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Synthesis and structures of lithium, aluminium, gallium and lanthanide amidinates containing a γ-pendant amine functionality

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Lithium, aluminium, gallium, lanthanum and cerium complexes of the new amidinato ligand $^{-}N(SiMe_3)C(Ph)N(CH_2)_3NMe_2$ (≡ L^-), having a γ-pendant amine functionality, have been prepared. The dimeric lithium amidinate **1** was obtained in four steps from 1-amino-3-(dimethylamino)propane. Using **1** and MCl_3 in appropriate stoichiometry led to the mononuclear $M(L)Cl_2$ (M = Al **2** or Ga **3**) and the dinuclear $[\{M(L)_2(\mu\text{-}Cl)\}_2]$ (M = La **4** or Ce **5**). Structures of four of these (**1**, **2**, **3** and **5**) have been studied by X-ray crystallography. In crystalline **1** each amidinato ligand L^- is chelating with respect to one of the lithium atoms and bridging by virtue of its pendant γ-tertiary nitrogen atom to the second Li atom. In **2** and **3**, by contrast, L^- behaves as a tripodal chelating ligand, whereas in crystalline **5** the seven-co-ordinate Ce atom is bound by two bidentate benzamidinato fragments and only one of the pendant amines.

Introduction

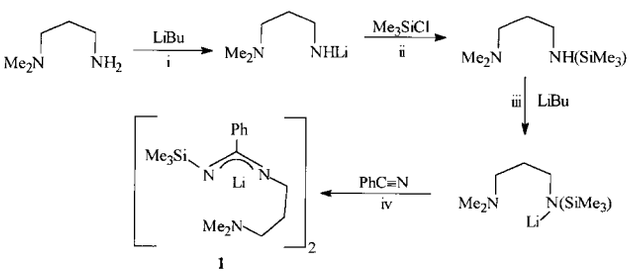
In recent years interest in amidines, especially *N*-silylated benzamidines, has increased significantly. Structures and chemistry of numerous metal benzamidinates have been reviewed.[1,2] Alkali metal salts have been shown to be excellent precursors for other main group element, as well as transition and f-metal, complexes. Cationic aluminium complexes containing amidinato ligands have shown remarkable catalytic activity in the polymerisation of olefins.[3] Group 13 metal amidinates are also promising precursors for MOCVD of III–V nitride semiconductor materials.[4] Additionally, amidinato ligands are of fundamental interest, because their steric and electronic properties can be modified by variation of substituents on either or both N and C atoms.

New types of amidinato ligands with pendant amine ($CH_2CH_2NMe_2$)[5] or pyridine[6] functionality have recently been reported. Several metal complexes of such ligands have been prepared and structurally characterised.[5,6]

We now report on the design of a new potentially tridentate benzamidinato ligand $^{-}N(SiMe_3)C(Ph)N(CH_2)_3NMe_2$ (≡ L^-) having an extended pendant amine function and its role in the synthesis of its lithium (**1**), aluminium (**2**), gallium (**3**), lanthanum (**4**) and cerium (**5**) derivatives, as well as the crystal structures of **1**–**3** and **5**.[14] An objective, not yet realised, was to establish whether the remote amine might serve as a donor to stabilise unusual metal complexes, such as $M(L)_2$ (M = Al, Ga, La or Ce).

Results and discussion

The starting amine $HN(SiMe_3)(CH_2)_2NMe_2$ was prepared in good yield from commercially available 1-amino-3-(dimethylamino)propane by treatment successively with LiBu^n and Me_3SiCl (steps i and ii of Scheme 1). The corresponding lithium salt $LiN(SiMe_3)(CH_2)_3NMe_2$ was prepared (step iii of Scheme 1) by reaction of this amine with LiBu^n. The white, crystalline lithium amidinate $[Li\{N(SiMe_3)C(Ph)N(CH_2)_3NMe_2\}]_2$ [≡ $(LiL)_2$] **1** was obtained (step iv of Scheme 1) from the foregoing lithium amide by treatment with an equivalent portion of benzonitrile.



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Scheme 1 Synthesis of the lithium amidinate $[Li\{N(SiMe_3)C(Ph)N(CH_2)_3NMe_2\}]_2$ [≡ $(LiL)_2$] **1**.

The lithium amidinate **1** was characterised by elemental analysis, IR and ^1H and ^7Li-$\{^1H\}$ NMR spectroscopy and by single crystal X-ray diffraction. The ^1H NMR spectrum in C_6D_6 revealed only a single set of signals assignable to the amidinato ligand L^-. The ^7Li-$\{^1H\}$ NMR spectrum showed a single sharp signal at δ 0.19, whereas its lithium amide precursor had a broad peak at δ 1.97. The IR spectral bands at 1645 and 1577 cm^{-1} were appropriate for an amidinate; the ν(C≡N) region at >2100 cm^{-1} was transparent.

