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Coordination Chemistry Reviews 233–234 (2002) 131–155

COORDINATION CHEMISTRY REVIEWS

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Non-cyclopentadienyl ancillaries in organogroup 3 metal chemistry: a fine balance in ligand design

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Received 5 October 2001; accepted 11 January 2002

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PII: S0010-8545(02)00016-4

Abstract

Over the past decade, several groups have targeted well-defined organometallic Group 3 metal complexes with ancillary ligand supporting environments alternative to the ubiquitous bis-Cp donor set. In addition to a desire to develop the fundamental organometallic chemistry of Group 3 bis-alkyl derivatives, these compounds are of interest as catalyst precursors for olefin and lactide polymerization processes, as well as olefin hydrosilation, amination and hydrogenation cycles. This review surveys the non-Cp organometallic chemistry of the ligands which have so far been explored for this purpose, commenting on the fine balance of steric and electronic properties necessary to stabilize monomeric, base-free organometallic compounds of these metals. While *bona fide* organometallic compounds have not been explicitly prepared in all cases, promising ligands in this regard are also included. The review covers the literature from about 1994 forward, encompassing 35 new ligand systems.

Keywords: Organometallic chemistry; Scandium; Yttrium; Lanthanum; Ligand design

1. Introduction

1.1. Scope of the review

Compared to other transition metals, the organometallic chemistry of the Group 3 triad has been slow to develop. In the first *Comprehensive Organometallic Chemistry* series, for example, the combined citations for the organometallic chemistry of scandium, yttrium, lanthanum *and the lanthanides* numbered only ≈233 [1], in comparison to 751 for organogroup 4 metal chemistry and 2632 for organogroup 8 metal compounds. Early work in organogroup 3 metal chemistry was dominated by complexes supported by cyclopentadienyl type donors of varying substitution and modification [2]. While these ligands are suitable for preparing and examining well defined, monomeric organometallic complexes, generally two Cp donors are required. This dianionic ligand set leaves only one valence in the M^{3+} metals for a reactive hydrocarbyl ligand, limiting the chemistry to reactions involving one M–C bond in neutral complexes. While much elegant chemistry was uncovered [3], the limitations inherent to the bis-Cp ancillary set triggered the search for new supporting ligand environments. This search has been a fruitful one, and in particular the last 5–10 years has seen a cornucopia of new ligands for use with Group 3 metals. While not all the ligand systems tested have been entirely successful, the combined efforts of researchers in this area have delineated the challenges inherent to ligand design for Group 3 metals.

In this review, we will cover the recent developments in the organometallic chemistry of Sc, Y and La, as supported by non-Cp ligand environments. More comprehensive treatments (including all of the lanthanides) of the literature up to ≈1994 appeared in 1995 [4], so we will emphasize the work produced since that period. Our perspective on these complexes derives primarily from their potential as olefin polymerization catalyst precursors, so the accent will be placed on those systems for which well characterized organometallic derivatives have been prepared; some mention of promising ligand systems for which only precursors to organometallic derivatives have been synthesized will also be made. However, non-organometallic chemistry dealing with coordination compounds [5], and low valent complexes or endohedral fullerenes, will be excluded. Furthermore, we do not intend to cover any of the 'modified Cp' ligand literature, for example the Cp-amido, 'constrained geometry' ligand systems and other Cp ligands modified by pendant donors of some type. The Group 3 organometallic chemistry of these ligand systems have been covered recently in other reviews [6] and in any case they still rely on a Cp donor as the primary ancillary anchor. Group 3 porphyrin complexes, although an important class of non-Cp organometallic compounds, are mentioned only briefly because little advancement has occurred since their chemistry was last reviewed [7]. Finally, we also exclude homoleptic alkyl complexes [8] and heterocyclopentadienyl complexes, including boratabenzene [9] derivatives. This latter area has also been partially covered in a recent review [10].

1.2. The challenges of ligand design for Group 3 metals

To the extent that challenges are defined by goals, let us assume that the goal is to prepare thermally stable, donor solvent-free organometallic complexes with 1–3 M–R groups, in which the ancillary ligand is completely inert and non-labile. Realization of this goal allows for the study of these organometallic compounds, but this has been accomplished in relatively few non-cyclopentadienyl systems and remains a vibrant area of research. Group 3 metals are highly Lewis acidic and the heavier members of the triad, Y and La, are relatively large (ionic radii for M^{3+}: Sc = 0.89; Y = 1.04; La = 1.17 Å [11]). This renders their complexes prone to ligation by weak Lewis bases, such as THF, which can be problematic since the primary starting materials for synthesis of complexes are often THF adducts of MX_3 (X = halide, amido, alkyl). Related to this is the tendency of Group 3 metal complexes to aggregate into (primarily) dimeric structures; often, if THF free complexes are obtained, dimerization is observed. A consequence of this ability to aggregate are low energy pathways for ligand exchange, resulting in facile ligand redistribution processes for sterically unprotected ancillaries. This is another challenge which must be overcome, since desirable targets such as LMR_2 (where L is a monoanionic ligand) can spontaneously redistribute to L_2MR and MR_3 (the latter compound class is generally thermally unstable). A final consideration related to the elevated Lewis acidity of these compounds is the well-known tendency to occlude salts generated as byproducts in synthetic procedures. Thus, structural motifs such as $L_nM(\mu\text{-Cl})_2M'(THF)_x$ are often encountered (M′ = an alkali metal), and the presence of this occluded salt can be deleterious to further reactivity studies.

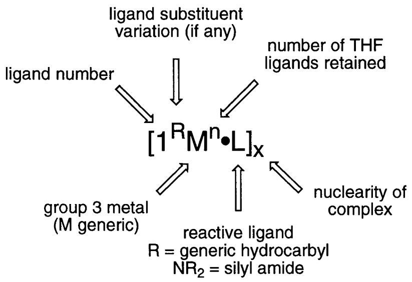
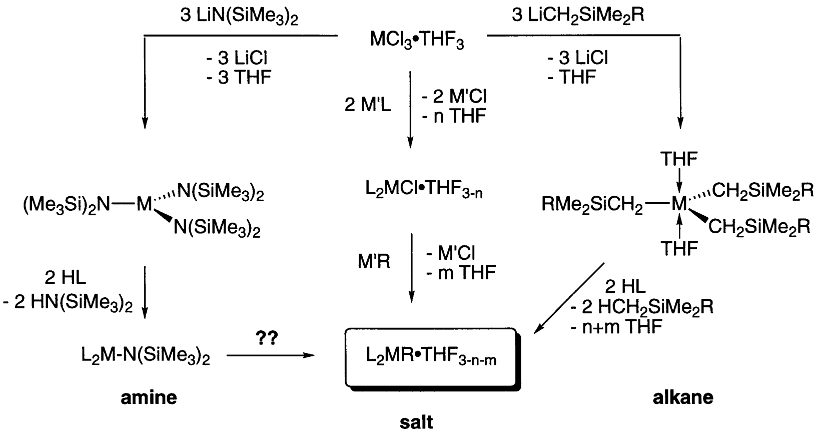


Fig. 1. Compound labeling scheme for the review. The number of anionic ligands 'L' in combination with the overall charge of the complex allows for determination of whether the derivative is a mono- or bis-ligand complex.

Addressing these challenges is mainly a question of providing the right steric environment about the metal center. Electronic saturation is less important, although the amount of electronic saturation can have an effect on the properties of the M–C bond(s) in the complex. Careful ligand design is therefore crucial. Ideally, a ligand system must provide enough steric bulk to prevent THF ligation, dimerization and ligand redistribution, but not so much as to shut down the organometallic reactivity that is the goal of the chemistry. Many ligand systems have failed in walking this fine line. Due to the hard, Lewis acidic nature of the M^{3+} ions, ligands based on the hard donor elements oxygen and nitrogen have tended to dominate in the ligand employed (with some notable exceptions). In order to prevent ligand distribution, multidentate ligands are generally favored, particularly those with donors that do not readily engage in bridging bonding modes. However, ligands of higher denticity occupy more coordination sites and begin to dampen reactivity, so again a fine balance is necessary.

A final consideration in ligand design is the formal charge of the ligand set. Since we are dealing with metals that are invariably in the +3 oxidation state, ligand sets of formal charge −2 or −1 are the most desirable in the context of organometallic chemistry. The dianionic ligand set allows for preparation of neutral mono-organo complexes related to those supported by the bis-cyclopentadienyl platform, while a mono anionic ligand makes possible the study of bis-hydrocarbyl derivatives. This latter, elusive family of compounds is of interest because of the potential for generating Group 3 metal alkyl cations related to the Group 4 cations which have been so important in the field of olefin polymerization [12].

Since this area is dominated by ligand design, we will organize the review according to ligand type. The primary taxonomy will be based upon denticity, with subsequent divisions based on the donor atom set and



Scheme 1.

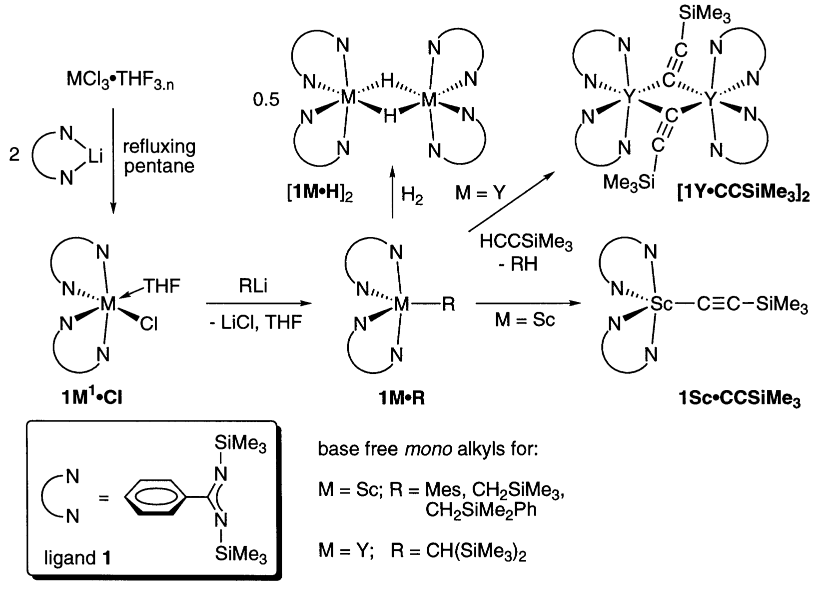
the formal charge of the ligands. Compounds will be labeled according to the system shown in Fig. 1, based on the ancillary ligand, metal and reactive ligand present. Since many of the compounds discussed retain THF donors, the number present is indicated by a superscript after the metal designation; no number indicates a THF free complex.

1.3. Synthetic and other considerations

With few exceptions, organometallic compounds of the scandium triad are prepared by three general methods: salt, amine and alkane eliminations (Scheme 1). The first method is the most time-honored and involves the reaction of alkali metal salts of the ligand with metal halide precursors, usually the metal chloride THF adducts. For M = Sc, the octahedral tris-THF adduct is conveniently available in large quantities from the oxide Sc_2O_3 [13]. For M = Y, the yttrium speciation in the trichloride depends on how it is prepared; the octahedral analog of the scandium trichloride is not conveniently available and the most common yttrium reagent exists as the ion pair $[YCl_2\cdot THF_5]^+[YCl_4\cdot THF_2]^-$, often depicted as $YCl_3\cdot THF_{3.5}$ [14]. Dissolving this material into CH_2Cl_2 and pumping to dryness gives a polymeric chloride of empirical formula $[YCl_3\cdot THF_2]_n$. The solubility and reactivity properties of the ion pair and the polymeric species are quite different and can affect the outcome of salt elimination procedures. In some cases, anhydrous, base-free YCl_3 beads in diethylether have been employed to good effect. $LaCl_3$, dissolved in THF is a typical starting material for salt eliminations involving this metal. Typically, salt elimination reactions for all three metals require forcing conditions, especially for sterically bulky ligands, and generate ligand–metal chloride precursors which may be subsequently converted to organometallic compounds via standard alkylation techniques. However, as mentioned above, occlusion of the eliminated salt is sometimes a problem.

Amine elimination using the homoleptic tris-amido compounds $M[N(SiMe_3)_2]_3$ [15] which have been known for some time, is a more recent method of ligand institution. In some instances, the amido derivative $M[N(SiHMe_2)_2]_3\cdot THF_2$ [16] has been used, particularly for more bulky ligands. Overall, this method has been less successful than amine elimination protocols in Group 4 organometallic chemistry [17], since the steric bulk of the amido groups used here raises the barrier towards amine elimination. Also, general routes for converting the resulting metal amides (i.e. $L_nM[N(R)_2]_{3-n}$) to organometallic compounds are not available. The last method, alkane elimination, circumvents this problem by preparing organometallic derivatives directly. Most protocols utilize $M(CH_2SiMe_3)_3\cdot THF_2$ derivatives [18], either generated in situ or isolated, but these compounds are thermally unstable even as solids and are difficult to isolate due to their high solubility in hydrocarbon solvents. Thus, these precursors are not amenable to alkane eliminations which require heating. Reactions using the more stable, crystalline compounds $M(CH_2SiMe_2Ph)_3\cdot THF_2$ (M = Sc, Y) [19] tend to proceed more cleanly because of the better control over reaction stoichiometry, and in our laboratory, these are now the reagents of choice for alkane elimination reactions. The major drawback of these protocols, however, is that one is limited to producing organometallic derivatives where the alkyl group is CH_2SiMe_2R (R = CH_3 or C_6H_5) [20].

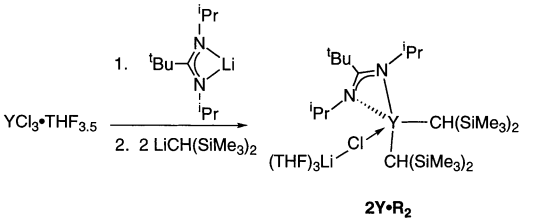
NMR spectroscopy is a primary tool for solution structure determination in organogroup 3 metal chemistry and each metal has NMR active isotopes [21]. For scandium, atoms bonded directly to the metal are sometimes difficult to detect due to the quadrupolar nature of the ^{45}Sc nucleus ($I = 7/2$, 100%), and the signals for α-protons in scandium hydrocarbyl groups are broadened to varying degree. Carbon atoms directly



Scheme 2.

attached to Sc are best detected using 2D-HMQC experiments. For yttrium, the situation is at the opposite end of the spectrum, in that the ^{89}Y nucleus has a spin of 1/2 (100%) and the coupling information available is highly informative. For hydrides, the $^{1}J_{Y-H}$ values range from 25 to 35 Hz, and the multiplicity provides information on the nuclearity of the complex. $^{2}J_{Y-H}$ and $^{1}J_{Y-C_{sp3}}$ values in hydrocarbyl groups range from 1.8 to 2.8 and 30 to 46 Hz, respectively. ^{89}Y-NMR spectroscopy itself can be informative, although long relaxation times and the negative nOe effect require the use of fairly concentrated samples, limiting the utility of this technique. The situation for lanthanum is similar to that of scandium in that ^{139}La, although 100% abundant, has a spin of 7/2 and a significant quadrupole moment. Although it has a high relative sensitivity, few reports including ^{139}La-NMR data have appeared.

We raise one final issue before surveying the chemistry. In many of the studies described below, the very bulky bis-trimethylsilylmethyl alkyl group is used to stabilize base free organogroup 3 compounds. Many of these compounds have been structurally characterized, and invariably, because of the three bulky substituents on it, the α carbon atom has a near-planar geometry. As a result, the lone C–H bond has high p-character and low $^{1}J_{CH}$ values ($\approx$80 Hz) are often reported for this group. This low $^{1}J_{CH}$ value is often ascribed to the presence of an α-agostic interaction; however, Schaverien and co-workers have recently shown definitively that CH agostic interactions are not a general feature of this alkyl group [22]. Rather, β-SiC agostic interactions are significant and frequently observed in the complexes of this alkyl group.



Scheme 3.

