Zirconium Complexes incorporating the New Tridentate Diamide Ligand $[(Me_3Si)N\{CH_2CH_2N(SiMe_3)\}_2]^{2-}$ (L); the Crystal Structures of $[Zr(BH_4)_2L]$ and $[ZrCl\{CH(SiMe_3)_2\}L]$ †

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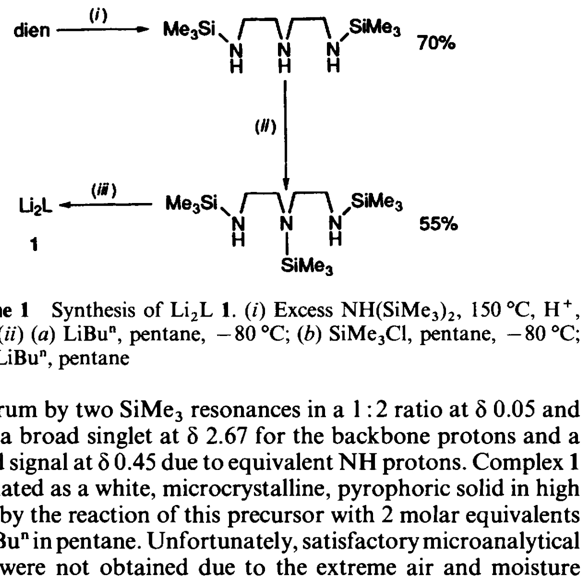
The lithium complex of the sterically demanding, polyfunctional amide ligand $[(Me_3Si)N\{CH_2CH_2N(SiMe_3)\}_2]^{2-}$, Li_2L reacted with $[ZrCl_4(thf)_2]$ (thf = tetrahydrofuran) to form dimeric $[(ZrCl_2L)_2]$ **2**, in which the ligand is facially co-ordinated in a tridentate manner. Treatment of **2** with $LiBH_4$ or $Li[CH(SiMe_3)_2]$ generated $[Zr(H_3BH)L]$ **3** and $[ZrCl\{CH(SiMe_3)_2\}L]$ **4**, respectively. Variable-temperature NMR studies on **4** give evidence for restricted rotation of both the alkyl and amino $SiMe_3$ groups. The crystal structures of **3** and **4** have been determined.

The search for alternatives to cyclopentadienyl-based spectator ligand systems which can facilitate the isolation of novel early transition-metal, lanthanide and actinide complexes has recently focused on multidentate, chelating amides. Such ligands are electronically compatible with highly Lewis-acidic metal centres and can be designed sterically to saturate the co-ordination sphere of the metal.[1] Particularly successful have been the potentially tetrapodal $[(RNCH_2CH_2)_3N]^{3-}$ and tripodal $[(RNCH_2)_3CR']^{3-}$ (R = $SiMe_3$, R' = H or Me) amides which form a variety of complexes across the transition-metal[2] and actinide[3] series. In order to extend the use of tripodal amides to tetravalent transition metal complexes in which two halide groups remain for subsequent manipulations, thus potentially mimicking zirconacene dihalide complexes, one amido function must be substituted for a neutral two-electron donor function, *e.g.* a tertiary amine. Such a compound $[CH(2\text{-}C_5H_4N)\{CH_2N(SiMe_3)\}_2]^{2-}$, incorporating a pyridyl function, has been successfully employed in the synthesis of the titanium complexes $[TiX_2\{CH(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2\}]$ (X = Cl or Br).[4] Herein, we report the synthesis of the bulky, multidentate amine *N,N′,N″*-tris(trimethylsilyl)diethylenetriamine (H_2L) for the preparation of novel amidozirconium complexes.

Results and Discussion

Synthesis of Li_2L **1**.—Although the synthesis of H_2L, *via* a transilylation reaction between diethylenetriamine and $NEt_2(SiMe_3)$, has been reported,[5] it was found that this route repeatedly gave mixtures of products that could not easily be separated. An alternative synthesis was therefore devised as described in Scheme 1.



Scheme 1 Synthesis of Li_2L **1**. (*i*) Excess $NH(SiMe_3)_2$, 150 °C, H^+, 16 h; (*ii*) (*a*) $LiBu^n$, pentane, −80 °C; (*b*) $SiMe_3Cl$, pentane, −80 °C; (*iii*) $2LiBu^n$, pentane

The transilylation reaction between diethylenetriamine and a slight molar excess of $NH(SiMe_3)_2$ in the presence of a catalytic amount of H_2SO_4 resulted in the formation of the bis(trimethylsilylated) product in good yield. The ^1H NMR spectrum is consistent with trimethylsilylation at the primary amine sites, displaying a singlet for the two $SiMe_3$ groups at δ 0.02 and related multiplets at δ 2.80 and 2.55 for the backbone protons. The NH protons are observed as broad signals at δ 1.25 (1 H) and 0.50 (2 H). A low-temperature lithiation/silylation reaction proved an effective route to the triply silylated product, which is characterised in the ^1H NMR spectrum by two $SiMe_3$ resonances in a 1 : 2 ratio at δ 0.05 and 0.04, a broad singlet at δ 2.67 for the backbone protons and a broad signal at δ 0.45 due to equivalent NH protons. Complex **1** is isolated as a white, microcrystalline, pyrophoric solid in high yield by the reaction of this precursor with 2 molar equivalents of $LiBu^n$ in pentane. Unfortunately, satisfactory microanalytical data were not obtained due to the extreme air and moisture sensitivity of this salt. The effect of lithiation is immediately apparent in the ^1H NMR spectrum, in which no resonances due to NH protons are observed. Also, the signals due to the $SiMe_3$ groups have become more distinct, now observed at δ 0.30 (18 H) and 0.03 (9 H), and those due to the backbone protons more complex, showing a broad singlet at δ 3.29 (4 H) and multiplets at δ 2.63 (2 H) and 2.48 (2 H).

