Synthesis and Structural Characterisation of the First Neutral Homoleptic Lanthanide Metal(III) Alkyls: [LnR_3] [Ln = La or Sm, R = $CH(SiMe_3)_2$]†

Peter B. Hitchcock,[a] Michael F. Lappert,[a] Richard G. Smith,[a] Ruth A. Bartlett,[b] and Philip P. Power[b]

[a] *School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, England, U.K.*
[b] *Department of Chemistry, University of California, Davis, California 95616, U.S.A.*

The alkylating agent LiR [R = $CH(SiMe_3)_2$] reacts with [$Ln(OC_6H_3Bu^t{}_2\text{-}2,6)_3$] (Ln = La or Sm) under ambient conditions to yield [LnR_3] [Ln = La (**1**) or Sm (**2**)], the first structurally characterised neutral homoleptic alkyls of the lanthanide metals; the crystalline compounds (**1**) and (**2**) have C_3 symmetry and almost tetrahedral CLnC′ angles, with Ln–C bonds of 2.515(9) (**1**) or 2.33(2) Å (**2**), and unusually short Ln $\cdots$ CH_3 contacts [3.121(9) (**1**) or 2.85(3) Å (**2**)].

Although much work on organolanthanide chemistry has recently been published,[1] the chemistry of compounds free from stabilising π-ligands, such as $\bar{C}_5Me_5$ or $\bar{C}_5H_3(SiMe_3)_2$-1,3, remains poorly developed. Where π-ligands are absent, stability has been attained through increasing the metal co-ordination number. This was achieved by means of (a) chelating ligands, as in [$Lu\{C_6H_4(CH_2NMe_2\text{-}2)\}_3$][2] or [$La\{CH(PPh_2)_2\}_3$];[3] (b) for-

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† No reprints available.

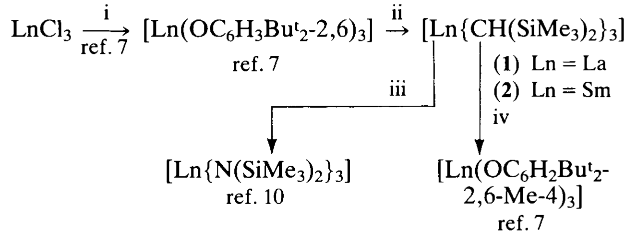
mation of a six-co-ordinate bimetallic complex, as in $[\mathrm{La\{(\mu\text{-}Me)_2Li(tmeda)\}_3}]$ [tmeda = *N,N,N′,N′*-tetramethylethylenediamine, and Ln = Sc, Y, or La—Lu (not Pm)];[4] (c) sterically demanding ligands together with sufficient neutral ligand to achieve co-ordination saturation, as in $[\mathrm{Y(CH_2SiMe_3)_3L_2}]$ [$\mathrm{L_2}$ = $\mathrm{(thf)_2}$ or tmeda (thf = tetrahydrofuran)];[5] or (d) anionic complexes, such as $[\mathrm{Li(thf)_4}][\mathrm{LnBu^t{}_4}]$ (Ln = Sm or Eu).[6]

We now report the synthesis and structural characterisation of the first neutral homoleptic alkyls of the lanthanide metals, the three-co-ordinate metal complexes $[\mathrm{Ln\{CH(SiMe_3)_2\}_3}]$ [Ln = La (**1**) or Sm (**2**)], and demonstrate their potential as precursors for other neutral homoleptic lanthanide metal(III) complexes.

Tris[bis(trimethylsilyl)methyl]samarium(III) $[\mathrm{SmR_3}]$ [R = $\mathrm{CH(SiMe_3)_2}$] (**2**) was obtained by treating a solution of $[\mathrm{Sm(OC_6H_3Bu^t{}_2\text{-}2,6)_3}]$[7] in pentane with 3 LiR at room temperature (ii in Scheme 1). The insoluble lithium aryloxide was removed by filtration, and extremely dioxygen- and moisture-sensitive crystals of (**2**) were obtained from pentane at −30 °C. The isoleptic lanthanum compound $[\mathrm{LaR_3}]$ (**1**) was obtained similarly. The key to our success in the present synthesis of $[\mathrm{LnR_3}]$ was the choice of an appropriate starting material. The anhydrous metal chloride $\mathrm{LnCl_3}$, with 3 LiR in thf, had been shown to yield $[\mathrm{Li(thf)_4}][\mathrm{LnClR_3}]$ (Ln = Er or Yb),[8a] although a claim to have obtained $\mathrm{YR_3}$ by this route has been made.[8b] In addition, we now find that $[\mathrm{Sm\{N(SiMe_3)_2\}_3}]$ does not react with 3 LiR at *ca.* 25 °C. An $\bar{\mathrm{O}}\mathrm{Ar}/\bar{\mathrm{A}}\mathrm{lk}$ exchange reaction has precedent in tin(II) chemistry.[9]