2. Group 3 organometallic compounds supported by bidentate ligands

2.1. NN donors, monoanionic

2.1.1. Amidinates

One of the first alternatives to Cp donors to support organoyttrium derivatives was the benzamidinato ligand framework [23]. Teuben and co-workers utilized the *N*-silylated ligand [PhC(NSiMe$_3$)$_2$] to prepare the bis-ligand yttrium chloride as the mono-THF adduct **1Y^1·Cl** (see Fig. 1 for the legend for the numbering system) via salt elimination as shown in Scheme 2. Initially, a LiCl adduct was formed, but the lithium chloride could be precipitated by refluxing the compound in pentane. Neutral organometallic derivatives **1Y·R** could be prepared via standard alkylation procedures, and other groups (alkoxides, amides or hydridoborate) could be similarly instituted. The ligand binds to the metal in a symmetrical fashion, with the four electrons fully delocalized over the CN$_2$M framework; in solution, a dynamic process consistent with rapid rotation about the M–C vector is observed. A detailed analysis of the structures [24] and reactivity patterns [25] for these compounds lead to the conclusion that, sterically, the

[PhC(NSiMe$_3$)$_2$] ligand has comparable properties to Cp* (Cp* = η^5-C$_5$Me$_5$), but electronically the Y center in these compounds is more electropositive than in metallocenes. The resulting contraction of the orbitals about Y impacts the reactivity of the alkyl derivatives **1Y·R**; for example, the rates of hydrogenolysis to dimer **[1Y·H]$_2$** are qualitatively much slower than those found for Cp$_2^*$YR, and, unlike the metallocenes, intermolecular σ-bond metathesis reactions with C_6D_6 are not observed. However, both **1Y·R** and **[1Y·H]$_2$** undergo σ-bond metathesis with the C_{sp}–H bonds of terminal acetylenes to give interesting μ-alkyne dimers as shown in Scheme 2. For acetylenes with bulkier groups, these compounds react with further terminal acetylene to effect catalytic head-to-tail dimerization of alkynes, albeit sluggishly. Nonetheless, these compounds exhibit a rich chemistry and, because they are thermally stable towards ligand redistribution reactions, provide a satisfactory platform for the study of non-Cp supported Y–R reactivity patterns.

The scandium congeners **1Sc** were reported by Arnold and Hagadorn [26] and prepared in a similar manner. The crystal structure of the dimeric hydride **[1Sc·H]$_2$** was determined; remarkably, this hydride did not undergo exchange with D$_2$ and exhibited low reactivity towards olefins and terminal alkynes, attesting to the low tendency of this dimer to dissociate. The reaction of **1Sc·R** with HCCSiMe$_3$ proceeds with loss of RH to yield the *monomeric* terminal acetylide, in contrast to the dimeric structures obtained for the larger yttrium congener. Organolanthanum derivatives with this ligand set have not been reported; however, the homoleptic tris-ligand complex has been synthesized [27].

Modifications of this parent benzamidinato ligand system have recently appeared, with the goals being to add steric bulk such that mono-ligand complexes might be supported, or to provide modified steric environments capable of controlling the stereochemical course of lactide polymerization catalysis. Two potential sites for ligand modification are the groups bonded to the central carbon and the nitrogen substituents. Hessen and co-workers have prepared a more sterically demanding amidinato ligand incorporating a ^{t}Bu group on carbon and iso-propyl groups on the nitrogen donor and generated a diorgano derivative of yttrium using the one-pot procedure outlined in Scheme 3 [28]. Compound **2Y·R$_2$** was isolated in a very respectable 83% using this protocol, but the compound retains one molecule of LiCl, as shown, even with the use of the large CH(SiMe$_3$)$_2$ alkyl group. This led to further modifications of the amidinato ligand framework, described below in Section 3.3.3.

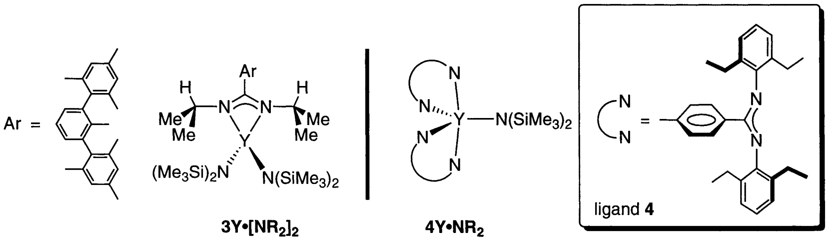
Arnold has incorporated a bulky terphenyl group onto the central carbon atom to form a highly sterically imposing amidinato ligand which stabilizes monomeric mono-ligand complexes such as **3Y·[NR$_2$]$_2$** (Chart 1) [29] Tolman and co-workers, on the other hand, used ligands with bulky nitrogen substituents to form monomeric yttrium amides (such as **4Y·NR$_2$**) and alkoxides which are active initiators for the ring opening polymerization of D,L-lactide [30]. Several discrete yttrium and lanthanum alkoxides have found utility for this particular application [31]. Both of these compounds were prepared via standard salt metathesis techniques. Although these compounds are not strictly organometallic derivatives, this work illustrates the potential of these bulkier amidinato ligands for the stabilization of **3Y·R$_2$** and **4Y·R** type compounds.

A related ligand system to the amidinates is the amidopyridinato ligand reported recently by Kempe and co-workers Although no organometallic derivatives were prepared, yttrium 'ate' complexes of this potentially more rigid (but less sterically bulky) ligand system were reported and used as a ligand transfer agent in the preparation of palladium complexes [32].

2.1.2. Guanidinates

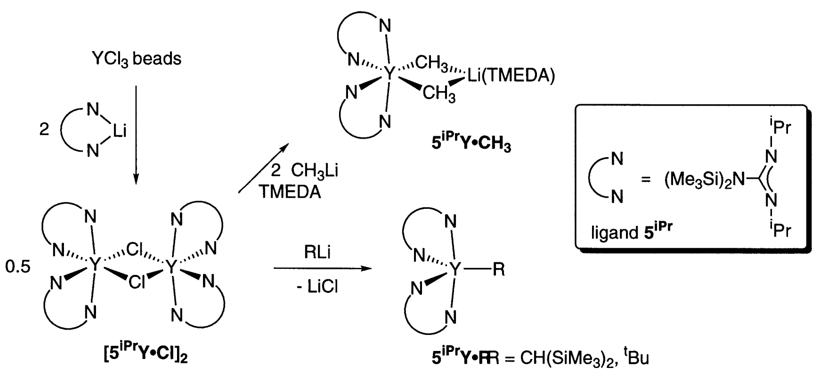
A related family of ligands containing an NR$_2$ group on the central carbon atom are the guanidinates [33]. In principle, these ligands should be more electron donating than the amidinato ligands by participation of an iminium/diamide resonance structure available through conjugation of the exogenous nitrogen's lone pair. In practice, the bulky groups necessary in guanidinato ligands for use with Group 3 metals preclude such conjugation and the non-coordinating NR$_2$ does not electronically participate in the bonding via conjugation.

Richeson and co-workers have developed some organoyttrium chemistry supported by the in situ generated guanidinato ligand [(Me$_3$Si)$_2$NC(N^{i}Pr)$_2$]$^-$ (Scheme 4)



3Y•[NR$_2$]$_2$ **4Y•NR$_2$**

Chart 1.



Scheme 4.

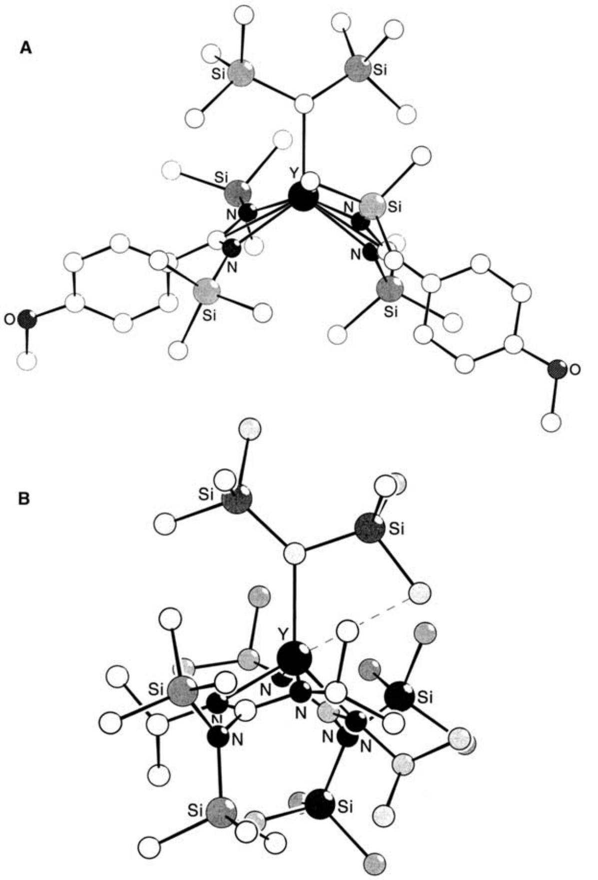
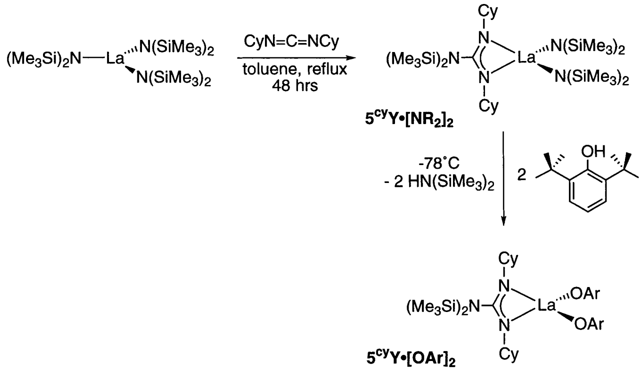


Fig. 2. Views $\mathbf{1^{OMe}Y \cdot CH(SiMe_3)_2}$ (A) and $\mathbf{5^{^iPr}Y \cdot CH(SiMe_3)_2}$ (B) illustrating the absence of a β-SiC agostic interaction in the former and its presence in the latter.



Scheme 5.

[34]. Reacting the lithium salt of this ligand with anhydrous YCl_3 beads in diethylether allowed for the high yield synthesis of the chloro bridge dimer $\mathbf{[5^{^iPr}Y \cdot Cl]_2}$, a notable method for producing a THF free starting material. Despite the dimeric structure, alkylation with RLi (R = $CH(SiMe_3)_2$, ${}^tBu$ and CH_3) proceeds smoothly to give monomeric organometallic compounds $\mathbf{5^{^iPr}Y \cdot R}$, although in the case of R = CH_3, a second equivalent of MeLi was incorporated into the product. All three of these compounds were crystallographically characterized, and an analysis of the C–N bond lengths and the observed orthogonal orientation of the $N(SiMe_3)_2$ substituent suggests that the ligand binds exclusively as a 1,3-diazaallyl moiety in these complexes. In contrast to the benzamidinato congener $\mathbf{1Y \cdot CH(SiMe_3)_2}$, the alkyl group in $\mathbf{5^{^iPr}Y \cdot CH(SiMe_3)_2}$ is asymmetrically bonded to the yttrium center (Fig. 2), indicating the presence of an agostic interaction between the yttrium and the β-SiC and γ-CH bonds of the alkyl group in the latter compound. Using the arguments of Teuben and co-workers [23], this observation might suggest that the yttrium centers in compounds $\mathbf{5^{^iPr}}$ are less electropositive than those in benzamidinates **1**. However, no evidence for β-CH agostic interactions was found in the structure of the ${}^tBu$ substituted compound, a rare example of a metal-tertiary hydrocarbyl derivative. The reactivity of these compounds awaits further investigation.

Arnold and co-workers have incorporated a related cyclohexyl substituted guanidinato ligand into lanthanum's coordination sphere via a novel and elegant method which serves as one of the few exceptions to the routes outlined in Scheme 1. Direct reaction of $La[N(SiMe_3)_2]_3$ with the carbodiimide CyN=C=NCy lead to insertion into one of the La–N bonds to form $\mathbf{5^{cy}Y \cdot [NR_2]_2}$ in good yield, along with a small amount of a bis-ligand amido complex (Scheme 5) [35]. Very few examples of base-free lanthanum complexes exist and this method may have some potential for the preparation of organometallic derivatives, albeit with a limited scope. Treatment of $\mathbf{5^{cy}Y\cdot[NR_2]_2}$ with a bulky phenol gave a bis-phenoxide complex which was tested for activity as a lactide polymerization catalyst.

2.1.3. Aminotroponiminates

Roesky et al. have begun development of the aminotroponiminato ligand framework as an alternative to Cp donors in Group 3 chemistry [36]. While no discrete organometallic derivatives of Sc/Y/La have been prepared (aside from some complexes containing Cp donors [37]), they are deserving of mention due to their potential as supporting ligands for organometallic chemistry, particularly in view of their successful deployment in organoaluminum chemistry [38]. These ligands are bidentate donors with a 10π electron, seven-membered ring backbone, forming a five-membered chelate upon binding to a metal center. Mono- and bis-ligand chloro complexes were prepared via salt elimination by reaction of the potassium salts of the *N*,*N*-*iso*-propyl substituted ligand and YCl_3 in THF. Because of unfavorable steric interactions between the seven-membered ring backbone, the nitrogen ^{i}Pr substituents are oriented such that the methyl groups point in towards the metal, providing steric shielding where it is most beneficial. Substitution of the remaining chloride ligands with the bulky $N(SiMe_3)_2$ ligand was trivially effected to yield $\mathbf{6Y\cdot NR_2}$ and $\mathbf{6Y\cdot[NR_2]_2}$ derivatives which are THF-free. These compounds are both active catalysts for the cyclohydroamination of amino alkynes, e.g. $H_2N(CH_2)_3C\equiv CH$ [39]. First reported for lanthanocene precatalysts [40], this reaction presumably proceeds via amide exchange (with loss of $HN(SiMe_3)_2$), followed by intramolecular insertion of the pendant alkyne into the newly formed Y–N bond, giving a vinyl organoyttrium intermediate. Alkane elimination via σ-bond metathesis with amino alkyne substrate completes the cycle. In comparison to $Cp_2^*YCH(SiMe_3)_2$ [41], both the mono- and bis-aminotroponiminato complexes are inferior catalysts, exhibiting turnover numbers 5–7 times lower than the metallocene. Nonetheless, as a first generation alternative catalyst system, the results are promising, particularly the stability of the ligand platform under the catalytic conditions employed.

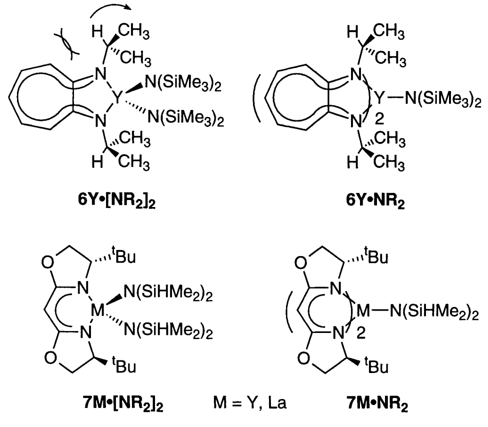


Chart 2.

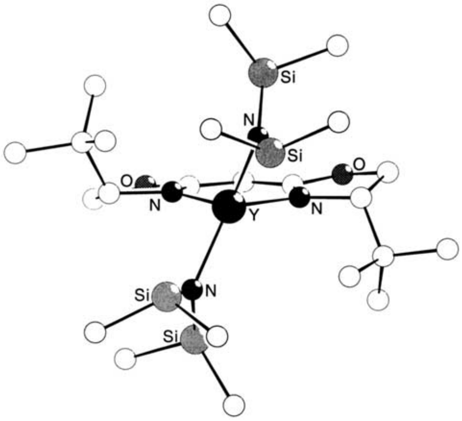


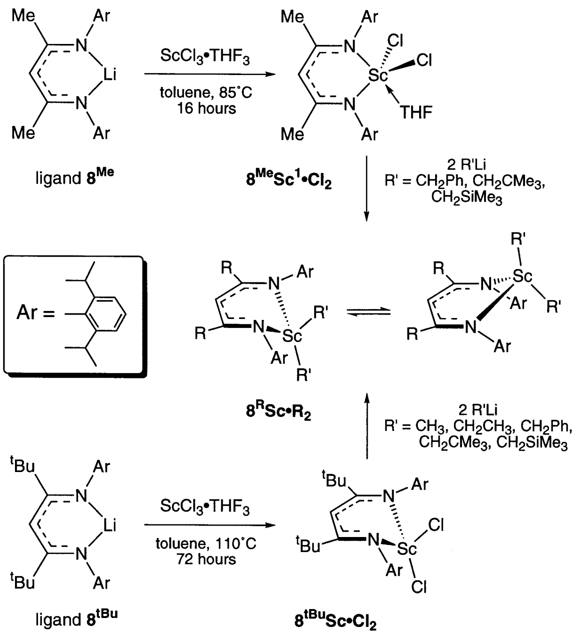
Fig. 3. Molecular structure of the C_2 symmetric bis-oxazolinato complex $\mathbf{7Y\cdot[NR_2]_2}$.

