

# Lithium and lanthanoid(III) complexes of the chelating *N,N*-dimethyl-*N'*-trimethylsilylethane-1,2-diaminate(1<sup>-</sup>) ligand

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Deprotonation of *N,N*-dimethyl-*N'*-trimethylsilylethane-1,2-diamine (HL<sup>1</sup>) with LiBu<sup>n</sup> in hexane yielded solvent-free LiL<sup>1</sup>, whilst in diethyl ether the dinuclear complex [LiL<sup>1</sup><sub>2</sub>Li(OEt<sub>2</sub>)] 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 [{LiL<sup>1</sup>LiClLiL<sup>1</sup>(thf)}<sub>2</sub>] (thf = tetrahydrofuran) was formed as a side product of a reaction of [LiL<sup>1</sup>(thf)<sub>n</sub>] with [LuCl<sub>3</sub>(thf)<sub>2</sub>] in thf. In the solid state the structure shows a LiCl bonded between LiL<sup>1</sup> and LiL<sup>1</sup>(thf) units generating a 'three-rung ladder', which is further connected, by Li–Cl bonds, to a second LiL<sup>1</sup>LiClLiL<sup>1</sup>(thf) moiety. The dimer has two rare Li<sub>4</sub>Cl units. Three equivalents of [LiL<sup>1</sup>(thf)<sub>n</sub>], prepared *in situ* in thf, reacted with [LuCl<sub>3</sub>(thf)<sub>2</sub>], anhydrous LnCl<sub>3</sub> (Ln = Er, Eu, Sm or Nd) or [LaBr<sub>3</sub>(thf)<sub>3</sub>] to form the hexane-soluble [LnL<sup>1</sup>]<sub>3</sub>. Monomeric six-co-ordinate, distorted-octahedral complexes with three chelating L<sup>1</sup> ligands in a *fac* orientation were found for Ln = Lu, Er or Eu by single-crystal X-ray studies. Reaction of 2 equivalents of LiL<sup>1</sup> with ErCl<sub>3</sub> in thf generated heteroleptic [ErL<sup>1</sup><sub>2</sub>Cl].

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 chemistry<sup>1</sup> and as strong bases in organic syntheses.<sup>2</sup> Numerous X-ray diffraction studies of lithium amide complexes have revealed a fascinating structural diversity.<sup>3</sup> Early research in diorganoamidolanthanoid compounds was dominated by the bis(trimethylsilyl)amide complexes [Ln{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>], the first examples of three-co-ordination for these large and electro-positive metals,<sup>4</sup> and there have been recent extensions to [Ln{NBu<sup>t</sup>(SiMe<sub>2</sub>H)}<sub>2</sub>]<sub>3</sub> and [Ln{N(SiMe<sub>2</sub>H)}<sub>2</sub>]<sub>3</sub> derivatives.<sup>5</sup> These and related compounds have found applications as synthetic precursors of other lanthanoid complexes<sup>6</sup> or lanthanoid nitrides,<sup>7</sup> and as potential MOCVD sources.<sup>8</sup>

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.<sup>9</sup> Prevalent amongst these new ligands are bidentate nitrogen donor anions such as benzamidates,<sup>10a–c</sup> β-diketiminates,<sup>10d,e</sup> and aminotropimines<sup>10f</sup> [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 NCH<sub>2</sub>CH<sub>2</sub>N 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 [LnL<sub>4</sub>Li] [L = N(Me)CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>] have been obtained upon reactions of lithium *N,N,N'*-trimethylethane-1,2-diaminate(1<sup>-</sup>) with lanthanoid trihalides.<sup>11</sup> Similarly, reactions of LiL with [Y(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl] and [Lu(Bu<sup>t</sup>C<sub>8</sub>H<sub>7</sub>)Cl] generated [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>YL<sub>2</sub>Li] and [(Bu<sup>t</sup>C<sub>8</sub>H<sub>7</sub>)LuL<sub>2</sub>Li].<sup>11</sup> Complex amides with one or two

SiMe<sub>2</sub> functions replacing backbone CH<sub>2</sub> groups are known, *e.g.* [N(SiMe<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>]<sup>-</sup> (giving Group IV complexes)<sup>12a</sup> and [RNSiMe<sub>2</sub>SiMe<sub>2</sub>NR]<sup>2-</sup> (R = Bu<sup>t</sup> or Ph) (giving Group IV<sup>12b</sup> and lanthanoid<sup>12c</sup> complexes). We have now investigated application of the bulky *N,N*-dimethyl-*N'*-trimethylsilylethane-1,2-diaminate ion,<sup>13</sup> 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.

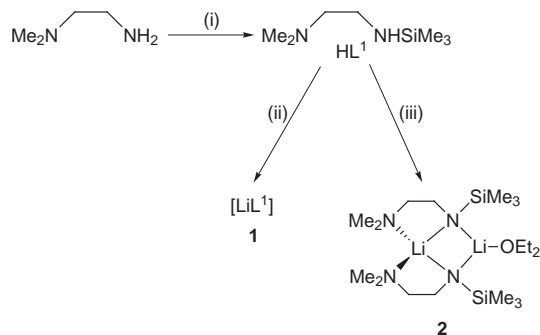
We now report the synthesis of lithium derivatives of HN-(SiMe<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (HL<sup>1</sup>), the crystal structures of [Li<sub>2</sub>L<sup>1</sup><sub>2</sub>(OEt<sub>2</sub>)] and [{LiL<sup>1</sup>LiClLiL<sup>1</sup>(thf)}<sub>2</sub>], the synthesis of [LnL<sup>1</sup>]<sub>3</sub> (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 [ErL<sup>1</sup><sub>2</sub>Cl].

