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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 diphenylphosphinous 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 Au_3-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% 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 $[R_2P(OH)–Au–P(O)R_2]_2$.[13]

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

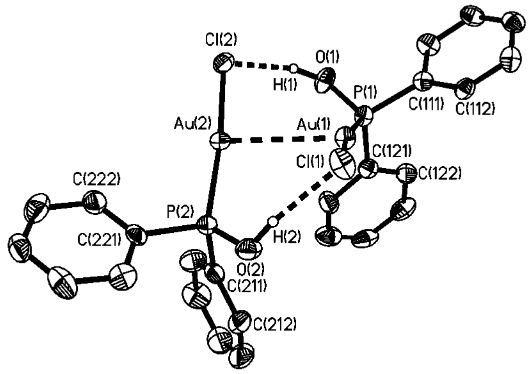

Fig. 1 Molecular structure of compound **1** (ORTEP[20] drawing with 50% probability ellipsoids, C–H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Au(1)–P(1) 2.218(2), Au(1)–Cl(1) 2.306(2), P(1)–O(1) 1.597(5), Au(1) · · · Au(2) 3.1112(7), Au(2)–P(2) 2.224(2), Au(2)–Cl(2) 2.309(2), 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.

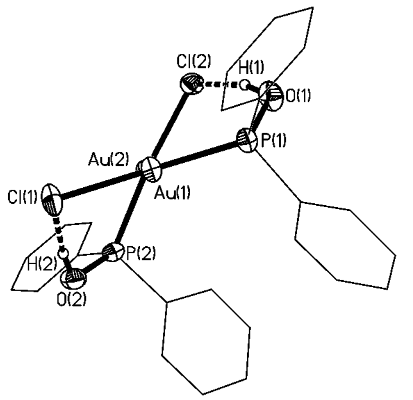

Fig. 2 Projection of the molecular structure of compound **1** along the Au(1) · · · Au(2) axis.

$$\underset{\mathbf{1}}{3\,[Ph_2P(OH)AuCl]_2} \xrightarrow[-3\,HCl/-3\,HF]{BF_3{\cdot}OEt_2\,(excess)} \underset{\mathbf{2}}{[FB(OPPh_2Au)_3Cl_3(AuPPh_2O)_3BF]^+BF_4^-} \quad (2)$$

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

Crystals of $\mathbf{2}{\cdot}3CH_2Cl_2$ (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 bridgeheads 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

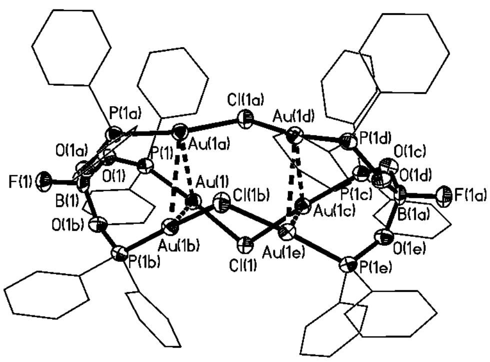

Fig. 3 Molecular structure of the cation of compound **2** (ORTEP drawing with 50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Au(1)–P(1) 2.238(2), Au(1)–Cl(1) 2.357(2), Au(1) · · · Au(1a) 3.1725(5), P(1)–O(1) 1.576(5), O(1)–B(1) 1.464(7), B(1)–F(1) 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.

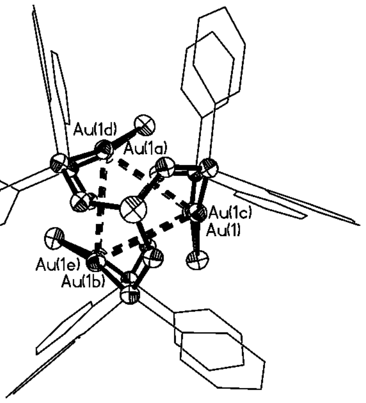

Fig. 4 Projection of the molecular structure of the cation of compound **2** along the threefold axis.

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·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.

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Notes and references

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

‡ Preparations. **1**: $(Me_2S)AuCl$ (177 mg, 0.60 mmol) and $Ph_2P(O)H$ (121 mg, 0.60 mmol) were dissolved in CH_2Cl_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_2Cl_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. ^1H NMR ($CDCl_3$, 20 °C): δ 8.70 (br s, OH); 7.21–7.91 (m, C_6H_5). ^{13}C-{^1H} NMR ($CDCl_3$, 20 °C): δ 134.7 (d, $^1J_{PC}$ = 74.4, *i*-C_6H_5), 132.1 (d, $^4J_{PC}$ = 2.3, *p*-C_6H_5), 131.4 (d, $^2J_{PC}$ = 16.1, *o*-C_6H_5), 128.8 (d, $^3J_{PC}$ = 13.0 Hz, *m*-C_6H_5). ^{31}P-{^1H} NMR ($CDCl_3$, 20 °C): δ 90.4 (s). MS (FAB): *m*/*z* 1000 $[\{Ph_2P(OH)\}_3Au_2]^+$, 833 $[2M - Cl]^+$, 601 $[\{Ph_2P(OH)\}_2Au]^+$, 399 $[M - Cl]^+$, 202 $[M - AuCl]^+$ (Found: C, 34.11; H, 2.79. Calc. for $C_{12}H_{11}AuClOP$·$0.125C_5H_{12}$: C, 34.18; H, 2.84%).

2: a solution of compound **1** (140 mg, 0.32 mmol) in CH_2Cl_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_2O was added to precipitate the product **2**, which was recrystallized from CH_2Cl_2–Et_2O 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. ^1H NMR (CD_2Cl_2, 20 °C): δ 7.25–8.00 (m, C_6H_5). ^{13}C-{^1H} NMR (CD_2Cl_2, 20 °C): δ 132.6 (s, *p*-C_6H_5), 131.2 (d, $^2J_{PC}$ = 16.9, *o*-C_6H_5), 128.9 (d, $^3J_{PC}$ = 13.8 Hz, *m*-C_6H_5), *i*-C_6H_5 not detected. ^{31}P-{^1H} NMR (CD_2Cl_2, 20 °C): δ 82.3 (s). ^{11}B-{^1H} NMR (CD_2Cl_2, 20 °C): δ −0.75 [s, $(PO)_3BF$], −1.05 (s, BF_4^-) (Found: C, 32.45; H, 2.44. Calc. for $C_{72}H_{60}Au_6B_3Cl_3F_6O_6P_6$: 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, ρ_{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 [$(\sin \theta/\lambda)_{max}$ = 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 $C_{75}H_{66}Au_6B_3Cl_9F_6O_6P_6$ (**2**·$3CH_2Cl_2$), M_r = 2896.38, colorless crystals (0.40 × 0.35 × 0.35 mm), hexagonal, a, b = 15.709(1), c = 23.705(1) Å, space group $P6_3/m$, Z = 2, V = 5066.0(5) Å^3, ρ_{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 [$(\sin \theta/\lambda)_{max}$ = 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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