

Gold and silver cations in the “Procrustean Bed” of the bis[2-(diphenylphosphino)phenyl]phenylphosphine ligand. Observations and conclusions †

Johann Zank, Annette Schier and Hubert Schmidbaur *

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

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Reaction of $[\text{Au}(\text{Me}_2\text{S})\text{Cl}]$ or AgCl with equimolar quantities of bis[2-(diphenylphosphino)phenyl]phenylphosphine (TP) gave isomorphous crystalline 1 : 1 complexes with a greatly distorted tetrahedral environment for Au^{I} and Ag^{I} . The large differences in the metal-to-phosphorus interactions are also obvious from the NMR parameters in solution. The complex $[\text{Au}(\text{TP})\text{Cl}]$ is converted into the tetrafluoroborate $[\text{Au}_2(\text{TP})_2][\text{BF}_4]_2$ when treated with AgBF_4 . This ionic compound has a dinuclear dication with grossly different environments for the two gold atoms: one is trigonally planar three-co-ordinated with a short intramolecular $\text{Au} \cdots \text{Au}$ bond [2.8776(4) Å]. The second gold atom is five-co-ordinated with the other gold atom as an equatorial contact. By contrast, the dicationic part $[\text{Ag}_2(\text{TP})_2]^{2+}$ of the product obtained by reaction of TP with AgBF_4 has equivalent silver atoms (related by a center of inversion) which are in a tetrahedral environment including a very short intramolecular $\text{Ag} \cdots \text{Ag}$ distance [2.8569(8) Å]. The temperature dependence of the NMR spectra of $[\text{M}_2(\text{TP})_2][\text{BF}_4]_2$ ($\text{M} = \text{Au}$ or Ag) reflects the fluxional behaviour of these highly strained units in solution.

Introduction

Most of the current research in co-ordination chemistry is generally focused on complexes with “tailor-made” ligands, which perfectly fit a given metal or its clusters.^{1–5} In standard cases this “fit” is beneficial to the stability of the complex and may help to generate certain chemical and physical properties.⁶ Much less interest has been paid to cases where a ligand does not fit a metal at all, although this may frequently generate an “active centre” owing to an “open” geometry and a much lower stability of the system.⁷ The situation there is reminiscent of a chapter in ancient Greek mythology, where the monster Procrustes made his victims (metals) “fit” to his bed (ligand), the infamous “Procrustean Bed”, by very cruel methods.⁸

The ligand geometry is most crucial for the stability of a complex if, on the one hand, the metal is rather inflexible in its preferences for a certain co-ordination number and geometry. This is true in particular for metals with low oxidation states, low co-ordination numbers, and high atomic numbers associated with strong relativistic effects.^{9–13} Gold(I) is a prototype for this group of metals, and it comes as no surprise that linear two-co-ordination is by far the dominant mode for this heaviest of the coinage metals.¹⁴ For gold(I) this geometry is rarely realized with bidentate ligands, because this would require exceedingly long loops between the donor atoms, especially so if the ligand does not tolerate any bending of its framework.^{15,16}

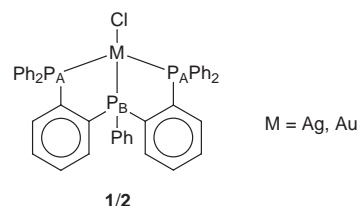
Bis[2-(diphenylphosphino)phenyl]phenylphosphine (TP), on the other hand, is a very inflexible ligand with a rigid backbone based solely on arene substituents with very little freedom for internal molecular motion.^{17,18} Only a few rotational movements are possible and simple models clearly show the groups to be always in each others way. Recently we have demonstrated for TP complexes of gallium and indium that there is virtually no strain-free arrangement for the TP tripod to co-ordinate with all three donor centres to a tetrahedral metal centre.¹⁹

Now we report the results of our studies with univalent gold and silver as their chloride and tetrafluoroborate salts. Very unusual co-ordination geometries involving intriguing metal–metal interactions have been observed, that are generated out of the dilemma that the individual preferences of the metals and the ligands cannot be reconciled in the given system.

Results and discussion

The TP complexes of AuCl and AgCl

Treatment of chloro(dimethyl sulfide)gold(I) with an equimolar quantity of TP in dichloromethane at room temperature gives a yellow solution, from which a yellow crystalline product [mp 332 °C (decomp.)] can be precipitated in 84% yield by addition of diethyl ether. The silver analogue is prepared similarly from silver chloride and TP in the same solvent as green crystals in 68% yield [mp 343 °C (decomp.)]. Both products give satisfactory elemental analysis data. The mass spectra (CI) show the molecular ions of the monomers in low intensity and with the correct isotope patterns. The ¹H NMR spectra contain only complex multiplets of C₆H₅/C₆H₄ resonances which have not been analysed any further.