## Results and Discussion

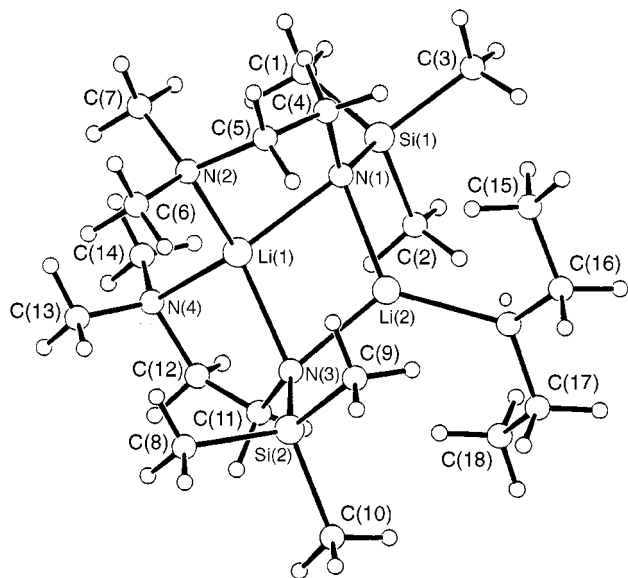
The amine HN(SiMe<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> HL<sup>1</sup> was readily prepared on multigram scale by an acid-catalysed reaction of *N,N*-dimethylethane-1,2-diamine with NH(SiMe<sub>3</sub>)<sub>2</sub> (Scheme 1). This synthesis was based on an analogous reaction of NH(SiMe<sub>3</sub>)<sub>2</sub> with (H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NH<sup>14</sup> and is similar to the method used for the silylation of ethane-1,2-diamine<sup>15</sup> but using H<sub>2</sub>SO<sub>4</sub> rather than SiMe<sub>3</sub>Cl as the catalyst. The above procedure was more convenient than that previously reported, *viz.* lithiation of H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> followed by addition of SiMe<sub>3</sub>Cl.<sup>13</sup> The compound HL<sup>1</sup> was characterised by infrared and <sup>1</sup>H NMR spectroscopy, such data not having been reported with the original preparation.<sup>13</sup>

### Synthesis and characterisation of lithium amides 1–3

Reaction of LiBu<sup>n</sup> with HL<sup>1</sup> in hexane at 0 °C followed by warming to room temperature gave a pale yellow solution, from which colourless crystals of LiL<sup>1</sup> **1** were isolated after evaporation of the solvent. A similar synthesis in diethyl ether yielded



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



**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  $^1\text{H}$  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  $^7\text{Li}$  NMR resonance, at  $\delta$  1.54 (**1**) and  $-0.76$  (**2**), even at low ( $-80\text{ }^\circ\text{C}$ ) 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  $[\text{N}(1)$  and  $\text{N}(3)]$  and  $\text{Et}_2\text{O}$  in a planar array with a geometry (Table 1) similar to one of the lithium centres in  $[\{\text{LiN}(\text{SiMe}_3)_2(\text{OEt}_2)\}_2]$ .<sup>16</sup> 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,  $\text{N}(1)$  and  $\text{N}(3)$ , to

**Table 1** Selected intramolecular distances ( $\text{\AA}$ ) 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)		

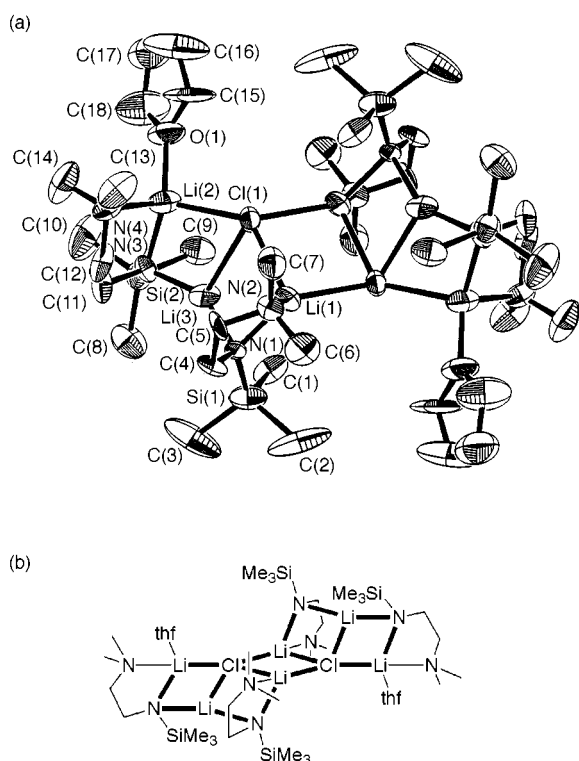
$\text{Li}(2)$ . The  $\text{Li}\text{--N}$  (amide),  $\text{Li}\text{--N}$  (amine) and  $\text{Li}\text{--O}$  distances (Table 1) do not differ significantly from those in related complexes<sup>1,16–19</sup> within the limits of their standard deviations. With observation of two different lithium centres in crystalline **2**, the single  $^7\text{Li}$  NMR resonance of the complex in  $\text{CD}_3\text{C}_6\text{D}_5$  at both room temperature and  $-80\text{ }^\circ\text{C}$  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.  $[\{\text{Li}(\mu\text{-qtsa})(\text{OEt}_2)\}_2]$  [ $\text{qtsa} = 8\text{-quinolyl}(\text{trimethylsilyl})\text{amide}$ ]<sup>17</sup> and  $[\{\text{Li}(\mu\text{-dtf})(\text{OEt}_2)\}_2]$  [ $\text{dtf} = N,N'\text{-di-}p\text{-tolylformamidinate}$ ].<sup>18</sup> The  $8\text{-quinolyl}(\text{trimethylsilyl})\text{amide}$  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.  $[\text{Li}\{(\text{RN})_2\text{SR}'\}_2\text{Li}(\text{OEt}_2)]$ ,<sup>19</sup> 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)<sup>19a</sup>]. The  $8\text{-quinolyl}(\text{trimethylsilyl})\text{amide}$  analogue of **1** has also been structurally characterised yielding dimeric  $[\{\text{Li}(\mu\text{-qtsa})\}_2]$ , with three-coordinate  $\text{Li}$ .<sup>17</sup> The structure of **1** is expected to be similar.