Synthesis of $[(ZrCl_2L)_2]$ **2**.—The reaction between complex **1** and $[ZrCl_4(thf)_2]$ in tetrahydrofuran (thf) at −80 °C results in the rapid formation of a pale yellow solution from which, after evaporation, extraction into diethyl ether and sublimation at 120 °C (10^{-6} mbar) yields $[(ZrCl_2L)_2]$ **2** as a white, microcrystalline solid in moderate yield (see Scheme 2).

That complex **2** is dimeric in the solid state was ascertained from the mass spectrum, in which the parent ion at *m*/*z* 959 with an appropriate isotopic pattern was observed. Also, the fragment for $[ZrCl(L)]^+$ at *m*/*z* 478 (90%) is a product of dimer cleavage and the loss of one Cl. The ^1H NMR spectrum suggests that the amide ligand is co-ordinated in a facial manner, with two $SiMe_3$ resonances observed in a 2 : 1 ratio at δ 0.37 and 0.10 respectively. Such a co-ordination mode results in the observed inequivalence of each proton on each ethylene arm of the chelate, with four related multiplets apparent in the ^1H NMR spectrum. This is reinforced by the ^{13}C-$\{^1H\}$ NMR spectrum,

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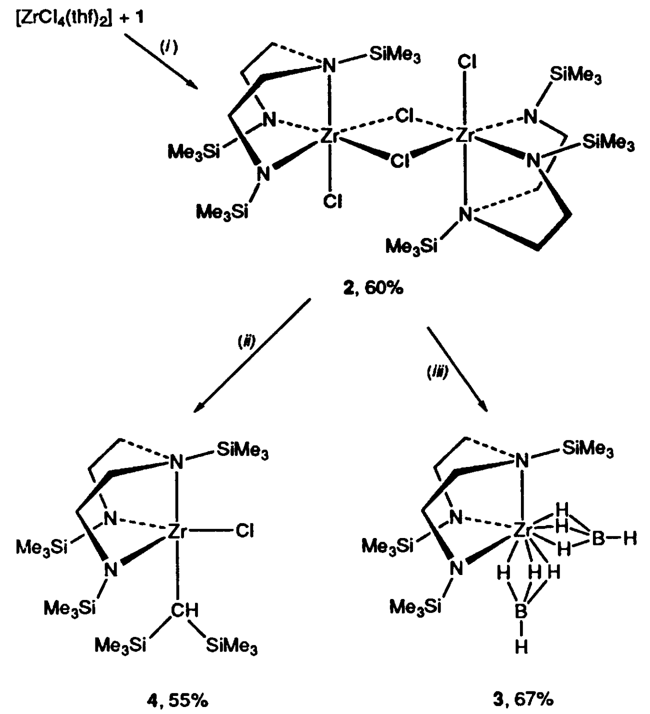
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: bar = 10^5 Pa.



Scheme 2 Synthesis of zirconium complexes incorporating the ligand L. (*i*) thf, −80 °C; (*ii*) excess Li[CH(SiMe$_3$)$_2$], Et$_2$O, 0 °C; (*iii*) 4LiBH$_4$, Et$_2$O, 0 °C

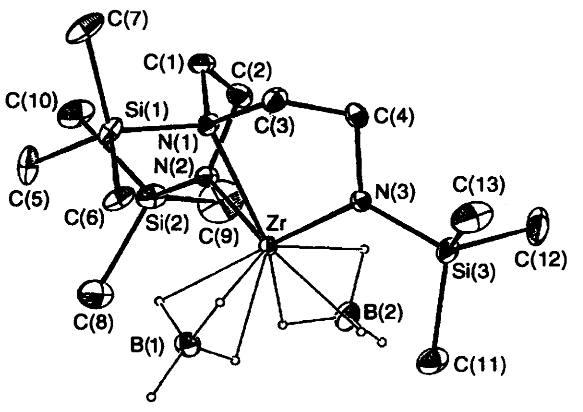


Fig. 1 Crystal structure of [Zr(BH$_4$)$_2$L] **3**, showing the non-H atoms as 20% thermal vibration ellipsoids and the H atoms as arbitrary sized spheres

which displays two resonances in a 2:1 ratio for the amido and amino SiMe$_3$ groups and two for the ethylene backbone carbons. A similar structure was observed in the structurally characterised C_2-symmetric chloro-bridged dimer [{ZrCl(μ-Cl)[η-C$_8$H$_6$(SiMe$_3$)$_2$-1,4]}$_2$] where each cyclooctatetraene ligand can be thought of as occupying a pseudo-octahedral face of the zirconium centre.[6]

Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy showed the presence of a second, uncharacterised product (*ca.* 25%) in which the SiMe$_3$ protons are observed at δ 0.33 and 0.40, again in a 2:1 ratio, but with only two resonances at δ 3.23 (m) and 3.78 (br s) visible for the chelate backbone. Attempts to isolate this complex from the crude reaction mixture by fractional crystallisation were unsuccessful. The presence of only two backbone resonances suggests that co-ordination of the aminodiamide ligand occurs through the amido nitrogens only, with the amino nitrogen pendant, thus rendering the geminal protons equivalent. The mass spectrum of the crude reaction mixture also displayed a new fragment at *m*/*z* 724, consistent with the zirconaspirabicyclic complex [ZrL$_2$]. A similar by-product was isolated from the reaction between the tripod Li$_2$[CH(2-C$_5$H$_4$N){CH$_2$N(SiMe$_3$)}$_2$] and [TiCl$_4$(thf)$_2$], for which NMR studies suggested a structure consistent with pendant pyridyl arms.[4]

