Cyclopentadienyl-Free Organolanthanide Chemistry

Frank T. Edelmann*

Dedicated to Professor Herbert W. Roesky on the occasion of his 60th birthday

During the past ten years the organometallic chemistry of the lanthanides has witnessed enormous growth. One of the main reasons for this development was the finding that lanthanide metallocenes can exhibit an unusually high catalytic activity. Considerable advances have also been achieved in the chemistry of organolanthanide complexes that are not stabilized by cyclopentadienyl ligands. For example, the successful synthesis of the first unsolvated homoleptic trialkyllanthanides, $[Ln\{CH(SiMe_3)_2\}_3]$, has recently been reported. Anionic allyl complexes of the lanthanides show promising catalytic properties and cyclooctatetraene complexes of these elements are also under active investigation. This review is intended to provide an overview of this rapidly developing area of research.

Keywords: cyclooctatetraene complexes · homogeneous catalysis · lanthanides · organolanthanide compounds

1. Introduction

Organolanthanide chemistry is currently one of the most rapidly developing areas of organometallic chemistry. This is even more surprising, as only twenty years ago it was stated in inorganic chemistry textbooks that the lanthanide elements do not form stable organometallic compounds. Meanwhile it has become quite clear that organolanthanide chemistry follows its own rules and often differs significantly from organometallic chemistry of the 3d transition metals. In recent years numerous unprecedented reaction pathways and novel molecular structures have been discovered, which demonstrate the unique character of organolanthanide chemistry. The impressive advance in this area has already been documented in several reviews.[1–6] The current research in the field of homogeneous catalysis with organolanthanide complexes is particularly exciting. It is now well established that certain lanthanide metallocenes can exhibit an unusually high catalytic activity. This is particularly true for olefin transformations such as hydrogenations, cyclizations, polymerizations, and addition reactions. Traditionally, for these purposes attention focused on cyclopentadienyl complexes of the lanthanides. Approximately 90% of all previously described organometallic complexes of the 4f elements are compounds containing cyclopentadienyl ligands.[4–6] Anionic π ligands are ideally suited for stabilizing highly reactive alkyl- and hydridolanthanide complexes. More recently, however, increasing use has been made of other ligand systems in organolanthanide chemistry. Among these ligands are bulky σ-alkyl groups and allyl ligands as well as pentadienyl anions ("open cyclopentadienyl"), neutral arenes, and anionic heterocycles. η^8-Cyclooctatetraene complexes of the lanthanides are a particularly large class of compounds. This review is intended to provide an overview of the current developments by illustrating synthetic and structural aspects as well as possible applications. Without trying to be fully comprehensive, it will present the most interesting results and show the main objectives.

Table 1 shows the assignment of the various lanthanide elements in the numbering of the compounds. As usual, scandium and yttrium have been included because of their chemical similarity with the lanthanides. The radioactive element promethium has been omitted as no organometallic compound without cyclopentadienyl ligands has so far been reported.[6] Compounds in which the formal oxidation state of the lanthanide is zero have also been excluded.

Table 1. Numbering scheme of the lanthanide elements in this article.

Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
a	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**j**	**k**	**l**	**m**	**n**	**o**	**p**

2. Carbonyl Complexes

In sharp contrast to the organometallic chemistry of the 3d transition metals, binary carbonyllanthanide compounds are unstable under normal conditions.[5] Ln^{3+} ions are considered good σ acceptors but poor π donors. Simple lanthanide carbonyls $[Ln(CO)_n]$ have so far only been detected in matrix inves-

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tigations.[1] The only structurally characterized compound, for which coordination of a CO ligand to a lanthanide element was proven, is the heteronuclear erbium complex **1m** (Fig. 1).[7] Weak

$[Er(EtOH)(H_2O)_4\{Mo(CO)_3(C_5H_5)\}_3]$ **1m**

metal–metal interactions and semibridging carbonyl ligands between molybdenum and erbium characterize this compound, which resembles the previously described heterobimetallic complexes with isocarbonyl bridges between lanthanides and transition metals.[8] Even today there is still a long way to go before the main goal is reached, namely, the synthesis of "true" carbonyl complexes of the lanthanides with C-bonded CO.

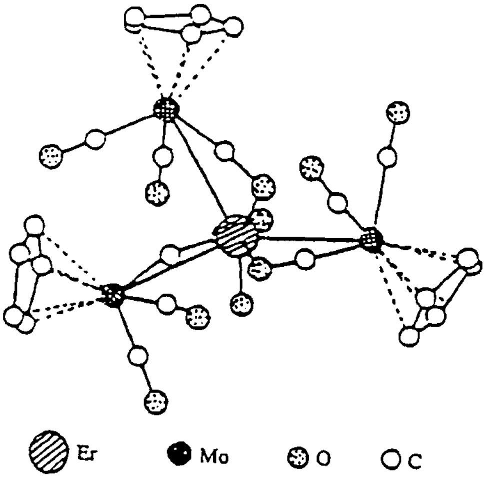

Fig. 1. Molecular structure of $[Er(EtOH)(H_2O)_4\{Mo(CO)_3(C_5H_5)\}_3]$ **1m** in the crystal.

3. Alkyl and Aryl Complexes

Once again in contrast to the countless π complexes of 3d transition metals, the lanthanides exhibit virtually no tendency to coordinate neutral alkenes, dienes, allenes, or alkynes.[1–6] The reasons for this behavior are the limited radial extension of the 4f orbitals and the fact that the Ln–C bond in organolanthanide complexes is predominantly ionic. Thus early attempts to prepare lanthanide complexes of unsaturated hydrocarbons were mostly unsuccessful. Likewise, the synthesis of simple organolanthanide complexes containing only σ-bonded ligands is quite problematic. One of the major challenges in the field of organolanthanide chemistry was (and continues to be) the synthesis of unsolvated, homoleptic trialkyl- and triaryllanthanides LnR_3. The main reason for the instability of such compounds is the tendency of the lanthanide to adopt high coordination numbers. Because of the large ionic radii of the Ln^{3+} ions, three-coordinate compounds with simple alkyl or aryl ligands are stericaly highly unsaturated. Normally this leads to the formation of solvent adducts, "ate" complexes, or oligomeric species. A significant breakthrough was achieved only very recently through the use of sterically demanding alkyl ligands such as $CH(SiMe_3)_2$.

3.1. Neutral Homoleptic Compounds

In addition to neutral, unsolvated compounds of the composition LnR_2 and LnR_3, solvent adducts thereof will also be discussed in this section, although per definition these materials are heteroleptic complexes. The most thoroughly investigated lanthanide(II) compound in this group is bis(pentafluorophenyl)ytterbium(II), $[Yb(C_6F_5)_2]$ **2o**, which was described by Deacon et al.[8–10] This compound is easily accessible by a

$[Yb(C_6F_5)_2]$ **2o** $[Yb(o\text{-}C_6F_4H)_2]$ **3o** $[Yb(p\text{-}C_6F_4H)_2]$ **4o**

transmetalation reaction between metallic ytterbium and bis(pentafluorophenyl)mercury. The corresponding europium(II) compound **2h** can be obtained analogously [Eq. (1)].

$$Ln + [Hg(C_6F_5)_2] \longrightarrow \underset{\mathbf{2},\ Ln\,=\,Eu,\,Yb}{[Ln(C_6F_5)_2]} + Hg \qquad (1)$$

The comparably high stability of the pentafluorophenyl derivatives has been explained by the formation of metal–fluorine interactions. Partially fluorinated derivatives such as **3o** and **4o** are significantly less stable than **2o**. Compounds **2h** and **2o** are both very useful intermediates in various subsequent reactions, for example, as starting materials for the preparation of lanthanide(II) amides and phenoxides.[11] Furthermore, the σ-bonded pentafluorophenyl groups in **2o** can be transferred to

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transition metals.[10, 12] Recently Lappert et al. reported on an interesting new representative of this small class of compounds.[13] The first well-characterized dialkyllanthanide(II) compound **5o**, was prepared according to Equation (2). The

$[Yb\{CH(SiMe_3)_2\}_2(Et_2O)_2]$ **5o**

coordinated diethyl ether can be replaced by the chelating phosphane ligand 1,2-bis(dimethylphosphino)ethane (DMPE) [Eq. (3)]. Subsequent reactions with pivalonitrile or anionic azaallylic ligands indicate that **5o** is a very promising starting material for the preparation of novel organolanthanide(II) complexes.

$$YbI_2 + 2\,NaCH(SiMe_3)_2 \xrightarrow[-2\,NaI]{Et_2O} \underset{\mathbf{5o}}{[Yb\{CH(SiMe_3)_2\}_2(Et_2O)_2]} \qquad (2)$$

$$\mathbf{5o} + DMPE \longrightarrow \underset{\mathbf{6o}}{[Yb\{CH(SiMe_3)_2\}_2(dmpe)]} + 2\,Et_2O \qquad (3)$$

By using the sterically more demanding tris(trimethylsilyl)methyl ligand it was even possible to isolate an unsolvated homoleptic dialkyllanthanide(II) compound. The reaction of YbI_2 with two equivalents of $KC(SiMe_3)_3$ in benzene afforded **7o** in the form of orange, sublimable crystals, which were

$[Yb\{C(SiMe_3)_3\}_2]$ **7o**

characterized by X-ray structure analysis (Fig. 2).[14] A particularly surprising and interesting structural feature of **7o** is the C-Yb-C angle of 137°. All other bis[tris(trimethylsilyl)methyl] metal species, for example $[Mg\{C(SiMe_3)_3\}_2]$[15] and $[Na\{C(SiMe_3)_3\}_2]^-$[16], have been reported to be linear. Just a few years ago an unsolvated dialkyllanthanide(II) compound like **7o** was considered to be impossible to isolate.

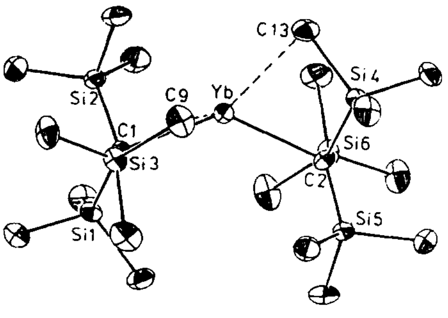


Fig. 2. Molecular structure of $[Yb\{C(SiMe_3)_3\}_2]$ **7o** in the crystal.

Organolanthanide(II) complexes can also be stabilized by σ-bonded carborane ligands.[17] The compound **8o** was synthesized by a transmetalation reaction [Eq. (4)], but an unambiguous structural characterization is still lacking.

$$Yb + [Hg(o\text{-}C_2H_2B_{10}H_9)_2] \xrightarrow[-Hg]{THF} \underset{\mathbf{8o}}{[Yb(o\text{-}C_2H_2B_{10}H_9)_2]} \qquad (4)$$

Attempts at synthesizing homoleptic trialkyllanthanides were made some 50 years ago.[1] The first indications that such compounds might form came from the observation that lanthanum reacts with methyl radicals.[18] However, it was not possible to isolate a product of the composition $LaMe_3$. Early reports on the synthesis of $ScEt_3$ and YEt_3 have also never been verified.[19] It is anticipated that the reported triphenyl derivatives $ScPh_3$ **9a** and YPh_3 **10b** are oligomeric or polymeric materials.[20, 21] The reason for the inherent instability of all such compounds is that the formally three-coordinate central atom is sterically unsaturated. Only recently a well-defined σ-phenyl derivative of ytterbium became available in which the metal atoms attain the formal coordination number 6 through formation of a dinuclear complex. The highly remarkable mixed-valent Yb^{II}/Yb^{III} compound **11o** was obtained by treatment of "naphthalene-ytterbium" **12o** with either diphenylmercury or triphenylbismuth.[22, 23] The crystal structure analysis revealed the presence of an asymmetric complex, in which both ytterbium atoms are coordinated in a distorted octahedral fashion (Fig. 3). Three phenyl groups act as bridging ligands by forming σ bonds to the first ytterbium atom, while being η^2-coordinated to the second ytterbium atom.

$ScPh_3$	YPh_3	$[Ph_2(thf)Yb(\mu\text{-}Ph)_3Yb(thf)_2]$	$[(C_{10}H_8)Yb(thf)_2]$
9a	**10b**	**11o**	**12o**

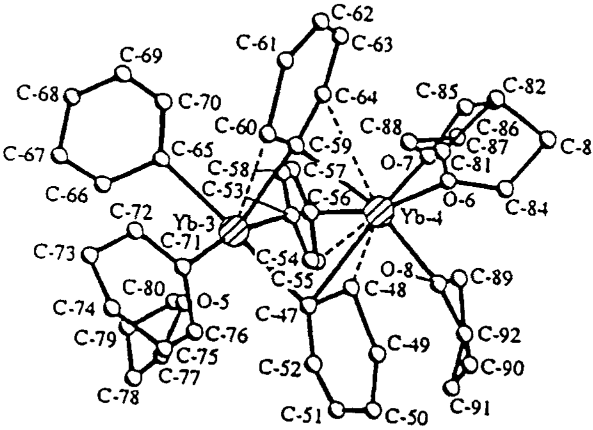


Fig. 3. Molecular structure of $[Ph_2(thf)Yb(\mu\text{-}Ph)_3Yb(thf)_2]$ **11o** in the crystal.

Recently the first structural characterization of two triphenyllanthanide complexes was reported by Bochkarev et al.[24] The THF adducts **13** were obtained according to Equation (5) by

$$2\,Ln + 3\,Ph_2Hg \xrightarrow{THF,\ LnI_3} 2\,[Ph_3Ln(thf)_3] + 3\,Hg \qquad (5)$$

13, Ln = Er, Tm

treatment of elemental lanthanides with diphenylmercury in the presence of small amounts of LnI_3. After reaction times of approximately 120–150 h, the products were isolated as pink (**13m**) or colorless (**13n**) highly air-sensitive crystals. Monomeric, distorted octahedral molecules with a facial arrangement of the ligands are present in the erbium derivative **13m** (Fig. 4).

Generally, however, low-coordinate organolanthanide complexes with simple σ-bound alkyl or aryl ligands are unstable. Compounds with a significantly higher stability are obtained by

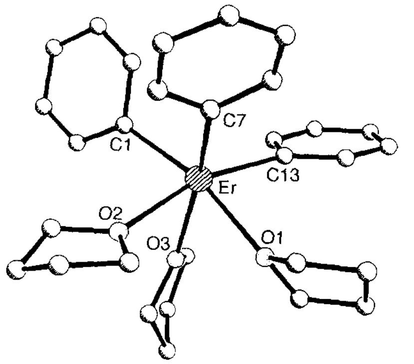


Fig. 4. Molecular structure of $[Ph_3Er(thf)_3]$ **13m** in the crystal.

using chelating ligands. Especially useful for this purpose are chelating ligands that contain an additional donor function and thus allow a coordinative saturation of the central metal atom. In this way homoleptic lanthanide complexes containing the chelating *o*-dimethylaminomethylphenyl substituent and related ligands were prepared in the 1970s. The six-coordinate complexes **14** and **15** can be isolated without any additional donor

$[Ln(o\text{-}Me_2NCH_2C_6H_4)_3]$ **14** $[Ln(o\text{-}Me_2NC_6H_4CH_2)_3]$ **15**

Ln = Sc, Y, La, Nd, Er, Yb, Lu

ligands such as THF.[25–27] Methoxy groups function as the additional donors in the complexes **16**.[28] A novel development

$[Ln(o\text{-}MeOC_6H_4)_3]$ **16**, Ln = Ce, Pr, Nd

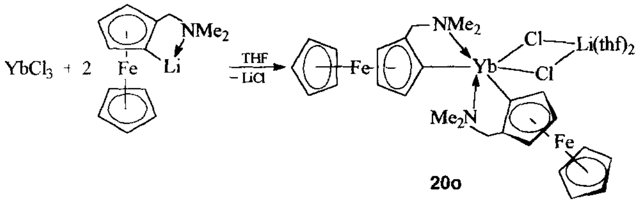
in this area is the use of the chelating 2-dimethylaminomethylferrocenyl (FcN) ligands. FcN compounds contain cyclopentadienyl ligands, but these are not *pentahapto* coordinated to the lanthanide central atoms. Among the hitherto described organolanthanide complexes with σ-bonded FcN ligands are the compounds **17c**, **18**, and **19o**,[29] which were obtained by treatment of anhydrous lanthanide trichlorides with Li(FcN) [Eqs. (6)–(8)].

$$LaCl_3 + 2\,Li(FcN) \longrightarrow \underset{\mathbf{17c}}{[(FcN)_2LaCl]} + 2\,LiCl \qquad (6)$$

$$LnCl_3 + 3\,Li(FcN) \xrightarrow{THF} \underset{\mathbf{18},\ Ln\,=\,Ce,\,Pr,\,Nd}{[(FcN)_3Ln \cdot LiCl \cdot THF]} + 2\,LiCl \qquad (7)$$

$$YbCl_3 + 3\,Li(FcN) \longrightarrow \underset{\mathbf{19o}}{[Yb(FcN)_3]} + 3\,LiCl \qquad (8)$$

The crystallographically characterized ytterbium "ate"-complex **20o** was obtained by reacting anhydrous ytterbium trichloride with two equivalents of Li(FcN) [Eq. (9)].[30] The product **20o** is the first bis(organo)lanthanide(III) halide containing only σ-bonded ligands (Fig. 5, Yb–C 265.1, 237.2 pm). This compound resembles the lanthanide metallocenes $[(C_5Me_5)_2Ln(\mu\text{-}Cl)_2Li(thf)_2]$[1–6] and thus an interesting derivative chemistry is also expected in this case.



