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Synthesis and structural characterization of a novel C_3-chiral triamine and its trilithium triamide

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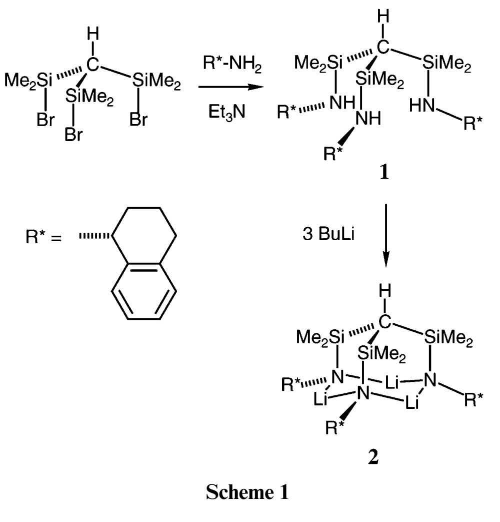
The novel C_3-chiral tripodal amine $HC(SiMe_2NHR^*)_3$ (1) and the corresponding trilithium triamide $HC(SiMe_2N(Li)R^*)$ (2) [$R^* = (R)$-tetrahydronaphthyl] have been synthesized and characterized by X-ray diffraction; the latter was found to have a central adamantoid cage structure in which the two-coordinate Li atoms are internally solvated by the peripheral aryl groups.

Whereas twofold rotational symmetry has been a leading principle in the design of a large number of chiral reagents and catalysts,[1] comparatively little is still known about the efficiency of systems possessing higher rotational symmetry.[2] During the past decade there has been a rapid increase of interest in C_3-chiral complexes and their application in catalysis.[3] However, the majority of the studies involved complexes of the late transition elements while C_3-chirality in compounds of the early transition metals is barely explored. These require highly charged σ and π donor ligands, such as alkoxides and amides in order to stabilize the high-valent metal centres. The introduction of chirality into the backbones of tripodal alkoxides and amides has been reported recently along with first results of their application in homogeneous catalysis.[4] Here we report the synthesis of a novel C_3-symmetric tridentate amido ligand in which the chiral centres are located in the peripheral groups and thus close to the potential reactive centre in metal complexes containing this ligand.

In the presence of an excess of triethylamine as auxiliary base, reaction of three molar equivalents of (*R*)-1-aminotetralene with the previously characterized trisilylmethane derivative $HC(SiMe_2Br)_3$,[5] after work up, gave the corresponding triamine $HC(SiMe_2NHR^*)_3$ (**1**) in good yield (Scheme 1). The ^1H, ^{13}C and ^{29}Si NMR spectra of **1** are consistent with a molecule of C_3 symmetry on the time scale of the experiment.† The ^1H NMR spectroscopic shift of the apical CH proton in the trisilylmethane backbone is characteristically at high field (δ −0.83 recorded in C_6D_6). The methyl groups of the $SiMe_2$ units are diastereotopic as a result of the chirality and occur at δ 0.34 and 0.38. Evidence for intramolecular hydrogen bonding may be deduced from the ν(N–H) infrared band which is observed at 3362 cm^{-1}, considerably lower than the value expected for a non-associated amine.[6] This notion is consistent with the molecular structure of **1** which was determined in a single crystal X-ray diffraction study (Fig. 1).‡