The ³¹P-¹H NMR spectra show A₂B spin systems indicating virtual equivalence of the terminal Ph₂P groups in solution at ambient temperature. There is rapid site exchange of the metal atom in $[\text{Ag}(\text{TP})\text{Cl}]$ as indicated by the absence of Ag–P coupling in the room temperature spectrum of the compound (Fig. 1). Upon cooling the sample to –70 °C the A₂B pattern is

† Dedicated to Professor Ernst Otto Fischer on the occasion of his 80th birthday.

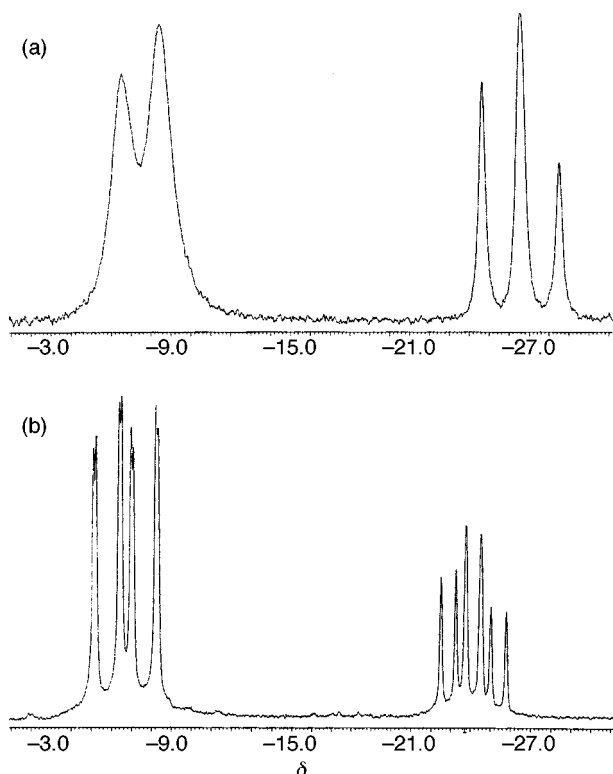


Fig. 1 $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of $[\text{Ag}(\text{TP})\text{Cl}]$ in CD_2Cl_2 at 20 (a) and -70°C (b).

turned into two closely spaced A_2BX spin systems with $\text{X} = ^{107,109}\text{Ag}$: $J(^{107}\text{Ag}-\text{P}) = 280$, $J(^{109}\text{Ag}-\text{P}) = 317$ Hz for P_A and $J(^{107,109}\text{Ag}-\text{P}) = 123$ Hz (average) for P_B , while the $J(\text{P},\text{P})$ coupling constant and the chemical shifts show only minor variations with temperature ($\delta_\text{A} -6.6$, $\delta_\text{B} -24.6$, $J = 204$ Hz). For the spectrum of the gold compound no significant temperature-dependence is observed. The two compounds are photoluminescent showing a yellow emission at λ_max 580 (1) and 503 nm (2), respectively, upon UV excitation at 258 nm. The phosphorescence is stronger for $\text{M} = \text{Ag}$ than for $\text{M} = \text{Au}$.

Single crystals of yellow $[\text{Au}(\text{TP})\text{Cl}]$ and green $[\text{Ag}(\text{TP})\text{Cl}]$ were grown by slow diffusion of diethyl ether into solutions in dichloromethane at 20°C . The crystals are isomorphous (monoclinic, space group $\text{P}2_1/n$, $Z = 4$) with only minor variations in the cell dimensions. The lattices are composed of mononuclear complex molecules with no significant sub-van der Waals contacts (Fig. 2). The individual molecules have no crystallographically imposed symmetry. The maximum attainable (mirror) symmetry is violated mainly by the relative orientation of the phenyl groups (Fig. 3).

The metal atoms are in the centre of a distorted tetrahedral environment of one chlorine and three phosphorus atoms. The distortions are obvious from the spread of the angles $\text{P}-\text{M}-\text{P}$ and $\text{P}-\text{M}-\text{Cl}$, which range from $85.40(3)$ to $121.37(3)^\circ$ for $\text{M} = \text{Au}$ and from $81.03(2)$ to $122.98(2)^\circ$ for $\text{M} = \text{Ag}$. The two smallest $\text{P}-\text{M}-\text{P}$ angles ($\text{P}1-\text{M}-\text{P}2/\text{P}3$) are endocyclic angles of the two fused five-membered rings and require large angles $\text{P}2-\text{M}-\text{P}3$ not spanned by the ligand.