20o

(9)

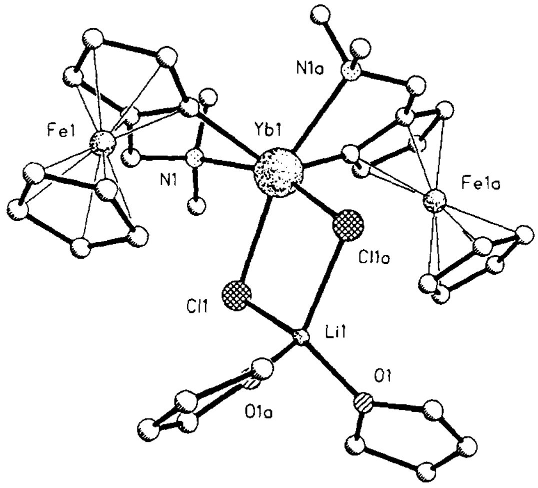


Fig. 5. Molecular structure of $[(FcN)_2Yb(\mu\text{-}Cl)_2Li(thf)_2]$ **20o** in the crystal.

Chelating phosphorus ylide anions should also be suitable for the synthesis of six-coordinate organolanthanide complexes. However, the products made according to Scheme 1 were polymeric and no structural characterization could be achieved. Even with the sterically demanding ligand $[(CH_2)_2PtBu_2]^-$ only oligomeric products were obtained.[31]

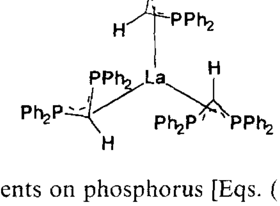
$$LnCl_3 + 3\,Me_3P{=}CH_2 \longrightarrow [Ln\{CH_2PMe_3Cl\}_3]$$

$$\xrightarrow[\substack{-3C_4H_{10}\\ -3LiCl}]{+3nBuLi} [Ln\{(CH_2)_2PMe_2\}_3] \quad \mathbf{21},\ Ln = La, Pr, Nd, Sm, Gd, Ho, Er, Lu$$

Scheme 1. Synthesis of $[Ln\{(CH_2)_2PMe_2\}_3]$ **21**.

Allyl-like diphosphinomethanide ligands have been demonstrated to be much better suited for the synthesis of homoleptic organolanthanide complexes. The lanthanum derivative **22c** was structurally characterized in 1986.[32]

With samarium as the central atom mono- or dinuclear diphosphinomethanide complexes can be isolated depending on the nature of the substituents on phosphorus [Eqs. (10) and (11), respectively].[33, 34] Both products have been unequiv-



22c

$$[SmCl_3(thf)_3] + 3\,LiCH(PPh_2)_2 \xrightarrow[\substack{-3\,LiCl\\ -3\,THF}]{} \underset{\mathbf{23g}}{[Sm\{CH(PPh_2)_2\}_3]} \qquad (10)$$

$$2\,Sm(O_3SCF_3)_3 + 6\,LiCH(PMe_2)_2 \xrightarrow[-6\,LiO_3SCF_3]{} \underset{\mathbf{24g}}{[\{\mu\text{-}\eta^2\text{-}CH(PMe_2)_2\}_2\{Sm[CH(PMe_2)_2]_2\}_2]} \qquad (11)$$

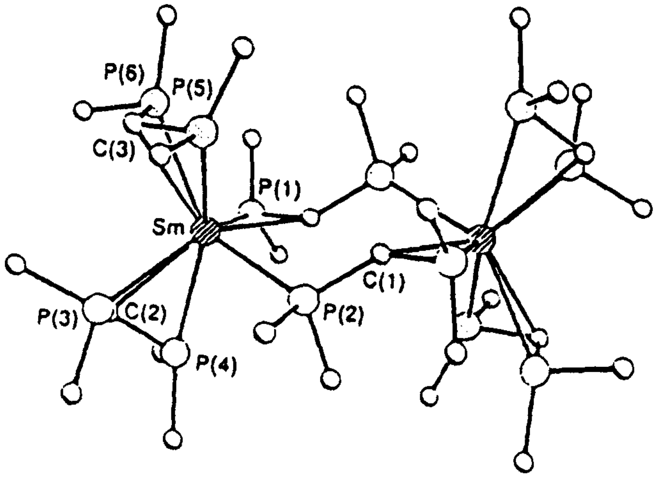


Fig. 6. Molecular structure of $[\{\mu\text{-}\eta^2\text{-CH(PMe}_2)_2\}_2\{\text{Sm[CH(PMe}_2)_2]_2\}_2]$ **24g** in the crystal.

ocally characterized by crystal structure analyses. In the centrosymmetric dimer **24g** the two samarium atoms are bridged by two diphosphinomethanide ligands through a carbon and a phosphorus atom (Fig. 6).

A second strategy for stabilizing lanthanide compounds with low coordination numbers (3–6) is the use of sterically demanding alkyl ligands. However, for this, alkyl groups such as *tert*-butyl, neopentyl, or trimethylsilylmethyl are not sufficiently bulky to allow the isolation of unsolvated trialkyllanthanides.[1] For example, treatment of lanthanide trichlorides with $LiCH_2SiMe_3$ in THF solution affords the THF adducts **25** as the final products [Eq. (12)], from which the coordinated solvent cannot be removed without decomposition.[35–39] The products are thermolabile and decompose upon heating under elimination of THF and tetramethylsilane. It was proposed that the resulting pyrophoric and presumably polymeric materials are lanthanide carbene complexes, although nothing is known about the molecular structure of these products.

$$\mathrm{LnCl_3 + 3\,LiCH_2SiMe_3 \xrightarrow{THF} [(Me_3SiCH_2)_3Ln(thf)_2] + 3\,LiCl} \tag{12}$$

25, Ln = Er, Tm, Yb, Lu

The results discussed above make quite clear that base-free homoleptic alkyllanthanide compounds are accessible only with the use of very bulky alkyl substituents. The synthesis of the trialkyl compounds $[Ln\{CH(SiMe_3)_2\}_3]$ **26** by Lappert et al. can be considered a milestone in organolanthanide chemistry.[40–42] Their successful preparation was made possible by a combination of two favorable factors: First, the bis(trimethylsilyl)methyl substituent was employed as a sterically highly demanding alkyl ligand. In addition, by using the low-coordinate phenoxides $[Ln(2,4,6\text{-}tBu_3C_6H_2O)_3]$ as starting materials it was possible to avoid the formation (and incorporation) of alkali metal halides. When the reactions are carried out in pentane, the lithium phenoxide by-product precipitates quantitatively and can be separated readily from the highly soluble trialkyllanthanide **26** [Eq. (13)].

$$\mathrm{[Ln(2,4,6\text{-}\mathit{t}Bu_3C_6H_2O)_3] + 3\,LiCH(SiMe_3)_2 \xrightarrow[-3\;2,4,6\text{-}\mathit{t}Bu_3C_6H_2OLi]{pentane} [Ln\{CH(SiMe_3)_2\}_3]} \tag{13}$$

26, Ln = Y, La, Sm, Lu

The molecular structures of the lanthanum (Fig. 7) and samarium derivative have been determined by X-ray diffraction.[40–42] Like the homoleptic silylamides $[Ln\{N(SiMe_3)_2\}_3]$ the trialkyl compounds **26** adopt a flat pyramidal coordination geometry. The average metal–carbon distances for **26c** and **26g** are 251.5(9) (La–C) and 233(2) (Sm–C) pm, respectively.

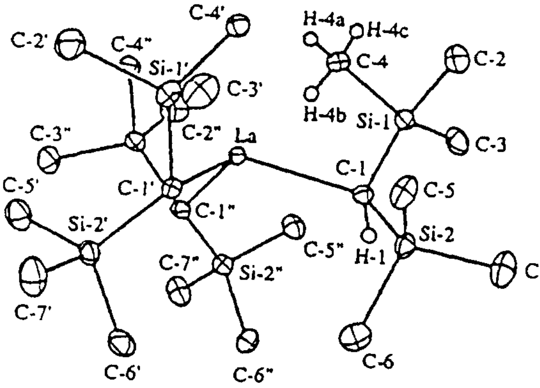


Fig. 7. Molecular structure of $[La\{CH(SiMe_3)_2\}_3]$ **26c** in the crystal.

The deviation from trigonal-planar coordination in the complexes **26** is somewhat surprising. Several explanations have been proposed for this unexpected coordination geometry. Initially, it was proposed that interligand repulsion would be minimized in a pyramidal structure. More important, however, is the possibility of forming agostic Ln-H-C interactions. In fact, short γ-agostic Ln ··· Me interactions have been found in both structurally characterized compounds (La ··· C 312.1 pm, Sm ··· C 285 pm). In this way, the extreme electronic and coordinative unsaturation can be diminished. A different, yet just as plausible, explanation would be the creation of a dipole moment in the pyramidal geometry which would then result in a higher lattice energy in the crystal.

Interestingly, the complexes **26** are not accessible directly from lanthanide trichlorides by conventional reactions. Instead of homoleptic trialkyl compounds, products containing incorporated lithium chloride are formed in these reactions [Eq. (14); PMDETA = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine].[40]

$$\mathrm{LaCl_3 + 3\,LiCH(SiMe_3)_2 \xrightarrow[-2\,LiCl]{PMDETA} [\{(Me_3Si)_2CH\}_3La(\mu\text{-}Cl)Li(pmdeta)]} \tag{14}$$

27c

The LiCl adduct **27c** contains a nearly linear La-Cl-Li unit (La-Cl-Li 165.1°, La–Cl 276.2 pm, Li–Cl 228 pm). In comparison with the neutral compound **26c**, the $[Ln\{CH(SiMe_3)_2\}_3]$ fragment in **27c** exhibits no significant structural changes. An analogous reaction with ytterbium trichloride affords the salt-like product **28o**, which consists of separated ions in the solid state.[35] Evidently, the formation of the various types of complexes depends on a subtle balance of certain factors. These factors include the nature of the alkali metal, the presence of

$[Li(thf)_4][YbCl\{CH(SiMe_3)_2\}_3]$ **28o** halide ions, and the ionic radius of the lanthanide element. A similar situation was recently described for some low-coordinate lanthanide alkoxides and amides.[43] For example, the chloro-bridged **27c** is closely related to the neodymium compounds **29f** and **30f**, whereas **28o** is comparable to the compound **31f**.

$[\{(Me_3Si)_2N\}_3Nd(\mu\text{-}Cl)Li(thf)_3]$ **29f**

$[(tBu_3CO)_3Nd(\mu\text{-}Cl)Li(thf)_3]$ **30f**

$[Li(thf)_4][NdOSiMe_3\{N(SiMe_3)_2\}_3]$ **31f**

Recent papers by Schaverien et al. provided additional evidence on how minor changes of the reaction conditions or the choice of the reagents can influence the product formation.[44,45] In this case instead of $LiCH(SiMe_3)_2$, the more reactive $KCH(SiMe_3)_2$ was allowed to react with the lanthanide trichlorides. Owing 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 2).

$$\begin{tikzcd}
LuCl_3 + 3\,KCH(SiMe_3)_2 \arrow[r, "ether"] & \underset{\textbf{32p}}{[Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)K(Et_2O)]} \arrow[d, shift left, "-ether"] \\
\underset{\textbf{34p}}{[Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)K(\eta^6\text{-}C_7H_8)]} & \underset{\textbf{33p}}{[Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)K]} \arrow[l, "toluene"'] \arrow[u, shift left, "ether"]
\end{tikzcd}$$

Scheme 2. Interconversion of alkyllutetium compounds.

In contrast to the analogous LiCl adduct **27c**, the coordinated diethyl ether in **32p** can easily be removed under vacuum to produce the complex **33p**. In this compound the potassium is coordinatively unsaturated and readily adds solvent molecules such as diethyl ether or even toluene.[44,45]

Very little is known about heavier homologues of the alkyllanthanides such as homoleptic silyl and germyl derivatives or their solvent adducts. In the case of divalent ytterbium the preparation of such compounds was achieved by reacting metallic ytterbium with Ph_3ECl (E = Si, Ge) [Eq. (15)].[46] In both

$$2\,Yb + 2\,Ph_3ECl \xrightarrow{THF} \underset{\mathbf{34o},\ E = Si;\ \mathbf{35o},\ E = Ge}{[(Ph_3E)_2Yb(thf)_4]} + [YbCl_2(thf)_2] \quad (15)$$

cases the crystal structure determination showed the presence of centrosymmetric octahedral molecular structures, in which the Ph_3E ligands are arranged in the axial positions.

A small number of σ-stannyl complexes are also known. The ytterbium(II) compound **36o** was prepared by treatment of YbI_2 with the stannylpotassium reagent $K[Sn(CH_2tBu)_3]$ and structurally characterized by X-ray diffraction.[47] The structures were determined also for the stannyl complexes **37** (DME = 1,2-dimethoxyethane);[48,49] however, thus far no further reactions of these interesting products have been reported.

$[Yb\{Sn(CH_2tBu)_3\}_2(thf)_2]$ **36o**

$[Ln\{Sn(CH_2SiMe_3)_3\}_3(dme)]$ **37**, Ln = Pr, Nd

3.2. Anionic Homoleptic Compounds

As a result of the desire of the lanthanide ions to achieve high coordination numbers in their complexes, simple alkyllanthanide(III) complexes very easily add solvent molecules or anionic ligands and form so-called "ate" complexes. Such anionic alkyl complexes are often the only isolable products, when anhydrous lanthanide trichlorides are treated with alkyl- or aryllithium reagents. Quite often the anionic ate complexes are formed preferentially, regardless of the stoichiometric ratio of the starting materials. In a series of fundamental papers, Schumann et al. described the most simple compounds of this type, which formally contain $[LnMe_6]^{3-}$ ions.[50,51] The octahedral complexes **38** and **39** are formed when anhydrous lanthanide trichlorides are treated with six equivalents of methyllithium in the presence of a coordinating solvent. It was possible to prepare the complexes **38** for the entire lanthanide series except promethium and europium.(Owing to the subsequent facile reduction to undefined europium(II) species, the europium derivative **38h** cannot be isolated.) The chelate ligands TMEDA (TMEDA = *N,N,N′,N′*-tetramethylethylene-1,2-diamine) and DME serve to coordinatively saturate the lithium ion.

$$LnCl_3 + 6\,MeLi + 3\,TMEDA \xrightarrow[-3\,LiCl]{Et_2O} [Li(tmeda)]_3[LnMe_6] \quad (16)$$

38, Ln = Sc, Y, La–Sm, Gd–Lu

$$LnCl_3 + 6\,MeLi + 3\,DME \xrightarrow[-3\,LiCl]{Et_2O} [Li(dme)]_3[LnMe_6] \quad (17)$$

39, Ln = Ce, Pr, Gd, Tb, Dy, Er, Lu

The crystalline compounds are extremely air sensitive and reveal the characteristic colors of the respective lanthanide ions. The X-ray crystal structures were determined for the complexes **38l** (Fig. 8), **38m**, and **39p**.[50,51] Six methyl groups surround the central lanthanide ion in a slightly distorted octahedral arrangement. Two methyl ligands form bridges between the lanthanide ion and each lithium ion, which, in turn, is coordinatively saturated by chelating TMEDA or DME. All Ln–C bonds are the same length.

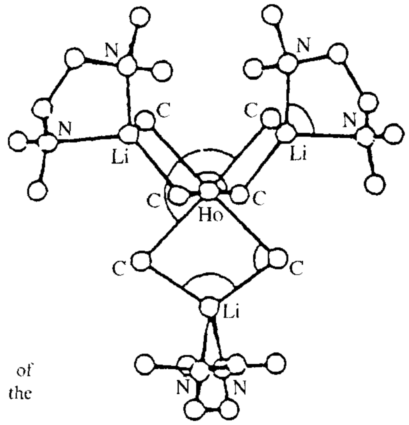


Fig. 8. Molecular structure of $[Li(tmeda)]_3[HoMe_6]$ **38l** in the crystal.

