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Syntheses and crystal structures of binuclear gold(I), silver(I) and copper(I) complexes containing bulky pyridyl functionalised alkyl ligands

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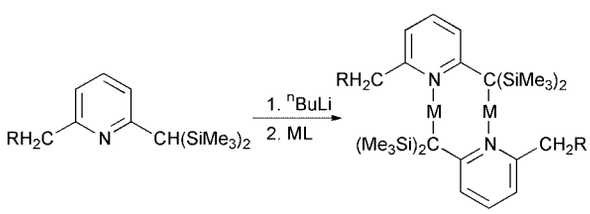
Treatment of (CO)AuCl, CuCl or $AgNO_3$ with 2-LiC($SiMe_3$)$_2$-Py-6-CH_2R gives the binuclear metal compounds [M_2(μ-2-C($SiMe_3$)$_2$-6-CH_2RPy)$_2$] [R = H, M = Au (**1**), Cu (**2**) and Ag (**3**); R = Me_3Si, M = Cu (**4**)]. The dimeric structures of complexes **1**, **2** and **4** have been established by single-crystal X-ray diffraction studies. The complexes are centrosymmetric with each ligand bridging the two metal centres which are in close proximity to each other [M · · · M 2.690(2) Å in **1**, 2.436(1) Å in **2** and 2.431(1) Å in **4**].

Introduction

A large variety of binuclear gold complexes containing two gold(I) atoms held in close proximity by a pair of bifunctional ligands are known. Examples of such ligands include dithiocarbamate,[1] bis(diphenylphosphino)methane,[2] (2-pyridyl)-dimethylphosphine,[3] methylenethiophosphinate[4] and phosphorus bis(ylides).[5,6] The digold(I) complexes exhibit a rich and varied chemistry, undergoing oxidative addition reactions with halogens, pseudohalogens, and, in the case of the bis(ylides), alkyl halides to give either metal–metal bonded digold(II) compounds or heterovalent gold(I)–gold(III) compounds; sometimes both can be isolated depending on the conditions.[4–13] Reaction with two equivalents of halogen can give binuclear gold(III) compounds.[7,14,15] In contrast to the large number of binuclear gold(I) compounds known of this type, very few analogous binuclear copper(I) and silver(I) complexes have been reported and structurally authenticated.[16–18] One of the main reasons for this is their thermal instability and/or susceptibility to photolytic decomposition.[19] By enhancing the bulk/steric hindrance of the bridging ligands and by blocking decomposition pathways, such as β-hydrogen elimination, thermal stability can be greatly increased. Compounds containing Me_3Si substituted alkyls are often much more thermally stable than simple alkyl compounds.[20–22] In our investigations of cyclometallated binuclear gold(I) compounds containing *n*-$MeC_6H_3PPh_2$ (*n* = 3, 4 and 5), we have found marked changes in reactivity when a methyl substituent is introduced *ortho* to the metal centre.[23] A combination of the increased bulk of the extra methyl substituent *and* the presence of Me_3Si substituents in both 2- and 6-positions on a particular ligand should give rise to ligands that are able to stabilise binuclear copper(I) and silver(I) complexes. The results of our continuing[18] investigation of binuclear coinage metal complexes containing the pyridyl functionalised alkyl ligands 2-CH($SiMe_3$)$_2$-6-MePy and 2-CH($SiMe_3$)$_2$-6-CH_2($SiMe_3$)Py ligands are presented here.

Results and discussion

The preparation of the coinage metal complexes **1**–**4** is summarised in Scheme 1. Addition of one equivalent of metal precursor