The $\text{M}-\text{P}$ distances average 2.3834 \AA for $\text{M} = \text{Au}$ and 2.5123 \AA for $\text{M} = \text{Ag}$, making silver the larger atom as compared to gold. Again, this result is in excellent agreement with recent redeterminations of the ionic radii of these two elements in other pairs of isomorphous species.²¹ In this context it is worth noting that the volume of the unit cell is greater for the silver than for the gold compound (Table 1).

The distance between the central phosphorus atom of the ligand ($\text{P}1$ in both structures) and the metal M is larger than the distance between M and the two terminal phosphorus atoms. The difference Δ_r is more significant for $\text{M} = \text{Au}$ (0.14 \AA) than

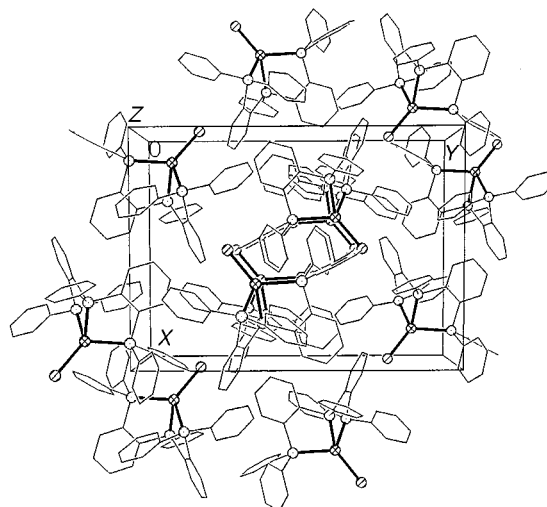


Fig. 2 Packing of the isomorphous compounds $[\text{Au}(\text{TP})\text{Cl}]$ 1 and $[\text{Ag}(\text{TP})\text{Cl}]$ 2 in the crystal lattice.

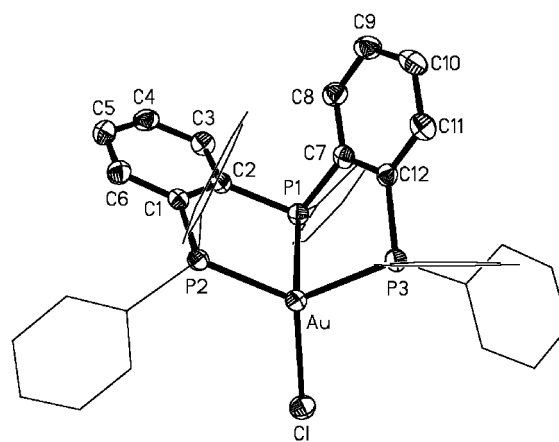


Fig. 3 Molecular structure of compound $[\text{Au}(\text{TP})\text{Cl}]$ 1 (ORTEP²⁰ drawing with 50% probability ellipsoids, H atoms omitted for clarity). The structure of the silver compound 2 is very similar. Selected bond lengths (\AA) and angles ($^\circ$) (the corresponding values of the isomorphous silver compound 2 are given in square brackets): $\text{Au}-\text{Cl}$ $2.5119(10)$ [$2.4663(5)$], $\text{Au}-\text{P}1$ $2.4608(9)$ [$2.5469(5)$], $\text{Au}-\text{P}2$ $2.3206(10)$ [$2.5049(5)$] and $\text{Au}-\text{P}3$ $2.3687(10)$ [$2.4852(5)$]; $\text{P}1-\text{Au}-\text{Cl}$ $118.17(3)$ [$123.09(2)$], $\text{P}2-\text{Au}-\text{Cl}$ $120.68(3)$ [$121.60(2)$], $\text{P}3-\text{Au}-\text{Cl}$ $114.00(3)$ [$122.98(2)$], $\text{P}1-\text{Au}-\text{P}2$ $86.77(3)$ [$81.03(2)$], $\text{P}1-\text{Au}-\text{P}3$ $85.40(3)$ [$82.32(2)$] and $\text{P}2-\text{Au}-\text{P}3$ $121.37(3)$ [$111.57(2)$].

for $\text{M} = \text{Ag}$ (0.06 \AA). These data reflect the weaker acceptor properties of two-co-ordinated gold. This effect is even more obvious from the two $\text{M}-\text{Cl}$ distances: $\text{Au}-\text{Cl}$ $2.5119(10)$ is found longer than $\text{Ag}-\text{Cl}$ $2.4663(5) \text{ \AA}$, which is clear evidence that the chloride anion is drawn towards the gold atom less strongly than towards the silver atom. This conclusion is even more obvious since gold is the smaller atom of the two. With the three $\text{M}-\text{P}$ bonds longer and the $\text{M}-\text{Cl}$ bond shorter for $\text{M} = \text{Ag}$, the volume required by the silver compound is still larger than that needed for the gold compound.

