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Article

Cationic Methyl Complexes of the Rare-Earth Metals: An Experimental and Computational Study on Synthesis, Structure, and Reactivity

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Synthesis, structure, and reactivity of two families of rare-earth metal complexes containing discrete methyl cations $[\mathrm{LnMe}_{(2-x)}(\mathrm{thf})_n]^{(1+x)+}$ ($x = 0, 1$; thf = tetrahydrofuran) have been studied. As a synthetic equivalent for the elusive trimethyl complex $[\mathrm{LnMe}_3]$, lithium methylates of the approximate composition $[\mathrm{Li}_3\mathrm{LnMe}_6(\mathrm{thf})_n]$ were prepared by treating rare-earth metal trichlorides $[\mathrm{LnCl}_3(\mathrm{thf})_n]$ with 6 equiv of methyllithium in diethyl ether. Heteronuclear complexes of the formula $[\mathrm{Li}_3\mathrm{Ln}_2\mathrm{Me}_9\mathrm{L}_n]$ (Ln = Sc, Y, Tb; L = $\mathrm{Et}_2\mathrm{O}$, thf) were isolated by crystallization from diethyl ether. Single crystal X-ray diffraction studies revealed a heterometallic aggregate of composition $[\mathrm{Li}_3\mathrm{Ln}_2\mathrm{Me}_9(\mathrm{thf})_n(\mathrm{Et}_2\mathrm{O})_m]$ with a $[\mathrm{LiLn}_2\mathrm{Me}_9]^{2-}$ core (Ln = Sc, Y, Tb). When tris(tetramethylaluminate) $[\mathrm{Ln}(\mathrm{AlMe}_4)_3]$ (Ln = Y, Lu) was reacted with less than 1 equiv of $[\mathrm{NR}_3\mathrm{H}][\mathrm{BPh}_4]$, the dimethyl cations $[\mathrm{LnMe}_2(\mathrm{thf})_n][\mathrm{BPh}_4]$ were obtained. The coordination number as well as *cis*/*trans* isomer preference was studied by crystallographic and computational methods. Dicationic methyl complexes of the rare-earth metals of the formula $[\mathrm{LnMe}(\mathrm{thf})_n][\mathrm{BAr}_4]_2$ (Ln = Sc, Y, La−Nd, Sm, Gd−Lu; Ar = Ph, $\mathrm{C}_6\mathrm{H}_4\mathrm{F}$-4) were synthesized, by protonolysis of either the ate complex $[\mathrm{Li}_3\mathrm{LnMe}_6(\mathrm{thf})_n]$ (Ln = Sc, Y, Gd−Lu) or the tris(tetramethylaluminate) $[\mathrm{Ln}(\mathrm{AlMe}_4)_3]$ (Ln = La−Nd, Sm, Dy, Gd) with ammonium borates $[\mathrm{NR}_3\mathrm{H}][\mathrm{BAr}_4]$ in thf. The number of coordinated thf ligands varied from $n = 5$ (Ln = Sc, Tm) to $n = 6$ (Ln = La, Y, Sm, Dy, Ho). The configuration of representative examples was determined by X-ray diffraction studies and confirmed by density-functional theory calculations. The highly polarized bonding between the methyl group and the rare-earth metal center results in the reactivity pattern dominated by the carbanionic character and the pronounced Lewis acidity: The dicationic methyl complex $[\mathrm{YMe}(\mathrm{thf})_6]^{2+}$ inserted benzophenone as an electrophile to give the alkoxy complex $[\mathrm{Y}(\mathrm{OCMePh}_2)(\mathrm{thf})_5]^{2+}$. Nucleophilic addition of the soft anion X^- ($\mathrm{X}^- = \mathrm{I}^-$, BH_4^-) led to the monocationic methyl complexes $[\mathrm{YMe}(\mathrm{X})(\mathrm{thf})_5]^+$.

Introduction

Since the report of dimethylzinc ZnMe_2 as one of the first organometallic complexes by Frankland,[1] methyl complexes have been considered as the exemplary organometallic compound for any electropositive element.[2] The transition metal-methyl bond exhibits polarity that critically depends on the electronegativity and oxidation state of the metal center, as well as on the ancillary ligand sphere and the charge. In some cases, the polarity reflects carbanionic, radical, as well as carbocationic, behavior. An example is methylcobaltamine with a formally cationic cobalt(III) center that can show all three reactivity patterns within the identical macrocyclic corrin-type ligand scaffold, depending on the substrate.[3] An overall positive charge may result in enhanced Brønsted acidity of the C−H bond, enabling an entry into doubly bonded methylene ligands, as exemplified by Schrock's synthesis of $[\mathrm{Ta}(\eta^5\text{-}\mathrm{C}_5\mathrm{H}_5)_2\mathrm{Me}(=\mathrm{CH}_2)]^+$ by deprotonation of the dimethyl cation $[\mathrm{Ta}(\eta^5\text{-}\mathrm{C}_5\mathrm{H}_5)_2\mathrm{Me}_2]^+$.[4]

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Group 3 metal−carbon bonds are generally considered to be "ionic", as rare-earth metals (group 3 metals Sc, Y, La to Lu) are located between the electropositive alkaline-earth metals and the more electronegative early transition metals of group 4.[5] Because of the large ionic radii of these metals and the small steric size of the methyl group, the synthesis of polymeric trimethyl complex $[\mathrm{LnMe_3}]_n$[6a−c] has only recently been claimed for Ln = Y and Lu by a cleavage reaction of $[\mathrm{Ln(AlMe_4)_3}]$.[6d,e] Apart from the apparent synthetic challenge, fundamental knowledge on the carbanionic methyl group at a strongly electropositive, Lewis-acidic cationic metal center is limited. Historically the organometallic chemistry of the rare-earth metals has been dominated by neutral and anionic compounds.[7] Although trianionic hexamethylate complexes $[\{\mathrm{Li(L_2)}\}_3\mathrm{LnMe_6}]$ ($\mathrm{L_2}$ = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, tmeda; 1,2-dimethoxyethane, dme) have been known since the early 1980s through the work by Schumann et al. for nearly the complete range of rare-earth metals,[8] they have not been considered as a synthetic equivalent for the elusive trimethyl $[\mathrm{LnMe_3}]$. We and others have found evidence that methyl and other hydrocarbyl cations are involved as active species in the homogeneous polymerization of α-olefins and 1,3-dienes by rare-earth metal catalyst precursors.[9] Such cationic hydrocarbyl complexes of the rare-earth metals can now be prepared by the reaction of neutral hydrocarbyls with a Lewis or Brønsted acid.[9,10] We report here on the preparation and structural characterization of a series of discrete mono- and dicationic rare-earth metal methyl complexes of the type $[\mathrm{LnMe}_{(2-x)}(\mathrm{thf})_n]^{(1+x)+}$ ($x = 0,1$). The dicationic methyl complexes $[\mathrm{LnMe(thf)}_n]^{2+}$ have been prepared for all rare-earth metals except promethium and europium. To establish a reactivity pattern for this unique type of organometallic cations that combines both carbanionic and Lewis acidic behavior, the reactivity of the representative complex $[\mathrm{YMe(thf)_6}]^{2+}$ has been examined.

Results and Discussion

Methylate Complexes. Initial studies on the reactivity of Schumann's hexamethylate complexes $[\{\mathrm{Li(L_2)}\}_3\mathrm{LnMe_6}]$ ($\mathrm{L_2}$ = tmeda, dme)[8] toward various Brønsted acids in different stoichiometric ratios suggested no straightforward formation of any neutral or cationic methyl species. However, protonolysis of the hexamethylate complexes $[\mathrm{Li_3LnMe_6(thf)}_n]$ (**1**), generated in situ in thf solution, with 5 equiv of $[\mathrm{NEt_3H}][\mathrm{BPh_4}]$ gave the dicationic methyl complexes $[\mathrm{LnMe(thf)}_n][\mathrm{BPh_4}]_2$ (**4**).[11]

To explore the nature of the hexamethylate complexes $[\mathrm{Li_3LnMe_6(thf)}_n]$ (**1**), we isolated compounds **1** by reacting the trichlorides $[\mathrm{LnCl_3(thf)}_n]$ with 6 equiv of methyllithium in diethyl ether (Scheme 1). The products are thermally extremely sensitive and could so far only be isolated for the smaller metals Sc, Y, and Gd−Lu. This kind of size dependence on the thermal stability was also observed during the preparation of compounds of the type $[\mathrm{Ln(CH_2SiMe_3)_3(thf)}_x]$ which could only be isolated for metals up to Sm.[12] Broad peaks in the NMR spectra of the diamagnetic complexes **1-Sc**, **1-Y**, and **1-Lu** down to −80 °C suggest an

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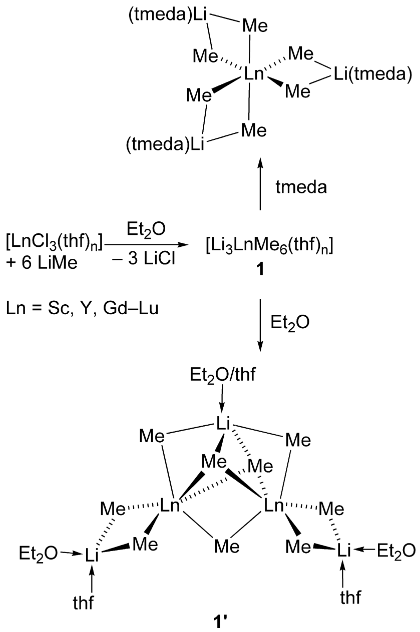
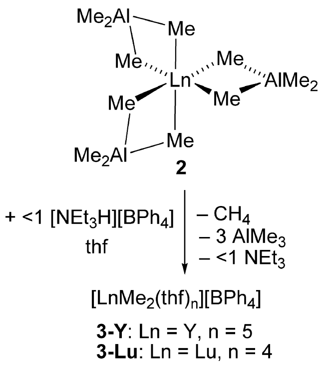
Scheme 1



Scheme 2



equilibrium between several fluxional species. This contrasts to the crystallographically characterized tmeda and dme adducts [{Li(L$_2$)}$_3$LnMe$_6$], which display narrower ^{1}H NMR signals for the methyl groups.[8] Crystallizing **1-Sc**, **1-Y**, and **1-Tb** from saturated diethyl ether solutions gave the heteronuclear complexes [Li$_3$Ln$_2$Me$_9$(thf)$_n$(Et$_2$O)$_m$] (**1′-Sc′ n = 2, m = 3**; **1′-Y**, **1′-Tb n = 3, m = 2**) as shown by X-ray diffraction studies (Figure 1).

The three C_2-symmetrical structures with a LiLn$_2$ core are similar (**1′-Y** and **1′-Tb** are isotypical). Each lanthanide center is surrounded by six methyl groups describing a distorted octahedral geometry. The Sc−μ_2-Me bond distances ranging from 2.294(4) to 2.397(4) Å are longer than Sc−Me(terminal) bonds reported,[13a−j] as found in β-diketiminato scandium methyl complexes, ranging from 2.162 to 2.245 Å,[13a−f] in [ScCp*$_2$Me] (2.243 Å),[13g] in [ScCp*Me$_2$-(^{t}Bu$_3$PO)] (2.251 and 2.252 Å),[13h] in [ScCp*Me(^{t}Bu$_3$PO)(μ-Me)B(C$_6$F$_5$)$_3$] (2.201 Å),[13h] in [Sc(OEP)Me] (2.246 Å, OEP = octaethylporphyrin),[13i] and [Sc(η^5-C$_5$Me$_4$H)(η^5-C$_5$H$_4$CH$_2$N-Me$_2$-κN)Me] (2.346 Å).[13j] The relatively long Sc−C distances can be explained by the formally anionic nature of the [Sc$_2$Me$_9$]$^{3-}$ unit, as well as by the steric crowding around the octahedrally coordinated Sc centers. As expected, the Sc−μ_3-Me bond lengths are longer (Sc−C3: 2.487(4) Å and Sc−C3′: 2.500(4) Å).[8c,14] Similar bond lengths were observed in the sterically encumbered compounds [(ScCp*$_2$)$_2$(μ_2-Me)][B(C$_6$F$_5$)$_4$] (2.519 and 2.454 Å),[13k] as well as in silylene-bridged metallocene aluminate complexes [{(Me$_2$Si)$_2$(η^5-C$_5$H$_2$^{t}Bu)(η^5-C$_5$H^{i}Pr$_2$)}Sc(μ_2-Me)$_2$(AlMe$_2$)] and [{Me$_2$Si(η^5-C$_5$H$_3$^{t}Bu)$_2$}Sc(μ_2-Me)$_2$(AlMe$_2$)] (2.414 and 2.442 Å,[13l] 2.490 and 2.425 Å[13m]).

