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Synthesis and Structural Chemistry of Non-Cyclopentadienyl Organolanthanide Complexes

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1. Introduction

About 30 years ago organometallic compounds of the rare earth metals were a curiosity. That changed slowly in the late 1970s and the early 1980s after the availability of modern preparative and analytical techniques. Especially access to single-crystal X-ray diffraction made it possible to handle these compounds, which are all extremely sensitive to oxygen and water, and to understand the structural features of these fascinating complexes. The area developed faster and faster in the late 1980s with the discovery of the high potential of these compounds as reagents in organic synthesis and as very active catalysts.

Following the discovery of the tricyclopentadienyl derivatives of the lanthanides by Wilkinson and Birmingham,[1] most of the organolanthanide compounds prepared have been sandwich complexes, containing unsubstituted or substituted cyclopentadienyl ligands. Their relatively high stability against moisture and air caused numerous research groups to develop the area of lanthanocene chemistry during the last two decades. In contrast, cyclopentadienyl-free organolanthanide compounds, like alkyl or aryl derivatives, alkenyl and alkynyl complexes, or organolanthanides with heterocyclic ligands have been very rare. Early review articles give them only minor reference[2,3] or deal only with cyclopentadienyl and π-complexes of the lanthanides with aromatic ligands.[4]

Recent work in the organolanthanide area shows a turn away from the cyclopentadienyl chemistry. Homoleptic alkyl, allyl, hydrido, and carbene derivatives of the lanthanides as well as cyclooctatetraenyl, pentadienyl, and lanthanoidocenes with nitrogen- and phosphorus-containing heterocycles are incredibly active catalysts, which developed new fields in organolanthanide chemistry recently, demanding a survey of this interesting new area of organometallic chemistry. Recent reviews concerning "non-cyclopentadienyl" organolanthanide compounds have been given by Edelmann,[5] Eaborn,[6] van Koten,[7] Cotton,[8] Zakharov,[9] Evans,[10] and Nief.[11] This article provides a review of the chemistry done with "non-cyclopentadienyl" organolanthanide compounds during the past decade. It does not cover syntheses, properties, and reactions from this area of chemistry described in the review article of Edelmann,[5] except where it is essential for understanding.

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Frank T. Edelmann was born in Hamburg, Germany, in 1954. He studied chemistry from 1974 to 1979 at the University of Hamburg, where he obtained his Diplom in 1979 and doctoral degree in 1983. His Ph.D. thesis entitled “The chemistry of the tricarbonyl(fulvene) chromium complexes” was carried out under the supervision of Prof. Ulrich Behrens. This was followed by two years (1983–1985) of postdoctoral research as a Feodor Lynen Fellow of the Alexander-von-Humboldt Foundation in the groups of Professors Josef Takats (University of Alberta, Edmonton, Canada), John W. Gilje (University of Hawaii at Manoa, Honolulu, HI), and Tristram Chivers (University of Calgary, Calgary, Canada). In 1991 he finished his Habilitation in the group of Prof. Herbert W. Roesky at the University of Göttingen, Göttingen, Germany, and in 1995 he was appointed Full Professor of Inorganic Chemistry at the Otto-von-Guericke-University in Magdeburg, Germany. More than 200 original papers in refereed journals document his research interests in the areas of organolanthanide and -actinide chemistry, silicon chemistry (silsesquioxanes and metallasilsesquioxanes), and fluorine chemistry.

Dominique M. M. Freckmann was born in Cologne, Germany, in 1975. In 1994, she began studying chemistry at the Universität zu Köln, financially supported by the scholarship foundation Cusanuswerk. In 1997/98, she became an exchange student at the Universität Bern in Switzerland, under the guidance of Professor Hans U. Güdel. During her Diploma work supervised by Professor Gerd Meyer, she carried out her research work in the laboratories of Professor Glen B. Deacon at Monash University, Clayton, Australia. Following graduation from the Universität zu Köln in 1999, she joined the group of Professor Sandro Gambarotta at the University of Ottawa, Ottawa, Canada. After 2000, as a scholar of the Graduiertenkolleg “Synthetische, mechanistische und reaktionstechnische Aspekte von Metallkatalysatoren” she has been preparing for her Ph.D. focusing on lanthanide alkyls under the direction of Professor Herbert Schumann.

Herbert Schumann was born in Coburg, Germany, in 1935. He received his degree Diplom-Chemiker in 1961 and Dr. rer. nat. in 1962 at the Ludwigs-Maximilians-Universität München under the direction of Max Schmidt. He spent 3 years at the Universität Marburg and 5 years at the Universität Würzburg, Germany, as Wissenschaftlicher Assistent until he obtained his Habilitation to Privatdozent in Würzburg in 1967. In 1970 he took over the Chair of Inorganic Chemistry at the Technische Universität Berlin, where he is now Chairman of the Department of Chemistry. He started his scientific work in 1967 in organotin chemistry, followed by preparative and X-ray structural investigations in the area of organometallic compounds of the main group and transition elements with main focus on group 13 for MOCVD precursors, use as reagents in organic synthesis and as cocatalysts for olefin polymerization, and rhodium complexes for homogeneous catalysis. Since 1975 his main interests are in organolanthanide chemistry. Together with his wife, Ingeborg Schumann, he is author of 25 volumes of Gmelin Handbook of Inorganic and Organometallic Chemistry “Organotin Compounds”. In 1992 he was a Lady Davies Professor and in 1998 a Forchheimer Visiting Professor at the Hebrew University of Jerusalem besides other Guest-Professorships at Zhejiang University in Hangzhou/China and Monash University, Clayton, Australia.

2. *σ-Alkyl and Aryl Complexes*

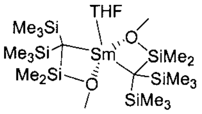
Over the years one major challenge has remained in organolanthanide chemistry: the synthesis of homoleptic alkyl and aryl complexes. The simplest organometallic compounds of the rare earths are the species LnR_2 or LnR_3 with the rare earth metals in their common oxidation states Ln^{2+} and Ln^{3+} which imply the coordination of only two or three ligands to the metal center. This is usually insufficient to meet the lanthanides’ demands of steric saturation through high coordination numbers.

Hence for a long time, only indirect evidence could be found for the existence of simple homoleptic organolanthanide compounds; the isolation and characterization of compounds belonging to this class were first achieved recently using pentafluorophenyl for Ln^{2+} derivatives[12] and very bulky alkyl ligands for Ln^{3+} species.[13−15] Especially for alkyls, very little structural data are available for compounds without any trimethylsilyl-substituted ligands which generally ensure higher stability. But nevertheless, due to the difficulties of their synthesis and their high reactivity alkyls and aryls still represent an interesting class of compounds.[16]

2.1. Homoleptic *σ*-Alkyl Complexes

Shortly after the synthesis of the first divalent solvent-free Ln alkyl, $[(Me_3Si)_3C]_2Yb$,[17] the Eu analogue was prepared similarly by the reaction of EuI_2 and $KC(SiMe_3)_3$ in benzene.[18] It also features the bent structure displayed by the Yb complex but with a slightly smaller C−Eu−C angle (C−Eu−C = 136°, C−Yb−C = 137°) and longer Eu−C bonds (Eu−C = 261 pm, Yb−C = 249/250 pm). Salt metathesis was then again applied successfully to synthesize the first divalent Sm alkyl, $Sm[C(SiMe_3)_2(SiMe_2OMe)]_2(THF)$

(**1**), with Sm−C distances of 279/285 pm.[19] The ligand has been slightly changed: one of the Si atoms bears now a methoxy instead of a methyl group. This leads to additional coordination by the ligand through the O atoms to the Sm center. One THF molecule completes the coordination sphere.



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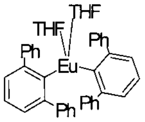
Though the synthesis of likewise silyl-stabilized but solvent-free $[(Me_3Si)_2CH]_3Yb$ was already reported by Schaverien et al. in 1991, its monomeric structure was only recently determined.[20] The trimethylsilyl ligands coordinate trigonal pyramidally to the Y atom (Y−C = 236 pm). An attempt to prepare a mixed alkyl alkoxide with the less bulky CH_2SiMe_3 ligand led to isolation of the ion pair $[(Me_3SiCH_2)_x(Me_3CO)_{1-x}Y(OCMe_3)_4(Li(THF))_4Cl][Y(CH_2SiMe_3)_4]$.[21] In the homoleptic anion the four trimethylsilyl ligands are arranged tetrahedrally around the metal center (Y−C = 238−242 pm).

For the neutral THF-solvated $Y(CH_2SiMe_3)_3(THF)_3$ an average Y−C distance of 243 pm is reported.[22a] First reports on the corresponding complexes of some late lanthanides (Ln = Tb, Er, Yb) showed up in the literature a long time ago.[22b,c] but no structural data were given. The structures of the THF-solvated derivatives $Ln(CH_2SiMe_3)_3(THF)_2$ were recently determined for Ln = Lu (Lu−C = 235−238 pm), Yb (Yb−C = 234−237 pm), and Er (Er−C = 239−242 pm). The coordination geometry is trigonal bipyramidal with the THF molecules in the axial positions. In the case of the larger Sm^{3+} ion, three molecules of THF coordinate to the metal center (Sm−C = 248−249 pm).[22d]

Treatment of Yb metal with neopentyl iodide in THF gives a neutral, surprisingly trivalent lanthanide alkyl, $Yb(CH_2tBu)_3(THF)_2$.[16] It is the first compound of this type without any trimethylsilyl substituents. The coordination geometry around the metal center is trigonal bipyramidal with the neopentyl groups in the equatorial positions (Yb−C = 236−239 pm). Finally, addition of MMe_3 to $Ln(NMe_2)_3(LiCl)_3$ (M = Ga and Al for Ln = Nd and M = Al for Ln = Y) leads to formation of homoleptic tetramethylaluminates $Ln[(\mu\text{-}Me)_2MMe_2]_3$ in which the Ln center is exclusively surrounded by methyl groups (M = Ga, Nd−C = 258−262 pm; M = Al, Nd−C = 256−261 pm). With excess $AlMe_3$ 2:1 cocrystallization products $Ln[AlMe_4]_3(Al_2Me_6)_{0.5}$ (Ln = Nd, Y) are obtained (Nd−C = 257−260 pm, Y−C = 206−251 pm).[22e,f]

2.2. Homoleptic σ-Aryl Complexes

Reaction of the sterically demanding aryl iodide IDpp (Dpp = 2,6-$Ph_2C_6H_3$) with Eu metal in THF afforded the first divalent lanthanide aryl $Eu(Dpp)_2(THF)_2$ (**2**).[23] The Eu atom is distorted tetrahedrally coordinated by two ligands (Eu−C = 261/262 pm) and two THF molecules.



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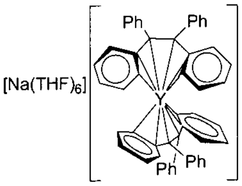
Recently crystals of $Eu(C_6F_5)_2(THF)_5$, obtained from solutions of $Eu(C_6F_5)_2$ in THF/light petroleum enabled the first single-crystal X-ray structure determination of a lanthanide(II) perfluoroaryl complex.[24] The C_6F_5 ligands are found in the axial positions of a pentagonal-bipyramidal europium center. With 282.2(3) pm the Eu−C distance is quite long due to the fluorine substitution of the aryl groups. Solutions of $Eu(C_6F_5)_2$ were prepared via a well-established metal-exchange route as outlined in eq 1.[25]

$$Eu + Hg(C_6F_5)_2 \rightarrow Eu(C_6F_5)_2 + Hg \qquad (1)$$

After Bochkarev et al. already reported in 1995 on the structural characterization of the first phenyl lanthanides with Er and Tm,[26] a third representative of this class of compounds, $ScPh_3(THF)_2$, followed in 1999.[27] Its synthesis involves salt metathesis of $ScCl_3(THF)_3$ with 3 equiv of PhLi. As only two molecules of THF coordinate to the Sc center, due to its smaller size, a trigonal-bipyramidal geometry is adopted (Sc−C = 224−227 pm).

The formation of "ate" complexes is a common phenomenon in lanthanide chemistry as high coordination numbers are preferred. So next to solvent molecules additional anionic ligands find their way easily to the central metal atom. Though Yasuda et al. managed to synthesize a solvent-free Sm−aryl, they only succeeded in the structural characterization of its "ate" complex $Li[Sm\{C_6H_3(OiPr_2)\text{-}2,6\}_4]$.[28] The formal coordination number 8 is reached through bidentate coordination of the four aryl ligands (Sm−C = 258−262 pm).

A new type of ligand, the dianion of tetraphenylethylene, forming a sandwichlike complex was introduced by Evans et al. Reaction of its potassium salt with YCl_3 and subsequent cation exchange with $NaBH_4$ affords $[Na(THF)_6][Y(Ph_2CCPh_2)_2]$ (**3**).[29] The Y atom being closest to the C atoms of the former double bond is coordinated in a η^6 fashion to each $[Ph_2CCPh_2]^{2-}$ ligand (Y−C = 252−269 pm).



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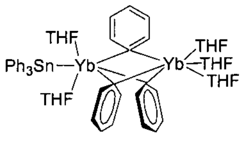
2.3. Complexes with Heavier Group 14 Elements

Still, little is known about lanthanide compounds with the heavier group 14 elements directly bonded to rare earth elements. After the group of Bochkarev presented the first silyl− and germyl−lanthanide compounds with Yb,[30] a germyl−europium complex followed. While silyl− and germyl−ytterbium complexes were synthesized starting from the metal itself, $(Ph_3Ge)_2Eu(DME)_3$ was obtained by reacting europium naphthalenide with Ph_3GeH.[31] The coordination polyhedron resembles a hexagonal bipyramid with the germyl groups in the axial positions (Eu−Ge = 335 pm, Ge−Eu−Ge′ = 180°) and a crownlike equatorial plane consisting of the three chelating DME molecules. Although chelating triarylgermyl ligands have been used in metathetical reactions with divalent Sm and Yb derivatives, no structural information on those compounds has been reported.[32] However, structural analyses of stannyl−ytterbium complexes have been more successful. Treatment of a THF solution of Ph_4Sn with $(C_{10}H_8)Yb(THF)_2$ at room temperature results in the formation of two compounds. Yellow $(Ph_3Sn)_2Yb(THF)_4$ was obtained from an ether solution (Yb−Sn = 331 pm, Sn−Yb−Sn = 165°), whereas dark-ruby, almost black $(Ph_3Sn)Yb(THF)_2(\mu\text{-}Ph)_3Yb(THF)_3$ (**4**) was isolated from ether−THF (Yb−Sn = 338 pm).[33,34]



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Starting from the corresponding lanthanide metals, polynuclear stannyl−lanthanide complexes $[(Me_3Sn)_3Sn]_2Ln(THF)_4$ (Ln = Sm, Yb) could be synthesized by the use of Me_3SnCl in THF. A longer reaction time, 100 instead of 60−70 h, leads to formation of another Yb compound with the same composition but a different structure. In the latter case, the $(Me_3Sn)_3Sn$ groups are in an eclipsed arrangement (tetragonal crystals, Yb−Sn = 330 pm, Sn−Yb−Sn = 176°) in contrast to a staggered one in the former case (orthorhombic crystals, Sm−Sn = 339/340 pm, Yb−Sn = 329/330 pm, Sn-Ln-Sn = 179°).[35]

2.4. Heteroleptic σ-Alkyl and Aryl Complexes

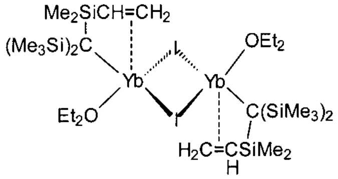
Formally, adducts of lanthanide alkyls with solvent donor ligands such as THF, DME, or TMEDA should be considered heteroleptic complexes. However, these solvated species are closely related with the unsolvated species LnR_3. Thus, only organolanthanide compounds containing additional *anionic* ligands will be discussed in this section. Until about 1990 this class of compounds was little investigated, and the small number of known compounds were mere laboratory curiosities. However, more recently a substantial number of highly interesting results in this area have been reported. It has become evident that especially various types of nitrogen-coordinated ancillary ligands (e.g. chelating amide ligands, benzamidinates, aminotroponiminates, porphyrinates, etc.) are highly suited for stabilizing such heteroleptic organolanthanide complexes.

2.4.1. Divalent Lanthanide Derivatives

Very little is known about well-defined heteroleptic organolanthanide(II) derivatives. Grignard-type organolanthanide halides represent a synthetically important though structurally not fully understood class of compounds. Grignard analogues of the type “RLnX” (R = alkyl, aryl; Ln = Sm, Eu, Yb; X = halide) have been thoroughly investigated as useful reagents since 1970 and are now widely used in organic synthesis.[2,3,5] Especially the ytterbium species “RYbI” are readily accessible from metallic ytterbium and the corresponding alkyl iodides in THF. Normally the resulting deeply colored THF solutions are used in situ for subsequent reactions. These organolanthanide(II) compounds behave like typical Grignard compounds, although there are several interesting differences in reactivity. Until recently compounds of the type “RLnX” had never been isolated as pure materials nor had they been characterized spectroscopically or by X-ray diffraction. This was first made possible through the use of very bulky trimethylsilyl-substituted σ-alkyl ligands. It was in 1994 that Eaborn et al. reported the first preparation and structural characterization of such compounds.[36] The unsolvated, homoleptic dialkylytterbium(II) complex $[(Me_3Si)_3C]_2Yb$ reacts with iodomethane or 1,2-diiodoethane to afford the ytterbium Grignard compound $[\{(Me_3Si)_3C\}Yb(\mu\text{-}I)(Et_2O)]_2$ in the form of yellow-green, exceedingly air-sensitive crystals (^{171}Yb NMR: δ 812 ppm). It is also possible to prepare $[\{(Me_3Si)_3C\}Yb(\mu\text{-}I)(Et_2O)]_2$ via a “normal” Grignard route by direct reaction of elemental ytterbium with the corresponding silyl-substituted alkyliodide according to eq 2.[18,36] This appears to be the most straightforward synthetic pathway to such compounds. An X-ray crystal structure determination of $[\{(Me_3Si)_3C\}Yb(\mu\text{-}I)(Et_2O)]_2$ revealed planarity of the central Yb_2I_2 ring (Yb−I 308.4(2), Yb−O 234.8(13), Yb−C 247(2) pm; I−Yb−I 91.92(4), Yb−I−Yb 88.08(4)°).

$$2Yb + 2(Me_3Si)_3CI \xrightarrow{Et_2O} [\{(Me_3Si)_3C\}Yb(\mu\text{-}I)(Et_2O)]_2 \quad (2)$$

Other representatives of this unusual class of compounds have become available through variation of the substituents.[18] The ytterbium complexes $[\{(Me_3Si)_2(Me_2XSi)C\}Yb(\mu\text{-}I)(Et_2O)]_2$ (X = OMe, Ph, $CH{=}CH_2$ (**5**)) have been prepared in an analogous manner as shown in eq 2. These molecules too are dimeric with a planar, almost squareYb_2I_2 ring. In the case of **5** (X = $CH{=}CH_2$) an X-ray structure analysis revealed an unusual molecular structure involving a very rare example of a weak lanthanide−vinyl π-interaction (Yb···C 298(2) pm):



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Typically the solid-state structure of an isolated organolanthanide halide is that of a halide-bridged dimer. In unpolar organic solvents (e.g. toluene) all these Grignard-type ytterbium(II) complexes exist in a typical Schlenk equilibrium as shown in eq 3.

$$[\mathrm{RYbI}]_2 \Leftrightarrow \mathrm{YbR}_2 + \mathrm{YbI}_2 \qquad (3)$$

The complexes $[\{(Me_3Si)_2(Me_2XSi)C\}Yb(\mu\text{-}I)(Et_2O)]_2$ (X = OMe, Ph, $CH{=}CH_2$ (**5**)) also decompose when heated under reduced pressure to give the corresponding dialkylytterbiums and YbI_2.[18]

In combination with the well-tried trimethylsilyl-substituted σ-alkyl ligands, heteroleptic organolanthanide(II) alkoxides can also be prepared. The dimeric alkylytterbium(II) ethoxide $[\{(Me_3Si)_3C\}Yb(\mu\text{-}OEt)(OEt_2)]_2$ (^{171}Yb NMR: δ 764 ppm) was made by treatment of ytterbium diiodide with equimolar amounts of $KC(SiMe_3)_3$ and KOEt in diethyl ether (eq 4) and crystallographically characterized.[17,36,37]

$$\mathrm{YbI_2 + KC(SiMe_3)_3 + KOEt \rightarrow {}^{1}/_{2}[\{(Me_3Si)_3C)\}Yb(\mu\text{-}OEt)(OEt_2)]_2 + 2KI} \qquad (4)$$

It has been found that the ethoxide-bridged species is also accessible through an alternative route from the homoleptic dialkyl $[(Me_3Si)_3C]_2Yb$ via an ether cleavage reaction according to eq 5.[36,37]

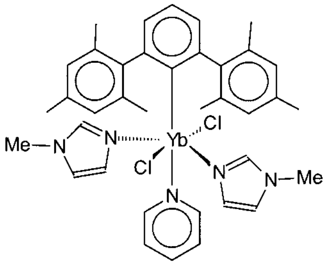
$$\mathrm{2[(Me_3Si)_3C]_2Yb + 4Et_2O \rightarrow [\{(Me_3Si)_3C)\}Yb(\mu\text{-}OEt)(OEt_2)]_2 + (Me_3Si)_3CH + CH_2{=}CH_2} \qquad (5)$$

Treatment of $Yb(OAr)_2(THF)_3$ with $KCH(SiMe_3)_2$ afforded the monomeric aryloxide derivative $[(Me_3Si)_2CH]Yb(OAr)(THF)_3$. In this case the very bulky ArO ligand prevents the formation of an aryloxide-bridged binuclear complex (Ar = C_6H_2tBu$_2$-2,6-Me-4).[17] A binuclear mixed alkyl amido species of divalent ytterbium was isolated as a brown solid (^{171}Yb NMR: δ 596 ppm) by protonation of 2 equiv of $Yb[CH(SiMe_3)_2]_2(OEt_2)_2$ with *N*,*N*′-bis(trimethylsilyl)-1,4-phenylenediamine as shown in eq 6.[37]

$$\mathrm{2Yb[CH(SiMe_3)_2]_2(OEt_2)_2 + C_6H_4(NHSiMe_3)_2\text{-}1,4 \xrightarrow{Et_2O} \{\mu\text{-}C_6H_4(NSiMe_3)_2\text{-}1,4\}[Yb\{CH(SiMe_3)_2\}(OEt_2)]_2 + 2CH_2(SiMe_3)_2} \qquad (6)$$

2.4.2. Trivalent Lanthanide Derivatives

A. Organolanthanide Halides and Mixed-Ligand Organolanthanides. Monoorganolanthanide(III) dihalides of the type $RLnX_2$ can also be regarded as Grignard analogues. These reagents are readily prepared in situ by alkylation of $LnCl_3$ or LnI_3 with organolithium compounds.[2,3,5] However, as with their lanthanide(II) counterparts, pure crystalline materials are often difficult to isolate and structural information is scarce. Thus, a remarkable result from an organometallic point of view was the first crystal structure determination of such a “lanthanide(III) Grignard compound”, which was reported by Chen et al.[38] Treatment of anhydrous gadolinium trichloride with phenyllithium in a 1:1 molar ratio afforded the well-defined seven-coordinate phenyl complex $PhGdCl_2(THF)_4$. The gadolinium−carbon σ-bond distance is 242(2) pm as determined by X-ray diffraction. More recently the sterically highly demanding terphenyl ligand 2,6-dimesitylphenyl (=Dmp) has been successfully employed to synthesize mono-(σ-aryl)lanthanide complexes.[39] Anhydrous $YbCl_3$ reacts slowly with 1 equiv of Li(Dmp) in THF to give a purple compound of the approximate composition $(Dmp)Yb(\mu\text{-}Cl_3)Li(THF)_2$. Treatment of the latter with pyridine and *N*-methylimidazole (=*N*-MeIm) afforded an orange crystalline material which was shown by X-ray crystallography to be hexacoordinated $(Dmp)YbCl_2(N\text{-}MeIm)_2(py)$ (**6**). The Yb−C distance in this monomeric complex is 244.7(9) pm.[39]



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A second monomeric ytterbium complex containing the very bulky terphenyl ligand Dmp was prepared in a one-pot synthesis by reacting $YbCl_3$ with Li(Dmp) in a 1:1 molar ratio followed by addition of $KN(SiMe_3)_2$. Orange-red $(Dmp)Yb[N(SiMe_3)_2](\mu\text{-}Cl)_2Li(THF)_2$ was obtained in 50% yield and structurally characterized by an X-ray analysis. This is a typical “ate” complex in which the coordination number around the central lanthanide ion is increased by retention of an alkali metal halide (LiCl). The Yb−C distance in this compound is 240.3(4) pm.[39]

Interestingly most recent variations of this terphenyl-type ligand system include the use of the donor-functionalized terphenyl ligand 2,6-di-*o*-anisylphenyl (=Danip)[40a] as well as the very bulky 2,6-di-1-naphthylphenyl derivative (=Dnp).[40b] Reactions of equimolar amounts of DanipLi with $LnCl_3$ (Ln = Yb, Y, Sm) afforded the novel mono(aryl)lanthanide “ate” complexes $[DanipYb(\mu\text{-}Cl)_2(\mu_3\text{-}Cl)Li(THF)]_2$ and $[DanipLn(\mu\text{-}Cl)\{(\mu\text{-}Cl)_2Li(THF)_2\}]_2$ (Ln = Y, Sm). The complexes are dimeric in the solid state. They are composed of lithium chloride bridged $DanipLnCl_2$ moieties (Ln = Yb, Y, Sm) stabilized through additional coordination of the two methoxy functions of each Danip ligand to the lanthanide ion.[40a] In a similar manner the mono(terphenyl)lanthanide dihalides $DnpLnCl_2(THF)_2$ were synthesized by reaction of 1 equiv of DnpLi with 1 equiv of $LnCl_3$ (Ln = Yb, Tm, Y).[40b]

It is well established that the lanthanide ions have a strong tendency to increase their coordination numbers through formation of “ate” complexes, e.g. by incorporation of alkali metal halide byproducts. For example, it was found that the homoleptic complexes $Ln[CH(SiMe_3)_2]_3$ are not accessible directly from lanthanide trichlorides via conventional metathetical reactions. Instead of the expected homoleptic trialkyls, products containing incorporated lithium chloride are formed in these reactions (eq 7).[13]

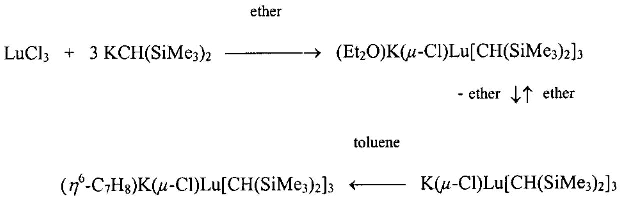
$$\mathrm{LaCl_3 + 3LiCH(SiMe_3)_2 \xrightarrow[-2LiCl]{PMDETA} (PMDETA)Li(\mu\text{-}Cl)La[CH(SiMe_3)_2]_3} \quad (7)$$

PMDETA = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine

The central structural unit of the resulting LiCl adduct is a nearly linear La−Cl−Li group (La−Cl−Li = 165.1°, La−Cl = 276.2 pm, Li−Cl = 228 pm). The Ln[CH(SiMe$_3$)$_2$]$_3$ part of the molecule exhibits no significant structural changes when compared with the neutral compound. A similar synthetic route, i.e. treatment of YCl$_3$ with 3 equiv of LiCH(SiMe$_3$)$_2$ in diethyl ether, was employed to prepare the related bimetallic complex (Et$_2$O)$_3$Li(μ-Cl)Y[CH(SiMe$_3$)$_2$]$_3$. The average Y−C bond length in this complex is 242.3 pm.[41] The analogous reaction with ytterbium trichloride in THF solution afforded the saltlike product [Li(THF)$_4$][YbCl{CH(SiMe$_3$)$_2$}$_3$], which consists of separated ions in the solid state.[42] Apparently the formation of different types of complexes depends on a subtle balance of certain factors. These factors can be the nature of the alkali metal, the presence of halide ions, or the ionic radius of the lanthanide element. A similar situation has also been described for some low-coordinate lanthanide alkoxides and amides.[43] For example, the chloro-bridged lanthanide alkyl complex (PMDETA)Li(μ-Cl)La[CH(SiMe$_3$)$_2$]$_3$ is closely related to the neodymium amide and alkoxide compounds (THF)$_3$Li(μ-Cl)Nd[N(SiMe$_3$)$_2$]$_3$ and (THF)$_3$-Li(μ-Cl)Nd[OC(tBu)$_3$]$_3$, whereas [Li(THF)$_4$][YbCl{CH-(SiMe$_3$)$_2$}$_3$] is comparable to the compound [Li(THF)$_4$]-[NdOSiMe$_3${N(SiMe$_3$)$_2$}$_3$].

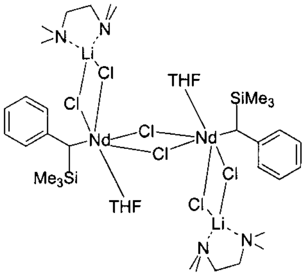
Another example of how minor changes of the reaction conditions or the choice of the reagents can influence the product formation was provided by Schaverien et al.[44] In this case the more reactive alkylpotassium derivative KCH(SiMe$_3$)$_2$ was reacted with lanthanide trichlorides. Due to the enhanced solubility of the potassium compound, it was possible to perform the reaction with lutetium trichloride in diethyl ether instead of THF (Scheme 1). Significant differences where observed in comparison to the analogous reaction sequence using LiCH(SiMe$_3$)$_2$.

Scheme 1. Interconversion of Alkyllutetium Compounds



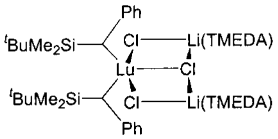
Unlike the analogous LiCl adduct (PMDETA)Li-(μ-Cl)La[CH(SiMe$_3$)$_2$]$_3$ the coordinated diethyl ether in (Et$_2$O)K(μ-Cl)Lu[CH(SiMe$_3$)$_2$]$_3$ can easily be removed under vacuum to produce the unsolvated complex K(μ-Cl)Lu[CH(SiMe$_3$)$_2$]$_3$. In this compound the potassium is coordinatively unsaturated and readily adds solvent molecules such as diethyl ether or even toluene (Scheme 1).[44] Formation of "ate" complexes on one hand and monosubstitution on the other hand are observed when (silylbenzyl)lithium reagents are reacted with LnCl$_3$.[45] Treatment of 3 equiv of Li(TMEDA)CH(SiMe$_2$R)Ph (R = Me, tBu) with LnCl$_3$ (Ln = Sm, Lu) in THF gives ionic Li(TMEDA)$_2$[Ln{CH(SiMe$_2$R)Ph}$_3$Cl] (Ln = Sm, R = Me, purple with Sm−C = 248−256 pm; Ln = Lu, R = tBu, light green with Lu−C = 236−240 pm).

In the case of Ln = Nd, two differently colored dimeric neutral complexes are obtained.[45] Green [Nd{CH(SiMe$_3$)Ph}Cl$_2$(LiCl·TMEDA)$_2$]$_2$ (**7**) (Nd−C = 253 pm) contains two TMEDA-solvated LiCl molecules; one of them is replaced by one molecule of THF in orange [Nd{CH(SiMe$_3$)Ph}Cl$_2${LiCl·TMEDA}-(THF)]$_2$ (**8**) (Nd−C = 257 pm).



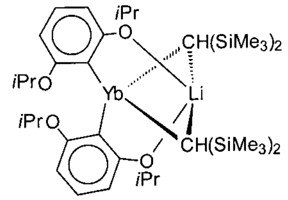
8

When LuCl$_3$ is reacted with 2 equiv of Li(TMEDA)-CH(SiMe$_2t$Bu)Ph in THF, monomeric [Lu{CH(SiMe$_2t$Bu)Ph}$_2$Cl{LiCl·TMEDA}$_2$] (**9**) is isolated. Two LiCl·TMEDA units are built in this highly symmetric structure (Lu−C = 239 pm).[45]



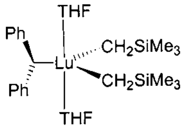
9

Little is known about organolanthanide complexes containing different σ-alkyl ligands. It has been found that a halide ligand bridging an alkali metal and a lanthanide ion can be replaced a bridging methyl group. A structurally characterized example is the heteroleptic anionic samarium complex (PMDETA)-Li(μ-Me)Sm[CH(SiMe$_3$)$_2$]$_3$ with a methyl group bridging Sm and Li (PMDETA = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine).[46] An interesting approach to mixed-ligand organolanthanides containing both σ-alkyl and σ-aryl ligands has been reported by Yasuda et al.[47] This was made possible through the use of the special 2,6-dialkoxyphenyl ligand containing additional donor sites. Ytterbium was chosen from the heavy rare earth metals because of its small ionic radius (0.87 Å). A 2:1 reaction of LiC$_6$H$_3$(OiPr)$_2$-2,6 with anhydrous YbCl$_3$ produced the halide precursor [2,6-(iPrO)$_2$C$_6$H$_3$]$_2$YbCl, which was subsequently treated with 2 equiv of LiCH(SiMe$_3$)$_2$ to give the dark red bimetallic alkyl/aryl complex [2,6-(iPrO)$_2$C$_6$H$_3$]$_2$Yb[μ-CH(SiMe$_3$)$_2$]$_2$Li (**10**). According to molecular weight measurements the compound is monomeric in solution. The coordination sphere around lithium is completed by two interactions between lithium and isopropoxy groups.



10

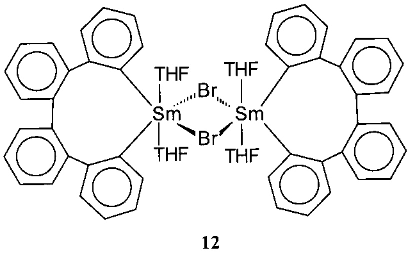
The first neutral lanthanide compound containing two different σ-bonded alkyl ligands (**11**) was synthesized by adding successively 2 equiv of $LiCH_2SiMe_3$ and 1 equiv of $KCHPh_2$ to $LuCl_3$. As two molecules of THF coordinate as well to the Lu center, a trigonal bipyramidal geometry is adopted which is only slightly distorted (Lu−C($CHPh_2$) = 245 pm, O−Lu−O′ = 177°).[22d]



11

Yet another very rare species comprises carbon metallacycles containing a lanthanide atom in the ring. Five-membered "lanthanols" of the composition $(THF)_nLi(\mu\text{-}Cl)_2LnC_4Ph_4$ have been reported for Ln = Nd and Gd but have not been fully characterized.[48] The situation was similar for the metallacyclic products which were obtained from reactions of anhydrous lanthanide tribromides with *o,o*-dilithiobiphenyl. The resulting products were initially formulated as the five-membered metallacycles (biph)LnBr$(THF)_n$.[49] Later a reinvestigation of the reaction of $SmBr_3$ with *o,o*-dilithiobiphenyl revealed the true nature of these materials.[50] Contrary to the originally proposed structure, the product does not contain a five-membered metallacycle. Instead, a dimetalated *o-quater*phenyl ligand is formed through dimerization of the biphenyl dianion (eq 8). Subsequent coordination to samarium results in the formation of a nine-membered metallacyclic ring system. Finally, dimerization via bromide ligands leads to the formation of the binuclear product. Intercalated in the crystal lattice is the hydrocarbon dibenzonaphthacene ($C_{24}H_{14}$) which is formed as a byproduct during the reaction.

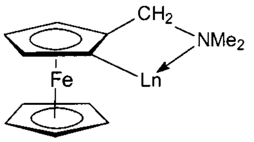
$$6SmBr_3 + 6Li_2(biph) \rightarrow \underset{\mathbf{12}}{[(C_{24}H_{16})Sm(\mu\text{-}Br)(THF)_2]_2\cdot[C_{24}H_{14}]} + 2Sm + 2SmBr_3 + H_2 + 12LiBr \quad (8)$$



12

A highly useful chelating ligand which has been introduced into organolanthanide chemistry about 10 years ago is the 2-((dimethylamino)methyl)ferrocenyl ligand (=FcN).[51] Although FcN derivatives contain cyclopentadienyl rings, there is no η^5 coordination to the lanthanide central atoms involved (Scheme 2). Heteroleptic lanthanide FcN complexes are therefore included in this section.

Scheme 2. Schematic View of Ln−FcN Coordination



Among the hitherto reported organolanthanide complexes with σ-bonded 2-((dimethylamino)methyl)ferrocenyl ligands is the heteroleptic organolanthanide halide derivative $(FcN)_2LaCl$ of unknown structure.[51b] Such heterobimetallic complexes are generally prepared by treatment of anhydrous lanthanide trichlorides with the stoichiometric amounts of Li(FcN) as shown in eq 9.

$$LaCl_3 + 2Li(FcN) \rightarrow (FcN)_2LaCl + 2LiCl \quad (9)$$

Several related heteroleptic organocerium(III) complexes containing FcN ligands have been prepared starting with cerium(IV) precursors.[51c] During the course of these reactions Ce^{4+} is reduced to Ce^{3+} while the dimer $(FcN)_2$ is formed as oxidation product. Equation 10 illustrates a remarkable reaction in which an organocerium(III) compound was prepared for the first time by using CeF_4 as starting material.

$$CeF_4 + 3Li(FcN) \xrightarrow{THF} Li_3[(FcN)_2CeF_4(THF)_3] + {}^1/_2(FcN)_2 \quad (10)$$

The saltlike species $Li_3[(FcN)_2CeF_4(THF)_3]$ contains 3 equiv of LiF, which can be removed by extraction with DME to afford the organocerium(III) fluoride derivative $(FcN)_2CeF(DME)_2$ in form of red-brown, paramagnetic crystals (eq 11).[51c]

$$Li_3[(FcN)_2CeF_4(THF)_3] + 2DME \rightarrow (FcN)_2CeF(DME)_2 + 3LiF \quad (11)$$

The reaction of another cerium(IV) precursor, $[C_5H_5NH]_2[CeCl_6]$, with Li(FcN) is more complex but again involves reduction of Ce^{4+} to trivalent species. $[C_5H_5NH]_2[CeCl_6]$ reacts with 2 or 3 equiv of Li(FcN) finally resulting in the anionic organocerium(III) complex $Li[(FcN)CeCl_3(DME)]$. Scheme 3 illustrates the reaction sequence.[51c]

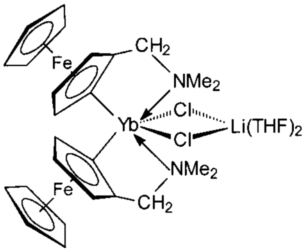
Scheme 3. Formation of $Li[(FcN)CeCl_3(DME)]$[52]

$$[C_5H_5NH]_2[CeCl_6] + 2\,Li(FcN) \xrightarrow{THF} Li_2[CeCl_6] + 2\,C_5H_5N + 2\,FcNH$$

$$Li_2[CeCl_6] + Li(FcN) \longrightarrow Li_3[CeCl_6] + {}^1/_2\,(FcN)_2$$

$$Li_3[CeCl_6] + Li(FcN) \longrightarrow Li_4[(FcN)CeCl_6] \xrightarrow[-3\,LiCl]{DME} Li[(FcN)CeCl_3(DME)]$$

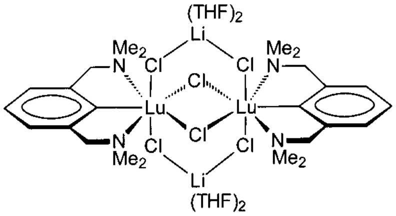
The ytterbium "ate" complex $(FcN)_2Yb(\mu\text{-}Cl)_2Li(THF)_2$ (**13**) was obtained in a similar manner by reacting anhydrous $YbCl_3$ with 2 equiv of Li(FcN).[52] In contrast to $(FcN)_2LaCl$ the heteroleptic ytterbium complex has been accessible to an X-ray structure analysis.