The molecular structure, shown in Fig. 3, indicates that the distortions of the tetrahedral structure in the complexes $[\text{M}(\text{TP})\text{Cl}]$ are mainly due to the restraints imposed by the ligand, which reduce two of the three $\text{P}-\text{M}-\text{P}$ angles to values well below 90° . The chloride anion is filling the resulting large gap in the co-ordination sphere of the metal in a symmetrical way with all $\text{Cl}-\text{M}-\text{P}$ angles slightly above 120° . It is thus clear that in the absence of this auxiliary ligand (Cl^-) serious consequences for the stability of the complexes are to be expected.

The TP complexes of AuBF_4 and AgBF_4

Treatment of a solution of $[\text{Au}(\text{TP})\text{Cl}]$ in dichloromethane with

a solution of equimolar quantities of silver tetrafluoroborate in methanol at room temperature leads to a precipitation of silver chloride. From the supernatant orange solution the product can be isolated after evaporation of the filtrate to dryness and recrystallized from dichloromethane–diethyl ether [orange crystals, mp 310 °C (decomp.), yield 87%]. A suspension of AgBF_4 in dichloromethane becomes clear after addition of equimolar quantities of TP and stirring of the mixture in the dark for 4 d. The crude product, isolated after removal of the solvent, can also be recrystallized from dichloromethane–diethyl ether [colourless crystals, mp 215 °C (decomp.), yield 74%].

The two tetrafluoroborate salts give satisfactory elemental analysis data after careful drying in a vacuum. Single crystals of $[\text{Au}_2(\text{TP})_2][\text{BF}_4]_2$ **3** contain two molecules of dichloromethane; $[\text{Ag}_2(\text{TP})_2][\text{BF}_4]_2$ **4** crystallizes free of solvent molecules. Both compounds are photoluminescent showing yellow emissions at λ_{max} 554 nm for $M = \text{Au}$ and λ_{max} 460 nm for $M = \text{Ag}$ upon UV excitation at 259 nm, the intensity being higher for the silver compound.

The mass spectra (FAB) of the compounds show the uni- and di-positive cations with the expected isotope distributions. The ^1H NMR spectra (in CD_2Cl_2 at 20 °C) contain only extremely complex multiplet resonances in the arene region, which could not be resolved. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of compound **3**, in CD_2Cl_2 at 20 °C, exhibits a broad peak at δ 26.2 (2 P) and a pseudo-quintet signal at δ 16.4 (1 P). At -60 °C the broad hump at δ 26.2 is split into two resonances, one of which is a virtual triplet at δ 33.8 (1 P), while the other is a multiplet centred at δ 19.4 (1 P) (Fig. 4). The third resonance at δ 15.6 (1 P) is now part of a complex multiplet together with a new resonance at δ 19.4. At the high temperature end of the range investigated ($+125$ °C, in *o*-dichlorobenzene– DMSO-d_6) the hump of the 20 °C spectrum (δ 26.2) is sharpened to a virtual triplet at δ 25.6 (2 P), while the former quintet (at 20 °C) is largely retained, but broadened at δ 16.9 (1 P).

Considering the solid state structure (see below and Scheme 1), it is possible to assign this spectrum and its changes as a function of temperature as follows: at the low temperature limit the six phosphorus atoms exist as three pairs of mutually chemically equivalent atoms, which owing to strong coupling and concomitant magnetic inequivalence generate an AA'BB'CC' spin system. The signal at lowest field (δ 33.8), well separated from the other two, is assigned to the pair of P atoms (P2 and P6) at the low-co-ordinate gold centre (Au1, Fig. 5). Owing to the particularly strong coupling A–A' for *trans* positions at low-co-ordinate gold(i) this resonance has the pronounced coupling pattern of a virtual triplet [$J(\text{A}-\text{A}') - J(\text{A}-\text{B}) = ca.$ 232 Hz]. The upfield resonance (δ 15.6) must be assigned to the central P atoms (B, B'; P1 and P4 in Fig. 5), because this signal remains largely unaffected in its chemical shift during the coalescence occurring as the temperature is increased. At low temperature it represents the complex BB' part of the spectrum with extensive coupling to A, A', C, C' and only a small shift difference relative to C/C' (complex multiplet at δ 19.4). It should be noted that the assignments proposed for $[\text{Au}_2(\text{TP})_2][\text{BF}_4]_2$ are in full agreement with published data for $[(\text{AuCl})_3(\text{TP})]$: this molecule also has the resonance of the central P atom at highest field (δ 18.5).¹⁸

As the temperature is raised the A/A' and C/C' resonances collapse at δ 25.6. This result indicates that there is an intramolecular "toothbrush movement" of the two ligands at the metal "teeth" which renders the two peripheral phosphorus atoms equivalent on the NMR timescale (Scheme 1). By the same token the two gold atoms become equivalent, but unfortunately there is no way to observe this consequence directly in solution. Clearly, the dynamic process does not involve a complete dissociation of a ligand from the gold atoms, because some virtual P,P coupling across the metal atoms is retained. This effect causes the pseudo-quintet structure of the

