Inorg. Chem. **2005**, *44*, 6777–6788

Inorganic Chemistry
Article

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

Benjamin R. Elvidge, Stefan Arndt, Peter M. Zeimentz, Thomas P. Spaniol, and Jun Okuda*

Institut für Anorganische Chemie, RWTH Aachen University, Landoltweg 1,
D-52074 Aachen, Germany

Received July 6, 2005

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 $[BPh_4]^-$, $[BPh_3(CH_2SiMe_3)]^-$, $[B(C_6F_5)_4]^-$, $[B(C_6F_5)_3(CH_2SiMe_3)]^-$, and $[Al(CH_2SiMe_3)_4]^-$ anions were prepared from corresponding neutral precursors $[Ln(CH_2SiMe_3)_3L_n]$ (Ln = Sc, Y, Lu; L = THF, n = 2 or 3; L = 12-crown-4, n = 1) as solvent-separated ion pairs. The syntheses of the monocationic derivatives $[Ln(CH_2SiMe_3)_2(12\text{-crown-4})_n(THF)_m]^+[A]^-$ 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 $[Ln(CH_2SiMe_3)(12\text{-crown-4})_n(THF)_m]^{2+}[A]^-_2$ 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 $[NMe_2PhH]^+[B(C_6F_5)_4]^-$ abstracts a third alkyl group from $[Ln(CH_2SiMe_3)(12\text{-crown-4})_2(THF)_x]^{2+}[B(C_6F_5)_4]^-_2$ (Ln = Y, 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 $[Ln(CH_2SiMe_3)_3(12\text{-crown-4})]$ (Ln = Sc, Y, Sm, Gd–Lu) in the solid and solution states. The X-ray structure of $[Sc(CH_2SiMe_3)_3(12\text{-crown-4})]$ 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 $[Y(CH_2SiMe_3)(12\text{-crown-4})(THF)_3]^{2+}[BPh_4]^-_2$ 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 $^{13}C\{^1H\}$ NMR resonances arising from the Ln-CH_2 groups and, in the case of yttrium, the $^1J_{YC}$ 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 $[Ln(L_nX)_2L_m]^+[A]^-$ [1] (Ln = rare-earth metal, L_nX = monoanionic ligand, L = neutral ligand, A = anion), a single σ-bound alkyl, and another monoanionic ligand $[Ln(L_nX)RL_m]^+[A]^-$ [2] or two σ-bound alkyls $[LnR_2L_m]^+[A]^-$ [3] 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,[1o,u,v] intramolecular hydroamination,[4] and alkyne dimerization.[2l] Compounds of the form $[LnR_2L_n]^+[A]^-$ have the advantage that a second alkyl group is available for abstraction to give a mono(alkyl) dication of the form $[LnRL_n]^{2+}[A]^-_2$, 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

---

* Corresponding author. E-mail: Jun.Okuda@ac.rwth-aachen.de.

10.1021/ic0511165 CCC: $30.25

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 [Ln(CH_2SiMe_3)$_3$(12-crown-4)] (Ln = Sc (**4**), Y (**5**), and Lu (**6**)) via reaction of [Ln(CH_2SiMe_3)$_3$(THF)$_n$] (Ln = 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, $[NEt_3H]^+[BPh_4]^-$, or $[NMe_2PhH]^+[BPh_4]^-$ 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 Al(CH_2SiMe_3)$_3$ resulted in the formation of the solvent-separated, crystallographically characterized ion pair $[Y(CH_2SiMe_3)_2(THF)_4]^+[Al(CH_2SiMe_3)_4]^-$.[3c]

The monocationic compounds here presented have various anions (**x** = **a**: $[BPh_4]^-$; **b**: $[B(C_6F_5)_4]^-$; **c**: $[BPh_3(CH_2SiMe_3)]^-$; **d**: $[B(C_6F_5)_3(CH_2SiMe_3)]^-$; **e**: $[Al(CH_2SiMe_3)_4]^-$) and either coordinated THF ($[Ln(CH_2SiMe_3)_2(THF)_n]^+[A]^-$: Ln = Sc (**7a**): $n = 3$; Y (**8x**): $n = 3$, 4; **x** = **a**−**e**; Lu (**9x**): $n = 3$, **x** = **a**−**d**) or 12-crown-4 ligands ($[Ln(CH_2SiMe_3)_2(12\text{-crown-}4)(THF)_n]^+[A]^-$: Ln = Sc (**10x**): $n = 0$, 1; **x** = **a**, **c**; Y (**11x**): $n = 1$; **x** = **a**−**e**; Lu (**12x**): $n = 1$, **x** = **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 $[NEt_3H]^+[BPh_4]^-$ (**a**), $[NMe_2PhH]^+[B(C_6F_5)_4]^-$ (**b**), or the Lewis acids BPh_3 (**c**), $B(C_6F_5)_3$ (**d**), or Al(CH_2SiMe_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 ($[Ln(CH_2SiMe_3)(THF)_n]^{2+}[A]^-{}_2$: Ln = Y (**13x**): $n = 5$; **x** = **a**; Lu (**14x**): $n = 4$, **x** = **a**) and 12-crown-4 ligands ($[Ln(CH_2SiMe_3)(12\text{-crown-}4)(THF)_n]^{2+}[A]^-{}_2$: Ln = Y (**15x**): $n = 2$, 3; **x** = **a**−**c**; Ln = Lu (**16b**); $[Ln(CH_2SiMe_3)(12\text{-crown-}4)_2]^{2+}[A]^-{}_2$: Ln = Y (**17x**): **x** = **b**, **c**; Lu (**18x**): **x** = **a**, **b**; Scheme 2) were synthesized in good yields. All complexes

---

(1) Cationic rare-earth metal complexes incorporating *only* π-bound hydrocarbyl ligands utilize three ligand types: "Cp": (a) Evans, W. J.; Bloom, I.; Grate, J. W.; Hughes, L. A.; Hunter, W. E.; Atwood, J. L. *Inorg. Chem.* **1985**, *24*, 4620. (b) Hazin, P. N.; Bruno, J. W.; Schulte, G. K. *Organometallics* **1990**, *9*, 416. (c) Evans, W. J.; Ulibarri, T. A.; Chamberlain, L. R.; Ziller, J. W.; Alvarez, D., Jr. *Organometallics* **1990**, *9*, 2124. (d) Heeres, H. J.; Meetsma, A.; Teuben, J. H. *J. Organomet. Chem.* **1991**, *414*, 351. (e) Evans, W. J.; Kociok-Köhn, G.; Ziller, J. W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1081. (f) Deng, D.; Zheng, X.; Qian, C.; Sun, J.; Dormond, A.; Baudry, D.; Visseaux, M. *J. Chem. Soc., Dalton Trans.* **1994**, 1665. (g) Schumann, H.; Winterfeld, J.; Keitsch, M. R.; Herrmann, K.; Demtschuk, J. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1457. (h) Yuan, F.; Shen, Q.; Sun, J. *J. Organomet. Chem.* **1997**, *538*, 241. (i) Song, X.; Thornton-Pett, M.; Bochmann, M. *Organometallics* **1998**, *17*, 1004. (j) Evans, W. J.; Seibel, C. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1998**, *120*, 6745. (k) Evans, W. J.; Seibel, C. A.; Forrestal, K. J.; Ziller, J. W. *J. Coord. Chem.* **1999**, *48*, 403. (l) Xie, Z.; Liu, Z.; Chui, K.; Xue, F.; Mak, T. C. W. *J. Organomet. Chem.* **1999**, *588*, 78. (m) Molander, G. A.; Rzasa, R. M. *J. Org. Chem.* **2000**, *65*, 1215. (n) Evans, W. J.; Davis, B. L.; Ziller, J. W. *Inorg. Chem.* **2001**, *40*, 6341. (o) Kaita, S.; Hou, Z. M.; Nishiura, M.; Doi, Y.; Kurazumi, J.; Horiuchi, A. C.; Wakatsuki, Y. *Macromol. Rapid Commun.* **2003**, *24*, 179. (p) Evans, W. J.; Perotti, J. M.; Brady, J. C.; Ziller, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 5204. (q) Evans, W. J.; Perotti, J. M.; Ziller, J. W. *J. Am. Chem. Soc.* **2005**, *127*, 3894. "η^8-C_8H_8": (r) Cendrowski-Guillaume, S. M.; Nierlich, M.; Lance, M.; Ephritikhine, M. *Organometallics* **1998**, *17*, 786. (s) Cendrowski-Guillaume, S. M.; Le Gland, G.; Nierlich, M.; Ephritikhine, M. *Organometallics* **2000**, *19*, 5654. (t) Cendrowski-Guillaume, S. M.; Nierlich, M.; Ephritikhine, M. *Eur. J. Inorg. Chem.* **2001**, 1495. "allyl": (u) Taube, R.; Maiwald, S.; Sieler, J. *J. Organomet. Chem* **2001**, *621*, 327. (v) Kaita, S.; Hou, Z.; Wakatsuki, Y. US2002/0119889A1.

(2) Cationic rare-earth metal complexes incorporating one σ-bound alkyl and another different monoanionic ligand utilize four ligand types: "LX": (a) Bambirra, S.; van Leusen, D.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Chem. Commun.* **2003**, 522. (b) Bambirra, S.; Bouwkamp, M. W.; Meetsma, A.; Hessen, B. *J. Am. Chem. Soc.* **2004**, *126*, 9182. "L_2X": (c) Schaverien, C. J. *Organometallics* **1992**, *11*, 3476. (d) Lee, L. W. M.; Piers, W. E.; Elsegood, M. R. J.; Clegg, W.; Parvez, M. *Organometallics* **1999**, *18*, 2947. (e) Hayes, P. G.; Piers, W. E.; McDonald, R. *J. Am. Chem. Soc.* **2002**, *124*, 2132. (f) Hayes, P. G.; Piers, W. E.; Parvez, M. *J. Am. Chem. Soc.* **2003**, *125*, 5622. (g) Hayes, P. G.; Welch, G. C.; Emslie, D. J. H.; Noack, C. L.; Piers, W. E.; Parvez, M. *Organometallics* **2003**, *22*, 1577. (h) Cameron, T. M.; Gordon, J. C.; Michalczyk, R.; Scott, B. L. *Chem. Commun.* **2003**, 2282. (i) Henderson, L. D.; MacInnis, G. D.; Piers, W. E.; Parvez, M. *Can. J. Chem.* **2004**, *82*, 162. (j) Luo, Y.; Baldamus, J.; Hou, Z. *J. Am. Chem. Soc.* **2004**, *126*, 13910. "L_3X": (k) Bambirra, S.; van Leusen, D.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Chem. Commun.* **2001**, 637. (l) Tazelaar, C. G. J.; Bambirra, S.; van Leusen, D.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2004**, *23*, 936. (m) Bambirra, S.; Boot, S. J.; van Leusen, D.; Meetsma, A.; Hessen, B. *Organometallics* **2004**, *23*, 1891. (n) Hessen, B.; Bambirra, S., WO2002032909. (o) Christopher, J. N.; Squire, L. R.; Canich, J. A. M.; Schaffer, T. D., WO0018808. "L_5X": (p) Lee, L.; Berg, D. J.; Einstein, F. W.; Batchelor, R. J. *Organometallics* **1997**, *16*, 1819.

