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Silylmethylamines and Their Derivatives: Chemistry and Biological Activities

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The Chemistry of Perfluoroaryl Boranes

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I

INTRODUCTION AND SCOPE

It has been just over 40 years since the first pentafluorophenyl substituted boranes were prepared using transmetallation reactions of $C_6F_5SnMe_3$ and BCl_3.[1] Although investigated fairly thoroughly at the time, the rise to prominence of this family of boranes by virtue of their efficacy as activators for olefin polymerization pre-catalysts has occurred only in the past 15 years and is well documented.[2] Indeed, the propensity of the parent tris-(pentafluorophenyl)borane,[3] $B(C_6F_5)_3$, to abstract anionic moieties from transition metals has opened up the chemistry of a wide variety of electrophilic organotransition metal cations and led to important commercial advances in the production of high quality polyolefin resins with superior properties when compared with plastics prepared traditionally *via* Ziegler–Natta technology.[4] The properties of $B(C_6F_5)_3$ that make it an excellent activator and its ready availability have led to a renewed interest in the chemistry of perfluoroaryl boranes, not only as catalyst activators but also as strong Lewis acids for other purposes.

Already in the early days of $B(C_6F_5)_3$ chemistry, Massey and Park demarked its remarkable thermal stability and high affinity for even weak Lewis bases.[5,6] It was

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ADVANCES IN ORGANOMETALLIC CHEMISTRY
VOLUME 52 ISSN 0065-3055/DOI 10.1016/S0065-3055(04)52001-4

noted at the time that, generally, perfluoroalkyl boranes were not particularly stable due to the strong thermodynamic driving force for the formation of B–F bonds and (relatively) stable fluorinated carbenes. The pentafluorophenyl group, however, resisted this pathway and $B(C_6F_5)_3$ was observed to be stable up to temperatures of 270 °C with only minor decomposition. Furthermore, by virtue of the strongly electron withdrawing perfluoroaryl groups (the C_6F_5 group is estimated to have σ_p and σ^- parameters of 0.4[7] and 0.99,[8] respectively), $B(C_6F_5)_3$ and related boranes are very strong Lewis acids, of comparable strength to BF_3 and BCl_3. Unlike the haloboranes, however, the B–C bonds in the perfluoroaryl compounds are resistant to cleavage by protic acids, giving these Lewis acids more chemical integrity. The perfluoroaryl substituents also provide steric protection to the boron center and raise the potential for $-C_6F_5/-C_6H_5$ π–π stacking interactions with incoming Lewis bases, which augment the primary Lewis acid/Lewis base dative interaction. The aryl groups also impart greater crystallinity to the adducts formed and many complexes have been studied crystallographically as a result, allowing for detailed analysis of the solid-state structures of the adducts of a variety of Lewis bases. Together, these attractive features have contributed to the increased use of this borane. The one inhibitor is the cost of the reagent; at the time of this writing it is available for 15–80 USD/g, depending on the quantities purchased, which is something of a deterrent for routine use in place of, for example, $BF_3{\cdot}Et_2O$.

Because the use of $B(C_6F_5)_3$ and related boranes in olefin polymerization applications has been reviewed extensively,[2] this aspect of their chemistry will not serve as the focus of this chapter. The aspects of perfluoroaryl borane chemistry that fall outside the domain of olefin polymerization by single site catalysts will be covered, drawing parallels only where necessary. The article will begin with a brief discussion of methods for quantifying Lewis acidity followed by a survey of the chemistry of X_2BAr^F, $XB(Ar^F)_2$ and $B(Ar^F)_3$ (Ar^F = perfluoroaryl group) compounds and their adducts, a section on polyfunctional perfluoroaryl boranes and conclude with applications that do not involve α-olefin polymerization by single site catalysts *via* a coordination polymerization mechanism. The role of perfluoroaryl borates as weakly coordinating anions (WCAs) will be touched on, but since this topic has also been adequately covered in the recent literature, it will not be emphasized here.

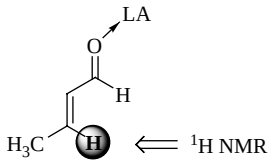
II

LEWIS ACID STRENGTH MEASUREMENT

Unlike Bronsted acidity, which can be quantitatively assessed accurately using the pK_a scale, quantitative measurement of Lewis acid strength is a more nebulous undertaking. Steric factors encompassing the structural features of the LA (Lewis acid) and the LB (Lewis base) play a much more significant role in the effective LA strength of a given acid and establishing an absolute scale of Lewis acid strength is difficult, since it is situation dependent. Therefore, in general, such methods are of diminished utility compared to pK_a measurements.

Nonetheless, several attempts to quantify Lewis acidity have been made and a few methods are useful in the context of perfluoroaryl borane chemistry. The Childs method[9] involves measurement of the perturbation of the ^1H NMR signal for the β-proton

in crotonaldehyde upon complexation to a given LA *via* the carbonyl oxygen (**I**).



I

The assumption here is that, because this proton is remote from the locus of coordination, it will be more or less immune to steric factors engendered upon complexation, and the chemical shift will be influenced primarily by the electronic effects caused by the electron withdrawing LA. The stronger the LA, the greater the perturbation from the chemical shift of this proton in free crotonaldehyde. Technical challenges include the need to exclude water completely and to use an excess of LA in measuring the complex's chemical shift, but aside from these potential pitfalls, the method provides a useful scale of Lewis acidity by which to judge main group Lewis acids relative to BBr_3.

This empirical method has been validated thermochemically and computationally. Childs observed a moderate correlation between the observed heats of formation of the crotonaldehyde·LA adducts and the scale of acidity developed by the NMR method.[10] Laszlo and Teston[11] found a strong correlation between the Lewis acidities determined *via* the Childs' method and the change in the computed energy of the π^* orbital of the carbonyl function upon complexation by the LA, suggesting a viable non-experimental method for assessing LA strength given the ready availability of the necessary computational resources in most modern laboratories.

Recently, Beckett *et al*. has used the Gutmann acceptor number[12] (GAN) scale to assess the Lewis acidity of $B(C_6F_5)_3$ in particular.[13] This scale uses the perturbation in the ^{31}P chemical shift of $Et_3P{=}O$ in hexane observed when the phosphine oxide is immersed in a Lewis acidic medium. Excellent correlation is observed between the GAN and the Childs' Lewis acidity for a variety of LAs, perhaps not too surprising given that they are related NMR methods.

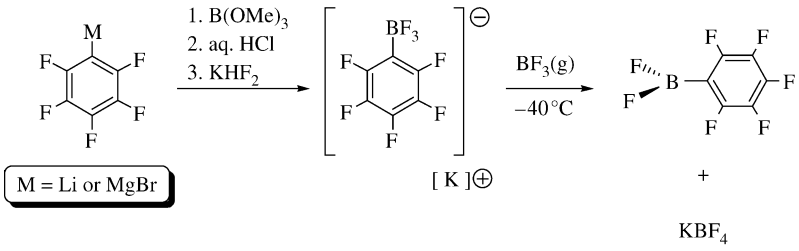
Where these methods tend to falter is in sterically more demanding LAs—such as perfluoroaryl boranes with bulkier groups than C_6F_5—in that they tend to overestimate the strength of an LA. Thus, Marks *et al*. have observed less distinct correlations between Childs' acidities and enthalpic data for larger perfluoroaryl boranes,[14] reflecting the steric back-strain that arises as a boron center is pyramidalized upon interaction with an LB. It is thus important to realize that, in assessing a pair of Lewis acids for comparative Lewis acid strength towards a given Lewis base, a competition experiment provides the most accurate information. Indeed, the relative LA strengths may flip depending on the base used. Thus, while the Childs' scale and the Laszlo/Teston methods described are qualitatively useful and will be referred to throughout the review, they may not reflect an absolute assessment of a given borane's LA strength, particularly in the more sterically significant members of the perfluoroaryl family of compounds.

III

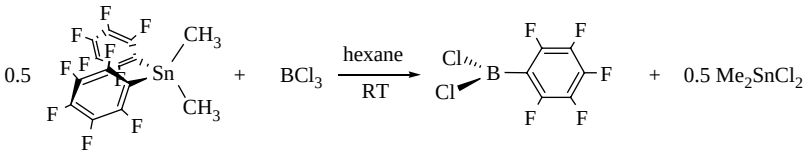
SYNTHESIS AND CHEMISTRY OF X_2BAr^F COMPOUNDS

Because they serve as versatile starting materials for a variety of other boranes, the dihalo boranes, particularly the fluoro and chloro derivatives, are the most important members of this class of compounds. Their chemistry, along with other pentafluorophenyl boron halides, has been reviewed recently from a personal perspective by Chivers,[15] whose PhD thesis described early explorations into the chemistry of these compounds. Most of the known literature on these compounds deals with pentafluorophenyl compounds, but the chemistry is likely extendable to other compounds with different Ar^F groups.

Early synthetic routes to $Cl_2BC_6F_5$ utilized a tin–boron transmetallation reactions [Eq. (1)] and this is still the method of choice for this compound, which is a distillable clear liquid material.[1,16] However, this method is not as effective for the preparation of $Br_2BC_6F_5$.[17] The difluoride was originally prepared from the dichloride using SbF_3, but this procedure is temperamental and prone to $-C_6F_5$ group transfer to antimony. Alternatively, treatment of the dibromide $Br_2BC_6F_5$ with HF gives the difluoride in acceptable yields, but the preparation of $Br_2BC_6F_5$ involves the reaction of highly toxic and undesirable organomercury reagents C_6F_5HgBr[18] or C_6F_5HgEt with BBr_3.[19] A new, general method for preparing F_2BAr^F compounds that overcomes these problems was recently reported by Fröhn *et al.* (Scheme 1).[19] Here, C_6F_5M (M=Li or MgBr) is treated with $B(OMe)_3$ to give a boronic ester that is easily converted to the potassium trifluoroperfluoroaryl borate by sequential treatment with aqueous HCl and KHF_2. A primary advantage is the ability to employ the Grignard reagent, since pentafluorophenyllithium is an explosive material at temperatures above $-40\,^{\circ}C$, whereas the Grignard can be safely handled at ambient temperatures. Key to success, however, is the fresh preparation of the Grignard reagent, from bromopentafluorobenzene and $^{i}PrMgBr$ or EtMgBr.[20] Upon workup, the product trifluoroborates are air- and moisture-stable white solids that are conveniently handled and serve as precursors to the desired F_2BAr^F products when treated with an excess of BF_3 under anhydrous conditions. $F_2BC_6F_5$ is a clear liquid that is purified by distillation and can serve as a starting material for a variety of perfluoroaryl derivatives. Furthermore, this method is widely applicable for the preparation of many F_2BAr and F_2BAr^F derivatives.

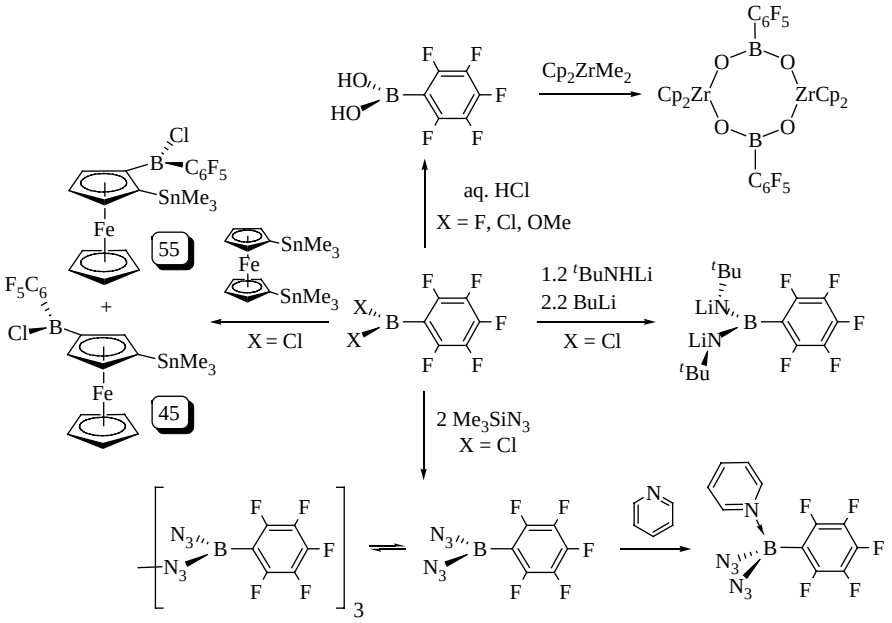


SCHEME 1.



(1)

The reactivity of these compounds largely focuses on functionalization of the halide groups (Scheme 2). Hydrolysis gives the isolable pentafluorophenyl boronic acid, $(HO)_2BC_6F_5$ which can also be apprehended as an intermediate in the Fröhn synthesis of $F_2BC_6F_5$.[21] This compound has been reacted with Cp_2ZrMe_2 to effect loss of CH_4 and form a zirconocene dimer which features an 8-membered $Zr_2B_2O_4$ heterocyclic core.[22] The halides in $X_2BC_6F_5$ can be metathetically replaced with *tert*-butyl amide groups, which can be subsequently deprotonated to give the dianionic boraamidinate ligand as its lithium salt. Reaction with Me_2SnBr_2 results in a boraamidinate tin derivative.[23] Treatment of $Cl_2BC_6F_5$ with TMS azide is a convenient route to the explosive pentafluorophenylboron diazide.[24] The solid-state structure of this species indicates it is trimeric, with bridging and terminal azide ligands, but solution spectroscopic data (^{11}B NMR, 34.6 ppm) suggest that the monomer is accessible. The pyridine adduct of the monomer has been prepared and characterized crystallographically. Finally, the LA properties of $Cl_2BC_6F_5$ have been demonstrated in the electrophilic substitution of $SnMe_3$ in the 1,1′ distannyl substituted ferrocene derivative shown.[25] The reaction is unusual in that the boron group ends up on the same Cp ring as the remaining



SCHEME 2.

trimethylstannyl moiety; although the mechanism of this process is unclear, the resulting compounds are interesting heterobifunctional Lewis acids.

The dichloro derivative has also played an important role in the chemistry of monomeric boron imides, $RB{=}NR'$, the first example of which was prepared by a dehydrohalogenation reaction involving $Cl_2BC_6F_5$ and H_2N^tBu.[26] It was thought that the electronic properties of the C_6F_5 group were a key factor in the stabilization of this function, but subsequent investigations suggested that these were not especially relevant. Indeed, reactions with other amines, such as mesidine, did not form boron imides but rather a series of products stemming from HCl evolution from initially formed amine–borane adducts.[27]

Bis-alkyl or aryl pentafluorophenyl boranes have been reported as by-products of reactions, but remain relatively poorly characterized. For example, methide abstraction from Cp_2ZrMe_2 using $MeB(C_6F_5)_2$ results in an unstable ion pair which transfers a $-C_6F_5$ group to zirconium, producing $Me_2BC_6F_5$, which has been characterized spectroscopically.[28] Attempts to prepare pure samples of the diphenyl borane $Ph_2BC_6F_5$ were foiled by its tendency to undergo group redistribution reactions.[29]

IV

SYNTHESIS AND CHEMISTRY OF $XB(Ar^F)_2$ COMPOUNDS

Examples of bis-(pentafluorophenyl)boranes and related compounds are more plentiful than the $X_2BC_6F_5$ boranes described above, so this discussion will be broken down according to the nature of X.

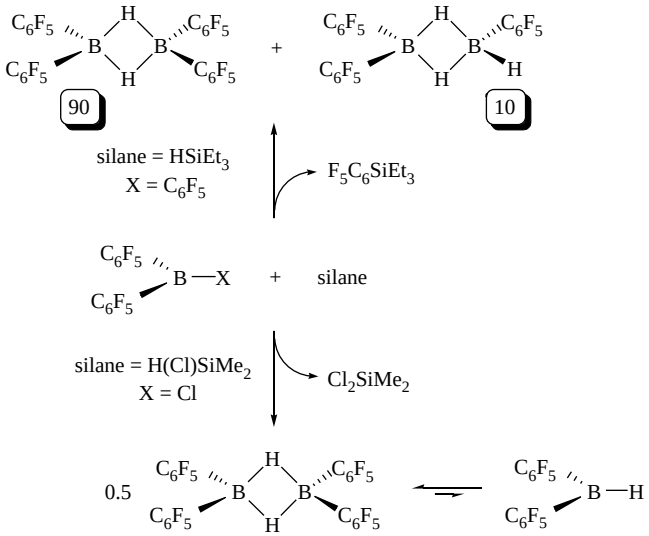
A. *Bis-(pentafluorophenyl)haloboranes (X = Halide)*

Again, the bis-(pentafluorophenyl)haloboranes are crucial compounds for accessing other members of this class, and they have been known for some time. The fluoroborane $FB(C_6F_5)_2$ is accessible *via* thermolysis of $F_2B(C_6F_5)$ at 95 °C,[16] or can be prepared as its ether adduct by treatment of $BF_3{\cdot}OEt_2$ with C_6F_5MgBr.[18] The etherate is a convenient starting material for further reactions, but thermally converts to $EtOB(C_6F_5)_2$ if heated above 100 °C or left to stand in solution for lengthy periods. The chloroborane $ClB(C_6F_5)_2$ is prepared *via* an organotin route analogous to that shown in Eq. (1), with appropriately altered stoichiometry. The original procedure was performed with no solvent, but subsequently it was found that using hexanes as a solvent allowed for more efficient separation of the Me_2SnCl_2 by-product and improved yields of highly pure product.[30] Sublimation of $ClB(C_6F_5)_2$ prepared in this way gave a clear crystalline material whose structure was solved by X-ray crystallography.[31] In this planar bis-pentafluorophenylborane, the B–C bond distances of 1.566(6) and 1.551(7) Å are slightly shorter than the typical distances of ≈1.65 Å observed in four coordinate boranes. The bromoborane $BrB(C_6F_5)_2$ [32] is accessible from BBr_3 and pentafluorophenyl mercury reagents as described above, but not (unfortunately!) from disproportionation of BBr_3 and $B(C_6F_5)_3$ as reported,[33] and later recanted,[18] by Bochmann *et al.*

B. *Bis-(pentafluorophenyl)borane (X = H)*

The haloboranes discussed above are excellent starting materials for a variety of bis-(pentafluorophenyl) derivatives. Dissolution of $ClB(C_6F_5)_2$ into $Me_2Si(Cl)H$ results in almost immediate precipitation of a white solid which can be isolated by filtration, providing the borane $[HB(C_6F_5)_2]_2$ in nearly quantitative yield (Scheme 3).[30,34] Alternatively, the same material can be obtained by a more prolonged reaction between commercially available $B(C_6F_5)_3$ and Et_3SiH in benzene. Although somewhat more convenient, this route is not as high yielding or atom economical as the one stemming from $ClB(C_6F_5)_2$. Both routes can also produce varying amounts of the unsymmetrical borane dimer $[(C_6F_5)_2B(\mu\text{–}H)_2B(H)(C_6F_5)]$ resulting from further $-C_6F_5/H$ exchange, but this impurity can be minimized by optimizing the reaction times and it can be removed completely by washing the product with a mixture of toluene and hexanes (3:1).

In the solid state, $[HB(C_6F_5)_2]_2$ is dimeric, but is distinguished from other diorganoboranes in that observable amounts of the monomeric species $HB(C_6F_5)_2$ appear in solution. This is clearly demonstrated by the ^{11}B NMR spectra in benzene, which show a minor peak centered around 60 ppm (three coordinate boron) and a major peak at 18 ppm (four coordinate, neutral boron).[35] Recent quantitative analysis of this monomer/dimer equilibrium using variable temperature ^{19}F NMR spectroscopy[36] at various temperatures confirmed our earlier, more qualitative assessment that the dissociation enthalpy in benzene is much less (4.6 kcal mol^{-1}) than that observed for $[(Mes)_2BH]_2$ (16.7 kcal mol^{-1}),[37] the only other borane for which this monomer/dimer equilibrium is assessable in solution. As expected, the ΔS° for this equilibrium is positive (15.3 cal K^{-1} mol^{-1}), but less so than that observed for dissociation of $[(Mes)_2BH]_2$

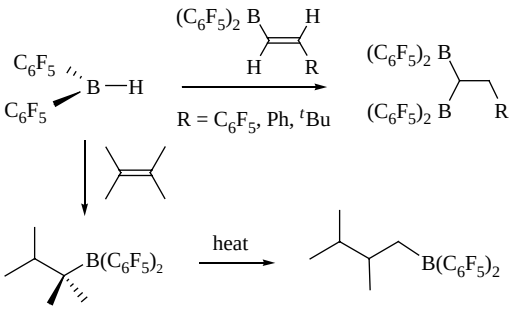


SCHEME 3.

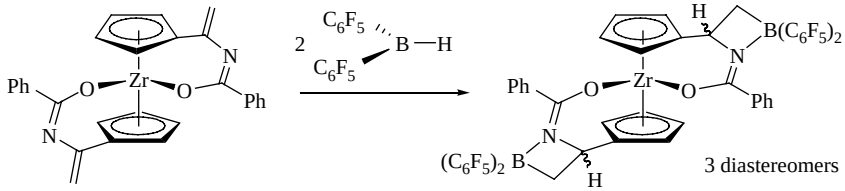
(50.7 cal K^{-1} mol^{-1}), suggesting that solvation of the monomeric $HB(C_6F_5)_2$ *via* C_6F_5–C_6D_6 π stacking interactions[38] may be playing a role in the stabilization of the monomer. The electron withdrawing $-C_6F_5$ groups lower the polarity of the B–H bond in the monomer, perhaps destabilizing the dimer by diminishing the electrostatic component of the three-center, two-electron bonds.

Since the activity of a given diorganoborane is generally dependent on the accessibility of the more reactive monomeric species, it is not surprising that $HB(C_6F_5)_2$ is a *highly* reactive hydroboration reagent. Regioselective addition to carbon–carbon double and triple bonds is rapid and quantitative in most instances, including substrates such as tetrasubstituted or electron poor olefins[30] (Scheme 4) for which other hydroboration reagents are ineffective. Another unique characteristic of this reagent is the facility with which retrohydroboration occurs, allowing for facile isomerization pathways to thermodynamically more favored products. The hydroboration products $RB(C_6F_5)_2$ are prone to protic loss of RH, so oxidation procedures to give ROH products involve use of H_2O_2 (4.4 M) under alkaline conditions (pH ≈ 12) or amine *N*-oxide reagents.

Since it is not trivially accessible, the properties of $HB(C_6F_5)_2$ make it worth considering for specialty hydroboration applications only. These include its use to install Lewis acid centers into ligand frameworks *via* hydroboration of tethered functions on coordinated ligands. For example, we[39] and others[40] have used $HB(C_6F_5)_2$ to hydroborate propenyl groups dangling from Cp ligands in bent zirconocene complexes in an effort to prepare self-activating zwitterionic olefin polymerization catalysts.[41] While this proved partially successful, the tendency for anions of general formula $[R_2B(C_6F_5)_2]^-$ to redistribute alkyl and $-C_6F_5$ groups between boron and the transition metal prevents these zwitterions from operating as stable platforms for olefin polymerization. Erker has also used $HB(C_6F_5)_2$ to functionalize the periphery of group 4 metallocene frameworks by hydroboration of the enamine group in the complex shown in Eq. (2).[42] Whereas the starting metallocene is inactive as a propylene polymerization catalyst, the hydroborated species is effective in this regard, probably because the Lewis acidic boron center "protects" the highly basic imine nitrogen, preventing it from poisoning the catalyst.



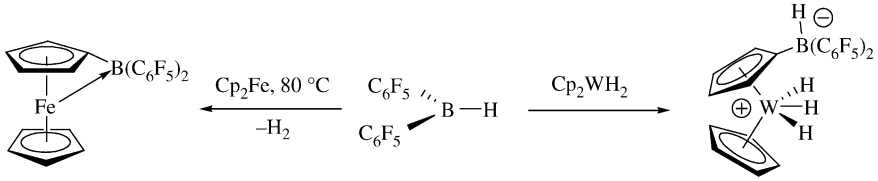
SCHEME 4.



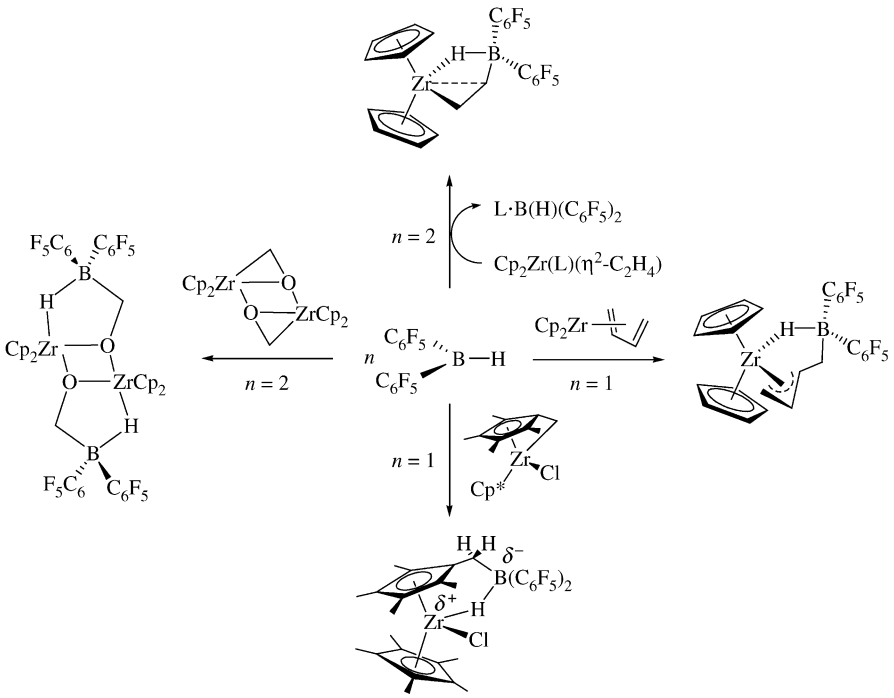
(2)

Bis-(pentafluorophenyl)boryl groups directly attached to coordinated Cp rings can be introduced by electrophilic attack of a Cp ring by $HB(C_6F_5)_2$. Ferrocene is directly borylated at 80 °C with loss of H_2,[43] while for Cp_2WH_2, the borane attacks the Cp ring from the *exo* face and transfers a Cp hydrogen to metal center, forming the zwitterion shown; apparently this material is stable towards loss of H_2 (Scheme 5).[44]

Coordinated olefins,[45] dienes,[46] metallated Cp rings[47] or η^2-formaldehyde[46] ligands in zirconocene complexes are attacked by $HB(C_6F_5)_2$ to give products formally arising from H−B addition to a Zr−C linkage of the metallacyclic resonance form of the organometallic compound (Scheme 6). The resulting heterocycles feature a stabilizing hydridoborate linkage to the zirconium center, and in the case of the olefinic compounds, a residual interaction between the Zr and the olefinic carbon now attached to B is indicated by the close Zr−C distance of 2.455(7) Å. For σ-bonded hydrocarbyl ligands M−R, reaction with $HB(C_6F_5)_2$ often results in complete alkyl/hydride exchange (Scheme 7),[48] a process which has been shown to be reversible in some cases. Experiments using the stereochemically defined *erythro*-CH(D)CH(D)^{t}Bu alkyl group in $Cp_2Zr(R)Cl$ produced inverted stereochemistry at the alpha carbon in the resulting $RB(C_6F_5)_2$ compound, suggesting that $HB(C_6F_5)_2$ abstracts the alkyl group *via* backside attack and transfers H^- back to the resulting Zr cation, although the intermediate ion pair has not been observed. A concerted, four-centered σ bond metathesis pathway would be expected to yield retained stereochemistry in the probe. In the presence of excess $HB(C_6F_5)_2$, the metal hydrides that are produced are rapidly complexed, forming very stable $M[(\mu\text{-}H)_2B(C_6F_5)_2]$ hydrido borate complexes. This is a reactivity pattern that has been observed in organoscandium,[49] titanium[50] and iridium[51] derivatives. Reaction between $[Cp_2Zr(H)Cl]$[48b] or Cp_2MoH_2 [44] and $HB(C_6F_5)_2$ gives $Cp_2Zr[(\mu\text{-}H)_2\text{-}B(C_6F_5)_2]Cl$ or $Cp_2Mo[(\mu\text{-}H)_2B(C_6F_5)_2](H)$, and the salt $[Li(OEt_2)][H_2B(C_6F_5)_2]$ can be prepared by reacting $HB(C_6F_5)_2$ with LiH,[52] indicating that metal hydrides are susceptible to complexation by $HB(C_6F_5)_2$ directly. In general, these hydridoborate complexes do not readily eject $HB(C_6F_5)_2$ or react with Lewis bases to liberate $L{\cdot}HB(C_6F_5)_2$. In fact, the compound $Cp_2Ti[H_2B(C_6F_5)_2]$ reacts with excess PMe_3 to give the ion pair



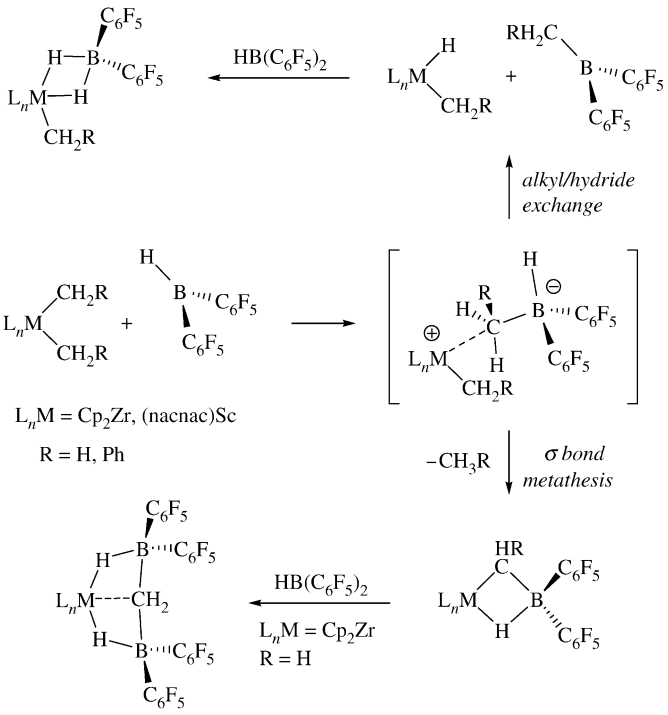
Scheme 5.



SCHEME 6.

$[Cp_2Ti(PMe_3)_2]^+[H_2B(C_6F_5)_2]^-$,[52] illustrating the high ionic character of the hydridoborate-early transition metal interaction in these compounds.

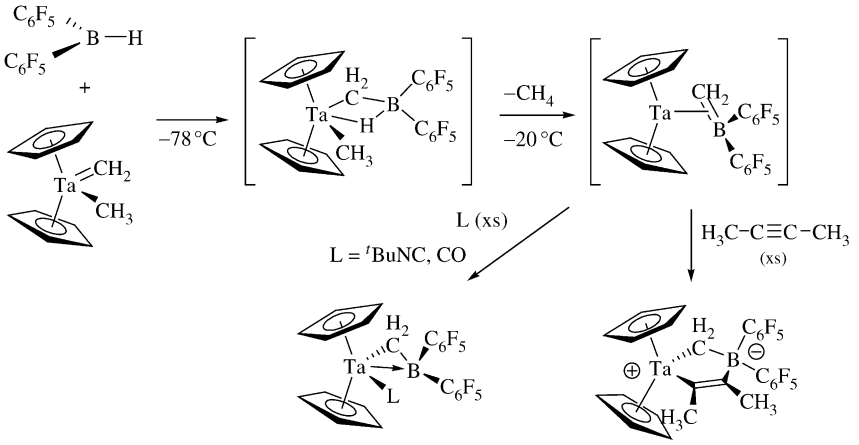
Another reaction pathway is available in the reactions of $HB(C_6F_5)_2$ with metal alkyls when two hydrocarbyl ligands are present.[48] In this scenario, the putative ion pair $[L_nM–CH_2R]^+[(RCH_2)BH(C_6F_5)_2]^-$ undergoes elimination of RCH_3 *via* a σ bond metathesis reaction involving a C–H bond of the abstracted alkyl group and the M–C bond of the remaining hydrocarbyl ligand, rather than transfer of H^- from B to M. This pathway is most prevalent for dimethyl compounds (i.e., R = H), for example, Cp_2ZrMe_2 or (nacnac)$ScMe_2$ [53] (Scheme 7; nacnac = 2,6-^{i}Pr$_2$C$_6$H$_3$NC(R)CHC(R)N-2,6-^{i}Pr$_2$C$_6$H$_3$) and is a process related to decomposition pathways observed in $[L_nM–CH_3]^+[H_3CB(C_6F_5)_3]^-$ ion pairs.[54] The products may be regarded as $HB(C_6F_5)_2$ stabilized methylidene compounds, where the H–B bond has complexed to M=CH_2 in a similar fashion to the $ClAlMe_2$ stabilization of "Cp_2Ti=CH_2" observed in Tebbe's reagent.[55] Interestingly, in the zirconocene case, where an open coordination site exists addition of another equivalent of $HB(C_6F_5)_2$ results in the complex shown in the Scheme, featuring a unique dianionic $CH_2[(\mu\text{-}H)B(C_6F_5)_2]_2$ ligand with significant donation from the central carbon to the Zr center. The bonding in this pentacoordinate carbon donor has been treated computationally,[56] showing that a significant amount of the electron density in this dianionic ligand resides on the central carbon for donation into the $1a_1$ orbital of the bent metallocene fragment.[57]



Scheme 7.

These compounds suggested that reaction with *bona fide* methylidene compounds might lead to compounds with interesting boron-based ligands. This proved to be the case; in a study of the reactions of Schrock's methylidene methyl complex $Cp_2Ta(=CH_2)CH_3$ [58] with $HB(C_6F_5)_2$, we observed rapid addition of the borane to the $Ta=CH_2$ moiety, followed by facile reductive elimination of CH_4.[59] The product, a Ta(III) complex of a new class of borataalkene ligand, is not isolable due to its tendency to slip between an η^1 (triplet) and η^2 (singlet) bonding mode, but could be trapped with π-acids such as CO or CN^tBu (Scheme 8). Computational investigation of these adducts showed that the bonding of the borataalkene ligand was topologically similar to the familiar Dewar-Chatt-Duncanson model of η^2 olefin binding to metals.[60] Furthermore, in trapping "$Cp_2Ta[CH_2=B(C_6F_5)_2]$" with selected alkynes, olefin-like reactivity was observed in the reductive coupling of the borataalkene ligand to form tantala-3-boratacyclopentenes.[61] Some of these products undergo further rearrangement to $HB(C_6F_5)_2$ stabilized vinyl alkylidenes of tantalocene. Alternatively, the borataalkene reacts with more basic isonitriles through an η^1 configuration *via* insertion into the B–C bond of the $Ta-CH_2-B(C_6F_5)_2$ moiety.[62]

Further surveys of the reactivity of $HB(C_6F_5)_2$ with simple organometallic compounds have led to the discovery of more novel boron-based ligand systems. For example, reactions with Schrock's tungsten methylidyne family $L_4W(X)\equiv CH$[63] (L = phosphine, X = Cl, OTf) result in electrophilic attack on the methylidyne ligand; hydride abstraction



SCHEME 8.

from this product with $[Ph_3C]^+[B(C_6F_5)_4]^-$ gives a novel borylalkylidyne cation, $[L_4(H)W(X)\equiv C-B(C_6F_5)_2]^+[B(C_6F_5)_4]^-$.[64] Adducts of Heppert's ruthenium carbide $(Pcy_3)_2Cl_2Ru\equiv C$:[65] with $HB(C_6F_5)_2$ have also been made and observed to undergo subsequent reactivity.

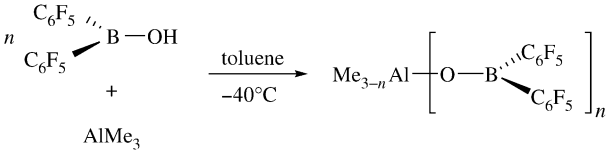
C. *Bis-(pentafluorophenyl)borinic acid (X = OH) and Related Compounds*

Researchers working with the highly water sensitive $HB(C_6F_5)_2$ and haloboranes described above have undoubtedly encountered bis-(pentafluorophenyl)borinic acid and its derivatives at some point, either purposely or unwittingly. While something of an annoyance in this regard, $HOB(C_6F_5)_2$ is an interesting and useful compound in its own right. In addition to having a strongly Lewis acidic site, it is also a Bronsted acid and possesses Lewis basicity through the OH lone pairs.

The compound can be synthesized on a large scale by the controlled hydrolysis of $ClB(C_6F_5)_2$ at 0 °C with one equivalent of water in 96% yield as a white solid; the HCl by-product is removed by evaporation.[66] Alternatively, it may be prepared by treatment of $HB(C_6F_5)_2$ with water, although these samples are contaminated with the anhydride $(C_6F_5)_2BOB(C_6F_5)_2$ in varying amounts, since $HOB(C_6F_5)_2$ reacts quite rapidly with $HB(C_6F_5)_2$.[2b] Two procedures that do not necessitate $ClB(C_6F_5)_2$ have also been developed and implemented on a large scale. Starting from BCl_3 and *n*-propanol, the dichloro borinic ester Cl_2BO^nPr is generated and treated with two equivalents of $BrMgC_6F_5$; aqueous acidic work-up of $^nPrOB(C_6F_5)_2$ yields the borinic acid.[67] Finally, although $B(C_6F_5)_3$ forms a stable adduct with water under ambient conditions (see below), heating $B(C_6F_5)_3$ in the presence of water to >80 °C results in the elimination of C_6F_5H and clean production of the borinic acid.[68] Since $B(C_6F_5)_3$ is more accessible than $ClB(C_6F_5)_2$, this is a somewhat more convenient method, but is rather wasteful of a precious $-C_6F_5$ group.

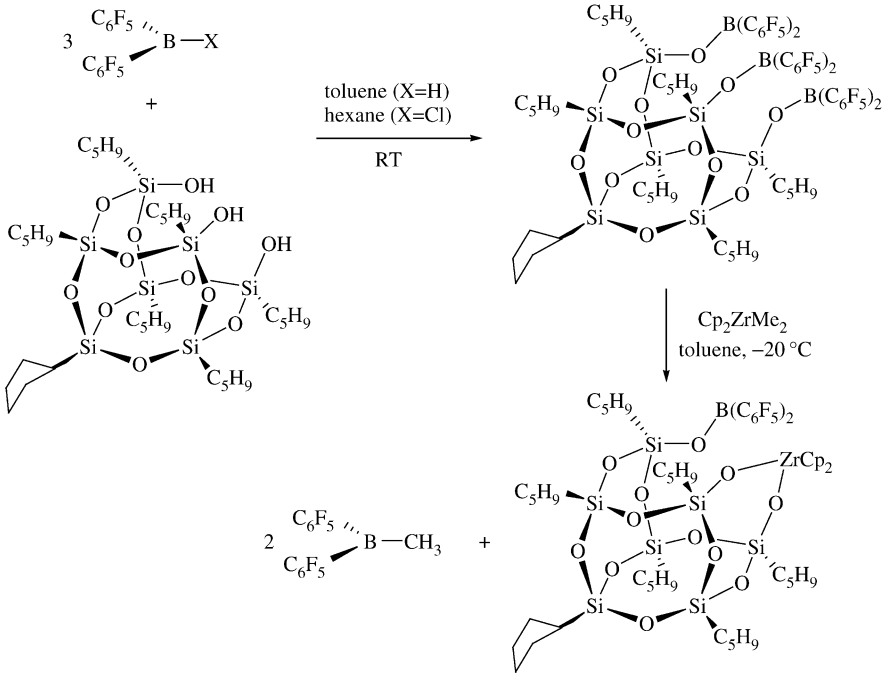
The X-ray structure of $HOB(C_6F_5)_2$ has recently been determined.[69] The compound assumes a trimeric structure *via* B–O(H)–B bridges and six O–H···F hydrogen bonds. Given the dimeric nature of $HB(C_6F_5)_2$ and the monomeric structure found for $ClB(C_6F_5)_2$, it is clear that subtle factors influence the nuclearity of the solids of $XB(C_6F_5)_2$ compounds. In solution, however, the trimer is disrupted and $HOB(C_6F_5)_2$ exists as a monomer whose properties have been studied in detail *via* multinuclear NMR spectroscopy. Most interesting is the observation of restricted rotation about the B–O bond, which creates chemically distinct C_6F_5 groups in the ^{19}F NMR spectrum at low temperatures. The authors attribute these observations to strong π donation of an oxygen lone pair into the empty p orbital on boron and estimate a barrier of 39(1) kJ mol^{-1} for this process.

The Lewis and Bronsted acid characteristics of $HOB(C_6F_5)_2$ are borne out in its capacity to mediate the Oppenauer oxidation of allylic and benzylic alcohols[68a] and the dehydration of β-hydroxy carbonyl compounds,[70] since it is able to activate alcohols and carbonyl functions *via* the Lewis acidic boron center, and facilitate proton transfers *via* the OH group. The closely related borinic acid incorporating partially fluorinated 3,4,5-trifluorophenyl groups is also an effective catalyst for dehydrogenation reactions. The protic nature of the OH group has also been employed to generate a number of novel boronoxy Lewis acids for use as olefin polymerization activators by reaction with organoaluminum reagents, as exemplified by the reaction in Eq. (3).[71] Little characterizational data was presented for these compounds, and their structures are likely more complex than depicted, but they are of interest as alternatives to the poorly understood conventional LA activator MAO. Other alternative activators have been derived from $(C_6F_5)_2BOB(C_6F_5)_2$, which can be prepared cleanly by heating solid $HOB(C_6F_5)_2$ to 100 °C under high vacuum.[72] The X-ray structure of $(C_6F_5)_2BOB(C_6F_5)_2$ reveals that the B–O–B angle is not linear but bent by 154.05(12)° by virtue of a B···F interaction between one of the boron centers and an *ortho* fluorine atom of a C_6F_5 group on the adjacent boron.[73]



(3)

The high strength of the B–O bond drives formation of $ROB(C_6F_5)_2$ derivatives *via* a variety of routes. Treatment of $HB(C_6F_5)_2$ with alcohols, epoxides, THF or carbonyl functions yields the borinic esters rapidly and cleanly. Ether cleavage has also been observed when heating the OEt_2 adduct of $FB(C_6F_5)_2$ to give $EtOB(C_6F_5)_2$. Detailed spectroscopic studies on the simple derivatives of this family have not been carried out to determine their nuclearity and probe the dynamics of B–O bond rotation. This mode of reactivity has also been used to functionalize the silanol groups of silica surfaces[28a] or silsesquioxane surface models[28b,c] with $-OB(C_6F_5)_2$ groups. While treatment of partially dehydroxylated silica with $HB(C_6F_5)_2$ or $ClB(C_6F_5)_2$ gives active co-catalysts, the silsesquioxane supported boranes are susceptible to ligand redistribution processes that nullify the catalyst's activity (Scheme 9).



SCHEME 9.

The chloroborane $ClB(C_6F_5)_2$ serves as a convenient starting material for the preparation of bis(pentafluorophenyl)boron triflate, $TfOB(C_6F_5)_2$, when treated with AgOTf or Me_3SiOTf.[74] The compound is monomeric in the solid and presumably in solution. The B–O distance of 1.403(4) Å is longer than the average B–O bond length of 1.331(3) Å in the silsesquioxane triborane of Scheme 9, indicating lower π bonding to the boron center from the OTf ligand. Boron triflates of general formula $TfOBR_2$ (R = alkyl) are excellent electrophiles for the formation of mono and bis boron enolates from esters and acids,[75] but the chemistry of $TfOB(C_6F_5)_2$ as a $-B(C_6F_5)_2$ synthon is largely unexplored to date.

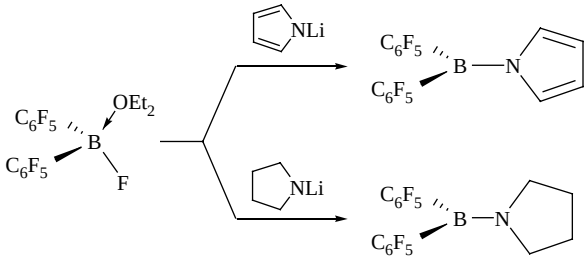
D. *Amino bis-(pentafluorophenyl)boranes (X = NR_2) and Related Compounds*

Amino boranes R_2NBR_2 are of interest because they are N,B analogs of olefins, and much of the work in this area centers around probing the multiple bond character of the N–B bond. The electron withdrawing nature of the $-B(C_6F_5)_2$ moiety was expected to enhance π bonding between N and B and indeed, the B–N bond length in the compound $[(Me_3Si)_2NB(C_6F_5)_2]$ was found by Green *et al.* to be on the short end of the normal range for such linkages at 1.400(3) Å.[76] The compound was prepared by reaction of $MN(SiMe_3)_2$ (M = Na or K) with $ClB(C_6F_5)_2$. Interestingly, when a reaction between $ClB(C_6F_5)_2$ and $HN(SiMe_3)_2$ was carried out, $ClSiMe_3$ was eliminated exclusively to form

the mono trimethylsilyl amino borane [$(Me_3SiN(H)B(C_6F_5)_2$]. The ^{11}B NMR spectrum shows signals in both the tricoordinate and tetracoordinate boron regions (38.2 ppm and −2.8 ppm, ratio ≈4:1) suggesting a monomer–dimer equilibrium for this species in solution. Further reaction with $ClB(C_6F_5)_2$ is observed at 70 °C, in which another equivalent of $ClSiMe_3$ is eliminated to form the bifunctional Lewis acid $(C_6F_5)_2B(H)NB(C_6F_5)_2$, the NH analog of the borinic anhydride $(C_6F_5)_2BOB(C_6F_5)_2$ described above.

The compounds were made to explore their potential as reagents for installing "=N–$B(C_6F_5)_2$" boron substituted imido groups on transition metals by reaction with L_nMCl_2 compounds. Elimination of $ClSiMe_3$ or HCl would be expected to lead to these novel species. Several metal chlorides were tested, but the amino bis-(pentafluorophenyl)boranes proved not to be basic enough to engender reaction. Interestingly, attempts to remove a TMS group with fluoride from $[(Me_3Si)_2NB(C_6F_5)_2]$ led to a fluoroborate, indicating the perfluoroaryl borane center has a greater affinity for F^- than the two silicon atoms in this molecule. The quest for $L_nM{=}N{-}B(C_6F_5)_2$ thus remains unfulfilled, although some of the approaches to boryl alkylidyne compounds mentioned above may be appropriate for this purpose.

Manipulation of the π character of the B–N bond by modifying the aromaticity of the NR_2 group allowed Erker and co-workers to develop a new pentafluorophenyl substituted organometallic Lewis acid for use as an activator of olefin polymerization catalyst precursors.[77] By sequestering the nitrogen lone pair into an aromatic pyrrolyl heterocycle, π bonding to boron is reduced and the boron center's Lewis acidity is influenced partially by the inductive electron withdrawing power of the electronegative N atom. The non-aromatic pyrrolidinyl derivative was prepared for comparison; the synthetic route to these compounds is straightforward and shown in Scheme 10. Structural determinations for both show that the B–N bond in the pyrrolyl compound is significantly longer (1.401(5) Å) than the saturated compound (B–N = 1.366(3) Å), supporting the notion that the N lone pair is less available for π donation to B. Furthermore, while $(C_4H_8N)B(C_6F_5)_2$ is unreactive towards various $Zr{-}CH_3$ compounds, $(C_4H_4N)B(C_6F_5)_2$ exhibits analogous methide abstraction reactivity to $B(C_6F_5)_3$ in this chemistry, generating active ethylene polymerization catalysts. Unfortunately, the $[(C_4H_4N)B(C_6F_5)_2(CH_3)]^-$ anion interacts with the transition metal cation through the relatively electron-rich π system of the pyrrolyl ring, dampening activity and opening up catalyst deactivation pathways. Nonetheless, this is an intriguing strategy for enhancing Lewis acidity at B whose potential has yet to be explored in other applications for perfluoroaryl borane Lewis acids.



Scheme 10.

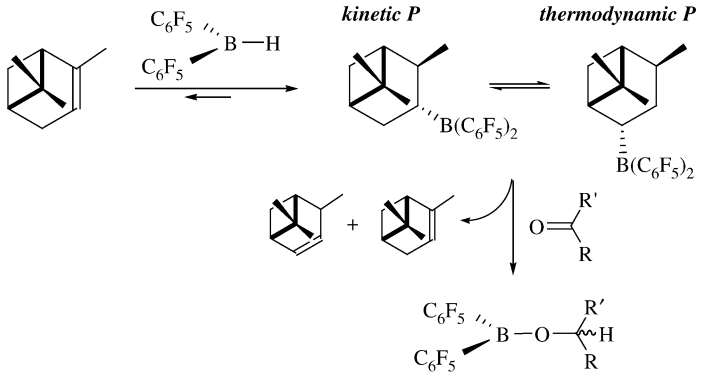
Recently, a four coordinate derivative incorporating a 5-(2-pyridyl) pyrazolate ligand was prepared by treating $B(C_6F_5)_3$ with the proteo ligand.[78] Loss of C_6F_5H was observed and the ligand was instituted, forming a compound with interesting photophysical properties.

In azido chemistry related to that described above,[24] Klapötke *et al*. have prepared and characterized bis-(pentafluorophenyl)boron azide by treatment of $ClB(C_6F_5)_2$ with $TMSN_3$.[79] The compound is monomeric in solution (^{11}B NMR = 43.9), but crystallizes as a μ-N_3 dimer, a unique nuclearity for boron azides. The pyridine adduct was also prepared and the compound is an intermediate in the synthesis of various azidoborates.[80]

E. *Hydrocarbyl bis-(pentafluorophenyl)boranes (X = Ar, CR_3) and Related Compounds*

Although substantially less Lewis acidic and more sensitive to adventitious water, compounds of general formula $RB(C_6F_5)_2$ have found some application as Lewis acids. One of the most effective ways to prepare examples of these compounds is hydroboration of olefins or alkynes using $HB(C_6F_5)_2$ as described above; the products of olefin hydroboration, however, are prone to facile retrohydroboration due to the presence of β-hydrogen groups. The problems this creates are illustrated in Scheme 11; the chiral LA derived from $HB(C_6F_5)_2$ and (+)-α-pinene is not stable towards equilibration between the kinetic and thermodynamic products. Furthermore, attempts to use either one of these to activate a carbonyl function results in regeneration of olefins and trapping of $HB(C_6F_5)_2$ as the $ROB(C_6F_5)_2$ borinic ester formed upon hydroboration of the carbonyl containing substrate. Thus, the utility of β-hydrogen containing $RB(C_6F_5)_2$ as Lewis acids is limited. However, when rearrangements to thermodynamic products of hydroboration are desirable, the $HB(C_6F_5)_2$ reagent proves advantageous. This is particularly true for silicon-containing substrates, since the high electrophilicity of the $-B(C_6F_5)_2$ group leads to a thermodynamic preference for R_3Si groups to occupy positions on the α carbon of the R group due to its ability to provide stabilization through hyperconjugation.[81]

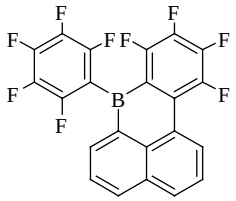
Preparation of alkyl boranes $RB(C_6F_5)_2$ which do not contain β-hydrogens can be accomplished by transmetallation between Cp_2ZrR_2 and $ClB(C_6F_5)_2$.[48b] The methyl, benzyl and trimethylsilyl methyl bis-(pentafluorophenyl) boranes have been prepared in



Scheme 11.

this way, and the methyl derivative can be made on gram scale in this fashion. It is purified by sublimation at 30–40° under high vacuum. These compounds have also been observed as decomposition products of ion pairs $[L_nM{-}R]^+[RB(C_6F_5)_3]^-$ that undergo $-C_6F_5$ back transfer to the metal. Limited exploration into their utility as olefin polymerization co-catalysts revealed that anions of the form $[R_2B(C_6F_5)_2]^-$ have an even greater propensity for transferring $-C_6F_5$ groups to the cationic metal center than the tris-(pentafluorophenyl)alkyl borates.

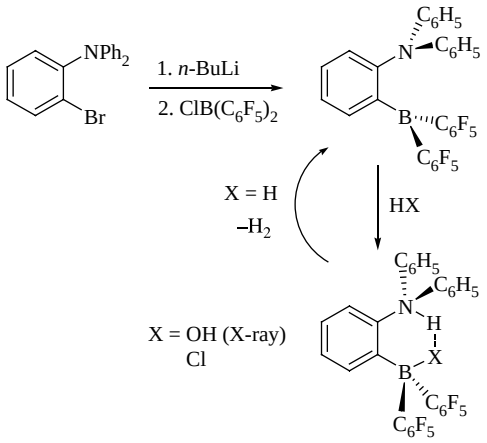
Although non-fluorinated aryl groups contain β-hydrogens, elimination is discouraged by the high energy of benzynes, and so boranes of general formula $ArB(C_6F_5)_2$ are relatively stable and useful when weaker Lewis acidity is desired. To evaluate the effect of reduced Lewis acidity on the thermodynamics of metallocenium ion pair formation, Marks *et al*. prepared the derivatives $PhB(C_6F_5)_2$, 3,5-$F_2C_6H_3B(C_6F_5)_2$ and 3,5-$(CH_3)_2$-$C_6H_3B(C_6F_5)_2$ by treating the $ArBX_2$ (X = Br or Cl) with *in situ* generated C_6F_5Li.[82] Overall yields using the procedure published here were rather poor, and we have found that $ArBF_2$ derivatives prepared *via* the Fröhn methodology shown in Scheme 1 serve as better precursors to $ArB(C_6F_5)_2$ boranes using freshly prepared C_6F_5MgBr as the pentafluorophenyl source.[83] As expected, these boranes exhibit moderated Lewis acid strength compared to $B(C_6F_5)_3$, which hampers their efficacy as olefin polymerization co-catalysts. However, in the case of $PhB(C_6F_5)_2$, the markedly lower Lewis acidity (the Childs' scale acidity is 0.54 vs. 0.68 for $B(C_6F_5)_3$) actually leads to greater efficacy as a catalyst for the allylstannation of benzaldehydes. The reasons for this phenomenon are discussed in Section VII.E.3. Another, more unusual member of this class of boranes was prepared by reaction of $Et_2O{\cdot}FB(C_6F_5)_2$ with 1,8-dilithionaphthalene·TMEDA, incorporating the B center in a planar, fused tetracyclic ring system, **II**.



II

This compound has been shown to be a substantially weaker LA than $B(C_6F_5)_3$, likely due to its reluctance to undergo pyramidalization.[84] Finally, the aminoborane 1-(NPh_2)-2-$[B(C_6F_5)_2]C_6H_4$ was prepared according to the procedure shown in Scheme 12.[85] This amphoteric species is intensely red colored and reacts rapidly with H_2O or HCl to give the colorless zwitterionic compounds shown. However, *in situ* generated 1-$(HNPh_2)$-2-$[(H)B(C_6F_5)_2]C_6H_4$ spontaneously releases H_2.

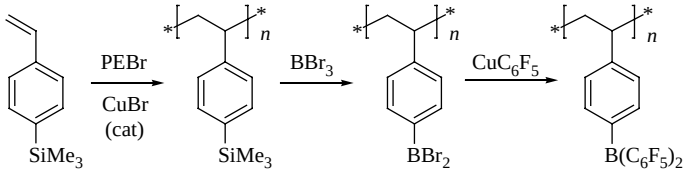
Jäkle and co-workers have recently incorporated the $PhB(C_6F_5)_2$ framework into a polymeric matrix, giving the first perfluoroaryl borane functionalized polymers (Scheme 13).[86] The Lewis acid centers in this polymer were judged to have a Childs' acidity of 0.60, a comparable value to that obtained for monomeric $PhB(C_6F_5)_2$. Of note in this work is that the reagent $[Cu(C_6F_5)]_4$ [87] was used to institute the pentafluorophenyl



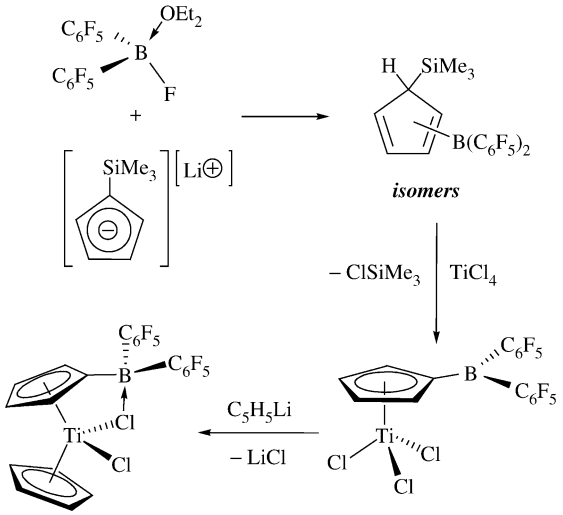
SCHEME 12.

groups; in monomeric systems, reagents like this and the related $Zn(C_6F_5)_2$ [88] have a tendency to be rather unselective[89] and/or catalyze redistribution of groups on boron centers, but since they are immobilized on the polymer backbone here, the copper reagent serves as a very convenient means of installing the desired C_6F_5 groups. The utility of these promising Lewis acid functionalized polymers awaits further investigation.

A related class of $RB(C_6F_5)_2$ derivatives are the cyclopentadienyl or dienide substituted perfluoroaryl boranes. These compounds are of interest due to their potential as Lewis acid substituted Cp ligands for forming "ring-type" zwitterionic metallocenes[41,90] that are essentially self-activated catalysts for olefin polymerization. Bochmann *et al.* have explored this area most thoroughly, preparing a variety of cyclopentadienyl, indenyl and fluorenyl derivatives $Cp^HB(C_6F_5)_2$ by reaction appropriate CpLi reagents with $Et_2O{\cdot}FB(C_6F_5)_2$.[18] While several derivatives were fully characterized alone or as H_2N^tBu adducts, most attempts to attach these Cp ligands to Ti or Zr failed completely. Deprotonation of the $Cp^HB(C_6F_5)_2$ group was not successful due to the preference for attack by the base at the electrophilic boron center. Attachment by amine elimination *via* reaction of $Cp^HB(C_6F_5)_2$ with $M(NMe_2)_4$ led to η^5-Cp complexes with $B(C_6F_5)NMe_2$ substituents; the fate of the other $-C_6F_5$ groups was not determined. Finally, $-SiMe_3$ substituted compounds $Cp^{SiMe3}B(C_6F_5)_2$ were prepared and reacted with MCl_4 (M = Ti, Zr) in an attempt to effect attachment by $ClSiMe_3$ elimination. This proved successful only



SCHEME 13.



SCHEME 14.

for the preparation of $[\eta^5\text{-}C_5H_4B(C_6F_5)_2]TiCl_3$ (Scheme 14).[91] The boron center in this compound is clearly three coordinate based on the ^{11}B NMR chemical shift of 59.8 ppm, and the authors judge it to be of comparable Lewis acidity to $B(C_6F_5)_3$ based on this observation; measurement of its Childs' acidity was not reported. Treatment of $[\eta^5\text{-}C_5H_4B(C_6F_5)_2]TiCl_3$ with CpLi derivative yields bis-Cp compounds in which the boron center now contacts one of the remaining Ti–Cl groups; these compounds are active olefin polymerization catalysts when alkylated with $AlEt_3$. A related Zr compound has also been reported.[92]

V

TRIS-PERFLUOROARYL BORANE DERIVATIVES: $B(C_6F_5)_3$ AND RELATED COMPOUNDS

A. *Lewis Acid Strength of $B(Ar^F)_3$ Derivatives*

The high Lewis acidity, thermal stability and resistance to protic B–C bond cleavage conspire to make $B(C_6F_5)_3$ an extremely effective activator of organometallic precatalysts for olefin polymerization and other reactions. As a result, other related boranes incorporating perfluoro biphenyl (Chart 1, **III**,[93] **IV**[94]), naphthyl (**V**[95]) or fluorinated 9-borafluorene (**VI**[96]) frameworks have been prepared in an effort to increase the Lewis acidity of the boron center and studied in the context of olefin polymerization.

The LA strength of $B(C_6F_5)_3$ has been assessed using the Childs' method by three groups, with some variation in the values obtained evident. We find a Childs' acidity of 0.68 ± 0.02, while Erker and co-workers assign a value of 0.72[97] and Marks and Luo report 0.77.[14] In light of the fact that Erker's value appears to be relative to $BCl_3 = 1.00$

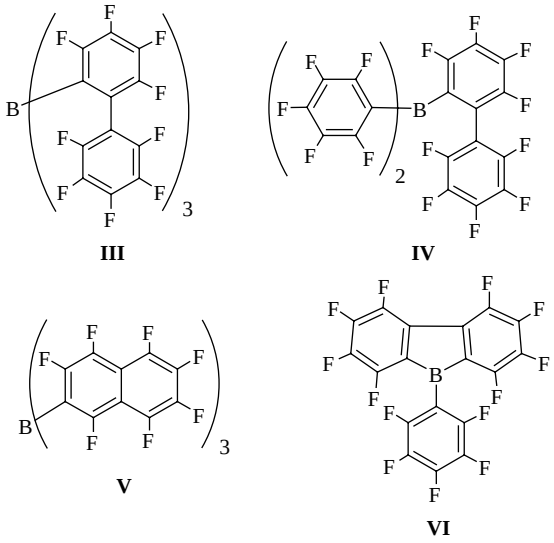


CHART 1.

instead of BBr_3, and that a Childs' acidity of 0.67 results upon correction, our assessment is in agreement with the Erker experiment. It is not clear why Marks and Luo find a substantially higher value, but given the very high affinity of $B(C_6F_5)_3$ for water (see below), it is possible that protic impurities may distort the measurement if rigorously dry $B(C_6F_5)_3$ and freshly distilled crotonaldehyde are not employed. At any rate, the compound clearly has a substantial Childs' Lewis acidity, roughly similar to BF_3 or $TiCl_4$.

Incorporation of bulkier, more highly fluorinated aryl groups increases the Childs' Lewis acidity, but calorimetric measurements on the reactions of **III** and **V** with simple Lewis bases or metallocenes reveal that back-strain upon pyramidalization at boron limits the effective Lewis acidity of these compounds. This notion is supported computationally.[98] As an alternative to bulky, exhaustively fluorinated aryl groups, incorporation of the boron atom into an anti-aromatic 9-borafluorene ring, **VI**, results in comparable LA strength (Childs acidity = 0.70 ± 0.02) to $B(C_6F_5)_3$, despite the loss of two fluorine atoms.

B. *Synthetic Methods*

Synthetic routes to perfluoroaryl boranes are invariably modifications of the original route reported by Stone, Massey and Park[5a] for the preparation of $B(C_6F_5)_3$ using *in situ* generated C_6F_5Li and BCl_3 in ethereal solvents, or a procedure using the Grignard reagent reported shortly thereafter by Pohlmann and Brinckmann.[99] Safety concerns[100] around the generation of C_6F_5Li on the large scales involved in industrial production of the borane have led to the development of processes that either minimize the reactor residence time of this reactive reagent[101] or utilize less dangerous alternatives, most commonly C_6F_5MgX reagents but also the zinc reagent $Zn(C_6F_5)_2$.[102] Other variations focus on the source of the $-C_6F_5$ groups; procedures which generate the C_6F_5M reagents from

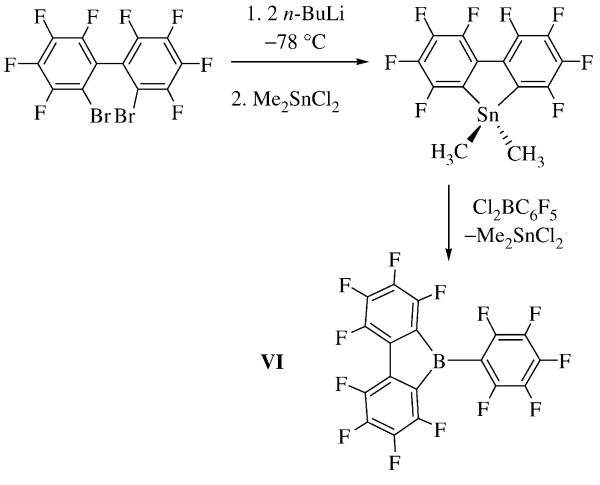
C_6F_5X (X = Cl,[103] Br[104]), C_6F_5H[105] or C_6F_6 [106] have all been reported in the patent literature. Since these reactions most often are performed in ethereal solvents such as diethylether or THF, the primary product of the reaction is the ether or THF adduct of $B(C_6F_5)_3$, which must be dissociated to produce the desired base-free borane. Since most Lewis base adducts of $B(C_6F_5)_3$ are labile (see below), this is typically done on an industrial scale by distilling off the ethereal species by refluxing a solution of $LB{\cdot}B(C_6F_5)_3$ in toluene or some high boiling hydrocarbon.[107] The ethereal base (and any residual water) is removed as an azeotrope, leaving the base-free borane. It can be employed as a solution, or isolated as a white, sublimable solid by precipitation and filtration.

The level of base remaining is easily assessed on a qualitative level by ^{19}F NMR spectroscopy. Pure, base-free $B(C_6F_5)_3$ exhibits three sharp multiplets for the *ortho*, *para* and *meta* F atoms in C_6D_6. The chemical shift of the *para* F is particularly sensitive to the presence of any Lewis base in the system, shifting upfield by $\approx$10 ppm upon complexation. This resonance is thus visibly broadened even in the presence of 5–10% of THF or water and provides a convenient qualitative assessment of the level of basic impurities.

The boranes **III**, **IV** and **V** were all prepared by reacting perfluoroaryl lithium reagents with either BCl_3 (**III** and **V**) or $ClB(C_6F_5)_2$ (**IV**). The 9-borafluorene derivative, however, could not be prepared by reaction of $C_{12}F_8Li_2$ with $Cl_2B(C_6F_5)$, because ether solvent was required and the resulting Et_2O adduct of **VI** could not be conveniently freed of the base without decomposition. The milder, hexane soluble fluorinated stannole reagent[108] (Scheme 15) proved to be a suitable reagent for this synthesis.

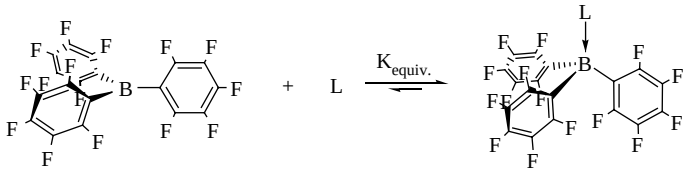
C. *Lewis Base Adducts of $B(C_6F_5)_3$ and Related Compounds*

Due to its thermal and protic stability, $B(C_6F_5)_3$ forms stable, isolable adducts with many Lewis bases [Eq. (4)], including weak Lewis bases often activated by Lewis acids for selective organic transformations. Because of the high LA strength of the borane,



SCHEME 15.

the equilibrium of Eq. (4) generally strongly favors the adducts, which can often be isolated and crystallized. Many adducts have, therefore, been characterized crystallographically, providing a bank of structural information that gives insights not only into the primary LA·LB interaction but also secondary bonding contacts that influence the behavior of these complexes. Although thermodynamically favored, kinetically these adducts are generally quite labile, with bound LB exchanging rapidly with free ligand in most instances. Solution NMR studies have, therefore, provided detailed information on the dynamic behavior of these species.



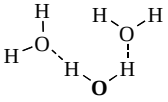
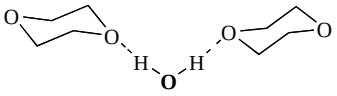
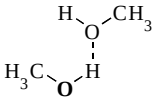
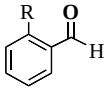
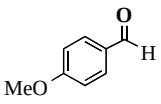
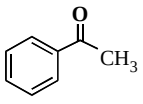
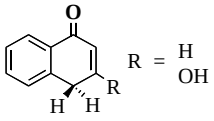
(4)

Adducts of $B(C_6F_5)_3$ that have been studied in detail either in solution or the solid state are collected in Table I along with selected solution NMR spectroscopic data and metrical parameters. In particular, both the ^{11}B NMR chemical shift[35] and the separation between the resonances for the *meta* and *para* fluorine atoms in the ^{19}F NMR spectrum[109] are quite sensitive to the environment about the boron center and the strength of the $LB{\cdot}B(C_6F_5)_3$ interaction. Indeed, as shown in Fig. 1, a rough empirical correlation between these two NMR parameters is observed. Anomalies arise for two classes of LB: more linear bases like nitriles or isonitriles that do not pyramidalize the boron center as severely and the RM^I adducts (M = Al, Ga).

1. O-Bound Adducts (Table I, Entries 1–15)

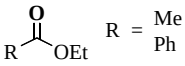
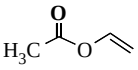
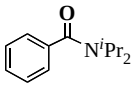
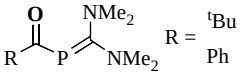
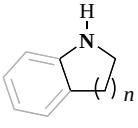
Although it was noted early on that $B(C_6F_5)_3$ is stable to hydrolysis, the chemistry of the water adduct of $B(C_6F_5)_3$ was not seriously pursued until the early 1990s when it was recognized that it may have utility as a Bronsted acid initiator for carbocationic polymerizations and other applications. Siedle and co-workers appear to be among the first to report that, when treated with excess water, $B(C_6F_5)_3$ forms a trihydrate in which one water coordinates directly to the boron center, and two others ligate in the second coordination sphere *via* strong hydrogen bonds.[110] This was initially supported by ^{17}O NMR spectroscopy on the labeled material, which showed resonances at 22.0 and 2.3 ppm in a 1:2 ratio. Later, Green *et al*. confirmed the trihydrate structure crystallographically by crystallizing the compound from a wet solution of $B(C_6F_5)_3$ in chloroform.[111] The dihydrate has also been characterized in solution and in the solid state as a DMSO solvate[112] (Entry 2). Clearly, the Lewis acidity of the borane imparts strong Bronsted acidity on the water molecule directly bonded to the boron center. Parkin and Norton have measured the pK_a of the dihydrate, which forms preferentially in acetonitrile solution, to be 8.4.[113] This is about the same acid strength as HCl in this medium. Thus, the polarized O–H bonds readily ligate further Lewis bases, including ^tBuOH,[113] the $[HOB(C_6F_5)_3]^-$ anion,[114] the amino alcohol $BzN(H)C_6H_{10}OH$[115] and dioxane[116] (Entries 2 and 4); the structures of these derivatives have been determined. Even in the monohydrate, whose structure has also been reported,[117] the ligated H_2O is stabilized by O–H···F hydrogen bonds to *meta* fluorine atoms on adjacent molecules.

TABLE I
NEUTRAL LEWIS BASE ADDUCTS OF $B(C_6F_5)_3$ WITH SELECTED NMR AND METRICAL DATA

E	Lewis base[a]	$\delta\,^{11}B$ (ppm)[b]	$\Delta\,\delta_{m,p}$ (ppm)[c]	B − X (Å)	Σ_{C-B-C} (°)[d]	References
1		6.65		1.597(2)	341.3	117
			8.9			110
			8.68			113
2	 B = H_2O		7.7			118
	H_2O·DMSO	−0.6		1.565(2)	338.75	112
	^{t}BuOH		7.6	1.583(3)	340.5	113
	$(C_6F_5)_3BOH$		4.7	1.529(6)		114
	$BzN(H)C_6H_{10}OH$			1.498(5)		115
3				1.577(1)	339.1	111a
			7.4			118
			7.9			111b
4			7.7	1.565(3)	338.0	116
5			7.9	1.557(2)	336.7	113
6		2.6	7.8			125
7	 R = H	5.0	8.2	1.610(8)	340.2	127
	OMe	3.3	8.2	1.589(5)	340.6	265
	F		7.6	1.603(4)	341.4	130
8		3.2	7.5	1.574(1)	340.2	
9		2.3	7.5	1.576(5)	337.7	127
10	 R = H	0.1	6.8	1.547(3)	335.3	131
	OH	−0.6	6.8	1.553(5)	335.6	

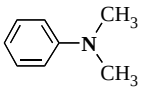
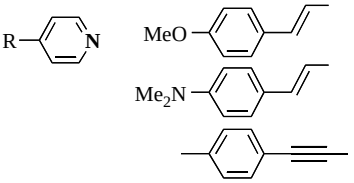
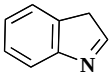
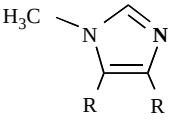
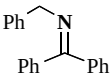
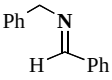
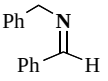
(*Continued*)

TABLE I
CONTINUED

E	Lewis base[a]	$\delta\,^{11}B$ (ppm)[b]	$\Delta\,\delta_{m,p}$ (ppm)[c]	B − X (Å)	Σ_{C-B-C} (°)[d]	References
11	 R = Me, Ph	−0.7 19.2	 10.7	 1.594(6)	 339.3	133 127
12		15.6	10.3			132
13		−0.1	7.0	1.52(1)	330.0	127
14	 R = ^{t}Bu, Ph			1.506(3)	334.3	129
15	 R = R′ = Et	−2.6		1.533(3)	338.3	
	Ph	−9.2	6.2	1.538(3)	340.6	
	^{n}Pr	−2.6	6.2			
	^{n}Oct	−3.8	5.9			
	OMe	−1.7	6.8			
	OEt	−3.7	7.2			
	OPh	−1.2	7.0			
	R = H; R′ = OEt	−2.1	6.8			
	H, O^{n}Bu	−2.2	7.0			133
	H, OPh	−0.2	7.0			
	Me, OMe	−1.2	6.9			
	Me, OEt	−2.5				
	Ph, OEt	−1.6				
	OEt, Me	−9.3				
16	 R = H, R′ = ^{t}Bu	 −9.1	6.6 5.0 7.1	 1.633(4)	 331.8	 6 137
	R = R′ = CH_3					
	Et					
17	 n = 1, 2	−3.1 −2.1	6.9	1.628(2) 1.630(3) 1.650(2)	330.8 332.4 333.5	135 135 136
	Ph					

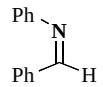
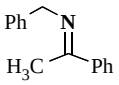
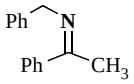
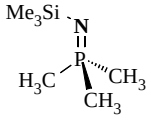
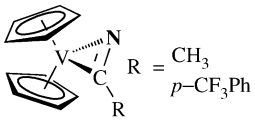
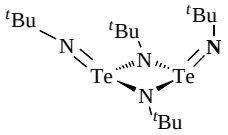
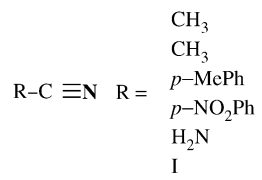
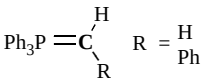
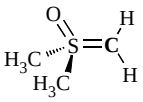
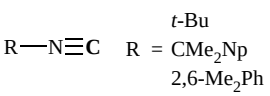
(*Continued*)

TABLE I
CONTINUED

E	Lewis base[a]	δ ^{11}B (ppm)[b]	$\Delta\ \delta_{m,p}$ (ppm)[c]	B − X (Å)	Σ_{C-B-C} (°)[d]	References
18		−2.9	6.3			140
19	 R = H		6.4			6
	R = H		7.11			18
	R = Me_2N	−5.3	5.9	1.602(6)	333.4	142
		−4.1	6.3			142
	R = MeO	−4.2	6.3			142
	R = Me_2N	−2.8	6.5	1.620(3)	334.9	142
20	 1	−4.0	7.3	1.644(3)	336.3	
	2	4.5	8.5	1.678(3)	338.2	143
				1.687(3)	339.0	
	3	18.6	11.4			
21		−7.6	6.9	1.608(2)	336.0	144
22		−3.5	7.5	1.613(3)	333.4	136
23	 R = H	−8.0	6.0	1.605(6)	334.0	146a
				1.597(6)	332.5	
	R = H	−8.7	7.1	1.588(2)	333.0	146b
	R = CH_3	−7.9	6.8	1.600(3)	333.2	146b
	R = 1,2-C_6H_4					
24		−3.7	6.7 (−40 °C)	1.642(8)	330.3	148
25		−6.6	7.5 (−40 °C)			148
26		−3.3	7.1 (−40 °C)	1.627(3)	332.5	148

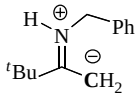
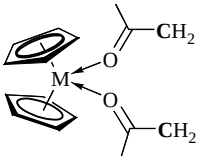
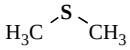
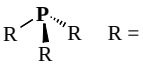
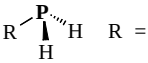
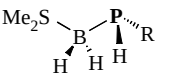
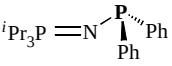
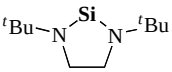
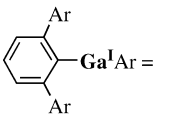
(*Continued*)

TABLE I
CONTINUED

E	Lewis base[a]	$\delta\,^{11}B$ (ppm)[b]	$\Delta\,\delta_{m,p}$ (ppm)[c]	B − X (Å)	Σ_{C-B-C} (°)[d]	References
27			8.2 (−20 °C)	1.649(4)	334.1	148
28			7.0 (−40 °C)	1.630(6) 1.658(6)	330.2 332.2	148
29		−4.7	7.0 (−40 °C)	1.640(2)	330.3	148
30		−11.2[e]	6.1	1.623(6)	324.9	149
31				1.586(3) 1.588(3)	334.1 333.4	150
32		−6.1	6.43	1.632(4)		151
33			7.8	1.610	342.6	113
		−10.3	8.4	1.616(3)	342.9	152a
		−9.6	7.6			152a
		−10.2	8.0	1.595(3)	342.0	152a
		−12.0	6.8	1.573(4)	338.0	152b
		−8.0	7.5	1.608(5)	342.0	152b
34		−14.9	4.2	1.675(2)	329.9	154
		−11.0	4.9	1.717(3)	325.4	
35		−16.3 (100 °C)	5.5	1.674(3)	330.7	153
36			7.6	1.624(4)	340.5	
		−21.8	7.6	1.624(4)	339.5	152a
		−21.7	7.5			
		−21.0				

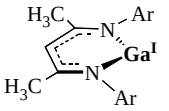
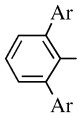
(*Continued*)

TABLE I
CONTINUED

E	Lewis base[a]	δ ^{11}B (ppm)[b]	$\Delta\ \delta_{m,p}$ (ppm)[c]	B − X (Å)	Σ_{C-B-C} (°)[d]	References
37		− 12.2	5.36	1.715(2)	326.8	148
38	 M = Ti, Zr, Hf			1.696 1.710(9)	329.0 330.2	155
39		− 2.3	19.7	2.091(5)	340.5	158
40				2.084(1)	341.4	159
41	 R = H, CH_3, Ph	− 2.5	7.1	2.046(8) 2.061(4) 2.180(6)	343.0 337.2 339.9	160 162 152a
42	 R = ^{i}Bu, Ph	− 15.5	7.2	2.015(3) 2.039	336.9 338.2	29 158
43	 R = H, Ph	− 17.4 − 14.5	5.4	2.049	339.0	158
44		34.8[e]	6.5	2.135(5)	336.4	163
45		− 14.3	7.4 7.1			164
46	 R = Al, Ga, Ga	− 32.9 − 19.6 − 17.9	4.9 6.7 9.24	2.169(3) 2.153(6) 2.160(2)	339.8 342.3 342.2	165 166b 166a
47	 Ar = 2,4,6–^{i}PrPh, 2,6–^{i}Pr–4–^{t}BuPh, 2,6–^{i}PrPh	− 18.9 − 18.0 − 17.7	5.27 5.24 4.82	2.110(3) 2.108(2) 2.129(3)	337.0 340.1 337.5	167

(*Continued*)

TABLE I
CONTINUED

E	Lewis base[a]	δ ^{11}B (ppm)[b]	$\Delta\ \delta_{m,p}$ (ppm)[c]	B − X (Å)	Σ_{C-B-C} (°)[d]	References
48	 Ar = 2,6-^{i}PrPh	− 20.3	4.01	2.156(1) 2.142(3)	334.3 332.8	169
49	 Ar = 2,4,6–^{i}PrPh 2,6–^{i}PrPh	− 13.7 − 14.1	4.52 5.05	2.322(2) 2.153(6)	337.8 338.9	168

[a]Atom bonded to boron is indicated in bold.
[b]Referenced to $BF_3{\cdot}OEt_2$ unless otherwise indicated.
[c]The difference in chemical shift between the *meta* and *para* fluorine atoms in the ^{19}F NMR spectrum. Some values are averaged over inequivalent $-C_6F_5$ rings.
[d]The sum of the B–C–B angles.

In solution, $B(C_6F_5)_3$ is a powerful water scavenger, and each of the mono, di and trihydrates are observable by ^{1}H and ^{19}F NMR spectroscopy. Beringhelli *et al*. have performed careful titrations of $B(C_6F_5)_3$ solutions to fully characterize the dynamic behavior of these adducts in toluene solution.[118] Their results are corroborated by the Parkin and Norton study. These experiments demonstrate that, while equilibria strongly

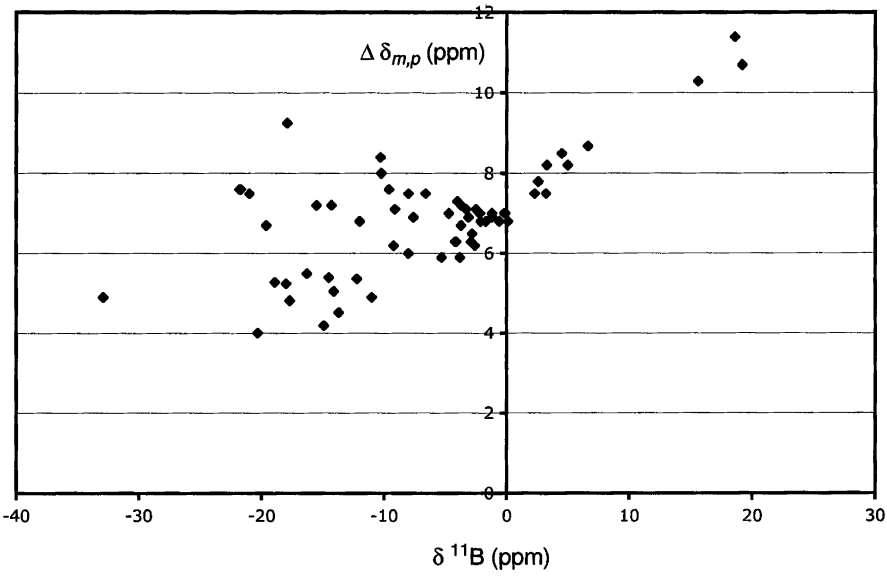
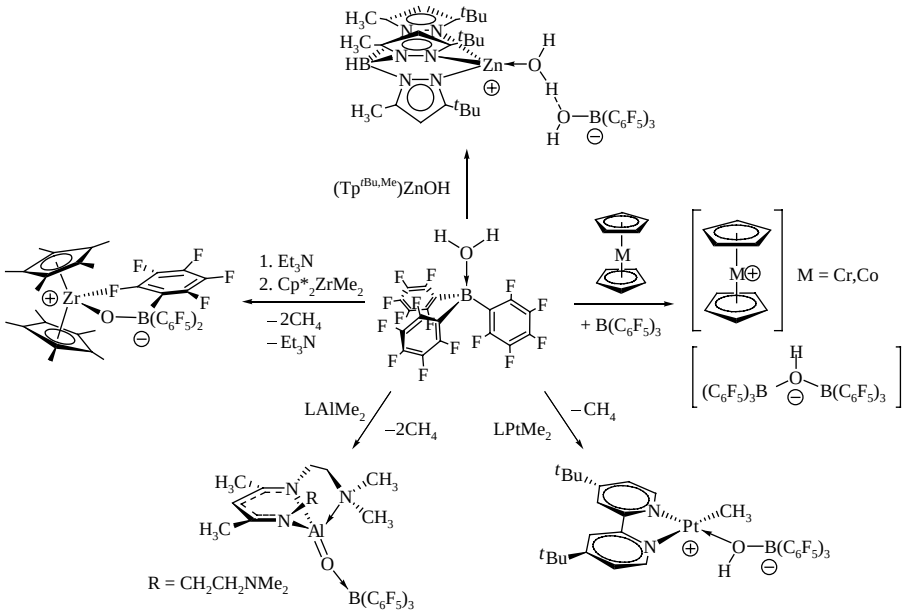


FIG. 1. Plot of δ ^{11}B vs. $\Delta_{m,p}$ (the difference in ppm between the chemical shifts of the *meta* and *para* fluorine atoms in the ^{19}F NMR spectrum).

favor the hydrates, the compounds are highly dynamic in solution. Exchange between bound and free H_2O *via* a dissociative mechanism is observed, along with rapid intra and intermolecular exchange of H-bound water and intramolecular exchange of H-bound with B-bound water. Interestingly, the calculated binding energy of the first H_2O (-9.4 kcal mol^{-1}) is somewhat less than that for the second (-12.9 kcal mol^{-1}) and third (-9.6 kcal mol^{-1}) water ligands, reflecting the energy required to pyramidalize the boron center in the first water binding event.

The monohydrate is a useful Bronsted acid reagent whose conjugate base is the weakly coordinating $[HOB(C_6F_5)_3]^-$ anion. It can be prepared either by careful stoichiometric reaction of $B(C_6F_5)_3$ with one equivalent of water in pentane, or by reaction of the trihydrate with two equivalents of pure, dry $B(C_6F_5)_3$. Examples of its utility are shown in Scheme 16. Protonation of TpZnOH results in the cationic Zn hydrate in a study modeling carbonic anhydrase function.[119] Green and Doerrer have used the reagent to protonate and oxidize metallocenes Cp_2M (M = Cr, Fe, Co); these reactions are aided by the presence of an extra equivalent of $B(C_6F_5)_3$, which generates the even more WCA $[(C_6F_5)_3B(\mu\text{-}OH)B(C_6F_5)_3]^-$.[117] Alkyl groups in organometallic compounds can be removed protolytically to form reactive cations. In the bipyridyl platinum derivative, one methyl group is lost as methane, leaving a contact ion pair with one remaining Pt–Me group[120] while Roesky has observed loss of two equivalents of methane from the β-diketiminato dimethyl aluminum complex shown, to yield what is effectively the $LAl{=}O{\cdot}B(C_6F_5)_3$ adduct, a stabilized monoalumoxane.[121]

This chemistry is related to the reaction of $[Et_3NH]^+[HOB(C_6F_5)_3]^-$ with $Cp^*_2ZrMe_2$, reported 10 years ago by Siedle in his early explorations of the chemistry of the water adducts of $B(C_6F_5)_3$ (Scheme 16).[122] The motivation for this work was to devise



SCHEME 16.

new ways to generate the active cationic species in olefin polymerization reactions, but the $[HOB(C_6F_5)_3]^-$ anion proved too reactive and a major decomposition pathway involved further protonation of the remaining alkyl group to form the observed zirconoxyborane, essentially an adduct between $Cp^*_2Zr{=}O$[123] and $B(C_6F_5)_3$. Use of Bronsted acidic alcohol adducts (for example, Entry 5, Table I) eliminates this problem and several of these adducts have been explored as co-catalyst systems in some detail.[110a] Unfortunately, transfer of the RO^- group to the cationic metal center is a significant drawback in these catalyst systems at higher temperatures. Longer chain alcohols and thiols have also been examined in this regard.[124] While the $[REB(C_6F_5)_3]^-$ (E = O, S) anions are not overly compatible with metallocenium ions, they can be effective in cationic polymerization applications (see Section VII.D.1).

Because ethereal solvents are used in the synthesis of $B(C_6F_5)_3$, the Et_2O and THF adducts are known, but have not been fully characterized.[125] However, several adducts between $B(C_6F_5)_3$ and molecules with carbonyl functions have been studied in detail (Table I, Entries 7–14) due to the importance of such complexes in LA catalyzed transformations of the C=O group.[126] The strength of the interaction between the carbonyl compound and $B(C_6F_5)_3$ tends to be dominated by steric effects, although the organic amide of Entry 13 binds the strongest, indicating the electronic effects can be important as well. Indeed, this is one of the few $B(C_6F_5)_3$ adducts for which exchange between free and bound Lewis base is slow on the NMR timescale.[127] The X-ray crystal structure (Fig. 2) offers some insight into the origins of the observed strength of this adduct. The borane coordinates *syn* to the Ph group of $PhC(=O)N^iPr_2$ and is able to do so because the phenyl group is twisted out of conjugation with the C=O moiety. Pi donation from the amide nitrogen and the C=O function further polarizes the C–O bond and

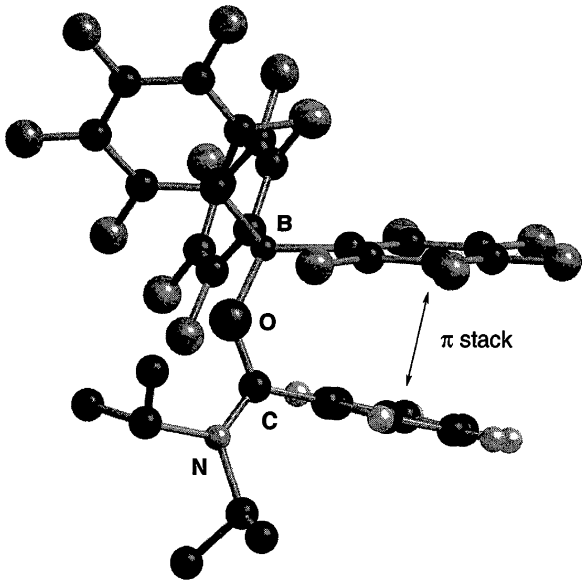
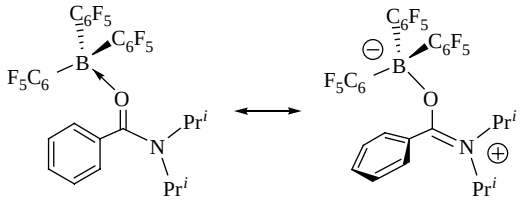
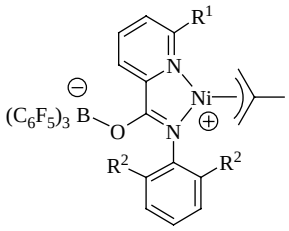


FIG. 2. Solid-state structure of the $PhC(O)N^iPr_2{\cdot}B(C_6F_5)_3$ adduct, illustrating the π stacking interaction.



SCHEME 17.

strengthens the B–O linkage in the adduct. This is reflected in a short C–N (1.28(1) Å) bond with significant double bond character and a shorter B–O (1.52(1) Å) bond than in comparable adducts. These observations are supportive of a significant contribution from a zwitterionic iminium/alkoxyborate resonance structure to the ground state of this adduct (Scheme 17). Bazan and Lee have instituted a similar strategy for generating olefin polymerization catalysts through a strong zwitterionic $B(C_6F_5)_3$ linkage with an electron-rich C=O moiety incorporated into the ligand backbone of a family of nickel based complexes, for example, the family of catalysts **VII**.[128] The adducts of Entry 14,



VII

involving electron-rich carbonyl functionalized phosphaalkenes, also make use of the tendency towards and alkoxyborate resonance structure, forming strong adducts; the example where R = Ph exhibits a very short B–O distance of 1.506(3) Å.[129]

The view of the $B(C_6F_5)_3{\cdot}PhC(=O)N^iPr_2$ in Fig. 2 brings to light another relatively common feature of adducts between $B(C_6F_5)_3$ and Lewis bases containing phenyl moieties in that the adduct is further stabilized by a $-C_6F_5/-C_6H_5$ π-stacking interaction. One of the borane's C_6F_5 rings is nearly parallel to the amide phenyl group and an analysis of the bond angles in the complex indicates that this arrangement is not due simply to packing forces. Typically, such interactions are worth about 3–4 kcal mol^{-1},[38] and, therefore, do not contribute significantly to the overall bonding picture, but to the extent that such interactions have the potential to orient the Lewis base in specific ways, there is potential to exploit this structural motif in stereoselective transformations.

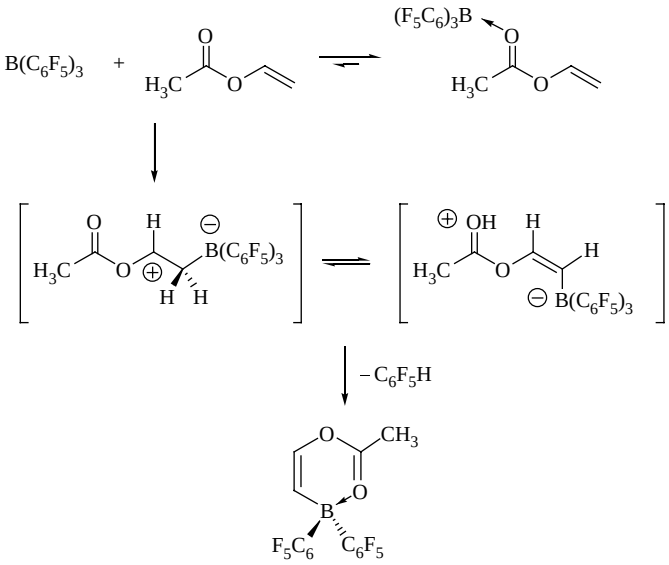
In other aromatic carbonyl compounds, the relative binding strength is based mainly on steric considerations. For benzaldehydes (Entries 7 and 8),[127,130] equilibrium constants are on the order of 10^4 for adduct formation and the borane binds *syn* to the sterically insignificant aldehyde proton. In the acetophenone adduct, the borane binds *syn* to the methyl group, but the equilibrium constant is an order of magnitude lower due to

the greater steric bulk of the methyl group relative to the proton. Finally, in esters such as ethyl benzoate (Entry 11), the borane is forced to coordinate *syn* to the phenyl group due to unfavorable interactions with the OEt group, which prefers a *Z* geometry, when coordinated *syn* to this group. While this engenders a $-C_6F_5/-C_6H_5$ stacking interaction, this is the weakest adduct in the series with a K_{eq} of about 10^2.

The keto tautomers of two 1-naphthols may be apprehended by treatment with $B(C_6F_5)_3$, forming the adducts of the α,β unsaturated ketones shown in Entry 10.[131] Whereas phenol forms a modestly stable adduct with $B(C_6F_5)_3$,[110a] dearomatization of the naphthyl framework is more favored so as to form a stronger adduct with the ketone function. Since the adducts are labile, the thermodynamically most favored adduct forms preferentially even though the keto tautomer is much less stable than the naphthol form of the substrate. Further reaction of the adduct where R = H with Schwartz's reagent, $[Cp_2Zr(H)Cl]_n$, results in selective reduction of the OH functionalized aromatic ring of the naphthol framework.

The dynamism of these systems is further illustrated in the chemistry of the adduct of vinyl acetate (Entry 12), where reversible coordination of the C=O function dominates, but competes with electrophilic attack of the vinyl group of the ester moiety (Scheme 18).[132] Irreversible proton transfer from the OH tautomer of this minor olefin adduct results in the expulsion of C_6F_5H and formation of the internally coordinated adduct shown as the eventual thermodynamic product in the reaction. A related chelating RC(=O)OR species results from the hydroboration of $H_2C{=}C(H)CH_2CH_2C(=O)OEt$ using $HB(C_6F_5)_2$.[30]

Beckett *et al*. have prepared and studied a range of related phosphine oxide adducts of $B(C_6F_5)_3$ (Entry 15).[133] Phosphorus substituent effects influence the strength of the $R_3P{=}O{\cdot}B(C_6F_5)_3$ interaction, with donor R groups increasing the contributions from



SCHEME 18.

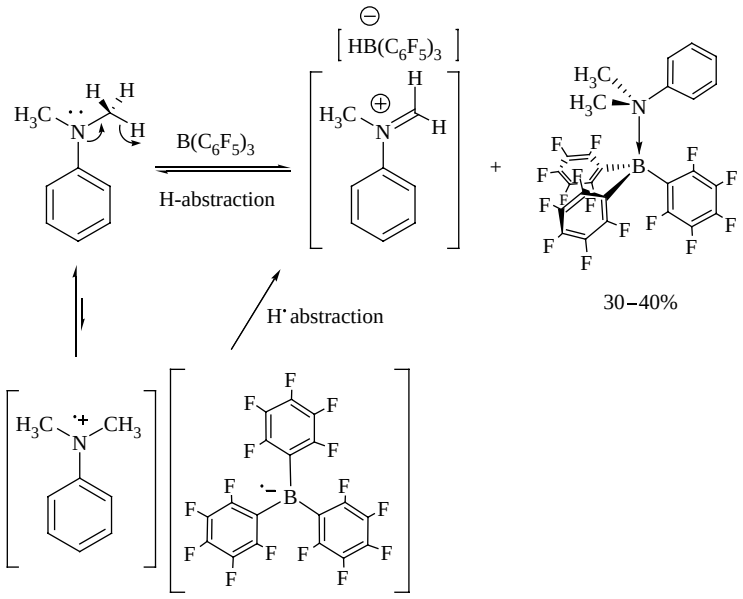
a zwitterionic resonance structure, i.e., $[R_3P^+–O–B^-(C_6F_5)_3]$. The X-ray structure of the $Ph_3P{=}O$ adduct again reveals π-stacking interactions between $–C_6F_5$ and C_6H_5 groups.

2. N-Bound Adducts (Table I, Entries 16–33)

The simple ammonia, trimethylamine and triethylamine adducts[5,6] were among the first reported in early studies by Massey and Park. The most interesting, the NH_3 adduct, is remarkably stable, but unlike the water adduct has not been subsequently explored in detail as a Bronsted acid reagent. It is a white, crystalline solid that can be purified by recrystallization or sublimation at 170 °C under high vacuum, attesting to its high thermal stability. Indeed, prolonged thermolysis at 220° led only to small amounts of C_6F_5H, with no evidence of tris-(pentafluorophenyl)borazine formation as expected on the basis of analogous chemistry with $H_3N{\cdot}BR_3$ adducts. Tris-(pentafluorophenyl)borazine was prepared by another route.[134]

Although pK_a measurements have not been performed on $H_3N{\cdot}B(C_6F_5)_3$, a recent structural study on the adducts of the cyclic secondary amines of Entry 17 provides evidence that the N–H protons of coordinated amines should be reasonably acidic,[135] although the indole adduct was not deprotonated by Et_3N.[136] Strong N–H···F hydrogen bonds involving the *ortho* F atoms of two of the $–C_6F_5$ rings are observed in the solid-state structures of these adducts and variable temperature ^{19}F NMR spectroscopy demonstrates that these interactions are maintained in solution. Similar contacts have been observed in the structure of the $^tBuNH_2$ adduct (Entry 16).[137] Further C–H···F hydrogen bonding is observed in the C_4H_5NH adduct between an *ortho* F and a C–H bond α to the nitrogen. These weak C–H···F contacts highlight a second structural motif that provides a higher degree of secondary structure ordering in the adducts of $B(C_6F_5)_3$, and similar interactions have recently been proposed as playing a role in the stereo directing behavior of a family of single site olefin polymerization catalysts.[138] Weak C–H···F contacts have also been identified in $B(C_6F_5)_3$ adducts of aldehydes RCHO.[127]

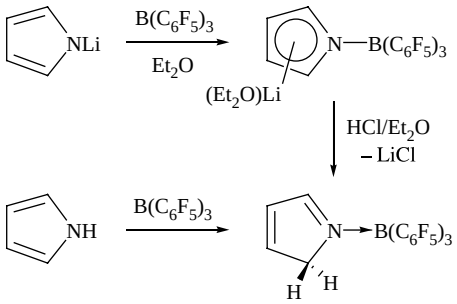
N,N-dialkylanilines are often used in conjunction with $B(C_6F_5)_3$ and the protic silica surface to introduce anilinium-based activators on the support surface.[139] In this context, Santini and Basset reported a detailed study on the reactions between $B(C_6F_5)_3$ and R_2NPh (R = Me, Et).[140] The chemistry is more complex than straightforward adduct formation and the products observed led the authors to propose hydride abstractions to explain the formation of iminium ions with $[HB(C_6F_5)_3]^-$ counteranions. For R = Et, in fact, no adduct formation is observed, while in the case of the dimethyl aniline, the equilibrium concentration of the adduct is only about 30–40% (Scheme 19). It should be noted, however, that solutions of $R_2NPh/B(C_6F_5)_3$ are pale pink in color, reminiscent of the intense red color observed for the chelating amino borane shown in Scheme 12. In our hands, the $R_2NPh/B(C_6F_5)_3$ solutions are ESR active,[141] suggesting charge transfer to form a radical cation/radical anion pair to some small degree. It is, therefore, conceivable that the formation of the observed products involves transfer of hydrogen atoms rather than hydride abstractions. The use of $B(C_6F_5)_3$ as a one electron oxidizing agent has been reported (see Section V.B). In any case, the addition of protic sources such as R′OH to these complex mixtures results in the complete formation of an $[R_2N(H)Ph]^+$ $[R'OB(C_6F_5)_3]^-$ ion pair, believed to be the activator species on the silica surfaces.



SCHEME 19.

Several pyridine Lewis bases form strong adducts with $B(C_6F_5)_3$ (Entry 19).[6,28c] Marder *et al*. have prepared adducts with pyridines incorporating extended conjugation for testing in non-linear optical applications.[142] Incorporation of the electron withdrawing borane into these molecules results in highly fluorescent molecules with enhanced dipole moments and second order non-linear optical coefficients. Up to three equivalents of $B(C_6F_5)_3$ can be added to trifunctional Lewis base 1,3,5-triazine, Entry 20, but halogenated derivatives ($C_3X_3N_3$) are too weak to form adducts.[143]

Imines also form adducts with $B(C_6F_5)_3$, and Erker *et al.*[144] and Resconi and coworkers[136] have used this to clever advantage in preparing a new family of Bronsted acids comprised essentially of the $B(C_6F_5)_3$ adducts of the thermodynamically less stable tautomers of pyrrole and derivatives (Entries 21 and 22, Scheme 20). Erker's preparation of the compound relies on protonation of the lithium pyrrolyl borate with HCl; Resoni has



SCHEME 20.

found that the direct reaction of pyrrole with $B(C_6F_5)_3$ leads rapidly to the same compound, circumventing the need to proceed *via* the lithium pyrrolyl reagent. The metrical and NMR parameters associated with this species are close to other genuine imine adducts and suggest that the compound is best formulated as an imine adduct, rather than an iminium borate. The compound is a strong enough Bronsted acid to protonate off alkyl groups from typical group 4 metallocene ethylene polymerization precatalysts, and the resulting pyrrolylborate anion is relatively robust and weakly coordinating.[145] This type of Bronsted acid has been incorporated directly into metallocene ligand structure by treatment of a pendant $-B(C_6F_5)_2$ group directly with pyrrole.[40] Related adducts of *N*-methylimidazole derivatives (Entry 23) have also been structurally characterized and deprotonated to generate borate substituted analogs of Arduengo carbenes.[146] The adduct of the parent imidazole base is a strong Bronsted Lewis acid capable of activating Cp_2ZrMe_2 with loss of CH_4, but the $[(C_3H_3N_2)B(C_6F_5)_3]^-$ anion is quite strongly coordinating *via* the free imidazole nitrogen.[147]

Erker and Resoni have both pointed out a general feature of the adducts of $B(C_6F_5)_3$ in their analysis of the crystal structures of the pyrrolyl and imidazolyl adducts of Entries 21–23. In many $LB{\cdot}B(C_6F_5)_3$ compounds, two of the $-C_6F_5$ groups exist in a two-bladed propeller array, while the other is more or less aligned with the LB → B vector, serving as a "pivot" group for the propeller. This structural feature is manifested in wide ranging values for the C–B–C angles; one of the three is invariably close to $104 \pm 2°$, while the other two are $\approx 115 \pm 2°$. Thus, the boron center is generally not smoothly pyramidalized and there is always some asymmetry in the C–B–C angles, possibly to accommodate secondary hydrogen bonding or π–π stacking interactions and the rigid two blade propeller conformation. Exceptions to this general observation involve LB that exhibit C_3 symmetry, for example, the R_3P bases (see below).

The structures of several aryl aldimine and ketimine adducts of $B(C_6F_5)_3$ have been determined and correlated with solution structures (Entries 24–29).[148] In solution, the thermodynamically more stable *E* imines are initially complexed as a kinetic adduct (e.g., Entries 25 and 28) that slowly converts to the thermodynamic adduct of the *Z* imines (e.g., Entries 26 and 29) as the borane traps the less thermodynamically stable isomer of the imine. In the presence of excess $B(C_6F_5)_3$ the conversion from the kinetic adduct to the thermodynamic product is slowed considerably, indicating that the isomerization occurs *via* the free imines rather than *via* the adduct itself. In the solid state, the subtle effects that $-C_6F_5/-C_6H_5$ π stacking interactions exert on adduct stability are particularly apparent in these compounds. For example, the adducts of Entries 26 and 27 differ only in the N-substituent, which is benzyl for Entry 26 and phenyl for 27. For the *N*-benzyl derivative, a strong π-stack is observed, while the *N*-phenyl compound is geometrically precluded from such an interaction (Fig. 3). ^{19}F NMR studies confirm that the stacking interaction persists in solution. In a competition experiment, the borane selectively binds to the more basic *N*-benzyl imine; the stability of the adduct is undoubtedly enhanced by the favorable stacking interaction possible for this substrate.

Other imine-like adduct structures reported include the phosphinimine of Entry 30[149] and the coordinated nitrile in the vanadocene complex shown in Entry 31.[150] The tellurium diimide dimer (Entry 32) also coordinates one equivalent of $B(C_6F_5)_3$ and this adduct has been crystallographically characterized.[151] The structure features weak

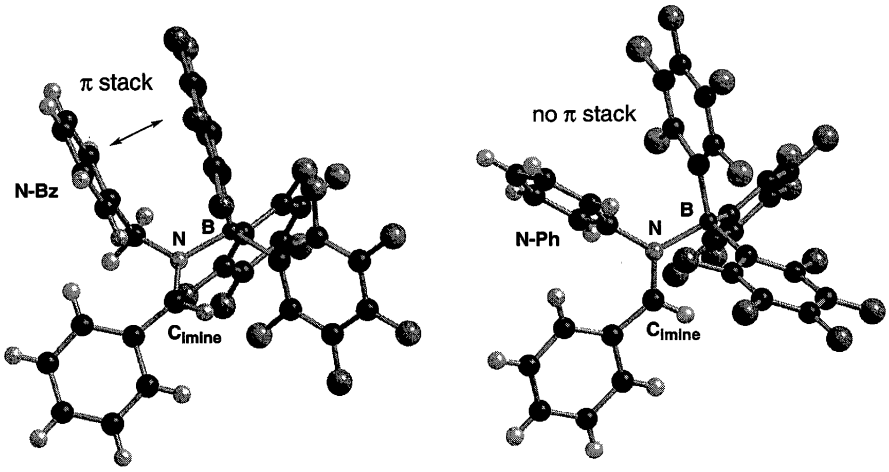


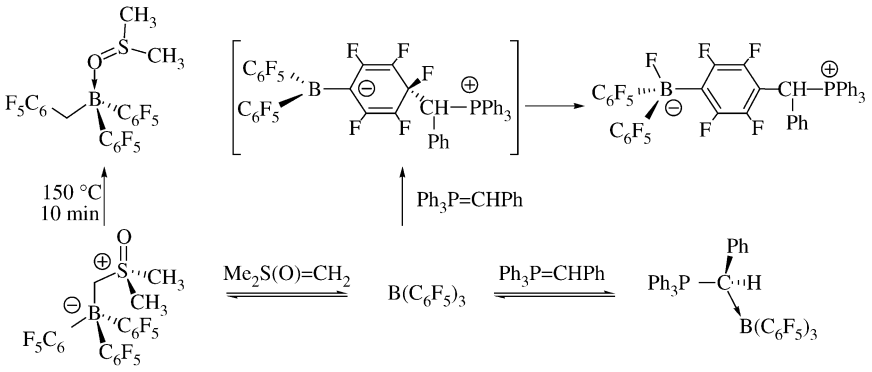
FIG. 3. Solid-state structures of the $Ph_2C{=}N(Bz){\cdot}B(C_6F_5)_3$ and $Ph_2C{=}N(Ph){\cdot}B(C_6F_5)_3$ adducts.

C–F···Te contacts, but the adduct is labile as evidenced by the observed ring opening of THF by the $B(C_6F_5)_3$/base combination in this system. Simply dissolving the adduct in THF results in the rapid formation of a zwitterionic product in which an iminium center is separated from an alkoxyborate by the atoms of the opened THF molecule.

Nitriles also coordinate readily to $B(C_6F_5)_3$ and several have been structurally characterized and studied in solution. Indeed, acetonitrile is a sterically innocuous Lewis base that is often used in competition experiments to ascertain the relative Lewis acid strength of two perfluoroaryl boranes. Berke, Erker and co-workers have studied these adducts in some detail, along with the related isonitrile adducts of Entry 36.[152] Upon coordination to $B(C_6F_5)_3$, the C≡N bonds contract slightly, suggesting a significant σ component to the bonding. This was confirmed computationally, in studies which also showed that there is a strong electrostatic component to the bonding between $B(C_6F_5)_3$ and these bases. The authors conclude that, like BF_3, $B(C_6F_5)_3$ is a hard Lewis acid, but because of diminished π overlap between the $-C_6F_5$ substituents on boron with the empty Lewis acidic orbital on boron, there is more overlap with the donor orbital, making for stronger bonding between the LA and LB.

3. C-Bound Adducts (Table I, Entries 34–38)

In addition to the aforementioned isonitrile adducts,[152a] C-bound sulfur[153] and phosphorus[154] ylides have been characterized for $B(C_6F_5)_3$. While both sulfur and phosphorus ylides insert into B–C bonds to homologate the alkyl groups attached to boron, in the case of $B(C_6F_5)_3$, migration of $-C_6F_5$ to the ylid carbon has a high barrier. In fact, for the phosphorus ylid adducts, the thermal reactivity involves dissociation of the ylid which engages in the nucleophilic aromatic substitution on one of the borane perfluoroaryl rings (Scheme 21). In the case of the sulfur ylid adduct, migration can be induced, but only with heating to 150 °C. The product is the DMSO adduct of the novel perfluoroaryl borane $C_6F_5CH_2B(C_6F_5)_2$. The strong Lewis acidity of the boron center,



SCHEME 21.

and the lower the energy of the HOMO orbital of the migrating group (i.e., $-C_6F_5$) serve to raise the barrier to migration substantially in these compounds relative to non-fluorinated borane analogs.

The bulky ketimine $BzN{=}C(^tBu)CH_3$ does not bind $B(C_6F_5)_3$ at the nitrogen, rather, the iminolate tautomer is trapped as the C-bound adduct shown in Entry 37.[148] Excess borane is required to drive the equilibrium far enough towards the adduct to isolate it as a solid. The bis-(propenolato) group 4 bent metallocene compounds of Entry 38 react directly with excess $B(C_6F_5)_3$ by electrophilic attack at the enolate carbons to give the zwitterionic products, two of which have been crystallographically characterized.[155] Lability again plays an important role in the chemistry of these compounds, which serve as initiators for the polymerization of methylvinyl ketone *via* a group transfer mechanism;[156] dissociation of the borane from the enolate complexes to free it up to activate the monomer is key to the chain propagation step.

Surprising addition of $B(C_6F_5)_3$ to the carbon atom of coordinated CO in $Cp_2Ti(CO)_2$ was recently reported and the bonding in these unusual complexes discussed.[157]

4. Adducts Bound Through Heavier Main Group Elements (Table I, Entries 39–49)

The final Entries of Table I show adducts of heavier element bases that have been prepared. Adducts of the simple thioethers dimethylsulfide[158] and THT[159] have been reported. Phosphine adducts were among the first prepared, and several have been fully characterized including the PH_3 adduct (Entry 41). Bradley and co-workers studied this adduct in some detail due to its potential to act as a storage molecule for PH_3, an important phosphorus source in semiconductor synthesis by MOVCD. Although adduct formation is facile, heating the solid gently at 50 °C results in quantitative release of PH_3; based on static vapor pressure measurements, an enthalpy of dissociation of $\approx 80\ kJ\ mol^{-1}$ was estimated.[29,160] This is substantially higher than the calculated value of $52\ kJ\ mol^{-1}$ reported by Berke and Erker for this adduct,[152] but the X-ray structure of $H_3P{\cdot}B(C_6F_5)_3$ reveals extensive intermolecular P–H···F hydrogen bonding, indicating that the crystal environment is providing added stability to the P–B interaction. In solution, the rate of exchange between free and bound PH_3 was measured

using 2D NMR techniques and a rate of $3.60 \pm 0.15\ s^{-1}$ (254 K) was obtained,[161] corresponding to a barrier to exchange of $126\ kJ\ mol^{-1}$. Given that the energy of pyramidalizing the boron center in planar $B(C_6F_5)_3$ has been calculated to be $94\ kJ\ mol^{-1}$ in forming the $H_3P{\cdot}B(C_6F_5)_3$ adduct,[152a] a solution bond energy of $\approx 32\ kJ\ mol^{-1}$ is predicted, in reasonable agreement with the calculated value of $52\ kJ\ mol^{-1}$, which would be expected to drop somewhat when the zero point energy correction is applied. This example again illustrates the importance of the crystal environment in stabilizing adducts of $B(C_6F_5)_3$, particularly for weaker Lewis bases.

Intramolecular, rather than intermolecular, C–H···F hydrogen bonds play a role in the structure of the $Me_3P{\cdot}B(C_6F_5)_3$ adduct (Fig. 4).[162] This material is highly insoluble in most organic solvents and irreversibly precipitates from systems where free PMe_3 and borane are potentially present. As a result, NMR data is not available for this species. As the view of the structure in Fig. 4 shows, the B–C and P–C bonds are nearly eclipsed, with essentially equal C–B–P–C dihedral angles of 16.4°. The C–B–C angles are also more or less equal at 112°; this is unusual, since most of the other adducts in Table I exhibit a much wider range of C–B–C angles due to attractive stacking interactions (see above) or repulsive steric contacts. The eclipsed geometry and high symmetry of the PMe_3 adduct appears to stem from two sets of three C–H···F hydrogen bonds, with distances of 2.475 and 2.566 Å as shown in the Figure. Such interactions appear to be absent in the Ph_3P adduct.[152a]

Adducts of secondary phosphines have also been studied in the context of MOVCD precursors,[29] as well as the dehydrocoupling of borane and phosphines to form B–P bond-based polymers.[158] Low to medium molecular weight poly(phenylphosphinoboranes) were isolated in the $B(C_6F_5)_3$ catalyzed dehydrocoupling of $PhPH_2{\cdot}BH_3$.

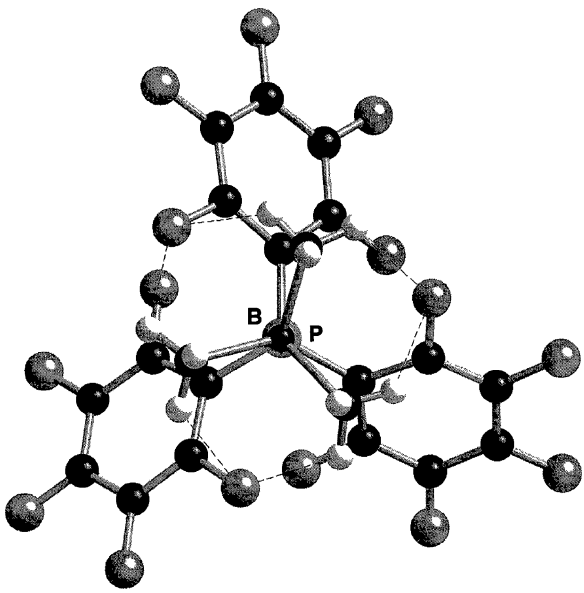


FIG. 4. Solid-state structure of the $Me_3P{\cdot}B(C_6F_5)_3$ adduct, illustrating the nearly eclipsed bonds and close C–H···F contacts.

The enhanced acidity of the P–H bonds upon coordination to $B(C_6F_5)_3$ is believed to lead to H_2 elimination in the presence of "BH_3", whose bonds are hydridic in character. The adducts of Entries 41 and 42 were isolated in connection with this preliminary study. The adduct of the phosphinimide–phosphine in Entry 44[163] has also been reported.

The stable silylene forms an adduct with $B(C_6F_5)_3$ that slowly (20 days) decomposes *via* transfer of a $-C_6F_5$ group to silicon, forming a novel silylborane (Entry 45).[164] Only partial adduct formation is observed when weaker Lewis acids such as $BPh(C_6F_5)_2$ or $ClB(C_6F_5)_2$ are reacted with the silylene.

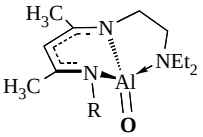
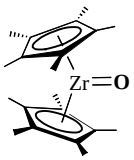
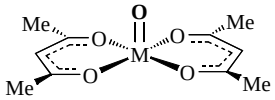
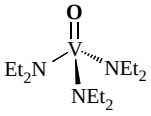
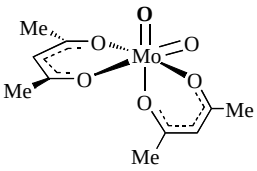
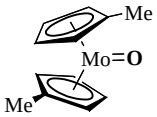
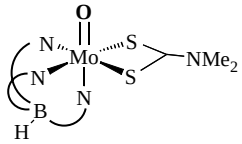
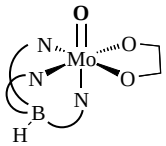
Various group 13 compounds in the +1 oxidation state have been stabilized *via* strong σ donation of their lone pair of electrons to $B(C_6F_5)_3$ to form the novel adducts of Entries 46–49.[165,166,167,168] Although all of these bases are either tetrameric or dimeric (with the exception of the (nacnac)Ga^I derivative of Entry 48[169]), the M–M interactions are weak enough that the monomeric compounds are rapidly trapped by the Lewis acid when treated with $B(C_6F_5)_3$. The fact that these compounds form so readily is indicative of the character of the LM(I) bases as strong σ donors; π back donation is negligible for the boron-based LA. Generally, shortening of the L–M bond distances are observed upon complexation, as the boron center withdraws electron density from the basic metal center, increasing the ionic component of the L–M interaction. In some instances, particularly for the heavier Ga and In derivatives, short F···M contacts involving the *ortho* fluorines are observed in the solid-state structures of the compounds.

5. Adducts of $L_nM{=}O$, $L_nM{\equiv}N$ and $L_nM{=}C$ Complexes

The role of M=O and M≡N bonds (Table II) in both hetero and homogeneous oxidation reactions has been a historically important question in organometallic chemistry. The observation that addition of Lewis acids to such systems often leads to enhanced activities has prompted several studies involving the reaction of $B(C_6F_5)_3$ with metal oxo and nitrido compounds. Consequently, several adducts have been prepared and studied; those that have been crystallographically characterized are collected in Table II. While most of these studies are straightforwardly synthetic and structural in nature, evidence that the action of the LA on the M=E bond and the resulting electronic perturbations at the metal center strongly influence the reactivity of the compounds hint at the role that LAs play in enhancing the performance of these compounds in small molecule chemistry.

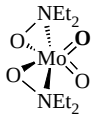
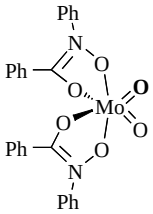
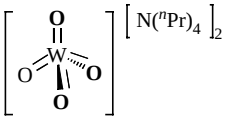
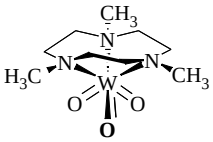
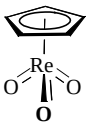
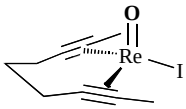
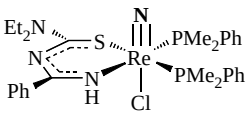
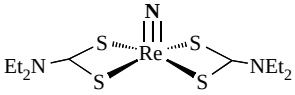
Entries 1 and 2 illustrate how $B(C_6F_5)_3$ can stabilize potentially highly reactive $L_nM{=}O$ compounds.[121,122] As described in Section V.C.1 these species were obtained indirectly *via* the reaction of polarized early transition metal alkyls with the water adduct of $B(C_6F_5)_3$, resulting in the elimination of CH_4 and trapping of the M=O species with the liberated LA (Scheme 16). Other compounds in Table II were invariably prepared by simple reaction of a stable $L_nM{=}O$ complex with $B(C_6F_5)_3$. For example, the vanadyl, titanyl and molybdyl compound of Entries 3,[170] 4[171] and 5 all form stable but labile adducts with $B(C_6F_5)_3$ in which the M=O bond is significantly elongated upon coordination of the LA. An adduct with the molybdocene $Cp'_2Mo{=}O$ ($Cp'{=}C_5H_4Me$) is also readily formed, but unlike the $Cp^*_2Zr{=}O$ adduct,[122] there are no close Mo–F contacts in this d^2 metallocene complex.[172] The LA does not dramatically affect the reactivity of

TABLE II
$B(C_6F_5)_3$ ADDUCTS WITH $L_nM{=}E$ (E = O, N, CR_2)

E	Lewis base[a]	$\delta\ ^{11}B$ (ppm)[b]	$\Delta\ \delta_{m,p}$ (ppm)[c]	B–X (Å)	Σ_{C-B-C} (°)[d]	References
1		−4.83	2.8	1.444(3)	327.4	121
2		3.3	5.3	1.460(6)	326.8	122
3	 M = Ti, V	1.5 −1.9	6.1 7.2	1.496(3) 1.527(2)	334.7 338.2	170
4		1.2	5.8	1.698(2)	336.9	171
5		4.7	6.8	1.521(3)	337.1	170
6		2.3		1.484(2)	330.5	172
7		2.5 −9.7		1.531(2)	332.7	174
8				1.538(7)	336.1	174

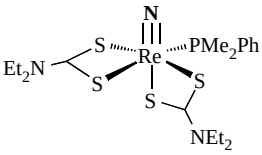
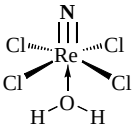
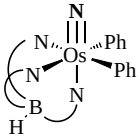
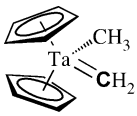
(*Continued*)

Table II
CONTINUED

E	Lewis base[a]	$\delta\ ^{11}B$ (ppm)[b]	$\Delta\ \delta_{m,p}$ (ppm)[c]	B–X (Å)	Σ_{C-B-C} (°)[d]	References
9		2.4		1.510(2)	332.3	175
10		3.3		1.508(2)	336.2	175
11		1.0	5.2	1.491(3) 1.508(3) 1.494(3)	335.4 336.3 337.5	176
12		0.3	5.1	1.499(5) 1.513(5)	328.1 328.7	176
13		5.2	7.1	1.568(5)	341.5	176
14				1.563	340.1	177
15				1.594(7)	330.1	178
16				1.58(3)	337.6	179

(*Continued*)

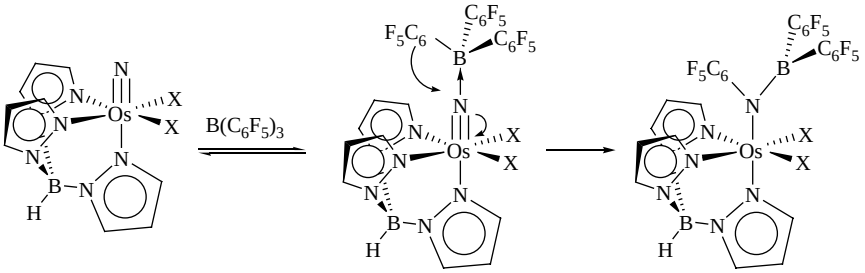
Table II
CONTINUED

E	Lewis base[a]	δ ^{11}B (ppm)[b]	Δ $\delta_{m,p}$ (ppm)[c]	B–X (Å)	Σ_{C-B-C} (°)[d]	References
17		−3.9		1.548(7)	332.5	174
18				1.589(7)	336.3	179
19			6.7	1.591(5)	335.9	180
20		−9.4	4.7	1.649(6)	326.5	181

[a]Atom bonded to boron is indicated in bold.
[b]Referenced to $BF_3{\cdot}OEt_2$ unless otherwise indicated.
[c]The difference in chemical shift between the *meta* and *para* fluorine atoms in the ^{19}F NMR spectrum.
[d]The sum of the B–C–B angles.

the molybdenum oxo moiety towards isocyanates; a similar 2 + 2 addition product is observed in both cases.[173] Given that this reaction is proposed to be governed by the high nucleophilicity of the Mo=O group, it may be that dissociation of the $B(C_6F_5)_3$ and activation of the isocyanate reagent is the path to the product.

Several vanadium, rhenium and molybdenum oxo compounds supported by Tp and dithiocarbamate ligands also form isolable adducts (Entries 7 and 8).[174] Despite the presence of several nucleophilic sites in these compounds, reaction at the oxo ligand occurs exclusively. The study reporting the adducts of the dioxo molybdenum derivatives in Entries 9 and 10 also indicates that an adduct of a molybdenum peroxo compound was observed in solution.[175] The oxo anions $[WO_4]^{2-}$ and $[ReO_4]^{1-}$ also add $B(C_6F_5)_3$ (Entry 11),[176] the tungsten derivative up to three equivalents by virtue of its higher nucleophilicity, while adducts of the neutral trioxo compounds of Entries 12 and 13 have also been characterized. Finally, in an effort to model the protonation of the oxo ligand in the rhenium dialkyne complex of Entry 14, Norton *et al*. characterized the adduct of $B(C_6F_5)_3$, inferring the oxo ligand as the site of protonation.[177]



X = Cl; not observed
X = Ph; X-ray structure

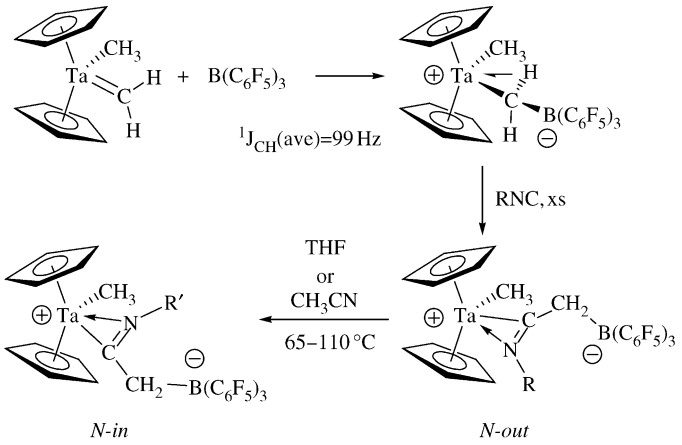
SCHEME 22.

Several adducts of terminal nitrides have been prepared (Entries 15–19).[178,179] Nitride ligands are strong π donors that often stabilize metals in their highest oxidation states, and complexation with Lewis acids such as $B(C_6F_5)_3$ can potentially have a dramatical influence the chemistry of these compounds. For example, the rhenium nitrido complex of Entry 16 is monomeric, but upon addition of $B(C_6F_5)_3$ the metal center becomes significantly more electrophilic, and the structure is a dimer associated through the dithiocarbamate ligands *via* S → V linkages. The ambivalent reactivity of the nitride ligand is further illustrated by the behavior of the Tp osmium nitrides (Entry 19, Scheme 22) towards boranes.[180] For the dichloride, the nitride is electrophilic in nature and cleaves B–C bonds *via* nucleophilic transfer of the Ar^- group from B to N *via* the nitrido-borane adduct. In the diphenyl derivative, the electrophilicity of the nitride nitrogen is dampened enough to stabilize the intermediate adduct, which was isolated and characterized. DFT calculations led the authors to draw a comparison between the $TpOs(X)_2{\equiv}N$ complex and CO, which undergoes similar reactivity towards boranes *via* weak $R_3B{\cdot}CO$ adducts.

The notion that LA coordination to an M=E donor enhances the electrophilicity of the metal center is underscored in the reactions of classical nucleophilic Schrock carbenes with $B(C_6F_5)_3$ and related boranes (Entry 20). Addition of the borane to the methylene group is rapid and the zwitterionic product features a strong α-agostic interaction in both the solid state and in solution (Scheme 23).[181] Insertion of isonitriles occurs exclusively into the $Ta{-}CH_2$ bond, relieving steric congestion about the metal, but further separating charge in the compound.[182] An inverse kinetic isotope effect observed for the $Ta{-}CD_2$ labeled compound indicates that dissociation of the α-agostic interaction is required to allow for isonitrile coordination prior to insertion. The resulting iminoacyls are formed as kinetic *N-out* isomers that isomerizes very slowly to the thermodynamic *N-in* species due to the high electrophilicity of the tantalum center.

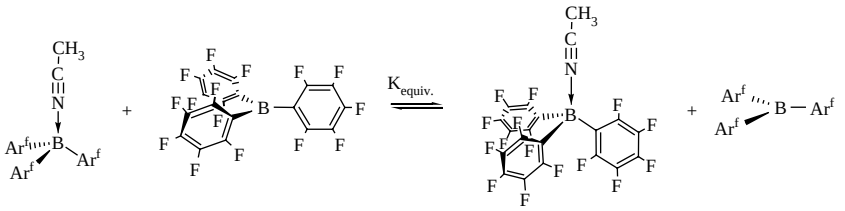
6. Lewis Base Adducts of Other $B(Ar^F)_3$ Derivatives

The Lewis base chemistry of the $B(Ar^F)_3$ derivatives **III**–**VI** is not nearly as diverse as that of the parent $B(C_6F_5)_3$, but some chemistry with simple donors has been reported, mainly in the context of comparative Lewis acid strength experiments. Competition



SCHEME 23.

equilibria between $B(C_6F_5)_3$ and $B(Ar^F)_3$ for CH_3CN [Eq. (5)] have been examined for LAs **III**, **V**, and **VI** and indicate that the position of the equilibrium is influenced not only by the intrinsic LA strength of the borane, but also steric effects. For example, for the equilibrium involving **V** thermodynamic parameters of $\Delta H^\circ = 0.7(2)$ kcal mol^{-1} and $\Delta S^\circ = +4.3(5)$ eu were obtained, indicating that although CH_3CN binds more strongly to **V**, the entropy gained upon release of steric constraints in the bulkier LA drives the equilibrium to slightly favor the $CH_3CN{\cdot}B(C_6F_5)_3$ side.[95] These effects are strong enough such that for the even more bulky **III**, the equilibrium strongly favors the right hand side. For the more equisteric 9-borafluorene LA **VI**, the equilibrium is almost thermoneutral ($K_{eq} = 0.77$ at 25 °C) with very little temperature dependence.[96]



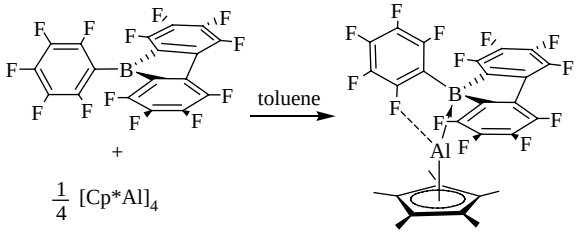
(5)

$B(Ar^f)_3$ = **III,V,VI**

This latter observation is interesting given the fact that $C_{12}F_8B(C_6F_5)$, **VI**, has two fewer F atoms than $B(C_6F_5)_3$. The antiaromaticity of the borole ring[183] compensates for the reduced cumulative influence of the electronegative fluorine complement, and makes for an LA of comparable strength to the borane LA. Furthermore, the flatness of the borafluorene ring reduces steric problems engendered upon pyramidalization of the boron center. This is illustrated in the competition between $C_{12}F_8B(C_6F_5)$ and $B(C_6F_5)_3$ for more sterically bulky Lewis bases such as crotonaldehyde and THF. For crotonaldehyde, the K_{eq} for the equation analogous to Eq (5) falls to 0.12 (i.e., favoring the $C_{12}F_8B(C_6F_5)$

adduct), while for THF, no evidence of the THF·$B(C_6F_5)_3$ adduct appears in the ^{19}F NMR spectrum in the competition experiment. These observations provide a nice demonstration of the subtle balance between steric and electronic effects and illustrate the need to judge LA strength on a system by system basis.

Adducts between $C_{12}F_8B(C_6F_5)$ (**VI**) and CH_3CN, THF, OEt_2 and PMe_3 have been synthesized and fully characterized by multinuclear NMR spectroscopy and, in the case of the CH_3CN adduct, by X-ray crystallography.[184] NMR spectroscopic and metrical parameters are similar to those found for $CH_3CN{\cdot}B(C_6F_5)_3$. A particularly interesting adduct of **VI**, however, is that of "Cp^*Al".[185] Although it was anticipated that the highly reducing Al(I) base might engage in an η^5 bonding mode with the 9-borafluorene acid, only a strong η^1 adduct similar to that observed for $B(C_6F_5)_3$ (Entry 46, Table II) was observed [Eq. (6)]. The metrical parameters were similar to the $B(C_6F_5)_3$ adduct,[165] but the 9-borafluorene adduct features a strong C–F···Al interaction in both solution and the solid state (Al–F = 2.800 Å). The preference for η^1 bonding was thermodynamic as well as kinetic and DFT calculations revealed that the observed stability is related to the fact that the aromatization of the C_4B core necessary for η^5 bonding leads to a loss of aromaticity in the flanking C_6 rings.



(6)

VI

BI- AND POLYFUNCTIONAL PERFLUOROARYL BORANES

Chelating Lewis bases have a long history of application in many areas of chemistry. Conversely, multifunctional compounds with two or more LA sites available for anion or LB binding are more rare and difficult to study. Nonetheless, due to their potential as precursors to large WCAs, chelating activation of organic substrates and supramolecular nuclearity effects, interest in polyfunctional perfluoroaryl boranes has been strong over the past 5–10 years. In an earlier Microreview, we highlighted many of these developments,[186] and for the sake of brevity the reader is referred to that article for a good introduction into this topic; here, we simply update that discussion.

While structures of many polyfunctional perfluoroaryl boranes have appeared in the patent literature, the few that have actually been made and published in the open literature (Chart 2) are for the most part bifunctional. Isomeric 1,2- and 1,4-(*bis*-pentafluorophenylboryl)tetrafluorobenzene (**VIII**[187] and **IX**,[188] respectively) have both been prepared. The *ortho* isomer is prepared starting from the organomercury trimer –$[Hg(C_6F_4)]_3$–;[189] the dibromoboryl complex is formed upon treatment with BBr_3, which

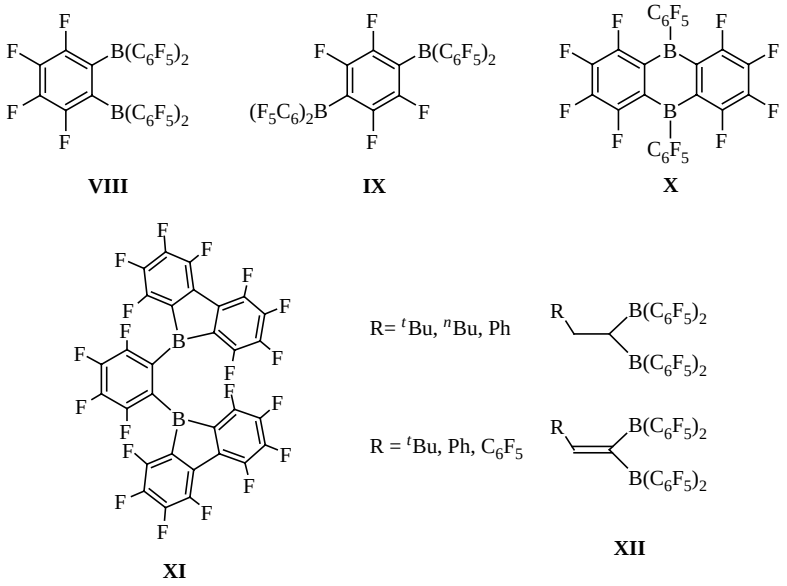
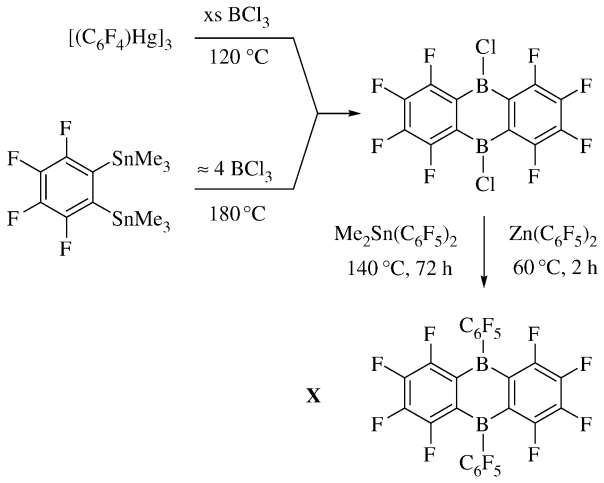


CHART 2.

is converted to **VIII** with $Zn(C_6F_5)_2$ as a $-C_6F_5$ transfer agent.[88] The *para* derivative **IX** can be prepared directly by heating 1,4-$(Me_3Sn)_2C_6F_4$ and four equivalents of $ClB(C_6F_5)_2$ to 140 °C for 72 h; two boryl equivalents are lost as $CH_3B(C_6F_5)_2$. This approach does not work for the 1,2 isomer.

The 9,10-diboraanthracene compound **X**[190] is related to **VIII**, but exhibits enhanced Lewis acidity by virtue of its antiaromaticity. Computational predictions of high Lewis acidity were born out experimentally in competition reactions with $B(C_6F_5)_3$, where the equilibrium constant for Eq. (5) using **X** was 5.6×10^{-3}. This compound is thus the most Lewis acidic perfluoroaryl borane reported to date, and there is evidence that the remaining boron center is also strongly Lewis acidic. Viable routes to its preparation were discovered in attempts to develop a synthesis of **VIII** (Scheme 24). Boron–tin transmetallation reactions between 1,2$(Me_3E)_2C_6F_4$ (E = Si, Sn) require harsh thermal conditions to proceed, and under these conditions condensation reactions to form the 9,10-diboraanthracene framework are facile. From the dichloro derivative, institution of $-C_6F_5$ groups is trivial using $Me_2Sn(C_6F_5)_2$ or $Zn(C_6F_5)_2$. The mono acetonitrile adduct of this compound has been characterized crystallographically; aside from applications in olefin polymerization, the chemistry of this interesting LA is largely unexplored.

A bifunctional LA combining the attributes of **VIII** and the 9-borafluorene LA **VI** has also been prepared by treating 1,2-$(BBr_2)_2C_6F_4$ with the stannole reagent shown in Eq (7).[191] This chelating LA is more sterically open than **VIII**, and this is reflected in the greater propensity of **XI** to coordinate sterically moderate Lewis bases like THF. In fact, the diborane **VIII** does not react with THF, while diborole **XI** is able to coordinate two



SCHEME 24.

molecules of THF, forming a bis-THF adduct that is stable in the solid state (Fig. 5). In solution, dissociation of the second equivalent of THF is extremely facile, but the flatness of the borole ring system allows for coordination to each boron center from the *exo* faces of the two BC_3 planes. Chelation of neutral difunctional Lewis bases in the *endo* pocket has not been observed, but anionic Lewis bases are chelated by this species in a like fashion to that observed for diborane **VIII**.[192]

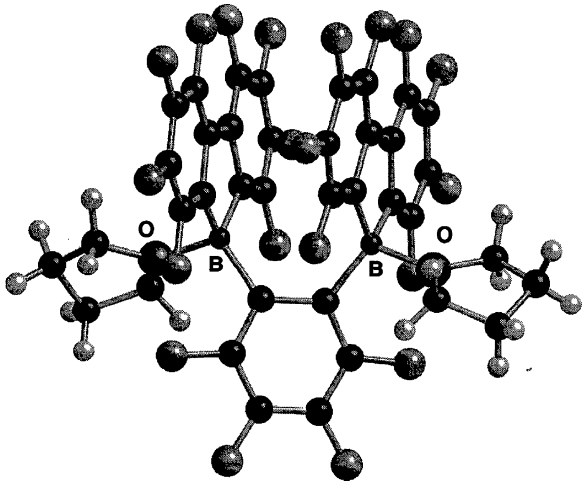
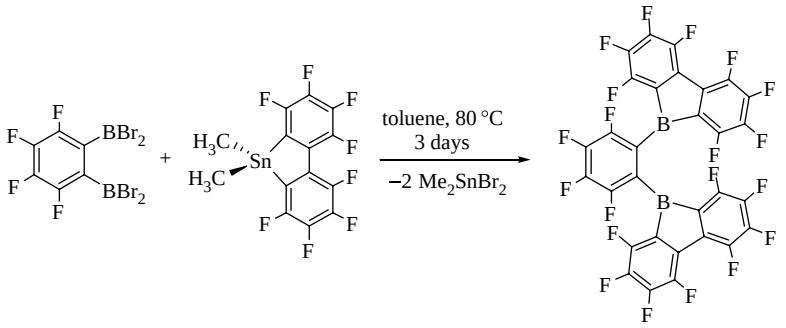


FIG 5. Solid-state structure of the bis-THF adduct of 1,2-$C_6F_4[B(C_{12}F_8)]_2$.



XI (7)

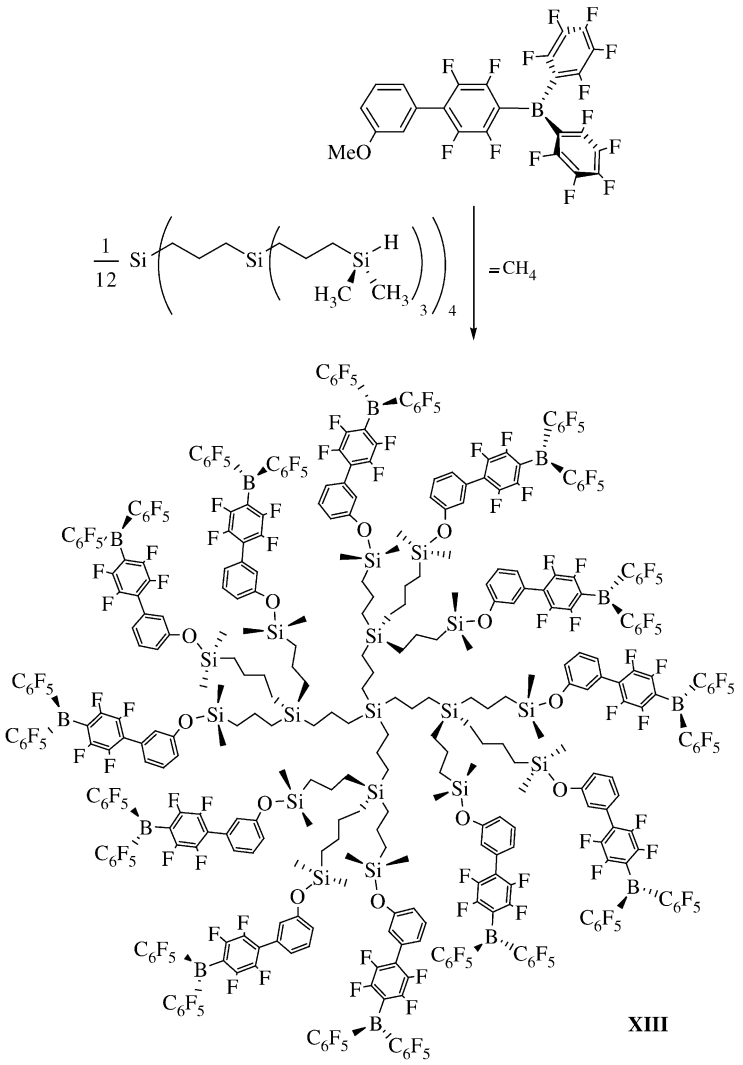
Bifunctional boranes linked by a one-carbon bridge (**XII**) are available *via* hydroboration of terminal alkynes using $HB(C_6F_5)_2$ [30,34] or by using $HBCl_2$ followed by a $-C_6F_5$ instituting step.[193] The bite angle of these chelating LAs is appropriate for binding H^-. Hydroboration of derivatives $RC{\equiv}C{-}B(C_6F_5)_2$ yields a family of LAs incorporating an unsaturated linker that is more resistant to retrohydroboration.[194] These compounds are not overly effective as olefin polymerization co-catalysts, and because of the small B–C–B bite angle and steric crowding about the boron centers have limited application as chelating LAs.[195]

Multifunctional perfluoroaryl boranes containing more than two boron centers remain a relatively unexplored area. Small dendrimers with 4, 8 and 12 borane centers have been prepared using borane catalyzed hydrosilation of methoxy aryl ethers (see Section VII.E.2) as exemplified in Scheme 25.[196] Carbosilane dendrimers are a well explored class of macromolecules with Si–H moieties on the periphery that can be used to affix the borane using the functionalized $B(C_6F_5)_3$ derivative **XIII**. The phenyl spacer and *meta* disposition of the OMe group minimizes the dampening effect of the donor group on the boron LA; the Childs acidity of **XIII** is similar to that of $B(C_6F_5)_3$ itself. In the hydrosilation of acetophenone, the dendrimers are less effective than $B(C_6F_5)_3$, and degradation of the dendrimers *via* hydrosilation of the Si–O–C linking point is problematic for this class of compounds.

VII

SELECTED APPLICATIONS OF PERFLUOROARYL BORANES

The use of $B(C_6F_5)_3$ and related compounds as co-catalysts for olefin polymerization reactions in so-called single site catalyst systems is probably the most well known application of this family of compounds and one that is utilized on a significant scale worldwide. This story has been well documented in the literature and will not be dealt with here. There are, however, several other applications for $B(C_6F_5)_3$ and its derivatives that have been explored in some detail or are undergoing development, and this section will highlight these less appreciated applications.



XIII

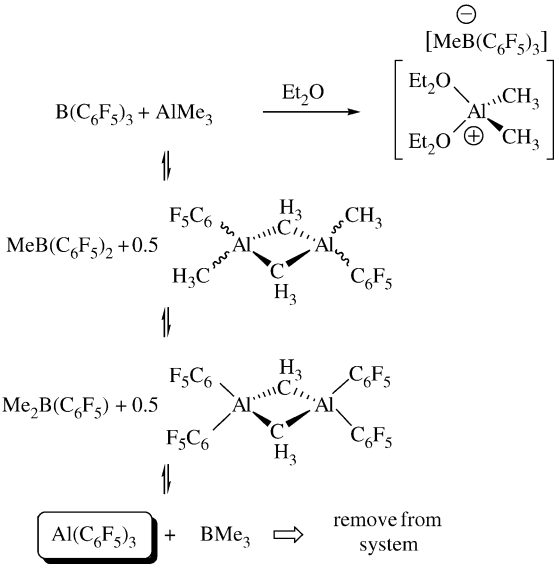
SCHEME 25.

A. *$B(C_6F_5)_3$ as a $-C_6F_5$ Transfer Agent*

Although much of the utility of $B(C_6F_5)_3$ stems from the stability and weakly coordinating properties of its borate anions $[(X)B(C_6F_5)_3]^-$ (X = H, R, C_6F_5), in certain instances, synthetically useful back-transfer of a C_6F_5 group is observed. For metallocenium cations, this process is generally slow for $[RB(C_6F_5)_3]^-$ and slower still for $[B(C_6F_5)_4]^-$ anions, but represents a known decomposition pathway for these catalysts under extreme conditions. Pentafluorophenyl back transfer from anions of the type $[R_2B(C_6F_5)_2]^-$ is rapid, indicating that as the electron richness of the anion

increases, its stability decreases. This can be in part ameliorated by the chelate effect; $[Me_2B(C_6F_5)_2]^-$ rapidly back transfers a pentafluorophenyl group, while $[Me_2B(C_{12}F_8)]^-$, derived from **VI**, is an appropriate anion for use in olefin polymerization catalysis.

The tendency to transfer $-C_6F_5$ groups increases when the metal ion is larger or extremely electrophilic, such that $B(C_6F_5)_3$ becomes useful as a reagent for synthesizing new $M(C_6F_5)_n$ derivatives. An early example was the preparation of the first organoxenon derivatives from XeF_2 and $B(C_6F_5)_3$, which likely proceeds *via* an ion pair formed upon F^- abstraction from Xe by the borane.[197] More recently, $B(C_6F_5)_3$ has been used as a reagent for the preparation of its alane analog $Al(C_6F_5)_3$ by treatment of $AlMe_3$ with stoichiometric amounts of borane (Scheme 26);[198] removal of the gaseous BMe_3 product *in vacuo* drives this reaction to completion.[199] Klosin and Chen have observed and characterized dimeric mixed methyl/$-C_6F_5$ Al intermediates, for example, $[(C_6F_5)_2Al(\mu\text{-}Me)_2Al(Me)(C_6F_5)]$, by carrying out the reaction in a closed system and with superstoichiometric amounts of $AlMe_3$.[200] By introducing donor solvents such as Et_2O, the ion pairs that form as intermediates upon abstraction of Me^- from aluminum can be apprehended as solvent separated alumocenium ion pairs. The base effectively negates the process by dampening the electrophilicity of the Al center and sterically blocking the metal. A similar exchange reaction is observed between $AlEt_3$ and $B(C_6F_5)_3$ and it has been observed that these mixtures are active for "transition metal free" olefin polymerization, although it is less than clear what the nature of the active species is in these novel systems.[201] Furthermore, the $AlEt_3/B(C_6F_5)_3$ activator system has been used in conjunction with Ni and Pd(II) halide precatalysts for norbornene polymerization.[202] Again, although it was assumed that the initiation follows an alkylation/abstraction sequence, in light of the observed reactivity of the two co-catalyst components, the actual



SCHEME 26.