Very little has been reported about the reactivity of the complexes **38** and **39**. The first applications in organic synthesis were the reactions with α,β-unsaturated aldehydes and ketones. The reaction of the samarium derivative **38g** with *tert*-butyl alcohol in diethyl ether afforded the alkoxide $[Li_5Sm(O\mathit{t}Bu)_8]$.[52]

$[Li(tmeda)]_3[SmMe_6]$ **38g**

Lower coordination numbers than those in the $[LnMe_6]^{3-}$ ions can be achieved with sterically demanding alkyl ligands such as *tert*-butyl or trimethylsilymethyl. The synthesis of anionic tetra-*tert*-butyl complexes was achieved in a conventional way by reaction of $LnCl_3$ or $Ln(O\mathit{t}Bu)_3$ with four equivalents $\mathit{t}BuLi$ [Eqs. (18)-(20)]. Diethyl ether, THF, or TMEDA can be used as the coordinating solvent in these reactions.[50, 53, 54] An X-ray crystal structure determination of the lutetium compound **40p** revealed the presence of solvent-separated ions in the crystal.[55]

$$LnCl_3 + 4\,\mathit{t}BuLi \xrightarrow[-3\,LiCl]{pentane/Et_2O} [Li(Et_2O)_4][Ln\mathit{t}Bu_4] \qquad (18)$$

40, Ln = Tb, Er, Lu

$$LnCl_3 + 4\,\mathit{t}BuLi \xrightarrow[-3\,LiCl]{THF} [Li(thf)_n][Ln\mathit{t}Bu_4] \qquad (19)$$

41, Ln = Er ($n = 4$), Yb ($n = 3$)

$$Ln(O\mathit{t}Bu)_3 + 4\,\mathit{t}BuLi \xrightarrow[-3\,LiO\mathit{t}Bu]{pentane/TMEDA} [Li(tmeda)_2][Ln\mathit{t}Bu_4] \qquad (20)$$

42, Ln = Er, Lu

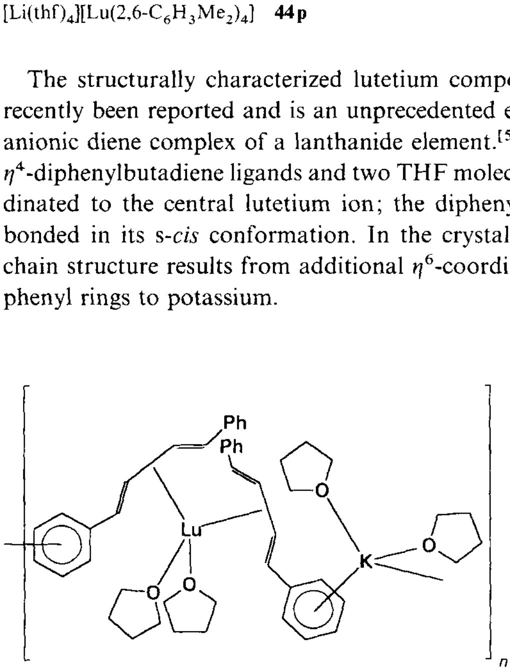
Four-coordinate anionic lanthanide(III) complexes are also accessible with σ-aryl ligands.[21] A typical example is the reaction of anhydrous lanthanide trichlorides with excess phenyllithium, which affords the tetraphenyl complexes **43** [Eq. (21)]. The proposed tetrahedral coordination geometry has been confirmed unambiguously by a crystal structure analysis of the ring-substituted derivative **44p**.[56]

$$LnCl_3 + 4\,PhLi \xrightarrow[-3\,LiCl]{THF} Li[LnPh_4] \qquad (21)$$

43, Ln = La, Pr

$[Li(thf)_4][Lu(2,6\text{-}C_6H_3Me_2)_4]$ **44p**

The structurally characterized lutetium compound **45p** has recently been reported and is an unprecedented example of an anionic diene complex of a lanthanide element.[57] In **45p** two η^4-diphenylbutadiene ligands and two THF molecules are 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.



45p

3.3. Heteroleptic Compounds

Although THF adducts of alkyllanthanide compounds are formally heteroleptic complexes, only organolanthanide compounds containing additional anionic ligands will be discussed in this section. Until just a few years ago this class of compounds was fairly obscure; however, more recently a substantial number of highly interesting results in this area have been reported. Well-defined lanthanide(II) derivatives are still virtually unknown. The dimeric alkylytterbium(II) ethoxide **46o** was made by treatment of ytterbium(II) iodide with $KC(SiMe_3)_3$ in diethyl ether and characterized by X-ray crystallography.[13] Alternatively, **46o** is also accessible from **7o** by an ether cleavage reaction [Eq. (22)].[14]

$$\underset{\mathbf{7o}}{2[Yb\{(Me_3Si)_3C\}_2]} + 4\,Et_2O \xrightarrow[-CH_2=CH_2]{-(Me_3Si)_3CH} \underset{\mathbf{46o}}{[(Me_3Si)_3CYb(OEt)(OEt_2)]_2} \qquad (22)$$

$[(Me_3Si)_2CHYb(OAr)(thf)_3]$ **47o**

The monomeric phenoxide **47o** is formed in the reaction of $[Yb(OAr)_2(thf)_3]$ with $KCH(SiMe_3)_2$. In this case the very bulky ArO ligand prevents the formation of a phenoxide-bridged dinuclear complex (Ar = $2,6\text{-}\mathit{t}Bu_2\text{-}4\text{-}MeC_6H_2$).[13]

Grignard-type organolanthanide complexes 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 = halogen) have been thoroughly investigated since 1970 and are now widely used in organic synthesis.[5] The ytterbium compounds RYbI, in particular, are easily accessible from RI and elemental ytterbium in THF. The resulting deeply colored THF solutions are usually used in situ for subsequent reactions. These organolanthanide(II) compounds behave somewhat 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. In 1994 Eaborn et al. reported the first preparation and structural characterization of such compounds.[14] The homoleptic dialkylytterbium(II) complex $[Yb\{(Me_3Si)_3C\}_2]$ **7o** reacts with iodomethane or 1,2-diiodoethane to give the ytterbium Grignard compound **48o**, which can be isolated in the form of greenish-yellow, exceedingly air-sensitive crystals. In complete analogy to normal Grignard compounds, **48o** could be prepared by direct reaction of elemental ytterbium with the corresponding silyl-substituted alkyl iodide [Eq. (23)].[14, 58] The crystal structure determination of **48o** revealed that the central Yb_2I_2 ring is planar (Fig. 9).

$$2\,Yb + 2(Me_3Si)_3CI \xrightarrow{Et_2O} \underset{\mathbf{48o}}{[\{[(Me_3Si)_3C]Yb(\mu\text{-}I)(Et_2O)\}_2]} \qquad (23)$$

Several other compounds of this class were synthesized by varying the substituents.[58] The ytterbium complexes **49o**

$[\{[(Me_3Si)_2(Me_2XSi)C]Yb(\mu\text{-}I)(Et_2O)\}_2]$ **49o**, X = OMe, Ph, CH=CH$_2$

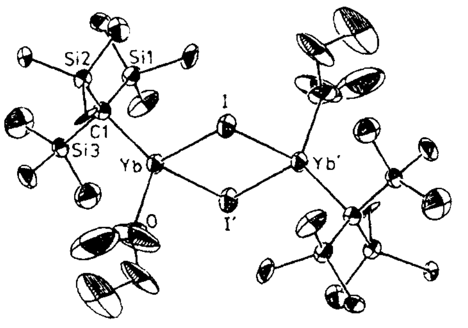


Fig. 9. Molecular structure of $[\{[(Me_3Si)_3C]Yb(\mu\text{-}I)(Et_2O)\}_2]$ **48o** in the crystal.

have been prepared according to Equation (23). Figure 10 depicts the unusual molecular structure of **49o** ($X = CH{=}CH_2$), in which the very rare lanthanide-vinyl π interaction occurs.

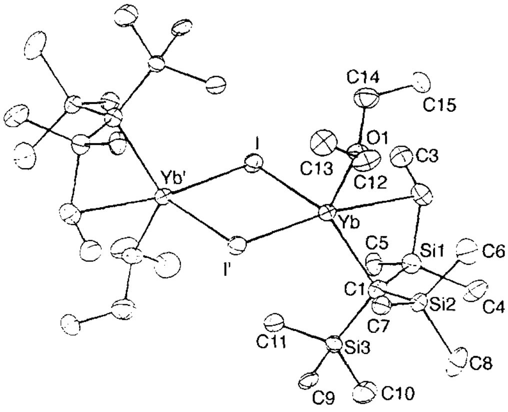


Fig. 10. Molecular structure of $[\{[(Me_3Si)_2(Me_2SiCH{=}CH_2)C]Yb(\mu\text{-}I)(Et_2O)\}_2]$ **49o** ($X = CH{=}CH_2$) in the crystal.

A typical Schlenk-equilibrium could be detected for all Grignard-type ytterbium(II) complexes in nonpolar organic solvents such as toluene [Eq. (24)].

$$[RYbI]_2 \rightleftharpoons R_2Yb + YbI_2 \qquad (24)$$

Until recently monoorganolanthanide(III) dihalides, $RLnX_2$, were still only poorly characterized. These compounds can likewise be considered as Grignard-type analogous compounds. They can be easily prepared in situ by alkylation of $LnCl_3$ or LnI_3 with organolithium compounds.[5] A remarkable result from an organometallic viewpoint was the first crystal structure determination of a "lanthanide(III) Grignard compound" of this type, which was reported by Chen et al.[59] Anhydrous gadolinium trichloride reacts with phenyllithium in a 1:1 molar ratio to give the well-defined seven-coordinate phenyl complex **50i**. The length of the gadolinium–carbon σ bond is 242(2) pm (Fig. 11).

$[PhGdCl_2(thf)_4]$ **50i**

Organolanthanide complexes containing different σ-alkyl ligands are still virtually unknown. A structurally characterized example is the heteroleptic anionic samarium complex **51g** with

$[\{(Me_3Si)_2CH\}_3Sm(\mu\text{-}Me)Li(pmdeta)]$ **51g**

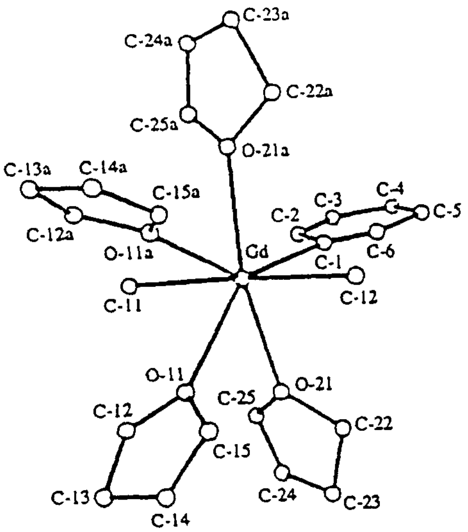
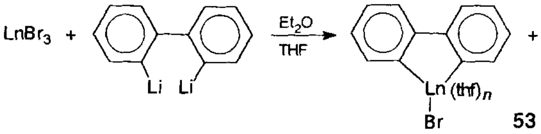


Fig. 11. Molecular structure of $[PhGdCl_2(thf)_4]$ **50i** in the crystal.

a methyl group bridging samarium and lithium.[60] Likewise, metallacycles containing a lanthanide atom in the ring are very rare species. Five-membered "lanthanols" such as **52f** and **52i** have been described, but are insufficiently characterized.[61]

$[Ph_4C_4Ln(\mu\text{-}Cl)_2Li(thf)_n]$, **52f**, Ln = Nd; **52i**, Ln = Gd

The same was true until recently for the metallacyclic products obtained by reacting anhydrous lanthanide tribromides with *o*-dilithiobiphenyl. The compounds **53** isolated as THF adducts were initially thought to be five-membered metallacycles [Eq. (25)].[62]



(25)

The reaction of $SmBr_3$ with *o*-dilithiobiphenyl $Li_2C_{12}H_8$ was recently reinvestigated and the true nature of the reaction product **54g** elucidated.[63] Contrary to the originally proposed structure, the product does not contain a five-membered metallacycle. Instead, a dimetalated *o*-quaterphenyl ligand is formed through dimerization [Eq. (26), Fig. 12], which with samarium

$$6\,SmBr_3 + 6\,Li_2C_{12}H_8 \xrightarrow[\substack{-2\,Sm,\ -2\,SmBr_3\\ -H_2,\ -12\,LiBr}]{} \underset{\textbf{54g}}{[(C_{24}H_{16})Sm(\mu\text{-}Br)(thf)_2]_2 \cdot C_{24}H_{14}} \qquad (26)$$

forms a nine-membered metallacycle. Dimerization through bromide ligands leads to the formation of the dinuclear product. The hydrocarbon dibenzonaphthacene ($C_{24}H_{14}$), which is formed as a by-product during the reaction, is intercalated in the crystal lattice.

Alkyllanthanide(III) alkoxides form a 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

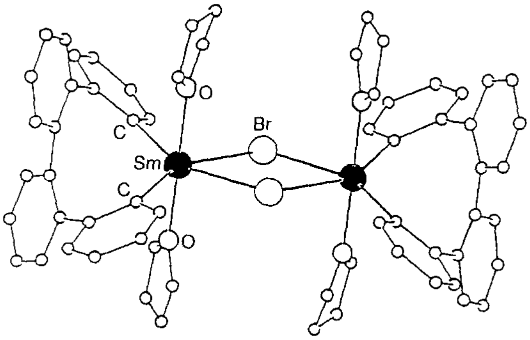


Fig. 12. Molecular structure of $[(C_{24}H_{16})Sm(\mu\text{-}Br)(thf)_2]_2 \cdot C_{24}H_{14}$ **54g** in the crystal (intercalated $C_{24}H_{14}$ omitted).

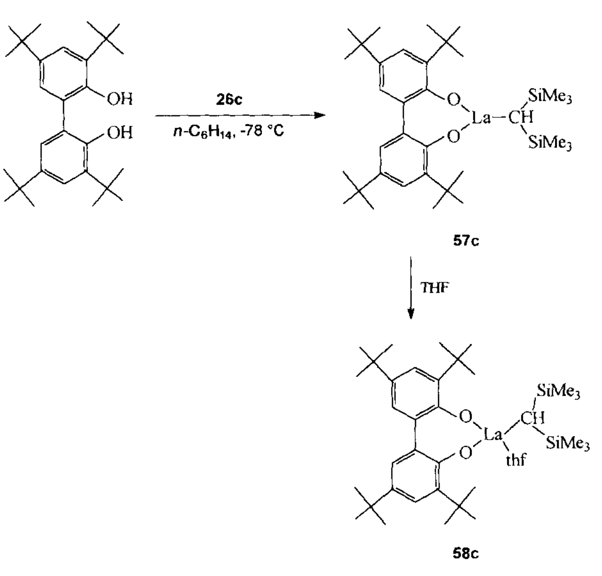
for diene polymerization is $Nd(O\textit{i}Pr)_3/AlEt_3/Et_2AlCl$. The heterobimetallic alkyllanthanide(III) alkoxide **55f** could be isolated

$[\{Nd_6Al_3(\mu\text{-}Cl)_6(\mu\text{-}Et)_9Et_5(O\textit{i}Pr)\}_2]$ **55f**

from this system and characterized by X-ray crystallography.[64] The complex structure of this catalytically active intermediate underlines the fact that lanthanide alkoxides tend to aggregate as clusters. Only in very rare cases is the constitution of lanthanide alkoxides as simple as implied by the formula $Ln(OR)_3$.[65] A series of heterobimetallic alkyllanthanide(III) alkoxides has been synthesized in a simple way by alkylation of lanthanide alkoxides [Eq. (27)].[66] The yttrium compound **56b** is also obtained by alkylation of the alkoxide cluster $[Y_3(O\textit{t}Bu)_9(thf)]$ with excess $AlMe_3$.[67]

$$Ln(O\textit{t}Bu)_3 + 3\,AlMe_3 \longrightarrow \underset{\textbf{56},\ Ln\,=\,Y,\ Pr,\ Nd}{[Ln\{(\mu\text{-}O\textit{t}Bu)(\mu\text{-}Me)AlMe_2\}_3]} \qquad (27)$$

The stabilization of monomeric alkyllanthanide(III) alkoxides was first achieved by employing the sterically demanding chelate ligand 3,3′,5,5′-tetra-*tert*-butyl-biphenyl-2,2′-diolate. In this case unsolvated $[La\{CH(SiMe_3)_2\}_3]$ **26c** served as a useful starting material (Scheme 3).[68]



Scheme 3. Synthesis of alkyllanthanum(III) diolates.

