

Lithium and lanthanoid(III) complexes of the chelating *N,N*-dimethyl-*N'*-trimethylsilylethane-1,2-diaminate(1⁻) ligand

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Deprotonation of *N,N*-dimethyl-*N'*-trimethylsilylethane-1,2-diamine (HL¹) with LiBuⁿ in hexane yielded solvent-free LiL¹, whilst in diethyl ether the dinuclear complex [LiL¹₂Li(OEt₂)] was obtained. A single-crystal structure determination of the etherate showed one four-co-ordinate Li atom bound to two chelating amide ligands which were further bound, through the amide nitrogens, to a three-co-ordinate lithium centre which also has a co-ordinated diethyl ether molecule. The complex [{LiL¹LiClLiL¹(thf)}₂] (thf = tetrahydrofuran) was formed as a side product of a reaction of [LiL¹(thf)_n] with [LuCl₃(thf)₂] in thf. In the solid state the structure shows a LiCl bonded between LiL¹ and LiL¹(thf) units generating a 'three-rung ladder', which is further connected, by Li–Cl bonds, to a second LiL¹LiClLiL¹(thf) moiety. The dimer has two rare Li₄Cl units. Three equivalents of [LiL¹(thf)_n], prepared *in situ* in thf, reacted with [LuCl₃(thf)₂], anhydrous LnCl₃ (Ln = Er, Eu, Sm or Nd) or [LaBr₃(thf)₃] to form the hexane-soluble [LnL¹]₃. Monomeric six-co-ordinate, distorted-octahedral complexes with three chelating L¹ ligands in a *fac* orientation were found for Ln = Lu, Er or Eu by single-crystal X-ray studies. Reaction of 2 equivalents of LiL¹ with ErCl₃ in thf generated heteroleptic [ErL¹₂Cl].

Monoanionic, unidentate diorganoamide ligands have played a significant role in the chemistry of metals which form mainly ionic compounds, *i.e.* those from Groups I–III and the lanthanoids. Indeed for Li alone, diorganoamide complexes are extensively utilised as amide transfer reagents in inorganic chemistry¹ and as strong bases in organic syntheses.² Numerous X-ray diffraction studies of lithium amide complexes have revealed a fascinating structural diversity.³ Early research in diorganoamidolanthanoid compounds was dominated by the bis(trimethylsilyl)amide complexes [Ln{N(SiMe₃)₂}₂], the first examples of three-co-ordination for these large and electro-positive metals,⁴ and there have been recent extensions to [Ln{NBu^t(SiMe₂H)}₂]₃ and [Ln{N(SiMe₂H)}₂]₃ derivatives.⁵ These and related compounds have found applications as synthetic precursors of other lanthanoid complexes⁶ or lanthanoid nitrides,⁷ and as potential MOCVD sources.⁸

A recent surge of new interest in diorganoamide ligation has been driven by the search for non-cyclopentadienyl-based reactive lanthanoid (and also Group IV metal) compounds and catalysts.⁹ Prevalent amongst these new ligands are bidentate nitrogen donor anions such as benzamidates,^{10a–c} β-diketiminates,^{10d,e} and aminotropimines^{10f} [see also ref. 10(g) for related (alkoxydimethylsilyl)bis(*tert*-butyl)amido-*N,O* ligation]. Such ligands would be expected to improve the stability of the resulting complexes relative to monodentate amides through chelation and increased electron donation to the metal centre whilst retaining relatively low (less than six) co-ordination numbers. The development of lanthanoid chemistry based on monodeprotonated ethane-1,2-diamine derivatives, however, has been notably neglected. The flexible NCH₂CH₂N backbone of these amide ligands should be amenable to lanthanoid co-ordination and is in contrast to the more rigid and partially delocalised architecture of the bidentate amides noted above. Bimetallic lanthanoid–lithium complexes of the type [LnL₄Li] [L = N(Me)CH₂CH₂NMe₂] have been obtained upon reactions of lithium *N,N,N'*-trimethylethane-1,2-diaminate(1⁻) with lanthanoid trihalides.¹¹ Similarly, reactions of LiL with [Y(C₅H₅)₂Cl] and [Lu(Bu^tC₈H₇)Cl] generated [(C₅H₅)₂YL₂Li] and [(Bu^tC₈H₇)LuL₂Li].¹¹ Complex amides with one or two

SiMe₂ functions replacing backbone CH₂ groups are known, *e.g.* [N(SiMe₂CH₂NMe₂)₂]⁻ (giving Group IV complexes)^{12a} and [RNSiMe₂SiMe₂NR]²⁻ (R = Bu^t or Ph) (giving Group IV^{12b} and lanthanoid^{12c} complexes). We have now investigated application of the bulky *N,N*-dimethyl-*N'*-trimethylsilylethane-1,2-diaminate ion,¹³ a relatively neglected ligand, for the synthesis of diorganoamido-lithium and -lanthanoid(III) complexes. With the steric bulk imparted by the two methyls and the trimethylsilyl groups, stabilisation of monomeric lanthanoid complexes is feasible and the lipophilic functional groups should give the metal complexes good hydrocarbon solubility.

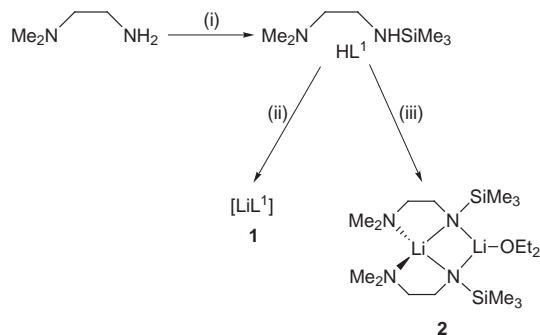
We now report the synthesis of lithium derivatives of HN-(SiMe₃)CH₂CH₂NMe₂ (HL¹), the crystal structures of [Li₂L¹₂(OEt₂)] and [{LiL¹LiClLiL¹(thf)}₂], the synthesis of [LnL¹]₃ (Ln = Lu, Er, Eu, Sm, Nd or La), the structures of the first three members of this series, and the preparation of a functionalised heteroleptic derivative [ErL¹₂Cl].