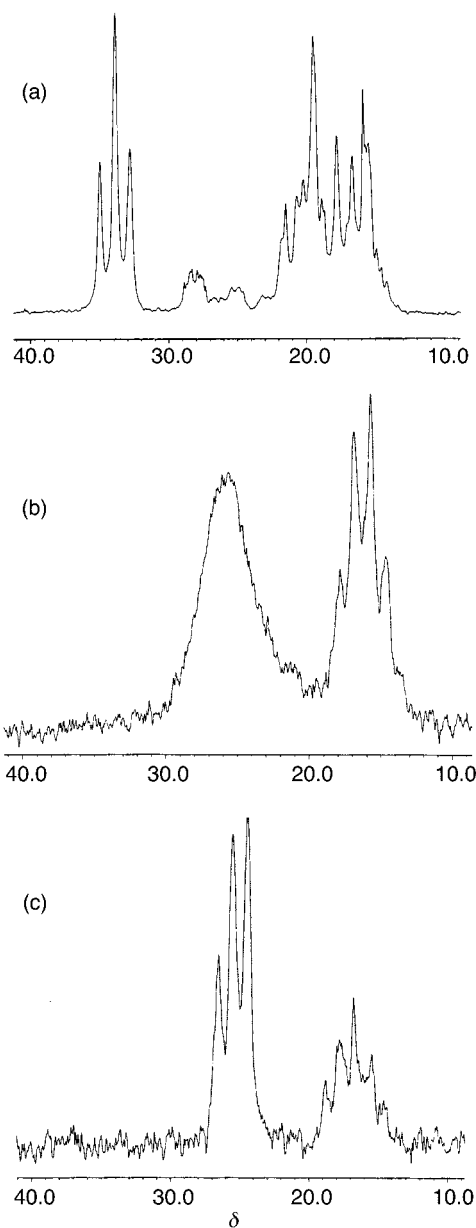
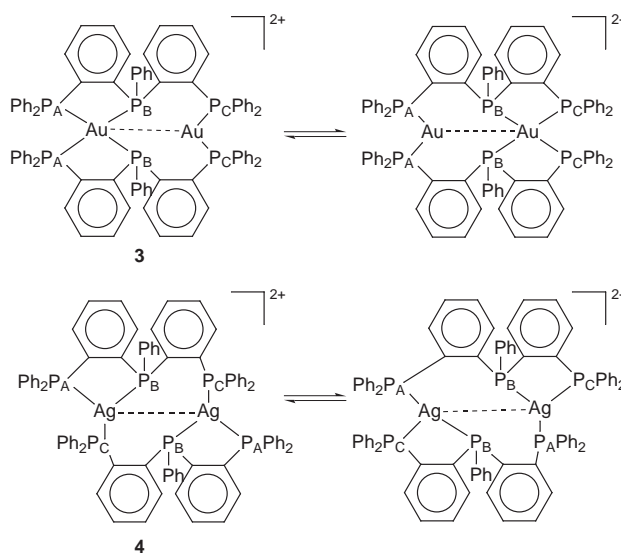


Fig. 4 $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of $[\text{Au}_2(\text{TP})_2][\text{BF}_4]_2$ **3** in CD_2Cl_2 at -60 °C (a), 20 °C (b) and in 1,2-dichlorobenzene at 125 °C (c).



Scheme 1 Representation of the co-ordination in the dicationic complexes $[\text{Au}_2(\text{TP})_2][\text{BF}_4]_2$ **3** and $[\text{Ag}_2(\text{TP})_2][\text{BF}_4]_2$ **4** and their fluxionality.

