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Homoleptic Rare-Earth Metal Complexes Containing Ln−C σ-Bonds†

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1. Introduction

1.1. General Introduction—Need of This Review

The past decade has witnessed an enormous growth in the chemistry of σ-bonded rare-earth metal (Ln) alkyls, particularly due to their relevance for Ziegler-type anionic polymerization catalysis and related catalytic transformations such as olefin hydrogenation, hydrosilylation, and alkyne dimerization. A highly desirable feature of these application-driven research efforts was the new fundamental organorare-earth metal chemistry, which has been developing in parallel. It is only the availability and utilization of pure ("well-characterized") σ-bonded rare-earth metal alkyl complexes of the type $Ln^{II}R_2$ and $Ln^{III}R_3$ that ensures advanced precatalyst synthesis and design and, hence, a meaningful interpretation of fundamental structure−reactivity relationships. Because the reactivity and catalytic activity of organolanthanide complexes are highly dependent on the size of the rare-earth metal center, it was of utmost importance to gain access to structurally characterized derivatives, with $Ln^{III}R_3$-trivalent derivatives being the most relevant for catalytic transformations, spanning the entire size range (Sc^{III} → La^{III}). This, however, turned out to be a major challenge because the thermodynamic and/or kinetic stability of such homoleptic complexes crucially depends on the size of the rare-earth metal cation and the synthesis protocol applied. While the catalytic performance of σ-bonded rare-earth metal (Ln) alkyls has been an integral part and the main focus of several recent surveys on organolanthanide chemistry (see Table 1),[1−25] more fundamental aspects of the lanthanide−carbon σ-bond were described lately in a 1997 review by S. A. Cotton.[1] Albeit giving some consideration to important catalytic applications, the main emphasis of our presentation is clearly on the synthesis, structure, and properties of homoleptic alkyl complexes and their utilization as synthesis precursors.

1.2. Scope of This Review

To restrict the range of this review, several assumptions, limitations, and definitions were carried out. The term "rare-earth metal" will be used for the group 3 elements scandium, yttrium, and the 14 lanthanides (lanthanum−lutetium) excluding promethium. The elements will be abbreviated by Ln. The only work which will be surveyed is that related to the chemistry of homoleptic rare-earth metal complexes with a single type of monovalent (hydro)carbyl ligand, that is, forming Ln−C σ-bonds (Chart 1 shows examples of (hydro)carbyl complexes, which are beyond the scope of this review).[26−41] Compounds containing donor solvent molecules (solv) as the only additional ligands are also referred to as homoleptic (e.g., $Ln(CH_2SiMe_3)_3(thf)_x$). Only isolated and characterized derivatives will be included. In this regard, the discussion of in situ generated compounds is omitted; however, some examples are included in sections 8 and 14 paying tribute to their value as rare-earth metal alkyl synthesis precursors.

Main emphasis will be put on synthesis approaches toward homoleptic rare-earth metal (hydro)carbyl complexes, whereas consideration is given to difficulties/imponderabilities of the respective synthesis strategies. The (thermal) stability as well as properties in solution and in the solid state will be presented. Moreover, the derivatization of the homoleptic (hydro)carbyl complexes with (ancillary) proligands will be surveyed and important catalytic applications will be emphasized. Only heteroleptic complexes of the type [**L**]Ln[(hydro)carbyl]$_x$(solv)$_y$ (**L** = ancillary ligand) directly derived from homoleptic rare-earth metal (hydro)carbyl precursors are included (for clarification, see Scheme 1). The present review is based on peer-reviewed papers written in English or German; patents are, however, not considered. Relevant literature is covered up until the end of 2008.

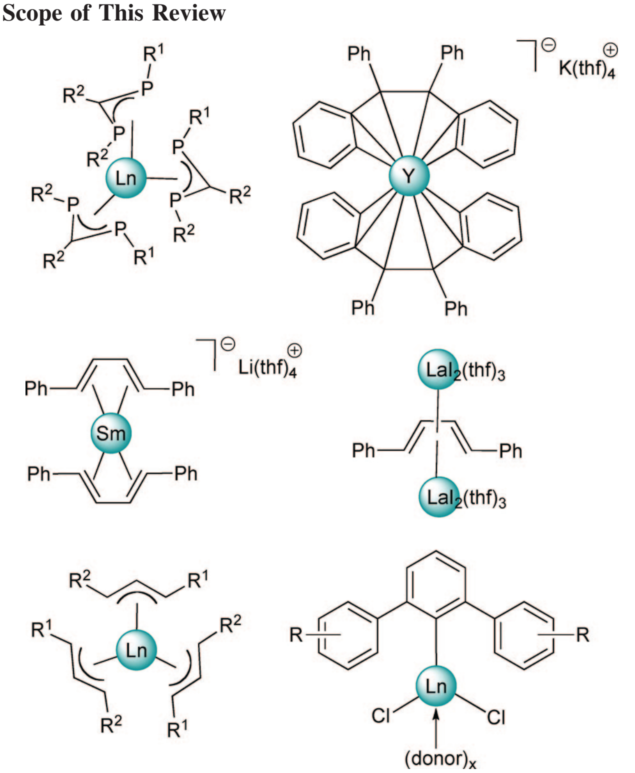
Melanie Zimmermann, born in 1977, studied chemistry at the Technische Universität München, Germany, where she received her diploma in 2003. She earned her Ph.D. in organometallic chemistry under the guidance of Reiner Anwander as a joint degree from the Technische Universität München, Germany, and the University of Bergen, Norway. In 2005, she spent four months as a fellow of the Bayerische Forschungsstiftung at Stanford University, Stanford, California, U.S.A., in the group of Robert M. Waymouth. Her Ph.D. thesis dealt with rare-earth metal alkyls, which is also part of this review. She spent her postdoctoral work as a fellow of the Norwegian Research Foundation in the group of Reiner Anwander at the University of Bergen, Norway, and the Eberhard-Karls-University in Tübingen, Germany. In 2009, she moved to John E. Bercaw's group at the California Institute of Technology, Pasadena, California, U.S.A. Among several fellowships, she received the Birkeland Award in Physics and Chemistry in 2009.

Reiner Anwander was born in 1961 in Schwabmünchen (Bavaria, Germany). He studied chemistry at the Technische Universität München TUM, where he also obtained his Diploma in 1989 and Dr. rer. nat. degree in 1992, both under the supervision of Wolfgang A. Herrmann. This was followed by postdoctoral research on organolanthanide chemistry with Bill Evans at the University of California, Irvine, California, U.S.A. Then he spent three years at the Universität Stuttgart starting his "habilitation" on "surface organometallic chemistry on nanoporous materials", which he completed in 2000 at TUM. From 2005 until 2008, he held the position "Heterogeneous Catalysis" at the University of Bergen, Norway. He joined the faculty of the Eberhardt-Karls University Tübingen, Germany, in 2009. His research interests include organometallic chemistry, nanostructured materials, and catalysis.

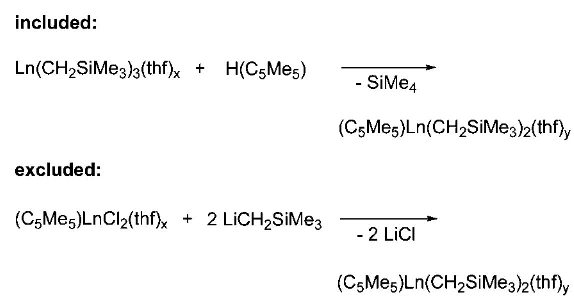
Table 1. Review Articles Covering Predominantly Ln−C Based Organorare-Earth Metal Chemistry

authors	title	year	ref
Cotton, F. A.	Alkyls and Aryls of Transition Metals	1955	2
Davidson, P. J.; Lappert, M. F.; Pearce R.	Stable Homoleptic Metal Alkyls	1974	3
Davidson, P. J.; Lappert, M. F.; Pearce R.	Metal σ-Hydrocarbyls, MR_n. Stoichiometry, Structures, Stabilities, and Thermal Decomposition Pathways	1976	4
Tsutsui, M.; Ely, N.; Dubois, R.	σ-Bonded Organic Derivatives of f Elements	1976	5
Lappert, M. F.	Unusual Metal Alkyls	1978	6
Schumann, H.	Organolanthanoid Compounds	1984	7
Schumann, H.	Organometallic Compounds of the Rare Earths	1985	8
Bochkarev, M. N.; Kalinina, G. S.; Bochkarev, L. N.	Advances in the Chemistry of Organolanthanides	1985	9
Evans, W. J.	The organometallic chemistry of the lanthanide elements in low oxidation states	1987	10
Koschmieder, S. U.; Wilkinson, G.	Homoleptic and Related Aryls of Transition Metals	1991	11
Steinborn, D.	On the Influence of Heteroatoms in α- and β-Functionalized Alkyl Transition-Metal Compounds	1992	12
Schaverien, C. J.	Organometallic Chemistry of the Lanthanides	1994	13
Edelmann, F. T.	Cyclopentadienyl-free Organolanthanide Chemistry	1995	14
Edelmann, F. T.	Comprehensive Organometallic Chemistry II	1995	15
Eaborn, C.; Izod, K.; Smith, J. D.	Synthesis, structure and reactions of organometallic compounds of Groups 1−3 containing bulky silicon-substituted alkyl groups	1995	16
Zakharov, L. N.; Struchkov, Y. T.	X-ray study of organic and organoelement compounds of the lanthanides	1997	17
Cotton, S. A.	Aspects of the lanthanide−carbon σ-bond	1997	1
Edelmann, F. T.; Freckmann, D. M. M.; Schumann, H.	Synthesis and Structural Chemistry of Non-Cyclopentadienyl Organolanthanide Complexes	2002	18
Deacon, G. B.; Forsyth, C. M.; Nickel, S.	Bis(pentafluorophenyl)mercury−A versatile synthon in organo-, organooxo-, and organoamido-lanthanoid chemistry	2002	19
Piers, W. E.; Emslie, D. J. H.	Noncyclopentadienyl ancillaries in organogroup 3 metal chemistry: A fine balance in ligand design	2002	20
Arndt, S.; Okuda, J.	Mono(cyclopentadienyl) Complexes of the Rare-Earth Metals	2002	21
Hou, Z.; Wakatsuki, Y.	Science of Synthesis	2002	22
Hou, Z.	Recent Progress in the Chemistry of Rare Earth Metal Alkyl and Hydrido Complexes Bearing Mono(cyclopentadienyl) Ligands	2003	23
Mountford, P.; Ward, B. D.	Recent developments in the noncyclopentadienyl organometallic and related chemistry of scandium	2003	24
Zeimentz, P. M.; Arndt, S.; Elvidge, B. R.; Okuda, J.	Cationic Organometallic Complexes of Scandium, Yttrium, and the Lanthanoids	2006	25

Chart 1. Examples of (Hydro)carbyl Complexes beyond the Scope of This Review



Scheme 1. Heteroleptic Complexes Included and Excluded in This Review



1.3. Nomenclature

The review will be organized according to the type of monovalent (hydro)carbyl ligand and the oxidation state of the rare-earth metal center. Compounds will be labeled following the system shown in Figure 1. Ligand variations and cations are indicated by superscripts after the complex type designation; rare-earth metal centers and retained donor solvent molecules are specified by a subscript.

Homoleptic rare-earth metal (hydrocarbyl) complexes will be named **A**−**AH** (Table 2). Heteroleptic derivatives derived thereof will be numbered with Arabic numerals **1**−**263** (Figure 2).

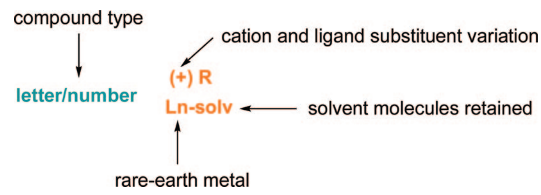


Figure 1. Compound labeling scheme for this review.

1.4. History of Homoleptic Rare-Earth Metal (Hydro)Carbyl Complexes

The way in which a metal atom and a carbon moiety establish a chemical bond between themselves is the contrary of a Romeo and Juliet story! The two elements can get together, but actually they do not want to.[42] This rather romantic description by Schlosser of the supposedly inherent thermodynamic instability and/or kinetic lability of metal alkyl complexes reflects not only the long search for stable derivatives of the *d*-transition and rare-earth metals.[43] In fact, the statement nicely scenarizes the main motivation why chemists have not been desperate in pursuing research in this field: lack of thermodynamic/kinetic stability means a high reactivity and hence catalytic potential!

After Frankland's epoch-making discovery of the spontaneously inflammable $ZnEt_2$ in 1849,[44] it was not until 60 years later when Pope and his co-worker Peachy isolated heteroleptic Me_3PtCl as the first stable solid metal complex bearing single bonds to saturated carbon.[45,46] Another 40 years later, the solid-state structures of $[Me_3PtX]_4$ (X = Me, I) were determined by X-ray diffraction analyses.[47] Until the 1960s, homoleptic metal σ-hydrocarbyls were described for most of the main group elements, albeit only in the higher oxidation states for elements such as Hg, Tl, Sn, or Pb.[48] Unsuccessful attempts to prepare other simple transition metal alkyl derivatives were still attributed to the low stability of such compounds[2,49] The following decade was marked by significant progress in the transition metal chemistry of σ-hydrocarbyl ligands, and the long established view that the transition metal-to-carbon bond is weak became untenable and had to be discarded.[50,51] However, homoleptic transition metal compounds were unusual and the known compounds were highly unstable ($TiMe_4$, $ZrMe_4$).[52−54] A breakthrough in organo-transition metal alkyl chemistry was independently

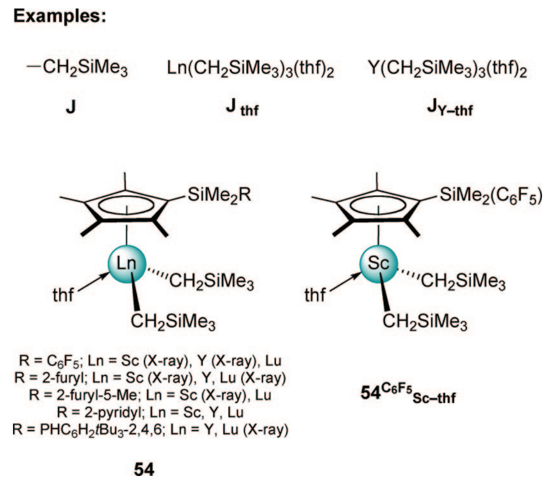


Figure 2. Examples of the compound labeling in this review.

Table 2. Compound Labeling According to the Type of Monovalent (Hydro)Carbyl Ligand

label	monovalent hydrocarbyl ligand	Ln oxidation state
A	Me (anionic complexes)	III
B	Me	III
C	AlR_4 (R = Me, Et)	II
D	AlR_4 (R = Me, Et)	III
E	$GaMe_4$	III
F	$(CH_2)_3NMe_2$	III
G	*t*Bu	III
H	CH_2tBu$_3$	III
J	CH_2SiMe_3	III
K	CH_2SiMe_3 (anionic complexes)	III
L	CH_2SiMe_2Ph	III
M	$CH(SiMe_3)_2$	II
N	$CH(SiMe_3)_2$ (anionic complexes)	II
O	$CH(SiMe_3)_2$	III
P	$CH(SiMe_3)(SiMe_2OMe)$	III
Q	$C(SiMe_3)_3$	II
R	$C(SiMe_3)_2(SiMe_2R)$ (R = OMe, $CHCH_2$, $(CH_2)_2OEt$)	II
S	$(Me_3Si)_2CSiMe_2(CH_2)_2SiMe_2C(SiMe_3)_2$	II
T	$(Me_3Si)_2CSiMe_2OSiMe_2C(SiMe_3)_2$	II
U	$(Me_3Si)(SiMe_2OMe)CSiMe_2(CH_2)_2SiMe_2C(SiMe_3)(SiMe_2OMe)$	II
V	CH_2Ph^R (R = H, Me-4, Me_2-3,5, *t*Bu-4)	III
W	$CH(SiMe_3)C_6H_4$-*o*-NMe_2	II
X	$CH_2C_6H_4$-*o*-NMe_2	III
Y	$CH_2C_6H_4$-*o*-$SiMe_3$ (anionic complexes)	III
Z	Ph^R (Ph^R = C_6H_5, C_6F_5, C_6F_4-*p*-H, $C_6H_3Ph_2$-2,6)	II
AA	Ph^R (Ph^R = C_6H_5, C_6F_5, C_6H_4-*p*-Me, C_6H_4-*p*-Et, $C_6H_3(OiPr)_2$-2,6, $C_6H_3(OC_6H_{11})_2$-2,6)	III
AB	Ph^R (anionic complexes) (Ph^R = C_6H_5, $C_6H_3Me_2$-2,6, $C_6H_3(OiPr)_2$-2,6)	III
AC	*o*-$C_6H_4CH_2NMe_2$	III
AD	Ph (mixed-valent complexes)	II/III
AE	C≡CR (R = Ph, *t*Bu, Me)	II
AF	C≡CR (anionic complexes) (R = C_4H_9)	II
AG	C≡CR (R = Ph, *t*Bu, dendrit)	III
AH	C≡CR (R = Ph, *t*Bu, C_4H_9)	III

achieved by the groups of Lappert and Wilkinson. With the introduction of bulky alkyl groups like $[CH_2SiMe_3]$, $[CH(SiMe_3)_2]$, $[CH_2CMe_3]$, or $[CH_2Ph]$, stable transition metal alkyl complexes became accessible, suggesting that transition metal carbon bonds are not inherently weak.[55−58] The synthesis of kinetically stable complexes rather depends on the choice of a suitable ligand.

The first attempted preparation of an organorare-earth metal compound surfaced most likely as early as 1902 in the Anorganisch-Chemisches Laboratorium at Königlich Technische Hochschule zu München. Back then, Muthmann and Kraft investigated, among others, into the reactivity of metallic cerium and lanthanum—freshly prepared from $LnCl_3$ by way of electrolysis—toward hydrogen and ethylene, affording the binary rare-earth metal hydrides.[59] In a footnote of this paper, it is stated that, in the same laboratory, Dr. J. Brunner has conducted a series of experiments in order to synthesize trimethylcerium. Accordingly, the most promising results were obtained when metallic cerium was treated with $HgMe_2$ in a sealed ampule. Upon distilling off unreacted dimethylmercury under a current of carbonic acid, a material remained that, when exposed to air, took fire, instantaneously releasing an exceedingly unpleasant smell. It was also noted that the material, putative $CeMe_3$, could not be isolated in a pure form. Because of the fact that the valence electrons of the rare-earth elements can reside in orbitals with different main quantum numbers, A. v. Grosse concluded in 1925 that these elements do not qualify to form alkyl complexes.[60] Certainly, such theoretical statements further stirred the inventive talent of synthesis-driven chemists, true to the motto "the importance of questioning scientific assumptions".[61] Ten years later, Rice and Rice provided further positive evidence for the formation of alkyl compounds when exposing a lanthanum mirror to methyl radicals in an experiment utilizing the Paneth technique.[62] Next, the synthesis of $LnEt_3(OEt_2)_x$ (Ln = Sc, Y) from the respective chlorides $LnCl_3$ and EtMgBr in ether followed by purification via distillation at 200 °C under a current of nitrogen had been claimed by Plets in 1938.[63] The synthesis, however, could never be repeated. In connection with the Manhattan project, Gilman and Jones attempted the preparation of organolanthanide compounds. Reacting $LaCl_3$ with phenyllithium in ether or lanthanum metal with diphenylmercury at 135 °C in a sealed tube for 100 days yielded biphenyl rather than benzoic acid after treating the reaction mixture with CO_2.[64] The formation of a "thick brown syrup" accompanied by evolution of methane was described when $LaCl_3$ and methyllithium reacted at ambient temperature. In 1955, an evaluation of the hitherto existing studies on rare-earth metal σ-bonded hydrocarbyls led to the conclusion *that the existence of isolable, well-defined (at least in composition) alkyl or aryl derivatives is extremely meager or nonexistent*.[2] This was stated one year after Wilkinson and Birmingham succeeded in the synthesis, isolation, and comprehensive characterization (except X-ray structure analysis) of $Ln(C_5H_5)_3$ (Ln = Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb), the first "π-bonded" complexes of the rare-earth metals.[65] In 1968, Hart and Saran reported the synthesis of $Sc(C_6H_5)_3$ as the first genuine σ-bonded organometallic compound of a rare-earth element.[66] With $[Li(thf)_4][Lu(C_6H_3\text{-}Me_2\text{-}2,6)_4]$, Hart and co-workers further provided the first structural proof of a σ-bonded *f*-transition metal alkyl/aryl in 1972.[67] Attempts to obtain permethylated rare-earth metal complexes "$LnMe_3$" as the simplest organometallic derivatives are strongly related to Schumann.[8,68,69] In the early 1980s, Schumann and Müller succeeded in the synthesis of thermally stable ate complexes $[Li(donor)]_3[LnMe_6]$,[70] but it took another 20 years until the elusive neutral rare-earth metal methyl complexes $[LnMe_3]_n$ were isolated and characterized by us.[71]

In accordance with *d*-transition metal chemistry, the introduction of "neopentyl"-type ligands $[CH_2CMe_3]$, and particularly the silyl-substituted variants $[CH_2SiMe_3]$, $[CH(SiMe_3)_2]$, and $[C(SiMe_3)_3]$, by the groups of Lappert and Eaborn opened up prolific organorare-earth metal chemistry.[72−74] It was not until 1988 when the structural characterization of the first neutral homoleptic rare-earth metal σ-bonded hydrocarbyl complexes $Ln[CH(SiMe_3)_2]_3$ (Ln = La, Sm) was reported by Hitchcock et al.[75] Until today, such (trimethylsilyl)methane derivatives are the most widely applied alkyl ligands in rare-earth metal chemistry.

1.5. Synthesis Protocols and Other Considerations

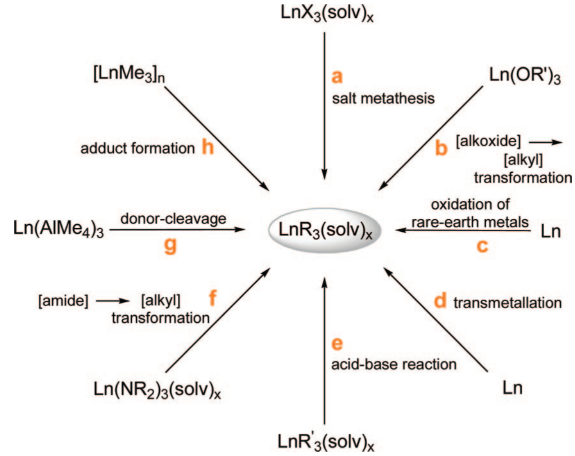
Associated with the exceptional progression in the field of rare-earth metal hydrocarbyls, several synthesis routes to homoleptic rare-earth metal alkyl, aralkyl, and alkynyl complexes have been developed. Scheme 2 indicates common synthesis pathways toward the formation of Ln(III)−C(hydrocarbyl) bonds. Important compound-specific details and differing synthesis protocols are mentioned in the following sections.

Rare-earth metal halides are suitable precursors for a variety of rare-earth metal hydrocarbyl compounds. Traditional salt-metathesis reaction of $LnX_3(solv)_x$ and an organoalkali metal compound therefore remains by far the predominant synthesis route (Scheme 2a). However, incorporation of alkali metal salts and ate complex formation are often observed (vide infra). As this is usually an undesired feature and particularly pronounced in rare-earth metal alkyl chemistry, alternative synthesis routes involving well-defined metalorganic precursors have been developed.

The transformation of lanthanide alkoxide bonds to lanthanide alkyl bonds in some cases is an attractive alternative to the traditional salt-metathesis reaction (Scheme 2b). The outcome of this kinetically controlled metathesis reaction is very sensitive toward slight changes of reaction conditions and the properties of the reactants, though.

Oxidation of rare-earth metals (Scheme 2c) and transmetalation reactions (Scheme 2d) as synthesis protocols are

Scheme 2. Synthesis Routes to Homoleptic Rare-Earth Metal(III) Hydrocarbyls



so far limited to the few lanthanide elements with readily available divalent oxidation states (Sm, Eu, Yb). Because of the comparatively low acidity of hydrocarbon acids (vide infra), an [alkyl] → [alkyl] exchange as a synthesis route toward homoleptic rare-earth metal hydrocarbyl complexes could only be utilized for relatively Brønsted acidic alkynes (Scheme 2e).

Peralkylation of rare-earth metal amide complexes ([amide] → [alkyl] transformation) using Lewis acidic group 13 alkyls (AlR_3, $GaMe_3$) offers an elegant route to heterobimetallic Ln/M alkyl compounds (Scheme 2f). Strongly connected to the intrinsic properties of such heterobimetallic compounds, the donor cleavage of a tetraalkylaluminate moiety was found to be a unique route to highly reactive rare-earth metal methyl compounds (Scheme 2g). The reverse adduct formation displays an economic pathway toward several other bimetallic compounds (Scheme 2h).

The large rare-earth metal cations are characterized by high electrophilicity and the ability to support high coordination numbers (8−12).[76] The 4*f* valence orbitals of the lanthanides are embedded in the interior of the ion, well shielded by the $5s^2$ and $5p^6$ orbitals.[77] Consequently, their poor overlap with ligand orbitals contributes to the predominant ionic character of organolanthanide complexes. Thus, the chemistry of the rare-earth metal complexes is rather governed by electrostatic and steric requirements than by filled orbital considerations. The gradual decrease in ionic radius (lanthanide contraction) and the limited radial extension of the valence orbitals are manifested in subtle reactivity changes of complexes with analogous ligand environments but different rare-earth metal centers.[78−81]

The given intrinsic properties of rare-earth metal cations imply challenges inherent to the accessibility and stability of homoleptic rare-earth metal hydrocarbyl complexes. Besides extreme sensitivity toward air and moisture, the large size of the rare-earth metal cation and its preference for high coordination numbers are the main challenges to be met by the hydrocarbyl ligand.[42] Potential ligands have to provide enough steric bulk and/or additionally coordinating groups to achieve steric and electronic saturation of the rare-earth metal center. In the absence of such bulky ligands, steric and electronic saturation is achieved by various methods, severely influencing the complex stability and reactivity:

Formation of Anionic or Ate Complexes

The formation of anionic rare-earth metal ligand moieties or ate complexation are commonly observed features of salt-metathesis reactions when alkali metal hydrocarbyl derivatives are employed (vide infra). Ate complexation, as the main reaction pathway or as contamination, occurs via coordination of additional counterligands or alkali metal halide incorporation. Because of the additional electronic and steric saturation of the metal environment, as a rule the reactivity of ate complexes is significantly decreased.

Donor Interactions/Solvent Complexation

Solvent complexation usually results from salt-metathesis reactions carried out in ethereal solvents such as Et_2O or tetrahydrofuran (thf) (vide infra). Solvent coordination usually decreases the reactivity of Ln−R bonds by depolarization, steric saturation, and competitive reactions. As the majority of organic transformations mediated/catalyzed by lanthanide centers depends on the precoordination of a neutral, functionalized substrate, solvent coordination possibly competes or even suppresses substrate coordination by stereoelectronic saturation of the rare-earth metal center. However, donor coordination in many cases allows for the isolation of otherwise labile homoleptic rare-earth metal hydrocarbyl complexes. It can further enforce crystallization and disrupt polymeric networks.

Formation of Polymeric Networks

Steric and electronic factors often force the stabilization of monometallic species via agglomerization (vide infra). Formation of di- and multinuclear species is achieved by intermolecular bridging of the smallest, most reactive, and labile Ln−R bond and, hence, leads to decreased reactivity. Formation of polymeric networks can further result in low solubility of the respective compounds, frustrating characterization and further reactions.

Despite the requirements for a suitable ligand system, a variety of hydrocarbyl ligands has been successfully applied to organorare-earth metal chemistry. One of the concepts applied includes hydrocarbyl ligands containing "built-in" chelating donor functionalities. Intramolecular ring formation via dative bonds stabilizes mononuclear complexes by the chelate and entropy effect. Ligand-bonded donor groups successfully compete with donor solvent molecules for coordination sites, implying improved thermal stability. The interaction of strong donor groups significantly decreases the reactivity of an adjacent Ln−R bond but enhances the complex stability.

Introduction of bulky neopentyl-type ligands and particularly the use of silyl-substituted derivatives [CH_2SiMe_3], [$CH(SiMe_3)_2$], and [$C(SiMe_3)_3$] resulted in very high stability of the respective rare-earth metal complexes. As the β-elimination pathway is an important decomposition route in early transition metal chemistry, ligand degradation reactions are impeded by the absence of β-hydrogen atoms. The remarkable stabilizing effect of the silyl substituents is further attributed to the stabilization of the respective carbanion by $(p \rightarrow d)_\pi$ or $(p \rightarrow \sigma^*)$ interaction with the silicon atom.[82−84]

Measurement of the gas-phase acidity of the corresponding carbon acids indeed revealed a significant stabilization of the α-silyl substituted carbanions. The acidity, relative to neopentane, increases by about 20 and 36 kcal/mol for the addition of one or two silyl groups, respectively.[84,85] (The gas-phase proton affinity (gas-phase acidity) is defined as the enthalpy change for the heterolytic H−R bond dissociation, ΔH°_{acid} (HR) = D°(H−R) − EA(R) + IP(H). The smaller the ΔH°_{acid} value, the more acidic the compound.)

Rare-earth metal alkyl compounds are important alkyl transfer reagents and initiate a variety of catalytic reactions. The Ln−C(hydrocarbyl) bond is significantly weaker than Ln−O(alkoxide) bonds and, however, as strong as Ln−N(amide) bonds, which markedly affects the synthesis chemistry and derivatization of rare-earth metal hydrocarbyl complexes.

This has been confirmed by the determination of absolute bond disruption enthalpies *D* by means of calorimetric titrations for the representative systems Cp*Sm−X (X = O*t*Bu, *D* = 82.4 kcal/mol; NMe_2 = 48.2 kcal/mol; $CH(SiMe_3)_2$ = 47.0 kcal/mol).[87] In addition to the comparably low thermodynamic stability, the Ln−C(hydrocarbyl) bond displays kinetic lability. Acid−base exchange reactions are fundamental for the derivatization of rare-earth metal hydrocarbyl complexes and the formation of catalytically active species. Therefore,

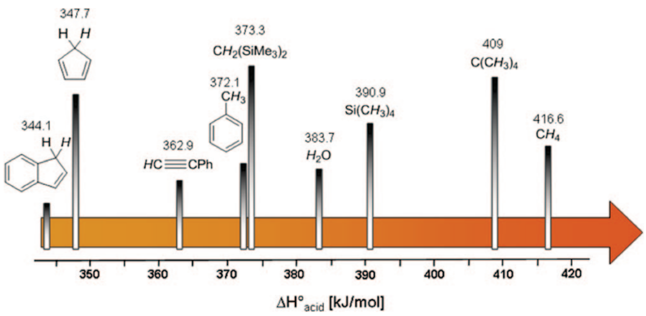


Figure 3. Gas-phase acidities of several C−H acidic compounds relevant for rare-earth metal hydrocarbyl chemistry.[84−86]

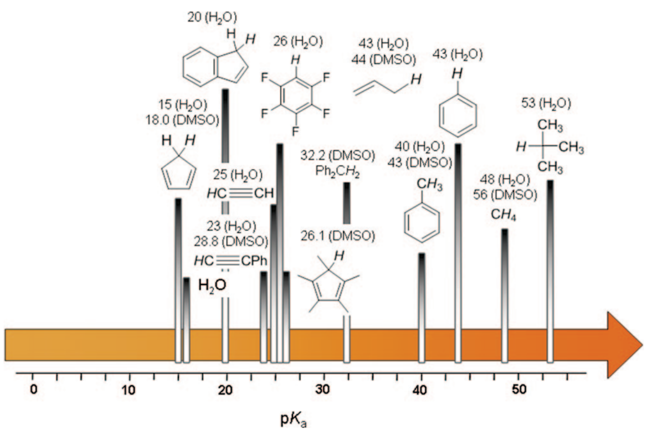


Figure 4. pK_a values of several C−H acidic compounds relevant for rare-earth metal hydrocarbyl chemistry (solvent indicated in parentheses).[88−90]

the most common hydrocarbyl proligands are depicted in Figure 4 according to their increasing pK_a values in H_2O or dimethylsulfoxide (DMSO).[88−90] Under certain restrictions, this scale might be used as a measure of reactivity.

Because of the weak acidity of organosilanes and competitive nucleophilic displacement reactions, pK_a values of the organosilicon compounds could so far not be measured by the usual proton-transfer equilibria studies.[91] A good estimation of relative acidities, however, can be obtained from the respective gas-phase acidities as depicted in Figure 3.[84−86] Hydrocarbyl proligands display (with some exceptions) relatively high pK_a values. In an acid−base type reaction, a hydrocarbyl ligand and particularly alkyl ligands can therefore be displaced by a proligand with lower pK_a. This applies for almost all known classes of ligands, be it hydrido, amido, and alkoxo ligands. Even though the reactivity of a Ln−C bond is critically dependent on several additional kinetic/steric and thermodynamic factors, shown characteristics give an impression of the high potential of rare-earth metal hydrocarbyl complexes in synthesis.

2. Methyl Complexes

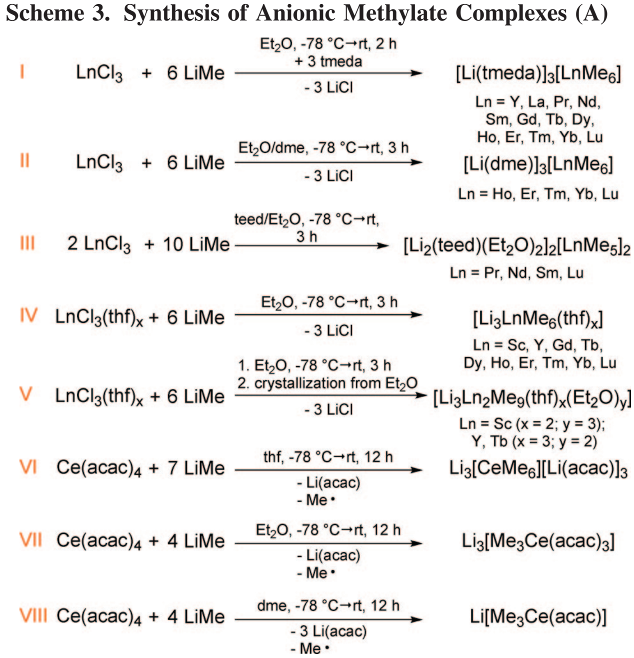
Unsolvated methyl complexes are classified as the most reactive organorare-earth metal compounds. Enhanced basicity and the small size of the methyl ligand promote extraordinary reactivity,[4,92] enabling, e.g., methane activation[93] and multiple hydrogen abstraction.[94] Permethylated transition-metal complexes, as represented by neutral $M(CH_3)_n$ and anionic $[M(CH_3)_n]^{m-}$, have attracted considerable interest not only for displaying the simplest organometallic derivatives but also for their intrinsic bonding phenomena.[4,95] While structural and theoretical investigations on homoleptic group 4, 5, 6, and 7 derivatives proceeded remarkably, group 3 and lanthanide congeners remained elusive until very recently.[71,95] Commonly, stable homoleptic rare-earth alkyl compounds involve sterically demanding or chelating alkyl groups to meet the rare-earth metal's need for steric saturation. Apparently, the small methyl ligand cannot provide such stereoelectronic protection, often resulting in fast secondary reactions and decomposition.

2.1. Synthesis, Structure, and Properties of $[Li(donor)_x]_3[LnMe_6]$, $Li_3Ln_2Me_9(thf)_x(Et_2O)_y$, and $[LnMe_3]_n$

Early attempts to obtain permethylated rare-earth metal complexes by reaction of methyllithium with $LnCl_3$ (Ln = Sc, Y, La) gave evidence for the formation of such compounds as non-volatile, pyrophoric products. Isolation from ethereal solutions, however, was not successful.[68,69] In the 1980s, Schumann and co-workers reported on the synthesis of thermally stable anionic permethylated complexes $[Li(donor)]_3[LnMe_6]$ (**A**) stabilized by chelating bases (donor = tmeda (*N,N,N′,N′*-tetramethylethylenediamine), dme (1,2-dimethoxyethane), and teed (tetraethylethylenediamine)).[70,96−98]

Dropwise addition of ethereal LiMe solutions to suspensions of the rare-earth metal trichlorides in the presence of stoichiometric amounts of the respective donor molecules resulted in the formation of hexamethylate complexes for the entire series of rare-earth metals except Sc, Ce, Pm, and Eu (Scheme 3, I−III). Following a slightly modified synthesis procedure using $LnCl_3(thf)_x$ as the rare-earth metal source, Okuda and co-workers obtained $[Li_3LnMe_6(thf)_x]$ as powdery solids for the smaller metal centers Sc, Y, and Gd−Lu (Scheme 3, IV).[99,100] Crystallization of $[Li_3LnMe_6(thf)_x]$ (Ln = Sc, Y, Tb) from saturated diethyl ether solutions gave the heteronuclear complexes $[Li_3Ln_2Me_9(thf)_x(Et_2O)_y]$ (Scheme 3, V).[100] In an attempt to synthesize permethylated compounds of Ce(IV), Thiele et al. reacted cerium(IV) acetylacetonate with varying amounts of methyllithium in ethereal solvents.[101] Because of the high oxidation potential of Ce^{3+}/Ce^{4+} combined with the high polarity of lithiumorganyls,

Scheme 3. Synthesis of Anionic Methylate Complexes (A)



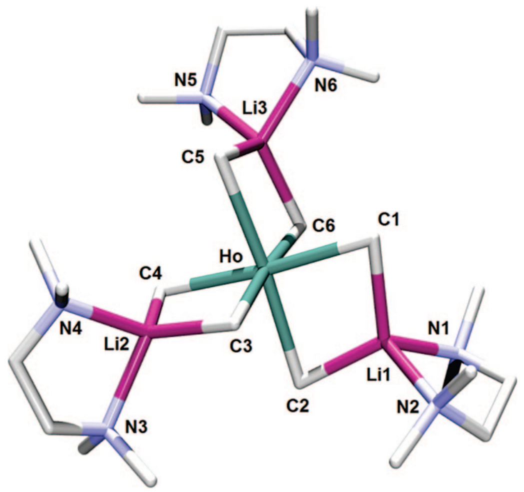


Figure 5. Solid-state structure of $[Li(tmeda)]_3[HoMe_6]$ ($\mathbf{A}_{Ho-tmeda}$), adapted from ref 97.

only cerium(III) compounds could be isolated (Scheme 3, VI−VIII). Common to all methylated Ce(III) products was the incorporation of Li(acac) (Li(acetylacetonate)), while the extent of the salt incorporation was governed by the reaction conditions.

Compounds $[Li(donor)]_3[LnMe_6]$ (**A**) are soluble in ethereal solvents, slightly soluble in aromatic solvents, but insoluble in aliphatic solvents.[97] The thermal stability decreases with increasing effective radius of the rare-earth metal cation. Hence, derivatives of the small ions (Lu−Ho) decompose over 120 °C, whereas all larger ions form complexes that are less stable.[97] The cerium(III) compounds $Li_3[CeMe_6][Li(acac)]_3$, $Li_3[Me_3Ce(acac)_3]$, and $Li[Me_3Ce(acac)]$ decompose at temperatures above 110 °C,[101] while hexamethylates $[Li_3LnMe_6(thf)_x]$ are reported as thermally extremely sensitive.[100]

In the solid state, the rare-earth metal cation of $[Li(donor)]_3[LnMe_6]$ is surrounded by six methyl groups in a slightly distorted octahedral arrangement (Figure 5). The lithium atoms are located at the center of tetrahedra made up of two methyl groups and the two nitrogen or oxygen donors of tmeda and dme, respectively.[8,96−98] $[Li_2(teed)(Et_2O)_2]_2[LnMe_5]_2$ appear to be dinuclear complexes featuring bridging methyl groups between the two rare-earth metal cations and between Ln and Li.[8,96] Heteronuclear complexes $[Li_3Ln_2Me_9(thf)_x(Et_2O)_y]$ display a $LiLn_2$ core structure and show an overall C_2-symmetry. Each rare-earth metal center is surrounded by six methyl groups, describing a distorted octahedral geometry (Figure 6).[100]

Hexamethyl rare-earth metal complexes are extremely sensitive toward moisture and oxygen. Upon hydrolysis, all ligands are displaced from the rare-earth metal with concurrent formation of $Ln(OH)_3$, CH_4, and tmeda/dme/teed. Further investigations on the chemical reactivity of $[Li(donor)]_3[LnMe_6]$ (**A**) are limited to preliminary studies on the methylation of α,β-unsaturated ketones and aldehydes. 1,2-Methylation was found to be favored over 1,4-methylation of the tested substrates.[97] Protonolysis of compounds $[Li_3LnMe_6(thf)_x]$ with borate reagents yielded cationic species active in isoprene polymerization (vide infra).[99,100]

Twenty years after Schumann's discovery of ionic permethylated compounds $[Li(donor)]_3[LnMe_6]$, we succeeded in the synthesis of neutral homoleptic trimethylyttrium and trimethyllutetium (**B**).[71] Adding stoichiometric amounts of

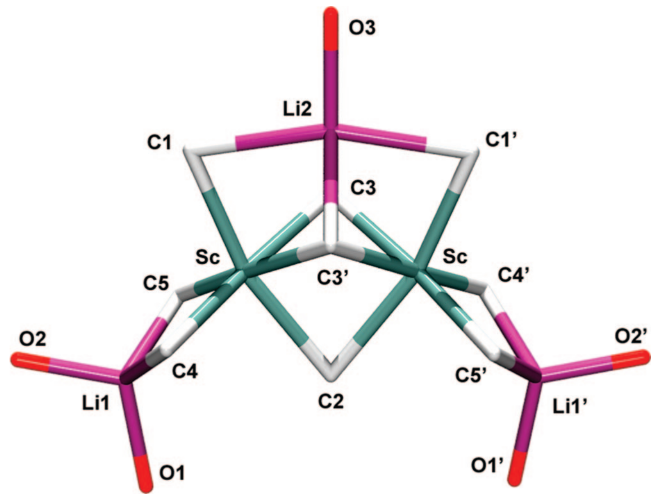
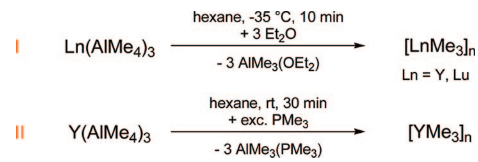


Figure 6. Solid-state structure of $[Li_3Sc_2Me_9(thf)_2(Et_2O)_3]$ ($\mathbf{A}_{Sc-thf,Et_2O}$), adapted from ref 100.

Scheme 4. Synthesis of $[LnMe_3]_n$ (B)



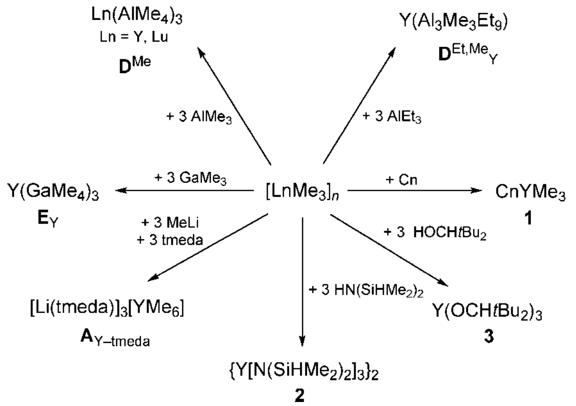
thf (3 equiv) to a solution of $Ln(AlMe_4)_3$ ($\mathbf{D}^{Me}$) in hexane instantly produced a white precipitate of $[LnMe_3]_n$ (**B**). Optimized conditions for the donor-induced tetramethylaluminate cleavage reaction (see also section 3.4) comprise the use of freshly sublimed $Ln(AlMe_4)_3$ and the less Lewis basic donor diethyl ether, as well as low reaction temperature (Scheme 4, I). Homoleptic $Y(AlMe_4)_3$ was also successfully cleaved by the softer donor PMe_3 (Scheme 4, II).[102] The production of $[YMe_3]_n$ is accompanied by formation of thermally stable $Me_3Al(PMe_3)$; the microanalytical data, however, clearly show that diethyl ether is a superior cleavage agent for $Y(AlMe_4)$.

Compounds $[LnMe_3]_n$ (**B**) are insoluble in aliphatic and aromatic solvents and slowly decompose in the presence of donor solvents (thf, Et_2O). Insolubility prevents the characterization of $[LnMe_3]_n$ by solution NMR spectroscopy and single-crystal X-ray diffraction studies. Solid-state Fourier transform infrared (FTIR) and magic-angle spinning (MAS) NMR spectroscopy revealed a uniform coordination environment at the rare-earth metal center, suggesting a polymeric network of rare-earth metals connected by bridging methyl groups. So far, only trimethylyttrium and trimethyllutetium could be obtained following the synthesis routes depicted in Scheme 4. Applying similar synthesis protocols to $Ln(AlMe_4)_3$ of the larger rare-earth metals resulted in the formation of powdery materials with low solubility. The obtained solid materials contain mixtures of rare-earth metal cluster compounds, which are the result of incomplete tetramethylaluminate cleavage and extensive C−H bond activation reactions.[102]

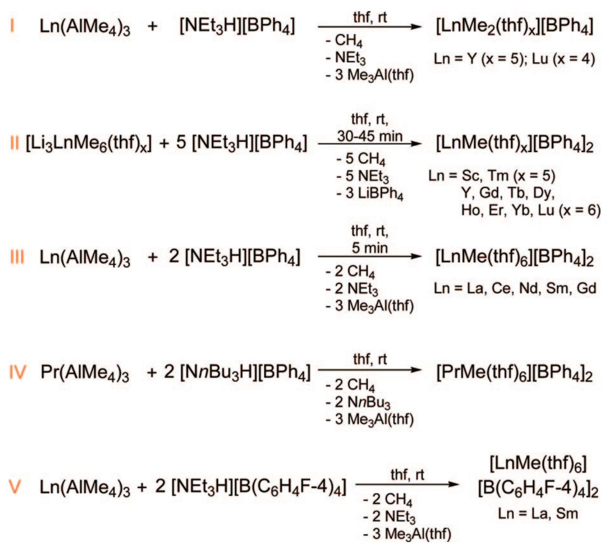
2.2. $[Li(donor)_x]_3[LnMe_6]$ and $[LnMe_3]_n$ as Synthesis Precursors

The donor-cleavage reaction of $Ln(AlMe_4)_3$ ($\mathbf{D}^{Me}$) (Ln = Y, Lu) as described above was found to be completely reversible. Treatment of $[LnMe_3]_n$ (**B**) with 3 equiv of $AlMe_3$

Scheme 5. Derivatization of $[LnMe_3]_n$ (B) by Lewis Acid/Donor Addition



Scheme 6. Synthesis of Cationic Methyl Complexes from $[Li_3LnMe_6(thf)_x]$ (A) and $Ln(AlMe_4)_3$ (D)



led to quantitative reformation of $Ln(AlMe_4)_3$ ($\mathbf{D}^{Me}$) (Scheme 5).[71] Accordingly, other strong Lewis acids like $AlEt_3$ and $GaMe_3$ redissolved $[YMe_3]_n$ to yield heterobimetallic $Y(Al_3Me_3Et_9)$ ($\mathbf{D}^{Et,Me}{}_{Y}$) and $Y(GaMe_4)_3$ ($\mathbf{E}_Y$),[71,103] respectively. In the presence of tmeda as donor solvent, $[YMe_3]_n$, and 3 equiv of LiMe, the anionic hexamethylate $[Li(tmeda)]_3[YMe_6]$ ($\mathbf{A}_{Y-tmeda}$) formed in moderate yield. Reaction with 1,4,7-trimethyl-1,4,7-triazacyclononane (Cn) gave $[CnYMe_3]$ (**1**) which has previously been prepared in the group of Bercaw following a salt metathesis protocol (Scheme 5).[104]

Homoleptic $[LnMe_3]_n$ further proved to react with Brønsted acids $HN(SiHMe_2)_2$ and $HOCH\textit{t}Bu_2$, forming homoleptic solvent-free amide $\{Y[N(SiHMe_2)_2]_3\}_2$ (**2**)[103] and alkoxide $Y(OCH\textit{t}Bu_2)_3$ (**3**),[71] respectively. Highly efficient methylation of the carbonylic functionality in 9-fluorenone (high yield, high group transfer economy) was observed, demonstrating the multifaceted applicability of $[LnMe_3]_n$ as rare-earth metal precursor and in organic synthesis.[103]

Dimethyl monocations $[LnMe_2(thf)_x][BPh_4]$ ($\mathbf{B}^{+}{}_{thf}$) can be prepared from the ate complexes $[Li_3LnMe_6(thf)_x]$ (**A**) by protonolysis with $[NEt_3H][BPh_4]$, by nucleophilic attack of the methyl dications $[LnMe(thf)_x][BPh_4]_2$ ($\mathbf{B}^{2+}{}_{thf}$) (vide infra) with methyllithium, or by protonolysis of $Ln(AlMe_4)_3$ (**D**) with $[NEt_3H][BPh_4]$ (Scheme 6, I). Only the latter method allowed isolation of the monocations ($\mathbf{B}^+$) as these compounds cannot be separated from $LiBPh_4$, which is formed by the former two methods.[99,100,105]

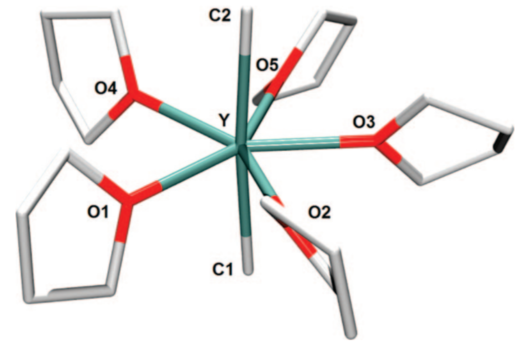


Figure 7. Solid-state structure of cation $[YMe_2(thf)_5]^+$ in $[YMe_2(thf)_5][BPh_4]$ ($\mathbf{B}^{+}{}_{Y-thf}$), adapted from ref 99.

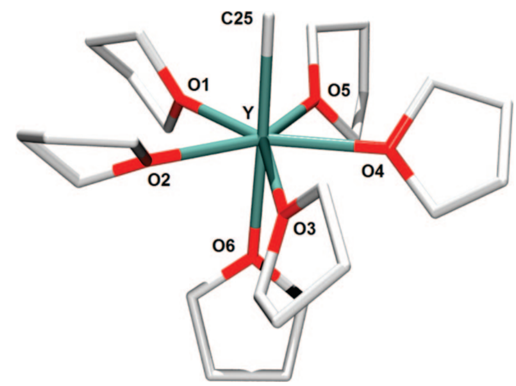


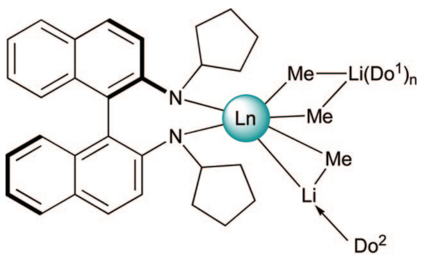
Figure 8. Solid-state structure of bis(cation) $[YMe(thf)_6]^{2+}$ in $[YMe(thf)_6][BPh_4]_2$ ($\mathbf{B}^{2+}{}_{Y-thf}$), adapted from ref 105.

When 5 equiv of $[NEt_3H][BPh_4]$ are added to thf solutions of $[Li_3LnMe_6(thf)_x]$ (**A**), compounds $[LnMe(thf)_x][BPh_4]_2$ ($\mathbf{B}^{2+}{}_{thf}$) precipitate (Scheme 6, II).[100,106] Because of the unavailability of the methylate complexes **A** for the larger rare-earth metal centers La, Ce, Pr, Nd, and Sm, dicationic methyl complexes were prepared by protonolysis of the homoleptic tetramethylaluminates $Ln(AlMe_4)_3$ ($\mathbf{D}^{Me}$) using $[NR_3H][BPh_4]$ (R = Et, *n*Bu) or $[NEt_3H][B(C_6H_4\text{-}F\text{-}4)_4]$ as Brønsted acids (Scheme 6, III−V).[100,106]

Methyl dications $[LnMe(thf)_x][BPh_4]_2$ of the larger rare-earth metals La−Sm are significantly less stable than their smaller analogues.[100] A ring-opening reaction of tetrahydrofuran to form a pentoxy complex was reported for Nd as the metal center,[106] whereas a suspension of the samarium derivative in thf gradually dissolved at ambient temperature and in daylight to give divalent $[Sm(thf)_7][BPh_4]_2$ (**4**).[100,107]

The solid-state structure of ion pair $[LuMe_2(thf)_4][BPh_4]$ ($\mathbf{B}^{+}{}_{Lu-thf}$) revealed a distorted octahedral coordination geometry around the lutetium metal center with four coordinating solvent molecules and a *cis*-arrangement of the methyl groups.[100] On the contrary, the structure of $[YMe_2(thf)_5][BPh_4]$ ($\mathbf{B}^{+}{}_{Y-thf}$) shows *trans*-disposed methyl groups, a pentagonal bipyramidal coordination geometry around the yttrium metal center, and the coordination of five thf molecules (Figure 7).[99]

Replacing one methyl group by thf leads to the solid-state structure of ion triple $[YMe(thf)_6][BPh_4]_2$ ($\mathbf{B}^{2+}{}_{Y-thf}$), showing a similar geometric arrangement of the methyl ligand and donors around the Y metal center (Figure 8).[105] The remaining methyl group occupies the apical position of the pentagonal bipyramid. Analogous solid-state structures were also found for the small to medium sized rare-earth metal



Ln = Y (X-ray), Yb; Do^1 = Do^2 = thf (n = 2)
Ln = Y (X-ray), Yb (X-ray); Do^1 = tmeda (n = 1), Do^2 = Et_2O (n = 1)
5

Figure 9. Structure of (binam)Ln(μ-Me)$_2$Li(Do)$_x$(μ-Me)Li(Do) (**5**).

centers Sc, Dy,[100] Ho,[106] and Tm.[100] The solid-state structures of $[LnMe(thf)_6][B(C_6H_4F\text{-}4)_4]_2$ (Ln = La, Sm) display a methyl-capped octahedral geometry. According to density functional theory (DFT) calculations, the preference for this capped octahedral structure is electrostatically driven because the shorter Ln−Me distance allows for a stronger electrostatic interaction.

In situ generated dications $[YMe(solv)_n]^{2+}$ ($\mathbf{B}^{2+}_{Y-tol}$) (solv = toluene) catalyzed the polymerization of 1,3-dienes when applying $[PhNMe_2H][B(C_6F_5)_4]$ as the cationizing agent, while the activation by $[PhNMe_2H][BPh_4]$ did not result in catalytically active species.[99] This marked reactivity difference was attributed to the comparatively weak coordination of fluorinated anions, resulting in solvent-separated ion pairs in aromatic solvents. On the contrary, a strong η^6-coordination of the $[BPh_4]$ anions would lead to inactive-contact ion pairs. Investigating the catalytic performance of in situ prepared $[YMe_2(solv)_n]^+$ ($\mathbf{B}^{+}_{Y}$) and $[YMe(solv)_n]^{2+}$ ($\mathbf{B}^{2+}_{Y}$) toward dienes revealed remarkably higher activity and *cis*-selectivity for the dicationic species (monocation, 90% *cis*-PBD; dication, 97% *cis*-PBD; PBD = polybutadiene). Activities and polymer properties further displayed a strong dependence on the use of Al*i*Bu$_3$ as a scavenger (100 equiv). Initial studies further revealed a high reactivity of the cationic complexes, including the C−H bond activation of pyridine.[108]

Recently, in situ generated anionic complexes $[Li(donor)]_3[LnMe_6]$ (**A**) were reported to form chiral amide alkyl complexes **5** (Figure 9), which display active catalysts for the enantioselective hydroamination of aminoolefins.[109]

3. Tetraalkylaluminate Complexes

3.1. Synthesis, Structure, and Properties of [Ln(II)(AlR$_4$)$_2$]$_n$

Early investigations by Boncella and Andersen regarding the reactivity of dimeric $\{Yb(II)[N(SiMe_3)_2]_2\}_2$ (**6**) toward molecules with Lewis acidic sites fundamentally contributed to the development of lanthanide tetraalkylaluminate compounds.[110] Reaction of compound **6** with equimolar amounts of AlR_3 (R = Me, Et) resulted in the formation of bis(trialkylaluminum) adducts $Yb(II)[N(SiMe_3)_2]_2(AlR_3)_2$ (**7**). Determination of the solid-state structure of $Yb[N(SiMe_3)_2]_2(AlMe_3)_2$ (**7**^{Me}) revealed a monomeric $Yb[N(SiMe_3)_2]_2$ fragment in which each lone pair of electrons on the nitrogen atoms is coordinated to aluminum atoms (Figure 10).[110] Steric saturation of the large divalent ytterbium metal center is achieved by four additional γ-CH agostic interactions with adjacent methyl protons.

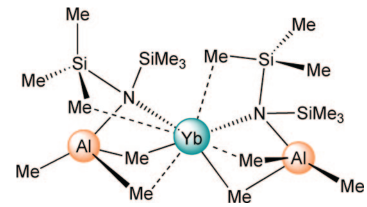
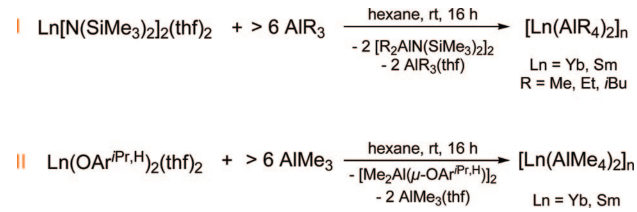


Figure 10. Structure of $Yb(II)[N(SiMe_3)_2]_2(AlMe_3)_2$ (**7**^{Me}).

Scheme 7. Synthesis of [Ln(II)(AlR$_4$)$_2$]$_n$ (C)



In 2001, the above-mentioned reactions were reinvestigated our group using an excess of the trialkylaluminum reagents (Scheme 7, I).[111,112] The obtained peralkylated heterobimetallic complexes [Ln(II)(AlR$_4$)$_2$]$_n$ (**C**) (R = Me, Et, *i*Bu) are the products of a complete [amide] → [alkyl] transformation, proceeding via intermediately formed AlR_3 adducts as found by Boncella and Andersen (Scheme 7).[110]

While the methyl derivatives [Ln(AlMe$_4$)$_2$]$_n$ (**C**^{Me}) precipitate quantitatively from hexane reaction mixtures to give analytically pure solids, [Ln(AlEt$_4$)$_2$]$_n$ (**C**^{Et}) and [Ln(Al*i*Bu$_4$)$_2$]$_n$ (**C**^{iBu}) display excellent solubility in aliphatic media and can be separated from the byproduct $[R_2AlN(SiMe_3)_2]_2$ by fractional crystallization.[111−113] Homoleptic [Ln(AlMe$_4$)$_2$]$_n$ (**C**^{Me}) could further be obtained by complete alkylation of lanthanide(II) bis(2,6-diisopropylphenolates) with an excess of $AlMe_3$ (Scheme 7, II).[114]

Structure determination of the methyl derivatives [Ln(AlMe$_4$)$_2$]$_n$ (**C**^{Me}) is frustrated by the insolubility in aliphatic and aromatic solvents, but single crystals suitable for X-ray crystallographic structure determination could be obtained for the higher alkylated congeners [Ln(AlEt$_4$)$_2$]$_n$ (**C**^{Et}).[111,113] Both divalent metal centers ytterbium and samarium show isotypic structures in the solid state consisting of a polymeric network of interconnected anionic $[Ln(AlEt_4)_3]^-$ (Figure 11) and cationic $[Ln(AlEt_4)]^+$ (Figure 12) fragments. In the anionic unit, the lanthanide(II) metal center is coordinated by six carbon atoms in a pseudo-octahedral geometry (Figure 11). Each [AlEt$_4$] unit is coordinated in an η^2 fashion. While

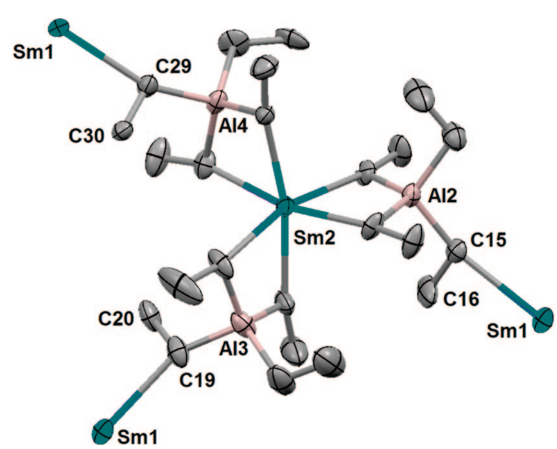


Figure 11. Solid-state structure of the anionic molecular fragment $[Sm(AlEt_4)_3]^-$ of $\mathbf{C}^{Et}_{Sm}$ showing the interconnection of the formally anionic and cationic fragments, adapted from ref 113.