2.1.4. Bis-oxazolinates

A promising family of compounds was recently reported by Anwander et al. incorporating the C_2 symmetric bis-oxazolinato ligand framework. Yttrium and lanthanum mono- and bis-ligand complexes were prepared conveniently by amine elimination using the sterically less bulky tris-amido derivatives $M[N(SiHMe_2)_2]_3\cdot THF_2$ introduced by the Anwander group a few years ago [16]. Both molecules of THF are lost in the reactions using the ^{t}Bu substituted bis-oxazolinato ligand, giving compounds $\mathbf{7M\cdot NR_2}$ and $\mathbf{7M\cdot[NR_2]_2}$ (Chart 2) [42]. Group 3 and lanthanide metal compounds incorporating the $N(SiHMe_2)_2$ ligand are often stabilized by β(SiH) agostic interactions [43]; however, in compound $\mathbf{7Y\cdot[NR_2]_2}$, which was structurally characterized, no evidence for such an interaction was obtained. In this compound, the remaining two amido groups are rotated away from the ^{t}Bu groups above and below the ligand plane (Fig. 3). The loss of THF and the absence of agostic interactions attests to the high electron donation from the bis-oxazolinato ligand and its favorable steric properties. These two features auger well for the generation of dialkyl derivatives of Y and La, for which well defined examples remain a rarity.

2.1.5. β-Diketiminates, or 'nacnac' ligands

β-Diketiminato ligands, popularly referred to as 'nacnac' ligands [44] since they are isoelectronic with the acac ligand family, have recently been exploited in the coordination chemistry of a wide variety of metals. We viewed them as attractive ligands for Group 3 metals since, on the face of it, they resemble the dianionic bis-



Scheme 6.

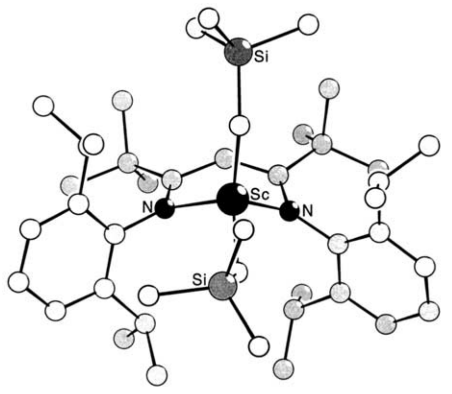
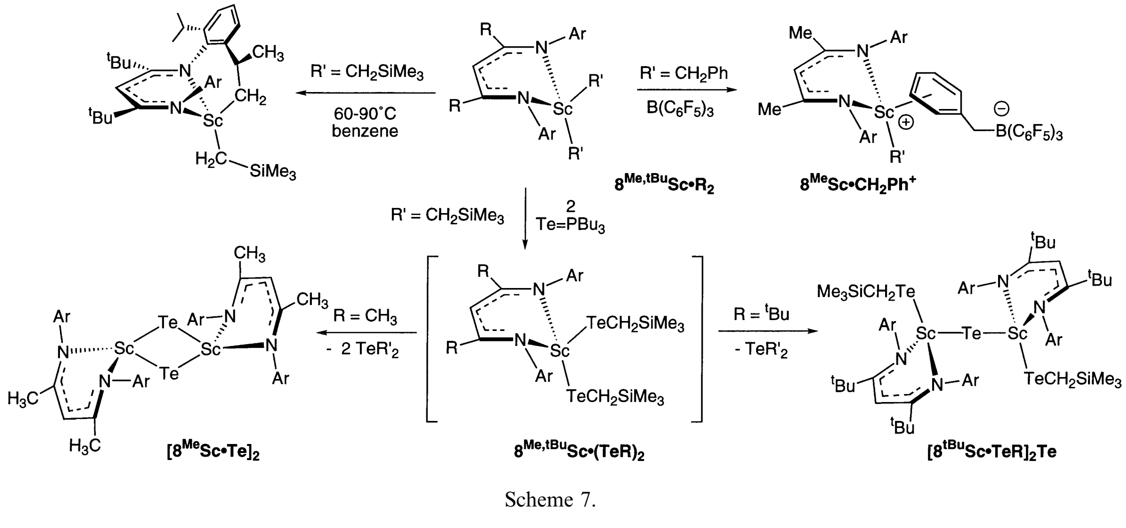


Fig. 4. Molecular structure of the diethyl nacnac derivative $8^{^t\mathrm{Bu}}$Sc·Et$_2$.

amido donors McConville developed for use in titanium and zirconium based olefin polymerization catalyst precursors [45]. However, since they bear only one negative charge, their use with Group 3 metals allow for the production of dialkyl derivatives, which in turn can be used to generate cationic organoscandium compounds [46]. Such dialkyl derivatives can be straightforwardly prepared as shown in Scheme 6 employing the bulky nacnac ligands incorporating 2,6-^{i}Pr$_2$C$_6$H$_3$ aryl groups on nitrogen, and either CH$_3$ or ^{t}Bu groups on the diketiminato ligand backbone [47]. The latter ligand has a slightly higher steric impact than the methyl substituted ligand, holding the aryl groups more upright with respect to the ligand C$_3$N$_2$ plane and pushing them forward by 5–6°. This effect is already manifested in that the dichloride incorporating the ^{t}Bu subsituted ligand is isolated THF free while the methyl substituted ligand dichloride retains one THF ligand. Alkylation of the dichlorides give compounds **8$^{\mathrm{Me}}$Sc·R$_2$** and **8$^{^t\mathrm{Bu}}$Sc·R$_2$** where R = CH$_3$, CH$_2$CH$_3$, CH$_2$Ph, CH$_2$CMe$_3$, CH$_2$SiMe$_3$. Notably, the diethyl species shows no tendency to undergo β-hydrogen transfer processes, either to the metal or to the other alkyl ligand, and no evidence for β-agostic interactions could be found.

Several of these compounds have been crystallographically characterized, and the structures invariably show that the Sc atom lies out of the C$_3$N$_2$ ligand plane by 1.10–1.25 Å. This occurs mainly so that the alkyl groups and the iso-propyl aryl groups avoid steric interaction (Fig. 4). These structures are maintained in solution, but at room temperature a dynamic process which equilibrates the diastereotopic alkyl and ligand groups gives the compounds the appearance of C_{2v} symmetry. However, at low temperatures, spectra consistent with the C_s symmetric solid state structure are obtained. Thus, the steric environment provided by these nacnac ligands is less rigid than that engendered by the McConville diamido ligand system.



Scheme 7.

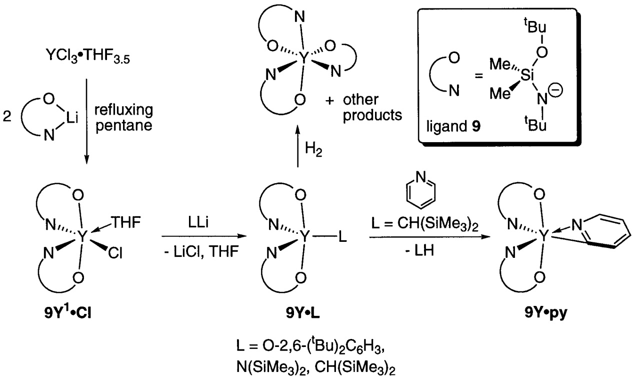
The availability of several THF-free, thermally stable scandium bis-alkyls have allowed for study of the reactivity of this largely unexplored family of compounds (i.e. Group 3 metal dialkyls). Scheme 7 illustrates some of the chemistry we have observed so far. Thermolysis leads to the metallated compounds shown, with loss of RH, via an intramolecular σ-bond metathesis reaction. However, in contrast to the chemistry of Cp_2^*ScR derivatives [3a], intermolecular σ-bond metathesis reactions with, for example, C_6D_6 are not observed. Insertion of tellurium into the Sc–R bonds of $\mathbf{8^{R}Sc\cdot(CH_2EMe_3)_2}$ (E = C, Si) give bis-tellurolates which decompose via bimolecular loss of TeR_2, ultimately giving the dimeric μ-tellurido species $\mathbf{[8^{Me}Sc\cdot Te]_2}$ [48]. In these dimeric compounds, the fluxionality of the ligand is slowed on the NMR timescale in comparison to the parent dialkyls, resulting in the observation of three isomers in the NMR spectra which differ in the relative orientations of the nacnac ligand with respect to each other and the molecular core (only one isomer is shown in Scheme 7). Finally, thermally stable cationic alkyl compounds can be prepared by treatment with the borane $B(C_6F_5)_3$, giving a variety of ion pairs $\mathbf{8^{Me,\mathit{t}Bu}Sc\cdot R^+}$, the dynamic behavior and chemistry of which we are currently studying. Although the benzyl cation $\mathbf{8^{Me}Sc\cdot CH_2Ph^+}$ depicted is relatively inert due to the strong coordination of the phenyl group in the benzylborate counteranion to the scandium center, other alkyl cations are much more reactive. Indeed, compound $\mathbf{8^{\prime Bu}Sc\cdot Me_2}$, in combination with the $B(C_6F_5)_3$ borane activator, is a highly active ethylene polymerization catalyst, exhibiting activities of ≈ 3.0 × 10^5 g PE mol^{-1} Sc h at 50 °C and 300 psi ethylene pressure [49].

2.2. *NO donors, monoanionic*

2.2.1. *N,O-bis(tert-butyl)(alkoxydimethylsilyl)amides*

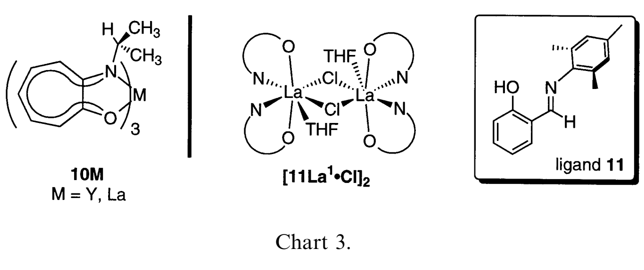
In another detailed study from the Teuben group, the yttrium chemistry of a chelating *N,O* system based on a siloxy amido donor framework has been described [50]. Forming a four-membered chelate, this ligand system is topologically related to the benzamidinato and guanidinato ligands described in Sections 2.1.1 and 2.1.2 above, but with some important differences which influence the reactivity of the resulting organoyttrium derivatives. Molecular models suggest that the bis-*tert*-butyl substituted siloxy amido ligand is slightly more sterically bulky than the bis-trimethylsilyl benzamidinato ligand, giving a smaller coordination gap aperture. However, since delocalization of the uninegative charge of the ligand is not possible through the dimethylsilyl linker, the charge is localized on the amide nitrogen, making it significantly more basic than the nitrogens of the amidinato ligands. In compounds substituted by bulky hydrocarbyl ligands, the oxygen donor of the siloxyamido ligand is more loosely bound to the yttrium and in some instances, evidence for dissociation of this part of the ligand is found.

As shown in Scheme 8, the compounds **9Y·L** [L = OAr, $N(SiMe_3)_2$ and $CH(SiMe_3)_2$] can be prepared via methodology which mirrors that used for the synthesis of compounds **1Y·L** (Scheme 2 above). A crystal structure determination of $\mathbf{9Y\cdot CH(SiMe_3)_2}$ shows that one of the Y–O bond distances is ≈ 0.2 Å longer than the other. However, in solution, the compounds are fluxional, with equilibration of the diastereotopic Si–Me groups observed at higher temperatures ($\Delta G^{\ddagger} = 73–78$ kJ mol^{-1} at 57–90 °C, depending on L). The presence of an Si–O bond in the ligand framework renders these compounds susceptible to thermal decomposition processes involving Si–O bond cleavage. Furthermore, ligand redistribution processes are kinetically facile for smaller L ligands in the *N,O* system; thus, the hydride formed upon hydrogenolysis is unstable towards formation of the tris-ligand compound and other unidentified species. The higher basicity of the amido nitrogen is manifested in the reactivity of $\mathbf{9Y\cdot CH(SiMe_3)_2}$ with terminal alkynes. Whereas, benzamidinato complex $\mathbf{1Y\cdot CH(SiMe_3)_2}$ gives products arising from σ-bond metathesis, deprotonation of the alkyne by the ligand nitrogen competes in the chemistry of **9Y·R**. The alkyl derivative does, however, react with pyridine and substituted pyridines via *ortho*-metallative σ-bond metathesis to give pyridyl compounds exemplified by **9Y·py** in Scheme 8. These compounds undergo a variety



L = O-2,6-(^{t}Bu)$_2$C$_6$H$_3$, N(SiMe$_3$)$_2$, CH(SiMe$_3$)$_2$

Scheme 8.



10M
M = Y, La

[11La^1•Cl]$_2$

Chart 3.

of stoichiometric insertion reactions with nitriles, alkynes and carbon monoxide [51].

2.2.2. Aminotroponates

A related ligand system to the *N*,*N* chelate described in Section 2.1.3 above are the aminotropinato ligands. Roesky has prepared the homoleptic complexes **10M** (Chart 3) to augment his studies on the related aminotropiniminato complexes discussed above [52]. No organometallic derivatives of the *N*,*O* ligand have been reported. The exposed nature of the O donor in this ligand system could render it susceptible to facile ligand redistribution processes, although this remains to be determined.

2.2.3. Salicylaldiminates

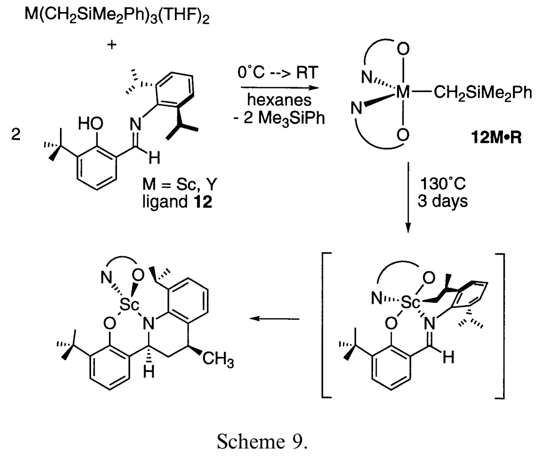
Several years ago, Floriani and co-workers reported the use of the salicylaldiminato ligand framework [53]. Although no organometallic compounds were reported, this was one of the first papers which purported to prepare non-Cp supported organogroup 3 compounds. A bulky mesityl group was incorporated on nitrogen and two phenoxyimine ligands were instituted via salt metathesis using the sodium salt of the ligand. The resulting bis-ligand chloride compound retained one THF donor and dimerized to form **[11La^1·Cl]$_2$**, Chart 3, where the La centers are seven-coordinate, mono-capped trigonal prismatic in geometry.

The recent successful use of this ligand system to support Group 4 [54] and Group 10 [55] metal-based olefin polymerization catalysts suggested that incorporation of a bulky group in the *ortho*-phenoxy position is critical for stabilizing electrophilic metal species. Thus, the complexes of ligand **12**, incorporating a 2,6-^{i}Pr$_2$C$_6$H$_3$ group on nitrogen and an *ortho*-^{t}Bu group on the phenoxy portion of the ligand were prepared by alkane elimination using the precursors $M(CH_2SiMe_2Ph)_3 \cdot THF_2$ (Scheme 9) [56]. Five-coordinate, pseudo C_2 symmetric bis-ligand complexes of both Sc and Y were formed as one isomer, **12M·R**, with the oxygen atoms occupying the axial sites of the trigonal bipyrimid. These organo scandium and yttrium derivatives are remarkably thermally stable, undergoing a metallation reaction only by heating at 130 °C for 3 days. For M = Sc, the reaction cleanly produces the neutral salicylaldiminato phenoxyamide complex shown in Scheme 9. This process is >98% diastereoselective and the CH_2SiMe_2Ph group does not undergo 1,3 migration to the aldiminato carbon. Notably, no reaction with the aromatic solvents these thermolyses are conducted in was observed. Mono-ligand complexes of yttrium can be prepared, but retain either one or two molecules of THF and exist as a mixture of geometric isomers. These compounds (i.e. **12M^{1,2}·R$_2$**) also exhibit a tendency towards ligand distribution and are thermally labile compared to the more well behaved bis-ligand derivatives. The reactivity of these compounds is under exploration, but hydrides are formed upon hydrogenolysis with four atmospheres of H_2.