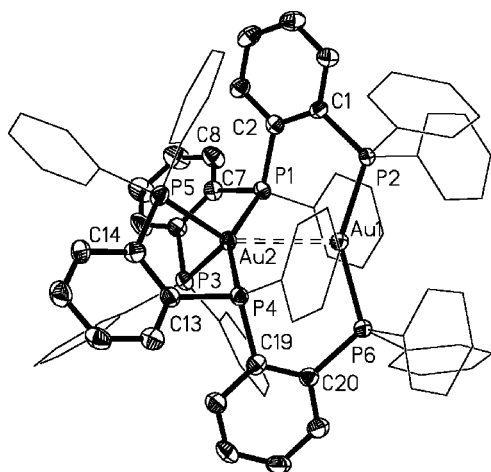


Fig. 5 Molecular structure of the dication of compound **3** (ORTEP drawing with 50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Au1...Au2 2.8776(4), Au1–P2 2.325(2), Au1–P6 2.329(2), Au2–P1 2.367(2), Au2–P3 2.468(2), Au2–P4 2.363(2) and Au2–P5 2.469(2); P2–Au1–P6 147.43(6), P2–Au1...Au2 106.11(4), P6–Au1...Au2 106.44(4), P1–Au2–P3 82.87(6), P1–Au2–P4 150.74(6), P1–Au2–P5 114.61(6), P3–Au2–P4 115.05(6), P3–Au2–P5 107.35(6), P4–Au2–P5 83.26(6), P1–Au2...Au1 75.52(4), P3–Au2...Au1 126.56(4), P4–Au2...Au1 75.22(4) and P5–Au2...Au1 126.09(4).

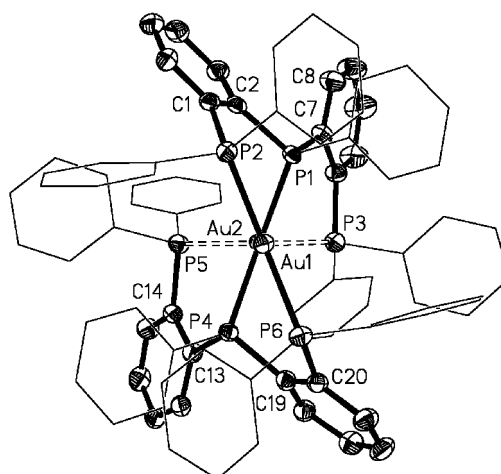


Fig. 6 Molecular structure of compound **3** projected along the Au–Au axis revealing the close approximation of the structure to the symmetry of a twofold axis.

high-field resonance at room temperature and above. This signal would have to be reduced to a triplet if the phenomenon were caused by dissociation and concomitant intermolecular exchange (scrambling) of 'free' and complexed ligands.

The ^{31}P - $\{^1\text{H}\}$ NMR spectrum of the silver compound **4** in CD_2Cl_2 at 20 °C shows only two resonances: a broad pseudo-quartet at δ 0.6 (2 P, $J = ca.$ 180 Hz) and a complex, symmetrical multiplet at δ –14.8 (1 P). At –75 °C the stronger signal (2 P) is also split and the multiplicity becomes more complex. This observation requires a ground-state structure with inequivalent phosphorus atoms (A, B, C) (Scheme 1), which is borne out by the crystal structure of the compound (Fig. 7). The temperature dependence of the spectra is due to a reduction of the coupling of the phosphorus and silver nuclei with increasing temperature (^{31}P , $^{107/109}\text{Ag}$). Owing to partial (but not complete) dissociation of Ag–P co-ordination as the central P atoms (P_B) start to oscillate between the two silver atoms, the terminal P atoms are rendered equivalent (AC collapse to A_2).

Crystals of the gold compound $[\text{Au}_2(\text{TP})_2][\text{BF}_4]_2$ **3** (from CH_2Cl_2 – Et_2O ; monoclinic, space group $P2_1/c$, $Z = 4$) contain two molecules of dichloromethane solvent per formula unit. The lattice is composed of dinuclear dications $[\text{Au}_2(\text{TP})_2]^{2+}$ and two BF_4^- anions, with no significant sub-van der Waals contacts between these components. The anions and the solvent molecules have standard geometries. The dication (Fig. 5) has no crystallographically imposed symmetry, but a projection along the axis connecting the two gold atoms reveals a close approximation of the molecular structure to the symmetry of a twofold axis (Fig. 6). The two ligands are therefore mutually equivalent. An inspection of the projection onto the Au–Au axis shows, however, that the two metal atoms are in completely different environments, both of which are highly unusual and merit a detailed discussion.

Gold atom Au1, on the one hand, is co-ordinated to one peripheral phosphorus atom (P2, P6) of each TP ligand, but the axis P2–Au1–P6 is strongly bent [147.43(6)°] owing to an approach of the second gold atom (Au2) to an Au1...Au2 contact distance as short as 2.8776(4) Å. This distance must definitely be considered as representing gold–gold bonding between closed shell cations. Auophilic bonding of this kind is now well established in the chemistry of low-valent gold compounds and is known to influence significantly many molecular

