

Synthesis and structures of compounds of Groups 11 and 12 containing the ligand $C(SiMe_3)_2(SiMe_2C_5H_4N-2)^\dagger$

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The compound $\overline{Li(thf)C(SiMe_3)_2(SiMe_2C_5H_4N-2)}$ (**1**) reacts with CuI or $AuCl-SMe_2$ to give the dimeric compounds $[MC(SiMe_3)_2(SiMe_2C_5H_4N-2)]_2$ ($M = Cu$ or Au), in which the bidentate ligand bridges two metal centres. Reactions of **1** with Group 12 halides of the form MX_2 give the compounds $\overline{MX\{C(SiMe_3)_2(SiMe_2C_5H_4N-2)\}}$ ($M = Zn, X = Br$; $M = Cd, X = Cl$; $M = Hg, X = Cl$). In the solid state, the zinc and cadmium compounds are halogen-bridged dimers, but the mercury compound is monomeric, with only weak interaction between mercury and nitrogen.

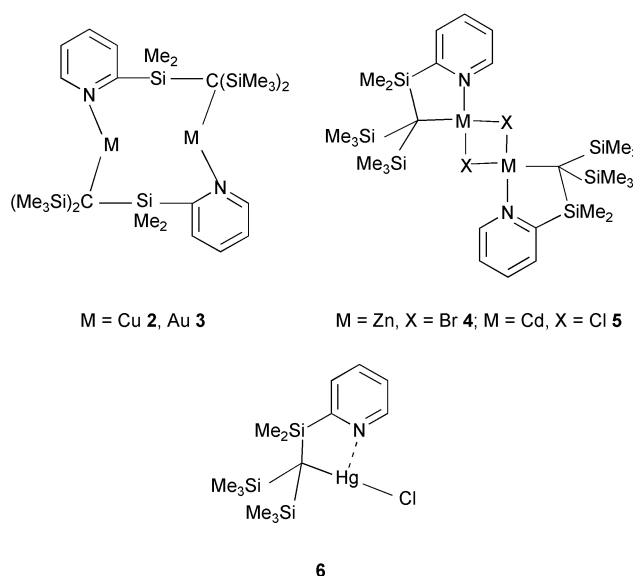
We have shown that the ligand $C(SiMe_3)_2(SiMe_2C_5H_4N-2)$, **R**, can be attached to a wide range of main group and open shell transition metals so that it is possible to study trends in structural parameters within series of closely related isostructural compounds.¹⁻³ The ligand is similar in size to the widely studied $C(SiMe_3)_3$ group⁴ and has a larger bite angle than the less sterically demanding bidentate ligands $C(SiMe_3)_2(C_5H_3XN-2)$ ($X = H, Me$ or CH_2SiMe_3), which have also been attached to a series of metal centres.⁵⁻¹¹ We considered that it would be of interest to attach the $C(SiMe_3)_2(SiMe_2C_5H_4N-2)$ group to some d^{10} metals (a) in order to study trends in the balance between C- and N-ligation in the resulting compounds and compare these with data obtained previously for derivatives of other elements, and (b) because the d^{10} Cu^I compounds have potential as precursors to novel d^9 species. As we have already isolated and structurally characterised a stable Ni^I derivative $\overline{Ni\{C(SiMe_3)_2(SiMe_2C_5H_4N-2)\}(PPh_3)}$,² we considered that it might be possible to isolate Cu^{II} species containing the same ligand. A recently described calix[4]phyrin Cu^{II} compound¹² is the only previously reported crystallographically characterised d^9 σ -bonded organometallic Cu^{II} compound, although EPR data have been given for two Cu^{II} 2-aza-21-carbaporphyrin derivatives.¹³

We now report the copper and gold species **2** and **3**, the first examples of compounds in which the ligand **R** bridges two metal centres, and the Group 12 derivatives **4-6**. Preliminary experiments on the oxidation of compound **2** are also described.

Results and discussion

The copper and gold compounds

Compounds **2** and **3**, containing ten-membered rings, were obtained from reactions between $\overline{Li(thf)\{C(SiMe_3)_2(SiMe_2C_5H_4N-2)\}}$ (**1**) and CuI or $AuCl-SMe_2$, respectively. Compound **2** was isolated as a toluene solvate, but there appear to be no chemically significant interactions between the toluene and the dimeric molecules. Attempts to synthesise the Ag analogue from **1** and $AgCl$ or $AgOSO_2C_6H_4Me-4$ gave black precipitates of metallic Ag, and



the only isolated organic product was the ligand precursor $CH(SiMe_3)_2(SiMe_2C_5H_4N-2)$.

Although several dimeric organocopper and -gold derivatives have been reported, this class of compound is still quite rare. The most important species for comparison with the ten-membered ring compounds **2** and **3** are the alkyl (**7** and **8**)^{7,11} and the azaallyl (**9**¹⁴ and **10**¹⁵) compounds, containing eight-membered rings, and the aryl derivatives **11**¹⁶ and **12**,¹⁷ containing ten-membered rings. As far as we are aware, no other structurally characterised alkylcopper compound containing a ten-membered ring has been reported.