The relatively low yield of  $[\text{LuL}^1]_3$  from reaction of  $\text{LiL}^1$  with  $\text{LuCl}_3$  in  $\text{thf}$  (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  $\text{LiL}^1$  and  $\text{LiCl}$ , identified by a single-crystal X-ray diffraction study. There has been recent interest in the structural identification of related  $\text{LiNR}_2/\text{LiX}$  species, in part due to the observed improved reactivity of lithium amide bases in organic synthesis upon addition of a lithium salt.<sup>20</sup> The molecular structure of **3** (Fig. 2) consists of a  $\text{LiCl}$  bonded between  $\text{LiL}^1$  and  $\text{LiL}^1(\text{thf})$  units through  $\text{N}$  (amide) $\text{--Li--N}$  (amide) and  $\text{Li--Cl--Li}$  bridges. The resulting three-rung ladder of  $\text{Li}$ ,  $\text{N}$  and  $\text{Cl}$  atoms is a typical structural motif of  $\text{LiNR}_2/\text{LiX}$  complexes.<sup>20,21</sup> A unique feature of the present structure is the dimerisation of two of these ladders through formation of further  $\text{Li--Cl}$  bonds between one of the terminal  $\text{Li}$  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,<sup>20,21</sup> as is the case for the remaining terminal  $\text{Li}$  in **3**, hence these have a  $\mu_3\text{-Cl}$  rather than the  $\mu_4\text{-Cl}$  of **3**. The  $\text{Li}_4\text{Cl}$  arrangements are uncommon in structures of lithium complexes.<sup>22</sup> A centrosymmetric dimer structure was recently described for  $[\{\{\text{LiTe}(\text{NBu}^t)_2(\text{NHBu}^t)\}_2\text{LiCl}\}_2]$ ,<sup>23</sup> 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  $\text{LiL}^1$  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)

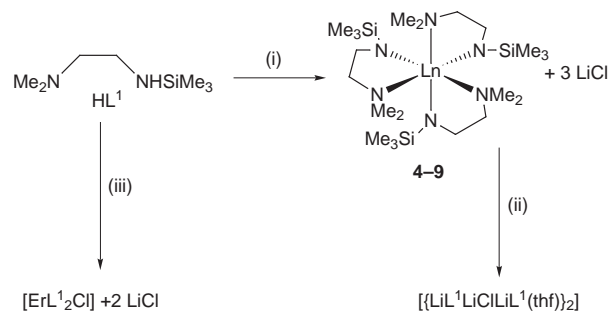
Li(1)–Cl(1)	2.50(3)	Li(2)–N(3)	1.97(3)
Li(1')–Cl(1)	2.40(3)	Li(2)–N(4)	2.08(3)
Li(2)–Cl(1)	2.48(3)	Li(2)–O(1)	1.92(3)
Li(3)–Cl(1)	2.44(2)	Li(3)–N(1)	1.96(3)
Li(1)–N(1)	2.03(3)	Li(3)–N(3)	1.97(3)
Li(1)–N(2)	2.01(3)		
Li(1)–Cl(1)–Li(1')	81.7(9)	N(2)–Li(1)–Cl(1')	117(1)
Li(1)–Cl(1)–Li(2)	130.7(9)	Cl(1)–Li(2)–O(1)	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 **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.<sup>23,24</sup> The three-rung ladder does not possess the pseudo- $C_2$  symmetry about the Li–Cl rung of earlier  $\text{LiNR}_2/\text{LiX}$  complexes<sup>20,21</sup> 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.<sup>21a</sup> 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  $^7\text{Li}$  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  $\delta$  1.49. Decoalescence occurred on cooling to 10 °C and two well resolved  $^7\text{Li}$  resonances at  $\delta$  1.60 and 1.30, in an

