Phosphorus-Centered Gold Clusters: A Novel Pentanuclear Species $\{[(Ph_3P)_6Au_5]P\}^{2+}$

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The reaction of tris[(triphenylphosphane)gold]oxonium tetrafluoroborate with phosphane gas in tetrahydrofuran leads to a mixture of products, one of which has now been isolated and identified as the complex $\{[(Ph_3P)_6Au_5]P\}^{2+}$ $(BF_4^-)_2$ (**1**). This cluster can be described as an adduct of $[(Ph_3PAu)_4P]^+$ and $[(Ph_3P)_2Au]^+$. Crystals of $(\mathbf{1})_2 \cdot (CH_2Cl_2)_3 \cdot Et_2O$ contain two crystallographically independent formula units of very similar structure. The dications are centered by pentacoordinate phosphorus atoms in an irregular coordination geometry. In the crystal one of the five gold atoms is attached to two triphenylphosphane ligands, while the other four bear only one such ligand. In solution rapid ligand exchange renders the ligands equivalent on the NMR time scale. This stoichiometry and structure of **1** are indicative of the strong basicity of the $[(Ph_3PAu)_4P]^+$ cation probably owing to its square-pyramidal structure with strong Au···Au bonding, as suggested by the structure of its arsenic analogue.

The tetrakis[(triphenylphosphane)gold(I)]*ammonium* cation $[(Ph_3PAu)_4N]^+$ is known to have the expected tetrahedral structure in at least three of its salts with F^-, BF_4^-, and PF_6^- counterions[1-3]. By contrast, the corresponding *arsonium* cation $[(Ph_3PAu)_4As]^+$ has been found to have an unusual square-pyramidal structure in no less than three crystalline modifications of its BF_4^- salt (containing different amounts of solvent molecules in the lattice)[3,4]. This non-tetrahedral structure is at variance with conventional rules of structure and bonding, but could be rationalized in a recent theoretical treatment by considering significant metal-metal interactions between seemingly closed-shell (d^{10}) gold centers through relativistic effects[5-9]. From these theoretical studies it has been deduced that the corresponding tetranuclear *phosphonium* cation $[(H_3PAu)_4P]^+$ should also adopt the non-classical square-pyramidal structure, but salts of this cation are unknown and therefore this prediction has not yet been confirmed[9].

In an attempt to prepare $[(Ph_3PAu)_4P]^+$ BF_4^- and to elucidate its structure we have obtained a salt with an unusual dicationic *penta*nuclear species with *six* phosphane ligands, the interesting structural features of which are reported in this contribution. In a related study[10], using tri(*tert-butyl*)phosphane instead of tri*phenyl*phosphane, the free tetranuclear cation could be isolated and structurally characterized. Owing to the steric bulk of the ligands, this cation cannot adopt a square-pyramidal structure and is found to be tetrahedral, but with severe distortions which allow at least for some weak Au···Au contacts.

Formation of the Pentanuclear Gold Cluster $\{[(Ph_3P)_6Au_5]P\}^{2+}$ $(BF_4^-)_2$

When phosphane gas, PH_3, is admitted into a slurry of tri[(triphenylphosphane)gold]oxonium tetrafluoroborate[11], $[(Ph_3PAu)_3O]^+$ BF_4^-, and $Na[BF_4]$ in tetrahydrofuran at −78 °C the *supernatant* solution turns lemon yellow immediately. Workup with a series of precipitation and crystallization steps affords yellow crystals of the title compound **1**. Other products are $\{[(Ph_3P)Au]_5P\}^{2+}$ $2\,BF_4^-$ and $[\{[(Ph_3P)Au]_4P\}_2Au]^{3+}$ $3\,BF_4^-$ (ref.[4,12]).

$$[(Ph_3PAu)_3O]^+\,BF_4^- \xrightarrow[-H_2O]{PH_3/NaBF_4} \underset{\mathbf{1}}{\{[(Ph_3P)_6Au_5]P\}^{3+}}(BF_4^-)_3 \qquad (1)$$