The molecular structure of **2** is shown in Fig. 1 and bond lengths and angles are given in Table 1. The Cu–C distances are the same within the experimental uncertainties as those in **7** and **9**, and, as expected for bonds to sp^3 rather than sp^2 carbon, are slightly longer than those in the aryl compounds **11** and **12**. The Cu–N distance is similar in all of the compounds **2**, **7**, **9**, **11** and **12**. The C–Cu–N angle in **2** [$161.9(5)^\circ$] is significantly narrower than those in **7** [$172.7(1)$ to $178.0(5)^\circ$], **12** [$177.8(2)^\circ$], **9** [$166.2(2)^\circ$] and **11** [$167.8(2)^\circ$]. The molecules of compound **2** have approximate C_2 symmetry and the ring is twisted, with the two C–Cu–N fragments pointing inwards towards each other. It has been argued that inward pointing bent C–Cu–N fragments

[†] Electronic supplementary information (ESI) available: full experimental details. See <http://www.rsc.org/suppdata/dt/b2/b200473a/>

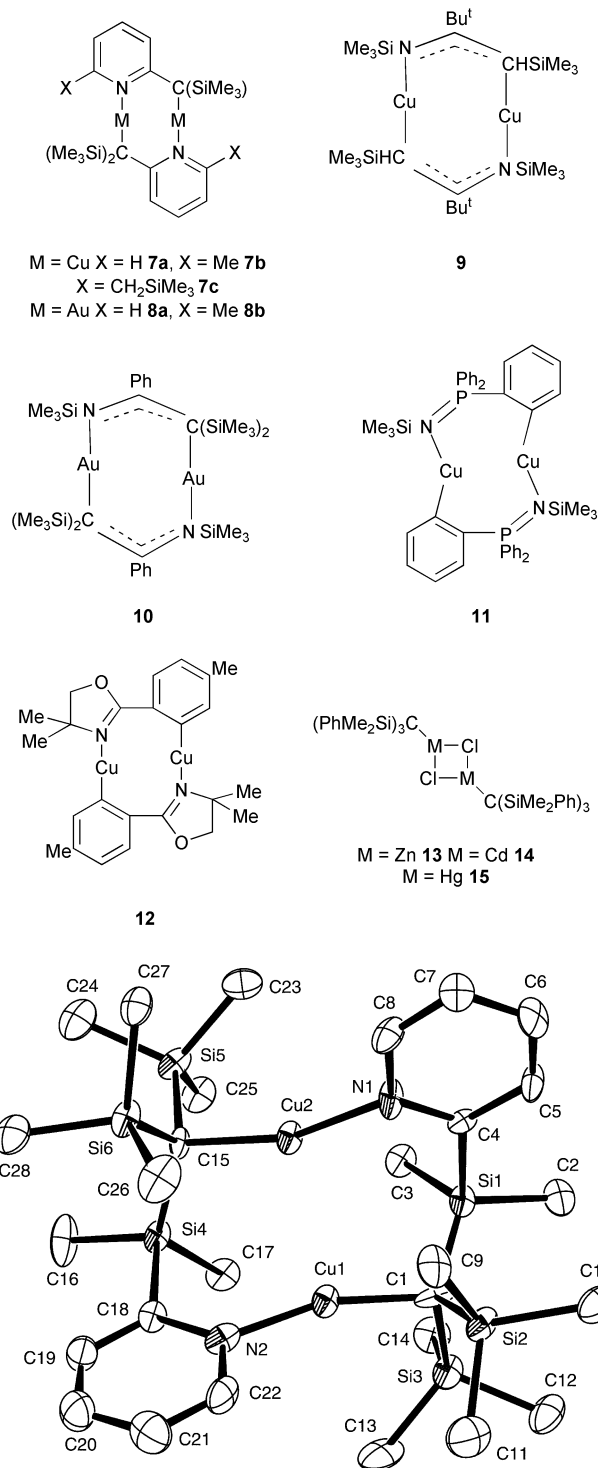


Fig. 1 Molecular structure of $[\text{CuC}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N-2})]_2$ (**2**).

provide evidence for $\text{Cu} \cdots \text{Cu}$ attraction,¹⁶ but the $\text{Cu} \cdots \text{Cu}$ distance in **2** [2.839(3) Å] is significantly longer than those in **7**, **9**, **11** and **12** [2.412(1) to 2.499(2) Å] and $[\text{CuCH}_2\text{SiMe}_3]_4$ (2.417 Å).¹⁸ A similar distance [2.843(3) Å] in $[\text{CuCH}_2\text{PMe}_2\text{CH}_2]_2$ is associated with a wider C–Cu–C angle [175.8(8)].¹⁹ The data indicate that there is little evidence for correlation between short $\text{Cu} \cdots \text{Cu}$ distances, non-linear C–Cu–N angles and ring size, and reflect the fact that the molecular parameters are determined by the balance between $\text{Cu} \cdots \text{Cu}$ interactions, attractive if 3d orbitals mix with 4s and 4p,²⁰ and geometrical constraints imposed by bridging ligands.^{21,22}