(3) Cationic rare-earth metal complexes incorporating two σ-bound alkyls "CH_2SiMe_3": (a) Arndt, S.; Spaniol, T. P.; Okuda, J. *Chem. Commun.* **2002**, 896. (b) Arndt, S.; Zeimentz, P. M.; Spaniol, T. P.; Okuda, J.; Honda, M.; Tatsumi, K. *Dalton Trans.* **2003**, 3622. (c) Arndt, S.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 5075. (d) Okuda, J.; Arndt, S.; Matsui, S., JP2005015579. (e) Ward, B. D., Bellemin-Laponnaz, S.; Gade, L. H. *Angew. Chem., Int. Ed.* **2005**, *44*, 1668. (f) Lawrence, S. C.; Ward, B. D.; Dubberley, S. R.; Kozak, C. M.; Mountford, P. *Chem. Commun.* **2003**, 2880. "CH_3": (g) Hajela, S.; Schaefer, W. P.; Bercaw, J. E. *J. Organomet. Chem.* **1997**, *532*, 45.

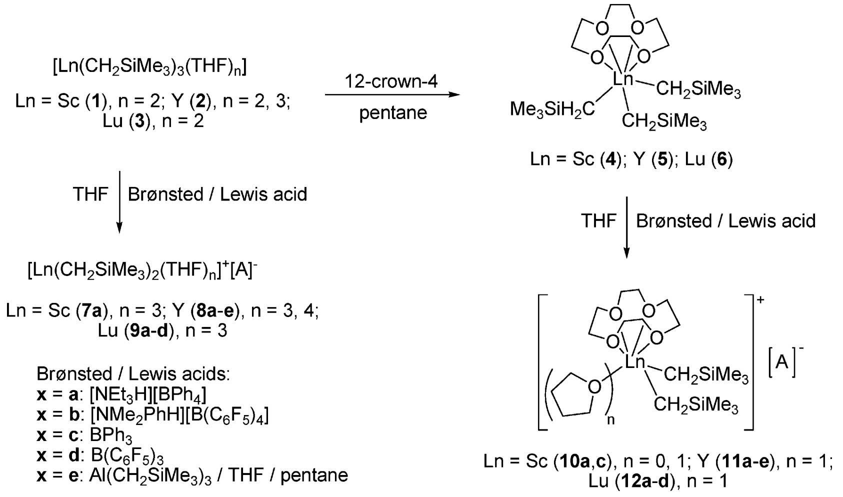
(4) Lauterwasser, F.; Hayes, P. G.; Bräse, S.; Piers, W. E.; Schafer, L. L. *Organometallics* **2004**, *23*, 2234.

(5) Taube, R. In *Metalorganic Catalysts for Synthesis and Polymerisation*; Kaminsky, W., Ed.; Springer: Berlin, Germany, 1999; p 531.

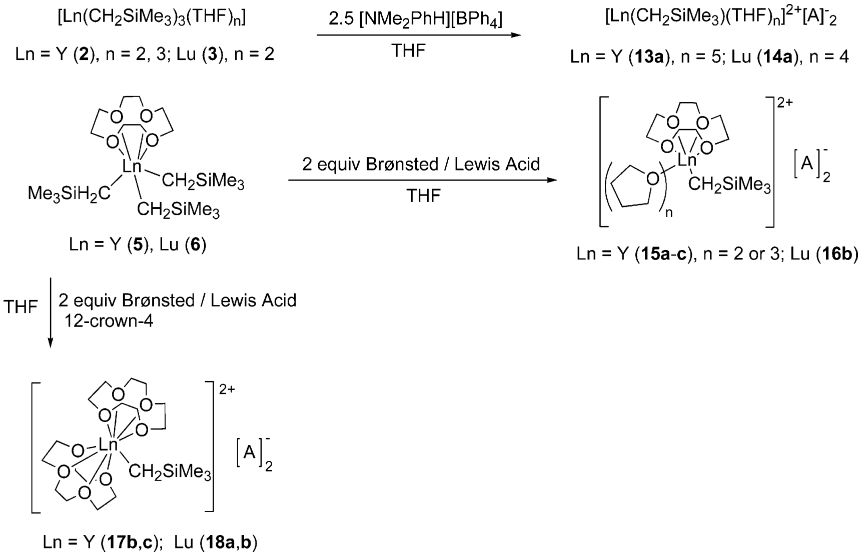
(6) Arndt, S.; Okuda, J. *Adv. Synth. Catal.* **2005**, *347*, 339.

(7) Pyridine activation processes involving rare-earth metal alkyl and hydride complexes are known, see Kirillov, E.; Lehmann, C. W.; Razavi, A.; Carpentier, J.-F. *Eur. J. Inorg. Chem.* **2004**, 943 and references therein.

Scheme 1



Scheme 2



are highly soluble in pyridine-d_5, but their solubility in other solvents such as THF-d_8 and CD_2Cl_2 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 $[NMe_2PhH]^+[BPh_4]^-$ was used for the synthesis.[8] **15a** was isolated from a mixture of **5** and 2.1 equiv of $[NEt_3H]^+[BPh_4]^-$ 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 $[NEt_3H]^+[BPh_4]^-$.[10]

A series of dicationic mono- and bis(12-crown-4) (**15b**, **16b**, **17b**, and **18b**) yttrium and lutetium complexes supported by the $[B(C_6F_5)_4]^-$ anion were prepared in THF-d_8 by reaction of **5** or **6** with 2 equiv of $[NMe_2PhH]^+[B(C_6F_5)_4]^-$. 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 $[NMe_2PhH]^+[B(C_6F_5)_4]^-$ to give a trimethylsilylmethyl-free complex and a third equiv of tetramethylsilane.[11] The $[B(C_6F_5)_4]^-$ anion afforded dicationic complexes of a much higher THF solubility than the borate $[BPh_4]^-$.

When 2 equiv of BPh_3 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 BPh_4, 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 BPh_4, coordinated 12-crown-4 and THF. Titration for Lu content gave 12.08%; $[Lu(12\text{-crown-}4)_2(THF)]^{3+}[BPh_4]^-{}_3$ ($C_{92}H_{100}B_3LuO_9$) requires 11.24%.

(10) The analogous procedure for yttrium gave a mixture tentatively assigned by NMR spectroscopy as $[Y(CH_2SiMe_3)(12\text{-crown-}4)_2]^{2+}[BPh_4]^-{}_2$, **15a** and an alkyl-free byproduct.

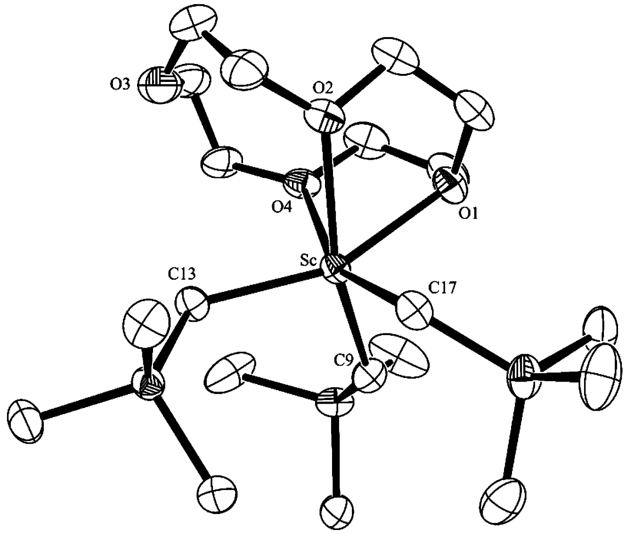


Figure 1. ORTEP representation of the molecular structure of [Sc(CH_2SiMe_3)$_3$(12-crown-4)] (**4**). Thermal ellipsoids are drawn at 30%, and hydrogen atoms have been omitted for clarity.

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 Al(CH_2SiMe_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 (Sc−O(1) = 2.276(2), Sc−O(2) = 2.423(3), and Sc−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)°, 161.41(10)°, and 156.46(11)°, respectively (Table 1). The Sc−C(alkyl) separations (Sc−C(9) = 2.219(3), Sc−C(13) = 2.243(3), and Sc−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 complexes including the [Sc(12-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 [$ScCl_2$(15-crown-5)]$^+_2$[$CuCl_4$]$^{2-}$, [$ScCl_2$(18-crown-6)]$^+$[$SbCl_6$]$^-$, and [$ScCl_2$(benzo-15-crown-5)]$^+$[$SbCl_6$]$^-$ 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 [$ScCl_2$(18-crown-6)]$^+$[$FeCl_4$]$^-$, only five of the six oxygen atoms coordinate to the Sc center; the average Sc−O(coordinated) bond length is 2.215 Å.[17]

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)

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 (Y−C(21) = 2.424(4) Å) is very similar to that recorded for [Y(CH_3)(THF)$_6$]$^{2+}$[BPh_4]$^-_2$.[3c] Surprisingly, it is also similar to the two Y−C separations in the monocationic complex [Y(CH_2SiMe_3)$_2$(THF)$_4$]$^+$[Al(CH_2SiMe_3)$_4$]$^-$,[3c] the neutral 12-crown-4 supported tris(trimethylsilylmethyl) [Y(CH_2SiMe_3)$_3$(12-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 [Ln(12-crown-4)$_2$(THF)$_x$]$^{3+}$[B(C_6F_5)$_4$]$^-_3$ (Ln = Y, Lu). The yttrium compound was alkyl-free on a preparative scale (residual NMe_2Ph was noted). The ^1H and $^{13}C\{^1H\}$ 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 [Y(CH_2SiMe_3)(THF)$_n$]$^{2+}$[BPh_3(CH_2SiMe_3)]$^-_2$ after 2 days at room temperature.

(14) (a) Estler, F.; Eickerling, G.; Herdtweck, E.; Anwander, R. *Organometallics* **2003**, *22*, 1212. (b) Lara-Sanchez, A.; Rodriguez, A.; Hughes, D. L.; Schormann, M.; Bochmann, M. *J. Organomet. Chem.* **2002**, *663*, 63. (c) Ward, B. D.; Dubberley, S. R.; Maisse-Francois, A.; Gade, L. H.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **2002**, 4649. (d) Emslie, D. J. H.; Piers, W. E.; Parvez, M.; McDonald, R. *Organometallics* **2002**, *21*, 4226 and references therein. (e) Hayes, P. G.; Piers, W. E.; Lee, L. W. M.; Knight, L. K.; Parvez, M.; Elsegood, M. R. J.; Clegg, W. *Organometallics* **2001**, *20*, 2533.

(15) (a) Willey, G. R.; Meehan, P. R.; Drew, M. G. B. *Polyhedron* **1996**, *15*, 1397. (b) Nishihara, S.; Takamatsu, N.; Akutagawa, T.; Hasegawa, T.; Nakamura, T. *Synth. Met.* **2001**, *121*, 1806.

(16) (a) Willey, G. R.; Lakin, M. T.; Alcock, N. W. *J. Chem. Soc., Chem. Commun.* **1992**, 1619. (b) Willey, G. R.; Lakin, M. T.; Alcock, N. W. *J. Chem. Soc., Dalton Trans.* **1993**, 3407.

(17) Brown, M. D.; Levason, W.; Murray, D. C.; Popham, M. C.; Reid, G.; Webster, M. *Dalton Trans.* **2003**, 857.