It should be noted that in previous studies[12] the reaction of the same oxonium precursor with tris(trimethylsilyl)phosphane[13], $(Me_3Si)_3P$, instead of PH_3, was found to yield another pentanuclear *di*cationic complex $\{[(Ph_3P)Au]_5P\}^{2+}$ with *five* phosphane ligands. The structure of this species has not yet been determined, but satisfactory analytical and spectroscopic data are available, which confirm the stoichiometry and suggest a trigonal-bipyramidal structure similar to that of the nitrogen analogue[14]. The *tert*-butyl analogue $[(tBu_3PAu)_5P]^{2+}$ $(BF_4^-)_2$ has meanwhile also been isolated and characterized[15].

The ^{31}P-NMR spectrum of solutions of compound **1** in $[D_2]$dichloromethane shows a broad Ph_3P resonance at $\delta = 41.26$ and an even broader signal at $\delta = -99.2$ (width at half height 200 Hz) for the interstitial phosphorus atom. At −90 °C these resonance signals transform into a broad doublet [$\delta = 40.01$, $^2J(P, P) = 95.2$ Hz] and a complex multiplet ($\delta = -95$), respectively, indicating ill-resolved nonequivalency of the Ph_3P ligands in solution.

The ^1H-NMR spectra (in CD_2Cl_2) show a broad aryl multiplet structure over the whole range of temperature with little variations. $^{13}C\{^1H\}$-NMR spectra (in CD_2Cl_2) show signals for only one set of aryl carbon atoms at 20 °C suggesting virtually equivalent Ph groups in solution under these conditions. At −90 °C a very complex pattern appears, which could not be resolved.

The FAB mass spectrum of compound **1** shows no parent peak for the intact dication. Fragment ions $[(Ph_3PAu)_4P]^+$

[m/z (%) = 1868.1 (13.4)], $[(Ph_3PAu)_3PAu]^+$ [m/z = 1605.9 (8.9)], $[(Ph_3P)_2Au]^+$ [m/z = 721.4 (100)], and $[(Ph_3PAu)]^+$ [m/z = 459.3 (99.7)] appear instead, which indicate a primary dissociation according to equation (2).

$$\{[(Ph_3P)_6Au_5]P\}^{2+} \rightarrow [(Ph_3PAu)_4P]^+ + [(Ph_3P)_2Au]^+ \qquad (2)$$

This result is supported by the structure of the dication in the crystal (below), which clearly features the two components. The same dissociation may be responsible for the exchange processes in polar solvents (CH_2Cl_2) as observed by NMR spectroscopy (above). Clearly, however, this will not be the only process leading to equilibration of the Ph_3P ligands at elevated temperatures.

The appearance of peaks attributed to the cation *$[(Ph_3PAu)_4P]^+$* in the mass spectra is an important observation which demonstrates the inherent stability of this species under the given experimental conditions. From this finding the stoichiometry of compound **1** can be rewritten as $[(Ph_3PAu)_4P \cdot Au(PPh_3)_2]^{2+}$, suggesting unexpected donor properties of $[(Ph_3PAu)_4P]^+$ at the phosphorus atom. While a tetrahedral cation of this stoichiometry is not expected to be a nucleophile, a square-pyramidal cation could well exhibit such behavior. The results of the X-ray structure determination have shown, that this is indeed the case.

