Gold–Phosphanyl Structures

Synthesis and Structure of Cyclic Gold(I) Phosphanyl Complexes [{Au(PR_2)}$_n$]**

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Since their discovery in 1976, homoleptic gold(I) phosphanyl complexes of the form [{Au(PR_2)}$_n$] have remained a mysterious class of compounds.[1] The parent, and most investigated of the family, [{Au(PPh_2)}$_n$], is insoluble; its color was reported to depend on the base used in its preparation from [Au($PHPh_2$)(Cl)] or related precursors.[2] Parish and co-workers prepared several related [{Au(PR_2)}$_n$] complexes (R = Et, *n*-octyl, *p*-MeC_6H_4, *p*-(*t*Bu)C_6H_4), which could be obtained in soluble and insoluble forms, that were proposed to be either cyclic or linear chain polymers.[2d] NMR studies of these materials, although made difficult by precipitate formation, suggested that several species were present in solution. Mössbauer spectra indicated the expected linear coordination with two phosphanyl ligands binding to a gold center, but structural details were not available.[2d,f] We report here that using bulkier R groups enables the synthesis of soluble gold phosphanyl complexes of the form [{Au(PR_2)}$_n$] (PR_2 = PCy_2 (**1**, Cy = c-C_6H_{11}), P(*t*Bu)$_2$ (**2**), $PMes_2$ (**3**, Mes = 2,4,6-$Me_3C_6H_2$), and PIs_2 (**4**, Is = 2,4,6-(*i*Pr)$_3C_6H_2$)), whose novel cyclic structures were determined by X-ray crystallography.[3]

Treatment of the known compounds [Au(PHR_2)(Cl)][4] and the novel [Au($PHIs_2$)(Cl)] (**5**) with aqueous ammonia in THF or CH_2Cl_2 caused precipitation of the white, toluene-soluble and air-stable [{Au(PR_2)}$_n$] complexes **1**–**4** (Scheme 1). ^{31}P NMR spectra of these crude products showed the presence of several species (for **1** and **3**: four species; for **2**: five or ten species depending on reaction time; for **4**: only one form). Recrystallization of **1** from toluene gave a mixture of two compounds which could not be separated, but on one occasion crystals of one of these forms were isolated. Recrystallization of **2** from toluene yielded a mixture of two compounds; the less soluble one was isolated after further recrystallization. Heating **3** in toluene caused partial conversion to a major product, which then crystallized preferentially. After isolation, these materials were characterized by elemental analyses, multinuclear NMR and IR spectroscopies, and MALDI mass spectrometry (molecular ions were observed).

$$[\mathrm{Au(PHR_2)Cl}] \xrightarrow{\mathrm{NH_4OH}} [\{\mathrm{Au(PR_2)}\}_n]$$

PR_2 = PCy_2 (**1**), P(*t*Bu)$_2$ (**2**),
$PMes_2$ (**3**), PIs_2 (**4**)

Scheme 1. Synthesis of Au^{I}–Phosphanyl Complexes.

The crystal structures of cyclic [{Au(PCy_2)}$_6$]·2 C_7H_8 (**1**·2 C_7H_8), [{Au(P(*t*Bu)$_2$)}$_6$]·C_7H_8 (**2**·C_7H_8), [{Au($PMes_2$)}$_4$] (**3**), and [{Au(PIs_2)}$_3$](**4**) are shown in Figures 1–4.[5] Toluene molecules are not illustrated in these figures, but in both **1**·2 C_7H_8 and **2**·C_7H_8, they are present in the channels between the rings, which stack to yield an extended structure. Not surprisingly, an increase in the size of the P substituents leads

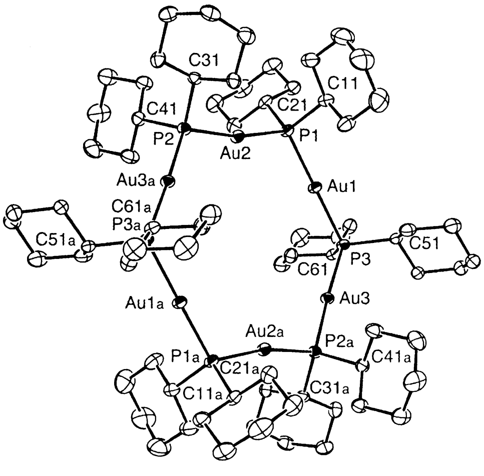

Figure 1. ORTEP diagram of [Au(PCy_2)]$_6$·2 C_7H_8 (**1**·2 C_7H_8). The hydrogen atoms and solvent molecules are not shown. Selected bond lengths [Å] and angles [°]: Au1-P1 2.3116(12), Au1-P3 2.3150(12), Au2-P2 2.3132(12), Au2-P1 2.3166(13), Au3-P2a 2.3145(12), Au3-P3 2.3223(12); P1-Au1-P3 174.09(4), P2-Au2-P1 168.83(4), P2a-Au3-P3 174.39(4).

