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Aggregation of a Neutral Gold(I) Complex through Cooperative Action of Hydrogen Bonding and Auriophilicity
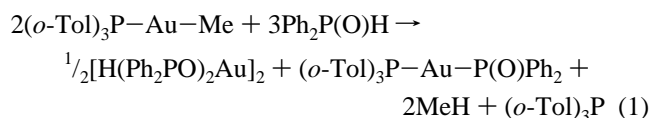
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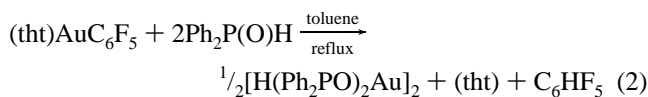
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Bonding interactions between seemingly closed-shell two-coordinate gold(I) centers (auriophilicity)[1] is now recognized as a widespread phenomenon of great relevance to the structural chemistry of individual molecules[2] and supramolecular aggregates.[3] The energies involved have been measured[4,5] or estimated[6,7] and were found, quite consistently, to be of the same order as the energies of standard hydrogen bonds (ca. 6–12 kcal/Au···Au at gold–gold distances of 3.0 ± 0.2 Å). State-of-the-art quantum chemical calculations including relativistic and correlation effects have given results that are in excellent agreement with experimental data for various gold(I) compounds.[8–10] Finally, similar phenomena are now also emerging in the structural chemistry of mercury(II).[11]

In exploratory experiments we have started to construct multidimensional systems, in which auriophilicity and hydrogen bonding are codetermining molecular, chain, ring, or network structures. Following a report on a chainlike aggregate of this type,[12] we now present a novel molecular "package" tied together by a central Au···Au bond and two peripheral hydrogen bonds.

Treatment of a solution of methyl[tri(*o*-tolyl)phosphine]gold-(I)[13] with equimolar quantities of diphenylphosphinous acid affords along with some (*o*-Tol)$_3$P−Au−P(O)Ph$_2$ a crystalline, colorless precipitate of a compound with the composition H(Ph$_2$-PO)$_2$Au (**1**) (eq 1). Methane is evolved, and (*o*-Tol)$_3$P is

$$2(o\text{-Tol})_3\text{P}−\text{Au}−\text{Me} + 3\text{Ph}_2\text{P(O)H} \rightarrow$$
$$\tfrac{1}{2}[\text{H(Ph}_2\text{PO)}_2\text{Au}]_2 + (o\text{-Tol})_3\text{P}−\text{Au}−\text{P(O)Ph}_2 +$$
$$2\text{MeH} + (o\text{-Tol})_3\text{P} \quad (1)$$

liberated as demonstrated by the ^{31}P NMR spectra.[14] The same product (**1**) is also obtained from the reaction of (tht)AuC$_6$F$_5$ (tht = tetrahydrothiophene)[15] with 2 mol equiv of Ph$_2$P(O)H in toluene under reflux (eq 2). The tht ligand is readily replaced by a neutral Ph$_2$P(O)H ligand while the second Ph$_2$P(O)H

$$(\text{tht})\text{AuC}_6\text{F}_5 + 2\text{Ph}_2\text{P(O)H} \xrightarrow[\text{reflux}]{\text{toluene}}$$
$$\tfrac{1}{2}[\text{H(Ph}_2\text{PO)}_2\text{Au}]_2 + (\text{tht}) + \text{C}_6\text{HF}_5 \quad (2)$$

molecule is coordinated as an anionic Ph$_2$P(O)$^-$ ligand with concomitant formation of C$_6$HF$_5$.[16]

Crystals of **1** are orthorhombic, space group *Pbca*, with 16 formula units in the unit cell.[17] The lattice contains discrete dimers, which have no crystallographically imposed symmetry. However, a projection along the Au···Au axis of the dinuclear complex reveals that the overall geometry of the dimer is close to point group C_2 symmetry (Figure 1). The two monomeric units are paired with an average dihedral angle P1−Au1··· Au2−P3/P2−Au1···Au2−P4 of 62.8°. In the dimerization process only one of the two P−Au−P axes remains quasi-linear [P3−Au2−P4 = 176.53(6)°], while the other is more strongly bent to P1−Au1−P2 = 167.56(7)°. From Figure 1a it is immediately obvious how the two gold atoms are virtually drawn together in order to attain the "magic distance" Au1···Au2 = 3.0308(4) Å.

Each of the two gold atoms bears a diphenylphosphinite anion and a diphenylphosphinous acid molecule as ligands, both P-bound to leave an oxo and a hydroxy function, respectively, ready for P−O−H···O=P hydrogen bonding. In the periphery of the dinuclear complex there are thus generated two strong hydrogen bonding clamps, which support the Au···Au bonding in the core of the dimer. The conformation of the Ph$_2$PO units is adjusted in such a way that strain-free bonding O2−H···O4 and O1···H−O3 is possible.