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

compound	Sc−C (Å)	reference
	Neutral Tris(alkyl) Complexes	
$[Sc(CH_2SiMe_2Ph)_3(THF)_2]$	2.248(2), 2.254(2), 2.2498(19)	14d
$[Sc(CH_2SiMe_3)_3(12\text{-crown-}4)]$	2.219(3), 2.243(3), 2.251(3)	this work
	Neutral Bis(alkyl) Complexes	
$[Sc(ArNC(Ph)NAr)(CH_2SiMe_3)_2(THF)]^a$	2.229(3), 2.195(3)	2b
$[Sc(Ar'O)(CH_2SiMe_3)_2(THF)]^b$	2.236(2), 2.246(2)	14b
$[Sc\{ArNC(Me)CHC(Me)NAr\}(CH_2SiMe_3)_2]^a$	2.2446(13), 2.1954(14)	14e
$[Sc\{ArNC(tBu)CHC(tBu)NAr\}(CH_2SiMe_3)_2]^a$	2.229(7), 2.202(7)	14e

^{a} Ar = 2,6-*i*Pr−C_6H_3. ^{b}Ar'O = {2-(2,4,6-$Me_3C_6H_2N$═CH)(6-*t*Bu)C_6H_3O}.

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

	4	**15a**
chemical formula	$C_{20}H_{49}O_4ScSi_3$	$C_{76}H_{99}B_2O_8SiY$
formula weight	482.82	1279.17
T	293(2) K	110(2) K
λ	0.71073 Å	0.71073 Å
crystal system, space group	monoclinic, $P2_1/n$ (No. 14)	monoclinic, $P2_1/c$ (No. 14)
a	10.849(4) Å	21.857(5) Å
b	15.690(2) Å	16.632(4) Å
c	17.256(3) Å	18.846(5) Å
α	90°	90°
β	97.50(2)°	94.451(5)°
γ	90°	90°
V	2912.2(12) Å^3	6830(3) Å^3
Z	4	4
D_{calc}	1.101 Mg/m^3	1.244 Mg/m^3
$R(F_o^2)$, $R_w(F_o^2)$ [$I > 2\sigma(I)$]	0.0503, 0.1055	0.0636, 0.1695
$R(F_o^2)$, $R_w(F_o^2)$ (all data)	0.0944, 0.1227	0.1171, 0.2019

^{a} $R(F_o^2)$ and $Rw(F_o^2)$ are defined as the final R indices [$I > 2\sigma(I)$].

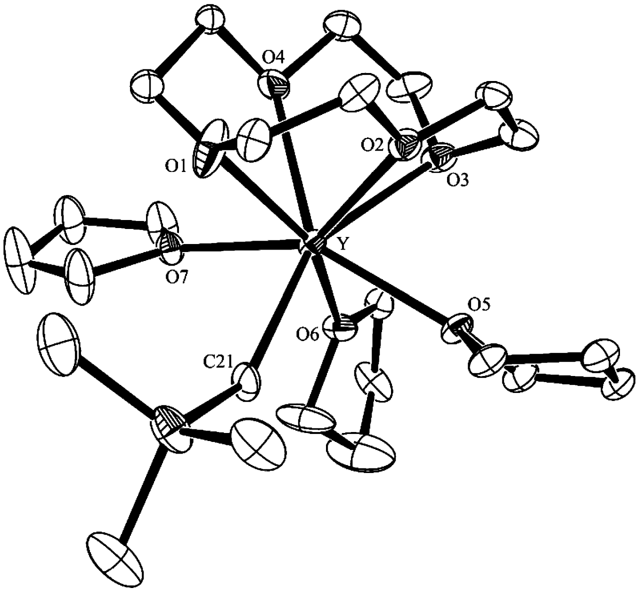


Figure 2. ORTEP representation of the molecular structure of $[Y(CH_2SiMe_3)(12\text{-crown-}4)(THF)_3]^{2+}[BPh_4]^-{}_2$ (**15a**). Thermal ellipsoids are drawn at 30%, and hydrogen atoms and borate anions have been omitted for clarity.

are comparable to those in $[Y(OH_2)_5(12\text{-crown-}4)]^{3+}(Cl)^-{}_3{\cdot}2H_2O$ (2.42(1)−2.59(1) Å) and $[YCl_2(OH_2)(OHMe)(12\text{-crown-}4)]^+(Cl)^-$ (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 CD_2Cl_2 and THF-d_8 solution is labile. The ^1H NMR spectrum of **4** (CD_2Cl_2, 25 °C) showed two sharp singlets arising from the Sc−CH_2 (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-CH_2 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−CH_2 (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 $^{13}C\{^1H\}$ NMR spectra. The 12-crown-4 ligand in the previously reported yttrium analogue **5** is not labile in CD_2Cl_2 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 $^{13}C\{^1H\}$ NMR spectra in pyridine-d_5. Trace $Si(CH_3)_3(CH_2D)$ was observed after a few

---

(18) (a) Westerhausen, M.; Hartmann, M.; Schwarz, W. *Inorg. Chim. Acta* **1998**, *269*, 91. (b) den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojicprodic, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726. (c) den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Smeets, W. J. J.; Spek, A. L. *J. Organomet. Chem.* **1987**, *327*, 31. (d) Coughlin, E. B.; Henling, L. M.; Bercaw, J. E. *Inorg. Chim. Acta* **1996**, *242*, 205. (e) Arndt, S.; Beckerle, K.; Zeimentz, P. M.; Spaniol, T. P.; Okuda, J. Unpublished work.

(19) Rogers, R. D.; Rollins, A. N.; Benning, M. M. *Inorg. Chem.* **1988**, *27*, 3826.

(20) (a) Evans, W. J.; Olofson, J. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2308. (b) Sobota, P.; Utko, J.; Szafert, S. *Inorg. Chem.* **1994**, *33*, 5203. (c) Chiu, K. Y.; Zhang, Z. Y.; Mak, T. C. W.; Xie, Z. W. *J. Organomet. Chem.* **2000**, *614*, 107.

(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
$[Y(CH_2SiMe_3)_3(THF)_3]$	2.427(19) (mean)	29b
$[Y(CH_2SiMe_3)_3(12\text{-crown-4})]$	2.399(6)−2.430(6)	3b
Neutral Metallocenes		
$[Y(\eta^5\text{-}C_5Me_5)_2\{CH(SiMe_3)_2\}]$	2.468(7)	18b
$[Y(\eta^5\text{-}C_5Me_5)_2(CH_3)(THF)]$	2.44(2)	18c
$[Y\{(\eta^5\text{-}C_5Me_4)_2SiMe_2\}\{CH(SiMe_3)_2\}]$	2.418(6)	18d
Alkyl Monocations		
$[Y(CH_2SiMe_3)_2(THF)_4]^+[Al(CH_2SiMe_3)_4]^-$	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
$[Y(CH_2SiMe_3)(12\text{-crown-4})(THF)_3]^{2+}[BPh_4]^-{}_2$	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
$[YCl_2(THF)_5]^+[C_2B_9H_{12}]^-$	2.309(7)−2.401(7)	20c
$[Y(CH_2SiMe_3)_2(THF)_4]^+[Al(CH_2SiMe_3)_4]^-$	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
$[Y(CH_2SiMe_3)(12\text{-crown-4})(THF)_3]^{2+}[BPh_4]^-{}_2$	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 $Si(CH_3)_3(CH_2D)$ as the only resonance in the $\delta < 1$ ppm region of the ^1H NMR spectrum. The resonance arising from the Y−CH_2 group was also lost in the $^{13}C\{^1H\}$ 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 $[Ln(L_2X)_2(\eta^2\text{-}(C,N)\text{-}C_5H_4N)]$ ($L_2X = C_5Me_5$, Ln = Sc,[22] Y,[23] Lu;[24] $LX_2 = C_5H_4R$ (R = H, Me), Ln = Y[25]) 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 $[Y(\eta^2\text{-}(C,N)\text{-}C_5D_4N)(12\text{-crown-4})(C_5D_5N)_n]^{2+}[BPh_4]^-{}_2$, based on the observed formation of $Si(CH_3)_3(CH_2D)$ and the appearance of a low intensity doublet in the $^{13}C\{^1H\}$ 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 ^{11}B and ^{19}F NMR spectroscopy, the ions are separated in solution. The ^{11}B 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 ^{19}F NMR spectrum, which has been previously used as an indicator of solvent-separated ion pairs.[27] The ^{19}F NMR resonances arising from both $[B(C_6F_5)_4]^-$ and $[B(C_6F_5)_3(CH_2SiMe_3)]^-$ are clearly cation independent.

We have found a strong effect on the ^{89}Y 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). $^{13}C\{^1H\}$ and ^1H NMR spectra also give similar evidence for an increase in nuclear charge concomitant with cation formation. For instance, the Y−CH_2 ^{13}C 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-

---

(22) Thomson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.M Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

(23) Deelman, B.-J.; Stevels, W. M.; Teuben, J. H.; Lakin, M. T.; Spek, A. L. *Organometallics* **1994**, *13*, 3881.

(24) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276.

(25) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291.

(26) $[YCp^*{}_2(2\text{-pyridyl})]$, synthesized from $[YCp^*{}_2(CH(SiMe_3)_2)]$ and pyridine, gives rise to a doublet in the $^{13}C\{^1H\}$ NMR spectrum (225.5 ppm, $^1J_{YC} = 33.2$ Hz) for the pyridine α-carbon (see ref 23).

(27) ^{19}F chemical shift differences between meta and para fluorine atoms of less than 3 ppm are indicative of a noncoordinating anion for $[RB(C_6F_5)_3]^-$ ($R = Me, CH_2Ph$): 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)	$^2J_{YH}$ (Hz)	δ (^{13}C) Ln−CH$_2$ (ppm)	$^1J_{YC}$ (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 CD$_2$Cl$_2$. [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−CH$_2$ groups of the monocationic THF-supported scandium, yttrium, and lutetium complexes give rise to higher frequency resonances in the ^{1}H 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−CH$_2$, THF-d_8: δ −0.78 ppm; Lu−CH$_2$, THF-d_8: δ −0.99 ppm) to dicationic (Y−CH$_2$, THF-d_8: δ −0.67 ppm; Lu−CH$_2$, 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−CH$_2$ 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 ^{11}B or ^{19}F 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 multinuclear 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 ^{89}Y and ^{13}C{^{1}H} 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 ^{1}H and ^{13}C{^{1}H} 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(CH$_2$SiMe$_3$)$_3$(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 1i,j,o and 2c. BPh$_4$ 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(CH$_2$SiMe$_3$)$_3$(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 (^{1}H, 400.1 MHz,^{13}C, 100.6 MHz, ^{11}B, 128.4 MHz, ^{19}F, 376.4 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, ^{19}F 470.1 MHz). Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. ^{11}B NMR spectra were referenced externally to a 1 M solution of NaBH$_4$ in D$_2$O. ^{19}F NMR spectra were referenced externally to CCl$_3$F. ^{89}Y spectra were referenced externally to a 1 M solution of YCl$_3$ in D$_2$O.