Special nitrogen ligands are also suitable for stabilizing heteroleptic alkyllanthanide compounds. In recent years porphyrin ligands have been successfully employed. For example, treatment of $[ScCl_3(thf)_3]$ with $[Li(thf)_4][Li(oep)]$ or $[Li_2(OEP)(thf)_2]$ affords the chloro complex [ScCl(oep)] **59a** (oep = octaethylporphyrin dianion). Substitution of the chloride ligand in **59a** leads to the corresponding scandium amides, alkoxides, or σ-alkyl derivatives. Alkylation affords the unsolvated alkyl complexes [ScR(oep)] **60**.[69, 70] Evidently, the small ionic radius

[ScCl(oep)] **59a**

[ScR(oep)] **60**, R = Me, $CH_2\textit{t}Bu$, $CH(SiMe_3)_2$

of the respective lanthanide facilitates the synthesis of porphyrin derivatives. Thus porphyrin-stabilized alkyllanthanide compounds can also be obtained with yttrium and lutetium as central atoms.[41] The thermal reaction of the homoleptic alkyl complexes $[Ln\{CH(SiMe_3)_2\}_3]$ with H_2oep in toluene has been demonstrated to be an elegant and effective access to such complexes [Eq. (28)]. This method completely circumvents complications that may arise from the formation of solvent adducts and/or incorporation of halide ions. The lutetium derivative **61p** has been characterized by an X-ray crystal structure analysis. Figure 13 depicts the square-planar coordination geometry.

$$\underset{\textbf{(26b, p)}}{[Ln\{CH(SiMe_3)_2\}_3]} + H_2oep \xrightarrow[-2\,CH_2(SiMe_3)_2]{} \underset{\textbf{61},\ Ln\,=\,Y,\ Lu}{[(oep)LnCH(SiMe_3)_2]} \qquad (28)$$

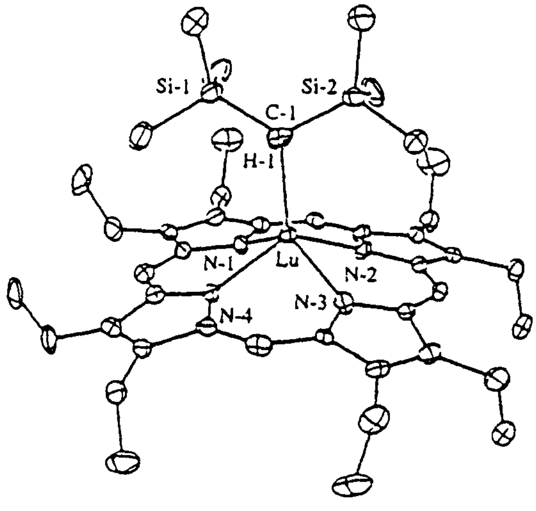


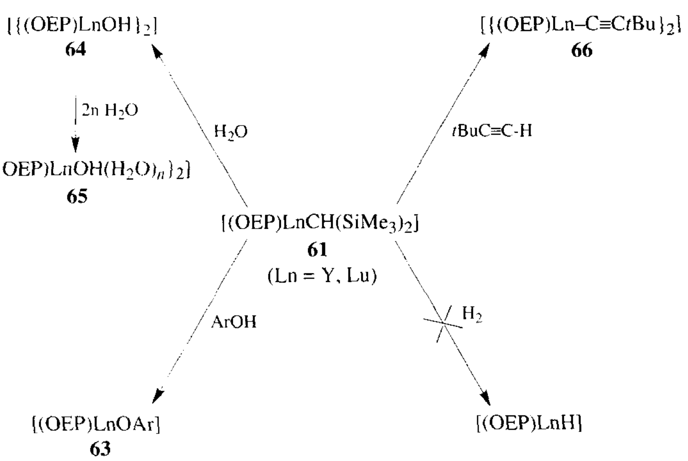
Fig. 13. Molecular structure of $[(oep)LuCH(SiMe_3)_2]$ **61p** in the crystal.

Alternatively, the porphyrin-stabilized alkyllanthanide(III) compounds **61** are accessible by a two-step synthetic procedure, in which the presence of coordinating solvent or alkali metal halides can also be avoided [Eqs. (29) and (30)].[41]

$$\underset{\textbf{62}}{[Ln(2,6\text{-}\textit{t}Bu_2C_6H_3O)_3]} + H_2oep \xrightarrow[-2\ 2,6\text{-}\textit{t}Bu_2C_6H_3OH]{} \underset{\textbf{63}}{[(oep)LnOC_6H_3\textit{t}Bu_2]} \qquad (29)$$

$$\textbf{63} + LiCH(SiMe_3)_2 \xrightarrow[-2,6\text{-}\textit{t}Bu_2C_6H_3OH]{} \underset{\textbf{61},\ Ln\,=\,Y,\ Lu}{[(oep)LnCH(SiMe_3)_2]} \qquad (30)$$

Just like other highly reactive alkyllanthanide(III) compounds, the complexes **61** are interesting starting materials for subsequent reactions, which are summarized in Scheme 4.[41] The very facile hydrolysis leads to the dimeric hydroxo complexes **64**, and the σ-alkyl groups are easily substituted in reactions with phenols or terminal alkynes. In contrast, hydrogenolysis to the corresponding hydrides cannot 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 hydrogen at normal pressure to give the dimeric hydrides $[\{(C_5Me_5)_2Ln(\mu\text{-}H)\}_2]$.[71–73]



Scheme 4. Derivative chemistry of the complexes **61**.

The heteronuclear alkyl complexes **68b** can be prepared by stepwise reaction of the yttrium alkoxide **63b** with methyllithium and trimethylaluminum (Scheme 5).[41]

$$\underset{\mathbf{63b}}{[(oep)YOC_6H_3tBu_2]} + 2\,MeLi \xrightarrow[-\,LiOC_6H_3tBu_2]{Et_2O} \underset{\mathbf{67b}}{[(oep)Y(\mu\text{-}Me)_2Li(Et_2O)]} \xrightarrow{Al_2Me_6} \underset{\mathbf{68b}}{[(oep)Y(\mu\text{-}Me)_2AlMe_2]}$$

Scheme 5. Synthesis of $[(oep)Y(\mu\text{-}Me)_2AlMe_2]$ **68b**.

The reaction sequence shown in Scheme 5 parallels the multistep synthesis of $[(C_5Me_5)_2LuMe]$[74] with the only exception that the final step, that is the elimination of trimethylaluminum with Lewis bases, cannot be reproduced in the porphyrin series. Treatment of **68b** with Lewis bases such as pyridine only leads to the formation of adducts and not to unsolvated [YMe(oep)]. O_2 selectively attacks the bridging methyl groups in **68b** leading to the formation of the YAl alkoxide **69b**.

$[(oep)Y(\mu\text{-}OMe)_2AlMe_2]$ **69b**

More recently several other auxiliary ligands have been found that are capable of stabilizing σ-alkyllanthanide(III) complexes. These ligands include sterically demanding amido ligands as well as benzamidinate and pyrazolylborate ions. For example, an alkyllanthanide(III) amide is formed upon treatment of $[Yb_2\{N(SiMe_3)_2\}_4]$ with two equivalents of Al_2Me_6.[75] The reaction product **70o** contains four Yb-Me-Al and two Yb-Me-Si bridges (Fig. 14).

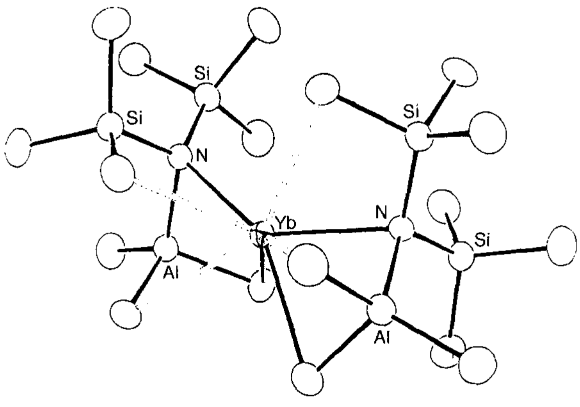


Fig. 14. Molecular structure of $[Yb\{N(SiMe_3)_2\}_2(AlMe_3)_2]$ **70o** in the crystal.

$[Yb\{N(SiMe_3)_2\}_2(AlMe_3)_2]$ **70o**

The potentially tridentate silylamide ion $[N(SiMe_2CH_2PMe_2)_2]^-$ developed by Fryzuk et al. has also been successfully employed in organolanthanide chemistry.[76–78] The stepwise preparation of heteroleptic alkyllanthanide(III) amides is illustrated in Scheme 6. The σ-alkyl complexes **72** are fluxional in solution and decompose upon heating under elimination of the hydrocarbon RH.

$$LnCl_3 + 2\,KN(SiMe_2CH_2PMe_2)_2 \xrightarrow[-2\,KCl]{} \underset{\mathbf{71}}{[LnCl\{N(SiMe_2CH_2PMe_2)_2\}_2]} \xrightarrow[-LiCl]{RLi} \underset{\mathbf{72}}{[LnR\{N(SiMe_2CH_2PMe_2)_2\}_2]}$$

(Ln = La, Lu)

Scheme 6. Synthesis of $[LnR\{N(SiMe_2CH_2PMe_2)_2\}_2]$ **72**.

The synthesis of bis-σ-alkyllanthanide complexes containing only one chelating ligand proved to be more difficult. Such complexes have only become available by combining the very bulky silylamide ion $[N(SiMe_2CH_2PiPr_2)_2]^-$ with the small Sc^{3+} ion.[79] The complexes **73a** and **74a** have been prepared (cf. Scheme 6) and structurally characterized by X-ray diffraction (Fig. 15). A high reactivity and catalytic activity can be expected for these 10-electron complexes.

$[\{N(SiMe_2CH_2PiPr_2)_2\}ScEt_2]$ **73a**

$[\{N(SiMe_2CH_2PiPr_2)_2\}Sc(CH_2SiMe_3)_2]$ **74a**

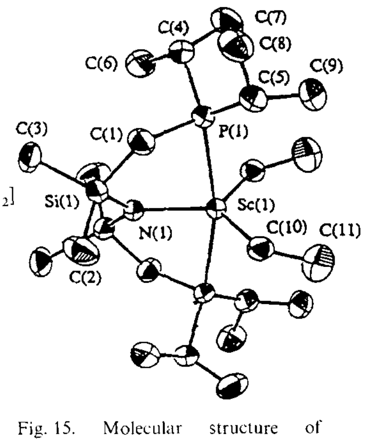


Fig. 15. Molecular structure of $[\{N(SiMe_2CH_2PiPr_2)_2\}ScEt_2]$ **73a** in the crystal.

Hydrotris(pyrazol-1-yl)borate ligands are enjoying increased popularity in the organometallic chemistry of lanthanides. By using the sterically demanding anion $[HB(3\text{-}t Bu\text{-}5\text{-}Me\text{-}pz)_3]^-$, Takats et al. recently succeeded in preparing soluble, monosubstituted ytterbium(II) alkyl complexes.[80] The compounds **76o** (Fig. 16) and **77o** have been made by treatment of the precursor

$[\{HB(3\text{-}t Bu\text{-}5\text{-}Me\text{-}pz)_3\}YbI(thf)]$ **75o**

$[\{HB(3\text{-}t Bu\text{-}5\text{-}Me\text{-}pz)_3\}YbCH(SiMe_3)_2]$ **76o**

$[\{HB(3\text{-}t Bu\text{-}5\text{-}Me\text{-}pz)_3\}Yb\{CH(SiMe_3)_2\}(Et_2O)]$ **77o**

75o with alkyllithium reagents. These compounds are rare examples of organolanthanide(II) complexes with σ-bonded alkyl ligands.

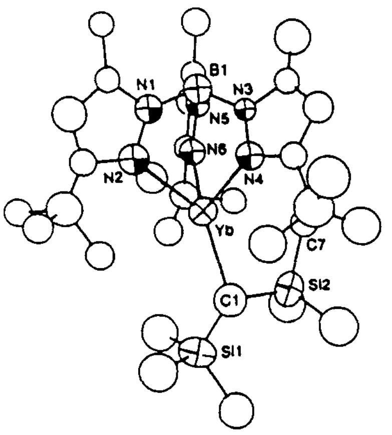


Fig. 16. Molecular structure of $[\{HB(3\text{-}t Bu\text{-}5\text{-}Me\text{-}pz)_3\}YbCH(SiMe_3)_2]$ **76o** in the crystal.

Bulky heteroallylic ligands such as the benzamidinate ions $[RC_6H_4C(NSiMe_3)_2]^-$ have recently been established as useful alternatives to the cyclopentadienyl ligands. Thus, the yttrium(III) benzamidinates **80b** can be regarded as analogues of the metallocene $[(C_5Me_5)_2YCH(SiMe_3)_2]$. All these compounds exhibit comparable catalytic activities, for example, in olefin polymerizations. The alkyl derivatives **80b** are easily accessible by alkylation of the corresponding chloride or triflate precursors [Eq. (31)].[81–83]

$$[\{RC_6H_4C(NSiMe_3)_2\}_2YX(thf)_n] + LiCH(SiMe_3)_2 \quad (31)$$

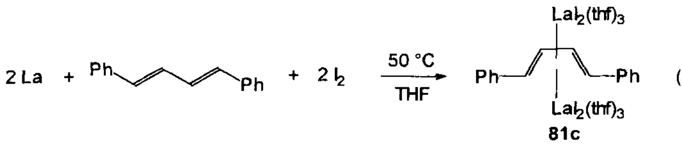
78b, X = Cl, $n = 1$

79b, X = O_3SCF_3, $n = 0$

$$\xrightarrow[-LiX]{} [\{RC_6H_4C(NSiMe_3)_2\}_2YCH(SiMe_3)_2]$$

80b, R = H, OMe, CF_3

In contrast to the organometallic chemistry of the d-block transition metals, diene complexes are particularly rare in the case of the lanthanides.[1–6] This is especially true for complexes without supporting cyclopentadienyl ligands. The first successful approaches in this direction have been reported in two recent papers: The diene-bridged dilanthanum complex **81c** was obtained by reacting finely divided elemental lanthanum with 1,4-diphenylbutadiene and iodine in THF [Eq. (32)].[84] The samarium analogue **81g** had already been made earlier using a similar synthetic procedure.[85]



(32)

81c

An X-ray structure determination of the isolated red crystals of **81c** revealed the presence of an "inverse sandwich complex" in which the two lanthanum atoms are symmetrically bridged by the $\eta^4:\eta^4$-coordinated diene ligand.[84] Structurally related "inverse sandwich complexes" have been prepared according to Equations (33) and (34) from naphthalene ($C_{10}H_8$).[86]

$$2[LaI_3(thf)_3] + 2Li + C_{10}H_8 \xrightarrow[-2LiI]{THF} [(\mu_2\text{-}\eta^4:\eta^4\text{-}C_{10}H_8)\{LaI_2(thf)_3\}_2] \quad (33)$$

82c

$$2[EuI_2(thf)_2] + 2C_{10}H_8Li \xrightarrow[-2LiI,\ -C_{10}H_8]{DME} [(\mu_2\text{-}\eta^4:\eta^4\text{-}C_{10}H_8)\{EuI(dme)_2\}_2] \quad (34)$$

83h

The complexes **82c** (Fig. 17) and **83h** have been characterized by X-ray structure analyses. In both cases the lanthanide atoms are bridged by nonplanar naphthalene units bonded in diene-like fashion.

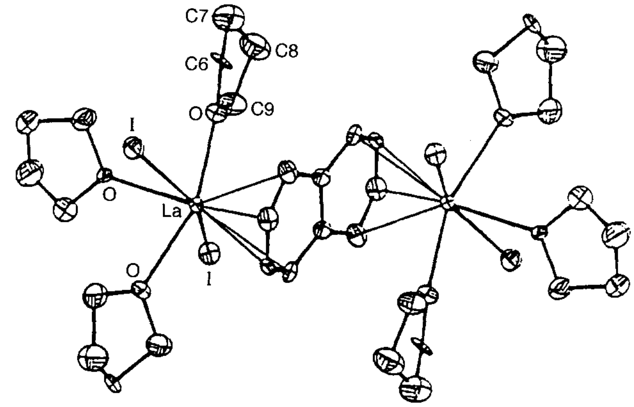


Fig. 17. Molecular structure of $[(\mu_2\text{-}\eta^4:\eta^4\text{-}C_{10}H_8)\{LaI_2(thf)_3\}_2]$ **82c** in the crystal.