The two acid hydrogen atoms (H1, H2) have been located unequivocally in the structure refinement, and each of them is

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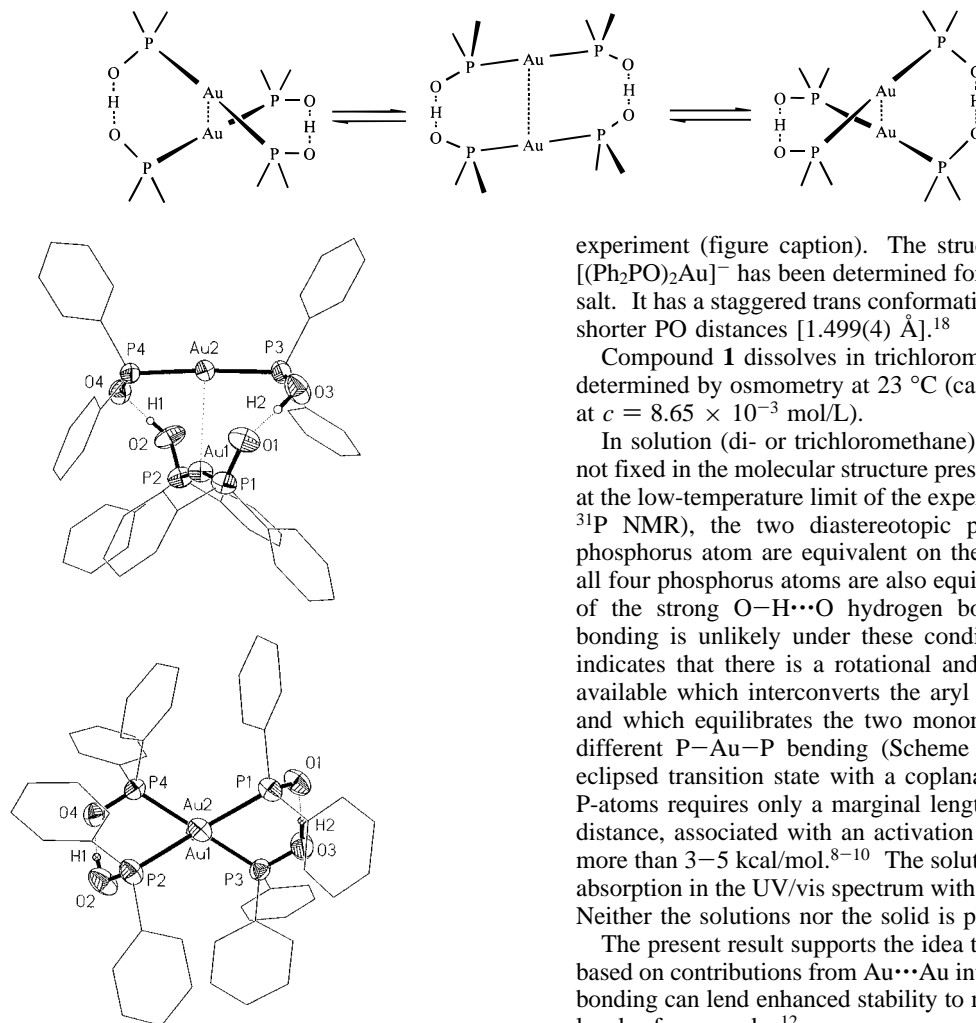(10) Rösch, N.; Görling, A.; Ellis, D. E.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1357.
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(14) A mixture of methyl[tri(*o*-tolyl)phosphine]gold(I), *o*-Tol$_3$PAuMe[13] (155 mg, 0.3 mmol), and diphenylphosphinous acid, Ph$_2$P(O)H (61 mg, 0.3 mmol), was dissolved in toluene (20 mL), and the resulting colorless solution was kept under reflux for 5 h with stirring until its color turned gold. The resulting mixture of products was fractionally crystallized from toluene/pentane to yield 65 mg of **1** (36%) as colorless crystals, mp 195 °C dec. ^{1}H NMR (CDCl$_3$, 20 °C): δ = 7.13–7.52 [m, Ph]. ^{1}H NMR (CD$_2$Cl$_2$, −80 °C): δ = 7.10–7.50 [m, Ph]. ^{31}P{^{1}H} NMR (CDCl$_3$, 20 °C): δ = 101.6 [s, P(O)Ph$_2$]. ^{31}P{^{1}H} NMR (CDCl$_3$, −60 °C): δ = 101.6 [s, P(O)-Ph$_2$]. ^{31}P NMR (CDCl$_3$, −60 °C): δ = 101.6 [s, P(O)Ph$_2$]. MS (FAB): *m/z* = 999 [Au$_2$(POPh$_2$)$_3$]$^+$, 797 [Au$_2$(POPh$_2$)$_2$]$^+$, 600 [Au(POPh$_2$)$_2$]$^+$. IR (KBr, Film): ν (cm^{-1}) = 1014 [ν(PO)]; 1376 [δ(O···H···O)]; 1306 [γ-(O···H···O)]; 750 [ν$_{as}$(O···H···O)]. Anal. Calcd for C$_{24}$H$_{21}$AuO$_2$P$_2$ (600.31): C, 48.02; H, 3.53. Found: C, 48.10; H, 3.63. See also: Hollatz, C.; Schier, A.; Schmidbaur, H. *Chem. Ber.*, submitted for publication.
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(16) A suspension of (tht)AuC$_6$F$_5$ (136 mg, 0.3 mmol) in toluene (20 mL) was treated with 2 equiv of diphenylphosphinous acid, Ph$_2$P(O)H (121 mg, 0.6 mmol), and the resulting suspension was kept under reflux for 3 h with stirring. After filtration the colorless solution was concentrated to a volume of ca. 5 mL, and pentane (30 mL) was added to precipitate product **1** as a white solid. Recrystallization from toluene/pentane yielded 155 mg of **1** (86%).
(17) **Crystal Structure Determination.** The sample was mounted in a glass capillary on an Enraf Nonius CAD4 diffractometer and used for measurements of precise cell constants and intensity data collection. During data collection three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. Graphite-monochromated Mo Kα radiation was used. The structure was solved by direct methods and refined by full matrix least-squares calculations on F^2. Crystal data for C$_{24}$H$_{21}$O$_2$P$_2$Au: M_r = 600.31, colorless crystals, orthorhombic, a = 17.655(1) Å, b = 20.596(1) Å, c = 24.345(2) Å, space group *Pbca*, Z = 16, V = 8852.4(10) Å^3, ρ_{calcd} = 1.802 g cm^{-3}, $F(000)$ = 4640; T = 25 °C. Data were corrected for Lorentz, polarization, and absorption effects [μ(Mo Kα) = 68.09 cm^{-1}, ψ-scans, T_{min}/T_{max} = 0.734/0.999]. 7168 measured reflections [(sin θ/λ)$_{max}$ = 0.62 Å^{-1}]; 531 refined parameters, wR_2 = 0.0644, R = 0.0345 for 7167 reflections with $F_o \geq 4\sigma(F_o)$. Residual electron densities: +1.244/−0.749. The function minimized was wR_2 = {[∑$w(F_o^2 - F_c^2)^2$]/∑[$w(F_o^2)^2$]}$^{1/2}$; w = 1/[$\sigma^2(F_o^2) + (ap)^2 + bp$]; p = ($F_o^2 + 2F_c^2$)/3; a = 0.0332, b = 0. All non-hydrogen atoms were refined with anisotropic displacement parameters. All phenyl hydrogen atoms were calculated and allowed to ride on their corresponding C-atoms with fixed isotropic contributions [$U_{iso(fix)}$ = 1.5U_{eq} of the attached C]; O−H atoms were located and refined with isotropic displacement parameters.

