

Neutral and cationic trimethylsilylmethyl complexes of the rare earth metals supported by a crown ether: synthesis and structural characterization

Stefan Arndt,^a Peter M. Zeimentz,^a Thomas P. Spaniol,^a Jun Okuda,^{*†a} Masaru Honda^b and Kazuyuki Tatsumi^b

^a Institut für Anorganische Chemie und Analytische Chemie,

Johannes Gutenberg-Universität Mainz, Duesbergweg 10–14, D-55099 Mainz, Germany

^b Department of Chemistry, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan

Received 27th May 2003, Accepted 21st July 2003

First published as an Advance Article on the web 8th August 2003

The synthesis of a series of thermally robust, isolable trimethylsilylmethyl complexes of the rare earth metals stabilized by 12-crown-4 [$\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(12\text{-crown-4})$] ($\text{Ln} = \text{Sc, Y, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu}$) is reported. The crystallographically characterized yttrium and lutetium complexes [$\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(12\text{-crown-4})$] exhibit facial coordination of the crown ether at the neutral lanthanide trialkyl unit. The coordination geometry can be derived from a capped octahedron. VT NMR spectroscopic studies revealed a labile coordination of the crown ether in thf solution. Reaction of the diamagnetic derivatives with triethylammonium tetraphenylborate in thf results in the clean formation of the cationic dialkyl complexes [$\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(12\text{-crown-4})(\text{thf})_y][\text{BPh}_4]$ ($\text{Ln} = \text{Sc, Y, } y = 0$; $\text{Ln} = \text{Lu, } y = 1$), which also exhibit an exocyclic coordination of the crown ether to the cationic dialkyl lanthanide fragment.

Introduction

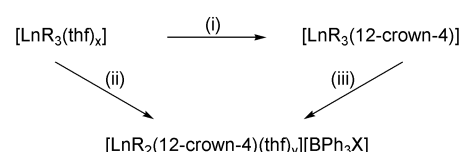
Cationic alkyl complexes of the rare earth metals are becoming increasingly important as active homogeneous ethylene polymerization catalysts.¹ A number of monoanionic ancillary ligands L such as deprotonated aza-18-crown-6, N,N' - R_2 -tacn- N'' -(CH_2) $_2$ $N^t\text{Bu}$ (tacn = 1,4,7-triazacyclononane, $R = ^i\text{Pr, Me}$), benzamidinate $\text{ArN}=\text{CPh}-\text{NAr}$ ($\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$), $\text{C}_3\text{Me}_4\text{SiMe}_2(\text{C}_5\text{H}_3\text{O}-2)$ have been used to stabilize the cationic alkyl rare earth metal fragments [$\text{Ln}(\text{L})\text{R}$]⁺.^{1,2} Because of the synthetic difficulty of preparing and handling even simple trialkyl complexes such as [$\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_x$],³ the development of structurally well-characterized alkyl cations has been rather slow.⁴ Recently we have succeeded in stabilizing *in situ* generated dialkyl cations [$\text{Ln}(\text{CH}_2\text{SiMe}_3)_2$]⁺ for $\text{Ln} = \text{Y}$ and Lu using crown ethers as ancillary ligands.⁵ We report here that the use of 12-crown-4 also results in the stabilization of the thermally sensitive [$\text{Ln}(\text{CH}_2\text{SiMe}_3)_3$] unit, giving a series of isolable complexes [$\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(12\text{-crown-4})$].

Results and discussion

Synthesis and structure in solution

When [$\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2$] is treated in pentane with one equivalent of 12-crown-4, careful workup at lower temperatures allowed the isolation of the new compound [$\text{Y}(\text{CH}_2\text{SiMe}_3)_3(12\text{-crown-4})$] in good yield as analytically pure, colorless crystals (Scheme 1). Due to the tedious isolation of the thf complex [$\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2$], a practically simple one-pot method was developed starting with anhydrous yttrium trichloride. The thermal stability is evidently enhanced over that of the thf complex, crystals of [$\text{Y}(\text{CH}_2\text{SiMe}_3)_3(12\text{-crown-4})$] being unchanged after standing for 2 weeks at room temperature. This complex is sparingly soluble in hydrocarbons and soluble in thf, dichloromethane and 1,2-dichloroethane. However, when a solution in dichloromethane is left standing in daylight for 1 h, the formation of a mixture of chlorinated products [$\text{Y}(\text{CH}_2\text{SiMe}_3)_{3-n}\text{Cl}_n(12\text{-crown-4})$] ($n = 1, 2$) was observed.

[†] Present address: Institute of Inorganic Chemistry, Aachen University of Technology (RWTH), Prof.-Pirlet-Strasse 1, D-52056 Aachen, Germany.



Scheme 1 $x = 2$ ($\text{Ln} = \text{Sc, Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu}$); $x = 3$ ($\text{Ln} = \text{Sm}$); $y = 0$ ($\text{Ln} = \text{Sc, Y}$), $y = 1$ ($\text{Ln} = \text{Lu}$). Conditions: i. 12-crown-4 in pentane, 15 min, -20 to 25°C ; ii. (a) BPh_3 in thf, 20 min, 25°C , (b) 12-crown-4, 5 min, 25°C , $\text{X} = \text{R}$; iii. $[\text{NEt}_3\text{H}][\text{BPh}_4]$ in thf, 24 h, 25°C , $\text{X} = \text{Ph}$.

