# Self-assembly of triatomic gold units as supporting frames for a large gold diphenylphosphinite cage molecule†

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A novel hexanuclear cage-type double-decker cation [FB-$(OPPh_2Au)_3Cl_3(AuPPh_2O)_3BF]^+$ is obtained in high yield as the tetrafluoroborate salt from a dinuclear diphenyl-phosphinous acid complex $[Ph_2P(OH)AuCl]_2$ upon treatment with $BF_3 \cdot OEt_2$.
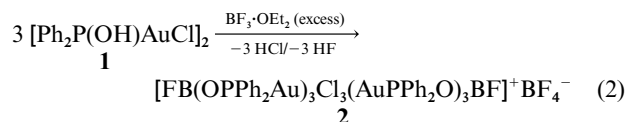
Intra- and inter-molecular metal–metal contacts between the closed-shell Au(I) centres of two-coordinate gold complexes are now recognized to contribute significantly to the stoichiometry, structure and conformation of all compounds of this type.[1–3] The energy associated with these interactions is similar to the energetics of hydrogen bonds,[4–9] and therefore this phenomenon has a great influence on the molecular and supramolecular chemistry of gold.[10] Small complex molecules are found to associate into pairs, rings, chains, or multidimensional frameworks the structural pattern of which is often solely determined by "aurophilic" Au···Au attractions.[11] There are also systems where hydrogen bonding and aurophilic bonding are cooperative forces.[12,13]

We now report another striking case where the build-up of gold–gold contacts induces the formation of large cage-type molecules in which two Au₃-triples represent supporting framework units.

The reaction of diphenylphosphinous acid with chloro-(dimethyl sulfide)gold(I) in dichloromethane at room temperature gives the 1:1 complex $[Ph_2P(OH)AuCl]_2$ **1**, with liberation of dimethyl sulfide [eqn. (1)]. The colourless product (93%

$$2(Me_2S)AuCl + 2Ph_2P(O)H \xrightarrow[-2\,Me_2S]{CH_2Cl_2} [Ph_2(OH)AuCl]_2 \quad (1)$$

**1**
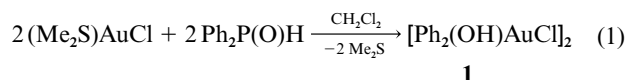
yield, mp 128 °C) has been fully characterized by standard analytical and spectroscopic data.‡ In the crystal (triclinic, space group $P\bar{1}$, $Z = 4$),§ the compound is a dimer the monomeric units of which are tied together by a central Au···Au bond [3.1112(7) Å] and two peripheral O–H···Cl hydrogen bonds (Fig. 1). It is obvious that the two Cl–Au–P units are bent to allow a close contact of the metal atoms. The structure approaches quite closely non-crystallographic twofold symmetry as shown in Fig. 2. Related structures have recently been found for compounds of the type $[R_2P(OH)\text{–}Au\text{–}P(O)R_2]_2$.[13]

$$3[Ph_2P(OH)AuCl]_2 \xrightarrow[-3\,HCl/-3\,HF]{BF_3 \cdot OEt_2\ (excess)}$$

**1**

$$[FB(OPPh_2Au)_3Cl_3(AuPPh_2O)_3BF]^+BF_4^- \quad (2)$$

**2**

Treatment of compound **1** with an excess of $BF_3 \cdot OEt_2$ in dichloromethane at 20 °C leads to the liberation of HCl and HF, the latter being trapped by the excess $BF_3$ to give $HBF_4$ and $BF_4^-$ counter ions. The net reaction is represented by eqn. (2). The only gold-containing product in this reaction, **2**, is isolated almost quantitatively (96% yield) as a colourless, crystalline solid (mp 152 °C with decomposition), soluble in dichloromethane. The solutions are stable only at lower temperatures and the NMR spectra show a singlet resonance for $^{31}P$ and two singlet $^{11}B$ resonances (intensity ratio 2:1). There is only one
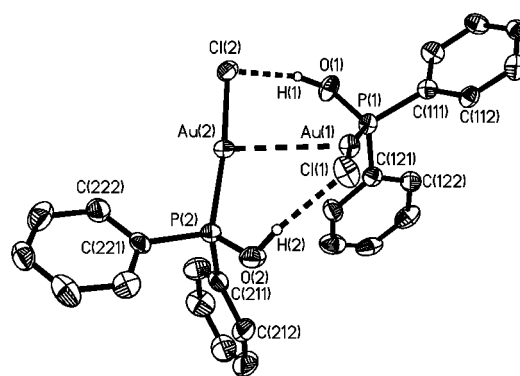