The structure of **3** is shown in Fig. 2. Although species containing ten-membered rings having P–Au–S^{23,24} or P–Au–Co²² sequences have been reported, we are not aware of any structurally characterised Au^I alkyl containing a ten-membered

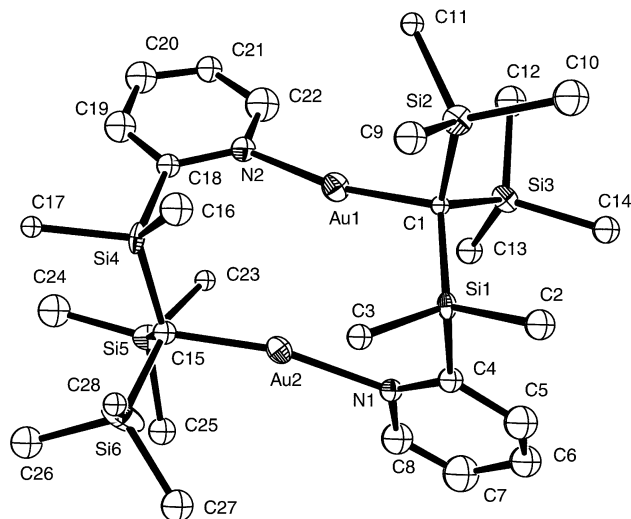
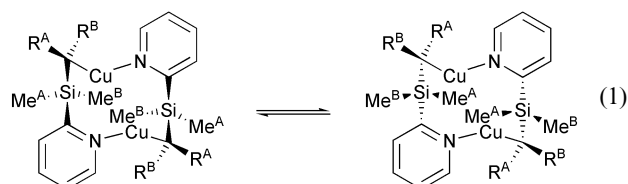


Fig. 2 Molecular structure of $[\text{AuC}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N-2})]_2$ (**3**).

ring, other than **3**. The $\text{Au} \cdots \text{Au}$ distance in **3** [3.0749(16) Å] (Table 1) is significantly longer than those in **8** [2.672(1) to 2.690(2) Å],^{8,11} **10** [2.6887(8) Å]¹⁵ and two 1,2-dithiolato-*o*-carborane complexes [2.9771(10) and 3.0195(5) Å],²⁴ but similar to that in $(\text{AuSCH}_2\text{CH}_2\text{PEt}_2)_2$ [3.104 Å (no esd)]²³ and those in gold compounds generally.^{25,26} The C–Au–N angle is narrower than those in **8** and **10**, so that, as in the copper compounds and presumably for the same reasons, narrow angles are not necessarily associated with shorter metal–metal contacts.

The ¹H, ¹³C and ²⁹Si NMR spectra of **2** and **3** in benzene or toluene show that each signal ascribed to the SiMe₂ and SiMe₃ groups is split into two, as required if the species in solution are dimeric and have puckered rings like those in the crystal. Saturation transfer experiments show that there is exchange between the signals in each pair, indicating that, at room temperature, the dimers are readily converted by inversion of the ring into mirror images in which the environments of the groups A and B are interchanged, as shown in eqn. (1).



Preliminary cyclic voltammetric measurements on a solution of **2** in THF at 25 °C with 0.2 M $[\text{NBu}_4][\text{BF}_4]$ as supporting electrolyte showed an oxidation process at vitreous carbon, with a peak potential *ca.* 100 mV from ferrocenium/ferrocene. The oxidation process showed some reversibility at moderate scan rates, but the shape of the curves suggests that two overlapping one-electron steps are involved. However, more work is necessary to define these precisely. The electrochemical oxidation of **2** appears to be similar to that of **7a**, described previously.⁸ Attempts to oxidize **2** on a preparative scale with O₂ or AgBPh₄ gave intractable products.

A 1 : 2 mixture of **2** and tetracyanoquinodimethane (tcnq) in toluene gave a solution from which thin blue crystals separated. These were not suitable for an X-ray structure determination, but their IR spectrum showed sharp peaks at 2182 and 2158 cm⁻¹. These are quite different from the absorptions of the neutral tcnq (2222 and 2226 cm⁻¹), but similar to those (2175 and 2150 cm⁻¹) in $[\text{Fe}(\text{C}_9\text{Me}_7)_2][\text{tcnq}]$ (C₉Me₇ = η⁵-heptamethylindenyl), in which the presence of the tcnq radical anion has been confirmed by an X-ray structure determination.²⁷ The EPR spectrum, which persisted for several days, comprised a broad feature ($\Delta w_{1/2} = \text{ca. } 40 \text{ G}$) at $g = 2.0035$, which could arise from a paramagnetic copper species, and a sharp signal at

Table 1 Selected bond lengths (Å) and angles (°)

