Synthesis and Characterization of Silazoxy Metallacycles†

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Novel transition-metal-containing metallacycles of the type $[\{M[O(SiMe_2NBu^t)_2]\}_2]$ (M = Mn^{II} **2**, Fe^{II} **3**, Ni^{II} **4** or Cr^{II} **5**) as well as six-membered heterocycles of the type $O(SiMe_2NBu^t)_2M$ (M = Te^{II} **8**, Ge^{II} **9** or Sn^{II} **10**) have been synthesised by the reaction of $O(SiMe_2NBu^tLi)_2$ with the corresponding metal halides. Reaction of $CuCl_2$ and CuCl with $O(SiMe_2NBu^tLi)_2$ yielded a novel copper amide $[Cu_4\{O(SiMe_2NBu^t)_2\}_2]$ **7** having four copper atoms in a square plane bridged symmetrically from above and below by the diamide ligand. This compound was also prepared by the reaction of $O[SiMe_2N(Bu^t)SnMe_3]_2$ with $CuCl_2$ and CuCl. X-Ray crystallographic data obtained are as follows: **2**, triclinic, space group $P\bar{1}$, $a = 8.550(2)$, $b = 9.838(2)$, $c = 11.668(2)$ Å, $\alpha = 83.81(3)$, $\beta = 70.35(3)$, $\gamma = 72.55(3)°$, $Z = 1$; **3**, triclinic, space group $P\bar{1}$, $a = 11.201(5)$, $b = 11.579(4)$, $c = 14.946(9)$ Å, $\alpha = 106.90(3)$, $\beta = 97.59(2)$, $\gamma = 101.27(2)°$, $Z = 2$.

As part of our attempts to make a symbiosis between main-group and transition-metal chemistry, we have been developing the synthetic and structural chemistry of metal-containing inorganic heterocycles for some years.[1] Previous reports from this laboratory have discussed the synthesis and structural characterization of a wide variety of these unusual ring compounds, many of them potential candidates as catalysts as well as precursors for new types of inorganic macromolecules.[2] In continuation of this study we have recently reported the synthesis of novel B–N–Ti[3] and Si–N–Zn[4] ring systems. The vast majority of these ring systems have the metal centres in their highest oxidation states; we have recently observed that the novel bidentate amide ligand $O(SiMe_2NBu^t)_2{}^{2-}$ stabilizes low oxidation and co-ordination states. In our search for novel ligands for synthesising metallacycles with the metal centres in low co-ordination states we have prepared complexes of Zn and Co with $O(SiMe_2NBu^t)_2{}^{2-}$ in the form of twelve-membered silazoxy metallacycles.[5] Herein we report the reactions of this ligand with a set of transition (Cr, Mn, Fe, Ni, Cu) and main group (Ge, Sn, Te) metal halides which have resulted in the formation of novel six- and twelve-membered metallacycles.

Experimental

Reactions were performed and worked up using modified Schlenk techniques and products handled under dry oxygen-free nitrogen, in a vacuum or using a Braun MB105B dry-box. Solvents, dried, distilled and stored using standard procedures, were freshly distilled into the reaction flasks using the vacuum manifold whenever needed. Infrared spectra were obtained using a Bio-Rad FTS7 spectrometer, NMR spectra on a Brucker 250M spectrometer [standards used: $SiMe_4$(^1H, ^{13}C, ^{29}Si), $TeMe_2$(^{125}Te) and $SnMe_4$(^{119}Sn)]. Mass spectra were measured on a Finnigan MAT System 8230 spectrometer in the electron-impact mode unless otherwise specified. The characteristic isotopic distribution pattern of the molecular ion was compared with the calculated molecular formula using a Commodore 3016 computer accessory. Microanalyses were done by the analytical laboratories of the University of Göttingen. The compounds $MnCl_2$, $SnCl_2$, $TeCl_4$, CuCl, $LiBu^n$ (2.3 mol dm^{-3} in hexane) (Jannssen), $FeCl_2$, $NiCl_2$, $CrCl_2$, $SnMe_3Cl$ and $CuCl_2$ (Aldrich) were used as commercially available; $GeCl_2{\cdot}C_4H_8O_2$ was synthesised using literature methods.[6] The preparation and characterization of the ligand $O(SiMe_2NHBu^t)_2$ has been described elsewhere.[5]

Syntheses.—$[\{Mn[O(SiMe_2NBu^t)_2]\}_2]$ **2**. A degassed suspension of $MnCl_2$ (0.26 g, 2.07 mmol) in tetrahydrofuran (10 cm^3) was frozen using a liquid-nitrogen bath in one arm of an H-shaped Schlenk vessel, and under a flow of nitrogen the amine $O(SiMe_2NHBu^t)_2$ **1** (0.58 g, 2.07 mmol) dilithiated using $LiBu^n$ (1.8 cm^3 of a 2.3 mol dm^{-3} solution in hexane) in tetrahydrofuran (25 cm^3) was added slowly using a syringe. The mixture was allowed to warm to room temperature over 15 min and stirred vigorously for 6 h under static vacuum. Afterwards the volatiles were removed *in vacuo* and hexane (30 cm^3) was distilled in. The mixture was stirred, insolubles allowed to settle and then carefully filtered over to the other arm of the reaction vessel through the frit separating the two arms. It was then slowly evaporated to yield pale pink crystalline blocks of compound **2** (0.35 g, 51%), m.p. 230 °C (decomp.) (Found: C, 43.2; H, 8.2; N, 8.1. $C_{24}H_{60}Mn_2N_4O_2Si_4$ requires C, 43.75; H, 9.15; N, 8.50%); ν_{max}(Nujol) 1364m, 1353m, 1263s, 1255m, 1208m, 1180m, 1068s, 986vs, 964vs, 850s, 845m, 798vs, 790s, 744m, 700m, 521m and 427m cm^{-1}; *m/z* 658 (M^+, 7), 643 (*M* − Me, 24) and 188 (100%).