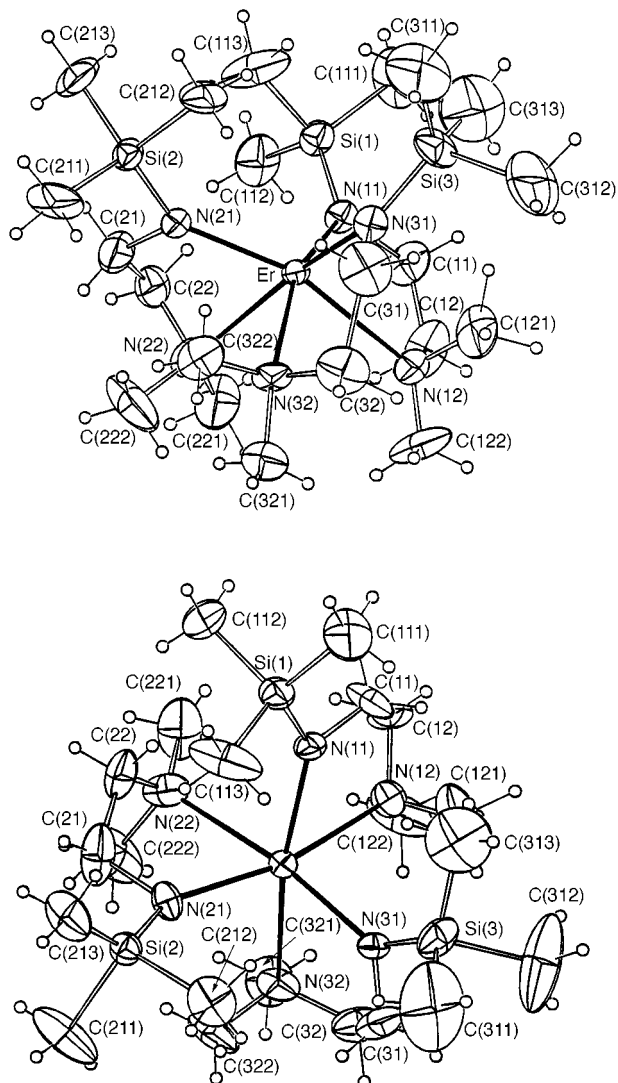


**Scheme 2** Reagents and conditions: (i)  $\text{LiBu}^t$ , thf, 0 °C, 0.33 equivalent  $[\text{LuCl}_3(\text{thf})_2]$ ,  $\text{LnCl}_3$  ( $\text{Ln} = \text{Er}, \text{Eu}, \text{Sm}$  or  $\text{Nd}$ ) or  $[\text{LaBr}_3(\text{thf})_3]$ , followed by crystallisation from hexane at –30 °C; (ii)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

approximate 1:2 ratio, were evident at –20 °C, in addition to three much weaker features at  $\delta$  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  $[\{\text{Li}(\mu\text{-NPr}^i_2)(\text{tmen})\}_2\text{Li}(\mu_3\text{-Cl})]$ <sup>20a</sup> 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  $^7\text{Li}$  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.<sup>21b</sup> In addition,  $[\{\text{LiN}(\text{SiMe}_3)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{NHSiMe}_3)_2\}_2\text{Li}(\mu_3\text{-Cl})]$ <sup>21b</sup> 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 $\text{La}$ ) **4–9** and $[\text{ErL}^1_2\text{Cl}]$ **10**

The homoleptic diorganoamidolanthanoid complexes  $[\text{LnL}^1_3]$  ( $\text{Ln} = \text{Lu}$  **4**,  $\text{Er}$  **5**,  $\text{Eu}$  **6**,  $\text{Sm}$  **7**,  $\text{Nd}$  **8** or  $\text{La}$  **9**) were prepared under mild conditions from 3 equivalents of  $\text{LiL}^1$ , 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.<sup>11</sup> Although both compound classes contain  $\text{LnN}_6$  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  $\text{SiMe}_3$  substituent prevents the addition of a further  $\text{LiL}^1$  moiety to  $\text{LnL}^1_3$  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  $\text{LuCl}_3$  is a rate limiting and subsequent



**Fig. 3** Molecular structure of  $[\text{ErL}_3] \mathbf{5}$ , projected down and normal to the pseudo-3 axis; 20% thermal ellipsoids are shown for the non-hydrogen atoms. Hydrogen atoms have arbitrary radii of 0.1 Å. Compounds **4** and **6** are isostructural

replacement of Cl by  $\text{L}^1$  is rapid. One example of a heteroleptic complex,  $[\text{ErL}_2\text{Cl}] \mathbf{10}$  was obtained by reaction of 2 equivalents of  $\text{LiL}^1$  with  $\text{ErCl}_3$  in thf. This is an important class of compound since it allows further derivatisation through replacement of the chloride and we are currently pursuing additional examples and examining their reactivity.

Analytical data for compounds **4–9** were consistent with their proposed  $[\text{LnL}_3]$  formulation. Their infrared spectra showed peaks attributable to  $\text{L}^1$  and no evidence of co-ordinated  $\text{thf}^{25}$  at  $900\text{--}850\text{ cm}^{-1}$ . The spectra of **4–8** were identical which suggests they are isostructural, as was found at least for **4–6** (see below). Minor differences with the spectrum of the lanthanum derivative **9** may suggest some structural variation in this case. The mass spectra of **4–9** all gave a base peak of  $m/z$  58 derived from fragmentation of  $\text{L}^1$  ( $\text{Me}_2\text{NCH}_2^+$ ), and all gave an ion for  $\text{LnL}_2^+$ . The highest-mass fragment observed for most of the  $[\text{LnL}_3]$  complexes was attributable to loss of  $\text{Me}_2\text{NCH}_2$  from the molecular ion. Characterisation of the heteroleptic complex **10** was supported by the analytical data, the infrared spectrum which showed marked differences to those of  $[\text{LnL}_3]$ , and the mass spectrum which gave a clear monomer molecular ion. Significantly, no higher-mass ions, indicative of a higher-nuclearity species, were observed in the mass spectrum of **10**.