Results and Discussion

The amine HN(SiMe₃)CH₂CH₂NMe₂ HL¹ was readily prepared on multigram scale by an acid-catalysed reaction of *N,N*-dimethylethane-1,2-diamine with NH(SiMe₃)₂ (Scheme 1). This synthesis was based on an analogous reaction of NH(SiMe₃)₂ with (H₂NCH₂CH₂)₂NH¹⁴ and is similar to the method used for the silylation of ethane-1,2-diamine¹⁵ but using H₂SO₄ rather than SiMe₃Cl as the catalyst. The above procedure was more convenient than that previously reported, *viz.* lithiation of H₂NCH₂CH₂NMe₂ followed by addition of SiMe₃Cl.¹³ The compound HL¹ was characterised by infrared and ¹H NMR spectroscopy, such data not having been reported with the original preparation.¹³

Synthesis and characterisation of lithium amides 1–3

Reaction of LiBuⁿ with HL¹ in hexane at 0 °C followed by warming to room temperature gave a pale yellow solution, from which colourless crystals of LiL¹ **1** were isolated after evaporation of the solvent. A similar synthesis in diethyl ether yielded



Scheme 1 Reagents and conditions: (i) $\text{NH}(\text{SiMe}_3)_2$, H^+ (catalyst), 150°C ; (ii) LiBu^9 , hexane, 0°C ; (iii) LiBu^9 , diethyl ether, 0°C

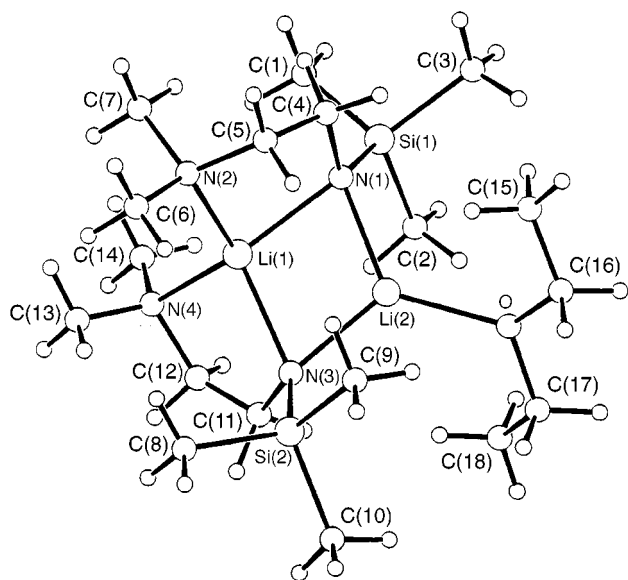


Fig. 1 Molecular structure of $[\text{LiL}^1]_2\text{Li}(\text{Et}_2\text{O})_2$ **2**

$[\text{LiL}^1]_2\text{Li}(\text{OEt}_2)_2$ **2** (Scheme 1). The compositions of the products were established by NMR spectroscopy and elemental analyses (C, H, N). The room-temperature ^1H NMR spectra showed resonances due to a single amide ligand environment for each complex and, for **2** one diethyl ether per two amide ligands. Both lithium complexes exhibited one ^7Li NMR resonance, at δ 1.54 (**1**) and -0.76 (**2**), even at low (-80°C) temperatures. These data suggest either a single lithium site for each amide, or rapid (on the NMR timescale) fluxional behaviour leading to time-averaged spectra.

Given the limited structural information available from the NMR data, conclusive identification of one lithium amide was obtained by a single-crystal X-ray diffraction study of **2**. High R but low R' values were obtained for the refinement, consistent with the use of a limited quantity of weak data, possibly consequent on partial dissolution of the specimen in the heavy oil used to cover the air-sensitive crystal for low-temperature data collection (as was also, but to a lesser extent, the case for **3** below). Nonetheless the key structural features of **2** were clearly established, and are shown, with the atom numbering scheme, in Fig. 1. The molecule is an exquisite example of a discrete dinuclear species with two different lithium centres. Four-coordinate $\text{Li}(1)$ is surrounded by two bidentate $\text{N}(\text{SiMe}_3)\text{CH}_2\text{CH}_2\text{NMe}_2$ ligands with the four nitrogen atoms in a distorted tetrahedral array, whereas $\text{Li}(2)$ is co-ordinated by the bridging amido nitrogens [N(1) and N(3)] and Et_2O in a planar array with a geometry (Table 1) similar to one of the lithium centres in $[\{\text{LiN}(\text{SiMe}_3)_2(\text{OEt}_2)\}_2]$.¹⁶ Deviations from a regular tetrahedron for $\text{Li}(1)\text{N}_4$ (Table 1) presumably arise from the restrictions of the bite angles [$89(1)$, $90(1)^\circ$] of the bidentate ligands and the bridging of the amide nitrogens, N(1) and N(3), to

Table 1 Selected intramolecular distances (\AA) and angles ($^\circ$) with estimated standard deviations in parentheses for $[\text{LiL}^1]_2\text{Li}(\text{OEt}_2)_2$ **2**