As shown in Fig. 1, the ^1H NMR spectrum of [$\text{Y}(\text{CH}_2\text{SiMe}_3)_3(12\text{-crown-4})$] in $\text{thf}-d_8$ at 25°C shows broad signals for all three equivalent trimethylsilylmethyl groups and a broad resonance for the methylene protons of the crown ether. At -10°C , separate signals are observed for coordinated and non-coordinated crown ether. The diastereotopic methylene protons of the coordinated crown ether give rise to two broad resonances at 3.88 and 4.04 ppm, whereas the methylene protons of the noncoordinated crown ether appear as a singlet at 3.61 ppm. In addition, at lower temperatures the ^1H and ^{13}C NMR spectra exhibit separate signals for the alkyl groups of [$\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_x$] and [$\text{Y}(\text{CH}_2\text{SiMe}_3)_3(12\text{-crown-4})$], indicating

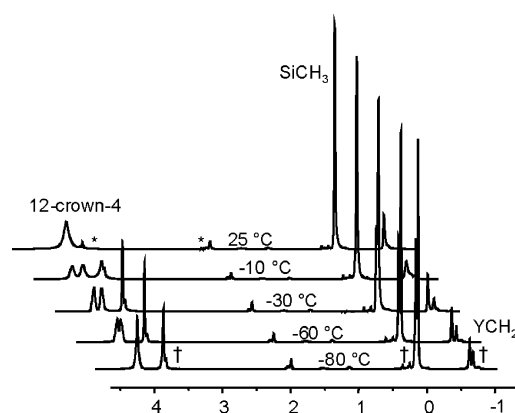


Fig. 1 ^1H NMR spectra of [$\text{Y}(\text{CH}_2\text{SiMe}_3)_3(12\text{-crown-4})$] in $\text{thf}-d_8$ at various temperatures. Signals denoted with (*) are due to the residual protons of $\text{thf}-d_8$. Signals denoted with (†) are assigned to non-coordinated crown ether and [$\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_x$], respectively.

reversible dissociation of the crown ether. The dissociation constant in thf-d_8 at -80°C was estimated to be $0.05 \pm 0.5 \text{ mol L}^{-1}$.

In the less Lewis basic solvent CD_2Cl_2 no dissociation of the crown ether was observed even at -80°C . In the ^1H NMR spectrum at 25°C , the methylene protons at yttrium appear as a doublet at -0.81 ppm with $J(\text{YH}) = 3.1 \text{ Hz}$, whilst the trimethylsilyl groups are observed as a sharp singlet at -0.09 ppm . The methylene protons of 12-crown-4 at 3.74 and 4.12 ppm are recorded as higher-order multiplets. These features indicate that 12-crown-4 is coordinated to the trivalent yttrium center in an exocyclic fashion analogous to that reported for the numerous 12-crown-4 complexes of lanthanide chlorides and nitrates.⁶

Following the analogous one-pot procedure scandium and an extensive series of lanthanide complexes $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{12-crown-4})]$ ($\text{Ln} = \text{Sc, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu}$) could be prepared and isolated. The only exceptions are the larger elements La, Ce, Pr and Nd, for which the formation of the starting complex $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_3]$ appeared to be not possible. Also the europium derivative could not be prepared, probably due to the facile reduction to the divalent state;⁷ cf.: $E^0(\text{Eu}^{3+}/\text{aq} + \text{e}^- \rightarrow \text{Eu}^{2+}/\text{aq}) = -0.35 \text{ V}$ versus SHE at pH = 0 in aqueous solution.^{7a} The diamagnetic scandium and lutetium complexes as well as the paramagnetic samarium complex show similar NMR spectroscopic features as those described for the yttrium complex.

Crystal structure

Single crystals of $[\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{12-crown-4})]$ suitable for an X-ray diffraction study were obtained from a saturated CD_2Cl_2 solution at ambient temperature. Fig. 2 depicts the ORTEP diagram of the molecular structure in the crystal. The overall structure resembles that of a three-legged piano-stool with 12-crown-4 coordinating to yttrium in a facial manner. The coordination geometry around the central atom can be best described as a capped octahedron, with one of the oxygen donors (O(3)) acting as the cap (Fig. 3). Notably, the cationic complex $[\text{Lu}(\text{CH}_2\text{SiMe}_3)_2(\text{12-crown-4})(\text{thf})][\text{BPh}_3(\text{CH}_2\text{SiMe}_3)]$ shows a configuration derived from a capped trigonal prism.⁵

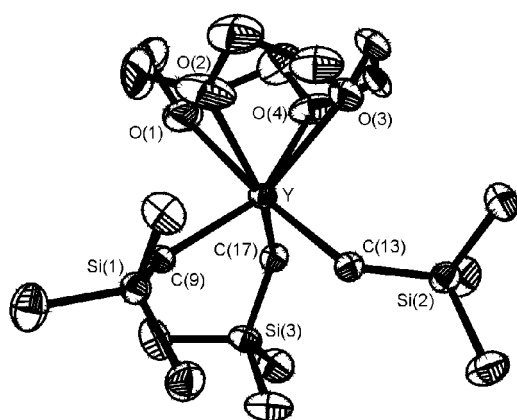


Fig. 2 ORTEP diagram of $[\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{12-crown-4})]$. Hydrogen atoms omitted for clarity, thermal ellipsoids drawn at 30% probability level. Y–C(9) 2.422(7), Y–C(13) 2.399(6), Y–C(17) 2.430(6), Y–O(1) 2.600(6), Y–O(2) 2.571(7), Y–O(3) 2.626(7), Y–O(4) 2.627(6) Å; C(13)–Y–O(1) 174.4(2), C(17)–O(4)–O(2) 90.3(2), O(4)–O(2)–C(9) 90.4(2), O(2)–C(9)–C(17) 88.5(2), C(9)–C(17)–O(4) 90.8(2)°.