13

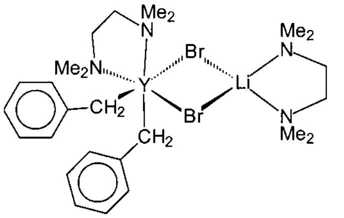
$(FcN)_2Yb(\mu\text{-}Cl)_2Li(THF)_2$ (**13**) was the first bis(organo)lanthanide(III) halide derivative containing only σ-bonded ligands (Yb−C = 265.1, 237.2 pm). This compound resembles the lanthanide metallocenes $(THF)_2Li(\mu\text{-}Cl)_2Ln(C_5Me_5)_2$,[2,3,5] and one can thus expect a comparable reactivity.

Related to the FcN derivatives are complexes containing the chelating tridentate aryldiamine ligand 2,6-bis(dimethylaminomethyl)phenyl, which has been intensively investigated by van Koten et al. A series of lutetium and yttrium complexes of this ligand has been prepared by reacting the corresponding metal trihalides with $2,6\text{-}(Me_2NCH_2)_2C_6H_3Li$. Reactions in a 1:1 molar ratio produced the "ate" complexes $[Ln\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(\mu\text{-}Cl)\{\mu\text{-}Li(THF)_2\}]_2$ (**14**, Ln = Lu, Y) in which the tridentate ligand is coordinated in *mer* fashion and all three chloride ions are retained in the product.[53] The dimeric monoalkyl complex $[Lu\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(\mu\text{-}Cl)(CH_2SiMe_3)]_2$ is accessible by treatment of the lutetium precursor with $LiCH_2SiMe_3$.



14

Due to the comparatively low steric bulk of the σ-benzyl ligand, benzyl complexes of the rare earth elements are little investigated. This is quite in contrast to the situation in the organometallic chemistry of the early transition metals, where σ-benzyl complexes are quite common. A structurally characterized σ-benzyl derivative of yttrium is yellow $(TMEDA)(PhCH_2)_2Y(\mu\text{-}Br)_2Li(TMEDA)$ (**15**), which was prepared by reacting YBr_3 with $PhCH_2Li(TMEDA)$. The coordination geometry around yttrium is distorted octahedral, and the Y−C bond lengths are 241.8(6) and 244.0(6) pm, respectively. Similar reactions of $SmBr_3$ with benzyllithium reagents led to reduction of the Sm^{3+} ion and formation of TMEDA adducts or "ate" complexes of samarium dibromide.[54]



15

B. Organolanthanide Alkoxides and Related Species. Alkoxide ligands have also been demonstrated to stabilize heteroleptic non-cyclopentadienyl organolanthanide complexes. Alkyllanthanide(III) alkoxides form a fairly small, though very promising, class of compounds. Such compounds are of great interest as intermediates in the lanthanide-catalyzed polymerization of 1,3-dienes. A typical multicomponent catalyst system for diene polymerization is $Nd(OiPr)_3/AlEt_3/Et_2AlCl$. From this system the heterobimetallic alkyllanthanide(III) alkoxide $[Nd_6Al_3(\mu\text{-}Cl)_6(\mu\text{-}Et)_9Et_5(OiPr)]_2$ could be isolated and structurally characterized.[55] The complex nature of this catalytically active intermediate underlines the fact that lanthanide alkoxides tend to aggregate as clusters. In most cases the constitution of lanthanide alkoxides is not as simple as implied by the formula "$Ln(OR)_3$".[56] An interesting series of heterobimetallic alkyllanthanide(III) alkoxides has been synthesized in a simple manner by alkylation of lanthanide alkoxides according to eq 12.[57] An alternative route to the yttrium compound $Y[(\mu\text{-}OtBu)(\mu\text{-}Me)AlMe_2]_3$ involves alkylation of the alkoxide cluster $Y_3(OtBu)_9(THF)$ with an excess of trimethylaluminum.[57]

$$Ln(OtBu)_3 + 3AlMe_3 \rightarrow Ln[(\mu\text{-}OtBu)(\mu\text{-}Me)AlMe_2]_3 \quad (12)$$
$$Ln = Y, Pr, Nd$$

The combination of sterically demanding alkyl ligands with bulky alkoxides and phenoxides has led to some interesting heteroleptic cyclopentadienyl-free organolanthanide complexes. One of the first examples was obtained unexpectedly according to eq 13 upon alkylation of a mixed indenylyttrium alkoxide derivative. Lithium indenide is eliminated in the course of the reaction.[59]

$$[(C_9H_7)Y(\mu\text{-}OtBu)(OtBu)]_2 + 4LiCH_2SiMe_3 \xrightarrow[2.\ THF]{1.\ hexane} 2(Me_3SiCH_2)Y[(\mu\text{-}CH_2)_2SiMe_2][(\mu\text{-}OtBu)Li(THF)_2]_2 + 2LiC_9H_7 \quad (13)$$

Other types of mixed-ligand complexes containing both alkyl and alkoxide ligands can be formally anionic "ate" complexes as well as neutral molecules. An anionic alkyl/alkoxide derivative of samarium was made according to eq 14 by treatment of a samarium aryloxide with $LiCH_2SiMe_3$. The product results from an addition reaction of the two components in a molar ratio of 1:2.[60]

$$\mathrm{Sm(OC_6H_3\mathit{i}Pr_2\text{-}2,6)_3(THF)_2 + 2LiCH_2SiMe_3 \xrightarrow{THF} [Li(THF)]_2[Sm(OC_6H_3\mathit{i}Pr_2\text{-}2,6)_3(CH_2SiMe_3)_2]} \quad (14)$$

As shown by Evans et al. such compounds can also be prepared in a more deliberate way directly from the metal trichlorides by reaction with the appropriate amounts of lithium alkyls and lithium alkoxides. Equation 15 illustrates the synthesis of a typical yttrium species.[61]

$$\mathrm{YCl_3 + 2LiCH(SiMe_3)_2 + 2LiO\mathit{t}Bu \xrightarrow{THF} [(Me_3Si)_2CH]_2Y(\mu\text{-}O\mathit{t}Bu)_2Li(THF) + 3LiCl} \quad (15)$$

The colorless crystalline solid was isolated in 54% yield and characterized by X-ray diffraction. The molecule has the expected coordination geometries with a distorted tetrahedral arrangement around yttrium and trigonally planar coordinated lithium.[61]

The combination of a less bulky alkyl group with a sterically highly demanding aryloxide ligand allowed the straightforward preparation of a neutral organoyttrium species (eq 16).[61,62]

$$\mathrm{YCl_3 + 2LiCH_2SiMe_3 + LiOC_6H_3\mathit{t}Bu_2\text{-}2,6 \xrightarrow{THF} (Me_3SiCH_2)_2Y(OC_6H_3\mathit{t}Bu_2\text{-}2,6)(THF)_2 + 3LiCl} \quad (16)$$

Using the proper stoichiometry $\mathrm{(Me_3SiCH_2)_2Y(OC_6H_3\mathit{t}Bu_2\text{-}2,6)(THF)_2}$ is formed in >90% yield. In the solid state the molecule forms a slightly distorted trigonal bipyramid with a O(THF)−Y−O(THF) angle of 172.6° between the axial ligands. The Y−C distances of 241.1(13) and 242.7(16) pm, respectively, are in the normal range.[61]

By adjusting the stoichiometry in eq 16 to a molar ratio of 1:2:2, it was possible to isolate an "ate" complex with this "small alkyl−large aryloxide" ligand combination as well (eq 17).[62] According to a single-crystal X-ray structure analysis the saltlike species contains the unusual $\mathrm{[\{(THF)_3Li\}_2Li]^+}$ cation.

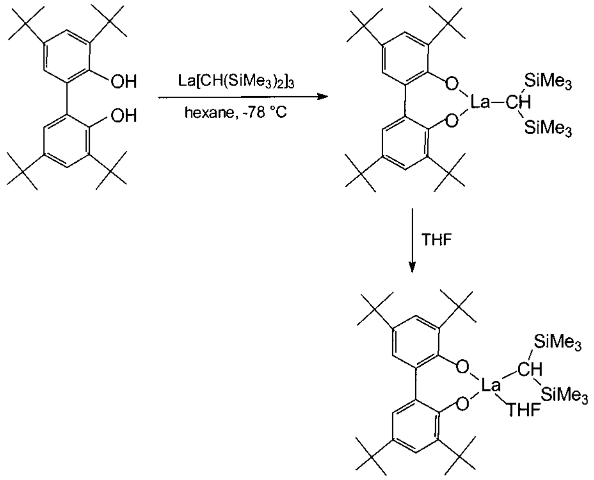
$$\mathrm{YCl_3 + 2LiCH_2SiMe_3 + 2LiOC_6H_3\mathit{t}Bu_2\text{-}2,6 \xrightarrow{THF} [\{(THF)_3Li\}_2Cl][(Me_3SiCH_2)_2Y(OC_6H_3\mathit{t}Bu_2\text{-}2,6)_2] + LiCl} \quad (17)$$

When the same reaction was carried out with lutetium trichloride a closely related saltlike product was isolated which, however, contained a conventional $\mathrm{[Li(THF)_4]^+}$ cation (eq 18). Both the yttrium and lutetium derivatives were structurally characterized by X-ray diffraction. The two ionic complexes as well as $\mathrm{(Me_3SiCH_2)_2Y(OC_6H_3\mathit{t}Bu_2\text{-}2,6)(THF)_2}$ catalyze the ring-opening polymerization of ϵ-caprolactone, but only the latter was found to polymerize ethylene. It also reacts with a large variety of reagents under metalation or insertion. However, isolation of new organoyttrium species from these reactions proved to be difficult due to the complexity of the resulting mixtures.[62]

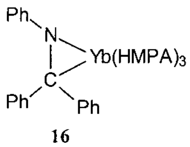
$$\mathrm{YCl_3 + 2LiCH_2SiMe_3 + 2LiOC_6H_3\mathit{t}Bu_2\text{-}2,6 \xrightarrow{THF} [Li(THF)_4][(Me_3SiCH_2)_2Y(OC_6H_3\mathit{t}Bu_2\text{-}2,6)_2]\cdot 2THF + 3LiCl} \quad (18)$$

The use of the sterically demanding chelate ligand 3,3′,5,5′-tetra-*tert*-butylbiphenyl-2,2′-diolate has been found to be an effective way of stabilizing monomeric alkyllanthanide(III) alkoxides. Treatment of the free diol with $\mathrm{La[CH(SiMe_3)_2]_3}$ in hexane solution as shown in Scheme 4 afforded the unsolvated lanthanum σ-alkyl complex $\mathrm{(C_{28}H_{40}O_2)LaCH(SiMe_3)_2}$. This material is still coordinatively unsaturated and readily adds a THF ligand to give the corresponding mono-THF solvate.[63]

Scheme 4. Synthesis of Alkyllanthanum(III) Diolates

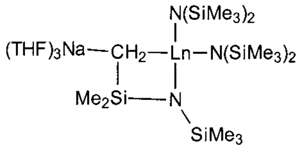


C. Organolanthanide Amides and Related Species. In recent years it has become evident that various types of nitrogen ligands are also capable of stabilizing heteroleptic lanthanide alkyls. Among these ancillary ligands are porphyrins, benzamidinates, alkoxysilylamides, aminotroponiminates, and certain bidentate amide ligands. A very simple though quite unusual organolanthanide compound involving both Ln−C and Ln−N bonding is the ytterbium(II)−imine azametallacyclopropane complex $\mathrm{Yb(\eta^2\text{-}Ph_2CNPh)(HMPA)_3}$ (**16**, HMPA = hexamethylphosphoramide), which has been directly synthesized by reacting Yb metal with $\mathrm{Ph_2C{=}NPh}$ in THF/HMPA and structurally characterized by X-ray diffraction.[64a] Compound **16** is isolated in the form of red-black, extremely air- and moisture-sensitive needles. The Yb−C bond length within the three-membered ring is 267.9(18) pm. The closely related, although dimeric, complex $\mathrm{[Yb(\mu\text{-}\eta^2\text{-}Ph_2CO)(HMPA)_2]_2}$, derived from the benzophenone dianion, had been reported earlier.[64b]



16

Four-membered metallacycles containing rare-earth elements have been reported by Dehnicke et al.[65] Deprotonation of the well-known lanthanide tris[bis(trimethylsilyl)amides] $Ln[N(SiMe_3)_2]_3$ with $NaN(SiMe_3)_2$ afforded the cyclometalated complexes **17** (Ln = Sc, Yb, Lu).



17

In these compounds the lanthanide atoms are constituents of planar four-membered LnCSiN rings. In addition, the carbon atom of the CH_2 group forms a linear Ln–C–Na axis through coordination to the sodium ion. The coordination sphere around sodium is completed by coordination of three THF ligands.

Porphyrin ligands are typical examples of polydentate nitrogen ligands which have been successfully employed in the case of scandium, yttrium, and lutetium as central metals. For example, the chloro complex ScCl(OEP) (OEP = octaethylporphyrin dianion) was made by treatment of $ScCl_3(THF)_3$ with either $[Li(THF)_4][Li(OEP)]$ or $Li_2(OEP)(THF)_2$. ScCl(OEP) is a highly useful starting material for metathetical reactions. The corresponding scandium amides, alkoxides, or σ-alkyl derivatives can be prepared by substitution of the chloride ligand in ScCl(OEP). Alkylation affords the unsolvated alkyl complexes ScR(OEP) (R = Me, CH_2tBu, $CH(SiMe_3)_2$).[66] Apparently the small ionic radius of scandium facilitates the synthesis of porphyrin derivatives. Thus, it is not surprising that porphyrin-stabilized lanthanide alkyls can also be obtained with yttrium and lutetium as central atoms.[66] Thermal reaction of the homoleptic alkyl complexes $Ln[CH(SiMe_3)_2]_3$ with octaethylporphyrin in toluene has been demonstrated to be an elegant and effective access to such complexes (eq 19). This method completely circumvents complications which may arise from solvate formation and/or incorporation of halide ions. Only volatile $CH_2(SiMe_3)_2$ is produced as a byproduct in these reactions.

$$\mathrm{Ln[CH(SiMe_3)_2]_3 + H_2(OEP) \rightarrow (OEP)LnCH(SiMe_3)_2 + 2CH_2(SiMe_3)_2} \quad (19)$$

$$\mathrm{Ln = Y, Lu}$$

An X-ray crystal structure analysis performed on the lutetium derivative $(OEP)LuCH(SiMe_3)_2$ revealed that, as expected, the coordination geometry around lutetium is square-pyramidal. The porphyrin-stabilized lanthanide(III) alkyls $(OEP)LnCH(SiMe_3)_2$ are alternatively accessible by a two-step synthetic procedure, in which the presence of coordinating solvent or alkali metal halides can also be avoided (eqs 20 and 21).[66] Protonation of homoleptic lanthanide tris(aryloxides) with free octaethylporphyrin gave the mono(alkoxide) derivative $(OEP)LnOC_6H_3tBu_2$, which could be treated with $LiCH(SiMe_3)_2$ to produce the desired σ-alkyl complexes besides hydrocarbon-insoluble $LiOC_6H_3tBu_2$-2,6.

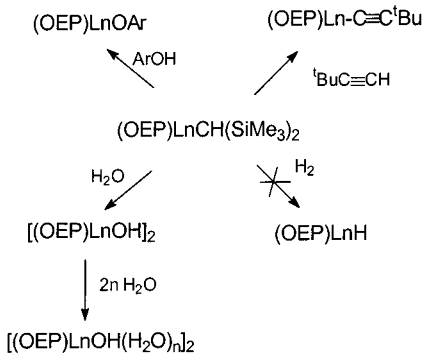
$$\mathrm{Ln(OC_6H_3\mathit{t}Bu_2\text{-}2,6)_3 + H_2(OEP) \rightarrow (OEP)LnOC_6H_3\mathit{t}Bu_2 + 2HOC_6H_3\mathit{t}Bu_2\text{-}2,6} \quad (20)$$

$$\mathrm{(OEP)LnOC_6H_3\mathit{t}Bu_2\text{-}2,6 + LiCH(SiMe_3)_2 \rightarrow (OEP)LnCH(SiMe_3)_2 + LiOC_6H_3\mathit{t}Bu_2\text{-}2,6\downarrow} \quad (21)$$

$$\mathrm{Ln = Y, Lu}$$

The complexes $(OEP)LnCH(SiMe_3)_2$ are highly reactive and thus represent interesting starting materials for subsequent reactions, which are summarized in Scheme 5.[66] Hydrolysis occurs readily and leads to the dimeric hydroxo complexes $[(OEP)LnOH]_2$, while the σ-alkyl groups are easily substituted in reactions with phenols or terminal alkynes. Hydrogenolysis, which was anticipated to afford the corresponding hydrides, could not be achieved even under a hydrogen pressure of 20 bar. This unexpected result is in marked contrast to the chemistry of the related metallocenes $(C_5Me_5)_2LnCH(SiMe_3)_2$, which readily react with molecular hydrogen at normal pressure to give the dimeric hydrides $[(C_5Me_5)_2Ln(\mu\text{-}H)]_2$.[67–69]

Scheme 5. Derivative Chemistry of the Complexes $(OEP)LnCH(SiMe_3)_2$ (Ln = Y, Lu)



The heterobimetallic tetramethylaluminate complex $(OEP)Y(\mu\text{-}Me)_2AlMe_2$ was prepared by subsequent reaction of the yttrium alkoxide (OEP)-$YOC_6H_3tBu_2$ precursor with methyllithium and trimethylaluminum (Scheme 6).[66]

Scheme 6. Synthesis of $(OEP)Y(\mu\text{-}Me)_2AlMe_2$

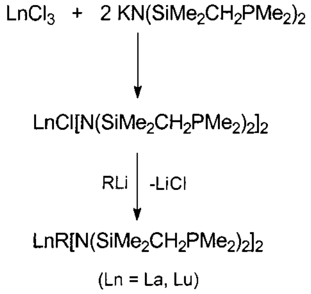
$$\mathrm{(OEP)YOC_6H_3\mathit{t}Bu_2 + 2\,MeLi \xrightarrow{Et_2O} (OEP)Y(\mu\text{-}Me)_2Li(Et_2O) + LiOC_6H_3\mathit{t}Bu_2 \xrightarrow{Al_2Me_6} (OEP)Y(\mu\text{-}Me)_2AlMe_2}$$

The reaction sequence outlined in Scheme 6 parallels the multistep synthesis of $(C_5Me_5)_2LuMe$[70] with the only exception that the final step, i.e. the elimination of trimethylaluminum in the presence of Lewis bases, cannot be reproduced in the porphyrin series. Treatment of $(OEP)Y(\mu\text{-}Me)_2AlMe_2$ with Lewis bases (e.g. pyridine) only leads to the formation of adducts instead of unsolvated (OEP)YMe. O_2 selectively attacks the bridging methyl groups in (OEP)-

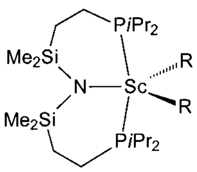
Y(μ-Me)$_2$AlMe$_2$ thereby forming the heterobimetallic alkoxide (OEP)Y(μ-OMe)$_2$AlMe$_2$.

In recent years several heteroleptic organolanthanide complexes containing specially designed amido ligands have been prepared and characterized. For example, a heterobimetallic alkyllanthanide(III) amide is formed upon treatment of Yb$_2$[N(SiMe$_3$)$_2$]$_4$ with 2 equiv of Al$_2$Me$_6$.[71] The reaction product Yb[N(SiMe$_3$)$_2$]$_2$(AlMe$_3$)$_2$ contains four Yb−Me−Al and two Yb−Me−Si bridges. Fryzuk et al. developed the potentially tridentate silylamide anion [N(SiMe$_2$CH$_2$PMe$_2$)$_2$]$^-$ and were able to successfully employ this ligand in organolanthanide chemistry.[72−74] The stepwise preparation of heteroleptic alkyllanthanide(III) amides is illustrated in Scheme 7. The σ-alkyl complexes LnR[N(SiMe$_2$CH$_2$PMe$_2$)$_2$] (Ln = La, Lu) are fluxional in solution and decompose upon heating under elimination of the hydrocarbon RH.

Scheme 7. Synthesis of LnR[N(SiMe$_2$CH$_2$PMe$_2$)$_2$]$_2$



While the preparation of bis(ligand) lanthanide alkyls was straightforward, the synthesis of bis(σ-alkyl)lanthanide complexes containing only *one* chelating ligand proved to be more difficult. Finally such complexes became available by combining the very bulky silylamide anion [N{SiMe$_2$(CH$_2$)$_2$P*i*Pr$_2$}$_2$]$^-$ with the small Sc^{3+} ion.[75] The complexes [N{SiMe$_2$(CH$_2$)$_2$P*i*Pr$_2$}$_2$]ScR$_2$ (**18**; R = Me, Et, CH$_2$SiMe$_3$) have been prepared be alkylation of the chloro precursor [N{SiMe$_2$(CH$_2$)$_2$P*i*Pr$_2$}$_2$]ScCl$_2$(THF). The resulting colorless dialkyl derivatives are extremely soluble in all hydrocarbons and can only be recrystallized with difficulty from hexamethyldisiloxane. Two representatives (R = Et and CH$_2$SiMe$_3$) were structurally characterized by X-ray diffraction. The dialkyls are mononuclear in the solid state with distorted trigonal-bipyramidal geometries. These materials are 12-electron complexes assuming that the chelating amido ligand is a four-electron donor.



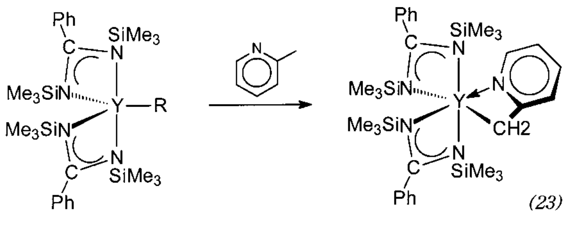
18

Hydrotris(pyrazol-1-yl)borate anions (scorpionates) have become quite popular ligands in lanthanide coordination chemistry. Takats et al. made use of the sterically demanding anion [HB(3-*t*Bu-5-Me-pz)$_3$]$^-$ to prepare soluble, monosubstituted ytterbium(II) alkyl complexes.[76] The compounds [HB(3-*t*Bu-5-Me-pz)$_3$]YbCH(SiMe$_3$)$_2$ and [HB(3-*t*Bu-5-Me-pz)$_3$]Yb[CH(SiMe$_3$)$_2$](Et$_2$O) have been made by treatment of the halide precursor [HB(3-*t*Bu-5-Me-pz)$_3$]YbI(THF) with the corresponding alkyllithium reagents. These two compounds represent rare examples of heteroleptic organolanthanide(II) complexes with σ-bonded alkyl ligands.

Bulky heteroallylic ligands such as the benzamidinate anions [RC$_6$H$_4$C(NSiMe$_3$)$_2$]$^-$ have recently been established as useful alternatives to the cyclopentadienyl ligands. Thus, the yttrium(III) benzamidinates [RC$_6$H$_4$C(NSiMe$_3$)$_2$]$_2$YCH(SiMe$_3$)$_2$ can be regarded as analogues of the metallocene alkyls (C$_5$Me$_5$)$_2$YCH(SiMe$_3$)$_2$. All these compounds exhibit comparable catalytic activities, e.g. in olefin polymerizations. Synthetically the alkyl derivatives are easily accessible by alkylation of the corresponding chloride or triflate precursors according to eq 22.[77−80]

$$\begin{gathered}[RC_6H_4C(NSiMe_3)_2]_2YX(THF)_n + LiCH(SiMe_3)_2 \\ X = Cl,\ n = 1 \\ X = O_3SCF_3,\ n = 0 \\ \xrightarrow{-LiX} [RC_6H_4C(NSiMe_3)_2]_2YCH(SiMe_3)_2 \quad (22) \\ R = H,\ OMe,\ CF_3\end{gathered}$$

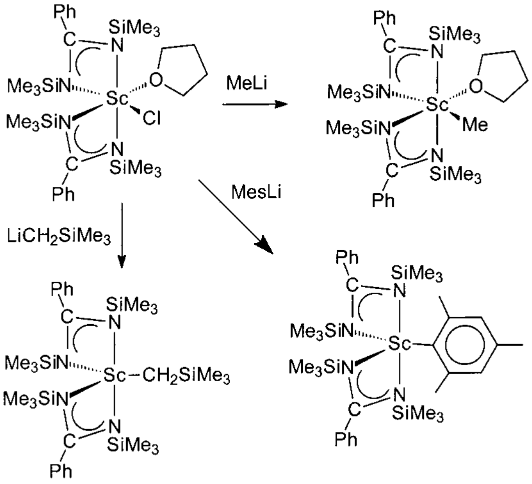
Other σ-alkyl yttrium complexes of this type include [PhC(NSiMe$_3$)$_2$]$_2$YCH$_2$Ph(THF) and [PhC(NSiMe$_3$)$_2$]$_2$Y(μ-Me)$_2$Li(TMEDA). The *p*-methoxy-substituted derivative [MeOC$_6$H$_4$C(NSiMe$_3$)$_2$]$_2$YCH(SiMe$_3$)$_2$ has been characterized by an X-ray structure determination. This study confirmed that the bis[*N*,*N*′-bis(trimethylsilyl)benzamidinate] ligand system sterically resembles more the bis(pentamethylcyclopentadienyl) than the bis(cyclopentadienyl) ligand set. The reactivity of the benzamidinate-stabilized yttrium complexes toward various reagents including hydrogen, ethylene, terminal alkynes, nitriles, and pyridine derivatives has been investigated in detail.[80,81] Hydrogenolysis of the yttrium alkyls in benzene under 4 bar of H$_2$ afforded the dimeric hydride [{RC$_6$H$_4$C(NSiMe$_3$)$_2$}$_2$Y(μ-H)]$_2$.[80] Both [PhC(NSiMe$_3$)$_2$]$_2$YCH$_2$Ph(THF) and [{RC$_6$H$_4$C(NSiMe$_3$)$_2$}$_2$Y(μ-H)]$_2$ are modestly active in ethylene polymerization but do not react with propylene and 1-hexene. Acetylide derivatives will be discussed in section 3. Treatment of [PhC(NSiMe$_3$)$_2$]$_2$YR with acetonitrile gives either C−H bond activation or insertion, but the resulting products do not contain Y−C bonds and will thus not be considered here. The alkyls and the hydride react with α-picoline according to eq 23 to give an α-picolyl derivative.[81]



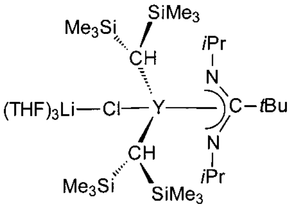
(23)

Closely related benzamidinate chemistry has also been investigated with scandium as central ion.[82] Due to its small ionic radius Sc^{3+} readily forms disubstituted benzamidinate complexes, which give rise to some interesting derivative chemistry. The main starting material is the chloro complex $[PhC(NSiMe_3)_2]_2ScCl(THF)$, which is easily obtained by the reaction of $Na[PhC(NSiMe_3)_2]$ with $ScCl_3(THF)_3$ in THF. The preparation of alkyl and aryl derivatives is illustrated in Scheme 8.

Scheme 8. Preparation of Bis(benzamidinato)scandium Alkyls and Aryls[82]



In the case of the methyllithium reaction the product is a THF solvate while with bulky hydrocarbyls unsolvated complexes are obtained. The compound $[PhC(NSiMe_3)_2]_2ScCH_2SiMe_3$ readily reacts with H_2 to form the dimeric hydride $[\{PhC(NSiMe_3)_2\}_2Sc(\mu\text{-}H)]_2$.[82] Especially notable among the most recent developments in lanthanide amidinate chemistry is the successful synthesis of stable *mono*-(amidinato)yttrium *di*alkyls. The synthetic strategy involved the use of the sterically hindered amidinate ligand $[tBuC(NiPr)_2]^-$ as well as a tridentate "pendant-arm" amidinate.[83,84] The first complex was prepared by a sequential reaction of $YCl_3(THF)_{3.5}$ with $Li[tBuC(NiPr)_2]$ (1 equiv) and 2 equiv of $LiCH(SiMe_3)_2$ followed by pentane extraction. Large crystals of $[tBuC(NiPr)_2]Y[CH(SiMe_3)_2]_2(\mu\text{-}Cl)Li(THF)_3$ (**19**) were isolated in 83% yield and structurally characterized by X-ray methods.



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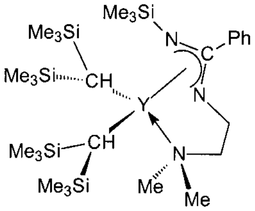
An interesting and very promising variation is the synthesis and use of potentially tridentate aminoamidinate ligands, $[PhC(NSiMe_3)N(CH_2)_nNMe_2]^-$ (n = 2, 3), which resemble the well-known "pendant-arm" substituted cylopentadienyl ligands. In the same manner as outlined above the salt-free mono(amidinato)yttrium dialkyls $[PhC(NSiMe_3)N(CH_2)_nNMe_2]Y[CH(SiMe_3)_2]_2$ (n = 2, 3) were synthesized, of which the derivative with n = 2 (**20**) was characterized by single-crystal X-ray diffraction. As expected, the new ligand is indeed tridentate adopting an approximately meridional coordination mode.[83,84]

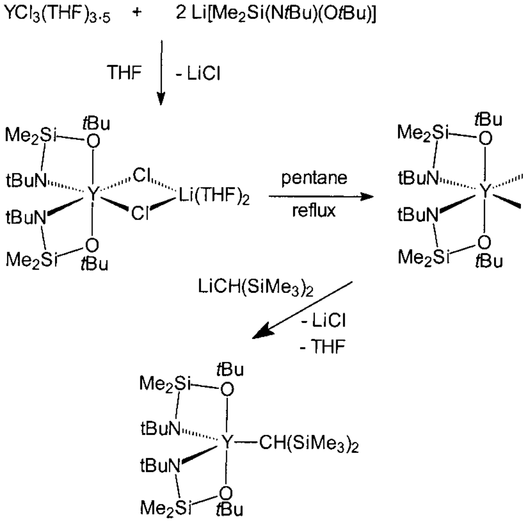


20

Closely related to the benzamidinates are guanidinato complexes which contain an amine functional group at the central carbon atom of the NCN chelate system. Such anions have also been found to stabilize certain heteroleptic lanthanide alkyls.[85] A suitable guanidinate ancillary ligand was generated by the reaction of 1,3-dicyclohexylcarbodiimide with 1 equiv of $LiN(SiMe_3)_2$ in diethyl ether. Subsequent reaction with anhydrous lanthanide trichlorides (molar ratio 2:1) afforded the "ate" complexes $[CyNC\{N(SiMe_3)_2\}NCy]_2Ln(\mu\text{-}Cl)_2Li(Et_2O)_2$ (Ln = Sm, Yb). Replacement of chloride and formation of solvent-free alkyl complexes was achieved by metathetical reactions with $LiCH(SiMe_3)_2$. The compounds $[CyNC\{N(SiMe_3)_2\}NCy]_2LnCH(SiMe_3)_2$ were obtained in high yields. The molecular structure of the samarium derivative was established by X-ray diffraction (Sm−C = 247.2(5) pm).

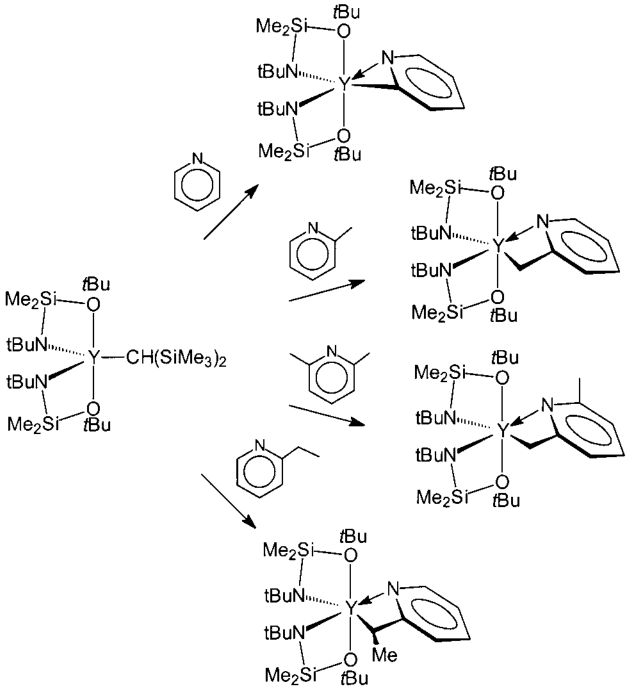
A diverse organoyttrium chemistry has been developed by Teuben et al.[86,87] using the bidentate, anionic *N*,*O*-bis(*tert*-butyl)(alkoxydimethylsilyl)amido ligand which is based on earlier work by Veith et al.[88] Scheme 9 illustrates the preparation of the starting materials and a monomeric yttrium alkyl stabilized by the $[Me_2Si(NtBu)(OtBu)]_2$ ligand set.[86]

Scheme 9. Preparation of the Yttrium Alkyl $[Me_2Si(NtBu)(OtBu)]_2YCH(SiMe_3)_2$[86]



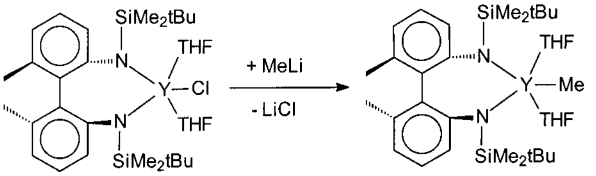
Multigram quantities of the bimetallic chloro complex $[Me_2Si(NtBu)(OtBu)]_2Y(\mu\text{-}Cl)_2Li(THF)_2$ could be obtained by reacting $YCl_3(THF)_{3.5}$ with the lithium salt of the ligand in a 1:2 molar ratio. The compound is very similar to the related bis[(alkoxysilyl)amido] derivatives $[Me_2Si(N\mathit{t}Bu)(O\mathit{t}Bu)]_2Ln(\mu\text{-}X)_2Li(THF)_2$ (Ln = Yb, X = Cl; Ln = Sm, X = I) reported earlier.[89] The complexed LiCl can easily be removed by refluxing the "ate" complex in pentane to give $[Me_2Si(N\mathit{t}Bu)(O\mathit{t}Bu)]_2YCl(THF)$. Subsequent alkylation with $LiCH(SiMe_3)_2$ afforded monomeric, unsolvated $[Me_2Si(N\mathit{t}Bu)(O\mathit{t}Bu)]_2YCH(SiMe_3)_2$, which was characterized by an X-ray structure determination (Y−C = 255.8(19) pm). All these complexes are thermally stable at room temperature though highly air sensitive.[86] The reactivity of the alkyl complex $[Me_2Si(N\mathit{t}Bu)(O\mathit{t}Bu)]_2YCH(SiMe_3)_2$ toward various reagents has been investigated in great detail.[86,87] Novel organoyttrium species are formed in C−H activation reactions with pyridines and substituted pyridines. These are summarized in Scheme 10.

Scheme 10. C−H Activation of Pyridine Derivatives by $[Me_2Si(N\mathit{t}Bu)(O\mathit{t}Bu)]_2YCH(SiMe_3)_2$[87]



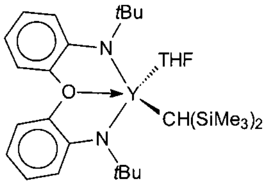
All products shown in Scheme 10 can be alternatively prepared by salt metathesis reactions between $[Me_2Si(N\mathit{t}Bu)(O\mathit{t}Bu)]_2YCl(THF)$ and the corresponding lithiopyridines. An X-ray crystal structure determination of the α-picolyl derivative $[Me_2Si(N\mathit{t}Bu)(O\mathit{t}Bu)]_2Y[\eta^3\text{-}(\mathit{C,C,N})\text{-}CH_2\text{-}2\text{-}NC_5H_4]$ revealed that the picolyl group is bonded to yttrium in a distorted η^3-(*C,C,N*)-azaallylic fashion. The reactivity of these C−H activation products toward various reagents such as ethylene, phenylacetylene, nitriles, and CO has been investigated in detail. In the case of phenylacetylene well-defined yttrium alkynyl complexes are formed (cf. section 3).[87]

In recent years several other chelating amido ligands have been designed to be used as alternative ligand sets in organolanthanide chemistry, especially with the aim of synthesizing highly reactive non-cyclopentadienyl organolanthanide alkyls and hydrides. A typical example of such chelating amides is 2,2′-bis[(*tert*-butyldimethylsilyl)amido]-6,6′-dimethylbiphenyl) (=DADMB).[90,91] This chelating, C_2-symmetric ligand is readily available via standard procedures starting from 2,2′-diamino-6,6′-biphenyl and used as its dilithium derivative. The dilithium salt reacts with $YCl_3(THF)_3$ in refluxing THF to give the chloro precursor $(DADMB)YCl(THF)_2$ in 92% yield. The corresponding methyl derivative was synthesized according to eq 24 in 60% yield as an off-white crystalline solid by subsequent treatment with MeLi in Et_2O/THF.[90]



(24)

$(DADMB)YMe(THF)_2$ reacts with phenylsilane or H_2 to give the insoluble, dimeric yttrium hydride $[(DADMB)Y(\mu\text{-}H)(THF)]_2\cdot C_6H_6$, which is an effective olefin hydrosilylation catalyst.[90,91] A closely related, though potentially tridentate diamido ligand, $[(\mathit{t}BuN\text{-}\mathit{o}\text{-}C_6H_4)_2O]^{2-}$ $(=[NON]^{2-})$, was introduced into organolanthanide chemistry by Schrock et al.[92] The dilithium salt $Li_2[NON]$ reacts with YCl_3 in THF to give $[NON]YCl(THF)_2$ in high yield (75%). Starting from this chloro precursor two stable yttrium alkyls, $[NON]Y(CH_2SiMe_3)(THF)_2$ and $[NON]Y[CH(SiMe_3)_2](THF)$ (**21**), could be prepared straightforwardly by treatment with the respective alkyllithium reagents. An X-ray structure analysis of $[NON]Y[CH(SiMe_3)_2](THF)$ revealed the presence of a distorted five-coordinate species in which the nitrogen atoms of the $[NON]^{2-}$ ligand approximately occupy apical sites in a trigonal bipyramid.