X-Ray quality crystals of $(LiL)_2$ **1** were prepared by recrystallisation from a concentrated hexane solution at −22 °C. The X-ray structure of **1** shows it to be a C_2-symmetric dimer, Fig. 1. Selected bond lengths and angles are presented in Table 1. There is a central puckered N(2)LiN(2′)Li′ ring, with Li–N(2) and Li–N(2′) bond lengths of 2.015(3) and 2.232(3) Å, respectively and the angle subtended at Li [106.1(2)°] wider than that at N, 69.3(2)°. Each lithium atom is chelated with respect to a benzamidinato ligand [*e.g.* Li with respect to N(1)′, C(1)′ and N(2)′] and also another *N*,*N*-centred fragment [*e.g.* Li with respect to N(2) and N(3)]. The Li′–N(1)–C(1)–N(2) ring is puckered, the angles subtended at C(1), N(1), N(2) and Li being 119.0(2), 89.9(2), 79.80(13) and 65.12(11)°, respectively; and the Li′–N(1), N(1)–C(1) and C(1)–N(2) bond lengths being 1.989(3), 1.321(2) and 1.327(2) Å, respectively. The Li–N(3) bond distance is 2.050(3) Å. Thus, each delocalised benzamidinato moiety of the L^- ligand is chelating with respect to one lithium atom and bridging *via* the central nitrogen atom N(2) [or N(2)′] and NMe_2 nitrogen atom N(3) [or N(3)′]. In

Table 1 Selected bond lengths (Å) angles (°) for $(LiL)_2$ **1**

Li–N(1)′	1.989(3)	Li–N(2)	2.015(3)
Li–N(2)′	2.232(3)	Li–N(3)	2.050(3)
Li–C(1)	2.386(3)	Li···Li′	2.420(6)
N(1)–C(1)	1.321(2)	N(2)–C(2)	1.461(2)
N(2)–C(1)	1.327(2)	Si–N(1)	1.698(2)
N(1)′–Li–N(2)	137.6(2)	N(1)′–Li–N(3)	116.3(2)
N(2)–Li′–N(3)	104.7(2)	N(1)′–Li–N(2)′	65.12(11)
N(2)–Li–N(2)′	106.1(2)	N(3)–Li–N(2)′	117.2(2)
N(1)–C(1)–N(2)	119.0(2)		

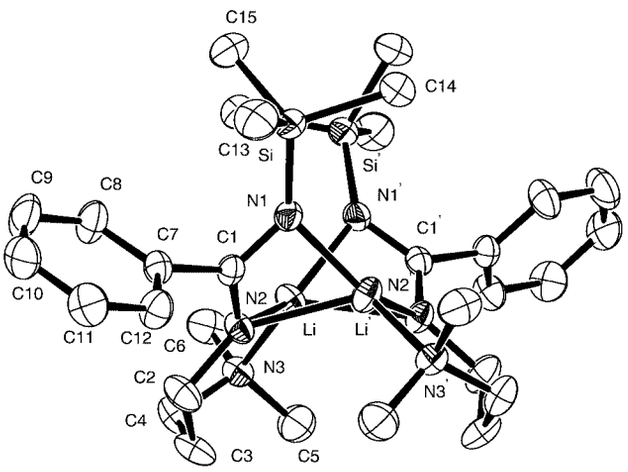
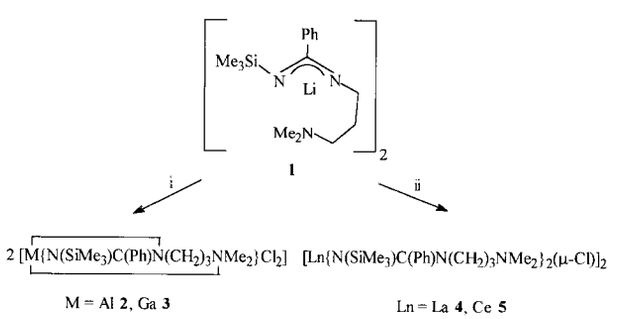


Fig. 1 The molecular structure of $(LiL)_2$ **1**.