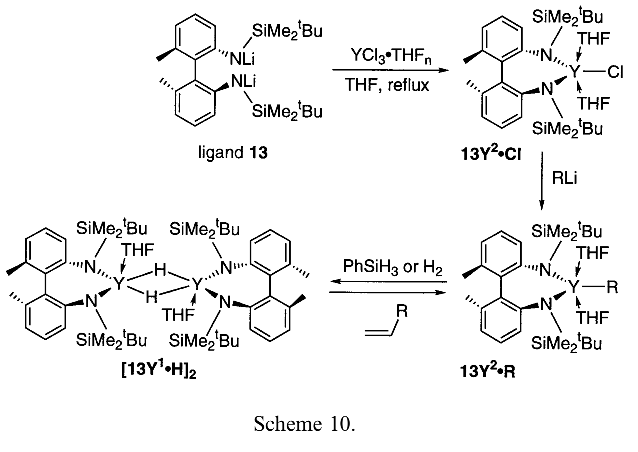
2.3. NN donors, dianionic

2.3.1. Diamides

As been briefly mentioned, chelating diamido ligands have been introduced by McConville in Group 4 metal chemistry to support living ethylene polymerization catalysts [45]. Such ligands have had less impact in Group 3 metal chemistry, but a few recent reports have concerned the use of C_2 symmetric diamides as ligands for organoyttrium complexes. For example, Gountchev and Tilley have prepared a chelating disilylamido ligand based on an axially chiral biphenyl framework, and, using salt elimination procedures, prepared the monomeric, bis-THF ligated yttrium chloride **13Y^2·Cl** complex shown in Scheme 10 [57]. Alkylation with MeLi or $LiCH(SiMe_3)_2$ yields the organo derivatives, again with two THF ligands remaining ligated. A crystal structure determination of **13Y^2·Cl** (Fig. 5) shows that the diamide ligand interacts with the yttrium center not only through the nitrogen atoms, but also the biphenyl backbone carbon atoms. This has the effect of directing



Scheme 9.



Scheme 10.

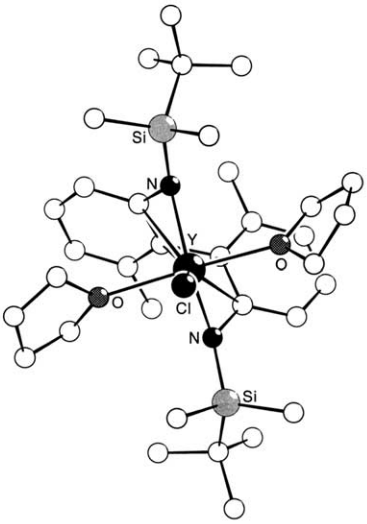


Fig. 5. Molecular structure of the C_2 symmetric diamido complex $\mathbf{13Y^2 \cdot Cl}$.

the bulky silyl groups on the amide nitrogens away from the molecular core, providing a very open coordination environment for the two THF ligands to exploit. One ligand of THF is even retained in the dimeric hydride complex formed upon hydrogenolyis of $\mathbf{13Y^2 \cdot R}$ or by treatment of the alkyls with $PhSiH_3$. The hydride resonance in the ^{1}H-NMR spectrum decays slowly over the course of a few days, indicating exchange with the deuterium in the d_8-THF solvent.

Insertion reactions are observed when hydride $\mathbf{[13Y^1 \cdot H]_2}$ is treated with α-olefins or pyridine, but the products formed are inert towards further reactions; thus, these compounds are inactive as olefin polymerization catalysts. However, the facility of one olefin insertion along with σ-bond metathesis of the alkyls with silanes allows these compounds to be effective catalysts for the hydrosilation of olefins [58]. Turnover numbers for 1-hexene were comparable to those found for metallocene based d^0 hydrosilation catalysts, whereas those for styrenic substrates were markedly lower. For the hydrosilation of norbornene using $PhSiH_3$ and enantomerically pure $\mathbf{13Y^2 \cdot Me}$, ee's on the order of 90% were obtained, substantially better than similar reactions using C_1 symmetric lanthanocene catalysts [59].

Another C_2 symmetric bis-sulfonamide ligand system based on a 1,2-*trans* disubstituted cyclohexyl backbone has recently been utilized to support scandium, yttrium and lanthanum complexes as reported by Anwander and co-workers [60] Although structural investigations indicate that the sulfonyl moieties are engaged in weak bonding interactions with the metal centers, this ligand system is essentially a diamido donor. Amine elimination using the precursors $M[N(SiHMe_2)_2]_3 \cdot THF_2$, gives the THF free complexes $\mathbf{14M \cdot NR_2}$ (Chart 4) for M = Sc and Y, but one THF is retained for the larger lanthanum derivative. Again, organometallic derivatives have not been reported, but this remains a promising chiral ligand system for these metals.

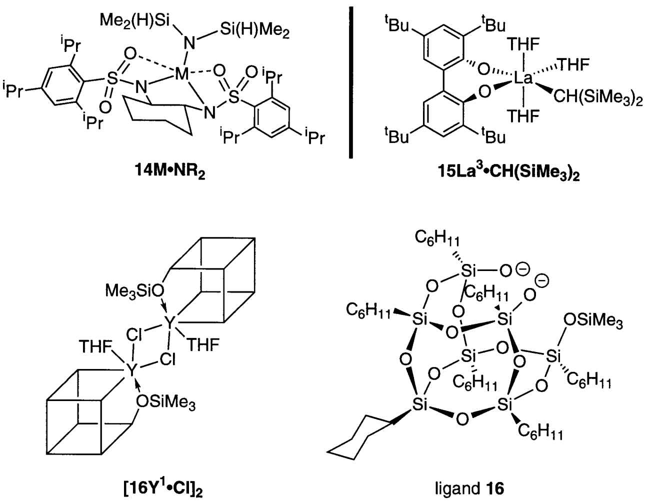


Chart 4.

2.4. OO donors, dianionic

2.4.1. Dialkoxides

Although first reported in 1992, and covered in his 1995 review, Schaverien's use of C_2 symmetric biphenolate ligands in organolanthanum chemistry is worthy of mention for completeness. Compound $\mathbf{15La^3 \cdot CH(SiMe_3)_2}$ (Chart 4) was prepared as a tris-THF adduct in one of the first reported alkane elimination procedures. A footnote in the paper remarks that this route was not successful for the Y or Lu analogs, but in the case of La, smooth loss of two equivalents of alkane gave the neutral mono-organolanthanum derivative shown; a bulky binaphthyl ligand system was also used in this chemistry. Unlike monodentate alkoxides, these ligands show no tendency to undergo redistribution processes. Insertion of CO into the La–C bond was observed to be facile in this system. To our knowledge, subsequent reports concerning the chemistry of these compounds have not appeared.

2.4.2. Silsesquioxanes

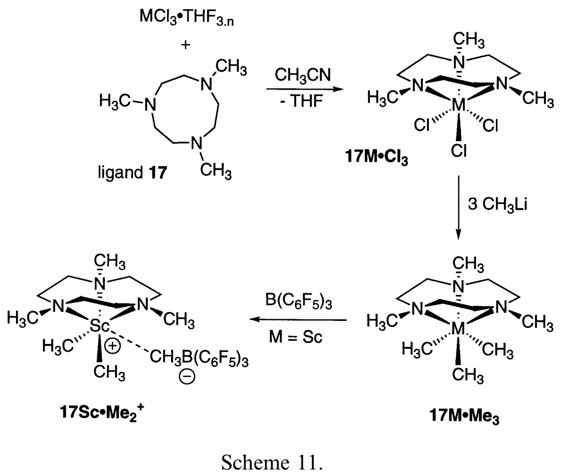
These ligands are cube shaped siloxy cage frameworks with a vertex missing such that three silanol groups are available to coordinate a metal in a strictly facial binding mode. As such, they are potentially trianionic OOO donors, and indeed, this is their most commonly observed ligation mode. In this mode, of course, the potential to support organogroup 3 chemistry is minimal since all the valences of the metal are 'used up' by a trianionic supporting ligand. Indeed, complexes of both yttrium and lanthanum with the ligand functioning in this way have been reported and touted as models for lanthanide doped silica catalysts [61,62]. However, as a dianionic donor, where one of the silanol groups of the silsesquioxane is protected in some fashion, there is potential for organometallic chemistry. Aspinall and co-workers have shown that when the THF adduct of **16Y^1** is treated with Me_3SiCl, cleavage of a Y–O bond takes place to form the chlorobridged dimer **[16Y^1·Cl]$_2$** (Chart 4), a compound with potential for elaboration into organoyttrium derivatives; this has not been achieved to date [63].

3. Group 3 organometallic compounds supported by tridentate ligands

3.1. NNN donors, neutral

3.1.1. 1,4,7-Triazacyclononane

The six electron donor bearing three amines in a cyclic array provided by the triazacyclononane heterocyle has found notable applications as a facially coordinating neutral ancillary ligand. Bercaw and co-workers reported its coordination to both Sc and Y chlorides to provide compounds **17M·Cl$_3$**, which can be readily alkylated with methyllithium to provide the intriguing trimethyl compounds **17M·Me$_3$** (Scheme 11) [64]. These compounds are the antecedents of some more recent chemistry from the Hessen group, discussed below in Section 4.1.1, and the Bercaw report is one of the first to implicate cationic Group 3 alkyl derivatives. Although compounds **17M·Me$_3$** are remarkably non-reactive towards olefins and alkynes as neutral species, when the scandium derivative is treated with $B(C_6F_5)_3$ or $[PhN(H)Me_2]^+[B(C_6F_5)_4]^-$, a species with physical and spectroscopic properties consistent with a **17Sc·Me$_2^+$** $[A]^-$ formulation is generated which polymerizes ethylene (slowly) and oligomerizes 1-pentene ($M_w = 4000$, PDI = 1.32). Although these cationic species were not fully characterized, the physical observations recorded indicate their presence as liquid clathrate like materials.



Scheme 11.

3.2. NCN donors, monoanionic

3.2.1. σ-Aryldiamine

Many of the monoanionic tridentate ligands discussed in the following sections are characterized by a central anionic donor flanked by two neutral donors. In so called ‘pincer’ ligands, the central donor is an aryl species with donor subsitutents in the *ortho* positions. van Koten and co-workers have employed such ligands with a variety of metals, and have reported the lanthanum complex **18La·Cp$_2$**, Chart 5 [65]. This complex was prepared via salt elimination, but with a twist; the eliminated salt is CpLi, utilizing $Cp_3La·THF$ as the starting material. In this case, reaction of the aryl lithium reagent with the trichlorides resulted only in ‘ate-complex’ formation, and was not effective for ligand attachment. More reactive hydrocarbyl ligands have not been instituted for this ligand system.

3.3. NNN donors, monoanionic

3.3.1. Bis(N-aryliminomethyl)pyrrolyls

Various yttrium complexes of the bis-imine pyrrolyl ligand system have recently been prepared via amine elimination using $Y[N(SiMe_3)_2]_3$ [66]. The complex **19Y·[NR$_2$]$_2$** (Chart 5) is one example of several which vary in the substitution pattern on the imine aryl substituent. Less bulky aryl groups favor the formation of bis-ligand and homoleptic tris-ligand complexes, while when Ar = 2,6-$^i Pr_2C_6H_3$, the ligand binds only through the pyrrolyl nitrogen and one of the imine donors. The X-ray structure of **19Y·[NR$_2$]$_2$** shows that the ligand binds in a planar, meridional fashion, with the *N*-aryl groups roughly perpendicular to the ligand plane; however, the rather long Y–N$_{imine}$ bonds of 2.702(3) and 2.776(3) Å show why more steric crowding induces dissociation of one of the imine donors. The well-defined mono-ligand compound **19Y·[NR$_2$]$_2$** was shown to be a viable catalyst precursor for the polymerization of ε-caprolactone.

3.3.2. Tris(pyrazolyl)borates

Next to cyclopentadienyl donors, tris-pyrazolylborates are probably the most common supporting ligands

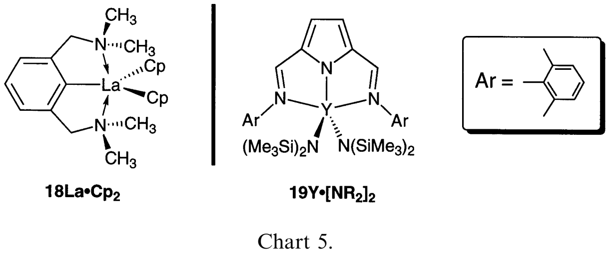
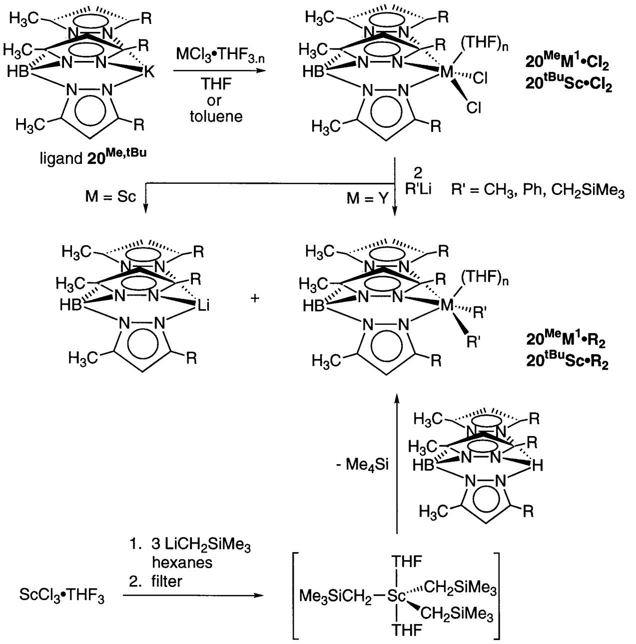


Chart 5.



Scheme 12.

in lanthanide chemistry. Much of this research has focussed on coordination chemistry, with few studies on organometallic complexes reported. This is somewhat surprising, given the inherent tunability of this versatile ligand system. For the Group 3 metals, organoscandium and yttrium derivatives have been reported only recently; synthetic routes to these compounds are shown in Scheme 12. Sterically bulky Tp ligands with the pyrazolyl rings substituted in the 3 and 5 positions are required to afford monomeric compounds. Bianconi and co-workers have used the potassium salts of some Tp ligands to prepare mono-THF adducts of dichlorides [67], $\mathbf{20^{Me}Y^{1}\cdot Cl_2}$ which are convenient starting materials for the preparation of alkyl derivatives [68]. We found that the analogous $\mathbf{20^{Me}Sc^{1}\cdot Cl_2}$ and $\mathbf{20^{^{\mathit{t}}Bu}Sc\cdot Cl_2}$ compounds could be prepared in a similar manner, but these dichlorides proved to be unsuitable as precursors to alkyl derivatives. Treatment of either of these dichlorides with RLi, resulted in competitive production of **20Li**, the extent of which was dependent on the nature of the Tp ligand and the alkylating hydrocarbyl group R. Thus, the organoscandium compounds $\mathbf{20^{Me,^{\mathit{t}}Bu}Sc^{0,1}\cdot R_2}$ are only available cleanly via alkane elimination procedures using in situ generated samples of $Sc(CH_2SiMe_3)_3\cdot THF_2$ from which LiCl has been completely removed. Using the more bulky $\mathbf{20^{^{\mathit{t}}Bu}}$ ligand, the resulting alkyl derivative is THF free; for the $\mathbf{20^{Me}}$ substituted compounds (where M = Sc and Y), one THF remains ligated to the metal center, although variable temperature NMR experiments show that this donor is quite labile. Indeed, many of these compounds exhibit dynamic behavior on the NMR timescale.

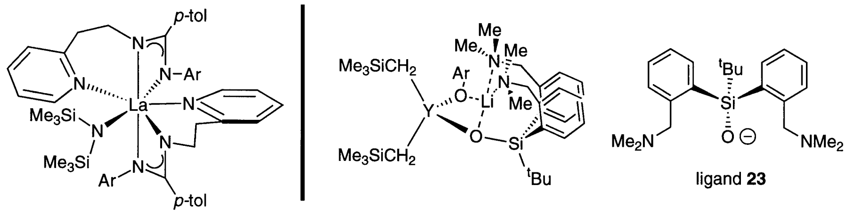
Bianconi has shown the yttrium derivatives $\mathbf{20^{Me}Y^{1}\cdot R_2}$ (R = Ph, CH_2SiMe_3 and in situ generated CH_3 and H derivatives) to be active ethylene polymerization catalysts (120 psi ethylene, 25 °C). Although turnover numbers are low in comparison to commercial catalysts, these polymerization reactions do not require any cocatalyst. Development of an ‘activatorless’ catalyst system with activities comparable to metallocene technology remains a sought after goal in the area of olefin polymerization catalysis. This work represents a step in this direction, but the high molecular weight and linearity of the polymer produced, with its itinerant processability problems, and the low activities remain significant challenges. Unfortunately, the scandium derivatives proved to be quite unreactive and prone to loss of the tris-pyrazolylborate ligand.