The yttrium–carbon bond distances range from 2.399(6) to 2.430(6) Å, comparable to those reported for other yttrium complexes with a trimethylsilylmethyl ligand.⁸ The yttrium–oxygen bond distances range from 2.571(7) to 2.627(6) Å and correspond to values found in other related complexes.⁹

The analogous lutetium complex is isostructural with the yttrium complex. Lutetium–carbon bond distances range from 2.36(1) to 2.40(1) Å, comparable to those reported for other

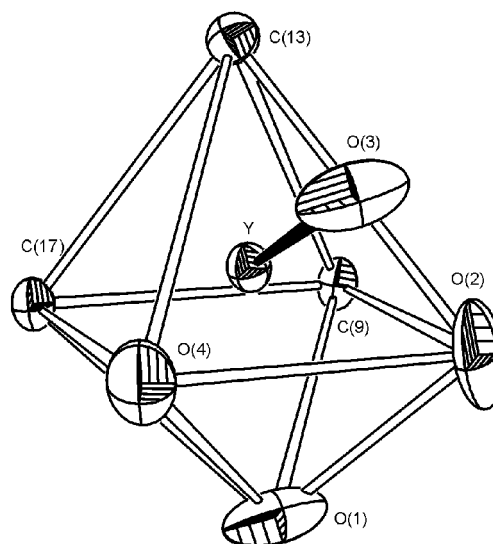


Fig. 3 ORTEP diagram of $[\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{12-crown-4})]$ illustrating the geometry of a distorted capped octahedron (open bonds) around the yttrium center. Noncoordinating atoms omitted for clarity.

lutetium complexes with a trimethylsilylmethyl ligand.¹⁰ The lutetium–oxygen bond distances range from 2.52(1) to 2.60(1) Å and are slightly elongated compared to those in the related cationic complex¹¹ in accordance with a tighter coordination.

The puckered conformation of the coordinated crown ether corresponds to that found in other related complexes. No significant change in bond parameters upon coordination was observed.⁶

Cation formation

Previously we reported that the lutetium dialkyl cation $[\text{Lu}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})_2]^+$ *in situ* generated from the reaction of the trialkyl $[\text{Lu}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2]$ and triphenyl borane in thf can be trapped by the addition of a crown ether and easily isolated as ion pairs $[\text{Lu}(\text{CH}_2\text{SiMe}_3)_2(\text{12-crown-4})(\text{thf})][\text{B}(\text{CH}_2\text{SiMe}_3)_3\text{Ph}_3]$.⁵ We found that the use of the neutral crown ether trialkyl complexes $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{12-crown-4})]$ as starting material for the cation formation instead of the corresponding bis(thf) complexes is advantageous because of its enhanced thermal stability. The trialkyl complexes $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{12-crown-4})]$ of scandium, yttrium and lutetium smoothly react with triethylammonium tetraphenylborate to give the dialkyl tetraphenylborate $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{12-crown-4})(\text{thf})_y][\text{BPh}_4]$ ($y = 0$ for $\text{Ln} = \text{Sc, Y}$; $y = 1$ for $\text{Ln} = \text{Lu}$) in high yields. These complexes are thermally stable and insoluble in aliphatic or aromatic hydrocarbons and highly soluble in pyridine. In contrast to $[\text{Lu}(\text{CH}_2\text{SiMe}_3)_2(\text{12-crown-4})(\text{thf})][\text{B}(\text{CH}_2\text{SiMe}_3)_3\text{Ph}_3]$,⁵ the dialkyl tetraphenylborates are only sparingly soluble in thf.

The lutetium and yttrium complexes $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{12-crown-4})(\text{thf})_y][\text{BPh}_4]$ exhibit NMR spectroscopic features for the cations that are essentially identical to those found for $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{12-crown-4})(\text{thf})][\text{B}(\text{CH}_2\text{SiMe}_3)_3\text{Ph}_3]$, consistent with the presence of isolated ion pairs in solution. The resonance of the methylene protons of the scandium complex $[\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{12-crown-4})][\text{BPh}_4]$ appears at -0.21 ppm and is slightly shifted to higher field in comparison with the analogous lutetium and yttrium compounds. Similar to the values observed for the cationic complexes of lutetium and yttrium, the diastereotopic protons of the crown ether ligand at scandium give rise to two multiplets at 3.33 and 3.65 ppm in the ^1H NMR spectrum at 25°C in thf-d_8 . In contrast to the neutral complex $[\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{12-crown-4})]$, the NMR spectra in thf-d_8 of the cationic alkyl $[\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{12-crown-4})][\text{BPh}_4]$ show no significant temperature dependence (-80 to 60°C),

indicating that crown ether dissociation is slow. In accordance with these findings, in the presence of excess crown ether the NMR spectrum in thf- d_8 shows well separated signals for coordinated and noncoordinated crown ether. There was also no indication for the formation of a bis(crown ether) complex $[\text{Y}(\text{CH}_2\text{SiMe}_3)_2(12\text{-crown-4})_2][\text{BPh}_4]$.

In contrast to the lutetium complex, the isolated scandium and yttrium complexes do not contain a thf ligand. For the scandium complex, this may be due to steric factors. The isolation of the yttrium complex $[\text{Y}(\text{CH}_2\text{SiMe}_3)_2(12\text{-crown-4})][\text{BPh}_4]$ as a thf-free complex after drying *in vacuo* may be due to the more labile nature of the thf, since yttrium is less Lewis acidic/electrophilic as compared with lutetium.¹² The ion pairs presented here are not active in olefin polymerization.

Conclusion

We have shown that tris(trimethylsilylmethyl) complexes of a rather extensive series of rare earth elements can be isolated in a one-pot method as their thermally robust 12-crown-4 complexes $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(12\text{-crown-4})]$ starting from the rare earth metal trichloride. This type of compounds may become useful for further derivatizations, as could be demonstrated for the smooth alkyl abstraction to form the dialkyl cations $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(12\text{-crown-4})(\text{thf})_n]^+$.