	2	3 ^a	4 ^b	5 ^c	6 ^d
M–C	1.945(12) ^e	2.06(3) ^e	2.037(4)	2.210(6)	2.124(3)
M–N	1.931(10) ^e	2.11(3) ^e	2.077(4)	2.312(6)	2.611(3)
M···M	2.839(3)	3.0749(16) ^e			
M–X, M–X'			2.5398(7), 2.4601(6)	2.5966(14), 2.5617(14)	2.3466(9)
Si–C	1.863(12) ^e	1.89(3) ^e	1.865(5) ^e	1.861(7) ^e	1.887(4) ^e
Si–Me	1.881(14) ^e	1.87(3) ^e	1.875(7) ^{e,f}	1.877(11) ^e	1.876(4) ^e
Si–C(py)	1.908(12) ^e	1.91(3) ^e	1.902(5)	1.905(7)	1.907(4)
C–M–N	161.9(5) ^e	168.1(10) ^e	98.97(15)	92.0(2)	87.46(11)
M–N–C4	126.0(8) ^e	127.7(18) ^e	110.3(3)	111.6(4)	109.3(2)
N–C4–Si	117.5(9) ^e	120(2) ^e	116.5(3)	116.3(4)	115.5(3)
C4–Si–Cl	109.2(5) ^e	108.4(13) ^e	106.50(19)	109.6(3)	109.24(15)
Si–Cl–M	111.9(6) ^e	111.8(12) ^e	97.92(18), 111.7(2), 104.6(2)	99.3(3), 103.4(3), 110.9(3)	104.47(15), 107.85(16), 103.11(15)
Si–Cl–Si	113.4(6) ^e	112.3(14) ^e	116.5(2), 113.6(2), 110.7(2)	113.9(3) ^e	113.66(17), 114.84(17), 111.70(17)
C1–Si–Me	112.8(6)–119.1(6)	113.8(13) ^e	111.2(3)–116.7(2)	110.6(4)–115.9(4)	111.8(2)–114.3(2)
Me–Si–Me	104.9(7) ^e	105.5(13) ^e	103.8(4)–106.9(3)	106.6(6) ^e	104.6(2)–108.1(2)

^a For one of the independent molecules in the asymmetric unit; values for the other molecule are not significantly different. ^b C–Zn–Br 124.99(12), C–Zn–Br' 131.30(11), N–Zn–Br 98.45(10), N–Zn–Br' 106.42(11), Br–Zn–Br' 91.79(2), Zn–Br–Zn' 88.21(2)°. ^c C–Cd–Cl 132.42(18), C–Cd–Cl' 132.08(18), N–Cd–Cl 99.32(16), N–Cd–Cl' 105.21(15), Cl–Cd–Cl' 89.06(4), Cd–Cl–Cd' 90.94(4)°. ^d C–Hg–Cl 173.43(9)°. All intermolecular distances to Hg are >4 Å. ^e Average values with e.s.d. for individual measurements in parentheses. ^f The value for Si2–C9, 1.911(9) Å, lies outside the limit implied by the quoted e.s.d.

$g = 2.0025$ with fine structure identical with that seen in the spectrum of the $[\text{tcnq}]^{\cdot -}$ radical ion.²⁸ The mass spectrum of the blue crystals indicated the presence of both the ligand R and tcnq . There is thus some evidence that **2** can be oxidised to the diradical cation, and further experiments to substantiate this postulate are in progress. A similar two-step oxidation of **7** was proposed previously.⁸

The zinc, cadmium and mercury compounds

The compounds **4–7** were obtained without difficulty. We have not had the opportunity to examine their chemistry in detail, but since they all formed good crystals suitable for X-ray diffraction studies we discuss their structures (Fig. 3–5) here.

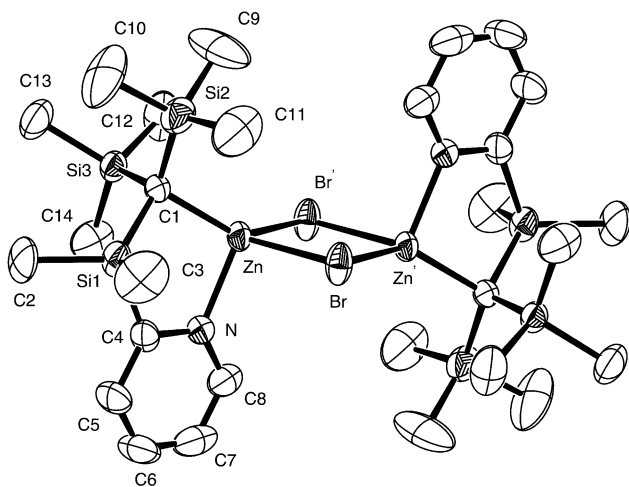


Fig. 3 Molecular structure of $[\text{ZnBr}\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)\}]_2$ (**4**).