Reactions of [(ZrCl$_2$L)$_2$] **2**.—Complex **2** proved to be a versatile reagent for the synthesis of new amidozirconium compounds, *via* halide displacement (see Scheme 2). Thus, the reaction with an excess of LiBH$_4$ in Et$_2$O resulted in the deposition of LiCl and the formation of the mononuclear bis(tetrahydroborate) complex [Zr(BH$_4$)$_2$L] **3** in good yield. X-Ray-quality crystals were isolated from the pentane extract, and the low-temperature crystal structure is shown in Fig. 1. Selected bond lengths and angles are in Table 1 and fractional atomic coordinates in Table 2.

The simplified ligand arrangement around the zirconium(IV) centre, with the BH$_4$ groups occupying one co-ordination site each, is distorted trigonal bipyramidal, with N(2), N(3) and B(1) occupying equatorial sites and N(1) and B(2) in approximate axial positions [N(1)–Zr–B(2) 157.5(2)°]. However, if the tridentate nature of the BH$_4$ ligand is incorporated the Zr becomes nine-co-ordinate and complex **3** can be described as either a monocapped square antiprism or a tricapped trigonal prism. Molecular-modelling experiments suggest that **3** is best viewed as a distorted monocapped square antiprism with N(1), N(2), N(3) and H(23) occupying the basal square face and H(13) capping the square face described by H(11), N(12), H(21) and H(22). The zirconium–amido nitrogen bonds are similar in length to those in the structurally characterised complex [Zr$_2$(μ-Cl)$_2$Cl$_2${N(SiMe$_2$H)$_2$}$_4$],[7] and consistent with strong N(p$_\pi$) to Zr(d$_\pi$) donation in low-co-ordinate Group 4 complexes.[8] The amido nitrogen atoms are observed to have an almost planar geometry. The amino nitrogen has near-tetrahedral geometry and a bond distance of 2.561(4) Å to the Zr. A similar bond length of 2.52(1) Å was observed for the zirconium–diethylamino bond in the complex [{Zr[Mo(CO)$_3$(η-C$_5$H$_5$)]$_2$(NEt$_2$)$_2$(NHEt$_2$)}$_2$],[9] although for [Zr(η^8-C$_8$H$_8$)(η^4-C$_8$H$_8$)(NH$_3$)] a much shorter distance of 2.434(3) Å is observed,[10] presumably due to the relative lack of steric congestion in the latter. The borohydride hydrogens were located from the Fourier-difference map, with the BH$_4$ groups both observed to be co-ordinated in an H$_3$BH fashion which, compared to the denticity observed for the metallocycles [Zr(H$_2$BH$_2$)$_2$(η-C$_5$H$_5$)$_2$][11] and [Zr(H$_3$BH)(H$_2$BH$_2$){C$_8$H$_6$(SiMe$_3$)$_2$-1,4}],[12] is probably the result of the increased Lewis acidity of the metal centre in **3**. The Zr–B distances are consistent with this co-ordination mode,[12,13] although the Zr–B(2) bond at 2.404(7) Å, *trans* to the amino nitrogen N(1), is appreciably longer than Zr–B(1) at 2.370(7) Å, '*trans*' to the amido nitrogens.

This difference in the borohydride groups is also observed in solution studies of complex **3**. In the ^{1}H NMR spectrum the ligand L displays similar resonances to that for **2**, with four multiplets observed for the backbone and 2:1 singlets for the SiMe$_3$ protons, implying facial co-ordination. The borohydride ligands are seen as broad, overlapping 1:1:1:1 quartets, which are reduced to two broad singlets at δ 1.60 and 1.34 in the ^{1}H-{^{11}B} NMR spectrum, thus showing the presence of two distinct borohydride ligands in solution and in the solid state. This is reinforced by the ^{11}B NMR spectrum, which displays two quintets at δ −12.6 and −19.3. The IR spectrum of **3** also shows the presence of two BH$_4$ groups, with strong ν(B–H$_t$) absorptions at 2519 and 2494 cm^{-1} and overlapping ν(B–H$_b$) absorptions between 2240 and 2150 cm^{-1}, consistent with tridentate co-ordination of the BH$_4$ group.[13] Attempts to remove a borohydride ligand from the d^0 metal by the addition of an excess of PMe$_3$, so potentially forming PMe$_3$·BH$_3$ and a zirconium hydride complex,[14] were unsuccessful, with no reaction observed by NMR spectroscopy.

The synthesis of zirconium alkyl complexes from **2** was seen to be dependent on the alkylating agent. Reaction with LiMe or Mg(CH$_2$Ph)Cl yielded mixtures of intractable products.