Experimental

General considerations

All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. Diethyl ether and thf were distilled from sodium benzophenone ketyl. Pentane was purified by distillation from sodium/triglyme benzophenone ketyl. Anhydrous lanthanide trichlorides (Aldrich or Strem) were used as received. 12-crown-4 was dried over sodium and distilled before use. All other chemicals were commercially available and used after appropriate purification. NMR spectra were recorded on a Bruker DRX 400 spectrometer at 25 °C (^1H , 400.1 MHz; ^{13}C , 100.6 MHz; ^{11}B , 128.4 MHz) unless otherwise stated. Chemical shifts for ^1H 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 $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in CDCl_3 . Elemental analyses were performed by the Microanalytical Laboratory of this department. 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 to the extreme sensitivity of the material. Metal analysis was performed by complexometric titration using xylenol orange as indicator.^{2e}

Syntheses

$[\text{Sc}(\text{CH}_2\text{SiMe}_3)_3(12\text{-crown-4})]$. Anhydrous scandium trichloride (0.454 g, 3.00 mmol) was stirred in thf (10 mL) at 40 °C overnight. After removal of thf the residue was taken up in a mixture of thf (3 mL), pentane (23 mL) and Et_2O (23 mL) and treated dropwise at ambient temperature with a solution of $\text{LiCH}_2\text{SiMe}_3$ (0.806 g, 8.56 mmol) in pentane (9 mL). The resulting colourless suspension was stirred at this temperature for 2 h. After filtration the solvent was removed from the clear colourless filtrate at 0 °C *in vacuo*. The resulting oily yellow residue was extracted twice with pentane (45 and 30 mL) at 0 °C and the extracts treated with a solution of 12-crown-4 (0.502 g, 2.85 mmol) in pentane (5 mL) at 0 °C to form a precipitate immediately. The supernatant was decanted, the product washed with pentane (10 mL) and dried *in vacuo* to afford a colourless powder of $[\text{Sc}(\text{CH}_2\text{SiMe}_3)_3(12\text{-crown-4})]$ (0.499 g,

36%) (Found C, 46.0; H, 10.1; Sc, 9.2. $\text{C}_{20}\text{H}_{49}\text{O}_4\text{ScSi}_3$ requires C, 49.8; H, 10.2; Sc, 9.3%). $\delta_{\text{H}}(\text{thf-}d_8)$ -0.59 (3×2 H, br s, $\text{ScCH}_2\text{SiCH}_3$), -0.11 (3×9 H, s, $\text{ScCH}_2\text{SiCH}_3$) and 3.59 (16 H, br s, 12-crown-4); $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$ -0.40 (3×2 H, br s, $\text{ScCH}_2\text{SiCH}_3$), -0.06 (3×9 H, s, $\text{ScCH}_2\text{SiCH}_3$) and 4.03 (16 H, br s, 12-crown-4); $\delta_{\text{C}}(\text{CD}_2\text{Cl}_2)$ 3.8 ($\text{ScCH}_2\text{SiCH}_3$), 40.0 (br, $\text{ScCH}_2\text{SiCH}_3$) and 70.0 (12-crown-4).

$[\text{Y}(\text{CH}_2\text{SiMe}_3)_3(12\text{-crown-4})]$. Anhydrous yttrium trichloride (0.586 g, 3.00 mmol) was stirred in thf (10 mL) at 45 °C overnight. After removal of thf the residue was taken up in pentane (20 mL) and treated dropwise at -78 °C with a solution of $\text{LiCH}_2\text{SiMe}_3$ (0.856 g, 9.09 mmol) in pentane (20 mL). The resulting colourless suspension was allowed to warm to 0 °C and stirred at this temperature for 2 h. After filtration at 0 °C the clear colourless filtrate was treated with a solution of 12-crown-4 (0.529 g, 3.00 mmol) in pentane (5 mL) to form a precipitate immediately. Decanting off the supernatant, washing the residue with pentane (10 mL) and drying *in vacuo* afforded a colourless powder of $[\text{Y}(\text{CH}_2\text{SiMe}_3)_3(12\text{-crown-4})]$ (1.261 g, 80%) (Found C, 44.5; H, 9.2; Y, 17.4. $\text{C}_{20}\text{H}_{49}\text{O}_4\text{Si}_3\text{Y}$ requires C, 45.6; H, 9.4; Y, 16.9%). $\delta_{\text{H}}(\text{thf-}d_8)$ -0.86 (3×2 H, br, $\text{YCH}_2\text{SiCH}_3$), -0.09 (3×9 H, s, SiMe_3) and 3.67 (16 H, br s, 12-crown-4); $\delta_{\text{H}}(\text{thf-}d_8, -10$ °C) -0.83 (3×2 H, br, $\text{YCH}_2\text{SiCH}_3$), -0.11 (3×9 H, s, SiMe_3), 3.61 (6 H, br s, free 12-crown-4) and $3.88, 4.04$ (10 H, $2 \times$ br s, coordinated 12-crown-4); $\delta_{\text{H}}(\text{thf-}d_8, -30$ °C) -0.92 ($0.5 \times 3 \times 2$ H, br, $\text{YCH}_2\text{SiCH}_3(\text{thf})$), -0.83 (3×2 H, br, $\text{YCH}_2\text{SiCH}_3(12\text{-crown-4})$), -0.11 (3×9 H, s, $\text{SiMe}_3(12\text{-crown-4})$), -0.09 ($0.5 \times 3 \times 9$ H, s, $\text{SiMe}_3(\text{thf})$), 3.62 (0.5×16 H, br s, free 12-crown-4) and $3.93, 4.03$ (16 H, $2 \times$ br s, coordinated 12-crown-4); $\delta_{\text{H}}(\text{thf-}d_8, -60$ °C) -0.94 ($0.5 \times 3 \times 2$ H, br, $\text{YCH}_2\text{SiCH}_3(\text{thf})$), -0.87 (3×2 H, br, $\text{YCH}_2\text{SiCH}_3(12\text{-crown-4})$), -0.13 (3×9 H, s, $\text{SiMe}_3(12\text{-crown-4})$), -0.10 ($0.5 \times 3 \times 9$ H, s, $\text{SiMe}_3(\text{thf})$), 3.60 (0.5×16 H, br s, free 12-crown-4) and $3.96, 4.00$ (16 H, $2 \times$ br s, coordinated 12-crown-4); $\delta_{\text{H}}(\text{thf-}d_8, -80$ °C) -0.95 ($0.5 \times 3 \times 2$ H, br, $\text{YCH}_2\text{SiCH}_3(\text{thf})$), -0.90 (3×2 H, br, $\text{YCH}_2\text{SiCH}_3(12\text{-crown-4})$), -0.14 (3×9 H, s, $\text{SiMe}_3(12\text{-crown-4})$), -0.11 ($0.5 \times 3 \times 9$ H, s, $\text{SiMe}_3(\text{thf})$), 3.60 (0.5×16 H, br s, free 12-crown-4) and 3.98 (16 H, br s, coordinated 12-crown-4); $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$ -0.81 (3×2 H, d, $J(\text{YH}) = 3.1$ Hz, $\text{YCH}_2\text{SiCH}_3$), -0.09 (3×9 H, s, $\text{YCH}_2\text{SiCH}_3$), and $3.74, 4.12$ (2×8 H, 2 m, 12-crown-4); $\delta_{\text{C}}(\text{thf-}d_8, -80$ °C) 4.8 ($\text{YCH}_2\text{SiCH}_3(\text{thf})$), 5.0 ($\text{YCH}_2\text{SiCH}_3(12\text{-crown-4})$), 29.8 (d, $J(\text{YC}) = 33.6$ Hz, $\text{YCH}_2\text{SiCH}_3(12\text{-crown-4})$), 30.9 (d, $J(\text{YC}) = 34.7$ Hz, $\text{YCH}_2\text{SiCH}_3(\text{thf})$), 69 (br, 12-crown-4); $\delta_{\text{C}}(\text{CD}_2\text{Cl}_2)$ 4.4 ($\text{YCH}_2\text{SiCH}_3$), 32.5 (d, $J(\text{YC}) = 35.7$ Hz, $\text{YCH}_2\text{SiCH}_3$) and 67.2 (12-crown-4). Single crystals suitable for X-ray analysis were obtained from a saturated CD_2Cl_2 solution at ambient temperature.

