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The first structurally characterized cationic lanthanide–alkyl complexes†

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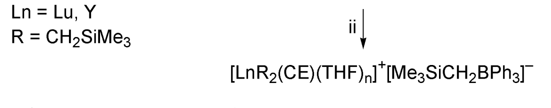
Reaction of rare earth metal–alkyl complexes [Ln(CH_2SiMe_3)$_3$(THF)$_2$] (Ln = Y, Lu) with B(C_6X_5)$_3$ (X = H, F) in the presence of crown ethers gives crystallographically characterized ion pairs [Ln(CH_2SiMe_3)$_2$(CE)(THF)$_n$]$^+$[B(CH_2SiMe_3)(C_6X_5)$_3$]$^-$(CE = [12]-crown-4, n = 1; CE = [15]-crown-5 and [18]-crown-6, n = 0).

In contrast to the intensely investigated chemistry of the group 4 metal–alkyl cations in the context of homogeneous olefin polymerization catalysis,[1] related cationic alkyl complexes of the group 3 metals and lanthanides have not attracted much attention.[2–5] Recently, yttrium–alkyl cations [Y(L)(CH_2SiMe_3)]$^+$[B(C_6F_5)$_4$]$^-$ (L = *N*,*N′*-R$_2$-tacn-*N″*-(CH_2)$_2$N^{t}Bu; tacn = 1,4,7-triazacyclononane, R = ^{i}Pr, Me) were reported as single-site polymerization catalysts for ethylene.[2] However, these and other alkyl cations of the rare earths reported in the literature, such as [Y(L)(CH_2SiMe_3)$_2$]$^+$ (L = deprotonated aza-[18]-crown-6) were generated *in situ* and only characterized by NMR spectroscopy.[2,4] The thermal sensitivity coupled with the extreme electrophilicity of the metal center due to its low valence electron count were cited as reasons for the difficulty in isolating such species. We present here, surprisingly robust rare earth metal–dialkyl cations supported by crown ethers, which allow full crystallographic characterization. Crown ethers have long been known to coordinate the cations of lanthanide chlorides and nitrates,[6] but their use in organolanthanide chemistry has only been described recently.[7]

When a THF solution of the lutetium–trialkyl complex [Lu(CH_2SiMe_3)$_3$(THF)$_2$][8] was treated at 25 °C with one equivalent of the borane B(C_6X_5)$_3$ (X = H, F), followed by one equivalent of crown ether CE, analytically pure, colorless crystals of the ion pair [Lu(CH_2SiMe_3)$_2$(CE)(THF)$_n$]$^+$[B(CH_2SiMe_3)(C_6X_5)$_3$]$^-$ were isolated in practically quantitative yield (Scheme 1). In contrast to cationic d^0 metal–benzyl complexes,[1,5] the anions were shown to be non-coordinating. Irrespective of the anion, the LuCH$_2$ resonances shift to higher field in the ^{1}H and ^{13}C NMR spectra with increasing size of the crown ether; this indicates enhanced shielding in this series. The ion pairs are soluble in THF and CH_2Cl_2, but insoluble in aliphatic or aromatic hydrocarbons. Surprisingly, THF solutions of the ionic complexes are stable for more than 12 h. As alkyl abstraction with triphenylborane resulted in complete conversion at ambient temperature, there was no obvious advantage in using the more electrophilic perfluorinated triphenylborane. The ^{11}B{^{1}H} NMR spectra of all cations with [B(CH_2SiMe_3)Ph_3]$^-$ as anion, at 25 °C in THF-*d*$_8$, contains a signal at δ −10.4, whilst in the ^{1}H NMR spectra the BCH$_2$ resonance appears as a quartet at δ 0.17 with $^2J_{BH}$ = 4.7 Hz, indicating the presence of the identical anion.



Scheme 1 *Conditions*: i. THF, 25 °C, 20 min; ii. crown ether (CE), 25 °C, 5 min. CE = [12]-crown-4, n = 1; CE = [15]-crown-5, n = 0; CE = [18]-crown-6, n = 0.