3.3.3. *Modified amidinates*

As discussed in Section 2.1.1 above, amidinato ligands have featured prominently in the development of non-Cp organogroup 3 metal chemistry. While bis-ligand complexes exhibit a rich chemistry, mono-ligand complexes have been more difficult to develop given the relatively small size and chelate bite of this ligand. Consequently, some groups have attempted to modify this ligand system by incorporating pendant donors (forming tridentate ligands) or by covalently attaching two amidinato moieties together (forming tetradentate ligands, see Section 4.2.1 below). The former systems have been found to be quite flexible in their mode of binding; while meridional arrangements are perhaps favored, in sterically more demanding situations, facial coordination modes are possible.

A family of amidinato ligands with a pendant 2-pyridylethyl donor dangling from one of the nitrogen atoms has been prepared by Arnold and co-workers, and the versatility of the new ligands demonstrated through their coordination to a variety of metals, including lanthanum [69]. The bis-ligand, seven-coordinate compound $\mathbf{21La\cdot NR_2}$ (Chart 6) was prepared by amine elimination, but the product was somewhat prone to ligand redistribution since both mono- and tris-ligand species were also observed. The utility of this ligand for the larger La nucleus is therefore questionable; however, it may be more suitable for the smaller Sc or Y elements.

Hessen and co-workers have employed benzamidinato ligands with pendant $-(CH_2)_nNMe_2$ donors ($n = 2$, 3) in an effort to make mono-ligand complexes of yttrium [25]. Using the protocol established for compound $\mathbf{2Y\cdot R_2}$ (Section 2.1.1), $YCl_3\cdot THF_{3.5}$ was treated sequentially with **22Li** (one equivalent) and $LiCH(SiMe_3)_2$ (two equivalents) to yield the base-free, dialkyl complex $\mathbf{22Y\cdot R_2}$ (Scheme 13) in good yield. In



$\mathbf{21La{\bullet}NR_2}$ $\mathbf{23Y{\bullet}R_2(OAr)^-Li^+}$ **ligand 23**

Chart 6.

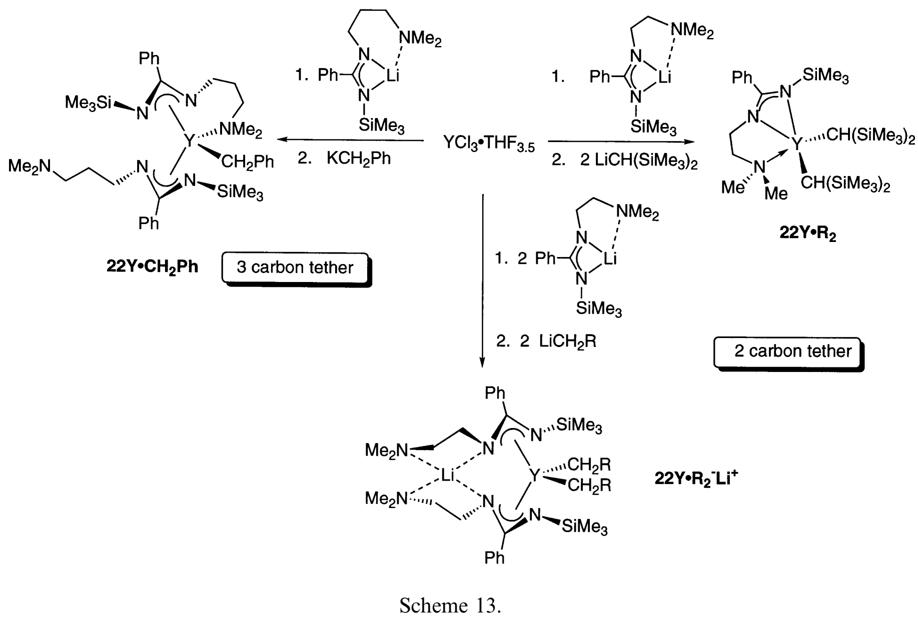
this complex, the ligand adopts an approximately meridional coordination arrangement, where the pendant donor has essentially replaced the coordinated LiCl moiety found in $\mathbf{2Y\cdot R_2}$. In an effort to produce analogous compounds with smaller and more reactive hydrocarbyl groups, the same protocol was attempted using KCH_2Ph or $LiCH_2SiMe_3$ as the alkylating reagents. Unfortunately, ligand redistribution reared its ugly head once again, and the bis-ligand complexes $\mathbf{22Y\cdot R_2^-Li^+}$ were isolated. In these compounds, the ligand exhibits bidentate coordination to the yttrium center, while the pendant amine donors sequester a Li^+ cation in concert with one of the amidinato nitrogens from each ligand. The compounds have an aesthetically pleasing pseudo-C_2 symmetry, and do contain two alkyl groups for further reactivity studies. The possibility that ligand redistribution is driven by the occlusion of Li^+ was investigated by using exclusively potassium salts and increasing the length of the tether; in these instances, bis-ligand compounds were also isolated, but without ion occlusion. Indeed, in the compounds containing the longer tether, the tendency of the amine donor to dissociate was marked. Thus the structure found for $\mathbf{22Y\cdot R_2^-Li^+}$ is specific to this combination of ion and tether length.

Recently, Lappert and co-workers reported a bis-ligand lanthanum chloride complex with this ligand system [70].

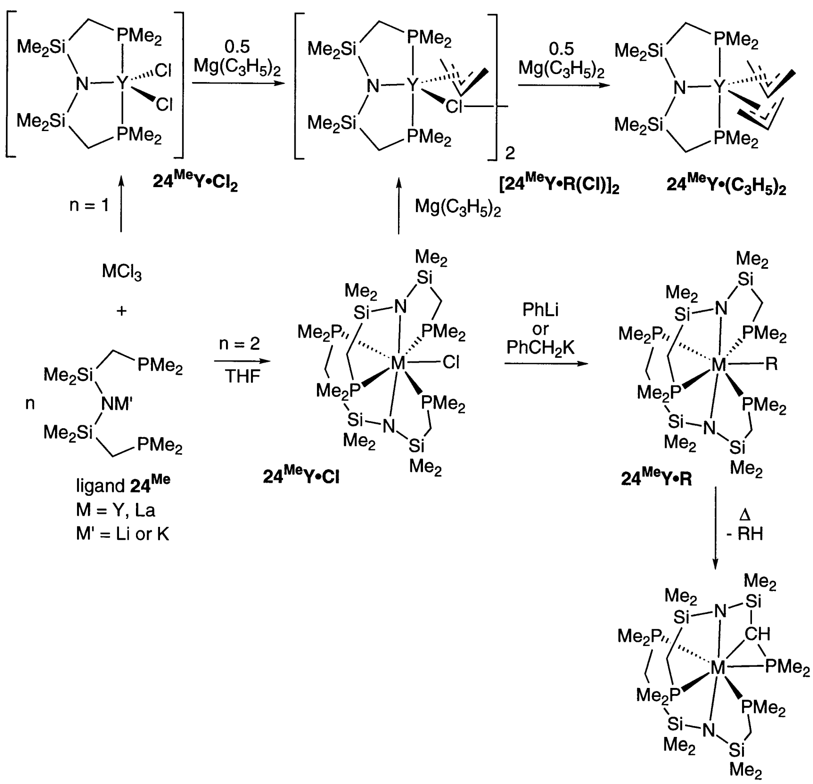
3.4. NON donors, monoanionic

3.4.1. Arylsiloxide with pendant donors

Berg and co-workers have explored the use of bulky alkoxides with pendant donors as ligands for a variety of lanthanides, including yttrium. The aryl siloxide ligand shown in Chart 6 is trivially synthesized, and instituted into yttrium's coordination sphere via amine elimination [71]. A crystal structure of $\mathbf{23Y\cdot[NR_2]_2}$ indicates that one of the pendant amine arms is not coordinated to the yttrium and replacement of the remaining silylamide groups with bulky phenoxides (to give $\mathbf{23Y\cdot[OAr]_2}$) does not change the coordination mode of this ligand. The bis-alkoxide, however, reacts with two equivalents of $LiCH_2SiMe_3$ to eliminate *one* equivalent of LiOAr; the other Li^+ cation is retained in the structure of the resulting organoyttrium complex $\mathbf{23Y\cdot R_2(OAr)^-Li^+}$. The authors speculate that the pendant amines play a role in coordinating the Li^+ cation, but detailed structural data was not obtained. In light of the more concrete structural determination of $\mathbf{22Y\cdot R_2Li^+}$ (see



Scheme 13.



Scheme 14.

Scheme 13), a structure such as that depicted in Chart 6 is not unreasonable. These two systems illustrate that pendant NMe_2 groups may be more effective at stabilizing occluded Li^+ cations than yttrium centers.

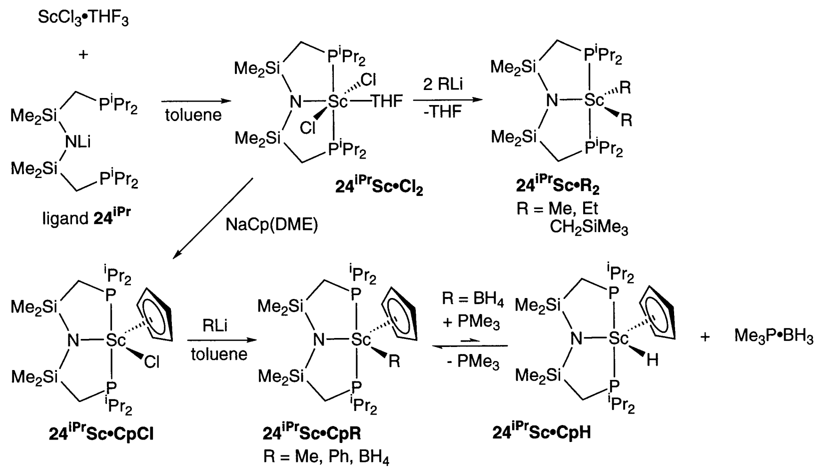
3.5. PNP donors, monoanionic

3.5.1. Fryzuk's amidodiphosphines

One of the first successful alternatives to Cp for Group 3 metal chemistry was the PNP ligand system developed by Fryzuk in the early 1980s. This ligand, which contains a hard amido donor and two soft phosphine donors, is an extraordinarily versatile ligand for use in both late and early transition metal chemistry [72]. For metals on the left side of the Periodic Table, the hard amido donor anchors the ligand, while for the softer metals to the right, the phosphine donors stabilize rare late metal amido metal linkages. This simple strategy has led to a remarkable body of chemistry that is still bearing fruit today.

Early success in Group 3 chemistry was attained by Haddad and Fryzuk using the larger metals in the group, Y [73–75] and La [76]. Some of this chemistry has been covered in earlier reviews [72,77], but will be briefly summarized here for comparison to the more recently published organoscandium chemistry. The PNP chemistry of Y and La mainly involves seven-coordinate bis-ligand complexes which are synthesized via salt elimination (Scheme 14); no complications involving retention of Li^+ cations are observed with these softer pendant donors. Compounds $\mathbf{24^{Me}M\cdot Cl}$ can be readily alkylated to form hydrocarbyl derivatives. Although several crystal structure determinations show that all phosphines are bound to the metals in the ground state, detailed ^{31}P-NMR studies reveal that dynamic behavior involving phosphine dissociation is facile. Indeed, evidence for one dangling PR_2 in complexes of the less basic diphenyl phosphine ligand $\mathbf{24^{Ph}}$ was garnered via ^{31}P-NMR spectroscopy. These hydrocarbyl derivatives undergo a clean metallation process involving the methylene C–H bonds of the ligand backbone to form a very stable metallacyclic product with loss of RH. Interestingly, when $\mathbf{24^{Me}Y\cdot Cl}$ was alkylated with allylmagnesium chloride, loss of '$\mathbf{24^{Me}Mg}$' was observed and a mono-ligand allyl derivative was formed as a chloro bridged dimer $\mathbf{[24^{Me}Y\cdot R(Cl)]_2}$. The mono-ligand bis-allyl compound $\mathbf{24^{Me}Y\cdot [C_3H_5]_2}$ was therefore also accessible and reported to be active for ethylene polymerization, in contrast to the bis-ligand hydrocarbyls, where only metallation was observed.

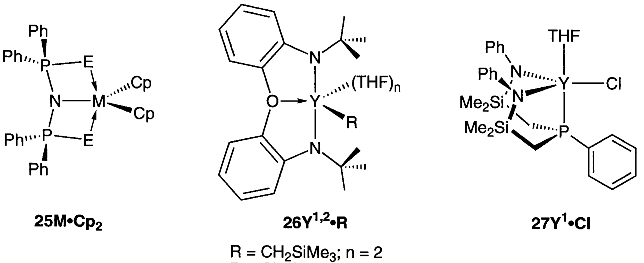
Unlike the chemistry of these larger metals, mono-ligand compounds are readily accessible for scandium (Scheme 15). Using the PNP ligand substituted with ^{i}Pr groups on phosphorus, the dichloride $\mathbf{24^{^iPr}Sc\cdot Cl_2}$ can be obtained as a THF adduct or free; the former compound is more soluble in hydrocarbons and therefore is the



Scheme 15.

reagent of choice for alkylation reactions [78]. These proceed readily, although the reactions are sensitive to choice of solvent, and the products tend to retain LiCl under certain conditions. Nonetheless, THF free dialkyl compounds $\mathbf{24}^{i\mathrm{Pr}}\mathbf{Sc}\cdot\mathbf{R}_2$ for R = Me, Et and CH_2SiMe_3 are obtainable as five-coordinate, distorted trigonal bipyramidal complexes where the PNP ligand coordinates in an approximately meridional mode. These derivatives were the first non-Cp Group 3 bis-alkyl derivatives to be reported.

Unfortunately, a survey of the reactivity of these compounds yielded disappointing results. When treated with small molecules like H_2, CO, ethylene and others, no clean reactions were observed. In all cases, the products formed appear to 'self destruct' and ligand loss occurs in many instances. In an attempt to rationalize this behavior, a low-level molecular orbital analysis suggested that the LUMO orbitals of these compounds lack appropriate symmetry for reaction with nucleophiles, especially in comparison with the frontier orbitals of metallocene fragments. To rectify this unfavorable situation, a Cp ligand was introduced to provide more electronic saturation at the scandium center and the resulting mixed ligand $\mathbf{24}^{i\mathrm{Pr}}$/Cp system's reactivity probed [79]. Somewhat more positive results were obtained in that the methyl complex $\mathbf{24}^{i\mathrm{Pr}}\mathbf{Sc}\cdot\mathbf{CpCH}_3$ undergoes clean σ-bond metathesis with primary amines (with loss of CH_4) to form amido complexes. More interestingly, the BH_4 derivative reacts reversibly with PMe_3 to give detectable amounts of a species assigned as a monomeric Sc-hydrido species. Although it must be said that the nuclearity of this species was not unequivocally established, if the assignment is correct, this is only the second monomeric scandium hydride species in the literature, the other being Cp^*_2Sc–H [80]. Monomeric Group 3 metal hydrides are expected to be highly reactive compounds and have yet to be observed for M = Y and La; ligand environments which support such moieties are of interest. Unfortunately the complex $\mathbf{24}^{i\mathrm{Pr}}\mathbf{Sc}\cdot\mathbf{Cp(H)}$ as generated in this fashion is on the unfavorable side of the equilibrium depicted in Scheme 15; also unfortunate is the fact that the hydrocarbyl derivative $\mathbf{24}^{i\mathrm{Pr}}\mathbf{Sc}\cdot\mathbf{CpCH}_3$ fails to react with H_2.



25M•Cp$_2$ **26Y^{1,2}•R** **27Y^1•Cl**

R = CH_2SiMe_3; n = 2
R = $CH(SiMe_3)_2$; n = 1

Chart 7.

3.6. ENE (E = S, Se) donors, monoanionic

3.6.1. Imidodiphosphinochalcogenides

In an effort to prepare volatile precursors to Group 3 metal and lanthanide chalcogenides, Ibers and coworker have prepared complexes of yttrium and lanthanum with imidodiphosphinochalcogenido ligands **25** (Chart 7). Bis-Cp complexes of this ligand were prepared by alkane elimination by treating Cp_3M derivatives (M = Y [81]; La [82]) with the ligands $HN[P(Ph)_2{=}E]_2$ (E = S, Se). The ligands bind to these large metals in an η^3-bonding mode with a strong M–N interaction evident in the structures as determined by X-ray diffraction. Tris-ligand complexes of these ligands have also been prepared for yttrium [83]. Other than these metallocene derivatives, no organometallic chemistry supported by these ligands has been reported.