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(CH$_2$SiMe$_3$)$_2$(THF)$_3$]$^+$[BPh$_4$]$^-$ (7a). A mixture of **1** (451 mg, 1.00 mmol) and [NEt$_3$H][BPh$_4$] (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%). ^{1}H NMR (THF-d_8, 25 °C): δ −0.21 (s, 2 × 2 H, ScC*H*$_2$SiCH$_3$), −0.04 (s, 2 × 9 H, ScCH$_2$SiC*H*$_3$), 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). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 3.5 (ScCH$_2$Si*C*H$_3$), 15.3 (β-CH$_2$, NEt$_3$), 45.0 (s (br), Sc*C*H$_2$SiCH$_3$), 65.9 (α-CH$_2$, NEt$_3$), 121.6 (Ph-4), 125.4 (Ph-3), 136.7 (Ph-2), 164.8 (q, $^1J_{BC}$ = 49.3 Hz).^{11}B{^{1}H} NMR (THF-d_8, 25 °C): δ −6.6. Anal. Calcd for C$_{44}$H$_{66}$BO$_3$Si$_2$Sc: C, 70.00; H, 8.81; Sc, 5.95. Found: C, 67.22; H, 8.26; Sc, 5.93.

[Y(CH$_2$SiMe$_3$)$_2$(THF)$_x$]$^+$[BPh$_4$]$^-$ (8a) (x = 3 or 4). A mixture of **2** (1000 mg, 1884 μmol) and [NEt$_3$H][BPh$_4$] (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(CH$_2$SiMe$_3$)$_2$(THF)$_3$]$^+$[BPh$_4$]$^-$ (1484 mg, 99%). The alternative product [Y(CH$_2$SiMe$_3$)$_2$(THF)$_4$]$^+$[BPh$_4$]$^-$ can be regenerated by a final washing with THF (5 mL) and drying under vacuum. ^{1}H NMR (THF-d_8, 25 °C): δ −0.78 (d, $^2J_{YH}$ = 3.3 Hz, 2 × 2 H, YC*H*$_2$SiCH$_3$), −0.06 (s, 2 × 9 H, YCH$_2$SiC*H*$_3$), 1.76 (m, 4 × 4 H, β-CH$_2$, THF), 3.60 (m, 4 × 4 H, α-CH$_2$, 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).^{1}H NMR (pyridine-d_5, 25 °C): δ −0.08 (d, $^2J_{YH}$ = 2.3 Hz, 2 × 2 H, YC*H*$_2$SiCH$_3$), 0.19 (s, 2 × 9 H, YCH$_2$SiC*H*$_3$), 1.65 (m, 4 × 4 H, β-CH$_2$, THF), 3.68 (m, 4 × 4 H, α-CH$_2$, 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). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 4.1 (YCH$_2$Si*C*H$_3$), 36.9 (d, $^1J_{YC}$ = 41.2 Hz, Y*C*H$_2$SiCH$_3$), 122.0 (Ph-4), 125.8 (Ph-3), 137.1 (Ph-2), 165.2 (q, $^1J_{BC}$ = 49.3 Hz).^{13}C NMR (pyridine-d_5, 25 °C): δ 4.5 (YCH$_2$Si*C*H$_3$), 25.8 (β-CH$_2$, THF), 30.9 (dt, $^1J_{YC}$ = 36.5 Hz, $^1J_{CH}$ = 97.2 Hz, Y*C*H$_2$SiCH$_3$) 67.8 (α-CH$_2$, THF), 122.3 (Ph-4), 126.2 (Ph-3), 137.2 (Ph-2), 165.0 (q, $^1J_{BC}$ = 49.3 Hz, Ph-1). ^{11}B{^{1}H} NMR (THF-d_8, 25 °C): δ −6.6. ^{89}Y NMR (THF-d_8, 25 °C): δ 660.0. Anal. Calcd for C$_{48}$H$_{74}$BO$_4$Si$_2$Y: C, 66.19; H, 8.56; Y, 10.21. Found: C, 65.91; H, 8.44; Y, 9.74.

[Y(CH$_2$SiMe$_3$)$_2$(THF)$_x$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (8b). An NMR tube was charged with a solution of **2** (37 mg, 75 μmol) and [NMe$_2$PhH][B(C$_6$F$_5$)$_4$] (60 mg, 75 μmol) in THF-d_8 (0.5 mL). NMR spectra were recorded after 40 min at 25 °C: ^{1}H NMR (THF-d_8, 25 °C): δ −0.69 (d, $^2J_{YH}$ = 3.2 Hz, 2 × 2 H, YCH$_2$), −0.05 (s, 2 × 9 H, YCH$_2$SiC*H*$_3$), 0.02 (s, 12 H, SiMe$_4$), 2.87 (s, 2 × 3 H, N*Me*$_2$Ph-3), 6.57 (t, $^3J_{HH}$ = 7.2 Hz, 1 H, NMe$_2$*Ph*-4), 6.65 (d, $^3J_{HH}$ = 8.4 Hz, 2 H, NMe$_2$*Ph*-2), 7.09 (m, 2 H, NMe$_2$*Ph*-3). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ −0.1 (SiMe$_4$), 3.9 (YCH$_2$Si*C*H$_3$), 37.4 (d, $^1J_{YC}$ = 41.6 Hz, YCH$_2$), 40.4 (N*Me*$_2$Ph), 113.1, 116.9 (NC$_6$H$_5$), 125.0 (br m, C$_6$F$_5$-1), 129.3 (NMe$_2$*Ph*), 137.0 (d, $^1J_{CF}$ = 241.6 Hz, C$_6$F$_5$-3), 139.0 (d, $^1J_{CF}$ = 242.8 Hz, C$_6$F$_5$-4), 149.0 (d, $^1J_{CF}$ = 243.4 Hz, C$_6$F$_5$-2).^{11}B{^{1}H} NMR (THF-d_8, 25 °C): δ −16.7. ^{19}F NMR (THF-d_8, 25 °C): δ −168.8, −165.2, −133.1.

[Y(CH$_2$SiMe$_3$)$_2$(THF)$_x$]$^+$[BPh$_3$(CH$_2$SiMe$_3$)]$^-$ (8c) (x = 3 or 4). A mixture of **2** (600 mg, 1130 μmol) and BPh$_3$ (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(CH$_2$SiMe$_3$)$_2$(THF)$_4$]$^+$[BPh$_3$(CH$_2$SiMe$_3$)]$^-$ and dried under vacuum to give colorless microcrystals of [Y(CH$_2$SiMe$_3$)$_2$-

---

(29) (a) Lappert, M. F.; Pearce, R. *J. Chem. Soc., Chem. Commun.* **1973**, 126. (b) Evans, W. J.; Brady, J. C.; Ziller, J. W. *J. Am. Chem. Soc.* **2001**, *123*, 7711. (c) Schumann, H.; Freckmann, D. M. M.; Dechert, S. *Z. Anorg. Allorg. Chem.*, **2002**, *628*, 2422.

(30) Farrugia, L. J. *J. Appl. Crystallogr*. **1999**, *32*, 837.

(31) Siemens. *ASTRO, SAINT and SADABS. Data Collection and Processing Software for the SMART System*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1996.

(32) Sheldrick, G. M. *SHELXS-86*, *Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1986.

(33) Sheldrick, G. M. *SHELXL-97*, *Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

(34) *International Tables for X-ray Crystallography*, Vol. C; Kluwer Academic Publishers: Dordrecht, 1992.

(35) (a) Mitchell, J. P.; Hajela, S.; Brookhart, S. K.; Hardcastle, K. I.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 1045. (b) Bambirra, S.; Brandsma, M. J. R.; Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H.; *Organometallics* **2000**, *19*, 3197.

(36) Arndt, S.; Spaniol, T. P.; Okuda, J. *Organometallics* **2003**, *22*, 775 and references therein.

$(\mathrm{THF})_3]^+[\mathrm{BPh_3(CH_2SiMe_3)}]^-$ (792 mg, 87%). NMR data (for $x = 3$): ^{1}H NMR (THF-d_8, 25 °C): δ −0.80 (d, $^2J_{\mathrm{YH}} = 3.2$ Hz, 2 × 2 H, $\mathrm{YCH_2}$), −0.49 (s, 9 H, $\mathrm{BCH_2SiC}\mathit{H}_3$), −0.07 (s, 2 × 9 H, $\mathrm{YCH_2SiC}\mathit{H}_3$), 0.18 (q, $^2J_{\mathrm{BH}} = 4.8$ Hz, 2 H, $\mathrm{BCH_2}$), 6.67 (t, $^3J_{\mathrm{HH}} = 7.1$ Hz, 3 × 1 H, Ph-4), 6.83 (m, 3 × 2 H, Ph-3), 7.38 (m (br), 3 × 2 H, Ph-2). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 2.7 ($\mathrm{BCH_2Si}\mathit{C}\mathrm{H_3}$), 4.0 ($\mathrm{YCH_2Si}\mathit{C}\mathrm{H_3}$), 36.7 (d, $^1J_{\mathrm{YC}} = 41.6$ Hz, $\mathrm{YCH_2}$), 121.5 (Ph-4), 125.6 (Ph-3), 135.7 (Ph-2), 167.8 (q, $^1J_{\mathrm{BC}} = 48.5$ Hz, Ph-1). The signal of the $\mathrm{BCH_2}$ group was not detected.^{11}B{^{1}H} NMR (THF-d_8, 25 °C): δ −10.3.^{89}Y{^{1}H} NMR (THF-d_8, 25 °C): δ 660.2. Anal. Calcd for $\mathrm{C_{42}H_{72}BO_3Si_3Y}$: C, 62.36; H, 8.97; Y, 10.99. Found: C, 61.52; H, 9.34; Y, 10.48.

$[\mathrm{Y(CH_2SiMe_3)_2(THF)}_x]^+[\mathrm{B(C_6F_5)_3(CH_2SiMe_3)}]^-$ (8d). An NMR tube was charged with a solution of **2** (37 mg, 75 μmol) and $\mathrm{B(C_6F_5)_3}$ (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: ^{1}H NMR (THF-d_8, 25 °C): δ −0.70 (d, $^2J_{\mathrm{YH}} = 2.9$ Hz, 2 × 2 H, $\mathrm{YCH_2}$), −0.38 (s, 9 H, $\mathrm{BCH_2SiC}\mathit{H}_3$), −0.06 (s, 2 × 9 H, $\mathrm{YCH_2SiC}\mathit{H}_3$), 0.58 (br, 2 H, $\mathrm{BCH_2}$). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 1.3 ($\mathrm{BCH_2Si}\mathit{C}\mathrm{H_3}$), 3.9 ($\mathrm{YCH_2Si}\mathit{C}\mathrm{H_3}$), 37.3 (d, $^1J_{\mathrm{YC}} = 43.0$ Hz, $\mathrm{YCH_2}$), 129.8 (br, $\mathrm{C_6F_5}$-1) 137.0 (d, $^1J_{\mathrm{CF}} = 243.6$ Hz, $\mathrm{C_6F_5}$-3), 138.2 (d, $^1J_{\mathrm{CF}} = 241.2$ Hz, $\mathrm{C_6F_5}$-4), 149.1 (d, $^1J_{\mathrm{CF}} = 236.8$ Hz, $\mathrm{C_6F_5}$-2). The signal of the $\mathrm{BCH_2}$ group was not detected.^{11}B{^{1}H} NMR (THF-d_8, 25 °C): δ −14.2. ^{19}F NMR (THF-d_8, 25 °C): δ −169.3, −167.1, −132.0.