^{1}H and ^{13}C NMR spectroscopy have shown that the cationic lutetium complex derived from [12]-crown-4 contains one molecule of THF that is labile on the NMR timescale.[9] In the yttrium analogue [Y(CH_2SiMe_3)$_2$([12]-crown-4)(THF)]$^+$, the CH$_2$ protons of the two equivalent alkyl groups at the yttrium center in CD_2Cl_2 give rise to a doublet at δ −0.86 with $^2J_{YH}$ = 3.2 Hz, whilst the carbon atoms were recorded as a doublet at δ 39.8 with $^1J_{YC}$ = 41.0 Hz. The CH$_2$ protons of the facially coordinated [12]-crown-4 appear in the ^{1}H NMR spectrum as two separate broad multiplets at δ 3.27 and 3.65, suggesting rigid coordination at the yttrium center. The lutetium complex shows similar NMR spectra. As shown in Fig. 1, the lutetium derivative exhibits a seven-coordinate metal center best described as a capped trigonal prism. Two parallel trigonal planes are formed by the atoms O(1), O(2), C(9) and O(3), O(4), C(13). The capping atom O(5) is located over the square plane O(2), O(3), C(9), C(13). The angles at the alkyl carbon atoms, 127.3(1) and 135.4(1)°, suggest the absence of any strong agostic interaction.

[15]-Crown-5 stabilizes the formally four-electron dialkyl cation fragment without an additional molecule of THF.[9] The CH$_2$ resonance of the alkyl groups at the lutetium center of [Lu(CH_2SiMe_3)$_2$([15]-crown-5)]$^+$ in CD_2Cl_2 appear in the ^{1}H NMR spectrum as a sharp singlet at δ −1.17. The diastereotopic methylene protons of the [15]-crown-5 give rise to two broad multiplets at δ 4.46 and 3.75. Again, the coordination polyhedron around the seven-coordinate metal center can be regarded as a capped trigonal prism (Fig. 2). Two parallel trigonal planes are formed by the atoms O(2), O(3), C(15) and O(4), O(5), C(11), with the capping atom O(1) located over the square plane O(2), O(5), C(11), C(15).

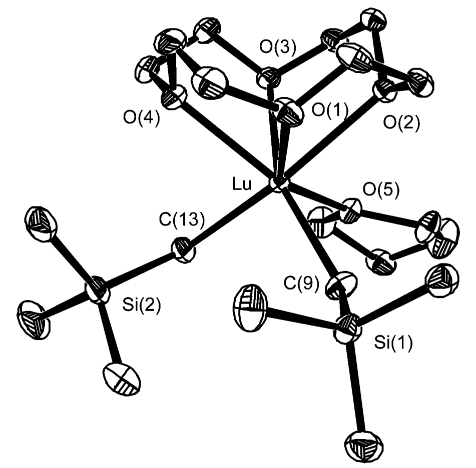


Fig. 1 ORTEP diagram of [Lu(CH_2SiMe_3)$_2$([12]-crown-4)(THF)]$^+$[B(CH_2SiMe_3)Ph_3]$^-$. Anion and hydrogen atoms omitted for clarity, thermal ellipsoids drawn at 30% probability level. Selected bond lengths (Å): Lu–O(1) 2.438(1), Lu–O(2) 2.451(1), Lu–O(3) 2.503(1), Lu–O(4) 2.406(1), Lu–O(5) 2.307(1), Lu–C(9) 2.340(2), Lu–C(13) 2.354(2).

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† Electronic supplementary information (ESI) available: experimental and spectroscopic details. See http://www.rsc.org/suppdata/cc/b2/b201613n/

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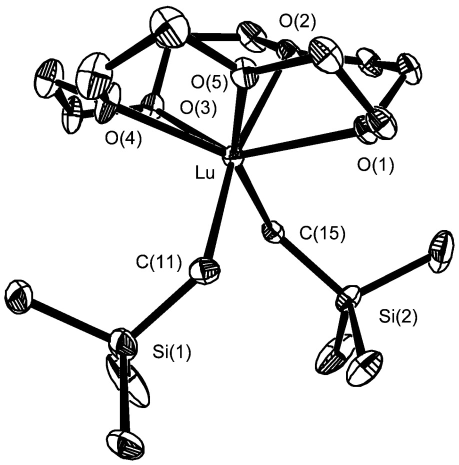

