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A silver(I) center solely bonded to four gold(I) atoms

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(Trimethylsilylmethyl)gold(I) complexes $[\{Au(CH_2SiMe_3)\}_2(\mu\text{-}P{-}P)]$ (P–P = dppm or dppe) reacted with silver derivatives ($AgOClO_3$ or $AgOSO_2CF_3$) affording trinuclear $[Au_2Ag(CH_2SiMe_3)_2(\mu\text{-}P{-}P)A]$ (A = $OClO_3$ or OSO_2CF_3) or pentanuclear $[Au_4Ag(CH_2SiMe_3)_4(\mu\text{-}dppm)_2]SO_3CF_3$ complexes; the cation of the latter consists of a novel Au_4Ag core with four Ag^I–Au^I non-supported bonds.

In the recently developed field of gold–silver heteronuclear chemistry,[1] only a few complexes containing non-supported silver–gold bonds have been reported.[2–10] Most of them are gold clusters[2–7] where the gold and silver atoms can be formally considered in an oxidation state between 0 and 1. Gold(I)–silver(I) compounds with non-supported bonds $\{[AuAg(C_6F_5)_2L_2]_n$ (*e.g.* L = tetrahydrothiophene or benzene) or $[Au_2Ag_2(CH_2PPh_3)_4(OClO_3)_4]\}$ have been prepared by reaction of $[NBu_4][Au(C_6F_5)_2]$[9] or $[Au(CH_2PPh_3)_2]ClO_4$[10] with appropriate silver derivatives. The gold centers in these complexes donate electron density to the silver atom, which is also stabilized by co-ordination to other C-, P-, O- or S-donor ancillary ligands.

In order to extend the synthesis of these type of complexes we have selected as starting materials the previously reported bimetallic gold(I) compounds $[\{Au(CH_2SiMe_3)\}_2(\mu\text{-}P{-}P)]$ (P–P = $Ph_2PCH_2PPh_2$, dppm; $Ph_2PCH_2CH_2PPh_2$, dppe).[11] The trimethylsilylmethyl group should confer a higher electron density to the gold atom than those previously chosen for the unbridged gold–silver bond formation mentioned above. Firstly, the CH_2SiMe_3 group is less electron withdrawing than the pentafluorophenyl ligand ($C_6F_5^-$) and secondly, the silicon-based group gives neutral gold compounds instead of the cationic ones obtained with ylide ligands (CH_2PR_3). In addition, the well studied β-effect of the $SiMe_3$ group[12] should presumably give rise to more stable organometallic complexes.

Herein we report on the synthesis of novel heteronuclear compounds containing Au_2Ag, Au_4Ag and Au_4Cu cores. The crystal structure of the complex $[Au_4Ag(CH_2SiMe_3)_4(\mu\text{-}dppm)_2]SO_3CF_3$ **3** confirms the presence of a silver(I) center solely bonded to four gold atoms. Only recently, one example of a naked silver atom bonded to six gold(I) centers has been reported.[13]

Reactions of the compounds $[\{Au(CH_2SiMe_3)\}_2(\mu\text{-}P{-}P)]$ (P–P = dppm or dppe)[11] with nearly 'naked' silver centres ($AgOClO_3$ or $AgOSO_2CF_3$) in dichloromethane–diethyl ether (1 : 1 molar ratio, Scheme 1) afford trinuclear yellow complexes of stoichiometry $[Au_2Ag(CH_2SiMe_3)_2(\mu\text{-}P{-}P)A]$ [P–P = dppm, A = $OClO_3$ (**1a**), A = OSO_2CF_3 (**1b**); P–P = dppe, A = $OClO_3$ (**2**)]. The IR spectra of complexes **1a**, **1b** and **2** show absorptions that can be assigned to covalent $OClO_3$[14] and OSO_2CF_3[15] groups. The ^1H NMR spectra are in accordance with the proposed formulation.‡ Interestingly, the resonances due to the protons of the CH_2Si, $SiMe_3$ and PCH_2 fragments appear to be displaced further downfield than those found in the spectra of the dinuclear gold starting materials. The $^{31}P\text{-}\{^1H\}$ NMR spectra follow a similar behavior. The positive-ion liquid secondary ionization mass spectra (nitrobenzyl alcohol as matrix) of the complexes **1a**, **1b** and **2** show the parent ion with loss of the anions ClO_4^- and $SO_3CF_3^-$ at *m*/*z* (%) = 1061 (100) **1a**, 1061 (100) **1b** and 1075 (90) **2**. It is noteworthy that among other peaks, those corresponding to pentanuclear $[Au_4Ag(CH_2SiMe_3)_4(\mu\text{-}P{-}P)_2]^+$ species at *m*/*z* (%) = 2014 (3) **1a** and **1b** and 2042 (4) **2**, are observed indicating that such species could be stable.

