

Cationic Rare-Earth Metal Trimethylsilylmethyl Complexes Supported by THF and 12-Crown-4 Ligands: Synthesis and Structural Characterization

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To expand the limited range of rare-earth metal cationic alkyl complexes known, a series of mono- and dicationic trimethylsilylmethyl complexes supported by THF and 12-crown-4 ligands with $[\text{BPh}_4]^-$, $[\text{BPh}_3(\text{CH}_2\text{SiMe}_3)]^-$, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, $[\text{B}(\text{C}_6\text{F}_5)_3(\text{CH}_2\text{SiMe}_3)]^-$, and $[\text{Al}(\text{CH}_2\text{SiMe}_3)_4]^-$ anions were prepared from corresponding neutral precursors $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3\text{L}_n]$ ($\text{Ln} = \text{Sc}, \text{Y}, \text{Lu}$; $\text{L} = \text{THF}$, $n = 2$ or 3 ; $\text{L} = 12\text{-crown-4}$, $n = 1$) as solvent-separated ion pairs. The syntheses of the monocationic derivatives $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(12\text{-crown-4})_n(\text{THF})_m]^+[A]^-$ are all high yielding and proceed rapidly in THF solution at room temperature. A “one pot” procedure using the neutral species directly for the syntheses of a number of lutetium and yttrium dicationic derivatives $[\text{Ln}(\text{CH}_2\text{SiMe}_3)(12\text{-crown-4})_n(\text{THF})_m]^2+[A]^-_2$ with a variety of different anions, a class of compounds previously limited to just a few examples, is presented. When BPh_3 is used to generate the ion triple, the presence of 12-crown-4 is required for complete conversion. Addition of a second equiv of 12-crown-4 and a third equiv of $[\text{NMe}_2\text{PhH}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ abstracts a third alkyl group from $[\text{Ln}(\text{CH}_2\text{SiMe}_3)(12\text{-crown-4})_2(\text{THF})_x]^2+[\text{B}(\text{C}_6\text{F}_5)_4]^-_2$ ($\text{Ln} = \text{Y}, \text{Lu}$). X-ray crystallography and variable-temperature (VT) NMR spectroscopy reveal a structural diversity within the known series of neutral 12-crown-4 supported tris(trimethylsilylmethyl) complexes $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(12\text{-crown-4})]$ ($\text{Ln} = \text{Sc}, \text{Y}, \text{Sm}, \text{Gd-Lu}$) in the solid and solution states. The X-ray structure of $[\text{Sc}(\text{CH}_2\text{SiMe}_3)_3(12\text{-crown-4})]$ exhibits incomplete 12-crown-4 coordination. VT NMR spectroscopy indicates fluxional 12-crown-4 coordination on the NMR time scale. X-ray crystallography of only the second structurally characterized dicationic rare-earth metal alkyl complex $[\text{Y}(\text{CH}_2\text{SiMe}_3)(12\text{-crown-4})(\text{THF})_3]^2+[\text{BPh}_4]^-_2$ shows exocyclic 12-crown-4 coordination at the 8-coordinate metal center with well separated counteranions. ^{11}B and ^{19}F NMR spectroscopy of all mono- and dicationic rare-earth metal complexes reported demonstrate that the anions are symmetrical and noncoordinating on the NMR time scale. A series of trends within the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR resonances arising from the Ln-CH_2 groups and, in the case of yttrium, the $^1J_{\text{YC}}$ coupling constants at the Y-CH_2 group and the ^{89}Y chemical shift values are discussed.

Introduction

Cationic complexes of the rare-earth metals containing only π -bound hydrocarbyl ligands $[\text{Ln}(\text{L}_n\text{X})_2\text{L}_m]^+[A]^-$ ($\text{Ln} = \text{rare-earth metal}$, $\text{L}_n\text{X} = \text{monoanionic ligand}$, $\text{L} = \text{neutral ligand}$, $\text{A} = \text{anion}$), a single σ -bound alkyl, and another monoanionic ligand $[\text{Ln}(\text{L}_n\text{X})\text{RL}_m]^+[A]^-$ or two σ -bound alkyls $[\text{LnR}_2\text{L}_m]^+[A]^-$ have been shown to be isolable species. Complexes in the latter group in particular show enhanced thermal stability with respect to the neutral tris(alkyl) precursors and often incorporate neutral macrocyclic ligands.³ Improved catalytic behavior has been noted for monocationic rare-earth metal complexes in comparison

to the parent neutral species, including ethylene and α -olefin polymerization,^{2a–b,e,k,m–o;3c–g} styrene polymerization and styrene–ethylene copolymerization,^{2j} diene polymerization,^{10a,v} intramolecular hydroamination,⁴ and alkyne dimerization.²ⁱ Compounds of the form $[\text{LnR}_2\text{L}_n]^+[A]^-$ have the advantage that a second alkyl group is available for abstraction to give a mono(alkyl) dication of the form $[\text{LnRL}_n]^2+[A]^-_2$, which has been implicated as the active species in the polymerization of ethylene.^{3c–e} Allyl dications have also been discussed in the context of diene polymerization.⁵ Despite the fact that cationic rare-earth metal complexes containing a σ -bound alkyl were first reported in 1992,^{2c} these species still remain relatively unexplored.⁶ We report here a systematic multinuclear study of neutral, monocationic, and

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dicationic rare-earth metal trimethylsilylmethyl complexes supported by THF and 12-crown-4, which expands the relatively small number of such complexes hitherto known in the literature. In particular, we present here that dicationic complexes with a trimethylsilylmethyl ligand are generally

accessible and report on the second structurally authenticated example of this type of cation.

Results and Discussion

Syntheses. We have previously reported the synthesis and characterization of neutral rare-earth metal trimethylsilylmethyl complexes supported by crown ether ligands $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(12\text{-crown-4})]$ ($\text{Ln} = \text{Sc}$ (**4**), Y (**5**), and Lu (**6**)) via reaction of $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_n]$ ($\text{Ln} = \text{Sc}$ (**1**), $n = 2$; Y (**2**), $n = 2, 3$, and Lu (**3**), $n = 2$) with 12-crown-4.^{3a,b} We have also previously reported solution and solid-state characterization of certain mono- and dicationic trimethylsilylmethyl rare-earth metal complexes incorporating solvent separated ion pairs supported by THF and crown ether ligands that are formed by reaction of BPh_3 , $[\text{NEt}_3\text{H}]^+[\text{BPh}_4]^-$, or $[\text{NMe}_2\text{PhH}]^+[\text{BPh}_4]^-$ with the appropriate THF- and crown ether-supported neutral rare-earth metal precursors **1–6**.^{3a–c} Furthermore, the alkyl abstraction reaction of **2** with $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$ resulted in the formation of the solvent-separated, crystallographically characterized ion pair $[\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_4]^+[\text{Al}(\text{CH}_2\text{SiMe}_3)_4]^-$.^{3c}

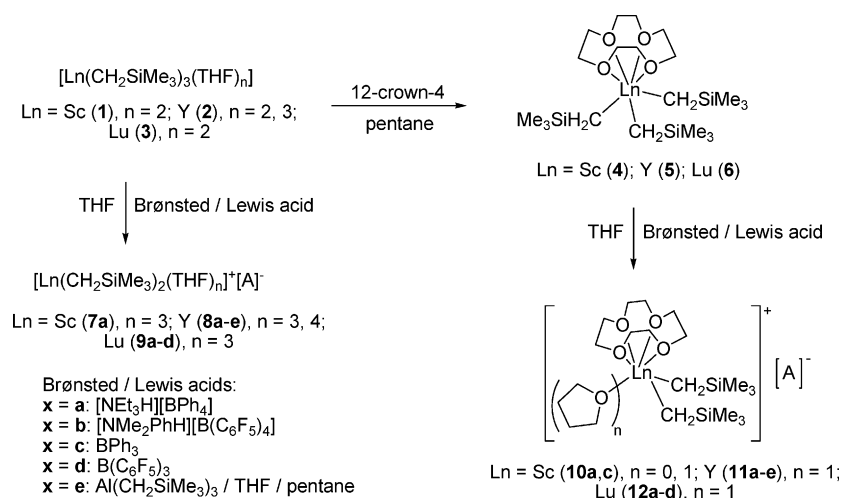
The monocationic compounds here presented have various anions ($\mathbf{x} = \mathbf{a}$: $[\text{BPh}_4]^-$; \mathbf{b} : $[\text{B}(\text{C}_6\text{F}_5)_4]^-$; \mathbf{c} : $[\text{BPh}_3(\text{CH}_2\text{SiMe}_3)]^-$; \mathbf{d} : $[\text{B}(\text{C}_6\text{F}_5)_3(\text{CH}_2\text{SiMe}_3)]^-$; \mathbf{e} : $[\text{Al}(\text{CH}_2\text{SiMe}_3)_4]^-$) and either coordinated THF ($[\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_n]^+[\text{A}]^-$; $\text{Ln} = \text{Sc}$ (**7a**): $n = 3$; Y (**8x**): $n = 3, 4$; $\mathbf{x} = \mathbf{a–e}$; Lu (**9x**): $n = 3$, $\mathbf{x} = \mathbf{a–d}$) or 12-crown-4 ligands ($[\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(12\text{-crown-4})(\text{THF})_n]^+[\text{A}]^-$; $\text{Ln} = \text{Sc}$ (**10x**): $n = 0, 1$; $\mathbf{x} = \mathbf{a, c}$; Y (**11x**): $n = 1$; $\mathbf{x} = \mathbf{a–e}$; Lu (**12x**): $n = 1$, $\mathbf{x} = \mathbf{a–d}$; Scheme 1) at the metal center. Their syntheses proceed in 74–99% yield from the neutral rare-earth metal precursors **1–6** by reaction with the Brønsted acids $[\text{NEt}_3\text{H}]^+[\text{BPh}_4]^-$ (**a**), $[\text{NMe}_2\text{PhH}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**b**), or the Lewis acids BPh_3 (**c**), $\text{B}(\text{C}_6\text{F}_5)_3$ (**d**), or $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$ (**e**). All complexes are highly soluble in THF-*d*₈, CD_2Cl_2 , and pyridine-*d*₅ and show higher thermal stability in THF-*d*₈ than the neutral precursor compounds. The slow appearance of tetramethylsilane in the NMR spectrum when CD_2Cl_2 and pyridine-*d*₅ are used was assigned to decomposition processes in these solvents.⁷

While these monocationic compounds are in principle useful precursor compounds for a study of dication formation, their laborious isolation led us to consider “one-pot” procedures. Thus all syntheses of dicationic compounds here reported proceed from the neutral rare-earth metal precursors **1–6** by reaction with 2 or more equiv of Brønsted or Lewis acids. Under this regimen, dicationic rare-earth mono(trimethylsilylmethyl) complexes of both yttrium and lutetium with various counteranions supported by THF ($[\text{Ln}(\text{CH}_2\text{SiMe}_3)(\text{THF})_n]^{2+}[\text{A}]_2^-$; $\text{Ln} = \text{Y}$ (**13x**): $n = 5$; $\mathbf{x} = \mathbf{a}$; Lu (**14x**): $n = 4$, $\mathbf{x} = \mathbf{a}$) and 12-crown-4 ligands ($[\text{Ln}(\text{CH}_2\text{SiMe}_3)(12\text{-crown-4})(\text{THF})_n]^{2+}[\text{A}]_2^-$; $\text{Ln} = \text{Y}$ (**15x**): $n = 2, 3$; $\mathbf{x} = \mathbf{a–c}$; $\text{Ln} = \text{Lu}$ (**16b**); $[\text{Ln}(\text{CH}_2\text{SiMe}_3)(12\text{-crown-4})_2]^{2+}[\text{A}]_2^-$; $\text{Ln} = \text{Y}$ (**17x**): $\mathbf{x} = \mathbf{b, c}$; Lu (**18x**): $\mathbf{x} = \mathbf{a, b}$; Scheme 2) were synthesized in good yields. All complexes

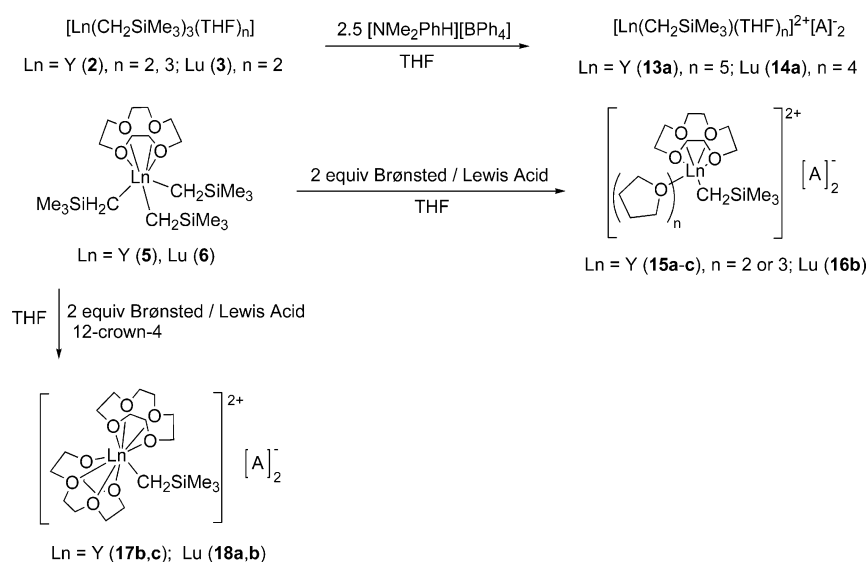
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Scheme 1



Scheme 2



are highly soluble in pyridine-*d*₅, but their solubility in other solvents such as THF-*d*₈ and CD₂Cl₂ is highly dependent on the choice of anion and the presence of 12-crown-4. Compound **15a** is only the second example of a crystallographically characterized alkyl dication.^{3c}

Both **13a** and its lutetium analogue **14a** proceeded to 90% conversion to the dication in THF-*d*₈ after 1.5 h when [NMe₂PhH]⁺[BPh₄][−] was used for the synthesis.⁸ **15a** was isolated from a mixture of **5** and 2.1 equiv of [NEt₃H]⁺[BPh₄][−] in THF as large, colorless crystals in 94% yield after standing for 3 days at room temperature.⁹ The THF-free bis(12-crown-4) dicationic lutetium compound **18a** was synthesized from a stirred equimolar mixture of **6** and 12-crown-4 with 2 equiv of [NEt₃H]⁺[BPh₄][−].¹⁰

A series of dicationic mono- and bis(12-crown-4) (**15b**, **16b**, **17b**, and **18b**) yttrium and lutetium complexes sup-

ported by the [B(C₆F₅)₄][−] anion were prepared in THF-*d*₈ by reaction of **5** or **6** with 2 equiv of [NMe₂PhH]⁺[B(C₆F₅)₄][−]. Furthermore, the bis(12-crown-4) complexes **17b** and **18b**, but notably not the mono(12-crown-4) analogues **15b** and **16b**, reacted with a third equiv of [NMe₂PhH]⁺[B(C₆F₅)₄][−] to give a trimethylsilylmethyl-free complex and a third equiv of tetramethylsilane.¹¹ The [B(C₆F₅)₄][−] anion afforded dicationic complexes of a much higher THF solubility than the borate [BPh₄][−].