$[\{Fe[O(SiMe_2NBu^t)_2]\}_2]$ **3**. A slurry of $FeCl_2$ (0.32 g, 2.50 mmol) in tetrahydrofuran (15 cm^3) was treated with dilithiated **1** (0.69 g, 2.50 mmol) under the conditions described for the synthesis of **2**. Slow evaporation of the final brown hexane solution gave dark yellow crystals of compound **3** (0.31 g, 38%), m.p. 185 °C (decomp.) (Found: C, 43.6; H, 9.2; N, 8.5. $C_{24}H_{60}Fe_2N_4O_2Si_4$ requires C, 43.60; H, 9.15; N, 8.50%); ν_{max}(Nujol) 1364s, 1353m, 1260vs, 1255s, 1204s, 1177s, 1044s, 1035m, 1007s, 943s, 846vs, 840s, 797vs, 752s, 701m and 678m cm^{-1}; δ_{Si}(C_6D_6) 308.2 (s) and 581.9 (s); *m/z* 660 (M^+, 15), 645 (*M* − Me, 12) and 188 (100%).

$[\{Ni[O(SiMe_2NBu^t)_2]\}_2]$ **4**. The reaction of $NiCl_2$ (0.42 g, 3.20 mmol) with the dilithiated amine **1** (0.90 g, 3.20 mmol) proceeded quite slowly in contrast to the cases of **2** and **3**. After stirring the reaction mixture for 48 h at room temperature the solvents were removed and the residue extracted in hexane (20 cm^3). Slow evaporation of the solution gave dark pinkish red needles of compound **4** (0.23 g, 21%), m.p. 178 °C (decomp.) (Found: C, 42.9; H, 8.9; N, 8.4. $C_{24}H_{60}N_4Ni_2O_2Si_4$ requires

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: mmHg ≈ 133 Pa.

C, 43.25; H, 9.05; N, 8.40%); ν_{max}(Nujol) 1363s, 1352m, 1260s, 1251vs, 1192s, 1171s, 1035s, 1003vs, 913m, 829vs, 800m, 787s, 783s, 745s and 711m cm^{-1}; $\delta_H(C_6D_6)$ 1.84, 1.78 (18 H, Bu^t), 1.50, 1.49 (18 H, Bu^t) and 0.88–0.21 (24 H, m, Me$_2$Si); $\delta_{Si}(C_6D_6)$ 13.62 (s) and -35.46 (s); *m/z* 664 (M^+, 22), 651 (M − Me, 6) and 302 (100%).

[{Cr[O(SiMe$_2$NBu^t)$_2$]}$_2$] **5**. The reaction of CrCl$_2$ (0.33 g, 2.69 mmol) with dilithiated **1** (0.74 g, 2.67 mmol) in tetrahydrofuran (30 cm^3) proceeded similarly to the cases of **2** and **3** yielding dark green leaflike crystals of compound **5** (0.35 g, 40%), m.p. 110 °C (decomp.) (Found: C, 44.6; H, 9.2; N, 7.1. $C_{24}H_{60}Cr_2N_4O_2Si_4$ requires C, 44.15; H, 9.30; N, 8.60%); ν_{max}(Nujol) 1358s, 1355s, 1251s, 1220s, 1191s, 1036vs, 1009vs, 984vs, 939s, 836vs, 785s, 778vs, 737s, 542m and 513m cm^{-1}; *m/z* 652 (M^+, 9), 637 (M − Me, 3) and 188 (100%).

The ligand O[SiMe$_2$N(Bu^t)SnMe$_3$]$_2$ **6**. A solution of compound **1** (2.38 g, 8.61 mmol) in tetrahydrofuran (40 cm^3) was dilithiated using LiBu^n (7.3 cm^3 of a 2.3 mol dm^{-3} solution in hexane), briefly warmed to reflux and cooled to room temperature. After cooling the mixture to −40 °C, SnMe$_3$Cl (3.43 g, 17.22 mmol) in tetrahydrofuran (15 cm^3) was added dropwise over a period of 10 min. The solution was brought to room temperature, stirred for 12 h and volatiles were removed in vacuum. The residue was vacuum distilled to yield compound **6** as a colourless oil (3.9 g, 75.3%), b.p. 128–130 °C (0.01 mmHg); ν_{max}(Nujol) 1469w, 1389w, 1360s, 1257vs, 1229m, 1204m, 1190vs, 1042vs, 992vs, 862s, 859vs, 843s, 813s, 786vs, 725w, 670w, 528s, 518s and 509m cm^{-1}; $\delta_H(C_6D_6)$ 1.36 (18 H, s, Bu^t), 0.36, 0.35 (30 H, 2s, Me$_3$Sn, Me$_2$Si); $\delta_{Si}(C_6D_6)$ -15.97 (s); *m/z* (field ionization FI), 602 (M^+, 100), 572 (M − 2Me) and 440 (M − SnMe$_3$).