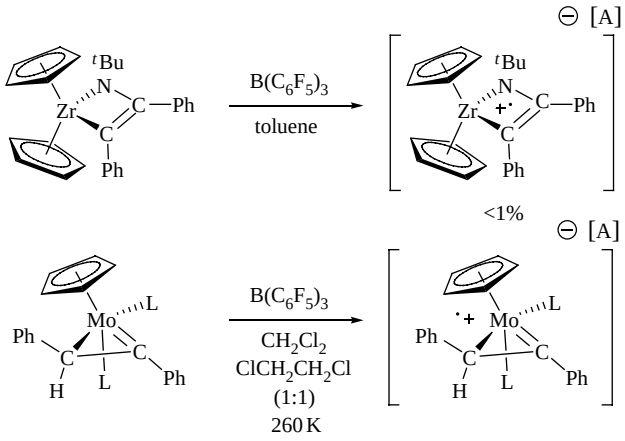
activating species could be any number of species. In all of these systems, it is likely that the high electrophilicity of the alumocenium ions induce rapid $-C_6F_5$ transfer in the absence of stabilizing bases, since Bochmann has observed rapid pentafluorophenyl group transfer even from the usually robust $[B(C_6F_5)_4]^-$ anion in putative $[Me_2Al]^+[B(C_6F_5)_4]^-$ ion pairs formed upon reaction of $[Ph_3C]^+[B(C_6F_5)_4]^-$ with $AlMe_3$.[203] Indeed, while more stabilized alumocenium ions like $[Cp_2Al]^+$ can tolerate perfluoroarylborate anions,[204] even moderately sterically open aluminum cations like $[(^iPr_2-ATI)Al-R]^+$ (ATI = *N,N′*-diisopropylaminotroponiminate) are prone to neutralization by $-C_6F_5$ back transfer from $[XB(C_6F_5)_3]^-$ (X = H, R, or C_6F_5).[205]

Similar chemistry is observed in the reactions of dialkyl zinc reagents and related compounds with $B(C_6F_5)_3$.[206] In hydrocarbon solvents, this reaction may be used as a convenient method to prepare $Zn(C_6F_5)_2$, while ion pairs of general formula $[RZn(OEt_2)_3]^+[RB(C_6F_5)_3]^-$ (R = Me, Et) can be generated and characterized in solution. The facility of $-C_6F_5$ back transfer is clearly dampened by the presence of donors in both the alkyl zinc and alkyl aluminum cations.

B. *Perfluoroaryl Boranes as Oxidizing Agents*

Triarylboranes can act as one electron acceptors and the resulting radical anions are relatively stable and observable as bright blue compounds with intense boron p orbital $\rightarrow \pi^*$ absorptions.[207] Intuitively, one would expect that $B(C_6F_5)_3$, with its electron withdrawing pentafluorophenyl groups, would be inherently easier to reduce and should act as a stronger oxidizing agent than, for example, BPh_3. Surprisingly, attempts to reduce $B(C_6F_5)_3$ with alkali metals in donor solvents such as THF resulted in only slow decomposition of the borane with no evidence that reduction had taken place.

However, it is clear that $B(C_6F_5)_3$ can behave as an electron acceptor, as evidenced by the oxidation of the metallacyclic organometallic derivatives shown in Scheme 27. Norton *et al.* have observed about 1–2% production of the radical cation of



SCHEME 27.

the azazirconacyle upon treatment with $B(C_6F_5)_3$.[208] Furthermore, Green, Connelly and co-workers observed near quantitative production of the 17-electron molybdenum species upon treatment of the metallacyclopropene with $B(C_6F_5)_3$.[209] This radical cation underwent further transformation at higher temperatures. Neither of these studies was able to directly implicate the radical anion of $B(C_6F_5)_3$, but Norton *et al.* subsequently showed that the borane could be reduced with Cp^*_2Co at $-50\,^{\circ}C$ in THF to give $[B(C_6F_5)_3]^{-\cdot}$ cleanly enough to establish its ESR and UV-vis spectra ($\lambda_{max} \approx 600$ nm).[210] The species is only transiently stable, decomposing at temperatures above $-50\,^{\circ}C$. Unfortunately, electrochemical measurements on $B(C_6F_5)_3$ have thus far been inconclusive, a common problem in the electrochemistry of triarylboranes.[211] It is clear from these studies that the $B(C_6F_5)_3$ radical anion is highly reactive.

The 9-borafluorene derivative **VI** was expected to be easily reducible to a borrolide dianion, consistent with the generally observed behavior of boroles. However, similar difficulties to those observed for $B(C_6F_5)_3$ were encountered in attempts to reduce **VI** with Li, Na or K in coordinating solvents like THF or Et_2O.[184b] Only unreacted THF or Et_2O adducts of **VI**, along with some decomposition products, were isolated from these reactions. Unlike $B(C_6F_5)_3$, reduction of **VI** with Cp^*_2Co in THF did not proceed, a reflection of the borole LAs higher affinity for THF (see Section V.6). When carried out in CH_2Cl_2, however, an immediate reaction was observed, cleanly producing the decamethylcobaltocenium complex $[Cp^*_2Co]^+[ClB(C_6F_5)(C_{12}F_8)]^-$, which contains a chloroborate counteranion. This nature of the product was unambiguously established by NMR spectroscopy and X-ray crystallography. This product is observed even when an excess of the Cp^*_2 Co reagent is employed. Thus, one-electron reduction of **VI** gives a highly reactive radical anion that rapidly abstracts Cl· from the solvent to form a stable chloroborate counteranion. In light of these results, it seems likely that the anion formed in the Green/Connelly chemistry depicted in Scheme 27 is also a chloroborate, given that that reaction was done in a 1:1 mixture of $CH_2Cl_2/ClCH_2CH_2Cl$.

The ability of $B(C_6F_5)_3$ to act as an oxidizing agent raises questions regarding the role of electron transfer reactions involving abstraction of hydride or alkide groups by $B(C_6F_5)_3$ and related LAs. An example where such an electron transfer pathway seems reasonable was discussed in connection with Scheme 19. Probably, $B(C_6F_5)_3$ is not a strong enough oxidizing agent for this pathway to be important in the abstraction of alkide groups from early transition metal organometallic compounds, where typically oxidizing agents like Ag^+ or $[Cp'_2Fe]^+[A]^-$ ($Cp' = C_5H_4Me$) are required to effect oxidation of the M–R σ bonding electrons.[2a,2d] The observed inversion of configuration at the α-carbon of an abstracted group using $HB(C_6F_5)_2$ (see Section IV.B) supports this notion.[48b] Nonetheless, for the abstraction of bulkier alkyl groups, or in more easily oxidized organometallics, an electron transfer pathway must be considered as a reasonable possibility based on these studies.

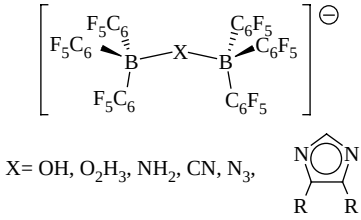
C. *Perfluoroaryl Boranes in the Synthesis of Novel Weakly Coordinating Anions*

Perfluoroarylborates are among the most WCAs known, and are certainly the most easily accessible and widely available. As such, they have been applied to numerous

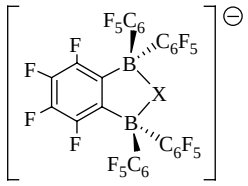
long-standing problems in the synthesis of electrophilic compounds as detailed in an excellent recent review.[212] Tris-(pentafluorophenyl)borates, $[XB(C_6F_5)_3]^-$, are formed as a consequence of abstraction of X (X = H, R, Cl[213]) from a metal or main group element center, and are generally more coordinating than, for example, the *tetrakis*-(pentafluorophenyl)borate, since the X group can facilitate contact with the cation *via* M···X–B bridges. This can provide a useful stabilizing effect to the electrophilic metal center, while still allowing for high reactivity.

When X possesses one or more lone electron pairs, excess borane can lead to formation of even more WCAs of general form $[(C_6F_5)_3B(\mu\text{-}X)B(C_6F_5)_3]^-$. This observation leads to the rational synthesis of several examples of such anions, generally as trityl or ammonium salts, for use as WCA's (**XIV**, Chart 3). A significant attribute of all of these compounds are that they are readily accessible in one step from $B(C_6F_5)_3$ by treatment of an alkali metal salt of X with two equivalents of $B(C_6F_5)_3$. Metathesis with Ph_3CCl or $[HNR_3]^+[Cl]^-$ yields reagents capable of instituting WCAs into metallocenium systems for X = OH,[117] NH_2,[214] CN,[215] N_3,[216] and imidazolide.[217] The cyano[215] and imidazolide[218] anions have also been prepared as their $[(Et_2O)_2H]^+$ salts, adding other Bronsted acids to the series that includes the Brookhart[219] and Jutzi[220] acids.

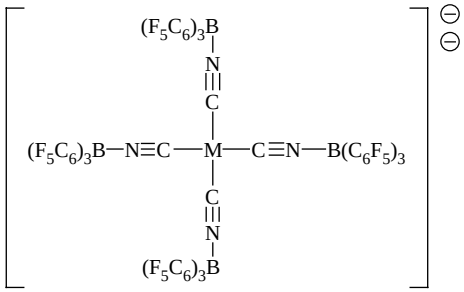
The effectiveness of these anions depends to a large degree on the integrity of the μ–X linkage. The μ-NH_2 compound is air and moisture stable and exhibits a particularly strong bridge, possibly by virtue of four N–H···F hydrogen bonds between *ortho* fluorine atoms and the amido NH protons. Activation of common metallocenes with the trityl salt



XIV



XVI



XV

Chart 3.

of this anion gives stable metallocenium ion pairs that exhibit high activity for propene polymerization. The bent nature of the bridge distinguishes it from the μ-CN anion, which arranges the two borate centers in a linear fashion across the cyano linkage. This anion affords extraordinarily active catalysts for propene polymerization, yet in the absence of monomer tends to give unstable ion pairs based on the $[L_2ZrMe(\mu\text{-}Me)MeZrL_2]^+$ cation[221] (L_2 = some bis-Cp framework). This initially formed species tends to dissociate to give $[L_2ZrMe]^+[MeB(C_6F_5)_3]^-$ and a second metallocenium ion stabilized as the contact ion pair $[L_2ZrMe(\mu\text{-}N{\equiv}C)B(C_6F_5)_3]$. The μ-azide anions are generally less effective, as they rapidly transfer the azide anion to metallocenium ions. Finally, the imidazolide family is also an effective series of WCAs for use in olefin polymerization applications.

Bochmann has also produced a novel class of large *dianionic* borates **XV** based on the non-labile *tetra*-cyano Ni and Pd(II) metallates $[K]_2^+[M(CN)_4]^{2-}$.[215a] The metals in these WCAs are strictly square planar and as such the anion assumes a flat rather than spherical shape, with a torus of fluorination on the periphery of the plane. The bis-trityl salts of these dianions afford catalysts that are not as productive as those formed from the **XIV** class (X = CN), although they are still much more active than borane activated catalysts. The lower activity was attributed to the inherently greater cation/anion attraction in a monocation/dianion pair.

All of these species (**XIV**, **XV**) have been for the most part applied towards function in the olefin polymerization arena; use of these novel anions for the stabilization of other electrophilic species remains to be explored. Recently, the imidazolide anion **XVI**, as well as the perfluorinated tetraaryl borate derived from the diborane **IX** of Chart 2, have been used to stabilize iodonium cations.[222] These cations are used as photoinitiators for cationic polymerization of epoxy resins in photolithography applications. While use of the $[B(C_6F_5)_4]^-$ led to a breakthrough in this area of research,[223] higher activities are observed for more WCAs.

The chelating diborane **VIII** and diborole **IX** shown in Chart 2 also readily afford highly effective WCAs (exemplified by **XVI**, Chart 3) upon treatment of the base-free acids with a variety of trityl-X reagents. Trityl ethers are especially good reagents in this regard, forming μ-alkoxide compounds that are quite resistant to transfer of the OR group to the cationic center. In fact, these Lewis acids are capable of abstracting an OMe group from $Cp_2Zr(OMe)_2$. Activation of common metallocenes with $[Ph_3C]^+[C_6F_4\text{-}1,2\text{-}\{B(C_6F_5)_2\}_2(\mu\text{-}OR)]^-$ proceeds quite cleanly in the absence of monomer, providing ion pairs of general formula $[L_2ZrMe]^+[C_6F_4\text{-}1,2\text{-}\{B(C_6F_5)_2\}_2(\mu\text{-}OR)]^-$ whose dynamic behavior can be studied in detail.[224] In addition to stabilizing metallocenium ions (and providing catalysts that are up to four times more active than those activated with $[Ph_3C]^+[B(C_6F_5)_4]^-$), the $[C_6F_4\text{-}1,2\text{-}\{B(C_6F_5)_2\}_2(\mu\text{-}OCH_3)]^-$ anion can be isolated as its $[(Et_2O)_2H]^+$ salt and can stabilized stannylinium ions $[R_3Sn(s)]^+$.[225] Transfer of OMe^- to $[R_3Si(s)]^+$ cations is facile, however, establishing some limits to the utility of this class of WCAs. Anions $[C_6F_4\text{-}1,2\text{-}\{B(C_6F_5)_2\}_2(\mu\text{-}X)]^-$ with other chelated anionic bases have been generated. For $X = F^-$, Cl^-, or N_3^-, the chelated group is rapidly transferred to the electrophilic cation center, but the μ-halides are effective as anions in cationic polymerizations (see Section V.D). Interestingly, attempts to prepare the μ-hydride met with failure; although the anion could be generated *in situ* at low temperatures, it was not stable upon warming.

The μ-OH anion can also be prepared by treating the diborane with KOH; it often appears in small quantities *via* adventitious water.

A moderately effective perfluoroaryl borate WCA incorporating the exhaustively fluorinated *para*-C_6F_4-C(F)$(C_6F_5)_2$ has also been prepared and fully characterized as its $[PhNMe_2H]^+$ salt.[226]

D. *Perfluoroaryl Boranes as Polymerization Initiators*

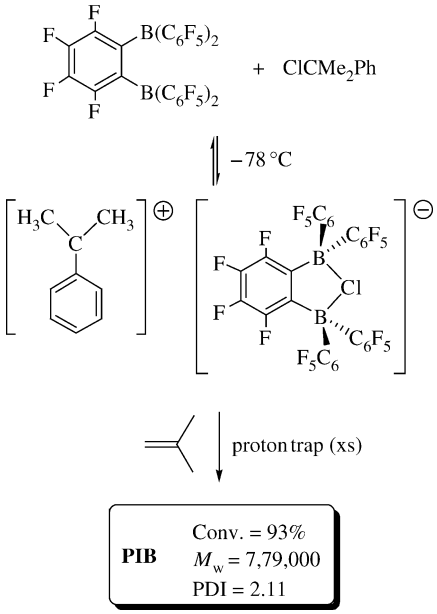
In addition to the familiar and extensive role perfluoroaryl boranes and borates fill as co-catalysts for the coordination polymerization of ethylene and α-olefins, these compounds can act as initiators for other polymerization reactions due to their high Lewis acidity.

1. Cationic Polymerizations

Under certain conditions, $B(C_6F_5)_3$ is an effective initiator for the carbocationic polymerization of isobutylene. The delineation of these conditions began with reports that a catalyst system comprised of Cp^*TiMe_3 and $B(C_6F_5)_3$ was capable of initiating polystyrene production *via* a carbocationic mechanism.[227] The observation that the polymer was largely syndiotactic led the researchers to propose that the $[MeB(C_6F_5)_3]^-$ was playing a key role in determining the stereochemistry of the polymer. Subsequent studies, however, indicated that, for this system, the syndiotactic polystyrene was being produced by a coordination polymerization mechanism[228] and the question as to whether carbocationic polymerizations were possible at all with metal cations like $[Cp^*TiMe_2]^+[MeB(C_6F_5)_3]^-$ or metallocenium compounds arose.

To this end, Shaffer and Ashbaugh studied isobutylene polymerizations,[229,230] since this monomer is unambiguously polymerized by a carbocationic mechanism, using a variety of cationic organometallic compounds $[L_nMCH_3]^+[RB(C_6F_5)_3]^-$ and $B(C_6F_5)_3$ alone as initiators. Their findings confirm that the $[Cp^*TiMe_2]^+$ cation, stabilized by the $[MeB(C_6F_5)_3]^-$ WCA, can act as an initiator for isobutylene polymerizations, but that protons produced by reaction of adventitious water with the metal cation play a significant role as a competing initiation process. Nonetheless, when this possibility is negated by the addition of the effective proton trap 2,6-di-*tert*-butylpyridine, these cations still initiate polymerization. For bulkier metallocenes such as $Cp^*_2MMe_2/[Ph_3C]^+[B(C_6F_5)_4]^-$ (M = Zr, Hf), direct initiation by the metal is slower and most of the polymer is produced by protons released upon reaction of water with $[Cp^*_2MMe]^+$.

Interestingly, $B(C_6F_5)_3$ itself can initiate isobutylene polymerization, but the initiation is only effective in polar solvents such as chlorobenzene. When done in the presence of the proton trap, polymerization does not occur. This indicates that the water adduct, $H_2O{\cdot}B(C_6F_5)_3$, is likely the initiator in these experiments, and the carbocationic end of the chain is stabilized by the $[HOB(C_6F_5)_3]^-$, or possibly the $[(F_5C_6)_3B(\mu\text{-}OH)B(C_6F_5)_3]^-$ anion. The dependence of this $B(C_6F_5)_3$ initiated polymerization on solvent polarity is an indication that the propagation equilibrium is quite sensitive and requires a polar medium for effective ionization.



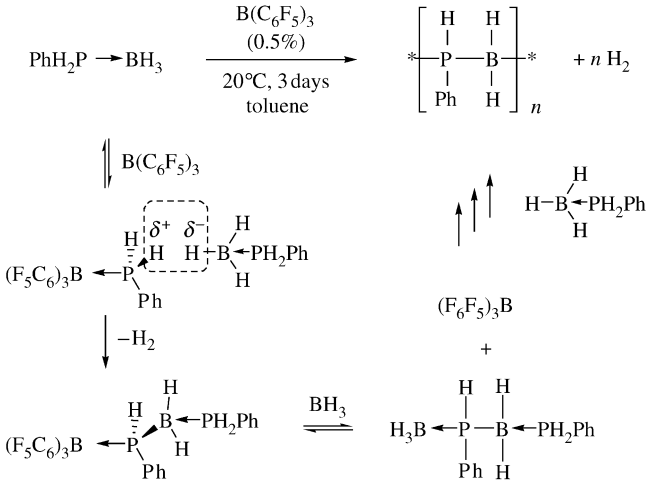
SCHEME 28.

Baird *et al*. have explored the use of $B(C_6F_5)_3$ in conjunction with long chain alcohols and thiols as proton sources for the initiation of isobutylene polymerization using Cp^*TiMe_3.[231] The anions that form upon initiation, $[REB(C_6F_5)_3]^-$ are comparable in effectiveness to the $[B(C_6F_5)_4]^-$ anion,[232] producing high MW polymer with excellent conversion.

Given the acknowledged effect of the counteranion on isobutylene polymerizations, Collins *et al*. have begun to explore the use of the chelating diborane **VIII** as an initiator in conjunction with cumyl chloride, the idea being that chelation of the chloride ion should favor the desired side of the propagation equilibrium.[233] The diborane reversibly abstracts Cl^- from $PhMe_2CCl$ at -60 °C in CH_2Cl_2 in the absence of monomer, and this catalyst system is highly active for the production of high molecular weight PIB *even in the presence of the proton trap* (Scheme 28). Thus, although protic initiation with **VIII** is also facile, when this is eliminated by the 2,6-di-*tert*-butylpyridine proton trap, the system remains highly active, in contrast to the non-chelating $B(C_6F_5)_3$ system. Even in the presence of cumyl chloride, $B(C_6F_5)_3$ is inactive in the absence of protons, emphasizing the advantage provided by the chelating diborane array.

2. Dehydropolymerizations

Neutral dimethyl metallocenes of group 4, Cp_2MMe_2, are effective catalysts for the dehydropolymerization of primary silanes, *via* a σ bond metathesis pathway.[234] Given the topological similarities between the four centered transition states for olefin insertion into M–C bonds and σ bond metathesis reactions, it was postulated that activation of these metallocenes by $B(C_6F_5)_3$ might enhance dehydropolymerization of silanes in



SCHEME 29.

the same way that olefin polymerization rates are boosted. While it turns out that metallocenium ions are somewhat less active dehydropolymerization catalysts than the neutral systems, when $B(C_6F_5)_3$ is the co-catalyst, higher molecular weight polysilane polymers are obtained in comparison to the neutral systems.[235] The more coordinating $[MeB(C_6F_5)_3]^-$ anion may be playing a role in discouraging low molecular weight cyclooligomers in these systems.

Recently, it has been shown that $B(C_6F_5)_3$ can be directly enlisted as a catalyst for the heterodehydropolymerization of RPH_2 (R = Ph, H) and BH_3.[158] Previously, the high molecular weight polyphosphinoboranes were prepared at moderately high temperatures using a Rh(I) catalyst,[236] but Denis and co-workers have shown that $B(C_6F_5)_3$ (0.5–5%) produces similar materials at ambient temperatures. Model studies (Scheme 29) suggest that propagation *via* the borane/phosphine adduct; coordination enhances the acidity of the PH moiety enough such that reaction with the hydridic BH bond to eliminate hydrogen is facile. The lability of the $RP(H)\cdot B(C_6F_5)_3$ bond is critical for polymer formation, since dissociation of borane from the growing polymer chain is necessary for activation of further phosphine monomers. In addition to the phosphorus substituted polymers prepared *via* Rh catalysis, the $B(C_6F_5)_3$ catalyzed process allows for preparation of samples of the parent polyphosphinoborane $H_3P{-}(BH_2PH_2)_n{-}BH_3$ as an air and moisture sensitive solid.

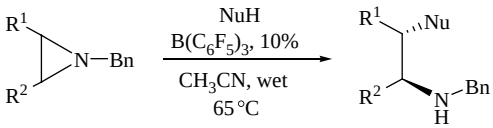
E. *Perfluoroaryl Boranes in Organic Synthesis*

1. Use of $B(C_6F_5)_3$ as a Conventional Lewis Acid

Due to its superior hydrolytic stability and high Lewis acidity, $B(C_6F_5)_3$ has been explored extensively as an alternative to more commonly employed haloborane Lewis acids such as $BF_3\cdot OEt_2$. Hisashi Yamamoto and co-workers were among the first to explore the utility of this borane in such commonly LA enhanced reactions as

the Mukaiyama aldol reaction,[237] conjugate additions of silyl enol ethers to α,β-unsaturated ketones,[238] addition of ketene silyl acetals to imines[239] and the Diels–Alder reaction.[238] More recently, Kalesse *et al*. have shown that use of $B(C_6F_5)_3$ instead of $BF_3{\cdot}OEt_2$ in the vinylogous Mukaiyama aldol leads to significantly higher diastereoselectivities and furthermore can be employed in substoichiometric amounts.[240] This study emphasizes the steric advantages of $B(C_6F_5)_3$ over $BF_3{\cdot}OEt_2$ and this chemistry has been applied to the rapid preparation of complex polyketide scaffolds.[241] Although anhydrous grade $B(C_6F_5)_3$ is not necessary in most cases (indeed some Mukaiyama aldols were carried out in water), generally the rate of reaction was enhanced when dry borane was used. Other reactions explored by the H. Yamamoto group include the catalytic rearrangement of epoxides to aldehydes using $B(C_6F_5)_3$ [242] and the Oppenauer oxidation of aldehydes using the diarylboronic acid $HOB(C_6F_5)_2$.[68a] H. Yamamoto and Ishihara have reviewed their work in this area and the reader is referred to this article for further information on these reactions.[243]

Recently, other groups have investigated $B(C_6F_5)_3$ as an LA for a variety of transformations. In the presence of allylic or propargylic alcohols, aniline or benzene thiol, a variety of epoxides are smoothly and regiochemically opened and trapped under mild conditions.[244] The mechanism has not been investigated, but the role of a Bronsted acid pathway may be important in light of a study by Watson and Yudin[115] on the use of $B(C_6F_5)_3$ as a catalyst for a similar ring-opening of inactivated aziridines [Eq. (8)]. No special precautions for the exclusion of water were taken, and the chemistry proceeded smoothly, but when molecular sieves or proton sponge were introduced, the reaction became sluggish. Detailed ^{19}F NMR studies supported the proposal that the water adduct of $B(C_6F_5)_3$ mediates the majority of catalysis in this chemistry; the relatively polar solvent acetonitrile was also required for optimal reactivity, facilitating ionization in the critical step in the reaction.



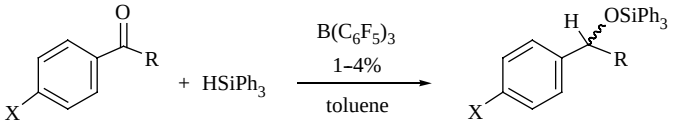
(8)

Gansäuer *et al*. have used the ability of $B(C_6F_5)_3$ to cleave ethers to devise a novel enolate alkylation process.[245] Upon addition of $B(C_6F_5)_3$ to enol ethers in which the ether group is the one capable of stabilizing a carbocationic charge, the group is rapidly transferred to the enol carbon, forming a new carbon–carbon bond. As little as 0.1% catalyst was employed, and turnover numbers in excess of $800\ h^{-1}$ were achieved. Deuterium labeling experiments demonstrated the stepwise nature of the process, which could be applied to enol ethers incorporating the *para*-methoxybenzyl, adamantyl, MOM and most significantly, the allyl group.

2. Hydrosilations and Related Reactions

Although detailed mechanistic studies have for the most part not been carried out, it is likely that in all of the above-mentioned $B(C_6F_5)_3$ mediated reactions, the LA behaves in a conventional manner, that is to say it activates the organic functional target to

nucleophilic attack or cleavage by coordination of the function's lone pair. Several years ago, we discovered that $B(C_6F_5)_3$ serves as a very active catalyst for the hydrosilation of carbonyl functions [Eq. (9)].[246] Initially, we assumed that the mode of action for the LA in this chemistry was also a conventional one, but several observations implied a more complex mechanistic picture.

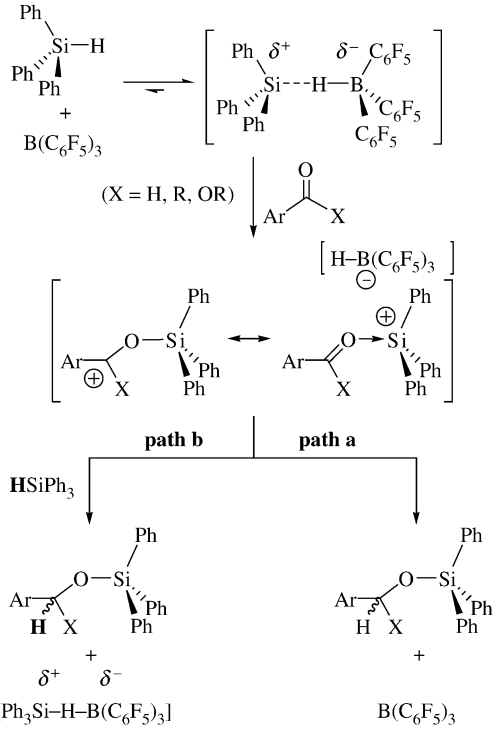


(9)

First, it was observed that substrates of lower basicity were hydrosilated by Ph_3SiH much more rapidly than substrates of higher basicity. Thus, for the substrates benzaldehyde, acetophenone and ethylbenzoate, observed turnover numbers were 19, 45 and 637 h^{-1}, respectively, while the measured equilibrium constants for adduct formation of these substrates with $B(C_6F_5)_3$ were 2.1×10^4, 1.1×10^3 and 1.9×10^2. A similar inverse correlation between turnover number and equilibrium constant was observed for a series of *para*-substituted acetophenone derivatives, where much faster hydrosilation rates were observed for substrates with strongly electron withdrawing groups in the *para* position. Clearly, if activation of the substrate *via* adduct formation is important in the hydrosilation reaction, the opposite correlation between TON and K_{eq} should be observed.

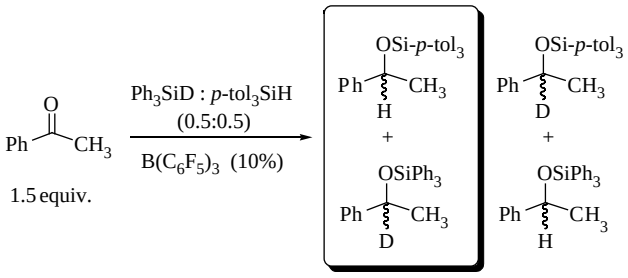
A second puzzling observation was the inverse dependence of hydrosilation rates on the concentration of substrate. In a rate study in which the concentration of acetophenone was varied, rate suppression was observed as [acetophenone] increased. Since raising [acetophenone] is expected to shift the equilibrium for adduct formation towards the adduct, this phenomenon argues against direct involvement of the adduct in the catalytic cycle for hydrosilation. Finally, it was observed that, in a competition experiment between benzaldehyde and ethylbenzoate, benzaldehyde was hydrosilated almost exclusively at a comparable rate to the non-competitive hydrosilation of the aldehyde. This observation shows that the relative basicity of the substrate does play an important role in the reaction, determining the chemoselectivity of the reaction.

A mechanism that is consistent with all of these observations is shown in Scheme 30.[247] In this picture of the reaction, dissociation of borane from the $Ar(R)C{=}O{\cdot}B(C_6F_5)_3$ adduct is necessary so the borane can activate the *silane* towards nucleophilic attack by the substrate. This explains the higher activities observed for less basic substrates and the inverse dependence on [substrate]; more free borane results in enhanced reaction rates since more silane is activated under these conditions. Although the borane/silane adduct is not observed directly spectroscopically, the borane catalyzes rapid H/D exchange between silane centers, and computational studies support the feasibility of such a process.[81] The well established behavior of $B(C_6F_5)_3$ towards organotransition metal alkyl and hydride compounds lends credence to the proposed abstraction of H^- from Si by $B(C_6F_5)_3$ as a crucial step in this reaction. The abstraction is aided by displacement of the $[HB(C_6F_5)_3]^-$ by the Lewis basic substrate, offering a rationale for the observed selectivity of the reaction towards more basic substrates.



SCHEME 30.

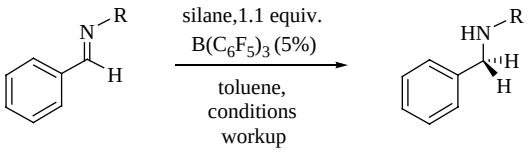
A remaining critical mechanistic question deals with the mode of product formation from the ion pair formed upon H^- abstraction. At this point, the reaction can be consummated either by transfer of H^- from B to the carbonyl carbon (path a, Scheme 30), or direct abstraction of H^- from another R_3SiH reagent (path b).[248] In this latter scenario, the borane becomes a spectator in the reaction, and the true catalyst is the $[R_3Si]^+$ cation. To probe this question, we performed the experiment depicted in Scheme 31. In the case of path b, both pairs of isotopomers should be observed, while if path a is operative, only the unscrambled products should be present. In fact, the product mixture consistent with



SCHEME 31.

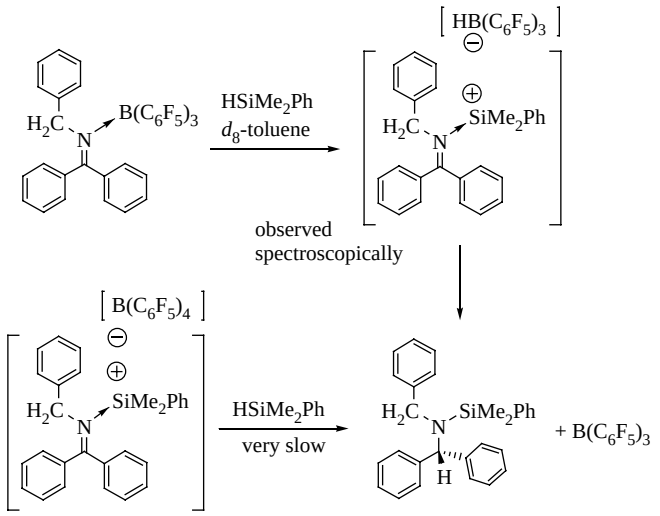
path a was observed, strongly suggesting that $[HB(C_6F_5)_3]^-$ is the delivery agent. This eventuality has implications for the potential effectiveness of chiral boranes in asymmetric versions of this reaction, since $[R_3Si]^+$ catalysis would relegate the chiral borane to a secondary role.

Direct spectroscopic observation of a silyliminium ion in analogous $B(C_6F_5)_3$ catalyzed hydrosilations of imine substrates provided further evidence for the "silane activation" mechanism.[249] $B(C_6F_5)_3$ is an effective catalyst for the hydrosilation of a variety of imine substrates [Eq. (10)], and again rate trends (albeit semiquantitative) indicate that more basic substrates are hydrosilated much more slowly than less basic imines. This is particularly illustrated by the effect of changing the imine nitrogen substituents, where bulky and/or electron withdrawing groups significantly enhance the production of silylamine product. In a stoichiometric experiment, dropwise addition of silane to a toluene solution of the *N*-benzyl imine of benzophenone leads to precipitation of a liquid clathrate-like oil that can be examined directly by multinuclear NMR spectroscopy (Scheme 32). The NMR data is completely consistent with the silyliminium ion structure shown, incorporating a hydrido borate counteranion. This material converts to the amine produce and free $B(C_6F_5)_3$ at a much faster rate than the silyliminium ion stabilized by $[B(C_6F_5)_4]^-$, generated as shown in the Scheme, reacts with silane. This again suggests that $[HB(C_6F_5)_3]^-$ serves as the H^- delivery agent in completing the hydrosilation.

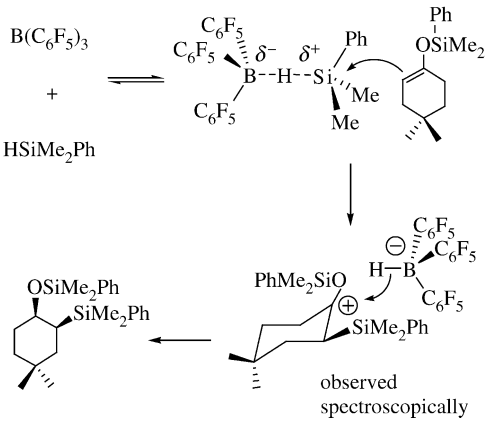


(10)

Silylium ion intermediates were also observed in the chemistry involving the hydrosilation of α,β-unsaturated ketones.[250] For most substrates, the H-SiR_3 reagent is



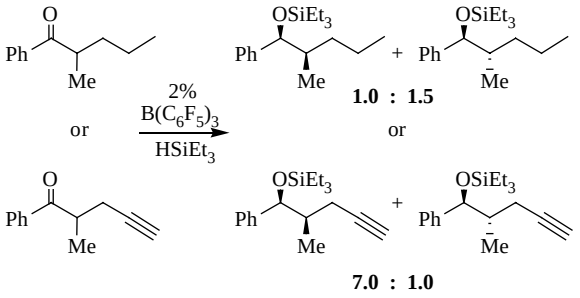
SCHEME 32.



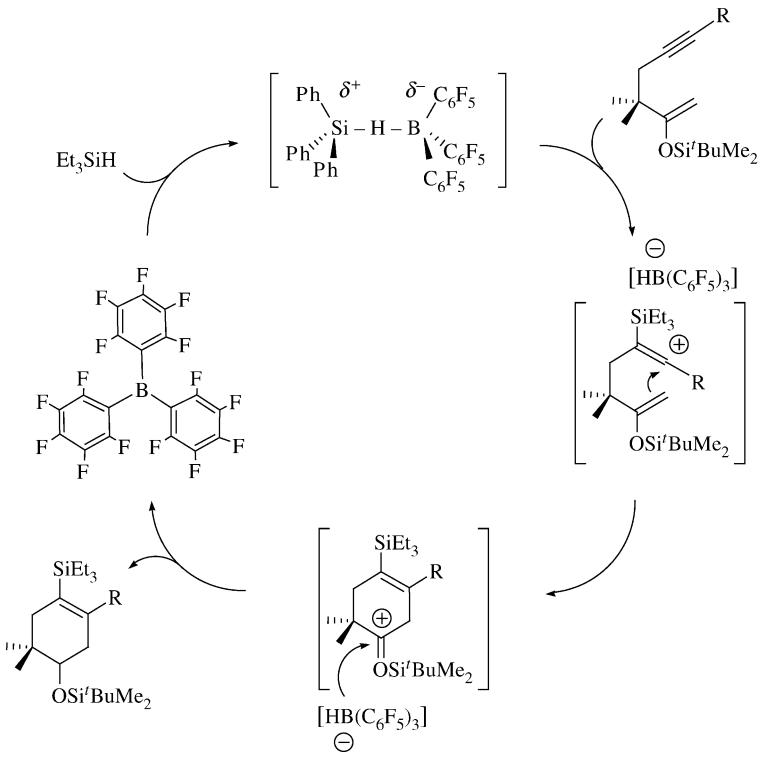
SCHEME 33.

delivered with 1,4 regiochemistry, forming silyl enol ethers as the main products. Thus, there is potential to use this chemistry in tandem with the $B(C_6F_5)_3$ catalyzed addition of silyl enol ethers to aldehyde and imine substrates discussed above.[243] Furthermore, the hydrosilation of the silyl enol ethers was observed in some instances (Scheme 33) and for this particular substrate a silylcarboxonium ion intermediate was observed spectroscopically. This mechanism is also consistent with the observed *cis* geometry in the disilated cyclohexyl product.

Although somewhat counterintuitive, a growing body of evidence from other groups supports the silane activation mechanism. For example, Yoshinori Yamamoto and co-workers have developed some highly diastereoselective ketone hydrosilations by exploiting the availability of $[SiR_3]^+$ for chelation of pendant alkyne donors (Scheme 34).[251] The substrate without the alkyne demonstrates poor diastereoselectivity, while incorporation of the alkyne leads to good selectivity. Since chelation of the boron center by this substrate is unlikely, the observed selectivity was rationalized on the basis of a silane activation mechanism. Another interesting system reported by Y. Yamamoto *et al*. involves the LA catalyzed intramolecular addition of silyl enol ethers to alkynes,



SCHEME 34.



SCHEME 35.

Scheme 35.[252] Although this process is promoted by $EtAlCl_2$, $B(C_6F_5)_3$ itself is ineffective probably due to a lack of labile groups. However, addition of Et_3SiH to the reaction results in rapid cyclization to the cyclohexenyl product shown *via* a silane activation mechanism.

Gevorgyan and co-workers have utilized the $B(C_6F_5)_3$/silane system to hydrosilate a variety of olefins[253] and offer several mechanistic experiments that support a mechanism involving rate limiting addition of the olefin to the borane/silane complex, followed by rapid quenching of the β-silyl carbocation intermediate by the hydridoborate counter-anion. No polymerization of styrenic substrates was observed, attesting to the rapidity of the hydride transfer step. This chemistry is related to the hydrosilation of simple olefins as mediated by $[Et_3Si{\cdot}C_6H_6]^+[B(C_6F_5)_4]^-$,[254] but the $B(C_6F_5)_3/R_3SiH$ system is much more active again suggesting that $[HB(C_6F_5)_3]^-$ is a more effective H^- donor than R_3SiH.

The silanolysis of alcohols to form silyl ethers is an attractive method since the only by-product, H_2, is easily removed making workup procedures trivial. Many transition metal catalysts for this exothermic process have been introduced, but most suffer from low activities and inconvenient preparations. The silane activation mechanism has parallels to the mechanisms by which transition metal compounds bring about this transformation and the $B(C_6F_5)_3$/silane catalytic system turns out to be highly active for this transformation.[255] In contrast to the normal procedures involving silyl chlorides

and base for protection of alcohol functions as their silyl ethers, the $B(C_6F_5)_3$ catalyzed silanolysis is more rapid for sterically bulky alcohols, again reflecting the kinetic benefit of increasing the amount of free borane. This is again suggestive of a silane activation mechanism; in this case, the substrate alcohol coordinates the incipient $[R_3Si]^+$ cation, and the now more acidic alcohol proton reacts rapidly with $[HB(C_6F_5)_3]^-$ to eliminate H_2. Since alcohol functions in general are quite Lewis basic in comparison to other organic functions, this reaction is tolerant of a wide variety of functional groups. Thus, ROH silanolysis can be performed in the presence of olefins, alkynes, halogens, esters, lactones, ethers and in some instances ketones. The reaction can be employed with a variety of silanes, with the exception of the most sterically hindered examples, in particular the $^{i}Pr_3SiH$ reagent. For this silane, there is simply too much front strain in the $B(C_6F_5)_3/^{i}Pr_3SiH$ complex. Nonetheless, the reaction is quite general and offers the widest scope of reactivity in the reductions catalyzed by the $B(C_6F_5)_3/R_3SiH$ system.

It is important, however, not to use excess silane in these reactions because the silyl ethers formed are susceptible to exhaustive reduction by the $B(C_6F_5)_3$/silane reagent system, with elimination of $(R_3Si)_2O$.[255] Gevorgyan and Y. Yamamoto have utilized this chemistry to develop protocols for the complete deoxygenation of ROH, ArOR,[256] R(H)C=O, RR′C=O and R(X)C=O (X = OR, OH, Cl) [257] functions. These reactions offer relatively mild reaction conditions for conversion of these functions to fully saturated hydrocarbons; in the case of carboxylic acids, complete reduction to a methyl group is accomplished, an otherwise difficult transformation. Several examples of these sorts of reactions for aldehyde and ketone substrates have been carried out using the relatively cheap silane reagent polymethylhydrosiloxane.[258]

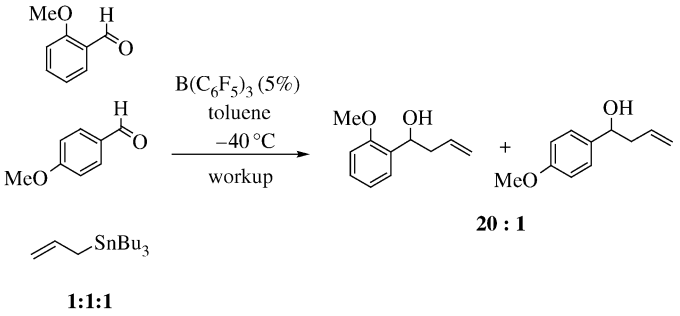
Phenolic substrates are not readily reduced to benzene derivatives, and this fact can be used to effect the transformation of methyl or benzyl ethers of phenols to their silyl ethers with elimination of CH_4 or toluene as the only by-products. These studies include detailed mechanistic studies that support and corroborate our experiments and support the silane activation mechanism. The reaction is clean and high yielding enough to be applied towards the functionalization of the periphery of carbosilane dendrimers with perfluoroaryl borane moieties (Scheme 25).[196]

In related chemistry, the borane/silane catalytic system can cleanly dealkylate phosphonic and phosphinic esters $RPO(OR')_2$ or $R_2PO(OR')$ to give silyl esters with trialkyl silanes.[259] If more active silane reagents like Ph_2SiH_2 or $PhSiH_3$ are employed, catalytic reduction to primary or secondary phosphines is observed. Mechanistic experiments strongly support a silane activation pathway for this chemistry.

Since complete hydride abstraction by $B(C_6F_5)_3$ from Bu_3SnH has been observed,[260] it is not surprising that the borane mediates hydrostannation reactions as well. Y. Yamamoto also reported the use of $B(C_6F_5)_3$ in the hydrostannation of alkynes; the hydrostannane is generated *in situ* from silane in the presence of $B(C_6F_5)_3$.[261] Furthermore, Maruoka *et al*. have reported $B(C_6F_5)_3$ mediated hydrostannation of ketones, chemistry which is discussed in more detail in the next section.

3. Allylstannations and Related Reactions

Allylation of carbonyl or imine functions is an important carbon–carbon bond forming methodology that also adds functionality for further elaboration and offers



SCHEME 36.

opportunity to effect asymmetric transformations. Lewis acids are often required to encourage addition of soft allyl nucleophiles like allyl tin reagents to carbonyl electrophiles, and the rules governing selectivity are relatively well understood.[262]

Not surprisingly, $B(C_6F_5)_3$ is an effective catalyst for allylation of carbonyl functions. In a provocative *J. Am. Chem. Soc.* communication, Maruoka and co-workers reported the chemoselective allylstannation of *ortho*-anisaldehyde in the presence of *para*-anisaldehyde as mediated by $B(C_6F_5)_3$ (Scheme 36).[263] By way of rationale, they proposed that the *ortho* substituted substrate is selectively activated by the LA through chelation at boron; this explanation was also used to explain the high diastereoselectivity observed for X = O in the hydrostannation of $PhC(O)CH(CH_3)XCH_3$ but not for $X = CH_2$.

Given the likelihood of a stannane activation pathway for the latter hydrostannation chemistry, and the unprecedented nature of the hypercoordinate boron intermediate proposed we examined the mechanism of allylstannation of the anisaldehyde substrates in detail.[130] The chemoselectivity for allylation of the *ortho* substituted substrate appears to be quite general as long as an *ortho* substituent capable of electron pair donation is present and furthermore does not depend greatly on the nature of the LA. After a detailed spectroscopic and mechanistic investigation of this reaction, a mechanism consistent with all observations was proposed and is depicted in Scheme 37. Taken together, these and other observations argue against a chelation-based explanation for the selectivity,[264] and suggests that the *ortho* donor plays a role in stabilizing the generally accepted antiperiplanar transition state[265] for allyl delivery in these reactions.

Note that the mechanism in Scheme 37 does not involve abstraction of the allyl group from the tin, which was our original hypothesis in light of the mechanistic picture for the hydrosilation chemistry. True, in the absence of other reagents $B(C_6F_5)_3$ is capable of partially abstracting an allyl group from $Bu_3Sn(C_3H_5)$[266] and catalyzing the isomerization of more substituted allyl tin reagents.[267] However, in contrast to the hydrosilation chemistry, this does not appear to be a kinetically important process in the $B(C_6F_5)_3$ mediated allystannation reactions. Thus, attack of the more nucleophilic (than R_3SiH) organotin reagent on the borane/aldehyde adduct results in an irreversible C–C bond forming reaction to form an ion pair (IP) consisting of a tributylstannylium ion solvated by two substrate molecules and an alkoxyborate counteranion. This ion pair is quite stable at low temperatures (−78 °C) where turnover of the reaction is very slow.

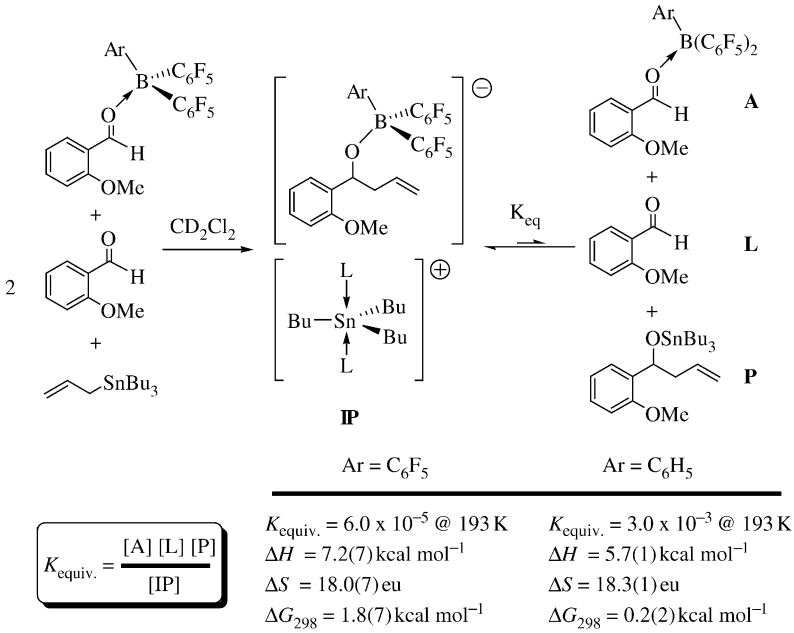
B(C6F5)3
L
OMe
A
xs L
SnBu3
X =
OB(C6F5)3
OMe
L
SnBu3
OB(C6F5)3
OMe
Bu—Sn—Bu
L
L
δ119Sn = 91.0 ppm
IP
L
Sn
Bu
Bu
δ119Sn = 300.5 ppm
– 40 °C
OSnBu3
SnBu3
OMe
δ119Sn = 220, 240 ppm
L
OSnBu3
OMe
P
δ119Sn = 104.5 ppm

SCHEME 37.

As the reaction mixture is warmed to temperatures of about −40 °C, product formation begins mainly *via* an $[R_3Sn]^+$ catalyzed mechanism as indicated in the scheme. Thus, the $B(C_6F_5)_3$ functions here primarily as an initiator, while the majority of the catalysis is mediated by the tin cation generated upon initial attack of allyltributyltin on the borane activated substrate.

Similar mechanistic pathways have been implicated in LA catalyzed allylsilation reactions[268], but have not generally been thought to be important for the more nucleophilic allyl tin reagents. The dominance of a tin cation catalyzed pathway has obvious implications for the potential efficacy of chiral perfluoroaryl borane catalysts for asymmetric induction in this reaction and suggests that "turning on" a pathway involving true borane catalysis is a key challenge for the deployment of such catalysts.

Such a borane catalyzed pathway would necessitate direct collapse of the IP formed upon C–C bond formation to product *via* transfer of the alkoxy group from boron to tin. This would regenerate the adduct A for further reaction with allyltin reagent. It is possible to isolate and study this product forming step upon generation of the ion pair in the absence of excess allyltin reagent by mixing the aldehyde, $B(C_6F_5)_3$ and tin reagents in a 3:1:1 ratio as shown in Scheme 38. When this reaction is performed at −80 °C in CD_2Cl_2, the IP is generated smoothly and, upon warming, an equilibrium is established in which product P is generated along with the $B(C_6F_5)_3$/*ortho*-anisaldehyde adduct A and free aldehyde L. The equilibrium constant can be evaluated at various temperatures by determining the concentrations of the various components by ^1H and ^{19}F NMR spectroscopy.[269] An identical experiment can be performed using the less Lewis



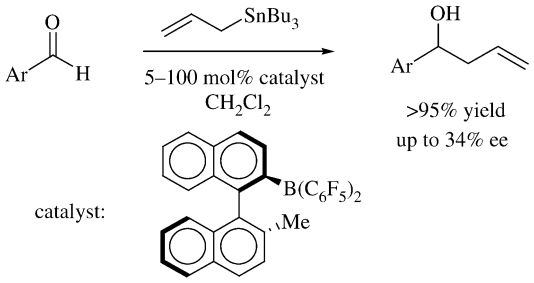
SCHEME 38.

acidic borane $PhB(C_6F_5)_2$. This experiment allows for a rare glimpse into the thermodynamic factors affecting the product-forming step of a LA catalyzed reaction as a function of the Lewis acidity of the catalyst. As shown in Scheme 38, this equilibrium, in the product forming direction, is enthalpically disfavored but entropically favored. Although there are obviously ill-defined kinetic factors that come into play, use of the weaker LA $PhB(C_6F_5)_2$ lowers the enthalpy of the equilibrium such that it is now more favored towards the product side of the equation. Thus, despite being a demonstrably weaker LA than $B(C_6F_5)_3$, the phenyl substituted borane is a superior allylation catalyst for allylation of benzaldehyde substrates. For example, at temperatures where tin cation catalysis of the allylstannation of *ortho*-anisaldehyde is known to be slow, the $PhB(C_6F_5)_2$ catalyzed reaction is finished while the $B(C_6F_5)_3$ mediated reaction is only 21% complete.

This observation is an unusual one since it is a largely accepted tenet of LA catalysis that stronger LAs should result in enhanced rates of reaction, and not decrease activity. At least part of the explanation for this phenomenon lies in the effect of substituting a phenyl group for a pentafluorophenyl group on the equilibrium described in Scheme 38. Whereas the stronger LA $B(C_6F_5)_3$ is "leveled" to the strength of $[Bu_3Sn(L)]^+$, $PhB(C_6F_5)_2$ provides a closer match to the tin cation in terms of LA strength, allowing for more facile transfer of the alkoxy group from boron to tin and turnover *via* a "true" borane catalyzed pathway.

These detailed spectroscopic and mechanistic studies have thus delineated two competing mechanistic pathways for turnover in the catalytic allylstannation of benzaldehyde substrates. The first is a tin cation mediated pathway as depicted in Scheme 37 in which the borane is effectively sequestered in the counteranion of the stannylium species responsible for the majority of the catalysis. This pathway dominates in the $B(C_6F_5)_3$ initiated reactions, since reaction turnover is not generally observed until the medium is warmed to temperatures where it is known that tin cations are effective catalysts for this reaction. The second pathway involves genuine borane catalysis with steps as shown in Scheme 38. These observations are critical for the goal of using chiral perfluoroaryl boranes for effecting these allylations in an enantioselective way. Catalysis by $[R_3Sn(L)]^+$ has little hope of influencing the C–C bond forming step beyond the first turnover—the initiation step. However, in true borane catalysis, a chiral borane comes into play in each turnover and thus provides hope that a chiral borane will exert sufficient asymmetric influence for high enantioselectivity.

Preliminary results towards this goal suggest that this is the case. We have prepared the chiral perfluoroaryl borane shown in Scheme 39, which incorporates a binaphthyl group as the chiral element.[270] This material can be prepared in five steps from enantiopure (*R*)-(+)-2,2′-dibromobinaphthyl[271] in an overall yield of 56% ($[\alpha]_D = +448$) using the Fröhn methodology of Scheme 1. Assessment of the diastereopurity of (−)-diethyltartrate derivatives of two intermediates in the synthesis indicates that the 2′-Me-BNB has >99% enantiopurity. (*R*)-(+)-2′-Me-BNB is an effective catalyst for the allylstannation of benzaldehydes (Scheme 39), giving high yields of the allylic alcohol products upon work-up. Furthermore, while observed ee's are modest, the fact that any enantioselection is observed at all is indicative that some measure of borane catalysis is operative. We are currently modifying the structure of the chiral borane to optimize its performance in this and other reactions.



(*R*)-(+)-2′-Me-BNB

SCHEME 39.

$B(C_6F_5)_3$ catalyzed reactions involving allylsilanes are now beginning to be explored. For example, Gevorgyan *et al*. have reported the allylation of secondary benzylic alcohol derivatives, particularly the acetates, using 5% $B(C_6F_5)_3$ as a catalyst.[272] The mechanism of this process is unknown, but the reaction is clean and high yielding.

Clearly, the applications of $B(C_6F_5)_3$ in organic synthesis are growing in number, and the advantages the reagent offers are beginning to outweigh the detrimental aspects of its use (primarily the cost). The opportunities to effect asymmetric transformations are tremendous, justifying the development of chiral boranes such as that shown in Scheme 39.

VIII

SUMMARY AND CONCLUSIONS

"From Obscurity to Applications" was the subtitle of the Piers and Chivers 1997 *Chem. Soc. Rev.* article highlighting the chemistry of perfluoroaryl boranes.[2b] The discovery that $B(C_6F_5)_3$ is an effective co-catalyst for olefin polymerization processes has led to the proverbial explosion of research activity in its chemistry and that of its derivatives. The unique properties of $B(C_6F_5)_3$ (thermal and hydrolytic stability coupled with strong Lewis acidity) have led to extensive applications in widely varying areas of chemistry. Most of what has been discussed above has focused on applications as Lewis acids, but emerging applications such as anion transport additives in lithium batteries[273] suggest even broader utility for this remarkable class of compounds. As $B(C_6F_5)_3$ and its derivatives become more broadly available, this should continue to be an active area of research.

ACKNOWLEDGEMENTS

I would like to start by thanking the many undergraduate and graduate students and postdoctoral fellows who have studied perfluoroaryl boranes in my group. Their names are in the citations and I am indebted to them not only for their hard work and talent but also for making my life as a chemist incredibly rich and fulfilling. I am also grateful for the contributions of our crystallographic collaborators, particularly my colleague Dr. Masood Parvez and Dr. Robert MacDonald of the University of Alberta. Our work on perfluoroaryl boranes has been funded by the Natural Sciences and Engineering Research Council of Canada, Nova Chemicals Ltd., of Calgary, Alberta, and the Merck Frosst Centre for Therapeutic Research, of Dorval, Quebec. Finally, I would like

to dedicate this article in thanks to my colleague, Prof. Tris Chivers, for his mentorship and support during my career at the University of Calgary. It is a happy coincidence that, although perhaps better known for his contributions to sulfur–nitrogen and chalcogen chemistry, he is also one of the pioneers of perfluoroaryl borane chemistry.[1]

References

(1) Chambers, R. D.; Chivers, T. *Proc. Chem. Soc.* **1963**, 208.
(2) (a) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391. (b) Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, 345. (c) Erker, G. *Chem. Commun.* **2003**, 1469.
(3) (a) Massey, A. G.; Park, A. J.; Stone, F. G. A. *Proc. Chem. Soc.* **1963**, 212. (b) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325.
(4) (a) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253. (b) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223. (c) Brintzinger, H.-H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143.
(5) (a) Massey, A. G.; Park, A. J.; Stone, F. G. A. *Proc. Chem. Soc.* **1963**, 212. (b) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245.
(6) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1966**, *5*, 218.
(7) De Pasquale, R. J.; Tamborski, C. *J. Org. Chem.* **1967**, *32*, 3163.
(8) (a) Miller, J.; Ho, K. C. *Aust. J. Chem.* **1966**, *19*, 423. (b) Miller, J.; Yeung, H. W. *Aust. J. Chem.* **1967**, *20*, 379.
(9) Childs, R. F.; Mulholland, D. L.; Nixon, A. *Can. J. Chem.* **1982**, *60*, 801.
(10) Childs, R. F.; Mulholland, D. L.; Nixon, A. *Can. J. Chem.* **1982**, *60*, 809.
(11) Laszlo, P.; Teston, M. *J. Am. Chem. Soc.* **1990**, *112*, 8750.
(12) (a) Mayer, U.; Gutmann, V.; Gerger, W. *Monatshefte Chemie.* **1975**, *106*, 1235. (b) Gutmann, V. *Coord. Chem. Rev.* **1976**, *18*, 225.
(13) Beckett, M. A.; Brassington, D. S.; Coles, S. J.; Hursthouse, M. B. *Inorg. Chem. Commun.* **2000**, *3*, 530.
(14) Luo, L.; Marks, T. J. *Top. Catal.* **1999**, *7*, 97.
(15) Chivers, T. *J. Fluorine Chem.* **2002**, *115*, 1.
(16) Chambers, R. D.; Chivers, T. *J. Chem. Soc.* **1965**, 3933.
(17) Pohlmann, J. L. W.; Brinckmann, F.; Tesi, G.; Donadio, R. E. *Z. Naturforsch B* **1965**, *20*, 1.
(18) Duchateau, R.; Lancaster, S. J.; Thornton-Pett, M.; Bochmann, M. *Organometallics* **1997**, *16*, 4995.
(19) Frohn, H.-J.; Franke, H.; Fritzen, P.; Bardin, V. V. *J. Organomet. Chem.* **2000**, *598*, 127.
(20) Abarbri, M.; Dehmel, F.; Knochel, P. *Tetrahedron Lett.* **1999**, *40*, 7449.
(21) Fröhn, H.-J.; Adonin, N. Y.; Bardin, V. V.; Starichenko, V. F. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2827.
(22) Balkwill, J. E.; Cole, S. C.; Coles, M. P.; Hitchcock, P. B. *Inorg. Chem.* **2002**, *41*, 3548.
(23) (a) Habben, C. D.; Herbst-Irmer, R.; Noltemeyer, M. *Z. Naturforsch.* **1991**, *46b*, 625. (b) Habben, C. D.; Heine, A.; Sheldrick, G. M.; Stalke, D. *Z. Naturforsch.* **1992**, *47b*, 1367.
(24) Fraenk, W.; Klapötke, T. M.; Krumm, B.; Nöth, H.; Suter, M.; Warchold, M. *J. Chem. Soc., Dalton Trans.* **2000**, 4635.
(25) Gamboa, J. A.; Sundararaman, A.; Kakalis, L.; Lough, A. J.; Jäkle, F. *Organometallics* **2002**, *21*, 4169.
(26) Paetzold, P.; Richter, A.; Thijssen, T.; Wurtenberg, S. *Chem. Ber.* **1979**, *112*, 3811.
(27) Morse, J. G.; Glanville, W. K. *Inorg. Chem.* **1984**, *23*, 11.
(28) (a) Tian, J.; Wang, S.; Feng, Y.; Li, J.; Collins, S. *J. Mol. Cat. A: Chemical* **1999**, *144*, 137. (b) Metcalfe, R. A.; Kreller, D. I.; Tian, J.; Kim, H.; Taylor, N. J.; Corrigan, J. F.; Collins, S. *Organometallics* **2002**, *21*, 1719. (c) Duchateau, R.; van Santen, R. A.; Yap, G. P. A. *Organometallics* **2000**, *19*, 809.
(29) Bradley, D. C.; Harding, I. S.; Keefe, A. D.; Motevalli, M.; Zheng, D. H. *J. Chem. Soc., Dalton Trans.* **1996**, 3931.
(30) Parks, D. J.; Piers, W. E.; Yap, G. P. A. *Organometallics* **1998**, *17*, 5492.
(31) Spence, R. E. vH.; Piers, W. E.; MacGillivray, L. R.; Zaworotko, M. J. *Acta Cryst. Ser. C* **1995**, *C51*, 1688.
(32) Chambers, R. D.; Coates, G. E.; Livingstone, J. G.; Musgrave, W. K. R. *J. Chem. Soc.* **1962**, 4367.
(33) Bochmann, M.; Lancaster, S. J.; Robinson, O. B. *J. Chem. Soc., Chem. Commun.* **1995**, 2081.
(34) Parks, D. J.; Spence, R. E. vH.; Piers, W. E. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 809.

(35) Kidd, R. G. (P. Laszlo, Ed.) *NMR of Newly Accessible Nuclei*, Vol. 2. Academic Press, New York, 1983.
(36) Romero, P.E.; Piers, W.E. Unpublished results.
(37) Entwistle, C. D.; Marder, T. B.; Smith, P. S.; Howard, J. A. K.; Fox, M. A.; Mason, S. A. *J. Organomet. Chem.* **2003**, *680*, 165.
(38) Willams, J. H. *Acc. Chem. Res.* **1993**, *26*, 593.
(39) Spence, R. E. vH.; Piers, W. E. *Organometallics* **1995**, *14*, 4617.
(40) Hill, M.; Kehr, G.; Fröhlich, R.; Erker, G. *Eur. J. Inorg. Chem.* **2003**, 3583.
(41) Piers, W. E. *Chem. Eur. J.* **1998**, *4*, 13.
(42) Kunz, D.; Erker, G.; Fröhlich, R.; Kehr, G. *Eur. J. Inorg. Chem.* **2000**, 409.
(43) Carpenter, B. E.; Piers, W. E.; Parvez, M.; Yap, G. P. A.; Rettig, S. J. *Can. J. Chem.* **2001**, *78*, 857.
(44) Doerrer, L. H.; Graham, A. J.; Haussinger, D.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **2000**, 813.
(45) (a) Sun, Y.; Piers, W. E.; Rettig, S. J. *Organometallics* **1996**, *15*, 4110. (b) Lee, L. W. M.; Piers, W. E.; Elsegood, M. R. J.; Clegg, W.; Parvez, M. *Organometallics* **1999**, *18*, 2947.
(46) Blaschke, U.; Erker, G.; Fröhlich, R.; Meyer, O. *Eur. J. Inorg. Chem.* **1999**, 2243.
(47) Sun, Y.; Spence, R. E. vH.; Piers, W. E.; Parvez, M.; Yap, G. P. A. *J. Am. Chem. Soc.* **1997**, *119*, 5132.
(48) (a) Spence, R. E. vH.; Parks, D. J.; Piers, W. E.; MacDonald, M.; Zaworotko, M. J.; Rettig, S. J. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1230. (b) Spence, R. E. vH.; Piers, W. E.; Sun, Y.; Parvez, M.; MacGillivray, L. R.; Zaworotko, M. J. *Organometallics* **1998**, *17*, 2459.
(49) Hayes, P.G.; Piers, W.E., Parvez, M. Unpublished results.
(50) (a) Chase, P. A.; Piers, W. E.; Parvez, M. *Organometallics* **2000**, *19*, 2040. (b) Plecnik, C. E.; Liu, F.-C.; Liu, S.; Liu, J.; Meyers, E. A.; Shore, S. G. *Organometallics* **2001**, *20*, 3599.
(51) Iverson, C. N.; Smith, M. R. III *J. Am. Chem. Soc.* **1999**, *121*, 7696.
(52) Douthwaite, R. E. *Polyhedron* **2000**, *19*, 1579.
(53) Hayes, P. G.; Lee, L. W. M.; Knight, L. K.; Piers, W. E.; Parvez, M.; Elsegood, M. R. J.; Clegg, W.; MacDonald, R. *Organometallics* **2001**, *20*, 2533.
(54) (a) Zhang, S.; Piers, W. E.; Gao, X.; Parvez, M. *J. Am. Chem. Soc.* **2000**, *122*, 5499, and references therein. (b) Zhang, S.; Piers, W. E. *Organometallics* **2001**, *20*, 2088.
(55) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611.
(56) Radius, U.; Silverio, S. J.; Hoffmann, R.; Gleiter, R. *Organometallics* **1996**, *15*, 3737.
(57) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.
(58) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.
(59) Cook, K. S.; Piers, W. E.; Rettig, S. J. *Organometallics* **1999**, *18*, 1575.
(60) Cook, K. S.; Piers, W. E.; Woo, T. K.; Rettig, S. J.; McDonald, R. *Organometallics* **2001**, *20*, 3927.
(61) Cook, K. S.; Piers, W. E.; McDonald, R. *J. Am. Chem. Soc.* **2002**, *124*, 5411.
(62) Cook, K. S.; Piers, W. E.; Hayes, P. G.; Parvez, M. *Organometallics* **2002**, *22*, 2422.
(63) Sharp, P. R.; Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 965.
(64) van de Eide, E. F.; Romero, P.E.; Piers, W.E.; Parvez, M.; McDonald, R. *Organometallics* **2004**, *23*, 314.
(65) (a) Carlson, R. G.; Gile, M. A.; Heppert, J. A.; Mason, M. H.; Powell, D. R.; Vander Velde, D.; Vilain, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 1580. (b) Heil, A.; Trnka, T. M.; Day, M. W.; Grubbs, R. H. *Chem. Commun.* **2002**, 2524.
(66) Bohnen, H.; Hahn, U., Patent WO0017208, 2000 (Aventis R&T GMBH).
(67) Kratzer, R. Patent DE 10059717, **2000** (Basell).
(68) (a) Ishihara, K.; Kurihara, H.; Yamamoto, H. *J. Org. Chem.* **1997**, *62*, 5664. (b) Schottek, J.; Fritze, C. Patent DE 10009714, **2001** (Targor). (c) Ikeno, I.; Mitsui, H.; Iida, T.; Moriguchi, T.; Hara, K. Patent WO 02/44185, **2000** (Nippon Shokubai Co.).
(69) Beringhelli, T.; D'Alfonso, G.; Donghi, D.; Maggioni, D.; Mercandelli, P.; Sironi, A. *Organometallics* **2003**, *22*, 1588.
(70) Ishihara, K.; Kurihara, H.; Yamamoto, H. *Synlett* **1997**, 597.
(71) Bohnen, H. Patent DE 19733017, **1999** (Hoechst AG).
(72) Schottek, J.; Fritze, C.; Bohnen, H.; Moers, D.E.; Becker, P. Patent DE 19845240, **2000** (Aventis R&T GMBH).
(73) Collins, S.; Taylor, N.J. Unpublished results.
(74) Parks, D.J.; van de Eide, E.; Piers, W.E. Unpublished results.
(75) Abiko, A.; Inoue, T.; Masamune, S. *J. Am. Chem. Soc.* **2002**, *124*, 10759, and references therein.

(76) Galsworth, J. R.; Green, M. L. H.; Williams, V. C.; Chernega, A. N. *Polyhedron* **1998**, *17*, 119.
(77) Kehr, G.; Fröhlich, R.; Wibbeling, B.; Erker, G. *Chem. Eur. J.* **2000**, *6*, 258.
(78) Wu, P.-C.; Yu, J.-K.; Song, Y.-H.; Chi, Y.; Chou, P.-T.; Peng, S.-M.; Lee, G.-H. *Organometallics* **2003**, *22*, 4938.
(79) Fraenk, W.; Klapötke, T. M.; Krumm, B.; Mayer, P. *Chem. Commun.* **2000**, 667.
(80) Fraenk, W.; Klapötke, T. M.; Krumm, B.; Nöth, H.; Suter, M.; Vogt, M.; Warchold, M. *Can. J. Chem.* **2002**, *80*, 1444.
(81) Parks, D. J.; Piers, W. E. *Tetrahedron* **1998**, *54*, 15469.
(82) Deck, P. A.; Beswick, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *129*, 1772.
(83) (a) Morrison, D. J.; Piers, W. E. *Org. Lett.* **2003**, *5*, 2857. (b) Morrison, D. J.; Blackwell, J. M.; Piers, W. E. *Pure Appl. Chem.* **2004**, *76*, 615.
(84) Schulte, M.; Gabbaï, F. P. *J. Organomet. Chem.* **2002**, *634–644*, 164.
(85) Roesler, R.; Piers, W. E.; Parvez, M. *J. Organomet. Chem.* **2003**, *680*, 218.
(86) Qin, Y.; Cheng, G.; Sundararaman, A.; Jäkle, F. *J. Am. Chem. Soc.* **2002**, *124*, 12672.
(87) Sundararaman, A.; Lalancette, R. A.; Zakharov, L. V.; Rheingold, A. L.; Jäkle, F. *Organometallics* **2003**, *23*, 3526, and references therein.
(88) Sun, Y.; Piers, W. E.; Parvez, M. *Can. J. Chem.* **1998**, *76*, 513.
(89) Sundararaman, A.; Jäkle, F. *J. Organomet. Chem.* **2003**, *681*, 134.
(90) Piers, W. E.; Sun, Y.; Lee, L. W. M. *Topics in Catalysis* **1999**, *7*, 133.
(91) Lancaster, S. J.; Al-Benna, S.; Thornton-Pett, M.; Bochmann, M. *Organometallics* **2000**, *19*, 1599.
(92) Reetz, M. T.; Brümmer, H.; Kessler, M.; Kuhnigk, J. *Chimia* **1995**, *49*, 501.
(93) Chen, Y.-X. E.; Metz, M. V.; Li, L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 6287.
(94) Li, L.; Stern, C. L.; Marks, T. J. *Organometallics* **2000**, *19*, 3332.
(95) Li, L.; Marks, T. J. *Organometallics* **1998**, *17*, 3996.
(96) Chase, P. A.; Piers, W. E.; Patrick, B. O. *J. Am. Chem. Soc.* **2000**, *122*, 12911.
(97) Döring, S.; Erker, G.; Fröhlich, R.; Meyer, O.; Bergander, K. *Organometallics* **1998**, *17*, 2183.
(98) Vanka, K.; Chan, M. S. W.; Pye, C. C.; Ziegler, T. *Organometallics* **2000**, *19*, 1841.
(99) Pohlmann, J. L. W.; Brinckmann, F. E. *Z. Naturforsch. B* **1965**, *20*, 5.
(100) Spence, R. E. vH. *Chem. Eng. News* **1996**, *74*, 21, 4.
(101) Kraft, T. US Patent 5,679,289, **1996** (Boulder Scientific Company).
(102) Wilson, D. R.; Lapointe, R. E. WO 97/39003, **1997**; US Patent 5,744,646 (Dow Chemical Company).
(103) Asai, T.; Nakajima, Y. WO99/64427, **1999** (Asahi Glass Company Ltd.).
(104) Diefenbach, S. P. EP 0728761A2, **1996** (Albemarle Corporation).
(105) Ikeda, Y., Yamane, T.; Kaji, E.; Ishamaru, K. EP 0604959A2, EP 0604962A1, EP 0604963A1, **1993** (Tosoh Akzo Corporation).
(106) (a) Frazier, K. A.; Meier, L. B. WO 97/14698, **1996** (Dow Chemical Company). (b) Ashkam, F. WO 98/22475, **1997** (Boulder Scientific Company).
(107) (a) Lee, J. Y.; Diefenbach, S. P.; Power, J. M.; Lin, R. W. US Patent 5,959,151, **1998** (Albemarle Corporation). (b) Lee, J. Y.; Strickler, J. R. WO 00/64907, 1999 (Albermarle Corporation).
(108) Cohen, S. C.; Massey, A. G. *J. Organomet. Chem.* **1967**, *10*, 471.
(109) Horton, A. D.; de With, J. *Organometallics* **1997**, *16*, 5424.
(110) (a) Siedle, A. R.; Lamanna, W. M. U.S. Patent No. 5,296,433, March 22, 1994. (b) Siedle, A. R.; Lamanna, W. M.; Newmark, R. A.; Stevens, J.; Richardson, D. E.; Ryan, M. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 215.
(111) (a) Danopoulos, A. A.; Galsworthy, J. R.; Green, M. L. H.; Cafferkey, S.; Doerrer, L. H.; Hursthouse, M. B. *Chem. Commun.* **1998**, 2529. (b) Kalamarides, H. A.; Iyer, S.; Lipian, J.; Rhodes, L. F. *Organometallics* **2000**, *19*, 3983.
(112) Coles, S. J.; Hursthouse, M. B.; Beckett, M. A.; Dutton, M. *Acta Cryst. Ser. E* **2003**, *E59*, o1354.
(113) Bergquist, C.; Bridgewater, B. M.; Harlan, C. J.; Norton, J. R.; Friesner, R. A.; Parkin, G. *J. Am. Chem. Soc.* **2000**, *122*, 10581.
(114) Drewitt, M. J.; Neidermann, M.; Baird, M. C. *Inorg. Chim. Acta* **2002**, *340*, 207.
(115) Watson, I. D. G.; Yudin, A. K. *J. Org. Chem.* **2003**, *68*, 5160.
(116) Janiak, C.; Braun, L.; Scharmann, T. G.; Girgsdies, F. *Acta Cryst.* **1998**, *C54*, 1722.
(117) Doerrer, L. H.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1999**, 4325.
(118) Beringhelli, T.; Maggioni, D.; D'Alfonso, G. *Organometallics* **2001**, *20*, 4927.

(119) (a) Bergquist, C.; Parkin, G. *J. Am. Chem. Soc.* **1999**, *121*, 6322. (b) Bergquist, C.; Fillebeen, T.; Morlok, M. M.; Parkin, G. *J. Am. Chem. Soc.* **2003**, *125*, 6189.
(120) Hill, G. S.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 525.
(121) Neculai, D.; Roesky, H. W.; Neculai, A. M.; Magull, J.; Walfort, B.; Stalke, D. *Angew. Chem. Int. Ed.* **2002**, *41*, 4294.
(122) Siedle, A. R.; Newmark, R. A.; Lamanna, W. M.; Huffman, J. C. *Organometallics* **1993**, *12*, 1491.
(123) Howard, W. A.; Parkin, G. *J. Am. Chem. Soc.* **1994**, *116*, 606.
(124) Drewitt, M. J.; Niedermann, M.; Kumar, R.; Baird, M. C. *Inorg. Chim. Acta* **2002**, *335*, 43.
(125) Data in Table I, Entry 6: Chase, P.A.; Piers, W.E. Unpublished results.
(126) Shambayati, S.; Crowe, W. E.; Schrieber, S. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 256.
(127) Parks, D. J.; Piers, W. E.; Parvez, M.; Atencio, R.; Zaworotko, M. J. *Organometallics* **1998**, *17*, 1369.
(128) (a) Lee, B. Y.; Bu, X.; Bazan, G. C. *Organometallics* **2001**, *20*, 5425. (b) Kim, Y. H.; Kim, T. H.; Lee, B. Y.; Woodmansse, D.; Bu, X.; Bazan, G. C. *Organometallics* **2002**, *21*, 3082. (c) Komon, Z. J. A.; Bu, X.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 12379. (d) Lee, B. Y.; Bazan, G. C.; Vela, J.; Komon, Z. J. A.; Bu, X. *J. Am. Chem. Soc.* **2001**, *123*, 5352.
(129) Weber, L.; Uthmann, S.; Stammler, H.-G.; Neumann, B.; Schoeller, W. W.; Boese, R.; Bläser, D. *Eur. J. Inorg. Chem.* **1999**, 2369.
(130) Blackwell, J. M.; Piers, W. E.; McDonald, R. *J. Am. Chem. Soc.* **2002**, *124*, 1295.
(131) Vagedes, D.; Fröhlich, R.; Erker, G. *Angew. Chem. Int. Ed.* **1999**, *38*, 3362.
(132) Dash, A. K.; Jordan, R. F. *Organometallics* **2002**, *21*, 777.
(133) Beckett, M. A.; Brassington, D. S.; Light, M. E.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **2001**, 1768.
(134) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 461.
(135) Mountford, A. J.; Hughes, D. L.; Lancaster, S. *J. Chem. Commun.* **2003**, 2148.
(136) Guidotti, S.; Camurati, I.; Focante, F.; Angellini, L.; Moscardi, G.; Resconi, L.; Leardini, R.; Nanni, D.; Mercandelli, P.; Sironi, A.; Beringhelli, T.; Maggioni, T. *J. Org. Chem.* **2003**, *68*, 5445.
(137) Chivers, T.; Schatte, G. Manuscript in preparation for *Inorg. Chem.*
(138) Mitani, M.; Furuyama, R.; Mohri, J.-I.; Saito, J.; Ishii, S.; Terao, H.; Nakano, T.; Tanaka, H.; Fujita, T. *J. Am. Chem. Soc.* **2003**, *125*, 4293.
(139) Millot, N.; Cox, A.; Santini, C. C.; Molard, Y.; Basset, J.-M. *Chem. Eur. J.* **2002**, *8*, 1438, and references therein.
(140) Millot, N.; Santini, C. C.; Fenet, B.; Basset, J.-M. *Eur. J. Inorg. Chem.* **2002**, 3328.
(141) Henderson, L.D.; Piers, W.E. Unpublished results.
(142) Lesley, M. J. G.; Woodward, A.; Taylor, N. J.; Marder, T. B.; Cazenobe, E.; Ledoux, I.; Zyss, J.; Thornton, A.; Bruce, D. W.; Kakkar, A. K. *Chem. Mater.* **1998**, *10*, 1355.
(143) Fraenk, W.; Klapötke, T. M.; Krumm, B.; Mayer, P.; Piotrowski, H.; Vogt, M. Z. *Anorg. Allg. Chem.* **2002**, *628*, 745.
(144) Kehr, G.; Roesmann, R.; Fröhlich, R.; Holst, C.; Erker, G. *Eur. J. Inorg. Chem.* **2001**, 535.
(145) Resconi, L.; Guidotti, S. Int. Patent Appl. WO 01/62764, **2001** (Basell).
(146) (a) Vagedes, D.; Kehr, G.; König, D.; Wedeking, K.; Fröhlich, R.; Erker, G.; Mück-Lichtenfeld, C.; Grimme, S. *Eur. J. Inorg. Chem.* **2002**, 2015. (b) Vagedes, D.; Erker, G.; Kehr, G.; Bergander, K.; Kataeva, O.; Fröhlich, R.; Grimme, S.; Mück-Lichtenfeld, C. *Dalton Trans.* **2003**, 1337.
(147) Röttger, D.; Erker, G.; Fröhlich, R.; Kotila, S. *J. Organomet. Chem.* **1996**, *518*, 17.
(148) Blackwell, J. M.; Piers, W. E.; Parvez, M.; McDonald, R. *Organometallics* **2002**, *21*, 1400.
(149) Courtenay, S.; Ong, C. M.; Stephan, D. W. *Organometallics* **2003**, *22*, 818.
(150) Choukroun, R.; Lorber, C.; Donnadieu, B. *Chem. Eur. J.* **2002**, *8*, 2700.
(151) Chivers, T.; Schatte, G. *Eur. J. Inorg. Chem.* **2003**, 3314.
(152) (a) Jacobsen, H.; Berke, H.; Döring, S.; Kehr, G.; Erker, G.; Fröhlich, R.; Meyer, O. *Organometallics* **1999**, *18*, 1724. (b) Fraenk, W.; Klapötke, T. M.; Krumm, B.; Mayer, P.; Piotrowski, H.; Vogt, M. *Z. Anorg. Allg. Chem.* **2002**, *628*, 745.
(153) Stoddard, J. M.; Shea, K. J. *Organometallics* **2003**, *22*, 1124.
(154) Döring, S.; Erker, G.; Fröhlich, R.; Meyer, O.; Bergander, K. *Organometallics* **1998**, *17*, 2183.
(155) Spaether, W.; Klass, K.; Erker, G.; Zippel, F.; Fröhlich, R. *Chem. Eur. J.* **1998**, *4*, 1411.
(156) (a) Collins, S.; Ward, D. G.; Suddaby, K. H. *Macromolecules* **1994**, *27*, 7222. (b) Giardello, M. A.; Yamamoto, Y.; Brard, L.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 3776. (c) Yasuda, H.; Yamamoto, H.;

Yamashima, M.; Yokata, K.; Nakamura, A.; Miyake, S.; Kai, Y.; Kanehisa, N. *Macromolecules* **1993**, *26*, 7134.
(157) Choukroun, R.; Lorber, C.; Lepetit, C.; Donnadieu, B. *Organometallics* **2003**, *22*, 1995.
(158) Denis, J.-M.; Forintos, H.; Szelke, H.; Toupet, L.; Pham, T.-N.; Madec, P.-J.; Gaumont, A.-C. *Chem. Commun.* **2003**, 54.
(159) Schaper, F.; Brintzinger, H.-H. *Acta Cryst. Ser. E* **2002**, *E58*, o77.
(160) Bradley, D. C.; Hursthouse, M. B.; Motevalli, M.; Zheng, D. H. *J. Chem. Soc., Chem. Commun.* **1991**, 7.
(161) Bradley, D. C.; Hawkes, G. E.; Haycock, P. R.; Sales, K. D.; Zheng, D. H. *Phil. Trans. R. Soc. Lond. A* **1994**, *348*, 315.
(162) Chase, P.A.; Piers, W.E.; Parvez, M. Unpublished results.
(163) Yue, N. L. S.; Stephan, D. W. *Organometallics* **2001**, *20*, 2303.
(164) Metzler, N.; Denk, M. *Chem. Commun.* **1996**, 2657.
(165) Gorden, J. D.; Voigt, A.; MacDonald, C. L. B.; Silverman, J. S.; Cowley, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 950.
(166) (a) Hardman, N. J.; Power, P. P.; Gorden, J. D.; Macdonald, C. L. B.; Cowley, A. H. *Chem. Commun.* **2001**, 1866. (b) Jutzi, P.; Neumann, B.; Reumann, G.; Schebaum, L. O.; Stammler, H.-G. *Organometallics* **2001**, *20*, 2854.
(167) Hardman, N. J.; Wright, R. J.; Phillips, A. D.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 2667.
(168) Wright, R. J.; Phillips, A. D.; Hardman, N. J.; Power, P. P. *J. Am. Chem. Soc.* **2002**, *124*, 8538.
(169) Hardman, N. J.; Eichler, B.; Power, P. P. *Chem. Commun.* **2000**, 1991.
(170) Galsworthy, J. R.; Green, M. L. H.; Müller, M.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1997**, 1309.
(171) Wolff, F.; Choukron, R.; Lorber, C.; Donnadieu, B. *Eur. J. Inorg. Chem.* **2003**, 628.
(172) Galsworthy, J. R.; Green, J. C.; Green, M. L. H.; Müller, M. *J. Chem. Soc., Dalton Trans.* **1998**, 15.
(173) Jernakoff, P.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1610.
(174) Doerrer, L. H.; Galsworthy, J. R.; Green, M. L. H.; Leech, M. A. *J. Chem. Soc., Dalton Trans.* **1998**, 2483.
(175) Doerrer, L. H.; Galsworthy, J. R.; Green, M. L. H.; Leech, M. A.; Müller, M. *J. Chem. Soc., Dalton Trans.* **1998**, 3191.
(176) Barrado, G.; Doerrer, L.; Green, M. L. H.; Leech, M. A. *J. Chem. Soc., Dalton Trans.* **1999**, 1061.
(177) Han, Y.; Harlan, C. J.; Stoessel, P.; Frost, B. J.; Norton, J. R.; Miller, S.; Bridgewater, B.; Xu, Q. *Inorg. Chem.* **2001**, *40*, 2942.
(178) Doerrer, L. H.; Graham, A. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1998**, 3941.
(179) (a) Abram, U.; Kohl, F. J.; Öfele, K.; Herrmann, W. A.; Voigt, A.; Kirmse, R. *Z. Anorg. Allg. Chem.* **1998**, *624*, 934. (b) Abram, U. *Z. Anorg. Allg. Chem.* **1999**, *625*, 839. (c) Abram, U.; Schmidt-Brücken, B.; Ritter, S. *Polyhedron* **1999**, *18*, 831.
(180) (a) Crevier, T. J.; Mayer, J. M. *Angew. Chem. Int. Ed.* **1998**, *37*, 1891. (b) Crevier, T. J.; Bennett, B. K.; Soper, J. D.; Bowman, J. A.; Dehestani, A.; Hrovat, D. A.; Lovel, S.; Kaminsky, W.; Mayer, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 1059.
(181) Cook, K. S.; Piers, W. E.; Rettig, S. J.; McDonald, R. *Organometallics* **2000**, *19*, 2243.
(182) Cook, K. S.; Piers, W. E.; Patrick, B. O.; McDonald, R. *Can. J. Chem.* **2003**, *81*, 1137.
(183) Eisch, J. J.; Galle, J. E.; Kozima, S. *J. Am. Chem. Soc.* **1986**, *108*, 379.
(184) (a) Chase, P.A. PhD Thesis, University of Calgary, 2003. (b) Chase, P.A.; Romero, P.E.; Piers, W.E.; Parvez, M. Unpublished results.
(185) Romero, P. E.; Piers, W. E.; Decker, S.; Chau, D.; Woo, T. K.; Parvez, M. *Organometallics* **2003**, *22*, 1266.
(186) Piers, W. E.; Irvine, G. J.; Williams, V. C. *Eur. J. Inorg. Chem.* **2000**, 2131.
(187) Williams, V. C.; Piers, W. E.; Clegg, W.; Collins, S.; Marder, T. B. *J. Am. Chem. Soc.* **1999**, *121*, 3244.
(188) Li, H.; Li, L.; Marks, T. J.; Liable-Sands, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 10788.
(189) Sartori, P.; Golloch, A. *Chem. Ber.* **1968**, *101*, 2004.
(190) (a) Williams, V. C.; Dai, C.; Li, Z.; Collins, S.; Piers, W. E.; Clegg, W. C.; Elsegood, M. R. J.; Marder, T. B. *Angew. Chem. Int. Ed.* **1999**, *39*, 3695. (b) Metz, M. V.; Schwartz, D. J.; Stern, C. L.; Nickias, P. N.; Marks, T. J. *Angew. Chem. Int. Ed.* **2000**, *39*, 1312. (c) McAdon, M.H.; Nickias, P.N.; Marks, T.J.; Schwartz, D.J. WO-A9906413A1, **1999** (The Dow Chemical Co., Northwestern University). (d) Metz, M. V.; Schwartz, D. J.; Stern, C. L.; Marks, T. J.; Nickias, P. N. *Organometallics* **2002**, *21*, 4159.
(191) Chase, P.A.; Piers, W.E.; Parvez, M. Unpublished results.
(192) Williams, V. C.; Irvine, G. J.; Piers, W. E.; Li, Z.; Collins, S.; Clegg, W.; Elsegood, M. R. J.; Marder, T. B. *Organometallics* **2000**, *19*, 1619.

(193) Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1994**, *13*, 3755.
(194) Köhler, K.; Piers, W. E.; Xin, S.; Feng, Y.; Bravakis, A. M.; Jarvis, A. P.; Collins, S.; Clegg, W.; Yap, G. P. A.; Marder, T. B. *Organometallics* **1998**, *17*, 3557.
(195) Köhler, K.; Piers, W. E. *Can. J. Chem.* **1998**, *76*, 1249.
(196) Roesler, R.; Piers, W. E.; Har, B. J. N. *Organometallics* **2002**, *21*, 4300.
(197) (a) Naumann, D.; Tyrra, W. *J. Chem. Soc., Chem. Commun.* **1989**, 47. (b) Fröhn, H.-J.; Jakobs, S. *J. Chem. Soc., Chem. Commun.* **1989**, 625. (c) Fröhn, H.-J.; Jakobs, S.; Henkel, G. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1506.
(198) Biagini, P.; Lugli, G.; Abis, L.; Andreussi, P.; Eur. Patent Appl. EP o 694 548 A1, 1996 (Enichem Elastomeri S.r. l.).
(199) Lee, C. H.; Lee, S. J.; Park, J. W.; Kim, K. H.; Lee, B. Y.; Oh, J. S. *J. Mol. Cat. A: Chem.* **1998**, *132*, 231.
(200) Klosin, J.; Roof, G. R.; Chen, E. Y.-X.; Abboud, K. A. *Organometallics* **2000**, *19*, 4684.
(201) Kim, J. S.; Wojcinski, L. M.; Liu, S.; Sworen, J. C.; Sen, A. *J. Am. Chem. Soc.* **2000**, *122*, 5668.
(202) Lassahn, P.-G.; Janiak, C.; Oh, J.-S. *Macromol. Rapid. Commun.* **2002**, *23*, 16.
(203) Bochmann, M.; Sarsfield, M. J. *Organometallics* **1998**, *17*, 5908.
(204) Dawson, D. M.; Bochmann, M. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2226.
(205) (a) Korolev, A. V.; Ihara, E.; Guzei, I. A.; Young, V. G. Jr.; Jordan, R. F. *J. Am. Chem. Soc.* **2001**, *123*, 8291. (b) Spitzmesser, S. K.; Gibson, V. C. *J. Organomet. Chem.* **2003**, *673*, 95.
(206) (a) Walker, D. A.; Woodman, T. J.; Hughes, D. L.; Bochmann, M. *Organometallics* **2001**, *20*, 3772. (b) Walker, D. A.; Woodman, T. J.; Schormann, M.; Hughes, D. L.; Bochmann, M. *Organometallics* **2003**, *22*, 797.
(207) (a) Leffler, J. E.; Watts, G. B.; Tanigaki, T.; Dolan, E.; Miller, D. S. *J. Am. Chem. Soc.* **1970**, *92*, 6825. (b) Eisch, J. J.; Dluzniewski, T.; Behrooz, M. *Heteroatom Chem.* **1993**, *4*, 235. (c) DuPont, T. J.; Mills, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 6375.
(208) Harlan, C. J.; Hascall, T.; Fujita, E.; Norton, J. R. *J. Am. Chem. Soc.* **1999**, *121*, 7274.
(209) Beddows, C. J.; Burrows, A. D.; Connelly, N. G.; Green, M.; Lynam, J. M.; Paget, T. *J. Organometallics* **2001**, *20*, 231.
(210) Kwaan, R. J.; Harlan, C. J.; Norton, J. R. *Organometallics* **2001**, *20*, 3818.
(211) Schulz, A.; Kaim, W. *Chem. Ber.* **1989**, *122*, 1863.
(212) Krossing, I.; Raabe, I. *Angew. Chem. Int. Ed.* **2004**, *43*, 2066.
(213) (a) Bosch, B. E.; Erker, G.; Fröhlich, R.; Meyer, O. *Organometallics* **1997**, *16*, 5449. (b) Bellabarba, R. M.; Clancy, G. P.; Gomes, P. T.; Martins, A. M.; Rees, L. H.; Green, M. L. H. *J. Organomet. Chem.* **2001**, *640*, 93.
(214) Lancaster, S. J.; Rodriguez, A.; Lara-Sanchez, A.; Hannant, M. D.; Walker, D. A.; Hughes, D. H.; Bochmann, M. *Organometallics* **2002**, *21*, 451.
(215) (a) Zhou, J.; Lancaster, S. J.; Walker, D. A.; Beck, S.; Thornton-Pett, M.; Bochmann, M. *J. Am. Chem. Soc.* **2001**, *123*, 223. (b) Lancaster, S. J.; Walker, D. A.; Thornton-Pett, M.; Bochmann, M. *Chem. Commun.* **1999**, 1533.
(216) LaPointe, R.E. PCT Int. Application WO 9942467 **1999** (Dow Chemical Co.).
(217) Lapointe, R. W.; Roof, G. R.; Abboud, K. A.; Klosin, J. *J. Am. Chem. Soc.* **2000**, *122*, 9560.
(218) Vagedes, D.; Erker, G.; Fröhlich, R. *J. Organomet. Chem.* **2002**, *641*, 148.
(219) Brookhart, M.; Grant, B.; Volpe, A. F. Jr. *Organometallics* **1992**, *11*, 3920.
(220) Jutzi, P.; Müller, A.; Stammler, H.-G. *Organometallics* **2000**, *19*, 1442.
(221) Bochmann, M.; Lancaster, S. J. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1634.
(222) Ren, K.; Malpert, J. H.; Li, H.; Gu, H.; Neckers, D. C. *Macromolecules* **2002**, *35*, 1632.
(223) Castellanos, F.; Fouassier, J. P.; Priou, C.; Cavezzan, J. *J. Appl. Polym. Sci.* **1996**, *60*, 705.
(224) Henderson, L.D.; Piers, W.E. Unpublished results.
(225) Henderson, L. H.; Piers, W. E.; McDonald, R. *Organometallics* **2002**, *21*, 340.
(226) Rodriguez, G.; Brant, P. *Organometallics* **2001**, *20*, 2417.
(227) Quyoum, R.; Wang, Q.; Tudoret, M.-J.; Baird, M. C.; Gillis, D. J. *J. Am. Chem. Soc.* **1994**, *116*, 6435.
(228) (a) Pellecchia, C.; Pappalardo, D.; Oliva, L.; Zambelli, A. *J. Am. Chem. Soc.* **1995**, *117*, 6539. (b) Wang, Q.; Quyoum, R.; Gillis, D. J.; Tudoret, M.-J.; Jeremic, D.; Hunter, B. K.; Baird, M. C. *Organometallics* **1996**, *15*, 693.
(229) Shaffer, T. D.; Ashbaugh, J. R. *J. Polym. Sci: Part A: Polym. Chem.* **1997**, *35*, 329.
(230) Shaffer, T.D. US Patent Appl. 08 234 782, **1994** (Exxon).

(231) Kumar, K. R.; Hall, C.; Penciu, A.; Drewitt, M. J.; Mcinenly, P. J.; Baird, M. C. *J. Polym. Sci., Part A: Polymer Chem.* **2002**, *40*, 3302.
(232) Pi, Z.; Jacob, S.; Kennedy, J. P. (J. E. Puskas, Ed.) *Ionic Polymerizations and Related Processes*, Kluwer, Dordrecht, 1999.
(233) Lewis, S. P.; Taylor, N. J.; Piers, W. E.; Collins, S. *J. Am. Chem. Soc.* **2003**, *125*, 14686.
(234) (a) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22. (b) Gauvin, F.; Harrod, J. F.; Woo, H. G. *Adv. Organomet. Chem.* **1998**, *42*, 363.
(235) (a) Dioumaev, V. K.; Harrod, J. F. *Organometallics* **1996**, *15*, 3859. (b) Sadow, A. D.; Tilley, T. D. *Organometallics* **2003**, *22*, 3577.
(236) Dorn, H.; Singh, R. A.; Massey, J. A.; Nelson, J. M.; Jaska, C. A.; Louhg, A. J.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 6669.
(237) Ishihara, K.; Hanaki, N.; Yamamoto, H. *Synlett* **1993**, 577.
(238) Ishihara, K.; Hanaki, N.; Funahashi, M.; Miyata, M.; Yamamoto, H. *Bull. Chem. Soc. Jpn* **1995**, *68*, 1721.
(239) Ishihara, K.; Funahashi, M.; Hanaki, N.; Miyata, M.; Yamamoto, H. *Synlett* **1994**, 963.
(240) Christmann, M.; Kalesse, M. *Tetrahedron Lett.* **2001**, *42*, 1269.
(241) (a) Hassfeld, J.; Christmann, M.; Kalesse, M. *Org. Lett.* **2001**, *3*, 3561. (b) Bhatt, U.; Christmann, M.; Quitschalle, M.; Claus, E.; Kalesse, M. *J. Org. Chem.* **2001**, *66*, 1885.
(242) Ishihara, K.; Hanaki, N.; Yamamoto, H. *Synlett* **1995**, 721.
(243) Ishihara, K.; Yamamoto, H. *Eur. J. Org. Chem.* **1999**, 527.
(244) Chandrasekhar, S.; Reddy, C. R.; Babu, B. N.; Chandrashekar, G. *Tetrahedron Lett.* **2002**, *43*, 3801.
(245) Gansäuer, A.; Fielenbach, D.; Stock, C. *Adv. Synth. Catal.* **2002**, *344*, 845.
(246) Parks, D. J.; Piers, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 9440.
(247) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090.
(248) Mayr, H.; Basso, N.; Hagen, G. Silanes are good hydride donors to carbocations, *J. Am. Chem. Soc.* **1992**, *114*, 3060.
(249) Blackwell, J. M.; Sonmor, E.; Scoccitti, T.; Piers, W. E. *Org. Lett.* **2000**, *2*, 3921.
(250) Blackwell, J. M.; Piers, W. E.; Morrison, D. J. *Tetrahedron* **2002**, *58*, 8247.
(251) (a) Asao, N.; Ohishi, T.; Sato, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **2001**, *123*, 6931. (b) Asao, N.; Ohishi, T.; Sato, K.; Yamamoto, Y. *Tetrahedron* **2002**, *58*, 8195.
(252) Imamura, K.-I.; Yoshikawa, E.; Gevorgyan, V.; Sudo, T.; Asao, N.; Yamamoto, Y. *Can. J. Chem.* **2001**, *79*, 1624.
(253) Rubin, M.; Schwier, T.; Gevorgyan, V. *J. Org. Chem.* **2002**, *67*, 1936.
(254) (a) Lambert, J. B.; Zhao, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7876. (b) Lambert, J. B.; Zhao, Y.; Wu, H. *J. Org. Chem.* **1999**, *64*, 2729.
(255) Blackwell, J. M.; Foster, K. L.; Beck, V. H.; Piers, W. E. *J. Org. Chem.* **1999**, *64*, 4887.
(256) (a) Gevorgyan, V.; Liu, J.-X.; Rubin, M.; Benson, S.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 8919. (b) Gevorgyan, V.; Rubin, M.; Benson, S.; Liu, J.-X.; Yamamoto, Y. *J. Org. Chem.* **2000**, *65*, 6179.
(257) Gevorgyan, V.; Rubin, M.; Liu, J.-X.; Yamamoto, Y. *J. Org. Chem.* **2001**, *66*, 1672.
(258) Chandrasekhar, S.; Reddy, C. R.; Babu, B. N. *J. Org. Chem.* **2002**, *67*, 9080.
(259) Denis, J.-M.; Forintos, H.; Szelke, H.; Keglevich, G. *Tetrahedron Lett.* **2002**, *43*, 5569.
(260) Lambert, J. B.; Kuhlmann, B. *J. Chem. Soc., Chem. Commun.* **1992**, 931.
(261) Gevorgyan, V.; Liu, J.-X.; Yamamoto, Y. *Chem. Commun.* **1998**, 37.
(262) (a) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207. (b) Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31.
(263) Ooi, T.; Uraguchi, D.; Kagoshima, N.; Maruoka, K. *J. Am. Chem. Soc.* **1998**, *120*, 5327.
(264) Maruoka, K.; Ooi, T. *Chem. Eur. J.* **1999**, *5*, 829.
(265) Yamamoto, Y. *Acc. Chem. Res.* **1987**, *20*, 243.
(266) Blackwell, J. M.; Piers, W. E.; Parvez, M. *Org. Lett.* **2000**, *2*, 695.
(267) Gill, K.; Marshall, J. A. *J. Organomet. Chem.* **2001**, *624*, 294.
(268) Denmark, S. E.; Fu, J. *Chem. Rev.* **2003**, *103*, 2763.
(269) Morrison, D. J.; Piers, W. E. *Org. Lett.* **2003**, *5*, 2857.
(270) Morrison, D.J.; Piers, W.E.; Parvez, M. *Synlett* **2004**, in press.
(271) Brown, K. J.; Berry, M. S.; Murdoch, J. R. *J. Org. Chem.* **1985**, *50*, 4345.
(272) Rubin, M.; Gevorgyan, V. *Org. Lett.* **2001**, *3*, 2705.
(273) Sun, X.; Lee, H. S.; Yang, X.-Q.; McBreen, J. *Electrochem. Solid-State Lett.* **2003**, *6*, A43, and references therein.

Recent Developments in Arylgold(I) Chemistry

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I
INTRODUCTION

Organogold derivatives have been known for almost a century.[1,2] Although their chemistry initially developed very slowly and no reviews of these derivatives were published until 1970,[3] interest in this field of study has grown considerably since the 1970s. Consequently, new material became the subject matter of other reviews on organogold chemistry, including general surveys[4–10] as well as more specialized research into topics such as univalent gold,[11] methanides,[12] ferrocene[13] and bis(diphenylphosphino)-ferrocene or -dicarba-*closo*-dodecaborane derivatives.[14]

Similarly, the chemistry of arylgold compounds initially developed only slowly and the first arylgold compounds[15] were well characterized 29 years after they were synthesized.[16] The use of polyhalophenyl groups has contributed greatly to the more rapid development of this area in recent decades, leading to thermodynamically and kinetically stable species.

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ADVANCES IN ORGANOMETALLIC CHEMISTRY
VOLUME 52 ISSN 0065-3055/DOI 10.1016/S0065-3055(04)52002-6

Thus, some revisions of arylgold chemistry were published in the 1980s,[17–19] the last update coming in 1994.[20]

This review focuses on recent developments in monovalent arylgold derivatives and covers research on arylgold(I) chemistry since 1995. While traditionally mononuclear complexes are the most plentiful arylgold(I) derivatives, the growing interest in the study and understanding of closed-shell metal–metal interactions have led to the synthesis of numerous examples of homo- (which include gold(I)/(III) derivatives) or hetero-atomic associations in which the presence of intra- or inter-molecular metal–metal interactions may play an important role and lead to interesting optical properties. This review will therefore focus not only on the different synthetic routes to arylgold(I) derivatives, but also on their crystal structures in an increasing order of nuclearity from mononuclear species to polynuclear complexes and according to the neutral or ionic nature of the arylgold species.

II
MONONUCLEAR COMPLEXES

A. *Neutral*

A common method to form transition metal to carbon bonds generally involves the use of organolithium reagents and, accordingly, the unsubstituted phenyl gold(I) compounds $[AuPh(PPh_3)]$[21] and $[AuPh(P^tBu_3)]$[22] can be prepared following this synthetic route, starting from the corresponding chloro gold(I) derivative [Eq. (1)].

$$[AuCl(PR_3)] + PhLi \rightarrow [AuPh(PR_3)] + LiCl \quad (1)$$

Interestingly, $[AuPh(P^tBu_3)]$ can also be obtained in quantitative yield in a slow reaction of tris{[tri(*tert*-butyl)phosphine]gold(I)}oxonium tetrafluoroborate with sodium tetraphenylborate as phenylating agent[22] [Eq. (2)].

$$[O\{Au(P^tBu_3)\}_3][BF_4] + Na[BPh_4] \xrightarrow[15\ days]{EtOH} 3[AuPh(P^tBu_3)] + Na[BF_4] + PhBO \quad (2)$$

Also [AuPh(TPA)] (TPA = 1,3,5-triaza-7-phosphaadamantane) is obtained in a similar phenyl-transfer reaction using $Na[BPh_4]$ and $[Au(TPA)_3]Cl$[23] [Eq. (3)]. Although the $[BPh_4]^-$ anion is well known for participating in phenyl-transfer reactions with other transition metals,[24] these appear to be the first reported examples of phenyl transfer to a gold center.

$$[Au(TPA)_3]Cl + Na[BPh_4] \rightarrow [AuPh(TPA)] + NaCl + BPh_3 + 2TPA \quad (3)$$

These three phenyl gold(I) derivatives have been structurally characterized by X-ray diffraction methods, showing discrete linear molecules with similar Au–C and Au–P

TABLE I
MONONUCLEAR NEUTRAL COMPLEXES

Complex	Au–C (Å)	Au–P/N (Å)	C–Au–P/N (°)	Ref.
[AuPh(PPh_3)]	2.045(6)	2.296(2)	175.5(2)	25
			176.8(4)	
[AuPh(P^tBu_3)]	2.055(6)	2.305(1)	177.9(2)	22
[AuPh(TPA)]	2.040(2)	2.289(5)	170.1(5)	23
[Au(NCN)(PPh_3)]	2.055(9)	2.282(2)	178.6(3)	26
	2.045(9)	2.287(2)	176.0(3)	
[Au(mes)($AsPh_3$)]				27
[Au(mes)(PPh_3)]				27
[Au(mes)(PPh_2Me)]				27
[Au(mes)(dppm)]				27
[Au(Fmes)($AsPh_3$)]				28
[Au(Fmes)(dppm)]				28
[Au(Fmes)(tht)]				29
[Au(Fmes)(PPh_3)]				29
[Au(Fmes){P(*o*-tol)$_3$}]				29
[Au(Fmes)(2,6-lut)]				29
[Au(Fmes)(NCMe)]				29
[Au(Dmp)(PPh_3)]	2.046(3)	2.2799(8)	174.21(8)	32
[Au(trip)($AsPh_3$)]				31
[Au(C_6F_5)($PPh_2C{\equiv}CH$)]	2.059(8)	2.283(2)	176.6(2)	33
[Au(C_6F_5){$PPh_2C(=S)N(H)Me$}]				34
[Au(C_6F_5)(PPh_2CH_2SPh)]				35
[Au(C_6F_5){PPh_2(2-OHC_6H_4)}]				36
[Au(C_6F_5){PPh_2(2-$OSiMe_3C_6H_4$)}]				36
[Au(C_6F_5){$N(H){=}CPh_2$}]	2.002(10)	2.044(8)	178.0(3)	37
[Au(C_6F_5)(3-$MeNC_5H_4$)]	1.995(6)	2.066(5)	178.4(2)	38
[Au(C_6F_5)(2-amt)]				39
[Au(3,5-$Cl_2C_6F_3$)(tht)]				40

distances (see Table I) ranging from 2.040(2) Å (PR_3 = TPA)[23] to 2.055(6) Å (PR_3 = P^tBu_3)[22] and from 2.289(5) Å (PR_3 = TPA)[23] to 2.305(1) Å (PR_3 = P^tBu_3),[22] respectively. The highest deviation from linearity is observed in the TPA derivative (P–Au–C 170.1(5)°).[23] While the distance between the closest gold centers (3.774 Å) is too long for any significant interaction to be invoked, the two gold centers appear to be deviating slightly from linear coordination toward each other.

The bis(*ortho*-amine)arylgold(I) compound [Au(NCN)(PPh_3)] (NCN = 2,6-(CH_2NMe_2)$_2C_6H_3$), obtained through the corresponding aryllithium derivative, has shown excellent properties in transmetalation reactions with Au^{III}, M^{II} (M = Ni, Pd, Pt), Fe^{III}, and Ti^{IV} halide-containing precursors.[26] Moreover, the use of this complex as an arylating agent has certain advantages over traditional organolithium or Grignard reagents: the reactions can be performed in air and even at reflux; the complexes formed can be easily separated from the coproduct; and the reaction does not require excess transmetalating reagent. In addition, this method circumvents the use of environmentally unacceptable Hg and Tl analogs.

Similarly, mesityl (mes) and 2,4,6-tris(trifluoromethyl)phenyl (Fmes) derivatives [Au(mes)($AsPh_3$)],[27] [Au(Fmes)($AsPh_3$)],[28] and [Au(Fmes)(tht)][29] have been synthesized by the reaction of [AuClL] (L = $AsPh_3$, tht) with the corresponding aryllithium. Other monoarylated complexes are readily obtained when the labile ligand L is displaced by different neutral phosphorus or nitrogen donor ligands, such as PPh_3, PPh_2Me, dppm, P(*o*-tol)$_3$ or 2,6-lutidine [Eq. (4)],[27–29] although some of them had previously been prepared by other synthetic procedures.

$$[AuArL] + L' \longrightarrow [AuArL'] + L \tag{4}$$

In the case of the complex [Au(Fmes)(NCMe)], containing a poorer donor ligand, it must be obtained by removing halogen from NBu_4[Au(Fmes)Cl] with $TlBF_4$ in the presence of the desired ligand [see Eq. (5)].

$$NBu_4[Au(Fmes)Cl] + Tl[BF_4] \xrightarrow{NCMe} [Au(Fmes)(NCMe)] + TlCl + NBu_4[BF_4] \tag{5}$$

The crystal structures of these mes, Fmes or 2,6-lutidine derivatives have not been described previously. In the case of the 2,6-lutidine complex a rigid structure with the two phenyl rings perpendicular to each other, in order to diminish crowding, is proposed based on its NMR spectra, which do not show any signs of fluxionality.[29]

There is currently a huge amount of interest in the chemistry of sterically demanding ligands because they have been found to be suitable for stabilizing main group element complexes in unusual coordination geometries and unprecedented bonding situations.[30] Thus, the bulkier aryl groups tris(isopropyl)phenyl (trip, 2,4,6-$(CHMe_2)_3C_6H_2$)[31] and dimesitylphenyl (Dmp, 2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3$)[32] have been employed for the synthesis of neutral monoarylated complexes using the traditional organo-lithium[32] or -magnesium[31] method.

The molecular structure of [Au(Dmp)(PPh_3)][32] (Fig. 1) features an almost linear C–Au–P arrangement and displays no intermolecular Au···Au interactions. The Au–C distance of 2.046(3) Å, the Au–P distance of 2.2799(8) Å, as well as the C–Au–P angle of 174.21(8)° compare well with the corresponding values in [AuPh(PPh_3)][25] and [Au(NCN)(PPh_3)][26] (see Table I). Besides the Au–C_{ipso} distance, there are weak

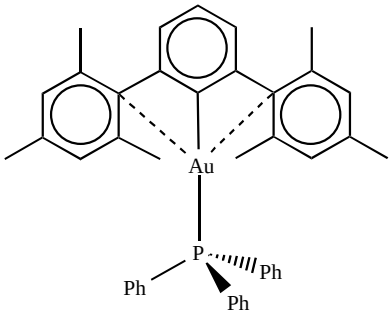


FIG. 1. Structure of [Au(Dmp)(PPh_3)].

secondary interactions between the metal atom and the *ipso* carbon atoms of the mesityl rings of 3.166(3) and 3.271(3) Å. Thus, the Dmp ligand is slightly tilted.

The perhalophenyl groups represent a very common type of aryl ligands that seem to enhance the stability of gold compounds. Among them, the use of pentafluorophenyl is widely extended and, accordingly, a large number of mononuclear complexes of the type $[Au(C_6F_5)L]$ (L = $PPh_2C{\equiv}CH$,[33] $PPh_2C(=S)N(H)Me$,[34] PPh_2CH_2SPh,[35] $PPh_2(2\text{-}OHC_6H_4)$,[36] $PPh_2(2\text{-}OSiMe_3C_6H_4)$,[36] benzophenoneimine,[37] 3-picoline[38] or 2-aminothiazoline(2-amino-4,5-dihydrothiazole) (2-amt)[39]) have recently been prepared by rapid displacement of the weakly coordinated tetrahydrothiophene ligand from the precursor with the phosphorus or nitrogen donor atom [Eq. (6)].

$$[Au(C_6F_5)(tht)] + L \longrightarrow [Au(C_6F_5)L] + tht \tag{6}$$

The crystal structures of three of these complexes have been established by X-ray diffraction, all of them showing a typical linear environment for the metal atom. The Au–C distances of 2.059(8) Å for L = $PPh_2C{\equiv}CH$,[33] 2.002(10) Å for L = $N(H){=}CPh_2$,[37] and 1.995(6) Å for L = 3-picoline[38] indicate a lower *trans* influence for the nitrogen donor ligands.

The benzophenoneimine derivative shows an interesting molecular packing, which displays discrete dimers in an antiparallel conformation. Both Au···Au interactions (3.5884(7) Å) and N–H···F hydrogen bonds (H···F 2.75 Å, N–H···F 116°) are present within the dimeric units. Both types of interactions are present in the polymeric structure of the analogous silver derivative (see Fig. 2).[37]

The other two compounds display no intermolecular Au···Au interactions, although the molecular packing of $[Au(C_6F_5)(PPh_2C{\equiv}CH)]$ involves an Au···H contact from the acidic alkynyl proton (Au···H distance of 3.07 Å, C–H–Au angle of 143°) that links the molecules by translation parallel to the *a*-axis.[33]

Another polyhalophenyl gold(I) complex, $[Au(3,5\text{-}C_6Cl_2F_3)(tht)]$, has been found to be a very efficient catalyst for the isomerization of *trans*-$[Pd(3,5\text{-}C_6Cl_2F_3)_2(tht)_2]$ to *cis*-$[Pd(3,5\text{-}C_6Cl_2F_3)_2(tht)_2]$.[40] The reaction takes place through a novel reversible aryl exchange between Pd(II) and Au(I). The mechanism involves associative substitution of

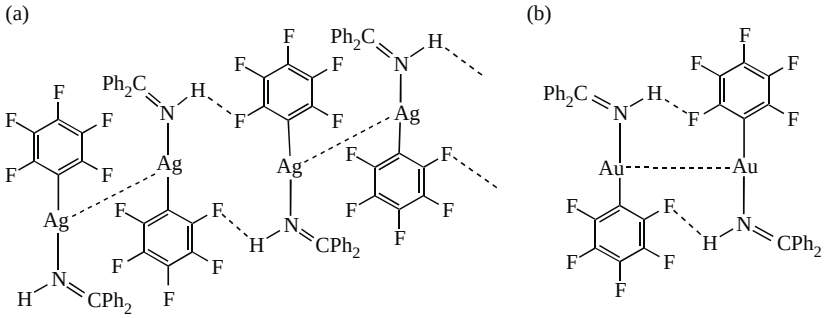
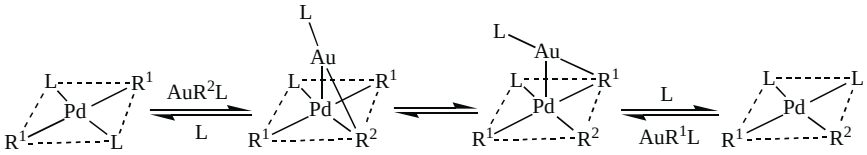


FIG. 2. Structures of $[Ag(C_6F_5)\{N(H){=}CPh_2\}]$ (a) and $[Au(C_6F_5)\{N(H){=}CPh_2\}]$ (b).



SCHEME 1.

the neutral ligand L in *trans*-[PdR_2L_2] by the nucleophilic Au(I) complex and formation of an aryl-bridged intermediate *trans*-[$LR_2Pd(\mu\text{-}R)AuL$] (see Scheme 1).

B. *Anionic*

This group of mononuclear compounds also contains a large number of examples, although no phenyl derivative has been described recently. The simplest aryl group is the monosubstituted 4-$NO_2C_6H_4$, which, together with 2,4,6-$(NO_2)_3C_6H_2$, has led to the synthesis of anionic species $[AuArCl]^-$ by the reaction of dichloroaurate(I) with the corresponding diarylmercury(II), as shown in Eq. (7).[41]

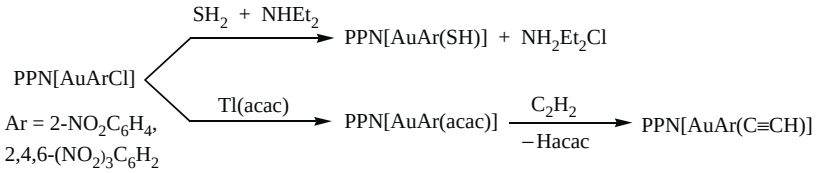
$$2PPN[AuCl_2] + HgAr_2 + NMe_4Cl \xrightarrow{\text{acetone}} 2PPN[AuArCl] + NMe_4HgCl_3 \qquad (7)$$

Treatment of these with SH_2 or C_2H_2 in the presence of a deprotonating agent leads to the homologous hydrosulfido[41] and ethynylgold(I)[42] derivatives (Scheme 2).

The complex PPN[Au{2,4,6-$(NO_2)_3C_6H_2$}(C≡CH)], together with its pentafluorophenyl analog, are the first ethynylgold(I) complexes characterized by X-ray diffraction methods. Both crystal structures display the dicoordinate gold atom in a quasi-linear environment with C–Au–C angles of 175.5(2) and 176.9(2)°, respectively. The Au–C≡C angles (175.6(5) and 174.6(5)°, respectively) are slightly bent, as in most alkynylgold(I) complexes.

A lengthening of the $Au-C_{ethynyl}$ bond distance is also observed with respect to the mean value of 1.97 Å found for a series of alkynylgold complexes.[43–53] This could be due to the greater *trans* influence of the aryl ligand (even greater for 2,4,6-$(NO_2)_3C_6H_2$ than for C_6F_5) than the usual ligands in other alkynylgold complexes.

Finally, the $Au-C_{aryl}$ bond distance—2.039(5) Å in PPN[Au{2,4,6-$(NO_2)_3C_6H_2$}(C≡CH)] and 2.049(5) Å in PPN[Au(C_6F_5)(C≡CH)]—is, in both cases, longer than in



SCHEME 2.

TABLE II
MONONUCLEAR ANIONIC COMPLEXES OF THE TYPE $[AuRX]^-$

Complex	Au–C_{aryl} (Å)	Au–C/Br (Å)	C–Au–C/Br (°)	Ref.
PPN[Au(2-$NO_2C_6H_4$)Cl]				41
PPN[Au{2,4,6-$(NO_2)_3C_6H_2$}Cl]				41
PPN[Au(2-$C_6H_4NO_2$)(SH)]				41
PPN[Au{2,4,6-$(NO_2)_3C_6H_2$}(SH)]				41
PPN[Au(2-$NO_2C_6H_4$)(C≡CH)]				42
PPN[Au{2,4,6-$(NO_2)_3C_6H_2$}(C≡CH)]	2.0392(54)	2.0148(56)	175.5(2)	42
PPN[Au(trip)Cl]				31
$BzPh_3P$[Au(mes)Cl]				27
PPN[Au(mes)Br]				27
NBu_4[Au(Fmes)Cl]				29
NBu_4[Au(Fmes)Br]				29
NBu_4[Au(Fmes)I]				29
PPN[Au(C_6F_5)Cl]				41
NMe_4[Au(C_6F_5)Cl]				41
TTF[Au(C_6F_5)Cl]				55
$MePh_3P$[Au(C_6F_5)Br]	2.009(5)	2.4137(7)	177.90(13)	56
PPN[Au(C_6F_5)(SH)]				41
NBu_4[Au(C_6F_5)(SH)]				41
NEt_4[Au(C_6F_5)(SH)]				41
PPN[Au(C_6F_5)(C≡CH)]	2.049(5)	1.984(6)	176.9(2)	42

complexes with sulfur[41] or nitrogen[37,38,54] donor ligands, consistent with the stronger *trans* influence of carbon donor ligands.

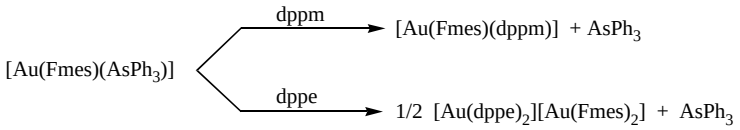
Apart from the chloro complexes discussed previously, a number of haloderivatives of the type Q[AuArX] have been described (see Table II). They include aryl groups such as the bulky tris(isopropyl)phenyl ligand (trip),[31] mes,[27] Fmes[29] or pentafluorophenyl[41,55,56] and have generally been obtained by displacement of the labile $AsPh_3$ or tht ligand with the halogenide anion, as shown above:

$$[AuArL] + QX \longrightarrow Q[AuArX] + L \tag{8}$$

In contrast, the cation-radical salt (TTF)[Au(C_6F_5)Cl] (TTF = tetrathiafulvalene) was prepared by combination of tetrathiafulvalene with an organoaurate(I) salt, under a controlled current[55] [Eq. (9)].

$$TTF + BzPPh_3[Au(C_6F_5)Cl] \xrightarrow[14\ days]{1.6\ \mu A} (TTF)[Au(C_6F_5)Cl] \tag{9}$$

Only one of these haloderivatives, $[MePh_3P][Au(C_6F_5)Br]$,[56] has been structurally characterized showing a typical linear disposition of the ligands around the metal center in the anion (C–Au–Br 177.9°). The Au–C distance of 2.009(5) Å is similar to those observed in the pentafluorophenyl derivatives $[Au(C_6F_5)\{N(H)=CPh_2\}]$ (2.002(10) Å)[37] or $[Au(C_6F_5)(3\text{-}MeNC_5H_4)]$ (1.995(6) Å),[38] suggesting an



SCHEME 3.

analogous *trans* influence for bromide and the nitrogen donor ligands benzophenoneimine and 3-picoline.

Also, the pentafluorophenyl derivatives Q[Au(C_6F_5)(SH)] (Q = PPN, NBu_4, NEt_4)[41] and PPN[Au(C_6F_5)(C≡CH)][42] (whose crystal structure has been described previously) can be obtained following the synthetic procedure represented in Scheme 2.

The second main class of compounds included in this section is bis(aryl)aurate(I) anions. Of these, salts containing the anion $[Au(Fmes)_2]^-$ have been described with usual cations, such as NBu_4 or NEt_4, and have been prepared by treatment of dibromoaurate(I) with Li(Fmes).[29] The reaction of the latter with $AgBF_4$ was carried out in order to determine whether it could bring out linear polymers $[AuAgR_2]_n$ or $[AuAgR_2L]_n$ similar to those reported for C_6F_5.[57] However, only $[Ag(4\text{-Mepy})_2][Au(Fmes)_2]$ could be obtained after the addition of 4-methylpyridine[29] [Eq. (10)].

$$NEt_4[Au(Fmes)_2] + AgBF_4 + 2\ 4\text{-Mepy} \longrightarrow [Ag(4\text{-Mepy})_2][Au(Fmes)_2] + NEt_4BF_4 \quad (10)$$

A similar complex with $[Au(dppe)_2]^+$ as cation is also obtained when [Au(Fmes)($AsPh_3$)] is treated with dppe in a 1:1 molar ratio, reaction that in the case of dppm affords the neutral complex [Au(Fmes)(dppm)] with the diphosphine acting as monodentate, as described previously[28] (Scheme 3).

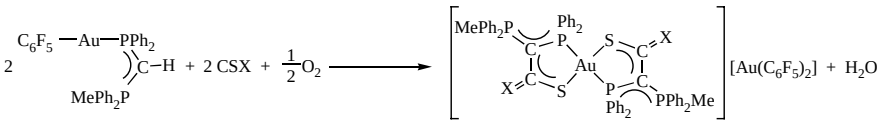
The latter, as well as the NBu_4 derivative, have been structurally characterized and both of them are very similar, with one exception (see Table III). The exception concerns

TABLE III
MONONUCLEAR ANIONIC COMPLEXES OF THE TYPE $[AuR_2]^-$

Complex	Au–C_{aryl} (Å)	C–Au–C (°)	Ref.
$NBu_4[Au(Fmes)_2]$	2.057(5) 2.060(5)	178.2(2)	29
$NEt_4[Au(Fmes)_2]$			29
$[Ag(4\text{-Mepy})_2][Au(Fmes)_2]$			29
$[Au(dppe)_2][Au(Fmes)_2]$	2.054(2) 2.065(2)	179.58(9)	28
$[Au\{PPh_2C(PPh_2Me)CS_2\}_2][Au(C_6F_5)_2]$	2.054(7)	180.0	61
$[Au\{PPh_2C(PPh_2Me)C(4\text{-}ClC_6H_4N)S\}_2][Au(C_6F_5)_2]$			61
$[Au\{PPh_2C(PPh_2Me)C(PhN)S\}_2][Au(C_6F_5)_2]$			61
$(TTFPh_2)_2[Au(C_6F_5)_2]$	2.040(3)	180.0	55
$(TTFPh_2)_2[Au(C_6F_3H_2)_2]$			55

the angle between the two aryl ligand planes, which is 27° in the NBu_4 complex and 19° in the $[Au(dppe)_2]^+$ derivative. Whereas other $[Au(aryl)_2]^-$ complexes are planar,[28,55,58–61] these two cations are not. Hence, this twist angle is the most striking feature of both structures.

In the case of $[Au(C_6F_5)_2]^-$, the most recent complexes described contain Au(III) cations[61] or the cation-radical $TTFPh_2$ ($TTFPh_2$ = 4,4′-diphenyltetrathiafulvalene).[55] The first of these complexes is obtained in a singular reaction in which the methanide carbon atom of $[Au(C_6F_5)(PPh_2CHPPh_2Me)]$ acts as nucleophilic center toward reagents such as carbon disulfide or isothiocyanates [Eq. (11)],[61] while the latter, as well as its 2,4,6-$C_6F_3H_2$ homologue, is synthesized following the same procedure than in Eq. (9) for $(TTF)[Au(C_6F_5)Cl]$.[55]



(11)

As discussed previously, the anion $[Au(C_6F_5)_2]^-$, both in the crystal structures of $[Au\{PPh_2C(PPh_2Me)CS_2\}_2][Au(C_6F_5)_2]$ and $(TTFPh_2)_2[Au(C_6F_5)_2]$, displays both aryl rings parallel to each other, similarly to the anion in $NBu_4[Au(C_6F_5)_2]$,[60] with only one difference: the Au–C distance in the cation-radical salt is 2.040(3) Å, shorter than in other $[AuAr_2]^-$ anions (see Table III). Besides, in this structure each gold center is involved in four short Au···S contacts (3.253 and 3.490 Å) to four different $TTFPh_2$ units of two different stacks.

Finally, the conductivity of $(TTFPh_2)_2[Au(C_6F_5)_2]$ has been studied at different temperatures showing semiconductor behavior in the range of 300–200 K.[55] The reduction of Au(I) to Au(0) was observed in the study by cyclic voltammetry of $NBu_4[Au(C_6F_5)_2]$ and $NBu_4[Au(C_6Cl_5)_2]$.[62]

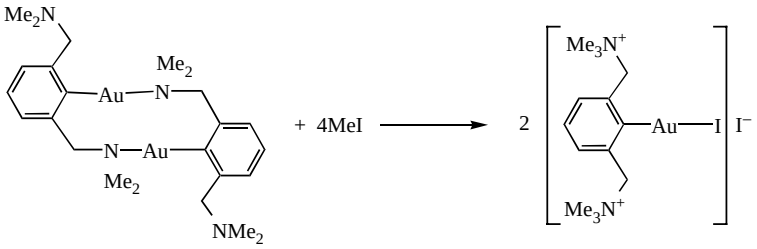
C. *Cationic*

These types of compounds are scarcely represented due to the low number of cationic ligands available and no general method for their synthesis exists. One example is $[AuPh(MeTPA)]BPh_4$, which contains the cationic ligand $MeTPA^+$, derived from 1,3,5-triaza-7-phosphaadamantane, synthesized through an unusual phenyl-transfer reaction in aqueous solution [Eq. (12)].[23]

$$[AuI(MeTPA)_3]I_3 + 4Na[BPh_4] \rightarrow [AuPh(MeTPA)]BPh_4 + 4NaI + 2(MeTPA)[BPh_4] + BPh_3 \quad (12)$$

The heteroaurate(I) $[Au\{2,6\text{-}(CH_2NMe_3)_2C_6H_3\}I]I$ is obtained in a different transfer reaction, a methyl group is transferred from MeI to the nitrogen atom of the *ortho* amino ligand, at the same time the quantitative precipitation

of the gold(I)–ammonium salt occurs [Eq. (13)].[63]



(13)

The phosphoranium salt $[CH(PPh_2Me)_2]TfO$ reacts with $[Au(C_6F_5)(tht)]$ to afford its first metallic complex, $[Au(C_6F_5)\{CH(PPh_2Me)_2\}]TfO$, which, despite the weak nucleophilic character of the ylidic carbon, is stable.[64]

The crystal structures of these three products display $Au–C_{aryl}$ distances from 2.04(1) to 2.029(6) Å (see Table IV), the latter being of the same order as those found in related complexes with C_6F_5 groups *trans* to an ylidic carbon atom (mean distance 2.024 Å)[65–67] and close to that reported for the $Au–C_{aryl}$ distances (2.049(5) Å) in $PPN[Au(C_6F_5)(C{\equiv}CH)]$.[42] The three cations show an approximately linear coordination around the gold(I) center, with the maximum deviation for the iodo derivative (C–Au–I 171.7(3)°).[63] None of them display intermolecular gold···gold interactions, with the shortest Au–Au distance (4.581 Å) found in the MeTPA complex.[23]

III

DINUCLEAR COMPLEXES

A. *Homonuclear Complexes*

1. Neutral Gold(I) or Gold(I)/(III)

A number of gold(I)···gold(I) dimers of the type $[Au(o\text{-}C,P)]_2$ containing *ortho*-metallated arylphosphanes (see Table V) have been prepared by reaction of the organolithium reagents with $[AuBr(PEt_3)]$ in diethyl ether at low temperature

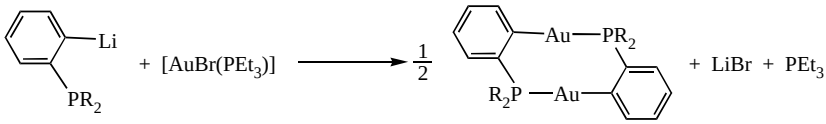
TABLE IV
MONONUCLEAR CATIONIC COMPLEXES

Complex	Au–C (Å)	Au–P/I/C (Å)	C–Au–P/I/C (°)	Ref.
$[AuPh(MeTPA)]BPh_4$	2.04(1)	2.274(3)	176.5(5)	23
$[Au\{2,6\text{-}(CH_2NMe_3)_2C_6H_3\}I]I$	2.034(9)	2.575(1)	171.7(3)	63
$[Au(C_6F_5)\{CH(PPh_2Me)_2\}]TfO$	2.029(6)	2.112(6)	175.9(2)	64

TABLE V
HOMODINUCLEAR NEUTRAL COMPLEXES WITH BRIDGING ARYL LIGANDS

Complex	Au–C (Å)	Au–P/S (Å)	C–Au–P/S (°)	Au···Au_{intra} (Å)	Ref.
$[Au(o\text{-}PPh_2C_6H_4)]_2$	2.056(3)	2.300(1)	172.8(1)	2.8594(3)	68
$[Au(o\text{-}PEt_2C_6H_4)]_2$	2.087	2.309	178.58	2.861	69
	2.057	2.296	177.98	2.850	
$[Au(2\text{-}PPh_2\text{-}5\text{-}MeC_6H_3)]_2$					70
$[Au(2\text{-}PPh_2\text{-}6\text{-}MeC_6H_3)]_2$	2.061(7)	2.302(2)	174.3(2)	2.861(2)	70
$[Au\{2,6\text{-}(CH_2NMe_2)_2C_6H_3\}]_2$					63
$[Au_2\{\mu\text{-}(o\text{-}C_6H_4)_2CH_2\}(\mu\text{-dppe})]$	2.06(3)	2.30(1)	178.8(9)	3.012(3)	74
	2.05(3)	2.30(1)	168.7(9)		
	2.05(2)	2.296(4)	179.0(5)	3.012(2)	75
	2.04(2)	2.296(5)	168.6(4)		
$[Au_2(\mu\text{-}2\text{-}PPh_2\text{-}5\text{-}MeC_6H_3)(\mu\text{-}S_2CN^nBu_2)]$	$2.039(6)_C$	$2.338(2)_S$	174.6(2)	2.8331(3)	73
	$2.264(2)_P$	$2.316(2)_S$	178.2(1)	2.8243(3)	
$[Au_2(\mu\text{-}2\text{-}PPh_2\text{-}6\text{-}MeC_6H_3)(\mu\text{-}S_2CN^nBu_2)]$					73
$[\{Au(PPh_3)\}_2\{\mu\text{-}(o\text{-}C_6H_4)_2CH_2\}]$					75
$[\{Au(PPh_3)\}_2\{\mu\text{-}(o\text{-}C_6H_4)_2CH_2CH_2\}]$	2.05(2)	2.279(8)	174.5(5)		75
$[\{Au(PPh_3)\}_2\{\mu\text{-}(2,2\text{-}C_{12}H_7\text{-}4\text{-}^tBu)\}]$	2.051(9)	2.302(2)	172.8(3)	3.1691(6)	80
	2.063(8)	2.301(3)	176.3(3)		

as shown in Eq. (14).[68–70]



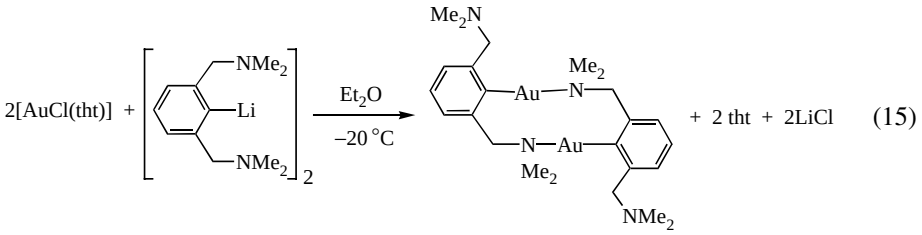
(14)

The oxidative addition reactions of the methyl-substituted dinuclear gold(I) complexes $[Au(2\text{-}PPh_2\text{-}n\text{-}MeC_6H_3)]_2$ ($n = 5, 6$) has been studied by X-ray photoelectron spectroscopy and it can clearly be seen that the Au binding energy values increase in magnitude as the formal oxidation state of gold increases from I to III.[71] Also, the oxidation states and structures of a series of cyclometallated gold complexes derived from oxidative addition reactions of the digold(I) complex $[Au(2\text{-}PPh_2\text{-}6\text{-}MeC_6H_3)]_2$ have been determined by ^{197}Au Mössbauer spectroscopy.[72]

This type of cycloaurated complexes display short transannular Au···Au interactions, as observed in the crystal structures of $[Au(o\text{-}PR_2C_6H_4)]_2$ (R = Ph,[68] Et[69]) and $[Au(2\text{-}PPh_2\text{-}6\text{-}MeC_6H_3)]_2$,[70] where Au···Au distances of about 2.86 Å have been found (see Table V), suggesting a substantial bonding interaction between the metal centers. This attractive interaction is probably the reason for the distortion of the linear environment of the gold atoms. The metallacycle has a twist conformation, probably as a consequence of the steric requirements of the fairly bulky phenyl substituents.

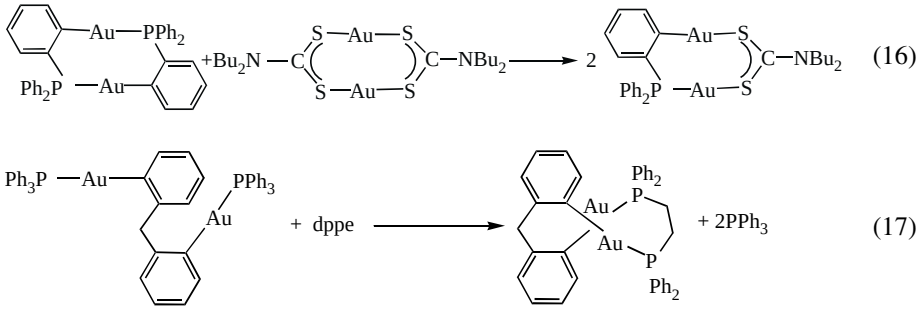
Also the C,N-donor ligand $2,6\text{-}(CH_2NMe_2)_2C_6H_3$ forms a similar dimer obtained by treatment of [AuCl(tht)] with [2,6-bis{(dimethylamino)methyl}phenyl]lithium in diethyl

ether at −20 °C [Eq. (15)].[63]



(15)

Apart from these dimers, cycloaurated complexes containing two different bidentate ligands, such as $[Au_2(\mu\text{-}2\text{-}PPh_2\text{-}n\text{-}MeC_6H_3)(\mu\text{-}S_2CN^nBu_2)]$ ($n = 5$, 6) or $[Au_2\{\mu\text{-}(o\text{-}C_6H_4)_2CH_2\}(\mu\text{-dppe})]$, have been synthesized in a metathesis reaction between $[Au(2\text{-}PPh_2\text{-}n\text{-}MeC_6H_3)]_2$ ($n = 5, 6$) with $[Au(S_2CN^nBu_2)]_2$[73] [Eq. (16)] or by displacement of triphenylphosphine from $[\{Au(PPh_3)\}_2\{\mu\text{-}(o\text{-}C_6H_4)_2CH_2\}]$ with dppe[74,75] [Eq. (17)].



(16)

(17)

The dithiocarbamate derivative $[Au_2(\mu\text{-}2\text{-}PPh_2\text{-}5\text{-}MeC_6H_3)(\mu\text{-}S_2CN^nBu_2)]$ has been structurally characterized. The main difference from the other cycloaurated complexes described is the presence of not only intra but also intermolecular gold···gold interactions of 2.8331(3) and 2.8243(3) Å (two independent molecules) and 3.0653(3) and 3.1304(3) Å, respectively. Thus, as observed in dinuclear gold(I)–dtc complexes,[76,77] the molecules pack in the crystal to generate an infinite zigzag chain of gold atoms. The intramolecular Au–Au separations are similar to those observed in $[Au(o\text{-}PPh_2C_6H_4)]_2$[68] and $[Au(2\text{-}PPh_2\text{-}6\text{-}MeC_6H_3)]_2$[70] (see Table V).

The crystal structure of the dppe derivative has been described in two papers (in 1995[74] and 1997[75]) with small differences in bond lengths, angles and geometry. It consists of a 11-membered ring with both gold(I) centers at a distance of 3.012(2) Å, consistent with direct aurophilic interaction. The macro ring is asymmetrical and has a twist conformation at which the linear C–Au–P fragments are mutually rotated around the Au···Au vector (see Fig. 3). Such an arrangement of two linear C–Au–P fragments was theoretically predicted to be necessary in order to achieve a Au···Au interaction.[78] The Au–C and Au–P distances (see Table V) both coincide with normal values, but while one of the gold atoms presents an almost exactly linear coordination (C–Au–P 179.0(5)°), the collinear arrangement of the bonds at the second gold(I) center is

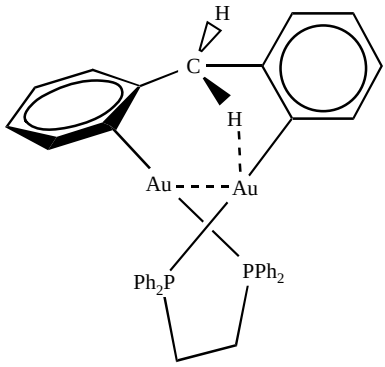


FIG. 3. Structure of $[Au_2\{\mu\text{-}(o\text{-}C_6H_4)_2CH_2\}(\mu\text{-dppe})]$.

noticeably disrupted (C–Au–P 168.6(4)°). Moreover, the linearly coordinated gold atom is involved in an agostic interaction with one hydrogen of the methylene bridge of the diphenylmethane ligand (Au···H 2.62 Å).

The same types of agostic interactions are also found in the crystal structures of the related complexes $[\{Au(PPh_3)\}_2\{\mu\text{-}(2\text{-}C_6H_4)_2CH_2\}]$[75,79] and $[\{Au(PPh_3)\}_2\{\mu\text{-}(2\text{-}C_6H_4)_2CH_2CH_2\}]$,[75] obtained *via* the corresponding organolithium reagents, and show three (3.01, 2.92 and 3.06 Å) or four (2.75 and 3.00 Å) Au···H distances, respectively. However, no intramolecular gold···gold interaction is observed in these structures, as a consequence of the *trans*-type conformation of 2,2′-diaurated phenyl fragments (see Fig. 4).

In the ongoing study of the possibility of formation on secondary bonds involving the gold atom in these types of species (Au···Au or Au···H contacts), the crystal structure of $[\{Au(PPh_3)\}_2\{\mu\text{-}(2,2\text{-}C_{12}H_7\text{-}4\text{-}^tBu)\}]$ was also determined (Fig. 5),[80] revealing bond lengths and angles around the metal centers similar to those observed in the cyclic complexes described above (see Table V) and no agostic Au···H interaction. The only difference is the intramolecular Au···Au distance of 3.1691(6) Å, which is clearly longer

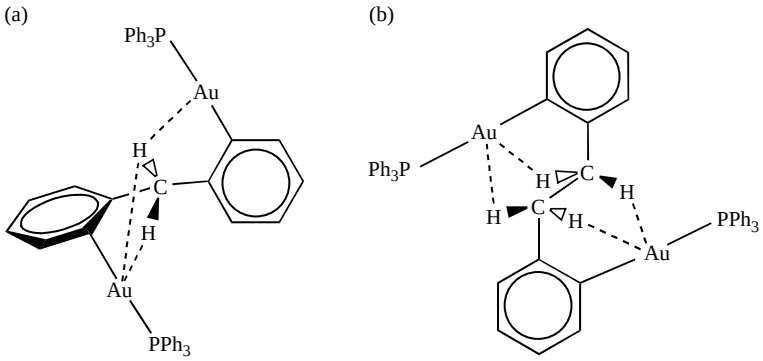


FIG. 4. Structure of $[\{Au(PPh_3)\}_2\{\mu\text{-}(o\text{-}C_6H_4)_2CH_2\}]$ (a) and $[\{Au(PPh_3)\}_2\{\mu\text{-}(o\text{-}C_6H_4)_2CH_2CH_2\}]$ (b).

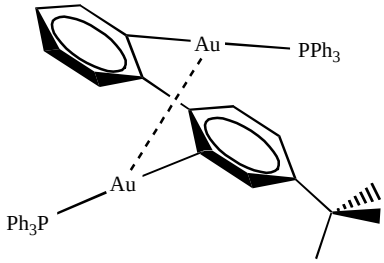


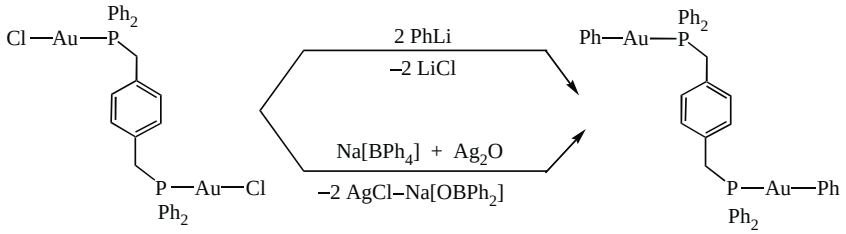
FIG. 5. Structure of [{Au(PPh$_3$)}$_2${μ-(2,2-C$_{12}$H$_7$-4-^{t}Bu)}].

than the other aurophilic intramolecular interactions described, probably due to the absence of an aurated cycle in this case.

The homodinuclear neutral complexes also contain a large number of non-cyclic products containing a non-aryl bidentate bridging ligand, which is in most cases a phosphorus donor ligand. These include aryl groups as simple as phenyl, as in the case of [(PhAu)$_2${μ-1,4-(PPh$_2$CH$_2$)$_2$C$_6$H$_4$}], that can be prepared using phenyllithium or sodium tetraphenylborate in the presence of silver oxide as phenylating agents, as shown in Scheme 4.[22]

This compound and its dppm analog, which were synthesized 9 years previously,[81] have been characterized by X-ray diffraction showing two-coordinated gold(I) atoms with P–Au–C angles of 174.8(2) and 175.8(4)°, respectively. The conformation of the AuPh fragments, which is *trans* in the former and *cis* in the latter, represents the main difference between them. This is the reason for the absence of intramolecular Au···Au interactions in the former, while the dppm derivative displays an intramolecular Au···Au separation of 3.154(1) Å, a distance similar to that found in its pentafluorophenyl analog (3.163(1) Å).[82]

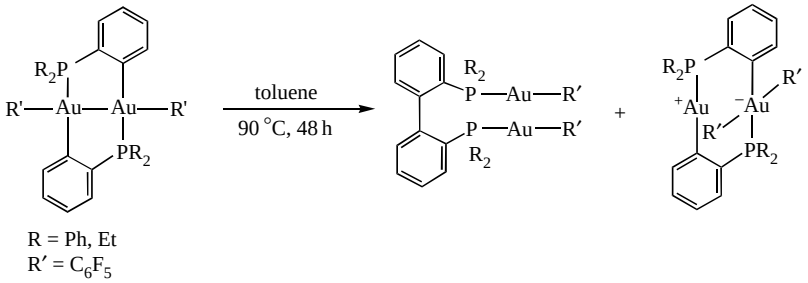
As described above, treatment of [Au(Fmes)(AsPh$_3$)] with an equimolecular amount of dppm or dppe results in the formation of [Au(Fmes)(dppm)] or [Au(dppe)$_2$] [Au(Fmes)$_2$], respectively. However, when these reactions are carried out in a 2:1 molar ratio, the dinuclear complexes [{(Fmes)Au}$_2$(μ-dppm)] or [{(Fmes)Au}$_2$(μ-dppe)] are obtained.[28] Similarly, by displacement of the weakly coordinated tht ligand from [Au(Fmes)(tht)], the bipyridyl complex [{(Fmes)Au}$_2$(μ-2,2′-bipy)] can also be prepared.[29]



SCHEME 4.

X-ray diffraction studies of the diphosphine complexes were carried out in order to determine whether the bulkiness of the ligands affects the geometry of the molecule, compared to other less hindered complexes such as the phenyl derivative described above. As expected, the high steric demand of the Fmes ligands leads to an unusual *gauche* conformation in the dppm complex, displaying an intramolecular distance as long as 7.041 Å, which contrasts with the *cis* conformation preferred in other complexes containing a single dppm bridge, as in the phenyl (3.154(1) Å)[25] or pentafluorophenyl (3.162(1) Å)[82] derivatives. The intramolecular gold···gold distance of 5.092 Å in the dppe derivative is also associated with the symmetry-imposed *trans* conformation of the diphosphine. This conformation is, by contrast, the most common in complexes containing a single dppe bridge, such as, for example, the related derivative [{(mes)Au}$_2$(μ-dppe)].[83] The Au–P and Au–C distances are very similar in both structures and compare well with those observed in alkyl or aryl derivatives with a dppm bridge and in [{(mes)Au}$_2$(μ-dppe)].

When the aryl group is pentafluorophenyl, numerous examples of compounds having the general formula [{(C_6F_5)Au}$_2$(μ-LL′)] (LL′ = bidentate ligand) have been reported in recent years[34,84–88] (see Table VI). Phosphorus donor ligands, such as vdpp ((PPh_2)$_2$C=CH_2)[84] or tdppmeO ((PPh_2CH_2)$_2$C(Me)CH_2PPh_2O),[86] among others, are very common in these types of complexes, although methylenebis(dialkyldithiocarbamates) has also been employed.[88] Most of them are prepared by reaction of the free neutral ligand with two equivalents of [Au(C_6F_5)(tht)] with displacement of the labile ligand from the gold(I) starting material.[34,84,86–88] However, [{(C_6F_5)Au}$_2${μ-2,2′-($PR_2C_6H_4$)$_2$}] (R = Ph, Et) are obtained after prolonged heating in toluene of the gold(II) complexes [Au(C_6F_5)(μ-2-$PR_2C_6H_4$)]$_2$ in a reaction that takes place with a rearrangement of ligands and the carbon–carbon coupling of the $PR_2C_6H_4$ units, as shown in Eq. (18).[85] Nevertheless, this reaction occurs with the simultaneous formation of a small amount of zwitterionic heterovalent complexes [(C_6F_5)$_2$Au^{III}{μ-2,2′-($PR_2C_6H_4$)}$_2$Au^{I}].