When 2 equiv of BPh₃ were added to **5**, clean conversion to the dication **15c** was observed after 2 h at room temperature.¹² Addition of a second equiv of 12-crown-4

(8) The analogous scandium experiment gave a ¹H NMR spectrum with peaks arising from residual monocation and other unidentified resonances. Attempted introduction of a 12-crown-4 ligand to **13a** or **14a** failed; **13a** and 12-crown-4 in THF-*d*₈ gave a greasy, insoluble solid inconsistent (by ¹H NMR spectroscopy in pyridine-*d*₅) with clean 12-crown-4 incorporation.

(9) A concentration of between 0.05 and 0.10 mol·L^{−1} gave **15a** in 90–95% yield. A weaker solution (0.01 mol·L^{−1}) deposited only trace **15a**. At 0.01 mol·L^{−1} the major insoluble component was an alkyl-free byproduct; NMR spectroscopy (pyridine-*d*₅) indicated BPh₄, coordinated 12-crown-4 and THF, in a 2:1:1.5 ratio. The analogous procedures with scandium and lutetium deposit only alkyl-free products also with BPh₄, coordinated 12-crown-4 and THF. Titration for Lu content gave 12.08%; [Lu(12-crown-4)₂(THF)]³⁺[BPh₄]^{−3} (C₉₂H₁₀₀B₃LuO₉) requires 11.24%.

(10) The analogous procedure for yttrium gave a mixture tentatively assigned by NMR spectroscopy as [Y(CH₂SiMe₃)(12-crown-4)₂]²⁺[BPh₄]^{−2}, **15a** and an alkyl-free byproduct.

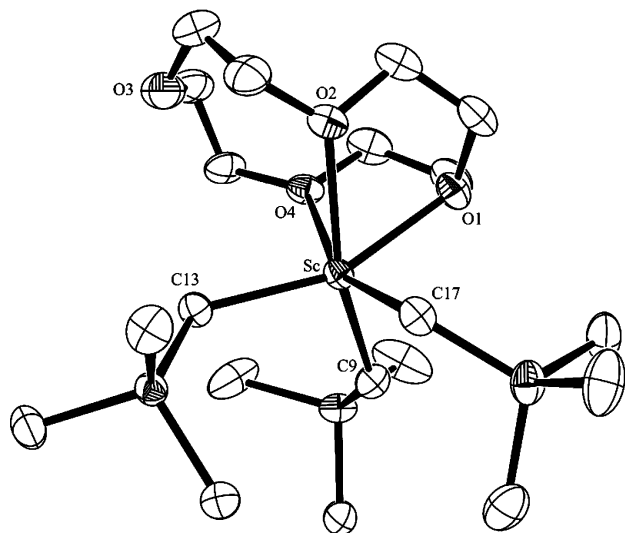


Figure 1. ORTEP representation of the molecular structure of $[\text{Sc}(\text{CH}_2\text{SiMe}_3)_3(12\text{-crown-4})]$ (**4**). Thermal ellipsoids are drawn at 30%, and hydrogen atoms have been omitted for clarity.

gave the THF-free species **17c**. Both **15c** and **17c** were synthesized on a preparative scale in good yield.¹³ Neither of the aluminate-supported yttrium monocations **8e** nor **11e** reacted with excess $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$ at room temperature after 7 days in THF-*d*₈ solution.

Crystal Structures. Neutral tris(trimethylsilylmethyl) complexes **5** and **6** adopt a three-legged “piano-stool” geometry in the solid state, with facial 12-crown-4 coordination, as determined by X-ray crystallography.^{3b} We have now isolated crystals of the scandium derivative **4** suitable for an X-ray diffraction study from dichloromethane at -30°C . In this case, the crown ether ligand only coordinates through three oxygen atoms ($\text{Sc}-\text{O}(1) = 2.276(2)$, $\text{Sc}-\text{O}(2) = 2.423(3)$, and $\text{Sc}-\text{O}(4) = 2.396(2)$ Å) to give a 6-coordinate metal center; the fourth 12-crown-4 oxygen was found 3.923(3) Å from the metal center (Figure 1). The geometry at scandium in **4** is best described as distorted octahedral, with angles along the C13–Sc–O1, C9–Sc–O2, and C17–Sc–O4 axes of $157.91(11)^\circ$, $161.41(10)^\circ$, and $156.46(11)^\circ$, respectively (Table 1). The Sc–C(alkyl) separations ($\text{Sc}-\text{C}(9) = 2.219(3)$, $\text{Sc}-\text{C}(13) = 2.243(3)$, and $\text{Sc}-\text{C}(17) = 2.251(3)$ Å) lie within the range of distances found for other scandium trimethylsilylmethyl complexes (2.195(3)–2.295(3), Table 2),¹⁴ although many of these complexes have a lower coordination number, commonly 5. Selected crystallographic data for **4** can be found in Table 3. Tricationic Sc

Table 1. Selected Bond Lengths and Angles for **4** and **15a**

4		15a	
Sc–C(9)	2.219(3)	Y–C(21)	2.424(4)
Sc–C(13)	2.243(3)	Y–O(1)	2.414(3)
Sc–C(17)	2.251(3)	Y–O(2)	2.423(3)
Sc–O(1)	2.276(2)	Y–O(3)	2.491(3)
Sc–O(2)	2.423(3)	Y–O(4)	2.527(3)
Sc–O(3)	3.923(3)	Y–O(5)	2.425(2)
Sc–O(4)	2.396(2)	Y–O(6)	2.370(2)
C(9)–Sc–C(13)	98.63(13)	Y–O(7)	2.396(2)
C(9)–Sc–C(17)	100.22(12)	C(21)–Y–O(7)	83.10(11)
C(13)–Sc–C(17)	105.40(12)	O(7)–Y–O(6)	75.29(9)
O(1)–Sc–O(4)	68.62(8)	O(6)–Y–O(5)	77.59(9)
O(1)–Sc–O(2)	68.77(9)	O(5)–Y–C(21)	79.58(11)
O(2)–Sc–O(4)	76.15(8)	O(1)–Y–O(4)	65.07(13)
C(13)–Sc–O(1)	157.91(11)	O(4)–Y–O(3)	64.16(9)
C(9)–Sc–O(2)	161.41(10)	O(3)–Y–O(2)	66.14(9)
C(17)–Sc–O(4)	156.46(11)	O(2)–Y–O(1)	66.63(9)

complexes including the $[\text{Sc}(12\text{-crown-4})_2]^{3+}$ unit with symmetrical *exo*-crown ether coordination have been reported in which the Sc–O bond lengths lie in the region 2.160(8)–2.274(9) Å.¹⁵ By contrast, the monocationic complexes $[\text{ScCl}_2(15\text{-crown-5})]_2^+[\text{CuCl}_4]^{2-}$, $[\text{ScCl}_2(18\text{-crown-6})]^+[\text{SbCl}_6]^-$, and $[\text{ScCl}_2(\text{benzo-15-crown-5})]^+[\text{SbCl}_6]^-$ include an almost linear ScCl_2^+ unit that is threaded through the crown cavity such that the Sc and O centers are essentially planar. Average Sc–O bond lengths for these compounds are 2.125, 2.210, and 2.188 Å, respectively.¹⁶ In $[\text{ScCl}_2(18\text{-crown-6})]^+[\text{FeCl}_4]^-$, only five of the six oxygen atoms coordinate to the Sc center; the average Sc–O(coordinated) bond length is 2.215 Å.¹⁷

X-ray crystallography of single crystals of the yttrium dication **15a** confirmed the coordination of the 12-crown-4 in a face-capping manner as well as three THF units; the geometry at the 8-coordinate yttrium center is best described as square antiprismatic (Figure 2). There are no close interactions between the dicationic metal center and the borate anions in the solid state. The yttrium–carbon bond length ($\text{Y}-\text{C}(21) = 2.424(4)$ Å) is very similar to that recorded for $[\text{Y}(\text{CH}_3)(\text{THF})_6]^{2+}[\text{BPh}_4]_2^{3-}$.^{3c} Surprisingly, it is also similar to the two Y–C separations in the monocationic complex $[\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_4]^+[\text{Al}(\text{CH}_2\text{SiMe}_3)_4]^-$,^{3c} the neutral 12-crown-4 supported tris(trimethylsilylmethyl) $[\text{Y}(\text{CH}_2\text{SiMe}_3)_3(12\text{-crown-4})]$,^{3b} and other representative neutral yttrium complexes (Table 4).¹⁸ The Y–O(12-crown-4) bond lengths (2.414(3)–2.527(3) Å) are shorter than those observed in the neutral complex **5** (2.571(7)–2.627(6) Å),^{3b} despite an increase in coordination number from 7 to 8 but

- (11) The alkyl-free products were tentatively assigned as $[\text{Ln}(12\text{-crown-4})_2(\text{THF})_4]^{3+}[\text{B}(\text{C}_6\text{F}_5)_4]_3^-$ (Ln = Y, Lu). The yttrium compound was alkyl-free on a preparative scale (residual NMe_2Ph was noted). The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are similar to those of the co-product observed at low concentration in the formation of **15a**. Alkyl-free tricationic rare-earth metal borate complexes are known: (a) Sauro, L. J.; Moeller, T. *J. Inorg. Nucl. Chem.* **1968**, *30*, 953. (b) Thomas, R. R.; Chebolu, V.; Sen, A. *J. Am. Chem. Soc.* **1986**, *108*, 4096.
- (12) Addition of two equiv of BPh_3 to **6** in THF-*d*₈ required 10 days for complete loss of monocation resonances. The Lu analysis of the worked-up product was 2–3% too high in Lu for the dication.
- (13) A mixture of **2** and 2 equiv of BPh_3 in THF-*d*₈ gave a mixture of the monocation **8c** and another yttrium species tentatively assigned as the dication $[\text{Y}(\text{CH}_2\text{SiMe}_3)(\text{THF})_n]^{2+}[\text{BPh}_3(\text{CH}_2\text{SiMe}_3)]_2^-$ after 2 days at room temperature.

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Table 2. Selected Sc–C(alkyl) Bond Lengths in Neutral Tris- and Bis(alkyl) Complexes

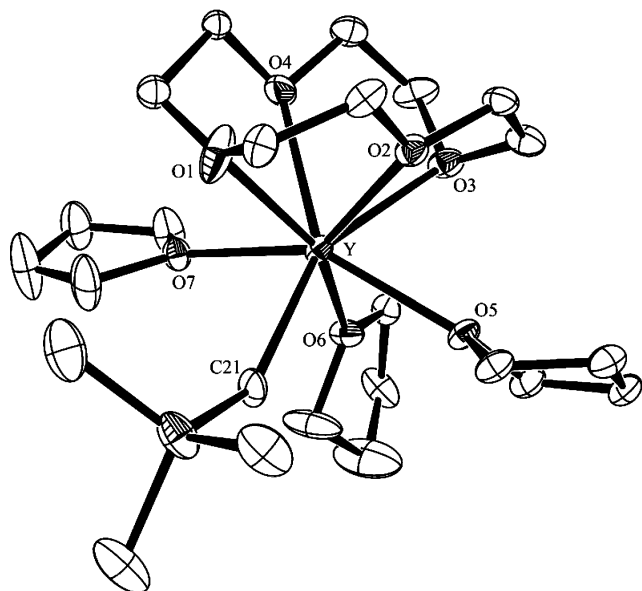
compound	Sc–C (Å)	reference
Neutral Tris(alkyl) Complexes		
[Sc(CH ₂ SiMe ₂ Ph) ₃](THF) ₂]	2.248(2), 2.254(2), 2.2498(19)	14d
[Sc(CH ₂ SiMe ₃) ₃ (12-crown-4)]	2.219(3), 2.243(3), 2.251(3)	this work
Neutral Bis(alkyl) Complexes		
[Sc(ArNC(Ph)NAr)(CH ₂ SiMe ₃) ₂](THF)] ^a	2.229(3), 2.195(3)	2b
[Sc(Ar' O)(CH ₂ SiMe ₃) ₂](THF)] ^b	2.236(2), 2.246(2)	14b
[Sc{ArNC(Me)CHC(Me)NAr}(CH ₂ SiMe ₃) ₂] ^a	2.2446(13), 2.1954(14)	14e
[Sc{ArNC(<i>i</i> Bu)CHC(<i>i</i> Bu)NAr}(CH ₂ SiMe ₃) ₂] ^a	2.229(7), 2.202(7)	14e

^a Ar = 2,6-*i*Pr–C₆H₃. ^b Ar' O = {2-(2,4,6-Me₃C₆H₂N=CH)(6-*i*Bu)C₆H₃O}.