general, the Li–N bond lengths [1.989(3), 2.232(3) and 2.015(3) Å] are either similar or slightly shorter than in most other lithium benzamidinates or guanidinates: *e.g.* 1.993(9), 2.387(9) and 2.051(10) Å in $[Li\{(NSiMe_3)_2CC_6H_4Me\text{-}4\}(thf)_2]_2$,[7a] 2.076(6), 2.188(6), 2.162(6), 2.235(6) and 2.139(6) Å in $[Li\{(NPh)_2CPh\}(pmdeta)]_2$,[7b] 1.995(10), 2.080(7), 2.108(10) and 2.260(19) Å in $[Li\{(NSiMe_3)_2CC_6H_4Me\text{-}4\}(NCC_6H_4Me\text{-}4)]_2$,[7c] 2.046(7), 2.054(7) and 2.173(7) Å in $[Li\{(NPh)_2CPh\}(hmpa)]_2$,[7d] 2.034(3), 2.023(4), 2.003(4) in $[Li\{(NPh)_2CPh\}(tmen)]$,[7d] or 1.98(3), 2.03(3) and 2.03(3) Å in $[Li\{(NC_6H_{11}\text{-}c)_2C\text{-}[N(SiMe_3)_2]\}]_2$.[7e]

Reaction of equimolar portions of $(LiL)_2$ **1** and Al_2Cl_6 in diethyl ether (i in Scheme 2) yielded the white crystalline com-



Scheme 2 Preparation of compounds **2**–**5**. *Reagents and conditions*: (i) Al_2Cl_6 for **2** or Ga_2Cl_6 for **3**, *ca.* 20 °C, Et_2O and crystallisation from hexane; (ii) $LaCl_3$ for **4** or $CeCl_3$ for **5**, *ca.* 20 °C, thf and crystallisation from hexane.

plex $Al(L)Cl_2$ **2**. The IR spectrum showed characteristic bands (1658 and 1543 cm^{-1}) of a chelating amidinatometal complex. The ^1H NMR spectrum revealed only one set of signals of the $[L]^-$ ligand.

The crystal structure of complex **2** shows it to be a monomer (Fig. 2), having the central five-co-ordinated Al atom, in a very distorted trigonal bipyramidal arrangement. The N(1) and N(3) atoms are in "axial" [N(1)–Al–N(3) 151.64(7)°] and N(2),

Table 2 Selected bond lengths (Å) angles (°) for $Al(L)Cl_2$ **2** and $Ga(L)Cl_2$ **3**

	M = Al (**2**)	M = Ga (**3**)
M–N(1)	2.0182(16)	2.1130(17)
M–N(2)	1.9053(15)	1.9592(15)
M–N(3)	2.0929(16)	2.1407(18)
M···C(1)	2.3738(17)	2.4486(18)
M–Cl(1)	2.1782(6)	2.2085(5)
M–Cl(2)	2.1610(8)	2.1940(6)
N(1)–C(1)	1.324(2)	1.317(3)
N(2)–C(1)	1.322(2)	1.325(3)
N(2)–C(11)	1.451(2)	1.453(3)
Si–N(1)	1.7396(16)	1.7364(18)
N(2)–M–N(1)	67.53(6)	65.08(6)
N(1)–M–N(3)	151.64(7)	149.47(6)
N(2)–M–N(3)	88.17(7)	88.18(7)
N(1)–M–Cl(2)	103.00(6)	103.58(5)
N(2)–M–Cl(1)	139.95(7)	138.69(6)
N(3)–M–Cl(1)	92.59(5)	93.20(5)
N(2)–M–Cl(2)	108.90(6)	109.78(6)
N(3)–M–Cl(2)	98.48(5)	99.07(5)
N(1)–M–Cl(1)	96.92(5)	97.58(5)
Cl(2)–M–Cl(1)	110.56(3)	110.73(2)
N(2)–C(1)–N(1)	111.20(15)	112.27(16)

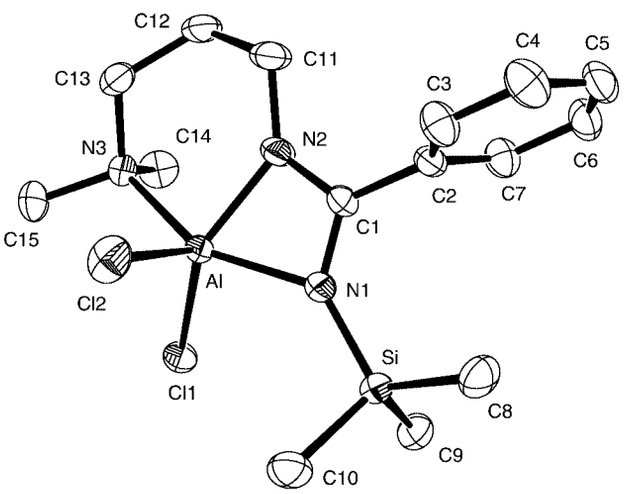


Fig. 2 The molecular structure of $Al(L)Cl_2$ **2**.