**Fig. 1** Molecular structure of compound **1** (ORTEP[20] drawing with 50% probability ellipsoids, C–H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Au(1)–P(1) 2.218(2), Au(1)–Cl(1) 2.306(2), P(1)–O(1) 1.597(5), Au(1)···Au(2) 3.1112(7), Au(2)–P(2) 2.224(2), Au(2)–Cl(2) 2.309(2), P(2)–O(2) 1.582(6); P(1)–Au(1)–Cl(1) 169.18(7), P(2)–Au(2)–Cl(2) 170.85(7); hydrogen bridges: O(1)––H(1)···Cl(2): O(1)–H(1) 0.986, H(1)···Cl(2) 2.029, O(1)···Cl(2) 2.994; O(1)–H(1)···Cl(2) 165.6; O(2)–H(2)···Cl(1): O(2)–H(2) 0.921, H(2)···Cl(1) 2.105, O(2)···Cl(1) 3.004; O(2)–H(2)···Cl(1) 168.1.
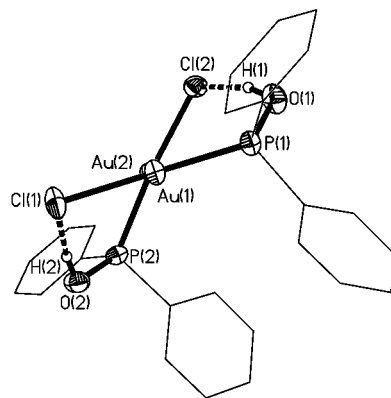


**Fig. 2** Projection of the molecular structure of compound **1** along the Au(1)···Au(2) axis.

set of phenyl $^{13}C$ and $^1H$ resonances with the expected $^1H$- and $^{13}C\text{-}^{31}P$ splittings, respectively.‡ These data suggest a very high symmetry for the components of the product in solution.

Crystals of **2**·$3CH_2Cl_2$ (from $CH_2Cl_2$–$Et_2O$, hexagonal, space group $P6_3/m$, $Z = 2$)§ contain cage-like hexanuclear cations with crystallographically imposed point group $C_{3h}$ symmetry (Fig. 3). At the opposite ends of the cation two BF bridgehead units are each connected to three diphenylphosphinite units via the oxygen atoms. The tentacles of the resulting tripodal donor anions $[FB(OPPh_2)_3]^-$ are attached via their phosphorus atoms to three V-shaped digoldchloronium groups $[Au_2Cl]^+$ to close three 16-membered rings which have only the two BF bridge-heads in common. In the lattice the $BF_4^-$ counter ions are disordered and associated with the $CH_2Cl_2$ molecules via weak F···H–C hydrogen bonds (virtual $C_{3h}$ symmetry).

The structure of the cation is remarkable mainly for two
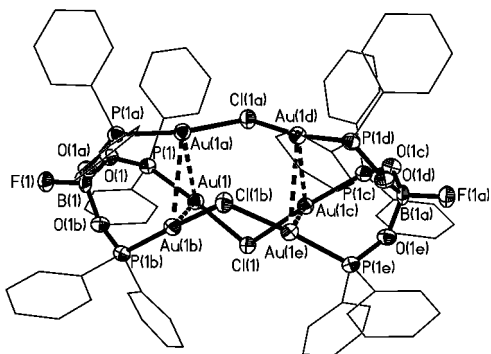
**Fig. 3** Molecular structure of the cation of compound **2** (ORTEP drawing with 50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Au(1)–P(1) 2.238(2), Au(1)–Cl(1) 2.357(2), Au(1)···Au(1a) 3.1725(5), P(1)–O(1) 1.576(5), O(1)–B(1) 1.464(7), B(1)–F(1) 1.38(2); P(1)–Au(1)–Cl(1) 171.38(8), Au(1)–Cl(1)–Au(1c) 106.51(10), Au(1a)···Au(1)···Au(1b) 60.0.
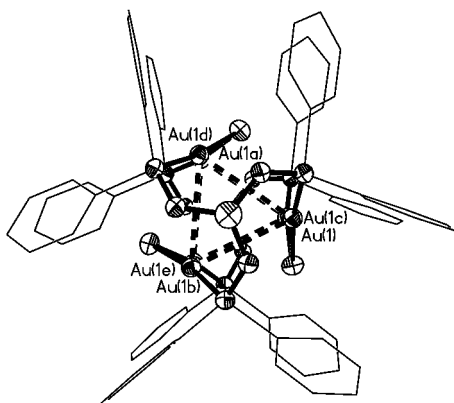