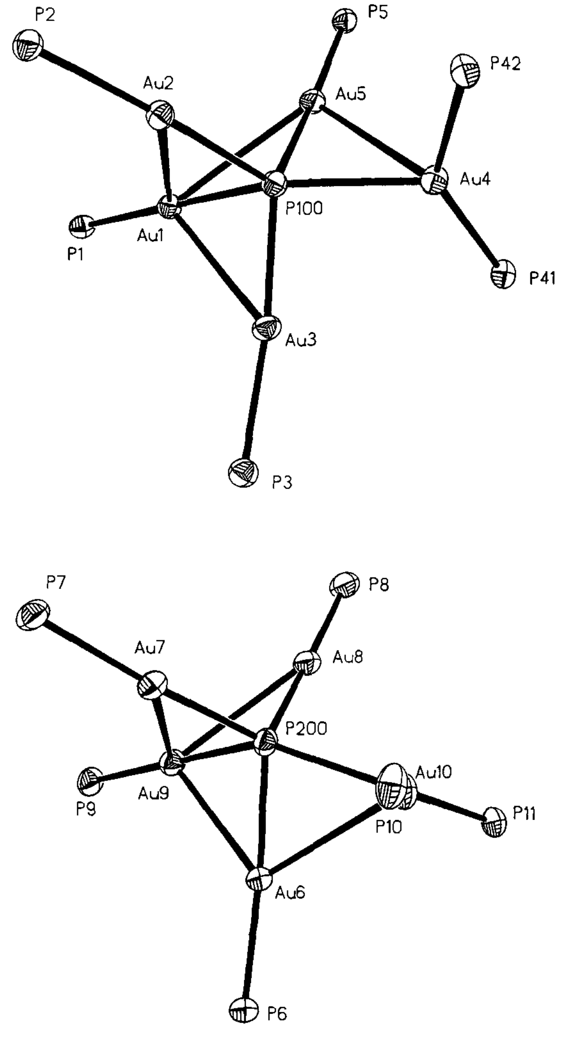

Figure 1. Molecular structure of the gold/phosphorus core in the two crystallographically independent dications $\{[(Ph_3P)Au]_4PAu(PPh_3)_2\}^{2+}$ [**A**: Figure 1a (top); **B**: Figure 1b (bottom)] of compound $(\mathbf{1})_2(CH_2Cl_2)_3(Et_2O)$ (for selected distances and angles see Table 1)

Crystal Structure of Compound $(\mathbf{1})_2 \cdot (CH_2Cl_2)_3 \cdot Et_2O$

Crystallization of compound **1** from a mixture of dichloromethane and diethyl ether affords colorless triclinic plates, space group $P\bar{1}$, with two formula units (above) in the unit cell. The asymmetric unit contains two crystallographically independent dications of very similar structure (**A** and **B**, Figures 1a, 1b) with their counterions and solvent molecules. The lattice features no unusual interionic or intermolecular contacts.

In **A** and **B** the interstitial phosphorus atoms (P100, P200) are coordinated to five gold atoms in the centers of strongly distorted trigonal bipyramides. The gold atoms Au3/Au5 and Au6/Au8 can be assigned axial positions, and the remainder six gold atoms equatorial positions. Two of these gold atoms are unique in that they bear *two* phosphane ligands in each case (Au4 in **A**, Au10 in **B**), whereas all other gold atoms bear only one phosphane ligand. The contacts of the interstitial phosphorus atoms with the unique three-coordinate gold atoms [Au4—P100 2.546(4), Au10—P200 2.566(4) Å] are much longer (and probably weaker) than those with the two-coordinate gold atoms (average 2.344 Å). As suggested by the spectroscopic data, it appears justified to view the complex as composed of units $[(Ph_3PAu)_4P]^+$ and $[(Ph_3P)_2Au]^+$. However, with the contacts Au4···Au5 and Au6··Au10 as short as 3.0320(9) and 3.051(1) Å, respectively, the interaction between the units $[(Ph_3PAu)_4P]^+$ and $[(Ph_3P)_2Au]^+$ clearly also involves some metal-metal bonding. An examination of the phosphorus-centered clusters shows, that the atoms Au1 and Au9 have no less than three such short contacts with neighboring gold atoms, Au5 and Au6 have two, and the remaining gold atoms have only one.

