Lanthanide Metal(III) Heteroleptic Alkyls: Synthesis of [$\mathrm{LnR_3(\mu\text{-}Me)Li(pmdeta)}$] [Ln = La or Sm, R = {$\mathrm{CH(SiMe_3)_2}$}, pmdeta = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine] and *X*-Ray Structure of the Samarium Complex†

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The first 'mixed' lanthanide metal(III) alkyls [$\mathrm{LnR_3(\mu\text{-}Me)Li(pmdeta)}$] [Ln = La or Sm, R = $\mathrm{CH(SiMe_3)_2}$, pmdeta = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine] were prepared from [$\mathrm{LnR_3}$], LiMe, and pmdeta; crystalline [$\mathrm{SmR_3(\mu\text{-}Me)Li(pmdeta)}$] has approximately tetrahedral environments for Sm and Li, an almost linear Sm–Me–Li unit [Sm–Me–Li 174(2)°], and short Sm–Me [2.33(3) Å] but long Li–Me [2.42(6) Å] distances.

We report on the preparation, equation (1), and characterisation of the heteroleptic lanthanide metal(III) alkyls [$\mathrm{LnR_3(\mu\text{-}Me)Li(pmdeta)}$] [R = $\mathrm{CH(SiMe_3)_2}$, pmdeta = $\mathrm{MeN(CH_2CH_2NMe_2)_2}$, and Ln = La (**1**) or Sm (**2**)], including the *X*-ray structure of the samarium complex (**2**).

$$[\mathrm{LnR_3}] \xrightarrow[\text{ii, pmdeta}]{\text{i, LiMe, Et}_2\text{O–C}_5\text{H}_{12}\text{, 293 K}} \begin{array}{l}[\mathrm{LnR_3(\mu\text{-}Me)Li\text{-}}\\ \mathrm{(pmdeta)}]\\ \text{Ln = La } (\mathbf{1})\\ \text{or Sm } (\mathbf{2})\end{array} \qquad (1)$$

Compounds (**1**) and (**2**) are of interest *inter alia* because they are the first: (i), complexes having two different alkyl

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† No reprints available.

Table 1. Comparative structural data for some 4f element (Ln) alkyls [$R = CH(SiMe_3)_2$; X = Cl or Me].

Compound	<Ln–C> (Å)	<R–Ln–R> (°)	Ln–X–Li (°)	Ref.
$[SmR_3(\mu\text{-}Me)Li(pmdeta)]$ (**2**)	2.51	107	174(2)	This work
$[Li(thf)_4][Yb(Cl)R_3]$ (**3**)	2.378	110.2	—	9
$[LaR_3(\mu\text{-}Cl)Li(pmdeta)]$ (**4**)	2.60	107.2	165(1)	10
$[SmR_3]$ (**5**)	2.33	110	—	12
$[LaR_3]$	2.515	110	—	12

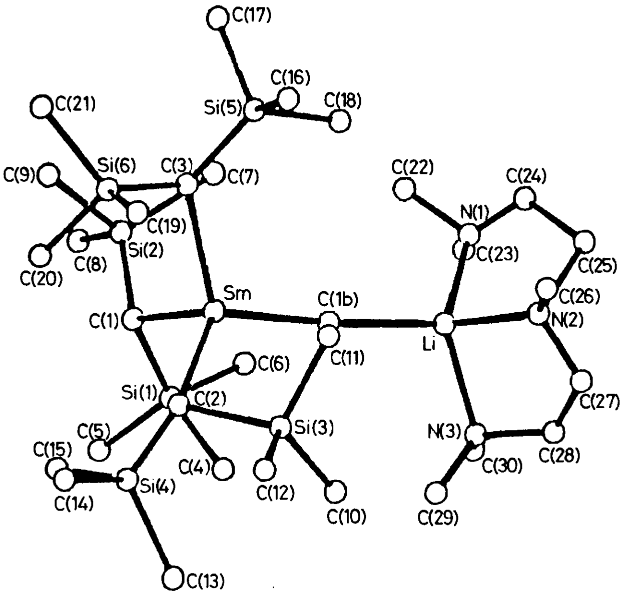

Figure 1. Molecular structure and atom numbering scheme for $[SmR_3(\mu\text{-}Me)Li(pmdeta)]$ (**2**). Selected bond distances (Å) and angles (°) are as follows: Sm–C(1) 2.53(3), Sm–C(2) 2.49(3), Sm–C(3) 2.52(3), Sm–C(1b) 2.33(3), Li–N(1) 2.13(7), Li–N(2) 2.02(7), Li–N(3) 2.17(8), Li–C(1b) 2.42(6); C(1)–Sm–C(2) 111(1), C(1)–Sm–C(3) 104(1), C(3)–Sm–C(2) 106(1), C(1)–Sm–C(1b) 103(1), C(2)–Sm–C(1b) 116(1), C(3)–Sm–C(1b), 115(1), Sm–C(1b)–Li 174(2).