Cl(1) and Cl(2) in "equatorial" [N(1)–Al–Cl(1) 96.92(5); N(1)–Al–Cl(2) 103.00(6)°] positions. Selected bond lengths and angles are listed in Table 2. The N(2)–Al–N(1) bite angle of 67.53(6)° is narrower than that reported for aluminium amidinates with a pendant pyridine moiety [72.3°],[6] but quite close to those reported for various other aluminium bis(amidinate)s [67.18 to 70.0(4)°].[8] The Al–N(1)–C(1)–N(2) ring is planar, the angles subtended at C(1), N(1) and N(2) being 111.20(15), 87.96(11) and 92.93(11)°, respectively; the N(1) [or N(2)]–C(1) bonds lengths are equal, 1.322(2) Å, and similar to those in **1**. The Al–N [2.018(2), 1.905(2), and 2.093(2) Å] bond lengths are unexceptional.[8] The two Al–Cl bond distances are almost equal and slightly longer than those reported for other benzamidinatoaluminium dichlorides, but very close to those for bis(amidinato)aluminium chlorides.[8a]

The gallium amidinate $Ga(L)Cl_2$ **3** was prepared (step i in Scheme 2) analogously to the aluminium complex **2**, from Ga_2Cl_6 and **1** in diethyl ether. The IR and ^1H NMR spectra were closely similar to those for **2**. The structure of the gallium complex **3** shows it to be isostructural and isomorphous to **2** (Fig. 2). Selected bond lengths and angles for **3** are presented in Table 2. The N(2)–Ga–N(1) bite angle of 65.08(6)° is quite acute and narrower than that in either the aluminium analogue **2** or other amidinatogallium dichlorides [68.1 and 69.4°].[8b,9]

Table 3 Selected bond lengths (Å) angles (°) for [{Ce(L)$_2$(μ-Cl)}] **5**

Ce–N(1)	2.492(4)	Ce–N(2)	2.438(4)
Ce–N(3)	2.761(4)	Ce–N(4)	2.503(4)
Ce–N(5)	2.496(4)	Ce–Cl	2.866(2)
Ce–Cl′	2.884(2)	Ce···Ce′	4.540
N(1)–C(1)	1.332(6)	N(2)–C(1)	1.314(7)
N(4)–C(16)	1.344(6)	N(2)–C(1)	1.314(6)
Cl–Ce–Cl′	75.71(4)	Ce–Cl–Ce′	104.29(4)
N(2)–Ce–N(1)	54.2(1)	N(2)–Ce–N(5)	92.9(2)
N(1)–Ce–N(5)	79.6(1)	N(2)–Ce–N(4)	141.0(2)
N(1)–Ce–N(4)	125.5(1)	N(5)–Ce– N(4)	54.0(1)
N(2)–Ce–N(3)	73.2(1)	N(1)–Ce–N(3)	123.8(1)
N(5)–Ce–N(3)	85.1(1)	N(4)–Ce–N(3)	82.9(1)
N(2)–Ce–Cl	128.9(1)	N(1)–Ce–Cl	88.6(1)
N(5)–Ce–Cl	115.7(1)	N(4)–Ce–Cl	87.7(1)
N(3)–Ce–Cl	145.2(1)	N(2)–Ce–Cl′	88.1(1)
N(1)–Ce–Cl′	113.9(1)	N(5)–Ce–Cl′	163.4(1)
N(4)–Ce–Cl′	117.6(1)	N(3)–Ce–Cl′	79.3(1)

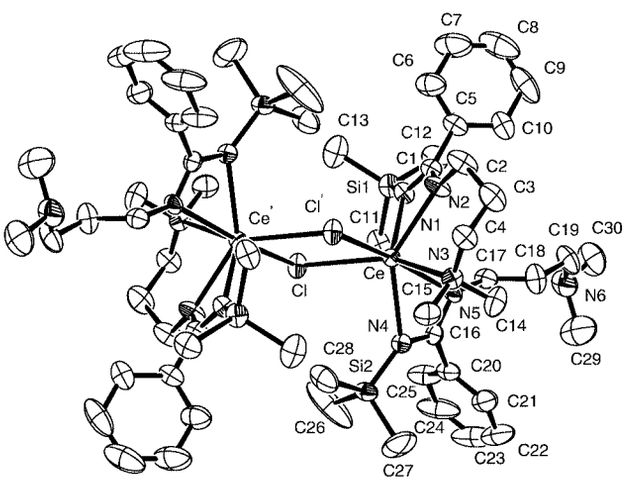


Fig. 3 The molecular structure of [{Ce(L)$_2$(μ-Cl)}$_2$] **5**.