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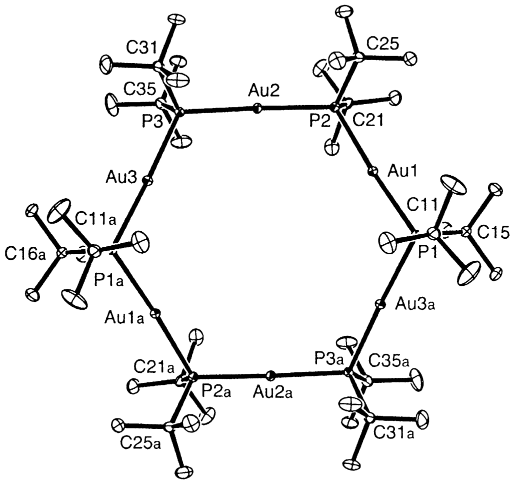

Figure 2. ORTEP diagram of $[\{Au(P(tBu)_2)\}_6]\cdot C_7H_8$ (**2**$\cdot C_7H_8$). The hydrogen atoms and solvent molecule are not shown. Selected bond lengths [Å] and angles [°]: Au1-P1 2.3287(12), Au1-P2 2.3306(12), Au2-P2 2.3324(12), Au2-P3 2.3363(12), Au3-P1a 2.2380(12), Au3-P3 2.3295(12); P1-Au1-P2 174.85(4), P2-Au2-P3 178.12(4), P1a-Au3-P3 176.86(4).

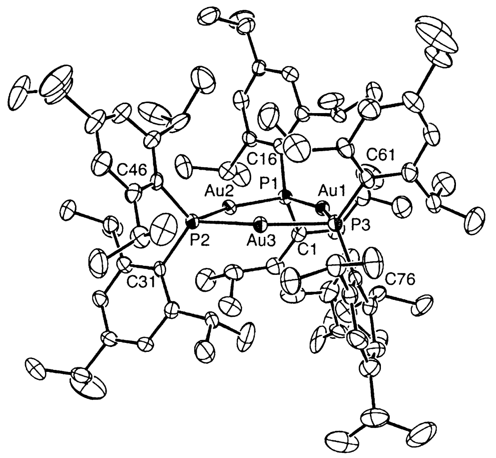

Figure 4. ORTEP diagram of $[\{Au(PIs_2)\}_3]$ (**4**). The hydrogen atoms and disorder in the isopropyl groups are not shown. Selected bond lengths [Å] and angles [°]: Au1-P3 2.332(2), Au1-P1 2.335(2), Au1···Au3 3.0661(4), Au1···Au2 3.0821(4), Au2-P1 2.314(2), Au2-P2 2.319(2), Au2···Au3 3.0970(5), Au3-P3 2.321(2), Au3-P2 2.323(2); P3-Au1-P1 157.30(7), P1-Au2-P2 156.47(8), P3-Au3-P2 157.02(8).

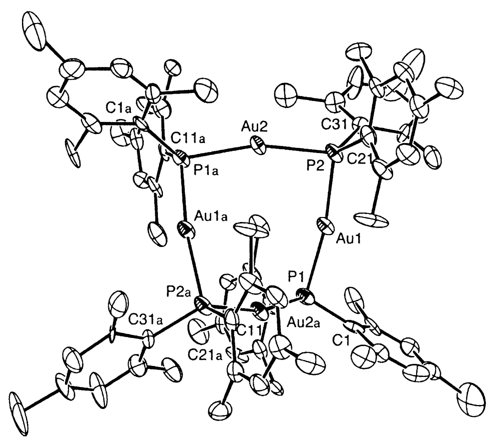

Figure 3. ORTEP diagram of $[\{Au(PMes_2)\}_4]$ (**3**). The hydrogen atoms are not shown. Selected bond lengths [Å] and angles [°]: Au1-P1 2.311(6), Au1-P2 2.318(6), Au1···Au2 3.3414(14), Au2-P1a 2.312(6), Au2-P2 2.320(6); P1-Au1-P2 170.3(2), P1a-Au2-P2 163.8(2).

to a decreased ring size, presumably to reduce unfavorable steric interactions.