R = Ph, Et
R′ = C_6F_5

(18)

In the crystal structures of [{(C_6F_5)Au}$_2${μ-2,2′-($PR_2C_6H_4$)$_2$}] (R = Ph, Et) the bis(tertiary phosphine) bridges a pair of linearly coordinated gold atoms and the biphenyl backbone is twisted about the central C–C bond (dihedral angles between the planes of the phenyl groups 90° (R = Ph) or 95° (R = Et)).[85] Despite the great similarity of both complexes, their structures display noticeable differences (see Fig. 6). Thus, while in the phenyl derivative (as well as in the related complex [{(SCN)Au}$_2${μ-2,2′-($PEt_2C_6H_4$)$_2$}])

TABLE VI
HOMODINUCLEAR NEUTRAL COMPLEXES WITH NO ARYL BRIDGING LIGANDS

Complex	Au–C (Å)	Au–P/S (Å)	C–Au–P/S (°)	Au···Au$_{intra}$ (Å)	Au···Au$_{inter}$ (Å)	Ref.
[(PhAu)$_2$(μ-dppm)]	2.07(2)	2.300(2)	175.8(4)	3.154(1)		25
[(PhAu)$_2${μ-1,4-(PPh$_2$CH$_2$)$_2$C$_6$H$_4$}]	2.044(4)	2.284(1)	174.8(2)			22
[{(Fmes)Au}$_2$(μ-dppm)]	2.069(3)	2.284(1)	174.6(1)	7.041		28
[{(Fmes)Au}$_2$(μ-dppe)]	2.064(2)	2.280(1)	178.7(1)	5.092		28
[{(Fmes)Au}$_2$(μ-2,2′-bipy)]						29
[{(C$_6$F$_5$)Au}$_2$(μ-vdpp)]						84
[{(C$_6$F$_5$)Au}$_2${μ-2,2′-(PPh$_2$C$_6$H$_4$)$_2$}]	2.02(1)	2.278(3)	168.0(4)	3.0688(8)		85
	2.04(1)	2.285(3)	172.3(4)			
[{(C$_6$F$_5$)Au}$_2${μ-2,2′-(PEt$_2$C$_6$H$_4$)$_2$}]	2.056(7)	2.271(2)	176.5(3)	5.3469(7)		85
[{(C$_6$F$_5$)Au}$_2$(μ-η^2-tdppmeO)]						86
[{(C$_6$F$_5$)Au}$_2${μ-1,2-(PPh$_2$NH)$_2$C$_6$H$_4$}]						87
[{(C$_6$F$_5$)Au}$_2${μ-1,2-(PPh$_2$NH)$_2$-4-MeC$_6$H$_3$}]						87
[{(C$_6$F$_5$)Au}$_2${μ-PPh$_2$C(=S)N(H)Me}]	2.068(8)	2.273(2)$_P$	175.9(2)	3.1631(5)		34
	2.029(8)	2.315(2)$_S$	174.8(2)		3.2712(5)	
	2.041(8)	2.316(2)$_S$	175.1(2)	3.0391(5)		
	2.074(7)	2.270(2)$_P$	176.4(2)			
[{(C$_6$F$_5$)Au}$_2${μ-CH$_2$(S$_2$CNMe$_2$)}]						88
[{(C$_6$F$_5$)Au}$_2${μ-CH$_2$(S$_2$CNEt$_2$)}]						88
[{(C$_6$F$_5$)Au}$_2${μ-CH$_2$(S$_2$CN^{n}Bu$_2$)}]						88
[{(C$_6$F$_5$)Au}$_2${μ-CH$_2$(S$_2$CNBz$_2$)}]						88

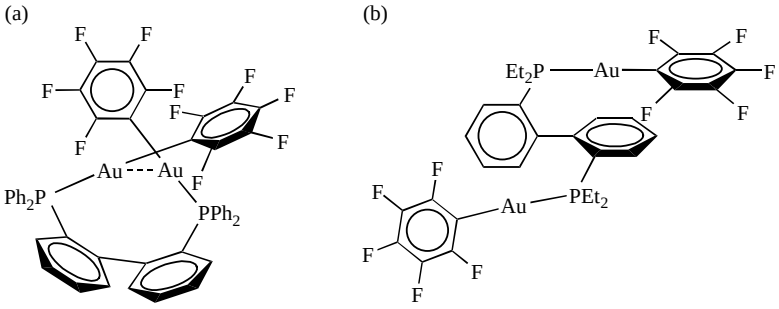


FIG. 6. Structure of [{$(C_6F_5)Au$}$_2${μ-2,2′-$(PPh_2C_6H_4)_2$}] (a) and [{$(C_6F_5)Au$}$_2$(μ-2,2′-$(PEt_2C_6H_4)_2$}] (b).

this torsion brings the gold atoms into fairly close contact (Au···Au 3.0688(8) Å), the torsion in the ethyl derivative is in the opposite direction, causing gold atoms to adopt an *anti* rather than a *syn* orientation with respect to the biphenyl backbone and separated by 5.3469(7) Å. The presence of the aurophilic interaction is presumably the reason for the greater deviation of the linearity around the gold centers in the phenyl complex (see Table VI).

In the case of [{$(C_6F_5)Au$}$_2${μ-$PPh_2C(=S)N(H)Me$}],[34] although it is included in this section and considered as a dinuclear compound, it crystallizes forming tetranuclear units formed by an intermolecular Au···Au interaction of 3.2712(5) Å between two dinuclear units (Fig. 7) and it is described in the paper as a tetranuclear complex. The shortest intermetallic distances between adjacent tetranuclear units are of approximately 6 Å. The intermolecular Au···Au contact is longer than the intramolecular ones, which present distances of 3.1631(5) and 3.0391(5) Å. These intramolecular distances are associated with the *cis* conformation observed in the complex, which is also the preferred conformation in dinuclear products containing a single dppm bridge, such as the phenyl and pentafluorophenyl compounds [$(PhAu)_2$(μ-dppm)] (3.154(1) Å)[25] and [{$(C_6F_5)Au$}$_2$(μ-dppm)] (3.162(1) Å)[82] or in the biphenyl derivative [{$(C_6F_5)Au$}$_2$ {μ-2,2′-$(PPh_2C_6H_4)_2$}] (3.0688(8) Å).[85]

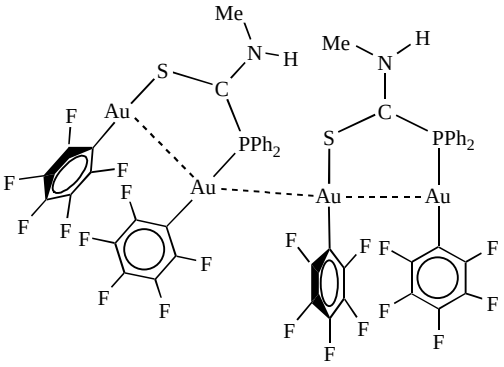
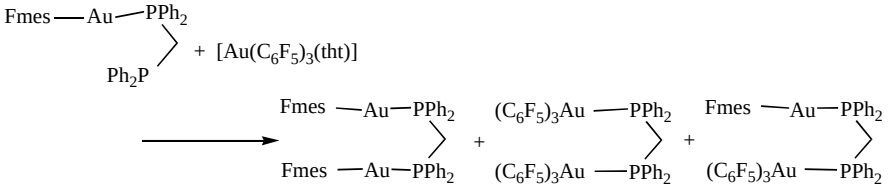


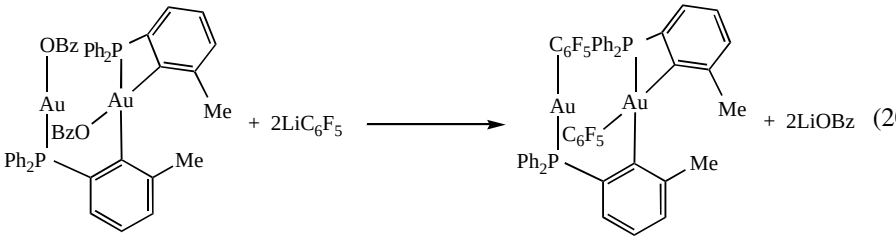
FIG. 7. Structure of [{$(C_6F_5)Au$}$_2${μ-$PPh_2C(=S)N(H)Me$}].

The products described in this section contain two gold(I) centers linked by one or two bridging ligands, but there are also some examples of mixed Au^{I}/Au^{III} species containing an aryl group bonded to the gold(I) atom, such as the 2,4,6-tris(trifluoromethyl)phenyl derivative [(Fmes)Au(μ-dppm)Au(C_6F_5)$_3$], obtained by reaction of [Au(Fmes)(dppm)] with [Au(C_6F_5)$_3$(tht)] (1:1). The process, however, leads to a mixture of three dinuclear complexes[28] [Eq. (19)], which means that this compound cannot be isolated as a pure substance.



(19)

Similarly, but now as pure products, the reaction of the corresponding mononuclear gold(I) complex with the same gold(III) reagent as before affords the heterovalent species [(C_6F_5)Au(μ-vdpp)Au(C_6F_5)$_3$][84] and [(C_6F_5)Au{μ-1,2-(PPh_2NH)$_2$-4-MeC_6H_3}Au(C_6F_5)$_3$].[87] In contrast, the cycloaurated complex [(C_6F_5)Au(μ-2-PPh_2-6-MeC_6H_3)Au(C_6F_5)(η^2-2-PPh_2-6-MeC_6H_3)] is obtained from the reaction of its benzoate analog (prepared *in situ* by treatment of the iodo derivative with silver benzoate) with pentafluorophenyllithium in a ca. 40% yield [Eq. (20)].[89]



(20)

The bond distances and angles around the gold(I) center in the crystal structures of this cycloaurated[89] compound and in the vinylidenebis(diphenylphosphine)[84] are almost identical (see Table VII), with one exception: the intramolecular Au···Au distance in the vdpp derivative is 6.157(1) Å, while in the cyclic complex the gold centers are at a distance of 3.1948(2) Å, suggesting a weak interaction between them. This presumably causes the distortion observed in the linearity of the gold(I) atom (C–Au–P 169.1(1)°), although the same deviation is found in the diphosphine complex without any apparent reason for this (C–Au–P 169.0(2)°).

2. Anionic

A series of dinuclear anionic gold(I) or mixed gold(I)/gold(III) compounds have been reported recently, all of them containing C_6F_5 as aryl group, probably due to the stabilizing

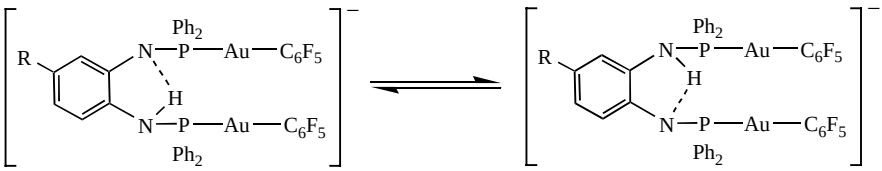
TABLE VII
HOMODINUCLEAR NEUTRAL MIXED Au^{I}/Au^{III} COMPLEXES WITH NO ARYL BRIDGING LIGANDS

Complex	Au–C (Å)	Au–P (Å)	C–Au–P (°)	Au···Au (Å)	Ref.
[(Fmes)Au(μ-dppm) Au(C_6F_5)$_3$]					28
[(C_6F_5)Au(μ-vdpp)Au(C_6F_5)$_3$]	2.054(7)	2.270(2)	169.0(2)	6.157(1)	84
[(C_6F_5)Au{μ-1,2-(PPh_2NH)$_2$-4-MeC_6H_3}Au(C_6F_5)$_3$]					87
[(C_6F_5)Au(μ-2-PPh_2-6-MeC_6H_3) Au(C_6F_5)(η^2-2-PPh_2-6-MeC_6H_3)]	2.056(4)	2.274(1)	169.1(1)	3.1948(2)	89

effect of this perhalophenyl ligand (Table VIII). The reaction of the corresponding diphosphino or diphosphinoamine starting complex with an acetylacetonate salt as a deprotonating agent afforded the anionic methanide or amide species PPN[(C_6F_5)-Au(PPh_2CHPPh_2)Au(C_6F_5)$_3$][90] or NBu_4[{(C_6F_5)Au}$_2${μ-1-(PPh_2NH)-2-(PPh_2N)-4-RC_6H_3}] (R = H, Me).[87]

The former is one of the few anionic methanides reported to date, probably due to their low stability. In fact, this complex is obtained as a yellow air and moisture-sensitive oil, which makes its complete characterization difficult.

In contrast, the phosphino amide derivatives are isolated as air and moisture stable solids. Although they still have an aminic proton, the use of excess acetylacetonate does not produce further deprotonation. Their $^{31}P\{^{1}H\}$ NMR spectra suggest the presence of a rapid exchange equilibrium in solution, in which the remaining aminic hydrogen changes its position from one nitrogen to the other, even at low temperature [Eq. (21)].



(21)

TABLE VIII
HOMODINUCLEAR ANIONIC COMPLEXES

Complex	Ref.
PPN[(C_6F_5)Au(PPh_2CHPPh_2)Au(C_6F_5)$_3$]	90
NBu_4[{(C_6F_5)Au}$_2${μ-1-(PPh_2NH)-2-(PPh_2N)C_6H_4}]	87
NBu_4[{(C_6F_5)Au}$_2${μ-1-(PPh_2NH)-2-(PPh_2N)-4-MeC_6H_3}]	87
PPN[{(C_6F_5)Au}$_2$(μ-$PPh_2C{\equiv}C$)]	33
(PPN)$_2$[{(C_6F_5)Au}$_2$(μ-dmit)]	91
(NBu_4)$_2$[{(C_6F_5)Au}$_2$(μ-dmit)]	91
(PPh_3Me)$_2$[{(C_6F_5)Au}$_2$(μ-$S_2C_2B_{10}H_{10}$)]	92

Moreover, a phosphino alkynyl derivative, PPN[{$(C_6F_5)Au$}$_2$(μ-$PPh_2C{\equiv}C$)], has recently been prepared by treatment of [$Au(C_6F_5)(PPh_2C{\equiv}CH)$] with sodium methoxide in the presence of chloropentafluorophenylaurate(I), as shown in Eq. (22).[33]

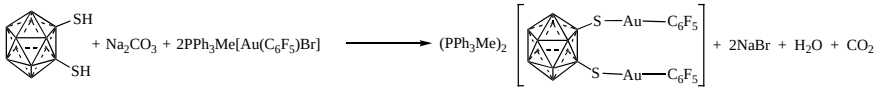
$$[Au(C_6F_5)(PPh_2C{\equiv}CH)] + NaOMe/MeOH + PPN[Au(C_6F_5)Cl] \rightarrow PPN[\{(C_6F_5)Au\}_2(\mu\text{-}PPh_2C{\equiv}C)] + NaCl + MeOH \quad (22)$$

This dinuclear complex luminesces at both 77 K and room temperature in solid state and emission seems to be related to the fragment Au^I–$PPh_2C{\equiv}C$ rather than to aurophilic interactions, which are commonly responsible for the luminescent properties of dinuclear species.

Apart from these complexes with phosphorus donor ligands, several dianionic species containing the sulfur donor ligands 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit)[91] and 1,2-dithiolate-*o*-carborane[92] can be prepared by reaction of the anion pentafluorophenylhaloaurate(I) with the ligand (deprotonated *in situ*) in a 2:1 molar ratio, as shown in the following equations.

$$2Q[Au(C_6F_5)X] + Na_2dmit \rightarrow Q_2[\{(C_6F_5)Au\}_2(\mu\text{-dmit})] + 2NaX \quad (23)$$

where $Q = NBu_4$, PPN and $X = Cl, Br$.



(24)

Finally, the dinuclear cycloaurated compounds [Au(2-PPh_2-*n*-MeC_6H_3)]$_2$ ($n = 5, 6$) react with the digold(I) complex [Au(μ-dppm)]$_2Cl_2$ and the subsequent addition of NH_4PF_6 affords the heterobridged cationic complexes [Au_2(μ-2-PPh_2-*n*-MeC_6H_3)(μ-dppm)](PF_6) ($n = 5, 6$).[73] From their $^{31}P\{^1H\}$ NMR spectra it is apparent that the PF_6^- counterion forces the equilibrium to the right by means of selectivity by precipitating the heterobridged cations.

B. *Heteronuclear Complexes*

1. Neutral

The use of gold(I) reagents containing weakly coordinated ligands, such as [$Au(C_6F_5)$(tht)] or [Au(Fmes)(SMe_2)], has enabled the synthesis of certain heterodinuclear complexes (see Table IX) by treatment of these gold(I) species with different metallic complexes of Mo,[93] W,[93,94] Fe[95,96] or Ti[97,98] with donor ability.

Some of them contain the triphosphine tdppme (($PPh_2CH_2)_3CMe$) in a μ-η^3 coordination mode as a bridge between Au(I) and Mo(0) or W(0).[93] Also, some ferrocenyl derivatives, such as ferrocenyl phosphine PPh_2CH_2Fc[95] [Fc = (η^5-C_5H_5)Fe(μ^5-C_5H_4)] or 3-ferrocenylpyridine,[96] have been employed as non-aryl bridging ligands.

TABLE IX
HETERODINUCLEAR NEUTRAL COMPLEXES

Complex	Au–C (Å)	Au–P/N/C (Å)	C–Au–P/N/C (°)	Au···M (Å)	Au···Au_{inter} (Å)	Ref.
$[(C_6F_5)Au(\mu\text{-}\eta^3\text{-tdppme})Mo(CO)_4]$						93
$[(C_6F_5)Au(\mu\text{-}\eta^3\text{-tdppme})W(CO)_4]$						93
$[(C_6F_5)Au(PPh_2CH_2Fc)]$	2.070(5)	2.284(2)	174.3(2)		5.560	95
$[(C_6F_5)Au(Fcpy)]$	2.00(2)	2.124(15)	176.3(6)		3.301(2)	96
$[(Fmes)Au\{(Me_3SiC{\equiv}C)_2Ti(\eta^5\text{-}C_5H_4SiMe_3)_2\}]$	2.079(7)	2.217–2.245	179.4(2)	2.9948(14)		97
			[Ti–Au–C]			98
$[(C_6F_5)Au\{\mu\text{-}CN(Et)Me\}W(\eta^5\text{-}C_5H_5)(CO)_2]$	2.07(2)	2.13(2)	$162.9(6)_C$	2.727(1)		94
			$150.3(4)_W$			

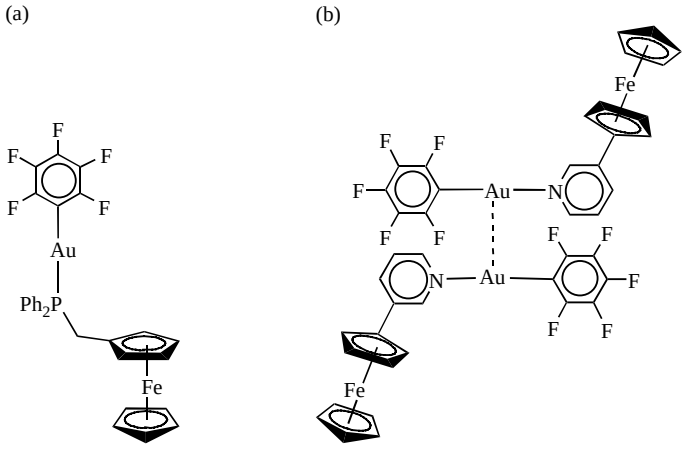


FIG. 8. Structure of $[(C_6F_5)Au(PPh_2CH_2Fc)]$ (a) and $[(C_6F_5)Au(Fcpy)]$ (b).

The crystal structures of the Au^{I}/Fe^{II} complexes have been determined by X-ray diffraction methods showing a typical linear environment for the gold(I) center and none of them display intramolecular Au···Fe interactions (see Fig. 8). The phosphino derivative does not display intermolecular Au···Au interactions either (the shortest gold–gold distance is 5.560 Å), but the lattice shows F···F (2.858 Å) and F···H (2.55 and 2.60 Å) contacts. In contrast, ferrocenylpyridine complex molecules are associated into pairs across inversion centers *via* a weak intermolecular Au···Au interaction of 3.301(2) Å, similar to that observed in the case of the (thiophenylmethyl)diphenylphosphine derivative $[\{(C_6F_5)Au\}_2\{\mu\text{-}PPh_2C(=S)N(H)Me\}]$ described above (Au···Au 3.2712(5) Å).[34]

The Au–C distance of 2.070(5) Å in the former compares well with those obtained for other pentafluorophenyl phosphino complexes, such as $[Au(C_6F_5)(PPh_3)]$ (2.07(2) Å)[99] or $[Au(C_6F_5)(PPh_2C{\equiv}CH)]$ (2.059(8) Å),[33] and is longer than the Au–C distance in the pyridine derivative (2.00(2) Å), in accordance with the greater *trans* influence of the phosphorus donor ligands. This Au–C distance is almost identical to those observed in complexes $[Au(C_6F_5)\{N(H){=}CPh_2\}]$ (2.002(10) Å),[37] $[Au(C_6F_5)(3\text{-}MeNC_5H_4)]$ (1.995(6) Å)[38] and $[Au(C_6F_5)(Ph_2C{=}N{-}N{=}CPh_2)]$ (1.992(9) Å).[54]

In contrast, an unusual coordination mode for gold(I) is observed in the crystal structures of $[(Fmes)Au\{(Me_3SiC{\equiv}C)_2Ti(\eta^5\text{-}C_5H_4SiMe_3)_2\}]$[97,98] and $[(C_6F_5)Au\{\mu\text{-}CN(Et)Me\}W(\eta^5\text{-}C_5H_5)(CO)_2]$.[94] In the first complex, prepared by reaction of $[Au(Fmes)(SMe_2)]$ with the 3-titanopenta-1,4-diyne $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2]$, the gold(I) center possesses a trigonal-planar environment comprising two η^2-coordinated C≡C building blocks and the η^1-bonded ligand 2,4,6-$(CF_3)_3C_6H_2$ (see Fig. 9).

The alkyne carbon atoms, the silicon atoms bonded to them, the metal centers and the aryl C_{ipso} carbon atom are arranged in-plane, which is consistent with η^2-alkyne-to-group 11 metal bonding, observed in other copper(I) and silver(I) derivatives.[100–102] Likewise, the η^2-coordination results in a C≡C bond lengthening from the distance observed in the starting compound and a significant change in the initially linear arrangement

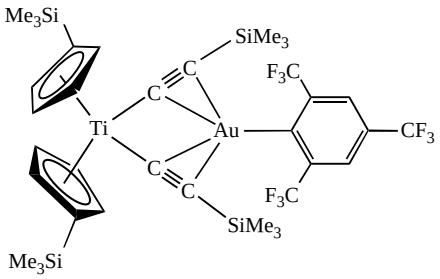


FIG. 9. Structure of [(Fmes)Au{$(Me_3SiC{\equiv}C)_2Ti(\eta^5\text{-}C_5H_4SiMe_3)_2$}].

of the Ti–C≡C–Si entities. However, the most striking feature of the η^2-coordination of the alkynyl ligands is the decrease in the bite angle C–Ti–C′ from 102.8(2)° in the parent compound to 95.4(3)°. Moreover, the Au–Ti distance of 2.9948(14) Å is relatively short and suggests the possibility of a direct Ti···Au interaction.

The aminocarbyne complex $[(C_6F_5)Au\{\mu\text{-}CN(Et)Me\}W(\eta^5\text{-}C_5H_5)(CO)_2]$[94] is also synthesized in a displacement reaction of $[W\{{\equiv}CN(Et)Me\}(\eta^5\text{-}C_5H_5)(CO)_2]$ with $[Au(C_6F_5)(tht)]$. This adduct exhibits a molecule of the starting product bonded to the $Au(C_6F_5)$ fragment through one of the $W-C_{carbyne}$ π bonds, with the formation of a WCAu ring (see Fig. 10). The tungsten atom acquires its closed electronic configuration through a mechanism which is somewhere in between the resonance structures N–C≡W and $N^+{=}C{=}W^-$. The $Au(C_6F_5)$ fragment achieves the preferred two-coordinative 14-electron configuration by accepting an electron pair from the in-plane localized $W-C_{carbyne}$ π orbital, resembling the coordination of an olefin ligand. This interaction perturbs, but does not disrupt, the electronic structure of the donor.

The Au–W and $Au-C_{carbyne}$ distances of 2.727(1) and 2.13(2) Å, respectively, can be compared with the corresponding values in the related compound $[AuWBr(bipy)(C_6F_5)(CO)_2(\mu\text{-}CC_6H_4Me\text{-}4)]$ (2.783(1) and 2.080(3) Å)[103] and the $Au-C_{aryl}$ distance of 2.07(2) Å compares well with that observed in $[(Fmes)Au\{(Me_3SiC{\equiv}C)_2Ti(\eta^5\text{-}C_5H_4SiMe_3)_2\}]$ (2.079(7) Å)[97,98] described previously.

Apart from these complexes, a number of heterodinuclear neutral compounds containing ferrocenyl derivatives as aryl ligands have also been prepared in recent years (see Table X). Most of them contain the ligand 2-(dimethylaminomethyl)ferrocenyl (FcN)[104–106] and, with the sole exception of $[(FcN)Au\{P(4\text{-}ClC_6H_4)_3\}]$,[106] have been

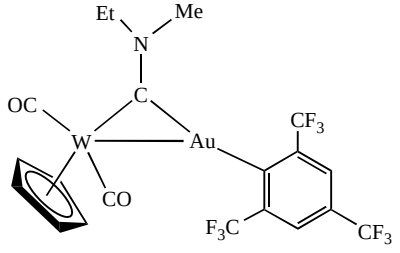
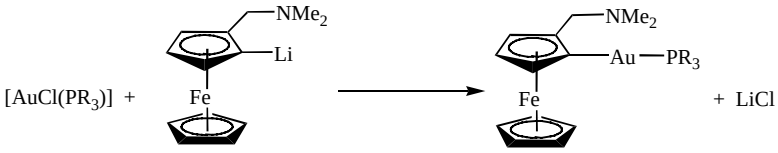


FIG. 10. Structure of $[(C_6F_5)Au\{\mu\text{-}CN(Et)Me\}W(\eta^5\text{-}C_5H_5)(CO)_2]$.

TABLE X
HETERODINUCLEAR NEUTRAL COMPLEXES WITH FERROCENYL DERIVATIVES AS ARYL LIGANDS

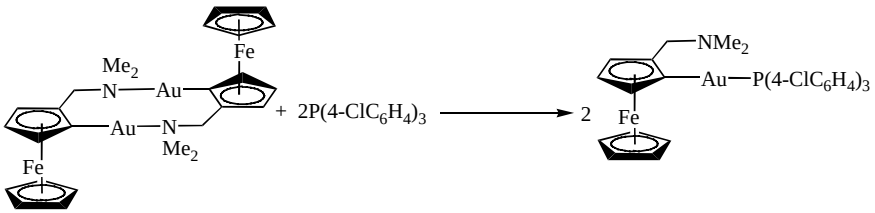
Complex	Au–C (Å)	Au–P (Å)	C–Au–P (°)	Au···Au_{inter} (Å)	Ref.
[(FcN)Au(PEt_3)]					104
[(FcN)Au(PPh_3)]	2.027(6)	2.287(2)	174.5(2)		105
[(FcN)Au{P(3-FC_6H_4)$_3$}]					105
[(FcN)Au{P(4-FC_6H_4)$_3$}]					105
[(FcN)Au{P(3-ClC_6H_4)$_3$}]	2.029(6)	2.285(2)	174.4(2)	3.068(1)	104
[(FcN)Au{P(4-ClC_6H_4)$_3$}]					106
[(FcN)Au{P(2-MeC_6H_4)$_3$}]					104
[(FcN)Au{P(3-MeC_6H_4)$_3$}]					104
[(FcN)Au{P(4-MeC_6H_4)$_3$}]					104
[(FcN)Au{P(3,4-$F_2C_6H_3$)$_3$}]					104
[(FcN)Au{P(3,5-$F_2C_6H_3$)$_3$}]	2.050(10)	2.285(2)	175.3(3)	3.052(1)	104
[(FcN,N)Au(PPh_3)]	2.039(3)	2.286(1)	178.1(1)		107
[(η^5-C_5H_5)Fe(η^5-2-$NO_2C_5H_3$)Au(PPh_3)]	2.021	2.279	177.91		108
[(η^5-C_5H_5)Ru(η^5-C_5H_4)Au(PPh_3)]	1.977	2.268	179.78		108

prepared by reaction of equimolecular amounts of the corresponding chloro-tertiaryphosphine-gold(I) with (FcN)Li, as shown in Eq. (25).



(25)

In contrast, the tris(*p*-chlorophenyl)phosphine homologue is obtained by treatment of the dimer $[(FcN)Au]_2$ with the free phosphine in a 1:2 molar ratio [Eq. (26)].[106]



(26)

Other heterobimetallic aryl-phosphine-gold(I) complexes with different ferrocenyl derivatives, such as *N*-[2-*N*′,*N*′-(dimethylaminoethyl)-*N*-methyl-aminoethyl]-ferrocenyl (FcN,N),[107] 2-nitroferrocenyl[108] or ruthenocenyl,[108] have also been reported.

Some of these compounds have been structurally characterized, all of them showing very similar features. They all display a linear P–Au–C fragment, with very similar values in terms of C–Au–P bond angles (see Table X) and similar Au–C and Au–P

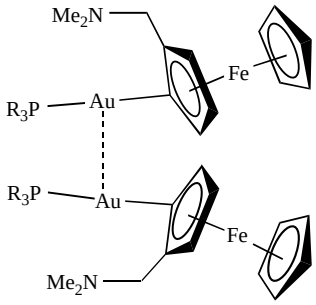
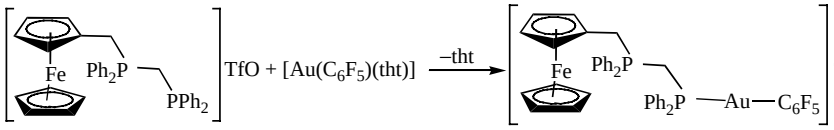


FIG. 11. Structure of [(FcN)Au(PR_3)] (R=3-ClC_6H_4, 3,5-$F_2C_6H_3$).

bond distances (1.977–2.050(10) Å and 2.268–2.287(2) Å, respectively), the shortest corresponding to the ruthenium derivative. None of them show intramolecular Au···M (M = Fe, Ru) interactions as a consequence of the restrictions imposed by the aryl ligand, but two of them, [(FcN)Au{P(3-$ClC_6H_4)_3$}] and [(FcN)Au{P(3,5-$F_2C_6H_3)_3$}],[104] are associated into dimers in the lattice through intermolecular Au···Au interactions of 3.068(1) and 3.052(1) Å, respectively (see Fig. 11).

2. Cationic

Cationic heterodinuclear complexes derived from ferrocenyl are not as common as their neutral analogs, and only the pentafluorophenyl derivative [(C_6F_5)Au($PPh_2CH_2PPh_2CH_2Fc$)]TfO has recently been prepared by treatment of the phosphonium-phosphine salt [$FcCH_2PPh_2CH_2PPh_2$]TfO with equimolecular amounts of [Au(C_6F_5) (tht)] [Eq. (27)] (Table XI).[109]



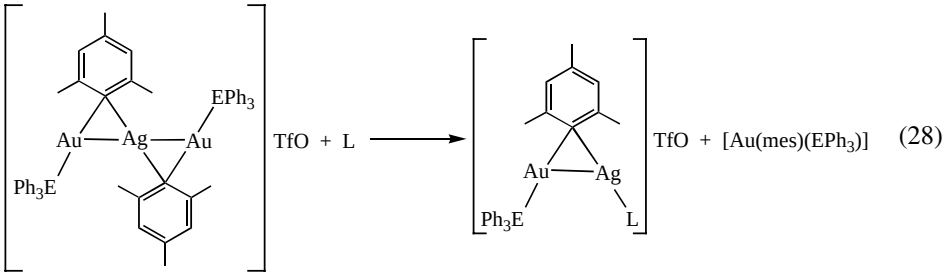
(27)

However, a number of species with the general formula [(Ph_3E)Au(μ-mes)AgL]TfO (E = P, As; L = P-, S-, N- or As-donor ligand) have been described.[27,110]

TABLE XI
HETERODINUCLEAR CATIONIC COMPLEXES

Complex	Ref.
[(C_6F_5)Au($PPh_2CH_2PPh_2CH_2Fc$)]TfO	109
[(Ph_3P)Au(μ-mes)Ag(PPh_3)]TfO	27,110
[(Ph_3P)Au(μ-mes)Ag(tht)]TfO	110
[(Ph_3P)Au(μ-mes)Ag(bipy)]TfO	110
[(Ph_3P)Au(μ-mes)Ag($SPPh_3$)]TfO	110
[(Ph_3As)Au(μ-mes)Ag($AsPh_3$)]TfO	110

The triphenylphosphine derivative $[(Ph_3P)Au(\mu\text{-mes})Ag(PPh_3)]TfO$ was first synthesized in 1994 by treatment of $[Au(mes)(PPh_3)]$ with $[Ag(OSO_2CF_3)L]$ in equimolecular amounts,[27] but it can also be isolated as the product of the reaction between the trinuclear complex $[\{Au(\mu\text{-mes})(PPh_3)\}_2Ag]TfO$ with PPh_3.[110] This method is, as shown in Eq. (28), the general procedure for the synthesis of the remaining compounds included in this section, the only difference being the neutral donor ligand employed.[110] Moreover, it has the advantage of allowing the recovery of $[Au(mes)(EPh_3)]$ formed as a by-product from the mother liquors.



(28)

Despite the absence of crystal structures, the presence of the mesityl bridging groups is confirmed in their IR spectra, which display the characteristic absorptions of these groups.

IV
TRINUCLEAR COMPLEXES

A. *Homonuclear Complexes*

1. Neutral

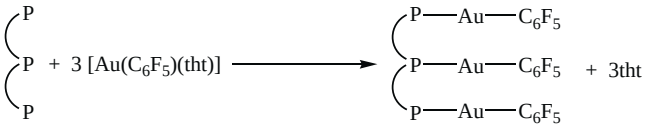
The majority of homotrinuclear complexes are pentafluorophenyl derivatives of gold containing bridging ligands, usually triphosphines (Table XII). One of the few recently described examples of neutral homotrinuclear species without C_6F_5 ligands is the complex $[\{(Fmes)Au\}_3(\mu_3\text{-triphos})]$ (triphos = $PPh(CH_2CH_2PPh_2)_2$), which is obtained by reaction of the corresponding chloro derivative with an excess of freshly prepared diethyl ether solution of Li(Fmes).[111]

The corresponding pentafluorophenyl derivative,[111] as well as the analogous compounds containing other triphosphines, such as dpmp $(PPh(CH_2PPh_2)_2)$[112] or tdppme $((PPh_2CH_2)_3CCH_3)$,[86] can be easily prepared by treatment of the free tridentate ligand with the stoichiometric amount of $[Au(C_6F_5)(tht)]$ [see Eq. (29)]. Likewise, these complexes are luminescent at low temperature in solid state, which is usually related to the presence of $Au^I\cdots Au^I$ interactions, although in these cases no X-ray crystal structure

TABLE XII
HOMOTRINUCLEAR NEUTRAL COMPLEXES

Complex	Ref.
[{(Fmes)Au}$_3$(μ_3-triphos)]	111
[{(C_6F_5)Au}$_3$(μ_3-triphos)]	111
[{(C_6F_5)Au}$_3$(μ_3-dpmp)]	112
[{(C_6F_5)Au}$_3$(μ_3-tdppme)]	86
[{(C_6F_5)Au}{(C_6F_5)$_3$Au}$_2$(μ_3-dpmp)]	112
[{(C_6F_5)Au}$_2$({(C_6F_5)$_3$Au}(μ_3-tdppme)]	86
[Au$_3$(C_6F_5)Cl(μ-S_2CNMe$_2$)(μ_3-dpmp)]	113
[{(C_6F_5)Au}$_2${μ-$PPh_2CH(AuPPh_3)PPh_2$}]	90
[{(C_6F_5)Au}{(C_6F_5)$_3$Au}{μ-$PPh_2CH(AuPPh_3)PPh_2$}]	90

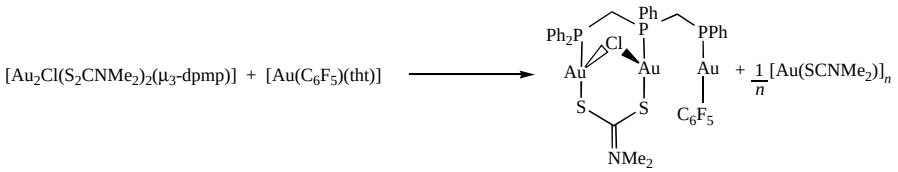
has been determined in order to confirm the presence of such interactions.



(29)

Apart from these products, the mixed-valence complexes [{(C_6F_5)Au}{(C_6F_5)$_3$Au}$_2$(μ_3-dpmp)][112] and [{(C_6F_5)Au}$_2${(C_6F_5)$_3$Au}(μ_3-tdppme)][86] have also been synthesized *via* displacement reactions of the same gold(I) reagent with the appropriate di- or mononuclear gold(III) phosphino derivative. Significantly, these complexes do not display the same optical properties as gold(I) species and are therefore not luminescent, signaling the absence of any interaction between gold(I) and gold(III) atoms.

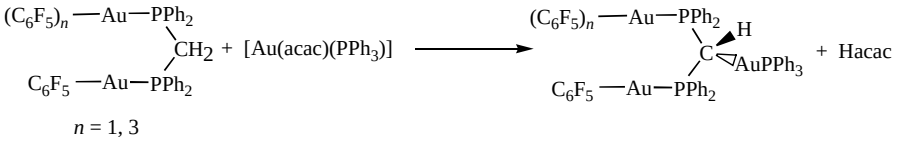
The insolubility of the polymeric species [Au(S_2CNMe$_2$)]$_n$ allows the synthesis of [Au$_3$(C_6F_5)Cl(μ-S_2CNMe$_2$)(μ_3-dpmp)] by reaction of [Au$_3$Cl(μ-S_2CNMe$_2$)$_2$(μ_3-dpmp)] with [Au(C_6F_5)(tht)], as shown in Eq. (30).[113] This arrangement of ligands, with dithiocarbamate and chloride acting as bridges, is proposed on the basis of its $^{31}P\{^1H\}$ NMR spectrum, which implies that this complex should be a racemic mixture.



(30)

Also certain trinuclear phosphino methanide derivatives containing gold(I) centers bonded to C_6F_5 groups have been reported. These species were prepared by substitution of one methylenic hydrogen of [(C_6F_5)Au($PPh_2CH_2PPh_2$)Au(C_6F_5)$_n$] ($n = 1, 3$) by treatment with one equivalent of [Au(acac)(PPh_3)], affording the trinuclear compounds shown in Eq. (31).[90] In both cases, the use of an excess of

deprotonating agent does not produce a double deprotonation and the monosubstituted product is formed again.

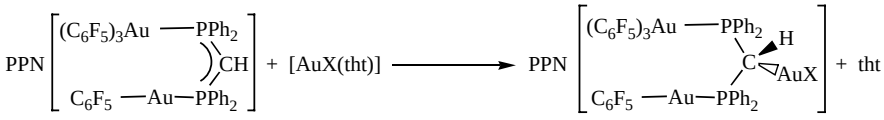


(31)

The mixed-valence complex can also be obtained by coordination of the non-saturated methanide carbon atom of the anionic species PPN[(C_6F_5)Au(PPh_2 CHPPh_2)Au$(C_6F_5)_3$] to a Au$(PPh_3)^+$ fragment when reacted with an equimolecular amount of [Au(PPh_3)(tht)]ClO_4.[90]

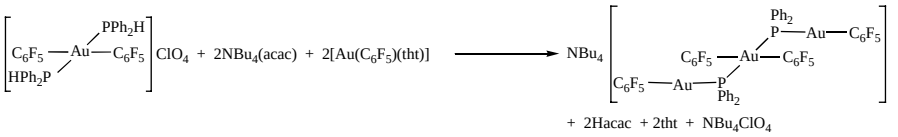
2. Anionic

Similarly, the trinuclear anionic Au^I/Au^{III} complexes PPN[(C_6F_5)Au{μ-PPh_2 CH(AuX)PPh_2}Au$(C_6F_5)_3$] (X = Cl, C_6F_5) are obtained when the same dinuclear methanide is treated with one equivalent of [AuX(tht)] instead of [Au(PPh_3)(tht)]ClO_4 [Eq. (32)].[90]



(32)

Acetylacetonate has been employed as a deprotonating agent not only for the synthesis of phosphino methanides, but also for obtaining phosphide derivatives. Thus, the hydrogen atoms of the diphenylphosphanylgold(III) complex *trans*-[Au$(C_6F_5)_2$(PPh_2 H$)_2$]ClO_4 can be easily removed by adding NBu_4(acac) and [Au(C_6F_5)(tht)] to a solution of the gold(III) complex in a 2:2:1 molar ratio [Eq. (33)].[114] The IR spectra seem to indicate a *trans* disposition of the ligands around the gold(III) center in this complex as well as the starting material. In contrast, its analogous triphenylphosphine derivative is described as the *cis* isomer also based on its IR spectrum, although no crystal structure has been determined in order to confirm this proposal.



(33)

In an attempt to obtain single crystals, the reaction of SH_2 with complexes of the type Q[AuArCl] (containing various aryl groups as well as cations) and in the presence

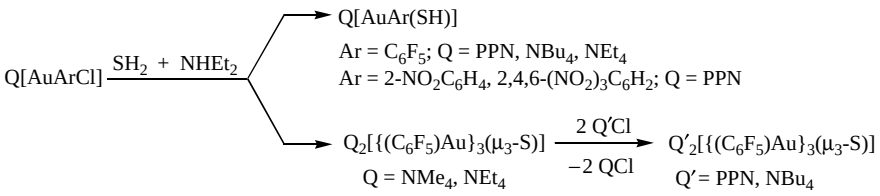
TABLE XIII
HOMOTRINUCLEAR ANIONIC COMPLEXES

Complex	Au–C (Å)	Au–S (Å)	C–Au–S (°)	Au···Au_{intra} (Å)	Ref.
PPN[(C_6F_5)Au{μ-PPh_2CH(AuCl)PPh_2}Au$(C_6F_5)_3$]					90
PPN[(C_6F_5)Au{μ-PPh_2CH(AuC_6F_5)PPh_2}Au$(C_6F_5)_3$]					90
trans-NBu_4[{(C_6F_5)Au(μ-PPh_2)}$_2$Au$(C_6F_5)_2$]					114
$(PPN)_2$[{(C_6F_5)Au}$_3$(μ_3-S)]					41
$(NMe_4)_2$[{(C_6F_5)Au}$_3$(μ_3-S)]					41
$(NEt_4)_2$[{(C_6F_5)Au}$_3$(μ_3-S)]	2.017(14)	2.301(4)	176.6(4)	3.2773(9)	41
	2.019(14)	2.321(4)	177.7(3)	3.4772(9)	
	2.042(13)	2.319(4)	177.0(3)	3.1844(9)	
$(NBu_4)_2$[{(C_6F_5)Au}$_3$(μ_3-S)]					41

of diethylamine was studied. However, this reaction gives the mononuclear complexes Q[AuAr(SH)] described previously (see Table II) or trinuclear derivatives of the type Q_2[{(C_6F_5)Au}$_3$(μ_3-S)] (see Table XIII) depending on the reaction conditions and, surprisingly, also on the cation.[41] Thus, whereas compounds containing the PPN or NBu_4 cations lead to hydrosulfido complexes, the NMe_4 derivative always yields the trinuclear sulfido product. When the cation is NEt_4, the complex obtained is mono- or trinuclear depending on the reaction conditions (see Scheme 5).

Lastly, the crystal structure of one of these trinuclear derivatives was determined by X-ray diffraction methods (see Fig. 12), showing the sulfur atom in a distorted trigonal pyramidal environment with Au···Au contacts between 3.1844(9) and 3.4772(9) Å and, correspondingly, a narrow Au–S–Au angle, (86.68(12)–97.65(13)°). Two of these pairs of parameters are in the normal range observed for related complexes [$(AuPR_3)_3$(μ_3-S)]X[115–117] or [Au{(μ_3-S)$(AuPPh_3)_2$}$_3$]$^+$[118] (Au···Au 2.990(1)–3.420(1) Å; Au–S–Au 79.5(1)–95.0(3)°). All these Au···Au and Au–S–Au values are similar to those calculated for $S(AuPH_3)_3^+$ using relativistic potentials (Au···Au 3.05, 3.52 Å; Au–S–Au 82.3, 98.5°).[119]

The gold centers are essentially linear with Au–C and Au–S distances in the range 2.017(14)–2.042(13) and 2.301(4)–2.321(4) Å, respectively. The latter are similar to those found in the above-mentioned complexes [$(AuPR_3)_3$(μ_3-S)]X[115–117] or [Au{(μ_3-S)$(AuPPh_3)_2$}$_3$]$^+$[118] (2.303(7)–2.342(7) Å) and they are intermediate between those



SCHEME 5.

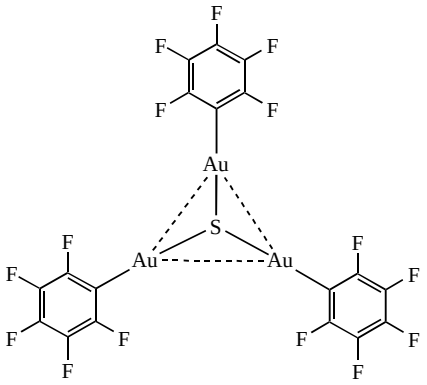
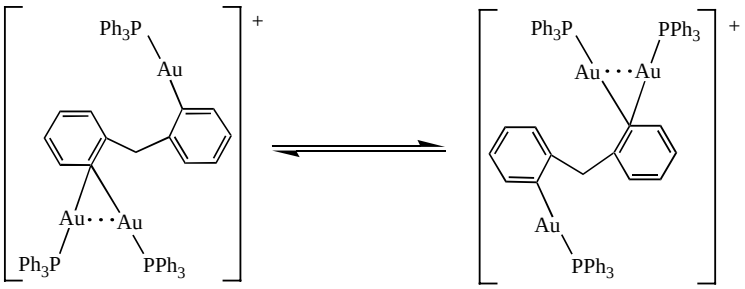


FIG. 12. Structure of $(NEt_4)_2[\{(C_6F_5)Au\}_3(\mu_3\text{-}S)]$.

observed in $[(AuPPh_3)_2(\mu_2\text{-}S)]$ (2.161(5) and 2.157(5) Å)[120] and in $[(AuPPh_3)_4(\mu_4\text{-}S)]^{2+}$ (2.362(5)–2.429(5) Å).[121] Thus, the Au–S distances increase with the number of gold atoms attached to sulfur.

3. Cationic

One of the few examples of homotrinuclear species without C_6F_5 ligands is the organogold *ortho* derivative of diphenylmethane $[CH_2(o\text{-}C_6H_4)_2(AuPPh_3)_3]BF_4$, obtained by the addition of one equivalent of $[AuPPh_3]BF_4$ to the dinuclear product $[CH_2(o\text{-}C_6H_4)_2(AuPPh_3)_2]$ previously commented (Table XIV).[75] The temperature dependence of its $^{31}P\{^1H\}$ NMR spectrum allows the observation of its conformational non-rigidity in solution, indicating that a rotation around the single C–C bonds occurs simultaneously with rapid intramolecular exchanges due to transfer between the gold-containing groups of the cation [Eq. (34)].



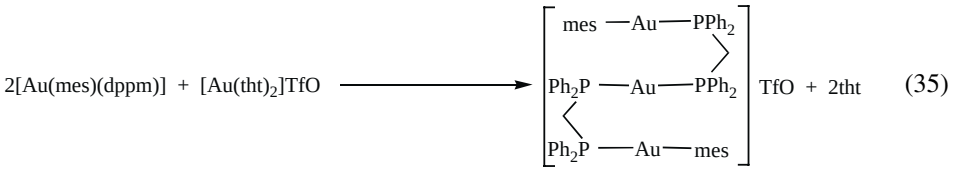
(34)

Also, a cationic homotrinuclear organogold(I) complex with mesityl ligands as aryl groups has recently been prepared by reaction of [Au(mes)(dppm)], which contains two potentially bidentate ligands, with bis(tetrahydrothiophene)gold(I)

TABLE XIV
HOMOTRINUCLEAR CATIONIC COMPLEXES

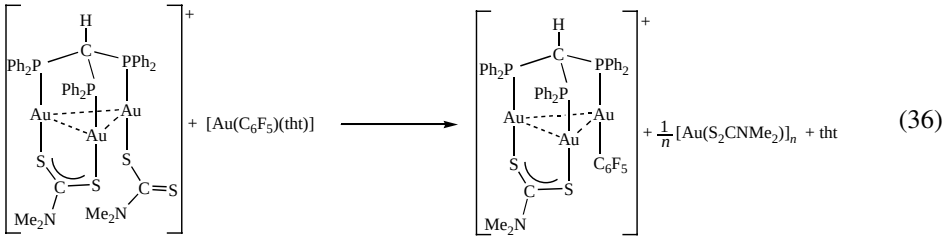
Complex	Ref.
$[CH_2(o\text{-}C_6H_4)_2(AuPPh_3)_3]BF_4$	75
$[\{(\mu\text{-mes})Au\}_2Au(\mu\text{-dppm})_2]TfO$	122
$[Au_3(C_6F_5)(\mu\text{-}S_2CNMe_2)\{\mu_3\text{-}(PPh_2)_3CH\}]ClO_4$	123
$[Au_3(C_6F_5)(\mu\text{-}S_2CNMe_2)(\mu_3\text{-dpmp})]TfO$	113
$[(C_6F_5)Au\{PPh_2C(AuPPh_3)_2PPh_2Me\}]ClO_4$	90

trifluoromethylsulfonate in a 2:1 molar ratio [Eq. (35)].[122]



(35)

In order to test the coordinative ability of the free sulfur atom of $[Au_3(\mu\text{-}S_2CNMe_2)_2\{\mu_3\text{-}(PPh_2)_3CH\}]ClO_4$, it was treated with $[Au(C_6F_5)(tht)]$. However, this reaction, instead of promoting coordination of the new metallic center to the sulfur, results in the precipitation of gold(I) dimethyldithiocarbamate and the coordination of the pentafluorophenyl group to the gold center previously bonded to $S_2CNMe_2^-$, as shown in Eq. (36).[123]

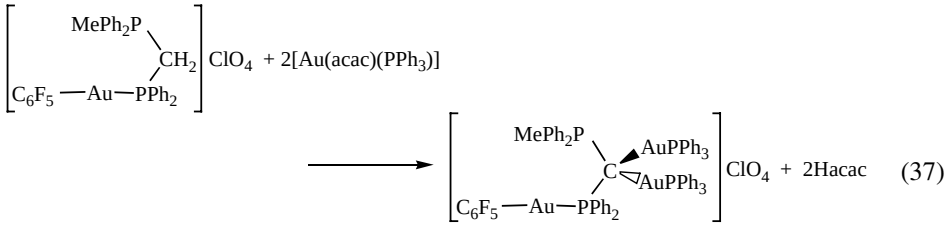


(36)

This reaction is similar to that previously described for the synthesis of the neutral $[Au_3(C_6F_5)Cl(\mu\text{-}S_2CNMe_2)(\mu_3\text{-dpmp})]$ [see Eq. (30)]. This complex can also be transformed into a cationic derivative, $[Au_3(C_6F_5)(\mu\text{-}S_2CNMe_2)(\mu_3\text{-dpmp})]TfO$, by elimination of the chlorine atom as silver chloride when reacted with AgTfO.[113]

Although the crystal structure of these two new cationic species has not been determined, those corresponding to the related complexes $[Au_3(\mu\text{-}S_2CNMe_2)_2\{\mu_3\text{-}(PPh_2)_3CH\}]ClO_4$,[123] $[Au_3(\mu\text{-}S_2CNMe_2)_3\{\mu_3\text{-}(PPh_2)_3CH\}]$[123] or $[(ClAu)_3(\mu_3\text{-dpmp})]$[113] display intramolecular Au···Au interactions with distances between 2.892(2) and 3.3961(8) Å, the shortest of them corresponding to the gold atoms coordinated to the bridging dithiocarbamate in the first compound.

Finally, in contrast with what happens when $[(C_6F_5)Au(PPh_2CH_2PPh_2)Au(C_6F_5)_n]$ ($n = 1$, 3) is treated with an excess of $[Au(acac)(PPh_3)]$ (see above), the reaction of $[(C_6F_5)Au(PPh_2CH_2PPh_2Me)]ClO_4$ with two equivalents of the same deprotonating agent affords the trinuclear methanide derivative $[(C_6F_5)Au\{PPh_2C(AuPPh_3)_2PPh_2Me\}]ClO_4$, probably favored by the positive charge of the complex.[90]

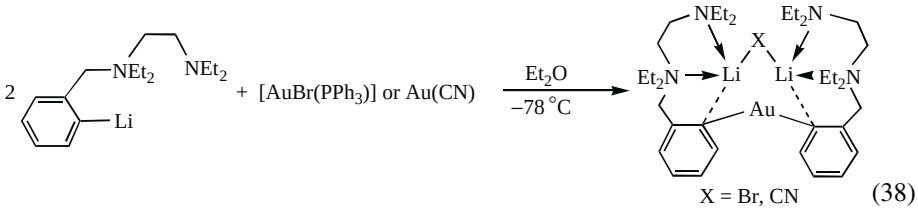


(37)

B. *Heteronuclear Complexes*

1. Neutral

Probably the most interesting complexes of this section are the aryl bromo- and aryl cyanoaurates $[AuLi_2BrAr_2]$ and $[AuLi_2(C{\equiv}N)Ar_2]$ ($Ar = [2\text{-}CH_2NEtCH_2CH_2NEt_2C_6H_4]^-$) recently synthesized by the addition of $[AuBr(PPh_3)]$ or Au(CN), respectively, to a diethyl ether solution of the corresponding aryllithium as shown in Eq. (38).[124]



(38)

Similarly, homologous cuprate and argentate derivatives have also been prepared and the crystal structures of both bromocuprate and -argentate species have been established by X-ray diffraction (Fig. 13). They consist of a MLi_2 core, and each aryl ligand bridging

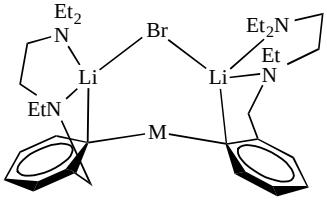
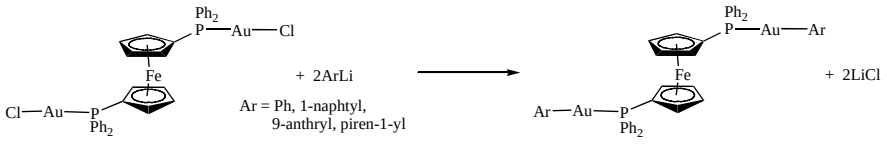


FIG. 13. Structure of $[MLi_2Br\{2\text{-}CH_2NEtCH_2CH_2NEt_2C_6H_4\}_2]$ (M=Cu, Ag).

the 11 group metal and one lithium atom *via* electron deficient bonding. The bromine atom exclusively bridges the lithium atoms and each of the *ortho*-$CH_2NEtCH_2CH_2NEt_2$ moieties is *N*,*N*′-chelate bonded to one lithium.

Molecular weight determinations by cryoscopy in benzene revealed that the MLi_2BrAr_2 stoichiometry found in the solid state is retained in solution. On the basis of NMR and cryoscopy, it can be concluded that the structural features of the bromoaurate are similar to those of the bromocuprate and -argentate. A multinuclear NMR study shows that the bonding between the [Li–Br–Li] and [Ar–M–Ar] is intermediate between ionic and covalent, with a more covalent Au–C_{ipso} bond than the Cu–C_{ipso} or Ag–C_{ipso} ones. A similar trend has also been reported previously by van Koten for tetranuclear compounds of the type $[M_2Li_2\{2\text{-}CH_2NMe_2C_6H_4\}_4]$ (M = Cu, Ag, Au).[125]

The use of ferrocenyl derivatives has also led to the synthesis of other trinuclear organogold(I) complexes that usually contain the fragment C–Au–P. Some of them contain 1,1′-bis(diphenylphosphino)ferrocene (dppf) bridging two gold(I) atoms and a variety of aryl groups (see Table XV). They have been prepared by treatment of the trinuclear chloro derivative [$(ClAu)_2$(dppf)] with two equivalents of the corresponding aryllithium [Eq. (39)] and their photophysical and electrochemical properties have been studied.[126]



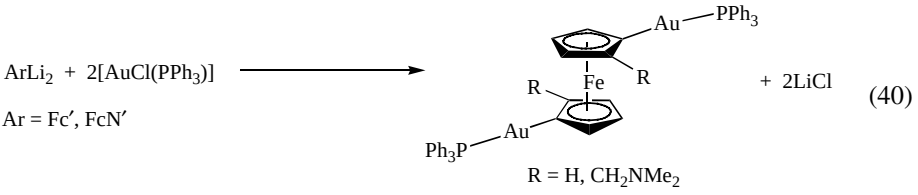
(39)

TABLE XV
HETEROTRINUCLEAR NEUTRAL COMPLEXES

Complex	Au–C (Å)	Au–P (Å)	C–Au–P (°)	Au···M_{intra} (Å)	Ref.
$[AuLi_2Br\{2\text{-}CH_2NEtCH_2CH_2NEt_2C_6H_4\}_2]$					124
$[AuLi_2(C{\equiv}N)\{2\text{-}CH_2NEtCH_2CH_2NEt_2C_6H_4\}_2]$					124
$[(PhAu)_2(dppf)]$					126
$[\{(1\text{-naphthyl})Au\}_2(dppf)]$					126
$[\{(9\text{-anthryl})Au\}_2(dppf)]$					126
$[\{(pyren\text{-}1\text{-}yl)Au\}_2(dppf)]$	2.061(8)	2.295(2)	172.1(3)	8.3315	126
$[Fc'(AuPPh_3)_2]$					106
$[FcN'(AuPPh_3)_2]$					106
$[\{(C_6F_5)Au\}_2\{Fc(Spy)_2\}]$					132
$[\{(C_6F_5)Au\}_2(dptpf)]$					133
$[(C_6F_5)Au(PFc_2Ph)]$					134
$[\{(C_6F_5)Au(o\text{-}PPh_2C_6H_4S)\}_2SnMe_2]$					135
$[\{(C_6F_5)Au(o\text{-}PPh_2C_6H_4S)\}_2Sn^tBu_2]$	2.052(10) 2.013(11)	2.269(3) 2.270(3)	177.5(3) 179.0(3)	5.08 5.48	135
$[\{(C_6F_5)Au(o\text{-}PPh_2C_6H_4S)\}_2SnPh_2]$					135
$[AuAg_2(C_6F_5)(CF_3CO_2)_2(PPh_2CH_2SPh)]$					35

The crystal structure of the pyren-1-yl derivative was determined by X-ray diffraction methods, being basically similar to that of the starting material.[127] The gold(I) centers display their typical linear environment with normal Au–C and Au–P distances (see Table XV). The two PPh_2 groups are oriented in an *anti* configuration, which precluded any possible intramolecular Au···Au contact (Au–Au 8.3315 Å). Although the cyclopentadienyl rings can rotate freely, a *syn* configuration is not observed in either this or in other reported non-chelating Au(dppf) complexes.[127–131]

Apart from these compounds with 1,1′-bis(diphenylphosphino)ferrocene, other organogold(I) complexes containing 1,1′-ferrocenediyl (Fc′) or 2,2′-bis(dimethylaminomethyl)ferrocenediyl (FcN′), such as bidentate aryl ligands, have been reported.[106] They are also obtained *via* the organolithium, which is treated in this case with $[AuCl(PPh_3)]$ in a 1:2 molar ratio [see Eq. (40)].



(40)

The electrochemical behavior of the ferrocenediyl complex has also been studied and from its cyclic voltammetric profile it can be deduced that it exhibits a ferrocene-centered one-electron oxidation, followed by the decomposition of the electrogenerated cation $[Fc'(AuPPh_3)_2]^+$.

As observed in other previous sections, a large number of heterotrinuclear complexes contain pentafluorophenylgold(I) fragments that are usually isolated from reaction of $[Au(C_6F_5)(tht)]$ with a metal-containing product with donor atoms that can coordinate the gold(I). The most recent ones are shown in Fig. 14 and contain functionalized ferrocene derivatives as 1,1′-bis(2-pyridylthio)ferrocene ($Fc(Spy)_2$),[132] 1,1′-bis(diphenylthiophosphoryl)ferrocene (dptpf)[133] or diferrocenylphenylphosphine (PFc_2Ph).[134]

Also following the same synthetic pathway, a series of heterometallic phosphinethiolate Sn^{IV}/Au^{I} derivatives of the type $[\{(C_6F_5)Au(o\text{-}PPh_2C_6H_4S)\}_2SnR_2]$ were obtained

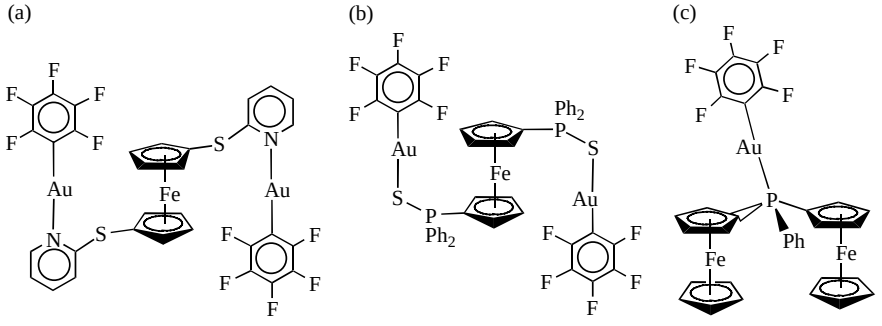


FIG. 14. Structure of $[\{(C_6F_5)Au\}_2\{Fc(Spy)_2\}]$ (a),$[\{(C_6F_5)Au\}_2(dptpf)]$ (b) and $[(C_6F_5)Au(PFc_2Ph)]$ (c).

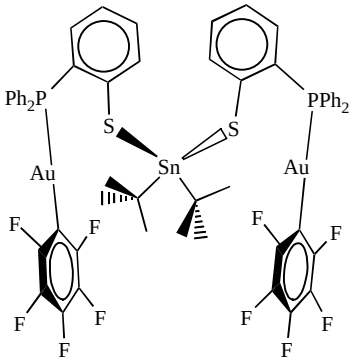


FIG. 15. Structure of $[\{(C_6F_5)Au(o\text{-}PPh_2C_6H_4S)\}_2Sn^tBu_2]$.

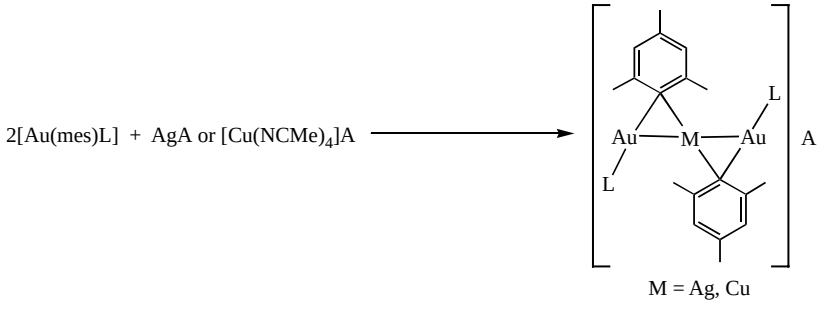
(see Table XV).[135] The crystal structure of the ^{t}Bu derivative (Fig. 15) shows every phosphinethiolate ligand bridging the tin(IV) center and one of the gold(I) atoms.

The Sn^{IV} is in a distorted tetrahedral geometry, while the Au^I atoms are linearly coordinated to the phosphorus of one of the bidentate ligands and to one C_6F_5 group. The Au–P (2.269(3) and 2.270(3) Å) and Au–C (2.052(10) and 2.013(11) Å) distances are similar to those found in the previously commented pentafluorophenyl complexes $[(C_6F_5)Au(\mu\text{-vdpp})Au(C_6F_5)_3]$,[84] $[\{(C_6F_5)Au\}_2\{\mu\text{-}2,2'\text{-}(PR_2C_6H_4)_2\}]$ (R = Et, Ph)[85] or $[(C_6F_5)Au(\mu\text{-}2\text{-}Ph_2P\text{-}6\text{-}MeC_6H_3)Au(C_6F_5)(\eta^2\text{-}2\text{-}Ph_2P\text{-}6\text{-}MeC_6H_3)]$[89] (Au–P = 2.270 (2)–2.285(3) Å; Au–C 2.02(1)–2.056(4) Å). The Au–Sn distances are 5.08 and 5.48 Å, so there are no significant interactions between the metallic centers.

Finally, a mixed Au/Ag complex of stoichiometry $[AuAg_2(C_6F_5)(CF_3CO_2)_2(PPh_2CH_2SPh)]$, in which the thioether ligand (thiophenylmethyl)diphenylphosphine is expected to be coordinated to two silver trifluoroacetate moieties through the silver atoms, has also been reported as a result of treatment of the mononuclear $[(C_6F_5)Au(PPh_2CH_2SPh)]$ with two equivalents of $Ag(CF_3CO_2)$.[35]

2. Cationic

A series of heterotrinuclear Au_2Ag or Au_2Cu complexes containing mesityl bridging ligands and general formula compounds $[\{LAu(\mu\text{-mes})\}_2M]A$ (see Table XVI) are obtained by reaction of [Au(mes)L] with weakly coordinated silver or copper compounds such as AgTfO, $Ag(OClO_3)$ or $[Cu(NCMe)_4]PF_6$ in a 2:1 molar ratio [Eq. (41)].[110]



(41)

TABLE XVI
HETEROTRINUCLEAR CATIONIC COMPLEXES

Complex	Au–C (Å)	Au–P/As (Å)	C–Au–P/As (°)	Au···Ag_{intra} (Å)	Au···Au_{inter} (Å)	Ref.
$[\{(Ph_3P)Au(\mu\text{-mes})\}_2Ag]TfO$						110
$[\{(Ph_3As)Au(\mu\text{-mes})\}_2Ag]ClO_4$	2.09(2)	2.425(2)	166.8(4)	2.7758(8)	3.132(2)	110
$[\{(Ph_3As)Au(\mu\text{-mes})\}_2Ag]TfO$						110
$[\{(Ph_3P)Au(\mu\text{-mes})\}_2Cu]PF_6$						110
$[\{(Ph_3As)Au(\mu\text{-mes})\}_2Cu]PF_6$						110
$[\{(mes)Au\}_2Ag(\mu\text{-dppm})_2]ClO_4$	2.080(9)	2.315(5)	176.4(3)	2.944(2)	4.768	122
	2.083(10)	2.315(5)	177.0(3)	2.946(2)		
$[\{(C_6F_5)Au\}_2Ag(\mu\text{-}PPh_2CH_2SPh)_2]TfO$						35
$[\{(C_6F_5)Au\}_2Cu(\mu\text{-}PPh_2CH_2SPh)_2]TfO$						35

The X-ray diffraction analysis of $[\{(Ph_3As)Au(\mu\text{-}mes)\}_2Ag]ClO_4$ shows the central silver atom to be coordinated to two Au–Ag bridging mesityl groups, which bring the metals in close contact (Au–Ag distance of 2.7758(8) Å). This distance is of the same order as those found in complexes with formal gold–silver bonds, such as $[Au_{13}Ag_{12}Cl_8\{P(4\text{-}MeC_6H_4)_3\}_{10}]PF_6$ (average 2.883 Å),[136] $[AuAg(C_6F_5)_2(C_6H_6)]_n$ (2.702(2), 2.792(2) Å)[57] or $[Pt(AgNO_3)(AuPPh_3)_8](NO_3)_2$ (2.714(5)–2.786(5) Å).[137]

The deviation from the linearity at the gold atom (C–Au–As angle of 166.8(4)°) is only moderate if compared with other complexes with bridging mesityl groups, e.g., $[Au_5(mes)_5]$.[83] It is noteworthy that the mesityl bridge is not symmetrically disposed, in contrast with the usual symmetrical disposition of the aryl ligand in the examples mentioned above.

Finally, although this complex is described as a trinuclear entity, in the crystal packing it appears as an unidimensional chain polymer parallel to the *y*-axis (Fig. 16) formed by intermolecular Au···Au contacts of 3.132(2) Å.

A cationic mesityl Au_2Ag derivative, namely, $[\{(mes)Au\}_2Ag(\mu\text{-}dppm)_2]ClO_4$, has also been described, but now containing the aryl ligands acting as terminals instead of as bridges.[122] It is the silver homologue to the homotrinuclear gold derivative described in Section IV.A.3. Similarly, its synthesis takes place by reaction of the same mesitylgold(I) starting material than in Eq. (35) with silver perchlorate, instead of $[Au(tht)_2]TfO$.

Its crystal structure shows the silver center in the middle of the molecule with Ag–P distances (2.413(5) and 2.423(5) Å) similar to those observed in certain three-coordinated silver complexes (2.419(3), 2.4244(12) Å).[138,139] This fact, together with a P–Ag–P angle of 148.3(2)°, indicates a highly distorted geometry around the silver atom caused by the Au···Ag interactions of 2.944(2) and 2.946(2) Å (see Fig. 17). These distances are similar to those found in $[(AuPPh_3)_2\{\mu\text{-}C(PPh_3)(C_5H_4N)\}\{\mu\text{-}Ag(O_2NO)(OClO_3)\}]$ (2.926(1) and 3.006(1) Å)[140,141] and longer than in the pentafluorophenyl complex $[AuAg(C_6F_5)_2(C_6H_6)]_n$ (2.702(2) and 2.792(2) Å).[57]

The gold atoms are two-coordinate, with P–Au–C angles of 177.0(3) and 176.4(3)°, and Au–C distances similar to those observed in $[\{(Ph_3As)Au(\mu\text{-}mes)\}_2Ag]ClO_4$[110] (see Table XVI). Lastly, the intermolecular Au···Au distance of 4.768 Å indicates the absence of further intermetallic interactions, contrasting with the observations made in the case of $[\{(Ph_3As)Au(\mu\text{-}mes)\}_2Ag]ClO_4$.[110]

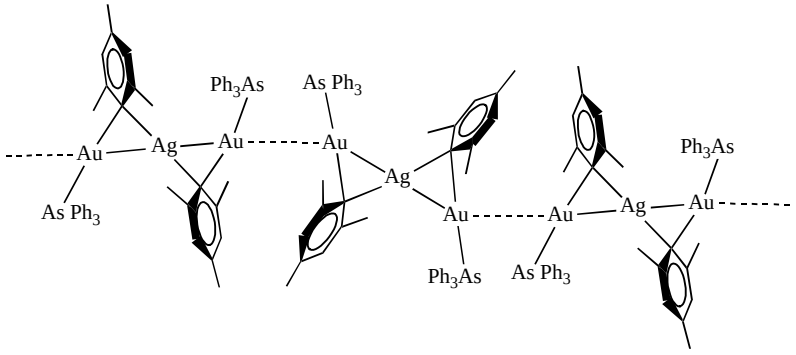


FIG. 16. Structure of $[\{(Ph_3As)Au(\mu\text{-}mes)\}_2Ag]ClO_4$.

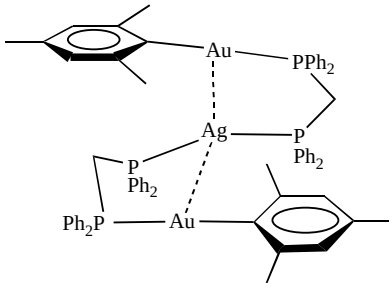


FIG. 17. Structure of [{(mes)Au}$_2$Ag(μ-dppm)$_2$]TfO.

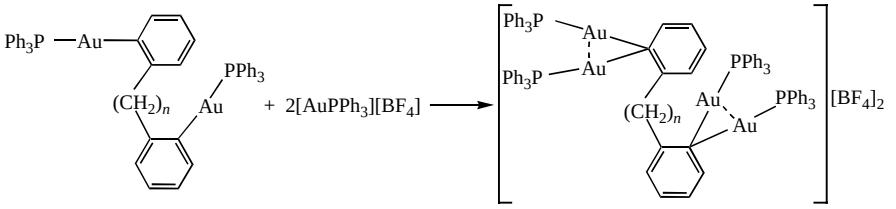
A similar reaction to that described for [{(mes)Au}$_2$Ag(μ-dppm)$_2$]TfO prompts the synthesis of the related pentafluorophenyl complexes [{(C$_6$F$_5$)Au}$_2$M(μ-PPh$_2$CH$_2$SPh)$_2$]TfO (M = Cu, Ag)[35] [see Eq. (42)]. These species contain the asymmetric bidentate ligand PPh$_2$CH$_2$SPh instead of dppm as a bridge between the metallic centers and, although none of them have been crystallographically characterized, the presence of intramolecular Au···M contacts is also probable in these compounds.

V

TETRANUCLEAR COMPLEXES

A. *Homonuclear*

The hypercoordinated diphenylmethane and diphenylethane derivatives [{CH$_2$(*o*-C$_6$H$_4$)$_2$}(AuPPh$_3$)$_4$][BF$_4$]$_2$ and [{CH$_2$CH$_2$(*o*-C$_6$H$_4$)$_2$}(AuPPh$_3$)$_4$][BF$_4$]$_2$ can be synthesized by auration of the corresponding dinuclear neutral species with [AuPPh$_3$][BF$_4$] (1:2) as shown in Eq. (42).[75]



(42)

The crystal structure of the latter has been reported in two papers (in 1997[75] and 1998[142]), with small differences in the bond lengths and angles although the crystal data were quite different. The diphenylethane ligand has a strictly *trans* configuration (determined by the crystallographically centrosymmetric nature of the dication) with the C(AuPPh$_3$)$_2$ fragments spaced at the greatest possible distance (see Fig. 18).

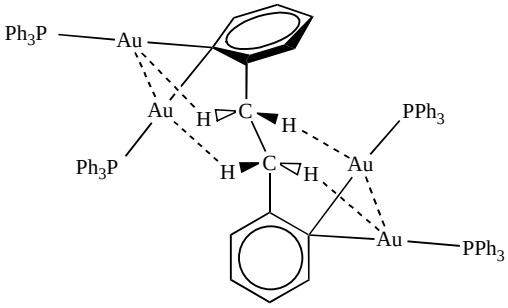


FIG. 18. Structure of $[\{CH_2CH_2(o\text{-}C_6H_4)_2\}(AuPPh_3)_4](BF_4)_2$.

The Au–C and Au–P distances (see Table XVII) found in this complex are similar to those observed in the starting materials $[\{CH_2(o\text{-}C_6H_4)_2\}(AuPPh_3)_2]$[75,79] and $[\{CH_2CH_2(o\text{-}C_6H_4)_2\}(AuPPh_3)_2]$[75] or in the related complexes $[(2,2\text{-}C_{12}H_7\text{-}4\text{-}^tBu)(AuPPh_3)_2]$[80] and $[\{CH_2(o\text{-}C_6H_4)_2\}Au_2(\mu\text{-dppe})]$[74,75] previously commented (Au–C 2.04(2)–2.06(3) Å and Au–P 2.279(8)–2.30(1) Å). Thus, no significant lengthening of the Au–C bonds is observed when a second $AuPPh_3$ fragment is incorporated in the same carbon atom. The main difference lies, as expected, in the intramolecular Au···Au distance of 2.727(3)[75] or 2.7440(8) Å,[142] which corresponds to the intermetallic distance in each Au–C–Au triangle.

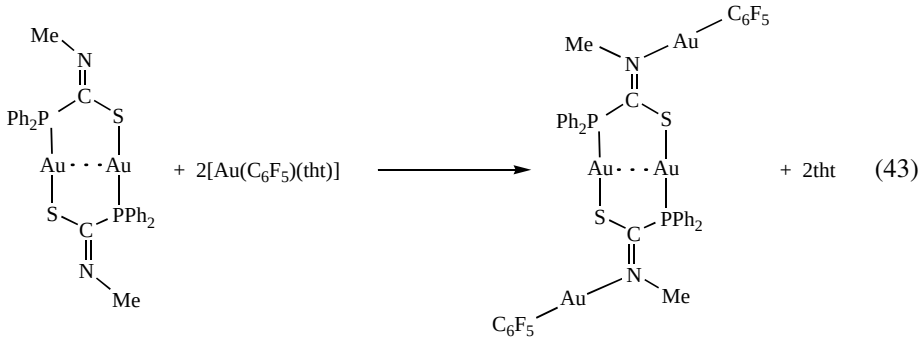
Lastly, one of the most important features of the structure of this complex is the presence of Au···H agostic interactions of 2.6 and 3.0 Å[75] or 2.71 and 2.88 Å[142] between each gold center and one hydrogen of the ethylene bridge. These interactions are also present in the crystal structures of the related complexes $[\{CH_2(o\text{-}C_6H_4)_2\}(AuPPh_3)_2]$,[75,79] $[\{CH_2CH_2(o\text{-}C_6H_4)_2\}(AuPPh_3)_2]$[75] and $[\{CH_2(o\text{-}C_6H_4)_2\}Au_2(\mu\text{-dppe})]$[74,75] (Au–H 2.62–3.06 Å), but absent in those of $[(2,2\text{-}C_{12}H_7\text{-}4\text{-}^tBu)(AuPPh_3)_2]$,[80] where the conformation observed in the molecule is stabilized by an aurophilic interaction of 3.1691(6) Å.

Again, the use of $[Au(C_6F_5)(tht)]$ has been shown as a useful pathway for the synthesis of new arylgold(I) compounds. Thus, its treatment with species with donor capacity, such as the diphenylphosphinothioformamide derivative $[Au\{PPh_2C(=S)NMe\}]_2$ affords

TABLE XVII
HOMOTETRANUCLEAR COMPLEXES

Complex	Au–C (Å)	Au–P/S (Å)	C–Au–P/S (°)	Au···Au_{intra} (Å)	Ref.
$[\{CH_2(o\text{-}C_6H_4)_2\}(AuPPh_3)_4](BF_4)_2$					75
$[\{CH_2CH_2(o\text{-}C_6H_4)_2\}(AuPPh_3)_4](BF_4)_2$	2.13(4)	2.27(1)	172(1)	2.727(3)	75
	2.12(4)	2.26(1)	172(1)		
	2.18(1)	2.281(5)	170.6(4)	2.7440(8)	142
	2.17(1)	2.273(5)	171.7(4)		
$[Au\{PPh_2C(=S)N(AuC_6F_5)Me\}]_2$					34

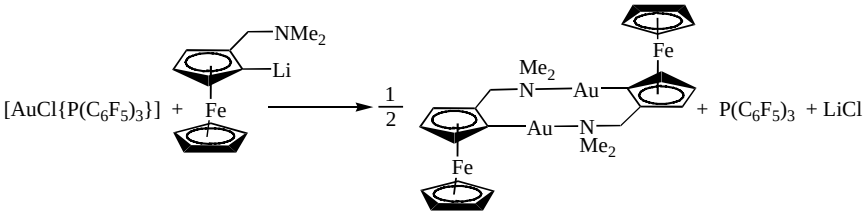
the neutral species $[Au\{PPh_2C(=S)N(AuC_6F_5)Me\}]_2$[34] [Eq. (43)].



(43)

B. *Heteronuclear*

In Section III.B.1 we discussed the synthesis of certain heterodinuclear neutral compounds of the type $[(FcN)Au(PR_3)]$[104–106] (FcN = 2-(dimethylaminomethyl)ferrocenyl) by reaction of $[AuCl(PR_3)]$ (see Table X) with (FcN)Li (1:1) [Eq. (25)]. In contrast, when the same reaction takes place with $[AuCl\{P(C_6F_5)_3\}]$ as a starting material, in which a larger number of electronegative fluorine atoms are present, the phosphine is displaced by the nitrogen atom of the FcN ligand affording the dimer $[Au(FcN)]_2$ [Eq. (44)].[105]

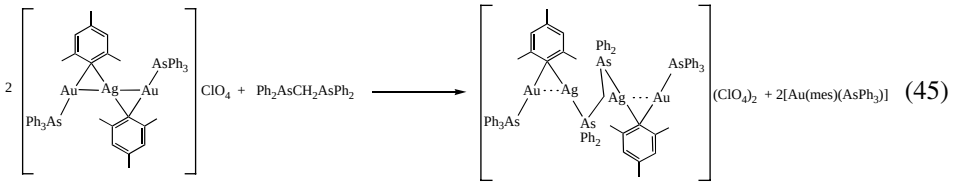


(44)

The formation of a 10-membered ring, in which the bidentate ligand adopts a head-to-tail conformation, yields gold(I) centers at a distance of 3.122(1) Å(see Table XVIII), longer than the aurophilic intramolecular interactions commented for other cyclic complexes in Section III.A.1 (see Table V), probably due to the higher number of atoms participating in the ring. No deformation of the linear environment of the gold atoms is observed and the Au–C distance of 2.021(6) Å is similar to those found in related heterodinuclear ferrocenyl derivatives (see Table X), in which the Au–C distances range from 2.021 to 2.050(10) Å.[104–108]

It is clear from the previous sections that the capacity of mesityl groups to act as bridges fosters the isolation of homo- or heteropolynuclear complexes. Thus, tetranuclear dicationic derivatives $[\{(Ph_3As)Au(\mu\text{-mes})Ag\}_2(\mu\text{-dpam})](ClO_4)_2$[110] (dpam = $Ph_2AsCH_2AsPh_2$) and $[(Ph_3P)Au(\mu\text{-mes})Ag(tht)]_2(TfO)_2$[27] have been prepared by reaction

of $[\{(Ph_3As)Au(\mu\text{-}mes)\}_2Ag]ClO_4$ with dpam (2:1) recovering $[Au(mes)(AsPh_3)]$ from the mother liquors [Eq. (45)] or by treatment of the related phosphino derivative $[Au(mes)(PPh_3)]$ with the equimolecular amount of $[Ag(OSO_2CF_3)(tht)]$ [Eq. (46)].



(45)

$$[Au(mes)(PPh_3)] + [Ag(TfO)(tht)] \rightarrow \tfrac{1}{2}[(Ph_3P)Au(\mu\text{-}mes)Ag(tht)]_2(TfO)_2 \qquad (46)$$

Figure 19 shows the crystal structure of the latter, which shows a dimer with the tetrahydrothiophene ligands acting as bridge between the two silver atoms, which are bonded to a mesityl ligand and two sulfur atoms from tht molecules in a distorted trigonal environment. As observed in other complexes with bridging mesityl ligands,[83,110,143–145] the planar mesitylene groups are nearly perpendicular to the plane through atoms Au–Ag–C_{ipso}.

The gold atoms are two-coordinate, with P–Au–C angles of 177.34(9)°, which contrasts with the angle of 166.8(4)° observed in $[\{(Ph_3As)Au(\mu\text{-}mes)\}_2Ag]ClO_4$.[110] The Au–C bond distances, 2.086(3) Å, are similar to those found in $[\{(Ph_3As)Au(\mu\text{-}mes)\}_2Ag]ClO_4$ (2.09(2) Å)[110] or in $[\{(mes)Au\}_2Ag(\mu\text{-}dppm)_2]TfO$ (2.080(9) and 2.083(10) Å),[122] the latter containing terminal mesityl ligands, which indicates that the Au–C distances seem to be substantially independent of the bonding mode displayed by the C-donor ligand. Lastly, the Au–Ag distance, 2.8245(6) Å, indicates appreciable metal–metal bonding, while the transannular Ag–Ag distance of 3.826 Å is too long to allow bonding interaction.

The synthesis of the tetranuclear complex $[(C_6F_5)Au(\mu\text{-}PPh_2CH_2SPh)Ag(\mu\text{-}CF_3CO_2)]_2$ by the addition of $AgCF_3CO_2$ to a solution of $[Au(C_6F_5)(PPh_2CH_2SPh)]$ (1:1 or 1:2)[35] is an example of how changes in a counterion can significantly affect the

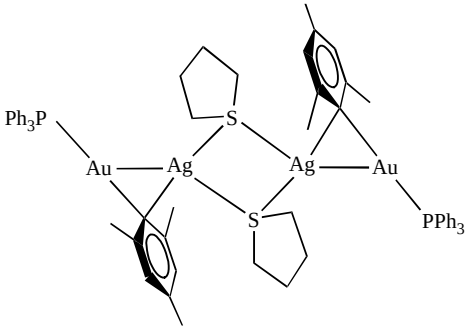


FIG. 19. Structure of $[(Ph_3P)Au(\mu\text{-}mes)Ag(tht)]_2(TfO)_2$.

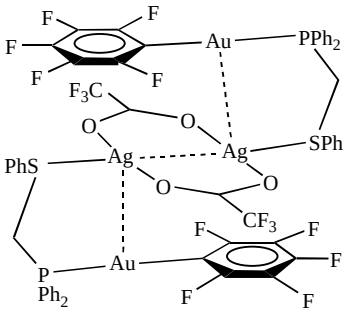
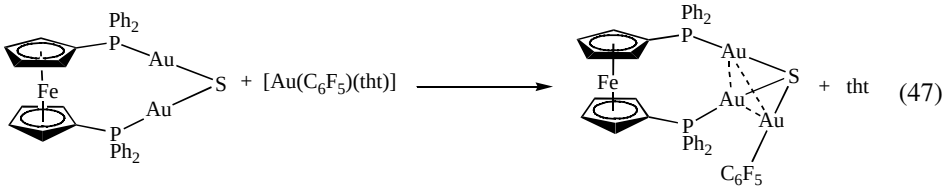


FIG. 20. Structure of $[(C_6F_5)Au(\mu\text{-}PPh_2CH_2SPh)Ag(\mu\text{-}CF_3CO_2)]_2$.

final geometry of a product. Thus, when the same reaction takes place using silver triflate instead of the trifluoroacetate salt, the "snake"-type complex $[\{(C_6F_5)Au\}_2Ag(\mu\text{-}PPh_2CH_2SPh)_2]TfO$, described above, is isolated.[35]

The crystal structure of this Au_2Ag_2 species (Fig. 20) shows the metallic centers forming a zigzag chain with the Ph_2PCH_2SPh ligands bridging the gold and silver atoms (with Au–P and Ag–S bonds) and the silver atoms bridged by the trifluoroacetate ligands. There are short Au···Au and Ag···Ag bonding interactions of 3.0335(8) and 2.8155(9) Å. The former is slightly longer than in the related $[AuAg(\mu\text{-}PPh_2CH_2SPh)_2](TfO)_2$ (2.9314(5) Å),[35] whereas the latter is shorter than in the homodinuclear $[Ag(\mu\text{-}PPh_2CH_2SPh)]_2(ClO_4)_2$ (2.9732(9) Å)[146] and even shorter than the values found in metallic silver (2.89 Å) or in many silver oxides.[147] The geometry at the gold centers is distorted from the linearity (C–Au–P 170.16(9)°) perhaps as a consequence of the Au···Ag interaction, while the silver atoms present a more irregular geometry.

As on other occasions, the reaction of a metallic complex, such as the trinuclear $[\mu\text{-}S\{Au_2(\mu\text{-dppf})\}]$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene), with $[Au(C_6F_5)(tht)]$ leads to the preparation of a new organometallic gold(I) complex of higher nuclearity, $[\mu_3\text{-}S\{Au(C_6F_5)\}\{Au_2(\mu\text{-dppf})\}]$ [Eq. (47)], in which the sulfur atom bridges the three gold centers.[148]



(47)

The most interesting compounds in this section are probably the Au_2Tl_2 species $[\{AuTl(C_6Cl_5)_2\}_2(O{=}CMe_2)]$[149] and $[\{AuTl(C_6Cl_5)_2(C_6H_5Me)\}_2(O_2C_4H_8)]$,[150] resulting from recent interest in the study of the reactivity of the basic anion $[Au(C_6Cl_5)_2]^-$. Thus, its treatment with Lewis acids, such as thallium(I) or silver(I) salts, leads to the formation of oligomers or polymers containing Au···Tl or Au···Ag interactions. These tetranuclear complexes are isolated from the acetone or toluene solutions in which

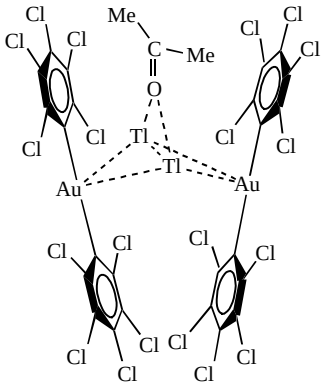


FIG. 21. Structure of $[\{AuTl(C_6Cl_5)_2\}_2(O{=}CMe_2)]$.

the reaction takes place [see Eqs. (48) and (49)].

$$NBu_4[Au(C_6Cl_5)_2] + Tl[PF_6] \xrightarrow{\text{acetone}} \tfrac{1}{2}[Au_2Tl_2(C_6Cl_5)_4(O{=}CMe_2)] + NBu_4[PF_6] \tag{48}$$

$$\frac{2}{n}[AuTl(C_6Cl_5)_2]_n + \text{dioxane} \xrightarrow{\text{toluene}} [\{AuTl(C_6Cl_5)_2(C_6H_5Me)\}_2(O_2C_4H_8)] \tag{49}$$

These complexes present a different disposition of the metals in their striking crystal structures, which display very interesting features. In the acetone derivative the metals are held together through four unsupported Au···Tl interactions and an additional Tl···Tl contact resulting in a loosely bound butterfly cluster (Fig. 21), while in the second complex there are only two Au···Tl contacts and a bridging dioxane molecule between

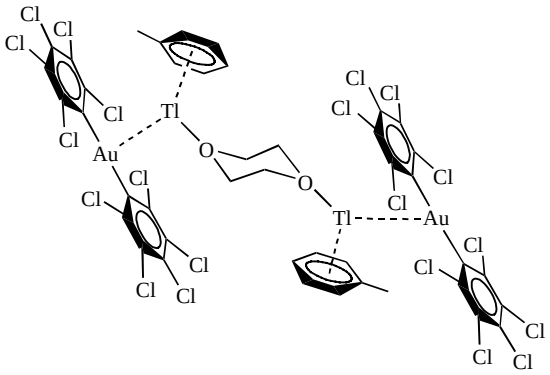


FIG. 22. Structure of $[\{AuTl(C_6Cl_5)_2(C_6H_5Me)\}_2(O_2C_4H_8)]$.

the thallium centers *via* unsupported Tl···O interactions, thus resulting a Au–Tl–dioxane–Tl–Au arrangement (Fig. 22).

In both structures the gold atoms are linearly coordinated to two pentachlorophenyl rings with similar Au–C distances and C–Au–C angles (see Table XVIII). A remarkable difference is observed in Au···Tl distances, which range from 3.0331(6) to 3.1887(6) Å in the butterfly-type compound while the dioxane derivative displays the shortest Au···Tl distance described to date (2.8935(3) Å),[149,151–157] being even shorter than the sum of Au and Tl covalent radii (3.08[158] or 2.92 Å[159]). The first complex also presents an intramolecular Tl···Tl interaction of 3.6027(6) Å, similar to the distances observed in dimeric $[Tl(S_2CNEt)_2]_2$ (3.60 and 3.62 Å).[160]

There are also remarkable differences in the environment of the Tl^I centers in each structure. Thus, in the first derivative the thallium atoms show weak interactions with the oxygen atom of an acetone molecule (Tl···O 2.968(9) and 2.903(9) Å), whereas in the second one each Tl(I) is only weakly coordinated to one oxygen atom of the bridging dioxane molecule (Tl–O 2.827(4) Å) and completes its coordination sphere with an unusual η^6-like π-arene contact to a toluene molecule. This results in a nearly trigonal-planar environment for the Tl^I (sum of angles of 355.2°), which implies that, very surprisingly, the stereoactivity of the inert pair, usually stereochemically active,[161] is not apparent in this case.

Finally, it is worth mentioning that both complexes luminesce in the solid state both at room temperature and at 77 K, showing different luminescent behavior, the dioxane derivative being one of the still scarce blue luminescent materials. In contrast, the acetone complex is also luminescent in solution and shows a solvent dependence on the emission. Luminescence and conductivity measurements suggest that the Tl···Tl interaction also exists in solution (probably stabilized by solvent molecules) and TD-DFT calculations seem to indicate that this interaction is responsible for luminescence in this case. This contrasts with other pentahalophenyl Au/Tl complexes, in which the optical properties are associated with the Au···Tl contacts.[149,151–154]

VI
HIGHER NUCLEARITY COMPLEXES

A. *Penta-, Hexa- and Heptanuclear Complexes*

Probably the best-known pentanuclear organogold complex is the homoleptic complex $[Au(\mu\text{-mes})]_5$, whose synthesis by reaction of [AuCl(CO)] with the appropriate Grignard reagent in tetrahydrofuran solution [Eq. (50)] was first reported in 1983 by Floriani.[143] An alternative synthetic procedure that takes place with precipitation of insoluble byproducts and uses a mesitylgold(I) derivative as a starting material [Eq. (51)] has been described more recently.[31]

$$[AuCl(CO)] + (mes)MgBr \rightarrow \tfrac{1}{5}[Au(\mu\text{-mes})]_5 + CO + MgClBr \qquad (50)$$

$$[BzPPh_3][Au(mes)Cl] + AgTfO \rightarrow \tfrac{1}{5}[Au(\mu\text{-mes})]_5 + [BzPPh_3]TfO + AgCl \qquad (51)$$

TABLE XVIII
HETEROTETRANUCLEAR COMPLEXES

Complex	Au–C (Å)	Au–N/P (Å)	C–Au–N/P/C (°)	Au···M (Å)	M···M (Å)	Ref.
$[(FcN)Au]_2$	2.021(6)	2.148(5)	175.9(3)		3.122(1) [Au···Au]	105
$[\{(Ph_3As)Au(\mu\text{-mes})Ag\}_2(\mu\text{-dpam})](ClO_4)_2$						110
$[(Ph_3P)Au(\mu\text{-mes})Ag(tht)]_2(TfO)_2$	2.086(3)	2.2886(9)	177.3(1)	2.8245(6)		27
$[(C_6F_5)Au(\mu\text{-}PPh_2CH_2SPh)Ag(\mu\text{-}CF_3CO_2)]_2$	2.056(3)	2.2886(10)	170.2(1)	3.0335(8)	2.8155(9) [Ag···Ag]	35
$[\mu_3\text{-}S\{Au(C_6F_5)\}\{Au_2(\mu\text{-dppf})\}]$						148
$[\{AuTl(C_6Cl_5)_2\}_2(O{=}CMe_2)]$	2.058(10)		177.0(3)	3.0331(6)	3.6027(6)	149
	2.062(9)			3.1887(6)	[Tl···Tl]	
	2.061(9)		176.5(3)	3.1164(6)		
	2.073(9)			3.0733(5)		
$[\{AuTl(C_6Cl_5)_2(C_6H_5Me)\}_2(O_2C_4H_8)]$	2.055(5)		177.6(2)	2.8935(3)		150
	2.052(5)					

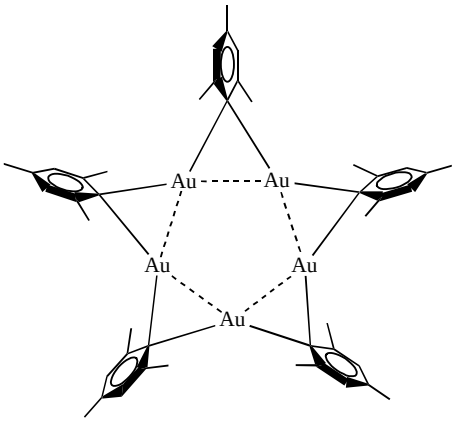


FIG. 23. Structure of $[Au(\mu\text{-mes})]_5$.

Its pentanuclear nature was confirmed by X-ray diffraction,[83,143] showing a beautiful star-shaped molecule with a 10-membered ring of alternating carbon and gold atoms, similar to that found for its copper analog.[144,162] The mesitylene ring planes are nearly perpendicular to the mean plane through the polynuclear ring, in which the metallic centers approach each other so closely (2.697(1)–2.708(1) Å) that the compound could be considered to be a pentanuclear gold(I) cluster (Fig. 23). These intramolecular Au···Au distances are slightly shorter than those found in $[\{CH_2CH_2(o\text{-}C_6H_4)_2\}(AuPPh_3)_4][BF_4]_2$ (2.727(3)[75] or 2.7440(8) Å[142]), where two gold(I) atoms are bridged by an aromatic carbon. Both complexes show similar Au–C distances (2.12(4)–2.18(1) Å for $[\{CH_2CH_2(o\text{-}C_6H_4)_2\}(AuPPh_3)_4](BF_4)_2$ and 2.12(2)–2.20(2) Å for $[Au(\mu\text{-mes})]_5$), while the latter displays significant deviations from the expected linear coordination at gold (C–Au–C 148.3(7)–152.9(8)°) that seem to be attributable to the presence of Au^I–Au^I bonds.

The crystal structure of the pentanuclear cycloaurated cation $[Au_5(\mu\text{-}o\text{-}PPh_2C_6H_4)_4]^+$ (see Fig. 24), which was the unexpected result of the reaction of $[Au(\mu\text{-}o\text{-}PPh_2C_6H_4)]_2$

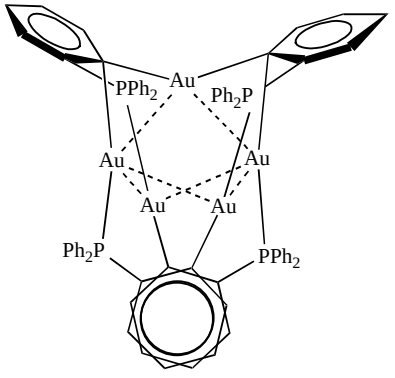


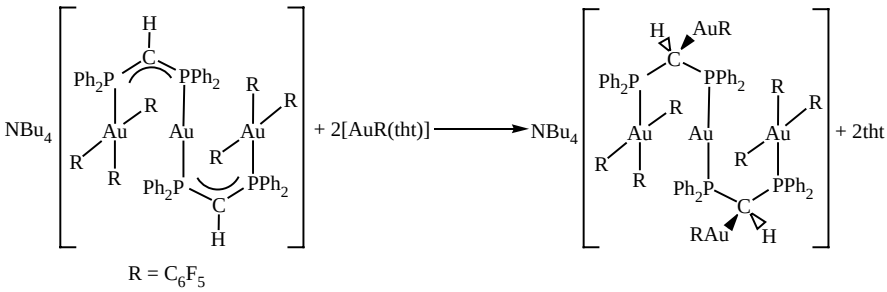
FIG. 24. Structure of $[Au_5(\mu\text{-}o\text{-}PPh_2C_6H_4)_4]TfO$.

TABLE XIX
PENTANUCLEAR COMPLEXES

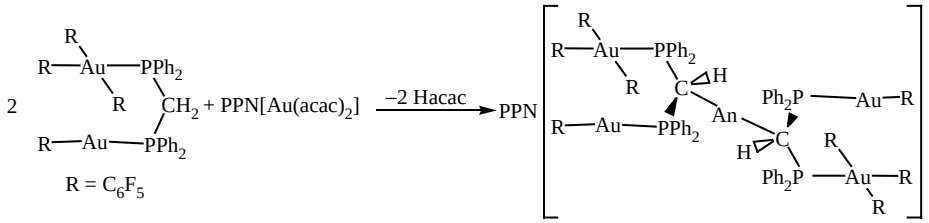
Complex	Au–C (Å)	Au–P (Å)	C–Au–C/P (°)	Au···Au_{intra} (Å)	Ref.
$[Au(\mu\text{-mes})]_5$	2.13(3)		150.4(6)	2.697(1)–2.708(1)	83
	2.20(2)		152.9(8)		143
	2.19(2)		148.3(7)		
	2.12(2)				
	2.18(2)				
$[Au_5(\mu\text{-}o\text{-}PPh_2C_6H_4)_4]TfO$	2.10(4)		164(1)	2.709(2)	163
	2.26(2)	2.263(8)	161(1)	3.186(2)	
	2.01(3)	2.306(8)	168.5(7)	3.158(3)	
	2.11(3)		168(1)	2.701(2)	
	2.25(3)	2.264(9)	157.1(7)	3.225(3)	
	2.06(3)	2.297(9)	170(1)	3.101(3)	
$NBu_4[Au\{(C_6F_5)_3Au\{PPh_2CH(AuC_6F_5)PPh_2\}\}_2]$					164
$PPN[Au\{(C_6F_5)Au(PPh_2CHPPh_2)Au(C_6F_5)_3\}_2]$					90

with methyl triflate,[163] shows some similar characteristics. The cation consists of a butterfly arrangement of four gold atoms bridged by the *o*-$PPh_2C_6H_4$ ligands with Au···Au distances in the range 3.101(3)–3.225(3) Å. The fifth metallic center binds two bridging carbon atoms of two aryl rings thus forming a pair of Au–C–Au triangles with Au–Au distances shorter than those found in the tetranuclear fragment (2.709(2) and 2.701(2) Å). These distances compare well with those mentioned above for $[Au(mes)]_5$ (see Table XIX), as well as the corresponding Au–C distances (2.10(4)–2.26(2) Å) and Au–C–Au angles (77(1)° for $[Au_5(\mu\text{-}o\text{-}PPh_2C_6H_4)_4]^+$ and 75.9(7)° for $[Au(mes)]_5$).

Also, a couple of pentanuclear anionic phosphino methanide derivatives, $NBu_4[Au\{(C_6F_5)_3Au\{PPh_2CH(AuC_6F_5)PPh_2\}\}_2]$[164] and $PPN[Au\{(C_6F_5)Au(PPh_2CHPPh_2)Au(C_6F_5)_3\}_2]$[90] containing Au^I and Au^{III} centers, have been synthesized by coordination of two $Au(C_6F_5)$ units to the C-donor atoms of $NBu_4[Au\{(C_6F_5)_3Au(PPh_2CHPPh_2)\}_2]$ or by deprotonation of $[(C_6F_5)Au(PPh_2CH_2PPh_2)Au(C_6F_5)_3]$ with $PPN[Au(acac)_2]$, as shown in Eqs. (52) and (53).



(52)



(53)

Although none of them have been structurally characterized by X-ray diffraction, no intramolecular Au···Au interaction is expected in these species because of the presence of a large number of pentafluorophenyl rings in each anion. Thus, in the crystal structure of the trinuclear starting methanide, which is less hindered, the shortest intramolecular Au···Au separation is 6.10 Å.[90]

Although the pyridine-based trimer $[Au_3(\mu\text{-}NC_5H_4)_3]$ was originally prepared in 1970,[165] its crystal structure was not reported until 2002.[166] Its structural characterization by X-ray diffraction reveals that the individual molecules self-associate through aurophilic interactions into two structural motifs, one of them consisting in discrete hexanuclear units formed by pairwise Au···Au contacts of 3.105(2) Å between two molecules of $[Au_3(\mu\text{-}NC_5H_4)_3]$ as shown in Fig. 25. The gold centers in each trinuclear molecule show weaker interactions, with distances of 3.308(2) and 3.345(3) Å, similar to the range of distances (3.274–3.339 Å) found in a number of solids containing the related triangular complex $[Au_3(\mu\text{-}MeN{=}COMe)_3]$.[167] The formation of a dimer through pairwise interactions had also been observed previously in the structure of $[Au_3(\mu\text{-}MeC_6H_4N{=}COMe)_3]$ and other complexes.[157,168,169]

Reaction of the pentanuclear $[Au(\mu\text{-}mes)]_5$ with $AgClO_4$ or $[Cu(NCMe)_4]PF_6$ (1:1) at 0 °C affords the heterometallic species $[Au_5Ag(\mu\text{-}mes)_5]ClO_4$ or $[Au_5Cu(\mu\text{-}mes)_5]PF_6$, which are isolated as green or red solids, respectively.[31] The mass spectra (LSIMS +) of such complexes showed the parent ions $[Au_5M(\mu\text{-}mes)_5]^+$ (M = Ag, Cu) as the base peaks.

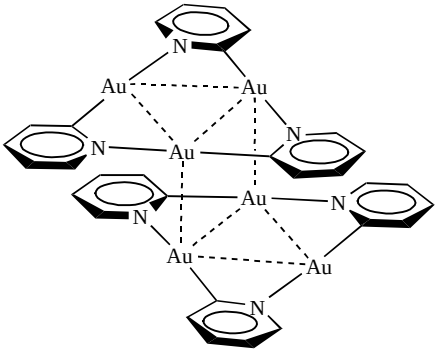


FIG. 25. One of the structural motifs of $[Au_3(\mu\text{-}NC_5H_4)_3]$: $[Au_3(\mu\text{-}NC_5H_4)_3]_2$.

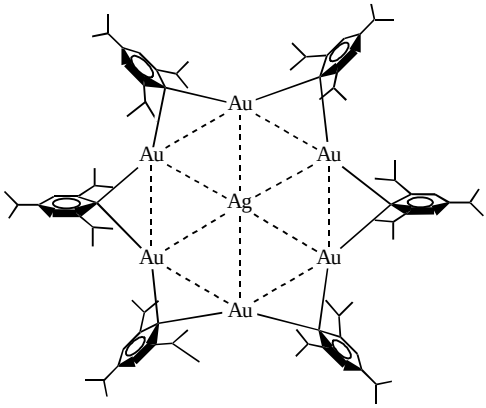


FIG. 26. Structure of $[Au_6Ag(\mu\text{-trip})_6]TfO$.

Hence, analogous reactions with an alternative gold(I) precursor containing the bulkier aryl ligand tris(isopropyl)phenyl (trip) were carried out. Surprisingly, treatment of PPN[Au(trip)Cl] with silver triflate did not afford the homoleptic trip derivative homologous to $[Au(\mu\text{-mes})]_5$ but rather the heterometallic heptanuclear deep green complex $[Au_6Ag(\mu\text{-trip})_6]TfO$ [see Eq. (54)].[31]

$$6PPN[Au(trip)Cl] + 7AgTfO \rightarrow [Au_6Ag(trip)_6]TfO + 6AgCl + 6PPNTfO \qquad (54)$$

Its crystal structure shows a beautiful Au_6Ag wheel in which the six gold atoms form a hexagon with the silver atom in the center (Fig. 26). As observed in other aryl bridging complexes,[27,83,110,143–145] the planar tris(isopropyl)phenyl groups are nearly perpendicular to the mean plane through the metallic atoms. The Au–C distances, with values between 2.111(7) and 2.200(7) Å, are also similar to those in the previously mentioned mesityl complexes.

The Au–Ag distances within the Au_6Ag core (2.797(1)–2.809(1) Å) compare well with those found in the tri- or tetranuclear mesityl-bridged compounds $[\{(Ph_3As)Au(\mu\text{-mes})\}_2Ag]ClO_4$ (2.7758(8) Å)[110] or $[(Ph_3P)Au(\mu\text{-mes})Ag(tht)]_2(TfO)_2$ (2.8245(6) Å)[27] or in other complexes in which a formal gold–silver bond is proposed.[57,136,137] The intramolecular Au–Au contacts, which range over 2.795(1) and 2.817(1) Å, are slightly longer than the gold–gold distances observed for the pentamer $[Au(\mu\text{-mes})]_5$[83,143] or than the separation between the gold(I) atoms bridged by an aryl group in $[Au_5(\mu\text{-}C_6H_4PPh_2)_4]TfO$[163] (see Table XIX).

B. *Polynuclear Complexes*

1. Complexes Derived from $[Au_3(\mu\text{-}NC_5H_4)_3]$

In the previous section it was commented that in the solid state individual molecules of $[Au_3(\mu\text{-}NC_5H_4)_3]$ self-associate through aurophilic interactions into two distinct motifs that involve both the already described hexanuclear units formed by pairwise Au···Au

contacts and extended chains of molecules connected by pairwise Au···Au contacts and individual Au···Au contacts (see Figs. 25 and 27).[166]

Each trinuclear molecule of the polymer is planar and displays a very similar structure to that of the individual molecule of $[Au_3(\mu\text{-}NC_5H_4)_3]_2$ with Au···Au distances of 3.309(2) and 3.346(3) Å within the molecule. As in the case of the hexanuclear unit, the intermolecular Au···Au contacts are closer than the intramolecular ones, with a pairwise Au···Au distance of 3.146(3) Å and a single Au···Au interaction at the other end of the molecular triangle of 3.077(2) Å. It is worth noting that the presence of two different types of intermolecular aurophilic interactions in one crystal is unusual. However, in the solid state $[S\{Au(PMe_3)\}_3]^+$ does display a chain motif that includes alternating single and double sets of Au···Au contacts.[117]

The crystals are remarkable for the gradual formation of a hourglass shape within the crystals that develops after months in the atmosphere or after immersion in HCl for a few days. These hourglass figures appear to result from the deposition of gold. Moreover, solutions of $[Au_3(\mu\text{-}NC_5H_4)_3]$ are luminescent, as well as the colorless or pale-yellow crystals, but the luminescence differs in solid state and in solution. This would seem to result from the extended supramolecular aggregation observed in the solid.

In the last few years trinuclear cyclic organogold(I) compounds, such as $[Au_3(\mu\text{-}C^2,N^3\text{-bzim})_3]$ ($\mu\text{-}C^2,N^3$-bzim = 1-benzylimidazolate) or $[Au_3(\mu\text{-}C^2,N^3\text{-meim})_3]$ ($\mu\text{-}C^2,N^3$-meim = 1-methylimidazolate), have been shown to interact with metal cations such as Ag^+ or Tl^+,[157,170] with the neutral inorganic Lewis acid $[Hg(C_6F_4)]_3$[171] or even with the organic electron acceptor 7,7,8,8-tetracyanoquinodimethane (TCNQ).[172] Such acid–base reactions afford stacked supramolecular entities of trinuclear gold(I) complexes sandwiching the small inorganic or organic acids (see Table XXI).

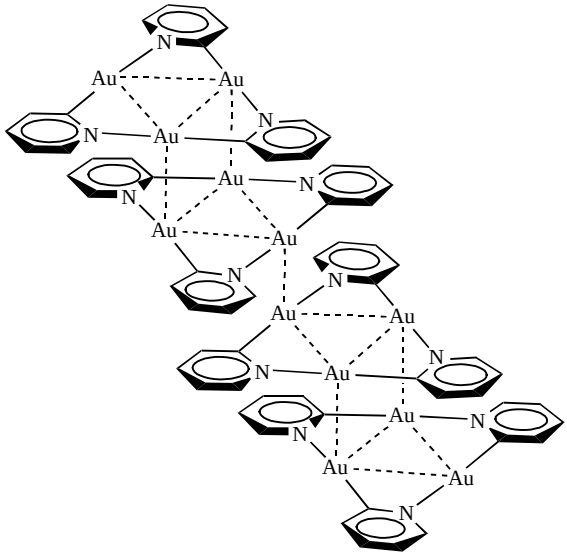


FIG. 27. One of the structural motifs of $[Au_3(\mu\text{-}NC_5H_4)_3]$: $[Au_3(\mu\text{-}NC_5H_4)_3]_n$.

TABLE XXI
POLYNUCLEAR COMPLEXES DERIVED FROM $[Au_3(\mu\text{-}NC_5H_4)_3]$

Complex	Au–C (Å)	Au–N (Å)	C–Au–N (°)	Au···Au$_{intra}$ (Å)	Au···M (Å)	Au···Au$_{inter}$ (Å)	Ref.
$\{[Au_3(\mu\text{-}NC_5H_4)_3]\}_n$	2.11(2)	2.07(2)	174.8(9)	3.309(2)		3.146(3)	166
		2.03(2)	174.3(13)	3.346(3)		3.077(2)	
$\{[Ag\{Au_3(\mu\text{-}C^2,N^3\text{-}bzim)_3\}_2]BF_4\}_n$	2.00(2)	2.02(2)	173.9(8)	3.19 (average)	2.731(2)	3.2678(12)	170
	1.98(2)	2.04(2)	177.2(8) (average)		2.747(2)	3.1157(11)	157
	2.01(2)	2.03(2)	172.9(7)		2.796(2)		
					2.801(2)		
					2.866(2)		
					2.922(2)		
$\{[Ag\{Au_3(\mu\text{-}C^2,N^3\text{-}bzim)_3\}_2]PF_6\}_n$							157
$\{[Ag\{Au_3(\mu\text{-}C^2,N^3\text{-}meim)_3\}_2]BF_4\}_n$							157
$\{[Tl\{Au_3(\mu\text{-}C^2,N^3\text{-}bzim)_3\}_2]PF_6\}_n$	2.031(12)	2.061(10)	173.7(5)	3.08 (average)	2.9711(7)	3.1089(7)	157
	1.999(12)	2.047(9)	176.4(4) (average)		2.9905(7)	3.0658(7)	
	1.967(13)	2.041(10)	171.5(5)		3.0184(7)		
					3.0240(7)		
					3.0433(7)		
					3.0448(7)		
$\{[Au_3(\mu\text{-}C^2,N^3\text{-}bzim)_3]_2[Hg(C_6F_4)]_3\}_n$	1.980(13)	2.028(9)	(average)	3.456 (average)	3.6531(6)	3.3298(5)	171
					3.2749(6)		
$\{[Au_3(\mu\text{-}C^2,N^3\text{-}bzim)_3]_2TCNQ\}_n$	2.013	2.028	173.78	3.493 (average)		3.152	172
	1.995	2.051	176.03 (average)			3.152	
	1.996	2.082	175.69				
$\{[Au_3(\mu\text{-}C^2,N^3\text{-}bzim)_3][AgClO_4]\}_n$							157
$\{[Au_3(\mu\text{-}C^2,N^3\text{-}bzim)_3][AgClO_4]_2\}_n$							157

The crystal structures of some of these species, $\{[Ag\{TR(bzim)\}_2]BF_4\}_n$ (TR(bzim) = $[Au_3(\mu\text{-}C^2,N^3\text{-bzim})_3]$),[157,170] $\{[Tl\{TR(bzim)\}_2]PF_6\}_n$,[157] $\{[TR(bzim)]_2[Hg(C_6F_4)]_3\}_n$[171] and $\{[TR(bzim)]_2TCNQ\}_n$,[172] have been established by X-ray diffraction, all of them showing sandwich units consisting of a Ag^+ or Tl^+ ion or a molecule of the inorganic $[Hg(C_6F_4)]_3$ or organic TCNQ π-acid sandwiched between two nine-membered rings of TR(bzim) (see Fig. 28).

Each central naked Ag^I or Tl^I atom in $\{[M\{TR(bzim)\}_2]BF_4\}_n$ is bonded to six Au^I centers forming a distorted trigonal prism (Fig. 28a) with Au···M distances ranging from 2.731(2) to 2.922(2) Å or from 2.9711(7) to 3.0448(7) Å, respectively, indicative of appreciable metal–metal interaction. In the case of the mercury(II) derivative, the Hg^{II} atoms interact with the Au^I centers in adjacent rings (four Au···Hg contacts in each sandwich) with Hg···Au distances 3.2749(6) and 3.6531(6) Å. Lastly, in the TCNQ derivative the cyanide groups are clearly not coordinated to the gold atoms and the distance from the centroid of the TCNQ to the centroid of the Au_3 unit is 3.964 Å.

Stacking in all of these complexes is the result of additional intermolecular aurophilic interactions between four of the six Au^I atoms in adjacent units giving rise to stacked linear-chain structures with a ···BBABBA··· pattern. The intermolecular $Au^I\cdots Au^I$ distances, between 3.0658(7) and 3.3298(5) Å, are usually similar or slightly shorter (in the case of the mercury derivative) than the intramolecular ones, with average distances between 3.08 and 3.493 Å (see Table XXI). Only in the case of the TCNQ derivative the intermolecular aurophilic contacts (3.152 Å) are clearly shorter than the intramolecular ones (3.457, 3.471 and 3.534 Å), which could be ascribed to charge-transfer from the electron-rich gold center to the electron acceptor TCNQ.

In addition, the optical properties of these materials, which include luminescence and thermochromism, are promising for optoelectronic applications, specifically the TCNQ species as a candidate for new semiconducting materials in view of the clear scanning electron microscope (SEM) image observed for crystals of this product.[173]

2. Complexes Derived from $[AuR_2]^-$ ($R = C_6F_5$, C_6Cl_5)

The use of bis(perhalophenyl)aurate(I) as Lewis base in order to generate unsupported Au···M interactions between closed-shell metal atoms by acid–base reactions has increased continually in recent years. A number of polymeric Au^I/Ag^I complexes of stoichiometry $[Au_2Ag_2R_4L_2]_n$ ($R = C_6F_5$, $C_6F_3H_2$) were prepared about 20 years ago using this strategy, as shown in Eq. (55).[57,174] Although they were isolated as solids whose colors varied from pale yellow to red while in solution they were colorless ($R = C_6F_5$) or pale yellow ($R = C_6F_3H_2$), the optical properties of such materials were not studied until 2000.[175]

$$NBu_4[AuR_2] + AgClO_4 \xrightarrow{-NBu_4ClO_4} [AuAgR_2] \xrightarrow{nL} \tfrac{1}{2n}[Au_2Ag_2R_4L_2]_n \qquad (55)$$

where $R = C_6F_5, C_6F_3H_2$.

The X-ray crystal structure of the acetone derivative, recently determined,[175] shows polymeric chains by repetition of $[Au_2Ag_2(C_6F_5)_4(O{=}CMe_2)_2]$ units through Au···Au

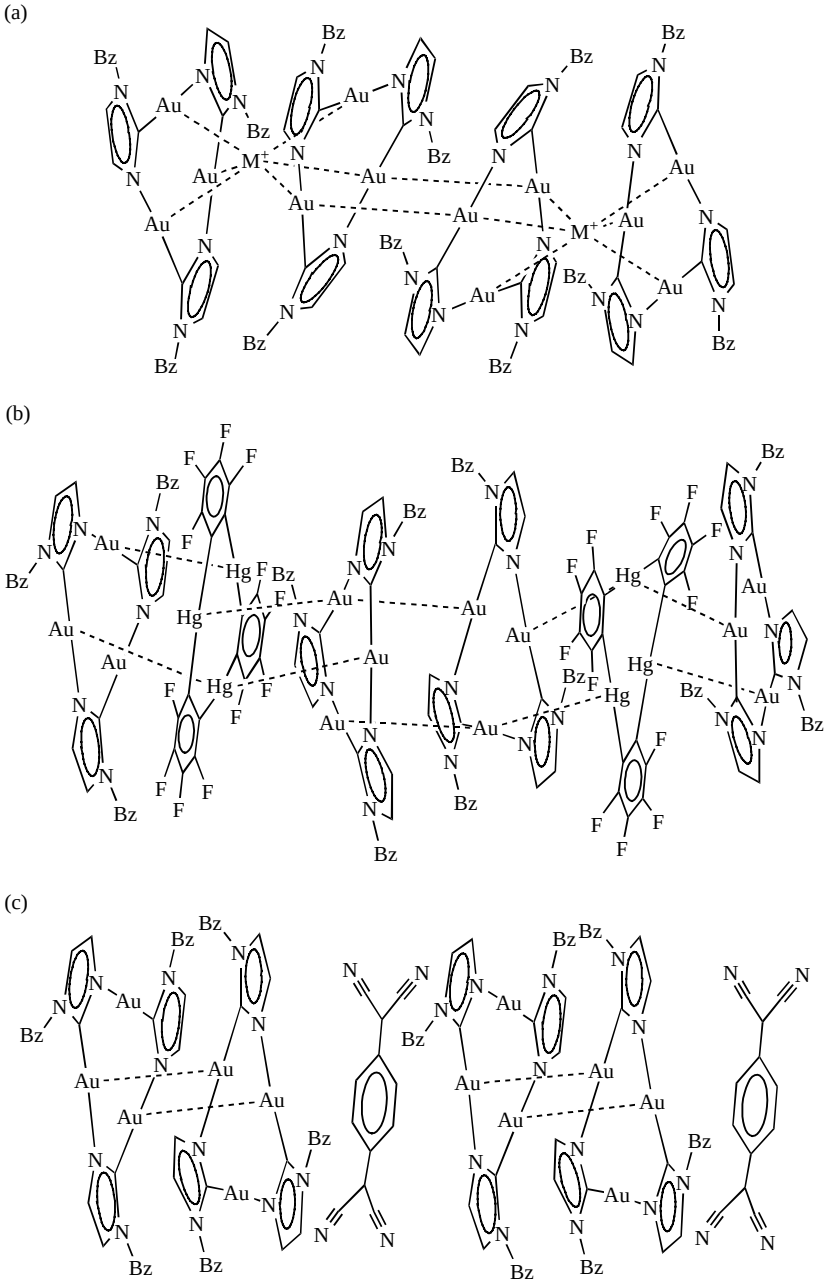


FIG. 28. Structure of $\{[M\{Au_3(\mu\text{-}C^2,N^3\text{-bzim})_3\}_2]^+\}_n$(M=Ag,Tl)(a), $\{[Au_3(\mu\text{-}C^2,N^3\text{-bzim})_3]_2[Hg(C_6F_4)]_3\}_n$ (b) and $\{[Au_3(\mu\text{-}C^2,N^3\text{-bzim})_3]_2TCNQ\}_n$(c).

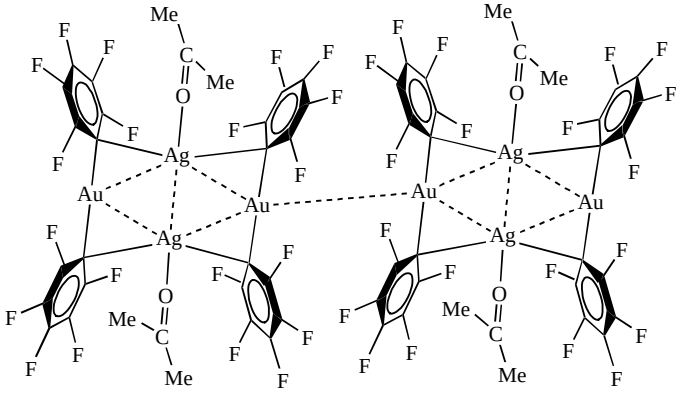


FIG. 29. Structure of $[Au_2Ag_2(C_6F_5)_4(O{=}CMe_2)_2]_n$.

contacts of 3.1674(11) Å as shown in Fig. 29. Each silver atom is bonded to two gold centers with Au–Ag distances of 2.7829(9) and 2.7903(9) Å, which are very similar to those observed in the tetrahydrothiophene (2.726(2) and 2.718(2) Å)[57,174] or benzene (2.702(2) and 2.792(2) Å)[57] derivatives. However, there are several differences in the bonding scheme in comparison with the latter compounds: there is a bonding interaction of 3.1810(13) Å between the two silver atoms of each tetranuclear unit, and the pentafluorophenyl groups bridge the gold and silver atoms asymmetrically with Au–C and Ag–C distances of 2.086(8) and 2.092(7) Å and 2.440(8) and 2.506(8) Å, respectively, the latter ones being slightly longer than those found in mesityl-bridged silver derivatives such as $[\{(Ph_3As)Au(\mu\text{-mes})\}_2Ag]ClO_4$ (2.27(2) Å)[110] or $[(Ph_3P)Au(\mu\text{-mes})Ag(tht)]_2(TfO)_2$ (2.326(3) Å).[27] Furthermore, each silver atom is also bound to the oxygen atom of the acetone ligand.

Moreover, the optical properties of this complex have been studied in the solid state at room temperature and at 77 K as well as in acetone solution leading to very interesting results.[175] The most striking one is the observation of a band that does not obey the Lambert–Beer law in its absorption and emission spectra in acetone registered at different temperatures. Such a deviation is consistent with an oligomerization process in solution through Au···Au interactions. Moreover, there is a clear correlation between the emission wavelength and the structure of $[Au_2Ag_2(C_6F_5)_4(O{=}CMe_2)_2]_n$ in solid state and in solution.

When the reaction shown in Eq. (55) is carried out in dichloromethane in the presence of excess pyridine, a colorless solid of stoichiometry $[AuAg(C_6F_5)_2(py)_4]$ is obtained.[176] The single-crystal X-ray diffraction study of this species shows the silver atom distorted over two positions (50% each one), which does not enable a valid analysis of its bond distances and angles. Anyway, it univocally shows an extended unsupported one-dimensional chain of alternating gold and silver atoms of the $[Ag(py)_3]^+$ and $[Au(C_6F_5)_2]^-$ units with the fourth pyridine molecule non-coordinated to the metal centers (Fig. 30). This arrangement is the result of the formation of molecular Au–Ag ion

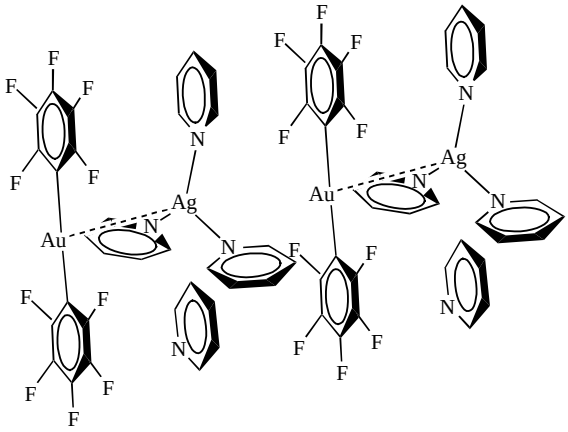


FIG. 30. Structure of $[AuAg(C_6F_5)_2(py)_4]_n$.

pairs, to the π-stacking interactions between C_6F_5 and pyridine arene ligands and to packing effects.

Moreover, theoretical calculations based on approximate distances and angles have been carried out, revealing the presence of both metallophilic $Au^I\cdots Ag^I$ and aromatic C_6F_5–py interactions.[176]

The same synthetic acid–base strategy has been employed to prepare Au^I/Tl^I polymeric species. The simplest one is that resulting from treatment of $NBu_4[Au(C_6Cl_5)_2]$ with $TlPF_6$ in tetrahydrofuran [Eq. (56)].[152]

$$NBu_4[Au(C_6Cl_5)_2] + Tl[PF_6] \xrightarrow{THF} \frac{1}{n}[AuTl(C_6Cl_5)_2]_n + NBu_4[PF_6] \qquad (56)$$

Its X-ray crystal structure consists of one-dimensional linear chains that run parallel to the crystallographic *z*-axis. Its polymeric nature is a consequence of unsupported Au···Tl interactions of 3.0044(5) and 2.9726(5) Å between $[Au(C_6Cl_5)_2]^-$ and Tl^+ ions as shown in Fig. 31.

The Au–Tl distances in this complex are shorter than the sum of Au(I) and Tl(I) ionic radii (2.96 Å)[177,178] and Au–Tl distances in related polymeric systems (see Table XXII). Including the metal–metal interactions the geometry at gold is square planar and that at thallium is exactly linear. The low coordination mode of the thallium is probably stabilized by eight long Tl···Cl contacts (3.2441(15)–3.6786(15) Å). Finally, it is worth noting that this crystal structure presents channels parallel to the *z*-axis (Fig. 32) with diameters as large as 10.471 Å which could allow the entrance of small molecules into the net.

The complex is luminescent in the solid state both at room temperature and at 77 K, showing a temperature dependence similar to other gold–thallium extended linear chains[151,153–155] that is assumed to be a result of the thermal contraction that occurs when temperature is lowered. But the most interesting spectral feature is the shift of the

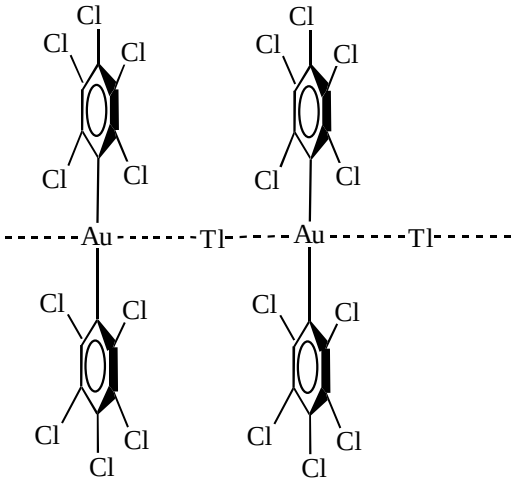


FIG. 31. Structure of $[AuTl(C_6Cl_5)_2]_n$.

emission energy observed when varying the particle size. Besides, the clear SEM images observed without coating with a conductor suggest that the material is not an insulator.[173]

Moreover, the complex displays a completely reversible vapochromic behavior with reversible changes of color when the solid is exposed to a variety of organic vapors, which is even deeper under UV light. These results illustrate the potential applications of this complex for the detection of VOCs.

When the bis(pentahalophenyl)aurate(I) salt is treated with thallium(I) hexafluorophosphate in the presence of $OPPh_3$, the phosphine oxide is incorporated into the polymeric chain affording species with different stoichiometry depending on the aryl group (see Scheme 6).[151]

Their crystal structures confirm the polymeric nature showing one-dimensional chains formed *via* short unsupported interactions between alternating Au^I and Tl^I centers that range from 3.0358(8) Å (R = C_6F_5)[153] to 3.3205(3) Å (R = C_6Cl_5).[151] They all display linear gold(I) atoms by coordination of two aryl groups with typical Au–C and C–Au–C bond distances and angles (see Table XXII).

In the pentafluorophenyl derivative, the geometry at thallium(I) is distorted trigonal bipyramidal with a vacant coordination site presumably associated with the stereochemically active lone pair (Fig. 33), whilst in the pentachlorophenyl complexes the thallium(I) centers show two different types of geometrical environments: pseudotetrahedral and distorted trigonal bipyramidal (also with a vacant coordination site) due to the presence of molecules of solvent acting as ligands in the solid state structure (Fig. 34). Nevertheless, the solvent molecules are only weakly coordinated, with Tl–O distances of 2.766(5) (THF) or 2.828(7) Å (acetone), clearly longer than the Tl–$OPPh_3$ distances (2.471(3) and 2.582(4) Å).

These complexes are also luminescent in the solid state both at room temperature and at 77 K but not in solution, where the intermetallic contacts are no longer present, which,

TABLE XXII
POLYNUCLEAR COMPLEXES DERIVED FROM $[AuR_2]^-$ (R = C_6F_5, C_6Cl_5)

Complex	Au–C (Å)	C–Au–C (°)	Tl–Au–Tl (°)	Au–Tl–Au (°)	Au···Au (Å)	Au···M (Å)	Ref.
$[Au_2Ag_2(C_6F_5)_4(O{=}CMe_2)_2]_n$	2.086(8)	177.3(3)			3.1674(11)	2.7829(9)	175
	2.092(7)				3.1810(13)	2.7903(9)	
					[Ag···Ag]		
$[AuAg(C_6F_5)_2(py)_4]_n$							176
$[AuTl(C_6Cl_5)_2]_n$	2.063(6)	177.9(3)	180.0	180.0		3.0044(5)	152
						2.9726(5)	
$[AuTl(C_6F_5)_2(OPPh_3)_2]_n$	2.058(5)	180.0	180.0	163.2(1)		3.0358(8)	153
	2.053(6)					3.0862(8)	
$[Au_2Tl_2(C_6Cl_5)_4(OPPh_3)_2(THF)]_n$	2.055(5)	178.1(2)	142.61(1)	156.56(1)		3.0529(3)	151
	2.058(4)	176.7(2)	168.53(1)	131.60(1)		3.1452(3)	
	2.041(5)					3.1630(3)	
	2.051(5)					3.3205(3)	
$[Au_2Tl_2(C_6Cl_5)_4(OPPh_3)_2(O{=}CMe_2)]_n$	2.055(6)	178.2(2)	143.88(1)	158.31(1)		3.0937(3)	151
	2.055(6)	178.6(2)	166.74(1)	135.72(1)		3.1492(3)	
	2.038(7)					3.2438(3)	
	2.041(7)					3.2705(4)	
$[AuTl(C_6F_5)_2(bipy)]_n$	2.048(3)	177.6(1)	164.92(1)		3.4092(3)	3.0161(2)	154
	2.049(3)		[Tl–Au–Au]				
$[Au_2Tl_2(C_6Cl_5)_4(bipy)_{1.5}(THF)]_n$	2.052(8)	173.9(3)	133.77(1)	163.16(1)		3.0323(4)	154
	2.050(8)	176.1(3)	160.99(1)	129.97(1)		3.0485(4)	
	2.051(7)					3.0534(4)	
	2.062(7)					3.0540(4)	

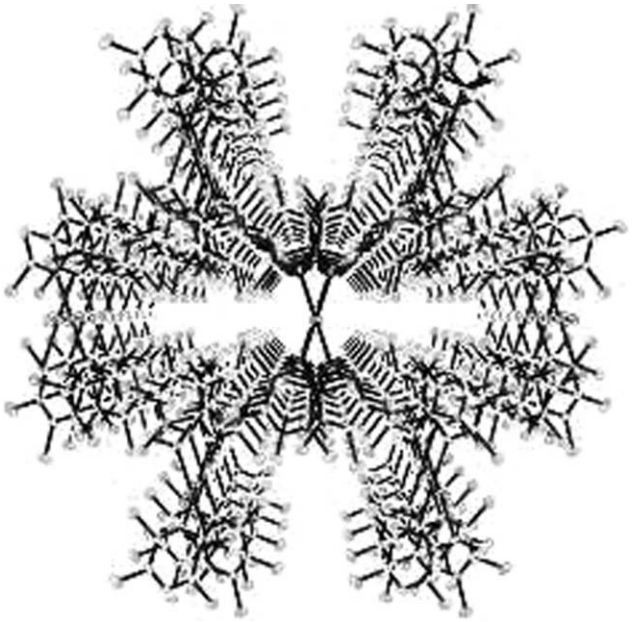
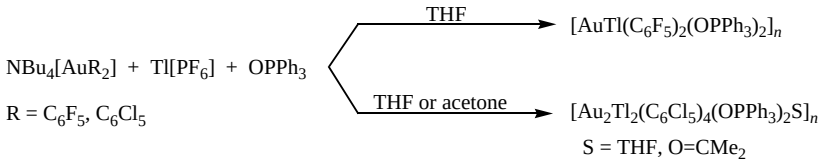


FIG. 32. Crystal structure of $[AuTl(C_6Cl_5)_2]_n$ viewed down the crystallographic z axis.

as in other cases, suggests that the luminescence is a result of the interactions between the metals. Moreover, the C_6Cl_5 derivatives show a site-selective excitation, behavior which, based on single-point DFT and TD-DFT calculations, is due to the different geometrical environment around the Tl^I atoms.[151]

Finally, a couple of Au^I/Tl^I derivatives with the bidentate ligand 4,4′-bipyridine have also been recently synthesized through similar acid–base reactions carried out in tetrahydrofuran and in the presence of bipy.[154] Again, the aryl group is a key factor in the stoichiometry ($[AuTl(C_6F_5)_2(bipy)]_n$ or $[Au_2Tl_2(C_6Cl_5)_4(bipy)_{1.5}(THF)]_n$) and in the crystal structure of the complex. Thus, while the pentafluorophenyl derivative is formed by tetranuclear units with a sequence Tl–Au–Au–Tl linked through bridging bipyridine ligands forming planar polymers (see Fig. 35), the pentachlorophenyl derivative shows polymeric layers formed by the repetition of Tl–Au–Tl′–Au moieties similarly linked



SCHEME 6.

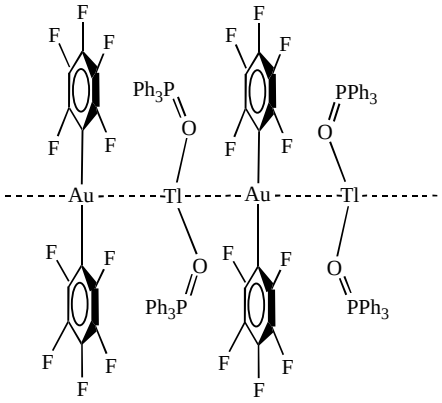


FIG. 33. Structure of $[AuTl(C_6F_5)_2(OPPh_3)_2]_n$.

by bridging bipyridines (Fig. 36). In the latter case, every two layers are linked through additional bipy molecules.

The Au–Tl distances in the C_6Cl_5 derivative range from 3.0323(4) to 3.0540(4) Å, whereas in the C_6F_5 complex they are slightly shorter (3.0161(2) Å). It is worth noting that in the latter case there are also additional Au···Au contacts of 3.4092(3) Å that account for the unusual Tl–Au–Au–Tl arrangement where repulsive instead of attractive forces could be expected.

Once again, these complexes are strongly luminescent at room temperature and at 77 K in solid state, losing this characteristic in solution. This luminescence can therefore be attributed to the intermetallic interactions, which is also suggested by DFT calculations that show the nature of the orbital involved in each transition.

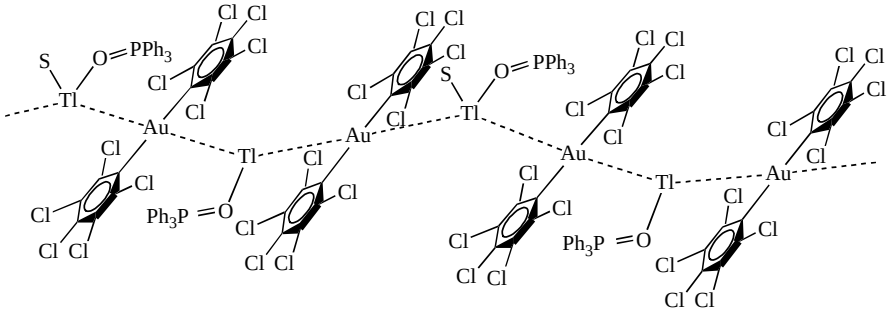


FIG. 34. Structure of $[Au_2Tl_2(C_6Cl_5)_4(OPPh_3)_2S]_n$ (S=THF, O=CMe_2).

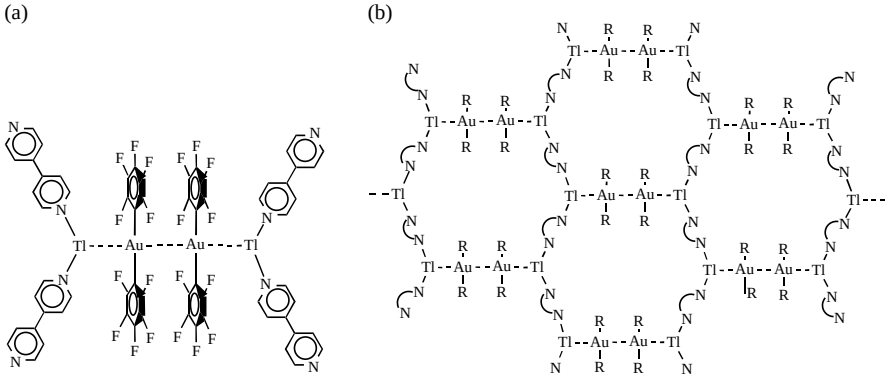


FIG. 35. Structure of $[AuTl(C_6F_5)_2(bipy)]_n$.

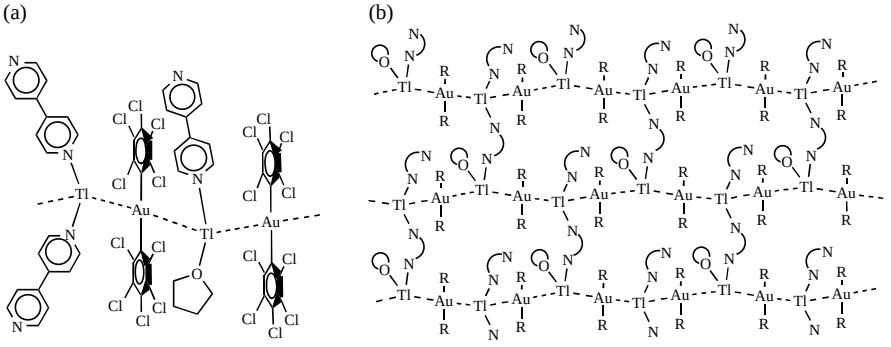


FIG. 36. Structure of $[Au_2Tl_2(C_6Cl_5)_4(bipy)_{1.5}(THF)]_n$.

ACKNOWLEDGEMENTS

We thank the Dirección General de Investigación Científica y Técnica (Project BQU2001-2409-C02) for financial support.

REFERENCES

(1) Pope, W. P.; Gibson, C. S. *J. Chem. Soc.* **1907**, 2061.
(2) Pope, W. P.; Gibson, C. S. *Proc. Chem. Soc.* **1908**, *23*, 245.
(3) Armer, B.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 101.
(4) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 728.
(5) Usón, R.; Laguna, A.; Vicente, J. *Synth. React. Inorg. Met.-Org. Chem.* **1977**, *7*, 463.
(6) Schmidbaur, H. *Gmelin Handbuch der Anorganischen Chemie. Organogold Compounds*, Springer Verlag, Berlin, 1980.
(7) Anderson, G. K. *Adv. Organomet. Chem.* **1982**, *20*, 39.
(8) Parish, R. V. *Gold Bull.* **1997**, *30*, 3, **1997**, *30*, 55; **1998**, *31*, 14.
(9) Schmidbaur, H.; Grohmann, A.; Olmos, M. E. *Gold: Progress in Chemistry, Biochemistry and Technology. Organogold Chemistry*, Wiley, Chichester, 1999.

(10) Schmidbaur, H.; Grohmann, A.; Olmos, M. E.; Schier, A. *The Chemistry of Organic Derivatives of Gold and Silver. Synthesis and Uses of Organogold Compounds*, Wiley, Chichester, 1999.
(11) Grandberg, K. I.; Dyadchenko, V. P. *J. Organomet. Chem.* **1994**, *474*, 1.
(12) Laguna, A.; Laguna, M. *J. Organomet. Chem.* **1990**, *394*, 743.
(13) Gimeno, M. C.; Laguna, A. *Gold Bull.* **1999**, *32*, 90.
(14) Crespo, O.; Gimeno, M. C.; Laguna, A. *Appl. Organometal. Chem.* **2000**, *14*, 644.
(15) Kharasch, M. S.; Isbell, H. S. *J. Am. Chem. Soc.* **1931**, *53*, 3053.
(16) Calvin, G.; Coates, G. E.; Dixon, P. S. *Chem. Ind. (London)* **1959**, 1628.
(17) Usón, R.; Laguna, A. *Coord. Chem. Rev.* **1986**, *70*, 1.
(18) Usón, R. *Pure & Appl. Chem.* **1986**, *58*, 647.
(19) Usón, R. *J. Organomet. Chem.* **1989**, *372*, 171.
(20) Laguna, A.; Gimeno, M. C. *Trends Organomet. Chem.* **1994**, *1*, 231.
(21) Coates, G. E.; Parkin, C. *J. Chem. Soc.* **1962**, 3220.
(22) Sladek, A.; Hofreiter, S.; Paul, M.; Schmidbaur, H. *J. Organomet. Chem.* **1995**, *501*, 47.
(23) Forward, J. M.; Fackler, J. P. Jr.; Staples, R. J. *Organometallics* **1995**, *14*, 4194.
(24) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927, and references therein.
(25) Hong, X.; Cheung, K. K.; Guo, C. X.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1994**, 1867.
(26) Contel, M.; Stol, M.; Casado, M. A.; van Klink, G. P. M.; Ellis, D. D.; Spek, A. L.; van Koten, G. *Organometallics* **2002**, *21*, 4556.
(27) Contel, M.; Jiménez, J.; Jones, P. G.; Laguna, A.; Laguna, M. *J. Chem. Soc., Dalton Trans.* **1994**, 2515.
(28) Bardají, M.; Jones, P. G.; Laguna, A.; Moracho, A.; Fischer, A. K. *J. Organomet. Chem.* **2002**, *648*, 1.
(29) Espinet, P.; Martín-Barrios, S.; Villafañe, F.; Jones, P. G.; Fischer, A. K. *Organometallics* **2000**, *19*, 290.
(30) Twamley, B.; Haubrich, S. T.; Power, P. P. *Adv. Organomet. Chem.* **1999**, *44*, 1, and references therein.
(31) Cerrada, E.; Contel, M.; Valencia, A. D.; Laguna, M.; Gelbrich, T.; Hursthouse, M. B. *Angew. Chem. Int. Ed.* **2000**, *39*, 2353.
(32) Rabe, G. W.; Mitzel, N. W. *Inorg. Chim. Acta* **2001**, *316*, 132.
(33) Bardají, M.; Jones, P. G.; Laguna, A. *J. Chem. Soc., Dalton Trans.* **2002**, 3624.
(34) Crespo, O.; Fernández, E. J.; Jones, P. G.; Laguna, A.; López-de-Luzuriaga, J. M.; Monge, M.; Olmos, M. E.; Pérez, J. *Dalton Trans.* **2003**, 1076.
(35) Fernández, E. J.; López-de-Luzuriaga, J. M.; Monge, M.; Rodríguez, M. A.; Crespo, O.; Gimeno, M. C.; Laguna, A.; Jones, P. G. *Chem. Eur. J.* **2000**, *6*, 636.
(36) Hollatz, C.; Schier, A.; Schmidbaur, H. *Z. Naturforsch.* **1999**, *54b*, 30.
(37) Codina, A.; Fernández, E. J.; Jones, P. G.; Laguna, A.; López-de-Luzuriaga, J. M.; Monge, M.; Olmos, M. E.; Pérez, J.; Rodríguez, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 6781.
(38) Jones, P. G.; Ahrens, B. *Z. Naturforsch.* **1998**, *53b*, 653.
(39) Bardají, M.; Laguna, A.; Pérez, M. R.; Jones, P. G. *Organometallics* **2002**, *21*, 1877.
(40) Casado, A. L.; Espinet, P. *Organometallics* **1998**, *17*, 3677.
(41) Vicente, J.; Chicote, M. T.; González-Herrero, P.; Grünwald, C.; Jones, P. G. *Organometallics* **1997**, *16*, 3381.
(42) Vicente, J.; Chicote, M. T.; Abrisqueta, M. D.; Jones, P. G. *Organometallics* **2000**, *19*, 2629.
(43) Jia, G. C.; Puddephatt, R. J.; Scott, J. D.; Vital, J. J. *Organometallics* **1993**, *12*, 3565.
(44) Bruce, M. I.; Grundy, K. R.; Liddell, M. J.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1988**, *344*, C49.
(45) Li, D.; Hong, X.; Che, C. M.; Lo, W. C.; Peng, S. M. *J. Chem. Soc., Dalton Trans.* **1993**, 2929.
(46) Payne, N. C.; Ramachandran, R.; Puddephatt, R. J. *Can. J. Chem.* **1995**, *73*, 6.
(47) Bruce, M. I.; Horn, E.; Matisons, J. G.; Snow, M. R. *Aust. J. Chem.* **1984**, *37*, 1163.
(48) Carriedo, G. A.; Riera, V.; Solans, X.; Solans, J. *Acta Crystallogr. C* **1988**, *44*, 978.
(49) Vicente, J.; Chicote, M. T.; Abrisqueta, M. D.; Jones, P. G. *Organometallics* **1997**, *16*, 5628.
(50) Whittall, I. R.; Humphrey, M. G.; Houbrechts, S.; Persoons, A.; Hockless, D. C. R. *Organometallics* **1996**, *15*, 5738.
(51) Müller, T. E.; Choi, S. W. K.; Mingos, D. M. P.; Murphy, D.; Williams, D. J.; Yam, V. W. W. *J. Organomet. Chem.* **1994**, *484*, 209.
(52) Shieh, S. J.; Hong, X.; Peng, S. M.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1994**, 3067.
(53) Bruce, M. I.; Duffy, D. N. *Aust. J. Chem.* **1986**, *39*, 1697.
(54) Bordoni, S.; Busetto, L.; Cassani, M. C.; Albano, V. G.; Sabatino, P. *Inorg. Chim. Acta* **1994**, *222*, 267.

(55) Cerrada, E.; Laguna, M.; Bartolomé, J.; Campo, J.; Orera, V.; Jones, P. G. *Synth. Met.* **1998**, *92*, 245.
(56) Jones, P. G.; Villacampa, M. D. *Z. Kristallogr.—New Cryst. Struct.* **1997**, *212*, 121.
(57) Usón, R.; Laguna, A.; Laguna, M.; Manzano, B. R.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1984**, 285.
(58) Usón, R.; Laguna, A.; Vicente, J.; García, J.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1981**, 655.
(59) Jones, P. G. *Z. Naturforsch. B* **1982**, *37*, 937.
(60) Jones, P. G. *Z. Kristallogr.* **1993**, *208*, 347.
(61) Bardají, M.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; Merchán, F.; Romeo, I. *Organometallics* **1997**, *16*, 1083.
(62) Koelle, U.; Laguna, A. *Inorg. Chim. Acta* **1999**, *290*, 44.
(63) Contel, M.; Nobel, D.; Spek, A. L.; van Koten, G. *Organometallics* **2000**, *19*, 3288.
(64) Romeo, I.; Bardají, M.; Gimeno, M. C.; Laguna, M. *Polyhedron* **2000**, *19*, 1837.
(65) Usón, R.; Laguna, A.; Laguna, M.; Manzano, B. R.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1984**, 839.
(66) Usón, R.; Laguna, A.; Laguna, M.; Gimeno, M. C.; Jones, P. G.; Fittschen, C.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1986**, 509.
(67) Usón, R.; Laguna, A.; Laguna, M.; Lázaro, I.; Morata, A.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1986**, 669.
(68) Bennett, M. A.; Bhargava, S. K.; Griffiths, K. D.; Robertson, G. B.; Wickramasinghe, W. A.; Willis, A. C. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 258.
(69) Marsh, R. E. *Acta Crystallogr. B* **1999**, *55*, 931.
(70) Bhargava, S. K.; Mohr, F.; Bennett, M. A.; Welling, L. L.; Willis, A. C. *Organometallics* **2000**, *19*, 5628.
(71) Bhargava, S. K.; Mohr, F.; Gorman, J. D. *J. Organomet. Chem.* **2000**, *607*, 93.
(72) Bhargava, S. K.; Mohr, F.; Takahashi, M.; Takeda, M. *Bull. Chem. Soc. Jpn* **2001**, *74*, 1051.
(73) Bhargava, S. K.; Mohr, F.; Bennett, M. A.; Welling, L. L.; Willis, A. C. *Inorg. Chem.* **2001**, *40*, 4271.
(74) Baukova, T. V.; Kuz'mina, L. G.; Oleinikova, N. A.; Lemenovskii, D. A. *Russ. Chem. Bull.* **1995**, *44*, 1952.
(75) Baukova, T. V.; Kuz'mina, L. G.; Oleinikova, N. A.; Lemenovskii, D. A.; Blumenfel'd, A. L. *J. Organomet. Chem.* **1997**, *530*, 27.
(76) Hesse, R.; Jennische, P. *Acta Chem. Scand.* **1972**, *26*, 3855.
(77) Heinrich, D. D.; Wang, J. C.; Fackler, J. P. Jr. *Acta Crystallogr. C* **1990**, *46*, 1444.
(78) Pyykko, P.; Zhao, Y. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 604.
(79) Baukova, T. V.; Dyadchenko, V. P.; Oleinikova, N. A.; Lemenovskii, D. A.; Kuz'mina, L. K. *Russ. Chem. Bull.* **1994**, *43*, 1063.
(80) Kuz'mina, L. G.; Churakov, A. V.; Howard, J. A. K. *Russ. J. Coord. Chem.* **1998**, *24*, 435.
(81) Cross, R. J.; Davidson, M. F. *J. Chem. Soc., Dalton Trans.* **1986**, 411.
(82) Jones, P. G.; Thöne, C. *Acta Crystallogr. C* **1992**, *48*, 1312.
(83) Meyer, E. M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1989**, *8*, 1067.
(84) Fernández, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; López-de-Luzuriaga, J. M.; Olmos, M. E. *Chem. Ber.* **1997**, *130*, 1513.
(85) Bennett, M. A.; Hockless, D. C. R.; Rae, A. D.; Welling, L. L.; Willis, A. C. *Organometallics* **2001**, *20*, 79.
(86) Fernández, E. J.; Gimeno, M. C.; Laguna, A.; Laguna, M.; López-de-Luzuriaga, J. M.; Olmos, M. E. *J. Organomet. Chem.* **1996**, *514*, 169.
(87) Bella, P. A.; Crespo, O.; Fernández, E. J.; Fischer, A. K.; Jones, P. G.; Laguna, A.; López-de-Luzuriaga, J. M.; Monge, M. *J. Chem. Soc., Dalton Trans.* **1999**, 4009.
(88) Gimeno, M. C.; Jambrina, E.; Laguna, A.; Laguna, M.; Murray, H. H.; Terroba, R. *Inorg. Chim. Acta* **1996**, *249*, 69.
(89) Bennett, M. A.; Bhargava, S. K.; Mohr, F.; Welling, L. L.; Willis, A. C. *Aust. J. Chem.* **2002**, *55*, 267.
(90) Fernández, E. J.; Gimeno, M. C.; Laguna, A.; López-de-Luzuriaga, J. M.; Olmos, M. E. *Polyhedron* **1998**, *17*, 3919.
(91) Cerrada, E.; Jones, P. G.; Laguna, A.; Laguna, M. *Inorg. Chem.* **1996**, *35*, 2995.
(92) Crespo, O.; Gimeno, M. C.; Jones, P. G.; Ahrens, B.; Laguna, A. *Inorg. Chem.* **1997**, *36*, 495.