Fig. 2 ORTEP diagram of $[Lu(CH_2SiMe_3)_2([15]\text{-crown-5})]^+[B(CH_2SiMe_3)Ph_3]^-\cdot 0.5(CH_2Cl)_2$. Anion, non-coordinating solvent molecule and hydrogen atoms omitted for clarity, thermal ellipsoids drawn at 30% probability level. Selected bond lengths (Å): Lu–O(1) 2.359(5), Lu–O(2) 2.419(5), Lu–O(3) 2.376(5), Lu–O(4) 2.406(5), Lu–O(5) 2.421(5), Lu–C(11) 2.364(7), Lu–C(15) 2.345(7).

Use of [18]-crown-6 makes further expansion of the coordination sphere of the dialkyl–lanthanide complex possible.[9] The NMR spectroscopic features are similar to those of the related cations with smaller crown ethers. As Fig. 3 shows, the lutetium center adopts a coordination polyhedron of a doubly capped trigonal prism, where all six oxygen atoms of [18]-crown-6 are coordinated to the eight-coordinate lutetium ion. The two parallel trigonal planes are formed by the atoms O(1), O(6), C(13) and O(3), O(4), C(17). The oxygen atoms O(2) and O(5) cap the square planes formed by O(1), O(3), C(13), C(17), and by O(4), O(6), C(13), C(17), respectively.

In the absence of crown ethers, the reaction of $[Lu(CH_2SiMe_3)_3(THF)_2]$ with $B(C_6F_5)_3$ in THF-d_8 gives $[Lu(CH_2SiMe_3)_2(THF)_n]^+[B(CH_2SiMe_3)(C_6F_5)_3]^-$, whose ^{19}F NMR spectrum exhibits *meta*/*para* chemical shift differences $\Delta\delta$ of 2.2 ppm, consistent with solvent-separated ion pairs.[10] However, reaction between $[Lu(CH_2SiMe_3)_3(THF)_2]$ and BPh_3 in THF at ambient temperature resulted in colorless crystals of $[Lu(CH_2SiMe_3)_2(THF)_3]^+[B(CH_2SiMe_3)Ph_3]^-$. The ^1H NMR spectrum in CD_2Cl_2 shows that the cation of this complex contains three THF molecules. Comparison of its ^1H and ^{13}C NMR data with that of $[Lu(CH_2SiMe_3)_2(THF)_n]^+[B(CH_2SiMe_3)(C_6F_5)_3]^-$ shows that the $LuCH_2$ resonances appear at significantly higher field (δ −1.03 *vs.* −0.92 and δ 39.8 *vs.* 40.4, respectively). This finding strongly suggests that the $[B(CH_2SiMe_3)Ph_3]^-$ anion is loosely coordinating in the absence of crown ethers.[11]

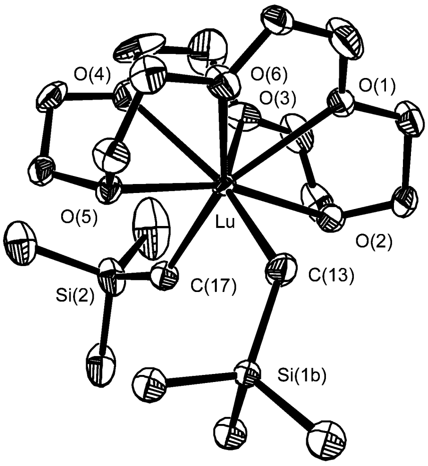

Fig. 3 ORTEP diagram of $[Lu(CH_2SiMe_3)_2([18]\text{-crown-6})]^+[B(CH_2SiMe_3)Ph_3]^-\cdot 0.5(CH_2Cl)_2$. Anion, non-coordinating solvent molecule and hydrogen atoms omitted for clarity, thermal ellipsoids drawn at 30% probability level. Selected bond lengths (Å): Lu–O(1) 2.532(5), Lu–O(2) 2.422(5), Lu–O(3) 2.431(5), Lu–O(4) 2.433(5), Lu–O(5) 2.399(5), Lu–O(6) 2.524(5), Lu–C(13) 2.366(8), Lu–C(17) 2.371(8).