Table 1 Selected bond distances (Å) and angles (°) for $[Zr(BH_4)_2L]$ **3** and $[ZrCl\{CH(SiMe_3)_2\}L]$ **4**

	3	**4**
Zr–N(1)	2.561(4)	2.770(5)
Zr–N(2)	2.048(4)	2.035(5)
Zr–N(3)	2.060(4)	2.041(5)
Zr–B(2)/C(14)	2.404(7)	2.286(7)
Zr–B(1)/C(1)	2.370(7)	2.390(2)
Zr–H(11)	2.04(7)	
Zr–H(12)	2.10(5)	
Zr–H(13)	2.03(6)	
Zr–H(21)	2.21(4)	
Zr–H(22)	2.20(8)	
Zr–H(23)	2.31(5)	
N(1)–Zr–N(2)	71.9(1)	70.9(2)
N(1)–Zr–N(3)	74.1(2)	71.3(2)
N(2)–Zr–N(3)	123.2(2)	120.2(9)
N(1)–Zr–B(2)/C(14)	157.5(2)	164.7(2)
N(1)–Zr–B(1)/C(1)	95.9(2)	91.5(1)
N(2)–Zr–B(2)/C(14)	95.0(2)	100.4(2)
N(3)–Zr–B(2)/C(14)	99.9(2)	104.6(2)
N(2)–Zr–B(1)/C(1)	115.4(2)	112.8(1)
N(3)–Zr–B(1)/C(1)	112.1(2)	111.9(1)
B(2)/C(14)–Zr–B(1)/C(1)	106.3(2)	103.6(2)

Table 2 Fractional atomic coordinates for $[Zr(BH_4)_2L]$ **3**

Atom	*x*	*y*	*z*
Zr	0.205 30(5)	0.189 68(4)	0.258 69(3)
Si(1)	−0.157 52(15)	0.129 392(13)	0.264 18(8)
Si(2)	0.253 22(18)	0.166 65(13)	0.454 97(9)
Si(3)	0.277 69(16)	0.135 43(13)	0.081 46(8)
N(1)	0.003 7(4)	0.078 2(3)	0.252 4(2)
N(2)	0.203 9(4)	0.129 2(3)	0.363 0(2)
N(3)	0.204 4(4)	0.109 2(3)	0.161 7(2)
C(1)	0.047 6(6)	0.007 9(4)	0.314 7(3)
C(2)	0.189 4(6)	0.026 2(4)	0.034 72(3)
C(3)	−0.000 6(6)	0.029 6(4)	0.177 1(3)
C(4)	0.136 0(6)	0.015 2(4)	0.158 8(3)
C(5)	−0.150 3(6)	0.187 5(6)	0.354 7(3)
C(6)	−0.219 0(6)	0.202 2(5)	0.045(3)
C(7)	−0.271 0(6)	0.017 8(6)	0.264 3(4)
C(8)	0.220 6(8)	0.298 6(5)	0.461 0(4)
C(9)	0.142 8(7)	0.484 7(5)	0.091(5)
C(10)	0.157 3(8)	0.098 6(5)	0.519 8(3)
C(11)	0.302 2(7)	0.267 2(5)	0.069 9(3)
C(12)	0.043 85(6)	0.072 0(6)	0.087 0(4)
C(13)	0.169 0(8)	0.095 2(6)	−0.005 2(4)
B(1)	0.083 1(7)	0.335 0(5)	0.236 7(4)
B(2)	0.434 6(6)	0.235 6(6)	0.280 4(4)
H(11)	0.183(6)	0.334(5)	0.237(3)
H(12)	0.059(5)	0.278(4)	0.199(3)
H(13)	0.086(6)	0.294(4)	0.292(3)
H(14)	0.036(6)	0.411(5)	0.299(3)
H(21)	0.377(4)	0.268(3)	0.319(2)
H(22)	0.388(7)	0.251(6)	0.226(4)
H(23)	0.428(5)	0.153(4)	0.284(3)
H(24)	0.537(5)	0.250(4)	0.294(4)

However, an excess of $Li[CH(SiMe_3)_2]$ in Et_2O resulted in the precipitation of LiCl and the formation of the chloroalkyl complex $[ZrCl\{CH(SiMe_3)_2\}L]$ **4** (see Scheme 2) which was isolated from pentane as colourless prisms suitable for X-ray crystallography. The crystal structure is shown in Fig. 2. Selected bond lengths and angles are in Table 1 and fractional atomic coordinates in Table 3.

A comparison of the bond angles of complexes **3** and **4** (see Table 1) shows that both adopt a similarly distorted trigonal-bipyramidal co-ordination geometry. For **4**, atoms N(2), N(3) and Cl are in the equatorial plane, with N(1) and C(14) in approximate axial sites [N(1)–Zr–C(14) 164.7(2)°]. The amido nitrogen atoms again adopt approximate trigonal geometry and, as with **3**, are at normal bond distances to the Lewis-acidic Zr^{IV}. An approximate tetrahedral arrangement around the amino nitrogen atom is observed, at a distance of 2.770(5) Å from the Zr, which is considerably longer than that observed for **3** and other aminozirconium complexes. It is probable that this