In order to prepare these pentanuclear complexes, reactions of $[\{Au(CH_2SiMe_3)\}_2(\mu\text{-}P{-}P)]$ with $AgOClO_3$ or $AgOSO_2CF_3$ (2 : 1) were carried out. Only in the case of P–P = dppm and $AgOSO_2CF_3$ could a pure pentanuclear white compound $[Au_4Ag(CH_2SiMe_3)_4(\mu\text{-}dppm)_2]SO_3CF_3$ **3** be isolated and characterized (Scheme 1). The ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectra of **3** show all the signals slightly displaced downfield from the dinuclear starting material.‡ In this case, absorptions due to anionic triflate[16] can be observed in the IR spectra. The mass spectrum displays the parent ion $[M - SO_3CF_3]^+$ at *m*/*z* (%) = 2014 (6).

The crystal structure of the cation of compound **3** is shown in Fig. 1.§ It consists of two $[\{Au(CH_2SiMe_3)\}_2(\mu\text{-}dppm)]$ units (starting material) directly bonded to a silver center through four gold–silver bonds. The novel Au_4Ag core exhibits a distorted tetrahedral environment for the silver atom. The four silver–gold distances lie between the values of 2.7179(13) and 2.7822(13) Å and therefore, can be considered as formal silver–gold bonds.[1–3] Moreover, these values are almost identical to those found in the three examples of non-supported silver(I)–gold(I) bonds described in the literature.[9,10,13] The dinuclear $[\{Au(CH_2SiMe_3)\}_2(\mu\text{-}dppm)]$ units can be described as 'bidentate ligands' whose bite angles are tighter [average 72.30(3)°] than the other two Au–Ag–Au angles [average 112.99(4)°]. The linear co-ordination around the gold centres and the values of Au–P [average 2.277(4) Å] and Au–C [2.067(13) Å] are similar

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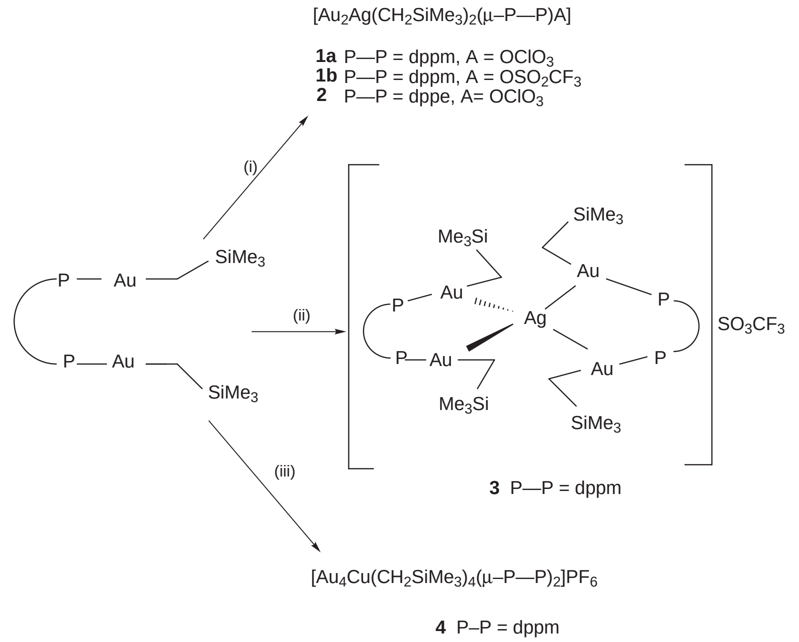
‡ Selected NMR data. **1a**: ^1H (300 MHz, $CDCl_3$, $SiMe_4$), δ 3.83 (t, 2 H, PCH_2P, $^2J_{PH}$ 11.4 Hz), 1.05 (s br, 4 H, CH_2Si), 0.06 [s, 18 H, $Si(CH_3)_3$]; $^{31}P\text{-}\{^1H\}$ (120 MHz, $CDCl_3$, H_3PO_4), δ 38.0 (s, dppm). **1b**: ^1H, δ 3.66 (t, 2 H, PCH_2P, $^2J_{PH}$ 11.2 Hz), 0.93 (s br, 4 H, CH_2Si), 0.05 [s, 18 H, $Si(CH_3)_3$]; $^{31}P\text{-}\{^1H\}$ δ 37.3 (s, dppm). **2**: ^1H, δ 2.69 (d, 4 H, PCH_2, $^2J_{PH}$ 6.2), 0.87 (d br, 4 H, CH_2Si, $^3J_{PH}$ 3.6 Hz), 0.05 [s, 18 H, $Si(CH_3)_3$]; $^{31}P\text{-}\{^1H\}$ δ 44.1 (s, dppe). **3**: ^1H, δ 3.52 (t, 4 H, PCH_2P, $^2J_{PH}$ 10.9 Hz), 0.87 (s br, 8 H, CH_2Si), 0.06 [s, 36 H, $Si(CH_3)_3$]; $^{31}P\text{-}\{^1H\}$ δ 37.1 (s, dppm). **4**: ^1H, δ 3.51 (t, 4 H, PCH_2P, $^2J_{PH}$ 9.0), 0.86 (s br, 8 H, CH_2Si), 0.11 [s, 36 H, $Si(CH_3)_3$]; $^{31}P\text{-}\{^1H\}$ δ 35.6 (s, dppm), −143.5 (sept, $^1J_{PF}$ 714 Hz, PF_6).