4. Alkenyl and Alkynyl Complexes

Well-characterized alkenyl- and alkynyllanthanide complexes remain a relatively unexplored class of compounds. Ytterbium reacts with $Hg(CH{=}CHCl)_2$ to give the insufficiently characterized bis(β-chlorovinyl)ytterbium **84o**.[87] However, a well-defined alkynyl complex of divalent ytterbium could be synthesized by using the sterically demanding hydrotris(3,5-dimethylpyrazol-1-yl)borate ligand. The dark red phenylacetylide **86o** was obtained in good yield by reaction of the amide **85o** with phenylacetylene.[80]

$[Yb(CH{=}CHCl)_2]$ **84o**

$[\{HB(3,5\text{-}Me_2pz)_3\}Yb\{N(SiMe_3)_2\}]$ **85o**

$[\{HB(3,5\text{-}Me_2pz)_3\}YbC{\equiv}CPh]$ **86o**

It was reported that the blue solutions of elemental europium or ytterbium in liquid ammonia react with alkynes with terminal triple bonds to give bis(alkynyl)lanthanide(II) complexes. Alkynyl derivatives of divalent europium and ytterbium are also available by transmetalation of $Hg(C{\equiv}CR)_2$ with the respective metals [Eq. (35)].[88, 89]

$$Ln + Hg(C{\equiv}CR)_2 \xrightarrow{THF} [Ln(C{\equiv}CR)_2] + Hg \quad (35)$$

87h, o

R = nBu; Ln = Eu, Yb

R = Ph; Ln = Yb

In the case of trivalent lanthanides the tris(alkynyl) complexes **88p**[27] and **89**[90, 91] have been described. Virtually nothing is known about the molecular structures of all these compounds; however, it is likely that the unsolvated complexes $[Ln(C{\equiv}CR)_2]$ and $[Ln(C{\equiv}CR)_3]$ are polymeric materials with bridging alkynyl ligands.

$[Lu(C{\equiv}C\textit{t}Bu)_3]$ **88p**

$[Ln(C{\equiv}CPh)_3]$ **89**, Ln = Pr, Sm, Eu, Gd, Tb, Er, Yb

A well-defined μ-ethynyl complex of yttrium is formed by protolysis of the alkyl derivative **80b** (R = H) with acetylene [Eq. (36)]. Figure 18 shows the dimeric structure of **90b** with bridging ethynyl ligands.

$$\underset{\textbf{80b}}{2[\{PhC(NSiMe_3)_2\}_2YCH(SiMe_3)_2]} \xrightarrow[-2\,CH_2(SiMe_3)_2]{2\,HC{\equiv}CH} \underset{\textbf{90b}}{[\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}C{\equiv}CH)\}_2]} \quad (36)$$

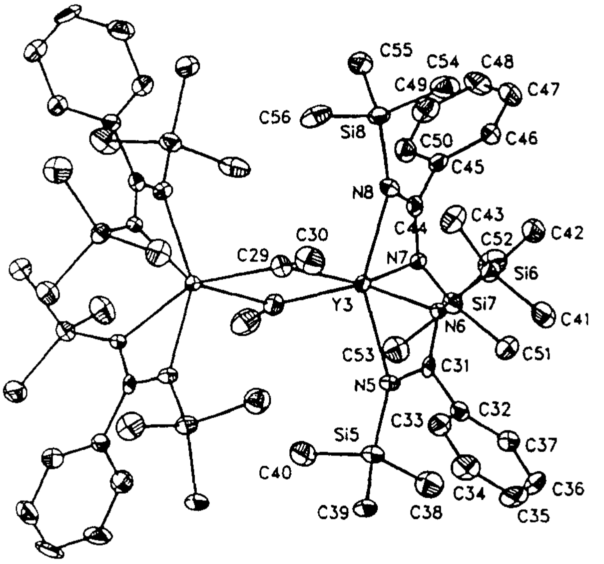


Fig. 18. Molecular structure of $[\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}C{\equiv}CH)\}_2]$ **90b** in the crystal.

5. Allyl Complexes

Homoleptic tris(η^3-allyl)lanthanides are unknown. Evidently, the steric bulk of three relatively small allyl ligands is not sufficient to coordinatively saturate the large lanthanide ions. Instead, reactions of anhydrous lanthanide trichlorides with allyllithium have produced a series of interesting anionic allyl complexes. The complexes **91**–**93** have been obtained depending on the reaction conditions and the solvents used.[92–94]

$[Li(dioxane)_n][Ln(\eta^3\text{-}C_3H_5)_4]$ **91**, Ln = Ce, Pr, Nd, Sm, Gd, $n = 2$; Ln = Y, $n = 2.5$; Ln = La, $n = 3$

$[Li_2(thf)_n][Ln(\eta^3\text{-}C_3H_5)_5]$ **92**, Ln = Y, La, $n = 2.5$; Ln = Ce, Pr, Nd, Sm, $n = 3$

$[Li_2(dioxane)_n][Ln(\eta^3\text{-}C_3H_5)_5]$ **93**, Ln = Ce, Nd, Sm, Gd, Dy, Ho, Er; $n = 1{,}3$

Only recently it has been shown that such complexes are also available by a one-pot reaction in which the allyllithium reagent is prepared in situ from tetraallyltin and *n*-butyllithium [Eq. (37)].[92]

$$LaCl_3 + 2\,Sn(C_3H_5)_4 + 4\,\textit{n}BuLi \xrightarrow[2.\ Et_2O/dioxane]{1.\ toluene} [Li(\mu\text{-}dioxane)_{3/2}][La(\eta^3\text{-}C_3H_5)_4] + 3\,LiCl + 2\,\textit{n}Bu_2Sn(C_3H_5)_2 \quad (37)$$

In compound **94c** the central lanthanum atom is surrounded by the four η^3-allyl ligands in a distorted tetrahedral fashion (Fig. 19). The bridging dioxane molecules and the lithium ions form a two-dimensional sheet in the crystal lattice.

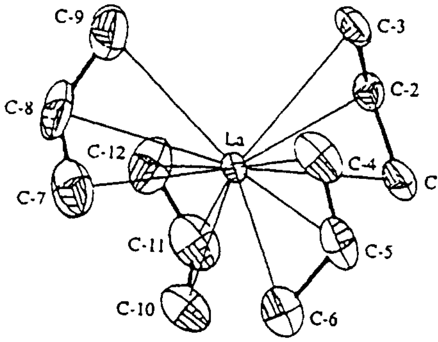


Fig. 19. Structure of the anion in $[Li(\mu\text{-}dioxane)_{3/2}][La(\eta^3\text{-}C_3H_5)_4]$ **94c** in the crystal.

By partial protolysis one allyl ligand in **94c** can be selectively replaced by a cyclopentadienyl derivative, and in this way, the complexes **95c** can be isolated.[95] Such anionic allyllanthanide(III) complexes are valuable homogeneous catalysts for diene polymerizations.[5] More complicated coordination compounds containing η^3-allyl ligands have been obtained by reactions of anhydrous lanthanide trichlorides with allyl-Grignard reagents in the presence of TMEDA.[96] Among the structurally characterized products are **96d** and **97**.

$[Li(dioxane)_2][CpLa(C_3H_5)_3]$ **95c**, Cp = C_5H_5, C_5Me_5, indenyl, fluorenyl

$[(\eta^3\text{-}C_3H_5)_2Ce(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_3Mg_2(tmeda)_2]$ **96d**

$[(\eta^3\text{-}C_3H_5)_2Ln(\mu_3\text{-}Br)_2(\mu\text{-}Br)_3Mg_2(Et_2O)_4]$ **97**, Ln = Ce, Nd

The use of the tridentate amido ligand $[N(SiMe_2CH_2PMe_2)_2]^-$ also allowed the synthesis of a heteroleptic allyllanthanide complex.[77, 78] Treatment of **71b** with $(C_3H_5)MgCl$ led to elimination of one chelating amido ligand and formation of the chloro-bridged binuclear complex **98b**.

$[(\eta^3\text{-}C_3H_5)Y\{N(SiMe_2CH_2PMe_2)_2\}(\mu\text{-}Cl)]_2$ **98b**

6. Complexes Containing Cyclopentadienyl Analogues as Ligands

Cyclopentadienyl-analogous ligands are increasingly being employed in organolanthanide chemistry. Among these ligands are pentadienyl anions as well as five-membered anionic heterocycles containing nitrogen, phosphorus, or arsenic in the ring. η^5-Cyclohexadienyl ligands, which have been reported to form interesting coordination compounds with uranium,[97, 98] have so far not been used in organolanthanide chemistry.

6.1. Pentadienyl Complexes

In many cases transition metal complexes with 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" was synthesized as long ago as 1982. Bright green tris(2,4-dimethylpentadienyl)neodymium **99f** is formed when anhydrous neodymium trichloride is treated with three equivalents of potassium 2,4-dimethylpentadienide (KC_7H_{11}) in THF [Eq. (38)].[99]

$$\mathrm{NdCl_3 + 3\,KC_7H_{11} \xrightarrow{THF} \underset{\textbf{99f}}{[Nd(C_7H_{11})_3]} + 3\,KCl} \qquad (38)$$

A crystal structure analysis of the homoleptic complex **99f** revealed the presence of three equivalent η^5-coordinated 2,4-dimethylpentadienyl ligands. Meanwhile several other pentadienyllanthanide complexes have been reported, including the compounds **99**–**101**.[100, 101] The tris(η^5-2,4-dimethylpentadienyl) complexes **99f**, **99i**, and **99p** have been structurally characterized.

$[Ln(C_7H_{11})_3]$ **99**, Ln = La, Sm, Gd, Tb, Lu

$[(C_7H_{11})LnCl_2(thf)_3]$ **100**, Ln = Nd, Sm, Gd

$[(C_7H_{11})_2LnCl(thf)]$ **101**, Ln = Nd, Sm, Gd

While the gadolinium complex adopts the same molecular structure as the neodymium compound, an interesting structural difference is found for the coordination mode of the three pentadienyl ligands in **99p**. Due to the smaller ionic radius of lutetium only two 2,4-dimethylpentadienyl ligands in this molecule are η^5-coordinated, while the third ligand is η^3-bonded (Fig. 20). This example nicely illustrates how the flexible pentadienyl ligands are able to adapt to the different ionic radii of the lanthanides.[101]

A novel way of modifying pentadienyl ligands involves the connection of two of these anions through a hydrocarbon chain.[102] A bridged bis(pentadienyl) dianion (bpd) of this kind could be generated by deprotonation of two methyl groups in 2,4,7,9-tetramethyl-1,3,7,9-decatetraene. Subsequent reaction of the resulting potassium salt with ytterbium diiodide afforded the "open" ytterbium(II) metallocene **102o** (Fig. 21), which can

$[(bpd)Yb(thf)_2]$ **102o**

be regarded as a pentadienyl analogue of $[(C_5Me_5)_2Yb(thf)_2]$. Thus far nothing has been reported about the reactivity of **102o**.

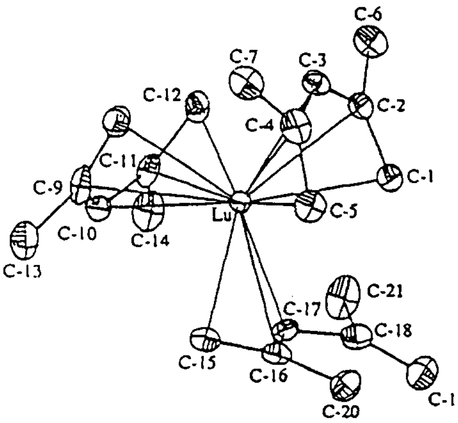


Fig. 20. Molecular structure of $[Lu(C_7H_{11})_3]$ **99p** in the crystal.

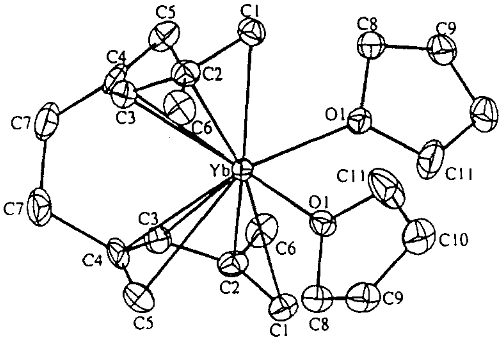


Fig. 21. Molecular structure of $[(bpd)Yb(thf)_2]$ **102o** in the crystal.

6.2. Complexes Containing Five-Membered Heterocycles as Ligands

A completely new development in organolanthanide chemistry is the use of anionic nitrogen, phosphorus, or arsenic heterocycles as ligands. Substituted pyrrolyl, phospholyl, or arsolyl ligands may turn out to be interesting alternatives to the ubiquitous pentamethylcyclopentadienyl ligands. Furthermore, the additional donor function could open up new possibilities for the construction of heteronuclear complexes.

At first glance nitrogen heterocycles appear to be less suited as π ligands for lanthanide complexes. Since the Ln^{3+} ions are known to be hard Lewis acids one would expect a preferred σ-coordination through the nitrogen atom. By introducing suitable substituents at the ring Schumann et al. succeeded in the first synthesis of organolanthanide complexes with π-bonded pyrrolyl ligands. Pyrrolyl-analogues of the known bis(pentamethylcyclopentadienyl)lanthanide(II) complexes are easily accessible according to Equation (39).[103]

$$\mathrm{[LnI_2(thf)_x] + 2\,Na[2,5\text{-}\mathit{t}Bu_2C_4H_2N] \xrightarrow[-2\,NaI]{} \underset{\textbf{103},\ Ln\,=\,Sm,\ Yb}{[(2,5\text{-}\mathit{t}Bu_2C_4H_2N)_2Ln(thf)]}} \qquad (39)$$

Mono- and bis(2,5-di-*tert*-butylpyrrolyl) complexes have been synthesized starting from anhydrous lanthanide trichlorides [Eqs. (40) and (41), respectively].[103, 104] Complex **104o**

$$\mathrm{[YbCl_3(thf)_2] + Na[2,5\text{-}\mathit{t}Bu_2C_4H_2N] \xrightarrow[-NaCl]{} \underset{\textbf{104o}}{[(2,5\text{-}\mathit{t}Bu_2C_4H_2N)YbCl_2(thf)_2]}} \qquad (40)$$

$$\mathrm{2\,NdCl_3 + 4\,Na[2,5\text{-}\mathit{t}Bu_2C_4H_2N] \xrightarrow[-2\,NaCl]{THF} \underset{\textbf{105f}}{[(2,5\text{-}\mathit{t}Bu_2C_4H_2N)_2Nd(\mu\text{-}Cl)_2\{Na(thf)\}_2(\mu\text{-}Cl)_2Nd(2,5\text{-}\mathit{t}BuC_4H_2N)_2]}} \qquad (41)$$

is monomeric in the crystal (Fig. 22); in **105f** two [2,5-$tBu_2C_4H_2N]_2NdCl$ units are connected by two NaCl "molecules". These results demonstrate that *N*-coordination of pyrrolyl ligands can be successfully avoided by introduction of bulky substituents, thus allowing the preparation of η^5-azacyclopentadienyl complexes of the lanthanides.

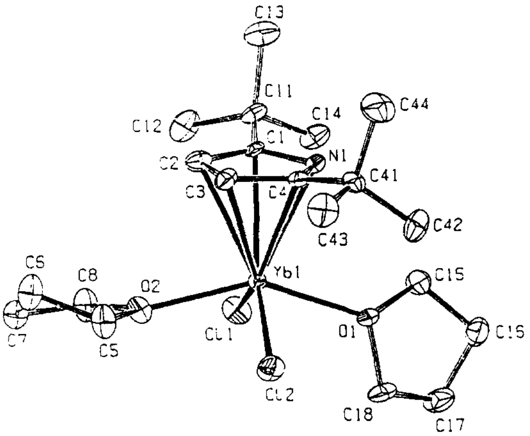


Fig. 22. Molecular structure of [(2,5-$tBu_2C_4H_2N)YbCl_2(thf)_2$] **104o** in the crystal.