Table 3. Crystal Data for **4** and **15a**^a

	4	15a
chemical formula	C ₂₀ H ₄₉ O ₄ ScSi ₃	C ₇₆ H ₉₉ B ₂ O ₈ SiY
formula weight	482.82	1279.17
<i>T</i>	293(2) K	110(2) K
λ	0.71073 Å	0.71073 Å
crystal system,	monoclinic,	monoclinic,
space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i>	10.849(4) Å	21.857(5) Å
<i>b</i>	15.690(2) Å	16.632(4) Å
<i>c</i>	17.256(3) Å	18.846(5) Å
α	90°	90°
β	97.50(2)°	94.451(5)°
γ	90°	90°
<i>V</i>	2912.2(12) Å ³	6830(3) Å ³
<i>Z</i>	4	4
<i>D</i> _{calc}	1.101 Mg/m ³	1.244 Mg/m ³
<i>R</i> (<i>F</i> _o ²), <i>R</i> _w (<i>F</i> _o ²) [<i>I</i> > 2σ(<i>I</i>)]	0.0503, 0.1055	0.0636, 0.1695
<i>R</i> (<i>F</i> _o ²), <i>R</i> _w (<i>F</i> _o ²) (all data)	0.0944, 0.1227	0.1171, 0.2019

^a *R*(*F*_o²) and *R*_w(*F*_o²) are defined as the final *R* indices [*I* > 2σ(*I*)].

**Figure 2.** ORTEP representation of the molecular structure of [Y(CH₂SiMe₃)(12-crown-4)(THF)₃]¹²⁺[BPh₄]₂[−] (**15a**). Thermal ellipsoids are drawn at 30%, and hydrogen atoms and borate anions have been omitted for clarity.

are comparable to those in [Y(OH₂)₅(12-crown-4)]³⁺(Cl)[−]·2 H₂O (2.42(1)–2.59(1) Å) and [YCl₂(OH₂)(OHMe)(12-crown-

4)]⁺(Cl)[−] (2.430(3)–2.472(3) Å).¹⁹ The Y–O(THF) bond lengths (Y–O5: 2.425(2), Y–O6: 2.370(2), and Y–O7: 2.396(2) Å) in **15a** are within the range reported for Y–O(THF) bond lengths at cationic yttrium centers (Table 5).²⁰

Structures in Solution. Variable-temperature (VT) NMR studies reveal that the coordination of 12-crown-4 in the neutral scandium complex **4** in both CD₂Cl₂ and THF-*d*₈ solution is labile. The ¹H NMR spectrum of **4** (CD₂Cl₂, 25 °C) showed two sharp singlets arising from the Sc–CH₂ (δ −0.24 ppm) and trimethylsilyl (δ −0.06 ppm) groups as well as a broad, poorly resolved signal at δ 4.03 ppm due to the crown ether. At −10 °C, the broad resonance of the 12-crown-4 changed into two higher order multiplets at δ 3.83, 4.19 ppm.²¹ The resonance arising from the Sc–CH₂ group was only slightly affected in its position (δ −0.28 ppm). In THF-*d*₈ solution, the ¹H NMR spectrum at 25 °C gave sharp singlets for the 12-crown-4 (δ 3.65 ppm) and the Sc–methylene (δ −0.59 ppm) and trimethylsilyl (δ −0.12 ppm) groups; the same chemical shift values were noted for the THF-adduct **1** and free crown ether. At −60 °C, both the above peaks and new broad peaks arising from 12-crown-4 (δ 4.01, 4.14 ppm) and Sc–CH₂ (δ −0.28 ppm) and trimethylsilyl (δ −0.09 ppm) were observed. These new resonances are assigned to the complex with coordinated 12-crown-4 and have a relative intensity of about 10%. Corresponding new resonances were noted in the variable temperature ¹³C{¹H} NMR spectra. The 12-crown-4 ligand in the previously reported yttrium analogue **5** is not labile in CD₂Cl₂ solution (two higher-order multiplets at δ 3.74 and 4.12 ppm were noted at 25 °C) but dissociates reversibly in THF-*d*₈ solution, with complete coordination observed at −80 °C.^{3b}

All of the expected peaks for the yttrium dication **15a** are cleanly resolved in the ¹H and ¹³C{¹H} NMR spectra in pyridine-*d*₅. Trace Si(CH₃)₃(CH₂D) was observed after a few

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- (21) Higher order downfield multiplets for crown ether ligands have been observed in similar compounds and arise from the diastereotopic methylene protons of the exocyclic crown ether when the coordination is rigid on the NMR time scale (see ref 3a,b). The apparent discrepancy with the solid-state structure can be explained by a carousel-like 12-crown-4 oxygen rotation that is fast on the NMR time scale. A very low intensity signal at 3.62 ppm, slightly broad at 25 °C and sharp at −10 °C, was assigned to a trace free 12-crown-4 impurity.

Table 4. Selected Y–C(alkyl) Bond Lengths in Neutral and Cationic Complexes

compound	Y–C (Å)	reference
Neutral Tris(alkyl) Complexes		
[Y{CH(SiMe ₃) ₂ }] ₃	2.357(7) (mean)	18a
[Y(CH ₂ SiMe ₃) ₃ (THF) ₃]	2.427(19) (mean)	29b
[Y(CH ₂ SiMe ₃) ₃ (12-crown-4)]	2.399(6)–2.430(6)	3b
Neutral Metallocenes		
[Y(η ⁵ -C ₅ Me ₅) ₂ {CH(SiMe ₃) ₂ }]	2.468(7)	18b
[Y(η ⁵ -C ₅ Me ₅) ₂ (CH ₃)(THF)]	2.44(2)	18c
[Y{(η ⁵ -C ₅ Me ₄) ₂ SiMe ₂ }{CH(SiMe ₃) ₂ }]	2.418(6)	18d
Alkyl Monocations		
[Y(CH ₂ SiMe ₃) ₂ (THF) ₄] ⁺ [Al(CH ₂ SiMe ₃) ₄] [–]	2.384(6), 2.411(6)	3c
[Y(CH ₃) ₂ (THF) ₅] ⁺ [BPh ₄] [–]	2.508(2), 2.526(2)	18e
Alkyl Dications		
[Y(CH ₃)(THF) ₆] ²⁺ [BPh ₄] ^{–2}	2.418(3)	3c
[Y(CH ₂ SiMe ₃)(12-crown-4)(THF) ₃] ²⁺ [BPh ₄] ^{–2}	2.424(4)	this work

Table 5. Selected Y–O(THF) Bond Lengths in Cationic Yttrium Complexes

compound	Y–O (Å)	reference
[YCl(OCMe ₃)(THF) ₅] ⁺ [BPh ₄] [–]	2.391(5)–2.422(5)	20a
[YCl ₂ (THF) ₅] ⁺ [YCl ₄ (THF) ₂] [–]	2.368(5)–2.382(6)	20b
[YCl ₂ (THF) ₅] ⁺ [C ₂ B ₉ H ₁₂] [–]	2.309(7)–2.401(7)	20c
[Y(CH ₂ SiMe ₃) ₂ (THF) ₄] ⁺ [Al(CH ₂ SiMe ₃) ₄] [–]	2.354(4)–2.479(4)	3c
[Y(CH ₃) ₂ (THF) ₅] ⁺ [BPh ₄] [–]	2.395(2)–2.418(2)	18e
[Y(CH ₃)(THF) ₆] ²⁺ [BPh ₄] ^{–2}	2.352(3)–2.427(3)	3c
[Y(CH ₂ SiMe ₃)(12-crown-4)(THF) ₃] ²⁺ [BPh ₄] ^{–2}	2.370(2)–2.425(2)	this work

minutes at room temperature in the ¹H NMR spectrum, indicating that **15a** is unstable in pyridine-*d*₅. The clear, colorless pyridine-*d*₅ solution of **15a** reacts completely after 10 h at room temperature to give a deep yellow solution that shows Si(CH₃)₃(CH₂D) as the only resonance in the δ < 1 ppm region of the ¹H NMR spectrum. The resonance arising from the Y–CH₂ group was also lost in the ¹³C{¹H} NMR spectrum, while the peaks arising from the 12-crown-4 protons in the ¹H NMR spectrum changed from a complicated multiplet to a slightly higher frequency singlet after this reaction. Rare-earth metal alkyl and hydride complexes are known to react with pyridine, as well as other aromatic heterocycles, to give in the case of pyridine a range of products including ortho-metalated pyridyl complexes of the general form [Ln(L₂X)₂(η²-(C,N)-C₅H₄N)] (L₂X = C₅Me₅, Ln = Sc,²² Y,²³ Lu;²⁴ LX₂ = C₅H₄R (R = H, Me), Ln = Y²⁵) or, via insertion/rearrangement, 1,2- and 1,4-addition products.²⁵ The reaction product from **15a** and pyridine-*d*₅ was thus tentatively concluded to be [Y(η²-(C,N)-C₅D₄N)-(12-crown-4)(C₅D₅N)_n]²⁺[BPh₄]^{–2}, based on the observed formation of Si(CH₃)₃(CH₂D) and the appearance of a low intensity doublet in the ¹³C{¹H} NMR spectrum (δ 212.6 ppm, ¹J_{YC} = 28.9 Hz) for the pyridyl α-carbon.²⁶

Qualitative evidence for a steady increase in positive charge from neutral to dicationic complexes at the rare-earth metal center can be gained from multinuclear NMR studies

(Table 6). Secondary effects are seen in the difference between ¹H NMR chemical shift values of comparable complexes with or without 12-crown-4 and between complexes with different anions, from which tentative conclusions about the extent of anion–cation association can also be drawn.

We found that, on the NMR time scale as determined by ¹¹B and ¹⁹F NMR spectroscopy, the ions are separated in solution. The ¹¹B nucleus gave rise to a single, cation-independent resonance in each case of both mono- and dicationic complexes (THF-*d*₈, 25 °C: **a**: δ –6.6 ppm; **b**: δ –16.7 ppm; **c**: δ –10.3 ppm; **d**: δ –14.2 ppm). These chemical shift values show a small solvent dependency (pyridine-*d*₅, 25 °C: **a**: δ –5.7 ppm). The perfluorinated anion **d** gives rise in every case to a meta–para chemical shift difference of only δ 2.3 ppm in the ¹⁹F NMR spectrum, which has been previously used as an indicator of solvent-separated ion pairs.²⁷ The ¹⁹F NMR resonances arising from both [B(C₆F₅)₄][–] and [B(C₆F₅)₃(CH₂SiMe₃)][–] are clearly cation independent.

We have found a strong effect on the ⁸⁹Y frequencies arising from the change in charge at the metal center from the neutral complex **2** (δ 882.7 ppm) to the monocations **8a**, **8c**, and **8e** (δ 660.0, 660.2, and 666.4 ppm) and then further to the dication **13a** (δ 409.2 ppm). ¹³C{¹H} and ¹H NMR spectra also give similar evidence for an increase in nuclear charge concomitant with cation formation. For instance, the Y–CH₂ ¹³C nuclei at yttrium (δ 34.4–39.8 ppm) were recorded at a higher frequency from the neutral precursors (δ 32.4–32.5 ppm, Table 6), an effect that has also been noted for cationic mono(amidinate) trimethylsi-

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(26) [YCp*₂(2-pyridyl)], synthesized from [YCp*₂(CH(SiMe₃)₂)] and pyridine, gives rise to a doublet in the ¹³C{¹H} NMR spectrum (225.5 ppm, ¹J_{YC} = 33.2 Hz) for the pyridine α-carbon (see ref 23).

(27) ¹⁹F chemical shift differences between meta and para fluorine atoms of less than 3 ppm are indicative of a noncoordinating anion for [RB(C₆F₅)₃][–] (R = Me, CH₂Ph): Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672.

Table 6. Selected NMR Data for Neutral, Mono- and Dicationic Sc, Y, and Lu Complexes^a

compound	δ (¹ H) Ln—CH ₂ (ppm)	² J _{YH} (Hz)	δ (¹³ C) Ln—CH ₂ (ppm)	¹ J _{YC} (Hz)	δ (⁸⁹ Y) Y (ppm)	reference
Neutral Yttrium Complexes						
2	−0.92	2.9	32.5	35.4	882.7	29
5	−0.83	2.1	32.4	35.0		3b
Monocationic Yttrium Complexes						
8a	−0.78	3.3	36.9	41.2	660.0	
8b	−0.69	3.2	37.4	41.6		
8c	−0.80	3.2	36.7	41.6	660.2	
8d	−0.70	2.9	37.3	43.0		
8e	−0.73	3.1	37.2	42.1	666.4	3c
11a	−0.89	2.9	34.4	40.5		3b
11b	−0.73	3.1	35.3	42.4		
11c	−0.88	3.0	39.8 ^b	41.0 ^b		3a
11d	−0.73	3.4	35.1	40.8		
11e	−0.73	2.8	35.1	40.2		
Dicationic Yttrium Complexes						
13a	0.73 ^c	3.3 ^c	44.5 ^c	44.9 ^c	409.2 ^c	3a
15a	0.02 ^c	3.0 ^c	40.1 ^c	42.2 ^c		
15b	−0.58	3.4	39.0	37.1		
15c	−0.91	2.8	36.9	43.8		
17b	−0.68	2.8	nd ^d			
17c	−1.05	3.2	26.1	53.3		
Neutral Lutetium Complexes						
3	−1.15		40.2			29
6	−1.12		39.6 ^b			3b
Monocationic Lutetium Complexes						
9a	−0.99		40.0			
9b	−0.93		40.4			
9c	−1.03		39.8			
9d	−0.92		40.4			
12a	−1.12		38.5			3b
12b	−0.97		39.1			
12c	−1.12 ^b		39.5 ^b			3a
12d	−0.97		39.1			
Dicationic Lutetium Complexes						
14a	0.47 ^c		44.3 ^c			
16b	−0.68		39.8			
18a	−0.17 ^c		nd			
18b	−0.73		nd			
Neutral Scandium Complexes						
1	−0.65		36.3			29
4	−0.40 ^b		40.0 ^b			3b
Monocationic Scandium Complexes						
7a	−0.22		45.0			
10a	−0.21		nd			3b
10c	−0.21		46.3			

^a Unless otherwise noted, NMR measurements were made in THF-*d*₈ at 25 °C. ^b Measured in CD₂Cl₂. ^c Measured in pyridine-*d*₅. ^d nd, not detected.

lylmethyl complexes.^{2b} The range of chemical shift values for the dicationic yttrium complexes and the mono- and dicationic lutetium compounds is much broader and reveals no discernible trends. The ¹J_{YC} coupling constants are significantly larger in the case of the monocations (δ 40.2–43.0 Hz) than the neutral complexes (δ 35.0–35.4 Hz).