Compounds **4–6** were examined by single-crystal X-ray diffraction and found to be isostructural discrete homoleptic  $[\text{LnL}_3]$  complexes with three bidentate amide ligands surround-

**Table 3** Metal atom environments (distances in Å, angles in °) in  $[\text{LnL}_3] \mathbf{4–6}$

	Eu ( <b>6</b> )	Er ( <b>5</b> )	Lu ( <b>4</b> )
Ln–N(11)	2.22(1)	2.24(1)	2.10(3)
Ln–N(21)	2.28(1)	2.24(1)	2.23(3)
Ln–N(31)	2.32(1)	2.25(1)	2.25(1)
Average	2.29	2.24	2.19
Ln–N(12)	2.78(1)	2.67(1)	2.62(4)
Ln–N(22)	2.73(1)	2.81(2)	2.84(4)
Ln–N(32)	2.92(1)	2.67(2)	2.62(4)
Average	2.81	2.72	2.69
N(11)–Ln–N(21)	108.6(5)	106.8(5)	109(1)
N(21)–Ln–N(31)	107.1(5)	104.8(5)	106(1)
N(31)–Ln–N(11)	106.6(5)	106.2(5)	105(1)
Average	107.4	105.9	107
N(12)–Ln–N(22)	83.5(3)	86.2(5)	91(1)
N(22)–Ln–N(32)	89.3(4)	89.4(4)	92(1)
N(32)–Ln–N(12)	90.1(4)	87.4(5)	85(2)
Average	86	87.7	89
N(11)–Ln–N(12)	72.3(4)	73.9(4)	72(1)
N(21)–Ln–N(22)	74.8(4)	73.5(5)	67(1)
N(31)–Ln–N(32)	77.0(5)	77.7(5)	80(1)
Average	74.7	75.0	73
N(11)–Ln–N(22)	85.4(4)	86.4(5)	85(1)
N(21)–Ln–N(32)	86.3(4)	89.6(5)	91(1)
N(31)–Ln–N(12)	93.1(4)	94.3(4)	94.6(9)
Average	88	90	90
N(11)–Ln–N(32)	162.2(5)	161.1(4)	157(1)
N(21)–Ln–N(12)	158.1(4)	159.5(4)	158(1)
N(31)–Ln–N(22)	166.0(5)	167.0(5)	169(1)
Average	162	163	163
Si(1)–N(11)–Ln	134.9(7)	135.4(8)	134(1)
Si(2)–N(21)–Ln	136.3(7)	143(1)	133(1)
Si(3)–N(31)–Ln	130.9(8)	133.4(8)	131(1)
Average	134	137	133
Si(1)–N(11)–C(11)	106(1)	112(1)	108(3)
Si(2)–N(21)–C(21)	110(1)	103(1)	109(3)
Si(3)–N(31)–C(31)	109(1)	112(1)	111(3)
Average	108	109	109
Ln–N(11)–C(11)	119(1)	113(1)	118(3)
Ln–N(21)–C(21)	114(1)	113(1)	115(3)
Ln–N(31)–C(31)	120(1)	115(1)	118(3)
Average	118	113	117
Ln–N(12)–C(12)	100(1)	109(1)	107(3)
Ln–N(22)–C(22)	91(1)	90(1)	92(3)
Ln–N(32)–C(32)	85(1)	106(1)	105(3)
Average	92	102	102
Torsion angles			
N(11)–C(11)–C(12)–N(12)	–58(3)	–37(3)	–58(5)
N(21)–C(21)–C(22)–N(22)	69(2)	67(2)	75(5)
N(31)–C(31)–C(32)–N(32)	–19(8)	–50(3)	–46(6)
Si(1)–N(11)–C(11)–C(12)	–146(2)	–157(2)	–145(4)
Si(2)–N(21)–C(21)–C(22)	148(2)	151(2)	140(3)
Si(3)–N(31)–C(31)–C(32)	–174(3)	–150(2)	–144(4)

ing the six-co-ordinate distorted-octahedral lanthanoid centre in a *fac* configuration (Fig. 3). Structural characterisation of other  $[\text{LnL}_3]$  species, where L = a bidentate N,N monoanion, have revealed both distorted octahedral (e.g.  $[\text{Ln}(\text{aip})_3]$ , Ln = Sm or Gd; Haip = 2-phenylamino-4-phenyliminopent-2-ene)<sup>26</sup> and trigonal-prismatic (e.g.  $[\text{Gd}\{\text{CH}(\text{C}_5\text{H}_4\text{N}-2)_2\}_3]$ )<sup>27</sup> co-ordination. The considerable difficulties experienced with the current  $[\text{LnL}_3]$  structure solutions (see Experimental section) render their fine detail unreliable, but a number of well defined general trends are apparent. First, there is a lengthening of the  $\langle\text{Ln–N}\rangle$  distances (Table 3) from Lu to Eu, consistent with the increase in the ionic radii of the metals (co-ordination number = 6;  $\text{Lu}^{3+}$ , 0.86;  $\text{Er}^{3+}$ , 0.89;  $\text{Eu}^{3+}$ , 0.95 Å).<sup>28</sup> Secondly, shorter  $\langle\text{Ln–N}(\text{amide})\rangle$  than  $\langle\text{Ln–N}(\text{amine})\rangle$  bond lengths presumably reflect greater Coulombic attraction between the positively charged lanthanoid centre and the negatively charged amide N(SiMe<sub>3</sub>) *versus* the neutral amine NMe<sub>2</sub>. Thirdly, the N (amide)–Ln–N