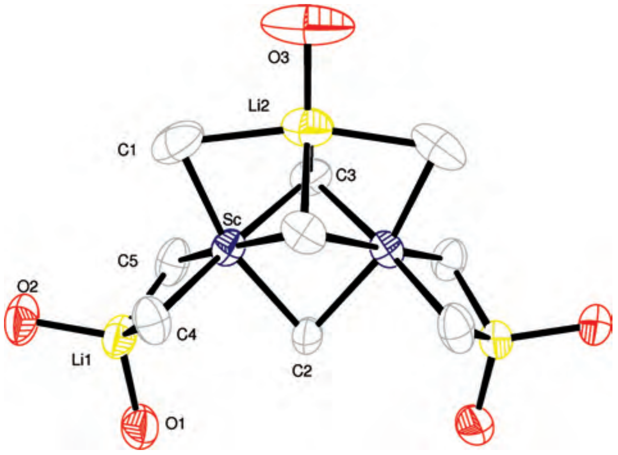


Figure 1. ORTEP drawing of **1′-Sc** with thermal ellipsoids at the 50% level. Hydrogen atoms and all carbon atoms of the thf and Et$_2$O ligands are omitted for clarity.

NMR spectra of the diamagnetic complexes **1′-Sc** and **1′-Y** in thf-d_8 do not differ significantly from those of the parent substances **1-Sc** and **1-Y**, indicating that the aggregate structure is highly fluxional in solution. The reactivity of **1** and **1′** is similar and both can be regarded as synthetic equivalent for [LnMe$_3$]. Treatment of **1** with 5 equiv of [NEt$_3$H][BPh$_4$] gave the dicationic species **4** (vide infra). When using **1′**, only 3.5 equiv of acid per rare-earth metal Ln are needed, in agreement with the formulation [Ln$_2$-Me$_9$]$^{3-}$. In the absence of chelating ligands such as dme or tmeda, apparently exhaustive methylation of the rare-earth metal center to give [LnMe$_6$]$^{3-}$ does not occur or upon crystallization from diethyl ether, the equilibrium is shifted toward [LnMe$_3$].

Synthesis and Structure of Dimethyl Monocations. Dimethyl monocations of the type [LnMe$_2$(thf)$_n$][BPh$_4$] (**3**) have been isolated and fully characterized for Ln = Y (**3-Y**)[11b,c] and Lu (**3-Lu**). They can be prepared from the ate complex [Li$_3$LnMe$_6$(thf)$_n$] (**1**) by protonolysis with [NEt$_3$H]-[BPh$_4$], by nucleophilic attack of the methyl dication [LnMe(thf)$_n$][BPh$_4$]$_2$ (**4**) (vide infra) with methyllithium, or by protonolysis of [Ln(AlMe$_4$)$_3$] (**2**) with [NEt$_3$H][BPh$_4$]. Only the latter method allowed isolation of the monocations **3**, as these compounds cannot be separated from LiBPh$_4$ that is formed by the former two methods. We have obtained analytically pure **3-Y** and **3-Lu** from the reactions of **2-Y** and **2-Lu** in thf using less than 1 equiv of [NEt$_3$H][BPh$_4$] (Scheme 2). The methyl groups in **3-Lu** give rise to one sharp singlet at δ −0.94 ppm in the ^{1}H NMR spectrum and

δ 27.3 ppm in the ^{13}C NMR spectrum in thf-d_8.[15] The sharp signals indicate that there is no fast exchange of methyl groups between Lu centers on the NMR-time scale. The previously communicated yttrium dimethyl cation **3-Y** exhibits two doublets at 1.07 and 0.95 with $^2J_{YH} = 1.7$ Hz, indicative of the presence of two isomers, one ^{13}C NMR resonance at 17.5 ppm ($^1J_{YC} = 46.8$ Hz), and a peak in the $^{89}Y\{^1H\}$ NMR spectrum in thf-d_8 at 650.9 ppm. This value is similar to the ^{89}Y NMR chemical shift of $[Y(CH_2SiMe_3)_2(thf)_4][BPh_4]$ (660.0 ppm)[15] and in remarkable agreement with Hanusa's empirical study on the contribution of charges and ligands on the ^{89}Y NMR chemical shifts: The expected shift in thf-d_8 is 651 ppm (a Me group "contributes" 288 ppm, a positive charge 75 ppm).[16]

Recrystallization from saturated thf solutions afforded single crystals of **3-Lu**. The structure of **3-Lu** differs significantly from that of previously reported *trans*-$[YMe_2(thf)_5][BPh_4]$ (**3-Y**).[11b,c] Instead of five coordinating thf molecules, **3-Lu** contains only four solvent molecules. The C−Lu−C angle of 96.39(12)° leaves the alkyl groups in a *cis*-geometry in a distorted octahedron (Figure 2). The average Lu−O(thf) distances of 2.316 Å are comparable to the distances found in $[Lu(\eta^5\text{-}C_5Me_4{}^iPr)_2Me(thf)]$ (2.325 Å)[17] and $[LuCp^*(CH_2SiMe_3)_2(thf)]$ (2.255 Å).[18] Both Lu−O bonds *trans* to the Lu−C bonds are significantly longer (average 2.366 Å) than the two Lu−O bonds *trans* to each other (average 2.266 Å). Similar structural features were observed in the six-coordinated monocationic complexes $[Y(CH_2SiMe_3)_2(thf)_4][E(CH_2SiMe_3)_4]$ (E = Al,[11a] Ga[10e]) and $[ScPh_2(thf)_4][BPh_4]$.[19] A strong structural *trans*-influence is ascribed to methyl groups, but these observations are usually explained by molecular-orbital considerations, which do not apply to rare-earth metal coordination chemistry.[20] An elongation of the Lu−O bonds *trans* to the Me groups was also observed in the results of density-functional theory (DFT) calculations (vide infra).

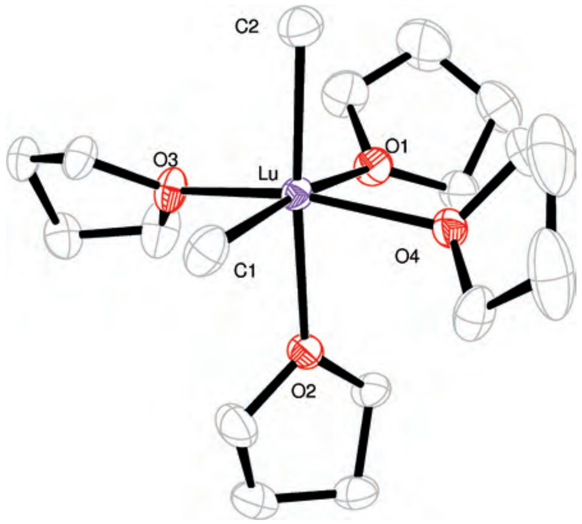


Figure 2. ORTEP drawing of the cation portion of **3-Lu** at the 50% probability level. Hydrogen atoms are omitted for clarity.

Both Lu−Me distances are virtually identical (2.343(3) and 2.347(3) Å) and shorter than those of reported neutral and anionic compounds, such as $[Lu(\eta^5\text{-}C_5Me_4{}^iPr)_2Me(thf)]$ (2.369 Å)[17] or $[Li(tmeda)_2][LuCp^*Me_3]$ (2.59, 2.56, and 2.39 Å).[21] This mirrors previous observations of shortening metal−carbon bond distances with increasing cationic charge.[11] The structure of **3-Y**, displaying a pentagonal bipyramidal *trans*-geometry around the yttrium centers, appears to be unusual. Monocationic dialkyl complexes $[Y(CH_2SiMe_3)_2(thf)_4][E(CH_2SiMe_3)_4]$ (E = Al,[11a] Ga[10e]) display a *cis*-geometry of the alkyl groups around the yttrium centers, similar to **3-Lu**.

To explain this structural difference, calculations for the experimentally found six- and seven-coordinated **3-Lu** and **3-Y** as well as a hypothetical six-coordinated $[YMe_2(thf)_4]^+$ were carried out at the DFT level. In all cases both the *cis* and the *trans* complexes were found as minima on the potential energy surface (PES). Selected bond lengths and angles of the experimentally found and calculated structures of **3-Lu** and **3-Y** and their respective *cis* and *trans* calculation results are given in Table 1 (See details in the Supporting Information).

The calculated geometry parameters for **3-Lu** are in good agreement with the experimental values. The Lu−Me distances are reproduced within 0.01Å. The Lu−O(thf) distances are less satisfactory (maximum deviation of 0.1 Å for the Lu−O distances *trans* to the methyl groups; 0.06 Å for those *cis*). The longer Lu−O distances for the thf ligands *trans* to the methyl group are found both in the experiment and in the calculation.

The bond between lutetium and the methyl group is found to be strongly polarized at the Natural Bond Orbital (NBO)

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Table 1. Selected Experimentally Observed and Calculated Bond Lengths (Å) and Bond Angles (deg) for **3-Lu** and **3-Y**[11b]

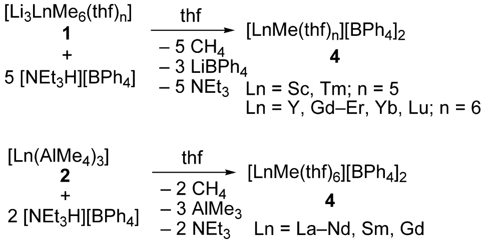
	3-Lu	$[LuMe_2(thf)_4]^+_{calc}$ [b]	**3-Y**[c]	$[YMe_2(thf)_5]^+_{calc}$ [d]
Ln−C1	2.343(3)	2.332	2.526(2) [2.513(3)]	2.481
Ln−C2	2.347(3)	2.334	2.508(2) [2.516(3)]	2.486
Ln−O1	2.367(2)[a]	2.459[a]	2.397(2) [2.393(3)]	2.467
Ln−O2	2.3655(19)[a]	2.483[a]	2.399(2) [2.422(2)]	2.460
Ln−O3	2.260(2)	2.329	2.406(2) [2.380(2)]	2.451
Ln−O4	2.271(2)	2.329	2.395(2) [2.392(3)]	2.471
Ln−O5			2.418(2) [2.377(2)]	2.453
C−Ln−C	96.39(12)	105.3	174.03(8) [178.46(11)]	178.1

[a] thf *trans* to Me group. [b] *cis* isomer. [c] values in square brackets correspond to second molecule in unit cell. [d] *trans* isomer.

level (contribution of 89% from the methyl sp^3 and 11% from the metal 5d for the *cis* isomer) and is found to be quite similar for both isomers (contribution of 91% of the methyl sp^3 and 9% from the lutetium 5d for the *trans* isomer). This is different from the situation in neutral species $[LnMe_3]$ where the bonds are almost purely ionic,[6c] in line with more contracted atomic orbitals for a monocationic complex than for a neutral complex. The two Ln−Me bonds are found to be equivalent, in agreement with the two similar Ln−C distances (Table 1). This bonding situation leads to a highly positive charge at the Lu center (*cis* isomer, +2.01, and *trans* isomer, +2.10) and strong negative charges at the methyl groups (−0.73 and −0.79, respectively). The Lu−Me bonds in $[LuMe_2(thf)_4][BPh_4]$ are calculated to be much shorter for the *cis* than for the hypothetical *trans* isomer (the important electrostatic part of the bonding has been verified by a NBO analysis, see charge given above). Thus, the electrostatic attractions are found to be stronger in the *cis* than in the *trans* isomer. The smaller C−Ln−C angle leads to an important electrostatic repulsion between the two negatively charged methyl groups. Moreover, the longer Ln−O distances in the *cis* than in the *trans* isomer reduce the energy difference between the two isomers. The energy difference between the two isomers results from a subtle mixing of these effects (demonstrated by a smaller lutetium charge for the *cis* than for the *trans* isomer despite a shorter Lu−C distance for the former than the latter). As a result, both the six-coordinated isomers are found to be almost isoenergetic with only a slight preference for the *cis* isomer (around 0.2−0.3 kcal·mol^{-1}).