Lanthanide(II) complexes containing tetrasubstituted phospholyl and arsolyl ligands have been obtained by treatment of lanthanide diiodides with two equivalents of $K(C_4Me_4E)$ (*E* = P,As) [*Eq.* (42)].[105,106]

$$[LnI_2(thf)_2] + 2\,K(C_4Me_4E) \xrightarrow[-2\,KI]{} [(C_4Me_4E)_2Ln(thf)_2] \qquad (42)$$

106, **107**, Ln = Sm, Yb; E = P, As

$[(2,5\text{-}Ph_2C_4H_2P)_2Yb(thf)_2]$ **108o**

Reductive cleavage of the E–E bond in the corresponding biphospholyl or biarsolyl derivatives by ytterbium affords the same products. The molecular structure of **108o** (Fig. 23) was determined by X-ray diffraction and illustrates the close relationship to analogous lanthanide(II) metallocenes such as $[(C_5Me_5)_2Sm(thf)_2]$.[105]

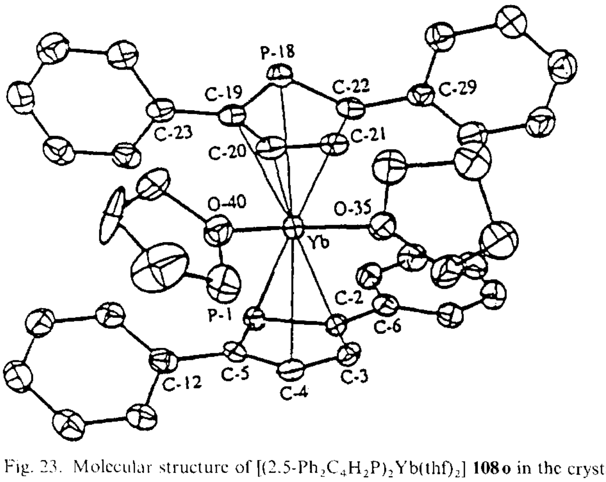


Fig. 23. Molecular structure of [(2,5-$Ph_2C_4H_2P)_2Yb(thf)_2$] **108o** in the crystal.

Of special interest with regard to derivative chemistry and possible catalytic applications are phospholyl analogues of the well-known bis(pentamethylcyclopentadienyl)lanthanide(III) halides $[(C_5Me_5)_2Ln(\mu\text{-}Cl)_2Li(solv.)_2]$ (solv. = solvent). First examples of such complexes have already been reported.[107] Thus, $Li(C_4Me_4P)$ was generated in situ from bis(tetramethylphospholyl)butane, and subsequent treatment with $LnCl_3$ in a 2:1 molar ratio afforded the disubstituted products **109** in moderate yields [Eq. (43)].

$$LnCl_3 + 2\,Li(C_4Me_4P) \xrightarrow[-LiCl]{solv.} [(C_4Me_4P)_2Ln(\mu\text{-}Cl)_2Li(solv.)_2] \qquad (43)$$

109b, Ln = Y; solv. = 1/2 DMF
109p, Ln = Lu; solv. = Et_2O

These reactions are not always as straightforward as implied by Equation (43). This was demonstrated by the recently reported reaction of $SmCl_3$ with three equivalents of $K(C_4Me_4P)$ in toluene, which led to the polymeric product **110g** (Fig. 24).[108]

$[(C_4Me_4P)_6Sm_2(KCl)_2(C_7H_8)_3]_n$ **110g**

A different result was obtained when the sterically less demanding 3,4-dimethylphospholyl ligand was used. The reaction of $SmCl_3$ with $K(C_4Me_2H_2P)$ in a 1:3 molar ratio yielded a red crystalline material which was shown by X-ray diffraction to be dimeric **111g**.[108]

$[(\eta^5\text{-}C_4Me_2H_2P)_4\{\mu\text{-}(\eta^5,\eta^1)\text{-}(C_4Me_2H_2P)\}_2Sm_2]$ **111g**

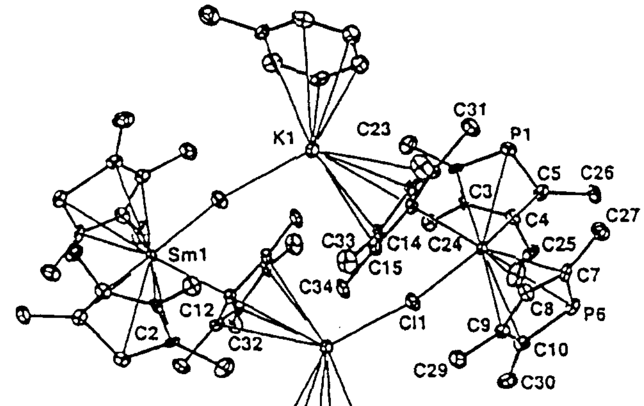


Fig. 24. Molecular structure of $[(C_4Me_4P)_6Sm_2(KCl)_2(C_7H_8)_3]_n$ **110g** in the crystal.

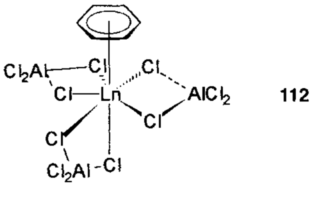
7. Arene Complexes

Lanthanide ions can participate in η^6 interactions with benzene derivatives, although the number of well-characterized arene complexes is still fairly small. The most important and best-known compounds are bimetallic arene complexes of the type $[(\eta^6\text{-arene})Ln(AlCl_4)_3]$ **112**–**114**.[109–114] In contrast to the anhydrous lanthanide trichlorides, these substances 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 these preparations are carried out in the appropriate benzene derivative as solvent [Eq. (44)].

$$\mathrm{LnCl_3 + 3\,AlCl_3 + C_6R_6 \longrightarrow [(\eta^6\text{-}C_6R_6)Ln(AlCl_4)_3]} \qquad (44)$$

112, **113**, Ln = La, Nd, Sm, Gd, Yb;
R = H, Me

The bonding in these arene complexes can be described as an ion–dipole interaction between the Ln^{3+} ion and the π-electron system of the aromatic ring. Preferably electron-rich arenes such as benzene, toluene, and hexamethylbenzene are used. Among the well-characterized and in some cases structurally analyzed examples are the complexes **112**–**114**, which are usually monomeric in the crystal.[111,112] The compounds **112f** and **112g** are isostructural with the uranium(III) analogue $[(\eta^6\text{-}C_6H_6)U(AlCl_4)_3]$. An exception is the tetramer $[\{(\eta^6\text{-}C_6H_6)Er(AlCl_4)_3\}_4]$ **112m**, in which the erbium ions are bridged by η^2-tetrachloroaluminate ligands.[115]



112

$[(\eta^6\text{-}C_6H_6)Ln(AlCl_4)_3]$ **112**, Ln = Nd, Sm, Yb

$[(\eta^6\text{-}C_6Me_6)Ln(AlCl_4)_3]$ **113**, Ln = Sm, Er, Yb

$[(\eta^6\text{-}C_6H_5Me)Ln(AlCl_4)_3]$ **114**, Ln = Y, Pr, Nd, Sm, Gd

Recently the first derivatization reactions of the arene complexes were reported. Addition of AlR_3 (R = Me, Et) to a toluene suspension of **114** results in the formation of clear solutions from which the alkylated products **115** and **116** can be isolated in good yields [Eq. (45)]. The synthesis of the complexes

$$\underset{\mathbf{114}}{[(\eta^6\text{-}C_6H_5Me)Ln(AlCl_4)_3]} + 3\,AlR_3 \xrightarrow[-3\,AlCl_2R]{} [(\eta^6\text{-}C_6H_5Me)Ln(AlCl_3R)_3] \qquad (45)$$

115, R = Me; Ln = Y, Nd, Sm
116, R = Et; Ln = Pr, Nd

$[(\eta^6\text{-}C_6H_2Me_4)Nd(AlCl_3R)_3]$ **117f**, R = Me, Et

117f has been achieved in a similar way.[116] The neodymium complex **115f** was characterized by an X-ray crystal structure determination (Fig. 25). Initial experiments show that the complexes **115** and **116** catalyze the polymerization of ethylene and butadiene.

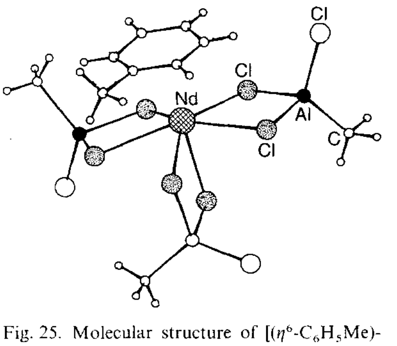
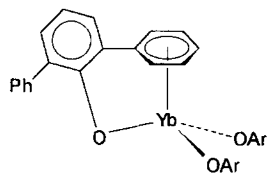


Fig. 25. Molecular structure of $[(\eta^6\text{-}C_6H_5Me)Nd(AlCl_3Me)_3]$ **115f** in the crystal.

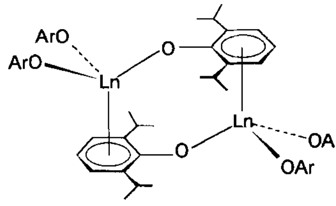
In several recent papers some interesting cases of η^6-arene coordination between lanthanide ions and phenyl groups of certain phenoxide ligands have been reported. Thus far two types of this novel bonding have been described.[117,118] Treatment of lanthanide metal powders with $[Hg(C_6F_5)_2]$ and 2,6-diphenylphenol in THF affords the lanthanide(III) phenoxides **118** and their THF adducts **119**. No unusual structural features were noted in the crystallographically characterized THF adduct **119o**. However, in the unsolvated compound **118o** 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. The reason for this additional η^6-arene coordination most likely lies in the sterically unsaturated character of the three-coordinate species $[Ln(2,6\text{-}OC_6H_3Ph_2)_3]$.

$[Ln(2,6\text{-}OC_6H_3Ph_2)_3]$ **118**, Ln = Nd, Sm, Er, Yb, Lu

$[Yb(2,6\text{-}OC_6H_3Ph_2)_3(thf)_2]$ **119o**



118o, Ar = 2,6-$Ph_2C_6H_3$



120, Ar = 2,6-*i*$Pr_2C_6H_3$

Another variant was found in the lanthanide derivatives **120** (Ln = Nd, Sm, Er, Yb) of 2,6-diisopropylphenol, which have been synthesized in an analogous manner.[118] Centrosymmetric dimers are present in the crystal; the monomeric units are each linked through a Ln–O bond and η^6-arene coordination. These results demonstrate that the formation of lanthanide arene complexes occurs more frequently than originally anticipated.

8. Cyclooctatetraene Complexes

The first cyclooctatetraene lanthanide complexes were reported in 1969.[1–6] These materials were lanthanide(II) compounds of the type $[Ln(C_8H_8)]$ **121** (Ln = Eu, Yb). Initial synthetic achievements in this area were followed by a period of stagnation, which in recent years has been replaced by a significant increase in the research activity. Today it is generally accepted that the large, flat cyclooctatetraene ligand is an especially valuable alternative to the cyclopentadienyl ligands. This is an area of organolanthanide chemistry where numerous interesting results can be expected in the future.[119]

8.1. Lanthanide(II) Complexes

Well-defined lanthanide(II) complexes with cyclooctatetraene ligands are rare. Cyclooctatetraene reacts with the dark blue solutions of europium or ytterbium in liquid ammonia to give $[Ln(C_8H_8)]$ **121** [Eq. (46)].[1] The orange products are extremely

$$\mathrm{Ln + C_8H_8 \xrightarrow{NH_3\,(l)} [Ln(C_8H_8)]} \qquad (46)$$

121, Ln = Eu, Yb

$[(C_8H_8)Yb(C_5H_5N)_3]$ **122o**

air sensitive and insoluble in organic solvents. This behavior suggests a polymeric structure of the compounds. Polymeric $[Sm(C_8H_8)]$ **121g** is more easily available by reacting $[SmI_2(thf)_2]$ with $K_2C_8H_8$.[120]

The polymeric structure can be broken up by treatment of **121o** with pyridine. This results in the formation of soluble, monomeric **122o**, for which a crystal structure determination has been reported (Fig. 26).[121] The structural characterization of the anionic sandwich complexes **123o** and **124o** revealed that

$[K(diglyme)]_2[Yb(C_8H_8)_2]$ **123o** $[K(dme)]_2[Yb(C_8H_8)_2]$ **124o**

in these compounds cyclooctatetraene dianions act as bridging ligands between ytterbium and potassium.[122]

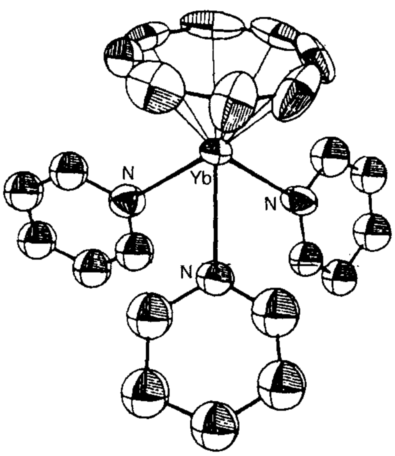


Fig. 26. Molecular structure of $[(C_8H_8)Yb(C_5H_5N)_3]$ **122o** in the crystal.

8.2. Lanthanide(III) Complexes

The first mono(cyclooctatetraene)lanthanide(III) halides were reported in 1971.[119, 123, 124] They are still among the most important starting materials for the preparation of other half-sandwich complexes of the lanthanides with cyclooctatetraene ligands. The complexes **125** are easily accessible by reaction of anhydrous lanthanide trichlorides with $K_2C_8H_8$ in a molar ratio of 1:1 [Eq. (47)].[125]

$$2\,LnCl_3 + 2\,K_2C_8H_8 \longrightarrow [\{(C_8H_8)Ln(\mu\text{-}Cl)(thf)_2\}_2] + 4\,KCl \qquad (47)$$

125

Purification of the crystalline, intensely colored products can be achieved by Soxhlet extraction with THF. A crystal structure determination of the cerium compound **125d** revealed the presence of centrosymmetric, Cl-bridged dimers with η^8-coordinated cyclooctatetraene ligands.[1, 2, 119, 123, 124] The coordinated THF cannot be removed from the compounds without extensive decomposition.

An interesting change in the molecular structure is observed when the sterically highly demanding 1,4-bis(trimethylsilyl)cyclooctatetraene ligand is used.[126, 127] 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(cyclooctatetraene)lanthanide(III) chlorides **126**, of which the holmium derivative **126l** was characterized by X-ray crystallography. The single-crystal X-ray structural analysis of the scandium complex **127a** revealed the presence of an

$[\{Ln[1{,}4\text{-}(Me_3Si)_2C_8H_6](\mu\text{-}Cl)(thf)\}_2]$ **126**, Ln = Y, Sm, Ho, Lu

$[(\mu\text{-}Cl)_2(\mu\text{-}thf)\{Sc[1{,}4\text{-}(Me_3Si)_2C_8H_6]\}_2]$ **127a**

unusual semibridging THF ligand (Fig. 27). Evidently, the reason for the coordination of only one THF molecule is the increased steric demand of the substituted cyclooctatetraene ligands.[126]

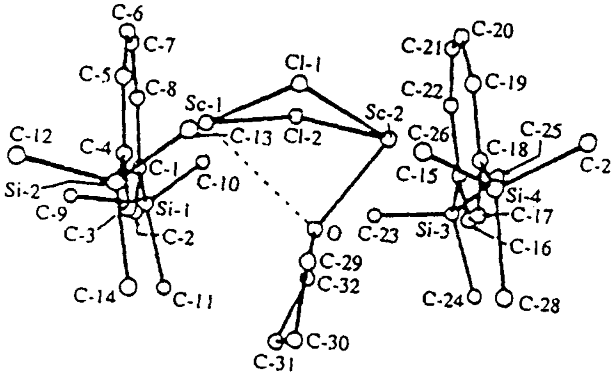


Fig. 27. Molecular structure of $[(\mu\text{-}Cl)_2(\mu\text{-}thf)\{Sc[1{,}4\text{-}(Me_3Si)_2C_8H_6]\}_2]$ **127a** in the crystal.

The complexes **125** are often used as starting materials for subsequent reactions because the bridging chloro ligands are easily replaced by other anions.[119] A certain disadvantage, however, is the very low solubility of these compounds even in THF. In the search for more soluble alternatives, preparative routes to mono(cyclooctatetraene)lanthanide(III) iodides and triflates have been developed. Mononuclear iodo complexes **128** are accessible in two ways [Eqs. (48) and (49)].[128–130] The

$$LnI_3 + K_2C_8H_8 \longrightarrow [(C_8H_8)LnI(thf)_n] + 2\,KI \qquad (48)$$

128, Ln = Nd, Sm

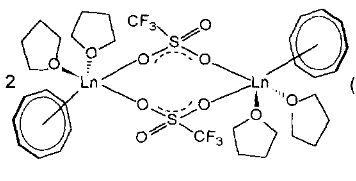
$$Ln + C_8H_8 + 1/2\,I_2 \xrightarrow{THF} [(C_8H_8)LnI(thf)_n] \qquad (49)$$

128
Ln = La, Ce, Pr, Nd, Sm,
$n = 1, 2, 3$

second procedure offers the advantage that the metal powders can be directly used as starting materials.[129, 130] Depending on the ionic radius of the lanthanide, the complexes are coordinated by a different number of THF molecules. The molecular structures of **128d** and **128f** have been determined by X-ray diffraction.