(93) Fernández, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; Olmos, M. E. *J. Chem. Soc., Dalton Trans.* **1996**, 3603.
(94) Albano, V. G.; Busetto, L.; Cassani, M. C.; Sabatino, P.; Schmitz, A.; Zanotti, V. *J. Chem. Soc., Dalton Trans.* **1995**, 2087.
(95) Barranco, E. M.; Crespo, O.; Gimeno, M. C.; Laguna, A.; Jones, P. G.; Ahrens, B. *Inorg. Chem.* **2000**, *39*, 680.
(96) Barranco, E. M.; Crespo, O.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Villacampa, M. D. *J. Organomet. Chem.* **1999**, *592*, 258.
(97) Lang, H.; Köhler, K.; Zsolnai, L. *Chem. Commun.* **1996**, 2043.
(98) Köhler, K.; Silverio, S. J.; Hyla-Kryspin, I.; Gleiter, R.; Zsolnai, L.; Driess, A.; Huttner, G.; Lang, H. *Organometallics* **1997**, *16*, 4970.
(99) Baker, R. W.; Pauling, J. P. *J. Chem. Soc., Dalton Trans.* **1972**, 2264.
(100) Lang, H.; Weinmann, M. *Synlett* **1996**, 1.
(101) Lang, H.; Köhler, K.; Blau, S. *Coord. Chem. Rev.* **1995**, *143*, 113.
(102) Lang, H.; Köhler, K.; Büchner, M. *Chem. Ber.* **1995**, *128*, 525.
(103) Carriedo, G. A.; Riera, V.; Sánchez, G.; Solans, X. *J. Chem. Soc., Dalton Trans.* **1988**, 1957.
(104) Jacob, K.; Voigt, F.; Merzweiler, K.; Wagner, C.; Zanello, P.; Fontani, M.; Pietzsch, C. *J. Organomet. Chem.* **1998**, *552*, 265.
(105) Jacob, K.; Voigt, F.; Merzweiler, K.; Pietzsch, C. *J. Organomet. Chem.* **1997**, *545–546*, 421.
(106) Jacob, K.; Zanello, P.; Voigt, F.; Fontani, M. *Monatsh. Chem.* **1998**, *129*, 1213.
(107) Voigt, F.; Fischer, A.; Pietzsch, C.; Jacob, K. *Z. Anorg. Allg. Chem.* **2001**, *627*, 2337.
(108) Kuz'mina, L. G. *Koord. Khim.* **1995**, *21*, 542.
(109) Barranco, E. M.; Gimeno, M. C.; Laguna, A. *Inorg. Chim. Acta* **1999**, *291*, 60.
(110) Contel, M.; Garrido, J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M. *Organometallics* **1996**, *15*, 4939.
(111) Bardají, M.; Laguna, A.; Vicente, J.; Jones, P. G. *Inorg. Chem.* **2001**, *40*, 2675.
(112) Bardají, M.; Laguna, A.; Orera, V. M.; Villacampa, M. D. *Inorg. Chem.* **1998**, *37*, 5125.
(113) Bardají, M.; Laguna, A.; Jones, P. G.; Fischer, A. K. *Inorg. Chem.* **2000**, *39*, 3560.
(114) Blanco, M. C.; Fernández, E. J.; López-de-Luzuriaga, J. M.; Olmos, M. E.; Crespo, O.; Gimeno, M. C.; Laguna, A.; Jones, P. G. *Chem. Eur. J.* **2000**, *6*, 4116.
(115) Jones, P. G.; Sheldrick, G. M.; Hädicke, E. *Acta Crystallogr. B* **1980**, *36*, 2777.
(116) Schmidbaur, H.; Kolb, A.; Zeller, E.; Schier, A.; Beruda, H. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1575.
(117) Angermaier, K.; Schmidbaur, H. *Chem. Ber.* **1994**, *127*, 2387.
(118) Jones, P. G.; Lensch, C.; Sheldrick, G. M. *Z. Naturforsch.* **1982**, *37B*, 141.
(119) Pyykkö, P.; Angermaier, K.; Assmann, B.; Schmidbaur, H. *J. Chem. Soc., Chem. Commun.* **1995**, 1889.
(120) Lensch, C.; Jones, P. G.; Sheldrick, G. M. *Z. Naturforsch.* **1982**, *37B*, 944.
(121) Canales, F.; Gimeno, M. C.; Jones, P. G.; Laguna, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 769.
(122) Contel, M.; Garrido, J.; Gimeno, M. C.; Jiménez, J.; Jones, P. G.; Laguna, A.; Laguna, M. *Inorg. Chim. Acta* **1997**, *254*, 157.
(123) Fernández, E. J.; López-de-Luzuriaga, J. M.; Monge, M.; Olmos, E.; Laguna, A.; Villacampa, M. D.; Jones, P. G. *J. Clust. Sci.* **2000**, *11*, 153.
(124) Kronenburg, C. M. P.; Jastrzebski, J. T. B. H.; Boersma, J.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **2002**, *124*, 11675.
(125) van Koten, G.; Jastrzebski, J. T. B. H.; Stam, C. H.; Brevard, C. *Copper Coordination Chemistry; Biochemical and Inorganic Perspectives*, Adenine Press, Guilderland, NY, 1985, p. 267.
(126) Yam, V. W. W.; Choi, S. W. K.; Cheung, K. K. *J. Chem. Soc., Dalton Trans.* **1996**, 3411.
(127) Hill, D. T.; Girard, G. R.; McCabe, F. L.; Johnson, R. K.; Stupik, P. D.; Zhang, J. H.; Reiff, W. M.; Eggleston, D. S. *Inorg. Chem.* **1989**, *28*, 3529.
(128) Viotte, M.; Gautheron, B.; Kubicki, M. M.; Mugnier, Y.; Parish, R. V. *Inorg. Chem.* **1995**, *34*, 3465.
(129) Gimeno, M. C.; Laguna, A.; Sarroca, C.; Jones, P. G. *Inorg. Chem.* **1993**, *32*, 5926.
(130) Phang, L. T.; Hor, T. S. A.; Zhau, Z. Y.; Mak, T. C. W. *J. Organomet. Chem.* **1994**, *469*, 253.
(131) Houlton, A.; Mingos, D. M. P.; Murphy, D. M.; Williams, D. J.; Phang, L. T.; Hor, T. S. A. *J. Chem. Soc., Dalton Trans.* **1993**, 3629.
(132) Barranco, E. M.; Crespo, O.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Sarroca, C. *J. Chem. Soc., Dalton Trans.* **2001**, 2523.

(133) Gimeno, M. C.; Jones, P. G.; Laguna, A.; Sarroca, C. *J. Organomet. Chem.* **2000**, *596*, 10.
(134) Gimeno, M. C.; Jones, P. G.; Laguna, A.; Sarroca, C. *J. Organomet. Chem.* **1999**, *579*, 206.
(135) Fernández, E. J.; Hursthouse, M. B.; Laguna, M.; Terroba, R. *J. Organomet. Chem.* **1999**, *574*, 207.
(136) Teo, B. K.; Zhang, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 445.
(137) Kanters, R. P. F.; Schlebos, P. P. J.; Bour, J. J.; Bosman, W. P.; Smits, J. M. M.; Beurskens, P. T.; Steggerda, J. J. *Inorg. Chem.* **1990**, *29*, 324.
(138) Borrow, M.; Bürgi, H. B.; Camalli, M.; Caruso, F.; Fischer, E.; Venanzi, L. M.; Zambonelli, L. *Inorg. Chem.* **1983**, *22*, 2356.
(139) Gimeno, M. C.; Jones, P. G.; Laguna, A.; Sarroca, C. *J. Chem. Soc., Dalton Trans.* **1995**, 1473.
(140) Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G. *J. Chem. Soc., Chem. Commun.* **1991**, 1730.
(141) Vicente, J.; Chicote, M. T.; Lagunas, M. C. *Inorg. Chem.* **1993**, *32*, 3748.
(142) Kuz'mina, L. G.; Churakov, A. V.; Howard, J. A. *Russ. J. Coord. Chem.* **1998**, *24*, 282.
(143) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1983**, 1304.
(144) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1983**, 1156.
(145) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1983**, 1087.
(146) Fernández, E. J.; López-de-Luzuriaga, J. M.; Monge, M.; Rodríguez, M. A.; Crespo, O.; Gimeno, M. C.; Laguna, A.; Jones, P. G. *Inorg. Chem.* **1998**, *37*, 6002.
(147) Jansen, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1098.
(148) Canales, F.; Gimeno, M. C.; Laguna, A.; Jones, P. G. *J. Am. Chem. Soc.* **1996**, *118*, 4839.
(149) Fernández, E. J.; López-de-Luzuriaga, J. M.; Monge, M.; Olmos, M. E.; Pérez, J.; Laguna, A. *J. Am. Chem. Soc.* **2002**, *124*, 5942.
(150) Fernández, E. J.; Laguna, A.; López-de-Luzuriaga, J. M.; Olmos, M. E.; Pérez, J. *Chem. Commun.* **2003**, 1760.
(151) Fernández, E. J.; Laguna, A.; López-de-Luzuriaga, J. M.; Mendizábal, F.; Monge, M.; Olmos, M. E.; Pérez, J. *Chem. Eur. J.* **2003**, *9*, 456.
(152) Fernández, E. J.; López-de-Luzuriaga, J. M.; Monge, M.; Olmos, M. E.; Pérez, J.; Laguna, A.; Mohamed, A. A.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **2003**, *125*, 2022.
(153) Crespo, O.; Fernández, E. J.; Jones, P. G.; Laguna, A.; López-de-Luzuriaga, J. M.; Mendía, A.; Monge, M.; Olmos, M. E. *Chem. Commun.* **1998**, 2233.
(154) Fernández, E. J.; Jones, P. G.; Laguna, A.; López-de-Luzuriaga, J. M.; Monge, M.; Olmos, M. E.; Pérez, J. *Inorg. Chem.* **2002**, *41*, 1056.
(155) Wang, S.; Garzón, G.; King, C.; Wang, J. C.; Fackler, J. P. Jr. *Inorg. Chem.* **1989**, *28*, 4623.
(156) Catalano, V. J.; Bennett, B. L.; Kar, H. M. *J. Am. Chem. Soc.* **1999**, *121*, 10235.
(157) Burini, A.; Bravi, R.; Fackler, J. P. Jr.; Galassi, R.; Grant, T. A.; Omary, M. A.; Pietroni, B. R.; Staples, R. J. *Inorg. Chem.* **2000**, *39*, 3158.
(158) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1997.
(159) http://www.webelements.com.
(160) Pritzkow, H.; Jennische, P. *Acta Chem. Scand.* **1975**, *A29*, 60.
(161) Kristiansson, O. *Eur. J. Inorg. Chem.* **2002**, 2355, and references therein.
(162) Belli-Dell'Amico, D.; Calderazzo, F. *Gazz. Chim. Ital.* **1973**, *103*, 1099.
(163) Bennett, M. A.; Welling, L. L.; Willis, A. C. *Inorg. Chem.* **1997**, *36*, 5670.
(164) Fernández, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; López-de-Luzuriaga, J. M. *Organometallics* **1995**, *14*, 2918.
(165) Vaughan, L. G. *J. Am. Chem. Soc.* **1970**, *92*, 730.
(166) Hayashi, A.; Olmstead, M. M.; Attar, S.; Balch, A. L. *J. Am. Chem. Soc.* **2002**, *124*, 5791.
(167) Vickery, J. C.; Olmstead, M. M.; Fung, E. Y.; Balch, A. L. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1179.
(168) Tsunoda, M.; Gabbaï, F. P. *J. Am. Chem. Soc.* **2000**, *122*, 8335.
(169) Tiripicchio, A.; Tiripicchio, M.; Minghetti, G. *J. Organomet. Chem.* **1979**, *171*, 399.
(170) Burini, A.; Fackler, J. P. Jr.; Galassi, R.; Pietroni, B. R.; Staples, R. J. *Chem. Commun.* **1998**, 95.
(171) Burini, A.; Fackler, J. P. Jr.; Galassi, R.; Grant, T. A.; Omary, M. A.; Rawashdeh-Omary, M. A.; Pietroni, B. R.; Staples, R. J. *J. Am. Chem. Soc.* **2000**, *122*, 11265.

(172) Rawashdeh-Omary, M. A.; Omary, M. A.; Fackler, J. P. Jr.; Galassi, R.; Pietroni, B. R.; Burini, A. *J. Am. Chem. Soc.* **2001**, *123*, 9689.
(173) Goldstein, J. I.; Newbury, D. E.; Echlin, P.; Joy, D. C.; Fiori, C.; Lifshin, E. (Eds.). *Scanning Electron Microscopy and X-Ray Microanalysis*, Plenum Press, New York, **1992**.
(174) Usón, R.; Laguna, A.; Laguna, M.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1981**, 1097.
(175) Fernández, E. J.; Gimeno, M. C.; Laguna, A.; López-de-Luzuriaga, J. M.; Monge, M.; Pyykkö, P.; Sundholm, D. *J. Am. Chem. Soc.* **2000**, *122*, 7287.
(176) Fernández, E. J.; Laguna, A.; López-de-Luzuriaga, J. M.; Monge, M.; Pyykkö, P.; Runeberg, N. *Eur. J. Inorg. Chem.* **2002**, 750.
(177) Pauling, L. *The Chemical Bond*, Cornell University Press, Ithaca, NY, 1967.
(178) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 73rd ed., CRC Press, Boca Raton, FL, 1993.

Dehydrocoupling, Redistributive Coupling, and Addition of Main Group 4 Hydrides

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I

INTRODUCTION

Organic polymers can be classified as two major categories: natural biopolymers and synthetic industrial polymers. Natural biopolymers have been used frequently since the advent of humankind. Many industrial polymers have been synthesized using dazzling organic synthetic methodology during the past 50 years and are used heavily in daily life.[2] The backbones of organic polymers consist mainly of carbon atoms linked together or separated by heteroatoms such as oxygen or nitrogen. Organic polymers are generally available in large quantities and at moderate cost because of easy accessibility of their raw materials (i.e., monomers) derived from relatively cheap natural resources. At the same

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ADVANCES IN ORGANOMETALLIC CHEMISTRY
VOLUME 52 ISSN 0065-3055/DOI 10.1016/S0065-3055(04)52003-8

time, organic polymers degrade to lose their advantageous properties (light weight, flexibility, fabricability, etc.) in the presence of oxygen, ozone, ultraviolet radiation or long heating at high temperature. Most organic polymers burn with the release of toxic chemicals, leading to environmental pollution. Furthermore, the availability of raw materials for organic polymers is confined by the anticipated shortage of petroleum/coal resources. We need ideal materials, which have most of the advantageous properties of the three materials. Therefore, research on the design, synthesis, characterization, and applications of inorganic polymers or inorganic–organic hybrid polymers is needed, leading to the development of new advanced materials which may avoid some or all of these problems.[3] Inorganic polymers are made up of mainly silicon, germanium, tin, phosphorus, and sulfur atoms, which do not originate from petroleum/coal resources.[1] In particular, silicon-containing polymers exhibit quite unusual properties as advanced materials.[4]

For the heavier elements in main group 4 the formation of E–E bonds to produce a long chain polymer has proven to be difficult. The main reason is that stable unsaturated E=E species, analogues of vinyl compounds, can be prepared only in the presence of sterically bulky substituents, which obviously will deter their polymerization.[5] Intriguing methodologies to avoid this difficulty are the use of masked disilanes [6] and cyclic oligosilanes.[3a,4a] Wurtz-type reductive coupling of dihalosilanes using an alkali metal dispersion has widely been used in industry, but has some problems. As an alternative method, dehydrocoupling and redistributive coupling of group 4 hydrides to their polymers are useful routes to the synthesis of E–E bonds.

Group 4 hydrides (hydrosilanes, hydrogermanes, hydrostannanes) possess an E–H bond (E=Si, bond energy of 320 kJ/mole; E=Ge, 289 kJ/mole; E=Sn, 263 kJ/mole) that is more reactive than the C–H bond of hydrocarbons (bond energy of 416 kJ/mol).[7] For example, hydrosilanes undergo diverse reactions more easily than hydrocarbons, using catalysts to produce organic compounds and polymers containing silicon. In the following sections, this review describes some of the recent advances that have been made by other researchers with respect to dehydrocoupling, redistributive coupling, and addition of group 4 hydrides along with selective examples of our recent research developments in silicon materials chemistry. In other words, this article is rather comprehensive with a partial focus on our recent research developments.

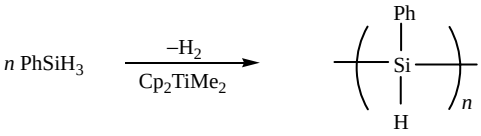
II

DEHYDROCOUPLING

A. *Linear-selective Dehydrocoupling of Hydrosilanes to Polysilanes*

Polysilanes have proved to be an intriguing class of inorganic polymers with many versatile applications in ceramics, photoelectronics, photoresistors, and nonlinear optics.[8,9] The unusual optoelectronic properties of polysilanes are attributed to sigma-conjugation of the silicon atoms in the polymer backbone chain, depending on the molecular weight, conformation, and substituents of the polymer.[10a] Wurtz-type

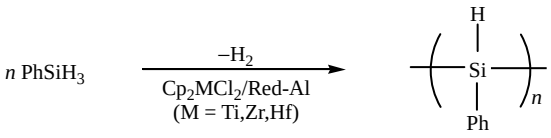
reductive coupling of dihalosilanes using an alkali metal dispersion in toluene- or xylene-refluxing temperature has some critical problems including intolerance of certain functional groups, lack of reproducibility, and has some limitations for controlling stereochemistry and molecular weights although some advances have been made by tuning several factors with use of ultrasonic activation.[10b] As an alternative synthetic method to the conventional Wurtz-type dehalogenative coupling method, the transition metal group 4 metallocene-catalyzed dehydrocouping of hydrosilanes using dimethyltitanocene was first discovered by Harrod [Eq. (1)], followed by intensive studies by many researchers worldwide.[11–13]



(1)

However, the dehydrocoupling of hydrosilanes generally produces a mixture of linear polymers and cyclic oligomers, resulting in decrease of polymer molecular weights. Therefore, the careful design of new group 4 metallocene catalytic systems for the selective production of linear polymer is important along with proper tuning of other factors such as addition rate/order of reagents, reaction temperature, etc.[12a] Linear high molecular weight polysilanes can be used as precursors for making functional polysilanes by introducing functional groups on the linear polysilane. The properties of linear polysilanes could be different from those of cyclic oligosilanes. Tilley[12a] and Waymouth[14] successfully synthesized high molecular weight polyphenylsilanes with number-average molecular weight (M_n) of ca. 5300 and 4700, respectively, by carefully controlling dehydrocoupling reaction conditions of phenylsilane using zirconocene-based catalysts. Tanaka[15] and Harrod[16] also prepared polyphenylsilanes with M_n of ca. 4600 and 7300, respectively, from the dehydrocoupling of phenylsilane by using the zirconocene-based combination catalysts of $[Me_2N(CH_2)_3-H_4C_5](Me_5C_5)ZrCl_2/2MeLi$ and $Cp(Me_5C_5)ZrCl_2/2n$-BuLi/$(C_6F_5)_3B$, respectively. Corey[13b] carried out a recent survey of the catalytic dehydrocoupling of hydrosilanes under the influence of a range of early and late transition metal complexes.

Woo recently developed a rapid, highly linear-selective dehydrocoupling catalyst system of phenylsilane: Cp'_2MCl_2/Hydride ($Cp' = C_5H_5$ or C_5Me_5; M = Ti, Zr, Hf; Hydride = Red-Al, Selectride, Super Hydride) combination catalysts [Eq. (2)].[11,17]



(2)

Woo's combinative catalyst system of Cp'_2MCl_2/Hydride is different from the catalyst systems using $Cp'_2MCl_2/2$ alkyllithiums of Corey, Tanaka, and Harrod. Real catalytic species in the dehydrocoupling of hydrosilanes could be a metallocene hydride based on a sigma-bond metathesis mechanism.[12,13b] Inorganic hydrides effectively produce a metallocene hydride whereas alkyllithium can produce a metallocene hydride *via*

a complex process (e.g., reductive elimination of metallocene alkyls or reaction with hydrosilane). Thus, no appreciable induction period was observed for the Cp'_2MCl_2/Hydride combination catalyst. The molecular weight distributions obtained from the GPC traces were bimodal shapes, implying the existence of linear polysilanes (which generally means $>Si_{10}$) and cyclic oligosilanes (M_w ca. 500). The formation of cyclic oligosilanes was estimated by integration of the GPC peaks. The peaks corresponding to SiH in the ^{1}H NMR spectrum were visually separated as linear polysilane (4.2 $\sim$ 4.8 ppm range) and cyclic oligosilane (4.9 $\sim$ 5.3 ppm range). Thus, the formation of the cyclic oligosilanes was also estimated by the integration of the ^{1}H NMR peaks, and was used as a means of cross-checking the cyclic/linear ratio. The two cross-checking methods were roughly correlative. Woo and Song[17b] also tested the other group 4 metallocene-based combination catalysts for the dehydrocoupling of phenylsilane under various reaction conditions. The dehydrocoupling of phenylsilane with Cp'_2MCl_2/Red-Al combination catalysts rapidly produces linear polyphenylsilanes. The linear selectivity increases in the order of Cp_2Ti (64%) $<$ Cp_2Zr (92%) $<$ $Cp(C_5Me_5)Zr$ (95%) $<$ Cp_2Hf (99%) $<$ $Cp(C_5Me_5)Hf$ ($<$99%). The higher linear-selectivity of the hafnocene relative to the zirconocene is likely due to the lower intrinsic dehydrocoupling activity (originating from stronger Hf–H and Hf–Si bond strengths). The lower linear-selectivity of titanocene relative to zirconocene and hafnocene is probably due to the combined effect of greater intrinsic dehydrocoupling activity (stemming from much weaker Ti–H and Ti–Si bond strengths) and much smaller atomic size (overriding steric crowding around the metal center) of Ti.[18] The change in linear selectivity is more outstanding than in other catalytic combination systems: Cp_2TiCl_2/2MeLi (55%) $<$ Cp_2ZrCl_2/2MeLi (75%), Cp_2TiCl_2/2*n*-BuLi (75%) $<$ $Cp(C_5Me_5)ZrCl_2$/2*n*-BuLi (80%) $<$ Cp_2HfCl_2/2MeLi (85%).[16,18] The coordinating environment around the metal center of the Cp_2MCl_2/Red-Al combination catalysts could be different from other catalytic systems such as Cp_2MCl_2/2R′Li.[14,15,18,20] Red (or Vitride; sodium bis(2-methoxyethoxy)aluminum hydride; $Na[H_2Al(OCH_2CH_2OMe)_2]$) will be quantitatively converted into $Na[Cl_2Al(OCH_2CH_2OMe)_2]$ after reacting with dichlorometallocene. The coordinating structure of the present catalytic system could be similar to or different from the zwitterionic structure of the Cp_2ZrCl_2/2*n*-BuLi/$(C_6F_5)_3B$ catalytic system.[16,19] The $Na[Cl_2Al(OCH_2CH_2OMe)_2]$ moiety may influence by simply coordinating to the metal through an H, Cl-bridge or H, OMe-bridge between the group 4 metal and Al metal. In any case, the favorable steric demands exerted by the Cp ring and cocatalyst moiety could prevent the formation of the inactive dimer of metallocene hydride and suppress the cyclic oligomer formation by chain cleavage reaction, leading to greater chain elongation.[15,16] However, an overriding steric demand should result in low dehydrocoupling activity. The order of dehydrocoupling activity for the various zirconocenes was found to be the same as the sequence of Tilley[12] and Harrod[16]: $(C_5Me_5)_2Zr \ll Cp_2Zr <$ $Cp(C_5Me_5)Zr$. The $(C_5Me_5)_2ZrCl_2$/Red-Al combination catalyst thus slowly produces a mixture of dimer, trimer, and tetramer. In addition, the order of linear-selectivity for the dehydrocoupling of phenylsilane catalyzed by hydrides with Cp_2ZrCl_2 was found to be Super Hydride (82%) $<$ *N*-Selectride (88%) $<$ Red-Al (92%).[17c] The dehydrocoupling of $PhCH_2SiH_3$ yields only low-molecular weight oligomers (i.e., no appreciable linear-selectivity was observed) because the alkylsilane $PhCH_2SiH_3$ is less reactive than an arylsilane $PhSiH_3$, as seen in other catalyst systems.[20] The molecular weight of polymer

is increased by higher catalyst concentration (1 mol% *versus* 5 mol%), but it is affected little by longer reaction times (1 day *versus* 5 days).[17b] Linear selectivity and molecular weights decrease with addition of solvent and with heating, which was similarly observed in other catalytic systems.[12a,16] This is because dilution and heating could hamper the tight coordination of the $Na[Cl_2Al(OCH_2CH_2OMe)_2]$ moiety to the metal center. Interestingly, linear selectivity and molecular weights decrease drastically by adding 4 Å molecular sieve (MS 4Å). Woo suggested that the interaction of the $Na[Cl_2Al(OCH_2CH_2OMe)_2]$ moiety with MS 4Å might prevent the close coordination of $Na[Cl_2Al(OCH_2CH_2OMe)_2]$ moiety to the metal center.[17b] An exact molar ratio of Red-Al to dichlorometallocene is necessary to replace both chlorines to attain high reactivity. The inactivity observed for higher molar ratios of Red-Al to dichlorometallocene could be attributed to over-complexation of Red-Al moieties to the metal, blocking the empty coordination site necessary for the dehydrocoupling of silane.[18] All the experimental results described above strongly suggest that better catalysts affording higher linear-selectivity and higher-molecular-weight polymer can be properly designed by tuning the steric and electronic character of the catalyst environment, including ligand and co-catalyst moieties.

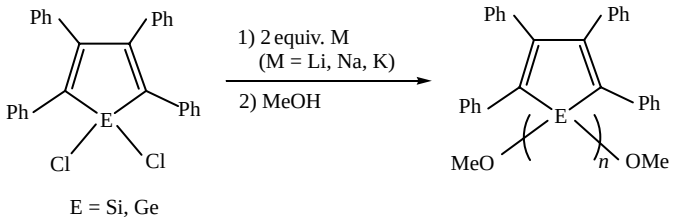
It is interesting to note that the dehydrocoupling of *p*-fluorophenylsilane using Cp_2ZrCl_2/Red-Al produced soluble amorphous polysilane (ca. 75%) and sparingly-soluble crystalline polysilane (ca. 25%) in toluene and chloroform. The two polysilanes were soluble in THF and pyridine. In comparison, the dehydrocoupling of *p*-fluorophenylsilane using Cp_2TiCl_2/Red-Al gave soluble polysilane only.[17c] The crystalline polysilane may have interactions[17b] in the polymer molecules either between Si and F (high possibility) or between F and phenyl ring (low possibility).

Linear high molecular weight polysilanes can be used as precursors for making functional polysilanes by introducing functional groups on the linear polysilane. The Si–H bonds in the backbone chain of poly(hydrophenylsilane) were transformed to Si–Cl bonds using a mild chlorinating reagent, CCl_4. The Si–Cl bonds in the poly(chlorophenylsilane) can be replaced by various nucleophiles such as cyclopropyl, epoxy, aziridinyl, pyridyl, bipyridyl, phosphinyl, poly(ethylene oxide), thiol, etc. to give new functional polymers which can be used for applications in sensors, ion-exchange resins, batteries, drug delivery, metal nanomaterials preparation, etc.[17e]

B. *Homodehydrocoupling of 1,1-Dihydrotetraphenylsilole and 1,1-Dihydrotetraphenylgermole to Electroluminescent Polymers*

Polysilanes[21–23] with low oxidation potentials and a high-lying HOMO exhibit peculiar optoelectronic properties due to sigma-conjugation along the silicon backbone chain in the polymer.[10,24] Siloles (silacyclopentadienes), with low reduction potential and low-lying LUMOs, have attracted considerable attention because of their peculiar electronic properties.[25,26] They may be used for electron-transporting materials in devices.[27] A silole did not luminesce in diluted solution, but did luminesce in concentrated solution.[25] Polysiloles could thus show different luminescent behavior from that of monomeric siloles. Polysiloles, which are expected to have hybrid properties

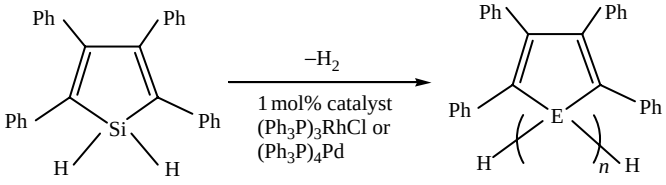
of polysilane and silole by nature in the structure, can be prepared by 1,1- or 2,5-coupling reactions of siloles using various synthetic coupling methods.[28] Electroluminescent poly(silole-*co*-silane)s have also been synthesized in several laboratories.[29] West *et al.* reported recently the synthesis of polysiloles and polygermole (M_w ca. 5200–5700) that have methoxy end groups in 30–37% yield by heterogeneous Wurtz 1,1-dehydrocoupling of 1,1-dichlorotetraphenylsilole with 2.0 equivalents of Li, Na, K metal in refluxing THF for 3 days [Eq. (3)].[28a]



E = Si, Ge (3)

Some oligomers were also isolated along with the polysilole when 1.2 equiv of the metal was used at room temperature for 1 day. Tamao and collaborators had earlier reported the Wurtz coupling synthesis of polysiloles.[28d]

As an alternative to Wurtz coupling, the homogeneous dehydrocoupling methodology was demonstrated in Tanaka's earlier report of the dehydrocoupling synthesis of poly(dibenzosilole).[30a] Trogler and co-workers recently reported the 1,1-dehydrocoupling of 1,1-dihydrotetraphenylsilole (**1**) to an electroluminescent polysilole (**2**) (M_w ca. 4000–6000), having hydrogen end groups, in high yield 80–90% yield using 1 mol% of the late transition metal complexes [$((Ph_3P)_3RhCl$ and $((Ph_3P)_4Pd$) as catalysts [Eq. (4)].[29b,30b]



1 **2** (4)

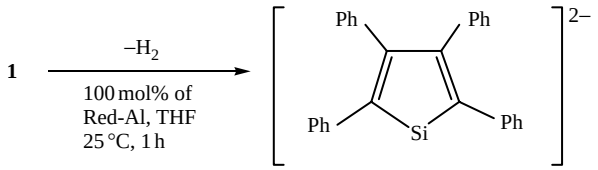
Similarly, Woo and co-workers prepared **2** (M_w ca. 5500–6200) in >95% yield by dehydrocoupling of **1** using $[RhCl(COD)_2]_2$ and $Pt(PMe_3)_4$ as catalyst.[31] Woo also synthesized poly(tetraphenylgermole) (M_w ca. 5800–6500) in >92% yield by dehydrocoupling of 1,1-dihydrotetraphenylgermole using the same catalysts. The UV-vis spectrum of poly(tetraphenylgermole) shows an absorption at 377 nm, which is assignable to both the $\sigma-\sigma^*$ transition of the Ge–Ge backbone chain and $\pi-\pi^*$ transition of the germole ring. The polygermole is intensively photoluminescent, emitting green light at 487 nm.[31] The hydrogen end groups of the polysiloles

and polygermoles can then be transformed to other useful functional groups by various chemical reactions.

As an alternative to the heterogeneous Wurtz reductive coupling of dichlorosilole and the homogeneous late-transition-metal-complex-catalyzed dehydrocouplig of **1**, Woo also synthesized **2** in high yield by homogeneous dehydrocoupling of **1** under mild conditions, catalyzed with inorganic hydrides such as Selectrides $\{MB[CH(CH_3)C_2H_5]_3H;\ M = Li,\ Na,\ K\}$, Red-Al $\{Na[H_2Al(OCH_2CH_2OCH_3)_2]\}$, and Super-Hydride $[LiB(C_2H_5)_3H]$ as shown in Eq. (5).[32a,b]

$$\mathbf{1} \xrightarrow[< 50\ \text{mol\% of Hydride, THF 25 °C, 24 h}]{-H_2} \mathbf{2} \tag{5}$$

Dehydrocoupling of **1** catalyzed by <50 mol% (i.e., M–H/Si–H ≤ 0.5) of Red-Al yielded **2** as light yellow powders. Polymers with molecular weights (M_w) of 4600 and 4100 were isolated in 86 and 78% yields when 15 mol% and 50 mol% of Red-Al were used, respectively. Polymer yields and molecular weights when 15 mol% of Red-Al was used were higher compared to polymers obtained when 50 mol% of Red-Al was used. Products from the reaction of **1** with 15 mol% 25 mol%, and 50 mol% Red-Al were separated by preparative GPC and were characterized by NMR spectroscopy. Shorter oligomers such as silole dimer or trimer were not found in products. However, when 100 mol% of Red-Al (i.e., M–H/Si–H = 1) was used, the formation of silole dianion **3**[33] was observed without forming **2** [Eq. (6)].



3 (6)

In similar dehydrocoupling of **1** to **2** carried out using 15 mol% of Selectrides and Super-Hydride at 25 °C for 24 h, the polysiloles were obtained in 77–78% isolated yield. The molecular weight (M_w) and polydispersity index (PDI) of all the polysiloles were in the range of 4300–5800 and 1.1–1.2, respectively. Endgroup analysis was performed to determine the chain length by integrating the peak area for the phenyl protons and Si–H proton in the ^1H NMR spectra. A ratio of about 15–17 siloles to 2 Si–H groups was observed. In order to confirm the results of the end group analysis, the Si–H end groups were transformed to Si–OMe by reacting **2** with an excess of CCl_4 for 48 h to convert Si–H to Si–Cl, followed by reaction with methanol. A ratio of about 14–16 siloles to 2 Si–OMe groups was found, which is in reasonably good agreement with the Si–H derived value. The chain length from the endgroup analysis is consistent with the polymer molecular weight determined by GPC. Polymerization yield and polymer molecular weight increased in the order of L-Selectride < *N*-Selectride < K-Selectride. The trend seems to be related to the ionic character of the Selectrides. The polymerization

yields were almost equal for Red-Al, K-Selectride, and Super-Hydride, but the molecular weight increased in the order of Red-Al < K-Selectride < Super-Hydride. Like the polysiloles prepared by West and co-workers,[28a] these polysiloles have a characteristic UV absorption around 300 nm, assigned to the $\sigma-\sigma^*$ transition of the Si–Si backbone chain. They are photoluminescent, emitting green light at 520 nm when the excitation is at 330 nm. These polysiloles are strongly electroluminescent around 520 nm. No appreciable characteristic Si–O–Si band was observed in the IR spectra of the polysiloles.

For the dehydrocoupling reaction of **1** to **2**, K-Selectride and Super-Hydride were the most active catalysts examined. **2** was prepared in high yield directly from the reaction of 1,1-dichlorotetraphenylsilole (instead of **1**) in the presence of <1.5 equiv. of Red-Al (instead of <0.5 equiv).[32c] Unlike in the case of late-transition-metal-complex-catalyzed dehydrocoupling,[30,31] catalysis for the conversion of **1** to **2** by early transition metal complexes, Cp_2MCl_2/Red-Al (M = Ti, Zr, Hf) (a catalytic system which was recently found to give predominantly linear polysilanes[17]) was ineffective, as expected, in the dehydrocoupling of **1** because **1** is sterically hindered, considering the four-centered transition state in the sigma-bond metathesis mechanism. The sterically demanding silane is expected to be difficult in forming a four-centered transition state in the sigma-bond metathesis mechanism.[12] Thus, we know the dehydrocoupling mechanism should be different from the sigma-bond metathesis mechanism. Woo proposed a mechanism involving the preferential attack of a hydride ion on either the silicon atom or silole ring of **1** to form an activated anionic intermediate such as a pentacoordinated sigma-complex or pi-complex.[32]

The activated anionic intermediate could lose both a dihydrogen molecule and a hydride ion (this hydride may participate again in the catalytic cycle) sequentially to form a silylene type of silole. If the activated anionic intermediate accepts another hydride ion, a silole dianion **3** will be formed after losing two dihydrogen molecules. The silylene type of silole will then either self-couple or keep inserting into the Si–H bond of **1**, forming **2** (Fig. 1).

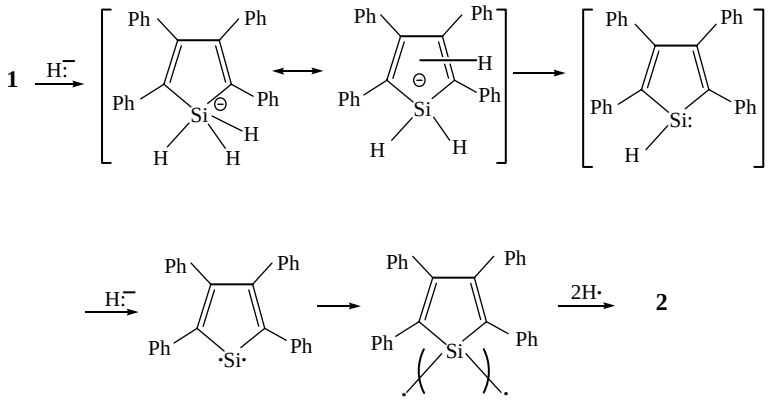
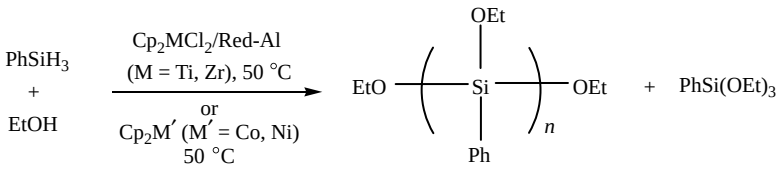


FIG. 1. Possible mechanism for the formation of polysilole **2** from the dehydrocoupling of **1**.

C. *Combinative Si–O/Si–Si Dehydrocoupling of Hydrosilane with Alcohol to Poly(alkoxysilane)*

A wide range of catalysts have been involved for the Si–O dehydrocoupling of alcohols with silanes.[34] These catalysts include acids, bases, and both homogeneous and heterogeneous transition metal catalysts. Corey and Bedard carried out a comprehensive survey of the dehydrocoupling of a range of hydrosilanes and alcohols under the influence of $Cp_2TiCl_2/2n$-BuLi.[13a,35a] The Si–O dehydrocoupling of bis-hydrosilanes with diols, catalyzed by rhodium complex, yielding polymers was reported.[35b,c] The Si–S dehydrocoupling of hydrosilanes with benzene dithiol to produce polymers was also reported.[35d] Harrod reviewed the recent dehydrocoupling of hydrosilanes with alcohols.[11] The transition metal complexes of group VIII (Ni, Co, Rh, Pd, Ir, Pt, etc.) have been extensively applied in the catalytic dehydrocoupling of hydrosilanes with various nucleophilic reagents.[36] Corey also carried out a recent survey of the catalytic dehydrocoupling of hydrosilanes in the presence of a range of early and late transition metal complexes.[13b] Si–Si dehydrocoupling of hydrosilanes with late transition metal complex catalysts produces a mixture of oligomers along with significant amounts of redistributed by-products.[13b]

Numerous studies were reported on the alcoholysis of hydrosilanes or on the dehydropolymerization of silanes in the presence of transition metal complex catalysts[13,34,35a–c,36]. Nonetheless, Woo first reported the interesting one-pot synthesis of poly(alkoxysilane)s by combinative Si–Si/Si–O dehydrocoupling of hydrosilanes with alcohols. Poly(alkoxysilane)s can be used as precursors for preparing interesting polysilane–siloxane hybrids by sol–gel methods.[37a] The sol–gel processing of poly(alkoxysilane)s in the presence of acid/base catalyst with (or without) a surfactant (anionic: AOT, dioctyl sulfosuccinate sodium salt; cationic: CETAB, cetyl trimethyl ammonium bromide) as a template produced polysilane–siloxane hybrid gels. Woo and co-workers described the combinative Si–Si/Si–O dehydrocoupling reaction of hydrosilanes with alcohols (1:1.5 mole ratio) at 50 °C, catalyzed by Cp_2MCl_2/Red-Al (M = Ti, Zr) and Cp_2M' (M = Co, Ni), producing poly(alkoxysilane)s in one-pot in high yield, as shown in Eq. (7).



(7)

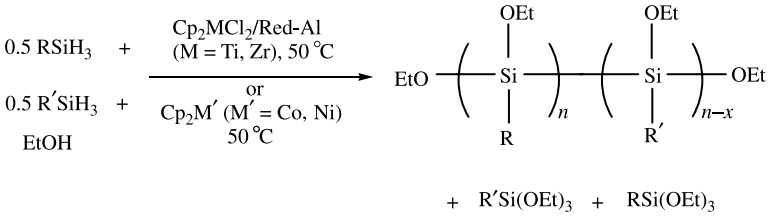
The hydrosilanes included p-$C_6H_4SiH_3$ (X = H, CH_3, OCH_3, F), $PhCH_2SiH_3$, and $(PhSiH_2)_2$. The alcohols included MeOH, EtOH, i-PrOH, PhOH, and $CF_3(CF_2)_2CH_2OH$. The weight average molecular weights of the poly(alkoxysilane)s ranged from 600 to 8000. In comparison, Cp_2M' (M′ = Co, Ni) did not have any catalytic activity toward Si–Si homodehydrocoupling of primary silanes.[37b] The dehydrocoupling reactions of phenylsilane with ethanol (1:1.5 mole ratio) using Cp_2HfCl_2/Red-Al, and phenylsilane

with ethanol (1:3 mole ratio) using Cp_2TiCl_2/Red-Al gave only triethoxyphenylsilane as product [Eqs. (8a) and (8b)].[38]

$$PhSiH_3 + 1.5\ EtOH \xrightarrow[50\ ^\circ C]{Cp_2HfCl_2/Red\text{-}Al} PhSi(OEt)_3 \tag{8a}$$

$$PhSiH_3 + 3.0\ EtOH \xrightarrow[50\ ^\circ C]{Cp_2TiCl_2/Red\text{-}Al} PhSi(OEt)_3 \tag{8b}$$

Similarly, Woo *et al*. carried out the combinative Si–Si/Si–O dehydrocoupling reactions of mixed hydrosilanes with alcohols (two different hydrosilanes were used in the same mole ratio; 0.5:0.5:1.5 mole ratio) at 50 °C, catalyzed by Cp_2MCl_2/Red-Al (M = Ti, Zr) and Cp_2M' (M′ = Co, Ni), producing copoly(alkoxysilane)s in one-pot in high yield [Eq. (9)].[37a]



$$+\ R'Si(OEt)_3 + RSi(OEt)_3 \tag{9}$$

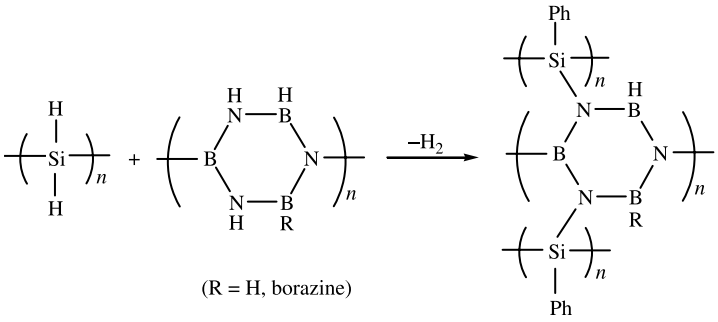
In a similar manner, Woo and co-workers performed the combinative Si–Si/Si–O dehydrocoupling reactions of hydrosilanes with mixed alcohols (two different alcohols were used in the same mole ratio; 1:0.75:0.75 mole ratio) at 50 °C, catalyzed by Cp_2MCl_2/Red-Al (M = Ti, Zr) and Cp_2M' (M′ = Co, Ni), producing copoly(alkoxysilane)s in one-pot in high yield.[37a] The bonding characters [mixing interaction between σ (silicon) and n (oxygen)] of Si–O bonds in poly(dialkoxysilylene)s were studied by molecular orbital calculations.[37c]

D. *Si–N Dehydrocoupling of Poly(hydrosilane) with Polyborazine Additive*

Harrod and co-workers recently reviewed the Si–N dehydrocoupling of various hydrosilanes with amines (including ammonia, alkyl amines, and aromatic amines, hydrazines), catalyzed by early and late transition metal complexes in detail.[11] Eisen reported the dehydrocoupling of phenylsilane with various amines catalyzed by $[(Et_2N_3)$-$U[BPh_4]$.[39a] Although B–N dehydrocoupling of borazine and poly(vinylborazine) was reported by Sneddon *et al*.[39b] Si–N dehydrocoupling of poly(hydrosilane)s with polyborazine (PBN) has been reported very recently by Woo and co-workers.[41] No Si–B dehydrocoupling of hydrosilane with borazine has been reported up to date although it may possibly occur.

SiC is an excellent nonoxide ceramic with high-temperature stability and suitable mechanical properties. Since silicon-containing polymers are generally used for preparing nonoxide ceramics, various polymeric precursors with different structures have been designed. Preceramic polycarbosilane (PCS), used for preparing commercial Nicalon fiber,

is synthesized by the poorly efficient thermolysis of polydimethylsilane (PDMS) due to the formation of hazardous gaseous compounds (leading to low yield) and irregularity of the composition of the resulting PCS.[39c] As an alternative precursor for SiC ceramics, Woo and co-workers studied polyphenylsilane (PPS,[-Si(Ph)H-]$_n$) and polyvinylsiane (PVS, [$CH_2CH(SiH_3)$]$_n$). An ideal preceramic precursor for Si–C ceramics should exhibit: (1) high ceramic residue yield, to minimize the cost and volume change associated with pyrolytic conversion to ceramics and consequently to maximize the control of porosity and densification, and (2) a suitable processability (i.e., viscosity) allowing it to be shaped into the needed forms prior to pyrolysis. In this context, it is disadvantageous that the low viscosity PPS and PVS undergo drastic mass loss during pyrolysis, which leads to low ceramic residue yields (20–40 wt%).[39d,40a] To improve the ceramic residue yields and processabilities of PPS and PVS, the Seyferth group tried to use many additives including transition metal complex catalysts, urea, and decaborane.[39d,e] Woo and co-workers also reported the increase of thermal stability (i.e., increase of TGA ceramic residue yield) of PCS and oligocarbosilane (OCS) by dehydrocoupling of Si–H bonds in the PCS and OCS using group 4 and 6 transition metal complex catalysts.[40b,c] Woo described the additive effect of PBN on the improvement of ceramic residue yield of the polysilane, as depicted in Eq. (10).[41]



(10)

The ceramic residue yield of PPS increases from an original 39 to 65 wt%, and PVS from an original 26 to 64 wt% by simply heating with 1 wt% PBN at 70 °C for $<$6 h. Furthermore, the low viscosity PPS and PVS were transformed into highly viscous polymers, which are suitable for hand drawing into green fibers. Analysis using NMR spectroscopy suggests that dehydrocoupling of SiH_3 in PVS and Si–H in PPS by PBN is responsible for the improved ceramic residue yields.[41] When the added amount of PBN was increased, the resulting materials were found to be B, N-incorporated SiC ceramics which can be used for diverse applications.

E. *Homodehydrocoupling of Hydrogermanes and Hydrostannanes to Polymers*

Harrod and co-workers recently reviewed the catalytic dehydrocoupling of hydrogermanes and hydrostannanes with transition metal complex catalysts.[11] Braunstein and Morise very recently reviewed the dehydrocoupling of hydrostannanes catalyzed by transition metal complex catalysts.[42] Although polygermanes and polystannanes are anticipated to have similar intriguing properties to polysilanes, great

attention has not been paid to them until very recently. As in the case of polysilanes, polygermanes and polystannanes have been conventionally prepared by the Wurtz-type dehalocoupling of halogermanes and halostannanes using alkali metals (Li, Na, K) or alkaline earth metal (Mg).[43] Harrod and co-workers first reported the catalytic dehydrocoupling of $PhGeH_3$ to a cross-linked gel type of polygermane (without noticeable formation of soluble polygermane) using Cp_2TiMe_2 catalyst.[44a] The formation of the highly cross-linked insoluble gel product might be caused by further dehydrocoupling of backbone Ge–H bonds or by partial redistribution of $[PhGeH]_n$ moiety to $[Ph_2Ge]_x[GeH_2]_{n-x}$, followed by further dehydrocoupling of $[GeH_2]_{n-x}$ moiety. The first one seems to be more likely to occur. The catalytic dehydrocoupling of Ph_2GeH_2 formed a mixture of oligomer and $(Ph_2GeH)_2$ using Cp_2TiMe_2 catalyst.[44a] Tanaka and co-worker synthesized partially cross-linked soluble poly(phenylgermane) in 67% isolated yield after precipitation of the polymer solution in THF with pentane by the catalytic dehydrocoupling of $PhGeH_3$ using $CpCp'ZrCl_2/2n$-BuLi ($Cp' = Cp$ or Cp^*) combination catalyst.[44b] Similarly, Kim and co-worker prepared soluble poly(phenylgermane) and insoluble poly(phenylgermane) by the catalytic dehydrocoupling of $PhGeH_3$ using Cp_2MCl_2/Red-Al (M = Ti, Zr, Hf) combination catalyst.[44c] From the catalytic reaction the percentage of the soluble poly(phenylgermane) decreased in the order of Hf (89%) > Zr (82%) > Ti (25%). After removing all the volatiles from the reaction mixture 24 h later, the weights of the resulting materials were measured. The materials were subject to column chromatography, evaporation of solvent and measurement of the weights of resulting soluble polymers. The percentages were calculated from an equation of (second weight/first weight) × 100.

Tilley and co-worker prepared linear polystannanes (M_w, ca. 70,000) by dehydrocoupling of R_2SnH_2 (R = *n*-Bu, *n*-Hex, *n*-Oct) using $CpCp^*Zr[Si(SiMe_3)_3]Me$ catalyst.[45] Tilley *et al*. studied the properties of sigma-conjugated polystannanes such as low band gap,[46a] $\sigma-\sigma^*$ transition energy,[46b] and order–disorder phase transition.[46c] Braunstein and Morise reported the efficient dimerization of R_3SnH (R = Ph, *n*-Bu) by a Fe–Pd heterobimetallic alkoxysilyl and siloxysilyl complex.[47] The mechanism for the dehydrocoupling of hydrogermanes and hydrostannanes by the transition metal group metallocene catalysts could be similar to the mechanism for dehydrocoupling of hydrosilanes by those catalysts.[11,12] Tilley and Neale recently proposed a modified mechanism comprising steps of σ-elimination and σ-bond metathesis based on their kinetic study of hafnium hydrostannyl complexes by ^1H NMR spectroscopy.[48]

III

REDISTRIBUTIVE COUPLING

A. *Desilanative Coupling of Multisilylmethanes to Oligomers*

Inorganic hydrides are usually soluble in polar solvent such as THF, but sparingly soluble in nonpolar solvents. Red-Al (or Vitride; sodium bis(2-methoxyethoxy)aluminum hydride) is a toluene-soluble inorganic hydride and efficiently promotes the polymerization

of lactams and olefins and the trimerization of isocyanates.[49] Corriu and co-workers reported the desilanative proportionation reactions of di- and trihydrosilanes[50a] and the desilanative oligomerization of disilanes[50b] with exchanging their substituents [Eqs. (11) and (12)], catalyzed by inorganic hydrides (e.g., NaH, KH, *etc*).

$$3\ RSiH_3 \xrightarrow[-SiH_4]{H:^-} R_2SiH_2 \xrightarrow[-SiH_4]{H:^-} R_3SiH \tag{11}$$

$$R_3Si-Si(Me)_2H \xrightarrow{H:^-} R_3SiH + (Me_2Si)_6 + Me_3Si(SiMe_2)_nH \tag{12}$$

The authors suggested a mechanism *via* the intermediacy of a reactive pentacoordinated hydrosilyl anion,[50c] which is formed by the addition of hydride (H^-) on the silanes, for the redistribution reactions.

Riviere and co-workers prepared oligogermane $(PhHGe)_n$ by redistributive coupling of PhH_2GeGeH_2Ph under the influence of a Lewis base PhH_2GeLi.[51] The Lewis acid $AlCl_3$ catalyzes a redistribution reaction of hydroarylsilane to afford quaternary arysilane and SiH_4.[52] Woo *et al*. reported the intriguing desilanative coupling of bis- and tris(silyl)methanes to oligomers, catalyzed by Red-Al.[53] The bis- and tris(silyl)methanes are multisilylmethanes which have reactive Si−C−Si linkages. 2-Phenyl-1,3-disilapropane (**4**) underwent desilanative coupling at ambient temperature in the presence of 1 mole% Red-Al (3.4 M solution in toluene) within 1 h to produce benzylsilane as the major product and as yet uncharacterized high-boiling oligomers as minor products with SiH_4 gas, as shown in Eq. (13). Similarly, the bis(silyl)methane, 1-phenyl-3,5-disilapentane **5**, was quantitatively converted to methylphenethylsilane and phenethylsilane (7:3 ratio, identified by GC/MS analysis) as the major product and uncharacterized high-boiling oligomers as minor products with SiH_4 and $MeSiH_3$ gases [Eq. (14)]. Likewise, the tris(silyl)methane, 1-phenyl-4-silyl-3,5-disilapentane **6**, was quantitatively transformed to **5**, methylphenethylsilane, and phenethylsilane (3:12:4 ratio identified by GC/MS analysis) as major products and uncharacterized high-boiling oligomers as minor products along with the formation of SiH_4, $MeSiH_3$, and $CH_2(SiH_3)_2$ molecules [Eq. (15)].[53]

$$\underset{\mathbf{4}}{PhCH(SiH_3)_2} \xrightarrow{\text{Red-Al}} PhCH_2SiH_3 + SiH_4 + \text{Oligomers} \tag{13}$$

$$\underset{\mathbf{5}}{Ph(CH_2)_2SiH_2CH_2SiH_3} \xrightarrow{\text{Red-Al}} Ph(CH_2)_2SiH_2CH_3 + Ph(CH_2)_2SiH_3 + SiH_4 + CH_3SiH_3 + \text{Oligomers} \tag{14}$$

$$\underset{\mathbf{6}}{Ph(CH_2)_2SiH_2CH(SiH_3)_2} \xrightarrow{\text{Red-Al}} \mathbf{5} + Ph(CH_2)_2SiH_2CH_3 + Ph(CH_2)_2SiH_3 + SiH_4 + CH_3SiH_3 + CH_2(SiH_3)_2 + \text{Oligomers} \tag{15}$$

Benzylsilane did not appreciably undergo further redistribution (i.e., to dibenzylsilane and tribenzylsilane) under the mild redistribution conditions.

Methylphenethylsilane can be obtained *via* Si−C bond cleavage of **4**, evolving SiH_4 gas in the redistribution reaction of **5**. However, phenethylsilane cannot be obtained *via* the direct Si−C bond cleavage of methylphenethylsilane, but *via* the direct Si−C bond cleavage of **5** with CH_3SiH_3 gas evolution. Methylphenethylsilane was obtained in higher yield than phenethylsilane, implying that SiH_4 formation is easier than CH_3SiH_3 formation, likely due to less steric hindrance exerted upon adding hydride to the silanes. On the other hand, methylphenethylsilane can be formed *via* consecutive Si−C bond scissions of **6**, giving off SiH_4 gas in the redistribution reaction of **6**. However, phenethylsilane cannot be obtained by the direct Si−C bond cleavage of methylphenethylsilane, but can be obtained either by the direct Si−C bond cleavage of **5** with release of CH_3SiH_3 or by the direct Si−C bond cleavage of **6** with the formation of $CH_2(SiH_3)_2$. The yield for methylphenethylsilane was higher than for phenethylsilane, suggesting that SiH_4 formation is easier than $CH_2(SiH_3)_2$, probably due to different steric hindrance upon the addition of hydride to the silane. The as yet uncharacterized high-boiling oligomers could be obtained only during the redistribution process because the reactions of benzylsilane, methylphenethylsilane, and phenethylsilane with Red-Al do not yield oligomeric mixture of silanes under the reaction conditions. The oligomers might be oligocarbosilanes or a mixture of oligocarbosilanes and oligosilanes (Fig. 2).

Methylene bridges between two silicon atoms are more readily deprotonated by strong organometallic bases than are methyl groups bonded to a single silicon atom because two silicon centers jointly can stabilize the resulting anion better than one silicon center *via* pπ−dπ interaction between p-orbital of carbon and d-orbital of silicon[54] (but other explanation based on some MO calculation may be possible.[37c]), but cleavage of the Si−C bond takes place normally under extremely harsh conditions.[55] No appreciable redistribution of multisilylmethanes **4**–**6** under these reaction conditions was observed with *n*-BuLi and $AlCl_3$. Attempts at trapping silylene or silene using 2,3-dimethyl-1,3-butadiene, cyclohexene, and trimethylmethoxysilane were unsuccessful, probably due to the presence of good-hydrogen donor, hydrosilane species possessing active Si−H bonds, in the reaction mixture.[53]

Woo *et al*. suggested a mechanism (Fig. 2) involving the preferential addition of the hydride to the silicon at the less hindered site, forming an active intermediate and SiH_4 gas.[53] The α-silyl carbanion pentacoordinated anionic species which then collapses to give an *α*-silyl carbanion may then pick up a hydrogen from a hydrogen source (e.g., silane or solvent) to form a silane or may lose a hydride to produce a silene, associating to produce some oligo(carbosilane)s, or isomerizing to a silyl anion. The silyl anion may lose a hydride to give an unstable silylene, which can add to silane or an associate, producing some linear or cyclic oligosilanes. The regenerated hydride may add to **4** to participate again in the catalytic cycle.

Interestingly, the reactions of **4** with Red-Al, Cp_2MCl_2/Red-Al, and Cp_2MCl_2/ 2*n*-BuLi (M = Ti, Zr, Hf) give different results. The redistribution-dehydrocoupling of **4** catalyzed by Cp_2MCl_2/Red-Al gives polymer (M_w = 550 for Ti; 750 for Zr; 2040 for Hf) with low TGA ceramic residue yield (ca. 3% at 800 °C for Ti, Zr, Hf) in moderate yield (20% for Ti; 25% for Zr; 28% for Hf)[56,57] as shown in Eq. (16) whereas the redistributive coupling [Eq. (13)] of **4** catalyzed by Red-Al gives oligomer ($M_w < 500$) in very low yield (less than 3%).[53]

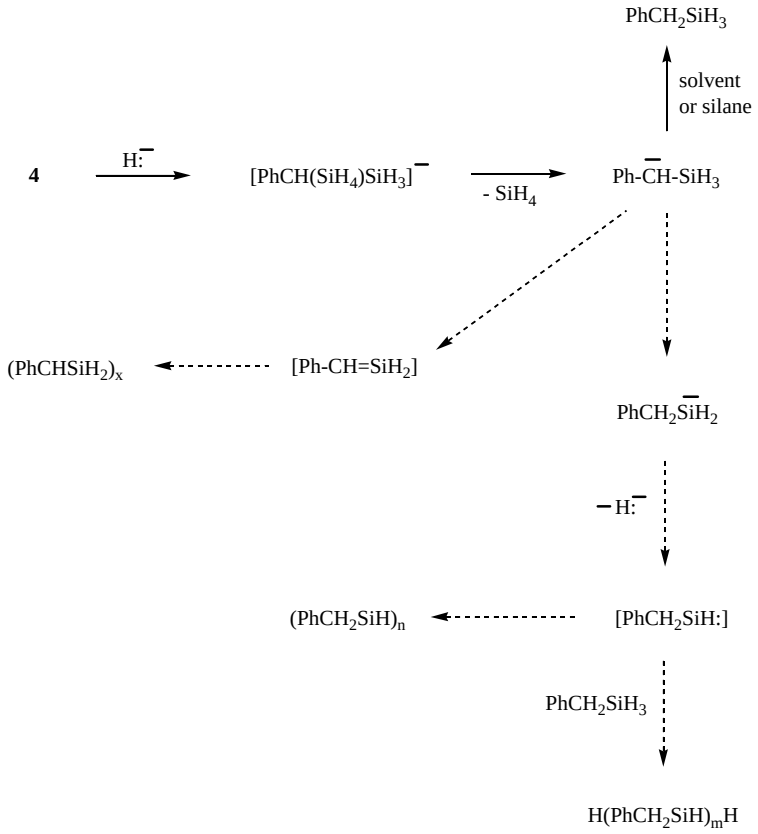


FIG. 2. Postulated mechanism for the catalytic desilanative coupling of **4** in the presence of Red-Al.

$$\mathbf{4} \xrightarrow[\substack{Cp_2MCl_2/\text{Red-Al}\\(M=Ti,Zr,Hf)}]{-H_2/-SiH_4} \text{copolymer} + \underset{\mathbf{7}}{PhCH_2SiH_3} + \underset{\mathbf{8}}{(PhCH_2)_2SiH_2}$$
$$+ \underset{\mathbf{9}}{H_3SiCH(Ph)SiH_2CH_2Ph} + \underset{\mathbf{10}}{H_3SiCH(Ph)SiH_2CH(Ph)SiH_3}$$
$$+ \underset{\mathbf{11}}{H_3SiCH(Ph)SiH_2SiH_2CH(Ph)SiH_3} \qquad (16)$$

A plausible mechanism for the redistribution-dehydrocoupling of **4** with Cp_2ZrCl_2/Red-Al is shown in Fig. 3.[57]

The mechanism involves the preferential attack of the hydride on the less hindered silicon with formation of a pentacoordinated anionic species which collapses to give an α-silyl carbanion intermediate and SiH_4 gas. The α-silyl carbanion may then take up a hydrogen from the hydrogen source (e.g., silane or solvent) to yield **7** or may lose

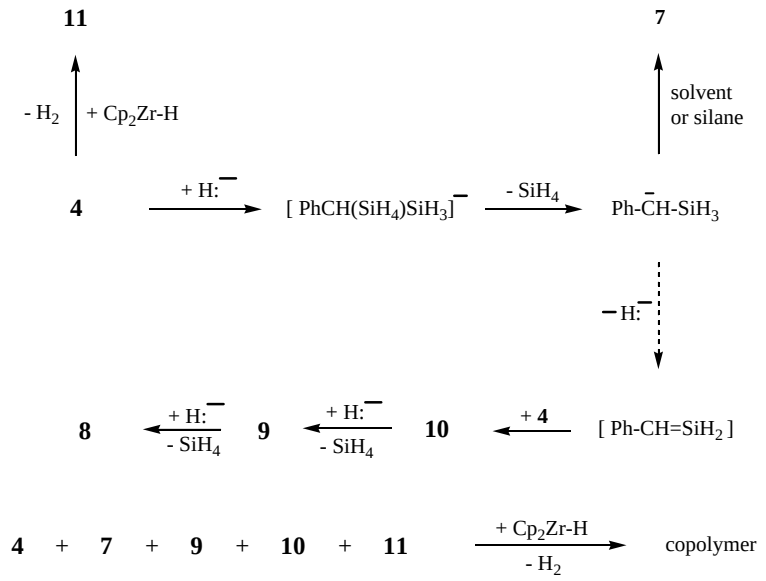
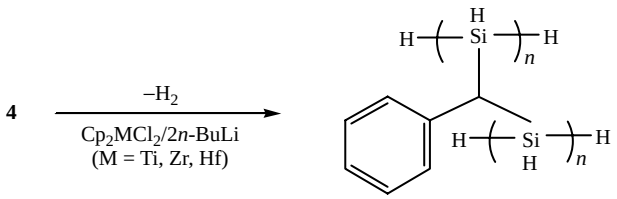


FIG. 3. Possible mechanism for the redistribution-dehydrocoupling of **4** catalyzed by Cp_2ZrCl_2/Red-Al.

a hydride, participating again in the catalytic cycle to produce phenylsilene. Experiments for trapping silene using 2,3-dimethyl-1,3-butadiene, cyclohexene, and trimethylmethoxysilane were unsuccessful, likely due to the active Si–H bonds which are abundant in the reaction mixture. Compound **4** may add to phenylsilene to give **10**, which will become **8** and **9** by sequentially losing SiH_4 gas. The silanes might then undergo catalytic dehydrocoupling to yield a copolymer.[56,57]

By comparison with the reactions as shown in Eqs. (15) and (16), dehydrocoupling (without redistribution) of **4** catalyzed by $Cp_2MCl_2/2n$-BuLi gives mostly highly cross-linked polysilanes along with soluble oily polymers as minor products [Eq. (17)].[56–58]

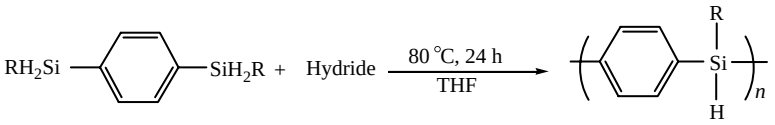


(17)

Insoluble solid polymers were isolated in 82% yield for Ti, 95% yield for Zr, and 80% yield for Hf. TGA ceramic residue yields were 72% for Ti, 73% for Zr, and 74% for Hf. The weight average molecular weights of the oily polymers were 4120 for Ti, 9020 for Zr, and 5010 for Hf. The TGA ceramic residue yields of the soluble oily polymers were ca. 14%. The dehydrocoupling mechanism of **4** should be similar to the sigma-bond metathesis for the dehydrocoupling of phenylsilane.[11,12]

B. *Redistributive Coupling of Bis(silyl)phenylenes to Hyperbranched Polymers*

As described in detail in the previous section, the desilanative coupling and desilanative-dehydrocoupling of **4** possessing a Si−C−Si connection (i.e., 1,1-bissilyl connection) in the molecule, catalyzed by Red-Al and Cp_2MCl_2/Red-Al (M = Ti, Zr, Hf), produce oligomers and polymers [Eqs. (13) and (16)], respectively.[53,56–58] In comparison, redistributive coupling of 1,4-$C_6H_4(SiH_3)_2$ **12** using 2 mol% Red-Al gave 33% of soluble polysilane (M_w: 2800; $M_w/M_n = 1.2$) and hyperbranched polysilane (TGA ceramic residue yield: 63%) which is insoluble in organic solvents because of the high degree of cross linking.[59] Similarly, redistributive coupling of **12** in the presence of 2 mol% inorganic hydride (*N*-Selectride, Super-Hydride) afforded soluble polysilane in moderate yield (30%, $M_w = 3100$ for *N*-Selectride; 27%, $M_w = 3500$ for Super-Hydride) and hyperbranched polysilane (TGA ceramic residue yield = 83% for *N*-Selectride; 67% for Super-Hydride) as shown in Eq. (18).



(18)

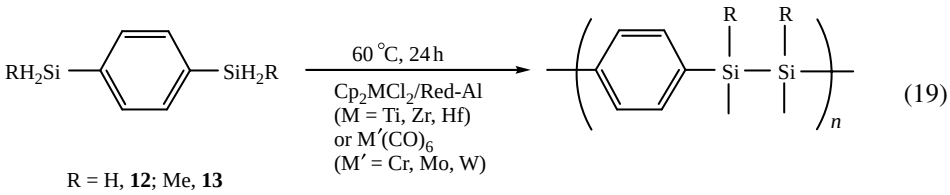
Hydride = Red-Al, N-Selectride Super-Hydride

R = H, **12**; Me, **13**; $CH{=}CH_2$, **14**

The redistributive coupling of 1,4-$C_6H_4(SiH_2Me)_2$ **13** using 2 mol% Red-Al gave 70% of soluble polysilane (M_w: 1500; $M_w/M_n = 1.5$) and hyperbranched polysilane (TGA ceramic residue yield: 70%).[59] Similarly, redistributive coupling of **13** under the influence of 2 mol% inorganic hydride (*N*-Selectride, Super-Hydride) afforded soluble polysilane in moderate yield (58%, $M_w = 2100$ for *N*-Selectride; 40%, $M_w = 2500$ for Super-Hydride) and hyperbranched polysilane (TGA ceramic residue yield: 75% for *N*-Selectride; 80% for Super-Hydride). The redistributive coupling of 1,4-$C_6H_4(SiH_2CH{=}CH_2)_2$ **14** with 2 mol% Red-Al yielded 70% of soluble polysilane (M_w: 1500, $M_w/M_n = 1.5$) and hyperbranched polysilane (TGA ceramic residue yield: 63%).[59] In the same manner, redistributive coupling of **14** in the presence of 2 mol% inorganic hydride (*N*-Selectride, Super-Hydride) afforded soluble polysilane in moderate yield (58%, $M_w = 2100$ for *N*-Selectride; 40%, $M_w = 2500$ for Super-Hydride) and hyperbranched polysilane (TGA ceramic residue yield: 75% for *N*-Selectride; 80% for Super-Hydride). Thus, steric hindrance on the silicon center increases the portion of soluble polymer as expected because it will retard the extensive redistributive coupling to form hyperbranched polysilane.

The dehydrocoupling of **12** using 1 mol% by Cp_2MCl_2/Red-Al (M = Ti, Zr, Hf) catalyst gave soluble polysilane (in 25%, $M_w = 2600$, $M_w/M_n = 1.1$ for Ti; in 15%, $M_w = 3300$, $M_w/M_n = 1.2$ for Zr; in 15%, $M_w = 3600$, $M_w/M_n = 1.1$ for Hf) and hyperbranched polysilane (TGA ceramic residue yield: ca. 60% for Ti, Zr, Hf) which is insoluble in organic solvents because of the high degree of cross linking.[60] The dehydrocoupling of **12** in the presence of 1 mol% $M'(CO)_6$ (M′ = Cr, Mo, W) catalyst also yielded soluble polysilane (in 65%, $M_w = 4100$, $M_w/M_n = 2.1$ for Cr; in 53%,

$M_w = 5100$, $M_w/M_n = 2.4$ for Mo; in 40%, $M_w = 5900$, $M_w/M_n = 2.0$ for W) and hyperbranched polysilane (TGA ceramic residue yield: ca. 70% for Cr, Mo, W).[60] The dehydrocoupling of **13** using 1 mol% Cp_2MCl_2/Red-Al (M = Ti, Zr, Hf) catalyst gave soluble polysilane (in 95%, $M_w = 1300$, $M_w/M_n = 1.4$ for Ti; in 90%, $M_w = 1400$, $M_w/M_n = 1.1$ for Zr; in 93%, $M_w = 2400$, $M_w/M_n = 1.1$ for Hf).[60] The dehydrocoupling of **13** in the presence of 1 mol% $M'(CO)_6$ (M′ = Cr, Mo, W) catalyst yielded soluble polysilane (in 75%, $M_w = 2500$, $M_w/M_n = 1.3$ for Cr; in 80%, $M_w = 2700$, $M_w/M_n = 1.1$ for Mo; in 50%, $M_w = 2720$, $M_w/M_n = 1.1$ for W) [Eq. (19)].[60]

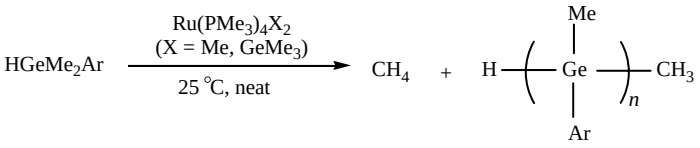


(19)

Similarly, other disilanes such as bis(1-sila-3-butyl)benzene,[57,58] 2,5-disilaoct-7-ene, 2,5-disilahexane[61] underwent dehydrocoupling in the presence of group 4 metallocene combination catalysts Cp_2MCl_2/Red-Al (M = Ti, Zr, Hf) and $Cp_2ZrCl_2/2n$-BuLi. Thus, types of substituent on silane and catalyst can make a difference in the coupling process.

C. *Demethanative Coupling of Tertiary Germanes to Polygermanes*

As described in Section II.E, polygermanes, which can be prepared by the Wurtz coupling of chlorogermanes with alkali metals and by the dehydrocoupling of hydrogermanes, show interesting physical properties. Berry and co-workers reported an extraordinary demethanative coupling of tertiary germanes to polygermanes ($M_w = 5000 \sim 10{,}000$ by light scattering measurements), catalyzed by $Ru(PMe_3)_4X_2$ (M = $GeMe_3$, Me) as shown in Eq. (20).[62]



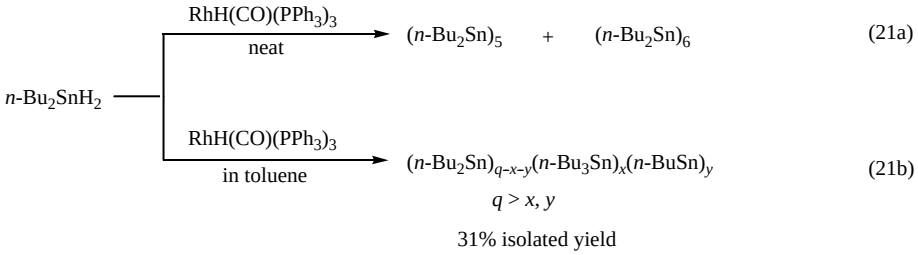
(20)

The hydrogermanes should have at least one methyl group in the molecule for demethanative coupling: $HGeMe_2Ar$ (Ar = methyl, phenyl, *p*-tolyl, *p*-fluoro, *p*-trifluorotolyl, *p*-anisyl, *m*-xylyl). Comparison of the properties of polygermanes prepared by catalytic demethanative coupling and Wurtz coupling of $MeArGeCl_2$ with sodium showed no significant differences. In principle, the demethanative coupling (removal of CH_4 gas) is similar to dehydrocoupling (removal of H_2 gas). According to the sigma-bond metathesis mechanism the dehydrocoupling of a tertiary germane should produce a digermane if the tertiary germane is not sterically demanding. If the tertiary germane is sterically demanding, no dehydrocoupling should take place.[11,12]

The authors proposed a mechanism for the demethanative coupling where Ge–C bond cleavage and Ge–Ge bond formation are attained by sequential α-CH_3 and germyl to germylene migration steps *via* an intermediacy of metal-germylene species.[62b]

D. *Redistributive Coupling of Hydrostannanes to Highly Branched Polystannanes*

As described in Section II.E, polystannanes, which can be prepared by the Wurtz coupling of chlorostannanes with alkali metals and by the dehydrocoupling of hydrostannanes, exhibit intriguing physical properties. The Sita group reported a peculiar polymerization of *n*-Bu_2SnH_2 with a $RhH(CO)(PPh_3)_3$ catalyst [Eqs. (21a) and (21b)].[63]



Normal dehydrocoupling reaction occurred to give only the cyclic oligomers (Sn_5 and Sn_6) when the reaction was carried out in neat hydrostannane with fast addition of the catalyst. However, redistributive dehydrocoupling took place to produce high molecular weight, moderately branched polystannane $[n\text{-}Bu_2Sn]_{q-x-y}(n\text{-}Bu_3Sn)_x(n\text{-}BuSn)_y$, $q > x$, y; $M_w = 50{,}240$, $M_w/M_n = 1.43$] in 31% yield without appreciable formation of cyclic oligomers when the reaction was performed in toluene with slow addition of the catalyst. The high molecular weight branched polystannane of Sita was different from the high molecular weight linear polystannane [$H(n\text{-}Bu_2Sn)_mH$; $M_w = 33{,}430$, $M_w/M_n = 2.26$] of Tilley that was produced by dehydropolymerization of *n*-Bu_2SnH_2 using Cp_2ZrMe_2 catalyst.[43c,45] The analysis of the two different polystannanes was performed using ^{119}Sn NMR, UV-vis, and GPC. The redistribution could occur *via* intermediacy of metal-stannylene species.

Woo *et al*. also described such unusual redistributive dehydrocoupling of *n*-Bu_2SnH_2 with Cp_2MCl_2/Red-Al (M = Ti, Zr, Hf) combination catalyst.[64a] The redistributive dehydrocoupling was carried out at ambient temperature for 30 min, producing soluble cyclic oligomers (Sn_5 and Sn_6) and insoluble hyperbranched polystannane $[n\text{-}Bu_2Sn]_{p-x}(n\text{-}BuSn)_x$] as depicted in Eq. (22).

$$n\text{-}Bu_2SnH_2 \xrightarrow[\text{neat, 25 °C, 30 min}]{Cp_2MCl_2/\text{Red-Al(M = Ti,Zr,Hf)}} (n\text{-}Bu_2Sn)_5 + (n\text{-}Bu_2Sn)_6 + (n\text{-}Bu_2Sn)_{q-x}(n\text{-}BuSn)_x \quad (22)$$

The insoluble products (TGA ceramic residue yield = ca. 33%) were obtained in moderate yield (for Ti, 39%; for Zr, 27%; for Hf, 26%) as a yellow solid. Similarly,

the Woo group carried out the redistributive dehydrocoupling of Bu_2SnH_2 with $M'(CO)_6$/Red-Al (M' = Cr, Mo, W) at ambient temperature for 16 h to give soluble oligomers and insoluble hyperbranched polystannane. The insoluble product (TGA ceramic residue yield = ca. 33%) was obtained in moderate yield (for Cr, 40%; for Mo, 48%; for W, 39%) as a yellow solid. The Woo group also reported the redistributive dehydrocoupling of Bu_3SnH with Cp_2MCl_2/Red-Al (M = Ti, Zr, Hf) and $M'(CO)_6$/Red-Al (M' = Cr, Mo, W) at 70 °C (for group 4 catalyst) or 90 °C (for group 6 catalyst) for 3 days to give soluble oligomer (mainly, Sn_2) and insoluble hyperbranched polystannane (TGA ceramic residue yield = ca. 33%; for Ti, 17%; for Zr, 14%; for Hf, 13%; for Cr, 23%; for Mo, 23%; for W, 7%).[64b]

IV
HYDROSILATION

A. *Hydrosilation*

The addition of Si–H bond to unsaturated bonds such as alkenes (including C=C, C=O, C=N, C=metal, etc.) and alkynes (including C≡C, C≡N, C≡metal, etc.) is termed *hydrosilation* (can be also termed *hydrosilylation*) and is promoted by many homogeneous transition-metal complex catalysts and heterogeneous supported metal catalysts.[65] Hydrosilation is an important reaction of forming Si–C bonds in organic chemistry.[66] The reactions are quite problematic due to many factors such as induction periods, irreproducible kinetics, apparent radical chain processes, olefin isomerization/dimerization, high sensitivity of the products to the nature of the hydrosilating reagent, and obscureness of the hydrosilation catalysts.[67] Catalytic hydrosilations are very complex processes and the overall mechanisms are not well understood although plausible mechanisms can be described for the hydrosilations based on known reaction steps (suggested from structural elucidation studies of intermediates) and kinetic studies. Chalk and Harrod proposed a simplified mechanism (Chalk–Harrod mechanism) for transition metal complex-catalyzed hydrosilation involving coordination of alkenes to a coordinatively unsaturated transition metal hydride residue, followed by metal-hydride insertion, oxidative addition of the silane to the metal alkyl, then reductive elimination of the alkylsilane to regenerate the metal-hydride (Fig. 4).[68]

Although the Chalk–Harrod mechanism has been widely accepted,[69] some phenomena (include an induction period for many precatalysts and the formation of vinylsilanes) cannot be explained well by the Chalk–Harrod mechanism. An alternative mechanism to the Chalk–Harrod mechanism involves insertion of the alkene into the M–Si bond instead of insertion of the alkene into the M–H bond (Fig. 5).[70]

The modified Chalk–Harrod mechanism was suggested by several researchers on the basis of identification of intermediates in hydrosilations catalyzed by metals such as Fe, Co, Rh, and Pd. Alternative mechanisms were also proposed by several researchers on the basis of their studies with their own catalytic systems such as Seitz–Wrighton mechanism

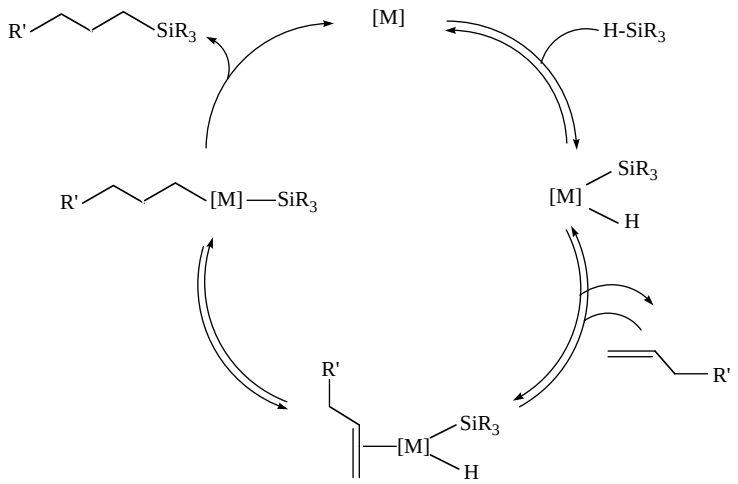


FIG. 4. Chalk–Harrod mechanism for the transition metal complex-catalyzed hydrosilation of olefin.

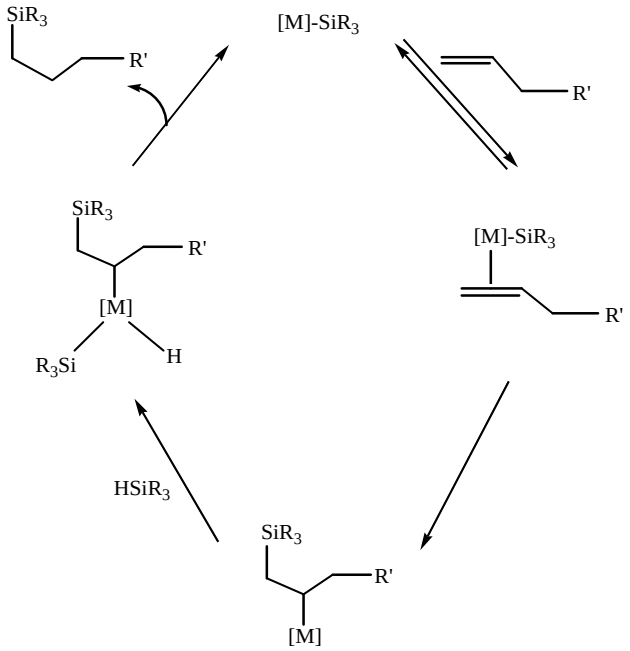
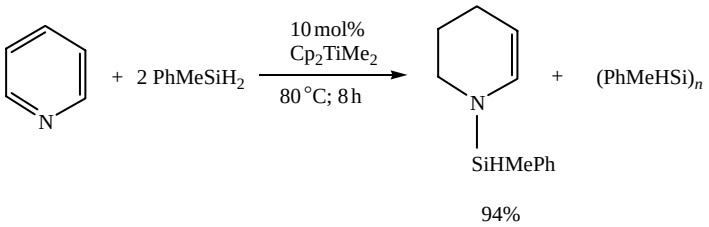


FIG. 5. Modified Chalk–Harrod mechanism for the transition metal complex-catalyzed hydrosilation of olefin.

(for hydrosilation–dehydrosilation of alkenes), Duckett–Perutz mechanism (for hydrosilation of alkenes using two-silicon cycle), Karstedt mechanism (for dehydrosilation of alkenes catalyzed by Karstedt type of Ni complex), and Brookhard–Grant mechanism (for silyl migration in the hydrosilation catalyzed by cobalt(III) cationic complex where an agostic interaction was involved).[71]

The Gevorgyan group recently reported the highly efficient $B(C_6F_5)_3$-catalyzed hydrosilation of differently substituted alkenes.[72] In the paper, the authors newly proposed a simple Lewis Acid-catalyzed hydrosilation mechanism unlike the known complex Lewis-Acid-catalyzed hydrosilation mechanisms proposed by Wetter, Yamamoto, and Lambert.[73] Several research groups reported the highly regioselective hydrosilation of terminal alkynes catalyzed by $Cp^*_2AnMe_2$ (An = Th, U), [74a] $Cp^*RuH_3(PPh_3)$,[74b] $[Cp^*Rh(BINAP)](SbF_6)_2$.[74c] Takahashi *et al*. described regioselective *syn*-hydrosilation of internal alkynes, catalyzed by $Cp_2TiCl_2/2n$-BuLi.[75] The Johannsen group reported the asymmetric hydrosilation of aromatic alkenes with $HSiCl_3$, catalyzed by a $[ClPd(C_3H_5)]_2$/chiral phosphoramidite complex.[76a] Hayashi and co-workers also reported the asymmetric hydrosilation of aromatic alkynes with $HSiCl_3$, promoted by $[Cl_2Pd(C_2H_4)]_2$/(*R*)-2-bis[3,5-bis(trifluoromethyl)phenyl]phosphino-1,1′-binaphthyl complex.[76b]

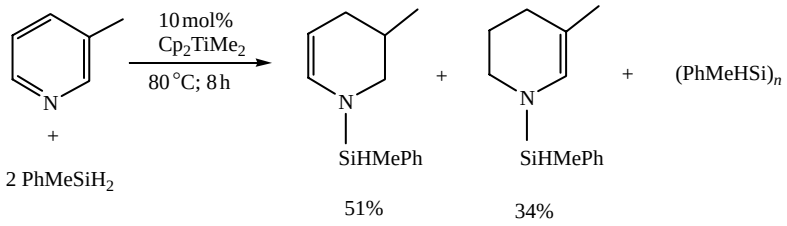
The Yoshida group reported an interesting $RhCl(PPh_3)_3$-catalyzed hydrosilation of alkenes and alkynes using dimethyl(2-pyridyl)silane.[77] Since the $PyMe_2Si$ group has the phase tag property due to the basicity of pyridyl substituent, hydrosilation products were readily isolated in greater than 95% purity by simple acid–base extraction. However, appreciable hydrosilation of the pyridyl ring of dimethyl(2-pyridyl)silane was not observed from the reaction. In comparison, Woo, Harrod and co-workers reported the hydrosilation–hydrogenation of various pyridine derivatives using Cp_2TiMe_2 catalyst and $PhMeSiH_2$ as the source of Si–H.[78] Typically, the reaction is carried out without solvent with a 2:1 molar ratio of silane to pyridine and 10 mol% (based on the mol of pyridine) of Cp_2TiMe_2, affording hydrogenation–hydrosilation product in 85% yield [Eq. (23)].[78a]



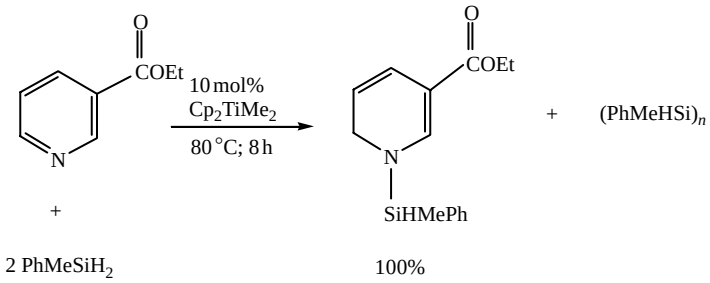
(23)

The initial step in the reaction could be the addition of a Ti–Si species across the C=N bond of the pyridine to give an *N*-silyldihydropyridine. An additional two hydrogen atoms can be transferred to produce the tetrahydropyridine, but complete reduction only occurs in the presence of H_2. On the other hand, electron-donating substituents and electron-withdrawing substituents on pyridine derivatives affect the reactions in different ways. 3-Picoline with electron-donating substituents gives two hydrogenation–hydrosilation isomers in a 3:2 ratio in 85% yield [Eq. (24)] whereas ethyl nicotinate with

electron-withdrawing substituents gives only the hydrosilation product in quantitative yield [Eq. (25)].[78b]



(24)



(25)

The reaction rate is strongly dependent on the electronic and steric effects of the substituents. The relative reaction rate decreases in the order of ethyl nicotinate (50) > pyridine (20) > 3-picoline (7) > 4-picoline (3) > 3,5-lutidine (1).[78b]

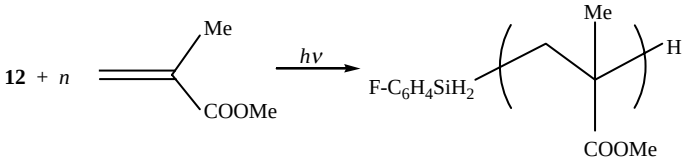
B. *Hydrosilapolymerization of Vinyl Monomers with Hydrosilanes to Organic Polymers Having Reactive Hydrosilyl End Groups*

The common *hydrosilation* of olefins described in Section IV.A is the *single* addition of Si–H bond to vinyl derivatives in the presence of organic or inorganic catalysts by adding more excess hydrosilanes than olefins. Versatile polymers can be prepared by continuous multiple hydrosilation: (a) hydrosilation of $CH_2{=}CH(CH_2)_xSiR_2H$ ($x = 0 \sim 2$; R = H, Me, OMe, Cl), (b) hydrosilation of $[CH_2{=}CH(CH_2)_x]_2Y$ ($x = 0 \sim 2$; Y = CH_2, CMe_2, $SiMe_2$, $GeMe_2$, phenylene, etc.) with R_2SiH_2 or $HSiMe_2{-}X{-}SiMe_2H$ [X = $(SiMe_2{-}O)_n$, CH_2, CMe_2, $SiMe_2$, $GeMe_2$, phenylene, etc.], (c) hydrosilation of olefin with $(RSiH)_n$, and (d) hydrosilapolymerization of vinyl monomer with hydrosilane or $(RSiH)_n$. For example, the Weber group prepared a series of new 3,3,3-trifluoropropyl substituted copoly(carbosiloxane)s by step-growth hydrosilation copolymerization of 1,9-dihydrido-1,1,3,5,7,9,9-heptamethyl-3,5,7-tris(3′,3′,3′-trifluoropropyl)pentasiloxane with various α,ω-divinylsilanes and siloxanes using Karsted's catalyst, Pt-divinyltetramethyldisiloxane.[79a] Weber *et al.* also synthesized copoly(arylene-1,2-dioxy/oligodimethylsiloxanylene)s by dehydrosilation condensation copolymerization of *o*-quinones with α,ω-dihydridooligodimethylsiloxanes catalyzed by $H_2(CO)Ru(PPh_3)_3$.[79b] Woo and co-workers prepared new preceramic

polymers (for making SiC ceramics) such as a copolymer of polycarbosilane–dichloromethylvinylsilane and a copolymer of polycarbosilane-γ-methacryloxypropyl-trimethoxysilane by hydrosilation copolymerization under the influence of Pt-based catalyst.[79c,d] Interestingly, Woo and co-workers reported a novel consecutive *multiple* addition (which has been coined *hydrosilapolymerization*) of vinyl monomers to hydrosilanes thermally and photochemically to produce the first organic polymers with reactive hydrosilyl end groups by the addition of excess olefin with respect to hydrosilane.[80a–m]

Green photopolymerization technology is widely used commercially in surface coatings, photoresists, adhesives, and holography.[81] Only a few vinyl monomers, including methyl methacrylate (MMA), absorb the most convenient wavelength of light in the range of 250–500 nm for common experimental work. Despite an incomplete understanding of the detailed mechanism of photochemically forming the propagating radicals, it seems to involve the transformation of an electronically excited singlet state of the vinyl monomer to a long-lived excited triplet state of propagating radical.[82]

The bulk photopolymerization of MMA with *para*-substituted phenylsilanes such as *p*-F-$C_6H_4SiH_3$ (**12**), *p*-H_3C-$C_6H_4SiH_3$ (**13**), and *p*-H_3CO-$C_6H_4SiH_3$ (**14**) produces poly(MMA)s containing the respective silyl moiety as an end group.[80l] Poly(MMA)s possessing the *p*-F-$C_6H_4SiH_2$ moiety as an end group with weight average molecular weight (M_w) of 6200–22,020 and TGA residue yields of 12–73% were prepared in 24–85% yields by 300 nm UV light-initiated bulk polymerization of MMA with different molar ratios of **12** (MMA: **12** = 9:1 through 3:7) as shown Eq. (26).



(26)

Similarly, poly(MMA)s possessing *p*-H_3C–$C_6H_4SiH_2$ end groups with weight average molecular weights (M_w) of 8130–28,090 and TGA residue yields of 12–67% were prepared in 30–93% yields by the bulk polymerization of MMA with different molar ratios of **13**. Poly(MMA)s possessing *p*-H_3CO–$C_6H_4SiH_2$ end groups with weight average molecular weights (M_w) of 6080–21,100 and TGA residue yields of 18–78% were also prepared in 21–73% yields by the bulk polymerization of MMA with different molar ratios of **14**. For all the hydrosilanes, the polymerization yields and the polymer molecular weights decreased, whereas the TGA residue yields and the relative intensities of Si–H IR stretching bands increased as the relative silane concentration compared to MMA increased. Thus, for all the hydrosilanes the highest polymerization yield and polymer molecular weight were obtained for MMA:hydrosilane = 9:1, but the highest TGA residue yield was obtained for MMA:hydrosilane = 3:7. The polymerization yields and polymer molecular weights of MMA with **12**–**14** increased in the order of **14** < **12** < **13**.

Weak resonances corresponding to the expected *para*-substituted phenylsilyl end groups appeared, but the resonances corresponding to the potential vinyl end groups were not observed in the ^1H NMR spectra of the poly(MMA)s within detectable limits. One may anticipate that the silane reactivity (which could be directly related to the hydrogen

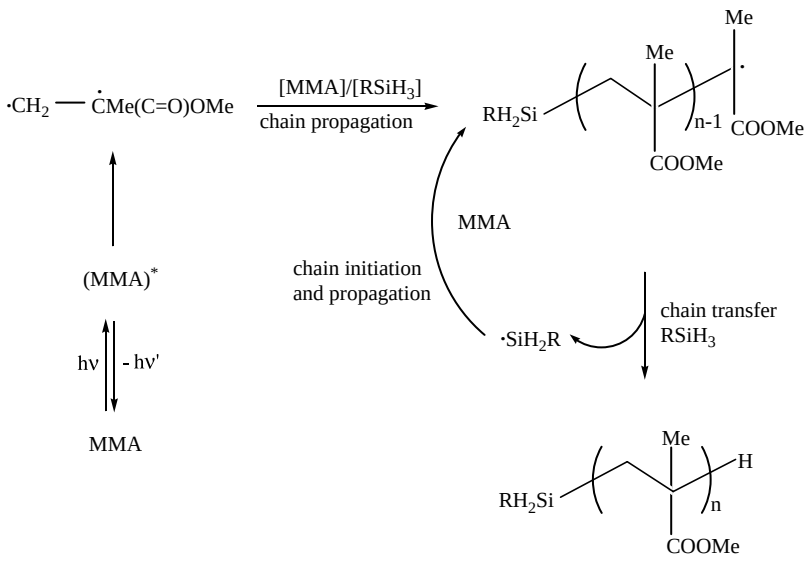


FIG. 6. Postulated mechanism for the photopolymerization of MMA with $RSiH_3$.

donation ability of the silane) would increase in the order **12** < **13** < **14** toward photopolymerization in consideration of only electronic effects because the steric effect of *para*-substituent should be negligible. However, the reactivity order was not observed. The mechanism for the photopolymerization of MMA with **12**–**14** could be similar to those with other hydrosilanes (Fig. 6).

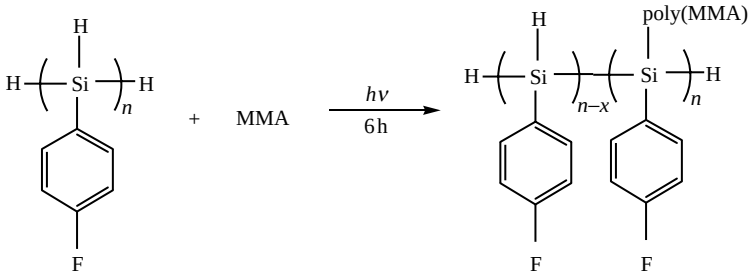
Light absorption of a MMA molecule is well known to produce an excited singlet state of MMA which may then either fluoresce with a return to the ground state of MMA or may be converted to a long-lived triplet excited state, the diradical of the MMA monomer.[82] Addition on another MMA by this diradical gives a new diradical of MMA dimer which either reverts to the ground state or continues attacking other MMAs to produce poly(MMA)s. Under neat conditions the latter will be a predominant process to produce poly(MMA) radicals. At high [MMA]/[silane] ratios, chain propagation will be able to compete with chain transfer over the poly(MMA) radicals. However, chain transfer will eventually rule over chain propagation with increasing silane concentration. Chain transfer might produce a silyl radical which, in turn, leads to chain initiation, resulting in the production of poly(MMA) containing silyl end groups. Higher concentrations of hydrosilane over MMA produces shorter chain lengths of poly(MMA), which contributes to the increase in thermal stability of poly(MMA).

Other hydrosilanes similarly exhibit the characteristic trends[80a–d,i,k] as the *p*-substituted phenylsilanes do in the photopolymerization of MMA[80l] while the polymer molecular weights and the polymerization yields decline, the relative intensities of Si–H IR stretching bands and the TGA residue yields increase when increasing the silane molar ratio over MMA. The increase of Si–H contents with respect to poly(MMA) moiety will result in the higher possibility of high temperature cross-linking hydrosilation with C=O groups in poly(MMA), which will give higher thermal stability (i.e., higher TGA ceramic

residue yield). The hydrosilanes include $PhSiH_3$, $PhCH_2SiH_3$, $PhMeSiH_2$, Ph_2SiH_2, $PhSiH_2SiH_2Ph$, $PhCH(SiH_3)_2$, and 1,4-$C_6H_4(SiH_{3-x}Me_x)_2$. The monomers include MMA, AA (acrylic acid), MA (methacrylic acid), HEMA (2-hydroxyethyl methacrylate), and styrene. The hydrosilapolymerization yield of styrene was lower than those of MMA, MA, and HEMA. No appreciable thermal and photopolymerizations of the vinyl monomers with $CH_2(CH_2)_5SiH_3$, $Ph(CH_2)_2SiH_3$, Ph_3SiH, and $(mesityl)_2SiH_2$ were observed, probably because of their steric and/or electronic effects. Therefore, the types of vinyl monomer and hydrosilane appear to be important for successful hydrosilapolymerization. The thermal polymerization of MMA with hydrosilanes also shows a similar trend.[80e,j] Furthermore, the thermal and photopolymerization of MA with hydrosilanes also exhibit a similar trend.[80f–h] The TGA ceramic residue yields of poly(MA)s were higher than those of poly(MMA)s probably because when compared to poly(MMA), which has a cross-linking site of C=O in a repeating unit, poly(MA) has two cross-linking sites (C=O and OH), leading to higher cross linking. The thermal and photocopolymerization of MMA and MA with the hydrosilanes show a similar trend.[80m]

C. *Graft Hydrosilacopolymerization of Vinyl Monomers on Poly(hydrophenylsilane)s to Inorganic–Organic Hybrid Polymers*

Chatgilialoglu *et al*. reported the reactivity study of alkyl peroxy radicals toward poly(hydrosilane)s.[83] The Woo group extended the above consecutive hydrosilation (*or hydrosilapolymerization*) methodology to poly(hydrophenylsilane)s instead of monomeric hydrosilanes for first making novel inorganic–organic hybrid graft copolymers. Such inorganic–organic hybrid graft copolymers can be used for many applications in contact lens, paints, etc. Poly(*p*-fluoro-substituted phenylsilane), H[(*p*-F-C_6H_4)SiH]$_n$H, ($M_w = 3300$; $M_w/M_n = 1.83$) was prepared by dehydropolymerization of *p*-F-$C_6H_4SiH_3$ using the Cp_2ZrCl_2/Red-Al combination catalyst. In a typical photopolymerization experiment, a quartz tube (15 mm × 120 mm) charged with MMA, poly(*p*-fluoro-substituted phenylsilane), and toluene (1 mL) was degassed, sealed, and irradiated with UV-light (280 nm) for 6 h. Precipitation with *n*-hexane and drying *in vacuo* give poly(*p*-fluoro-substituted phenylsilane)-*g*-poly(MMA), which is an inorganic–organic hybrid graft copolymer [Eq. (27)].[84a]



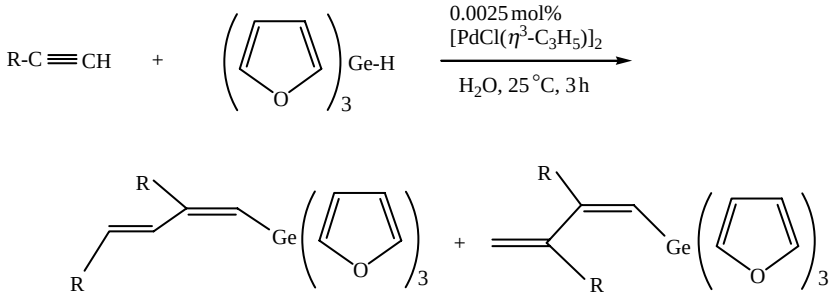
(27)

In this photopolymerization, various molar ratios of polysilane:MMA are used: 1:1, 1:5, 1:10, 1:20, 1:50. Similarly, in the graft photopolymerization, while the polymer molecular weights and the polymerization yields decrease, the relative

intensities of Si–H IR stretching bands and the TGA residue yields increase with the increase of silane molar ratio over MMA. The higher contents of Si–H moieties remaining in the graft copolymer backbone will result in the higher possibility of high temperature cross-linking hydrosilation with C=O groups in the graft chain of poly(MMA), swhich will give higher thermal stability (i.e., higher TGA ceramic residue yield). For the other vinyl monomers such as MA and styrene, similar trends are observed.[84b] Similar trends are also observed for the copolymerization of MMA–MA, MMA–styrene, and MA–styrene.[84c] Furthermore, for various other poly(hydroarylsilane)s prepared by Cp_2MCl_2/Red-Al (M = Ti, Zr, Hf) combination catalyst, similar trends are found.[84c]

D. *Hydrogermation/Hydrostannation*

Hydrogermation and hydrostannation are very important methods of forming E–C bonds (E = Ge, Sn) in organic chemistry which are similar to hydrosilation. The addition of E–H bond (E = Ge, Sn) to unsaturated bonds is termed *hydrogermation* (or also termed *hydrogermylation*) and *hydrostannation* (or also termed *hydrostannylation*), respectively, and is promoted by many homogeneous transition-metal complex catalysts and heterogeneous supported metal catalysts.[85] Recently Oshima and co-workers reported a highly stereo- and regioselective hydrogermation of terminal alkynes in water, catalyzed by 0.0025 mol% (unusually low catalyst loading) of $[PdCl(\eta^3 - C_3H_5)]_2$/tris(2-^{t}Bu-phenoxy)phosphine, to produce dienylgermanes [Eq. (28)].[86]



(28)

In the reaction, no phase transfer catalysts are needed. Furthermore, the reaction in water proceeds much faster than the reaction under neat conditions. (Germyl)stannanes and digermanes may be used for germylstannation and double germation, respectively.[87] The Hosomi group described the regio- and stereoselective hemolytic hydrostannation of propargyl alcohols and ethers with $HSnBu_2Cl$, catalyzed by the Lewis Acid Et_3B.[88] The regioselectivity was not as high as that with the propargyl alcohols. Catalytic hydrogermation and hydrostannation could be complex processes and the overall mechanisms are not well understood although plausible mechanisms could be similar to the Chalk and Harrod mechanism or modified Chalk–Harrod mechanism.[68] Hydrogermapolymerization and hydrostannation of MMA and MA on poly(hydroarylsilane)s gave similar trends as the hydrosilapolymerization of MMA and MA.[89]

V

CONCLUSIONS

Main group 4 hydrides possessing reactive E–H (E = Si, Ge, Sn) bonds can be used in synthesizing new functional materials with interesting physical properties under the influence of various promoters such as metals, organometallic complexes, inorganic hydrides, heat, and UV-irradiation. Catalytic coupling of hydrosilanes with molecules having active E′–H bonds (E′ = Si, O, N) or vinylic bonds through Si–Si/Si–O–Si–N dehydrocoupling, redistributive coupling, and addition processes is described in this chapter as selective examples of our recent research developments. Coupling–addition processes are shown to be effective approaches for the incorporation of useful group 14 element entities into both small to large molecules. Numerous possible reactions with group 14 hydrides remained to be examined with high expectation, and some are outlined in the body of the chapter.

Acknowledgements

We thank our co-workers (graduate students, postdoctoral associates, research professors, visiting scientists, and collaborating researchers), who appear as coauthors in the references cited, for their devoting contributions in evolving this remarkable coupling-addition chemistry of hydrosilanes, hydrogermanes, and hydrostannanes successfully. H. G. Woo is indebted to the Korea Science and Engineering Foundation (Grant Number R01-2001-000-00053-0;2003) for its generous support of his research reported herein. H. G. Woo is particularly grateful to his chemistry mentors (Prof. T. Don Tilley at U.C. Berkeley, Prof. John F. Harrod at McGill University, Prof. Dietmar Seyferth at M.I.T., Prof. Robert West at University of Wisconsin, Madison, and Prof. Ian Fleming at Cambridge University) working in organosilicon chemistry for their continuous support with encouragement and guidance, and to Prof. David Y. Son at Southern Methodist University for the scholastic exchange with stimulating communications in the field of organosilicon chemistry.

References

(1) Odian, G. *Principles of Polymerization*, 3rd ed., Wiley, New York, 1991.
(2) (a) Wisian-Neilson, P.; Allcock, H. R.; Wynne, K. J. (Eds.), *Inorganic and Organometallic Polymers II*, ACS Symposium Series 572, American Chemical Society, Washington, DC, 1994. (b) Laine, R. M. (Ed.), *Design, Activation, and Transformation of Organometallics into Common and Exotic Materials*, NATO ASI Series E, no. 141, Martinus Nijhof, Amsterdam, 1988.
(3) Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*, 2nd ed., Prentice-Hall, New York, 1990, Chapter 9.
(4) (a) Kricheldorf, H. R. (Ed.), *Silicon in Polymer Synthesis*, Springer, Berlin, 1996. (b) Jones, R. G. (Ed.), *Silicon-Containing Polymers*, The Royal Society of Chemistry, Cambridge, 1995.
(5) (a) Regitz, M.; Binger, P. *Angew. Chem. Int. Ed.* **1988**, *27*, 1484. (b) West, R. *Angew. Chem. Int. Ed.* **1987**, *26*, 1201.
(6) Sakamoto, K.; Yoshida, M.; Sakurai, H. *Macromolecules* **1990**, *23*, 4494.
(7) (a) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246. (b) Dewar, M. J. S. *Organometallics* **1986**, *5*, 375. (c) Jackson, R. A. J. *Organomet. Chem.* **1979**, *166*, 17.
(8) West, R. *J. Organomet. Chem.* **1986**, *300*, 327.
(9) Ziegler, J. M.; Fearon, F. W. G. (Eds.), *Silicon-Based Polymer Science*, Advances in Chemistry Series 224, American Chemical Society, Washington, DC, 1990.

(10) (a) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359, and references cited therein. (b) Matyjaszewski, K.; Chen, Y. L.; Kim, H. K. (M. Zeldin, K. J. Wynne, H. R. Allcock, Eds.) *Inorganic and Organometallic Polymers*, ACS Symposium Series 360, American Chemical Society, Washington, DC, 1988, 78.
(11) Gauvin, F.; Harrod, J. F.; Woo, H.-G. *Adv. Organomet. Chem.* **1998**, *42*, 363, and references cited therein.
(12) (a) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22, and references cited therein. (b) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10*, 37.
(13) (a) Corey, J. Y. *Adv. Silicon Chem.* **1991**, *1*, 327, and references cited therein. (b) Corey, J. Y. *Adv. Organomet. Chem.* **2004**, in press; and references cited therein.
(14) Banovetz, J. P.; Stein, R. M.; Waymouth, R. M. *Organometallics* **1991**, *10*, 3430.
(15) Choi, N.; Onozawa, S.-Y.; Sakakura, T.; Tanaka, M. *Organometallics* **1997**, *16*, 2765.
(16) Dioumaev, V. K.; Harrod, J. F. *Organometallic* **1994**, *13*, 1548.
(17) (a) Woo, H.-G.; Kim, S.-Y.; Han, M.-K.; Cho, E. J.; Jung, I. N. *Organometallics* **1995**, *14*, 2415. (b) Woo, H.-G.; Song, S.-J. *Chem. Lett.* **1999**, 457. (c) Woo, H.-G.; Kim, B.-H, in preparation. (d) Resel, R.; Leising, G.; Lunzer, F.; Marschner, Ch. *Polymer* **1998**, *39*, 5257. (e) Woo, H.-G.; Kim, B.-H., submitted.
(18) Li, H.; Gauvin, F.; Harrod, J. F. *Organometallics* **1993**, *12*, 575.
(19) Dioumaev, V. K.; Harrod, J. F. *Organometallics* **1996**, *15*, 3859.
(20) Campbell, W. H.; Hilty, T. K.; Yurga, L. *Organometallics* **1989**, *8*, 2615.
(21) (a) Aitken, C.; Harrod, J. F.; Gill, U. S. *Can. J. Chem.* **1987**, *65*, 1804. (b) Harrod, J. F.; Yun, S. S. *Organometallics* **1987**, *6*, 1381. (c) Aitken, C.; Barry, J.-P.; Gauvin, F.; Harrod, J. F.; Malek, A.; Rousseau, D. *Organometallics* **1989**, *8*, 1732. (d) Harrod, J. F.; Ziegler, T.; Tschinke, V. *Organometallics* **1990**, *9*, 897. (e) Woo, H.-G.; Harrod, J. F.; Henique, J.; Samuel, E. *Organometallics* **1993**, *12*, 2883. (f) Britten, J.; Mu, Y.; Harrod, J. F.; Polowin, J.; Baird, M. C.; Samuel, E. *Organometallics* **1993**, *12*, 2672.
(22) (a) Woo, H.-G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 3757. (b) Woo, H.-G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 8043. (c) Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *Macromolecules* **1991**, *24*, 6863. (d) Woo, H.-G.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 5698. (e) Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 7047. (f) Banovetz, J. P.; Suzuki, H.; Waymouth, R. M. *Organometallics* **1993**, *12*, 4700. (g) Imori, T.; Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *Chem. Mater.* **1993**, *5*, 1487. (h) Corey, J. Y.; Huhmann, J. L.; Zhu, X.-H. *Organometallics* **1993**, *12*, 1121.
(23) (a) Woo, H.-G.; Kim, S.-Y.; Kim, W.-G.; Cho, E. J.; Yeon, S. H.; Jung, I. N. *Bull. Korean Chem. Soc.* **1995**, *16*, 1109. (b) Woo, H.-G.; Song, S.-J.; Han, M.-K.; Cho, E. J.; Jung, I. N. *Bull. Korean Chem. Soc.* **1995**, *16*, 1242. (c) Woo, H.-G.; Song, S.-J. *Bull. Korean Chem. Soc.* **1996**, *17*, 494. (d) Woo, H.-G.; Song, S.-J. *Bull. Korean Chem. Soc.* **1996**, *17*, 1040. (e) Woo, H.-G.; Kim, B.-H.; Song, S.-J.; Han, M.-K.; Kim, S.-Y.; Kim, J.-H.; Lee, J. S. *Bull. Korean Chem. Soc.* **2000**, *21*, 935.
(24) West, R. (A. G. Davis, Ed.) *Comprehensive Organometallic Chemistry II*, Pergamon Press, Oxford, 1995. pp. 77–110.
(25) Luo, J.; Xie, Z.; Lam, J. W. Y.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D.; Tang, B. Z. *J. Chem. Soc., Chem. Commun.* **2001**, 1740.
(26) (a) Sohn, H.; Woo, H.-G.; Powell, D. R. *J. Chem. Soc., Chem. Commun.* **2000**, 697. (b) Woo, H.-G.; Kim, B.-H.; Sohn, H. *Chem. Lett.* **2000**, 544.
(27) Tamao, K.; Uchida, M.; Izumizawa, T.; Furukawa, K.; Yamaguchi, S. *J. Am. Chem. Soc.* **1996**, *118*, 11974.
(28) (a) Sohn, H.; Huddleston, R. R.; Powell, D. R.; West, R. *J. Am. Chem. Soc.* **1999**, *121*, 2935. (b) Tamao, K.; Yamaguchi, S. *Pure Appl. Chem.* **1996**, *68*, 139. (c) Yamaguchi, S.; Tamao, K. *J. Chem. Soc., Dalton Trans.* **1998**, 3693. (d) Yamaguchi, S.; Jin, R.-Z.; Tamao, K. *J. Am. Chem. Soc.* **1999**, *121*, 2937. (e) Kanno, K.; Ichinohe, M.; Kabuto, C.; Kira, M. *Chem. Lett.* **1998**, 99.
(29) (a) Sanji, T.; Sakai, T.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1998**, *120*, 4552. (b) Sohn, H.; Sailor, M. J.; Magde, D.; Trogler, W. C. *J. Am. Chem. Soc.* **2003**, *125*, 3821. (c) Woo, H.-G.; Kim, B.-H.; Song, S.-J., in preparation.
(30) (a) Chauhan, B. P. S.; Shimizu, T.; Tanaka, M. *Chem. Lett.* **1997**, 785. (b) Trogler, W. C.; Sohn, H.; Liu, S.; Toal, S. *Abstracts of Papers*, 225th ACS National Meeting, New Orleans, March 23–27, 2003, INOR-I746.
(31) Kim, B.-H.; Cho, M.-S.; Kong, J.-I.; Woo, H.-G., submitted.
(32) (a) Kim, B.-H.; Woo, H.-G. *Organometallics* **2002**, *21*, 2796. (b) Woo, H.-G.; Song, S.-J.; Kim, B.-H.; Yun, S. S. *Mol. Cryst. Liq. Cryst.* **2000**, *349*, 87. (c) Kim, B.-H.; Cho, M.-S.; Kong, J.-I.; Woo, H.-G.; Lee, S.-W.; Lee, C.-J. *Mol. Cryst. Liq. Cryst.* **2004**, in press.

(33) (a) Hong, J.-H.; Boudjouk, P. *J. Am. Chem. Soc.* **1993**, *115*, 5883. (b) Hong, J.-H.; Boudjouk, P.; Castellino, S. *Organometallics* **1994**, *13*, 3387. (c) West, R.; Sohn, H.; Bankwitz, U.; Calabrese, J.; Apeloig, Y.; Mueller, T. *J. Am. Chem. Soc.* **1995**, *117*, 11608.
(34) (a) Lukevics, E.; Dzintara, M. *J. Organomet. Chem.* **1985**, *295*, 265. (b) Pitt, C. G. (A. L. Rheingold, Ed.) *Homoatomic Rings, Chains, and Macromolecules of Main-Group Elements*, Elsevier, Amsterdam 1977, 203.
(35) (a) Bedard, T. C.; Corey, J. Y. *J. Organomet. Chem.* **1992**, *428*, 315. (b) Li, Y.; Kawakami, Y. *Macromolecules* **1999**, *32*, 6871. (c) Zhang, R.; Mark, J. E.; Pinhas, A. R. *Macromolecules* **2000**, *33*, 3508. (d) Baruah, J. B.; Osakada, K.; Yamamoto, T. *Organometallics* **1996**, *15*, 456.
(36) (a) Sommer, L. H.; Lyons, J. E. *J. Organomet. Chem.* **1967**, *89*, 1521. (b) Corriu, R. J. P.; Moreau, J. J. *J. Chem. Soc., Chem. Commun.* **1973**, 38. (c) Ojima, I.; Kogure, T.; Nihonyanagi, M.; Kono, H.; Inaba, S.; Nagai, Y. *Chem. Lett.* **1973**, 501.
(37) (a) Kim, B.-H.; Park, S.-H.; Kim, M.-S.; Woo, H.-G., in preparation. (b) Kim, B.-H.; Woo, H.-G., in preparation. (c) Koe, J. R.; Motonaga, M.; Fujiki, M.; West, R. *Macromolecules*, **2001**, *34*, 706.
(38) Kim, B.-H.; Cho, M.-S.; Kim, M.-A.; Woo, H.-G. *J. Organomet. Chem.* **2003**, *685*, 93.
(39) (a) Wang, J. X.; Dash, A. K.; Berthet, J. C.; Ephritikhine, M.; Eisen, M. S. *J. Organomet. Chem.* **2000**, *610*, 49. (b) Sneddon, L. G.; Kai, S.; Fazen, P.; Lynch, A. T.; Remsen, E. E.; Beck, J. S. (J. F. Harrod, R. M. Laine, Eds.) *Inorganic and Organometallic Polymers and Oligomers*, Kluwer Academic Publishers, Dordrecht, The Netherlands 1991, 199. (c) Laine, R. M.; Babonneau, F. *Chem. Mater.* **1993**, *5*, 260. (d) Woo, H.-G. *Postdoctoral Research Report*, Massachusetts Institute of Technology, MA, USA 1991. (e) Seyferth, D.; Tasi, M.; Woo, H.-G. *Chem. Mater.* **1995**, *7*, 236.
(40) (a) Cho, M.-S.; Kim, B.-H.; Kong, J.-I.; Woo, H.-G. *J. Organomet. Chem.* **2003**, *685*, 99. (b) Yang, S.-Y.; Park, J.-M.; Woo, H.-G.; Kim, W.-G.; Kim, I.-S.; Kim, D.-P.; Hwang, T.-S. *Bull. Korean Chem. Soc.* **1997**, *18*, 1264. (c) Woo, H.-G.; Yang, S.-Y.; Hwang, T.-S.; Kim, D.-P. *Bull. Korean Chem. Soc.* **1998**, *19*, 1310.
(41) Hong, L.-Y.; Cao, F.; Kim, D.-J.; Woo, H.-G.; Kim, B.-H.; Cho, M.-S.; Li, X.-D.; Kim, D.-P. *J. Organomet. Chem.* **2003**, *687*, 27.
(42) Braunstein, P.; Morise, X. *Chem. Rev.* **2000**, *100*, 3541.
(43) (a) Trefonas, P.; West, R. *J. Polym. Sci. Polym. Chem. Ed.* **1985**, *23*, 2099. (b) Szymanski, W. J.; Visscher, G. T.; Bianconi, P. A. *Macromolecules* **1993**, *26*, 869. (c) Imori, T.; Lu, V.; Cai, H.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 9931. (d) Kashimura, S.; Ishifune, M.; Yamashita, N.; Bu, H.-B.; Takebayashi, M.; Kitajima, S.; Yoshiwara, D.; Kataoka, Y.; Nishida, R.; Kawasaki, S.-I.; Murase, H.; Shono, T. *J. Org. Chem.* **1999**, *64*, 6615.
(44) (a) Aitken, C.; Harrod, J. F.; Malek, A. J. *J. Organomet. Chem.* **1988**, *249*, 285. (b) Choi, N.; Tanaka, M. *J. Organomet. Chem.* **1998**, *564*, 81. (c) Kim, B.-H.; Woo, H.-G., in preparation.
(45) Imori, T.; Tilley, T. D. *J. Chem. Soc. Chem. Commun.* **1993**, 1607.
(46) (a) Lu, V.; Tilley, T. D. *Macromolecules* **1996**, *29*, 5763. (b) Lu, V.; Tilley, T. D. *Macromolecules* **2000**, *33*, 2403. (c) Bukalov, S. S.; Leites, L. A.; Lu, V.; Tilley, T. D. *Macromolecules* **2002**, *35*, 1757.
(47) Braunstein, P.; Morise, X. *Organometallics* **1998**, *17*, 540.
(48) Neale, N. R.; Tilley, T. D. *J. Am. Chem. Soc.* **2002**, *124*, 3802.
(49) (a) Kralicek, J.; Kubanek, V.; Kondelikova, J. *German Patent*, **1973**, 2, 301, 784. (b) Kralicek, J.; Kubanek, V.; Kondelikova, J.; Casensky, B.; Machacek, J. *German Patent*, **1976**, 2, 445, 647. (c) Bukac, Z.; Sebenda, J. *U.S. Patent*, **1976**, 3, 962, 239.
(50) (a) Becker, B.; Corriu, R. J. P.; Guérin, C.; Henner, B. J. L. *J. Organomet. Chem.* **1989**, *369*, 147. (b) Becker, B.; Corriu, R.; Guérin, C.; Henner, B. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*(1), 409. (c) Corriu, R. J. P. *J. Organomet. Chem.* **1990**, *400*, 81.
(51) Riviere, P.; Satge, J.; Soula, D. *J. Organomet. Chem.* **1974**, *72*, 329.
(52) Speier, J. L.; Zimmerman, R. E. *J. Am. Chem. Soc.* **1955**, *77*, 6395.
(53) Woo, H.-G.; Song, S.-J.; Cho, E. J.; Jung, I. N. *Bull. Korean Chem. Soc.* **1996**, *17*, 123.
(54) Seyferth, D.; Lang, H. *Organometallics* **1991**, *10*, 551.
(55) Armitage, A. D. (G. Wilkinson, F. G. A. Stone, E. W. Abel, Eds.), *Comprehensive Organometallic Chemistry*, Vol. 2, Pergamon Press, Oxford, 1982, Chapter 1.
(56) Woo, H.-G.; Song, S.-J.; You, H.; Cho, E. J.; Jung, I. N. *Bull. Korean Chem. Soc.* **1996**, *17*, 475.
(57) Woo, H.-G.; Song, S.-J. *Bull. Korean Chem. Soc.* **1996**, *17*, 1040.
(58) Woo, H.-G.; Kim, S.-Y.; Kim, W.-G.; Yeon, S. H.; Cho, E. J.; Jung, I. N. *Bull. Korean Chem. Soc.* **1995**, *16*, 1109.

(59) Woo, H.-G.; Kim, B.-H.; Cho, M.-S.; Hwang, T. S. *Proceedings of International Symposium on Silicon-containing Polymers and Applications*; Kanagawa: Japan, 2001, p. 49.
(60) Woo, H.-G.; Kim, B.-H.; Cho, M.-S. *Proceedings of International Symposium on Silicon-containing Polymers and Applications*; Kanagawa: Japan, 2001, p. 53.
(61) (a) Woo, H.-G.; Song, S.-J.; Han, M.-K.; Cho, E. J.; Jung, I. N. *Bull. Korean Chem. Soc.* **1995**, *16*, 1242. (b) Woo, H.-G.; Kim, B.-H.; Cho, M.-S.; Song, S.-J.; Han, M.-K.; Kim, S.-Y.; Sung, A.-Y.; Kim, J. H.; Lee, J.-S. *Bull. Korean Chem. Soc.* **2000**, *21*, 935. (c) Shaltout, R. M.; Corey, J. Y. *Organometallics* **1996**, *15*, 2866.
(62) (a) Reichl, J. A.; Popoff, C. M.; Gallagher, L. A.; Remsen, E. E.; Berry, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 9430. (b) Katz, S. M.; Reichl, J. A.; Berry, D. H. *J. Am. Chem. Soc.* **1998**, *120*, 9844.
(63) Babcock, J. R.; Sita, L. R. *J. Am. Chem. Soc.* **1996**, *118*, 12481.
(64) (a) Woo, H.-G.; Park, J.-M.; Song, S.-J.; Yang, S.-Y.; Kim, I.-S.; Kim, W.-G. *Bull. Korean Chem. Soc.* **1997**, *18*, 1291. (b) Woo, H.-G.; Song, S.-J.; Kim, B.-H. *Bull. Korean Chem. Soc.* **1998**, *19*, 1161.
(65) (a) Speier, J. L. *Adv. Organomet. Chem.* **1978**, *17*, 407. (b) Pesek, J. J.; Matyska, M. T.; Pan, X. *J. Chromatography A* **2003**, *992*, 57.
(66) (a) Harrod, J. F.; Chalk, A. J. (I. Wender, P. Pino, Eds.) *Organic Synthesis via Metal Carbonyls*, Wiley, New York, 1977, p. 673. (b) Ojima, I. (S. Patai, Z. Rappoport, Eds.) *The Chemistry of Organic Silicon Compounds*, Wiley, New York, 1989, p. 1479. (c) Marciniec, B. *Comprehensive Handbook on Hydrosilylation*, Pergamon Press, Oxford, 1992.
(67) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, 1987, p. 564.
(68) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16.
(69) Roy, A. K.; Taylor, R. B. *J. Am. Chem. Soc.* **2002**, *124*, 9510.
(70) (a) Seitz, F.; Wrighton, M. S. *Angew. Chem. Int. Ed.* **1989**, *28*, 762. (b) Tanke, R. S.; Crabtree, R. H. *Organometallics* **1991**, *10*, 415. (c) Bergens, S. H.; Whelan, P. N. *J. Am. Chem. Soc.* **1992**, *114*, 2128. (d) Yasue, T. R. *Organometallics* **1996**, *15*, 2098. (e) LaPointe, A. M.; Rix, F. C.; Boorkhart, M. *J. Am. Chem. Soc.* **1997**, *119*, 906.
(71) Marciniec, B. *Appl. Organomet. Chem.* **2000**, *14*, 527, and references cited therein.
(72) Rubin, M.; Schwier, T.; Gevorgyan, V. *J. Org. Chem.* **2002**, *67*, 1936.
(73) (a) Oertle, K.; Wetter, H. *Tetrahedron Lett.* **1985**, *26*, 5511. (b) Asao, N.; Sudo, T.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 7654. (c) Lambert, J. B.; Zhao, Y.; Wu, H. *J. Org. Chem.* **1999**, *64*, 2729.
(74) (a) Dash, A. K.; Wang, J. Q.; Eisen, M. S. *Organometallics* **1999**, *18*, 4724. (b) Kawanami, Y.; Sonoda, Y.; Mori, T.; Yamamoto, K. *Org. Lett.* **2002**, *4*, 2825. (c) Faller, J. W.; D'Alliessi, D. G. *Organometallics* **2002**, *21*, 1743.
(75) Takahashi, T.; Bao, F.; Gao, G.; Ogasawara, M. *Org. Lett.* **2003**, *5*, 3479.
(76) (a) Jensen, J. F.; Svendsen, B. Y.; la Cour, T. V.; Pedersen, H. L.; Johannsen, M. *J. Am. Chem. Soc.* **2002**, *124*, 4558. (b) Shimada, T.; Mukaide, K.; Shinohara, A.; Han, J. W.; Hayashi, T. *J. Am. Chem. Soc.* **2002**, *124*, 1584.
(77) Itami, K.; Mitsudo, K.; Nishino, A.; Yoshida, J.-I. *J. Org. Chem.* **2002**, *67*, 2645.
(78) (a) Hao, L.; Harrod, J. F.; Lebuis, A.-M.; Mu, Y.; Shu, R.; Samuel, E.; Woo, H.-G. *Angew. Chem. Int. Ed.* **1998**, *37*, 3126. (b) Harrod, J. F.; Shu, R.; Woo, H.-G.; Samuel, E. *Can. J. Chem.* **2001**, *79*, 1075.
(79) (a) Grunlan, M. A.; Mabry, J. M.; Weber, W. P. *Polymer* **2003**, *44*, 981. (b) Mabry, J. M.; Runyon, M. K.; Weber, W. P. *Macromolecules* **2001**, *34*, 7264. (c) Hwang, T.-S.; Lim, J.-T.; Woo, H.-G. *Polymer (Korea)* **1999**, *23*, 197. (d) Hwang, T.-S.; Lim, J. H.; Woo, H.-G. *Polymer (Korea)* **1998**, *22*, 194.
(80) (a) Hong, L.-Y.; Woo, H.-G.; Ham, H.-S. *Bull. Korean Chem. Soc.* **1995**, *16*, 360. (b) Woo, H.-G.; Hong, L.-Y.; Kim, S.-Y.; Park, S.-H.; Song, S.-J.; Ham, H.-S. *Bull. Korean Chem. Soc.* **1995**, *16*, 774. (c) Woo, H.-G.; Hong, L.-Y.; Yang, S.-Y.; Park, S.-H.; Song, S.-J.; Ham, H.-S. *Bull. Korean Chem. Soc.* **1995**, *16*, 1056. (d) Woo, H.-G.; Hong, L.-Y.; Park, J.-Y.; Jeong, Y.-T.; Park, H.-R.; Ham, H.-S. *Bull. Korean Chem. Soc.* **1996**, *17*, 16. (e) Woo, H.-G.; Park, S.-H.; Park, J.-Y.; Yang, S.-Y.; Ham, H.-S. *Bull. Korean Chem. Soc.* **1996**, *17*, 373. (f) Woo, H.-G.; Park, S.-H.; Hong, L.-Y.; Kang, H.-G.; Song, S.-J.; Ham, H.-S. *Bull. Korean Chem. Soc.* **1996**, *17*, 376. (g) Woo, H.-G.; Park, S.-H.; Hong, L.-Y.; Yang, S.-Y.; Kang, H.-G.; Ham, H.-S. *Bull. Korean Chem. Soc.* **1996**, *17*, 532. (h) Woo, H.-G.; Park, J.-Y.; Hong, L.-Y.; Song, S.-J.; Ham, H.-S.; Kim, W.-G. *Bull. Korean Chem. Soc.* **1996**, *17*, 560. (i) Woo, H.-G.; Oh, E.-M.; Park, J.-H.; Kim, B.-H.; Kim, Y.-N.; Yoon, C.-H.; Ham, H.-S. *Bull. Korean Chem. Soc.* **2000**, *21*, 291. (j) Woo, H.-G.; Lee, M.-S.; Kim, Y.-J.;

Kim, B.-H.; Kong, J.-I. *Proceedings of International Symposium on Silicon-containing Polymers and Applications; Kanagawa: Japan* 2001, p. 81. (k) Woo, H.-G.; Lee, M.-S.; Kim, Y.-J.; Kim, B.-H.; Kim, Y.-S. *Proceedings of International Symposium on Silicon-Containing Polymers and Applications*; Kanagawa Japan 2001, p. 85. (l) Woo, H.-G.; Kim, B.-H.; Cho, M.-S.; Kim, D.-Y.; Choi, Y.-S.; Kwak, Y.-C.; Ham, H.-S.; Sung, A.-Y.; Kim, D.-P.; Hwang, T. S. *Bull. Korean Chem. Soc.* **2001**, *22*, 1337. (m) Woo, H.-G.; Kim, B.-H., in preparation.

(81) (a) Odian, G. *Principles of Polymerization*, 3rd ed. Wiley, New York, 1991, pp. 222–223. (b) Mimura, S.; Naito, H.; Kanemitsu, Y.; Matsukawa, K.; Inoue, H. *J. Organomet. Chem.* **2000**, *611*, pp. 40. (c) Peinado, C.; Alonso, A.; Catalina, F.; Schnabel, W. J. *Photochem. Photobiol. A.*; *Chem.* **2001**, *141*, pp. 85.

(82) Norrish, R. G.; Simons, J. P. *Proc. Roy. Soc. (London)* **1959**, *A251*, 4.

(83) Chatgilialoglu, C.; Timokhin, V. I.; Zaborovskiy, A. B.; Lutsyk, D. S.; Prystansky, R. E. *J. Chem. Soc., Perkin Trans.* **2000**, *2*, 577.

(84) (a) Woo, H.-G.; Lee, S.-E.; Kwak, Y.-C.; Kim, B.-H.; Ham, H.-S. *Proceedings of International Symposium on Silicon-containing Polymers and Applications*; Kanagawa: Japan, 2001, p. 69. (b) Woo, H.-G.; Cho, M.-S.; Lee, M.-S.; Jun, M.-J.; *Proceedings of International Symposium on Silicon-Containing Polymers and Applications*; Kanagawa: Japan, 2001, p. 97. (c) Woo, H.-G.; Kim, B.-H., submitted.

(85) (a) Tanaka, S.; Nakamura, T.; Yorimitsu, H.; Shinokubo, H.; Oshima, K. *Org. Lett.* **2000**, *2*, 1911. (b) Faller, J. W.; Kultyshev, R. G. *Organometallics* **2003**, *22*, 199. (c) Kadib, A. E.; Castel, A.; Delpech, F.; Riviere, P.; Riviere-Baudet, M.; Gornitzka, H.; Aguirre, P.; Manriquez, J. M.; Chavez, I.; Abril, D. *Inorg. Chem. Acta* **2004**, *357*, 1256. (d) Choi, K.; Buriak, J. M. *Langmuir* **2000**, *16*, 7737.

(86) Kinoshita, H.; Nakamura, T.; Kakiya, H.; Shinokubo, H.; Matsubara, S.; Oshima, K. *Org. Lett.* **2001**, *3*, 2521.

(87) (a) Nakano, T.; Ono, K.; Senda, Y.; Migita, T. *J. Organomet. Chem.* **2001**, *619*, 313. (b) Komoriya, H.; Kako, M.; Nakadaira, Y.; Mochida, K. *J. Organomet. Chem.* **2000**, *611*, 420.

(88) Miura, K.; Wang, D.; Matsumoto, Y.; Fujisawa, N.; Hosomi, A. *J. Org. Chem.* **2003**, *68*, 8730.

(89) Kim, B.-H.; Woo, H.-G., unpublished results.

Silylmethylamines and Their Derivatives: Chemistry and Biological Activities

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ADVANCES IN ORGANOMETALLIC CHEMISTRY
VOLUME 52 ISSN 0065-3055/DOI 10.1016/S0065-3055(04)52004-X

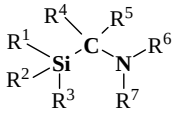
ACRONYMS

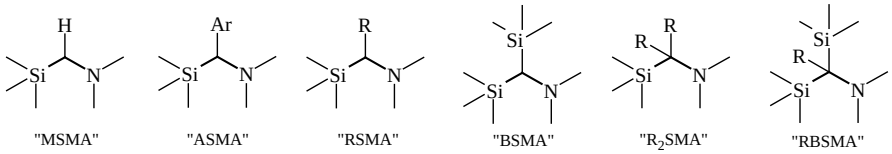
ASMA	arylsilylmethylamine
Boc or boc	*t*-butyloxycarbonate
BSMA	bis(silyl)methylamine
n-BuLi	*n*-butyllithium
s-BuLi	*s*-butyllithium
t-BuLi	*t*-butyllithium
CAN	cerium ammonium nitrate
DCA	9,10-dicyanoanthacene
DCN	1,4-dicyanonaphthalene
DMAD	dimethyl acetylenedicarboxylate
DME	ethylene glycol dimethylether
HMPA	hexamethylphosphoramide
LAH	lithium aluminum hydride
LDA	lithium diisopropylamide
Lidakor	Schlosser base: 1/1 mixture of LDA and *t*-BuOK
LiTMP	lithium 2,2,6,6-tetramethylpiperidine
MeCN	acetonitrile
MSMA	monosilymethylamine
PET	photoinduced electron transfer
RBSMA	alkylbissilylmethylamine
RSMA	alkylsilylmethylamine
R_2SMA	dialkylsilylmethylamine
SET	single electron transfer
SMA	silylmethylamine
TBAF	tetrabutylammonium fluoride
TASF	tris(dimethylamino)sulfur (trimethylsilyl)difluoride
THF	tetrahydrofuran
TMEDA	tetramethylethylenediamine
TMS	trimethylsilyl
TFA	trifluoroacetic acid
TfO	triflate

I
INTRODUCTION

In this chapter silylmethylamines are defined as compounds in which one silicon and one nitrogen atom are directly linked to an sp^3-carbon atom. This excludes, for example, enamines[1] or imines[2] of acylsilanes, α-silylpyridine[3] and α-silylpyrroles[4] derivatives (in which central carbon is sp^2 hybridized) and silyldiazomethanes.[5] In the literature, primary amines of this type are commonly referred to as aminomethylsilanes, silylmethylamines, 1-silylamines, α-silylamines, or 3-sila-1-aza-propanes derivatives. In this chapter,

the acronym SMA is used to denote silylmentylamine, and to represent the structure irrespective of its substituents. Furthermore, we have classified these amines, which in the more frequently encountered structures have at least one hydrogen on the central carbon atom, into four main classes according to their substitution patterns. These are monosilylmethylamines, arylsilylmethylamines, alkylsilylmethylamines and bissilylmethylamines, denoted MSMA, ASMA, RSMA and BSMA, respectively. The chapter also addresses alkyl-substituted derivatives of RSMA and BSMA, dialkylsilylmethylamines R_2SMA and alkylbissilylmethylamines RBSMA.

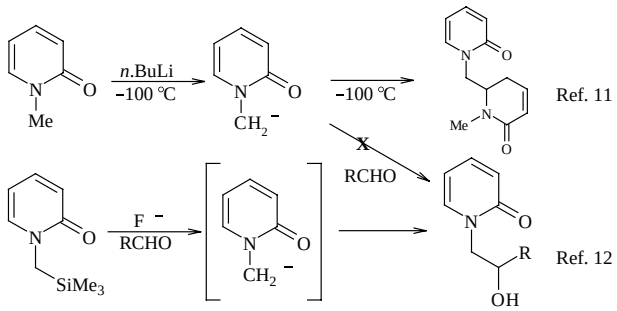




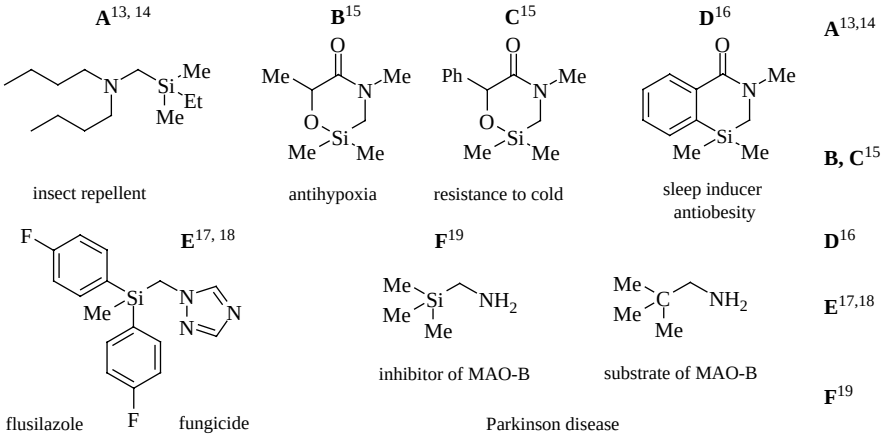
The utilization of SMA and their derivatives in a wide variety of synthetic transformations has exhibited considerable growth in recent years. The chemistry of BSMA and its derivatives has been extensively reviewed[6] and that of SMA, as members of silylmethyl functional compounds,[7,8] has been surveyed. Silylmethylamines have been known in the literature for almost 50 years since Speier[9] and Sommer[10] independently reported the first compounds of this type. These compounds have been the subject of nearly 1000 publications to date, including nearly 100 patents. For the first two decades after these initial reports, attention focused on the question of whether or not the nitrogen lone pair electrons interact with the silicon moiety.

In the 1970s, three main topics of interest in the SMAs emerged.

Firstly, the possibility of generating an α-aminomethyl anion equivalent under mild and neutral conditions and in the presence of the electrophilic receptor *via* the fluoride ion cleavage of the Si–C bond was investigated by Patel and Joule,[11] who observed the addition product of the anion to the starting material. Katritzsky and Sengupta[12] then found that fluoride-mediated desilylation could be carried out in the presence of an aldehyde, allowing the facile synthesis of aminoethanols.



The second important finding was that a number of silylmethylamino derivatives show significant biological activity.[13–19] For example, flusilazole (E) is an active fungicide, produced commercially in ton quantities and is a component of almost all agricultural fungicides.[17,18] Aminomethyl(trimethyl)silane (or trimethylsilylmethylamine) inhibits monoamine oxidase (MAO-B) whereas its carbon analogue, neopentylamine, is a substrate for the same enzyme.[19] Biological activity of SMAs is covered in detail in Section VIII.



The third area of interest has been the emergence of use of silylmethylamino derivatives as precursors to 1,3-dipolar, non-stabilized azomethine ylids. The ability of the α-aminosilanes to generate the azomethine ylids in the presence of the dipolarophile attracted the attention of organic chemists (See Section VII).

This chapter presents a comprehensive review of the chemistry of organosilanes which have a nitrogen atom on the α-carbon in their structures. After presenting some elements relative to the structure, the synthesis, and the reactivity of SMAs in terms of making and cleaving bonds, their physicochemical and biological behaviors will be detailed.

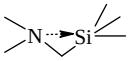
II

SOME ELEMENTS RELATIVE TO THE SUBSTRUCTURE

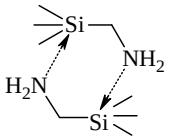
A. *Nitrogen to Silicon Chelation*

As soon as the first SMA was prepared, the question arose as to the structure and consequently of the basicity of this new type of amine. As is true for N-alkylamines, it could be expected that the silylmethyl group would make MSMA more basic than ammonia through its +I effect. Conversely, the ability of a silicon atom to accept electrons from a nucleophile, as is the case with silatranes and *o*-silylbenzylamines,[20]

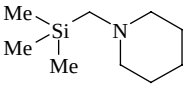
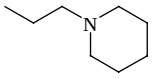
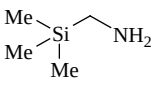
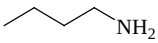
opens the possibility of an interaction between a vacant d-orbital of silicon and the lone pair of electrons on nitrogen. In such a case, the electron density on nitrogen is diminished, thus making SMA less basic than the corresponding non-silylated amines.



In order to get information, the base-strength of trimethylsilylmethylamine was measured by titration in dilute aqueous solution and compared with that of aliphatic amines. The silylmethylamine ($pK_a = 10.96$) was 5.7 times more basic than neopentylamine, its carbon analog ($pK_a = 10.21$) and 1.82 times more basic than methylamine.[10] This was confirmed by another independent study.[21] In both the cases, the authors concluded that silicon does not expand its valence shell and reject the existence of any intramolecular N → Si interaction. The possibility of a strong association through an intermolecular N → Si coordination was also eluded on the basis of molecular weight measurements.[21] In another study, potentiometric titration of a large series of SMA derivatives indicated that their pK_a varied from 10.14 up to 7.72, a range similar to that of the analogous carbon amines (10.16–6.20).[22] The basicity of SMA was also studied by infrared spectroscopy by looking at the shift $\Delta\nu$ [$\Delta\nu = \nu(C{-}D)_{free} - \nu(C{-}D\cdots N)$] of the C–D absorption band of deuterated chloroform when associated with SMA. It was concluded that these amines are less basic than their carbon analogs as indicated in the table, and that hyperconjugation and (p → d)π interactions should be considered to explain these results.[23–25]



Wavenumber shifts $\Delta\nu$ (in cm^{-1}) due to interaction between $CDCl_3$ and SMA[23,24]

SMA	$\Delta\nu$ (cm^{-1})	Reference amine	$\Delta\nu$ (cm^{-1})
	60		70
	36		43

However, solvation and entropy (which could be very different between these two types of amines) must be taken into account when comparing the two methods (titration and infrared spectroscopy). The ionization constants of a series of silylmethylpiperidines and their carbon analogs were measured potentiometrically in methanol. The data indicates a lower basicity for these compounds, compared to non-silylated analogs, which was explained in terms of inductive effects, three-center-bond formation and (p–d)σ interactions.[26] From a study of the effect of solvation by acetone on the basicity of

silylmethylamines, the dependence on the substitution at silicon was difficult to explain. It was proposed that the non-systematic changes in basicity could be due to inductive effects and solvation on one side, and hyperconjugation and steric hindrance on the other.[27] This is supported by a similar study on frequency shift of the N–H bond upon complexation of SMA R_3SiCH_2NHR' with THF relative to substituents R′ at nitrogen.[28] When these studies were collected and discussed in a review, it was concluded that "the lower basicity of $Me_3SiCH_2NH_2$ compared to its β-homolog, appears to result from an intramolecular interaction between the silicon and nitrogen".[29] More recently, however, ^{13}C, ^{15}N and ^{29}Si NMR studies led the authors to conclude the existence of a N → Si interaction in SMA which strongly depends on the substituents at the silicon atom.[30,31]

Until this point, results appear to be rather divergent, possibly because these studies were performed on SMA dissolved in various solvents and solvation might modify the distribution of electrons in the Si–C–N unit. In order to circumvent this problem, gas phase studies and theoretical approaches were developed. In the gas phase (ion cyclotron resonance mass spectroscopy), trimethylsilylmethyldimethylamine was reported to be more basic than the analogous neopentyldimethylamine from proton affinity measurements based upon proton affinity of ammonia (201.0 kcal/mol): 227.1 and 225.8 kcal/mol respectively.[32] Conversely, the ionization potential of MSMA indicates a basicity lower than that of its carbon analog and the authors emphasize the fact that this result is opposite to charge densities, p*K* values, IR studies and HOMO energies.[33]

The total protonation energy, defined as the difference, Δ*E*, between the total energy of the non-protonated molecule and that of its conjugated acid was analyzed *via* theoretical quantum chemical calculations. It was considered that this energy could be split into three additive contributions, electronic (Δε), electrostatic (ΔE_{elst}) and polarization (ΔE_{polar}). An increase was observed on going from carbon to silicon that was attributed mainly to the difference in the respective polarizabilities of carbon and silicon atoms.[34,35]

Comparison of the calculated proton energies and their individual components[34]

Compound	Δ*E* (atomic units)	Δε (atomic units)	ΔE_{elst} (atomic units)	ΔE_{polar} (atomic units)
H_3C–NH_2	−0.491	−0.383	0.049	−0.157
H_3Si–NH_2	−0.497	−0.385	0.049	−0.161
Variations (Si–C)	−0.006	−0.002	0.000	−0.004

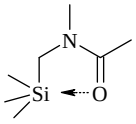
In a recent work, the gas-phase structure of $H_3SiCH_2NMe_2$ has been deduced from electron diffraction study (GED) and *ab initio* calculations (MP2/6-311G**). The Si–C–N angle is larger than in a tetrahedral sp^3 carbon atom [114.7° (GED) and 111.4° (MP2/6-311G**)] and the molecule adopts a gauche conformation with the lone pair of electrons on nitrogen away from the Si–C–N plane (torsion angle lp-N–C–Si 55.6°), eluding any N → Si interaction.[36] However, calculations made on $FH_2SiCH_2NMe_2$, taken as a model molecule, indicate that the Si–C–N unit tends to adopt a smaller bond angle.

In conclusion, it appears that substitution with electron releasing groups at nitrogen and with strong electron attracting groups at silicon favors the establishment of an interaction

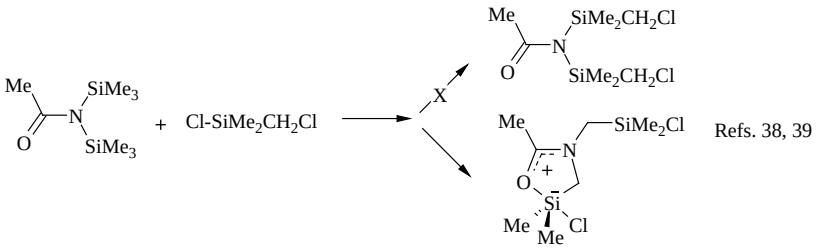
between N and Si, but the energy of this interaction is weak and can be overwhelmed by other phenomena such as solvation. This does not exclude the intermediacy of a possible interaction in the transition state of reactions of SMA and their derivatives.