(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(SiMe<sub>3</sub>) versus NMe<sub>2</sub> and/or the electronic repulsions of the N(SiMe<sub>3</sub>) anions. Examples of heteroleptic lanthanoid complexes analogous to **10** include the β-diketimate derivatives [Nd{N(SiMe<sub>3</sub>)C(Ph)CHC(Ph)N(SiMe<sub>3</sub>)Cl}]<sup>10d</sup> and [Ln{N(Pr<sup>i</sup>)C(Me)CHC(Me)N(Pr<sup>i</sup>)Br}] (Ln = Sm or Gd).<sup>10e</sup> 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 Na<sub>2</sub>H<sub>2</sub>edta 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 [LaBr<sub>3</sub>(thf)<sub>3</sub>] was prepared from La metal and CH<sub>2</sub>Br<sub>2</sub> in thf,<sup>29</sup> and [LuCl<sub>3</sub>(thf)<sub>2</sub>] from Lu metal and C<sub>2</sub>Cl<sub>6</sub> in thf,<sup>30</sup> 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 N<sub>2</sub> 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 <sup>1</sup>H resonances of the solvent (δ 7.15 and 6.98 respectively) or external 0.1 M LiCl in D<sub>2</sub>O for <sup>7</sup>Li 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

**HL<sup>1</sup>**. A drop of concentrated H<sub>2</sub>SO<sub>4</sub> was added to a mixture of freshly distilled H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (25 cm<sup>3</sup>, 0.23 mol) and NH(SiMe<sub>3</sub>)<sub>2</sub> (40 cm<sup>3</sup>, 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.,<sup>13</sup> room temperature (<10<sup>-2</sup> 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. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): <sup>1</sup>H, δ 0.09 [9 H, s, SiMe<sub>3</sub>], 0.97 (1 H, br s, NH), 2.06 [6 H, s, NMe<sub>2</sub>], 2.18 (2 H, t, Me<sub>2</sub>NCH<sub>2</sub>) and 2.74 [2 H, q, Me<sub>3</sub>SiN(H)CH<sub>2</sub>].

**LiL<sup>1</sup> 1**. To a stirred solution of compound HL<sup>1</sup> (0.88 g, 1.0 cm<sup>3</sup>, 5.5 mmol) in hexane (20 cm<sup>3</sup>) at 0 °C was slowly added LiBu<sup>n</sup> (3.75 cm<sup>3</sup>, 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. C<sub>7</sub>H<sub>19</sub>LiN<sub>2</sub>Si requires C, 50.6; H, 11.5; N, 16.9%). NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): <sup>1</sup>H, δ 0.30 (9 H, s, SiMe<sub>3</sub>), 1.94 (6 H, s, NMe<sub>2</sub>), 2.23 (2 H, br, Me<sub>3</sub>SiNCH<sub>2</sub>) and 3.16 (2 H, br, Me<sub>2</sub>NCH<sub>2</sub>); <sup>7</sup>Li (116.64 MHz), δ 1.54.

**[LiL<sup>1</sup><sub>2</sub>Li(OEt<sub>2</sub>)] 2**. To a stirred solution of compound HL<sup>1</sup>

(0.88 g, 1.0 cm<sup>-3</sup>, 5.5 mmol) in diethyl ether (20 cm<sup>-3</sup>) at 0 °C was slowly added LiBu<sup>n</sup> (3.75 cm<sup>3</sup>, 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. C<sub>18</sub>H<sub>48</sub>Li<sub>2</sub>N<sub>4</sub>OSi<sub>2</sub> requires C, 53.2; H, 11.9; N, 13.8%). NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): <sup>1</sup>H, δ 0.30 (18 H, s, SiMe<sub>3</sub>), 1.09 (6 H, t, OCH<sub>2</sub>Me), 1.98 (12 H, s, NMe<sub>2</sub>), 2.31 (4 H, br, Me<sub>3</sub>SiNCH<sub>2</sub>), 3.24 (4 H, br, Me<sub>2</sub>NCH<sub>2</sub>) and 3.28 (4 H, q, OCH<sub>2</sub>CH<sub>3</sub>); <sup>7</sup>Li (116.64 MHz), δ -0.76.

**[{LiL<sup>1</sup>Li(μ<sub>4</sub>-Cl)LiL<sup>1</sup>(thf)}<sub>2</sub>] 3**. From the preparation of [LuL<sup>1</sup><sub>3</sub>] (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, C<sub>6</sub>D<sub>6</sub>, 298 K): <sup>1</sup>H, δ 0.39 (36 H, s, SiMe<sub>3</sub>), 1.33 (8 H, m, thf), 2.04 (24 H, s, NMe<sub>2</sub>), 2.11 (8 H, t, Me<sub>3</sub>SiNCH<sub>2</sub>), 3.28 (8 H, q, CH<sub>2</sub>NMe<sub>2</sub>) and 3.59 (8 H, m, thf); <sup>7</sup>Li (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.

