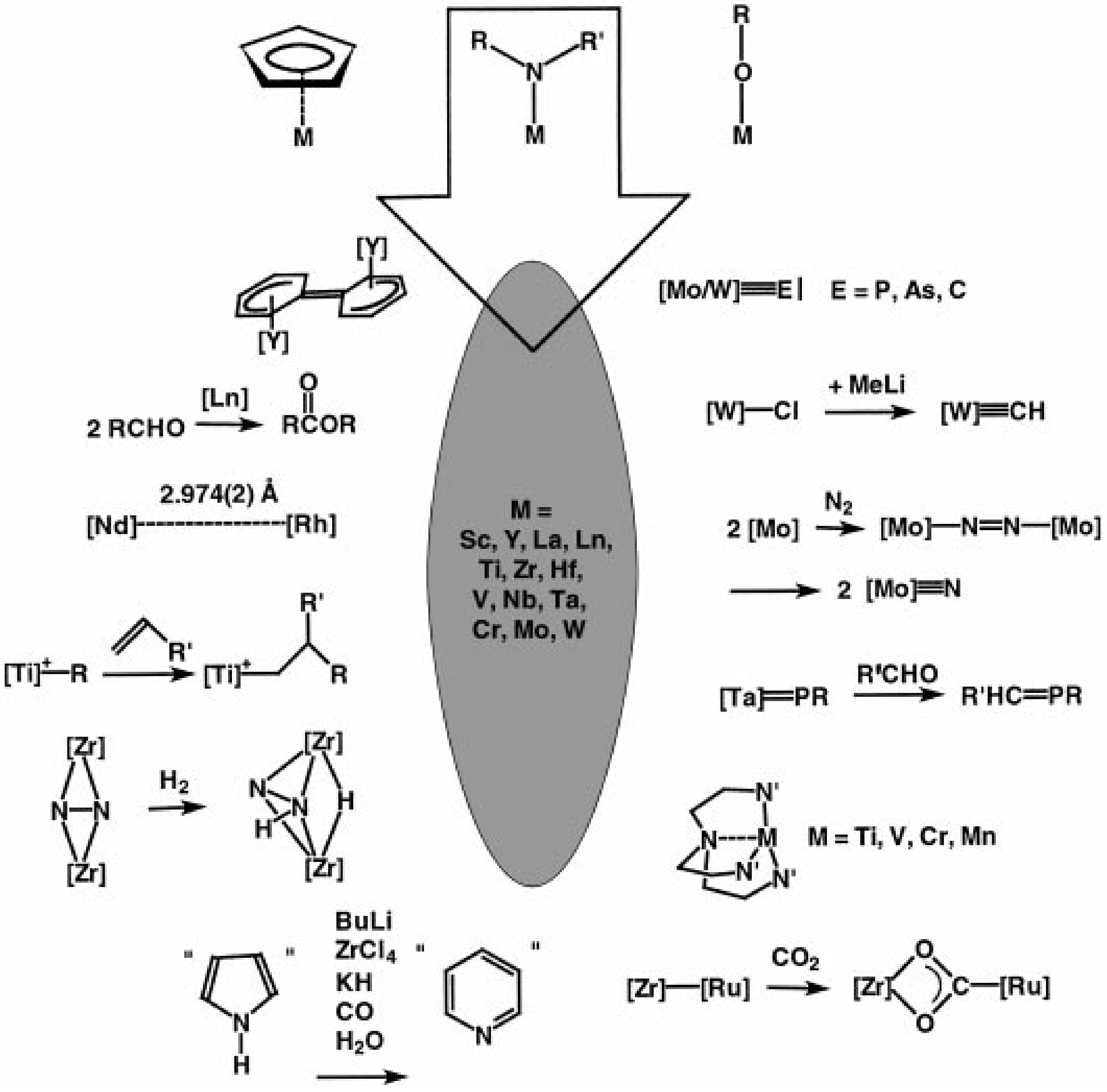
Amidometal Chemistry Today



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Highlights in the Renaissance of Amidometal Chemistry

Rhett Kempe*

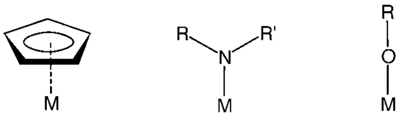
Dedicated to Professor Dirk Walther on the occasion of his 60th birthday

More than 30 years ago intensive work began on the reactivity of the amidometal bond, mainly as a comparison to the metal–carbon bond. The results of these investigations were rather sobering. The amidometal bond in the complexes of early transition metals is kinetically inert, thermodynamically more stable, and thus synthetically far less interesting than the corresponding metal–carbon bond. "Today" amidometal chemistry has come to mean the utilization of the presumed disadvantage of a stable amidometal bond to produce well-defined reaction centers in transition metal complexes. In this way the reactivity of the resulting compounds can be specifically tailored to allow applications in areas such as the activation of small, poorly reactive molecules, homogeneous catalysis, or organic synthesis. Insights into the mechanisms of elementary reactions such as C–H activation, α-H elimination, the cleavage of N–N triple bonds, reactions of N_2 with H_2 within the coordination sphere of transition metals, new routes for the synthesis of macrocycles, polar metal–metal bonds, and complexes with unusual terminal ligands such as phosphorus, arsenic, or carbon are, in addition to interesting transfer or polymerization reactions, just a few selected examples which illustrate what has become possible by the use of amido ligands. Thus, in addition to the cyclopentadienyl fragment, which as a "directing ligand" has dominated the chemistry of the early transition metals for decades, alternatives are now available for targeted studies. What amido ligands have brought us in new information over the last 5–10 years can be called the renaissance of amidometal chemistry, or the beginning of a "postmetallocene era".

Keywords: metal–metal interactions · N ligands · nitrogen fixation · nitrogen heterocycles · polymerizations

1. Introduction

In organometallic chemistry considerable effort is being expended on modifying the reactivity of metal–carbon bonds with coligands. The information thus obtained is being extensively used, for example in homogeneous catalysis.[1] In the choice of such coligands, the cyclopentadienyl (Cp) fragment and phosphanes have hitherto played the decisive role as anionic and neutral donor functions, respectively.[2] In addition to these classical possibilities for the control of reactivity of complexes, since the beginning of the 1990s exhaustive efforts have been devoted to the development of novel ligands.[3] As well as the Cp ligand (Scheme 1, left), alkoxy (Scheme 1, right) and amido ligands[4] (Scheme 1, center) have proved to be suitable for the stabilization of early, electron-poor transition metals in medium to high oxidation states. Of these two alternatives, the amido ligand is especially interesting since it offers the greater potential in ligand and complex design because of the potential for double substitution at the donor atom.



Scheme 1. The three most important ligand types for the stabilization of early transition metals in middle to high oxidation states (R = alkyl, aryl, silyl).

The foundations of amidometal chemistry were laid in the 1960s and 1970s and are associated with names such as Bürger, Wannagat, Bradley, and Lappert. The motivation for the investigations was mainly the exploration of the reactivity of amidometal bonds in comparison to the metal–carbon bond.[4] From the middle of the 1970s to the end of the 1980s interest in amidometal complexes stagnated as greater effort was devoted to the metallocenes. Compounds with essentially η^5-bound Cp ligands have been extensively investigated since their discovery,[5, 7] with special interest being devoted from the middle of the 1970s to complexes with metals of Group 4.

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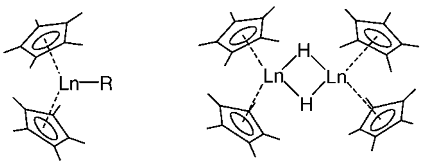
This was brought about by the discovery of their high alkene polymerization activities in combination with methylaluminoxane (MAO),[8, 9] the stability of the ligand–metal bond, and the frontier orbitals set up for the activation of small molecules. The renaissance of amidometal chemistry from the end of the 1980s to the middle of the 1990s is characterized mainly by the search for analogies between Cp and amido ligands. This search was later discontinued, and the actual advantages of amido ligands, that is the many uses in the construction of novel complex compounds with defined reactive centers, were exploited. Until now there has been little interest in the amido complexes of late transition metals. The chemistry of these compounds differs drastically from that of the early transition metals because of the energetically unfavorable combination of "soft" metals with "hard" amido ligands.[10]

Reviews on the chemistry of the amido complexes of early transition metals may be divided into two categories. On the one hand, there are the "cross-sectional works", publications in which different amido ligands are described;[4] on the other, there are the "amido ligand orientated" publications in which the chemistry of only a specific ligand type is described. A comprehensive presentation of amidometal chemistry up to 1981 was both useful and realizable.[4] Since 1990 this has been restricted to individual ligand types.[11–23] The plethora of the amido ligands used makes an exhaustive "cross-sectional discussion" difficult since not all compounds can be discussed. However, such scrutiny is desirable as a counterpart to the "ligand-orientated" reviews and in order to stress the significance of amidometal chemistry. A restriction to highlights appears appropriate since in this way trend-setting work can be discussed and the review held within discernible limits.

2. Scandium, Yttrium, and Lanthanoids

2.1. Cp-Free Organolanthanoid Chemistry

Amido chemistry of the Ln metals is greatly influenced by the analogy to metallocene chemistry. The fascination with lanthanoid complexes stabilized with Cp ligands comes from the opportunities for homogeneous catalytic processes for the formation of C–H, C–C, and C–X bonds.[24] Here, highly reactive alkyl and hydride species are used as precatalysts or as stoichiometric reagents (Scheme 2).



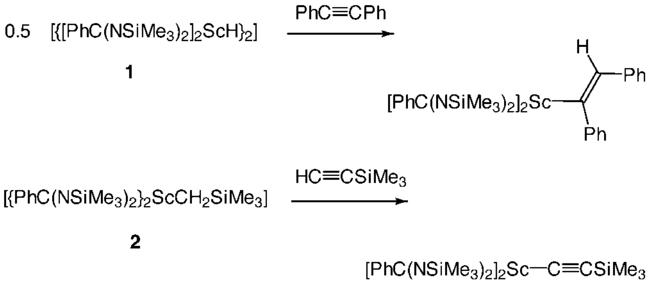
Scheme 2. Lanthocene catalysts for C–C, C–H, and C–X couplings (R = alkyl, X = heteroatom).

Typical examples of catalytic uses are polymerization,[25, 26] hydrogenation,[26, 27] hydroboration,[28] hydrosilylation,[29] and hydroamination/cyclization[30] of olefins. Analogous catalyses have also been described for alkynes (oligomerization,[31, 32] hydrogenation,[32] and hydroamination/cyclization[33]). With the aim of developing new and possibly more active catalysts, Cp-free ligand systems have become popular. Exchanging the Cp ligand for alkoxy or amido functionalities should lead, for example, to improved olefin polymerization catalysts. Chain termination by β-hydrogen transfer can be effectively suppressed at more electron-deficient metal centers because these alkyl complexes are thermodynamically more stable.[34] In addition to alkoxy ligands, amido ligands are especially good since they fulfill the requirement for effective steric shielding. Examples are the silyl-substituted benzamidinato ligands first described by Dehnicke et al.[35] and Roesky et al.[36] The foundations of lanthanoid chemistry were developed mainly by Edelmann et al.[13, 37] During these investigations it was demonstrated that in the case of central f element ions such ligands represent a steric equivalent to Cp ligands.[13, 38] Comprehensive spectroscopic measurements on tris(benzamidinato)- and tris(cyclopentadienyl)lanthanoid complexes also confirm an electronic equivalence if the central Ln atom possesses a low electron affinity.[39] On this basis, and because of the easy accessibility of silyl-substituted

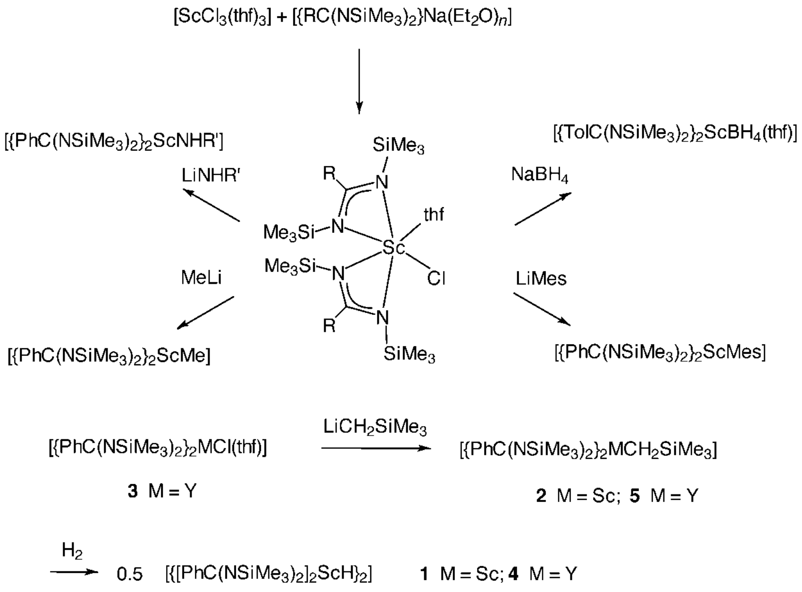
Rhett Kempe was born in Dresden in 1964. He studied chemistry at the Universität Leipzig and received his Diplom under the supervision of Professor J. Sieler in 1989. A subsequent research studentship allowed him to work at the Max-Planck-Institut für Festkörperforschung with Professor H.-G von Schnering and at the Friedrich-Schiller-Universität in Jena with Professor D. Walther. He received his doctorate from the Universität Leipzig in 1992 for work on the mechanisms of nickel complex catalyzed reactions. During a DAAD postdoctoral research fellowship at the Massachusetts Institute of Technology (1992/93) with Professor R. R. Schrock he became interested in N_2 activation. Then after a period at the Max-Planck-Institut für Kohlenforschung (1993/94) with Professor C. Krüger he began to study for his habilitation at the Max-Planck-Gesellschaft in the group "Complex Catalysis" led by Professor U. Rosenthal in 1994. Habilitation on aminopyridinato ligands, complexes of early transition metals and their use in homogeneous catalysis followed at the Universität Rostock in 1998. He is currently a group leader at the Institut für Organische Katalyseforschung in Rostock. His research interests include the development of novel catalysts and he is working at the interface between coordination chemistry and homogeneous catalysis. He is the author of more than 140 publications and in 1998 he was awarded the Karl-Winnacker-Stipendium.

benzamidinato ligands, the alkyl and hydride species, known to be highly reactive from metallocene chemistry, were synthesized. The preparative methodology is borrowed from metallocene chemistry[24] and was used successfully for the first time by Teuben et al. for yttrium complexes.[40] Corresponding scandium complexes are accessible as shown on Scheme 3 and have been described by Arnold et al.[41]

Compound **1** does not react with ethylene or propylene at room temperature. At 60 °C ethylene is only poorly polymerized. The reaction of **1** with internal alkynes such as PhC≡CPh gives the monoinsertion product (Scheme 4). Compound **2** reacts with terminal alkynes under σ-bond metathesis to give the σ-alkynyl complex.[41]



Scheme 4. Reactions of benzamidinatoscandium complexes with terminal alkynes.

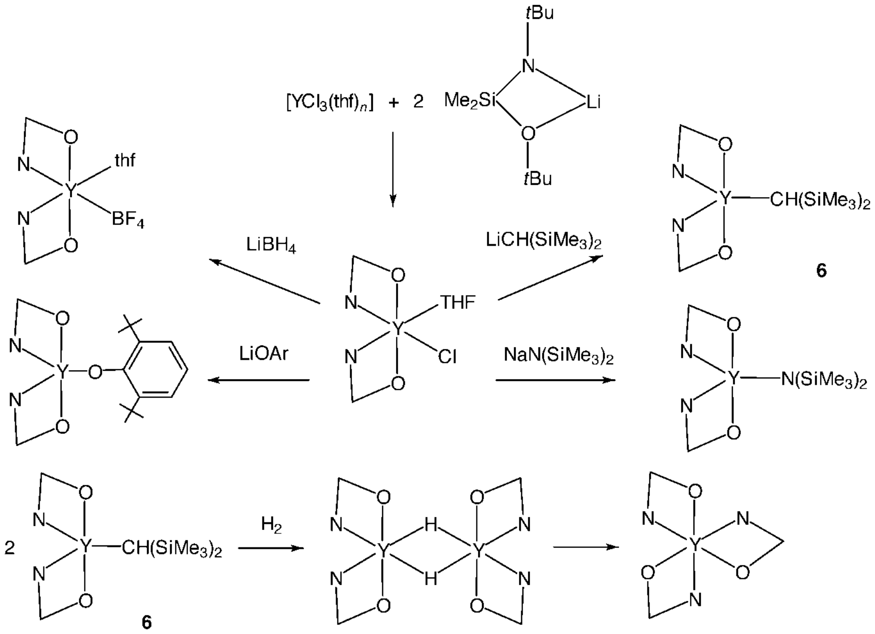


Scheme 3. Benzamidinatoscandium complexes (R = Ph, Tol ($H_3CC_6H_4$); R′ = C_6H_3-2,6-iPr$_2$; Mes = 2,4,6-$(H_3C)_3C_6H_2$).