Elemental analysis and $^{13}\mathrm{C}\text{-}\{^1\mathrm{H}\}$ and $^1\mathrm{H}$ n.m.r. data‡ for the product were consistent with their formulation as $\mathrm{Ln\{CH(SiMe_3)_2\}_3}$ [Ln = La (**1**) or Sm (**2**)], and single crystal *X*-ray diffraction studies§ confirmed them to be neutral, homoleptic, three-co-ordinate lanthanide metal(III) alkyls.

The *X*-ray structure of $[\mathrm{LaR_3}]$ (**1**) is illustrated in Figure 1; the samarium alkyl (**2**) is isostructural. The crystalline alkyls (**1**) and (**2**) show a pyramidal, rather than a trigonal planar, metal environment, with bond angles close to sp^3 [C(1)–Ln–C(1′) = 109.9(2)° (**1**) and 110(1)° (**2**)]. They are isoelectronic with the amides $[\mathrm{Ln\{N(SiMe_3)_2\}_3}]$,[10] and indeed isostructural {as they are with the alkyls $[\mathrm{MR_3}]$ (M = Cr[11a] or In[11b])}. The choice of a pyramidal geometry may be rationalised on steric grounds, the deviation from planarity occurring in order to maximise ligand–metal attractions and minimise ligand–ligand repulsions.



Scheme 1. *Reagents and conditions*: i, $[\mathrm{Li(OC_6H_3Bu^t{}_2\text{-}2,6)(OEt_2)}]_2$ (1.5 equiv.), thf, reflux 8 h, then sublime at 250 °C/10^{-3} mbar;[7] ii, $\mathrm{LiCH(SiMe_3)_2}$ (3 equiv.), $\mathrm{C_5H_{12}}$, 25 °C, 30 min; iii, Ln = Sm, excess $\mathrm{HN(SiMe_3)_2}$, $\mathrm{C_5H_{12}}$, < 1 min; iv, Ln = Sm, $\mathrm{HOC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4}$ (3 equiv.), $\mathrm{C_5H_{12}}$, < 1 min.

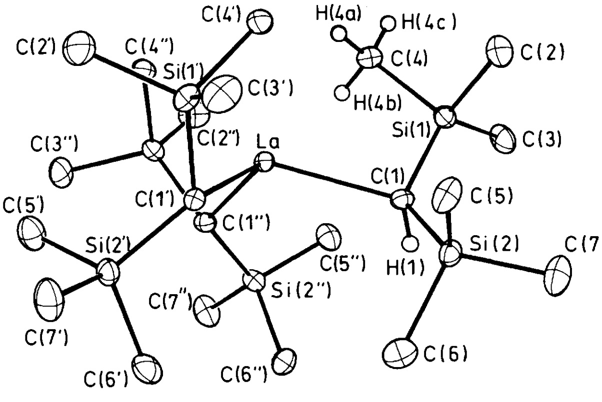


Figure 1. *X*-Ray structure and atom numbering scheme for $[\mathrm{La\{CH(SiMe_3)_2\}_3}]$ (**1**). The isoleptic samarium compound $[\mathrm{Sm\{CH(SiMe_3)_2\}_3}]$ (**2**) is isostructural with (**1**). Selected bond distances (Å) and angles (°) for (**1**) [(**2**)] are as follows: Ln–C(1) 2.515(9) [2.33(2)], <C(1)–Si> 1.85 [1.90], Ln · · · C(4) 3.121(9) [2.85(3)]; C(1)–Ln–C(1′) 109.9(2) [110(1)], Ln–C(1)–Si(1) 102.0(4) [107(1)], Ln–C(1)–Si(2) 121.0(4) [124(1)], Si(1)–C(1)–Si(2) 121.6(6) [118(1)].

The Ln–C bond lengths in the three-co-ordinate alkyls $[\mathrm{LnR_3}]$ [2.515(9) (**1**) and 2.33(2) Å (**2**)] are short by comparison with other known Ln–C σ-bonds. For example, the Lu–C bond length in $[\overline{\mathrm{Lu\{C_6H_4(CH_2N}}\mathrm{Me_2\text{-}2)\}_3}]$ of 2.435(14) Å (ref. 2) corresponds¶ to an expected value for the isoleptic La or Sm compound of 2.601 or 2.55 Å, respectively; while the Sm–C(σ) bond length of 2.511(8) Å in $[\mathrm{Sm(\eta\text{-}C_5Me_5)_2Ph(thf)}]$[13] leads¶ to an expectation of 2.56 Å for the lanthanum analogue. We suggest that the low metal co-ordination number in the alkyls (**1**) and (**2**) accounts for their having such short Ln–C bonds.