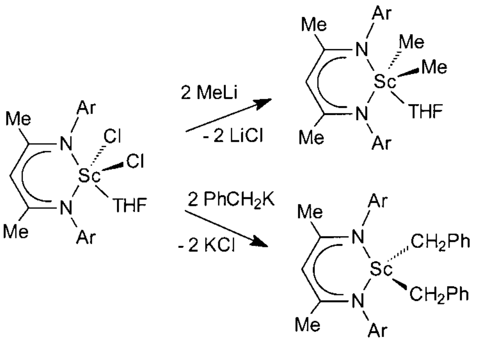


21

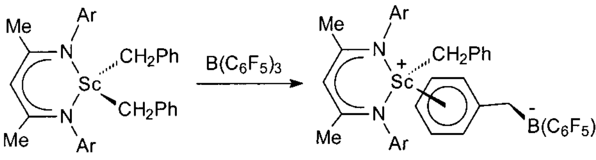
Monoanionic β-diketiminato ligands, ArNC(R)CHC(R)NAr, are ideal for use with metals in the +3 oxidation state and have recently been employed for the synthesis of novel dialkylscandium complexes.[93] Treatment of $ScCl_3(THF)_3$ with the lithium salt of the ligand with Ar = 2,6-$\mathit{i}Pr_2C_6H_3$ and R = Me gave $[ArNC(Me)CHC(Me)NAr]ScCl_2(THF)$, while in the case of R = *t*Bu the THF-free scandium dichloride derivative was obtained. The compound $[ArNC(Me)CHC(Me)NAr]ScCl_2(THF)$ could be smoothly alkylated with conventional alkyllithium or potassium reagents. Use of methyllithium affords the THF-ligated dimethyl derivative whereas an unsolvated dibenzyl complex is formed upon treatment with 2 equiv of benzylpotassium (Scheme 11).[93] Although the latter is formally an eight-electron complex, the NMR data suggest that there is no multihapto bonding between scandium and the benzyl ligands.

As part of the search for novel olefin polymerization catalysts, the dibenzyl compound was treated with

Scheme 11. Preparation of [ArNC(Me)CHC(Me)NAr]ScMe$_2$(THF) and [ArNC(Me)CHC(Me)NAr]Sc(CH$_2$Ph)$_2$[93]



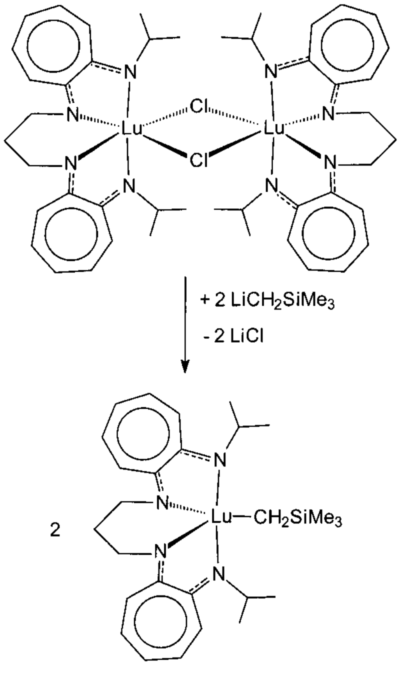
$B(C_6F_5)_3$. As depicted in eq 25, this reaction afforded an ion pair, in which the Sc^{3+} center is stabilized by an η^6-aryl interaction with the abstracted borate benzyl group. Apparently this η^6-coordinated benzyl group is quite strongly attached in this system as the compound was found to be totally unreactive toward H_2 or ethylene, even at elevated temperature.[93]



(25)

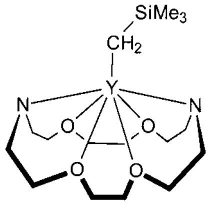
Aminotroponiminates are a most recent addition to the range of useful nitrogen-based ligands which are capable of stabilizing non-cyclopentadienyl organolanthanides. The tetradentate bis(aminotroponiminato) ligand 1,3-bis[2-(isopropylamino)-troponiminate]propane (=[*i*PrTP]$^{2-}$) has been successfully employed in the synthesis of a monomeric lutetium alkyl.[94] The reaction of K$_2$[*i*PrTP] with lutetium trichloride afforded the dimeric chloro-bridged complex [(*i*PrTP)Lu(μ-Cl)]$_2$, which was isolated in the form of yellow crystals (77% yield). Conversion into a stable lutetium alkyl complex was achieved by subsequent reaction with LiCH$_2$SiMe$_3$ in toluene to give (*i*PrTP)LuCH$_2$SiMe$_3$ in 60% yield (eq 26). The analogous lanthanum alkyl (*i*PrTP)LaCH$_2$-SiMe$_3$ was made by following the same reaction sequence.[95] Due to the larger ionic radius of La^{3+} as compared to Lu^{3+} the chloride precursor [(*i*PrTP)La-(μ-Cl)(THF)]$_2$ contains two additional THF ligands per dimeric unit. However, as in the lutetium case, a subsequent alkylation reaction with LiCH$_2$SiMe$_3$ afforded the unsolvated σ-alkyl derivative (iPrTP)-LaCH$_2$SiMe$_3$ (86% yield).

Other polydentate nitrogen-based ligands capable of stabilizing monomeric and solvent-free σ-alkyl complexes of the group 3 and rare earth elements are deprotonated azacrown ethers.[96,97] A convenient salt-free route (eq 27) was chosen to synthesize the yttrium alkyl species (DAC)Y(CH$_2$SiMe$_3$) (**22**, DAC = deprotonated 4,13-diaza-18-crown-6). Colorless crystalline **22** is very air and moisture sensitive and slowly decomposes at room temperature. The monomeric nature of this complex was confirmed by an X-ray diffraction analysis.[96]



(26)

$$Y(CH_2SiMe_3)_3(THF)_2 + H_2DAC \xrightarrow{\text{toluene}} \underset{\mathbf{22}}{(DAC)Y(CH_2SiMe_3)} + 2SiMe_4 + 2THF \quad (27)$$



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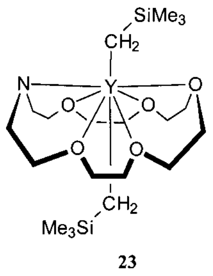
With 245(2) pm the Y−C bond length in (DAC)Y-(CH$_2$SiMe$_3$) is comparable to that found in (C$_5$Me$_5$)$_2$Y-[CH(SiMe$_3$)$_2$].[68] The use of the monoanionic ligand deprotonated aza-18-crown-6 (=MAC) allowed the synthesis of a related yttrium dialkyl species, *trans*-(MAC)Y(CH$_2$SiMe$_3$)$_2$ (**23**).[97] Once again Y(CH$_2$SiMe$_3$)$_3$-(THF)$_2$ was used as as convenient halide-free precursor and treated with the protonated free ligand as shown in eq 28.

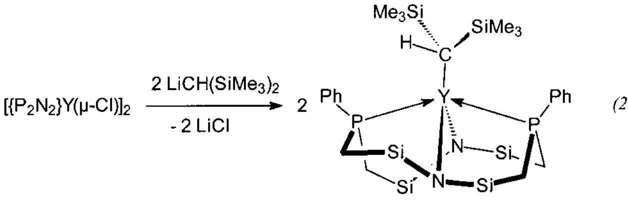
$$Y(CH_2SiMe_3)_3(THF)_2 + HMAC \xrightarrow{\text{toluene}} \underset{\mathbf{23}}{trans\text{-}(MAC)Y(CH_2SiMe_3)_2} + SiMe_4 + 2THF \quad (28)$$



23

The colorless crystalline dialkyl complex **23** was obtained in 76% yield, and its molecular structure was elucidated by an X-ray diffraction analysis. The Y−C distance in this compound is 246.1(4) pm. *trans*-(MAC)Y(CH_2SiMe_3)$_2$ (**23**) reacts smoothly with CO to yield the bis(enolate) complex *trans*-(MAC)-Y[OC($SiMe_3$)=CH_2]$_2$ via CO insertion and rearrangement of the originally formed acyl complex. The yttrium dialkyl was also found to undergo alkyl abstraction upon treatment with B(C_6F_5)$_3$ in THF to generate the cationic species [(MAC)Y(CH_2SiMe_3)]$^+$-[B(C_6F_5)$_3$(CH_2SiMe_3)]$^-$. However, this salt was found to be highly unstable and could not be isolated as a pure material.[97]

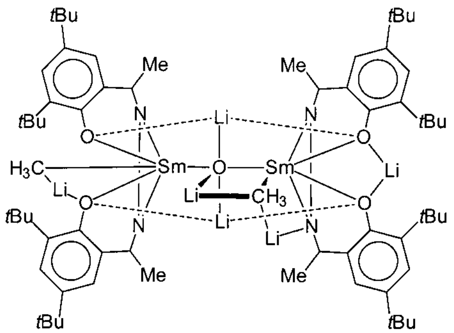
Fryzuk et al. have developed a remarkable organoyttrium chemistry around the phosphorus-containing macrocycle *syn*-{P_2N_2} ({P_2N_2} = [PhP(CH_2SiMe_2-$NSiMe_2CH_2$)$_2$PPh]$^{2-}$).[98] The starting material was the chloride-bridged dimer [{P_2N_2}Y(μ-Cl)]$_2$, which can be prepared in 95% yield by the reaction of *syn*-Li_2(THF){P_2N_2} with YCl_3(THF)$_3$ in THF solution. Straightforward metathesis using the very bulky alkyllithium reagent LiCH($SiMe_3$)$_2$ according to eq 29 (methyl groups on Si omitted for clarity) afforded the monomeric yttrium alkyl species {P_2N_2}YCH-($SiMe_3$)$_2$ in 92% yield.



(29)

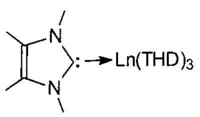
Use of the less sterically hindered alkyl moiety CH_2SiMe_3 followed by addition of THF resulted in formation of the THF adduct {P_2N_2}YCH_2SiMe_3-(THF), whereas the THF-free compound could only be isolated as a highly reactive oily material.[98]

A quite remarkable samarium alkyl complex of complicated molecular structure was reported by Gambarotta et al.[99] Samarium diiodide acted as reducing agent in the reaction with (phenylenebis(3,5-*t*Bu_4-salicylidene)iminato)sodium, (3,5-*t*Bu_4salophen)Na_2(THF)$_3$, to give dimeric [Sm_2(SB−SB)(THF)$_3$]·2toluene (SB−SB = C−C bonded 3,5-*t*Bu_4salophen dimer). The new ligand resulted from the reductive coupling of two imino functional groups of two 3,5-*t*Bu_4salophenSm units. Subsequent treatment with MeLi resulted in a novel oxo-bridged dimer (**24**), featuring alkylation of both samarium atoms and arising from cleavage of the C−C bond connecting the two units, as well as complete reduction of the imine groups of the salophen ligands and THF deoxygenation. In the formula drawing depicted here the bridging phenylene rings are omitted for clarity.[99]



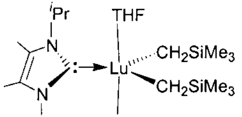
24

Carbene complexes of the lanthanide elements have first become available through the use of the stable Arduengo-type carbenes.[100,101] Organolanthanide derivatives are readily accessible by adding the heterocyclic carbene ligands to various di- and trivalent rare earth complexes such as decamethylsamarocene. Cyclopentadienyl-free derivatives have been obtained by reacting 1,3,4,5-tetramethylimidazol-2-ylidene with the tris(2,2,6,6-tetramethylheptane-3,5-dionato) complexes of yttrium and europium, Ln(THD)$_3$ (Ln = Y, Eu). The two carbene complexes **25** were isolated as white solids in quantitative yield. The europium complex was structurally characterized by X-ray analysis.



25, Ln = Y, Eu

Despite the differences in the ionic radii of the two metals 7-coordinate monocarbene adducts are formed in both cases. With 266.3(4) pm the Eu−C distance in (1,3,4,5-tetramethylimidazol-2-ylidene)Eu(THD)$_3$ is comparable to Pr(III)−C and Sm(III)−C distances reported for some isonitrile complexes.[102,103] In the ^{13}C NMR spectrum of the yttrium complex the resonance for the former carbene carbon is at δ 199.38 (cf. δ 214 for the free carbene ligand) and shows a ^{13}C−^{89}Y coupling of 33 Hz which indicates that the Y−C bond does not dissociate rapidly on the NMR time scale.[101] The bulkier 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (^{i}Pr−Carb) has been used to synthesize a mixed carbene−THF alkyl Lu(CH_2-$SiMe_3$)$_3$(THF)(^{i}Pr−Carb) (**26**).[22d] Due to its higher steric demand, the carbene ligand occupies an equatorial position (Lu−C(Carb) = 249 pm).



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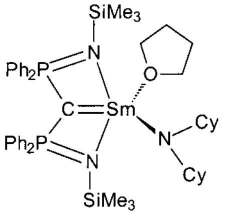
Somewhat related to the carbene complexes is a highly unusual monomeric samarium bis(iminophosphoranyl) chelate complex which has been reported by Cavell et al.[104] Addition of H_2C(Ph_2P=$NSiMe_3$)$_2$ to a toluene solution of samarium tris(dicyclohexylamide) afforded bright yellow [κ^3-*C*,*N*,*N'*-C(Ph_2P=$NSiMe_3$)$_2$]Sm(NCy_2)(THF) (**27**). The core of the molecule consists of two nearly planar, fused four-membered rings with a Sm−C shared edge. With 246.7(4) pm the Sm−C bond length is considerably shorter (10%) than the average samarium−carbon distances, indicating that **27** can be formulated as a carbene complex.



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3. Alkenyl and Alkynyl Complexes

Well-characterized alkenyl complexes remain a relatively unexplored class of organolanthanide complexes. Metallic ytterbium was reported to react with $Hg(CH{=}CHCl)_2$ to give the insufficiently characterized bis(β-chlorovinyl)ytterbium.[105] Cyclopentadienyl-free σ-alkenyl lanthanide complexes have been postulated as intermediates in the alkyne hydroamination catalyzed by (aminotroponiminato)yttrium amides.[106] A rare example of a well-characterized σ-alkenyl derivative is the bis(benzamidinato)scandium complex $[PhC(NSiMe_3)_2]_2ScC(Ph){=}C(Ph)H$, which was synthesized by reacting the dimeric hydride $[\{PhC(NSiMe_3)_2\}_2Sc(\mu\text{-}H)]_2$ with diphenylacetylene.[82]

Reaction of samarium diiodide with metallic Li and *trans*-stilbene (molar ratio 1:2:2) in DME according to eq 30 produced the stilbene complex of divalent samarium $(PhCHCHPh)Sm(DME)_2$. The dark brown crystalline product was isolated in 63% yield.[107]

$$SmI_2(THF)_2 + 2Li + 2\textit{trans}\text{-}PhCH{=}CHPh \xrightarrow{DME} (PhCHCHPh)Sm(DME)_2 + 2LiI + 2THF \quad (30)$$

$(PhCHCHPh)Sm(DME)_2$ is extremely sensitive to oxygen and moisture and is highly reactive. It reacts with hydrogen in THF solution under pressure to give a solvated samarium dihydride (red-brown amorphous powder) besides 1,2-diphenylethane (eq 31).[107]

$$(PhCHCHPh)Sm(DME)_2 + H_2 \xrightarrow{THF} SmH_2(THF)_2 + PhCH_2CH_2Ph + 2DME \quad (31)$$

Treatment of $(PhCHCHPh)Sm(DME)_2$ with hexamethyldisilazane according to eq 32 afforded the Sm(II) silylamide $[(Me_3Si)_2N]_2Sm(DME)_2$ as dark violet crystals in 60% yield.[107]

$$(PhCHCHPh)Sm(DME)_2 + 2(Me_3Si)_2NH \xrightarrow{DME} [(Me_3Si)_2N]_2Sm(DME)_2 + PhCH{=}CHPh + H_2 \quad (32)$$

The chemistry of lanthanide alkynyl complexes has made significant progress in recent years. A well-defined alkynyl complex of divalent ytterbium could be synthesized by using the sterically demanding hydrotris(3,5-dimethylpyrazol-1-yl)borate ligand. Dark red $[HB(3,5\text{-}Me_2pz)_3]YbC{\equiv}CPh$ was obtained in high yield by protonation of $[HB(3,5\text{-}Me_2pz)_3]Yb[N(SiMe_3)_2]$ with phenylacetylene.[76] There are also early reports in the literature that the blue solutions of metallic europium or ytterbium in liquid ammonia react with terminal alkynes to give bis(alkynyl)lanthanide(II) complexes. Alkynyl derivatives of divalent europium and ytterbium are also available via transmetalation reactions in which $Hg(C{\equiv}CR)_2$ is reacted with the corresponding metals according to eq 33.[108,109]

$$Ln + Hg(C{\equiv}CR)_2 \xrightarrow{THF} Ln(C{\equiv}CR)_2 + Hg \quad (33)$$

$$R = nBu,\ Ln = Eu, Yb; \quad R = Ph,\ Ln = Yb$$

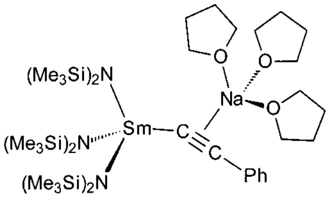
In the case of trivalent lanthanides the tris(alkynyl) complexes $Lu(C{\equiv}CtBu)_3$[110] and $Ln(C{\equiv}CPh)_3$ (Ln = Pr, Sm, Eu, Gd, Tb, Er, Yb)[111,112] have been described. Although virtually nothing is known about the molecular structures of all these compounds, it is very likely, however, that the unsolvated species $Ln(C{\equiv}CR)_2$ and $Ln(C{\equiv}CR)_3$ are polymeric materials with bridging alkynyl ligands.

In recent years various nitrogen-based donor ligands have been found to stabilize novel types of heteroleptic lanthanide alkynyl complexes. A straightforward access to a series of alkynyllanthanide amides has been reported by Dehnicke et al.[113] The homoleptic tris(silylamides) of cerium, samarium, and europium react with phenylacetylene in THF solution in the presence of $NaN(SiMe_3)_2$ as deprotonating agent according to eq 34 to give the novel bimetallic alkynyllanthanide amides $[(Me_3Si)_2N]_3Ln(\mu\text{-}C{\equiv}CPh)Na(THF)_3$.

$$Ln[N(SiMe_3)_2]_3 + PhC{\equiv}CH + NaN(SiMe_3)_2 \xrightarrow{THF} [(Me_3Si)_2N]_3Ln(\mu\text{-}C{\equiv}CPh)Na(THF)_3 + HN(SiMe_3)_2 \quad (34)$$

$$Ln = Ce, Sm, Eu$$

All three compounds have been isolated in excellent yields (95−98%) in the form of red, moisture-sensitive crystalline solids. A single-crystal X-ray structure determination of the samarium derivative revealed the presence of a bimetallic complex (**28**) with the phenylacetylide ligand bridging samarium and sodium.[113]



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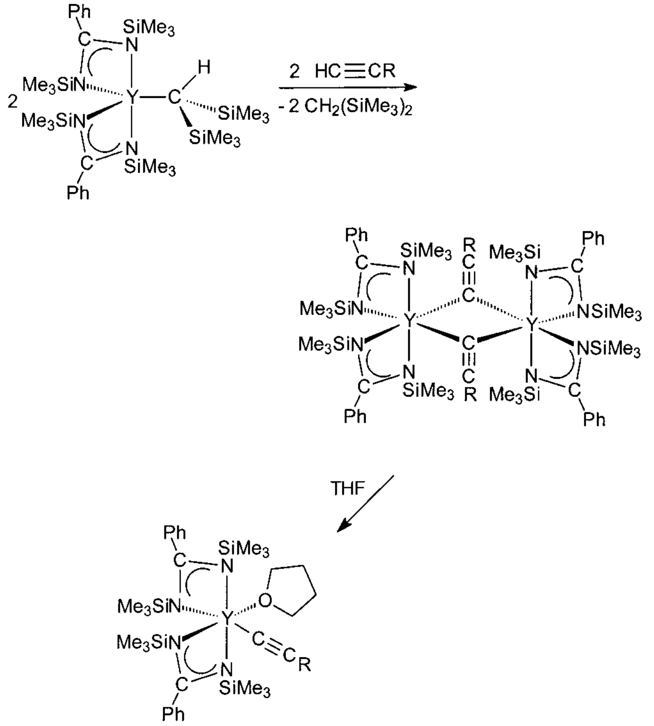
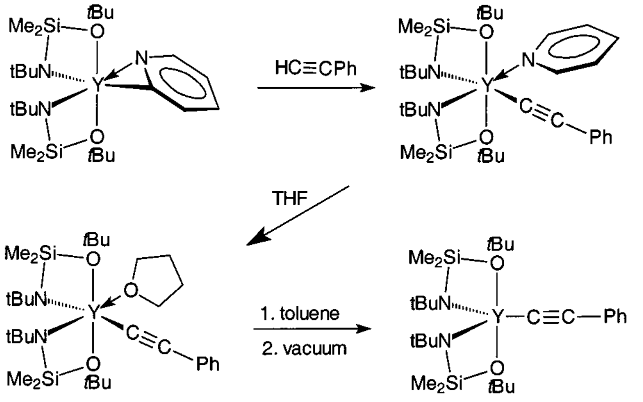
Well-defined dimeric μ-ethynyl complexes of yttrium are formed by protolysis of the alkyl derivative $[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2$ or the corresponding hydride with terminal alkynes (R = H, Me, *n*Pr, *t*Bu, $SiMe_3$, Ph) as illustrated in Scheme 12.[77,81] The solid-state structure of $[\{PhC(NSiMe_3)_2\}_2Y(\mu\text{-}C{\equiv}CH)]_2$ with bridging ethynyl ligands has been verified by an X-ray crystal structure analysis.

Scheme 12 shows that treatment with THF leads to cleavage of these dimers, yielding $[PhC(NSiMe_3)_2]_2YC{\equiv}CR(THF)$ (R = H, *t*Bu). Protonation of $[PhC(NSiMe_3)_2]_2Y(\mu\text{-}Me)_2Li(TMEDA)$ with $HC{\equiv}CtBu$ afforded the bimetallic acetylide complex $[PhC(NSiMe_3)_2]_2Y(\mu\text{-}C{\equiv}CtBu)_2Li(TMEDA)$. In addition,

Scheme 12. Preparation of Dimeric and Monomeric Bis(benzamidinato)yttrium Acetylides[77,81]



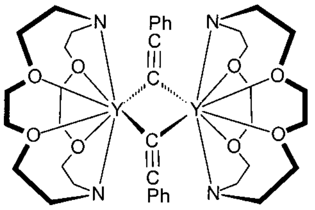
Scheme 13. Preparation of $[Me_2Si(NtBu)(OtBu)]_2YC{\equiv}CPh$[87]



$[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2$ was found to catalyze the dimerization of bulky 1-alkynes.[81] A related bis(benzamidinato)scandium acetylide, $[PhC(NSiMe_3)_2]_2ScC{\equiv}CSiMe_3$, was made by reacting $[PhC(NSiMe_3)_2]_2ScCH_2SiMe_3$ with $Me_3SiC{\equiv}CH$.[82]

Closely related, though monomeric alkynyl complexes have been synthesized starting from a bis(alkoxysilylamido)yttrium pyridyl complex.[87] The pyridyl compound $[Me_2Si(NtBu)(OtBu)]_2Y[\eta^3\text{-}(C,C,N)\text{-}2\text{-}NC_5H_4]$ reacts with $PhC{\equiv}CH$ to yield the corresponding phenylacetylide pyridine complex $[Me_2Si(NtBu)(OtBu)]_2YC{\equiv}CPh(Py)$. The coordinated pyridine can be replaced by THF to give $[Me_2Si(NtBu)(OtBu)]_2YC{\equiv}CPh(THF)$, which easily loses THF and forms the base-free, monomeric yttrium phenylacetylide $[Me_2Si(NtBu)(OtBu)]_2YC{\equiv}CPh$. The overall reaction sequence is illustrated in Scheme 13.[87]

The reaction of $(DAC)Y(CH_2SiMe_3)$ (DAC = deprotonated 4,13-diaza-18-crown-6) (cf. section 2) with phenylacetylene produced a deep purple solution from which the blue-purple alkynide-coupled butatrienediyl complex $(\mu\text{-}(Z)\text{-}PhC{=}C{=}C{=}CPh)[Y(DAC)]_2$ and the colorless phenylacetylide-bridged dimer $[(DAC)Y(\mu\text{-}C{\equiv}CPh)]_2$ (**29**) could be isolated.[114] In solution there is an equilibrium between the two complexes. In both cases the molecular structures could be confirmed by X-ray diffraction analyses although disorder in the butatrienediyl complex prevented full refinement. Nevertheless the *Z* conformation of the bridging butatrienediyl ligand was clearly established. The crystal structure determination of $[(DAC)Y(\mu\text{-}C{\equiv}CPh)]_2$ revealed the presence of a centrosymmetric dimer with asymmetric bridging alkynide groups.[114]



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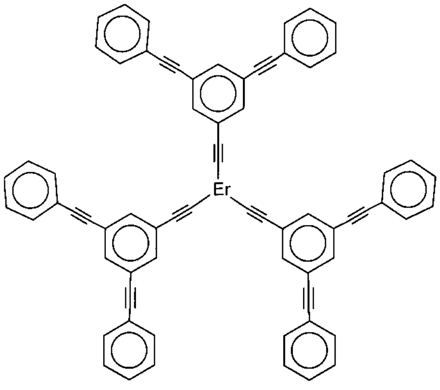
As demonstrated by Takats et al. the bis[hydrotris(3,5-dimethylpyrazol-1-yl)borate] ligand set is also highly useful in the stabilization of base-free monomeric lanthanide alkynyl complexes.[115] Treatment of a slurry of insoluble, purple $[HB(3,5\text{-}Me_2pz)_3]_2Sm$ in THF with mercury bis(phenylacetylide) resulted in gradual dissolution of the Sm(II) precursor and formation of a colorless solution besides a black precipitate of mercury (eq 35). $[HB(3,5\text{-}Me_2pz)_3]_2Sm(C{\equiv}CPh)$ was isolated as a colorless, crystalline solid in 55% yield.

$$2[HB(3,5\text{-}Me_2pz)_3]_2Sm + Hg(C{\equiv}CPh)_2 \xrightarrow{THF} 2[HB(3,5\text{-}Me_2pz)_3]_2Sm(C{\equiv}CPh) + Hg(l) \quad (35)$$

The monomeric molecular structure of $[HB(3,5\text{-}Me_2pz)_3]_2Sm(C{\equiv}CPh)$ was confirmed by an X-ray diffraction analysis (Sm−C = 249.4(9) pm).[115]

Unusual organoerbium complexes containing dendritic acetylide ligands have been reported by Bochkarev et al.[116] The compound $Er[C{\equiv}CC_6H_3(C{\equiv}CPh)_2\text{-}3,5]_3$ (**30**) was prepared in 75% yield by reacting $Er[N(SiMe_3)_2]_3$ with 3 equiv of the corresponding phenylacetylene derivative in toluene.



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In a similar manner the second generation organoerbium dendrimer, $Er[C{\equiv}CC_6H_3\{C{\equiv}CC_6H_3(C{\equiv}CPh)_2\text{-}3,5\}_2\text{-}3,5]_3$, was prepared and isolated as a dark brown solid in 84% yield.[116]

4. Allyl Complexes and Azaallyl Complexes

The chemistry of lanthanide allyl complexes has made significant progress in recent years in terms of preparative results as well as applications in organic synthesis and catalysis. Until recently, homoleptic tris(η^3-allyl)lanthanide complexes were unknown. Reactions of anhydrous lanthanide trichlorides with 4 or 5 equiv of allyllithium generally result in the formation of anionic allyl complexes. The complexes $[Li(dioxane)_n][Ln(\eta^3\text{-}C_3H_5)_4]$ (Ln = Ce, Pr, Nd, Sm, Gd, $n = 2$; Ln = Y, $n = 2.5$; Ln = La, $n = 3$), $[Li_2(THF)_n][Ln(\eta^3\text{-}C_3H_5)_5]$ (Ln = Y, La, $n = 2.5$; Ln = Ce, Pr, Nd, Sm, $n = 3$), and $[Li_2(dioxane)_n][Ln(\eta^3\text{-}C_3H_5)_5]$ (L = Ce, Nd, Sm, Gd, Dy, Ho, Er; $n = 1, 3$) have been obtained depending on the reaction conditions and the use of either THF or dioxane as solvents.[117-119] For example, a typical preparation involves treatment of anhydrous neodymium trichloride with the dioxane adduct of allyllithium in DME solution (eq 36).[118,120]

$$NdCl_3 + 4LiC_3H_5(dioxane) \xrightarrow[\text{2. }Et_2O/\text{dioxane}]{\text{1. DME, 50 °C}} [Li(\mu\text{-dioxane})_{1.5}][Nd(\eta^3\text{-}C_3H_5)_4] + 3LiCl \quad (36)$$

Following this procedure $[Li(\mu\text{-dioxane})_{1.5}][Nd(\eta^3\text{-}C_3H_5)_4]$ can be isolated in 80% yield as a yellow-green crystalline solid, which is highly sensitive toward air and moisture but can be stored at −25 °C without noticeable decomposition. Later it was found that such complexes are also available through a one-pot reaction in which the allyllithium reagent is prepared in situ from tetraallyltin and *n*-butyllithium (eq 37).[117]

$$LaCl_3 + 2Sn(C_3H_5)_4 + 4nBuLi \xrightarrow[\text{2. }Et_2O/\text{dioxane}]{\text{1. toluene}} [Li(\mu\text{-dioxane})_{1.5}][La(\eta^3\text{-}C_3H_5)_4] + 3LiCl + 2Sn(C_3H_5)_2nBu_2 \quad (37)$$

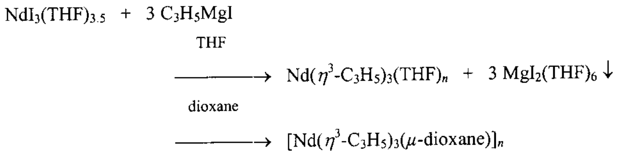
The lanthanum compound $[Li(\mu\text{-dioxane})_{1.5}][La(\eta^3\text{-}C_3H_5)_4]$ was structurally characterized by X-ray diffraction. In the solid state the central La^{3+} ion is surrounded by the four η^3-allyl ligands in a distorted tetrahedral fashion. Bridging dioxane molecules and the lithium cations form two-dimensional sheets in the crystal lattice. A major achievement in organolanthanide chemistry was the successful preparation of the first neutral tris(η^3-allyl)lanthanide complexes by Taube et al.[121] The compounds $La(\eta^3\text{-}C_3H_5)_3(dioxane)_{1.5}$(yellow) and $Nd(\eta^3\text{-}C_3H_5)_3(dioxane)$(green) were synthesized by allyllithium abstraction from the corresponding anionic tetrakis(allyl)lanthanide(III) complexes $[Li(\mu\text{-dioxane})_{1.5}][Ln(\eta^3\text{-}C_3H_5)_4]$ (Ln = La, Nd). As shown in eq 38, this was achieved by choosing BEt_3 in dioxane as the most suitable reagent. Isolated yields are in the range of 65−85%.

$$[Li(\mu\text{-dioxane})_{1.5}][Ln(\eta^3\text{-}C_3H_5)_4] + BEt_3 \xrightarrow{\text{dioxane}} Ln(\eta^3\text{-}C_3H_5)_3(dioxane)_n + Li[BEt_3(C_3H_5)]\cdot 1.5dioxane \quad Ln = La,\ n = 1.5;\ Ln = Nd,\ n = 1 \quad (38)$$

In both complexes the three allyl ligands are η^3-coordinated to the lanthanide metal. Additional coordination of dioxane leads to different crystal structures. X-ray crystal structure analyses revealed that the lanthanum compound adopts a dimeric structure of the type $(\mu\text{-dioxane})[La(\eta^3\text{-}C_3H_5)_3(dioxane)]_2$ with one bridging and two terminal dioxane ligands, while with neodymium the polymeric structure $[Nd(\eta^3\text{-}C_3H_5)_3(\mu\text{-dioxane})]_n$ is formed. It was found that the coordinated dioxane can be split off easily at 50 °C to give the unsolvated homoleptic lanthanide tris(allyls) $La(\eta^3\text{-}C_3H_5)_3$ and $Nd(\eta^3\text{-}C_3H_5)_3$ as light brown, microcrystalline solids. Stirring of the dioxane solvate with excess *n*-hexane at 40 °C also leads to quantitative formation of the donor-free tris(allyl) complexes.[122] In the presence of THF, DME, or dioxane they form the corresponding solvates again. Both allyl species $Ln(\eta^3\text{-}C_3H_5)_3(dioxane)_n$ (Ln = La, Nd) catalyze the 1,4-*trans*-polymerization of butadiene in toluene with high selectivity. Active catalysts for the 1,4-*cis*-polymerization of butadiene can be obtained by addition of suitable Lewis acids such as Et_2AlCl, $EtAlCl_2$, or methylaluminoxane (MAO).[121]

Most recently a further improved and essentially more simple synthetic procedure for the preparation of the catalytically interesting compound $[Nd(\eta^3\text{-}C_3H_5)_3(\mu\text{-dioxane})]_n$ has been reported. The new preparation involves treatment of neodymium triiodide with the easily accessible allyl Grignard reagent in THF followed by crystallization from dioxane (Scheme 14).[122]

Scheme 14. Improved Preparation of $[Nd(\eta^3\text{-}C_3H_5)_3(\mu\text{-dioxane})]_n$[122]



Following this procedure allows high-purity, halide-free $[Nd(\eta^3\text{-}C_3H_5)_3(\mu\text{-dioxane})]_n$ to be isolated in at least 70% yield, thus making this important starting material readily available.[122]

The dimeric molecular structure of $(\mu\text{-dioxane})[La(\eta^3\text{-}C_3H_5)_3(dioxane)]_2$ can be broken up into monomeric units by addition of hexamethylphosphoric triamide (HMPA) or chelating ligands such as DME or TMEDA. The mononuclear nature of $La(\eta^3\text{-}C_3H_5)_3(TMEDA)$ (intensely yellow crystals) was confirmed by a single-crystal X-ray structure analysis. These complexes show a similar catalytic activity in the polymerization of butadiene as the dioxane solvates. In toluene at 50 °C high 1,4-*trans*-selectivity is observed, while upon addition of MAO the catalytic activity increases and a 1,4-*cis*-selectivity of 40−60% is obtained.[123]

Partial protolysis of one allyl ligand in [Li(μ-dioxane)$_{1.5}$][La(η^3-C_3H_5)$_4$] by a cyclopentadiene derivative leads to selective formation of the complexes [Li(dioxane)$_2$][Cp′La(η^3-C_3H_5)$_3$] (Cp′ = C_5H_5, C_5Me_5, indenyl, fluorenyl).[120,124] This series of anionic allyllanthanum complexes as well as the neutral tris(allyls) have been studied by ^{139}La NMR spectroscopy. Typical ranges of the ^{139}La NMR chemical shifts were found for the different types of complexes dependent on the number and kind of organic ligands directly bonded to La.[125] For (μ-dioxane)[La(η^3-C_3H_5)$_3$(dioxane)]$_2$ and [Nd(η^3-C_3H_5)$_3$(μ-dioxane)]$_n$ the absorption spectra have been measured at room temperature and low temperatures. A truncated crystal field (CF) splitting pattern has been derived for the neodymium derivative and simulated by fitting the free parameters of an empirical Hamiltonian. The parameters derived allowed the construction of experimentally based nonrelativistic and relativistic molecular orbital schemes in the f range.[126]

The first cationic allyllanthanide complex has recently been reported by Taube et al.[122] Equations 39 and 40 illustrate the two-step procedure which has been employed to synthesize the cationic mono(allyl)neodymium species [Nd(η^3-C_3H_5)Cl(THF)$_5$][BPh$_4$]·THF:

$$2\mathrm{Nd}(\eta^3\text{-}C_3H_5)_3(\mathrm{dioxane}) + \mathrm{NdCl_3(THF)_2} \xrightarrow[-\mathrm{dioxane}]{\mathrm{THF},\ -20\ ^\circ\mathrm{C}} 3\mathrm{Nd}(\eta^3\text{-}C_3H_5)_2\mathrm{Cl(THF)}_x \quad (39)$$

$$\mathrm{Nd}(\eta^3\text{-}C_3H_5)_2\mathrm{Cl(THF)}_x + [\mathrm{NHMe_3}][\mathrm{BPh_4}] \xrightarrow{\mathrm{THF,\ rt}} [\mathrm{Nd}(\eta^3\text{-}C_3H_5)\mathrm{Cl(THF)_5}][\mathrm{BPh_4}]\cdot\mathrm{THF} + C_3H_6 + \mathrm{NMe_3} \quad (40)$$

Green, crystalline [Nd(η^3-C_3H_5)Cl(THF)$_5$][BPh$_4$]·THF has been isolated in 80% yield and structurally characterized by an X-ray diffraction analysis. The coordination geometry of the [Nd(C_3H_5)Cl(THF)$_5$]$^+$ cation is that of a pentagonal bipyramid with the five THF ligands occupying the equatorial positions. Quite unexpectedly the cationic complex proved to be catalytically inactive in butadiene polymerization.[122]

Several more complicated coordination compounds containing η^3-allyl ligands have been reported which are isolated from reactions of anhydrous lanthanide trichlorides with allyl-Grignard reagents in the presence of TMEDA.[127] Among the structurally characterized products are (η^3-C_3H_5)$_2$Ce(μ_3-Cl)$_2$(μ-Cl)$_3$Mg$_2$(TMEDA)$_2$ and (η^3-C_3H_5)$_2$Ln(μ_3-Br)$_2$(μ-Br)$_3$Mg$_2$(Et$_2$O)$_4$ (Ln = Ce, Nd). Allyllanthanide(III) complexes are valuable homogeneous catalysts for 1,4-diene polymerizations. Promising results in organolanthanide catalysis have been obtained in recent years with anionic allyl complexes of the type [Ln(η^3-C_3H_5)$_4$]$^-$.[124] Lithium salts of these anions catalyze the polymerization of butadiene and various alkylbutadienes with moderately to high activity and high *trans*-selectivity.