$[\mathrm{Y(CH_2SiMe_3)_2(THF)_4}]^+[\mathrm{Al(CH_2SiMe_3)_4}]^-$ (8e). A solution of **2** (100 mg, 202 μmol) in pentane (0.3 mL) was treated with THF (72 μL, 1 mmol) and $\mathrm{Al(CH_2SiMe_3)_3}$ (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. ^{1}H NMR (THF-d_8, 25 °C): δ −1.28 (br m, 4 × 2 H, $\mathrm{AlCH_2}$), −0.73 (d, $^2J_{\mathrm{YH}} = 3.1$ Hz, 2 × 2 H, $\mathrm{YCH_2}$), −0.16 (s, 4 × 9 H, $\mathrm{AlCH_2SiC}\mathit{H}_3$), −0.09 (s, 2 × 9 H, $\mathrm{YCH_2SiC}\mathit{H}_3$), 1.75 (m, 4 × 4 H, β-$\mathrm{CH_2}$, THF), 3.60 (m, 4 × 4 H, α-$\mathrm{CH_2}$, THF). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 3.8 ($\mathrm{YCH_2Si}\mathit{C}\mathrm{H_3}$), 3.9 ($\mathrm{AlCH_2Si}\mathit{C}\mathrm{H_3}$), 4.4 ($\mathrm{AlCH_2}$), 37.2 (d, $^1J_{\mathrm{YC}} = 42.1$ Hz, $\mathrm{YCH_2}$). ^{27}Al NMR (THF-d_8, 25 °C): δ 150.9. ^{89}Y NMR (THF-d_8, 25 °C): δ 666.4. Anal. Calcd for $\mathrm{C_{40}H_{98}AlO_4Si_6Y}$: C, 51.79; H, 10.65. Found: C, 51.82; H, 10.66.

$[\mathrm{Lu(CH_2SiMe_3)_2(THF)_3}]^+[\mathrm{BPh_4}]^-$ (9a). A mixture of **3** (1000 mg, 1720 μmol) and $[\mathrm{NEt_3H}][\mathrm{BPh_4}]$ (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%). ^{1}H NMR (THF-d_8, 25 °C): δ −0.99 (s, 2 × 2 H, $\mathrm{LuC}\mathit{H}_2\mathrm{SiCH_3}$), −0.05 (s, 2 × 9 H, $\mathrm{LuCH_2SiC}\mathit{H}_3$), 1.76 (m, 3 × 4 H, β-$\mathrm{CH_2}$, THF), 3.60 (m, 3 × 4 H, α-$\mathrm{CH_2}$, THF), 6.72 (t, $^3J_{\mathrm{HH}} = 7.0$ Hz, 4 × 1 H, Ph-4), 6.87 (m, 4 × 2 H, Ph-3), 7.28 (m (br), 4 × 2 H, Ph-2).^{1}H NMR (pyridine-d_5, 25 °C): δ −0.10 (s, 2 × 2 H, $\mathrm{LuC}\mathit{H}_2\mathrm{SiCH_3}$), 0.06 (s, 2 × 9 H, $\mathrm{LuCH_2SiC}\mathit{H}_3$), 1.62 (m, 3 × 4 H, β-$\mathrm{CH_2}$, THF), 3.66 (m, 3 × 4 H, α-$\mathrm{CH_2}$, THF), 7.11 (t, $^3J_{\mathrm{HH}} = 7.0$ Hz, 4 × 1 H, Ph-4), 7.28 (m, 4 × 2 H, Ph-3), 8.06 (m (br), 4 × 2 H, Ph-2). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 4.4 ($\mathrm{LuCH_2Si}\mathit{C}\mathrm{H_3}$), 40.0 ($\mathrm{Lu}\mathit{C}\mathrm{H_2SiCH_3}$), 121.9 (Ph-4), 125.7 (Ph-3), 137.0 (Ph-2), 165.0 (q, $^1J_{\mathrm{BC}} = 49.3$ Hz).^{13}C NMR (pyridine-d_5, 25 °C): δ 3.8 ($\mathrm{LuCH_2Si}\mathit{C}\mathrm{H_3}$), 25.5 ($\beta$-$\mathrm{CH_2}$, THF), 42.8 (s, $\mathrm{Lu}\mathit{C}\mathrm{H_2SiCH_3}$), 67.5 (α-$\mathrm{CH_2}$, THF), 122.0 (Ph-4), 125.9 (Ph-3), 136.8 (Ph-2), 164.7 (q, $^1J_{\mathrm{BC}} = 48.9$ Hz, Ph-1). ^{11}B{^{1}H} NMR (THF-d_8, 25 °C): δ −6.6. ^{11}B{^{1}H} NMR (pyridine-d_5, 25 °C): δ −5.7. Anal. Calcd for $\mathrm{C_{44}H_{66}BLuO_3Si_2}$ C, 59.72; H, 7.52; Lu, 19.77. Found: C, 59.24; H, 6.90; Lu, 19.35.

$[\mathrm{Lu(CH_2SiMe_3)_2(THF)}_x]^+[\mathrm{B(C_6F_5)_4}]^-$ (9b). An NMR tube was charged with a solution of **3** (44 mg, 75 μmol) and $[\mathrm{NMe_2PhH}][\mathrm{B(C_6F_5)_4}]$ (60 mg, 75 μmol) in THF-d_8 (0.5 mL). Recorded spectra after 2 h at 25 °C: ^{1}H NMR (THF-d_8, 25 °C): δ −0.93 (s, 2 × 2 H, $\mathrm{LuCH_2}$), −0.05 (s, 2 × 9 H, $\mathrm{LuCH_2SiC}\mathit{H}_3$), 0.02 (s, 12 H, $\mathrm{SiMe_4}$), 2.87 (s, 2 × 3 H, $\mathrm{N}\mathit{Me}_2\mathrm{Ph}$), 6.57 (t, $^3J_{\mathrm{HH}} = 7.2$ Hz, 1 H, $\mathrm{NMe_2}\mathit{Ph}$-4), 6.66 (d, $^3J_{\mathrm{HH}} = 8.4$ Hz, 2 H, $\mathrm{NMe_2}\mathit{Ph}$-2), 7.09 (m, 2 H, $\mathrm{NMe_2}\mathit{Ph}$-3). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ −0.1 ($\mathrm{SiMe_4}$), 4.1 ($\mathrm{LuCH_2Si}\mathit{C}\mathrm{H_3}$), 40.4 ($\mathrm{LuCH_2}$, $\mathrm{N}\mathit{Me}_2\mathrm{Ph}$), 113.1, 116.9, ($\mathrm{NC_6H_5}$), 125.0 (br m, $\mathrm{C_6F_5}$-1), 129.3 ($\mathrm{NMe_2}\mathit{Ph}$), 137.0 (d, $^1J_{\mathrm{CF}} = 242.8$ Hz, $\mathrm{C_6F_5}$-3), 139.0 (d, $^1J_{\mathrm{CF}} = 242.2$ Hz, $\mathrm{C_6F_5}$-4), 149.0 (d, $^1J_{\mathrm{CF}} = 241.6$ Hz, $\mathrm{C_6F_5}$-2). ^{11}B{^{1}H} NMR (THF-d_8, 25 °C): δ −16.7. ^{19}F NMR (THF-d_8, 25 °C): δ −168.8, −165.2, −133.1.

$[\mathrm{Lu(CH_2SiMe_3)_2(THF)_3}]^+[\mathrm{BPh_3(CH_2SiMe_3)}]^-$ (9c). A mixture of **3** (500 mg, 861 μmol) and $\mathrm{BPh_3}$ (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%). ^{1}H NMR (THF-d_8, 25 °C): δ −1.03 (s, 2 × 2 H, $\mathrm{LuCH_2}$), −0.49 (s, 9 H, $\mathrm{BCH_2SiC}\mathit{H}_3$), −0.06 (s, 2 × 9 H, $\mathrm{LuCH_2SiC}\mathit{H}_3$), 0.18 (q, $^2J_{\mathrm{BH}} = 4.8$ Hz, 2 H, $\mathrm{BCH_2}$), 6.67 (t, $^3J_{\mathrm{HH}} = 7.1$ Hz, 3 × 1 H, 4-Ph), 6.83 (m (br), 3 × 2 H, Ph-3), 7.38 (br, 3 × 2 H, Ph-2). ^{1}H NMR (pyr-d_5, 25 °C): δ −0.12 (s, 2 × 2 H, $\mathrm{LuCH_2}$), 0.04 (s, 2 × 9 H, $\mathrm{LuCH_2SiC}\mathit{H}_3$), 0.08 (s, 9 H, $\mathrm{BCH_2SiC}\mathit{H}_3$), 0.96 (q, $^2J_{\mathrm{BH}} = 4.8$ Hz, 2 H, $\mathrm{BCH_2}$), 1.60 (m, 3 × 4 H, β-$\mathrm{CH_2}$, THF), 3.64 (m, 3 × 4 H, α-$\mathrm{CH_2}$, THF), 7.06 (t, $^3J_{\mathrm{HH}} = 7.1$ Hz, 3 × 1 H, 4-Ph), 7.29 (m, 3 × 2 H, Ph-3), 8.13 (m (br), 3 × 2 H, Ph-2). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 2.8 ($\mathrm{BCH_2Si}\mathit{C}\mathrm{H_3}$), 4.2 ($\mathrm{LuCH_2Si}\mathit{C}\mathrm{H_3}$), 39.8 ($\mathrm{LuCH_2}$), 121.5 (Ph-4), 125.6 (Ph-3), 135.7 (Ph-2), 167.8 (q, $^1J_{\mathrm{BC}} = 48.7$ Hz, Ph-1). The signal of the $\mathrm{BCH_2}$ group was not detected.^{11}B{^{1}H} NMR (THF-d_8, 25 °C): δ −10.3. Anal. Calcd for $\mathrm{C_{42}H_{72}BO_3Si_3Lu}$: C, 56.36; H, 8.11; Lu, 19.55. Found: C, 47.29; H, 7.67; Lu, 19.54.

$[\mathrm{Lu(CH_2SiMe_3)_2(THF)}_x]^+[\mathrm{B(C_6F_5)_3(CH_2SiMe_3)}]^-$ (9d). An NMR tube was charged with a solution of **3** (40 mg, 69 μmol) and $\mathrm{B(C_6F_5)_3}$ (35 mg, 69 μmol) in THF-d_8 (0.5 mL). NMR spectra were recorded after 12 h at 40 °C: ^{1}H NMR (THF-d_8, 25 °C): δ −0.92 (s, 2 × 2 H, $\mathrm{LuCH_2}$), −0.37 (s, 9 H, $\mathrm{BCH_2SiC}\mathit{H}_3$), −0.05 (s, 2 × 9 H, $\mathrm{LuCH_2SiC}\mathit{H}_3$), 0.59 (br, 2 H, $\mathrm{BCH_2}$). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 1.3 ($\mathrm{BCH_2Si}\mathit{C}\mathrm{H_3}$), 4.1 ($\mathrm{LuCH_2Si}\mathit{C}\mathrm{H_3}$), 40.4 ($\mathrm{LuCH_2}$), 129.8 ($\mathrm{C_6F_5}$-1), 137.0 (d, $^1J_{\mathrm{CF}} = 242.8$ Hz, $\mathrm{C_6F_5}$-3), 138.3 (d, $^1J_{\mathrm{CF}} = 241.2$ Hz, $\mathrm{C_6F_5}$-4), 149.2 (d, $^1J_{\mathrm{CF}} = 226.1$ Hz, $\mathrm{C_6F_5}$-2). The signal of the $\mathrm{BCH_2}$ group was not detected. ^{11}B{^{1}H} NMR (THF-d_8, 25 °C): δ −14.2. ^{19}F NMR (THF-d_8, 25 °C): δ −169.4, −167.1, −132.0.