R = H, M = Au **1**, Cu **2**, Ag **3**

R = Me_3Si, M = Cu **4**

Scheme 1

to a THF solution of the lithiated ligand at −78 °C gives air and moisture stable solids (except for **3**, which is light and air sensitive) of empirical formula [M_2(2-C($SiMe_3$)$_2$-6-CH_2RPy)$_2$] [R = H, M = Au (**1**), Cu (**2**) and Ag (**3**); R = Me_3Si, M = Cu (**4**)] in *ca.* 50% yield. The ^{1}H NMR spectra show the same features for all four complexes: singlets at *ca.* δ 0.38 and 2.5 due to Me_3Si and Me protons, respectively, as well as aromatic multiplets at δ 6.3–7.3. These data are consistent with the proposed dimeric structure, which has been established by X-ray diffraction studies of complexes **1**, **2** and **4**, the molecular structures of which are shown in Figs. 1, 2 and 3, respectively; selected bond distances and angles are collected in Table 1. Compounds **1**–**4** each consist of two metal atoms bridged linearly by a pair of ligands through the pyridyl nitrogen atom and the carbon atom of the di-substituted methylene group. The metal–metal

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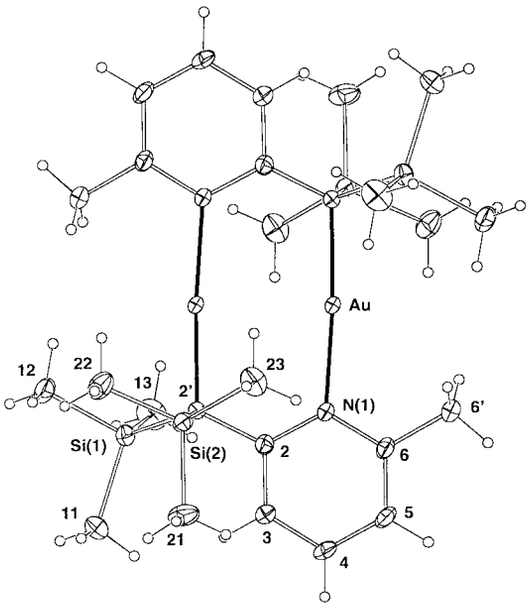

Fig. 1 Molecular structure of **1**.

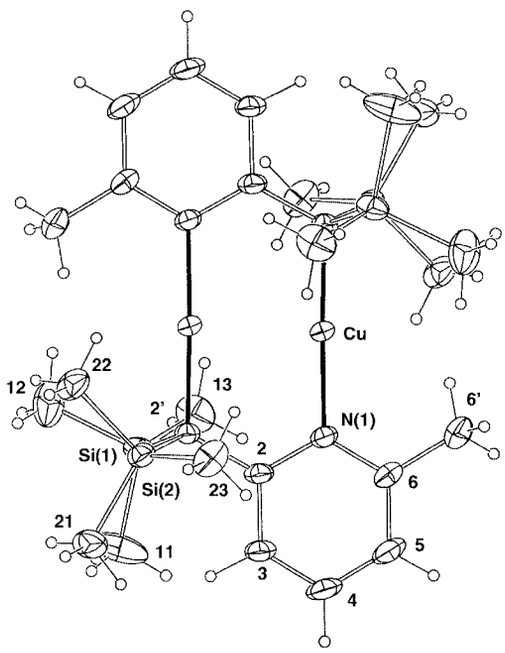

Fig. 2 Molecular structure of **2**.

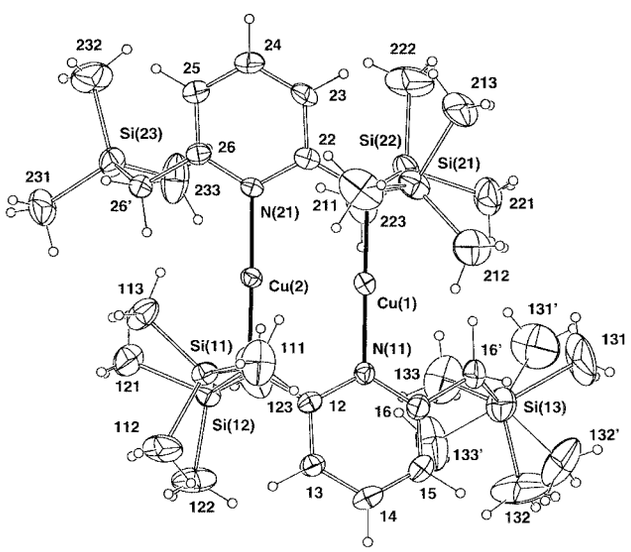

Fig. 3 Molecular structure of **4**.

