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Neutral and Monocationic Half-Sandwich Methyl Rare-Earth Metal Complexes: Synthesis, Structure, and 1,3-Butadiene Polymerization Catalysis

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Dedicated to Professor Wolfgang A. Herrmann on the occasion of his 60th birthday

Keywords: Rare-earth metals / Half-sandwich complexes / Alkyl complexes / Cationic complexes / Butadiene polymerization

Half-sandwich rare-earth metal tetramethylaluminate complexes [Ln(η^5-$C_5Me_4SiMe_3$){(μ-Me)$_2$(AlMe$_2$)}$_2$] (Ln = Y, La, Nd, Sm, Gd, Lu) were obtained by reaction of the neutral homoleptic tetramethylaluminate complex [Ln{(μ-Me)$_2$(AlMe$_2$)}$_3$] with tetramethyl(trimethylsilyl)cyclopentadiene, (C_5Me_4H)SiMe$_3$. Protonolysis reaction of the neutral mono(cyclopentadienyl) complexes with the Brønsted acid [NEt$_3$H]$^+$[BPh$_4$]$^-$ in thf led to the formation of the monocationic methyl complexes [Ln(η^5-$C_5Me_4SiMe_3$)Me(thf)$_3$]$^+$[BPh$_4$]$^-$ (Ln = Y, La, Nd, Sm, Lu). Single-crystal X-ray diffraction study on the Y, Sm, and Lu derivatives showed a four-legged piano-stool configuration. Upon activation with [Ph$_3$C]$^+$[B(C_6F_5)$_4$]$^-$, the neutral half-sandwich tetramethylaluminate complex [La(η^5-$C_5Me_4SiMe_3$){(μ-Me)$_2$(AlMe$_2$)}$_2$] catalyzed the polymerization of butadiene in the presence of [Al*i*Bu$_3$] to give *trans*-1,4-polybutadiene with narrow polydispersities (M_n/M_w = 1.05–1.09).

Introduction

Half-sandwich complexes of the rare-earth elements have been far less studied than their bis(cyclopentadienyl) homologues.[1] Despite the higher tendency towards ligand redistribution, they may exhibit enhanced reactivity through increased electronic and steric unsaturation.[2] Cationic alkyl mono(cyclopentadienyl) complexes [Ln(η^5-$C_5R'_5$)R]$^+$ have been reported to be key intermediates in catalytic polymerizations of unsaturated hydrocarbons.[3,4a] Although the report of the first cationic alkyl half-sandwich rare-earth complex by Schaverien dates back to 1992,[4b] only a limited number of this type of potentially reactive complexes has so far been reported in the literature.[5] The neutral tris[(trimethylsilyl)methyl] precursors [Ln(CH$_2$SiMe$_3$)(thf)$_n$] and the corresponding half-sandwich complexes [Ln(η^5-$C_5Me_4SiMe_3$)(CH$_2$SiMe$_3$)$_2$(thf)] turned out to be exceedingly sensitive and not reported for metal centers larger than Sm[6] and Gd.[4a,5e,7] Moreover, the cationic derivatives [Ln(η^5-$C_5R'_5$)(CH$_2$SiMe$_3$)(thf)$_m$]$^+$[A]$^-$ were so far only generated in situ and could not be structurally characterized.[5] Methyl cations were expected to be easier to handle and to facilitate the access to catalytically active cationic methyl species. Prompted by the reports on half-sandwich bis(aluminate) complexes as synthetic equivalents for bis(alkyl) half-sandwich complexes,[8b,8d] we report here the synthesis of monocationic methyl complexes from mono(cyclopentadienyl) bis(aluminate) complexes and their catalytic behavior in homogeneous 1,3-butadiene polymerization.

Results and Discussion

Mono(cyclopentadienyl) Bis(aluminate) Complexes

Neutral mono(cyclopentadienyl) bis(aluminate) complexes [Ln(η^5-$C_5Me_4SiMe_3$){(μ-Me)$_2$(AlMe$_2$)}$_2$] [Ln = Y (**1-Y**), La (**1-La**), Nd (**1-Nd**), Sm (**1-Sm**), Gd (**1-Gd**), Lu (**1-Lu**)] were obtained by alkane elimination reaction between the homoleptic tris(aluminate) precursors [Ln{(μ-Me)$_2$(AlMe$_2$)}$_3$] and (C_5Me_4H)SiMe$_3$ (Scheme 1). All the complexes (except for **1-Gd**) display a pattern of four resonances in their ^{1}H NMR spectra: one singlet for the SiMe$_3$ group and two singlets for the two pairs of methyl groups at the cyclopentadienyl ring, along with another signal for the eight methyl groups of the aluminate moieties, indicating a rapid exchange of the bridging and terminal methyl groups on the NMR timescale. Broad signals were observed in the ^{13}C NMR spectra for the methyl carbon atoms in the aluminate fragments. This high fluxionality of the aluminate group was already reported in the literature.[8]

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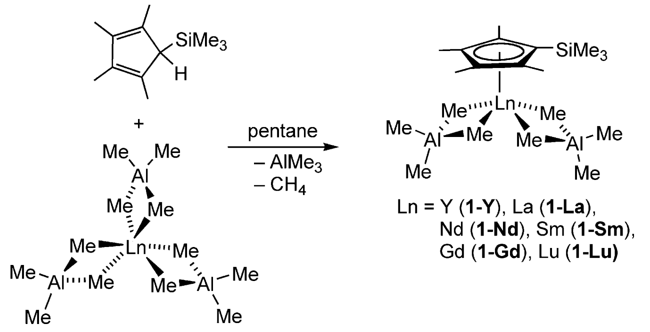


Scheme 1.

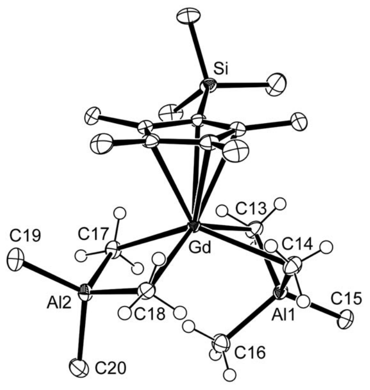


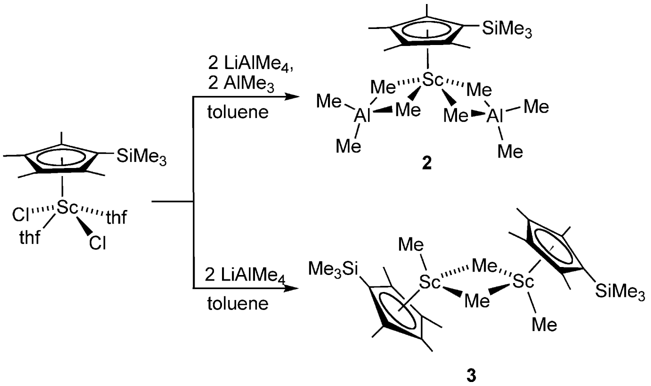
Figure 1. ORTEP view of $[Gd(\eta^5\text{-}C_5Me_4SiMe_3)\{(\mu\text{-}Me)_2(AlMe_2)\}_2]$ (**1-Gd**). Displacement ellipsoids are drawn at the 50% probability level. Only selected hydrogen atoms (all refined in their positions) are shown. Selected bond lengths [Å] and angles [°]: Gd–C13 2.704(2), Gd–C14 2.720(2), Gd–C17 2.563(2), Gd–C18 2.565(2), Gd···Al1 2.9367(9), Gd···Al2 3.1333(7), Al1–C13 2.056(2), Al1–C14 2.051(2), Al1–C15 1.9557(19), Al1–C16 1.993(2), Al2–C17 2.092(2), Al2–C18 2.077(2), Al2–C19 1.977(2), Al2–C20 1.979(2), Gd–Cp_{cent} 2.393(2), Gd···C16 3.213(2); Gd–C13–Al1 74.81(6), Gd–C14–Al1 74.49(6), C13–Al1–C14 107.66(9), C15–Al1–C16 114.42(9), Gd–C17–Al2 83.97(7), Gd–C18–Al2 84.21(7), C17–Al2–C18 108.76(8), C19–Al2–C20 115.33(9).

