The 6-amino-6-methyl-1,4-diazepine group as an ancillary ligand framework for neutral and cationic scandium and yttrium alkyls†

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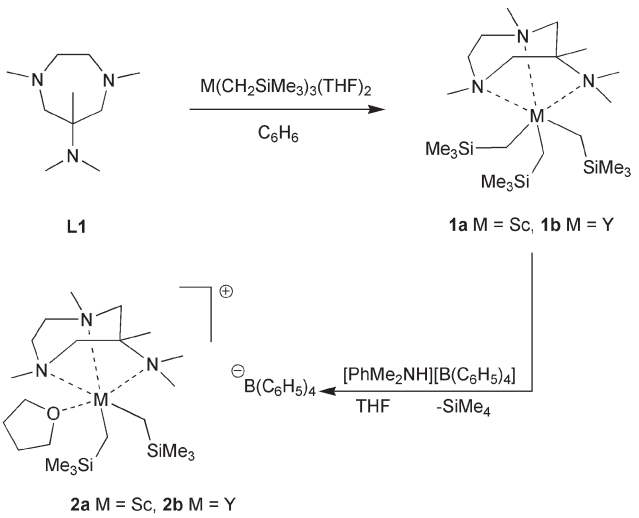
The 6-amino-6-methyl-1,4-diazepine framework is a readily available neutral 6-electron ligand moiety, suitable to support cationic group 3 metal alkyl catalysts; it also provides convenient access to tri- and tetradentate monoanionic ligand derivatives.

In contrast to their transition-metal analogues (which have long been known as active catalysts for olefin polymerisation), the chemistry of cationic rare-earth metal alkyl species has only recently been developed.[1] The use of nitrogen-based facial tridentate ligand moieties (such as 1,4,7-triazacyclononane, tris(pyrazolyl)methane and tris(oxazolinyl)methane) has played an important role in opening up this chemistry.[2] A disadvantage of these ligand systems is that stepwise modification and extension of these moieties is synthetically quite elaborate. Very recently, the use of the 6-amino-6-methyl-1,4-diazepine group as a facially coordinating moiety in biomimetic complexes was described.[3] This framework is readily obtained by reaction of 1,2-diaminoethanes with nitroethane and formaldehyde, followed by reduction of the nitro group. Here we show that this group provides an accessible and versatile basis for neutral and anionic tri- and tetradentate ligands for use in rare-earth metal organometallic chemistry.

To test the suitability of the 6-amino-6-methyl-1,4-diazepine group as an ancillary ligand moiety for rare-earth metal alkyl chemistry, the known permethylated 6-amino-6-methyl-1,4-diazepine (**L1**)[3b] was reacted with the group 3 metal trialkyls $M(CH_2SiMe_3)_3(THF)_2$ (M = Sc, Y). This afforded the complexes (**L1**)$M(CH_2SiMe_3)_3$ (M = Sc **1a** or Y **1b**, Scheme 1) in high isolated yields (**1a**: 94%; **1b**: 95%). Solution NMR spectroscopy of these compounds (C_7D_8) showed that the three alkyl groups on the metal centre are equivalent down to −50 °C. The M–CH_2 resonances (C_6D_6, 20 °C) for **1a** are found at δ −0.14 ppm (^{1}H) and δ 40.0 ppm (^{13}C), for **1b** at δ −0.56 (d, $^1J_{YH}$ = 2.9 Hz) and δ 36.9 ppm (J_{YC} = 35 Hz, $^1J_{CH}$ = 97.9 Hz) respectively.

A crystal structure determination of **1a** was performed, and its molecular structure is shown in Fig. 1.‡ The crystal contains two independent molecules in the asymmetric unit that do not differ significantly; only one is explicitly discussed here. The three nitrogen atoms of **L1** are bound to the scandium centre in a *fac*-arrangement and the geometry at Sc is approximately octahedral. The average Sc–N bond length of 2.497 Å in **1a** is slightly longer



Scheme 1 Synthesis of complexes **1** and **2**.