$\text{Li}(1)\text{--N}(1)$	2.09(3)	$\text{Li}(2)\text{--N}(1)$	2.00(3)
$\text{Li}(1)\text{--N}(2)$	2.09(3)	$\text{Li}(2)\text{--N}(3)$	2.02(3)
$\text{Li}(1)\text{--N}(3)$	2.10(3)	$\text{Li}(2)\text{--O}$	2.04(3)
$\text{Li}(1)\text{--N}(4)$	2.13(3)		
$\text{N}(1)\text{--Li}(1)\text{--N}(2)$	89(1)	$\text{N}(1)\text{--Li}(2)\text{--N}(3)$	109(1)
$\text{N}(3)\text{--Li}(1)\text{--N}(4)$	90(1)	$\text{N}(1)\text{--Li}(2)\text{--O}$	127(1)
$\text{N}(1)\text{--Li}(1)\text{--N}(3)$	102(1)	$\text{N}(3)\text{--Li}(2)\text{--O}$	123(1)
$\text{N}(2)\text{--Li}(1)\text{--N}(4)$	115(1)	$\text{Li}(1)\text{--N}(1)\text{--Li}(2)$	74(1)
$\text{N}(1)\text{--Li}(1)\text{--N}(4)$	134(1)	$\text{Li}(1)\text{--N}(3)\text{--Li}(2)$	73(1)
$\text{N}(2)\text{--Li}(1)\text{--N}(3)$	129(1)		

$\text{Li}(2)$. The $\text{Li}\text{--N}$ (amide), $\text{Li}\text{--N}$ (amine) and $\text{Li}\text{--O}$ distances (Table 1) do not differ significantly from those in related complexes^{1,16–19} within the limits of their standard deviations. With observation of two different lithium centres in crystalline **2**, the single ^7Li NMR resonance of the complex in $\text{CD}_3\text{C}_6\text{D}_5$ at both room temperature and -80°C must result from rapid exchange.

The structure of compound **2** differs from the classical 'dimer' arrangement observed for other diethyl ether complexes of lithiated bidentate amides, e.g. $[\{\text{Li}(\mu\text{-qtsa})(\text{OEt}_2)\}_2]$ [qtsa = 8-quinolyl(trimethylsilyl)amide]¹⁷ and $[\{\text{Li}(\mu\text{-dtf})(\text{OEt}_2)\}_2]$ (dtf = N,N' -di-*p*-tolylformamidate).¹⁸ The 8-quinolyl(trimethylsilyl)amide is related to the present ligand, but it has a much more rigid backbone, and is apparently less sterically hindered, allowing greater solvation of the lithium complex by diethyl ether. Structures analogous to that of **2** have previously been observed for lithium sulfinimidamides with co-ordinated diethyl ether, e.g. $[\text{Li}\{\text{R}(\text{N})_2\text{SR}'\}_2\text{Li}(\text{OEt}_2)]$,¹⁹ albeit with distinctly unsymmetrical binding of the bidentate amide [e.g. $\text{R} = \text{SiMe}_3$, $\text{R}' = \text{Ph}$; $\text{Li}\text{--N}$ 1.994(3), 2.245(5)^{19a}]. The 8-quinolyl(trimethylsilyl)amide analogue of **1** has also been structurally characterised yielding dimeric $[\{\text{Li}(\mu\text{-qtsa})\}_2]$, with three-coordinate Li .¹⁷ The structure of **1** is expected to be similar.

The relatively low yield of $[\text{LuL}^1]_3$ from reaction of LiL^1 with LuCl_3 in thf (below) led to an investigation of by-products. Crystallisation from the mother-liquor after isolation of $[\text{LuL}^1]_3$ gave $[\{\text{LiL}^1\text{LiClLiL}^1(\text{thf})\}_2]$ **3**, a mixed aggregate of LiL^1 and LiCl , identified by a single-crystal X-ray diffraction study. There has been recent interest in the structural identification of related LiNR_2/LiX species, in part due to the observed improved reactivity of lithium amide bases in organic synthesis upon addition of a lithium salt.²⁰ The molecular structure of **3** (Fig. 2) consists of a LiCl bonded between LiL^1 and $\text{LiL}^1(\text{thf})$ units through N (amide) --Li--N (amide) and Li--Cl--Li bridges. The resulting three-rung ladder of Li, N and Cl atoms is a typical structural motif of LiNR_2/LiX complexes.^{20,21} A unique feature of the present structure is the dimerisation of two of these ladders through formation of further Li--Cl bonds between one of the terminal Li atoms of the three-rung ladder and the chloride of the neighbouring ladder [shown schematically in Fig. 2(b)]. In previous examples co-ordination of lithium sites is completed by other donor bases,^{20,21} as is the case for the remaining terminal Li in **3**, hence these have a $\mu_3\text{-Cl}$ rather than the $\mu_4\text{-Cl}$ of **3**. The Li_4Cl arrangements are uncommon in structures of lithium complexes.²² A centrosymmetric dimer structure was recently described for $[\{\{\text{LiTe}(\text{NBU}^t)_2(\text{NHBu}^t)\}_2\text{LiCl}\}_2]$,²³ where the $\text{Te}(\text{NBU}^t)_2(\text{NHBu}^t)$ monoanion essentially acts as a tridentate amide, but this does not contain a three-rung ladder as the monomeric unit. The two halves of the dimer structure of **3** are crystallographically related by inversion through the centre of the $(\text{LiCl})_2$ four-membered ring. Selected bond distances and angles are listed in Table 2. As with **2**, the relatively low precision of the structure determination precludes a detailed comparison of the intramolecular parameters. Suffice it to say that the LiL^1 geometries (Table 2) compare well

Table 2 Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for $[\{\text{LiL}^1\text{Li}(\mu_4\text{-Cl})\text{LiL}^1(\text{thf})\}_2] \mathbf{3}$ (atoms generated through symmetry operations are denoted by primes)