The Ln—CH₂ groups of the monocationic THF-supported scandium, yttrium, and lutetium complexes give rise to higher frequency resonances in the ¹H NMR spectrum (Sc: δ −0.22 ppm, Y: δ −0.69 to −0.80 ppm, Lu: δ −0.92 to −1.03 ppm) compared with the respective neutral species (Sc: δ −0.65 ppm, Y: δ −0.92 ppm, Lu: δ −1.15 ppm). In situ-generated dications **13a** and **14a** in THF-*d*₈ demonstrate a further higher frequency shift from monocationic (Y—CH₂,

THF-*d*₈: δ −0.78 ppm; Lu—CH₂, THF-*d*₈: δ −0.99 ppm) to dicationic (Y—CH₂, THF-*d*₈: δ −0.67 ppm; Lu—CH₂, THF-*d*₈: δ −0.85 ppm) species. The extent of the higher frequency shift depends on the anion used and is greater in the case of perfluorinated borate anions than for the perprotonated analogues. The Ln—CH₂ groups of the monocationic and dicationic mono(12-crown-4) yttrium and lutetium compounds also show an anion dependency, in this case a high-frequency shift with respect to the neutral compound is noted for complexes with perfluorinated anions while a low-frequency shift occurs with the perprotonated anions. These small anion influences not detectable by ¹¹B or ¹⁹F NMR spectroscopy may be due to weak cation–anion association that is fluxional on the NMR time scale.²⁸

Conclusion

We have demonstrated that a series of mono- and dicationic rare-earth metal trimethylsilylmethyl complexes stabilized by either THF or 12-crown-4 ligands can be prepared from neutral tris(alkyl) precursors. We have shown that the preparation of the monocationic complexes is general for Sc, Y, and Lu and that a range of anions and ether ligands can stabilize these metal centers. The syntheses of the dicationic complexes show a strong dependency on the rare-earth metal, anion, and ether ligand, both on the feasibility of the reaction, its rate and the solubility of the resultant complexes. The crystallographic study of the dicationic complex **15a** with 12-crown-4 and THF ligands revealed well-separated ions in the crystalline state. Detailed multi-nuclear NMR studies also indicated solvent separated ion pairs for all mono- and dicationic complexes. These studies also showed that there is a systematic influence of the charge at the yttrium center on the chemical shift values in the ⁸⁹Y and ¹³C{¹H} NMR spectra. In the case of all rare-earth metals examined, a change from THF to 12-crown-4 or to a different anion gave rise to a small variation in the ¹H and ¹³C{¹H} frequencies. Our ongoing studies in this area include the further assessment of these novel species as catalysts for a range of polymerizations and organic transformations or as starting materials for the synthesis of organometallic complexes inaccessible via more conventional routes.^{1q}

Experimental Section

General Considerations. All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. THF and toluene were distilled from sodium benzophenone ketyl. Pentane was purified by distillation from sodium/triglyme benzophenone ketyl. Anhydrous trichlorides of scandium, yttrium, and lutetium (ALFA or Strem) were used as received. All other chemicals were commercially available and used after appropriate purification. [Ln(CH₂SiMe₃)₃(THF)_{*n*}] (*n* = 2 for Ln = Sc, Lu, *n* = 3 for Ln = Y) were prepared according to

- (28) Anion coordination via the phenyl group has been noted in Lewis base-free rare-earth metal complexes with both fluorinated and nonfluorinated anions—see refs 11,j,o and 2c. BPh₄ coordination has also been noted in cationic zirconium complexes: (a) Bochmann, M.; Karger, G.; Jaggar, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1038. (b) Horton, A. D.; Frijns, J. H. G. *Angew. Chem., Int. Ed. Engl.* **1991**, 30, 1152.

literature procedures.²⁹ [Ln(CH₂SiMe₃)₃(12-crown-4)] (Ln = Sc, Y, Lu) were prepared according to literature procedures.^{3b} X-ray diffraction data of **4** were collected with an Enraf Nonius CAD4 diffractometer, and the program system WinGX was used for the data reduction.³⁰ The data of **15a** were collected on a Bruker CCD platform diffractometer equipped with a CCD detector. The SMART program package was used to determine the unit-cell parameters and for data collection; the raw frame data was processed using SAINT and SADABS to yield the reflection data file.³¹ The structures were solved by direct methods and difference Fourier syntheses (SHELXS-86).³² All independent reflections were used in the refinement by full-matrix least-squares against all F_o^2 data (SHELXL-97).³³ Analytical scattering factors for neutral atoms were used throughout the analysis.³⁴ All non-hydrogen atoms were refined with anisotropic thermal parameters; the hydrogen atoms were included into idealized positions. In the structure refinement of **15a**, the carbon atoms C7 and C8 were refined with split positions and isotropic thermal parameters. For the graphical representation, the program ORTEP-III was used as implemented in the program system WinGX.

NMR spectra were recorded on a Bruker DRX 400 spectrometer (¹H, 400.1 MHz, ¹³C, 100.6 MHz, ¹¹B, 128.4 MHz, ¹⁹F, 376.4 MHz, ⁸⁹Y 19.6 MHz) or on a Varian Unity 500 spectrometer (¹H, 500 MHz, ¹³C, 125.6 MHz, ¹¹B, 160.3 MHz, ¹⁹F 470.1 MHz). Chemical shifts for ¹H and ¹³C NMR spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. ¹¹B NMR spectra were referenced externally to a 1 M solution of NaBH₄ in D₂O. ¹⁹F NMR spectra were referenced externally to CCl₃F. ⁸⁹Y spectra were referenced externally to a 1 M solution of YCl₃ in D₂O.

Elemental analyses were performed by the Microanalytical Laboratory of the Johannes Gutenberg—University Mainz, Germany. In many cases the results were not satisfactory, and the best values from repeated runs were given. Moreover the results were inconsistent from run to run and therefore not reproducible. We ascribe this difficulty observed also by other workers to the extreme sensitivity of the material.³⁵ Metal analysis was performed by complexometric titration.³⁶ The sample (20–30 mg) was dissolved in THF (2 mL) or 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).

[Sc(CH₂SiMe₃)₂(THF)₃]⁺[BPh₄][−] (**7a**). A mixture of **1** (451 mg, 1.00 mmol) and [NEt₃H][BPh₄] (421 mg, 1.00 mmol) was suspended in THF (50 mL) at −78 °C and stirred at this temperature. The reaction mixture was allowed to slowly warm to ambient temperature and stirred for 15 h to give a colorless clear

solution. After the volatiles were removed under reduced pressure, the resultant slightly oily solid was washed with diethyl ether (2 × 20 mL) and pentane (2 × 20 mL) and dried under vacuum to give colorless microcrystals (561 mg, 74%). ¹H NMR (THF-*d*₈, 25 °C): δ −0.21 (s, 2 × 2 H, ScCH₂SiCH₃), −0.04 (s, 2 × 9 H, ScCH₂SiCH₃), 6.73 (t, ³J_{HH} = 7.0 Hz, 4 × 1 H, Ph-4), 6.87 (m, 4 × 2 H, Ph-3), 7.28 (m (br), 4 × 2 H, Ph-2). ¹³C{¹H} NMR (THF-*d*₈, 25 °C): δ 3.5 (ScCH₂SiCH₃), 15.3 (β-CH₂, NEt₃), 45.0 (s (br), ScCH₂SiCH₃), 65.9 (α-CH₂, NEt₃), 121.6 (Ph-4), 125.4 (Ph-3), 136.7 (Ph-2), 164.8 (q, ¹J_{BC} = 49.3 Hz). ¹¹B{¹H} NMR (THF-*d*₈, 25 °C): δ −6.6. Anal. Calcd for C₄₄H₆₆BO₃Si₂Sc: C, 70.00; H, 8.81; Sc, 5.95. Found: C, 67.22; H, 8.26; Sc, 5.93.

[Y(CH₂SiMe₃)₂(THF)_x]⁺[BPh₄][−] (**8a**) (x = 3 or 4). A mixture of **2** (1000 mg, 1884 μmol) and [NEt₃H][BPh₄] (794 mg, 1884 μmol) was suspended in THF (30 mL) at −78 °C and stirred at this temperature. The reaction mixture was allowed to slowly warm to ambient temperature and stirred for 2 h to give a colorless clear solution. After the volatiles were removed under reduced pressure, the resultant slightly oily solid was washed with pentane (2 × 30 mL) and dried under vacuum to give colorless microcrystals of [Y(CH₂SiMe₃)₂(THF)₃]⁺[BPh₄][−] (1484 mg, 99%). The alternative product [Y(CH₂SiMe₃)₂(THF)₄]⁺[BPh₄][−] can be regenerated by a final washing with THF (5 mL) and drying under vacuum. ¹H NMR (THF-*d*₈, 25 °C): δ −0.78 (d, ²J_{YH} = 3.3 Hz, 2 × 2 H, YCH₂SiCH₃), −0.06 (s, 2 × 9 H, YCH₂SiCH₃), 1.76 (m, 4 × 4 H, β-CH₂, THF), 3.60 (m, 4 × 4 H, α-CH₂, THF), 6.74 (t, ³J_{HH} = 7.0 Hz, 4 × 1 H, Ph-4), 6.87 (m, 4 × 2 H, Ph-3), 7.28 (m (br), 4 × 2 H, Ph-2). ¹H NMR (pyridine-*d*₅, 25 °C): δ −0.08 (d, ²J_{YH} = 2.3 Hz, 2 × 2 H, YCH₂SiCH₃), 0.19 (s, 2 × 9 H, YCH₂SiCH₃), 1.65 (m, 4 × 4 H, β-CH₂, THF), 3.68 (m, 4 × 4 H, α-CH₂, THF), 7.12 (t, ³J_{HH} = 7.0 Hz, 4 × 1 H, Ph-4), 7.28 (m, 4 × 2 H, Ph-3), 8.05 (m (br), 4 × 2 H, Ph-2). ¹³C{¹H} NMR (THF-*d*₈, 25 °C): δ 4.1 (YCH₂SiCH₃), 36.9 (d, ¹J_{YC} = 41.2 Hz, YCH₂SiCH₃), 122.0 (Ph-4), 125.8 (Ph-3), 137.1 (Ph-2), 165.2 (q, ¹J_{BC} = 49.3 Hz). ¹³C NMR (pyridine-*d*₅, 25 °C): δ 4.5 (YCH₂SiCH₃), 25.8 (β-CH₂, THF), 30.9 (dt, ¹J_{YC} = 36.5 Hz, ¹J_{CH} = 97.2 Hz, YCH₂SiCH₃), 67.8 (α-CH₂, THF), 122.3 (Ph-4), 126.2 (Ph-3), 137.2 (Ph-2), 165.0 (q, ¹J_{BC} = 49.3 Hz, Ph-1). ¹¹B{¹H} NMR (THF-*d*₈, 25 °C): δ −6.6. ⁸⁹Y NMR (THF-*d*₈, 25 °C): δ 660.0. Anal. Calcd for C₄₈H₇₄BO₄Si₂Y: C, 66.19; H, 8.56; Y, 10.21. Found: C, 65.91; H, 8.44; Y, 9.74.

[Y(CH₂SiMe₃)₂(THF)_x]⁺[B(C₆F₅)₄][−] (**8b**). An NMR tube was charged with a solution of **2** (37 mg, 75 μmol) and [NMe₂PhH]-[B(C₆F₅)₄] (60 mg, 75 μmol) in THF-*d*₈ (0.5 mL). NMR spectra were recorded after 40 min at 25 °C: ¹H NMR (THF-*d*₈, 25 °C): δ −0.69 (d, ²J_{YH} = 3.2 Hz, 2 × 2 H, YCH₂), −0.05 (s, 2 × 9 H, YCH₂SiCH₃), 0.02 (s, 12 H, SiMe₄), 2.87 (s, 2 × 3 H, NMe₂Ph-3), 6.57 (t, ³J_{HH} = 7.2 Hz, 1 H, NMe₂Ph-4), 6.65 (d, ³J_{HH} = 8.4 Hz, 2 H, NMe₂Ph-2), 7.09 (m, 2 H, NMe₂Ph-3). ¹³C{¹H} NMR (THF-*d*₈, 25 °C): δ −0.1 (SiMe₄), 3.9 (YCH₂SiCH₃), 37.4 (d, ¹J_{YC} = 41.6 Hz, YCH₂), 40.4 (NMe₂Ph), 113.1, 116.9 (NC₆H₅), 125.0 (br m, C₆F₅-1), 129.3 (NMe₂Ph), 137.0 (d, ¹J_{CF} = 241.6 Hz, C₆F₅-3), 139.0 (d, ¹J_{CF} = 242.8 Hz, C₆F₅-4), 149.0 (d, ¹J_{CF} = 243.4 Hz, C₆F₅-2). ¹¹B{¹H} NMR (THF-*d*₈, 25 °C): δ −16.7. ¹⁹F NMR (THF-*d*₈, 25 °C): δ −168.8, −165.2, −133.1.