$[\mathrm{Sc(CH_2SiMe_3)_2(12\text{-}crown\text{-}4)}]^+[\mathrm{BPh_3(CH_2SiMe_3)}]^-$ (10c). A solution of $\mathrm{BPh_3}$ (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%). ^{1}H NMR (THF-d_8, 25 °C): δ −0.50 (s, 9 H, $\mathrm{BCH_2SiC}\mathit{H}_3$), −0.21 (s, 2 × 2 H, $\mathrm{ScC}\mathit{H}_2$), −0.10 (s, 2 × 9 H, $\mathrm{ScCH_2SiC}\mathit{H}_3$), 0.19 (q, $^2J_{\mathrm{BH}} = 4.9$ Hz, 2 H, $\mathrm{BCH_2}$), 3.34, 3.65 (m, 2 × 8 H, 12-crown-4), 6.74 (t, $^3J_{\mathrm{HH}} = 6.8$ Hz, 3 × 1 H, Ph-4), 6.91 (m, 3 × 2 H, Ph-3), 7.43 (m (br), 3 × 2 H, Ph-2). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 2.6 ($\mathrm{BCH_2Si}\mathit{C}\mathrm{H_3}$), 3.6 ($\mathrm{ScCH_2Si}\mathit{C}\mathrm{H_3}$), 14.4 (q, $^1J_{\mathrm{BC}} = 39.3$ Hz, $\mathrm{B}\mathit{C}\mathrm{H_2SiCH_3}$), 46.3 (s(br), $\mathrm{Sc}\mathit{C}\mathrm{H_2SiCH_3}$), 68.8 (12-crown-4), 121.7 (Ph-4), 125.8 (Ph-3), 135.7 (Ph-2), 167.9

(q, $^{1}J_{BC}$ = 49.1 Hz, Ph-1). ^{11}B{^{1}H} NMR (THF-d_8, 25 °C): δ −10.4. Anal. Calcd for $C_{38}H_{64}BO_4Si_3Sc$: C, 62.96; H, 8.90; Sc, 6.20. Found: C, 60.64; H, 9.16; Sc, 6.24.

$[Y(CH_2SiMe_3)_2(12\text{-crown-4})(THF)_x]^+[B(C_6F_5)_4]^-$ (11b). An NMR tube was charged with **5** (25 mg, 47 μmol) and $[NMe_2PhH][B(C_6F_5)_4]$ (25 mg, 47 μmol) in THF-d_8 (500 μL). NMR spectra were recorded after standing for 10 min at room temperature: ^{1}H NMR (THF-d_8, 25 °C): δ −0.73 (d, $^{2}J_{YH}$ = 3.1 Hz, 2 × 2 H, YCH_2), −0.06 (s, 2 × 9 H, YCH_2SiCH_3), 0.00 (s, 12 H, $SiMe_4$), 2.88 (s, 2 × 3 H, N*Me*$_2$Ph), 4.08, 4.20 (m, 2 × 8 H, 12-crown-4), 6.58 (t, $^{3}J_{HH}$ = 7.2 Hz, 1 H, NMe$_2$*Ph*-4), 6.68 (d, $^{3}J_{HH}$ = 8.4 Hz, 2 H, NMe$_2$*Ph*-2), 7.11 (m, 2 H, NMe$_2$*Ph*-3). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 0.0 ($SiMe_4$), 4.2 (YCH_2SiCH_3), 35.3 (d, $^{1}J_{YC}$ = 42.4 Hz, YCH_2), 40.6 (N*Me*$_2$Ph), 68.9 (12-crown-4), 113.3, 117.1, 124.8 (m (br), C_6F_5-1), 129.5, 151.8 (NMe$_2$*Ph*), 137.9 (m, C_6F_5-3, C_6F_5-4), 148.9 (d, $^{1}J_{CF}$ = 247.4 Hz, C_6F_5-2). ^{11}B{^{1}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.

$[Y(CH_2SiMe_3)_2(12\text{-crown-4})(THF)_x]^+[B(C_6F_5)_3(CH_2SiMe_3)]^-$ (11d). An NMR tube was charged with **5** (50 mg, 95 μmol) and $B(C_6F_5)_3$ (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: ^{1}H NMR (THF-d_8, 25 °C): δ −0.73 (d, $^{2}J_{YH}$ = 3.4 Hz, 2 × 2 H, YCH_2), −0.37 (s, 9 H, BCH_2SiCH_3), −0.07 (s, 2 × 9 H, YCH_2SiCH_3), 4.08, 4.20 (m, 2 × 8 H, 12-crown-4). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 1.2 (BCH_2SiCH_3), 3.9 (YCH_2SiCH_3), 9.5 (BCH_2SiCH_3), 35.1 (d, $^{1}J_{YC}$ = 40.8 Hz, YCH_2), 68.7 (12-crown-4), 129.8 (m (br), C_6F_5-1), 137.0 (d, $^{1}J_{CF}$ = 246.2 Hz, C_6F_5-3), 138.3 (d, $^{1}J_{CF}$ = 243.6 Hz, C_6F_5-4), 149.2 (d, $^{1}J_{CF}$ = 238.6 Hz, C_6F_5-2). ^{11}B{^{1}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.

$[Y(CH_2SiMe_3)_2(12\text{-crown-4})(THF)]^+[Al(CH_2SiMe_3)_4]^-$ (11e). To a solution of **5** (200 mg, 380 μmol) in THF (7 mL) was added neat $Al(CH_2SiMe_3)_3$ (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%). ^{1}H NMR (THF-d_8, 25 °C): δ −1.23 (br, 4 × 2 H, $AlCH_2$), −0.73 (d, $^{2}J_{YH}$ = 2.80 Hz, 2 × 2 H, YCH_2), −0.11 (s, 4 × 9 H, $AlCH_2SiCH_3$), −0.06 (s, 2 × 9 H, YCH_2SiCH_3), 1.77 (m, 4 H, β-CH_2, THF), 3.60 (m, 4 H, α-CH_2, THF), 4.10, 4.22 (br, 2 × 8 H, 12-crown-4). ^{1}H NMR (CD_2Cl_2, 25 °C): δ −1.29 (br, 4 × 2 H, $AlCH_2$), −0.70 (d, $^{2}J_{YH}$ = 2.40 Hz, 2 × 2 H, YCH_2), −0.09 (s, 4 × 9 H, $AlCH_2SiCH_3$), −0.07 (s, 2 × 9 H, YCH_2SiCH_3), 2.11 (m, 4 H, β-CH_2, THF), 3.97 (br, 8 H, 12-crown-4), 4.22 (br, 8 + 4 H, 12-crown-4 + α-CH_2, THF). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 3.0 ($AlCH_2$), 4.2 (YCH_2SiCH_3 + $AlCH_2SiCH_3$), 35.1 (d, $^{1}J_{YC}$ = 40.2 Hz, YCH_2), 68.9 (12-crown-4). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ 3.86 (YCH_2SiCH_3 + $AlCH_2SiCH_3$), 37.2 (d, $^{1}J_{YC}$ = 42.0 Hz, YCH_2), 72.4 (12-crown-4). Anal. Calcd for $C_{34}H_{86}O_{4.5}AlSi_6Y$ (corresponding to 0.5 THF): C, 47.96; H, 10.18. Found: C, 47.23; H, 10.11.

$[Lu(CH_2SiMe_3)_2(12\text{-crown-4})(THF)_x]^+[B(C_6F_5)_4]^-$ (12b). An NMR tube was charged with **6** (50 mg, 82 μmol) and $[NMe_2PhH][B(C_6F_5)_4]$ (65 mg, 82 μmol) in THF-d_8 (500 μL). NMR spectra were recorded after standing for 15 min at room temperature: ^{1}H NMR (THF-d_8, 25 °C): δ −0.97 (s, 2 × 2 H, $LuCH_2$), −0.06 (s, 2 × 9 H, $LuCH_2SiCH_3$), 0.00 (s, 12 H, $SiMe_4$), 2.88 (s, 2 × 3 H, N*Me*$_2$Ph), 4.04, 4.19 (m, 2 × 8 H, 12-crown-4), 6.58 (t, $^{3}J_{HH}$ = 7.2 Hz, 1 H, NMe$_2$*Ph*-4), 6.68 (d, $^{3}J_{HH}$ = 8.4 Hz, 2 H, NMe$_2$*Ph*-2), 7.11 (m, 2 H, NMe$_2$*Ph*-3). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 0.0 ($SiMe_4$), 4.1 ($LuCH_2SiCH_3$), 39.1 ($LuCH_2$), 40.3 (N*Me*$_2$Ph), 68.8 (12-crown-4), 113.3, 117.1, 129.5, 151.8 (NMe$_2$*Ph*), 125.0 (m (br), C_6F_5-1), 137.9 (m, C_6F_5-3, C_6F_5-4), 148.9 (d, $^{1}J_{CF}$ = 243.4 Hz, C_6F_5-2). ^{11}B{^{1}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.

$[Lu(CH_2SiMe_3)_2(12\text{-crown-4})(THF)_x]^+[B(C_6F_5)_3(CH_2SiMe_3)]^-$ (12d). An NMR tube was charged with **6** (50 mg, 82 μmol) and $B(C_6F_5)_3$ (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: ^{1}H NMR (THF-d_8, 25 °C): δ −0.97 (s, 2 × 2 H, $LuCH_2$), −0.36 (s, 9 H, BCH_2SiCH_3), −0.06 (s, 2 × 9 H, $LuCH_2SiCH_3$), 4.06, 4.20 (m, 2 × 8 H, 12-crown-4). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 1.2 (BCH_2SiCH_3), 4.1 ($LuCH_2SiCH_3$), 9.5 (BCH_2SiCH_3), 39.1 ($LuCH_2$), 68.7 (12-crown-4), 129.8 (C_6F_5-1), 137.0 (d, $^{1}J_{CF}$ = 242.4 Hz, C_6F_5-3), 138.2 (d, $^{1}J_{CF}$ = 242.4 Hz, C_6F_5-4), 149.2 (d, $^{1}J_{CF}$ = 237.4 Hz, C_6F_5-2). ^{11}B{^{1}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.