In contrast to the dimeric chloro complexes **125**, the iodides **128** are highly soluble in THF. The same is true for the recently described triflates. Schumann et al. and Fischer et al. had already shown that triflates are valuable alternatives to the previously used chloro complexes in the cyclopentadienyl chemistry of the lanthanides.[131, 132] Dimeric organolanthanide triflates **129** [Eq. (50)] are obtained in good yields in a smooth reaction between anhydrous lanthanide(III) triflates and equimolar

$$2\,K_2C_8H_8 + 2\,Ln(O_3SCF_3)_3 \xrightarrow[-4\,KO_3SCF_3]{THF} 2$$



(50)

129, Ln = Ce, Pr, Nd, Sm

amounts of $K_2C_8H_8$.[128, 133] The intensely colored products which crystallize well are also highly soluble in THF. With yttrium as central atom the bis(tetrahydrofuran) complex **130b** is isolated due to the smaller ionic radius of the metal.[133]

$[\{(C_8H_8)Y(\mu\text{-}O_3SCF_3)(thf)\}_2]$ **130b**

The molecular structures of **129d** (Fig. 28) and **129f** have been determined by X-ray diffraction. A central eight-membered $Ln_2O_4S_2$ ring is formed by bridging of the lanthanide ions by bidentate triflate ligands. Thus, the compounds **129** are structurally closely related to the bis(cyclopentadienyl)lanthanide(III) triflates $[\{(C_5H_5)_2Ln(\mu\text{-}O_3SCF_3)\}_2]$.[132] As expected, the cyclooctatetraene ligands are η^8-coordinated. Besides the improved solubility, the triflate complexes **129** and **130b** offer additional preparative advantages. First, the triflate anion is a good leaving group and thus facilitates substitution reactions with other ligands, second, LiO_3SCF_3 and NaO_3SCF_3 are more easily removed by filtration than finely divided LiCl or NaCl. Most of the subsequent reactions of the chloro complexes **125** described below have already been carried out with the corresponding triflates, and in many cases higher yields have been obtained.

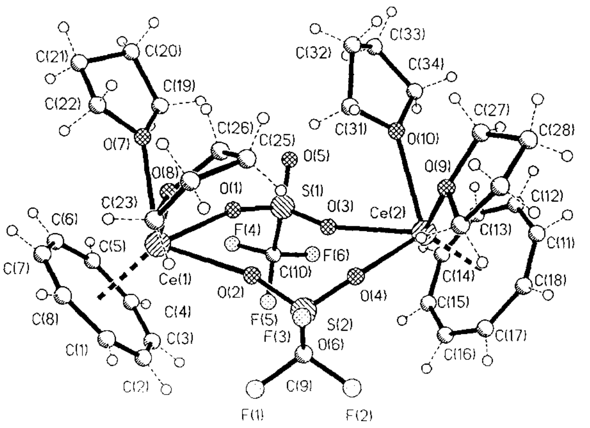


Fig. 28. Molecular structure of $[\{(C_8H_8)Ce(\mu\text{-}O_3SCF_3)(thf)_2\}_2]$ **129d** in the crystal.

In a series of recent papers an impressive number of mono(cyclooctatetraene)lanthanide(III) complexes has been reported. For example, the synthesis of some dinuclear complexes with bridging alkoxide ligands has been achieved according to Equation (51). The derivatives **131b** and **133k** have been structurally characterized.[134, 135] The compounds **134** and **135** were prepared with sterically more demanding alkoxide and siloxide ligands. These compounds are monomeric in the solid state,[134] as are the 1,4-bis(trimethylsilyl)cyclooctatetraene complexes $[Ln\{1,4\text{-}(Me_3Si)_2C_8H_6\}(2,6\text{-}tBu_2\text{-}4\text{-}MeOC_6H_2)(thf)]$ (Ln = Sc, Y).[127]

$$\underset{\textbf{125}}{[\{(C_8H_8)Ln(\mu\text{-}Cl)(thf)_2\}_2]} \xrightarrow[-2\,NaCl]{2\,NaOR} [\{(C_8H_8)Ln(\mu\text{-}OR)(thf)\}_2] \quad (51)$$

131, R = Ph; Ln = Y, Lu
132, R = 2,6-$Me_2C_6H_3$; Ln = Y, Lu
133k, R = $(CH_2)_3CH{=}CH_2$; Ln = Dy

$[(C_8H_8)Ln(OCtBu_3)(thf)]$ **134**, Ln = Y, Lu
$[(C_8H_8)Ln(OSiPh_3)(thf)]$ **135**, Ln = Y, Lu

The heterodinuclear alkoxide **136d** is formed in the reaction of $Ce(OiPr)_4$ with triethylaluminum in the presence of cyclooctatetraene [Eq. (52)].[11] During the course of this reaction Ce^{IV} is reduced to Ce^{III}. In the product, isopropoxide ligands act as bridges between cerium and aluminum.

$$Ce(OiPr)_4 \xrightarrow{AlEt_3,\ C_8H_8} \underset{\textbf{136d}}{[(C_8H_8)Ce(\mu\text{-}OiPr)_2AlEt_2]} \quad (52)$$

The synthesis of mono(cyclooctatetraene)lanthanide(III) thiolates and selenolates has been reported very recently.[130] Their preparation was achieved by using a procedure similar to that in Equation (49); diaryldisulfides or diaryldiselenides were used as oxidizing agents instead of iodine [Eq. (53)]. Catalytic amounts of iodine accelerate the reactions by activating the metal surface. The X-ray structure analysis of $[\{(C_8H_8)Sm(\mu\text{-}SePh)(thf)_2\}_2]$ **138g** (EAr = SePh) revealed the presence of a dimer with phenylselenolate bridges (Fig. 29).

$$2\,Sm + C_8H_8 + ArEEAr \xrightarrow{THF} [\{(C_8H_8)Sm(\mu\text{-}EAr)(thf)_n\}_2] \quad (53)$$

137g, $n = 1$, EAr = 2,4,6-$iPr_3C_6H_2S$
138g, $n = 2$, EAr = SPh,
2,4,6-$Me_3C_6H_2S$, SePh

Nitrogen donor ligands are also increasingly used in connection with lanthanide cyclooctatetraene complexes. For example, interesting results were obtained with the sterically demanding

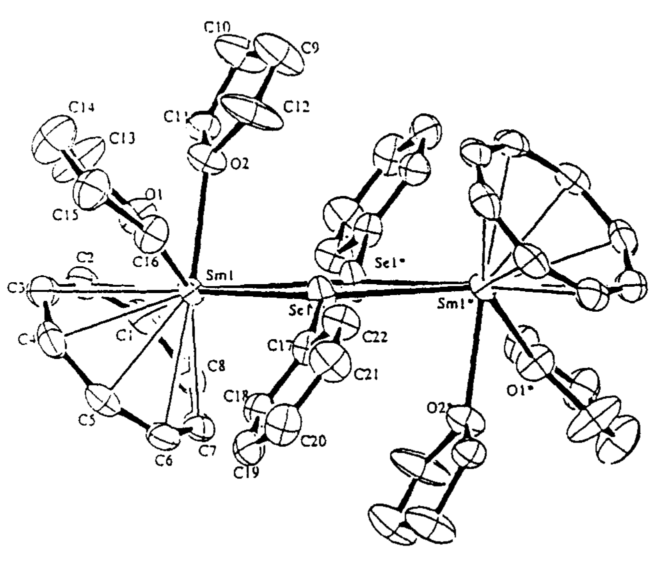


Fig. 29. Molecular structure of $[\{(C_8H_8)Sm(\mu\text{-}SePh)(thf)_2\}_2]$ **138g** (EAr = SePh) in the crystal.

bis(trimethylsilyl)amido ligand. The monomeric amido complexes **139** were isolated for yttrium and the "late" lanthanides [Eq. (54)].[136]

$$\underset{\mathbf{125}}{[\{(C_8H_8)Ln(\mu\text{-}Cl)(thf)_2\}_2]} + 2\,NaN(SiMe_3)_2 \xrightarrow[-2\,NaCl]{} \underset{\mathbf{139},\ Ln\,=\,Y,\ Gd,\ Er,\ Lu}{2[(C_8H_8)Ln\{N(SiMe_3)_2\}(thf)]} \quad (54)$$

When the same reaction is carried out with the samarium derivative **125g** [Eq. (55)], an unusual "inverse sandwich complex" is formed, in which two $Sm[N(SiMe_3)_2]_2$ units are symmetrically bridged by a cyclooctatetraene ligand (Fig. 30).[136]

$$\underset{\mathbf{125g}}{3[\{(C_8H_8)Sm(\mu\text{-}Cl)(thf)_2\}_2]} + 8\,NaN(SiMe_3)_2 \xrightarrow[-6\,NaCl]{toluene} \quad (55)$$
$$\underset{\mathbf{140g}}{[(\mu\text{-}C_8H_8)\{Sm[N(SiMe_3)_2]_2\}_2]} + 2[Na(thf)_n][Sm(C_8H_8)_2]$$

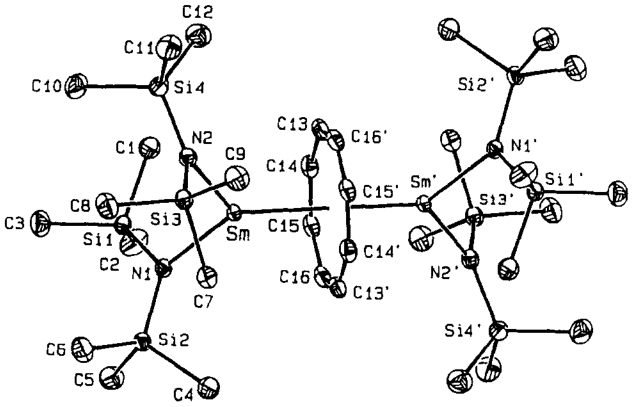
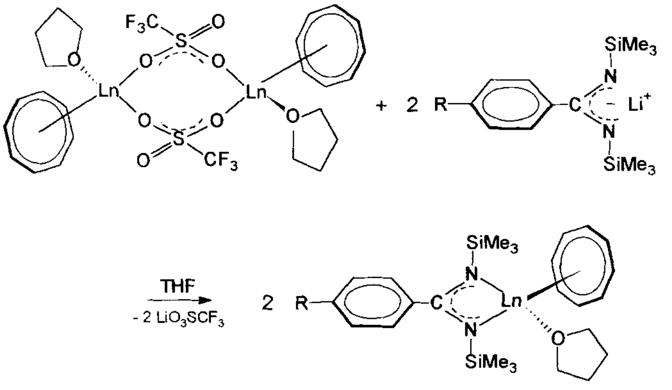


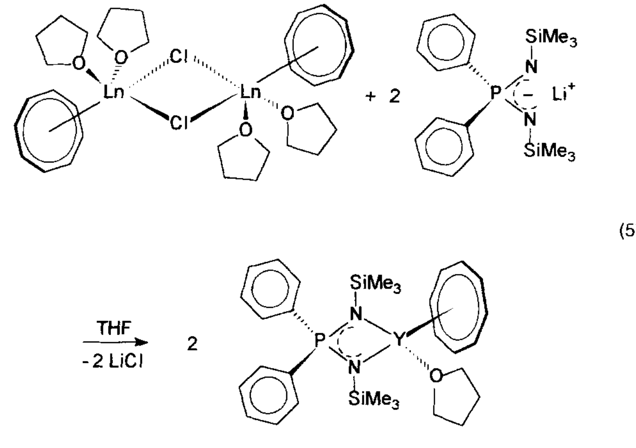
Fig. 30. Molecular structure of $[(\mu\text{-}C_8H_8)\{Sm[N(SiMe_3)_2]_2\}_2]$ **140g** in the crystal.

Mono(cyclooctatetraene)lanthanide(III) complexes containing polydentate nitrogen ligands are also currently being investigated. These include silylated benzamidinate and diiminophosphinate anions as well as tridentate pyrazolylborate ligands.[133, 137-140] Typical preparations are outlined in the Equations (56)-(58).



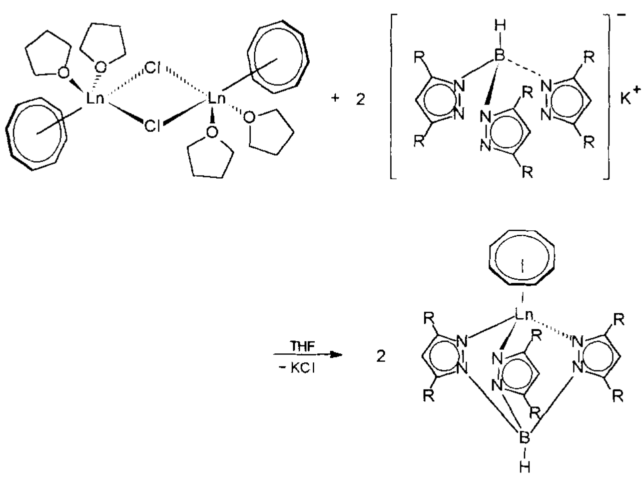
(56)

141, R = H; **142**, R = MeO; **143**, R = CF3
Lw = Y, Ce, Pr, Nd, Sm, Tm, Lu



(57)

144, Ln = Ce, Pr, Nd, Sm



(58)

145, R = H; **146**, R = Me,
Ln = Ce, Pr, Nd, Sm

The first pyrazolylborate complexes of the type **145** had already been synthesized some years ago by Takats et al.[138] Depending on the ionic radius of the lanthanide element, these compounds can either be unsolvated or may contain a coordinated THF molecule. The complexes **145** and **146** are formed as highly crystalline, intensely colored substances and several representatives have already been characterized by crystal structure analyses.[140] Figure 31 shows the molecular structure of the THF adduct of the cerium compound **146d**.

The first σ-alkyl complexes with η^8-cyclooctatetraene ligands were isolated starting from the lutetium compound **125p** [Eq. (59)].[141, 142] The formation of mononuclear complexes is facilitated by the small ionic radius of lutetium as well as the high steric demand of the organic ligands.

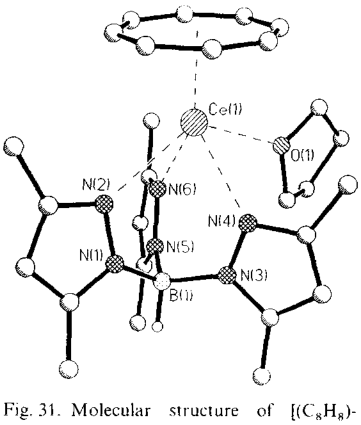


Fig. 31. Molecular structure of $[(C_8H_8)Ce\{HB(3,5\text{-}Me_2pz)_3\}(thf)]$ **146d** in the crystal.

$$\underset{\textbf{125p}}{[\{(C_8H_8)Lu(\mu\text{-}Cl)(thf)_2\}_2]} + 2\,LiR \xrightarrow[-2\,LiCl \atop -2\,THF]{} 2[(C_8H_8)LuR(thf)] \tag{59}$$

$\textbf{147p}$, R = CH_2SiMe_3

$\textbf{148p}$, R = $o\text{-}Me_2NCH_2C_6H_4$

Similar alkylations of **125** (Ln = Y, Sm, Lu) with $LiCH(SiMe_3)_2$ did not lead to the expected neutral σ-alkyl complexes.[143] Instead, the "inverse sandwich complexes" **149** were

$[Li(thf)_2\{\mu\text{-}\eta^2,\eta^8\text{-}C_8H_8\}Ln\{CH(SiMe_3)_2\}]$ **149**

formed. Figure 32 shows the unusual zwitterionic structure of the samarium compound **149g** with a bridging cyclooctatetraene ligand which is η^2-coordinated to a $Li(thf)_2$ unit. The question of whether σ-alkyl complexes containing η^8-cyclooctatetraene ligands such as **147**, **148**, and **149** exhibit catalytic activities still remains to be answered.

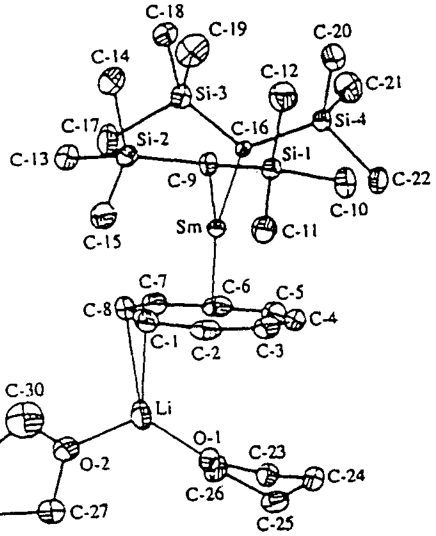


Fig. 32. Molecular structure of $[Li(thf)_2\{\mu\text{-}\eta^2,\eta^8\text{-}C_8H_8\}Sm\{CH(SiMe_3)_2\}]$ **149g** in the crystal.