$[\text{Sm}(\text{CH}_2\text{SiMe}_3)_3(12\text{-crown-4})]$. Anhydrous samarium trichloride (0.770 g, 3.00 mmol) was stirred in thf (3 mL) at room temperature for 20 min. After removal of thf, Et_2O (23 mL) and pentane (23 mL) were added. To this suspension was added dropwise at room temperature a solution of $\text{LiCH}_2\text{SiMe}_3$ (0.806 g, 8.56 mmol) in pentane (9 mL) and the resulting yellow suspension stirred for 1 h. After filtration the clear yellow filtrate was cooled to -40 °C and the solvent was removed *in vacuo*. The resulting oily yellow residue was extracted with pentane (3×30 mL) at -30 °C and the extracts treated with a solution of 12-crown-4 (0.502 g, 2.85 mmol) in pentane (5 mL) at -20 °C to form a precipitate immediately. Decanting off the supernatant, washing with pentane (10 mL) and drying *in vacuo* at 0 °C afforded a yellow powder of $[\text{Sm}(\text{CH}_2\text{SiMe}_3)_3(12\text{-crown-4})]$ (0.636 g, 38%) (Found C, 39.8; H, 8.0; Sm, 27.7. $\text{C}_{20}\text{H}_{49}\text{O}_4\text{Si}_3\text{Sm}$ requires C, 40.8; H, 8.4; Sm, 25.6%). $\delta_{\text{H}}(\text{thf-}d_8)$ -0.28 (3×2 H, s, $\text{SmCH}_2\text{SiCH}_3$), -0.09 (3×9 H, s, $\text{SmCH}_2\text{SiCH}_3$) and 3.60 (16 H, br, 12-crown-4); $\delta_{\text{C}}(\text{thf-}d_8)$ 3.0 ($\text{SmCH}_2\text{SiCH}_3$) and 70.0 (br, 12-crown-4). The signal of the methylene group attached to samarium could not be detected.

[Gd(CH₂SiMe₃)₃(12-crown-4)]. Anhydrous gadolinium trichloride (0.791 g, 3.00 mmol) was stirred in thf (3 mL) at room temperature for 15 min. Et₂O (23 mL) and pentane (23 mL) were added. To this suspension was added dropwise at 0 °C a solution of LiCH₂SiMe₃ (0.808 g, 8.58 mmol) in pentane (9 mL) and the reaction mixture stirred at 0 °C for 2.5 h. After filtration at 0 °C the solvent was removed from the clear yellow filtrate. The resulting oily yellow residue was extracted with pentane (45 and 30 mL) at 0 °C and the extracts treated with a solution of 12-crown-4 (0.500 g, 2.84 mmol) in pentane (5 mL) at 0 °C to form a precipitate immediately. Decanting off the supernatant, washing with pentane (10 mL) and drying *in vacuo* at 0 °C afforded a colourless powder of [Gd(CH₂SiMe₃)₃(12-crown-4)] (1.214 g, 72%) (Found C, 38.8; H, 6.9; Gd, 26.1. C₂₀H₄₉GdO₄Si₃ requires C, 40.4; H, 8.3; Gd, 26.4%).

[Tb(CH₂SiMe₃)₃(12-crown-4)]. Anhydrous terbium trichloride (0.796 g, 3.00 mmol) was stirred in thf (2 mL) at room temperature for 15 min. Et₂O (23 mL) and pentane (23 mL) were added. To this suspension was added dropwise at 0 °C a solution of LiCH₂SiMe₃ (0.805 g, 8.55 mmol) in pentane (9 mL) and the reaction mixture stirred at 0 °C for 1 h and at room temperature for 45 min. After filtration at 0 °C the solvent was removed from the clear yellow filtrate *in vacuo*. The resulting oily yellow residue was extracted with pentane (60 and 20 mL) at 0 °C and the extracts treated with a solution of 12-crown-4 (0.529 g, 3.00 mmol) in pentane (5 mL) at 0 °C to form a precipitate immediately. Decanting off the supernatant, washing with pentane (10 mL) and drying *in vacuo* at 0 °C afforded a colourless powder of [Tb(CH₂SiMe₃)₃(12-crown-4)] (0.910 g, 54%) (Found C, 39.5; H, 7.6; Tb, 26.5. C₂₀H₄₉O₄Si₃Tb requires C, 40.3; H, 8.3; 26.6%).