Halide-bridged compounds of the type $[\text{MX}\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)\}]_2$, with X = halogen, M = Cr,¹ Co²⁹ or Pd,² having tetrahedral or square planar coordination at the metal centres, have been described previously. The compounds **4** and **5**, which have crystallographically imposed $\bar{1}$ symmetry and tetrahedral coordination at the metal centre, belong to this general class. Few organozinc or -cadmium halides have been structurally characterised. As far as we are aware, the only previous examples of halogen-bridged species are the compounds $[(\text{PhMe}_2\text{Si})_3\text{CMCl}]_2$ (M = Zn **13**, Cd **14**,

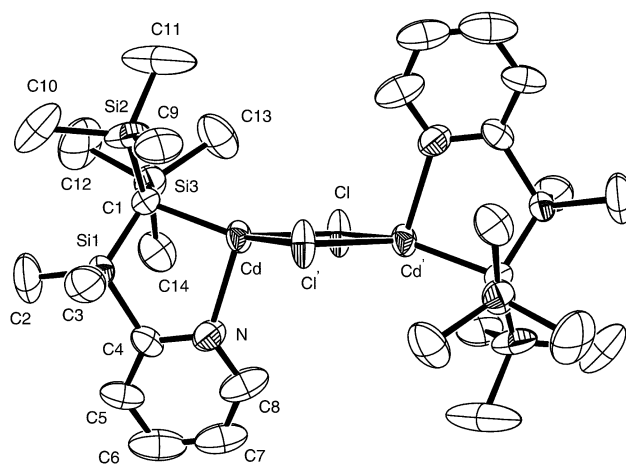


Fig. 4 Molecular structure of $[\text{CdCl}\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)\}]_2$ (**5**).

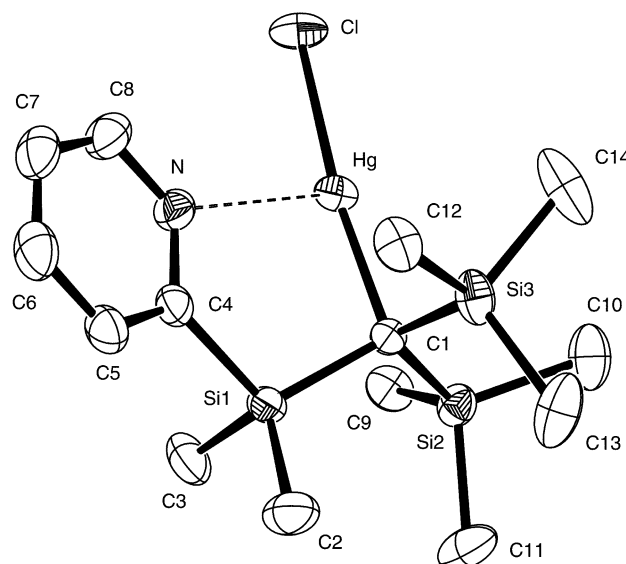


Fig. 5 Molecular structure of $\text{HgCl}\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)\}$ (**6**).

Hg **15**)³⁰ and $[(\text{PhMe}_2\text{Si})_3\text{CCdBr}]_2$,³¹ which contain three-coordinate metal centres, and $\{(\text{PhMe}_2\text{Si})_3\text{CCdBr}(\text{H}_2\text{O})\}_2(\text{thf})$ and $[(\text{Me}_3\text{Si})_3\text{CCdCl}]_4$, in which the metal is four-coordinate.³¹

There are thus few data in the literature with which the structural parameters of **4** and **5** can be compared. A search that included all compounds, not just organometallic derivatives, yielded only two examples of structures containing Zn_2Br_2 ^{32,33} and three examples containing Cd_2Cl_2 cores with tetrahedral coordination at the metal.^{34–36}

The Zn–Br [2.4601(6) and 2.5398(7) Å] and Cd–Cl bond lengths [2.5966(14) and 2.5617(14) Å], in **4** and **5** respectively, (Table 1) are similar to those in previously described compounds [Zn–Br 2.430(2) to 2.545(1) Å^{32,33} and Cd–Cl 2.532(6) to 2.570(4) Å^{34–36}] so that there is nothing to suggest that these bonds are in any way unusual. The Cd–Cl bond in **5** is similar to that of the longer bond [2.558(2) Å] in the unsymmetrical Cd_2Cl_2 core of **14**.³⁰ The M–C bond lengths involving four-coordinate M in **4** [2.037(4) Å] and **5** [2.210(6) Å] can be compared with those involving three-coordinate M in **13** [1.977(8) Å] and **14** [2.195(6) Å] and the sum of the covalent radii [Zn–C 2.02 and Cd–C 2.18 Å].³⁷ The data in Table 1 show that for compounds **3–6**, the M–N are greater than the M–C bond lengths. In this respect, these compounds resemble those of Ge, Sn and Pb³ rather than those of the more electropositive main group or middle transition metals [cf. $\text{Mg}(\text{thf})\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)\}$, in which Mg–C = 2.189(9) and Mg–N = 2.097(9) Å].¹