A heteroleptic allyllanthanide complex has also been successfully prepared with the use of the abovementioned tridentate amido ligand [N(SiMe$_2$CH$_2$PMe$_2$)$_2$]$^-$.[73,74] Treatment of YCl[N(SiMe$_2$CH$_2$PMe$_2$)$_2$]$_2$ with (C_3H_5)MgCl caused elimination of one chelating ligand and formation of the chloro-bridged binuclear complex [(η^3-C_3H_5)Y{N(SiMe$_2$CH$_2$PMe$_2$)$_2$}(μ-Cl)]$_2$. Heteroleptic allyllanthanide complexes also play a role as intermediates in organic synthesis.[128] For example, allylsamarium diiodide can be generated according to eq 41 by adding allyl iodide to a slurry of SmI$_2$ in THP (=tetrahydropyran) at 0 °C. Under these conditions allylsamarium iodide can be isolated as a turquoise suspension which is stable at 0 °C and can be readily used for subsequent reactions.

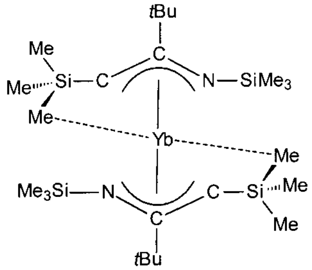
(41)

The formal replacement of one or more carbon atoms in an allyl unit e.g. by nitrogen or phosphorus leads to heteroallyl ligands. Lappert et al. demonstrated that 1,3-bis(trimethylsilyl)-1-azaallyl ligands are suitable of stabilizing a variety of di- and trivalent lanthanide complexes.[129,130] A typical ligand can be prepared as the lithium or potassium salt as outlined in eq 42:

$$\mathrm{MCH(SiMe_3)_2} + t\mathrm{BuCN} \rightarrow \mathrm{M[N(SiMe_3)C(}t\mathrm{Bu)CHSiMe_3]} \quad (42)$$

$$\mathrm{M = Li,\ K}$$

These salts have been empolyed in metathetical reactions with lanthanide(II) and lanthanide(III) halides to give the corresponding azaallyl lanthanide complexes in which the ligands are generally η^3-coordinated. Reaction with SmI$_2$ and YbI$_2$ afforded the divalent species [N(SiMe$_3$)C(tBu)CHSiMe$_3$]$_2$Sm(THF) (dark green) and [N(SiMe$_3$)C(tBu)CHSiMe$_3$]$_2$Yb (**31**, dark red), respectively. According to an X-ray crystal structure determination the unsolvated ytterbium complex is monomeric in the solid state. There is an agostic intramolecular interaction between Yb and two of the methyls in the SiMe$_3$ groups bonded to the terminal carbons of the azaallyl ligand (Yb−C = 284(2) and 290(2) pm).[129]



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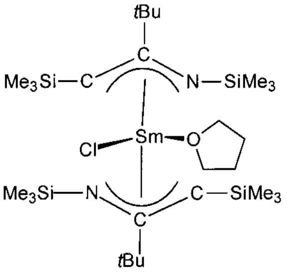
The series of trivalent lanthanide azaallyl derivatives includes the chloro complexes [N(SiMe$_3$)C(tBu)CHSiMe$_3$]$_2$LnCl(THF) (Ln = Ce (yellow), Nd (blue)) as well as the iodides [N(SiMe$_3$)C(tBu)CHSiMe$_3$]$_2$LnI(THF) (Ln = Sm (yellow), Yb (dark red)). An alternative route to the latter species involves oxidation of [N(SiMe$_3$)C(tBu)CHSiMe$_3$]$_2$Yb with elemental iodine. As a typical representative the samarium complex [N(SiMe$_3$)C(tBu)CHSiMe$_3$]$_2$SmCl(THF) (**32**) has been structurally characterized by X-ray diffraction. If one takes each azaallyl ligand as occupying a single coordination site, the coordination geometry around samarium can be described as distorted tetrahedral.[129]



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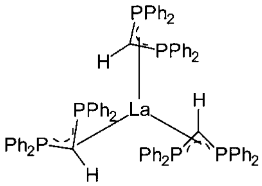
Other heteroallyl ligands which have been employed in the synthesis of homoleptic organolanthanide complexes are the diphosphinomethanides. The structurally characterized lanthanum derivative La[η^3-CH(PPh$_2$)$_2$]$_3$ (**33**) was reported in 1986.[131]



33

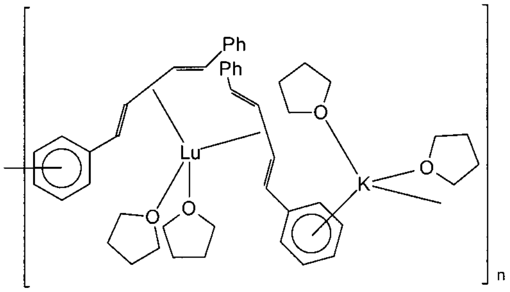
In the case of the smaller samarium ion mono- and dinuclear diphosphinomethanide complexes were isolated depending on the nature of the substituents on phosphorus (eqs 43 and 44).[132,133] The molecular structures of both products have been unequivocally elucidated by X-ray diffraction analyses. {μ-η^2-CH(PMe$_2$)$_2$}$_2$[Sm{CH(PMe$_2$)$_2$}$_2$]$_2$ can be obtained from samarium triflate and isolated as a red solid in 54% yield. In the centrosymmetric dimer the two samarium atoms are bridged by two diphosphinomethanide ligands via a carbon and a phosphorus atom, while Sm[η^3-CH(PPh$_2$)$_2$]$_3$ is a monomeric heteroallyl complex like the lanthanum homologue.

$$2Sm(O_3SCF_3)_3 + 6LiCH(PMe_2)_2 \rightarrow \{\mu\text{-}\eta^2\text{-}CH(PMe_2)_2\}_2[Sm\{\eta^3\text{-}CH(PMe_2)_2\}_2]_2 + 6LiO_3SCF_3 \quad (43)$$

$$SmCl_3(THF)_3 + 3LiCH(PPh_2)_2 \rightarrow Sm[CH(PPh_2)_2]_3 + 3LiCl + 3THF \quad (44)$$

5. Diene Complexes

Quite in contrast to the organometallic chemistry of the d-transition metals, diene complexes are a particularly rare species in organolanthanide chemistry.[2,3,5] Lanthanide ions show only a negligible tendency to coordinate neutral dienes. Thus the few examples of fully characterized members of this class of compounds generally contain the diene ligands formally in the form of their corresponding dianions. For example, the reaction of lanthanide metal powders with 1,4-diphenylbutadiene in the presence of iodine or diiodoethane have been reported to yield complexes of the type (1,4-Ph$_2$C$_4$H$_4$)LnI(THF)$_3$, but none of them has been structurally characterized.[134,135] In a few recent papers the first successful approaches toward well-characterized lanthanide diene complexes have been reported. The structurally characterized lutetium compound [(μ-PhCHCHCHCHPh)$_2$Lu(THF)$_2$K(THF)$_2$]$_n$ (**34**) is an example of an anionic diene complex of a lanthanide element.[136] Compound **34** contains two η^4-tetraphenylbutadiene ligands and two THF molecules coordinated to the central lutetium ion. The diphenylbutadiene is bonded in its s-*cis* conformation. In the crystal, a polymeric chain structure results from additional η^6-coordination of two phenyl rings to potassium. Since the oxidation state of lutetium is +3, the two diene ligands must be formally dianions to result in a monoanionic species with potassium as the counterion.



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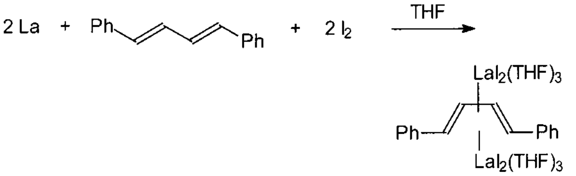
The dilanthanum complex (μ-PhCHCHCHCHPh)[LaI$_2$(THF)$_3$]$_2$ with a bridging diene ligand was obtained by reacting finely divided elemental lanthanum with 1,4-diphenyl-1,3-butadiene and iodine in THF as shown in eq 45.[137] The samarium analogue (μ-PhCHCHCHCHPh)[SmI$_2$(THF)$_3$]$_2$ had already been made earlier using a similar synthetic procedure.[138]



(45)

(μ-PhCHCHCHCHPh)[LaI$_2$(THF)$_3$]$_2$ forms red crystals which have been accessible to an X-ray structure determination. It showed the presence of an “inverse sandwich complex” in which the two lanthanum ions are symmetrically bridged by the η:$^4\eta^4$-coordinated diene ligand.[137]

1,4-Diphenylbutadiene and some of its *p*-substituted derivatives have been used as ligands in a systematic study on lanthanide diene complexes published by Thiele et al.[139] In all cases the butadiene ligands are coordinated in the form of their butenediyl dianions. It was found that the (pentamethylcyclopentadienyl)lanthanide dichlorides (C$_5$Me$_5$)LnCl$_2$ (Ln = Sm, Lu) react with these diarylbutadienes and lithium under elimination of the pentamethylcyclopentadienyl ligand and formation of anionic (butadiene)lanthanide complexes (eqs 46 and 47). The black-red (Sm) or orange-red (Lu) compounds are soluble in ethers and hydrocarbons.

$$(C_5Me_5)SmCl_2 + 2\ 1,4\text{-}Ph_2C_4H_4 + 2Li \xrightarrow{THF} [Li(THF)_3][Sm(1,4\text{-}Ph_2C_4H_4)_2] + LiCl + ... \quad (46)$$

$$(C_5Me_5)LuCl_2 + 1,4\text{-}R_2C_4H_4 + 2Li \xrightarrow{DME} [Li(DME)][(1,4\text{-}R_2C_4H_4)LuCl_2] + Li(C_5Me_5) + ... \quad (47)$$

$$R = C_6H_4Me\text{-}p,\ C_6H_4OMe\text{-}p$$

A slightly different lithium salt (higher THF content) of the $[Sm(1,4\text{-}Ph_2C_4H_4)_2]^-$ anion was isolated in the form of black-red crystals starting directly from samarium trichloride (eq 48).[139]

$$SmCl_3(THF)_3 + 2\ 1,4\text{-}Ph_2C_4H_4 + 4Li \xrightarrow{THF} [Li(THF)_4][Sm(1,4\text{-}Ph_2C_4H_4)_2] + 3LiCl \quad (48)$$

A mono(iodo)samarium complex containing a 1,4-di-*p*-tolylbutadiene ligand was made by reacting metallic samarium with iodine and the butadiene derivative in THF according to eq 49.[131]

$$2Sm + I_2 + 1,4\text{-}(p\text{-}MeC_6H_4)_2C_4H_4 \xrightarrow{THF} [1,4\text{-}(p\text{-}MeC_6H_4)_2C_4H_4]SmI(THF)_3 \quad (49)$$

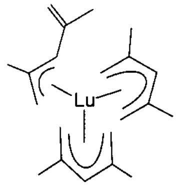
6. Pentadienyl Complexes

There are many examples in the organometallic chemistry of the d-transition metals showing that pentadienyl ligands closely resemble the corresponding cyclopentadienyl complexes. Due to this relationship bis(pentadienyl)metal complexes are often termed "open metallocenes". One lanthanide derivative with "open cyclopentadienyl ligands" has already been described 1982. Bright green tris(2,4-dimethylpentadienyl)neodymium is formed upon treatment of anhydrous neodymium trichloride with 3 equiv of potassium 2,4-dimethylpentadienide in THF solution according to eq 50:[140]

$$NdCl_3 + 3KC_7H_{11} \xrightarrow{THF} Nd(\eta^5\text{-}C_7H_{11})_3 + 3KCl \quad (50)$$

$$C_7H_{11} = 2,4\text{-dimethylpentadienyl}$$

An X-ray crystal structure analysis of the homoleptic complex $Nd(\eta^5\text{-}C_7H_{11})_3$ revealed the presence of three equivalent η^5-coordinated 2,4-dimethylpentadienyl ligands. Meanwhile several other series of pentadienyllanthanide complexes have been reported, including the mono(pentadienyl) derivatives $(\eta^5\text{-}C_7H_{11})LnCl_2(THF)_3$ (Ln = Nd, Sm, Gd), bis(pentadienyl)lanthanide halides $(\eta^5\text{-}C_7H_{11})_2LnCl(THF)$ (Ln = Nd, Sm, Gd), and homoleptic $Ln(C_7H_{11})_3$ (Ln = La, Sm, Gd, Tb, Lu).[141,142] Of the latter, the tris(2,4-dimethylpentadienyl) complexes with Ln = Nd, Gd, and Lu have been structurally characterized. The gadolinium complex adopts the same molecular structure as the neodymium compound containing three η^5-coordinated pentadienyl ligands. An interesting structural difference is found for the coordination mode of the three pentadienyl ligands in $Lu(C_7H_{11})_3$ (**35**). Due to the smaller ionic radius of Lu^{3+} only two 2,4-dimethylpentadienyl ligands in this molecule are η^5-coordinated, while the third ligand is bonded to lutetium in an η^3-allyl-like fashion. These examples nicely illustrate how the flexible pentadienyl ligands are able to adapt to the different coordination spheres of the lanthanide elements.[142]



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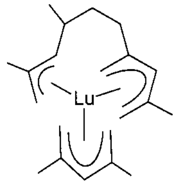
The metathesis reaction of anhydrous $LuCl_3$ with 3 equiv of potassium 2,4-dimethylpentadienide is in fact not as straightforward as originally anticipated. The compound $Lu(\eta^5\text{-}C_7H_{11})_2(\eta^3\text{-}C_7H_{11})$ (**35**) is isolated from the reaction mixture only in 46% yield.[142] A careful reexamination of this reaction revealed the formation of an unusual minor byproduct, which has been shown by X-ray crystallography to be the novel pentadienyllutetium complex $Lu(\eta^5\text{-}C_7H_{11})[\eta{:}^5\eta^3\text{-}MeC_5H_5CH_2CH_2CH(Me)C_3H_3(Me)]$ (**36**).[143] The pale orange-yellow crystals have been isolated in 5% yield. This compound contains a dimeric chelate ligand derived from end-to-end fusion of two 2,4-dimethylpentadienyl groups.



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Some promising catalytic applications have also been reported for lanthanide pentadienyl complexes. Highly active catalysts for the production of *cis*-1,4-polybutadiene are obtained by combining tris(2,4-dimethylpentadienyl)neodymium with various Lewis acids such as $AlEtCl_2$, $AlBr_3$, $SnCl_4$, or Ph_2SnCl_2. In this case the crystal structure analysis provided valuable insight about the structural constitution of an active precatalyst, when it became possible to isolate and structurally characterize the hexanuclear complex $Nd_6Cl_{12}(C_7H_{11})_6(THF)_2$ (C_7H_{11} = 2,4-dimethylpentadienyl).[144] In the solid state this compound forms an unusual cluster, in which two hexagonal-bipyramidal Nd_3Cl_5 units are connected via two chloride bridges. The coordination mode of all six 2,4-dimethylpentadienyl ligands to neodymium is η^5.

Pentadienyl ligands can be modified in an interesting manner by formally connecting two of these anions through a hydrocarbon chain.[145] Such a bridged bis(pentadienyl) dianion has been generated by deprotonation of two methyl groups in the precursor 2,4,7,9-tetramethyl-1,3,7,9-decatetraene. Subsequent reaction of the resulting potassium salt with ytterbium diiodide afforded the "open" *ansa*-ytterbocene

$[4,4'\text{-}(CH_2)_2(2\text{-}C_6H_8)_2]Yb(THF)$, which can be regarded as a pentadienyl analogue of $(C_5Me_5)_2Yb(Et_2O)$.[145] Thus far very little is known about the derivative chemistry of pentadienyllanthanide complexes. In a recent study the homoleptic tris(2,4-dimethylpentadienyl) derivatives of gadolinium and erbium have been used to synthesize phenylalkynyl derivatives via reactions with equimolar amounts of phenylacetylene (eq 51). Single-crystal X-ray structure analyses of the resulting red crystals established the presence of μ-alkynyl-bridged dimeric molecules for both compounds.[146]

$$2Ln(\eta^5\text{-}C_7H_{11})_3 + 2PhC{\equiv}CH \xrightarrow{\text{toluene}} [(\eta^5\text{-}C_7H_{11})_2Ln(\mu\text{-}C{\equiv}CPh)]_2 + 2\ 2,4\text{-}C_7H_{12} \quad (51)$$

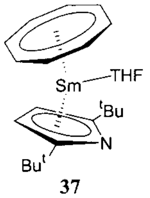
It should be mentioned that η^5-cyclohexadienyl ligands, which have been reported to form interesting coordination compounds with uranium,[147,148] have so far not been used in the organometallic chemistry of the lanthanides.

7. Complexes of Nitrogen Heterocycles

Interestingly it is possible to achieve π-bonding of five-membered N-heterocycles to Ln^{3+} ions although in the first place σ-coordination through the N atom to the hard lanthanide ions should be more preferred. Examples of pyrazolate complexes with Ln−N bonds are numerous, but very little is reported on complexes containing pyrrole or pyrazole ligands having a hapticity of higher than 2.

7.1. Pyrrolyl and Pyrazolate Complexes

After reporting on homo- and heteroleptic pyrrolyl complexes exhibiting σ- and π-bonding modes, Schumann et al. also succeeded in the synthesis of a mixed pyrrolyl−COT species. Treatment of the dimeric COT−chloride $[(C_8H_8)LnCl(THF)]_2$ with $Na[NC_4H_2tBu_2\text{-}2,5]$ affords $(C_8H_8)Ln(2,5\text{-}tBu_2py)(THF)$ (Ln = Sm (**37**), Tm, Lu).[149] In the purple Sm representative the metal ion is pseudo trigonal planar coordinated by one η^8-bonded COT unit, one pyrrole ring, and one THF molecule.



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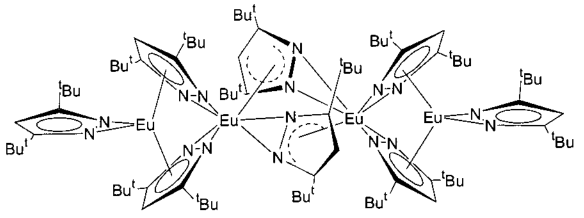
Homoleptic solvent-free lanthanide pyrazolates have been conveniently prepared in high-temperature reactions using sealed tubes. A mixture of the ligand, excess lanthanide metal, and a few drops of mercury is heated at 200−250 °C for 1−5 days followed by extraction with toluene. But only for Ln = Eu and 3,5-di-*tert*-butylpyrazole a new bonding fashion other than η^2 is observed. Bright yellow crystals of $[Eu_4(tBu_2pz)_8]$ (**38**) are isolated in almost quantitative yield after a reaction time of 15.5 h.[150]



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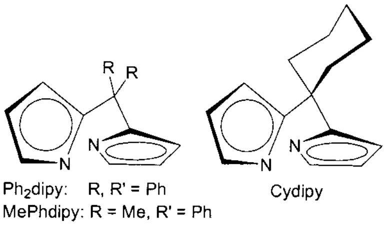
The outer Eu^{II} ions are sandwiched between two pyrazolate rings which bind μ-η:$^5\eta^2$ to the outer and the inner Eu atoms. The ligands in the middle connect the two inner Eu atoms by adopting μ-η^2:η^3 and μ-η^2:η^4 bonding modes.

7.2. Dipyrrolyl Complexes

Though examples of lanthanide compounds with the “simple” pyrrolyl ligand remain still rare, the dipyrrolyl−lanthanide chemistry has recently experienced a tremendous development. The dianionic ligand introduced by Gambarotta et al. is similar to the *ansa*-cyclopentadienyl ligand which might be responsible for the big variety of new and interesting structural features displayed in its complexes.[151] It has also revealed some more of the remarkable reactivity of Sm.

Three dipyrrolyl systems have been used so far; they differ by the substituents at the bridging carbon atom (Scheme 15). Whereas Ph_2dipy and Cydipy were extensively studied, there exists only one structure with MePhdipy. Except for two reported Yb compounds, research was so far mainly focused on Sm. In general a THF solution of the alkali-metalated ligand is added to the di- or trivalent lanthanide, in the latter case followed by reduction with the corresponding alkali metal.

Scheme 15. Dipyrromethane Ligands



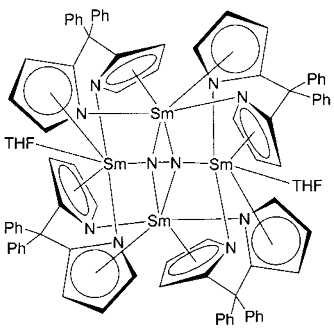
Apart from one monomer and one polymer mostly cyclic polynuclear structures are obtained with nuclearity reaching from 4 to 8, ionic or neutral, and with or without interstitials.

In these clusters each dipyrromethanyl dianion bridges two metal atoms; usually one pyrrol ring is σ-bonded to one metal atom and π-bonded to the other metal atom. For the second pyrrole ring the bonding situation is exactly vice versa. Especially worth mentioning are the dinitrogen complexes which were isolated in three cases.

Despite all the different reactions that were carried out to understand the reaction behavior of this ligand system, there seems to be still no correlation established between ligand substituents, alkali metal, and the resulting structure.

7.2.1. Diphenyldipyrromethane (Ph_2dipy)

Treatment of SmI_2 with $K_2(Ph_2dipy)$ in the presence of N_2 leads to the formation of the first dipyrrole−dinitrogen complex $[\{[\mu\text{-}Ph_2C(\eta^1{:}\eta^5\text{-}C_4H_3N)_2]Sm\}_4(\mu\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}N_2)]$ (**39**).[152] The cooperative attack of four Sm(II) atoms allowed the four-electron reduction of one dinitrogen molecule resulting in this Sm(III)−N_2 complex.



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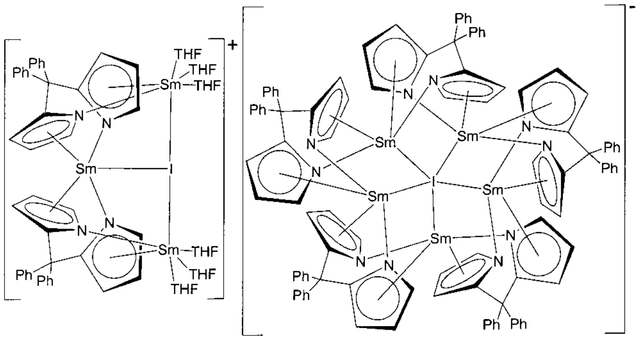
When the same reaction is carried out under an Ar atmosphere, an ionic Sm(II) compound $[\{[\mu\text{-}Ph_2C(\eta^1{:}\eta^5\text{-}C_4H_3N)_2][(Sm(THF)_3)_2Sm]\}(\mu_3\text{-}I)]^+[\{[\mu\text{-}Ph_2C(\eta^1{:}\eta^5\text{-}C_4H_3N)_2]\,Sm\}_5(\mu_5\text{-}I)]^-$ (**40**) is obtained.[152] It can be converted into **39** by reaction with KH under a N_2 atmosphere.



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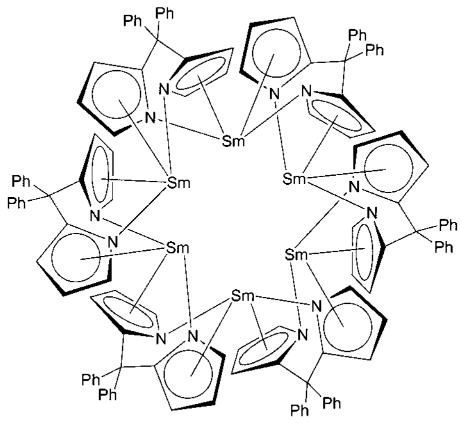
By using a halide and alkali metal free route via $Sm[N(SiMe_3)_2]_2$ and the neutral ligand with no N_2 present, it is possible to trap the highly reactive divalent precursor $[\{[Ph_2C(\alpha\text{-}C_4H_3N)_2]Sm\}_6(THF)_3]\cdot 6.5THF$ (**41**). The six Sm atoms of this "empty" cluster form a regular flat hexagon. Upon exposure to N_2 **39** is formed again.

Reaction of $Li_2/Na_2(Ph_2dipy)$ with $SmCl_3(THF)_3$ and subsequent reduction with Li/Na in the presence of Ar gives octameric mixed-valent Sm(II/III) clusters $\{[Ph_2C(C_4H_3N)_2Sm]_8(LiCl_4)\}^{2-}[Li_2Cl(THF)_4]^+[Li(THF)_4]^+$ (**42**)/$[Na(THF)_5]^+\{[Ph_2C(C_4H_3N)_2Sm]_8(NaCl_4)\}^-$ (**43**). Like **40**, the Li complex **42** where *one* Sm atom retained its trivalent state can be transformed to **39** by reaction with KH/N_2. This is not possible for the Na complex **43** with *two* remaining trivalent Sm ions.[154]



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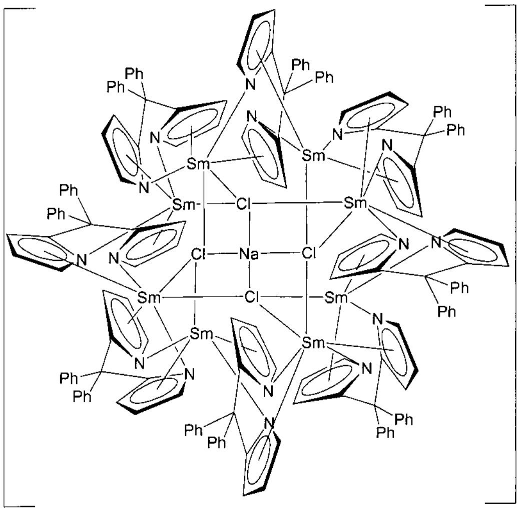

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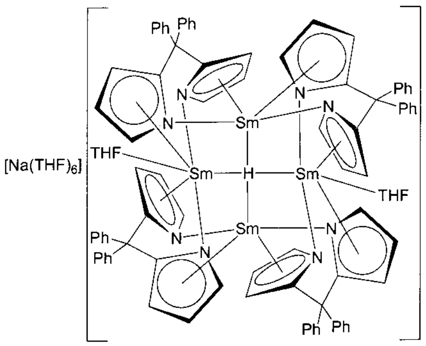
In the presence of N_2 the reactions with $Na_2/K_2(Ph_2dipy)$, $SmCl_3(THF)_3$, and Na/K lead to the formation of ionic divalent tetrameric clusters. In the case of Na a hydride $\{Na(THF)_6\}\{[Ph_2C(C_4H_3N)_2Sm]_4(H)(THF)_2\}$ (**44**)[155] and with K a chloride $[\{[\mu\text{-}Ph_2C(\eta^1{:}\eta^5\text{-}C_4H_3N)_2]Sm\}_4(\mu_4\text{-}Cl)\{K(THF)_2\}]$ (**45**)[152] are formed. Treatment of the dilithium and the disodium salt with trivalent Yb and subsequent reduction with the corresponding alkali metal affords the divalent octameric cluster $\{[Ph_2C(C_4H_3N)_2Yb]_8(\mu^3\text{-}Cl)_2\}\{Li(THF)_4\}_2\cdot 10THF$ (**46**) as well as divalent monomeric $\{[Ph_2C(C_4H_3N)_2]Na(THF)_2\}_2Yb$ (**47**), respectively. In **46** two Cl ions are built into the $(Yb(Ph_2dipy))_8$ core leading to a 2-fold negative charge counterbalanced by two $Li(THF)_4^+$ cations. On the other hand, complex **47** containing two Na ions is neutral.[156]

7.2.2. 1,1-Cyclohexyldipyrromethane (Cydipy)

Starting again from halide- and alkali-free $Sm[N(SiMe_3)_2]_2$ and $H_2(Cydipy)$ under an Ar atmosphere, Gambarotta et al. managed to isolate another "empty" divalent, this time octameric Sm cluster $[\{[1,1\text{-}(\alpha\text{-}C_4H_3N)_2C_6H_{10}]Sm\}_8(THF)_4]\cdot$ hexane (**48**).[153] Just like **41** it reacts rapidly with N_2 to form the dinitrogen complex $\{[(CH_2)_5C(C_4H_3N)_2]Sm\}_4(THF)_2(\mu\text{-}N_2)\cdot 0.5THF$ (**49**) previously obtained by the same reaction in the presence of N_2.[155]

Addition of Na to **49** affords another dinitrogen compound $\{[(CH_2)_5C(C_4H_3N)_2]Sm\}_4(THF)_2(\mu\text{-}N_2)[Na(THF)]_2\cdot 2THF$ (**50**).[155]

In both cases, **49** and **50**, it is difficult to determine the exact oxidation state of the Sm ions. These two neutral complexes hardly differ in the N−N bonding distance of their encapsulated dinitrogen molecules



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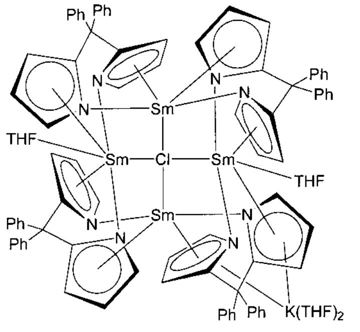

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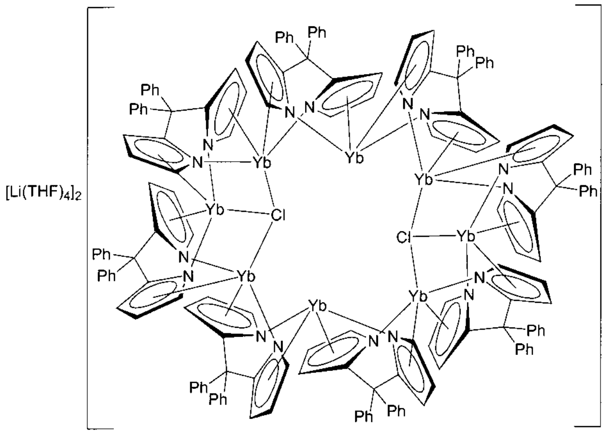

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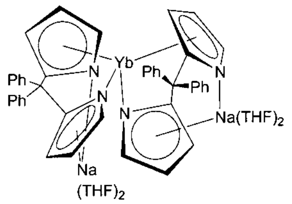
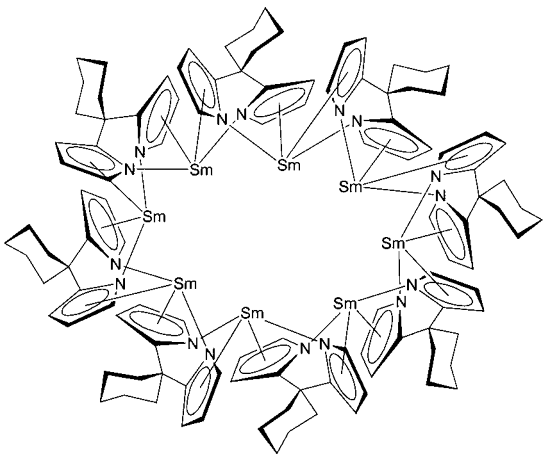


47

(**49**, N−N = 139 pm; **50**, N−N = 137 pm). Assuming a two electron reduction of N_2 by Na in **50** the Sm ions should be in the divalent state which contradicts the measured magnetic moment. But with the proximity of the metal atoms magnetic coupling cannot be excluded. For the Sm ions in Na-free **49**, a greater extent of reduction is expected which is consistent with the observed lower magnetic moment (**49**, μ_{eff} = 3.24 μ_B; **50**, μ_{eff} = 4.05 μ_B).[155]



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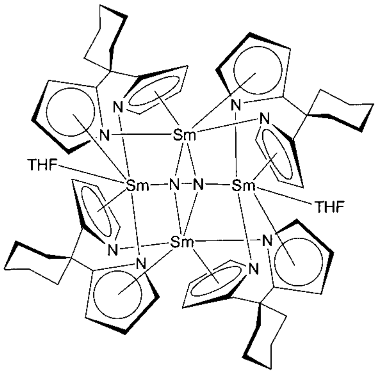

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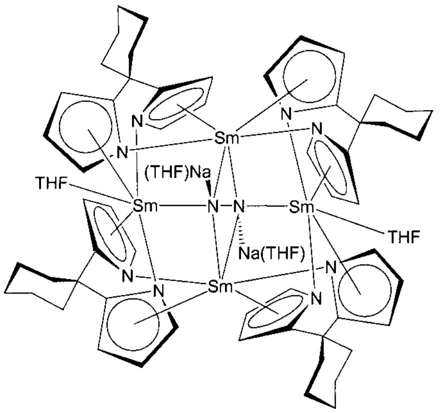
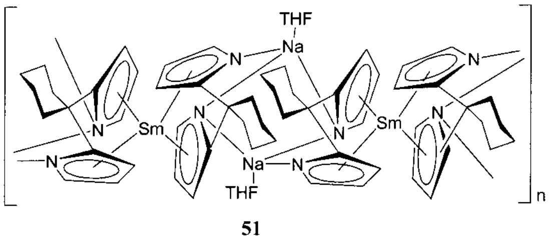


50

Further reduction of **50** by Na gives a linear polymeric divalent Sm compound $\{[1,1\text{-}H_{10}C_6(\alpha\text{-}C_4H_3N)_2]_2Sm[Na(THF)]_2\}_n$ (**51**).[151] The coordination geometry is (pseudo)tetrahedral for both Sm (four π-bonds from the pyrrolide rings) and Na (three σ-bonds from the N atoms of the pyrrolide rings and one from the O atom of the coordinated THF).



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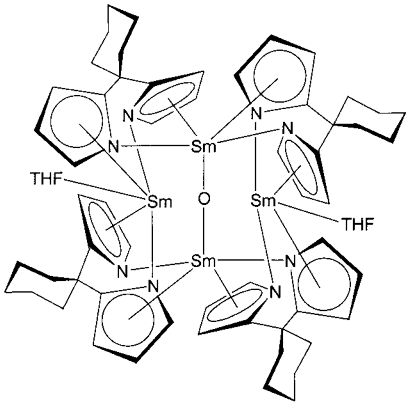
Complex **50** was also obtained by reaction of $SmCl_3(THF)_3$ with Na_2(Cydipy) and subsequent reaction with Na in the presence of N_2.[155] If the same reaction is carried out under an Ar atmosphere an O atom is built into the tetrameric mixed-valent cluster $\{[(CH_2)_5C(C_4H_3N)_2]Sm\}_4(\mu\text{-}O)$ (**52**). Treatment of $SmI_2(THF)_2$ with K_2(Cydipy) also gives **52**.[157]



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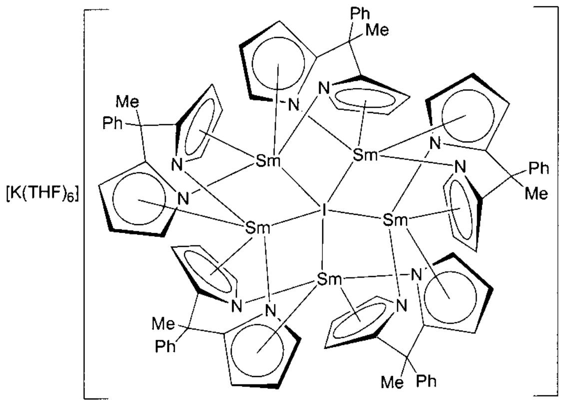
7.2.3. Methylphenyldipyrromethane (MePhdipy)

Only one reaction was carried out with the MePh derivative. The conversion of its dipotassium salt with $SmI_2(THF)_2$ leads to formation of ionic $\{[(MePhC(C_4H_3N)_2]Sm\}_5(\mu\text{-}I)][K(THF)_6]$ (**53**), which pentameric anion resembles the anion of **40**.[154]



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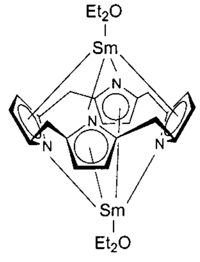
7.3. Calix-Tetrapyrroles

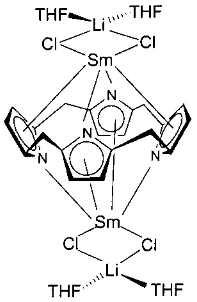
Next to the dipyrrolyl ligand, the cyclic system consisting of four pyrrol rings, the calix-tetrapyrrolyl or porphyrinogen ligand, has been the subject of intense investigations. Mainly reactions with the trivalent lanthanide halides and the tetralithium or tetrasodium salt of the octaethyl- (oepg) or cyclohexylporphyrinogen (cypg) have been carried out. In general monomeric or dimeric structures are obtained and except for two cases they contain additional solvent molecules and alkali and/or halide atoms. Usually the Ln atom is placed in the center of the macrocyle and is bonded to the four pyrrole rings by adopting alternately σ- and π-bonding modes.