[Y(CH₂SiMe₃)₂(THF)_x]⁺[BPh₃(CH₂SiMe₃)][−] (**8c**) (x = 3 or 4). A mixture of **2** (600 mg, 1130 μmol) and BPh₃ (274 mg, 1130 μmol) was suspended in THF (20 mL) at −78 °C and stirred at this temperature. The reaction mixture was allowed to slowly warm to ambient temperature and stirred for 6 h to give a very pale yellow solution. After the volatiles were removed under reduced pressure, the resultant yellow oil was washed with pentane (2 × 30 mL) to give [Y(CH₂SiMe₃)₂(THF)₄]⁺[BPh₃(CH₂SiMe₃)][−] and dried under vacuum to give colorless microcrystals of [Y(CH₂SiMe₃)₂-

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(THF)₃]⁺[BPh₃(CH₂SiMe₃)₃][−] (792 mg, 87%). NMR data (for *x* = 3): ¹H NMR (THF-*d*₈, 25 °C): δ −0.80 (d, ²*J*_{YH} = 3.2 Hz, 2 × 2 H, YCH₂), −0.49 (s, 9 H, BCH₂SiCH₃), −0.07 (s, 2 × 9 H, YCH₂-SiCH₃), 0.18 (q, ²*J*_{BH} = 4.8 Hz, 2 H, BCH₂), 6.67 (t, ³*J*_{HH} = 7.1 Hz, 3 × 1 H, Ph-4), 6.83 (m, 3 × 2 H, Ph-3), 7.38 (m (br), 3 × 2 H, Ph-2). ¹³C{¹H} NMR (THF-*d*₈, 25 °C): δ 2.7 (BCH₂SiCH₃), 4.0 (YCH₂SiCH₃), 36.7 (d, ¹*J*_{YC} = 41.6 Hz, YCH₂), 121.5 (Ph-4), 125.6 (Ph-3), 135.7 (Ph-2), 167.8 (q, ¹*J*_{BC} = 48.5 Hz, Ph-1). The signal of the BCH₂ group was not detected. ¹¹B{¹H} NMR (THF-*d*₈, 25 °C): δ −10.3. ⁸⁹Y{¹H} NMR (THF-*d*₈, 25 °C): δ 660.2. Anal. Calcd for C₄₂H₇₂BO₃Si₃Y: C, 62.36; H, 8.97; Y, 10.99. Found: C, 61.52; H, 9.34; Y, 10.48.

[Y(CH₂SiMe₃)₂(THF)₃]⁺[B(C₆F₅)₃(CH₂SiMe₃)₃][−] (8d). An NMR tube was charged with a solution of **2** (37 mg, 75 μmol) and B(C₆F₅)₃ (38 mg, 75 μmol) in THF-*d*₈ (0.5 mL). NMR spectra were recorded after 4 h at 25 °C and 0.5 h at 50 °C: ¹H NMR (THF-*d*₈, 25 °C): δ −0.70 (d, ²*J*_{YH} = 2.9 Hz, 2 × 2 H, YCH₂), −0.38 (s, 9 H, BCH₂SiCH₃), −0.06 (s, 2 × 9 H, YCH₂SiCH₃), 0.58 (br, 2 H, BCH₂). ¹³C{¹H} NMR (THF-*d*₈, 25 °C): δ 1.3 (BCH₂SiCH₃), 3.9 (YCH₂SiCH₃), 37.3 (d, ¹*J*_{YC} = 43.0 Hz, YCH₂), 129.8 (br, C₆F₅-1), 137.0 (d, ¹*J*_{CF} = 243.6 Hz, C₆F₅-3), 138.2 (d, ¹*J*_{CF} = 241.2 Hz, C₆F₅-4), 149.1 (d, ¹*J*_{CF} = 236.8 Hz, C₆F₅-2). The signal of the BCH₂ group was not detected. ¹¹B{¹H} NMR (THF-*d*₈, 25 °C): δ −14.2. ¹⁹F NMR (THF-*d*₈, 25 °C): δ −169.3, −167.1, −132.0.

[Y(CH₂SiMe₃)₂(THF)₄]⁺[Al(CH₂SiMe₃)₄][−] (8e). A solution of **2** (100 mg, 202 μmol) in pentane (0.3 mL) was treated with THF (72 μL, 1 mmol) and Al(CH₂SiMe₃)₃ (73 μL, 202 μmol). After the mixture was stirred for 5 min at 25 °C, the turbid suspension was cooled to −40 °C. After 7 days at this temperature, colorless crystals (140 mg, 75%) formed. ¹H NMR (THF-*d*₈, 25 °C): δ −1.28 (br m, 4 × 2 H, AlCH₂), −0.73 (d, ²*J*_{YH} = 3.1 Hz, 2 × 2 H, YCH₂), −0.16 (s, 4 × 9 H, AlCH₂SiCH₃), −0.09 (s, 2 × 9 H, YCH₂SiCH₃), 1.75 (m, 4 × 4 H, β-CH₂, THF), 3.60 (m, 4 × 4 H, α-CH₂, THF). ¹³C{¹H} NMR (THF-*d*₈, 25 °C): δ 3.8 (YCH₂SiCH₃), 3.9 (AlCH₂-SiCH₃), 4.4 (AlCH₂), 37.2 (d, ¹*J*_{YC} = 42.1 Hz, YCH₂). ²⁷Al NMR (THF-*d*₈, 25 °C): δ 150.9. ⁸⁹Y NMR (THF-*d*₈, 25 °C): δ 666.4. Anal. Calcd for C₄₀H₉₈AlO₄Si₆Y: C, 51.79; H, 10.65. Found: C, 51.82; H, 10.66.

[Lu(CH₂SiMe₃)₂(THF)₃]⁺[BPh₄][−] (9a). A mixture of **3** (1000 mg, 1720 μmol) and [NEt₃H][BPh₄] (726 mg, 1720 μmol) was suspended in THF (35 mL) at −78 °C and stirred at this temperature. The reaction mixture was allowed to slowly warm to ambient temperature and stirred for 2 h to give a colorless clear solution. After the volatiles were removed under reduced pressure, the resultant colorless solid was washed with pentane (2 × 30 mL) and dried under vacuum to give colorless microcrystals (1485 mg, 98%). ¹H NMR (THF-*d*₈, 25 °C): δ −0.99 (s, 2 × 2 H, LuCH₂-SiCH₃), −0.05 (s, 2 × 9 H, LuCH₂SiCH₃), 1.76 (m, 3 × 4 H, β-CH₂, THF), 3.60 (m, 3 × 4 H, α-CH₂, THF), 6.72 (t, ³*J*_{HH} = 7.0 Hz, 4 × 1 H, Ph-4), 6.87 (m, 4 × 2 H, Ph-3), 7.28 (m (br), 4 × 2 H, Ph-2). ¹H NMR (pyridine-*d*₅, 25 °C): δ −0.10 (s, 2 × 2 H, LuCH₂SiCH₃), 0.06 (s, 2 × 9 H, LuCH₂SiCH₃), 1.62 (m, 3 × 4 H, β-CH₂, THF), 3.66 (m, 3 × 4 H, α-CH₂, THF), 7.11 (t, ³*J*_{HH} = 7.0 Hz, 4 × 1 H, Ph-4), 7.28 (m, 4 × 2 H, Ph-3), 8.06 (m (br), 4 × 2 H, Ph-2). ¹³C{¹H} NMR (THF-*d*₈, 25 °C): δ 4.4 (LuCH₂SiCH₃), 40.0 (LuCH₂SiCH₃), 121.9 (Ph-4), 125.7 (Ph-3), 137.0 (Ph-2), 165.0 (q, ¹*J*_{BC} = 49.3 Hz). ¹³C NMR (pyridine-*d*₅, 25 °C): δ 3.8 (LuCH₂-SiCH₃), 25.5 (β-CH₂, THF), 42.8 (s, LuCH₂SiCH₃), 67.5 (α-CH₂, THF), 122.0 (Ph-4), 125.9 (Ph-3), 136.8 (Ph-2), 164.7 (q, ¹*J*_{BC} = 48.9 Hz, Ph-1). ¹¹B{¹H} NMR (THF-*d*₈, 25 °C): δ −6.6. ¹¹B{¹H} NMR (pyridine-*d*₅, 25 °C): δ −5.7. Anal. Calcd for C₄₄H₆₆BLuO₃-Si₂: C, 59.72; H, 7.52; Lu, 19.77. Found: C, 59.24; H, 6.90; Lu, 19.35.

[Lu(CH₂SiMe₃)₂(THF)₃]⁺[B(C₆F₅)₄][−] (9b). An NMR tube was charged with a solution of **3** (44 mg, 75 μmol) and [NMe₂PhH]-[B(C₆F₅)₄] (60 mg, 75 μmol) in THF-*d*₈ (0.5 mL). Recorded spectra after 2 h at 25 °C: ¹H NMR (THF-*d*₈, 25 °C): δ −0.93 (s, 2 × 2 H, LuCH₂), −0.05 (s, 2 × 9 H, LuCH₂SiCH₃), 0.02 (s, 12 H, SiMe₄), 2.87 (s, 2 × 3 H, NMe₂Ph), 6.57 (t, ³*J*_{HH} = 7.2 Hz, 1 H, NMe₂Ph-4), 6.66 (d, ³*J*_{HH} = 8.4 Hz, 2 H, NMe₂Ph-2), 7.09 (m, 2 H, NMe₂Ph-3). ¹³C{¹H} NMR (THF-*d*₈, 25 °C): δ −0.1 (SiMe₄), 4.1 (LuCH₂SiCH₃), 40.4 (LuCH₂, NMe₂Ph), 113.1, 116.9, (NC₆H₅), 125.0 (br m, C₆F₅-1), 129.3 (NMe₂Ph), 137.0 (d, ¹*J*_{CF} = 242.8 Hz, C₆F₅-3), 139.0 (d, ¹*J*_{CF} = 242.2 Hz, C₆F₅-4), 149.0 (d, ¹*J*_{CF} = 241.6 Hz, C₆F₅-2). ¹¹B{¹H} NMR (THF-*d*₈, 25 °C): δ −16.7. ¹⁹F NMR (THF-*d*₈, 25 °C): δ −168.8, −165.2, −133.1.

[Lu(CH₂SiMe₃)₂(THF)₃]⁺[BPh₃(CH₂SiMe₃)₃][−] (9c). A mixture of **3** (500 mg, 861 μmol) and BPh₃ (209 mg, 861 μmol) was suspended in THF (20 mL) at −78 °C and stirred at this temperature. The reaction mixture was allowed to slowly warm to ambient temperature and stirred for 4 h to give a very pale yellow solution. After the volatiles were removed under reduced pressure, the resultant yellow oil was washed with heptane (2 × 30 mL) and dried under vacuum to give colorless microcrystals (700 mg, 91%). ¹H NMR (THF-*d*₈, 25 °C): δ −1.03 (s, 2 × 2 H, LuCH₂), −0.49 (s, 9 H, BCH₂SiCH₃), −0.06 (s, 2 × 9 H, LuCH₂SiCH₃), 0.18 (q, ²*J*_{BH} = 4.8 Hz, 2 H, BCH₂), 6.67 (t, ³*J*_{HH} = 7.1 Hz, 3 × 1 H, 4-Ph), 6.83 (m (br), 3 × 2 H, Ph-3), 7.38 (br, 3 × 2 H, Ph-2). ¹H NMR (pyr-*d*₅, 25 °C): δ −0.12 (s, 2 × 2 H, LuCH₂), 0.04 (s, 2 × 9 H, LuCH₂SiCH₃), 0.08 (s, 9 H, BCH₂SiCH₃), 0.96 (q, ²*J*_{BH} = 4.8 Hz, 2 H, BCH₂), 1.60 (m, 3 × 4 H, β-CH₂, THF), 3.64 (m, 3 × 4 H, α-CH₂, THF), 7.06 (t, ³*J*_{HH} = 7.1 Hz, 3 × 1 H, 4-Ph), 7.29 (m, 3 × 2 H, Ph-3), 8.13 (m (br), 3 × 2 H, Ph-2). ¹³C{¹H} NMR (THF-*d*₈, 25 °C): δ 2.8 (BCH₂SiCH₃), 4.2 (LuCH₂SiCH₃), 39.8 (LuCH₂), 121.5 (Ph-4), 125.6 (Ph-3), 135.7 (Ph-2), 167.8 (q, ¹*J*_{BC} = 48.7 Hz, Ph-1). The signal of the BCH₂ group was not detected. ¹¹B{¹H} NMR (THF-*d*₈, 25 °C): δ −10.3. Anal. Calcd for C₄₂H₇₂BO₃Si₃Lu: C, 56.36; H, 8.11; Lu, 19.55. Found: C, 47.29; H, 7.67; Lu, 19.54.

[Lu(CH₂SiMe₃)₂(THF)₃]⁺[B(C₆F₅)₃(CH₂SiMe₃)₃][−] (9d). An NMR tube was charged with a solution of **3** (40 mg, 69 μmol) and B(C₆F₅)₃ (35 mg, 69 μmol) in THF-*d*₈ (0.5 mL). NMR spectra were recorded after 12 h at 40 °C: ¹H NMR (THF-*d*₈, 25 °C): δ −0.92 (s, 2 × 2 H, LuCH₂), −0.37 (s, 9 H, BCH₂SiCH₃), −0.05 (s, 2 × 9 H, LuCH₂SiCH₃), 0.59 (br, 2 H, BCH₂). ¹³C{¹H} NMR (THF-*d*₈, 25 °C): δ 1.3 (BCH₂SiCH₃), 4.1 (LuCH₂SiCH₃), 40.4 (LuCH₂), 129.8 (C₆F₅-1), 137.0 (d, ¹*J*_{CF} = 242.8 Hz, C₆F₅-3), 138.3 (d, ¹*J*_{CF} = 241.2 Hz, C₆F₅-4), 149.2 (d, ¹*J*_{CF} = 226.1 Hz, C₆F₅-2). The signal of the BCH₂ group was not detected. ¹¹B{¹H} NMR (THF-*d*₈, 25 °C): δ −14.2. ¹⁹F NMR (THF-*d*₈, 25 °C): δ −169.4, −167.1, −132.0.