The Ga–N, Ga–C and Ga–Cl distances in **3** are slightly longer [0.030–0.095 Å] than those in the isoleptic aluminium complex **2**, due to the larger ionic radius of Ga.

Reaction of $LaCl_3$ with complex **1** in THF, followed by extraction of the products with hexane, gave the colourless compound [{La(L)$_2$(μ-Cl)}$_2$] **4** (step ii in Scheme 2), which was characterised by satisfactory elemental analysis and IR spectral bands at 1676, 1625, 1604 and 1566 cm^{-1}. The ^{1}H NMR spectrum in C_6D_6 showed two sets of closely similar signals, attributed to two magnetically inequivalent amidinato ligands. This is consistent with the view (see below) that one of the L$^-$ ligands is bidentate and the other tridentate. The cerium(III) f^1 complex [{Ce(L)$_2$(μ-Cl)}$_2$] **5** was prepared analogously. Crystals of **5** (from pentane) showed an identical IR spectrum to those of **4** and analysed satisfactorily. The ^{1}H NMR spectrum in C_6D_6 revealed a number of very broad and paramagnetically shifted signals between δ 11.92 and −4.29. Although the spectrum was quite complicated (integration clearly demonstrated (see Experimental section) the presence of two sets of signals as in the spectrum of **4**) due to inequivalent $(CH_2)_3NMe_2$ groups, consistent with the crystal structure showing that one of the L$^-$ ligands is bidentate and the other tridentate.

From the above data we conclude that the structures of complexes **4** and **5** are very similar. It was considered adequate crystallographically to characterise only one of them and the choice fell on the paramagnetic cerium complex **5**. The structure is illustrated in Fig. 3 and selected bond lengths and angles are shown in Table 3. Complex **5** is dinuclear, having an inversion centre at the midpoint of the planar CeClCe′Cl′ ring, which has endocyclic bond lengths and angles very similar to those in [{Ce(η^5-C$_5$H$_3$Bu$^t_2$-1,3}$_2$(μ-Cl)}$_2$].[10] Each of the cerium atoms is bound in a chelate manner by the amidinato fragments [N(1)C(1)N(2) and N(4)C(16)N(15)] of the two L$^-$ ligands, only one of which is tridentate [having a Ce–N(3) bond]. Both the CeN(1)C(1)N(2) and CeN(4)C(16)N(5) rings are planar, having almost identical endocyclic angles, that at Ce being the narrowest, 54.2(1)°, and that at C(1) or C(16) the widest, 116.9(9)°. Three of the endocyclic Ce–N distances in the two rings are closely similar [2.492(4), 2.496(4), Ce–N(4) 2.503(4) Å] but the Ce–N(2) bond of 2.438(4) Å is much shorter, while the Ce–NMe$_2$ [*i.e.* Ce–N(3)] bond is rather longer, 2.716(4) Å. The seven-co-ordinate Ce atom may be regarded as being at the centre of a distorted N(4)-monocapped octahedron, with N(5) and Cl′ in axial and N(1), N(2), N(3) and Cl in equatorial positions. An example of a bis(amidinato)metal complex having a ligand containing a pendant NMe$_2$ group is known; [Cr{N(C$_6$H$_{11}$-*c*)C(C$_6$H$_4$CH$_2$NMe$_2$-2)NC$_6$H$_{11}$-*c*}$_2$(thf)$_2$], but the NMe$_2$ substituent has no close Cr···N contact.[11] Various lanthanide metal amidinates are known,[2,6,12] but there is only one which is structurally similar, namely [La{N(CH$_2$CH$_2$-C$_5$H$_4$N-2)C(C$_6$H$_4$Me-4)NPh}$_2${N(SiMe$_3$)$_2$}];[6] in the latter the seven-co-ordinate lanthanum atom has La–N bond distances [2.491(4), 2.753(4), 2.609(4), 2.747(4) and 2.453(4) Å] which are close to the Ce–N distances in **5**.

Owing to the presence of a non-co-ordinating $(CH_2)_3$-NMe$_2$ group the complexes **4** and **5** are potential precursors for novel intermolecular aggregates. We plan to treat the compounds with various Lewis acids in order to gain access to heterometallic oligomers or polymers. In summary, the amidinate [N(SiMe$_3$)C(Ph)N(CH$_2$)$_3$NMe$_2$]$^-$ has been shown to be a versatile ligand, which can behave in either a bridging or chelating fashion and function in either a bi-(4-electron) or tri-(6-electron) dentate mode. Depending on the nature of the metal, it can adopt either a facial (**2**, **3**) or a meridional (**5**) geometry. At present, it does not seem that an expansion of the chain length of the pendant amine functionality from β [(CH$_2$)$_2$NMe$_2$)] to γ [(CH$_2$)$_3$NMe$_2$] has a significant effect on the structures of several of their derived metal amidinate complexes. The versatility of such amidinato ligands makes it likely that they will fulfil an increasingly useful role in co-ordination chemistry.