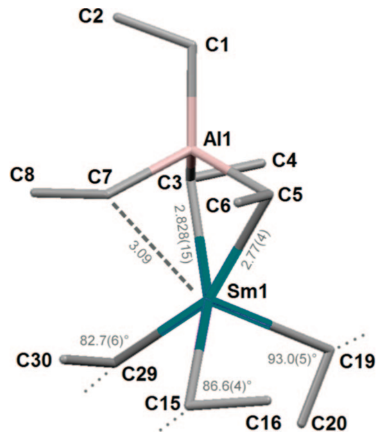
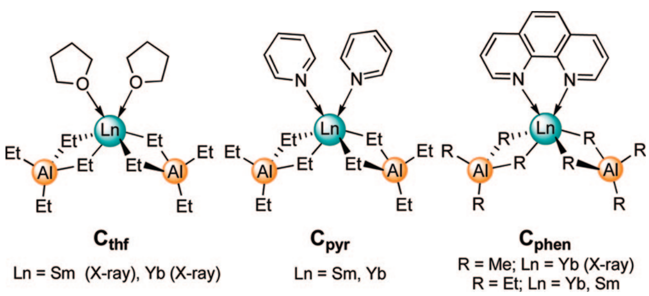


Figure 12. Solid-state structure of the cationic molecular fragment $[Sm(AlEt_4)]^+$ of $\mathbf{C}^{Et}{}_{Sm}$ showing the interconnection of the formally anionic and cationic fragments, adapted from ref 113.

Chart 2. Donor Adducts $Ln(AlR_4)_2(Do)_x$



the $[AlEt_4]$ coordination in the cationic moiety $[Yb(AlEt_4)]^+$ was described as a slightly distorted η^3-coordination,[111] the respective cationic samarium unit is rather approaching a bent η^2-coordination mode with one significantly longer Sm−(μ-CH_2) contact (Figure 12).[113] Interconnection of the formally anionic and cationic molecular fragments into a three-dimensional network is accomplished via the "terminal" ethyl groups of $[Ln(AlEt_4)_3]^-$, resulting in an overall $\mu,\eta^1:\eta^2$ coordination mode.

Because of dynamic exchange processes in solution (see section 3.3), the ^{1}H NMR spectrum of diamagnetic $[Yb(AlEt_4)_2]_n$ ($\mathbf{C}^{Et}{}_{Yb}$) exhibits only two resonances for the $[AlEt_4]$ ligands.[113] Variable-temperature ^{1}H NMR studies did not reveal decoalescence of the proton signals for the bridging and nonbridging alkyl groups over the temperature range of −100 to +90 °C.[111] MAS NMR spectroscopic investigations of insoluble $[Yb(AlMe_4)_2]_n$ ($\mathbf{C}^{Me}{}_{Yb}$) were indicative of two distinct bridging methyl groups in the solid state.[113]

Contrary to the reactivity observed for trivalent homoleptic $Ln(AlMe_4)_3$ ($\mathbf{D}^{Me}$), donor-induced aluminate cleavage[115] (see section 3.4) does not occur at lanthanide(II) metal centers. Interaction of polymeric $[Ln(AlR_4)_2]_n$ with donor molecules (donor = thf, pyridine (pyr), 1,10-phenanthroline (phen)) leads to the formation of discrete monomeric lanthanide donor adducts $Ln(AlR_4)_2(donor)_x$ ($\mathbf{C}_{thf}$, $\mathbf{C}_{pyr}$, and $\mathbf{C}_{phen}$) (Chart 2).[112,113]

The observed divergent reactivity of heterobimetallic homoleptic $[Ln(II)(AlR_4)_2]_n$ and $Ln(III)(AlMe_4)_3$ toward Lewis basic molecules accounts for a different nature of the lanthanide−carbon bonding. Whereas the latter display true aluminate complexes (E_N scale according to Pauling: Ln(III) = 1.1−1.3, Al(III) = 1.6), divalent derivatives are better described as lanthanidate complexes $[AlEt_2]_2[LnEt_4(donor)_x]$ similar to $[Li(donor)_x]_3[Ln(III)Me_6]$ (see section 2). The Ln−C bonding nature cannot be rationalized on the basis of Pauling's electronegativity scale.[116,117] Neither can the Lewis acidity criterion (Al(III) > Ln(III) > Ln(II)), commonly considered as the driving force for AlR_3(donor) separation, be applied. Increased covalent contributions to the Ln(II)−C bonding rather seem to control the observed Lewis base addition reactions.

3.2. $[Ln(II)(AlR_4)_2]_n$ as Synthesis Precursors

Studies on the reactivity of peralkylated $[Ln(II)(AlR_4)_2]_n$ (**C**) toward protic substrates were performed only recently. A suspension of $[Yb(AlMe_4)_2]_n$ in thf reacted with excess HC_5Me_5 to yield the solvent-separated ion pair $[(C_5Me_5)Yb(thf)_4][AlMe_4]$ (**8**) according to a methane elimination reaction.[113] A similar structural motif has previously been found in the solid-state structure of $[\eta^5$-(fluorenyl)$Yb(thf)_4][AlMe_4]$ (**9**).[118] Complexes $[Ln(AlR_4)_2]_n$ (**C**) readily undergo protonolysis reactions with bulky phenolic substrates $HOAr^{tBu,Me}$ ($OAr^{tBu,Me}$ = $OC_6H_2tBu_2$-2,6-Me-4) and $HOAr^{iPr,H}$ ($OAr^{iPr,H}$ = $OC_6H_3iPr_2$-2,6) (Scheme 8).[119] Generally, the reactions give complicated product mixtures containing up to three alkylation products. The reaction outcome is hereby sensitively balanced by the sterical demand of the phenolate ligands. Two prevalent secondary reaction pathways have been unambiguously identified, TMA(TEA) (TMA = trimethylaluminum; TEA = triethylaluminum) adduct formation and ligand rearrangement under formation of the bidentate ligand $[(\mu\text{-}OAr^{iPr,H})_2AlR_2]$. The bulkiness of the *tert*-butyl-substituted aryloxides, however, seems to suppress such ligand rearrangement.[114,119,120]

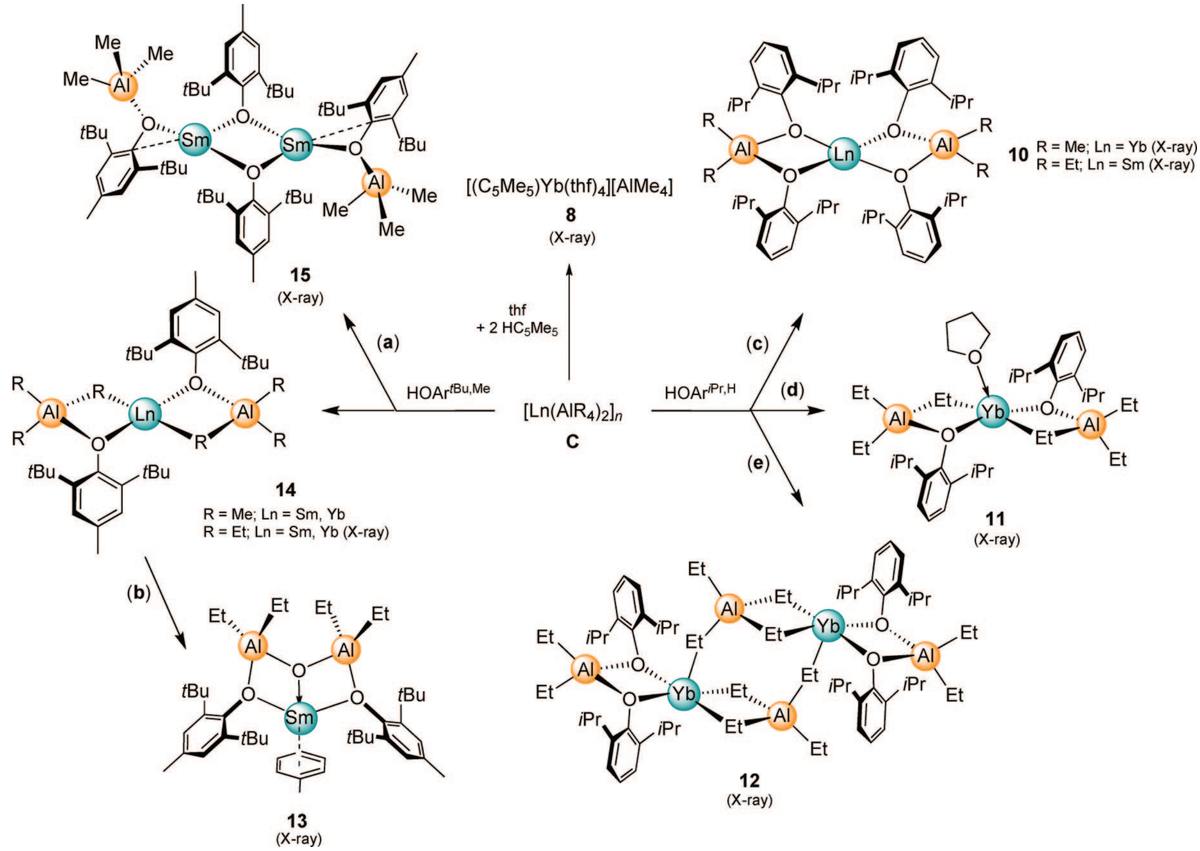
3.3. Synthesis, Structure, and Properties of $Ln(III)(AlR_4)_3$

When investigating the reactivity of homoleptic rare-earth metal alkylamides toward Lewis acidic highly reactive organoaluminum reagents, Evans and co-workers discovered the formation of heterobimetallic Ln(III)/Al alkyl species.[121−123] The degree of alkylation in the generated heterobimetallic compounds is hereby strongly dependent on the amount of alkylaluminum reagent present in the reaction mixture and the steric/electronic properties of the alkylamide ligands. Whereas homoleptic $AlMe_3$ adducts $Ln[(\mu\text{-}NMe_2)(\mu\text{-}Me)AlMe_2]_3$ (**16**) were isolated from $Ln(NMe_2)_3(LiCl)_3$ in the presence of 3 equiv of $AlMe_3$,[121] peralkylated tris(tetramethylaluminates) $Ln(AlMe_4)_3$ ($\mathbf{D}^{Me}$) formed with an excess of trimethylaluminum.[122] Such $AlMe_3$-mediated complete $[NR_2] \rightarrow [AlMe_4]$ transformations were found to be a viable route for the synthesis of several tetramethylaluminate-containing organorare-earth metal complexes.[124−127]

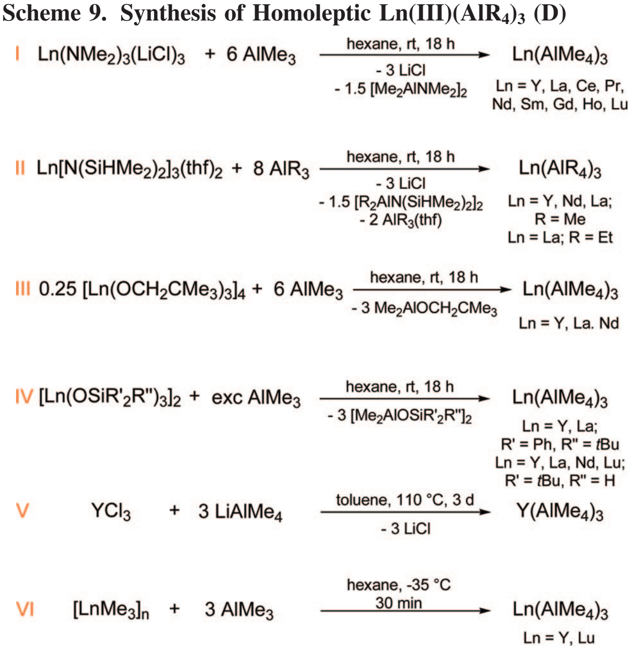
Since the discovery of $Ln(AlMe_4)_3$ ($\mathbf{D}^{Me}$) in 1995,[122] the general synthesis protocol has been optimized and applied to the entire size range of Ln^{3+} metal centers (Scheme 9, I).[128,129] The hetereobimetallic compounds can be obtained in high yield. Several crystallization steps are, however, necessary to obtain crystalline, trimethylaluminum-free $Ln(AlMe_4)_3$. The high volatility of the alkylated amide byproduct $[Me_2AlNMe_2]_2$ is one of the main advantages of this synthesis strategy, allowing for easy separation of the desired product.

Although rare-earth metal tetramethylaluminates are accessible by alkylation of a number of other Ln(III) precursors, like silylamide complexes $Ln[N(SiHMe_2)_2]_3(thf)_2$ (**17**),[130] tetrameric

Scheme 8. Alkane Elimination Reactions of Peralkylated Complexes $[Ln(AlR_4)_2]_n$: All Reactions Performed in Toluene (R = Me) or Hexane (R = Et) with 2 equiv of $HOAr^R$: (a) 1 equiv $HOAr^{tBu,Me}$; (b) Degradation Product Most Likely by Traces of H_2O; (c) Also Obtained with 4 equiv of $HOAr^{iPr,H}$; (d) thf Possibly Originates from $Yb(AlEt_4)_2(thf)_2$ Present As Minor Impurity; (e) Main Product but Slower Crystallization

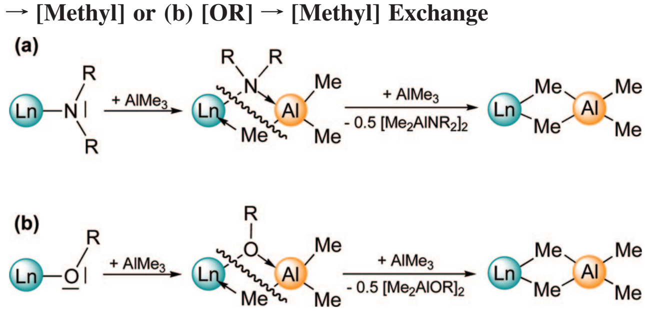


Scheme 9. Synthesis of Homoleptic $Ln(III)(AlR_4)_3$ (D)



$[Ln(OCH_2CMe_3)_3]_4$ (**18**),[120] aryloxide $[Y(OAr^{iPr,H})_3]_2$ (**19**),[114] and siloxides $[Ln(OSiR'_2R'')_3]_2$ (**20**),[131] separation of peralkylated $Ln(AlMe_4)_3$ from the alkylated byproducts has proven to be difficult (Scheme 9, II−IV). Because of the high solubility of tetraethylaluminate complexes $Ln(AlEt_4)_3$ ($\mathbf{D}^{Et}$), separation from residual $AlEt_3$ and the byproduct $[Et_2AlNR_2]_2$ was not successful. Only reaction of $La[N(SiHMe_2)_2]_3(thf)_2$ ($\mathbf{17}_{La}$) with $AlEt_3$ produced separable single

Scheme 10. Two-Step Mechanistic Scenario for the Formation of Tetramethylaluminate Ligands by (a) [Amide] → [Methyl] or (b) [OR] → [Methyl] Exchange



crystals of $La(AlEt_4)_3$ ($\mathbf{D}^{Et}_{La}$) (Scheme 9, II).[128] Salt metathesis as a one-step synthesis protocol for the preparation of $Ln(AlMe_4)_3$ could be applied for anhydrous YCl_3 and 3 equiv of lithium tetramethylaluminate (Scheme 9, V).[129] Suspensions in toluene yielded 7% of $Y(AlMe_4)_3$ after seven days. Derivatives of the larger rare-earth metals could not be obtained by this method. Alternatively, $Ln(AlMe_4)_3$ of very high purity can be obtained by $AlMe_3$-adduct formation to polymeric trimethyl compounds $[LnMe_3]_n$ (**B**) (Ln = Y, Lu). Adding 3 equiv of $AlMe_3$ to a hexane suspension of $[LnMe_3]_n$ yielded crystalline $Ln(AlMe_4)_3$ in almost quantitative yield (Scheme 9, VI).[71,102]

Formation of tetramethylaluminate ligands by [amido] → [methyl] or [OR] → [methyl] exchange, respectively, likely proceeds via a two-step mechanistic scenario (Scheme 10). In a first step, the strong Lewis acid $AlMe_3$ coordinates to the basic amide−nitrogen/OR. Such adduct formation apparently results in a weakening of the originally strong

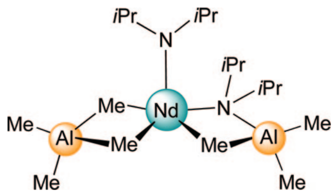


Figure 13. Structure of Nd(N*i*Pr$_2$)[(μ-N*i*Pr$_2$)(μ-Me)AlMe$_2$][(μ-Me)$_2$AlMe$_2$] (**21**).

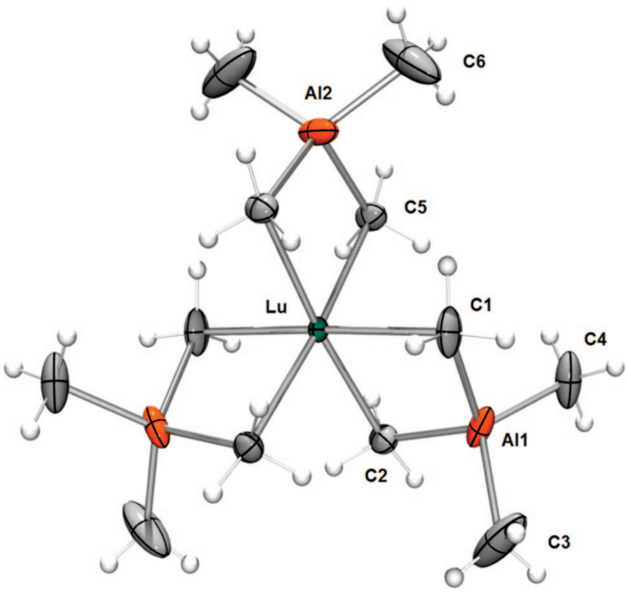


Figure 14. Solid-state structure of Lu[(μ-Me)$_2$AlMe$_2$]$_3$ ($\mathbf{D}^{Me}{}_{Lu}$), adapted from ref 129.

Ln−N/Ln−O bond. Intermediate formation of a four-membered Ln−N−Al−Me ring[110,121,123] (Ln−O−Al−Me ring)[114,131−134] containing a bridging methyl group allows for partial saturation of the mildly Lewis acidic rare-earth metal center. Addition of a second $AlMe_3$ molecule results in the complete [amido] → [methyl] ([OR] → [methyl]) exchange under the formation of a tetramethylaluminate ligand and the thermodynamically very stable $[Me_2AlNR_2]_2$ ($[Me_2AlOR]_2$).[135−138] It is suggested that the rates of the individual steps are controlled by the amido/OR group, the aluminum alkyl, their concentrations, and the reaction conditions. Stepwise addition of 4 equiv of $AlMe_3$ to Nd(N*i*Pr$_2$)$_3$(thf) allowed for the isolation of Nd(N*i*Pr$_2$)[(μ-N*i*Pr$_2$)(μ-Me)AlMe$_2$][(μ-Me)$_2$AlMe$_2$] (**21**) containing three different types of ligands (Figure 13).[123] This mixed ligand compound is acting as a model for the two-step tetramethylaluminate formation.

The [amido/OR] → [alkyl] transformation is a versatile synthesis procedure, reported for several heteroleptic Ln/Al heterobimetallic organorare-earth complexes. A high-yield synthesis of rare-earth metal tetramethylaluminates, though, underlies steric restrictions, and the choice of monoanionic lanthanide amide/OR precursors is often limited to small functionalities (NMe_2, NEt_2). Contrary to divalent Ln(II)[N(SiMe$_3$)$_2$]$_2$(thf)$_2$, steric constraints hamper the adduct formation/alkylation when using homoleptic Ln(III)[N(SiMe$_3$)$_2$]$_3$.[130,139]

The solid-state structures of homoleptic Y,[122] La, Pr,[129] Nd,[122] Sm, and Lu[129] tetramethylaluminates have been determined, showing a rare-earth metal cation size-dependent aluminate coordination. Ln(AlMe$_4$)$_3$ of the small- to middle-sized Ln(III) ions (Lu−Sm) crystallize in the centrosymmetric space group *C*2/c (Figure 14). The slightly larger

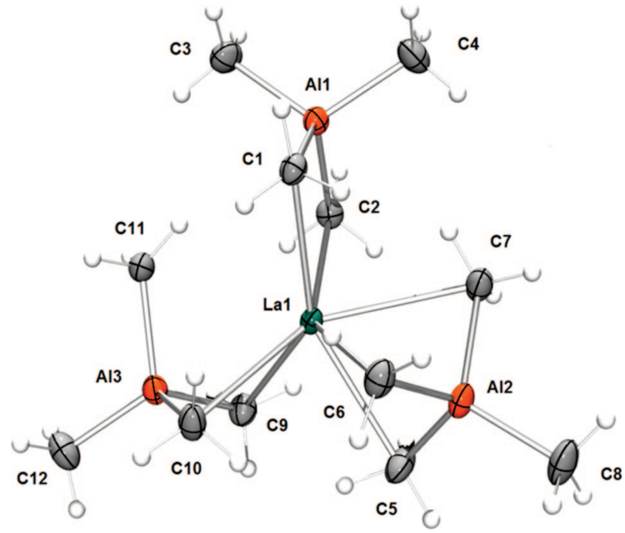


Figure 15. Solid-state structure of La[(μ-Me)$_2$AlMe$_2$]$_2$[(μ-Me)$_3$AlMe] ($\mathbf{D}^{Me}{}_{La}$), adapted from ref 129.

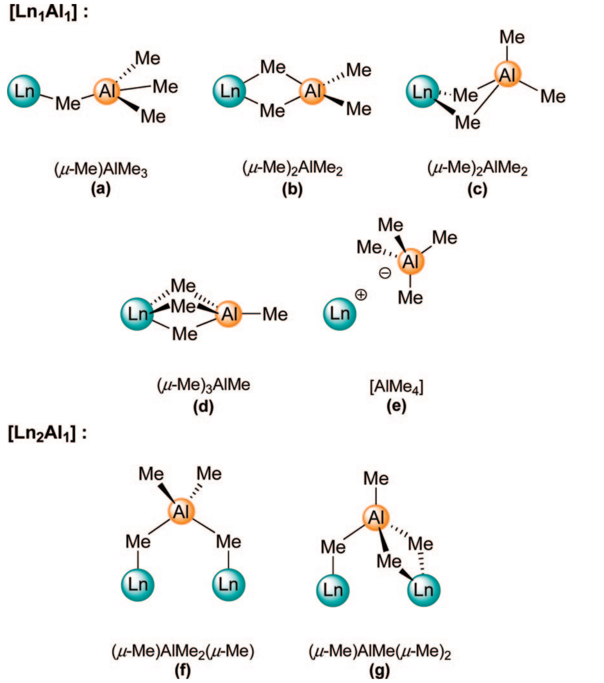
praseodymium and neodymium derivatives (monoclinic space group $P2_1/c$) crystallize with two independent molecules in the unit cell. All solid-state structures show a 6-fold coordination of carbon atoms around the Ln(III) metal centers, resulting in a pseudo-octahedral coordination geometry (Figure 14). Each [AlMe$_4$] unit coordinates to the central Ln metal through two bridging methyl groups, forming planar or almost planar [Ln(μ-Me)$_2$Al] metallacycles. The bridging carbon atoms revealed a heavily distorted trigonal-bipyramidal coordination geometry. Because of steric unsaturation of the rare-earth metal center, two of the three H atoms in each bridging methyl group are directed toward the Ln atom.

X-ray crystallographic structure analysis of La(AlMe$_4$)$_3$ revealed the presence of three different [AlMe$_4$] coordination modes (Figure 15). While one ligand coordinates in the routinely observed η^2 fashion to form an almost planar [La(μ-Me)$_2$Al] heterobimetallic unit, the second [AlMe$_4$] ligand shows a bent η^2 coordination with an additional La−(μ-Me) contact. The third tetramethylaluminate ligand coordinates through three bridging methyl groups to the lanthanum metal center, providing additional stereoelectronic saturation.[129]

In the course of X-ray crystallographic investigations of homoleptic and heteroleptic organorare-earth metal complexes with tetramethylaluminate ligands, different types of [AlMe$_4$] coordination modes were observed (Chart 3). Among these, terminal (b) and bridging η^1:η^1 coordinated ligands (f) seem to be favored.[114,126,129,133,140−143] However, in the presence of sterically highly unsaturated rare-earth metal centers, bent [Ln(μ-Me)$_2$Al] moieties (c)[125,144−148] as well as terminal η^3 (d)[129] and bridging (μ-Me)AlMe(μ-Me)$_2$-coordinated aluminate ligands (g) appeared.[129,149] A few examples of terminal η^1-coordinated [AlMe$_4$] ligands (a) were reported for sterically very constrained environments.[150−152] Noncoordinating [AlMe$_4$] units (e) were found for solvent separated lanthanide(II) ion pairs.[113,118]

Homoleptic tris(tetramethylaluminates) are soluble in aliphatic and aromatic solvents. Because of immediate donor-induced aluminate cleavage, ethereal solvents have to be avoided. Ln(AlMe$_4$)$_3$ are thermally stable, and derivatives of the small- to middle-sized rare-earth metals can be sublimed (Ln = Y, 80 °C at 10^{-3} mbar; Ln = Lu, 90 °C at 10^{-3} mbar).

Chart 3. Structurally Characterized Coordination Modes of the [AlMe$_4$] Ligand in Organorare-Earth Metal Chemistry



Despite their solid-state structures, the ^{1}H NMR spectra of Ln(AlMe$_4$)$_3$ show only one signal for the [AlMe$_4$] moieties at ambient temperature.[122] This is indicative of a very fast exchange of bridging and terminal methyl groups (Figure 16). However, different types of methyl groups could be resolved at lower temperature for complexes of the smaller Ln(III) metals. Consistent with increased steric unsaturation and therefore more rapid alkyl exchange, decoalescence temperatures decreased with increasing size of the rare-earth metal center (Lu = 278 K, Y = 229 K, and Sm = 216 K). The methyl group exchange mechanism was studied by dynamic NMR spectroscopy and line-shape analysis, revealing activation parameters indicative of an associative methyl group exchange for Ln(AlMe$_4$)$_3$ (Ln = Sm, Y, Lu).

3.4. Ln(III)(AlMe$_4$)$_3$ as Synthesis Precursors

An important reactivity concept of heterobimetallic Ln/Al alkyl complexes, the donor(Do)-induced aluminate cleavage was reported by Lappert and co-workers in 1979 (Scheme 11).[115]

Originally applied for lanthanidocene complexes (C$_5$H$_5$)$_2$Ln(AlMe$_4$), the donor(pyridine)-cleavage gave access to dimeric (μ-Me)$_2$-bridged complexes [(C$_5$H$_5$)$_2$Ln(μ-Me)]$_2$.[115] Lappert's concept of donor-induced aluminate cleavage recently allowed for the generation of solvent-free [LnMe$_3$]$_n$ (**B**) from homoleptic Ln(AlMe$_4$)$_3$ (Ln = Y, Lu) (section 2.1).[71,102] The previously mentioned formation of ion pairs [LnMe$_2$(thf)$_x$][BPh$_4$] ($\mathbf{B^{+}_{thf}}$) and ion triples [LnMe(thf)$_6$][BAr$^R_4$]$_2$ ($\mathbf{B^{2+}_{thf}}$) (section 2) can also be assigned to a donor(thf)-induced cleavage of Ln(AlMe$_4$)$_3$ followed by protonolysis reaction with [NR$_3$H][BAr$^R_4$].[99,100,105]

The reversibility of the tetraalkylaluminate cleavage reaction is another important detail of the early work by Lappert and co-workers.[115] It was later exploited for the synthesis of mixed-alkylated complexes, e.g., mixed methyl/ethyl aluminate complexes.[124]

Further, the above-mentioned donor-induced cleavage reactions imply another important concept of the [AlMe$_4$] moiety. Thus, tetramethylaluminates can also be described as adducts LnMe$_3$(AlMe$_3$)$_3$ ("alkyls in disguise"). In accordance with this bonding feature, several alkane elimination reactions have been reported, leading to heteroleptic Ln/Al tetramethylaluminate rare-earth metal complexes (Scheme 12a).

Reaction with substituted cyclopentadienes H(Cp^R) gave access to a variety of mono(cyclopentadienyl) bis(aluminate) complexes (Chart 4).[144−146] Metallocene formation, even for the large rare-earth metal centers, could successfully be suppressed by adjusting the reaction time and temperature. The reaction of Ln(AlMe$_4$)$_3$ with potassium salts K(PC$_4$Me$_4$) and K[PC$_4$Me$_2$(SiMe$_3$)$_2$] was found to produce mono-(PC$_4$Me$_2$R$_2$) bis(tetramethylaluminate) complexes **26** under concomitant formation of KAlMe$_4$ (Scheme 12b).[147] This reaction adds another bonding concept describing the Ln(III)-AlMe$_4$ bonding as predominantly ionic, readily engaging in salt-metathesis reactions. All half-sandwich complexes depicted in Chart 4 form active catalysts for the polymerization

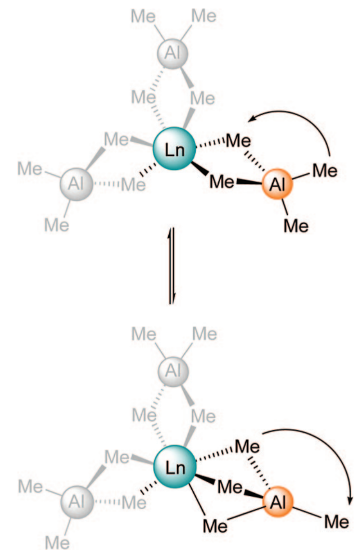
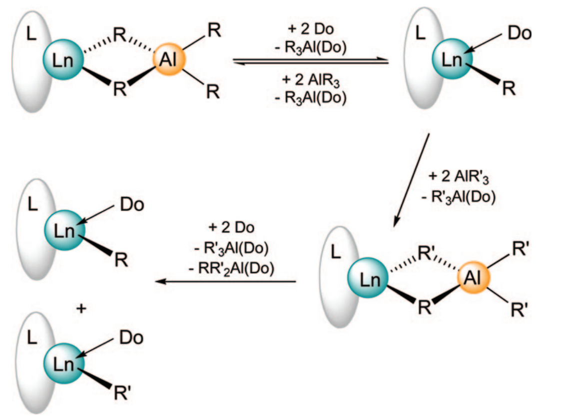


Figure 16. Proposed associative methyl exchange in homoleptic Ln(AlMe$_4$)$_3$ complexes.

Scheme 11. Donor(Do)-Induced Aluminate Cleavage and the Reversibility Phenomenon in Aluminate Chemistry



Scheme 12. Ln(AlMe$_4$)$_3$ as Synthesis Precursors

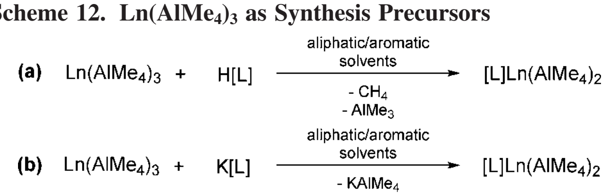
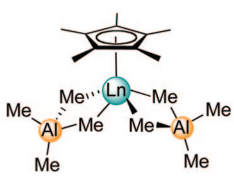
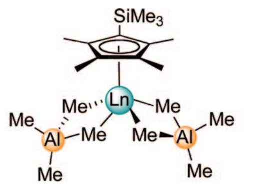


Chart 4. $Ln(AlMe_4)_3$ Derivatives Containing Cp^R Ligands



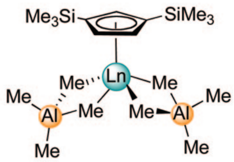
Ln = Y, La (X-ray), Nd, Lu (X-ray)

22



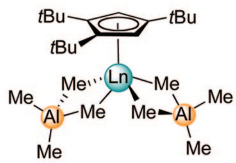
Ln = Y (X-ray), La, Nd, Sm, Gd (X-ray), Lu

23



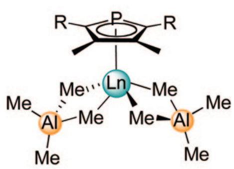
Ln = Y (X-ray), La, Nd (X-ray), Sm, Lu (X-ray)

24



Ln = La (X-ray), Nd (X-ray), Sm (X-ray)

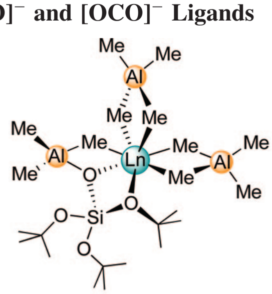
25



R = Me; Ln = La (X-ray), Nd (X-ray)
R = $SiMe_3$; Ln = La, Nd (X-ray)

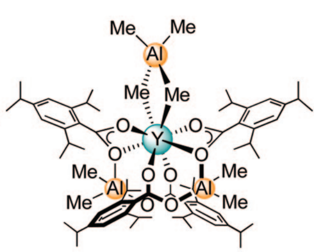
26

Chart 5. $Ln(AlMe_4)_3$ Derivatives Containing Monoanionic $[O]^-$ and $[OCO]^-$ Ligands



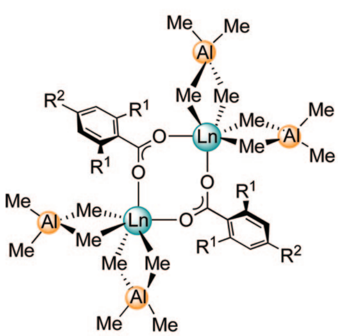
Ln = La (X-ray), Nd

27



(X-ray)

28



R^1 = Ph, R^2 = H; Ln = Y, La (X-ray), Nd (X-ray)
R^1 = R^2 = *t*Bu; Ln = Y, La (X-ray), Nd (X-ray)

29

$Ln[(O_2CAr^{Me})_2(AlMe_2)]_3$

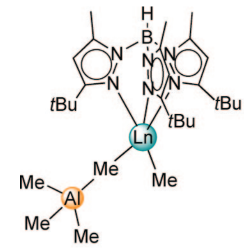
Ar^{Me} = C_6H_2-2,4,6-Me
Ln = Y, La

30

of isoprene upon activation with $B(C_6F_5)_3$, $[Ph_3C][B(C_6F_5)_4]$, or $[PhNMe_2H][B(C_6F_5)_4]$. The catalyst activities and stereoselectivities are governed by the size of the rare-earth metal center, the substituents at the cyclopentadienyl ancillary ligand, and the borane/borate activator employed. Excellent *trans*-1,4-stereoselectivity was found for the catalyst mixture $(C_5Me_5)La(AlMe_4)_2/B(C_6F_5)_3$ (99.5% *trans*-1,4 PIP, M_w/M_n = 1.19).

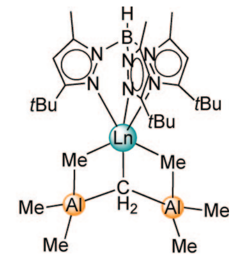
Homoleptic $Ln(AlMe_4)_3$ readily undergoes protonolysis reactions with Brønsted acidic proligands, e.g., alcohols, silanols, carboxylic acids, and amines, to generate heteroleptic Ln/Al bimetallic complexes (Charts 5−7).[126,128,129,133,140,150−152] Particularly, mixed alkoxide/aluminate and carboxylate/aluminate complexes were extensively used as model systems to study structure−reactivity relationships in commonly used Ziegler-type catalysts. Upon "cationization" with R_2AlCl reagents (R = Me, Et), such compounds provide highly active catalysts for the *cis*-1,4 stereospecific polymerization of 1,3-dienes.[114,128,129,131−134]

Chart 6. $Ln(AlMe_4)_3$ Derivatives Containing Monoanionic $[NNN]^-$ Ligands



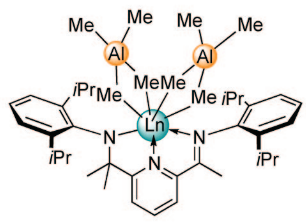
Ln = Y (X-ray), Lu

31



Ln = La (X-ray), Nd

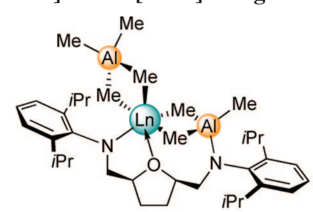
32



Ln = Y, La, Nd

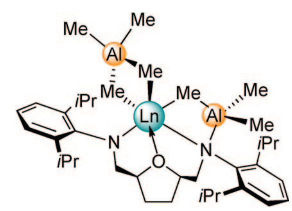
33

Chart 7. $Ln(AlMe_4)_3$ Derivatives Containing Dianionic $[NON]^{2-}$ and $[NNN]^{2-}$ Ligands



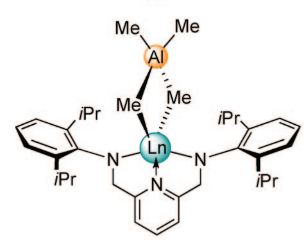
Ln = Y (X-ray)

34



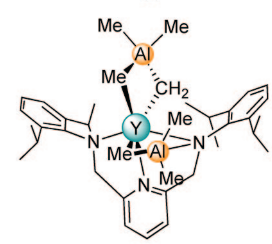
Ln = Nd, La (X-ray)

35



Ln = Y, La, Lu (X-ray)

36



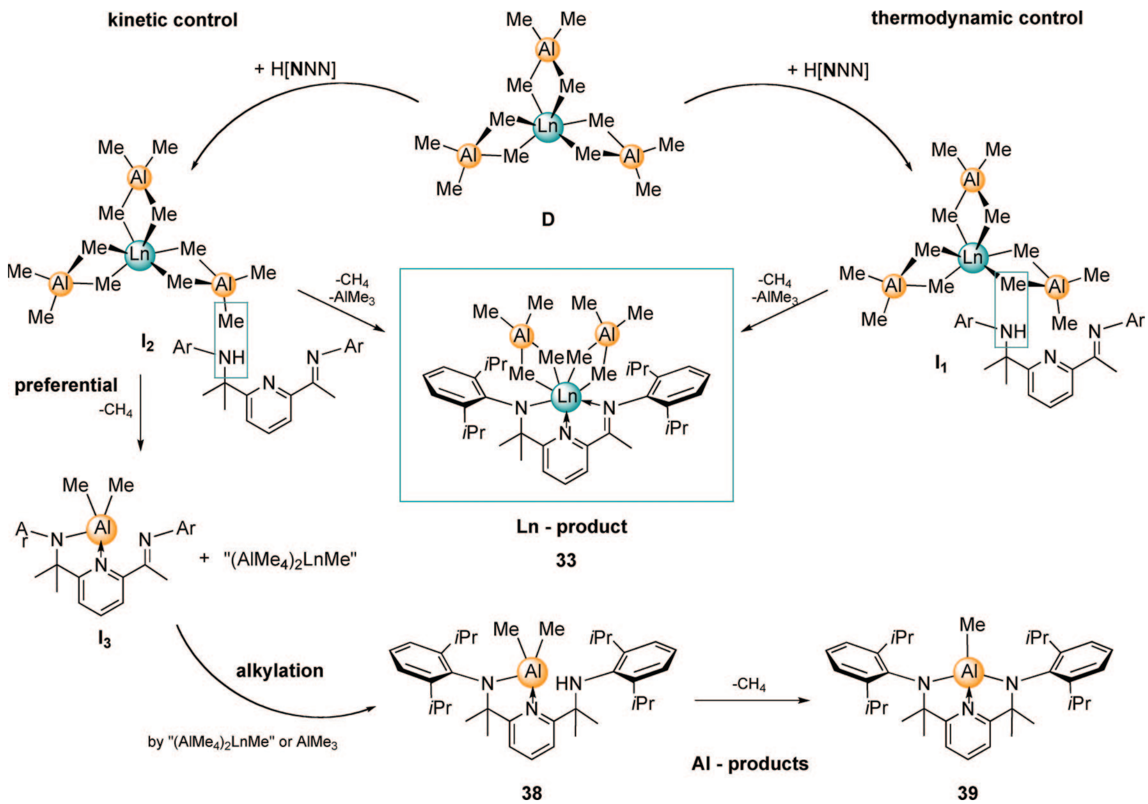
(X-ray)

37

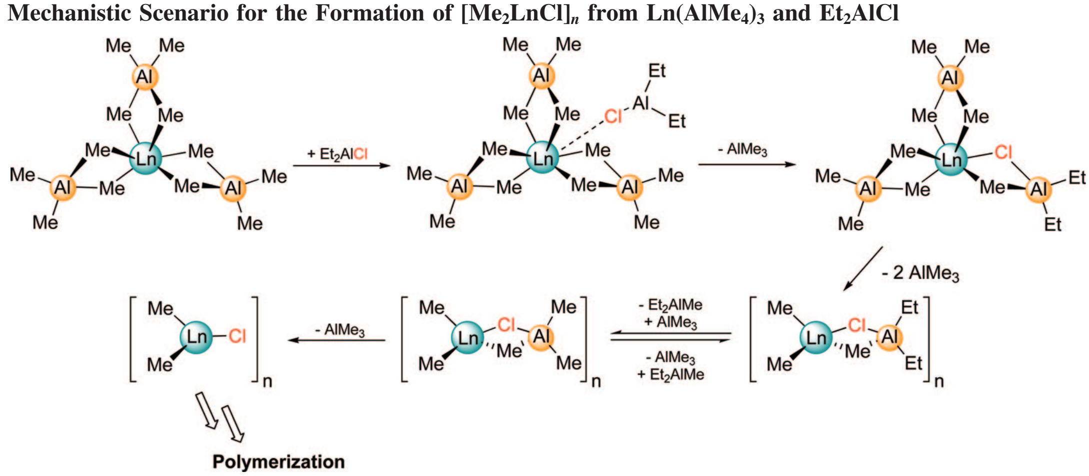
The reactivity of $Ln(AlMe_4)_3$ toward several monoanionic (Chart 6)[150−152] and dianionic chelating nitrogen donor ligands (Chart 7)[126,140] has been investigated. Reaction according to Scheme 12 was observed in all cases, leading to rare-earth metal complexes that contain $[AlMe_4]$ moieties or cleavage (**31**) and C−H bond activation products (**32** and **37**) thereof.

The overall yields of rare-earth metal containing products, however, were significantly dependent on the rare-earth metal size. Competitive formation of aluminum complexes ap-

Scheme 13. Proposed Mechanistic Scenario of Kinetically and Thermodynamically Controlled Ligand Attack Occurring in Reactions between the Imino−Amido−Pyridine Ligand Precursor and $Ln(AlMe_4)_3$ (D) (H[NNN] = Imino−Amido−Pyridine; According to Ref 150)



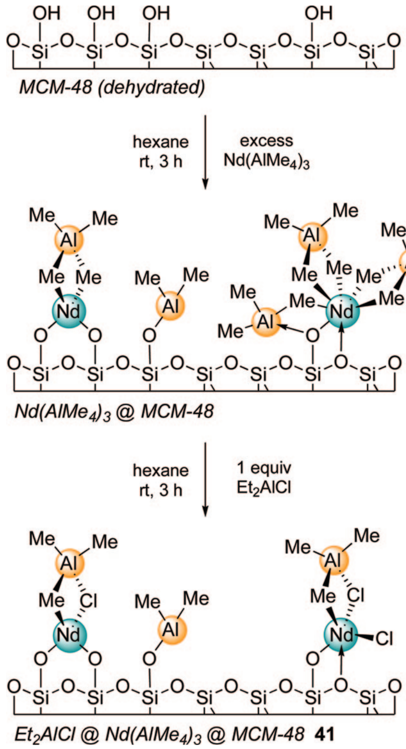
Scheme 14. Mechanistic Scenario for the Formation of $[Me_2LnCl]_n$ from $Ln(AlMe_4)_3$ and Et_2AlCl



peared to be inherent to the interaction of nitrogen donor ancillary ligands and $Ln(AlMe_4)_3$. The product distributions seem to be the result of kinetically controlled reaction sequences (Scheme 13). The key feature appears to be the kinetically controlled initial attack of the ancillary ligand's amine functionality at a bridging *or* terminal methyl group of one tetramethylaluminate moiety. In the presence of easily accessible bridging methyl groups, particularly for the larger rare-earth metal centers (La−Nd), methane elimination reaction between a bridging methyl group and the amine functionality (Scheme 13, $\mathbf{I}_1$) results in the formation of thermodynamically stable Ln−N(ancillary ligand) bonds (Scheme 13, **33**). Because of enhanced steric crowding, the thermodynamically less favored attack at a terminal methyl group appears to be pronounced for $Ln(AlMe_4)_3$ of the small rare-earth metal centers (Lu−Y) (Scheme 13, $\mathbf{I}_2$). Consequent bond formation to the adjacent aluminum atom proceeds under loss of methane and leads to preferential formation of the respective aluminum complexes (Scheme 13, $\mathbf{I}_3$ → **38** → **39**). A significantly increased yield of aluminum side-products with decreasing metal cation size (La < Nd < Y ≪ Lu) is inherent to all investigated systems, substantiating the proposed mechanistic scenario.[126,140,150,151]

Homoleptic $Ln(AlMe_4)_3$ reacts with R_2AlCl (R = Me, Et) under formation of polymeric/ionic mixed-methyl/chloride rare-earth metal compounds $[Me_2LnCl]_n$/$[MeLnCl_2]_n$ (**40**).[128,153] Such compounds are discussed as possible polymerization-initiating species in the industrial *cis*-1,4 stereospecific polymerization of dienes. Mixtures containing $Nd(AlMe_4)_3$ and Et_2AlCl initiate the stereospecific polymerization of isoprene with very high activities. The resulting polyisoprene shows very high *cis*-1,4 content (99%) and narrow molecular weight distributions ($M_n/M_w = 2.11$).[153] On the basis of NMR spectroscopic investigations and catalytic studies, a mecha-

Scheme 15. Proposed Surface Species of Hybrid Materials after Immobilization of $Nd(AlMe_4)_3$ and Et_2AlCl on Dehydrated MCM-48



nistic scenario for the formation of $[Me_2LnCl]_n$ from $Ln(AlMe_4)_3$ and Et_2AlCl has been proposed (Scheme 14).[153]

In a preliminary study, cubic mesoporous silica MCM-48 featuring a three-dimensional mesopore arrangement was applied to heterogenize binary $[Nd(AlMe_4)_3/Et_2AlCl]$ precatalyst systems (Scheme 15).[128] The organometallic−inorganic hybrid material **41** was characterized by means of FTIR spectroscopy, elemental analysis, and nitrogen physisorption. The neodymium-grafted materials performed as efficient single-component catalysts in the slurry polymerization of isoprene. Polymer analysis revealed high-*cis*-1,4-stereospecificities (>99% *cis*) and narrow molecular weight distributions ($M_n/M_w = 1.33-1.88$).

4. Tetramethylgallate Complexes $Ln(GaMe_4)_3$

In 1994, Evans et al. reported the synthesis and molecular structure of neodymium(III) tris(tetramethylgallate) ($\mathbf{E}_{Nd}$) as the first structurally characterized molecular lanthanide−gallium heterobimetallic complex.[121] The reaction of 6 equiv or an excess of $GaMe_3$ with a suspension of $Nd(NMe_2)_3(LiCl)_3$ in hexane afforded the solvent-free heterobimetallic alkyl compound $Nd(GaMe_4)_3$ in high yield (Scheme 16, I).

Scheme 16. Synthesis of $Ln(GaMe_4)_3$ (E)

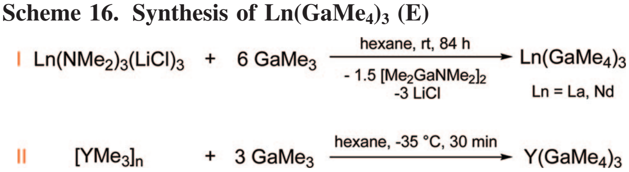
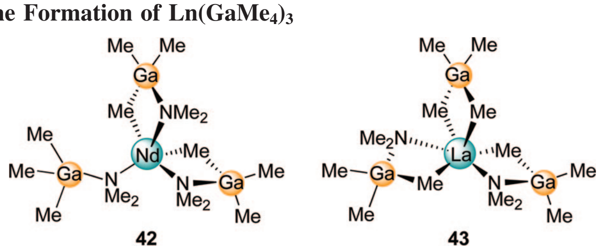


Chart 8. Isolated Reaction Intermediates Occurring during the Formation of $Ln(GaMe_4)_3$



The formation of tetramethylgallate ligands is likely to occur through intermediate coordination of Lewis acidic $GaMe_3$ to the basic amido-nitrogen atoms of $Ln(NMe_2)_3(LiCl)_3$. An additional equivalent of $GaMe_3$ triggers the complete [amido] → [methyl] exchange, leading to $[GaMe_4]$ ligands (see section 3.3). Successful isolation and characterization of the $GaMe_3$ adduct $Nd(NMe_2)_3(GaMe_3)_3$ (**42**) (Chart 8) and partially exchanged complex $La(GaMe_4)[(NMe_2)(GaMe_3)]_2$ (**43**) (Chart 8) support the proposed stepwise mechanism.[121]

Ligand transformation is further driven by the formation of very stable $[Me_2GaNMe_2]_2$, which can be separated from $Ln(GaMe_4)_3$ by fractional crystallization. With the discovery of $[LnMe_3]_n$ (**B**), an alternative and economic synthesis route toward homoleptic $Ln(GaMe_4)_3$ evolved.[71,103] Polymeric compound $[YMe_3]_n$ could be redissolved by $GaMe_3$, yielding very pure $Y(GaMe_4)_3$ in almost quantitative yield (Scheme 16, II). The stoichiometric use of expensive trimethylgallium and the avoidance of undesired gallium-containing byproducts are clearly favorable attributes. However, the applicability of this synthesis approach is so far limited to yttrium as a rare-earth metal center.

Tris(tetramethylgallate) complexes of the rare-earth metals are soluble in hydrocarbons and aromatic solvents. Donor solvents lead to immediate donor cleavage of the $[GaMe_4]$ ligand (see section 3.4). Single crystals of the neodymium and yttrium derivatives have been obtained from hexane solutions and revealed octahedrally coordinated rare-earth metal cations and a tetrahedral geometry about the gallium metal centers (Figure 17).[103,121] All three Ln−C−Ga−C rings are almost planar, and two of the hydrogen atoms at the five-coordinate bridging carbon atoms are tilted toward the rare-earth metal center. Compared with structurally related $Ln(AlMe_4)_3$, the LnGa distances are considerably shorter than the respective LnAl distances, which is further reflected in less acute C−Ln−C angles.

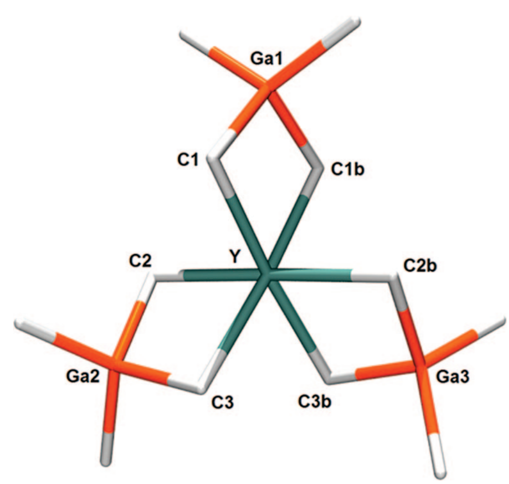
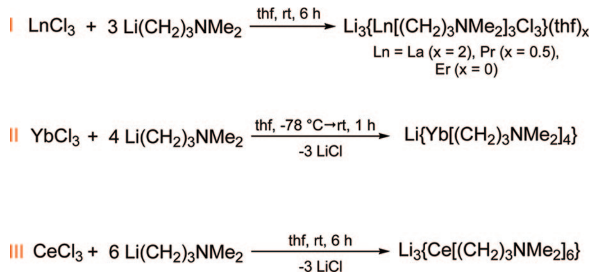


Figure 17. Solid-state structure of $Y(GaMe_4)_3$ ($\mathbf{E}_Y$), adapted from ref 103.

Scheme 17. Synthesis of Dimethylaminopropyl Complexes (F)



5. Dimethylaminopropyl Complexes $Li_3\{Ce[(CH_2)_3NMe_2]_6\}$ and $Li\{Yb[(CH_2)_3NMe_2]_4\}$

The large size of the rare-earth metal cation and its preference for high coordination numbers challenges the development of potential hydrocarbyl ligands. One concept to achieve steric and electronic saturation of the rare-earth metal center is the use of ligands containing "built-in" chelating donor functionalities. Intramolecular ring formation via dative bonds stabilizes mononuclear complexes by the chelate and entropy effect. Ligand-bonded donor groups can further compete with donor-solvent molecules for coordination sites, enhancing the thermal stability of the resulting compounds. The 3-(*N*,*N*-dimethylamino)propyl moiety appeared as well suited for the formation of a multiplicity of main group[154−157] and transition metal chelates.[158−160] The envisaged synthesis of neutral homoleptic dimethylaminopropyl complexes of the rare-earth metals by reaction of anhydrous $LnCl_3$ (Ln = La, Pr, Er) with $Li(CH_2)_3NMe_2$ did not yield the desired products but resulted in the formation of LiCl containing compounds $Li_3\{Ln[(CH_2)_3NMe_2]_3Cl_3\}(thf)_x$ (**F**) (Scheme 17, I).[161] Salt contamination was found irrespective of the amount of lithium alkyl used, and attempted separation of lithium chloride by extraction and recrystallization was unsuccessful. Analogous reactions of $NdCl_3$ and $DyCl_3$ with $Li(CH_2)_3NMe_2$ revealed the decomposition of the organic ligands already at ambient temperature. When treating $YbCl_3$ with 4 equiv of $Li(CH_2)_3NMe_2$, red crystals of the homoleptic dimethylaminopropyl complex $Li\{Yb[(CH_2)_3NMe_2]_4\}$ ($\mathbf{F}_{Yb}$) could be isolated in moderate yield (Scheme 17, II).[162] Applying a similar synthesis procedure to cerium(III) chloride in the presence of 6 equiv of the lithium alkyl gave anionic $Li_3\{Ce[(CH_2)_3NMe_2]_6\}$ ($\mathbf{F}_{Ce}$) (Scheme 17, III).

Anionic rare-earth metal dimethylaminopropyl complexes are soluble in aliphatic and ethereal solvents. The described compounds are thermally stable and decompose at temperatures above 110 °C under formation of dimethylamine, propene, and small amounts of higher hydrocarbons. Despite the presence of β-hydrogen atoms, β-hydride elimination as a decomposition pathway has not been observed.[161,162]

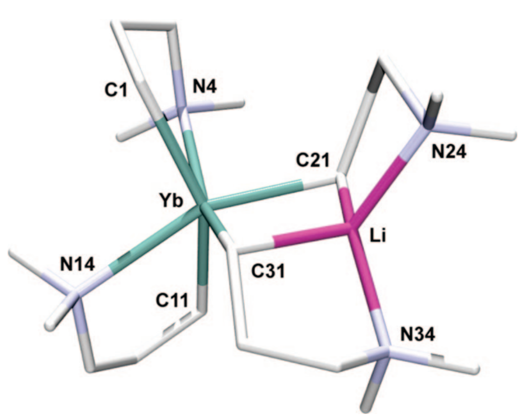


Figure 18. Solid-state structure of $Li\{Yb[(CH_2)_3NMe_2]_4\}$ ($\mathbf{F}_{Yb}$), adapted from ref 162.

The solid-state structure of $Li\{Yb[(CH_2)_3NMe_2]_4\}$ ($\mathbf{F}_{Yb}$) revealed a distorted octahedral geometry at the ytterbium metal center (Figure 18).[162] Two $[(CH_2)_3NMe_2]$ ligands coordinate in a chelating fashion to the ytterbium metal center, while the dimethylamine functionalities of the other two alkyl ligands form a dative bond toward the lithium cation. On the basis of the atomic distances C21−Li and C31−Li, multicentered bonding has been proposed, which results in a distorted tetrahedral coordination of lithium.

Derivatization of dimethylaminopropyl rare-earth metal complexes by means of alkane elimination has not been reported so far.

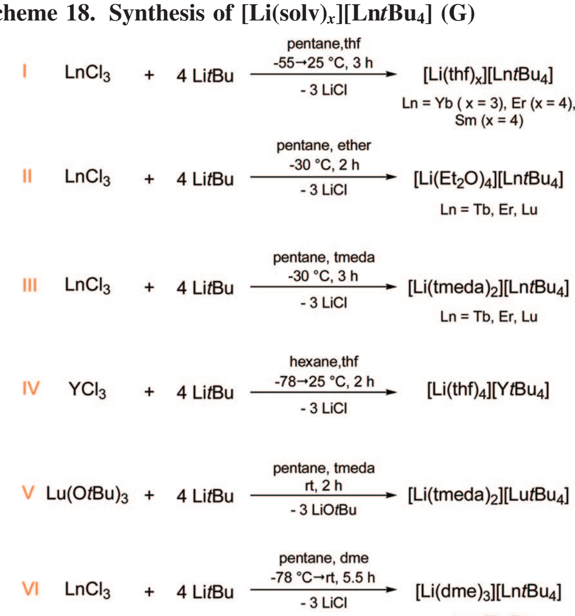
6. tert-Butylate Complexes $[Li(solv)_x][LntBu_4]$

The first synthesis of homoleptic *tert*-butylate complexes of the rare-earth metals was reported in 1978 by Evans.[163] Following the synthesis approach in Scheme 18, I, thf adducts $[Li(thf)_x][Ln\mathit{t}Bu_4]$ (Ln = Sm, Er, Yb) have been isolated and characterized by means of elemental analysis, IR spectroscopy, magnetic susceptibility, and ^1H NMR spectroscopy (Sm).

Several years later, Schumann et al. synthesized the diethyl ether analogues $[Li(Et_2O)_4][Ln\mathit{t}Bu_4]$ of lutetium, erbium, and terbium (Scheme 18, II).[97] Ate complex formation was reported regardless of the stoichiometric ratio of the starting materials. Exchanging the ether donors by tmeda allowed for the isolation of compounds $[Li(tmeda)_2][Ln\mathit{t}Bu_4]$ (Scheme 18, III).[97] An alternative synthesis protocol starting from $Ln(O\mathit{t}Bu)_3$ and 4 equiv of Li*t*Bu in the presence of tmeda yielded products of the same composition (Scheme 18, V).[97] Aiming at the synthesis of tetravalent *tert*-butylate rare-earth metal complexes, the preparation of dme analogues $[Li(dme)_3][Ln\mathit{t}Bu_4]$ (Ln = Tb, Er) was reported (Scheme 18, VI).[164]

Compounds $[Li(solv)_x][Ln\mathit{t}Bu_4]$ are insoluble in hydrocarbon solvents and form oils in aromatic solvents. They are completely soluble in ethereal solvents (Et_2O, thf).

Scheme 18. Synthesis of $[Li(solv)_x][Ln\mathit{t}Bu_4]$ (G)



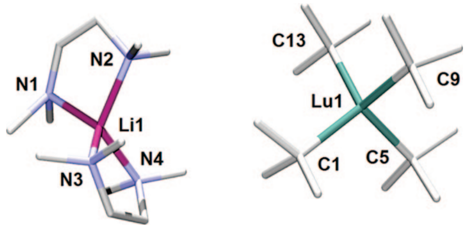
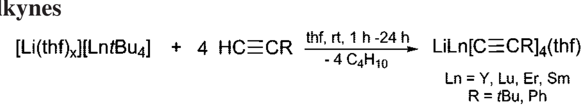


Figure 19. Solid-state structure of [Li(tmeda)$_2$][Lu*t*Bu$_4$] ($\mathbf{G}_{\text{Lu-tmeda}}$), adapted from ref 165.