B. *O–Si Internal Chelation in N-Silylmethylamides*

Interaction between silicon and the oxygen atom of a carbonyl moiety linked to the nitrogen atom of these compounds has been shown to be a reality. A number of studies dealing with this topic have been reviewed.[37]

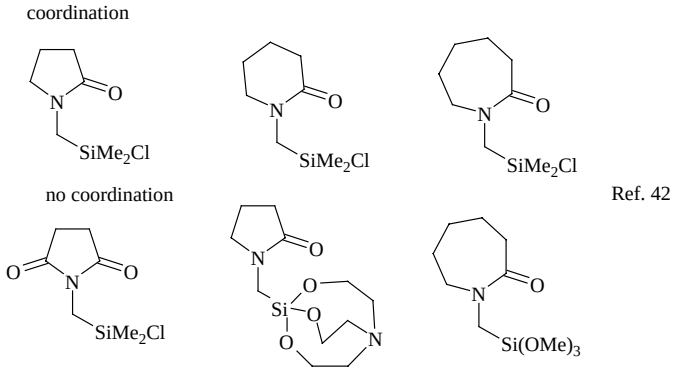


The first evidence was provided by Yoder *et al*., who demonstrated (X-ray analysis) that the result of the reaction between *N*,*N*-bis(trimethylsilyl)acetamide with chloromethyldimethylchlorosilane was not *N*,*N*-bis(chloromethyldimethylsilyl)acetamide as erroneously reported,[38] but a five-membered ring containing a five-coordinated silicon atom.[39] This synthesis was extended to other model molecules.[40,41]



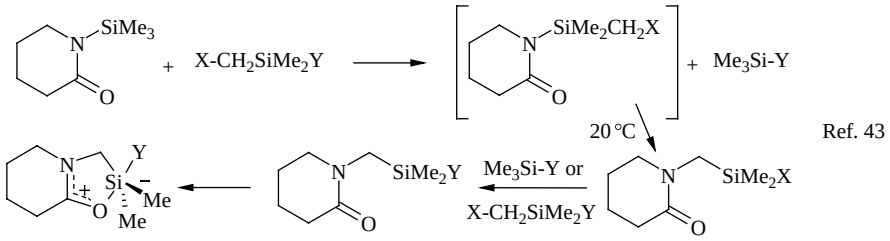
Refs. 38, 39

Several studies are devoted to this structural feature, in particular on the effect of the ring size in lactams or the substitution at silicon on the coordination. It is found by ^{29}Si NMR that the size has little effect and that replacement of the chlorodimethylsilyl group by a trimethoxy or silatranyl group does not lead to coordinated species.[42]

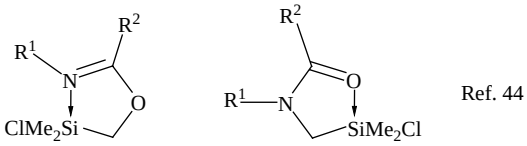


Ref. 42

Information has been obtained on the formation of these compounds. Condensation of *N*-trimethylsilyl-δ-lactam with an halomethyldimethylhalosilane at low temperatures led to the transsilylation reaction at nitrogen. The *N*-halomethyldimethylsilylated lactam then isomerizes at −40 °C into the *N*-silylmethylated derivative susceptible to halogen exchange with the starting halosilane, and finally, internally coordinated.[43]



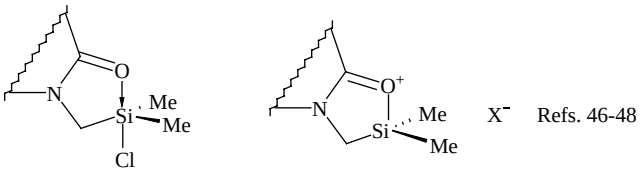
Using careful NMR monitoring, the reaction starting with amide or lactams was confirmed to be multistage including a previously non-described O-[(dimethylchlorosilyl)methyl]imidate showing a N → Si coordination. The chelated imidate is formed under kinetic control whereas the chelated amide is formed under thermodynamic control.[44]



kinetic product thermodynamic product

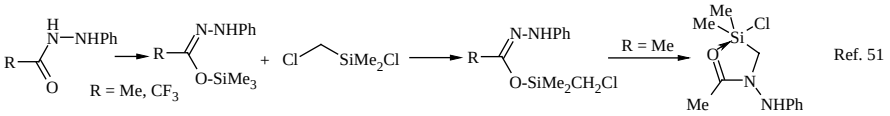
Starting from *N*-trimethylsilylated amides or lactams is not necessary as these chelates can be formed directly from the non-silylated amide or lactam in a one-pot reaction with the same chloromethylchlorosilane in the presence of hexamethyldisilazane.[45]

X-ray studies show the silicon to be trigonal bipyramidal coordinated with the oxygen and chlorine in the apical positions.[46–48] Variations in the substitution at silicon are reflected in variations in the strength of the O → Si coordination bond, sometimes resulting in the loss of the pentacoordination at silicon and formation of a salt.[49] These studies have been reviewed.[50]

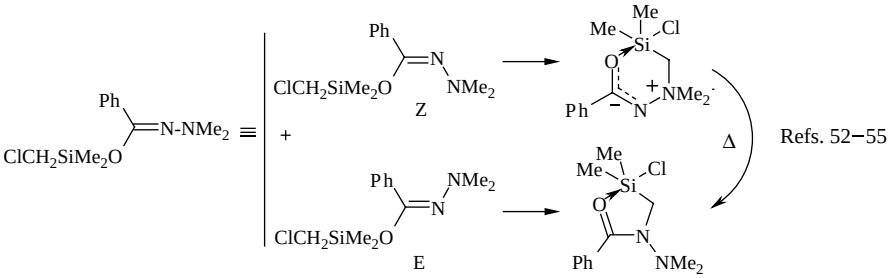


trigonal bipyramide salt

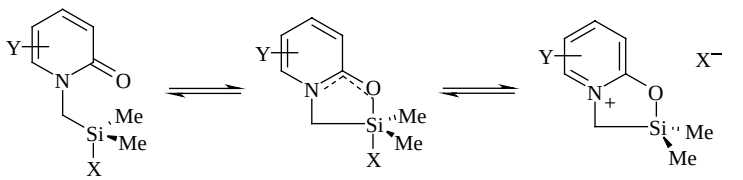
A similar type of internal coordination has been observed starting from hydrazine derivatives. Thus, reaction of dimethylchloromethylsilyl chloride with trimethylsilyl-derivative of 1-phenyl-2-acetylhydrazine leads to transsilylation product that rearranges into the O ⟶ Si compound. However, this isomerization did not occur when starting from 1-phenyl-2-trifluoroacetylhydrazine.[51]



In reality, two compounds are formed,[52] the five- and a six-membered rings shown to arise from the E and Z forms of the O-trimethylsilylated derivative of the starting acylhydrazine.[53] Moreover, the six-membered chelate isomerized irreversibly upon heating into the five-membered chelate.[54] The six-membered chelate has also been shown to exhibit a trigonal bipyramidal silicon atom.[55]



In order to gain insight into the nucleophilic substitution at silicon, a new method of mapping its progress has been reported. It is based on compounds derived from pyridone with various substituents at the ring (Y) and at the silicon atom (X). Intramolecular displacement of X (X = OR, F, Cl, Br, OSO_2CF_3) by oxygen was followed by ^{29}Si NMR spectroscopy and is correlated with displacement of the pyridone ring carbon shifts (^{13}C NMR analysis).[56–59] These important observations have been used for a thermodynamic study of pentacoordination at silicon[60] and a kinetic and stereochemical study of nucleophilic substitution at the same atom.[46e,61]



III

SYNTHESES OF THE SUBSTRUCTURE

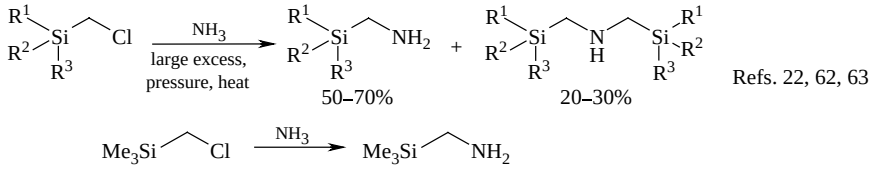
A. *Formation of the C–N Bond*

Essentially all of the classical methods for the synthesis of organic amines can be successfully applied to the synthesis of α-silylamines. However, the lack of good general methods for the preparation of halomethylsilanes remains a serious drawback.

1. Nucleophilic Amination of Chloromethylsilanes

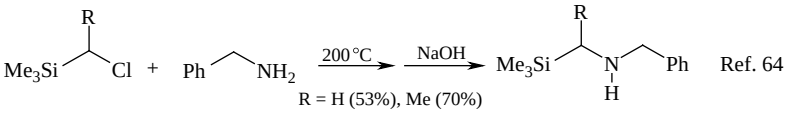
The condensation of ammonia or primary or secondary amines with halocarbons is the oldest and simplest general method for forming the C–N bond. This technique has been applied with success to the preparation of a series of aminomethylsilanes from chloromethylsilanes diversely substituted at silicon. As in purely organic synthesis, the hydrogen chloride formed is either trapped by an excess of the starting amine (in the case of ammonia) or by a base (for more expensive amines).

- *Primary amines*.[9,22,62] Direct amination of chloromethyl-trimethylsilane illustrates the difficulty of stopping the reaction at the monoalkylation level with the formation of up to 30% of the bis(trimethylsilylmethyl) amine even when a large excess of ammonia is employed. The same process has been used to prepare aminomethylsiloxanes where the formation of a small amount of the secondary amine is also observed.[63] See also Ref. 24.



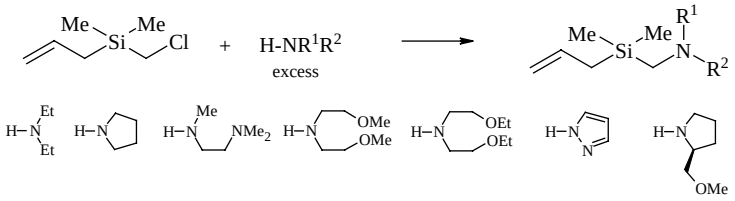
Refs. 22, 62, 63

- *Secondary amines*.[64,65]

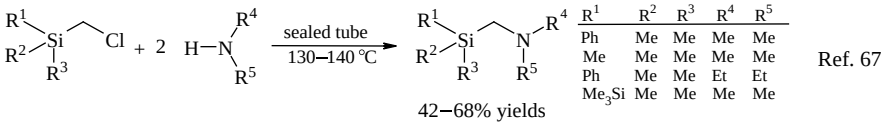


Ref. 64

- *Tertiary amines*.[22,66,67]



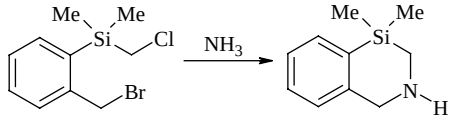
Ref. 22



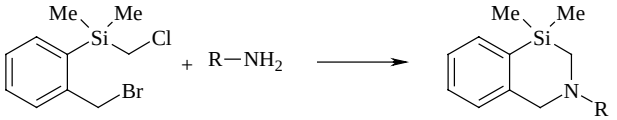
R^1	R^2	R^3	R^4	R^5
Ph	Me	Me	Me	Me
Me	Me	Me	Me	Me
Ph	Me	Me	Et	Et
Me_3Si	Me	Me	Me	Me

Ref. 67

- *Cyclic amines*[68–70] *including triazoles*[71] *and aziridines*.[72,73] Good yields of the desired N-substituted 4,4-dimethyl-4-sila-1,2,3,4-tetrahydroisoquinolines are obtained from primary amines and the benzyl bromide derivative. However, due to further reaction, the formation of the non-substituted parent isoquinoline occurs in very low yield.



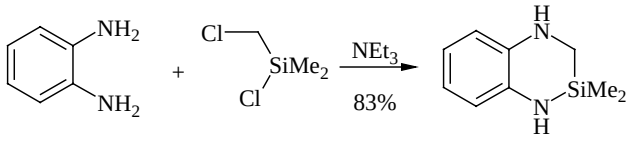
5.8% yield Ref. 70



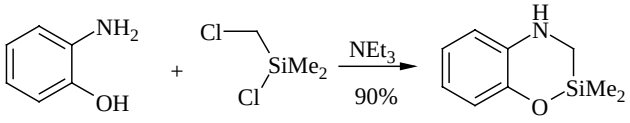
Ref. 70

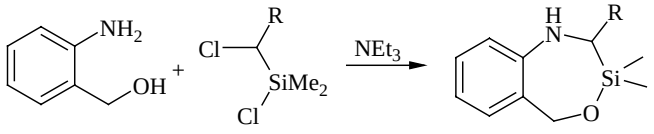
R = Me (74%), Ph (73%), Bn (76%)

Condensation of chloromethyldimethylchlorosilane with *o*-phenylene diamine and *o*-aminophenol leads almost quantitatively to 4-aza- and 4-oxo-3,3-dimethyl-3-silaquinoline. With aminophenol, it should be noted that the O–Si bond is formed first. This same observation may be made starting from *o*-aminobenzyl alcohol.



Ref. 68

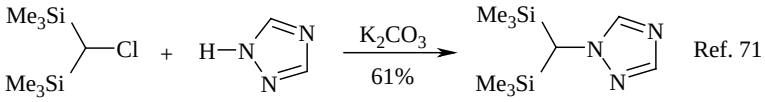




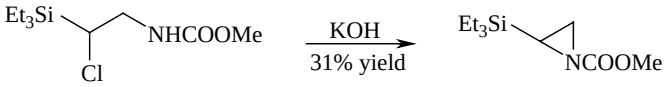
Refs. 69, 70

R = H (35%), Ph (35%)

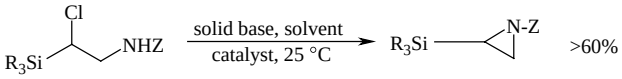
Dehydrochlorination using a base allows the synthesis of triazine and aziridine derivatives. Sonication was shown to be good activator of the reaction in some instances.



Ref. 71



Ref. 72

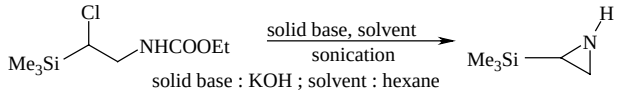


solvent : hexane, MeCN ; catalyst : $(C_8H_{17})_4N^+Br^-$

Z = COOEt, SO_2Tol; R = Me, Et

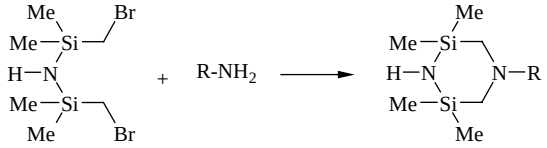
solid base : NaOH, K_2CO_3;

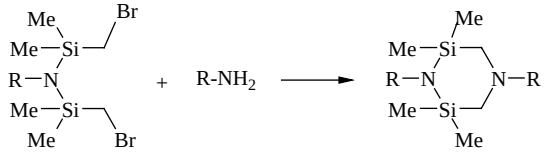
Ref. 73



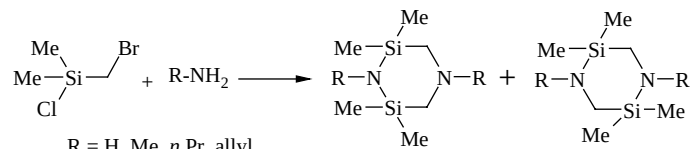
solid base : KOH ; solvent : hexane

Also prepared were 2,6- and 2,5-disilapiperazines, as shown in the examples below.[74,75]



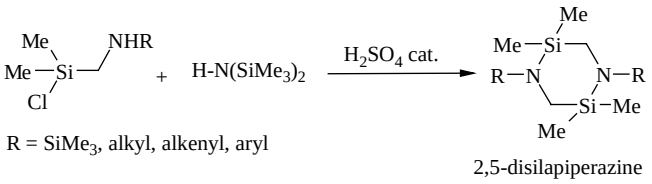


Ref. 74



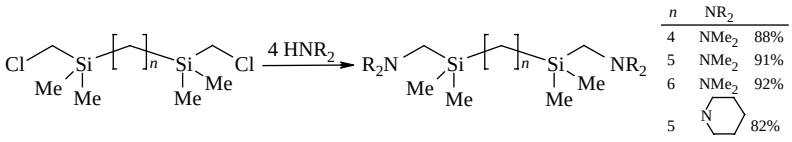
R = H, Me, *n*.Pr, allyl

2,6-disilapiperazine 2,5-disilapiperazine



Ref. 75

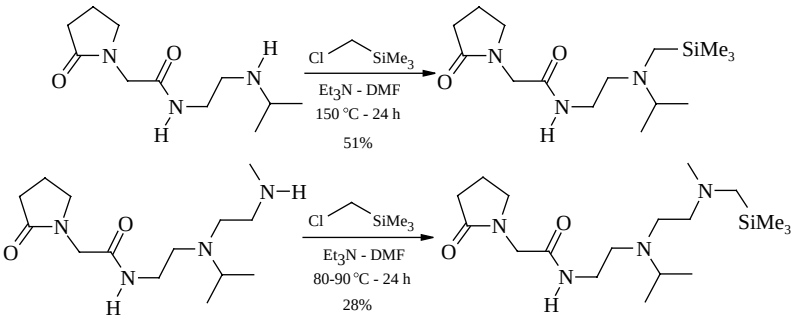
- *Polyamines through amination reaction.*[76] α,γ-Bischloromethylsilanes are converted to the corresponding bis-SMA upon reaction with a secondary amine.



n	NR_2	
4	NMe_2	88%
5	NMe_2	91%
6	NMe_2	92%
5	N	82%

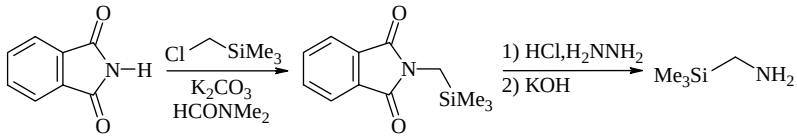
Ref. 76

- *Polyamines through alkylation reaction with chloromethylsilane.*[77] The secondary amine function of polyaza derivatives are alkylated using chloromethyltrimethylsilane.



Ref. 77

- *Gabriel's synthesis using phthalimide.*[10]

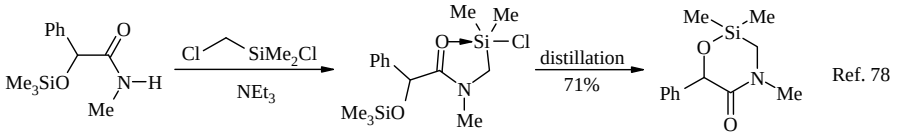


Ref. 10

The normal conditions without solvent do not work. The authors emphasized the necessity of using a highly polar DMF solvent to obtain a good reaction. Using this method a 57% overall yield of trimethylsilymethylamine is obtained.

2. Condensation of Chloromethylchlorosilane with Amides (*via* Rearrangement)

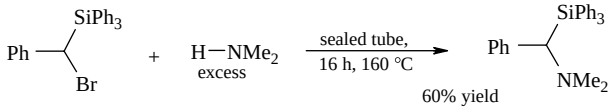
Condensation of an α-hydroxy amide with chloromethyldimethylchlorosilane leads to a pentacoordinated silicon species that isomerizes upon distillation into the corresponding oxazasilacyclohexanone.[78] See also Section II.B.



Ref. 78

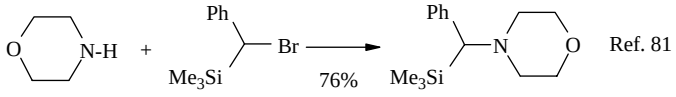
3. Nucleophilic Amination of Bromo- or Iodomethylsilanes

α-Triphenylsilylbenzylbromide has been treated with an excess of dimethylamine in a sealed tube, and the corresponding ASMA is obtained in 60% yield (for a less effective synthesis see Section III.B.2.f).[79]

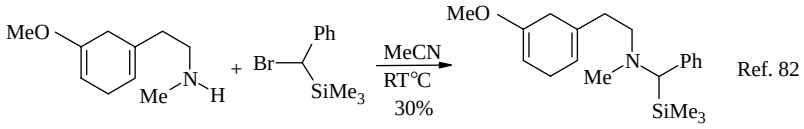


Ref. 79

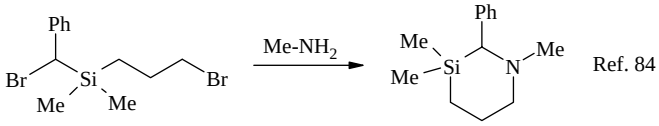
The same technique has been used to react trimethylsilylmethyl iodide and *t*-butylamine to prepare the corresponding secondary amine.[80] Several other examples have been published on the use of bromo-[81–84] or iodomethylsilanes.[83,85,86]



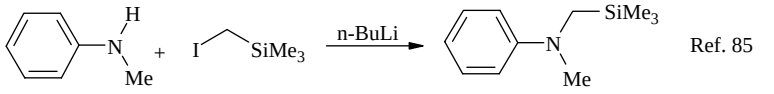
Ref. 81



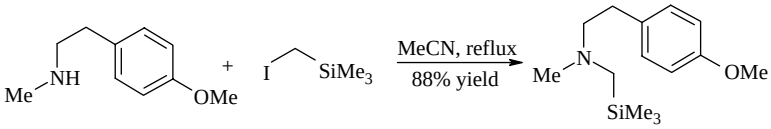
Ref. 82



Ref. 84

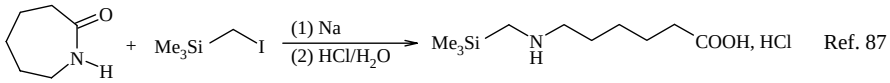


Ref. 85



Ref. 86

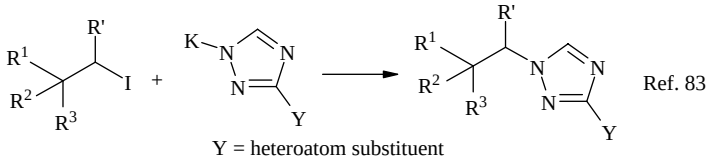
Condensation of the sodium salt of a lactam with iodomethyltrimethylsilane leads to a *N*-trimethylsilylmethyl-ω-aminoacid.[87]



Ref. 87

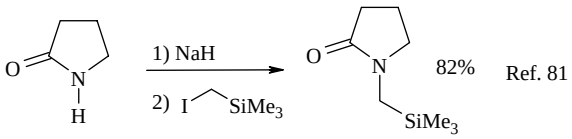
4. Nucleophilic Amination of Chloromethylsilanes with Alkali Metal Amides

The use of alkali-metal amides instead of the amine itself has the advantages of avoiding polyaddition reactions and the need of using an excess of amines (see above). This process has been applied to the synthesis of SMA. A chloromethylsilane was condensed with an amide preformed from an acidic amine function. In general, good yields were obtained.[17,81,88–91]

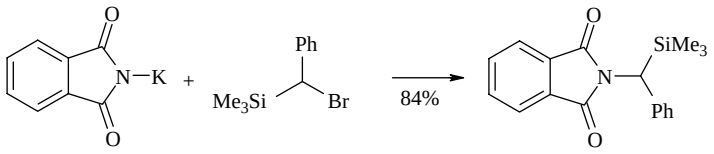


Ref. 83

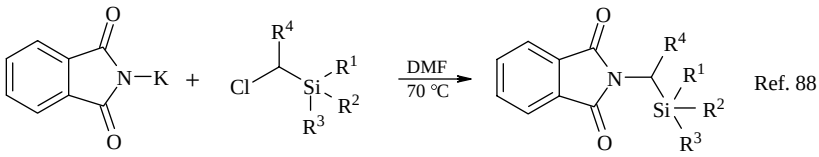
Y = heteroatom substituent

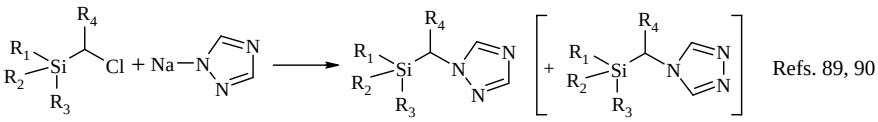


82% Ref. 81

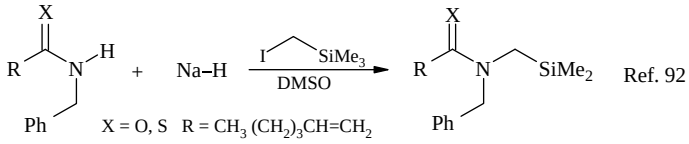


Ref. 81



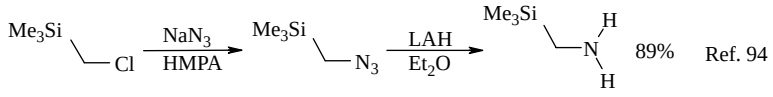


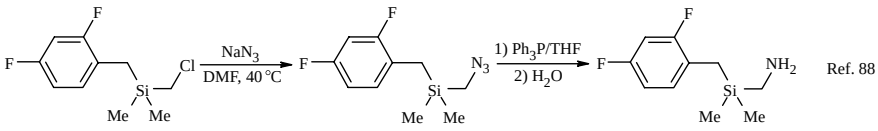
Similarly, *N*-silylmethyl-*N*-benzylamides and thioamides are prepared in relatively high yields by reacting iodomethyltrimethylsilane with the sodium salt of the *N*-benzylamides or thioamides.[92]



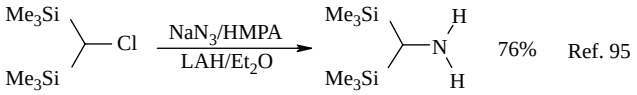
5. Nucleophilic Amination of Chloromethylsilanes with Azides

Amination of chloromethylsilanes with sodium azide occurs readily in an aprotic solvent (DMF or HMPA[93]). The new azides formed afford the corresponding primary amines in excellent yield after treatment with LAH or PPh_3.[88,94]





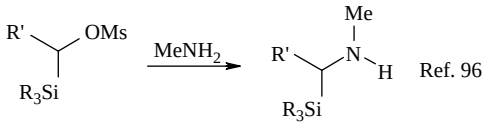
By the same procedure, bis(trimethylsilyl)methylamine has been prepared in fairly good yield.[95]



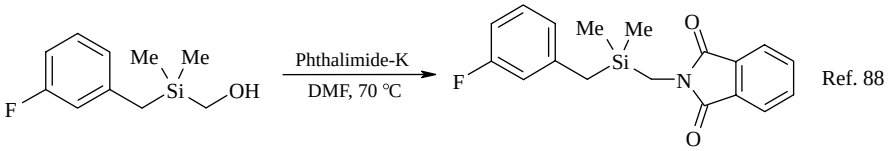
76% Ref. 95

6. Nucleophilic Displacement of Oxygen from Silylmethyloxy Derivatives

Two examples are found for the preparation of α-silylamine derivatives by nucleophilic displacement of an oxygen functionality by an amino compound.[88,96]

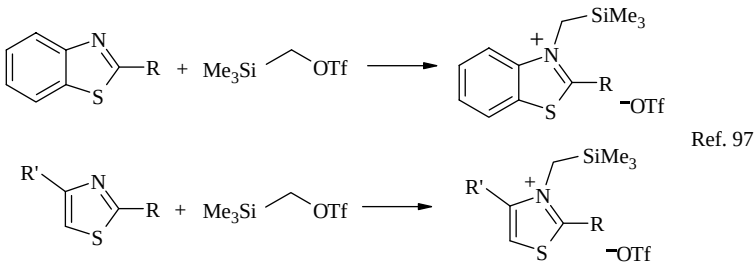


Ref. 96



Ref. 88

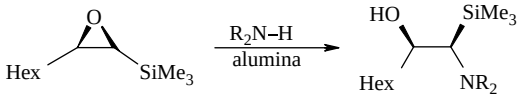
N-Silylmethylthiazolium triflates are quantitatively obtained by the condensation of thiazole derivatives with trimethylsilylmethyl triflate.[97]



Ref. 97

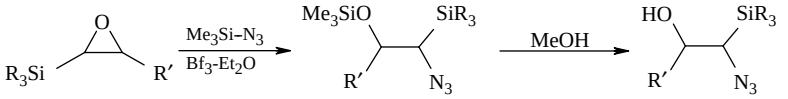
7. From α-Silylepoxides

Interaction of α-silylepoxides with various nitrogen reactants leads either to 2-silyl-2-aminoalcohols or to α-silylnitrogen heterocycles. Nitrogen reactants were amines[98] or azides.[99,100]



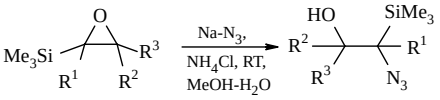
Ref. 98

$R_2N–H$ = N–H, O N–H



Ref. 99

R/R′ = Me/H (86%), Et/ OH (74%)



R^1	R^2	R^3	R^1/R^2
H	H	CH_2OH	*trans*
H	CH_2OH	H	*cis*
H	H	CHOHPh	*trans*
H	H	$CHOHCHMe_2$	*trans*
H	H	Ph	*trans*
H	Ph	H	*cis*
Me	H	Ph	*trans*

Ref. 100

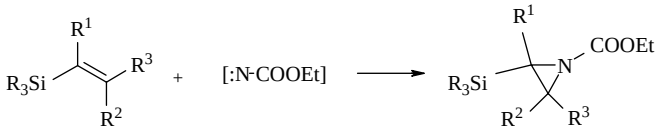
For the amination of chiral epoxides see Section V.G.

8. From Vinylsilanes

Vinylsilanes also serve as a starting material for various SMA derivatives, mostly silylaziridines or their precursors silylpyrazolines *via* insertion of nitrenes, diazomethanes, azides, nitrile imine and nitrogen oxide, N_2O_3.

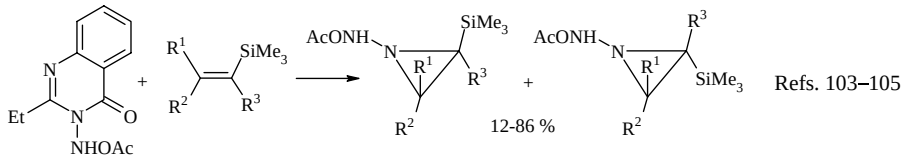
a. Nitrenes

Using *p*-nitrobenzene sulfonyl carbamates as the source of nitrene, the reaction needs to be activated either by a carbonate in the presence of phase-transfer reagent or by sonication. Yields are only moderate and this reaction cannot be regarded as being preparatively useful.[101,102]



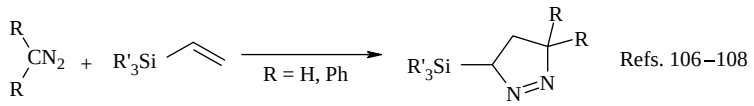
Refs. 101, 102

On the other hand using *N*-acetoxyaminoquinazolone as a nitrene equivalent, silylaziridines are formed in useful, though variable, yields.[103–105] The aziridines obtained are a mixture of two stereoisomers (AcONH/$SiMe_3$) where the Z form predominates.

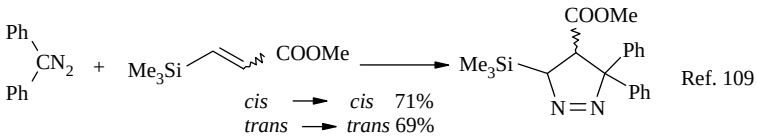


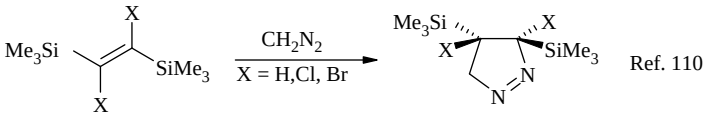
b. Diazomethanes

The cycloaddition of diazomethanes under different conditions leads to 3-silyl-1-pyrazoline derivatives in yields variable according to the conditions employed and the substituents on the reactants.[106–108]

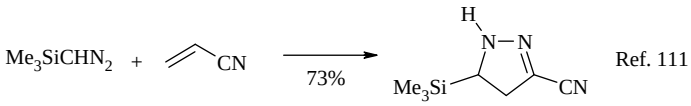


This condensation has been shown to be stereospecific.[109,110]

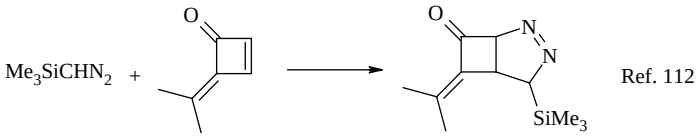




1,3-Cycloaddition of trimethylsilyldiazomethane with activated olefins leads to pyrazoline derivatives that have the SMA substructure. Two examples are reported in the literature. The first concerns addition to acrylonitrile that gives 5-trimethylsilyl-3-cyano-Δ^2-pyrazoline in good yield.[111]

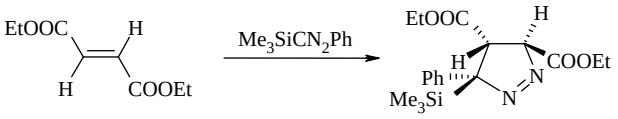


The second reports the addition to a cyclobutanone derivative that leads to the formation of a Δ^1-pyrazoline derivative.[112]



Ref. 112

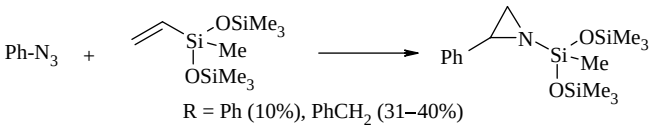
Other silyldiazomethanes have been reacted with several functional alkenes leading to the synthesis of the 3-silyl-1-pyrazoline skeleton. This pyrazoline evolves rapidly to 1-silyl-3-pyrazoline (see Section VI.B.8).[113]



Ref. 113

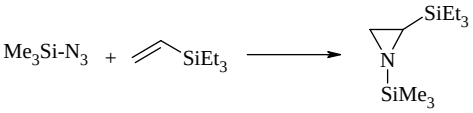
c. Azides

The cyclocondensation of azides with vinylsilanes has been shown to lead to silylaziridines.[106,114,115]



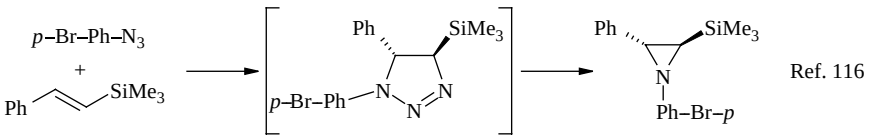
R = Ph (10%), $PhCH_2$ (31–40%)

Refs. 106–114

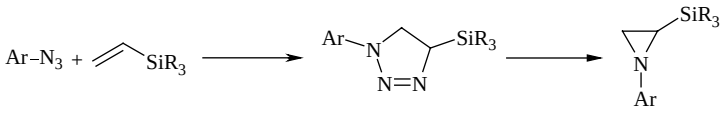


Ref. 115

In reality, 4-silyl-[1,2,3]-triazoles are the true addition products, silylaziridines being formed after decomposition with loss of nitrogen.[116,117]

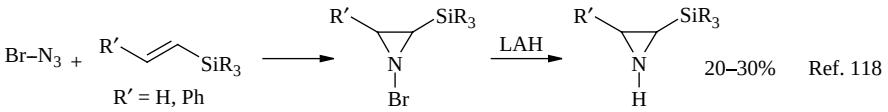


Ref. 116



Ref. 117

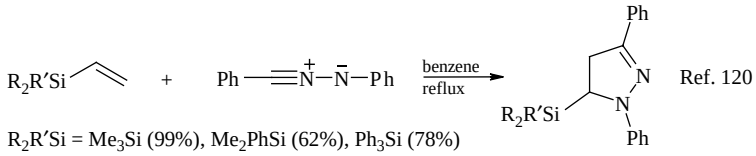
The use of bromoazide allows the synthesis of N-non-substituted silylaziridines after condensation and reduction with lithium aluminum hydride.[118]



Similar results are obtained using iodoazide. The reaction occurs with excellent stereocontrol.[119]

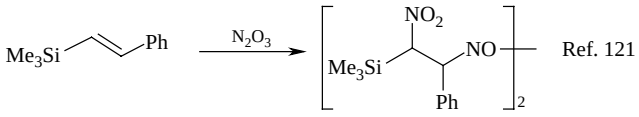
d. Diphenylnitrile Imine

5-Silyl-2-pyrazolines are obtained in moderate to excellent yields by the [2 + 3] cycloaddition of a vinylsilane with diphenylnitrile imine.[120]



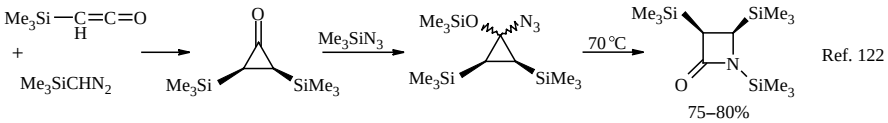
e. Nitrogen Oxide N_2O_3

α-Silyl nitroalkanes, under the form of pseudonitrosite dimers, result from the addition of nitrogen oxide N_2O_3 to vinylsilanes.[121]



9. Ring Enlargement of Silylcyclopropanone

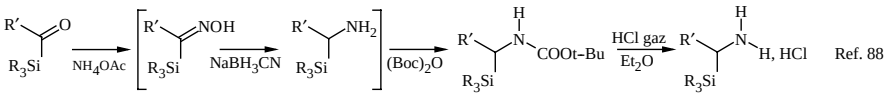
Reaction between trimethylsilyldiazomethane and trimethylsilylketene produces the disilylcyclopropanone. This was reacted with trimethylsilylazide to form the corresponding azetidinone in high yields after heating.[122]



10. Reduction of an Oxime of Acylsilane

Reduction of the imine or oxime of an acylsilane provides an appropriate route to SMA derivatives, as several routes to acylsilanes are now available. This process is

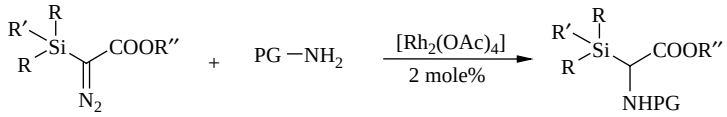
effective using the oxime of an acylsilane.[88]



Ref. 88

11. Silylcarbene Insertion into the N–H

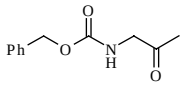
The ruthenium-catalyzed insertion of the carbene derived from an α-diazosilylacetate led to the formation for the first time, of a stable 1-silylaminoester in moderate to high yields.[123]



R = Me, Et R′ = Me, Et, *t*-Bu R″ = Et, Bn 47–86%

Ref. 123

PG = Tosyl, Boc, BnOCO and



B. *Formation of the Si–C Bond*

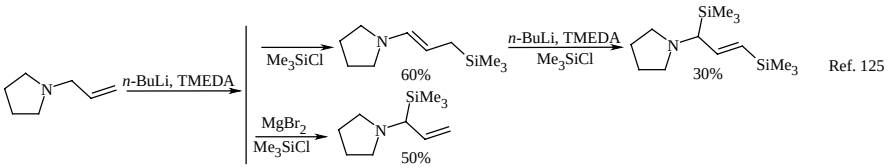
Ideally, the introduction of a silyl moiety to the α-position of a nitrogen atom would be carried out through the reaction of a chlorosilane with a α-nitrogen carbanion. However, obtaining anions with a suitable α-nitrogen moiety is difficult, restricting this approach to nitrogen derivatives wherein the α-position is further activated.

1. Silylation of a α-Nitrogen Carbanion

Metallation of amine derivatives adjacent to nitrogen and further electrophilic substitution is a well-documented process to elaborate amines, provided that the starting amines are activated.[124]

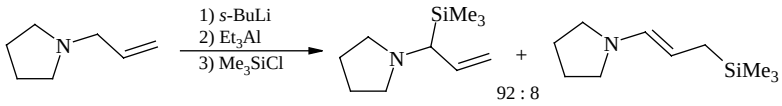
a. Allylamines

Reaction of allylpyrrolidine with *n*-butyllithium in TMEDA leads, after silylation, to a silylated enamine; further treatment with *n*-butyllithium results in the 1,3-migration of the trimethylsilyl group to the corresponding SMA derivative in poor yield after silylation. In the presence of magnesium bromide, 1-trimethylsilylallylpyrrolidine is formed selectively in moderate yield.[125]



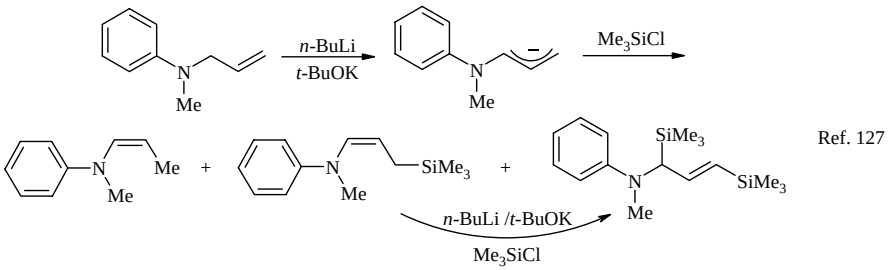
Ref. 125

The use of an alanate intermediate instead of a lithium reagent is not specific as a mixture of both isomers is obtained, with the SMA structure being predominant.[126]



Ref. 126

Similar results are observed starting from *N*-phenyl-*N*-methylallylamine.[127]

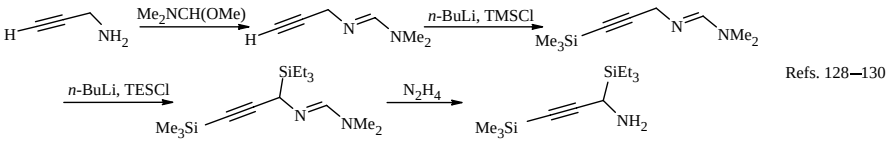


Ref. 127

A similar synthesis has been described involving partial hydrogenation of the triple bond of a 1-silyl propargyl amine (see Section III.B.1.b).

b. Propargyl Amine

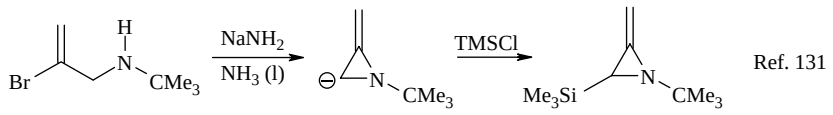
After protection of the amine function under the form of a formamidine, silylation (80% yield) and deprotection *via* hydrazonolysis, propargyl amine is converted to the corresponding bis(silyl)propargylamine.[128–130]



Refs. 128–130

c. 2-Bromoallylamine

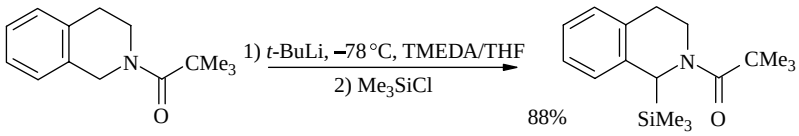
The reaction of 2-bromoallylamine with sodium amide in liquid ammonia forms a cyclic anion that reacts with trimethylchlorosilane to provide 1-trimethylsilyl-2-methylene aziridine.[131]



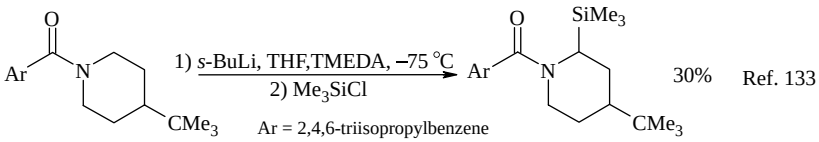
Ref. 131

d. Amides and Thioamides

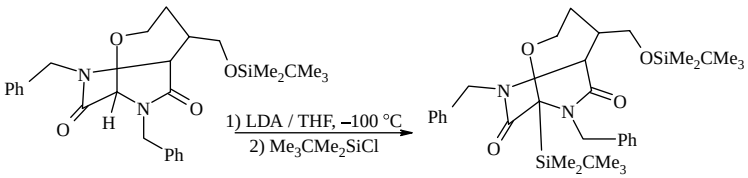
The first example of the silylation reaction of amides to form *N*-silylmethylamides was published in 1983.[132] Later, *s*-BuLi was substituted for *t*-BuLi and the yield was lower.[133] Next, activation by a carbonyl group (from another amide function) allowed the use of LDA at low temperatures.[134]



Ref. 132

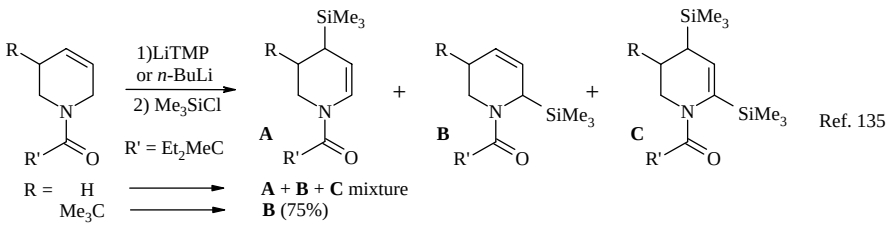


30% Ref. 133



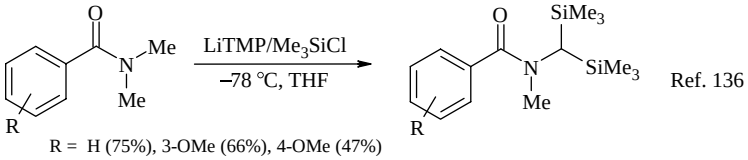
Ref. 134

When *N*-acyl-3,4-dehydropiperidine (R = H) is deprotonated and trimethylsilylated, three compounds are formed, among which only **B** is an SMA. However, starting from the 5-*t*-butyl-*N*-acyl-3,4-dehydropiperidine (R = *t*-butyl), compound **B** is obtained as the sole product.[135]

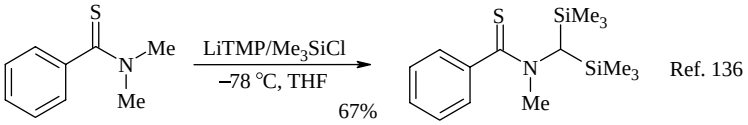


Ref. 135

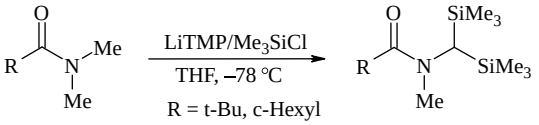
The use of lithium tetramethylpiperidide (LiTMP) as the base, followed by a quench with trimethylchlorosilane, has been shown to effectively silylate *N*,*N*-dimethylamides. With two equivalents of base the reaction occurs on the same methyl group, probably because the first trimethylsilyl group favors the formation of and stabilizes the anion on the same carbon atom.[136,137] The process has been extended to thiobenzamide[136] and aliphatic amides.[137]



Ref. 136

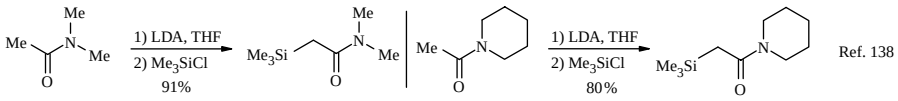


Ref. 136



Refs. 136, 137

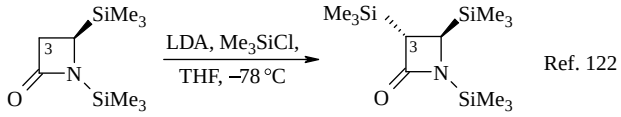
This last result is in contrast with the one of silylation of amide with LDA in solvent THF that give α-silylated amides.[138]



Ref. 138

e. Azetidinones

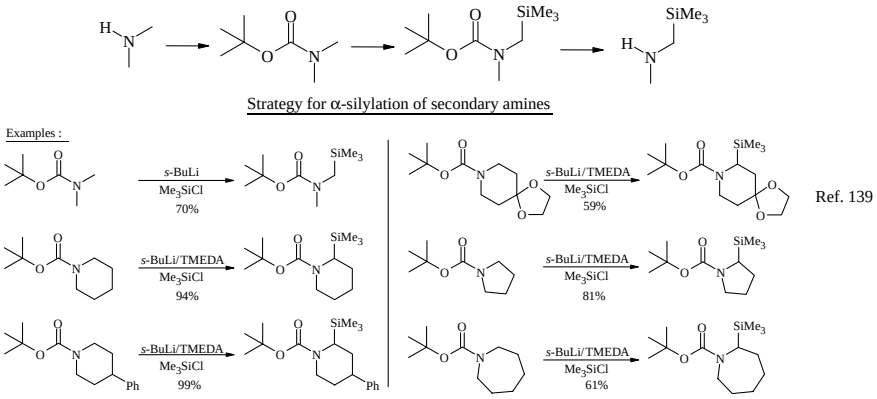
A similar process was used to silylate 1,4-bis(trimethylsilyl)azetidinone in position 3 as the final step of transformation of the *trans*-1,3,4-trissilylazetidinone into its *cis* isomer.[122]



Ref. 122

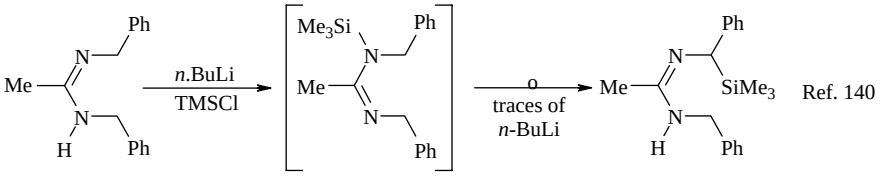
f. Carbamates (N-Boc-amines)

Protection of secondary amines as *t*-butylcarbamates activates the α-position to nitrogen. Lithiation of this position with *s*-butyllithium in TMEDA followed by silylation leads to the desired α-silylated amine.[139]

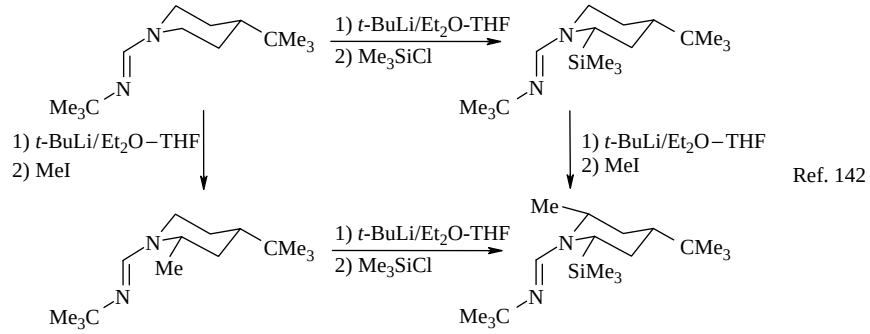


g. Amidines

Silylation of *N*,*N*-dibenzylacetamidine has been explored. Reaction occurred first at a nitrogen atom giving a *N*-silyl derivative that isomerized *via* a base-catalyzed N to C silyl migration into the silylbenzyl derivative.[140]

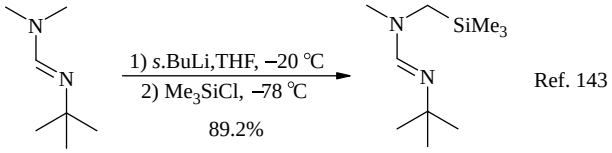


Formamidines have been recognized as good activators for the α-deprotonation of amines at the α-position.[141] Trapping the anions with trimethylchlorosilane led to the corresponding SMA.[142]



In this procedure, two substituents were introduced in diequatorial relationship. This contrasts with the results from the N-Boc procedure (see above) that led to the axial/equatorial substitution.[135]

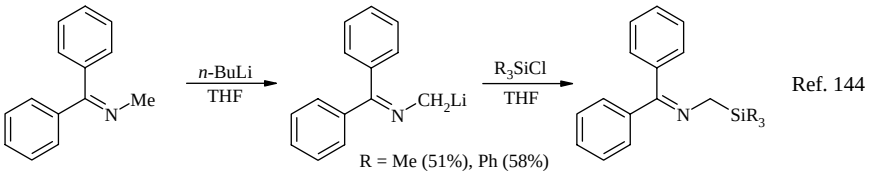
Another example was given as a step in a process for homologation of carbonyl compounds, in which treating *N*′-*t*-Bu-*N*,*N*-dimethylformamidine with *s*-BuLi in THF at −20 °C and quenching the intermediate anion led to the corresponding aminomethylsilane.[143]



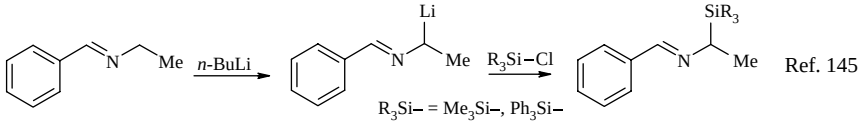
Ref. 143

h. Aliphatic Imines

Trimethyl- and triphenylchlorosilanes have been used to trap the lithium reagent that resulted from the action *n*-butyllithium in THF on the *N*-methyl benzophenone imine.[144,145] More recently, this technique has been applied to the synthesis of polystyrene-grafted silylmethylimines.[146]



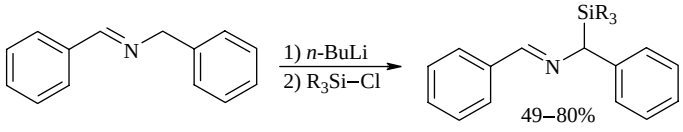
Ref. 144



Ref. 145

i. Benzylamines

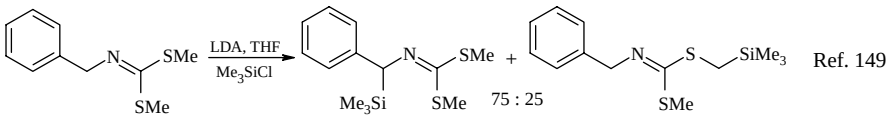
Benzylamines have been transformed into their benzaldimines in order both to protect the primary amine function and to enhance the acidity of the proton at the sp^3 carbon atom. Deprotonation–silylation of the benzaldimines led to the corresponding SMA in yields which depend on the substituents on the silicon.[147]



Ref. 147

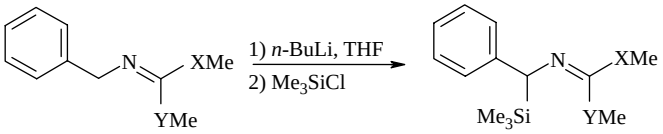
However, this reaction is not regiospecific with systems made dissymmetrical by introducing a substituent in *para* on one of the phenyl groups.[148] *S*,*S*′-Dimethyl-*N*-(benzyl)imidothiocarbonate was deprotonated by means of lithium diisopropylamide

in THF at both benzylic methylene and methyl as evidenced after quenching with TMSCl.[149]



Ref. 149

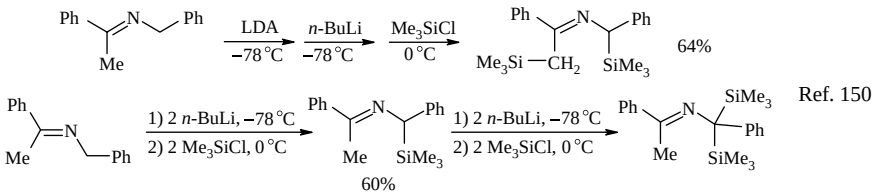
Deprotonation with *n*-butyllithium in THF/HMPA/hexane provided a regiospecific silylation at the benzylic position. Similar results are obtained starting from *O*,*O*′ and *O*,*S*′-dimethyl derivatives. These derivatives are not very stable.[149]



Ref. 149

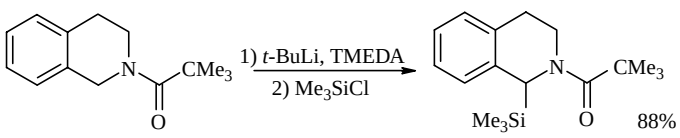
X,Y = S,S (40%), O,O (40%), S,O (60%)

A similar study on the deprotonation/silylation process of *N*-benzyl acetophenone imine led to similar results. Again *n*-butyllithium was shown to be regioselective. A second deprotonation–trimethylsilylation sequence leads to the expected BSMA derivative.[150]

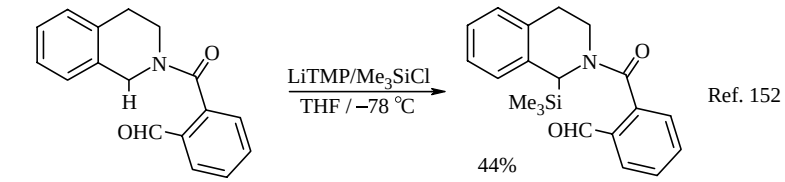


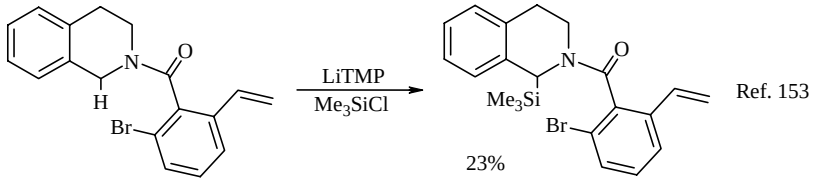
Ref. 150

N-Boc-4H-isoquinoline reacted quantitatively within 5 min with *t*-butyllithium in TMEDA to lead to the product silylated at the benzylic position.[151] Another 4H-isoquinoline-type product has been silylated using lithium tetramethylpiperidide (LiTMP) in THF and the resulting compound has served as an intermediate in the synthesis of protoberberine.[136,152] Interestingly, the intermediate lithium reagent did not react with the aldehyde group prior to silylation. A similar reaction has been done with the corresponding bromo derivative.[153]



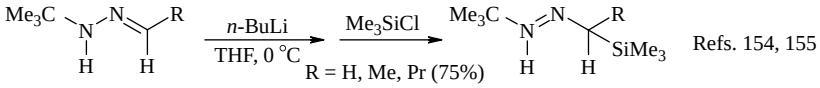
Ref. 151





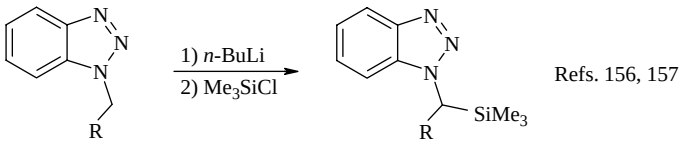
j. Hydrazones

Deprotonation–silylation of hydrazones with n-butyllithium in THF as the base followed by quenching with trimethylchlorosilane has been reported to afford the desired SMA derivative in good yield.[154,155]



k. Benzotriazoles

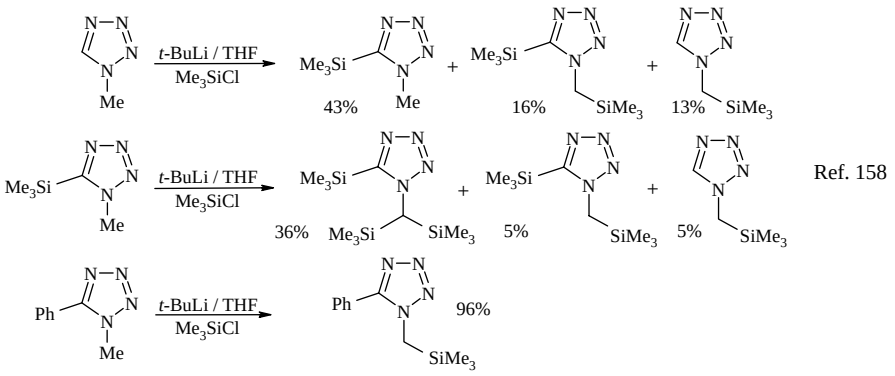
The deprotonation–silylation of *N*-alkylated benzotriazoles has been tested. Successive deprotonation–silylation of benzotriazoles leads to *N*-trimethylsilylmethyl- and *N*-bis(trimethylsilyl)methylbenzotriazole.[156,157]



l. Tetrazoles

Deprotonation–silylation of 1-methyl-1H-tetrazole exhibits predominant C-silylation at the 5-position to form 1-methyl-5-trimethylsilyl-1H-tetrazole (it is not a SMA, silylated carbon atom being sp^2). When this position is blocked by a silyl or a phenyl group, silylation occurs on the *N*-methyl to yield SMA derivatives.[158]

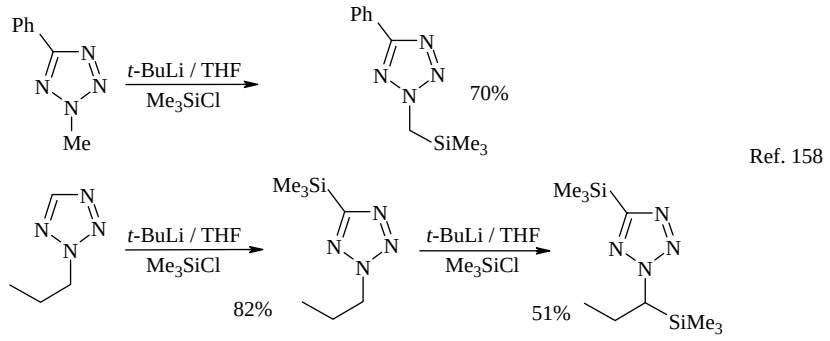
1-Methyl-1H-tetrazoles



Ref. 158

Similar to these results, 2-alkyl-2H-tetrazoles substituted at the 5-position leads to deprotonation–silylation on the alpha position of the alkyl chain on the nitrogen.[158]

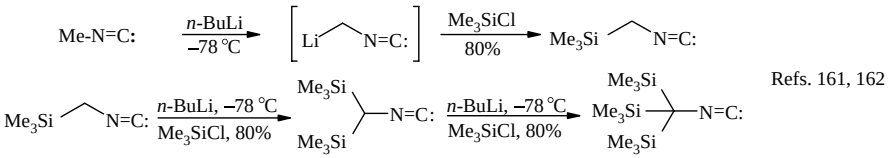
2-Methyl-2H-tetrazoles



Ref. 158

m. Isonitriles

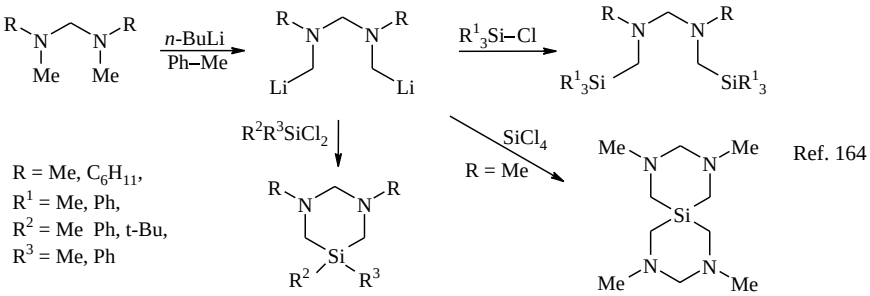
The insertion of isonitriles with bulky substituents and no α-hydrogen, (i.e., *t*-butyl), into the C–Li bond of a lithium reagent is a convenient route to aldimines and other functional organic compounds.[159] C-trimethylsilylimines result from deprotonation–silylation of isonitriles containing an α-hydrogen[2a,160] (See Section III.B.5.d). The reaction of *n*-butyllithium at low temperatures with alkyl α-hydrogen containing isonitriles leads to deprotonation. Trapping the intermediate with trimethylchlorosilane yields the α-silylisonitrile. Starting from methylisonitrile, the reaction can be repeated to synthesize bis- and tris-silylisonitriles.[161,162]



Refs. 161, 162

n. Diaminomethanes

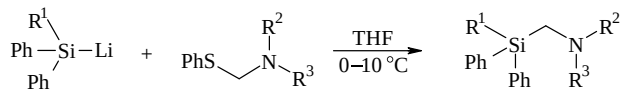
Due to the −I effect of the nitrogen atoms, diaminomethane derivatives (aminals) seem to be good candidates for the metallation at the methylene group, as is the case with tetramethylmethylenediphosphine, $Me_2PCH_2PMe_2$.[163] In practice, however, the reaction does not occur at the methylene group but at the *N*-methyl group instead, giving access to a variety of bis-silylmethyl diamino derivatives after silylation.[164] In the examples shown, activation is probably provided by α-nitrogen that coordinates to lithium and silicon atoms successively.



Ref. 164

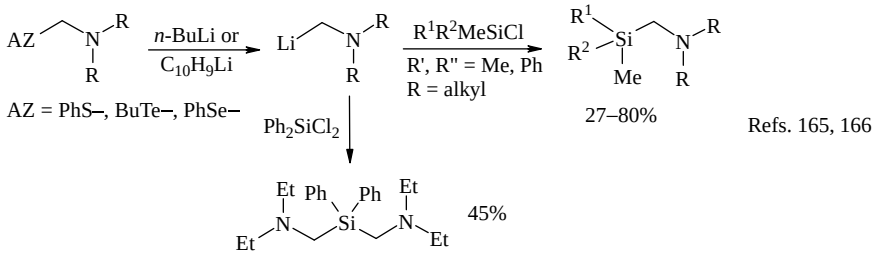
o. α-Element Amino Derivatives

Cleavage of a carbon to sulfur bond by a lithium reagent is a well known entry to organolithium reagents. This process has been used to synthesize α-nitrogen carbanions, and hence SMA derivatives.[67,165] This study has been extended to tellurium and selenium starting materials as well.[166]

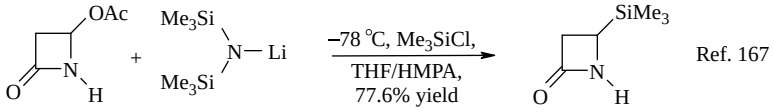


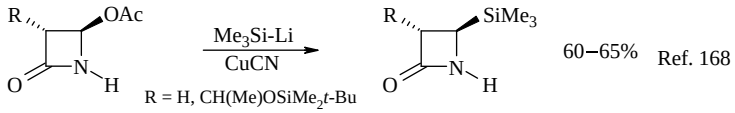
Ref. 67

R^1, R^2, R^3 = Ph, Me, Me (48%); Me, Me, Me (70.8%); Ph, Et, Et (48.2%); Me, Et, Et (74%); Ph, $–(CH_2)_4–$ (44.7%); Ph, $–(CH_2)_2O(CH_2)_2–$ (38%)

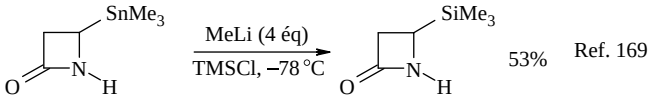


An acetoxy group at the 4-position of an azetinone ring is the precursor for the corresponding carbanion that can be readily trimethylsilylated.[167,168]



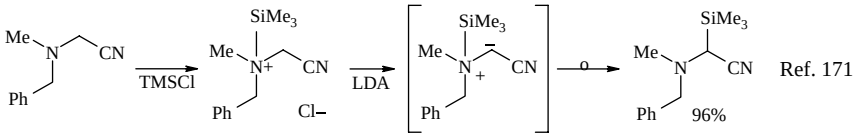


Substitution of the silyl group for a tin group gives access to azetidinones having the SMA fragment in the skeleton.[169]



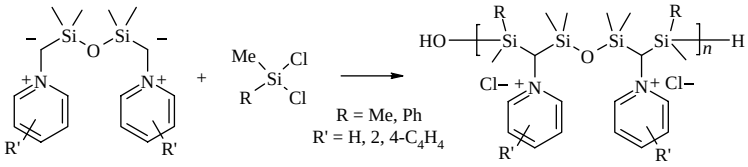
p. Aminoacetonitriles

Generally, α-aminoacetonitriles can be readily deprotonated with LDA and the resulting α-lithioaminonitrile alkylated in high yields.[170] In contrast, trimethylsilylation gives poor yields, probably because the lithio derivative reacts with the starting aminonitrile before being silylated. This drawback has been cleverly circumvented by the addition of trimethylchlorosilane to *N*-benzyl-*N*-methylaminoacetonitrile to form the silylammonium salt. Treatment of this salt with LDA/THF leads to silylcyanoamine in quantitative yield *via* the rearrangement of the ylid formed.[171] This procedure is particularly interesting because silylcyanoamines can be considered as excellent precursors of α-silyaminoacids.



Ref. 171

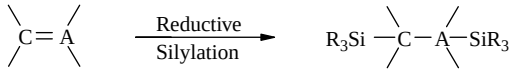
A similar process has been used in the case of polysiloxanes with pendant pyridinium groups.[172] In this instance, an MSMA derivative was transformed into a BSMA derivative.



Ref. 172

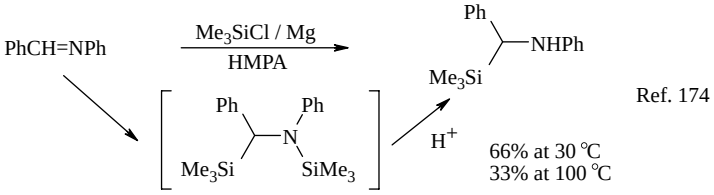
2. Reductive Silylation of Imines, Nitriles and Cyano Derivatives

Reductive silylation is a very fruitful technique that consists of the treatment of an unsaturated organic molecule with a chlorosilane (generally trimethylsilyl chloride) and a metal (magnesium or lithium) in an aprotic solvent (THF or HMPA or mixture of both). The result is that the unsaturation C=A or C≡A is reduced and two silyl groups are introduced at the termini.[173] A large variety of unsaturated organic functionalities have been reductively silylated in this manner. Among these, C=N and C≡N derivatives were the starting materials of choice for the synthesis of SMAs.



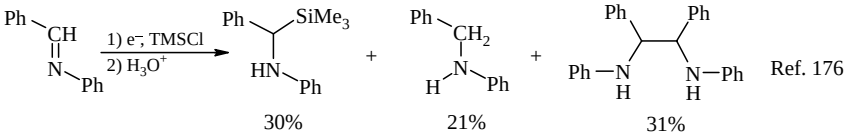
a. Schiff Bases

The reductive silylation of Schiff bases is reported to yield (trimethylsilyl)benzylaniline (ASMA), after hydrolysis of the reaction medium. The reaction is highly sensitive to temperature.[174] An anion-radical mechanism was postulated. Similar results are obtained from diversely N-substituted benzaldimines.[175]



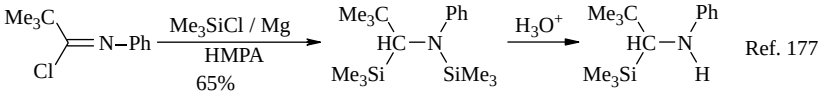
Ref. 174

The role of the metal is to provide the organic substrate with electrons. These electrons could be provided electrochemically, and it has been shown that electrosynthesis can afford the same products, although reduction and dimerization are concurrent reactions.[176]

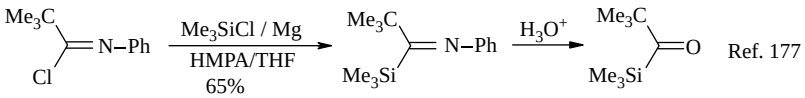


b. Iminoyl Chloride

The reductive silylation of *N*-phenylpivalimidoyl chloride has been studied in HMPA as the solvent and (1-trimethylsilyl)*t*-amylaniline is obtained in 65% yield along with some of the non-silylated aniline (15%).[177]



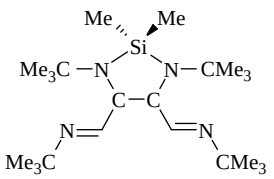
If HMPA is used in stoichiometric amount in THF as the solvent, then substitution of the chlorine atom occurs providing the corresponding C-silylated imine, the precursor of the acylsilane pivaloylsilane. This imine can also be regarded as a good precursor of an SMA through its reduction. Reduction of the iminoylchloride into the non-silylated imine is a side reaction.

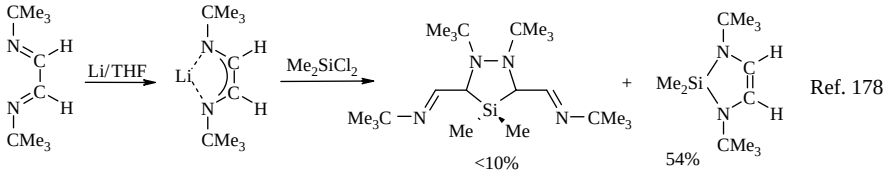


c. Diimine

When glyoxal diimine is reacted with lithium in THF and in the presence of a chlorosilane, formation of an SMA is not expected. It has been postulated, however, that a 1,2-diaza-4-silacyclopentane derivative (SMA) is formed in low yield* in addition to the expected product, 1,3-diaza-2-sila-4-cyclopentene.[178]

*Note of the author: NMR data given by the authors[178] fit equally well with the following 1,3-diaza-2-silacyclopentane isomeric structure.

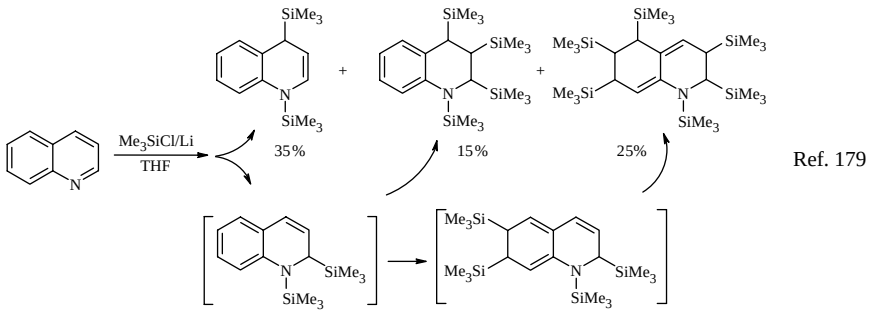




Ref. 178

d. Quinoline

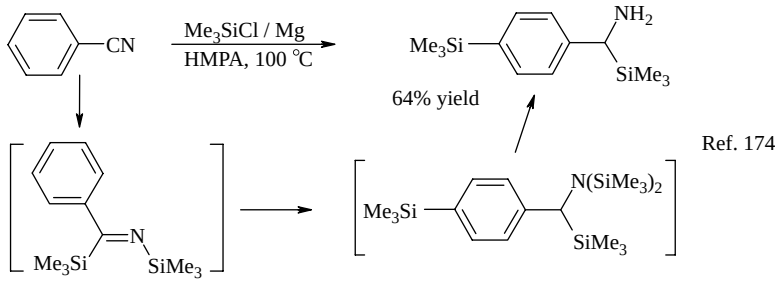
The reductive-trimethylsilylation of quinoline has been studied. Among the products isolated are two RSMA derivatives.[179] For further oxidation and protolysis see Section VI.B.3.d.



Ref. 179

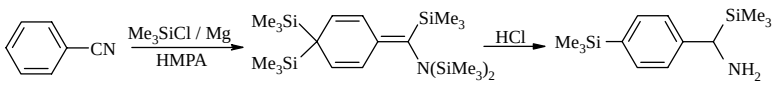
e. Benzonitrile

The less reactive magnesium reagent allows the complete reductive trimethylsilylation of the nitrile function of benzonitrile. Hydrolysis of the obtained silazane into the ammonium chloride followed by its neutralization afforded the α-trimethylsilylbenzylamine (ASMA) in good yield.[174]



Ref. 174

The intermediacy of an imine was postulated. In order to test this hypothesis and to find an explanation to the introduction of one silyl group on the *para*-position on the ring, this reaction has been revisited. Avoiding hydrolysis of the reaction medium, the real reaction product was identified as being an enamine, the likely precursor of the ASMA.[180]

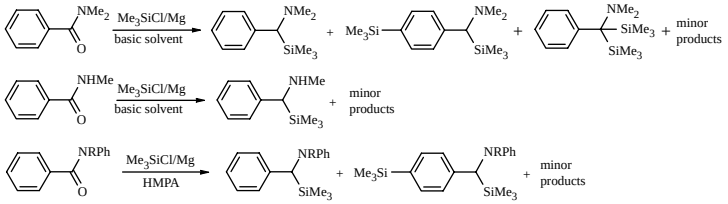


Ref. 180

Similar enamines were obtained from α- and β-naphtonitriles,[180] and the same ASMA has been prepared from *p*-chlorobenzonitrile.[181]

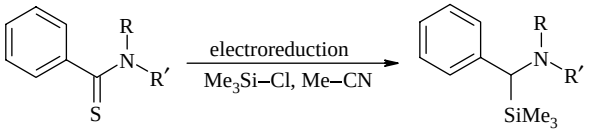
f. Benzamides

Benzamides have been subjected to reductive-trimethylsilylation and ASMA derivatives were obtained, though mixed with other compounds in ratios which depend on the solvent used and on the nature of the R group on nitrogen.[182,183]



Refs. 182, 183

A parallel study of the silylation of thiobenzamides in acetonitrile has been done, utilizing a constant potential electroreductive-trimethylsilylation technique.[184] The corresponding α-(trimethylsilyl)benzyl-amines were obtained in yields that depended on the nature of the substituents at nitrogen.

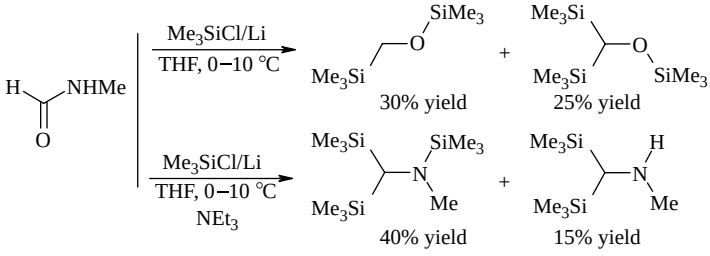


R	R′	yield
Me	Me	80%
Me	Ph	30%

Ref. 184

g. Aliphatic Amides

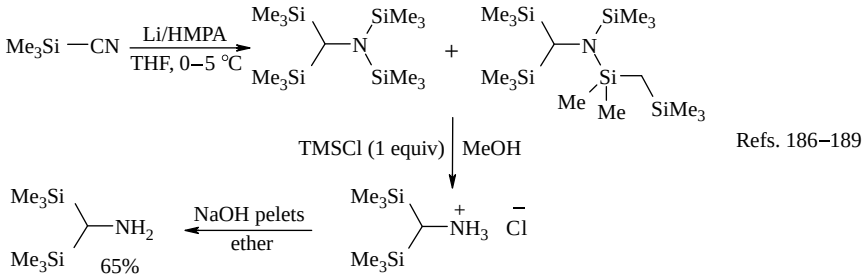
Reductive-trimethylsilylation of formamides, using trimethylsilyl chloride and lithium in tetrahydrofurane lead to complex mixtures of O- and N-substituted derivatives that depend upon the conditions of the reaction and the substituents at nitrogen. However, in the presence of triethylamine, the reaction is oriented toward the unique formation of the α-silylamine. In general, the yields are moderate.[185]



Ref. 185

h. Cyanides

Trimethylsilylcyanide has been reductively trimethylsilylated.[80,186,187] A mixture of two silazanes is obtained in 65–70% yield and in a ratio that varies with the conditions of the reaction. No free rotation was observed along the C–N bond. Treatment of the reaction mixture with one equivalent of trimethylchlorosilane in methanol provides, after evaporation of the low boiling materials, a quantitative yield of bis(trimethylsilyl) methylamine (BSMA), that was entirely recovered after neutralization of its hydrochloride with solid sodium hydroxide in diethyl ether.[188] An electrochemical version of this synthesis, with similar results, has been described.[189]

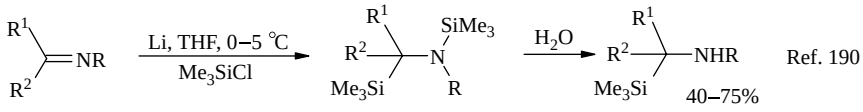


Refs. 186–189

In an extension of these studies substitution of trimethylsilylcyanide for other silylcyanides (e.g., ethyldimethylsilylcyanide), isocyanides or cyanamides led to the same results. Among these, dimethylcyanamide was found to be an advantageous starting material for the preparation of BSMA.

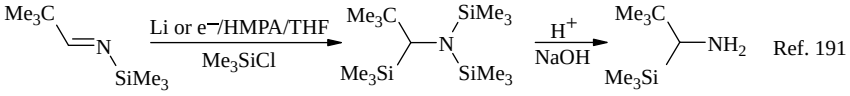
i. Aliphatic Imines and Nitriles

The reductive-trimethylsilylation of imines by means of granulated lithium in THF at 0–5 °C is a good method to synthesize ASMA and RSMA. This process was applied to aldimines and ketimines, lower yields being obtained in the latter case.[190]



Ref. 190

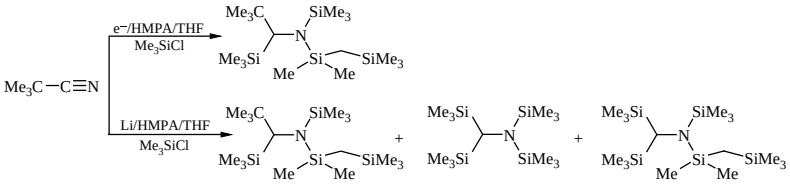
The reductive-trimethylsilylation, *via* either a chemical (Li/HMPA/THF) or an electrochemical (undivided cell/sacrificial anode) process, led to the synthesis of 1-(trimethylsilyl)alkylamines (RSMAs).[191] Thus, 1-(trimethylsilyl)*t*-amylamine was prepared in 67% yield from pivalaldehyde *N*-(trimethylsilyl)imine, after hydrolysis of the intermediate silazane.



Ref. 191

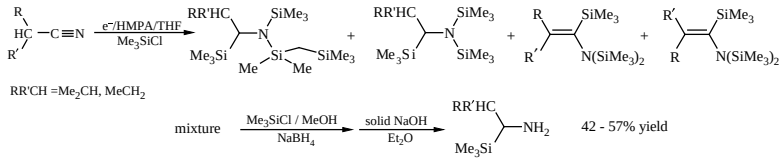
Using the same electrochemical process, pivalonitrile affords a silazane similar to this one in a comparable yield of 60%. However, the chemical process is not as selective

producing in addition to the expected silazane in 63% yield, other silazanes corresponding to those obtained previously from cyanides in yields of approximately 20% yield each, indicating that this nitrile behaves as a cyanide in this instance.[191]



Ref. 191

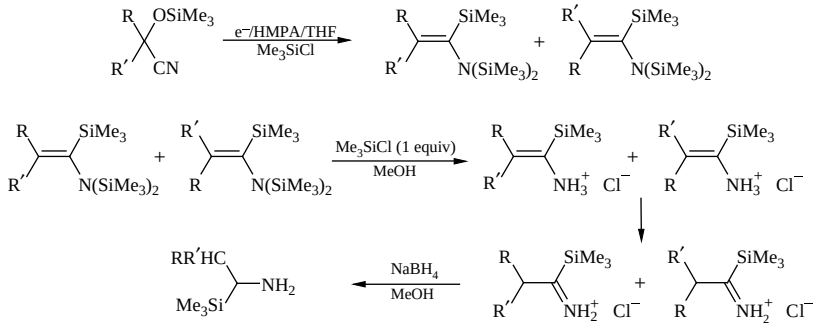
Nitriles having at least one hydrogen on the functional carbon, react with trimethylchlorosilane under electrochemical conditions to provide a mixture of silazanes and enamines of acylsilanes. These enamines have been suggested to be formed from the isomeric ketene imine form of the nitrile. They were obtained as a mixture of Z (major) and E isomers. Treatment of the silazane–enamine mixture with trimethylchlorosilane/methanol and sodium borohydride followed by neutralization of the salt gives the corresponding RSMA.[191]



Ref. 191

j. Cyanohydrins

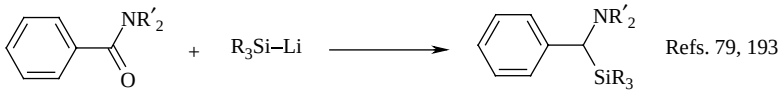
Enamines have been prepared through reductive-trimethylsilylation of cyanohydrins as precursors of acylsilanes.[1a,192] As indicated above, these enamines are also excellent starting materials for synthesizing RSMAs *via* reduction of the corresponding iminium chlorides with sodium borohydride.[1a,1b]



Ref. 1a

3. Reductive Silylation of Benzamides Using Silyllithium Reagent

The reaction of silyllithium reagents with *N*,*N*-dialkylated benzamides has been investigated. The corresponding *N*,*N*-dialkyl-α-(silyl)-benzylamines (ASMA) were obtained in low yields.[79,193]

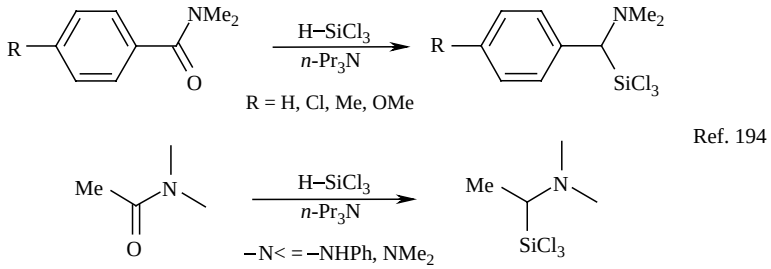


Refs. 79, 193

This process leads to products identical to those obtained through nucleophilic amination of α-silyl benzyl halides (See Section III.A.3), but this method of synthesis is less satisfactory as far as convenience and yields are concerned (See Section III.B.4).

4. Reductive Silylation of Amides Using Trichlorosilane/Tertiary Amine Mixture

A trichlorosilane/tertiary amine mixture has been shown to reduce the carbonyl moiety of aromatic amides to give ASMAs. This constitutes an alternative to the reductive silylation described in Section III.B.2.f.[194] This work has been reviewed[195] and extended to aliphatic amides to give RSMA.



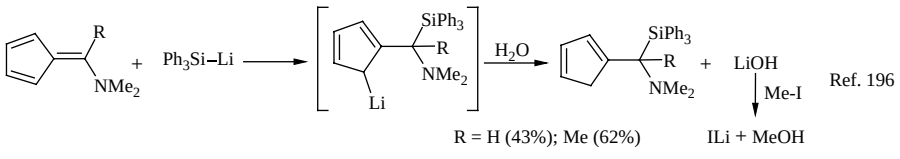
Ref. 194

5. Miscellaneous

Various chemical transformations have led to the formation of the SMA structure. However, they have not been considered of preparative value, mostly because the starting materials were of limited access and yields were low.

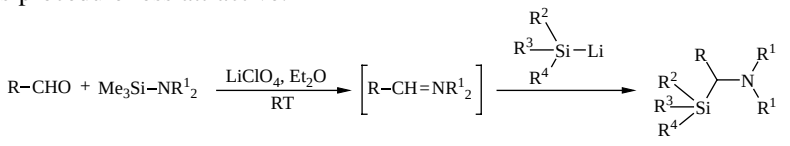
a. Addition of Silyllithium Reagents to Enamines and Iminium Salts

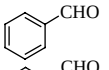
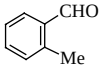
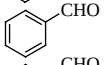
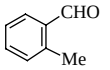
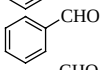
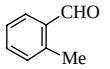
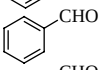
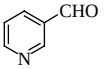
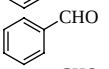
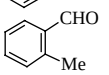
Cyclopentadienyl-SMA have been obtained through addition of triphenylsilylithium reagent to 6-(dimethylamino)fulvenes, hydrolysis and final treatment of the residue with methyl iodide.[196]



Ref. 196

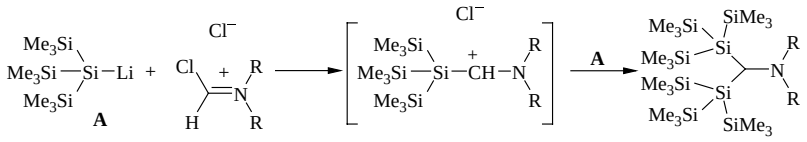
N,*N*-Dialkyl-RSMAs have been prepared by addition of silyllithium reagents to iminium salts formed *in situ* by reacting aldehydes with silylamines in the presence of lithium perchlorate. Although excellent yields have been obtained, except when starting from enolizable aldehydes, the use of the dangerous reagent lithium perchlorate makes this procedure less attractive.[197]



RCHO	NR^1_2	R^4, R^3, Si, R^2	yield (%)	RCHO	NR^1_2	R^4, R^3, Si, R^2	yield (%)
		$SiPh_2Me$	95		NMe_2	$SiPh_2Me$	95
	NMe_2, HCl	$SiPh_2Me$	70		NMe_2, HCl	$SiPh_2Me$	83
		$SiPh_3$	80		NMe_2	$SiPh_3$	70
	NH_2	$SiPhMe_2$	80			$SiPhMe_2$	76
	NMe_2	$SiPhMe_2$	85				
	NMe_2	$SiPhMe_2$	74			$SiPh_3$	50

Ref. 197

Similarly, dimethylamino-bis[tris(trimethylsilyl)silyl]methane has been obtained.[198]

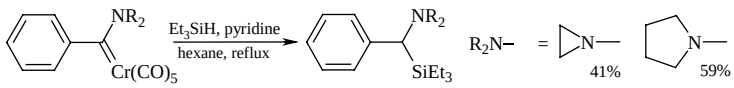


Ref. 198

NR_2 = Me_2 (54%), Et_2 (impure), $(CH_2)_5$ (43%)

b. Insertion of an α-aza-Carbene/Chromium Complex into the Si–H Bond

Treatment of this complex with triethylsilane gives the corresponding ASMA in moderate yield.[199,200]

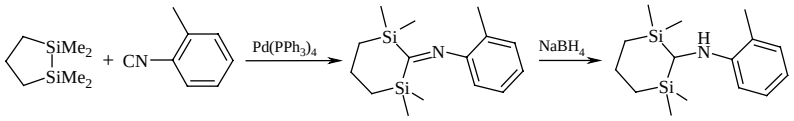


Refs. 199, 200

c. Insertion of Isonitriles into the Si–Si Bond Followed by Reduction

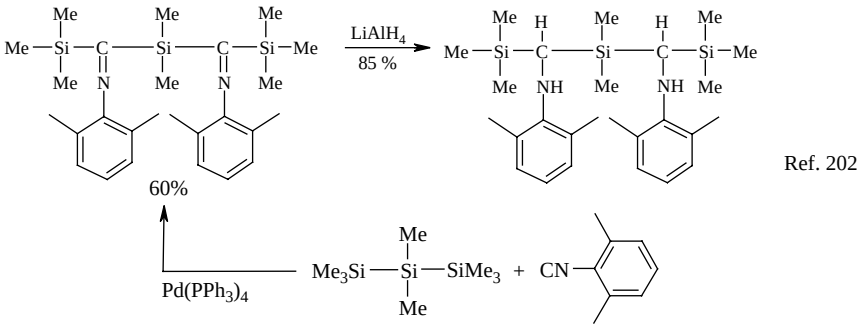
When a disilane is reacted with an isocyanide in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0), an imine is formed. Subsequent reduction by

an hydride leads to the corresponding BSMA derivative.[201]



Ref. 201

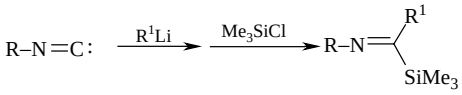
This synthesis has been used to prepare polycarbosilanes with pendant aniline substituents.[202]



Ref. 202

d. Insertion of an Isonitrile into the C–Li Bond Followed by Silylation

Imines of acylsilanes are excellent precursors of SMA (See Section III.B.1.m). Insertion of an isonitrile into the C–Li bond of a lithium reagent, followed by the silylation of the resulting vinyllithium derivative affords such imines.[160]

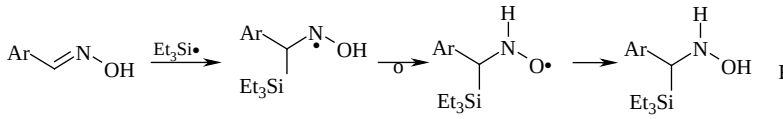


Ref. 160

R,R[1] = Ar,Me (41%); Ar,Et (41%); Ar,*i*-Pr (52%); Ar,*t*-Bu (73%); *t*-Oct,n-Bu (51%); *t*-Oct,Ph (30%); *t*-Bu,*n*-Bu (31%)

e. Radical Addition of Si–H to >C=N of Oximes, N-Oxides or Nitrones

The interaction between oxime and triethylsilyl radical has been investigated by ESR, which showed that an α-silylated hydroxylamine is formed. In spite of the lack of any further detail, this reaction may constitute an excellent access to this type of SMA derivatives, which are otherwise difficult to obtain.[203]

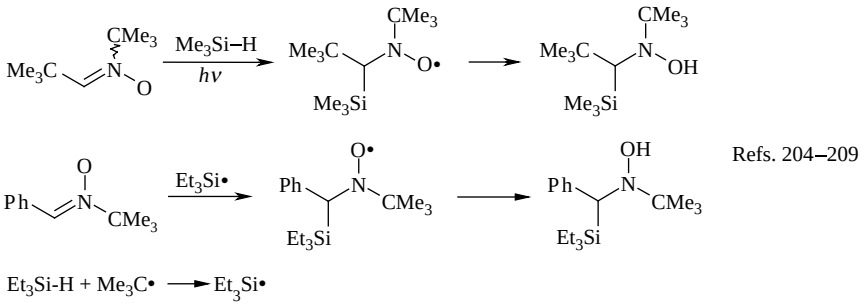


Ref. 146

Ar = Ph, *p*-MePh, *p*-MeOPh, *m*-pyridyl, *p*-pyridyl, α-furyl, β-thienyl, α-thienyl

Similarly, for the purpose of studying silyl radicals in the gas phase in the presence of a spin trap, it has been established that the trimethylsilyl radical added to the double bond of a nitrone to yield the α-trimethylsilylated hydroxylamine.[204] Other studies have been

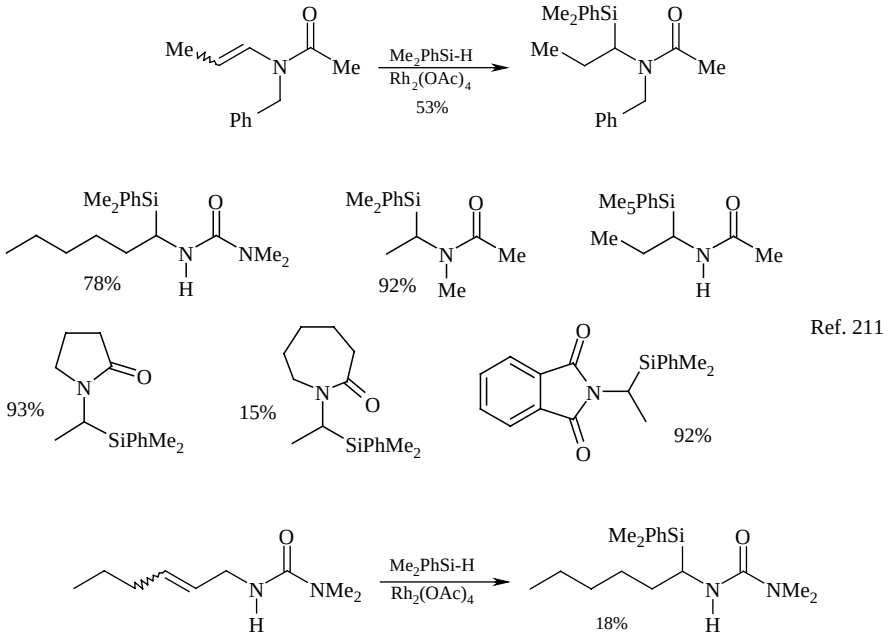
reported where silyl radicals were generated by action of di-*t*-butyl peroxide or light.[205–209] A related study using the diphenylchlorosilyl radical has been reported.[210]



Refs. 204–209

f. Rhodium Catalyzed Addition of Si–H to Enamides

The addition of phenyldimethylsilane to the double bond of enamides (or vinyl ureas) in the presence of catalytic amounts of rhodium acetate, leads to *N*(α-silyl)alkyl amides (or ureas). Rhodium catalyst are known to move double bonds, and indeed the same type of RSMA are obtained from an *N*-allyl urea, albeit in low yield. On the other hand, hydrosilylation of *N*-allyl imides takes place at the terminal carbon atom in high yields.[211]

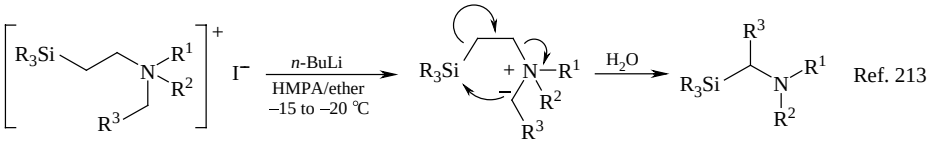


Ref. 211

g. 1,4-Isomerization of β-Silyl Quaternary Ammonium Salts

β-Silylated quaternary ammonium salts when treated with *n*-butyllithium in HMPA/Et_2O solvent mixture at low temperatures leads to RSMA as the major

products.[212–214] This 1,4-rearrangement, which can be compared to the Sommelet–Hauser [3,2] sigmatropic rearrangement, can be explained in the following way: anion formation α- to nitrogen on one of its substituents, which would attack silicon inducing the elimination of ethylene.

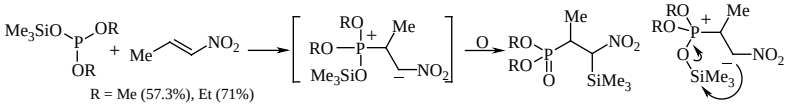


Ref. 213

When LDA was used in place of butyllithium, 1,1-bis(trimethylsilyl)ethylene (Hoffmann-type elimination product) was obtained as the main product (71%).[214]

h. Isomerization of O-Silylnitrophosphonate Ylids

A 1,4-rearrangement similar to that of β-silyl quaternary ammonium salts shown in Section III.B.5.g leading to α-silylated nitroalkanes has been reported.[215]



R = Me (57.3%), Et (71%)

Ref. 215

i. Palladium Catalyzed Addition of Disilanes to Imines

In the catalytic presence of tetrakis(triphenylphosphine)palladium imines condenses with disilanes in toluene after 5 h at 120 °C in a sealed tube to give high yields of the corresponding α-silyl-*N*-silylamine.[216]

j. Addition of C–H (from >N–CH) to a Silanimine and [2 + 2]Cycloaddition of Si=Si to C=N

BSMA and RSMA derivatives are formed by the addition of the C–H bond of the >N–CH substructure to a silanimine (>Si=N–)[217] and [2 + 2]cycloaddition of disilene (>Si=Si<) to the azomethine linkage, respectively.[218]

IV

TRANSFORMATIONS WITHOUT CLEAVAGE OF THE SUBSTRUCTURE

Transformations without cleavage of the α-silyl amine substructure present two advantages. First, they provide methods to convert one SMA derivative to another SMA derivative. Secondly, they illustrate numerous aspects of the reactivity of SMA derivatives.

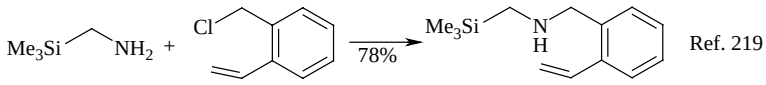
A. *Transformations at Nitrogen*

Silylmethylamines and their derivatives have been the subject of many transformations. The results parallel those obtained from pure organic amines and derivatives.

1. Amines to Amines

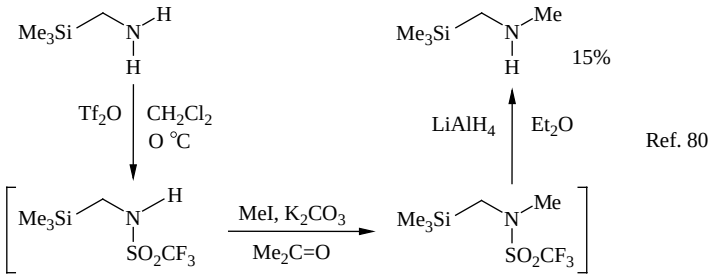
a. Alkylation of a Primary SMA

The classical alkylation of a primary amine with an alkyl halide in the presence of a base has been used to prepare *N*-trimethylsilyl benzylamines efficiently.[219]



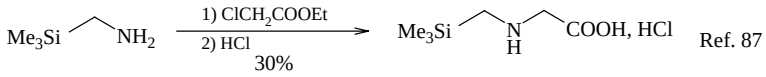
Ref. 219

Another route consists of a three-step process: the protection of the amine under the form of its triflate,[220], followed by a classical alkylation and finally reductive release of the amine. Although this route gives selectively the *N*-monomethylated derivative, the low yield (possibly due to its volatility) of the final step makes this synthesis not very attractive.[80]



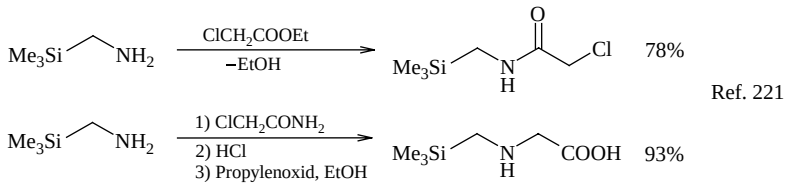
Ref. 80

The reaction of MSMAs with chloroacetates has been studied. It was stated that mixing trimethylsilylmethylamine with ethyl chloroacetate leads to the formation of the corresponding sarcosine after treatment with dilute hydrochloric acid.[87]



Ref. 87

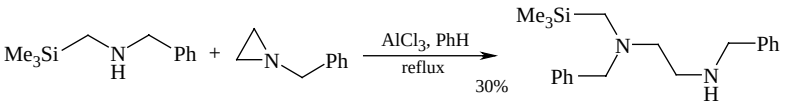
In another study, the experiment could not be reproduced and instead the corresponding chloroacetamide was obtained in 73% yield. Under similar conditions, *N*-trimethylsilylmethylglycine has been obtained *via* its amide.[221]



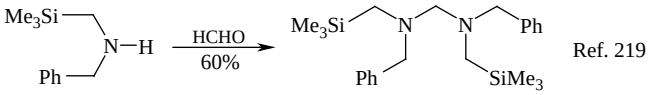
Ref. 221

b. Alkylation of Secondary SMAs

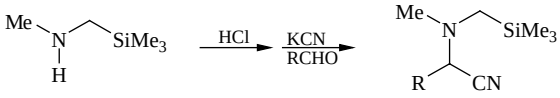
No direct alkylation of a secondary SMA has been reported. However, indirect methods have been described. Albeit the yield was not very high[†], the condensation of *N*-benzyl MSMA with an aziridine in the presence of aluminum chloride, provided a route to a *N*-silyl-1,2-diamine.[219]



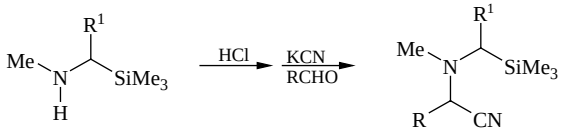
Another route is based on the well-known property of amines to add to aldehydes to form aminals. The conversion of these intermediates provides entries to tertiary SMAs. For example, simple treatment of *N*-benzyl MSMA with formaldehyde gives the corresponding diaminomethane derivative in good yield.[219]



Classical treatment of the aminals with potassium cyanide leads to the corresponding α-amino nitriles in high yields.[64]



RCHO = HCHO (92%); nicotinaldehyde (90%)



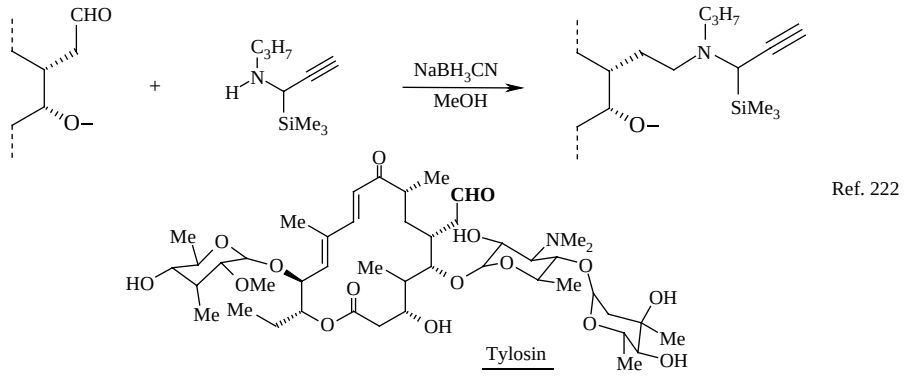
Ref. 64

R,R[1] = H,H (94%); Me,H (73%); H,Me (80%)

Reduction of an aminal (derived from tylosine[‡]) with sodium cyanoborohydride has also been used to prepare the corresponding tertiary RSMA.[222]

[†]Probably, partial desilylation has occured through quaternarization of the nitrogen atom of the MSMA with chloride (see Section V).

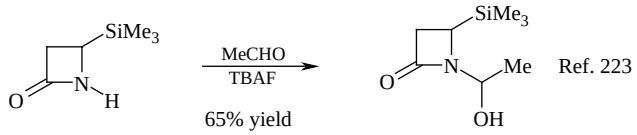
[‡]Tylosine is an important antibiotic in veterinary medicine.



2. Amines to Derivatives

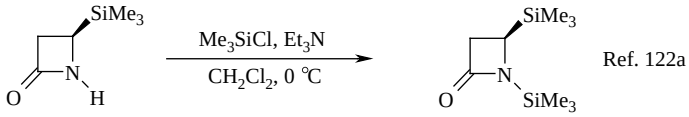
a. Aminals

In an effort to cleave the silyl group (see Section VI.B.2), 4-trimethylsilyl azetidinone was treated with tetrabutylammonium fluoride, TBAF, in the presence of acetaldehyde. The corresponding aminal was obtained instead in 65% yield.[223]



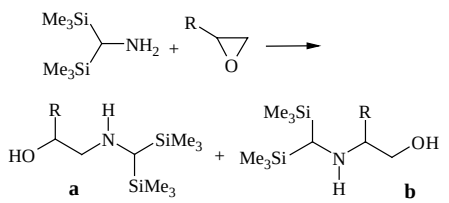
b. Silylation of SMA

The amidic proton of the same azetidinone has been silylated in a classical way, almost quantitatively, using chlorosilane/triethylamine mixture at 0 °C.[122a]



c. Addition to Epoxides and Epichlorohydrin

Aminolysis of dissymmetric epoxides by BSMA has been shown to regio- and stereospecifically yield the corresponding *N*-bis(trimethylsilyl)methyl β-aminoalcohols.[224] Double addition has not been observed in these transformations.

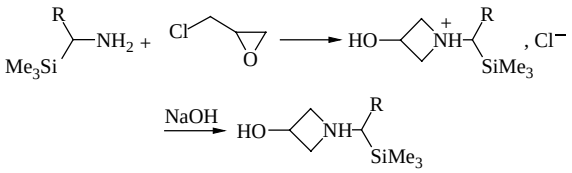


R	a/b ratio	Yield (%)[c]
Ethyl	100/0[a] (100/0)[b]	90
Vinyl	100/0[a] (96/04)[b]	86
Phenyl	100/0[a] (90/10)[b]	80
o-Cl-Phenyl	100/0[a] (96/04)[b]	90

[a] reaction performed in dichloromethane.
[b] reaction performed in ethanol.
[c] yields after distillation.

Ref. 224

In contrast to alkylamines in general and methylamine in particular, BSMA and RSMA reacted with epichlorhydrin to give the corresponding azetidinol as the sole product in high yields after neutralization of the chlorohydrate primarily formed.[224]



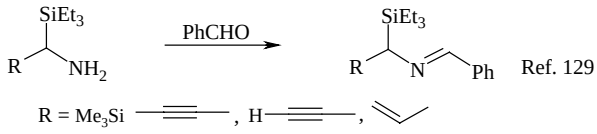
R	Yield (%)[a]
$SiMe_3$	70
Ethyl	72
n-Propyl	74
i-Propyl	72
c-Hexyl	83

[a] isolated yields after distillation...

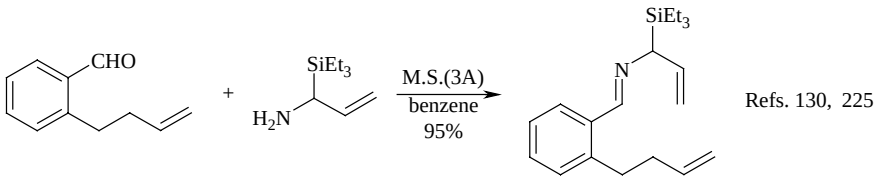
Ref. 224

d. Formation of Imines

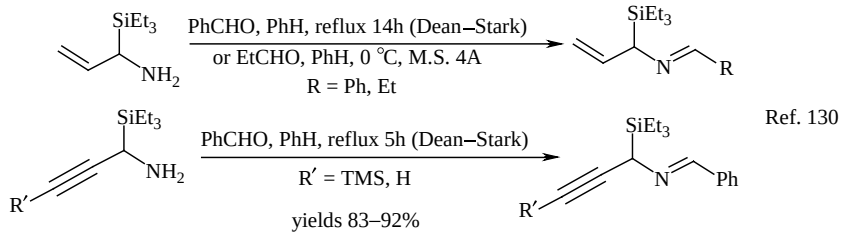
As pure organic primary amines, SMA readily condense with aldehydes to form (*E*)-aldimines. Sometimes various desiccants such as molecular sieves may be used to advantage.[95,129,130,225–230]



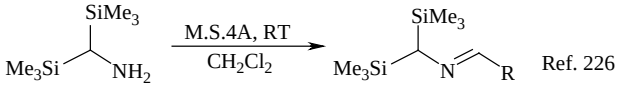
Ref. 129



Refs. 130, 225

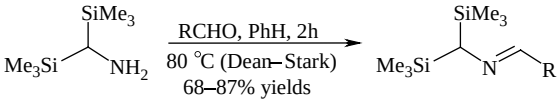


Ref. 130

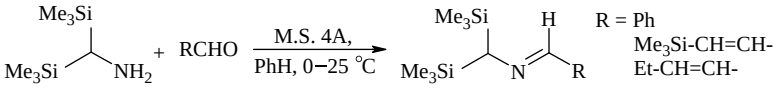


Ref. 226

R = *t*-Bu, Ph, *p*-Me-Ph, C(Me)=CHPh, CH=CHPh

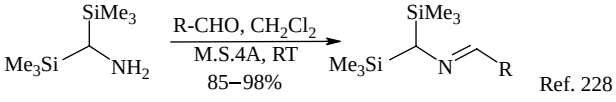


Ref. 95



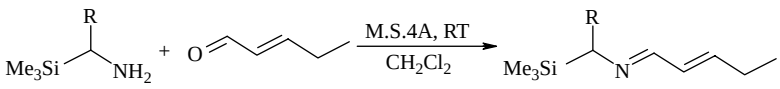
Ref. 227

almost quantitative yields



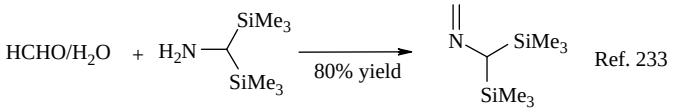
Ref. 228

R = Me, Et, *n*-Pr, CH_2CH_2Ph, *i*-Bu, *i*-Pr, $CHEt_2$, *c*-Hexyl, Ph, CH=CHPh, COOMe, $CH_2OCH^{\cdot\cdot}Ph$, CH_2Ph,



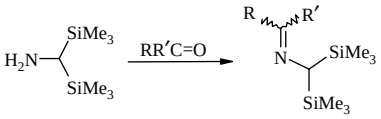
Ref. 229

In contrast to the behavior of alkylamines[231] or trimethylsilylmethylamine[232], the imine formed from the reaction of BSMA with aqueous formaldehyde does not trimerize at room temperature.[233]



Ref. 233

Ketones, when used in large excess, also gave easily the corresponding imines in good yields, with the *E* conformation being predominant.[234]



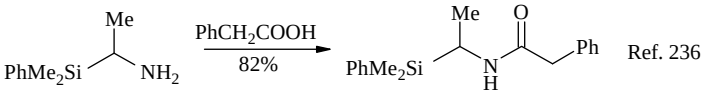
R	R′	Yield (%)	E:Z
Me	Me	91	–
Me	Et	90	86:14
Et	Et	80	–
n-Pr	*n*-Pr	75	–
Me	COOMe	95	76:24
Me	CH_2CH_2Ph	60	–

Ref. 234

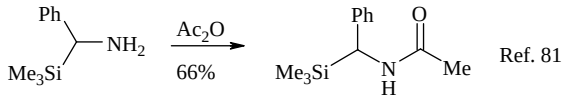
Imines have also been prepared by the reaction of iminophosphoranes with aromatic, heteroaromatic, aliphatic and α,β-unsaturated aldehydes at reflux in dry benzene. Reactions with ketones were rather sluggish. Acetone was used as the reagent and the solvent and cyclohexanone was reacted at reflux in toluene for a prolonged period of time.[235]

e. Formation of Amides

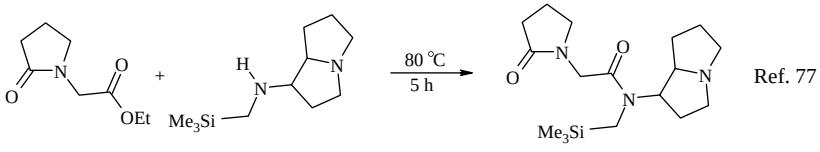
Using classical procedures, SMAs were transformed into the corresponding amides, using acids,[236] acid anhydrides,[81] esters,[77] or acid chlorides.[95,237,238]



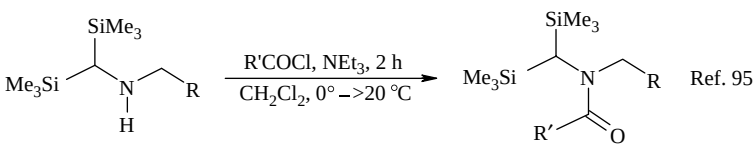
Ref. 236



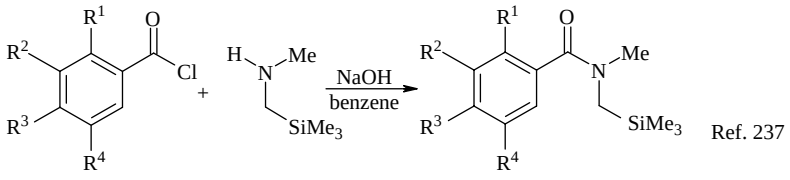
Ref. 81



Ref. 77

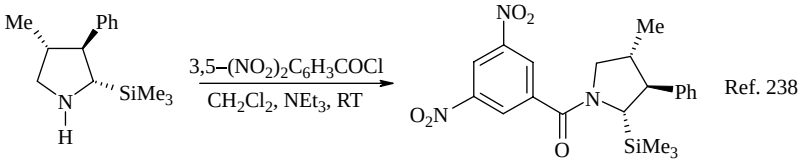


Ref. 95



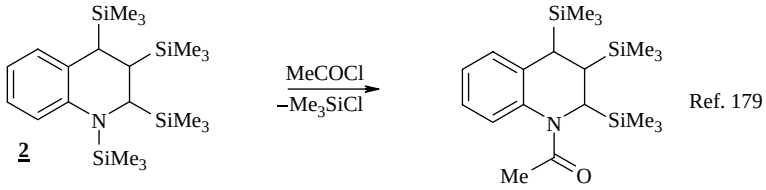
Ref. 237

	R^1	R^2	R^3	R^4	Rdt (%)
a	OMe	OMe	H	H	91
b	OMe	H	OMe	H	78
c	H	OMe	OMe	H	89
d	H	OMe	H	OMe	87
e	H	OMe	OMe	OMe	79



Ref. 238

Cleavage of the N–Si bond of silylamines by acyl chloride constituted a valuable approach to the corresponding amides.[179]



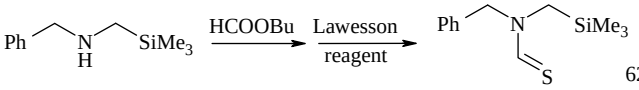
Ref. 179

f. Formation of Heterocumulenes

Trimethylsilylmethyl azide serves *via* its iminophosphorane derivative, as a source of heterocumulenes, i.e., isocyanate, isothiocyanate, carbodiimide, ketenimine.[235,239] Parallel procedures were used to synthesize BSMA-derived heterocumulenes[240] although other synthetic routes have been used to prepare BSMA's isocyanate [BSMA + $(Cl_3CO)_2C{=}O$][241] and isothiocyanate (sulfur + BSMA isocyanide).[242]

g. Formation of Thioformamides

Formylation of the SMA followed by the treatment of the formamide with Lawesson's reagent leads to the corresponding thioformamide with good yield.[64,171]

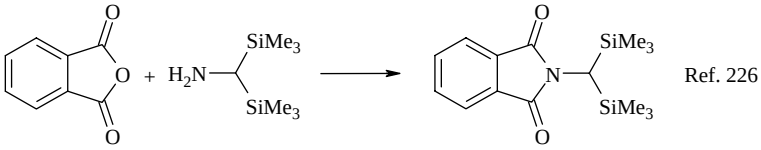


Refs. 64, 171

62%

h. Direct Formation of SMA Phthalimides

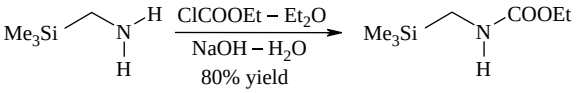
BSMA phthalimide is prepared efficiently by the reaction of BSMA to phthalic anhydride.[226]



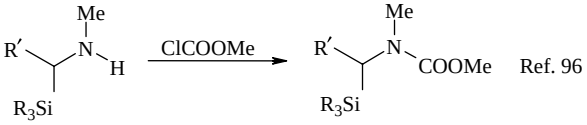
Ref. 226

i. Formation of SMA Carbamates

Condensation of methyl chloroformate with SMA leads to the nearly quantitative yield of the corresponding carbamate.[96,243]



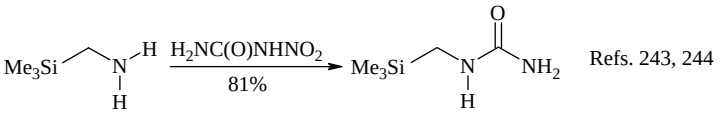
Ref. 243



Ref. 96

j. Ureas from SMA

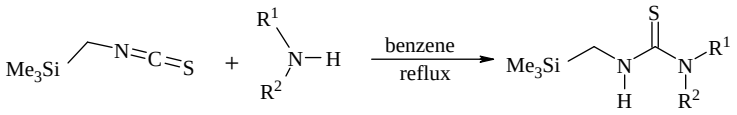
Similarly, ureas are obtained by the treatment of SMA with nitrourea in ethanol as the solvent.[243,244]



Refs. 243, 244

k. Formation of Thioureas

SMA thioureas were prepared in nearly quantitative yield by the addition of primary or secondary amines to *N*-silylmethyl isothiocyanates.[245]

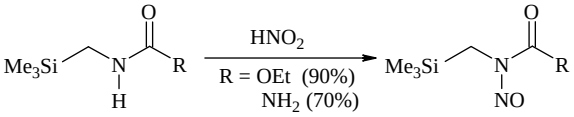


Ref. 245

$R^1R^2N–H$ = Ph–NH_2 (**a**), N–H (**b**), N–H (**c**), O N–H (**d**), 93–98%

l. *N*-Nitroso Derivatives

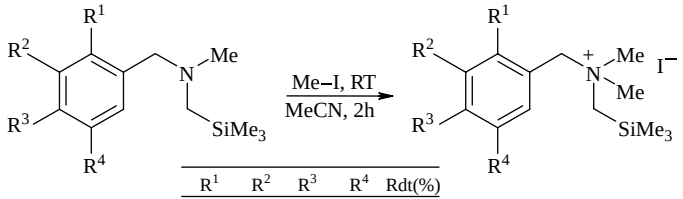
When reacted with nitrous acid, carbamates and ureas are transformed with excellent yields into the corresponding *N*-nitroso derivatives.[243,244]



Refs. 243, 244

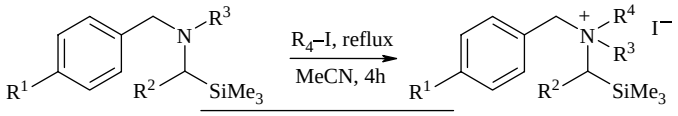
m. *N*-Methiodides and Other Ammonium Salts

N-methiodides, resulting from the addition of methyl iodide with tertiary amines, are valuable intermediates in synthesis, particularly in heterocyclic chemistry. Those derived from tertiary SMA have been prepared in high yields in the same way.[70,164,237,246–248]



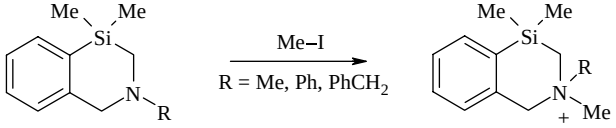
R^1	R^2	R^3	R^4	Rdt(%)
OMe	OMe	H	H	83
OMe	H	OMe	H	94
H	OMe	OMe	H	96
H	OMe	H	OMe	97
H	OMe	OMe	OMe	67

Ref. 237

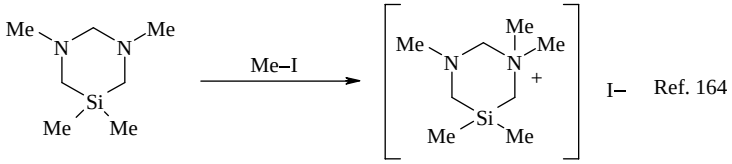


R^1	R^2	R^3	R^4	Rdt(%)
H	Me	Me	Me	93
H	Me	Me	Et	44
H	Me	Et	Me	83
H	Et	Me	Me	94
H	n.Bu	Me	Me	97
MeO	Me	Me	Me	80

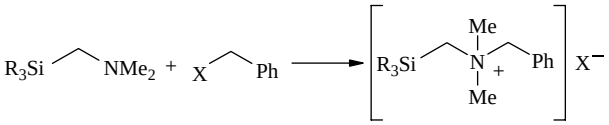
Ref. 246



Ref. 70

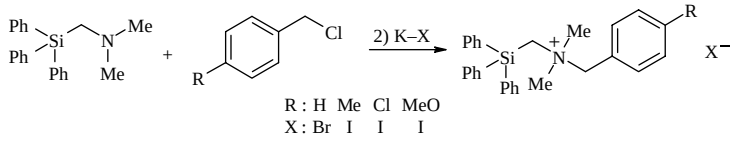


Ref. 164



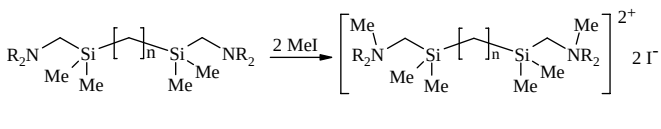
Ref. 247

	R_3	X	Yield		R_3	X	Yield
a	Me_3	Br	85%	c	Ph_2Me	Br	81%
b	$PhMe_2$	Br	95%	d	Ph_3	Cl	87%



Ref. 248

Similarly, methiodides were prepared from diamines.[76]

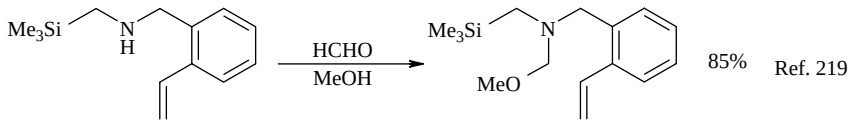


n	R	
4	NMe_2	90%
5	NMe_2	88%
6	NMe_2	87%
5	N	89%

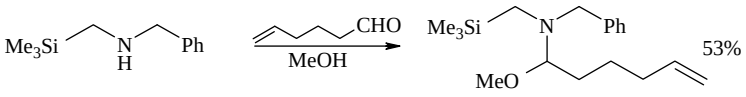
Ref. 76

n. Formation of Aminomethyl Ethers

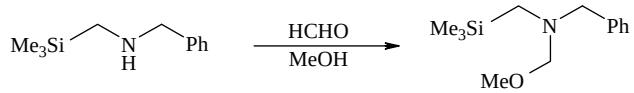
Classical action of an aldehyde on primary or secondary SMA in methanol leads to the corresponding aminomethyl ethers.[219]



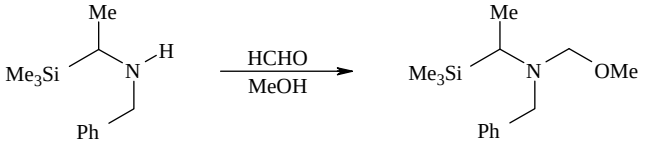
85% Ref. 219



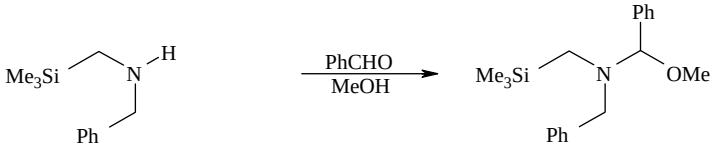
53% Ref. 219



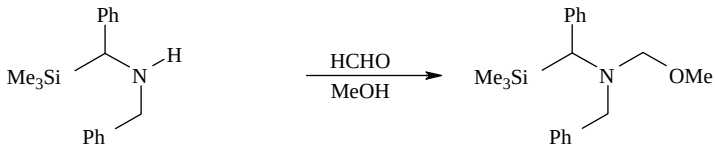
72% Ref. 219



95% Ref. 219



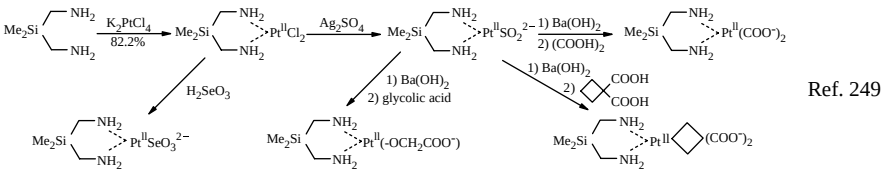
Ref. 219



Ref. 219

o. Formation of Metallic Complexes

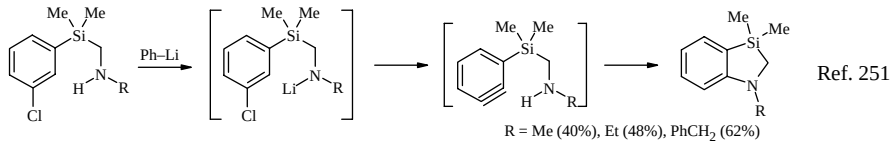
Platinum complexes are easily prepared from bis(aminomethyl)dimethylsilane.[249]



Ref. 249

p. Arylation

N-Arylation of an amine generally consists in the condensation of the amine with an aryl substrate in the presence of a transition metal catalyst.[250] Another strategy has been used, however, to obtain 3,3-dimethylbenzo[*d*]-1,3-azasilolines in moderate yields. It consists in the internal insertion of an N–H bond to the triple bond of a benzyne.[251,252]



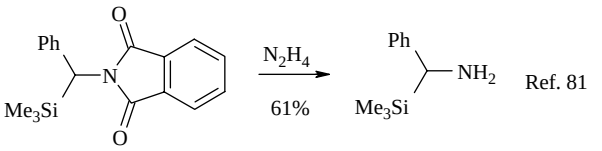
Ref. 251

Similar compounds are formed when *N*,*N*-dimethyl-2-silylethylamines are reacted with benzyne.[253]

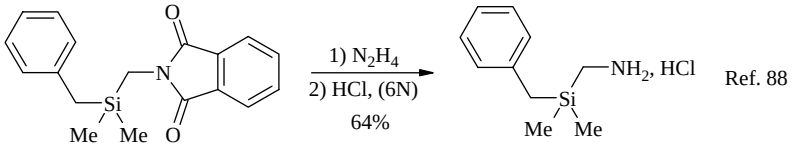
3. Derivatives to Amines (Deprotection of SMA)

a. Hydrazinolysis of SMA Phthalimides and Formamidines

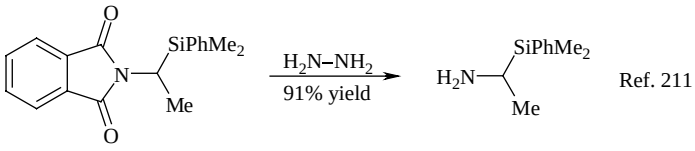
We have already seen various syntheses of SMA phthalimides, either through nucleophilic amination of α-chlorosilanes (see Sections III.A.1 and III.A.2), hydrosilylation of *N*-vinyl phthalimide (see Section III.B.5.f) or by reaction of SMA with phthalic anhydride (see Section IV.A.2.h). The deprotection and recovery of free SMA has been conducted in the usual way by reaction with hydrazine.[81,88,211]



Ref. 81

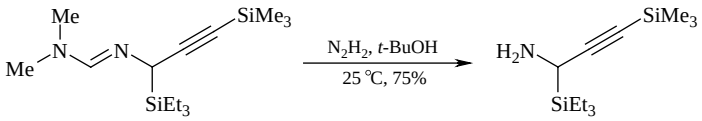


Ref. 88



Ref. 211

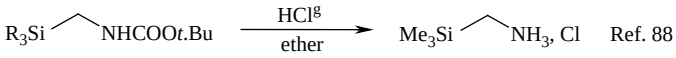
Formamidines are well known as protecting groups for primary amines. Hydrazinolysis has been used to recover the corresponding SMA.[130]



Ref. 130

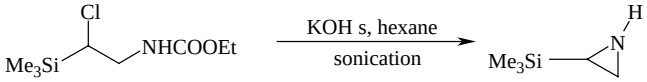
b. Deprotection of SMA from Their Carbamates

Carbamates are often used as protecting and activating groups for amines. Their treatment in acidic medium allows the release of SMA from their carbamates.[88]



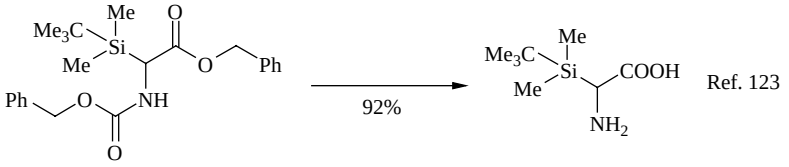
Ref. 88

Such deprotection has occurred spontaneously during the course of the preparation of an aziridine using sonication. The use of a base instead led to a mixture of protected and deprotected aziridines.[73,101]



Ref. 73

Another recent example is twofold debenzylation of this protected aminoester.[123]

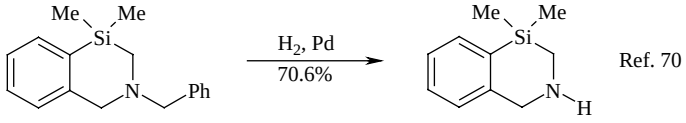


Ref. 123

As these esters are easily separable by chiral HPLC, the aminoacid has been obtained in its enantiomerically pure (S) and (R) forms.

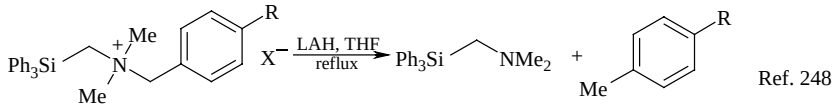
c. Debenzylation of SMA

The use of the benzyl group to protect an amine during a synthetic sequence is common. The benzyl group is easily removed under hydrogenolysis conditions. This technique has been applied with success to the chemistry of SMA.[70]



Ref. 70

After a SMA has been reacted with a benzyl halide, SMA might be recovered by reaction of the salt with an excess of lithium aluminum hydride (LAH) in THF at reflux. However, the elimination of toluene was a minor feature in this reaction (2–6% yields) that cannot be considered of synthetic value.[248]



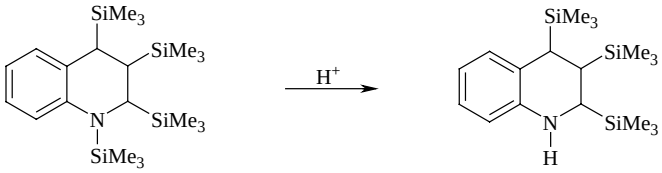
Ref. 248

R : H Me Cl MeO
X : Br I I I

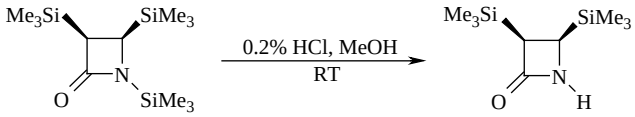
benzylic group elimination

d. SMA from Aminosilanes

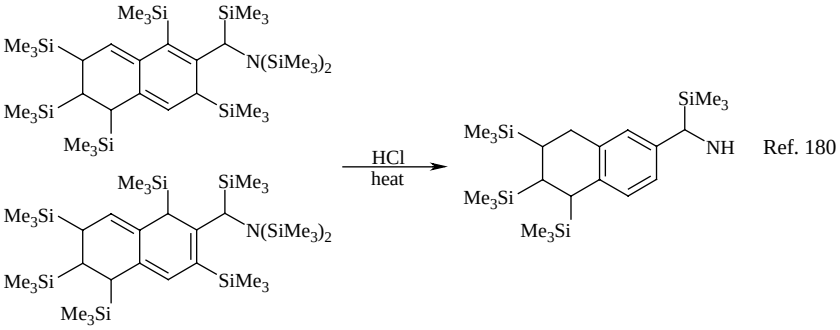
The protection of amines with a silyl group is of wide use not only in organic synthesis but also in chromatographic analysis. Deprotection generally occurs in acidic medium. This has been applied to the chemistry of SMAs.[122,177,179,180,186,187,189,191]



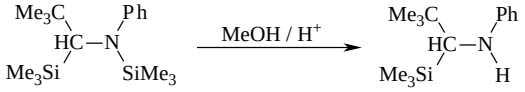
Ref. 179



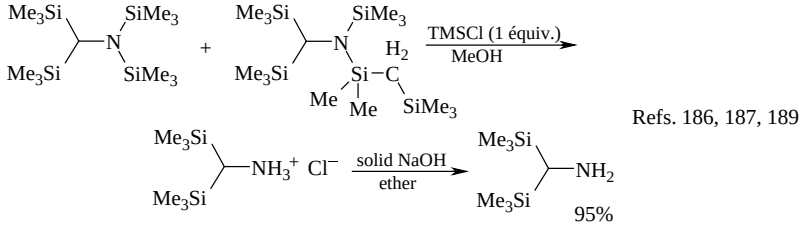
Ref. 122



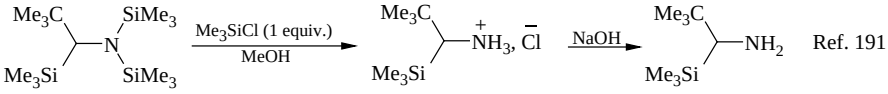
Ref. 180



Ref. 177



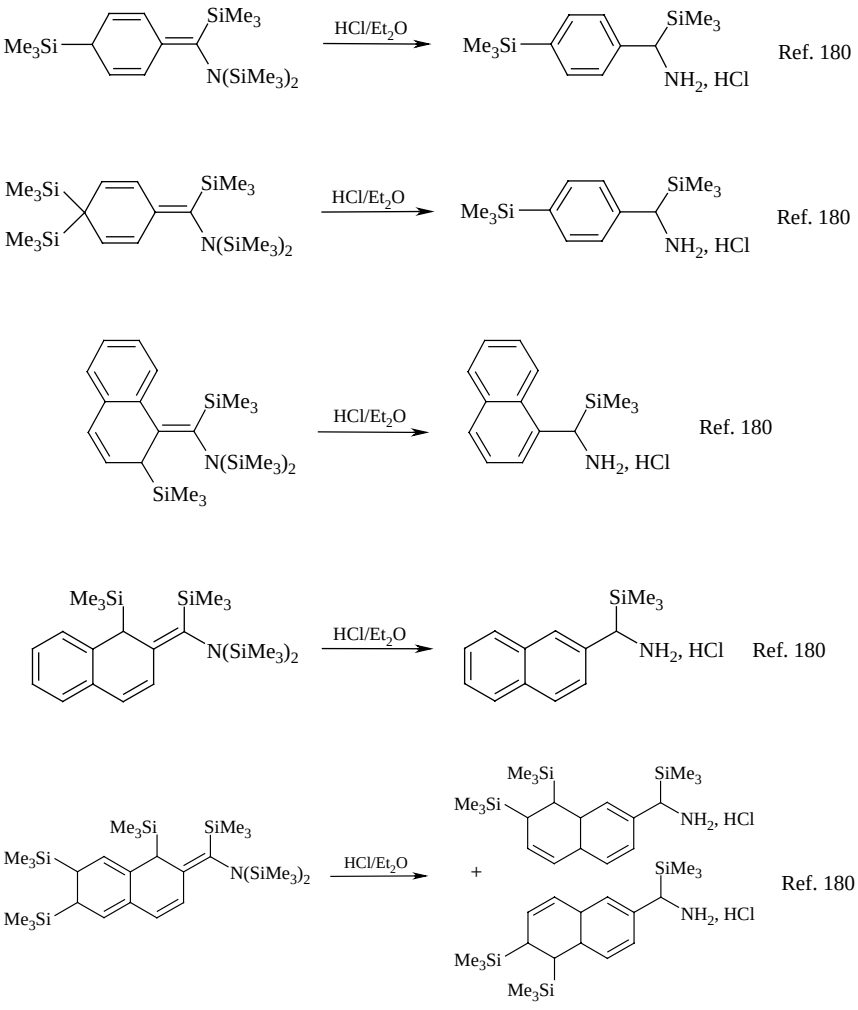
Refs. 186, 187, 189



Ref. 191

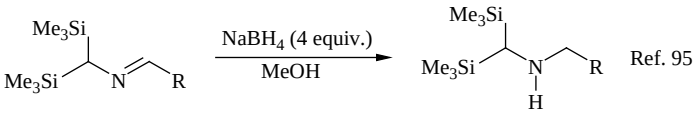
e. SMA from Aromatic Acylsilane Enamines

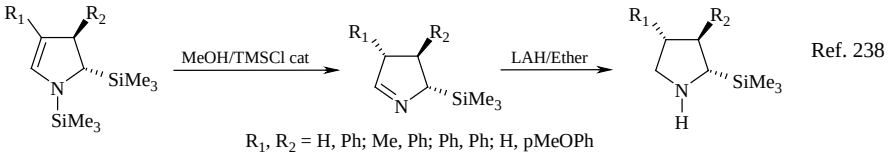
It has already been shown that aliphatic acylsilane enamines serve as precursors for RSMA (See Sections III.B.2.i and III.B.2.j) *via* reduction of their iminium chloride. Transformation of aromatic acylsilane enamines into the corresponding ASMA does not require a reduction step. Their protonolysis leads directly to ASMA, aromatization occurring during the process, sometimes with migration of a silyl group.[180]



f. Reduction of SMA Imines into SMA

Reduction of SMA imines with sodium borohydride or lithium aluminum hydride allows the synthesis of the corresponding secondary amine in good yields.[95,238]

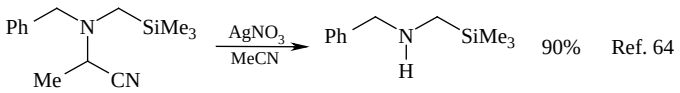




R_1, R_2 = H, Ph; Me, Ph; Ph, Ph; H, pMeOPh

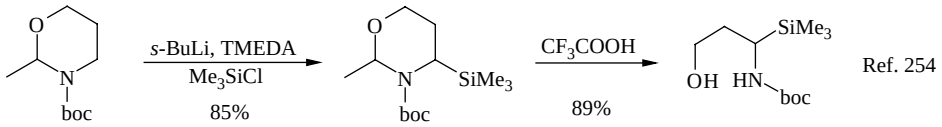
g. From α-Amino Nitriles

Protected temporarily as an α-amino nitrile, SMA can be recovered in excellent yield after treatment with silver nitrate in acetonitrile.[64]



h. From N-Boc-6-silyl-2-methyltetrahydro-1,3-oxazine

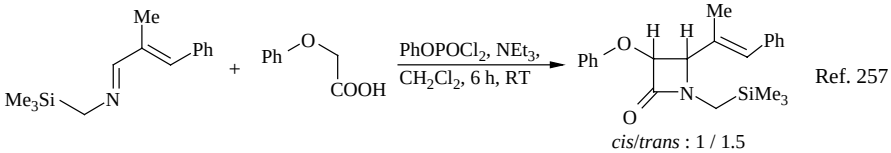
N-Boc-2-methyltetrahydro-1,3-oxazine has been silylated and the resulting 6-silylated derivative transformed into N-Boc-1-trimethylsilyl-3-hydroxy-1-propylamine.[254]



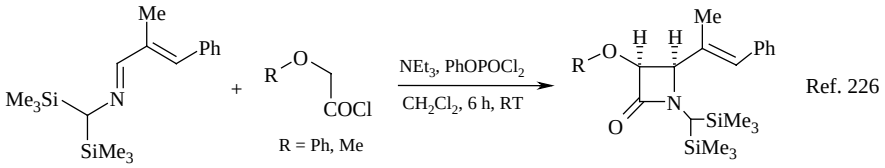
4. Derivatives to Other Derivatives

a. Formation of β-Lactams from SMA Imines (Staudinger Condensation)

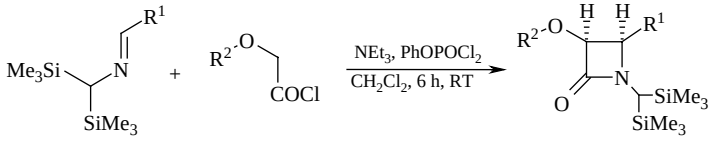
The Staudinger's condensation of ketenes with imines is a well-known process to synthesize β-lactams. SMA imines have been tested with success, leading to *N*-silylmethyl protected β-lactams.[226,228,230,234,255–258] High yields are generally obtained, in particular with the bissilylmethyl group. This is probably due to the high solubility of reactants, intermediates and final products. Moreover, contrary to the monosilylmethyl group, the bissilylmethyl group induced a complete (aldimines) or high (ketimines) stereocontrol during the formation of C_3–C_4 bond to predominantly yield *cis*-β-lactams.



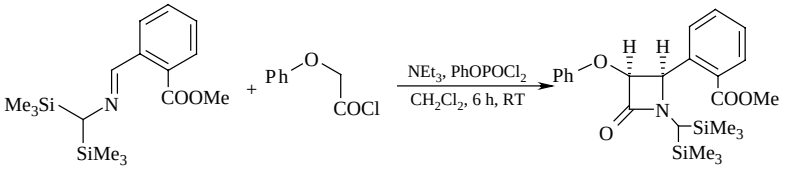
cis/*trans* : 1 / 1.5



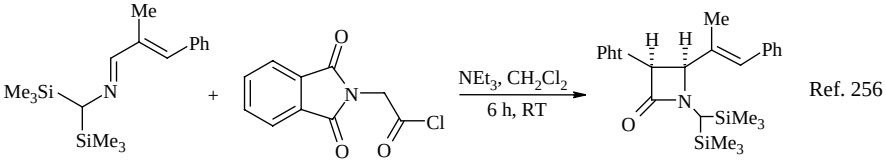
Ref. 226



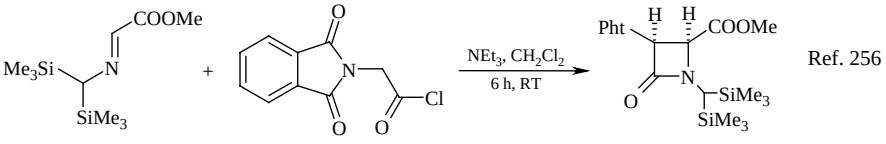
Ref. 228



Ref. 255

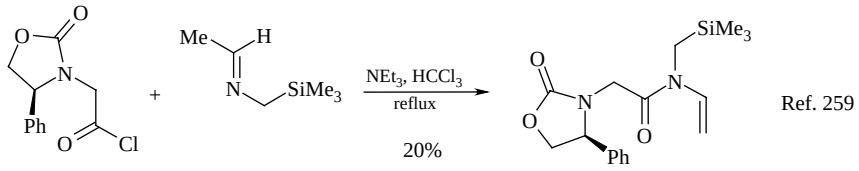


Ref. 256



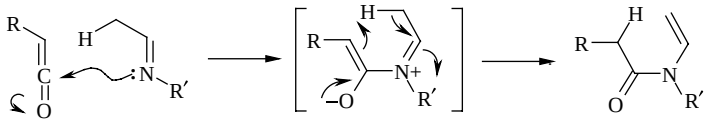
Ref. 256

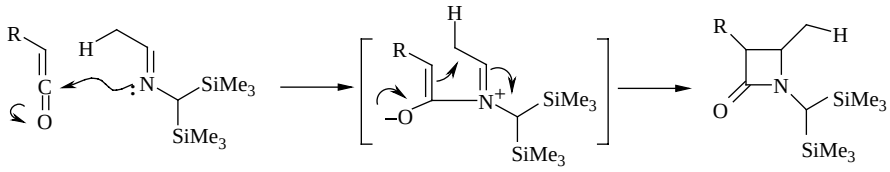
Imines derived from enolizable aliphatic aldehydes are well known to lead to *N*-vinyl amides. The reaction of such aldehydes with MSMA gave *N*-vinyl amides in low yields.[259]



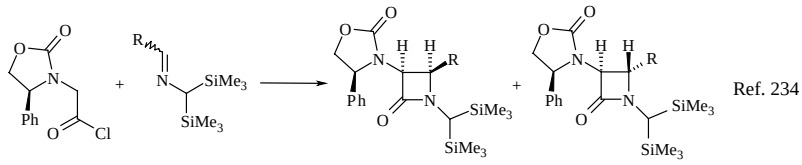
Ref. 259

Surprisingly, BSMAs that form aliphatic enolizable imines led to 4-alkyl-β-lactams. The bissilylmethyl group reducing the acidity of the β-proton was probably the cause of this highly interesting result, which has opened new synthetic potential in the β-lactam chemistry.





Moreover, chiral inductors have been efficiently used (Evans' acid chloride, for instance), giving highly stereospecific entries into this important class of compounds.

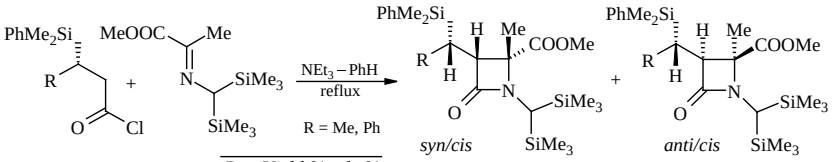


Ref. 234

Imine R	Yield (%)[a]	*cis*:*trans*[b]
Et	75	98:2
n-Pr	75	90:10
i-Pr	78	98:2
CH_2CH_2Ph	82	98:2
CH_2CHMe_2	70	85:15
CH_2OCH_2Ph	70	98:2
CH_2Ph	45	98:2
CH_2CH_2COO*t*-Bu	65	88:12

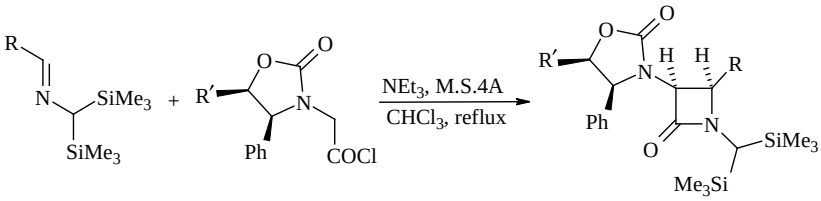
Ref. 234

[a] Mixture after purification on silica gel.
[b] From NMR analysis on the crude product.

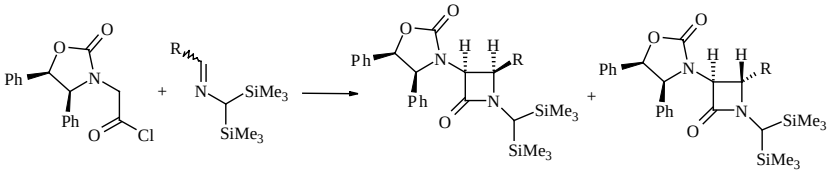


R	Yield %	de %
Me	68	54
Ph	62	91

Ref. 234



Ref. 228



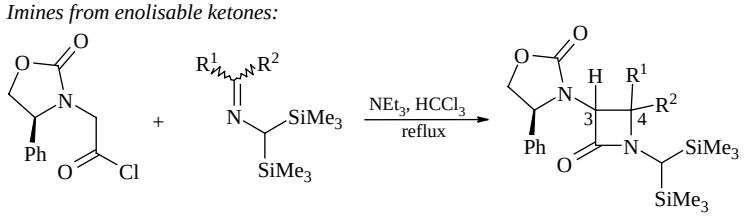
Ref. 259

Imine R	Yield (%)[a]	*cis*:*trans*[b]
Et	65	85:15
n-Pr	71	95:5
i-Pr	79	91:9
CH_2CH_2Ph	80	≥ 98:2
CH_2CHMe_2	70	≥ 98:2
$CHEt_2$	70	≥ 98:2
c-C_6H_{11}	70	≥ 98:2
Ph	70	≥ 98:2
CH=CHPh (*E*)	72	≥ 98:2
CH_2OCH_2Ph	74	≥ 98:2

Ref. 259

[a] Mixture after purification on silica gel.
[b] From NMR analysis on the crude product.

Imines from enolisable ketones:



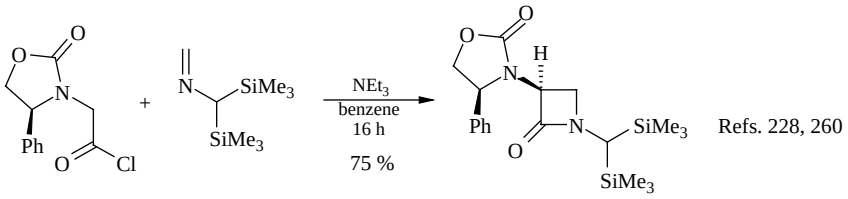
Ref. 234

R	Imine	R′	Yield (%)[a]	de (%)
Me		Me	70	>98
Me		Et	80	80[b]
Et		Et	69	>98
n-Pr		*n*-Pr	70	>98
Me		CH_2CH_2Ph	69	44[b]

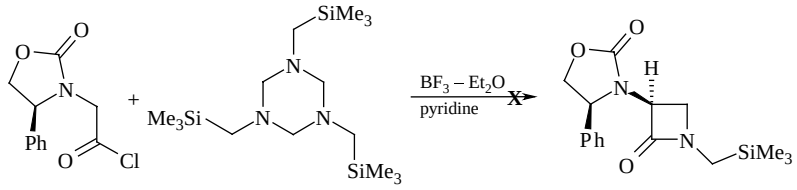
Ref. 234

[a] Mixture after purification on silica gel.
[b] From NMR analysis on the crude, to determine the diastereoisomeric ratio (3S,4R):(3S,4S).