The formation of neutral σ-alkyl complexes should be facilitated by the increased steric demand of the cyclooctatetraene ligand. This was recently verified by Cloke et al. with the 1,4-bis(trimethylsilyl)cyclooctatetraene complexes. Alkylation of the dimeric chloro complexes **126** with $LiCH(SiMe_3)_2$ afforded the monomeric σ-alkyl derivatives **150**.[127]

$[Ln\{1,4\text{-}(Me_3Si)_2C_8H_6\}\{CH(SiMe_3)_2\}(thf)]$ **150**, Ln = Sc,Y

Symmetrical sandwich complexes containing $[Ln(C_8H_8)_2]^-$ ions have been described previously for a series of lanthanides.[119, 123, 124] Potassium salts of these anions are easily accessible by treatment of anhydrous lanthanide trichlorides with two equivalents of $K_2C_8H_8$ [Eq. (60)]. The products are readily soluble in THF and can be isolated by extraction with this solvent. The potassium salts **151** are thermally very robust, but decompose almost explosively upon contact with traces of oxygen.

$$LnCl_3 + 2\,K_2C_8H_8 \xrightarrow[-3\,KCl]{} K[Ln(C_8H_8)_2] \tag{60}$$

151, Ln = Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb

All structurally characterized compounds of this series contain coordinated solvent molecules. The structural chemistry of the cerium(III) anion $[Ce(C_8H_8)_2]^-$ has been investigated in detail. The crystallographically characterized lithium salt of this anion (**152d**) was obtained in the form of needlelike, bright green crystals as a by-product in the reaction of **125d** with $LiCH(SiMe_3)_2$.[144] The crystal structure reveals the presence of separated ions; the Li^+ ion is coordinated by four THF molecules (Fig. 33).

$[Li(thf)_4][Ce(C_8H_8)_2]$	$[Na(thf)_3][Ce(C_8H_8)_2]$	$[K(diglyme)][Ce(C_8H_8)_2]$
152d	**153d**	**154d**

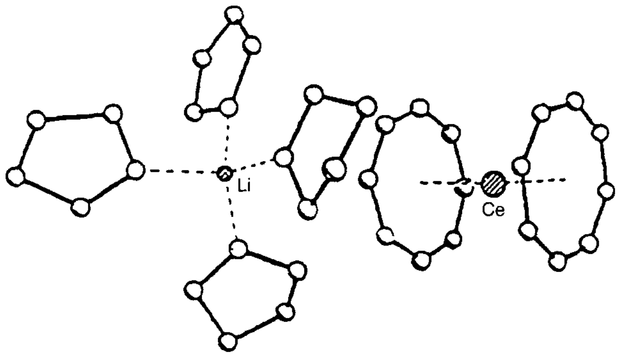


Fig. 33. Molecular structure of $[Li(thf)_4][Ce(C_8H_8)_2]$ **152d** in the crystal.

The sodium salt forms a sort of "double sandwich" **153d** (Fig. 34).[144] Two cyclooctatetraene ligands and the two metal ions are arranged as a linear unit. In this case three THF ligands are sufficient for the coordinative saturation of the sodium. A very similar structure was reported for the potassium salt **154d**.[145]

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 **155m** (Fig. 35).[146] However, compounds of this type are not accessible by rational syntheses. The compound **155m** was isolated serendipitously from a reaction of $[(C_5H_4CH_2Ph)ErCl_2(thf)_3]$ with $K_2C_8H_8$.

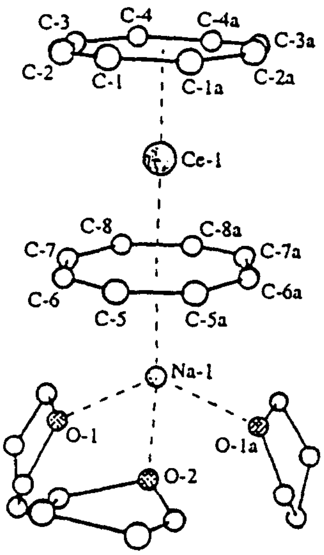


Fig. 34. Molecular structure of $[Na(thf)_3][Ce(C_8H_8)_2]$ **153d** in the crystal.

$[(C_8H_8)Er(\mu\text{-}C_8H_8)K(\mu\text{-}C_8H_8)Er(\mu\text{-}C_8H_8)K(thf)_4]$ **155m**

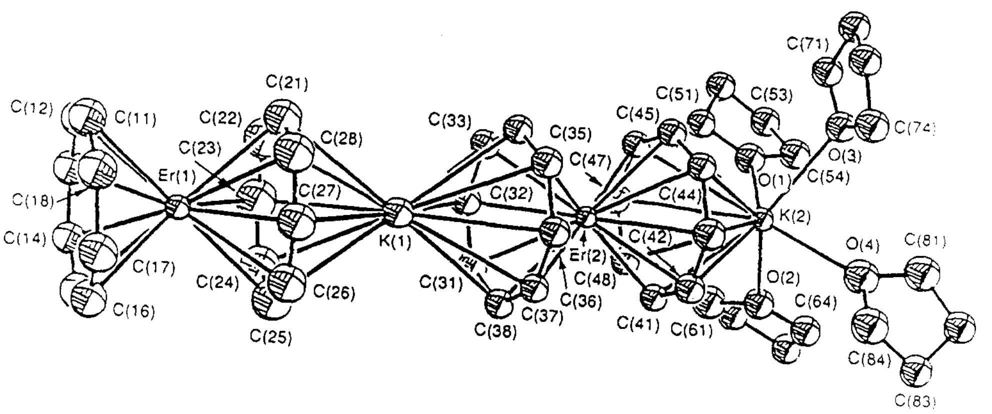


Fig. 35. Molecular structure of $[(C_8H_8)Er(\mu\text{-}C_8H_8)K(\mu\text{-}C_8H_8)Er(\mu\text{-}C_8H_8)K(thf)_4]$ **155m** in the crystal.

8.3. Lanthanide(IV) Complexes

Cerium is the only lanthanide that has been shown to form stable organometallic complexes in the formal oxdation state + IV; however, even well-defined organocerium(IV) compounds are very rare.[119, 123, 124] Many organic ligands are simply oxidized in the presence of Ce^{IV} ions. The longest known compound of this type is the so-called cerocene **156d**.[145–147]

$[Ce(C_8H_8)_2]$ **156d** $[Ce(MeC_8H_7)_2]$ **157d**

Cerocene was first made by the reaction of $Ce(O\textit{i}Pr)_4$ with cyclooctatetraene in the presence of triethylaluminum and isolated as a black-red, pyrophoric product.[1, 119] An improved synthetic route to cerocene involves controlled oxidation of the anionic sandwich complex with silver iodide or allyl iodide.[150] A thorough investigation of this interesting complex was complicated by its difficult accessibility as well as by its low solubility and pyrophoric nature. Except for the reduction by alkali metals, which leads to known derivatives of the cerium(III) anion $[Ce(C_8H_8)_2]^-$, 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. For instance, with the 1,1'-dimethyl compound **157d** Streitwieser et al. succeeded in the first structural characterization of a cerocene derivative; the result clearly established the proposed sandwich structure.[145] 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.[151] Schemes 7 and 8 illustrate the syntheses of the silyl-substituted cerocene derivatives **159d** and **161d**. In both cases silver iodide has proven successful as the mild oxidizing agent. The compound **159d** is isolated as a dark purple oil, while **161d** forms permanganate-colored crystals. The two cerocenes are highly soluble in nonpolar organic solvents due to the presence of the trimethylsilyl substituents.

$$\mathrm{CeCl_3 + 2[Li(thf)_n]_2[1,4\text{-}(Me_3Si)_2C_8H_6]} \xrightarrow[-3\,\mathrm{LiCl}]{\mathrm{THF}}$$

$$\underset{\mathbf{158d}}{\mathrm{Li[Ce\{1,4\text{-}(Me_3Si)_2C_8H_6\}_2]}} \xrightarrow[-\mathrm{Ag},\ -\mathrm{LiI}]{+\mathrm{AgI}} \underset{\mathbf{159d}}{\mathrm{[Ce\{1,4\text{-}(Me_3Si)_2C_8H_6\}_2]}}$$

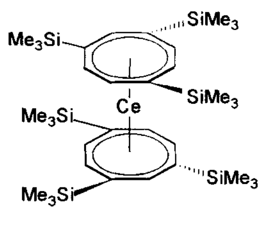
Scheme 7. Synthesis of $[Ce\{1,4\text{-}(Me_3Si)_2C_8H_6\}_2]$ **159d**.

$$\mathrm{Ce(O_3SCF_3)_3 + 2[K(thf)_n]_2[1,3,6\text{-}(Me_3Si)_3C_8H_5]}$$

$$\xrightarrow[-3\,\mathrm{KO_3SCF_3}]{\mathrm{THF}} \underset{\mathbf{160d}}{\mathrm{K[Ce\{1,3,6\text{-}(Me_3Si)_3C_8H_5\}_2]}}$$

$$\xrightarrow[-\mathrm{Ag},\ -\mathrm{KI}]{+\mathrm{AgI}} \underset{\mathbf{161d}}{\mathrm{[Ce\{1,3,6\text{-}(Me_3Si)_3C_8H_5\}_2]}}$$

Scheme 8. Synthesis of $[Ce\{1,3,6\text{-}(Me_3Si)_3C_8H_5\}_2]$ **161d**.



161d

The crystalline hexakis(trimethylsilyl)cerocene **161d** was characterized by a crystal structure analysis (Fig. 36);[151] the angle between cerium and the ring centroids is 176.1°. The compounds **159d** and **161d** are the first cerocene derivatives that are reproducibly accessible in synthetically useful amounts; thus, they allow the study of what is expected to be interesting derivative chemistry.[152]

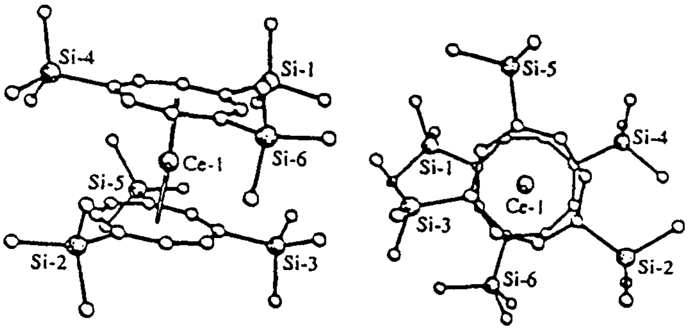


Fig. 36. Molecular structure of $[Ce\{1,3,6\text{-}(Me_3Si)_3C_8H_5\}_2]$ **161d** in the crystal.

9. Organolanthanides in Homogeneous Catalysis

Applications of organolanthanide complexes in homogeneous catalysis have been initiated by the observation that some of these complexes exhibit high catalytic activities in olefin polymerizations.[5, 74, 153] In the preliminary experiments in that direction the catalytically active species were generated by activating lanthanide oxides, halides, or alkoxides with co-catalysts such as alkyllithium or alkylaluminum compounds. The intermediately formed σ-alkyl complexes were capable of catalyzing the cracking of hydrocarbons as well as oligomerizations and polymerizations of olefins. Since then well-defined organolanthanide complexes have become available, and many other cases of interesting catalytic activities have been discovered. It was found, for example, that (cyclooctatetraene)cerium complexes catalyze the polymerization of ethylene and butadiene.[153] Anionic tetrakis(η^3-allyl)lanthanide complexes are also highly active catalysts for the production of polybutadiene. In the meantime, however, it has become quite clear that catalytic activity is almost generally limited to cyclopentadienyl complexes of the lanthanides. Metallocene derivatives of trivalent lanthanides such as $[(C_5Me_5)_2LnCH(SiMe_3)_2]$ or $[\{(C_5Me_5)_2Ln(\mu\text{-}H)\}_2]$, in particular, have been found to display very high activities.[5] In contrast, the number of catalytically useful organolanthanide complexes without cyclopentadienyl ligands is still very limited.

The majority of the hitherto investigated reactions that are catalyzed by organolanthanide complexes are olefin transformations such as hydrogenations, polymerizations, or addition reactions. For example, a catalyst for the hydrogenation of ethylene was prepared from a samarium/magnesium alloy.[1] $SmMg_3$ reacts with anthracene in THF to afford a complex of unknown structure. This product absorbs hydrogen and is then able to catalyze the hydrogenation of ethylene.

The main field of application for organolanthanide catalysts without cyclopentadienyl ligands is diene polymerization. In earlier reports on the polymerization of butadiene, catalyst systems such as "$Ph_3Nd_2/Al_2Et_2Cl_3$",[154] neodymium-2-ethylhexanoate/$AlEt_2Cl/AlEt_3$,[155] or $LnCl_3$/*n*BuLi[156] were used. However, very little is known about the nature of the intermediately formed σ-alkyllanthanide species. Only in one case, that is the catalyst system $Nd(O\textit{i}Pr)_3/AlEt_3/AlEt_2Cl$, could a defined intermediate be "fished out" and structurally characterized.[64, 157] It was shown to be the heteronuclear alkyllanthanide(III) alkoxide **55f** (see Section 3.3). Promising results have been obtained in recent years with anionic allyl complexes of the type $[Ln(\eta^3\text{-}C_3H_5)_4]^-$.[95] Lithium salts of these anions catalyze the polymerization of butadiene and alkylbutadienes with moderate to high activity and high *trans* selectivity. Highly active catalysts for the production of *cis*-1,4-polybutadiene have been obtained by combining tris(2,4-dimethylpentadienyl)-neodymium **99f** with 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 constitution of an active pre-catalyst, since the hexanuclear complex **162f** could be isolated and characterized by X-ray diffraction.[158] Figure 37 shows the molecular structure of this unusual cluster, in which two hexagonal-bipyramidal Nd_3Cl_5 units are linked through two chloro bridges. All 2,4-dimethylpentadienyl ligands are η^5-coordinated to neodymium.

$[Nd_6Cl_{12}(C_7H_{11})_6(thf)_2]$ **162f** (C_7H_{11} = 2,4-dimethylpentadienyl)

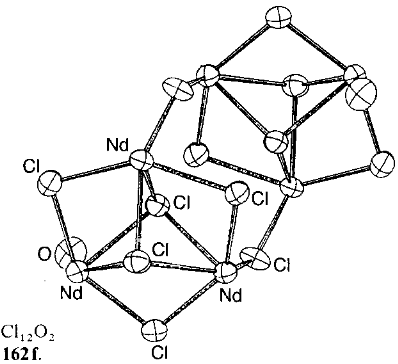


Fig. 37. Structure of the $Nd_6Cl_{12}O_2$ unit in $[Nd_6Cl_{12}(C_7H_{11})_6(thf)_2]$ **162f**.

10. Future Outlook

In the past 10–15 years organolanthanide chemistry has been developed into a highly dynamic area of research that continues to produce fascinating novel results. Until recently most of the research was focused mainly on the discovery of new types of structures and reaction pathways. Indeed, organolanthanide chemistry is characterized by a great diversity of novel and unusual molecular structures, and the extraordinarily high reactivity of certain organolanthanide complexes is without precedent in the chemistry of the d-block transition metals. Today an increased interest in possible applications of organolanthanides is apparent. For example, an enormous potential lies in the use of organolanthanide complexes in homogeneous catalysis. Lanthanide catalysts combine several favorable aspects such as very high activities, excellent environmental compatibility, and low costs. Possible applications in the area of materials science are also apparent and it should be worthwhile to consider future work in that direction. A conceivable application, for example, is the use of organolanthanide complexes in the doping of semiconductor materials, which has already been successful in the case of cyclopentadienyl lanthanide complexes.[5] There is a good chance that volatile organocerium compounds will turn out to be useful precursors for the vapor deposition of cerium dioxide. In addition, many interesting questions of a more academic nature still warrant further investigation: To what degree do f-orbitals participate in the bonding in (cyclooctatetraene)lanthanide complexes? Is it possible to construct multidecker sandwich complexes with cyclooctatetraene ligands? Will it ever be possible to synthesize organometallic complexes containing a direct Ln–Ln bond or to realize unusual oxidation states (e.g. Nd^{II}, Pr^{IV}, Tb^{IV}, Tm^{II}) in organolanthanide complexes? What are the structures of "Grignard-like" complexes RLnX with simple alkyl substituents? In any case, research in the area of "lanthanide chemistry without cyclopentadienyl" will continue to be exciting.

Our own investigations which have been carried out in Göttingen would not have been possible without the enthusiasm of my highly talented co-workers, whose names appear in the list of references. To them I owe my sincere gratitude. Special thanks are also due to Prof. Dr. H. W. Roesky for his continuing generous support. I have learned a lot from him. I also thank Prof. Dr. Josef Takats (University of Alberta, Edmonton, Canada) for initiating my interest in organo-f-element chemistry. Many stimulating discus-

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