groups bonded to a group 3 or 4f element; (ii), neutral tetra-alkyl-Ln^{III} complexes; and (iii), singly alkyl-bridged-Ln^{III} or -binuclear Li^{I} complexes. Heteroleptic metal alkyls or μ-alkyldimetal complexes[1] are exceedingly rare throughout the Periodic Table. The only previous example of a singly alkyl-bridged lithium compound appears to be $[\{Li(\mu\text{-}R)\}_\infty]$, a chain polymer in the solid state, Li–C 2.19(5) Å.[2] Among d and f block elements, the following singly-methyl-bridged complexes are known: $[Lu_2(\eta\text{-}C_5Me_5)_4(\mu\text{-}Me)Me]$,[3] $[Zr_2(\eta\text{-}C_5H_5)_4(\mu\text{-}Me)(OCHCH_2Bu^t)_2AlMe_2]$,[4] and $[Yb(\eta\text{-}C_5Me_5)_2(\mu\text{-}Me)Be(\eta\text{-}C_5Me_5)]$.[5] Di(μ-methyl)-heterobimetallic Ln–M compounds (M = an electron-deficient main group metal) have precedent but, except for the series $[Ln\{(\mu\text{-}Me)_2Li(tmeda)\}_3]$ [Ln = Sc, Y, and La–Lu (except Pm); tmeda = $(CH_2NMe_2)_2$],[6] they have contained cyclopentadienyl ligands, as in $[Ln(\eta\text{-}C_5H_5)_2(\mu\text{-}Me)_2AlMe_2]$[7] and $[Y(\eta\text{-}C_5Me_5)_2(\mu\text{-}Me)_2Li(OEt_2)_2]$.[8] *X*-Ray data on two quasi-tetrahedral lanthanide metal(III) alkyls are available: $[Li(thf)_4][Yb(Cl)R_3]$ (**3**)[9] (thf = tetrahydrofuran) and $[LaR_3(\mu\text{-}Cl)Li(pmdeta)]$ (**4**);[10] and reference has also been made to the series $[Li(thf)_4][LnBu^t_4]$ (Ln = Sm, Er, or Lu).[11]

Addition of a solution of LiMe in Et_2O to the deep red-orange pentane solution of $[SmR_3]$ (**5**)[12] gave a pale yellow solution. Addition of pmdeta caused precipitation of a yellow microcrystalline solid. Pyrophoric yellow cubic crystals of $[SmR_3(\mu\text{-}Me)Li(pmdeta)]$ (**2**) were obtained after recrystallisation from toluene. Colourless crystals of $[LaR_3(\mu\text{-}Me)Li(pmdeta)]$ (**1**) were prepared similarly, and both (**1**) and (**2**) were identified by satisfactory elemental analyses, and ^1H, ^7Li, and ^{13}C n.m.r.‡ spectroscopy.

Characterisation of the samarium complex $[SmR_3(\mu\text{-}Me)Li(pmdeta)]$ (**2**) was completed by *X*-ray diffraction.§ It was shown to be monomeric, with each metal in an approximately tetrahedral environment, and isomorphous with the μ-chloro complex (**4**). The metals were linked *via* an almost linear [174(2)°] Sm–Me–Li bridge, Figure 1. Some comparative structural data for complexes (**2**)—(**5**) are listed in Table 1.

In $[SmR_3]$ (**5**) there was a close metal–methyl interaction [2.85(3) Å] involving one methyl from each alkyl group.[12] There was no crystallographic evidence for such agostic interactions in $[SmR_3(\mu\text{-}Me)Li(pmdeta)]$ (**2**), the closest Sm · · · Me(R) contact being > 3.4 Å.