[Sc(CH₂SiMe₃)₂(12-crown-4)]⁺[BPh₃(CH₂SiMe₃)₃][−] (10c). A solution of BPh₃ (83 mg, 345 μmol) in THF (2 mL) was added to a solution of **4** (166 mg, 345 μmol) at room temperature. The solution was stirred at this temperature for 3 h, the solvent was removed under reduced pressure, and the slightly sticky, off-white crude product was washed with heptane (2 × 15 mL). Removing the volatiles under reduced pressure gave **10c** as colorless microcrystals (210 mg, 84%). ¹H NMR (THF-*d*₈, 25 °C): δ −0.50 (s, 9 H, BCH₂SiCH₃), −0.21 (s, 2 × 2 H, ScCH₂), −0.10 (s, 2 × 9 H, ScCH₂SiCH₃), 0.19 (q, ²*J*_{BH} = 4.9 Hz, 2 H, BCH₂), 3.34, 3.65 (m, 2 × 8 H, 12-crown-4), 6.74 (t, ³*J*_{HH} = 6.8 Hz, 3 × 1 H, Ph-4), 6.91 (m, 3 × 2 H, Ph-3), 7.43 (m (br), 3 × 2 H, Ph-2). ¹³C{¹H} NMR (THF-*d*₈, 25 °C): δ 2.6 (BCH₂SiCH₃), 3.6 (ScCH₂SiCH₃), 14.4 (q, ¹*J*_{BC} = 39.3 Hz, BCH₂SiCH₃), 46.3 (s(br), ScCH₂SiCH₃), 68.8 (12-crown-4), 121.7 (Ph-4), 125.8 (Ph-3), 135.7 (Ph-2), 167.9

(q, $^1J_{BC} = 49.1$ Hz, Ph-1). $^{11}\text{B}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ -10.4. Anal. Calcd for $\text{C}_{38}\text{H}_{64}\text{BO}_4\text{Si}_3\text{Sc}$: C, 62.96; H, 8.90; Sc, 6.20. Found: C, 60.64; H, 9.16; Sc, 6.24.

[Y(CH₂SiMe₃)₂(12-crown-4)(THF)_x]⁺[B(C₆F₅)₄]⁻ (11b). An NMR tube was charged with **5** (25 mg, 47 μmol) and [NMe₂PhH]-[B(C₆F₅)₄] (25 mg, 47 μmol) in THF- d_8 (500 μL). NMR spectra were recorded after standing for 10 min at room temperature: ^1H NMR (THF- d_8 , 25 °C): δ -0.73 (d, $^2J_{YH} = 3.1$ Hz, 2 \times 2 H, YCH₂), -0.06 (s, 2 \times 9 H, YCH₂SiCH₃), 0.00 (s, 12 H, SiMe₄), 2.88 (s, 2 \times 3 H, NMe₂Ph), 4.08, 4.20 (m, 2 \times 8 H, 12-crown-4), 6.58 (t, $^3J_{HH} = 7.2$ Hz, 1 H, NMe₂Ph-4), 6.68 (d, $^3J_{HH} = 8.4$ Hz, 2 H, NMe₂Ph-2), 7.11 (m, 2 H, NMe₂Ph-3). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ 0.0 (SiMe₄), 4.2 (YCH₂SiCH₃), 35.3 (d, $^1J_{YC} = 42.4$ Hz, YCH₂), 40.6 (NMe₂Ph), 68.9 (12-crown-4), 113.3, 117.1, 124.8 (m (br), C₆F₅-1), 129.5, 151.8 (NMe₂Ph), 137.9 (m, C₆F₅-3, C₆F₅-4), 148.9 (d, $^1J_{CF} = 247.4$ Hz, C₆F₅-2). $^{11}\text{B}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ -16.7. ^{19}F NMR (THF- d_8 , 25 °C): δ -168.7, -165.1, -133.1.

[Y(CH₂SiMe₃)₂(12-crown-4)(THF)_x]⁺[B(C₆F₅)₃(CH₂SiMe₃)]⁻ (11d). An NMR tube was charged with **5** (50 mg, 95 μmol) and B(C₆F₅)₃ (49 mg, 95 μmol) in THF- d_8 (500 μL). NMR spectra were recorded after standing for 24 h at room temperature and 1 h at 50 °C: ^1H NMR (THF- d_8 , 25 °C): δ -0.73 (d, $^2J_{YH} = 3.4$ Hz, 2 \times 2 H, YCH₂), -0.37 (s, 9 H, BCH₂SiCH₃), -0.07 (s, 2 \times 9 H, YCH₂SiCH₃), 4.08, 4.20 (m, 2 \times 8 H, 12-crown-4). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ 1.2 (BCH₂SiCH₃), 3.9 (YCH₂SiCH₃), 9.5 (BCH₂SiCH₃), 35.1 (d, $^1J_{YC} = 40.8$ Hz, YCH₂), 68.7 (12-crown-4), 129.8 (m (br), C₆F₅-1), 137.0 (d, $^1J_{CF} = 246.2$ Hz, C₆F₅-3), 138.3 (d, $^1J_{CF} = 243.6$ Hz, C₆F₅-4), 149.2 (d, $^1J_{CF} = 238.6$ Hz, C₆F₅-2). $^{11}\text{B}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ -14.2. ^{19}F NMR (THF- d_8 , 25 °C): δ -168.9, -166.6, -131.6.

[Y(CH₂SiMe₃)₂(12-crown-4)(THF)]⁺[Al(CH₂SiMe₃)₄]⁻ (11e). To a solution of **5** (200 mg, 380 μmol) in THF (7 mL) was added neat Al(CH₂SiMe₃)₃ (137 μL , 380 μmol). After the solution was stirred overnight, the solvent was removed under reduced pressure. The residue was washed with pentane to give colorless microcrystals (297 mg, 92%). ^1H NMR (THF- d_8 , 25 °C): δ -1.23 (br, 4 \times 2 H, AlCH₂), -0.73 (d, $^2J_{YH} = 2.80$ Hz, 2 \times 2 H, YCH₂), -0.11 (s, 4 \times 9 H, AlCH₂SiCH₃), -0.06 (s, 2 \times 9 H, YCH₂SiCH₃), 1.77 (m, 4 H, β -CH₂, THF), 3.60 (m, 4 H, α -CH₂, THF), 4.10, 4.22 (br, 2 \times 8 H, 12-crown-4). ^1H NMR (CD₂Cl₂, 25 °C): δ -1.29 (br, 4 \times 2 H, AlCH₂), -0.70 (d, $^2J_{YH} = 2.40$ Hz, 2 \times 2 H, YCH₂), -0.09 (s, 4 \times 9 H, AlCH₂SiCH₃), -0.07 (s, 2 \times 9 H, YCH₂SiCH₃), 2.11 (m, 4 H, β -CH₂, THF), 3.97 (br, 8 H, 12-crown-4), 4.22 (br, 8 \times 4 H, 12-crown-4 + α -CH₂, THF). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ 3.0 (AlCH₂), 4.2 (YCH₂SiCH₃ + AlCH₂SiCH₃), 35.1 (d, $^1J_{YC} = 40.2$ Hz, YCH₂), 68.9 (12-crown-4). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂, 25 °C): δ 3.86 (YCH₂SiCH₃ + AlCH₂SiCH₃), 37.2 (d, $^1J_{YC} = 42.0$ Hz, YCH₂), 72.4 (12-crown-4). Anal. Calcd for C₃₄H₈₆O_{4.5}AlSi₆Y (corresponding to 0.5 THF): C, 47.96; H, 10.18. Found: C, 47.23; H, 10.11.

[Lu(CH₂SiMe₃)₂(12-crown-4)(THF)_x]⁺[B(C₆F₅)₄]⁻ (12b). An NMR tube was charged with **6** (50 mg, 82 μmol) and [NMe₂PhH]-[B(C₆F₅)₄] (65 mg, 82 μmol) in THF- d_8 (500 μL). NMR spectra were recorded after standing for 15 min at room temperature: ^1H NMR (THF- d_8 , 25 °C): δ -0.97 (s, 2 \times 2 H, LuCH₂), -0.06 (s, 2 \times 9 H, LuCH₂SiCH₃), 0.00 (s, 12 H, SiMe₄), 2.88 (s, 2 \times 3 H, NMe₂Ph), 4.04, 4.19 (m, 2 \times 8 H, 12-crown-4), 6.58 (t, $^3J_{HH} = 7.2$ Hz, 1 H, NMe₂Ph-4), 6.68 (d, $^3J_{HH} = 8.4$ Hz, 2 H, NMe₂Ph-2), 7.11 (m, 2 H, NMe₂Ph-3). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ 0.0 (SiMe₄), 4.1 (LuCH₂SiCH₃), 39.1 (LuCH₂), 40.3 (NMe₂Ph), 68.8 (12-crown-4), 113.3, 117.1, 129.5, 151.8 (NMe₂Ph), 125.0 (m (br), C₆F₅-1), 137.9 (m, C₆F₅-3, C₆F₅-4), 148.9 (d, $^1J_{CF} = 243.4$ Hz,

C₆F₅-2). $^{11}\text{B}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ -16.7. ^{19}F NMR (THF- d_8 , 25 °C): δ -168.3, -164.8, -132.8.

[Lu(CH₂SiMe₃)₂(12-crown-4)(THF)_x]⁺[B(C₆F₅)₃(CH₂SiMe₃)]⁻ (12d). An NMR tube was charged with **6** (50 mg, 82 μmol) and B(C₆F₅)₃ (42 mg, 82 μmol) in THF- d_8 (500 μL). NMR spectra were recorded after standing for 24 h at room temperature and 1 h at 50 °C: ^1H NMR (THF- d_8 , 25 °C): δ -0.97 (s, 2 \times 2 H, LuCH₂), -0.36 (s, 9 H, BCH₂SiCH₃), -0.06 (s, 2 \times 9 H, LuCH₂SiCH₃), 4.06, 4.20 (m, 2 \times 8 H, 12-crown-4). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ 1.2 (BCH₂SiCH₃), 4.1 (LuCH₂SiCH₃), 9.5 (BCH₂SiCH₃), 39.1 (LuCH₂), 68.7 (12-crown-4), 129.8 (C₆F₅-1), 137.0 (d, $^1J_{CF} = 242.4$ Hz, C₆F₅-3), 138.2 (d, $^1J_{CF} = 242.4$ Hz, C₆F₅-4), 149.2 (d, $^1J_{CF} = 237.4$ Hz, C₆F₅-2). $^{11}\text{B}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ -14.2. ^{19}F NMR (THF- d_8 , 25 °C): δ -168.9, -166.6, -131.6.

[Y(CH₂SiMe₃)₂(THF)₅]²⁺[BPh₄]⁻² (13a). A mixture of **2** (400 mg, 808 μmol) and [NEt₃H][BPh₄] (1022 mg, 2430 μmol) was suspended in THF (30 mL) at -78 °C. The stirred reaction mixture was allowed to slowly warm to ambient temperature and stirred for 48 h. Removing small amounts of insoluble impurities by filtration gave a colorless clear solution, the volume of which was reduced to 10 mL under reduced pressure. Cooling to -30 °C recovered colorless crystals of [NEt₃H][BPh₄] (323 mg). Evaporation of the volatiles of the supernatant gave a colorless solid residue. Washing with Et₂O (2 \times 20 mL) and removing the solvent under reduced pressure yielded **13a** as a colorless powder (690 mg, 77%). ^1H NMR (pyridine- d_5 , 25 °C): δ 0.17 (s, 9 H, YCH₂SiCH₃), 0.73 (d, $^2J_{YH} = 3.3$ Hz, 2 H, YCH₂SiCH₃), 1.62 (m, 4 \times 4 H, β -CH₂, THF), 3.66 (m, 4 \times 4 H, α -CH₂, THF), 7.10 (t, $^3J_{HH} = 7.3$ Hz, 8 \times 1 H, Ph-4), 7.27 (m, 8 \times 2 H, Ph-3), 8.06 (m (br), 8 \times 2 H, Ph-2). ^{13}C NMR (pyridine- d_5 , 25 °C): δ 4.0 (YCH₂SiCH₃), 25.9 (β -CH₂, THF), 44.5 (dt, $^1J_{YC} = 44.9$ Hz, $^1J_{CH} = 93.8$ Hz, YCH₂-SiCH₃), 67.9 (α -CH₂, THF), 122.4 (Ph-4), 126.2 (Ph-3), 137.1 (Ph-2), 165.0 (q, $^1J_{BC} = 49.2$ Hz, Ph-1). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ 3.9 (YCH₂SiCH₃), 25.5 (β -CH₂, THF), 67.8 (α -CH₂, THF), 122.2 (Ph-4), 125.9 (Ph-3), 137.1 (Ph-2), 165.1 (q, $^1J_{BC} = 49.2$ Hz, Ph-1). The signal for the methylene group attached to yttrium was not detected. $^{11}\text{B}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ -6.7. ^{89}Y NMR (THF- d_8 , 25 °C): δ 409.2. Anal. Calcd for C₇₂H₉₁B₂O₅-SiY: C, 73.59; H, 7.81; Y, 7.57. Found: C, 74.62; H, 8.37; Y, 7.16.