Scheme 19. Reactivity of [Li(thf)$_x$][Ln*t*Bu$_4$] ($\mathbf{G}_{\text{thf}}$) toward Alkynes



The solid-state structures of [Li(tmeda)$_2$][Lu*t*Bu$_4$] ($\mathbf{G}_{\text{Lu-tmeda}}$) and [Li(dme)$_3$][Er*t*Bu$_4$] ($\mathbf{G}_{\text{Er-dme}}$) revealed solvent-separated ion pairs (Figure 19).[164,165] The rare-earth metal center of the anionic [Ln*t*Bu$_4$] unit is ligated by the four *tert*-butyl groups in an approximately tetrahedral arrangement. The Ln−C distances and the C−Ln−C angles (107.3−111.2°) are in the expected range.

Despite the presence of *β*-hydrogen atoms, compounds [Li(solv)$_x$][Ln*t*Bu$_4$] provide relatively high stability. [Li(thf)$_x$][Ln*t*Bu$_4$] (Ln = Yb, Sm) were reported to be stable for several days at ambient temperature.[163] Thermal decomposition of the respective samarium compound was monitored by NMR spectroscopy, and it was suggested that dissociation of Li*t*Bu occurs as one of the initial decomposition steps. The absence of equivalent quantities of 2-methylpropene and 2-methylpropane after decomposition led to the conclusion that *β*-hydride elimination is not the most facile degradation pathway.[166] This phenomenon is in contrast to transition metal organometallic chemistry, where *β*-hydride elimination usually prevents the formation of stable *t*Bu species.

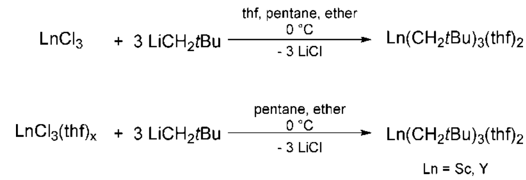
[Li(thf)$_x$][Ln*t*Bu$_4$] react with alkynes according to an acid−base reaction under formation of tetra(alkynide) anions [Ln(C≡CR)$_4$]$^-$ (Scheme 19). The *t*Bu ligands are hereby completely displaced under concomitant formation of 2-methylpropane.[167,168]

Already under mild conditions, [Li(tmeda)$_2$][Ln*t*Bu$_4$] reacts with α,*β*-unsaturated aldehydes and ketones under formation of 1,2-addition products.[165] All four *t*Bu groups can be transferred, but rare-earth metal containing reaction intermediates could not be isolated. Attempts to oxidize *tert*-butylate complexes [Li(dme)$_3$][Ln*t*Bu$_4$] to neutral tetra(*tert*-butyl) rare-earth metal(IV) compounds by common oxidizing agents (dry O$_2$, Ag-salts, 1,1′-dimethylferrocenium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) did not yield isolable compounds.[164]

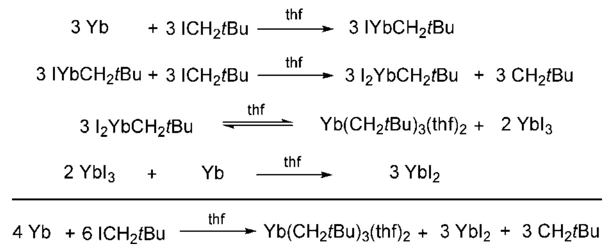
7. Neopentyl Complexes Ln(CH$_2$tBu)$_3$(thf)$_2$

Lappert and Pearce reported the first group 3 neopentyl complexes Ln(CH$_2$*t*Bu)$_3$(thf)$_2$ (**H**) together with their silyl analogues Ln(CH$_2$SiMe$_3$)$_3$(thf)$_2$ (**I**) in 1973.[72] A trigonal-bipyramidal arrangement of the ligands around the metal center was anticipated by the ^{1}H NMR spectra of Sc(CH$_2$*t*Bu)$_3$(thf)$_2$ and Y(CH$_2$*t*Bu)$_3$(thf)$_2$, but final structural proof was not supplied until 30 years later when Niemeyer successfully crystallized the respective ytterbium compound Yb(CH$_2$*t*Bu)$_3$(thf)$_2$.[169]

Scheme 20. Synthesis of Ln(CH$_2$*t*Bu)$_3$(thf)$_2$ (H) by Salt Metathesis



Scheme 21. Synthesis of Yb(CH$_2$*t*Bu)$_3$(thf)$_2$ ($\mathbf{H}_{\text{Yb}}$)



Whereas Lappert and Pearce followed the widely used synthesis procedure starting from lanthanide tris(halides) and lithium alkyl reagents (Scheme 20), Yb(CH$_2$*t*Bu)$_3$(thf)$_2$ was synthesized directly from Yb metal and organohalides (Scheme 21).[169]

Such a direct approach is more common for the synthesis of divalent organolanthanide complexes, and reaction mixtures often provide complex mixtures of Ln(II) and Ln(III) organyls. Purple crystals of Yb(CH$_2$*t*Bu)$_3$(thf)$_2$ were obtained from reaction mixtures containing Yb chips and 2,2-dimethylpropyliodide (neopentyliodide).

^{1}H NMR spectroscopy and magnetic-susceptibility measurements confirmed the presence of a paramagnetic Yb(III) metal center. The expected trigonal-bipyramidal structure could finally be proven by X-ray structure determination (Figure 20).[169]

Structural details are in very good agreement with those found in the respective Yb(CH$_2$SiMe$_3$)$_3$(thf)$_2$ structure. The O−Yb−O angle (178.8°) between the axial thf donor molecules is very close to the ideal value, but the highest possible C_{3h} symmetry is not accomplished. Two [CH$_2$*t*Bu] ligands are facing each other. Steric repulsion is reflected in the nonuniform C−Yb−C angles (110.3°−133.5°) and Yb−C bond lengths (2.36−2.39 Å).

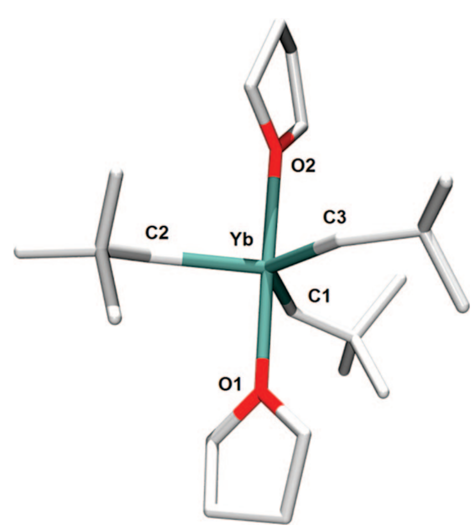
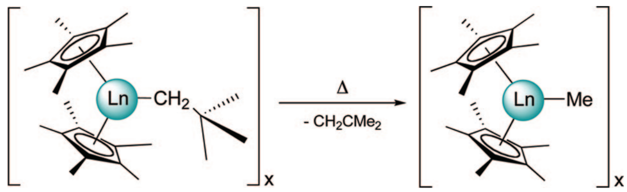


Figure 20. Solid-state structure of Yb(CH$_2$*t*Bu)$_3$(thf)$_2$ ($\mathbf{H}_{\text{Yb}}$), adapted from ref 169.

Scheme 22. Decomposition of $[(C_5Me_5)_2Ln(CH_2tBu)]_x$ (44) via β-Methyl Elimination



Very little is known about rare-earth metal neopentyl complexes. Considering the wide application of the respective tris(trimethylsilyl)methyl complexes, this is especially surprising. Further derivatizations of lanthanide alkyls $Ln(CH_2tBu)_3(thf)_2$ by means of alkane elimination have not been reported so far. The low thermal stability of $[CH_2tBu]$ containing compounds could be a reasonable explanation for the low number of reported representatives. Metallocenes $(C_5Me_5)_2Ln(CH_2tBu)$ (**44**) (Ln = Sc, Lu) could be obtained by salt-metathesis reaction of $[(C_5Me_5)_2LnCl]_x$ and $LiCH_2tBu$.[170,171] Such compounds decompose at ambient temperature, and their solutions are sensitive to ambient light. The stability of **44** the hereby decreases with increasing size of the lanthanide cation, and decomposition occurs under formation of the β-methyl elimination products $[(C_5Me_5)_2LnMe]_x$ (Scheme 22)[170,171] No α-agostic interaction of the neopentyl ligand and the lanthanide metal center—providing further stabilization—was observed in the solid-state structure of monomeric $(C_5Me_5)_2Sc(CH_2tBu)$. These findings substantiate the low thermal stability of the homoleptic compounds and demonstrate possible decomposition pathways, regardless of the absence of a β-hydrogen atom.

8. (Trimethylsilyl)methyl Complexes

In 1969, trimethylsilyl-substituted methyls were recognized as valuable ligands for main group and transition metal organometallic chemistry.[172] Useful properties like thermal stability, solubility, and chemical reactivity are conferred on their metal complexes. Steric bulk, the stabilizing effect of the silyl group, and the absence of β-hydrogen or β-alkyl substituents characterize this important class of alkyl ligands.[55]

8.1. Synthesis, Structure, and Properties of $Ln(III)(CH_2SiMe_3)_3(solv)_x$ and $[cation(solv)_x][Ln(CH_2SiMe_3)_4]$

The application of homoleptic (trimethylsilyl)methyl rare-earth metal complexes $Ln(CH_2SiMe_3)_3(thf)_x$ ($\mathbf{J}_{thf}$) underwent an exceptional development during the past decade. Today, $Ln(CH_2SiMe_3)_3(thf)_x$ are among the most widely used starting materials in organorare-earth metal chemistry. Although first synthesized as early as 1973 by Lappert and Pearce,[72] detailed investigations into structure and reactivity of these lanthanide hydrocarbyls were presented only recently.

The initial synthesis of group 3 (trimethylsilyl)methyl complexes $Sc(CH_2SiMe_3)_3(thf)_2$ and $Y(CH_2SiMe_3)_3(thf)_2$[72] was extended to the lanthanide metals some years later. Main contributions were made by the groups of Lappert and Schumann describing the respective lutetium,[173] ytterbium,[174] thulium, erbium,[174,175] and terbium[174] compounds. The representative of the medium-sized lanthanide metal center samarium[173] was described and characterized in 2002, marking the upper cation size limit for isolable compounds $Ln(CH_2SiMe_3)_3(thf)_x$ ($\mathbf{J}_{thf}$).

Scheme 23. Synthesis of $Ln(CH_2SiMe_3)_3(solv)_x$ (J)

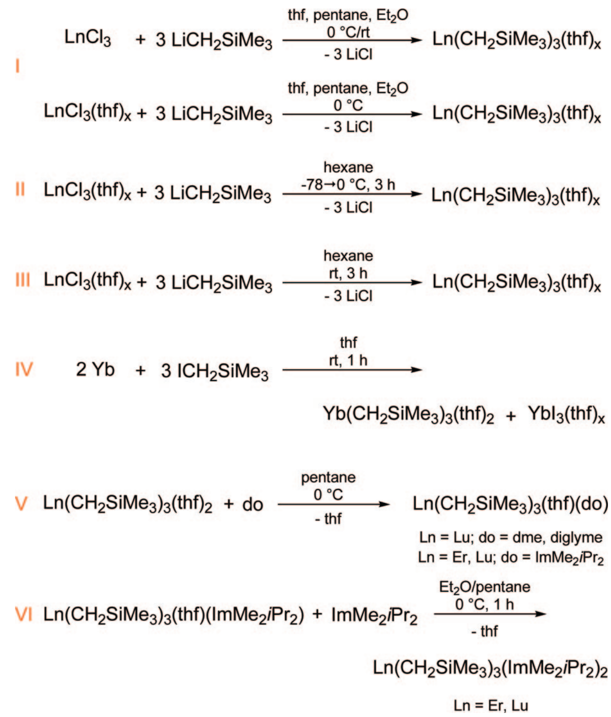


Table 3. $Ln(CH_2SiMe_3)_3(thf)_x$ ($\mathbf{J}_{thf}$): Synthesis, thf Coordination, Yield, And Characterization

Ln	synthesis	$thf_{coord.}(x)$	yield	characterization	ref
Sc	I	2		^1H, ^{13}C, IR, elemental analysis (EA), mp	72
	II	2			
	III	2	71%		179
Y	I	2		^1H, ^{13}C, ^{29}Si, IR, EA, mp, X-ray ($x = 3$)	72
	II	2	82%		176, 180
	III	3	69%		179
Lu	I	2		^1H, ^{13}C, IR, EA, X-ray	177, 181
	II	2	63%		177
	III	2	65%		179
Yb	I	2		^1H, IR, EA, mp, X-ray	174, 181
	II	2			
	IV	2	48%		178
Tm	I	2		IR, EA	181, 182
	II	2			
Er	I	2	29%	IR, EA, mp, X-ray	174, 175
Tb	I	2		IR, mp, EA	174
	II	2			
Sm	I	3	50%	^1H, ^{13}C, IR, EA, mp, X-ray	173

Several synthesis procedures for $Ln(CH_2SiMe_3)_3(thf)_x$ have been described, the majority following a salt-metathesis reaction of the anhydrous rare-earth metal halides $LnCl_3$ or the thf adducts $LnCl_3(thf)_x$ and 3 equiv of $LiCH_2SiMe_3$ (Scheme 23, I−III). The original syntheses reported by the groups of Lappert and Schumann follows eq I in Scheme 23 using hexane (pentane)/diethylether mixtures combined with (stoichiometric) amounts of thf.[72,175] Reactions were performed at ca. 0 °C and ambient temperature, respectively. With the introduction of compounds $Ln(CH_2SiMe_3)_3(thf)_x$ as rare-earth metal alkyl precursors, slightly modified synthesis protocols II and III have been applied using hexane suspensions of $LnCl_3(thf)_x$ and $LiCH_2SiMe_3$.[176,177]

Synthesis route IV starting from Yb chips and ICH_2SiMe_3 is limited to this redox-active Yb metal center.[178] In situ preparation of the rare-earth metal alkyls has also proved suitable when further reacting $Ln(CH_2SiMe_3)_3(thf)_x$ in alkane elimination reactions with protic reagents. Table 3 sum-

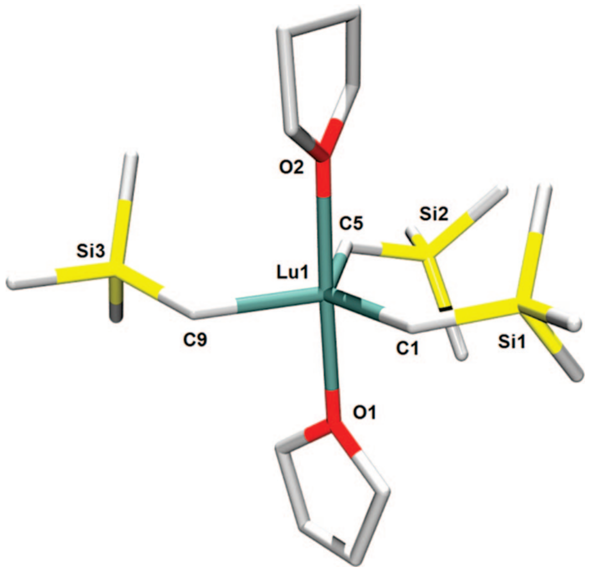


Figure 21. Solid-state structure of $Lu(CH_2SiMe_3)_3(thf)_2$ ($\mathbf{J}_{Lu-thf}$), adapted from ref 173.

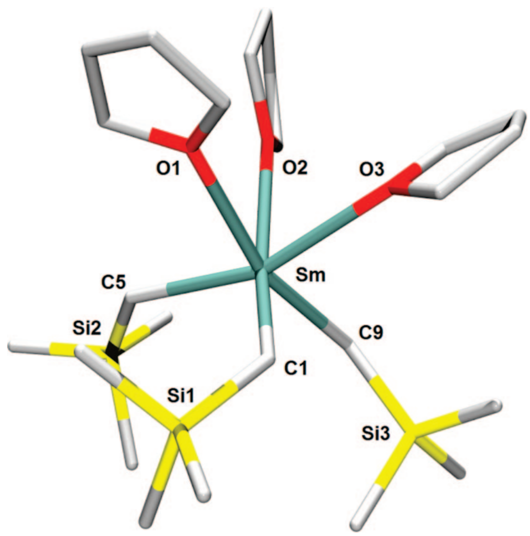


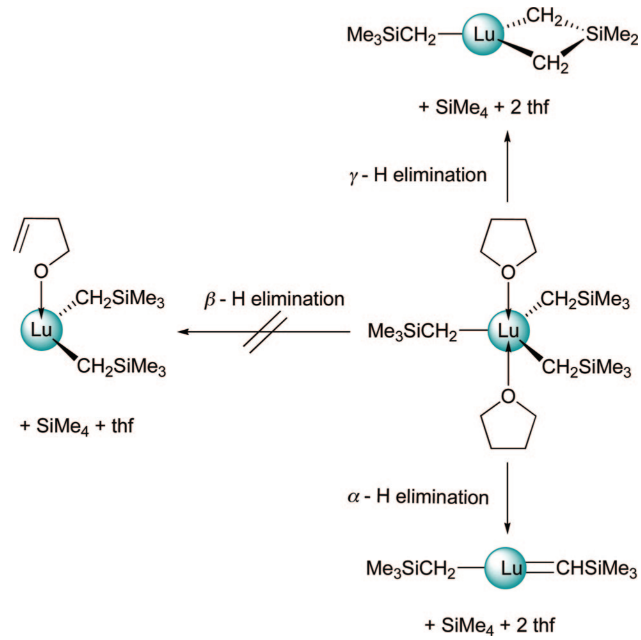
Figure 22. Solid-state structure of $Sm(CH_2SiMe_3)_3(thf)_3$ ($\mathbf{J}_{Sm-thf}$), adapted from ref 173.

marizes the reported synthesis approaches, the number of coordinating thf molecules, yields, and characterization of compounds $\mathbf{J}_{thf}$.

Because of inefficient steric shielding of the rare-earth metal center by the $[CH_2SiMe_3]$ ligands, complexes **J** require stabilizing donor molecules, usually thf. The number of thf molecules coordinated increases with increasing size of the rare-earth metal cation (Table 3).

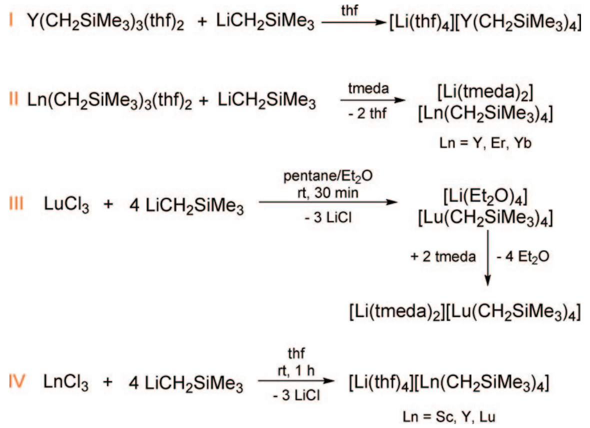
Solvation affects the solid-state structures of Ln-$(CH_2SiMe_3)_3(thf)_x$ (Figures 21 and 22). The representatives of the smaller rare-earth metals $Ln(CH_2SiMe_3)_3(thf)_2$ (Ln = Lu,[173] Yb,[178] and Er[173]) feature a five-coordinate metal center with the three $[CH_2SiMe_3]$ ligands occupying the equatorial positions and the thf oxygen atoms occupying the axial positions of a trigonal bipyramid (Figure 21). A propeller-like arrangement of the alkyl ligands around the metal center (C_{3h} symmetry) is not realized. Rather, two of the silyl groups are facing each other, causing nonuniform angles C−Ln−C (max. 110°−134°) and Ln−C distances. X-ray structure analyses of $Y(CH_2SiMe_3)_3(thf)_3$[180] and $Sm(CH_2SiMe_3)_3$-$(thf)_3$[173] revealed a distorted *fac*-octahedral coordination of alkyl ligands and the three donor thf molecules (Figure 22). The angles O−Ln−O (74°−81°) are considerably smaller than angles C−Ln−C (101°−108°). Such octahedral coordination can also be enforced by thf → diglyme ligand exchange as reported for $Lu(CH_2SiMe_3)_3(thf)(diglyme)$ (Scheme 23, V).[183] Replacement of one thf molecule by 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene ($ImMe_2iPr_2$) according to Scheme 23, VI, yielded $Ln(CH_2SiMe_3)_3(thf)$-$(ImMe_2iPr_2)$ (Ln = Er, Lu).[184] In the solid state, the carbene adducts display a distorted trigonal-bipyramidal coordination sphere around the metal center. Contrary to the respective thf adducts, the thf oxygen and the third alkyl ligand occupy the axial positions of $\mathbf{J}_{thf/Im}$ while steric requirements force two alkyl ligands and one $ImMe_2iPr_2$ ligand into the equatorial positions of the trigonal bipyramid. Displacement of thf in $Ln(CH_2SiMe_3)_3(thf)(ImMe_2iPr_2)$ by a second $ImMe_2iPr_2$ donor molecule (Scheme 23, VI) results in five-coordinate complexes that resemble a strongly distorted square pyramid.[184] The edges of the basal plane are occupied by two alkyl and two $ImMe_2iPr_2$ ligands, and the apical position is occupied by the third alkyl ligand.

Scheme 24. Thermal Decomposition Pathways of $Lu(CH_2SiMe_3)_3(thf)_2$ (According to Ref 183)



A major drawback of homoleptic alkyls **J** is their thermal instability. At ambient temperature, solid and dissolved samples of $Ln(CH_2SiMe_3)_3(thf)_x$ decompose within hours, leading to oily insoluble products and the formation of $SiMe_4$.[173] Especially the derivatives of the larger lanthanides are prone to ligand degradation reactions, limiting the availability of these useful precursors to the small- and middle-sized rare-earth metals (Sc−Sm). Nevertheless, the synthesis of $Nd(CH_2SiMe_3)_3$ was published in 1980. The authors claimed a dimeric structure of the insufficiently characterized product.[185] The synthesis and isolation of the neodymium compound, however, has not been reproduced so far. In some cases, in situ alkylation of $LnBr_3(thf)_x$ with $LiCH_2SiMe_3$ followed by the addition of a protic ligand precursor yielded the desired alkylated compound in moderate yields, even for the large rare-earth metal centers.[186−189] Monitoring the reaction of $LaBr_3(thf)_4$ with 3, 4, and 5 equiv of $LiCH_2SiMe_3$ in thf-d_8 by ^1H NMR spectroscopy revealed a highly dynamic system with rapid interconversion of

Scheme 25. Formation of Ate Complexes $[Li(solv)_x][Ln(CH_2SiMe_3)_4]$ (K)



different alkyl species in solution, whereas the products derived from a 1:4 stoichiometry are the thermodynamically most stable species.[189]

Three reasonable elimination pathways have been proposed for the thermal decomposition of $Ln(CH_2SiMe_3)_3(thf)_x$, all involving the evolution of $SiMe_4$ (Scheme 24).[183] While α-H elimination from a [Ln−CH_2Si] moiety was first assumed to be the preferred decomposition pathway,[175] more detailed investigations on the thermal degradation of $Lu(CH_2SiMe_3)_3(thf)_2$ corroborate γ-H elimination to be predominant. The "face-to-face" arrangement of two of the $SiMe_3$ groups in trigonal-bipyramidal compounds $\mathbf{J}_{thf}$ (Figure 21) seems to impede the α-H elimination of $SiMe_4$, and octahedrally coordinated $Lu(CH_2SiMe_3)_3$(thf)(diglyme) proved to be thermally robust.[183] A β-H elimination mechanism involving the donor (thf) ligands could be ruled out by studies on $Lu(CH_2SiMe_3)_3(thf\text{-}d_8)_2$.

Carbene adducts $Ln(CH_2SiMe_3)_3(ImMe_2iPr_2)_2$ slowly decompose at ambient temperature under formation of so far unidentified decomposition products.[184] Tetramethylsilane, however, could not be detected, which excludes degradation via an α- or γ-elimination process yielding carbene-stabilized organorare-earth alkylidene complex $(Me_3SiCH_2)Ln({=}CHSiMe_3)(ImMe_2iPr_2)_2$.

Besides thermal instability, ate complex formation is a complicating side-effect in the synthesis of **J**. Already the earliest publications reported on the occurrence of anionic complexes $[Li(solv)_4][Ln(CH_2SiMe_3)_4]$ (**K**) regardless of the stoichiometry of $LnCl_3$ and $LiCH_2SiMe_3$.[174,181] Direct synthesis of the lithium salts **K** was achieved by reaction of $Ln(CH_2SiMe_3)_3(thf)_x$ with $LiCH_2SiMe_3$ (Scheme 25, I and II)[174,190] and $LnCl_3$ with 4 equiv of $LiCH_2SiMe_3$ (Scheme 25, III and IV),[181,190] respectively. The ate complexes are insoluble in nonpolar solvents but are readily soluble in ethers. The diethylether adducts $[Li(Et_2O)_4][Ln(CH_2SiMe_3)_4]$ are kinetically labile and follow an α-H elimination pathway, leading to lanthanide alkylidenes $Li[Ln(CH_2SiMe_3)_2(CHSiMe_3)]$, but can be stabilized by donor exchange with tmeda (Scheme 25, III).[181]

However, the use of such ate complexes as alkyl precursor is limited. So far there is only one report on the successful application of $[Li(thf)_4][Ln(CH_2SiMe_3)_4]$ for the synthesis of rare-earth metal bis(alkyl) complexes bearing a fluorenyl functionalized *N*-heterocyclic carbene ligand (Chart 10, **45**).[190]

Alkylation of homoleptic rare-earth metal aryloxide complexes proved to be an excellent synthesis approach toward

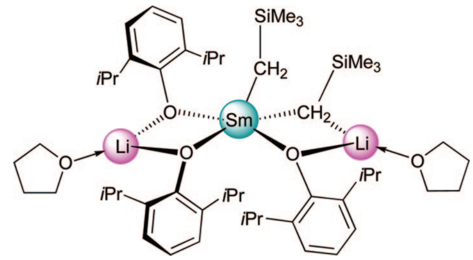
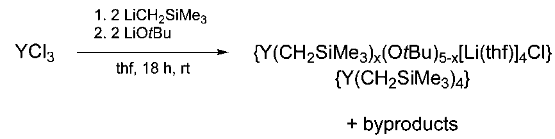


Figure 23. Structure of $[Li(thf)]_2[Sm(OAr^{iPr,H})_3(CH_2SiMe_3)_2]$ (**46**).

Scheme 26. Formation of $\{Y(CH_2SiMe_3)_x(OtBu)_{5-x}[Li(thf)_4]Cl\}\{Y(CH_2SiMe_3)_4\}$ (47)



neutral compounds $Ln[CH(SiMe_3)_2]_3$ (**O**).[75] Attempts to synthesize neutral $Sm(CH_2SiMe_3)_3(thf)_3$ following a similar synthesis protocol starting from monomeric aryloxide $Sm(OAr^{iPr,H})_3(thf)_2$ and 3 equiv of $LiCH_2SiMe_3$, however, gave the mixed aryloxide−alkyl ate complex $[Li(thf)]_2[Sm(OAr^{iPr,H})_3(CH_2SiMe_3)_2]$ (**46**) in moderate yield.[191] The ionic compound can rather be described as the product of an addition reaction of 2 equiv of $LiCH_2SiMe_3$ than that of a ligand-substitution reaction. The solid-state structure displays a distorted square-based pyramidal samarium metal ligated by one terminal and one bridging [CH_2SiMe_3] ligand. The three [$OAr^{iPr,H}$] ligands are bridging between the lanthanide metal and the lithium cations (Figure 23).

Interesting reactivity patterns were observed when combining [CH_2SiMe_3] and alkoxide ligands. In an attempt to make a mixed alkyl/alkoxide compound starting from YCl_3 with 2 equiv of $LiCH_2SiMe_3$ and 2 equiv of Li*Ot*Bu, the product of a nearly complete segregation of alkyl and alkoxide ligands into anionic and cationic compounds was observed (Scheme 26).[192]

X-ray crystallography revealed the ion pair $\{Y(CH_2SiMe_3)_x(OtBu)_{5-x}[Li(thf)_4]Cl\}\{Y(CH_2SiMe_3)_4\}$ (**47**) to be the outcome of this intricate reaction. While the cationic unit shows a complex structure of a central five-coordinate yttrium atom surrounded by [O*t*Bu] ligands (the cation contains a disordered ligand, which is a mixture of ∼75% O*t*Bu and 25% CH_2SiMe_3), the anionic part contains an anionic homoleptic yttrium tetrakis(trimethylsilyl)methyl complex. The geometry about the yttrium central metal describes a tetrahedron with C−Y−C angles ranging from 105.9° to 113.2° (Figure 24).

8.2. $Ln(CH_2SiMe_3)_3(thf)_x$ as Synthesis Precursors

Despite the aforementioned drawbacks (cation size restrictions, thermal instability, and ate complex formation), $Ln(CH_2SiMe_3)_3(thf)_x$ ($\mathbf{J}_{thf}$) are widely used rare-earth metal alkyl synthesis precursors. Protonolysis of one, two, or all three [CH_2SiMe_3] ligands under loss of $SiMe_4$ allowed for the synthesis of an impressive variety of heteroleptic rare-earth metal (alkyl) compounds. Particularly, the access to catalytically highly active alkyl compounds including cationic variants led to extensive derivatization of $Ln(CH_2SiMe_3)_3(thf)_x$.

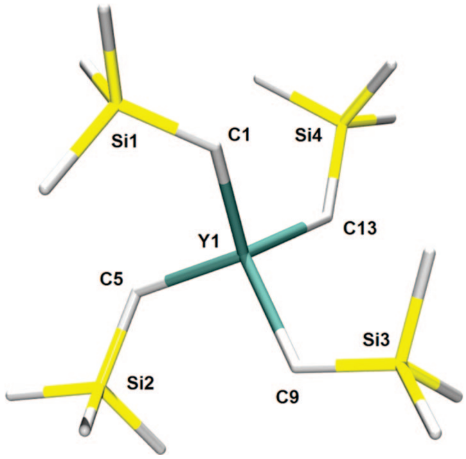


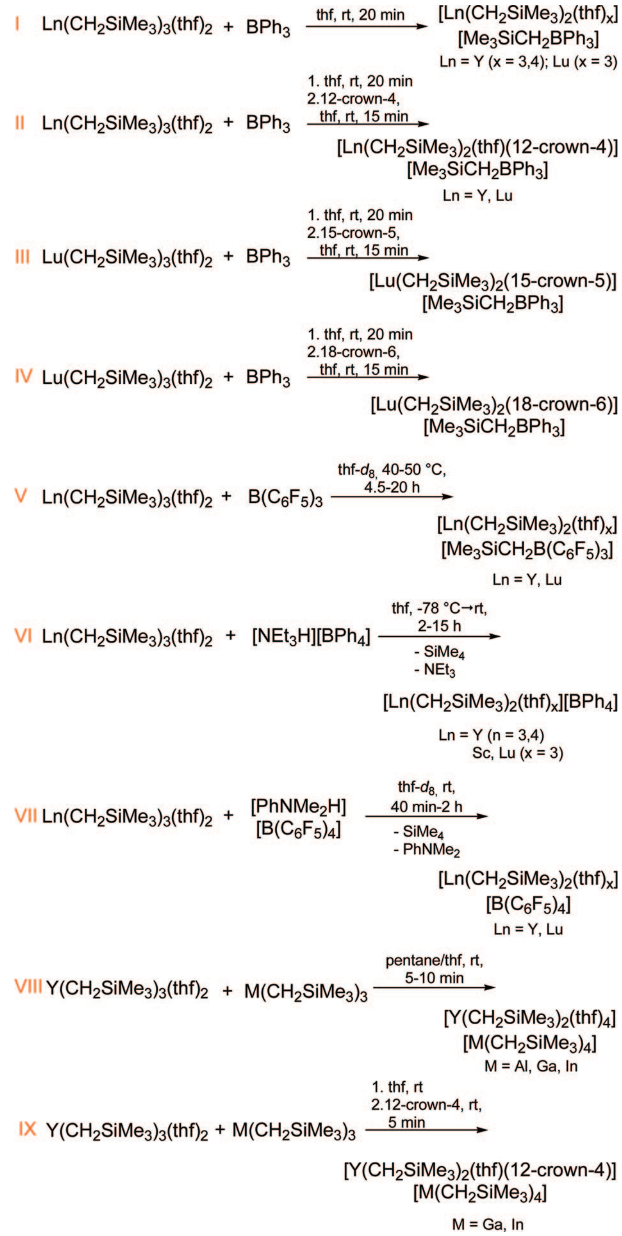
Figure 24. Solid-state structure of anionic $\{Y(CH_2SiMe_3)_4\}$ in **47**, adapted from ref 192.

8.2.1. Cationic Complexes $[Ln(CH_2SiMe_3)_{3-n}(donor)_x]^{n+}[anion]^{n-}$

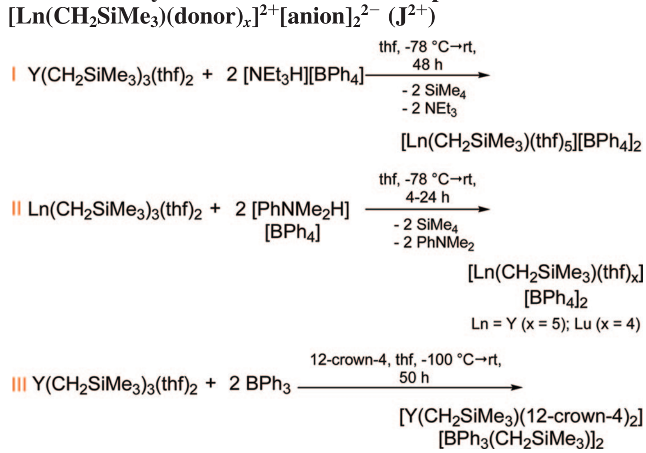
Okuda et al. found that toluene solutions of $Ln(CH_2SiMe_3)_3(thf)_2$ (Ln = Y, Tm, Er, Ho, Dy, and Tb) effectively catalyze the polymerization of ethylene upon activation with Brønsted acid $[PhNMe_2H][B(C_6F_5)_4]$ in the presence of Al*i*Bu_3.[105] The obtained polymerization activities were well correlated to the effective ionic radius of the rare-earth metal. Monocationic complexes $[Ln(CH_2SiMe_3)_2(solv)_x][B(C_6F_5)_4]$ ($\mathbf{J}^+$) and dicationic compounds $[Ln(CH_2SiMe_3)(solv)_x][B(C_6F_5)_4]_2$ ($\mathbf{J}^{2+}$) were discussed as the catalytically active species, and a series of such ionic rare-earth metal (trimethylsilyl)methyl compounds was investigated.[193−198] Neutral tris(alkyl) complexes $Ln(CH_2SiMe_3)_3(thf)_2$ react via alkyl abstraction with neutral Lewis acids, in particular group 13 organometallics such as BPh_3, $B(C_6F_5)_3$, and $M(CH_2SiMe_3)_3$ (M = Al, Ga, In), to form monocationic complexes of the type $[Ln(CH_2SiMe_3)_2(donor)_x]^+[anion]^-$ (Scheme 27, I−V, VIII, and IX).[105,193−197] The compounds display solvent-separated ion pairs while the number of coordinated donor molecules is governed by the size of the rare-earth metal cation and the type of donor ligands (thf, 12-crown-4, 15-crown-5, 18-crown-6). The reaction of the tris(alkyls) with $B(C_6F_5)_3$ in thf-d_8 requires forcing conditions (several hours at 40−50 °C; Scheme 27, V), and the resulting monocations can only be characterized in situ. Ion pairs $[Y(CH_2SiMe_3)_2(thf)_4][M(CH_2SiMe_3)_4]$ (Scheme 27, VIII and IX) are stable as thf solutions but recombine in the presence of aromatic hydrocarbons to form the respective neutral precursor compounds.[197] Cationic (trimethylsilyl)methyl complexes can further be obtained by protonolysis reaction of $Ln(CH_2SiMe_3)_3(thf)_2$ with weak Brønsted acids such as $[NEt_3H][BPh_4]$, $[PhNMe_2H][BPh_4]$, and $[PhNMe_2H][B(C_6F_5)_4]$ (Scheme 27, VI and VII).[105,195,196] Thermally fairly robust compounds can hereby be obtained with $[BPh_4]^-$ counterions, whereas mono(cations) containing the $[B(C_6F_5)_4]^-$ anion are only observable by NMR spectroscopy.

The respective two equivalent reactions of **J** with BPh_3, $[NEt_3H][BPh_4]$, and $[PhNMe_2H][BPh_4]$ result in the clean formation of thermally robust dicationic alkyl complexes $[Ln(CH_2SiMe_3)(donor)_x]^{2+}[anion]_2^{2-}$ (Scheme 28, I−III).[105,195,196] The residual alkyl group of the thf solvates is resistant to a third equivalent of $[NR_2H][BPh_4]$.

Scheme 27. Synthesis of Cationic Complexes $[Ln(CH_2SiMe_3)_2(donor)_x]^+[anion]^-$ ($\mathbf{J}^+$)



Scheme 28. Synthesis of Dicationic Complexes $[Ln(CH_2SiMe_3)(donor)_x]^{2+}[anion]_2^{2-}$ ($\mathbf{J}^{2+}$)



While cationic rare-earth metal alkyls $[Ln(CH_2SiMe_3)_{3-n}(solv)_x]^{n+}[anion]^{n-}$ are insoluble in hydrocarbons and aromatic solvents, they were reported to be soluble and stable

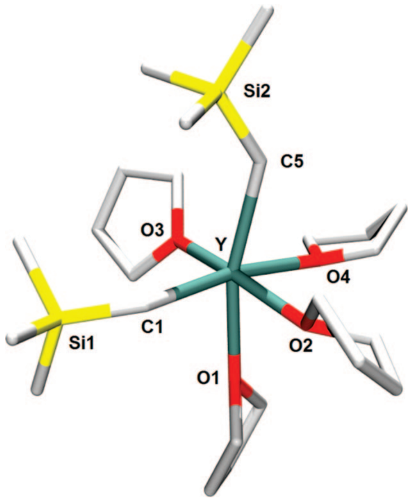
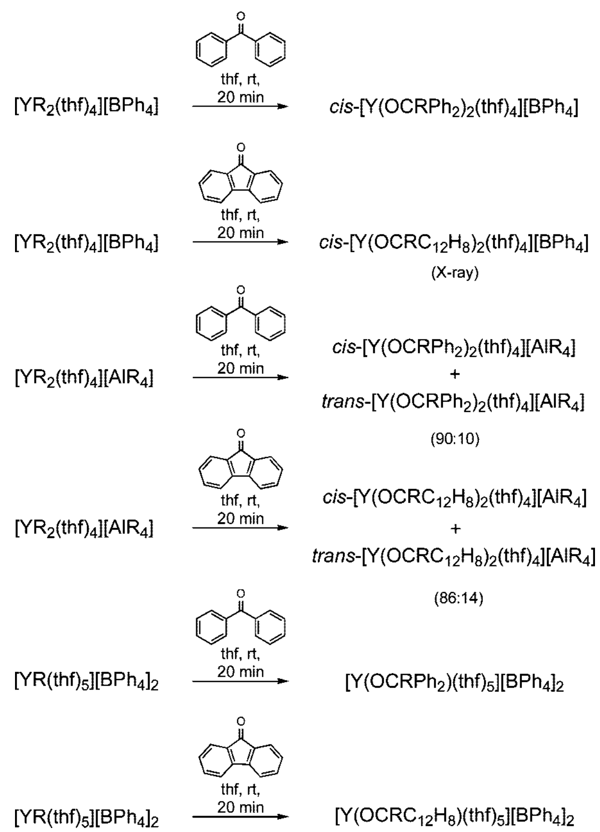


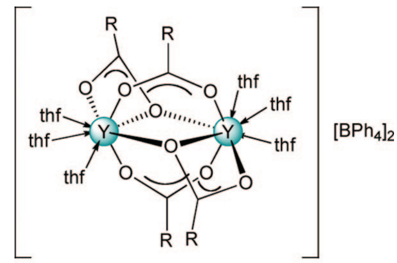
Figure 25. Solid-state structure of the cationic moiety of $[Y(CH_2SiMe_3)_2(thf)_4][Al(CH_2SiMe_3)_4]$ ($J^+_{Y-thf}/Al(CH_2SiMe_3)_4$), adapted from ref 105.

Scheme 29. Reaction of $[Y(CH_2SiMe_3)_2(thf)_4][BPh_4]$, $[Y(CH_2SiMe_3)_2(thf)_4][Al(CH_2SiMe_3)_4]$, and $[Y(CH_2SiMe_3)(thf)_5][BPh_4]_2$ with Benzophenone/Fluorenone

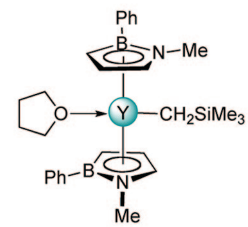


in the presence of donor solvents (thf, pyridine). Ion pair $[Y(CH_2SiMe_3)_2(thf)_4][Al(CH_2SiMe_3)_4]$ ($J^+_{Y-thf}/Al(CH_2SiMe_3)_4$) could further be activated by $[PhNMe_2H][B(C_6F_5)_4]$, providing high activity in the polymerization of ethylene. Single crystals of $J^+_{Y-thf}/Al(CH_2SiMe_3)_4$ were obtained from a pentane/thf mixture, revealing a distorted octahedral coordination geometry about the yttrium metal center (Figure 25).[105] The two remaining alkyl ligands of the cationic unit are arranged in a *cis* fashion while four thf donor molecules stabilize the yttrium metal center. Such a *cis* arrangement of the alkyl ligands was further

Chart 9. Complexes Derived from $[Y(CH_2SiMe_3)_2(thf)_4][BPh_4]$

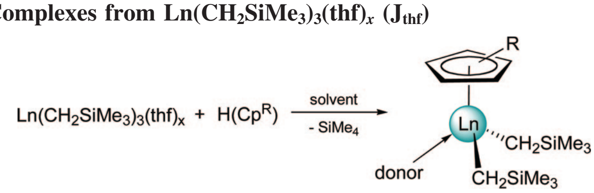


48



49

Scheme 30. General Synthesis Procedure for Half-Sandwich Complexes from $Ln(CH_2SiMe_3)_3(thf)_x$ (J_{thf})



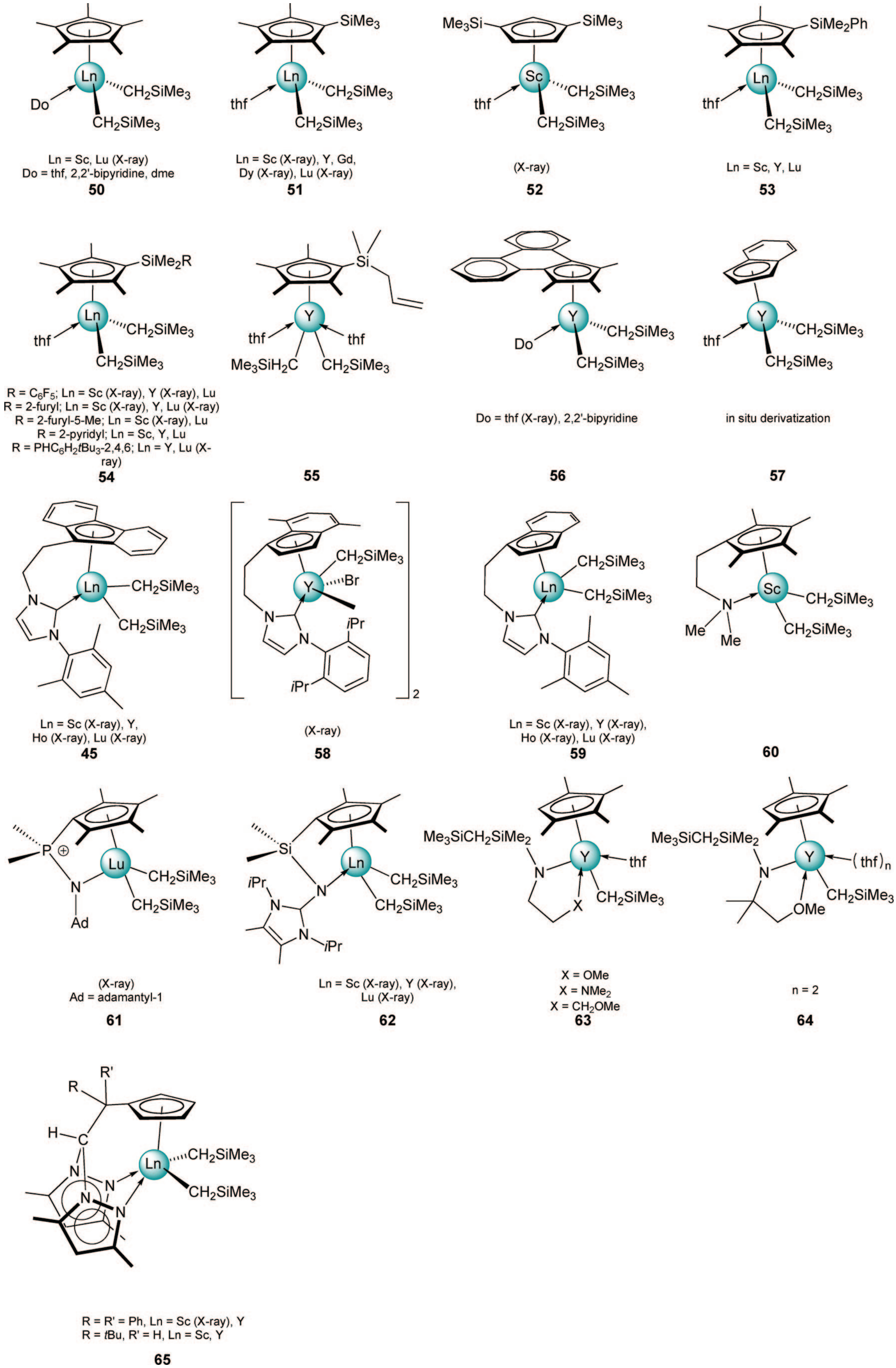
observed in the solid-state structure of $[Y(CH_2SiMe_3)_2(thf)_4][Ga(CH_2SiMe_3)_4]$.[197]

Since a highly polarized rare-earth metal−carbon bond is combined with a Lewis acidic cationic metal center, both nucleophilic and electrophilic properties can be anticipated for cationic bis(alkyl) and mono(alkyl) complexes. Accordingly, monocationic complexes $[Y(CH_2SiMe_3)_2(thf)_4][BPh_4]$ and $[Y(CH_2SiMe_3)_2(thf)_4][Al(CH_2SiMe_3)_4]$, as well as dication $[Y(CH_2SiMe_3)(thf)_5][BPh_4]_2$, were found to be highly reactive toward ketones in thf solutions at ambient temperature.[198] Whereas reactions with aliphatic ketones (acetone, pentanone-3, acetophenone) resulted in intractable mixtures of several compounds, the reactions with excess of benzophenone and fluorenone gave the expected alkylation products in high yield (Scheme 29). In the presence of carbon dioxide (1 bar), $[Y(CH_2SiMe_3)_2(thf)_4][BPh_4]$ produced dinuclear cationic complex **48** as the product of a CO_2 insertion into the rare-earth metal alkyl bond (Chart 9). Further, the yttrium monocation proved to be a suitable precursor for the synthesis of bis(1,2-azaborolyl)yttrium alkyl complex **49** (Chart 9).[199] Treatment of the rare-earth metal compound with 1 equiv of the respective lithium azaborolyl yielded the thermodynamically stable bis(1,2-azaborolyl)yttrium compound as the result of ligand redistribution.

8.2.2. Half-Sandwich Complexes

Structurally well-characterized organorare-earth metal complexes based on cyclopentadienyl ligands are of considerable interest, particularly for catalytic hydroamination and as homogeneous polymerization catalysts for both nonpolar and polar monomers. Compared with bis(cyclopentadienyl) complexes, half-sandwich rare-earth metal complexes that contain only one cyclopentadienyl ligand show an increased potential for functionalization at the metal

Chart 10. Complexes $(Cp^R)Ln(CH_2SiMe_3)_2(donor)_x$ Derived from $Ln(CH_2SiMe_3)_3(thf)_x$ (J_{thf})



center. Allowing for two σ-bonded alkyl ligands, such compounds retain one alkyl ligand upon cation formation by treatment with, e.g., organoboron reagents. Hence, they display potential catalyst precursors for polymerization reactions or organic transformations. The conventional synthesis of mono(cyclopentadienyl) rare-earth metal com-

Table 4. Further Applications of Half-Sandwich Complexes $(Cp^R)Ln(CH_2SiMe_3)_2(donor)_x$

compound	further application	ref
50	$[CH_2SiMe_3]$ exchange reactions formation of mono(cations) alternating ethylene−norbornene copolymerization insertion of CO intramolecular C−H bond activation formation of Lu/Ru heterobimetallic dihydrido complexes	205−209
51	$[CH_2SiMe_3]$ exchange reactions synthesis of hydride compounds synthesis of mixed hydride/aryloxide compounds formation of mono(cations) syndiospecific polymerization of styrene ethylene−styrene copolymerization ethylene−norbornene copolymerization (alternating and poly(ethylene-*alt*-norbornene) block-copolymers) homo- and alternating copolymerization of cyclohexene oxide with CO_2 polymerization of isoprene (3,4-enriched) styrene−isoprene copolymerization ethylene−dicyclopentadiene copolymerization ethylene, dicyclopentadiene, and styrene terpolymerization	204, 206, 210−222
52	formation of mono(cations) ethylene−norbornene copolymerization	206
53	synthesis of hydride compounds formation of mono(cations) syndiospecific polymerization of styrene ethylene−norbornene copolymerization	204, 216, 217
54	intramolecular C−H bond activation formation of mono(cations) syndiospecific polymerization of styrene ethylene−norbornene copolymerization	204, 216−218, 223−226
55	insertion of CO_2 formation of a cyclopentadienyl−allyl ligand by multiple metalation	180
56	$[CH_2SiMe_3]$ exchange reactions donor exchange formation of mono(cations) insertion of CO_2 insertion of Me_3SiNCO insertion of *i*PrN=C=N*i*Pr polymerization of ethylene	227
57	$[CH_2SiMe_3]$ exchange reactions	221
45	formation of mono(cations) polymerization of isoprene (3,4-selective)	228
58	no further application	229
59	formation of mono(cations) polymerization of isoprene (3,4-enriched)	190
60	formation of mono(cation) polymerization of ethylene	230
61	no further application	231
62	hydroamination	232
63	no further application	176
64	no further application	176
65	ROP of ε-caprolactone formation of monocations $[CH_2SiMe_3]$ exchange reactions	233, 234

plexes by salt-metathesis reactions is often hampered by ate complex formation with concomitant alkali metal salt incorporation.[200−202] Alkane elimination was found to be a facile synthesis route to complexes of the type $(Cp^R)Ln(CH_2SiMe_3)_2(donor)_x$. Reaction of $Ln(CH_2SiMe_3)_3(thf)_x$ ($\mathbf{J}_{thf}$) with the respective substituted cyclopentadiene $H(Cp^R)$ (Scheme 30) gave access to a large variety of mono(cyclopentadienyl)−bis(alkyl) complexes (Chart 10 and Table 4). Metallocene formation,[203] even in the presence of excess $H(Cp^R)$, was not observed when silyl-substituted cyclopentadienes were employed.[204] The use of silyl-free cyclopentadienes $H(C_5Me_5)$ and $H(C_5Me_4H)$ often results in mixtures of mono- and bis(cyclopentadienyl) complexes.[203]

Mono(cyclopentadienyl) complexes **51** and **53** can undergo hydrogenolysis of both alkyl ligands, affording isolable hydrido clusters.[204,210,212,219] The in situ generation of cationic mono(cyclopentadienyl) rare-earth metal complexes by alkyl abstraction using borate reagents $[Ph_3C][B(C_6F_5)_4]$ and $[PhNMe_2H][B(C_6F_5)_4]$, respectively, results in highly active polymerization catalysts (Table 4). Scandium bis(alkyl) complex $\mathbf{51}_{Sc}$ shows excellent activity for the syndiospecific styrene homopolymerization (activity, 1.36×10^4 (kg PS)/(mol Sc h); $M_w/M_n = 1.37$), and complexes **51**, **53**, and **54** proved suitable for the co- and terpolymerization of a series of monomers.[204,206,210−225]

8.2.3. Constraint Geometry Complexes

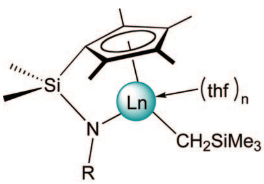
Incorporation of the cyclopentadienyl ancillary ligand into a chelate array of (pendant) donor functionalities gives access to prominent Cp derivatives. Since the original introduction by the Bercaw group, the linked amido−cyclopentadienyl (Cp) ligand has advanced to be one of the most versatile ligands for group 4 metal polymerization catalysts.[235] Catalysts based on this type of ligand provide a constrained ligand environment but are anticipated to be more active toward sterically demanding monomers than metallocenes. Amine−cyclopentadiene proligands react with $Ln(CH_2SiMe_3)_3(thf)_x$ ($\mathbf{J}_{thf}$) according to an alkane-elimination reaction in a similar manner as shown in Scheme 30. Because of the dianionic nature of the resulting ligand, only one $[CH_2SiMe_3]$ ligand is retained in the resulting compounds, which allows for further derivatization (Chart 11).

In the presence of Ph_3SiH or H_2, complexes **66**−**73** form dimeric hydrido complexes,[176,177,204,236] showing high potential in the catalytic hydrosilylation of olefins.[226,237,238] Catalytic activities and stereoselectivities are hereby influenced by the length of the linker between the cyclopentadienyl and the amido-functionality and the substituents at the amido-nitrogen.[237] Remarkable catalytic activity was observed for complexes $\mathbf{68}^{cyclohexyl}$. Upon activation with equimolar amounts of $[Ph_3C][B(C_6F_5)_4]$, such compounds polymerized ethylene and isoprene, regiospecifically yielding 3,4-polyisoprene with isotactic-rich stereo microstructures and relatively narrow molecular weight distribution ($M_w/M_n = 1.8$).[222] Complex $\mathbf{67}_Y$ was found to initiate the polymerization of the polar monomers *tert*-butyl acrylate and acrylonitrile, however, yielding atactic polymeric products (see Table 5).[204]

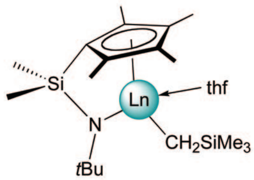
8.2.4. Complexes with Neutral Nitrogen- and Oxygen-Based Ligands

While early work in organorare-earth metal chemistry was dominated by complexes supported by cyclopentadienyl-type ligands of varying substitution and modification, the limitations inherent to these ligand sets triggered the development of alternative ancillary ligands. Particularly in the past 15 years, advanced ligand design gave access to a wide variety of rare-earth metal complexes supported by noncyclopentadienyl ligand environments. Because of the Lewis acidic nature of the rare-earth metal ions, ligands based on the hard donor elements oxygen and nitrogen are most commonly used, while some notable exceptions have been reported. To avoid ligand redistribution, multidentate ligands are generally favored. Since rare-earth metal cations are invariable in the +3 oxidation state (except Eu(II), Sm(II), Yb(II), and Ce(IV)), neutral, monoanionic, or dianionic ligand sets are the most desirable.

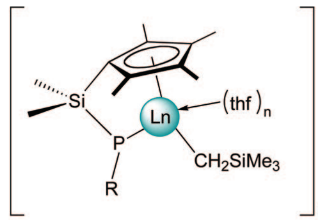
Chart 11. Constrained Geometry Complexes Derived from $Ln(CH_2SiMe_3)_3(thf)_x$ (J_{thf})



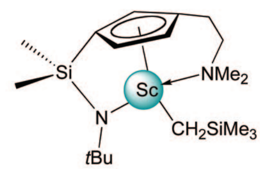
R = CMe$_2$Et; Ln = Y (X-ray); n = 1
R = Ph; Ln = Y (X-ray), Yb, Lu; n = 2
R = C$_6$H$_2$Me$_3$-2,4,6; Ln =Y, Lu; n = 1
R = C$_6$H$_3$Me$_2$-2,6; Ln = Lu; n = 1
66



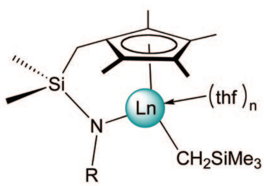
Ln = Y, Yb, Lu
67



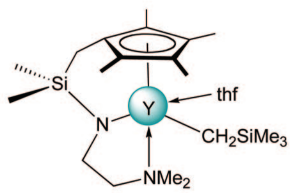
R = Ph; Y (n = 1,2), Yb (n = 0), Lu (n = 0) (X-ray); (x = 2)
R = C$_6$H$_{11}$; Ln = Y, Yb, Lu (X-ray); (n = 0); (x = 2)
R = C$_6$H$_2$-*t*Bu-2,4,6; Y, Lu (only intermediates)
68



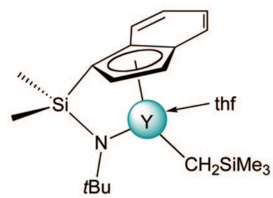
69



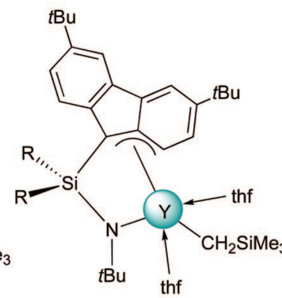
R = *t*Bu; Ln = Y (X-ray), Lu; (n = 1)
R = Ph; Ln = Y, Lu (n = 2)
R = C$_6$H$_4$-*t*Bu-4; Ln = Y (n = 2), Lu (n = 1.5)
R = C$_6$H$_4$-*n*Bu-4; Ln = Y (n = 2), Lu (n = 1.5)
70



(X-ray)
71



72



R = Me (X-ray), Ph
73

Table 5. Further Applications of Complexes with Functionalized Cp^R Ligands

compound	further application	ref
66	synthesis of hydride compounds [CH_2SiMe_3] exchange reactions dimerization of terminal alkynes cross-coupling of terminal alkynes with isocyanides catalytic addition of amine N−H, alkyne C−H, and phosphine P−H bonds to carbodiimines hydrosilylation of olefins	176, 177, 237, 239−244
67	synthesis of hydride compounds [CH_2SiMe_3] exchange reactions donor-exchange reactions hydrosilylation of olefins polymerization of *t*Bu-acrylate polymerization of acrylonitrile dimerization of terminal alkynes catalytic addition of amine N−H, alkyne C−H, and phosphine P−H bonds to carbodiimines cross-coupling of terminal alkynes with isocyanides	176, 177, 204, 237, 239, 241, 243−246
68	synthesis of hydride compounds hydrosilylation of olefins polymerization of ethylene isospecific 3,4-polymerization of isoprene	215, 222, 226
69	synthesis of hydride compounds	247
70	synthesis of hydride compounds [CH_2SiMe_3] exchange reactions hydrosilylation of olefins	237, 238, 248
71	synthesis of hydride compounds hydrosilylation of olefins	236, 237
72	synthesis of hydride compounds	176
73	synthesis of hydride compounds polymerization of methyl methacrylate (low activity)	249

Neutral macrocyclic and tripodal ancillary ligands containing oxygen, nitrogen, or sulfur donors were found suitable to stabilize tris(alkyl) rare-earth metal complexes (Chart 12). Moreover, such facially coordinating ancillary ligands allow for the formation of stable monocationic and in some cases even dicationic rare-earth metal alkyl species.

Complexes **74**−**84** were prepared by the reaction of tris(alkyl) precursors $Ln(CH_2SiMe_3)_3(thf)_x$ (J_{thf}) with equimolar amounts of the respective neutral donor ligand (Chart 12 and Table 6).