The coordination of a fifth thf molecule in the seven-coordinated **3-Y** leads to an energy stabilization of 7.5 kcal·mol^{-1}. The *trans* isomer has been calculated to be slightly more stable than the *cis* isomer (1.3 kcal·mol^{-1}). As was the case for the six-coordinated species, shorter Y−Me distances are found for the *cis* than for the *trans* isomer, but Y−O(thf) distances are shorter for the *trans* than for the *cis* isomer. Similarly, the Y−Me bonds are also strongly polarized (contribution of 93% of the methyl sp^3 and 7% from the yttrium 4d for the *trans* isomer and of 91% of the methyl sp^3 and 9% from the metal 4d for the *cis* isomer). This leads to an yttrium charge of +2.13 and of −0.76 for the methyl groups in the *trans* isomer (+2.03 and −0.73 in the *cis* isomer). Thus, similar effects to those presented for the six-coordinated species should apply here and one would expect the *cis* configuration to be slightly more stable. However, the presence of the fifth thf molecule is increasing the steric hindrance around the metal center. The additional stability caused by the C_5 arrangement of the five thf molecules makes the *trans* isomer more stable than the *cis* isomer.

Scheme 3



Synthesis and Structure of Methyl Dications. When 5 equiv of $[NEt_3H][BPh_4]$ were added to thf solutions of **1**, compounds **4** precipitated (Scheme 3). Because of the unavailability of the ate complex **1** for the larger metals La, Ce, Pr, Nd, and Sm, these dicationic methyl complexes were prepared by protonolysis of the homoleptic aluminates $[Ln(AlMe_4)_3]$ (**2**) using $[NEt_3H][BPh_4]$ as Brønsted acid. An excess of acid did not lead to abstraction of the last remaining methyl group. A similar observation had been made for the trimethylsilylmethyl cations,[15] whereas exhaustive protonolysis of neutral $[La(CH_2C_6H_4Me\text{-}4)_3(thf)_3]$ and anionic $[Li(thf)_4][La(CH_2C_6H_4Me\text{-}4)_4]$ with an excess of $[NPhMe_2H][B(C_6F_5)_4]$ was reported to give La^{3+}.[10d]

Compounds **4-La**, **4-Ce**, **4-Pr**, **4-Nd**, and **4-Sm** are significantly less stable at room temperature and in thf than their smaller analogues. A colorless suspension of **4-La** in thf turned orange when left at room temperature for several hours. Previously the thf ring opening reaction by **4-Nd** to the pentoxy complex $[Nd\{O(CH_2)_4Me\}(thf)_6][BPh_4]_2$ was reported.[11b] When a suspension of **4-Sm** in thf was left at room temperature and in daylight, solid **4-Sm** gradually dissolved to give the purple divalent complex $[Sm(thf)_7][BPh_4]_2$.[22] This was ascribed to the homolysis of the Sm−Me bond to give Sm(II) and a methyl radical, but attempts to trap this radical with TEMPO remained unsuccessful.

Single crystals of **4-Sc**, **4-Y**,[11a] **4-Dy**, **4-Ho**,[11b] and **4-Tm** could be obtained when thf solutions of the corresponding compounds **1** were reacted with less than 4 equiv of acid, followed by layering the remaining acid as a thf solution on top of the reaction mixture. The yttrium, dysprosium, and holmium dicationic complexes crystallized isostructurally with six thf molecules surrounding the metal centers. Although the crystal quality of **4-Sc** and **4-Tm** was poor, the composition and connectivity of both compounds was unequivocally established. Both cationic parts crystallized with five thf molecules coordinating to the Ln center in an octahedral geometry.

In crystalline **4-Dy** the metal center adopts a pentagonal bipyramidal geometry (for details, see Supporting Information). The methyl group is situated in the axial position with five thf molecules in the equatorial plane. Even though

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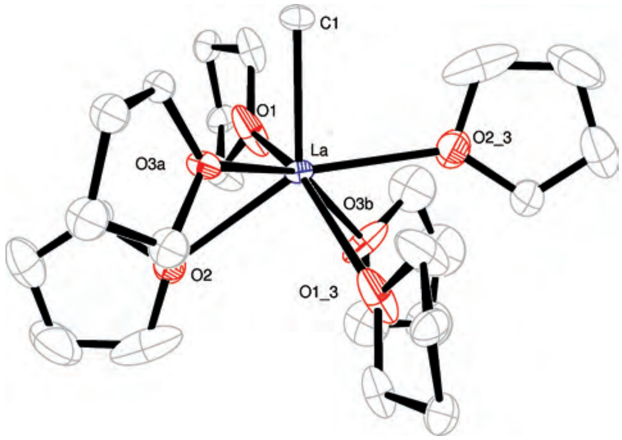

Figure 3. ORTEP drawing of the cationic portion of **4′-La** at the 30% level of probability. Hydrogen atoms are omitted for clarity.

dysprosium has a slightly larger ionic radius (91 pm, CN 6) than yttrium and holmium (90 pm),[23] the Dy−C bond distance (2.401(10) Å) has the same length (within the standard error) as was found in **4-Y** (2.418(3) Å) and in **4-Ho** (2.378(4) Å).[11] In all three cases, no elongation of the bond length of the thf *trans* to the methyl groups relative to the equatorial thf ligands is observed, since the equatorial thf molecules are located further away from the metal center because of greater steric repulsions in the equatorial plane.

Crystals of [LaMe(thf)$_6$][B(C$_6$H$_4$F-4)$_4$]$_2$ (**4′-La**) and [SmMe(thf)$_6$][B(C$_6$H$_4$F-4)$_4$]$_2$ (**4′-Sm**) were grown by reaction of **2-La** and **2-Sm** with substoichiometric amounts of [NEt$_3$H][B(C$_6$H$_4$F-4)$_4$] in thf and subsequent layering with thf solutions of the acid (for the structure of **4′-La** see Figure 3, for **4′-Sm** see Supporting Information). Unexpectedly, the two compounds are not isostructural to the smaller rare-earth metal derivatives with six thf ligands. Instead of the pentagonal bipyramidal structure, a methyl-capped octahedral geometry is adopted. This structure allows a closer metal-alkyl contact, which is clearly visible when the structure of **4-Y** is compared to that of **4′-Sm**. The Y−C distance of 2.418(3) Å[11a] is longer than the Sm−C distance of 2.385(8) Å even though the ionic radius of Y is 6 pm smaller than that of Sm (90 pm versus 96 pm).[23] The La−C distance of 2.456(6) Å reflects the increase in ionic radius from Sm to La (103 pm).[23] The average La−O(thf) bond distance of 2.593 Å is longer than in the dicationic benzyl complex [La(CH$_2$C$_6$H$_4$Me-4)(thf)$_6$][BPh$_4$]$_2$ (2.586 Å).[10d]

For seven-coordinate complexes, the commonly adopted geometries (capped octahedron, capped trigonal prism, and pentagonal bipyramid) are similar in energy with the Repulsion Energy Coefficients X ranging from X = 3.230 to 3.266.[24] DFT calculations led to minima on the PES for both the observed capped octahedral and pentagonal bipyramidal structures of [LnMe(thf)$_6$]$^{2+}$ (Ln = La, Sm, Y). According to calculations for Ln = Y, the pentagonal bipyramidal structure is more stable by 2.0 kcal·mol^{-1} than the capped octahedron. The calculated Y−Me distance of 2.361 Å is in good agreement with the experimentally found value of 2.418 Å. A comparison of bond distances and angles is given in Table 2. As was the case for the monocationic complex, the bond between Y and the methyl group is strongly polarized toward methyl (contribution of 93% of the methyl sp^3 and 7% from the metal 4d). This leads to a charge of +2.19 for Y and −0.74 for the methyl group. When the bonding situation in **3-Y** and **4-Y** is compared, the Y−Me bonds are similar, and the charge at the metal center and the charge of the methyl group are marginally different in the two complexes. The metal charge is slightly more positive in **4-Y** leading to shorter Y−Me distance in **4-Y** than in **3-Y**.

For Ln = La, the capped octahedral structure was found to be more stable than the pentagonal bipyramid (1.37 kcal·mol^{-1}). The calculated La−Me distance of 2.480 Å is similar to the experimental value of 2.456(6) Å. As expected, such an arrangement allows a closer metal−methyl contact and the La−Me distance for a hypothetical pentagonal bipyramidal structure would be 2.506 Å. The preference for the capped octahedral structure is electrostatically driven, since the shorter La−Me distance allows a stronger electrostatic interaction (as in the previous section, the highly polarized nature of the bonding has been verified by a NBO analysis). The longer La−O distances indicate a smaller contribution from the steric hindrance around the metal center, in contrast to the situation for Ln = Y where the Y−O distances are shorter by up to 0.2 Å. The bond is also found to be highly polarized in this system and similar to the bonding in **4-Y** (contribution of 93% of the methyl sp^3 and 7% from the metal 4d). The charge is, however, higher in **4-La** than in **4-Y** (+2.6 for La and −0.74 for Me) despite the longer La−Me distance with respect to Y−Me. The charge of the methyl group indicates that the bond is similar for **4-Y** and **4-La**. The difference of metal charge is in agreement with the fact that La−O(THF) distances are much longer than the Y−O(THF) bonds.

For Ln = Sm, both calculated structures are isoenergetic. The ionic radius of Sm (96 pm) is almost midway between that of La and that of Y (103 and 90 pm, respectively).[23] A subtle balance between the reduced steric hindrance around the metal center and increased electrostatic Sm−Me attractions is indicated. For the capped octahedral structure, the Sm−Me distance was calculated to be 2.406 Å (to be compared with 2.385(8) Å found experimentally) whereas a value of 2.430 Å is expected for the pentagonal bipyramid.

Reactivity of the Yttrium Methyl Cations. Three representative reaction types were found for the cationic metal complexes: (a) because of its carbanionic nature, the methyl group acts as a nucleophile toward electrophiles (Scheme 4); (b) the Lewis acidic cationic metal center reacts with a nucleophile (Scheme 4); (c) the methyl group reacts as a Brønsted base in deprotonation reactions.[25] Owing to the diamagnetic nature and medium sized ionic radius (Sc: 75 pm, Y: 90 pm, La: 103 pm),[23] methyl cations of yttrium **3-Y** and **4-Y** were chosen to explore the reactivity of this family of compounds.

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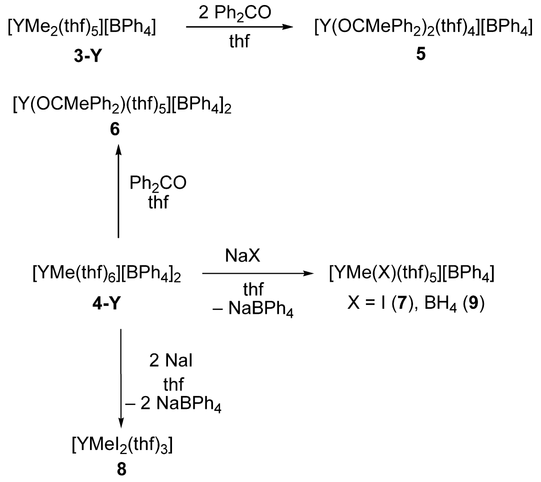
Table 2. Selected Bond Lengths (Å) and Angles (deg) of **4-Y**,[11a] **4′-La**, and **4′-Sm** and Their Calculated Structures

	4-Y	$[YMe(thf)_6]^{2+}$ [a]	**4′-La**	$[LaMe(thf)_6]^{2+}$ [b]	**4′-Sm**	$[SmMe(thf)_6]^{2+}$ [b]
Ln−C	2.418(3)	2.361	2.456(6)	2.480	2.385(8)	2.406
Ln−O	2.352(3)[c]	2.436	2.556(2)[e]	2.631	2.411(4)[e]	2.520
	2.426(3)[c]	2.456	2.679(3)[f]	2.644	2.472(3)[e]	2.534
	2.355(3)[c]	2.437	2.664(3)[f]	2.649	2.495(6)[e]	2.559
	2.427(3)[c]	2.474	2.578(4)[e]	2.638	2.573(4)[f]	2.566
	2.377(3)[c]	2.456	2.583(5)[f]	2.648	2.603(4)[f]	2.576
	2.427(3)[d]	2.598	2.497(3)[e]	2.609	2.512(8)[f]	2.593
C−Ln−O[g]	176.5(1)	175.4				

[a] Calculated pentagonal bipyramidal isomer. [b] Calculated capped octahedral isomer. [c] Equatorial thf. [d] Axial thf. [e] thf in top plane. [f] thf in bottom plane. [g] thf *trans* to Me.