In contrast to the (trimethylsilyl)methyl complex $[Y(\eta^5\text{-}C_5Me_4SiMe_3)(CH_2SiMe_3)_2(thf)]$, which was reported to slowly decompose at room temperature,[7a,9] complexes **1-Ln** could all be isolated as thermally robust microcrystals in excellent yields and high purity. In addition, the yttrium complex **1-Y** could also be characterized by $^{89}Y\{^1H\}$ NMR spectroscopy in [D$_6$]benzene and [D$_8$]thf, showing singlets at δ = 171.5 and 312.6 ppm, respectively. The strong difference in chemical shifts obtained in deuterated benzene and thf stems from the nature of the species present in solution: whilst the structure of complex **1-Y** is maintained in benzene, the aluminate moieties are split by thf with formation of the dimethyl complex $[Y(\eta^5\text{-}C_5Me_4SiMe_3)Me_2(thf)_n]$ along with the trimethylaluminum adduct $[AlMe_3(thf)]$.[8d,10–12]

Complex **1-Gd** could not be characterized by NMR spectroscopy due to paramagnetism of the metal ion. Diffraction-quality crystals were grown from a saturated pentane solution (Figure 1). As was observed in $[La(\eta^5\text{-}C_5Me_5)\{(\mu\text{-}Me)_2(AlMe_2)\}_2]$[8d] or, to a lesser extent, in $[Lu(\eta^5\text{-}C_5Me_5)\{(\mu\text{-}Me)_2(AlMe_2)\}_2]$,[8b] the two $AlMe_4$ groups in **1-Gd** display a rather different coordination mode (Figure 1).

Whilst one $AlMe_4$ moiety (Al2, C17, C18, C19 and C20) coordinates the metal center in a classical η^2 fashion with an almost planar $Ln(\mu\text{-}Me)_2Al$ skeleton [torsion angle Ln–C–Al–C: Ln = La: 3.0°;[8d] Gd: 3.91(6)°; Lu: 6°[8b]], the second aluminate moiety (Al1, C13, C14, C15 and C16) is strongly distorted towards an η^3 coordination mode with rather small Ln–C–Al angles [torsion angle Ln–C–Al–C: Ln = La: 47.3°;[8d] Gd: 45.55(8)°; Lu: 28°[8b]] and a short Ln···C contact between the metal center and the carbon atom of a terminal methyl group [Ln = La: 3.140(3) Å;[8d] Gd: 3.213(2) Å; Lu: 3.447 Å[8b]]. It appears that the bending of the aluminate group and the length of the additional Ln···C contact vary proportionally to the ionic radius of the metal center: the larger the metal atom, the smaller the Ln–C–Al angles and the shorter the Ln···C agostic contact.

In order to access the scandium analogue $[Sc(\eta^5\text{-}C_5Me_4SiMe_3)\{(\mu\text{-}Me)_2(AlMe_2)\}_2]$, attempts to synthesize the neutral precursor $[Sc\{(\mu\text{-}Me)_2(AlMe_2)\}_3]$ were undertaken.[13] Reaction of $ScCl_3$ with 3 equiv. of $[Li(AlMe_4)]$ in non-coordinating solvents such as CH_2Cl_2, toluene, or hexamethyldisiloxane all failed to provide the desired product. An alternative method was found by employing the pentane-soluble half-sandwich dichlorido complex $[Sc(\eta^5\text{-}C_5Me_4SiMe_3)Cl_2(thf)_2]$, easily synthesized from $ScCl_3$ and $[Li(C_5Me_4SiMe_3)]$ in thf.[14] Reaction of the dichlorido precursor with 2 equiv. of $[Li(AlMe_4)]$ and 2 equiv. of $[AlMe_3]$ in toluene yielded a red oil whose NMR spectroscopic data fit with the formula $[Sc(\eta^5\text{-}C_5Me_4SiMe_3)\{(\mu\text{-}Me)_2(AlMe_2)\}_2]$ (**2**) (Scheme 2).



Scheme 2.

A broad signal typical for the $AlMe_4$ moiety is observed in the ^1H NMR spectrum at δ = –0.39 ppm in [D$_6$]benzene. The compound could, however, not be isolated in pure form. The presence of $[AlMe_3]$ is required to trap the two thf molecules coordinated in $[Sc(\eta^5\text{-}C_5Me_4SiMe_3)Cl_2(thf)_2]$. This quantity of thf would be sufficient to induce the splitting of both $AlMe_3$ moieties in **2**. If the same reaction is carried in the absence of $[AlMe_3]$, a product of formula $[Sc(\eta^5\text{-}C_5Me_4SiMe_3)Me_2]_n$ (**3**) is isolated as crystalline material from pentane. The ^1H NMR spectrum of **3** in [D$_6$]benzene displays the three-signal pattern for the C_5Me_4-

$SiMe_3$ ring and a sharp singlet at $\delta = 0.13$ ppm for the two methyl groups at the scandium center. In addition, no coordination of thf is observed, suggesting a polynuclear structure, as was observed for $[Y(\eta^5\text{-}C_5Me_5)Me_2]_3$.[10] Mass spectrometry showed **3** to be a dimer, an intense signal being observed for $m/z = 537.4$, corresponding to the $[M - H]^+$ fragment generated from $[Sc(\eta^5\text{-}C_5Me_4SiMe_3)Me_2]_2$. Single-crystal X-ray structure determination of **3** revealed a dimeric complex of C_i symmetry in the solid state (Figure 2). A typical dimer configuration of the type *trans*-**M**[2a] with two three-legged piano-stool fragments can be recognized.[15]

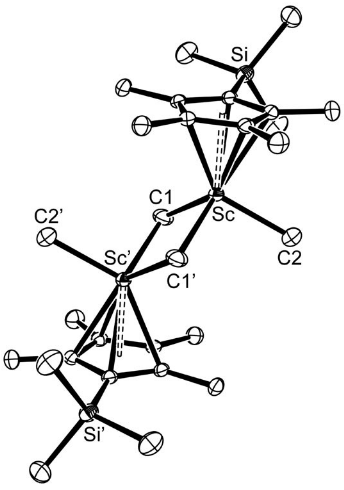


Figure 2. ORTEP view of $[Sc(\eta^5\text{-}C_5Me_4SiMe_3)Me(\mu\text{-}Me)]_2$ (**3**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Primed atoms are related to the unprimed ones by a center of inversion located in the center of the Sc–C1–Sc′–C1′ ring. Selected bond lengths [Å] and angles [°]: Sc–C1 2.3129(15), Sc–C2 2.1982(15), Sc–C1′ 2.3415(16); Sc–Cp_{cent} 2.152, Sc···Sc′ 3.1392(5); Cp_{cent}–Sc–C1 122.97(15), Cp_{cent}–Sc–C2 117.45(15), Cp_{cent}–Sc–C1′ 114.61(15), C1–Sc–C2 103.38(6), C2–Sc–C1′ 98.61(6), C1–Sc–C1′ 95.18(5).

The Sc–C bond of the bridging methyl group is longer than that of the terminal one by more than 0.11 Å [Sc–C1 2.3129(15) Å and Sc–C2 2.1982(15) Å], whereas an even longer contact is established with the methyl group belonging to the other half of the molecule [Sc–C1′ 2.3415(16) Å]. The bond length to the terminal methyl group is in the range of commonly observed values, such as in $[Sc(\eta^5\text{-}C_5Me_5)Me_2(tBu_3P{=}O)]$ [2.251(2) Å and 2.252(2) Å][16] or in neutral "nacnac" complexes where contacts of 2.225 Å on average are observed.[17]

As ^1H NMR spectroscopic data in $[D_6]$benzene revealed only one signal for two equivalent methyl groups, the dimeric nature of **3** must be lost in solution where the compounds only exists as a monomeric species with C_s symmetry. Alternatively, a fast exchange of the bridging and terminal methyl groups on the NMR timescale might explain the presence of a single signal for the two different methyl moieties.

Cationic Mono(cyclopentadienyl) Methyl Complexes

The ease with which the $[Ln(\mu\text{-}Me)_2(AlMe_2)]$ moiety can be dissociated into $[AlMe_3]$ and an [Ln–Me] fragment in the presence of donor solvent such as diethyl ether, thf, or pyridine makes it useful as synthon for the trimethyl complex.[10,11] We have established that the homoleptic rare-earth aluminates $[Ln\{(\mu\text{-}Me)_2(AlMe_2)\}_3]$ cleanly react in thf with either 1 equiv. of $[NEt_3H]^+[BPh_4]^-$ to yield the monocationic dimethyl complex $[LnMe_2(thf)_n]^+[BPh_4]^-$ or with 2 equiv. of $[NEt_3H]^+[BPh_4]^-$ to generate the dicationic monomethyl complex $[LnMe(thf)_n]^{2+}[BPh_4]^-{}_2$.[3a,3b,18] Applying this protonolytic methodology to compounds **1-Y**, **1-La**, **1-Nd**, **1-Sm**, and **1-Lu** enabled easy access to cationic half-sandwich compounds **4-Ln**.