When ketones are symmetrical, a single isomer is obtained, indicative of total asymmetric induction at C3. In the case of unsymmetrical ketones, two isomers are formed that may be separated by LC on silica gel. An important feature is that β-lactams are easily formed from formaldimine BSMA offering for the first time a direct entry to C4-unsubstituted β-lactam ring (monobactams).[228,260] In contrast, its monosilylated counterpart, under the form of its trimer, leads only to traces of the expected β-lactam.[259] This demonstrates the great utility of the bissilylmethyl group for preparing β-lactams.



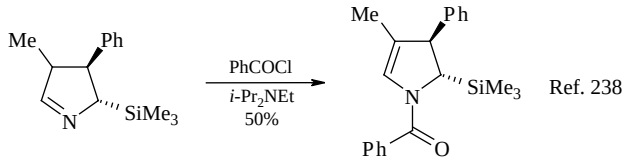
Refs. 228, 260



Ref. 259

b. Transformation of Imines into Enamides

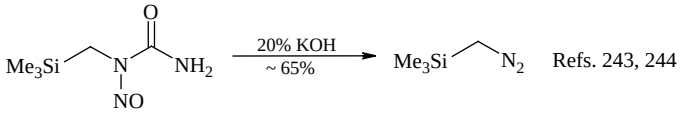
No cleavage of the Si–C bond occurs when a 5-silyl-Δ^1-pyroline reacts with benzoyl chloride in the presence of a tertiary amine. The corresponding enamide is obtained.[238]



Ref. 238

c. Silyl Diazomethanes from *N*-Nitroso Derivatives

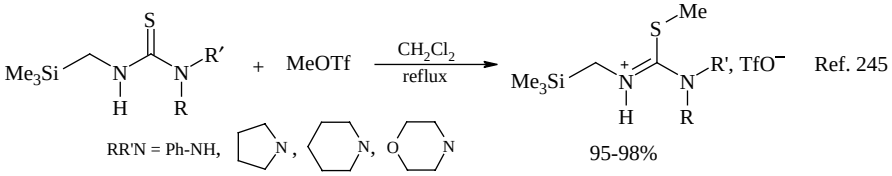
Treatment of a nitrosourea with a base comprises the final step in a preparation of a diazomethane derivative. This has been successfully applied to the synthesis of trimethylsilyl diazomethane.[243,244]



Refs. 243, 244

d. Iminium Triflates from Thioureas

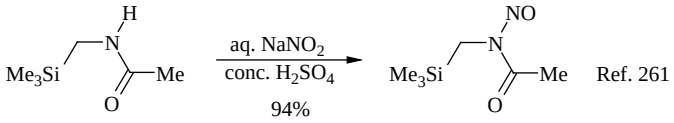
Selective *S*-methylation of *N*-(trimethylsilylmethyl)thioureas with methyl triflate proceeds smoothly to give the corresponding *N*-(trimethylsilylmethyl)iminium triflates in almost quantitative yields.[245]



Ref. 245

e. *N*-Nitroso Amides from Amides

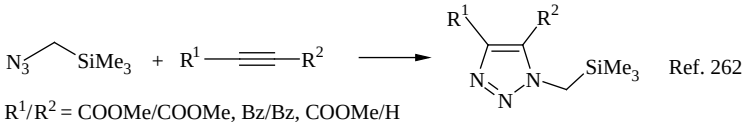
Nitrous acid quantitatively converts *N*-trimethylsilylmethyl acetamide into the corresponding *N*-nitroso derivative.[261]



Ref. 261

f. 1-Trimethylsilylmethyl-1H-1,2,3-triazoles from Trimethylsilylmethylazide

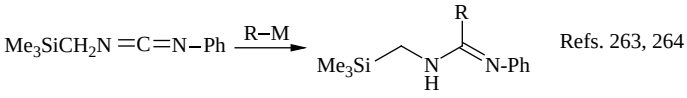
Trimethylsilylmethylazide condenses easily with acetylenic dipolarophiles as dimethyl acetylendicarboxylate (DMAD) to give corresponding trimethylsilylmethyl-1H-1,2,3-triazoles.[262]



Ref. 262

g. Amidines from Carbodiimides

Addition of an organometallic reagent to carbodiimides provides excellent access to formamidines with high yields.[263,264]



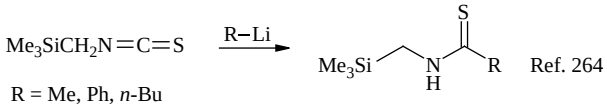
Refs. 263, 264

R	Yields	R	Yields
Me	91	Ph	95
Et	95	CH_2COOEt[a]	92
n-Bu	90		

[a]Obtained as a 7:3 mixture of two tautomers.

h. Thioamides from Isothiocyanates

Similarly, reaction of various alkyllithium reagents on SMA's isothiocyanates is a good way to prepare the corresponding thioamides.[264,265]

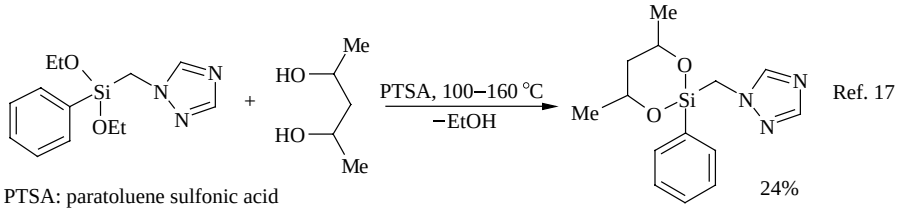


R = Me, Ph, *n*-Bu

Ref. 264

B. *Transformations at Silicon*

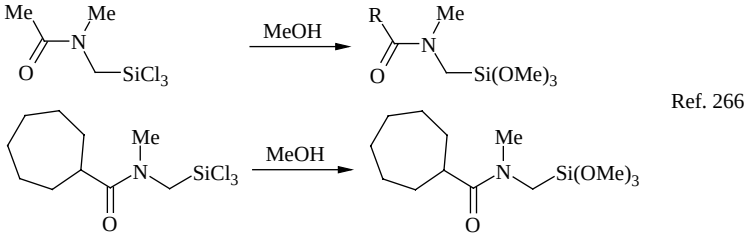
Some transformations at silicon atom have been performed in order to prepare a series of SMA derivatives. They consist of the nucleophilic substitutions of heteroatoms directly linked to silicon, such as the hydrolysis of alkoxysilanes and chlorosilanes into silanols or siloxanes, or the transesterification of alkoxysilanes.[17,266–268]



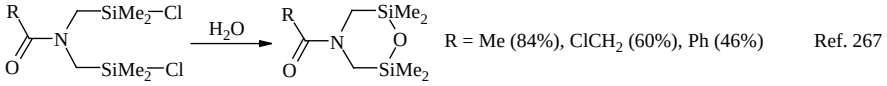
PTSA: paratoluene sulfonic acid

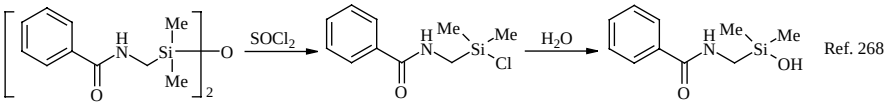
Ref. 17

24%

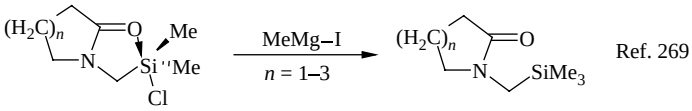


Ref. 266



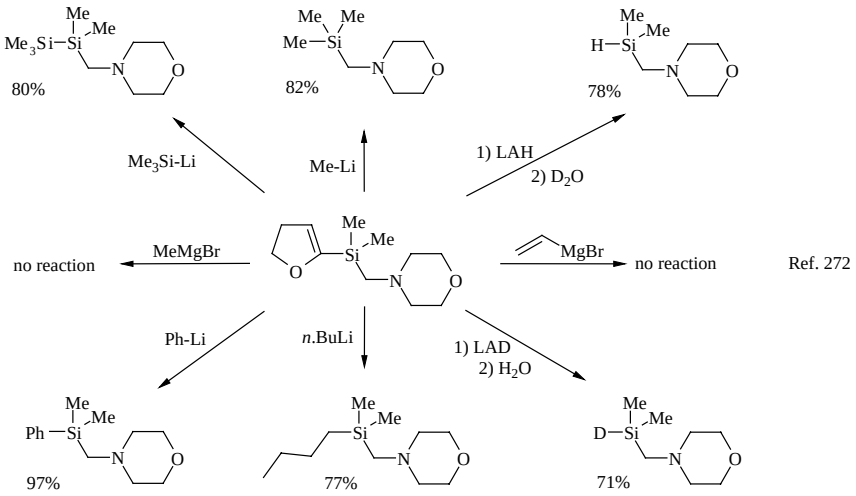


Alkylations are also possible by nucleophilic displacement of a chlorine atom using an organometallic reagent. Substitution occurs faster when the silicon atom is pentacoordinated and the rate of the reaction depends upon the size of the ring, reflecting the strength of the coordination.[269]

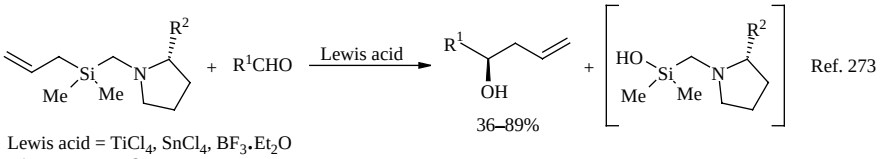


These chelates are more reactive than non-chelated chlorosilanes in forming a silyl enol ether from ketones.[270] Moreover, careful hydrolysis of a pentacoordinated chlorosilane was shown to give a pentacoordinate protonated silanol that resembles the intermediate in the aqueous hydrolysis of silanes.[271]

Of interest also is the synthesis of aminomethylsilanes that have been designed to bear a labile substituent namely [2-(4,5-dihydrofuryl)] at the silicon atom. They are the source of a series of diversely substituted aminomethylsilanes as, for example, Me_2HSi-substituted aminomethylsilanes, not readily available in pure form by other means.[272]



Chiral pyrrolidinylmethylallylsilanes have been shown to be good reagents that transfer their allyl group to aldehydes to synthesize chiral homoallylic alcohols.[273]



Ref. 273

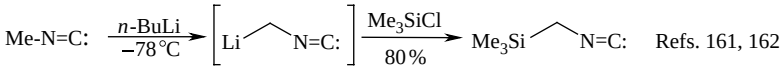
Lewis acid = $TiCl_4$, $SnCl_4$, $BF_3.Et_2O$
R^1 = Pr, Oct. R^2 = COOMe, $CH_2OOCNHPh$, CH_2OMe

C. *Transformations at Carbon*

Transformations at the central carbon atom are interesting and useful reactions that allow for the conversion of one SMA into another. For instance, silylation transformed a MSMA into a BSMA and alkylation a MSMA into a RSMA.

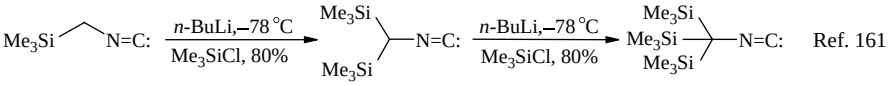
1. Silylation of Carbanions ⊖CHSiN (MSMA to BSMA) and ⊖CSi_2N (BSMA to TSMA)

Silylation of the anion obtained by treatment of methyl isocyanide with *n*-butyllithium at low temperature followed by quenching the anion with trimethylchlorosilane has already been described (see Section III.B.1.m). This constitutes a good, large-scale preparation of trimethylsilylmethyl isocyanide.[161,162]



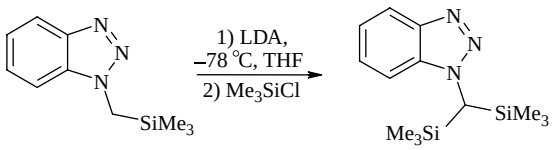
Refs. 161, 162

The same process when applied to trimethylsilylmethyl isocyanide leads to the obtention of the bis- and trissilylated derivatives with high yields (~80%).[161]



Ref. 161

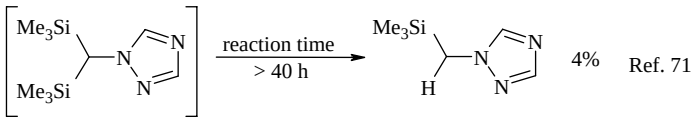
Using a similar technique, trimethylsilylmethyl benzotriazole transforms into its bissilylated homologue.[156]



Ref. 156

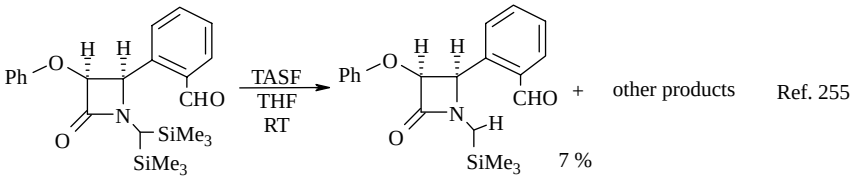
2. Partial Desilylation of BSMA Derivatives (to MSMA)

Partial desilylation of BSMA derivatives has been reported to occur in low yields as the result of a side reaction either during their preparation or their reaction, for example, formation of trimethylsilyl-methyltriazole during the preparation of [bis(trimethylsilyl)-methyl]triazole.[71] It was conjectured that this could be the result of a nucleophilic attack on the disilyl compound.



4% Ref. 71

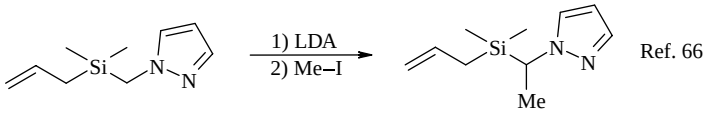
Similarly, partial desilylation is observed during the Peterson annelation reaction (see Section VI.B.3.b) starting from an *N*-[bis(trimethylsilyl)methyl]azetidinone.[255]



7 % + other products Ref. 255

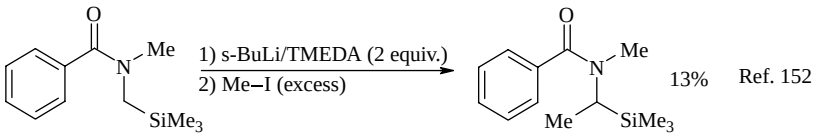
3. Alkylation of Carbanion ⊖CHSiN (MSMA to RSMA)

Several authors have demonstrated the feasibility of the alkylation of a MSMA substrate to obtain the homologous RSMA *via* reaction of the corresponding α-silylcarbanion with an alkyl halide. Treatment with LDA of (allyl)(pyrrazolylmethyl) silane gives a carbanion that on trapping with methyl iodide, leads to the unique formation of the corresponding RSMA derivative without traces of compounds that could have resulted from the allylic system. However, when *s*-butyllithium is used instead of LDA, partial methylation of this system also occurs.[66]

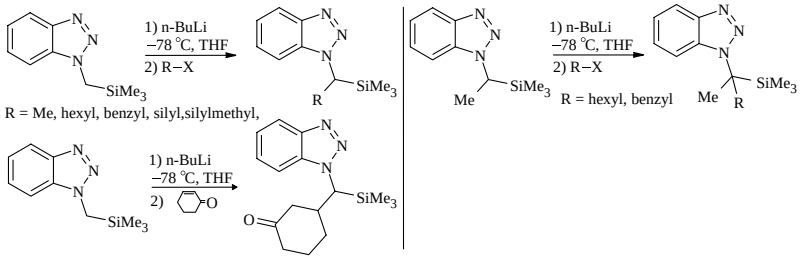


Ref. 66

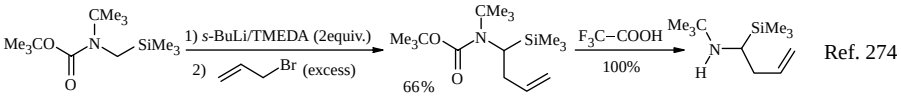
s-Butyllithium in conjunction with an excess of methyl iodide in TMEDA as the solvent, can be utilized to methylate *N*-methyl-*N*-trimethylsilylmethyl benzamide. The yield is quite low.[152]



Similarly, *N*-silylmethylbenzotriazole derivatives have been prepared, using in this case *n*-butyllithium as the base and various electrophiles including cyclohexenone. Even alkylation of RSMA-type benzotriazole derivatives can be performed, leading to a new class of SMA (R_2SMA).[157]

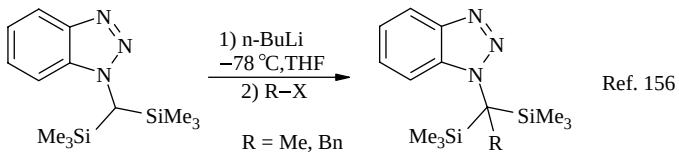


t-Butyl carbamates of MSMAs undergo facile metallation between nitrogen and silicon and reaction of electrophiles with the intermediate lithio derivative efficiently give access to RSMAs. Benzylic deprotonation competes with deprotonation next to silicon when a benzyl group is attached to nitrogen.[274]

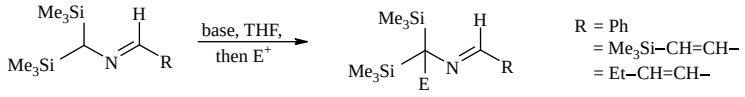


4. Alkylation of Carbanion ⊖$CHSi_2N$ (BSMA to BRSMA)

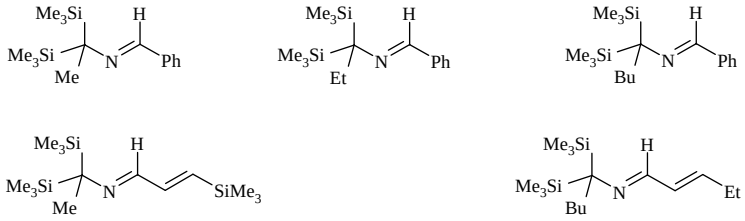
The same process has been applied towards the alkylation of *N*-[bis(trimethylsilyl) methyl]benzotriazole to obtain a new class of SMA derivative, RBSMA.[156]



BSMA imines have been shown to be excellent candidates for alkylation. Treatment of such aldimines, first with methyllithium at room temperature or Lidakor ("Schlosser base")[275] at low temperatures followed by quenching with excess of alkyl halide, is an excellent means to original RBSMA imines.[227]

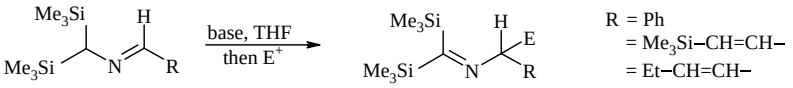


base = MeLi(25 °C), LIDAKOR (–78 °C) E–X = Me–I, Et–I, n.Bu–I

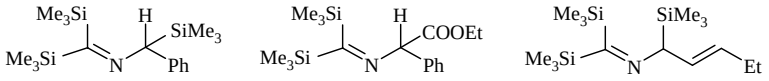


Ref. 227

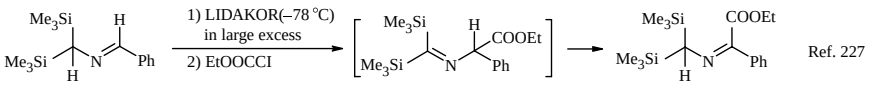
However, the result is dependent on the nature of the electrophile. Thus, TMSCl and ethyl chloroformate leads to products of alkylation after migration of the double bond.[227] These products, imines of bis(trimethylsilyl)carbonyl, have been previously obtained by the insertion of isonitriles into the Si–Si bond of disilanes.[201]



base = MeLi (25 °C), LIDAKOR (–78 °C) E-X = Me_3Si–Cl, EtOOC–Cl Ref. 227



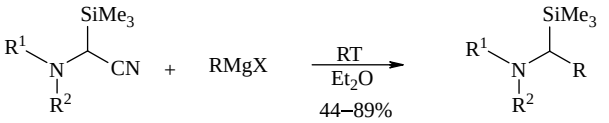
In the presence of excess of base, this type of imine was not observed.[227]



Ref. 227

5. Alkylation through Nucleophilic Displacement of the Cyano Group in >N–CH(Si)–CN

It has been shown (see Section III.B.1.p) that α-silyl aminoacetonitriles are readily accessible.[171] Reacting a Grignard reagent with these compounds gives access to RSMA in 44–89% yields.[276]



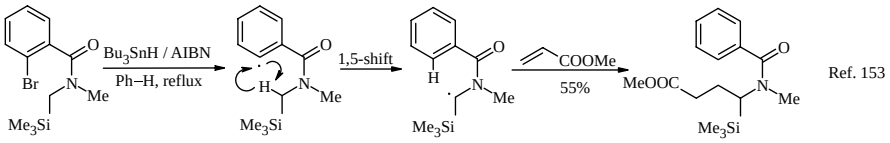
Ref. 276

R^1 = Me, Et, Bn, *p*-MeO-Bn; R^2 = Me, Et; R^1R^2 = $(CH_2)_4$, $(CH_2)_5$

R = Me, *n*-Bu, Bn, *c*-Hex

6. Alkylation of Radical · CHSiN (MSMA to RSMA)

Rare examples exist of this transformation. However, when the substrate is well-suited for such a purpose, a radical can be prepared and reacted with acrylonitrile to produce the corresponding γ-silyl-γ-aminoester in moderate yield.[153]

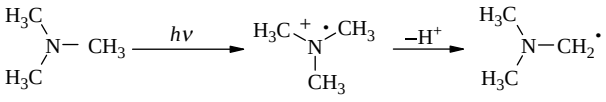


Ref. 153

7. Light-induced Electron Transfer: C–H Addition to Enones (MSMA to RSMA)

Single Electron Transfer (SET) has an important place in many bimolecular reactions.[277] Several types of initiation have been employed. When this transfer is induced by light, which provides sufficient redox potential difference between the two interacting molecules to initiate it, the process is known as the Photoinduced Electron Transfer (PET) process.[278,279] Light-induced electron transfer provides an excellent synthetic means to alkylate MSMA.

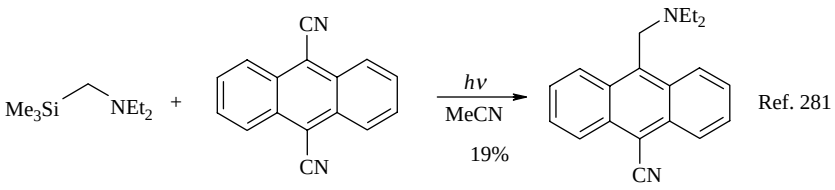
Under irradiation with light ($\lambda > 290$ nm), tertiary amines are able to transfer one of the electrons of the lone pair on nitrogen to a molecule to produce a cation radical that loses a proton α- to nitrogen to form an α-amino radical.[280]



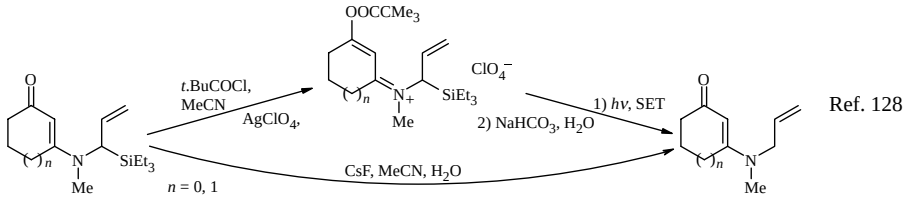
Ref. 280

Under the same conditions, it has been shown that tertiary SMAs undergo α-C–Si bond cleavage to produce the same type of cation radicals.

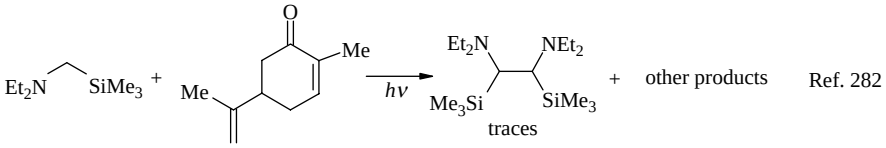
Thus, when a saturated solution of 9,10-dicyanoanthracene (DCA) in acetonitrile and (trimethylsilyl)methyldiethylamine is irradiated, the 9-aminomethylanthracene derivative is obtained (with other non-silylated products) in 19% yield that differs from that resulting from the same irradiation of DCA and methyldiethylamine (2% yield).[281]



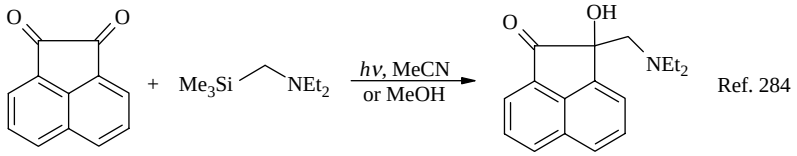
Another study reported that desilylation occurs when α-triethylsilylated imminium perchlorates are irradiated. *N*-Alkyl-α-enaminones are obtained after treatment of the photolysates with aqueous sodium bicarbonate (~70% yield). These enones are also formed upon fluoride-induced desilylation with cesium fluoride in acetonitrile.[128]



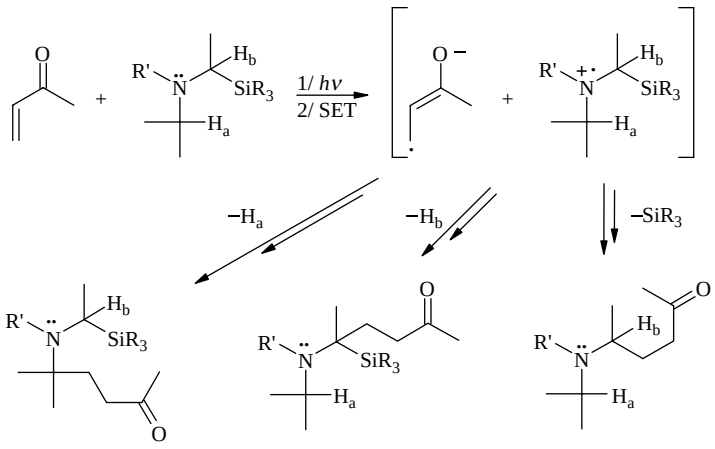
In one instance, minor formation of the original 1,2-diamine (the dimer of the starting MSMA) has been observed, indicative of the radical character of the reaction.[282]



Sequential SET desilylation has been used to generate α-amino radicals. The mechanistic and synthetic aspects of the reaction have been briefly surveyed.[283] Thus irradiation of *N*,*N*-diethyltrimethylsilylmethylamine with acenaphthenequinone in acetonitrile or methanol produces 2-hydroxy-2-[(diethylamino)methyl]acenaphthylen-1-one.[284]

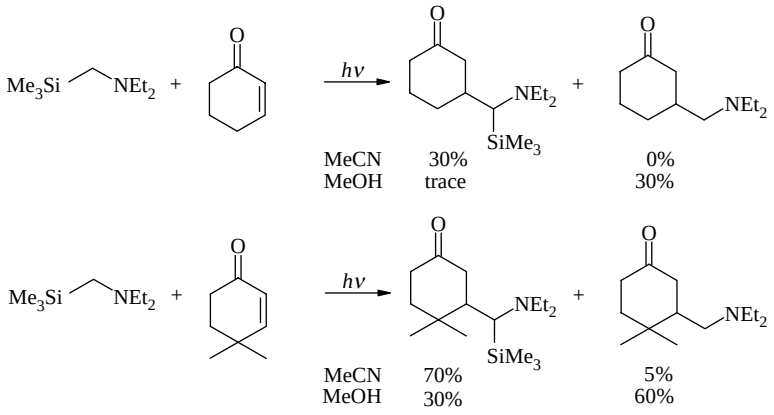


In fact, unique cleavage of the C−Si bond from a tertiary SMA is not a general feature as cleavage of C−H bond can also occur. This is illustrated with the reaction of methylvinylketone with tertiary SMAs, leading either to silylated or non-silylated products or both.[285]



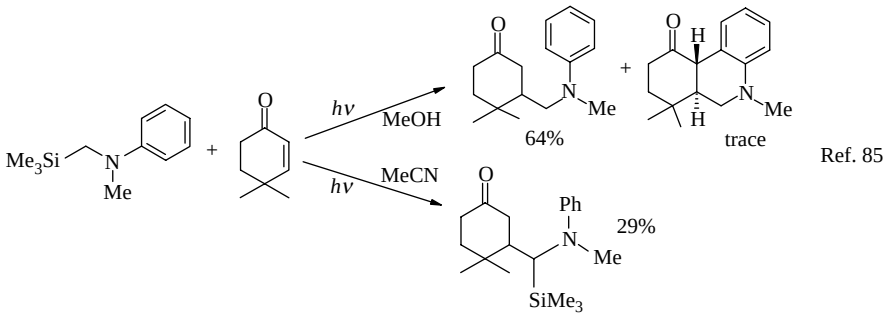
Ref. 285

Conditions of the reaction govern its result and solvent plays an important role. As an example, irradiation of cyclohexenones in the presence of trimethylsilylmethyldiethylamine leads to a mixture of silylated and non-silylated aminocyclohexanes with a ratio that depends on the solvent used: acetonitrile yields silylated compounds as the major products, whereas they are the minor products in methanol.[285,286]



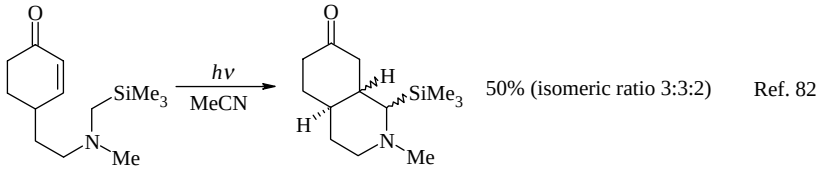
Ref. 285

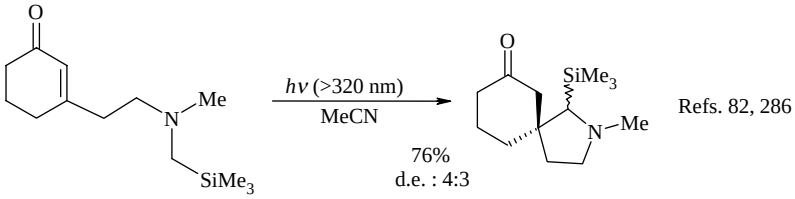
The same phenomenon has been observed when tertiary *N*-(trimethylsilyl)methylaniline is used.[85]

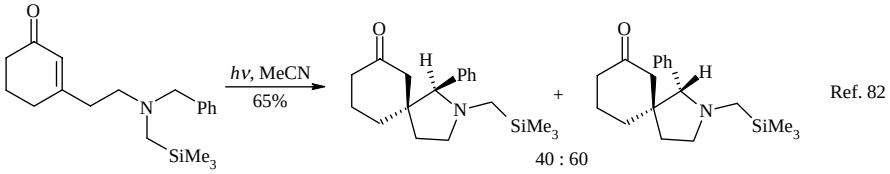


Hereafter, non-desilylative SET reaction is considered as an alkylation reaction of MSMA into RSMA. Later in the text (see Section VI.B.7), desilylative SET reaction will be detailed.

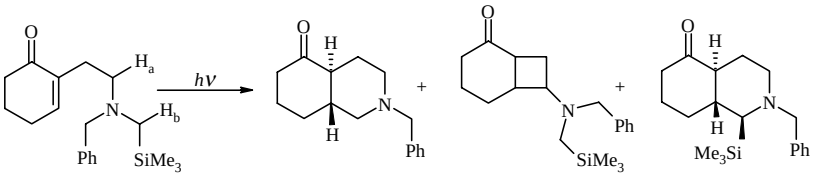
When the enone and SMA moieties are in the same molecule, cyclization reactions have occurred under irradiation in acetonitrile giving a bicyclic amino ketone.[82,286,287]







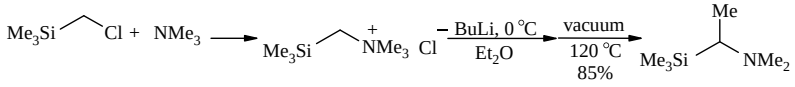
However, this is not always the case, as exemplified by the following results where the major product from the direct irradiation in acetonitrile results in the elimination of the radical $H_a^{\cdot}$, and in the elimination of H_b in methanol.[82]



Ref. 82

8. Alkylation *via* Isomerization of Quaternary Ammonium Salts (MSMA to RSMA)

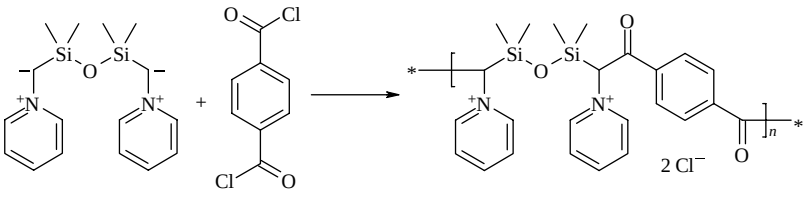
The pioneering work of Miller has shown that the treatment of trimethylsilylmethyl-trimethylammonium chloride with butyllithium induces a 1,2-sigmatropic Stevens rearrangement[288] to give 1-(trimethylsilyl-methyl)ethyldimethylamine in excellent yield.[289]



Ref. 289

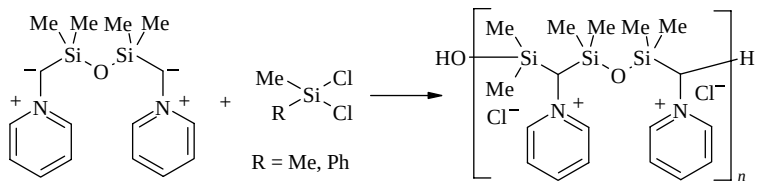
9. Acylation of the Ylid $N^+–CH–Si^-$

Action of terephthaloyl chloride on an *N*-(silylmethyl)pyridine ylid leads to alkylation with the formation of a polyterephthalic siloxane material.[290]



Ref. 290

A similar reaction with chlorosilanes leads to corresponding salts.[291]



Ref. 291

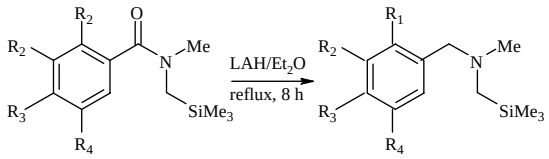
D. *Transformations away from the Substructure*

Transformations remote from the basic α-aminomethylsilane group are reactions of great interest because they indicate the conditions in which the SMA framework is stable. They are mainly concerned with functionalization in the α-, β-, γ- (or further away) with respect to the nitrogen atom.

1. Transformations α- to an Atom of the Substructure

a. Transformations α- to N

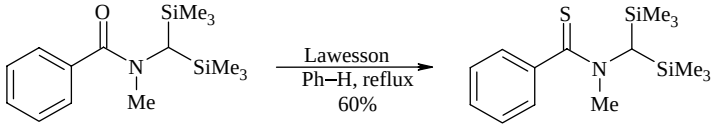
Almost quantitative yields are obtained when MSMA benzamide is reduced by LAH to yield a series of *N*-benzyl MSMAs.[237]



	R_1	R_2	R_3	R_4	Yield(%)
a	OMe	OM	H	H	89
b	OMe	H	OMe	H	91
c	H	OMe	OMe	H	89
d	H	OMe	H	OMe	84
e	H	OMe	OMe	OMe	75

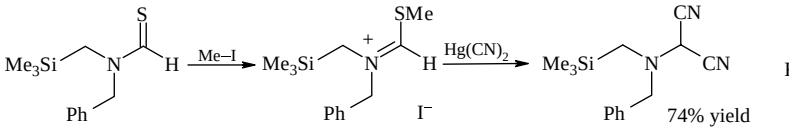
Ref. 237

Under treatment with Lawesson's reagent, BSMA benzamide has been converted in good yield into the corresponding thiobenzamide.[136] This bis(silyl)thio derivative has been already prepared by silylation of *N*,*N*-dimethylbenzothioamide (see Section III.B.1.d).



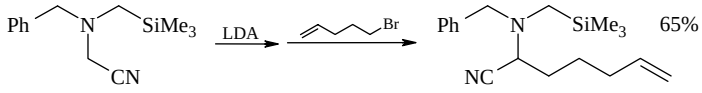
Ref. 136

Quaternization of the sulfur atom followed by reaction with mercuric cyanide produces the corresponding 2-aminomalononitrile.[64,171]



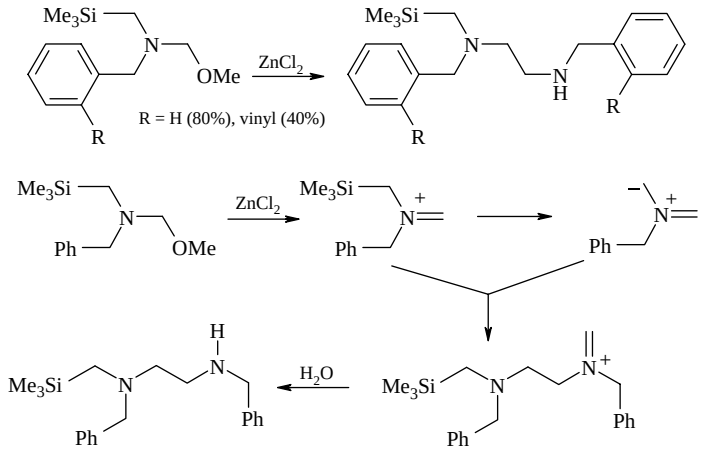
Refs. 64, 171

As is the case of non-silylated *N*,*N*-dialkylaminoacetonitriles, the MSMA derivative has been alkylated with 5-bromopentene without any trace of a product that could result from alkylation of the α-trimethylsilyl- or the benzylic carbon atom.[64]



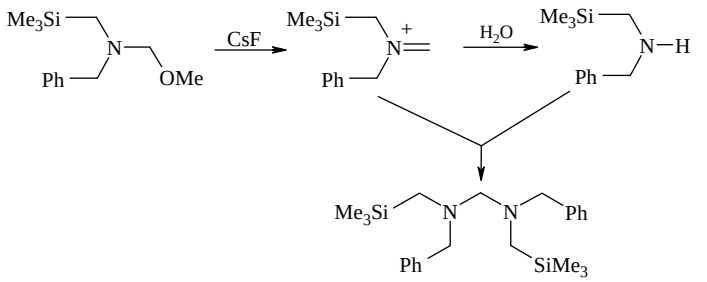
Ref. 64

N-Methoxymethyl SMAs have been the substrate of choice for numerous other SMA derivatives. Action of zinc chloride transforms this compound into an original 1,2-diamine, with the yield being dependent on the substituent on the phenyl ring. This is explained by the following scheme.[219]



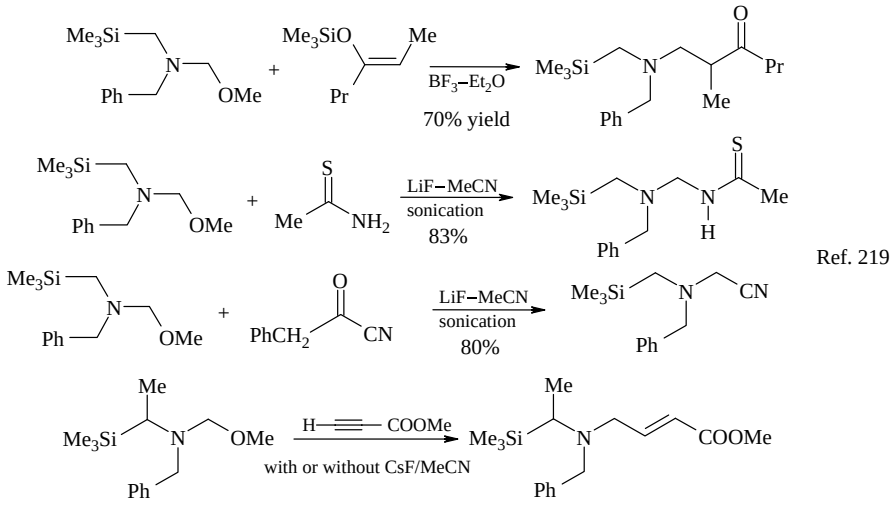
Ref. 219

When cesium fluoride is used instead of zinc chloride, a diaminomethane derivative is obtained, whose formation is explained by the addition of the iminium salt to the secondary amine resulting from its hydrolysis.[219]



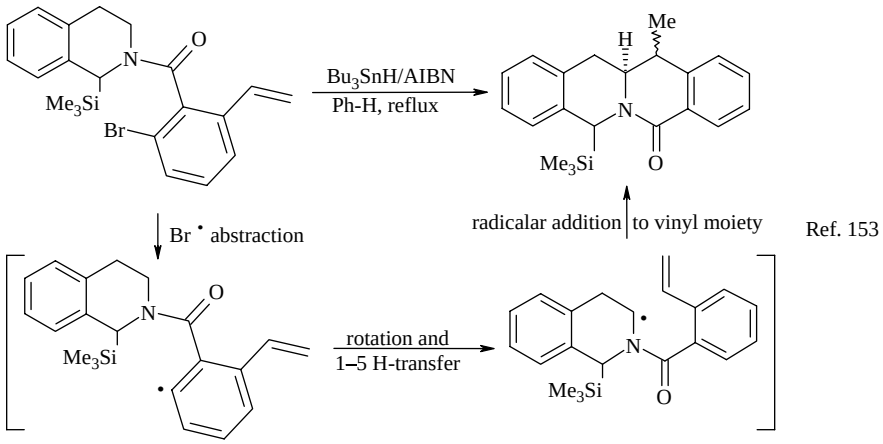
Ref. 219

The intermediate immonium cation has been intercepted by an enoxysilane to yield a β-amino ketone and by thioacetamide, phenacetyl cyanide and methyl propiolate to yield functionalized derivatives.[219]



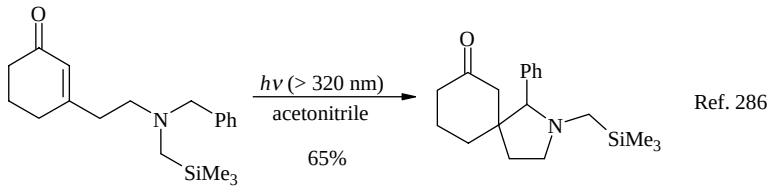
Ref. 219

In a study dealing with the construction of a 5*a*-aza-naphthacene derivative, conditions of the radical reaction did not affect the SMA framework present in the starting material. This result could be explained either by the steric hindrance of the silyl group that inhibits the abstraction of the benzylic hydrogen atom to create the corresponding radical species, or this radical, if created, is too stable to react efficiently.[153]



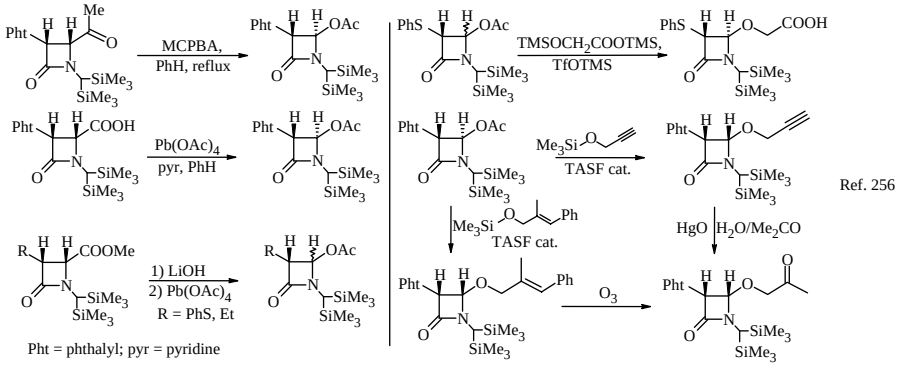
Ref. 153

Another example is the irradiation of the cyclohexenone below in acetonitrile, where the spiro compound formed is an *N*-silylmethyl derivative. The same reaction performed in methanol gives a non-silylated spiro compound (see Section VI.B.7).[82,286]



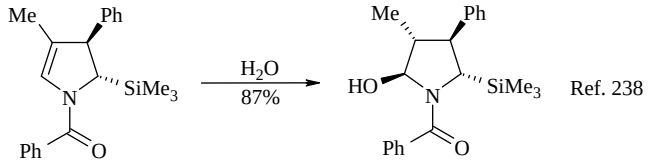
Ref. 286

The chemistry of *N*-[bis(trimethylsilyl)methyl]-β-lactams provides interesting insight into the stability of these systems. The bis(trimethylsilyl)methyl group is not affected by conditions of the Bayer–Villiger reaction, by oxidation with lead tetraacetate or ester hydrolysis with lithium hydroxide.[256] The acetoxy group could be displaced to form ether derivatives.[256]



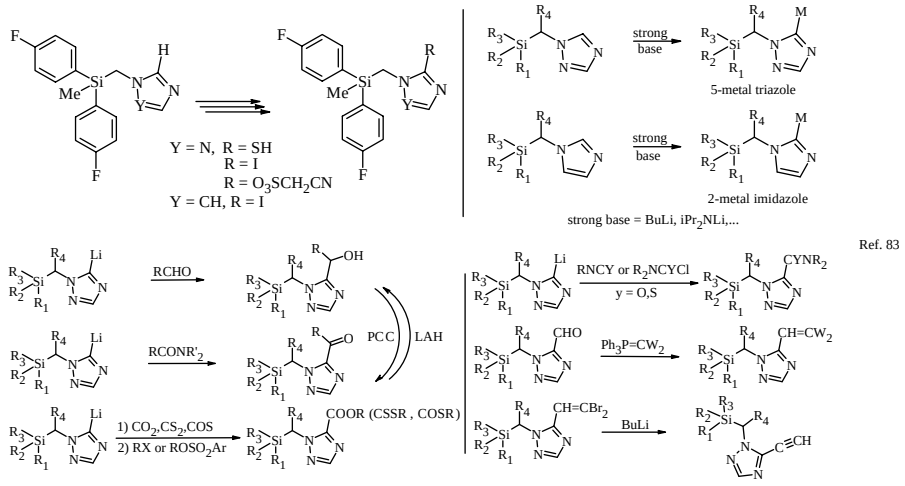
Ref. 256

Similarly, the SMA framework of *N*-vinyl amide is not affected during hydration of the double bond.[238]



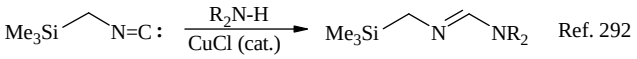
Ref. 238

A large number of transformations have been made on a series of silylmethyltriazoles or imidazoles, as shown below.[83]



Ref. 83

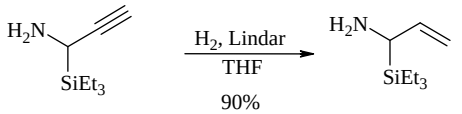
Trimethylsilyl-*iso*-acetonitrile has been shown to be highly versatile in the presence of cuprous chloride. Amines lead to formamidines through the insertion into their N–H bond whereas alcohols lead to desilylation products (see Section VI.B).[292]



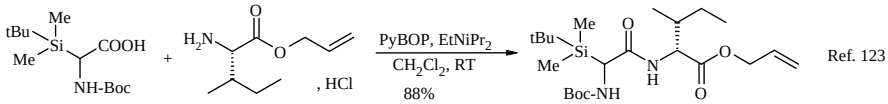
Ref. 292

b. Transformations α- to C

Several of the transformations α- to the carbon of the silylmethylamines giving access to differently substituted SMAs have been reported. Thus, an ethynyl derivative has been reduced quantitatively to its vinyl congener or peptide has been prepared in high yield from the corresponding aminoacid.[123,130]

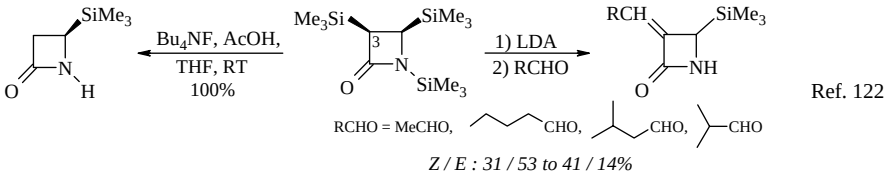


Ref. 130



Ref. 123

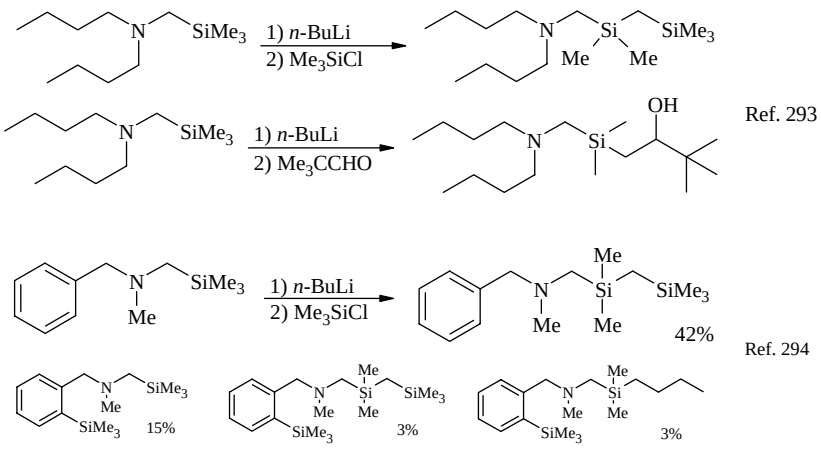
In the chemistry of β-lactams, the silyl group at the 3-position on the ring, has been used as a good precursor for the introduction of an alkylidene group through a Peterson-type reaction. Protodesilylation of this position is also possible.[122]



Ref. 122

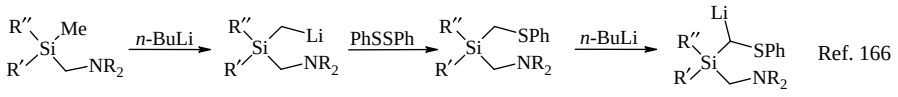
c. Transformations α-to Si

Lithiation of a methyl group of the silyl group of an SMA could be easily performed using *n*-butyllithium as shown in the following sequence of reactions.[166,293,294]



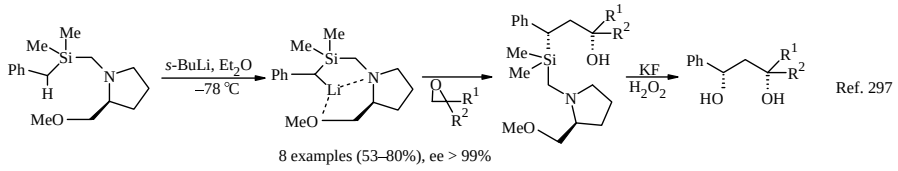
Ref. 293

Ref. 294



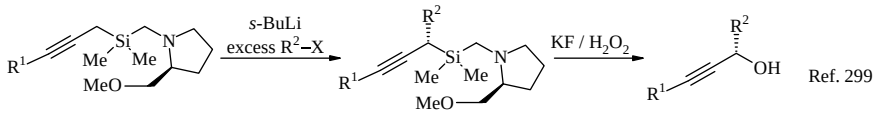
Ref. 166

If nitrogen is included in a chiral auxiliary, chirality is transferred with excellent enantiomeric excesses to the new C–C bond formed. Thus, alcohols are prepared with excellent enantioselectivity after oxidative cleavage[295] of the Si–C bond,[296] and a chiral 1,3-diol is obtained with high optical purity.[297,298]



Ref. 297

This strategy has been applied to the highly enantioselective synthesis (up to >99% ee) of propargyl alcohols.[299]

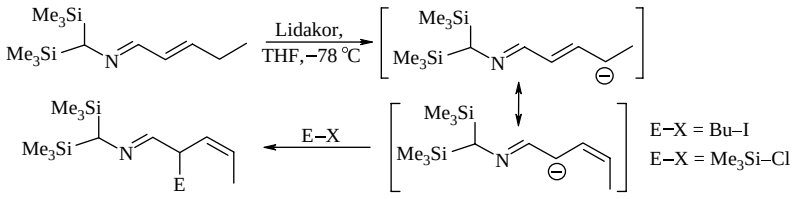


Ref. 299

2. Transformations β to an Atom of the Substructure

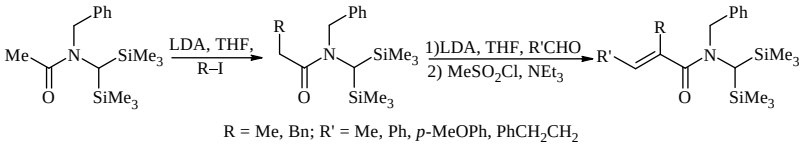
a. Alkylation

Deprotonation of BSMA imines followed by trapping with an electrophile of the intermediate anion has been described (see Section IV.C.4). However, when these imines derive from conjugated carbonyl compounds, attack of the base takes place at the end of the conjugated system to give delocalized bis(allyl) anion that could be alkylated or silylated in the β-position from the nitrogen.[227]



Ref. 227

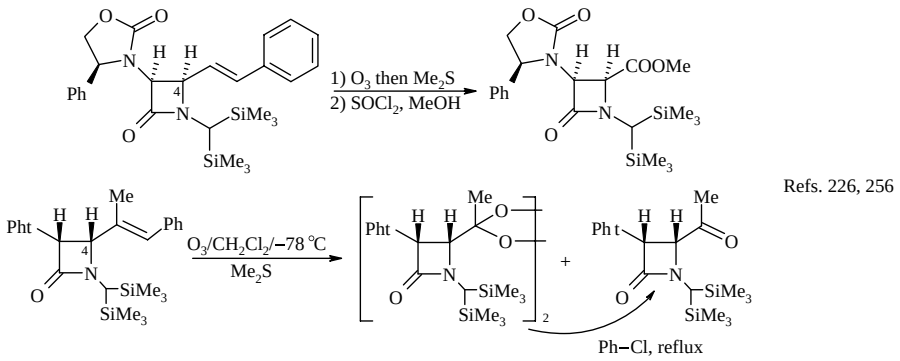
Homologation of this acetamide into other alkyl or aryl amides has been performed successfully. Their transformation into α,β-unsaturated amides is also possible.[95]



Ref. 95

b. Ozonolysis

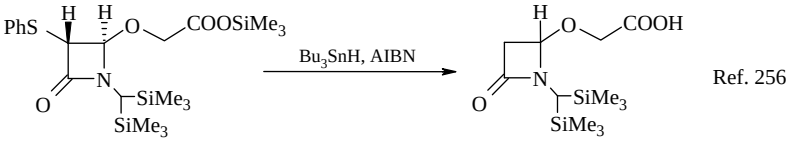
As exemplified by the chemistry of *N*-[bis(trimethylsilyl)methyl]azetidinones, the bissilylmethyl group are stable to ozonolysis conditions, allowing chemical transformations to be carried out on the substituents at the 4-position of the ring.[228,256]



Refs. 226, 256

c. Desulfuration

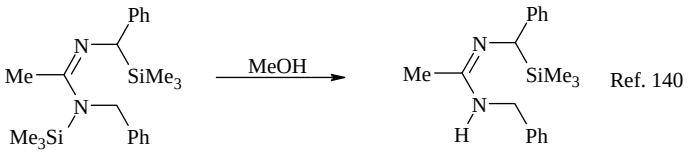
Similarly, desulfuration of 3-phenylthio azetidinone under radical conditions has been performed to yield its 3-non-substituted homolog without affecting the α-silylamine group.[256]



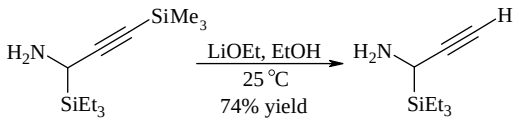
Ref. 256

d. Hydrolysis

Conditions which serve to desilylate an *N*-trimethylsilyl group or an ethynyltrimethylsilyl group do not result in the loss of a trimethylsilyl group α- to an amine.[130,140] Another example is the hydrolysis of BSMA precursors with methanol in the presence of one equivalent of trimethylsilyl chloride (see Section III.B.2.h).[186–189]



Ref. 140

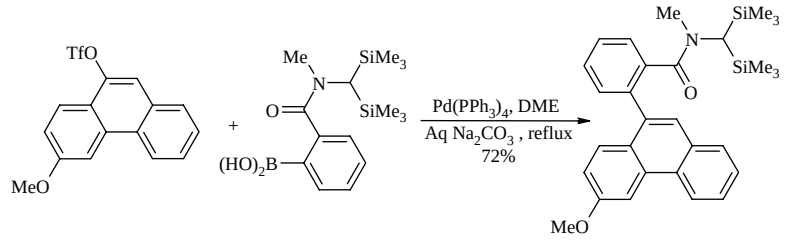


Ref. 130

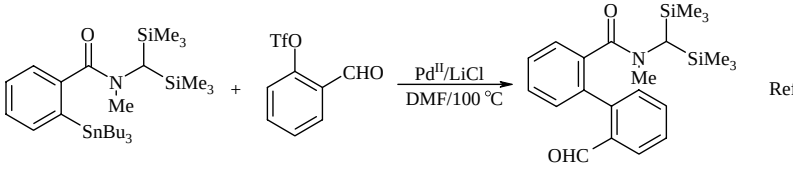
3. Transformations γ to an atom of the substructure

a. Aryl coupling

The BSMA amide framework has been shown to be unaffected under the conditions of either the Suzuki or the Stille cross-coupling reactions.[137,152,300]



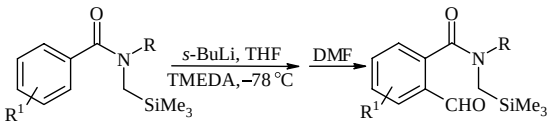
Ref. 300



Refs. 137, 152

b. Formylation and functionalization

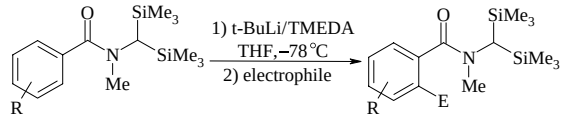
Formylation of the aryl group of MSMA benzamide to produce *o*-formylbenzamides has also been performed without observation of side reactions.[137,152]



R^1=	H	R = Et
R^1=	H	R = *i*.Pr
R^1=	4-MeO	R = *i*.Pr
R^1 =	3-MeO	R = *i*.Pr
R^1 =	6-MeO	R = Me
R^1 =	4,6-diMeO	R = Me
R^1 =	6-Ph	R = *i*.Pr
R^1 =	6-Cl	R = Me

Refs. 137, 152

The same has been observed during the introduction of a functional group at the *ortho*-position of the aryl ring of these amides, even if *s*-BuLi has been replaced by *t*-BuLi.[137,152]

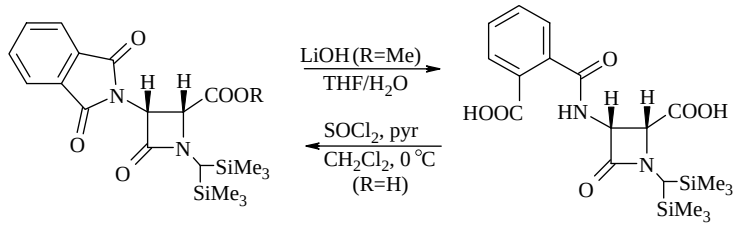


R	E	electrophile
H	D	MeOD
H	Me	MeI
H	Allyl	Br-allyl
H	CHO	DMF
H	$CONEt_2$	Cl-$CONEt_2$
H	Br	Br_2
H	$SnBu_3$	Cl$SnBu_3$
H	S-*t*-Bu	$(t.BuS)_2$
3-OMe	$SiMe_3$	Cl-$SiMe_3$
4-OMe	CHO	DMF

Refs. 137–152

c. Hydrolysis of phthalimide

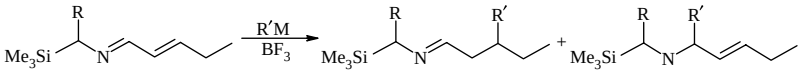
Partial hydrolysis of phthalimide ring has been realized on an *N*-[bis(trimethylsilyl)methyl]azetidinone, as well as ring closure, the reverse reaction.[256]



Ref. 256

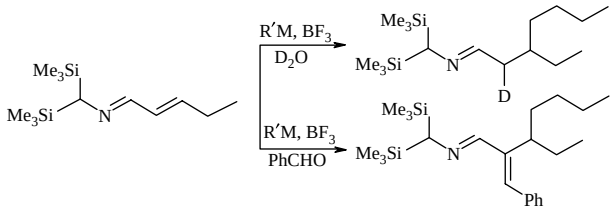
d. Conjugate addition to conjugated imines

In the presence of boron trifluoride, organocuprates are added to 1-aza-1,3-butadiene derivatives to give 1,4 addition products in moderate to good yields after reaction with nucleophiles. When the nucleophile is 2-thienyl or 2-furyl, alkylation results in a simple addition on the imine double bond. The intermediate anion is also trapped by an electrophile.[229]



R= H, $SiMe_3$

R′M = R'_2CuLi (with R′ = Bu, Ph, $PhMe_2Si$) or $R'_2Cu(CN)Li_2$ (with R′ = Bu, 2-thienyl, 2-furyl)

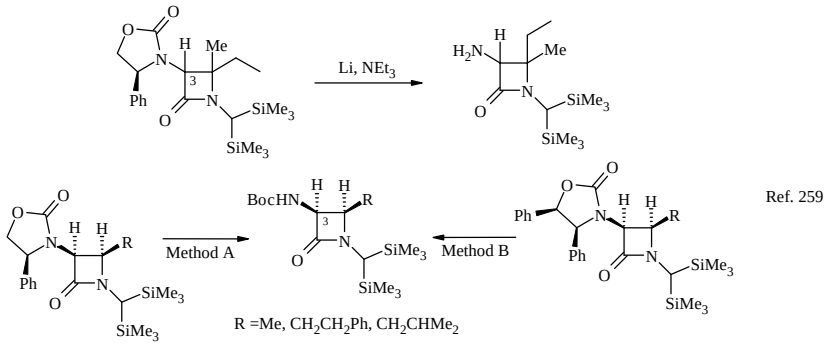


Ref. 229

R′M = n Bu_2 $Cu(CN)Li_2$

e. Conversion of oxazolidinones

Formation of a 3-amino azetidinone and its N-Boc protected form from oxazolidinone precursors shows that various reactions can be performed with good yields (67–95%) without affecting the *N*-[bis(trimethylsilyl)methyl] group.[259]



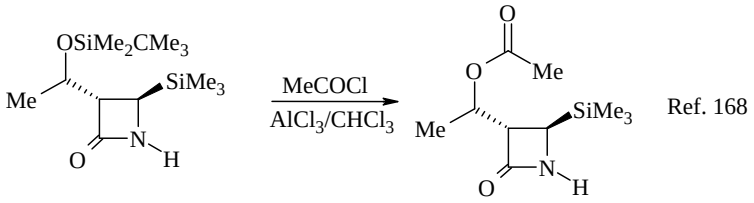
Ref. 259

R =Me, CH_2CH_2Ph, CH_2CHMe_2

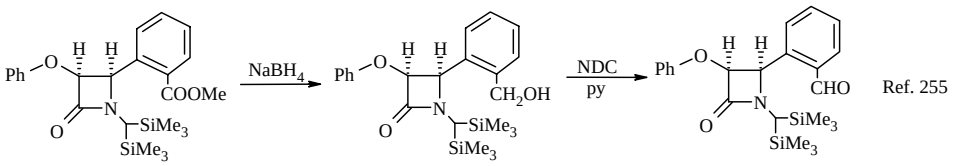
Method A: a) Li/NH_3, THF, t-BuOH,–78 °C; b) NH_4Cl; c) HCl 1N; d) NaOH; e) Boc_2O, CH_2Cl_2.
Method B: EtOH, $Pd(OH)_2$, Boc_2O, 60psi,

4. Transformations at an atom away from the substructure

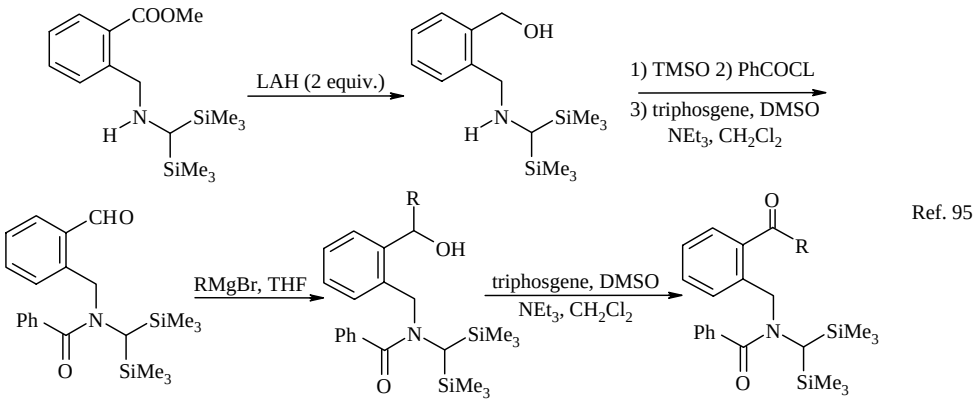
A variety of functional transformations occurring far from the SMA framework have been described. Acylation of a silyl ether, sodium borohydride or LAH reduction of an ester into a carbinol, oxidation of a carbinol into an aldehyde or a ketone, and the addition of Grignard reagents to a carbonyl are some examples.[95,168,255]



Ref. 168



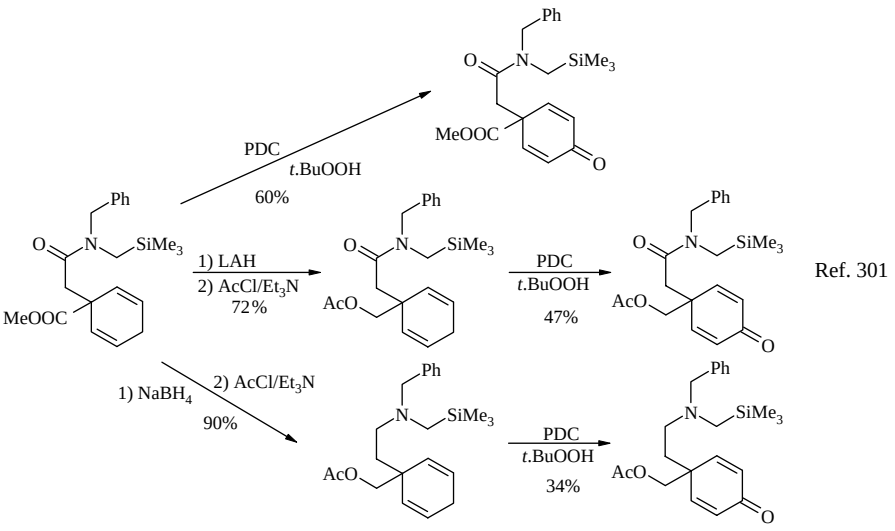
Ref. 255



Ref. 95

TMSO : *N*-trimethylsilyloxazolidinone

Another illustration is the chemistry developed from MSMA amides where oxidation with pyridinium dichromate (PDC) of a methylene unit, LAH or sodium borohydride reduction of an ester moiety is performed without affecting the SMA's framework.[301]



These α-silylamino- and α-silylamido-2,5-cyclohexadien-1-one have been submitted to SET photochemistry (see Sections IV.C.7 and VI.B.7) to synthesize functional hydroisoquinolines.[301]

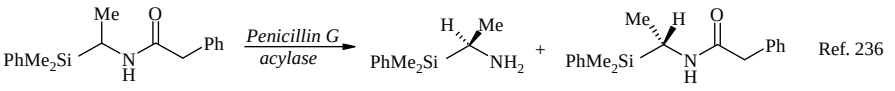
V

SYNTHESES OF CHIRAL SMA

It has already been reported (see Section IV.A.3.b) that the two enantiomers of a racemic C-silyl aminoacetic ester have been easily separated by chiral HPLC.[123] Various chiral SMAs have been prepared using classical methods. SMAs where the chiral center is not part of their framework are not considered here.

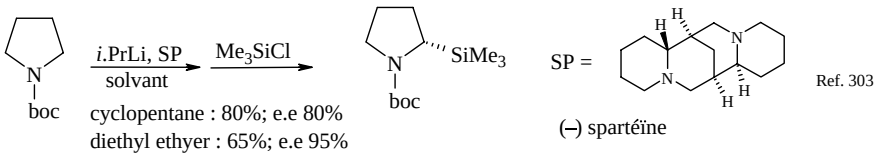
A. *Enzymatic hydrolysis of amides*

Enzymatic treatment with Penicillin G acylase of the phenylacetamide of a RSMA leads to the specific hydrolysis of one enantiomer forming the amine in good yield and high enantiomeric purity (92%).[236] Absolute configuration (R) and enantiomeric purity are determined by H^1 NMR, after derivatization with (*S*)-α-trifluoromethylphenylacetic acid (Mosher's salt).[302]



B. *Asymmetric deprotonation followed by silylation of the "chiral" anion*

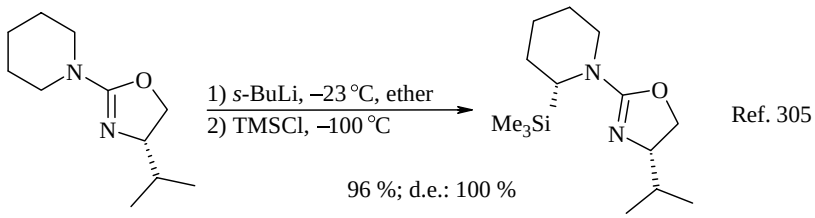
During the course of work on the asymmetric deprotonation of boc-protected pyrrolidine with lithium reagents in the presence of the chiral base (−)-sparteine, α-[R]-trimethylsilylpyrrolidine was obtained in good yield and excellent enantiomeric excess.[303]



Sparteine appears to be the best ligand examined to date in studies on the effect of ligand structure on the enantioselective deprotonation.[304] The *t*-butoxycarbonyl group stabilizes the anion and renders α-protons more acidic.

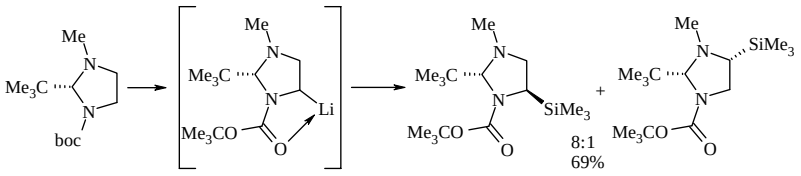
C. *Use of a chiral inductor*

In early work, difficulty in applying the method towards the silylation of six-membered heterocycles was noticed.[133] This may be circumvented by using an oxazolidine as the protective group. Through the use of a chiral oxazolidine, this approach leads to complete diastereoselection in quantitative yields.[305] Unfortunately, the silylpiperidine could not be recovered after deprotection.



D. *Silylation of a chiral molecule*

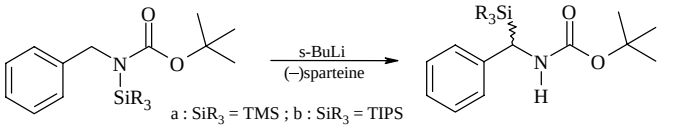
Using the previous methodology, silylation of [R]-*N*-methyl-*N*-boc-2-*t*-butylimidazoline led to a mixture of 4- and 5-trimethylsilylimidazoline in which the latter predominates. No details were given on the diastereoselectivity nor on the possible separation of the two regioisomers. Optical antipodes were accessible from the [*S*]-form of the starting imidazoline.[306]



Ref. 306

E. *Silylation of an α-nitrogen carbanion through a retro-Brook rearrangement*

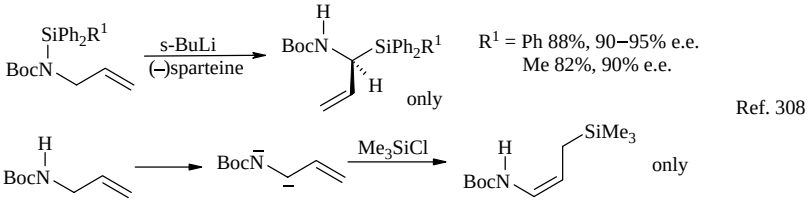
The Brook rearrangement is a well-known and useful process in organosilicon synthetic organic chemistry. A silicon atom on a carbon atom exchanges with a negative charge on a heteroatom (O or N) attached to this same carbon. The reverse rearrangement, oftentimes referred to as the retro-Brook rearrangement, has also been established[140,307,308] and was utilized to synthesize chiral SMAs from *N*-Boc-*N*-trimethylsilylbenzylamine and *s*-butyllithium/sparteine.[309] It is notable that the non-silylated allyl amine leads to a result different from the one obtained from *N*-silylated allylamine.[308]



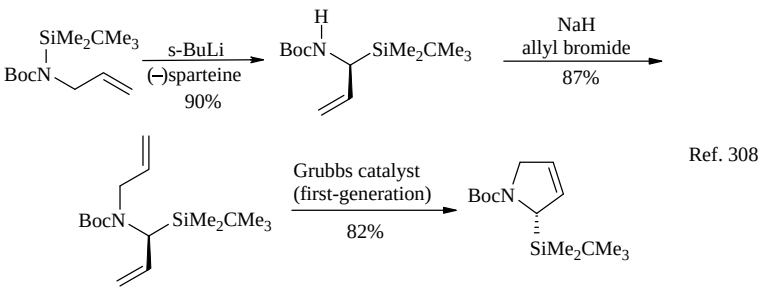
a : SiR_3 = TMS ; b : SiR_3 = TIPS

Ref. 309

	a(%)	b(%)
Yield	51–67	72–80
e.e.	35–70	30–72



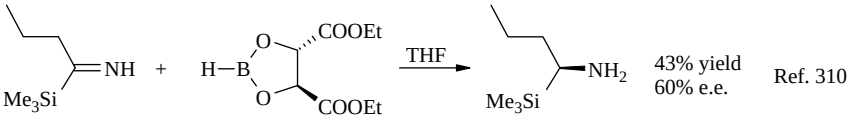
Ref. 308



Ref. 308

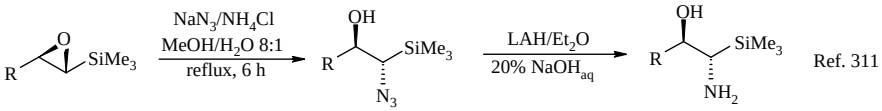
F. *Asymmetric reduction of acylsilane imines*

Aliphatic acylsilane imines and their salts are readily accessible (see Sections III.B.2.i and III.B.2.j). Their reduction by a chiral boronate provides ready access to the corresponding chiral RSMAs.[310]

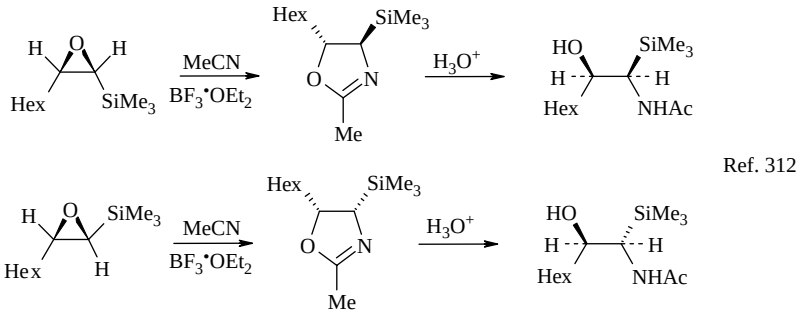


G. *Amination of chiral epoxysilanes*

Chiral α-hydroxy RSMAs are obtained from α-chiral silyl epoxides by classical *trans* addition of sodium azide followed by reduction of the intermediate α-hydroxy azide (see Section III.A.7).[311]

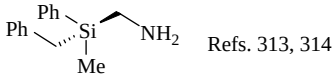


Stereochemically well-defined silylaminoalcohols can also be prepared through the hydrolysis of intermediate oxazolines obtained by treating chiral α-silylepoxides with acetonitrile in the presence of boron trifluoride etherate.[312]



H. *Chiral SMA as NMR shift reagents*

Aminomethylbenzylphenylmethylsilane, chiral at the silicon center, has been used as an NMR shift and relaxation reagent.[313] Both enantiomers are obtained from the racemic material by fractional crystallization of the (+)-tartaric acid salts.[314]



VI

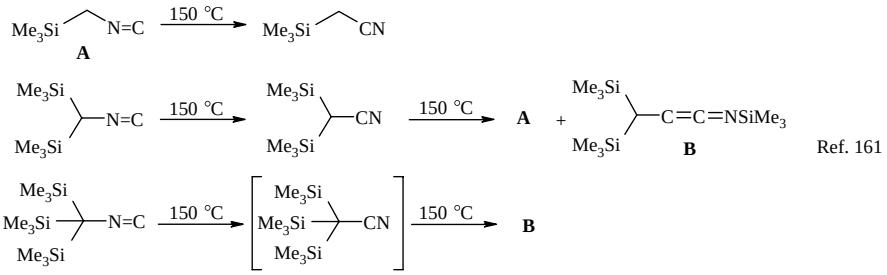
TRANSFORMATIONS WITH CLEAVAGE OF THE SUBSTRUCTURE

A. *Cleavage of the C–N bond*

Generally, the cleavage of the C–N bond in silylmethylamines occurs with the formation of a new C–C bond.

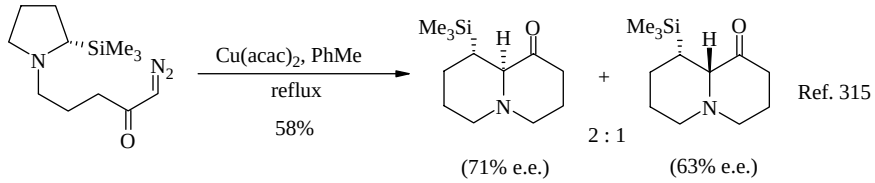
1. Isomerization of isonitriles into nitriles

When heated at 150 °C, trimethylsilylmethylisonitriles undergo an isomerization into the corresponding trimethylsilylacetonitriles. The tris(trimethylsilyl) derivative, not very stable at this temperature, undergoes further isomerization to the ketene imine structure.[161]



2. Insertion of carbenes into the C–N bond: ring enlargement of α-silylpyrrolidines

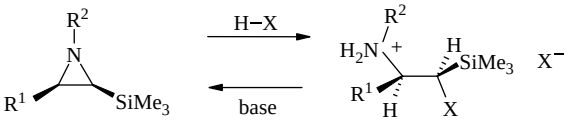
Catalyzed insertion of a carbene into the SiC–N bond of a α-trimethylsilylpyrrolidine results, *via* a Stevens rearrangement, in the expansion of the ring to form the 3-trimethylsilylpiperidine derivative. Thus a mixture of *cis* and *trans* 9-trimethylsilyl-hexahydro-quinolizin-1-ones can be obtained from N-(5-diazopentan-4-onyl)-2-trimethylsilylpyrrolidine.[315]



3. Ring opening of 2-silylaziridines: synthesis of β-silylamines and α-silyl-β-aminoalcohols

2-Trimethylsilylaziridines have proven to be difficult to open by purely nucleophilic reagents (LAH, MeONa, etc.). However, prior protonation with hydrogen halides facilitates ring opening to stereospecifically form β-silylamines (46–96%). Ring closure

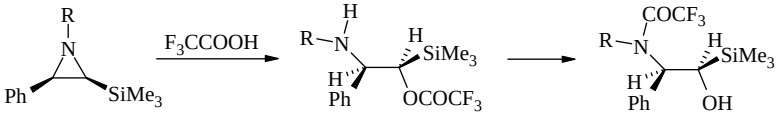
back to the aziridine ring occurs when these β-silylamines are treated with a base.[316]



Ref. 316

R^1 = Ph, H R^2 = *n*-Pr, Ph, H, COOEt X = Cl, Br

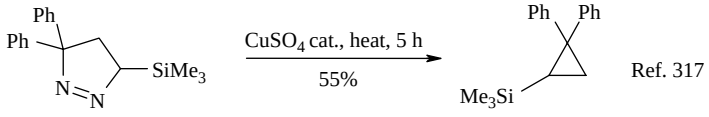
In the presence of trifluoroacetic acid, these aziridines undergo protonation at room temperature and ring opening at reflux in methanol, diethyl ether or hexane under nucleophilic attack of the trifluoroacetate anion followed by acyl exchange to give the corresponding α-silyl-β-aminoalcohol derivative.[316]



Ref. 316

4. Decomposition of 3-silylpyrazoline

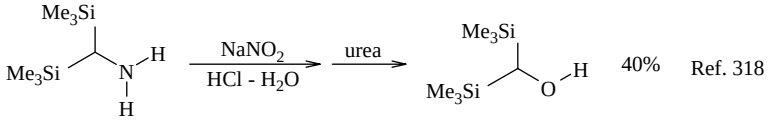
Under heating in the presence of a catalytic amount of copper sulfate, 3,3-diphenyl-5-trimethylsilyl-4,5-dihydro-3H-pyrazole loses nitrogen to form the corresponding cyclopropane derivative[317] that can be prepared directly (yield 85%) through reaction of diphenyldiazomethane with vinyltrimethylsilane.



Ref. 317

5. Nitrous deamination reaction

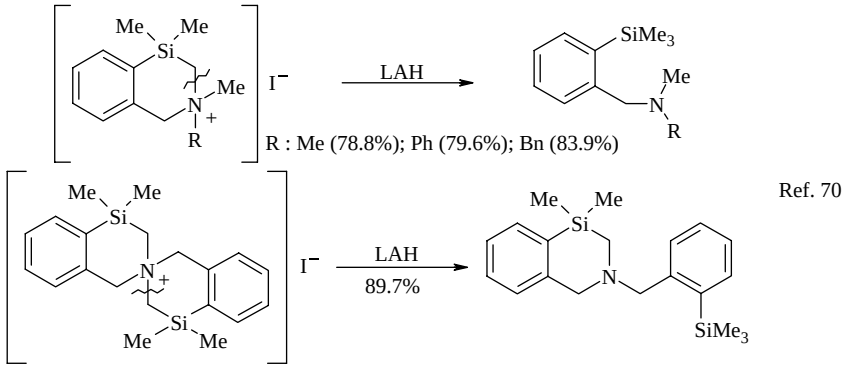
Bis(trimethylsilyl)methanol is obtained when BSMA is subjected to the usual conditions of a nitrous deamination reaction.[318] Neither starting material nor a monosilylated compound are recovered.



40% Ref. 318

6. Reduction of ammonium salts

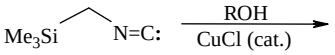
Lithium aluminum hydride reduction of 1,1,3-trimethyl-3-substituted-1,2,3,4-tetrahydrobenzo[*d*]-1,3-azoniasiline iodide gives 2-trimethylsilylbenzylamine derivatives in good yields through cleavage of the C–N bond of the framework.[70]



Ref. 70

B. *Cleavage of the Si–C bond*

Cleavage of the Si–C bond has gained tremendous importance in organic synthesis because of the diversity of the reactions in which organosilicon compounds can be engaged and the very mild conditions of these reactions.[319] In some instances, total or partial desilylation is observed as a side or unexpected reaction. For instance, attempted cuprous ion-catalyzed insertion of trimethylsilylmethylisocyanide into the O–H bond of alcohols fails and desilylation occurs whereas insertion in the N–H bond of amines takes place in high yield (see Section IV.D.1.a).[292]



desilylation products Ref. 292

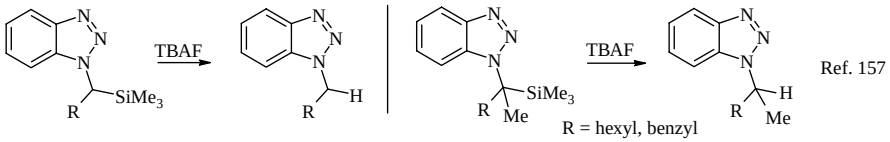
More efficient desilylations have been obtained that constitute interesting and versatile steps in organic synthesis, for instance, where the silyl group is substituted by a hydrogen or a heteroatom.

1. Protodesilylation (C–Si to C–H)

a. Fluoride-assisted protodesilylation

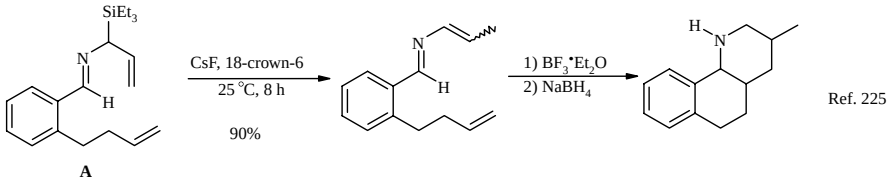
The use of a strong nucleophile capable of coordinating with the silicon atom has provided the key for cleaving the Si–C bond. Partial desilylation reaction of BSMA derivatives has already been described (see Section IV.C.2). Desilylation-protonation of MSMA derivatives is presented here.

N-(α-Trimethylsilyl)alkylbenzothiazoles are easily desilylated by reaction with tetrabutylammonium fluoride (TBAF) and quenching with water.[157]



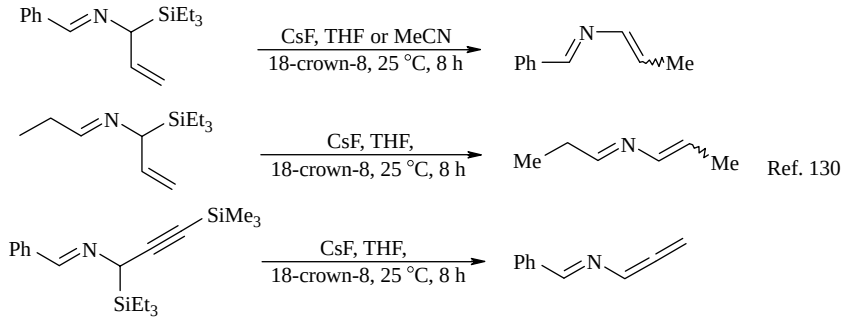
Ref. 157

Treating α-triethylsilylallylimine **A** with cesium fluoride in the presence 18-crown-6 ether provides excellent access to the corresponding 2-azadiene that is further cyclized into 3-methyl-octahydrobenzo-[h]quinoline.[225]



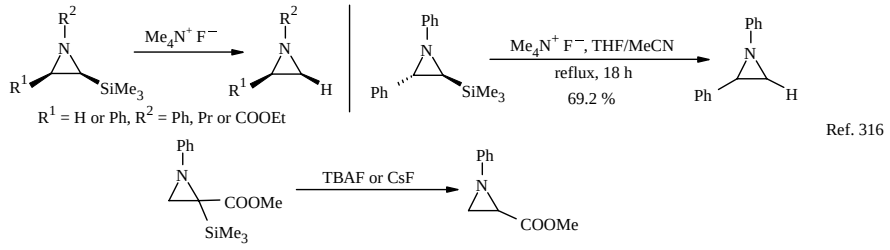
Ref. 225

This method has been applied to the synthesis of other 2-azadienes. The corresponding non-silylated *N*-allylimine is not formed and does not isomerize into the azadiene under the conditions of the reaction. The stereochemistry (E/Z:E/E) of the diene depends on the reaction conditions.[130]



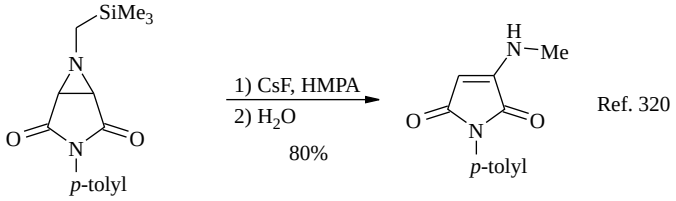
Ref. 130

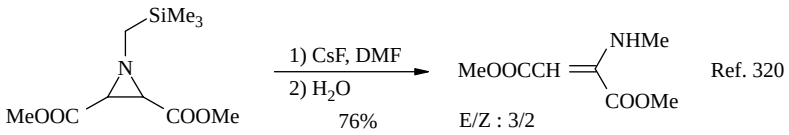
Although fluorodesilylation of 2-silylaziridines is reported to be not easy to perform, some of these compounds undergo such a reaction.[316]

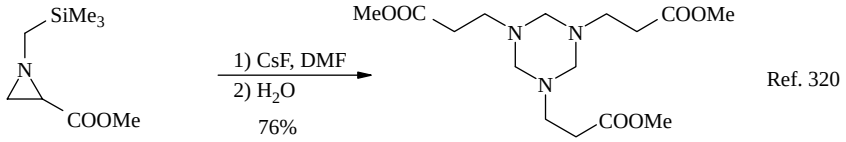


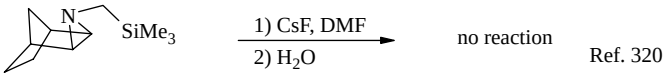
Ref. 316

Similar to these results, but accompanied with ring opening, are the desilylation reactions of substituted aziridines. Treatment with cesium fluoride (1 equiv.) in HMPA (tetrabutylammonium fluoride in THF or DME gives lower yields) at room temperature followed by aqueous work-up, yields desilylated open-chain compounds.[320]



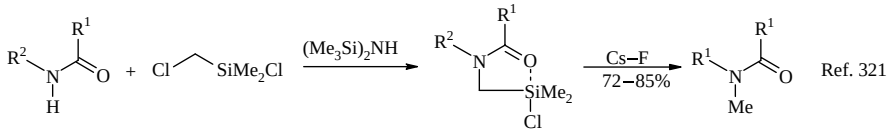






Noticeable is the absence of reaction when the aziridine ring does not bear at least one anion-stabilizing moiety. Noticeable also is the influence of the position of the trimethylsilyl group in the molecule as silyl group directly attached to the ring does not induce ring opening (see above).

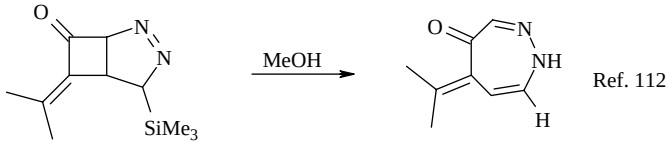
Taking advantage of the peculiar reactivity of pentacoordinated *N*-(amidomethyl)-chlorosilanes (see Section II.B), they were easily desilylated in the presence of an equivalent amount of cesium fluoride into the *N*-methylamide.[321]



b. Protodesilylation

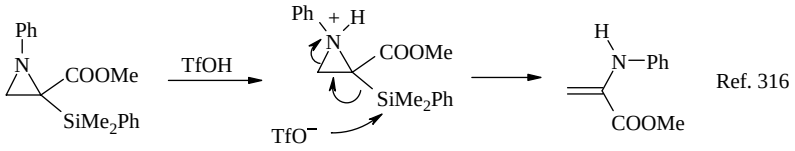
Sometimes, the structure of the silylated molecule is such that desilylation can be performed under the action of an acid as weak as methanol. Thus 3-trimethylsilyl-Δ^1-pyrazoline when dissolved in methanol loses the silyl group with

ring expansion to provide the corresponding 1,5-dihydro-[1,2]diazepin-4-one.[112]



Ref. 112

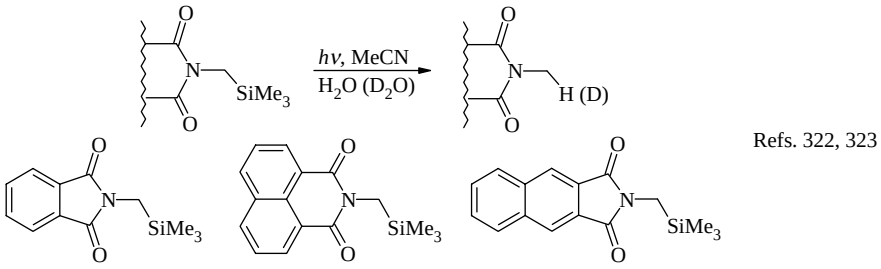
It has been mentioned that hydracids ring-opened 2-silylaziridines to yield silylated amino derivatives (see Section VI.A.3). However, triflic acid is reported to open the ring of 2-silylaziridines with elimination of the silyl group. An α-amino crotonate is formed.[316]



Ref. 316

c. Photodesilylation

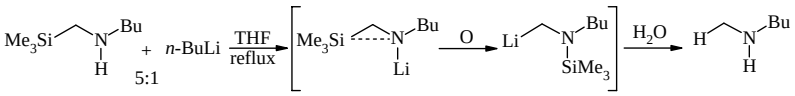
Irradiation of trimethylsilylmethylamino derivatives in wet acetonitrile leads to the desilylated product. Deuterated products are obtained by substituting H_2O for D_2O.[322,323]



Refs. 322, 323

d. Brook rearrangement

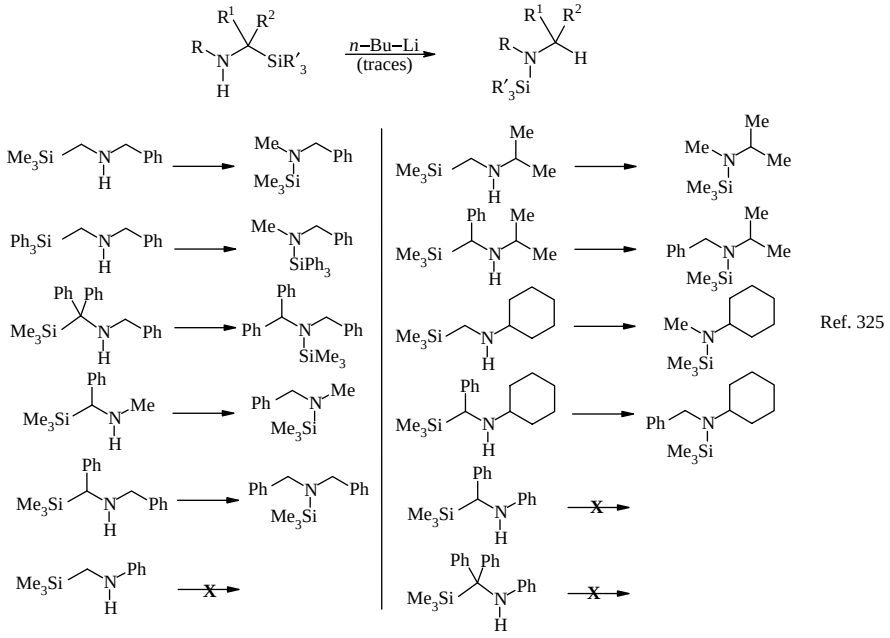
What is known as the aza-Brook rearrangement deals uniquely with monosubstituted MSMAs. When it was reported for the first time that *n*-butyllithium reacted with excess *N*-trimethylsilylmethyl-*n*-butylamine to yield *N*-methyl-*n*-butylamine, it was assumed that the intermediate lithium amide underwent a metal exchange.[324]



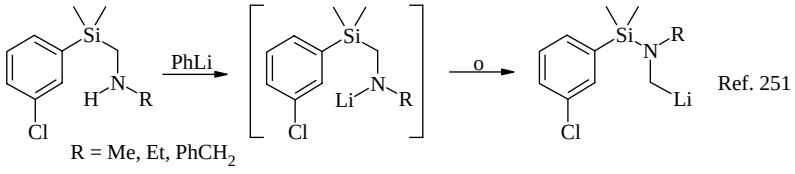
Ref. 324

This preliminary result has been the subject of an extensive study that confirms the catalytic nature of this rearrangement. It was observed that aniline derivatives do not undergo the rearrangement, probably because the aza-anion is more stabilized than

the isomeric carbanion.[325]



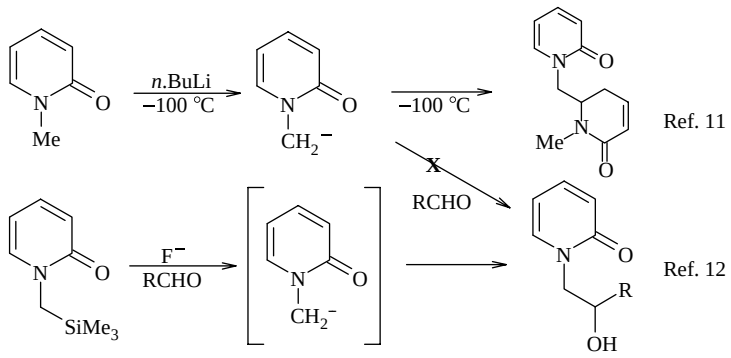
Such a rearrangement was observed to occur as a side reaction when *N*-alkylamino-*m*-chlorophenyldimethylsilane is reacted with phenyllithium. *m*-Chlorophenyldimethylsiloxane was obtained in low yield after hydrolysis.[251]



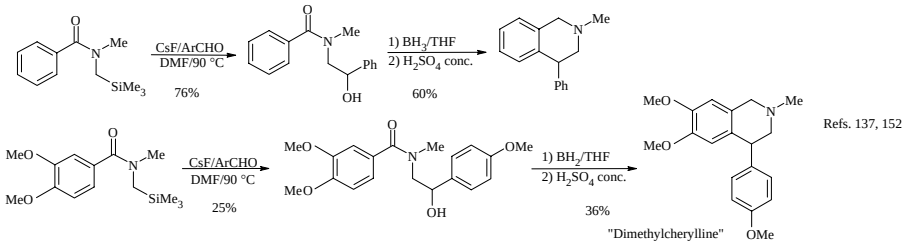
Another example of 1,2-silatropy is found with *N*-silylindole which isomerizes into 2-silylindole in the presence of *n*-butyl lithium.[326]

2. *Formation of aminoalcohols: N–C–Si → N–C–C–OH*

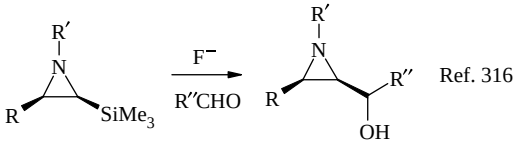
Preparation of aminoalcohols derived from *N*-methylpiperidone has been successfully performed by condensation of aldehydes with the carbanion obtained by fluorodesilylation of *N*-(trimethylsilyl)-methylpiperidone (*vide supra* Section I).[11,12]

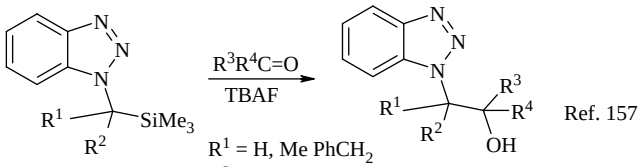


Dimethylcherylline, dimethylether of alkaloid cherylline, has been prepared (15% total yield) from the appropriately substituted *N*-methylbenzamide, *via* condensation with the corresponding benzaldehyde and subsequent cyclization.[137,152]

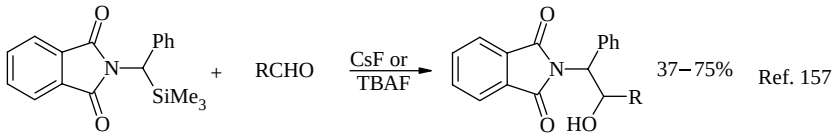


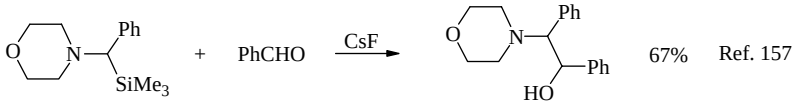
Other examples:

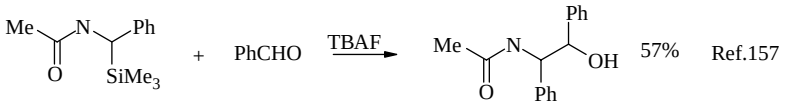


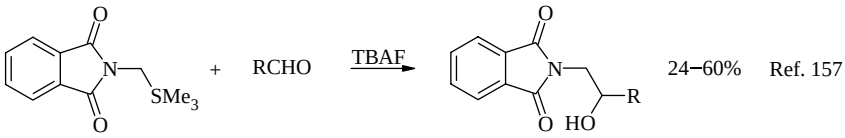


R^1 = H, Me $PhCH_2$
R^2 = H, $PhCH_2$
R^3, R^4 = p.MePh,H; Pr,H; $(CH_2)_5$





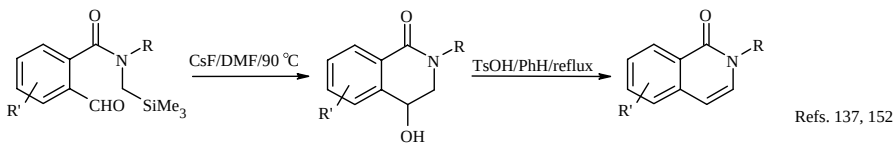




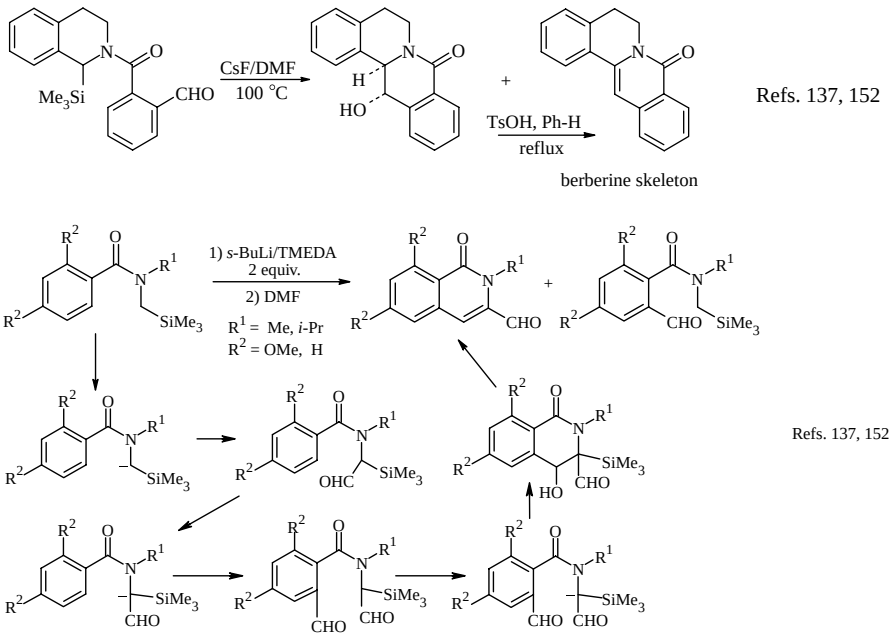
3. *Formation of the C=C*

a. Dehydration of amino alcohols

N-Vinyl amides have been obtained through dehydration of aminoalcohols resulting from the addition on an aldehyde of the carbanion formed under desilylative conditions (see Section VI.B.2).[137,152]



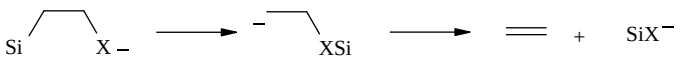
a R' = H	R = Et	e R' = 6-MeO	R = Me
b R' = H	R = *i*.Pr	f R' = 4,6-diMeO	R = Me
c R' = 4-MeO	R = *i*.Pr	g R' = 6-Ph	R = *i*.Pr
d R' = 3-MeO	R = *i*.Pr	h R' = 6-Cl	R = Me



In this last example, when $R^1 = i$.Pr and $R^2 = H$, the yield of bicyclic compound is 40 and 10% for the non-cyclized compound. With R = Me and R′ = OMe, the bicyclic derivative is obtained alone in 49% yield. It is noteworthy that this compound bears a formyl group which means that double formylation reaction occurs. A plausible mechanism would be that indicated in the scheme.

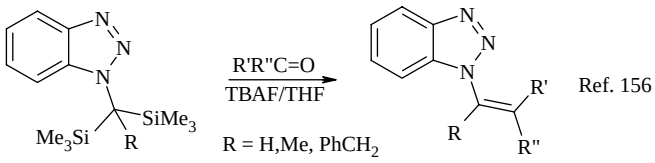
b. Peterson/Chan olefination

Wittig olefination reaction ("the phosphorus way") has been a very popular reaction in organic synthesis. However, it is now in competition with Peterson/Chan olefination reaction[327] ("the silicon way"). Formally, this latter involves the formation of a β-silyl heteroatomic anion, which in the absence of an electrophile undergoes a β-shift of the silyl moiety to the heteroatom (usually oxygen) with final elimination of silylated heteroatomic anion and formation of the olefin.

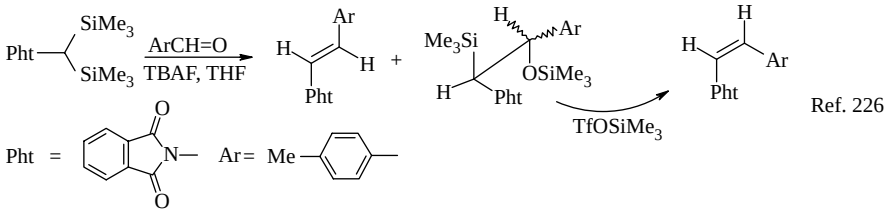


i. From BSMA derivatives

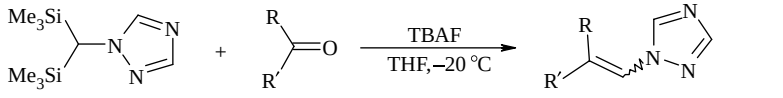
The formation of alkenes can happen when a BSMA derivative is partially desilylated in the presence of a carbonyl compound, finally giving the corresponding enamine. Many examples have been given of this useful and easily applicable technique. Starting from benzotriazole derivatives, the corresponding enamines are obtained after reaction with carbonyl compounds in the catalytic presence of fluoride anion.[156]

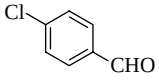
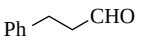
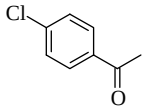
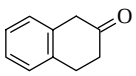


N-Bis(trimethylsilyl)methylphthalimide was treated similarly with *p*-tolyl aldehyde. After acidic work-up, the reaction afforded a mixture of the *trans*-alkene together with *threo* and *erythro* diastereoisomers (from NMR studies) of the addition product (not isolated). Upon treatment with trimethylsilyl trifluoromethylsulfonate ($TfOSiMe_3$), this last yields the *cis*-alkene.[226]



Similarly *N*-bis(trimethylsilyl)methyltriazoles lead to the corresponding *N*-bis(trimethylsilyl)methyltriazoles with yields which are generally good to excellent, except in the case where highly enolizable ketones (cyclohexanone and β-tetralone) are used as an electrophile. This olefination reaction is not stereoselective, except in the case of γ-phenylpropionaldehyde.[71]



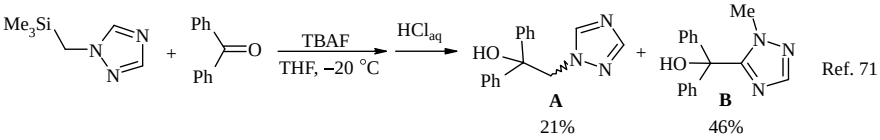
	Yield (%)	Isomer ratio[a]		Yield (%)	Isomer ratio[a]
	98	1:1		82	3:2
	89	–		40	–
	80	1:1		0	–

Ref. 71

[a] Isomer ratios measured by NMR (structures have not been attributed).

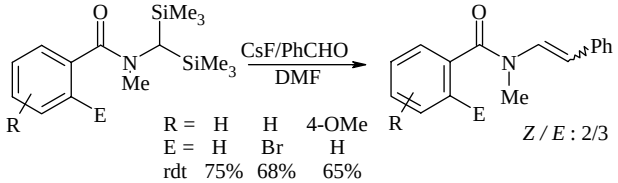
This result has to be compared with that of the reaction starting from the monosilylated triazole where two isomeric carbinols A and B are obtained. This is probably due to

the fact that the intermediate anion resulting from the desilylation is both nucleophilic (Π**A**) and basic (Π**B**) in character, whereas the presence of a second silyl group stabilizes the corresponding anion making it less basic than the non-silylated anion.[71]

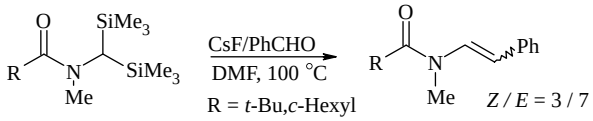


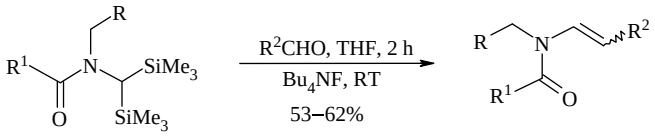
Ref. 71

A series of aryl and alkyl vinyl amides can also be prepared in good to excellent yields by this method.[95,137]



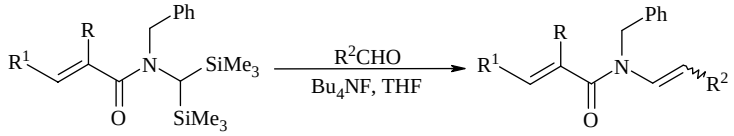
Ref. 137





R = H, Me, $PhCH_2$; R^1 =Me, Ph, *p*.MeOPh, $PhCH_2CH_2$; R^2 =Ph, *t*.Bu,

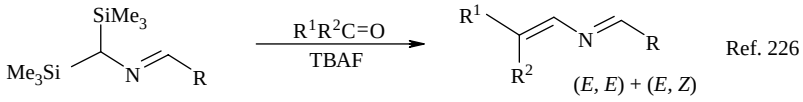
Ref. 95



R^2 = Ph,*p*.MePh, *p*.MeOPh,*t*.Bu, PhCH=C(Me)

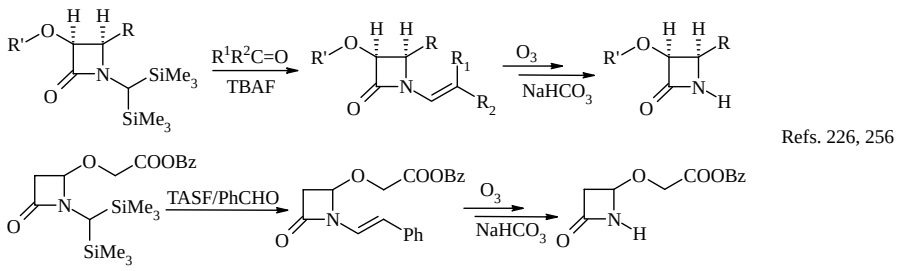
Even α,β-unsaturated amides lead to the corresponding vinyl amides obtained as Z + E mixtures where the Z isomer is the major isomer.[95]

An excellent illustration of the mildness of the olefination reaction is provided by the efficient synthesis of 2-aza-1,3-butadienes, compounds which are known to be highly susceptible to polymerization and thus difficult to prepare and isolate.[226]



Ref. 226

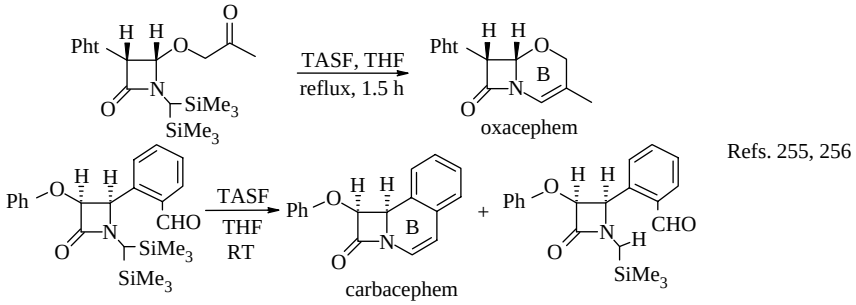
This transformation has been used to prepare, from *N*-bis(trimethylsilyl)methyl β-lactams, *N*-vinyl β-lactams precursors of N–H β-lactams *via* ozonolysis.[226,256] This constitutes a valuable deprotection of *N*-bis(trimethylsilyl)methyl β-lactams. For an alternate deprotection technique see Section VI.B.11.



Refs. 226, 256

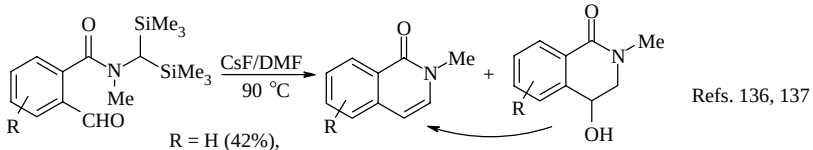
Olefination reaction can be internal to a molecule bearing the bisilylmethylamino group and the carbonyl moiety, to form a ring of appropriate size. Many examples exist in the literature.

B-cycle of β-lactamic structures have been easily prepared, namely, oxa- and carbacephems. In this last instance, cyclization is accompanied by partial desilylation of the starting material.[255,256]

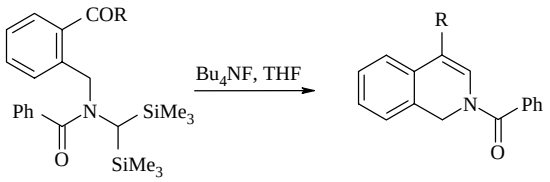


Refs. 255, 256

Peterson olefination reaction has been utilized to create a new access to dihydroisoquinoline derivatives.[95,136,137]



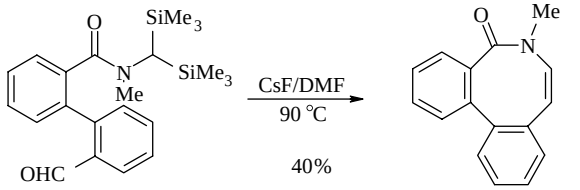
Refs. 136, 137



Ref. 95

R = H (50%), Me (58%), Ph (67%), $PhCH_2$ (46%), $CH_2{=}CH{-}CH_2$ (42%)

A cyclooctane ring ("benzocaine") has also been obtained in moderate yield by this route.[136,137]

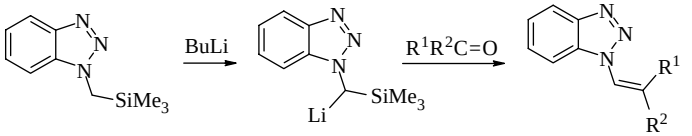


Refs. 136, 137

It is notable that strong steric hindrance affects neither the *syn*/*anti* rotation of the amide function nor the rotation in the biphenyl system.

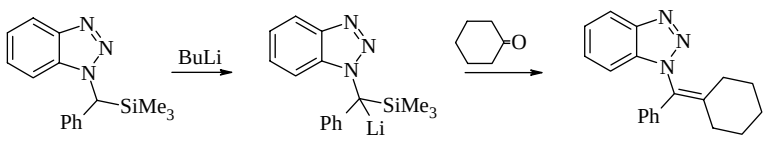
ii. From a MSMA derivative

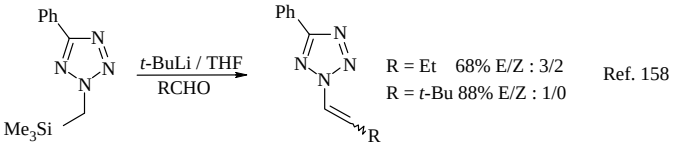
Abstraction of a proton from the methylene of an MSMA leads to an α-silyl-α′-nitrogen carbanion that can be silylated or alkylated (see Section IV.C) when reacted with a carbonyl compound; vinyl amino derivatives were readily obtained.[157,158]



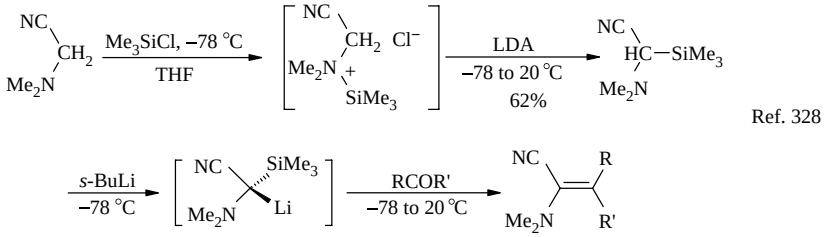
$R^1R^2 = (CH_2)_5$; Me,Me; Ph,Me; Ph,Ph

Ref. 157



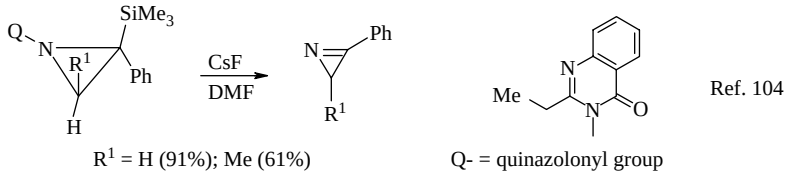


Also interesting is the recent preparation of α-amino acrylonitriles from amino acetonitrile *via* its corresponding trimethylsilyl derivative.[328]

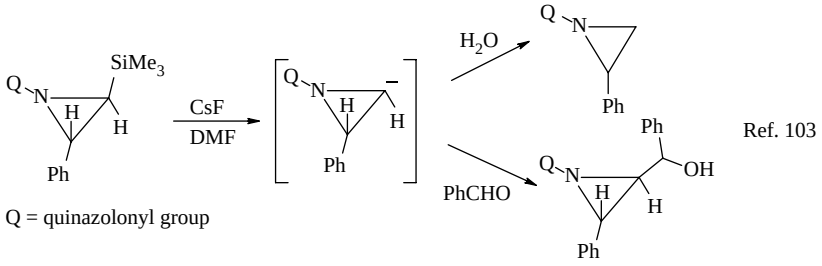


c. Formation of azirines from 2-silyl aziridines

Treating *N*-quinazolonyl-2-trimethylsilylaziridines with cesium fluoride for 5 h at room temperature in DMF as the solvent leads to the elimination of quinazolonyl-trimethylsilane and the formation of corresponding azirines in good to medium yield under very mild conditions.[104]

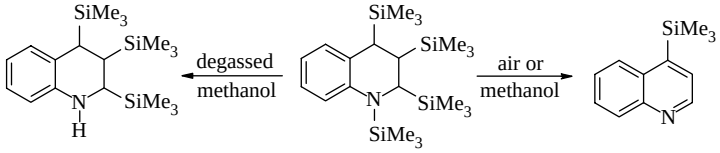


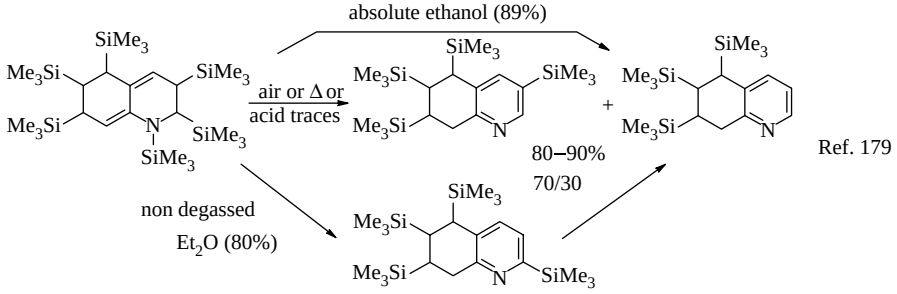
A carbanion has been postulated in this reaction that has been intercepted, for instance, by performing the reaction in the presence of an electrophile, water and benzaldehyde.[103]



d. Pyridines from polysilylpiperidines

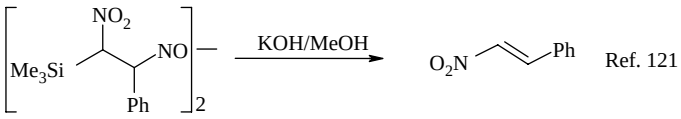
Polytrimethylsilylated piperidines have been obtained through the reductive silylation of quinoline (Section III.B.2.d). Among these compounds are SMA derivatives that are readily oxidized in the presence of air and hydrolyzed into pyridine derivatives. Trimethylsilyl groups on the non-aromatic ring were found to be in an all-*trans* relationship.[179]





e. Formation of nitroalkenes

Section III.A.8.e describes the synthesis of an α-trimethylsilylnitroalkane (pseudonitrosite dimer). When treated with potassium hydroxide in methanol, this dimer is desilylated to give β-nitrostyrene (conformation of the double bond not given), a result which ascertains the structure of the starting dimer.[121]

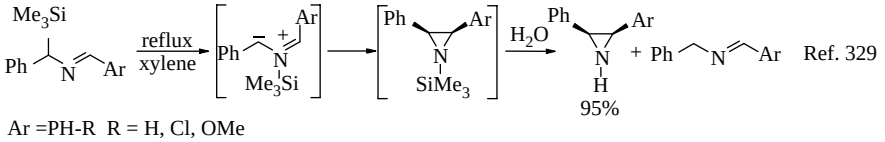


4. *Thermal migration from C to N (C–Si to C–H or to C–C)*

Under thermal conditions, the silyl group of conjugated SMA imines undergoes 1,2-migration from C to N with concomitant cyclization when the structure is favorable.

a. Aziridine formation

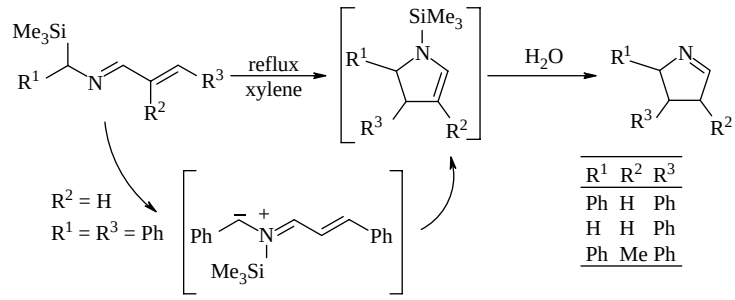
When refluxed for 15 h in xylene, aryl-substituted *N*-(trimethylsilylmethyl)imines rearrange to *N*-trimethylsilylaziridines with high *cis*-selectivity. It has been demonstrated that the reaction proceeds *via* an ylid that can be trapped with diethylacetylene-dicarboxylate (DEAD), for example. The more stable *trans*-geometry of the ylid and conrotatory cyclization would be responsible for the *cis*-aziridines. The authors note that no reaction occurs when the reaction is run in a polar solvent such as THF or acetonitrile, and that treatment of the imine with cesium fluoride in THF leads to protodesilylation only, as does 1 equiv. of water in HMPA.[329]



Ar =PH-R R = H, Cl, OMe

b. Δ^1- and Δ^2-Pyrrolines formation

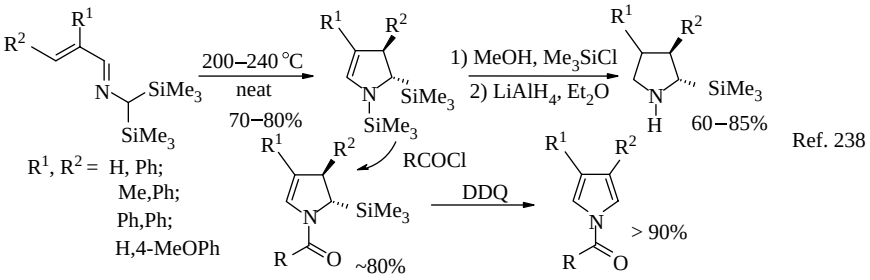
Generalization of this result to imines of conjugated aldehydes provides a good synthesis of the Δ^2-pyrroline ring. The intermediacy of an ylid is confirmed by trapping with *N*-phenylmaleimide, which takes place with excellent stereocontrol.[330]



R^1	R^2	R^3
Ph	H	Ph
H	H	Ph
Ph	Me	Ph

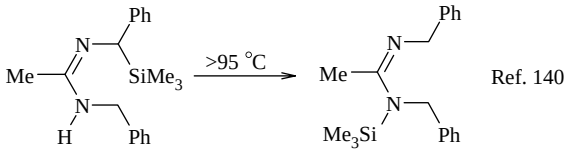
Ref. 330

Similarly, when *N*-[bis(trimethylsilyl)methyl]-1-aza-1,3-dienes are heated neat at 200–240 °C, ring closure occurs with the migration of one trimethylsilyl group from carbon to nitrogen to yield Δ^2-pyrroline derivatives in high yields and high stereoselectivity (*trans* only). From these Δ^2-pyrrolines, corresponding 1-trimethylsilyl-2,3-disubstituted pyrrolines can be prepared with total stereocontrol. After treatment with an acyl chloride, the same Δ^2-pyrrolines are converted into the corresponding *N*-acyl pyrroles upon oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), providing a novel route to 3,4-disubstituted pyrroles.[238,331]



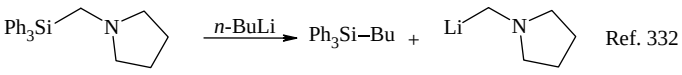
c. Enamines

The C to N shift of a trimethylsilyl group has also been reported to occur quantitatively when *N*-benzyl-*N*′-(trimethylsilyl)benzyl acetamidine is heated at temperatures above 95 °C.[140]



5. *Transmetallation (C–Si to C–Li)*

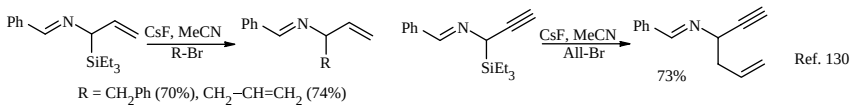
If the amine is tertiary instead of secondary, transmetallation can take place.[332]

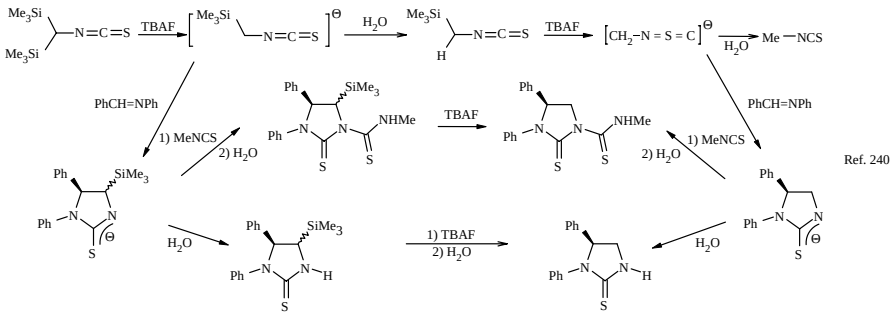


6. *Formation of a C–C bond (C–Si to C–C)*

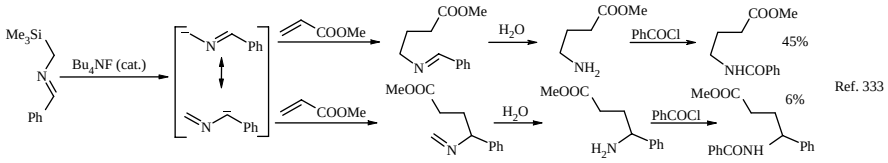
a. Alkylation *via* fluoride anion assisted cleavage of the C–Si bond

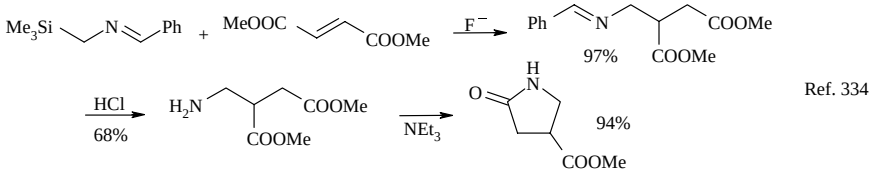
Very few reports deal with the substitution reaction of a silyl group by an alkyl group. In this instance, the intermediate carbanion resulting from the cleavage of a C–Si is intercepted by an electrophile that can be a very reactive bromide or a Schiff base, as in the following examples.[130,240]

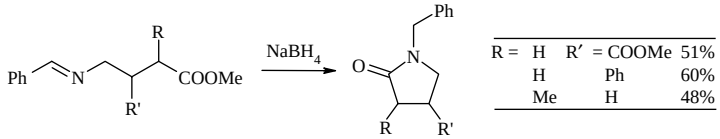




In the catalytic presence of tetrabutylammonium fluoride, a trimethylsilyl group is cleaved from *N*-(trimethylsilyl)methylbenzylimine to form the resonance-stabilized 2-aza-allyl anion which undergoes a Michael addition reaction with, for example, methyl acrylate, giving γ-aminoesters.[333] These types of aminoesters serve as a starting material for the elaboration of diversely substituted pyrrolidones.[334]

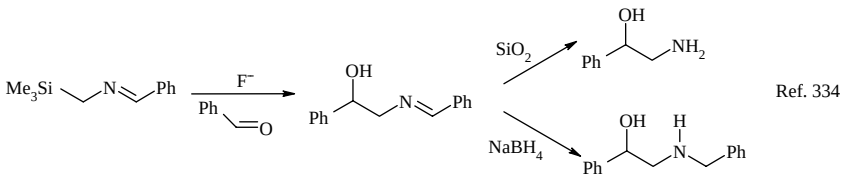






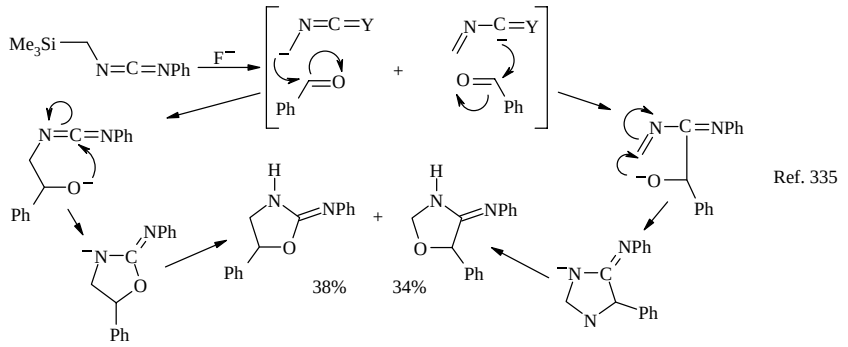
R =	H	R′ = COOMe	51%	Ref. 334
	H	Ph	60%	
	Me	H	48%	

Aza-allyl anions also react with carbonyl derivatives to give *N*-protected β-hydroxyamines and β-amino alcohols after reduction or hydrolysis.[334]



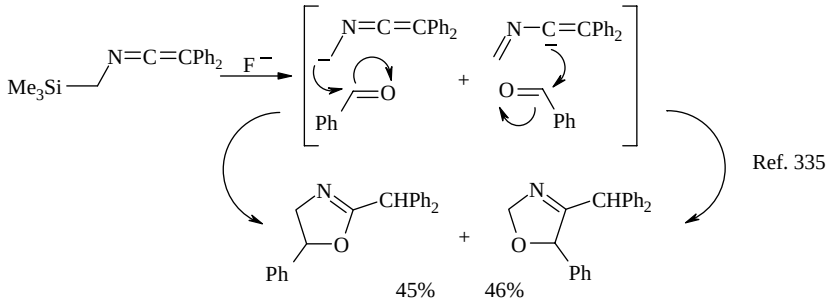
Ref. 334

Other *N*-(trimethylsilyl)methylnitrogen compounds like carbodiimides give the corresponding anion which reacted with benzaldehyde to give 1,3-oxazolidine derivatives (almost 1-to-1 mixture of regioisomers).[335]



Ref. 335

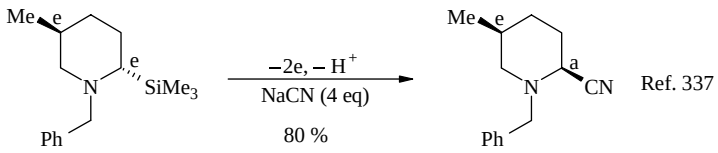
Following the same reaction pathways, *N*-silylmethylketenimines leads to Δ^1-1, 3-oxazoline derivatives (1-to-1 mixture of two regioisomers) when reacted with benzaldehyde.[335]



Ref. 335

b. Anodic oxidation: α-cyanoamines from SMAs

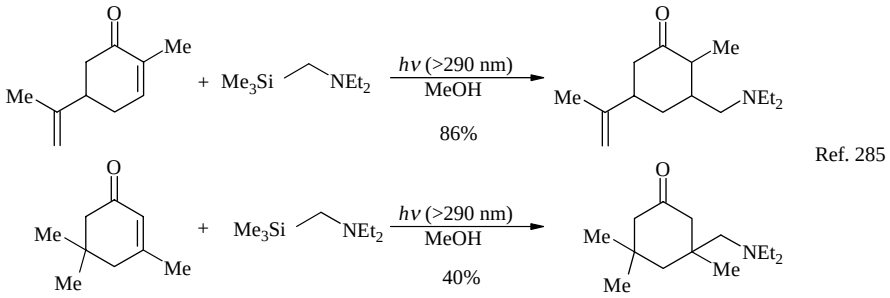
Under anodic oxidation conditions, α-cyanopiperidines can be prepared in high yield from α-trimethylsilylpiperidines. The reaction is conducted in a flow cell (graphite anode),[336] in methanol as the solvent containing $LiOAc(H_2O)_2$ as the supporting electrolyte and sodium cyanide as the cyanating agent. The reaction does not need activation and is regio- and stereospecific with cyanation occurring with total inversion of configuration.[337]



Ref. 337

7. *Desilylative radical alkylation via an electron transfer process*

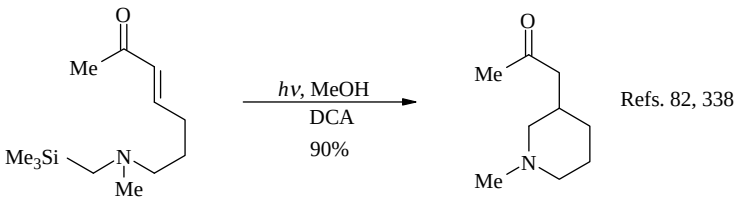
It has already been explained that irradiation of a tertiary SMA can produce an α-amino radical by rupture of a C−H or the C−Si bond. The former case allows the transformation of an MSMA into an RSMA (see Section IV.C.7). Here are disclosed the results of the irradiation of tertiary SMAs under conditions in which cleavage of the C−Si bond occurs to yield a non-silylated adduct. Thus, the reaction of *N*-(trimethylsilylmethyl)diethylamine with various cyclohexenones leads to a mixture of the silylated and non-silylated β-adducts, depending upon the solvent used (see Section IV.C.7). In methanol, protodesilylation predominated.[285,286]



Ref. 285

This SET-induced photocondensation has been used to internally cyclize enones bearing the α-silylamino functionality in the molecule. This leads to cyclic, bicyclic and spirobicyclic compounds.[82,338]

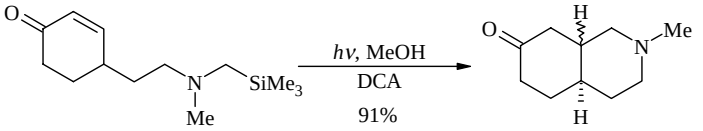
Open-chain enones (one example among 17 examples)



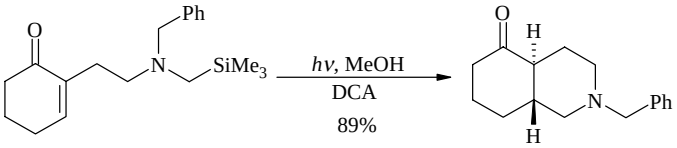
Refs. 82, 338

DCA = 9,10-dicyanoanthracene

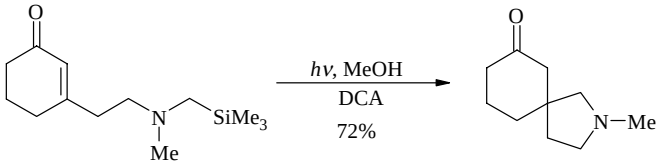
Cyclic enones



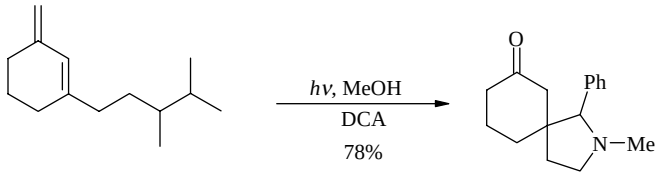
Refs. 82, 338



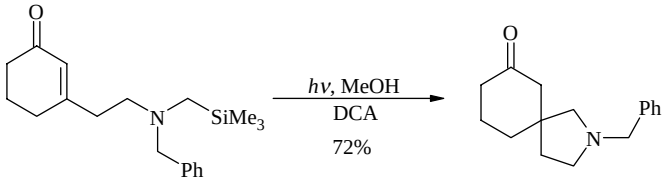
Refs. 82, 338



Refs. 82, 338

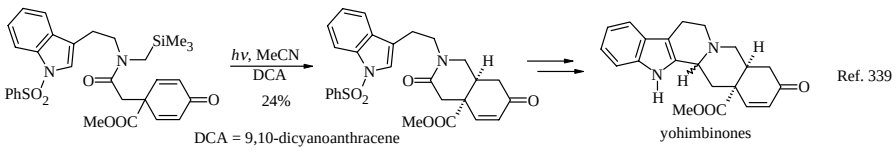


Refs. 82, 338



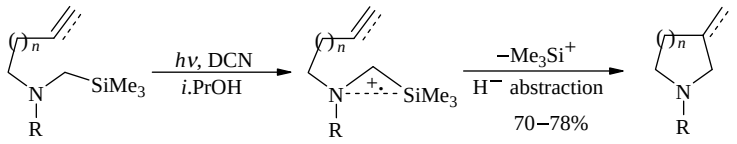
Refs. 82, 338

The process has been applied to the synthesis of derivatives of the yohimbane alkaloid providing a new strategy.[339]

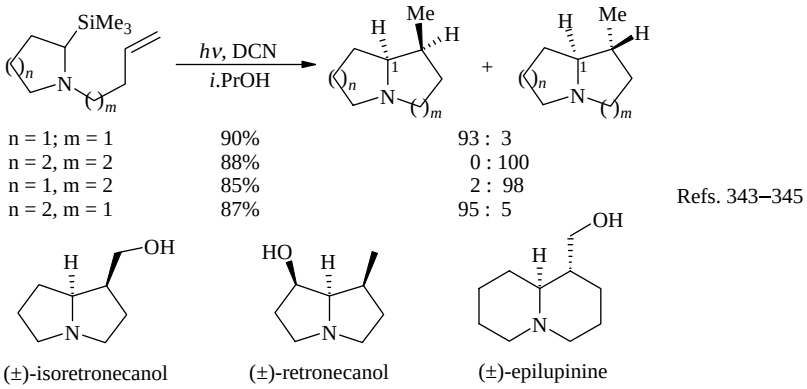


Ref. 339

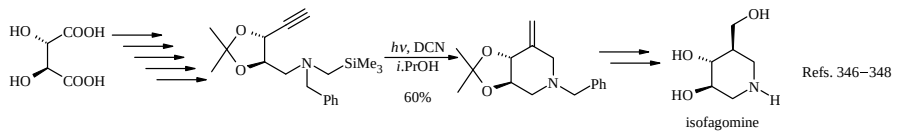
A similar study has been reported on the 1,4-dicyanonaphthalene (DCN)-sensitized light-induced desilylation (PET process) of *N*-alkenyl-substituted RSMA to form pyrrolidine and piperidine derivatives in high yields, involving a delocalized α-silylmethylamine cation as the key intermediate in these cyclization reactions.[279,340,341]



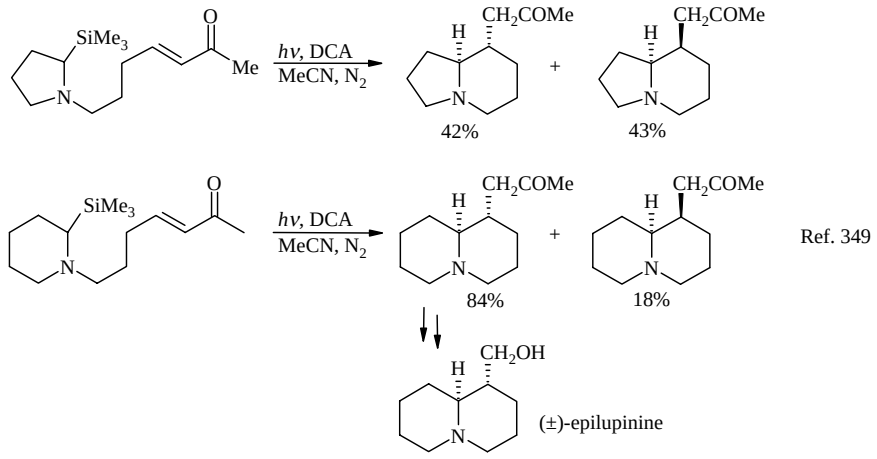
The stereochemical aspect of these cyclizations has been investigated. They have been found to be non-stereoselectives.[342] On the contrary, diastereoselective 1-azabicycloalkanes have been prepared in the same way, the stereochemistry being dependent upon the size of the ring formed, namely, 1,5-*cis* and 1,6-*trans*.[343] This methodology has been applied to the synthesis of (±)-isoretronecanol, (±)-epilupinine[344] and retronecanol.[345]



Interestingly, this photochemical process was used to synthesize 1-*N*-iminosugar isofagomine (D-Glc type), an inhibitor of β-glycosidase with high activity, from tartaric acid in 5.3% are yield.[346–348]

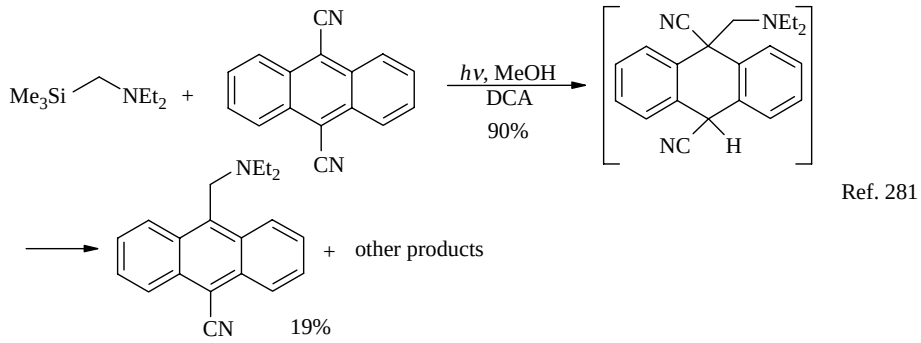


In a study aimed at the scope and limitations of SET-photoinduced synthesis of indilizidine and quinolizidine ring forming, α-amino radical cyclization reactions are explored.[349] It was shown that 2-silyl-pyrrolidyl and piperidyl enones react nicely under DCA-sensitized irradiation ($\lambda > 320$ nm) in degassed acetonitrile to produce indolizidine and quinolizidine compounds. This technique appears as efficient as the preceding one (DCN in protic medium).[344]



Ref. 349

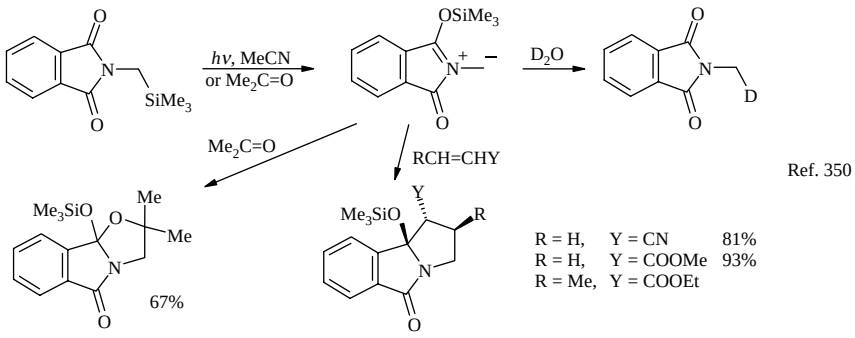
In the photoreactions performed in the absence of enone and sensitized with 9,10-dicyanoanthracene (DCA), this derivative has been demonstrated to react with the intermediate *N*,*N*-diethylaminomethyl radical-cation. The adduct forms spontaneously and is dehydrocyanated under the reaction conditions to yield 10-diethylaminomethyl-9-cyanoanthracene. This transformation is not of synthetic value because the yield is low and other products are formed.[281]



Ref. 281

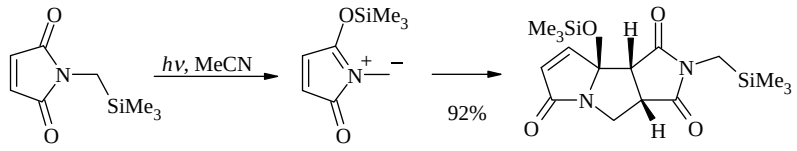
When $MeNEt_2$ was used, the amino derivative was formed in 2% yield.

Irradiation of *N*-(trimethylsilylmethyl)phthalimide has been shown to induce migration of the silyl moiety from methylene to oxygen. The resulting azomethine ylid can be trapped by a dipolarophile to give a pyrrolidine ring.[350]



Ref. 350

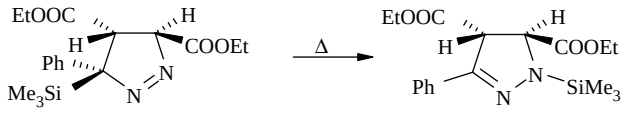
The same type of azomethine ylid can be obtained from *N*-(trimethylsilylmethyl) maleimide. Because this imide is also a dipolarophile, self-condensation takes place leading to the pyrrolo [3,4-a]pyrrolizine skeleton in excellent yield.[351]



Ref. 351

8. *Imination via 1,3-silyl migration (C–Si to C=N)*

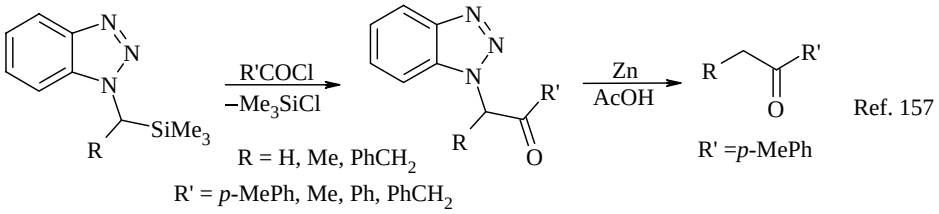
Formation of the 3-silyl-1-pyrrazoline ring has already been mentioned (see Section III.A.8.b). This ring readily isomerizes to give the corresponding 1-silyl-3-phenyl-3-pyrrazoline.[113]



Ref. 113

9. *Acylation (C–Si to C–C=O)*

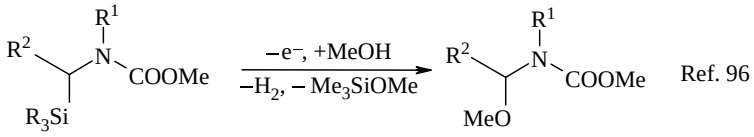
The Si–C bonds of α-benzotriazolylsilanes ($BtCHRSiMe_3$ and $BtCH_2SiMe_3$) are easily cleaved by acyl chlorides to give ketones after reductive cleavage of the C–N bond with zinc in acetic acid medium. This transformation cannot be performed starting from the bisalkyl congener $BtCR_2SiMe_3$.[157]



Ref. 157

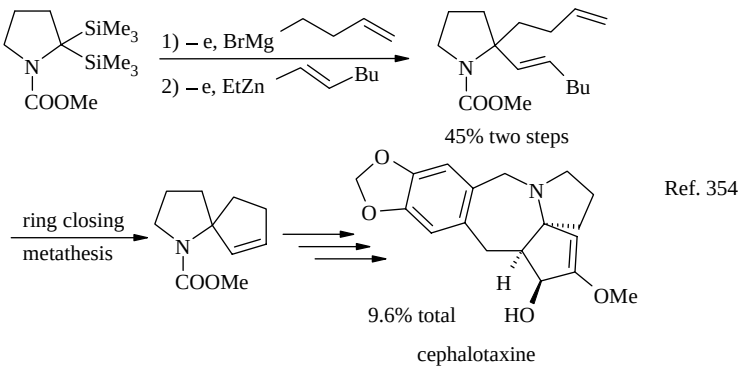
10. *Electrochemical anodic oxidation (C−Si to C−nucleophile)*

Anodic oxidation of amines has been extensively studied, in particular because of the importance of the degradation process of biological amines. Aliphatic amines have a relatively low oxidation potential and, therefore, they are easily oxidized. In the presence of water, anodic oxidation leads generally to dealkylation products until ammonia is formed. This is mainly due to the instability of the intermediates, whereas amides and more evidently carbamates lead to more stable intermediates. This opened the use of anodic oxidation of amines in the field of organic synthesis. The reaction mechanism involves direct one-electron removal from the lone-pair electrons on the nitrogen in the initial step. Capture of a second electron results in the loss of a proton from one C−H bond α- to nitrogen formation of the corresponding cation. For the purpose of synthesis, it is advantageous to regioselectively control the formation of this cation. It has been shown that the replacement of a hydrogen by a trimethylsilyl group, i.e., use of an SMA carbamate, meets this requirement nicely as the cation is created at the carbon that was linked to the silicon atom. When the anodic oxidation is conducted in methanol as the solvent, a methoxy group is finally introduced at the position where the silyl group was.[96,352,353]



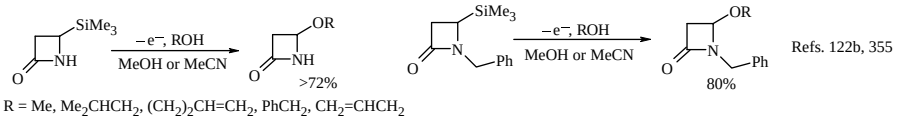
Ref. 96

In addition to the regiocontrol, the use of SMA carbamates provides activation to the reaction through overlapping of the lone-pair electrons on the nitrogen with the s-orbital of the C−Si bond.[96] In this process, the trimethylsilyl group is replaced by a methoxy group. In fact any nucleophile can be used. Thus, various carbanions were utilized for the synthesis of spiro compounds that are synthons, for example, in an excellent route to cephalotaxine.[354]



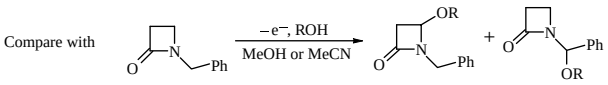
Ref. 354

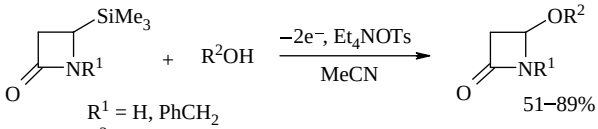
The same technique can be applied to regioselectively prepare 4-alkoxy substituted azetidinones. Non-silylated azetidinones have oxidation potentials, which are too high for this process. Introduction of a silyl group lowers these potentials, rendering the reaction easier and more regiospecific. Note that in the case of *N*-benzyl azetidinones, the methoxylation reaction occurs also at the benzylic position.[122b,355]



Refs. 122b, 355

R = Me, Me_2CHCH_2, $(CH_2)_2CH{=}CH_2$, $PhCH_2$, $CH_2{=}CHCH_2$

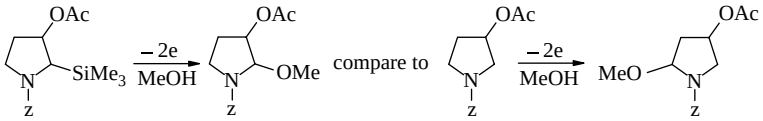




Refs. 122b, 355

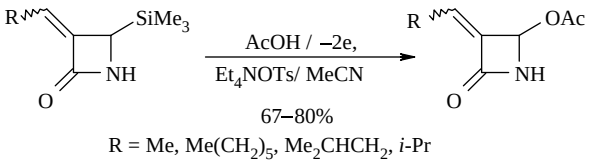
R^1 = H, $PhCH_2$
R^2= Ac, Me, Me_2CHCH_2, $(CH_2)_2CH{=}CH_2$, $PhCH_2$, $CH_2{=}CHCH_2$

The trimethylsilyl-directed regiocontrol is also illustrated by the conversion of 3-acetoxypyrrolidines into 2-methoxy-3-acetoxypyrrolidines *via* the 2-trimethylsilyl derivative. In its absence, methoxylation occurs at the 5-position of the ring.[356]



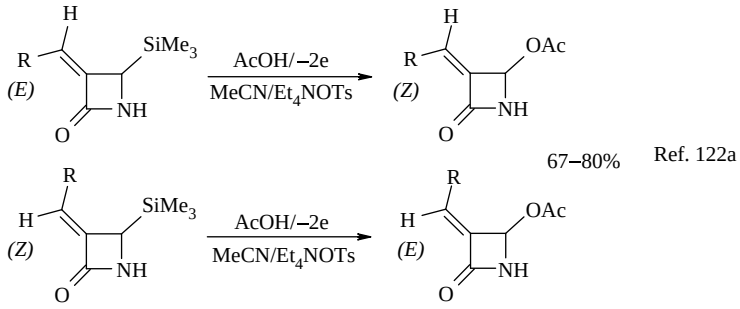
Ref. 356

Other nucleophiles, like acetoxy ion, can be introduced electochemically.[122b,357] Electrolysis is conducted with graphite electrodes in an undivided cell and a constant electric current (50 mA) is applied to the solution.