Scheme 4



A typical reaction for the insertion of unsaturated molecules into Ln−C bonds is the reaction with benzophenone or fluorenone.[6b,26] Upon reaction of **3-Y** with 2 equiv of benzophenone the dialkoxy complex $[Y(OCMePh_2)_2(thf)_4][BPh_4]$ (**5**) formed. When 1 equiv of benzophenone was reacted with **4-Y** in thf, the reaction mixture instantaneously turned clear and crystals of $[Y(OCMePh_2)(thf)_5][BPh_4]_2$ (**6**) precipitated out of solution. The structure of the cationic part of the compound **6** is depicted in Figure 4. In the distorted octahedral cation the central yttrium atom is coordinated by the alkoxy ligand and five thf molecules. The Y−O bond distance to the alkoxy ligand (1.9990(16) Å) is slightly shorter than that reported for terminal alkoxo ligands in the monocationic *cis*-$[Y(OCRC_{12}H_8)_2(thf)_4][BPh_4]$ (R = CH_2SiMe_3, 2.0533 and 2.0680 Å)[26] and the neutral $[Y(OC_{14}H_{11})_2(\mu\text{-}OC_{14}H_{11})]_2$(9-fluorenone) (2.028 and 2.049 Å),[6b] because of the dicationic charge of the compound. The thf molecule *trans* to the alkoxy ligand is situated further away from the metal center, as was the case in **3-Lu** (vide supra).

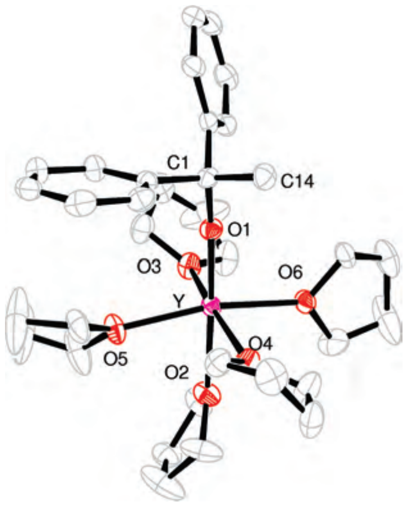


Figure 4. ORTEP drawing of the cationic portion of **6** at 50% probability level. Hydrogen atoms are omitted for clarity.

The results of a DFT investigation of the reaction between benzophenone and both **3-Y** and **4-Y** resulted in the free energy profile depicted in Figure 5. The reactions are calculated to be kinetically and thermodynamically favorable for **3-Y** and **4-Y**, in agreement with the experimental observation. It should be noted that, for **3-Y**, only insertion into one Y−Me bond has been considered. The reaction is both thermodynamically and kinetically slightly more favorable for the dicationic rather than for the monocationic complex with respect to the separated reactants. As the MOs are more contracted in the dicationic complex, the insertion would be expected to be less facile than in the monocationic complex. On the other hand, the higher metal charge leads to stronger electrostatic interactions. Analyzing the energy profile and in agreement with the metal charge (related to mainly electrostatic interaction), the benzophenone adduct is found to be more stable for **4-Y** than **3-Y**. With respect to the adduct formation, the barrier is higher for **4-Y** (35.7 kcal·mol^{-1}) than for **3-Y** (21.3 kcal·mol^{-1}), in line with the charge effect.

When the dication **4-Y** was reacted with soft nucleophiles of the type M^+X^- (M = Li, Na, K) in thf, monocationic yttrium compounds of the type $[YMeX(thf)_n][BPh_4]$ were formed. Isolation of the resulting cations was difficult, as $[YMeX(thf)_n][BPh_4]$ had to be separated from $[M(thf)_m][BPh_4]$. Upon reaction of **4-Y** with 1 equiv of NaI in thf, the iodo methyl yttrium cation $[YMeI(thf)_5][BPh_4]$ (**7**) could be isolated. Further reaction with 1 equiv of NaI resulted in the formation of neutral $[YMeI_2(thf)_3]$ (**8**). Comparable to **7** is the η^3-allyl chloro monocation $[Nd(\eta^3\text{-}C_3H_5)Cl(thf)_5][BPh_4]$.[27] A number of divalent and trivalent compounds of the general formula LnRX and $LnRX_2$/LnR_2X (X = halide) were generated by direct reaction of Ln^0 with RX.[28] In

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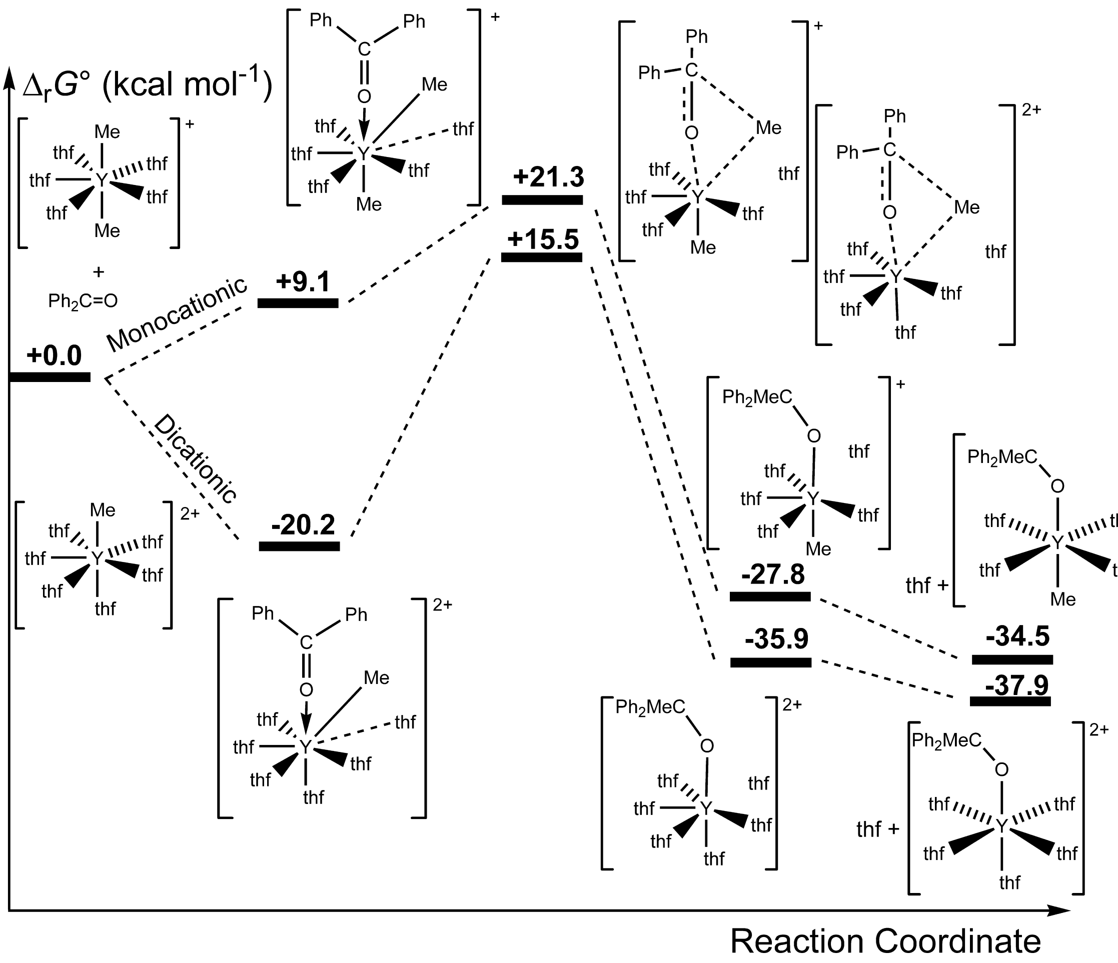

Figure 5. Calculated energy profile for benzophenone insertion into the Y−Me bond for both **3-Y** and **4-Y**.

addition, a series of [$LnPhCl_2(thf)_n$] (Ln = Pr, Sm, Gd)[29] and some complexes of the type [$LnRCl_2(thf)_n$] with bulky aryl groups (R = 2,6-dimesitylphenyl or 2,6-di(1-naphtyl)phenyl)[30,31] were prepared by reacting LiR with $LnCl_3$ in 1:1 ratio. A further example is the η^3-allyl dichloro complex [$Nd(C_3H_5)Cl_2(thf)_2$] prepared by the comproportionation of the homoleptic tri(allyl) complex [$Nd(\eta^3\text{-}C_3H_5)_3(diox)$] with [$NdCl_3(thf)_2$].[32] Recently, Anwander et al. reported on mixed rare-earth methyl chloro compounds either isolated as [$Ln_aAl_bMe_cCl_d$]$_n$ ($a + b = 1$, $a > b$, $c + d = 3$, $d > c$; Ln = Sc, Y, La, Nd) or prepared in situ from compounds **2-Ce**, **2-Pr** and **2-Nd** and Et_2AlCl in varying amounts as a chlorinating agent.[6e,33] Compound **8** is an analogue to cerium reagents of the type LiR/CeX_3 or MgRX/CeX_3, used as a source of nucleophilic alkyls, where pure lithium alkyls or Grignard reagents undergo undesirable side reactions such as enolization of the carbonyl substrates. The exact nature of these compounds is, however, not well understood.[34]

Unlike Grignard reagents, **7** and **8** are not involved in Schlenk equilibria in pyridine-d_5 because a fast exchange (on the NMR-time scale) of the methyl groups can be excluded on the basis of a coupling of both ^{1}H and ^{13}C to ^{89}Y ($I = {}^1/_2$).[35] A single, well defined peak in the ^{89}Y NMR spectrum at δ 543 ppm confirmed that only one species is present in pyridine-d_5 solution. This is analogous to the ^{47}Ti and ^{49}Ti spectra of [$TiMeCl_3$], where also only one species was detected.[36] Single crystals of a pyridine adduct of **8** could be grown from a pyridine/pentane solution of **8**. The resulting crystals of [YMeI(py)$_5$]I (**8′**) were pseudomerohedrically twinned with strong disorder of iodo and methyl ligands. The result of the structure determination confirmed the composition and atomic connectivity, in particular, the *trans* arrangement of the methyl group and the iodo ligand. Within the crystal, the second iodide is separated from the yttrium

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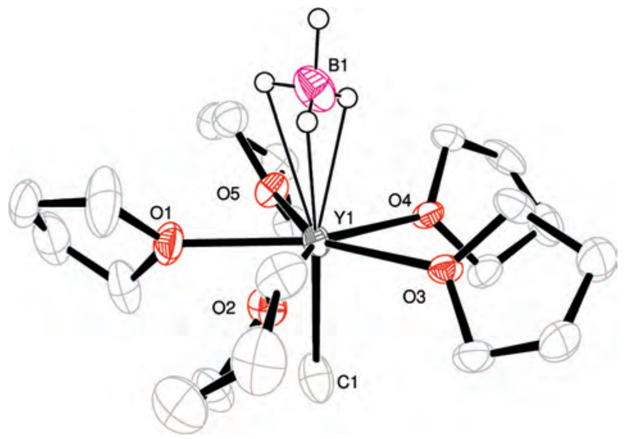

Figure 6. ORTEP drawing of the cationic portion of **9** at the 50% probability level. Only those hydrogen atoms of the BH_4 group are shown for clarity.

center, affording a charge separated ion pair [YMeI(py)$_5$]I. Accordingly, the identical ^{1}H NMR shifts of the methyl groups in **7** and **8**/**8′** suggest a charge separated ion pair in solution. Complex **8** is relatively stable in pyridine-d_5 and neither pyridine orthometalation[15,25] nor methyl group transfer to a pyridine ring[19] occurred within 24 h.