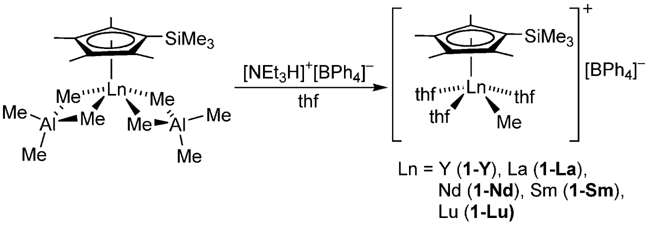
Upon treatment of the neutral complexes **1-Ln** with a substochiometric amount of the Brønsted acid $[NEt_3H]^+$-$[BPh_4]^-$ in thf, the monocationic derivatives $[Ln(\eta^5\text{-}C_5Me_4\text{-}SiMe_3)Me(thf)_3]^+[BPh_4]^-$ [Ln = Y (**4-Y**), La (**4-La**), Nd (**4-**

Table 1. Structurally characterized cationic methyl complexes of the rare-earth metals.

Compound	Ln–Me [Å]	Ref.
$[Y(\eta^5\text{-}C_5Me_4SiMe_3)Me(thf)_3]^+[BPh_4]^-$ (**4-Y**)	2.374(3)	this work
$[Sm(\eta^5\text{-}C_5Me_4SiMe_3)Me(thf)_3]^+[BPh_4]^-$ (**4-Sm**)	2.406(5)	this work
$[Lu(\eta^5\text{-}C_5Me_4SiMe_3)Me(thf)_3]^+[BPh_4]^-$ (**4-Lu**)	2.331(4)	this work
trans-$[YMe_2(thf)_5]^+[BPh_4]^-$	2.526(2)/2.508(2)	[18]
$[YMe_2(12\text{-crown-}4)(thf)]^+[BPh_4]^-$	2.438(2)/2.443(2)	[18]
cis-$[LuMe_2(thf)_5]^+[BPh_4]^-$	2.343(3)/2.347(3)	[18]
$[Sc(\eta^5\text{-}C_5Me_5)Me(tBu_3P{=}O)(\mu\text{-}Me)B(C_6F_5)_3]$	2.201(2)/2.529(11)[a]	[16]
$[Sc(nacnac)Me(\mu\text{-}Me)B(C_6F_5)_3]$[b]	2.221(5)/2.703(6)[a]	[20a]
$[Sc(nacnac')(C_6F_5)(\mu\text{-}Me)B(C_6F_5)_3]$[c]	2.699(4)	[20c]
$[Sc(nacnac)(R)(\mu\text{-}Me)B(C_6F_5)_3]$[b,d]	2.499(2)	[20c]
$[Sc(nacnac)(NH^tBu)(\mu\text{-}Me)B(C_6F_5)_3]$[b]	2.521(3)/2.537(3)[e]	[20d]
$[Sc(nacnac')Me(\eta^6\text{-}C_6X_5Br)]^+[B(C_6F_5)_4]^-$[c,f]	2.162(5)	[20b,20e]
$[Sc(nacnac')Me(\eta^6\text{-}C_6H_5CH_3)]^+[B(C_6F_5)_4]^-$[c]	2.186(4)	[20e]
$[Sc(nacnac')Me(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)]^+[B(C_6F_5)_4]^-$[c]	2.212(4)	[20e]
$[Sc(nacnac)Me(\mu\text{-}H)BMe(C_6F_5)_2]$[b]	2.193(3)	[20f]

[a] First value for the terminal methyl group, second value for the bridging one. [b] nacnac = η^3-ArNC(tBu)CHC(tBu)NAr; Ar = $C_6H_3iPr_2$-2,6. [c] nacnac′ = η^3-ArNC(Me)CHC(Me)NAr; Ar = $C_6H_3iPr_2$-2,6. [d] R = $CH_2SiMe_2CH_2SiMe_3$. [e] Value for each of the two crystallographically independent molecules in the unit cell. [f] X = H, D.

Nd), Sm (**4-Sm**), Lu (**4-Lu**)] were isolated in good yields and high purity as thermally robust thf-supported monocations (Scheme 3).



Scheme 3.

Apart from the series of thf-supported monocationic dimethyl and dicationic monomethyl complexes $[LnMe_2(thf)_x]^+[BPh_4]^-$ and $[LnMe(thf)_y]^{2+}[BPh_4]^-_2$,[18] only few rare-earth cationic methyl complexes bearing non-cyclopentadienyl ligands are known, bulky substituents such as neutral macrocycles[19] or β-diketiminato ligands[20] being required for their stabilization (Table 1). So far, the only reported cationic half-sandwich methyl complex is the crystallographically characterized scandium complex $[Sc(\eta^5\text{-}C_5Me_5)Me(t\text{Bu}_3P{=}O)(\mu\text{-}Me)B(C_6F_5)_3]$ reported by Piers et al. as a contact ion pair.[16,21] Complexes **4-Ln** are the first examples of charge-separated cationic half-sandwich methyl complexes.

Crystals suitable for X-ray diffraction analysis could be obtained for the three complexes **4-Y**, **4-Sm** and **4-Lu** from saturated thf solutions. Representative bond lengths and angles are given in Table 2. Despite the large ionic radius difference of 10 pm (CN = 6) between lutetium and samarium,[22] the three compounds show all a coordination number of five and adopt a distorted square-pyramidal geometry (Figures 3 and 4).

The arrangement of the three thf molecules and the methyl group in the base plane of the structure is very similar in all three products. However, the SiMe$_3$ group at the cyclopentadienyl ligand is found in two different positions. It is found above the portion of the plane defined by O1, Ln and O2 in **4-Y** and **4-Sm** (which crystallize isotypically), inducing enlarged Cp$_{cent}$–Ln–O angles with the thf molecule nearest to the SiMe$_3$ group in **4-Y** and **4-Sm** [Cp$_{cent}$–Y–O2 127.92(8)°, cf. 114° mean in **4-Y**; Cp$_{cent}$–Sm–O2 131.56(15)°, cf. 114° mean in **4-Sm**). In **4-Lu**, it is found above the portion of the plane defined by C1 and O3. As a result of the reduced steric hindrance around the methyl group, no particular influence of the SiMe$_3$ group on the geometry of the structure can be seen in **4-Lu**, where similar Cp$_{cent}$–Lu–X angles (X = Me, thf) are observed. The Ln–Me bonds are rather short compared to those reported in the literature (Table 1), indicating a tighter bonding of the methyl group to the cationic metal center.

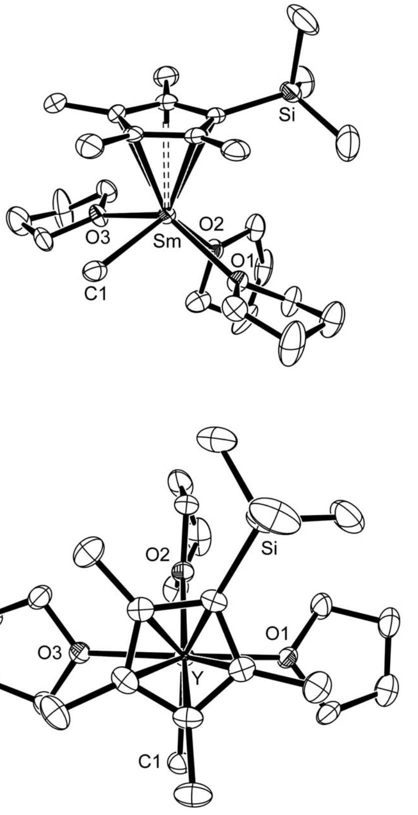


Figure 3. ORTEP view of the cationic part of $[Sm(\eta^5\text{-}C_5Me_4SiMe_3)Me(thf)_3]^+[BPh_4]^-$ (**4-Sm**) (top) and top view of the cationic part of $[Y(\eta^5\text{-}C_5Me_4SiMe_3)Me(thf)_3]^+[BPh_4]^-$ (**4-Y**) (bottom). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths [Å] and angles [°] for complexes **4-Y**, **4-Sm** and **4-Lu**.