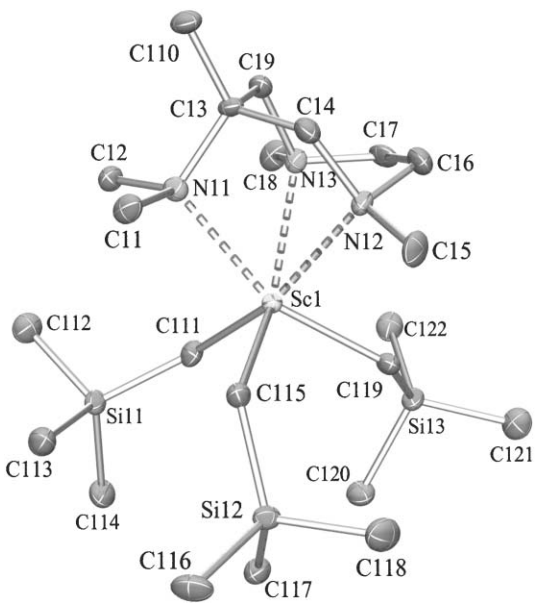


Fig. 1 Molecular structure of one of the independent molecules of **1a** (hydrogen atoms omitted for clarity, thermal ellipsoids drawn at 50% probability level). Selected bond distances (Å) and angles (°): Sc1–N11 2.504(3), Sc1–N12 2.465(3), Sc1–N13 2.521(3), Sc1–C111 2.267(3), Sc1–C115 2.256(4), Sc1–C119 2.309(4); N11–Sc1–N12 73.91(8), N11–Sc1–N13 69.63(8), N12–Sc1–N13 66.45(8), C111–Sc1–C115 100.87(13), C111–Sc1–C119 96.68(13), C115–Sc1–C119 102.31(13), N11–Sc1–C119 159.47(11), N12–Sc1–C111 163.19(11), N13–Sc1–C115 153.24(11).

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than that reported for the triazacyclononane complex $Sc(Me_3[9]aneN_3)(CH_2SiMe_3)_3$[4] (average 2.463 Å), while the average Sc–CH_2 distances are very similar. There is no notable asymmetry in the bonding of the three amine donors in **1a**: the Sc–N distance for the NMe_2-group is intermediate between the other two Sc–N distances in the complex. The smallest N–Sc–N angle involves the amine nitrogens linked by the $(CH_2)_2$-bridge, N(12)–Sc–N(13) of 66.45(8)°.

The neutral trialkyl complexes **1** can be converted in THF solvent to the dialkyl cations $[(\mathbf{L1})M(CH_2SiMe_3)_2(THF)]^+$ (M = Sc, **2a**; Y, **2b**) by reaction with $[PhMe_2NH][BAr_4]$ (Ar = Ph, C_6F_5). This was seen by NMR spectroscopy when performing these reactions in THF-d_8, and the BPh_4-salt of the Sc cation **2a** was isolated in 75% yield from THF–cyclohexane.§ The ^{13}C NMR resonances of the M–CH_2 groups in **2** relative to those in **1** show the typical downfield shift and (for Y) increase in $^1J_{YC}$ associated with conversion to the cationic species (for **2b**: δ 42.3 ppm, J_{YC} = 41 Hz).

Ethene polymerisation experiments with **1a** and **1b** activated by $[PhMe_2NH][B(C_6F_5)_4]$ were performed in toluene, and the results are listed in Table 1. For both metals active polymerisation catalysts are obtained. This shows that the 6-amino-6-methyl-1,4-diazepine group is suitable as an ancillary ligand moiety for cationic rare-earth metal alkyl catalysts. Remarkably, the activity of the Sc system increases substantially when the temperature is increased from 50 °C to 70 °C, but this is accompanied by a strong broadening of the polymer molecular weight distribution. This might be due to the transformation of the initially formed cation into another species that is also active, and of which the nature is presently unclear.

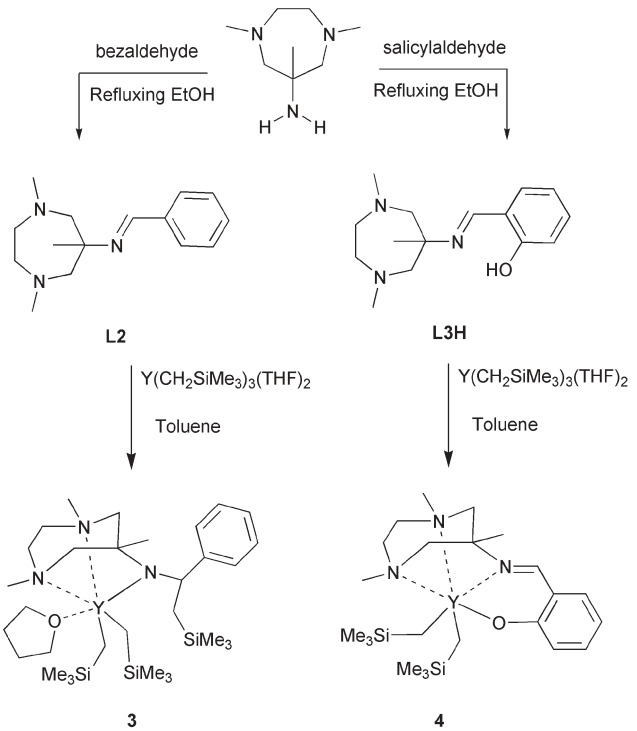
Two new ligand derivatives were prepared by the acid-catalysed condensation of the 1,4-dimethylated 6-amino-6-methyl-1,4-diazepine with benzaldehyde and with *o*-hydroxybenzaldehyde. This produced the 6-imino-6-methyl-1,4-diazepines **L2** and **L3**H (Scheme 2).