In situ formation of mono- and dicationic rare-earth metal alkyl species by treatment with $[Ph_3C][B(C_6F_5)_4]$, $[PhNMe_2H][B(C_6F_5)_4]$, or $B(C_6F_5)_3$, respectively, was reported for compounds **74**−**80**, **82**, and **83**.[182,193−195,250−256] The borate/borane activated complexes (except **74**−**76**, and **81**) polymerized ethylene with moderate to high activities. Activated complex **78** stabilized by 1,4,7-trithiacyclononane further initiated the polymerization of 1-hexene and styrene with very high activities but yielded atactic polymers with poor control of the molecular weights.[252]

Bis(cations) formed by **83**$_{Sc}$ and 2 equiv of $[Ph_3C][B(C_6F_5)_4]$ are highly active in the polymerization of 1-hexene, producing highly isotactic poly(1-hexene) (2030 kg/(mol h); *mmmm* = 90%) (see Table 6).[254]

8.2.5. Complexes with Monoanionic Nitrogen-, Oxygen-, and Phosphorus-Based Ligands

A large number of monoanionic ancillary ligand sets has been developed, well suitable to stabilize alkyl complexes of the rare-earth metals. The monoanionic ancillary ligand allows for organometallic rare-earth metal complexes with two hydrocarbyl or hydride ligands that can be converted into the corresponding cationic monoalkyl/monohydride species by activation with borate/borane reagents like $[Ph_3C][B(C_6F_5)_4]$, $[PhNMe_2H][B(C_6F_5)_4]$, or $B(C_6F_5)_3$. The resulting cationic species have demonstrated encouraging catalytic activities for a range of polymerization reactions including olefins, conjugated dienes, and polar monomers. Homoleptic $Ln(CH_2SiMe_3)_3(thf)_x$ (J_{thf}) are the most widely used alkyl precursors for the synthesis of rare-earth metal bis(alkyl) complexes supported by such monoanionic ancil-

Chart 12. Ln(CH$_2$SiMe$_3$)$_3$(thf)$_x$ Derivatives Containing Neutral [OOOO], [OOOOO], [OOOOOO], [NN], [NNN], [SSS], and [ONO] Ligands

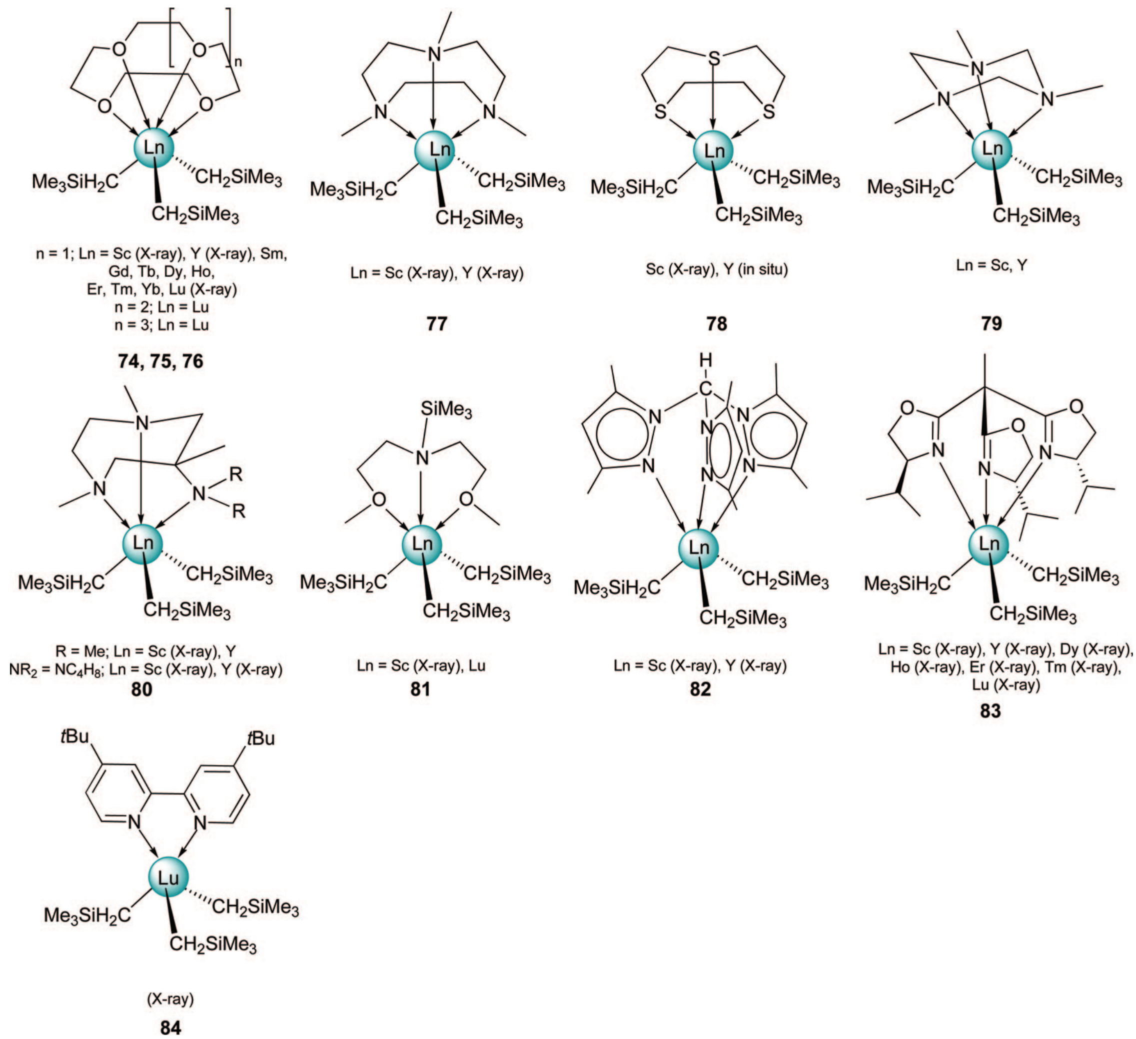


Table 6. Further Applications of Complexes Containing Neutral N- and O-Based Ligands

compound	further application	ref
74	formation of mono- and dications	193−195
75	formation of monocations	193
76	formation of monocations	193
77	formation of mono- and dications polymerization of ethylene	250, 251, 255, 257
78	formation of mono- and dications polymerization of ethylene polymerization of 1-hexene polymerization of styrene	252, 255
79	formation of monocations polymerization of ethylene	251, 255
80	formation of monocations polymerization of ethylene hydroamination/cyclization of aminoalkenes	253, 258
81	formation of monocations	259
82	formation of monocations polymerization of ethylene	250, 251, 255
83	formation of mono- and dications polymerization of α-alkenes (1-hexene, 1-heptene, 1-octene)	182, 254, 256
84	[CH$_2$SiMe$_3$] exchange reactions insertion of carbodiimines	260

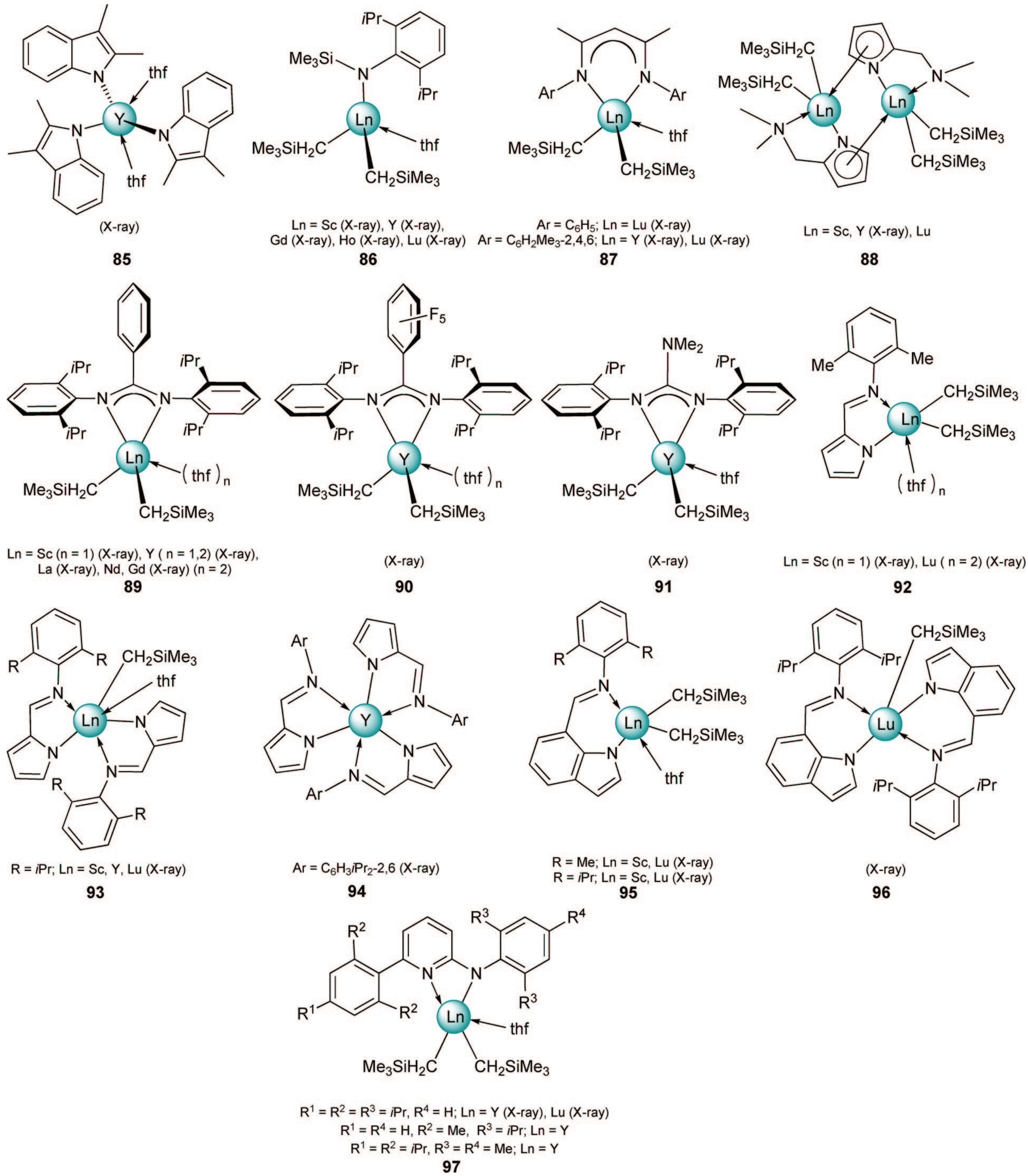
lary ligands. Routinely, alkane-elimination reaction of equimolar equimolar amounts of the respective proligand and Ln(CH$_2$SiMe$_3$)$_3$(thf)$_x$ gave access to a large variety of complexes [L]Ln(CH$_2$SiMe$_3$)$_x$(thf)$_n$ (Charts 13−16).

One of the first monoanionic nitrogen-donor ancillaries applied in this alkane elimination reaction is the benzamidinato ligand. The Hessen group reported benzamidinato−bis(alkyl) complexes **89** and **90** as well as the formation of cationic species upon activation with [PhNMe$_2$H][B(C$_6$F$_5$)$_4$].[186,261,262] In situ prepared cations effectively catalyzed the polymerization of ethylene, yielding polyethylene with a narrow polydispersity (**89**$_{Y}$/[PhNMe$_2$H][B(C$_6$F$_5$)$_4$]/TiBAO: 3 × 10^{3}kg/(mol bar h); $M_w/M_n = 2.0$).[261]

Remarkably, the benzamidinato ligand proved suitable to form bis(alkyl) complexes of the entire rare-earth metal cation size range. One-pot reaction of LaBr$_3$(thf)$_4$, NdCl$_3$(thf)$_3$, or GdCl$_3$(thf)$_3$ with 3 equiv of LiCH$_2$SiMe$_3$ and 1 equiv of the amidine yielded the respective complexes **89**$_{La}$, **89**$_{Nd}$, and **89**$_{Gd}$—the first neosilyl complexes of the early lanthanide metals.[186]

Active ethylene polymerization catalysts were further obtained from complexes **97**,[263] **98**,[264,265] **105**,[266] **106**,[187] **107**,[267] **109**,[268] **115**,[269] and **129**[270] when activated with borate reagents. Whereas cationic species derived from **92** and [Ph$_3$C][B(C$_6$F$_5$)$_4$] showed no activity in the polymerization of isoprene, addition of AlEt$_3$ as a third component resulted in versatile activity depending on the molar ratio of [Al]/

Chart 13. $Ln(CH_2SiMe_3)_3(thf)_x$ Derivatives Containing Monoanionic $[N]^-$ and $[NN]^-$ Ligands



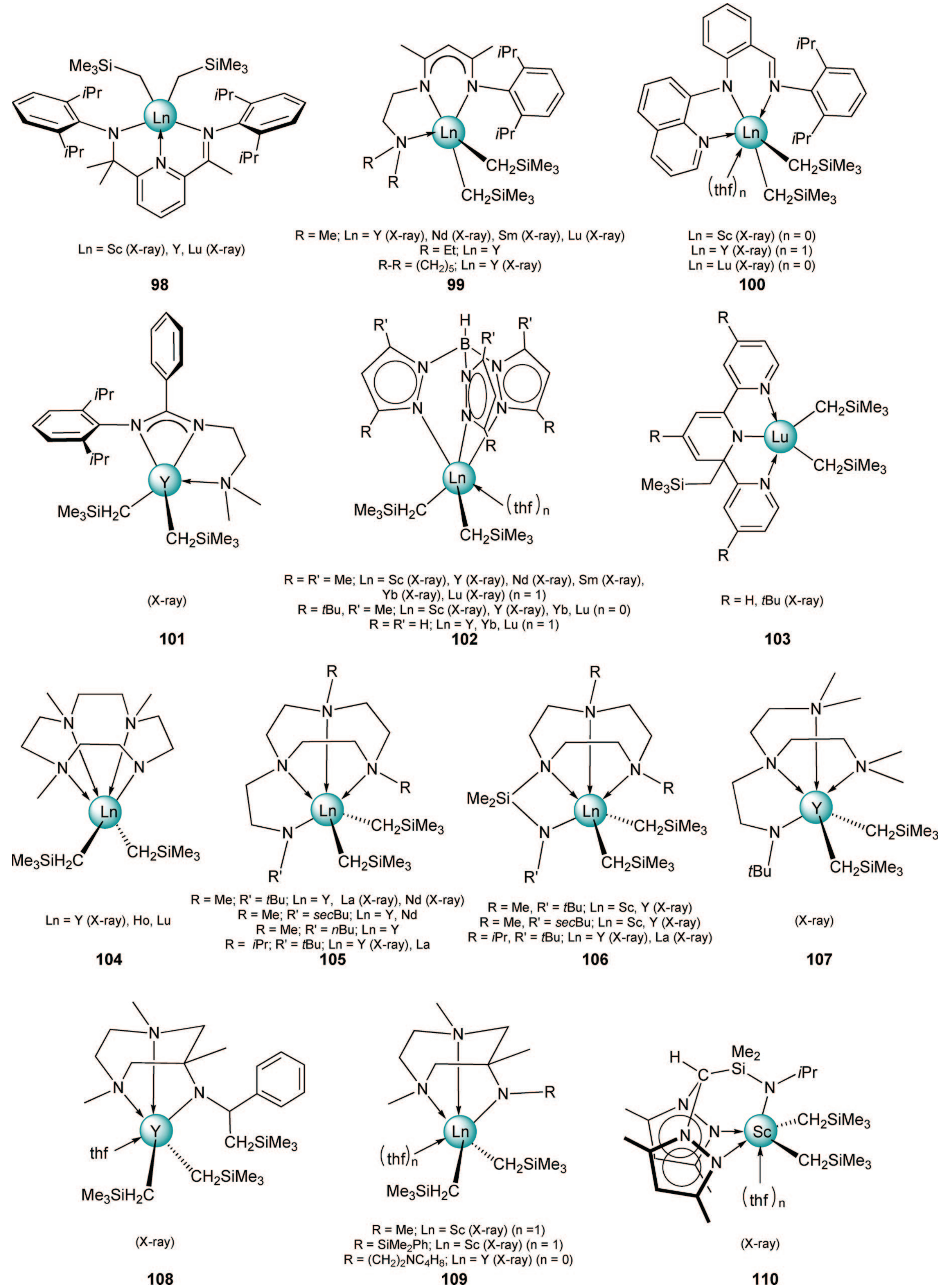
[Ln], however, producing polyisoprene with low stereoregularity.[271] High *cis*-1,4-polyisoprene (*cis*-1,4: 99%; M_w/M_n = 1.05−1.13) could be obtained from catalyst mixtures **124**/[$PhNMe_2H$][$B(C_6F_5)_4$] and **124**/[Ph_3C][$B(C_6F_5)_4$], rare examples of high catalytic activity in the absence of an organoaluminum cocatalyst.[272] Further, **86**,[273] **95**,[274] **126** (3,4-enriched),[275] **131** (*trans*-1,4-enriched),[276] and **132**[276] (*trans*-1,4-enriched) polymerize isoprene when activated by borate cocatalysts.

Neutral complexes **93**,[271,277] **114**,[278,279] **117**,[280] **118**,[279] **121**,[280] and **127**[281] are active catalysts for the ring-opening polymerization (ROP) of lactide, whereas **99**,[282] **100**,[283] **119**,[284] and **120**[284] polymerize ε-caprolactone. For further applications of complexes [L][Ln]$_{3-x}$(CH_2SiMe_3)$_x$(thf)$_n$, see Table 7.

8.2.6. Complexes with Dianionic Nitrogen- and Oxygen-Based Ligands

Reaction of $Ln(CH_2SiMe_3)_3(thf)_x$ (**J**$_{thf}$) with multidentate proligands containing two acidic functionalities yielded a series of very stable mono(alkyl) rare-earth metal complexes (Charts 17−19). The dianionic ligand set allows for the preparation of complexes related to bis(cyclopentadienyl) (= metallocene) derivatives. The catalytic application of complexes supported by dianionic ancillary ligands therefore depends on the initiating property of the remaining alkyl actor ligand. Compound **142**$_{Sc}$ bearing a tridentate diamide−pyridine ancillary ligand initiated the polymerization of the polar monomer methyl methacrylate (MMA). The resulting PMMA

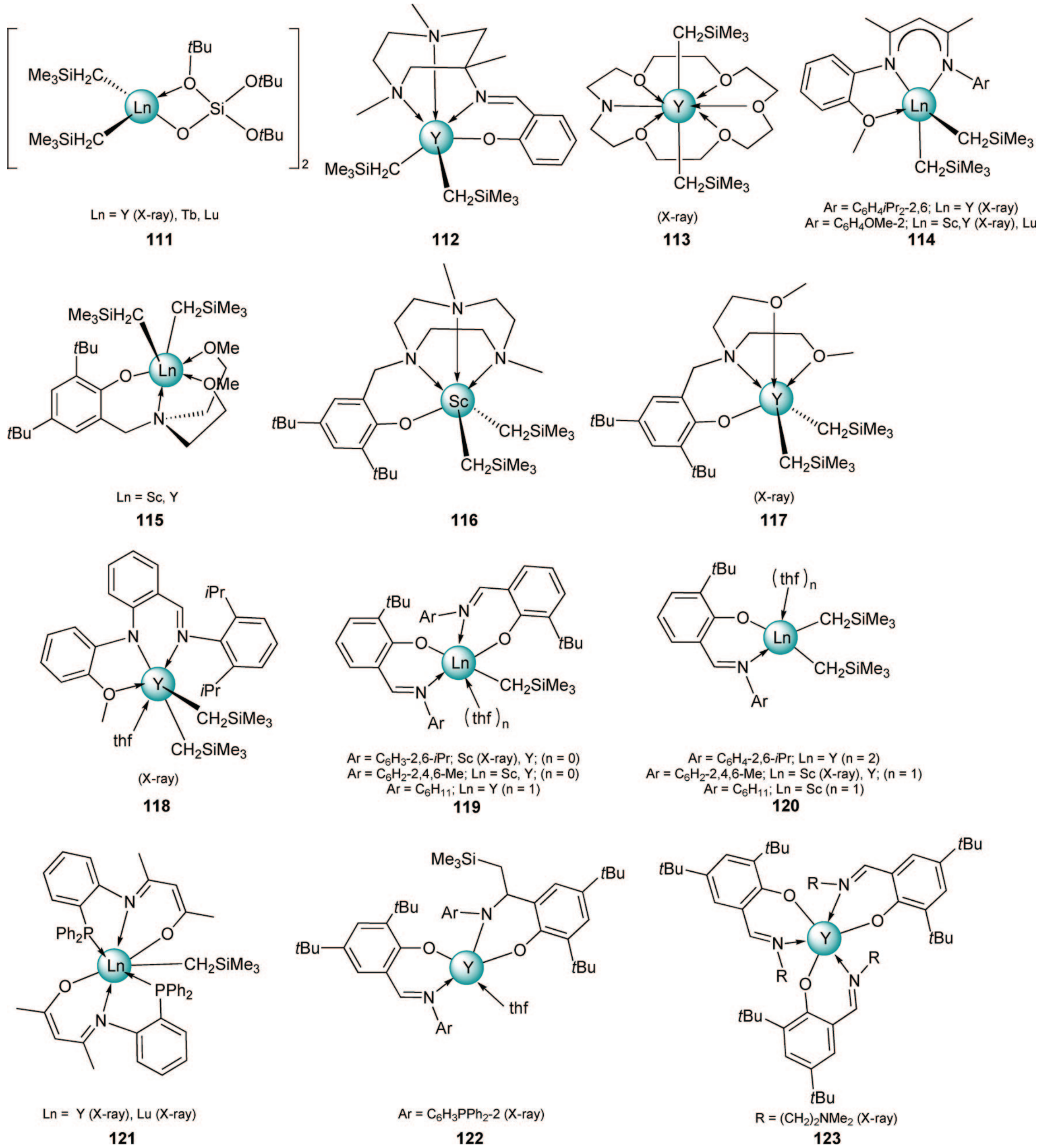
Chart 14. $Ln(CH_2SiMe_3)_3(thf)_x$ Derivatives Containing Monoanionic $[NNN]^-$ and $[NNNN]^-$ Ligands; Complexes 102 Featuring the Large Lanthanides Nd and Sm Were Obtained Only by Alkyl Abstraction Using $TlTp^{Me,Me}$



showed a narrow molecular weight distribution (M_w/M_n = 1.28) but low control of the tacticity.[306] Further, complexes **133** and **137** proved to be efficient initiators for the polymerization of MMA.[307] The chiral binaphthylamido alkyl complex **139** and aminotroponiminato complex **145** performed as catalysts for the asymmetric intramolecular hydroamination/cyclization of terminal aminoolefins.[109,308]

Polylactides are among the most promising biodegradable and biocompatible synthetic macromolecules. Such polymers are most conveniently accessible by ring-opening polymer-

Chart 15. $Ln(CH_2SiMe_3)_3(thf)_x$ Derivatives Containing Monoanionic $[OO]^-$, $[ONN]^-$, $[ONNN]^-$, $[ONOO]^-$, and $[NOOOOO]^-$ Ligands



ization of lactide. Mono(alkyl) complexes **138**, **140**, **153**, and **157**−**159** initiate the polymerization of *rac*-lactide under mild conditions.[277,278,281,309,310] Compounds **153** and **157**−**159** displayed living polymerization and produced polymers with very high stereoselectivity affording heterotactic polylactide from racemic lactide mixtures.[278,309,310] Complexes **161** and **162** bearing thioether-functionalized bis(phenolato) ligands proved to be efficient catalysts for the hydrosilylation of olefins.[311,312] For further applications of complexes $[L]Ln(CH_2SiMe_3)(thf)_n$, see Table 8.

9. [Dimethyl(phenyl)silyl]methyl Complexes

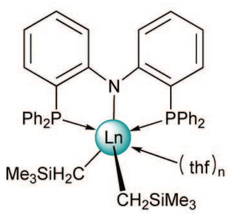
9.1. Synthesis, Structure, and Properties of $Ln(CH_2SiMe_2Ph)_3(thf)_2$

Triggered by the thermal instability of lanthanide alkyls $Ln(CH_2SiMe_3)_3(thf)_x$ ($\mathbf{J}_{thf}$), more bulky $[CH_2SiMe_2Ph]$ groups have been introduced to prepare homoleptic alkyls $Ln(CH_2SiMe_2Ph)_3(thf)_2$ ($\mathbf{L}_{thf}$). The scandium and yttrium derivatives were first reported in 2002 by Piers et al. as easily accessible by a salt-metathesis reaction of $LnCl_3(thf)_x$ and $LiCH_2SiMe_2Ph$ (Scheme 31).[302,322]

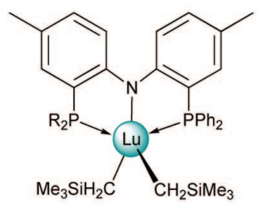
The $[CH_2SiMe_2Ph]$ ligands impart higher stability of complexes **L** reflected in high isolable yields and significantly reduced thermal degradation. However, decomposition giving an unidentified, insoluble brown precipitate accompanied by the loss of Me_3SiPh occurred after 24 h at 65 °C in toluene-d_8. The lower solubility of compounds $Ln(CH_2SiMe_2Ph)_3(thf)_2$ ($\mathbf{L}_{thf}$) compared to $Ln(CH_2SiMe_3)_3(thf)_x$ ($\mathbf{J}_{thf}$) facilitates crystallization and purification of these alkyl derivatives.

In the solid state, $Sc(CH_2SiMe_2Ph)_3(thf)_2$ ($\mathbf{L}_{Sc-thf}$) features a trigonal-bipyramidal coordination geometry upon the scandium metal center.[302] The two thf molecules are axially coordinated, whereas the alkyl groups are arranged in a pinwheel array (Figure 26). The trigonal bipyramid is nearly regular, and the Sc−C bond lengths are essentially identical.

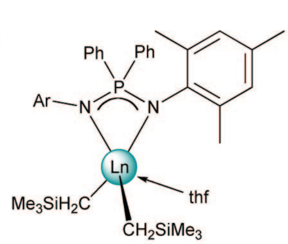
Chart 16. $Ln(CH_2SiMe_3)_3(thf)_x$ Derivatives Containing Monoanionic $[PNP]^-$, $[NPN]^-$, and $[NP]^-$ Ligands



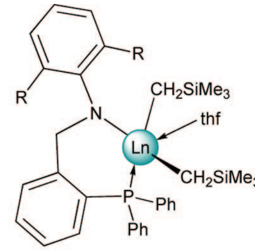
Ln = Sc; (n = 0)
Y, Lu (X-ray) (n = 1)
124



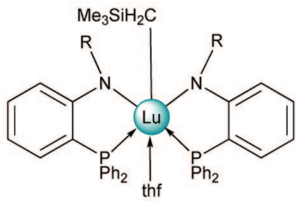
R = *i*Pr (X-ray)
R = Ph
125



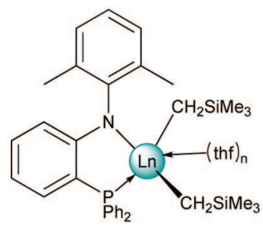
Ar = C_6H_5; Ln = Sc (X-ray), Y (X-ray), Lu (X-ray)
Ar = C_5H_4N; Ln = Sc (X-ray)
126



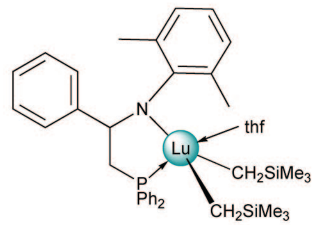
R = Me; Ln = Y (X-ray), Lu
R = *i*Pr; Ln = Y (X-ray), Lu
127



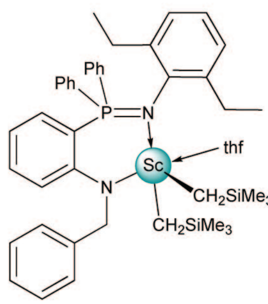
R = Me
R = $CH_2C_6H_5$ (X-ray)
128



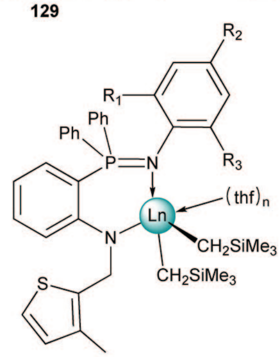
Ln = Sc (X-ray) (n = 1), Y (n = 2),
Tm (X-ray), Yb (X-ray), Lu (X-ray) (n = 1)
129



Ln = Sc (X-ray) (n = 1), Y (n = 2),
Tm (X-ray), Yb (X-ray), Lu (X-ray) (n = 1)
130



(X-ray)
131



$R_1 = R_2 = R_3$ = Me; Ln = Sc, Lu (X-ray) (n = 1)
$R_1 = R_3$ = Ethyl, R_2 = H; Ln = Sc (X-ray), Y, Lu (n = 1)
$R_1 = R_3$ = *i*Pr, R_2 = H; Ln = Sc (X-ray) (n = 0)
132

According to NMR spectroscopic studies, the solid-state structure is also retained in solution. Very recently, the respective thulium and lutetium compounds have been synthesized following the procedure depicted in Scheme 31.[182,256] Because of the unexpected low stability, compounds $\mathbf{L}_{Tm-thf}$ and $\mathbf{L}_{Lu-thf}$ were not isolated but used in situ at −80 °C in an alkane-elimination reaction. Attempts to synthesize complexes **L** with the larger rare-earth metals have not been reported so far.

$LiCH_2SiMe_2Ph$ is commercially not available and has to be synthesized from $Me_2PhSiCH_2Cl$ and lithium powder. This and the low volatility of the Me_3SiPh side-product of alkane-elimination reactions (bp. 170 °C vs 27 °C for $SiMe_4$) are obvious drawbacks of the presented lanthanide alkyls.[302]

9.2. $Ln(CH_2SiMe_2Ph)_3(thf)_2$ as Synthesis Precursors

Like their less-bulky analogues, complexes $Ln(CH_2SiMe_2Ph)_3(thf)_2$ ($\mathbf{L}_{thf}$) have been used as starting materials for alkane-elimination reactions. The number of reported applications, however, is so far limited to monoanionic multidentate N,O-donor and neutral multidentate N-donor ligands (Chart 20).

A series of salicylaldiminato complexes **164−169** has been investigated with respect to the ancillary ligand impact on the (thermal) stability of complexes $[L]_2Ln(CH_2SiMe_2Ph)(thf)_x$ (Ln = Sc, Y) (**164−167**) and $[L]Y(CH_2SiMe_2Ph)_2(thf)_x$ (x = 1, 2) (**168**).[302,303,322] The stability of bis[L] complexes **164−167** increases with increasing steric bulk on the aldimine functionality. Insufficient steric shielding and elevated temperatures lead to rapid decomposition via ligand metalation and/or 1,3-migration of the entire $[CH_2SiMe_2Ph]$ group to the aldimine carbon.

A series of monoanionic, tripodal ancillary ligands featuring various neutral O-, N-, and S- donors has been synthesized by the group of Bercaw.[269] The reaction of in situ generated $Ln(CH_2SiMe_2Ph)_3(thf)_2$ ($\mathbf{L}_{thf}$) (Ln = Sc, Y) with the respective ligand precursors cleanly produced compounds **171−174**. Cationization of compounds **171−174** with $[PhNMe_2H][B(C_6F_5)_4]$ and/or MAO generated mono(alkyl) species displaying low activity in the polymerization of ethylene.

With the objective to obtain a catalytically active cationic lanthanide alkyl species, in situ prepared $Ln(CH_2SiMe_2Ph)_3(thf)_2$ (Ln = Tm, Lu) was treated with the C_3-chiral tris(oxazolinyl)ethane to form donor-free **175**.[182] The reaction

Table 7. Further Applications of Complexes Containing Monoanionic N-, O-, and P-Based Ligands

compound	further application	ref
85	no further application	285
86	formation of monocations polymerization of isoprene	273
87	alternating copolymerization of cyclohexene oxide and CO_2	279, 286
88	formation of monocations polymerization of isoprene	271
89	formation of monocations polymerization of ethylene intramolecular hydroamination/cyclization hydrosilylation of alkenes	186, 261, 287, 288
90	formation of monocations polymerization of ethylene	262
91	hydrosilylation of alkenes	288
92	formation of monocations polymerization of isoprene	271
93	formation of monocations ROP of D,L-lactide	271, 277
94	no further application	277
95	insertion of carbodiimines formation of monocations polymerization of isoprene	274
96	insertion of carbodiimines	274
97	formation of monocations formation of hydride compounds polymerization of ethylene	263, 289
98	formation of monocations polymerization of ethylene	264, 265
99	ROP of ε-caprolactone	282
100	ROP of ε-caprolactone	283
101	no further application	262
102	formation of hydride compounds	290−292
103	$[CH_2SiMe_3]$ exchange reactions	293, 294
104	formation of hydride compounds	295
105	formation of monocations polymerization of ethylene *cis*-selective linear alkyne dimerization intramolecular hydroamination/cyclization thermal stability investigations	187, 188, 266, 287, 296
106	formation of monocations polymerization of ethylene thermal stability investigations	187, 188
107	formation of monocations polymerization of ethylene	267, 287
108	no further application	253
109	formation of monocations intramolecular C−H bond activation ethylene insertion polymerization of ethylene Z-selective head-to-head alkyne dimerization	268, 297
110	formation of monocations	298
111	formation of mono- and dications hydrosilylation of olefins	299
112	no further application	253
113	formation of monocations insertion of CO	300
114	ROP of *rac*-lactide $[CH_2SiMe_3]$ exchange reactions alternating copolymerization of cyclohexene oxide and CO_2	278, 279, 286
115	formation of monocations polymerization of ethylene	269
116	no further application	301
117	ROP polymerization of L-lactide	280
118	$[CH_2SiMe_3]$ exchange reactions ROP of *rac*-lactide	279
119	hydride compounds ROP of ε-caprolactone	284, 302, 303
120	ROP of ε-caprolactone	284, 302
121	ROP polymerization of L-lactide	280
122	no further application	280
123	no further application	280
124	formation of monocations polymerization of isoprene and butadiene copolymerization of isoprene and butadiene	272
125	$[CH_2SiMe_3]$ exchange reactions	304
126	formation of monocations polymerization of isoprene (3,4)	275
127	polymerization of D,L-lactide $[CH_2SiMe_3]$ exchange reactions	281
128	no further application	270
129	formation of monocations polymerization of ethylene	270
130	insertion of carbodiimines	305
131	formation of monocations polymerization of butadiene (*trans*-1,4)	276
132	formation of monocations polymerization of butadiene (*trans*-1,4)	276

of **175** with either 1 or 2 equiv of $[Ph_3C][B(C_6F_5)_4]$, however, failed to produce an active catalyst for the polymerization of 1-hexene, 1-heptene, or 1-octene (see Table 9).

10. Bis(trimethylsilyl)methyl Complexes

The introduction of the $[CH(SiMe_3)_2]$ ligand to group 3 metal chemistry by Barker and Lappert in 1974 marked the beginning of a new era of organolanthanide chemistry.[73] With $Y[CH(SiMe_3)_2]_3$, the first neutral homoleptic solvent-free lanthanide alkyl species had been isolated and the synthesis protocol could successfully be extended to the whole series of rare-earth metals. Further, steric shielding and the stabilizing effect of the trimethylsilyl methyl goups contributed significantly to the development of low-valent organolanthanide chemistry.

10.1. Synthesis, Structure, and Properties of Ln(II)[CH(SiMe$_3$)$_2$]$_2$(solv)$_x$ and {M(solv)$_x$}{Ln(II)[CH(SiMe$_3$)$_2$]$_3$}

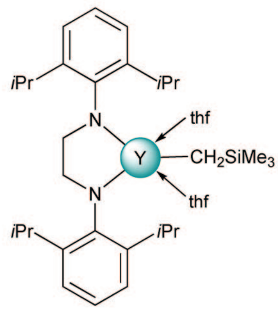
Because of their high reactivity and their potential as one-electron reducing agents, complexes of the divalent ytterbium and samarium are valuable compounds not only in organic syntheses but also as polymerization catalysts. As shown by Lappert and co-workers, bis(trimethylsilyl)methyl ligands provide enough steric bulk to stabilize bis(alkyl) complexes of divalent ytterbium.[324] Several synthesis approaches have been developed to produce neutral homoleptic complexes $Yb[CH(SiMe_3)_2]_2(solv)_x$ (**M**$_{Yb}$) and ionic $Yb[CH(SiMe_3)_2]_3$-$M(solv)_x$ (**N**$_{Yb}$) (Schemes 32 and 33). YbI_2 and $Yb(OAr^{tBu,Me})_2(Et_2O)_2$ ($Ar^{tBu,Me} = C_6H_2$-4-Me-2,6-*t*Bu) proved to be convenient synthesis precursors for $Yb[CH(SiMe_3)_2]_2(Et_2O)_2$ (**M**$_{Yb-Et_2O}$) via salt-metathesis reaction with the respective sodium or potassium alkyls (Scheme 32, I and II). (The mixed ytterbium(II) mono(alkyl)−mono(aryloxide) $Yb[CH(SiMe_3)_2](OAr^{tBu,Me})(thf)_3$ (**176**) was obtained when $Yb(OAr^{tBu,Me})_2(thf)_3$ was treated with 1 equiv of $KCH(SiMe_3)_2$ in thf.)[324,325] The bis(alkyl) products are stabilized by two molecules of weakly bound Et_2O donors. The reaction of $(C_5Me_5)_2Yb(Et_2O)$ with 2 equiv of $LiCH(SiMe_3)_2$ in diethyl ether afforded a red oil, which upon dissolving in toluene and an excess of tmeda yielded the tmeda adduct $Yb[CH(SiMe_3)_2]_2(tmeda)$ (**M**$_{Yb-tmeda}$) (Scheme 32, III).[325]

So far, the organometallic chemistry of low-valent lanthanides carrying the $[CH(SiMe_3)_2]$ ligand has been limited to the smallest ytterbium(II) metal center. Apparently, the ligand does not provide enough steric and electronic protection to satisfy the larger metal centers Eu(II) and Sm(II).

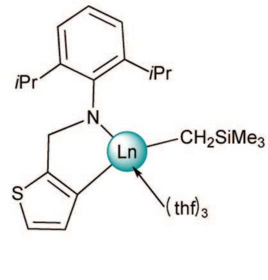
The neutral solvates have been characterized by means of ^{1}H, ^{13}C, $^{29}Si\{H\}$, and $^{171}Yb\{H\}$ NMR spectroscopy, but final structural proof is frustrated by the unavailability of suitable single crystals. The lanthanide cation's desire for higher coordination numbers is impressively reflected by the reactions depicted in Scheme 33. The formation of ate complexes with lithium, sodium, and potassium cations has been reported irrespective of the stoichiometry applied. High yields and the formation of crystalline material substantiate higher stability of such ionic compounds $Yb[CH(SiMe_3)_2]_3M(solv)_x$ (**N**$_{Yb}$) (M = Li, Na, K) compared to their neutral analogues.[325]

The solid-state structure of the potassium salt $\{Yb[CH(SiMe_3)_2]_3K\}_n$ revealed double chains of $\{Yb[CH(SiMe_3)_2]_3\}$ anions linked by potassium cations along one axis (Figure

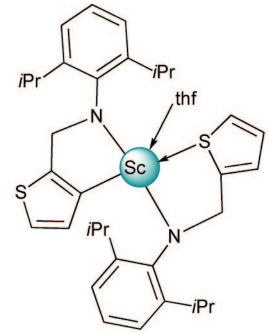
Chart 17. $Ln(CH_2SiMe_3)_3(thf)_x$ Derivatives Containing Dianionic $[NN]^{2-}$, $[NC]^{2-}$, $[NCN]^{2-}$, and $[NNNN]^{2-}$ Ligands



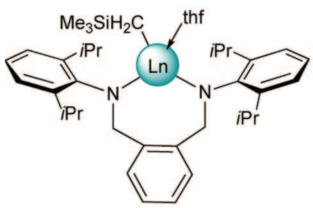
133



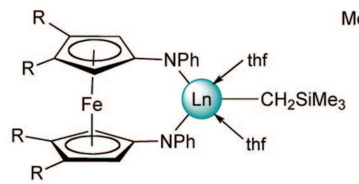
Ln = Y (X-ray), Lu (X-ray)
134



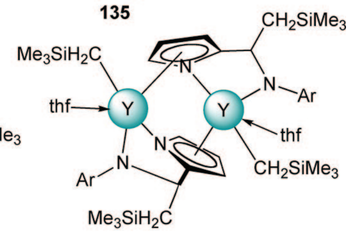
(X-ray)
135



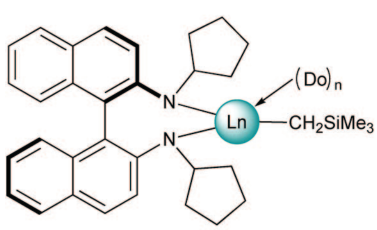
Ln = Sc (X-ray), Y, Lu
136



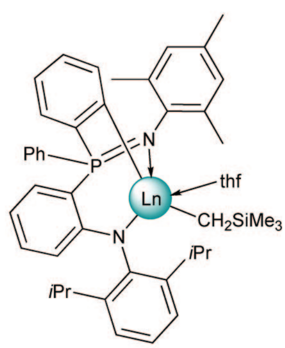
R = H, Ln = Y, Lu
R = Ph, Ln = Y, Lu (X-ray)
137



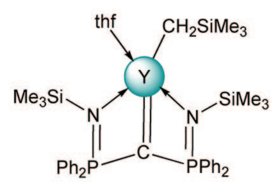
Ar = $C_6H_3iPr_2$-2,6 (X-ray)
138



Ln = Y, Yb, Do = thf (n = 2)
Ln = Y (X-ray), Do = Et_2O (n = 1)
139



Ln = Y (X-ray), Lu
140



(X-ray)
141

27).[326] Each potassium has four additional close contacts to methyl carbon atoms.

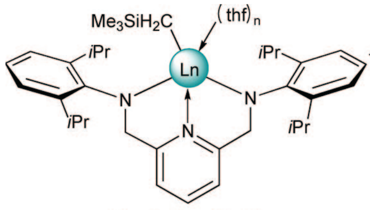
Stabilization by metal−methyl interactions is also prominent in the solid-state structure of $Yb[CH(SiMe_3)_2]_3Li(thf)_4$ (Figure 28).[326] The solvent-separated ion pair consists of a $\{Li(thf)_4\}$ cationic unit and a $\{Yb[CH(SiMe_3)_2]_3\}$ anion. A trigonal-pyramidal environment about the ytterbium atom is accomplished, and each of the $[CH(SiMe_3)_2]$ groups shows one additional close Yb methyl contact (Figure 28). Other than the lithium and potassium containing ate complexes, the sodium compound was reported to be stable at −30 °C but slowly decomposed at ambient temperature.

The coordinating Et_2O molecules in neutral Yb[CH-$(SiMe_3)_2]_2(Et_2O)_2$ ($\mathbf{M}_{Yb-Et_2O}$) can easily be displaced by a chelating 1,2-bis(dimethylphosphino)ethane (dmpe), to yield the respective $Yb[CH(SiMe_3)_2]_2$(dmpe) ($\mathbf{M}_{Yb-dmpe}$).[325] The observed reactivity is in good agreement with loosely bound diethyl ether donors. Exchange of one alkyl ligand in an alkane elimination reaction was found when reacting $Yb[CH(SiMe_3)_2]_2(Et_2O)_2$ with *N*,*N*-bis(trimethylsilyl)-1,4-phenylenediamine (Scheme 34).[325] In the presence of 2 equiv of Bu*t*CN, in situ prepared $Yb[CH(SiMe_3)_2]_2(Et_2O)_2$ can be converted into Yb(II) 1-azaallyl complexes (**178**), whereas the respective reaction with 4 equiv of PhCN yielded Yb(II) β-diketiminates (**179**) (Scheme 35).[324,327,328]

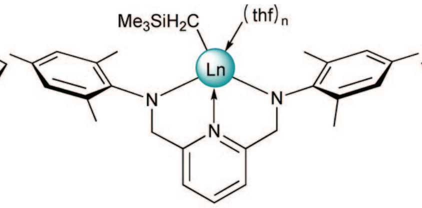
10.2. Synthesis, Structure, and Properties of $Ln(III)[CH(SiMe_3)_2]_3$ and $Ln(III)[CH(SiMe_3)(SiMe_2OMe)]_3$

Cation size limitations have not been observed for the homoleptic bis(trimethylsilyl)methyl complexes of the trivalent rare-earth metals. Already the first publication on $Ln[CH(SiMe_3)_2]_3$ (**O**) described the synthesis of Sc[CH-$(SiMe_3)_2]_3(thf)_2$ as the respective compound of the smallest rare-earth metal.[73] Salt metathesis reaction of $LnCl_3$ and the organolithium compound $LiCH(SiMe_3)_2$ in a mixture of thf and Et_2O further yielded the yttrium analogue as a thf solvate (Scheme 36, I).[73] Solvent-free $Y[CH(SiMe_3)_2]_3$ could be obtained from a toluene/diethylether mixture, which is, remarkably, the first successful synthesis of a neutral homoleptic solvent-free lanthanide alkyl compound (Scheme 36, II).[73] As ate complex formation under these reaction conditions is favored with increasing size of the metal cation, salt metathesis of $Ln(OAr^{tBu})_3$ and $LiCH(SiMe_3)_2$ became the predominant synthesis route (Scheme 36, III).[75] Insolubility of the byproduct $Li(OAr^{tBu})$ in hydrocarbon solvents allows for easy separation and additionally shifts the equilibrium to the product side. Applying this procedure, complexes $Ln[CH(SiMe_3)_2]_3$ have been synthesized for Ln

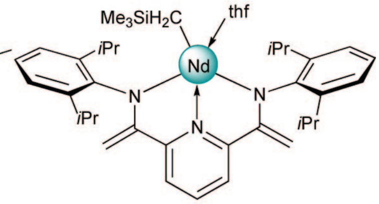
Chart 18. $Ln(CH_2SiMe_3)_3(thf)_x$ Derivatives Containing Dianionic $[NNN]^{2-}$ and $[NNNN]^{2-}$ Ligands



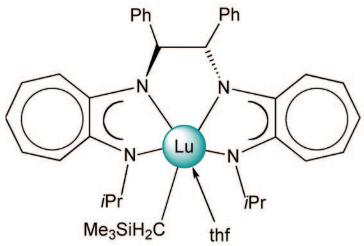
Ln = Sc (X-ray) (n = 1)
Y, Lu; (n = 2)
142



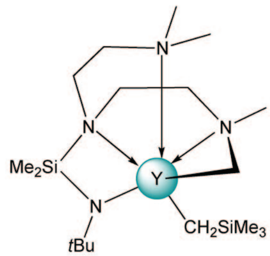
Ln = Sc (n = 1), Lu (n = 2)
143



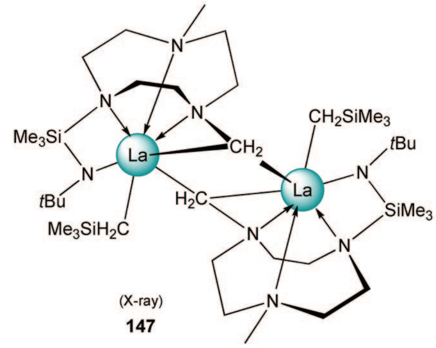
(X-ray)
144



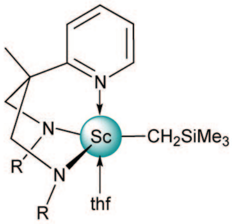
145



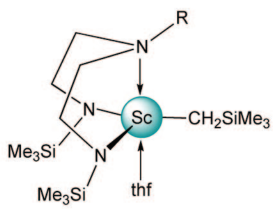
146



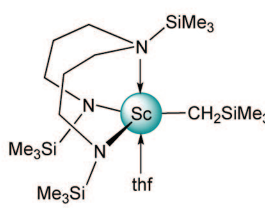
(X-ray)
147



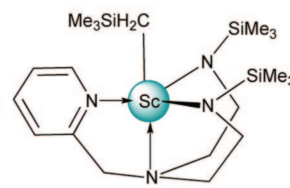
R = $SiMe_3$, C_6H_4-4-Me, C_6H_2-2,4,6-Me (X-ray)
148



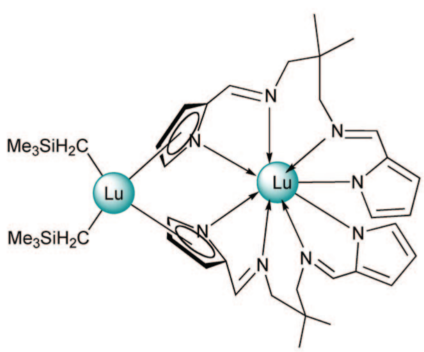
R = Me, $SiMe_3$
149



NMR tube scale only
150



(X-ray)
151



(X-ray)
152

= Y,[329] La,[75] Ce,[330] Pr,[331] Nd,[331] Sm,[75] Er,[332] and Lu[329] covering the whole cation size range of the rare-earth metals.

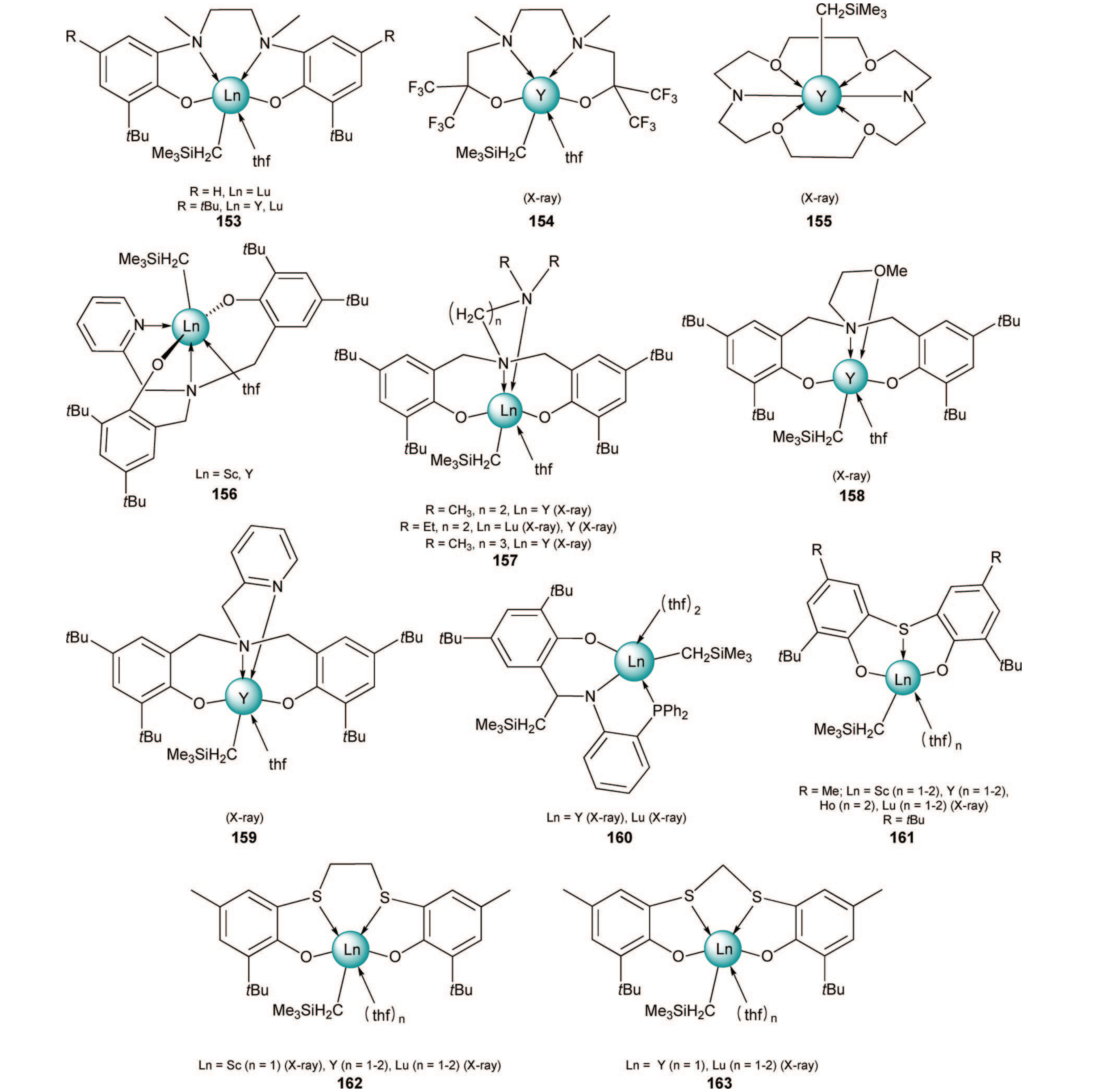
The solid-state structures of $Ln[CH(SiMe_3)_2]_3$ (Ln = Y,[330] La,[75] Ce,[330] and Sm[75]) have been determined and revealed isomorphous structures with a pyramidal geometry about the metal center (Figure 29). The deviation from the anticipated planarity might be rationalized by steric reasons. By adopting a pyramidal structure, repulsion between the ligands is minimized and the ligand−metal attractions are maximized. Indeed, each metal center achieves coordination saturation by forming three additional close $Ln-CH_3$ contacts. On the basis of DFT calculations of $La[CH(SiMe_3)_2]_3$, the most likely explanation for the observed short contacts are agostic $(Si-C_\beta)\cdots Ln$ rather than $(C_\gamma-H)\cdots Ln$ interactions.[333,334]

Because of dynamic exchange processes, the different methyl groups cannot be distinguished by solution NMR spectroscopy even at low temperature. The ^{13}C CPMAS NMR spectrum of $La[CH(SiMe_3)_2]_3$, however, showed two peaks for the interacting and noninteracting trimethylsilyl groups.[335] Compounds $Ln[CH(SiMe_3)_2]_3$ are soluble in hydrocarbon, aromatic, and ethereal solvents, but thermal instability has been reported. Accordingly, the thermal stability decreases with increasing size of the rare-earth metal center, and decomposition leads to formation of $CH_2(SiMe_3)_2$ and insoluble material, which has not been further characterized.

The methoxy analogues $Ln(III)[CH(SiMe_3)(SiMe_2OMe)]_3$ (**P**) were synthesized from anhydrous $LnCl_3$ (Ln = Y, Ce) and $Li[CH(SiMe_3)(SiMe_2OMe)]$ (Scheme 37).[330] Interestingly, no LiCl containing products were obtained from this reaction, which is attributed to the intramolecular interaction of the OMe group with the rare-earth metal center.

The solid-state structures of the yttrium and cerium compounds are isostructural (Figure 30).[330] The rare-earth

Chart 19. $Ln(CH_2SiMe_3)_3(thf)_x$ Derivatives Containing Dianionic $[ONNO]^{2-}$, $[ONOO]^{2}$, $[NOONOO]^{2-}$, $[ONP]^{2-}$, $[OSO]^{2-}$, and $[OSSO]^{2-}$ Ligands



metal center is surrounded by the three chelating alkyl ligands adopting distorted trigonal-prismatic geometry. Solution NMR spectroscopic experiments revealed an equilibrium of two different isomers with *cis*- and *trans*-OMe groups.

As mentioned earlier, the usability of $LiCH(SiMe_3)_2$ as starting material for the synthesis of neutral $Ln[CH(SiMe_3)_2]_3$ is limited. Particularly in the presence of polar donor solvents, ate complexes are the most favored reaction products. Such ionic compounds have been obtained throughout the entire rare-earth metal series (Scheme 38, I).[336,337] The molecular structure of $\{La[CH(SiMe_3)_2]_3(\mu\text{-Cl})\}\{Li(pmdeta)\}$ shows a monomer where the La and the Li atoms are linked via a single, almost linear chloride bridge.[336] The chloride anion resides in the vacant coordination site of $La[CH(SiMe_3)_2]_3$ without significantly distorting the $La[CH(SiMe_3)_2]_3$ skeleton.

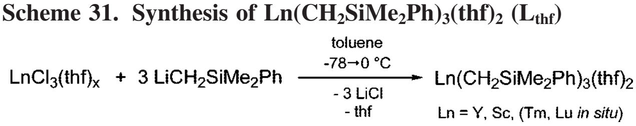
Alkali metal halide containing $\{Ln[CH(SiMe_3)_2]_3(\mu\text{-}X)\}\{K(Et_2O)\}$ (X = Cl, Br) can further be synthesized by direct adduct formation of KX and $Ln[CH(SiMe_3)_2]_3$ (Scheme 38, II and III).[338] The coordinating ether can readily be removed by heating the solid compound under reduced pressure. With toluene, the solvent-free compound $\{Lu[CH(SiMe_3)_2]_3(\mu\text{-Cl})\}\{K\}$ formed a solvent adduct with two toluene molecules coordinated in an η^6 mode to the potassium cations.

The reaction of $Ln[CH(SiMe_3)_2]_3$ with 1 equiv of LiMe in the presence of pmdeta yielded monomeric $\{Ln[CH(SiMe_3)_2]_3(\mu\text{-Me})\}\{Li(pmdeta)\}$ (**181**$_{pmdeta}$).[339] Characterization of the samarium complex by X-ray diffraction showed a structure isomorphous to μ-chloro compound $\{La[CH(SiMe_3)_2]_3(\mu\text{-Cl})\}\{Li(pmdeta)\}$ with an almost linear but asymmetric $Sm-CH_3-Li$ bridge (Figure 31).

Table 8. Further Applications of Complexes Containing Dianionic N- and O-Based Ligands

compound	further application	ref
133	polymerization of methyl methacrylate	307
134	no further application	313
135	no further application	313
136	no further application	306
137	polymerization of methyl methacrylate	307
138	ROP of *rac*-lactide	277
139	enantioselective hydroamination/ cyclization of terminal amino olefins (max. 83% ee at 25 °C)	109
140	ROP of *rac*-lactide	281
141	no further application	314
142	polymerization of methyl methacrylate	306
143	no further application	306
144	polymerization of butadiene (cocatalyst methylalumoxane (MAO))	315
145	enantioselective hydroamination/ cyclization of terminal amino olefins (max. 44% ee at 100 °C)	308
146	no further application	267
147	no further application	296
148	no further application	316
149	no further application	316
150	no further application	316
151	no further application	301
152	polymerization of isoprene	271
153	ROP of *rac*-lactide O_2 activation hydrolysis	278, 317
154	no further application	318
155	no further application	319
156	no further application	301, 320
157	ROP of *rac*-lactide	278
158	ROP of *rac*-lactide	309, 310, 321
159	ROP of *rac*-lactide	278
160	ROP of L-lactide	280
161	formation of hydride compounds hydrosilylation	312
162	formation of hydride compounds donor-exchange reactions $[CH_2SiMe_3]$-exchange reactions hydrosilylation	311, 312
163	formation of hydride compounds	312

Scheme 31. Synthesis of $Ln(CH_2SiMe_2Ph)_3(thf)_2$ (L_{thf})



10.3. Ln(III)[CH(SiMe$_3$)$_2$]$_3$ as Synthesis Precursors

Homoleptic rare-earth metal alkyls $Ln[CH(SiMe_3)_2]_3$ (**O**) are valuable precursors allowing for protonolysis reactions with a variety of protic substrates under mild conditions. Their "alkyl-only" nature prevents salt coordination as well as the coordination of donor solvents. $[CH(SiMe_3)_2]$-exchange reactions are usually kinetically controlled and very sensitive to the reactivity and steric bulk of the reactants. Thus, alkane-elimination reactions are basically limited to the respective early and middle lanthanide tris(alkyls).

Aiming at the synthesis of a mono(cyclopentadienyl) bis(alkyl) complex, $(C_5Me_5)H$ has been reacted with $Ln[CH(SiMe_3)_2]_3$ (Ln = La, Ce) to give mixtures of $(C_5Me_5)_2Ln[CH(SiMe_3)_2]$ (**182**), $(C_5Me_5)Ln[CH(SiMe_3)_2]_2$ (**183**), and $Ln[CH(SiMe_3)_2]_3$ (**O**).[340] The mixture of products was found to be the result of a competitive introduction of cyclopentadienyl ligands rather than a disproportionation of $(C_5Me_5)Ln[CH(SiMe_3)_2]_2$. Reaction of $(C_5Me_5)H$ with the sterically more congested $Y[CH(SiMe_3)_2]_3$ revealed a high kinetic barrier for the introduction of a cyclopentadienyl ligand and did not give the desired product. Compounds $(Cp^R)_2Ln[CH(SiMe_3)_2]$ have been successfully applied as catalysts for the hydroamination/cyclization and hydrophosphination/cyclization of a variety of substrates.[341,342] The used sandwich complexes were, however, exclusively synthesized following a salt-metathesis approach.