The mercury compound **6** differs significantly from the zinc and cadmium analogues **4** and **5** in that the coordination of the ligand is markedly asymmetric. The Hg–Cl and Hg–C bond lengths are similar to those in **15** and other alkyl- and dialkyl-mercury derivatives,³⁸ but the Hg–N distance [2.611(3) Å], though shorter than the sum of the van der Waals radii (3.0–3.2 Å),^{38,39} is considerably longer than the sum of the covalent radii (2.19 Å), indicating that the bond is weak. The distance is similar to that [2.63(1) Å] in 2-pyridylphenylmercury chloride (**16**),⁴⁰ but shorter than those in $\text{Hg}\{\text{C}(\text{SiMe}_3)_2(\text{C}_5\text{H}_4\text{N}-2)\}_2$ (**17**) (2.78 Å)⁴¹ or $\text{Hg}\{\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2\}_2$ [2.89(1) Å].⁴² The weak Hg...N interaction in **5** is associated with bending of the C–Hg–Cl angle from linearity to 173°. The data given here for the compounds **4–6** may be compared with those for **13–15** and the derivatives $\text{M}\{\text{C}(\text{SiMe}_3)_2(\text{C}_5\text{H}_4\text{N}-2)\}_2$.⁴¹ For each set of compounds, the M–C and M–Cl distances increase from Mg to Cd and decrease from Cd to Hg. Compound **15** forms chloride-bridged dimers and compound **16** tetramers, but **6** shows no such association. Although the data for the compounds **16–18** are less precise than those given here, they too show the same trends: the M–C distance reaches a maximum for M = Cd and the M–N distances increase systematically from M = Mg to M = Hg as the acceptor power of the metal towards nitrogen decreases.

Ligand geometry

The selected molecular parameters given in Table 1 indicate that bond lengths and angles within the ligand are similar for all five complexes and similar to those in previously described compounds containing the ligand R.^{1,3} The Si–Cl distances in the copper and zinc compounds are shorter than those in the mercury and (probably) the gold derivatives (there is a large uncertainty in the bond lengths in **3**), in accord with the previously established generalisation⁴³ that the distance becomes shorter as the electronegativity of the atom adjacent to carbon decreases. The increase in bite distance from 3.13 in **4** to 3.58–3.66 Å in **2–3** required by the change from a chelating to a bridging configuration is accommodated by changes in the M–C–Si and M–N–C angles. The Si–C(py) bonds are consistently longer than the Si–Me distances. The results presented in this paper, taken along with those reported earlier,^{1–3} cover compounds of the ligand $\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)$ with metals from most groups of the Periodic Table from 1 to 14. They indicate that carbanionic charge is delocalised mainly into

adjacent Si–C bonds with little effect on the Si–Me or Si–C(py) bonds. However, the more electropositive metals, which form the most ionic bonds to ligating carbon are also the best acceptors for the lone pair on nitrogen and form shorter M–N bonds. The ligand is thus strongly bidentate and more sterically demanding than it is in compounds containing less electropositive metals.

Experimental

Air and moisture were excluded as far as possible by the use of Schlenk techniques and Ar as blanket gas. Glassware was flame-dried under vacuum and solvents were dried and distilled immediately before use. NMR spectra were recorded at 300.13 (¹H), 125.8 (¹³C), 99.4 (²⁹Si) and 110.97 MHz (¹¹³Cd), and chemical shifts are given relative to SiMe_4 or CdMe_2 . Except where indicated, solutions in C_6D_6 at 298 K were used. EI mass spectra were obtained at 70 eV and data are given for species containing ⁶³Cu, ⁶⁴Zn, ¹⁰⁷Ag, ¹¹⁴Cd and ²⁰²Hg. In assignments, R = $\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)$. Compound **1** was made as described previously.¹

Synthesis

[CuC(SiMe₃)₂(SiMe₂C₅H₄N-2)]₂ (2**).** A solution of **1** (2.10 mmol) in thf (20 cm³) was added at –78 °C to a stirred slurry of CuI (0.40 g, 2.10 mmol) in thf (20 cm³). The mixture was allowed to warm to room temperature and the solvent was removed from the dark grey solution to give a sticky grey solid that was extracted with a mixture of hexane and toluene (40 cm³, ca. 5 : 1). The extract was filtered and the pale yellow filtrate reduced in volume to ca. 15 cm³. This was kept at –30 °C for 3 days to give yellow needles of **2**·(toluene) suitable for X-ray diffraction analysis (0.55 g, 62%). The toluene of crystallisation could not be completely removed, even by prolonged pumping under vacuum, so satisfactory elemental analyses could not be obtained. Found: C, 49.35; H, 8.76; N, 3.70; C₂₈H₅₆N₂Cu₂Si₆ requires C, 47.00; H, 7.83; N, 3.92%. NMR: δ_{H} 0.14 and 0.50 (18 H, s, SiMe₃), 0.60 and 1.11 (6 H, s, SiMe₂), 6.39 (2 H, m, 4-H), 6.78 (2H, t, 5-H), 7.40 (2H, t, 3-H), 8.70 (2H, d, 6-H); δ_{C} 0.4 (CSi₃), 3.2 (SiMe₃), 7.3 (SiMe₃), 8.7 (SiMe₂), 14.3 (SiMe₂), 123.4 (4-C), 131.4 (5-C), 135.9 (3-C), 149.8 (6-C), 174.5 (*ipso*-C); δ_{Si} –7.0, –8.7 and –10.3 (SiMe₃ and SiMe₂). EI-MS: *m/z* 716 (15, M), 701 (6, M – Me), 358 (55, RCu), 342 (70, RCu – CH₄), 294 (55, R), 279 (45, R – Me), 264 (100, R – Me – CH₄), 248 (15), 220 (20), 136 (25), 73 (45, SiMe₃).