[Cu$_4${O(SiMe$_2$NBu^t)$_2$}$_2$] **7**. (*i*) *From the reaction of* CuCl$_2$ *with* O(SiMe$_2$NBu^{t}Li)$_2$ (1:1). To a suspension of CuCl$_2$ (0.41 g, 3.05 mmol) in tetrahydrofuran (15 cm^3) kept at −40 °C was added an equimolar amount of dilithiated **1** over a period of 15 min. An instantaneous reaction with the formation of a deep violet solution was observed. Over a period of 3 h the solution changed from purple, wine red and pale brown to colourless. All solvents were removed in vacuum and the residue was extracted with hexane (30 cm^3), filtered over Celite, partially concentrated and cooled at 0 °C for 48 h to yield colourless diamond-shaped crystals of compound **7** (0.25 g, 41%), m.p. 180–182 °C (decomp.) (Found: C, 36.2; H, 7.6; N, 7.0. $C_{24}H_{60}Cu_4N_4O_2Si_4$ requires C, 35.90; H, 7.55; N, 7.00%); ν_{max}(Nujol) 1360s, 1355s, 1254vs, 1219w, 1185m, 1055vs, 1029s, 989m, 974vs, 838s, 801s, 776s, 750s, 674s, 585w, 424w and 379s cm^{-1}; $\delta_H(C_6D_6)$ 1.47 (36 H, s, Bu^t) and 0.42 (24 H, s, Me$_2$Si); $\delta_C(C_6D_6)$ 64.66 (4 C, Me$_3$*C*), 38.90 (12 C, *Me*$_3$C) and 7.99 (8 C, Me$_2$Si); $\delta_{Si}(C_6D_6)$ -13.34 (s); *m/z* 802 (M^+, 94) and 787 (M − Me, 100%).

(*ii*) *From the reaction of* CuCl *with* O(SiMe$_2$NBu^{t}Li)$_2$ (2:1). To a suspension of CuCl (0.69 g, 6.97 mmol) in tetrahydrofuran (15 cm^3) at −10 °C was added after dilithiation **1** (0.96 g, 3.47 mmol) over a period of 15 min. The solution turned dark violet and afterwards pale green over 4 h. After stirring for 12 h the volatiles were removed and the residue was extracted with hexane (30 cm^3), filtered over Celite, concentrated and cooled at 0 °C for 48 h to yield compound **7** as colourless crystals (0.73 g, 53%).

(*iii*) *From the reaction of* CuCl$_2$ *with* O[SiMe$_2$N(Bu^t)SnMe$_3$]$_2$ (1:1). To a suspension of CuCl$_2$ (0.22 g, 1.64 mmol) in hexane (15 cm^3) was added dropwise at room temperature compound **6** (1.00 g, 1.65 mmol) in hexane (15 cm^3). The solution which turned green on stirring was set to a gentle reflux (bath temperature 75 °C) for 12 h whereupon it became colourless. The volatiles were pumped off at 0.01 mmHg and collected in a trap, which on cooling at −40 °C crystallized out SnMe$_3$Cl. The residue was extracted with hexane (30 cm^3), filtered and cooled at 0 °C for 48 h to yield compound **7** (0.19 g, 57%) as colourless crystals.

(*iv*) *From the reaction of* CuCl *with* O[SiMe$_2$N(Bu^t)SnMe$_3$]$_2$ (2:1). The compound CuCl (0.33 g, 3.33 mmol) in hexane (25 cm^3) was treated with **6** (1.00 g, 1.65 mmol) in hexane (25 cm^3) under similar conditions to reaction (*iii*). No colour change was observed throughout the reaction and work-up. Cooling of the final hexane extract at 0 °C for 48 h yielded compound **7** (0.28 g, 42%).

O(SiMe$_2$NBu^t)$_2$Te **8**. To a dilithiated solution of compound **1** (1.90 g, 6.87 mmol) in tetrahydrofuran (20 cm^3) kept at −78 °C was added slowly a solution of TeCl$_4$ (0.93 g, 3.44 mmol) in tetrahydrofuran (30 cm^3) over a period of 30 min. The mixture was allowed slowly to warm up to room temperature and stirred for 12 h. On removing the volatiles in vacuum a dark brown semisolid residue with a white solid remained. On vacuum distillation this yielded two fractions: a colourless liquid (31 °C, 0.01 mmHg) which was spectroscopically identified as **1** and a dark yellow extremely air-sensitive liquid, which was characterized as compound **8** (1.03 g, 75%), b.p. 78 °C (0.01 mmHg); ν_{max}(neat) 2963vs, 2928m, 2905m, 2869w, 1465m, 1413m, 1379s, 1361s, 1259vs, 1231s, 1197m, 1043vs, 1023vs, 997m, 850vs, 803s, 787s and 645w cm^{-1}; $\delta_H(C_6D_6)$ 1.24 (18 H, s, Bu^t) and 0.40 (12 H, s, Me$_2$Si); $\delta_{Si}(C_6D_6)$ -7.31 (s); $\delta_{Te}(C_6D_6)$ 1522.7 (s); *m/z* 404 (M^+, 3), 389 (M − Me, 6) and 188 (100); (FI) 404 (M^+, 100%).