7.3.1. Complexes Derived from Li_4(pg)

The first alkali-metal- and halide-free compound $[(oepg)Sm_2(Et_2O)_2]$ (**54oe**) was synthesized by reacting $Sm[N(SiMe_3)_2]_2$ with 0.5 equiv of the protonated ligand H_4(oepg). The pg ligand is centered between an almost linear $(Et_2O)Sm\cdots Sm(Et_2O)$ unit.[158]



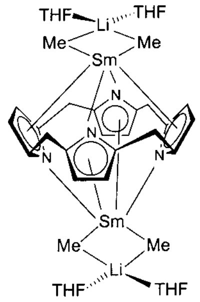
54oe



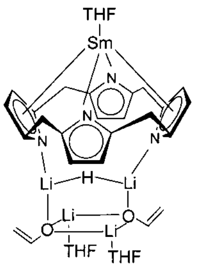
55oe

Another reaction sequence with the same stoichiometry implies the use of 1 equiv of $SmCl_3(THF)_3$ and 0.5 equiv of the metalated ligand Li_4(oepg) to give $(oepg)Sm_2[(\mu\text{-}Cl)_2\{Li(THF)_2\}]_2\cdot 2THF$ (**55oe**). Again the pg ligand bridges two Sm atoms connected via two Cl atoms to one Li atom, respectively.[159]

Alkylation with MeLi gives the corresponding methyl complex $(oepg)Sm_2[(\mu\text{-}CH_3)_2\{Li(THF)_2\}]_2\cdot 2THF$ (**56oe**). Further reaction with $PhSiH_3$ afforded the structurally not characterized hydride $(oepg)Sm(H)Li_2(THF)_6$ (**57oe**) as major product and the enolate $(oepg)(THF)Sm(\mu\text{-}H)[\mu\text{-}OCH{=}CH_2]_2Li_4(THF)_2$ (**58oe**) as minor product. The enolate groups are easily lost in THF, and **57oe** is formed, which can also be obtained by hydrogenation of **56oe**.[159]

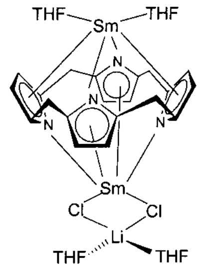


56oe

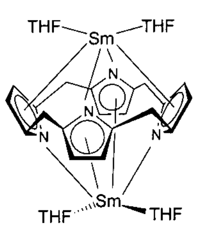


58oe

Reduction of the trivalent precursor **55oe** with $LiAlH_4$ at room temperature leads to formation of the mixed-valent $(oepg)Sm_2(THF)_2(\mu\text{-}Cl)_2\{Li(THF)_2\}$ (**59oe**) whereas reflux conditions or treatment with metallic Li yields the divalent $(oepg)Sm_2(THF)_4\cdot 3THF$ (**60oe**). This THF analogue of **54oe** can be also synthesized by a metathesis reaction of $SmI_2(THF)_2$ with Li_4(oepg).[159]



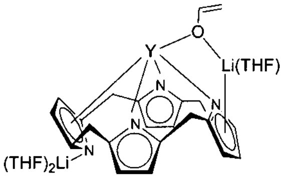
59oe



60oe

The stoichiometric reaction of $LnCl_3(THF)_x$ and Li_4(oepg) gives an enolate complex $\{Li(THF)_2\}[(oepg)Y$-

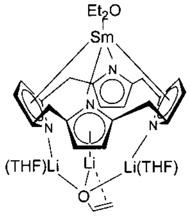
(μ-OCH=CH$_2$)Li(THF)] (**61oe**) for Ln = Y[160] and a chloride complex (oepg)(Cl)Sm{Li$_2$(THF)$_3$} (**62oe**) for Ln = Sm, which has not been structurally characterized thus far.[161]



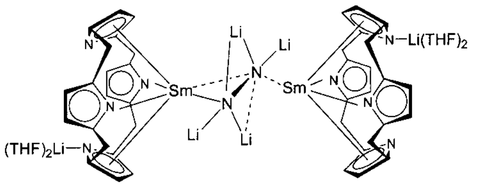
61oe

In contrast to the otherwise observed η:$^5\eta^1$:η:$^5\eta^1$ bonding fashion the Y atom is η:$^5\eta^1$:η^1:η^1-bonded to the oepg ligand and connected via the enolate group to a Li ion, which is π-bonded to a pyrrole ring. Whereas only one additional reaction was carried out with **61oe**, an alkylation which led to the formation of a Li–oepg compound, **62oe**, served as a precursor for various subsequent reactions.

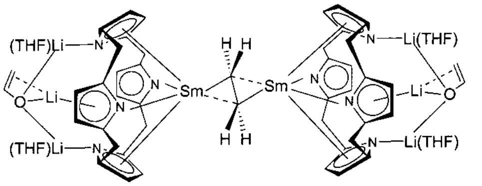
Reduction of trivalent **62oe** with Li under Ar affords the green divalent enolate [(Et$_2$O)Sm(oepg)-(Li){Li(THF)}$_2$(μ_3-OCHCH$_2$)(Et$_2$O)$_{1.5}$] (**63oe**).[162] Upon exposure to N$_2$, a four-electron reduction takes place and the tetralithium hydrazide complex [(THF)$_2$Li-(oepg)Sm]$_2$(N$_2$Li$_4$) (**64oe**) is formed.[163] With ethylene only a two-electron reduction happens to yield the dimer [(CH$_2$CHO)(Li){Li(THF)}$_2$(oepg)Sm]$_2$(μ-CH$_2$CH$_2$) (**65oe**), which unlike **64oe** still contains the enolate groups.[162]



63oe

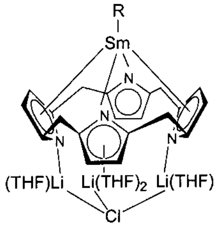


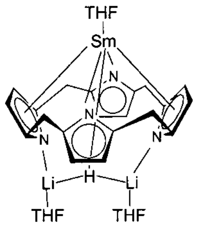
64oe



65oe

Alkylation of **62oe** with RLi affords the alkyl (oepg)(R)Sm(μ_3-Cl){Li(THF)}$_2${Li(THF)$_2$} (**66oe**, R = Me) and the alkenyl (**67oe**, R = vinyl). Treatment with H$_2$ or PhSiH$_3$ transforms them into the hydride (oepg)(THF)Sm{Li(THF)}$_2$(μ_3-H) (**68oe**), which can also be obtained by reaction of **62oe** with LiAlH$_4$ or NaHBEt$_3$.[161]

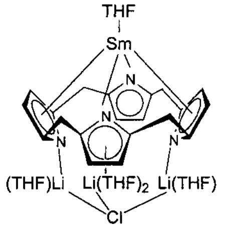


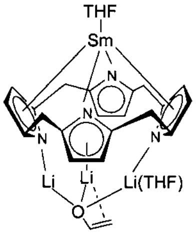


66oe R = Me, **67oe** R = vinyl **68oe**

In the presence of LiCl the addition of ethylene to the hydride triggers a C–H σ-bond metathetic reaction to recover **67oe**. However, this vinyl derivative is temperature sensitive and rapidly decomposes under loss of ethylene to a divalent species from which only the cypg derivative (cypg)(THF)Sm(μ_3-Cl)-{Li(THF)}{Li(THF)$_2$} (**69cy**) was structurally characterized.

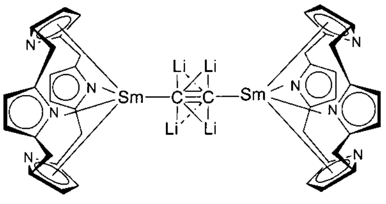
Reaction of SmCl$_3$(THF)$_3$ with Li$_4$(cypg) and subsequent treatment with Li under Ar also gives **69cy** after recrystallization from Et$_2$O.[161] Yet, thorough drying and recrystallization from toluene yields the enolate (cypg)Sm(THF)(Li$_2${Li(THF)}(μ_3-OCH=CH$_2$) (**70cy**), the cy analogue of **63cy**.[164,165]





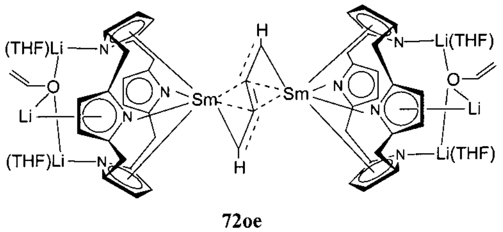
69cy **70cy**

Both enolates react with acetylene to form different compounds. In both cases H$_2$ is released and the Sm atoms are oxidized to the trivalent state. In the pale yellow cy complex [{(cypg)Sm}$_2$(μ-C$_2$Li$_4$)]·Et$_2$O (**71cy**) the acetylide dianion surrounded by 4 Li atoms is placed end-on between two Sm–cypg units. But with the oepg ligand a coupling of two acetylene molecules takes place and the cherry-red dimer [(oepg)Sm(Li-{Li(THF)}$_2$)(μ_3-OCH=CH$_2$)]$_2$(μ_3-η^2:η^2-HC=C=C=CH) (**72oe**) is obtained.[165]



71cy

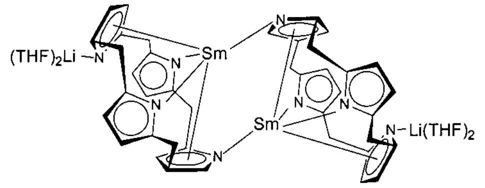
73oe



72oe

This result is consistent with the previously made observation that ethylene fixation also occurs more strongly with the oepg ligand.[162] Therefore, the degree of complexation is obviously very much dependent on the nature of the substituents at the ligand.[165]

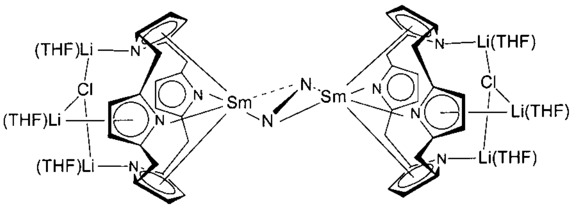
Exposure of acetylene to the methyl complex **66oe** or the hydride **68oe** affords both the coupling product **72oe** and the C_2Li_4 encapsulation product $[\{(oepg)Sm\}_2(\mu\text{-}C_2Li_4)]\cdot Et_2O$ (**73oe**). During the search for the source of the enolate groups in **72oe**, which were not present in the starting materials, another dimer $[(oepg)Sm\{Li(THF)_2\}]_2$ (**74oe**) was isolated.



74oe

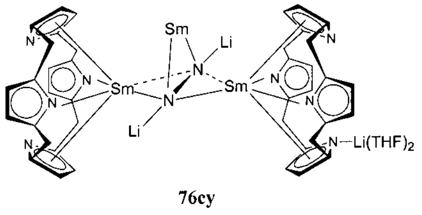
This "N-confused" porphyrinogen is the dimerization product of a $(oepg)SmLi(THF)_2$ species formed through formal abstraction of "LiH" from **66oe** or **68oe** which could initiate the THF cleavage supplying the enolate groups.

Like **62oe** the cy–chloride **69cy** serves as precursor for further transformations. Reflux of a THF solution of **69cy** under nitrogen leads to formation of the labile dimer $[(cypg)Sm\{Li(THF)\}_3(\mu_3\text{-}Cl)]_2(\mu\text{-}N_2)\cdot 2THF$ (**75cy**). Interestingly the N_2 molecule which retained its triple bond is side-on coordinated.[164]

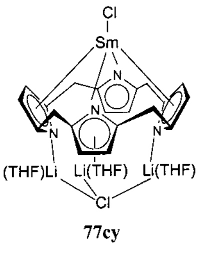


75cy

Subsequent reaction of **75cy** with two additional molecules of **69cy** causes reduction of the N_2 molecule to give the trinuclear complex $[(cypg)_2Sm_3Li_2](\mu\text{-}N_2)\{Li(THF)_2\}\cdot THF$ (**76cy**). Side products are the chloride $(cypg)Sm(Cl)\{Li(THF)\}_3(\mu_3\text{-}Cl)$ (**77cy**) with trivalent Sm and $\{Li(THF)\}_4(cypg)$ which upon reaction with $SmCl_3(THF)_3$ affords **77cy**.[164]



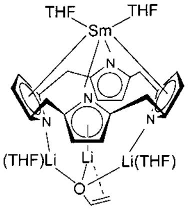
76cy



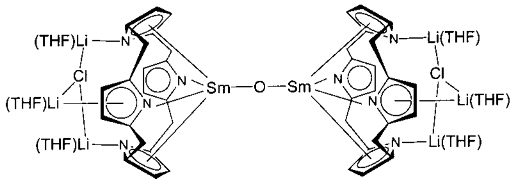
77cy

Besides N_2 fixation in **75cy** THF cleavage also occurs and the above-mentioned enolate **70cy** is formed. Recrystallization of THF causes additional solvation of the Sm atom with a second THF molecule, $(cypg)Sm(THF)_2(Li)\{Li(THF)\}_2(\mu_3\text{-}OCH{=}CH_2)\cdot THF$ (**78cy**). In both complexes the enolate group obviously affects the redox potential of the metal centers to such an extent that no further reaction with N_2 takes place.[164]

Finally, slow decomposition of the N_2 complexes **75cy** and **76cy** in THF, accelerated under reflux conditions, affords the O-bridged dimer $[(cypg)Sm\{Li(THF)\}_3(\mu_3\text{-}Cl)]_2(\mu\text{-}O)$ (**79cy**).[164]



78cy



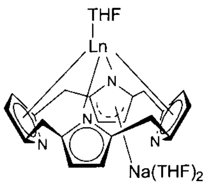
79cy

7.3.2. Complexes Derived from $Na_4(pg)$

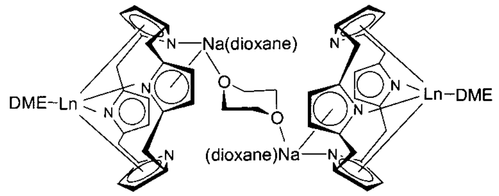
Next to the reaction conditions, the solvent of crystallization plays an important role for reactions using the sodium salt of the oepg ligand. The structures obtained are mostly dimeric and usually contain coordinated sodium ions and solvent molecules but no anionc ligands other than the pg ligand.

Treatment of $Na_4(oepg)$ with $LnCl_3(THF)_x$ affords a Na–Ln–pg precursor which can be monomeric if crystallized from THF, $[\{(oepg)Ln(THF)\}\text{-}\eta^3\text{-}Na(THF)_2]$ (**80oe**, Ln = Pr, Nd, Sm, Eu, Gd, Yb), or dimeric if recrystallized from DME/dioxane. The two units can be connected by a dioxane molecule between the sodium ions $[\{(oepg)Ln(DME)\text{-}\eta^3\text{-}Na\}_2(dioxane)_{1.5}]$ (**81oe**, Ln = Nd, Sm). Solvent-free bridging can also occur only through the sodium ions as in $[\{(oepg)Ln(THF)\text{-}\eta^2{:}\eta^3\text{-}Na\}_2]$ (**82oe**, Ln = Pr, Sm).

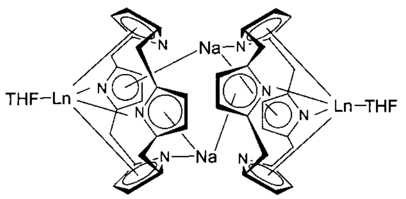
Recrystallization of **80oe** from DME gives an ionic dimeric species $[\{(Hoepg)Ln\}_2][Na(DME)_2]_2$ (**83oe**, Ln = Pr, Sm, Eu, Nd, Gd), which is also formed by reaction of $Na_4(oepg)$ with the Ln metal in DME. The compound **83oe** is the result of an attack of the Ln metal center to the β-carbon of a pyrrol ring of an adjacent Ln–pg moiety. This causes the formation of the bridging Ln–C σ-bond and a hydrogen shift from this carbon to the nitrogen of the same pyrrole.



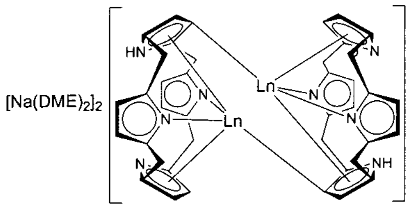
80oe



81oe

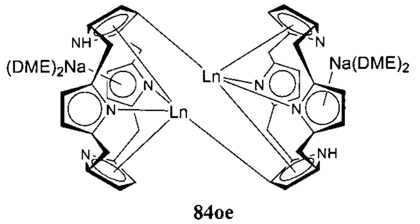


82oe



83oe

Complex **83oe** can be converted into a neutral dimer $[\{(Hoepg)Ln(THF)\}\text{-}\eta^2\text{-}Na(S)_2]$ (**84oe**, Ln = Pr, Sm, S = DME, Ln = Nd, Gd, S = THF) by additional recrystallization from DME.[166]

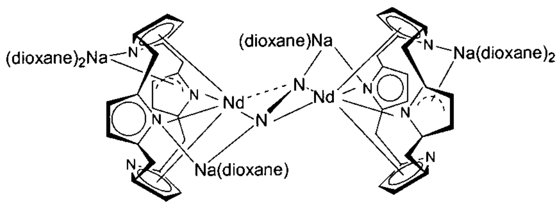


84oe

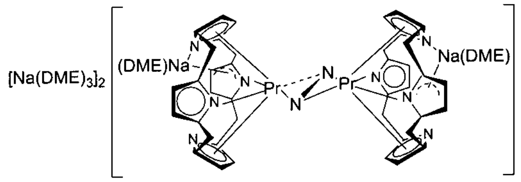
Reduction of **80oe** (Ln = Nd, Pr) with $Na/C_{10}H_8$ in THF affords fixation and two-electron reduction of N_2. Again, the solvent used for crystallization has a strong influence on the solid-state structures of the complexes: with dioxane neutral **85oe** is isolated while DME causes ion-pair formation in $[\{(DME)Na(oepg)Pr\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)][Na(DME)_3]_2$ (**86oe**).[167]

Exposure of **80oe** to ethylene in the presence of $Na/C_{10}H_8$ and 18-crown-6 in THF affords ionic $[\{(THF)_2Na(oepg)Ln\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_2H_4)][\{Na(THF)(18\text{-}crown\text{-}6)\}_2(\mu\text{-}dioxane)]$ (**87oe**, Ln = Pr, Nd) with the $CH_2\text{-}CH_2$ unit bonded side-on. **87oe** can also be isolated upon treatment of the THF precursor of **85oe** or **86oe** with C_2H_4/18-crown-6.

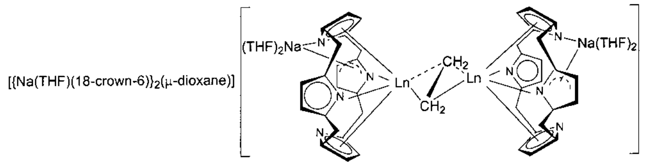
On the other hand, reaction of **80oe** with acetylene and Na gives the neutral dimers $[(oepg)Ln]_2[(\mu\text{-}C_2)(\mu\text{-}Na)_4]$ (**88oe**) in which the acetylide dianion is bonded end-on. The two Ln–pg moieties are also bridged by four Na ions.[168] During every transformation of **80oe** two additional Na^+ ions are built into the structures as they provide the two electrons needed for the N_2 and C_2H_4 reduction and the C_2H_2 deprotonation.



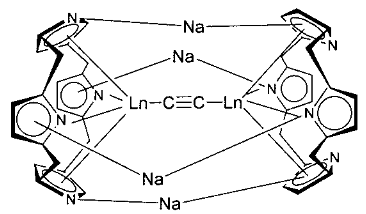
85oe



86oe



87oe



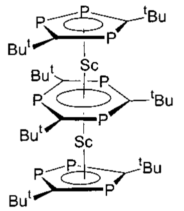
88oe

8. Complexes of Phosphorus Heterocycles

In recent years cocondensation, redox metalation, and transmetalation as well as ligand metathesis reactions were carried out to react different types of phosphorus containing ligands (excluding phosphides) with lanthanides. In their coordination behavior P-heterocycles, especially the permethylated ones, resemble the Cp* and similar ligands. As the electronegativity of P is smaller than that of N, the probability of σ-coordination to the Ln^{3+} ions is lower.

At 77 K the reaction of vaporized scandium with *t*BuCP triggers cyclization of the phosphaalkyne. The resulting two products were separated by flash sublimation. From the sublimate the forest-green triple decker $[\{(\eta^5\text{-}P_3C_2tBu_2)Sc\}_2(\mu\text{-}\eta\text{:}^6\eta^6\text{-}P_3C_3tBu_3)]$ (**89**) was isolated. In addition to oily byproducts the sublimate also contained dark purple $Sc(\eta^5\text{-}P_2C_3tBu_3)_2$ (**90**). Its double decker structure was deduced from magnetic and EPR studies.[169,170]

Structural data are available for the purple double decker formed in the reaction of holmium vapor with excess 2,4,6-tri-tert-butylphosphorin at −196 °C. $[Ho(\eta\text{-}PC_5H_2tBu_3\text{-}2,4,6)_2]$ represents the first zero-valent heteroarene complex of a lanthanide.[171]



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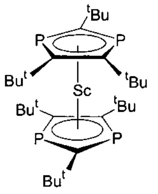

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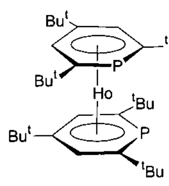
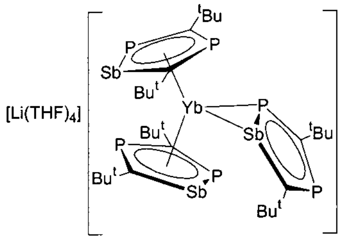


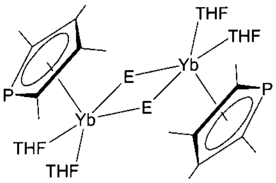
91

Redox transmetalation between ytterbium metal and the thallium species $[Tl(1,4,2\text{-}P_2EC_2tBu_2)]$ (E = Sb, P) containing presumably a substantial amount of Li impurities leads to formation of $[Li(THF)_4][Yb(1,4,2\text{-}P_2EC_2tBu_2)_3]$ (**92**). Two of the low-symmetry $[P_2SbC_2tBu_2]$ ligands are bonded in a η^5 fashion while the third is η^2 bonded. Due to two different arrangements there is a positional disorder in the side-on ligand with phosphorus and antimony having mutual partial occupancies. The best refinement corresponds to a 2:1 ratio of $[P_2SbC_2tBu_2]$ to $[P_3C_2tBu_2]$.[172]



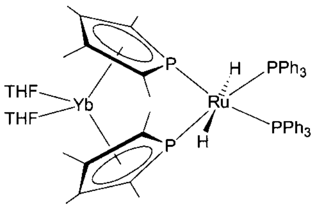
92

Another reaction possibility starting from the metal itself implies conversion of ytterbium metal with 1-chloro- or 1-phenylthio-2,3,4,5-tetramethylphosphole (TmPE, E = Cl, SPh). It comes to direct cleavage of the P−Cl and P−S bonds, respectively, and formation of divalent dimers $[Yb(\mu\text{-}E)(\eta^5\text{-}TmP)(THF)_2]_2$ (**93**). The chloride is also the comproportionation product of $YbCl_2$ and homoleptic $Yb(TmP)_2$. Further treatment with NaSPh in THF at room temperature gives the thiolate as well.[173]



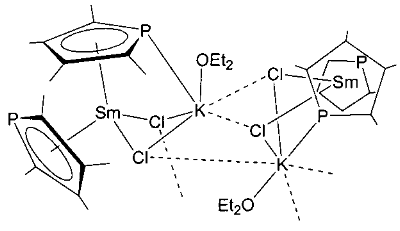
93

$Yb(TmP)_2(THF)_2$ can be converted into the phospholyl-bridged heterobimetallic ruthenium hydride $(THF)_2Yb[\mu\text{-}(\eta^5{:}\eta^1\text{-}TmP)_2Ru(H)_2(PPh_3)_2]$ (**94**) by equimolar reaction with $RuH_4(PPh_3)_3$ in THF. The TmP ligands are π-bonded to the ytterbium and P-σ-bonded to the ruthenium atom.[174]



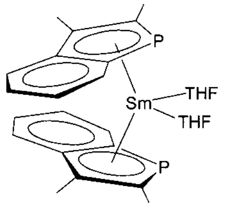
94

Carbene adducts of solvent free homoleptic $Yb(TmP)_2$ as well as their reaction products with $RuH_4(PPh_3)_3$ were synthesized, but no X-ray structures were reported.[175] Sm halides were also treated with the potassium salt of the TmP ligand causing the formation of some interesting polymers. THF-solvated $SmCl_3(THF)_x$ reacts immediately with 2 equiv of C_4Me_4PK in THF to form $[(TmP)_2SmCl_2K]$, whose ether complex $[(\eta^5\text{-}TmP)Sm(\mu_3\text{-}Cl)_2(\mu\text{-}\eta{:}^5\eta^1\text{-}TmP)K(Et_2O)]_n$ (**95**) was structurally characterized. The ligands are π-bonded to the Sm center, and it is the triply bridging chlorine atoms that cause the cross-linkage in the polymer chain.



95

π- and σ-complexes were obtained with the phosphorus analogues of indene and fluorene. Treatment of $SmI_2(THF)_2$ with 2 equiv of potassium 2,3-dimethylphosphindolide gives π-bonded bis(η^5-2,3-dimethylphosphindolyl)$Sm(THF)_2$ (**96**). On the other side, the reaction of $HgCl_2$ activated Sm with bis(1,1′-dibenzophospholyl) leads to formation of the phosphide bis(η^1-dibenzophospholyl)$Sm(THF)_4$ (**97**).[177]



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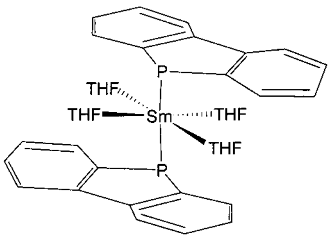


97

9. Lanthanacarboranes

Over 30 years ago Hawthorne et al. introduced carboranes as ligands in organometallic chemistry. Pointing out the electronic resemblance between dicarbollyl and cyclopentadienyl ions, Hawthorne and co-workers started to explore the transition metal−carborane chemistry.[178,179] They also reported on the first carborane complex with a lanthanide metal.[180]

Despite the different charges of the ligands the dicarbollide dianions seem to be promising candidates to develop a new alternative area of cyclopentadienyl-analogous chemistry. Still there exist a lot of differences between the two aromatic systems. The bonding between the carborane faces to the metal center should be more covalent due to the orientation of their frontier orbitals, the softer boron atoms, and the greater negative charge of the ligand.[181,182]

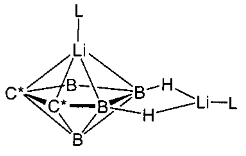
The most commonly used carboranes, dianions of the *nido*-carboranes $2,3\text{-}R_2C_2B_4H_6$ (2,3CB) and $7,8\text{-}R_2C_2B_9H_{11}$,[181] have been mainly applied in lanthanacarborane chemistry. In recent years, the groups of

Hosmane et al. and Xie et al. have undertaken intense research on the fields of the $C_2B_4^-$ and the C_2B_9/C_2B_{10} system, respectively.

9.1. Complexes with the Dicarba-*nido*-hexaborane (C_2B_4) Cage

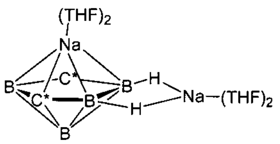
The smaller carbon−boron cage 2,3-bis(trimethylsilyl)-2,3-dicarba-*nido*-hexaborane(8) is easily deprotonated by BuLi in THF or TMEDA to give *closo-exo*-4,5-[(μ-H)$_2$Li(L)]-1-Li(L)-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$, L = (THF)$_2$ and TMEDA ([Li(L)]$_2$(2,3CB), **98**).[183]

Treatment of [Li(THF)]$_2$(2,3CB) with NiCl$_2$ and Na/C$_{10}$H$_8$ yields the disodium salt *closo-exo*-4,5-[(μ-H)$_2$Na(THF)$_2$]-1-Na(THF)$_2$-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$ ([Na(THF)$_2$]$_2$(2,4CB), **99**).



L = (THF)$_2$, TMEDA; C* = C-SiMe$_3$

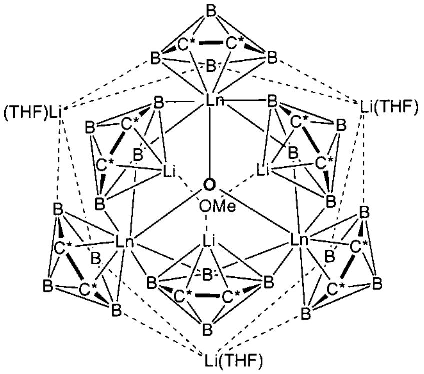
98



99

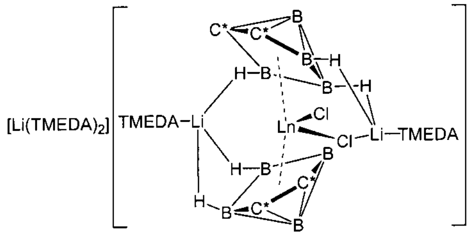
Typical reaction procedures include the treatment of a solution of the dilithiocarborane with anhydrous LnCl$_3$ in molar ratios of 2:1 in dry benzene. Different structures are obtained depending on the nature of the ligating solvents of the lithium salt.

The reactions using [Li(THF)$_2$]$_2$(2,3CB) result in the formation of heteronuclear clusters {[η^5-1-Ln-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$]$_3$[(μ_2-1-Li-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$)$_3$-(μ_3-OMe)][μ_2-Li(THF)]$_3$(μ_3-O)} (**100**) (for Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er).[185−187]



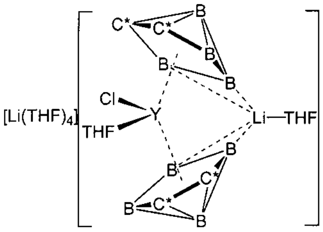
100

A methoxy group links three lithiocarborane moieties which connect three Ln atoms capped by one carborane, respectively. An oxygen atom is located almost in the center of the Ln$_3$ trigonal plane. On the outside the carboranes belonging to the Ln atoms are bridged by three Li(THF). As THF seems to be the source of the oxygen atom as well as of the methoxy group, the same reactions were carried out using the TMEDA-solvated lithium salt of the ligand [Li(TMEDA)]$_2$(2,3CB). The resulting anionic species [Li(TMEDA)$_2$][1-Cl-1-(μ-Cl)-2,2′,3,3′-(SiMe$_3$)$_4$-5,6-[(μ-H)$_2$Li(TMEDA)]-4,4′,5′-[(μ-H)$_3$Li(TMEDA)]-1,1′-*commo*-Ln(2,3-C$_2$B$_4$H$_4$)$_2$] (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er) (**101**) resemble bent metallocenes: a Ln, with additional Cl, LiCl, or solvent ligands, is bonded to two carborane units which are bridged by one Li(TMEDA).[185,188−190] Repeated crystallization causes the loss of one LiCl(TMEDA) moiety.[185]



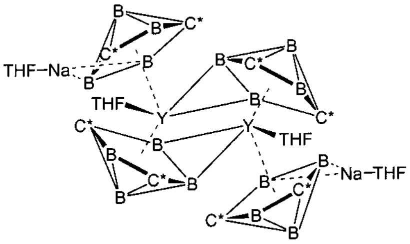
101

A very similar structure is presented by the reaction product [Li(THF)$_4$]{1-Cl-1-(THF)-2,2′-(SiMe$_3$)$_2$-3,3′-(SiMe$_3$)$_2$-4,4′,5,5′-Li(THF)[1,1′-*commo*-Y(2,3-C$_2$B$_4$H$_4$)$_2$]} (**102**) of the THF-solvated dilithiocarborane and YCl$_3$.[184]



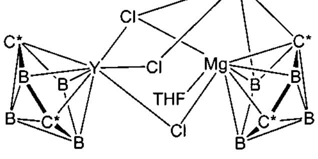
102

On the other side [Na(THF)$_2$]$_2$(2,4CB) reacts with YCl$_3$ to form a halide-free dimer {Na(THF)$_3$}$_2${[1-(THF)-1-(μ-H)$_2$-2,2′,4,4′-(SiMe$_3$)$_4$-1,1′-*commo*-Y(2,4-C$_2$B$_4$H$_4$)$_2$]$_2$} (**103**).[184]



103

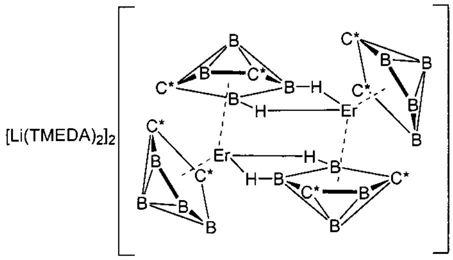
An attempt to synthesize an alkyl-substituted yttracarborane with a Grignard reagent yielded a mixed Y−Mg cluster *closo*-1-Y-{1,1′-(μ-Cl)$_2$-*exo*-[5,6-(μ-H)$_2$-Mg(THF)$_2$]-1,1′-(μ-Cl)[*closo*-1-Mg(THF)-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$]}-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$·3.5C$_6$H$_6$ (**104**), whose formation mechanism is still not fully understood.[184]



104

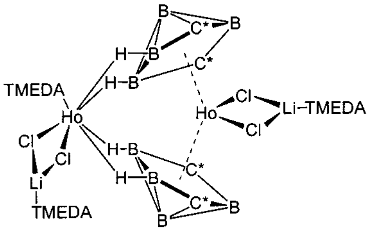
Additional treatment of **101** with [Li(TMEDA)]$_2$(2,4CB) allowed the high-yield synthesis of the first mixed (2,3CB)(2,4CB)Ln−carborane derivative {Li-

$(TMEDA)_2\}_2\{$*commo*-1-$[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]$-1-Er-$[2,4\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_4]\}_2$ (**105**), which is a dianionic dimer in the solid state. Each Er is capped by one (2,3CB) and one (2,4CB) unit, respectively. The two halves are linked via two Er−H−B bridging interactions of the (2,4CB) moieties.[188]



105

A dinuclear cluster 1-$[(\mu\text{-}Cl)_2Li(TMEDA)]$-2,2′,4,4′-$(SiMe_3)_4$-5,5′,6,6′$[(\mu\text{-}H)_4Ho(TMEDA)(\mu\text{-}Cl)_2Li(TMEDA)]$-1,1′-*commo*-$Ho(2,4\text{-}C_2B_4H_4)_2{\cdot}(C_{10}H_8)$ (**106**) is the result of an equimolar reaction of $[Li(TMEDA)]_2$(2,4CB) and $HoCl_3$.[191] Whereas one Ho and two (2,4CB) moieties form a bent-sandwich complex, the second *exo*-polyhedral Ho atom is bridged to via two B−H(terminal) groups.



106

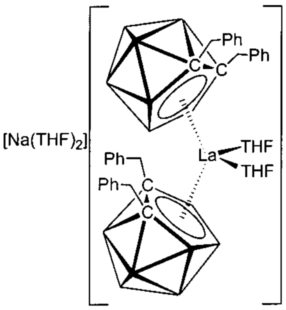
9.2. Complexes with C_2B_9 and C_2B_{10} Cages

In the case of the larger cage systems, only Na- or K-metalated ligands are used. $[NH_3][C_2B_9H_{12}]$ is deprotonated with NaH to give $Na_2[7,8\text{-}R_2\text{-}$*nido*-$7,8\text{-}R_2C_2B_9H_9]$ ($Na_2[R_2C_2B_9H_9]$), whereas K metal is necessary to make $K_2[R_2C_2B_{10}H_{10}]$ (R = H, $C_6H_5CH_2$). Reactions with lanthanide halides are carried out in THF.

9.2.1. C_2B_9 Derivatives

Treatment of equimolar amounts of $Na_2[R_2C_2B_9H_9]$ and $LaCl_3$ in THF affords the sandwich complex *closo*-$\{(THF)_2Na\}\{(R_2C_2B_9H_9)_2La(THF)_2\}$ (R = H, $C_6H_5CH_2$ (**107**)).[192] In the case of the smaller lanthanides Y and Yb, a half-sandwich lanthanacarborane chloride seems to be formed. But only the recrystallization product from a wet THF solution was characterized for Yb, which is the ionic compound $[YbCl_2(THF)_5]$[*nido*-$C_2B_9H_{12}$] (**108**).[193]

The outcome of the reactions using divalent lanthanides is slightly different depending on the stoichiometry. At first sight all three structures which were determined from reactions of $Na_2[(C_6H_5CH_2)_2C_2B_9H_9]$ and divalent lanthanides seem to be the same. However, there are small differences as to the coordination of the carborane ligands to the Ln ions though all the compounds are dimeric with exclusive Ln−H−B bonds.



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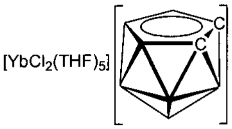
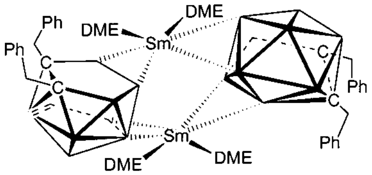


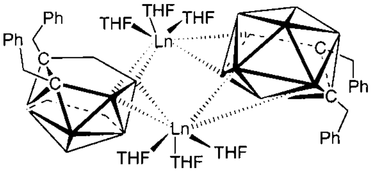
108

Equimolar conversion of $Na_2[(C_6H_5CH_2)_2C_2B_9H_9]$ with a THF solution of SmI_2 gives *exo*-*nido*-$[((C_6H_5CH_2)_2C_2B_9H_9)Sm(DME)_2]_2{\cdot}DME$ (**109**) after crystallization from DME. Bonding occurs to the Sm atoms via two B−H bonds from the upper and two from the lower CB belt, respectively.[192]



109

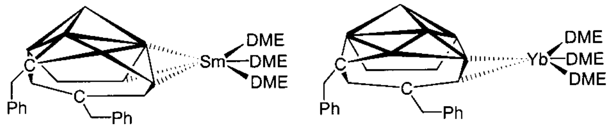
Treatment of 2 equiv of $Na_2[(C_6H_5CH_2)_2C_2B_9H_9]$ with divalent Sm and Yb gives isomorphous structures [*exo*-*nido*-$\{(C_6H_5CH_2)_2C_2B_9H_9\}Ln(THF)_3]_2$ (**110**, Ln = Sm, Yb), where the bonding situation is more complicated. The metal atoms are bonded to both belts and there again in different fashions as well.[194]



110

9.2.2. $R_2C_2B_{10}$ Derivatives

Xie et al. also studied the reaction behavior of the benzyl-substituted potassium salt $K_2[(C_6H_5CH_2)_2C_2B_{10}H_{10}]$ with di- and trivalent halides of Sm and Yb.[194] Equimolar reactions with LnI_2 give monomeric DME-solvated compounds *exo*-*nido*-$[(C_6H_5CH_2)_2C_2B_{10}H_{10}]Ln(DME)_3$ (**111**, Ln = Sm, Yb). Probably due to the different sizes of the Ln^{2+} ions the coordination mode to the carboranyl ligand varies.



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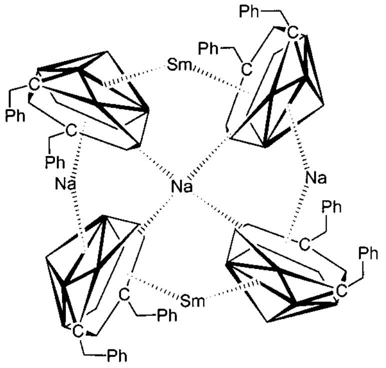
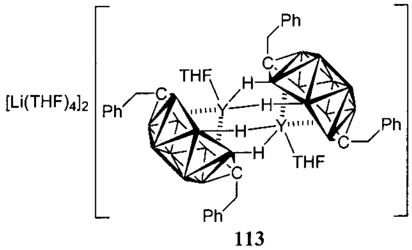
Reduction takes place when $LnCl_3$ is reacted with the dianion of the $C_2B_{10}H_{12}$ carborane. It is complete for Ln = Yb affording divalent **111** as above, but it stops halfway for Ln = Sm yielding a novel mixed-valent heteronuclear cluster *closo*-*exo*-$[(C_6H_5CH_2)_2C_2B_{10}H_{10}]_4Sm_2Na_3$ (**112**). The metal atoms are connected via bonds from the B_5 belt and the open hexagonal C_2B_4 bonding face. As the two Sm atoms cannot be distinguished in terms of bond distances, the formal oxidation state for each one of them should be +2.5.