Scheme 1

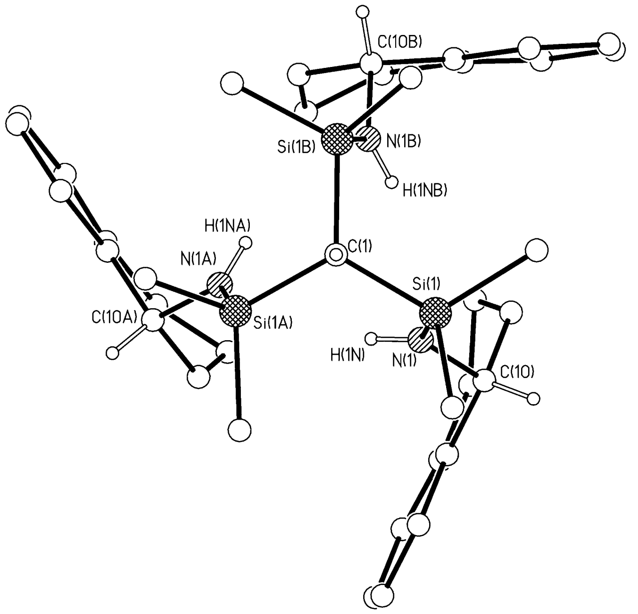


Fig. 1 Molecular structure of **1** viewed along the molecular axis of the tripod cage. Selected bond lengths (Å) and angles (°) (mean values); all H-atoms except those on methine and amido atoms have been omitted for clarity: C(1)–Si(1) 1.888, Si(1)–N(1) 1.715, Si(1)–C(2) 1.888, Si(1)–C(3) 1.892, N(1)–C(10) 1.485; Si(1)–C(1)–Si(1A) 113.8, N(1)–Si(1)–C(1) 104.3, C(10)–N(1)–Si(1) 125.1, C(15)–C(10)–N(1) 110.3, C(11)–C(10)–N(1) 108.9.

Compound **1** crystallizes in the polar hexagonal space group $P6_3$, and X-ray diffraction studies reveal three independent molecules of exact C_3 symmetry. The three molecules have virtually identical structures which are illustrated in Fig. 1 for the first molecule. Chemically equivalent metric parameters are equal within experimental error for the three molecules, and the mean values of selected bond lengths and angles are given in the caption to Fig. 1. In the solid state the tripodal ligand adopts a "claw-like" arrangement which is part of an adamantane-related cage structure. The base of the cage is formed by the three NH groups and, in contrast to the infrared data, the structure shows evidence of only extremely weak

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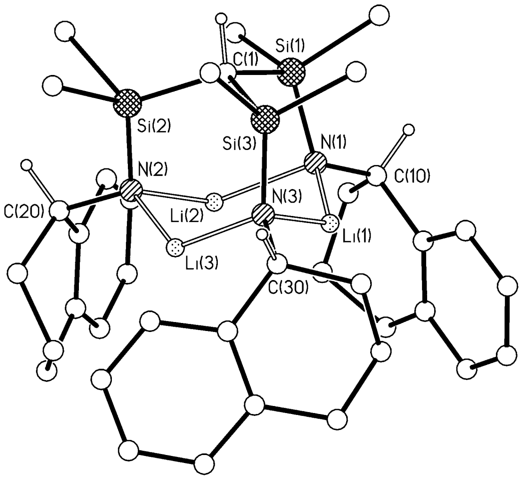

Fig. 2 Molecular structure of **2**. Selected bond lengths (Å) and angles (°); all H-atoms except those on methine atoms have been omitted for clarity: C(1)–Si(1) 1.879(8), C(1)–Si(2) 1.894(9), C(1)–Si(3) 1.887(9), Si(1)–N(1) 1.713(7), N(1)–Li(1) 1.943(16), N(1)–Li(2) 1.997(19), N(1)–C(10) 1.483(9); Si(1)–C(1)–Si(3) 115.0(4), Si(1)–C(1)–Si(2) 112.9(4), Si(2)–C(1)–Si(3) 113.9(5), N(1)–Si(1)–C(1) 108.9(4), N(1)–Li(1)–N(3) 121.7(8), Li(1)–N(1)–Li(2) 97.4(7), Si(1)–N(1)–Li(1) 111.9(6), C(10)–N(1)–Li(1) 111.3(7), Si(1)–N(1)–Li(2) 98.9(5).

intramolecular hydrogen bonding with N–H · · · N and N · · · N distances in the ranges 2.465–2.767 and 3.257–3.323 Å, respectively.