As expected, the P-Au-P angles are close to linear, and the phosphorus atoms are approximately tetrahedral (Table 1). The Au–P bond lengths are similar in all four complexes, and the average Au–P bond length in **2**$\cdot C_7H_8$ (2.3309(12) Å) is slightly longer than that in the precursor $[Au(PH(tBu)_2)(Cl)]$ (2.230(2) Å).[4] Aurophilic interactions[6] are clearly present in the $\{Au_3\}$ triangle of **4**, with Au···Au separations ranging from 3.0661(4) to 3.0970(5) Å, and may also be important in **3**, with Au···Au separations of 3.3414(14) and 3.4448(12) Å observed. In contrast, the shortest Au···Au separations in **1**$\cdot 2\,C_7H_8$ and **2**$\cdot C_7H_8$ are 3.8992(3) and 3.9183(3) Å, respectively.

Although the ring in **1**$\cdot 2\,C_7H_8$ is almost planar (mean deviation from the plane is 0.1116 Å) and that in **4** is planar (mean deviation 0.0075 Å), **2**$\cdot C_7H_8$ and **3** adopt puckered structures (Figure 5). The structure of **3** may be described as "butterfly-like", with an angle between the planes of 125.24(9)°, or as a plane of Au atoms with P atoms alternating above and below the plane. In the twisted **2**$\cdot C_7H_8$, two planes of P atoms (P1, P2, P3, P1a and P1, P2a, P3a, P1a) intersect at an angle of 34.15(2)°.

Hexameric **1**$\cdot 2\,C_7H_8$ and **2**$\cdot C_7H_8$ have the same nuclearity as $[\{Au(S(2,4,6\text{-}(iPr)_3C_6H_2)\}_6]$, in which the $\{Au_6S_6\}$ ring adopts a chair conformation.[3a,e] However, **1**$\cdot 2\,C_7H_8$ is almost planar and the twisted ring in **2**$\cdot C_7H_8$ is closer to a boat conformation. The structure of the cyclic tetramer **3** may be compared to that of $[\{Au(N(SiMe_3)_2)\}_4]$, which contains a planar $\{Au_4N_4\}$ core. The shorter Au–N bond length (2.082(3) Å) is accompanied by reduced Au···Au distances (3.0100(3) and 3.0355(3) Å).[3f] In contrast, the $\{Au_4S_4\}$ core in $[\{Au(S\{SiO(tBu)_3\})\}_4]$ is folded as in **3** with an angle of 157.3° with respect to the S–S diagonal,[3c] but $[\{Au(SC(SiMe_3)_3)\}_4]$ is planar and $[\{Au(TeC(SiMe_3)_3)\}_4]$ adopts a butterfly structure with a dihedral angle of 144.98(6)°.[3b]

Several planar complexes with a $\{Au_3\}$ triangle supported by bridging ligands are known, but these include two-atom bridges and nine-membered rings.[7] In contrast,

Table 1: Selected bond lengths [Å] and angles [°] in the gold(I) phosphanyl complexes **1**$\cdot 2\,C_7H_8$, **2**$\cdot C_7H_8$, **3**, and **4**.

Complex	**1**$\cdot 2\,C_7H_8$	**2**$\cdot C_7H_8$	**3**	**4**
Au–P (av)	2.3155(13)	2.3309(12)	2.315(6)	2.324(2)
P-Au-P (av)	172.44(4)	176.61(4)	167.0(2)	156.93(8)
Au-P-C (av)	108.18(18)	106.93(17)	114.6(7)	115.2(3)
Au-P-Au (av)	117.51(5)	115.76(5)	94.2(2)	83.06(7)
C-P-C (av)	105.8(2)	113.5(2)	105.4(9)	110.9(4)

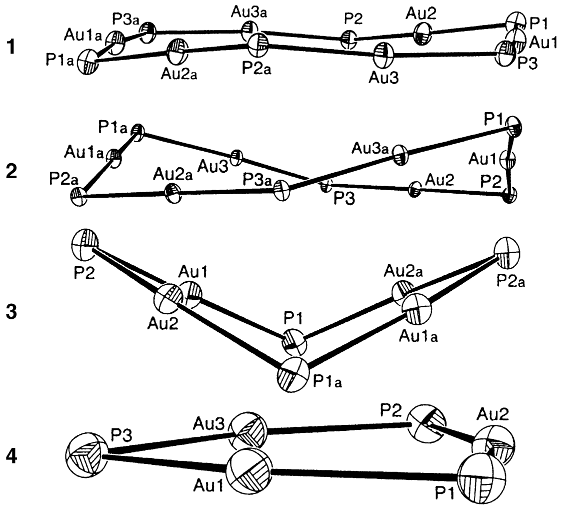

Figure 5. The Au–P rings have different shapes: almost planar in $\mathbf{1}\cdot 2\,C_7H_8$, twisted in $\mathbf{2}\cdot C_7H_8$, butterfly in **3**, and planar in **4**.

the shorter bridges in **4** lead to unusually bent P-Au-P angles (average 156.93(8)°). We are not aware of other simple $[\{AuX\}_n]$ complexes with trinuclear structures; the closest precedent is the Au–Nb raft cluster $[\{Au(Cp'_2NbH_2)\}_3]$ ($Cp' = \eta^5\text{-}C_5H_4SiMe_3$), which also features bridging hydrides.[8] These comparisons suggest that ring size and conformation in these classes of homoleptic compounds depend strongly on the substituents and the possibility of Au···Au interactions.