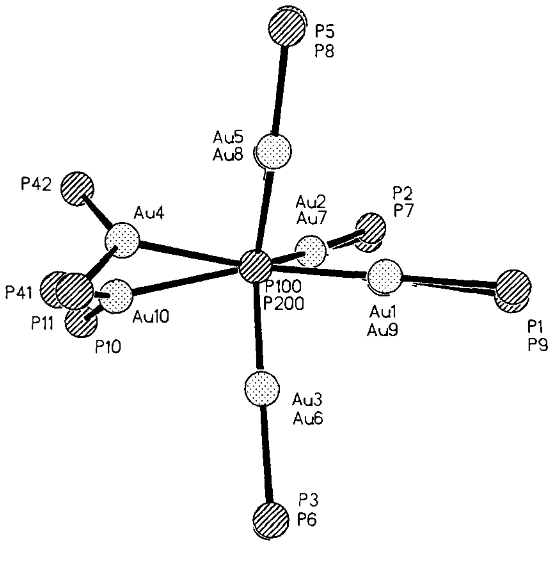

Figure 2. Superposition of the gold/phosphorus cores of the dications **A** and **B** (see Figures 1a, b)

This system of peripheral metal-metal bonding no doubt strongly contributes to the stability of the cluster units. It is also to be held responsible for the severe distortions of the polyhedra, which make these Au···Au contacts possible[15,16].

A superposition of the core structures of **A** and **B** illustrates the similarity of the two structures. While the skeleton of the $[(Ph_3PAu)_4P]^+$ units is almost superimposible, the orientation of the $[(Ph_3P)_2Au]^+$ units is different (Figure 2).

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Experimental

All experiments were carried out in dry and pure N_2. Solvents were dried, distilled, and saturated with N_2. Glassware was oven-dried and filled with N_2. The apparatus was protected against incandescent light. – NMR: Jeol GX 270. – MS: Varian MAT 311A.

Preparation of Compound **1**: A slurry of tris[(triphenylphosphane)gold]oxonium tetrafluoroborate (1.00 g, 0.68 mmol) and sodium tetrafluoroborate (0.10 g, 9.1 mmol) in tetrahydrofuran (25 ml) is cooled to −78°C and 11.0 ml (0.49 mmol) of phosphane gas is admitted with stirring. The colorless solution turns lemon yellow and finally orange when allowed to warm to room temperature over a period of 3 h. The solvent is removed in vacuo and the residue treated with dichloromethane. Undissolved material (mainly $NaBF_4$) is filtered off, and pentane (20 ml) is added to the filtrate to precipitate a red-brown solid, which is discarded. Addition of another 20 ml portion of pentane to the yellow solution affords yellow crystals of the product on standing, yield 0.15 g (14%), dec. temp. 155°C. – $^{31}P\{H\}$ NMR (CD_2Cl_2, 20°C): $\delta = 41.26$ (br., PPh_3), −99.2 (br. s, $w_h = 200$ Hz, PAu_5); (−90°C): 40.01 (br. d, PPh_3), −95.0 (br. m, $w_h = 500$ Hz, PAu_5). – ^1H NMR (CD_2Cl_2, 20°C): $\delta = 7.08-7.42$ (m, PPh_3); (−90°C): 7.05−7.58 (br. m, PPh_3). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20°C): $\delta = 129.7$ [d, J(P,C) = 11.0 Hz, C3], 130.1 [d, J(P,C) = 50.9 Hz, C1], 132.2 (s, C4), 134.3 [d, J(P,C) = 13.8 Hz, C2]; (−90°C): br. and more complex signals. – MS (FAB): m/z (%) = 1868.1 (13.4) $[(Ph_3PAu)_4P^+]$, 1605.9 (8.9) $[(Ph_3PAu)_3PAu^+]$, 721.4 (100) $[(Ph_3P)_2Au^+]$, 459.3 (99.7) $[Ph_3PAu^+]$.