	$[Y(\eta^5\text{-}C_5Me_4SiMe_3)Me(thf)_3]^+[BPh_4]^-$ (**4-Y**)	$[Sm(\eta^5\text{-}C_5Me_4SiMe_3)Me(thf)_3]^+[BPh_4]^-$ (**4-Sm**)	$[Lu(\eta^5\text{-}C_5Me_4SiMe_3)Me(thf)_3]^+[BPh_4]^-$ (**4-Lu**)
Ln–C1	2.374(3)	2.406(5)	2.331(4)
Ln–O1	2.3757(18)	2.454(3)	2.324(3)
Ln–O2	2.3479(18)	2.435(3)	2.300(2)
Ln–O3	2.3808(18)	2.458(3)	2.356(3)
Ln–Cp$_{cent}$	2.359(3)	2.419(5)	2.314(4)
C1–Ln–O1	85.46(8)	85.42(16)	85.72(12)
O1–Ln–O2	78.22(6)	78.35(11)	77.23(9)
O2–Ln–O3	75.41(6)	75.08(11)	75.25(9)
O3–Ln–C1	83.78(8)	83.86(16)	83.67(12)
Cp$_{cent}$–Ln–C1	107.82(9)	104.94(18)	114.55(15)
Cp$_{cent}$–Ln–O1	112.23(8)	112.72(15)	108.56(12)
Cp$_{cent}$–Ln–O2	127.92(8)	131.56(15)	116.62(12)
Cp$_{cent}$–Ln–O3	108.94(8)	108.13(15)	116.60(12)

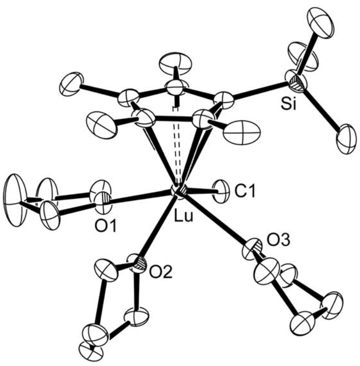


Figure 4. ORTEP view of the cationic part of [Lu(η^5-$C_5Me_4SiMe_3$)Me(thf)$_3$]$^+$[BPh_4]$^-$ (**4-Lu**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

The ^{1}H NMR spectrum of the yttrium derivative **4-Y** shows a doublet ($^2J_{YH}$ = 2.1 Hz) at δ = –0.74 ppm for the protons of the methyl group coupled with the yttrium center, and a well-resolved quartet ($^2J_{YH}$ = 2.1 Hz) is observed in the ^{1}H-coupled ^{89}Y NMR spectrum at δ = 265.3 ppm. As a result of the contribution of the positive charge at the yttrium center, this value appears to be slightly shifted to high field ($\Delta\delta$ = –47.3 ppm) compared to the value observed for the neutral complex **1-Y** (δ = 312.6 ppm in [D$_8$]thf). This observation confirms the trend initially observed in ^{89}Y NMR chemical shifts for the series of alkyl complexes [Y(CH_2SiMe_3)$_n$(thf)$_x$]$^{(3-n)+}$[BPh_4]$^-_{(3-n)}$ in which successive abstraction of the alkyl groups from the neutral tris(alkyl) complex results in upfield shifts of the resonance of δ = –223 and –251 ppm, respectively (Table 3).[3a,23] In the lutetium complex **4-Lu**, a singlet at δ = –0.72 ppm is observed for the methyl group, whereas a broad signal at δ = 7.01 ppm is detected in the samarium derivative **4-Sm**.

Table 3. ^{89}Y{^{1}H} NMR chemical shifts (ppm) for neutral, mono- and dicationic derivatives of the same series.

Compound	Shift	Solvent	Ref.
[Y(η^5-$C_5Me_4SiMe_3$){(μ-Me)$_2$($AlMe_2$)}$_2$] (**1-Y**)	171.5	[D$_6$]benzene	this work
[Y(η^5-$C_5Me_4SiMe_3$){(μ-Me)$_2$($AlMe_2$)}$_2$] (**1-Y**)	312.6	[D$_8$]thf	this work
[Y(η^5-$C_5Me_4SiMe_3$)Me(thf)$_3$]$^+$[BPh_4]$^-$ (**4-Y**)	265.3	[D$_8$]thf	this work
[Y(η^5-$C_5Me_4SiMe_3$)(thf)$_4$]$^{2+}$[BPh_4]$^-_2$	45.0	[D$_5$]pyridine	[3c]
[Y(CH_2SiMe_3)$_3$(thf)$_2$]	882.7	[D$_8$]thf	[18]
[Y(CH_2SiMe_3)$_2$(thf)$_4$]$^+$[BPh_4]$^-$	660.0	[D$_8$]thf	[18]
[Y(CH_2SiMe_3)(thf)$_5$]$^{2+}$[BPh_4]$^-_2$	409.2	[D$_5$]pyridine	[18]

Complex **4-Y** could also be synthesized in lower yield by salt elimination reaction between the dicationic methyl precursor [YMe(thf)$_6$]$^{2+}$[BPh_4]$^-_2$ and a stoichiometric amount of [K($C_5Me_4SiMe_3$)].

Polymerization of Butadiene

Upon activation with 1 equiv. of [Ph_3C]$^+$[B(C_6F_5)$_4$]$^-$ in toluene, the neutral precursors **1-La**, **1-Nd** and **1-Gd**, were found to efficiently initiate stereoselective 1,4-polymerization of butadiene in the presence of 5 equiv. of [Al*i*Bu$_3$] (Table 4). A dependence of the stereoselectivity on the ionic radius of the metal center in the catalyst was observed. Thus, mainly 1,4-*cis*-polybutadiene was obtained with **1-Gd** (Run 9). The neodymium analogue **1-Nd** gave an increased 1,4-*trans* microstructure (Run 7), and the lanthanum complex **1-La** gave high 1,4-*trans* contents (Run 3).[24] The catalytic system **1-La**/[Ph_3C]$^+$[B(C_6F_5)$_4$]$^-$ was found to be inactive at –40 °C even with a reaction time of up to 4 h. Upon addition of a second equivalent of [Ph_3C]$^+$[B(C_6F_5)$_4$]$^-$ to **1-La** or **1-Nd**, deactivation of the catalytic system was observed (Runs 6 and 8), consistent with the abstraction of both methyl groups at the metal center and formation of an inactive dicationic half-sandwich complex.[24–26] Remarkably narrow molecular-weight distributions were obtained using **1-La** (M_n/M_w = 1.05–1.09). Less control was achieved by its neutral parent complex [La{(μ-Me)$_2$-($AlMe_2$)}$_3$] (M_n/M_w = 2.45) which also afforded low-molecular-weight polymers (M_n = 7000 g mol^{-1}). In the case of the gadolinium system, going from the neutral homoleptic [Gd{(μ-Me)$_2$($AlMe_2$)}$_3$] to the half-sandwich complex **1-Gd** induces a significant increase in stereoselectivity (from 42.2 to 91.1% 1,4-*cis*). This, however, was accompanied by a loss in control of molecular-weight distributions (M_n/M_w from 3.09 to 4.24).

Table 4. 1,3-Butadiene polymerization catalyzed by complexes **1-La**, **1-Nd** and **1-Gd**, activated by [Ph_3C]$^+$[B(C_6F_5)$_4$]$^-$.[a]

Run	Complex	Activator	[BD]/[Ln]	t[b]	T[c]	Yield[d]	*cis*/*trans*/1,2[e]	M_n[f]	M_n/M_w
1	**1-La**	1	200	5	19	0	–	–	–
2	**1-La**	1	200	10	19	67	8.5/90.9/0.6	19	1.08
3	**1-La**	1	200	15	19	77	7.5/91.9/0.6	24	1.05
4[g]	**1-La**	1	1000	15	19	95	15.1/84.8/0.1	66	1.09
5	**1-La**	1	200	240	–40	0	–	–	–
6	**1-La**	2	200	15	19	11	9.4/90.1/0.5	5	1.20
7	**1-Nd**	1	200	15	19	82	69.1/30.2/0.7	28	1.20
8	**1-Nd**	2	200	15	19	0	–	–	–
9	**1-Gd**	1	200	15	19	68	91.1/8.2/0.7	49	4.24
10	**LaAl$_3$**[h]	1	200	15	19	16	16.5/83.3/0.2	7	2.45
11	**GdAl$_3$**[i]	1	200	15	19	40	42.2/57.3/0.5	23	3.09

[a] Conditions: 50 µmol of catalyst; solvent: toluene; V_{total} = 21 mL. [b] In min. [c] In °C. [d] In % (isolated polymer). [e] Determined by ^{1}H and ^{13}C NMR spectroscopy. [f] In g mol^{-1}. [g] V_{total} = 36 mL. [h] LaAl$_3$ represents [La{(μ-Me)$_2$($AlMe_2$)}$_3$]. [i] GdAl$_3$ represents [Gd{(μ-Me)$_2$($AlMe_2$)}$_3$].