112

Whereas **112** incorporates the carboranyl ligand in a η^6-fashion, a higher hapticity of 7 is reached in compounds formed during reactions with the lithium or sodium salt of the same carborane. $LnCl_3$ reacts with 1 equiv of lithium- or sodium-reduced 1,2-$(C_6H_5CH_2)_2$-1,2-$C_2B_{10}H_{10}$ in the presence of excess alkali metal in THF to give neutral or ionic dimeric 13-vertex *closo*-lanthanacarboranes. With Li dianionic $[\{(C_6H_5CH_2)_2C_2B_{10}H_{10}\}Ln(THF)]_2[Li(THF)_4]_2$ (Ln = Y (**113**), Er) is formed while the use of Na produces neutral $\{[(C_6H_5CH_2)_2C_2B_{10}H_{10}]Ln(THF)\}_2\{Na(THF)_3\}_2 \cdot 2THF$ (Ln = Dy, Y (**114**), Er) with two Na atoms attached to the carboranyl ligands. Recrystallization of the Er complex from DME affords DME-solvated $\{[(C_6H_5CH_2)_2C_2B_{10}H_{10}]Er(DME)\}_2\{Na(DME)_2\}_2$ (**115**).[195]



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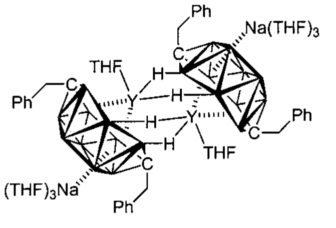

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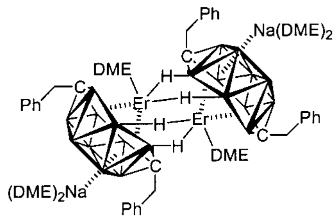
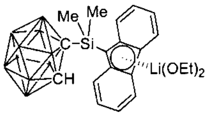


115

The synthesis of a full-sandwich η^7-C_2B_{10}-lanthanacarborane was achieved by use of the carborane−fluorene ligand $[Me_2Si(C_{13}H_8)(C_2B_{10}H_{11})]Li(OEt)_2$ (**116**) made from $Li_2[C_2B_{10}H_{10}]$ and $Me_2Si(C_{13}H_9)Cl$. Reaction of equimolar amounts of **116**, $YbCl_3$, Na metal, and Me_3NHCl in THF results in formation of $\{\{[\eta^7\text{-}Me_2Si(C_{13}H_9)(C_2B_{10}H_{11})]_2Yb^{III}\}_2Yb^{II}\}\{Na_8(THF)_{20}\}$ (**117**).[196] Addition of Me_3NHCl is essential for isolation of **117**. It is assumed that the ammonium salt protonates the appended fluorenyl anion leaving the core structure intact.



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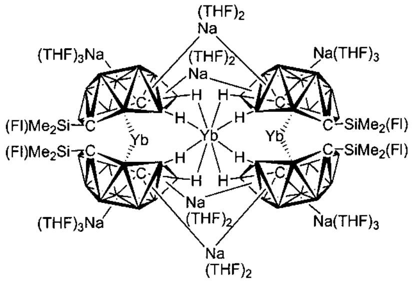


117

In the structure two units consisting of trivalent Yb ions sandwiched between *arachno*-$R_2C_2B_{10}H_{10}$ ligands are connected by a divalent Yb ion via two sets of four B−H−Yb bonds. Obviously the tetra-anionic carboranyl ligand can protect trivalent Yb from being reduced by Na.

10. π-Arene Complexes

By now it is well-established that lanthanide ions are capable of participating in η^6-interactions with benzene derivatives. The number of well-characterized lanthanide arene complexes has increased steadily in recent years. Among the non-cyclopentadienyl organolanthanides the π-arene complexes form a particularly important class of compounds, especially due to their very interesting derivative chemistry. Bis(arene)lanthanide(0) sandwich complexes have been reviewed elsewhere and thus will not be considered here.[197,198]

Naphthalene complexes of the general formula $(C_{10}H_8)Ln(THF)_n$ (Ln = Sm, Eu, Yb) are known for many years, and their derivative chemistry has been compiled in an excellent recent review article by Bochkarev.[197] A typical preparation involves the reaction of ytterbium diiodide with lithium naphthalenide in THF or DME solution (eq 52).[197] It is now generally accepted that these compounds are lanthanide(II) complexes of the naphthalene dianion.

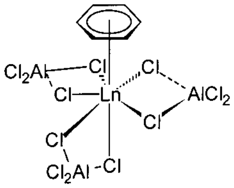
$$YbI_2 + 2Li(C_{10}H_8) \xrightarrow{THF} (C_{10}H_8)Ln(THF)_n + 2LiI \tag{52}$$

In a series of studies Bochkarev et al. have also demonstrated that these complexes exhibit high reactivities toward a large variety of reagents and may thus serve as highly useful starting materials for the preparation of various organolanthanides.[197] A most recent addition to the diverse derivative chemistry of $(C_{10}H_8)Ln(THF)_n$ complexes is the reaction of $(C_{10}H_8)Yb(THF)_2$ with cyclopentadienyl-substituted alcohols and amines, which leads to novel half-sandwich complexes of divalent ytterbium.[199,200]

The longest known organolanthanide complexes involving η^6-arene coordination are bimetallic complexes of the type (η^6-arene)Ln($AlCl_4$)$_3$.[201−206] Unlike the anhydrous lanthanide trichlorides, these compounds are soluble in hydrocarbons. The synthetic route involves treatment of anhydrous lanthanide trichlorides with $AlCl_3$ in the presence of the arene ligand. Most conveniently the appropriate benzene derivative is used directly as a solvent in these preparations (eq 53).

$$LnCl_3 + 3AlCl_3 + C_6R_6 \rightarrow (\eta^6\text{-}C_6R_6)Ln(AlCl_4)_3 \quad R = H\ (\mathbf{118}),\ Me \qquad (53)$$

$$Ln = La,\ Nd,\ Sm,\ Gd,\ Yb$$



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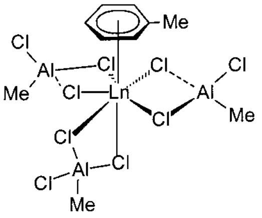
The bonding situation in these arene complexes has been described as an electrostatically induced dipole interaction between the Ln^{3+} cation and the π-electron system of the aromatic ring. Preferable ligands are electron-rich arenes such as benzene, toluene, and hexamethylbenzene. Well-characterized and in some cases structurally characterized examples are the complexes (η^6-C_6H_6)Ln($AlCl_4$)$_3$ (**118**, Ln = Nd, Sm, Yb), (η^6-C_6H_5Me)Ln($AlCl_4$)$_3$ (Ln = Y, Pr, Nd, Sm, Gd), and (η^6-C_6Me_6)Ln($AlCl_4$)$_3$ (Ln = Sm, Er, Yb), most of which are monomeric in the solid state.[203,204] Interestingly, the structurally investigated toluene complex (η^6-C_6H_5Me)Nd($AlCl_4$)$_3$ was isolated during an attempt to synthesize [η^6-$C_6H_3(tBu)_3$]Nd($AlCl_4$)$_3$ in toluene solution.[207] The η^6-benzene compounds of neodymium and samarium are isostructural with the uranium(III) analogue (η^6-C_6H_6)U($AlCl_4$)$_3$. A notable exception from the normal monomeric, pentagonal-bipyramidal structure is tetrameric [(η^6-C_6H_6)Er($AlCl_4$)$_3$]$_4$, in which the erbium ions are bridged by η^2-tetrachloroaluminate ligands.[208]

Derivatization of the tetrachloroaluminate ligands has been achieved by addition of AlR_3 (R = Me, Et) to a toluene suspension of (η^6-C_6H_5Me)Ln($AlCl_4$)$_3$, which results in the formation of clear solutions from which the alkylated products (η^6-C_6H_5Me)Ln($AlCl_3R$)$_3$ (R = Me, Et) can be isolated in good yields (eq 54). The complexes (η^6-$C_6H_2Me_4$)Nd($AlCl_3R$)$_3$ (R = Me, Et) have been made in an analogous manner, and the neodymium complex (η^6-C_6H_5Me)Nd($AlCl_3Me$)$_3$ was structurally characterized by X-ray diffraction.[209] It has also been found that these alkyltrichloroaluminate complexes catalyze the polymerization of ethylene and butadiene.

$$2(\eta^6\text{-}C_6H_5Me)Ln(AlCl_4)_3 + 3AlR_3 \rightarrow (\eta^6\text{-}C_6H_5Me)Ln(AlCl_3R)_3 + 3AlCl_2R \qquad (54)$$

$$\mathbf{119}:\ R = Me,\ Ln = Y,\ Nd,\ Sm;\quad R = Et,\ Ln = Pr,\ Nd$$



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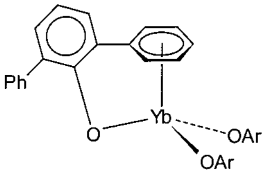
Interesting cases of η^6-arene coordination between lanthanide ions and phenyl groups of certain phenoxide ligands have been detected in some unsolvated lanthanide aryloxide derivatives. Two different types of this novel bonding situation have been reported so far.[210,211] Lanthanide metal powders react with $Hg(C_6F_5)_2$ and 2,6-diphenylphenol in THF to afford the lanthanide(III) phenoxides Ln(2,6-$OC_6H_3Ph_2$)$_3$ (Ln = Nd, Sm, Er, Yb, Lu) or the corresponding THF solvates. The structurally characterized THF adduct Yb(2,6-$OC_6H_3Ph_2$)$_3$(THF)$_2$ exhibits no unusual π-bonding features. However, in the unsolvated compound Yb(2,6-$OC_6H_3Ph_2$)$_3$ (**120**) one phenyl substituent is in a geometrically favorable position which allows this ring to engage in a novel π-interaction with the central ytterbium atom (Ar = 2,6-$C_6H_3Ph_2$). The reason for this additional η^6-arene coordination is most likely the sterically unsaturated character of the three-coordinate species Ln(2,6-OC_6H_3-Ph_2)$_3$ (**120**).



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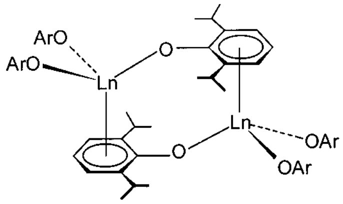
The second variety was found in related lanthanide derivatives of 2,6-diisopropylphenol, which have been prepared using a similar synthetic route.[211] The complexes [Ln(2,6-$OC_6H_3iPr_2$)$_3$]$_2$ (**121**: Ln = Nd (pale blue), Sm (deep yellow), Er (light pink)) were prepared in good yield by the reaction of 3 equiv of 2,6-diisopropylphenol with Ln[N($SiMe_3$)$_2$]$_3$ in refluxing toluene. X-ray analyses revealed that these compounds consist of centrosymmetric dimers in which the monomeric units are connected through η^6-arene coordination of two phenyl substituents.



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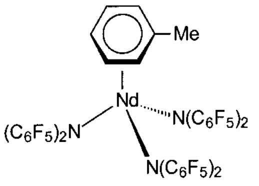
Interesting "inverse sandwich complexes" have been prepared according to eqs 55 and 56 from naphthalene (=$C_{10}H_8$):[212]

$$2LaI_3(THF)_3 + 2Li + C_{10}H_8 \xrightarrow{THF} (\mu_2\text{-}\eta^4{:}\eta^4\text{-}C_{10}H_8)[LaI_2(THF)_3]_2 + 2LiI \quad (55)$$

$$2EuI_2(THF)_2 + 2C_{10}H_8Li \xrightarrow{DME} (\mu_2\text{-}\eta^4{:}\eta^4\text{-}C_{10}H_8)[EuI(DME)_2]_2 + 2LiI + C_{10}H_8 \quad (56)$$

Both naphthalene complexes have been characterized by single-crystal X-ray structure analyses. These compounds are not typical π-arene complexes involving η^6-coordination of the aromatic ligands. Instead, the lanthanide atoms are bridged by nonplanar naphthalene units bonded in diene-like fashion.

The recent literature also has several interesting examples of lanthanide amido complexes involving η^6-arene coordination.[213] Reaction of $Nd[N(SiMe_3)_2]_3$ with 3 equiv of decafluorodiphenylamine, $HN(C_6F_5)_2$, in toluene followed by recrystallization from the same solvent led to isolation of $(\eta^6\text{-}C_6H_5Me)Nd[N(C_6F_5)_2]_3$ (**122**) in good yield. An X-ray diffraction analysis revealed a distorted three-legged piano-stool geometry around neodymium. The toluene ligand is coordinated rather unsymmetrically with Nd−C distances in the range of 298(2)−332.4(13) pm. In addition there are three significant Nd···F interactions, resulting in a formal coordination number of 9 at neodymium.



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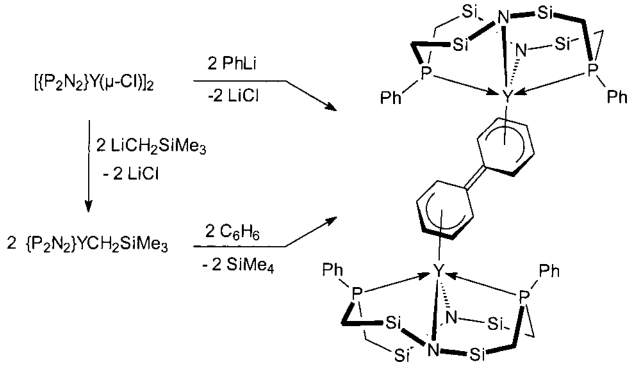
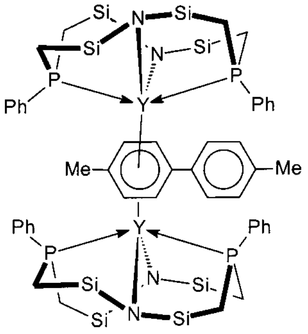
The formation of highly colored yttrium arene complexes with macrocyclic ancillary ligands has been reported by Fryzuk et al.[98] The compound $[\{P_2N_2\}Y(\mu\text{-}Cl)]_2$ ($\{P_2N_2\} = [PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh]^{2-}$) reacts with phenyllithium to give a dark blue product comprising the empirical formula $\{P_2N_2\}Y(C_6H_5)$. The same product was obtained in a C−H activation reaction between $\{P_2N_2\}YCH(SiMe_3)_2$ and benzene. An X-ray structure determination of the isolated deep blue crystals revealed the presence of an unusual dimeric complexes of the composition $(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_5C_6H_5)[\{P_2N_2\}Y]_2$ as depicted in Scheme 16.

The compound $(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_5C_6H_5)[\{P_2N_2\}Y]_2$ is a dinuclear complex with a biphenyl dianion bridging two $\{P_2N_2\}Y$ fragments with each of these units bound in an η^6-fashion to the opposite faces of the biphenyl moiety. While the same type of dark blue compound could be generated using *m*-tolyllithium, the reaction of $[\{P_2N_2\}Y(\mu\text{-}Cl)]_2$ with *p*-tolyllithium had a different outcome affording a dark brown crystalline product (**123**). In this case an X-ray diffraction study showed again the presence of a dinuclear complex containing a bridging bi-*p*-tolyl ligand. However, in this case the two $\{P_2N_2\}Y$ fragments are sandwiching one tolyl group leaving the second uncoordinated.[98]

Scheme 16. Synthesis of $(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_5C_6H_5)[\{P_2N_2\}Y]_2$ with Methyl Groups on Si Omitted for Clarity[98]





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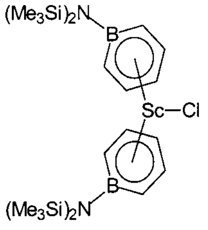
Closely related dinuclear π-complexes of yttrium and lutetium with sandwiched naphthalene and anthracene ligands have been reported more recently.[214] Here the synthetic route involves treatment of the chloro precursors $[\{P_2N_2\}Ln(\mu\text{-}Cl)]_2$ (Ln = Y, Lu) with the respective polyarenes in the presence of potassium graphite (C_8K) in toluene/diethyl ether.

An interesting new addition to the chemistry of lanthanide π-arene complexes is the use of monoanionic boratabenzene ligands. Boratabenzene anions are six-membered aromatic heterocycles which can serve as 6π-electron ligands and thus form organolanthanide derivatives similar to certain classes of rare earth cyclopentadienyl complexes. Solvent-free lithium boratabenzenes, $Li(C_5H_5BR)$ (R = Me, NMe_2, $N(SiMe_3)_2$), were reacted with $ScCl_3$ in toluene under rather drastic reaction conditions (110 °C, 3 days) to give the disubstituted complexes.[215] All three compounds were structurally characterized by X-ray analyses. In the cases of R = Me or NMe_2, the products are chloro-bridged dimers while with the bulky $N(SiMe_3)_2$ substituent the monomeric chloro complex $ScCl[C_5H_5BN(SiMe_3)_2]_2$ (**124**) was obtained.

In a similar manner a dimeric yttrium complex containing the 1-methylboratabenzene ligand was prepared in 85% yield in the form of moisture-sensitive pale yellow crystals.[216] In this case, too, drastic reaction conditions had to be employed due to the lower nucleophilicity of $Li(C_5H_5BMe)$ in comparison to cyclopentadienide.



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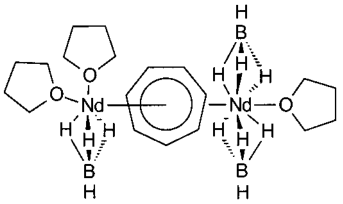
11. Cycloheptatrienyl Complexes

f-element cycloheptatrienyl complexes were first mentioned in 1981 by Miller and Dekock who reacted cycloheptadienyllithium (=Li[C_7H_9]) with actinide and lanthanide chlorides. However, the presence of metal-coordinated $C_7H_7^{3-}$ was deduced only from chemical reactivity and spectroscopy. Until recently, well-characterized cycloheptatrienyl complexes have been completely absent from organolanthanide chemistry. Thus, the first successful synthesis of such a species by Ephritikhine et al. was a particularly remarkable achievement.[217] Treatment of $Nd(BH_4)_3(THF)_2$ with K[C_7H_9] gave the neutral compound $(THF)_2(BH_4)Nd(\mu\text{-}\eta^7{:}\eta^7\text{-}C_7H_7)Nd(BH_4)_2(THF)$ as green microcrystals. Green single crystals could be obtained by recrystallization from THF−pentane. The formation of the cycloheptatrienyl ligand resulted from the disproportionation reaction outlined in eq 57.

$$3C_7H_9^{\ -} \rightarrow C_7H_7^{\ 3-} + 2C_7H_{10} \qquad (57)$$

An X-ray crystal structure determination of $(THF)_2(BH_4)Nd(\mu\text{-}\eta^7{:}\eta^7\text{-}C_7H_7)Nd(BH_4)_2(THF)$ (**125**) revealed the presence of an inverse sandwich complex in which two different neodymium fragments are bridged by a $\mu\text{-}\eta^7{:}\eta^7\text{-}C_7H_7$ ligand. The cycloheptatrienyl ring is planar and perpendicular to the axis defined by the two Nd centers and the ring centroid. According to the IR data the coordination mode of the tetrahydroborate ligands is tridentate.



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12. Cyclooctatetraenyl Complexes

Lanthanide(II) cyclooctatetraenyl compounds of the type Ln(C_8H_8) (Ln = Eu, Yb) were reported as early as 1969.[2,3,5] The initial synthetic achievements in this area were followed by a period of relative stagnation, which in recent years has been replaced by significantly increased research activities. Today it is generally accepted that the large, flat cyclooctatetraene ligand represents an especially valuable alternative to the popular cyclopentadienyl ligands. Among the non-cyclopentadienyl organolanthanide complexes, cyclooctatetraenyl derivatives form a large and well-investigated group of compounds. This is an area of organolanthanide chemistry where numerous interesting results can be expected in the future.[218]

12.1. Divalent Lanthanide Derivatives

Well-defined lanthanide(II) complexes with cyclooctatetraenyl ligands are rare. Metallic europium or ytterbium are known to dissolve in liquid ammonia to give dark blue solutions. Cyclooctatetraene reacts with these solutions to give $[Ln(C_8H_8)]_n$ (Ln = Eu, Yb) according to eq 58.[2,3,5,218] The orange products are exceedingly air-sensitive and insoluble in common organic solvents. The latter property suggests that the compounds are polymeric in the solid state. A more straightforward synthetic route to polymeric $[Sm(C_8H_8)]_n$ involves treatment of $SmI_2(THF)_2$ with 1 equiv of $K_2C_8H_8$.[219]

$$Ln + C_8H_8 \xrightarrow{NH_3(l)} [Ln(C_8H_8)]_n \qquad (58)$$

$$Ln = Eu,Yb$$

Treatment of $[Yb(C_8H_8)]_n$ with pyridine breaks up the polymeric structure and results in the formation of soluble $(C_8H_8)Yb(C_5H_5N)_3$. The monomeric nature of this complex has been established by an X-ray structure analysis.[220] The anionic sandwich complexes $[K(diglyme)]_2[Yb(C_8H_8)_2]$ and $[K(DME)]_2[Yb(C_8H_8)_2]$ have also been structurally characterized. In these compounds cyclooctatetraene dianions act as bridging ligands between ytterbium and potassium.[221]

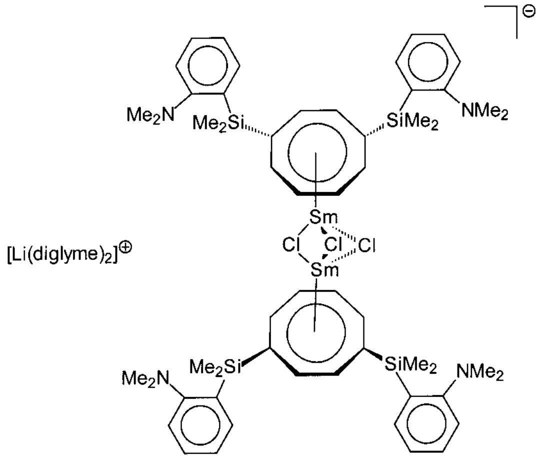
12.2. Trivalent Lanthanide Derivatives

Mono(cyclooctatetraenyl)lanthanide(III) halides of the type $[(C_8H_8)Ln(\mu\text{-}Cl)(THF)_2]_2$ are the most important precursors for the preparation of other half-sandwich complexes with cyclooctatetraenyl ligands.[218,222,223] These complexes are readily accessible by reacting anhydrous lanthanide trichlorides with $K_2C_8H_8$ in a molar ratio of 1:1 according to eq 59. Purification of the crystalline, intensely colored products is usually achieved by Soxhlet extraction with THF.[224]

$$2LnCl_3 + 2K_2C_8H_8 \rightarrow [(C_8H_8)Ln(\mu\text{-}Cl)(THF)_2]_2 + 4KCl \qquad (59)$$

As exemplified by a crystal structure determination of the cerium compound $[(C_8H_8)Ce(\mu\text{-}Cl)(THF)_2]_2$ the compounds consist of centrosymmetric, chloro-bridged dimers with η^8-coordinated cyclooctatetraenyl ligands.[2,3,5,218,222,223] The coordinated THF cannot be removed from the solvates without extensive decomposition. Thus far the unsolvated parent compounds have not been synthesized. The use of the sterically highly demanding 1,4-bis(trimethylsilyl)cyclooctatetraenyl ligand has allowed the synthesis of a related series of organolanthanide halides.[225,226] The THF adducts $LnCl_3(THF)_3$ (Ln = Y, Sm, Ho, Lu) react with equimolar amounts of the dilithium salt $[Li(THF)]_2[1,4\text{-}(Me_3Si)_2C_8H_6]$ to afford the dimeric mono(cyclooctatetraenyl)lanthanide(III) chlorides $[Ln\{(1,4\text{-}(Me_3Si)_2C_8H_6)\}(\mu\text{-}Cl)(THF)]_2$ (Ln = Y, Sm, Ho, Lu).

An X-ray diffraction study of the holmium derivative showed that due to the steric bulk of the silyl-substituted COT ligands these complexes now contain only two THF ligands/molecule. In the case of scandium another interesting change takes place. Here the composition of the reaction product is (μ-Cl)$_2$(μ-THF)[Sc{1,4-(Me$_3$Si)$_2$C$_8$H$_6$)}]$_2$. A single-crystal X-ray structural analysis showed the presence of an unusual semibridging THF ligand. Obviously the reason for the coordination of only one THF molecule is the increased steric demand of the substituted cyclooctatetraene ligands in combination to the small ionic radius of Sc^{3+}.[225] An interesting novel development in this area is the use of functionally substituted cyclooctatetraenyl ligands.[227,228] Treatment of *o*-(chlorodimethylsilyl)-*N*,*N*-dimethylaniline with $K_2C_8H_8$ (molar ratio 2:1) selectively gave 1,4-bis[(*o*-*N*,*N*-(dimethylamino)methylpheny)dimethylsilyl]-cycloocta-2,5,7-triene. Subsequent metalation with 2 equiv of *n*-butyllithium afforded the new functionalized cycloctatetraenide Li$_2$(1,4-R$_2$C$_8$H$_6$) (R = *o*-*N*,*N*-Me$_2$NC$_6$H$_4$SiMe$_2$). Treatment of this salt with anhydrous SmCl$_3$ (molar ratio 2:1) in diglyme solution resulted in formation of the anionic complex [Li(diglyme)$_2$][(1,4-R$_2$C$_8$H$_6$)$_2$Sm$_2$(μ-Cl)$_3$] (**126**), which was isolated in the form of purple crystals. A single-crystal X-ray diffraction study revealed the presence of a unique triply chlorine-bridged complex.



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The mono(cyclooctatetraenyl)lanthanide chlorides [(C$_8$H$_8$)Ln(μ-Cl)(THF)$_2$]$_2$ are useful precursors for subsequent reactions, because the bridging chloro ligands are easily replaced by various other anions.[218] A certain disadvantage, however, is the very low solubility of these compounds even in THF. A search for better soluble alternatives led to the development of preparative routes to mono(cyclooctatetraenyl)-lanthanide(III) iodides and triflates. Mononuclear iodo complexes can be prepared in two different ways (eqs 60 and 61).[229−232] The second procedure (eq 61) has the advantage that metal powders can be directly used as starting materials.[229,230] Depending on the ionic radius of the lanthanide element, the products are solvated with various amounts of THF. The molecular structures of samarium and neodymium derivatives have been determined by X-ray diffraction. Both are monomeric in the solid state. In contrast to the dimeric chloro complexes [(C$_8$H$_8$)Ln-(μ-Cl)(THF)$_2$]$_2$ the iodides (C$_8$H$_8$)LnI(THF)$_n$ are highly soluble in THF.

$$\mathrm{LnI_3 + K_2C_8H_8 \xrightarrow{THF} (C_8H_8)LnI(THF)_{\mathit{n}} + 2KI} \quad (60)$$

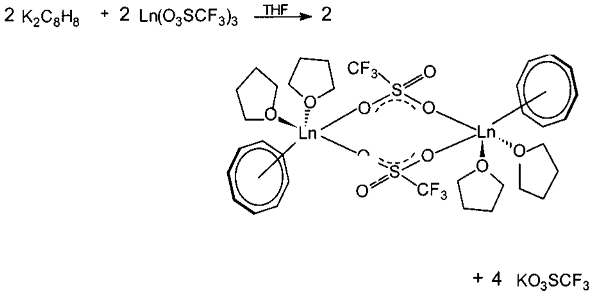
$$\mathrm{Ln = Nd, Sm}$$

$$\mathrm{Ln + C_8H_8 + 1/2I_2 \xrightarrow{THF} (C_8H_8)LnI(THF)_{\mathit{n}}} \quad (61)$$
$$n = 1-3$$

$$\mathrm{Ln = La, Ce, Pr, Nd, Sm}$$

The iodo complexes (C$_8$H$_8$)LnI(THF)$_3$ have been used as model compounds for the evaluation of the electronic structure of related actinide half-sandwich complexes of the type (C$_8$H$_8$)An(I)$_2$(THF)$_2$ (An = actinide element).[233] For this purpose the absorption spectra of (C$_8$H$_8$)LnI(THF)$_3$ (Ln = Pr, Nd, Sm) have been measured at ambient and low temperatures. It was found that the spectra obtained were nearly identical with those of the pyrazolylborate derivatives (C$_8$H$_8$)Ln[HB(3,5-Me$_2$pz)$_3$], where the f-electrons experience essentially a crystal field (CF) associated with the cyclooctatetraenyl ligand.

Greatly improved solubility in polar organic solvents was also found for the corresponding mono-(cyclooctatetraenyl)lanthanide triflates. According to Schumann and Fischer et al. triflates can be valuable alternatives to chloro complexes as demonstrated for various bis(cyclopentadienyl)lanthanide derivatives.[234,235] Dimeric organolanthanide triflates [(C$_8$H$_8$)Ln(μ-O$_3$SCF$_3$)(THF)$_2$]$_2$ (eq 62) are obtained in good yields in a straightforward reaction between anhydrous lanthanide(III) triflates and equimolar amounts of K$_2$C$_8$H$_8$.[229,236] The intensely colored (Ce, Pr, bright yellow; Nd, green; Sm, purple), well-crystallized products are highly soluble in THF. In the case of yttrium the bis(THF) solvate [(C$_8$H$_8$)Y(μ-O$_3$SCF$_3$)(THF)]$_2$ is isolated due to the smaller ionic radius of Y^{3+}.[236]

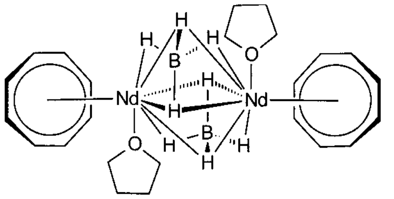


(62)

Ln = Ce, Pr, Nd, Sm

The cerium and neodymium derivatives have been structurally characterized by X-ray diffraction. The central part of the molecule central eight-membered Ln$_2$O$_4$S$_2$ ring is formed by bridging of the lanthanide ions by the bidentate triflate ligands. Thus, there is a close structural relation between the COT compounds [(C$_8$H$_8$)Ln(μ-O$_3$SCF$_3$)(THF)$_2$]$_2$ and the corresponding bis(cyclopentadienyl)lanthanide(III) triflates [Cp$_2$Ln(μ-O$_3$SCF$_3$)]$_2$.[235] As expected the cyclooctatetraene ligands are η^8-coordinated. In addition to better solubility the triflate complexes $[(C_8H_8)Ln(\mu\text{-}O_3SCF_3)(THF)_2]_2$ offer other preparative advantages. The triflate ligand is a good leaving group which facilitates substitution reactions. Furthermore, it was found that LiO_3SCF_3 and NaO_3SCF_3 are easier to remove by filtration than finely divided LiCl or NaCl. Most of the subsequent reactions of the chloro complexes $[(C_8H_8)Ln(\mu\text{-}Cl)(THF)_2]_2$ described below have already been carried out with the corresponding triflates and in many cases higher yields have been obtained.

The number of well-defined mono(cyclooctatetraenyl)lanthanide(III) complexes without additional cyclopentadienyl ligands has greatly increased in recent years. An interesting new development is the use of borohydride ligands which led to the development of some highly versatile starting materials, including the first cationic mono(cyclooctatetraenyl)lanthanide(III) derivative.[237,238] In addition, this was the first example of a chemical transformation of the long-known lanthanide borohydrides, $Ln(BH_4)_3(THF)_n$. Reaction of $Nd(BH_4)_3(THF)_3$ with $K_2C_8H_8$ in THF afforded the monomeric compound $(C_8H_8)Nd(BH_4)(THF)_2$ as a green solid in 87% yield. Upon recrystallization of this material, loss of one THF ligand/Nd and formation of the green organoneodymium borohydride $[(C_8H_8)Nd(\mu\text{-}BH_4)(THF)]_2$ (**127**) were observed. The dimeric structure of **127** with bridging borohydride ligands was established by X-ray crystallography. The coordination mode of the BH_4^- ligands is unusual in that the boron atom is linked to each Nd center via a μ_2-hydrogen, while the other two H atoms bridge the boron and both Nd ions in a μ_3 fashion:



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Protonation of $(C_8H_8)Nd(BH_4)(THF)_2$ with acidic ammonium salts provided a convenient access to novel cationic mono(cyclooctatetraenyl)lanthanide(III) complexes. Treatment of $(C_8H_8)Nd(BH_4)(THF)_2$ with $[NHEt_3][BPh_4]$ afforded pale green $[(C_8H_8)Nd(THF)_4][BPh_4]$ in 75% yield. An X-ray crystal structure of this material revealed the presence of discrete cation−anion pairs in the solid state with the Nd ions being in a slightly distorted square-pyramidal coordination environment.[237,238] Both $(C_8H_8)Nd(BH_4)(THF)_2$ and $[(C_8H_8)Nd(THF)_4][BPh_4]$ are valuable precursors for the synthesis of other $(C_8H_8)NdX$ derivatives.[238]

Mono(cyclooctatetraenyl)lanthanide(III) complexes containing additional group 16 donor ligands are now well-established in non-cyclopentadienyl organolanthanide chemistry. For example, a series of binuclear complexes with bridging alkoxide ligands has been prepared according to eqs 63−65. Three representatives, $[(C_8H_8)Y(\mu\text{-}OPh)(THF)]_2$, $[(C_8H_8)Nd(\mu\text{-}OEt)(THF)]_2$ (pale blue crystals), and $[(C_8H_8)Dy\{\mu\text{-}O(CH_2)_3\text{-}CH{=}CH_2\}(THF)]_2$ (bright yellow crystals), have been structurally characterized.[238−240] With the use of sterically more demanding alkoxide and siloxide ligands the monomeric compounds $(C_8H_8)Ln(OCtBu_3)(THF)$ (Ln = Y, Lu) and $(C_8H_8)Ln(OSiPh_3)(THF)$ (Ln = Y, Lu) have been prepared.[239] Also monomeric are the 1,4-bis(trimethylsilyl)cyclooctatetraene derivatives $Ln[1,4\text{-}(Me_3Si)_2C_8H_6](OC_6H_2\text{-}2,6\text{-}tBu_2\text{-}4\text{-}Me)(THF)$ (Ln = Sc, Y) due to the increased steric bulk of the silyl-substituted COT ligand.[226]

$$\begin{gathered}[(C_8H_8)Ln(\mu\text{-Cl})(THF)_2]_2 + 2NaOR \rightarrow \\ [(C_8H_8)Ln(\mu\text{-OR})(THF)]_2 + 2NaCl \\ R = Ph,\ Ln = Y, Lu \\ R = 2,6\text{-}C_6H_3Me_2,\ Ln = Y, Lu \\ R = (CH_2)_3CH{=}CH_2,\ Ln = Dy\end{gathered} \quad (63)$$

$$(COT)Nd(BH_4)(THF)_2 + NaOEt \xrightarrow{THF} 1/2[(C_8H_8)Nd(\mu\text{-OEt})(THF)]_2 + NaBH_4 \quad (64)$$

$$[(C_8H_8)Nd(THF)_4][BPh_4] + NaOEt \xrightarrow{THF} 1/2[(C_8H_8)Nd(\mu\text{-OEt})(THF)]_2 + NaBPh_4 \quad (65)$$

An interesting synthetic route using a Ce^{4+} precursor has been employed to prepare the heterobimetallic alkoxide $(C_8H_8)Ce(\mu\text{-}OiPr)_2AlEt_2$. This compound is formed when $Ce(OiPr)_4$ is treated with triethylaluminum in the presence of cyclooctatetraene.[2,3,5,218] During the course of this reaction according to eq 66 cerium is reduced to the trivalent oxidation state. In the mononuclear product cerium and aluminum are bridged by isopropoxide ligands.

$$Ce(OiPr)_4 \xrightarrow{AlEt_3,\ C_8H_8} (C_8H_8)Ce(\mu\text{-}OiPr)_2AlEt_2 \quad (66)$$

Only one example of a mono(cyclooctatetraenyl)lanthanide alkoxide complex containing a ring-substituted cyclooctatetraenyl ligand has been reported in the literature.[214] As outlined in the eqs 67 and 68, the red dimeric complex $[\{1,4\text{-}(Me_3Si)_2C_8H_6\}Sm(\mu\text{-}OAr)]_2$ (Ar = $C_6H_2(tBu)_2\text{-}2,6,\text{-}Me\text{-}4$) can be prepared in two different ways. The first method (eq 67) using the homoleptic samarium aryloxide $Sm(OAr)_3$ as precursor benefits from the fact the byproduct LiOAr is insoluble in nonpolar solvents and can be readily separated from the reaction mixture.

$$2Sm(OAr)_3 + 2Li_2[C_8H_6(SiMe_3)_2\text{-}1,4] \xrightarrow{hexane} [\{1,4\text{-}(Me_3Si)_2C_8H_6\}Sm(\mu\text{-OAr})]_2 + 2LiOAr\downarrow \quad (67)$$

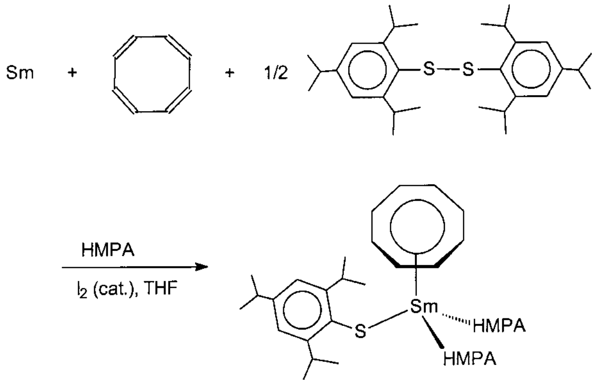
The second method is a salt-free route (eq 68) involving protonation of the anionic sandwich complex $[Li(THF)_4][Sm\{1,4\text{-}(Me_3Si)_2C_8H_6\}_2]$ with the free phenol ArOH. Here too hexane-insoluble LiOAr is eliminated besides the protonation product 1,4-bis(trimethylsilyl)cyclooctatriene. With 36% the yield is considerably lower in this case as compared to the route depicted in eq 67 (69%).

$$2[\mathrm{Li(THF)_4}][\mathrm{Sm\{1,4\text{-}(Me_3Si)_2C_8H_6\}_2}] + 4\mathrm{ArOH} \xrightarrow{\text{toluene/hexane}} [\{1,4\text{-}(\mathrm{Me_3Si})_2\mathrm{C_8H_6}\}\mathrm{Sm}(\mu\text{-OAr})]_2 + 2\mathrm{LiOAr}\downarrow + 2\mathrm{C_8H_8(SiMe_3)_2\text{-}1,4} \quad (68)$$

The preparation of mono(cyclooctatetraenyl)lanthanide(III) thiolates and selenolates has been achieved by the procedure similar to eq 61 using diaryl disulfides or diselenides as oxidizing agents instead of iodine (eq 69).[231] The reactions can be accelerated by activating the metal surface with catalytic amounts of iodine. The molecular structure of $[(\mathrm{C_8H_8})\mathrm{Sm}(\mu\text{-SePh})(\mathrm{THF})_2]_2$ has been determined by X-ray diffraction revealing a dimeric molecule with phenylselenolate bridges.

