

Aurophilicity-impaired internal molecular motion of trinuclear gold(I) complexes †

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The trinuclear (chloro)gold(I) complex of the tritertiary phosphine $\text{PhP}[\text{C}_6\text{H}_4(\text{PPh}_2)_2]$ was found to have a compact unsymmetrical structure in the crystalline state which is retained in solution owing to the fixation of the gold atoms through intermetallic contacts.

Bis[2-(diphenylphosphino)phenylene]phenylphosphine (TP, **I**)¹ is a tritertiary phosphine ligand with mirror symmetry. This symmetry is borne out by two phosphorus resonances [$\delta -13.9$ (2 P) and -16.7 (1 P)] in the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum representing an A_2B spin system ($J_{\text{PP}} = 154.8$ Hz) for a dichloromethane solution over the temperature range -80 to $+20$ °C. The spectra of the corresponding trisulfide (TPS₃, **II**) are also compatible with this symmetry [$\text{CH}_2\text{Cl}_2\text{-C}_6\text{D}_6$: $\delta 49.3$ (t), 47.7 (d), $J_{\text{PP}} = 8.1$ Hz at 20 °C], and it is only at the low temperature limit (-60 °C) that for compound **II** signs of non-equivalence of the two terminal phosphorus atoms become discernible [$\text{CH}_2\text{Cl}_2\text{-C}_6\text{D}_6$: $\delta 49.4$ (d), 47.4 (d), 46.9 (t), $J_{\text{PP}} = 8.0$ Hz]. This result shows that although **II** has an unsymmetrical ground-state conformation, there is little steric hindrance of the rotation of the structural units about the P–C bonds in solution at ambient temperature. An estimation of the activation barrier of the hindered motion in **II** from the coalescence parameters gives a ΔG^\ddagger value of *ca.* 7.5 kcal mol⁻¹, and of course even less for **I**. Introduction of a sizable acceptor atom (S) at each phosphorus donor atom in TP thus means only a small curtailment to the flexibility of the ligand skeleton (Fig. 1).

Treatment of TP with 3 equivalents of chloro(dimethyl sulfide)gold(I)² in dichloromethane at 25 °C leads to the liberation of the Me_2S ligands and formation of the trinuclear complex $(\text{TP})(\text{AuCl})_3$ **1** in 60% yield.‡ Colourless needles of **1** [from $\text{CH}_2\text{Cl}_2\text{-pentane}$, m.p. 220 °C (decomp.)] are orthorhombic, space group *Pccn*, with $Z = 8$ formula units in the unit cell (at 181 K).§ The lattice contains equivalent electroneutral trinuclear molecules which possess no crystallographic symmetry (Fig. 2). In these molecules the ligand is folded in such a way as to allow two short contacts between the three gold atoms: Au1-Au2 $2.9671(4)$, Au1-Au3 $2.9250(4)$ Å; Au2-Au1-Au3

$126.88(2)^\circ$. The configuration at the gold atoms is close to linear, and the individual atom P–Au–Cl triples are crossed like swords with their neighbouring units. The environment of the phosphorus atoms is close to tetrahedral and shows no anomalies.

As often observed for $\text{Au}\cdots\text{Au}$ bonded polynuclear gold(I) complexes,⁴ crystals of compound **1** are strongly luminescent: UV excitation (λ_{max} 305 nm) leads to an intense blue emission (λ_{max} 457 nm).

While the solid-state properties are more or less as expected in the light of previous findings in the structural chemistry of polynuclear gold compounds,^{5,6} the observations in the solution state are unusual: the solubility of compound **1** in CDCl_3 or CD_2Cl_2 is poor, but the complex can be dissolved in *o*-dichlorobenzene and in this solvent it shows three separate