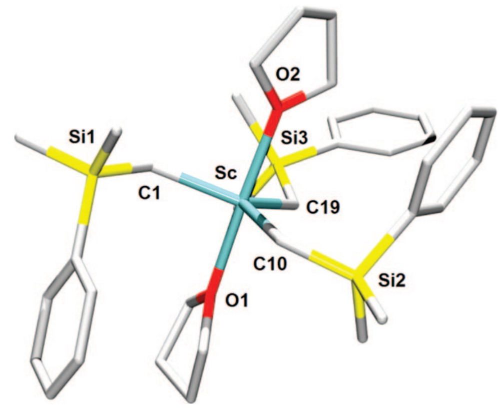


Figure 26. Molecular structure of $Sc(CH_2SiMe_2Ph)_3(thf)_2$ ($\mathbf{L}_{Sc-thf}$), adapted from ref 302.

Remarkably, homoleptic alkyls $Ln[CH(SiMe_3)_2]_3$ of the late lanthanide metals ytterbium and lutetium reacted with $(C_5Me_4H)Me_2Si(tBuNH)$ to form constrained geometry complexes **184** (Chart 21).[343] Heating, however, is necessary to activate the tetramethylcyclopentadiene C−H group for alkane elimination. Complexes **184** are active catalysts for aminoalkene hydroamination/cyclization and hydrophosphination/cyclization.[341,342,344,345] The attempted synthesis of a mono(alkyl) compound using a linked alkoxide−cyclopentadienyl ligand and in situ prepared $Y(OAr^{tBu})[CH(SiMe_3)_2]_2$ only yielded the "alkyl-free" ate complex $\{\eta^5:\eta^1\text{-}C_5H_4[CH_2CO(3,5\text{-}C_6H_3(CF_3)_2)_2]\}_2YLi(thf)_n$ (**185**).[346]

Schaverien et al. first reported the applicability of $Ln[CH(SiMe_3)_2]_3$ for the synthesis of noncyclopentadienyl complexes. The reaction of octaethylporphyrin ($OEPH_2$) and $Ln[CH(SiMe_3)_2]_3$ (Ln = Y, Lu) afforded purple, hexane-soluble $[OEP]Ln[CH(SiMe_3)_2]$ (**186**) in good yields (Chart 22).[329]

Mild protonolysis reactions of $La[CH(SiMe_3)_2]_3$ and chiral, chelating binaphthols and biphenols resulted in the smooth formation of mono(alkyl) binaphtholate lanthanum complex **187** and mono(alkyl) biphenolate lanthanum complexes **188** and **189**, respectively (Chart 22).[347,348] Whereas biphenolate **189** revealed a dimeric structure in the absence of donor solvents, the sterically quite undemanding ancillary ligand allows for coordination of up to three donor molecules in the presence of thf (**188**). Compounds **187**−**189** show good catalytic activity for the hydroamination/cyclization of aminoalkenes, but the practical use for asymmetric hydroamination is limited by the low enantiomeric excesses in the produced heterocycles. In contrast, the C_2 symmetric bis(oxazolinato)lanthanide complex $[(4S)\text{-}tBuBox]Lu[CH(SiMe_3)_2]_2$ (**190**), synthesized via alkane elimination from $Lu[CH(SiMe_3)_2]_3$, displays an efficient enantioselective nonmetallocene hydroamination catalyst.[349]

Chart 20. Ln(CH$_2$SiMe$_2$Ph)$_3$(thf)$_2$ Derivatives Containing Neutral N-Donor- and Monoanionic N,O-Ancillary Ligands

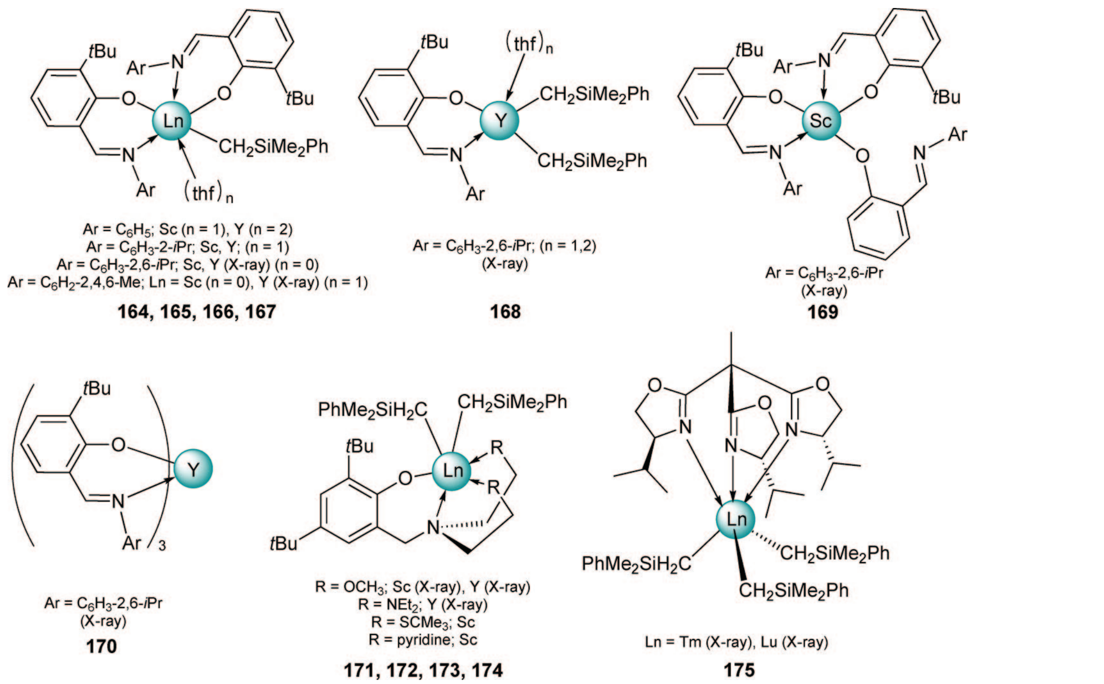
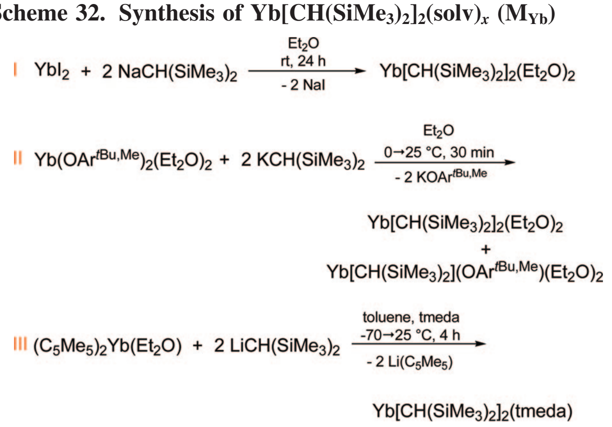


Table 9. Further Applications of Complexes Derived from Ln(CH$_2$SiMe$_2$Ph)$_3$(thf)$_2$ (L$_{thf}$)

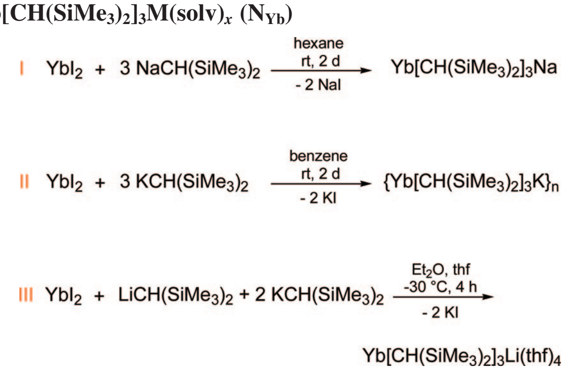
compound	further application	ref
164−167	formation of hydride compounds investigations on the thermal decomposition hydroamination of aminoalkynes and alkenes	302, 303, 322, 323
168	no further application	302
169	no further application	302
170	no further application	302
171−174	formation of monocations polymerization of ethylene	269
175	no further application	182, 256

Scheme 32. Synthesis of Yb[CH(SiMe$_3$)$_2$]$_2$(solv)$_x$ (M$_{Yb}$)



Contrary to the formation of Yb(II) 1-azaallyl and β-diketiminates when reacting divalent Yb[CH(SiMe$_3$)$_2$]$_2$-(Et$_2$O)$_2$ with nitriles NCPh and NC*t*Bu, respectively,[330] only 1:2 (**191**) and 1:1 (**192**) adducts of the nitrile to the rare-earth metal center have been observed starting from trivalent Ln[CH(SiMe$_3$)$_2$]$_3$ (Scheme 39).[330] Even when heated in toluene, no nitrile insertion into the Ln−C bond was evidenced, presumably due to effective steric shielding and the resulting high kinetic barrier for the insertion reaction. Acid−base reaction of Ln[CH(SiMe$_3$)$_2$]$_3$ (Ln = La, Y) with

Scheme 33. Synthesis of Ionic Compounds Yb[CH(SiMe$_3$)$_2$]$_3$M(solv)$_x$ (N$_{Yb}$)



perfluorobiphenols quantitatively produced compounds **194** (Scheme 39) capable of forming stable ion pairs with metallocene dimethyl complexes. Such ion pairs provided extremely active ethylene polymerization catalysts.[350] Complete ligand exchange was further observed for the reaction of bis(trimethylsilyl)phosphane and Y[CH(SiMe$_3$)$_2$]$_3$, yielding dimeric {Y[P(SiMe$_3$)$_2$]$_3$}$_2$ (**195**) and CH$_2$(SiMe$_3$)$_2$ (Scheme 39).[351]

Marks et al. found that homoleptic Ln[CH(SiMe$_3$)$_2$]$_3$ catalyzes the phosphinoalkyne cyclization with turnover

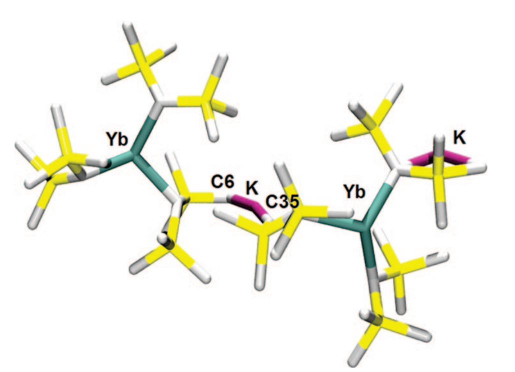


Figure 27. Solid-state structure of {Yb[CH(SiMe$_3$)$_2$]$_3$K}$_n$, adapted from ref 326.

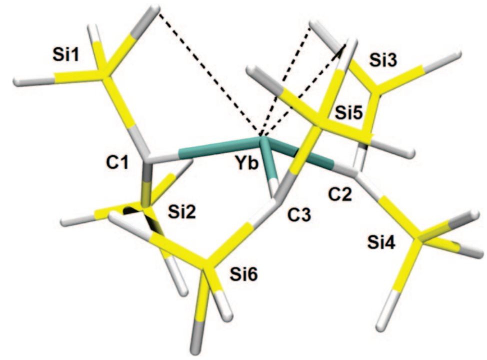
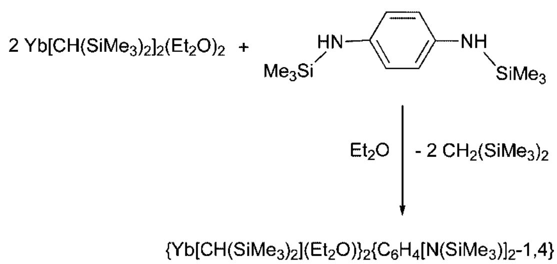


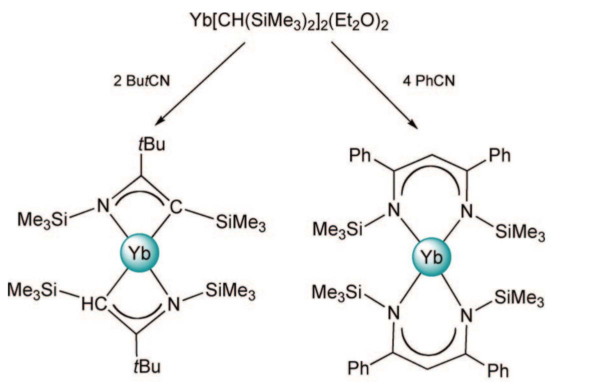
Figure 28. Solid-state structure of the $\{Yb[CH(SiMe_3)_2]_3\}$ anion in $Yb[CH(SiMe_3)_2]_3Li(thf)_4$, adapted from ref 326.

Scheme 34. Reaction of $Yb[CH(SiMe_3)_2]_2(Et_2O)_2$ with $C_6H_4(NH(SiMe_3))_2$-1,4



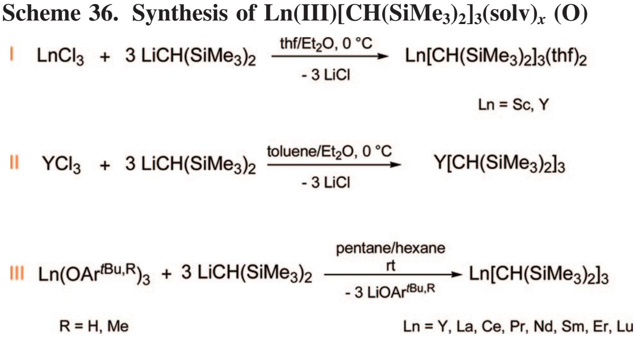
177

Scheme 35. Reaction of $Yb[CH(SiMe_3)_2]_2(Et_2O)_2$ with Bu*t*CN and PhCN



(X-ray)
178 179

Scheme 36. Synthesis of $Ln(III)[CH(SiMe_3)_2]_3(solv)_x$ (O)



frequencies comparable to the most active lanthanidocene catalysts. In an initiating step, complete Ln−$[CH(SiMe_3)_2]$ protonolysis is observed according to ^1H NMR spectroscopic investigations.[352]

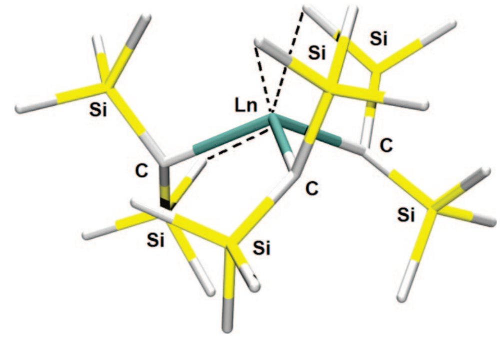
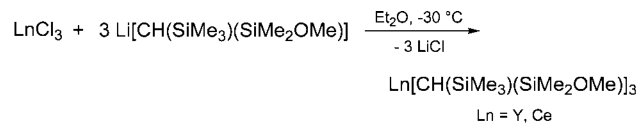


Figure 29. Solid-state structure of $Ln[CH(SiMe_3)_2]_3$ (**O**), adapted from refs 75 and 330.

Scheme 37. Synthesis of $Ln(III)[CH(SiMe_3)(SiMe_2OMe)]_3$ (P)



The treatment of lanthanum tris(alkyl) $La[CH(SiMe_3)_2]_3$ with 2 equiv of the secondary phosphine $HP(NMe_2CH_2\text{-}2\text{-}C_6H_4)[CH(SiMe_3)_2]$ revealed the product of a cyclometalation reaction (**196**) with the intramolecular elimination of $CH_2(SiMe_3)_2$ from transiently formed $\{[CH(SiMe_3)_2](C_6H_4\text{-}2\text{-}CH_2NMe_2)P\}_2La[CH(SiMe_3)_2]$ (Scheme 39).[353]

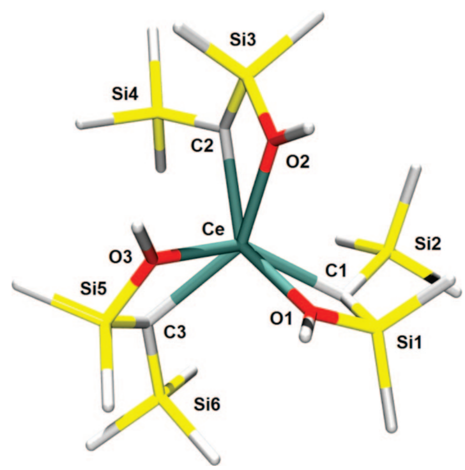
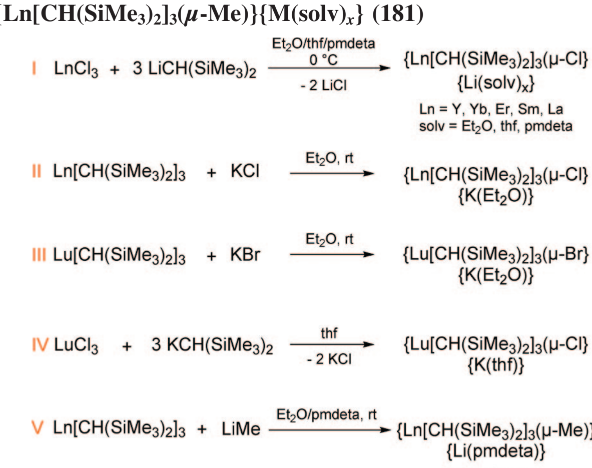


Figure 30. Solid-state structure of $Ce[CH(SiMe_3)(SiMe_2OMe)]_3$ (O_{Ce}), adapted from ref 330.

Scheme 38. Synthesis of Ate Complexes $\{Ln[CH(SiMe_3)_2]_3(\mu\text{-}X)\}\{M(solv)_x\}$ (180) and $\{Ln[CH(SiMe_3)_2]_3(\mu\text{-}Me)\}\{M(solv)_x\}$ (181)



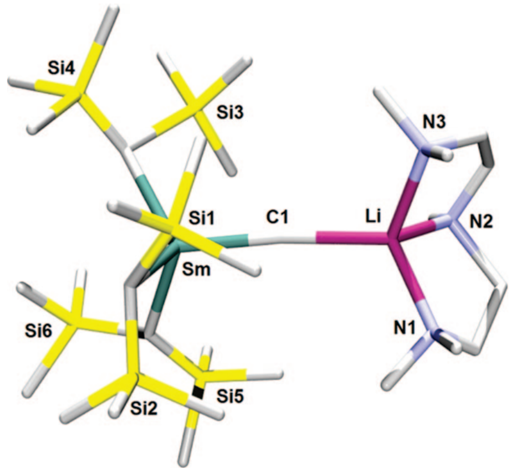
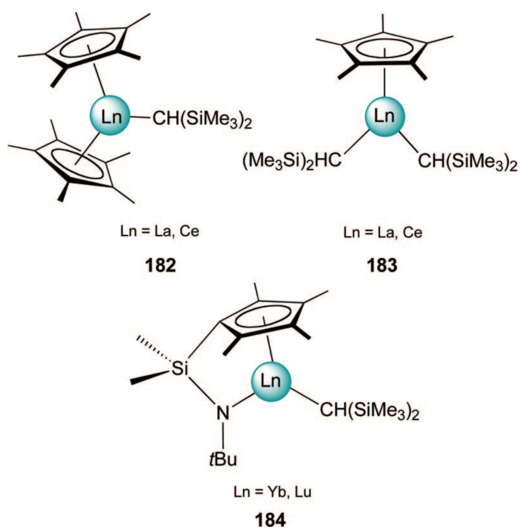


Figure 31. Solid-state structure of {Sm[CH(SiMe$_3$)$_2$]$_3$(μ-Me)}{Li(pmdeta)} (**181**$_{Sm-pmdeta}$), adapted from ref 339.

Chart 21. Sandwich (182), Half-Sandwich (183), and Constrained Geometry Complexes (184) Derived from Ln[CH(SiMe$_3$)$_2$]$_3$ (O)



11. Tris(trimethylsilyl)methyl Complexes

11.1. Synthesis, Structure, and Properties of Ln(II)[C(SiMe$_3$)$_3$]$_2$ and Ln(II)[C(SiMe$_3$)$_2$(SiMe$_2$R)]$_2$

Extending the series of trimethylsilyl-substituted methyl ligands to the highest possible substitution at the methyl carbon atom leads to extremely bulky [C(SiMe$_3$)$_3$] ligands.[74] Because of their high steric demand, such ligands are well suited to stabilize lanthanide metal centers in the divalent oxidation state. While ate complex formation was indicative of insufficient steric protection for the divalent ytterbium complexes carrying [CH(SiMe$_3$)$_2$] ligands, such salt formation is effectively suppressed in Eaborn complexes Ln(II)[C(SiMe$_3$)$_3$]$_2$ (**Q**).

However, the first attempts to synthesize a homoleptic ytterbium alkyl complex applying the reaction conditions that yield Yb[CH(SiMe$_3$)$_2$]$_2$(Et$_2$O)$_2$ (**M**$_{Yb-Et_2O}$) were not successful. Reaction of YbI$_2$ with 2 equiv of KC(SiMe$_3$)$_3$ in Et$_2$O rather gave orange−red crystals of the dimeric ether cleavage product {Yb[C(SiMe$_3$)$_3$](μ-OEt)(Et$_2$O)}$_2$ (**197**) than the putative Yb[C(SiMe$_3$)$_3$]$_2$ (Scheme 40).[324,325]

Further attempts to synthesize Yb[C(SiMe$_3$)$_3$]$_2$ were undertaken in the absence of ethereal solvents. A suspension of YbI$_2$ in benzene reacted with a solution of KC(SiMe$_3$)$_3$ to yield the homoleptic, solvent-free ytterbium alkyl complex Yb[C(SiMe$_3$)$_3$]$_2$ (**Q**$_{Yb}$) (Scheme 41, I).[74]

The respective europium(II)[354] and samarium(II)[355] complexes were synthesized the same way, with yields decreasing with increasing size of the metal cation (Yb > Eu > Sm). The crystal structures of all three compounds have been determined and revealed solvent-free monomers (Figures 32 and 33).

The most interesting feature of the solid-state structures is the bent C−Ln−C angles (137°, Yb; 136°, Eu; 143°, Sm). Similar bending is also observed for the respective bis(cyclopentadienyls) Ln(C$_5$Me$_5$)$_2$.[356−359] There have been intensive discussions about whether the bending is caused by electronic factors[360,361] or by ligand interactions.[362] As the latter would be significantly reduced by lengthening of the metal−carbon bond, the similarity of the observed angles in the ytterbium and europium compounds suggests that the factor determining the C−Ln−C angles is electronic rather than steric. A contribution of the metal d-orbitals has been discussed.[354]

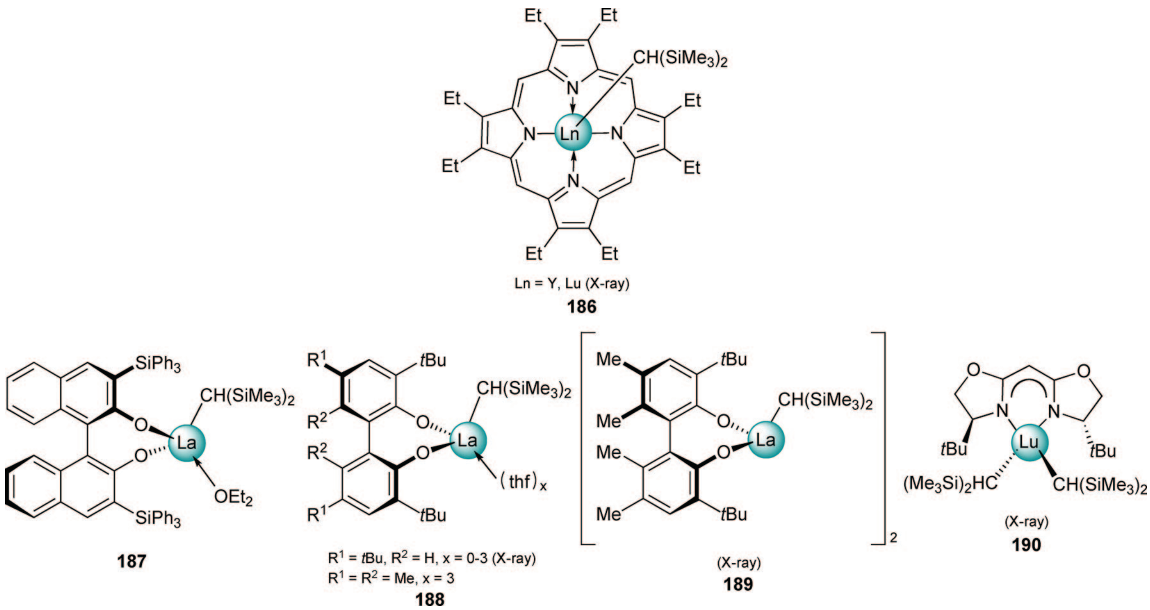
The mean metal−carbon distances in complexes Ln[C(SiMe$_3$)$_3$]$_2$ (**Q**) are long compared to those observed in other "two-coordinate" divalent species,[363,364] reducing the interactions between the SiMe$_3$ groups. The ytterbium compound shows two short Yb−methyl secondary interactions in the solid state, which contribute to a stabilization of the molecule (Figure 33).[74] Three similar interactions were observed for the larger europium metal center (Figure 32).[354] Attempts to distinguish the methyl groups by low-temperature NMR spectroscopy were not successful. All protons appeared to be equivalent even at −95 °C.

In order to provide further stabilization of complexes Ln[C(SiMe$_3$)$_3$]$_2$ (**Q**), a series of ligand modifications has been carried out and the ligand contribution on the complex stability and reactivity has been studied.[354] Reaction of YbI$_2$ with the modified potassium salts KC(SiMe$_3$)$_2$(SiMe$_2$R) (R = CH=CH$_2$ and CH$_2$CH$_2$OEt) in benzene afforded Yb[C(SiMe$_3$)$_2$(SiMe$_2$R)]$_2$ (**R**) in good yields (Scheme 41, II). A methoxy derivative of ytterbium was obtained by heating {Yb[C(SiMe$_3$)$_2$(SiMe$_2$OMe)]I(Et$_2$O)$_2$}$_2$ (Scheme 41, IV) under reduced pressure. More intuitive seems the synthesis of the samarium analogue starting from SmI$_2$(thf)$_2$ and the potassium salt KC(SiMe$_3$)$_2$(SiMe$_2$OMe) (Scheme 41, III).[365] Sm[C(SiMe$_3$)$_2$(SiMe$_2$OMe)]$_2$(thf) (**R**$^{OMe}_{Sm-thf}$) could be obtained in high yield as green−black single crystals grown from cyclohexane (Figure 34). The five-coordinate samarium metal center is surrounded by the two chelating alkyl ligands and one thf molecule. Additional coordination of the OMe groups results in the formation of two four-membered chelate rings.

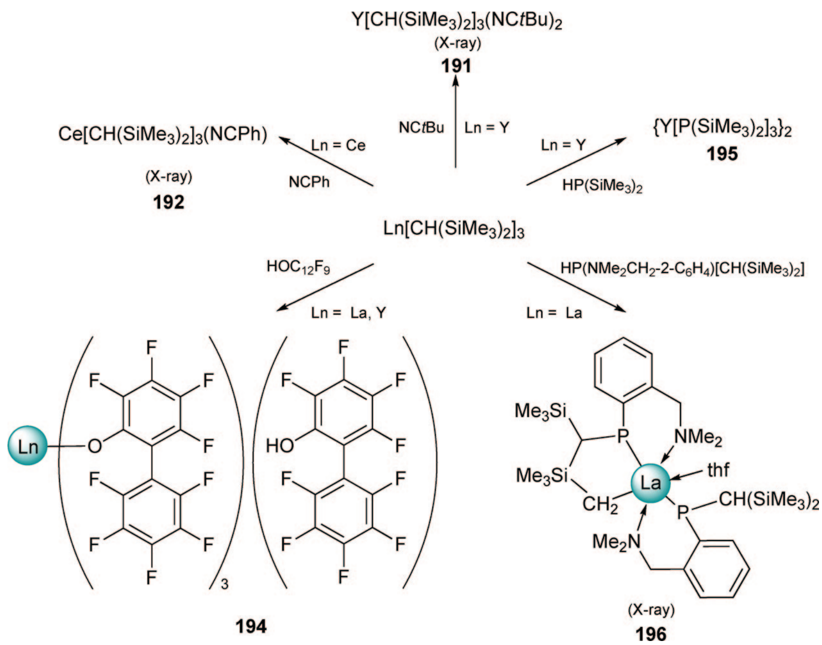
Because of the higher coordination numbers of the divalent metal center, the tendency to ether cleavage as found for Yb[C(SiMe$_3$)$_3$]$_2$ (**Q**$_{Yb}$) (Scheme 40) could be reduced dramatically. The additional interaction with the chelating ligand, even the weak vinyl−Yb interaction (for R = CH=CH$_2$), inhibits the coordination of Et$_2$O and consecutive ether cleavage reactions.

SmI$_2$ is a commonly used reagent in organic syntheses. Presumably, organosamarium intermediates play a key role in the SmI$_2$ mediated addition of alkylhalogenides to ketones (samarium Barbier reaction (SBR)). The reactivity of Sm[C(SiMe$_3$)$_2$(SiMe$_2$OMe)]$_2$(thf) (**R**$^{OMe}_{Sm-thf}$) toward benzophenone has therefore been investigated but revealed the

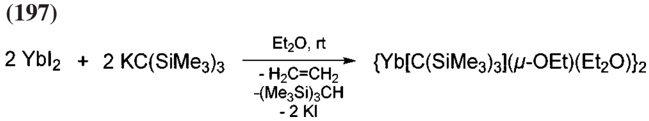
Chart 22. Porphyrinato, Binaphtholato, Biphenolato, And Bis(Oxazolinato) Complexes Derived from $Ln[CH(SiMe_3)_2]_3$ (O)



Scheme 39. Derivatization of $Ln[CH(SiMe_3)_2]_3$ (O)



Scheme 40. Synthesis of $\{Yb[C(SiMe_3)_3](\mu\text{-}OEt)(Et_2O)\}_2$ (197)

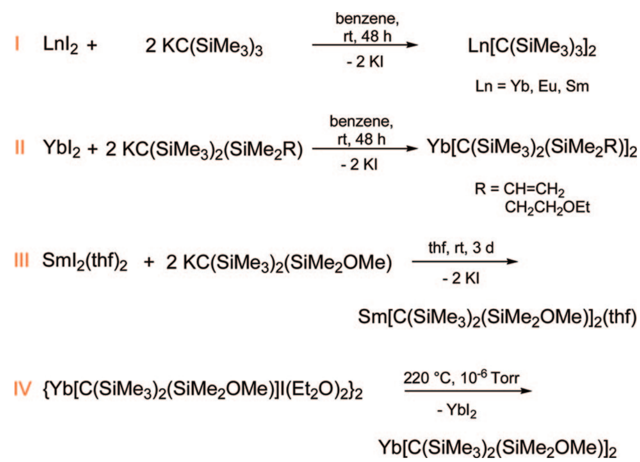


formation of a ketyl−radical anion complex $Sm[C(SiMe_3)_2(SiMe_2OMe)]_2(OCPh_2)$ (**198**) rather than a Grignard-like addition product.[365]

A series of Grignard reagent analogues with the general formula $\{Yb[C(SiMe_3)_2(SiMe_2R)]I(Et_2O)_2\}_2$ (**199**$_{Et_2O}$) has been reported. The reaction of $Yb[C(SiMe_3)_3]_2$ with iodomethane led to the cleavage of one Yb−C bond and formation of $\{Yb[C(SiMe_3)_3]I(Et_2O)_2\}_2$ (Scheme 42, I).[74]

The multiplicity of products/byproducts arising from this reaction, especially the formation of side-product $HC(SiMe_3)_3$, suggests a radical reaction pathway (not shown in Scheme 42). The same compound was isolated from the

Scheme 41. Synthesis of $Ln(II)[C(SiMe_3)_3]_2$ (Q) and $Ln(II)[C(SiMe_3)_2(SiMe_2R)]_2$ (R)



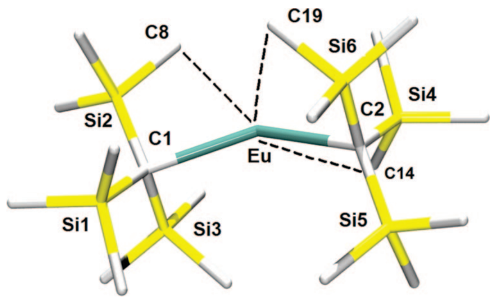


Figure 32. Solid-state structure of Eu[C(SiMe$_3$)$_3$]$_2$ (**Q**$_{Eu}$), adapted from ref 354.

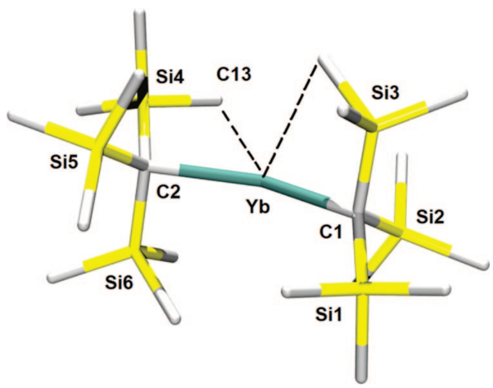


Figure 33. Solid-state structure of Yb[C(SiMe$_3$)$_3$]$_2$ (**Q**$_{Yb}$), adapted from ref 355.

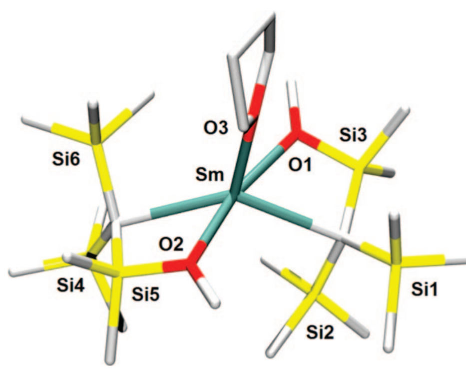
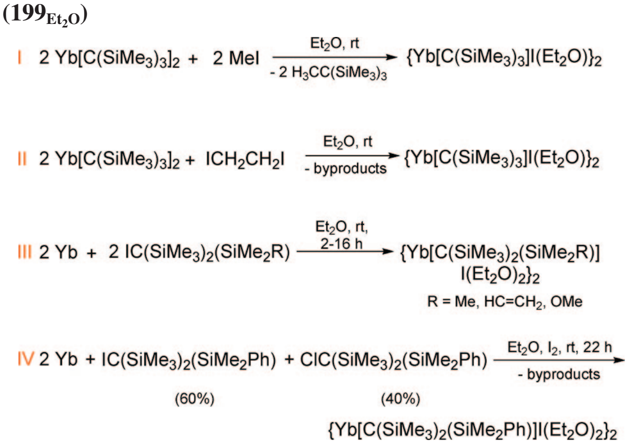


Figure 34. Solid-state structure of Sm[C(SiMe$_3$)$_2$(SiMe$_2$OMe)]$_2$-(thf) (**R**^{OMe}$_{Sm-thf}$), adapted from ref 365.

Scheme 42. Synthesis of {Yb[C(SiMe$_3$)$_2$(SiMe$_2$R)]I(Et$_2$O)$_2$}$_2$ (199$_{Et_2O}$)



reaction between Yb[C(SiMe$_3$)$_3$]$_2$ and an excess of ICH$_2$CH$_2$I as well as the reaction with IC(SiMe$_3$)$_3$ in Et$_2$O, respectively (Scheme 42, II and III).[74] The use of alkyl iodides and Yb powder further allowed for the synthesis of derivatives

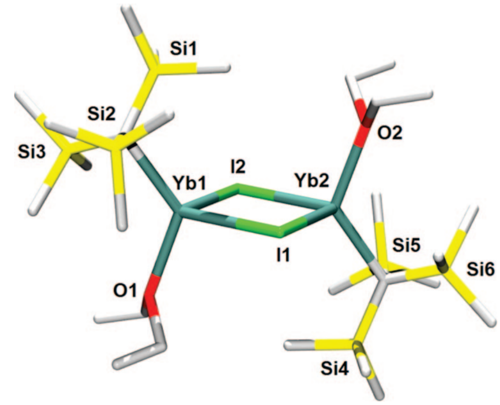


Figure 35. Solid-state structure of {Yb[C(SiMe$_3$)$_3$]I(Et$_2$O)}$_2$ (**199**^{Me}$_{Yb-Et_2O}$), adapted from ref 74.

{Yb[C(SiMe$_3$)$_2$(SiMe$_2$R)]I(Et$_2$O)$_2$}$_2$ (R = CH=CH$_2$, OMe) (Scheme 42, III).[354] {Yb[C(SiMe$_3$)$_2$(SiMe$_2$Ph)]I(Et$_2$O)$_2$}$_2$ was obtained from a mixture of the respective iodoalkyl and the chloroalkyl (Scheme 42, IV).[354] All “lanthanide Grignard” reagents (**199**$_{Et_2O}$) are stable in Et$_2$O solutions and can be stored as such for several weeks. The alkyl ytterbium iodides decompose when heated under reduced pressure to give Yb[C(SiMe$_3$)$_2$(SiMe$_2$R)]$_2$ and YbI$_2$ (see Scheme 42, IV). In nonpolar organic solvents, all Grignard-type ytterbium complexes exist in a typical Schlenk equilibrium.

The solid-state structures of several alkyl iodides have been determined, all substantiating dimeric structures (Figure 35).[74,354] The molecules usually have a center of symmetry due to an almost square-planar Yb$_2$I$_2$ ring. Analogue structures are adopted by a number of Grignard reagents.

Besides their occurrence in organic synthesis (in situ formation), probably the most interesting application of complexes Ln[C(SiMe$_3$)$_3$]$_2$ is their ability to polymerize methylmethacrylate and acrylonitrile.[355,366,367] Of several tested divalent ytterbium alkyl, amide, and alkynide complexes, Yb[C(SiMe$_3$)$_3$]$_2$ produced poly(MMA) with the highest isotacticity (97%) and excellent yield. The obtained polymer showed high molecular weights ($M_n = 51 \times 10^4$ g/mol) and very narrow molecular weight distributions ($M_w/M_n = 1.1$).[355]

11.2. Synthesis, Structure, and Properties of Related Ln(II) Silylmethyl Complexes

In 1999, a closely related bidentate ligand [(Me$_3$Si)$_2$CSiMe$_2$-CH$_2$CH$_2$SiMe$_2$C(SiMe$_3$)$_2$] had been introduced to low-valent lanthanide organometallic chemistry.[368] This ligand can be regarded as two trimethylsilyl groups (“trisyl”) joined together like Siamese twins and thus is referred to as a “trisamyl” ligand. Treatment of YbI$_2$ with the potassium salt of the trisamyl ligand gave the solvent-free chelate complex Yb[(Me$_3$Si)$_2$CSiMe$_2$CH$_2$CH$_2$SiMe$_2$C(SiMe$_3$)$_2$] (**S**$_{Yb}$) (Figure 36). Because of high disorder, detailed structural data could not be obtained. The reaction of **S**$_{Yb}$ with Et$_2$O was investigated and found to be slower than the one with Yb[C(SiMe$_3$)$_3$]$_2$.

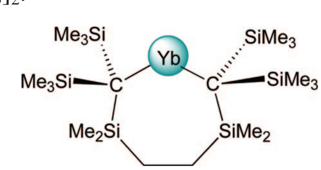
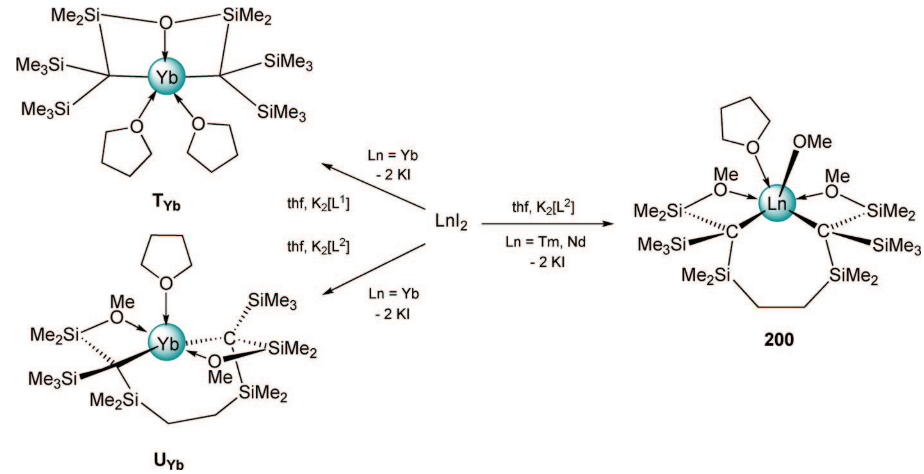


Figure 36. Structure of Yb[(Me$_3$Si)$_2$CSiMe$_2$CH$_2$CH$_2$SiMe$_2$C-(SiMe$_3$)$_2$] (**S**$_{Yb}$).

Scheme 43. Synthesis of Yb(II), Tm(III), and Nd(III) Complexes with [L^1] and [L^2]



Scheme 44. Synthesis of $Lu(CH_2SiMe_3)_2(CHPh_2)(thf)_2$ (201)

$$LuCl_3(thf)_3 + 2\ LiCH_2SiMe_3 + KCHPh_2 \xrightarrow[-\ 2\ LiCl,\ -\ KCl]{thf/pentane/Et_2O} Lu(CH_2SiMe_3)_2(CHPh_2)(thf)_2$$

Very recently, the ytterbium(II) complexes of the dicarbanionic sterically hindered, O-functionalized ligands [L^1] and [L^2] (see Scheme 43) have been reported.[369] YbI_2 and either of the dipotassium agents $K_2[L^1]$ and $K_2[L^2]$ cleanly formed the corresponding bisalkylytterbium(II) compounds $\mathbf{T}_{Yb}$ and $\mathbf{U}_{Yb}$.

Both compounds react instantaneously with Et_2O as known for $Yb[C(SiMe_3)_3]_2$ (Scheme 40) but can be isolated as thf adducts. Upon standing at ambient temperature for several days, $\mathbf{T}_{Yb}$ partly forms a paramagnetic Yb(III) species, as evidenced by NMR spectroscopic experiments.

In contrast to the ready isolation of ytterbium(II) compounds, reactions between LnI_2 (Ln = Tm, Nd) and $K_2[L^2]$ were accompanied by oxidation of the divalent metal center to form Tm(III) and Nd(III) complexes **200** (Scheme 43). The additional metal methoxy ligand coordinated to the metal in complex **200** is most likely derived from Si−O cleavage of a second dicarbanion ligand.[369]

12. Mixed Alkyl Complex $Lu(CH_2SiMe_3)_2(CHPh_2)(thf)_2$

Because of its steric demand and the flexible bonding modes, the [$CHPh_2$] anion appeared to be a promising candidate for the synthesis of stable lanthanide alkyl complexes. The anticipated formation of homoleptic complexes $Ln(CHPh_2)_3(solv)_x$, however, was not observed.[370] Attempted synthesis by reaction of 2/3 equiv of $KCHPh_2$ with $YbI_2(thf)_2$, $LuCl_3$, $YbCl_3$, and YCl_3, respectively, only resulted in dark-colored oils. The heteroleptic lutetium alkyl complex $Lu(CH_2SiMe_3)_2(CHPh_2)(thf)_2$ (**201**) could be obtained according to the equation depicted in Scheme 44.[370]

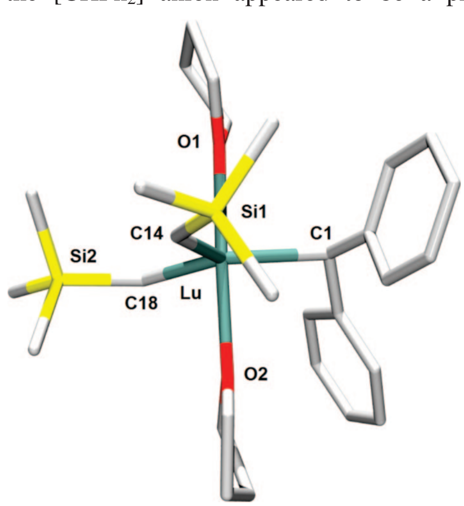


Figure 37. Solid-state structure of $Lu(CH_2SiMe_3)_2(CHPh_2)(thf)_2$ (**201**), adapted from ref 370.

The mixed alkyl compound shows a solid-state structure comparable to its homoleptic analogue $Lu(CH_2SiMe_3)_3(thf)_2$ (cf., Figure 21). The three alkyl ligands occupy the equatorial positions of a distorted trigonal bipyramid (Figure 37).

Because of the steric requirement of the benzylhydryl ligand, the lutetium methine carbon distance (Lu−C1, 2.45 Å) is considerably longer than the lutetium methylene carbon distances in the same molecule (Lu−C14, 2.35 Å; Lu−C18, 2.34 Å).

The alkyl compound is extremely air- and water-sensitive but is stable for some days if kept in evacuated sealed tubes. So far, literature provides no further information on the derivatization or reactivity of $Lu(CH_2SiMe_3)_2(CHPh_2)(thf)_2$.

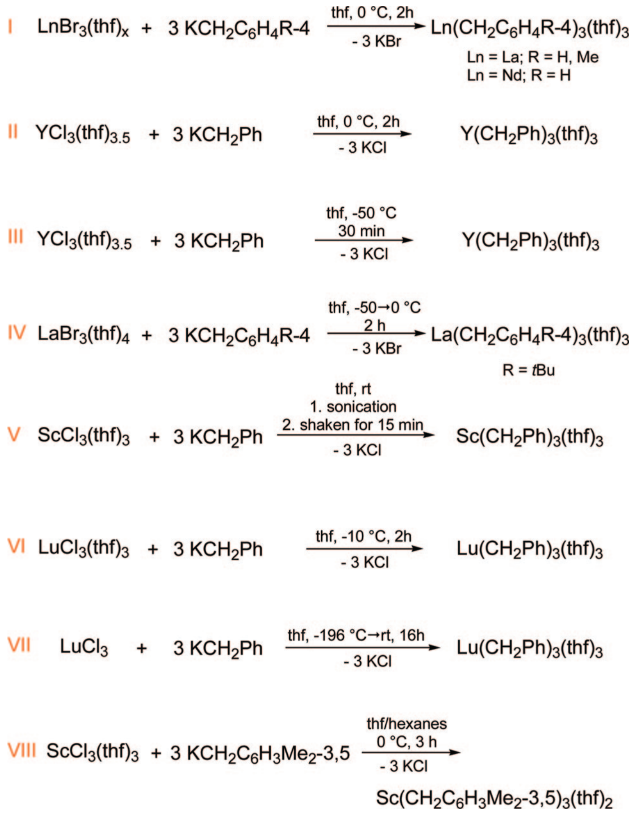
13. Benzyl Complexes

13.1. Synthesis, Structure, and Properties of $Ln(III)(CH_2Ph^R)_3(donor)_x$

Because of the need for suitable homoleptic alkyl precursors especially of the larger rare-earth metals, benzyl ligands [CH_2Ph] experienced a revival. The first reports on homoleptic tris(benzyl) complexes of neodymium[371,372] and lanthanum[373] were published in the 1980s but were inconclusive as to the existence of these species. Both compounds were characterized as (thermally) labile and decomposition by an α-elimination pathway, producing alkylidene products [$PhCH_2Nd{=}CHPh$] and carbine-like species [$Nd{\equiv}CPh$], was proposed for the neodymium compound, whereas the formation of [$PhCH_2La(H)OCH{=}CH_2(thf)_2$] was suggested in the lanthanum case. Recently, the straightforward synthesis of neutral, salt-free lanthanum tris(benzyl) complexes $La(CH_2Ph)_3(thf)_3$ ($\mathbf{V}_{La-thf}$) and $La(CH_2C_6H_4\text{-}4\text{-}Me)_3(thf)_3$ ($\mathbf{V}^{Me}_{La-thf}$) was described by the group of Hessen (Scheme 45).[374]

Reaction of $LaBr_3(thf)_4$ with 3 equiv of potassium benzyls $KCH_2C_6H_4\text{-}4\text{-}R$ (R = H, Me) in thf afforded lanthanum tris(benzyls) $\mathbf{V}_{La-thf}$ and $\mathbf{V}^{Me}_{La-thf}$ as orange−yellow crystals (Scheme 45, I). Under the same reaction conditions,

Scheme 45. Synthesis of $Ln(CH_2Ph)_3(thf)_3$ (V_{thf}), $Ln(CH_2C_6H_4Me\text{-}4)_3(thf)_3$ (V^{Me}_{La-thf}), and $Sc(CH_2C_6H_3Me_2\text{-}3,5)_3(thf)_2$ ($V^{Me,Me}_{Sc-thf}$)

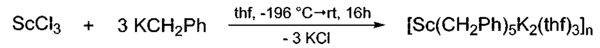


$NdBr_3(thf)_{3.5}$ or $YCl_3(thf)_{3.5}$ and KCH_2Ph formed the respective neodymium and yttrium compounds (Scheme 45, I and II).[375,376] Single crystals of the yttrium tris(benzyl) were obtained by performing the reaction at −50 °C (Scheme 45, III).[377] Higher solubility of benzyl compounds in apolar solvents was anticipated by the introduction of *tert*-butyl substituents in the 4-position of a homoleptic lanthanum benzyl complex (Scheme 45, IV).[377] Lately, the suitability of the benzyl ligand to stabilize homoleptic complexes of the smallest rare-earth metals scandium and lutetium has been demonstrated. $ScCl_3(thf)_3$ and $LuCl_3(thf)_3$ react with 3 equiv of the potassium benzyl at ambient temperature (Sc) or in a cooled thf solution (Lu) to yield the respective homoleptic rare-earth metal benzyl compounds $Ln(CH_2Ph)_3(thf)_3$ in good yield (Scheme 45, V and VI).[378] Trituration of the scandium and lutetium tris(benzyl) complexes in toluene results in ready loss of one thf donor ligand, leading to pentacoordinate complexes $Ln(CH_2Ph)_3(thf)_2$. Aiming at the synthesis of Ln–benzyls with increased solubility in hydrocarbon solvents, $ScCl_3(thf)_3$ was reacted with $KCH_2C_6H_3Me_2$-3,5, which allowed for the isolation of the tris(dimethylbenzyl) compound $Sc(CH_2C_6H_3Me_2\text{-}3,5)_3(thf)_2$ (Scheme 45, VIII).[379]

Performing the salt-metathesis reaction between anhydrous $LuCl_3$ and KCH_2Ph at −196 °C followed by warming the reaction mixture to ambient temperature proved to be an alternative synthesis for neutral $Lu(CH_2Ph)_3(thf)_3$ (Scheme 45, VII).[378] On the contrary, anhydrous $ScCl_3$ and 3 equiv of potassium benzyl yielded a two-dimensional coordination polymer of the composition $[Sc(CH_2Ph)_5K_2(thf)_3]_n$, in which the scandium atom is surrounded by five benzyl groups in a trigonal-bypyramidal fashion (Scheme 46).

The crystal structure of $Ln(CH_2Ph)_3(thf)_3$ has been determined for Sc,[378] Y,[377] Nd,[375] and La.[374] In the solid state,

Scheme 46. Synthesis of $[Sc(CH_2Ph)_5K_2(thf)_3]_n$



$La(CH_2Ph)_3(thf)_3$ and $Nd(CH_2Ph)_3(thf)_3$ revealed a *fac*-octahedral coordination of the benzyl and thf ligands. Interaction of the *ipso*-carbon atoms of each benzyl moiety with the large rare-earth metal center results in an η^2 coordination, thus providing additional steric stabilization (Figure 38).[374,375] The *p*-tolyl derivatives $La(CH_2C_6H_4Me\text{-}4)_3(thf)_3$[374] and $La(CH_2C_6H_4tBu\text{-}4)_3(thf)_3$[377] are essentially isostructural with $\mathbf{V}_{La-thf}$.

The solid-state structure of $Sc(CH_2Ph)_3(thf)_3$ revealed also a distorted *fac*-octahedral coordination of the three benzyl groups and three thf molecules (Figure 39).[378] In contrast to the lanthanum tris(benzyl) complex, an η^1 coordination of the benzyl groups is observed in $Sc(CH_2Ph)_3(thf)_3$[378] and $Y(CH_2Ph)_3(thf)_3$,[377] in agreement with the significantly smaller ionic radius of scandium.

$La(CH_2Ph)_3(thf)_3$ and $La(CH_2C_6H_4\text{-}4\text{-}Me)_3(thf)_3$ are poorly soluble in hydrocarbons but can be dissolved in thf. On the NMR time scale, all benzyl methylene protons are equivalent, suggesting an average C_{3v} symmetric solution structure.[374] The tris(benzyl) complexes of the smaller rare-earth metals Sc and Lu are reported to be soluble in hydrocarbons, whereas ionic $[Sc(CH_2Ph)_5K_2(thf)_3]_n$ needs to be dissolved in thf. ^1H NMR spectra of the latter recorded in thf-d_8 show only one singlet for the methylene protons in accordance with a monomeric structure.[378]

13.2. $Ln(CH_2Ph^R)_3(donor)_x$ as Synthesis Precursors

Mono(cationic) and di(cationic) lanthanum benzyl species could be obtained when reacting $\mathbf{V}_{La-thf}$ and $\mathbf{V}^{Me}_{La-thf}$ with 1 or 2 equiv of the Brønsted acid $[PhNMe_2H][B(C_6F_5)_4]$. To facilitate crystallization of the ionic lanthanum compounds, the corresponding tetraphenylborate salts were prepared using $[PhNMe_2H][BPh_4]$. Remarkably, both mono(cation) $\mathbf{V}^{+}_{La-thf}$ and di(cation) $\mathbf{V}^{2+,Me}_{La-thf}$ could be crystallized and showed two tilted η^3 coordinated benzyl groups in the mono(cationic)

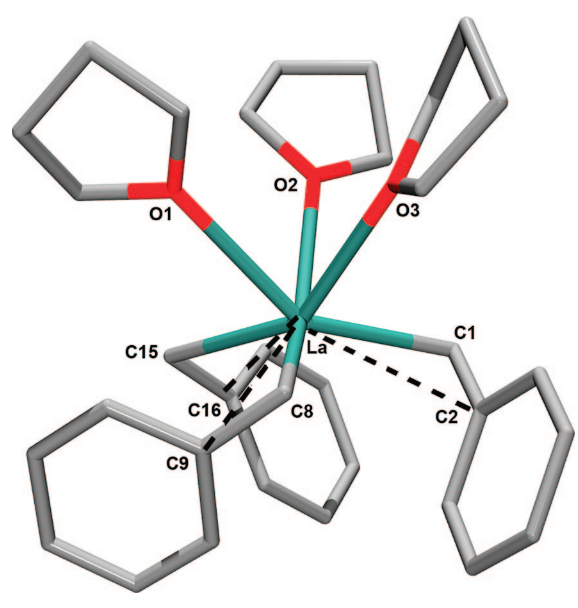


Figure 38. Solid-state structure of $La(CH_2Ph)_3(thf)_3$ ($\mathbf{V}_{La-thf}$), adapted from ref 374.

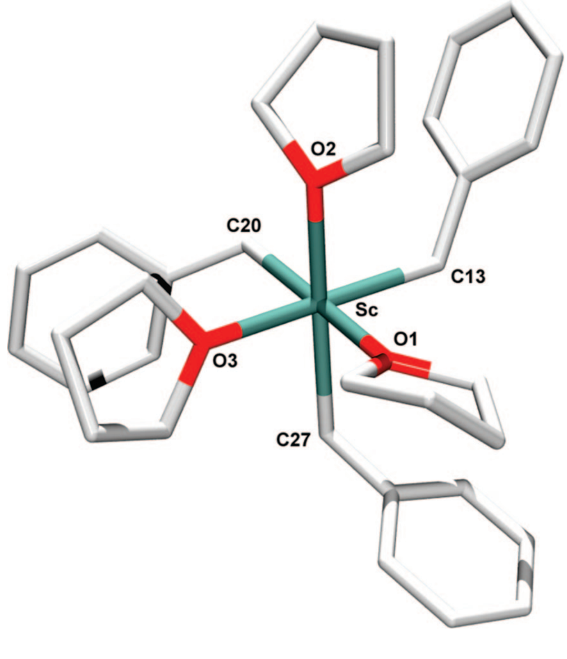


Figure 39. Solid-state structure of $Sc(CH_2Ph)_3(thf)_3$ ($\mathbf{V}_{Sc-thf}$), adapted from ref 378.

species $\mathbf{V}^{+}_{La-thf}$, whereas the remaining benzyl ligand in the di(cation) $\mathbf{V}^{2+,Me}_{La-thf}$ is essentially η^2 bonded (Chart 23). In both molecules, the environments of the lanthanum metal centers are saturated by thf molecules.

Reactions of the tris(benzyl) complex $\mathbf{V}^{Me}_{La-thf}$ with $LiCH_2C_6H_4$-4-Me in thf led to the formation of the ionic compound $[La(CH_2C_6H_4\text{-4-Me})_4][Li(thf)_4]$ ($\mathbf{V}^{-}_{La}$). Crystal structure determination again revealed a stabilizing η^2 coordination of all four benzyl ligands in the anionic unit.

Application of lanthanum benzyls $\mathbf{V}_{La-thf}$ and $\mathbf{V}^{Me}_{La-thf}$ as alkyl precursors in a series of derivatization reactions demonstrates the versatility and synthetic value of these compounds (Chart 23).[189,374,380] Acid−base reaction with the amidine ArN=CR′NHAr (Ar = C_6H_3-2,6-*i*Pr; R′ = Ph, *t*Bu) in thf generated the mono(amidinate)−bis(benzyl) complexes $[R'C(NAr)_2]La(CH_2C_6H_4\text{-R})_2(thf)_n$ (**202** and **203**) and 1 equiv of toluene or *p*-xylene, respectively.[189,374] In complexes **202**, one benzyl ligand is coordinated in an η^2 mode whereas the second benzyl ligand is significantly tilted, suggesting an η^3-like bonding. The more sterically hindered amidine with a *tert*-butyl substituent in the backbone allows only for two η^2 coordinated benzyl ligands in complex **203**. By reaction with $[PhNMe_2H][BPh_4]$, compound **203** can be transferred into the respective mono(cationic) species.

Mixtures $La(CH_2Ph)_3(thf)_3/[PhNMe_2H][B(C_6F_5)_4]$ and **202**/$[PhNMe_2H][B(C_6F_5)_4]$ in toluene show low activities in the polymerization of ethylene and provide catalysts for the intramolecular hydroamination/cyclization.[374] In the presence of 1,4,7-trimethyl-1,4,7-triazacyclononane, $La(CH_2Ph)_3(thf)_3$ forms compound **204** with one η^2 bound $[CH_2Ph]$ ligand. Reaction with a silylamino-substituted triazacyclononane led to the clean formation of monomeric, donor-solvent-free lanthanum dibenzyl complex **205**.[376]

Scandium tris(dimethylbenzyl) $Sc(CH_2C_6H_3Me_2\text{-3,5})_3(thf)_2$ was successfully used as a synthesis precursor for the preparation of ferrocene diamide scandium complex **206**.[379] Subsequent ligand-exchange reactions have been carried out, and the performance of **206** as a catalyst for the ROP of L-lactide has been investigated.

13.3. Synthesis, Structure, Properties, and Derivatization of $Ln(II)[CH(SiMe_3)C_6H_4\text{-}o\text{-}NMe_2]_2(thf)_2$

The research on benzyl complexes of the divalent lanthanide metals was greatly influenced by the chemistry of heavy alkaline-earth metals.[381] Striking similarities between the chemistries of Ca(II) and Yb(II) have been evidenced in solid-state structures and the chemical behavior.[354,382−384] Considering these parallels, Harder introduced donor-functionalized benzyl ligands to the chemistry of divalent lanthanide metals, which were previously successfully applied for alkaline-earth metals.[381] Benzyl ligands, which kinetically and thermodynamically stabilize the large coordination spheres of divalent lanthanide metals but still provide enough nucleophilicity to initiate catalytic reactions, have been applied, in particular the [2-NMe_2-α-Me_3Si-benzyl] ligand.