Table 3 Fractional atomic coordinates for $[ZrCl\{CH(SiMe_3)_2\}L]$ **4**

Atom	*x*	*y*	*z*
Zr	0.097 80(3)	0.142 21(4)	0.0
Cl	−0.019 46(10)	0.171 01(15)	0.079 11(10)
Si(1)	0.120 97(13)	0.421 48(17)	0.121 77(14)
Si(2)	0.222 35(13)	0.001 41(19)	0.125 62(13)
Si(3)	0.023 91(15)	0.292 96(19)	−0.150 26(12)
Si(4)	0.144 21(15)	−0.073 59(21)	−0.128 78(13)
Si(5)	−0.020 93(16)	−0.120 10(17)	−0.044 03(15)
N(1)	0.170 0(3)	0.034 17(4)	0.049 7(3)
N(2)	0.202 0(3)	0.104 0(4)	0.058 6(3)
N(3)	0.100 8(3)	0.255 4(4)	−0.086 7(3)
C(1)	0.251 8(4)	0.300 7(6)	0.073 9(5)
C(2)	0.270 7(4)	0.183 9(6)	0.043 0(4)
C(3)	0.173 5(5)	0.407 6(6)	−0.021 8(4)
C(4)	0.174 2(5)	0.332 7(7)	−0.089 2(4)
C(5)	0.017 6(5)	0.467 0(6)	0.091 9(6)
C(6)	0.112 6(6)	0.333 0(8)	0.206 1(5)
C(7)	0.184 4(6)	0.550 9(7)	0.141 8(6)
C(8)	0.290 6(6)	−0.110 0(7)	0.086 4(6)
C(9)	0.276 6(7)	0.063 6(9)	0.208 0(5)
C(10)	0.125 3(7)	−0.060 7(10)	0.158 5(6)
C(11)	−6.070 6(6)	0.213 3(10)	−0.131 0(6)
C(12)	−0.001 6(9)	0.444 8(8)	−0.144 2(7)
C(13)	0.058 0(7)	0.263 9(11)	−0.247 7(5)
C(14)	0.071 8(5)	−0.029 0(6)	−0.055 6(4)
C(15)	0.235 8(5)	0.019 8(8)	−0.135 3(5)
C(16)	0.097 9(9)	−0.076 6(16)	−0.223 2(6)
C(17)	0.185 9(7)	−0.218 4(9)	−0.112 1(9)
C(18)[a]	−0.082 7(9)	−0.100 2(13)	0.045 1(9)
C(19)[a]	−0.020 2(12)	−0.262 9(18)	−0.067 4(11)
C(20)[a]	−0.107 4(14)	−0.707(20)	−0.113 0(14)
C(18A)[b]	−0.057 8(21)	−0.182 0(27)	−0.128 2(20)
C(19A)[b]	−0.106 1(13)	−0.070 8(18)	−0.002 0(19)
C(20A)[b]	0.020 3(15)	−0.256 4(22)	0.015 7(14)

[a] Occupancy 0.6. [b] Occupancy 0.4.

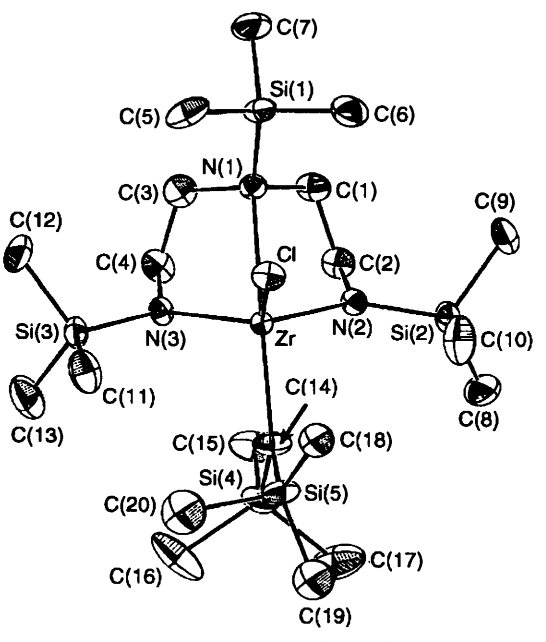


Fig. 2 Crystal structure of $[ZrCl(CH\{SiMe_3\}_2)L]$ **4**, showing the non-H atoms as 20% thermal vibrational ellipsoids

is a reflection of the steric influence of the bulky CH(SiMe$_3$)$_2$ group (see below). The alkyl carbon atom C(14) appears to have a planar arrangement of bonds but the hydrogen atom (which is unambiguously present in the ^{1}H NMR spectrum, see below) could not be located. Although C(14) has a small associated thermal parameter it seems likely that the planarity of this atom derives from disorder in the C(14), Si(4), Si(5) plane. However, on the available evidence it is not possible to discount the presence of an α-agostic interaction between the H atom and the Zr in the solid state so distorting the geometry around the carbon atom, even though no such interaction is observed in solution (see below). The Si(5) trimethylsilyl group is rotationally disordered between two orientations with 0.6:0.4 occupancy. The average Zr–C(14) bond distance of 2.286(7) Å is shorter than that observed in alkyl(cyclopentadienyl)-zirconium complexes, but is consistent with Zr–sp^3 C bond distances seen in low-co-ordinate zirconium(IV) complexes due to the decrease in atomic radius.[8,15]

Studies on complex **4** in solution by NMR spectroscopy indicate the presence of a dynamic process which is consistent with restricted rotation of the alkyl ligand. A similar process was observed for the bis(cyclopentadienyl) analogue, [Zr(η-C$_5$H$_5$)$_2$-Cl{CH(SiMe$_3$)$_2$}].[16] In the ^{1}H NMR spectrum of **4** at 298 K a 2:1 ratio of resonances at δ 0.33 and 0.11 due to the SiMe$_3$ groups of the amide ligand is observed; these overlap a very broad feature due to the SiMe$_3$ protons of the alkyl group which has virtually collapsed into the baseline at this temperature. The backbone protons appear as four, broad resonances of 2 H each, consistent with the ligand L adopting facial co-ordination at the Zr. The α-proton of the alkyl group is visible as a broad singlet at δ 1.17. On cooling the sample to 238 K the rotation of the alkyl group is halted, giving rise to an asymmetric solution structure in which all the SiMe$_3$ groups are different (*i.e.* five singlets of 9 H each); the α-proton is now resolved as a sharp singlet. All the protons of the backbone are inequivalent, giving rise to a series of overlapping multiplets. However, the spectrum at 238 K is not the low-temperature limit, as further cooling to 178 K results in collapse of the amino SiMe$_3$ protons (δ 0.05) into the baseline. Unfortunately, the low-temperature limiting spectrum could not be observed, so it is difficult to assign this fluxionality to a defined process. However, it is apparent from the number of resonances due to the backbone protons that the chelating ligand is still co-ordinated in a facial manner, so excluding the possibility of a mechanism involving dissociation of the amino nitrogen from the Zr. A more plausible explanation of this dynamic process may involve restricted rotation of the amino SiMe$_3$ group around the N(1)–Si(1) bond, caused by a steric interaction between the methyl protons and the chloride ligand as this would have little effect on the observed structure of the rest of the molecule. In the solid-state structure of **4** the methyl groups C(5), C(6) and C(7) are staggered relative to Cl, so minimising any steric interactions between them; this may also explain the unusually long Zr–N(1) bond (see above). The ^{13}C-{^{1}H} NMR spectrum of **4** at 234 K displays five resonances for the SiMe$_3$ carbons, the signal at δ −1.22 assignable to the amino SiMe$_3$ carbons, as on cooling to 188 K it collapses into the baseline. The low-temperature limiting spectrum could not be obtained. The alkyl group carbon is observed as a singlet at δ 56.1 at 234 K, verified by a DEPT (distortionless enhancement by polarisation transfer) experiment. The one-bond J_{CH} coupling constant of 86.6 Hz, measured from the ^{13}C proton-coupled spectrum, is consistent with an alkyl group ligated to a highly electropositive metal,[17] and is not indicative of an α-agostic interaction.