Reaction of **L2** with the yttrium trialkyl $Y(CH_2SiMe_3)_3(THF)_2$ is rapid and quantitative (NMR), and resulted in a product in which the imine carbon atom of the ligand has been alkylated to give the tridentate monoanionic ligand $\{(Me_3SiCH_2)PhC(H)NCMe[(CH_2NMeCH_2)_2]\}^-$. The coordination site on the metal that is vacated by the alkyl group that has migrated to the ligand is filled by one molecule of THF. The structure of this complex (**3**) was established by single-crystal X-ray diffraction (Fig. 2).‡ The compound contains a monoanionic *fac*-tridentate ligand in which the nitrogen on the 6-position of the 1,4-diazepine skeleton is an amide with a phenyl(trimethylsilylmethyl)methyl

Table 1 Catalytic ethene polymerization with $[(\mathbf{L1})M(CH_2SiMe_3)_3]$ (M = Sc **1a**, Y **1b**) activated with $[PhMe_2NH][B(C_6F_5)_4]$[a]

Trialkyl	T/°C	PE yield/g	Productivity/ 10^2 kg(PE) mol(M)$^{-1}$ h^{-1} bar^{-1}	$10^{-5}M_w$	M_w/M_n
1a	50	4.43	5.32	9.32	3.0
1a	70	9.66	11.60	2.35	9.4
1b	50	3.24	3.89	4.95	3.1
1b	70	4.57	5.48	1.43	2.6

[a] Conditions: 1 l steel autoclave (stirring rate 600 rpm), 250 ml toluene, 10 μmol trialkyl, 10 μmol $[PhMe_2NH][B(C_6F_5)_4]$, 5 bar ethene, 10 min run time.



Scheme 2 Synthesis of ligand **L2** and **L3**H and complex **3** and **4**.

substituent. The THF molecule is located in a *trans* position relative to the amide nitrogen. The Y–N(amide) distance of 2.215(3) Å is substantially shorter than the Y–N distances to the remaining ligand amine nitrogens. Low-temperature solution NMR studies on **3** show a fully asymmetric structure, with two resonances (δ 2.44, 2.12 ppm) for the diastereotopic methylene protons of the alkyl group transferred to the ligand, and four

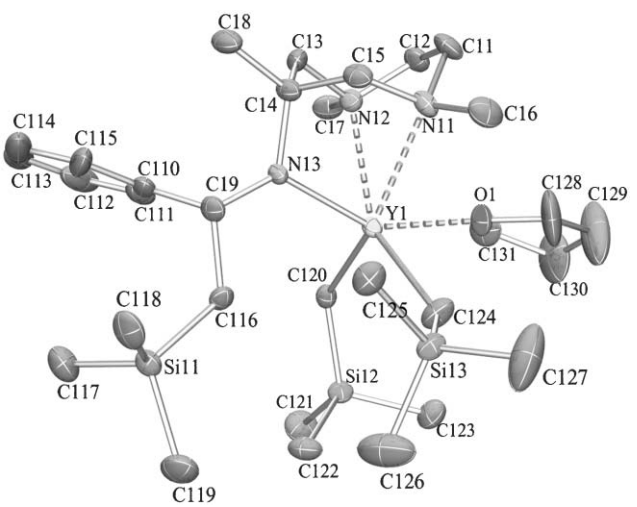


Fig. 2 Molecular structure of one of the independent molecules of **3** (hydrogen atoms omitted for clarity, thermal ellipsoids drawn at 50% probability level). Selected bond distances (Å) and angles (°): Y1–N11 2.695(3), Y1–N12 2.589(3), Y1–N13 2.215(3), Y1–C120 2.469(3), Y1–C124 2.446(4), Y1–O1 2.487(3); N11–Y1–N12 62.94(10), N11–Y1–N13 74.85(10), N12–Y1–N13 71.39(11), C120–Y1–C124 110.10(14), O1–Y1–C120 87.37(11), O1–Y1–C124 85.74(13), N11–Y1–C120 157.45(10), N12–Y1–C124 151.54(14), O1–Y1–N13 152.12(10).