More extensive studies on the reactivity of **3**[42] confirm the analogy to the chemistry of scandium (Scheme 3). The reaction of **3** with $LiAlH_4$ is surprising. There is no formation of an aluminum complex, but ligand transfer occurs from the yttrium center to the aluminum center. The activity of **4** during ethylene polymerization is to be classified as low.[84] At 55 °C only $4\,\mathrm{kg_{PE}\,mol_{cat.}^{-1}\,h^{-1}}$ is produced. Compound **4** does not react with propylene and 1-hexene.[43] One reason considered for the low polymerization activities is the strong ionic character of the central atom of the benzamidinatoyttrium complex. Compounds **4** and **5** catalyze the hydroboration of olefins in the presence of catecholborane. The activities are only about 5–10 % relative to the activity of $[Cp^*_2LaCH(SiMe_3)_2]$ (the best lanthanoid catalyst[28] Cp* = C_5Me_5), but are higher than that of $[Cp^*_2YCH_2SiMe_3]$.[44] Catalyst deactivation by reaction with the catecholborane is considered to be the reason. If **4** is exposed to an excess of terminal alkyne, selective dimerization occurs in the case of HC≡CR (R = tBu, Ph) with the formation of the head-to-tail coupled product $H_2C{=}C(R)C{\equiv}CR$ with a turnover frequency (TOF) of 35 h^{-1}.[40] In the case of $HC{\equiv}CSiMe_3$ the head-to-head product is formed exclusively. In contrast, the compounds $[Cp^*_2YR]$ (R = H, CH_2SiMe_3) do not form head-to-head or head-to-tail products selectively but instead show greater activity.

A similar alternative to Cp ligands are alkoxysilylamido ligands such as *N,O*-bis(*tert*-butyl)-(alkoxydimethylsilyl)amide (Scheme 5).[45]

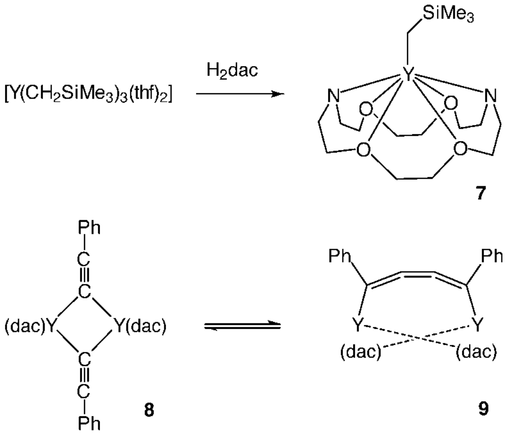
In addition to an alkyl complex, alkoxy, hydroboro and amido compounds may be prepared in good yields. The isolation of a hydrido complex is not possible since ligand redistribution occurs and a tris(alkoxysilylamido) complex is formed (Scheme 5, bottom). The steric demand of the *tert*-butyl-substituted ligand is not



Scheme 5. Alkoxysilylamidoyttrium complexes.

large enough to inhibit a hydrido-alkoxysilylamide exchange. Stoichiometric reactions of **6** with pyridine derivatives lead to η^2-pyridyl and η^2-α-picolyl complexes.[46] It was also demonstrated that the reactivity of these compounds corresponds to the analogous permethylated yttrocenes.

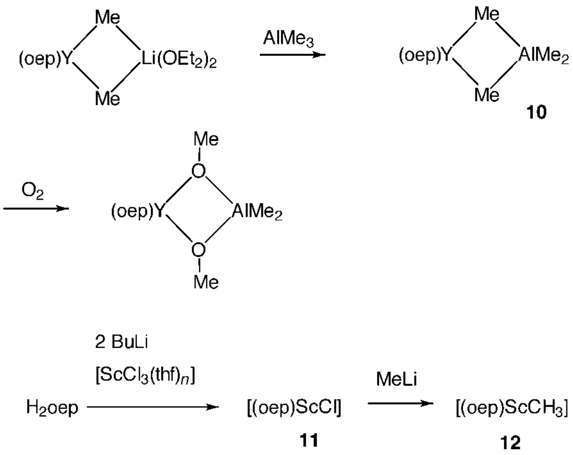
Reactive neutral monoalkyl complexes of the lanthanoids can also be stabilized by doubly deprotonated 4,13-diaza-[18]crown-6 (Scheme 6, top).[47] Compound **7** is stable as a solid, but decomposes in solution at room temperature.[48] The reaction of **7** with phenylacetylene (Scheme 6, bottom) is unusual since a color change to dark blue occurs. NMR investigations demonstrated an equilibrium between two compounds, **8** (colorless) and **9** (blue-violet). The equilibrium and hence the color can be reversibly displaced by change in temperature.[49] The bridging function of the 4,13-diaza-[18]crown-6 dianion (dac) ligand appears to play no role in the stabilization of **9** as analogous reversible coupling reactions have also been described for metallocenes.[31b, 50] Bisalkyl complexes can be stabilized by corresponding monoaza crown ethers (aza-[18]crown-6).[51]



Scheme 6. Alkane elimination in the synthesis of dac–yttrium complexes (top) and in the phenylacetylene complexes existing in equilibrium (bottom).

Reports on metalloporphyrins of lanthanoids were first published at the beginning of the 1970s by Buchler et al.[52] and Horrocks et al.[53] The entry into organometallic chemistry occurred 20 years later. Thus, for example, metalloorganyls $MR_3(R = CH(SiMe_3)_2$, M = Y, Lu) react with octaethylporphyrin (H2oep) to form monoalkyl compounds by alkane elimination. Protonolysis with sterically demanding alcohols, terminal alkynes, or water leads to the formation of monomeric alkoxy complexes, dimeric alkynyl or hydroxy complexes, respectively.[54]

The reaction of yttrium alkoxy compounds with MeLi gives a dimethylyttrate complex (Scheme 7, top) which reacts with $AlMe_3$ to form **10**. This compound shows an interesting selective reaction with one equivalent of O_2 with the formation of a bisalkoxy complex. Compound **11** can be isolated in over 90 % yield by salt metathesis, and the chloro ligand is efficiently substituted by reaction with lithium alkyls, amides, and alkoxy compounds (Scheme 7, bottom). The CH_3 resonance signal in the ^1H NMR spectrum of **12** is shifted markedly to high field (−5 ppm). Compound **12** reacts with CO_2 or acetone with the insertion of a carbonyl function into the Sc–C(methyl) bond.[55]



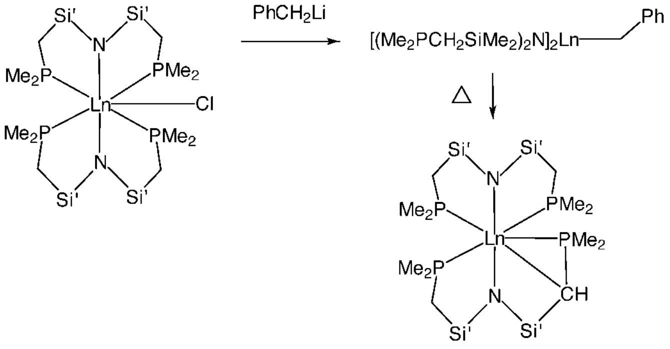
Scheme 7. Selective O_2 insertion in **10** and formation of **12**.

A comparison of the reactivity of the amidolanthanoid complexes with each other is complicated since there have been only individual reports on comparable reactions. Few ligands at all allow the synthesis of stable hydrido complexes. Hitherto, the most extensively investigated were the silyl-substituted benzamidinates, which, however, compare poorly with the corresponding metallocenes during catalytic use.

2.2. Lanthanoid–Phosphane Complexes

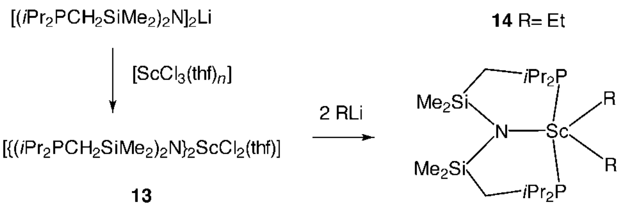
The synthesis of lanthanoid amidophosphane complexes is possible with the amidophosphane hybrid ligands developed by Fryzuk et al.[11, 12] Biligand complexes are accessible, depending upon the lanthanoid ion, by reaction of the lithiated ligand precursor or potassium salt with $LnCl_3$.[56] Alkylations with $LiCH_2Ph$ lead to unstable complexes which eliminate toluene at 50 °C (Scheme 8). In this way cyclometalation of the ligand occurs.[57]

Monoligand complexes are particularly interesting since now principally two chloro ligands are available for functionalization. Such compounds have been described for yttrium[58] and scandium.[59] Mono(amidophosphane)scandium complexes have been extensively studied, and *i*Pr substituents



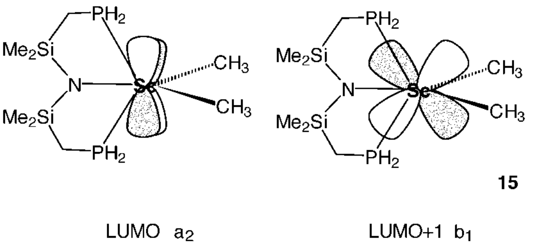
Scheme 8. Cyclometalation of amidophosphane ligands (Ln = Y, La, Ce, Lu).

on the phosphorus atom have been useful.[59] The reaction of $(iPr_2PCH_2SiMe_2)_2NLi$ ((‘P_2N’)Li) with $[ScCl_3(thf)_3]$ leads to **13** in high yield (Scheme 9). The use of toluene as the solvent is essential. Compound **13** reacts with alkyllithium compounds (LiR, R = Me, Et, CH_2SiMe_3) to form the corresponding bisalkyl complexes.



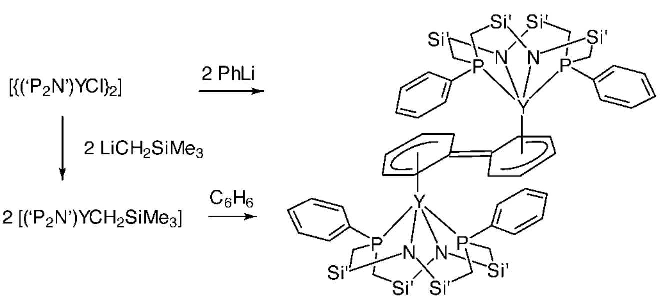
Scheme 9. Bisalkylscandium complexes stabilized by amidophosphane ligands (R = Me, Et, CH_2SiMe_3).

Analogous reactions with organozinc compounds or Grignard reagents fail. Salt-free bisalkyl complexes have thus far only been obtained by the use of sterically demanding substituents.[60] Comprehensive NMR investigations and X-ray crystallographic analysis suggested no agostic interactions with the extremely electron-deficient scandium ion. These can be regarded formally as 12 e^- complexes. It is also noteworthy that the bisalkyl compounds do not exist as “ate” complexes. The reactions of **14** with H_2, ethylene, CO, and CO_2 with ligand expulsion are rather sobering. Ethylene is slowly polymerized, whereas the reactions with H_2, CO, and CO_2 lead to indefinite products with ligand expulsion. That no agostic interactions and no stable products were observed in the reactions with H_2, CO, and CO_2 can be explained by the electronic structure of **15**. The LUMO and the LUMO + 1 are d orbitals with π symmetry (a_2 and b_1) which are incapable of accommodating the electron densities of molecules like CO (Scheme 10). In contrast, the LUMOs of $[Cp_2^*ScCH_3]$ ($1a_1$ and b_2) offer ideal conditions for interactions with electron-rich ligands or ligand fragments.[61]



Scheme 10. LUMOs of $[\{(H_2PCH_2SiMe_2)_2N\}_2ScMe_2]$ (a_2 and b_1).

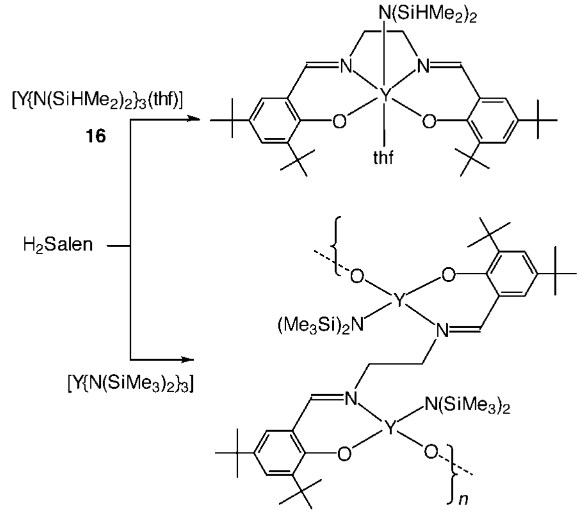
Compounds with diamidodiphosphane ligands possess totally different frontier orbitals.[102] The reactivity of such alkylyttrium complexes towards benzene is noteworthy for it leads to C–C bond formation and the formation of intensely colored (dark blue) arene complexes (Scheme 11).[62] Such arene complexes are untypical for yttrium, mainly σ-aryl complexes are known.[24] A comparison with arenechromium complexes, which are familiar as products of the Hein reaction, is obvious.[63]



Scheme 11. Areneyttrium complexes by phenyl coupling (Si′ = Me_2Si).

2.3. New Applications of the Classical Amine Elimination Reaction

Since the beginning of amidometal chemistry amine elimination reactions have been known to be an elegant synthesis variant for the preparation of compounds of Group 4 metals.[4] Particularly useful starting materials are mixed dimethylamidochloro complexes of the metals of this triad.[64] Comparable alkylamides of Group 3 metals or the lanthanoids do not exist.[65] Interesting prospects arise for these metals from the use of silyl amides. The key step here appears to be the choice of a suitable starting complex. Thus the reaction of **16** with bis(salicylidene)ethylenediamine (H_2Salen)[66] leads to a mononuclear complex which is very soluble in hexane. If $[Y\{N(SiMe_3)_2\}_3]$ is used, oligomers insoluble in THF are formed (Scheme 12).[67]

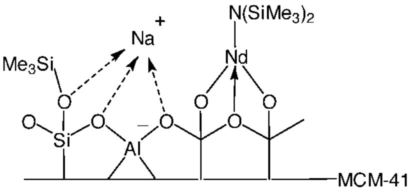


Scheme 12. Amine elimination for the preparation of salenyttrium complexes.

An efficient preparation of *ansa*-yttrocene complexes[68] and sulfonamide complexes[69] is similarly possible. Here too the formation of oligomers is observed with **16**.