O(SiMe$_2$NBu^t)$_2$Ge **9**. The compound GeCl$_2$·C$_4$H$_8$O$_2$ (0.60 g, 2.57 mmol) in tetrahydrofuran (15 cm^3) was treated with **1** (0.71 g, 2.57 mmol) after dilithiation at 0 °C. The reaction was complete in 4 h with the solution turning bright yellow. The volatiles were removed in vacuum, the residue extracted with hexane (25 cm^3) and filtered over Celite. Vacuum distillation of the oily residue obtained on removing the hexane gave a yellow oil (76 °C, 0.01 mmHg) which crystallized immediately (0.75 g, 84%), m.p. 54–55 °C (Found: C, 41.1; H, 8.8; N, 7.9. $C_{12}H_{30}GeN_2OSi_2$ requires C, 41.50; H, 8.75; N, 7.85%); ν_{max}(Nujol) 1363m, 1259vs, 1235w, 1193m, 1127w, 1100s, 1047vs, 1018s, 987s, 961m, 878m, 857s and 793vs cm^{-1}; δ_H 1.49 (18 H, s, Bu^t) and 0.40 (12 H, s, Me$_2$Si); $\delta_{Si}(C_6D_6)$ -12.09 (s); *m/z* 348 (M^+, 12), 333 (M − Me, 52) and 188 (100%); (FI) 348 (M^+).

O(SiMe$_2$NBu^t)$_2$Sn **10**. The compound SnCl$_2$ (0.64 g, 3.37 mmol) was treated with an equimolar quantity of dilithiated **1** in tetrahydrofuran (30 cm^3) similar to the case of **9**. The dark yellow residue obtained after removal of the volatiles was vacuum distilled to yield a dark yellow oil at 90–92 °C (0.01 mmHg) which crystallized on keeping at room temperature and was characterized as compound **10** (0.79 g, 60%), m.p. 54 °C (Found: C, 36.95; H, 7.6; N, 7.2. $C_{12}H_{30}N_2OSi_2Sn$ requires C, 36.65; H, 7.70; N, 7.10%); ν_{max}(Nujol) 1360s, 1254vs, 1227m, 1188m, 1044vs, 1005s, 980s, 854vs, 833s, 808m, 784vs, 751m, 735m, 678w, 520w, 425w and 380m cm^{-1}; $\delta_H(C_6D_6)$ 1.37 (18 H, s, Bu^t) and 0.37 (12 H, s, Me$_2$Si); $\delta_C(C_6D_6)$ 54.39 (Me$_3$*C*), 38.34 (*Me*$_3$C) and 7.07 (Me$_2$Si); $\delta_{Si}(C_6D_6)$ -12.00 (s); $\delta_{Sn}(C_6D_6)$ 785.6 (s); *m/z* 394 (M^+, 14), 379 (M − Me, 98) and 188 (100%).

X-Ray Crystallography.—The structures were determined from single-crystal X-ray diffraction data using graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å). Crystals suitable for measurement of compounds **2** (pale pink) and **3** (dark yellow) were grown overnight at room temperature by slowly condensing the solvent off a hexane solution. Data were collected at 153 K using a four-circle Siemens Stoe AED diffractometer. Crystallographic data are summarized in Table 1. Programs used for absorption correction, crystal structure solution and refinement were SHELXA 92, SHELXS 92 and SHELXL 92 respectively.[7] Diffraction measurements were carried out using ω scans and the structures were refined by full-matrix least squares on F^2 for all unique reflections. Anisotropic thermal parameters were refined for non-hydrogen atoms and hydrogen atoms were included in calculated positions with isotropic thermal parameters. Atomic scattering factors were taken from ref. 8. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + g_1P + g_2P^2]$ where P = [maximum of (0 or F_o^2) + $2F_c^2$]/3 and g_1 and g_2 were 0.0341, 0.5534 for **2** and 0.0434, 2.506 for **3**. Refined coordinates for compounds **2** and **3** are given in Tables 2 and 4 and selected bond distances in Tables 3 and 5.

Table 1 Crystallographic data for compounds **2** and **3**

Compound	**2**	**3**
Formula	$C_{24}H_{60}Mn_2N_4O_2Si_4$	$C_{24}H_{60}Fe_2N_4O_2Si_4$
M	659.00	660.82
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	8.550(2)	11.201(5)
b/Å	9.838(2)	11.579(4)
c/Å	11.668(2)	14.946(9)
α/°	83.81(3)	106.90(3)
β/°	70.35(3)	97.59(2)
γ/°	72.55(3)	101.27(2)
U/Å^3	881.7(3)	1781.7(15)
Z	1	2
F(000)	354	712
D_c/Mg m^{-3}	1.241	1.232
μ/mm^{-1}	0.887	0.974
Maximum and minimum transmission	0.94, 0.60	0.89, 0.29
Crystal size/mm	0.77 × 0.69 × 0.50	1.40 × 0.70 × 0.54
θ range for data collection/°	4.28–25.00	3.54–22.55
Reflections collected	4152	4383
Independent reflections	3090 (R_{int} 0.0168)	4383
Data/parameters for refinement	3090/198	4383/366
Goodness of fit on F^2	1.11	1.05
R, wR_2		
for $I > 2\sigma(I)$	0.025, 0.069	0.032, 0.083
for all data	0.025, 0.069	0.034, 0.086
Largest difference map peak, hole/e Å^{-3}	0.32, −0.31	0.56, −0.31