Experimental

General procedures

All manipulations were carried out under vacuum or argon by Schlenk techniques. Solvents were dried and distilled over sodium–potassium alloy under argon prior to use and then condensed into a reaction flask under vacuum shortly before use. 1-Amino-3-(dimethylamino)propane was obtained from Aldrich and distilled over CaH_2 prior to use. Microanalyses were carried out by Medac Ltd (Brunel University). The NMR spectra were recorded using a Bruker DPX 300 (^{1}H, 300.1; ^{7}Li, 116.64 MHz) or Varian 400 (^{1}H, 400 MHz) instrument in benzene-d$_6$ at ambient temperature unless stated otherwise and referenced for ^{1}H internally to residual solvent resonances; the ^{7}Li at 116.64 MHz in C_6D_6 at ambient temperature spectra was referenced externally to ^{7}Li[NO$_3$]. Deuteriated benzene was dried over a potassium metal mirror and distilled prior to use. IR spectra (500–4000 cm^{-1}) were recorded as "Nujol" mulls, using KBr discs and a Perkin-Elmer instrument. Melting points were taken in sealed capillaries under argon and are uncorrected.

Syntheses

HN(SiMe$_3$)(CH$_2$)$_3$NMe$_2$. A solution of LiBu^n in hexane (263 cm^3 of a 1.6 mol dm^{-3} solution, 0.42 mol) was added dropwise to a solution of 1-amino-3-(dimethylamino)propane (43.0 g, 0.42 mol) in diethyl ether (100 cm^3) at 0 °C. The mixture was stirred for *ca.* 12 h, then cooled to −78 °C and

Table 4 Crystal data and structure refinement for complexes **1**–**3** and **5**

	1	**2**	**3**	**5**
Formula	$C_{30}H_{52}Li_2N_6Si_2$	$C_{15}H_{26}AlCl_2N_3Si$	$C_{15}H_{26}GaCl_2N_3Si$	$C_{60}H_{104}Ce_2Cl_2N_{12}Si_4 \cdot 2C_5H_{12}$
M	566.80	374.36	417.10	1601.3
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c* (no. 15)	$P2_1$ (no. 4)	$P2_1$ (no. 4)	$P2_1/c$ (no. 14)
a/Å	17.151(4)	8.8881(3)	8.8921(3)	10.034(4)
b/Å	9.616(7)	11.4278(5)	11.4453(3)	18.888(3)
c/Å	22.314(9)	10.3472(5)	10.4095(3)	22.335(4)
β/°	105.27(4)	109.373(2)	109.221(2)	94.28(2)
U/Å^3, *Z*	3550(3), 4	991.47(7), 2	1000.35(4), 2	4221(2), 2
μ(Mo-Kα)/mm^{-1}	0.13	0.43	1.70	1.23
Reflections collected	3221	8799	8110	6230
Independent reflections (R_{int})	3122 (0.035)	4202 (0.032)	4427 (0.027)	5853 (0.027)
Reflections with [$I > 2\sigma(I)$]	2471	3972	4347	4426
Final *R*1	0.042	0.029	0.023	0.038
*wR*2	0.108	0.075	0.057	0.088

chlorotri(methyl)silane (45.6 g, 0.42 mol) added. It was stirred at ambient temperature for 12 h and filtered. Volatiles were removed from the filtrate *in vacuo*. Distillation of the residue afforded the diamine (45.3 g, 62%), bp 54–56 °C/15 mmHg: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.55 [t, 2 H, $^3J(^1H–^1H) = 6.9$, CH_2NSiMe$_3$], 2.1 [t, 2 H, $^3J(^1H–^1H) = 7.1$, CH_2NMe$_2$], 2.03 (s, 6 H, NMe$_2$), 1.38 [quin, 2 H, $^3J(^1H–^1H) = 7.1$ Hz, CCH$_2$C), 0.58 (br, 1 H, NH) and −0.16 (s, 9 H, SiMe$_3$).