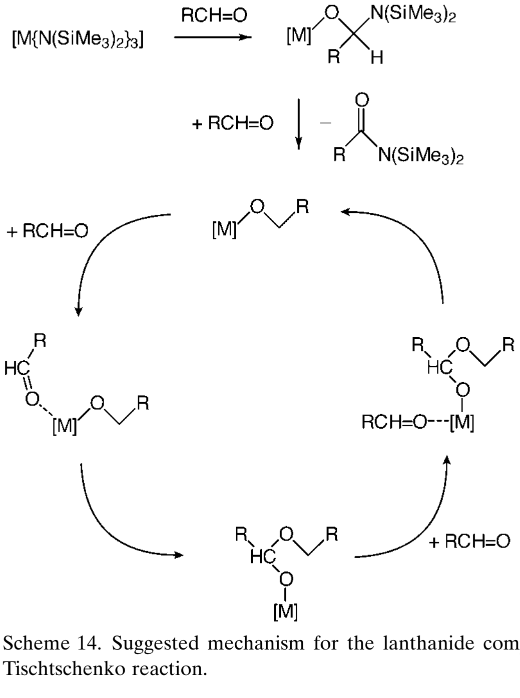
Homoleptic, trivalent selenates and tellurates of lanthanum and cerium are also preparatively readily accessible by amine elimination.[70] These compounds exist in toluene or hexane as triply coordinated mononuclear complexes, which was confirmed by the results of multidimensional $^{77}Se\{^1H\}$ NMR spectroscopy. Such chalcogenates are significant as precursors for the preparation of semiconductor materials with a lanthanoid–chalcogenide basis.[71]

Interesting applications in catalysis are promised by immobilizing amidolanthonide complexes on surfaces of mesoporous silicates.[72] Amine elimination reactions of silyl amides of lanthanoids with dehydrated MCM-41[73] led to immobilized lanthanoid complexes (Scheme 13). These are remarkable precatalysts in Danishefsky hetero-Diels–Alder reactions.[74]



Scheme 13. Immobilization of lanthanoid complexes by amine elimination on MCM-41.

The facile elimination of an amine is also responsible for the extremely high catalytic activity of $[M\{N(SiMe_3)_2\}_3]$[75] (M = Sc, Y, and Ln) in the Tischtschenko reaction (or Claisen–Tischtschenko reaction).[76] Alkoxy complexes are thought to be the intrinsically active species which are formed from catalyst precursors by amine elimination reactions (Scheme 14). If alkoxylanthanoid complexes or the corresponding aluminum compounds are used as precatalysts, very little or no activity is observed.[75]

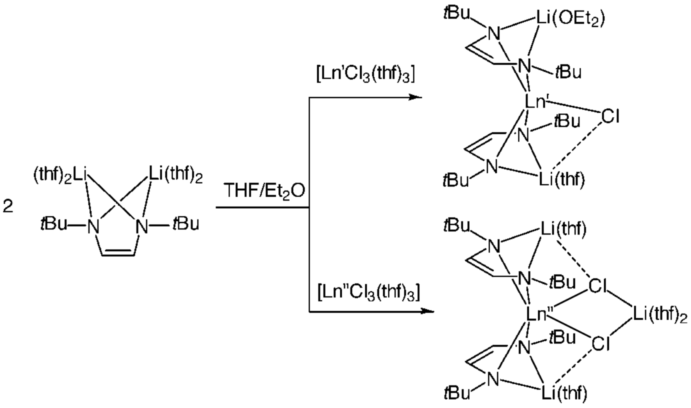


Scheme 14. Suggested mechanism for the lanthanide complex catalyzed Tischtschenko reaction.

2.4. Structure and Reactivity of “ate” Complexes

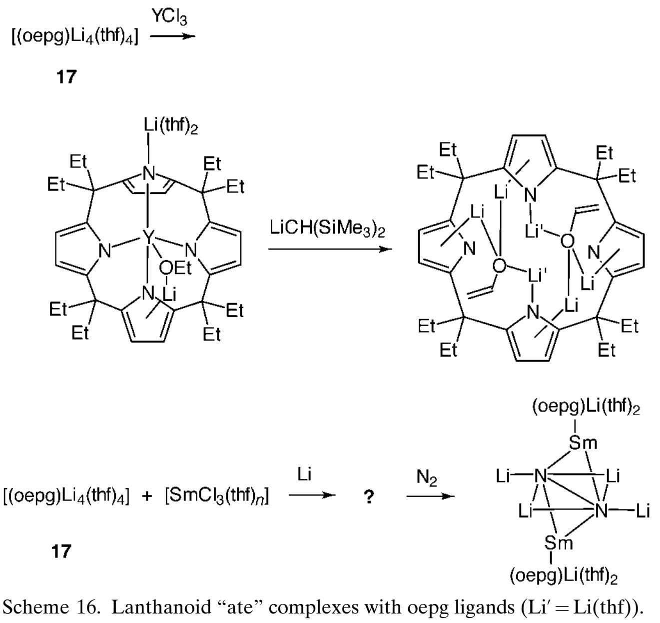
Most often sterically demanding, anionic ligands are used in the organometallic chemistry of the lanthanoids to accommodate the requirements of these large, electropositive metals.[24] Complex chemistry with ligands of low spatial requirement is underdeveloped because compounds with salt coordination, or “ate” complexes are formed preferentially.[65] That “ate” complexes are not to be regarded as useless byproducts, but have interesting properties in, for example, enantioselective catalysis was recently demonstrated with the alkoxy complexes developed by Shibasaki et al.[77]

The reaction of doubly lithiated diazadienes with lanthanoid trichlorides leads to “ate” complexes with chemically interesting structures (Scheme 15).[78] The synthetic potential of such compounds appears to be great since the halogen atoms are apparently readily substituted by organic moieties. The preparation of novel multimetal complexes could be achieved by the exchange of lithium for other metals. Reactions of “ate” complexes with $[CpZrCl_3]$ and $[Cp_2ZrCl_2]$ are noteworthy. In these cases mixed Cp–diazadiene–zirconium complexes are readily formed by ligand transfer.[78]



Scheme 15. Lanthanoid “ate” complexes with diazadiene ligands (Ln′ = Y, Lu; Ln″ = Sm).

Lanthanoid complexes with macrocyclic porphyrinogen ligands[15, 16] show remarkable reaction behavior as well as interesting structural chemistry. For example, **17** reacts with YCl_3 in THF to form a yttrate–lithium ethanolate complex (Scheme 16, top) in which the ethanolate is formed from



Scheme 16. Lanthanoid “ate” complexes with oepg ligands (Li′ = Li(thf)).

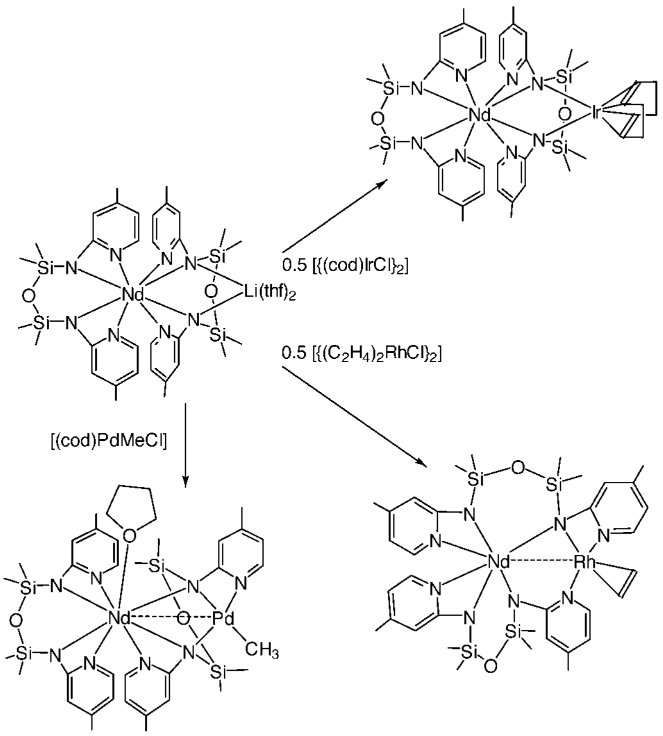
THF.[79] The addition of alkyllithium compounds leads to fragmentation of a further THF molecule and the formation of a dilithiated bisenolate salt with "loss" of the central yttrium ion. The reaction of **17** with [$SmCl_3(thf)_3$] in THF leads to a golden-yellow solution which becomes deep green on the addition of elemental lithium (Scheme 16, bottom). A green, crystalline compound, which is extremely air-sensitive and readily loses solvent, can be isolated. Reaction of the "green complex" with N_2 leads to an interesting dinitrogen compound.[80] The N–N distance of the complexed nitrogen is 1.525(4) Å, which is in agreement with an N–N single bond. This means that a four-electron reduction has taken place. Samarium is formally present as Sm^{III} since the magnetic moment of the whole complex is 2.72 μ_B.

Reactions of lithiated, silyl-substituted aminopyridines with YCl_3 also lead to "ate" complexes such as **18** (Scheme 17). Such compounds are reactive enough to react with the halogenides of late transition metals by salt elimination. In this way, ligand transfers also allowed the synthesis of the first homoleptic amidopalladium complex **19**.[81] The increase in the efficiency with a cyclic or catalytic reaction procedure in hexane is of interest (Scheme 17). The synthetic principle cited here is a new variant for the preparation of amido complexes of late transition metals where heterodinuclear compounds can be regarded as intermediates of ligand transfer reactions. Ligand transfer can be prevented by the use of bisaminopyridinato ligands, and new dinuclear complexes are accessible by this procedure (Scheme 18).[82]

In this way the spatial requirements for a metal–metal communication between lanthanoid and metals of the platinum group can be acquired.

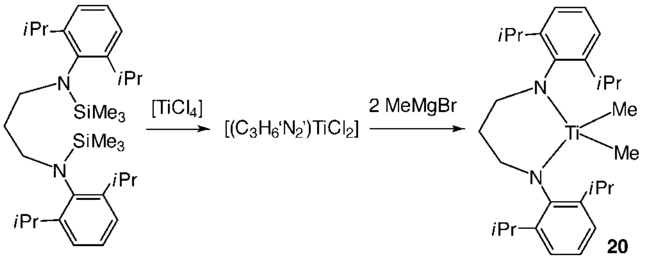
3. Titanium, Zirconium, and Hafnium

3.1. "Living" Olefin Polymerization

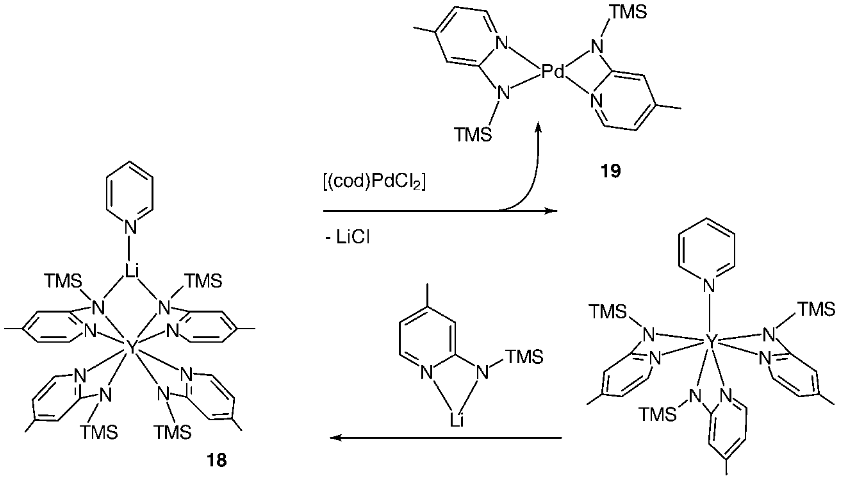


Scheme 18. Heterobinuclear complexes with bisaminopyridinato ligands.

In contrast to the amido chemistry of the lanthanoids, in the chemistry of Group 4 metals emphasis is not placed upon the analogy to metallocenes, but may be derived successfully from it, as, for example, in the development of olefin polymerization catalysts based on amido complexes. Sterically demanding bis(amido) chelate ligands, whose dichlorotitanium complexes are accessible in good yields by Me_3SiCl elimination (Scheme 19), show very high activities in the polymerization of 1-hexene if they are activated by Lewis acid cocatalysts.[83]



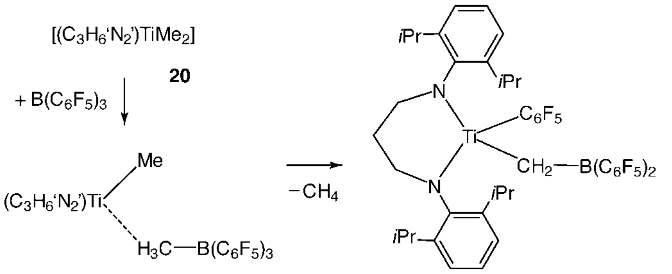
Scheme 19. Bis(amido) complexes with sterically demanding 2,6-diisopropylaryl substituents.



Scheme 17. Yttrate-mediated aminopyridine ligand transfer. cod = 1,5-cyclooctadiene; TMS = Me_3Si.

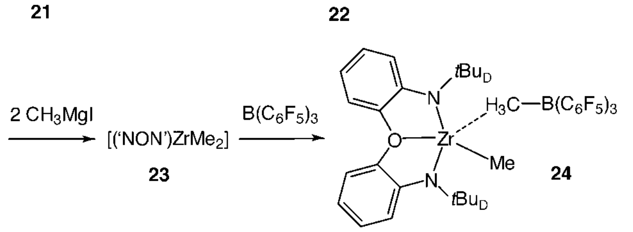
The activity of **20** after activation with MAO at 68 °C in pure hexene (polymerization time 0.5 min) also appears extraordinary in comparison to previously described Cp-free, homogeneous catalyst systems with metals of this triad.[84, 85] However, the activity is significantly lower when carried out at room temperature. If the polymerization is carried out in toluene as solvent the activity falls dramatically, which is explained by π coordination with the solvent.[85] The narrow molecular weight distribution suggests the presence of a uniformly active catalyst species. Particularly interesting is the observation that olefinic resonances in the NMR spectra of polymers have not been discovered. This means that chain transfer to aluminum is the dominant chain termination, not β-hydrogen transfer. If alkylaluminum cocatalysts are omitted chain termination can be prevented, which leads to "living" olefin polymerization. Such polymerizations are of special interest for they allow the synthesis of polymers with defined block structures.[86] There have been only isolated reports of catalyst systems which promote "living" olefin polymerization.[25g, 87, 88]

An equimolar ratio of **20** and $B(C_6F_5)_3$ catalyses the "living", aspecific polymerization of α-olefins at room temperature, which has been confirmed by a linear relationship between the molecular weight M_n and time.[89] If **20** is allowed to react stoichiometrically with $B(C_6F_5)_3$ in pentane (Scheme 20) methane elimination occurs with the formation of an aryl complex inactive in polymerizations, which is indicative of possible catalyst deactivation steps.[90] Studies on the mechanism of α-olefin insertion (1,2- or 2,1-insertion) with **20** ($Me = {}^{13}CH_3$), $B(C_6F_5)_3$, and 10 equivalents of 1-hexene as well as quenching of the unlabeled system with I_2 suggested a preferred 1,2-insertion. The resulting polymers were compared with model compounds such as 3-methylhexane and 2-iodobutane or 1-iodo-2-methylpropane by ^1H and ^{13}C NMR spectroscopy.[91]



Scheme 20. Catalyst deactivation steps in the $[(C_3H_6N_2)TiMe_2]$ and $B(C_6F_5)_3$ system.

The work of Schrock et al.[92] confirms that not only the system developed by McConville et al.[89] induced the "living" polymerization of higher olefins. The reaction of the tridentate diamido ligand precursor **21** with $[Zr(NMe_2)_4]$ leads to **22** by amine elimination (Scheme 21). Subsequent "iodination" can be carried out with CH_3I, and alkylation by reaction with two equivalents of CH_3MgI. If **23** is allowed to react with $B(C_6F_5)_3$ a cationic zirconium complex **24** is formed which polymerizes ethylene. The X-ray structure analysis of **24** shows an anion–cation separation of 2.487(12) Å. This distance is approximately 0.1 Å shorter than in structures of comparable metallocene compounds.



Scheme 21. Partial abstraction of a methyl group by $B(C_6H_5)_3$ in [('NON')Zr] complexes.