Table 2 Atomic coordinates (× 10^4) of compound **2**

Atom	x	y	z
Mn	601.9(3)	9 008.5(2)	5 852.9(2)
Si(1)	−1 247.4(6)	8 222.8(5)	8 296.6(4)
Si(2)	−2 816.4(6)	11 054.4(5)	7 050.7(4)
O	−2 307.6(15)	9 368.4(12)	7 460.7(10)
N(1)	816(2)	7 895(2)	7 350.2(13)
C(1)	2 390(3)	6 921(2)	7 542(2)
C(2)	3 680(7)	7 828(6)	7 359(6)
C(3)	2 162(13)	6 326(12)	8 784(6)
C(4)	3 270(7)	5 795(5)	6 583(5)
C(5)	−1 766(3)	9 092(2)	9 780(2)
C(6)	−2 223(3)	6 711(2)	8 625(2)
C(7)	−4 528(2)	11 281(2)	6 335(2)
C(8)	−3 906(3)	12 180(2)	8 441(2)
C(9)	−91(2)	12 363(2)	6 159(2)
C(10)	−1 280(3)	13 865(2)	6 143(2)
C(11)	363(3)	12 104(2)	7 341(2)
C(12)	1 582(3)	12 264(2)	5 114(2)
N(2)	−909(2)	11 274.4(14)	5 993.7(12)
C(2′)	2 408(16)	5 360(9)	7 280(13)
C(3′)	3 943(11)	7 196(15)	6 757(12)
C(4′)	2 219(20)	6 787(16)	8 870(11)

The terminal carbon atoms bonded to C(1) are disordered. The best model for this tertiary butyl group is shown in Fig. 1. Assuming tetrahedral bonding about C(1), the two alternative sets of atomic sites C(2), C(3), C(4) and C(2′), C(3′), C(4′) have occupancies of 63 and 37% respectively.

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

Results and Discussion

Reactions of $O(SiMe_2NBu^tLi)_2$ with metal halides in tetrahydrofuran proceed readily with the formation of the metallacycle and LiCl (Scheme 1). All compounds except $O(SiMe_2NBu^t)_2Te$ were solids which could be obtained as crystals on slow crystallization from hexane solutions. The six-membered ring systems $O(SiMe_2NBu^t)_2M$ (M = Te^{II} or Sn^{II}) were purified by vacuum distillation. Very stringent handling conditions were needed as all the compounds were extremely air and moisture sensitive. All are readily soluble in hydrocarbon and ether solvents without decomposition and except the copper cluster **7** are coloured. The colours are quite similar to those observed for the acyclic silylamides of the corresponding transition and main-group metals.[9]

Description of the Structures.—The crystal structures of $[\{Mn[O(SiMe_2NBu^t)_2]\}_2]$ **2** and $[\{Fe[O(SiMe_2NBu^t)_2]\}_2]$ **3** are shown in Figs. 1 and 2, respectively. Although from the available spectra similar structures could be ascribed to **2** and **3**, the X-ray diffraction studies show quite interesting differences. Compound **2** has a crystallographic centre of symmetry whereas **3** does not. The most significant difference between the two structures is that both the oxygen atoms of the manganese heterocycle are displaced towards the metal centres leading to a weak co-ordinative interaction, while in the iron heterocycle only one of the oxygens seems to be involved in such interaction. This fact is evident from the M–O distances. In **2** and **3** the co-ordinated Mn–O and Fe–O distances are 2.512(2) and 2.408(3) Å, respectively, while Fe(a)···O(a) distance involving the non-co-ordinated oxygen of the iron heterocycle is 3.024(3) Å. This ring is more staggered than rings involving co-ordinated oxygen which possess a butterfly-like configuration. These conformational differences are also evident in various bond angles in the six-membered rings. In particular the angles N(1)–Si(1)–O of **2** and **3** are 101.1(1) and 100.1(1)° while the two angles around Si(1a) and Si(2a) of **3** are more tetrahedral in nature [109.7(1) and 107.3(1)°] suggesting the energy gain in binding these oxygen atoms to their closest metal atoms is largely offset by distortions of the normal silicon stereochemical environment. Although the structure of **2** is similar to that of the cobalt analogue[5] we do not have a plausible explanation for the unusual structure of **3**. However, it may be noted that the normal co-ordinative bond distances of Mn←O(thf) and Fe←O(thf) [2.158–2.249(5)[10] and 2.071(6)[11]] are shorter than those observed in both **2** and **3**. The metal–nitrogen distances in the two compounds vary in the order M–N(1) < M–N(2a), M(a)–N(2) < M–N(2), M(a)–N(2a): for

Table 3 Selected bond lengths (Å) and angles (°) for compound **2**

Mn–N(1)	1.993(2)	Mn–N(2a)	2.119(2)
Mn–N(2)	2.208(2)	Mn–O	2.512(2)
Si(1)–O	1.670(2)	Si(1)–N(1)	1.692(2)
Si(2)–O	1.645(1)	Si(2)–N(2)	1.740(2)
N(1)–Mn–N(2a)	141.2(1)	N(1)–Mn–N(2)	119.9(1)
N(2)–Mn–N(2a)	97.4(1)	N(1)–Mn–O	69.3(1)
N(2a)–Mn–O	120.9(1)	N(2)–Mn–O	68.7(1)
Si(2)–O–Si(1)	142.8(1)	Si(2)–O–Mn	89.1(1)
Si(1)–O–Mn	85.6(1)	C(1)–N(1)–Si(1)	128.3(1)
C(1)–N(1)–Mn	127.6(2)	Si(1)–N(1)–Mn	103.9(1)
C(9)–N(2)–Si(2)	121.9(2)	C(9)–N(2)–Mn(a)	113.1(1)
Si(2)–N(2)–Mn(a)	115.8(1)	C(9)–N(2)–Mn	118.6(1)
Si(2)–N(2)–Mn	97.3(1)	Mn(a)–N(2)–Mn	82.6(1)