[AuC(SiMe₃)₂(SiMe₂C₅H₄N-2)]₂ (3**).** This was prepared similarly from **1** (1.15 mmol) and AuCl·SMe₂ (1.15 mmol) in thf (0.21 g, 37%). Found: C, 33.80; H, 4.85; N, 2.51; C₂₈H₅₆N₂Au₂Si₆ requires C, 34.22; H, 5.09; N, 2.85%. NMR: δ_{H} 0.16 and 0.57 (18 H, s, SiMe₃), 1.24 and 2.13 (6 H, s, SiMe₂), 6.35 (2 H, t, 4-H), 6.77 (2H, t, 5-H), 7.15 (2H, d, 3-H), 7.45 (2H, d, 6-H); δ_{C} –3.41 (CSi₃), 4.2 (SiMe₂), 6.7 (SiMe₂), 7.1 (SiMe₃), 7.4 (SiMe₂), 123.7 (4-C), 133.0 (5-C), 135.4 (3-C), 152.8 (6-C), 173.7 (*ipso*-C); δ_{Si} –2.4, –6.1 and –7.0 (SiMe₃, SiMe₂). EI-MS: *m/z* 982 (5, M), 967 (5, M – Me), 755 (60, R₂Au – 2Me), 350 (20), 294 (70, R), 279 (100, R – Me), 264 (70, R – Me – CH₄), 217 (15), 192 (20), 136 (65), 73 (50, SiMe₃), 57 (60).

[ZnBr{C(SiMe₃)₂(SiMe₂C₅H₄N-2)}]₂ (4**).** This was obtained from **1** (1.42 mmol) and ZnBr₂ (1.42 mmol) in 67% yield; m.p. 265 °C. Found: C, 37.89; H, 6.49; N, 2.99; C₂₈H₅₆N₂Br₂Si₆Zn₂ requires C, 38.19; H, 6.36; N, 3.18%. NMR: δ_{H} 0.28 (36 H, s, SiMe₃), 0.48 (12 H, s, SiMe₂), 6.60 (2 H, t, 4-H), 6.85 (2 H, t, 5-H), 7.03 (2 H, d, 3-H), 8.96 (2 H, d, 6-H); δ_{C} 1.4 (SiMe₃), 3.2 (CSi₃), 6.3 (SiMe₂), 124.1 (4-C), 128.8 (5-C), 137.5 (3-C), 147.5 (6-C), 172.8 (*ipso*-C); δ_{Si} –0.7 (SiMe₂), –3.1 (SiMe₃). EI-MS: *m/z* 439 (5, RZnBr), 424 (75, RZnBr – Me), 264 (100, RH – Me – CH₄), 220 (15), 164 (10), 125 (55), 73 (25, SiMe₃).

Table 2 Summary of crystallographic data for compounds **2–6**

	2 (toluene)	3	4	5	6
Chemical formula	C ₂₈ H ₅₆ Cu ₂ N ₂ Si ₆ ·(C ₇ H ₈)	C ₂₈ H ₅₆ Au ₂ N ₂ Si ₆	C ₂₈ H ₅₆ Br ₂ N ₂ Si ₆ Zn ₂	C ₂₈ H ₅₆ Cd ₂ Cl ₂ N ₂ Si ₆	C ₁₄ H ₂₈ ClHgNSi ₃
Formula weight	808.50	959.20	879.85	884.99	530.68
<i>T</i> /K	173(2)	173(2)	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	<i>C2/c</i> (no 15)	<i>Pca2₁</i> (no 29)	<i>P1</i> (no 2)	<i>P2_{1/c}</i> (no 14)	<i>P2_{1/n}</i> (no 14)
<i>a</i> /Å	23.022(8)	20.7045(6)	9.2402(9)	13.4324(4)	12.5563(3)
<i>b</i> /Å	9.069(6)	11.9894(3)	9.5269(8)	8.8552(3)	12.4249(3)
<i>c</i> /Å	41.20(4)	32.9397(5)	12.2376(11)	18.0063(5)	13.2254(3)
<i>a</i> °	90	90	79.992(6)	90	90
<i>β</i> °	90.47(3)	90	77.626(5)	100.072(2)	92.161(2)
<i>γ</i> °	90	90	87.953(6)	90	90
<i>U</i> /Å ³	8602(10)	8176.8(3)	1036.2(2)	2108.8(1)	2061.84(8)
<i>Z</i>	8	8	1	2	4
<i>μ</i> /mm ⁻¹	1.18	7.36	3.28	1.32	7.76
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.088, 0.215	0.076, 0.176	0.053, 0.136	0.058, 0.151	0.025, 0.064
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.146, 0.278	0.084, 0.181	0.066, 0.145	0.068, 0.161	0.031, 0.068
Meas./indep rflns/ <i>R</i> (int)	5370/5233/0.0833	27361/9715/0.082	7343/4655/0.045	25201/3711/0.104	17731/4880/ 0.043
Rflns with <i>I</i> > 2σ(<i>I</i>)	3361	8892	3806	3155	4353