§ Crystal data for compound **3**·$2CH_2Cl_2$: $C_{69}H_{92}AgAu_4Cl_4F_3O_3P_4SSi_4$, $M = 2332.26$, monoclinic, space group $P2_1/n$, $a = 16.695(3)$, $b = 24.469(5)$, $c = 21.076(4)$ Å, $\beta = 101.44(3)°$, $U = 8439(3)$ Å^3, $Z = 4$, $\mu = 7.489$ mm^{-1}, $F(000) = 4480$, $T = -100$ °C. 14 067 Reflections were collected of which 10 901 were independent (R_{int} 0.084). The final $wR(F^2)$ was 0.106 for 10 891 reflections, 823 parameters and 489 restraints, with a conventional $R(F)$ 0.047. CCDC reference number 186/916. See http://www.rsc.org/suppdata/dt/1998/1083/ for crystallographic files in .cif format.



Scheme 1 (i) $AgOClO_3$ or $AgOSO_2CF_3$; (ii) $\frac{1}{2}AgOSO_2CF_3$; (iii) $\frac{1}{2}[Cu(NCMe)_4]PF_6$

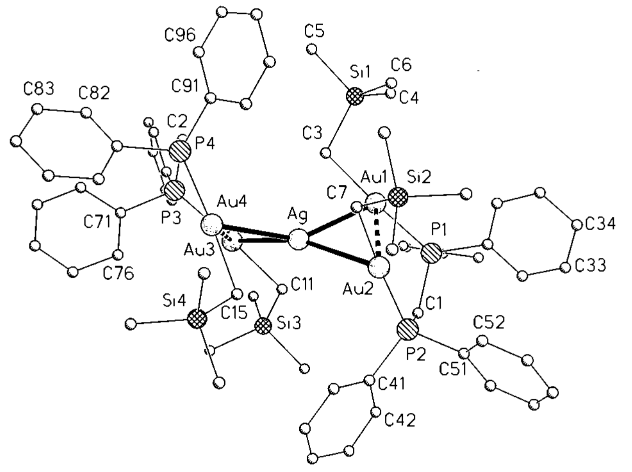


Fig. 1 The structure of the cation of complex **3** in the crystal. Radii are arbitrary, H atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag–Au1 2.7374(14), Ag–Au2 2.7714(13), Ag–Au3 2.7822(13) and Ag–Au4 2.7179(13), Au1–Au2 3.2170(9), Au3–Au4 3.2773(12); Au1–Ag–Au2 71.46(3), Au3–Ag–Au4 73.14(4), Au2–Ag–Au4 119.36(5), Au1–Ag–Au3 106.62(4), C3–Au1–P1 172.4(4), C7–Au2–P2 175.8(4), C11–Au3–P3 175.2(4), C15–Au4–P4 175.8(4)

to those previously reported. Only the carbon atom of the methylene group of one trimethylsilylmethyl ligand displays a shorter distance to the silver center than the others [Ag–C11 = 2.645(14) Å]. We cannot conclude whether or not this interaction is due to either electronic or packing effects, as the distance is too long to be considered a real Ag^I–C bond.

Reactions with $[Cu(NCMe)_4]PF_6$ (in order to prepare similar tri- and penta-metallic compounds), always gave the pentanuclear $[Au_4Cu(CH_2SiMe_3)_4(\mu\text{-dppm})_2]PF_6$ complex **4**, independently of the molar ratio employed (1 : 1 or 2 : 1). The ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectra of **4** show the signals assignable to CH_2SiMe_3 and dppm ligands slightly displaced downfield in comparison to those corresponding to the binuclear gold(I) starting material.‡ The mass spectra displays the parent ion $[M - PF_6]^+$ at m/z (%) = 1967 (1). All these data suggest a structure for this complex similar to that of the silver–gold derivative **3**.

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