LiN(SiMe$_3$)(CH$_2$)$_3$NMe$_2$. A solution of LiBu^n in hexane (163 cm^3 of a 1.6 mol dm^{-3} solution, 0.26 mol) was added dropwise to the above diamine (45.3 g, 0.26 mol) in diethyl ether (80 cm^3) at −33 °C. The mixture was allowed to warm to ambient temperature and stirred for *ca*. 12 h. The solvent was removed *in vacuo*. The residue was extracted with hexane (60 cm^3). The extract was concentrated to *ca*. 15 cm^3 and cooled at −22 °C, yielding white crystals of the lithium amide (41.6 g, 89%) (Found: C, 54.0; H, 12.02. $C_8H_{21}LiN_2Si$ requires C, 53.3; H, 11.67%); ^{1}H NMR (300 MHz): δ 3.27 [t, 2 H, $^3J(^1H–^1H) = 5.2$, CH_2NSiMe$_3$], 2.18 [t, 2 H, $^3J(^1H–^1H) = 5.2$, CH_2NMe$_2$], 1.92 (s, 6 H, NMe$_2$), 1.47 [quin, 2 H, $^3J(^1H–^1H) = 5.2$ Hz, CCH$_2$C] and 0.21 (s, 9 H, SiMe$_3$). ^{7}Li-{^{1}H} NMR: δ 1.97.

[Li{N(SiMe$_3$)C(Ph)N(CH$_2$)$_3$NMe$_2$}]$_2$ 1. Benzonitrile (3.61 g, 35 mmol) was added slowly (*ca*. 30 min) to a solution of LiN(SiMe$_3$)(CH$_2$)$_3$NMe$_2$ (6.30 g, 35 mmol) in diethyl ether (60 cm^3) at 0 °C. The mixture was stirred for *ca*. 12 h at ambient temperature. The solvent was removed *in vacuo* and the residue extracted with hexane (100 cm^3). The extract was concentrated to *ca*. 20 cm^3 and cooled at −30 °C, yielding white crystals of compound **1** (7.9 g, 80%) (Found: C, 62.8; H, 9.02. $C_{15}H_{26}LiN_3Si$ requires C, 63.5; H, 9.17%), mp *ca*. 150 °C. IR, $\tilde{\nu}_{max}$/cm^{-1}: 1645m, 1599m, 1577m, 1498w, 1403m, 1299m, 1240m, 1170w, 1071w, 1028s, 956w, 919m, 831m, 722m, 700m and 620w. ^{1}H NMR (300 MHz): δ 7.18–7.01 (m, 5 H, Ph), 2.87 [t, 2 H, $^3J(^1H–^1H) = 5.02$, CH_2NCPh], 2.16 (br, 2 H, CH_2NMe$_2$), 1.96 (s, 6 H, NMe$_2$), 1.24 [quin, 2 H, $^3J(^1H–^1H) = 5.02$ Hz, CCH$_2$C] and 0.07 (s, 9 H, SiMe$_3$). ^{7}Li-{^{1}H} NMR: δ 0.19.

[Al{N(SiMe$_3$)C(Ph)N(CH$_2$)$_3$NMe$_2$}Cl$_2$] 2. The lithium amide **1** (0.743 g, 2.6 mmol) was added slowly in portions to a solution of aluminium trichloride (0.35 g, 1.3 mmol) in diethyl ether (60 cm^3) at 0 °C. The mixture was stirred for *ca*. 24 h at ambient temperature. The solvent was removed *in vacuo*. The residue was extracted with hexane (80 cm^3). The extract was concentrated to *ca*. 20 cm^3 and cooled at −22 °C, yielding white crystals of compound **2** (0.83 g, 85%) (Found: C, 47.8; H, 6.72. $C_{15}H_{26}AlCl_2N_3Si$ requires C, 48.1; H, 6.95%), mp *ca*. 110 °C. IR $\tilde{\nu}_{max}$/cm^{-1}: 2240s, 1658s, 1543s, 1239m, 1180w, 1054s, 961s, 837m, 722m and 615w. ^{1}H NMR (400 MHz): δ 7.35–6.91 (m, 5 H, Ph), 2.68 [t, 2 H, $^3J(^1H–^1H) = 6.03$, CH_2NCPh], 2.25 [t, 2 H, $^3J(^1H–^1H) = 5.52$, CH_2NMe$_2$], 2.17 (s, 6 H, NMe$_2$), 0.98 [quin, 2 H, $^3J(^1H–^1H) = 6.03$ Hz, CCH$_2$C] and 0.023 (s, 9 H, SiMe$_3$).