Table 4 Atomic coordinates (× 10^4) for compound **3**

Atom	*x*	*y*	*z*
Fe	3243.3(3)	−880.9(3)	2291.9(2)
Fe(a)	1856.6(3)	772.7(3)	2806.8(2)
Si(1)	2844.0(7)	−3181.6(6)	823.8(5)
Si(1a)	2726.4(7)	3480.1(6)	4119.4(5)
Si(2)	636.9(7)	−2239.4(7)	1674.6(6)
Si(2a)	4613.9(6)	1935.9(7)	3375.5(5)
O	1703(2)	−2458(2)	1023.6(13)
O(a)	3980(2)	2972(2)	3975.2(14)
N(1)	4018(2)	−2184(2)	1706(2)
N(1a)	1488(2)	2353(2)	3353(2)
C(1)	5293(3)	−2315(3)	1959(2)
C(1a)	219(3)	2546(3)	3148(2)
C(2)	5432(4)	−2643(6)	2857(4)
C(2a)	123(4)	3050(5)	2326(4)
C(3)	5630(4)	−3263(4)	1159(3)
C(3a)	−74(4)	3463(4)	4002(3)
C(4)	6220(3)	−1089(4)	2124(3)
C(4a)	−723(3)	1332(4)	2908(4)
C(5)	2362(3)	−4785(3)	891(2)
C(5a)	3050(3)	5021(3)	3920(2)
C(6)	2981(3)	−3307(3)	−423(2)
C(6a)	2687(3)	3775(3)	5404(2)
C(7)	−557(3)	−1745(3)	987(2)
C(7a)	5063(3)	1021(3)	4149(2)
C(8)	−152(3)	−3787(3)	1726(3)
C(8a)	6115(3)	2763(3)	3194(3)
C(9)	1319(3)	−1197(3)	3687(2)
C(9a)	3426(3)	1210(2)	1431(2)
C(10)	−57(3)	−1543(3)	3741(3)
C(10a)	4455(3)	834(3)	924(2)
C(11)	1964(3)	−2176(3)	3882(2)
C(11a)	3471(3)	2587(3)	1581(2)
C(12)	1916(3)	41(3)	4481(2)
C(12a)	2181(3)	451(3)	791(2)
N(2)	1477(2)	−1069(2)	2732(2)
N(2a)	3545(2)	936(2)	2360.3(15)

Table 5 Selected bond lengths (Å) and angles (°) for compound **3**

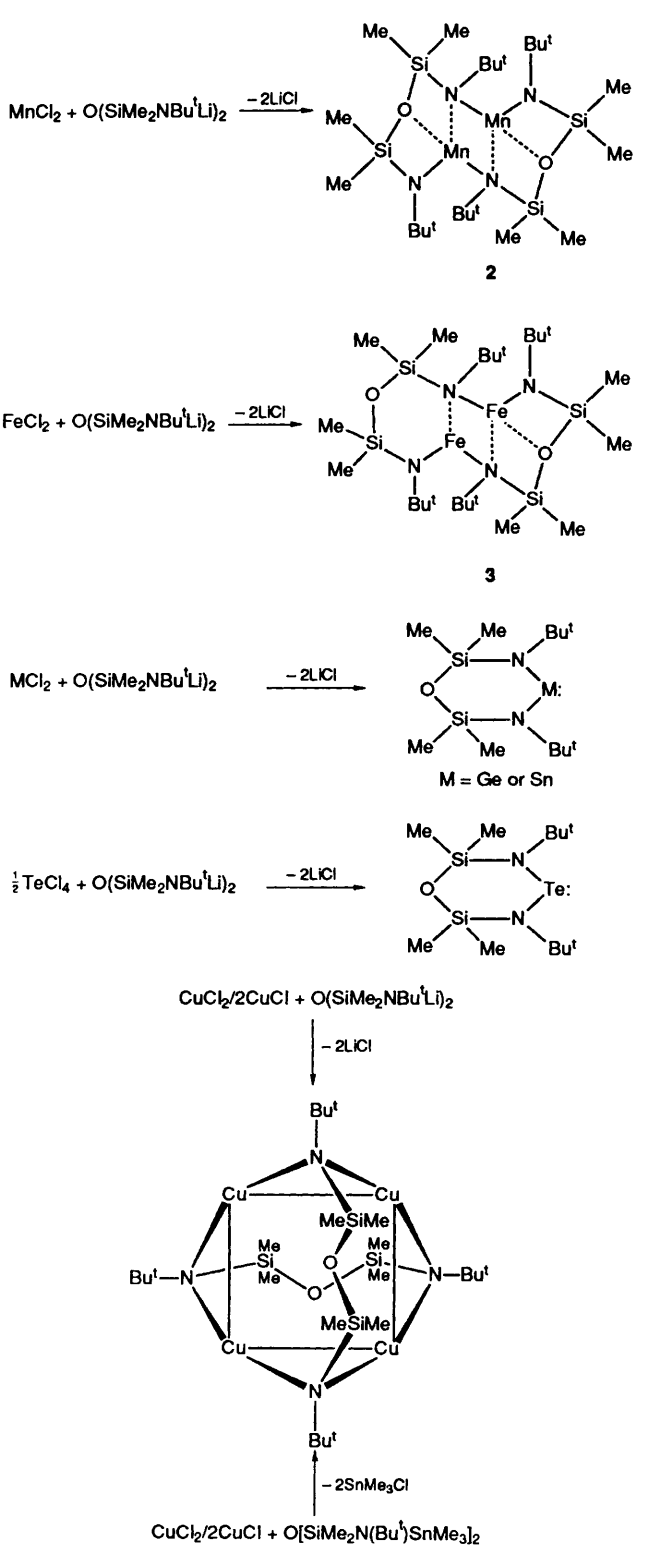
Fe–N(1)	1.934(3)	Fe–N(2a)	2.034(3)
Fe–N(2)	2.157(3)	Fe(a)–N(1a)	1.924(3)
Fe(a)–N(2)	2.058(3)	Fe(a)–N(2a)	2.079(3)
Si(1)–O	1.673(2)	Si(1)–N(1)	1.692(3)
Si(1a)–O(a)	1.641(2)	Si(1a)–N(1a)	1.715(3)
Si(2)–O	1.648(2)	Si(2)–N(2)	1.756(3)
Si(2a)–O(a)	1.619(2)	Si(2a)–N(2a)	1.742(3)
N(1)–Fe–N(2a)	131.7(2)	N(1)–Fe–N(2)	128.2(2)
N(2a)–Fe–N(2)	98.2(1)	N(1a)–Fe(a)–N(2)	144.7(1)
N(1a)–Fe(a)–N(2a)	113.1(1)	N(2)–Fe(a)–N(2a)	100.0(1)
Si(2)–O–Si(1)	144.3(1)	Si(2a)–O(a)–Si(1a)	148.4(1)
C(1)–N(1)–Si(1)	127.9(2)	C(1)–N(1)–Fe	129.9(2)
Si(1)–N(1)–Fe	102.2(1)	C(1a)–N(1a)–Si(1a)	123.7(2)
C(1a)–N(1a)–Fe(a)	122.0(2)	Si(1a)–N(1a)–Fe(a)	114.2(1)
C(9)–N(2)–Si(2)	120.1(2)	C(9)–N(2)–Fe(a)	110.9(2)
Si(2)–N(2)–Fe(a)	120.5(1)	C(9)–N(2)–Fe	122.8(2)
Si(2)–N(2)–Fe	95.8(1)	Fe(a)–N(2)–Fe	79.7(1)
C(9a)–N(2a)–Si(2a)	121.4(2)	C(9a)–N(2a)–Fe	117.5(2)
Si(2a)–N(2a)–Fe	112.9(1)	C(9a)–N(2a)–Fe(a)	110.5(2)
Si(2a)–N(2a)–Fe(a)	103.9(1)	Fe–N(2a)–Fe(a)	82.1(1)