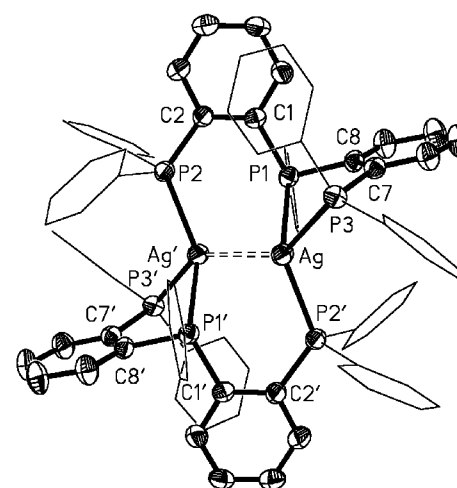


Fig. 7 Molecular structure of the dication of compound **4** (ORTEP drawing with 50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Ag...Ag' 2.8569(8), Ag–P1 2.5439(12), Ag–P2' 2.4301(12), Ag–P3 2.4997(12); P1–Ag–P2' 128.79(4), P1–Ag–P3 81.30(4), P2'–Ag–P3 116.49(4), P1–Ag...Ag' 73.22(3), P2'–Ag...Ag' 100.58(3), P3–Ag...Ag' 142.84(3).

structures and the packing of molecules and ions in the solid state.¹⁴ However, the present example is an extreme case of a trigonally planar three-co-ordinated gold(I) centre where a second gold atom appears as a true third (ligating) component.

Gold atom Au2, on the other hand, is five-co-ordinated and has this gold–gold contact as the fifth ligating interaction which is part of a distorted trigonal-bipyramidal environment. Both ligands are chelating Au2 with their central (P1, P4) and remaining peripheral phosphorus atoms (P3, P5), which form a distorted tetrahedron. Atom Au1 is inserted over one of the tetrahedral edges (P1–P4), the angle P1–Au2–P4 is widened to 150.74(6)° and a contact Au1...Au2 = 2.8776(4) Å is installed on a line exactly bisecting this angle: P1–Au2–Au1 75.52(4) and P4–Au2–Au1 75.22(4)°. To the best of our knowledge this is the first case not only of five-co-ordination at Au^I, but also of auophilic bonding at a high-co-ordinate metal centre.

Single crystals of the silver compound $[\text{Ag}_2(\text{TP})_2][\text{BF}_4]_2$ **4**, (from CH_2Cl_2 – Et_2O , monoclinic, space group $C2/c$, $Z = 8$) are not isomorphous with the gold analogue and contain no solvent. The lattice is composed of tetrafluoroborate anions and binuclear dications which enclose a crystallographic centre of inversion (Fig. 7). Each of the two equivalent silver atoms is chelated by two phosphorus atoms of one ligand (P1, P3) and further co-ordinated to one phosphorus atom (P2) of the

second ligand. However, the resulting AgP_3 core is not trigonal planar as expected for Ag^{I} , but trigonal pyramidal owing to a close mutual approach of the two silver atoms to a short contact of only 2.8569(8) Å, which provides each metal with a pseudo-tetrahedral environment. The Ag–P distances are in the range from 2.4301(12) to 2.5439(12) Å, in good agreement with standard Ag–P bond lengths (compare Fig. 3). The P–Ag–P angles show large deviations from the tetrahedral values, but their average (108.9°) agrees very well with a tetrahedral angle. The distortions are of course due to the constraints of the ligand.

The structure of the dication $[\text{Ag}_2(\text{TP})_2]^{2+}$ in **4** is unique in at least two features: (1) it is an extreme case of strong “metallophilic” bonding, the more general form of “aurophilic” bonding, between closed-shell cations with a higher co-ordination number;^{22,23} (2) the $\text{Ag}\cdots\text{Ag}$ contact is significantly shorter than the intermetallic distance in metallic silver (2.889 Å)²⁴ and in other cases where silver is involved in similar closed-shell interactions.^{22,23,25} This observation shows that this type of bonding between coinage metals is a much more general phenomenon than previously assumed. It is probably a semantic question if the two silver atoms in **4** are actually drawn together by a bonding force, or if they are simply pushed and held together in the “Procrustean Bed” of the ligand. Ample evidence for true bonding in gold chemistry, where several reliable estimates are now available for the bond energies involved, make it very unlikely that the two metal atoms in the dications $[\text{M}_2(\text{TP})_2]^{2+}$ are simply pressed into or onto each other by the TP ligands.^{18,26–30} It rather appears that the gain in bond energy associated with a metallophilic approach of two metal cations is not insignificant, even for lighter atoms with reduced relativistic effects, which were held mainly responsible for aurophilic bonding in the early discussions of the phenomenon.^{13,14}

Unfortunately, no model system has been found yet where the energy of this type of $\text{Ag}\cdots\text{Ag}$ bonding could be measured, or at least estimated, but all recent observations suggest that it may not be much smaller than for $\text{Au}\cdots\text{Au}$ contacts.^{18,26–30} Since we are dealing generally with weak forces, there must be a very delicate balance between several contributions to the overall energy of the system. This may also explain why the gold and silver tetrafluoroborates are not isostructural like the two chlorides. The small differences in the ionic radii of gold and silver may well be sufficient to induce a distortion of the dication. The observation that the unsymmetrical or symmetrical structure, respectively, is retained in solution at low temperature is convincing evidence that the distortion in $[\text{Au}_2(\text{TP})_2]^{2+}$ is not caused by crystal packing, solvation or other external influences, but is an intrinsic feature of the gold complex. For the silver complex the symmetrical structure is maintained, but both species have approximately the same $\text{M}\cdots\text{M}$ distance, in one case between two four-co-ordinate metal atoms, and in the other between a three- and a five-co-ordinated metal atom.