resonances (δ 0.18, −0.50, −0.74, −0.88 ppm) for the diastereotopic YCH_2Si methylene protons. Intermolecular alkylation of ligand imino functionalities by metal alkyl species has been observed previously for early transition metals.[5]

Reaction of **L3H** with $Y(CH_2SiMe_3)_3(THF)_2$ resulted in a product (**4**, Scheme 2) in which the phenolic –OH group of the ligand has been deprotonated, and where the imino ligand moiety remains intact (as evidenced by the ^{1}H and ^{13}C NMR resonances at δ 7.64 ppm and δ 161.1 ppm for the aldimine –CH=N group and the $\nu_{C=N}$ IR band at 1622 cm^{-1}).¶ Although suitable crystals of **4** for a single-crystal structure determination have not yet been obtained, the solution ^{1}H and ^{13}C spectra indicate a C_s symmetric structure with a tetradentate iminophenolatediazepine ligand and two alkyl groups attached to the metal centre. The yttrium is again 6-coordinate, as no additional THF is bound. The NMR resonances for the YCH_2Si groups are found at δ −0.51 and −0.55 ppm (^{1}H; $^2J_{HH}$ = 11.3 Hz, $^1J_{YH}$ = 2.9 Hz) and δ 30.0 ppm (^{13}C; $^1J_{YC}$ = 38 Hz). The compound is related to the triazacyclononanephenolate complexes of scandium reported by Mountford *et al.*[4]

In conclusion, the 6-amino-6-methyl-1,4-diazepine ligand framework proves to be a highly versatile and readily accessible ligand moiety for the synthesis of a range of neutral and monoanionic ancillary ligands that can be used in organo rare-earth metal chemistry. We also expect these ligands to be useful for the early transition metals. The synthesis of derivatives with larger rare-earth metals (especially La) and the study of the reactive and catalytic properties of these compounds and their cationic derivatives is in progress.

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Notes and references

‡ *Crystallographic data* **1a**: $C_{22}H_{56}N_3Si_3Sc$, M = 491.92, monoclinic, space group $P2_1/c$, a = 18.418(1), b = 17.990(1), c = 18.694(1) Å, β = 95.799(1)°, V = 6162.4(6) Å^3, Z = 8, D_x = 1.060 g cm^{-3}, F(000) = 2176, μ = 3.68 cm^{-1}, λ(MoKα) = 0.71073 Å, T = 100(1) K, 41674 reflections measured, GooF = 0.964, w$R(F^2)$ = 0.1084 for 12024 unique reflections and 971 parameters and $R(F)$ = 0.0544 for 7135 reflections obeying the $F_0 \geqslant 4.0\sigma(F_0)$ criterion of observability; **3**: $2(C_{31}H_{64}N_3OSi_3Y)\cdot 0.5(C_7H_8)$, M = 1382.13, triclinic, space group $P\bar{1}$, a = 10.653(1), b = 17.454(2), c = 21.730(2) Å, α = 80.864(2)°, β = 87.771(2)°, γ = 85.449(2)°, V = 3975.2(7) Å^3, Z = 2, D_x = 1.155 g cm^{-3}, F(000) = 1490, μ = 15.84 cm^{-1}, λ(MoKα) = 0.71073 Å, T = 100(1) K, 30900 reflections measured, GooF = 0.996, w$R(F^2)$ = 0.1154 for 15266 unique reflections and 729 parameters and $R(F)$ = 0.0534 for 10248 reflections obeying the $F_0 \geqslant 4.0\sigma(F_0)$ criterion of observability. CCDC 606108 and 606109. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606384e