Conclusions

Half-sandwich bis(aluminate) complexes [Ln(η^5-$C_5Me_4SiMe_3$){(μ-Me)$_2$($AlMe_2$)}$_2$] have been shown to be efficient precursors for the synthesis of thermally robust monocationic methyl complexes [Ln(η^5-$C_5Me_4SiMe_3$)Me(thf)$_3$]$^+$[BPh_4]$^-$ by protonolysis. The scandium bis(aluminate) [Sc(η^5-$C_5Me_4SiMe_3$){(μ-Me)$_2$($AlMe_2$)}$_2$] was obtained by salt metathesis between the dichlorido half-sandwich precursor and [Li($AlMe_4$)]. In the case of lanthanum and neodymium, activation of the neutral bis(aluminate) complexes [Ln(η^5-$C_5Me_4SiMe_3$){(μ-Me)$_2$($AlMe_2$)}$_2$] with [Ph_3C]$^+$[B(C_6F_5)$_4$]$^-$ generated active catalysts for the controlled 1,4-*trans* polymerization of 1,3-butadiene in toluene in the presence of [Al*i*Bu_3]. Thus, monocationic methyl complexes [Ln(η^5-$C_5Me_4SiMe_3$)Me(thf)$_3$]$^+$[BPh_4]$^-$ serve as functional models for rare-earth metal based 1,3-butadiene polymerization catalysts.

Experimental Section

General Remarks: All operations were performed under argon using standard Schlenk-line or glovebox techniques. The solvents thf and pentane were distilled from sodium benzophenone ketyl and sodium benzophenone ketyl triglyme, respectively; [D$_8$]thf and [D$_6$]benzene were dried with sodium and distilled prior to use; $CDCl_3$ was dried with CaH_2 and distilled prior to use. [Ln{(μ-Me)$_2$($AlMe_2$)}$_3$],[8a,27] [YMe(thf)$_6$]$^{2+}$[BPh_4]$^-{}_2$,[18] [Sc(η^5-$C_5Me_4SiMe_3$)Cl_2(thf)$_2$],[14] (C_5Me_4H)$SiMe_3$[28] and [K($C_5Me_4SiMe_3$)][29] were prepared according to literature procedures. [Li($AlMe_4$)] was prepared according to a modification of a literature procedure.[30] All other chemicals were commercially available and used after appropriate purification. NMR spectra were recorded at room temperature with a Bruker DRX 400 spectrometer (^{1}H 400.1 MHz, ^{13}C 100.6 MHz, ^{11}B 128.4 MHz, ^{89}Y 19.6 MHz) or a Varian Unity 500 spectrometer (^{1}H 499.6 MHz, ^{13}C 125.6 MHz, ^{11}B 160.3 MHz); all chemical shifts are given in ppm; chemical shifts for ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced internally using the residual solvent resonances and reported relative to $SiMe_4$; ^{11}B NMR spectra were referenced externally to a saturated solution of $NaBH_4$ in D_2O; ^{89}Y NMR spectra were referenced externally to a 1 mol L^{-1} solution of YCl_3 in H_2O.

General Polymerization Procedure: In a typical polymerization experiment, 50 µmol of the neutral mono(cyclopentadienyl) bis(aluminate) complex were dissolved in 10 mL of toluene. A fivefold excess of cocatalyst [Al*i*Bu_3] (250 µmol) was added, followed by 1 or 2 equiv. of activator [Ph_3C]$^+$[B(C_6F_5)$_4$]$^-$ (50 or 100 µmol). The resulting solution was stirred for 5 min, after which 200 equiv. of butadiene (12.8 wt.-% solution in toluene) was added. After 15 min, the reaction was quenched by pouring the polymerization mixture into 200 mL of methanol acidified with 4 mL of concentrated hydrochloric acid and containing 1 g of 2,6-di-*tert*-butylphenol as stabilisator. The precipitated polymer was isolated by decantation, washed with methanol and dried to constant weight. The microstructure of the polybutadienes was determined by ^{1}H (400.1 MHz) and ^{13}C (100.6 MHz) NMR spectroscopy in $CDCl_3$ with a Bruker DRX 400 spectrometer. The weight- and number-average molecular weights M_w and M_n were determined by GPC with an Agilent 1100 Series instrument at 35 °C in thf against polystyrene standards.

General Procedure for the Preparation of [Ln(η^5-$C_5Me_4SiMe_3$){(μ-Me)$_2$($AlMe_2$)}$_2$] (1-Ln): To a pentane solution (6 mL) of [Ln{(μ-Me)$_2$($AlMe_2$)}$_3$] was slowly added at room temperature a pentane solution (4 mL) of 1 equiv. of (C_5Me_4H)$SiMe_3$ under vigorous stirring. Gas evolution was instantaneously observed, and after stirring for 20 min, the solution was filtered. The volatiles were then removed under vacuum to leave oily products that crystallized within 1 h to yield the pure and microcrystalline compounds.

[Y(η^5-$C_5Me_4SiMe_3$){(μ-Me)$_2$($AlMe_2$)}$_2$] (1-Y): According to the general procedure, [Y{(μ-Me)$_2$($AlMe_2$)}$_3$] (700 mg, 2.0 mmol) was treated with (C_5Me_4H)$SiMe_3$ (389 mg, 2.0 mmol) to yield **1-Y** (809 mg, 89%) as a light yellow powder. ^{1}H NMR ([D$_6$]benzene): δ = –0.29 (d, $^2J_{YH}$ = 2.0 Hz, 24 H, $AlMe_4$), 0.23 (s, 9 H, $SiMe_3$), 1.74 (s, 6 H, C_5Me_4), 1.99 (s, 6 H, C_5Me_4) ppm. ^{13}C{^{1}H} NMR ([D$_6$]benzene): δ = 0.31 (br., $AlMe_4$), 2.16 ($SiMe_3$), 12.06 (C_5*Me*$_4$), 14.97 (C_5*Me*$_4$), 119.00 ($C_5Me_4SiMe_3$, C bonded to $SiMe_3$), 127.82 ($C_5Me_4SiMe_3$, C bonded to Me_4), 131.46 ($C_5Me_4SiMe_3$, C bonded to Me_4) ppm. ^{89}Y{^{1}H} NMR ([D$_6$]benzene): δ = 171.5 ppm. ^{89}Y{^{1}H} NMR ([D$_8$]thf): δ = 312.6 ppm. $C_{20}H_{45}Al_2SiY$ (456.52): calcd. C 52.62, H 9.94; found C 52.18, H 9.71.

[La(η^5-$C_5Me_4SiMe_3$){(μ-Me)$_2$($AlMe_2$)}$_2$] (1-La): According to the general procedure, [La{(μ-Me)$_2$($AlMe_2$)}$_3$] (600 mg, 1.5 mmol) was treated with (C_5Me_4H)$SiMe_3$ (292 mg, 1.5 mmol) to yield **1-La** (722 mg, 95%) as a light yellow powder. ^{1}H NMR ([D$_6$]benzene): δ = –0.25 (s, 24 H, $AlMe_4$), 0.24 (s, 9 H, $SiMe_3$), 1.81 (s, 6 H, C_5Me_4), 2.09 (s, 6 H, C_5Me_4) ppm. ^{13}C{^{1}H} NMR ([D$_6$]benzene): δ = 2.18 ($SiMe_3$), 2.36 (br., $AlMe_4$), 11.83 (C_5*Me*$_4$), 14.97 (C_5*Me*$_4$), 122.83 ($C_5Me_4SiMe_3$, C bonded to $SiMe_3$), 130.21 ($C_5Me_4SiMe_3$, C bonded to Me_4), 134.01 ($C_5Me_4SiMe_3$, C bonded to Me_4) ppm. $C_{20}H_{45}Al_2LaSi$ (506.53): calcd. C 47.42, H 8.95; found C 47.44, H 9.04.