A possible cause could be the lower spatial shielding of the 'NON' ligand ('NON' = $O[2\text{-}C_6H_4N\{C(CH_3)(CD_3)_2\}]_2$ dianion; $tBu_D = C(CH_3)(CD_3)_2$). The reaction of **23** with $[PhNMe_2H][B(C_6F_5)_4]$ leads to a cationic zirconium complex which polymerizes 1-hexene as well as ethylene. A linear relationship between the catalyst/1-hexene ratio and the mean molecular weight ($M_w/M_n < 1/1$) confirms the "living" character of the 1-hexene polymerization. NMR studies showed a preferred 1,2-insertion for the $[(\text{'NON'})ZrR]^+$ ion.[93]

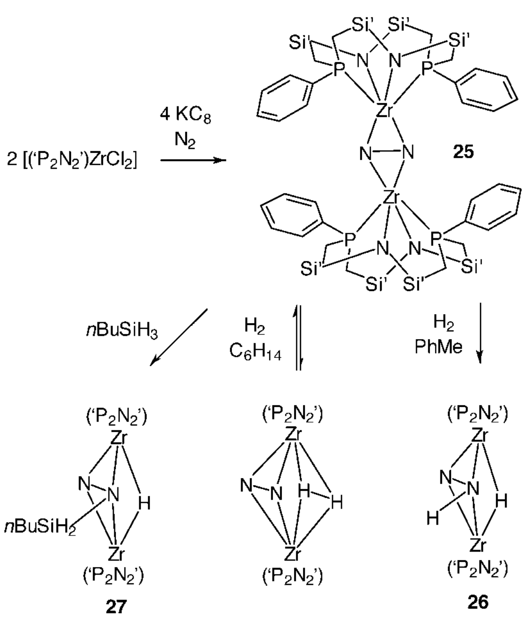
Unlike the metallocenes of Group 4, the amido ligands appear to suppress β-elimination as the chain termination step more effectively. In this way alkene polymerization can be "living" and efficient. With the extensive choice of available amido ligands, in addition to polymer modification, as is realizable with metallocenes,[94] it is also possible to synthesize different polymer blocks of defined length. Amidometal complexes which could polymerize α-olefins living and isotactically have not yet been described, although a rich selection of diamines with a C_2-symmetrical backbone are commercially available.

3.2. Reactions of Complexed Dinitrogen with Hydrogen

"The fixation of dinitrogen is one of the great discoveries awaiting the ingenuity of chemists." This statement by William Crookes (1898)[95] underlines the significance of the Haber–Bosch process for the manufacture of ammonia from N_2 and H_2 discovered shortly thereafter. Whereas the coordination chemistry of the chemically unreactive dinitrogen has been extensively investigated,[96] little is known about the reaction of both molecules (N_2 and H_2) with each other within the coordination sphere of a metal complex.

The use of macrocyclic diamidodiphosphane ligands allows a detailed investigation of reactions of complexed dinitrogen with hydrogen.[97] Hitherto, replacement of the bound nitrogen molecule has been mainly observed in the reactions of N_2 complexes with hydrogen.[98–100] For example, $[(Cp_2^*ZrN_2)_2(\mu\text{-}N_2)]$ reacts irreversibly with H_2 to form $[Cp_2^*ZrH_2]$.[100] Amidophosphane-stabilized[14] zirconium complexes are highly suitable for the activation of nitrogen. The unusual characteristic here is the μ-η^2 bonding mode of the N_2 ligand (*side-on* coordination).[101] Analogously, the use of macrocyclic diamidophosphane ligands[102] also leads to a *side-on* bound dinitrogen zirconium complex **25** (Scheme 22).

The X-ray structural analysis of **25** shows a N–N distance of 1.43(1) Å, similar to that of hydrazine (1.47 Å).[103] The presence of a fourfold deprotonated hydrazine ligand is also in agreement with the four-electron reduction which accompanied the formation of **25**. If the dark blue complex **25** is allowed to react with H_2 in toluene a color change to yellow-orange takes place. According to extensive NMR spectroscopic investigations a solution of **26** is formed. Recrystallization of **26** from hexane gave a compound whose structure does not agree with these NMR data, but is a (μ-η^2-N_2)-

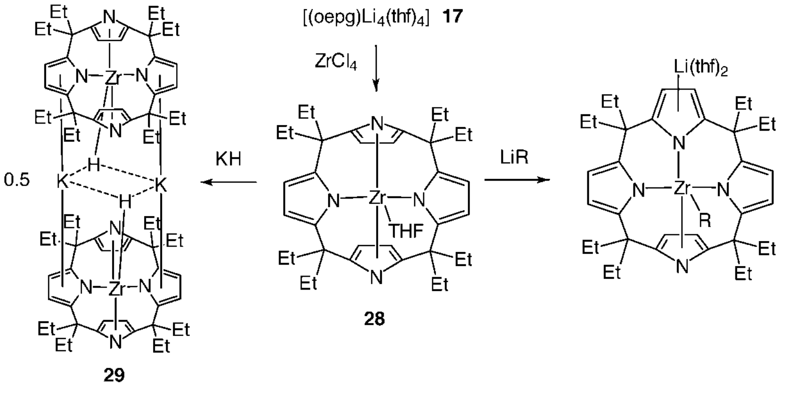


Scheme 22. Reactions of complexed N_2 with H_2 (Si' = Me_2Si).

(μ-η-H_2) complex according to X-ray structural analysis (Scheme 22). The reaction of **25** with n-butylsilane leads to **27**, a compound analogous to that of complex **26** detected in solution. The similarity of the reaction behavior of the H–H and Si–H bond could be helpful in the explanation of this analogy.[104]

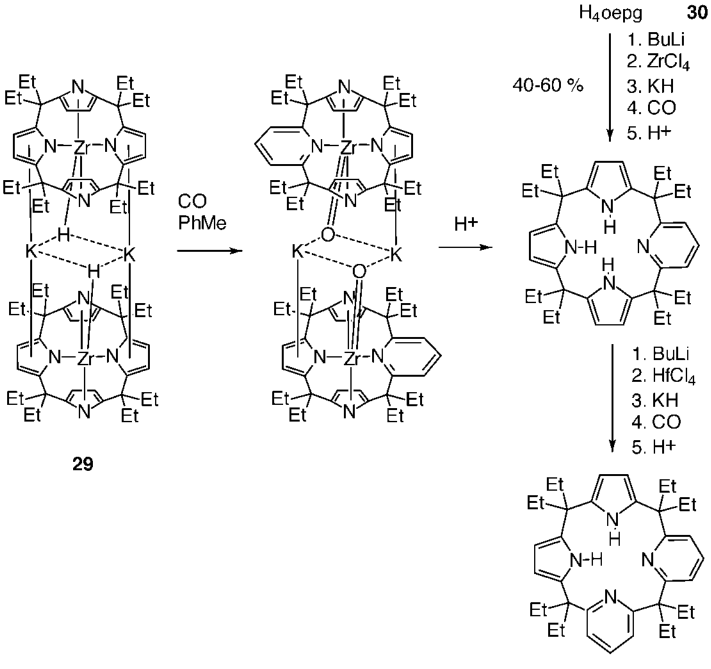
3.3. Modification at and with Porphyrinogen Ligands

Chemical modifications of porphyrinogens by the combined use of metals of Group 4 and the alkali metals are interesting. In this way novel macrocycles whose preparation was hitherto not possible by classical organic methods are now efficiently accessible preparatively. Porphyrinogens are starting materials or intermediates in the chemical and biochemical synthesis of porphyrins, as they are spontaneously oxidized to the corresponding porphyrin with the elimination of H_2 when H atoms are present as substituents in the *meso* positions.[105] Stable porphyrinogens are obtained by dialkyl substitution, as was demonstrated by Baeyer in 1886.[106] The reaction of **17** with $ZrCl_4$ leads to **28** (Scheme 23).[107]



Scheme 23. Activation of KH and alkyllithium complexes at [(oepg)Zr] complexes (R = alkyl, aryl, and allyl substituents).

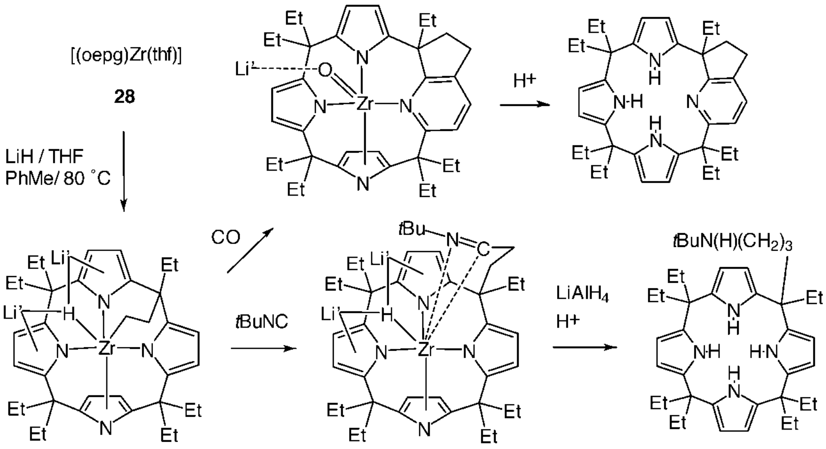
The (σ,σ,$\eta^5\eta^5$) bonding mode of the oepg ligands (oepg = octaethylphorphyrinogen tetraanion) is in the case of zirconium only slightly energetically more favorable relative to the (σ,σ,σ,σ) bond isomer.[108] Compound **28** appears to be an unreactive compound since it is coordinatively and electronically saturated. In reactions with ketones, however, zirconium-supported cleavage of the porphyrinogen framework takes place.[109] If **28** is allowed to react with LiR (R = alkyl, aryl, allyl) or KH, highly reactive bimetallic alkyl or hydrido complexes are formed (Scheme 23). The reactivity of this class of compounds is demonstrated by the insertion reactions into the bimetallically activated alkyl or hydrido functions (Scheme 24). Thus, for example, terminal olefins, isocyanides, and alkynes are inserted.[110] Particularly interesting is the reaction of **29** with carbon monoxide, the CO insertion reaction.[111] This is formally a conversion of a pyrrole ring of the oepg ligand into the pyridine fragment and thus the formation of the next highest homologue.[112] At the end, the modified ligand can be cleaved by hydrolysis. If **30** is allowed to react in an analogous sequence with four equivalents of BuLi, $ZrCl_4$, KH, CO, the simple pyridine-modified, protonated oepg ligand is obtained after hydrolytic workup. The total reaction yield is 40–60%. A subsequent, analogous transformation (BuLi, $HfCl_4$, KH, hydrolysis) leads to the doubly pyridine-modified, protonated oepg ligand (Scheme 24).



Scheme 24. Selective and sequential ring modifications at oepg ligands.

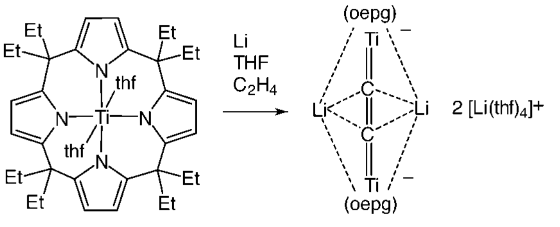
These modifications of the porphyrinogenic skeleton are not only a chemical curiosity, they are also suitable for the efficient preparation of novel, macrocyclic compounds and open up the way to artificial porphyrins. In addition to the modification of the ring system of the oepg ligands, the ligand periphery, in effect an ethyl substituent, can also be modified selectively. A combined transformation rearranges the ring system and the ligand periphery.[113] The reaction of **28** with LiH in the presence of one equivalent of THF in toluene at 80 °C leads, in analogy to **29**, to the formation of a zirconium–lithium hydrido complex, which by H_2 elimination and C–H activation coordinates an ethyl group of the oepg ligand periphery (Scheme 25).

Functionalization of the ligand periphery is carried out by isocyanide insertion. The thus formed imine coordinates at zirconium and can be reduced to the amine with $LiAlH_4$. Following hydrolytic workup, a macrocycle modified at an ethyl substituent is then formed. A combined transformation of the ligand environment and the heterocyclic system occurs analogously by CO insertion and subsequent hydrolytic workup (Scheme 25). The success of the unusual transformation is determined by two important properties of the oepg complexes. First, such compounds can coordinate cations in the electron-rich ligand periphery and thus act as carriers of reactive organometallic functionality. Here the considerable difference in the π-bond strength of the pyrrole units in porphyrinogens and in the less basic porphyrins, for which π complexation of alkali metal ions is untypical, must be stressed. Second, the oepg ligands are very flexible and consequently permit C–H bond activation of the ligand periphery.



Scheme 25. Modifications at the ring system and/or the oepg ligand periphery (Li′ = Li(thf)).

In addition to modifications of the ligands of the oepg complexes, such zirconium compounds can also act as an inert organic matrix. Thus the incorporation of Li_4H_4 and Li_2O by π-pyrrole complexation of the lithium ions through [(oepg)Zr] fragments is possible. In this way remarkable sandwich structures are formed.[114] The zirconium complex thus facilitates the "solubility" of the ionic compounds in a nonpolar organic phase. One interesting olefin activation reaction is the reduction of **31** with lithium in the presence of ethylene. (Scheme 26).[115] It appears remarkable that the oepg ligand is inert in spite of the drastic conditions. Unlike **28**, **31** exists as a (σ,σ,σ,σ) complex and is saturated coordinatively by two additional THF ligands. The reduction product is a dimetallacumulene.[116] Examples of metal-carbide systems with a C_2 bridge are rare and were hitherto mainly synthesized from alkynes.[117]

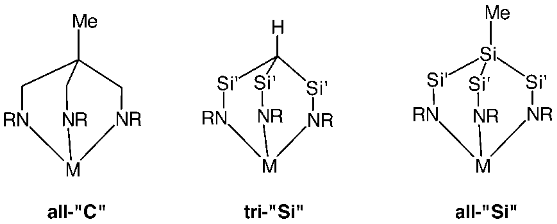


31

Scheme 26. A dititanacumulene from ethylene.

3.4. Polar Metal–Metal Bonds

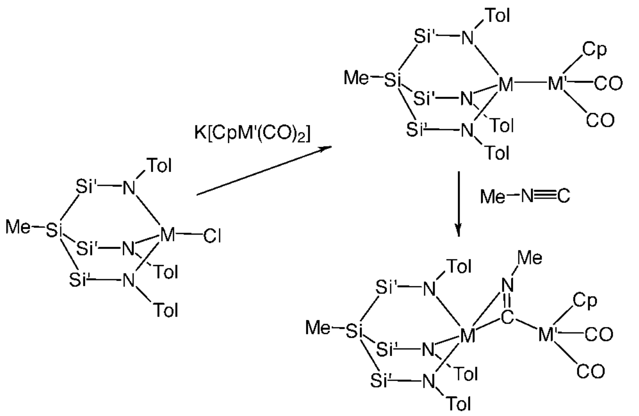
Systematic investigations into the reactivity of polar metal–metal bonds between metals of Group 4 and late transition metals were for a long time limited by the intrinsic instability of such compounds.[118] Moreover, the large number of different ligands bound to early transition metals made a comparison of the reactivity of such systems impossible.[119] As a consequence of this the work of Gade et al. was aimed at the development of a ligand system which prevented the self-destruction of the dinuclear compounds.[120] In this way the metal–metal bond can be kinetically stabilized so that its reactivity towards a large number of substrates can be specifically investigated. The key step is the use of a new class of tripodal, trianionic ligands (Scheme 27). The stability of these ligand–metal bonds and the steric protection of the reaction centers can be modified by variation of the substituent R. The variable geometry of the ligand backbone, all-"C",[120, 121] tri-"Si",[122, 123] and all-"Si",[123, 124] allows the reaction to be optimized to the different size of the metals of the titanium triad.



Scheme 27. Tripodal trisamido ligands with variable backbone (M = metal of Group 4; R = silyl, aryl or alkyl; Si′ = Me_2Si).

The reactions of monochloro complexes of titanium, zirconium, and hafnium stabilized by such tripod ligands with $K[(C_5H_5)M'(CO)_2]$ (M′ = Fe, Ru) gave heterodinuclear complexes with unbridged metal–metal bonds (Scheme 28).[125] These dinuclear compounds react with, for example, methylisocyanide with insertion and are examples of a bimetallic variant of α-addition.[126]

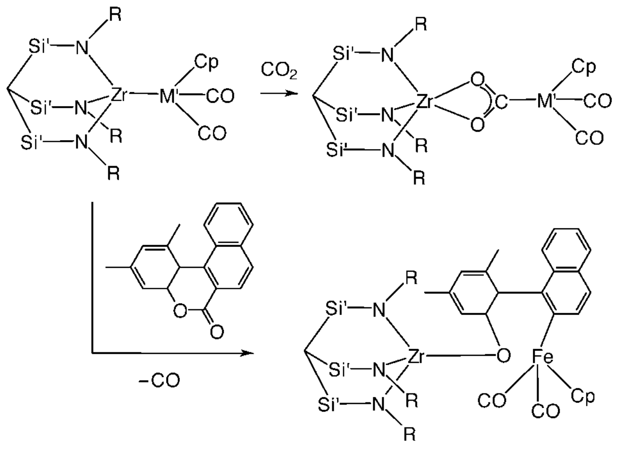
The general applicability of the concept of stabilization of bonds between metals of Group 4 and late transition metals by the use of multidentate amido ligands has also been



Scheme 28. Insertion of methyl isocyanide into polar metal–metal bonds (M = Ti, Zr, Hf; M' = Fe, Ru; Si' = Me_2Si).