**[LuL<sup>1</sup><sub>3</sub>] 4**. To a stirred solution of compound HL<sup>1</sup> (0.88 g, 1.0 cm<sup>-3</sup>, 5.5 mmol) in thf (40 cm<sup>-3</sup>) at 0 °C was slowly added LiBu<sup>n</sup> (3.75 cm<sup>-3</sup>, 1.6 M, 6.0 mmol), and the resulting solution was warmed to room temperature over *ca.* 1 h. The compound [LuCl<sub>3</sub>(thf)<sub>2</sub>] (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 cm<sup>3</sup> *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. C<sub>21</sub>H<sub>57</sub>LuN<sub>6</sub>Si<sub>3</sub> 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, C<sub>18</sub>H<sub>49</sub>LuN<sub>5</sub>Si<sub>3</sub><sup>+</sup>), 493 (14, LuL<sup>1</sup><sub>2</sub><sup>+</sup>), 73 (18, SiMe<sub>3</sub><sup>+</sup>) and 58 (100%, CH<sub>2</sub>NMe<sub>2</sub><sup>+</sup>). The filtrate yielded **4**.

**[ErL<sup>1</sup><sub>3</sub>] 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. C<sub>21</sub>H<sub>57</sub>ErN<sub>6</sub>Si<sub>3</sub> 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, C<sub>18</sub>H<sub>49</sub>ErN<sub>5</sub>Si<sub>3</sub><sup>+</sup>), 486 (15, ErL<sup>1</sup><sub>2</sub><sup>+</sup>), 73 (15, SiMe<sub>3</sub><sup>+</sup>) and 58 (100%, CH<sub>2</sub>NMe<sub>2</sub><sup>+</sup>).

**[EuL<sup>1</sup><sub>3</sub>] 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. C<sub>21</sub>H<sub>57</sub>EuN<sub>6</sub>Si<sub>3</sub> 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, C<sub>18</sub>H<sub>49</sub>EuN<sub>5</sub>Si<sub>3</sub><sup>+</sup>), 471 (22, EuL<sup>1</sup><sub>2</sub><sup>+</sup>), 312 (60, [EuL<sup>1</sup>]<sup>+</sup>), 73 (20, SiMe<sub>3</sub><sup>+</sup>) and 58 (100%, CH<sub>2</sub>NMe<sub>2</sub><sup>+</sup>).

**[SmL<sup>1</sup><sub>3</sub>] 7**. A similar preparation to that for compound **4** gave light yellow crystals of **7** (yield 75%) (Found: Sm, 23.2. C<sub>21</sub>H<sub>57</sub>N<sub>6</sub>Si<sub>3</sub>Sm 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, C<sub>18</sub>H<sub>49</sub>N<sub>5</sub>Si<sub>3</sub>Sm<sup>+</sup>), 468 (15, SmL<sup>1</sup><sub>2</sub><sup>+</sup>), 311 (10, [SmL<sup>1</sup>]<sup>+</sup>), 73 (12, SiMe<sub>3</sub><sup>+</sup>) and 58 (100%, CH<sub>2</sub>NMe<sub>2</sub><sup>+</sup>).

**[NdL<sup>1</sup><sub>3</sub>] 8**. A similar preparation to that for compound **4** gave light pink crystals of **8** (yield 65%) (Found: Nd, 22.6. C<sub>21</sub>H<sub>57</sub>N<sub>6</sub>NdSi<sub>3</sub> 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, C<sub>18</sub>H<sub>49</sub>N<sub>5</sub>NdSi<sub>3</sub><sup>+</sup>), 462 (60, NdL<sup>1</sup><sub>2</sub><sup>+</sup>), 73 (20, SiMe<sub>3</sub><sup>+</sup>) and 58 (100%, CH<sub>2</sub>NMe<sub>2</sub><sup>+</sup>).

**[LaL<sub>3</sub>]<sup>1</sup> 9.** A similar preparation to that for compound **4** gave colourless crystals of **9** (yield 62%) (Found: La, 22.0. C<sub>21</sub>H<sub>57</sub>LaN<sub>6</sub>Si<sub>3</sub> 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, LaL<sub>2</sub><sup>+</sup>), 73 (12, SiMe<sub>3</sub><sup>+</sup>) and 58 (100%, CH<sub>2</sub>NMe<sub>2</sub><sup>+</sup>).

**[ErL<sub>2</sub>Cl]<sup>1</sup> 10.** To a stirred solution of compound HL<sup>1</sup> (0.88 g, 1.0 cm<sup>3</sup>, 5.5 mmol) in thf (40 cm<sup>3</sup>) at 0 °C was slowly added LiBu<sup>n</sup> (3.75 cm<sup>3</sup>, 1.6 M, 6.0 mmol), and the resulting solution warmed to room temperature over ca. 1 h. The compound ErCl<sub>3</sub> (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 cm<sup>3</sup> under vacuum. Pink crystals deposited on standing overnight (yield 60%) (Found: C, 32.4; H, 7.6; Er, 31.7; N, 10.8. C<sub>14</sub>H<sub>38</sub>ClErN<sub>4</sub>Si<sub>2</sub> 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<sup>+</sup>), 486 (10, ErL<sub>2</sub><sup>+</sup>), 73 (53, SiMe<sub>3</sub><sup>+</sup>) and 58 (100%, CH<sub>2</sub>NMe<sub>2</sub><sup>+</sup>); there was no evidence for the presence of thf.