When **4-Y** was reacted with 1 equiv of $NaBH_4$ in thf, the mixed alkyl borohydride compound [YMe(BH_4)(thf)$_5$][BPh_4] (**9**) was isolated as colorless crystals. The IR spectrum exhibits a sharp band at $\nu = 2425$ cm^{-1} and a strong broad band at 2230 cm^{-1}, indicating a tridentate coordination of the BH_4 group.[37] The ^{1}H NMR spectrum of **9** in thf-d_8 shows a 1:1:1:1 quartet for the BH_4 group, suggesting a fast rearrangement of the coordination modes on the NMR time scale. Cationic borohydride complexes of the f-elements are rare and with the exception of a cationic uranium(IV) borohydride,[38] only recently have cationic rare-earth metal tetrahydridoborate complexes [Ln(BH_4)$_2$(thf)$_5$]$^+$ become accessible.[39]

Single crystals of **9** were obtained by slow cooling of a saturated thf solution (Figure 6). The geometry around the yttrium center is best described as a pentagonal bipyramid, as for **3-Y**. The BH_4 and Me groups are almost perfectly *trans* to each other with a C−Y−B angle of 179.1(3)°. The Y−C bond distance of 2.450(8) Å is slightly shorter than in **3-Y** (2.526 Å and 2.508 Å) and slightly longer than in **4-Y** (2.418 Å).[11] Within the standard deviation, the Y−B distance of 2.563(10) Å is equal to the corresponding distances in [Y(BH_4)$_3$(thf)$_3$] (2.58 Å).[40] Theoretical studies on [Y(BH_4)$_2$(H_2O)$_4$]$^+$ with different bonding modes of the borohydride (η^2 versus η^3) have shown a theoretical Y−B distance of 2.56 or 2.58 Å for the tridentate ligation.[41] The average Y−O distance of 2.413 Å is slightly longer than the averages observed in **3-Y** (2.403 and 2.393 Å for two independent ion pairs in the crystal lattice), comparable to one of the distances in [Y(BH_4)$_3$(thf)$_3$] (2.350 Å and 2.412 Å)[40] but longer than those observed in the six-coordinated cationic part of [Y(BH_4)$_2$(thf)$_4$][Y(BH_4)$_4$] (2.30, 2.33, 2.34 and 2.32 Å).[42]

Calculations at the DFT level have reproduced the structure of **9** well. The tridentate nature of the borohydride ligand, the *trans*-arrangement of the BH_4 and Me groups, as well as the Y−X (X = C, B, O) bond lengths are all in good agreement with the experimental results (for details, see Supporting Information).

Conclusion

The present study demonstrates that thf-solvated rare-earth metal methyl dications [LnMe(thf)$_n$][BAr_4]$_2$ can be prepared by protonolysis of synthetic equivalents of the elusive trimethyl metal compounds [$LnMe_3$] such as [Li_3LnMe_6(thf)$_n$] and [Ln($AlMe_4$)$_3$]. The configuration is either octahedral, pentagonal bipyramidal, or capped octahedral, depending on the radius of the metal center. Computations confirm a highly electrostatic bonding between the methyl group and the rare-earth metal center. Therefore the carbanionic character of the methyl group is pronounced despite the double positive charge. This is manifested in the facile nucleophilic attack on an electrophile such as benzophenone, whereas the Lewis acidic character is evidenced by the addition of soft nucleophiles, such as iodide or tetrahydroborate to give monocationic methyl complexes of the type [YMe(X)(thf)$_5$]$^+$ ($X^- = I^-, BH_4^-$). In conclusion, the methyl dications of the rare-earth metals contain a nucleophilic methyl group acting as methyl anion source, but at a relatively soft Lewis acidic metal center. This situation is related to that commonly associated with the active sites of Ziegler catalysts,[9,10] where both a Lewis acidic/electrophilic metal center and a (soft) nucleophilic alkyl (and hydride) chain are invoked for the polyinsertion of α-olefins. As recently demonstrated by Evans et al. in pioneering works on permethylcyclopentadienyl cations,[43] unsolvated alkyl cations of the rare-earth metals therefore promise even higher reactivity.

Experimental Section

General Considerations. All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. Diethyl ether, thf, and toluene were distilled from sodium benzophenone ketyl. Pentane was purified by distillation from sodium/triglyme benzophenone ketyl. Alternatively, the above solvents were dried using an MBraun SPS-800 solvent purification system. For the previously reported compounds **1-Sc**, **1-Y**, **1-Ho**, **1-Yb**, **1-Lu**, **4-Sc**, **4-Y**, **4-Nd**, **4-Ho**, **4-Yb**, and **4-Lu** optimized procedures are given for reasons of completeness.[11] The rare-earth metal aluminates **2** were prepared according to published procedures.[6e] [NR_3H][BAr_4] (Ar = Ph, C_6H_4F-4) was obtained by reaction of aqueous solutions of $NaBAr_4$ and of [NR_3H]Cl, followed

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Table 3. Crystallographic Data for **1′-Sc**, **3-Lu**, **4′-La**, and **9**

compound	**1′-Sc**	**3-Lu**	**4′-La**	**9**
empirical formula	$C_{29}H_{73}Li_3O_5Sc_2$	$C_{46}H_{66}BLuO_5$	$C_{73}H_{83}B_2F_8LaO_6$	$C_{45}H_{67}B_2O_5Y$
M_r	612.61	884.77	1368.92	798.52
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
crystal system	tetragonal	monoclinic	monoclinic	monoclinic
space group	$I4_1cd$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a (Å)	16.340(3)	12.6950(10)	14.4672(12)	13.5304(16)
b (Å)	16.340(3)	28.004(2)	12.7014(11)	13.0945(16)
c (Å)	29.970(2)	13.0130(10)	18.2100(15)	24.622(3)
α (deg)	90	90	90	90
β (deg)	90	111.0390(10)	103.8331(18)	90.700(2)
γ (deg)	90	90	90	90
V (Å^3)	8002(2)	4317.9(6)	3249.1(5)	4362.0(9)
Z	8	4	2	4
D_{calc} (g·cm^{-3})	1.017	1.361	1.399	1.216
T (K)	130(2)	130(2)	110(2)	120(2)
μ(Mo Kα) (mm^{-1})	0.367	2.329	0.733	1.379
F(000)	2704	1832	1416	1704
Crystal size (mm^3)	0.75 × 0.50 × 0.30	0.35 × 0.30 × 0.24	0.70 × 0.40 × 0.40	0.30 × 0.20 × 0.20
θ Range (°)	2.23−27.55	2.22−30.72	2.30−29.85	1.51−29.20
reflections collected	48000	52690	44720	61684
independent reflections (R_{int})	4610 (0.0369)	12660 (0.0805)	9115 (0.0493)	11731 (0.0822)
Max. and min. transmission	0.8979 and 0.7705	0.572 and 0.437	0.7428 and 0.6152	0.7623 and 0.6757
Data/restraints/parameters	4610/1/183	12660/0/480	9115/0/421	11731/0/495
goodness-of-fit on F^2	1.064	0.872	1.096	1.089
R_1, wR_2 [$I > 2\sigma(I)$]	0.0585, 0.1557	0.0354, 0.0626	0.0632, 0.1668	0.0838, 0.2281
R_1, wR_2 (all data)	0.0708, 0.1679	0.0613, 0.0663	0.0890, 0.1811	0.1250, 0.2495
largest diff. peak and hole (e Å^{-3})	0.456 and −0.251	2.082 and −0.653	0.928 and −0.558	3.428 and −0.674

by washing with H_2O and Et_2O (Ar = Ph) or pentane (Ar = C_6H_4F-4) and subsequent drying under vacuum. All other chemicals were commercially available and were used after appropriate purification. Solid methyllithium was obtained by removing all volatiles from 1.6 M solutions in diethyl ether (Acros). For the preparations of compounds **4** from **1**, idealized molecular weights according to mono-thf adducts of **1** are used, because of varying thf content from batch to batch.

NMR spectra were recorded at room temperature on 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 on a Varian Unity 500 spectrometer (^{1}H, 500 MHz; ^{13}C, 125.6 MHz; ^{11}B, 160.3 MHz). thf-d_8 (Aldrich) was distilled from sodium, and pyridine-d_5 was distilled from CaH_2. Chemical shifts for ^{1}H and ^{13}C NMR spectra are referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. ^{11}B NMR spectra are referenced externally to a 1 M solution of $NaBH_4$ in D_2O. ^{19}F NMR spectra are referenced externally to neat $CFCl_3$. ^{89}Y NMR spectra are referenced externally to a 1 M solution of YCl_3 in D_2O. Elemental analyses were performed by the Microanalytical Laboratory of the Organic Chemistry Department of RWTH Aachen University. Metal analysis was performed by complexometric titration. The sample (20−30 mg) was dissolved in acetonitrile (2 mL) and titrated with a 0.005 M aqueous solution of EDTA using xylenol orange as indicator and a 1 M ammonium acetate buffer solution (20 mL). IR spectra were recorded using KBr plates using a Nicolet Avatar 360 FT-IR spectrometer.

[$Li_3ScMe_6(thf)_{1.2}$] (1-Sc).[11b] Anhydrous $ScCl_3$ (757 mg, 5 mmol) was suspended in thf (20 mL) and stirred at 50 °C overnight. All volatiles were removed in vacuo and the solid residue was suspended in Et_2O (50 mL). The suspension was cooled to −78 °C and treated dropwise with a freshly prepared solution of methyllithium (659 mg, 30 mmol) in Et_2O (50 mL). The reaction mixture was stirred for 1 h at 0 °C and for further 2 h at room temperature. After filtering off a colorless precipitate and removing all volatiles under reduced pressure, the resulting sticky solid was triturated with pentane to give **1-Sc** as an off-white solid after drying; yield: 1.010 g (83%). ^{1}H NMR (400 MHz, thf-d_8): δ −0.90 (br s, 18H, ScMe), 1.77 (m, 4H, β-CH_2, thf), 3.62 (m, 4H, α-CH_2, thf). ^{13}C{^{1}H} NMR (100 MHz, thf-d_8): δ 14.2 (v br, ScMe), 26.3 (β-CH_2, thf), 68.2 (α-CH_2, thf). Anal. Calcd for $C_{10.8}H_{27.6}Li_3O_{1.2}Sc$: Sc, 18.54. Found: Sc, 18.74. Cooling a saturated Et_2O solution of **1-Sc** afforded **1′-Sc** as colorless crystals.

[$Li_3YMe_6(thf)_{1.3}$] (1-Y).[11b] Following the procedure described for **1-Sc**, anhydrous YCl_3 (5.260 g, 26.7 mmol) was reacted with methyllithium (3.516 g, 160 mmol) to afford **1-Y** after workup; yield: 6.350 g, (81%). ^{1}H NMR (500 MHz, thf-d_8): δ −1.10 (br s, 18H, YMe), 1.73 (m, 4H, β-CH_2, thf), 3.57 (m, 4H, α-CH_2, thf). ^{13}C{^{1}H} NMR (126 MHz, thf-d_8): δ 25.1 (β-CH_2, thf), 67.3 (α-CH_2, thf). Signals due to the YMe groups could not be detected. ^{7}Li{^{1}H} NMR (194 MHz, thf-d_8): δ 1.1. Anal. Calcd for $C_{11.2}H_{28.4}Li_3O_{1.3}Y$: Y, 30.27. Found: Y, 30.13. Cooling a saturated Et_2O solution of **1-Y** afforded **1′-Y** as colorless crystals.

[$Li_3GdMe_6(thf)_{2.4}$] (1-Gd). Following the procedure described for **1-Sc**, anhydrous $GdCl_3$ (1318 mg, 5 mmol) was reacted with methyllithium (659 mg, 30 mmol) to afford **1-Gd** after workup; yield: 989 mg, (45%). Anal. Calcd for $C_{15.6}H_{37.2}GdLi_3O_{2.4}$: Gd, 35.63. Found: Gd, 35.79.