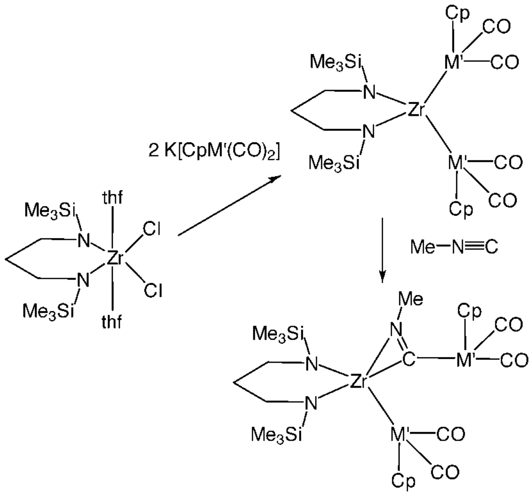
demonstrated by the synthesis of stable Ti–Co complexes.[127] The nature of the metal–metal bond between metals of the titanium triad and the late transition metals is to be regarded primarily as a classical σ bond. However, Fenske–Hall calculations on the system $[HC(CH_2NH)_3Ti{-}Fe(CO)_2Cp]$ also confirm π-donor–acceptor interactions which contribute to the stabilization of the metal–metal bond.[128] This partial multiple bond character is stronger than in the corresponding Sn–Fe bonds and is favored by the energetically low-lying π-acceptor orbitals on the titanium center. Additional π-bond contributions are in agreement with a restricted rotation of both complex fragments around the vector of the metal–metal bond.[125] Rotation barriers, however, can also be dictated by the steric interactions of the ligand peripheries. A good qualitative description of the bond polarity in unbridged Ti–Co or Zr–Co bimetal complexes[129] is also possible by Bader analysis of the electron density (Baders AIM)[130] and electron localization functions (ELF).[131] The high partial charges of the complex fragments emphasize the strong polar character of the Ti–Co bond. With polycyclic amido ligands the bimetal complexes are not only kinetically inert, but are also thermodynamically more stable.

An interesting bimetallic activation of poorly reactive molecules occurs in the reaction of Zr–M' bimetal complexes (M' = Fe, Ru) with heteroallenes such as carbon dioxide (Scheme 29, top).[132] Both the bonding mode and the bimetallic activation are unusual for carbon dioxide.[133] The reaction of Zr–Fe bimetal complexes with lactones leads to ring opening with subsequent decarbonylation in which the lactone is simultaneously and thus cooperatively activated by both metal centers (Scheme 29, bottom).[134]



Scheme 29. Cooperative reactivity of heterobinuclear complexes (M' = Fe, Ru; R = C_6H_4F; Si' = Me_2Si).

If bis(amido) chelate ligands are used in place of the tripod ligands there is the possibility to use both remaining chloro ligands for the preparation of trinuclear complexes (Scheme 30).[135] Analogous examples of metallocene-stabilized compounds[119b,c] show an extreme instability, and reactions with the Cp ligands of the zirconium fragment were observed. The introduction of the two $[M'(C_5H_5)(CO)]$ units (M' = Fe, Ru) can be carried out sequentially. It is not possible in this way, however, to prepare mixed Zr–Fe–Ru complexes with different potassium salts. A selective reaction with one equivalent of methyl isocyanide is possible.



Scheme 30. Heterobinuclear complexes and selective insertion of methyl isocyanide (M' = Fe, Ru).

Unbridged polar metal–metal bonds may be kinetically and thermodynamically stabilized with suitable amido ligands and thus allow insights into details of the reactivity of such compounds and into cooperative activation steps.

3.5. C–H Activation at d^0 Metal Centers

C–H activation at d^0 metal centers can be investigated very effectively with complexes of the type $[(t\mathrm{Bu}_3\mathrm{SiNH})_3\mathrm{MR}]$ (M = Ti, Zr; R = alkyl, aryl) since these complex compounds eliminate hydrocarbons reversibly.[136] The C–H activation mediated by transition metal complexes is one of the most fascinating sectors of organometallic chemistry.[137, 138] Numerous electronically unsaturated metal complexes can activate the C–H bond in different ways:

1) oxidative addition of a late transition metal[139, 140]

$$[L_nM] + RH \rightleftharpoons [L_n(H)MR]$$

2) heterolytic activation by late transition metals in polar media[141–143]

$$[L_nM] + RH \rightleftharpoons [L_nMR]^-H^+$$

3) σ-bond metathesis (early [25a, 144, 145] and late transition metal complexes[146])

$$[L_nMR] + R'H \rightleftharpoons [L_nMR'RH]$$

4) homolytic cleavage by UV-excited mercury atoms (Hg*)[147]

$$Hg^* + RH \rightleftharpoons Hg^* + R^\bullet + H^\bullet$$

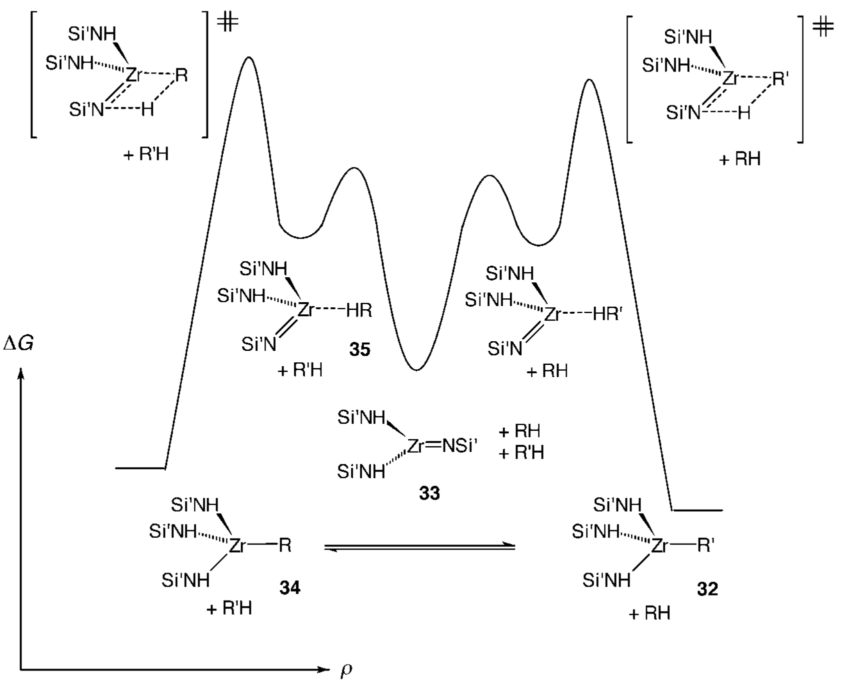
5) activation at porphyrin-Rh^{II} complexes[148]

$$2[L_nRh^{II}] + RH \rightleftharpoons [L_nRhR] + [L_nRhH]$$

6) 1,2-additions at M=X systems (X = O,[149] NR′,[150, 136] and CRR′[151]

$$[L_nM{=}X] + RH \rightleftharpoons [L_nM(R)XH] \qquad (X = O, N, C)$$

The possibilities for C–H activation listed here can be divided still further in principal into radical mechanisms without intermediate R–H bond interaction and concerted processes which involve such an interaction. The activation of C–H bonds at d^0 metal imido complexes belong to the latter category (Scheme 31).[152] Compounds of type **34** can be prepared by three synthetic routes: salt elimination reactions with alkyllithium or Grignard reagents, the addition of unsaturated substrates to the metal hydride, and C–H bond activation. In the case of C–H activation the intermediate **33** is generated from **32** by thermal 1,2-R′–H elimination, and the subsequent 1,2-R–H addition gives **34**. Kinetic investigations on 1,2-R–H elimination and addition give insights into the mechanism of this C–H activation (Scheme 31). The isolation and characterization of the THF complex of **33** confirms the existence of such an intermediate. Studies with deuterated compounds (primary kinetic isotope effect) gave ratios of rate constants of 1,2-R–H and 1,2-R–D elimination which comply with an almost linear H atom transfer[153] including a concerted C–H bond formation/N–H bond cleavage process with formation of a four-membered transition state. The existence of a four-membered transition state with a slightly deformed methyl group is confirmed by measurement of a secondary kinetic isotope effect. A linear relationship between $\Delta G^{\ddagger}$ of the 1,2-RH elimination step and the RH proton affinities verifies the existence of **35** as intermediate in the elimination and activation steps. If the bonding of an alkane or arene to a d^0 center is considered in analogy to the deprotonation of an RH unit, then such a correlation should arise. The calculation of the total energy of the hypothetical molecule $[(H_2N)_2HN{=}Zr(\eta^2\text{-}CH_4)]$ relative to $[(H_2N)_2Zr{=}NH] + CH_4$ confirms a considerable energy gain by methane coordination.[154] Also of interest is the comparison with d^8 systems, where alkane complexes are considered intermediates in the activation of C–H bonds.[155] Recently, such an intermediate could be directly established.[156] The course of the 1,2-RH elimination and activation is summarized in Scheme 31. Current investigations of C–H bond activation in homogeneous systems are highly diverse.[157] To allow technical application of C–H bond activation, catalytic process management must be coupled with the functionalization of substrates. The radical oxidation of hydrocarbons is the most important application, where selective transformations represent a problem. The results published by Wolczanski et al.[152] give an insight into the mechanistic details. Investigations on the selectivity of C–H activation at titanium d^0 complexes have been reported recently, where alkoxy ligands were used to stabilize the high oxidation states.[158]

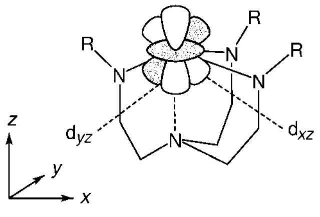


Scheme 31. C–H activation by reversible 1,2-R–H elimination starting from $[(tBu_3SiNH)_3ZrR]$ (Si′ = tBu_3Si; R = alkyl substituent).

4. Vanadium, Niobium, and Tantalum

4.1. Substrate Activation at "Half-Naked" Complexes

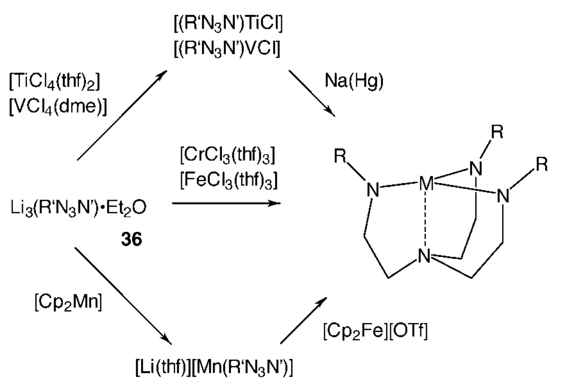
Trisamido amine ligands[17, 18] coordinate transition metals in a tetradentate manner such that a sterically shielded C_3-symmetric reaction center is formed in which principally three orbitals are concentrated for substrate activation (Scheme 32). Two of



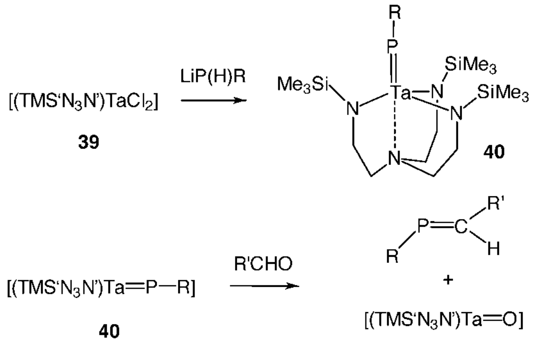
Scheme 32. Orbital relationships of the trisamidoamine complex fragment.

these can be regarded as π-type orbitals (≈ d_{xz} and d_{yz}) and one as a σ-type orbital (d_{z^2}).[18]

In trigonal-monopyrimidal M^{III} complexes of the type [(*t*Bu(Me)$_2$Si'N$_3$N')M] (M = Ti, V, Cr, Mn, Fe; *t*Bu(Me)$_2$-Si'N$_3$N' = [{(H$_3$C)$_3$C}(H$_3$C)$_2$SiN(CH$_2$)$_2$]$_3$N trianion), which can be synthesized as illustrated in Scheme 33, this "reactive pocket" is empty, and in this way "half-naked" transition metal complexes can be stabilized.[159] Of interest is the observation that the direct salt metathesis reaction between **36** and VCl$_3$ or TiCl$_3$ adducts does not lead to the desired end product. The titanium complex **37** binds CO reversibly, which is unusual for d^1 complexes.[160] The reactive pocket of the related **38** is set up for the oxidative addition of substrates. Thus, **38** reacts with aziridines, imines, or azides to form imido complexes, with propylene oxide, elemental selenium or sulfur, and TePMe$_3$ to form the corresponding chalcogenide complexes [(TMS'N$_3$N')V=X] (TMS'N$_3$N' = [(H$_3$C)$_3$SiN(CH$_2$)$_2$]$_3$ trianion; X = O, S, Se, Te).[161] Analogous tantalum compounds may be obtained by the reactions of **39** with one equivalent of [(Me$_3$Si)$_3$SiELi(thf)$_2$] (E = Se, Te) (Scheme 34).[162] There is currently considerable interest in terminal chalcogenides, particularly the higher homologues, with regard to the synthesis of semiconductors.[163] The reaction of **39** with LiPHR affords phosphanidene tantalum(v) complexes such as **40** (R = Ph, Cy, and *t*Bu), which react smoothly with aldehydes with the formation of phosphaalkenes (Scheme 34).

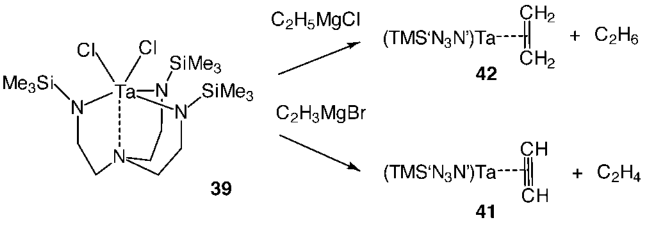


Scheme 33. Synthesis of "half-naked" transition metal complexes (R = *t*Bu(Me)$_2$Si, M = Ti (**37**), V, Cr, Mn; R = Me$_3$Si, M = V (**38**)). R'N$_3$N' = [RN(CH$_2$)$_2$]$_3$N trianion; dme = 1,2-dimethoxyethane; Tf = F$_3$CSO$_2$.



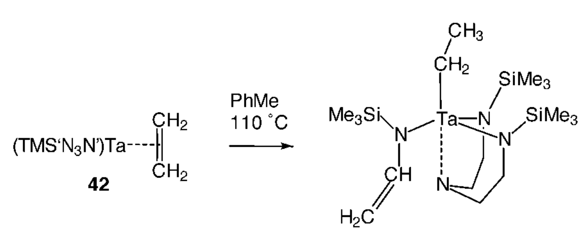
Scheme 34. Phosphinidenetantalum(v) complexes as phospha-Wittig reagents (R = Ph, *t*Bu; R' = *t*Bu).