distances are 2.690(2), 2.436(1) and 2.431(1) Å in **1**, **2** and **4**, respectively. The Au · · · Au distance in **1** is considerably less than that found in elemental gold (2.88 Å) and in binuclear gold(I) complexes containing bridging phosphine ligands (*ca.* 2.86 Å),[23,24] but of similar magnitude to that observed in other binuclear gold(I) complexes containing N-donor ligands.[3,16] Complex **1** represents one of the very few examples of cyclometallated binuclear gold(I) compounds containing alkyl-carbon–gold bonds. Other compounds of this type include the 10 membered ring phosphine complex $[Au_2(\mu\text{-}2\text{-}CH_2C_6H_4\text{-}PPh_2)_2]$[25] and the aforementioned pyridine complex $[Au_2(\mu\text{-}2\text{-}C(Me_3Si)_2Py)_2]$.[16] The Cu · · · Cu separations in **2** and **4** are very similar to that reported for $[Cu_2(\mu\text{-}2\text{-}C(SiMe_3)_2Py)_2]$ (2.412(1) Å),[16,26] and the Cu–C distances are comparable to those found in other copper alkyl complexes where the bonding is also two-electron, two-centred, *e.g.* $[Cu(Me_2P\{CH_2\}_2)_2]$.[27] The Cu–N bond lengths are typical for mononuclear, two-coordinate species containing pyridine ligands,[28] and all other bond lengths and angles are unexceptional. In all three structures the Me_3Si groups are directed away from the metal centres, minimising steric crowding; this is especially evident in complex **4**. Suitable crystals of the silver analogue (**3**) could not be obtained, but the spectral data strongly resembles that of **1** and **2**, so that a similar dimeric structure is proposed.

Of particular interest is the formation of complex **4** by this route. Lithiation of 2-$CH(SiMe_3)_2$-6-$CH_2(SiMe_3)$Py is expected to occur at the mono-substituted carbon atom and not at the $(Me_3Si)_2C$ carbon[29,30] so that a migration of the copper centre must have occurred to give complex **4**. It is most likely that lithiation has occurred at the mono-substituted carbon atom, followed by a copper migration to the thermodynamically more stable $(Me_3Si)_2C$ carbon.[31] However, the exact mechanism of how complex **4** is formed still remains to be fully investigated.

Experimental

General comments

All syntheses were carried out under an atmosphere of dry argon using standard Schlenk techniques, although the solid complexes (except **3**) were air stable once isolated. Solvents were dried over sodium–benzophenone under nitrogen. The ligands, 2-$CH(SiMe_3)_2$-6-MePy and 2-$CH(SiMe_3)_2$-6-$CH_2(SiMe_3)$Py were prepared following literature procedures.[29,30] All other chemicals were commercially available (Aldrich and Strem) and used as received. ^{1}H NMR (300 MHz) spectra were measured on a Bruker 250 WM instrument in C_6D_6 at room temperature. Chemical shifts (δ) are given in ppm internally referenced to residual solvent signals (δ 7.15). IR spectra were recorded on a Perkin Elmer 1725X instrument as KBr disks. Melting points were obtained on a Gallenkamp melting point apparatus in open glass capillaries. Elemental analysis data were obtained for complexes **2** and **3**. However, complexes **1** and **4** did not give reliable analytical data.

Preparations

$[Au_2(2\text{-}C(SiMe_3)_2\text{-}6\text{-}MePy)_2]$ 1. ^{n}BuLi (1.6 M in hexane) (5.3 mL, 3.3 mmol) was added to a cooled THF solution of 2-$CH(SiMe_3)_2$-6-MePy (0.76 g, 3 mmol). The resulting orange solution was added to a THF suspension of (CO)AuCl (0.80 g, 3 mmol) cooled to −78 °C. The mixture was stirred for 15 min at this temperature while protected from light. After warming to room temperature, the solvent was removed *in vacuo* and the dark brown oil extracted with hexane. Cooling the hexane extract to −30 °C afforded light brown crystals of complex **1**. The yield was 1.50 g (55%). Mp 127 °C (dec.); δ_H 0.38 [18H, s, 2 Me_3Si], 2.55 [3H, s, Me], 6.35–7.28 [3H, m, arom.].