M = Mn, 1.993(2) < 2.119(2) < 2.208(2), for M = Fe, 1.934(3) < 2.034(3) < 2.157(3). The shortest of these distances are longer than other two-co-ordinate M–N distances: 1.989(3) Å in $Mn[N(SiMePh_2)_2]_2$[12] and 1.903(7) in $Fe[N(SiMePh_2)_2]_2$.[13] The sums of the angles at N(1) for both structures are almost 360° indicating a trigonal-planar geometry, while the sums of the angles at N(2) [excluding M–N(2)] are 351.3 and 351.6°, respectively, for **2** and **3** indicating a slightly distorted tetrahedral geometry. The fact that the angles N(1)–Mn–N(2a) and N(1)–Fe–N(2a) are 141.2(1) and 131.7(2)° also shows that the metal centres are more than two-co-ordinate in nature. The four-membered ring formed by the metal atoms and the four-co-ordinated nitrogens seems to be puckered in the case of the iron compound as evidenced by the four different angles of this ring varying from 79.7(1) to 100.0(1)°.

Spectral Features of the Cyclometallasilazoxanes.—Electron-impact mass spectral analysis readily gave the molecular ion peaks for all the synthesised metallacycles in the expected isotopic distribution pattern. A common feature was the peak for *M* − Me and that at *m*/*z* 188 attributable to a rearranged fragment of the ligand $[O(SiMe_2)_2NBu^tMe]$ which is the base peak in almost all the cases.

Compounds **2**, **3** and **5** were found to be paramagnetic and no paramagnetically shifted NMR peaks were obtained in the case of manganese compound **2** and the chromium compound **5**. The ^{29}Si NMR spectra of the iron compound **3** showed two strong singlets (δ 308.25 and 581.9). Two singlets were also observed for the nickel compound **4** which was found to be diamagnetic. This observation, similar to those made for cycloaluminadisilatriazane[14] at room temperature and cyclozincadisilatriazane[4] at −10 °C, is indicative of the fact that the solid-state structure is retained in solution. It may be noted that many of the acyclic transition-metal silylamide dimers tend to remain as monomers in solution at room temperature.[11] The proton NMR spectra of the nickel compound also showed mainly a four-peak pattern for the Me_2Si groups and two peaks for the Bu^t groups. This is in accord with the data reported for cycloaluminadisilatriazane[14] which basically possesses a similar structural framework. However, since no suitable crystals for X-ray structural analysis could be grown for **4** and **5** we are unable to give a clearer picture of their structures.