Conclusion

The development of a viable route to the polyfunctional amide ligand Li$_2$[(Me$_3$Si)N{CH$_2$CH$_2$N(SiMe$_3$)}$_2$] has allowed access to a new area of amidozirconium chemistry, which may offer a viable alternative to the well known bis(cyclopentadienyl) system in, for example, functionalised olefin polymerisation. The tridentate chelation mode of the borohydride groups in complex **3** shows that the zirconium(IV) centre is highly Lewis-acidic, but stabilised by the steric requirements of the bulky, chelating amide ligand. The steric influence of this ligand is further demonstrated by **4**, which undergoes dynamic processes involving restricted rotation of both the alkyl ligand and the amino SiMe$_3$ group. Investigations into the synthesis of zirconium complexes, the reactions of **3** and **4**, and the catalytic activity of these systems are currently underway.

Experimental

General Considerations.—All experiments were carried out under pure argon using Schlenk techniques, or in a MBraun glove-box under an atmosphere of dinitrogen (< 5 ppm H$_2$O, < 1 ppm O$_2$). Diethyl ether, tetrahydrofuran and pentane were pre-dried over sodium wire, distilled from sodium–potassium alloy and stored over potassium mirrors. Deuteriated solvents (C$_6$D$_5$CD$_3$ and C$_6$D$_6$) were refluxed over potassium and distilled trap-to-trap prior to use. The compounds 1,1,1,3,3,3-hexamethyldisilazane, diethylenetriamine, 2.5 mol dm^{-3} LiBu^n in hexanes, trimethylsilyl chloride and lithium tetrahydroborate were obtained from Aldrich and used without further purification. The compounds [ZrCl$_4$(thf)$_2$][18] and Li[CH-(SiMe$_3$)$_2$][19] were prepared according to literature methods. The NMR spectra were recorded on Bruker AMX 500, WM 360 and AC 250 instruments and referenced internally to residual solvent resonances, infrared spectra as Nujol mulls on a Perkin-Elmer 1750 interferometer and mass spectra on solid samples using a Kratos MS80RF spectrometer. Elemental analyses were carried out by Medac Ltd., Brunel University and by the Canadian Microanalytical Service Ltd., Canada.

Preparations.—Li$_2$L **1**. (*i*) N,N′-*Bis*(*trimethylsilyl*)*diethylenetriamine*. A mixture of diethylenetriamine (20 g, 0.19 mol), 1,1,1,3,3,3-hexamethyldisilazane (72 cm^3, 0.34 mol) and H$_2$SO$_4$ (0.1 cm^3) was heated at 150 °C for 18 h. The mixture was allowed to cool, the volatiles evaporated *in vacuo* and the residues distilled at 0.5 mbar, yielding 33.1 g, 70% of the amine at 64–70 °C. ^{1}H NMR (CDCl$_3$, 360 MHz), δ 2.80 (m, 4 H, CH$_2$), 2.55 (m, 4 H, CH$_2$), 1.25 (br s, 1 H, NH), 0.50 (br s, 2 H, NH) and 0.02 (s, 18 H, SiMe$_3$).

(*ii*) N,N′,N″-*Tris*(*trimethylsilyl*)*diethylenetriamine*. The addition of a 2.5 mol dm^{-3} solution of LiBu^n (23.4 cm^3, 0.058 mol) in hexanes to a stirred solution of the disubstituted amine (14.49 g, 0.058 mol) in pentane (100 cm^3) at −78 °C caused the formation of a white precipitate which redissolved on warming the vessel to room temperature. The resultant solution was stirred for 0.5 h, cooled to −78 °C and treated with SiMe$_3$Cl (7.4 cm^3, 0.058 mol). The mixture was allowed to warm to ambient temperature and stirred for 18 h, during which LiCl had precipitated. The solids were filtered off through a frit, the filtrate evaporated to dryness *in vacuo* and the pale yellow oil distilled at 0.5 mbar, giving the trisubstituted amine at 73–76 °C, yield 10.1 g, 55%. ^{1}H NMR (CDCl$_3$, 360 MHz), δ 2.67 (br s, 8 H, CH$_2$), 0.45 (br s, 2 H, NH), 0.05 (s, 9 H, SiMe$_3$) and 0.04 (s, 18 H, SiMe$_3$).