3.7. NON donors, dianionic

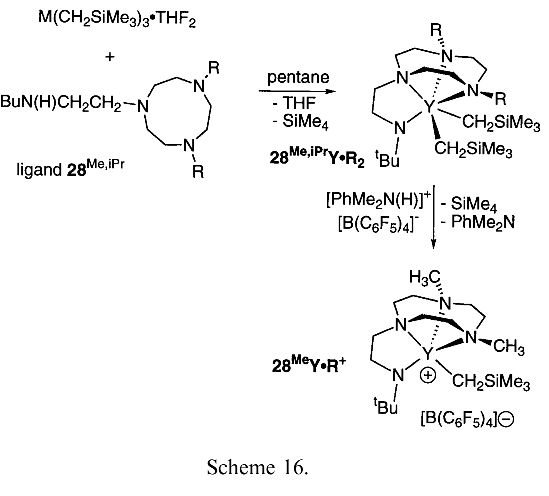
3.7.1. Schrock's diamido aryl ether

Two anilido donors linked by an *ortho*-aryl ether function have proven to be a flexible and versatile ancillary for a variety of early transition metal compounds. Developed by Schrock et al. initially for use in Group 4 chemistry [84], this ligand has also been ligated to yttrium, and organometallic derivatives prepared (Chart 7) [85]. Depending on the steric bulk of the alkylating agent, complexes $\mathbf{26^{^{i}Pr}Y''\cdot R}$ retain either one or two THF ligands, providing five- and six-coordinate complexes. Because of the relatively large size of the Y^{3+} metal, the ligand adopts a meridional structure, which is preferred on steric grounds to the facial isomer where ligand–ligand interactions are more severe. In other five-coordinate complexes where interaction between the amido *tert*-butyl groups and the other two metal ligands are significant, the NON ligand adopts a facial bonding arrangement. The THF ligated organoyttrium complexes $\mathbf{26^{^{i}Pr}Y''\cdot R}$ were unreactive towards H_2 or ethylene and attempts to generate more reactive compounds by removal of the THF resulted in decomposition. Thus, we again observe the phenomenon that THF complexes are not reactive enough, but THF free species are too reactive. Modifications to this ligand system, which walk this fine line, are necessary.

3.8. NPN donors, dianionic

3.8.1. Diamido phosphine

A ligand system recently reported is conceptually related to both Fryzuk's PNP ligand, and the Schrock NON system just discussed. Fryzuk et al. has inverted the donor pattern in the well-studied PNP ligand framework to generate a dianionic ligand system with outer amides anchoring a central phosphine donor [86]. Unlike the THF chloride of the Schrock ligand, in compound $\mathbf{27Y^{1}\cdot Cl}$ (Chart 7, prepared via salt elimination) the NPN ligand adopts an approximately *fac* bonding mode, as indicated by the solid state structure. Unfortunately, attempts to alkylate this material have thus far failed to yield clean products. Indeed, it appears that the bonding mode of the ligand is not maintained in the products of these reactions, calling into question the suitability of this ligand for supporting organoyttrium chemistry.



Scheme 16.

4. Group 3 organometallic compounds supported by tetra and polydentate ligands

Because the Group 3 metals support large coordination numbers, many polydentate ligands such as various Schiff bases, functionalized tris(pyrazolyl)borates, calixarenes, macrocycles (inc. polyethers and porphyrins) and cryptands, have been attached to scandium, yttrium and lanthanum. Some of these ligands have also been used to support organometallic chemistry.

4.1. NNNN donors, monoanionic

4.1.1. Triazacyclononane-amides

Hessen and co-workers have prepared the triazacyclononane-amide ligands $\mathbf{28^{Me,^{i}Pr}}$ which may be viewed as monoanionic analogs of the Cp-amido 'constrained geometry' ligand system originally developed as an ancillary for scandium [3a]. As shown in Scheme 16, compounds $\mathbf{28^{Me,^{i}Pr}Y\cdot R_2}$ ($R = CH_2SiMe_3$) can be synthesized by alkane elimination, although for the ^{i}Pr substituted ligand a 28% yield was obtained due to the extreme solubility of the product [87]. X-ray crystallography of this derivative shows the ancilliary ligand to be κ^4-coordinated, with the ^{i}Pr and Y-alkyl groups arranged in such a way as to prevent eclipsing (Fig. 6). This is a rare example of a THF free dialkyl organoyttrium complex, providing an opportunity to generate yttrium alkyl cations. Indeed, the dialkyl complexes $\mathbf{28^{Me,^{i}Pr}Y\cdot R_2}$ react cleanly with $[HNMe_2Ph][B(C_6F_5)_4]$

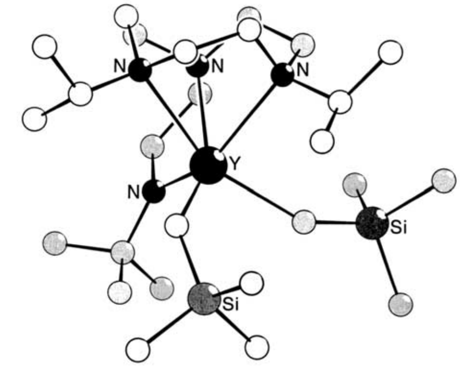


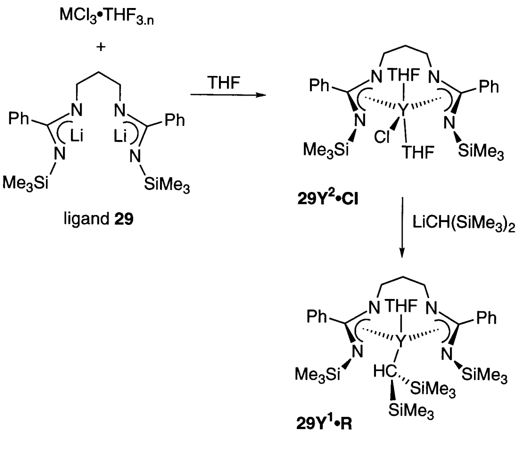
Fig. 6. Molecular structure of the amido-tacn bis-alkyl $\mathbf{28^{\,^{i}Pr}Y\cdot (CH_2SiMe_3)_2}$.

in C_6D_5Br to give RH, NMe_2Ph and cationic complexes $\mathbf{28^{Me,{}^{\mathit{i}}Pr}YR}^+$ $[A]^-$. However, only the cation generated from the methyl substituted ligand system is stable in the absence of olefin monomer; the ^{i}Pr-substituted cation is prone to metallative decomposition pathways. However, both are highly active olefin polymerization catalysts, with productivities approaching levels of commercial interest. These compounds represent a significant advance in Group 3 olefin polymerization catalyst design.

4.2. NNNN donors, dianionic

4.2.1. Linked bis-amidinates

A number of the NN bidentate monoanionic donors discussed above in Section 2.1 have been linked together to form tetradentate donors, mimicking the strategy used to develop *ansa*-metallocenes. For example Hessen and co-workers have extended their work with the benzamidinato ligand system to the linked bis-benzamidinato ligand **29** (Scheme 17) and explored its coordination chemistry with yttrium [88]. Salt metathesis using $\mathbf{29Li_2}$ and $YCl_3 \cdot THF_{3.5}$ smoothly gives $\mathbf{29Y^2 \cdot Cl}$ as a bis-THF adduct, which can be converted into the monoalkyl complex, $\mathbf{29Y^1 \cdot R}$ ($R = CH(SiMe_3)_2$) with one-coordinated THF donor. These derivatives are conceptually related to the non-linked bis-amidinates of Section 2.1.1 and Scheme 2 above, but comparison of the structures of $\mathbf{29Y^1 \cdot R}$ and a derivative of the non-linked bis(amidinate) complex $\mathbf{1Y \cdot R}$ reveals significant differences which indicate that tethering has two main affects. First, the amidinato fragments are not symmetrically bound to the Y center in **29**, with much longer (0.18 Å) distances to the nitrogens attached to the tether observed. A second and more profound effect is that tethering restricts the angle between the two Y–N–C–N planes, which is only 24.7(4)° in $\mathbf{29Y^1 \cdot R}$, but 75.6(2)° in the non-linked system. This opens up the coordination sphere around yttrium considerably, allowing for coordination of THF in $\mathbf{29Y^1 \cdot R}$, whereas $\mathbf{1Y \cdot R}$ is THF free. The more open environment in $\mathbf{29Y^1 \cdot R}$ also allows for a weak β-SiC agostic interaction (the Y–C–Si angles are 106.1(4) and 121.3(4)° in this complex), which was completely absent in $\mathbf{1Y \cdot R}$ (see Fig. 2).



Scheme 17.

4.2.2. Bis-amidopyridines

Bidentate amidopyridinato ligands are not tremendously effective for supporting organogroup 3 chemistry due to their lack of steric influence [32]. However, a linked bis-amidopyridinato system reported recently by Kempe and co-workers has proven sufficient in this regard [89]. Salt metathesis using $\mathbf{30Li_2}$ (generated in situ) and YCl_3 in THF gave $\mathbf{30Y^2 \cdot Cl}$ as a bis-THF adduct, whereas with $LaCl_3$, only an eight-coordinate bis-ligand 'ate-complex' was produced. As in the bis-amidinato linked ligand discussed above, this tetradentate donor tends to ligate in a planar fashion, opening coordination space above and below this plane and allowing for retention of the THF ligands. This is clearly illustrated by the X-ray crystal structure, which is pentagonal bipyramidal with the four nitrogen atoms of the ligand and the chloride in the equatorial plane. Reaction of $\mathbf{30Y^2 \cdot Cl}$ with LiR gave only the dialkyl ate complex $\mathbf{30Y \cdot R_2^-}$ cleanly (Chart 8), even with one equivalent of lithium 'big R'; complex $\mathbf{30Y \cdot R_2^-}$ ($R = CH(SiMe_3)_2$) was isolable and stable at low temperature. Some of the Y and La complexes supported by this ligand system were active towards the ring opening polymerization of lactones.

4.2.3. Bis-aminotroponiminates

Roesky has extended his work on organogroup 3 complexes of aminotroponiminato ligands to linked versions with higher denticity. Reaction of $\mathbf{31K_2}$ with $LaCl_3$ (1:1 ratio) in refluxing THF gave $[\mathbf{31La^1 \cdot Cl}]_2$ in good yield. In the solid state, each lanthanum center in dimeric $[\mathbf{31La^1 \cdot Cl}]_2$ is seven-coordinate with the bis-aminotroponiminato ligands adopting a bent geometry, in contrast to the ligating modes of the bis-amidinato and -amidopyridinato ligands discussed above. Reaction of $[\mathbf{31La^1 \cdot Cl}]_2$ with two equivalents of $LiCH(SiMe_3)_2$ or $KN(SiMe_3)_2$ in toluene afforded high yields of the THF free alkyl or amido derivatives, $\mathbf{31La \cdot E(SiMe_3)_2\}}$ ($E =$ CH, N), (Chart 8) which show diastereotopic splitting of the isopropyl CH_3 signals, indicating chirality at the

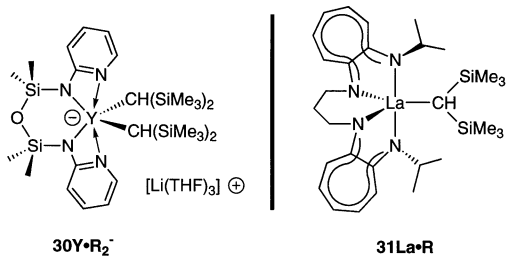
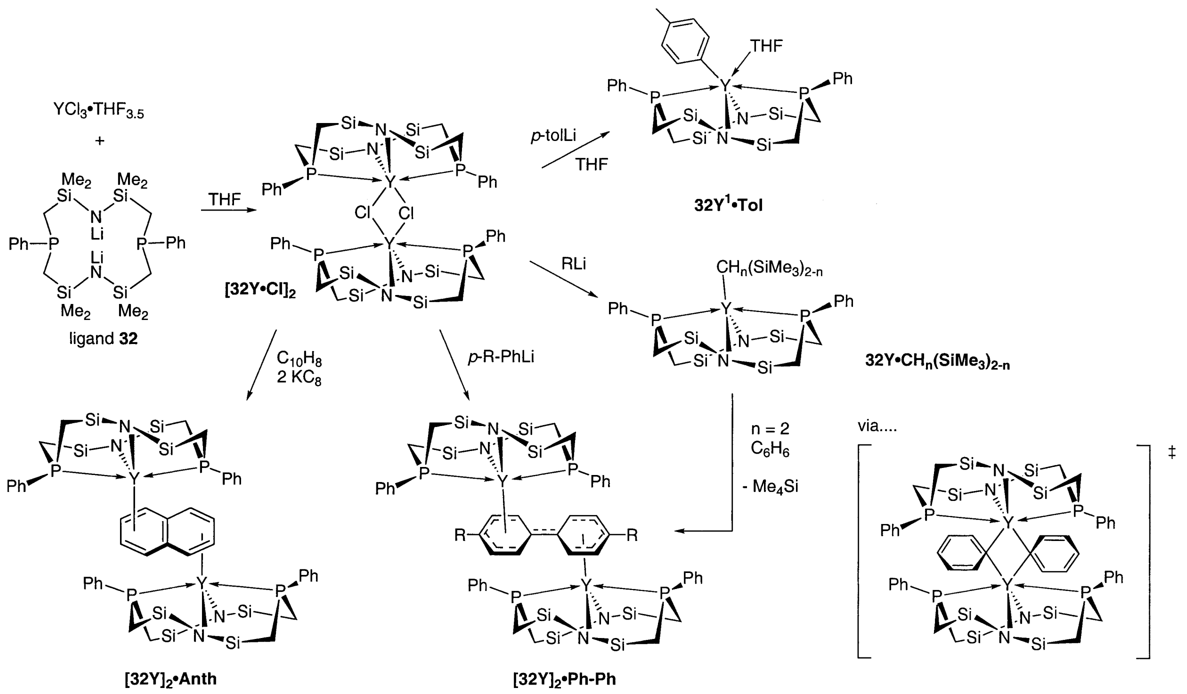


Chart 8.



Scheme 18.

five-coordinated lanthanum center. The reactivity of these derivatives awaits further investigation.

4.2.4. Porphyrins

Although the porphyrin ligand system was employed early on as an alternative to Cp in Group 3 metal chemistry, much of the organometallic chemistry of such derivatives was developed prior to 1994. As such, this material has been amply covered in the review literature [4,7] and will not be repeated here. Nonetheless, the importance of this ligand system as an alternative to the metallocene framework is such that it bears mention and the reader is directed to the above mentioned reviews and the following key papers for further details on this chemistry [90,91].

4.3. P_2N_2 donors, dianionic

4.3.1. P_2N_2 macrocycles

Using a template driven synthetic procedure, Fryzuk et al. have developed a macrocyclic P_2N_2 ligand system whose organoyttrium chemistry is among the most intriguing in the literature. The dilithium salt of ligand **32** [92] reacts with $YCl_3 \cdot THF_{3.5}$ to yield the chloro-bridged dimer [**32Y·Cl**]$_2$, which is isolated free of THF even though the reaction is performed in this medium (Scheme 18) [93]. Crystallographic studies show that this ancillary ligand effectively occupies one hemisphere of the coordination space about the yttrium center. Although the metrical parameters associated with each Y center in this dimer are quite different, in solution both metal centres are equivalent on the NMR timescale, attesting to the flexibility inherent to this ligand framework. Dichloride [**32Y·Cl**]$_2$ is a convenient starting material for monomeric, base free organoyttrium compounds such as **32Y·CH$_n$(SiMe$_3$)$_{2-n}$**. However, when attempts to institute organoaryl groups were made, a unique C–C bond coupling reaction was observed which lead to yttrium arene complexes [94].