$[Y(CH_2SiMe_3)(THF)_5]^{2+}[BPh_4]^-{}_2$ (13a). A mixture of **2** (400 mg, 808 μmol) and $[NEt_3H][BPh_4]$ (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 $[NEt_3H][BPh_4]$ (323 mg). Evaporation of the volatiles of the supernatant gave a colorless solid residue. Washing with Et_2O (2 × 20 mL) and removing the solvent under reduced pressure yielded **13a** as a colorless powder (690 mg, 77%). ^{1}H NMR (pyridine-d_5, 25 °C): δ 0.17 (s, 9 H, YCH_2SiCH_3), 0.73 (d, $^{2}J_{YH}$ = 3.3 Hz, 2 H, YCH_2SiCH_3), 1.62 (m, 4 × 4 H, β-CH_2, THF), 3.66 (m, 4 × 4 H, α-CH_2, THF), 7.10 (t, $^{3}J_{HH}$ = 7.3 Hz, 8 × 1 H, Ph-4), 7.27 (m, 8 × 2 H, Ph-3), 8.06 (m (br), 8 × 2 H, Ph-2). ^{13}C NMR (pyridine-d_5, 25 °C): δ 4.0 (YCH_2SiCH_3), 25.9 (β-CH_2, THF), 44.5 (dt, $^{1}J_{YC}$ = 44.9 Hz, $^{1}J_{CH}$ = 93.8 Hz, YCH_2SiCH_3), 67.9 (α-CH_2, THF), 122.4 (Ph-4), 126.2 (Ph-3), 137.1 (Ph-2), 165.0 (q, $^{1}J_{BC}$ = 49.2 Hz, Ph-1). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 3.9 (YCH_2SiCH_3), 25.5 (β-CH_2, THF), 67.8 (α-CH_2, THF), 122.2 (Ph-4), 125.9 (Ph-3), 137.1 (Ph-2), 165.1 (q, $^{1}J_{BC}$ = 49.2 Hz, Ph-1). The signal for the methylene group attached to yttrium was not detected. ^{11}B{^{1}H} NMR (THF-d_8, 25 °C): δ −6.7. ^{89}Y NMR (THF-d_8, 25 °C): δ 409.2. Anal. Calcd for $C_{72}H_{91}B_2O_5SiY$: C, 73.59; H, 7.81; Y, 7.57. Found: C, 74.62; H, 8.37; Y, 7.16.

$[Lu(CH_2SiMe_3)(THF)_4]^{2+}[BPh_4]^-{}_2$ (14a). A mixture of **3** (290 mg, 500 μmol) and $[NMe_2PhH][BPh_4]$ (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%). ^{1}H NMR (pyridine-d_5, 25 °C): δ 0.12 (s, 9 H, $LuCH_2SiCH_3$), 0.47 (s, 2 H, $LuCH_2SiCH_3$), 1.60 (m, 4 × 4 H, β-CH_2, THF), 3.64 (m, 4 × 4 H, α-CH_2, THF), 7.08 (t, $^{3}J_{HH}$ = 7.3 Hz, 8 × 1 H, Ph-4), 7.25 (m, 8 × 2 H, Ph-3), 8.03 (m (br), 8 × 2 H, Ph-2). ^{13}C NMR (pyridine-d_5, 25 °C): δ 3.8 ($LuCH_2SiCH_3$), 25.5 (β-CH_2, THF), 44.3 ($LuCH_2SiCH_3$), 67.5 (α-CH_2, THF), 122.1 (Ph-4), 125.9 (Ph-3), 136.8 (Ph-2), 164.6 (q, $^{1}J_{BC}$ = 49.2 Hz, Ph-1). ^{11}B{^{1}H} NMR (pyridine-d_5, 25 °C): δ −5.8. Anal. Calcd for $C_{68}H_{83}B_2LuO_4Si$: C, 68.69; H, 7.04; Lu, 14.71. Found: C, 62.40; H, 6.78; Lu, 15.13.

$[Y(CH_2SiMe_3)(12\text{-crown-4})(THF)_3]^{2+}[BPh_4]^-{}_2$ (15a). A mixture of **5** (44 mg, 84 μmol) and $[NEt_3H][BPh_4]$ (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%).

^{1}H NMR (pyridine-d_5, 25 °C): δ −0.19 (s, 2 × 9 H, YCH$_2$SiC*H*$_3$), 0.02 (d, $^2J_{YH}$ = 3.0 Hz, 2 H, YC*H*$_2$), 1.62 (m, 2 × 4 H, β-CH$_2$, THF), 3.65 (m, 2 × 4 H, α-CH$_2$, THF), 3.99 (m, 16 H, 12-crown-4), 7.11 (t, $^3J_{HH}$ = 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 (YCH$_2$Si*C*H$_3$), 25.5 (β-CH$_2$, THF), 40.1 (d, $^1J_{YC}$ = 42.2 Hz, Y*C*H$_2$SiCH$_3$), 67.5 (α-CH$_2$, THF), 69.4 (12-crown-4), 122.1 (Ph-4), 125.9 (Ph-3), 136.7 (Ph-2), 164.5 (q, $^1J_{BC}$ = 48.9 Hz, Ph-1). ^{11}B{^{1}H} NMR (pyridine-d_5, 25 °C): δ −5.9. Anal. Calcd for $C_{72}H_{91}B_2O_7SiY$ (3 × THF): C, 71.64; H, 7.60; Y, 7.37; $C_{68}H_{83}B_2O_6SiY$ (2 × THF): C, 71.96; H, 7.37; Y, 7.83. Found: C, 66.61; H, 8.31; Y, 8.29.

[Y(η^2-(*C*,*N*)-C$_5$D$_4$N)(12-crown-4)(C$_5$D$_5$N)$_n$]$^{2+}$[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. ^{1}H NMR (pyridine-d_5, 25 °C): δ 0.00 (s, 9 H, Si(C*H*$_3$)$_3$(CH$_2$D)), −0.03 (t, $^2J_{DH}$ = 2.1 Hz, 2 H, Si(CH$_3$)$_3$(C*H*$_2$D)), 1.62 (m, 2 × 4 H, β-CH$_2$, THF), 3.65 (m, 2 × 4 H, α-CH$_2$, THF), 4.06 (s, 16 H, 12-crown-4), 7.11 (t, $^3J_{HH}$ = 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, $^1J_{DC}$ = 18.2 Hz, Si(CH$_3$)$_3$(*C*H$_2$D)), −0.3 (Si(*C*H$_3$)$_3$(CH$_2$D)), 25.5 (β-CH$_2$, THF), 67.5 (α-CH$_2$, THF), 68.9 (12-crown-4), 122.1 (Ph-4), 125.9 (Ph-3), 136.7 (Ph-2), 164.5 (q, $^1J_{BC}$ = 48.9 Hz, Ph-1), 212.6 (d, $^1J_{YC}$ = 28.9 Hz, C$_5$D$_4$N-2). ^{11}B{^{1}H} NMR (pyridine-d_5, 25 °C): δ −5.9.

[Y(CH$_2$SiMe$_3$)(12-crown-4)(THF)$_x$]$^{2+}$[B(C$_6$F$_5$)$_4$]$^-_2$ (15b). An NMR tube was charged with **5** (25 mg, 47 μmol) and [NMe$_2$PhH][B(C$_6$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: ^{1}H NMR (THF-d_8, 25 °C): δ −0.58 (d, $^2J_{YH}$ = 3.4 Hz, 2 H, YC*H*$_2$), −0.04 (s, 9 H, YCH$_2$SiC*H*$_3$), 0.00 (s, 2 × 12 H, SiMe$_4$), 2.94 (s, 4 × 3 H, N*Me*$_2$Ph), 4.23, 4.32 (m, 4 × 8 H, 12-crown-4), 6.70 (t, $^3J_{HH}$ = 7.2 Hz, 2 × 1 H, NMe$_2$*Ph*-4), 6.78 (d, $^3J_{HH}$ = 8.4 Hz, 2 × 2 H, NMe$_2$*Ph*-2), 7.16 (m, 2 × 2 H, NMe$_2$*Ph*-3). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 0.0 (SiMe$_4$), 3.8 (YCH$_2$Si*C*H$_3$), 39.0 (d, $^1J_{YC}$ = 37.1 Hz, YCH$_2$), 41.0 (N*Me*$_2$Ph), 70.3 (12-crown-4), 113.9, 118.2, 129.6 (NMe$_2$*Ph*), 125.0 (m (br), C$_6$F$_5$-1), 138.2 (m, C$_6$F$_5$-3, C$_6$F$_5$-4), 149.1 (d, $^1J_{CF}$ = 242.2 Hz, C$_6$F$_5$-2). ^{11}B{^{1}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.

[Y(CH$_2$SiMe$_3$)(12-crown-4)(THF)$_2$]$^{2+}$[BPh$_3$(CH$_2$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%). ^{1}H NMR (THF-d_8, 25 °C): δ −0.91 (d, $^2J_{YH}$ = 2.8 Hz, 2 H, YC*H*$_2$), −0.50 (s, 2 × 9 H, BCH$_2$SiC*H*$_3$), −0.10 (s, 9 H, YCH$_2$SiC*H*$_3$), 0.18 (br q, $^2J_{BH}$ = 5.2 Hz, 2 × 2 H, BCH$_2$), 1.77 (m, 2 × 4 H, β-CH$_2$, THF), 3.16, 3.37 (br, 2 × 8 H, 12-crown-4), 3.61 (m, 2 × 4 H, α-CH$_2$, THF), 6.76 (t, $^3J_{HH}$ = 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). ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): δ −0.79 (d, $^2J_{YH}$ = 2.8 Hz, 2 H, YCH$_2$), −0.48 (s, 2 × 9 H, BCH$_2$SiC*H*$_3$), −0.16 (s, 9 H, YCH$_2$SiC*H*$_3$), 0.17 (br, 2 × 2 H, BCH$_2$), 2.00 (br, 2 × 4 H, β-CH$_2$, THF), 2.87, 3.17 (m, 2 × 8 H, 12-crown-4), 3.80 (br, 2 × 4 H, α-CH$_2$, THF), 6.88 (t, $^3J_{HH}$ = 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}C{^{1}H} NMR (THF-d_8, 25 °C): δ 2.75 (BCH$_2$Si*C*H$_3$), 4.03 (YCH$_2$Si*C*H$_3$), 26.4 (β-CH$_2$, THF), 36.9 (d, $^1J_{YC}$ = 43.8 Hz, YCH$_2$), 68.3 (α-CH$_2$, THF), 69.8 (12-crown-4), 122.1 (Ph-4), 126.1 (Ph-3), 136.0 (Ph-2), 168.3 (q, $^1J_{BC}$ = 48.1 Hz, Ph-1). The signal for the BCH$_2$ group was not detected. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C): δ 2.26 (BCH$_2$Si*C*H$_3$), 3.37 (YCH$_2$Si*C*H$_3$), 25.8 (β-CH$_2$, THF), 40.6 (d, $^1J_{YC}$ = 47.7 Hz, YCH$_2$), 69.4 (α-CH$_2$, THF), 72.3 (12-crown-4), 122.0 (Ph-4), 126.1 (Ph-3), 135.5 (Ph-2), 167.7 (q, $^1J_{BC}$ = 48.1 Hz, Ph-1). The signal for the BCH$_2$ group was not detected. Anal. Calcd for $C_{64}H_{95}B_2O_6Si_3Y$: C, 66.54; H, 8.29; Y, 7.70. Found: C, 65.15; H, 9.12; Y 8.07.