Li(1)–Cl(1)	2.50(3)	Li(2)–N(3)	1.97(3)
Li(1')–Cl(1)	2.40(3)	Li(2)–N(4)	2.08(3)
Li(2)–Cl(1)	2.48(3)	Li(2)–O(1)	1.92(3)
Li(3)–Cl(1)	2.44(2)	Li(3)–N(1)	1.96(3)
Li(1)–N(1)	2.03(3)	Li(3)–N(3)	1.97(3)
Li(1)–N(2)	2.01(3)		
Li(1)–Cl(1)–Li(1')	81.7(9)	N(2)–Li(1)–Cl(1')	117(1)
Li(1)–Cl(1)–Li(2)	130.7(9)	Cl(1)–Li(2)–O(1)	105(1)
Li(1)–Cl(1)–Li(3)	67.5(9)	Cl(1)–Li(2)–N(3)	101(1)
Li(2)–Cl(1)–Li(1')	139.1(9)	Cl(1)–Li(2)–N(4)	113(1)
Li(2)–Cl(1)–Li(3)	66.2(8)	O(1)–Li(2)–N(3)	134(1)
Li(3)–Cl(1)–Li(1')	123.2(8)	O(1)–Li(2)–N(4)	109(1)
Cl(1)–Li(1)–Cl(1')	98.3(9)	N(3)–Li(2)–N(4)	90(1)
Cl(1)–Li(1)–N(1)	100(1)	Cl(1)–Li(3)–N(1)	104(1)
Cl(1)–Li(1)–N(2)	112(1)	Cl(1)–Li(3)–N(3)	103(1)
N(1)–Li(1)–Cl(1')	133(1)	N(1)–Li(3)–N(3)	149(1)
N(1)–Li(1)–N(2)	93(1)		

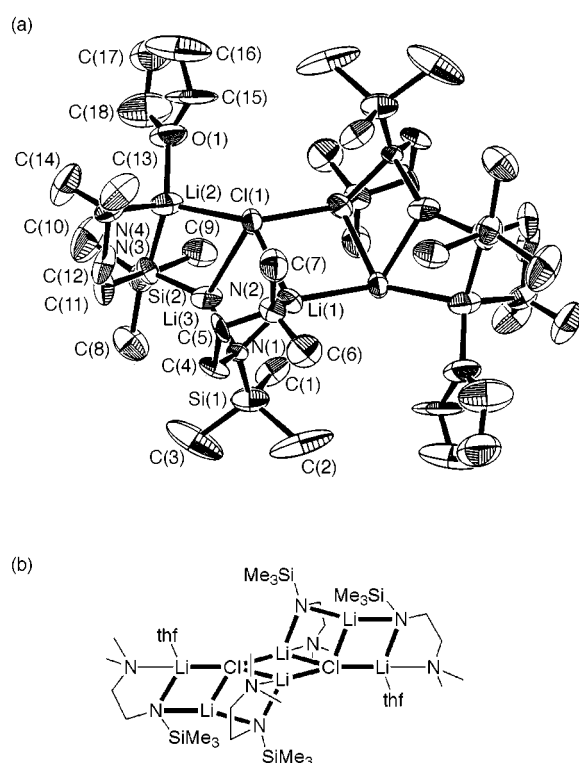
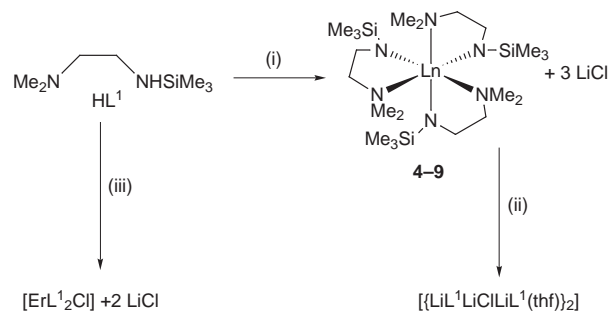


Fig. 2 (a) Molecular structure of $[\{\text{LiL}^1\text{Li}(\mu_4\text{-Cl})\text{LiL}^1(\text{thf})\}_2] \mathbf{3}$. Hydrogen atoms have been omitted for clarity. (b) Schematic representation of the ladder structure of $\mathbf{3}$

with those of **2** and the Li–Cl distances and the internal angles of the central $(\text{LiCl})_2$ core (Table 2) are within the ranges observed for other complexes containing this structural moiety in a primarily N-donor framework.^{23,24} The three-rung ladder does not possess the pseudo- C_2 symmetry about the Li–Cl rung of earlier LiNR_2/LiX complexes^{20,21} and this is reflected in the unequal displacement of Li(1) (0.63 Å) above and Li(2) (0.12 Å) below the anion plane [defined by Cl(1), N(1) and N(3)] although these values lie within the range (0.05–0.68 Å) previously observed.^{21a} Otherwise the bond distances and angles (Table 2) are unexceptional within the standard deviations.

The solution behaviour of compound **3** in $\text{CD}_3\text{C}_6\text{D}_5$ was probed by variable-temperature ^7Li NMR spectroscopy. At room temperature a peak with a broad shoulder was observed. Heating to 50 °C transformed this spectrum to a single narrow line at δ 1.49. Decoalescence occurred on cooling to 10 °C and two well resolved ^7Li resonances at δ 1.60 and 1.30, in an



Scheme 2 Reagents and conditions: (i) LiBu^n , thf, 0 °C, 0.33 equivalent $[\text{LuCl}_3(\text{thf})_2]$, LnCl_3 ($\text{Ln} = \text{Er}, \text{Eu}, \text{Sm}$ or Nd) or $[\text{LaBr}_3(\text{thf})_3]$, followed by crystallisation from hexane at –30 °C; (ii) for $\text{Ln} = \text{Lu}$, crystallisation from the mother-liquor after isolation of $[\text{LuL}^1_3]$; (iii) LiBu^n , thf, 0 °C, 0.50 equivalent ErCl_3 , followed by crystallisation from hexane