Phosphaalkenes[164] which are stabilized by conjugation[165] or by sterically demanding substituents[166] can be prepared by silyl migration[165] or dehalogenation.[166] Phosphaalkenes bound to a complex fragment are accessible by phospha-Wittig reactions.[167] Scheme 34 outlines a new route for the preparation of phosphaalkenes. Of interest is the possibility to modify substituent R.[168] In the first step "[(TMS'N$_3$N')Ta=PLi]" is generated in the presence of an excess of lithium and is then allowed to react selectively at low temperatures with R'X (X = Cl, Br; R' = Me, *n*Bu, SiMe$_3$, SiMe$_3$Ph). The reactions of **39** with alkyllithium or Grignard reagents are unusual.[169] In the case of MeLi a bisalkyl complex can be isolated, and the reaction with C$_6$H$_5$CH$_2$MgCl affords an alkylidene complex by α-elimination.[170] Analogously, lithium amides react smoothly to form the corresponding imido complex. Ethyl or vinyl Grignard reagents react with **39** to form the ethylene or acetylene complex, respectively (Scheme 35). Ethane or ethylene are eliminated simultaneously.

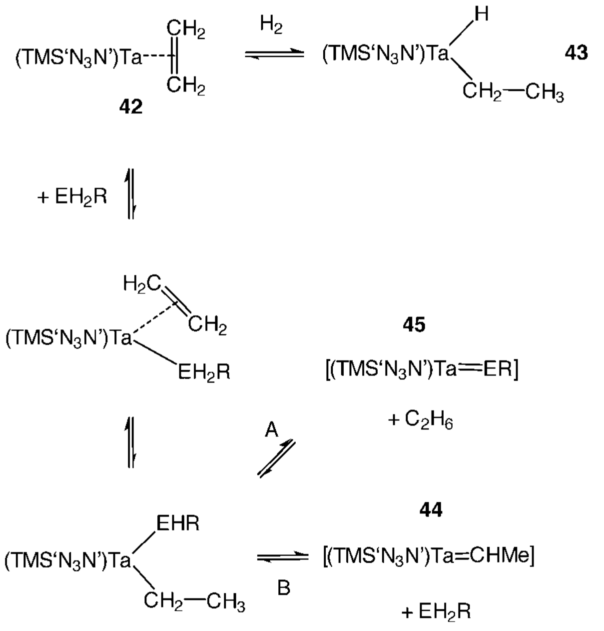


Scheme 35. Ethylene- and acetylenetantalum complexes by ethylene or acetylene elimination.

Unlike **41**, which is very stable and unreactive, **42** decomposes in solution (toluene) at room temperature by ligand decomposition in a first-order reaction (Scheme 36). Remarkably, there is no Si–N bond cleavage. Compound **42** is an excellent starting material for the preparation of a reactive [(TMS'N$_3$N')Ta] complex fragment and reacts reversibly, for example, with hydrogen to form **43**. A catalytic amount of phenylphosphane converts **42** into **44** (Scheme 37), a stoichiometric amount of aniline gives the corresponding imido complex, and trimethylsilylarsane an unstable arsinidene complex analogous to **45**. The mechanism of the reaction of **42** with amines, phosphanes, and arsanes is summarized in Scheme 37. Reaction path A is not observed for E = P, and a catalytic amount of phosphane suffices to give a carbene complex selectively. Reaction path A is preferred if E = N or As.



Scheme 36. Possible decomposition processes of triamidoamine ligands.



Scheme 37. Suggested mechanism for the reaction of [(TMS'N$_3$N')Ta(C$_2$H$_4$)] with EH$_2$R (E = N, P, As).

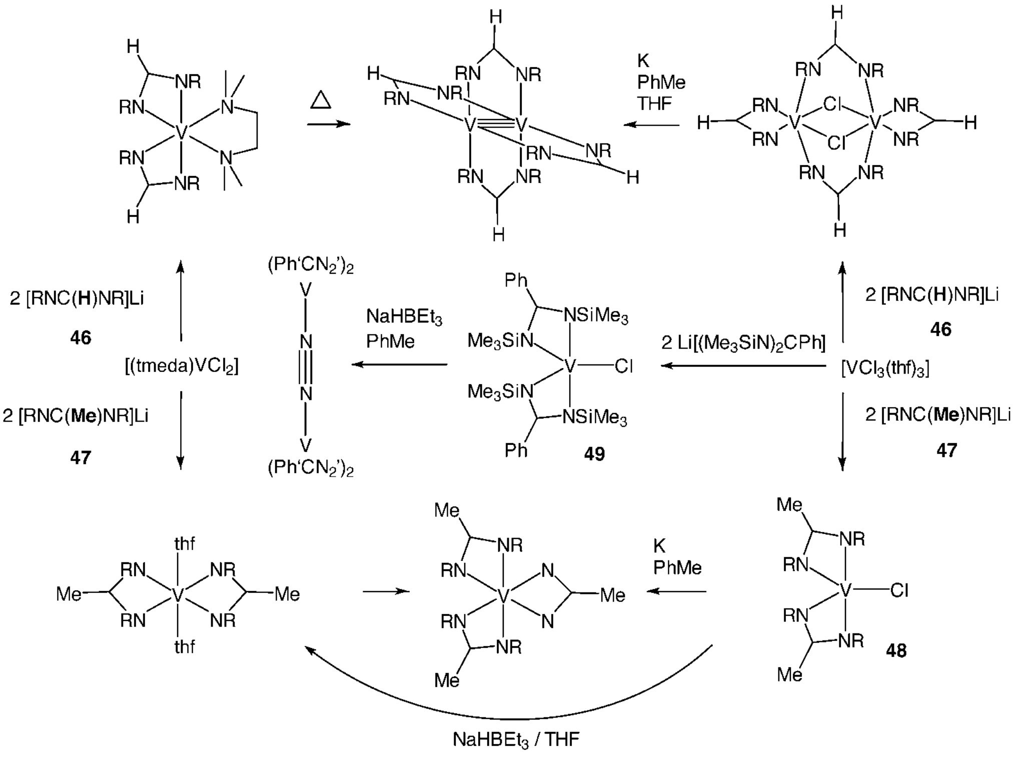
Similar imido, phosphinidene and arsinidine complexes were published recently by Wolczanski et al. with the use of the tri(silyloxy)tantalum complex core.[171]

4.2. The Chemistry of Low-Valent Vanadium Complexes

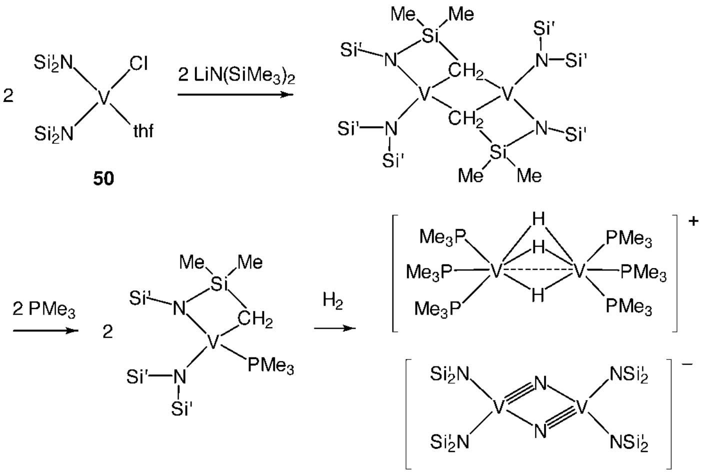
Disproportionation and electron transfer reactions are the most frequently observed reaction pathways when complex compounds whose metals are in an unstable oxidation state decompose. A possible strategy to prevent undesired disproportionation reactions is to embed the metal center into an inert organic matrix. Few possibilities then exist for the molecular ensemble to rearrange and thus modify the oxidation state. This procedure is based on biochemical systems, and was used in the past to isolate transition metal complexes in unusual oxidation states.[172] Sterically demanding, monodentate silyl or alkylamides or bidentate ligands such as amidinates are suitable for the stabilization of low-valent vanadium complexes. The reactivity of vanadium(II) amidinato complexes is only poorly understood since even the smallest change in the steric demand of this ligand results in the preference for different reaction channels. One fascinating area is the chemistry of vanadium(II) complexes since such compounds can fix N$_2$[173] and produce short V–V triple bonds.[174] Vanadium complexes are also interesting as olefin polymerization catalysts.[84] The products of the reactions of **46** and **47** with [(tmeda)VCl$_2$] or [VCl$_3$(thf)$_3$] differ drastically from each other, although the steric differences between the ligands are slight (Scheme 38).[175]

If instead of **48** the analogous complex **49** is reduced with NaHBEt$_3$ in toluene a dinitrogen complex is formed (Scheme 38).[176] Alkyl- and allylvanadium(III) complexes may be obtained in good yields by the reaction of **49** with alkyl or allyl Grignard reagents.[177] These compounds thus are characterized by an exceptionally high thermal stability.

The classical bis(trimethylsilyl)amido ligand, which was introduced into vanadium chemistry by Bradley et al.,[178] is not inert and tends towards σ-bond metathesis with the formation of a vanadacyclobutane ring (Scheme 39, top).[179] The V–C bond formed is very reactive.[180] Thus, for example, isocyanides,[181] CO, and alkynes are activated or inserted,[179, 182] and pyridine is partially hydrogenated.[182] Particularly noteworthy is the reaction of the vanadacyclobutane with H$_2$ in the presence of PMe$_3$ (Scheme 39, below).[183] The hydrido unit is probably formed by hydrogenolysis of both the V–CH$_2$ and the V–N(SiMe$_3$)$_2$ bonds. The formation of (Me$_3$Si)$_2$NH as by-product supports this. Silane is not found, which supports the supposition that the nitrido ligand of the anion originates from molecular nitrogen which is present during the hydrogenation. Attempts at the isolation of a dinitrogen intermediate have been unsuccessful. Analogous experiments without nitrogen gave only pyrophoric oils whose characterization was difficult due to paramagnetism. The corresponding alkyl complex may be synthesized from

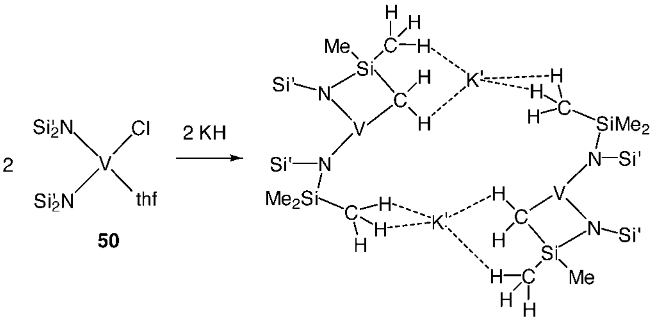


Scheme 38. Reactivity of amidinatovanadium complexes in relationship to the smallest ligand variations.



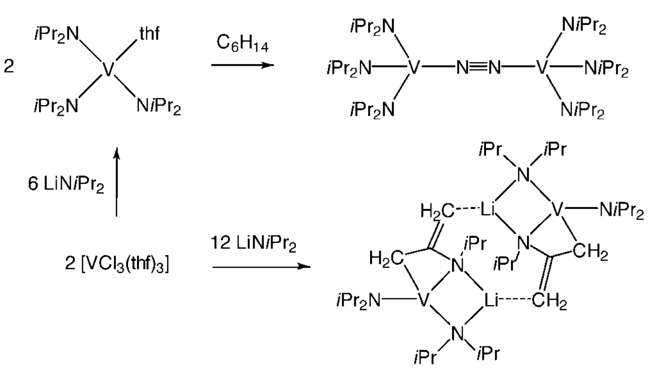
Scheme 39. Reactivity of silylamidovanadium(III) complexes (Si' = SiMe$_3$).

50[184] by reaction with MgMe$_2$.[185] The reactivity of this compound has been systematically and thoroughly investigated.[185, 186] The reaction of **50** with KH is interesting because supramolecular organization occurs through agostic C–H··· potassium interactions with the formation of a V$_2$K$_2$ ensemble (Scheme 40).[187]



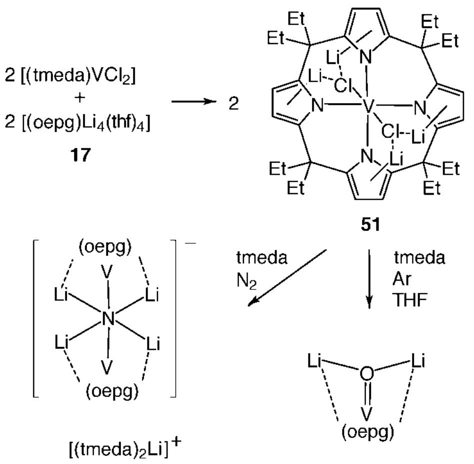
Scheme 40. Supramolecular organization by agostic C–H···potassium interactions (Si' = SiMe$_3$; K' = K(thf)$_2$).

When aryl- and alkylamido ligands are used in place of the (Me$_3$Si)$_2$N anion a vanadium–N$_2$ complex is isolated (Scheme 41).[188] An isostructural Nb–dinitrogen complex can be stabilized by Cy$_2$N ligands.[189] If an excess of lithiated amine (six equivalents) is used in the reaction of [VCl$_3$(thf)$_3$] with LiN*i*Pr$_2$ C–H activation of the amido ligand and generation of a vanadate complex occurs (Scheme 41).



Scheme 41. Reactivity of alkylamidovanadium(III) complexes.

In the reaction of **17** with [VCl$_3$(thf)$_3$] in toluene (room temperature) an inolate complex is formed and THF fragments together with C$_2$H$_6$ are eliminated.[190] The reaction of **17** with [(tmeda)VCl$_2$] gives the highly reactive complex **51** (Scheme 42)[191] in which the vanadium is surrounded octahedrally by four N atoms and two Cl atoms. Complex **51** reacts with N$_2$ in the presence of tmeda to afford nitrido clusters, and with THF in the absence of dinitrogen to give the terminal oxo complex.

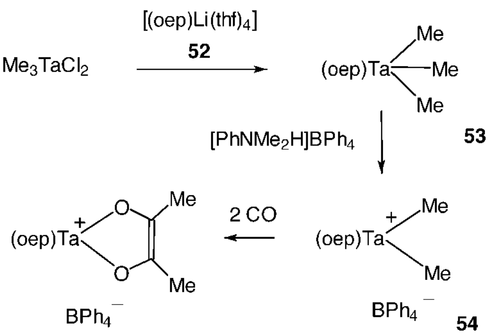


Scheme 42. Reactivity of oepg–vanadium complexes.

It can be generally said that amido complexes of low-valent vanadium are very reactive, amido ligands rarely behave inertly, and the numerous activation reactions are currently poorly understood. One of the main problems appears to be the frequent paramagnetism which makes targeted investigations of the compounds in solution complicated.

4.3. Compounds with Metals in the High Oxidation State and the Analogy to Group 4

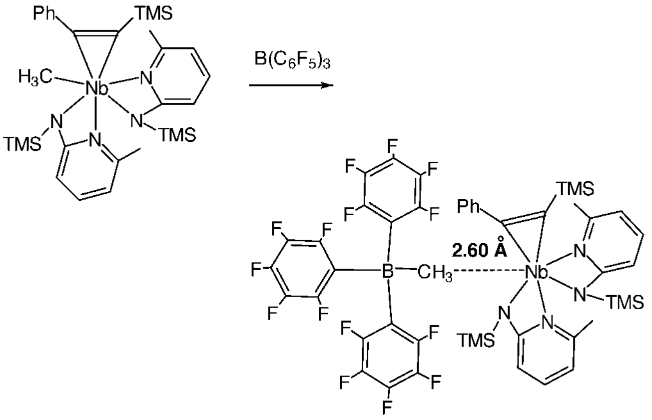
In contrast to vanadium, in the higher homologues of this triad, a tendency towards stabilization of the high oxidation state is observed. Niobium and tantalum compounds, unlike metal complexes of Group 4, have a shadowy existence. Noteworthy is the first ditantalum complex with a Ta–Ta bond which is not stabilized by further bridging ligands.[192] A homobimetal complex with an unbridged Ta–Ta bond is formed in the reaction of TaCl$_5$ with four equivalents of LiNCy$_2$. The metal–metal distance is 2.8484(7) Å. An efficient entry into tantalum–porphyrin chemistry is made possible with Me$_3$TaCl$_2$, which reacts with **52** to form **53** (Scheme 43).[193] In contrast, salt elimination routes with TaCl$_5$ fail. By reaction with [PhMeNH]BPh$_4$ **53** can be converted into **54**, which may be regarded to be a porphyrin analogue of



Scheme 43. CO insertion and coupling at cationic tantalum complexes.