[CdCl{C(SiMe₃)₂(SiMe₂C₅H₄N-2)}]₂ (5**).** A solution of **1** (0.98 mmol) in thf and CdCl₂ (0.18 g, 0.98 mmol) gave colourless crystals of **5** (0.30 g, 69%); m.p. 296–7 °C (dec). Found: C, 37.81; H, 6.27; N, 3.07; C₂₈H₅₆N₂Cd₂Cl₂Si₆ requires C, 37.97; H, 6.33; N, 3.16%. NMR: δ_H 0.38 (36 H, s, SiMe₃), 0.47 (12 H, s, SiMe₂), 6.55 (2 H, t, 4-H), 6.89 (2 H, t, 5-H), 7.13 (2 H, d, 3-H), 8.81 (2 H, m, 6-H); δ_C 1.3 (CSi₃), 3.4 (SiMe₂), 6.4 (SiMe₃), 123.5 (4-C), 128.9 (5-C), 136.8 (3-C), 148.6 (6-C), 172.6 (*ipso*-C); δ_{Si} -1.7 (²*J*_{SiCd} = 62.5 Hz, SiMe₃), -0.7 (²*J*_{SiCd} = 65 Hz, SiMe₂); δ_{Cd} 305. EI-MS: *m/z* 443 (15, RCdCl), 428 (40, RCdCl - Me), 294 (50, R), 279 (40, R - Me), 264 (100, RH - Me - CH₄), 217 (20), 136 (25), 73 (35, SiMe₃).

HgCl{C(SiMe₃)₂(SiMe₂C₅H₄N-2)} (6**).** A solution of **1** (3.05 mmol) in thf and HgCl₂ (3.05 mmol) gave **6** as large colourless crystals. (1.00 g, 62%); m.p. 129–130 °C. Found: C, 31.54; H, 5.36; N, 2.55; C₁₄H₂₈NClHgSi₃: requires C, 31.66; H, 5.28; N, 2.64%. NMR: δ_H 0.05 (18 H, s, SiMe₃), 0.22 (6 H, s, SiMe₂), 6.60 (2 H, t, 4-H), 6.95 (2 H, t, 5-H), 7.08 (2 H, d, 3-H), 8.68 (2 H, d, 6-H); δ_C 2.6 (SiMe₂), 5.5 (SiMe₃), 22.5 (¹*J*_{SiC} = 35.8 Hz, CSi₃), 113.9 (4-C), 128.7 (5-C), 135.7 (3-C), 148.3 (6-C), 168.1 (*ipso*-C); δ_{Si} -0.9 (SiMe₃), -2.1 (SiMe₂); δ_{Hg} -814.1. EI-MS: *m/z* 531 (3, *M*), 516 (70, *M* - Me), 495 (RHg), 329 (15) 294 (60, R), 279 (15, R - Me), 264 (100, RH - Me - CH₄), 220 (45), 162 (20), 136 (45), 73 (70, SiMe₃), 43 (25).

Crystallography

Data for **2** were collected on an Enraf-Nonius CAD4 diffractometer and for **3–6** on a Kappa CCD diffractometer using Mo-*K*α radiation (λ = 0.71073 Å), and an empirical absorption correction was applied. Further details are given in Table 2. Refinement was based on all *F*² by use of SHELXL-97.⁴⁴ For **2**, the data were affected by peak overlap, due to the long *c* axis, and constraints were placed on the anisotropic displacement parameters by use of DELU. There are two toluene molecules, both on symmetry elements and one disordered. The crystals of **3** were small plates, mostly intergrown, from which a reasonably clean specimen was chosen. There were a few very weak reflections, indicating a *b* axis of 23.98 Å, but analysis with this larger unit cell resulted in a structure with a repeat distance of half that axis. The weak reflections were therefore ignored. After the refinement, there were small residual peaks, which appeared to be low-occupancy images of the molecules reflected through a mirror plane perpendicular to *b*, but only the Au atoms were identifiable and included in the refinement. Only Au and Si atoms were refined anisotropically. There are two independent molecules of similar geometry in the asymmetric unit. In all diagrams, ellipsoids are drawn at 50% level.

CCDC reference numbers 177596–177600.

See <http://www.rsc.org/suppdata/dt/b2/b200473a/> for crystallographic data in CIF or other electronic format.

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