**Fig. 4** Projection of the molecular structure of the cation of compound **2** along the threefold axis.

reasons. (1) The gold atoms are arranged in two triangular groups with short Au···Au contacts [3.1725(5) Å]. These two units clearly stabilize the framework of the cage like two rings of a barrel. The same phenomenon, but with only one $Au_3$-triple, has recently been observed in the structure of the trinuclear cation $[FB(OPPh_2AuPPh_2O)_3BF]^+$.[14] (2) The two triangles of gold atoms, which together form a trigonal prism, are linked through three chloride anions which are thus converted into di(gold)chloronium centres already known in salts of the type $[Cl(AuPR_3)_2]^+$.[15] The Au–Cl–Au angles in **2** [106.51(10)°] are not as small as in open-chain reference compounds [82.7(2)° for R = Ph],[16] but probably still small enough to allow some weak Au···Au bonding. The overall double decker arrangement may thus be taken as a hexanuclear gold cluster with three chlorine atoms bridging the three vertical edges of the trigonal prism (Fig. 3 and 4). Triangular $Au_3$ units have previously been encountered with various other tripodal ligands.[9,14,17–19]

The mechanism of the formation of **2** probably involves stepwise substitution of fluoride in the $BF_3 \cdot OEt_2$ agent by phosphinite nucleophiles $[ClAuPPh_2O]^-$. The second and third steps are increasingly promoted by the opportunity to form pairs and triples of gold atoms. The reaction is terminated by closure of the cluster *via* only three chloride anions. The prismatic unit $Au_3Cl_3Au_3$ is remarkably robust and withstands attack by HCl and $HBF_4$, the by-products of the reaction. All P–Au–Cl units are close to linear, but nevertheless bent in the direction required for intimate Au···Au interactions.

## Acknowledgements

## Notes and references

† Dedicated to Professor E. Niecke on the occasion of his 60th birthday.

‡ Preparations. **1**: (Me$_2$S)AuCl (177 mg, 0.60 mmol) and Ph$_2$P(O)H (121 mg, 0.60 mmol) were dissolved in CH$_2$Cl$_2$ (15 mL) and the resulting mixture was stirred for 2 h at 20 °C. The solvent was evaporated under vacuum to leave a volume of 3 mL, and pentane (30 mL) was added to precipitate a white solid, which was recrystallized from CH$_2$Cl$_2$–pentane to give colourless crystals. Yield 243 mg, 93%; mp 128 °C, stable to air and moisture, soluble in tetrahydrofuran, di- and tri-chloromethane, and insoluble in diethyl ether and pentane. $^1$H NMR (CDCl$_3$, 20 °C): δ 8.70 (br s, OH); 7.21–7.91 (m, C$_6$H$_5$). $^{13}$C-{$^1$H} NMR (CDCl$_3$, 20 °C): δ 134.7 (d, $^1J_{PC}$ = 74.4, i-C$_6$H$_5$), 132.1 (d, $^4J_{PC}$ = 2.3, p-C$_6$H$_5$), 131.4 (d, $^2J_{PC}$ = 16.1, o-C$_6$H$_5$), 128.8 (d, $^3J_{PC}$ = 13.0 Hz, m-C$_6$H$_5$). $^{31}$P-{$^1$H} NMR (CDCl$_3$, 20 °C): δ 90.4 (s). MS (FAB): m/z 1000 [{Ph$_2$P(OH)}$_3$Au$_2$]$^+$, 833 [2M − Cl]$^+$, 601 [{Ph$_2$P(OH)}$_2$Au]$^+$, 399 [M − Cl]$^+$, 202 [M − AuCl]$^+$ (Found: C, 34.11; H, 2.79. Calc. for C$_{12}$H$_{11}$AuClOP·0.125C$_5$H$_{12}$: C, 34.18; H, 2.84%).