[Nd(η^5-$C_5Me_4SiMe_3$){(μ-Me)$_2$($AlMe_2$)}$_2$] (1-Nd): According to the general procedure, [Nd{(μ-Me)$_2$($AlMe_2$)}$_3$] (608 mg, 1.5 mmol) was treated with $HC_5Me_4SiMe_3$ (292 mg, 1.5 mmol) to yield **1-Nd** (660 mg, 86%) as a light blue powder. ^{1}H NMR ([D$_6$]benzene): δ = –3.03 (br. s, 9 H, $SiMe_3$), 5.24 (br. s, 24 H, $AlMe_4$), 8.83 (br. s, 6 H, C_5Me_4), 14.61 (br. s, 6 H, C_5Me_4) ppm. ^{13}C{^{1}H} NMR ([D$_6$]benzene): δ = –20.05 (C_5*Me*$_4$), –10.71 (C_5*Me*$_4$), 8.95 ($SiMe_3$), 232.57 (br., $AlMe_4$), 237.72 ($C_5Me_4SiMe_3$, C bonded to Me_4), 254.15 ($C_5Me_4SiMe_3$, C bonded to Me_4) ppm. The signal for the carbon atom bonded to the $SiMe_3$ group was not detected. $C_{20}H_{45}Al_2NdSi$ (511.86): calcd. C 46.93, H 8.86; found C 45.36, H 8.92.

[Sm(η^5-$C_5Me_4SiMe_3$){(μ-Me)$_2$($AlMe_2$)}$_2$] (1-Sm): According to the general procedure, [Sm{(μ-Me)$_2$($AlMe_2$)}$_3$] (412 mg, 1.0 mmol) was treated with (C_5Me_4H)$SiMe_3$ (195 mg, 1.0 mmol) to yield **1-Sm** (503 mg, 97%) as a deep red powder. ^{1}H NMR ([D$_6$]benzene): δ = –3.14 (br. s, 24 H, $AlMe_4$), –0.64 (s, 9 H, $SiMe_3$), –0.13 (s, 6 H, C_5*Me*$_4$), 2.69 (s, 6 H, C_5*Me*$_4$) ppm. ^{13}C{^{1}H} NMR ([D$_6$]benzene): δ = –19.53 (br., $AlMe_4$), 0.47 ($SiMe_3$), 14.92 (C_5*Me*$_4$), 21.65 (C_5*Me*$_4$), 110.71 ($C_5Me_4SiMe_3$, C bonded to $SiMe_3$), 122.27 ($C_5Me_4SiMe_3$, C bonded to Me_4), 129.57 ($C_5Me_4SiMe_3$, C bonded to Me_4) ppm. $C_{20}H_{45}Al_2SiSm$ (518.01): calcd. C 46.37, H 8.76; found C 45.83, H 8.92.

[Gd(η^5-$C_5Me_4SiMe_3$){(μ-Me)$_2$($AlMe_2$)}$_2$] (1-Gd): According to the general procedure, [Gd{(μ-Me)$_2$($AlMe_2$)}$_3$] (418 mg, 1.0 mmol) was treated with (C_5Me_4H)$SiMe_3$ (195 mg, 1.0 mmol) to yield **1-Gd** (427 mg, 82%) as a white powder. Crystals suitable for X-ray diffraction were grown from a saturated pentane solution at –35 °C. Due to the paramagnetism of the gadolinium center, no NMR spectroscopic data could be obtained for this compound.

$C_{20}H_{45}Al_2GdSi$ (524.87): calcd. C 45.77, H 8.64; found C 45.21, H 9.16.

[Lu(η^5-C$_5$Me$_4$SiMe$_3$){(μ-Me)$_2$(AlMe$_2$)}$_2$] (1-Lu): According to the general procedure, [Lu{(μ-Me)$_2$(AlMe$_2$)}$_3$] (655 mg, 1.5 mmol) was treated with (C$_5$Me$_4$H)SiMe$_3$ (292 mg, 1.5 mmol) to yield **1-Lu** (622 mg, 76%) as a pale yellow powder. ^{1}H NMR ([D$_6$]benzene): δ = –0.13 (s, 24 H, AlMe$_4$), 0.23 (s, 9 H, SiMe$_3$), 1.77 (s, 6 H, C$_5$Me$_4$), 2.01 (s, 6 H, C$_5$Me$_4$) ppm. ^{13}C{^{1}H} NMR ([D$_6$]benzene): δ = 1.69 (br. s, AlMe$_4$), 2.16 (SiMe$_3$), 12.02 (C$_5$*Me*$_4$), 14.85 (C$_5$*Me*$_4$), 117.45 (C$_5$Me$_4$SiMe$_3$, C bonded to SiMe$_3$), 126.53 (C$_5$Me$_4$SiMe$_3$, C bonded to Me$_4$), 130.10 (C$_5$Me$_4$SiMe$_3$, C bonded to Me$_4$) ppm. $C_{20}H_{45}Al_2LuSi$ (542.59): calcd. C 44.27, H 8.36; found C 43.54, H 8.23.

[Sc(η^5-C$_5$Me$_4$SiMe$_3$){(μ-Me)$_2$(AlMe$_2$)}$_2$] (2): To a toluene suspension (3 mL) of [Li(AlMe$_4$)] (188 mg, 2.00 mmol) and [AlMe$_3$] (144 mg, 2.00 mmol) was slowly added at room temperature a toluene solution (5 mL) of [Sc(η^5-C$_5$Me$_4$SiMe$_3$)Cl$_2$(thf)$_2$] (453 mg, 1 mmol). After stirring overnight, the mixture was filtered and dried under vacuum to afford an orange oil. ^{1}H NMR ([D$_6$]benzene): δ = –0.39 (br. s, 24 H, AlMe$_4$), 0.28 (s, 9 H, SiMe$_3$), 1.78 (s, 6 H, C$_5$Me$_4$), 2.11 (s, 6 H, C$_5$Me$_4$) ppm.

[Sc(η^5-C$_5$Me$_4$SiMe$_3$)Me(μ-Me)]$_2$ (3): To a toluene suspension (3 mL) of [Li(AlMe$_4$)] (193 mg, 2.05 mmol) was slowly added at room temperature a toluene solution (5 mL) of [Sc(η^5-C$_5$Me$_4$SiMe$_3$)Cl$_2$(thf)$_2$] (453 mg, 1.0 mmol). After stirring overnight, the mixture was filtered, dried under vacuum, and the resulting pale yellow solid extracted with pentane (2 × 4 mL). After filtration, the clear solution was stored at –40 °C. The product (180 mg, 44%) could be isolated as single crystals within a few hours. ^{1}H NMR ([D$_6$]benzene): δ = 0.13 (s, 6 H, ScMe), 0.36 (s, 9 H, SiMe$_3$), 1.89 (s, 6 H, C$_5$Me$_4$), 2.25 (s, 6 H, C$_5$Me$_4$) ppm. ^{13}C{^{1}H} NMR ([D$_6$]benzene): δ = 2.13 (SiMe$_3$), 11.62 (C$_5$*Me*$_4$), 15.13 (C$_5$*Me*$_4$), 120.18 (C$_5$Me$_4$SiMe$_3$, C bonded to SiMe$_3$), 126.31 (C$_5$Me$_4$SiMe$_3$, C bonded to Me$_4$), 130.58 (C$_5$Me$_4$SiMe$_3$, C bonded to Me$_4$) ppm. $C_{28}H_{54}Sc_2Si_2$ (536.82): calcd. C 62.65, H 10.14; found C 60.49, H 9.60.

General Procedure for the Preparation of [Ln(η^5-C$_5$Me$_4$SiMe$_3$)Me(thf)$_3$]$^+$[BPh$_4$]$^–$ (4-Ln) by Protonolysis: To a thf solution of [Ln(η^5-C$_5$Me$_4$SiMe$_3$){(μ-Me)$_2$(AlMe$_2$)}$_2$] (**1-Ln**) was slowly added at –35 °C a thf solution of [NEt$_3$H]$^+$[BPh$_4$]$^–$ under vigorous stirring. After the addition, the clear solution was warmed up to room temperature and stirred for 30 min. The volatiles were then removed under vacuum. Washing the oily residue with pentane (3 × 10 mL) and drying afforded the desired compound as microcrystalline solid.