approximate 1:2 ratio, were evident at –20 °C, in addition to three much weaker features at δ 2.40, 1.07, 0.35. Further cooling produced little change in the spectrum. Apart from the minor resonances, the variable-temperature spectra of **3** are similar to those observed for $[\{\text{Li}(\mu\text{-NPr}^i_2)(\text{tmen})\}_2\text{Li}(\mu_3\text{-Cl})]$ ^{20a} but, crystalline **3** has three inequivalent lithium sites (*cf.* two sites in a 1:2 ratio in $[\{\text{Li}(\mu\text{-NPr}^i_2)(\text{tmen})\}_2\text{Li}(\mu_3\text{-Cl})]$). The relatively narrow chemical shift range for the ^7Li nucleus may preclude the detection of two distinct resonances for Li(1) and Li(2). Alternatively, equalisation of the two terminal lithium sites on each ladder is plausible through a rapid process of thf dissociation, dimer cleavage by thf co-ordination, and recombination of the monomer ladders. Solution exchange phenomena were detected for $[\{\text{LiN}(\text{SiMe}_3\text{CH}_2\text{CH}_2\text{PPR}^i_2)_2\}_2\text{Li}(\mu_3\text{-Cl})]$ where the data were interpreted in terms of equalisation of the lithium sites through mobility of the neutral donors with retention of the ladder structure.^{21b} In addition, $[\{\text{LiN}(\text{SiMe}_3)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{NHSiMe}_3)_2\}_2\text{Li}(\mu_3\text{-Cl})]$ ^{21b} did not show evidence of dynamic solution behaviour up to 65 °C and indicated retention of the ladder structure observed in the solid state. Thus it is likely that in **3**, to a large extent, the three-rung ladder remains intact in solution, but the weaker lithium resonances may also indicate the existence of further processes involving partial or complete dissociation of the solid-state structure.

Synthesis and characterisation of $[\text{LnL}^1_3]$ ($\text{Ln} = \text{Lu}, \text{Er}, \text{Eu}, \text{Sm}, \text{Nd}$ or La) **4–9** and $[\text{ErL}^1_2\text{Cl}]$ **10**

The homoleptic diorganoamidolanthanoid complexes $[\text{LnL}^1_3]$ ($\text{Ln} = \text{Lu}$ **4**, Er **5**, Eu **6**, Sm **7**, Nd **8** or La **9**) were prepared under mild conditions from 3 equivalents of LiL^1 , generated *in situ* in thf, and suitable lanthanoid trihalides (Scheme 2). The products were highly soluble in aliphatic hydrocarbons and were crystallised with some difficulty from concentrated solutions at –30 °C. In contrast to these homoleptic lanthanoid complexes, bimetallic Ln/Li complexes of the type $[\text{LnL}_4\text{Li}]$, where $\text{L} = \text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2$, are formed under virtually identical conditions.¹¹ Although both compound classes contain LnN_6 co-ordination environments (see below) and bimetallic complexes of $\text{N}(\text{SiMe}_3)\text{CH}_2\text{CH}_2\text{NMe}_2$ are known (see **2**), it would appear likely that the larger SiMe_3 substituent prevents the addition of a further LiL^1 moiety to LnL^1_3 in the present reactions. Yields of $[\text{LnL}^1_3]$ were generally good to excellent (50–80%), being lowest for $\text{Ln} = \text{Lu}$ where the side product, **3**, was isolated in 40% yield from the mother-liquor after isolation of $[\text{LuL}^1_3]$. Since **3** was not detected in any of the syntheses with the larger lanthanoids, it would appear that the smaller size of Lu has significantly influenced the course of the reaction. In addition, the isolation of $[\text{LuL}^1_3]$ rather than a partially substituted derivative, *e.g.* $[\text{LuL}^1_2\text{Cl}]$, suggests that the dissolution of the sparingly soluble LuCl_3 is a rate limiting and subsequent

(amide) angles are larger than the N (amine)–Ln–N (amine) angles, possibly as a result of either greater steric repulsions of the bulky N(SiMe₃) versus NMe₂ and/or the electronic repulsions of the N(SiMe₃) anions. Examples of heteroleptic lanthanoid complexes analogous to **10** include the β-diketiminato derivatives [Nd{N(SiMe₃)C(Ph)CHC(Ph)N(SiMe₃)Cl}]^{10d} and [Ln{N(Prⁱ)C(Me)CHC(Me)N(Prⁱ)Br}] (Ln = Sm or Gd).^{10e} These were found to be monomeric and five-coordinate and hence the structure of **10** may be similar, consistent with the mass spectral data (above).

Experimental

Microanalyses were by Chemical and Microanalytical Services Pty. Ltd., Belmont, Australia, and lanthanoid metal analyses were determined by Na₂H₂edta titration. Diethyl ether, hexane and thf were freshly distilled from sodium–benzophenone prior to use. *N,N*-Dimethylethane-1,2-diamine (Aldrich) and 1,1,1,3,3,3-hexamethyldisilazane (Aldrich) were distilled under argon. *n*-Butyllithium (Aldrich) was a 1.6 M solution in hexanes, used as received. Anhydrous neodymium, samarium, europium and erbium chlorides were from Cerac Incorporated, Milwaukee, WI and were used without further purification. The compound [LaBr₃(thf)₃] was prepared from La metal and CH₂Br₂ in thf,²⁹ and [LuCl₃(thf)₂] from Lu metal and C₂Cl₆ in thf,³⁰ and the stoichiometries were established by lanthanoid analyses. The lanthanoid complexes are highly air- and moisture-sensitive and all preparations and manipulations were conducted under an inert atmosphere (purified N₂ or Ar) involving conventional glove-box and Schlenk techniques. The IR spectra of Nujol mulls between NaCl plates were obtained with a Perkin-Elmer 1600 FTIR spectrometer, NMR spectra on a Bruker 300 MHz spectrometer for samples in deuterated benzene or toluene and referenced to the residual ¹H resonances of the solvent (δ 7.15 and 6.98 respectively) or external 0.1 M LiCl in D₂O for ⁷Li spectra. Mass spectra (EI) were obtained on a VG Trio-1 spectrometer; samples were introduced under argon in a probe designed specifically for air-sensitive materials. For metal-containing ions, data reported correspond to the highest-intensity peak of a cluster with the correct isotope pattern.