Reaction of the triamine **1** with three molar equivalents of Bu^{n}Li gave the corresponding trilithium triamide HC(SiMe$_2$N(Li)R*)$_3$ (**2**). The molecule of **2** was shown by X-ray diffraction studies (Fig. 2) to have virtual C_3 symmetry in the solid state and to be again based on a heteroadamantane cage structure consisting of a puckered (LiN)$_3$ unit capped by the trisilylmethane unit.‡ The Li–N–Li′–N′ torsion angles in the basal unit lie between 60.8(10) and 66.2(10)° while the Li–N distances between 1.922(16) and 1.997(19) Å are similar to those found in other cyclic lithium amides.[7] The lithium atoms are two-coordinate [N–Li–N′ angles between 120.0(8) and 122.7(8)°] although short Li · · · H–C contacts of 2.667(18), 2.62(2) and 2.715(18) Å with the C(19), C(29) and C(39) of the tetralyl [the term tetralyl refers to the (*R*)-tetrahydronaphthyl moiety] units indicate "internal solvation" by the ligand periphery. Several cases of such interactions of low-coordinate lithium atoms and hydrocarbon units have previously been reported.[8]

In summary, we have prepared a novel C_3-chiral ligand system the application of which in the coordination chemistry of the early transition metals and their use in catalysis is part of current and future activities in our laboratory.

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Notes and references

† Selected analytical and spectroscopic data: **1**: ^{1}H NMR (400.14 MHz, C$_6$D$_6$, 295 K) δ −0.83 [s, 1 H, *H*C(Si . . .)$_3$], 0.34, 0.38 [2 × s, 2 × 9 H, Si(C*H*$_3$)$_2$], 1.19–1.36 (m, 6 H, tetralyl), 1.45–1.53 (m, 3 H, tetralyl), 1.56–1.66 (m, 3 H, tetralyl), 1.84 (d, 3 H, $^3J_{\mathrm{HCNH}}$ = 10.6 Hz, N*H*), 2.41–2.51 (m, 3 H, tetralyl), 2.52–2.61 (m, 3 H, tetralyl), 3.82 (dt, 3 H, $^3J_{\mathrm{HCNH}}$ = 10.6 Hz, $^3J_{\mathrm{HH}}$ = 5.2 Hz, H^1 of tetralyl), 6.89 (dd, 3 H, $^3J_{\mathrm{HH}}$ = 6.9 Hz, $^4J_{\mathrm{HH}}$ = 1.7 Hz, H$^{\mathrm{arom.}}$ of tetralyl), 7.01 (m, 6 H, H$^{\mathrm{arom.}}$ of tetralyl), 7.45 (dd, 3 H, $^3J_{\mathrm{HH}}$ = 8.9 Hz, $^4J_{\mathrm{HH}}$ = 2.1 Hz, H$^{\mathrm{arom.}}$ of tetralyl); ^{13}C{^{1}H} NMR (100.62 MHz, C$_6$D$_6$, 295 K) δ 4.2, 4.3 [Si(*C*H$_3$)$_2$], 4.5 [H*C*(Si . . .)$_3$], 19.8 (C^3 of tetralyl), 29.9 (C^4 of tetralyl), 35.2 (C^2 of tetralyl), 49.9 (C^1 of tetralyl), 126.0, 126.5, 128.9, 129.5 (C^{5,6,7,8} of tetralyl), 136.7, 142.2 (C^{4a,8a} of tetralyl); ^{29}Si{^{1}H} NMR (79.50 MHz, C$_6$D$_6$, 295 K) δ 0.3; IR (benzene, ν/cm^{-1}): 3362 s, 3062 m, 3018 m, 2942 vs, 2862 s, 1488 m, 1443 w, 1408 s, 1253 vs, 1096 s, 1007 s, 891 s, 838 vs, 825 vs, 753 vs, 669 m; C$_{37}$H$_{55}$N$_3$Si$_3$ (626.12): calc. C 70.98, H 8.85, N 6.71; found C 70.66, H 8.70, N 6.68%.