Accordingly, complexes $Ln(II)[CH(SiMe_3)C_6H_4\text{-}o\text{-}NMe_2]_2(thf)_2$ ($\mathbf{W}_{thf}$) could be obtained by salt-metathesis reaction of the respective LnI_2 and 2 equiv of $K[CH(SiMe_3)C_6H_4\text{-}o\text{-}NMe_2]$ in thf at ambient temperature (Scheme 47).[377,381]

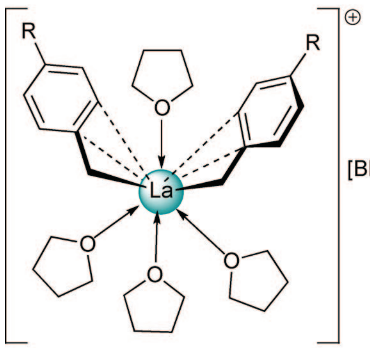
The solid-state structures of the Eu,[377] Sm,[381] and Yb[381] benzyl complexes have been determined and revealed diastereomers with *R* and *S* configuration at the benzylic carbons (Figure 40). The (2-Me_2N-α-Me_3Si-benzyl) ligand coordinates to the lanthanide metal center in a bidentate fashion. The coordination sphere might be described as a distorted octahedron with the carbanions in *trans* position and the four neutral coordinating groups in the equatorial plane. The benzylic carbons show a hybridization between sp^3 and sp^2. $Eu[CH(SiMe_3)C_6H_4\text{-}o\text{-}NMe_2]_2(thf)_2$ and $Sm[CH(SiMe_3)C_6H_4\text{-}o\text{-}NMe_2]_2(thf)_2$ revealed isomorphous structures, which, in contrast to the respective ytterbium structure, showed short contacts to the aryl rings.

In solution, the complexes $Ln(II)[CH(SiMe_3)C_6H_4\text{-}o\text{-}NMe_2]_2(thf)_2$ exist as a pair of diastereomers interconverting slowly. However, only one set of thf signals is observed, indicating fast exchange of the thf ligands.

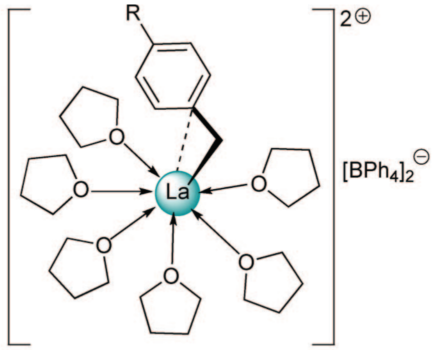
$Yb(II)[CH(SiMe_3)C_6H_4\text{-}o\text{-}NMe_2]_2(thf)_2$ has been used as a starting material for the formation of heteroleptic Yb(II) complexes. Following the synthesis procedure, which had previously been applied for calcium,[385] the ytterbium dibenzyl was reacted with 9-Me_3Si-fluorene to yield compound **207** (Chart 24), which has been applied as a catalyst for the polymerization of styrene.[381] Heteroleptic complexes can further be prepared by ligand exchange between two homoleptic compounds. The Schlenk-like equilibria present in such solutions are controlled by steric as well as electronic effects. When a reaction mixture of $Yb[CH(SiMe_3)C_6H_4\text{-}o\text{-}NMe_2]_2(thf)_2$ and $Yb(nacnac)_2$ was heated at 50 °C, the heteroleptic species **208** formed first but upon standing yielded the C−H activation product **209** (Chart 24).[381]

Homoleptic $Yb(II)[CH(SiMe_3)C_6H_4\text{-}o\text{-}NMe_2]_2(thf)_2$ and $Sm(II)[CH(SiMe_3)C_6H_4\text{-}o\text{-}NMe_2]_2(thf)_2$ initiate the polymerization of styrene.[381] For the ytterbium derivative, polystyrene of high syndiotacticity could be obtained, whereas a bimodal molecular weight distribution was found when the samarium-based catalyst was used. Oxidation of the Sm(II) metal center by styrene to a catalytically active Sm(III) species has been proposed.

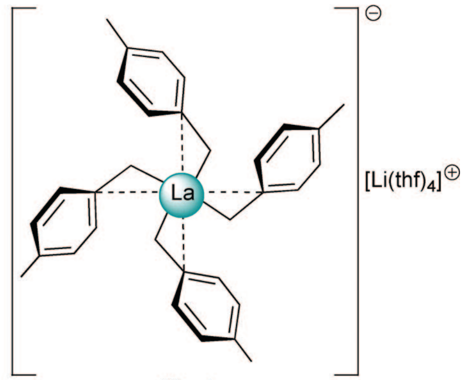
Chart 23. Derivatives of $La(CH_2Ph)_3(thf)_3$ (V_{La-thf}) and $La(CH_2C_6H_4\text{-}4\text{-}Me)_3(thf)_3$ (V^{Me}_{La-thf})



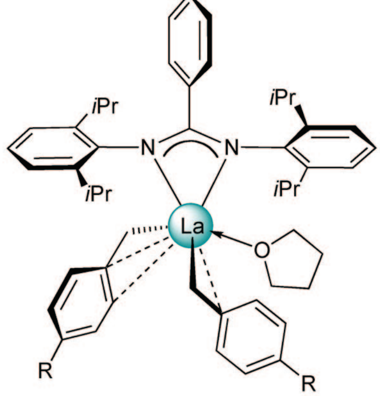
R = H (X-ray), Me
V^{+}_{La-thf}



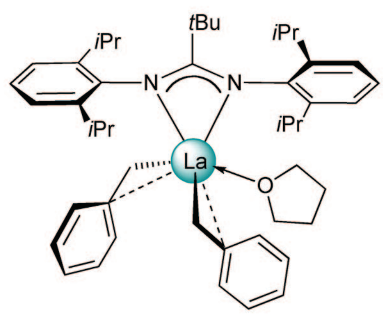
R = H, Me (X-ray)
V^{2+}_{La-thf}



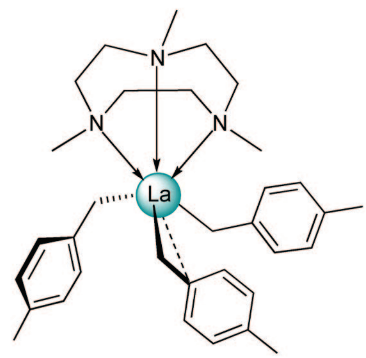
(X-ray)
V^{-}_{La}



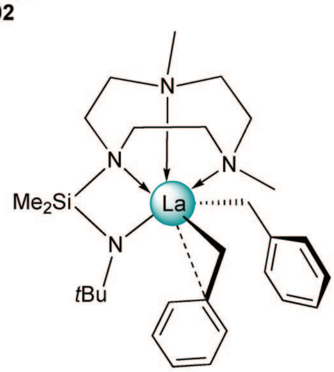
R = H (X-ray), Me
202



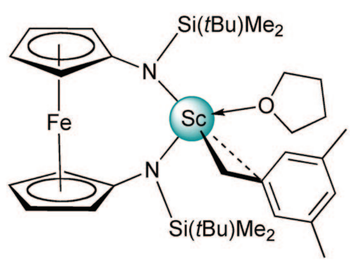
(X-ray)
203



(X-ray)
204



(X-ray)
205



(X-ray)
206

Scheme 47. Synthesis of $Ln(II)[CH(SiMe_3)C_6H_4\text{-}o\text{-}NMe_2]_2(thf)_2$ (W_{thf})

$LnI_2(thf)_n$ + 2 $K[CH(SiMe_3)C_6H_4\text{-}o\text{-}NMe_2]$ —(thf, rt, 40 h; − 2 KI)→ $Ln[CH(SiMe_3)C_6H_4\text{-}o\text{-}NMe_2]_2(thf)_2$

Ln = Eu, Sm, Yb

13.4. Synthesis, Structure, and Properties of $Ln(III)(CH_2C_6H_4\text{-}o\text{-}NMe_2)_3$ and $Ln(III)(CH_2C_6H_4\text{-}o\text{-}SiMe_3)_3$

Donor-functionalized benzyl ligands $[CH_2C_6H_4\text{-}o\text{-}NMe_2]$ have attracted attention very recently. The aminobenzyl ligand was especially developed to provide stability and steric shielding in complexes of the early transition metals. Because of its "built-in" chelating amino group, it was found suitable to stabilize homoleptic and heteroleptic titanium and chromium complexes.[386]

With the synthesis of the homoleptic solvent-free scandium compound $Sc(CH_2C_6H_4\text{-}o\text{-}NMe_2)_3$ (**X**$_{Sc}$), Manzer introduced these bidentate benzyl ligands to group 3 chemistry.[386,387] Straightforward synthesis starting from anhydrous $ScCl_3$ and $Li(CH_2C_6H_4\text{-}o\text{-}NMe_2)$ yielded the envisaged product as an extremely air-sensitive, pale-yellow, crystalline solid (Scheme 48, I). Further purification, however, was described as exceedingly difficult.

Almost 30 years later, Harder rediscovered the synthetic potential of $Ln(CH_2C_6H_4\text{-}o\text{-}NMe_2)_3$ (**X**).[388] Applying slightly modified reaction conditions and using the potassium salt $K(CH_2C_6H_4\text{-}o\text{-}NMe_2)$ rather than the lithium analogue, he succeeded in preparing the yttrium and lanthanum derivatives $Y(CH_2C_6H_4\text{-}o\text{-}NMe_2)_3$ and $La(CH_2C_6H_4\text{-}o\text{-}NMe_2)_3$, respectively (Scheme 48, II). Recently, the synthesis protocol could be extended to the entire lanthanide series, producing the respective Nd, Sm, Ho, Dy, and Yb tris(aminobenzyl) complexes (Scheme 48, II−IV).[377] Notably, in the case of

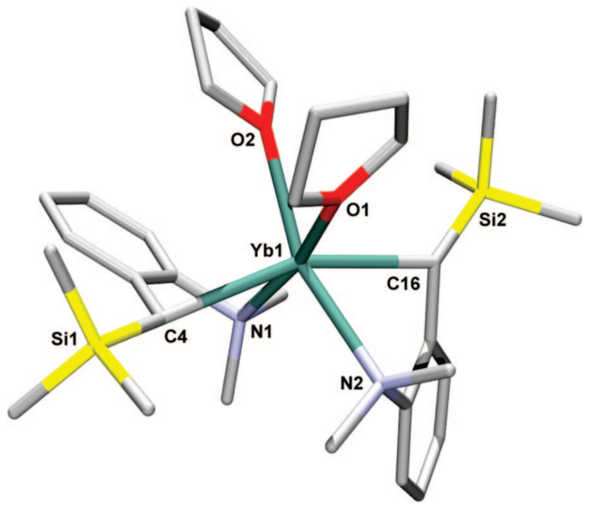
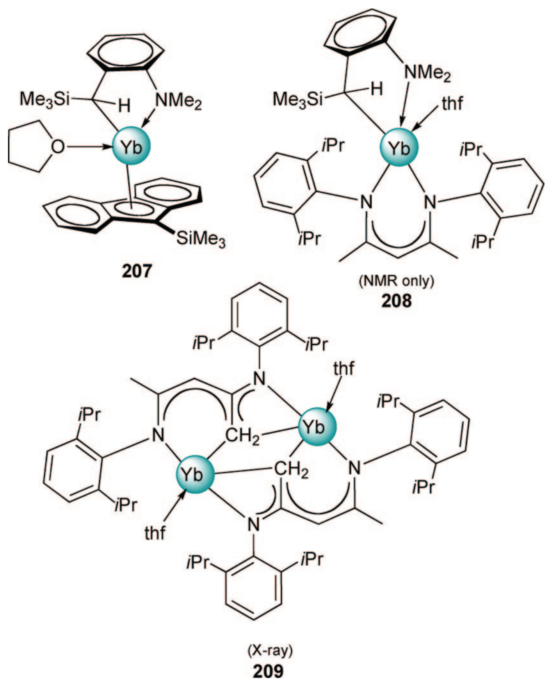


Figure 40. Solid-state structure of Yb[CH(SiMe$_3$)C$_6$H$_4$-*o*-NMe$_2$]$_2$(thf)$_2$ (**W**$_{Yb-thf}$), adapted from ref 381.

Chart 24. Complexes Derived from Yb(II)[CH(SiMe$_3$)C$_6$H$_4$-*o*-NMe$_2$]$_2$(thf)$_2$ (W$_{Yb-thf}$)

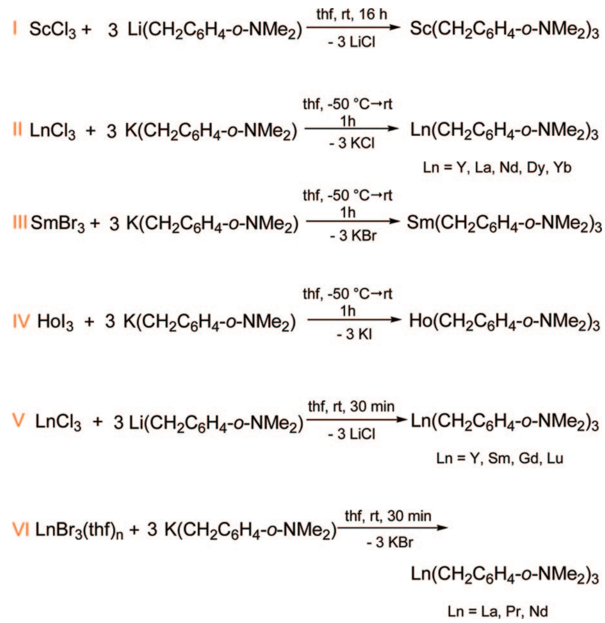


samarium and holmium, anhydrous SmBr$_3$ and HoI$_3$ have been used as lanthanide precursors (Scheme 48, III and IV).

Almost parallel to Harder's work, a slightly modified synthesis procedure for the homoleptic aminobenzyl complexes Ln(CH$_2$C$_6$H$_4$-*o*-NMe$_2$)$_3$ has been published by the group of Hou.[389] The Y, Sm, Gd, and Lu compounds were hereby accessed by reacting suspensions of the respective LnCl$_3$ in thf with solutions of Li(CH$_2$C$_6$H$_4$-*o*-NMe$_2$) in thf at ambient temperature (Scheme 48, V). LnBr$_3$(thf)$_n$ has been used under similar reaction conditions to access the derivatives of the larger rare-earth metals lanthanum, praseodymium, and neodymium (Scheme 48, VI).

The solid-state structures of Ln(CH$_2$C$_6$H$_4$-*o*-NMe$_2$)$_3$ (Ln = Y, La, Nd, Sm, Dy, Ho, and Yb) have been investigated and revealed isomorphous structures showing a paddle-wheel geometry with prismatically coordinated metal centers (Figure 41).[377,388] One of the benzyl ligands coordinates "upside down" and thus breaks up the 3-fold symmetry. The

Scheme 48. Synthesis of Ln(CH$_2$C$_6$H$_4$-*o*-NMe$_2$)$_3$ (X)



Ln−C and Ln−N bond lengths correlate with the ionic radii of the Ln^{3+} cations. Remarkably, the La−C$_{ipso}$ and La−C$_{ortho}$ distances are shorter than expected, demonstrating a pronounced multihapto bonding with increasing metal size. The benzyl ligands show a hybridization of the CH$_2$ group between sp^2 and sp^3. The parameters associated with delocalization of the negative charge from the benzylic carbon C$_\alpha$ into the ring do not vary significantly along the rare-earth metal series. However, comparison of these values for La and Yb confirm a slight decrease in charge delocalization with decreasing cation size.[377]

Compounds Ln(CH$_2$C$_6$H$_4$-*o*-NMe$_2$)$_3$ are soluble in aromatic solvents and thf. Sc(CH$_2$C$_6$H$_4$-*o*-NMe$_2$)$_3$ reacts violently with chlorinated solvents.[387] Noteworthy is the thermal stability of complexes **X**. Toluene solutions can be stored at ambient temperature for several months with only negligible decomposition of **X**. Even heated solutions show only minor decomposition of **X**.[377,388]

Further, variation of the donor functionality at the benzyl ligands *ortho*-position and the effect on complex stabilization was investigated. An extended steric shielding of the rare-earth metal's coordination sphere and additional stabilization by possible agostic Si−Me−Ln interactions was anticipated by the *o*-SiMe$_3$ substituents. The attempted preparation of a

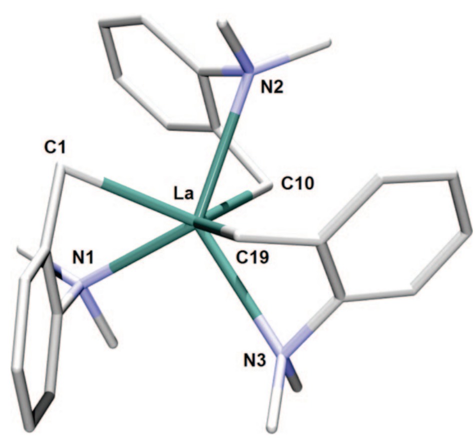
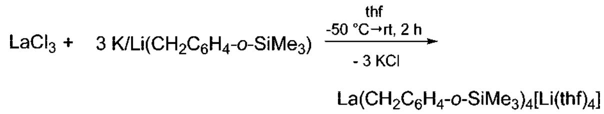


Figure 41. Solid-state structure of La(CH$_2$C$_6$H$_4$-*o*-NMe$_2$)$_3$ (**X**$_{La}$), adapted from ref 388.

Scheme 49. Synthesis of Ionic Complex [La($CH_2C_6H_4$-*o*-$SiMe_3$)$_4$][Li(thf)$_4$] ($\mathbf{Y}_{La}$)



neutral homoleptic lanthanum compound by reaction of $LaCl_3$ with K($CH_2C_6H_4$-*o*-$SiMe_3$) in thf yielded the ionic complex [La($CH_2C_6H_4$-*o*-$SiMe_3$)$_4$][Li(thf)$_4$] ($\mathbf{Y}_{La}$) due to lithium impurities in the starting material (Scheme 49).[388]

The solid-state structure of [La($CH_2C_6H_4$-*o*-$SiMe_3$)$_4$][Li-(thf)$_4$] shows a pseudo S_4-symmetric [La($CH_2C_6H_4$-*o*-$SiMe_3$)$_4$] anion with a distorted tetrahedral geometry about the lanthanum metal center (Figure 42). Two of the La−C

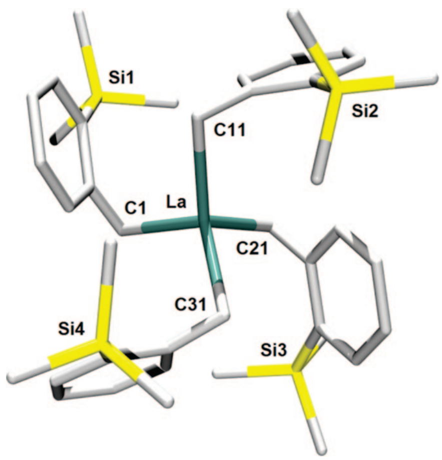


Figure 42. Solid-state structure of the [La($CH_2C_6H_4$-*o*-$SiMe_3$)$_4$] anion in $\mathbf{Y}_{La}$, adapted from ref 388.

bonds are distinctively shorter than the other two, substantiating a tendency toward η^2 bonding.

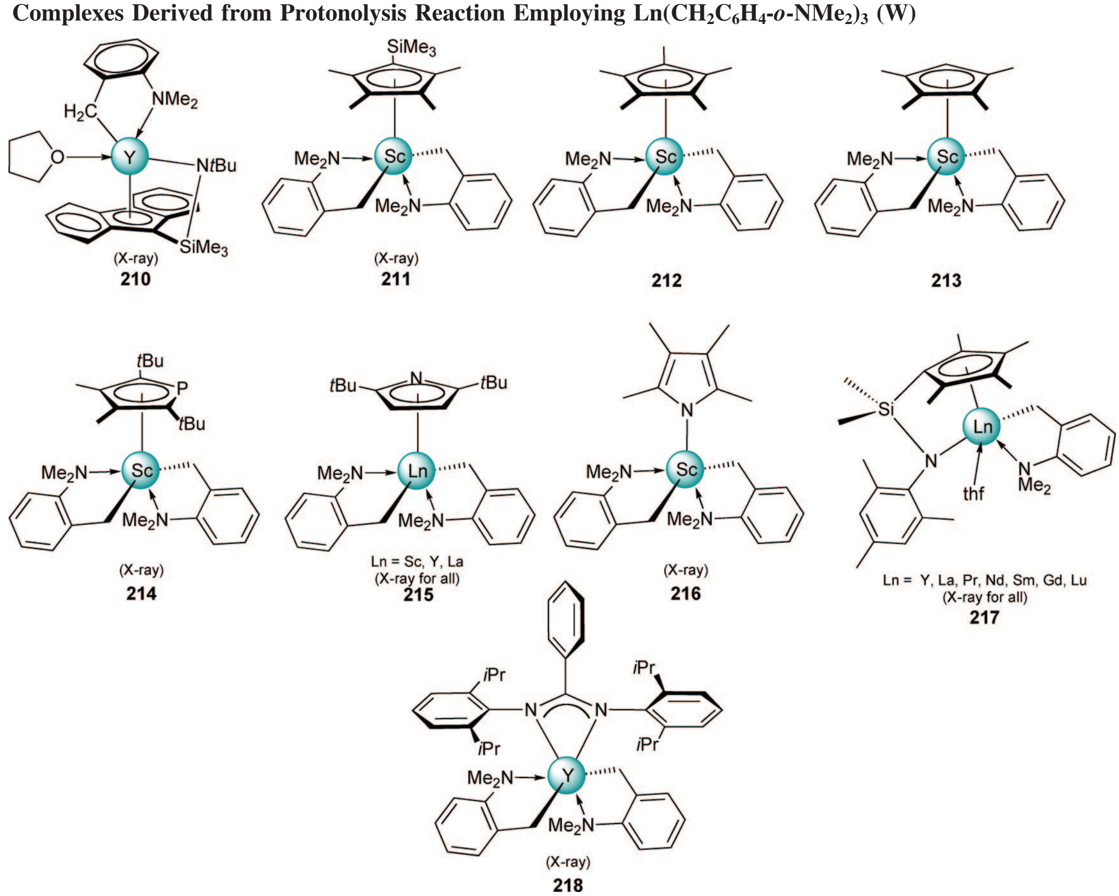
13.5. Ln($CH_2C_6H_4$-*o*-NMe_2)$_3$ as Synthesis Precursors

Homoleptic donor-free tris(aminobenzyl) complexes **W** were introduced as rare-earth metal alkyl precursors only very recently. The majority of reports on the derivatization of these rare-earth metal alkyls appeared in 2007−2008, but a multitude of applications is anticipated in the near future.

Despite the steric and electronic saturation of the rare-earth metal center by the aminobenzyl ligands, compounds Ln($CH_2C_6H_4$-*o*-NMe_2)$_3$ (**W**) easily undergo acid−base reactions with a variety of protic proligands. The yttrium derivative has been shown to deprotonate fluorenes and alkylamines and has been used as a precursor in the synthesis of a constrained-geometry yttrium benzyl compound (**210**), which could easily be converted into the respective hydride species (Chart 25).[388]

A series of scandium mono(cyclopentadienyl) bis(aminobenzyl) complexes was reported to be the outcome of acid−base reactions between Sc($CH_2C_6H_4$-*o*-NMe_2)$_3$ and the respective H(Cp^R) (Chart 25, **211**−**213**).[390] In the presence of 1 equiv of [$PhNMe_2H$][B(C_6F_5)$_4$] or [Ph_3C][B(C_6F_5)$_4$], compounds **211**−**213** form mono(cationic) species, which appeared to be active catalysts for the polymerization of olefins (ethylene, 1-hexene, styrene, norbornene, dicyclopentadiene). Further, copolymerization of 1-hexene/norbornene and 1-hexene/dicyclopentadiene was achieved. Remarkable catalytic activity in the polymerization of styrene was found for mono(cations) in situ prepared from mono(phospholyl) scandium complex **214** and [Ph_3C][B(C_6F_5)$_4$].[391]

Chart 25. Complexes Derived from Protonolysis Reaction Employing Ln($CH_2C_6H_4$-*o*-NMe_2)$_3$ (W)



Mono(pyrrolyl) bis(aminobenzyl) complexes of Sc, Y, and La can be accessed by acid−base reactions of the homoleptic rare-earth metal alkyls and the pyrrole derivative (Chart 25, **215** and **216**).[392] The coordination of the newly introduced ancillary ligand is governed by the substituents at the pyrrolyl. Scandium complex **216** is a rare example of a rare-earth metal complex with an η^1-bonded pyrrolyl ligand. The respective mono(cations) are formed upon treatment of **215**/**216** with $[Ph_3C][B(C_6F_5)_4]$ and have been applied as catalysts for the production of syndiotactic styrene. Benzamidinate ligands have successfully been used to synthesize bis(alkyl) complexes of the entire rare-earth metal series. Using $Y(CH_2C_6H_4$-*o*-$NMe_2)_3$ as alkyl precursor, yttrium complex **218** could be obtained.[393] Further cationization with $[Ph_3C][B(C_6F_5)_4]$ produced an active isoprene polymerization catalyst. Constrained-geometry complexes **217** could be accessed via the tris(aminobenzyl) precursors for the entire size range of rare-earth metals.[389] Compounds **217** serve as catalysts for the catalytic addition of phosphine P−H bonds to carbodiimides and have further been applied in the cross-coupling of terminal alkynes with isocyanides.[243,244]

14. Phenyl Complexes

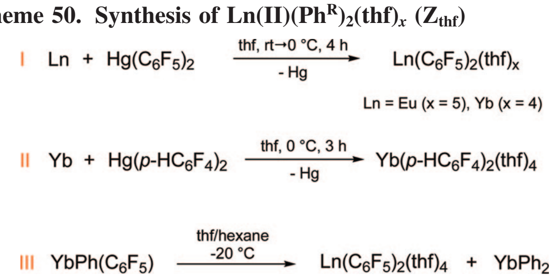
14.1. Synthesis, Structure, and Properties of $Ln(II)(Ph^R)_2(solv)_x$

Contrasting the predominant use of metathesis reactions for the synthesis of organorare-earth metal complexes, redox transmetalation/ligand-exchange reactions display a competitive route particularly for the preparation of low-valent lanthanide organometallics involving σ-bonded ligands. Major contributions to the early developments were made by Deacon and coworkers, introducing transmetalation reactions of organomercurials as a route to organolanthanides.[394,395]

Already 30 years ago, the redox transmetalation reaction of elemental ytterbium and europium with the appropriate diorganomercurial in a donor solvent, thf, at ambient temperature were reported to yield perfluoroaryllanthanide(II) compounds $Ln(C_6F_5)_2(thf)_{4/5}$ ($\mathbf{Z}^{C_6F_5}{}_{thf}$) (Scheme 50, I).[395−397] Although the reactivity of these compounds was studied in depth, structural data were not available until very recently. $Ln(C_6F_5)_2(thf)_x$ are thermally unstable, predominantly decomposing by fluoride abstraction within hours or days at ambient temperature. Attempts to synthesize the respective perfluorated Sm(II) diaryls yielded complex product mixtures caused by thermal decomposition of initially formed $Sm(C_6F_5)_2$.[395]

The reaction of $Hg(p\text{-}HC_6F_4)_2$ with ytterbium at ambient temperature showed features similar to the reaction with samarium, but cooling to 0 °C allowed for the isolation of $Yb(p\text{-}HC_6F_4)_2(thf)_4$ ($\mathbf{Z}^{C_6F_4}{}_{thf}$) (Scheme 50, II).[395,397] Satisfactory analytical characterization was, however, hampered by the low thermal stability of the compound.

Scheme 50. Synthesis of $Ln(II)(Ph^R)_2(thf)_x$ ($\mathbf{Z}_{thf}$)



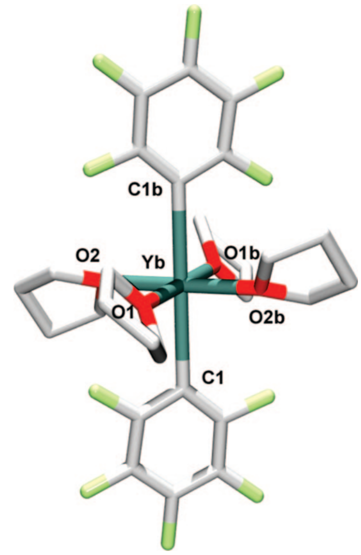
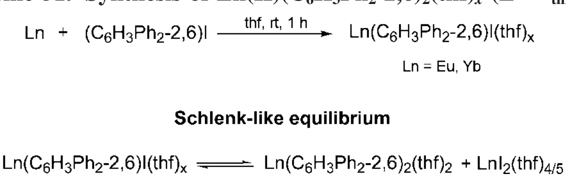


Figure 43. Solid-state structure of $Yb(C_6F_5)_2(thf)_4$ ($\mathbf{Z}^{C_6F_5}{}_{Yb-thf}$), adapted from ref 401.

Scheme 51. Synthesis of $Ln(II)(C_6H_3Ph_2\text{-}2,6)_2(thf)_x$ ($\mathbf{Z}^{terph}{}_{thf}$)



Reactions between rare-earth elements and $HgPh_2$ are harder to induce than those of their fluorinated analogues and usually require activation of the metal (Hg or CH_2I_2)[398,399] and heating.[400] The simplest ytterbium(II) diaryl $YbPh_2$ is accessible by transmetalation of $HgPh_2$ and activated Yb metal in thf, but it is noteworthy that a well-defined $YbPh_2$ complex has not yet been isolated.[399]

Previously, the composition of the perfluoroaryl lanthanide(II) compounds $Ln(C_6F_5)_2(thf)_{4/5}$ had been proven by IR, UV/vis, ^{171}Yb NMR, and ^{19}F NMR spectroscopy accompanied by metal titration and acidolysis.[395,397,401] Single crystals of $Eu(C_6F_5)_2(thf)_5$ ($\mathbf{Z}^{C_6F_5}{}_{Eu-thf}$) have been grown from thf solutions by addition of light petroleum at −20 °C. In the solid state, the europium environment approximates a pentagonal bipyramid with axial C_6F_5 groups and five coordinating thf molecules in the equatorial positions.[402] The C(*ipso*)−Eu−C(*ipso*) angle is near 180°, and competing *o*-F/*o*-F and/or *o*-F/thf repulsions cause rotation of the C_6F_5 groups (angle between C_6 ring planes = 65.7°).

The attempted crystallization of putative "$YbPh(C_6F_5)$" by cooling a concentrated thf/hexanes solution to −20 °C revealed the occurrence of a ligand-redistribution process (Scheme 50, III), yielding crystalline $Yb(C_6F_5)_2(thf)_4$ ($\mathbf{Z}^{C_6F_5}{}_{Yb-thf}$).[401] As predicted earlier, the six-coordinate ytterbium(II) is surrounded by two *trans*-C_6F_5 ligands with four equatorial thf ligands completing an octahedral coordination geometry (Figure 43). Contrary to the europium compound, the two C_6F_5 groups in $Yb(C_6F_5)_2(thf)_4$ are coplanar.

In 2000, Heckmann and Niemeyer introduced the sterically demanding *m*-terphenyl ligands ($C_6H_3Ph_2$-2,6) to low-valent rare-earth metals. σ-Bonded Ln(II) aryls were prepared by a direct synthesis route from organyl iodides and the ytterbium or europium metal, respectively (Scheme 51).[178,403] Using ^{171}Yb as a probe, a Schlenk-like equilibrium between

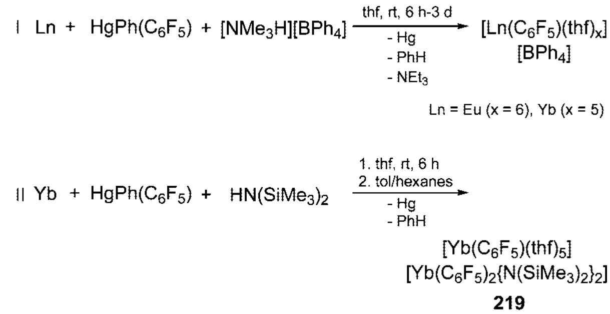
$Yb(C_6H_3Ph_2\text{-}2,6)I(thf)_3$, $Yb(C_6H_3Ph_2\text{-}2,6)_2(thf)_2$, and $YbI_2(thf)_4$ in thf solution has been detected (Scheme 51). Depending on the nature of the lanthanide metal center, the aryl substituent, and the solvent used, either the diaryl compound or the mixed aryl/iodide species may be obtained from solution. Thus, recrystallization of $Ln(C_6H_3Ph_2\text{-}2,6)I(thf)_3$ from aromatic solvents shifts the equilibrium shown in Scheme 51 toward homoleptic $Ln(C_6H_3Ph_2\text{-}2,6)_2(thf)_2$ ($\mathbf{Z}^{terph}{}_{thf}$). Further, using europium affords the europium(II) diaryl and $EuI_2(thf)_5$ as the main products.

The molecular structures of $Ln(C_6H_3Ph_2\text{-}2,6)_2(thf)_2$ ($\mathbf{Z}^{terph}{}_{thf}$) reveal monomeric units wherein two aryl ligands and two thf molecules form a strongly distorted tetrahedral environment of the lanthanide metal center (Figure 44).[178,403] High steric crowding and a high ionic character of the metal−carbon bonds were held responsible for the considerable displacement of the respective lanthanide atoms from the aromatic planes. In addition, a favorable arrangement allowing for secondary η^1-π-arene interactions to one o'-phenyl carbon atom of the terphenyl ligand is provided.

In 2004, Deacon and Forsyth published the synthesis of cations with the lanthanide metal in the divalent oxidation state and a residual Ln−C σ bond. Redox transmetalation/ligand-exchange reaction of ytterbium or europium metal, $HgPh(C_6F_5)$, and $[NMe_3H][BPh_4]$ yielded the tetraphenylborate salts $[Ln(C_6F_5)(thf)_x][BPh_4]$ ($\mathbf{Z}^{+/C_6F_5}{}_{thf}$) in good yields (Scheme 52, I).[404] Presumably, these reactions proceed by protonolysis of the more basic Ln−Ph site of intermediately formed $LnPh(C_6F_5)$ by $[NMe_3H][BPh_4]$. The $[Yb(C_6F_5)(thf)_x]^+$ fragment is also found in $[Yb(C_6F_5)(thf)_5][Yb(C_6F_5)_2\{N(SiMe_3)_2\}_2]$ (**219**), a mixed-valent species fortuitously isolated in low yield from Yb, $HgPh(C_6F_5)$, and $HN(SiMe_3)_2$ mixtures in thf (Scheme 52, **II**).

The organolanthanide(II) cations exhibit greater thermal stability than their neutral diorganolanthanide(II) counterparts and appear to be stable for several weeks at ambient temperature. Decomposition of solid $[Yb(C_6F_5)(thf)_5][BPh_4]$ upon heating was observed only above 130 °C, with evolution of thf. Heating a solution of the ionic ytterbium species in thf at 60 °C for 24 h gave a semicrystalline white solid, which was shown to be $[Yb(thf)_6][BPh_4]_2$. Even though the decomposition pathways are not entirely elucidated, the thermal reactions of $[Ln(C_6F_5)(thf)_x][anion]$ appear to be substantially different to those of other $Ln-C_6F_5$ species.

Scheme 52. Synthesis of Cationic $[Ln(II)(C_6F_5)(thf)_x][anion]$ ($\mathbf{Z}^{+/C_6F_5}{}_{thf}$ and 219)



The solvated cations $[Ln(C_6F_5)(thf)_x]^+$ display lanthanide(II) coordination geometries similar to the corresponding neutral $[Ln(C_6F_5)_2(thf)_x]$ derivatives but with significantly shorter metal−carbon bonds (Figure 45). In accordance with the larger ionic radius of Eu(II) than Yb(II), $[Eu(C_6F_5)(thf)_6]^+$ is solvated by six thf molecules, resulting in a distorted pentagonal-bipyramidal geometry upon the europium metal center, whereas only five donor thf molecules provide an octahedral arrangement at the smaller ytterbium metal center.

14.2. $Ln(II)(Ph^R)_2(solv)_x$ as Synthesis Precursors

The high reactivity of the Ln−C bond in complexes $Ln(Ph^R)_2(thf)_x$ ($\mathbf{Z}_{thf}$) has been used for the preparation of rare-earth metal cyclopentadienyl, aryloxide, and organoamide complexes through protonolysis reaction with the respective proligands. Because of the thermal instability of $Ln(Ph^R)_2(thf)_x$, ligand exchange can best be realized by reacting the in situ formed $Ln-Ph^R$ species immediately with the protic substrate to avoid the problematic isolation of $Ln(Ph^R)_2(thf)_x$.[395,397] The choice of $Hg(Ph^R)_2$ employed in such reactions is hereby subject to pK_a considerations. Substrates with high pK_a values (e.g., $HN(SiMe_3)_2$ =

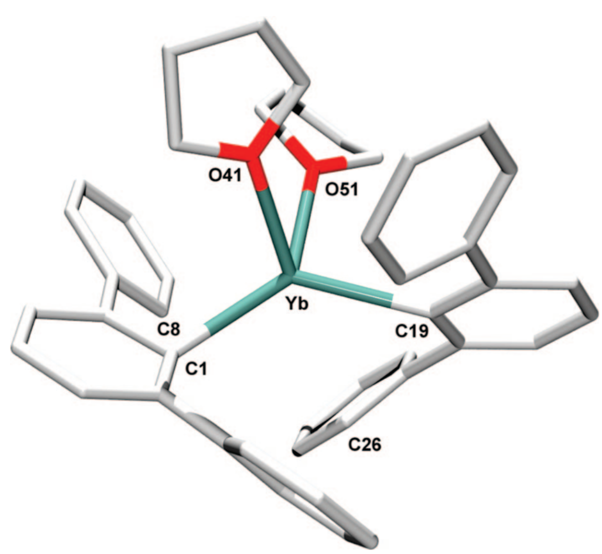


Figure 44. Solid-state structure of $Yb(C_6H_3Ph_2\text{-}2,6)_2(thf)_2$ ($\mathbf{Z}^{terph}{}_{thf}$), adapted from ref 178.

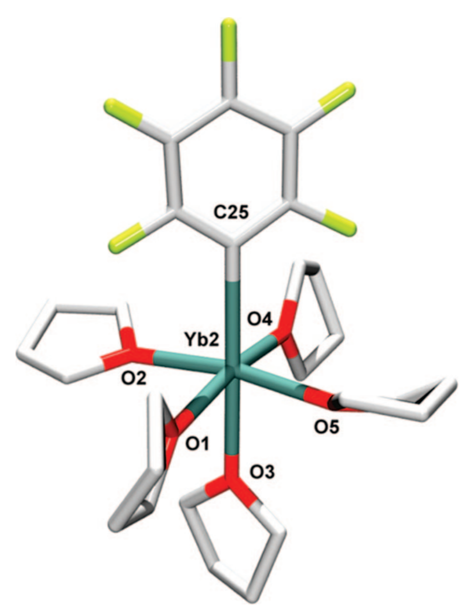
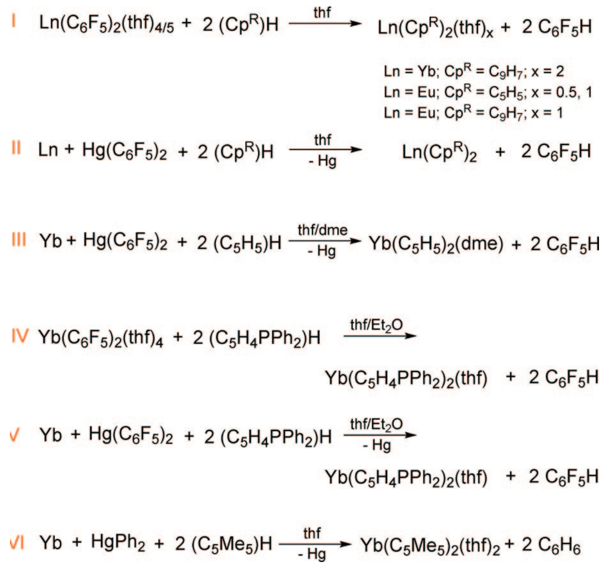


Figure 45. Solid-state structure of the cationic fragment $[Yb(C_6F_5)(thf)_5]^+$ in $[Yb(C_6F_5)(thf)_5][Yb(C_6F_5)_2\{N(SiMe_3)_2\}_2]$ (**219**), adapted from ref 404.

Scheme 53. Cyclopentadienyl Complexes Derived from $Ln(Ph^R)_2$ (Z)



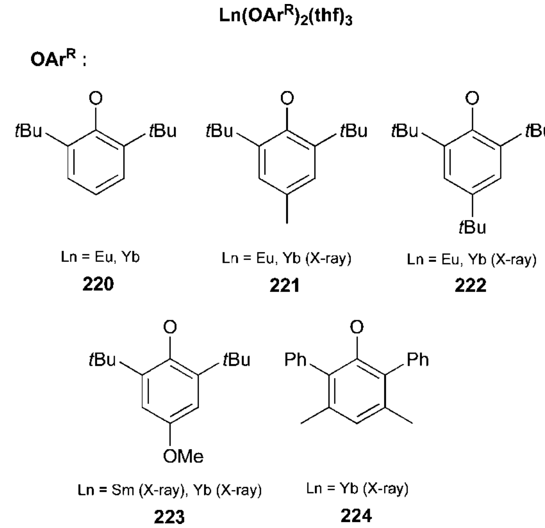
$\sim$25.8)[405] require the use of $HgPh_2$ rather than $Hg(C_6F_5)_2$ because the pK_a of C_6H_6 ($\sim$40) is considerably higher than that of C_6F_5H ($\sim$26).[90] In addition, $HgPh_2$ shows a weaker oxidizing ability than $Hg(C_6F_5)_2$, an important criterion for transmetalation−ligand-exchange reactions of rare-earth metals with accessible divalent and trivalent oxidation states.[406] The in situ preparation of $Ln(Ph^R)_2(thf)_x$ followed by ligand exchange further allowed for the synthesis of a few organosamarium(II) compounds, even though the respective $Sm(Ph^R)_2$ cannot be isolated.[406,407]

Initial studies addressed the reactivity of preformed $Ln(C_6F_5)_2(thf)_{4/5}$ toward cyclopentadienes, indene, and diphenylphosphinocyclopentadiene.[408,409] Accordingly, solutions of the perfluoroaryllanthanide(II) compounds in thf/Et_2O reacted with the respective proligands $(Cp^R)H$ to form complexes $Ln(Cp^R)_2(thf)_x$ (Scheme 53, I and IV). Performing the aforementioned ligand-exchange reactions with in situ prepared $Ln(C_6F_5)_2(thf)_{4/5}$ yielded the desired cyclopentadienyl complexes usually in higher yields (Scheme 53, II, III, and V).[19,408,409] Replacing thf as a solvent by pyridine in the mixtures of $Eu(C_6F_5)_2$/$Hg(C_6F_5)_2$ and CpH resulted in oxidation of the europium metal to yield $EuCp_3(pyr)$.[410] In accordance with the above mentioned pK_a criterion, $HgPh_2$ had to be used for the synthesis of $Yb(C_5Me_5)_2(thf)_2$ (Scheme 53, VI). The reaction of $Yb(C_6F_5)_2(thf)_4$ with C_5H_5Me intermediately formed the envisaged product, but attempts to isolate the compound gave an explosive solid, presumably due to contamination with a fluorocarbon−ytterbium impurity.[408]

$Yb(C_5H_4PPh_2)_2(thf)$ was subjected to donor-exchange reactions (thf → tmen) and was further used to prepare ytterbium−transition metal heterobimetallic compounds $Yb(C_5H_4PPh_2)_2(thf)_xMo(CO)_4$, $Yb(C_5H_4PPh_2)_2(thf)_xNi(CO)_2$, and $Yb(C_5H_4PPh_2)_2(thf)_xPtMe_2$.[409]

With the objective to obtain low-coordinate lanthanide(II) complexes, the redox transmetalation/ligand-exchange procedure was further applied to phenols. Reacting preformed $Ln(C_6F_5)_2(thf)_{4/5}$ ($\mathbf{Z}^{C_6F_5}{}_{thf}$) as well as the in situ formed species with bulky phenols $HOAr^R$ yielded complexes $Ln(OAr^R)_2(thf)_3$ (**220**−**224**) in good yields (Chart 26).[411−414] Complex **223**$_{Sm}$ was formed in very low yield along with the major product $Sm(OAr^{OMe})_3(thf)$ with samarium in the trivalent oxidation state (Chart 26).[414] The lower oxidizing ability of $HgPh_2$ compared with $Hg(C_6F_5)_2$ is demonstrated when using HOC_6Me_2-3,5-Ph_2-2,6 as a protic substrate. Whereas the mixture of Yb, $Hg(C_6F_5)_2$, and the phenol resulted in the formation of the trivalent ytterbium complex, the use of $HgPh_2$ produced complex **224** with ytterbium in the divalent oxidation state (Chart 26).[415]

Chart 26. Aryloxide Complexes Derived from $Ln(Ph^R)_2$ (Z)

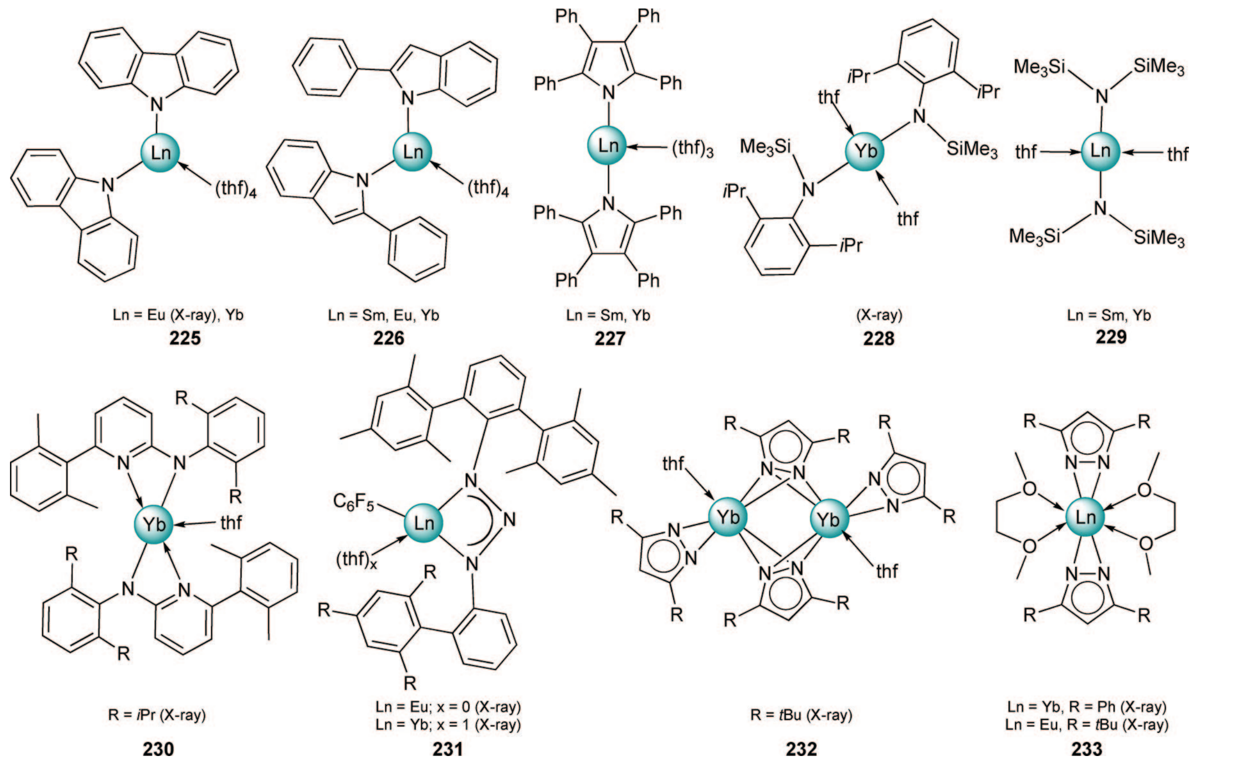


Reaction of bis(pentafluorophenyl)lanthanides or the in situ prepared complexes, respectively, with the heterocyclic amines carbazole, 2-phenylindole, or 2,3,4,5-tetraphenylpyrrole in thf gave access to homoleptic organoamidolanthanide(II) complexes $Ln(NR_2)_2(thf)_x$ (Chart 27, **225**−**227**).[406,407,411,416] Remarkably, divalent Sm species **226**$_{Sm}$ and **227**$_{Sm}$ are formed even when applying $Hg(C_6F_5)_2$ in the transmetalation reaction. The use of $HgPh_2$ was essential for the preparation of complexes $Ln[N(SiMe_3)(C_6H_3iPr_2\text{-}2,6)]_2(thf)_2$ (**228**) and $Ln[N(SiMe_3)_2]_2(thf)_2$ (**229**) because of the relatively high pK_a of the respective silylamines.[405,417] Moreover, the preparation of triazenide complexes (**231**) from the lanthanide metal, $Hg(C_6F_5)_2$, and a sterically crowded triazene[418] and the formation of an aminopyridinato ytterbium(II) complex (**230**) (prepared with $HgPh_2$) have been reported.[419]

Pyrazolate complexes represent a special class of organoamide complexes. Redox transmetalation of the lanthanide metal with $HgPh_2$ followed by ligand exchange with pyrazole gave the respective organoamide compounds with ytterbium and europium in the divalent oxidation state (Chart 27, **232**−**233**).[420−422] The use of $Hg(C_6F_5)_2$, however, exclusively yielded trivalent pyrazolate complexes.

In reactions with transition metal complexes, triphenyltin chloride, and mercuric chloride, bis(polyfluorophenyl)ytterbium compounds show reactivities comparable to those of the corresponding Grignard and organolithium reagents.[423] With aldehydes and ketones, the diorganoytterbium compounds are predominantly carbanion transfer reagents and can act as reducing reagents.[424] Further, the insertion of CO_2 into the Ln−Ph^R bond has been reported.[423] Ligand exchange of $Yb(C_6F_5)_2$ ($\mathbf{Z}^{C_6F_5}{}_{Yb}$) with phenylacetylene is a synthesis route to bis(phenylethynyl)ytterbium(II) (see section 15.1).[394] Further, $YbPh_2(thf)_2$ ($\mathbf{Z}^{Ph}{}_{Yb-thf}$) has been applied as a catalyst for the polymerization of styrene but only showed very low catalytic activity.[425]

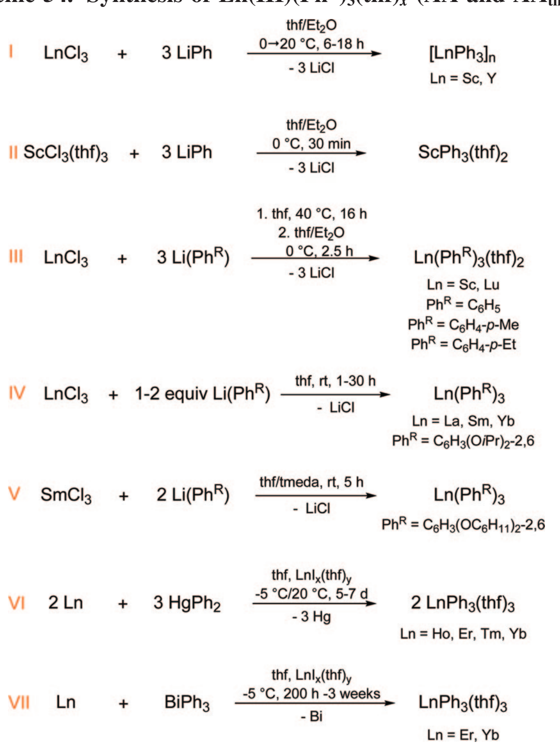
Chart 27. Amide and Pyrazolate Complexes Derived from $Ln(Ph^R)_2$ (Z)



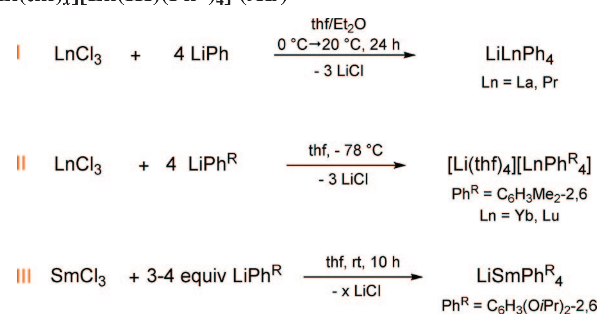
14.3. Synthesis, Structure, and Properties of $Ln(III)(Ph^R)_3(solv)_x$ and $[Li(solv)_x][Ln(III)(Ph^R)_4]$

The history of σ-bonded organometallic complexes of the rare-earth metals is strongly related to phenyl complexes. In 1968, Hart and Saran reported what appeared to be the first purely σ-bonded organorare-earth metal derivative by treating anhydrous scandium chloride with phenyllithium as shown in Scheme 54, I.[66] While YPh_3 ($\mathbf{AA}_Y$) could be prepared analogously, the larger rare-earth metals lanthanum

Scheme 54. Synthesis of $Ln(III)(Ph^R)_3(thf)_x$ (AA and $\mathbf{AA}_{thf}$)



Scheme 55. Formation of Ate Complexes $[Li(thf)_x][Ln(III)(Ph^R)_4]$ (AB)



and praseodymium yielded anionic lithium tetraphenyllanthanate $LiLaPh_4$ ($\mathbf{AB}_{La}$) and lithium tetraphenylpraseodymiate $LiPrPh_4$ ($\mathbf{AB}_{Pr}$), respectively (Scheme 55, I).[68] The neutral phenyl complexes were obtained as powdery solids consisting of polymeric $[LnPh_3]_n$ (**AA**), which were characterized by IR spectroscopy, elemental analyses, Michler's ketone test, and the reaction with $HgCl_2$. Structural proof was provided 30 years later, when $ScCl_3(thf)_3$ and 3 equiv of phenyllithium were reacted in thf/Et_2O solution to afford mononuclear $ScPh_3(thf)_2$ ($\mathbf{AA}_{Sc-thf}$) as crystalline material (Scheme 54, II).[426] Salt metathesis of rare-earth metal(III) chlorides and aryllithium reagents in thf/Et_2O further proved to be a viable route to $Ln(Ph^R)_3(thf)_x$ with differently substituted aryl ligands. Recently, a series of neutral scandium and lutetium tri(aryl) complexes with methyl and ethyl substituents in the *para* position have been isolated following this approach (Scheme 54, III).[427] The outcome of the reaction between $LnCl_3$ and $Li[C_6H_3(OiPr)_2\text{-}2,6]$ or $Li[C_6H_3(OC_6H_{11})_2\text{-}2,6]$ is determined by the amount of lithium reagent employed.[428] Neutral complexes of the type $Ln[C_6H_3(OiPr)_2\text{-}2,6]_3$ and $Ln[C_6H_3(OC_6H_{11})_2\text{-}2,6]_3$ require a substoichiometric use of the aryllithium reagent (1−2 equiv) (Scheme 54, IV and V), whereas anionic complex $LiSm[C_6H_3(OiPr)_2\text{-}2,6]_4$ was ob-

tained when 3−4 equiv of the lithium organyl were applied (Scheme 55, III).

Redox transmetalation as an alternative synthesis approach toward phenyl complexes of the trivalent rare-earth metals was introduced by Bochkarev et al. in the mid-1990s.[429] In the presence of catalytical amounts of rare-earth metal halides, metallic lanthanides react with $HgPh_2$ or $BiPh_3$ to form $LnPh_2(thf)_2$ (Ln = Eu, Yb) (see section 14.5) and $Ph_3Ln(thf)_3$ (Ln = Ho, Er, Tm, Yb), respectively (Scheme 54, VI and VII).[429,430]

The synthesis of neutral triphenyl rare-earth metal complexes is so far limited to the small- to middle-sized rare-earth metals. As mentioned above, the formation of anionic compounds $LiLnPh^R_4$ (**AB**) is a commonly observed phenomenon, particularly in the presence of a large rare-earth metal center or an excess of the lithium organyl.[68,428] Remarkably, $[Li(thf)_4][Lu(C_6H_3Me_2\text{-}2,6)_4]$, formed in the reaction of anhydrous lutetium chloride and 2,6-dimethylphenyl lithium in thf, was the first X-ray structurally authenticated example of a complex containing a lanthanide−carbon σ-bond (Scheme 55, II).[67]

Polymeric compounds $[LnPh_3]_n$ (**AA**) are insoluble in benzene and Et_2O but slightly soluble in tetrahydrofuran. They are reported to be thermally robust (decomposition above 140 °C in vacuo) and indefinitely stable at ambient temperature.[66,68] Solutions of $ScPh_3(thf)_2$ ($\mathbf{AA}_{Sc-thf}$) are, however, thermally unstable and decompose under formation of C_6H_6 and a dark-brown precipitate.[431] Crystalline material can be stored at −35 °C for months without decomposition. $LnPh_3(thf)_3$ of the larger metal centers erbium and thulium are described as thermally stable compounds even at elevated temperatures.[429] The thf adducts are insoluble in hexane, are poorly soluble in aromatic solvents, but can be dissolved in thf.

Because of inefficient steric shielding of the rare-earth metal center by the phenyl ligands, mononuclear complexes $LnPh_3(thf)_x$ coordinate stabilizing thf molecules. The number of additional thf molecules increases with increasing size of the rare-earth metal cation. The representative of the smallest rare-earth metal $ScPh_3(thf)_2$ ($\mathbf{AA}_{Sc-thf}$) features a five-coordinate metal center with the three [Ph] ligands occupying the equatorial positions and the thf oxygen atoms occupying the axial positions of a trigonal bipyramid (Figure 46).[431] In spite of the close contact of the *ortho*-H atoms, the phenyl groups are only slightly twisted with respect to the ScC_3 plane (0, 8, 18°). A sufficient explanation for this sterically disfavored arrangement of the phenyl rings could not be provided—some degree of anomeric hyperconjugation between the *ortho*-H atom at C2 and the phenyl ring (C13−C18) has been discussed, as well as the impact of the coordinated thf on the unique coplanar arrangement of the phenyl rings. X-ray structure analyses of $ErPh_3(thf)_3$, $TmPh_3(thf)_3$,[429] and $YbPh_3(thf)_3$[430] revealed a distorted *fac*-octahedral coordination of the phenyl ligands and the three donor thf molecules (Figure 47). The angles O−Ln−O (78°−81°) are considerably smaller than angles C−Ln−C (99°−104°).

[(Dimethylamino)methyl]phenyl ligands [$o\text{-}C_6H_4CH_2NMe_2$] were developed in parallel to the donor-substituted benzyl ligands described in section 13.4.[387] The first [(dimethylamino)methyl]phenyl lanthanide complex was reported in 1978.[387] Scandium compound $Sc(o\text{-}C_6H_4CH_2NMe_2)_3$ ($\mathbf{AC}_{Sc}$) was prepared from $ScCl_3$ and $Li(o\text{-}C_6H_4CH_2NMe_2)$ in refluxing thf and could be obtained as a

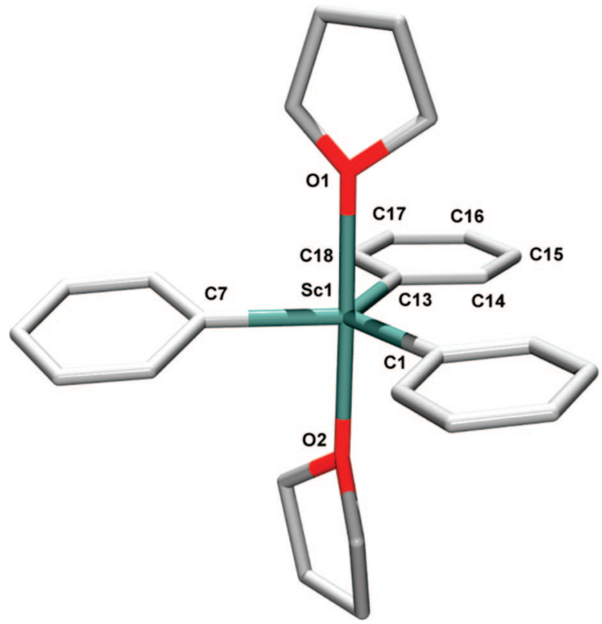


Figure 46. Solid-state structure of $ScPh_3(thf)_2$ ($\mathbf{AA}_{Sc-thf}$), adapted from ref 431.