Preparations

HL¹. A drop of concentrated H₂SO₄ was added to a mixture of freshly distilled H₂NCH₂CH₂NMe₂ (25 cm³, 0.23 mol) and NH(SiMe₃)₂ (40 cm³, 0.19 mol) under argon. After heating at 150 °C for 36 h the product was distilled under argon from the reaction mixture [fraction b.p. 143–146 °C; lit.,¹³ room temperature (<10⁻² mmHg, *ca.* 1.33 Pa)] as a colourless, moisture-sensitive liquid (yield 48%). IR (liquid film, $\tilde{\nu}/\text{cm}^{-1}$): 3386m, 2951vs, 2896s, 2855s, 2818vs, 2769vs, 1457s, 1400s, 1368m, 1248vs, 1175w, 1155m, 1123vs, 1050s, 1042s, 950s, 861vs, 836vs, 788m, 744m and 680m. ¹H NMR (300 MHz, C₆D₆, 298 K): ¹H, δ 0.09 [9 H, s, SiMe₃], 0.97 (1 H, br s, NH), 2.06 [6 H, s, NMe₂], 2.18 (2 H, t, Me₂NCH₂) and 2.74 [2 H, q, Me₃SiN(H)CH₂].

LiL¹ 1. To a stirred solution of compound HL¹ (0.88 g, 1.0 cm³, 5.5 mmol) in hexane (20 cm³) at 0 °C was slowly added LiBuⁿ (3.75 cm³, 1.6 M, 6.0 mmol), and the mixture was stirred until it had warmed to room temperature (*ca.* 1 h). The solvent volume was then reduced *in vacuo* until a solid began to form. The mixture was heated until dissolution occurred, and allowed to cool slowly overnight whereupon colourless crystals were deposited (yield 88%) (Found: C, 50.3; H, 11.6; N, 16.9. C₇H₁₉LiN₂Si requires C, 50.6; H, 11.5; N, 16.9%). NMR (300 MHz, C₆D₆, 298 K): ¹H, δ 0.30 (9 H, s, SiMe₃), 1.94 (6 H, s, NMe₂), 2.23 (2 H, br, Me₃SiNCH₂) and 3.16 (2 H, br, Me₂NCH₂); ⁷Li (116.64 MHz), δ 1.54.

[LiL¹₂Li(OEt₂)] 2. To a stirred solution of compound HL¹

(0.88 g, 1.0 cm⁻³, 5.5 mmol) in diethyl ether (20 cm⁻³) at 0 °C was slowly added LiBuⁿ (3.75 cm³, 1.6 M, 6.0 mmol), and the solution was stirred until it had warmed to room temperature (*ca.* 1 h). The solvent volume was reduced *in vacuo* and colourless crystals were deposited on standing overnight (yield 90%) (Found: C, 53.9; H, 12.3; N, 14.6. C₁₈H₄₈Li₂N₄OSi₂ requires C, 53.2; H, 11.9; N, 13.8%). NMR (300 MHz, C₆D₆, 298 K): ¹H, δ 0.30 (18 H, s, SiMe₃), 1.09 (6 H, t, OCH₂Me), 1.98 (12 H, s, NMe₂), 2.31 (4 H, br, Me₃SiNCH₂), 3.24 (4 H, br, Me₂NCH₂) and 3.28 (4 H, q, OCH₂CH₃); ⁷Li (116.64 MHz), δ -0.76.

[{LiL¹Li(μ₄-Cl)LiL¹(thf)}₂] 3. From the preparation of [LuL¹₃] (see next preparation) the mother-liquor, after separation from the lutetium complex by canula transfer, deposited further colourless crystals on standing (yield 40%). NMR (300 MHz, C₆D₆, 298 K): ¹H, δ 0.39 (36 H, s, SiMe₃), 1.33 (8 H, m, thf), 2.04 (24 H, s, NMe₂), 2.11 (8 H, t, Me₃SiNCH₂), 3.28 (8 H, q, CH₂NMe₂) and 3.59 (8 H, m, thf); ⁷Li (116.64 MHz, 293 K), δ 1.53 (1.35 shoulder). Variable-temperature spectra (see Results and Discussion) were obtained at 5 or 10 °C intervals from 50 to -65 °C.

[LuL¹₃] 4. To a stirred solution of compound HL¹ (0.88 g, 1.0 cm⁻³, 5.5 mmol) in thf (40 cm⁻³) at 0 °C was slowly added LiBuⁿ (3.75 cm⁻³, 1.6 M, 6.0 mmol), and the resulting solution was warmed to room temperature over *ca.* 1 h. The compound [LuCl₃(thf)₂] (0.78 g, 1.83 mmol) was then added, and the mixture rapidly stirred for 12 h. The solvent was removed *in vacuo*, and hexane added whereupon a white precipitate formed. The suspension was then filtered and the filtrate volume reduced to *ca.* 1 cm³ *in vacuo*. After standing undisturbed at -30 °C overnight, colourless crystals were deposited (yield 50%) (Found: C, 38.7; H, 9.1; N, 12.8. C₂₁H₅₇LuN₆Si₃ requires C, 38.6; H, 8.8; N, 12.9%). Infrared (Nujol, $\tilde{\nu}/\text{cm}^{-1}$): 1239s, 1172w, 1156w, 1087s, 1026m, 956s, 850s, 831s and 723m. Mass spectrum: *m/z* 594 (2, C₁₈H₄₉LuN₅Si₃⁺), 493 (14, LuL¹₂⁺), 73 (18, SiMe₃⁺) and 58 (100%, CH₂NMe₂⁺). The filtrate yielded **4**.

[ErL¹₃] 5. A similar preparation to that for compound **4** gave pink crystals of **5** (yield 76%) (Found: C, 39.0; H, 8.9; N, 12.9. C₂₁H₅₇ErN₆Si₃ requires C, 39.1; H, 8.9; N, 13.0%). Infrared (Nujol, $\tilde{\nu}/\text{cm}^{-1}$): 1355m, 1287w, 1239s, 1171w, 1156w, 1087s, 1026m, 956s, 927s, 849s, 829s, 794m, 763m, 736m and 660m. Mass spectrum: *m/z* 587 (0.5, C₁₈H₄₉ErN₅Si₃⁺), 486 (15, ErL¹₂⁺), 73 (15, SiMe₃⁺) and 58 (100%, CH₂NMe₂⁺).