### Crystallography

**[LiL<sub>2</sub>Li(OEt<sub>2</sub>)<sup>2</sup> 2 and {LiL<sup>1</sup>Li(μ<sub>4</sub>-Cl)LiL<sup>1</sup>(thf)}<sub>2</sub>]<sup>3</sup> 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-Kα 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 < 2θ < 15.00 (**2**) or 9.30 < 2θ < 21.40° (**3**). A total of *N* independent data were collected using the ω-scan technique to a maximum 2θ 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,<sup>31</sup> 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*<sub>o</sub> reflections with *I* > 2σ(*I*) for *n*<sub>v</sub> 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.<sup>32</sup>

*Crystal and refinement data.* **2**, C<sub>18</sub>H<sub>48</sub>Li<sub>2</sub>N<sub>4</sub>OSi<sub>2</sub>, *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) Å<sup>3</sup>, *D*<sub>c</sub> = 0.981 g cm<sup>-3</sup> (*Z* = 2), *F*(000) = 452, μ<sub>Mo</sub> = 1.41 cm<sup>-1</sup>, *N* = 3578 (*R*<sub>int</sub> = 0.091), *N*<sub>o</sub> = 1159, *R* = 0.139, *R'* = 0.067, *n*<sub>v</sub> = 144. **3**, C<sub>18</sub>H<sub>46</sub>ClLi<sub>3</sub>N<sub>4</sub>OSi<sub>2</sub>, *M* = 447.03, monoclinic, space group *P*2<sub>1</sub>/*n* (no. 14), *a* = 10.226(4), *b* = 17.827(7), *c* = 16.267(6) Å, β = 97.92(3)°, *U* = 2937(1) Å<sup>3</sup>, *D*<sub>c</sub> = 1.011 g cm<sup>-3</sup> (*Z* = 4), *F*(000) = 976, μ<sub>Mo</sub> = 2.25 cm<sup>-1</sup>, *N* = 3979 (*R*<sub>int</sub> = 0.099), *N*<sub>o</sub> = 1186, *R* = 0.089, *R'* = 0.056, *n*<sub>v</sub> = 262.

**[LnL<sub>3</sub>]<sup>1</sup> (Ln = Lu **4**, Er **5** or Eu **6**).** Unique room-temperature four-circle diffractometer data sets (2θ-θ scan mode; monochromatic Mo-Kα radiation, λ = 0.71073 Å; *T* ≈ 295 K) were measured yielding *N* independent reflections, *N*<sub>o</sub> with *I* > 3σ(*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*<sub>iso</sub>)<sub>H</sub> being constrained at estimated values. Conventional residuals *R*, *R'* at convergence are quoted, statistical weights being derivative of σ<sup>2</sup>(*I*) = σ<sup>2</sup>(*I*<sub>diff</sub>) + 0.0004σ<sup>4</sup>(*I*<sub>diff</sub>). Neutral atom complex scattering factors were employed, computation using the XTAL 3.4 program system.<sup>33</sup>

*Crystal and refinement data.* C<sub>21</sub>H<sub>57</sub>LnN<sub>6</sub>Si<sub>3</sub>, orthorhombic, putative space group *Pnma* (*D*<sub>2h</sub><sup>16</sup>, 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 Å<sup>3</sup>, *D*<sub>c</sub> = 1.264 g cm<sup>-3</sup>, *F*(000) = 1320, μ<sub>Mo</sub> = 20.2 cm<sup>-1</sup>, specimen 0.55 × 0.35 × 0.55 mm, *A*<sup>\*</sup><sub>min,max</sub> = 1.80, 2.40, 2θ<sub>max</sub> = 50°, *N* = 3011, *N*<sub>o</sub> = 1632, *R* = 0.047, *R'* = 0.053, *n*<sub>v</sub> = 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*<sub>int</sub> 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 *lel<sub>2</sub>ob* (ring 2 being 'ob').<sup>34</sup>

Ln = Er (**5**): *M* = 645.3, *a* = 19.08(1), *b* = 16.946(9), *c* = 10.156(4) Å, *U* = 3283 Å<sup>3</sup>, *D*<sub>c</sub> = 1.36 g cm<sup>-3</sup>, *F*(000) = 1340, μ<sub>Mo</sub> = 26.8 cm<sup>-1</sup>, specimen 0.50 × 0.28 × 0.50 mm, *A*<sup>\*</sup><sub>min,max</sub> = 2.04, 2.29, 2θ<sub>max</sub> = 55°, *N* = 3887, *N*<sub>o</sub> = 2383, *R* = 0.058, *R'* = 0.065, *n*<sub>v</sub> = 271.

Again, a duplicate data set was measured, *R*<sub>int</sub> 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 Å<sup>3</sup>, *D*<sub>c</sub> = 1.36 g cm<sup>-3</sup>, *F*(000) = 1352, μ<sub>Mo</sub> = 32.3 cm<sup>-1</sup>, specimen (est.) 0.22 × 0.26 × 0.26 mm, *A*<sup>\*</sup><sub>min,max</sub> = 1.40, 1.66, 2θ<sub>max</sub> = 45°, *N* = 2135, *N*<sub>o</sub> = 1032, *R* = 0.056, *R'* = 0.054, *n*<sub>v</sub> = 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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