[Y(η^5-C$_5$Me$_4$SiMe$_3$)Me(thf)$_3$]$^+$[BPh$_4$]$^–$ (4-Y). By Protonolysis: According to the general procedure, **1-Y** (809 mg, 1.77 mmol) in thf (15 mL) was treated with a thf solution (15 mL) of [NEt$_3$H]$^+$[BPh$_4$]$^–$ (709 mg, 1.68 mmol) to afford **4-Y** as an off-white powder (1335 mg, 95%). Crystals suitable for X-ray diffraction were obtained by cooling a saturated thf solution of **4-Y** to –35 °C. ^{1}H NMR ([D$_8$]thf): δ = –0.74 (d, $^2J_{YH}$ = 2.13 Hz, 3 H, YMe), 0.30 (s, 9 H, SiMe$_3$), 1.77 (m, 12 H, β-CH$_2$, thf), 1.99 (s, 6 H, C$_5$Me$_4$), 2.13 (s, 6 H, C$_5$Me$_4$), 3.62 (m, 12 H, α-CH$_2$, thf), 6.73 (t, $^3J_{HH}$ = 7.3 Hz, 4 H, Ph-4), 6.87 (t, $^3J_{HH}$ = 7.3 Hz, 8 H, Ph-3), 7.27 (br. m, 8 H, Ph-2) ppm. ^{13}C{^{1}H} NMR ([D$_8$]thf): δ = 2.35 (SiMe$_3$), 11.35 (C$_5$*Me*$_4$), 14.19 (C$_5$*Me*$_4$), 26.16 (β-CH$_2$, thf), 26.6 (d, $^1J_{YC}$ = 55.8 Hz, YMe), 68.21 (α-CH$_2$, thf), 110.97 (C$_5$Me$_4$SiMe$_3$, C bonded to SiMe$_3$), 121.85 (Ph-4), 125.08 (C$_5$Me$_4$SiMe$_3$, C bonded to Me$_4$), 129.57 (C$_5$Me$_4$SiMe$_3$, C bonded to Me$_4$), 125.69 (Ph-3), 137.11 (Ph-2), 165.20 (q, $^1J_{BC}$ = 49.4 Hz, Ph-1) ppm. ^{11}B{^{1}H} NMR ([D$_8$]thf): δ = –6.57 ppm. ^{89}Y NMR ([D$_8$]thf): δ = 265.3 (q, $^2J_{YH}$ = 2.10 Hz) ppm. $C_{49}H_{68}BO_3SiY$ (832.87): calcd. C 70.66, H 8.23, Y 10.67; found C 70.00, H 8.36, Y 10.45. **By Salt Metathesis:** To a thf suspension (3 mL) of [YMe(thf)$_6$]$^{2+}$[BPh$_4$]$^–_2$ (235 mg, 0.2 mmol) at –35 °C was added a thf suspension (3 mL) of [K(C$_5$Me$_4$SiMe$_3$)] (56 mg, 0.24 mmol). After completion of the addition, the suspension was warmed up to room temperature, stirred for 2 h, and filtered. The volatiles were removed under vacuum, the resulting solid washed with pentane (2 × 10 mL) and dried under vacuum to give **4-Y** (92 mg, 69%) as an off-white solid. ^{1}H, ^{13}C and ^{11}B NMR spectroscopic data matched those obtained for the product isolated by protonolysis.

[La(η^5-C$_5$Me$_4$SiMe$_3$)Me(thf)$_3$]$^+$[BPh$_4$]$^–$ (4-La): According to the general procedure, **1-La** (101 mg, 0.2 mmol) in thf (3 mL) was treated with a thf solution (3 mL) of [NEt$_3$H]$^+$[BPh$_4$]$^–$ (76 mg, 0.18 mmol) to afford **4-La** as a yellow powder (120 mg, 76%). ^{1}H NMR ([D$_8$]thf): δ = –0.61 (s, 3 H, LaMe), 0.27 (s, 9 H, SiMe$_3$), 1.77 (m, 12 H, β-CH$_2$, thf), 1.97 (s, 6 H, C$_5$Me$_4$), 2.13 (s, 6 H, C$_5$Me$_4$), 3.62 (m, 12 H, α-CH$_2$, thf), 6.72 (t, $^3J_{HH}$ = 7.3 Hz, 4 H, Ph-4), 6.86 (t, $^3J_{HH}$ = 7.3 Hz, 8 H, Ph-3), 7.27 (br. m, 8 H, Ph-2) ppm. ^{13}C{^{1}H} NMR ([D$_8$]thf): δ = 2.86 (SiMe$_3$), 11.64 (C$_5$*Me*$_4$), 14.69 (C$_5$*Me*$_4$), 26.37 (β-CH$_2$, thf), 68.22 (α-CH$_2$, thf), 117.95 (C$_5$Me$_4$SiMe$_3$, C bonded to SiMe$_3$), 121.63 (Ph-4), 125.69 (Ph-3), 126.20 (C$_5$Me$_4$SiMe$_3$, C bonded to Me$_4$), 130.05 (C$_5$Me$_4$SiMe$_3$, C bonded to Me$_4$), 137.10 (Ph-2), 165.12 (q, $^1J_{BC}$ = 49.4 Hz, Ph-1) ppm. The signal of the carbon atom of the methyl group bonded to the lanthanum center could not be located. ^{11}B{^{1}H} NMR ([D$_8$]thf): δ = –6.56 ppm. $C_{49}H_{68}BLaO_3Si$ (882.88): calcd. C 66.66, H 7.76; found C 65.55, H 6.98.

[Nd(η^5-C$_5$Me$_4$SiMe$_3$)Me(thf)$_3$]$^+$[BPh$_4$]$^–$ (4-Nd): According to the general procedure, **1-Nd** (103 mg, 0.20 mmol) in thf (3 mL) was treated with a thf solution (3 mL) of [NEt$_3$H]$^+$[BPh$_4$]$^–$ (76 mg, 0.18 mmol) to afford **4-Nd** as a pale green powder (125 mg, 78%). ^{1}H NMR ([D$_8$]thf): δ = 0.26 (br. s, 9 H, SiMe$_3$), 1.74 (br. s, 12 H, β-CH$_2$, thf), 3.43 (br. s, 6 H, C$_5$Me$_4$), 3.53 (br. s, 12 H, α-CH$_2$, thf), 6.57 (br. s, 12 H, Ph-3 + Ph-4), 6.73 (br. s, 8 H, Ph-2), 12.48 (br. s, 6 H, C$_5$Me$_4$) ppm. The signal of the methyl group bonded to the neodymium center was not detected. ^{13}C{^{1}H} NMR ([D$_8$]thf): δ = –19.93 (C$_5$*Me*$_4$), –11.03 (C$_5$*Me*$_4$), 10.69 (SiMe$_3$), 26.61 (β-CH$_2$, thf), 68.26 (α-CH$_2$, thf), 121.77 (Ph-4), 125.51 (Ph-3), 136.82 (Ph-2), 164.82 (q, $^1J_{BC}$ = 49.6 Hz, Ph-1), 203.98 (br., C$_5$Me$_4$SiMe$_3$, C bonded to Me$_4$), 214.53 (br., C$_5$Me$_4$SiMe$_3$, C bonded to Me$_4$), 251.34 (C$_5$Me$_4$SiMe$_3$, C bonded to SiMe$_3$) ppm. The signal of the carbon atom of the methyl group bonded to the neodymium center was not detected. ^{11}B{^{1}H} NMR ([D$_8$]thf): δ = –7.00 ppm. $C_{49}H_{68}BNdO_3Si$ (888.21): calcd. C 66.26, H 7.72; found C 65.97, H 7.33.