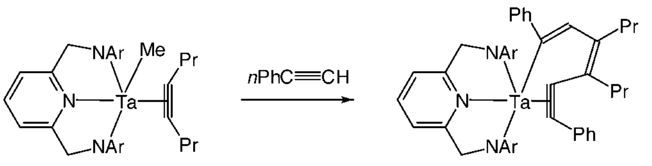
Schrock's dimethyltantalocene cation.[194] Compound **54** does not react with ethylene, acetone, or CO_2, but reacts smoothly with CO to form the enediolate complex. Benzamidinato complexes of tantalum are accessible by analogous routes.[195] The starting material of choice is again Me_3TaCl_2.

Reactions of olefins or even their polymerization are unsuccessful in spite of an analogy to cationic metallocenes of Group 4. The partial abstraction of a methyl group appears to be essential, and succeeds with aminopyridinato and niobium alkyne complexes (Scheme 44).[196] Such compounds polymerize ethylene as "one-component system" and dimerize higher alkenes selectively, for example 1-butene to 2-ethylhexene in the presence of MAO.



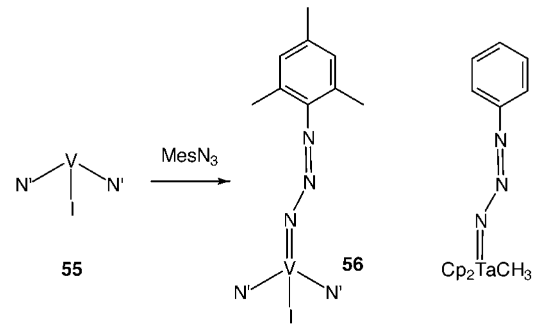
Scheme 44. Partial abstraction of a methyl group in aminopyridine(TMS-Ap)-alkyne complexes of niobium for the generation of active ethylene polymerization systems.

Alkynetantalum complexes with pyridine diamido ligands are suitable model systems to investigate the mechanism of the coordination polymerization of alkynes because successive alkyne insertion and coupling within the coordination sphere of tantalum occurs (Scheme 45).[197]



Scheme 45. Sequential alkyne insertion and coupling (Ar = 2,6-iPr$_2$C$_6$H$_3$).

A standard reaction for the preparation of imido complexes is the reaction of an organic azide with a metal complex which is capable of two-electron oxidation.[198] Although organoazide complexes have been assumed to be intermediates in such reactions, until now none has been completely characterized.[199] The isolation of such a compound (**56**) has been achieved with the vanadium-amido-iodide complex **55** and mesityl azide at low temperatures (Scheme 46).[200] The thuscomplexed $MesN_3$ can be regarded as a diazaenylimido ligand (Scheme 46, left). Compound **56** eliminates N_2 at temperatures above 50 °C and is converted into the corresponding mesitylimido complex. The stabilization of such an intermediate with the $[Cp_2TaCH_3]$ complex fragment was also published (Scheme 46, right).[201]



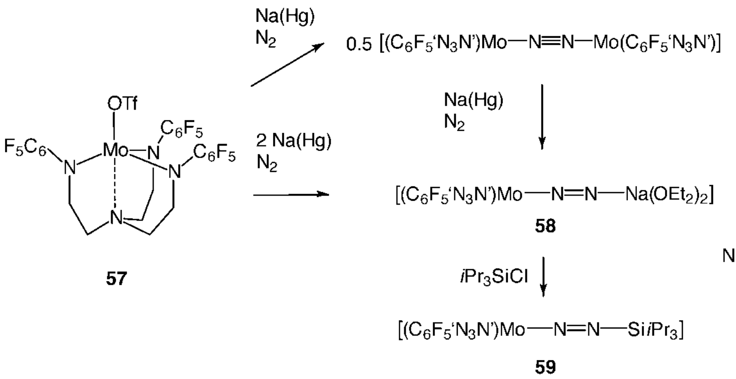
Scheme 46. Diazaenylimido complexes ($N' = N[C(CD_3)_2CH_3][3,5\text{-}(F,Me)C_6H_3]$).

Numerous mixed chalcogenide-chalcogenolate compounds of vanadium have been prepared and comprehensively characterized by Arnold et al. Of note is the systematics of the chemical shifts in the ^{51}V NMR spectra of such amido complexes,[202] which, for example, allow a quantification of electronic differences between terminal oxo, seleno, and telluro ligands.

5. Chromium, Molybdenum, and Tungsten

5.1. Cleavage of the Nitrogen–Nitrogen Triple Bond

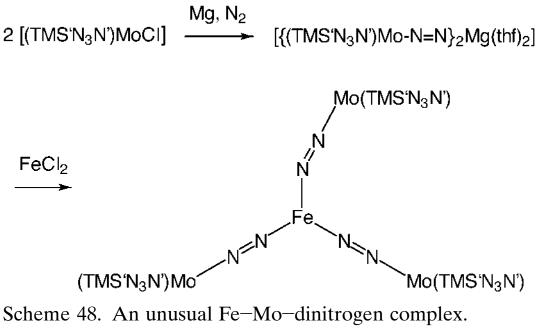
Trisamidoamine complexes of the type $[(C_6F_5\text{'}N_3N')MCl]$ (M = Mo, W; $C_6F_5\text{'}N_3N' = [C_6F_5N(CH_2)_2]_3N$ trianion) may be obtained in good yields by salt elimination reactions in which Et_3N acts as a base.[203] The reaction of the respective molybdenum complex with TMSOTf gives **57**, the reduction of which with one or two equivalents of Na(Hg) in the presence of N_2 leads to dinitrogen complexes (Scheme 47). Of note here is that N_2 can be activated stepwise and then partially reduced. Similarly, partially reduced dinitrogen ligands have already been described for vanadium complexes.[204] The reaction of **58** with iPr$_3$SiCl gives **59** and underlines the nucleophilic character of the β-nitrogen atom of **58** as well as the stability of the $[(C_6F_5\text{'}N_3N')Mo(N_2)]$ fragment. A comparison with the nitrogenase center of *Azotobacter vinelandii* is interesting in this respect. Its X-ray structure analysis[205] allowed for the first time a detailed insight into the structure of such enzymes, and posed the



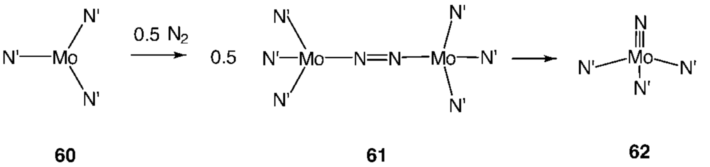
Scheme 47. Binuclear and partially reduced dinitrogen complexes.

question whether dinitrogen activation takes place at the Fe or the Mo center.[206] Here, molybdenum is coordinated with three sulfur atoms, a nitrogen donor, a histidine moiety, and homocitrate. A principle argument proposed against activation at the octahedrally coordinated Mo center is its coordination saturation. However, ligand cleavage, for example by protonation or electron transfer processes, must be considered. If the immediate environment of the molybdenum in the nitrogenase center is regarded as a combination of three anionic sulfide functions and a nitrogen donor. Parallels can be drawn with the $[(C_6F_5\text{‘}N_3N\text{’})Mo]$ fragment, which is stabilized by three anionic amido functions and one nitrogen donor function. This infers that the $[(\text{“}S_3N\text{”})Mo^{III}]$ unit of the enzyme could activate N_2 by homocitrate cleavage, analogous to the $[(C_6F_5\text{‘}N_3N\text{’})Mo]$ fragment. In the latter case it is not homocitrate that is expelled, but the anionic triflate ligand is reductively removed. The question whether N_2 in the $[(C_6F_5\text{‘}N_3N\text{’})Mo]$ system is fixed by a d^3 or d^4 center cannot be answered with certainty. However, activation at the molybdenum(III) fragment appears plausible since a dinitrogen complex is formed in the reaction of $[MoCl_3(thf)_3]$ with “$Li_3(t\text{Bu}Me_2SiNCH_2CH_2)_3N$” in the presence of N_2.[207] Equally interesting in respect to analogies with Fe–Mo nitrogenase centers are the heterodinuclear complexes with a dinitrogen ligand as bridge between the iron and the molybdenum center. A structurally interesting compound of this type is formed by an unusual salt elimination reaction (Scheme 48).[208] Furthermore, the synthesis and structure of a uranium–molybdenum–dinitrogen complex has been recently reported.[209]

The activation and partial reduction of N_2 at the $[(C_6F_5\text{‘}N_3N\text{’})Mo]$ fragment can be carried out, but not, however, cleavage of the N–N triple bond.[210] Compound **60** is suitable for this purpose (Scheme 49)[211] If **60** is exposed to an N_2 atmosphere at −35 °C the violet dinitrogen complex **61** is formed, which with a half-life of 35 min at 30 °C rearranges into two equivalents of the nitrido complex **62**.[212] The same reaction in an $^{15}N_2$ atmosphere give the isotopically labeled **62**, which confirms the source of the nitrido ligand. The thermodynamic driving force of dinitrogen cleavage is the formation of a nitrido complex, as the metal–nitrogen triple bond is the most stable of all metal–ligand bonds.[213] A comprehensive structural characterization of the violet, paramagnetic intermediate **61** or its analogous $^{15}N_2$ complex by EXAFS[214] and Raman spectroscopy together with kinetic data on the conversion to the corresponding nitrido complex gave a detailed insight into the course of the N– bond cleavage.[215] The conversion of **61** into two equivalents of **62** takes place by a first-order reaction. The data of the kinetic isotope effect of the bond cleavage, Mo_2N_2 versus $Mo_2{}^{15}N_2$, confirm that the N–N cleavage is the rate-determining step. Raman spectroscopic studies showed a bond order of two for the N_2 ligand in **61**, and EXAFS measurements showed a linear Mo–N=N–Mo arrangement. Amidomolybdenum complexes are suitable systems to model elemental steps of biological nitrogen activation at a molecular level. It was possible to demonstrate that the N–N bond cleavage need not take place via N–H compounds as intermediates.



Scheme 48. An unusual Fe–Mo–dinitrogen complex.

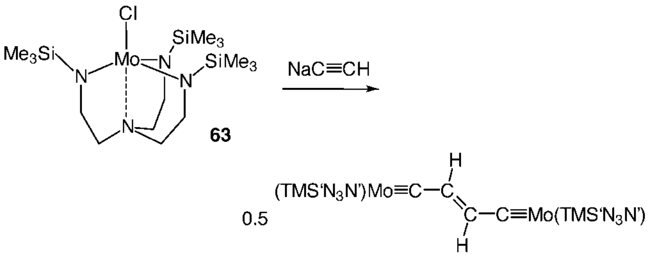


Scheme 49. The cleavage of the N–N triple bond by Mo^{III} complexes ($N' = Ar(t\text{Bu}_D)N$).

5.2. Spontaneous α-Elimination in the Formation of Carbyne Complexes

The classical decomposition reaction of a kinetically labile metal–carbon bond is β-H elimination with the formation of a hydrido complex and release of the corresponding olefin. There may also be parallel α-H elimination with the formation of carbene or carbyne complexes, familiar from the chemistry of the metals of Groups 5 and 6. Both α- and β-elimination has been observed with alkylmolybdenum complexes stabilized by TMS‘N$_3$N’ ligands.[216]

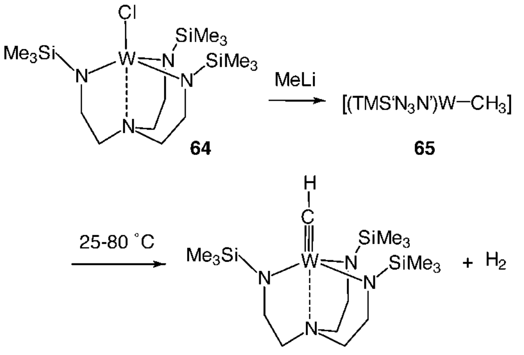
The reactions of **63** with MeLi or $LiC{\equiv}CR$ ($R = Me$, Ph, $SiMe_3$) give paramagnetic d^2-molybdenum methyl or alkynyl complexes, but the reaction with $NaC{\equiv}CH$ leads to a diamagnetic d^0-molybdenum acetylene coupling product (Scheme 50).[207] Such a coupling can be compared with acetonitrile couplings to d^2-tantalum and -niobium centers.[217] It confirms the high oxidation tendency of the $[(TMS\text{‘}N_3N\text{’})Mo]^+$ fragment. Paramagnetic molybdenum complexes of the type $[(TMS\text{‘}N_3N\text{’})MoR]$ ($R =$ alkyl substituent) are capable of both α- and β-eliminations if the corresponding H atoms are present. Where $R =$ cyclopentyl β-



Scheme 50. Alkyne coupling by the formation of carbyne complexes.

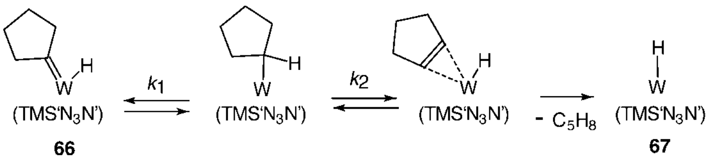
elimination leads to the formation of the hydridocyclopentene complex and the hydridocyclopentylidene complex is formed by α-elimination. The former process occurs more than six orders of magnitude more slowly than the formation of the carbene complex.[216]

The corresponding tungsten complexes are significantly more capable of α-elimination than alkylmolybdenum complexes. Thus carbyne complexes are formed by α,α-eliminations.[218] Compound **64** reacts with MeLi to form the alkyl complex **65** which in the temperature range of 25–80 °C is transformed into the corresponding methylidyne complex with loss of H_2 (Scheme 51).[219] Analogously the reaction of **64** with $LiCH_2R$ gives carbyne complexes of the type [(TMS‘N$_3$N’)W≡CR] (R = Me, Pr, CMe$_3$, SiMe$_3$). Because of the steric shielding of the three Me$_3$Si groups a unimolecular process which occurs via a carbenehydrido complex intermediate is assumed to take place here. In general, the formation of the catalytically active species in classical alkene or alkyne metathesis systems can be explained by such dehydrogenation reactions of alkyl ligands. Analogous to the reaction described in Scheme 51 is the reaction of [(PMe$_3$)$_4$WCl$_2$] with AlMe$_3$, which leads to *trans*-[Cl(PMe$_3$)$_4$W≡CH].[220]



Scheme 51. Spontaneous α,α-elimination.

The transformations of a polyhydridorhenium complex[221] and an allylmolybdenum compound[222] show only a distant relationship. If **64** is allowed to react with cyclopentyllithium α,α-elimination is blocked and the reaction remains at the stage of the carbene–hydrido complex **66** (Scheme 52).[223] Product **66** is unstable and changes into the paramagnetic compound **67** with the loss of cyclopentene. The reaction of **64** with α-D-cyclopentyllithium at low temperatures gives the kinetically preferred intermediate **66** with “deuterido ligand”, which confirms that in this system α-cleavage occurs faster than β-elimination under the given conditions.[224] At temperatures above 0 °C the D atom wanders to the cyclopentylidene ligand, first to the β-position, then to the γ-position. After cyclopentene cleavage and the formation of the thermodynamically stable final product **67**, statistical deuteration of the cyclopentene is found. Scheme 52 summarizes the equilibrium where $k_1 > k_2$. The preference of α-elimination[225] over β-H atom cleavage appears to occur more frequently than is assumed but is difficult to confirm.

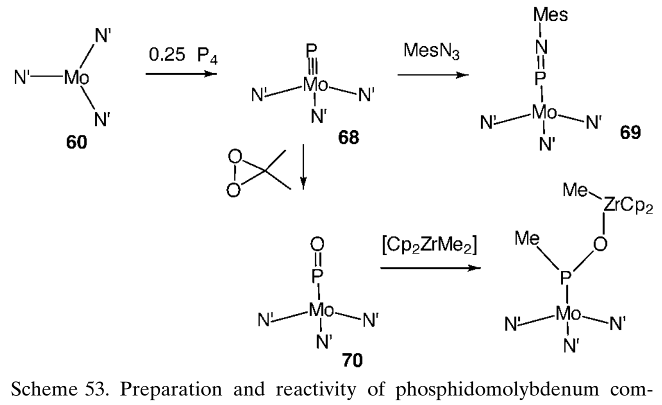


Scheme 52. α- versus β-elimination.