[$Li_3TbMe_6(thf)_{1.5}$] (1-Tb). Following the procedure described for **1-Sc**, anhydrous $TbCl_3$ (1.326 g, 5 mmol) was reacted with methyllithium (659 mg, 30 mmol) to afford **1-Tb** after workup; yield: 1.200 g, (63%). Anal. Calcd for $C_{12}H_{30}Li_3O_{1.5}Tb$: Tb, 42.03. Found: Tb, 42.12. Cooling a saturated Et_2O solution of **1-Tb** afforded **1′-Tb** as colorless crystals.

[$Li_3DyMe_6(thf)_{1.65}$] (1-Dy). Following the procedure described for **1-Sc**, anhydrous $DyCl_3$ (1.344 g, 5 mmol) was reacted with methyllithium (659 mg, 30 mmol) to afford **1-Dy** after workup; yield: 1.500 g, (76%). Anal. Calcd for $C_{12.6}H_{31.2}DyLi_3O_{1.65}$: Dy, 41.40. Found: Dy, 41.34.

[$Li_3HoMe_6(thf)_{1.2}$] (1-Ho).[11b] Following the procedure described for **1-Sc**, anhydrous $HoCl_3$ (1.356 g, 5 mmol) was reacted with methyllithium (659 mg, 30 mmol) to afford **1-Ho** after workup; yield: 920 mg, (53%). Anal. Calcd for $C_{10.8}H_{27.6}HoLi_3O_{1.2}$: Ho, 45.50. Found: Ho, 45.22.

[$Li_3ErMe_6(thf)_2$] (1-Er). Following the procedure described for **1-Sc**, anhydrous $ErCl_3$(1.368 g, 5 mmol) was reacted with methyllithium (659 mg, 30 mmol) to afford **1-Er** after workup; yield: 1.515 g, (72%). Anal. Calcd for $C_{14}H_{34}ErLi_3O_2$: Er, 39.58. Found: Er, 39.40.

[Li$_3$TmMe$_6$(thf)$_{1.7}$] (1-Tm). Following the procedure described for **1-Sc**, anhydrous $TmCl_3$ (1.376 g, 5 mmol) was reacted with methyllithium (659 mg, 30 mmol) to afford **1-Tm** after workup; yield: 1.495 g, (74%). Anal. Calcd for $C_{12.8}H_{31.6}Li_3O_{1.7}$: Tm, 41.97. Found: Tm, 41.49.

[Li$_3$YbMe$_6$(thf)] (1-Yb).^{11b} Following the procedure described for **1-Sc**, anhydrous $YbCl_3$ (1.397 g, 5 mmol) was reacted with methyllithium (659 mg, 30 mmol) to afford **1-Yb** after workup; yield: 720 mg, (40%). Anal. Calcd for $C_{10}H_{26}Li_3OYb$: Yb, 48.58. Found: Yb, 48.38.

[Li$_3$LuMe$_6$(thf)] (1-Lu).^{11b} Following the procedure described for **1-Sc**, anhydrous $LuCl_3$ (1.407 g, 5 mmol) was reacted with methyllithium (659 mg, 30 mmol) to afford **1-Lu** after workup; yield: 1.640 g, (92%). ^{1}H NMR (400 MHz, thf-d_8): δ −1.03 (br s, 18H, LuMe), 1.77 (m, 4H, β-CH$_2$, thf), 3.61 (m, 4H, α-CH$_2$, thf). ^{13}C{^{1}H} NMR (100 MHz, thf-d_8): δ 9.0, 17.1 (br, LuMe), 26.2 (β-CH$_2$, thf), 68.2 (α-CH$_2$, thf). Anal. Calcd for $C_{10}H_{26}Li_3LuO$: Lu, 48.86. Found: Lu, 48.98.

[YMe$_2$(thf)$_5$][BPh$_4$] (3-Y).^{11b} To a solution of [Y(AlMe$_4$)$_3$] (**2-Y**) (250 mg, 0.714 mmol) in thf (2.5 mL) was added dropwise a solution of [NEt$_3$H][BPh$_4$] (300 mg, 0.712 mmol) in thf (4 mL) under stirring. Upon complete addition, the clear solution was treated with pentane (7 mL), resulting in precipitation of a colorless solid. The supernatant solution was decanted, and the solid dried thoroughly under reduced pressure. Recrystallization from thf/pentane, subsequent washing with pentane (3 × 5 mL) and drying under vacuum gave **3-Y** as colorless microcrystals (395 mg, 69%). ^{1}H NMR (400 MHz, thf-d_8): δ −1.07 and −0.95 (d, $^2J_{YH}$ = 1.7 Hz, 6H, YMe$_2$), 1.77 (m, 20H, β-CH$_2$, thf), 3.62 (m, 20H, α-CH$_2$, thf), 6.73 (t, $^3J_{HH}$ = 7.1 Hz, 4H, Ph-4), 6.87 (t, $^3J_{HH}$ = 7.1 Hz, 8H, Ph-3), 7.28 (m, 8H, Ph-2). ^{13}C{^{1}H} (100 MHz, thf-d_8): δ 17.5 (d, $^1J_{YC}$ = 46.8 Hz, YMe$_2$), 26.3 (β-CH$_2$, thf), 68.2 (α-CH$_2$, thf), 121.8 (Ph-4), 125.6 (q, $^3J_{BC}$ = 2.6 Hz, Ph-3), 137.0 (Ph-2), 165.0 (q, $^1J_{BC}$ = 49.4 Hz, Ph-1). ^{11}B{^{1}H} (128 MHz, thf-d_8): δ 6.6. ^{89}Y{^{1}H} NMR (19.6 MHz, thf-d_8): δ 650.9. ^{1}H NMR (400 MHz, pyridine-d_5): δ −0.02 (d, $^2J_{YH}$ = 1.3 Hz, 6H, YMe$_2$), 1.67 (m, 20H, β-CH$_2$, thf), 3.67 (m, 20H, α-CH$_2$, thf), 7.08 (t, $^3J_{HH}$ = 7.0 Hz, 4H, Ph-4), 6.87 (t, $^3J_{HH}$ = 7.5 Hz, 8H, Ph-3), 7.28 (m, 8H, Ph-2). ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_5): δ 18.0 (d, $^1J_{YC}$ = 39.0 Hz, $^1J_{CH}$ = 102.5 Hz, YMe$_2$), 26.1 (β-CH$_2$, thf), 68.2 (α-CH$_2$, thf), 122.5 (Ph-4), 126.3 (q, $^3J_{BC}$ = 2.6 Hz, Ph-3), 137.3 (Ph-2), 165.1 (q, $^1J_{11(B)C}$ = 49.4 Hz, septet, $^1J_{10(B)C}$ = 16.5 Hz, Ph-1). ^{11}B{^{1}H} NMR (128 MHz, pyridine-d_5): δ −5.9. ^{89}Y{^{1}H} NMR (19.6 MHz, pyridine-d_5): 216.4 (Y(pyridyl)$_2$), 349.5 (YMe(pyridyl)), 571.8 (YMe$_2$). Anal. Calcd for $C_{46}H_{66}BO_5Y$: C, 69.17; H, 8.33. Found: C, 68.98; H, 8.22.

[LuMe$_2$(thf)$_4$][BPh$_4$] (3-Lu). To a stirred solution of [Lu(AlMe$_4$)$_3$] (**2-Lu**) (200 mg, 0.458 mmol) in thf (3 mL) was added dropwise a solution of [NEt$_3$H][BPh$_4$] (183 mg, 0.435 mmol) in thf (1.5 mL). After complete addition the reaction mixture was stirred for a further 10 min. All volatiles were removed under reduced pressure, and the resulting colorless solid was dissolved in a minimum amount of thf. The saturated solution was cooled to −20 °C overnight. The resulting diffraction quality crystals were washed with pentane and dried in vacuo. (230 mg, 65% based on [NEt$_3$H][BPh$_4$]). ^{1}H NMR (400 MHz, thf-d_8): δ −0.94 (s, 6H, LuMe$_2$), 1.77 (m, 16H, β-CH$_2$, thf), 3.62 (m, 16H, α-CH$_2$, thf), 6.72 (t, $^3J_{HH}$ = 7.3 Hz, 4H, Ph-4), 6.87 (t, $^3J_{HH}$ = 7.3 Hz, 8H, Ph-3), 7.27 (m, 8H, Ph-2). ^{13}C{^{1}H} NMR (126 MHz, thf-d_8): δ 26.3 (β-CH$_2$, thf), 27.3 (LuMe$_2$), 68.2 (α-CH$_2$, thf), 121.9 (Ph-4), 125.6 (q, $^3J_{BC}$ = 2.6 Hz, Ph-3), 137.1 (m, Ph-2), 165.1 (q, $^1J_{BC}$ = 49.4 Hz, Ph-1). ^{11}B{^{1}H} NMR (160 MHz, thf-d_8): δ −6.56. Anal. Calcd for $C_{42}H_{58}BLuO_4$: C, 62.07; H, 7.19. Found: C, 61.69; H, 7.31.

[ScMe(thf)$_5$][BPh$_4$]$_2$ (4-Sc).^{11b} A mixture of **1-Sc** (100 mg, 0.438 mmol) and [NEt$_3$H][BPh$_4$] (923 mg, 2.19 mmol) was treated at 25 °C with thf (10 mL), resulting in the evolution of gas. After the colorless suspension was stirred for 30 min at 25 °C, the supernatant was decanted. The volatiles were removed under reduced pressure to give colorless microcrystals of **4-Sc** (193 mg, 42%). ^{1}H NMR (500 MHz, pyridine-d_5): δ 0.87 (s, 3H, ScMe), 1.60 (m, 20H, β-CH$_2$, thf), 3.64 (m, 20H, α-CH$_2$, thf), 7.08 (t, $^3J_{HH}$ = 7.8 Hz, 8H, Ph-4), 7.26 (m, 16H, Ph-3), 8.04 (m, 16H, Ph-2). ^{13}C{^{1}H} NMR (126 MHz, pyridine-d_5): δ 25.5 (β-CH$_2$, thf), 46.6 (ScMe), 67.5 (α-CH$_2$, thf), 122.0 (Ph-4), 125.8 (Ph-3), 136.8 (Ph-2), 164.8 (q, $^1J_{BC}$ = 49.3 Hz, Ph-1). ^{11}B{^{1}H} NMR (160 MHz, pyridine-d_5): δ 5.8. Anal. Calcd for $C_{69}H_{83}B_2O_5Sc$: Sc, 4.25. Found: Sc, 4.20.

[YMe(thf)$_6$][BPh$_4$]$_2$ (4-Y).^{11} Following an analogous procedure to prepare **4-Sc**, **1-Y** (1.50 g, 5.51 mmol) and [NEt$_3$H][BPh$_4$] (11.6 g, 27.6 mmol) gave **4-Y** as colorless crystals (4.24 g, 65%). ^{1}H NMR (400 MHz, pyridine-d_5): δ 0.69 (d, $^2J_{YH}$ = 2.1 Hz, 3H, YMe), 1.63 (m, 24H, β-CH$_2$, thf), 3.67 (m, 24H, α-CH$_2$, thf) 7.10 (t, $^3J_{HH}$ = 7.0 Hz, 8H, Ph-4), 7.26 (t, $^3J_{HH}$ = 7.4 Hz, 16H, Ph-3), 8.04 (m, 16H, Ph-2). ^{13}C NMR (100 MHz, pyridine-d_5): δ 27.6 (β-CH$_2$, thf), 32.8 (dq, $^1J_{YC}$ = 53.6 Hz, $^1J_{CH}$ = 105.5 Hz, YMe), 69.7 (α-CH$_2$, thf), 124.2 (Ph-4), 128.0 (Ph-3), 139.0 (Ph-2), 166.8 (q, $^1J_{BC}$ = 49.2 Hz, Ph-1). ^{11}B{^{1}H} NMR (128 MHz, pyridine-d_5): δ −4.7. ^{89}Y{^{1}H} NMR (19.6 MHz, pyridine-d_5): δ 433.2. Anal. Calcd for $C_{73}H_{91}B_2O_6Y$: C, 74.16; H, 8.00; Y, 7.57. Found: C, 73.27; H, 7.22; Y, 7.33.