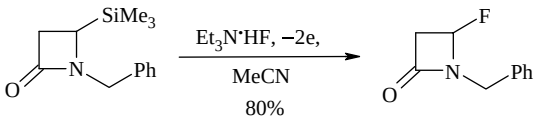
Ref. 122b

During the reaction, the geometry of the double bond was preserved.[122a]



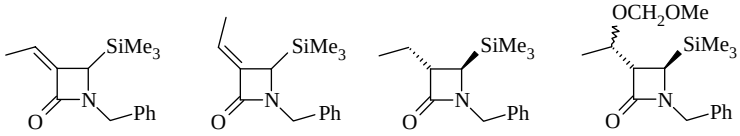
Ref. 122a

Similarly, fluoride ion has been used as the nucleophile to prepare 4-fluoro azetidinones in high yields. Triethylamine/hydrogen fluoride is the source of the fluoride anion.[122b,357]



Refs. 122b, 357

It is important to note that Bu_4NBF_4 leads to tar and that, if 8 $Fmol^{-1}$ are consumed in the case of *N*-benzyl derivatives, 20 $Fmol^{-1}$ are needed for *N*-butyl derivatives.[358] Diverse 4-trimethylsilyl-*N*-benzyl azetidinones have been successfully fluorinated using this technique.[358]

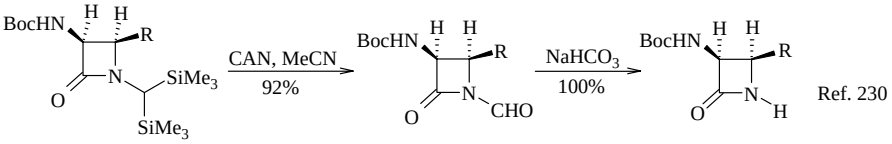


E 68% *Z* 80% *cis/trans 1/1* 88% *trans* 75%

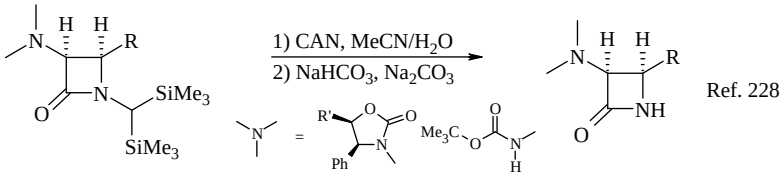
Ref. 358

11. *Chemical oxidation (to C–OSi and to C–C)*

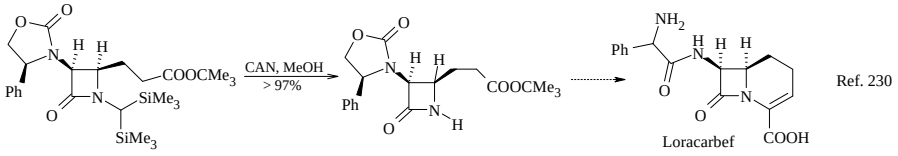
The C–Si bond of an SMA can also be cleaved by oxidizing reagents like cerium ammonium nitrate (CAN). Starting from *N*-bis(trimethylsilyl)methylazetidinones, treatment with CAN probably leads to the oxidation product of the two C–Si bonds, i.e., the corresponding disilylketal that is hydrolyzed into the formamide to give the N–H azetidinones (yields >80%). This constitutes an alternate and more efficient way to sequential fluoride-induced desilylation. Peterson olefination, ozonolysis, and formamide decomposition when deprotection of bis(trimethylsilyl)methylated azetidinones into NH-azetidinones is required.[228,230]



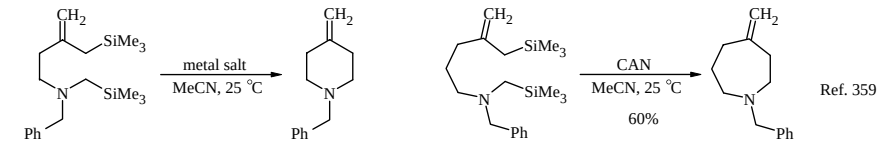
R = Me, Et, *n*-Pr, $PhCH_2CH_2$, $PhCH_2$, Me_2CH, $PhCH_2OCH_2$, *t*-$BuO_2CCH_2CH_2$



This process is used as one of the steps in a synthesis of the antibiotic loracarbef.[230]

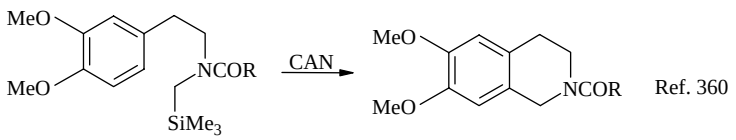


Another oxidation reactions have been reported that led to C–C bond formation. They deal with treatment of *N*-allylsilane-substituted SMAs with CAN, lead tetraacetate or manganese triacetate to form methylene piperidines and azepines. Yields are in the same range as those obtained using SET-photolytic or electrolytic processes.[359]



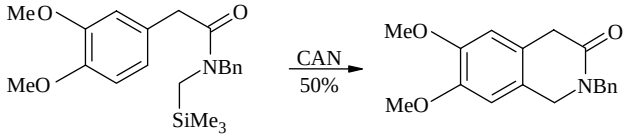
metal salt : CAN (62%), $Pb(OAc)_4$ (60%); $Mn(OAc)_3$ (55%)

Other examples include CAN oxidation of silylmethyl amines and amides with the synthesis of aryl-fused piperidine and pyrrolidine ring derivatives.[360]

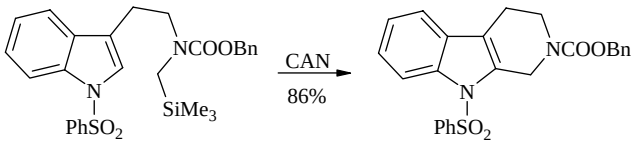


Ref. 360

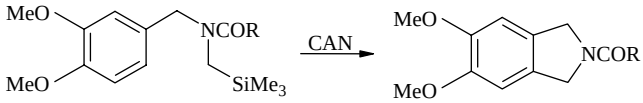
R = Ph (60%), OBn (60%)



Ref. 360



Ref. 360



Ref. 360

R = Ph (7%), OBn (13%)

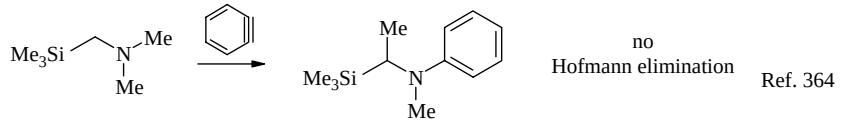
C. *Desilylation with rearrangements*

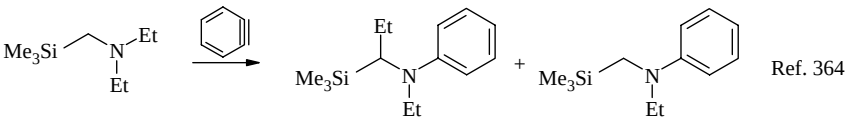
Sato has developed a series of works dealing with rearrangements occurring in various circumstances from SMA and their quaternary salts. They have been reviewed.[8,361] Base-induced rearrangement of quaternary β-silylethylammonium salts giving an SMA has already been detailed (see Section III.B.5.g).

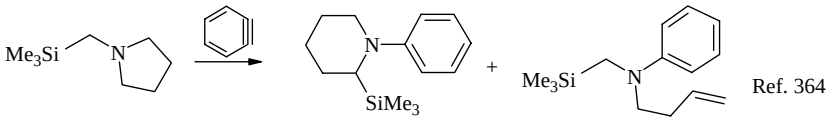
1. Reaction SMA with benzyne

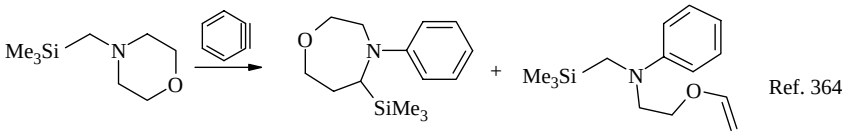
Reaction of benzyne with tertiary aliphatic amines to give anilines *via* Sommelet–Hauser and/or Stevens-type rearrangements of the intermediate ylid has been documented.[362,363]

Reaction with α-silyltertiary aliphatic amines leads to results of the same type, including silyl- and non-silyl-products, proceeding either from a Stevens rearrangement or a Hoffmann elimination.[364]

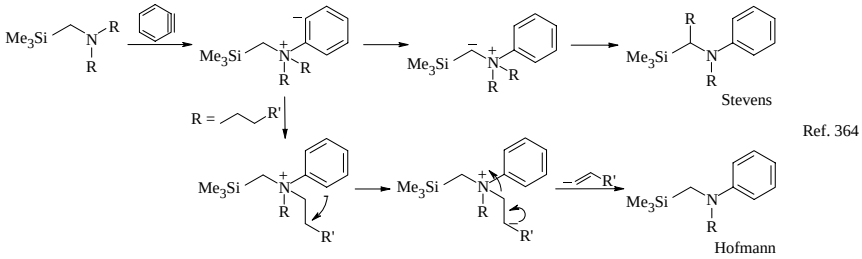




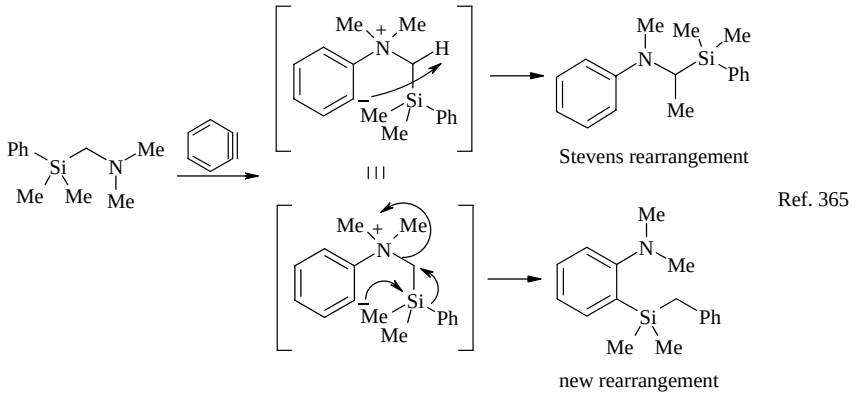




The initial step of the reaction is probably the electrophilic attack of benzyne on the tertiary amine to form a betaine. In the second step, Stevens rearrangement takes place to give the RSMA derivative. If the *N*-alkyl group has a β-hydrogen (NEt_2, pyrrolidine, morpholine), Hoffmann degradation competes with the rearrangement to give the MSMA.

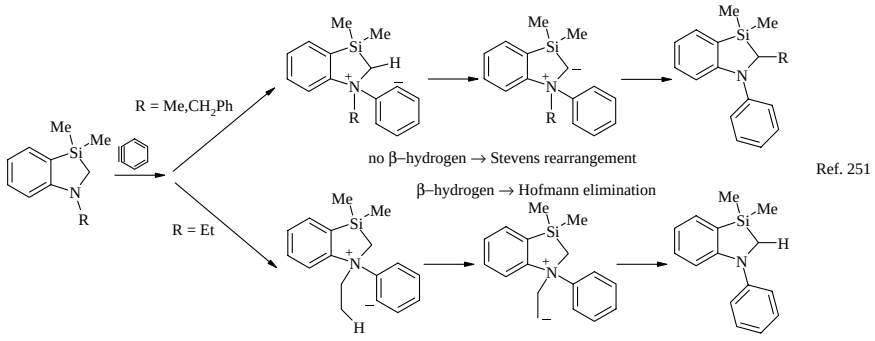


This study has been extended to other tertiary SMA systems.[67] It has been found that Stevens rearrangement competed, when silicon has at least one phenyl group, with the migration of the silyl group to the benzene ring accompanied by the shift of one phenyl group to the adjacent carbon.[365] If the Stevens rearrangement provides a means to transform an MSMA into an RSMA, the second rearrangement is totally new.



Ref. 365

Another example is the reaction of benzyne with 1-methyl- (and benzyl)-3, 3-dimethylbenzo[d]-1,3-azasiloline (see their preparation in Section IV.A.2.p). Stevens rearrangement product is obtained (48%) as a single compound. If a Me on nitrogen is replaced by an Et, then Hoffmann elimination occurs.[251] It should be noted that an *N*-alkyl MSMA is converted into an *N*-aryl RSMA in the former case and into a *N*-aryl MSMA in the latter case.



Ref. 251

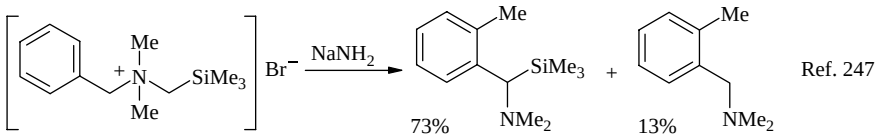
2. *Isomerization of ammonium salts*

Due to the presence of silicon which stabilizes the α-carbanion, strong bases such as butyllithium and sodium amide are able to give an ylid from silylmethylammonium halides. Fluoride ion-assisted desilylation of these salts represents another means to create an ylid. These ylids are prone to rearrange and the results differ upon the nature of

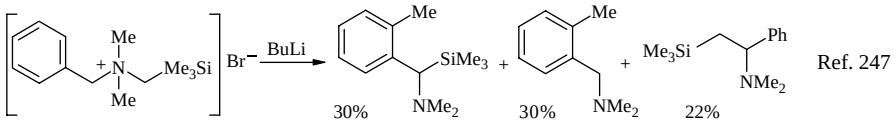
the reactant, the structure of the ylid and the conditions of the reaction. The subject has been reviewed by Sato who has published extensively in this field.[361]

a. Induced by base

Based on a previous study by Miller,[289] a series of *N*-benzyl-MSMA chlorides or bromides have been treated with a base and/or a nucleophile. For example, in the presence of the amide anion, the trimethylsilyl derivative yields *N*,*N*-dimethyl-2-methyl-α-(trimethylsilyl)benzylamine (a Sommelet–Hauser rearrangement product) as the main product and its non-silylated congener.[247]



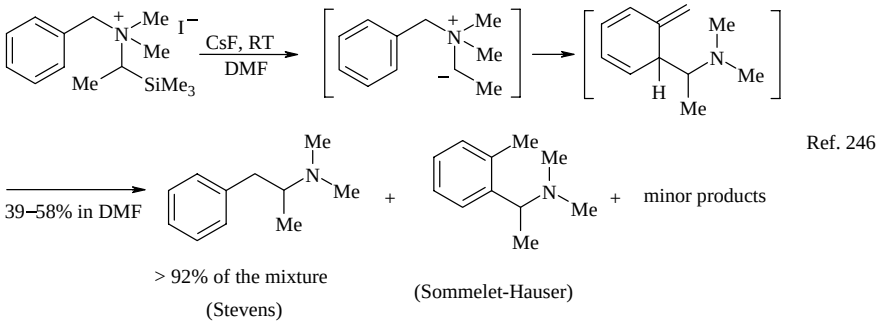
With phenylsilylated salts, the same type of *N*,*N*-dimethylbenzylamines are formed accompanied by *N*,*N*-dimethyl-2-trimethylsilylmethylbenzylamine. A mechanism involving silylated and non-silylated intermediate ylid has been proposed. Using LAH in place of sodium amide induces cleavage of the silyl group, especially in the triphenylsilyl case. With *n*-butyllithium, the same two products are obtained in equal amounts accompanied with a Stevens rearrangement product as a minor compound.



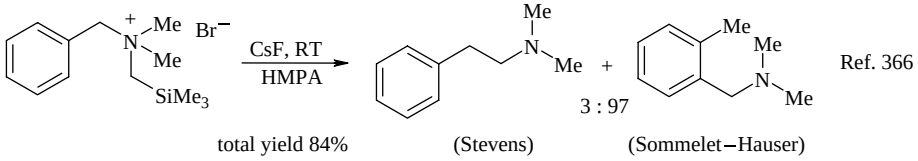
b. By fluoride ion-assisted desilylation

Fluoride ion-assisted desilylation has been extensively used to create an ylid from a *N*-silylmethyl-quaternary ammonium salt. Its evolution to final product(s) is variable and Sommelet–Hauser and Stevens rearrangement products were obtained (often as major products) in a ratio that can be shifted from one structure to another very close one, as in examples 1 and 2 dealing with *N*-benzyl salts.[246,366] Differences in the solvents used are not significant because in the first example, HMPA does not reverse the ratio, yields and selectivity being just a bit lower. *Iso*-toluene was proposed as an intermediate in example 1; it might also be the intermediate in example 2. Thus product partition reflects the relative ability of the C–H or the C–C bonds to be cleaved to produce aromatization with proton or α-amine carbocation migration.

example 1

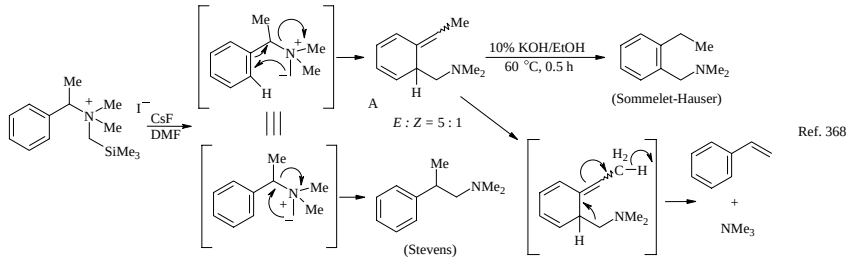


example 2

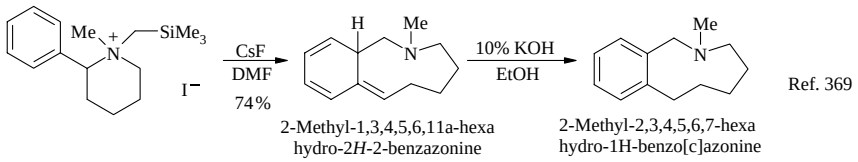


This study has been extended to model salts where the NMe_2 group is replaced by NMe(alkyl) or $N(alkyl)_2$ group with results identical to that of example 2.[367]

The presence of an alkyl group or not on the benzylic carbon atom has little influence on the result (example 2). The Sommelet–Hauser rearrangement product is not obtained as its *exo*-1-alkylidene-cyclohexadi-2,4-ene precursor is stable (allowed typical cyclohexadiene chemistry) and isolable as a 1:5 mixture (35% yield) of the two stereoisomers. Styrene is also obtained as the major product (50%) whereas the Stevens product is formed in trace amounts. Triene **A** is converted quantitatively into 2-ethylbenzylamine under treatment with diluted KOH at 60 °C for 0.5 h in ethanol.[368]

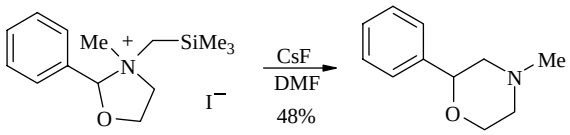


An illustration of the Sommelet–Hauser rearrangement is the synthesis of 2-methyl-2,3,4,5,6,7-hexahydro-1H-2-benzazonine from 2-phenyl-1-[(trimethylsilyl)methyl]-piperidine in good yield, where a stable trienic intermediate aromatized only after treatment with base for 24 h at room temperature.[369]



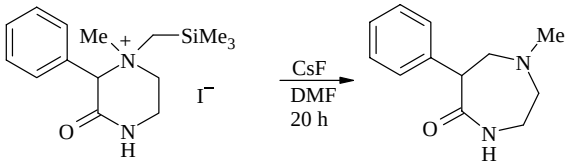
Ref. 369

However, when the piperidine ring is substituted for an oxazolidine ring, Stevens product, 2-phenyl-4-methylmorpholine, is formed after 48 h reaction at room temperature.[370]



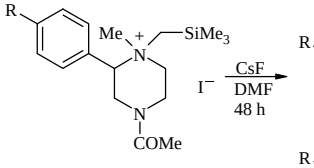
Ref. 370

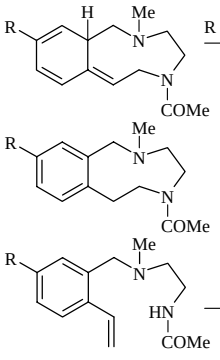
Treated similarly 3-phenylpiperarizin-2-one salt affords the Stevens rearrangement product in moderate yield.[371]



43% Ref. 371

2-Phenylpiperazine gives more complex results originating from both types of rearrangement. However, working in the presence of the strong base DBU, the reaction could be rendered regiospecific to synthesize nine-membered cyclic diamines.[371]



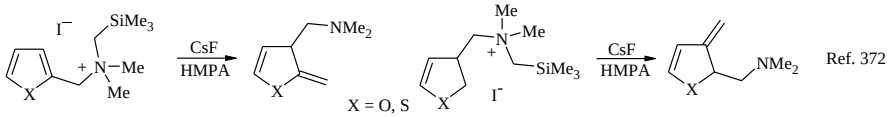


		DBU	
R = H (%)	OMe (%)	H (%)	OMe (%)
16	100	0	0
68	0	100	100
16	0	0	0

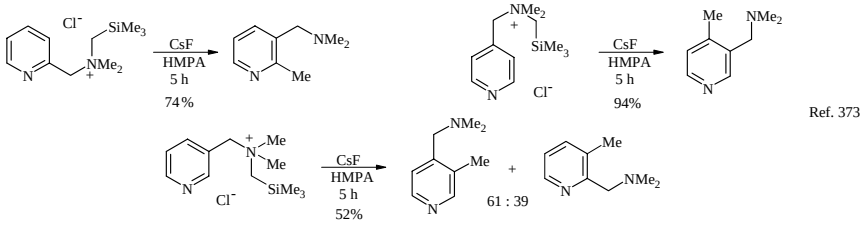
Ref. 371

Formation of exomethylene compounds is also observed (as the major products, $>84\%$) when *N*,*N*-dimethyl-*N*-[(trimethylsilyl)methyl](2-furylmethyl)ammonium iodide and its 2-thienylmethyl analogue and their 3-furylmethyl and 3-thienylmethyl isomers are

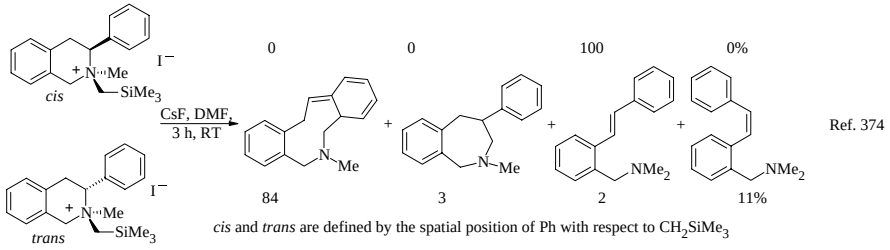
treated with cesium fluoride in HMPA.[372]



Heterocyclic nitrogen-derived ylids behaviors have been studied.[373] For instance, pyridine derivatives lead exclusively to [2,3]-sigmatropic rearrangement (Sommelet–Hauser) products.

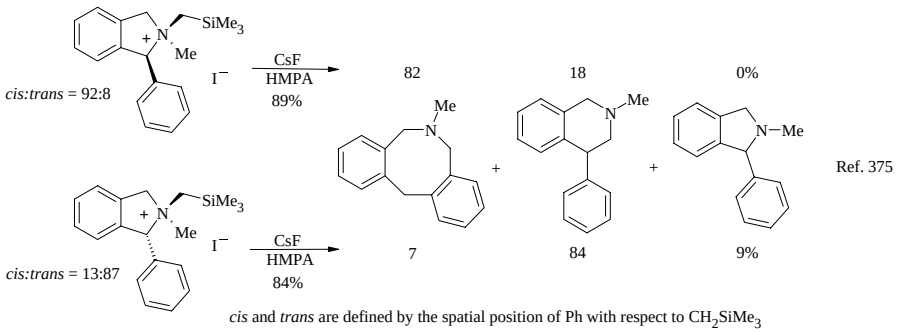


Modification of the stereochemistry of the reaction has been demonstrated by studying desilylation reaction of *cis*- and *trans*-2-methyl-1-(phenyl)isoindolinium 2-methylides. It has been established that *cis*-isomer leads preferentially to the Sommelet–Hauser rearrangement product (eight-membered ring formed) whereas the *trans*-isomer leads predominantly to the Stevens rearrangement product.[374]



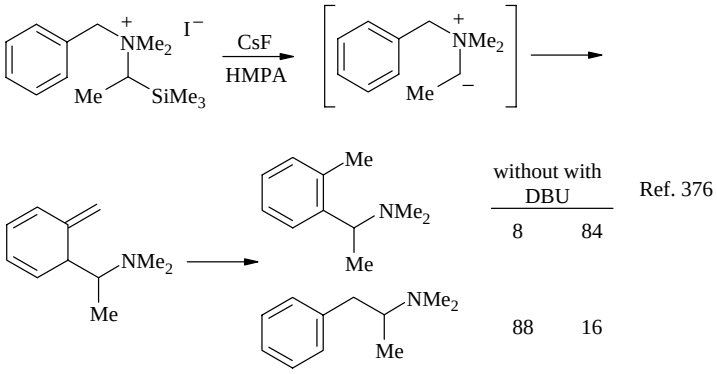
cis and *trans* are defined by the spatial position of Ph with respect to CH_2SiMe_3

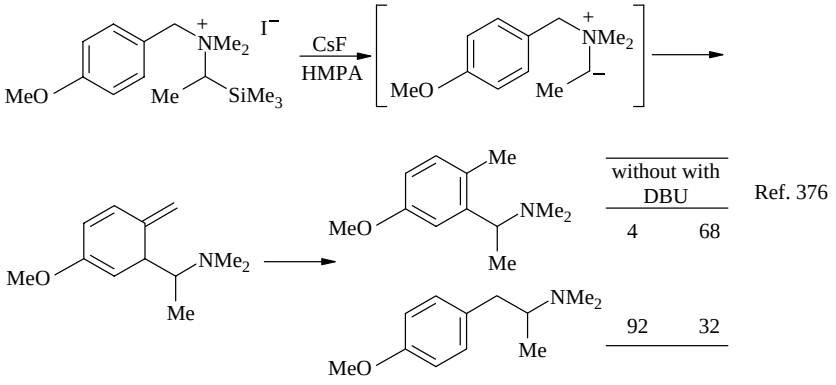
A similar study has been done on *cis*- and *trans*-2-methyl-3-(phenyl)-1,2,3,4-tetrahydroisoquinolinium 2-methylides.[375] The *cis*-isomer gives, in excellent yield, clean and stereospecific rearrangement to a (*E*)-1-phenyl-2-(2-dimethylaminobenzyl)phenyl ethylene whereas the *trans*-isomer gives a mixture (69% total yield) of four products. Among these products, the [2,3]-sigmatropic rearrangement product, (*Z*)-6-methyl-4a,5,6,7-tetrahydro-12H-dibenzo[*c*, *g*]azonine greatly predominates.



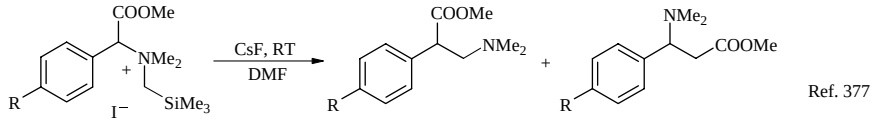
cis and *trans* are defined by the spatial position of Ph with respect to CH_2SiMe_3

In order to obtain information on the general mechanism of these rearrangements, studies have been devoted to the orientation of the reaction with the substituents on the phenyl group of *N*,*N*-dimethyl(substituted benzyl)ammonium *N*-alkylides. It has been shown that the ratio of Sommelet–Hauser to Stevens rearrangement products is influenced by the magnitude of the electron-donating effect of the substituents. This ratio can be changed by performing the reaction in the presence of DBU.[376]





The following result also illustrates the influence of the substituent on the phenyl ring. Ammonium iodide derived from α-carbomethoxybenzylamine has been desilylated. Essentially a mixture (81%) of two isomeric aminoesters, *N*,*N*-dimethyl-2-phenyl-2-carbomethoxyethylamine and methyl-2-phenyl-2-dimethylaminopropionate (70:30 ratio) has been obtained. Specific formation of an analog of the former rearrangement product is obtained by substituting hydrogen in position 4 on the ring by a methoxy group.[377]



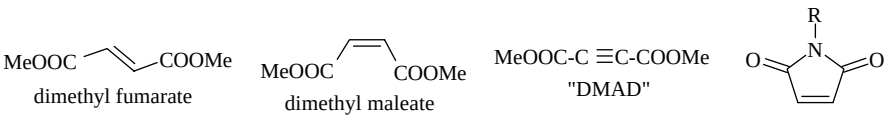
R =			
H :	70	30
MeO:	100	0

VII

DESILYLATIVE ROUTE TO AZOMETHINE YLIDS

Cycloaddition of a 1,3-dipole to an electron-deficient olefin or acetylene represents one of the most efficient approaches to the construction of five-membered ring molecules. When this dipole is an azomethine ylid, pyrrolidine, pyrroline and pyrrole derivatives can be obtained depending on the substituents on the ylid.[378] However, dipoles present generally some stabilization due to appropriate substituents, restricting the scope of applicability of this strategy. In order to circumvent this drawback, the need for suitable methods to generate non-stabilized azomethine ylids, i.e., those lacking an electron withdrawing group on carbon, becomes evident.[379] In the recent past several methods have appeared, and among these, desilylation of *N*-(silylmethyl)amino derivatives has given an excellent solution to this problem, mainly because of the ready availability of the ylid precursors, the mildness of reaction conditions and the chemoselectivity to generate the ylid compared with that of deprotonation with strong bases. Reviews have been published which deal with different aspects of this topic.[279,380–384]

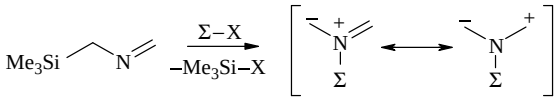
A large variety of silylmethylamino derivatives have been shown to be excellent starting materials for the *in situ* generation of non-stabilized azomethine ylids. Combined with a number of electron-deficient olefinic or acetylenic molecules that have been recognized as good dipolarophiles, ready access to diversely substituted five-membered ring nitrogen heterocycles has consequently been opened.



Commonly used dipolarophiles

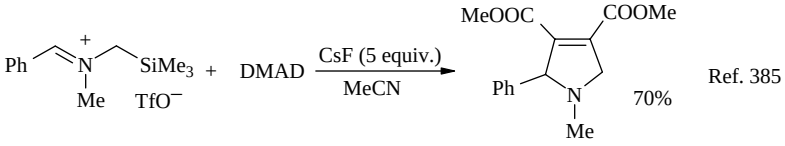
A. *Imines*

Conceptually, quaternarization of a *N*-(silylmethyl)imine with an halide would give the desired ylid. In reality, various means have been shown to induce quaternarization and desilylation of these imines.



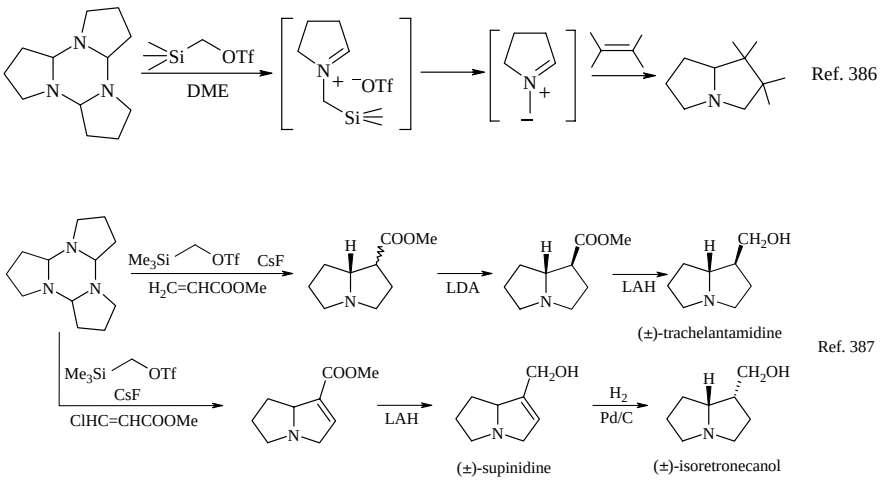
1. Methyl and (trimethylsilyl)methyl trifluorosulfonates

The first article on the desilylative route to azomethine ylids appeared in 1979.[385] It deals with the action of methyl trifluorosulfonate on *N*-(trimethylsilylmethyl)benzylidenimine to form the corresponding iminium salt which reacts with DMAD in the presence of cesium fluoride to yield corresponding Δ^3-pyrroline.

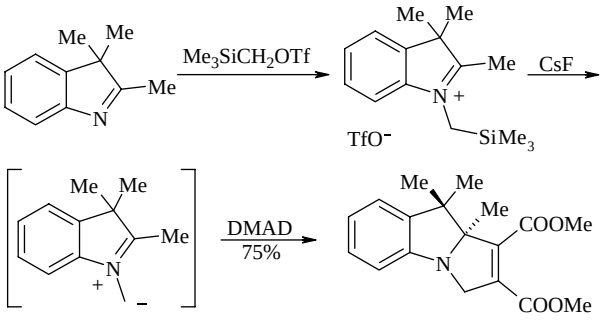


In some cases, protonation of the desilylated salt occurs under usual conditions (CsF, MeCN). This is due to the acidity of acetonitrile (which can be replaced by diglyme) and the basicity of the ylid.[381]

Triazines are trimers of unstable imines and may serve as imine precursors. Treatment of trimer of Δ^1-pyrroline with a trimethylsilylmethyl triflate gives trimethylsilylmethylimonium triflate which may be desilylated by cesium fluoride, providing an ylid suitable for 1,3-dipolar cycloaddition reactions and construction of the hexahydro-pyrrolizine framework.[386] This strategy has been applied to prepare trachelanthamidine, supinidine and isoretronecanol alkaloids.[387]

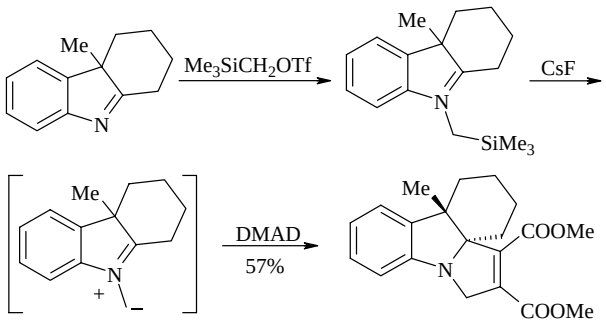


The pyrrolo [1,2-a] indoline nucleus, a central feature of the mytomycin class of antitumor antibiotics,[388] is accessible by this route from *N*-trimethylsilylmethyl indolium triflate.[389]



Ref. 389

Similarly, 4a-methyl-2,3;4,4a-tetrahydro-1H-carbazole give access to a tetracyclic derivative.[389]

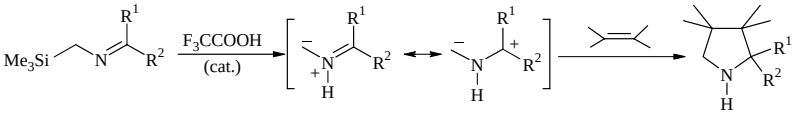


Ref. 389

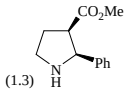
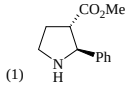
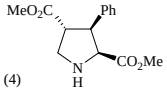
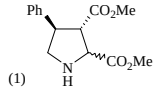
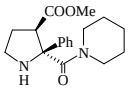
A list of classical dipolarophiles has been tested successfully and from the whole of the results it is concluded that the regioselectivity of cycloadditions involving non-symmetrical dipolarophiles is temperature dependent and that all cycloadditions are highly stereoselective and favor formation of the isomer resulting from an *exo* transition state.

2. Trifluoroacetic acid and trimethylsilyl triflate

This acid, used in catalytic amounts, easily generates azomethine ylids (this route is sometimes referred to as "Achiwa's procedure"). Excellent to complete regioselectivity has been established when both ylid and ethylenic dipolarophile are dissymmetrical, but stereochemical control is not so strong. From these data, *ab initio* calculations have been made and frontier molecular orbital theory used to explain the origin of these selectivities.[390]



Ref. 390

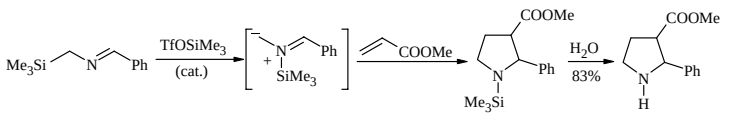
Substrate	Dipolarophile	Product[a]	Regio-selectivity (%)	Stereo-Selectivity (%)
$Me_3SiCH_2N{=}CHPh$	$H_2C{=}CHCO_2Me$	 (1.3)  (1)	100	57
$Me_3SiCH_2N{=}CHCO_2Me$	$PhHC{=}CHCO_2Me$	 (4)  (1)	80	100
$Me_3SiCH_2N{=}C(Ph)CON$	$H_2C{=}CHCO_2Me$		100	100

Ref. 390

[a]Ratio of isomers is given in parentheses

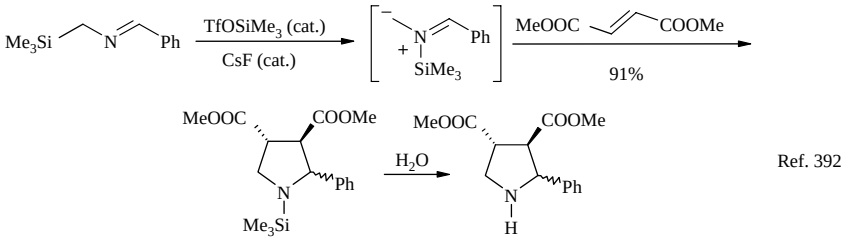
With this procedure, *N*-H pyrrolidines can be synthesized directly. An important observation is that the conservation of the geometry of the dipolarophile, such as methyl cinnamate, leads to *trans*-Ph/COOMe pyrrolidines. This feature appears to be a general characteristic of these cycloadditions.

Silyl triflates may also be used as the catalyst to the same goal. In both cases, conjugated base induces desilylation to create the ylid (compare with the action of tetrabutylammonium fluoride on the same imine which led to the anion; see Section VI.B.6.a).[333,391]



Refs. 333, 391

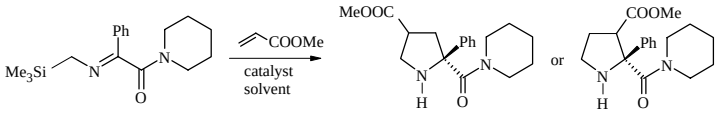
Co-catalysis with cesium fluoride (10 mol%) has been utilized. If the geometry of the ethylenic starting compounds is preserved, diastereoisomeric selectivity is not very high.[392]



Ref. 392

Other dipolarophiles (yield, ratio 2-Ph:3-COOMe *cis:trans*):
methyl maleate (91%, 5:4); methyl fumarate (83%, 2:3);
N-methyl maleimide (85%, 1:2); methyl acrylate (83%, 5:4).

A particular Schiff base serves as dipolarophile precursor leading to trisubstituted pyrrolidines through [1,3]-dipolar cycloaddition on methyl acrylate. Solvent and catalyst affect the course of the reactions studied. Depending on the catalyst, either 3- or 4-substituted pyrrolidines were obtained. The choice of the solvent is crucial; the greater the polarity, the higher the yield of ring formation. Thus the yield of the reaction catalyzed with trimethylsilyl chloride decreased from 80% in HMPA to 20% in refluxing benzene, with intermediate values of 30% in DMF and 20% in THF. The more spectacular effect is that TBAF gives the opposite orientation from the other catalysts tested. Noticeable also is the predominant *cis* stereochemistry (Ph/COOMe) observed whatever the regiochemistry was.[333,391]

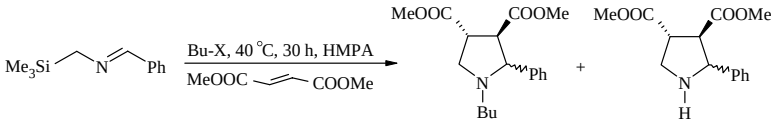


Catalyst	Solvent	Temperature (°C)	Time (h)	Yield (%)	Yield (%)
TBAF (10 mol%)	DMF	25	47	72	
Me_3Si-Cl (20 mol%)	HMPA	25	25		83
Me_3Si-OTf (20 mol%)	HMPA	60–65	24		90
TFAA (20 mol%)	HMPA	25	20		92

Refs. 333, 391

3. Alkyl halides

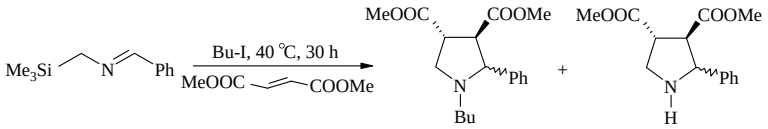
It has been demonstrated that quaternarization of nitrogen may be realized with alkyl halides or tosylates and iodide is found to be the best anion. Formation of N-unsubstituted pyrrolidines when using an alkyl chloride was tentatively explained by the formation of trimethylsilyl chloride in the reaction medium. This silyl halide participates in the quaternarization of nitrogen to give *N*-silyl pyrrolidine and finally *N*-H pyrrolidine under the hydrolytic conditions of the work-up. The fact that changing iodide for chloride allows formation of the N-unsubstituted pyrrolidine is a synthetically interesting feature.[393]



Ref. 393

Bu–X	Total yield (%)	Molar proportion	
Bu-I	100	99	1
Bu-Br	100	63	37
Bu-Cl	66	–	100
Bu-OTs	79	50	50

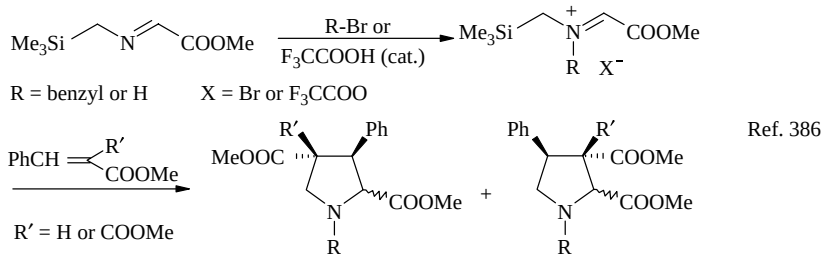
Using *n*-butyl iodide, the influence of the solvent has been examined and HMPA is found to be the most appropriate solvent giving a quantitative yield of N-substituted pyrrolidines exclusively.[393,394]



Ref. 393

Solvent	Total yield (%)		Molar proportion
HMPA	100	99	1
TMU	90	70	30
DMF	70	65	35
MeCN	20	70	30
THF	0	--	--

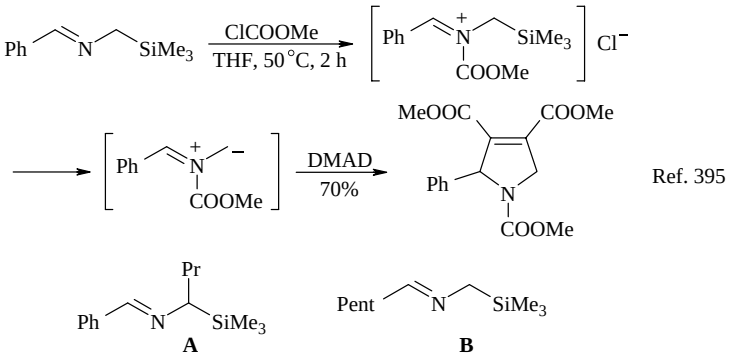
Methyl-(trimethylsilyl)methyliminoacetate, chosen as the azomethine ylid precursor, provides an elegant access to proline derivatives. However, the cycloaddition reaction has a low regiospecificity.[386]



Ref. 386

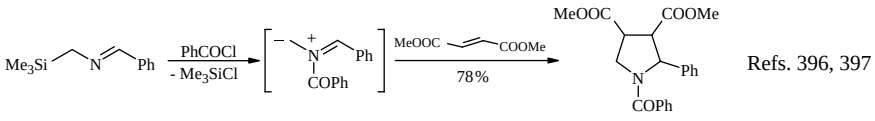
4. Chloroformiates

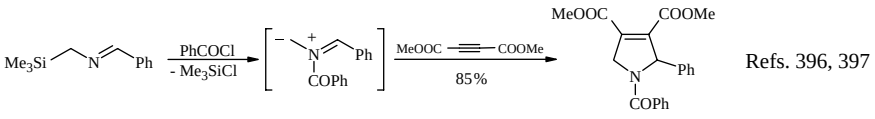
Chloroformiates are also able to induce formation of azomethine ylids from *N*-(trimethylsilylmethyl)benzylidenimine. But SMA imines such as **A** and **B** do not react under these conditions. The authors conclude that stabilization by an aryl group at the incipient carbanion center is necessary.[395]

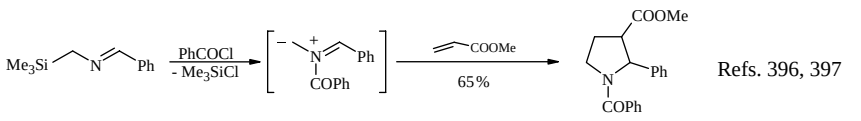


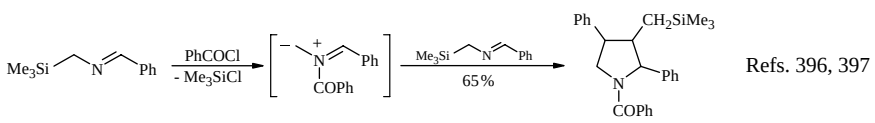
5. Acyl halides

When an SMA imine is treated with acyl and aroyl chlorides, quaternization occurs at the nitrogen atom with subsequent desilylation giving the corresponding ylid.[396,397] This is in marked contrast with the addition reaction occuring with the same chlorides and non-silylated imines.[398] This ylid is treated with ethylenic dipolarophiles to give *N*-acyl (or aroyl)pyrrolidines and with acetylenic dipolarophiles to give *N*-acyl (or aroyl)-2, 5-dihydropyrrols. In the absence of added dipolarophile the starting imine intercepts the ylid to give the corresponding imidazolidine.[396,397]

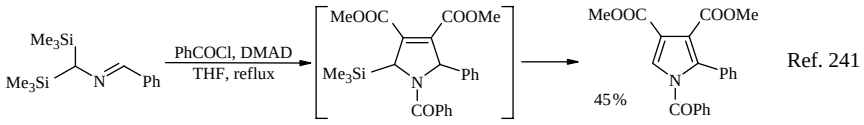






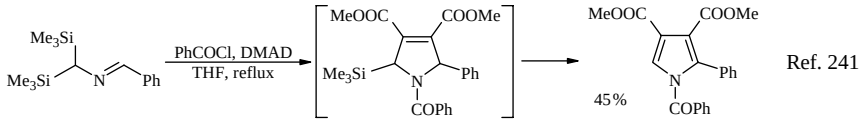


On the other hand, BSMA imines have been tested as precursors to azomethine ylids. When treated with DMAD in the presence of benzoyl chloride, in THF, *N*-benzylidene bis(trimethylsilyl)methylamine leads to the formation of *N*-benzoyl 2-phenyl-3, 4-dicarbomethoxypyrrole.[241]



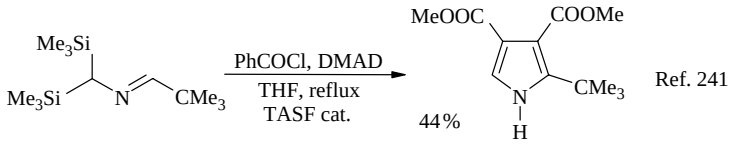
Ref. 241

BSMA imines derived from aliphatic carbonyl compounds lead to complex mixtures under these conditions.[241]

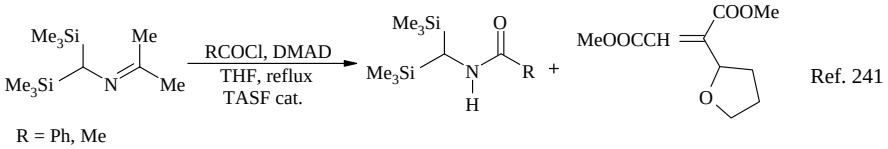


Ref. 241

However, in the presence of a catalytic amount of tris(dimethylamino)sulfonium difluorotrimethylsilicate ("TASF"), pivaldehyde imine yields the N-unsubstituted adduct, whereas acetone imine leads to the corresponding BSMA amides accompanied with the addition product of THF to DMAD. Formation of amides might be explained by the loss of HCl from the iminium resulting from condensation of acyl chloride with imine, leading to a vinyl amide which is easily hydrolyzed. No explanation was presented for the formation of the THF adduct.[241]



Ref. 241

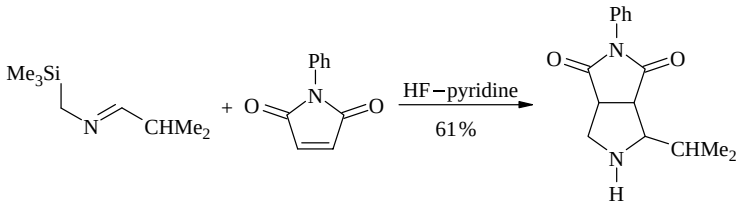


Ref. 241

R = Ph, Me

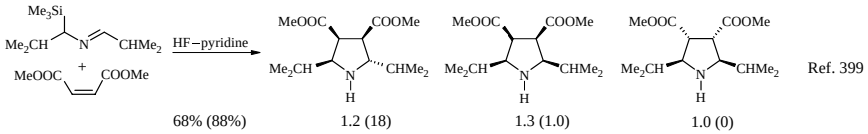
6. HF-pyridine

Similarly to the action of acids, HF-pyridine has been shown able to promote formation of azomethine ylids from SMA imines.[399] This is an interesting result compared with the action of fluoride anion which led to the formation of the corresponding anion (*vide supra*).

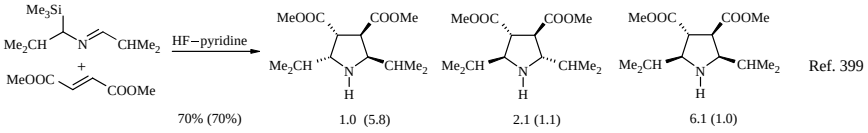


Ref. 399

The *cis*:*trans* stereoselectivity observed in theses cycloadditions is found to depend on the metallic group present in the starting imine, better selectivity being obtained when the Bu_3Sn group replaces the Me_3Si group (see values in brackets).



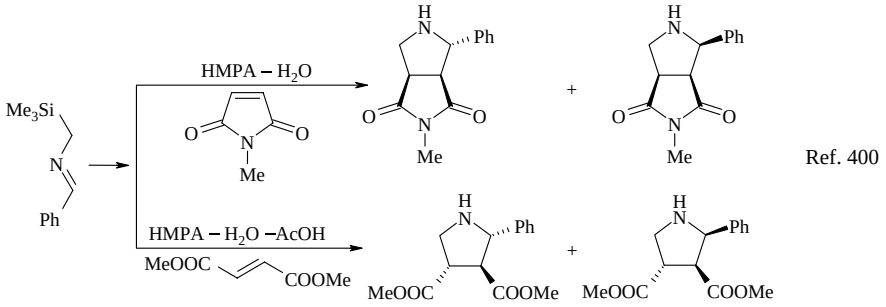
68% (88%) 1.2 (18) 1.3 (1.0) 1.0 (0) Ref. 399



70% (70%) 1.0 (5.8) 2.1 (1.1) 6.1 (1.0) Ref. 399

7. Water-HMPA

At room temperature, water also induces formation of 1,3-dipoles which undergoes a quantitative [3 + 2]cycloaddition reaction with maleimide. Cycloaddition with ethylenic derivatives requires the additional use of acetic acid.[400]

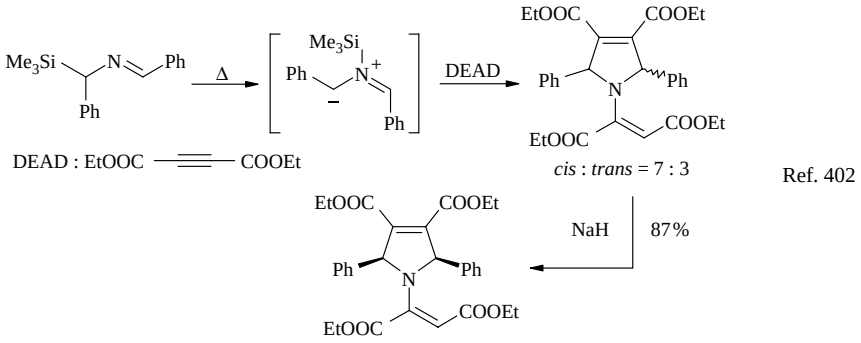


Ref. 400

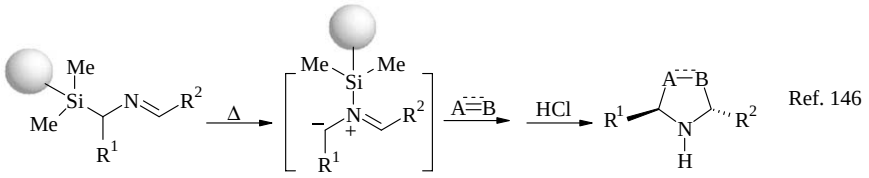
The reaction also works with dimethyl fumarate (100%), fumaronitrile (80%), methyl cinnamate (72%), crotonate (63%) and methacrylate (75%). Stereocontrol is poor or non-existent.[401]

8. Thermolysis

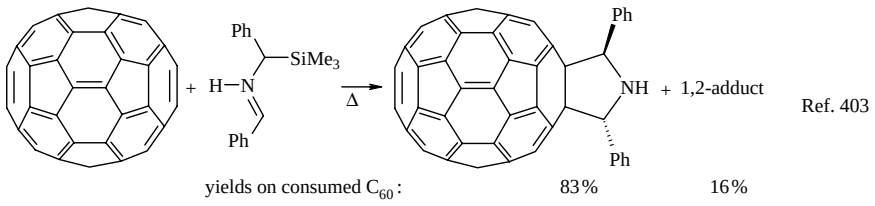
The silyl group in an SMA derivative is able to migrate from C to N under thermal conditions (see Section VI.B.4). This is the case with SMA imines, and such rearrangement leads directly to the corresponding azomethine ylid which may be intercepted by a dipolarophile.[402]



Polymer-supported azomethine ylids generated from α-silylimines through a 1,2-silatropic shift, are shown to be versatile reagents suitable for the synthesis of libraries of pyrrolidine derivatives after 1,3-dipolar cycloaddition with a series of dipolarophiles. Effectively substituents R^1, R^2 and dipolarophiles A=B and A≡B can be chosen to get the desired adduct.[146]



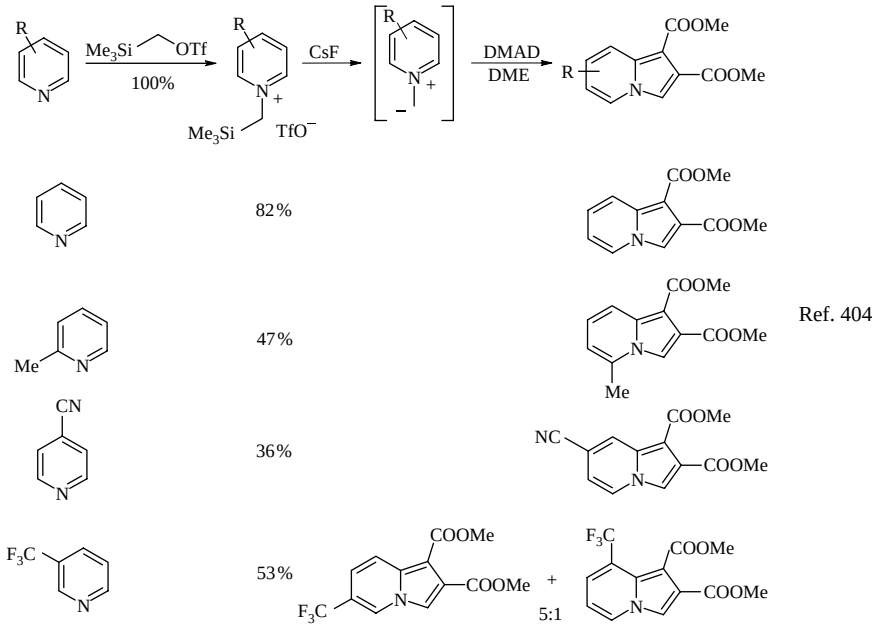
C_{60} behaves as a good dipolarophile under these conditions; high yields of the 1,3-adduct are formed.[403]



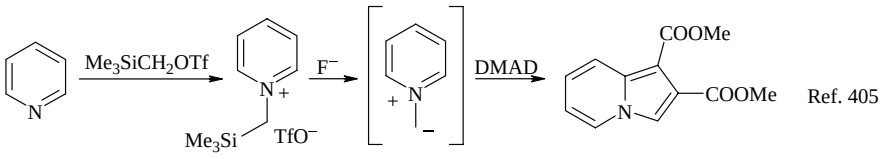
B. *Pyridine and quinoline derivatives*

When reacted with trimethylsilylmethyl triflate, pyridines give pyridinium methylides, a salt which is a good precursor for azomethine ylids under treatment with fluoride ion. Thus, indolizine derivatives can be prepared from non-stabilized pyridinium

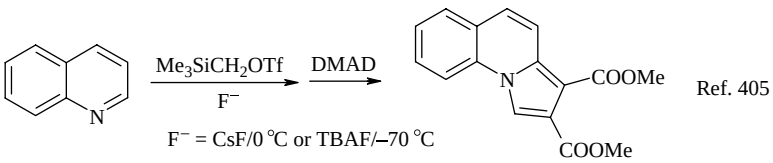
methylides *via* their *N*-(trimethylsilylmethyl)pyridinium trifluoromethane sulfonates and action of cesium fluoride and DMAD in dimethoxyethane.[404]



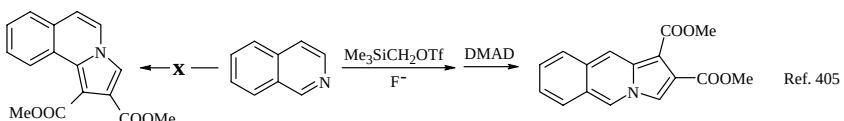
This study was extended to include quinoline and *iso*-quinoline, using either CsF at 0 °C or TBAF at −70 °C as the source of fluoride.[405]



F⁻ = CsF/0 °C or TBAF/–70 °C

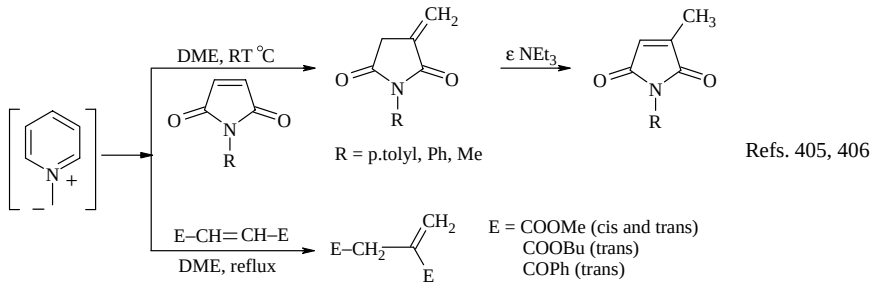


F⁻ = CsF/0 °C or TBAF/–70 °C



F⁻ = CsF/0 °C or TBAF/–70 °C

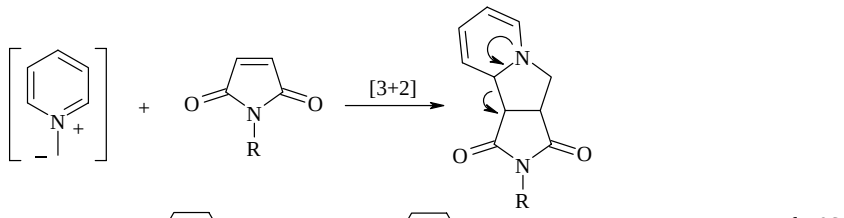
However, an unprecedented result is obtained when maleimide, fumarates, maleate and dibenzoylethylene are used as dipolarophiles, as hydromethylenation of olefins results.[405,406]



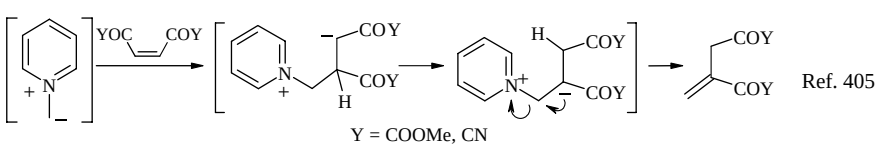
Refs. 405, 406

The reaction of maleimide does not work in dichloromethane and gives polymers in HMPA or MeCN at room temperature. Itaconides are transformed quantitatively into citraconimides on treatment with traces of NEt_3 in chloroform. 2,3-Dibenzoylpropene isomerizes rapidly into *cis* and *trans* 1,2-dibenzoylpropenes. Reactions with olefin need to be performed in refluxing solvent. However, reaction with methyl maleate does not appear to work at all.

The hydromethylenation reaction of maleimide may be explained by initial formation of the expected adduct followed by aromatization of the cyclohexa-1,3-diene ring (driving force of this reaction) and 1,2-hydrogen transfer (key step) followed by final elimination of pyridine. The same mechanism probably occurs with open-chain dipolarophiles.



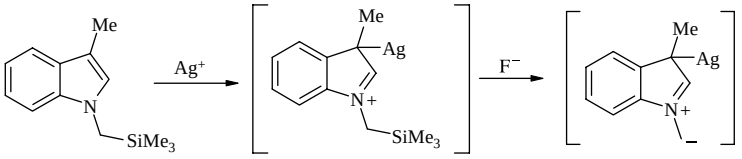
Ref. 406



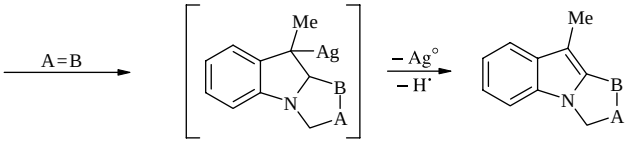
Ref. 405

C. *Indole*

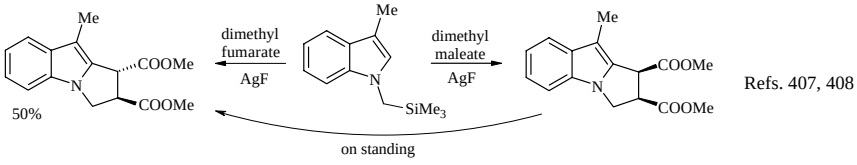
Silver fluoride, used in stoichiometric amount has been found to promote formation of azomethine ylid from *N*-(trimethylsilyl)methyl indole. To explain the role played by AgF, the following mechanism was proposed. Silver ion, acting as a Lewis acid, may attack the indole ring to give silver-bonded carbonium ion. Then fluoride anion may cleave the Si−C bond to form trimethylsilyl fluoride and silver-substituted azomethine which may undergo cycloaddition with the dipolarophile, the resulting silver-bonded intermediate finally losing metallic silver and one hydrogen to give the final adduct.[407,408]



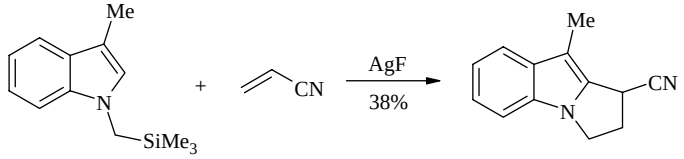
Ref. 408



The stereochemistry of the cycloaddition has been studied through the reaction with methyl fumarate and maleate. The geometry is preserved and *trans*- and *cis*-adducts are obtained. The *cis*-adduct isomerizes rapidly into the *trans*-adduct on standing at room temperature. Indications of the regiochemistry were obtained from reaction with acrylonitrile which gives 2,3-dihydro-1-cyano-9-methyl-1H-pyrrolo[1,2a]indole exclusively.[407,408]



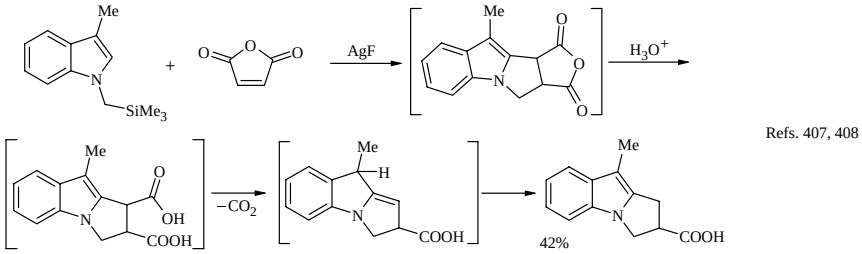
Refs. 407, 408



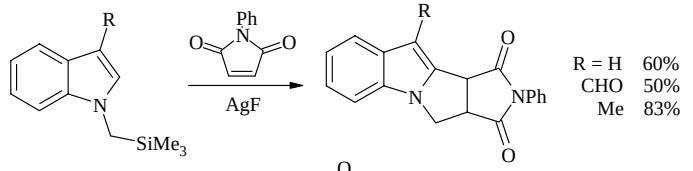
Refs. 407, 408

It is interesting to note that the reaction with maleic anhydride leads exclusively to a carboxylic acid, 2,3-dihydro-9-methyl-1H-pyrrolo[1,2a]indole-2-carboxylic acid, with a regiochemistry different from that observed in the case of acrylonitrile and from that

predicted for cycloaddition with acrylates.[407,408] This result led to interest in studies dedicated to new synthetic strategies toward the access to 2,3-dihydro-1H-pyrrolo[1,2-a]indole nucleus, which is a very important target since the emergence of structurally similar mitocyn C as a clinically useful anticancer agent has appeared.[409]

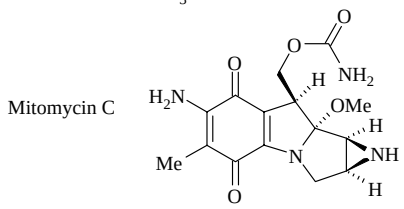


Refs. 407, 408

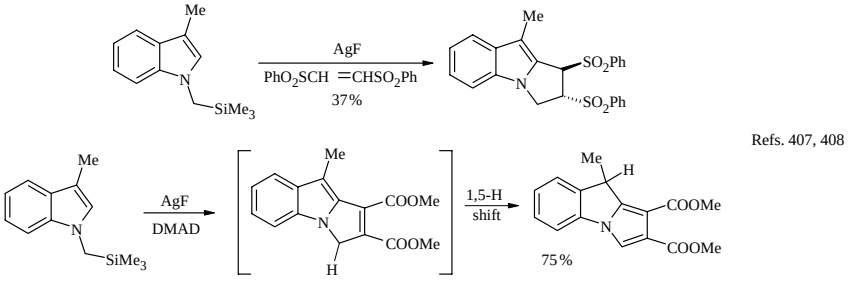


R = H 60%
CHO 50%
Me 83%

Refs. 407, 408



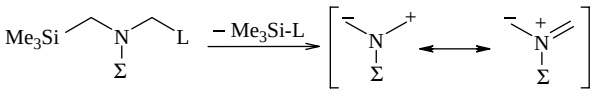
The reaction with (*E*) or (*Z*)-1,2-bis(phenylsulfonyl)ethylene leads to the exclusive formation of the *trans*-cycloadduct, the (*Z*)-dipolarophile rearranging into its thermodynamically more stable (*E*)-isomer before cycloaddition reaction takes place.[407,408] The reaction with DMAD leads to the corresponding pyrrol derivative with good yield, a 1,5-hydrogen shift taking place from the adduct.[407,408]



Refs. 407, 408

D. *Aminomethylethers*

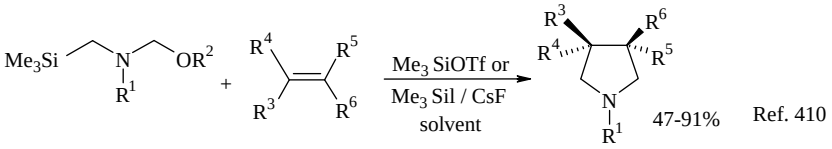
Other types of precursors for azomethine ylids are *N*-(silyl)methylamino derivatives in which the substituent α- to the nitrogen atom is a good leaving group.



Among these groups (siloxy, amino, benzotriazolyl, thiolate, cyanide) the methoxy group has been the subject of a large number of studies. To generate the azomethine ylid, essentialy three reagents have been utilized: silyl triflate (or iodide), trifluoroacetic acid and lithium fluoride (sometime combined with sonication). Thermal rearrangement has also proven to be efficient.

1. Silyl triflate or iodide

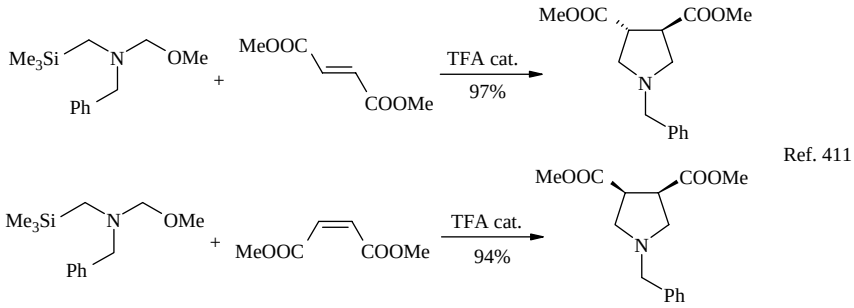
It has been demonstrated that TMS iodide (in combination with cesium fluoride) or TMS triflate in various solvents (THF, MeCN, HMPA) are excellent reagents to promote the generation of azomethine ylids from *N*-methoxymethyl-*N*-(trimethylsilylmethyl)alkylamines and their cycloaddition to electron deficient alkenes with yields ranging from moderate to nearly quantitative. The geometry of the double bond in the alkene is preserved in the cycloadduct.[410]



R^1 = cyclohexyl, benzyl R^2 = Me, *n*-Bu
alkenes = methyl (or ethyl) fumarate, maleate, acrylate, cinnamate and N-phenyl succinimide.

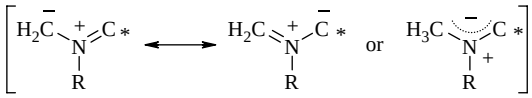
2. Trifluoroacetic acid ("Achiwa's procedure")

Trifluoroacetic acid (TFA) used in catalytic amount generates the azomethine ylid from *N*-benzyl-*N*-(methoxymethyl)trimethylsilylmethylamine.[1,3] Dipolar cycloaddition of this intermediate occurs in quantitative yields with excellent stereospecificity. Use of TBAF is not so efficient in terms of yield and stereoselectivity.[411] This procedure is often referred to as "Achiwa's procedure".

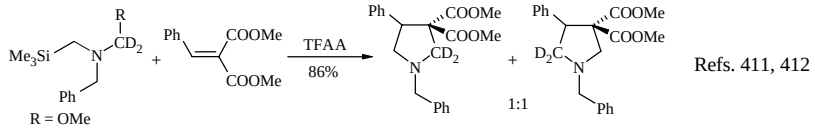


Ref. 411

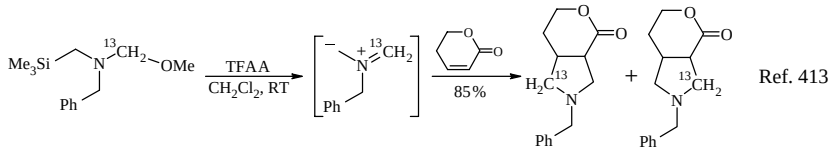
The ambivalence of an unsubstituted azomethine ylid is generally accepted as a fundamental property of 1,3-dipoles, though it had never been shown by any experimental work until reports affording clear evidence were published.[411–413] Both employed the silyl procedure, and precursors in which one carbon α- to nitrogen was distinguished from the other.



The first study consisted of labelling one of the reactive carbon centers with deuterium. Thus, cycloaddition with a dissymmetric dipolarophile led to a 1:1 mixture of two deuterated pyrrolidines, indicative of the ambivalence.[411,412] In the second study, ^{13}C was used to label one of the carbons α- to nitrogen, and once again a 1:1 mixture of labeled pyrrolidines was obtained.[413] These results demonstrate that free resonance of an unstabilized azomethine ylid occurs during the reaction.

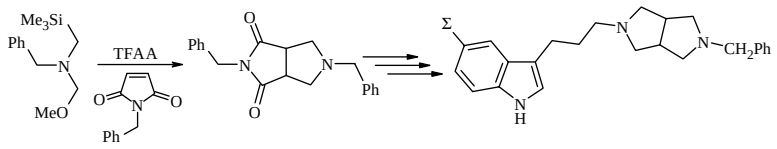


Refs. 411, 412



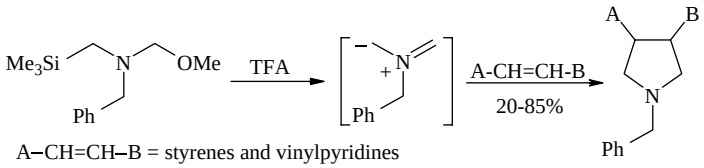
Ref. 413

This procedure has been utilized to condense *N*-benzyl protected azomethine ylid with *N*-benzyl maleimide as the initial step in the preparation of heterocyclyl-substituted diazabicyclooctanes having a $EC_{50} < 500$ nM, being selective agonists of 5-HT1-like receptors and potent agonists for the human 5-HT1Dα.[414]



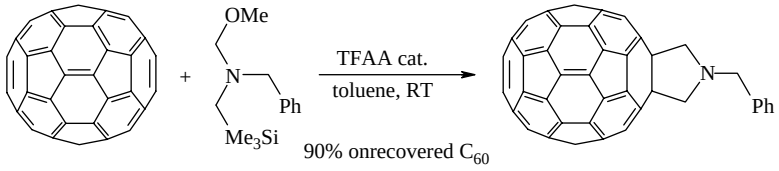
Ref. 414

Styrenes, vinyl pyridines and C_{60} (for another example: see Section VII.A.8 above) have been shown to be good dipolarophiles.[415,416]



Ref. 415

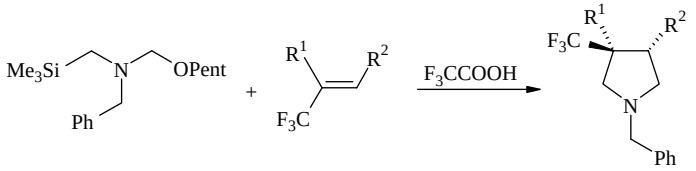
A–CH=CH–B = styrenes and vinylpyridines



Ref. 416

90% onrecovered C_{60}

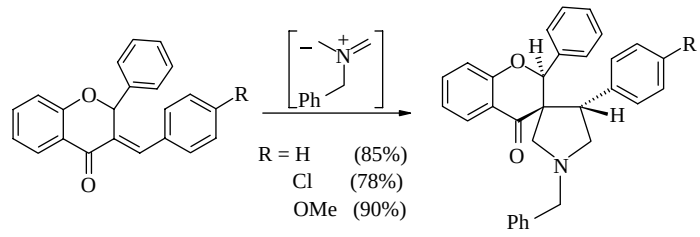
Trifluoromethyl ethylenic substrates have been used as dipolarophiles. The remarkable activation effect provided by the trifluoromethyl group is illustrated by the large increase in yield from the reaction of styrene (20%)[416] to that of α-trifluoromethylstyrene (80%).[417,418]



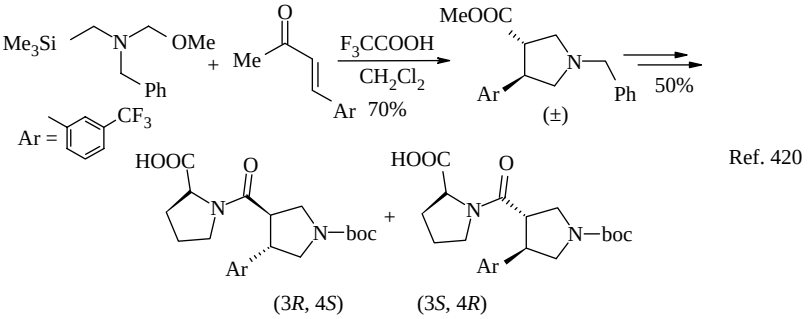
Refs. 417, 418

R^1,R^2 = H, COOEt (80%); Ph, H (80%); Ph, COOEt (70%); PrO, COOEt (30%)

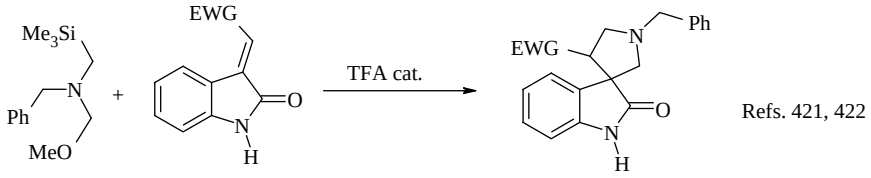
Excellent yields are also obtained in spiro-adducts formed by the condensation of azomethine ylid thus generated, with 3-arylidene-flavanone derivatives at room temperature in the presence of trifluomethylacetic acid in toluene. These molecules are both flavonoids and spiro compounds, two classes of naturally occurring substances which exhibit biological activities.[419]



Pyrrolidine-based thrombine inhibitors are prepared by condensation of the ylid derived from *N*-benzyl-*N*-(methoxymethyl)trimethylsilylmethylamine, with methyl *m*-trifluoromethyl cinnamate.[420]

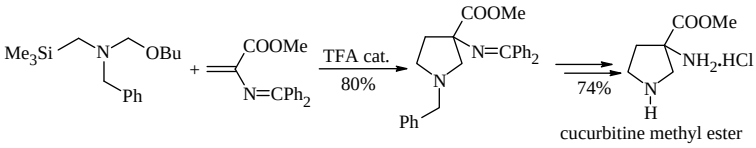


Other spiro pyrrolidine derivatives can be prepared from 2-oxoindolin-3-ylidine derivatives. Even the nitro derivative which is known to be extremely sensitive to base and heat, has been obtained in good yield.[421,422] The spiro-indolenine framework is frequently encountered in alkaloids such as horsfilline.[423]



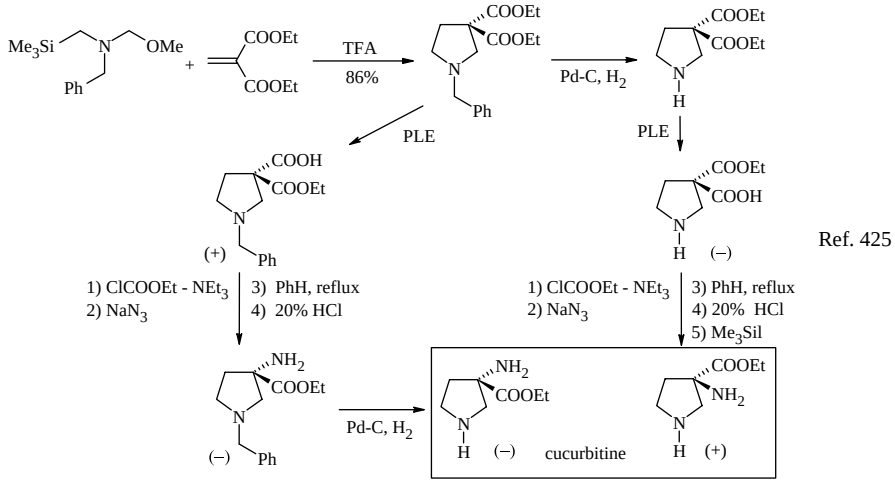
EWG = COOMe (92%), NO_2 (78%)

Achiwa's procedure has been utilized by several authors toward the synthesis of cucurbitine, an aminoacid extracted from pumpkin seeds which share structural features with arginine. Different precursors have been used in chiral and achiral synthetic pathways. First, cucurbitine methyl ester was obtained from an α-amino acrylate.[424] Other substituted acrylates were tested and 3,3-dimethyl-2-aminocarboxylate did not react at all.



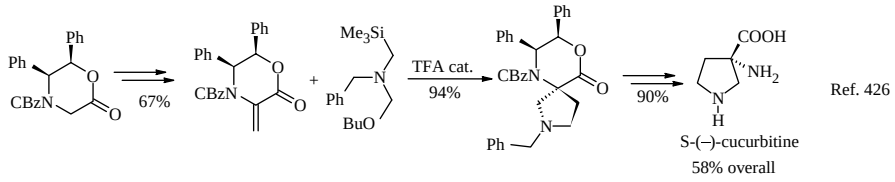
Ref. 424

Second, condensation of diethyl methylene malonate under the same conditions gives a high yield of diethyl *N*-benzylpyrrolidine-3,3-dicarboxylate. Semi-hydrolysis of N-protected and N-unprotected pyrrolidine diester with pork liver esterase (PLE) provides the route to a selective synthesis of (−)- and (+)-cucurbitine.[425]



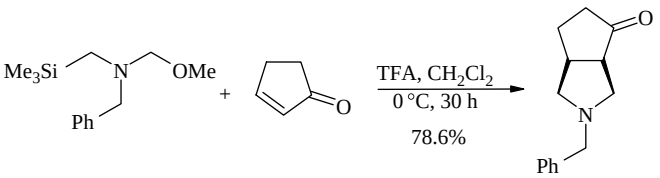
Ref. 425

Similarly, a spirolactone adduct can be quantitatively prepared from a chiral α-methylenlactone. Deprotection led to S-(−)-cucurbitine in excellent overall yield, with greater than 98% ee.[426]



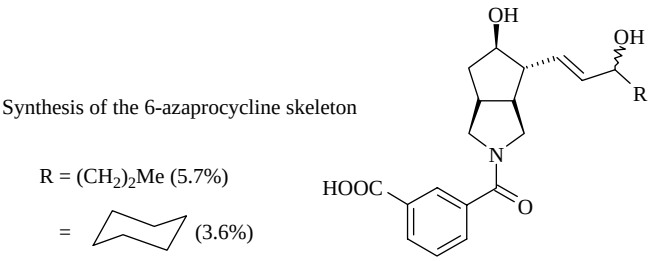
Ref. 426

Condensation of cyclopentenone with the same precursor under the same conditions gives a high yield of *N*-benzyl-3-azabicyclo[3.3.0]-octa-8-one, which serves as a building block for the elaboration of two compounds having the 6-azaprocycline skeleton, compounds which have shown weak inhibitory activities in blood platelet aggregation.[427]



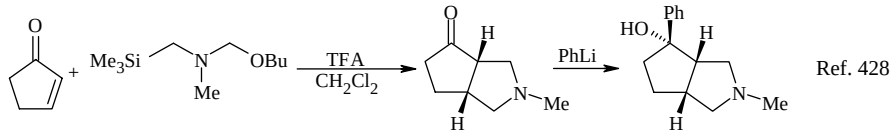
Ref. 427

Synthesis of the 6-azaprocycline skeleton



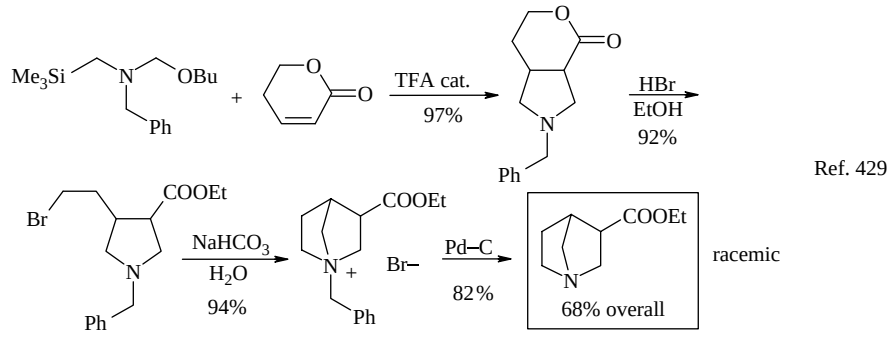
Ref. 427

A similar condensation of the modified ylid (benzyl substituted for methyl) allows the preparation of a compound which is an analgesic inhibiting abdominal contraction response in mice at 30 mg/kg (p.o.).[428]

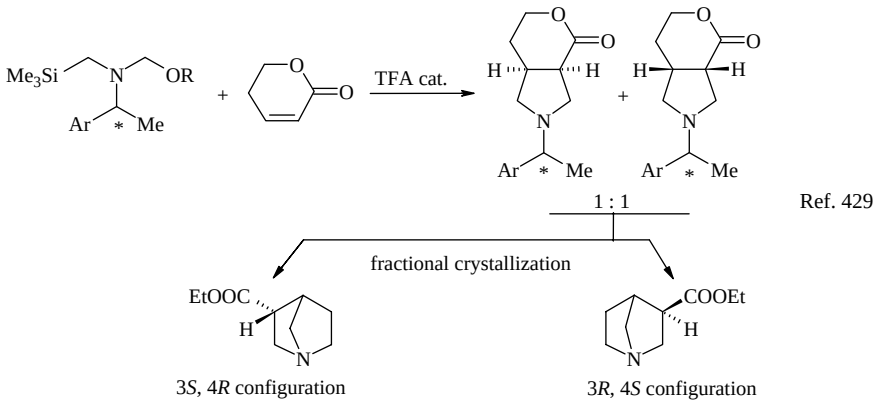


Ref. 428

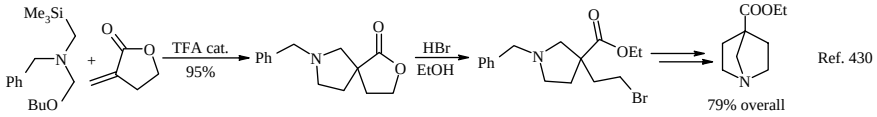
1-Azabicyclo[2.2.1]heptane-3-carboxylic acid esters have been prepared in good yields from 5,6-dihydro-pyran-2-one, in racemic and enantiomerically pure forms. To this goal a modified chiral azomethine ylid precursor having a chiral group as substituent on the nitrogen atom, has been used. It is inefficient in inducing any stereochemical preference. The diastereoisomeric adducts are separated by crystallization at the level of the pyrrolidinelactones or the N-protected bicyclic quaternary salt (large scale work). In this case, their hydrogenolysis gives enantiomerically pure (3*R*, 4*S*) and (3*S*, 4*R*)-aminoesters in 84 and 100% yields, respectively. The structures were determined by X-ray analysis.[429]



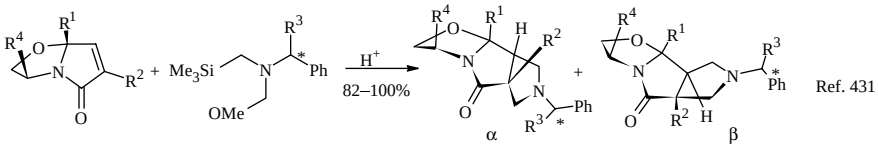
Ref. 429



Methylene butyrolactone has been used as a dipolarophile to synthesize, for the first time, ethyl-1-azabicyclo[2.2.1]hept-3-yl carboxylate using Achiwa's procedure. The synthetic pathway involves rearrangement of the spiropyrrolidine lactone resulting from the [1,3]dipolar addition.[430]

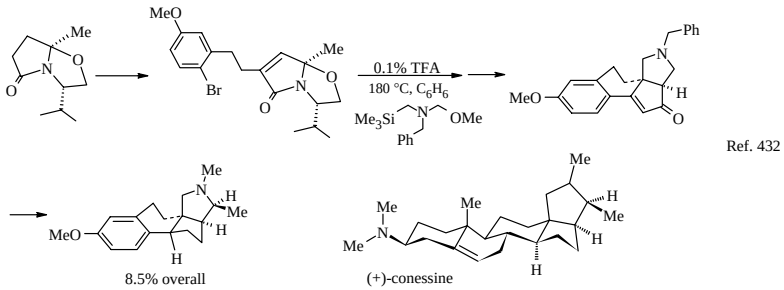


A chiral unsaturated lactam leads to the formation of a mixture of α- and β-adducts when it reacts with a chiral azomethine ylid. The α-adduct is predominant when R^1 = Me, Ph, and the β-adduct when R^1, R^2, R^3 = H and R^4 = Ph. The diastereofacial selectivity is a function of the non-bonded interaction between R^3 and R^2.[431]

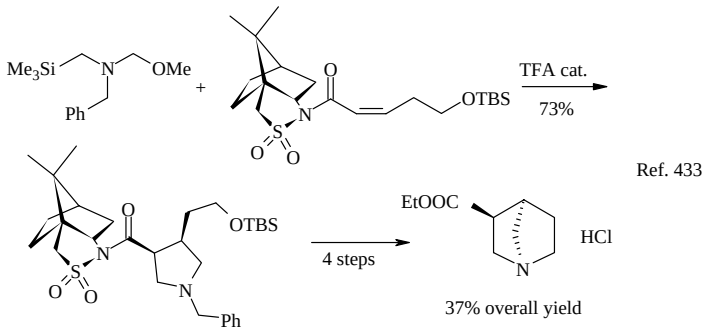


R^1= H, Me, Ph R^2= H, COOR (R= Me, *t*-Bu) R^3 = H, Me R^4 = *i*-Pr, Ph

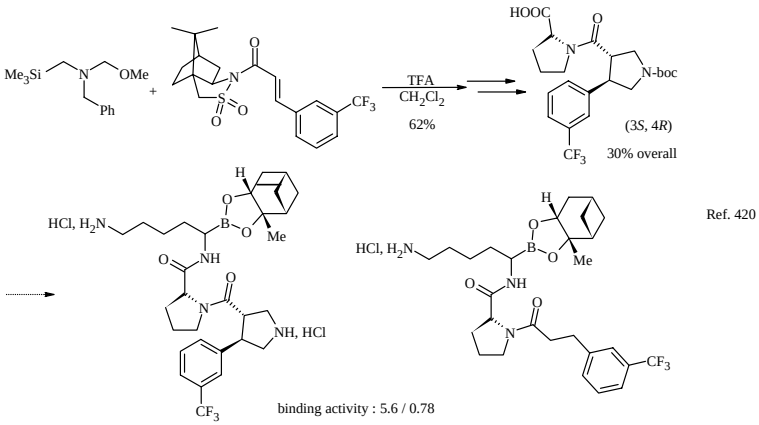
These preliminary results have been used to support a formal total synthesis of a precursor of (+)-conessine, a steroidal alkaloid used in the treatment of dysentery.[432]



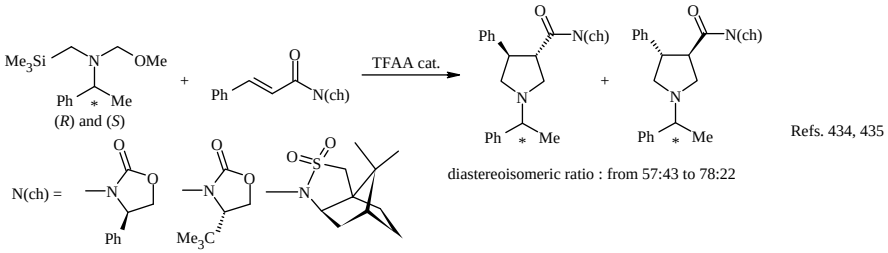
Utilization of α,β-unsaturated amides derived from the chiral amine, namely, camphor sultam, has been made by several groups to test the feasibility of [1,3]dipolar cycloaddition reactions with these chiral systems. This methodology has been applied to the synthesis of (3*S*, 4*R*)ethyl-1-azabicyclo[2.2.1]heptane-3-carboxylate (see above for non-specific syntheses).[433]



A similar result occurs in the synthesis of the stereochemically defined (3*S*, 4*R*) isomer of a pyrrolidine derivative which was transformed into the desired boropeptide thrombin inhibitor showing a binding affinity seven times greater than that of its non-pyrrolidinic congener.[420]

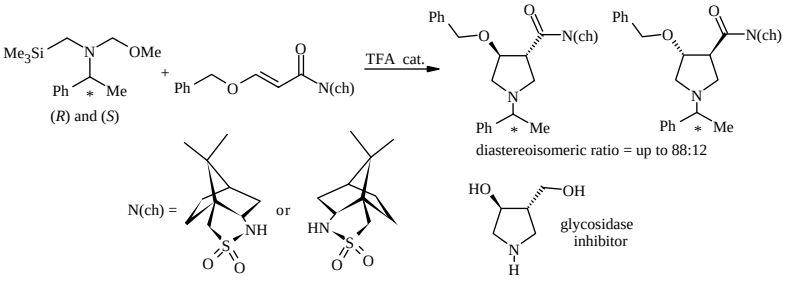


In a study dedicated to enantioselective approaches and their limitations, chiral dipolarophiles and chiral azomethine ylids precursors were used and it was established that the chirality of the adduct is largely controlled by the chirality of the dipolarophile while that of the azomethine ylid has a very weak influence.[434,435]



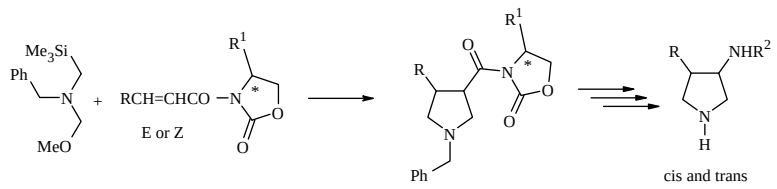
Refs. 434, 435

Results of a similar study on the enantiospecific synthesis of a glycosidase inhibitor, using chiral β-benzyloxy acrylamide, show that even electron-rich alkenes can serve as dipolarophiles. A large influence of the polarity of the solvent is observed: the greater the polarity the greater is the diastereoselectivity. Thus, DMF and acetonitrile are found to be the best solvents. On the basis of these observations, the desired enantiomerically pure glycosidase inhibitor, (3*R*, 4*R*)-4-(hydroxymethyl)pyrrolidin-3-ol, could be prepared in two steps in 87% overall yield.[436]



Ref. 436

Chiral oxazolidines have been used as chiral inductor in the cycloaddition of ethylenic amides with ylids formed from *N*-methoxymethyl-*N*-(trimethylsilylmethyl)benzylamine. Poor stereocontrol is observed as either the (*E*) or the (*Z*) isomer leads to a mixture of *cis* and *trans* pyrrolidine.[437]

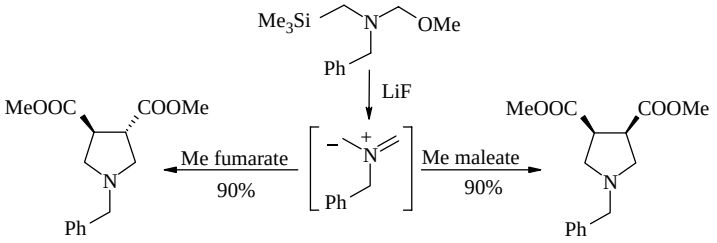


Ref. 437

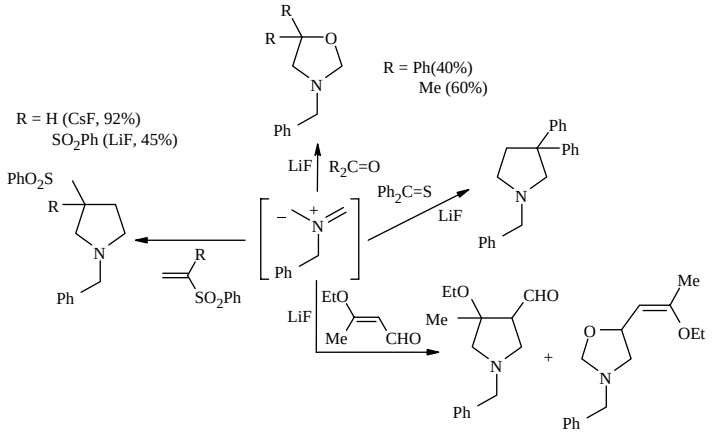
R = (cyclic)alkyl, phenyl(alkyl). R^1 = *i*-Pr, *t*-Bu, Ph, naphthyl, etc. R^2 = COO*t*-Bu, $COOCH_2Ph$, etc.

3. Lithium fluoride

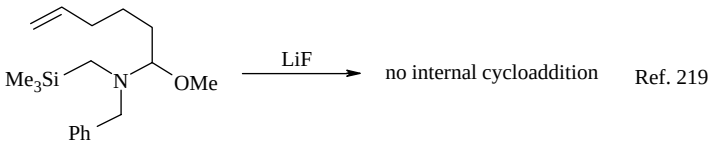
Lithium fluoride is able to promote the formation of azomethine ylids from *N*-benzyl-*N*-(methoxymethyl)trimethylsilylmethylamine. The reaction with methyl fumarate and maleate gives quantitative yields of *trans* and *cis* *N*-benzyl-3,4-dicarbomethoxypyrrolidines. Thus, the geometry of the alkenes is preserved during the cycloaddition reaction.[219,438] These results are identical to those obtained using Achiwa's procedure (see Section VII.D.2).

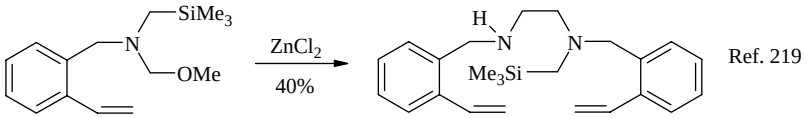


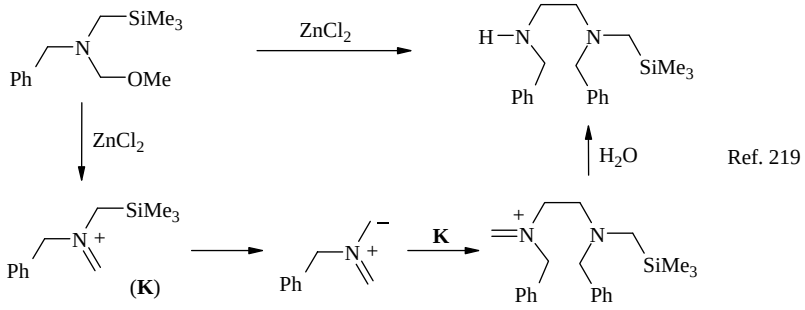
Other dipolarophiles have been tested leading to pyrrolidines (from vinyl sulfones),[219] oxazolidines (from ketones)[219] and thiazolidine (from a thioketone)[219] in moderate to good yields. Noteworthy is the isolation of two adducts from ethoxycrotonaldehyde: a pyrrolidine carbaldehyde implying cycloaddition onto the ethylenic double bond and an oxazolidine resulting from the cycloaddition on the carbonyl moiety of the dipolarophile.[219,438]



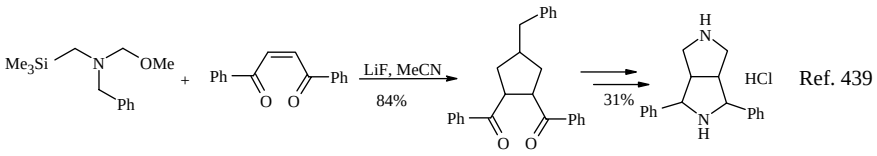
However, internal cycloaddition fails to give an adduct when an ethylenic moiety is linked to the ylid precursor. Even a styrene does not give any adduct and a diamine is obtained instead (note that in this instance zinc chloride was used instead of lithium fluoride). The same result is observed starting from the corresponding phenyl derivative, i.e., from *N*-benzyl-*N*-(methoxy methyl)trimethylsilylmethylamine. The proposed mechanism involves demethoxylation under the action of the Lewis acid to form cation, K, which adds to the ylid to give the ethylenediamine framework.[219]





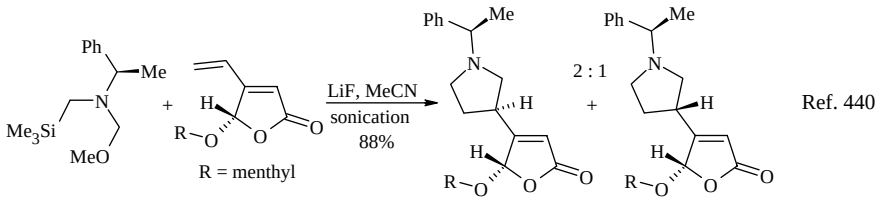


Condensation of (*Z*)-dibenzoylethylene has been studied to serve as a model reaction for the synthesis of a new series of non-sulfonyl potent and selective COX-2 inhibitors.[439]



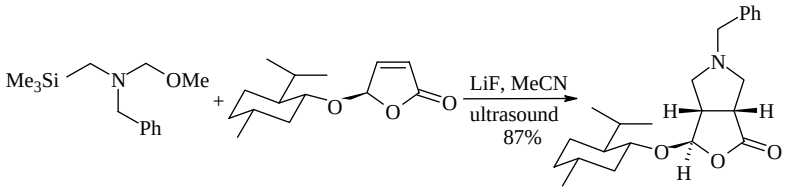
4. Lithium fluoride and sonication

In spite of the efficiency of lithium fluoride to initiate formation of an azomethine ylid from aminomethylethers, sonication of the reaction medium proved useful. It is likely that sonication improves the solubility of lithium fluoride in the solvent. This is illustrated by the following two examples. Chiral pyrrolidinylfuranones are obtained from 5-(*S*)-5-menthyloxy-4-vinylfuran-2(5H)-one. Sonication increases the yield from 55 to 88%, but does not change the stereoselectivity.[440]



Ref. 440

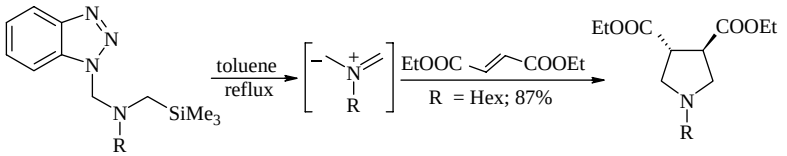
In a full study devoted to the use of 5-(*R*)-menthyloxy-2(5H)-furanone in 1,3-dipolar cycloadditions, use of ultrasonic conditions accelerates the reaction (30 min) giving diastereomerically pure adduct in high yield. This adduct has the *trans*-configuration (^{1}H NMR). Cesium fluoride leads to unidentifiable products.[441] The adduct may serve as a precursor to 3,4-*cis*-(bis) functionalized pyrrolidines.



Ref. 441

E. *Benzotriazolylmethylaminomethylsilane*

The benzotriazolyl group is a good leaving group. This feature was exploited in the use of benzotriazolylmethyl-aminomethyltrimethylsilane as a precursor of an azomethine ylid. At reflux in toluene, benzotriazolyltrimethylsilane was eliminated and formation of the ylid underwent quantitative [1,3]dipolar cycloaddition with diethyl fumarate, for example, giving a *trans*-3,4-dicarboethoxy pyrrolidine derivative exclusively. Other examples were reported as well.[442]



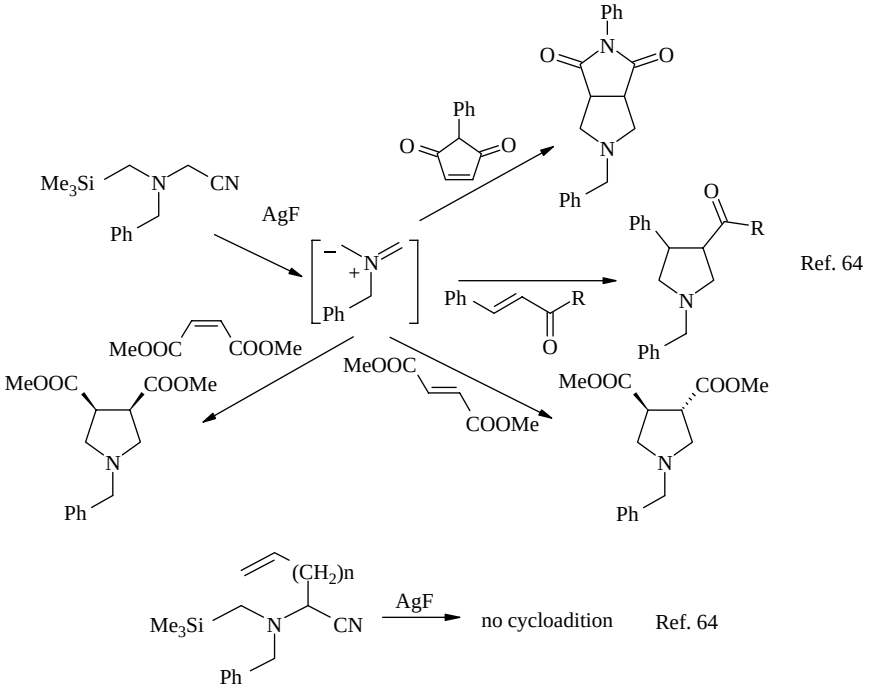
Ref. 442

F. *Aminoacetonitriles*

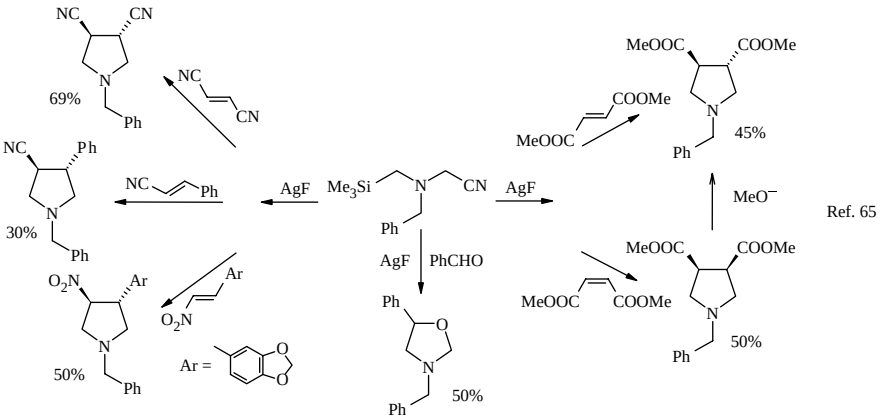
Achiwa's procedure is well suited to promote formation of an azomethine ylid from *N*-methoxymethyl-*N*-(trimethylsilylmethyl)alkylamines (see Section VII.D.2). It is also efficient and gives similar results when one uses *N*-cyanomethyl-*N*-(trimethylsilylmethyl) alkylamines as the precursor.[415]

Silver fluoride also provides access to the azomethine ylid from *N*-methoxymethyl-*N*-(trimethylsilylmethyl)benzylamine, with the intermediate being trapped with classical dipolarophiles. No internal cycloaddition occurs when a non-activated ethylenic moiety

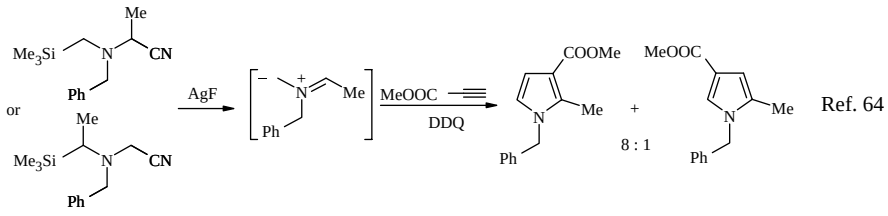
is present in the starting precursor.[64]



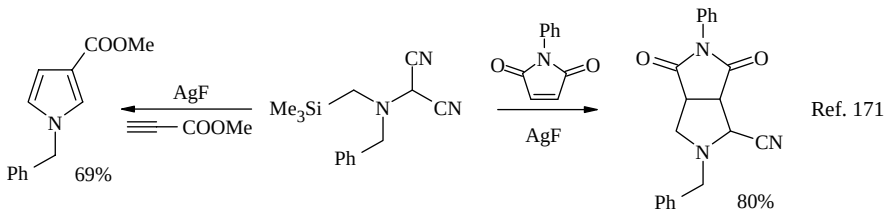
This result has been confirmed with other dipolarophiles. Conservation of the original geometry is observed as exemplified by reactions with methyl dimaleate and fumarate. In the presence of a base such as the methoxide anion, the *cis*-isomer issued from fumarate was transformed into the more stable *trans*-cycloadduct form from maleate. Cycloaddition of benzaldehyde leads to *N*-benzyl-5-phenyloxazolidine.[65,443]



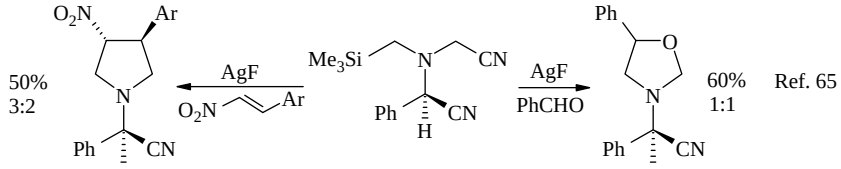
It was noted that using either the α- or α′-methylated precursor leads to the same mixture of the cycloaddition products. This demonstrates that the same azomethine ylid is generated as the common intermediate.[64]



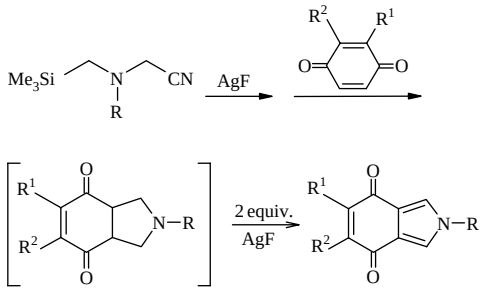
When the precursor is derived from malononitrile, reaction with maleimide leads to the expected α-cyano pyrrolidine adduct. However, methyl propiolate gives 3-carbomethoxy pyrrole, probably due to the acidity of hydrogen α- to the cyano group in the intermediate Δ^3-pyrrolinic adduct first formed.[171]



Substituting a benzyl group for the chiral α-cyanobenzyl group in the azomethine ylid provides insight into the diastereoselectivity of this cycloaddition. In fact, poor selection results, probably because the groups attached to the nitrogen atom of the ylid differ little in their size and electronic nature.[65]

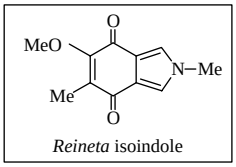


Quinones have also been used as dipolarophiles, giving pyrrole derivatives after oxidation with excess silver fluoride. *Reineta* isoindole, a naturally occurring antimicrobial compound, was synthesized by this route in good yield.[444]



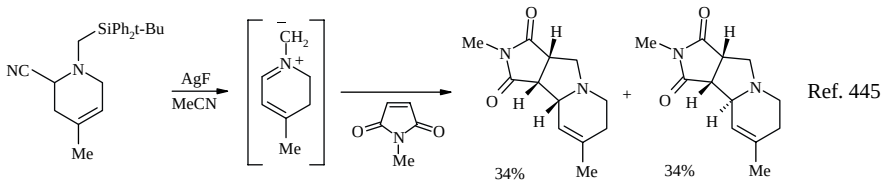
R	R^1	R^2	Yield (%)
Me	OMe	Me	68
H	H	Bn	60
H	H	Me	64
Me	Me	Bn	75
Me	Me	Me	72

Ref. 444



Reineta isoindole

Very close to this type of precursor is 1-silylmethyl-6-cyano-4-methyl-1,2,5,6-tetrahydropyridine, which upon treatment with silver fluoride and *N*-methyl maleimide gives equal amounts of two isomeric indolizidine derivatives.[445]



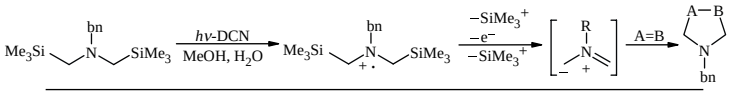
Ref. 445

G. *Bis(silylmethyl)amines*

Three techniques have been utilized to promote generation of an azomethine ylid from bis(trimethylsilmethyl)amines: photochemistry, chemistry with silver fluoride and electrochemistry.

1. Photochemical activation

Azomethine ylids can be generated photochemically by irradiating N-protected bis(trimethylsilylmethyl)amines in the presence of a sensitizer (1,4-dicyano-naphthalene, "DCN") in methanol as the solvent. The ylid reacted with a series of dipolarophiles to give adducts in moderate to good yields.[446,447]

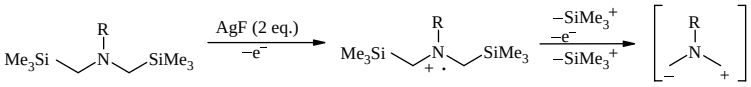


Refs. 446, 447

benzophenone	80%	ethyl acrylate	58%
dimethyl fumarate	60%	trans-1,2-bis(phenylsulfonyl)ethylene	82%
trans-methyl cinnamate	78%	phenylvinyl sulfone	75%
N-phenylmalimide	83%	dimethylacetylene dicarboxylate (DMAD)	55%

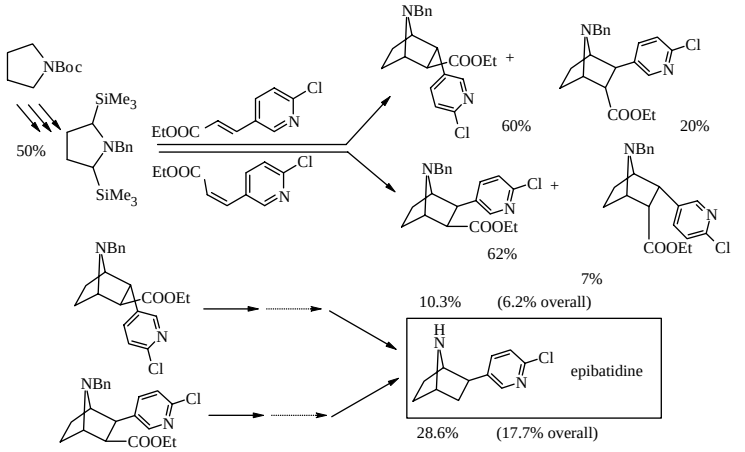
2. Chemical activation with AgF

In the presence of two equivalents of silver fluoride, N-protected bis[(trimethylsilyl)methyl]amines lead also to azomethine ylids which can be trapped by dipolarophiles. The mechanism of the cycloaddition reaction involves sequential electron–Me_3Si^+–electron transfer process from the amine to silver fluoride, which forms silver metal, ruling out a fluoride-induced desilylation process. Although silver is recovered at the end of the reaction, a cheaper oxidizing reagent is still lacking.[448,449]



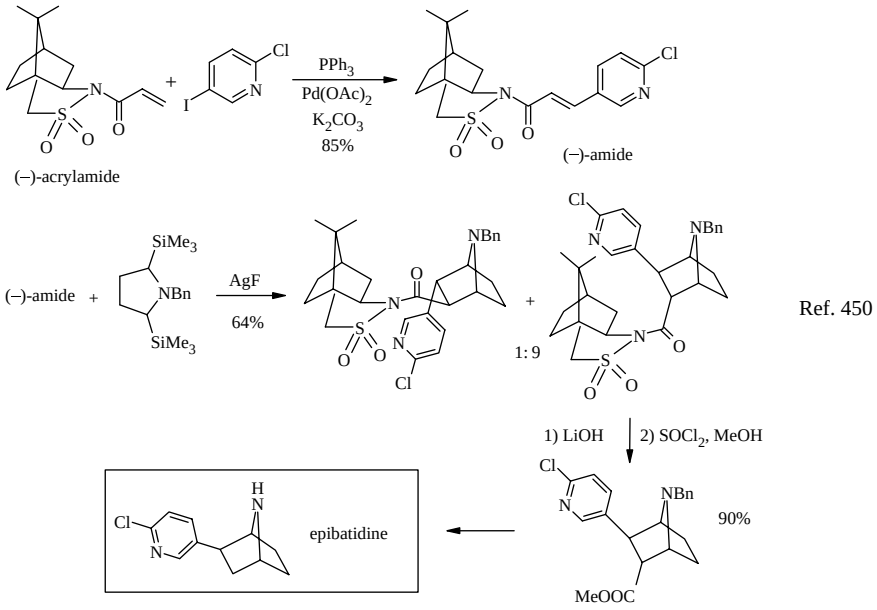
Refs. 448, 449

This technique has been applied to the synthesis of epibatidine, an alkaloid which exhibits nonopiod analgesic activity 200–500 times greater than that of morphine. Boc-protected 2,5-bis(trimethylsilyl)pyrrolidine has been chosen as the precursor of the azomethine ylid and *cis*- and *trans*-ethyl-(6-chloro-3-piperidyl)-2-propenoates as the dipolarophiles.[448,449]



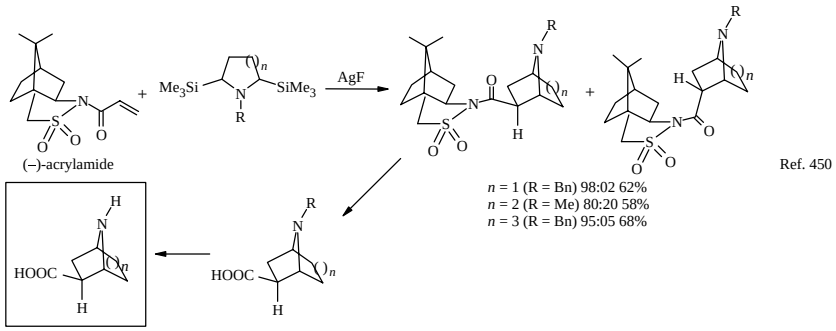
Refs. 448, 449

A chiral synthesis of epibatidine is achieved by using a chiral amide derived from camphorsultam instead of the ester.[450]

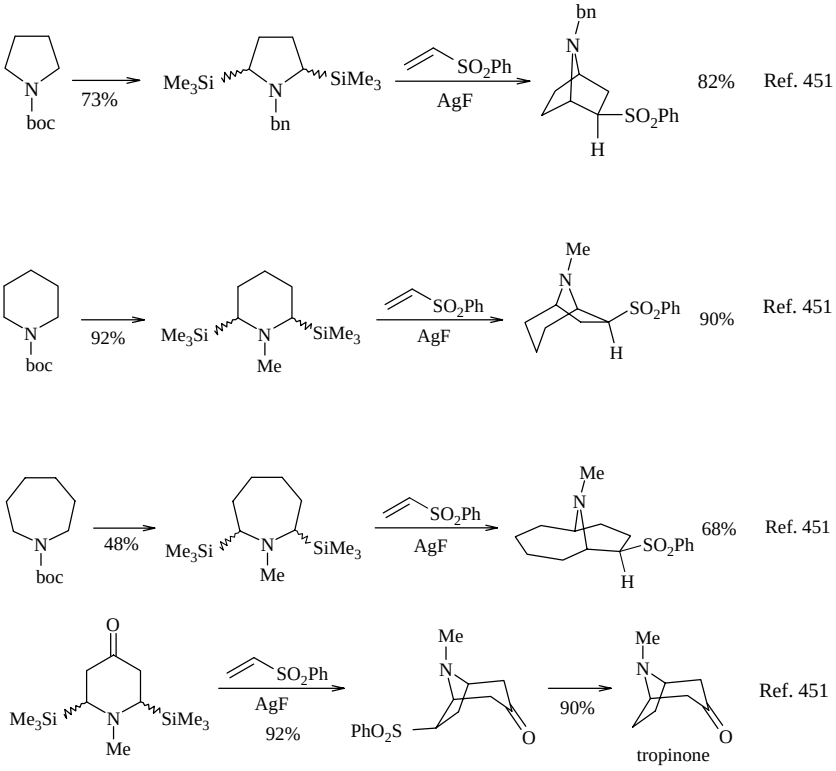


Ref. 450

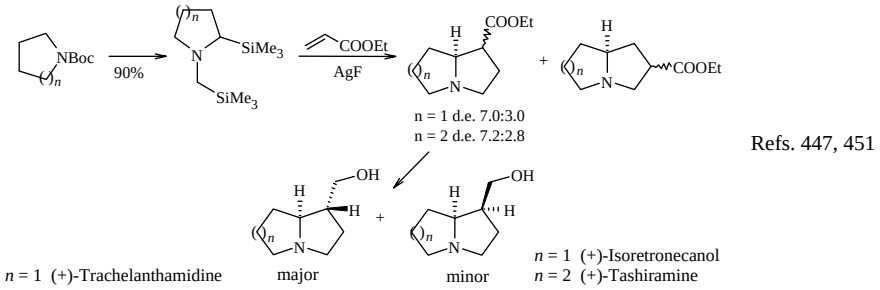
This same strategy has been extended to the synthesis of optically pure conformationally constrained amino acids.[450]



Conveniently N-protected 2,2′-bis(trimethylsilylmethyl)pyrrolidine, -piperidine and -azepane were prepared and reacted with phenylvinylsulfone in the presence of silver fluoride (2 equiv.). The X-azabicyclo[*m*.2.1]alkane framework in each case is obtained in good to excellent yields. Being very efficient, this technique provides a new strategy to synthesize tropinone, an important member of the tropane class of alkaloids.[451]



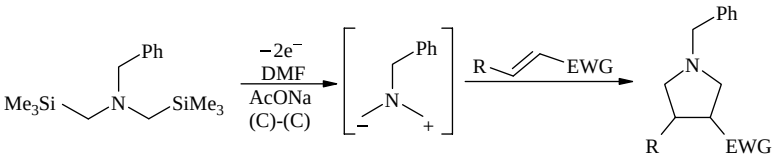
The use of another type of bis(trimethylsilylmethyl)amine leads to the synthesis of 1-azabicyclo[*m*.3.0]alkanes also present in the skeleton of a number of alkaloids as trachelanthamidine, isoretronecanol, and tashiramine.[447,451]



Refs. 447, 451

3. Electrochemical activation

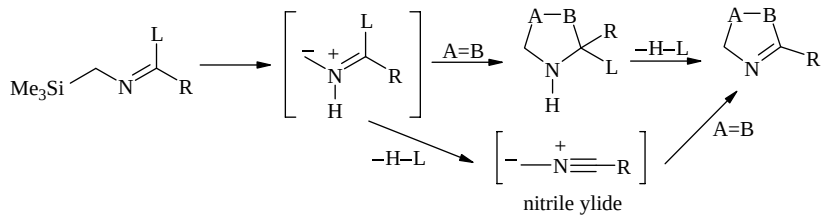
With the chemical activation process, the precursor is oxidized by silver ion. An electrochemical process using a carbon–carbon pair of electrodes, has been shown to promote the formation of the ylid which is reacted with electron-poor olefins.[452]



Ref. 452

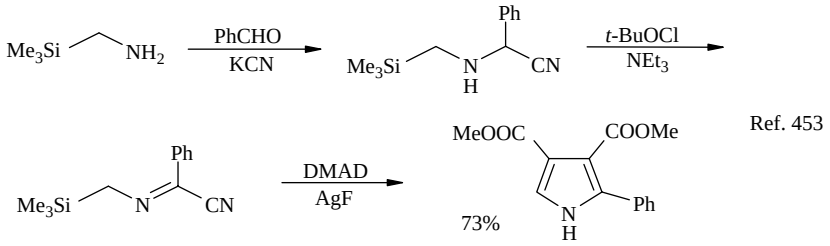
H. *Substituted imines*

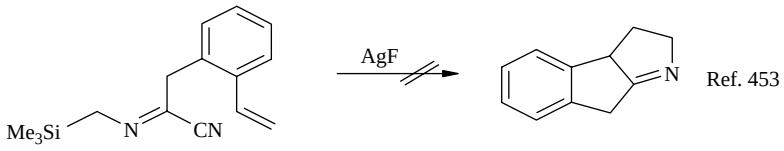
N-Silylmethylimines are excellent precursors of unstabilized azomethine ylids. Other compounds that have the imine framework, i.e., have one (or two) functional group(s) directly linked to the sp^2 carbon atom also provide access to this type of ylids. After the occurence of the [3 + 2]cycloaddition reaction, giving a functionalized pyrrolidine, this group (which is also a good living group) eliminates to give a Δ^1-pyrroline derivative. The final product might also be the result of a [3 + 2]cycloaddition reaction of an intermediate nitrile ylid onto the olefin A=B.



1. Cyanoimines

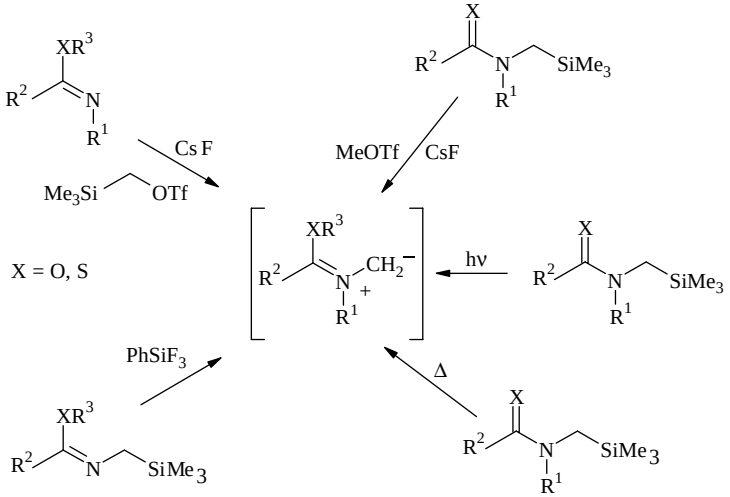
N-silylmethyl α-cyanoimines have been studied as a precursor of nitrile ylids. They undergo facile cycloaddition with dipolarophiles. Thus reaction with DMAD in the presence of silver fluoride leads to the formation of the corresponding pyrrole derivative in good yield, but no reaction occurs with the non-activated π-bond of styrene.[453]



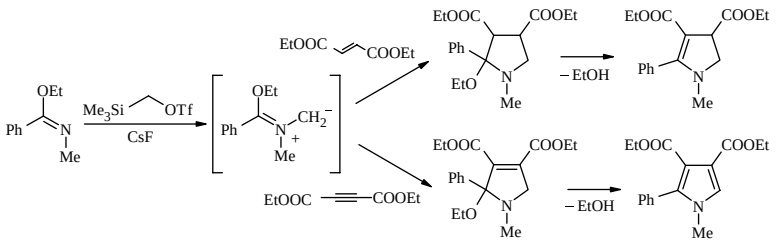


2. Imidates, amides, thioimidates, thioamides and thiocarbonates

Different approaches have been used to synthesize imidate- and thioimidate-derived azomethine ylids.

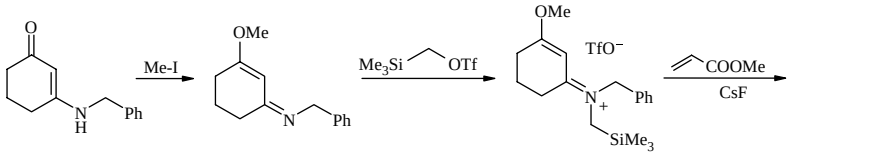


Imidates, generated from secondary amides, are treated with trimethylsilylmethyl triflate to give an azomethine ylid which reacts with electron-poor alkenes and acetylenes, yielding Δ^2-pyrroline and pyrrole derivatives.[54] Similar transformations are conducted from thioamides (*vide infra*).

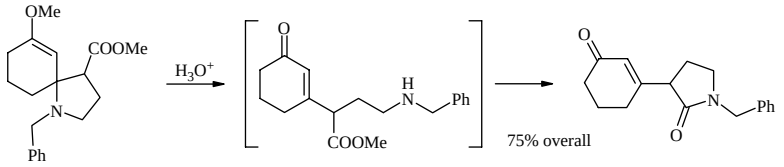


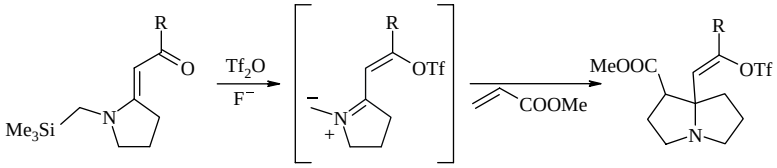
Ref. 454

This technique has been applied to a vinylogous imidate.[454,455]

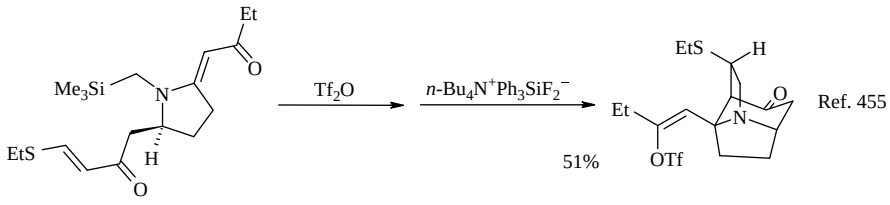


Ref. 454





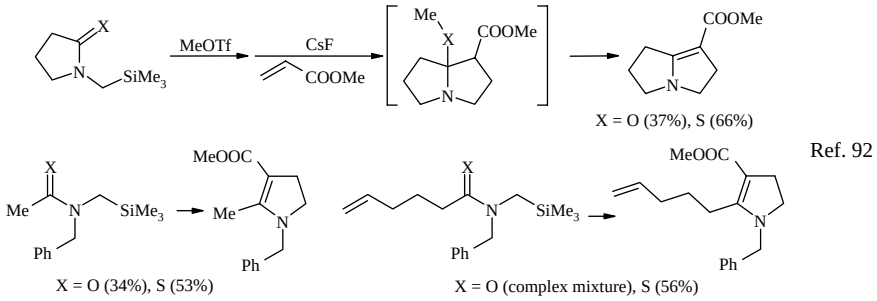
Ref. 455



Ref. 455

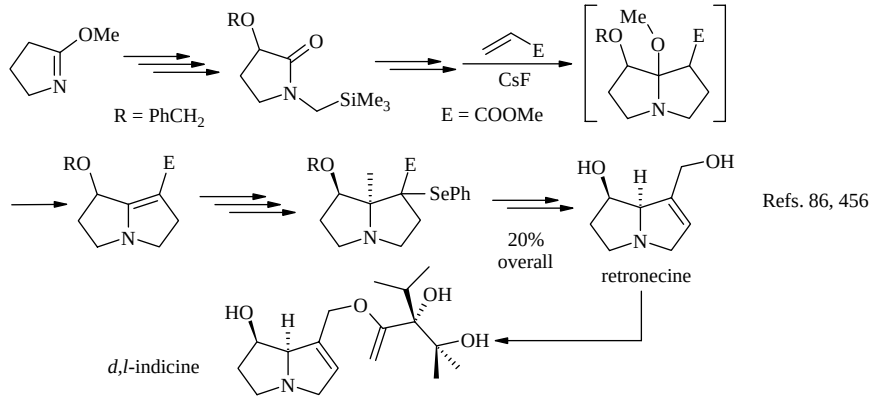
N-Silylmethyl amides and thioamides are sources of imidate methylides. Starting from pyrrolidine-2-one and thione, 2,5,6,7-tetrahydro-3H-pyrrolizine-1-carboxylic acid methyl ester can be prepared as can other Δ^2-pyrroline derivatives from amides and

thioamides. In spite of these successful syntheses, it has been found that working with thioamides instead of amides gives better yields, probably because methylthiolate anion is a better leaving group than methoxy anion. Noticeable is the absence of any internal trapping, acrylate being a better dipolarophile than a simple double bond.[92]



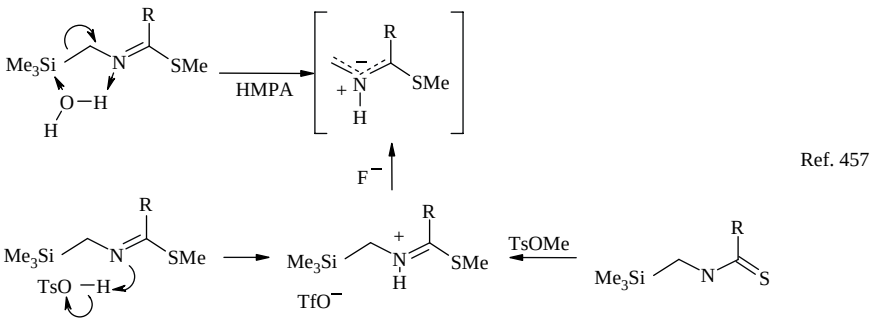
Ref. 92

This synthesis is complemented by that of *d*,*l*-indicine starting from retronecine. Indicine *N*-oxide has antitumor properties.[86,456]

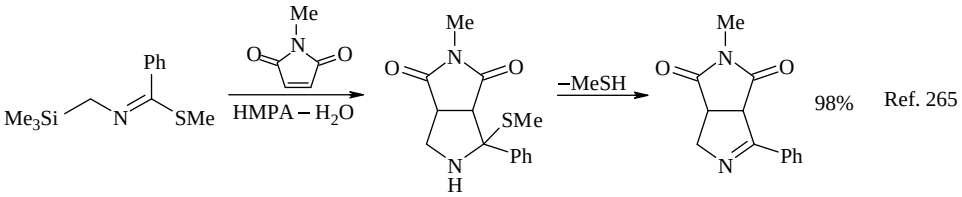


Refs. 86, 456

An important observation is that water in HMPA quaternarizes the nitrogen atom and cleaves the Si–C bond of thioimidates to give the same thioimidate methylide. This is an alternative to fluorodesilylation as the action of fluoride anion (CsF) directly onto the same reagent in HMPA did not lead to the ylid but to the corresponding aza-allyl anion.[457] Thus, reaction with *N*-methyl maleimide gives quantitative yields of the expected 2,5-diazabicyclo[3.3.0]octane derivative. Conventional generating methods (TMSOtf/CsF/HMPA/60 °C, PhCOF/MeCN/60 °C or AcOH/HMPA/25 °C) give poorer yields.[265]

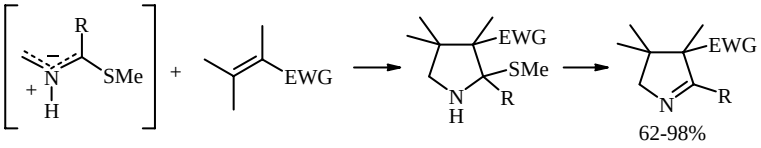


Ref. 457



Ref. 265

A series of electron deficient alkenes have been reacted with thioimidate methylide under these conditions. Corresponding Δ^1-pyrrolines are obtained in moderate to high yields.[457]

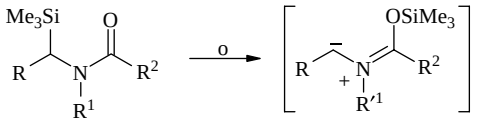


Ref. 457

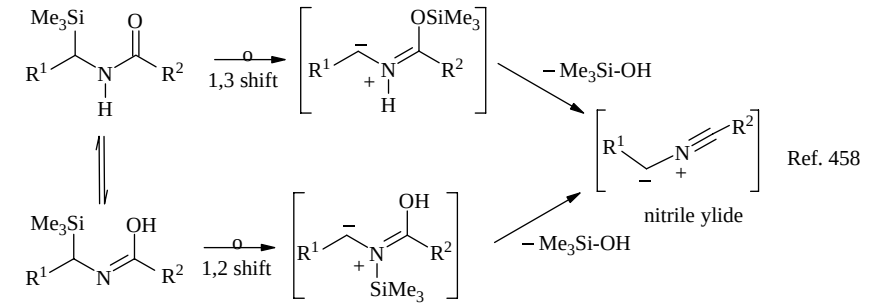
olefines : N-methyl maleimide, dimethyl and dibutyl fumarates and maleates, fumaronitrile, 3-buten-2-one, methylacrylate, methacrylate, crotonate and cinnamate

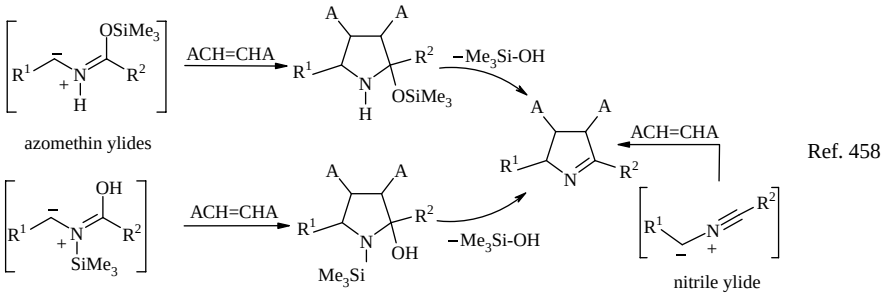
Under thermal treatment, one can expect the formation of an imidate methylide starting from a tertiary amide.

