Four-co-ordinate Lanthanide Metal(III) Chloro(alkyl)s: Synthesis and *X*-Ray Structure of [$LaR_3(\mu\text{-}Cl)Li(pmdeta)$] [$R = CH(SiMe_3)_2$, pmdeta = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine]†

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The lanthanum(III) chloro(alkyl) [$LaR_3(\mu\text{-}Cl)Li(pmdeta)$] [$R = CH(SiMe_3)_2$, pmdeta = $MeN(CH_2CH_2NMe_2)_2$] (**1**) was prepared from anhydrous $LaCl_3$ and 3LiR in tetrahydrofuran in the presence of pmdeta; compound (**1**) has approximately tetrahedral environments for the lanthanum and lithium ions [C–La–C′ (av.) = 108.8(6)°], an almost linear La–Cl–Li unit [La–Cl–Li = 165(1)°], and a mean La–C distance of 2.60(3) Å.

Although the term 'organolanthanide chemistry' is much used as a convenient method of classification, it is evident that the chemistry of complexes of the early lanthanides [La^{3+} (f^0), Ce^{3+} (f^1), Pr^{3+} (f^2), and Nd^{3+} (f^3)] differs markedly from that of the later analogues [Sm^{3+} (f^5) to Yb^{3+} (f^{13}), and Lu^{3+} (f^{14})].[1] This is due primarily to the progressive change in radius, from La^{3+} (r = 1.06 Å) to Lu^{3+} (r = 0.85 Å).[2] For a suite of ligands which co-ordinately satisfies a late lanthanide, it is often noted that data for the isoleptic early lanthanide analogue are elusive; *e.g.* (i) $LnCl_3 + 2LiCp \rightarrow [\{LnCp_2(\mu\text{-}Cl)\}_2]$ for the f^5 to f^{14} complexes but $LnCp_3$ for the f^0 to f^3 analogues ($Cp = \eta\text{-}C_5H_5)^-$;[1] or (ii) while $LuCl_3$ with $LiC_6H_3Me_2$-2,6 in tetrahydrofuran (thf) gave [$Li(thf)_4$][$Lu(C_6H_3Me_2\text{-}2,6)_4$], the analogous reaction with $LaCl_3$ yielded unidentified products.[3] There are only three published reports to date of *X*-ray-authenticated compounds containing an early lanthanide metal–carbon σ-bond, *viz.* [$Nd(\eta\text{-}C_5Me_5)_2R$] [$R = CH(SiMe_3)_2$],[4] [$Nd\{(\eta\text{-}C_5Me_4)_2SiMe_2\}R$],[5] and [$LaR_3$].[6]

A species of the type [$YbClR_3$]$^-$, with [$Li(thf)_4$]$^+$ as counterion, obtained from $YbCl_3$ + 3LiR in thf, was *X*-ray-characterised.[7] We now report that the related reaction with $LaCl_3$ yields [$LaR_3(\mu\text{-}Cl)Li(thf)_3$], which with pmdeta gave [$LaR_3(\mu\text{-}Cl)Li(pmdeta)$] (**1**) (pmdeta = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine) [equation (1)]. Recrystallisation from diethyl ether yielded extremely dioxygen- and moisture-sensitive colourless crystals of (**1**), identified by elemental analyses (C, H, N, and Cl), and ^1H and ^7Li n.m.r. spectra;‡ and by single-crystal *X*-ray analysis.§

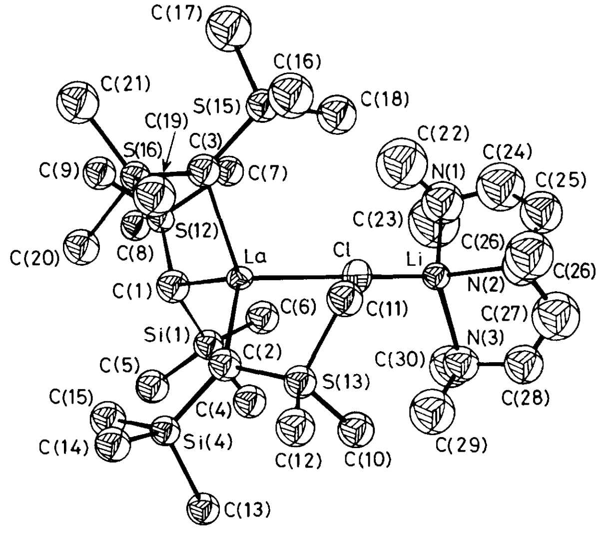

Figure 1. Molecular structure and atom numbering scheme for [$LaR_3(\mu\text{-}Cl)Li(pmdeta)$] (**1**). Selected bond distances (Å) and angles (°): La–C(1) 2.68(4), La–C(2) 2.55(2), La–C(3) 2.58(2), La–Cl 2.761(6), Li–N(1) 2.13(4), Li–N(2) 2.07(4), Li–N(3) 2.13(4), Li–Cl 2.28(4); C(1)–La–C(2) 116.2(6), C(1)–La–C(3) 108.8(6), C(3)–La–C(2) 107.4(6), C(1)–La–Cl 105.3(5), C(2)–La–Cl 115(2), C(3)–La–Cl 113.6(4), La–Cl–Li 165(1).