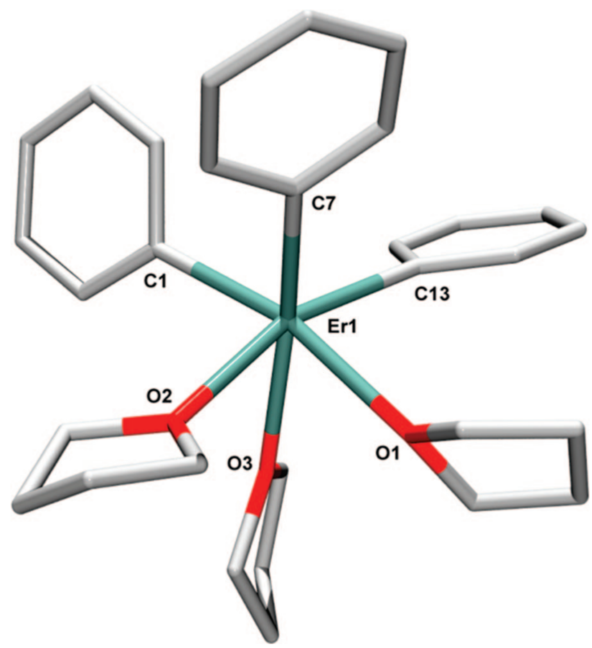


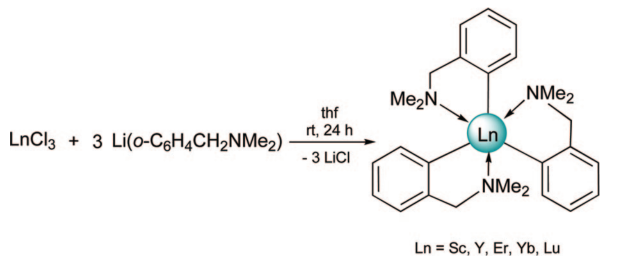
Figure 47. Solid-state structure of $ErPh_3(thf)_3$ ($\mathbf{AA}_{Er-thf}$), adapted from ref 429.

white, insoluble compound that decomposes violently in dichloromethane and methanol.

In 1984, Wayda et al. extended this synthesis protocol to the lanthanide metals lutetium, ytterbium, and erbium (Scheme 56).[432] Good isolable yields, purity, and easy characterization by standard analytical and spectroscopic techniques were reported. Crystal structure determination of the respective $Lu(o\text{-}C_6H_4CH_2NMe_2)_3$ finally proved the proposed structure and composition of compounds **AC** (Figure 48). Attempts to further extend the series to the early and middle lanthanide metals were not successful. Reaction of $LnCl_3$ (Ln = Pr, Nd, Sm, Tb) with the lithium salt $Li(o\text{-}C_6H_4CH_2NMe_3)$ only produced uncharacterizable mixtures of products.[433]

Phenyl complexes $Ln(o\text{-}C_6H_4CH_2NMe_2)_3$ (**AC**) are extremely air- and moisture-sensitive and marginally soluble

Scheme 56. Synthesis of Ln(o-$C_6H_4CH_2NMe_2$)$_3$ (AC)



in alkane solvents. They are, however, soluble in aromatic and ethereal solvents. In the solid state, the three bidentate phenyl ligands of Lu(o-$C_6H_4CH_2NMe_2$)$_3$ (**AC**$_{Lu}$) surround the lutetium metal center in a pedal-wheel manner (Figure 48).[432] Interestingly, the Lu−N distances fall into a two-short−one-long pattern, the origin of which was discussed to be of steric nature or due to packing effects.

Attempted hydrogenolysis of Lu(o-$C_6H_4CH_2NMe_2$)$_3$ with molecular hydrogen and reaction with simple olefins did not reveal the envisaged products. With terminal alkynes, Lu(o-$C_6H_4CH_2NMe_2$)$_3$ formed the metalation product, however (see section 15.2).[433]

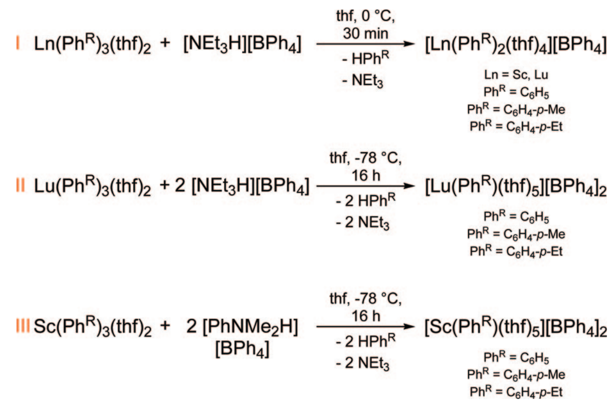
14.4. Ln(III)(Ph^R)$_3$(solv)$_x$ as Synthesis Precursors

Neutral tris(aryl) complexes Ln(Ph^R)$_3$(thf)$_2$ (**AA**) (Ln = Sc, Lu) react with 1 and 2 equiv of weak Brønsted acids such as [NEt_3H][BPh_4] and [$PhNMe_2H$][BPh_4] via arene elimination to form monocationic bis(aryl) complexes [Ln(Ph^R)$_2$(thf)$_4$][BPh_4] (**AA**$^+_{thf}$) (Scheme 57, I) and dicationic mono(aryl) complexes [Ln(Ph^R)(thf)$_5$][BPh_4]$_2$ (**AA**$^{2+}_{thf}$) (Scheme 57, II and III).[427] While Lu(Ph^R)$_3$(thf)$_2$ and 2 equiv of ammonium salt [NEt_3H][BPh_4] yielded the respective mono(aryl) dications, the same reactions carried out with the analogous scandium compounds gave only mixtures of the monocationic species and unreacted [NEt_3H][BPh_4]. The use of the more acidic anilinium salt [$PhNMe_2H$][BPh_4], however, allowed for the isolation of scandium dications [Sc(Ph^R)(thf)$_5$][BPh_4]$_2$.

All mono- and dications are obtained as solvent (thf)-separated ion pairs, which show poor solubility in hydrocarbons and aromatic solvents. The monocationic species [Ln(Ph^R)$_2$(thf)$_4$][BPh_4] (**AA**$^+_{thf}$) can be dissolved in tetrahydrofuran, but NMR spectra of the thf insoluble dications were recorded in pyridine-d_5.

The solid-state structure of ion pair [$ScPh_2$(thf)$_4$][BPh_4] (**AA**$^+_{Sc-thf}$) revealed a distorted octahedral coordination

Scheme 57. Synthesis of Monocationic and Dicationic Complexes [Ln(Ph^R)$_2$(thf)$_4$][BPh_4] (AA$^+_{thf}$) and [Ln(Ph^R)(thf)$_5$][BPh_4]$_2$ (AA$^{2+}_{thf}$)



geometry around the scandium metal center, with the phenyl groups displaying a *cis*-arrangement (Figure 49). Interestingly, the Sc−C(aryl) distances (2.259(2) and 2.298(2) Å) are slightly longer than in the neutral triphenyl complex $ScPh_3$(thf)$_2$ (2.240(3), 2.245(4), and 2.266(4) Å).[431] An increase of the coordination number from five to six upon cationization and/or some Sc−C(aryl) bond shortening in the ground state of the neutral triphenyl complex were discussed to explain this counterintuitive finding.[427] The Sc−O separations *trans* to the phenyl groups are significantly longer than those in *cis* positions.

Replacing one phenyl group in [$LnPh_2$(thf)$_4$][BPh_4] by thf led to the of ion triple [LuPh(thf)$_5$][BPh_4]$_2$ (**AA**$^{2+}_{Lu-thf}$), showing a similar octahedral arrangement of the ligands in the solid state (Figure 50).[427] The remaining phenyl group caps a slightly distorted octahedron. Because of the increased positive charge in the dication, the Lu−C(aryl) distance of 2.303(7) Å and the Lu−O distances are shorter than those reported for other lutetium aryl complexes. As for the monocationic scandium species, a significant *trans* influence of the aryl ligand is observed.

The activation of pyridine by dicationic aryl complexes was studied by NMR experiments. In contrast to the C−H bond activation observed for related methyl dications, evidence for a competition between C−H bond activation and insertion of pyridine into the aryl−Ln bond was found.[427]

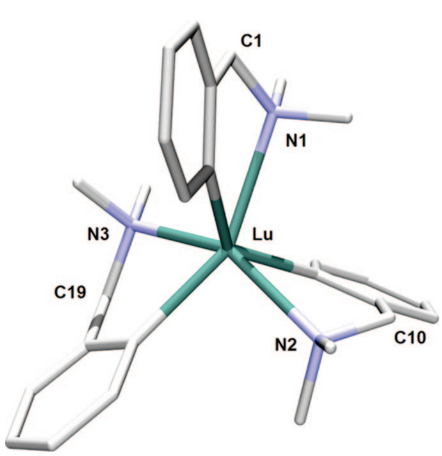


Figure 48. Solid-state structure of Lu(o-$C_6H_4CH_2NMe_2$)$_3$ (**AC**$_{Lu}$), adapted from ref 432.

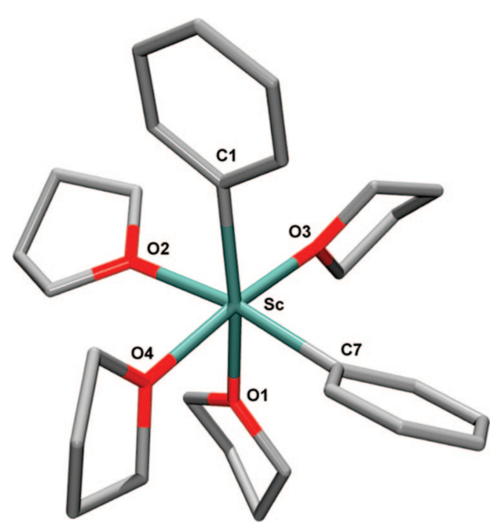


Figure 49. Solid-state structure of the cationic moiety of [$ScPh_2$(thf)$_4$][BPh_4] (**AA**$^+_{Sc-thf}$), adapted from ref 427.

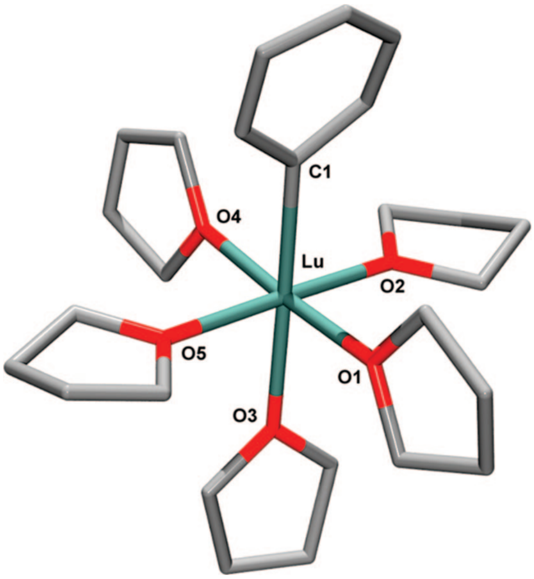
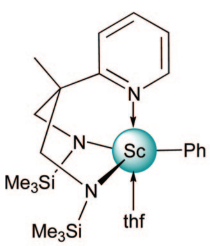


Figure 50. Solid-state structure of the cationic moiety of $[LuPh(thf)_5][BPh_4]_2$ ($\mathbf{AA}^{2+}_{Lu-thf}$), adapted from ref 427.

Chart 28. Complexes Derived from $ScPh_3(thf)_2$ ($\mathbf{AA}_{Sc-thf}$)



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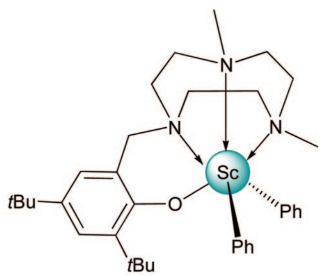

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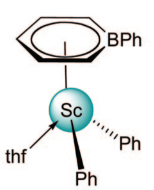
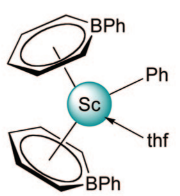


(X-ray)
236



237

There are some reports of employing $ScPh_3(thf)_2$ ($\mathbf{AA}_{Sc-thf}$) as a rare-earth metal precursor in arene-elimination reactions with protic proligands. Chart 28 shows the outcome of the acid−base reaction between $ScPh_3(thf)_2$ and a pyridine-functionalized diamine proligand (Chart 28, **234**)[316] or a functionalized triazacyclononane (Chart 28, **235**), respectively.[251] In the presence of the scandium triphenyl compound, a neutral borabenzene-base adduct $C_5H_5B\cdot PMe_3$ was converted into the formally monoanionic boratabenzene ligand to form the piano stool-shaped complex **236** or the respective bis(boratabenzene) scandium compound **237**.[431]

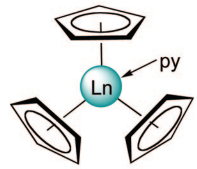
Homoleptic rare-earth metal phenyl complexes $LnPh_3(thf)_2$ (Ln = Y, Nd, Sm), $Ln[C_6H_3(OiPr)_2\text{-}2,6]_3$ (Ln = Sm, Yb), and $LiSm[C_6H_3(OiPr_2)_2\text{-}2,6]_4$ initiate the polymerization of ε-caprolactone.[428,434] The latter two complexes have also been tested as initiators for the polymerization of alkyl isocyanates and methyl methacrylate but showed only low activity.[428]

In the following sections, redox-transmetalation/ligand-exchange reactions as depicted in Scheme 58 will be discussed. The trivalent perfluorinated phenyl complexes $Ln(C_6F_5)_3$ ($\mathbf{AA}^{C_6F_5}$) are thermally very unstable and have not yet been isolated. Reaction mixtures that might generate such species undergo rapid decomposition into LnF_3 and complex organic products.[395] Nevertheless, the synthetic value of in situ prepared "$Ln(C_6F_5)_3$" has been the subject of detailed investigations mainly carried out by Deacon et al. and will therefore be presented here. For closer insight into mechanistic proposals, the original publications might be consulted.[19]

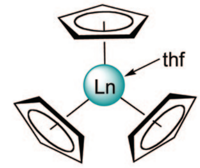
Scheme 58. General Redox-Transmetalation/Ligand Exchange Reaction Yielding Trivalent Rare-Earth Metal Derivatives

$$2\,Ln + 3\,Hg(C_6F_5)_2 + 6\,HL \xrightarrow[-3\,Hg,\ -6\,C_6F_5H]{thf/dme} 2\,Ln(L)_3(thf/dme)_x$$

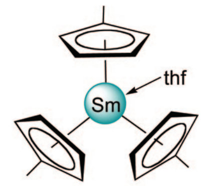
Chart 29. Cyclopentadienyl Complexes Synthesized by Redox-Transmetalation/Ligand-Exchange Reactions



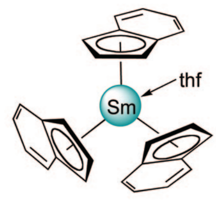
Ln = Eu, Yb
238



Ln = Ce, Nd, Sm, Gd, Dy, Er, Tm, Yb, Lu
239



240

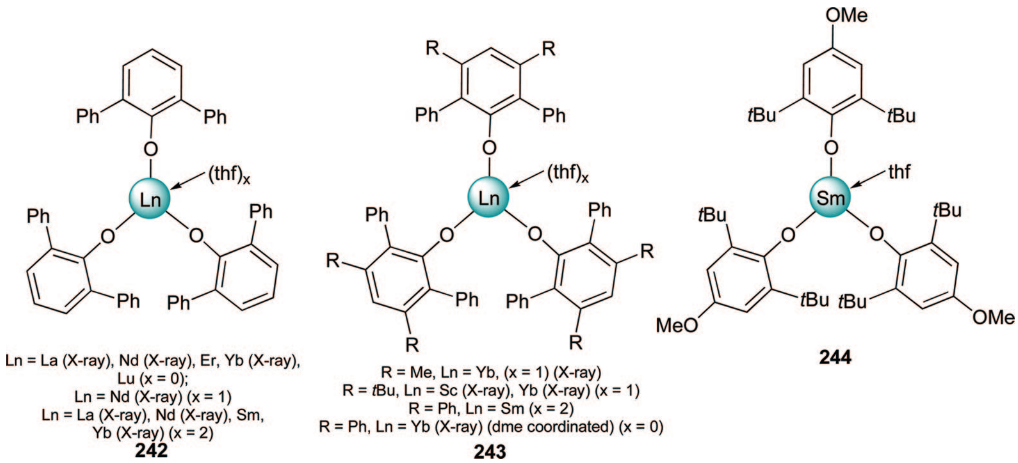


241

The preparation of tris(Cp) complexes of the rare-earth metals by reaction of europium or ytterbium, $Hg(C_6F_5)_2$, and CpH was first accomplished when pyridine was used instead of thf as solvent. While divalent products were isolated from ethereal solvents, the analogous reaction in pyridine yielded the trivalent pyridine solvates $LnCp_3(py)$ (Ln = Eu, Yb) (Chart 29, **238**).[410] In a more general application, the synthesis of $LnCp_3(thf)$ for a series of lanthanide metals (Ln = Ce, Nd, Sm, Gd, Dy, Er, Tm, Lu) has been reported using thf as a solvent (Chart 29, **239**).[19] The utility of this synthesis approach, however, seems to be limited to unsubstituted cyclopentadienes. Reactions with C_5H_5Me or indene were only successful when Sm was used as a metal center, but compounds **240** and **241** were produced in low yield.[408]

Redox-transmetalation followed by ligand exchange with 2,6-diphenylphenol exclusively yields phenolate complexes with trivalent rare-earth metals, even for the lanthanides with accessible divalent oxidation states. Depending on the workup and the crystallization procedures, homoleptic tris(phenolate) complexes $Ln(OC_6H_3Ph_2\text{-}2,6)_3(thf)_x$ with varying amounts of coordinating donor molecules have been isolated (Chart 30, **242**).[416,435,436] The corresponding divalent ytterbium phenolate $Yb(OC_6H_3Ph_2\text{-}2,6)_2(thf)_3$ could only be obtained by reduction of the Yb(III) species with ytterbium powder and mercury metal.[437] Further substitution in the 3- and 5-position of the phenolate ligand produced sterically hindered complexes **243** with low metal coordination numbers.[415] While the reaction of Yb, $Hg(C_6F_5)_2$, and $HOC_6H_2iPr_2$-

Chart 30. Aryloxide Complexes Synthesized by Redox-Transmetalation/Ligand-Exchange Reactions



2,6-OMe-4 gave a divalent aryloxide species (see section 14.2), the same reaction with samarium generated the divalent species in very low yield with the major product Sm[O(C_6H_2*t*Bu_2-2,6-OMe-4)]$_3$(thf) (**244**) in the Ln(III) oxidation state.[414]

Redox-transmetalation/ligand-exchange reactions have been extensively explored for the preparation of rare-earth metal pyrazolate complexes. Depending on the substitution pattern of the pyrazolato ligand in the 3- and 5-positions (e.g., H, Me, *t*Bu, Ph) and the size of the rare-earth metal cation, polymeric compounds (Nd, R = H),[438] complexes with both $\mu-\eta^1$-η^1 bridging and η^2-coordinated pyrazolato ligands (Nd, R = Me),[438] or exclusively η^2-coordinated pyrazolato ligands have been reported (Chart 31, **245**–**249**).[439–442] When the synthesis was carried out in dme or dme/$OPPh_3$, the corresponding donor adducts (**248** and **249**) were obtained.[440,443] It is noteworthy that utilization of $HgPh_2$ instead of $Hg(C_6F_5)_2$ in the transmetalation reaction followed by protonolysis with H(pz^R) produced the respective divalent pyrazolate compounds, in accordance with the lower oxidizing ability of $HgPh_2$ (see section 14.1).

The attempted synthesis of ytterbium(II) complexes carrying the bidentate N,O-ligands [N($SiMe_3$)C_6H_4-2-OMe] and [N($SiMe_3$)C_6H_4-2-OPh] from Yb and $Hg(C_6F_5)_2$ in the presence of the respective amines rather yielded the products of an O–C(Ar) bond activation.[444] The resulting trivalent ytterbium metal center is stabilized by the respective N,O- and [OR] ligands (Chart 31, **250** and **251**).

Following the synthesis strategy illustrated in Scheme 58, a series of rare-earth metal(III) formamidinates has been prepared (Chart 31, **252** and **253**).[445,446] Depending on the steric bulk of the formamidinato ligand, varying coordination numbers of the rare-earth metal center were observed. The use of a sterically demanding ligand bearing isopropyl groups in the 2- and 6- position of the aryl substituents induced the activation of a C–F bond, yielding a terminal Ln–F functionality (Chart 31, **252**).[445] Tris(formamidinato)lanthanum(III) complexes **253**$_{La}$ can be used as catalysts for the Tishchenko reaction.[447]

Targeting an arene-elimination reaction of Y(*o*-$C_6H_4CH_2N$-Me_2)$_3$ with H(C_5Me_5), the group of Teuben successfully synthesized a mono(cyclopentadienyl)–bis(phenyl) yttrium complex (**254**) (Chart 32) and investigated thermal decomposition pathways of such compounds.[340,448]

Besides the formation of cyclopentadienyl complexes, compounds **AC** were found to be suitable precursors for the synthesis of rare-earth metal complexes with multidentate binaphtholato (**255**) and amino–amido (**256**) ligands.[449–451] Compounds **255** and **256** (Chart 32) have successfully been applied as catalysts in the (asymmetric) intramolecular hydroamination/cyclization of aminoalkenes, with the former producing the highest enantiomeric excess so far. With the intention to synthesize a heteroleptic mono(phosphor–ylide), Y(*o*-$C_6H_4CH_2NMe_2$)$_3$ was reacted with Ph_3P=CH-(*o*-$CH_3OC_6H_4$), but compound **257** was rather obtained as the product of exhaustive protonolysis of the phosphoranylidene ligand (Chart 32).[452]

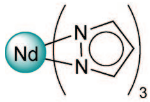
14.5. Synthesis, Structure, and Properties of Mixed-Valent Ph_2Yb(III)(thf)(μ-Ph)$_3$Yb(II)(thf)$_3$

As mentioned in section 14.1, reactions between rare-earth metals and $HgPh_2$ are harder to induce than those with $Hg(C_6F_5)_2$. Slow interaction was observed with amalgated metal,[398] and violent reaction was reported upon metal activation with CH_2I_2.[399] Naphthaleneytterbium Yb($C_{10}H_8$)-(thf)$_2$[453] can also be viewed as activated Yb metal, and the reactivity of such toward $HgPh_2$ was investigated by Bochkarev et al. Indeed, the reaction of diphenylmercury with the naphthalene species in thf is completed within 2 h at ambient temperature and yields mixed-valent Ph_2Yb(III)(thf)(μ-Ph)$_3$Yb(II)(thf)$_3$ (**AD**$_{Yb-thf}$) as the main product (Scheme 59, I).[454] Recrystallization from thf/Et_2O mixtures gave red crystals of **AD**$_{Yb-thf}$. The mixed-valent complex could further be obtained by the use of $BiPh_3$ as oxidizing reagent (Scheme 59, II). The reaction, however, gets considerably slowed down and produces the ytterbium complex with lower yield.

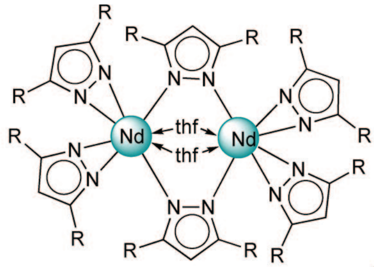
Compound Ph_2Yb(III)(thf)(μ-Ph)$_3$Yb(II)(thf)$_3$ has been characterized by IR spectroscopy, elemental analysis, X-ray crystallography, and the chemical reactivity toward various substrates (H_2O, HCl, Br_2, MeI, CO_2/H^+). The oxidation state of the two ytterbium metal centers was confirmed by measuring the μ_{eff} value.

The solid-state structure of the mixed-valent complex revealed a bimetallic structure with three bridging phenyl groups (Figure 51). The ytterbium(III) metal center additionally coordinates two terminal phenyl groups and one thf molecule, while additional stabilization of the ytterbium(II) metal center is achieved by coordination of three donor(thf) molecules. The geometry about both ytterbium metal centers can best be described as distorted octahedral.

Chart 31. Pyrazolate and Amide Complexes Synthesized by Redox-Transmetalation/Ligand-Exchange Reactions

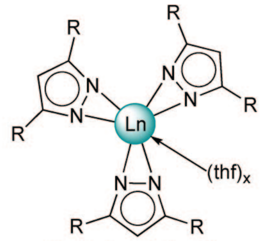


245



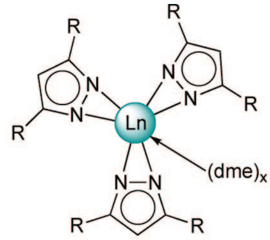
R = Me (X-ray)

246



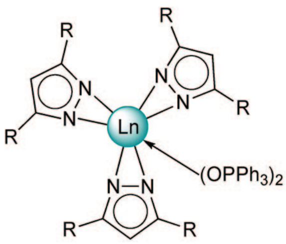
R = Me, Ln = Er (x = 1)
R = *t*Bu, Ln = Y, La, Pr, Nd (X-ray), Sm, Gd, Dy, Er (X-ray), Yb, Lu (x = 2)
R = Ph, Ln = La, Nd (X-ray), Lu (x = 3)
R = Ph, Ln = Sc, Y, Gd, Er (x = 2)

247



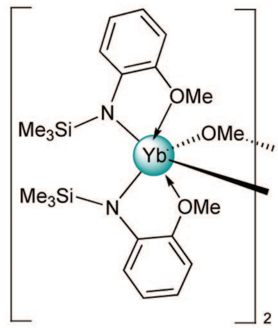
R = *t*Bu, Ln = La, Nd (X-ray), Er (x = 1)
R = Ph, Ln = La, Nd Er (X-ray) (x = 2)

248



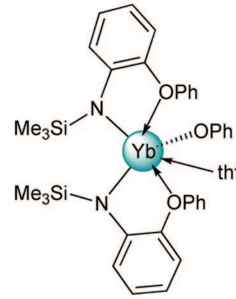
R = *t*Bu, Ln = La, Er
R = Ph, Ln = La, Nd (X-ray), Er (X-ray)

249



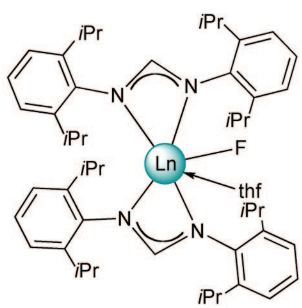
(X-ray)

250



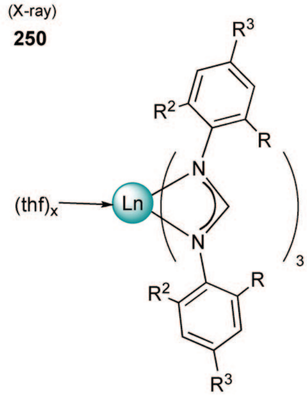
(X-ray)

251



Ln = La (X-ray), Ce (X-ray), Nd (X-ray), Sm, Tm (X-ray)

252



R = Me, $R^2 = R^3$ = H, Ln = La (X-ray) (x = 2), Er (x = 0);
R = R^2 = Me, R^3 = H, Ln = La (X-ray) (x = 1), Sm (X-ray) (x = 0);
R = $R^2 = R^3$ = Me, Ln = La, Nd (X-ray), Sm, Yb (X-ray) (x = 0);
R = R^2 = Et, R^3 = H, Ln = La (X-ray), Nd (X-ray), Sm (X-ray), Ho (X-ray), Yb (X-ray) (x = 0);
R = Ph, $R^2 = R^3$ = H, Ln = La, Nd, Sm (X-ray), Er (x = 0);

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15. Alkynide Complexes

15.1. Synthesis, Structure, and Properties of Ln(II)(C≡CR)$_2$ and H[Ln(II)(C≡CR)$_3$]

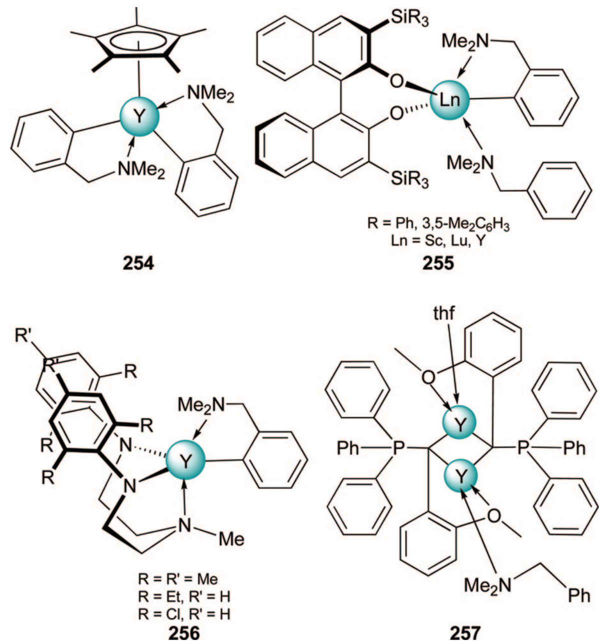
Even though the first examples of divalent lanthanide alkynides were reported more than 30 years ago, the chemistry of these σ-bonded hydrocarbyls developed sluggishly. This can partly be assigned to the advanced syntheses, the high reactivity of the divalent metal centers ("hot oxidation state"), and the challenging characterization.

Until today, a large variety of synthesis procedures has been developed, giving access to alkynide complexes of Yb(II), Eu(II), and Sm(II) (**AE**) (Scheme 60). Major contributions to the early developments were made by Deacon and co-workers, introducing transmetalation reactions of organomercurials as a route to organolanthanides.[394,395] Bis(phenylethynide) ytterbium and europium have been prepared by such transmetalations and were isolated solvent-free (Ln = Yb) or as Eu(C≡CPh)$_2$(thf)$_{0.25}$ (**AE**$^{Ph}_{Eu-thf}$) (Scheme 60, I). Following the same protocol, the respective Ln(C≡C*t*Bu)$_2$ (**AE**^{tBu}) compounds were accessible, even though bis(3,3-dimethylbut-1-ynide) mercury is less reactive than bis(phenylethynide) mercury.[455] Attempts to obtain the divalent samarium compounds and tris(alkynide)lanthanides by transmetalation failed.[455]

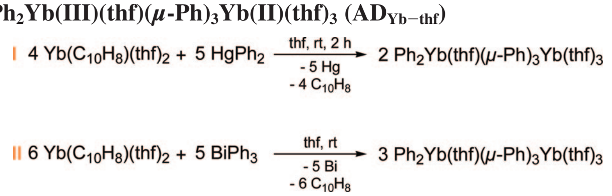
Bis(phenylethynide) ytterbium could further be prepared by ligand exchange of Yb(C_6F_5)$_2$ with phenylacetylene (Scheme 60, II).[394] Although reaction of Eu(C_6F_5)$_2$ and Ln(C≡C*t*Bu)$_2$ with phenylacetylene was indicated by IR and the hydrolysis behavior, no defined products could be isolated from such mixtures.

A very early report describes the reaction of metallic europium and ytterbium in liquid ammonia with propyne. Complex Eu(C≡CCH$_3$)$_2$ (**AE**$^{Me}_{Eu}$) could be isolated from a blue solution (Scheme 60, III), while in the ytterbium case,

Chart 32. Complexes Obtained from $Ln(o\text{-}C_6H_4CH_2NMe_2)_3$ (AC) by Arene-Elimination Reactions



Scheme 59. Synthesis of Mixed-Valent $Ph_2Yb(III)(thf)(\mu\text{-}Ph)_3Yb(II)(thf)_3$ (AD_{Yb-thf})



a mixture of the desired product $Yb(C{\equiv}CCH_3)_2$ and $Yb(NH_2)_2$ was obtained.[456]

In an effort to investigate the extent of low-valent lanthanide chemistry, Evans et al. applied the metal vaporization technique to examine zero-valent lanthanide metal reactivity.[457] Co-condensation of ytterbium metal vapor with 1-hexyne at −196 °C generated a black matrix of which several very similar products could be extracted with thf (Scheme 60, IV). IR spectroscopy indicated the formation of terminal hexynide ligands, and reactivity studies indicated the presence of hexynide and hydride ligands. Isopiestic molecular weight studies revealed the existence of highly associated complexes. The oligomerization presumably occurs via alkynide bridges as depicted in Figure 52a. Analogous reactions with the larger metal centers europium and samarium provided trivalent lanthanide species (vide infra).

Salt metathesis of divalent lanthanide iodides and phenylethynide sodium as applied by Bochkarev yielded the

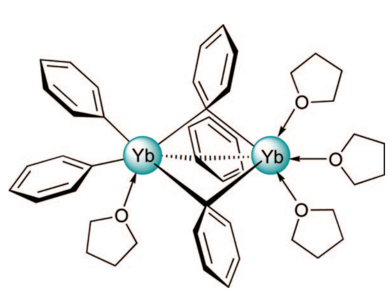
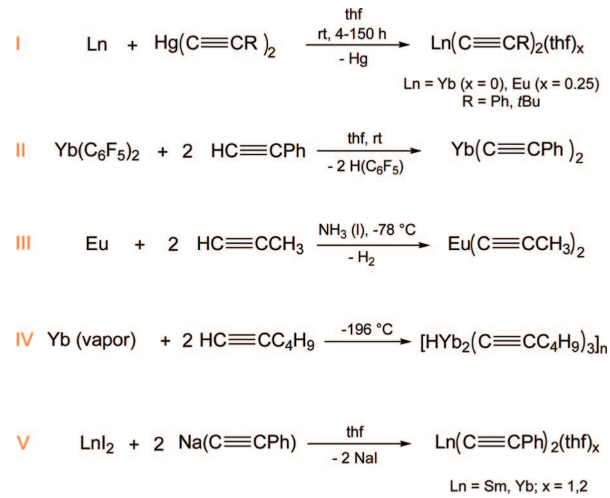


Figure 51. Schematic drawing of $Ph_2Yb(III)(thf)(\mu\text{-}Ph)_3Yb(II)(thf)_3$ (AD_{Yb-thf}) as found in the solid-state structure.

Scheme 60. Synthesis of Ln(II) Alkynides (AE and AF)



solvated $Ln(C{\equiv}CPh)_2(thf)_x$ compounds (AE^{Ph}_{thf}) (Ln = Yb, Sm) (Scheme 60, V). This is the only report of a samarium bis(alkynide) compound.[458]

The alkynide complexes of the low-valent lanthanides are indefinitely stable in inert atmosphere but extremely sensitive to oxygen and moisture.[394] $Ln(C{\equiv}CR)_2$ (**AE**) are insoluble in nonpolar solvents but can be dissolved in thf. A trimeric-tetrameric structure was found in boiling thf, indicative of an associated solid-state structure.[455] A polynuclear structure is further confirmed by significantly low $\nu(C{\equiv}C)$ frequencies, which can be assigned to bridging alkynide groups (Figure 52b). So far, all attempts to obtain structural information by crystallography have been frustrated by the inability to grow suitable crystals.

Alkynide ligands can be exchanged according to an acid−base reaction. For example, the [C≡C*t*Bu] ligand in $Yb(C{\equiv}CtBu)_2$ (AE^{tBu}_{Yb}) reacts with 2 equiv of the stronger Brønsted acid HC≡CPh to give $Yb(C{\equiv}CPh)_2$ (AE^{Ph}_{Yb}).[455] Considering the relatively high acidity of terminal alkynes, ligand-exchange reactions are of minor synthetic value, however.

Interesting reactivity was recently reported by Deacon and co-workers when reacting sterically very demanding H-

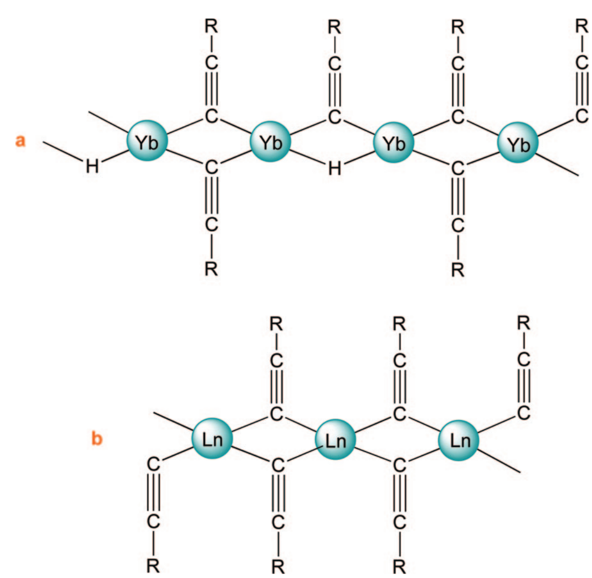
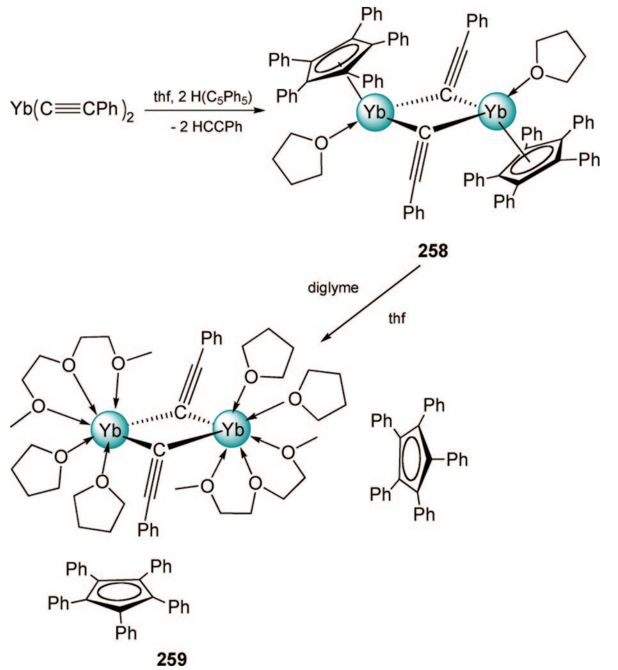


Figure 52. Proposed oligomeric structure of (a) $[HYb_2(C{\equiv}CR)_3]_n$ (AF_{Yb}) and (b) $[Ln(C{\equiv}CR)_2]_n$ (**AE**).

Scheme 61. Reaction of $Yb(C{\equiv}CPh)_2$ (AE^{Ph}_{Yb}) with $H(C_5Ph_5)$



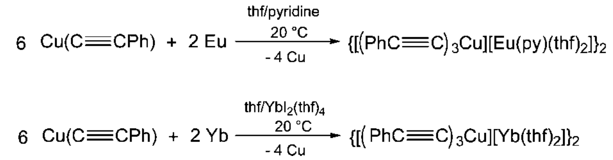
(C_5Ph_5) with a thf solution of $Yb(C{\equiv}CPh)_2$ (or in situ generated $Yb(C{\equiv}CPh)_2$) (Scheme 61).[459]

The resulting mono(cyclopentadienyl) complex [Yb-(C_5Ph_5)(μ-C≡CPh)(thf)$]_2$ (**258**) revealed a dimeric structure with bridging [C≡CPh] ligands. Slow addition of diglyme to **258** yielded solvent-separated ion pair [Yb(μ-C≡CPh)(diglyme)(thf)$_2]_2[C_5Ph_5]\cdot(thf)_4$ (**259**). The $[C_5Ph_5]$ anions are not bound to the metal but reside in the crystal lattice. A similar structural motif was also observed in [Eu(μ-C≡CPh)(diglyme)$_2]_2[P_2C_3tBu_3]_2\cdot C_6D_6\cdot$(diglyme)$_{0.5}$ (**260**). Transmetalation/ligand-exchange reaction of Yb, Hg-$(C{\equiv}CPh)_2$, and 2,6-diphenylphenol yielded the respective tri(phenolate) ytterbium(III) complex $Yb(OC_6H_3Ph_2\text{-}2,6)_3$, presumably involving the initial formation of the di(alkynide) Yb(II) compound followed by ligand exchange and oxidation.[435]

Alkynides $Ln(C{\equiv}CR)_2$ (**AE**) act as effective carbanion sources in reactions with aldehydes and ketones and can further act as reducing agents.[424,460] Commonly generated in situ, such compounds are valuable reagents in organic synthesis. Most widely used are organosamariums for carbon−carbon bond formations (samarium Barbier reaction, samarium Grignard reaction), due to their advantage of rapid, mild, and chemoselective reduction of organohalides.[461−463] Both inter- and intramolecular versions of these reactions using primary and secondary alkyl halides are well established.

A speciality with so far no further synthetic value is the formation of cuprate complexes of europium and ytterbium (**261**) (Scheme 62).[464] Redox-transmetalation reaction of the lanthanide metals with organocopper compound CuC≡CPh yielded the lanthanide cuprate complexes {[(C≡CPh)$_3$Cu]-[Eu(py)(thf)$_2$]}$_2$ ($\mathbf{261}_{Eu-thf}$) and {[(C≡CPh)$_3$Cu][Yb(thf)$_2$]}$_2$ ($\mathbf{261}_{Yb-thf}$). The outcome of the reactions is essentially dependent on the solvents used and the reaction conditions. Whereas reactions performed in pyridine/thf mixtures readily gave complexes **261**, the reactions in thf needed the presence of catalytic amounts of $YbI_2(thf)_4$. The solid-state structure of cuprates **261** revealed two $Eu(py)(thf)_2$ units and two

Scheme 62. Synthesis of Eu and Yb Cuprate Complexes (261)



$Yb(thf)_4$ units, respectively, that are bonded by two bridging $Cu(C{\equiv}CPh)_3$ fragments.[464]

15.2. Synthesis, Structure, and Properties of Ln(III)(C≡CR)$_3$ and [cation][Ln(III)(C≡CR)$_4$]

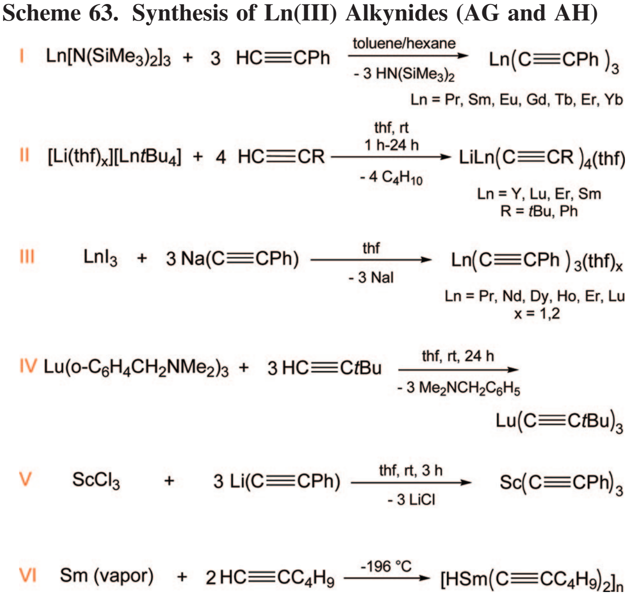
Compared to their divalent analogues, trivalent homoleptic alkynides have been even less studied. The number of reports on compounds $Ln(C{\equiv}CR)_3$ (**AG**) is basically limited to the description of synthesis approaches. Since transmetalation reactions did not afford alkynides of the trivalent rare-earth metals,[455] amine elimination, alkane elimination, and salt metathesis display potential synthesis procedures.

Synthesis according to the commonly used "silylamide route" was performed for a wide size range of rare-earth metal cations and gave compounds $Ln(C{\equiv}CPh)_3$ ($\mathbf{AG}^{Ph}$) in high yields (Scheme 63, I).[465,466] When investigating the general reactivity of Ln−C σ-bonds, the reactivity of ate complexes [Li(thf)$_x$][LntBu$_4$] (**G**) toward substrates containing acidic hydrogens was tested. Complete ligand exchange was observed with terminal alkynes HC≡CPh and HC≡CtBu yielding alkynide ate complexes $LiLn(C{\equiv}CR)_4$ (**AH**) (Scheme 63, II).[167,168]

Reactivity studies further revealed that treatment of Lu(o-$C_6H_4CH_2NMe_2)_3$ (**AC**) with HC≡CtBu gave solvent-free Lu(C≡CtBu)$_3$ ($\mathbf{AG}^{tBu}{}_{Lu}$) and N,N-dimethylbenzylamine (Scheme 63, IV).[433]

Starting from $ScCl_3$ and lithium alkynide, a representative of the smallest rare-earth metal scandium $Sc(C{\equiv}CPh)_3$ ($\mathbf{AG}^{Ph}{}_{Sc}$) could be obtained (Scheme 63, V).[68] Surprisingly, solutions of LnI_3 in thf react with Na(C≡CPh) under elimination of NaI to give the solvated lanthanide alkynides $Ln(C{\equiv}CPh)_3(thf)_x$ ($\mathbf{AG}^{Ph}{}_{thf}$) (Scheme 63, III).[467] Even though the donor solvent was present in all other reported synthesis routes, only solvent-free products have been reported.

Scheme 63. Synthesis of Ln(III) Alkynides (AG and AH)



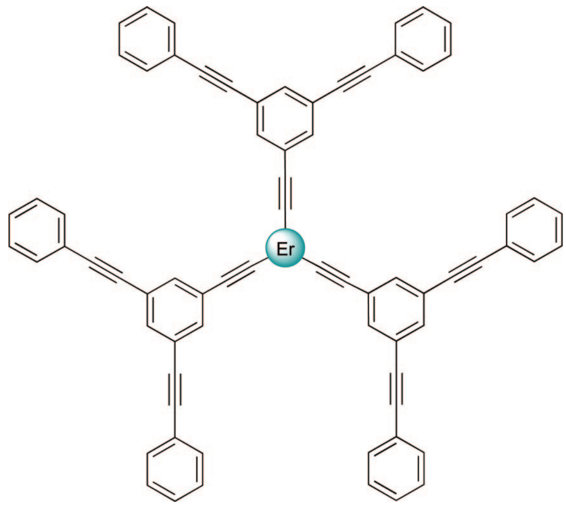


Figure 53. Proposed structure of Er[C≡CC$_6$H$_3$(C≡CPh)$_2$-3,5]$_3$ (**AG**$^{dend}{}_{Er}$).

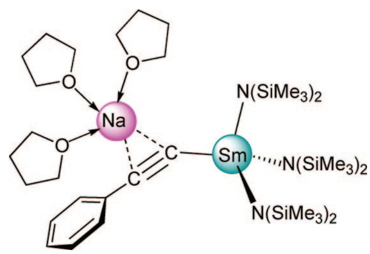


Figure 54. Structure of {Na(thf)$_3$}{Sm[N(SiMe$_3$)$_2$]$_3$(C≡CPh)} (**262**$_{Sm}$).

In contrast to the reactivity observed for ytterbium (section 15.1, Ln(II) alkynides), co-condensation of samarium metal with 1-hexyne at −196 °C produced an orange−black matrix from which a trivalent alkynide hydride of the possible composition [HSm(C≡CC$_4$H$_9$)$_2$]$_n$ (H**AH**$^{C_4H_9}{}_{Sm}$) could be extracted (Scheme 63, VI).[457] Like for the divalent ytterbium compound, a highly associated solid-state structure is anticipated (Figure 52a). Application of alkynide hydride **HAH**$^{C_4H_9}{}_{Sm}$ in the catalytic hydrogenation of 3-hexyne revealed formation of 3-hexene with low rates.

An exceptional organoerbium complex ligated by dendritic acetylide ligands has been published by Bochkarev et al. (Figure 53). Reacting Er[N(SiMe$_3$)$_2$]$_3$ with 3 equiv of dendron H[C≡CC$_6$H$_3$(C≡CPh)$_2$-3,5] in toluene gave Er[C≡CC$_6$H$_3$-(C≡CPh)$_2$-3,5]$_3$ in good yield (**AG**$^{dend}{}_{Er}$).[468]

The second-generation organoerbium dendrimer Er{C≡CC$_6$H$_3$[C≡C(C$_6$H$_3$(C≡CPh)$_2$-3,5)]$_2$-3,5}$_3$ could be prepared in a similar manner.[468] Both erbium dendrimers are soluble in thf, dme, and toluene but dissolve only poorly in hexane. They decompose above 330 °C without melting. The composition of the organoerbium compounds was determined by IR spectroscopy, their magnetic moments, and hydrolysis.

Reacting the tris(amides) Ln[N(SiMe$_3$)$_2$]$_3$ of cerium, samarium, and europium with phenylacetylene in the presence of 1 equiv of NaN(SiMe$_3$)$_2$ produced ion pairs {Na(thf)$_3$}{Ln-[N(SiMe$_3$)$_2$]$_3$(C≡CPh)} (**262**) (Ln = Ce, Sm, Eu).[469] The solvated sodium ion binds side-on to the acetylide ligand of the heteroleptic tris(amide)−mono(alkynide) complex (Figure 54). The cation interaction bends the Sm−C≡C angle in **262**$_{Sm}$ to a value of only 151.4°.

Heteroleptic bis(aryloxide)−mono(acetylide) complexes were further reported by Deacon et al.[414] Because of the extreme steric bulk provided by HOAr^{tBu,OMe} (Ar^{tBu,OMe} = C$_6$H$_2$*t*Bu$_2$-2,6-OMe-4), the transmetalation reaction of Hg(C≡CPh)$_2$ with the smaller rare-earth elements Y, Er, and Lu in the presence of the aryl alcohol cleanly produced Ln(OAr^{tBu,OMe})$_2$(C≡CPh)(thf)$_2$ (**263**$_{thf}$) (Figure 55). Isolation of these mixed-ligand complexes was attributed to steric inhibition of the cleavage of the final Ln(C≡CPh) group. Under the same reaction conditions, Yb with Hg(C≡CPh)$_2$ and HOAr^{tBu,OMe} gave divalent Yb(OAr^{tBu,OMe})$_2$(thf)$_3$ (**264**), which could be oxidized by additional Hg(C≡CPh)$_2$ to complete the series by Yb(OAr^{tBu,OMe})$_2$(C≡CPh) (**263**$_{Yb}$). The observed reactivity is remarkable because the homoleptic alkynides of the trivalent rare-earth metals were not accessible by transmetalation reaction (vide supra).[455]

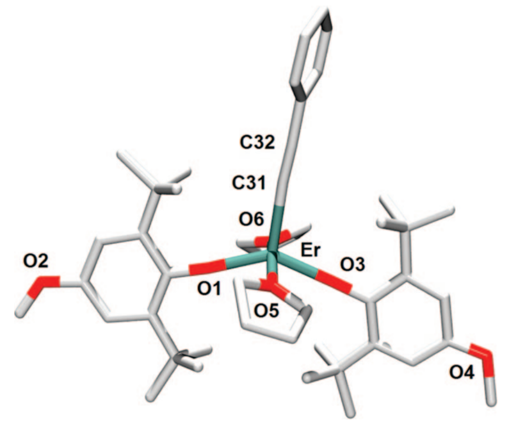


Figure 55. Solid-state structure of Er(OAr^{tBu,OMe})$_2$(C≡CPh)(thf)$_2$ (**263**$_{Er-thf}$), adapted from ref 414.

16. Conclusions and Perspectives

Polymerization catalysis has crucially advanced research in the field of rare-earth metal hydrocarbyl chemistry. In particular, the quest for suitable catalyst precursors pushed the development of new reaction protocols, accomplishing the synthesis and isolation of truly homoleptic rare-earth metal alkyl complexes. The hitherto only donor(solvent)- and ate-free Ln(III) representatives Ln[CH(SiMe$_3$)$_2$]$_3$ and [Ln-(CH$_3$)$_3$]$_n$ are accessible from tailor-made aryl(alk)oxide and amide precursors, seemingly achieving their thermal stability through kinetic constraints. Together with donor-stabilized neosilyl and benzyl derivatives, mainly Ln(CH$_2$SiMe$_3$)$_3$(thf)$_x$ and Ln(CH$_2$Ph)$_3$(thf)$_y$, as well as heterobimetallic Ln(MMe$_4$)$_3$ (M = Al, Ga)—so-called methyls in disguise or cryptomethyls "LnMe$_3$(MMe$_3$)$_3$"—such σ-bonded alkyl complexes emerged as versatile and powerful precursors for the synthesis of molecularly well-defined precatalysts. The traditional and still prevailing notion of the general low stability of such compounds is clearly thwarted by the thermal stability of homoleptic tetramethylaluminates Ln(AlMe$_4$)$_x$ (x = 2, 3). Complexes Ln(AlMe$_4$)$_3$ of the smaller-sized redox-stable Ln centers can even be sublimed (<100 °C/10^{-3} Torr), hence belonging to the most volatile rare-earth metal compounds. This thermal stability is reminiscent of that of the homoleptic alkaline-earth metal tetraalkylaluminate complexes Mg(AlMe$_4$)$_2$ and Ca(AlEt$_4$)$_2$.[470] The synergetic relationship between rare-earth metal centers and group 13 metals not only provides deeper insight into Ziegler−Natta-type catalysts but might be elaborated in organorare-earth synthesis. Further expansion of the chemistry of Ln(MR$_4$)$_2$ and Ln(MR$_4$)$_3$ (M = Al, Ga) might provide entry into unprecedented hydrocarbyl chemistry like the synthesis of novel donor(solvent)-free derivatives Ln−CH$_3$

and Ln−CH_2CH_3. Such complexes are potential candidates for alkane (methane) activation and can assist in elucidating and assessing fundamental organometallic reaction pathways such as β-hydrogen elimination and associated secondary (agostic) interactions. Methyl degradation to formerly elusive $Ln^{3+}-CH_2^{2-}$ (methylidene), $Ln^{3+}-CH^{3-}$ (methine), and $Ln^{3+}-C^{4-}$ (carbide) species already has been demonstrated to preferentially occur via organoaluminum-assisted proton abstraction, being controllable in the presence of sterically demanding ancillary ligands. More detailed investigations into such long-time neglected degradation processes of hydrocarbyl ligands will certainly enhance our knowledge of rare-earth metal complexes containing Ln−C σ-bonds, thus markedly contributing to the progress of this exciting area of organometallic chemistry.

17. Acknowledgments

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18. References

(1) Cotton, S. A. *Coord. Chem. Rev.* **1997**, *160*, 93.
(2) Cotton, F. A. *Chem. Rev.* **1955**, *55*, 551.
(3) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Acc. Chem. Res.* **1974**, *7*, 209.
(4) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Chem. Rev.* **1976**, *76*, 219.
(5) Tsutsui, M.; Ely, N.; Dubois, R. *Acc. Chem. Res.* **1976**, *9*, 217.
(6) Lappert, M. F. *Pure Appl. Chem.* **1978**, *50*, 703.
(7) Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 474.
(8) Schumann, H. *J. Organomet. Chem.* **1985**, *281*, 95.
(9) Bochkarev, M. N.; Kalinina, G. S.; Bochkarev, L. N. *Russ. Chem. Rev.* **1985**, *54*, 802.
(10) Evans, W. J. *Polyhedron* **1987**, *6*, 803.
(11) Koschmieder, S. U.; Wilkinson, G. *Polyhedron* **1991**, *10*, 135.
(12) Steinborn, D. *Angew. Chem.* **1992**, *104*, 392.
(13) Schaverien, C. J. In *Adv. Organomet. Chem.*; Academic Press: New York, 1994; Vol. 36.
(14) Edelmann, F. T. *Angew. Chem., Int. Ed.* **1995**, *34*, 2466.
(15) Edelmann, F. T. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Lappert, M. F., Eds.; Pergamon: Oxford, New York, Tokyo, 1995; Vol. 4, p 11.
(16) Eaborn, C.; Izod, K.; Smith, J. D. *J. Organomet. Chem.* **1995**, *500*, 89.
(17) Zakharov, L. N.; Struchkov, Y. T. *J. Organomet. Chem.* **1997**, *536−537*, 65.
(18) Edelmann, F. T.; Freckmann, D. M. M.; Schumann, H. *Chem. Rev.* **2002**, *102*, 1851.
(19) Deacon, G. B.; Forsyth, C. M.; Nickel, S. *J. Organomet. Chem.* **2002**, *647*, 50.
(20) Piers, W. E.; Emslie, D. J. H. *Coord. Chem. Rev.* **2002**, *233−234*, 131.
(21) Arndt, S.; Okuda, J. *Chem. Rev.* **2002**, *102*, 1953.
(22) Hou, Z.; Wakatsuki, Y. In *Science of Synthesis*; Imamoto, T., Noyori, R., Eds.; Thieme: Stuttgart, Germany, 2002; Vol. 2, p 849.
(23) Hou, Z. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 2253.
(24) Mountford, P.; Ward, B. D. *Chem. Commun.* **2003**, 1797.
(25) Zeimentz, P. M.; Arndt, S.; Elvidge, B. R.; Okuda, J. *Chem. Rev.* **2006**, *106*, 2404.
(26) Karsch, H. H.; Appelt, A.; Müller, G. *Angew. Chem.* **1986**, *98*, 832.
(27) Karsch, H. H.; Ferazin, G.; Steigelmann, O.; Kooijman, H.; Hiller, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1739.
(28) Karsch, H. H.; Ferazin, G.; Kooijman, H.; Steigelmann, O.; Schier, A.; Bissinger, P.; Hiller, W. *J. Organomet. Chem.* **1994**, *482*, 151.
(29) Hao, S.; Song, J.-I.; Aghabozorg, H.; Gambarotta, S. *Chem. Commun.* **1994**, 157.
(30) Roitershtein, D. M.; Ziller, J. W.; Evans, W. J. *J. Am. Chem. Soc.* **1998**, *120*, 11342.
(31) Kretschmer, W.; Thiele, K. H. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1304.
(32) Mashima, K.; Sugiyama, H.; Nakamura, A. *Chem. Commun.* **1994**, 1581.
(33) Taube, R.; Windisch, H.; Görlitz, F. H.; Schumann, H. *J. Organomet. Chem.* **1993**, *445*, 85.
(34) Taube, R.; Windisch, H.; Maiwald, S.; Hemling, H.; Schumann, H. *J. Organomet. Chem.* **1996**, *513*, 49.
(35) Taube, R.; Maiwald, S.; Sieler, J. *J. Organomet. Chem.* **2001**, *621*, 327.
(36) Kuehl, C. J.; Simpson, C. K.; John, K. D.; Sattelberger, A. P.; Carlson, C. N.; Hanusa, T. P. *J. Organomet. Chem.* **2003**, *683*, 149.
(37) Woodman, T. J.; Schormann, M.; Hughes, D. L.; Bochmann, M. *Organometallics* **2003**, *22*, 3028.
(38) Woodman, T. J.; Schormann, M.; Bochmann, M. *Organometallics* **2003**, *22*, 2938.
(39) Woodman, T. J.; Schormann, M.; Hughes, D. L.; Bochmann, M. *Organometallics* **2004**, *23*, 2972.
(40) Rabe, G. W.; Strissel, C. S.; Liable-Sands, L. M.; Concolino, T. E.; Rheingold, A. L. *Inorg. Chem.* **1999**, *38*, 3446.
(41) Rabe, G. W.; Zhang-Presse, M.; Riederer, F. A.; Golen, J. A.; Incarvito, C. D.; Rheingold, A. L. *Inorg. Chem.* **2003**, *42*, 7587.
(42) Hegedus, L., Lipshutz, B., Nozaki, H., Reetz, M., Rittmeyer, P., Smith, K., Totter, F., Yamamoto, H., Schlosser, M., Eds.; John Wiley & Sons Ltd.: *Organometallics in Synthesis. A Manual*; Schlosser, M. Editor, John Wiley & Sons, Chichester, U.K., 1994.
(43) Wilkinson, G. *Science* **1974**, *185*, 109.
(44) Frankland, P. F. *J. Chem. Soc.* **1848−1849**, *2*, 263.
(45) Pope, W. J.; Peachy, S. J. *Proc. Chem. Soc.* **1907**, *23*, 86.
(46) Pope, W. J.; Peachy, S. J. *J. Chem. Soc.* **1909**, 371.
(47) Rundle, R. E.; Sturdivant, J. H. *J. Am. Chem. Soc.* **1947**, *69*, 1561.
(48) Coates, G. E.; Wade, K. In *Organometallic Compounds*, 3rd ed.; Coates, G. E., Green, M. L. H., Wade, K., Eds.; Methuen: London, 1967; Vol. 1.
(49) Jaffe, H. H.; Doak, G. O. *J. Chem. Phys.* **1953**, *21*, 627.
(50) Green, M. L. H. In *Organometallic Compounds*, 3rd ed.; Coates, G. E., Green, M. L. H., Wade, K., Eds.; Methuen: London, 1968; Vol. 2.
(51) Wilkinson, G. *Chimia* **1973**, *27*, 165.
(52) Clauss, K.; Beermann, C. *Angew. Chem.* **1959**, *71*, 627.
(53) Berthold, H. J.; Groh, G. *Z. Anorg. Allg. Chem.* **1963**, *319*, 230.
(54) Berthold, H. J.; Groh, G. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 516.
(55) Collier, M. R.; Lappert, M. F.; Truelock, M. M. *J. Organomet. Chem.* **1970**, *25*, C36.
(56) Collier, M. R.; Lappert, M. F.; Pearce, R. *J. Chem. Soc., Dalton Trans.* **1973**, 445.
(57) Yagupsky, G.; Shortland, A.; Wilkinson, G. *Chem. Commun.* **1970**, 1369.
(58) Mowat, W.; Shortland, A.; Yagupsky, G.; Hill, N. J.; Yagupsky, M.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1972**, 533.
(59) Muthmann, W.; Kraft, K. *Liebigs Ann. Chem.* **1903**, *325*, 261.
(60) Grosse, A. v. *Z. Anorg. Allg. Chem.* **1926**, *152*, 133.
(61) Evans, W. J. *Inorg. Chem.* **2007**, *46*, 3435.
(62) Rice, F. O.; Rice, K. K. *The Aliphatic Free Radicals*; The John Hopkins Press: Baltimore, MD, 1935.
(63) Plets, V. M. *Dokl. Akad. Nauk SSSR* **1938**, *20*, 27.
(64) Gilman, H.; Jones, R. G. *J. Org. Chem.* **1945**, *10*, 505.
(65) Wilkinson, G.; Birmingham, J. M. *J. Am. Chem. Soc.* **1954**, *76*, 6210.
(66) Hart, F. A.; Saran, M. S. *J. Chem. Soc., Chem. Commun.* **1968**, 1614.
(67) Cotton, S. A.; Welch, A. J.; Hursthouse, M. B.; Hart, F. A. *J. Chem. Soc., Chem. Commun.* **1972**, 1225.
(68) Hart, F. A.; Massey, A. G.; Saran, M. S. *J. Organomet. Chem.* **1970**, *21*, 147.
(69) Müller, J. Dr. Thesis, Technische Universität Berlin, Germany, 1978.
(70) Schumann, H.; Müller, J. *Angew. Chem., Int. Ed.* **1978**, *17*, 276.
(71) Dietrich, H. M.; Raudaschl-Sieber, G.; Anwander, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 5303.
(72) Lappert, M. F.; Pearce, R. *J. Chem. Soc., Chem. Commun.* **1973**, 126.
(73) Barker, G. K.; Lappert, M. F. *J. Organomet. Chem.* **1974**, *76*, C45.
(74) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Smith, J. D. *J. Am. Chem. Soc.* **1994**, *116*, 12071.
(75) Hitchcock, P. B.; Lappert, M. F.; Smith, R. G.; Bartlett, R. A.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1988**, 1007.
(76) Thompson, L. C. In *Handbook on the physics and chemistry of the rare earths*; Gschneidner, K. A., Jr., Eyring, L., Eds.; North-Holland Publishing Company: Amsterdam, The Netherlands, 1979.
(77) Freeman, A. J.; Watson, R. E. *Phys. Rev.* **1962**, *127*, 2058.
(78) Seth, M.; Dolg, M.; Fulde, P.; Schwerdtfeger, P. *J. Am. Chem. Soc.* **1995**, *117*, 6597.
(79) Gibson, J. K. *J. Phys. Chem. A* **2003**, *107*, 7891.
(80) Cornehl, H. H.; Heinemann, C.; Schröder, D.; Schwarz, H. *Organometallics* **1995**, *14*, 992.