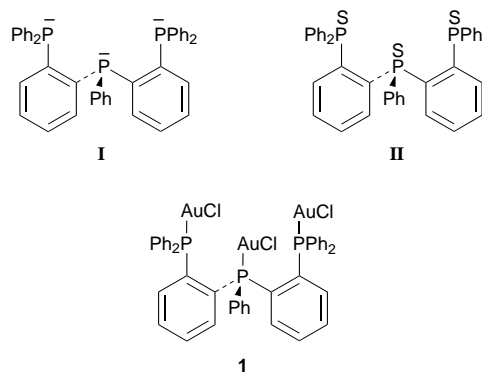


Fig. 1 Idealized representation of the structures of TP **I**, TPS₃ **II** and $(\text{TP})(\text{AuCl})_3$ **1**

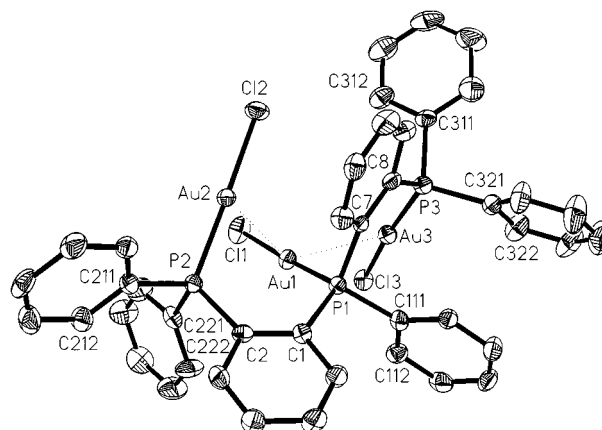


Fig. 2 Molecular structure of compound $(\text{TP})(\text{AuCl})_3$ **1** (ORTEP³, 50% probability ellipsoids, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Au1-Au2 $2.9671(4)$, Au1-Au3 $2.9250(4)$, Au1-P1 $2.243(2)$, Au1-Cl1 $2.296(2)$, Au2-P2 $2.228(2)$, Au2-Cl2 $2.283(2)$, Au3-P3 $2.233(2)$, Au3-Cl3 $2.303(2)$; Au2-Au1-Au3 $126.88(2)$, Cl1-Au1-P1 $175.60(9)$, Cl2-Au2-P2 $178.59(8)$, Cl3-Au3-P3 $172.54(8)$

† Non-SI unit employed: cal = 4.184 J.

‡ Synthesis of $(\text{TP})(\text{AuCl})_3$ **1**. A solution of TP (65 mg, 0.1 mmol) in CH_2Cl_2 (20 cm³) was treated with $[(\text{Me}_2\text{S})\text{AuCl}]$ (90 mg, 0.3 mmol) at 20 °C for 1 h. The solution turned green. A layer of pentane (40 cm³) was allowed to diffuse into this solution to precipitate colourless needles of $(\text{TP})(\text{AuCl})_3$ **1**, m.p. 220 °C, 80 mg (60% yield) (Found: C, 36.9; H, 2.9. $\text{C}_{42}\text{H}_{33}\text{Au}_3\text{Cl}_3\text{P}_3\cdot\text{CH}_2\text{Cl}_2$ requires C, 36.6; H, 2.5%); MS (Cl): m/z 1327.0 [M^+], 1291.9 [$M^+ - \text{Cl}$]. ^1H NMR [$(\text{CD}_3)_2\text{SO}$, 20 °C]: δ 6.67, 6.87, 7.70–7.84 (all m, C_6H_4 , C_6H_5). $^{31}\text{P}\{-^1\text{H}\}$ NMR [$(\text{CD}_3)_2\text{SO}$, 20 °C]: δ 22.7 (d), 22.4 (d), 20.6 (t), $J_{\text{PP}} = 50.1$ Hz.

§ Crystal data: $\text{C}_{42}\text{H}_{33}\text{Au}_3\text{Cl}_3\text{P}_3\cdot\text{CH}_2\text{Cl}_2$, $M_r = 1412.77$, orthorhombic, $a = 21.492(1)$, $b = 21.866(2)$, $c = 20.004(1)$ Å, space group *Pccn*, $Z = 8$, $U = 9400.8(11)$ Å³; $T = -92$ °C; $\mu(\text{Mo-K}\alpha) = 97.55$ cm⁻¹; 8784 measured reflections, 8778 independent reflections, $R1$ ($wR2$) value of 0.0372 (0.0799). CCDC reference number 186/836.