[LaMe(thf)$_6$][BPh$_4$]$_2$ (4-La). To a solution of [La(AlMe$_4$)$_3$] (**2-La**) (200 mg, 0.5 mmol) in cold thf (3 mL) was added dropwise [NEt$_3$H][BPh$_4$] (422 mg, 1 mmol) in thf (5 mL) under stirring. An immediate gas evolution and precipitation of an off-white solid was observed. Upon complete addition, the reaction mixture was stirred for a further 5 minutes. The suspension was decanted, and the solid was washed with thf and pentane. Drying of the solid under reduced pressure gave **4-La** as an off-white solid (434 mg, 71%). ^{1}H (400 MHz, pyridine-d_5): δ 0.11 (1:1:1 t, $^2J_{HD}$ = 2.0 Hz, CH$_3$D), 0.77 (s, LaMe), 1.63 (m, 24H, β-CH$_2$, thf), 3.66 (m, 24H, α-CH$_2$, thf), 7.08 (t, $^3J_{HH}$ = 7.3 Hz, 8H, Ph-4), 7.24 (t, $^3J_{HH}$ = 7.5 Hz, 16H, Ph-3), 8.03 (m, 16H, Ph-2). The sample was prepared at −40 °C and immediately frozen with liquid N$_2$ prior to measurement. Methane evolution due to decomposition was observed as soon as the solvent melted. The intensity of the LaMe protons was therefore found to be too low and the signal for CH$_3$D was detected. Because of the fast decomposition, no ^{13}C NMR was recorded. ^{1}H NMR (200 MHz, suspension in thf-d_8): δ −0.30 (s, 3H, LaMe), 1.77 (m, 28H, β-CH$_2$, thf), 3.61 (m, 28H, α-CH$_2$, thf), 6.73 (tt, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 2.2 Hz, 8H, Ph-4), 6.87 (t, $^3J_{HH}$ = 7.3 Hz, 16H, Ph-3), 7.27 (m, 16H, Ph-2). Anal. Calcd for $C_{73}H_{91}B_2LaO_6$: C, 71.57; H, 7.49. Found: C, 72.05; H, 7.66.

[LaMe(thf)$_6$][B(C$_6$H$_4$F-4)$_4$]$_2$ (4′-La). To a stirred solution of of [La(AlMe$_4$)$_3$] (**2-La**) (60 mg, 0.150 mmol) in thf (2 mL) was added dropwise a solution of [NEt$_3$H][B(C$_6$H$_4$F-4)$_4$] (67 mg, 0.135 mmol) in thf (2 mL). Upon complete addition, the solution was cooled to −30 °C and a second solution of [NEt$_3$H][B(C$_6$H$_4$F-4)$_4$] (81 mg, 0.165 mmol) in thf (2 mL) was carefully layered on top of the cold solution. The solution was kept at −30 °C overnight, after which diffraction quality crystals had formed. Washing with thf (2 × 5 mL) and pentane (2 × 5 mL) and drying in vacuo afforded a colorless solid (155 mg, 72%). ^{1}H NMR (400 MHz, thf-d_8): δ −0.22 (s, LaMe), 1.77 (m, 24H, β-CH$_2$, thf), 3.61 (m, 24H, α-CH$_2$, thf), 6.60 (t, $^3J_{HH}$ = 9.3 Hz, 16H, C_6H_4F-3), 7.16 (m, 16H, C_6H_4F-2). ^{13}C NMR (100 MHz, thf-d_8): δ 26.4 (β-CH_2, thf), 68.2 (α-CH_2, thf), 112.2 (C_6H_4F-3), 137.7 (C_6H_4F-2), 159.44 (q, $^1J_{BC}$ = 50.3 Hz, C_6H_4F-1), 162.1 (C_6H_4F-4). The signal of the methyl carbon was not observed. ^{19}F NMR (188 MHz, thf-d_8): δ −121.6. Anal. Calcd for $C_{73}H_{83}B_2F_8LaO_6$: C, 64.05; H, 6.11. Found: C, 64.16; H, 6.10.

[CeMe(thf)$_6$][BPh$_4$]$_2$ (4-Ce). To a stirred solution of [Ce(AlMe$_4$)$_3$] (**2-Ce**) (40 mg, 0.100 mmol) in thf (1 mL) was added dropwise a solution of [NEt$_3$H][BPh$_4$] (40 mg, 0.095 mmol) in thf (1 mL). Gas evolution was observed and upon complete addition the stirrer bar was removed and the solution cooled to −30 °C. A solution of [NEt$_3$H][BPh$_4$] (44 mg, 0.105 mmol) in thf (1 mL) was carefully layered on top, and the reaction was left to stand at −30 °C. Overnight colorless crystals of **4-Ce** formed which were washed with thf (2 × 3 mL) and pentane (2 × 3 mL) and subsequently dried under reduced pressure (104 mg, 85%). Anal. Calcd for $C_{73}H_{91}B_2CeO_6$: C, 71.50; H, 7.48. Found: C, 70.79; H, 7.45.

[PrMe(thf)$_6$][BPh$_4$]$_2$ (4-Pr). To a stirred solution of [Pr(AlMe$_4$)$_3$] (**2-Pr**) (50 mg, 0.124 mmol) in thf (1 mL) was added dropwise a solution of [N^{n}Bu$_3$H][BPh$_4$] (57 mg, 0.113 mmol) in thf (1 mL). Gas evolution was observed and upon complete addition the stirrer bar was removed and the green solution cooled to −30 °C. A solution of [N^{n}Bu$_3$H][BPh$_4$] (69 mg, 0.136 mmol) in thf (1 mL) was carefully layered on top, and the reaction was left to stand at −30 °C. Pale green crystals of **4-Pr** formed overnight which were washed with thf (2 × 3 mL) and pentane (2 × 3 mL) and dried under reduced pressure; yield: 120 mg (79%). Anal. Calcd for $C_{73}H_{91}B_2O_6Pr$: C, 71.46; H, 7.48. Found: C, 70.28; H, 7.34.

[NdMe(thf)$_6$][BPh$_4$]$_2$ (4-Nd).[11b] **4-Nd** was prepared analogous to **4-La** from [Nd(AlMe$_4$)$_3$] (**2-Nd**) (304 mg, 0.749 mmol) and [NEt$_3$H][BPh$_4$] (632 mg, 1.50 mmol) to afford **4-Nd** as a pale blue solid; yield: 650 mg (70%). Anal. Calcd for $C_{73}H_{91}B_2NdO_6$: C, 71.26; H, 7.45. Found: C, 70.22; H, 7.46.

[SmMe(thf)$_6$][BPh$_4$]$_2$ (4-Sm). To a solution of [Sm(AlMe$_4$)$_3$] (**2-Sm**) (180 mg, 0.437 mmol) in thf (2 mL) [NEt$_3$H][BPh$_4$] (162 mg, 0.384 mmol) in thf (1 mL) were added dropwise under stirring. An immediate gas evolution was observed. After complete addition, the reaction mixture was cooled to −30 °C. A solution of [NEt$_3$H][BPh$_4$] (207 mg, 0.491 mmol) in thf (1 mL) was then carefully layered on top, and the reaction mixture was left to stand overnight at −30 °C. The resulting dark-red crystals of **4-Sm** were washed thoroughly with thf and pentane and subsequently dried under reduced pressure; yield 476 mg (88%). Anal. Calcd for $C_{73}H_{91}B_2O_6Sm$: C, 70.91; H, 7.42. Found: C, 70.03; H, 7.59.

[SmMe(thf)$_6$][B(C$_6$H$_4$F-4)$_4$]$_2$ (4′-Sm). Following the same procedure as for **4′-La** diffraction quality single crystals were obtained overnight.

[GdMe(thf)$_6$][BPh$_4$]$_2$ (4-Gd). Method A. To a solution of **1-Gd** (150 mg, 0.441 mmol) in thf (4 mL) was slowly added solid [NEt$_3$H][BPh$_4$] (929 mg, 2.20 mmol) under stirring. An immediate gas evolution and precipitation of a solid toward the end of the addition was observed. Upon complete addition, the reaction mixture was stirred for a further 45 min. The suspension was decanted, and the solid washed thoroughly with thf and subsequently with pentane. Drying of the solid under reduced pressure yielded **4-Gd** as an off-white solid (207 mg, 38%).

Method B. To a stirred solution of **2-Gd** (80 mg, 0.191 mmol) in thf (2 mL) was added dropwise a solution of [NEt$_3$H][BPh$_4$] (73 mg, 0.172 mmol) in thf (1 mL). The solution was cooled to −40 °C. Subsequently a solution of [NEt$_3$H][BPh$_4$] (89 mg, 0.210 mmol) was layered on top of the reaction mixture and left at −40 °C. Diffraction quality crystals of **4-Gd** formed (152 mg, 64%) overnight. Anal. Calcd for $C_{73}H_{91}B_2GdO_6$: C, 70.52; H, 7.38; Gd, 12.64. Found: C, 69.94; H, 7.39; Gd, 12.52.

[TbMe(thf)$_6$][BPh$_4$]$_2$ (4-Tb). This compound was prepared analogous to **4-Gd** via route A by reaction of **1-Tb** (150 mg, 0.439 mmol) with [NEt$_3$H][BPh$_4$] (924 mg, 2.19 mmol) to yield **4-Tb** as an off-white solid; yield: 354 mg (65%). Anal. Calcd for $C_{73}H_{91}B_2O_6Tb$: Tb, 12.76. Found: Tb, 12.65.

[DyMe(thf)$_6$][BPh$_4$]$_2$ (4-Dy). This compound was prepared analogous to **4-Gd** via route A by reaction of **1-Dy** (150 mg, 0.434 mmol) with [NEt$_3$H][BPh$_4$] (914 mg, 2.17 mmol) to yield **4-Dy** as a very pale yellow solid; yield: 295 mg (54%). Anal. Calcd for $C_{73}H_{91}B_2DyO_6$: Dy, 13.01. Found: Dy, 12.69.

[HoMe(thf)$_6$][BPh$_4$]$_2$ (4-Ho).[11b] This compound was synthesized from **1-Ho** (100 mg, 0.287 mmol) and [NEt$_3$H][BPh$_4$] (605 mg, 1.437 mmol) analogous to the synthesis of **4-Sc** to yield pink microcrystals of **4-Ho** (359 mg, 100%). Anal. Calcd for $C_{73}H_{91}B_2HoO_6$: Ho, 13.18. Found: Ho, 13.23.

[ErMe(thf)$_6$][BPh$_4$]$_2$ (4-Er). This compound was prepared analogous to **4-Gd** via route A by reaction of **1-Er** (150 mg, 0.428 mmol) with [NEt$_3$H][BPh$_4$] (902 mg, 2.14 mmol) to yield **4-Er** as a pink solid (287 mg, 54%). Anal. Calcd for $C_{73}H_{91}B_2ErO_6$: Er, 13.34. Found: Er, 13.07.

[TmMe(thf)$_5$][BPh$_4$]$_2$ (4-Tm). This compound was prepared analogous to **4-Gd** via route A by reaction of **1-Tm** (150 mg, 0.426 mmol) with [NEt$_3$H][BPh$_4$] (898 mg, 2.13 mmol) to yield **4-Tm** as a yellow-green solid (414 mg, 82%). Anal. Calcd for $C_{69}H_{83}B_2O_5Tm$: Tm, 14.28. Found: Tm, 14.68.

[YbMe(thf)$_6$][BPh$_4$]$_2$ (4-Yb).[11b] This compound was synthesized from **1-Yb** (100 mg, 0.281 mmol) and [NEt$_3$H][BPh$_4$] (592 mg, 1.404 mmol) analogous to the synthesis of **4-Sc** to yield **4-Yb** as yellow microcrystals (339 mg, 96%). Anal. Calcd for $C_{73}H_{91}B_2YbO_6$: Yb, 13.74. Found: Yb, 13.69.