Although a relatively large amount of literature exists on acyclic amides of Te^{II},[15] Ge^{II}[16] and Sn^{II}, only a few examples of cyclic amides have been reported.[17] Wannagat and Rabet[18] have also reported the synthesis of silazoxy metallacycles of the type $O(SiMe_2NMe)_2MCl_2$ (M = Ge or Sn) where the metal centres are in the tetravalent state. The tellurium heterocycle **8** was synthesised by a method similar to that described for the synthesis of $Te[N(SiMe_3)_2]_2$ by Björgvinsson *et al.*[19] The mass spectral analysis of compounds **8**–**10** gave the molecular ion peak corresponding to the six-membered ring systems. In parallel with the observations by Gynane *et al.*,[20] we also prefer to assign monomeric structures to these low-melting (liquid in the case of **8**) coloured, thermally stable compounds. The proton NMR spectra for **8**–**10** are quite simple giving sharp singlets for the Me_2Si groups (δ 0.37–0.40) and the Bu^t groups (δ 1.24–1.49). The ^{29}Si NMR spectra give only a single sharp singlet at δ −7.31, −12.09 and −12.00 for **8**, **9** and **10**, respectively. Further evidence for the nature of **8** and **10** was obtained from the ^{125}Te NMR spectrum of **8** which gave a singlet (δ 1522.7). This observation is in accordance with ^{125}Te NMR data reported for the amides $Te[N(SiMe_3)_2]_2$ (δ 1912),



Scheme 1

Te[NBu^t(SiMe$_3$)]$_2$ (δ 1742)[21] and [TePhN(SiMe$_3$)$_2$] (δ 1629).[22] The ^{119}Sn NMR spectrum of **10** gave a singlet (δ 785.66). To the best of our knowledge this is one of the most highly deshielded ^{119}Sn NMR shifts reported.[23] Such a value, a clear indication of the monomeric state of the compound in solution,[24] has also been observed for the well known tin amide Sn[N(SiMe$_3$)$_2$]$_2$ (δ 772.6). As discussed by Wrackmeyer[24] for amides of Sn^{II} and Pb^{II}, a dimeric species is expected to give a signal at much lower δ value.

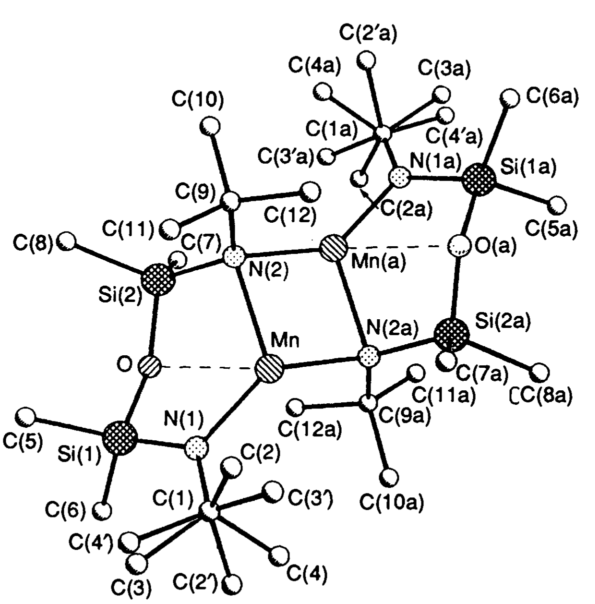


Fig. 1 Molecular structure of [{Mn[O(SiMe$_2$NBu^t)$_2$]}$_2$], hydrogen atoms being omitted

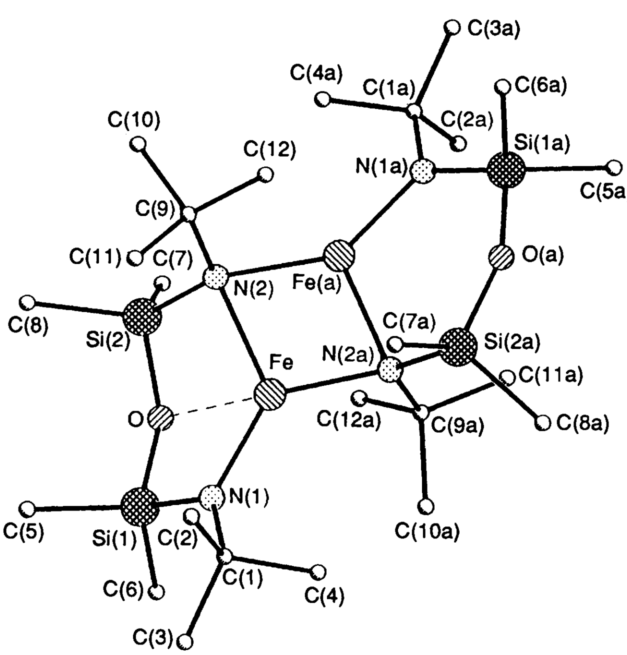


Fig. 2 Molecular structure of [{Fe[O(SiMe$_2$NBu^t)$_2$]}$_2$], hydrogen atoms being omitted

Interestingly, the reaction of O(SiMe$_2$NBu^{t}Li)$_2$ with CuCl$_2$ was found to give a compound the analytical and spectral data for which showed it to be entirely different from the type of heterocycles obtained from other divalent metal halides. The proton NMR spectra of this compound showed two singlets [δ 0.42 (Me$_2$Si) and 1.47 (Bu^t)]. The ^{29}Si NMR spectrum also showed only a singlet (δ −13.34). The mass spectrum, which gave an intense molecular ion peak (*m/z* 802), indicated that the molecule should have a minimum of four copper atoms and the structure was assigned as [Cu$_4${O(SiMe$_2$NBu^t)$_2$}$_2$] **7**.

As an alternative for ligands involving lithium metal, which imposes limitations in the selection of solvents, work-up and purification methods, in addition to bringing about reduction of the metal centres in many cases, we have been looking for suitable leaving groups capable of abstracting halogens from metal halides and leading to the formation of metal–nitrogen bonds. Our initial attempts with the Me$_3$Sn substituted ligand **6** show considerable promise in this direction. However, in the reaction of CuCl$_2$ with **6**, the reduction of Cu^{II} to Cu^I could not be avoided. Compound **7** was obtained from the reactions of compounds **1** and **6** with CuCl as well.

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