(81) Schinzel, S.; Bindl, M.; Visseaux, M.; Chermette, H. *J. Phys. Chem. A* **2006**, *110*, 11324.
(82) Eaborn, C.; Eidenschink, R.; Jackson, P. M.; Walton, D. R. M. *J. Organomet. Chem.* **1975**, *101*, C40.
(83) Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467.
(84) Brinkman, E. A.; Berger, S.; Brauman, J. I. *J. Am. Chem. Soc.* **1994**, *116*, 8304.
(85) Römer, B.; Gatev, G. G.; Zhong, M.; Brauman, J. I. *J. Am. Chem. Soc.* **1998**, *120*, 2919.
(86) Fu, Y.; Liu, L.; Li, R. Q.; Liu, R.; Guo, Q. X. *J. Am. Chem. Soc.* **2004**, *126*, 814.
(87) Nolan, S. P.; Stern, D.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7844.
(88) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.
(89) Bordwell, F. G. http://www.chem.wisc.edu/areas/reich/pkatable/index.htm.
(90) Streitwieser, A.; Scannon, P. J.; Niemeyer, H. M. *J. Am. Chem. Soc.* **1972**, *94*, 7936.
(91) Wetzel, D. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1988**, *110*, 8333.
(92) Ziegler, T.; Folga, E.; Berces, A. J. *J. Am. Chem. Soc.* **1993**, *115*, 636.
(93) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491.
(94) Dietrich, H. M.; Grove, H.; Törnroos, K. W.; Anwander, R. *J. Am. Chem. Soc.* **2006**, *128*, 1458.
(95) Seppelt, K. *Acc. Chem. Res.* **2003**, *36*, 147.
(96) Schumann, H.; Lauke, H.; Hahn, E.; Pickardt, J. *J. Organomet. Chem.* **1984**, *263*, 29.
(97) Schumann, H.; Müller, J.; Bruncks, N.; Lauke, H.; Pickardt, J. *Organometallics* **1984**, *3*, 69.
(98) Schumann, H.; Pickardt, J.; Bruncks, N. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 120.
(99) Arndt, S.; Beckerle, K.; Zeimentz, P. M.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 7473.
(100) Kramer, M. U.; Robert, D.; Arndt, S.; Zeimentz, P. M.; Spaniol, T. P.; Yahia, A.; Maron, L.; Eisenstein, O.; Okuda, J. *Inorg. Chem.* **2008**, *47*, 9265.
(101) Jacob, K.; Thiele, K. H. *Z. Anorg. Allg. Chem.* **1986**, *543*, 192.
(102) Gerber, L. C. H.; Le Roux, E.; Törnroos, K. W.; Anwander, R. *Chem.—Eur. J.* **2008**, *14*, 9555.
(103) Dietrich, H. M.; Meermann, C.; Törnroos, K. W.; Anwander, R. *Organometallics* **2006**, *25*, 4316.
(104) Hajela, S.; Schaefer, W. P.; Bercaw, J. E. *J. Organomet. Chem.* **1997**, *532*, 45.
(105) Arndt, S.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 5075.
(106) Arndt, S.; Beckerle, K.; Zeimentz, P. M.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 7473.
(107) Evans, W. J.; Johnston, M. A.; Greci, M. A.; Gummersheimer, T. S.; Ziller, J. W. *Polyhedron* **2003**, *22*, 119.
(108) Arndt, S.; Elvidge, B. R.; Zeimentz, P. M.; Spaniol, T. P.; Okuda, J. *Organometallics* **2006**, *25*, 793.
(109) Aillaud, I.; Lyubov, D.; Collin, J.; Guillot, R. g.; Hannedouche, J. r. m.; Schulz, E.; Trifonov, A. *Organometallics* **2008**, *27*, 5929.
(110) Boncella, J. M.; Andersen, R. A. *Organometallics* **1985**, *4*, 205.
(111) Klimpel, M. G.; Anwander, R.; Tafipolsky, M.; Scherer, W. *Organometallics* **2001**, *20*, 3983.
(112) Schrems, M. G.; Dietrich, H. M.; Tornroos, K. W.; Anwander, R. *Chem. Commun.* **2005**, 5922.
(113) Sommerfeldt, H.-M.; Meermann, C.; Schrems, M. G.; Törnroos, K. W.; Frøystein, N. A.; Miller, R. J.; Scheidt, E.-W.; Scherer, W.; Anwander, R. *Dalton Trans.* **2008**, 1899.
(114) Fischbach, A.; Herdtweck, E.; Anwander, R.; Eickerling, G.; Scherer, W. *Organometallics* **2003**, *22*, 499.
(115) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 54.
(116) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.
(117) Allred, A. L. *J. Inorg. Nucl. Chem.* **1961**, *17*, 215.
(118) Nakamura, H.; Nakayama, Y.; Yasuda, H.; Maruo, T.; Kanehisa, N.; Kai, Y. *Organometallics* **2000**, *19*, 5392.
(119) Sommerfeldt, H.-M.; Meermann, C.; Törnroos, K. W.; Anwander, R. *Inorg. Chem.* **2008**, *47*, 4696.
(120) Fischbach, A. Dr. Thesis, Technische Universität München, Germany, 2003.
(121) Evans, W. J.; Anwander, R.; Doedens, R. J.; Ziller, J. W. *Angew. Chem., Int. Ed.* **1994**, *33*, 1641.
(122) Evans, W. J.; Anwander, R.; Ziller, J. W. *Organometallics* **1995**, *14*, 1107.
(123) Evans, W. J.; Anwander, R.; Ziller, J. W.; Khan, S. I. *Inorg. Chem.* **1995**, *34*, 5927.
(124) Klimpel, M. G.; Eppinger, J.; Sirsch, P.; Scherer, W.; Anwander, R. *Organometallics* **2002**, *21*, 4021.
(125) Anwander, R.; Klimpel, M. G.; Dietrich, H. M.; Shorokhov, D. J.; Scherer, W. *Chem. Commun.* **2003**, 1008.
(126) Zimmermann, M.; Estler, F.; Herdtweck, E.; Törnroos, K. W.; Anwander, R. *Organometallics* **2007**, *26*, 6029.
(127) Xiang, L.; Wang, Q.; Song, H.; Zi, G. *Organometallics* **2007**, *26*, 5323.
(128) Fischbach, A.; Klimpel, M. G.; Widenmeyer, M.; Herdtweck, E.; Scherer, W.; Anwander, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 2234.
(129) Zimmermann, M.; Frøystein, N. Å.; Fischbach, A.; Sirsch, P.; Dietrich, H. M.; Törnroos, K. W.; Herdtweck, E.; Anwander, R. *Chem.—Eur. J.* **2007**, *13*, 8784.
(130) Anwander, R.; Runte, O.; Eppinger, J.; Gerstberger, G.; Herdtweck, E.; Spiegler, M. *J. Chem. Soc., Dalton Trans.* **1998**, 847.
(131) Fischbach, A.; Eickerling, G.; Scherer, W.; Herdtweck, E.; Anwander, R. *Z. Naturforsch. B: Chem. Sci.* **2004**, *59*, 1353.
(132) Fischbach, A.; Perdih, F.; Sirsch, P.; Scherer, W.; Anwander, R. *Organometallics* **2002**, *21*, 4569.
(133) Fischbach, A.; Perdih, F.; Herdtweck, E.; Anwander, R. *Organometallics* **2006**, *25*, 1626.
(134) Fischbach, A.; Meermann, C.; Eickerling, G.; Scherer, W.; Anwander, R. *Macromolecules* **2006**, *39*, 6811.
(135) Nagl, I.; Widenmeyer, M.; Herdtweck, E.; Raudaschl-Sieber, G.; Anwander, R. *Microporous Mesoporous Mater.* **2001**, *44*, 311.
(136) Byers, J. J.; Pennington, W. T.; Robinson, G. H.; Hrncir, D. C. *Polyhedron* **1990**, *9*, 2205.
(137) Hess, H.; Hinderer, A.; Steinhauser, S. *Z. Anorg. Allg. Chem.* **1970**, *377*, 1.
(138) McLaughlin, G. M.; Smith, J. D.; Sim, G. A. *J. Chem. Soc., Dalton Trans.* **1972**, 2197.
(139) Klimpel, M. G. Dr. Thesis, Technische Universität München, Germany, 2001.
(140) Zimmermann, M.; Törnroos, K. W.; Anwander, R. *Organometallics* **2006**, *25*, 3593.
(141) Holton, J.; Lappert, M. F.; Scollary, G. R.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1976**, 425.
(142) Busch, M. A.; Harlow, R.; Watson, P. L. *Inorg. Chim. Acta* **1987**, *140*, 15.
(143) Evans, W. J.; Kozimor, S. A.; Brady, J. C.; Davis, B. L.; Nyce, G. W.; Seibel, C. A.; Ziller, J. W.; Doedens, R. J. *Organometallics* **2005**, *24*, 2269.
(144) Dietrich, H. M.; Zapilko, C.; Herdtweck, E.; Anwander, R. *Organometallics* **2005**, *24*, 5767.
(145) Zimmermann, M.; Törnroos, K. W.; Anwander, R. *Angew. Chem., Int. Ed.* **2008**, *47*, 775.
(146) Zimmermann, M.; Törnroos, K. W.; Sitzmann, H.; Anwander, R. *Chem.—Eur. J.* **2008**, *14*, 7266.
(147) Le Roux, E.; Nief, F.; Jaroschik, F.; Törnroos, K. W.; Anwander, R. *Dalton Trans.* **2007**, 4866.
(148) Robert, D.; Spaniol, T. P.; Okuda, J. *Eur. J. Inorg. Chem.* **2008**, 2801.
(149) Dietrich, H. M.; Schuster, O.; Törnroos, K. W.; Anwander, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 4858.
(150) Zimmermann, M.; Törnroos, K. W.; Anwander, R. *Angew. Chem., Int. Ed.* **2007**, *46*, 3126.
(151) Zimmermann, M.; Takats, J.; Kiel, G.; Tornroos, K. W.; Anwander, R. *Chem. Commun.* **2008**, 612.
(152) Litlabø, R.; Zimmermann, M.; Saliu, K.; Takats, J.; Törnroos, K. W.; Anwander, R. *Angew. Chem., Int. Ed.* **2008**, *47*, 9560.
(153) Meermann, C.; Törnroos, K. W.; Nerdal, W.; Anwander, R. *Angew. Chem., Int. Ed.* **2007**, *46*, 6508.
(154) Bähr, G.; Müller, G. E. *Chem. Ber.* **1955**, *88*, 1765.
(155) Schumann, H.; Hartmann, U.; Wassermann, W. *Polyhedron* **1990**, *9*, 353.
(156) Dümichen, U.; Thiele, K.-H.; Gelbrich, T.; Sieler, J. *J. Organomet. Chem.* **1995**, *495*, 71.
(157) Thiele, K. H.; Herbrich, T. *Z. Anorg. Allg. Chem.* **1995**, *621*, 2025.
(158) Hofstee, H. K.; Boersma, J.; van der Meulen, J. D.; van der Kerk, G. J. M. *J. Organomet. Chem.* **1978**, *153*, 245.
(159) Langguth, E.; Van Thu, N.; Shakoor, A.; Jacob, K.; Thiele, K. H. *Z. Anorg. Allg. Chem.* **1983**, *505*, 127.
(160) Langguth, E.; Thiele, K. H. *Z. Anorg. Allg. Chem.* **1985**, *530*, 69.
(161) Shakoor, A.; Jacob, K.; Thiele, K. H. *Z. Anorg. Allg. Chem.* **1985**, *521*, 57.
(162) Herbrich, T.; Thiele, K. H.; Thewalt, U. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1609.
(163) Wayda, A. L.; Evans, W. J. *J. Am. Chem. Soc.* **1978**, *100*, 7119.
(164) Noh, W.; Girolami, G. S. *Polyhedron* **2007**, *26*, 3865.
(165) Schumann, H.; Genthe, W.; Hahn, E.; Pickardt, J.; Schwarz, H.; Eckart, K. *J. Organomet. Chem.* **1986**, *306*, 215.
(166) Qian, C.; Ye, C.; Li, Y. *J. Organomet. Chem.* **1986**, *302*, 171.

(167) Evans, W. J.; Drummond, D. K.; Hanusa, T. P.; Olofson, J. M. *J. Organomet. Chem.* **1989**, *376*, 311.
(168) Evans, W. J.; Wayda, A. L. *J. Organomet. Chem.* **1980**, *202*, C6.
(169) Niemeyer, M. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1027.
(170) Sadow, A. D.; Tilley, T. D. *J. Am. Chem. Soc.* **2003**, *125*, 7971.
(171) Evans, W. J.; Champagne, T. M.; Ziller, J. W.; Kaltsoyannis, N. *J. Am. Chem. Soc.* **2006**, *128*, 16178.
(172) Collier, M. R.; Kingston, B. M.; Lappert, M. F.; Truelock, M. M. Brit. Patent 36021, 1969.
(173) Schumann, H.; Freckmann, D. M. M.; Dechert, S. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2422.
(174) Atwood, J. L.; Hunter, W. E.; Rogers, R. D.; Holton, J.; McMeeking, J.; Pearce, R.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1978**, 140.
(175) Schumann, H.; Müller, J. *J. Organomet. Chem.* **1978**, *146*, C5.
(176) Hultzsch, K. C.; Voth, P.; Beckerle, K.; Spaniol, T. P.; Okuda, J. *Organometallics* **2000**, *19*, 228.
(177) Arndt, S.; Voth, P.; Spaniol, T. P.; Okuda, J. *Organometallics* **2000**, *19*, 4690.
(178) Niemeyer, M. *Acta Crystallogr.* **2001**, *E57*, m578.
(179) Estler, F. Dr. Thesis, Technische Universität München, Germany, 2002.
(180) Evans, W. J.; Brady, J. C.; Ziller, J. W. *J. Am. Chem. Soc.* **2001**, *123*, 7711.
(181) Schumann, H.; Müller, J. *J. Organomet. Chem.* **1979**, *169*, C1.
(182) Lukesova, L.; Ward, B. D.; Bellemin-Laponnaz, S.; Wadepohl, H.; Gade, L. H. *Dalton Trans.* **2007**, 920.
(183) Rufanov, K. A.; Freckmann, D. M. M.; Kroth, H.-J.; Schutte, S.; Schumann, H. *Z. Naturforsch. B: Chem. Sci.* **2005**, *60*, 533.
(184) Schumann, H.; Freckmann, D. M. M.; Schutte, S.; Dechert, S.; Hummert, M. *Z. Anorg. Allg. Chem.* **2007**, *633*, 888.
(185) Vollershtein, E. L.; Yakovlev, V. A.; Tinyakova, E. I.; Dolgoplosk, B. A. *Dokl. Akad. Nauk SSSR* **1980**, *250*, 365.
(186) Bambirra, S.; Bouwkamp, M. W.; Meetsma, A.; Hessen, B. *J. Am. Chem. Soc.* **2004**, *126*, 9182.
(187) Bambirra, S.; vanLeusen, D.; Tazelaar, C. G. J.; Meetsma, A.; Hessen, B. *Organometallics* **2007**, *26*, 1014.
(188) Bambirra, S.; Meetsma, A.; Hessen, B.; Bruins, A. P. *Organometallics* **2006**, *25*, 3486.
(189) Bambirra, S.; Perazzolo, F.; Boot, S. J.; Sciarone, T. J. J.; Meetsma, A.; Hessen, B. *Organometallics* **2008**, *27*, 704.
(190) Wang, B.; Wang, D.; Cui, D.; Gao, W.; Tang, T.; Chen, X.; Jing, X. *Organometallics* **2007**, *26*, 3167.
(191) Clark, D. L.; Gordon, J. C.; Huffman, J. C.; Watkin, J. G.; Zwick, B. D. *Organometallics* **1994**, *13*, 4266.
(192) Evans, W. J.; Shreeve, J. L.; Broomhalldillard, R. N. R.; Ziller, J. W. *J. Organomet. Chem.* **1995**, *501*, 7.
(193) Arndt, S.; Spaniol, T. P.; Okuda, J. *Chem. Commun.* **2002**, 896.
(194) Arndt, S.; Zeimentz, P. M.; Spaniol, T. P.; Okuda, J.; Honda, M.; Tatsumi, K. *Dalton Trans.* **2003**, 3622.
(195) Elvidge, B. R.; Arndt, S.; Zeimentz, P. M.; Spaniol, T. P.; Okuda, J. *Inorg. Chem.* **2005**, *44*, 6777.
(196) Arndt, S.; Okuda, J. *Adv. Synth. Catal.* **2005**, *347*, 339.
(197) Kramer, M. U.; Robert, D.; Nakajima, Y.; Englert, U.; Okuda, J. *Eur. J. Inorg. Chem.* **2007**, 665.
(198) Nakajima, Y.; Okuda, J. *Organometallics* **2007**, *26*, 1270.
(199) Fang, X.; Deng, Y.; Xie, Q.; Moingeon, F. *Organometallics* **2008**, *27*, 2892.
(200) Sulfab, Y.; Al-Shatti, N. J. *Inorg. Chim. Acta* **1984**, *87*, L23.
(201) Margerum, D. W. *Pure Appl. Chem.* **1983**, *55*, 23.
(202) Diddario, L. L.; Robinson, W. R.; Margerum, D. W. *Inorg. Chem.* **1983**, *22*, 1021.
(203) Butovskii, M. V.; Tok, O. L.; Wagner, F. R.; Kempe, R. *Angew. Chem., Int. Ed.* **2008**, *47*, 6469.
(204) Hultzsch, K. C.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 227.
(205) Cameron, T. M.; Gordon, J. C.; Scott, B. L. *Organometallics* **2004**, *23*, 2995.
(206) Li, X.; Baldamus, J.; Hou, Z. *Angew. Chem., Int. Ed.* **2005**, *44*, 962.
(207) Cameron, T. M.; Gordon, J. C.; Scott, B. L.; Tumas, W. *Chem. Commun.* **2004**, 1398.
(208) Jantunen, K. C.; Scott, B. L.; Gordon, J. C.; Kiplinger, J. L. *Organometallics* **2007**, *26*, 2777.
(209) Shima, T.; Hou, Z. *Chem. Lett.* **2008**, *37*, 298.
(210) Tardif, O.; Nishiura, M.; Hou, Z. *Organometallics* **2003**, *22*, 1171.
(211) Luo, Y.; Baldamus, J.; Hou, Z. *J. Am. Chem. Soc.* **2004**, *126*, 13910.
(212) Hultzsch, K. C.; Voth, P.; Spaniol, T. P.; Okuda, J. *Z. Anorg. Allg. Chem.* **2003**, *629*, 1272.
(213) Cui, D.; Nishiura, M.; Hou, Z. *Macromolecules* **2005**, *38*, 4089.
(214) Li, X.; Hou, Z. *Macromolecules* **2005**, *38*, 6767.
(215) Hou, Z.; Luo, Y.; Li, X. *J. Organomet. Chem.* **2006**, *691*, 3114.
(216) Hitzbleck, J.; Beckerle, K.; Okuda, J.; Halbach, T.; Mülhaupt, R. *Macromol. Symp.* **2006**, *236*, 23.
(217) Tritto, I.; Boggioni, L.; Ravasio, A.; Zampa, C.; Hitzbleck, J.; Okuda, J.; Bredeau, S.; Dubois, P. *Macromol. Symp.* **2007**, *260*, 114.
(218) Ravasio, A.; Zampa, C.; Boggioni, L.; Tritto, I.; Hitzbleck, J.; Okuda, J. *Macromolecules* **2008**, *41*, 9565.
(219) Cui, D.; Nishiura, M.; Tardif, O.; Hou, Z. *Organometallics* **2008**, *27*, 2428.
(220) Zhang, H.; Luo, Y.; Hou, Z. *Macromolecules* **2008**, *41*, 1064.
(221) Miao, W.; Li, S.; Zhang, H.; Cui, D.; Wang, Y.; Huang, B. *J. Organomet. Chem.* **2007**, *692*, 4828.
(222) Zhang, L.; Luo, Y.; Hou, Z. *J. Am. Chem. Soc.* **2005**, *127*, 14562.
(223) Arndt, S.; Spaniol, T. P.; Okuda, J. *Organometallics* **2003**, *22*, 775.
(224) Hitzbleck, J.; Okuda, J. *Z. Anorg. Allg. Chem.* **2006**, *632*, 1947.
(225) Hitzbleck, J.; Okuda, J. *Organometallics* **2007**, *26*, 3227.
(226) Tardif, O.; Nishiura, M.; Hou, Z. *Tetrahedron* **2003**, *59*, 10525.
(227) Sun, J.; Berg, D. J.; Twamley, B. *Organometallics* **2008**, *27*, 683.
(228) Wang, B.; Cui, D.; Lv, K. *Macromolecules* **2008**, *41*, 1983.
(229) Downing, S. P.; Guadano, S. C.; Pugh, D.; Danopoulos, A. A.; Bellabarba, R. M.; Hanton, M.; Smith, D.; Tooze, R. P. *Organometallics* **2007**, *26*, 3762.
(230) Canich, J. A. M.; Schaffer, T. D.; Christopher, J. N.; Squire, K. R. (Exxon) World Pat. WO0018808, 2000; Vol. 1.
(231) Rufanov, K. A.; Petrov, A. R.; Kotov, V. V.; Laquai, F.; Sundermeyer, J. *Eur. J. Inorg. Chem.* **2005**, 3805.
(232) Panda, T. K.; Hrib, C.; Jones, P. G.; Jenter, J.; Roesky, P. W.; Tamm, M. *Eur. J. Inorg. Chem.* **2008**, 4270.
(233) Otero, A.; Fernandez-Baeza, J.; Antinolo, A.; Lara-Sanchez, A.; Martinez-Caballero, E.; Tejeda, J.; Sanchez-Barba, L. F.; Alonso-Moreno, C.; Lopez-Solera, I. *Organometallics* **2008**, *27*, 976.
(234) Otero, A.; Fernandez-Baeza, J.; Lara-Sanchez, A. n.; Antinolo, A.; Tejeda, J.; Martinez-Caballero, E.; Marquez-Segovia, I.; Lopez-Solera, I.; Sanchez-Barba, L. F.; Alonso-Moreno, C. *Inorg. Chem.* **2008**, *47*, 4996.
(235) Shapiro, P. J.; Bunel, E. E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867.
(236) Voth, P.; Spaniol, T. P.; Okuda, J. *Organometallics* **2003**, *22*, 3921.
(237) Robert, D.; Trifonov, A. A.; Voth, P.; Okuda, J. *J. Organomet. Chem.* **2006**, *691*, 4393.
(238) Trifonov, A. A.; Spaniol, T. P.; Okuda, J. *Organometallics* **2001**, *20*, 4869.
(239) Nishiura, M.; Hou, Z.; Wakatsuki, Y.; Yamaki, T.; Miyamoto, T. *J. Am. Chem. Soc.* **2003**, *125*, 1184.
(240) Zhang, W. X.; Nishiura, M.; Hou, Z. *J. Am. Chem. Soc.* **2005**, *127*, 16788.
(241) Zhang, W. X.; Nishiura, M.; Hou, Z. *Chem.—Eur. J.* **2007**, *13*, 4037.
(242) Zhang, W.-X.; Nishiura, M.; Hou, Z. *Synlett* **2006**, *2006*, 1213.
(243) Zhang, W.-X.; Nishiura, M.; Hou, Z. *Angew. Chem., Int. Ed.* **2008**, *47*, 9700.
(244) Zhang, W.-X.; Hou, Z. *Org. Biomol. Chem.* **2008**, *6*, 1720.
(245) Arndt, S.; Spaniol, T. P.; Okuda, J. *Eur. J. Inorg. Chem.* **2001**, *2001*, 73.
(246) Arndt, S.; Trifonov, A.; Spaniol, T. P.; Okuda, J.; Kitamura, M.; Takahashi, T. *J. Organomet. Chem.* **2002**, *647*, 158.
(247) Mu, Y.; Piers, W. E.; MacQuarrie, D. C.; Zaworotko, M. J.; Young, V. G. *Organometallics* **1996**, *15*, 2720.
(248) Spaniol, T. P.; Okuda, J.; Kitamura, M.; Takahashi, T. *J. Organomet. Chem.* **2003**, *684*, 194.
(249) Kirillov, E.; Toupet, L.; Lehmann, C. W.; Razavi, A.; Carpentier, J. F. *Organometallics* **2003**, *22*, 4467.
(250) Lawrence, S. C.; Ward, B. D.; Dubberley, S. R.; Kozak, C. M.; Mountford, P. *Chem. Commun.* **2003**, 2880.
(251) Tredget, C. S.; Lawrence, S. C.; Ward, B. D.; Howe, R. G.; Cowley, A. R.; Mountford, P. *Organometallics* **2005**, *24*, 3136.
(252) Tredget, C. S.; Bonnet, F.; Cowley, A. R.; Mountford, P. *Chem. Commun.* **2005**, 3301.
(253) Ge, S.; Bambirra, S.; Meetsma, A.; Hessen, B. *Chem. Commun.* **2006**, 3320.
(254) Ward, B. D.; Bellemin-Laponnaz, S.; Gade, L. H. *Angew. Chem., Int. Ed.* **2005**, *44*, 1668.
(255) Tredget, C. S.; Clot, E.; Mountford, P. *Organometallics* **2008**, *27*, 3458.
(256) Lukesova, L.; Ward, B. D.; Bellemin-Laponnaz, S.; Wadepohl, H.; Gade, L. H. *Organometallics* **2007**, *26*, 4652.
(257) Bambirra, S.; Meetsma, A.; Hessen, B. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2006**, *62*, m314.
(258) Ge, S.; Meetsma, A.; Hessen, B. *Organometallics* **2008**, *27*, 5339.
(259) Zeimentz, P. M.; Spaniol, T. P.; Okuda, J. *Inorg. Chim. Acta* **2006**, *359*, 4769.
(260) Masuda, J. D.; Jantunen, K. C.; Scott, B. L.; Kiplinger, J. L. *Organometallics* **2008**, *27*, 1299.
(261) Bambirra, S.; Leusen, D. v.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Chem. Commun.* **2003**, 522.
(262) Bambirra, S.; Otten, E.; van Leusen, D.; Meetsma, A.; Hessen, B. *Z. Anorg. Allg. Chem.* **2006**, *632*, 1950.

(263) Kretschmer, W. P.; Meetsma, A.; Hessen, B.; Schmalz, T.; Qayyum, S.; Kempe, R. *Chem.—Eur. J.* **2006**, *12*, 8969.
(264) Cameron, T. M.; Gordon, J. C.; Michalczyk, R.; Scott, B. L. *Chem. Commun.* **2003**, 2282.
(265) Zimmermann, M.; Törnroos, K. W.; Waymouth, R. M.; Anwander, R. *Organometallics* **2008**, *27*, 4310.
(266) Bambirra, S.; Leusen, D. v.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Chem. Commun.* **2001**, 637.
(267) Bambirra, S.; Boot, S. J.; vanLeusen, D.; Meetsma, A.; Hessen, B. *Organometallics* **2004**, *23*, 1891.
(268) Ge, S.; Meetsma, A.; Hessen, B. *Organometallics* **2007**, *26*, 5278.
(269) Marinescu, S. C.; Agapie, T.; Day, M. W.; Bercaw, J. E. *Organometallics* **2007**, *26*, 1178.
(270) Li, S.; Miao, W.; Tang, T.; Cui, D.; Chen, X.; Jing, X. *J. Organomet. Chem.* **2007**, *692*, 4943.
(271) Yang, Y.; Liu, B.; Lv, K.; Gao, W.; Cui, D.; Chen, X.; Jing, X. *Organometallics* **2007**, *26*, 4575.
(272) Zhang, L.; Suzuki, T.; Luo, Y.; Nishiura, M.; Hou, Z. *Angew. Chem., Int. Ed.* **2007**, *46*, 1909.
(273) Luo, Y.; Nishiura, M.; Hou, Z. *J. Organomet. Chem.* **2007**, *692*, 536.
(274) Yang, Y.; Wang, Q.; Cui, D. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 5251.
(275) Li, S.; Miao, W.; Tang, T.; Dong, W.; Zhang, X.; Cui, D. *Organometallics* **2008**, *27*, 718.
(276) Wang, D.; Li, S.; Liu, X.; Gao, W.; Cui, D. *Organometallics* **2008**, *27*, 6531.
(277) Yang, Y.; Li, S.; Cui, D.; Chen, X.; Jing, X. *Organometallics* **2007**, *26*, 671.
(278) Liu, X.; Shang, X.; Tang, T.; Hu, N.; Pei, F.; Cui, D.; Chen, X.; Jing, X. *Organometallics* **2007**, *26*, 2747.
(279) Shang, X.; Liu, X.; Cui, D. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 5662.
(280) Miao, W.; Li, S.; Cui, D.; Huang, B. *J. Organomet. Chem.* **2007**, *692*, 3823.
(281) Liu, B.; Cui, D.; Ma, J.; Chen, X.; Jing, X. *Chem.—Eur. J.* **2007**, *13*, 834.
(282) Xu, X.; Xu, X.; Chen, Y.; Sun, J. *Organometallics* **2008**, *27*, 758.
(283) Gao, W.; Cui, D.; Liu, X.; Zhang, Y.; Mu, Y. *Organometallics* **2008**, *27*, 5889.
(284) Lara-Sanchez, A.; Rodriguez, A.; Hughes, D. L.; Schormann, M.; Bochmann, M. *J. Organomet. Chem.* **2002**, *663*, 63.
(285) Evans, W. J.; Brady, J. C.; Ziller, J. W. *Inorg. Chem.* **2002**, *41*, 3340.
(286) Zhang, Z.; Cui, D.; Liu, X. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6810.
(287) Bambirra, S.; Tsurugi, H.; Leusen, D. v.; Hessen, B. *Dalton Trans.* **2006**, 1157.
(288) Ge, S.; Meetsma, A.; Hessen, B. *Organometallics* **2008**, *27*, 3131.
(289) Lyubov, D. M.; Döring, C.; Fukin, G. K.; Cherkasov, A. V.; Shavyrin, A. S.; Kempe, R.; Trifonov, A. A. *Organometallics* **2008**, *27*, 2905.
(290) Blackwell, J.; Lehr, C.; Sun, Y. M.; Piers, W. E.; PearceBatchilder, S. D.; Zaworotko, M. J.; Young, V. G. *Can. J. Chem.* **1997**, *75*, 702.
(291) Cheng, J.; Saliu, K.; Kiel, G. Y.; Ferguson, M. J.; McDonald, R.; Takats, J. *Angew. Chem., Int. Ed.* **2008**, *47*, 4910.
(292) Rabe, G. W.; Rheingold, A. L. Cambridge Structural Database 2007, CCDC REFCODE: VIFREI.
(293) Jantunen, K. C.; Scott, B. L.; Hay, P. J.; Gordon, J. C.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2006**, *128*, 6322.
(294) Masuda, J. D.; Jantunen, K. C.; Scott, B. L.; Kiplinger, J. L. *Organometallics* **2008**, *27*, 803.
(295) Ohashi, M.; Konkol, M.; Del Rosal, I.; Poteau, R.; Maron, L.; Okuda, J. *J. Am. Chem. Soc.* **2008**, *130*, 6920.
(296) Tazelaar, C. G. J.; Bambirra, S.; vanLeusen, D.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2004**, *23*, 936.
(297) Ge, S.; Norambuena, V. F. Q.; Hessen, B. *Organometallics* **2007**, *26*, 6508.
(298) Howe, R. G.; Tredget, C. S.; Lawrence, S. C.; Subongkoj, S.; Cowley, A. R.; Mountford, P. *Chem. Commun.* **2006**, 223.
(299) Elvidge, B. R.; Arndt, S.; Spaniol, T. P.; Okuda, J. *Dalton Trans.* **2006**, 890.
(300) Lee, L.; Berg, D. J.; Einstein, F. W.; Batchelor, R. J. *Organometallics* **1997**, *16*, 1819.
(301) Skinner, M. E. G.; Tyrrell, B. R.; Ward, B. D.; Mountford, P. *J. Organomet. Chem.* **2002**, *647*, 145.
(302) Emslie, D. J. H.; Piers, W. E.; Parvez, M.; McDonald, R. *Organometallics* **2002**, *21*, 4226.
(303) Emslie, D. J. H.; Piers, W. E.; Parvez, M. *Dalton Trans.* **2003**, 2615.
(304) Masuda, J. D.; Jantunen, K. C.; Ozerov, O. V.; Noonan, K. J. T.; Gates, D. P.; Scott, B. L.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2008**, *130*, 2408.
(305) Liu, B.; Yang, Y.; Cui, D.; Tang, T.; Chen, X.; Jing, X. *Dalton Trans.* **2007**, 4252.
(306) Estler, F.; Eickerling, G.; Herdtweck, E.; Anwander, R. *Organometallics* **2003**, *22*, 1212.
(307) Eppinger, J.; Nikolaides, K. R.; Zhang-Presse, M.; Riederer, F. A.; Rabe, G. W.; Rheingold, A. L. *Organometallics* **2008**, *27*, 736.
(308) Meyer, N.; Zulys, A.; Roesky, P. W. *Organometallics* **2006**, *25*, 4179.
(309) Cai, C.-X.; Toupet, L.; Lehmann, C. W.; Carpentier, J.-F. *J. Organomet. Chem.* **2003**, *683*, 131.
(310) Amgoune, A.; Thomas, C. M.; Roisnel, T.; Carpentier, J.-F. *Chem.—Eur. J.* **2006**, *12*, 169.
(311) Konkol, M.; Spaniol, T. P.; Kondracka, M.; Okuda, J. *Dalton Trans.* **2007**, 4095.
(312) Konkol, M.; Kondracka, M.; Voth, P.; Spaniol, T. P.; Okuda, J. *Organometallics* **2008**, *27*, 3774.
(313) Wang, D.; Cui, D.; Miao, W.; Li, S.; Huang, B. *Dalton Trans.* **2007**, 4576.
(314) Liddle, S. T.; McMaster, J.; Green, J. C.; Arnold, P. L. *Chem. Commun.* **2008**, 1747.
(315) Sugiyama, H.; Gambarotta, S.; Yap, G. P. A.; Wilson, D. R.; Thiele, S. K. H. *Organometallics* **2004**, *23*, 5054.
(316) Ward, B. D.; Dubberley, S. R.; Maisse-Francois, A.; Gade, L. H.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **2002**, 4649.
(317) Liu, X.; Cui, D. *Dalton Trans.* **2008**, 3747.
(318) Lavanant, L.; Chou, T. Y.; Chi, Y.; Lehmann, C. W.; Toupet, L.; Carpentier, J. F. *Organometallics* **2004**, *23*, 5450.
(319) Lee, L.; Berg, D. J.; Bushnell, G. W. *Organometallics* **1995**, *14*, 8.
(320) Boyd, C. L.; Toupance, T.; Tyrrell, B. R.; Ward, B. D.; Wilson, C. R.; Cowley, A. R.; Mountford, P. *Organometallics* **2005**, *24*, 309.
(321) Cai, C.-X.; Amgoune, A.; Lehmann, C. W.; Carpentier, J.-F. *Chem. Commun.* **2004**, 330.
(322) Emslie, D. J. H.; Piers, W. E.; MacDonald, R. *J. Chem. Soc., Dalton Trans.* **2002**, 293.
(323) Lauterwasser, F.; Hayes, P. G.; Brase, S.; Piers, W. E.; Schafer, L. L. *Organometallics* **2004**, *23*, 2234.
(324) Hitchcock, P. B.; Holmes, S. A.; Lappert, M. F.; Tian, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2691.
(325) Van den Hende, J. R.; Hitchcock, P. B.; Holmes, S. A.; Lappert, M. F.; Tian, S. *J. Chem. Soc., Dalton Trans.* **1995**, 3933.
(326) Hitchcock, P. B.; Khvostov, A. V.; Lappert, M. F. *J. Organomet. Chem.* **2002**, *663*, 263.
(327) Hitchcock, P. B.; Lappert, M. F.; Tian, S. *J. Organomet. Chem.* **1997**, *549*, 1.
(328) Hitchcock, P. B.; Lappert, M. F.; Tian, S. *Dalton Trans.* **1997**, 1945.
(329) Schaverien, C. J.; Orpen, A. G. *Inorg. Chem.* **1991**, *30*, 4968.
(330) Avent, A. G.; Caro, C. F.; Hitchcock, P. B.; Lappert, M. F.; Li, Z.; Wei, X.-H. *Dalton Trans.* **2004**, 1567.
(331) Guttenberger, C.; Amberger, H. D. *J. Organomet. Chem.* **1997**, *545−546*, 601.
(332) Reddmann, H.; Guttenberger, C.; Amberger, H.-D. *J. Organomet. Chem.* **2000**, *602*, 65.
(333) Perrin, L.; Maron, L.; Eisenstein, O.; Lappert, M. F. *New J. Chem.* **2003**, *27*, 121.
(334) Clark, D. L.; Gordon, J. C.; Hay, P. J.; Martin, R. L.; Poli, R. *Organometallics* **2002**, *21*, 5000.
(335) Schaverien, C. J.; Nesbitt, G. J. *J. Chem. Soc., Dalton Trans.* **1992**, 157.
(336) Atwood, J. L.; Lappert, M. F.; Smith, R. G.; Zhang, H. M. *J. Chem. Soc., Chem. Commun.* **1988**, 1308.
(337) Westerhausen, M.; Hartmann, M.; Pfitzner, A.; Schwarz, W. *Z. Anorg. Allg. Chem.* **1995**, *621*, 837.
(338) Schaverien, C. J.; Van Mechelen, J. B. *Organometallics* **1991**, *10*, 1704.
(339) Hitchcock, P. B.; Lappert, M. F.; Smith, R. G. *J. Chem. Soc., Chem. Commun.* **1989**, 369.
(340) Booij, M.; Kiers, N. H.; Heeres, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1989**, *364*, 79.
(341) Müller, T. E.; Hultzsch, K. C.; Yus, M.; Foubelo, F.; Tada, M. *Chem. Rev.* **2008**, *108*, 3795.
(342) Douglass, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 10221.
(343) Tian, S.; Arredondo, V. M.; Stern, C. L.; Marks, T. J. *Organometallics* **1999**, *18*, 2568.
(344) Ryu, J.-S.; Marks, T. J.; McDonald, F. E. *Org. Lett.* **2001**, *3*, 3091.
(345) Ryu, J.-S.; Marks, T. J.; McDonald, F. E. *J. Org. Chem.* **2004**, *69*, 1038.
(346) Gendron, R. A. L.; Berg, D. J.; Shao, P.; Barclay, T. *Organometallics* **2001**, *20*, 4279.
(347) Schaverien, C. J.; Meijboom, N.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1992**, 124.
(348) Gribkov, D. V.; Hampel, F.; Hultzsch, K. C. *Eur. J. Inorg. Chem.* **2004**, 4091.
(349) Hong, S.; Tian, S.; Metz, M. V.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 14768.

(350) Metz, M. V.; Sun, Y.; Stern, C. L.; Marks, T. J. *Organometallics* **2002**, *21*, 3691.
(351) Westerhausen, M.; Hartmann, M.; Schwarz, W. *Inorg. Chim. Acta* **1998**, *269*, 91.
(352) Kawaoka, A. M.; Douglass, M. R.; Marks, T. J. *Organometallics* **2003**, *22*, 4630.
(353) Izod, K.; Liddle, S. T.; McFarlane, W.; Clegg, W. *Organometallics* **2004**, *23*, 2734.
(354) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Lu, Z. R.; Smith, J. D. *Organometallics* **1996**, *15*, 4783.
(355) Qi, G.; Nitto, Y.; Saiki, A.; Tomohiro, T.; Nakayama, Y.; Yasuda, H. *Tetrahedron* **2003**, *59*, 10409.
(356) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283.
(357) Andersen, R. A.; Boncella, J. M.; Burns, C. J.; Blom, R.; Haaland, A.; Volden, H. V. *J. Organomet. Chem.* **1986**, *312*, C49.
(358) Andersen, R. A.; Blom, R.; Boncella, J. M.; Burns, C. J.; Volden, H. V. *Acta Chem. Scand.* **1987**, *A41*, 24.
(359) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1285.
(360) DeKock, R. L.; Peterson, M. A.; Timmer, L. K.; Baerends, E. J.; Vernooijs, P. *Polyhedron* **1990**, *9*, 1919.
(361) Kaupp, M.; Schleyer, P. v. R.; Dolg, M.; Stoll, H. *J. Am. Chem. Soc.* **1992**, *114*, 8202.
(362) Hollis, T. K.; Burdett, J. K.; Bosnich, B. *Organometallics* **1993**, *12*, 3385.
(363) Al-Juaid, S. S.; Eaborn, C.; Hitchcock, P. B.; McGeary, C. A.; Smith, J. D. *J. Chem. Soc., Chem. Commun.* **1989**, 273.
(364) Al-Juaid, S. S.; Eaborn, C.; Hitchcock, P. B.; Izod, K.; Mallien, M.; Smith, J. D. *Angew. Chem., Int. Ed.* **1994**, *1994*, 1268.
(365) Clegg, W.; Eaborn, C.; Izod, K.; O'Shaughnessy, P.; Smith, J. D. *Angew. Chem.* **1997**, *109*, 2925.
(366) Yasuda, H. *J. Polym. Sci., Part A: Polym.Chem.* **2001**, *39*, 1955.
(367) Yasuda, H. *J. Organomet. Chem.* **2002**, *647*, 128.
(368) Eaborn, C.; Hill, M. S.; Hitchcock, P. B.; Smith, J. D.; Zhang, S.; Ganicz, T. *Organometallics* **1999**, *18*, 2342.
(369) Bowman, L. J.; Izod, K.; Clegg, W.; Harrington, R. W. *Organometallics* **2007**, *26*, 2646.
(370) Schumann, H.; Freckmann, D. M. M.; Dechert, S. *Organometallics* **2006**, *25*, 2696.
(371) Chigir, N. N.; Guzman, I. S.; Sharaev, O. K.; Tinyakova, E. I.; Dolgoplosk, B. A. *Dokl. Akad. Nauk SSSR* **1982**, *263*, 375.
(372) Guzman, I. S.; Chigir, N. N.; Sharaev, O. K.; Bondarenko, G. N.; Tinyakova, E. I.; Dolgoplosk, B. A. *Dokl. Akad. Nauk SSSR* **1979**, *249*, 860.
(373) Thiele, K. H.; Unverhau, K.; Geitner, M.; Jacob, K. *Z. Anorg. Allg. Chem.* **1987**, *548*, 175.
(374) Bambirra, S.; Meetsma, A.; Hessen, B. *Organometallics* **2006**, *25*, 3454.
(375) Döring, C.; Kempe, R. *Z. Kristallogr. NCS* **2008**, *223*, 397.
(376) Ge, S.; Meetsma, A.; Hessen, B. *Organometallics* **2009**, *28*, 719.
(377) Harder, S.; Ruspic, C.; Bhriain, N. N.; Berkermann, F.; Schürmann, M. *Z. Naturforsch. B: Chem. Sci.* **2008**, *63b*, 267.
(378) Meyer, N.; Roesky, P. W.; Bambirra, S.; Meetsma, A.; Hessen, B.; Saliu, K.; Takats, J. *Organometallics* **2008**, *27*, 1501.
(379) Carver, C. T.; Monreal, M. J.; Diaconescu, P. L. *Organometallics* **2008**, *27*, 363.
(380) Bambirra, S.; Meetsma, A.; Hessen, B. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2007**, *63*, m2891.
(381) Harder, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2714.
(382) Izod, K.; Clegg, W.; Liddle, S. T. *Organometallics* **2000**, *19*, 3640.
(383) Fedushkin, I. L.; Petrovskaya, T. V.; Bochkarev, M. N.; Dechert, S.; Schumann, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 2474.
(384) Weber, F.; Schultz, M.; Sofield, C. D.; Andersen, R. A. *Organometallics* **2002**, *21*, 3139.
(385) Harder, S.; Feil, F.; Knoll, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 4261.
(386) Manzer, L. E. *J. Organomet. Chem.* **1977**, *135*, C6.
(387) Manzer, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 8068.
(388) Harder, S. *Organometallics* **2005**, *24*, 373.
(389) Zhang, W.-X.; Nishiura, M.; Mashiko, T.; Hou, Z. *Chem.—Eur. J.* **2008**, *14*, 2167.
(390) Li, X.; Nishiura, M.; Mori, K.; Mashiko, T.; Hou, Z. *Chem. Commun.* **2007**, 4137.
(391) Jaroschik, F.; Shima, T.; Li, X.; Mori, K.; Ricard, L.; Le Goff, X.-F.; Nief, F.; Hou, Z. *Organometallics* **2007**, *26*, 5654.
(392) Nishiura, M.; Mashiko, T.; Hou, Z. *Chem. Commun.* **2008**, 2019.
(393) Zhang, L.; Nishiura, M.; Yuki, M.; Luo, Y.; Hou, Z. *Angew. Chem., Int. Ed.* **2008**, *47*, 2642.
(394) Deacon, G. B.; Koplick, A. J. *J. Organomet. Chem.* **1978**, *146*, C43.
(395) Deacon, G. B.; Koplick, A. J.; Raverty, W. D.; Vince, D. G. *J. Organomet. Chem.* **1979**, *182*, 121.
(396) Deacon, G. B.; Vince, D. G. *J. Organomet. Chem.* **1976**, *112*, C1.
(397) Deacon, G. B.; Raverty, W. D.; Vince, D. G. *J. Organomet. Chem.* **1977**, *135*, 103.
(398) Suleimanov, G. Z.; Khandozhko, R. N.; Mekhdiev, R. Y.; Petrovsky, P. V.; Agdamsky, T. A.; Kolobova, N. E.; Beletskaya, I. P. *Dokl. Akad. Nauk SSSR* **1985**, *284*, 1376.
(399) Starostina, T. A.; Shifrina, R. R.; Rybakova, L. F.; Petrov, E. S. *J. Gen. Chem. USSR* **1987**, *57*, 2148.
(400) *Organoderivatives of the Rare Earth Elements*; Bochkarev, M. N., Zakharov, L. N., Kalinina, G. S., Eds.; Kluwer: Dordrecht, The Netherlands, 1995.
(401) Deacon, G. B.; Forsyth, C. M. *Organometallics* **2003**, *22*, 1349.
(402) Forsyth, C. M.; Deacon, G. B. *Organometallics* **2000**, *19*, 1205.
(403) Heckmann, G.; Niemeyer, M. *J. Am. Chem. Soc.* **2000**, *122*, 4227.
(404) Deacon, G. B.; Forsyth, C. M. *Chem.—Eur. J.* **2004**, *10*, 1798.
(405) Fraser, R. R.; Mansour, T. S.; Savard, S. *J. Org. Chem.* **1985**, *50*, 3232.
(406) Deacon, G. B.; Forsyth, C. M. *Inorg. Chim. Acta* **1988**, *154*, 121.
(407) Deacon, G. B.; Forsyth, C. M.; Gatehouse, B. M.; White, A. H. *Aust. J. Chem.* **1990**, *43*, 795.
(408) Deacon, G. B.; Newnham, R. H. *Aust. J. Chem.* **1985**, *38*, 1757.
(409) Deacon, G. B.; Dietrich, A.; Forsyth, C. M.; Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1370.
(410) Deacon, G. B.; Forsyth, C. M.; Newnham, R. H.; Tuong, T. D. *Aust. J. Chem.* **1987**, *40*, 895.
(411) Deacon, G. B.; Forsyth, C. M.; Newham, R. H. *Polyhedron* **1987**, *6*, 1143.
(412) Deacon, G. B.; Hitchcock, P. B.; Holmes, S. A.; Lappert, M. F.; MacKinnon, P.; Newnham, R. H. *J. Chem. Soc, Chem. Commun.* **1989**, 935.
(413) Deacon, G. B.; Feng, T.; MacKinnon, P.; Newnham, R. H.; Nickel, S.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1993**, *46*, 387.
(414) Deacon, G. B.; Fallon, G. D.; Forsyth, C. M.; Harris, S. C.; Junk, P. C.; Skelton, B. W.; White, A. H. *Dalton Trans.* **2006**, 802.
(415) Deacon, G. B.; Fanwick, P. E.; Gitlits, A.; Rothwell, I. P.; Skelton, B. W.; White, A. H. *Eur. J. Inorg. Chem.* **2001**, 1505.
(416) Deacon, G. B.; Feng, T.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1995**, *48*, 741.
(417) Deacon, G. B.; Fallon, G. D.; Forsyth, C. M.; Schumann, H.; Weimann, R. *Chem. Ber.* **1997**, *130*, 409.
(418) Hauber, S.-O.; Niemeyer, M. *Inorg. Chem.* **2005**, *44*, 8644.
(419) Qayyum, S.; Haberland, K.; Forsyth, C. M.; Junk, P. C.; Deacon, G. B.; Kempe, R. *Eur. J. Inorg. Chem.* **2008**, 557.
(420) Deacon, G. B.; Delbridge, E. E.; Skelton, B. W.; White, A. H. *Angew. Chem., Int. Ed.* **1998**, *37*, 2251.
(421) Deacon, G. B.; Delbridge, E. E.; Skelton, B. W.; White, A. H. *Eur. J. Inorg. Chem.* **1999**, 751.
(422) Deacon, G. B.; Delbridge, E. E.; Skelton, B. W.; White, A. H. *Eur. J. Inorg. Chem.* **1998**, 543.
(423) Deacon, G. B.; MacKinnon, P. I.; Tuong, T. D. *Aust. J. Chem.* **1983**, *36*, 43.
(424) Deacon, G. B.; Tuong, T. D. *J. Organomet. Chem.* **1981**, *205*, C4.
(425) Kirillov, E. N.; Fedorova, E. A.; Trifonov, A. A.; Bochkarev, M. N. *Appl. Organomet. Chem.* **2001**, *15*, 151.
(426) Putzer, M. A.; Rogers, J. S.; Bazan, G. C. *J. Am. Chem. Soc.* **1999**, *121*, 8112.
(427) Zeimentz, P. M.; Okuda, J. *Organometallics* **2007**, *26*, 6388.
(428) Ihara, E.; Adachi, Y.; Yasuda, H.; Hashimoto, H.; Kanehisa, N.; Kai, Y. *J. Organomet. Chem.* **1998**, *569*, 147.
(429) Bochkarev, L. N.; Stepantseva, T. A.; Zakharov, L. N.; Fukin, G. K.; Yanovsky, A. I.; Struchkov, Y. T. *Organometallics* **1995**, *14*, 2127.
(430) Bochkarev, L. N.; Zheleznova, T. A.; Safronova, A. V.; Drozdov, M. S.; Zhil'tsov, S. F.; Zakharov, L. N.; Fukin, G. K.; Khorshev, S. Y. *Russ. Chem. Bull.* **1998**, *47*, 165.
(431) Putzer, M. A.; Bartholomew, G. P. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1777.
(432) Wayda, A. L.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1984**, *3*, 939.
(433) Wayda, A. L.; Rogers, R. D. *Organometallics* **1985**, *4*, 1440.
(434) Deng, X.; Yuan, M.; Xiong, C.; Li, X. *J. Appl. Polym. Sci.* **1999**, *73*, 1401.
(435) Deacon, G. B.; Nickel, S.; MacKinnon, P.; Tiekink, E. R. T. *Aust. J. Chem.* **1990**, *43*, 1245.
(436) Deacon, G. B.; Gatehouse, B. M.; Shen, Q.; Ward, G. N.; Thiekink, E. R. T. *Polyhedron* **1993**, *12*, 1289.
(437) Deacon, G. B.; Feng, T.; Junk, P. C.; Skelton, B. W.; White, A. H. *Chem. Ber.* **1997**, *130*, 851.
(438) Deacon, G. B.; Gatehouse, B. M.; Nickel, S.; Platts, S. N. *Aust. J. Chem.* **1991**, *44*, 613.
(439) Cosgriff, J. E.; Deacon, G. B.; Gatehouse, B. M.; Hemling, H.; Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 874.
(440) Cosgriff, J. E.; Deacon, G. B.; Gatehouse, B. M. *Aust. J. Chem.* **1993**, *46*, 1881.
(441) Cosgriff, J. E.; Deacon, G. B.; Gatehouse, B. M.; Hemling, H.; Schumann, H. *Aust. J. Chem.* **1994**, *47*, 1223.

(442) Cosgriff, J. E.; Deacon, G. B.; Gatehouse, B. M.; Lee, P. R.; Schumann, H. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1399.
(443) Cosgriff, J. E.; Deacon, G. B.; Fallon, G. D.; Gatehouse, B. M.; Schumann, H.; Weimann, R. *Chem. Ber.* **1996**, *129*, 953.
(444) Deacon, G. B.; Forsyth, C. M.; Scott, N. M. *Eur. J. Inorg. Chem.* **2000**, 2501.
(445) Cole, M. L.; Deacon, G. B.; Junk, P. C.; Konstas, K. *Chem. Commun.* **2005**, 1581.
(446) Cole, M. L.; Deacon, G. B.; Forsyth, C. M.; Junk, P. C.; Konstas, K.; Wang, J. *Chem.—Eur. J.* **2007**, *13*, 8092.
(447) Zuyls, A.; Roesky, P. W.; Deacon, G. B.; Konstas, K.; Junk, P. C. *Eur. J. Inorg. Chem.* **2008**, 693.
(448) Booij, M.; Klers, N. H.; Meetsma, A.; Teuben, J. H. *Organometallics* **1989**, *8*, 2454.
(449) Hultzsch, K. C.; Hampel, F.; Wagner, T. *Organometallics* **2004**, *23*, 2601.
(450) Gribkov, D. V.; Hultzsch, K. C. *Chem. Commun.* **2004**, 730.
(451) Gribkov, D. V.; Hultzsch, K. C.; Hampel, F. *J. Am. Chem. Soc.* **2006**, *128*, 3748.
(452) Rufanov, K. A.; Muller, B. H.; Spannenberg, A.; Rosenthal, U. *New J. Chem.* **2006**, *30*, 29.
(453) Bochkarev, M. N.; Trifonov, A. A.; Fedorova, E. A.; Emelyanova, N. S.; Basalgina, T. A.; Kalinina, G. S.; Razuvaev, G. A. *J. Organomet. Chem.* **1989**, *372*, 217.
(454) Bochkarev, M. N.; Khramenkov, V. V.; Rad'kov, Y. F.; Zakharov, L. N.; Struchkov, Y. T. *J. Organomet. Chem.* **1992**, *429*, 27.
(455) Deacon, G. B.; Koplick, A. J.; Tuong, T. D. *Aust. J. Chem.* **1982**, *35*, 941.
(456) Murphy, E.; Toogood, G. E. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 755.
(457) Evans, W. J.; Engerer, S. C.; Coleson, K. M. *J. Am. Chem. Soc.* **1981**, *103*, 6672.
(458) Gailiunas, G.; Biktimirov, R. K.; Nurtdinova, G. V.; Monakov, Y. B.; Tolstikov, G. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, *6*, 1435.
(459) Forsyth, C. M.; Deacon, G. B.; Field, L. D.; Jones, C.; Junk, P. C.; Kay, D. L.; Masters, A. F.; Richards, A. F. *Chem. Commun.* **2006**, 1003.
(460) Zhiltsov, S. F.; Shustov, S. B.; Shustova, L. V. *Metalloorgan. Khim.* **1992**, *5*, 729.
(461) Utimoto, K.; Nakamura, A.; Matsubara, S. *J. Am. Chem. Soc.* **1990**, *112*, 8189.
(462) Kunishima, M.; Tanaka, S.; Kono, K.; Hioki, K.; Tani, S. *Tetrahedron Lett.* **1995**, *36*, 3707.
(463) Kunishima, M.; Nakata, D.; Tanaka, S.; Hioki, K.; Tani, S. *Tetrahedron* **2000**, *56*, 9927.
(464) Bochkarev, L. N.; Druzhkova, O. N.; Zhiltsov, S. F.; Zakharov, L. N.; Fukin, G. K.; Khorshev, S. Y.; Yanovsky, A. I.; Struchkov, Y. T. *Organometallics* **1997**, *16*, 500.
(465) Shustov, S. B.; Bochkarev, L. N.; Zhiltsov, S. F. *Metalloorgan. Khim.* **1990**, *3*, 624.
(466) Bochkarev, L. N.; Shustov, S. B.; Guseva, T. V.; Zhiltsov, S. F. *Zh. Obshch. Khim.* **1988**, *58*, 923.
(467) Druzhkova, O. N.; Pimanova, N. A.; Bochkarev, L. N. *Russ. J. Gen. Chem.* **1999**, *69*, 1724.
(468) Bochkarev, M. N.; Katkova, M. A.; Khorshev, S. Y.; Makarenko, N. P. *Russ. Chem. Bull.* **1998**, *47*, 349.
(469) Karl, M.; Seybert, G.; Massa, W.; Harms, K.; Agarwal, S.; Maleika, R.; Stelter, W.; Greiner, A.; Heitz, W.; Neumüller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1301.
(470) Lehmkuhl, H. *Angew. Chem., Int. Ed.* **1964**, *3*, 107.

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