In conclusion, X-ray crystallographic studies of gold(I) phosphanyl complexes have for the first time established the structures of this class of compounds as cyclic oligomers. ^{31}P NMR spectroscopy showed that several species, presumably rings of different sizes, exist in solution, and that they can interconvert in some cases. These advances pave the way for further investigation of the structure and reactivity of Au^I phosphanyl complexes and their potential applications.[9]

Experimental Section

A representative synthesis is described. Full details of the synthesis and characterization of the other complexes are in the Supporting Information.

3: Aqueous ammonia (approximately 5 mL, 29.6 %, 78 mmol) was added to a solution of $[Au(PHMes_2)(Cl)]$ (340 mg, 0.68 mmol) in THF (10 mL); a white precipitate was formed. After stirring for 30 min, the solvent was pumped off, and the resulting white solid was washed with water (30 mL) to give **3** (220 mg, 69 %). $^{31}P\{^1H\}$ NMR ([D$_8$]toluene, 121.4 MHz): $\delta = -17.0$ (major), -18.8 (minor), -23.4 (minor), -36.1 ppm (minor). This material could be dissolved in heated toluene (70 °C). Slow evaporation of toluene at room temperature yielded a single product, shown to be a cyclic tetramer by X-ray crystallography (Yield 42 %).

Elemental analysis (%) calcd for $C_{72}H_{88}Au_4P_4$: C 46.36, H 4.76. Found: C 46.20, H 4.58. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.4 MHz): $\delta = -36.1$ ppm; ^{1}H NMR (C_6D_6, 300 MHz): $\delta = 6.70$ (16 H), 2.65 (48 H), 2.07 ppm (24 H). IR (KBr): $\tilde{\nu} = 3015$, 2954, 2915, 1715, 1592, 1546, 1454, 1392, 1292, 1246, 1015, 838, 700, 615, 554, 423 cm^{-1}. MALDI-TOF-MS (Cyano-4-hydroxycinnamic acid): *m*/*z* 2799.65 ($(AuPMes_2)_6$), 2529.86 ($Au_6(PMes_2)_5$), 2333.22 ($(AuPMes_2)_5$), 2202.19, 2153.50, 2108.03, 2063.85 ($Au_5(PMes_2)_4$), 1883.82, 1867.24 ($(AuPMes_2)_4$), 1783.39, 1717.12, 1641.44, 1597.32 ($Au_4(PMes_2)_3$), 1417.18, 1317.02, 1236.70, 1174.88, 951.23.

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[5] Crystallographic data for **1**–**4**: recorded at 223(2) K ($\mathbf{1}\cdot 2\,C_7H_8$ and **3**), 150(2) K ($\mathbf{2}\cdot C_7H_8$), and 218(2) K (**4**) with $Mo_{K\alpha}$ (0.71073 Å) radiation: $\mathbf{1}\cdot 2\,C_7H_8$: triclinic, space group $P\bar{1}$, $a = 11.7057(7)$, $b = 15.2817(9)$, $c = 15.3080(9)$ Å, $\alpha = 63.2510(10)$, $\beta = 73.1750(10)$, $\gamma = 88.0730(10)$°, $Z = 2$, $R1 = 0.0313$ for 10891 ($I > 2\sigma(I)$) data; $\mathbf{2}\cdot C_7H_8$: monoclinic, space group $C2/c$, $a = 30.0553(16)$, $b = 8.8627(5)$, $c = 29.4648(16)$ Å, $\beta = 115.4920(10)$°, $Z = 4$, $R1 = 0.0278$ for 8504 ($I > 2\sigma(I)$) data; **3**: monoclinic, space group $C2/c$, $a = 23.830(5)$, $b = 12.160(2)$, $c = 27.254(6)$ Å, $\beta = 108.322(4)$°, $Z = 8$, $R1 = 0.0728$ for 5526 ($I > 2\sigma(I)$) data; **4**: orthorhombic, space group $Pna2_1$, $a = 24.6277(14)$, $b = 15.3421(9)$, $c = 23.5866(14)$ Å, $Z = 4$, $R1 = 0.0474$ for 19538 ($I > 2\sigma(I)$) data; CCDC 196576–196579 (complexes $\mathbf{1}\cdot 2\,C_7H_8$, $\mathbf{2}\cdot C_7H_8$, **3**, and **4**, respectively) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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