$[Cu_2(2\text{-}C(SiMe_3)_2\text{-}6\text{-}MePy)_2]$ 2. This compound was prepared as described above using CuCl as metal precursor. The yield

Table 1 Selected bond lengths and angles in complexes **1**, **2** and **4**. Atoms in the alternate segment are italicised

	1	**2**	**4**
Distances (Å)			
M · · · M	2.690(2)	2.436(1)	2.431(1)
M–N(1)	2.111(5)	1.936(3)	1.931(3), 1.933(3)
M–*C*(2′)	2.084(5)	1.965(3)	1.959(5), 1.957(4)
Angles (°)			
C(2′)–M–N(1)	173.6(2)	177.9(2)	174.0(2), 172.7(1)
M–N(1)–C(2)	121.6(4)	118.4(3)	116.8(3), 116.8(3)
M–N(1)–C(6)	117.6(4)	121.8(3)	121.8(3), 121.9(3)
C(2)–N(1)–C(6)	199.9(5)	119.8(3)	119.3(4), 119.7(4)
N(1)–C(2)–C(2′)	122.9(6)	121.5(3)	120.1(3), 120.3(4)
C(2′)–C(2)–C(3)	119.2(6)	120.4(4)	122.0(4), 121.8(5)
C(2)–C(2′)–*M*	115.4(4)	118.0(3)	118.6(3), 118.3(3)
Si(1)–C(2′)–*M*	101.6(3)	100.4(2)	101.5(2), 101.8(2)
Si(2)–C(2′)–*M*	101.5(3)	102.5(2)	101.3(2), 100.7(2)
C(2)–C(2′)–Si(1)	114.2(5)	109.3(3)	111.5(3), 111.4(3)
C(2)–C(2′)–Si(2)	106.2(4)	107.0(4)	107.2(3), 107.4(3)
Si(1)–C(2′)–Si(2)	117.7(3)	120.1(3)	116.8(2), 117.2(3)
Atom deviations (Å) from the Py plane			
δM	0.49(1)	0.002(7)	0.567(6), 0.558(6)
δM′	0.39(1)	0.055(9)	0.171(8), 0.181(9)
δSi(1)	0.75(1)	−1.561(9)	1.218(8), 1.165(9)
δSi(2)	−2.10(1)	1.673(9)	−1.878(7), −1.911(7)
δSi(3)	—	—	−1.841(9), −1.756(8)

of greenish crystals was 2.1 g (58%). Mp 163 °C (dec.); Found C, 49.68, H, 7.80, N, 4.29%; $C_{26}H_{48}N_2Si_2Cu_2$ requires C, 49.72, H, 7.70, N, 4.46%; δ_H 0.39 [18H, s, 2 Me_3Si], 2.46 [3H, s, Me], 6.29–7.34 [3H, m, arom.].

[Ag_2(2-C($SiMe_3$)$_2$-6-MePy)$_2$] 3. This compound was also prepared as described above using $AgNO_3$ as metal precursor. The compound is very light and air sensitive and readily decomposed at room temperaure in solution. The solid can be stored under argon protected from light for several days. The yield of colourless crystals was 3.7 g (52%). Mp 29 °C (dec.); Found C, 43.18, H, 6.74%; $C_{26}H_{48}N_2Si_2Ag_2$ requires C, 43.57, H, 6.75%; δ_H 0.38 [18H, s, 2 Me_3Si], 2.53 [3H, s, Me], 6.25–7.18 [3H, m, arom.].