**2**: a solution of compound **1** (140 mg, 0.32 mmol) in CH$_2$Cl$_2$ (10 mL) was treated with 1 mL of BF$_3$·OEt$_2$ for 2 h at 20 °C. The solvent was evaporated to leave a volume of 2 mL, and Et$_2$O was added to precipitate the product **2**, which was recrystallized from CH$_2$Cl$_2$–Et$_2$O at 4 °C to give colourless crystals. Yield 135 mg, 96%; mp 152 °C (decomp.), stable to air and moisture, soluble in tetrahydrofuran and methanol, and insoluble in diethyl ether and pentane. Product **2** decomposes slowly in dichloromethane and rapidly in chloroform, at 20 °C. $^1$H NMR (CD$_2$Cl$_2$, 20 °C): δ 7.25–8.00 (m, C$_6$H$_5$). $^{13}$C-{$^1$H} NMR (CD$_2$Cl$_2$, 20 °C): δ 132.6 (s, p-C$_6$H$_5$), 131.2 (d, $^2J_{PC}$ = 16.9, o-C$_6$H$_5$), 128.9 (d, $^3J_{PC}$ = 13.8 Hz, m-C$_6$H$_5$), i-C$_6$H$_5$ not detected. $^{31}$P-{$^1$H} NMR (CD$_2$Cl$_2$, 20 °C): δ 82.3 (s). $^{11}$B-{$^1$H} NMR (CD$_2$Cl$_2$, 20 °C): δ −0.75 [s, (PO)$_3$BF], −1.05 (s, BF$_4^-$) (Found: C, 32.45; H, 2.44. Calc. for C$_{72}$H$_{60}$Au$_6$B$_3$Cl$_3$-F$_6$O$_6$P$_6$: C, 32.74; H, 2.29%).

§ Crystal structure determinations. Crystal data for C$_{12}$H$_{11}$AuClOP **1**. $M_r$ = 434.59, colorless crystals (0.45 × 0.35 × 0.30 mm), triclinic, a = 10.357(2), b = 10.806(2), c = 11.689(2) Å, α = 101.18(1), β = 98.49(2), γ = 98.00(2)°, space group P$\bar{1}$, Z = 4, V = 1250.2(4) Å$^3$, $\rho_{calc}$ = 2.309 g cm$^{-3}$, F(000) = 808; T = −78 °C. Data were corrected for Lorentz, polarization, and absorption effects [μ(Mo-Kα) = 120.83 cm$^{-1}$]. 5436 measured [(sin θ/λ)$_{max}$ = 0.64 Å$^{-1}$], 5435 unique reflections ($R_{int}$ = 0.0058); 289 refined parameters, wR2 = 0.0918, R = 0.0361 for 5166 reflections with $F_o \geq 4\sigma(F_o)$ used for refinement.

Crystal data for C$_{75}$H$_{66}$Au$_6$B$_3$Cl$_9$F$_6$O$_6$P$_6$ (**2**·3CH$_2$Cl$_2$), $M_r$ = 2896.38, colorless crystals (0.40 × 0.35 × 0.35 mm), hexagonal, a, b = 15.709(1), c = 23.705(1) Å, Z = 2, V = 5066.0(5) Å$^3$, $\rho_{calc}$ = 1.899 g cm$^{-3}$, F(000) = 2700; T = −77 °C. Data were corrected for Lorentz, polarization, and absorption effects [μ(Mo-Kα) = 90.40 cm$^{-1}$]. 7974 measured [(sin θ/λ)$_{max}$ = 0.64 Å$^{-1}$], 3755 unique reflections ($R_{int}$ = 0.0502); 175 refined parameters, wR2 = 0.0954, R = 0.0363 for 3265 reflections with $F_o \geq 4\sigma(F_o)$ used for refinement. CCDC reference number 186/1260. See http://www.rsc.org/suppdata/dt/1999/111/ for crystallographic files in .cif format.

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