[Dy(CH₂SiMe₃)₃(12-crown-4)]. Anhydrous dysprosium trichloride (0.811 g, 3.02 mmol) was stirred in thf (10 mL) at 40 °C overnight. After evaporation of the solvent, the residue was suspended in a mixture of thf (3 mL), pentane (23 mL) and Et₂O (23 mL), treated with a solution of LiCH₂SiMe₃ (0.811 g, 8.61 mmol) in pentane (9 mL) at 0 °C and the colourless reaction mixture stirred at this temperature for 2 h. After filtration at 0 °C the solvent was removed from the clear colourless filtrate at 0 °C. The resulting oily residue was extracted with pentane (45 and 30 mL) at 0 °C and the extracts treated with a solution of 12-crown-4 (0.508 g, 2.88 mmol) in pentane (5 mL) at 0 °C to form a precipitate immediately. Decanting off the supernatant, washing with pentane (2 × 10 mL) and drying *in vacuo* at 0 °C afforded a colourless solid of [Dy(CH₂SiMe₃)₃(12-crown-4)] (0.169 g, 10%) (Found C, 37.1; H, 8.3; Dy, 26.9. C₂₀H₄₉DyO₄Si₃ requires C, 40.0; H, 8.2; Dy, 27.1%).

[Ho(CH₂SiMe₃)₃(12-crown-4)]. [Ho(CH₂SiMe₃)₃(12-crown-4)] was synthesized in a manner analogous to that to prepare [Y(CH₂SiMe₃)₃(12-crown-4)] from holmium trichloride (0.814 g, 3.00 mmol), LiCH₂SiMe₃ (0.856 g, 9.09 mmol) and 12-crown-4 (0.529 g, 3.00 mmol) to yield 0.263 g (15%) of a pink powder (Found C, 39.9; H, 8.1; Ho, 27.4. C₂₀H₄₉HoO₄Si₃ requires C, 39.9; H, 8.1; Ho, 27.4%). The low yield is probably due to the difficulty in preparing the holmium starting materials in a reproducible way.

[Er(CH₂SiMe₃)₃(12-crown-4)]. Anhydrous erbium trichloride (0.822 g, 3.00 mmol) was stirred in thf (10 mL) at 45 °C overnight. After evaporation of the solvent the residue was suspended in pentane (20 mL) and treated with a solution of LiCH₂SiMe₃ (0.856 g, 9.09 mmol) in pentane (20 mL) at –78 °C. The resulting colourless suspension was allowed to warm to 0 °C and stirred at this temperature for 1 h and for additional 3 h at room temperature. After filtration at 0 °C the clear pink solution was treated with a solution of 12-crown-4 (0.529 g, 3.00 mmol) in pentane (5 mL) at 0 °C to form a

precipitate immediately. Decanting off the supernatant, washing with pentane (10 mL) and drying *in vacuo* afforded a slightly pink powder of [Er(CH₂SiMe₃)₃(12-crown-4)] (1.050 g, 58%) (Found C, 38.9; H, 8.0; Er, 27.4. C₂₀H₄₉ErO₄Si₃ requires C, 39.7; H, 8.2; Er, 27.6%).

[Tm(CH₂SiMe₃)₃(12-crown-4)]. [Tm(CH₂SiMe₃)₃(12-crown-4)] was synthesized in a manner analogous to that to prepare [Er(CH₂SiMe₃)₃(12-crown-4)] from thulium trichloride (0.826 g, 3.00 mmol), LiCH₂SiMe₃ (0.856 g, 9.09 mmol) and 12-crown-4 (0.529 g, 3.00 mmol) to yield 1.161 g (64%) of a colorless powder (Found C, 39.0; H, 7.3; Tm, 28.5. C₂₀H₄₉O₄Si₃Tm requires C, 39.6; H, 8.1; Tm, 27.8%).

[Yb(CH₂SiMe₃)₃(12-crown-4)]. Anhydrous ytterbium trichloride (0.838 g, 3.00 mmol) was stirred in thf (10 mL) at 45 °C overnight. After evaporation of the solvent, the residue was suspended in pentane (20 mL) and treated with a solution of LiCH₂SiMe₃ (0.856 g, 9.09 mmol) in pentane (20 mL) at –78 °C. The resulting brownish suspension was allowed to warm to 0 °C and stirred at this temperature for 1 h and for an additional 2 h at room temperature. After filtration at 0 °C the clear red filtrate was treated with 12-crown-4 (0.529 g, 3.00 mmol) in pentane (5 mL) at 0 °C to form a precipitate immediately. Decanting off the supernatant, washing with pentane (10 mL) and drying *in vacuo* afforded an orange powder of [Yb(CH₂SiMe₃)₃(12-crown-4)] (0.608 g, 33%) (Found C, 39.5; H, 7.6; Yb, 28.0. C₂₀H₄₉O₄Si₃Yb requires C, 39.3; H, 8.1; 28.3%). $\delta_{\text{H}}(\text{thf}-d_8)$ –18.2 (16 H, br, 12-crown-4), 5.5 (33 H, br overlap, YbCH₂SiCH₃).