From a secondary amide, formation of a nitrile ylid because of plausible elimination of trimethylsilanol prior to cyclization might be expected. However, it is possible that this elimination occurs after cyclization. Thus, the true 1,3-dipole would be the imidate methylide. In any case, the final product will be a Δ^1-pyrroline.[458]

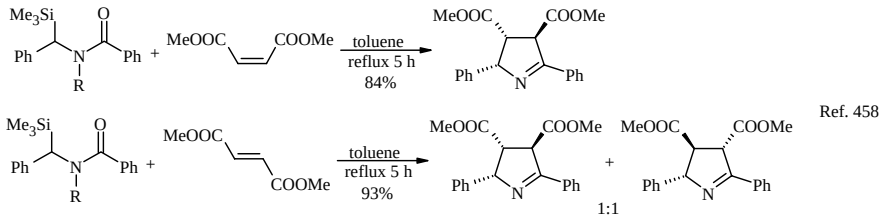


Ref. 458

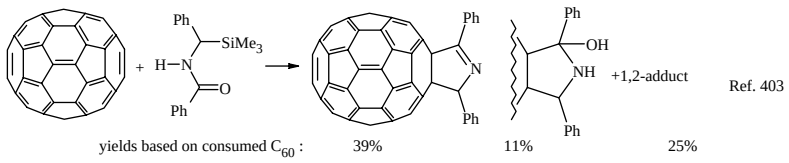




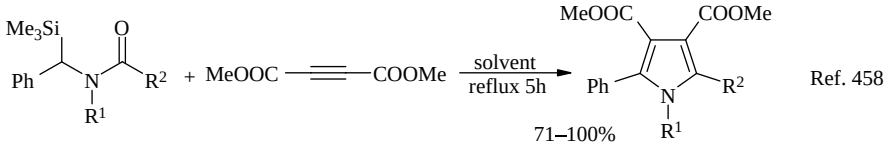
Apparent poor stereospecificity characterizes these 1,3-dipolar cycloaddition reactions. Formation of two diastereoisomers from fumarate might be the result of the possible two types of *endo* orientation of this olefin toward the ylid, and epimerization at the 3-position, due to the high acidity of the corresponding hydrogen might be responsible for the isomerization of the expected all-*cis* adduct to the final product.[458]



C_{60} reacts with the ylid generated thermally from *N*-(α-trimethylsilyl)benzylbenzamide.[403]

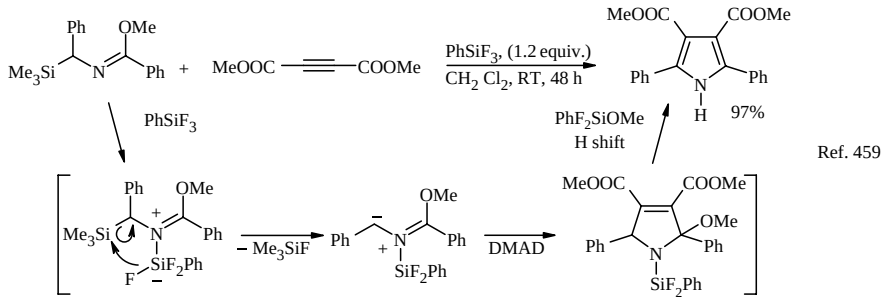


Five equivalents of DMAD were used in refluxing solvent. Best results are obtained in refluxing toluene, starting from secondary arylamides. Alkylamides ($R^2 = Me$) require higher temperature (refluxing xylene) to get yields in the same range.[458]



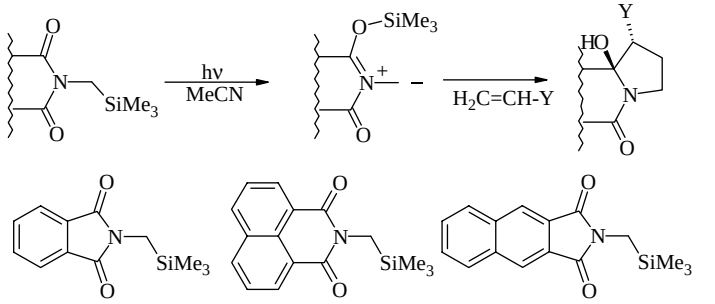
Ref. 458

Phenyltrifluorosilane is an excellent reagent for preparing imidate methylide from silylmethyl imidates. Several classical dipolarophiles have been tested, all giving excellent yields.[459]



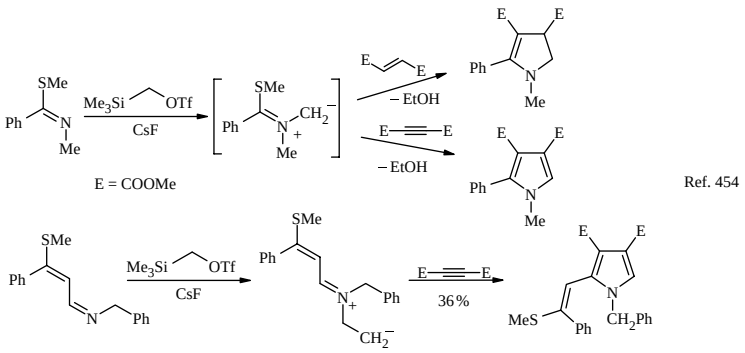
Ref. 459

The importance of the high regiospecificity of the photoinduced [3 + 2]cycloaddition reaction using silylmethylphthalimide should be emphasized. This reaction has opened the way to the synthesis of regio- and stereocontrolled substituted polycyclic compounds.[323,350,460]

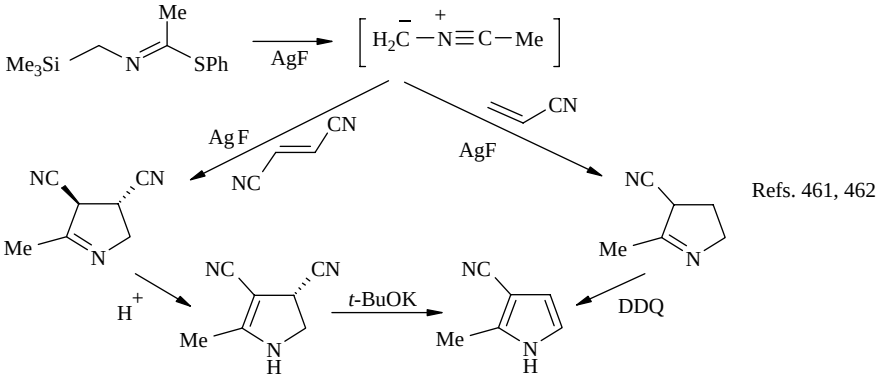


Refs. 323, 350, 460

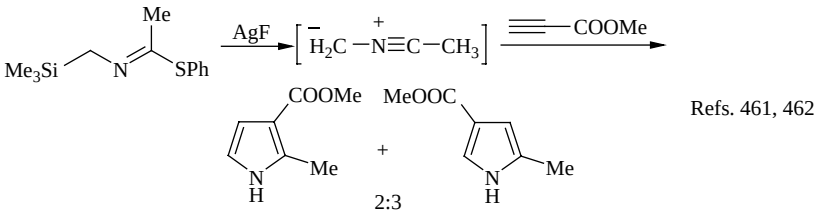
Like imidates, thioimidates were shown to be the precursors of azomethine ylids which lead to the formation of pyrroline and pyrrole derivatives through cycloaddition with dipolarophiles.[454]

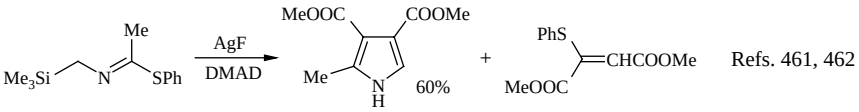


N-(Trimethylsilyl)methylthioimidates, readily obtained, for instance, by heating a 1:1 mixture of (trimethylsilyl)methyl triflate and acetonitrile followed by quenching with thiophenol, are nitrile ylid precursors which undergo facile cycloaddition reactions with dipolarophiles in the presence of a slight excess of silver fluoride to give Δ^1-pyrroline derivatives and pyrroles under further oxidation.[461,462]



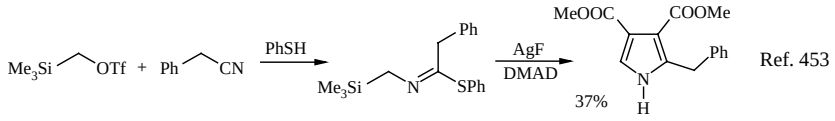
The reaction of the nitrile ylid with methyl propiolate in the presence of silver fluoride leads directly to the pyrrole derivative. In fact a 2:3 mixture of two regioisomers is obtained in contrast to the 1:1 mixture of the same isomers obtained by reaction with the nitrile ylid formed through condensation of methylene carbene with acetonitrile. It has also been observed that this ratio is strikingly dependent on the purity of the silylthioimidate: it changes from 2:3 to 9:1 when an aged sample is used. The reaction with DMAD leads to 2-methyl-3,4-dicarbomethoxypyrrole and a mixture of *cis* and *trans* dimethyl-2-(phenylthio)-2-butanedioate resulting from the addition of thiophenol to DMAD which has to be used in excess (2 equiv.).[461,462]

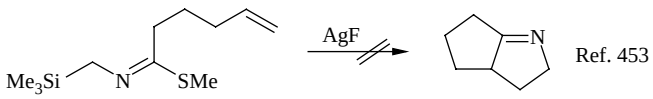


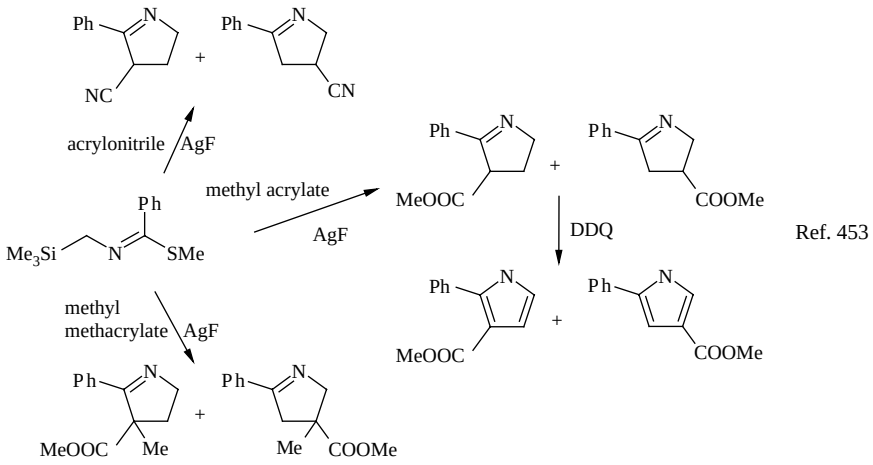


N-(Trimethylsilyl)methylthioimidates, readily obtained by heating a 1:1 mixture of (trimethylsilyl)methyl triflate and phenylacetonitrile followed by quenching with thiophenol, are nitrile ylid precursors which undergo facile cycloaddition reactions with dipolarophiles in the presence of a slight excess of silver fluoride to give pyrroles derivatives. Intramolecular cycloadditions have been attempted with silylmethyl thioimidates bearing an ethylenic (non-activated) or a styrenic moiety, but no adduct has been detected.[453] This contrasts with the known intramolecular cycloaddition occuring when nitrile ylids are generated from photolysis of azirines.[463]

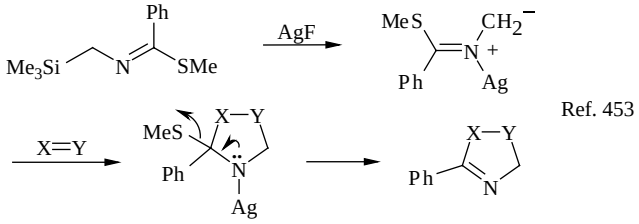
The same thioimidate can be reacted with unsymmetrical dipolarophiles to give mixtures of two regioisomeric pyrroline derivatives where the 2,3-disubstituted compound is predominant.[453]



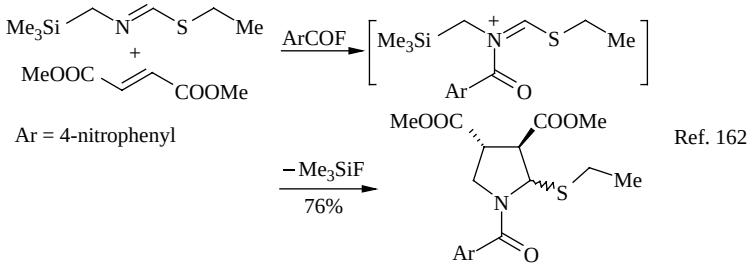




A mechanism accounting for these results was proposed that in fact excludes the intermediacy of a nitrile ylid.[453]

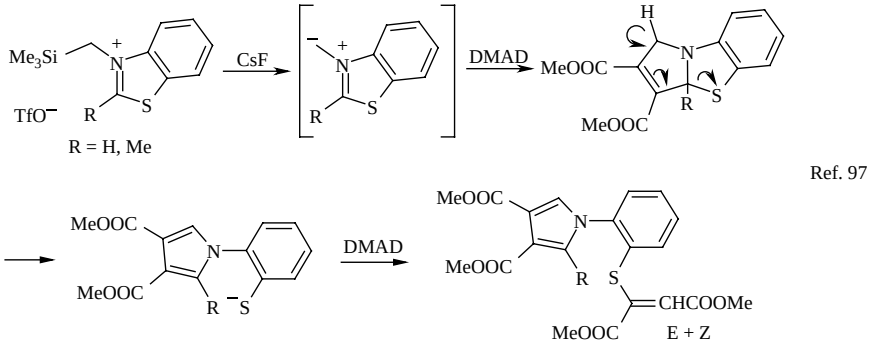


Aroyl fluorides promote dipolar cycloaddition of thioimide with dimethyl fumarate.[162]

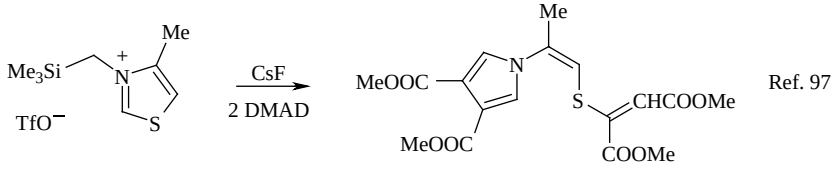


The thioimidate framework can be part of a ring as in benzothiazoles. Treated successively with TMS triflate to quaternarize the nitrogen atom and then with CsF, they give the benzothiazolium ylid which reacts with two equivalent of DMAD to form the corresponding pyrrole where the nitrogen bears an *ortho* vinylthio-substituted phenyl group. This result is explained by the initial formation of the expected cycloadduct which

oxidizes rapidly with the opening of the thiazole ring to leave a phenylthiolate species that undergoes Michael addition to DMAD. A similar reaction pathway occurs with thiazoles.[97]

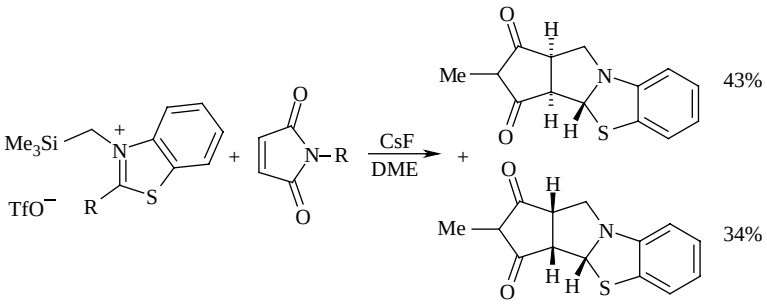


Ref. 97



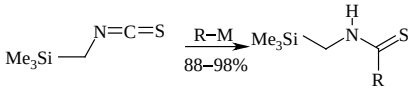
Ref. 97

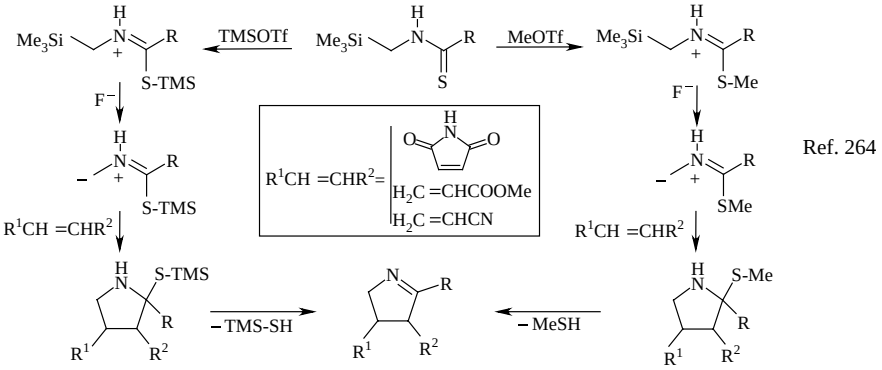
When maleic anhydride is used as the dipolarophile, simple condensation occurs with benzothiazole giving a five-membered cycloadduct as a mixture of *cis* and *trans* isomers.[97]



Ref. 97

Secondary thioamides, precursors of N-protonated azomethine ylids, give Δ^1-pyrroline derivatives (after elimination of thiol). When the dipolarophiles are dissymmetric alkenes, high regioselectivity is obtained. Reaction with alkynes leads to pyrrole derivatives in good to excellent yields and with ArCHO leads regioselectively to 2,5-disubstituted 2-oxazolidines in moderate yields.[264]

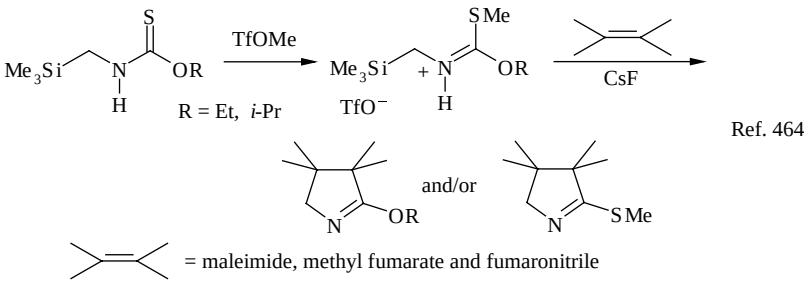




Ref. 264

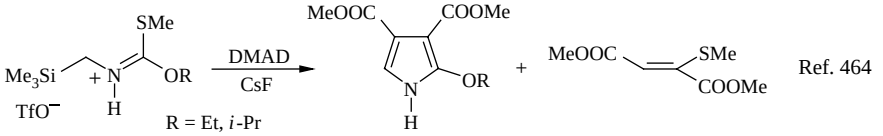
Solvent was acetonitrile or DME. DME was used only in case of MeOTf

Thiocarbamates have also been considered as precursors for the generation of a non-stabilized 1,3-dipole. Referring to the mechanism described for imidates and thioimidate (see above), a difficulty lies in the possibility of elimination of either an alcohol or a thiol. This is confirmed by the formation of a mixture of alkoxy- (elimination of thiol) and thiomethylpyrroline (elimination of alcohol) where the former always predominates. This is in good agreement with the known aptitude of methylthio and alkoxy groups as leaving groups. However, the use DME as the solvent (instead of acetonitrile) favors thio elimination and a much smaller quantity of thio derivative.[464]



Ref. 464

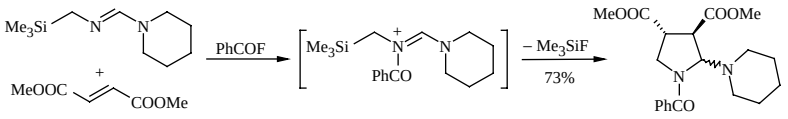
Reaction of these ylids with diaroyl- and aroylacetylenes fails even under forcing conditions. Reaction with DMAD, however, in the presence of cesium fluoride, leads to an alkoxypyrrole (no trace of thiopyrrole was observed) accompanied with the product of the addition of methylthiol to DMAD.[464]



Ref. 464

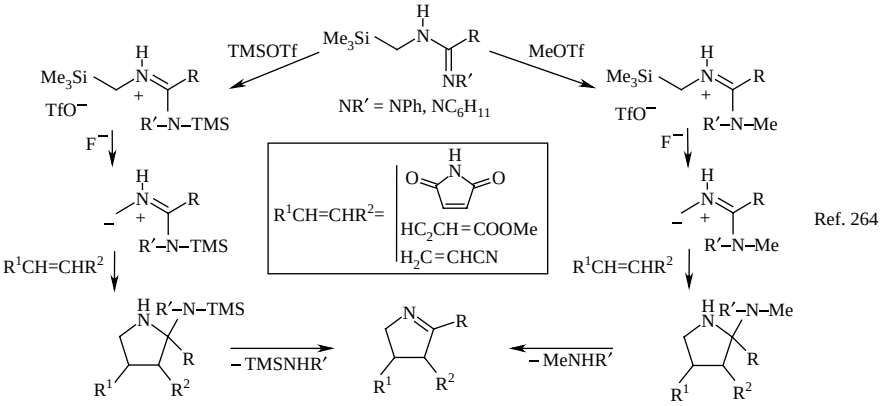
3. Amidines

As in the case of thioimidate, an aroyl fluoride is able to generate an ylid from *N*-trimethylsilylmethyl formamidine.[162]



Ref. 162

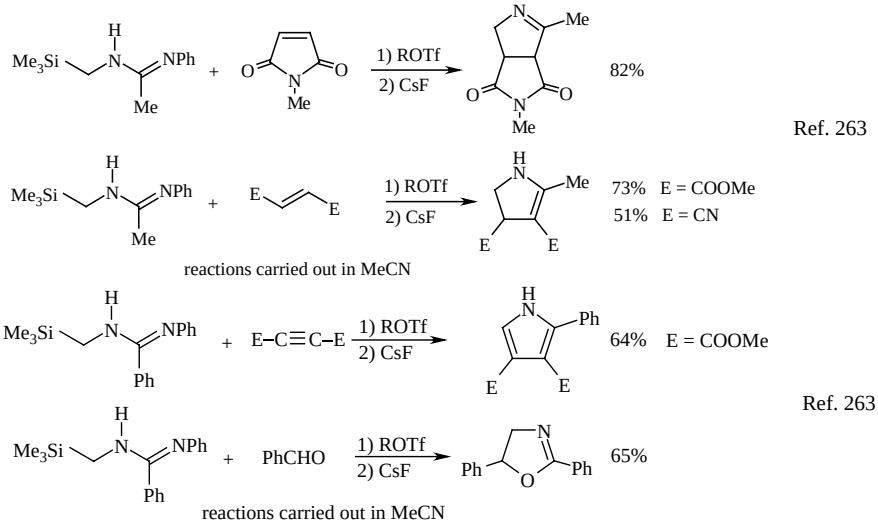
By a process similar to that described for the thioimidates, amidines give an intermediate ylid upon treatment with a triflate. The ylid is easily intercepted with a maleimide to give Δ^1-pyrroline with the elimination of amine.[264]



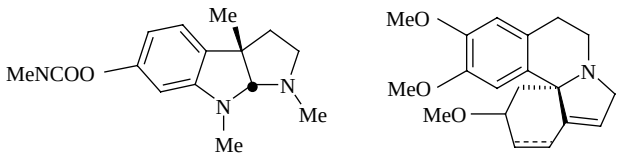
Ref. 264

Solvent was acetonitrile or DME, DME being used only in case of MeOTf

This above result was only obtained with maleimide as the dipolarophile. With dimethyl fumarate and fumaronitrile, Δ^2-pyrrolines are obtained, probably because of the acidity of the hydrogen atoms α- to ester and nitrile functionalities. Reaction with alkynes produces pyrrole derivatives in good to excellent yields and with aromatic aldehydes leads regioselectively to oxazolidines in moderate yields.[263]

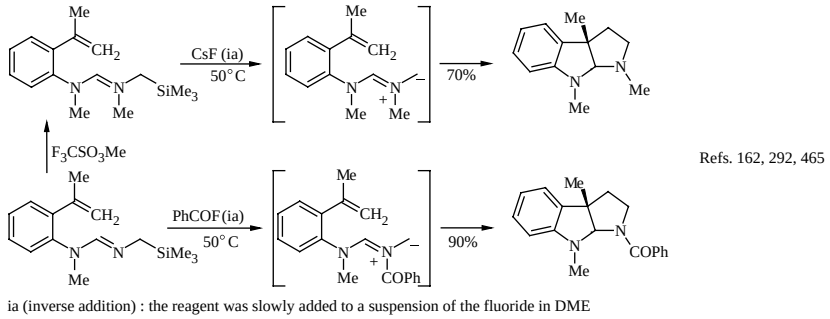


Azomethine ylids derived from amidines undergo internal [3 + 2]cyclization reactions with a styrenic double bond present in the starting amidine. This strategy has been applied to the synthesis of physostigmine and erythramine.

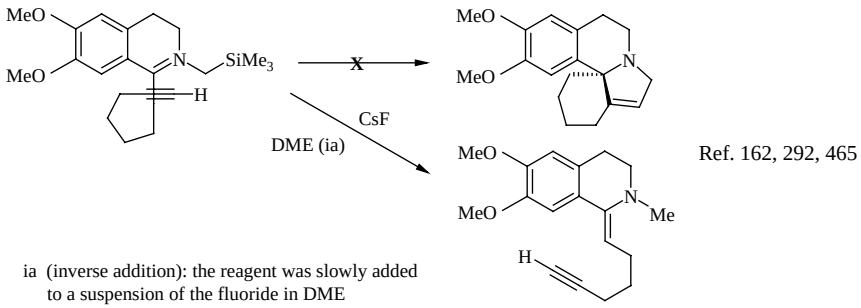


Physostigmine Erythramine

Physostigmine is one of the major alkaloids in calabar bean. It has been shown to inhibit acetylcholinesterase at low concentration and to reverse the toxic effects resulting from diazepam overdose. The phytostigmine skeleton is easily obtained in very good yields from an appropriate non-stabilized imidate methylide.[162,292,465]



Erythramine, a natural alkaloid extracted from bark of Mulungu tree, has a potent curariform activity. Unfortunately, the erythramine skeleton could not be formed using this cyclization process, and the acetylenic enamine is formed instead.[162,292,465]

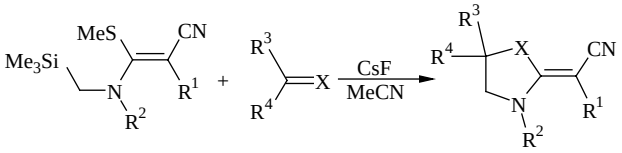


Ref. 162, 292, 465

ia (inverse addition): the reagent was slowly added to a suspension of the fluoride in DME

4. Ketene *N,S*-acetals

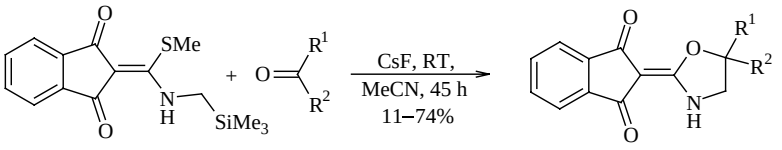
N-(Silylmethyl)-substituted ketene *N*,*S*-acetals are synthetic equivalents of alkylideneazomethine ylids which undergo facile [3 + 2]cycloadditions with aldehydes, ketones and thioketones to form alkylidenepyrrolidine, alkylideneoxazolidine and alkylidenethiazolidine derivatives. *N*-(Silylmethyl)-substituted ketene *N*,*S*-acetals are readily accessible.[466]



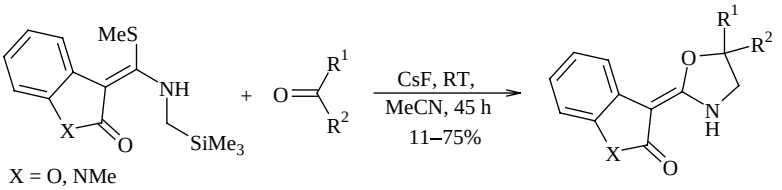
24–77% Ref. 466

X = CR_2, O, S
R^1 = CN, COOMe, COOEt, $CONH_2$,SO_2Ph
R^2 = Me, Et, Bn
R^3 = Aryl
R^4 = H, Aryl

A similar study reports using methylen-1,3-indandione, 2-coumarone and 1-methyloxindole substrates.[467,468]



Ref. 467

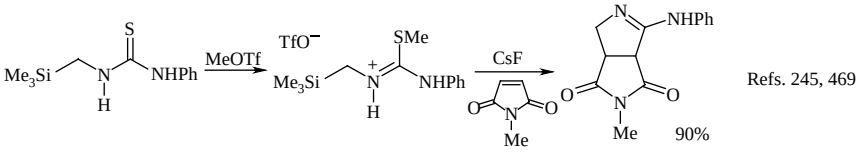


Ref. 468

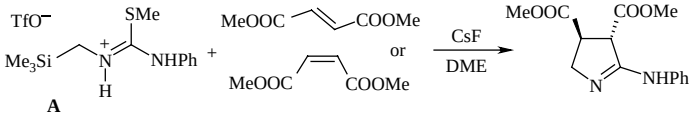
X = O, NMe

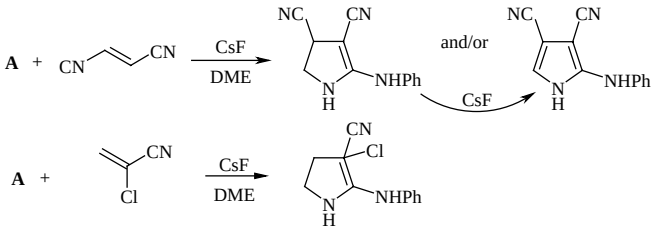
5. Thioureas and isothioureas

N-(Trimethylsilylmethyl)thioureas are readily accessible *via* the addition of an amine to the corresponding isothiocyanate. They are good starting materials for preparing 2-amino-Δ^1-pyrroline derivatives *via* their corresponding azomethine ylids. This is illustrated by condensation with maleimide and different alkenes.[245,469]



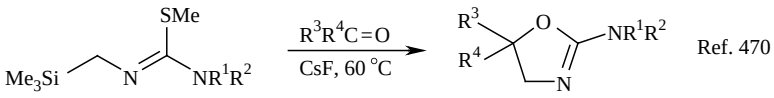
Refs. 245, 469



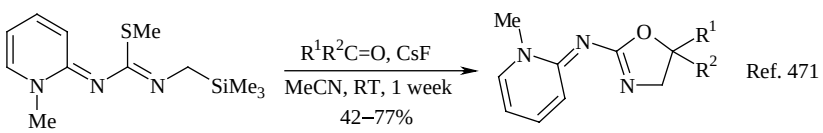


Refs. 245, 469

Aryl- and heteroaryl aldehydes give 2-amino-2-oxazolines, which are otherwise relatively inaccessible.[470,471]

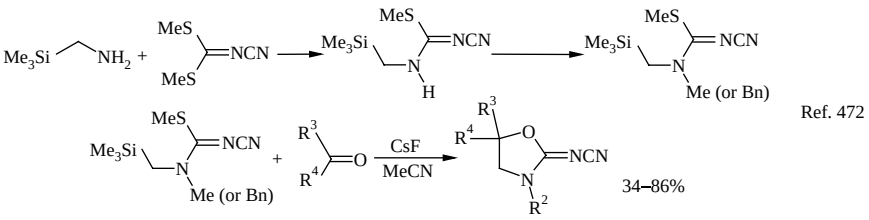


Ref. 470



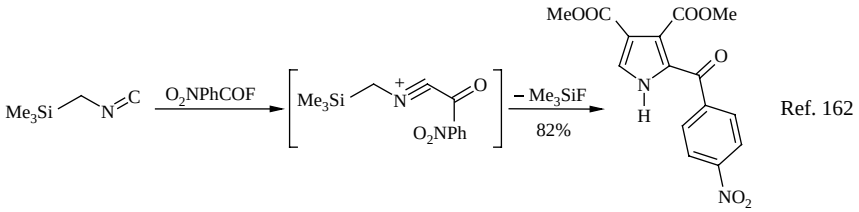
Ref. 471

N-(Trimethylsilylmethyl)isothioureas are readily available. They are easily converted into azomethine ylids (synthetic equivalents of iminoazomethine ylids) which, under reaction with aromatic aldehydes and ketones, undergo facile 1,3-cyloaddition to form iminooxazolidine derivatives.[472]



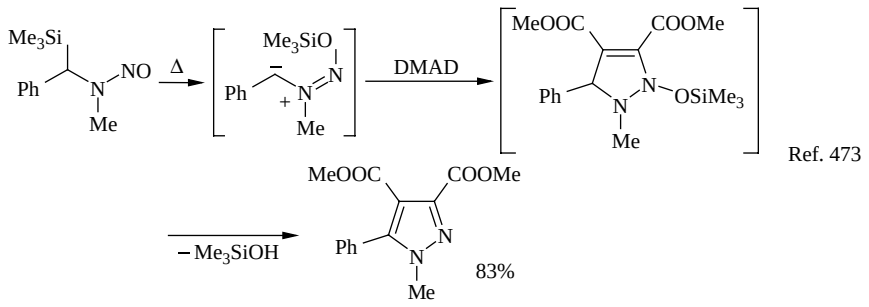
6. Isonitriles

Condensation of an MSMA isonitrile with an aroylfluoride gives a salt which undergoes loss of trimethylsilyl fluoride to form a nitrile ylid. This transient species reacts with DMAD to form 2-aroyl pyrrole in high yield.[162] Substitution of acyl chloride for acyl fluoride in the reaction affords only poor yields of adducts.[465]

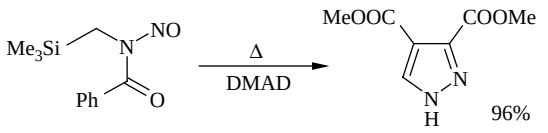


7. Nitrosamines and nitrosamides

N-Methyl-*N*-nitroso-α-(trimethylsilyl)benzylamine reacts thermally with DMAD to give 3,4-dicarbomethoxy-1-methyl-1H-pyrazole. The reaction is highly sensitive to the temperature: upon increasing the temperature from 25 to 110 °C, the reaction time drops from 168 h to 3 min and yields increase from 30 to 100%. No reaction occurs from non-silylated *N*-methyl-*N*-nitrosobenzylamine. Other acetylenic esters have been successfully tested. In contrast, phenylacetylene gives a poor yield of the adduct and diphenylacetylene does not react.[473]



α-(Trimethylsilyl)nitrosobenzamide behaves similarly but the benzoyl group is lost in the process in which 3,4-dicarbomethoxy-1H-pyrazole is obtained quantitatively.[473]



Ref. 473

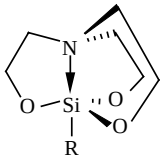
VIII

BIOLOGICALLY ACTIVE SMA

More than half a century ago, silicon, the most abundant element after oxygen on the crust of the Earth, was hardly recognized as having any biological activity. The same was true for many other elements (Ca, Mg, Fe, Zn, Cu, etc.). For a long time, attention was focused on silicones in medicine, pharmacy and surgery because of their biological inertness. Gradually, however, studies devoted to organosilicon compounds as possible drugs were initiated.[474]

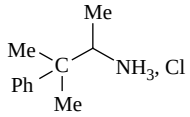
Initially, the purpose was to synthesize sila-analogs of known drugs for comparison of their efficiency and to get information on the mechanism of their action.[475] As investigations continued, an increasing number of biologically active molecules appeared. Perhaps the best known of these molecules are the silatranes, compounds that have no analogous carbon counterpart.[476]

silatranes

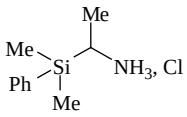


Ref. 476

Among these bioactive molecules, SMA derivatives have held an important place ever since Fessenden showed equivalent biological activities of the chlorohydrates of 3-methyl-3-phenyl-2-aminobutane, a sympathomimetic amine, and 1-dimethylphenysilyl-aminoethane, the silicon analog.[477] Both the enantiomers of this SMA have been synthesized.[478]



1,2-dimethyl-2-phenylpropylamine
(chlorohydrate)



1-dimethylphenylsilylethylamine
(chlorohydrate)

Ref. 477

Several reviews have been published on the bioactivity of organosilicon compounds in general and SMA derivatives in particular. Among these are those of Barcza,[479] Baukov,[480] Kichner,[481] Lukevics,[14b] Ricci,[482] Sakurai,[483] Tacke,[13,484] Voronkov,[485,486] and Wannagat.[487]

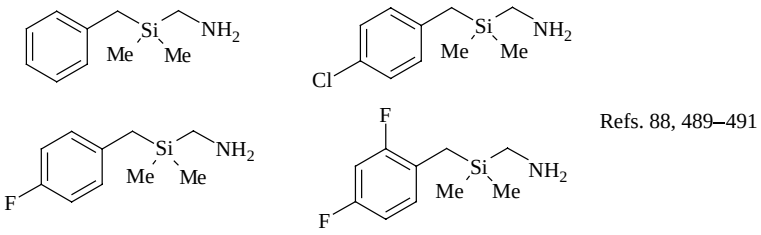
SMA derivatives exhibit a great variety of activities related to humans as well as animals and plants, some of which are detailed below.

A. *Amines*

1. Psychiatric Disorders: Inhibitors of Monoamine Oxidase (MAO)

MAO is an enzyme tightly bound to the outer membrane of mitochondria, closely related to the level of monoamines in the brain. It exists in two forms, A and B. Whereas MAO-A primarily oxidizes noreprinephrine and serotonin, MAO-B preferentially oxidizes dopamine.[488] Recently, an inhibitor of MAO-B as an adjunct to the L-DOPA treatment of Parkinson's disease has been used and L-deprenyl is usually the reference inhibitor for comparison.

Substituted benzylsilylmethylamines have been synthetized[88,489,490] and tested on rat brain MAO as potent and selective (MAO-B versus MAO-A) enzyme activated irreversible inhibitors of rat brain MAO-B *in vitro*.[490,491]

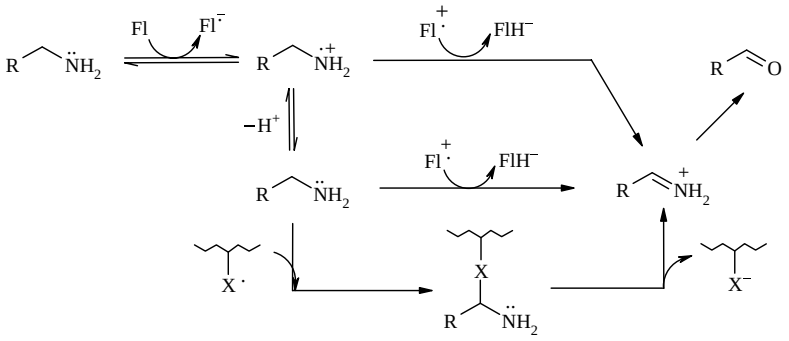


Refs. 88, 489–491

These compounds are shown to be excellent inhibitors of MAO, with a marked preference for MAO-B (selectivity MAO-B/MAO-A $\sim 3 \times 10^3$). Moreover, fluorinated derivatives have a high selectivity of about 100 times greater than that of L-deprenyl, for the monofluoro compound.

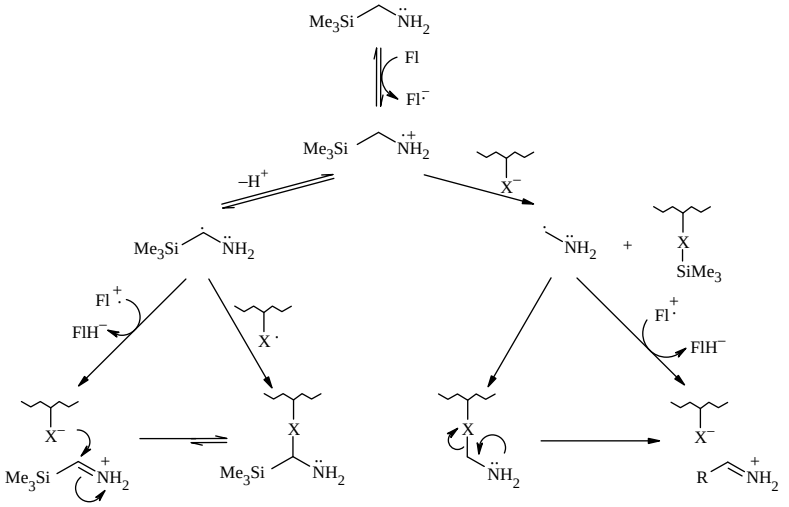
Trimethylsilylmethylamine itself has been shown to exert MAO inactivator activity. This is a remarkable finding, as the molecule is very simple and its activity should rely directly on the S–C–N framework. Oxidation of amines in the brain into aldimines and finally into aldehydes is a normal feature, but in diseases related to MAO, the level of its activity is not controlled inducing depletion of these amines. The mechanism proposed implies electron transfer from flavin (Fl) present in the membrane (〰) of the enzyme. With MSMA, potential mechanisms based on this concept have been proposed.[19,492]

Proposed mechanism for MAO-catalyzed amine oxidation



Ref. 19

Potential pathways for inactivation of MAO by MSMA



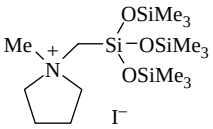
Ref. 19

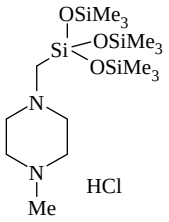
The key point is the deprotonation rather than the desilylation of the MSMA's cation radical, an unprecedented feature. Aimed at giving some support to this mechanism, the amine–flavine electron transfer photochemistry has been studied.[493] Later, a polar mechanistic pathway was established in place of the SET mechanism mentioned above.[494]

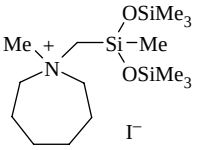
MSMA has also been shown to inactivate bovine plasma amine oxidase (BPAO).[495]

2. Antitumoral

Various [(heteroarylamino)methyl]siloxanes, their hydrochlorides and methiodides have been prepared (see some representative molecules below) and their antimicrobial activity studies. The nature of the heterocycle and number of siloxy groups affect their antitumoral activity.[496] They have also been tested for neurotropic and antimicrobial activity.



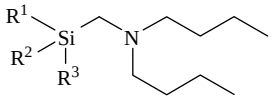




Ref. 496

3. Insect Repellents

The activity of a large series of *N*,*N*-di-*n*-butylaminomethylsilanes has been tested as insect repellents against *X. cheopsis*. The highest activity and the most extensive duration is seen with ethoxy derivatives.[14]



Ref. 14

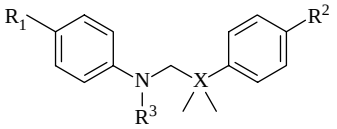
$R^1R^2R^3Si = (Me)_{3-n}(RO)_nSi$

R	*n*	Coefficient of repellent action (%) at dose g/m^2			Duration of action (days) at the dose g/m^2	
		5	20	40	20	40
$(Bu)_2NCH_2CH_2$	1	96	93	93	12	22
MeC=O	1	90	91	95	12	22
Et	1	98	98	100	13	20
Et	2	90	96	98	5	10
Et	3	90	94	75	28	85
Me	3	65	77	75	28	28
Pr	3	53	55	82	0	13
Bu	3	34	75	76	0	1
Me_3Si	1	90	97	96	5	10

4. Antioxidant

N-Aryl SMA (A–E) have been designed and synthesized as new hypocholesterolemic agents with antioxidant properties and compared with a carbon analog (F), vitamin E and probucol.[497,498] Compounds A and B are found to be, *in vitro*, potent inhibitors of copper-induced peroxidation of human LDL, especially when compared to results for vitamin E and probucol. IC_{50} was used as the test of effectiveness and was determined by measuring the extent of lipid peroxidation. The remarkable result was that A has a much stronger antioxidant effect than its carbon analog. Comparison of D and E shows that an electron-withdrawing group (CF_3) confers more antioxidant effect when substituted on the aryl

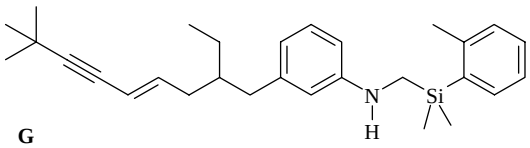
silicon ring than on the arylamine. Substitution of the arylsilicon ring by the electron-releasing OCH_3 group reduces the antioxidant property. This is in accordance with the stability of the corresponding cation-radical and, therefore, these SMA derivatives are believed to act as "chain breaking" antioxidants, because these molecules are oxidized more rapidly than lipids and the products formed are less prone to propagate radical reactions.[497]



Ref. 497

Compound	X	R^1	R^2	R^3	IC_{50} (μM)
A	Si	H	H	H	7.8
B	Si	OMe	H	H	3.0
C	Si	H	H	Et	15
D	Si	CF3	H	Et	100
E	Si	H	CF_3	H	20
F	C	H	H	H	100
Vitamin E	–	–	–	–	10
Probucol	–	–	–	–	5.3

However, none of compounds **A**–**E** was found to be able to inhibit squalene epoxidase. On the contrary, compound **G** has been shown to be an excellent antioxidant in this reaction. It presents a potential cure for atherosclerosis and other diseases related to oxidation.[497]



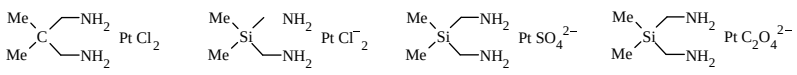
G

Ref. 497

B. *Polyamines*

1. Antitumoral Activity

The so-called "cis-platin" has been the subject of numerous studies related to its antitumoral activity (anti-cancerous). For comparison, "sila-cis-platin" under the form of its salts (chloride **A**, sulfate **B** and oxalate **C**) has been prepared and its anti-tumor activity tested against L-1210 leukemia in male mice.[499,500]



cis-platin A B C

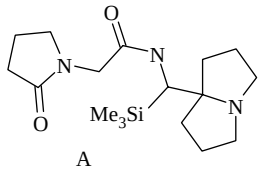
Ref. 499

Salt	A				B				C			cis-platine
Dose	5	10	15	20	5	10	15	20	5	10	15	4
T/G%	>273	>330	>302	>327	>271	>297	165	106	152	197	144	242
S/total	1/4	2/4	2/4	2/4	0/4	0/4	0/4	0/40/4	0/4	0/4	0/4	0/4

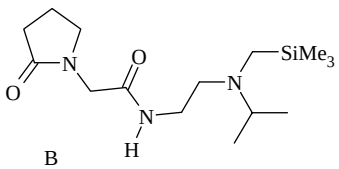
Dose: mg/kg. T/G% = (T/G) × 100, with mean survival time of the treated group (T) to that of the control group (G). S/total = number of survivors (*S*) after 30 days versus total number animals tested.

2. Memory Disruption

Molecules **A** and **B** were synthesized in order to compare their eventual activity against cerebral dysfunction, namely, memory disruption, with that of reference compound piracetam. Tested on mice, pyrrolizidine (**A**) delays this dysfunction better than piracetam (27.8% versus 21.7%). The ethylenediamine derivative (**B**) behaves similarly.[501]



A

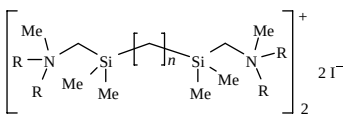


B

Ref. 501

3. Curare-like Activity

A series of ω-diamines and their methiodides have been synthesized and the potential curare-like activity of these salts has been evaluated in mice and compared to that of their C-analog (CH_2 instead of $SiMe_2$), decamethoniumiodide.[76,502] LD_{50} values are found to be 3–6 times greater than that of the reference compound (1 mg/kg). Maximal calculated interatomic distances N···N (in angstroms) are found very close to that of the carbon analogs [N···N(CH_2)], explaining the similarities of their muscle relaxant activity.



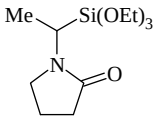
n	NR_2	mg/Kg	N...N	N...N (CH_2)
4	NMe_2	6.67	12.3	12.5
5	NMe_2	6.14	13.5	13.8
6	NMe_2	6.43	14.8	15.0
5		2.93		

Ref. 76

C. *Cyclic SMA*

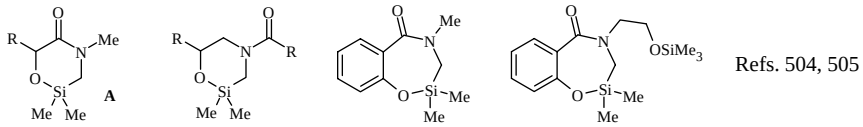
1. Silylmethylpyrrolidones: Neurotropic and Psychotropic Activity

N-[(α-Triethoxysilyl)ethyl] pyrrolidinone, prepared by $(EtO)_3Si-H$ addition to *N*-vinyl pyrrolidone in the presence of acetylacetonatodicarbonylrhodium, has been evaluated in terms of its neurotropic and psychotropic activity in mice.[503]



2. Monosilamorpholinones: Antihypoxic Activity against Chlorphos-poisoning

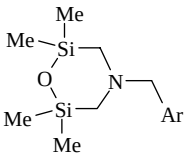
A series of 2-sila-5-morpholinones have been prepared and their biological activity evaluated. They are found to exhibit certain antihypoxic property in animals tested against chlorphos-poisoning.[504,505] 2,2,4-Trimethyl-6-phenyl-2-sila-5-morpholinone (**A** R = Ph) displays a cold-resistant activity.[504]



Refs. 504, 505

3. Disilamorpholines: Antifertility

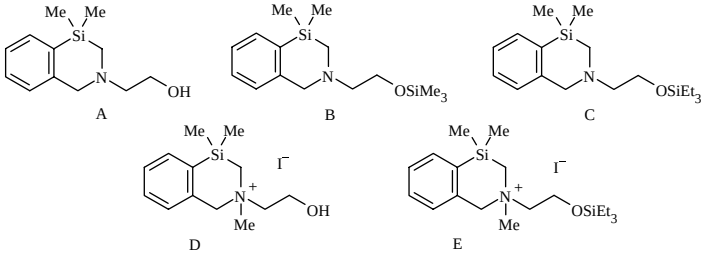
Disilamorpholines constitute another family of bioactive compounds. They have superior activity and are more easily prepared than their C-analogs. A series of compounds have been patented as muscle relaxants.[506] 4-(*m*-Methoxybenzyl)-1-oxa-4-aza-2,2,6,6-tetramethyl-2,6-disilacyclohexane, chosen for clinical muscle relaxant studies,[479] was found to induce antifertility in male mammals (dogs). After administration of the drug (12–120 mg/kg daily) is stopped, their sperm count returns to normal and no evidence of testicular damage or aspermatogenesis is observed.[507]



4. Silaisoquinolines: Neurotropic Activity

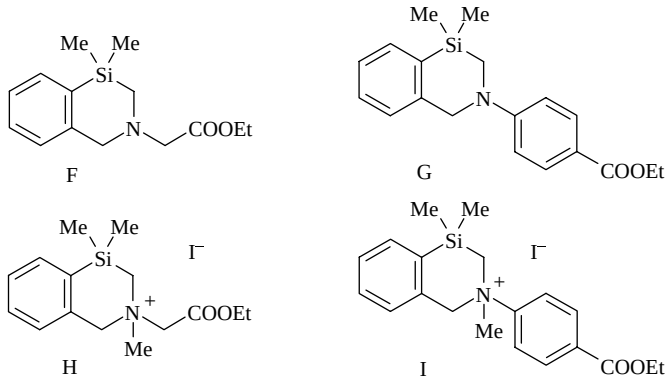
In order to evaluate the consequences of the replacement induced by substituting a $SiMe_2$ group for a methylene group on their biological activity, two series of tetrahydrosilaisoquinolines and tetrahydroisoquinolines derivatives have been synthesized and compared.[508–511]

Aminoethanols and their methiodides



Refs. 509–511

Aminoacids and their methiodides

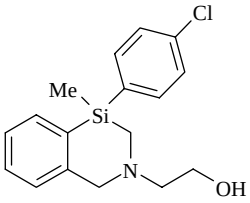


Refs. 509–511

All of the investigated aminoalcohol derivatives **A**–**E** possess antihypoxic activity to some degree (in the 30–55% range). However, differences appear with other neurotropic properties. Thus, the greatest depriming activity is encountered for **A**–**C**, with structure variations having little influence, on tone of skeletal and coordination movements (alkoxysilanes were supposed to pass through lipidic membranes most easily). Compounds **A**–**C** and methiodides do not possess analgesic properties although **E** does. Compounds **A**–**C** reduce the duration of ethanol-induced narcosis whereas **E** increases it. All compounds **A**–**E** have anticonvulsive action on clonic and tonic Corazole-induced convulsions with a most marked activity for **E** among the methiodides. Interestingly, all of these silicon derivatives exhibit a greater activity on processes of memory than do their carbon analogs. Thus, **A** completely (100%) prevents retrogade amnesia and improves the period of training by a factor of 2.4. Methiodides **D** and **E** decrease the level of retrograde amnesia and prolong the latent period of training. Acute toxicity has been evaluated. Silylation of the alcohol (**A** > **B** > **C**) decreases the acute toxicity and these silaisoquinolines are more toxic than their carbon analogs by a factor of 1.5–4.[509,510]

A comparison between aminoalcohol and aminoacid derivatives **F**–**I** reveals that the latter have equal potency in locomotive activity and muscles tests. They have prolonged ethanol anesthesia and are active only in the tonic phase of corazole convulsion tests. Methiodide **H** is highly effective against hypoxia.[511]

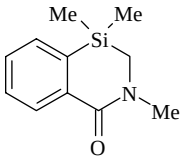
Arylsilaisoquinolines have been found useful as sedatives.[512]



Ref. 512

5. Silaisoquinolones: Sleep Inducer and Antiobesity

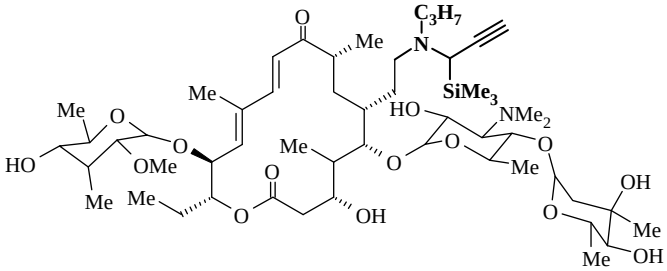
Small structural changes from these quinolines to quinolones shift the activity to inducing sleep and antiobesity in mice.[513]



Ref. 513

D. *Macrolide*

Biological activity of the macrolide derived from tylosin against *Pasteurella multocida* and *P. haemolytica* (in particular) *in vitro* and *P. multicida* (in particular) *in vivo* has been tested on chicks. Remarkable inhibition of these viruses is obtained. It is also found active against *Staphylococcus aureus*, *Streptococcus pyogenes and pneumoniae*, *Haemophilus influenzae*, *Mycoplasma gallisepticum*, *synoviae*, *hyorhinis* and *hyopneumoniae*.[222]

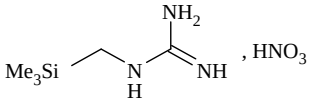


Ref. 222

E. *Silylmethylguanidinium Salts*

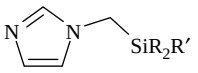
Trimethylsilylmethylguanidinium nitrate, which is easily prepared by displacement of the pyrazole moiety from 1-guanyl-3,5-dimethylpyrazole by MSMA, has been found to

be an effective anti-inflammant at 2–200 mg/kg (oral administration).[514]



F. *Silylmethylimidazoles*

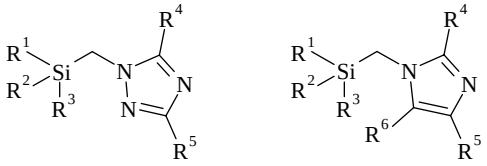
Silylmethylimidazoles, variously substituted at silicon, have been prepared. They are reported to be effective bactericides and fungicides.[515] See Section VIII.G for use of other silylmethyl imidazoles as fungicides.



R = Me, Ph
R′ = Ph, Me

G. *Triazoles: Fungicides*

Two decades ago, the effectiveness of silylmethyltriazoles and imidazoles as fungicides in plants was reported for the first time. These compounds are easily synthesized by condensation of suitable chloromethylsilanes with suitable imidazoles or 1,2,4-triazoles.[516]

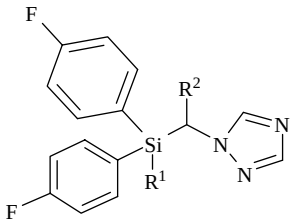


1. Triazoles

This preliminary work initiated a number of other investigations dealing with the synthesis and the evaluation of these types of derivatives in connection with an anthology of substitutents.[83,90,517–520]

The triazoles thus obtained are found to efficiently control a broad spectrum of plant diseases, particularly foliar pathogens of ornamental, vegetable, field, cereal and fruit crops, such as *Puccinia recondita* (wheat), *Sphaerotheca fuliginea* (cucumber), *Erisyphe graminis*, *Podosphaera leucotricha*, *Venturia inaequalis* (apple),[521] *Pyricularia orizae*, *Cercosporidium personatum* (peanut), *Bipolaris ryzae* (rice), *Cercospora arachidicola*, *Cercospora beticola*, *Monalinia fructicola* and *Rhizoctonia solani*. Among these derivatives, compound ($R^1 = H$, $R^2 =$ allyl) is the only one active against *Rhizoctonia*

solani (rice) whereas compound ($R^2 = H$, $R^1 = OSiMe_3$) is inactive against the same *Rhizoctonia solani.* A review article has been published on this topic.[522]

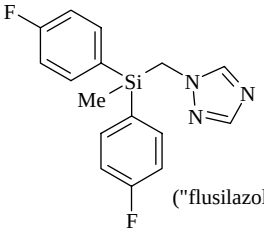


Ref. 90

$R^2 = H$, R^1 = allyl, H, $OSiMe_3$;
$R^2 = Me$, R^1 = allyl

2. Flusilazole

Among these compounds, the derivative in which $R^1 = Me$ and $R^2 = H$, the so-called "flusilazole", has met with great success. On the basis of patented procedures, a laboratory preparation of this triazole has been published.[18]



Bis(4-fluorophenyl)-methyl (1H-1,2,4-triazol-1-y1-methyl)silane ("flusilazole"), DPX H 6573

This fungicide is now prepared at the industrial level and is an ingredient in almost all of the fungicidal combinations on the market, Nustar®, Pundh®, Olymp®, Benocap®, among others. It has been shown to be successful in the treatment of *P. alba* (apple),[523] *Taphrina deformans* (peach leaf curl)[524] and *Erisiphe polygone* (powdery mildew), for example.[525]

3. Compositions Containing Flusilazole

Different laboratory or commercial mixtures of flusilazole with other fungicides have been tested, giving results exceeding those obtained without flusilazole. Among the increasing number of studies are those, for example, on *cercosporiasis* (banana),[526] *septoria tritici* (wheat leaf blotch and riband wheat).[527,528]

IX

CONCLUSIONS

Although this review-article does not pretend to be exhaustive, it reflects the richness of the chemistry of silylmethylamines. It also shows how from structural problems, such as whether or not there is any through-space interaction between Si and N atoms, studies

have led progressively through innovative synthetic applications to biological uses of properly designed SMA derivatives. In spite of an impressive number of studies, the author is convinced that the chemistry of SMA will continue to deserve much attention from organic synthetic chemists and biochemists.

Acknowledgements

The author is grateful to the Ministère de la Jeunesse, de l'Education Nationale et de la Recherche, to the Centre National de la Recherche (CNRS) and to the Region Aquitaine for support of our work in silylmethylamino derivatives. Collaboration with Jesus Maria Aizpurua, Séphane Grelier, Thierry Constantieux and Frédéric Fortis is deeply acknowledged as is the assistance of my colleague Marc Birot and of Gerald Larson, Gelest Co., in the preparation of the electronic version of this manuscript.

References

(1) (a) Picard, J. P.; Elyusufi, A.-A.; Calas, R.; Dunoguès, J.; Duffaut, N. *Organometallics* **1984**, *3*, 1660. (b) Picard, J.-P.; Aizpurua, J. M.; Elyusufi, A.; Kowalski, P. *J. Organometal. Chem.* **1990**, *391*, 13.
(2) (a) See, for instance: Brook, A. G.; Golino, C.; Mattern, E. *Can. J. Chem.* **1978**, *56*, 2286. (b) Sicker, U.; Meller, A.; Maringgele, W. *J. Organometal. Chem.* **1982**, *231*, 191. (c) Ito, Y.; Suginome, M.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1991**, *113*, 8899.
(3) See for example: Häbich, D.; Effenberger, F. *Synthesis* **1979**, 841.
(4) See for example: Moreau, C.; Serein-Spirau, F.; Bordeau, M.; Biran, C. *Synth. Commun.* **1998**, *28*, 3403.
(5) (a) For chemistry of trimethylsilyldiazomethane, see: Shioiri, T.; Aoyama, T. *Adv. Use Synthons Org. Chem.* **1993**, *1*, 51; and references cited therein. (b) Shioiri, T.; Aoyama, T. *J. Synth. Org. Chem. Jpn* **1986**, *44*, 149; *Chem. Abstr.* **1986**, *104*, 168525. (c) Shioiri, T.; Aoyama, T.; Mori, S. *Org. Syntheses* **1990**, *68*, 1. (d) Anderson, R.; Anderson, S. Trimethylsilyldiazomethane, G. L. Larson, Vol. 1, *Advances in Silicon Chemistry*, JAI Press, 1991, 303–326.
(6) Picard, J. P. *Can. J. Chem.* **2000**, *78*, 1363.
(7) Aizpurua, J. M.; Palomo, C. Silyl alcohols, ethers, and amines, (I. Fleming, S. V. Ley, Eds.), Vol. 4.4, *Science of Synthesis: Silicon Compounds*, Thieme Verlag, Stuttgart, 2001. p. 595.
(8) (a) See also: Sato, Y. *Yuki Gosei Kagaku Kyokaishi* **1978**, *36*, 834; *Chem. Abstr.* **1979**, *90*, 55000. (b) Sato, Y. *Nagoya-shiritsu Daigaku Yakugakubu Kenkyu Nenpo* **1984**, *32*, 1; *Chem. Abstr.* **1985**, *103*, 160550.
(9) Noll, J. E.; Speier, J. L.; Daubert, B. F. *J. Am. Chem. Soc.* **1951**, *73*, 3867.
(10) Sommer, L. H.; Rocket, J. *J. Am. Chem. Soc.* **1951**, *73*, 5130.
(11) Patel, P.; Joule, J. *J. Chem. Soc., Chem. Commun.* **1985**, 1021.
(12) Katritzky, A. R.; Sengupta, S. *Tetrahedron Lett.* **1987**, *28*, 5419.
(13) Tacke, R.; Wannagat, U. Syntheses and properties of bioactive organo-silicon compounds, *Top. Curr. Chem.* **1979**, *84*, 1.
(14) (a) Lukevics, E.; Dremona, V. P.; Simchenko, L. I.; Voronkov, M. G. *Khimiko-Farmatsevticheskii Zh.* **1974**, *8*, 29; *Chem. Abstr.* **1975**, *82*, 57805. (b) Lukevics, E. Biological activity of nitrogen-containing organosilicon compounds (G. Bendz, I. Lindqvist, Eds.) *Biochemistry of Silicon and Related Problems (Nobel Symposium)*, Plenum Press, New York 1978, 435.
(15) Mamayeva, Ye. A.; Agafonova, O. V.; Negrebetsky, V. N.; Shipov, A. G.; Baukov, Yu. I.; Losev, A. S. *Khim. Farm. Zh.* **1994**, *28*, 26; *Chem. Abstr.* **1995**, *122*, 10104.
(16) Barcza, S. US Patent 4132725 (to Sandoz), **1979**; *Chem. Abstr.* **1979**, *90*, 121795.
(17) Moberg, W.K. US Patent 4510136 (to du Pont de Nemours), **1985**; *Chem. Abstr.* **1986**, *104*, 207438.
(18) Tacke, R.; Becker, B.; Schomburg, D. *Appl. Organometal. Chem.* **1989**, *3*, 133.
(19) Banik, G. M.; Silverman, R. B. *J. Am. Chem. Soc.* **1990**, *112*, 4499.
(20) (a) For information on *N*-pentacoordinated silicon, see, for example: Pestunovich, V.; Kirppichenko, S.; Voronkov, M. G. Silatranes and their tricyclic analogues, (Z. Rappoport, Y. Apeloïg, Eds.), Vol. II, *The Chemistry of Organic Silicon Compounds*, Wiley, Chichester, UK, 1998, p. 1447; Chapter 24.

(b) Corriu, R. J. P.; Young, J. C. Hypervalent Silicon Compounds, (S. Patai, Z. Rappoport, Eds.) *The Chemistry of Organic Silicon Compounds*, Wiley, Chichester, UK, 1989, p. 1241; Part II, Chap. 20.
(21) Noll, J. E.; Daubert, B. F.; Speier, J. L. *J. Am. Chem. Soc.* **1951**, *73*, 3871.
(22) Andrianov, K. A.; Kopylov, V. M.; Chernyshev, A. I.; Andreeva, S. V.; Shragin, I. S. *Zh. Obshch. Khim.* **1975**, *45*, 351; *Chem. Abstr.* **1975**, *82*, 111427.
(23) (a) Lukevics, E.; Voronkov, M. G.; Shestakov, E. E.; Pestunovich, A. E. *Zh. Obshch. Khim.* **1971**, *41*, 2218. (b) Lukevics, E.; Voronkov, M. G.; Shestakov, E. E.; Pestunovich, A. E. *J. Gen. Chem. USSR* **1971**, *41*, 2243; *Chem. Abstr.* **1972**, *76*, 98875.
(24) Fialova, V.; Bazant, V.; Chvalovsky, V. *Coll. Czech. Chem. Commun.* **1973**, *38*, 3837; *Chem. Abstr.* **1974**, *80*, 81792.
(25) Popowski, E.; Zingler, G.; Kelling, H. *Z. Chem.* **1974**, *14*, 289; *Chem. Abstr.* **1974**, *81*, 1196724.
(26) (a) Voronkov, M. G.; Kashik, T. V.; Lukevits, E. Ya.; Deriglazova, E. S.; Pestunovich, A. E.; Moskovich, R. Ya. *Zh. Obshch. Khim.* **1974**, *44*, 778; *J. Gen. Chem. USSR*, **1974**, *44*, 749; *Chem. Abstr.* **1974**, *81*, 24871. See also:. (b) Voronkov, M. G.; Kashik, T. V.; Lukevits, E. Ya.; Deriglazova, E. S.; Pestunovich, A. E. *Zh. Obshch. Khim.* **1975**, *45*, 2200; *J. Gen. Chem. USSR*, **1975**, *45*, 2162; *Chem. Abstr.* **1976**, *84*, 43049. (c) Voronkov, M. G.; Kashik, T. V.; Deriglazova, E. S.; Lukevits, E. Ya.; Pestunovich, A. E.; Sturkovich, R. Ya. *Zh. Obshch. Khim.* **1976**, *46*, 1522; *J. Gen. Chem. USSR*, **1976**, *46*, 1487; *Chem. Abstr.* **1975**, *85*, 192013.
(27) Papouskova, Z.; Fialova, V.; Chvalovsky, V. *Coll. Czech. Chem. Commun.* **1979**, *44*, 2828.
(28) Egorochkin, A. N.; Skobeleva, S. E.; Sevast'yanova, E. I.; Kosolapova, I. G.; Sheludyakov, V. D.; Rodionov, E. S.; Kirilin, A. D. *Zh. Obshch. Khim.* **1976**, *46*, 1795; *Chem. Abstr.* **1977**, *86*, 54798.
(29) Pola, J. (V. Chvalovsky, J. M. Bellama, Eds.) *Carbon-Functional Organosilicon Compounds*, Plenum Press, New York, 1984. p. 55–59.
(30) Lukevics, E.; Sleiksa, I.; Liepins, E.; Shats, V. D.; Zicmane, I.; Purvina, A. *Geterosikl. Soedin.* **1991**, 1644; *Chem. Abstr.* **1993**, *118*, 102039.
(31) Brodskaya, E. I.; Voronkov, M. G.; Belyaeva, V. V.; Baryshok, V. P.; Lazareva, N. F. *Zh. Obshch. Khim.* **1993**, *63*, 2252; *Chem. Abstr.* **1994**, *121*, 205462.
(32) Shea, K. J.; Gobeille, R.; Bramblett, J.; Thompson, E. *J. Am. Chem. Soc.* **1978**, *100*, 161.
(33) Popowski, E.; Zingler, G. *Z. Chem.* **1981**, *21*, 139; *Chem. Abstr.* **1981**, *95*, 79852.
(34) Ponec, R.; Chvalovsky, V.; Voronkov, M. G. *J. Organometal. Chem.* **1984**, *264*, 163.
(35) Ponec, R. (V. Chvalovsky, J. M. Bellama, Eds.) *Carbon-Functional Organosilicon Compounds*, Plenum Press, New York, 1984. p. 271–275.
(36) Mitzel, N. W.; Kiener, C.; Rankin, D. W. H. *Organometallics* **1999**, *18*, 3477.
(37) Negrebetsky, V. V.; Baukov, Yu. I. *Russ. Chem. Bull.* **1997**, *46*, 1807; *Chem. Abstr.* **1998**, *128*, 140737.
(38) Kowalski, J.; Lazocki, Z. *J. Organometal. Chem.* **1976**, *116*, 75.
(39) Onan, K. D.; McPhail, A. T.; Yoder, C. D.; Hillyard, R. W. Jr. *J. Chem. Soc., Chem. Commun.* **1978**, 209.
(40) Hillyard, R. W. Jr.; Ryan, C. M.; Yoder, C. H. *J. Organometal. Chem.* **1978**, *153*, 369.
(41) Yoder, C. H.; Ryan, C. M.; Martin, G. F.; Ho, F. S. *J. Organometal. Chem.* **1980**, *190*, 1.
(42) Pestunovich, V. A.; Albanov, A. I.; Larin, M. F.; Voronkov, M. G.; Kramarova, E. P.; Baukov, Yu. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1980**, 2178; *Chem. Abstr.* **1981**, 94, 29677.
(43) Albanov, A. I.; Baukov, Yu. I.; Voronkov, M. G.; Kramarova, E. P.; Larin, M. F.; Pestunovich, V. A. *Zh. Obshch. Khim.* **1983**, *53*, 246; *Chem. Abstr.* **1983**, *98*, 215656.
(44) (a) Pestunovich, V. A.; Kalikhman, I. D.; Baukov, Yu. I.; Bannikova, O. B.; Albanov, A. I.; Belousova, L. I.; Kramarova, E. P.; Shipov, A. G.; Voronkov, M. G. *Metallorg. Khim.* **1988**, *1*, 719; *Chem. Abstr.* **1990**, *111*, 134346. (b) Kalikhman, I. D.; Albanov, A. I.; Bannikova, O. B.; Belousova, L. I.; Voronkov, M. G.; Pestunovich, V. A.; Shipov, A. G.; Kramarova, E. P.; Baukov, Yu. I. *J. Organometal. Chem.* **1989**, *361*, 147.
(45) (a) Shipov, A. G.; Kramarova, E. P.; Baukov, Yu. I. *Zh. Obshch. Khim.* **1994**, *64*, 1220; *Chem. Abstr.* **1995**, *122*, 314629. (b) Kramarova, E. P.; Shipov, A. G.; Negrebetskii, Vad. V.; Baukov, Yu. I. *Russ. J. Gen. Chem.* **1997**, *67*, 1315; *Chem. Abstr.* **1998**, 128, 321679.
(46) (a) See, for instance: Macharashvili, A. A.; Baukov, Yu. I.; Kramarova, E. P.; Oleneva, G. I.; Pestunovich, V. A.; Struchkov, Yu. T.; Shklover, V. E. *Zhur. Strukt. Khim.* **1987**, *28*, 114; *Chem. Abstr.* **1988**, *108*, 29802. (b) Macharashvili, A. A.; Shklover, V. E.; Struchkov, Yu. T.; Voronkov, M. G.; Gostevskii, B. A.; Kalikhman, I. D.; Bannikova, O. B.; Pestunovich, V. A. *Metallorg. Khim.* **1988**, *1*, 1131; *Chem. Abstr.* **1990**, *112*, 7552. (c) Macharashvili, A. A.; Shklover, V. E.; Struchkov, Yu. T.;

Pestunovich, V. A.; Baukov, Yu. I.; Kramarova, E. P.; Oleneva, G. I. *Zhur. Strukt. Khim.* **1988**, *29*, 121; *Chem. Abstr.* **1989**, *110*, 121. (d) Extension to ureas: Voronkov, M. G.; Pestunovich, A. E.; Albanov, A. I.; Vlassova, N. N.; Pestunovich, V. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1989**, 2841; *Chem. Abstr.* **1990**, *113*, 6424. (e) Bassindale, A. R.; Glynn, S. G.; Jiang, J.; Parker, D. J.; Turtle, R.; Taylor, P. G.; Brown, S. S. D.; (N. Auner, J. Weis, Eds.), Vol. II, *Organosilicon Chemistry: from Molecules to Materials*, Wiley-VCH, 1996, 411. (f) Albanov, A.; Bassindale, A.; Belogolova, E.; Chipanina, N.; Gavrilova, G.; Lazareva, N.; Pestunovich, V.; Sidorkin, V.; Taylor, P.; Turchaninov, V. *112th Int. Symp. Org. Chem.* **1999**, Sendaï (Japan) Abstr. P54 p.171. (g) Extension to piperazinediones: Shipov, A. G.; Artamkina, O. B.; Kramarova, E. P.; Oleneva, G. I.; Baukov, Yu. I. *Zh. Obshch. Khim.* **1991**, *61*, 1914; *Chem. Abstr.* **1992**, *116*, 214581. (h) Extension to oxazolidinones: Negrebetskii, V. V.; Kramarova, E. P.; Shipov, A. G.; Baukov, Yu. I. *Russ. J. Gen. Chem.* **2000**, *70*, 488; *Chem. Abstr.* **2000**, *133*, 335266. (i) Extension to diacylamides: Kalikhman, I. D.; Bannikova, O. B.; Gostevskii, B. A.; Vyazankina, O. A.; Vyazankin, N. S.; Pestunovich, V. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1985**, 1688; *Chem. Abstr.* **1986**, 104, 148977. (j) Belousova, L. I.; Gostevskii, B. A.; Kalikhman, I. D.; Vyazankina, O. A.; Bannikova, O. B.; Vyazankin, N. S.; Pestunovich, V. A. *Zh. Obshch. Khim.* **1988**, *58*, 407; *Chem. Abstr.* **1989**, *110*, 114908.

(47) Baukov, Yu. I.; Kramarova, E. P.; Shipov, E. P.; Oleneva, G. I.; Artamkina, O. B.; Albanov, A. I.; Voronkov, M. G.; Pestunovich, V. A. *Zh. Obshch. Khim.* **1989**, *59*, 127; *Chem. Abstr.* **1990**, *112*, 56003.

(48) (a) Sidorkin, V. F.; Vladimirov, V. V.; Voronkov, M. G.; Pestunovich, V. A. *THEOCHEM* **1991**, *74*, 1; *Chem. Abstr.* **1991**, *115*, 49789. (b) Mozzhukhin, A. O.; Antipin, M. Yu.; Struchkov, Yu. T.; Shipov, E. P.; Kromarova, E. P.; Baukov, Yu. I. *Metallorg. Khim.* **1992**, *5*, 917; *Chem. Abstr.* **1993**, *118*, 80993.

(49) (a) Macharashvili, A. A.; Baukov, Yu. I.; Kramarova, E. P.; Oleneva, G. I.; Pestunovich, V. A.; Struchkov, Yu. T.; Shklover, V. E. *Zhur. Strukt. Khim.* **1987**, *28*, 107; *Chem. Abstr.* **1988**, *108*, 14178. (b) Kalikhman, I. D.; Bannikova, O. B.; Belousova, L. I.; Gostevskii, B. A.; Liepinsh, E.; Vyazankina, O. A.; Vyazankin, N. S.; Pestunovich, V. A. *Metallorg. Khim.* **1988**, *1*, 683; *Chem. Abstr.* **1989**, *111*, 57840.

(50) Voronkov, M. G.; Pestunovich, V. A.; Baukov, Yu. I. *Metallorg. Khim.* **1991**, *4*, 1210; *Chem. Abstr.* **1992**, *116*, 41503.

(51) Kalikhman, I. D.; Bannikova, O. B.; Volkova, L. I.; Belousova, L. I.; Yushmanova, T. I.; Lopyrev, V. A.; Vyazankina, O. A.; Vyazankin, N. S.; Pestunovich, V. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1986**, 2781; *Chem. Abstr.* **1988**, *108*, 6068.

(52) Kalikhman, I. D.; Bannikova, O. B.; Petukhov, L. P.; Pestunovich, V. A.; Voronkov, M. G. *Doklady Akad. Nauk SSSR* **1986**, *287*, 870; *Chem. Abstr.* **1987**, *106*, 50289.

(53) Kalikhman, I. D.; Bannikova, O. B.; Gostevskii, B. A.; Volkova, L. I.; Vyazankina, O. A.; Vyazankin, N. S.; Yushmanova, T. I.; Lopyrev, V. A.; Pestunovich, V. A.; Voronkov, M. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, 459; *Chem. Abstr.* **1988**, *108*, 94657.

(54) Kalikhman, I. D.; Pestunovich, V. A.; Gostevskii, B. A.; Bannikova, O. B. *J. Organometal. Chem.* **1988**, *338*, 169.

(55) (a) Macharashvili, A. A.; Shklover, V. E.; Struchkov, Yu. T.; Voronkov, M. G.; Gostevskii, B. A.; Kalikhman, I. D.; Bannikova, O. B.; Pestunovich, V. A. *J. Organometal. Chem.* **1988**, *340*, 23. (b) Macharashvili, A. A.; Shklover, V. E.; Struchkov, Yu. T.; Gostevskii, B. A.; Kalikhman, I. D.; Bannikova, O. B.; Voronkov, M. G.; Pestunovich, V. A. *J. Organometal. Chem.* **1988**, *356*, 23.

(56) Bassindale, A. R.; Borbaruah, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1499.

(57) Bassindale, A. R.; Borbaruah, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1501.

(58) Bassindale, A. R.; Borbaruah, M.; Glynn, S. J.; Parker, D. J.; Taylor, P. G. *J. Chem. Soc., Perkin Trans.* **1999**, *2*, 2099.

(59) Bassindale, A. R.; Borbaruah, M.; Glynn, S. J.; Parker, D. J.; Taylor, P. G. *J. Organometal. Chem.* **2000**, *606*, 125.

(60) Bassindale, A. R.; Borbaruah, M. *J. Chem. Soc., Chem. Commun.* **1993**, 352.

(61) Bassindale, A. R. (B. Marciniec, J. Chojnowski, Eds.) *Progress in Organosilicon Chemistry*, Gordon & Breach, London, 1995, p. 191.

(62) Seyferth, D.; Dow, A. W.; Menzel, H.; Flood, T. C. *J. Am. Chem. Soc.* **1968**, *90*, 1080.

(63) George, P. D.; Elliott, J. R. *J. Am. Chem. Soc.* **1955**, *77*, 3493.

(64) Padwa, A.; Chen, Y.-Y.; Dent, W.; Nimmesgern, H. *J. Org. Chem.* **1985**, *50*, 4006.

(65) Padwa, A.; Chen, Y.-Y.; Chiacchio, U.; Dent, W. *Tetrahedron* **1985**, *41*, 3529.

(66) Horvath, R. F.; Chan, T. H. *J. Org. Chem.* **1989**, *54*, 317.

(67) Sato, Y.; Toyo'oka, T.; Aoyama, T.; Shirai, H. *J. Org. Chem.* **1976**, *41*, 3559.
(68) Wieber, M.; Schmidt, M. *J. Organometal. Chem.* **1963**, *1*, 22.
(69) Voss, P.; Meinicke, C.; Popowski, E.; Kelling, H. *J. Prakt. Chem.* **1978**, *320*, 34; *Chem. Abstr.* **1978**, *89*, 43557.
(70) Sato, Y.; Fukami, Y.; Shirai, H. *J. Organometal. Chem.* **1974**, *78*, 75.
(71) Shimizu, S.; Ogata, M. *J. Org. Chem.* **1987**, *52*, 2314.
(72) Vakhrushev, L. P.; Filippov, E. F.; Chernov, N. F.; Ageev, V. P. *Zh. Obshch. Khim.* **1975**, *45*, 1908; *Chem. Abstr.* **1975**, *83*, 193440.
(73) Lukevics, L.; Dirnens, V. V.; Goldberg, Y. S.; Liepinsh, E. E.; Gavars, M. P.; Kalvinsh, I. Y.; Shymanska, M. V. *Organometallics* **1985**, *4*, 1648.
(74) Niederprüm, H.; Simmler, W. *Chem. Ber.* **1963**, *96*, 965.
(75) (a) Mironov, V. F.; Sheludyakov, V. D.; Rodionov, E. S.; Popov, A. I. *Zhur. Obshch. Khim.* **1972**, *42*, 1651. (b) Mironov, V. F.; Sheludyakov, V. D.; Rodionov, E. S.; Popov, A. I. *J. Gen. Chem. USSR* **1972**, *42*, 1644; *Chem. Abstr.* **1972**, *77*, 140214.
(76) Tacke, R.; Niedner, R.; Frohnecke, J.; Ernst, L.; Sheldrick, W. S. *Liebigs Ann. Chem.* **1980**, 1859.
(77) Kurono, M.; Suzuki, T.; Suzuki, T.; Hirooka, K.; Matsumoto, Y.; Ozawa, H.; Sawai, K. *Eur. Pat. Appl.* **1989**, 299495; *Chem. Abstr.* **1989**, *111*, 7217.
(78) Shipov, A. G.; Kramarova, E. P.; Bylikin, S. Yu.; Mamaeva, E. A.; Zeitseva, G. S.; Sergeev, V. N.; Baukov, Yu. I. *Zhur. Obshch. Khim.* **1993**, *636*, 1195; *Chem. Abstr.* **1994**, 120, 8653.
(79) Gaj, B. J.; Gilman, H. *Chem. Ind. (London)* **1960**, 319.
(80) Harris, J. M.; Walton, J. C.; Maillard, B.; Grelier, S.; Picard, J.-P. *J. Chem. Soc., Perkin Trans. II* **1993**, 2119.
(81) Tsuge, O.; Tanaka, J.; Kanemasa, S. *Bull. Chem. Soc. Jpn* **1985**, *58*, 1991.
(82) Xu, W.; Zhang, X.-M.; Mariano, P. S. *J. Am. Chem. Soc.* **1991**, *113*, 8863.
(83) Olson, R.E. International Patent WO 06430 (to du Pont de Nemours), **1987**; *Chem. Abstr.* **1988**, *108*, 150712.
(84) Dedeyne, R.; Anteunis, M. J. O. *Bull. Soc. Chim. Belg.* **1976**, *85*, 319.
(85) Zhang, X.-M.; Mariano, P. S. *J. Org. Chem.* **1991**, *56*, 1655.
(86) Vedejs, E.; Larsen, S.; West, F. G. *J. Org. Chem.* **1985**, *50*, 2170.
(87) Duffaut, N.; Calas, R.; Bourgeois, P.; Dunoguès, J. *Third Silicon Symposium, Madison*, USA, **1972**.
(88) Schirlin, D.; Collard, J.-N.; Danzin, C. Eur. Patent 291787 (to Merrell Dow), 1988, *Chem. Abstr.* **1989**, *110*, 115113.
(89) Ashby, B.A. US Patent **1967**, 3346588; *Chem. Abstr.* **1968**, *68*, 78131.
(90) Moberg, W.K. Eur. Patent 148026 (to du Pont de Nemours), **1985**; *Chem. Abstr.* **1985**, *103*, 215540.
(91) Liebner, F.; Bankwitz, U.; Rühlmann, K. *Liebigs Ann. Chem.* **1994**, 145.
(92) Vedejs, E.; West, F. G. *J. Org. Chem.* **1983**, *48*, 4773.
(93) HMPA: hexamethylphosphoramide. This molecule that has been referred to as a "potential carcinogenic compound", is now referred to as a "useful aprotic solvent": cf for instance, Sigma-Aldrich catalogue since edition 2000–2001, p. 921.
(94) Letellier, M.; MacPhee, D. J.; Griller, D. *Synth. Commun.* **1988**, *18*, 1975.
(95) Palomo, C.; Aizpurua, J. M.; Legido, M.; Picard, J.-P.; Dunoguès, J.; Constantieux, T. *Tetrahedron Lett.* **1992**, *33*, 3903.
(96) Yoshida, J.-i.; Isoe, S. *Tetrahedron Lett.* **1987**, *28*, 6621.
(97) Tsuge, O.; Kanemasa, S.; Kuraoka, S. *Bull. Chem. Soc. Jpn* **1985**, *58*, 1570.
(98) Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. *Tetrahedron Lett.* **1985**, *26*, 139.
(99) Tomoda, S.; Matsumoto, Y.; Takeuchi, Y.; Nomura, Y. *Chem. Lett.* **1986**, 1193.
(100) Chakraborty, T. K.; Reddy, G. V. *Tetrahedron Lett.* **1990**, *31*, 1335.
(101) Lukevics, E.; Dirkens, V. V.; Goldberg, Y. S.; Liepinsh, E. E. *J. Organometal. Chem.* **1986**, *316*, 249.
(102) Dirkens, V. V.; Goldberg, Y. S.; Lukevics, E. *Dokl. Akad. Nauk SSSR.* **1988**, *298*, 116; *Chem. Abstr.* **1989**, *110*, 8270.
(103) Atkinson, R. S.; Kelly, B. J. *Tetrahedron Lett.* **1989**, *30*, 2703.
(104) Atkinson, R. S.; Kelly, B. J. *J. Chem. Soc., Chem. Commun.* **1989**, 836.
(105) Atkinson, R. S.; Kelly, B. J. *J. Chem. Soc., Perkin Trans.* **1989**, *I*, 1657.
(106) Andrianov, K. A.; Sidorov, V. I.; Khananashvili, L. M. *Dokl. Akad. Nauk SSSR* **1964**, *158*, 987; *Chem. Abstr.* **1965**, *62*, 15385.

(107) (a) D'yakonov, I. A.; Repinskaya, I. V.; Golodnikov, G. V. *Zhur. Organ. Khim.* **1966**, *2*, 2256. (b) D'yakonov, I. A.; Repinskaya, I. V.; Golodnikov, G. V. *J. Org. Chem. USSR* **1966**, *2*, 2212.
(108) Conlin, R. T.; Kwak, Y.-W. *J. Organometal. Chem.* **1985**, *293*, 177.
(109) Cunico, R.; Lee, M. L. *J. Am. Chem. Soc.* **1977**, *99*, 7613.
(110) Birkofer, L.; Kühn, T. *Chem. Ber.* **1981**, *114*, 2293.
(111) Seyferth, D.; Menzel, H.; Dow, A. W.; Flood, T. C. *J. Organometal. Chem.* **1972**, *44*, 279.
(112) Martin, H.-D.; Iden, R.; Mais, F.-J.; Kleefeld, G.; Steigel, A.; Fuhr, B.; Rümmele, O.; Oftring, A.; Schwichtenberg, E. *Tetrahedron Lett.* **1983**, *24*, 5469.
(113) Bassindale, A. R.; Brook, A. G. *Can. J. Chem.* **1974**, *52*, 3474.
(114) (a) Andrianov, K. A.; Sidorov, V. I.; Khananashvili, L. M. *Zhur. Obshch. Khim.* **1966**, *36*, 136; *Chem. Abstr.* **1966**, *64*, 75839. (b) Andrianov, K. A.; Sidorov, V. I.; Khananashvili, L. M. *J. Gen. Chem. USSR* **1966**, *36*, 178.
(115) Ettenhüber, E.; Rühlmann, K. *Chem. Ber.* **1968**, *101*, 743.
(116) Bassindale, A. R.; Brook, A. G.; Jones, P. F.; Stewart, J. A. G. *J. Organometal. Chem.* **1978**, *152*, C25.
(117) (a) Zanirato, P. *J. Chem. Soc., Perkin Trans. I* **1991**, 2789. (b) Funicello, M.; Spagnolo, P.; Zanirato, P. *J. Chem. Soc., Perkin Trans. I* **1990**, 2971. (c) Zanirato, P.; Funicello, M. *Gazz. Chim. Ital.* **1990**, *120*, 609. (d) Foresti, E.; Spagnolo, P.; Zanirato, P. *J. Chem. Soc., Perkin Trans. I* **1989**, 1354.
(118) Duboudin, F. *J. Organometal. Chem.* **1978**, *156*, C25.
(119) Duboudin, F. *J. Organometal. Chem.* **1979**, *174*, C18.
(120) (a) Kolokol'tseva, I. G.; Chistokletov, V. N.; Petrov, A. A. *Zhur. Obshch. Khim.* **1970**, *40*, 2612. (b) Kolokol'tseva, I. G.; Chistokletov, V. N.; Petrov, A. A. *J. Gen. Chem.* **1970**, *40*, 2605.
(121) Jolibois, H.; Doucet, A.; Perrot, R. *Helv. Chim. Acta* **1973**, *58*, 1801.
(122) (a) Suda, K.; Hotoda, K.; Iemuro, F.; Takanami, T. *J. Chem. Soc., Parkin Trans. I* **1993**, 1553. (b) Suda, K.; Hotoda, K.; Takanami, T. *International Symposium on Electroorganic Synthesis* **1994**, Kurahashi (Japan), *Abstr.* PI-27, p. 130.
(123) Bolm, C.; Kasyan, A.; Drauz, K.; Günther, K.; Raabe, G. *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 2288.
(124) Beak, P.; Zadjel, W. J.; Reitz, D. B. *Chem. Rev.* **1984**, *84*, 471.
(125) Corriu, R. J. P.; Huynh, V.; Moreau, J. J. E. *J. Organometal. Chem.* **1983**, *259*, 283.
(126) Yamamoto, Y.; Yatagai, H.; Saito, Y.; Maruyama, K. *J. Org. Chem.* **1984**, *49*, 1096.
(127) Ahlbrecht, H.; Eichler, J. *Synthesis* **1974**, 672.
(128) Chen, S.-F.; Ullrich, J. W.; Mariano, P. *J. Am. Chem. Soc.* **1983**, *105*, 6160.
(129) Chen, S.-F.; Mariano, P. *Tetrahedron Lett.* **1985**, *26*, 47.
(130) Chen, S.-F.; Ho, E.; Mariano, P. S. *Tetrahedron* **1988**, *44*, 7013.
(131) Quast, H.; Weise Velez, C. A. *Angew. Chem.* **1975**, *86*, 380.
(132) Seebach, D.; Lohmann, J.-J.; Syfrig, M. A.; Yoshifuji, M. *Tetrahedron* **1983**, *39*, 1963.
(133) Beak, P.; Zajdel, W. J. *J. Am. Chem. Soc.* **1984**, *106*, 1010.
(134) Williams, R. M.; Armstrong, R. W.; Dung, J.-S. *J. Am. Chem. Soc.* **1985**, *107*, 3253.
(135) Beak, P.; Lee, B. *J. Org. Chem.* **1989**, *54*, 458.
(136) Cuevas, J.-C.; Patil, P.; Snieckus, V. *Tetrahedron Lett.* **1989**, *30*, 5841.
(137) Snieckus, V. *Pure Appl. Chem.* **1990**, *62*, 671.
(138) Urayama, S.; Inoue, S.; Sato, Y. *J. Organometal. Chem.* **1988**, *354*, 155.
(139) Beak, P.; Lee, W.-K. *Tetrahedron Lett.* **1989**, *30*, 1197.
(140) Scherer, O. J.; Schnabl, G. *J. Organometal. Chem.* **1973**, *52*, C18.
(141) (a) Meyers, A. I.; Edwards, P. D.; Reiker, W. F.; Bailey, T. R. *J. Am. Chem. Soc.* **1984**, *106*, 3270. (b) Meyers, A. I. *Aldrichimica Acta* **1985**, *18*, 53.
(142) Shawe, T. T.; Meyers, A. I. *J. Org. Chem.* **1991**, *56*, 2751.
(143) Meyers, A. I.; Jagdmann, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 877.
(144) Hulot, P.; Cuvigny, T. *Bull. Soc. Chim. Fr.* **1973**, 2985.
(145) Popowski, E. *Z. Chem.* **1975**, *15*, 275.
(146) Komatsu, M.; Okada, H.; Akaki, T.; Oderaotoshi, Y.; Minakata, S. *Org. Lett.* **2002**, *4*, 3505.
(147) Popowski, E.; Konzempel, K.; Schott, G. *Z. Chem.* **1974**, *14*, 289.
(148) Popowski, E.; Franz, K. *Z. Chem.* **1979**, *19*, 103.
(149) Hoppe, D.; Beckman, L. *Liebigs Ann. Chem.* **1980**, 1751.
(150) Guan, Y.; Hu, C. *Gaodeng Xueziao Huazue Xuebao (Chem. J. Chin. Univ.)* **1987**, *8*, 905; *Chem. Abstr.* **1988**, *109*, 92366.

(151) Lohmann, J.-J.; Seebach, D.; Syfrig, M. A.; Yoshifugi, M. *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 128.
(152) Cuevas, J.-C.; Snieckus, V. *Tetrahedron Lett.* **1989**, *30*, 5837.
(153) Snieckus, V.; Cuevas, J.-C.; Sloan, C. P.; Liu, H.; Curran, D. P. *J. Am. Chem. Soc.* **1990**, *112*, 896.
(154) Adlington, R. M.; Baldwin, J. E.; Bottaro, J. C.; Perry, M. W. D. *J. Chem. Soc., Chem. Commun.* **1983**, 1040.
(155) Baldwin, J. E.; Adlington, R. M.; Bottaro, J. C.; Khol, J. N.; Perry, M. W. D.; Jain, A. U. *Tetrahedron* **1986**, *42*, 4223.
(156) Katritsky, A. R.; Offerman, R. J.; Cabildo, P.; Soleiman, M. *Rec. Trav. Chim. P-B* **1988**, *107*, 641.
(157) Katritsky, A. R.; Lam, J. N. *Heteroatom. Chem.* **1990**, *1*, 21.
(158) (a) Moody, C.; Rees, C. W.; Young, R. G. *Synlett* **1990**, 413. (b) Moody, C.; Rees, C. W.; Young, R. G. *J. Chem. Soc., Perkin Trans. I* **1991**, 323.
(159) (a) Walborsky, H. M.; Niznik, G. E. *J. Am. Chem. Soc.* **1969**, *91*, 7779. (b) Walborsky, H. M.; Morrison, W. H.; Niznik, G. E. *J. Am. Chem. Soc.* **1970**, *92*, 6675.
(160) Brook, A. G.; Golino, C.; Matern, E. *Can. J. Chem.* **1978**, *56*, 2286.
(161) West, R.; Gornowicz, G. A. *J. Organometal. Chem.* **1970**, *25*, 385.
(162) Livinghouse, T.; Smith, R. *J. Chem. Soc., Chem. Commun.* **1983**, 210.
(163) Karsch, H. H.; Schmidbaur, H. *Z. Naturforsch.* **1977**, *32*, B, 762.
(164) Karsch, H. H.; Schreiber, K. A. (N. Auner, J. Weis, Eds.), *Organosilicon Chemistry: from Molecules to Materials*, Vol. III, Wiley-VCH, London, 1997. p. 237; *Chem. Abstr.* **1998**, *128*, 179350.
(165) Strohmann, C.; Abele, B. C. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2378.
(166) Abele, B. C.; Strohmann, C. (N. Auner, J. Weis, Eds.), *Organosilicon Chemistry: from Molecules to Materials*, Vol. III, Wiley-VCH, London, 1997. p. 206.
(167) Suda, K. Jpn. Kokai Tokkyo Koho JP 05 17432, **1993**; *Chem. Abstr.* **1993**, *119*, 72426.
(168) Nativi, C.; Ricci, A.; Taddei, M. *Tetrahedron Lett.* **1990**, *31*, 2640.
(169) MacLeod, D.; Quayle, P.; Davies, G. M. *Tetrahedron Lett.* **1990**, *31*, 4927.
(170) Ahlbrecht, H.; Raab, W.; Vonderheid, C. *Synthesis* **1979**, 127.
(171) Padwa, A.; Eisenbarth, P.; Venkatramanan, M. K.; Wong, G. S. K. *J. Org. Chem.* **1987**, *52*, 2427.
(172) Kolesnik, I. R.; Koval, N. V. *Vysok. Soedin. Ser. B* **1990**, *32*, 137; *Chem. Abstr.* **1990**, *113*, 153131.
(173) See, in particular: Calas, R.; Dunoguès, J. *J. Organometal. Chem. Lib.* **1976**, *2*, 277.
(174) Biran, C.; Calas, R.; Dunoguès, J.; Duffaut, N. *J. Organometal. Chem.* **1970**, *22*, 557.
(175) Bolourtchian, M.; Saednya, A. *J. Sci., Islamic Repub. Iran* **1997**, *21*, 187; *Chem. Abstr.* **1997**, *126*, 259920.
(176) Shono, T.; Kise, N.; Kunimi, N.; Nomura, R. *Chem. Lett.* **1991**, 2191.
(177) Bourgeois, P. *J. Organometal. Chem.* **1974**, *76*, C1.
(178) tom Dieck, H.; Bruder, B.; Franz, K.-D. *Chem. Ber.* **1983**, *116*, 136.
(179) Grignon-Dubois, M.; Fialex, M.; Rezzonico, B. *Can. J. Chem.* **1990**, *68*, 2153.
(180) Biran, C.; Dédier, J.; Dunoguès, J.; Calas, R.; Duffaut, N.; Gerval, J. *J. Organometal. Chem.* **1972**, *35*, 263.
(181) Effenberger, F.; Häbich, D. *Liebigs Ann. Chem.* **1979**, 842.
(182) Bourgeois, P.; Calas, R.; Duffaut, N.; Dunoguès, J. *J. Organometal. Chem.* **1971**, *32*, 79.
(183) Bourgeois, P.; Duffaut, N. *J. Organometal. Chem.* **1972**, *35*, 63.
(184) Voss, J.; Wiegand, G.; Hülmeyer, K. *Chem. Ber.* **1985**, *118*, 4806.
(185) Ekouya, A.; Calas, R.; Dunoguès, J.; Biran, C.; Duffaut, N. *J. Organometal. Chem.* **1979**, *177*, 137.
(186) Picard, J.-P.; Grelier, S.; Dunoguès, J.; Aizpurua, J.-M.; Palomo, C. *J. Organometal. Chem.* **1991**, *419*, C1.
(187) Picard, J.-P.; Grelier, S.; Constantieux, T.; Dunoguès, J.; Aizpurua, J.-M.; Palomo, C.; Petraud, M.; Barbe, B.; Lunazzi, L.; Leger, J. M. *Organometallics* **1993**, *12*, 1378.
(188) BSMA's hydrochloride is soluble in water and most surprisingly in pentane (45 g/l): Picard, J.-P. unpublished, **1998**.
(189) Grelier, S.; Constantieux, T.; Deffieux, D.; Bordeau, M.; Dunoguès, J.; Picard, J.-P.; Aizpurua, J.-M.; Palomo, C. *Organometallics* **1994**, *13*, 3711.
(190) Bolourtchian, M.; Galeassadi, M. *J. Sci., Islamic Repub. Iran* **1993**, *4*, 183; *Chem. Abstr.* **1995**, *122*, 160749.
(191) Constantieux, T.; Grelier, S.; Picard, J.-P. *Main Group Metal Chem.* **1997**, *20*, 503.
(192) Constantieux, T.; Picard, J.-P. *Organometallics* **1996**, *15*, 1604.

(193) Bravo-Zhivotovskii, D. A.; Pigarev, S. D.; Kalikhman, I. D.; Vyazankina, O. A.; Vyazankin, N. S. *J. Organometal. Chem.* **1983**, *248*, 51.
(194) Benkeser, R.; Li, G. S.; Mezdzen, E. C. *J. Organometal. Chem.* **1979**, *178*, 21.
(195) Benkeser, R. *Acc. Chem. Res.* **1971**, *4*, 94.
(196) Weiner, M. A.; Kirschner, S. *Synth. Inorg. Metal-Org. Chem.* **1972**, *2*, 135.
(197) Reza Naimi-Jamal, M.; Mojtahedi, M. M.; Ipaktschi, J.; Saidi, M. *J. Chem. Soc., Perkin Trans. I* **1999**, 3709.
(198) (a) Gross, T.; Kempe, R.; Oehme, H. *Inorg. Chem. Commun.* **1998**, *1*, 128. (b) Gross, T.; Kempe, R.; Oehme, H. *Eur. J. Inorg. Chem.* **1999**, 21.
(199) Connor, J. A.; Rose, P. D. *J. Organometal. Chem.* **1970**, *24*, C45.
(200) Connor, J. A.; Rose, P. D.; Turner, R. M. *J. Organometal. Chem.* **1973**, *55*, 111.
(201) Ito, Y.; Nishimura, S.; Ishikawa, M. *Tetrahedron Lett.* **1987**, *28*, 1293.
(202) Ito, Y.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1988**, *110*, 3692.
(203) Grossi, L.; Lunazzi, L.; Placucci, G. *J. Chem. Soc., Perkin Trans. II* **1983**, 1831.
(204) Chandra, H.; Davidson, I. M. T.; Symons, M. C. R. *J. Chem. Soc., Faraday Trans. I* **1983**, *79*, 2705.
(205) Gasanov, R. G.; Ivanova, L. V.; Freidlina, R. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 938; *Chem. Abstr.* **1984**, *101*, 23585.
(206) Adeleke, B. B.; Wong, S.-K.; Wan, J. K. S. *Can. J. Chem.* **1974**, *52*, 2901.
(207) Haire, D.; Oehler, U. M.; Krygsman, P. H.; Janzen, E. G. *J. Org. Chem.* **1988**, *53*, 4535.
(208) Alberti, A.; Leardini, R.; Pedulli, G. F.; Tundo, A.; Zanardi, G. *Gazz. Chim. Ital.* **1983**, *113*, 869.
(209) Chandra, H.; Davidson, I. M. T.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. II* **1982**, 1353.
(210) Rivière, P.; Richelme, S.; Rivière-Baudet, M.; Satgé, J.; Riley, P. I.; Lappert, M. F.; Dunoguès, J.; Calas, R. *J. Chem. Res. (S)* **1981**, 130; *J. Chem. Res. (M)*, **1981**, 1663.
(211) Murai, T.; Kimura, F.; Tsutsui, K.; Hasegawa, K.; Kato, S. *Organometallics* **1998**, *17*, 926.
(212) Sato, Y.; Ban, Y.; Shirai, H. *J. Chem. Soc., Chem. Commun.* **1974**, 182.
(213) Sato, Y.; Ban, Y.; Shirai, H. *J. Organometal. Chem.* **1976**, *113*, 115.
(214) Inoue, S.; Urayama, S.; Sugiura, H.; Sato, Y. *J. Organometal. Chem.* **1989**, *363*, 25.
(215) Gareev, R. D.; Borisova, E. E.; Schermervorn, I. M. *Zhurn. Obshch. Khim.* **1975**, *45*, 944; *Chem. Abstr.* **1975**, *83*, 28337.
(216) Tanaka, M.; Uchimaru, J. Japan Patent 08134082 (to Kogyo Gijustuin, Japan) **1996**; *Chem. Abstr.* **1996**, *125*, 142993.
(217) (a) Wiberg, N.; Preiner, G.; Karampatses, P.; Kim, C.-K.; Schurz, K. *Chem. Ber.* **1987**, *120*, 1357. (b) Wiberg, N.; Schurz, K. *J. Organometal. Chem.* **1988**, *341*, 145.
(218) (a) Weidenbruch, M.; Flintjer, B.; Pohl, S.; Haase, D.; Martens, J. *J. Organometal. Chem.* **1988**, *338*, C1. (b) Weidenbruch, M.; Lesch, A.; Peters, K.; Georg von Schnering, H. *Chem. Ber.* **1990**, *123*, 1795. (c) Weidenbruch, M.; Lesch, A. *J. Organometal. Chem.* **1992**, *423*, 329.
(219) Padwa, A.; Dent, W. *J. Org. Chem.* **1987**, *52*, 235.
(220) Hendrickson, J. B.; Bair, K. W.; Bergeron, R.; Giga, A.; Skipper, P. L.; Sternbach, D. D. *Org. Prep. Proc. Int.* **1977**, *9*, 173.
(221) Fink, W. *Helv. Chim. Acta* **1974**, *57*, 1042.
(222) Kirst, H. A.; Willard, K. E.; Debono, M.; Toth, J. E.; Truedell, B. A.; Leeds, J. P.; Ott, J. L.; Felty-Druckworth, A. M.; Counter, F. T.; Ose, E. E.; Crouse, G. D.; Tustin, J. M. *J. Antibiot.* **1989**, *42*, 1676; *Chem. Abstr.* **1990**, *113*, 78860.
(223) Nativi, C.; Ricci, A.; Taddei, M. *Tetrahedron Lett.* **1990**, *31*, 2637.
(224) Constantieux, T.; Grelier, S.; Picard, J.-P. *Synlett* **1998**, 510.
(225) Ho, E.; Cheng, Y.-S.; Mariano, P. S. *Tetrahedron Lett.* **1988**, *29*, 4799.
(226) Lasarte, J.; Palomo, C.; Picard, J.-P.; Dunoguès, J.; Aizpurua, J.-M. *J. Chem. Soc., Chem. Commun.* **1989**, 72.
(227) Ricci, A.; Guerrini, A.; Seconi, G.; Mordini, A.; Constantieux, T.; Picard, J.-P.; Aizpurua, J.-M.; Palomo, C. *Synlett* **1994**, 955.
(228) Palomo, C.; Aizpurua, J.-M.; Legido, M.; Mielgo, A.; Galarza, R. *Chem. Eur. J.* **1997**, *3*, 1432.
(229) Bonini, B. F.; Fochi, M.; Comes Franchini, M.; Mazzanti, G.; Ricci, A.; Picard, J.-P.; Dunoguès, J.; Aizpurua, J.-M.; Palomo, C. *Synlett* **1997**, 1321.
(230) Palomo, C.; Aizpurua, J.-M.; Legido, M.; Galarza, R.; Deya, P. M.; Dunoguès, J.; Picard, J.-P.; Ricci, A.; Seconi, G. *Ang. Chem. Int. Ed. Engl.* **1996**, *35*, 1239.

(231) (a) Jewett, J. G.; Breeyear, J. J.; Brown, J. H.; Bushweller, C. H. *J. Am. Chem. Soc.* **2000**, *122*, 308; and references cited therein. (b) Barluenga, J.; Bayón, A. M.; Campos, P. *J. Chem. Soc., Perkin Trans.* **1988**, *2*, 1631. (c) Martinez-Aguilera, A. M. R.; Cadenas-Piego, G.; Contreras, R.; Flores-Parra, A. *Tetrahedron Asymm.* **1995**, *6*, 1585.
(232) Morimoto, T.; Nezu, Y.; Achiwa, K. *Chem. Pharm. Bull.* **1985**, *33*, 4596.
(233) Capperucci, A.; Ricci, A.; Seconi, G.; Dunoguès, J.; Grelier, S.; Picard, J.-P.; Palomo, C.; Aizpurua, J.-M. *J. Organometal. Chem.* **1993**, *458*, C1.
(234) Palomo, C.; Aizpurua, J.-M.; Garcia, J.-M.; Galarza, R.; Legido, M.; Urchegui, R.; Roman, P.; Luque, A.; Server-Carrio, J.; Linden, A. *J. Org. Chem.* **1997**, *62*, 2070.
(235) Tsuge, O.; Kanemasa, S.; Matsuda, K. *J. Org. Chem.* **1984**, *49*, 2688.
(236) Hengelsberg, H.; Tacke, R.; Fritsche, K.; Syldatk, C.; Wagner, F. *J. Organometal. Chem.* **1991**, *415*, 39.
(237) Maeda, Y.; Shirai, N.; Sato, Y.; Tatewaki, H. *J. Org. Chem.* **1994**, *59*, 7897.
(238) Palomo, C.; Aizpurua, J.-M.; Garcia, J.-M.; Legido, M. *J. Chem. Soc., Chem. Commun.* **1991**, 524.
(239) Tsuge, O.; Matsuda, K.; Kanemasa, S. *Heterocycles* **1996**, *24*, 240.
(240) Barbaro, G.; Battaglia, A.; Giorgianni, P.; Guerrini, A.; Seconi, G. *J. Org. Chem.* **1995**, *60*, 6032.
(241) Grelier, S. Thesis, University Bordeaux 1, **1991**, 633.
(242) (a) Hirao, T.; Yamada, A.; Ohshiro, Y.; Agawa, T. *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 126. (b) Oshiro, Y.; Hayashi, K.-i.; Yamada, A.; Ishibashi, G.-i.; Hirao, T.; Agawa, T. *Heterocycles* **1983**, *20*, 139.
(243) Seyferth, D.; Menzel, H.; Dow, A. W.; Flood, T. C. *J. Organometal. Chem.* **1972**, *44*, 279.
(244) Seyferth, D.; Menzel, H.; Dow, A. W.; Flood, T. C. *J. Am. Chem. Soc.* **1968**, *90*, 1080.
(245) Tsuge, O.; Hatta, T.; Tashiro, H.; Kakura, Y.; Maeda, H.; Kakehi, A. *Tetrahedron* **2000**, *56*, 7723.
(246) Okazaki, S.; Shirai, N.; Sato, Y. *J. Org. Chem.* **1990**, *55*, 334.
(247) Sato, Y.; Yagi, Y.; Koto, M. *J. Org. Chem.* **1980**, *45*, 613.
(248) Sato, Y.; Sakakibara, H. *J. Organometal. Chem.* **1979**, *166*, 303.
(249) Kurono, M.; Unno, R.; Matsumoto, Y.; Kondo, Y.; Mitani, T.; Jomori, T.; Mishichita, H.; Sawal, K. *Eur. Pat. Appl.*, 288002 (to Sanwa Kagaku Kenkyusho Co.), 1988; *Chem. Abstr.* **1988**, *90*, 75808.
(250) Desmarets, C.; Schneider, R.; Fort, Y. *J. Org. Chem.* **2002**, *67*, 3029; and Refs. 2 and 3 cited therein.
(251) Aoyama, T.; Sato, Y.; Shirai, H. *J. Organometal. Chem.* **1976**, *118*, 1.
(252) Aoyama, T.; Sato, Y.; Suzuki, T.; Shirai, H. *J. Organometal. Chem.* **1978**, *153*, 193.
(253) Sato, Y.; Ban, Y.; Aoyama, T.; Shirai, H. *J. Org. Chem.* **1976**, *41*, 1962.
(254) Beak, P.; Yum, E. K. *J. Org. Chem.* **1993**, *58*, 823.
(255) Palomo, C.; Aizpurua, J.-M.; Garcia, J.-M.; Ganboa, I.; Cossio, F. P.; Lecea, B.; Lopez, C. *J. Org. Chem.* **1990**, *55*, 2498.
(256) Palomo, C.; Aizpurua, J.-M.; Garcia, J.-M.; Picard, J.-P.; Dunoguès, J. *Tetrahedron Lett.* **1990**, *31*, 1921.
(257) Arrieta, A.; Cossio, F. P.; Garcia, J.-M.; Lecea, B.; Palomo, C. *Tetrahedron Lett.* **1988**, *29*, 3129.
(258) Palomo, C.; Aizpurua, J.-M.; Galarza, R.; Iturburu, M.; Legido, M. *Bioorg. Med. Chem. Lett.* **1993**, *3*, 2461.
(259) Galarza, R. Doctoral Thesis, University of Pais Vasco at San Sebastian (Spain) **1997**.
(260) Palomo, C.; Aizpurua, J.-M.; Legido, M.; Galarza, R. *Chem. Commun.* **1997**, 233.
(261) Schöllkopf, U.; Scholz, H.-U. *Synthesis* **1976**, 271.
(262) Tsuge, O.; Kanemasa, S.; Matsuda, K. *Chem. Lett.* **1983**, 1131.
(263) Tsuge, O.; Kanemasa, S.; Matsuda, K. *Chem. Lett.* **1985**, 1411.
(264) Tsuge, O.; Kanemasa, S.; Matsuda, K. *J. Org. Chem.* **1986**, *51*, 1411.
(265) Tsuge, O.; Kanemasa, S.; Yamada, T.; Matsuda, K. *Heterocycles* **1985**, *23*, 2489.
(266) Shipov, A. G.; Kramarova, E. P.; Artamkina, O. B.; Baukov, Yu. I. *Zhur. Obshch. Khim.* **1993**, *63*, 1434; *Russ. J. Gen. Chem.*, **1993**, *63*, 1002; *Chem. Abstr.* **1994**, *120*, 134614.
(267) Kramarova, E. P.; Negrebetskii, V. V.; Shipov, A. G.; Baukov, Yu. I. *Zhur. Obshch. Khim.* **1994**, *64*, 1222; *Chem. Abstr.* **1995**, *122*, 314630.
(268) Pogozhikh, S. A.; Zamyshlyaeva, O. A.; Kramarova, E. P.; Antipin, M. Yu.; Ovchinnikov, Yu. E.; Baukov, Yu. I. *Russ. Chem. Bull.* **1999**, *48*, 1595; *Chem. Abstr.* **1999**, *132*, 719510.
(269) Shipov, A. G.; Kramarova, E. P.; Artamkina, O. B.; Baukov, Yu. I. *Metalloorg. Khim.* **1991**, *4*, 1101; *Chem. Abstr.* **1992**, *116*, 106355.
(270) Shipov, A. G.; Kramarova, E. P.; Artamkina, O. B.; Oleneva, G. I.; Nepomnyashchaya, N. A.; Baukov, Yu. I. *Zh. Obshch. Khim.* **1995**, *65*, 272; *Chem. Abstr.* **1995**, *123*, 256814.
(271) Bassindale, A. R.; Parker, D. J.; Yaylor, P. G.; Auner, N.; Herrschaft, B. *Chem. Commun.* **2000**, 565.

(272) Labrecque, D.; Nwe, K. T.; Chan, T. H. *Organometallics* **1994**, *13*, 332.
(273) Chan, T. H.; Wang, D. *Tetrahedron Lett.* **1989**, *30*, 3041.
(274) Sieburth, S. McN.; Somers, J. J.; O'Hare, H. K. *Tetrahedron* **1996**, *52*, 5669.
(275) Mordini, A.; Ben Rayana, E.; Margot, C.; Schlosser, M. *Tetrahedron* **1990**, *46*, 2401.
(276) Okazaki, S.; Sato, Y. *Synthesis* **1990**, 36.
(277) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*, Springer, Berlin, 1987.
(278) Both acronyms are used in the literature: SET and PET processes are concerned with Mariano's and Pandey's work, respectively. See the references cited hereafter.
(279) Pandey, G. *Top. Curr. Chem.* **1993**, *168*, 175.
(280) (a) Brimage, D. R. G.; Davidson, R. S.; Steiner, P. R. *J. Chem. Soc., Perkin Trans.* **1972**, *1*, 1375. (b) Davidson, R. S.; Orton, S. P. *J. Chem. Soc., Chem. Commun.* **1974**, 209. (c) Shaefer, C. G.; Peters, K. S. *J. Am. Chem. Soc.* **1980**, *102*, 7566. (d) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 1048. (e) Manning, L. E.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, *105*, 5708. (f) Lewis, F. D.; Zebrowski, B. E.; Correa, P. E. *J. Am. Chem. Soc.* **1984**, *106*, 187. (g) Lewis, F. D.; Correa, P. E. *J. Am. Chem. Soc.* **1984**, *106*, 194. (h) Hub, W.; Schneider, S.; Doerr, F.; Oxman, J. D.; Lewis, F. D. *J. Am. Chem. Soc.* **1984**, *106*, 708. (i) Manning, L. E.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 6452. (j) Lee, L. Y. C.; Ci, X.; Giannotti, C.; Witten, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 175.
(281) Hasegawa, E.; Brumfield, M. A.; Mariano, P. S.; Yoon, U. C. *J. Org. Chem.* **1988**, *53*, 5435.
(282) Hasegawa, E.; Xu, W.; Mariano, P. S.; Yoon, U.-C.; Kim, J.-U. *J. Am. Chem. Soc.* **1988**, *110*, 8099.
(283) Yoon, U.-C.; Mariano, P. S. *Acc. Chem. Res.* **1992**, *25*, 233.
(284) Yoon, U.-C.; Kim, Y. C.; Choi, J. J.; Kim, D. U.; Mariano, P. S.; In, S.; Yoon, T. *J. Org. Chem.* **1992**, *57*, 1422.
(285) Yoon, U.-C.; Kim, J.-U.; Hasegawa, E.; Mariano, P. S. *J. Am. Chem. Soc.* **1987**, *109*, 4421.
(286) Xu, W.; Mariano, P. S. *J. Am. Chem. Soc.* **1991**, *113*, 1431.
(287) Xu, W.; Yoon, T. J.; Hasegawa, E.; Ung, C. Y.; Mariano, P. S. *J. Am. Chem. Soc.* **1989**, *111*, 406.
(288) Pine, S. H. *Org. React.* **1970**, *18*, 403.
(289) Miller, N. E. *Inorg. Chem.* **1965**, *4*, 1458.
(290) (a) Kolesnik, Yu. R.; Svetkin, Yu. V.; Grekov, A. P. *Vysokomol. Soedin., Ser. B* **1989**, *31*, 403; *Chem. Abstr.* **1990**, *112*, 36583. (b) See also: Kolesnik, Yu. R.; Teslenko, V. V.; Grekov, A. P. *Vysokomol. Soedin., Ser. A* **1989**, *32*, 756; *Chem. Abstr.* **1990**, *113*, 36583.
(291) Kolesnik, Yu. R.; Koval, I. V. *Vysokomol. Soedin., Ser. B* **1990**, *32*, 137; *Chem. Abstr.* **1990**, *113*, 153131.
(292) Smith, R.; Livinghouse, T. *Tetrahedron* **1985**, *41*, 3559.
(293) Marumo, K.; Inoue, S.; Sato, Y.; Kato, H. *J. Chem. Soc., Perkin Trans.* **1991**, *I*, 2275.
(294) Mitsui, S.; Marumo, K.; Inoue-Ando, S.; Kato, H.; Sato, Y. *Chem. Pharm. Bull.* **1993**, *41*, 2195.
(295) Tamao, K.; Takui, T.; Kumada, M. *J. Am. Chem. Soc.* **1978**, *100*, 2268.
(296) Chan, T. H.; Pellon, P. *J. Am. Chem. Soc.* **1989**, *111*, 8737.
(297) Chan, T. H.; Nwe, K. T. *J. Org. Chem.* **1992**, *57*, 6107.
(298) Chan, T. H.; Wang, D. *Chem. Rev.* **1992**, *92*, 995.
(299) Hartley, R. C.; Lamothe, S.; Chan, T. H. *Tetrahedron Lett.* **1993**, *34*, 1449.
(300) Fu, J.-M.; Snieckus, V. *Tetrahedron Lett.* **1990**, *31*, 1665.
(301) Jung, Y. S.; Swartz, W. H.; Xu, W.; Mariano, P. S. *J. Org. Chem.* **1992**, *57*, 6037.
(302) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512.
(303) (a) Gallagher, D. J.; Kerrick, S. T.; Beak, P. *J. Am. Chem. Soc.* **1992**, *114*, 5872. (b) See also: Kerrick, S. T.; Beak, P. *J. Am. Chem. Soc.* **1991**, *113*, 9708. (c) Bertini Gross, K. M.; Jun, Y. M.; Beak, P. *J. Org. Chem.* **1997**, *62*, 7679.
(304) Gallagher, D. J.; Wu, S.; Nikolic, N. A.; Beak, P. *J. Org. Chem.* **1995**, *60*, 8148.
(305) (a) Gawley, R. E.; Hart, G.; Goicoecha-Papas, M.; Smith, A. *J. Org. Chem.* **1986**, *51*, 3076. (b) Gawley, R. E.; Hart, G.; Bartolotti, L. J. *J. Org. Chem.* **1989**, *54*, 175.
(306) Pfammatter, E.; Seebach, D. *Liebigs Ann. Chem.* **1991**, 1323.
(307) Sieburth, S. McN.; Somers, J. J.; O'Hare, H. K.; Hewitt, G. W. *Appl. Organometal. Chem.* **1997**, *11*, 337.
(308) Sieburth, S. McN.; O'Hare, H. K.; Xu, J.; Chen, Y.; Liu, G. *Org. Lett.* **2003**, *5*, 1859.
(309) Barberis, C.; Voyer, N. *Tetrahedron Lett.* **1998**, *39*, 6807.
(310) (a) Picard, J.-P.; Fortis, F. *Tetrahedron Asymm.* **1998**, *9*, 3455. (b) See also: Fortis, F.; Barbe, B.; Pétraud, M.; Picard, J.-P. *Chem. Commun.* **1999**, 527.
(311) Bassindale, A. R.; Taylor, P. G.; Xu, Y. *Tetrahedron Lett.* **1996**, *37*, 555.

(312) Hudrlik, P. F.; Hudrlik, A. M.; Rona, R. J.; Misra, R. N.; Withers, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 1993.
(313) Terunuma, D.; Nohira, H. *Yuki Gosei Kagaku Kyokaishi* **1990**, *48*, 669; *Chem. Abstr.* **1991**, *114*, 163223.
(314) Terunuma, D.; Okada, T.; Araki, T.; Nohira, H. *Chem. Lett.* **1975**, 675.
(315) Vanecko, J. A.; West, F. G. *Org. Lett.* **2002**, *4*, 2813.
(316) Bassindale, A. R.; Kyle, P. A.; Soobramanien, M.-C.; Taylor, P. G. *J. Chem. Soc., Perkin Trans.* **2000**, *I*, 439.
(317) (a) D'yakonov, I. A.; Repinskaya, I. V.; Golodnikov, G. V. *Zhur. Organ. Khim.* **1966**, *2*, 2256. (b) D'yakonov, I. A.; Repinskaya, I. V.; Golodnikov, G. V. *J. Org. Chem. USSR* **1966**, *2*, 2212; *Chem. Abstr.* **1967**, *66*, 76060.
(318) Picard, J. P.; Ernst, R., unpublished results, **1999**.
(319) (a) Brook, M. A. *Silicon in Organic, Organometallic and Polymer Chemistry*, Wiley Interscience, New York, 2000. (b) Fleming, I.; Dunoguès, J.; Smithers, R. *Org. React.***1989**, p. 57. (c) Weber, W. P.; *Silicon Reagents in Organic Chemistry*, Springer, Weinheim, 1983. (d) Colvin, E. W.; *Silicon in Organic Synthesis*, Butterworths, London, 1981. (e) Fleming, I. (D. H. R. Barton, D. Ollis, J. D. Neville Eds.) Vol. 3, *Silicon Compounds in Comprehensive Organic Chemistry*, Pergamon Press, Oxford, 1979, p. 539.
(320) Tsuge, O.; Kanemasa, S.; Suga, H.; Matsuda, K. *Heterocycles* **1984**, *22*, 1955.
(321) Bassindale, A. R.; Parker, D. J.; Patel, P.; Taylor, P. G. *Tetrahedron Lett.* **2000**, *41*, 4933.
(322) Yoon, U. C.; Kim, D. U.; Lee, C. W.; Choi, Y. S.; Lee, Y.-J.; Ammon, H. L.; Mariano, P. S. *J. Am. Chem. Soc.* **1995**, *117*, 2698.
(323) Takahashi, Y.; Miyashi, T.; Yoon, U. C.; Oh, S. W.; Mancheno, M.; Su, Z.; Felvey, D. F.; Mariano, P. S. *J. Am. Chem. Soc.* **1999**, *121*, 3926.
(324) Nametkin, N. S.; Grushevenko, I. A.; Perchenko, V. N.; Kamneva, G. L. *Doklady Akad Nauk SSSR* **1972**, *207*, 865; *Chem. Abstr.* **1973**, *78*, 111422.
(325) (a) Brook, A. G.; Duff, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4692. (b) Duff, J. M.; Brook, A. G. *Can. J. Chem.* **1977**, *55*, 2589.
(326) Frenzel, A.; Klingebiel, U.; Lüttke, W.; Pieper, U. *J. Organometal. Chem.* **1994**, *11*, 73.
(327) (a) Peterson, D. J. *J. Org. Chem.* **1994**, *11*, 73. (b) Chan, T. H.; Chang, E.; Vinokur, E. *Tetrahedron Lett.* **1970**, 1137. (c) See also Review articles: Peterson, D. J. *Organometal. Chem. Rev.* **1972**, *A7*, 295. (d) Hudrlik, P. F. *J. Organometal. Chem. Library* **1976**, *1*, 127. (e) Chan, T. H. *Acc. Chem. Res.* **1977**, *10*, 442. (f) Ager, D. J. *Synthesis* **1984**, 384. (g) Colvin, E. W. *Silicon Reagents in Organic Synthesis*, Academic Press, London 1988.
(328) Adam, W.; Ortega-Schulte, C. M. *Synlett* **2003**, 414.
(329) Komatsu, M.; Ohno, M.; Tsuno, S.; Ohshiro, Y. *Chem. Lett.* **1990**, 575.
(330) Ohno, M.; Miyata, H.; Komatsu, M.; Ohshiro, Y. *Tetrahedron Lett.* **1991**, *32*, 5093.
(331) Constantieux, T. Thesis, Bordeaux (France) **1994**.
(332) Peterson, D. J. private communication cited by Sato, Y., **1976**, cf. Ref.212.
(333) Achiwa, K.; Imai, N.; Motoyama, T.; Sekiya, M. *Chem. Lett.* **1984**, 2041.
(334) Tsuge, O.; Kanemasa, S.; Hatada, A.; Matsuda, K. *Bull. Chem. Soc. Jpn* **1986**, *59*, 2537.
(335) Tsuge, O.; Kanemasa, S.; Matsuda, K. *Chem. Lett.* **1984**, 1984.
(336) Moinet, C.; Raoult, E. *Bull. Soc. Chem. Fr.* **1991**, 214.
(337) Le Gall, E.; Hurvois, J.-P.; Sinbandhit, S. *Eur. J. Org. Chem.* **1999**, 2645.
(338) Yoon, T. J.; Lee, C.-P.; Mariano, P. S. *J. Am. Chem. Soc.* **1991**, *113*, 8847.
(339) Jung, Y. S.; Mariano, P. S. *Tetrahedron Lett.* **1993**, *34*, 4611.
(340) Pandey, G.; Kumaraswamy, G.; Bhalerao, U. T. *Tetrahedron Lett.* **1989**, *30*, 6059.
(341) Pandey, G.; Reddy, G. D.; Kumaraswamy, G. *Tetrahedron* **1994**, *50*, 8185.
(342) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073.
(343) Pandey, G.; Reddy, G. D. *Tetrahedron Lett.* **1992**, *33*, 6533.
(344) Pandey, G.; Reddy, G. D.; Chakrabarti, D. *J. Chem. Soc., Perkin Trans.* **1996**, *1*, 219.
(345) Pandey, G.; Chakrabarti, D. *Tetrahedron Lett.* **1996**, *37*, 2285.
(346) Pandey, G.; Kapur, M. *Tetrahedron Lett.* **2000**, *41*, 8821.
(347) Pandey, G.; Kapur, M. *Synthesis* **2001**, 1263.
(348) Pandey, G.; Kapur, M. *Org. Lett.* **2002**, *4*, 3883.
(349) Hoegy, S. E.; Mariano, P. S. *Tetrahedron Lett.* **1994**, *35*, 8319.
(350) Yoon, U.-C.; Kim, D. U.; Kim, C. K.; Lee, J. G.; Mariano, P. S.; Lee, Y. J.; Ammon, H. L. *Tetrahedron Lett.* **1993**, *34*, 5859.

(351) Yoon, U.-C.; Cho, S. J.; Lee, Y.-J.; Mancheno, M. J.; Mariano, P. S. *J. Org. Chem.* **1995**, *60*, 2353.
(352) Yoshida, J. *Top. Curr. Chem.* **1994**, *170*, 39.
(353) Yoshida, J. *New Challenge Org. Electrochem. ED* **1998**, 155.
(354) Suga, S.; Watanabe, M.; Yoshida, J. *J. Am. Chem. Soc.* **2002**, *124*, 14824.
(355) Suda, K.; Hotoda, K.; Watanabe, J.; Shiozawa, K.; Takanami, T. *J. Chem. Soc., Perkin Trans.* **1992**, *1*, 1283.
(356) Matsumura, Y.; Furuse, T.; Tanaka, S.; Takeshima, Y. 67th Spring Meeting of the Chemical Society of Japan, 1994, Abstract 4N4 33, p. 1339.
(357) Suda, K. Japan Patent, 17432 (to Shiratori Pharmaceutical Co), **1993**; *Chem. Abstr.* **1993**, *119*, 72426.
(358) Suda, K.; Hotoda, K.; Aoyagi, M.; Takanami, T. *J. Chem. Soc., Perkin Trans.* **1995**, *1*, 1327.
(359) Zhang, X.; Young, S. Y.; Mariano, P. S.; Fox, M. A.; Martin, P. S.; Merkert, J. *Tetrahedron Lett.* **1993**, *34*, 5239.
(360) Kim, H. J.; Yoon, U. C.; Jung, Y.-S.; Park, N. S.; Cederstrom, E. M.; Mariano, P. S. *J. Org. Chem.* **1998**, *63*, 860.
(361) Sato, Y.; Shirai, N. *Yakugaku Zasshi* **1994**, *114*, 880; *Chem. Abstr.*, **1995**, *114*, 213867.
(362) (a) Lepley, A. R.; Becker, B. h.; Giumanini, A. G. *J. Org. Chem.* **1971**, *36*, 1222. (b) Hellmann, H.; Unseld, W. *Ann. Chem.* **1960**, *631*, 82; and references cited therein.
(363) Hellmann, H.; Unseld, W. *Ann. Chem.* **1960**, *631*, 89.
(364) Sato, Y.; Aoyama, T.; Shirai, H. *J. Organometal. Chem.* **1974**, *82*, 21.
(365) Sato, Y.; Toyo'oka, T.; Aoyama, T.; Shikai, H. *J. Chem. Soc., Chem. Commun.* **1975**, 640.
(366) (a) Nakano, M.; Sato, Y. *J. Org. Chem.* **1987**, *52*, 1844; *J. Chem. Soc., Chem. Commun.*, **1985**, 1684. (b) For a study of the intermediates in the Sommelet–Hauser rearrangement: Shirai, N.; Watanabe, Y.; Sato, Y. *J. Org. Chem.* **1990**, *55*, 2767. (c) For an extension to naphthalene homologs see: Koyama, S.; Shirai, N.; Sato, Y. *Chem. Pharm. Bull.* **1994**, *42*, 1331. (d) For an extension to *N*-allyl- and *N*-γ-(methoxycarbonyl or cyano)allylammonium analogous salts see: Sugiyama, H.; Sato, Y.; Shirai, N. *Synthesis* **1988**, 988. (e) Zhang, C.; Maeda, Y.; Sato, Y. *Chem. Pharm. Bull.* **1998**, *46*, 572.
(367) Shirai, N.; Sato, Y. *J. Org. Chem.* **1988**, *53*, 194.
(368) Machida, Y.; Shirai, N.; Sato, Y. *Synthesis* **1991**, 117.
(369) (a) Shirai, N.; Sumiya, F.; Sato, Y.; Hori, M. *J. Org. Chem.* **1989**, *54*, 836; *J. Chem. Soc., Chem. Commun.*, **1988**, 370. See also:. (b) Sumiya, F.; Shirai, N.; Sato, Y. *Chem. Pharm. Bull.* **1991**, *39*, 36. (c) Tomoko, K.; Shirai, N.; Sato, Y. *Synthesis* **1991**, 996.
(370) Kitano, T.; Shirai, N.; Sato, Y. *Chem. Pharm. Bull.* **1992**, *40*, 768.
(371) (a) Kitano, T.; Shirai, N.; Motoi, M.; Sato, Y. *J. Chem. Soc., Perkin Trans.* **1992**, *1*, 2851. (b) See also: Sato, Y.; Shirai, N.; Machida, Y.; Ito, E.; Tasui, T.; Kurono, Y.; Hatano, K. *J. Org. Chem.* **1992**, *57*, 6711.
(372) Usami, T.; Shirai, N.; Sato, Y. *J. Org. Chem.* **1992**, *57*, 5419.
(373) Maeda, Y.; Shirai, N.; Sato, Y. *J. Chem. Soc., Perkin Trans.* **1994**, *1*, 393.
(374) Sakuragi, A.; Shirai, N.; Sato, Y.; Kurono, Y.; Hatano, K. *J. Org. Chem.* **1994**, *59*, 148.
(375) Kawanishi, N.; Shirai, N.; Sato, Y.; Hatano, K.; Kurono, Y. *J. Org. Chem.* **1995**, *60*, 4272.
(376) (a) Tanaka, T.; Shirai, N.; Sugimori, J.; Sato, Y. *J. Org. Chem.* **1992**, *57*, 5034. (b) See also: Tanaka, T.; Shirai, N.; Sugimori, J.; Sato, Y. *Chem. Pharm. Bull.* **1992**, *40*, 518; and Ref.237.
(377) Zhang, C.; Ito, H.; Mada, Y.; Shirai, N.; Ikeda, S.-i.; Sato, Y. *J. Org. Chem.* **1999**, *64*, 581.
(378) Padwa, A. *1,3-Dipolar Cycloaddition Chemistry*, Vols. 1 and 2, Wiley-Interscience, New York, 1984.
(379) Vedejs, E. (D. P. Curran, Ed.), *Advances in Cycloaddition*, Vol. 1, JAI Press, Greenwich, CT, 1988. p. 33.
(380) Imai, N.; Terao, Y.; Achiwa, K. *Yuki Gosei Kagaku Kyokaishi (J. Synth. Org. Chem. Jpn)* **1985**, *43*, 862.
(381) Vedejs, E.; West, F. G. *Chem. Rev.* **1986**, *86*, 941.
(382) Terao, Y.; Aono, M.; Achiwa, K. *Heterocycles* **1988**, *27*, 981.
(383) Tominaga, Y.; Hojo, M.; Hosomi, A. *Yuki Gosei Kagaku Kyokaishi (J. Synth. Org. Chem. Jpn)* **1992**, *50*, 48; *Chem. Abstr.* **1992**, *118*, 1744188.
(384) Pandey, G. *Synlett* **1992**, 546.
(385) Vedejs, E.; Martinez, G. R. *J. Am. Chem. Soc.* **1979**, *101*, 6454.
(386) Imai, N.; Terao, Y.; Achiwa, K. *Chem. Pharm. Bull.* **1987**, *35*, 2085.
(387) Terao, Y.; Imai, N.; Achiwa, K.; Sekiya, M. *Chem. Pharm. Bull.* **1982**, *30*, 3167.
(388) See for instance: Remers, W. A.; Rao, S. N.; Singh, U. C.; Kollman, P. A. *J. Med. Chem.* **1986**, *29*, 1256.
(389) Fishwick, C. W. G.; Jones, A. D.; Mitchell, M. B.; Szantay, C. Jr. *Tetrahedron Lett.* **1988**, *29*, 5325.
(390) Imai, N.; Tokiwa, H.; Akahori, Y.; Achiwa, K. *Chem. Lett.* **1986**, 1113.

(391) Imai, N.; Achiwa, K. *Chem. Pharm. Bull.* **1987**, *35*, 2649.
(392) Achiwa, K.; Sugiyama, K.; Sekiya, M. *Chem. Pharm. Bull.* **1985**, *33*, 1975.
(393) Imai, N.; Achiwa, K. *Chem. Pharm. Bull.* **1987**, *35*, 593.
(394) Achiwa, K.; Imai, N.; Inaoka, T.; Sekiya, M. *Chem. Pharm. Bull.* **1984**, *32*, 2878.
(395) Anderson, W. K.; Dabrah, T. T. *Synth. Commun.* **1986**, *16*, 559.
(396) Achiwa, K.; Sekiya, M. *Chem. Lett.* **1981**, 1213.
(397) Achiwa, K.; Motoyama, T.; Sekiya, M. *Chem. Pharm. Bull.* **1983**, *31*, 3939.
(398) (a) Ikeda, K.; Morimoto, T.; Sekiya, M. *Chem. Pharm. Bull.* **1980**, *28*, 1178. (b) Ikeda, K.; Terao, Y.; Sekiya, M. *Chem. Pharm. Bull.* **1981**, *29*, 1747.
(399) Pearson, W. H.; Clark, R. B. *Tetrahedron Lett.* **1999**, *40*, 4467.
(400) Tsuge, O.; Kanemasa, S.; Hatada, A.; Matsuda, K. *Chem. Lett.* **1984**, 801.
(401) Tsuge, O.; Kanemasa, S.; Hatada, A.; Matsuda, K. *Bull. Chem. Soc. Jpn* **1986**, *59*, 2537.
(402) Komatsu, M.; Ohno, M.; Tsuno, S.; Ohshiro, Y. *Chem. Lett.* **1990**, 575.
(403) Iyoda, M.; Sultana, F.; Komatsu, M. *Chem. Lett.* **1995**, 1133.
(404) Tsuge, O.; Kanemasa, S.; Kuraoka, S.; Takenaka, S. *Chem. Lett.* **1984**, 279.
(405) Miki, Y.; Hachiken, H.; Takemura, S. *Heterocycles* **1984**, *22*, 701.
(406) Tsuge, O.; Kanemasa, S.; Kuraoka, S.; Takenaka, S. *Chem. Lett.* **1984**, 281.
(407) Padwa, A.; Gadaska, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 1104.
(408) Padwa, A.; Fryxell, G. E.; Gadaska, J. R.; Venkatramanan, M. K.; Wong, G. S. K. *J. Org. Chem.* **1989**, *54*, 644.
(409) See for instance: Luly, J. R.; Rapoport, H. *J. Org. Chem.* **1984**, *49*, 1671.
(410) Hosomi, A.; Sakata, Y.; Sakurai, H. *Chem. Lett.* **1984**, 1117.
(411) Terao, Y.; Kotaki, H.; Imai, N.; Achiwa, K. *Chem. Pharm. Bull.* **1985**, *33*, 896.
(412) Terao, Y.; Imai, N.; Achiwa, K. *Chem. Pharm. Bull.* **1987**, *35*, 1596.
(413) Bentley, J. M.; Smith, D. M.; Wadsworth, H. J.; Willis, C. L. *J. Chem. Res. (S)* **1993**, 240.
(414) Madin, A.; W.O. Patent, **1997**, 9711945; *Chem. Abstr.* **1997**, *126*, 317384.
(415) Laborde, E. *Tetrahedron Lett.* **1992**, *33*, 6607.
(416) Zhang, X.; Willems, M.; Foote, C. S. *Tetrahedron Lett.* **1993**, *34*, 8187.
(417) Bégué, J.-P.; Bonnet-Delpon, D.; Lequeux, T. *Tetrahedron Lett.* **1993**, *34*, 3279.
(418) Bonnet-Delpon, D.; Bégué, J.-P.; Lequeux, T.; Ourevitch, M. *Tetrahedron* **1996**, *52*, 59.
(419) Subramaniyan, G.; Raghunathan, R.; Martin Castro, A. M. *Synthesis* **2002**, 2440.
(420) Fevig, J. M.; Abelman, M. M.; Brittelli, D. R.; Kettner, C. A.; Knabb, R. M.; Weber, P. C. *Bioorg. Med. Chem. Lett.* **1996**, *6*, 295.
(421) Nyerges, M.; Gajdics, L.; Szöllosy, A.; Töke, L. *Synlett* **1999**, 111.
(422) Fejes, I.; Nyerges, M.; Szöllosy, A.; Blasko, G.; Töke, L. *Tetrahedron* **2001**, *57*, 1129.
(423) Jossang, P.; Jossang, A.; Hadi, H. A.; Sévenet, T.; Bodo, B. J. *J. Org. Chem.* **1991**, *56*, 6527.
(424) Mamoun, O.; Benhaoua, H.; Danion-Bougot, R.; Danion, D. *Synth. Commun.* **1995**, *25*, 1295.
(425) Morimoto, Y.; Achiwa, K. *Chem. Pharm. Bull.* **1987**, *35*, 3845.
(426) Williams, R. N.; Fegley, G. J. *Tetrahedron Lett.* **1992**, *33*, 6755.
(427) Miyajima, K.; Takemoto, M.; Achiwa, K. *Chem. Pharm. Bull.* **1991**, *39*, 3175.
(428) Carmosin, R. J.; Carson, J. R.; Pitis, P. M. US Patent **1996**, 5541217; *Chem. Abstr.* **1996**, *125*, 167784.
(429) Cottrell, I. F.; Hands, D.; Kennedy, D. J.; Paul, K. J.; Wright, H. B.; Hoogsteen, K. *J. Chem. Soc., Perkin Trans.* **1991**, *1*, 1091.
(430) Orlek, B. S.; Wadsworth, H.; Wyman, P.; King, F. D. *Tetrahedron Lett.* **1991**, *32*, 1245.
(431) Fray, A. H.; Meyers, A. I. *Tetrahedron Lett.* **1992**, *33*, 3575.
(432) Kopach, M. E.; Fray, A. H.; Meyers, A. I. *J. Am. Chem. Soc.* **1996**, *118*, 9876; NB: the conessine's formule given in this scheme is the correct one, the one given in scheme 1 of this publication seems to be erroneous, cf. for instance: *The Merck Index*, **1996**, 12th edition, p. 422.
(433) Carey, J. S. *J. Org. Chem.* **2001**, *66*, 2526.
(434) Karlsson, S.; Han, F.; Högberg, H.-E.; Caldirola, P. *Tetrahedron Asymm.* **1999**, *10*, 2605.
(435) Karlsson, S.; Högberg, H.-E. *Tetrahedron Asymm.* **2001**, *12*, 1975.
(436) Karlsson, S.; Högberg, H.-E. *Tetrahedron Asymm.* **2001**, *12*, 1977.
(437) Ma, Z.; Cooper, C. S.; Fung, A. K. L.; Chu, D. T. US Patent **1997**, 5618949; *Chem. Abstr.* **1997**, *126*, 262727.
(438) Padwa, A.; Dent, W. *Org. Synth.* **1988**, *67*, 133.

(439) Poitevin, B.; Tordjman, C.; Pastoureau, P.; Bonnet, J.; De Nanteuil, G. *J. Med. Chem.* **2000**, *43*, 4582.
(440) Gerlach, K.; Hoffmann, H. M. R.; Wartchow, R. *J. Chem. Soc., Perkin Trans.* **1998**, *1*, 3867.
(441) Rispens, M. T.; Keller, E.; de Lange, B.; Zijlistra, R. W. J.; Feringa, B. I. *Tetrahedron Asymm.* **1994**, *5*, 607.
(442) Katritsky, A. R.; Köditz, J.; Lang, H. *Tetrahedron* **1994**, *50*, 12571.
(443) Padwa, A.; Chen, Y.-Y. *Tetrahedron Lett.* **1983**, *24*, 3447.
(444) Parker, K. A.; Cohen, I. D.; Padwa, A.; Dent, W. *Tetrahedron Lett.* **1984**, *25*, 4917.
(445) Hat, D. J.; Huang, Y. *Synth. Commun.* **2000**, *30*, 3203.
(446) Pandey, G.; Lakshmaiah, G.; Kumaraswany, G. *J. Chem. Soc., Chem. Commun.* **1992**, 1313.
(447) Pandey, G.; Lakshmaiah, G.; Gadre, S. R. *Indian J. Chem.* **1996**, *35B*, 91.
(448) Pandey, G.; Bagul, T. D.; Lakshmaiah, G. *Tetrahedron Lett.* **1994**, *35*, 7439.
(449) Pandey, G.; Bagul, T. D.; Sahoo, A. K. *J. Org. Chem.* **1998**, *63*, 760.
(450) Pandey, G.; Laha, J. K.; Lakshmaiah, G. *Tetrahedron* **2002**, *58*, 3525.
(451) Pandey, G.; Lakshmaiah, G.; Ghatak, A. *Tetrahedron Lett.* **1993**, *34*, 7301.
(452) Torii, S.; Okumoto, H.; Genba, A. *Synlett* **1994**, 217.
(453) Padwa, A.; Gasdaska, J. R.; Haffmanns, G.; Rebello, H. *J. Org. Chem.* **1987**, *52*, 1027.
(454) Padwa, A.; Haffmanns, G.; Tomas, M. *Tetrahedron Lett.* **1983**, *24*, 4303.
(455) Epperson, M. T.; Gin, D. Y. *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 1778.
(456) Vedejs, E.; Martinez, G. R. *J. Am. Chem. Soc.* **1980**, *102*, 7994.
(457) Tsuge, O.; Kanemasa, S.; Yamada, T.; Matsuda, K. *J. Org. Chem.* **1987**, *52*, 2523.
(458) Ohno, M.; Komatsu, M.; Miyata, H.; Ohshiro, Y. *Tetrahedron Lett.* **1991**, *32*, 5813.
(459) Washizuka, K.; Minakata, S.; Ryu, I.; Komatsu, M. *Tetrahedron* **1999**, *55*, 12969.
(460) Yoon, U. C.; Kim, D. U.; Lee, C. W.; Choi, Y. S.; Lee, Y. J.; Ammon, H. L.; Mariano, P. S. *J. Am. Chem. Soc.* **1995**, *117*, 2698.
(461) Turro, N. J.; Cha, Y.; Gould, I. R.; Padwa, A.; Gasdaska, J. R.; Tomas, M. *J. Org. Chem.* **1985**, *50*, 4415.
(462) Padwa, A.; Gasdaska, J. R.; Tomas, M.; Turro, N. J.; Cha, Y.; Gould, I. R. *J. Am. Chem. Soc.* **1986**, *108*, 6739.
(463) Padwa, A.; Kamigata, N. *J. Am. Chem. Soc.* **1977**, *99*, 1871.
(464) Tsuge, O.; Hatta, T.; Shinozuka, M.; Tashiro, H. *Heterocycles* **2001**, *55*, 249.
(465) Smith, R.; Livinghouse, T. *J. Org. Chem.* **1983**, *48*, 1555.
(466) Hosomi, A.; Miyashiro, Y.; Yoshida, R.; Tominaga, Y.; Yanagi, T.; Hojo, M. *J. Org. Chem.* **1990**, *55*, 5308.
(467) Tominaga, Y.; Takada, S.; Kohra, S. *Chem. Pharm. Bull.* **1996**, *44*, 653.
(468) Tominaga, Y.; Takeda, S.; Kohra, S. *Heterocycles* **1994**, *39*, 15.
(469) Tsuge, O.; Hatta, T.; Kakura, Y.; Tashiro, H.; Maeda, H.; Kakehi, A. *Chem. Lett.* **1997**, 945.
(470) Oba, M.; Yoshihara, M.; Nishiyama, K. *Heterocycles* **1997**, *45*, 1405.
(471) Kohra, S.; Tominaga, Y. *Heterocycles* **1994**, *38*, 1217.
(472) Tominaga, Y.; Ogata, K.; Kohra, S.; Hojo, M.; Hosomi, A. *Tetrahedron Lett.* **1991**, *32*, 5987.
(473) Washikawa, K.; Nagai, K.; Minakata, S.; Ryu, I.; Komatsu, M. *Tetrahedron Lett.* **1999**, *40*, 8849.
(474) Levier, R. R.; Chandler, M. L.; Wendel, S. R. The pharmacology of silanes and siloxanes, (G. Bendz, I. Lindqvist, Eds.) *Biochemistry of Silicon and Related Problems (Nobel Symposium)*, Plenum Press, New York, 1978. p. 473.
(475) Fessenden, R. J.; Fessenden, J. S. Trends in organosilicon biological research, *Adv. Organometal. Chem.* **1980**, *18*, 275.
(476) Voronkov, M. G. Biological activity of silatranes, *Top. Curr. Chem.* **1979**, *84*, 77.
(477) Fessenden, R. J.; Coon, M. D. *J. Med. Chem.* **19864**, *7*, 561.
(478) Tacke, R.; Brakman, S.; Kropfgans, M.; Strohmann, C.; Wuttke, F.; Lambrecht, G.; Mutschler, E.; Proksch, P.; Schiebel, H.; Witte, L. Bioorganosilicon chemistry – recent results, (A. R. Bassindale, P. P. Gaspar, Eds.) *Frontiers of Organosilicon Chemistry*, Royal Society of Chemistry, London, 1991. p. 226.
(479) Barcza, S. Preparation of bioactive silicon compounds is feasible, *L'Actualité Chimique* **1986**, *3*, 83.
(480) Kurochka, A. V.; Agafonova, O. V.; Losev, A. S.; Mamaeva, E. A.; Bylikin, S. Y.; Negrebetsky, V. V.; Kramarova, E. P.; Shipov, A. G.; Baukov, Y. I. *Metal-Based Drugs* **1998**, *5*, 25; *Chem. Abstr.* **1968**, *129*, 49558.
(481) Garson, L. R.; Kirchner, L. K. *J. Pharm. Sci.* **1971**, *60*, 1113.

(482) Ricci, A.; Seconi, G.; Taddei, M. Bioorganosilicon chemistry: trends and perspectives, *Chimicaoggi* **1989**, *9*, 15.
(483) Sakurai, H. (H. Sakurai, Ed.) *Organosilicon and Bioorganosilicon Chemistry*, Ellis Horwood & Wiley, Toronto, 1985. p. 251.
(484) Tacke, R. Recent results in bioorganosilicon chemistry: novel siladrugs and microbial transformations of organosilicon compounds (H. Sakurai, Ed.) *Organosilicon and Bioorganosilicon Chemistry*, Ellis Horwood & Wiley, Toronto, 1985. p. 251; Chapter 23.
(485) Voronkov, M. G.; Alekseeva, L. N.; Brizga, B.; Zlle, A.; Krusmetra, L.; Kozuykov, V. P.; Lukevicz, E.; Lyashenko, I. N.; Mironov, V. F.; Fedotov, N. S. *Khim. Farm.* **1967**, 26; *Chem. Abstr.* **1968**, *68*, 38460.
(486) Voronkov, M. G. *XXIVth International Congress of IUPAC*, Butterworths, Hamburg, 1973, p. 45.
(487) Wannagat, U. Sila-Pharmaca, (G. Bendz, I. Lindqvist, Eds.) *Biochemistry of Silicon and Related Problems (Nobel Symposium)*, Plenum Press, New York, 1978. p. 447.
(488) Murphy, D. L.; Garrick, N. A.; Anlakh, C. S.; Cohen, R. M. *J. Clin. Psychiatry* **1984**, *45*, 37.
(489) Schirlin, D.; Collard, J. N.; Danzin, C.; Eur. Pat. Appl., 107312 (to Merell Dow Pharmaceutical Co), 1988; *Chem. Abstr.* **1989**, *110*, 115113. See also: Schirlin, D.; Collard, J.N.; Danzin, C. US Patent, **1995**, 690431; *Chem. Abstr.* **1995**, *122*, 205211.
(490) Danzin, C.; Zrelka, M.; Marchal, P.; Petty, M.; Collard, J. N.; Schirlin, D. *Biochem. Soc. Trans.* **1994**, *22*, 768.
(491) Danzin, C.; Collard, J. N.; Marchal, P.; Schirlin, D. *Biochem. Biophys. Res. Commun.* **1989**, *160*, 540.
(492) Silverman, R. B.; Banik, G. M. *J. Am. Chem. Soc.* **1987**, *109*, 2219.
(493) Kim, J.-M.; Cho, I.-S.; Mariano, P. S. *J. Org. Chem.* **1991**, *56*, 4943.
(494) Kim, J.-M.; Hoegy, S. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1995**, *117*, 100.
(495) Wang, F.; Venkataraman, B.; Klein, M. E.; Sayre, L. M. *J. Org. Chem.* **1992**, *57*, 6687.
(496) Lukevics, E.; Luse, V.; Zicmane, I.; Liepins, E.; Trusule, M.; Germane, S.; Augustane, I.; Verovski, V. N.; Prodenchuk, N. G.; Decneka, S. E.; Nivalov, V. H. *Khimiya Geterosiklicheskikh Soedinenii* **1991**, 1653; *Chem. Abstr.* **1991**, *117*, 191728.
(497) Gotteland, J. -P.; Delhon, A.; Junquéro, D.; Oms, P.; Halazy, S. *Bioorg. Med. Chem. Lett.* **1996**, *6*, 533.
(498) Halazy, S.; Gotteland, J.-P.; Delhon Oms, P. A.; Junquéro, D.; International Patent WO 01830 (to Pierre Fabre Medicaments), **1996**; *Chem. Abstr.* **1996**, *124*, 289877.
(499) Kurono, M.; Unno, R.; Matsumoto, Y.; Kondo, Y.; Mitani, T.; Jomori, T.; Michishita, H.; Sawai, K. Eur. Pat. Appl., **1988**, 288002; *Chem. Abstr.* **1989**, *110*, 75808.
(500) Anderson, W. K.; Haugwitz, R. D. US Patent **1991**, 4994591; *Chem. Abstr.* **1991**, *115*, 92600.
(501) Kurono, M.; Suzuki, T.; Suzuki, T.; Hirooka, K.; Matsumoto, Y.; Ozawa, H.; Sawai, K. Eur. Pat. Appl., **1989**, 299495; *Chem. Abstr.* **1989**, *111*, 7217.
(502) Tacke, R.; Linoh, H.; Attar-Bashi, M. T.; Scheldrick, W. S.; Ernst, L.; Niedner, R.; Frohnecke, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 1461.
(503) Shchekina, T. G.; Kopylov, V. M.; Voronkov, M. G. *Khim.-Farm. Zh.* **1985**, *19*, 165; *Chem. Abstr.* **1985**, *103*, 54137.
(504) Mamyeva, Y. A.; Agafonova, O. V.; Negrebetsky, V. N.; Shipov, A. G.; Baukov, Y. I.; Losev, A. S. *Khim.-Farm. Zh.* **1994**, *28*, 26; *Chem. Abstr.* **1995**, *122*, 10104.
(505) Kurochka, A. V.; Afganova, O. V.; Losev, A. S.; Mamaeva, E. A.; Bylikin, S. Y.; Negrebetsky, V. V.; Kramarova, E. P.; Shipov, A. G.; Baukov, Y. I. *Metal-based Drugs* **1998**, *5*, 25.
(506) Barcza, S. Eur. Patent **1979**, 4018 (to Sandoz, A.-G.); *Chem. Abstr.* **1980**, *92*, 94570; Barcza, S. US Patent **1980**, 4208408 (to Sandoz, A.-G.); *Chem. Abstr.* **1980**, *93*, 186554; Barcza, S. US Patent **1980**, 4224317 (to Sandoz, A.-G.); *Chem. Abstr.* **1980**, *94*, 103552.
(507) Barcza, S. US Patent **1985**, 4528151 (to Sandoz, A.-G.); *Chem. Abstr.* **1985**, *103*, 183585.
(508) Lukevics, E.; Segal, I.; Germane, S.; Veveris, M. *Lat. Kim. Z.* **1991**, 106; *Chem. Abstr.* **1991**, *115*, 49794.
(509) Lukevits, E.; Segal, I.; Zablotskaya, A.; Germane, S. *Chem. Heterocycl. Compounds* **1996**, *32*, 682.
(510) Lukevits, E.; Segal, I.; Zablotskaya, A.; Germane, S. *Molecules* **1997**, *2*, 180.
(511) Lukevits, E.; Germane, S.; Segal, I.; Zablotskaya, A. *Chem. Heterocycl. Compounds* **1996**, *33*, 234.
(512) Barcza, S. US Patent **1979**, 4175091 (to Sandoz, A.-G.); *Chem. Abstr.* **1980**, *92*, 76660.
(513) Barcza, S. US Patent **1979**, 4132725 (to Sandoz A.-G.); *Chem. Abstr.* **1979**, *90*, 121795.
(514) Barcza, S. US Patent **1972**, 3636025 (to Sandoz, A.-G.); *Chem. Abstr.* **1972**, *76*, 85915.
(515) Barcza, S. US Patent **1972**, 3692798 (to Sandoz, A.-G.); *Chem. Abstr.* **1973**, *78*, 43692.

(516) Moberg, W. K. Eur. Patent **1983**, 68813 (to du Pont de Nemours, E.I. & Co.); *Chem. Abstr.* **1983**, *98*, 198430.
(517) Moberg, W. K. US Patent **1985**, 4510136 (to du Pont de Nemours, E.I. & Co.); *Chem. Abstr.* **1986**, *104*, 207438.
(518) Barnum, C. S.; Olson, R. E.; Moberg, W. K. Eur. Patent, **1988**, 296745 (to du Pont de Nemours, E. I. & Co.); *Chem. Abstr.* **1988**, *110*, 173241.
(519) Aukenthaler, A.; Edlmayer, F.; Reiter, K.; Kores, D.; Graf, J.; Tramberger, H.; German Patent, **1989**, 3805117 (to Lentia G.m.b.H.); *Chem. Abstr.* **1990**, *112*, 56271.
(520) Jautelat, M.; Tieman, R.; Dutzmann, S.; Stenzel, K. German Patent, **1996**, 19520095 (to Bayer A.-G.); *Chem. Abstr.* **1997**, *126*, 41932.
(521) (a) Schnabel, G.; Parisi, L. *Z. Plflanzenkrankheiten Pflanzenschutz* **1996**, *104*, 36. (b) See also: Schnabel, G.; Parisi, L. *Acta Hortic.* **1996**, 83; *Chem. Abstr.* **1998**, *129*, 575051.
(522) Moberg, W. K.; Basarab, G. S.; Cuomo, J.; Liang, P. S. Biologically active organosilicon compounds: silicon-containing triazole fungicides, (R. Greenhaig, T. R. Roberts, Eds.) *Pesticides Science and Biotechnology*, Blackwell Scientific, Boston, 1986. p. 57.
(523) Bryk, H. *J. Fruit Ornamental Plant Res.* **1997**, *5*, 77.
(524) Ko, Y.; Sun, S. K.; Pan, C. M. *Zhiwu Baohu Xuehui Huikan* **1998**, *40*, 361; *Chem. Abstr.* **1999**, *130*, 10233.
(525) Gandhi, S. K.; Maheshwari, S. K.; Satyarvir. *Tests Agrochem. Cultiv*. **1997**, *18*, 10; *Chem. Abstr.* **1998**, *128*, 71887.
(526) Meunier, L.; Mercer, R. French Patent **1996**, 2732191; *Chem. Abstr.* **1997**, *126*, 743955.
(527) Kendal, S. J.; Hollomon, D. W.; Tolbutt, K. B.; Salter, A. C. *Brighton Crop Prot. Conf. Pest. Dis.* **1996**, *1*, 251; *Chem. Abstr.* **1997**, *126*, 71521.
(528) Mercer, P. C.; Ruddock, A. *Tests Agrochem. Cultiv*. **1995**, *16*, 32; *Chem. Abstr.* **1996**, *124*, 23918.

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