[LuMe(thf)$_6$][BPh$_4$]$_2$ (4-Lu).[11b] This compound was synthesized from **1-Lu** (100 mg, 0.279 mmol) and [NEt$_3$H][BPh$_4$] (588 mg, 1.396 mmol) analogous to the synthesis of **4-Sc** to yield **4-Lu** as off-white microcrystals (292 mg, 83%). ^{1}H NMR (500 MHz, pyridine-d_5): δ 0.68 (s, 3H, LuMe), 1.59 (m, 24H, β-CH_2, thf), 3.64 (m, 24H, α-CH_2, thf), 7.10 (t, $^3J_{HH}$ = 7.3 Hz, 8H, Ph-4), 7.24 (m, 16H, Ph-3), 8.07 (m, 16H, Ph-2). ^{13}C{^{1}H} NMR (126 MHz, pyridine-d_5): δ 25.5 (β-CH_2, thf), 34.5 (LuMe), 67.5 (α-CH_2, thf), 122.0 (Ph-4), 125.8 (Ph-3), 136.8 (Ph-2), 164.8 (q, $^1J_{BC}$ = 49.4 Hz, Ph-1). ^{11}B{^{1}H} NMR (160 MHz, pyridine-d_5): δ −5.8. Anal. Calcd for $C_{73}H_{91}B_2LuO_6$: C, 69.53; H, 7.27; Lu, 13.87. Found: C, 70.86; H, 7.49; Lu, 13.83.

[Y(OCMePh$_2$)$_2$(thf)$_4$][BPh$_4$] (5). To a stirred solution of **3-Y** (100 mg, 0.125 mmol) in thf (2.3 mL), solid benzophenone (46 mg, 0.250 mmol) was added. The reaction mixture was stirred for 5 min. Subsequently pentane (3 mL) was added to give a suspension of light pink microcrystals. Decanting the solvent and subsequently washing the solid with pentane and drying in vacuo yielded **5**; yield: 123 mg, (90%). ^{1}H NMR (400 MHz, pyridine-d_5): δ 1.61 (m, 16H, β-CH_2, thf), 1.97 (s, 6H, OC*Me*Ph$_2$), 3.64 (m, 16H, α-CH_2, thf), 7.10 (t, $^3J_{HH}$ = 7.0 Hz, 4H, Ph-4), 7.17−7.24 and 7.47−7.53 (various m, 20H, OCMe*Ph*$_2$), 7.28 (t, $^3J_{HH}$ = 7.3 Hz, 8H, Ph-3), 8.07 (m, 8H, Ph-2). ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_5): δ 25.9 (β-CH_2, thf), 33.3 (OC*Me*Ph$_2$), 67.9 (α-CH_2, thf), 80.5 (d, $^2J_{YC}$ = 6.1 Hz, O*C*MePh$_2$), 122.4 (Ph-4), 126.2 and 126.3 (OCMe*Ph*$_2$), 126.3 (Ph-3), 127.0 and 128.1 (OCMe*Ph*$_2$), 137.2 (Ph-2), 152.64 (OCMe*Ph*$_2$), 165.1 (q, $^1J_{YC}$ = 48.6 Hz, Ph-1). ^{11}B{^{1}H} NMR (128 MHz, pyridine-d_5): δ −5.7. Anal. Calcd for $C_{68}H_{78}BO_6Y$: Y, 8.15. Found: Y, 7.61.

[Y(OCMePh$_2$)(thf)$_5$][BPh$_4$]$_2$ (6). A stirred suspension of **4-Y** (60 mg, 51 μmol) in thf (4 mL) was reacted with solid benzophenone (9.3 mg, 51 μmol). The resulting colorless solution was heated to 50 °C overnight to give diffraction quality crystal of **6** (52 mg, 79%). ^{1}H NMR (400 MHz, pyridine-d_5): δ 1.66 (m, 20H, β-CH$_2$, thf), 2.00 and 2.26 (s, 3H, OC*Me*Ph$_2$), 3.68 (m, 20H, α-CH$_2$, thf), 7.09 (t, $^3J_{HH}$ = 7.3 Hz, 8H, Ph-4), 7.25 (t, $^3J_{HH}$ = 7.5 Hz, 16H, Ph-3), 7.33−7.61 (various m, 10H, OCMe*Ph*$_2$), 8.03 (m, 16H, Ph-2). ^{13}C{^{1}H} NMR (100 MHz, pyridine-d_5): δ 25.9 (β-CH$_2$, thf), 33.3 (OC*Me*Ph$_2$), 68.0 (α-CH$_2$, thf), 83.5 (d, $^2J_{YC}$ = 5.2 Hz, O*C*MePh$_2$), 122.5 (Ph-4), 126.2 (q, $^3J_{BC}$ = 3.4 Hz, Ph-3), 127.0, 127.4, 127.7, 128.1, 128.7 (all OCMe*Ph*$_2$), 137.2 (Ph-2), 165.1 (q, $^1J_{BC}$ = 49.4 Hz, Ph-1). ^{11}B{^{1}H} NMR (128 MHz, pyridine-d_5): δ −5.8. Anal. Calcd for $C_{82}H_{93}B_2O_6Y$: Y, 6.92. Found: Y, 7.02.

[YMeI(thf)$_5$][BPh$_4$] (7). To a stirred suspension of **4-Y** (1.500 g, 1.28 mmol) in thf (5 mL) was added solid sodium iodide (191 mg, 1.28 mmol) at once. After ~2 min the solid dissolved and a colorless precipitate formed quickly. The reaction mixture was stirred overnight. Filtration, thorough washing with thf (3 × 4 mL), pentane, and drying in vacuo yielded **7** as a colorless powder (908 mg, 78%). ^{1}H NMR (400 MHz, pyridine-d_5): δ 0.44 (d, $^2J_{YH}$ = 2.0 Hz, 3H, YMe), 1.60 (m, β-CH$_2$, thf), 3.64 (m, α-CH$_2$, thf), 7.12 (t, $^3J_{HH}$ = 7.3 Hz, 4H, Ph-4), 7.29 (t, $^3J_{HH}$ = 7.5 Hz, 8H, Ph-3), 8.07 (m, 8H, Ph-2). ^{13}C NMR (100 MHz, pyridine-d_5): δ 25.8 (α-CH$_2$, thf), 26.7 (d, $^1J_{YC}$ = 52.0 Hz, YMe), 67.9 (β-CH$_2$, thf), 122.4 (Ph-4), 126.6 (m, Ph-3), 137.2 (m, Ph-2), 165.1 (q, $^1J_{BC}$ = 49.4 Hz, Ph-1). ^{11}B{^{1}H} NMR (128 MHz, pyridine-d_5): δ −5.72. Anal. Calcd for $C_{45}H_{63}BIO_5Y$: Y, 9.76. Found: Y, 8.75.

[YMeI$_2$(thf)$_3$] (8). To a stirred suspension of **4-Y** (1.800 g, 1.53 mmol) in thf (6 mL) were added at once 2 equiv of dry sodium iodide (459 mg, 3.06 mmol) at room temperature. After a few min part of the solid dissolved but soon after a colorless precipitate formed. The reaction mixture was stirred overnight and filtered. Repeated washing of the precipitate with thf and pentane, followed by drying in vacuo afforded **8** as a colorless powder (440 mg, 50%). ^{1}H NMR (400 MHz, pyridine-d_5): δ 0.44 (d, $^2J_{YH}$ = 1.8 Hz, 3H, YMe), 1.60 (m, 12H, β-CH$_2$ thf), 3.63 (m, 12H, α-CH$_2$ thf).^{13}C NMR (100 MHz, pyridine-d_5): δ 25.86 (β-CH$_2$, thf), 27.23 (d, $^1J_{YC}$ = 52.0 Hz), 67.9 (α-CH$_2$, thf). ^{89}Y NMR (19.6 MHz, pyridine-d_5): δ 543.0. Anal. Calcd for $C_{13}H_{27}I_2O_3Y$: C, 27.20; H, 4.74. Found: C, 27.00; H, 4.56.

[YMeI(py)$_5$]I (8′). Solid **8** was dissolved in a minimum amount of pyridine, and pentane was layered on top of the solution. Cooling the mixture to −40 °C resulted in the formation of a biphasic mixture, which became homogeneous again upon warming to room temperature. From this mixture, single crystals of **8′** formed after standing overnight. Anal. Calcd for $C_{26}H_{28}I_2N_5Y$: C, 41.43; H, 3.75; N, 9.30. Found: C, 42.00; H, 3.84; N, 9.72.

[YMe(BH$_4$)(thf)$_5$][BPh$_4$] (9). To a stirred suspension of **4-Y** (2.400 g, 2.04 mmol) in thf (15 mL) was added at once solid NaBH$_4$ (77 mg, 2.04 mmol), and the resulting clear solution was stirred for 30 min, after which it was filtered. All volatiles were removed under reduced pressure, and the resulting solid was redissolved at room temperature in a minimum amount of thf. Cooling this saturated solution to −30 °C yielded a first crop of **9** (734 mg, 45%). This process of fractional crystallization could be repeated several times to increase the total yield. Diffraction quality crystals were grown from slow cooling of a saturated thf solution of **9**. ^{1}H NMR (400 MHz, thf-d_8): δ −0.89 (d, $^2J_{YH}$ = 1.8 Hz, 3H, YMe), −0.01 (q, $^1J_{BH}$ = 80.5 Hz, 4H, YBH$_4$), 1.76 (m, 20H, β-CH$_2$, thf), 3.61 (m, 20H, α-CH$_2$, thf), 6.71 (t, $^3J_{HH}$ = 7.3 Hz, 4H, Ph-4), 6.85 (t, $^3J_{HH}$ = 7.3 Hz, 8H, Ph-3), 7.27 (m, 8H, Ph-2). ^{13}C NMR (100 MHz, thf-d_8): δ 20.9 (d, $^1J_{YC}$ = 51.2 Hz, YMe), 26.2 (β-CH$_2$, thf), 68.2 (α-CH$_2$, thf), 121.7 (Ph-4), 125.5 (m, Ph-3), 137.0 (m, Ph-2), 165.0 (q, $^1J_{BC}$ = 49.4 Hz, Ph-1). ^{11}B NMR (128 MHz, thf-d_8): δ −6.52 (BPh$_4$), −30.2 (quintet, $^1J_{BH}$ = 80.5 Hz, BH$_4$). ^{89}Y{^{1}H} NMR (19.6 MHz, thf-d_8): δ 343.8. IR (KBr): ν = 2230 (strong br, BH$_4$), 2425 cm^{-1} (sharp, BH$_4$). Anal. Calcd for $C_{45}H_{67}B_2O_5Y$: Y, 11.13. Found: Y, 11.31.

Computational Method. On the basis of our previous work, it has been shown that the lanthanide center could be treated with f-in-core effective core potentials (ECPs).[44] Thus, La, Sm, and Lu were treated with a Stuttgart-Dresden pseudopotential in combination with its adapted basis set.[45] In both cases, the basis set has been augmented by a set of polarization functions. Carbon, oxygen, and hydrogen atoms have been described with a 6−31G(d,p) double-ζ basis set.[46] Calculations were carried out at the DFT level of theory using the hybrid functional B3PW91.[47,48] Geometry optimizations were carried out without any symmetry restrictions, and the nature of the *extrema* (*minima*) was verified with analytical frequency calculations. All these calculations were performed with the Gaussian 03[49] suite of programs. The electronic density has been analyzed using the Natural Bond Orbital (NBO) technique.[50]

Crystal Structure Determinations. All X-ray diffraction experiments were carried out at on a Bruker SMART diffractometer using Mo Kα X-radiation (λ = 0.71073 Å) and ω-scans. Diffracted intensities were integrated from several series of exposures.[51] Absorption corrections were based on multiple and symmetry-equivalent measurements. The structures were solved with the program SHELXS-86[52] using direct methods and were refined using SHELXL[53] against all F_o^2 data with hydrogen atoms riding in calculated positions. All other atoms were refined anisotropically. Only the structure of **4-La′** was solved by isotypic replacement using the coordinates of **4-Sm′**. The hydrogen atoms of the BH$_4$-group in **9** could be localized in a Fourier difference map and refined in their position. **4-Dy** contains co-crystallized thf in the lattice, **8** contains the solvent molecule pyridine. For the graphical representation, the Oak Ridge Thermal Ellipsoid Plot (ORTEP) program was used as implied in the program system WinGX.[54] Selected crystal parameters and results of the structure refinements are given in Table 3. Crystallographic information has been deposited to the Cambridge Crystallographic Data Centre.

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Supporting Information Available: Complete ref 49; complete CIF files giving full crystallographic data for **1′-Sc**, **1′-Y**, **1′-Tb**, **3-Lu**, **4′-La**, **4′-Sm**, **4-Dy**, **6**, **8′**, and **9**; lists of selected bond lengths and angles of all the above structures; crystallographic data of all structures; details of calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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