A feature of the molecular structures of the homoleptic alkyls of La (**1**) and Sm (**2**) is their unusually short Ln · · · Me contacts [3.121(9) (**1**) and 2.85(3) Å (**2**)] [however, even at 165 K, the $\mathrm{SiMe_3}$ $^1\mathrm{H}$ or $^{13}\mathrm{C}\text{-}\{^1\mathrm{H}\}$ n.m.r. signals for (**1**) were observed as singlets]. Such γ-agostic interactions have also been observed in $[\mathrm{Ln(\eta\text{-}C_5Me_5)_2\{CH(SiMe_3)_2\}}]$ (Ln = Nd[14] or Y[15]); this is attributed to their low metal co-ordination number.

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‡ *Selected n.m.r. data* (p.p.m. rel. to ext. $\mathrm{SiMe_4}$): for (**1**) (360 MHz for $^1\mathrm{H}$; 90 MHz for $^{13}\mathrm{C}$; $\mathrm{C_6D_{11}CD_3}$; 243 K) $^1\mathrm{H}$: 0.46 (s, $\mathrm{SiMe_3}$) and −0.14 (s, CH); $^{13}\mathrm{C}$: 5.20 [q, $^1J(^1\mathrm{H}\text{–}^{13}\mathrm{C})$ 117 Hz, $\mathrm{SiMe_3}$] and 75.2 [d, $^1J(^1\mathrm{H}\text{–}^{13}\mathrm{C})$ 95.2 Hz, CH]; for (**2**) (80 MHz for $^1\mathrm{H}$; 90 MHz for $^{13}\mathrm{C}$; $\mathrm{C_6D_5CD_3}$; 298 K) $^1\mathrm{H}$: −1.02 (br., s, $\mathrm{SiMe_3}$); $^{13}\mathrm{C}$: 0.35 [q, $^1J(^1\mathrm{H}\text{–}^{13}\mathrm{C})$ 118 Hz, $\mathrm{SiMe_3}$]; the methyne hydrogen and carbon signals were not observed owing to the paramagnetic nature of samarium(III) (f^5).

§ *Crystal data* for (**1**) [(**2**)]: $\mathrm{C_{21}H_{57}LaSi_6}$ [$\mathrm{C_{21}H_{57}Si_6Sm}$], *M* = 617.10 [628.6], trigonal, space group *P*31*c*, *a* = 16.366(9) [16.417(4)], *c* = 8.588(4) [8.708(4)] Å, *U* = 1992(2) [2032(2)] Å^3, *Z* = 2 [2], D_c = 1.03 [1.03] g cm^{-3}. Monochromated Mo-K_α radiation, λ = 0.71069 Å, μ = 12.75 [16.3] cm^{-1}.

For (**1**), *R* = 0.033, *R′* = 0.030 for 876 unique, absorption-corrected, reflections with $2\theta < 45°$ and $I > 2\sigma(I)$, measured at 130 K. Hydrogen atoms were refined using a riding model with C–H 0.96 Å. All non-hydrogen atoms were refined anisotropically.

For (**2**), *R* = 0.068, *R′* = 0.087 for 929 unique reflections with $2\theta <$ 50° and $I > \sigma(I)$, measured at room temperature with a large crystal (*ca.* 2.0 × 0.3 × 0.2 mm). No absorption correction was applied. Hydrogen atoms were omitted. In both (**1**) and (**2**) the crystal also contains a very disordered molecule of pentane for which only three carbon atom sites could be included. The absolute structure was checked for both structures.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ Some relevant ionic radii are $\mathrm{La^{3+}}$ 1.016, $\mathrm{Nd^{3+}}$ 0.995, $\mathrm{Sm^{3+}}$ 0.964, and $\mathrm{Lu^{3+}}$ 0.850 Å.[12]

We suggest that a neutral homoleptic lanthanide metal alkyl such as (**1**) or (**2**) will prove a useful source of other novel Ln complexes. For example, treatment with *n* equiv. of a protic reagent HA should lead to the series $LnA_n(R)_{3-n}$. For the present, we illustrate such behaviour by the mild reaction of $[SmR_3]$ (**2**) with either 3 $HN(SiMe_3)_2$ or 3 $HOC_6H_2Bu^t_2$-2,6-Me-4, to yield the known compounds $[Sm\{N(SiMe_3)_2\}_3]$[10] or $[Sm(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_3]$,[7] respectively (see iii or iv in Scheme 1).

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