[EuL¹₃] 6. A similar preparation to that for compound **4** gave deep red crystals of **6** (yield 80%) (Found: C, 39.9; H, 9.4; N, 13.4. C₂₁H₅₇EuN₆Si₃ requires C, 40.0; H, 9.1; N, 13.3%). Infrared (Nujol, $\tilde{\nu}/\text{cm}^{-1}$): 1355m, 1287w, 1240s, 1170w, 1157w, 1087s, 1054w, 1028m, 1013m, 953s, 924s, 847s, 828s, 794m, 763m, 736m, 668w and 659m. Mass spectrum: *m/z* 572 (2, C₁₈H₄₉EuN₅Si₃⁺), 471 (22, EuL¹₂⁺), 312 (60, [EuL¹]⁺), 73 (20, SiMe₃⁺) and 58 (100%, CH₂NMe₂⁺).

[SmL¹₃] 7. A similar preparation to that for compound **4** gave light yellow crystals of **7** (yield 75%) (Found: Sm, 23.2. C₂₁H₅₇N₆Si₃Sm requires Sm, 23.9%). Infrared (Nujol, $\tilde{\nu}/\text{cm}^{-1}$): 1354m, 1286w, 1241s, 1170w, 1157w, 1087s, 1029m, 1014m, 953s, 927m, 847s, 828s, 795s, 736m and 660m. Mass spectrum: *m/z* 571 (0.5, C₁₈H₄₉N₅Si₃Sm⁺), 468 (15, SmL¹₂⁺), 311 (10, [SmL¹]⁺), 73 (12, SiMe₃⁺) and 58 (100%, CH₂NMe₂⁺).

[NdL¹₃] 8. A similar preparation to that for compound **4** gave light pink crystals of **8** (yield 65%) (Found: Nd, 22.6. C₂₁H₅₇N₆NdSi₃ requires Nd, 23.2%). Infrared (Nujol, $\tilde{\nu}/\text{cm}^{-1}$): 1354s, 1285m, 1240vs, 1170m, 1157w, 1087s, 1055w, 1030m, 1013m, 954vs, 925s, 845vs, 828vs, 792s, 762m, 736s, 675m and 660m. Mass spectrum: *m/z* 563 (1, C₁₈H₄₉N₅NdSi₃⁺), 462 (60, NdL¹₂⁺), 73 (20, SiMe₃⁺) and 58 (100%, CH₂NMe₂⁺).

[LaL₃]¹ 9. A similar preparation to that for compound **4** gave colourless crystals of **9** (yield 62%) (Found: La, 22.0. C₂₁H₅₇LaN₆Si₃ requires La, 22.5%). Infrared (Nujol, $\tilde{\nu}/\text{cm}^{-1}$): 1348m, 1259m, 1246s, 1168w, 1103m, 1084m, 1068m, 1020m, 923s, 846vs, 828vs, 736m and 664m. Mass spectrum: m/z 457 (1.0, LaL₂⁺), 73 (12, SiMe₃⁺) and 58 (100%, CH₂NMe₂⁺).

[ErL₂Cl]¹ 10. To a stirred solution of compound HL¹ (0.88 g, 1.0 cm³, 5.5 mmol) in thf (40 cm³) at 0 °C was slowly added LiBuⁿ (3.75 cm³, 1.6 M, 6.0 mmol), and the resulting solution warmed to room temperature over *ca.* 1 h. The compound ErCl₃ (0.75 g, 2.75 mmol) was then added, and the reaction mixture rapidly stirred for 12 h. The solvent was then removed *in vacuo*, and hexane added giving a white precipitate. The pink solution was then filtered and the filtrate volume reduced to *ca.* 1 cm³ under vacuum. Pink crystals deposited on standing overnight (yield 60%) (Found: C, 32.4; H, 7.6; Er, 31.7; N, 10.8. C₁₄H₃₈ClErN₄Si₂ requires C, 32.3; H, 7.4; Er, 32.1; N, 10.8%). Infrared (Nujol, $\tilde{\nu}/\text{cm}^{-1}$): 1348m, 1258s, 1246m, 1170w, 1103m, 1094m, 1075m, 1032m, 1016m, 940m, 916s, 853s, 828s, 782m, 734m, 678w and 660w. Mass spectrum: m/z 521 (5, M⁺), 486 (10, ErL₂⁺), 73 (53, SiMe₃⁺) and 58 (100%, CH₂NMe₂⁺); there was no evidence for the presence of thf.

Crystallography

[LiL₂Li(OEt₂)] 2 and [LiL¹Li(μ₄-Cl)LiL¹(thf)]₂ 3. Representative, colourless prismatic crystals were covered with heavy oil, mounted on a glass fibre and cooled to -60 (**2**) or -100 °C (**3**). All measurements were made on a Siemens/Nicolet R3m/V diffractometer with graphite-monochromated Mo-K α radiation. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 centred reflections in the range 8.00 < 2 θ < 15.00 (**2**) or 9.30 < 2 θ < 21.40° (**3**). A total of *N* independent data were collected using the ω -scan technique to a maximum 2 θ value of 45.0°. The intensities of two (**2**) or three (**3**) representative reflections were measured every 198 (**2**) or 397 (**3**) reflections. A decay correction was applied for **3** only. Azimuthal scans of several reflections for **2** indicated no need for an absorption correction whilst an empirical absorption correction, using the program DIFABS,³¹ was applied to the data for **3** resulting in transmission factors ranging from 0.65 to 1.00. The solubility of the complexes in the mounting oil necessitated immediate cooling and prevented determination of the crystal dimensions. Both data sets were corrected for Lorentz polarisation effects. The structures were solved by direct methods and refined by full-matrix least-squares on $|F|$ using *N*_o reflections with $I > 2\sigma(I)$ for *n*_v variables. For **2** the Si atoms and for **3** all non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at calculated positions but not refined. Conventional *R*, *R'* are quoted on convergence. All calculations were performed using the TEXSAN crystallographic software package.³²