$$2\mathrm{Sm} + \mathrm{C_8H_8} + \mathrm{ArEEAr} \xrightarrow{\text{THF}} [(\mathrm{C_8H_8})\mathrm{Sm}(\mu\text{-EAr})(\mathrm{THF})_n]_2 \quad (69)$$
$$n = 1,\ \mathrm{EAr} = 2,4,6\text{-}\mathrm{SC_6H_2}i\mathrm{Pr_3}$$
$$n = 2,\ \mathrm{EAr} = \mathrm{SPh},\ 2,4,6\text{-}\mathrm{SC_6H_2Me_3},\ \mathrm{SePh}$$

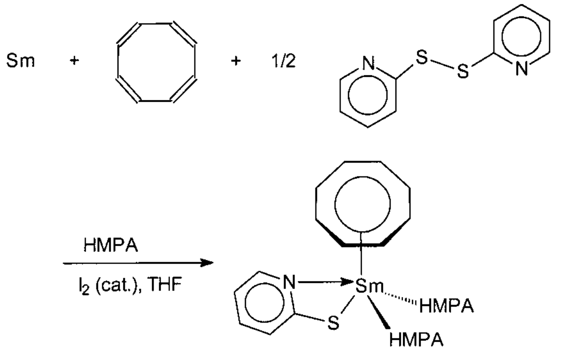
A similar reaction sequence has been employed to make monomeric organosamarium thiolates. However, this was only successful when either sterically demanding or potentially chelating thiolate ligands were used. For example, treatment of samarium metal, cyclooctatetraene, and bis(2,4,6-triisopropylphenyl) disulfide in HMPA as reaction medium produced the dark red thiolate complex $(\mathrm{C_8H_8})\mathrm{Sm}[\mathrm{SC_6H_2}(i\mathrm{Pr})_3\text{-}2,4,6](\mathrm{HMPA})_2$ (eq 70). According to an X-ray analysis this complex has a three-legged piano-stool geometry comprised of the planar η^8-$\mathrm{C_8H_8}$ ring, two HMPA ligands, and the bulky thiolate ligand.[232]



(70)

Dipyridyl disulfide was shown to be an interesting precursor for the synthesis of a related monomeric organosamarium thiolate complex. The heterogenic reaction outlined in eq 71 produced the red complex $(\mathrm{C_8H_8})\mathrm{Sm}(\mathrm{SC_5H_4N})$ which now contains a chelating pyridine-2-thiolate ligand. An X-ray crystal structure determination confirmed the proposed four-legged piano-stool geometry.[232]

The mono(cyclooctatetraenyl)neodymium bis(thiolate) derivative $\mathrm{Na}[(\mathrm{C_8H_8})\mathrm{Nd}(\mathrm{S}t\mathrm{Bu})_2]$ has been prepared via two different synthetic routes as outlined in eqs 72 and 73.[238]

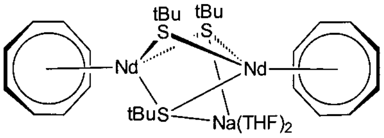


(71)

$$(\mathrm{COT})\mathrm{Nd}(\mathrm{BH_4})(\mathrm{THF})_2 + 2\mathrm{NaS}t\mathrm{Bu} \xrightarrow{\text{THF}} \mathrm{Na}[(\mathrm{C_8H_8})\mathrm{Nd}(\mathrm{S}t\mathrm{Bu})_2] + \mathrm{NaBH_4} \quad (72)$$

$$[(\mathrm{C_8H_8})\mathrm{Nd}(\mathrm{THF})_4][\mathrm{BPh_4}] + 2\mathrm{NaS}t\mathrm{Bu} \xrightarrow{\text{THF}} \mathrm{Na}[(\mathrm{C_8H_8})\mathrm{Nd}(\mathrm{S}t\mathrm{Bu})_2] + \mathrm{NaBPh_4} \quad (73)$$

Recrystallization of $\mathrm{Na}[(\mathrm{C_8H_8})\mathrm{Nd}(\mathrm{S}t\mathrm{Bu})_2]$ from THF–toluene afforded pale green crystals of $[\mathrm{Na(THF)_2}][\{(\mathrm{C_8H_8})\mathrm{Nd}\}_2(\mathrm{S}t\mathrm{Bu})_3]$ (**128**), which was structurally characterized by X-ray diffraction. In this bimetallic complex two $(\mathrm{C_8H_8})\mathrm{Nd}$ fragments are bridged by three S*t*Bu groups with two of these being coordinated to a $\mathrm{Na(THF)_2}$ moiety.[238]



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An increasing number of lanthanide mono(cyclooctatetraenyl) complexes has been synthesized with the use of additional nitrogen donor ligands. For example, interesting results have been obtained with the sterically demanding bis(trimethylsilyl)amido ligand. In the case of yttrium and the late lanthanides monomeric amido complexes are isolated according to eq 74.[242]

$$[(\mathrm{C_8H_8})\mathrm{Ln}(\mu\text{-Cl})(\mathrm{THF})_2]_2 + 2\mathrm{NaN(SiMe_3)_2} \xrightarrow{\text{THF}} 2(\mathrm{C_8H_8})\mathrm{Ln}[\mathrm{N(SiMe_3)_2}](\mathrm{THF}) + 2\mathrm{NaCl} \quad (74)$$

$$\mathrm{Ln} = \mathrm{Y, Gd, Er, Lu}$$

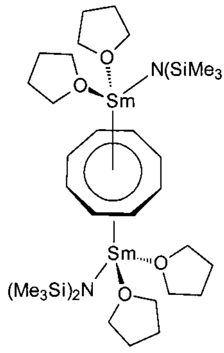
An unusual "inverse sandwich complex" is obtained when the same reaction is carried out with the samarium derivative $[(\mathrm{C_8H_8})\mathrm{Sm}(\mu\text{-Cl})(\mathrm{THF})_2]_2$ (eq 75). In the product two $\mathrm{Sm[N(SiMe_3)_2]_2}$ units are symmetrically bridged by a cyclooctatetraenyl ligand. The sodium salt of the anionic sandwich complex, $[\mathrm{Na(THF)}_n][\mathrm{Sm(C_8H_8)_2}]$, is formed as a byproduct.[242]

$$3[(\mathrm{C_8H_8})\mathrm{Sm}(\mu\text{-Cl})(\mathrm{THF})_2]_2 + 8\mathrm{NaN(SiMe_3)_2} \xrightarrow{\text{toluene}} (\mu\text{-}\mathrm{C_8H_8})[\mathrm{Sm\{N(SiMe_3)_2\}_2}]_2 + 2[\mathrm{Na(THF)}_n][\mathrm{Sm(C_8H_8)_2}] + 6\mathrm{NaCl} \quad (75)$$

A closely related "inverse sandwich complex" of divalent samarium was recently reported by Evans et al.[243] The synthetic route is outlined in eq 76. It involves the in situ generation of $[\{(Me_3Si)_2N\}Sm(THF)_2(\mu\text{-}I)]_2$ from samarium(II) bis[bis(trimethylsilyl)amide] and samarium diiodide followed by treatment with $K_2C_8H_8$ in THF solution.

$$[(Me_3Si)_2N]_2Sm(THF)_2 + SmI_2(THF)_2 + K_2C_8H_8 \xrightarrow{THF} (\mu\text{-}C_8H_8)[\{(Me_3Si)_2N\}Sm(THF)_2]_2 + 2KI \quad (76)$$

The dark blue-green complex $(\mu\text{-}C_8H_8)[\{(Me_3Si)_2N\}Sm(THF)_2]_2$ (**129**) was isolated in >80% yield. In the molecular structure a planar $(C_8H_8)^{2-}$ ring is sandwiched between two $[\{(Me_3Si)_2N\}Sm(THF)_2]^+$ cations. Thus, the overall structure is very similar to that of the pentamethylcyclopentadienyl derivative $(\mu\text{-}C_8H_8)[(C_5Me_5)Sm(THF)_2]_2$.[244]



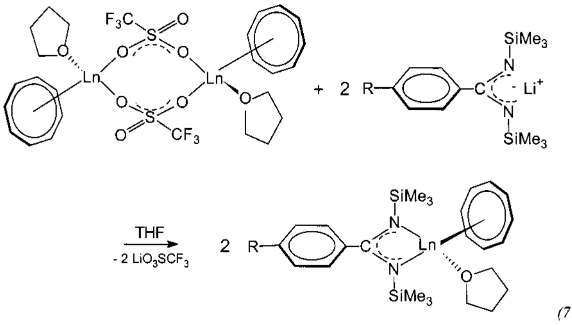
129

Polydentate nitrogen ligands have been found to be highly suited to stabilize mono(cyclooctatetraene)lanthanide(III) complexes. These include silylated benzamidinate and diiminophosphinate anions as well as tridentate pyrazolylborate ligands.[236,245-248] Typical preparations are outlined in the eqs 77−79.

The first "sandwich" complexes of the type $(C_8H_8)Ln[HB(pz)_3]$ had been synthesized earlier by Takats et al.[246] These compounds may either be unsolvated or can contain a coordinated THF molecule. Both series of complexes, $(C_8H_8)Ln[HB(pz)_3]$ and $(C_8H_8)Ln[HB(3,5\text{-}Me_2pz)_3]$, are formed as well-crystallized, intensely colored substances. Several representatives have already been characterized by crystal structure analyses.[248]

Two half-sandwich complexes containing the bulky 1,4-bis(trimethylsilyl)cyclooctatetraenyl ligand in combination with the chelating *N*,*N*′-bis(trimethylsilyl)diiminophosphinate ligand have been prepared. Equation 80 shows the "one-pot" reaction leading to the formation of these species. The blue-green cerium and the red samarium derivative were obtained in low yields due to their very high solubility even in hexane.[241]

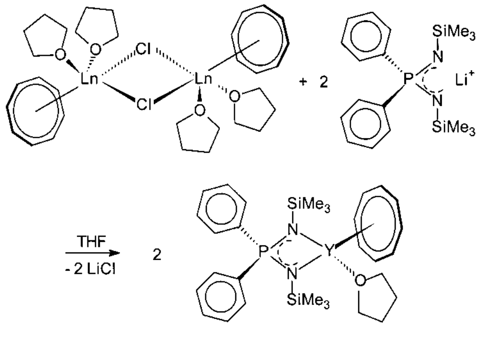
Complexes of the type $[1,4\text{-}(Me_3Si)_2C_8H_6]Ln(DAD)$ (Ln = Sm, Yb; DAD = 1,4-diazadiene) have been prepared in a "one-pot" reaction by treatment of elemental samarium or ytterbium with equimolar amounts of 1,4-bis(trimethylsilyl)cyclooctatriene and substituted 1,4-diazadiene ligands according to



(77)

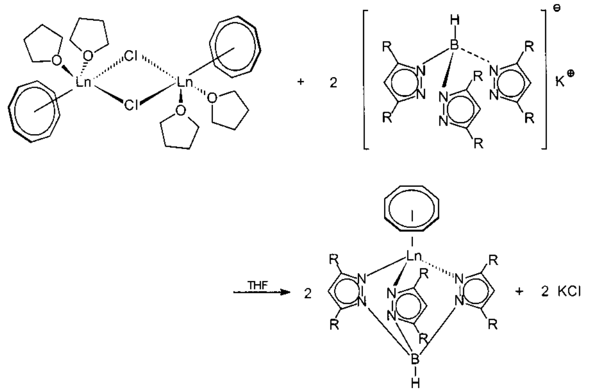
R = H, MeO, CF3

Ln = Y, Ce, Pr, Nd, Sm, Tm, Lu



(78)

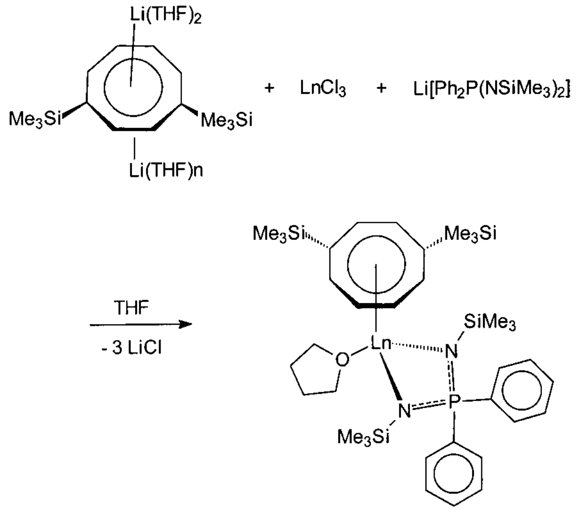
Ln = Ce, Pr, Nd, Sm



R = H, Me

(79)

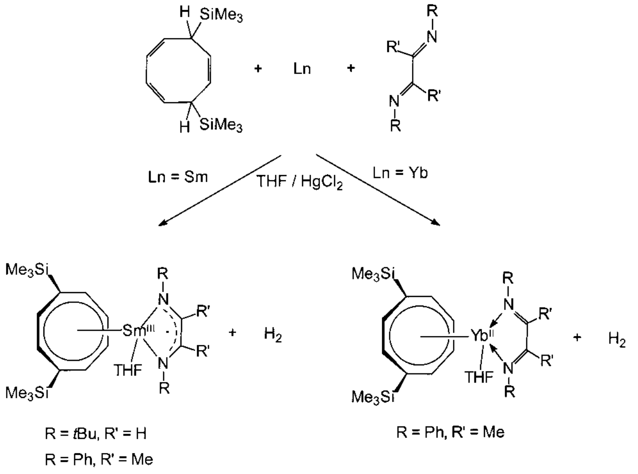
Ln = Ce, Pr, Nd, Sm



Ln = Ce, Sm

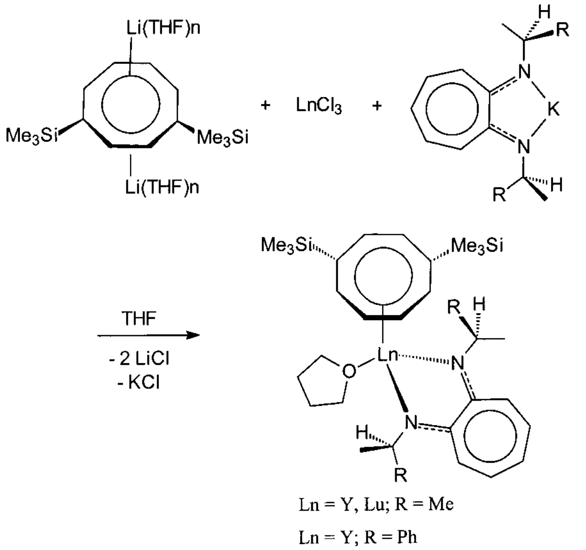
(80)

Scheme 17. Preparation of $[1,4\text{-}(Me_3Si)_2C_8H_6]Ln(DAD)$ Complexes



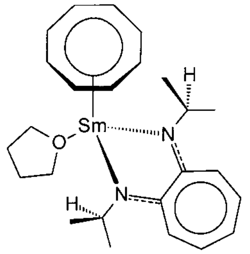
Scheme 17. ^{1}H and ^{171}Yb NMR data revealed that the Sm derivatives contain Sm^{3+} ions and coordinated DAD radical anions, while in the case of Yb the neutral DAD ligand is coordinated to divalent ytterbium. The ^{171}Yb NMR spectrum of $[1,4\text{-}(Me_3Si)_2C_8H_6]Yb[PhN{=}C(Me)C(Me){=}NPh]$ shows a single resonance at δ 224.3 ppm which is consistent with the presence of an Yb^{2+} complex.[249]

Recently a series of half-sandwich complexes containing the 1,4-bis(trimethylsilyl)cyclooctatetraenyl ligand in combination with aminotroponiminates have been prepared and characterized.[250] Equation 81 depicts the reaction sequence leading to such complexes.



(81)

With the diisopropyl-substituted aminotroponiminate ligand yttrium and lutetium complexes were synthesized, of which the Y derivative was structurally characterized by an X-ray analysis. Furthermore, a chiral yttrium complex containing the enantiomerically pure bis(1-phenylethyl)-substituted aminotroponiminate ligand was obtained using the same synthetic route. The method was also extended to a half-sandwich complex containing the unsubstituted cyclooctatetraenyl ring. The compound **130** was made by reacting $(C_8H_8)SmI(THF)$ with the potassium salt of the diisopropyl-substituted aminotroponiminato ligand.[250]



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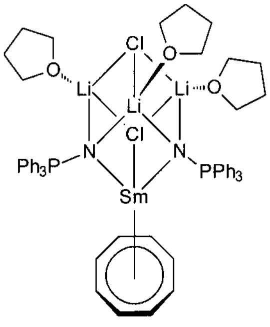
Unusual heterocubane structures containing a $(C_8H_8)Ln$ unit have been reported by Dehnicke et al.[251] $LiNPPh_3$ was found to react with the chloro-bridged dimers $[(C_8H_8)Ln(\mu\text{-}Cl)(THF)_2]_2$ (Ln = Ce, Sm) in THF solution to give the bimetallic phosphiniminato complexes $(C_8H_8)LnLi_3Cl_2(NPPh_3)_2(THF)_3$ (Ln = Ce (orange), Sm (**131**, red)). The proposed reaction leading to the formation of these unexpected products is outlined in eq 82. It was found that the product yields could be greatly improved by adding the required amounts of LiCl.

$$[(C_8H_8)Ln(\mu\text{-}Cl)(THF)_2]_2 + 4LiNPPh_3 + 2LiCl + 2THF \rightarrow (C_8H_8)LnLi_3Cl_2(NPPh_3)_2(THF)_3 \quad (82)$$
$$Ln = Ce,\ Sm\ (\mathbf{131})$$



131

The first σ-alkyl complexes with η^8-cyclooctatetraene ligands according to eq 83 starting from the lutetium precursor $[(C_8H_8)Lu(\mu\text{-}Cl)(THF)_2]_2$.[252,253] It is certainly the interplay of the small ionic radius of lutetium and the high steric demand of the organic ligands that facilitates the formation of mononuclear complexes.

$$[(C_8H_8)Lu(\mu\text{-}Cl)(THF)_2]_2 + 2LiR \rightarrow 2(C_8H_8)LuR(THF) + 2LiCl + 2THF \quad (83)$$

$$R = CH_2SiMe_3,\ o\text{-}Me_2NCH_2C_6H_4$$

Treatment of $[(C_8H_8)Ln(\mu\text{-}Cl)(THF)_2]_2$ (Ln = Y, Sm, Lu) with the alkyllithium reagent $LiCH(SiMe_3)_2$ did not lead to the expected neutral σ-alkyl complexes.[254] Instead, the "inverse sandwich complexes" $Li(THF)_2(\mu\text{-}\eta^2,\eta^8\text{-}C_8H_8)Ln[CH(SiMe_3)_2]$ were formed. An X-ray diffraction analysis established the unusual zwitterionic structure of the Sm derivative with a bridging cyclooctatetraene ligand which is η^2-coordinated to a Li(THF)$_2$ unit. Formation of neutral σ-alkyl complexes should be facilitated by an increased steric demand of the cyclooctatetraene ligand. This hypothesis was verified by Cloke et al. with the example of 1,4-bis(trimethylsilyl)cyclooctatetraenyl complexes. The monomeric σ-alkyl derivatives Ln[1,4-(Me$_3$Si)$_2$C$_8$H$_6$)][CH(SiMe$_3$)$_2$](THF) (Ln = Sc, Y) were prepared by alkylation of the dimeric chloro complexes [Ln{(1,4-(Me$_3$Si)$_2$C$_8$H$_6$)}(μ-Cl)(THF)]$_2$ with LiCH(SiMe$_3$)$_2$.[226]

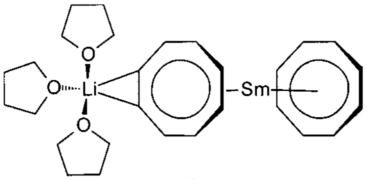
Among the longest known lanthanide COT complexes are symmetrical sandwich complexes containing [Ln(C$_8$H$_8$)$_2$]$^-$ anions.[218,222,223] The potassium salts of these anions are readily prepared by treatment of anhydrous lanthanide trichlorides with 2 equiv of K$_2$C$_8$H$_8$ according to eq 84 followed by extraction of the crude products with THF. The potassium derivatives K[Ln(C$_8$H$_8$)$_2$] are thermally very robust but decompose almost explosively upon contact with traces of oxygen. The latter property resembles the explosive decomposition which has been observed when K$_2$C$_8$H$_8$ comes into contact with air.

$$\mathrm{LnCl_3 + 2K_2C_8H_8 \rightarrow K[Ln(C_8H_8)_2] + 3KCl} \quad (84)$$

$$\mathrm{Ln = Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb}$$

X-ray diffraction studies showed that all representatives of these salts contain coordinated solvent molecules. The structural chemistry of the cerium(III) anion [Ce(C$_8$H$_8$)$_2$]$^-$ has been investigated in detail. Needlelike, bright green crystals of the lithium salt [Li(THF)$_4$][Ce(C$_8$H$_8$)$_2$] were obtained as a byproduct from a reaction of [(C$_8$H$_8$)Lu(μ-Cl)(THF)$_2$]$_2$ with LiCH(SiMe$_3$)$_2$.[255] The crystal structure consists of separated ions with the lithium cation being coordinated by four THF molecules. More recently, the red Sm analogue [Li(THF)$_4$][Sm(C$_8$H$_8$)$_2$] has also been structurally characterized.[251]

The sodium salt forms some kind of "double sandwich".[255] Two cyclooctatetraene ligands and the two metal ions are arranged as a linear unit. In this case only three THF ligands are sufficient to saturate the coordination sphere of sodium. A very similar molecular structure was reported for the solvated potassium salt [K(diglyme)][Ce(C$_8$H$_8$)$_2$].[256] The closely related samarium sandwich [Li(THF)$_3$][Sm(C$_8$H$_8$)$_2$] (**132**) was obtained by a somewhat serendipitous route and structurally characterized. The bridging cyclooctatetraenyl ring is η^8-coordinated to Sm and η^2-bonded to Li.[228]



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More recently several examples of anionic sandwich complexes containing substituted cyclooctatetraenyl ligands have been reported. Lithium salts of sandwich anions containing the 1,4-bis(trimethylsilyl)cyclooctatetraenyl ligand can be obtained in a straightforward manner by reacting anhydrous lanthanide trichlorides with Li$_2$[1,4-(Me$_3$Si)$_2$C$_8$H$_6$] in a 1:2 molar ratio (eq 85).[257]

$$\mathrm{LnCl_3 + 2Li_2[1,4\text{-}(Me_3Si)_2C_8H_6] \xrightarrow{THF} [Li(THF)_4][Ln\{1,4\text{-}(Me_3Si)_2C_8H_6\}_2] + 3LiCl} \quad (85)$$

$$\mathrm{Ln = Y, Ce, Pr, Nd, Sm}$$

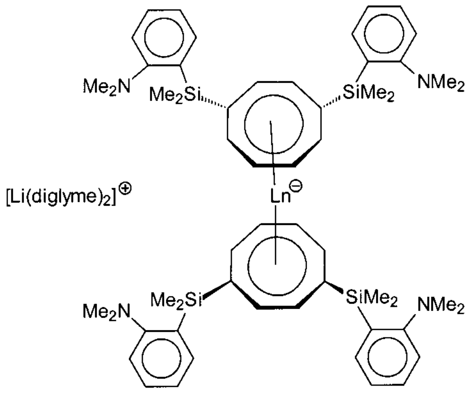
Salts containing other cations than [Li(THF)$_4$]$^+$ are also available as shown by the preparation of the dark red, crystalline [PPN]$^+$ derivative of the Sm sandwich anion ([PPN]$^+$ = [Ph$_3$PNPPh$_3$]$^+$). For this purpose it is not necessary to isolate the lithium salt. As shown in eq 86, [PPN]Cl can be added directly to the reaction mixture.[257]

$$\mathrm{SmCl_3 + 2Li_2[1,4\text{-}(Me_3Si)_2C_8H_6] + [PPN]Cl \xrightarrow{THF} [PPN][Sm\{1,4\text{-}(Me_3Si)_2C_8H_6\}_2] + 4LiCl} \quad (86)$$

The very bulky 1,3,6-tris(trimethylsilyl)cyclooctatetraenyl ligand also forms anionic sandwich complexes with rare earth elements as exemplified by the reaction of the dipotassium derivative with terbium triflate (eq 87).[257]

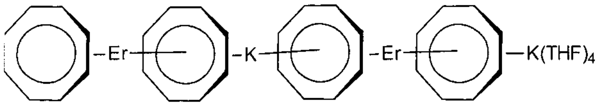
$$\mathrm{Tb(O_3SCF_3)_3 + 2K_2[1,3,6\text{-}(Me_3Si)_3C_8H_5] \xrightarrow{THF} [K(THF)_3][Tb\{1,3,6\text{-}(Me_3Si)_3C_8H_5\}_2] + 3KO_3SCF_3} \quad (87)$$

Yet another promising development is the use of functionally substituted cyclooctatetraenyl ligands.[227] Treatment of NdCl$_3$ or SmCl$_3$ with the new functionalized cyclooctatetraenide reagent Li$_2$(1,4-R$_2$C$_8$H$_6$) (R = *o*-*N*,*N*-Me$_2$NC$_6$H$_4$SiMe$_2$) in diglyme afforded the anionic sandwich complexes [Li(diglyme)$_2$][Ln(1,4-R$_2$C$_8$H$_6$)$_2$] (**133**) which were both structurally characterized by X-ray crystallography.



133: Ln = Nd, Sm

The stacking of cyclooctatetraene ligands in organolanthanide complexes can be further extended, as has been demonstrated by the structure determination of the unusual erbium complex [(C$_8$H$_8$)Er(μ-C$_8$H$_8$)K(μ-C$_8$H$_8$)Er(μ-C$_8$H$_8$)K(THF)$_4$] (**134**).[258] However, compounds of this type are not accessible by rational syntheses. The erbium derivative was isolated serendipitously from a reaction of (benzylcyclopentadienyl)erbium dichloride, [($C_5H_4CH_2Ph$)$ErCl_2$(THF)$_3$], with $K_2C_8H_8$.



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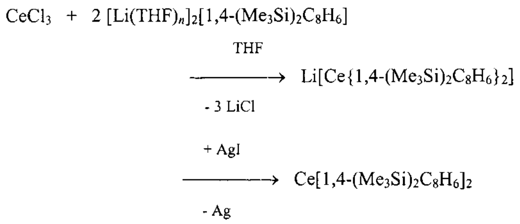
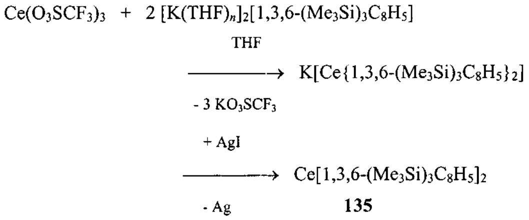
12.3. Neutral Sandwich Complexes

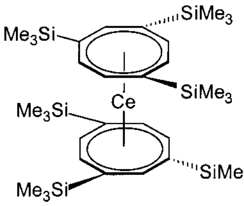
Cerium is the only lanthanide element which has been shown to form stable organometallic complexes in the formal oxdation state +4, and even in this case well-defined organolanthanide(IV) compounds are very rare.[218,222,223] Many organic ligands are simply oxidized in the presence of Ce^{4+} ions. The oldest compound of this type is the so-called “cerocene”, $Ce(C_8H_8)_2$.[256−261] Cerocene was first made by the reaction of Ce(O*i*Pr)$_4$ with cyclooctatetraene in the presence of triethylaluminum and isolated as a black-red, pyrophoric product.[2,3,5,218] An improved synthetic route to cerocene involves controlled oxidation of the anionic sandwich complex using silver iodide or allyl iodide.[262] A thorough investigation of this interesting complex was complicated by its difficult accessibility as well as low solubility and the pyrophoric nature of the material. Except for the reduction by alkali metals, which leads to known derivatives of the cerium(III) anion, no further reactions of cerocene have been reported. A novel development in the organometallic chemistry of tetravalent cerium was recently initiated through the use of substituted cyclooctatetraene ligands. The introduction of suitable substituents leads to an improved solubility as well as a significantly higher stability of the products toward oxygen. With the 1,1′-dimethyl compound $Ce(MeC_8H_7)_2$ Streitwieser et al. succeeded in the first structural characterization of a cerocene derivative, which clearly established the proposed sandwich structure.[256] In this case the angle between the central cerium atom and the ring centroids is 176.03°. Even better results can be obtained with the sterically demanding ligand 1,4-bis(trimethylsilyl)cyclooctatetraene as well as the novel 1,3,6-tris(trimethylsilyl) derivative.[263] The latter has been prepared in the form of its dipotassium salt by treatment of 1,3,6,6-tetrakis(trimethylsilyl)cyclooctatriene with excess KH in refluxing THF. Schemes 18 and 19 illustrate the syntheses of silyl-substituted cerocene derivatives. In both cases the mild oxidating agent silver iodide has proven successful. The compound $Ce[1,4\text{-}(Me_3Si)_2C_8H_6]_2$ is isolated as a dark purple oil, while the color of crystalline $Ce[1,3,6\text{-}(Me_3Si)_3C_8H_5]_2$ (**135**) resembles that of $KMnO_4$. Due to the presence of trimethylsilyl substituents both cerocenes are highly soluble in nonpolar organic solvents.

Scheme 18. Synthesis of $Ce[1,4\text{-}(Me_3Si)_2C_8H_6]_2$



Scheme 19. Synthesis of $Ce[1,3,6\text{-}(Me_3Si)_3C_8H_5]_2$ (135)





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The crystalline hexakis(trimethylsilyl)cerocene was characterized by a crystal structure analysis. In this molecule the angle between cerium and the ring centroids is 176.1°.[263] Sophisticated ab initio calculations on the cerocene sandwich carried out by Dolg et al. had the surprising result that $Ce(C_8H_8)_2$ is essentially a Ce(III) compound, i.e. a Ce^{3+} ion with a $4f^1$ configuration and two $C_8H_8{}^{1.5-}$ ligands.[261,264] The covalent contributions to metal−ring bonding in cerocene result mainly from the cerium 5d orbitals, whereas the 4f orbitals retain an atomic-like character in the molecular environment.[264] These conclusions were later supported experimentally by Edelstein et al.[265] X-ray absorption near-edge structure measurements (XANES) were used to determine the oxidation state of cerium in several inorganic and organic Ce(III) and Ce(IV) compounds, including organometallics. The XANES data were consistent with the assignment of the oxidation state of the cerium ion in cerocene molecules as trivalent.

The compounds $Ce[1,4\text{-}(Me_3Si)_2C_8H_6]_2$ and $Ce[1,3,6\text{-}(Me_3Si)_3C_8H_5]_2$ are the first cerocene derivatives which are reproducibly accessible in synthetically useful amounts and thus allow the study of an interesting derivative chemistry.[263,266,267] They offer an enormous potential for novel electron-transfer reactions. Initial experiments in that direction have already been carried out. For example, reduction of $Ce[1,4\text{-}(Me_3Si)_2C_8H_6]_2$ with cobaltocene readily afforded a dark green cobaltocenium salt (eq 88).

$$Co(C_5H_5)_2 + Ce[1,4\text{-}(Me_3Si)_2C_8H_6]_2 \rightarrow [Co(C_5H_5)_2][Ce\{1,4\text{-}(Me_3Si)_2C_8H_6\}_2] \quad (88)$$

The saltlike complex $[Co(C_5H_5)_2][Ce\{1,4\text{-}(Me_3Si)_2C_8H_6\}_2]$ is remarkable as in this compound both the cation and the anion are sandwich complexes. Redox chemistry of the new soluble cerocenes is just beginning to be developed. It has already been demonstrated that unusual new products can be obtained when metallic elements are used as reducing agents. The first experiment in this area has been carried out with ytterbium metal. Stirring of a THF solution of Ce[1,3,6-$(Me_3Si)_3C_8H_5]_2$ with excess ytterbium powder according to eq 89 results in a color change from purple to bright green while the metal slowly dissolves. Concentration of the filtered solution affords bright green, very air-sensitive crystals. This material has subsequently been shown to be the saltlike heterobimetallic complex $[Yb(THF)_6][Ce\{1,3,6\text{-}(Me_3Si)_3C_8H_5\}_2]_2$ (**136**).[267]

$$2Ce[1,3,6\text{-}(Me_3Si)_3C_8H_5]_2 + Yb \xrightarrow{THF} [Yb(THF)_6][Ce\{1,3,6\text{-}(Me_3Si)_3C_8H_5\}_2]_2 \quad (89)$$

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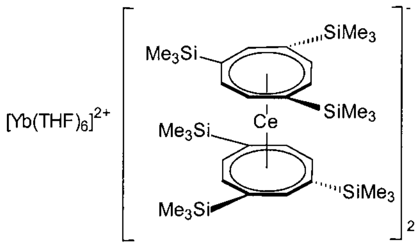
According to the X-ray crystal structure analysis the complex $[Yb(THF)_6][Ce\{1,3,6\text{-}(Me_3Si)_3C_8H_5\}_2]_2$ (**136**) consists of isolated $[Yb(THF)_6]^{2+}$ cations and $[Ce\{1,3,6\text{-}(Me_3Si)_3C_8H_5\}_2]^-$ sandwich anions. This is in fact the first structurally characterized organolanthanide complex with two different lanthanide elements in one compound.[267] Further studies have revealed that this reaction is not limited to ytterbium as reducing agent. Similar redox reactions have already been carried out with samarium, magnesium, and calcium. Apparently this is just the beginning of an exciting electron-transfer chemistry of cerium(IV) organometallics.



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13. Future Outlook

Although organolanthanide chemistry started after the synthesis of Wilkinson's tris(cyclopentadienyl)lanthanide complexes[1] in the middle of the last century, the first organic derivatives of the rare earth metals, triethylscandium and −yttrium, appeared in the literature in 1938,[268,269] before ferrocene, the parent complex of the metallocenes, was discovered and understood. But owing to their kinetic instability and because of the low level of synthetic and characterization techniques in that early time of organometallic chemistry, non-cyclopentadienyl organolanthanides remained a curiosity. Research groups worldwide focused their interest on the synthesis and characterization of lanthanidocenes with unsubstituted and substituted cyclopentadienyl,[4] indenyl,[270] fluorenyl,[271] cyclooctatetraenyl,[272] allyl,[118] π-arene,[204] and carborane ligands.[273] Most of this work exhibited a fascinating diversity in structure and reactivity, as well as in using the new compounds in organic synthesis and catalysis. In addition a great deal of interest has been drawn in the exploration of new ligand systems, with nitrogen-, phosphorus-, and arsenic-containing heterocycles, pyrrolyl, and pyrazolate, as well as a reinvestigation of neutral and anionic alkyl and aryl derivatives, using new techniques in synthesis and characterization. Organolanthanide chemistry is a well-established area of organometallic chemistry now after more or less half a century.

However, there is still a lot to do. There are many synthetic challenges that remain. The area of carbonyl and olefin complexes is still underdeveloped; there is still only one compound published containing a lanthanide to transition metal bond proved by an X-ray crystal structure analysis,[274] and not a single compound with a lanthanide to lanthanide bond is known. The availability of $NdI_2(DME)_3$,[275] $DyI_2(DME)_3$,[275] $TmI_2(DME)_3$,[276] $NdI_2(THF)_5$,[275,277] and $DyI_2(THF)_5$[275] opens a new field of organometallic compounds of Nd^{2+}, Dy^{2+}, and Tm^{2+} which promises unexpected results in structure and reactivity, together with a more intensive investigation of organometallic complexes of Sm^{2+}, Eu^{2+}, and Yb^{2+} as well as of Ce^{4+} and of organometallic compounds of zerovalent lanthanides.

Organolanthanides are useful reagents in organic synthesis.[278] Their potential as enantioselective reagents is far from being exhausted until now, as well as their use as catalysts for olefin and acrylate polymerizations. Perhaps the most exciting development is their use in manufacturing special polyolefins even without a cocatalyst.[279] Finally, organolanthanides promise to find important applications in MOCVD for thin films for semiconductors, superconductors, and as doping materials for optoelectronic devices.[280] Organometallic chemistry of the 4f elements will continue to be a real bonanza for synthetic, theoretical, and application interested scientists.

14. Acknowledgments

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15. References

(1) Wilkinson, G.; Birmingham, J. M. *J. Am. Chem. Soc.* **1954**, *76*, 6210.
(2) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283.
(3) Edelmann, F, T. In *Comprehensive Organometallic Chemistry II*; Stone, F. G. A., Wilkinson, G., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 4, Chapter 2.
(4) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 5, 865.
(5) Edelmann, F. T. *Angew. Chem.* **1995**, *107*, 2647; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2466.
(6) Eaborn, C.; Izod, K.; Smith, J. D. *J. Organomet. Chem.* **1995**, *500*, 89.
(7) Hogerheide, M. P.; Boersma, J.; van Koten, G. *Coord. Chem. Rev.* **1996**, *155*, 87.
(8) Cotton, S. A. *Coord. Chem. Rev.* **1997**, *160*, 93.
(9) Zakharov, L. N.; Struchkov, Y. T. *J. Organomet. Chem.* **1997**, *536*−*537*, 65.
(10) Evans, W. J. *New J. Chem.* **1995**, *19*, 525.
(11) (a) Nief, F. *Coord. Chem. Rev.* **1998**, *178*−*180*, 13. (b) Nief, F. *Eur. J. Inorg. Chem.* **2001**, 891.
(12) Deacon, G. B.; Vince, D. G. *J. Organomet. Chem.* **1976**, *112*, Cl.
(13) Hitchcock, P. B.; Lappert, M. F.; Smith, R. G.; Bartlett, R. A.; Power, P. P. J. *Chem. Soc., Chem. Commun.* **1988**, 1007.
(14) Schumann, H. *Comments Inorg. Chem.* **1983**, *2*, 247.