[Lu(CH₂SiMe₃)₂(THF)₄]²⁺[BPh₄]⁻² (14a). A mixture of **3** (290 mg, 500 μmol) and [NMe₂PhH][BPh₄] (552 mg, 1250 μmol) was suspended in THF (30 mL) at -78 °C. The reaction mixture was slowly warmed to room temperature, resulting in a clear, light brown solution, which was stirred for 4 h. Filtration, evaporation of the volatiles and washing with toluene (20 mL), pentane (60 mL) and THF (5 mL) gave **14a** as a colorless powder (370 mg, 62.3%). ^1H NMR (pyridine- d_5 , 25 °C): δ 0.12 (s, 9 H, LuCH₂SiCH₃), 0.47 (s, 2 H, LuCH₂SiCH₃), 1.60 (m, 4 \times 4 H, β -CH₂, THF), 3.64 (m, 4 \times 4 H, α -CH₂, THF), 7.08 (t, $^3J_{HH} = 7.3$ Hz, 8 \times 1 H, Ph-4), 7.25 (m, 8 \times 2 H, Ph-3), 8.03 (m (br), 8 \times 2 H, Ph-2). ^{13}C NMR (pyridine- d_5 , 25 °C): δ 3.8 (LuCH₂SiCH₃), 25.5 (β -CH₂, THF), 44.3 (LuCH₂SiCH₃), 67.5 (α -CH₂, THF), 122.1 (Ph-4), 125.9 (Ph-3), 136.8 (Ph-2), 164.6 (q, $^1J_{BC} = 49.2$ Hz, Ph-1). $^{11}\text{B}\{^1\text{H}\}$ NMR (pyridine- d_5 , 25 °C): δ -5.8. Anal. Calcd for C₆₈H₈₃B₂LuO₄Si: C, 68.69; H, 7.04; Lu, 14.71. Found: C, 62.40; H, 6.78; Lu, 15.13.

[Y(CH₂SiMe₃)₂(12-crown-4)(THF)₃]²⁺[BPh₄]⁻² (15a). A mixture of **5** (44 mg, 84 μmol) and [NEt₃H][BPh₄] (75 mg, 178 μmol) was dissolved in THF (1.5 mL), briefly stirred vigorously and left at 25 °C for 3 days. **15a** was isolated as large, colorless crystals, which were separated in the glovebox from a small amount of colorless needles (of an unidentified coproduct) and dried under vacuum to give **15a** as a white microcrystalline solid (95 mg, 94%).

^1H NMR (pyridine- d_5 , 25 °C): δ -0.19 (s, 2×9 H, $\text{YCH}_2\text{SiCH}_3$), 0.02 (d, $^2J_{\text{YH}} = 3.0$ Hz, 2 H, YCH_2), 1.62 (m, 2×4 H, $\beta\text{-CH}_2$, THF), 3.65 (m, 2×4 H, $\alpha\text{-CH}_2$, THF), 3.99 (m, 16 H, 12-crown-4), 7.11 (t, $^3J_{\text{HH}} = 7.0$ Hz, 8×1 H, Ph-4), 7.26 (m, 8×2 H, Ph-3), 8.00 (m (br), 8×2 H, Ph-2). ^{13}C NMR (pyridine- d_5 , 25 °C): δ 3.2 ($\text{YCH}_2\text{SiCH}_3$), 25.5 ($\beta\text{-CH}_2$, THF), 40.1 (d, $^1J_{\text{YC}} = 42.2$ Hz, $\text{YCH}_2\text{SiCH}_3$), 67.5 ($\alpha\text{-CH}_2$, THF), 69.4 (12-crown-4), 122.1 (Ph-4), 125.9 (Ph-3), 136.7 (Ph-2), 164.5 (q, $^1J_{\text{BC}} = 48.9$ Hz, Ph-1). $^{11}\text{B}\{^1\text{H}\}$ NMR (pyridine- d_5 , 25 °C): δ -5.9. Anal. Calcd for $\text{C}_{72}\text{H}_{91}\text{B}_2\text{O}_7\text{SiY}$ ($3 \times \text{THF}$): C, 71.64; H, 7.60; Y, 7.37; $\text{C}_{68}\text{H}_{83}\text{B}_2\text{O}_6\text{SiY}$ ($2 \times \text{THF}$): C, 71.96; H, 7.37; Y, 7.83. Found: C, 66.61; H, 8.31; Y, 8.29.

$[\text{Y}(\eta^2\text{-C}_5\text{N-C}_5\text{D}_4\text{N})(12\text{-crown-4})(\text{C}_5\text{D}_5\text{N})_n]^{2+}[\text{BPh}_4]^{-2}$. Complex **15a** (50 mg, 41 μmol) was dissolved in pyridine- d_5 (0.5 mL). NMR spectra were measured after standing for 24 h at 25 °C. ^1H NMR (pyridine- d_5 , 25 °C): δ 0.00 (s, 9 H, $\text{Si}(\text{CH}_3)_3(\text{CH}_2\text{D})$), -0.03 (t, $^2J_{\text{DH}} = 2.1$ Hz, 2 H, $\text{Si}(\text{CH}_3)_3(\text{CH}_2\text{D})$), 1.62 (m, 2×4 H, $\beta\text{-CH}_2$, THF), 3.65 (m, 2×4 H, $\alpha\text{-CH}_2$, THF), 4.06 (s, 16 H, 12-crown-4), 7.11 (t, $^3J_{\text{HH}} = 7.0$ Hz, 8×1 H, Ph-4), 7.26 (m, 8×2 H, Ph-3), 8.00 (m (br), 8×2 H, Ph-2). ^{13}C NMR (pyridine- d_5 , 25 °C): δ -0.7 (t, $^1J_{\text{DC}} = 18.2$ Hz, $\text{Si}(\text{CH}_3)_3(\text{CH}_2\text{D})$), -0.3 ($\text{Si}(\text{CH}_3)_3(\text{CH}_2\text{D})$), 25.5 ($\beta\text{-CH}_2$, THF), 67.5 ($\alpha\text{-CH}_2$, THF), 68.9 (12-crown-4), 122.1 (Ph-4), 125.9 (Ph-3), 136.7 (Ph-2), 164.5 (q, $^1J_{\text{BC}} = 48.9$ Hz, Ph-1), 212.6 (d, $^1J_{\text{YC}} = 28.9$ Hz, $\text{C}_5\text{D}_4\text{N-2}$). $^{11}\text{B}\{^1\text{H}\}$ NMR (pyridine- d_5 , 25 °C): δ -5.9.

$[\text{Y}(\text{CH}_2\text{SiMe}_3)(12\text{-crown-4})(\text{THF})_x]^{2+}[\text{B}(\text{C}_6\text{F}_5)_4]^{-2}$ (**15b**). An NMR tube was charged with **5** (25 mg, 47 μmol) and $[\text{NMe}_2\text{PhH}][\text{B}(\text{C}_6\text{F}_5)_4]$ (76 mg, 95 μmol) in THF- d_8 (500 μL). NMR spectra were recorded after standing for 10 min at room temperature: ^1H NMR (THF- d_8 , 25 °C): δ -0.58 (d, $^2J_{\text{YH}} = 3.4$ Hz, 2 H, YCH_2), -0.04 (s, 9 H, $\text{YCH}_2\text{SiCH}_3$), 0.00 (s, 2×12 H, SiMe_4), 2.94 (s, 4×3 H, NMe_2Ph), 4.23, 4.32 (m, 4×8 H, 12-crown-4), 6.70 (t, $^3J_{\text{HH}} = 7.2$ Hz, 2×1 H, $\text{NMe}_2\text{Ph-4}$), 6.78 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2×2 H, $\text{NMe}_2\text{Ph-2}$), 7.16 (m, 2×2 H, $\text{NMe}_2\text{Ph-3}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ 0.0 (SiMe_4), 3.8 ($\text{YCH}_2\text{SiCH}_3$), 39.0 (d, $^1J_{\text{YC}} = 37.1$ Hz, YCH_2), 41.0 (NMe_2Ph), 70.3 (12-crown-4), 113.9, 118.2, 129.6 (NMe_2Ph), 125.0 (m (br), $\text{C}_6\text{F}_5\text{-1}$), 138.2 (m, $\text{C}_6\text{F}_5\text{-3}$, $\text{C}_6\text{F}_5\text{-4}$), 149.1 (d, $^1J_{\text{CF}} = 242.2$ Hz, $\text{C}_6\text{F}_5\text{-2}$). $^{11}\text{B}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ -16.6. ^{19}F NMR (THF- d_8 , 25 °C): δ -168.7, -165.1, -133.1.

$[\text{Y}(\text{CH}_2\text{SiMe}_3)(12\text{-crown-4})(\text{THF})_2]^{2+}[\text{BPh}_3(\text{CH}_2\text{SiMe}_3)]^{-2}$ (**15c**). A solution of **5** (200 mg, 380 μmol) and BPh_3 (184 mg, 759 μmol) in THF (1 mL) was stirred for 2 h at 25 °C. After the solvent was removed under reduced pressure, the residue was washed with pentane to give **15c** as colorless microcrystals (371 mg, 86%). ^1H NMR (THF- d_8 , 25 °C): δ -0.91 (d, $^2J_{\text{YH}} = 2.8$ Hz, 2 H, YCH_2), -0.50 (s, 2×9 H, $\text{BCH}_2\text{SiCH}_3$), -0.10 (s, 9 H, $\text{YCH}_2\text{SiCH}_3$), 0.18 (br q, $^2J_{\text{BH}} = 5.2$ Hz, 2×2 H, BCH_2), 1.77 (m, 2×4 H, $\beta\text{-CH}_2$, THF), 3.16, 3.37 (br, 2×8 H, 12-crown-4), 3.61 (m, 2×4 H, $\alpha\text{-CH}_2$, THF), 6.76 (t, $^3J_{\text{HH}} = 7.2$ Hz, 6×1 H, Ph-4), 6.92 (m, 6×2 H, Ph-3), 7.44 (m (br), 6×2 H, Ph-2). ^1H NMR (CD_2Cl_2 , 25 °C): δ -0.79 (d, $^2J_{\text{YH}} = 2.8$ Hz, 2 H, YCH_2), -0.48 (s, 2×9 H, $\text{BCH}_2\text{SiCH}_3$), -0.16 (s, 9 H, $\text{YCH}_2\text{SiCH}_3$), 0.17 (br, 2×2 H, BCH_2), 2.00 (br, 2×4 H, $\beta\text{-CH}_2$, THF), 2.87, 3.17 (m, 2×8 H, 12-crown-4), 3.80 (br, 2×4 H, $\alpha\text{-CH}_2$, THF), 6.88 (t, $^3J_{\text{HH}} = 7.2$ Hz, 6×1 H, Ph-4), 7.04 (m, 6×2 H, Ph-3), 7.48 (m (br), 6×2 H, Ph-2). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ 2.75 ($\text{BCH}_2\text{SiCH}_3$), 4.03 ($\text{YCH}_2\text{SiCH}_3$), 26.4 ($\beta\text{-CH}_2$, THF), 36.9 (d, $^1J_{\text{YC}} = 43.8$ Hz, YCH_2), 68.3 ($\alpha\text{-CH}_2$, THF), 69.8 (12-crown-4), 122.1 (Ph-4), 126.1 (Ph-3), 136.0 (Ph-2), 168.3 (q, $^1J_{\text{BC}} = 48.1$ Hz, Ph-1). The signal for the BCH_2 group was not detected. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25 °C): δ 2.26 ($\text{BCH}_2\text{SiCH}_3$), 3.37 ($\text{YCH}_2\text{SiCH}_3$), 25.8 ($\beta\text{-CH}_2$, THF), 40.6 (d, $^1J_{\text{YC}} = 47.7$ Hz, YCH_2), 69.4

($\alpha\text{-CH}_2$, THF), 72.3 (12-crown-4), 122.0 (Ph-4), 126.1 (Ph-3), 135.5 (Ph-2), 167.7 (q, $^1J_{\text{BC}} = 48.1$ Hz, Ph-1). The signal for the BCH_2 group was not detected. Anal. Calcd for $\text{C}_{64}\text{H}_{95}\text{B}_2\text{O}_6\text{Si}_3\text{Y}$: C, 66.54; H, 8.29; Y, 7.70. Found: C, 65.15; H, 9.12; Y, 8.07.

$[\text{Lu}(\text{CH}_2\text{SiMe}_3)(12\text{-crown-4})(\text{THF})_x]^{2+}[\text{B}(\text{C}_6\text{F}_5)_4]^{-2}$ (**16b**). An NMR tube was charged with **6** (50 mg, 82 μmol) and $[\text{NMe}_2\text{PhH}][\text{B}(\text{C}_6\text{F}_5)_4]$ (130 mg, 164 μmol) in THF- d_8 (500 μL). NMR spectra were recorded after standing for 30 min at room temperature: ^1H NMR (THF- d_8 , 25 °C): δ -0.68 (s, 2 H, LuCH_2), -0.03 (s, 9 H, $\text{LuCH}_2\text{SiCH}_3$), 0.00 (s, 2×12 H, SiMe_4), 2.92 (s, 4×3 H, $\text{NMe}_2\text{-Ph}$), 4.36, 4.40 (m, 4×8 H, 12-crown-4), 6.66 (t, $^3J_{\text{HH}} = 7.2$ Hz, 2×1 H, $\text{NMe}_2\text{Ph-4}$), 6.75 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2×2 H, $\text{NMe}_2\text{Ph-2}$), 7.16 (m, 2×2 H, $\text{NMe}_2\text{Ph-3}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ 0.0 (SiMe_4), 3.3 ($\text{LuCH}_2\text{SiCH}_3$), 39.8 (LuCH_2), 40.6 (NMe_2Ph), 70.7 (12-crown-4), 113.4, 117.5, 129.3 (NMe_2Ph), 124.7 (m (br), $\text{C}_6\text{F}_5\text{-1}$), 137.9 (m, $\text{C}_6\text{F}_5\text{-3}$, $\text{C}_6\text{F}_5\text{-4}$), 149.1 (d, $^1J_{\text{CF}} = 240.4$ Hz, $\text{C}_6\text{F}_5\text{-2}$). $^{11}\text{B}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ -16.6. ^{19}F NMR (THF- d_8 , 25 °C): δ -168.3, -164.7, -132.7.