5.3. Complexes with Phosphorus and Arsenic as Terminal Ligands

Doubly or triply bridged P_1 ligands in binuclear or trinuclear metal complexes are well known.[226] An unbridged, terminal P_1 ligand (phosphido ligand) was first published simultaneously by Cummins et al. [227] and Schrock et al.[228] in 1995.[229] Ten years before the existence of the M≡P species had already been discussed.[230] The tendency of compound **60** to react with N_2[212] or N_2O[211] by N–N bond cleavage to form the nitrido complex and the affinity of the [(TMS‘N$_3$N’)W] fragment for the spontaneous formation of metal–carbon triple bonds[223, 219] suggest that both systems are set up for the stabilization of a terminal P_1 ligand.

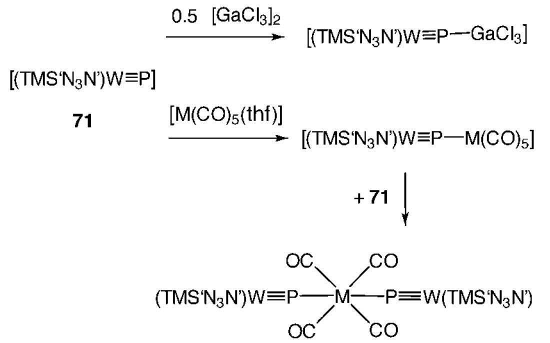
In analogy to dinitrogen cleavage, **60** reacts smoothly with 0.25 equivalents P_4 to form **68** (Scheme 53). The Mo–P distance is 2.119 (4) Å. The derivatization of **68** with mesityl azide leads to the diamagnetic complex **69** (Scheme 53). If **68** is reacted with elemental sulfur a phosphorus monosulfide complex can be isolated. Analogous to this is the reaction with dimethyldioxirane, which gives the corresponding phosphorus monooxide complex. Compound **70** reacts with Cp$_2$ZrMe$_2$ to afford the zircon oxane by methyl transfer (Scheme 53). The



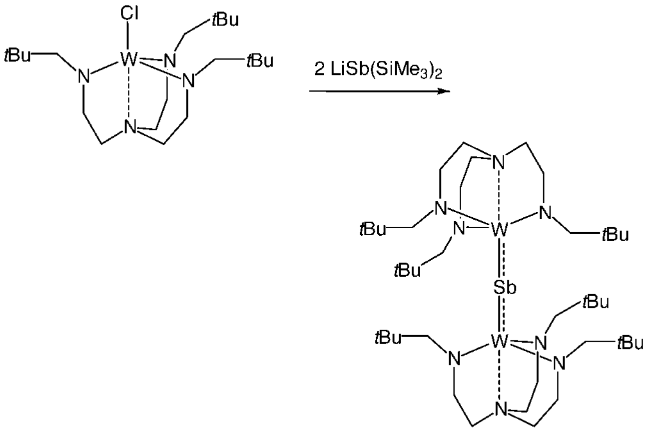
Scheme 53. Preparation and reactivity of phosphidomolybdenum complexes (N′ = Ar(tBu$_D$)N).

metal–phosphorus triple bond is also stabilized on the [(TMS‘N$_3$N’)M] fragment.[228] Thus **60** and **64** react with one equivalent of LiPPh(H) to give the intermediate [(TMS‘N$_3$N’)M–PPh(H)] (M = W, Mo), and with a second equivalent to give [(TMS‘N$_3$N’)M≡P] (W–P bond length 2.162(4) Å). The reaction proceeds significantly faster with the tungsten complex.[231]

The reaction of **71** with [M′(CO)$_5$(thf)] (M′ = Cr, W) leads to structurally interesting homo- and heterobimetal complexes[232] and with [GaCl$_3$]$_2$ to form a Ga–P adduct[233] (Scheme 54). With LiAsPh(H) a compound of the type [(TMS‘N$_3$N’)M≡As] (M = Mo, W) is obtained.[232, 234] The W–As distance is 2.2903 (11) Å. The [(TMS‘N$_3$N’)W] fragment cannot be used for the preparation of an antimonido or bismuthido complex since the steric demand of the TMS‘N$_3$N’ ligand is too large to enable a substitution of the chloro ligand. If a R‘N$_3$N’ anion (R = neopentyl) is used as ligand a compound is isolated in which the antimony atom acts as a symmetrical bridge between two tungsten centers (Scheme 55).[235]

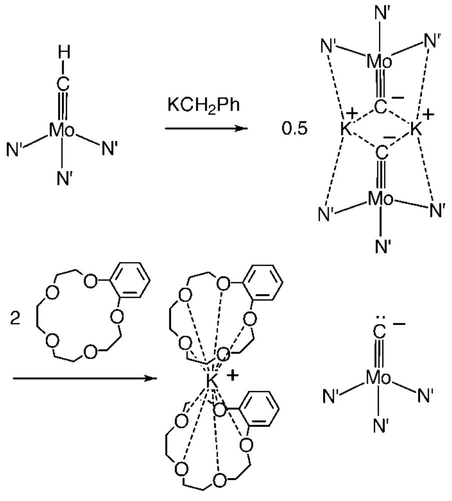


Scheme 54. Phosphido complexes as “neutral ligands” (M = Cr, W).



Scheme 55. Antimony as a bridging ligand.

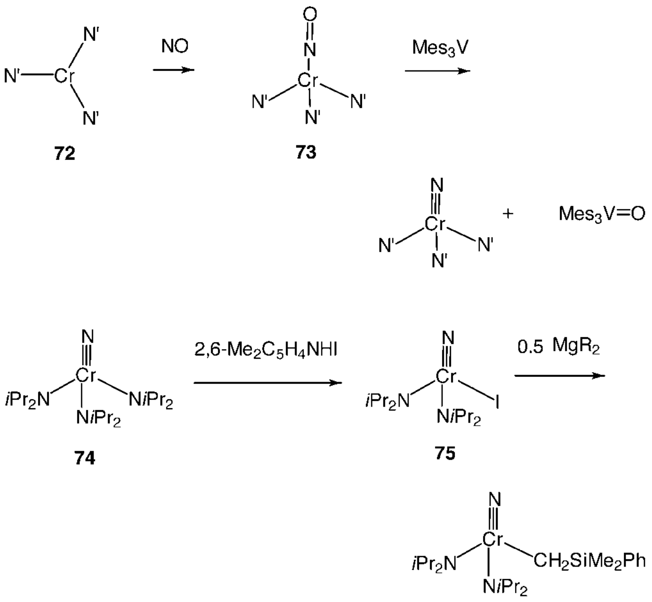
The use of multidentate amido ligands allowed the synthesis of stable phosphido and arsenido complexes for the first time. Not only metals of Group 15 can be terminal ligands, but also carbon. This leads to terminal carbides.[236] *tert*-Butylanilido ligands such as the Ar(*t*Bu$_D$)N anion (Ar(*t*Bu$_D$)N = [3,5-(CH$_3$)$_2$C$_6$H$_3$] [(H$_3$C)(D$_3$C)$_2$C]N anion; *t*Bu$_D$ = C(CH$_3$)(CD$_3$)$_2$) are suitable for the synthesis of such species (Scheme 56).



Scheme 56. Carbon as terminal ligand (N′ = Ar(*t*Bu$_D$)N).

5.4. Unusual Transfer Reactions between Metal Complexes

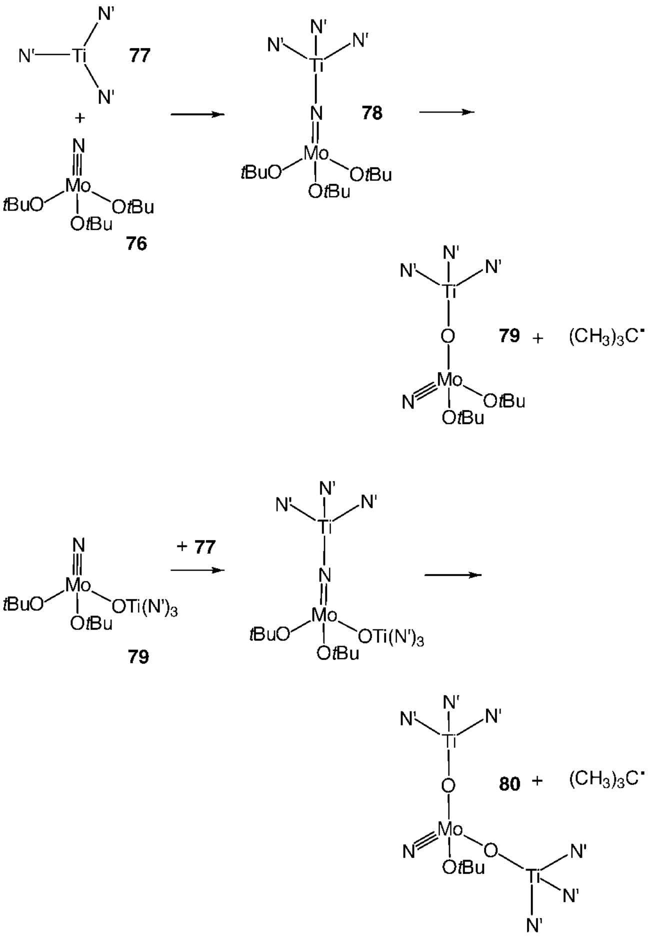
Intermetallic atom transfer reactions have until now been extensively investigated with the example of the nitrogen atom.[237] The synthetic potential of such reactions appears large if the parallel to organic chemistry is considered. Atom transfer reactions between different metal complexes is an excellent method for the preparation of chromium–nitrido complexes.[238] The reaction of, for example, **72** with NO leads to **73** (Scheme 57, top), a compound which then is transformed with Mes$_3$V into the nitrido complex by oxygen transfer when [Mes$_3$V=O] is formed. An intermetallic N–O bond cleavage is unusual[239] and must be regarded as the inversion of the oxidation of a terminal nitrido complex to a nitrosyl compound.[240] Compound **74** is formed analogously and reacts with 2,6-lutidinium iodide to form **75**, which can be



Scheme 57. N–O bond cleavage by two metal centers (N′ = Ar(*t*Bu$_D$)N, *i*Pr$_2$N; R = CH$_2$SiMe$_2$Ph).

alkylated with 0.5 equivalents of $Mg(CH_2SiMe_2Ph)_2$ (Scheme 57, bottom).[241]

A nitrogen atom transfer and the cleavage of the dinitrogen triple bond is observed in the system $[N'_3Mo]/[O'_3Mo]/N_2$ ($N' = Ar(t\mathrm{Bu}_D)N$, $O' = t\mathrm{BuO}$).[242] The reaction of $[O'_3Mo{\equiv}N]$ with $[N'_3Mo]$ in a N_2-free atmosphere affords $[O'_3Mo{\equiv}MoO'_3]$ and $[N'_3Mo{\equiv}N]$ quantitatively. This shows that the nitrido ligand transfer from alkoxy to the amido system is irreversible. The analogous reaction in a $^{15}N_2$ atmosphere leads quantitatively to a 1:1 mixture of $[N'_3Mo{\equiv}^{14/15}N]$ and $[O'_3Mo{\equiv}^{14/15}N]$ with the enrichment of both $^{15}N_2$ isotopomers being about 40 %. That means that in this system, the $[O'_3Mo]$ fragment is involved in the N_2 activation and cleavage of the N–N bond with formation of an nitrido complex. Since the nitrido ligand is transferred irreversibly from the alkoxy complex to $[N'_3Mo]$, the isotopomer $[O'_3Mo{\equiv}^{15}N]$ can only be formed by $^{15}N_2$ activation. Since the reaction of $[MoCl_3(thf)_3]$ with three equivalents of LiO*t*Bu in the presence of N_2 gives $[O'_3Mo{\equiv}MoO'_3]$ quantitatively, the "$[O'_3Mo]$" system alone is not capable of activating N_2. An intermediate $[N'_3Mo{-}N{=}N{-}MoO'_3]$ must be invoked. This decomposes into $[O'_3Mo{\equiv}N]$ and $[N'_3Mo{\equiv}N]$, when finally $[O'_3Mo{\equiv}N]$ transfers the nitrido ligand to $[N'_3Mo]$. Model compounds for such N and P atom transfer reactions have been described.[243] A novel transfer reaction is the constructional reaction of Mo–Ti-μ-oxo complexes by radical, homolytic C–O bond cleavage in alkoxy ligands. Formally, an alkyl radical in the periphery of a [Mo=O] or a [Mo≡N] fragment, for example a *t*Bu radical, is substituted by a titanium complex radical (Scheme 58).[244]



Scheme 58. Mo–Ti–μ-oxo complexes by radical C–O bond cleavage.

The reaction of **76** with **77** leads in the first step to the μ-nitrido complex **78**, which is stable at temperatures below −30 °C and which isomerizes to **79** with the release of a *t*Bu radical in a first-order reaction (Scheme 58). The addition of further **77** leads to **80** and decomposition products of the *t*Bu radical where again a μ-N intermediate can be observed. The addition of a further equivalent of **77** does not result in further substitution since the system is sterically "overloaded". A comparable reaction sequence is observed when instead of **76** the compound $[(t\mathrm{BuO})_2Mo(O)_2]$ is used. Analogous reactions between $[(i\mathrm{PrO})_3V{=}O]$ and **77** stop at the μ-oxo complex stage.[245]

6. Conclusions

Over the last few years especially, amido ligands have greatly enriched the chemistry of the early transition metals and have thus ended the fixation with cyclopentadienyl ligands as control units for the reactivity of such complexes. The real advantages of amido ligands lie in the wide scope of possibilities for the construction of complex compounds with well-defined reaction centers. Focusing on the construction of a Cp equivalent brought only little impetus. In addition to investigations of reaction mechanisms, the most significant advances of amidometal chemistry have been made in the activation and stabilization of unusual species and molecules. The question of consecutive stoichiometric reactions or even catalytic use is a topic for the future.

Little attention has hitherto been paid to the amido complexes of the later transition metals. The "hard" amido ligand is not adapted to the "soft" metals of these triads, which is why there are so few compounds of that type. The reactivity of the M–N bond of these metals should differ substantially from those of the early transition metals. Inert complex fragments probably cannot therefore be generated, although "reactive amido ligands", capable of inserting unsaturated substrates, remain a possibility. C–N couplings are amongst the most important of reactions.

Multidentate ligands play an important role in supramolecular chemistry. Hitherto little has been reported on the use of amido ligands. Can the many possibilities for the construction of polyfunctional ligands not also be used here, for example in the preparation of microporous metalloorganic materials and zeolite analogues (zeotypes)? Anionic ligands should stabilize structural frameworks more effectively than neutral donor functionalites.

7. Alphabetical List of the Abbreviations of the Amido Ligands Used

Abbrevation	***Meaning***
$Ar(t\mathrm{Bu}_D)N$	$[3,5\text{-}(CH_3)_2C_6H_3][(H_3C)(D_3C)_2C]N$ anion
$t\mathrm{BuMe_2Si'N_3N'}$	$[\{(H_3C)_3C\}(H_3C)_2SiN(CH_2)_2]_3N$ trianion

C_3H_6‘N_2’	$CH_2(CH_2N\text{-}2,6\text{-}i\mathrm{Pr}_2C_6H_3)_2$ dianion
C_6F_5‘N_3N’	$[F_5C_6N(CH_2)_2]_3N$ trianion
dac	4,13-diaza-[18]crown-6-dianion
‘NO’	*N*,*O*-bis(*tert*-butyl)(alkoxydimethylsilyl)amide
‘NON’	$O[2\text{-}\{C(CH_3)(CD_3)_2\}NC_6H_4]_2$ dianion
oep	octaethylphorphyrin dianion
oepg	octaethylphorphyrinogen tetraanion
Ph‘CN_2’	bis(trimethylsilyl)benzamidinato anion
‘P_2N’	$(i\mathrm{Pr}_2PCH_2SiMe_2)_2N$ anion
‘P_2N_2’	$PhP[CH_2Si(CH_3)_2NSi(CH_3)_2CH_2]_2PPh$ dianion
TMS-Ap	deprotonated *N*-trimethylsilyl-4-methyl-2-aminopyridine
TMS‘N_3N’	$[(H_3C)_3SiN(CH_2)_2]_3N$ trianion

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