(*iii*) Li$_2$[(Me$_3$Si)N{CH$_2$CH$_2$N(SiMe$_3$)}$_2$]. To a solution of the trisubstituted amine (2.41 g, 7.54 mmol) in pentane (30 cm^3) was added, dropwise, 2.5 mol dm^{-3} LiBu^n in hexanes (6.0 cm^3, 15.1 mmol) at −78 °C. The mixture was allowed to warm to ambient temperature and stirred for 1 h. Partial evaporation of the solvents caused complex **1** to precipitate as a white, microcrystalline solid, which was isolated by decanting the liquors and drying *in vacuo*. A second crop of **1** was isolated by cooling the liquors to −50 °C. Total yield 2.2 g, 86% (Found: C, 45.5; H, 10.1; N, 14.6. C$_{13}$H$_{35}$Li$_2$N$_3$Si$_3$ requires C, 47.1; H, 10.6; N, 12.7%). NMR (C$_6$D$_6$): ^{1}H (360 MHz), δ 3.29 (br s, 4 H, CH$_2$), 2.63 (m, 2 H, CH$_2$), 2.48 (m, 2 H, CH$_2$), 0.30 (s, 18 H, SiMe$_3$) and 0.03 (s, 9 H, SiMe$_3$); ^{13}C-{^{1}H} (125 MHz), δ 52.5 (br s, CH_2), 46.5 (s, CH_2), 2.41 (s, $SiMe_3$) and −1.34 (s, $SiMe_3$).

$[(ZrCl_2L)_2]$ **2**. To a solution of $[ZrCl_4(thf)_2]$ (0.58 g, 1.54 mmol) in thf (30 cm^3) at −78 °C was slowly added a solution of complex **1** (0.51 g, 1.5 mmol) in thf (30 cm^3). The resultant pale yellow solution was allowed to warm to room temperature and stirred for 18 h, after which the solvents were evaporated *in vacuo*. The residue was extracted into diethyl ether (20 cm^3), transferred into a sublimer tube, evaporated and sublimed at 120 °C, 10^{-6} mbar, yielding 0.44 g, 60% of complex **2** as white microcrystals (Found: C, 31.3; H, 7.30; N, 8.75. $C_{26}H_{70}Cl_4N_6Si_6Zr_2$ requires C, 32.5; H, 7.35; N, 8.75%). Mass spectrum (electron impact, EI): *m*/*z* 959 (M^+), 478 (90, ZrClL), 407 (75, ZrL) and 73 (100%, $SiMe_3$). NMR (C_6D_6): ^1H (360 MHz), δ 3.52 (ddd, 2 H, J_{HH} 14.2, 10.8 and 3.9), 2.94 (ddd, 2 H, J_{HH} 14.2, 5.0 and 2.5), 2.59 (ddd, 2 H, J_{HH} 12.2, 10.8 and 5.1), 2.10 (tt, 2 H, J_{HH} 12.3, 3.8 and 2.5 Hz), 0.37 (s, 18 H, $2SiMe_3$) and 0.10 (s, 9 H, $SiMe_3$); $^{13}C-\{^1H\}$ (125 MHz), δ 57.8 (s, CH_2), 49.3 (s, CH_2), 0.55 (s, $SiMe_3$) and −1.03 (s, $SiMe_3$).

$[Zr(BH_4)_2L]$ **3**. To a stirred solution of complex **2** (0.374 g, 0.39 mmol) in Et_2O (40 cm^3) at −78 °C was added, dropwise, a solution of $LiBH_4$ (0.05 g, 2.30 mmol) in Et_2O (15 cm^3). On warming to ambient temperature a white precipitate of LiCl formed. After stirring for 2 h the slurry was evaporated to dryness *in vacuo*, extracted into pentane (2 × 30 cm^3) and filtered through Celite. Partial evaporation of the filtrate resulted in the deposition of complex **3** as colourless prisms. Yield 0.23 g, 67% (Found: C, 35.00; H, 9.80; N, 9.20. $C_{13}H_{43}B_2N_3Si_3Zr$ requires C, 35.60; H, 9.90; N, 9.60%). Mass spectrum (EI): *m*/*z* 422 (75, $[M - BH_4]^+$), 407 (30, ZrL) and 73 (100%, $SiMe_3$). NMR ($C_6D_5CD_3$): ^1H (360 MHz), δ 3.30 (br m, 2 H), 3.15 (br m, 2 H), 2.55 (br m, 2 H), 2.20 (br m, 2 H, backbone of L), 2.0–1.0 (two overlapping 1:1:1:1 q, 10 H, BH_4), 0.17 (s, 18 H, $SiMe_3$) and 0.05 (s, 9 H, $SiMe_3$); $^1H-\{^{11}B\}$, δ 1.60 (s, BH_4) and 1.34 (s, BH_4); $^{13}C-\{^1H\}$ (125 MHz), δ 55.9 (s, CH_2), 49.5 (s, backbone CH_2), 1.36 (s, $SiMe_3$) and −1.00 (s, $SiMe_3$); ^{29}Si (99 MHz), δ 25.6 (s, amino $SiMe_3$) and 6.99 (s, amido $SiMe_3$); ^{11}B (80 MHz), δ −12.6 (qnt, J_{BH} 85.7) and −19.3 (qnt, J_{BH} 85.8 Hz). IR (Nujol): ν(B–H_t) 2519s, 2494s; ν(B–H_b) 2236s (sh), 2214s and 2162s cm^{-1}.