Crystal and refinement data. **2**, C₁₈H₄₈Li₂N₄OSi₂, *M* = 406.66, triclinic, space group *P* $\bar{1}$ (no. 2), *a* = 9.88(1), *b* = 10.21(1), *c* = 15.79(2) Å, α = 76.8(1), β = 78.65(9), γ = 63.28(9)°, *U* = 1377(3) Å³, *D*_c = 0.981 g cm⁻³ (*Z* = 2), *F*(000) = 452, μ_{Mo} = 1.41 cm⁻¹, *N* = 3578 (*R*_{int} = 0.091), *N*_o = 1159, *R* = 0.139, *R'* = 0.067, *n*_v = 144. **3**, C₁₈H₄₆ClLi₃N₄OSi₂, *M* = 447.03, monoclinic, space group *P*2₁/*n* (no. 14), *a* = 10.226(4), *b* = 17.827(7), *c* = 16.267(6) Å, β = 97.92(3)°, *U* = 2937(1) Å³, *D*_c = 1.011 g cm⁻³ (*Z* = 4), *F*(000) = 976, μ_{Mo} = 2.25 cm⁻¹, *N* = 3979 (*R*_{int} = 0.099), *N*_o = 1186, *R* = 0.089, *R'* = 0.056, *n*_v = 262.

[LnL₃]¹ (Ln = Lu **4, Er **5** or Eu **6**).** Unique room-temperature four-circle diffractometer data sets (2 θ - θ scan mode; monochromatic Mo-K α radiation, λ = 0.7107₃ Å; *T* \approx 295 K) were measured yielding *N* independent reflections, *N*_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-

matrix least-squares refinements on $|F|$ after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms, (*x*, *y*, *z*, *U*_{iso})_H being constrained at estimated values. Conventional residuals *R*, *R'* at convergence are quoted, statistical weights being derivative of $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.0004\sigma^4(I_{\text{diff}})$. Neutral atom complex scattering factors were employed, computation using the XTAL 3.4 program system.³³

Crystal and refinement data. C₂₁H₅₇LnN₆Si₃, orthorhombic, putative space group *Pnma* (*D*_{2h}¹⁶, no. 62), *Z* = 4.

Ln = Eu (**6**): *M* = 630.0, *a* = 19.164(7), *b* = 17.042(5), *c* = 10.136(7) Å, *U* = 3310 Å³, *D*_c = 1.26₄ g cm⁻³, *F*(000) = 1320, μ_{Mo} = 20.2 cm⁻¹, specimen 0.55 × 0.35 × 0.55 mm, *A**_{min,max} = 1.80, 2.40, 2 θ _{max} = 50°, *N* = 3011, *N*_o = 1632, *R* = 0.047, *R'* = 0.053, *n*_v = 267.

As with the Ln = Er adduct, the specimen was mounted in a capillary; twinning was widespread and some difficulty experienced in obtaining an untwinned specimen or deconvoluting a single reciprocal lattice component. Solution and refinement of the structures presented further features of considerable awkwardness. As modelled in space group *Pnma*, the large symmetrical pseudo-spherical molecule with its hydrocarbon exterior is disposed with the metal atom lying in a crystallographic mirror plane, so that it is disordered about that plane; attempts at refinement in non-centrosymmetric/lower symmetry space groups were unfruitful. For the present compound more than two octants of data were measured, *R*_{int} for merging of the total of 6922 measured reflections being 0.055. As modelled in the space group *Pnma*, a number of atoms lie in the proximity of the mirror images of others leading to some degree of correlation in the refinement; in consequence C(32) was refined with an isotropic thermal parameter. Atoms Ln, N(12), Si(2) were modelled as lying in the mirror plane, without abnormal refinement behaviour (all structures); the ligand ring configuration is tentatively assigned *lel₂ob* (ring 2 being 'ob').³⁴

Ln = Er (**5**): *M* = 645.3, *a* = 19.08(1), *b* = 16.946(9), *c* = 10.156(4) Å, *U* = 3283 Å³, *D*_c = 1.36₀ g cm⁻³, *F*(000) = 1340, μ_{Mo} = 26.8 cm⁻¹, specimen 0.50 × 0.28 × 0.50 mm, *A**_{min,max} = 2.04, 2.29, 2 θ _{max} = 55°, *N* = 3887, *N*_o = 2383, *R* = 0.058, *R'* = 0.065, *n*_v = 271.

Again, a duplicate data set was measured, *R*_{int} for merging of a total of 7853 measured independent reflections being 0.064. Atom C(313) was refined with an isotropic thermal parameter.

Ln = Lu (**4**): *M* = 653.0, *a* = 18.71(2), *b* = 16.78(1), *c* = 10.155(6) Å, *U* = 3188 Å³, *D*_c = 1.36₀ g cm⁻³, *F*(000) = 1352, μ_{Mo} = 32.3 cm⁻¹, specimen (est.) 0.22 × 0.26 × 0.26 mm, *A**_{min,max} = 1.40, 1.66, 2 θ _{max} = 45°, *N* = 2135, *N*_o = 1032, *R* = 0.056, *R'* = 0.054, *n*_v = 138.

In a fruitless attempt to improve the resolution and assist refinement of the structure, data measured at -100 °C as for the Li salts were employed; the specimen was oil-mounted, an estimate of its size proving difficult because of its ready solubility in the oil. The rather meagre body of data would support meaningful anisotropic thermal parameter refinement for Lu and Si only.

CCDC reference number 186/919.

See <http://www.rsc.org/suppdata/dt/1998/1381/> for crystallographic files in .cif format.

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