Crystal-Structure Determination: Crystals of **1** grown from a mixture of dichloromethane and diethyl ether contain three equivalents of dichloromethane and one equivalent of ether for two formula units of compound **1** $[(1)_2 \cdot (CH_2Cl_2)_3 \cdot (C_2H_5)_2O]$. Total molecular formula $C_{114}H_{196}Au_{10}B_4Cl_6F_{16}OP_{12}$, molecular mass 5855.28 gmol^{-3}. The colorless crystal used had the size 0.10 · 0.15 · 0.40 mm; a = 15.560(4), b = 20.851(5), c = 34.687(8) Å; α = 89.37(1), β = 85.76(2), γ = 74.567(2)°; V = 10819.0 Å^3; $d_{calcd.}$ = 1.797 gcm^{-3}; μ(Mo-K_α) = 69.71 cm^{-1}; Mo-K_α radiation; λ = 0.71069 Å; F(000) = 5628 e; Z = 2; crystal system: triclinic; space group: $P\bar{1}$ (No. 2, Int. Tables); Enraf-Nonius CAD4 diffractometer; scan mode: ω; $[\sin\Theta/\lambda]_{max}$ = 0.5497 Å^{-1}. 29964 reflections were measured in the hkl ranges 0−17/−22−22/−38−38, of which 29941 were unique [corrected for absorption; t_{min} = 0.081, t_{max} = 1.179 (DIFABS)[17]], and 14780 considered observed (with $F_o \geq 3\sigma F_o$). For 2328 refined parameters in 16 blocks the structure was solved by direct methods[18]. Refinement[19] of all non-hydrogen atoms of the two clusters A and B proceeded with aniostropic displacement parameters, for the remaining atoms with isotropic parameters; H-atom positions were calculated and kept fixed in the final refinement stages with U_{iso} = 0.05. The disorder of two BF_4^- anions was included in the refinement with partial occupancies (s.o.f. = 0.60/0.40). R = 0.045, R_w = 0.046 (using the weighting scheme of Prince[20]); residual electron density 5.2/−3.2 eÅ^{-3} (located at gold atoms). Selected bond distances and angles are listed in Table 1. Further details of the crystal-structure determination may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Zusammenarbeit mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-57601, the names of the authors, and the journal citation.

Table 1. Selected bond distances [Å] and angles [°] in crystals of $(1)_2(CH_2Cl_2)_3(Et_2O)$ (see Figures 1a, b for atomic numbering)