The putative phenyl derivative **32Y·Ph** is generated via σ-bond metathesis between **32Y·CH$_2$SiMe$_3$** and benzene or via salt metathesis between PhLi and the dichloride dimer [**32Y·Cl**]$_2$. However, this base free aryl

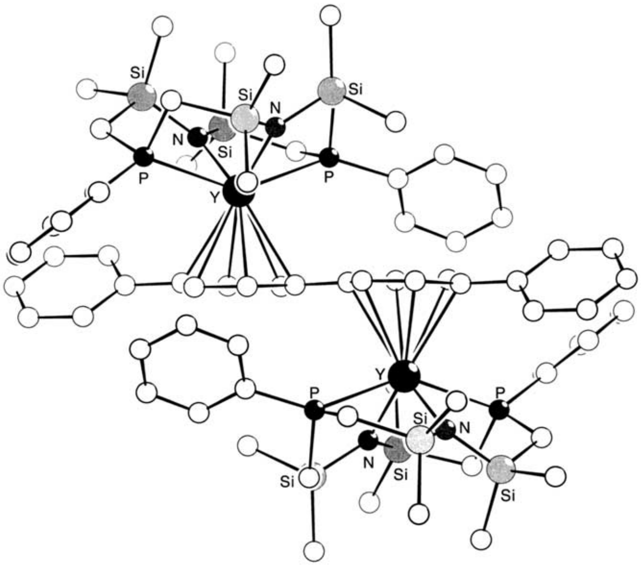


Fig. 7. Molecular structure of the dimer [**32Y**]$_2$·**Ph$_4$**.

yttrium species is not observed directly, as it converts to give dark blue $[\mathbf{32Y}]_2\cdot\mathbf{Ph{-}Ph}$ in a reaction involving dimerization, C–C bond formation and slippage of the **32Y** fragments into multihapto bonding modes with the resulting biphenyl dianion. The proposed intermediate, **32Y·Ph** was modeled by the trapped *para*-tolyl complex, which was fully characterized as a mono-THF adduct. The reaction is fairly general for other aryl groups, and the resulting arene complexes exhibit a low barrier dynamic process involving migration of the **32Y** moieties along the aromatic π-system. Thus, while the X-ray structure of the bis-biphenyl derivative shows the **32Y** fragments localized on the central rings (Fig. 7), NMR spectroscopy was consistent with averaged structures involving other linkage isomers.

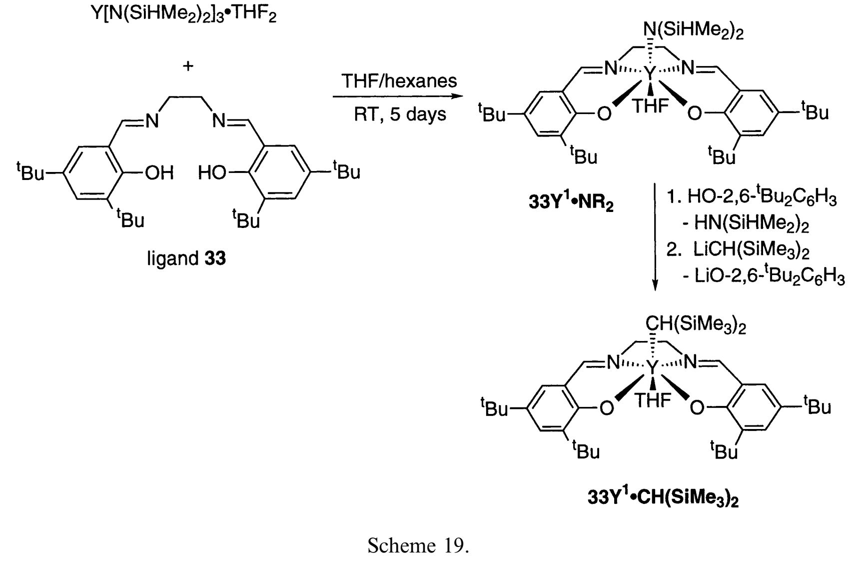
The coupling of aryl groups in compounds **32Y·Ar** is a new type of $C_{sp2}{-}C_{sp2}$ bond forming reaction for transition metals in which the metal does not change formal oxidation state and which does not involve migratory insertion. It is strongly related to the reversible coupling of acetylides observed in some lanthanide terminal acetylide complexes [95]. This coupling occurs at yttrium but not in related Yb complexes suggests that the large size of the yttrium ion plays a role in facilitating formation of the purported dimeric μ-phenyl intermediate (Scheme 18). In this regard, the unique hemispherical coverage of the macrocyclic P_2N_2 ligand framework must also be crucial for allowing this dimer to form, and to stabilize the resulting yttrium arene products. Related arene products are also accessible for extended aromatic systems such as naphathalene or anthracene, prepared by treatment of dichloride $[\mathbf{32Y}\cdot\mathbf{Cl}]_2$ with KAr reducing agents [96].

4.4. ONNO donors, dianionic

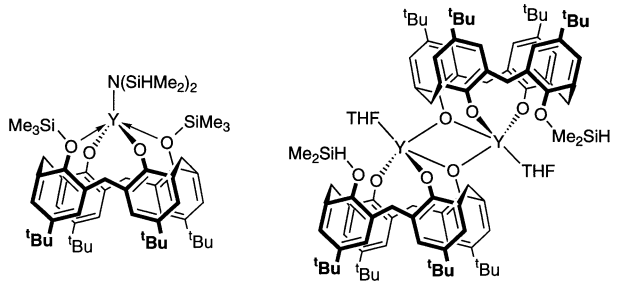
4.4.1. Bis-salicylaldiminates

Salen ligands have been applied in many areas of transition metal chemistry. They provide a rigid framework and their C_2 symmetric variants are therefore highly effective chiral auxiliaries. Two recent reports have detailed the preparation of both non-chiral and chiral salen complexes of yttrium, mainly for application as lactide polymerization catalysts. These complexes are related to the bidentate salicylaldiminato complexes of **12** described above in Section 2.2.3.

Using the extended silylamide route, Anwander and co-workers prepared the salen amido complex $\mathbf{33Y^1}\cdot\mathbf{NR_2}$ as a mono-THF adduct (Scheme 19) [97]. Interestingly, use of the more conventional yttrium amide reagent $Y[N(SiMe_3)_2]_3$ in reaction with $\mathbf{33H_2}$ gave a polymeric product which was insoluble in THF, but was determined to contain $N(SiMe_3)_2$ moieties. This contrasts with the near-quantitative formation of monomeric $\mathbf{33Y^1}\cdot\mathbf{NR_2}$ using the less bulky $Y[N(SiHMe_2)_2]_3$-$(THF)_2$ reagent, illustrating the utility of this variant in ligand institution protocols. The solid state structure of $\mathbf{33Y^1}\cdot\mathbf{NR_2}$ is distorted-trigonal prismatic with the ancilliary ligand adopting a bent coordination mode; the yttrium atom is displaced by 0.95 Å from the O_2N_2 plane and the dihedral angle between the two ligand aryl groups is 108°. Substitution chemistry of $\mathbf{33Y^1}\cdot\mathbf{NR_2}$ is reported, giving $\mathbf{33Y^1}\cdot\mathbf{OAr}$ (Ar = 2,6-^{t}Bu$_2$C$_6$H$_3$) with HOAr, which in turn reacts with $LiCH(SiMe_3)_2$ in hexane to give $\mathbf{33Y^1}\cdot\mathbf{CH(SiMe_3)_2}$. Both of these complexes occur as THF adducts, which contrasts with the observed chemistry of the bis-ligand salicylaldiminato alkyl complex **12Y·R** above in Section 2.2.3. This again illustrates that the strategy of linking two bidentate donors generally makes for a less bulky overall ligand environment than two non-linked donors. The Anwan-



Scheme 19.



$34^{Si2}Y{\bullet}NR_2$ $[34^{Si}Y^1]_2$

Chart 9.

der group has utilized this compound to make hybrid catalysts for the hetero Diels–Alder reaction by grafting it onto mesoporous MCM-41 silica [98].

While Anwander et al. report difficulty in using salt metathesis (with $\mathbf{33Li_2}$) to attach this ligand to yttrium, Evans et al. have shown that arene soluble species can be prepared using the potassium salt of the ligand $\mathbf{33K_2}$ [99]. Thus, the dimeric complex $[\mathbf{33Y^1 \cdot Cl}]_2$ was prepared and crystallographically characterized. The fact that this ligand, bulky though it is, girds the metal center in an equatorial binding mode, allows not only for retention of a THF donor, but also dimerization through the chloride ligand. Indeed, these authors report that a second ligand can be incorporated upon reaction of $[\mathbf{33Y^1 \cdot Cl}]_2$ with a further equivalent of $\mathbf{33K_2}$.

In related chemistry, Ovitt and Coates have recently prepared a C_2 symmetric salen yttrium alkoxide complex with a chiral binaphthyl backbone via alcohol exchange using $Y(OR)_3$ and the diproteo ligand [100]. Although it was a highly active catalyst for the ring opening polymerization of meso-lactide, it afforded no stereocontrol over the reaction and organometallic derivatives with this ligand were not prepared.

4.5. *OOOO donors, dianionic*

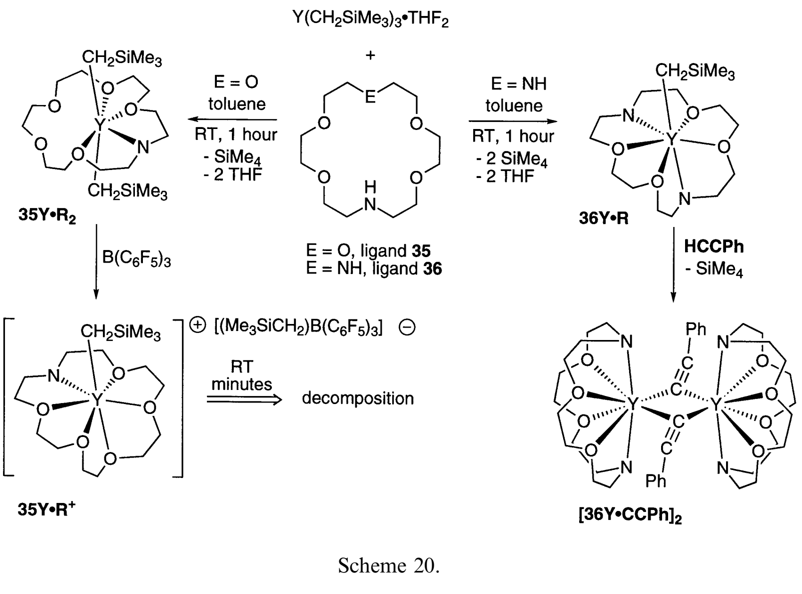
4.5.1. *Calixarenes*

Complexes of calixarene and silsesquioxane (section 2.4.2) ligands, which provide an oxo-quasiplanar ligand environment, have received much attention due to their potential as models for organometallic fragments grafted onto silanol rich surfaces. Although little calixarene supported Group 3 organometallic chemistry has been investigated, Anwander et al. have prepared some derivatives with potential for elaboration into an organometallic species [101]. The disilylated calixarene, $\mathbf{34^{H_2Si_2}}$ can be synthesized by reaction of $\mathbf{34^{H_4}}$ with hexamethyldisilazane. From this, the mononuclear amido-complex, $\mathbf{34^{H_2Si_2}Y \cdot NR_2}$ (Chart 9) was synthesized by straightforward amine elimination using $Y[N(SiHMe_2)_2]_3 \cdot (THF)_2$ at room temperature. By contrast, reaction of $Y[N(SiHMe_2)_2]_3 \cdot (THF)_2$ with $\mathbf{34^{H_4}}$ resulted in dimer formation to give $[\mathbf{34^{H_3Si}Y^1}]_2$ in which three phenolic oxygen atoms have been deprotonated, and the remaining oxygen has been silylated in situ by $HN(SiMe_3)_2$ produced as a byproduct. In the solid state structure, the silylated phenoxide does not interact with an yttrium center; rather, a THF ligand is retained as shown in Chart 9.

4.6. *Higher denticity macrocyclic donors*

4.6.1. *Mono-aza-18-crown-6 (MAC) macrocycles, monoanionic*

Berg and co-workers have explored the use of mono and dianionic aza-crown ethers as ligands to support organoyttrium chemistry (Scheme 20). The MAC (ligand **35**) was instituted using alkane elimination, giving the thermally stable dialkyl complex $\mathbf{35Y \cdot R_2}$ (R = CH_2SiMe_3), in which the two alkyl groups are coordi-



Scheme 20.

nated *trans* to one another, as confirmed by solution NMR studies and X-ray crystallography [102]. In the solid state, the nitrogen and three of the oxygen atoms in the ring are bonded to yttrium, with the remaining two oxygens considered to be weakly interacting.

The reaction of **35Y·R₂** with CO proceeds smoothly to give a bis-enolate complex [R = $OC(CH_2)(SiMe_3)$], but the starting bis-alkyl could be recovered unchanged after exposure to H_2 or ethylene. The complex does, however, appear to undergo alkyl abstraction with $B(C_6F_5)_3$ in the presence of THF to give a colorless material assigned as the cation **35Y·R**$^+$ $[A]^-$; decomposition of this species to give $SiMe_4$ and unidentified products occurs rapidly at room temperature. Direct abstraction of a CH_2SiMe_3 group is relatively rare, but is supported by the proton NMR data presented. Unfortunately, the high reactivity of this species even in the presence of stabilizing donors precluded full characterization and further reactivity studies.

4.6.2. Di-aza-18-crown-6 (DAC) macrocycles, dianionic

In addition to the monoanionic aza-18-crown-6 macrocycle, **35**, the Berg group have introduced a dianionic version, the DAC ligand **36**. Reaction of diproteo 4,15-diaza-18-crown, H_2**36**, with $[Y\{N(SiMe_3)_2\}_3]$ gave the amido complex **36Y·NR₂** [103] which was crystallographically characterized. Unsuccessful attempts to derivatize this material led these authors to prepare a monomeric alkyl derivative **36Y·R** via alkane elimination using $[Y(CH_2SiMe_3)_3(THF)_2]$ [104]. This alkyl complex is indefinitely stable as a solid at −30 °C, but at room temperature in solution decomposes autocatalytically to give $SiMe_4$ and unidentified products, probably as a result of ligand metallation. In contrast to the MAC ligand **35**, in complexes of the DAC ligand **36**, all donor atoms of the macrocycle are engaged in bonding to the yttrium center.

The alkyl complex **36Y·R** undergoes rapid σ-bond methathesis with phenylacetylene to give deep purple solutions containing an equilibrium mixture of a dimeric μ-acetylide complex, [**36Y·CCPh**]₂ (possibly in equilibrium with a monomeric species) and a butatrienediyl-dimer, related to the acetylide by a reversible C–C coupling reaction reminiscent of the chemistry discussed in Section 4.3.1 above [105]. Pure samples of both complexes could be prepared by crystallization; the structure of the dimeric form of the colorless acetylide complex is shown in Fig. 8. It is a centrosymmetric dimer in which all nitrogen and oxygen atoms of the ligands are coordinated and the acetylide groups are bridging (Fig. 7). The Y–C bond lengths are very long, lying outside the usual range, probably due to steric crowding at the metal centers. This is consistent with reports that acetylide couplings are promoted by a high degree of steric crowding. A structural investigation of the coupled product was also carried out, but satisfactory refinement of the structure was prevented by disorder in the backbone of the diaza-crown ligands. Some connectivity could however be determined; the butatrienediyl fragment clearly adopts a *Z*-conformation with the two yttrium atoms on the same side of the C4 chain, and one nitrogen atom from each diaza-crown ligand is in a bridging site between the two metal centers.

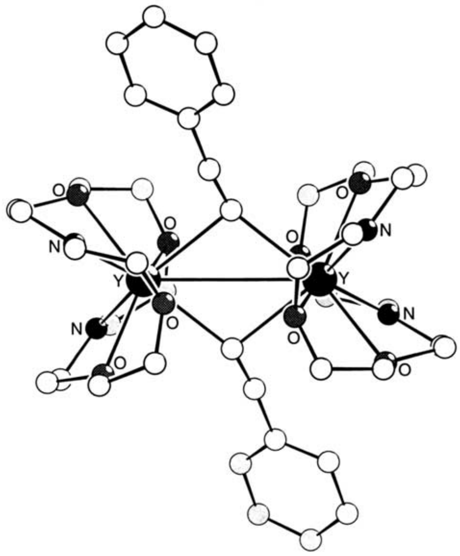


Fig. 8. Molecular structure of the dimer [**36Y·CCPh**]₂.

5. Concluding remarks

The past 5 years has been a wide-ranging hunt for suitable ligands for supporting base-free, monomeric organogroup 3 derivatives, particularly those with two reactive hydrocarbyl ligands. While this ‘ligand exploration’ phase will be ongoing, the successful ligand systems developed in this regard will now allow for a new phase of organogroup 3 metal research. Some of the challenges to be addressed include the development of the chemistry of Group 3 metal alkyl cations, the preparation and study of monomeric Group 3 metal hydrides, the preparation of highly active ‘activatorless’ olefin polymerization catalysts and the development of chiral versions of these families of compounds. In terms of synthetic methodology, the generality and effectiveness of the amine elimination protocols will be significantly enhanced if convenient and general methods for converting $LM(NR_2)_n$ compounds to organometallic compounds $LM(R)_n$ can be developed. A two step procedure involving alcoholysis and alkylation with organolithium reagents has some promise, but is not very atom economical and may be too harsh for ligands, which are also based on hard donors and prone to demetallation. Nonetheless, several promising ligand systems exist for supporting organogroup 3 metal chemistry, most notably the bulky amidinate donor **3**, the bis-oxazoline ancillary **7**, the nacnac ligands **8**, and the linked amido-tacn ligands **28**. This augurs well for the study of well defined LMR_2 compounds whose likely rich chemistry is now being explored.