(15) Schumann, H. *Angew. Chem.* **1984**, *96*, 475; *Angew. Chem., Int. Ed Engl.* **1994**, *23*, 474.
(16) Niemeyer, M. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1027.
(17) Hitchcock, P. B.; Holmes, S. A.; Lappert, M. F.; Tian, S. *Chem. Commun.* **1994**, 2691.
(18) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Smith, J. D. *J. Am. Chem. Soc.* **1994**, *116*, 12071.
(19) Clegg, W.; Eaborn, C.; Izod, K.; O'Shaughnessy, P.; Smith, J. D. *Angew. Chem.* **1997**, *109*, 2925; *Angew. Chem., Int. Ed Engl.* **1997**, *36*, 2815.
(20) Westerhausen, M.; Hartmann, M.; Schwarz, W. *Inorg. Chim. Acta* **1998**, *269*, 91.
(21) Evans, W. J.; Shreeve, J. L.; Broomhall-Dillard, R. N. R.; Ziller, J. W. *J. Organomet. Chem.* **1995**, *501*, 7.
(22) (a) Evans, W. J.; Brady, J. C.; Ziller, J. W. *J. Am. Chem. Soc.* **2001**, *123*, 7711. (b) Schumann, H.; Müller, J. *J. Organomet. Chem.* **1978**, *146*, C5. (c) Atwood, J. L.; Hunter, W. E.; Rogers, R. D.; Holton, J.; McMeeking, J.; Pearce, R.; Lappert, M. F. *Chem. Commun.* **1978**, 140. (d) Schumann, H.; Freckmann, D. M. M.; Dechert, S. *Z. Anorg. Allg. Chem.* **2002**, in press. (e) Evans, W. J.; Anwander, R.; Doedens, R. J.; Ziller, J. W. *Angew. Chem.* **1994**, *106*, 1725; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1641. (f) Evans, W. J.; Anwander, R.; Ziller, J. W. *Organometallics* **1995**, *14*, 1107.
(23) Heckmann, G.; Niemeyer, M. *J. Am. Chem. Soc.* **2000**, *122*, 4227.
(24) Forsyth, C. M.; Deacon, G. B. *Organometallics* **2000**, *19*, 1205.
(25) Deacon, G. B.; Raverty, W. D.; Vince, D. G. *J. Organomet. Chem.* **1977**, *135*, 103.
(26) Bochkarev, L. N.; Stepantseva, T. A.; Zakharov, L. N.; Fukin, G. K.; Yanovsky, A. I.; Struchkov, Y. T. *Organometallics* **1995**, *14*, 2127.
(27) Putzer, M. A.; Bartholomew, G. P. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1777.
(28) Ihara, E.; Adachi, Y.; Yasuda, H.; Hashimoto, H.; Kanehisa, N.; Kai, Y. *J. Organomet. Chem.* **1998**, *569*, 147.
(29) Roitershtein, D. M.; Ziller, J. W.; Evans, W. J. *J. Am. Chem. Soc.* **1998**, *120*, 11342.
(30) Bochkarev, L. N.; Makarov, V. M.; Hrzhanovskaya, Y. N. *J. Organomet. Chem.* **1994**, *467*, C3.
(31) Fedorova, E. E.; Trifonov, A. A.; Bochkarev, M. N.; Girgsdies, F.; Schumann, H. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1818.
(32) Berg, D. J.; Lee, C. K.; Walker, L.; Bushnell, G. W. *J. Organomet. Chem.* **1995**, *493*, 47.
(33) Bochkarev, M. N.; Khramenkov, V. V.; Rad'kov, Yu. F.; Zakharov, L. N.; Struchkov, Yu. T. *J. Organomet. Chem.* **1991**, *408*, 329.
(34) Bochkarev, M. N.; Khramenkov, V. V.; Rad'kov, Yu. F.; Zakharov, L. N.; Struchkov, Yu. T. *J. Organomet. Chem.* **1991**, *421*, 29.
(35) Bochkarev, L. N.; Grachev, O. V.; Molosnova, N. E.; Zhiltsov, S. F.; Zhakarov, L. N.; Fukin, G. K.; Yanovsky, A. I.; Struchkov, Y. T. *J. Organomet. Chem.* **1993**, *443*, C26.
(36) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Lu, Z.-R.; Smith, J. D. *Organometallics* **1996**, *15*, 4783.
(37) van den Hende, J. R.; Hitchcock, P. B.; Holmes, S. A.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1995**, 3933.
(38) Lin, G.; Jin, Z.; Zhang, Y.; Chen, W. *J. Organomet. Chem.* **1990**, *396*, 307.
(39) (a) Rabe, G. W.; Strissel, C. S.; Liable-Sands, L. M.; Concolino, T. E.; Rheingold, A. L. *Inorg. Chem.* **1999**, *38*, 3446. (b) Rabe, G. W.; Bérubé, C. D.; Yap, G. P. A.; Lam, K.-C.; Concolino, T. E.; Rheingold, A. L. *Inorg. Chem.* **2002**, *41*, 1446.
(40) (a) Rabe, G. W.; Bérubé, C. D.; Yap, G. P. A. *Inorg. Chem.* **2001**, *40*, 4780. (b) Rabe, G. W.; Bérubé, C. D.; Yap, G. P. A. *Inorg. Chem.* **2001**, *40*, 2682.
(41) Westerhausen, M.; Hartmann, M.; Pfitzner, A.; Schwarz, W. *Z. Anorg. Allg. Chem.* **1995**, *621*, 837.
(42) Atwood, J. L.; Hunter, W. E.; Rogers, R. D.; Holton, J.; McMeeking, J.; Pearce, R.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1978**, 140.
(43) Edelmann, F. T.; Steiner, A.; Stalke, D.; Gilje, J. W.; Jagner, S.; Håkansson, M. *Polyhedron* **1994**, *13*, 539.
(44) (a) Schaverien, C. J.; van Mechelen, J. B. *Organometallics* **1991**, *10*, 1704. (b) Schaverien, C. J.; Nesbitt, G. J. *J. Chem. Soc., Dalton Trans.* **1992**, 157.
(45) Schumann, H.; Freckmann, D. M. M. Unpublished results.
(46) Hitchcock, P. B.; Lappert, M. F.; Smith, R. G. *J. Chem. Soc., Chem. Commun.* **1989**, 369.
(47) Ihara, E.; Adachi, Y.; Yasuda, H.; Hashimoto, H.; Kanehisa, N.; Kai, Y. *J. Organomet. Chem.* **1998**, *569*, 147.
(48) Bao, X.; Chen, W. *Chin. Sci. Bull.* **1989**, *34*, 207.
(49) Syutkina, O. P.; Rybakova, L. F.; Egorova, E. N.; Sigalov, A. B.; Beletskaya, I. P. *Izv. Akad. Nauk SSSR* **1983**, 648; *Bull Acad. Sci. USSR* **1983**, 586.
(50) Boje, B.; Magull, J. *Z. Anorg. Allg. Chem.* **1994**, *620*, 703.
(51) (a) Jacob, K.; Edelmann, F. T. *J. Prakt. Chem. (Weinheim, Ger.)* **1998**, *340*, 393. (b) Jacob, K.; Kretschmer, W.; Thiele, K.-H.; Gornitzka, H.; Edelmann, F. T.; Pavlik, I.; Lycka, A.; Holecek, J. *J. Organomet. Chem.* **1992**, *436*, 231. (c) Jacob, K.; Edelmann, F. T.; Pietzsch, C. *Monatsh. Chem.* **1997**, *128*, 165.
(52) Gornitzka, H.; Steiner, A.; Stalke, D.; Kilimann, U.; Edelmann, F. T.; Jacob, K.; Thiele, K.-H. *J. Organomet. Chem.* **1992**, *439*, C6.
(53) Hogerheide, M. P.; Grove, D. M.; Boersma, J.; Jastrzebski, J. T. B. H.; Kooijman, H.; Spek, A. L.; van Koten, G. *Chem.—Eur. J.* **1995**, *1*, 343.
(54) Mandel, A.; Magull, J. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1542.
(55) Shen, Z. *Inorg. Chim. Acta* **1987**, *140*, 7.
(56) Mehrotra, R. C.; Singh, A.; Tripathi, U. M. *Chem. Rev.* **1991**, *91*, 1287.
(57) Biagini, P.; Lugli, G.; Abis, L.; Millini, R. *J. Organomet. Chem.* **1994**, *474*, C16.
(58) Evans, W. J. *New. J. Chem.* **1995**, *19*, 525.
(59) Evans, W. J.; Boyle, T. J.; Ziller, J. W. *J. Organomet. Chem.* **1993**, *462*, 141.
(60) Clark, D. L.; Gordon, J. C.; Huffman, J. C.; Watkin, J. G.; Zwick, B. D.; *Organometallics* **1994**, *13*, 4266.
(61) Evans, W. J.; Broomhall-Dillard, R. N. R.; Ziller, J. W. *Organometallics* **1996**, *15*, 1351.
(62) Evans, W. J.; Broomhall-Dillard, R. N. R.; Ziller, J. W. *J. Organomet. Chem.* **1998**, *569*, 89.
(63) Schaverien, C. J.; Meijboom, N.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1992**, 124.
(64) (a) Makioka, Y.; Taniguchi, Y.; Fujiwara, Y.; Takaki, K.; Hou, Z.; Wakatsuki, Y. *Organometallics* **1996**, *15*, 5476. (b) Hou, Z.; Yamazaki, H.; Kobayashi, K.; Fujiwara, Y.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1992**, 722.
(65) Karl, M.; Harms, K.; Seybert, G.; Massa, W.; Fau, S.; Frenking, G.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1999**, *625*, 2055.
(66) (a) Arnold, J.; Hoffman, C. G. *J. Am. Chem. Soc.* **1990**, *112*, 8620. (b) Arnold, J.; Hoffmann, C. G.; Dawson, D. Y.; Hollander, F. J. *Organometallics* **1993**, *12*, 3645. (c) Schaverien, C. J.; Orpen, A. G. *Inorg. Chem.* **1991**, *30*, 4968.
(67) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. W.; Vollmer, S. H.; Day, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 5393.
(68) den Haan, K. H.; De Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojic-Prodic, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726.
(69) Heeres, H. J.; Renkema, J.; Booij, M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1988**, *7*, 2495.
(70) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51.
(71) Boncella, J. M.; Andersen, R. A. *Organometallics* **1985**, *4*, 205.
(72) Fryzuk, M. D.; Haddad, T. S. *J. Chem. Soc., Chem. Commun.* **1990**, 1088.
(73) Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. *Organometallics* **1992**, *11*, 2967.
(74) Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. *Organometallics* **1991**, *10*, 2026.
(75) Fryzuk, M. D.; Giesbrecht, G.; Rettig, S. J. *Organometallics* **1996**, *15*, 3329.
(76) Hasinoff, L.; Takats, J.; Zhang, X. W.; Bond, A. H.; Rogers, R. D. *J. Am. Chem. Soc.* **1994**, *116*, 8833.
(77) Duchateau, R.; van Wee, C. T.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1993**, *115*, 4931.
(78) Edelmann, F. T. *J. Alloys Compd.* **1994**, *207/208*, 182.
(79) Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403.
(80) Duchateau, R.; van Wee, C. T.; Meetsma, A.; van Duijnen, P. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2279.
(81) Duchateau, R.; van Wee, C. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2291.
(82) Hagadorn, J. R.; Arnold, J. *Organometallics* **1996**, *15*, 984.
(83) Bambirra, S.; Brandsma, M. J. R.; Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2000**, *19*, 3197.
(84) Bambirra, S.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2001**, *20*, 782.
(85) Zhou, Y.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **1998**, *17*, 4387.
(86) Duchateau, R.; Tuinstra, T.; Brussee, E. A. C.; Meetsma, A.; van Duijnen, P. T.; Teuben, J. H. *Organometallics* **1997**, *16*, 3511.
(87) Duchateau, R.; Brussee, E. A. C.; Meetsma, A.; Teuben, J. H. *Organometallics* **1997**, *16*, 5506.
(88) Veith, M. *Angew. Chem.* **1987**, *99*, 1; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1.
(89) Recknagel, A.; Steiner, A.; Brooker, S.; Stalke, D.; Edelmann, F. T. *J. Organomet. Chem.* **1991**, *415*, 315.
(90) Gountchev, T. I.; Tilley, T. D. *Organometallics* **1999**, *18*, 2896.
(91) Gountchev, T. I.; Tilley, T. D. *Organometallics* **1999**, *18*, 5661.
(92) Graf, D. D.; Davis, W. M.; Schrock, R. R. *Organometallics* **1998**, *17*, 5820.
(93) Lee, L. W. M.; Piers, W. E.; Elsegood, M. R. J.; Clegg, W.; Parvez, M. *Organometallics* **1999**, *18*, 2947.
(94) Roesky, P. W. *J. Organomet. Chem.* **2000**, *603*, 161.
(95) Roesky, P. W. *Inorg. Chem.* **1998**, *37*, 4507.
(96) Lee, L.; Berg, D. J.; Bushnell, G. W. *Organometallics* **1995**, *14*, 8.
(97) Lee, L.; Berg, D. J.; Eisenstein, F. W.; Batchelor, R. J. *Organometallics* **1997**, *16*, 1819.
(98) Fryzuk, M. D.; Love, J. B.; Rettig, S. J. *J. Am. Chem. Soc.* **1997**, *119*, 9071.

(99) Dubé, T.; Gambarotta, S.; Yap, G. *Organometallics* **1998**, *17*, 3967.

(100) Schumann, H.; Glanz, M.; Winterfeld, J.; Hemling, H.; Kuhn, N.; Kratz, T. *Chem. Ber.* **1994**, *127*, 2369.

(101) Arduengo, A. J., III; Tamm, M.; McLain, S. J.; Calabrese, J. C.; Davidson, F.; Marshall, W. J. *J. Am. Chem. Soc.* **1994**, *116*, 7927.

(102) Burns, J. H.; Baldwin, W. H. *J. Organomet. Chem.* **1976**, *120*, 361.

(103) (a) Evans, W. J.; Drummond, D. K. *Organometallics* **1988**, *7*, 797. (b) Evans, W. J.; Drummond, D. K.; Hughes, L. A.; Zhang, H.; Atwood, J. L. *Polyhedron* **1988**, *7*, 1693.

(104) Aparna, K.; Ferguson, M.; Cavell, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 726.

(105) Suleimanov, G. Z.; Bogachev, Y. S.; Petrovskii, P. V.; Grishin, Y. K.; Zhuravleva, I. L.; Beletskaya, I. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 471.

(106) Bürgstein, M. R.; Berberich, H.; Roesky, P. W. *Organometallics* **1998**, *17*, 1452.

(107) Trifonov, A. A.; Fedorova, E. A.; Kirillov, E. N.; Bochkarev, M. N.; Girgsdies, F.; Schumann, H. *Russ. Chem. Bull. Int. Ed.* **2000**, *49*, 8.

(108) Deacon, G. B.; Koplick, A. J.; Tuong, T. D. *Aust. J. Chem.* **1982**, *35*, 941.

(109) Deacon, G. B.; Koplick, A. J. *J. Organomet. Chem.* **1978**, *146*, C43.

(110) Wayda, A. L.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1984**, *3*, 939.

(111) Bochkarev, L. N.; Shustov, S. B.; Guseva, T. V.; Shil'tsov, S. F. *Zh. Obshch. Khim.* **1988**, *58*, 923.

(112) Shustov, S. B.; Bochkarev, L. N.; Zhil'tsov, S. F. *Metalloorg. Khim.* **1990**, *3*, 624.

(113) Karl, M.; Seybert, G.; Massa, W.; Harms, K.; Agarwal, S.; Maleika, R.; Stelter, W.; Greiner, A.; Heitz, W.; Neumüller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1301.

(114) Lee, L.; Berg, D. J.; Bushnell, G. W. *Organometallics* **1995**, *14*, 5021.

(115) Lin, G.; McDonald, R.; Takats, J. *Organometallics* **2000**, *19*, 1814.

(116) Bochkarev, M. N.; Katkova, M. A.; Khorshev, S. Y.; Makarenko, N. P. *Russ. Chem. Bull.* **1998**, *47*, 349.

(117) Taube, R.; Windisch, H.; Görlitz, F. H.; Schumann, H. *J. Organomet. Chem.* **1993**, *445*, 85.

(118) Brunelli, M.; Poggio, S.; Pedretti, U.; Lugli, G. *Inorg. Chim. Acta* **1987**, *131*, 281.

(119) Huang, Z.; Chen, M.; Qiu, W.; Wu, W. *Inorg. Chim. Acta* **1987**, *139*, 203.

(120) Taube, R.; Maiwald, S.; Sieler, J. *J. Organomet. Chem.* **1996**, *513*, 37.

(121) Taube, R.; Windisch, H.; Maiwald, S.; Hemling, H.; Schumann, H. *J. Organomet. Chem.* **1996**, *513*, 49.

(122) Taube, R.; Maiwald, S.; Sieler, J. *J. Organomet. Chem.* **2001**, *621*, 327.

(123) Taube, R.; Windisch, H.; Weissenborn, H.; Hemling, H.; Schumann, H. *J. Organomet. Chem.* **1997**, *548*, 229.

(124) Taube, R.; Windisch, H. *J. Organomet. Chem.* **1994**, *472*, 71.

(125) Windisch, H.; Scholz, J.; Taube, R.; Wrackmeyer, B. *J. Organomet. Chem.* **1996**, *520*, 23.

(126) Reddmann, H.; Amberger, H.-D.; Kanellakopulos, B.; Maiwald, S.; Taube, R. *J. Organomet. Chem.* **1999**, *584*, 310.

(127) Wu, W.; Chen, M.; Zhou, P. *Organometallics* **1991**, *10*, 98.

(128) Hamann-Gaudinet, B.; Namy, J.-L.; Kagan, H. B. *J. Organomet. Chem.* **1998**, *567*, 39.

(129) Hitchcock, P. B.; Lappert, M. F.; Tian, S. *J. Organomet. Chem.* **1997**, *549*, 1.

(130) Caro, C. F.; Lappert, M. F.; Merle, P. G. *Coord. Chem. Rev.* **2001**, *219−221*, 605.

(131) Karsch, H. H.; Appelt, A.; Miller, G. *Angew. Chem.* **1986**, *98*, 832; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 823.

(132) Hao, S.; Song, J.-I.; Aghabozorg, H.; Gambarotta, S. *J. Chem. Soc., Chem. Commun.* **1994**, 157.

(133) Karsch, H. H.; Ferazin, G.; Bissinger, P. *J. Chem. Soc., Chem. Commun.* **1994**, 505.

(134) Mashima, K.; Takaya, H. *Tetrahedron Lett.* **1989**, *30*, 3697.

(135) Saussine, L.; Olivier, H.; Commereuc, D.; Chauvin, Y. *New. J. Chem.* **1988**, *12*, 13.

(136) Emel'yanova, N. S.; Trifonov, A. A.; Zakharov, L. N.; Bochkarev, M. N.; Shestakov, A. F.; Struchkov, Yu. T. *Metalloorg. Khim.* **1993**, *6*, 363.

(137) Mashima, K.; Sugiyama, H.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1581.

(138) Mashima, K.; Takaya, H. *Tetrahedron Lett.* **1989**, *30*, 3697.

(139) Kretschmer, W.; Thiele, K.-H. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1304.

(140) Ernst, R. D.; Cymbaluk, T. H. *Organometallics* **1982**, *1*, 708.

(141) Qiu, X.; Liu, J. *Chin. J. Chem.* **1991**, *9*, 10.

(142) Schumann, H.; Dietrich, A. *J. Organomet. Chem.* **1991**, *401*, C33.

(143) Zielinski, M. B.; Drummond, D. K.; Iyer, P. S.; Leman, J. T.; Evans, W. J. *Organometallics* **1995**, *14*, 3724.

(144) Sieler, J.; Simon, A.; Peters, K.; Taube, R.; Geitner, M. *J. Organomet. Chem.* **1989**, *362*, 297.

(145) Weng, W.; Kunze, K.; Arif, A. M.; Ernst, R. D. *Organometallics* **1991**, *10*, 3643.

(146) Zhang, S.; Zhuang, X.; Zhang, J.; Chen, W.; Liu, J. *J. Organomet. Chem.* **1999**, *584*, 135.

(147) Baudry, D.; Bulot, E.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1988**, 1369.

(148) Baudry, D.; Bulot, E.; Ephritikhine, M. *J. Organomet. Chem.* **1990**, *397*, 169.

(149) Schumann, H.; Rosenthal, E. C. E.; Winterfeld, J.; Weimann, R.; Demtschuk, J. *J. Organomet. Chem.* **1996**, *507*, 287.

(150) Deacon, G. B.; Gitlits, A.; Roesky, P. W.; Bürgstein, M. R.; Lim, K. C.; Skelton, B. W.; White, A. H. *Chem.—Eur. J.* **2001**, *7*, 127.

(151) Ganesan, M.; Lalonde, M. P.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2001**, *20*, 2443.

(152) Dubé, T.; Conoci, S.; Gambarotta, S.; Yap, G. P. A.; Vasapollo, G. *Angew. Chem.* **1999**, *111*, 3890; *Angew. Chem., Int. Ed.* **1999**, *38*, 3657.

(153) Ganesan, M.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem.* **2001**, *113*, 788; *Angew. Chem. Int. Ed.* **2001**, *340* 766.

(154) Dubé, T.; Gambarotta, S.; Yap, G. P. A.; Conoci, S. *Organometallics* **2000**, *19*, 115.

(155) Dubé, T.; Ganesan, M.; Conoci, S.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 3716.

(156) Dubé, T.; Freckmann, D.; Conoci, S.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 209.

(157) Dubé, T.; Conoci, S.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 1182.

(158) Song, J.-I.; Gambarotta, S. *Angew. Chem.* **1995**, *107*, 2319; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2141.

(159) Dubé, T.; Gambarotta, S.; Yap, G. P. A. *Organomet.* **2000**, *19*, 817.

(160) Jubb, J.; Gambarotta, S.; Duchateau, R.; Teuben, J. H. *Chem. Commun.* **1994**, 2641.

(161) Dubé, T.; Gambarotta, S.; Yap, G. *Organometallics* **2000**, *19*, 121.

(162) Dubé, T.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem.* **1999**, *111*, 1507; *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1432.

(163) Jubb, J.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 4477.

(164) Guan, J.; Dubé, T.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 4820.

(165) Dubé, T.; Guan, J.; Gambarotta, S.; Yap, G. P. A. *Chem.—Eur. J.* **2001**, *7*, 374.

(166) Campazzi, E.; Solari, E.; Scopelliti, R.; Floriani, C. *Inorg. Chem.* **1999**, *38*, 6240.

(167) Campazzi, E.; Solari, E.; Floriani, C.; Scopelliti, R. *Chem. Commun.* **1998**, 2603.

(168) Campazzi, E.; Solari, E.; Scopelliti, R.; Floriani, C. *Chem. Commun.* **1999**, 1617.

(169) Arnold, P. L.; Cloke, F. G. N.; Hitchcock, P. B.; Nixon, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7630.

(170) Arnold, P. L.; Cloke, F. G. N.; Nixon, J. F. *Chem. Commun.* **1998**, 797.

(171) Arnold, P. L.; Cloke, F. G. N.; Hitchcock, P. B. *Chem. Commun.* **1997**, 481.

(172) Deacon, G. B.; Delbridge, E. E.; Fallon, G. D.; Jones, C.; Hibbs, D. E.; Hursthouse, M. B.; Skelton, B. W.; White, A. H. *Organometallics* **2000**, *19*, 1713.

(173) Nief, F.; Ricard, L. *Chem. Commun.* **1994**, 2723.

(174) Desmurs, P.; Visseaux, M.; Baudry, D.; Dormond, A.; Nief, F.; Ricard, L. *Organometallics* **1996**, *15*, 4178

(175) Desmurs, P.; Dormond, A.; Nief, F.; Baudry, D. *Bull. Soc. Chim. Fr.* **1997**, *134*, 683.

(176) Nief, F.; Riant, P.; Richard, L.; Desmurs, P.; Baudry-Barbier, D. *Eur. J. Inorg. Chem.* **1999**, 1041.

(177) Nief, F.; Ricard, L. *J. Organomet. Chem.* **1994**, *464*, 149.

(178) Hawthorne, M. F.; Young, D. C.; Wegner, P. A. *J. Am. Chem. Soc.* **1965**, *87*, 1818.

(179) Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjes, M.; Warren, L. F., Jr.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879.

(180) Manning, M. J.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1988**, *110*, 4458.

(181) Hosmane, N. S.; Maguire, J. A. *Adv. Organomet. Chem.* **1990**, *30*, 99.

(182) Oki, A. R.; Zhang, H.; Hosmane, N. S. *Organometallics* **1991**, *10*, 3964.

(183) Hosmane, N. S.; Saxena, A. K.; Barreto, R. D.; Zhang, H.; Maguire, J. A.; Jia, L.; Wang, Y.; Oki, A. R.; Grover, K. V.; Whitten, S. J.; Dawson, K.; Tolle, M. A.; Siriwardane, U.; Demissie, T.; Fagner, J. S. *Organometallics* **1993**, *12*, 3001.

(184) Hosmane, N. S.; Zhu, D.; Zhang, H.; Oki, A. R.; Maguire, J. A. *Organometallics* **1998**, *17*, 3196.

(185) Hosmane, N. S.; Wang, Y.; Oki, A. R.; Zhang, H.; Zhu, D.; McDonald, E. M.; Maguire, J. A. *Phosphorus, Sulfur Silicon* **1994**, *93−94*, 253.

(186) Zhang, H.; Oki, A. R.; Wang, Y.; Maguire J. A.; Hosmane, N. S. *Acta Crystallogr.* **1995**, *C51*, 635.

(187) Hosmane, N. S.; Wang, Y.; Oki, A. R.; Zhang, H.; Maguire, J. A. *Organometallics* **1996**, *15*, 626.

(188) Hosmane, N. S.; Wang, Y.; Zhang, H.; Oki, A. R.; Maguire, J. A.; Waldhör, E.; Kaim, W.; Binder, H.; Kremer, R. K. *Organometallics* **1995**, *14*, 1101.

(189) Zhang, H.; Wang, Y.; Maguire, J. A.; Hosmane, N. S. *Acta Crystallogr.* **1996**, *C52*, 8.

(190) Hosmane, N. S.; Wang, Y.; Zhang, H.; Maguire, J. A.; McInnis, M.; Gray, T. G.; Collins, J. D.; Kremer, R. K.; Binder, H.; Waldhör, E.; Kaim, W. *Organometallics* **1996**, *15*, 1006.

(191) Zhang, H.; Wang, Y.; Maguire, J. A.; Hosmane, N. S. *Acta Crystallogr.* **1996**, *C52*, 640.

(192) Xie, Z.; Liu, Z.; Chiu, K.; Xue, F.; Mak, T. C. W. *Organometallics* **1997**, *16*, 2460.

(193) Chiu, K.; Zhang, Z.; Mak, T. C. W.; Xie, Z. *J. Organomet. Chem.* **2000**, *614*−*615*, 107.

(194) Xie, Z.; Liu, Z.; Yang, Q.; Mak, T. C. W. *Organometallics* **1999**, *18*, 3603.

(195) Chui, K.; Yang, Q.; Mak, T. C. W.; Lam, W. H.; Lin, Z.; Xie, Z. *Organometallics* **2000**, *122*, 5758.

(196) Wang, S.; Li, H.-W.; Xie, Z. *Organometallics* **2001**, *20*, 3842.

(197) Bochkarev, M. N. *Russ. Chem. Rev.* **2000**, *69*, 783.

(198) Cloke, F. G. N. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 4 (Lappert, M. F., Vol. Ed.), p 1.

(199) Trifonov, A. A.; Kirillov, E. N.; Fischer, A.; Edelmann, F. T.; Bochkarev, M. N. *Chem. Commun.* **1999**, 2203.

(200) Trifonov, A. A.; Kirillov, E. N.; Kurskii, Yu. A.; Bochkarev, M. N. *Russ. Chem. Bull.* **2000**, *49*, 744.

(201) Fan, B.; Shen, Q.; Lin, Y. *J. Organomet. Chem.* **1989**, *377*, 51.

(202) Fan, B.; Jin, S.; Shen, Q.; Lin, Y. *Chin. Sci. Bull.* **1991**, *36*, 84.

(203) Liang, H.; Shen, Q.; Guan, J.; Lin, Y. *J. Organomet. Chem.* **1994**, *474*, 113.

(204) Cotton, F. A.; Schwotzer, W. *J. Am. Chem. Soc.* **1986**, *108*, 4657.

(205) Fan, B.; Shen, Q.; Lin, Y. *J. Organomet. Chem.* **1989**, *376*, 61.

(206) Cotton F. A.; Schwotzer, W. *Organometallics* **1987**, *6*, 1275.

(207) Liu, Q.; Lin, Y.-H.; Shen, Q. *Acta Crystallogr.* **1977**, *C53*, 1579.

(208) Liang, H.; Shen, Q.; Jin, S.; Lin, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 480.

(209) Biagini, P.; Lugli, G.; Abis, L.; Millini, R. *New J. Chem.* **1995**, *19*, 713.

(210) Deacon, G. B.; Nickel, S.; MacKinnon, P.; Tiekink, E. R. T. *Aust. J. Chem.* **1990**, *43*, 3, 1245.

(211) Barnhart, D. M.; Clark, D. L.; Gordon, J. C.; Huffman, J. C.; Vincent, R. L.; Watkin, J. G.; Zwick, B. D. *Inorg. Chem.* **1994**, *33*, 3487.

(212) Fedushkin, I. L.; Bochkarev, M. N.; Schumann, H.; Esser, L.; Kociok-Köhn, G. *J. Organomet. Chem.* **1995**, *489*, 145.

(213) Click, D. R.; Scott, B. L.; Watkin, J. G. *Chem. Commun.* **1999**, 633.

(214) Fryzuk, M. D.; Jafarpour, L.; Kerton, F. M.; Love, J. B.; Rettig, S. J. *Angew. Chem.* **2000**, *112*, 783; *Angew. Chem., Int. Ed.* **2000**, *39*, 767.

(215) Herberich, G. E.; Englert, U.; Fischer, A.; Ni, J.; Schmitz, A. *Organometallics* **1999**, *18*, 5496.

(216) Zheng, X.; Wang, B.; Englert, U.; Herberich, G. E. *Inorg. Chem.* **2001**, *40*, 3117.

(217) Arliguie, T.; Lance, M.; Nierlich, M.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1997**, 2501.

(218) Edelmann, F. T. *New J. Chem.* **1995**, *19*, 535.

(219) Wayda, A. L.; Cheng, S.; Mukerji, I. *J. Organomet. Chem.* **1987**, *330*, C17.

(220) Wayda, A. L.; Mukerji, I.; Dye, J. L.; Rogers, R. D. *Organometallics* **1987**, *6*, 1328.

(221) Kinsley, S. A.; Streitwieser, A., Jr.; Zalkin, A. *Organometallics* **1985**, *4*, 52.

(222) Streitwieser, A., Jr. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragalà, I. L., Eds.; NATO ASI Series D; Reidel: Boston, MA, 1985; Vol. 155, p 77.

(223) Streitwieser, A., Jr.; Boussie, T. R. *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 399.

(224) Mares, F.; Hodgson, K. O.; Streitwieser, A., Jr. *J. Organomet. Chem.* **1971**, *28*, C24.

(225) Burton, N. C.; Cloke, F. G. N.; Hitchcock, P. B.; de Lemos, H. C.; Sameh, A. A. *J. Chem. Soc., Chem. Commun.* **1989**, 1462.

(226) Burton, N. C.; Cloke, F. G. N.; Joseph, S. C. P.; Karamallakis, H.; Sameh, A. A. *J. Organomet. Chem.* **1993**, *462*, 39.

(227) Wetzel, T. G.; Roesky, P. W. *Organometallics* **1998**, *17*, 4009.

(228) Wetzel, T. G.; Dehnen, S.; Roesky, P. W. *Organometallics* **1999**, *178*, 3835.

(229) Kilimann, U.; Schäfer, M.; Herbst-Irmer, R.; Edelmann, F. T. *J. Organomet. Chem.* **1994**, *469*, C10.

(230) Mashima, K.; Takaya, H. *Tetrahedron Lett.* **1989**, *30*, 3697.

(231) Mashima, K.; Nakayama, Y.; Nakamura, A.; Kanehisa, N,; Kai, Y.; Takaya, H. *J. Organomet. Chem.* **1994**, *473*, 85.

(232) Mashima, K.; Shibahara, T.; Nakayama, Y.; Nakamura, A. *J. Organomet. Chem.* **1998**, *559*, 197.

(233) Amberger, H.-D.; Jank, S.; Edelmann F. T. *J. Organomet. Chem.* **1998**, *559*, 209.

(234) Schumann, H.; Meese-Marktscheffel, J. A.; Dietrich, A. *J. Organomet. Chem.* **1989**, *377*, C5.

(235) Stehr, J.; Fischer, R. D. *J. Organomet. Chem.* **1992**, *430*, C1.

(236) Kilimann, U.; Edelmann, F. T. *J. Organomet. Chem.* **1994**, *469*, C5.

(237) Cendrowski-Guillaume, S. M.; Nierlich, M.; Lance, M.; Ephritikhine, M. *Organometallics* **1998**, *17*, 786.

(238) Cendrowski-Guillaume, S. M.; Le Gland, G.; Nierlich, M.; Ephritikhine, M. *Organometallics* **2000**, *19*, 5654.

(239) Schumann, H.; Winterfeld, J.; Köhn, R. D.; Esser, L.; Sun, J.; Dietrich, A. *Chem. Ber.* **1993**, *126*, 907.

(240) Zhang, S.; Wei, G.; Chen, W.; Liu, J. *Polyhedron* **1994**, *13*, 1927.

(241) Reissmann, U.; Poremba, P.; Noltemeyer, M.; Schmidt, H.-G.; Edelmann, F. T. *Inorg. Chim. Acta* **2000**, *303*, 156.

(242) Schumann, H.; Winterfeld, J.; Esser, L.; Kociok-Köhn, G. *Angew. Chem.* **1993**, *105*, 1212; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1208.

(243) Evans, W. J.; Johnston, M. A.; Clark, R. D.; Anwander, R.; Ziller, J. W. *Polyhedron* **2001**, *20*, 2483.

(244) Evans, W. J.; Clark, R. D.; Ansari, M. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1998**, *120*, 9555.

(245) Kilimann, U.; Edelmann, F. T. *J. Organomet. Chem.* **1993**, *444*, C15.

(246) Masino, A. Ph.D. Thesis, University of Alberta, 1978.

(247) Schumann, H.; Winterfeld, J.; Hemling, H.; Hahn, F. E.; Reich, P.; Brzezinka, K.-W.; Edelmann, F. T.; Kilimann, U.; Schäfer, M.; Herbst-Irmer, R. *Chem. Ber.* **1995**, *128*, 8, 395.

(248) Reissmann, U.; Amberger, H.-D.; Takats, J.; Schäfer, M.; Herbst-Irmer, R.; Edelmann, F. T. Manuscript in preparation.

(249) Poremba, P.; Edelmann, F. T. *J. Organomet. Chem.* **1997**, *549*, 101.

(250) Roesky, P. W. *J. Organomet. Chem.* **2001**, *621*, 277.

(251) Anfang, S.; Seybert, G.; Harms, K.; Geiseler, G.; Massa, W.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1187.

(252) Wayda, A. L. *Organometallics* **1983**, *2*, 565.

(253) Wayda, A. L.; Rogers, R. D. *Organometallics* **1985**, *4*, 1440.

(254) Schumann, H.; Winterfeld, J.; Görlitz, F. H.; Pickardt, J. *Organometallics* **1987**, *6*, 1328.

(255) Kilimann, U.; Schäfer, M.; Herbst-Irmer, R.; Edelmann, F. T. *J. Organomet. Chem.* **1994**, *469*, C15.

(256) Boussie, T. R.; Eisenberg, D. C.; Rigsbee, J.; Streitwieser, A., Jr.; Zalkin, A. *Organometallics* **1991**, *10*, 1922.

(257) Poremba, P.; Reissmann, U.; Noltemeyer, M.; Schmidt, H.-G.; Brüser, W.; Edelmann, F. T. *J. Organomet. Chem.* **1997**, *544*, 1.

(258) Xia, J.; Jin, Z.; Chen, W. *J. Chem. Soc., Chem. Commun.* **1991**, 1214.

(259) Rösch, N. *Inorg. Chim. Acta* **1984**, *94*, 297.

(260) Streitwieser, A., Jr.; Kinsley, S. A.; Rigsbee, J. T.; Fragalà, I. L.; Ciliberto, E.; Rösch, N. *J. Am. Chem. Soc.* **1985**, *107*, 7786.

(261) Dolg, M.; Fulde, P.; Küchle, W.; Neumann, C.-S.; Stoll, H. *J. Chem. Phys.* **1991**, *94*, 3011.

(262) Streitwieser, A., Jr.; Kinsley, S. A.; Rigsbee, J. T.; Fragalà, I. L.; Ciliberto, E.; Rösch, N. *J. Am. Chem. Soc.* **1985**, *107*, 641.

(263) Kilimann, U.; Herbst-Irmer, R.; Stalke, D.; Edelmann, F. T. *Angew. Chem.* **1994**, *106*, 1684; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1618.

(264) Dolg, M.; Fulde, P.; Stoll, H.; Preuss, H.; Chang, A.; Pitzer, R. M. *Chem. Phys.* **1995**, *195*, 71.

(265) Edelstein, N. M.; Allen, P. G.; Bucher, J. J.; Shuh, D. K.; Sofield, C. D. *J. Am. Chem. Soc.* **1996**, *118*, 13115.

(266) Fischer, R. D. *Angew. Chem.* **1994**, *106*, 2253; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 3, 2165.

(267) Reissmann, U.; Lameyer, L.; Stalke, D.; Poremba, P.; Edelmann, F. T. *Chem. Commun.* **1999**, 1865.

(268) Plets, W. M. *Dokl. Acad. Nauk SSSR* **1938**, *20*, 27.

(269) Afanasev, B. N.; Tsyganova, P. A. *Zh. Obshch. Khim.* **1948**, *18*, 306.

(270) Tsutsui, M.; Gysling, H. *J. Am. Chem. Soc.* **1968**, *90*, 6880.

(271) Rybakova, L. F.; Sigalov, A. B.; Syutkina, O. P.; Egorova, E. N.; Beletskaya, I. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 2415; *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1981**, 1995.

(272) Hayes, R. G.; Thomas, J. *J. Am. Chem. Soc.* **1969**, *91*, 6876.

(273) Suleimanov, G. Z.; Bregadze, V. I.; Kovalchuk, N. A.; Khalilov, K. S.; Beletskaya, I. P. *J. Organomet. Chem.* **1983**, *255*, C5.

(274) Beletskaya, I. P.; Voskoboynikov, A. Z.; Chuklanova, E. B.; Magomedov, G. K. I. *J. Am. Chem. Soc.* **1993**, *115*, 3156.

(275) Bochkarev, M. N.; Fagin, A. A. *Chem.*−*Eur. J.* **1999**, *5*, 2990.

(276) Bochkarev, M. N.; Fedushkin, I, L.; Fagin, A. A.; Petrovskaya, T. V.; Ziller, J. W.; Bromhall-Dillard, R. N. R.; Evans, W. J. *Angew. Chem.* **1997**, *109*, 123; *Angew. Chem., Int. Ed.* **1999**, *36*, 1133.

(277) Bochkarev, M. N.; Fedushkin, I. L.; Dechert, S.; Fagin, A. A.; Schumann, H. *Angew. Chem.* **2001**, *113*, 3268; *Angew. Chem., Int. Ed.* **2001**, *40*, 3176.

(278) Molander, G. A. *Chem. Rev.* **1992**, *92*, 29.

(279) Coughlin, E. B.; Bercaw, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 7606.

(280) Gun'ko, Yu. K.; Edelmann, F. T. *Comments Inorg. Chem.* **1997**, *19*, 153−184.

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