Au1 - Au2	3.0040(9)	Au6 - Au9	2.895(1)
Au1 - Au3	2.9446(9)	Au6 - Au10	3.051(1)
Au1 - Au5	2.9711(9)	Au6 - P6	2.301(5)
Au1 - P1	2.277(4)	Au6 - P200	2.348(5)
Au1 - P100	2.381(4)	Au7 - Au9	3.004(1)
Au2 - Au1	3.0040(9)	Au7 - P7	2.293(5)
Au2 - P2	2.288(4)	Au7 - P200	2.314(5)
Au2 - P100	2.318(4)	Au8 - Au9	3.002(1)
Au3 - Au1	2.9446(9)	Au8 - P8	2.293(5)
Au3 - P3	2.283(5)	Au8 - P200	2.329(5)
Au3 - P100	2.322(4)	Au9 - Au6	2.895(1)
Au4 - Au5	3.0320(9)	Au9 - Au7	3.004(1)
Au4 - P41	2.325(4)	Au9 - Au8	3.002(1)
Au4 - P42	2.350(4)	Au9 - P9	2.284(5)
Au4 - P100	2.546(4)	Au9 - P200	2.395(4)
Au5 - Au1	2.9711(9)	Au10 - Au6	3.051(1)
Au5 - Au4	3.0320(9)	Au10 - P10	2.347(5)
Au5 - P5	2.289(4)	Au10 - P11	2.327(5)
Au5 - P100	2.348(4)	Au10 - P200	2.566(4)
Au3 - Au1 - Au2	82.30(2)	Au10 - Au6 - Au9	105.57(3)
Au5 - Au1 - Au2	78.52(2)	P6 - Au6 - Au9	125.9(1)
Au5 - Au1 - Au3	88.57(2)	P6 - Au6 - Au10	127.5(1)
P1 - Au1 - Au2	132.1(1)	P200 - Au6 - Au9	53.1(1)
P1 - Au1 - Au3	128.9(1)	P200 - Au6 - Au10	54.9(1)
P1 - Au1 - Au5	128.8(1)	P200 - Au6 - P6	174.8(2)
P100 - Au1 - Au2	49.4(1)	P7 - Au7 - Au9	124.4(1)
P100 - Au1 - Au3	50.4(1)	P200 - Au7 - Au9	51.6(1)
P100 - Au1 - Au5	50.6(1)	P200 - Au7 - P7	172.7(2)
P100 - Au1 - P1	178.5(2)	P8 - Au8 - Au9	130.5(1)
P2 - Au2 - Au1	123.9(1)	P200 - Au8 - Au9	51.5(1)
P100 - Au2 - Au1	51.2(1)	P200 - Au8 - P8	175.4(2)
P100 - Au2 - P2	175.0(2)	Au7 - Au9 - Au6	83.44(3)
P3 - Au3 - Au1	128.3(1)	Au8 - Au9 - Au6	87.92(3)
P100 - Au3 - Au1	52.1(1)	Au8 - Au9 - Au7	78.39(3)
P100 - Au3 - P3	169.2(2)	P9 - Au9 - Au6	127.4(1)
P41 - Au4 - Au5	107.8(1)	P9 - Au9 - Au7	130.2(1)
P42 - Au4 - Au5	104.2(1)	P9 - Au9 - Au8	132.0(1)
P42 - Au4 - P41	139.7(2)	P200 - Au9 - Au6	51.6(1)
P100 - Au4 - Au5	48.8(1)	P200 - Au9 - Au7	49.2(1)
P100 - Au4 - P41	120.1(1)	P200 - Au9 - Au8	49.6(1)
P100 - Au4 - P42	99.2(1)	P200 - Au9 - P9	178.5(2)
Au4 - Au5 - Au1	101.50(3)	P10 - Au10 - Au6	107.2(1)
P5 - Au5 - Au1	131.4(1)	P11 - Au10 - Au6	48.5(1)
P5 - Au5 - Au4	124.9(1)	P11 - Au10 - P(10)	139.3(2)
P100 - Au5 - Au1	51.6(1)	P200 - Au10 - Au6	48.5(1)
P100 - Au5 - Au4	54.7(1)	P200 - Au10 - P10	101.4(2)
P100 - Au5 - P5	173.7(2)	P200 - Au10 - P11	119.3(2)
Au2 - P100 - Au1	79.5(1)	Au7 - P200 - Au6	114.8(2)
Au3 - P100 - Au1	77.5(1)	Au8 - P200 - Au6	122.2(2)
Au3 - P100 - Au2	115.0(2)	Au8 - P200 - Au7	109.7(2)
Au4 - P100 - Au1	141.3(2)	Au9 - P200 - Au6	75.2(1)
Au4 - P100 - Au2	136.3(2)	Au9 - P200 - Au7	79.3(1)
Au4 - P100 - Au3	93.9(1)	Au9 - P200 - Au8	78.9(1)
Au5 - P100 - Au1	77.9(1)	Au10 - P200 - Au6	76.6(1)
Au5 - P100 - Au2	108.3(2)	Au10 - P200 - Au7	131.6(2)
Au5 - P100 - Au3	124.4(2)	Au10 - P200 - Au8	99.7(2)
Au5 - P100 - Au4	76.5(1)	Au10 - P200 - Au9	145.3(2)

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