2: ^{1}H NMR (400.14 MHz, d_8-toluene, 295 K) δ −0.73 [s, 1 H, *H*C(Si . . .)$_3$], 0.43, 0.55 [2 × s, 2 × 9 H, Si(C*H*$_3$)$_2$], 0.70, 0.93, 1.21–1.30 (2 × m, 2 × 3 H, tetralyl), 2.22–2.31 (m, 6 H, tetralyl), 4.16 (t, 3 H, $^3J_{\mathrm{HH}}$ = 4.5 Hz, H^1 of tetralyl), 6.75 (d, 3 H, $^3J_{\mathrm{HH}}$ = 7.2 Hz, H$^{\mathrm{arom.}}$ of tetralyl), 6.85 (dt, 3 H, $^3J_{\mathrm{HH}}$ = 7.2 Hz, $^3J_{\mathrm{HH}}$ = 1.0 Hz, H$^{\mathrm{arom.}}$ of tetralyl), 7.00 (dt, 3 H, $^3J_{\mathrm{HH}}$ = 7.2 Hz, $^3J_{\mathrm{HH}}$ = 1.0 Hz, H$^{\mathrm{arom.}}$ of tetralyl), 7.41 (d, 3 H, $^3J_{\mathrm{HH}}$ = 7.2 Hz, H$^{\mathrm{arom.}}$ of tetralyl); ^{13}C{^{1}H} NMR (100.62 MHz, d_8-toluene, 295 K) δ 4.8, 9.1 [Si(*C*H$_3$)$_2$], 10.9 [H*C*(Si . . .)$_3$], 19.4 (C^3 of tetralyl), 29.8 (C^4 of tetralyl), 36.9 (C^2 of tetralyl), 52.7 (C^1 of tetralyl), 125.8, 127.0, 127.6, 130.2 (C^{5,6,7,8} of tetralyl), 135.4 (C^{8a} of tetralyl), 147.4 (C^{4a} of tetralyl); ^{29}Si{^{1}H} NMR (79.50 MHz, d_8-toluene, 295 K) δ −3.2; ^{7}Li{^{1}H} NMR (155.51 MHz, d_8-toluene, 295 K) δ 2.0; C$_{37}$H$_{52}$Li$_3$N$_3$Si$_3$ (643.92): calc. C 69.02, H 8.14, N 6.53; found C 68.69, H 7.94, N 6.58%.

‡ Crystal data for **1**: C$_{37}$H$_{55}$N$_3$Si$_3$, M = 626.11, hexagonal, space group $P6_3$, a = 18.392(4), c = 19.655(5) Å, V = 5758(2) Å^3, Z = 6, D_c = 1.083 g cm^{-3}, F(000) = 2040, μ(Mo-Kα) = 0.151 mm^{-1}, T = 301(2) K, 8267 reflections collected, 3705 unique ($R_{\mathrm{int.}}$ = 0.0868), R_1 = 0.0576 ($I > 2\sigma I$), wR_2 = 0.1127 (all data). **2**: C$_{37}$H$_{52}$Li$_3$N$_3$Si$_3$, M = 643.91, orthorhombic, space group $P2_12_12_1$, a = 11.323(2), b = 16.714(6), c = 19.535(3) Å, V = 3696.9(17) Å^3, Z = 4, D_c = 1.155 g cm^{-3}, F(000) = 1380, μ(Mo-Kα) = 0.157 mm^{-1}, T = 173(2) K, 3657 reflections collected, 3410 unique ($R_{\mathrm{int.}}$ = 0.0338), R_1 = 0.0745 ($I > 2\sigma I$), wR_2 = 0.2101 (all data). Data for **1** was collected on a Siemens P4 diffractometer with an oil-coated crystal mounted in a Lindemann capillary under argon, data for **2** using an Enraf-Nonius CAD4 diffractometer with an oil-coated, shock-cooled crystal[9] mounted on the top of a glass pin under nitrogen. All data for structure **2** were corrected for absorption using ψ-scans, no absorption correction was applied for structure **1**. Structures **1** and **2** were solved by direct methods (SHELXS-97) and refined on F^2 (SHELXL-97).[10] In the case of **2** all methyl groups of the SiMe$_2$ units and one tetralene group were found 50 : 50% disordered. In the case of **1** some disorder of the tetralene groups was found. In the final cycles of refinement all full occupancy non-hydrogen atoms of **1** and **2** were assigned anisotropic displacement parameters. The N-bonded H-atoms were directly located in a difference-Fourier based on low angle data (mean N–H 0.86 Å); all other H-atom positions were calculated. CCDC reference numbers 156829 and 156830. See http://www.rsc.org/suppdata/dt/b1/b100719j/ for crystallographic data in CIF or other electronic format.

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