Acknowledgements

Funding for our work in this area has been provided by Nova Chemicals (Calgary, Alberta) and NSERC of Canada's Research Partnerships Program. WEP would like to thank Professor Jan Teuben and Professor Bart Hessen for their gracious hospitality and the opportunity to spend time in their group (July–September 2001), where the bulk of this article was prepared. Given their many significant contributions to this area, the article is dedicated to them with respect and in friendship.

References

[1] The Group 3 metals have traditionally been grouped in with the rest of the lanthanides in monographs of this type; this number therefore includes citations for the rest of the lanthanide elements.

[2] In the book *Organoderivatives of the Rare Earth Elements*, M.N. Bochkarev, L.N. Zakharov, G.S. Kalinina, Kluwer, Boston, 1995, which covered the literature up to 1990, almost all the complexes discussed incorporated a Cp donor of some type. The exceptions were homoleptic coordination compounds, which do not classify as organometallic derivatives.

[3] (a) W.E. Piers, P.J. Shapiro, E.E. Bonet, J.E. Bercaw, Synlett 1 (1990) 74;
(b) S.A. Cotton, Polyhedron 18 (1999) 1691.

[4] (a) C.J. Schaverien, Adv. Organomet. Chem. 36 (1994) 289;
(b) F.T. Edelmann, Angew. Chem. Int. Ed. Engl. 34 (1995) 2466.

[5] P.R. Meehan, D.R. Aris, G.R. Willey, Coord. Chem. Rev. 181 (1999) 121.

[6] (a) U. Siemeling, Chem. Rev. 100 (2000) 1495;
(b) H. Butenschön, Chem. Rev. 100 (2000) 1565.

[7] H. Brand, J. Arnold, Coord. Chem. Rev. 140 (1995) 137.

[8] S.A. Cotton, Coord. Chem. Rev. 160 (1997) 93.

[9] (a) G.E. Herberich, U. Englert, A. Fischer, J. Ni, A. Schmitz, Organometallics 18 (1999) 5496;
(b) M.A. Putzer, J.S. Rogers, G.C. Bazan, J. Am. Chem. Soc. 121 (1999) 8112.

[10] F. Nief, Eur. J. Inorg. Chem. (2001) 891.

[11] For the 6 coordinate M^{3+} ions: R.D. Shannon, Acta Crystallogr. Sect. A 32 (1976) 751.

[12] A.S. Guram, R.F. Jordan, in: M.F. Lappert (Ed.), Comprehensive Organometallic Chemistry II, vol. 4, Elsevier Scientific Ltd, Oxford, 1995, p. 589.

[13] L. Manzer, Inorg. Synth. 21 (1982) 135.

[14] P. Sobota, J. Utko, S. Szafert, Inorg. Chem. 33 (1994) 5203.

[15] M = Sc: (a) J.S. Ghotra, M.B. Hursthouse, A.J Welch, J. Chem. Soc. Chem. Common. (1973) 669;
(b) E.C. Alyea, D.C. Bradley, R.G. Copperwaite, J. Chem. Soc. Dalton Trans. (1972) 1580;
(c) M = Y, La: D.C. Bradley, J.G. Ghotra, F.A. Hart, J. Chem. Soc. Dalton Trans. (1973) 1021;
(d) M = La: W.J. Evans, R.E. Golden, J.W. Ziller, Inorg. Chem. 30 (1991) 4963.

[16] R. Anwander, O. Runte, J. Eppinger, G. Gerstberger, E. Herdtweck, M. Spiegler, J. Chem. Soc. Dalton Trans. (1998) 847.

[17] (a) A.K. Hughes, A. Meetsma, J.H. Teuben, Organometallics 12 (1993) 1936;
(b) G.M. Diamond, S. Rodewald, R.F. Jordan, Organometallics 14 (1995) 5.

[18] (a) M = Sc, Y: M.F. Lappert, R.J. Pearce, J. Chem. Soc. Chem. Commun. (1973) 126;
(b) K.C. Hultzsch, J. Okuda, P. Voth, K. Beckerle, T.P. Spaniol, Organometallics 19 (2000) 228;
(c) W.J. Evans, J.C. Brady, J.W. Ziller, J. Am. Chem. Soc. 123 (2001) 7711.

[19] D.J. Emslie, W.E. Piers, M. Parvez, unpublished results.

[20] Potentially, the tris-neo-pentyl derivatives could be employed, but other $MR_3 \cdot THF_n$. derivatives (for example $R = CH_3$ or Ph) are oligomeric and not well-behaved compounds.

[21] R.K. Harris, B.E. Mann, NMR and the Periodic Table, Academic Press, 1978, p. 195.

[22] W.T. Klooster, L. Brammer, C.J. Schaverien, P.H.M. Budzelaar, J. Am. Chem. Soc. 121 (1999) 1381.

[23] R. Duchateau, C.T. van Wee, A. Meetsma, J.H. Teuben, J. Am. Chem. Soc. 115 (1993) 4931.

[24] (a) R. Duchateau, C.T. van Wee, A. Meetsma, P.T. van Duijen, J.H. Teuben, Organometallics 15 (1996) 2279;
(b) See also: R. Duchateau, A. Meetsma, J.H. Teuben, Organometallics 15 (1996) 1656.

[25] R. Duchateau, C.T. van Wee, J.H. Teuben, Organometallics 15 (1996) 2291.

[26] J.R. Hagadorn, J. Arnold, Organometallics 15 (1996) 984.

[27] E.A. Bijpost, R. Duchateau, J.H. Teuben, J. Mol. Catal. Sect. A 95 (1995) 121.

[28] S. Bambirra, M.J.R. Brandsma, E.A.C. Brussee, A. Meetsma, B. Hessen, J.H. Teuben, Organometallics 19 (2000) 3197.

[29] J.A.R. Schmidt, J. Arnold, Chem. Commun. (1999) 2149.

[30] K.B. Aubrecht, K. Chang, M.A. Hillmyer, W.B. Tolman, J. Polym. Sci. Part A 39 (2001) 284.

[31] For a nice perspective on this area, see: B.J. O'Keefe, M.A. Hillmyer, W.B. Tolman, J. Chem. Soc. Dalton Trans. (2001) 2215.

[32] A. Spannenberg, P. Arndt, R. Kempe, Angew. Chem. Int. Ed. 37 (1998) 832.

[33] P.J. Bailey, S. Pace, Coord. Chem. Rev. 214 (2001) 91.

[34] Z. Lu, G.P.A. Yap, D.S. Richeson, Organometallics 20 (2001) 706.

[35] G.R. Giesbrecht, G.D. Whitener, J. Arnold, J. Chem. Soc. Dalton Trans. (2001) 923.

[36] P.W. Roesky, Chem. Ber. 130 (1997) 859.

[37] P.W. Roesky, Eur. J. Inorg. Chem. (1998) 593.

[38] A.V. Korolev, E. Ihara, I.A. Guzei, V.G. Young, Jr., R.F. Jordan, J. Am. Chem. Soc. 123 (2001).

[39] M.R. Bürgsein, H. Berberich, P.W. Roesky, Organometallics 17 (1998) 1452.

[40] See Y. Li, T.J. Marks, J. Am. Chem. Soc. 118 (1996) 9295 for leading references.

[41] K.H. den Haan, J.L. de Boer, J.H. Teuben, A.L. Spek, B. Kojic-Prodic, G.R. Hayes, R. Huis, Organometallics 5 (1986) 1726.

[42] H.W. Görlitzer, M. Spiegler, R. Anwander, J. Chem. Soc. Dalton Trans. (1999) 4287.

[43] (a) W.A. Herrmann, J. Eppinger, M. Spiegler, O. Runte, R. Anwander, Organometallics 16 (1997) 1813;
(b) J. Eppinger, M. Spiegler, W. Hieringer, W.A. Herrmann, R. Anwander, J. Am. Chem. Soc. 122 (2000) 3080.

[44] W.-K. Kim, M.J. Fevola, L.M. Liable-Sands, A.L. Rheingold, K.H. Theopold, Organometallics 17 (1998) 4541.

[45] J.D. Scollard, D.H. McConville, J. Am. Chem. Soc. 118 (1996) 10008.
[46] L.W.M. Lee, W.E. Piers, M.R.J. Elsegood, W. Clegg, M. Parvez, Organometallics 18 (1999) 2947.
[47] P.G. Hayes, W.E. Piers, L.W.M. Lee, L.K. Knight, M. Parvez, M.R.J. Elsegood, W. Clegg, Organometallics 20 (2001) 2533.
[48] L.K. Knight, W.E. Piers, R. McDonald, Chem. Eur. J. 6 (2000) 4322.
[49] (a) W.E. Piers, P.G. Hayes, W. Clegg, Abstracts of OCOP 2000, Organometallic Catalysts and Olefin Polymerization, Oslo, Norway, June 18–22, 2000.;
(b) W.E. Piers, P.G. Hayes, R. McDonald, J. Am. Chem. Soc. (2002) 124.
[50] R. Duchateau, T. Tuinstra, E.A.C. Brussee, A. Meetsma, P.T. van Duijnen, J.H. Teuben, Organometallics 16 (1997) 3511.
[51] R. Duchateau, E.A.C. Brussee, A. Meetsma, J.H. Teuben, Organometallics 16 (1997) 5506.
[52] S. Dehnen, M.R. Bürgstein, P.W. Roesky, J. Chem. Soc. Dalton Trans. (1998) 2425.
[53] P. Blech, C. Floriani, A. Chiesi-Villa, C. Guastini, J. Chem. Dalton Trans. (1990) 3557.
[54] S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsure, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa, T. Fujita, J. Am. Chem. Soc. 123 (2001) 6847.
[55] C. Wang, S. Friedrich, T.R. Younkin, R.T. Li, R.H. Grubbs, D.A. Bansleben, M.W. Day, Organometallics 17 (1998) 3149.
[56] D.J.H. Emslie, W.E. Piers, R. McDonald, J. Chem. Soc. Dalton Trans. (2002) 293.
[57] T.I. Gountchev, T.D. Tilley, Organometallics 18 (1999) 2896.
[58] T.I. Gountchev, T.D. Tilley, Organometallics 18 (1999) 5661.
[59] P.-F. Fu, L. Brard, Y. Li, T.J. Marks, J. Am. Chem. Soc. 117 (1995) 7157.
[60] H.W. Görlitzer, M. Spiegler, R. Anwander, Eur. J. Inorg. Chem. (1998) 1009.
[61] W.A. Herrmann, R. Anwander, V. Dufaud, W. Scherer, Angew. Chem. Int. Ed. Engl. 33 (1994) 1285.
[62] J.A. Annand, H.C. Aspinall, A. Steiner, Inorg. Chem. 38 (1999) 3941.
[63] J.A. Annand, H.C. Aspinall, J. Chem. Soc. Dalton Trans. (2000) 1867.
[64] S. Hajela, W.P. Schaefer, J.E. Bercaw, J. Organomet. Chem. 532 (1997) 45.
[65] M.P. Hogerheide, J. Boersma, A.L. Spek, G. van Koten, Organometallics 15 (1996) 1505.
[66] Y. Matsuo, K. Mashima, K. Tani, Organometallics 20 (2001) 3510.
[67] D.P. Long, A. Chandrasekaran, R.O. Day, P.A. Bianconi, A.L. Rheingold, Inorg. Chem. 39 (2000) 4476.
[68] D.P. Long, P.A. Bianconi, J. Am. Chem. Soc. 118 (1996) 12453.
[69] K. Kincaid, C.P. Gerlach, G.R. Giesbrecht, J.R. Hagadorn, G.D. Whitener, J. Arnold, Organometallics 18 (1999) 5360.
[70] D. Doyle, Y.K. Gun'ko, P.B. Hitchcock, M.F. Lappert, J. Chem. Soc. Dalton Trans. (2000) 4093.
[71] P. Shao, D.J. Berg, G.W. Bushnell, Inorg. Chem. 33 (1994) 6334.
[72] For a personal account concerning the evolution and early chemistry of this ligand see: M.D. Fryzuk, Can. J. Chem. 70 (1992) 2839.
[73] M.D. Fryzuk, T.S. Haddad, S.J. Rettig, Organometallics 11 (1992) 2967.
[74] M.D. Fryzuk, T.S. Haddad, J. Am. Chem. Soc. 110 (1988) 8263.
[75] M.D. Fryzuk, T.S. Haddad, S.J. Rettig, Organometallics 10 (1991) 2026.
[76] M.D. Fryzuk, T.S. Haddad, J. Chem. Soc. Chem. Commun. (1990) 1088.
[77] M.D. Fryzuk, T.S. Haddad, D.J. Berg, Coord. Chem. Rev. 99 (1990) 137.
[78] M.D. Fryzuk, G.R. Giesbrecht, S.J. Rettig, Organometallics 15 (1996) 3329.
[79] M.D. Fryzuk, G.R. Giesbrecht, S.J. Rettig, Can. J. Chem. 78 (2000) 1003.
[80] M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer, J.E. Bercaw, J. Am. Chem. Soc. 109 (1987) 203.
[81] C.G. Pernin, J.A. Ibers, Inorg. Chem. 38 (1999) 5487.
[82] C.G. Pernin, J.A. Ibers, Inorg. Chem. 39 (2000) 1216.
[83] C.G. Pernin, J.A. Ibers, Inorg. Chem. 39 (2000) 1222.
[84] R.R. Schrock, Acc. Chem. Res. 30 (1997) 9.
[85] D.D. Graf, W.M. Davis, R.R. Schrock, Organometallics 17 (1998) 5820.
[86] M.D. Fryzuk, P. Yu, B.O. Patrick, Can. J. Chem. 79 (2001) 1194.
[87] S. Bambirra, D. van Leusen, A. Meetsma, B. Hessen, J.H. Teuben, Chem. Commun. (2001) 637.
[88] S. Bambirra, A. Meetsma, B. Hessen, J.H. Teuben, Organometallics 20 (2001) 782.
[89] H. Noss, M. Oberthür, C. Fischer, W.P. Kretschmer, R. Kempe, Eur. J. Inorg. Chem. (1999) 2283.
[90] J. Arnold, C.G. Hoffman, D.Y. Dawson, F.J. Hollander, Organometallics 12 (1993) 3645.
[91] C.J. Schaverien, A.G. Orpen, Inorg. Chem. 30 (1991) 4968.
[92] M.D. Fryzuk, J.B. Love, S.J. Rettig, Chem. Commun. (1996) 2783.
[93] M.D. Fryzuk, J.B. Love, S.J. Rettig, J. Am. Chem. Soc. 119 (1997) 9071.
[94] M.D. Fryzuk, L. Jafarpour, F.M. Kerton, J.B. Love, B.O. Patrick, S.J. Rettig, Organometallics 20 (2001) 1387.
[95] H.J. Heeres, J. Nijhoff, J.H. Teuben, R.D. Rogers, Organometallics 12 (1993) 2609.
[96] M.D. Fryzuk, L. Jafarpour, F.M. Kerton, J.B. Love, S.J. Rettig, Angew. Chem. Int. Ed. 39 (2000) 767.
[97] O. Runte, T. Priermeier, R. Anwander, Chem. Commun. (1996) 1385.
[98] R. Anwander, H.W. Görlitzer, G. Gerstberger, C. Palm, O. Runte, M. Spiegler, J. Chem. Soc. Dalton Trans. (1999) 3611.
[99] W.J. Evans, C.H. Fujimoto, J.W. Ziller, Chem. Commun. (1999) 311.
[100] T.M. Ovitt, G.W. Coates, J. Am. Chem. Soc. 121 (1999) 4072.
[101] R. Anwander, J. Eppinger, I. Nagl, W. Scherer, M. Tafipolsky, P. Sirsch, Inorg. Chem. 39 (2000) 4713.
[102] L. Lee, D.J. Berg, F.W. Einstein, R.J. Batchelor, Organometallics 16 (1997) 1819.
[103] L. Lee, D.J. Berg, G.W. Bushnell, Inorg. Chem. 33 (1994) 5302.
[104] L. Lee, D.J. Berg, G.W. Bushnell, Organometallics 14 (1995) 8.
[105] L. Lee, D.J. Berg, G.W. Bushnell, Organometallics 14 (1995) 5021.