[Lu(CH₂SiMe₃)₃(12-crown-4)]. Anhydrous lutetium trichloride (0.840 g, 3.00 mmol) was stirred in thf (10 mL) at 40 °C for 2 h. After evaporation of the solvent, the residue was suspended in pentane (20 mL) and treated with a solution of LiCH₂SiMe₃ (0.856 g, 9.09 mmol) in pentane (20 mL) at –78 °C. The resulting colourless suspension was allowed to warm to 0 °C and stirred at this temperature for 1 h and for additional 2 h at room temperature. After filtration at 0 °C the clear colourless filtrate was treated with 12-crown-4 (0.529 g, 3.00 mmol) in pentane (5 mL) to form a precipitate immediately. Decanting off the supernatant, washing with pentane (10 mL) and drying *in vacuo* afforded a colourless powder of [Lu(CH₂SiMe₃)₃(12-crown-4)] (1.237 g, 68%) (Found C, 39.1; H, 7.0; Lu, 28.3. C₂₀H₄₉LuO₄Si₃ requires C, 39.2; H, 8.1; Lu, 28.6%). $\delta_{\text{H}}(\text{thf}-d_8)$ –1.12 (3 × 2 H, s, LuCH₂SiCH₃), –0.09 (3 × 9 H, s, LuCH₂SiCH₃) and 3.61 (16 H, br, 12-crown-4); $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$ –1.02 (3 × 2 H, s, LuCH₂SiCH₃), –0.08 (3 × 9 H, s, LuCH₂SiCH₃) and 3.74, 4.14 (2 × 8 H, 2 m, 12-crown-4); $\delta_{\text{C}}(\text{CD}_2\text{Cl}_2)$ 4.4 (LuCH₂SiCH₃), 39.6 (LuCH₂SiCH₃) and 68.1 (12-crown-4). Single crystals suitable for X-ray analysis were obtained from a saturated CH₂Cl₂ solution at –40 °C.

[Sc(CH₂SiMe₃)₂(12-crown-4)][BPh₄]. A mixture of [Sc(CH₂SiMe₃)₃(12-crown-4)] (0.100 g, 0.207 mmol) and [NEt₃H][BPh₄] (0.870 g, 0.207 mmol) was stirred in thf (15 mL) at –100 °C and allowed to slowly warm to room temperature. After stirring for 24 h, the solvent was removed *in vacuo*, the crude product was washed with Et₂O (20 mL) and dried *in vacuo* to give colourless microcrystals (0.125 g, 85%) (Found: C, 66.5; H, 7.9; Sc, 6.4. C₄₀H₅₈BO₄ScSi₂ requires C, 67.2; H, 8.2; Sc, 6.3%). $\delta_{\text{H}}(\text{thf}-d_8)$ –0.21 (2 × 2 H, s, ScCH₂SiCH₃), –0.09 (2 × 9 H, s, ScCH₂SiCH₃), 3.33, 3.65 (2 × 8 H, 2 m, 12-crown-4), 6.80 (4 H, t, *J*(HH) = 7.3 Hz, 4-Ph), 6.94 (4 × 2 H, t, *J*(HH) = 7.3 Hz, 3-Ph), 7.33 (4 × 2 H, br, 2-Ph); $\delta_{\text{C}}(\text{thf}-d_8)$ 3.8 (ScCH₂SiCH₃), 68.9 (12-crown-4), 122.4 (4-Ph), 126.1 (3-Ph), 137.1 (2-Ph) and 165.0 (q, *J*(BC) = 49.1 Hz, 1-Ph). The signal of the methylene group at Sc could not be detected; $\delta_{\text{B}}(\text{thf}-d_8)$ –6.7.

[Y(CH₂SiMe₃)₂(12-crown-4)][BPh₄]. A mixture of [Y(CH₂SiMe₃)₃(thf)₂] (0.300 g, 0.606 mmol), [NEt₃H][BPh₄] (0.256 g,

0.606 mmol) and 12-crown-4 (0.096 mL, 0.606 mmol) was stirred in thf (50 mL) at -78°C and allowed to slowly warm to room temperature. After stirring for 24 h, a colourless byproduct was removed by filtration. All volatiles were removed from the filtrate *in vacuo*, the crude product was washed with Et_2O (20 mL) and dried *in vacuo* to give colourless microcrystals (0.402 g, 87%) (Found: C, 63.4; H, 7.9; Y, 11.6. $\text{C}_{40}\text{H}_{58}\text{BO}_4\text{Si}_2\text{Y}$ requires C, 63.3; H, 7.7; Y, 11.8%). $\delta_{\text{H}}(\text{thf}-d_8) -0.89$ (2×2 H, d, $J(\text{YH}) = 2.9$ Hz, $\text{YCH}_2\text{SiCH}_3$), -0.10 (2×9 H, s, $\text{YCH}_2\text{SiCH}_3$), 3.37, 3.61 (2×8 H, 2 m, 12-crown-4), 6.82 (4 H, t, $J(\text{HH}) = 7.2$ Hz, 4-Ph), 6.96 (4×2 H, t, $J(\text{HH}) = 7.2$ Hz, 3-Ph) and 7.35 (4×2 H, br, 2-Ph); $\delta_{\text{C}}(\text{thf}-d_8)$ 4.5 ($\text{YCH}_2\text{SiCH}_3$), 34.4 (d, $J(\text{YC}) = 40.5$ Hz, $\text{YCH}_2\text{SiCH}_3$), 68.5 (12-crown-4), 122.4 (4-Ph), 126.2 (3-Ph), 137.1 (2-Ph) and 165.0 (q, $J(\text{BC}) = 49.3$ Hz, 1-Ph); $\delta_{\text{B}}(\text{thf}-d_8) -6.7$.