$[ZrCl\{CH(SiMe_3)_2\}L]$ **4**. To a stirred mixture of complex **2** (0.16 g, 0.17 mmol) and an excess of $Li[CH(SiMe_3)_2]$ (0.11 g, 0.67 mmol) was added Et_2O (50 cm^3) at −78 °C. The resultant white slurry was allowed to warm to room temperature, during which the solids dissolved and a precipitate of LiCl formed. After being stirred for 4 h, the slurry was evaporated *in vacuo*, extracted into pentane and filtered through Celite. Partial evaporation of the filtrate and slow cooling to −50 °C resulted in the deposition of complex **4** as colourless prisms. Yield 0.11 g, 55% (Found: C, 39.85; H, 9.05; N, 6.90. $C_{20}H_{54}ClN_3Si_5Zr$ requires C, 39.80; H, 9.00; N, 6.95%). Mass spectrum (EI): *m*/*z* 588 (5, $[M - Me]^+$), 442 [100, $M - CH(SiMe_3)_2$], 407 (95, ZrL) and 73 (55, $SiMe_3$). NMR ($C_6D_5CD_3$): ^1H (360 MHz), δ 3.53 (br s, 2 H, CH_2), 3.00 (br d, 2 H, J_{HH} 12.2, CH_2), 2.55 (br t, 2 H, J_{HH} 12.2 Hz, CH_2), 2.03 (br m, 2 H, CH_2), 1.17 (s, 1 H, $C\mathit{H}(SiMe_3)_2$], 0.33 (br s, 36 H, $SiMe_3$) and 0.11 (s, 9 H, $SiMe_3$); (250 MHz, 238 K), δ 3.49 (m, 1 H, CH_2), 3.33 (m, 1 H, CH_2), 2.83 (br m, 2 H, CH_2), 2.28 (br m, 2 H, CH_2), 1.89 (br d, 1 H, J_{HH} 10, CH_2), 1.82 (br d, 1 H, J_{HH} 8 Hz, CH_2), 1.19 [s, 1 H, $C\mathit{H}(SiMe_3)_2$], 0.45 (s, 9 H, $SiMe_3$), 0.30 (s, 9 H, $SiMe_3$), 0.27 (s, 9 H, $SiMe_3$), 0.24 (s, 9 H, $SiMe_3$) and 0.05 (s, 9 H, $SiMe_3$); $^{13}C-\{^1H\}$ (125 MHz, 234 K), δ 56.3 (s, CH_2), 56.1 [s, $\mathit{C}H(SiMe_3)_2$], 55.5 (s, CH_2), 51.0 (s, CH_2), 49.5 (s, CH_2), 5.90 (s, $SiMe_3$), 4.75 (s, $SiMe_3$), 1.28 (s, $SiMe_3$), 0.72 (s, $SiMe_3$) and −1.22 (s, $SiMe_3$).

Crystallography.—Complex **3**. Data were collected on an Enraf-Nonius CAD4 diffractometer using a crystal of dimensions 0.35 × 0.35 × 0.3 mm mounted in mineral oil at 173 K. A total of 4591 unique reflections were measured for $4 < 2\theta < 50°$, 3323 reflections with $|F^2| > 2\sigma(F^2)$ being used in the refinement where $\sigma(F^2) = [\sigma^2(I) + (0.041I)^2]^{\frac{1}{2}}/L_p$. A correction (maximum 1.00, minimum 0.94) was applied for absorption using DIFABS[20] after isotropic refinement. The structure was solved *via* heavy-atom methods using SHELXS 86,[21] with non-H atoms refined anisotropically by full-matrix least squares. The H atoms of BH_4 were refined isotropically whilst other H atoms were held at fixed calculated positions with $U_{iso} = 1.3\ U_{eq}$ for the parent atom. With a weighting scheme $w = \sigma^2(F)$ the final residuals were $R = 0.051$ and $R' = 0.060$, the ratio of observations to variables 14.39:1.00 and $S = 1.5$.

Table 4 Crystal data for the complexes $[Zr(BH_4)_2L]$ **3** and $[ZrCl\{CH(SiMe_3)_2\}L]$ **4***

	3	**4**
Formula	$C_{13}H_{43}B_2N_3Si_3Zr$	$C_{20}H_{54}ClN_3Si_5Zr$
M	438.6	603.8
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$ (non-standard no. 14)	$Pna2_1$ (no. 33)
a/Å	10.200(2)	16.195(9)
b/Å	13.834(7)	11.774(4)
c/Å	17.895(5)	17.835(6)
β/°	97.79(2)	
U/Å³	2502	3401
D/g cm⁻³	1.16	1.18
F(000)	936	1288
μ/cm⁻¹	5.7	5.8
T/K	173	293

* Details in common: $Z = 4$; Mo-Kα radiation (λ = 0.710 69 Å).

Complex **4**. Data were collected on an Enraf-Nonius CAD4 diffractometer using a crystal of dimensions 0.3 × 0.3 × 0.3 mm mounted in a Lindeman capillary under argon. A total of 4582 unique reflections were measured for $4 < 2\theta < 56°$, 2944 reflections with $|F^2| > 2\sigma(F^2)$ being used in the refinement, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{\frac{1}{2}}/L_p$. An absorption correction (maximum 1.00, minimum 0.94) was applied and the structure was solved as for complex **3** except that atoms C(18)/C(18A), C(19)/C(19A) and C(20)/C(20A) were refined isotropically and in 0.6:0.4 occupancy ratio respectively. Hydrogen atoms were held at fixed calculated positions with $U_{iso} = 1.3\ U_{eq}$ for the parent atom; H(14) was omitted. With a weighting scheme of $w = \sigma^2(F)$ the final residuals were $R = 0.045$, $R' = 0.0439$, the ratio of observations to variables 11.03:1.00 and $S = 1.21$.

Other crystallographic parameters are given in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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