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Scheme 1

Figure 1. Molecular structure of compound **1** (ORTEP drawing with 50% probability ellipsoids, phenyl H-atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Au1···Au2 3.031(1), Au1−P1 2.317(2), Au1−P2 2.315(2), Au2−P3 2.320(2), Au2−P4 2.321(2), P1−O1 1.554(5), P2−O2 1.561(5), P3−O3 1.539(5), P4−O4 1.547(5); P1−Au1−P2 167.56(7), P3−Au2−P4 176.63(6). Hydrogen bonding: (O3−H2···O1) O3−H2 0.98(10), H2···O1 1.45(10); O3−H2···O1 174.3(10); (O2−H1···O4) O1−H1 0.90(7), H1···O4 1.54(10); O2−H1···O4 174.6(9).

found closer to one of the two neighboring oxygen atoms (O2 or O3) than to the other (O1 or O4, respectively, Figure 1a, top). Surprisingly, this orientation is not fully reflected by the corresponding P−O bond lengths, which show only minor differences, hardly exceeding the standard deviations of the

experiment (figure caption). The structure of the free anion $[(Ph_2PO)_2Au]^-$ has been determined for the crystal of the PPN salt. It has a staggered trans conformation of C_i symmetry with shorter PO distances [1.499(4) Å].[18]

Compound **1** dissolves in trichloromethane as the dimer as determined by osmometry at 23 °C (calcd 1200.7, found 1100 at $c = 8.65 \times 10^{-3}$ mol/L).

In solution (di- or trichloromethane) the two monomers are not fixed in the molecular structure present in the crystal. Even at the low-temperature limit of the experiment (−80 °C, ^{1}H and ^{31}P NMR), the two diastereotopic phenyl groups at each phosphorus atom are equivalent on the NMR time scale, and all four phosphorus atoms are also equivalent. Since a rupture of the strong O−H···O hydrogen bonds and the Au···Au bonding is unlikely under these conditions, the NMR result indicates that there is a rotational and a "breathing" process available which interconverts the aryl groups at the P-atoms, and which equilibrates the two monomers with their grossly different P−Au−P bending (Scheme 1). Note that a fully eclipsed transition state with a coplanar array of all Au- and P-atoms requires only a marginal lengthening of the Au···Au distance, associated with an activation energy of probably no more than 3−5 kcal/mol.[8−10] The solutions in CH_2Cl_2 have an absorption in the UV/vis spectrum with a maximum at 300 nm. Neither the solutions nor the solid is photoluminescent.

The present result supports the idea that synergistic bonding based on contributions from Au···Au interactions and hydrogen bonding can lend enhanced stability to molecular and supramolecular frameworks.[12]

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