The Sm–Me bond in $[SmR_3(\mu\text{-}Me)Li(pmdeta)]$ (**2**) was short [2.33(3) Å]. The Sc–Me distance of 2.24(1) Å in $[Sc(\eta\text{-}C_5Me_5)_2Me]$[13] leads[14] to a value of *ca.* 2.47 Å for a terminal Sm–Me bond; this compares with a terminal Sm–C(R) bond length in (**2**) of 2.49(3)—2.53(3) Å.[12] The Y–Me

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‡ *Selected n.m.r. data* {δ in p.p.m., rel. to external $SiMe_4$, or $Li[NO_3]$(aq.)}. For (**1**) (80 MHz for ^1H, 31 MHz for ^7Li; 298 K, C_6D_6; 90 MHz for ^{13}C, $C_6D_5CD_3$, 243 K): ^1H 0.40 (s, $SiMe_3$), −0.12 (s, CH), −2.01 (s, μ-Me), 2.05 (s, pmdeta-Me), 1.97 (s, pmdeta-Me_2), 1.77 (s, pmdeta-CH_2); ^{13}C 5.78 (q, J_{CH} 120 Hz, $SiMe_3$), 61.28 (d, J_{CH} 86.5 Hz, CH), 46.1 (m, pmdeta), 53.0 (m, pmdeta), 57.0 (m, pmdeta), the signal due to the μ-Me group was obscured by the pmdeta signals; ^7Li 0.43. For (**2**) (80 MHz for ^1H, 90 MHz for $^{13}C\{^1H\}$, 31 MHz for ^7Li; 298 K, C_6D_6); ^1H 0.30 (s, $SiMe_3$), 2.47 (s, CH), 1.13 (s, pmdeta-CH_2), 1.38 (s, pmdeta-Me), −4.13 (s, μ-Me); $^{13}C\{^1H\}$ 5.03 (s, $SiMe_3$), 45.4 (s, pmdeta-Me), 52.9 (s, pmdeta-CH_2), 56.7 (s, pmdeta-CH_2), the bridging methyl group and the methyne (CH) carbon were not observed owing to the paramagnetism of Sm^{3+} (f^5), coupling constants were not recorded in the ^{13}C spectrum; ^7Li 8.30 ($w_{\frac{1}{2}}$ 18 Hz).

§ *Crystal data for* (**2**): $C_{31}H_{83}LiN_3Si_6Sm$, $M = 823.8$, triclinic, space group $P\bar{1}$, $a = 11.975(2)$, $b = 13.384(3)$, $c = 16.923(6)$ Å, $\alpha = 79.84(3)$, $\beta = 87.11(3)$, $\gamma = 68.35(2)°$, $U = 2481.0$ Å^3, $Z = 2$, $D_c = 1.10$ g cm^{-3}. Monochromated Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu = 13.5$ cm^{-1}. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer. A total of 4614 unique reflections were measured for $2 < \theta < 20°$ and $+h \pm k \pm l$, and 3219 with $|F^2| > 3\sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = \{\sigma^2(I) + (0.04\ I)^2\}^{\frac{1}{2}}/Lp$. There was no crystal decay and no absorption correction. The structure was solved by routine heavy atom methods and refined by full matrix least squares, with anisotropic thermal parameters, except for the Li atom and the C and N atoms of the pmdeta ligand. An attempt was made to refine the pmdeta anisotropically, but the refinement became unstable with diverging atom positions. Hydrogen atoms were omitted. The weighting scheme was $w = 1/\sigma^2(F)$ and the final residuals were $R = 0.108$, $R_w = 0.161$. Programs from the Enraf-Nonius SDP-Plus package were run on a PDP 11/34 computer. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue 1.

distance of 2.545(11) Å in $[\{Y(\eta\text{-}C_5H_5)_2(\mu\text{-Me})\}_2]$[15] points[14] to a value of 2.62 Å for the doubly bridging Sm–Me bond. The Sm–Me distance in complex (**2**) was identical to the Sm–C bond length in $[SmR_3]$.[12] The Li–Me bond in (**2**) was significantly longer [2.42(6) Å] than the Li–C bond in [LiR(pmdeta)] [2.13(5) Å][16] or $[Er(\eta\text{-}C_5H_5)_2(\mu\text{-Me})_2Li\text{-}(tmeda)]$ [2.26(3) Å].[17] We conclude that in complex (**2**) the Sm–Me bond is strong, but the Li–Me bond is weak, implying an asymmetric 'Sm–Me · · · Li,' as opposed to a symmetric 'Sm–Me–Li,' bridge.

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