[Cu_2(2-C($SiMe_3$)$_2$-6-CH_2($SiMe_3$)Py)$_2$] 4. ^{n}BuLi (1.6 M in hexane) (2.75 mL, 4.4 mmol) was added to a cooled THF solution of 2-CH($SiMe_3$)$_2$-6-CH_2($SiMe_3$)Py (1.3 g, 4 mmol). The resulting orange solution was added to a THF suspension of CuCl (0.4 g, 4 mmol) cooled to −78 °C. The mixture was stirred for 15 min at this temperature while protected from light. After warming to room temperature, the solvent was removed *in vacuo* and the dark green oil extracted with hexane. Cooling the hexane extract to −30 °C gave 1.9 g green crystals of **4** in 61% yield. Mp 165 °C; δ_H 0.05 [9H, s, Me_3Si], 0.41 [18H, s, 2 Me_3Si], 2.75 [3H, s, Me], 6.40–7.17 [3H, m, arom.].

X-Ray crystallography

General. Unique single counter diffractometer data sets were measured (monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å, $2\theta/\theta$ scans, *T ca.* 295 K) yielding *N* independent reflections, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full matrix least squares refinement after Gaussian absorption correction, refining anisotropic displacement parameter forms for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimated values. Conventional residuals on |*F*| are quoted at convergence, statistical weight derivatives of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being employed. Pertinent results are given below and in Table 1 and the figures, which display 20% displacement ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å; carbon atoms are denoted by number only. Neutral atom complex scattering factors were employed within the context of the Xtal 3.4 program system.[32]

$C_{26}H_{48}Au_2N_2Si_4$ ***1****.* *M* = 895.0. Triclinic, space group $P\bar{1}$ (no. 2), *a* = 11.953(2), *b* = 8.732(8), *c* = 8.416(7) Å, *α* = 81.40(7), *β* = 76.82(5), *γ* = 72.22(5)°, *V* = 811 Å^3, D_c (*Z* = 1 dimer) = 1.832 g cm^{-3}, μ_{Mo} = 92 cm^{-1}; specimen: 0.58 × 0.42 × 0.14 mm, $A^*_{min,max}$ (analytical correction) = 3.4, 13.7. $2\theta_{max}$ = 65°; *N* = 4722, N_o = 4188; *R* = 0.038, R_w = 0.045.

$C_{26}H_{48}Cu_2N_2Si_4$ ***2****.* *M* = 628.1. Triclinic, space group $P\bar{1}$, *a* = 11.494(5), *b* = 9.257(3), *c* = 9.058(4) Å, *α* = 113.53(3), *β* = 97.07(4), *γ* = 104.56(3)°, *V* = 828 Å^3. D_c (*Z* = 1 dimer) = 1.260 g cm^{-3}. μ_{Mo} = 14.5 cm^{-1}; specimen: 0.34 × 0.24 × 0.60 mm, $A^*_{min,max}$ = 1.39, 1.66. $2\theta_{max}$ = 60°; *N* = 4803, N_o = 3349; *R* = 0.065, R_w = 0.073.

Variata. The two above structures, despite similar cell dimensions, differ sufficiently in atom disposition to be considered not isomorphous. In the latter, a second hemisphere of data to $2\theta_{max}$ = 50° was merged with the first, R_{int} = 0.067.

$C_{32}H_{64}Cu_2N_2Si_6$ ***4****.* *M* = 772.5. Monoclinic, space group $P2_1/c$ (no. 14), *a* = 12.156(5), *b* = 20.980(10), *c* = 18.848(6) Å, *β* = 110.78(3)°, *V* = 4494 Å^3. D_c (*Z* = 4 dimers) = 1.142 g cm^{-3}. μ_{Mo} = 11.7 cm^{-1}; specimen: 0.58 × 0.45 × 0.36 mm, $A^*_{min,\ max}$ = 1.36, 1.66. $2\theta_{max}$ = 50°; *N* = 7892, N_o = 4838; *R* = 0.048, R_w = 0.051.

Variata. One of the Me_3Si groups (no. 13) was modelled as disordered about its Si–C attachment, site occupancies of the methyl groups set at 0.5 after trial refinement. A hemisphere of data was measured (12497 reflections; R_{int} = 0.052).

CCDC reference numbers 165353–165355.

See http://www.rsc.org/suppdata/dt/b1/b103865f/ for crystallographic data in CIF or other electronic format.

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