[Lu(CH₂SiMe₃)₃(12-crown-4)(thf)][BPh₄]. A mixture of [Lu(CH₂SiMe₃)₃(12-crown-4)] (0.100 g, 0.163 mmol) and [NEt₃H][BPh₄] (0.069 g, 0.163 mmol) was stirred in thf (10 mL) at -100°C and allowed to slowly warm to room temperature. After stirring for 48 h, a colourless byproduct was removed by filtration. All volatiles were removed from the filtrate *in vacuo* to give colourless microcrystals (0.102 g, 70%) (Found: C, 57.1; H, 7.3; Lu, 19.2. $\text{C}_{44}\text{H}_{66}\text{BLuO}_5\text{Si}_2$ requires C, 57.6; H, 7.3; Lu, 19.1%). $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2) -1.11$ (2×2 H, s, $\text{LuCH}_2\text{SiCH}_3$), -0.12 (2×9 H, s, $\text{LuCH}_2\text{SiCH}_3$), 2.02 (4 H, m, $\beta\text{-CH}_2$, thf), 3.29, 3.67 (2×8 H, m, 12-crown-4), 4.04 (4 H, m, $\alpha\text{-CH}_2$, thf), 6.92 (4 H, t, $J(\text{HH}) = 7.3$ Hz, 4-Ph), 7.06 (4×2 H, t, $J(\text{HH}) = 7.3$ Hz, 3-Ph) and 7.37 (4×2 H, br, 2-Ph); $\delta_{\text{H}}(\text{thf}-d_8) -1.12$ (2×2 H, s, $\text{LuCH}_2\text{SiCH}_3$), -0.10 (2×9 H, s, $\text{LuCH}_2\text{SiCH}_3$), 1.76 (4 H, m, $\beta\text{-CH}_2$, thf), 3.36 (8 H, 2 m, 12-crown-4), 3.62 ($4 + 8$ H, m, $\alpha\text{-CH}_2$, thf and 12-crown-4), 6.82 (4 H, t, $J(\text{HH}) = 7.0$ Hz, 4-Ph), 6.95 (4×2 H, t, $J(\text{HH}) = 7.3$ Hz, 3-Ph) and 7.34 (4×2 H, br, 2-Ph); $\delta_{\text{C}}(\text{thf}-d_8)$ 4.4 ($\text{LuCH}_2\text{SiCH}_3$), 38.5 ($\text{LuCH}_2\text{SiCH}_3$), 71.4 (12-crown-4), 122.4 (4-Ph), 126.2 (3-Ph), 137.1 (2-Ph) and 165.0 (q, $J(\text{BC}) = 49.1$ Hz, 1-Ph). $\delta_{\text{B}}(\text{thf}-d_8) -6.7$.

Crystal structure analysis

Crystallographic data for [Y(CH₂SiMe₃)₃(12-crown-4)]: $\text{C}_{20}\text{H}_{49}\text{O}_4\text{Si}_3\text{Y}$, 526.77 g mol⁻¹, monoclinic, $a = 9.771(1)$ Å, $b = 16.2169(8)$ Å, $c = 19.137(1)$ Å, $\beta = 98.057(7)^{\circ}$, $U = 3002.4(4)$ Å³, $P2_1/n$ (non-standard setting of $P2_1/c$, no. 14), $Z = 4$, $T = 293(2)$ K, $\mu(\text{MoK}\alpha) = 2.081$ mm⁻¹; 12264 data, 7122 unique; structure solution by direct methods and difference Fourier syntheses; refinement converged with $R = 0.081$, $R_w = 0.137$ [$I > 2\sigma(I)$].

CCDC reference number 211480.

Crystallographic data for [Lu(CH₂SiMe₃)₃(12-crown-4)]: $\text{C}_{20}\text{H}_{49}\text{LuO}_4\text{Si}_3$, 612.83 g mol⁻¹, monoclinic, $a = 9.753(4)$ Å, $b = 16.163(2)$ Å, $c = 19.119(3)$ Å, $\beta = 99.24(2)^{\circ}$, $U = 2975(1)$ Å³, $P2_1/n$ (non-standard setting of $P2_1/c$, no. 14), $Z = 4$, $T = 293(2)$ K, $\mu(\text{MoK}\alpha) = 3.458$ mm⁻¹; 8027 data, 7596 unique; structure solution by isotopic replacement using the coordinates of the yttrium complex; the refinement converged with $R = 0.082$, $R_w = 0.174$ [$I > 2\sigma(I)$].

CCDC reference number 211481.

See <http://www.rsc.org/suppdata/dt/b3/b305964b/> for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support. M. H. was a fellow of the International Max Planck Research School for Polymer Science.

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- [$\text{Y}(\text{OH})_2(\text{12-crown-4})\text{Cl}_3 \cdot 2 \text{H}_2\text{O}$]: $\text{Y}-\text{O}(\text{12-crown-4}) = 2.42(1)-2.59(1)$ Å, see: R. D. Rogers, A. N. Rollins and M. M. Benning, *Inorg. Chem.*, 1988, **27**, 3826.
- [$\text{LuCp}_2(\text{CH}_2\text{SiMe}_3)(\text{thf})$]: $\text{Lu}-\text{C} = 2.376(16)$ Å, see: (a) H. Schumann, W. Genthe and N. Bruncks, *Angew. Chem.*, 1981, **93**, 126; H. Schumann, W. Genthe and N. Bruncks, *Angew. Chem., Int. Ed.*, 1981, **20**, 129; H. Schumann, W. Genthe, N. Bruncks and J. Pickardt, *Organometallics*, 1982, **1**, 1194; (b) [$\text{Li}(\text{thf})_3$] $\text{Lu}(\eta^5\text{-C}_5\text{Me}_5)(\text{CH}_2\text{SiMe}_3)\{\text{CH}(\text{SiMe}_3)_2\text{Cl}\}$: $\text{Lu}-\text{C} = 2.314(18)$, 2.344(18) Å (two crystallographically independent molecules), see: H. van der

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Å, see ref. 3(g); (f) $[Lu(CH_2SiMe_3)_2(12-crown-4)(thf)][B(CH_2SiMe_3)Ph_3]$: Lu–C = 2.340(2), 2.354(2) Å, see ref. 5.

11 $[Lu(CH_2SiMe_3)_2(12-crown-4)(thf)][B(CH_2SiMe_3)Ph_3]$: Lu–O(12-crown-4) = 2.438(1)–2.503(1) Å, see ref. 5.

12 Relative Lewis acidities of lanthanide compounds were determined by tandem mass spectrometry, see: H. Tsuruta, K. Yamaguchi and T. Imamoto, *Chem. Commun.*, 1999, 1703.