In conclusion, we have shown that in the presence of oxygen donors, thermally robust lutetium and yttrium alkyl cations $[Ln(CH_2SiMe_3)_2(CE)(THF)_n]^+$ become easily available. Preliminary experiments with these extremely oxygen- and moisture-sensitive cationic lanthanide alkyl complexes indicate that they not only react with Broensted acids such as $HOC_6H_2{}^tBu_2$-2,6-Me-4, but exhibit significant ethylene polymerization activity.

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9 See electronic supplementary information (ESI) for experimental and spectroscopic details. $[Ln(CH_2SiMe_3)_2([12]\text{-crown-4})(THF)]^+[B(CH_2SiMe_3)Ph_3]^-$ (Ln = Lu, Y) and $[Lu(CH_2SiMe_3)_2([18]\text{-crown-6})(THF)]^+[B(CH_2SiMe_3)Ph_3]^-$ were prepared according to the method used for the synthesis of $[Lu(CH_2SiMe_3)_2([15]\text{-crown-5})]^+[B(CH_2SiMe_3)Ph_3]^-$: A solution of $Lu(CH_2SiMe_3)_3(THF)_2$ (200 mg, 344 μmol) and BPh_3 (83 mg, 344 μmol) in THF (1 mL) was stirred for 20 min at 25 °C, and treated with [15]-crown-5 (75 μL, 344 μmol). After evaporation of the solvent, pentane (3 mL) was added to give a colorless powder which was washed with pentane (3 × 2 mL). Yield: 284 mg, 92%. ^1H NMR (CD_2Cl_2, 25 °C), δ −1.17 (s, 2 × 2 H, $LuCH_2$), –0.44 (s, 9 H, BCH_2SiCH_3), –0.07 (s, 2 × 9 H, $LuCH_2SiCH_3$), 0.18 (br, 2 H, BCH_2), 3,45, 3.75 (br m, 10 H, OCH), 6.87 (t, $^3J_{HH}$ 7.0 Hz, 3 H, 4-Ph), 7.03 (t, $^3J_{HH}$ 7.1 Hz, 3 × 2 H, 3-Ph), 7.45 (br 3 × 2 H, 2-Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C), δ 2.4 (BCH_2SiCH_3), 4.2 ($LuCH_2SiCH_3$), 36.7 ($LuCH_2$), 69.2 (OCH), 122.0 (4-Ph), 126.0 (3-Ph), 135.3 (2-Ph), 167.5 (q, $^1J_{BC}$ 48.3 Hz, 1-Ph). The signal of the BCH_2 group was not detected. $^{11}B\{^1H\}$ NMR (THF-d_8, 25 °C), δ −10.4. Anal. Calc. for $C_{40}H_{68}BLuO_5Si_3$: C, 53.44; H, 7.56. Found: C, 52.56; H, 8.32. *Crystallographic data*: CCDC reference number 179961, $[Lu(CH_2SiMe_3)_2([12]\text{-crown-4})(THF)]^+[B(CH_2SiMe_3)Ph_3]^-$; 179962, $[Lu(CH_2SiMe_3)_2([15]\text{-crown-5})]^+[B(CH_2SiMe_3)Ph_3]^-\cdot 0.5(CH_2Cl)_2$; 179963, $[Lu(CH_2SiMe_3)_2([18]\text{-crown-6})]^+[B(CH_2SiMe_3)Ph_3]^-\cdot 0.5(CH_2Cl)_2$. See http://www.rsc.org.suppdata/cc/b2/b201613n/ for crystallographic data in CIF or other electronic format.

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11 A strong η^n coordination of the aryl groups is unlikely because of the high fluxionality. Furthermore, no reduction of the anion's C_{3v} symmetry is observed on the NMR timescale.