[Ga{N(SiMe$_3$)C(Ph)N(CH$_2$)$_3$NMe$_2$}Cl$_2$] 3. Using the procedure of the preceding experiment, the white, crystalline compound **3** (1.04 g, 78%) (Found: C, 42.9; H, 6.12. $C_{15}H_{26}Cl_2GaN_3Si$ requires C, 43.2; H, 6.23%), mp *ca*. 120 °C, was obtained from **1** (0.90 g, 3.2 mmol) and gallium trichloride (0.56 g, 3.2 mmol). The IR spectrum **3** was identical to that of **2**. ^{1}H NMR (400 MHz): δ 6.99 (m, 5 H, Ph), 2.77 (br, 2 H, CH_2NCPh), 2.18 (br, 2 H, CH_2NMe$_2$), 2.13 (s, 6 H, NMe$_2$), 0.96 (br, 2 H, CCH$_2$C) and 0.21 (s, 9 H, SiMe$_3$).

[{La[N(SiMe$_3$)C(Ph)N(CH$_2$)$_3$NMe$_2$]$_2$(μ-Cl)}$_2$] 4. The lithium amide **1** (1.52 g, 2.68 mol) was added slowly in portions to a suspension of lanthanum(III) chloride (0.33 g, 1.34 mol) in thf (60 cm^3) at 0 °C. The mixture was stirred for 24 h at ambient temperature. The solvent was removed *in vacuo*. The residue was extracted with hexane (*ca*. 80 cm^3). The extract was concentrated to *ca*. 20 cm^3 and cooled at 0 °C, affording white crystals of compound **4** (1.30 g, 67%) (Found: C, 50.9; H, 7.34. $C_{30}H_{52}ClLaN_6Si_2$ requires C, 49.6; H, 7.16%). IR, $\tilde{\nu}_{max}$/cm^{-1}: 1676s, 1625m, 1604m, 1566m, 1376m, 1301m, 1238m, 1154w, 1043m, 967s, 838m, 733m, 682w and 590w. ^{1}H NMR (400 MHz): δ 7.4– 7.03 (m, 10 H, Ph), 3.25 and 3.14 [ts, 4 H + 4 H, $^3J(^1H–^1H)$ 6.48 and 6.99 Hz, CH_2NCPh], 2.40 (s + sh, 4 H + 12 H, CH_2N*Me*$_2$), 2.33 (br m, 4 H, CH_2NMe$_2$), 2.21 (s, 12 H, NMe$_2$), 1.88–1.74 (ms, 8 H, CCH$_2$C), 0.35 and 0.23 (ss, 18 H, SiMe$_3$).

[{Ce[N(SiMe$_3$)C(Ph)N(CH$_2$)$_3$NMe$_2$]$_2$(μ-Cl)}$_2$] 5. From compound **1** (0.64 g, 2.28 mmol) and cerium(III) chloride (0.28 g, 1.14 mmol), using the procedure of the preceding experiment, there were obtained pale yellow crystals (from C_5H_{12} at ambient temperature) of compound **5** (1.12 g, 58%) (Found: C, 50.1; H, 7.21. $C_{30}H_{52}CeClN_6Si_2$ requires C, 49.5; H, 7.15%). ^{1}H NMR (440 MHz): δ 11.92–9.16 (br ms, 20 H, Ph), 3.24 (m, 4 H, CH_2NMe$_2$), 2.11 (br m, 4 H, CH_2NMe$_2$), 1.22 (br, 12 H, NMe$_2$), 1.13 (m, 4 H, CCH$_2$C), 0.88 (s, 12 H, NMe$_2$), 0.35 (br m, 4 H, CCH$_2$C), −2.66 and −2.98 (br ms, 4 H + 4 H, CH_2NCPh), −4.29 (v br, 36 H, SiMe$_3$). The IR spectrum was identical to that of **4**.

X-Ray crystallography

Data sets for complexes **1** and **5** were measured on an Enraf-Nonius CAD4 and for **2** and **3** on Kappa CCD diffractometers at 173(2) K using monochromated Mo-Kα radiation. A crystal of each of the salts **1**, **2, 3** and **5** was coated in oil and cooled. Refinement was based on F^2, with H atoms in riding mode,

using SHELXL-93.[13] Further details on the crystal data are given in Table 4.

CCDC reference number 186/2189.

See http://www.rsc.org/suppdata/dt/b0/b005824f/ for crystallographic files in .cif format.

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14 Note added at proof. Since submission of this manuscript, a paper has appeared describing the preparation and structure of $[YL_2(CH_2Ph)]$, in which one of the chelating L^- ligands is bi- and the other tri-dentate (S. Bambirra, M. J. R. Brandsma, E. A. C. Brussee, A. Meetsma, B. Hessen and J. H. Teuben, *Organometallics*, 2000, **19**, 3197.