$$LaCl_3 + 3LiR \xrightarrow{\text{pmdeta, thf, } ca. \text{ 298 K}} \underset{(\mathbf{1})}{[LaR_3(\mu\text{-}Cl)Li(pmdeta)]} + 2LiCl \quad (1)$$

The molecular structure and atom-numbering scheme for [$LaR_3(\mu\text{-}Cl)Li(pmdeta)$] (**1**) are depicted in Figure 1. The molecule was shown to be monomeric, containing La^{3+} and Li^+, in approximately tetrahedral environments, linked *via* a rare example of a single chloride bridge.[8] The pmdeta was co-ordinated in a tridentate fashion to lithium.

The La–C(σ) bond lengths in the complex (**1**) were in the range 2.53(2)—2.60(2) Å. There is only one other lanthanum alkyl for which *X*-ray data are available; this is the three-co-ordinate homoleptic alkyl [LaR_3],[6] which had La–C(σ) bond lengths of 2.515(9) Å. The average C–La–C′ angle in (**1**) [108.8(6)°] showed a lanthanum(III) environment not significantly different from that in [LaR_3][6] [C–La–C′ 109.9(2)°]. It appears that the vacant co-ordination site in [LaR_3] is large enough to allow binding of the (μ-Cl)Li(pmdeta) moiety without significant distortion of the LaR_3 skeleton.

In [$Ln(\eta\text{-}C_5Me_5)_2R$] (Ln = Y[9] or Nd[4]) and [LnR_3][6] (Ln = La or Sm), a methyl carbon atom from one $SiMe_3$ group in each bis(trimethylsilyl)methyl ($\overline{R}$) ligand was located close to the metal centre. In [$LaR_3(\mu\text{-}Cl)Li(pmdeta)$] (**1**), no such

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† No reprints available.

‡ *Selected n.m.r. data* [rel. to ext. $SiMe_4$ (for ^1H) or aq. $LiNO_3$ (for ^7Li), 80 MHz for ^1H, 31 MHz for ^7Li, in C_6D_6 at *ca.* 298 K] for [$LaR_3(\mu\text{-}Cl)Li(pmdeta)$] (**1**); δ_H 0.52 (54H, s, $SiMe_3$), 1.92 (Me-pmdeta, 15H, m), and 1.62 (CH_2-pmdeta, 8H, m); the methyne (CH) signal could not be unambiguously assigned; δ_{Li} −0.20 p.p.m.

§ *Crystal data* for [$LaR_3(\mu\text{-}Cl)Li(pmdeta)$] (**1**): space group $P\bar{1}$, a = 12.066(6), b = 13.492(6), c = 16.936(8) Å, α = 79.24(5), β = 86.69(6), γ = 68.98(6)°, and D_c = 1.09 g cm^{-3} for U = 2528.41 Å^3 and Z = 2. Least-squares refinement based on 2616 observed reflections led to a final conventional R value of 0.072 (R' = 0.082). Anisotropic thermal parameters were used for La, Cl, and Si atoms. Hydrogen atoms were not located, but those on the La-bonded carbon atoms were placed in calculated positions. Details of data collection are given in *J. Chem. Soc., Dalton Trans.*, 1979, 45. 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.

agostic interactions were observed; the closest La $\cdots$ C(Me) approach was greater than 3.2 Å.

The La–Cl–Li moiety in (**1**) was approximately linear [165.1(1)°], with each of the La–Cl and Li–Cl interactions strong. Thus, the La–Cl distance of 2.762(2) Å was near the value found for a terminal La–Cl single bond, *cf.*[10] 2.72(1) Å in [$\{LaCl_3(2,6\text{-dmp})(OH_2)_n\}_m$] (2,6-dmp = 2,6-dimethyl-4-pyrone). The Yb–Cl bond distance of 2.486(6) Å[7] in [$YbClR_3$]$^-$ would lead to an expectation of 2.69 Å in the, as yet unknown, isoleptic lanthanate complex. We conclude that the La–Cl interaction in (**1**) is only slightly diminished by the presence of the [Li(pmdeta)]$^+$ fragment. Moreover, the Li–Cl distance in the complex (**1**), at 2.28(4) Å, is one of the shortest on record. The Li $\cdots$ Cl separation in crystalline LiCl is 2.56 Å,[11] and ranges from 2.33 to 2.42 Å in variously solvated LiCl complexes.[12] A mean Li–Cl distance of 2.405 Å was reported for the doubly Cl-bridged f^3 complex [$Nd\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(\mu\text{-}Cl)_2Li(thf)_2$].[13]

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