[Sm(η^5-C$_5$Me$_4$SiMe$_3$)Me(thf)$_3$]$^+$[BPh$_4$]$^–$ (4-Sm): According to the general procedure, **1-Sm** (104 mg, 0.20 mmol) in thf (3 mL) was treated with a thf solution (3 mL) of [NEt$_3$H]$^+$[BPh$_4$]$^–$ (76 mg, 0.18 mmol) to afford **4-Sm** as a pink powder (94 mg, 58%). Crystals suitable for X-ray diffraction were obtained by cooling a saturated thf solution of **4-Sm** to 6 °C. ^{1}H NMR ([D$_8$]thf): δ = 0.11 (s, 9 H, SiMe$_3$), 1.19 (s, 6 H, C$_5$Me$_4$), 1.81 (s, 6 H, C$_5$Me$_4$), 1.78 (m, 12 H, β-CH$_2$, thf), 3.62 (m, 12 H, α-CH$_2$, thf), 6.73 (t, $^3J_{HH}$ = 7.3 Hz, 4 H, Ph-4), 6.86 (t, $^3J_{HH}$ = 7.3 Hz, 8 H, Ph-3), 7.01 (br. s, 3 H, SmMe), 7.25 (br. m, 8 H, Ph-2) ppm. ^{13}C{^{1}H} NMR ([D$_8$]thf): δ = 1.80 (SiMe$_3$), 15.56 (C$_5$*Me*$_4$), 17.52 (C$_5$*Me*$_4$), 26.33 (β-CH$_2$, thf), 68.22 (α-CH$_2$, thf), 106.67 (C$_5$Me$_4$SiMe$_3$, C bonded to SiMe$_3$), 121.84 (Ph-4), 123.29 (C$_5$Me$_4$SiMe$_3$, C bonded to Me$_4$), 125.35 (C$_5$Me$_4$SiMe$_3$, C bonded to Me$_4$), 125.65 (Ph-3), 137.08 (Ph-2), 165.10 (q, $^1J_{BC}$ = 49.3 Hz, Ph-1) ppm. The signal of the carbon atom of the mehyl group bonded to the samarium center

Table 5. Crystallographic and data-collection parameters for compounds **1-Gd**, **3**, **4-Y**, **4-Sm**, and **4-Lu**.

	1-Gd	**3**	**4-Y**	**4-Sm**	**4-Lu**
Empirical formula	$C_{20}H_{45}Al_2GdSi$	$C_{14}H_{27}ScSi$	$C_{49}H_{68}BO_3SiY{\cdot}(C_4H_8O)$	$C_{49}H_{68}BO_3SiSm{\cdot}(C_4H_8O)$	$C_{49}H_{68}BLuO_3Si{\cdot}0.5(C_4H_8O)$
M_r	524.86	268.41	904.95	966.39	956.20
Crystal size [mm]	0.54 × 0.32 × 0.24	0.30 × 0.30 × 0.10	0.40 × 0.32 × 0.30	0.14 × 0.13 × 0.11	0.30 × 0.13 × 0.06
Crystal color and habit	colorless block	colorless block	colorless block	orange block	colorless fragment
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$C2/c$
a [Å]	10.189(3)	11.4405(11)	10.9037(7)	10.8822(6)	27.687(2)
b [Å]	13.439(3)	8.4494(8)	37.922(2)	37.917(2)	24.6089(19)
c [Å]	19.217(5)	16.3691(16)	11.9130(8)	11.9654(7)	16.4669(13)
α [°]	90	90	90	90	90
β [°]	105.021(4)	93.9675(14)	93.1600(10)	93.6190(10)	123.4570(11)
γ [°]	90	90	90	90	90
V [Å^3]	2541.5(11)	1578.5(3)	4918.4(6)	4927.3(5)	9360.6(12)
Z	4	4	4	4	8/2
$D_{\text{calcd.}}$ [g cm^{-3}]	1.372	1.129	1.222	1.303	1.357
T [K]	130(2)	130(2)	130(2)	110(2)	130(2)
μ(Mo-K_α) [mm^{-1}]	2.727	0.519	1.253	1.259	2.176
F(000)	1076	584	1936	2028	3975
θ range [°]	1.87–28.30	2.25–30.75	2.15–24.66	2.35–21.29	2.22–23.80
Number of reflections collected	22467	23073	73877	36560	52036
Number of reflections observed [$I > 2\sigma(I)$]	5899	3752	9911	4693	9945
Number of independent reflections (R_{int})	6301 (0.0316)	4701 (0.0454)	14467 (0.0688)	5455 (0.0858)	13650 (0.0724)
Data/restraints/parameters	6301/0/277	4701/0/176	14467/0/514	5455/2/544	13650/0/525
Goodness-of-fit on F^2	1.037	0.950	1.045	1.042	1.033
R_1, wR_2 [$I > 2\sigma(I)$]	0.0192, 0.0481	0.0335, 0.0813	0.0551, 0.1291	0.0376, 0.0820	0.0476, 0.0907
R_1, wR_2 (all data)	0.0213, 0.0490	0.0438, 0.0842	0.0966, 0.1462	0.0468, 0.0859	0.0777, 0.1015
Largest difference in peak and hole [e Å^{-3}]	0.739 and –1.279	0.485 and –0.273	1.033 and –0.674	0.891 and –0.597	0.1893 and –0.794

was not detected. $^{11}B\{^1H\}$ NMR ([D$_8$]thf): δ = –6.59 ppm. $C_{49}H_{68}BO_3SiSm$ (894.33): calcd. C 65.81, H 7.66; found C 64.99, H 7.68.

[Lu(η^5-C$_5$Me$_4$SiMe$_3$)Me(thf)$_3$]$^+$[BPh$_4$]$^-$ (4-Lu): According to the general procedure, **1-Lu** (163 mg, 0.30 mmol) in thf (3 mL) was treated with a thf solution (3 mL) of $[NEt_3H]^+[BPh_4]^-$ (114 mg, 0.27 mmol) to afford **4-Lu** as a pale yellow powder (232 mg, 94%). Crystals suitable for X-ray diffraction were obtained by cooling a saturated thf solution of **4-Lu** to –35 °C. ^1H NMR ([D$_8$]thf): δ = –0.70 (s, 3 H, LuMe), 0.29 (s, 9 H, SiMe$_3$), 1.77 (m, 12 H, β-CH$_2$, thf), 2.01 (s, 6 H, C$_5$Me$_4$), 2.14 (s, 6 H, C$_5$Me$_4$), 3.62 (m, 12 H, α-CH$_2$, thf), 6.72 (t, $^3J_{HH}$ = 7.5 Hz, 4 H, Ph-4), 6.86 (t, $^3J_{HH}$ = 7.5 Hz, 8 H, Ph-3), 7.27 (br. m, 8 H, Ph-2) ppm. $^{13}C\{^1H\}$ NMR ([D$_8$]thf): δ = 2.55 (SiMe$_3$), 11.69 (C$_5$*Me*$_4$), 14.40 (C$_5$*Me*$_4$), 26.37 (β-CH$_2$, thf), 30.94 (LuMe), 68.22 (α-CH$_2$, thf), 116.71 (C$_5$Me$_4$SiMe$_3$, C bonded to SiMe$_3$), 121.86 (Ph-4), 124.45 (C$_5$Me$_4$SiMe$_3$, C bonded to Me$_4$), 128.97 (C$_5$Me$_4$SiMe$_3$, C bonded to Me$_4$), 125.70 (Ph-3), 137.12 (Ph-2), 165.13 (q, $^1J_{BC}$ = 49.3 Hz, Ph-1) ppm. $^{11}B\{^1H\}$ NMR ([D$_8$]thf): δ = –6.57 ppm. $C_{49}H_{68}BLuO_3Si$ (918.94): calcd. C 64.05, H 7.46; found C 63.17, H 7.49.

X-ray Crystal-Structure Determination of 1-Gd, 3, 4-Y, 4-Sm, and 4-Lu: A summary of the crystallographic data is given in Table 5. The data were collected using Mo-K_α radiation of a Bruker AXS diffractometer with a CCD area detector using ω scans. The SMART program package was used to determine the unit-cell parameters and for data collection; the raw frame data were processed using SAINT and SADABS to yield the reflection data file.[31] Subsequent calculations were carried out using the SHELXS and SHELXL programs.[32] All hydrogen atoms were included into calculated positions; the hydrogen atoms of the bridging methyl groups in **1-Gd** were refined in their positions. The structure of **4-Y** was solved by isotypical replacement using the coordinates of **4-Sm**. The crystal structures of **4-Y**, **4-Sm** and **4-Lu** contain a co-crystallized molecule of thf. CCDC-671767 (**1-Gd**), -671768 (**3**), -671769 (**4-Y**), -671770 (**4-Sm**) and -671771 (**4-Lu**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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