$[\text{Y}(\text{CH}_2\text{SiMe}_3)(12\text{-crown-4})(\text{THF})_x]^{2+}[\text{B}(\text{C}_6\text{F}_5)_4]^{-2}$ (**17b**). An NMR tube was charged with **5** (25 mg, 47 μmol) and $[\text{NMe}_2\text{PhH}][\text{B}(\text{C}_6\text{F}_5)_4]$ (76 mg, 95 μmol) in THF- d_8 (500 μL). 12-Crown-4 (8 mg, 47 μmol) was added to the resultant clear, colorless solution. NMR spectra were recorded after standing for 1 h at room temperature: ^1H NMR (THF- d_8 , 25 °C): δ -0.68 (d, $^2J_{\text{YH}} = 2.8$ Hz, 2 H, YCH_2), -0.07 (s, 9 H, $\text{YCH}_2\text{SiCH}_3$), 0.00 (s, 2×12 H, SiMe_4), 2.89 (s, 4×3 H, NMe_2Ph), 4.15, 4.41 (m (br), 4×8 H, 12-crown-4), 6.59 (t, $^3J_{\text{HH}} = 7.2$ Hz, 2×1 H, $\text{NMe}_2\text{Ph-4}$), 6.68 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2×2 H, $\text{NMe}_2\text{Ph-2}$), 7.11 (m, 2×2 H, $\text{NMe}_2\text{Ph-3}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ 0.0 (SiMe_4), 4.0 ($\text{YCH}_2\text{SiCH}_3$), 40.6 (NMe_2Ph), 71.6 (12-crown-4), 113.3, 117.1, 129.4, 151.8 (NMe_2Ph), 125.0 (m (br), $\text{C}_6\text{F}_5\text{-1}$), 138.2 (m, $\text{C}_6\text{F}_5\text{-3}$, $\text{C}_6\text{F}_5\text{-4}$), 149.1 (d, $^1J_{\text{CF}} = 240.2$ Hz, $\text{C}_6\text{F}_5\text{-2}$). The signal for the YCH_2 group was not detected. $^{11}\text{B}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ -16.6. ^{19}F NMR (THF- d_8 , 25 °C): δ -168.6, -165.0, -132.1.

$[\text{Y}(\text{CH}_2\text{SiMe}_3)(12\text{-crown-4})]^{2+}[\text{BPh}_3(\text{CH}_2\text{SiMe}_3)]^{-2}$ (**17c**). A mixture of **2** (300 mg, 606 μmol), BPh_3 (294 mg, 1213 μmol), and 12-crown-4 (94 μL , 606 μmol) was suspended in THF (50 mL) at -100 °C. The stirred suspension was allowed to slowly warm to ambient temperature to give a clear colorless solution after 48 h. The reaction mixture was treated with 12-crown-4 (94 μL , 606 μmol) and stirred for additional 2 h. Evaporation of the volatiles gave a colorless solid residue. Washing with pentane and removing the solvent under reduced pressure afforded **16c** as a colorless powder (533 mg, 74%). ^1H NMR (THF- d_8 , 25 °C): δ -1.05 (d, $^2J_{\text{YH}} = 3.2$ Hz, 2 H, YCH_2), -0.48 (s, 2×9 H, $\text{BCH}_2\text{SiCH}_3$), -0.14 (s, 9 H, $\text{YCH}_2\text{SiCH}_3$), 0.20 (br, 2×2 H, BCH_2), 3.54, 3.68 (br, 2×16 H, 12-crown-4), 6.79 (t, $^3J_{\text{HH}} = 7.3$ Hz, 6×1 H, Ph-4), 6.95 (m, 6×2 H, Ph-3), 7.47 (m (br), 6×2 H, Ph-2). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ 2.8 ($\text{BCH}_2\text{SiCH}_3$), 4.2 ($\text{YCH}_2\text{SiCH}_3$), 26.1 (d, $^1J_{\text{YC}} = 53.3$ Hz, $\text{YCH}_2\text{SiCH}_3$), 71.1 (br, 12-crown-4), 122.1 (Ph-4), 126.2 (Ph-3), 136.0 (Ph-2), 168.3 (q, $^1J_{\text{BC}} = 48.6$ Hz, Ph-1). The signal for the BCH_2 group was not detected. $^{11}\text{B}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ -10.4. Anal. Calcd for $\text{C}_{64}\text{H}_{95}\text{B}_2\text{O}_8\text{-Si}_3\text{Y}$: C, 64.75; H, 8.07; Y, 7.49. Found: C, 64.63; H, 7.96; Y, 7.85.

$[\text{Lu}(\text{CH}_2\text{SiMe}_3)(12\text{-crown-4})]^{2+}[\text{BPh}_4]^{-2}$ (**18a**) and $[\text{Lu}(\text{CH}_2\text{SiMe}_3)(12\text{-crown-4})(\text{pyridine-}d_5)_2]^{2+}[\text{BPh}_4]^{-2}$. A mixture of **6** (200 mg, 326 μmol), 12-crown-4 (57 μL , 362 μmol), and $[\text{NEt}_3\text{H}][\text{BPh}_4]$ (275 mg, 653 μmol) was suspended in THF (10 mL) at -100 °C. The stirred mixture was allowed to slowly warm to ambient temperature. After 48 h a suspension containing colorless microcrystals was obtained. The supernatant was filtered off, and the precipitate was washed with Et_2O (25 mL). Removing the volatiles

under reduced pressure afforded **17a** as colorless microcrystals (333 mg, 82%). ^1H NMR (pyridine- d_5 , 25 °C): δ -0.21 (s, 9 H, $\text{LuCH}_2\text{-SiCH}_3$), -0.17 (s, 2 H, LuCH_2), 3.64 (s, 16 H, 12-crown-4), 4.15 (m, 2×8 H, 12-crown-4), 7.10 (t, $^3J_{\text{HH}} = 7.2$ Hz, 8×1 H, Ph-4), 7.26 (m, 8×2 H, Ph-3), 8.00 (m (br), 8×2 H, Ph-2). $^{13}\text{C}\{^1\text{H}\}$ NMR (pyridine- d_5 , 25 °C): δ 3.5 ($\text{LuCH}_2\text{SiCH}_3$), 70.2, 70.7 (12-crown-4), 122.5 (Ph-4), 126.3 (Ph-3), 137.0 (Ph-2), 164.9 (q, $^1J_{\text{BC}} = 49.4$ Hz, Ph-1). The signal for the LuCH_2 group was not detected. $^{11}\text{B}\{^1\text{H}\}$ NMR (pyridine- d_5 , 25 °C): δ -6.0. Anal. Calcd for $\text{C}_{68}\text{H}_{83}\text{B}_2\text{LuO}_8\text{Si}$: C, 65.18; H, 6.68; Lu, 13.96. Found: C, 64.77; H, 7.16; Lu, 14.11.

[Lu(CH₂SiMe₃)(12-crown-4)₂(THF)₄]₂²⁺[B(C₆F₅)₄]₂⁻ (18b**).** An NMR tube was charged with **6** (50 mg, 82 μmol) and $[\text{NMe}_2\text{PhH}][\text{B}(\text{C}_6\text{F}_5)_4]$ (130 mg, 164 μmol) in THF- d_8 (500 μL). 12-Crown-4 (14 mg, 82 μmol) was added to the resultant clear, colorless solution. NMR spectra were recorded after standing for 1 h at room temperature: ^1H NMR (THF- d_8 , 25 °C): δ -0.73 (2 H, LuCH_2), -0.03 (s, 9 H, $\text{LuCH}_2\text{SiCH}_3$), 0.00 (s, 2×12 H, SiMe_4), 2.88 (s, 4×3 H, NMe_2Ph), 3.61, 4.40 (m (br), 4×8 H, 12-crown-4), 6.59 (t, $^3J_{\text{HH}} = 7.2$ Hz, 2×1 H, $\text{NMe}_2\text{Ph-4}$), 6.69 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2×2 H, $\text{NMe}_2\text{Ph-2}$), 7.11 (m, 2×2 H, $\text{NMe}_2\text{Ph-3}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ 0.0 (SiMe_4), 3.5, 4.1 ($\text{LuCH}_2\text{SiCH}_3$), 40.3 (NMe_2Ph), 69.2, 70.8 (br, 12-crown-4), 113.3, 116.8, 129.2, 151.5 (NMe_2Ph), 125.0 (m (br), C_6F_5 -1), 137.9 (m, C_6F_5 -3, C_6F_5 -4), 148.9 (d, $^1J_{\text{CF}} = 242.3$ Hz, C_6F_5 -2). The signal for the LuCH_2 group was not detected. $^{11}\text{B}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ -16.6. ^{19}F NMR (THF- d_8 , 25 °C): δ -168.2, -164.6, -132.8.

Reaction between 13a and 12-crown-4 in THF- d_8 . 12-Crown-4 (8 μL , 49 μmol) was added to a solution of **13a** (48 mg, 41 μmol) in THF- d_8 , resulting in immediate deposition of an off-white, greasy product, which failed to redissolve under ultrasonication. Soluble fraction: ^1H NMR (THF- d_8 , 25 °C): δ -0.87 (d, $^2J_{\text{YH}} = 2.93$ Hz, 2×2 H, YCH_2 **11**), -0.75 (d, $^2J_{\text{YH}} = 3.17$ Hz, 2×2 H, YCH_2 **8**), -0.09 (s, 2×9 H, $\text{YCH}_2\text{SiCH}_3$ **11**), -0.06 (s, 2×9 H, $\text{YCH}_2\text{-SiCH}_3$ **8**) and other associated resonances. Insoluble fraction: ^1H NMR (pyridine- d_5 , 25 °C): δ -0.21 (s, 2×9 H, $\text{YCH}_2\text{SiCH}_3$), 0.02 (d, $^2J_{\text{YH}} = 2.0$ Hz, 2 H, YCH_2) and other associated resonances.

Reaction between 5, 3 [NMe₂PhH][B(C₆F₅)₄] and 12-crown-4 in THF- d_8 . An NMR tube was charged with **5** (25 mg, 47 μmol) and $[\text{NMe}_2\text{PhH}][\text{B}(\text{C}_6\text{F}_5)_4]$ (76 mg, 95 μmol) in THF- d_8 (500 μL). 12-Crown-4 (8 mg, 47 μmol) was added to the resultant clear, colorless solution, followed by $[\text{NMe}_2\text{HPh}][\text{B}(\text{C}_6\text{F}_5)_4]$ (38 mg,

47 μmol). NMR spectra were recorded after standing for 1 h at room temperature; no resonances due to alkyl groups at the yttrium center were recorded. ^1H NMR (THF- d_8 , 25 °C): δ 0.00 (s, 36 H, SiMe_4), 3.01 (s, 6×3 H, NMe_2Ph), 4.58 (m, 4×8 H, 12-crown-4), 6.84 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3×1 H, $\text{NMe}_2\text{Ph-4}$), 6.92 (d, $^3J_{\text{HH}} = 8.4$ Hz, 3×2 H, $\text{NMe}_2\text{Ph-2}$), 7.24 (m, 3×2 H, $\text{NMe}_2\text{Ph-3}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ 0.0 (SiMe_4), 42.3 (NMe_2Ph), 72.3 (12-crown-4), 115.3, 120.9, 130.1, 149.6 (NMe_2Ph), 125.2 (m (br), C_6F_5 -1), 138.1 (m, C_6F_5 -3, C_6F_5 -4), 149.1 (d, $^1J_{\text{CF}} = 240.2$ Hz, C_6F_5 -2). $^{11}\text{B}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ -16.6. ^{19}F NMR (THF- d_8 , 25 °C): δ -166.7, -163.1, -130.3.

Reaction between 6, 3 [NMe₂PhH][B(C₆F₅)₄] and 12-crown-4 in THF- d_8 . An NMR tube was charged with **6** (50 mg, 82 μmol) and $[\text{NMe}_2\text{PhH}][\text{B}(\text{C}_6\text{F}_5)_4]$ (130 mg, 164 μmol) in THF- d_8 (500 μL). 12-Crown-4 (14 mg, 82 μmol) was added to the resultant clear, colorless solution, followed by $[\text{NMe}_2\text{HPh}][\text{B}(\text{C}_6\text{F}_5)_4]$ (65 mg, 82 μmol). NMR spectra were recorded after standing for 1 h at room temperature; no resonances due to alkyl groups at the lutetium center were recorded. ^1H NMR (THF- d_8 , 25 °C): δ 0.00 (s, 36 H, SiMe_4), 2.95 (s, 6×3 H, NMe_2Ph), 4.62 (s, 4×8 H, 12-crown-4), 6.59 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3×1 H, $\text{NMe}_2\text{Ph-4}$), 6.69 (d, $^3J_{\text{HH}} = 8.4$ Hz, 3×2 H, $\text{NMe}_2\text{Ph-2}$), 7.11 (m, 3×2 H, $\text{NMe}_2\text{Ph-3}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ 0.0 (SiMe_4), 40.3 (NMe_2Ph), 71.6 (12-crown-4), 113.3, 116.8, 129.2, 151.5 (NMe_2Ph), 125.0 (m (br), C_6F_5 -1), 137.9 (m, C_6F_5 -3, C_6F_5 -4), 148.9 (d, $^1J_{\text{CF}} = 242.3$ Hz, C_6F_5 -2). $^{11}\text{B}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C): δ -16.6. ^{19}F NMR (THF- d_8 , 25 °C): δ -168.2, -164.6, -132.8.

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Supporting Information Available: Crystallographic data for the structural analyses of $\text{C}_{20}\text{H}_{49}\text{O}_4\text{ScSi}_3$ (**4**) and $\text{C}_{76}\text{H}_{99}\text{B}_2\text{O}_8\text{SiY}$ (**15a**). This material is available free of charge via the Internet at <http://pubs.acs.org>. Copies of this information may also be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ. Fax +44(1223)336-033 or e-mail deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>.

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