[Lu(CH$_2$SiMe$_3$)(12-crown-4)(THF)$_x$]$^{2+}$[B(C$_6$F$_5$)$_4$]$^-_2$ (16b). An NMR tube was charged with **6** (50 mg, 82 μmol) and [NMe$_2$PhH][B(C$_6$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: ^{1}H NMR (THF-d_8, 25 °C): δ −0.68 (s, 2 H, LuCH$_2$), −0.03 (s, 9 H, LuCH$_2$SiC*H*$_3$), 0.00 (s, 2 × 12 H, SiMe$_4$), 2.92 (s, 4 × 3 H, N*Me*$_2$Ph), 4.36, 4.40 (m, 4 × 8 H, 12-crown-4), 6.66 (t, $^3J_{HH}$ = 7.2 Hz, 2 × 1 H, NMe$_2$*Ph*-4), 6.75 (d, $^3J_{HH}$ = 8.4 Hz, 2 × 2 H, NMe$_2$*Ph*-2), 7.16 (m, 2 × 2 H, NMe$_2$*Ph*-3). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 0.0 (SiMe$_4$), 3.3 (LuCH$_2$Si*C*H$_3$), 39.8 (LuCH$_2$), 40.6 (N*Me*$_2$Ph), 70.7 (12-crown-4), 113.4, 117.5, 129.3 (NMe$_2$*Ph*), 124.7 (m (br), C$_6$F$_5$-1), 137.9 (m, C$_6$F$_5$-3, C$_6$F$_5$-4), 149.1 (d, $^1J_{CF}$ = 240.4 Hz, C$_6$F$_5$-2). ^{11}B{^{1}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.

[Y(CH$_2$SiMe$_3$)(12-crown-4)$_2$(THF)$_x$]$^{2+}$[B(C$_6$F$_5$)$_4$]$^-_2$ (17b). An NMR tube was charged with **5** (25 mg, 47 μmol) and [NMe$_2$PhH][B(C$_6$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: ^{1}H NMR (THF-d_8, 25 °C): δ −0.68 (d, $^2J_{YH}$ = 2.8 Hz, 2 H, YC*H*$_2$), −0.07 (s, 9 H, YCH$_2$SiC*H*$_3$), 0.00 (s, 2 × 12 H, SiMe$_4$), 2.89 (s, 4 × 3 H, N*Me*$_2$Ph), 4.15, 4.41 (m (br), 4 × 8 H, 12-crown-4), 6.59 (t, $^3J_{HH}$ = 7.2 Hz, 2 × 1 H, NMe$_2$*Ph*-4), 6.68 (d, $^3J_{HH}$ = 8.4 Hz, 2 × 2 H, NMe$_2$*Ph*-2), 7.11 (m, 2 × 2 H, NMe$_2$*Ph*-3). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 0.0 (SiMe$_4$), 4.0 (YCH$_2$Si*C*H$_3$), 40.6 (N*Me*$_2$Ph), 71.6 (12-crown-4), 113.3, 117.1, 129.4, 151.8 (NMe$_2$*Ph*), 125.0 (m (br), C$_6$F$_5$-1), 138.2 (m, C$_6$F$_5$-3, C$_6$F$_5$-4), 149.1 (d, $^1J_{CF}$ = 240.2 Hz, C$_6$F$_5$-2). The signal for the YCH$_2$ group was not detected. ^{11}B{^{1}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.

[Y(CH$_2$SiMe$_3$)(12-crown-4)$_2$]$^{2+}$[BPh$_3$(CH$_2$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%). ^{1}H NMR (THF-d_8, 25 °C): δ −1.05 (d, $^2J_{YH}$ = 3.2 Hz, 2 H, YC*H*$_2$), −0.48 (s, 2 × 9 H, BCH$_2$SiC*H*$_3$), −0.14 (s, 9 H, YCH$_2$SiC*H*$_3$), 0.20 (br, 2 × 2 H, BCH$_2$), 3.54, 3.68 (br, 2 × 16 H, 12-crown-4), 6.79 (t, $^3J_{HH}$ = 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}C{^{1}H} NMR (THF-d_8, 25 °C): δ 2.8 (BCH$_2$Si*C*H$_3$), 4.2 (YCH$_2$Si*C*H$_3$), 26.1 (d, $^1J_{YC}$ = 53.3 Hz, YCH$_2$SiCH$_3$), 71.1 (br, 12-crown-4), 122.1 (Ph-4), 126.2 (Ph-3), 136.0 (Ph-2), 168.3 (q, $^1J_{BC}$ = 48.6 Hz, Ph-1). The signal for the BCH$_2$ group was not detected. ^{11}B{^{1}H} NMR (THF-d_8, 25 °C): δ −10.4. Anal. Calcd for $C_{64}H_{95}B_2O_8Si_3Y$: C, 64.75; H, 8.07; Y, 7.49. Found: C, 64.63; H, 7.96; Y, 7.85.

[Lu(CH$_2$SiMe$_3$)(12-crown-4)$_2$]$^{2+}$[BPh$_4$]$^-_2$ (18a) and [Lu(CH$_2$SiMe$_3$)(12-crown-4)(pyridine-d_5)$_2$]$^{2+}$[BPh$_4$]$^-_2$. A mixture of **6** (200 mg, 326 μmol), 12-crown-4 (57 μL, 362 μmol), and [NEt$_3$H][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$_2$O (25 mL). Removing the volatiles under reduced pressure afforded **17a** as colorless microcrystals (333 mg, 82%). ^{1}H NMR (pyridine-d_5, 25 °C): δ −0.21 (s, 9 H, LuCH$_2$SiC*H*$_3$), −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, $^3J_{HH}$ = 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}C{^{1}H} NMR (pyridine-d_5, 25 °C): δ 3.5 (LuCH$_2$SiC*H*$_3$), 70.2, 70.7 (12-crown-4), 122.5 (Ph-4), 126.3 (Ph-3), 137.0 (Ph-2), 164.9 (q, $^1J_{BC}$ = 49.4 Hz, Ph-1). The signal for the LuCH$_2$ group was not detected. ^{11}B{^{1}H} NMR (pyridine-d_5, 25 °C): δ −6.0. Anal. Calcd for $C_{68}H_{83}B_2LuO_8Si$: C, 65.18; H, 6.68; Lu, 13.96. Found: C, 64.77; H, 7.16; Lu, 14.11.

$[Lu(CH_2SiMe_3)(12\text{-crown-}4)_2(THF)_x]^{2+}[B(C_6F_5)_4]^-{}_2$ (18b). An NMR tube was charged with **6** (50 mg, 82 μmol) and [NMe$_2$PhH][B(C$_6$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: ^{1}H NMR (THF-d_8, 25 °C): δ −0.73 (2 H, LuC*H*$_2$), −0.03 (s, 9 H, LuCH$_2$SiC*H*$_3$), 0.00 (s, 2 × 12 H, SiMe$_4$), 2.88 (s, 4 × 3 H, N*Me*$_2$Ph), 3.61, 4.40 (m (br), 4 × 8 H, 12-crown-4), 6.59 (t, $^3J_{HH}$ = 7.2 Hz, 2 × 1 H, NMe$_2$*Ph*-4), 6.69 (d, $^3J_{HH}$ = 8.4 Hz, 2 × 2 H, NMe$_2$*Ph*-2), 7.11 (m, 2 × 2 H, NMe$_2$*Ph*-3). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 0.0 (SiMe$_4$), 3.5, 4.1 (LuCH$_2$SiC*H*$_3$), 40.3 (N*Me*$_2$Ph), 69.2, 70.8 (br, 12-crown-4), 113.3, 116.8, 129.2, 151.5 (NMe$_2$*Ph*), 125.0 (m (br), C$_6$F$_5$-1), 137.9 (m, C$_6$F$_5$-3, C$_6$F$_5$-4), 148.9 (d, $^1J_{CF}$ = 242.3 Hz, C$_6$F$_5$-2). The signal for the LuCH$_2$ group was not detected. ^{11}B{^{1}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: ^{1}H NMR (THF-d_8, 25 °C): δ −0.87 (d, $^2J_{YH}$ = 2.93 Hz, 2 × 2 H, YC*H*$_2$ **11**), −0.75 (d, $^2J_{YH}$ = 3.17 Hz, 2 × 2 H, YC*H*$_2$ **8**), −0.09 (s, 2 × 9 H, YCH$_2$SiC*H*$_3$ **11**), −0.06 (s, 2 × 9 H, YCH$_2$SiC*H*$_3$ **8**) and other associated resonances. Insoluble fraction: ^{1}H NMR (pyridine-d_5, 25 °C): δ −0.21 (s, 2 × 9 H, YCH$_2$SiC*H*$_3$), 0.02 (d, $^2J_{YH}$ = 2.0 Hz, 2 H, YC*H*$_2$) and other associated resonances.

Reaction between 5, 3 [NMe$_2$PhH][B(C$_6$F$_5$)$_4$] and 12-crown-4 in THF-d_8. An NMR tube was charged with **5** (25 mg, 47 μmol) and [NMe$_2$PhH][B(C$_6$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 [NMe$_2$HPh][B(C$_6$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. ^{1}H NMR (THF-d_8, 25 °C): δ 0.00 (s, 36 H, SiMe$_4$), 3.01 (s, 6 × 3 H, N*Me*$_2$Ph), 4.58 (m, 4 × 8 H, 12-crown-4), 6.84 (t, $^3J_{HH}$ = 7.2 Hz, 3 × 1 H, NMe$_2$*Ph*-4), 6.92 (d, $^3J_{HH}$ = 8.4 Hz, 3 × 2 H, NMe$_2$*Ph*-2), 7.24 (m, 3 × 2 H, NMe$_2$*Ph*-3). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 0.0 (SiMe$_4$), 42.3 (N*Me*$_2$Ph), 72.3 (12-crown-4), 115.3, 120.9, 130.1, 149.6 (NMe$_2$*Ph*), 125.2 (m (br), C$_6$F$_5$-1), 138.1 (m, C$_6$F$_5$-3, C$_6$F$_5$-4), 149.1 (d, $^1J_{CF}$ = 240.2 Hz, C$_6$F$_5$-2). ^{11}B{^{1}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 [NMe$_2$PhH][B(C$_6$F$_5$)$_4$] and 12-crown-4 in THF-d_8. An NMR tube was charged with **6** (50 mg, 82 μmol) and [NMe$_2$PhH][B(C$_6$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 [NMe$_2$HPh][B(C$_6$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. ^{1}H NMR (THF-d_8, 25 °C): δ 0.00 (s, 36 H, SiMe$_4$), 2.95 (s, 6 × 3 H, N*Me*$_2$Ph), 4.62 (s, 4 × 8 H, 12-crown-4), 6.59 (t, $^3J_{HH}$ = 7.2 Hz, 3 × 1 H, NMe$_2$*Ph*-4), 6.69 (d, $^3J_{HH}$ = 8.4 Hz, 3 × 2 H, NMe$_2$*Ph*-2), 7.11 (m, 3 × 2 H, NMe$_2$*Ph*-3). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 0.0 (SiMe$_4$), 40.3 (N*Me*$_2$Ph), 71.6 (12-crown-4), 113.3, 116.8, 129.2, 151.5 (NMe$_2$*Ph*), 125.0 (m (br), C$_6$F$_5$-1), 137.9 (m, C$_6$F$_5$-3, C$_6$F$_5$-4), 148.9 (d, $^1J_{CF}$ = 242.3 Hz, C$_6$F$_5$-2). ^{11}B{^{1}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.

Acknowledgment. We would like to thank the Deutsche Forschungsgemeinschaft (DFG) and the Fonds der Chemischen Industrie for financial support, Prof. Dr. U. Englert for X-ray measurements, and Dr. B. Mathiasch and Mr. T. Gossen for NMR measurements.

Supporting Information Available: Crystallographic data for the structural analyses of $C_{20}H_{49}O_4ScSi_3$ (**4**) and $C_{76}H_{99}B_2O_8SiY$ (**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.

IC0511165