§ Synthesis of **2a**. THF (2 ml) was added to a mixture of 73.8 mg (150 μmol) of (**L1**)$Sc(CH_2SiMe_3)_3$ and 66.2 mg (150 μmol) of $[PhMe_2NH][B(C_6H_5)_4]$. The solution was homogenised by agitation and allowed to stand for about 20 min. The clear, slightly yellow solution was carefully layered with cyclohexane (3 ml). After standing overnight a white solid had precipitated. The solid was washed with pentane and dried under vacuum to give 90.4 mg (114 mmol, 76%) of pure **2a** as an off-white powder. ^{1}H NMR (400 MHz, THF-d_8, 298 K, δ): 7.33 (br, 4 × 2H, 2-*Ph*B), 6.92 (t, 4 × 2H, J_{HH} = 7.48 Hz, 3-*Ph*B), 6.78 (t, 4 × 1H, J_{HH} = 7.10 Hz, 4-*Ph*B), 3.04 (d, 2H, J_{HH} = 14.0 Hz, CC*H*H), 2.95 (m, 2H, NCH_2), 2.42 (s, 6H, NCH_3), 2.34 (m, 2H, NCH_2), 2.30 (s, 6H, $N(CH_3)_2$), 2.21 (d, 2H, J_{HH} = 14.0 Hz, CCH*H*), 0.64 (s, 3H, CCH_3), −0.01 (s, 18H, $Si(CH_3)_3$), −0.26 (s, 6H, $ScCH_2$). ^{13}C NMR (100.6 MHz, THF-d_8, δ): 166.4 (q, J_{BC} = 46.5 Hz, 1-*Ph*), 138.4 (d, J_{CH} = 153.1 Hz, 2-*Ph*), 127.1 (d, J_{CH} = 152.9 Hz, 3-*Ph*), 123.3 (d, J_{CH} = 155.6 Hz, 4-*Ph*), 69.7 (t, J_{CH} = 142.7 Hz, CCH_2), 63.5 (s, Me*C*), 60.6 (t, J_{CH} = 142.7 Hz, CH_2CH_2), 52.1 (q, J_{CH} = 136.3 Hz, NMe_2), 48.4 (br, $ScCH_2$), 43.2 (q, J_{CH} = 137.6 Hz, N*Me*), 12.5 (q, J_{CH} = 128.9 Hz, C*Me*), 4.8 (q, J_{CH} = 119.3 Hz, $SiMe_3$). Anal. calcd for $C_{46}H_{73}BN_3OSi_2Sc$: C, 69.41%; H, 9.24%; N, 5.28%. Found: C, 68.60%; H, 9.09%; N, 5.24%.

¶ Synthesis of **4**. $(Me_3SiCH_2)_3Y(THF)_2$ (0.495 g, 1.0 mmol) was dissolved in 20 ml of cold toluene (−30 °C). A solution of **L3H** (0.261 g, 1.0 mmol) in 6 ml of cold toluene (−30 °C) was added dropwise while stirring. The mixture was allowed to warm to room temperature and stirred for 30 min. The volatiles were removed under reduced pressure and the residue was washed with pentane yielding pure **4** (0.41 g, 0.78 mmol, 78%) as a slightly yellow solid. ^{1}H NMR (500 MHz, C_6D_6, δ): 7.64 (s, 1H, N=C*H*), 7.29 (t, 1H, J_{HH} = 7.26 Hz, *Ph*), 7.23 (d, 1H, J_{HH} = 7.75 Hz, *Ph*), 7.12 (d, 1H, J_{HH} = 7.75 Hz, *Ph*), 6.67 (t, 1H, J_{HH} = 7.26 Hz, *Ph*), 2.87 (m, 2H, NCH_2CH_2), 2.02 (s, 6H, N*Me*), 1.78 (d, 2H, J_{HH} = 13.3 Hz), 1.55 (m, 2H, NCH_2CH_2), 1.53 (d, 2H, J_{HH} = 13.3 Hz), 0.42 (s, 18H, $SiMe_3$), 0.33 (s, 3H, C*Me*), −0.51 (dd, 2H, J_{YH} = 2.9 Hz, J_{HH} = 11.3 Hz), −0.55 (dd, 2H, J_{YH} = 2.9 Hz, J_{HH} = 11.3 Hz). $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6, δ): 166.6 (O–*Ph*), 161.1 (N=*C*H), 135.5 (*Ph*), 134.7 (*Ph*), 122.6 (*Ph*), 122.6 (*Ph*), 115.7 (*Ph*), 71.5 (CCH_2), 62.1 (*C*Me), 57.2 (NCH_2CH_2), 49.4 (NMe_2), 30.3 (d, YCH_2, J_{YC} = 38.2 Hz), 17.1 (C*Me*), 4.7 ($SiMe_3$). Anal. calcd for $C_{23}H_{44}N_3OSi_2Y$: C, 52.75%; H, 8.47%; N, 8.02%. Found: C, 52.80%; H, 8.43%; N, 8.03%.

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