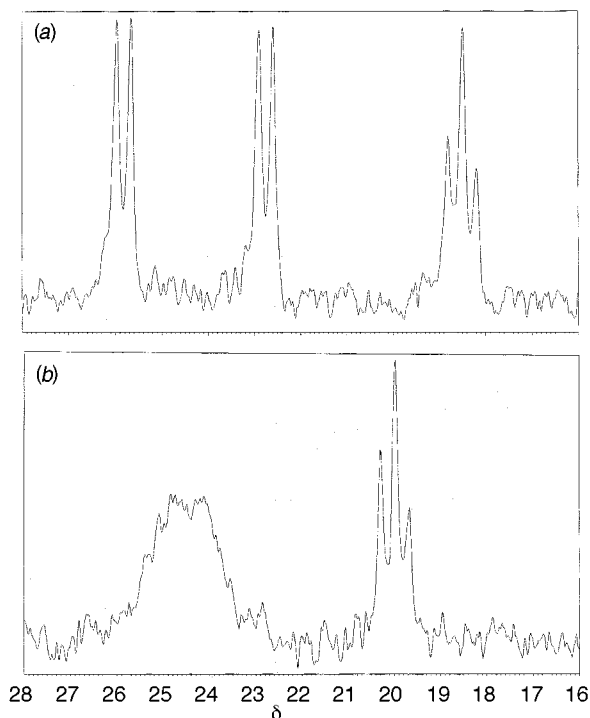


Fig. 3 The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of $(\text{TP})(\text{AuCl})_3$ **1** in *o*-dichlorobenzene at 20 °C (a) and at +110 °C (b)

resonances at 20 °C [as an ABC spin system, Fig. 3(a)], which indicate that an unsymmetrical structure persists in this solvent [δ 25.8 (d, 1 P), 22.7 (d, 1 P), 18.5 (t, 1 P), $J_{\text{PP}} = 49.4$ Hz]. A symmetrization by solvation, either through complete decoupling of the $\text{Au} \cdots \text{Au}$ contacts, or through alternating opening of one of the two contacts to give mirror symmetry or virtual mirror symmetry, respectively, is not rapid on the NMR time-scale at room temperature. Coalescence of the signals of the two peripheral phosphorus atoms (to give an AB_2 spin system) can only be induced by heating the compound to as much as +110 °C [Fig. 3(b)]. This process is reversible upon cooling.

Calculation on the basis of the corresponding NMR spectroscopic parameters give an activation energy for the equilibration process (leading to complete or virtual symmetrization) of no less than $\Delta G_{383}^\ddagger = 17.3 \pm 0.2$ kcal mol $^{-1}$. The $^{31}\text{P}\{-^1\text{H}\}$ NMR data sets for **I**, **II** and **1** thus give a new rough clue as to the bond energy of aurophilic bonding. Previous estimations^{7–11} yielded values between +7.5 and 11.5 kcal mol $^{-1}$ (all based on NMR spectroscopy). The present data, which in an extreme model, are valid for the decoupling of *two* $\text{Au} \cdots \text{Au}$ bonds, fit into this range very nicely, and again support the idea of a similarity (in energy) with hydrogen bonding.⁵

In the words of Pyykkö¹² and others, gold(I) centers are ‘sticky’ and become ‘glued together’ as they become closer than ca. 3.3 Å. This phenomenon, which meanwhile is classified^{12,13} also as a ‘super-van der Waals force’, has been treated with a variety of advanced theoretical methods and the results^{12,14} are in satisfactory agreement with the few quantitative^{7–11} and the plethora of qualitative experimental data.^{5,6} The calculations and recent observations with, e.g. compounds of mercury(II)¹⁵ also provide evidence that the effect is probably more general, but nevertheless most pronounced for gold, the ‘relativistic element *par excellence*’.¹⁶

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