Experimental

General procedure, measurements and materials

All experiments were carried out under dry, purified nitrogen. Solvents used for reactions and crystallizations were dried using appropriate agents, distilled and kept under nitrogen. Glassware was oven-dried and filled with nitrogen. The NMR spectra were obtained on JEOL GX 270 and GX 400 spectrometers. Tetramethylsilane, phosphoric acid and trifluoroacetic acid served as reference compounds for ^1H , ^{31}P and ^{19}F NMR, respectively (δ values in ppm). For mass spectroscopic measurements a Finnigan MAT 90 spectrometer was used. Microanalyses were performed on in-house equipment (by combustion). The ligand bis[2-(diphenylphosphino)phenyl]phenylphosphine¹⁷ and chloro(dimethyl sulfide)gold(I)³¹ were prepared according to literature procedures.

Syntheses

[Au(TP)Cl] 1. The compound $[\text{Au}(\text{Me}_2\text{S})\text{Cl}]$ (120 mg, 0.4 mmol) was dissolved in dichloromethane (10 ml). Addition of TP (250 mg, 0.4 mmol) gave a homogeneous yellow solution, which was stirred for 2 h. A yellow precipitate formed upon addition of pentane. Yellow needles of complex **1** were obtained by allowing diethyl ether to diffuse into a dichloromethane solution. Yield: 84%, mp 332 °C (decomp.) (Found: C, 56.44; H, 3.86; Cl, 6.23. Calc. for $\text{C}_{42}\text{H}_{33}\text{AuClP}_3$: C, 57.0; H, 3.81; Cl, 6.63%). MS (CI): m/z 826.5 $[\text{M}^+]$, 630.7 $[\text{M}^+ - \text{AuCl}]$ and 444.8 $[\text{M}^+ - \text{Ph}_2\text{PAuCl}]$. ^1H NMR (CDCl_3 , 20 °C): δ 6.74, 7.02–7.38, 7.8 and 7.98 (all m, C_6H_4 , C_6H_5). ^{31}P - $\{^1\text{H}\}$ NMR (CDCl_3 , 20 °C): A_2B spin system, δ_{A} 21.4 (d, 2 P), δ_{B} 5.1 (t, 1 P), $J(\text{P},\text{P}) = 190$ Hz.

Ag(TP)Cl 2. To a suspension of AgCl (11.4 mg, 0.08 mmol) in dichloromethane (5 ml) the ligand TP (50 mg, 0.08 mmol) was added and the reaction mixture stirred for 48 h. From the homogeneous green solution the compound was isolated as a green solid by removing the solvent in a vacuum. Diffusion of diethyl ether into a dichloromethane solution led to the formation of green needles. Yield: 68%, mp 343 °C (decomp.) (Found: C, 64.63; H, 4.2. Calc. for $\text{C}_{42}\text{H}_{33}\text{AgClP}_3$: C, 65.18; H, 4.3%; MS (CI): m/z 630.7 $[\text{M}^+ - \text{AgCl}]$ and 445.4 $[\text{M}^+ - \text{Ph}_2\text{PAuCl}]$. ^1H NMR (CD_2Cl_2 , 20 °C) δ 6.94, 7.05, 7.16, 7.24–7.3 and 7.62 (all m, C_6H_4 , C_6H_5). ^{31}P - $\{^1\text{H}\}$ NMR (CD_2Cl_2 , 20 °C) δ -7.5 (broad d, PPh_2), -26.6 (broad t, PPh), $J(\text{P},\text{P}) = 210$ Hz; (-70 °C) δ -6.7 (dd, $\text{PPh}_2 = \text{eP}$), -24.2 (dt, $\text{PPh} = \text{cP}$), $J(\text{eP},\text{cP}) = 204$, $J(\text{eP}^{109}\text{Ag}) = 317$, $J(\text{eP}^{107}\text{Ag}) = 280$, $J(\text{cP}^{109/107}\text{Ag}) = 123$ Hz.

[Au₂(TP)₂][BF₄]₂ 3. To a solution of $[\text{Au}(\text{TP})\text{Cl}]$ (140 mg, 0.15 mmol) in dichloromethane (10 ml) a solution of AgBF_4 (30 mg, 0.15 mmol) in methanol (10 ml) was added with stirring. A white solid (AgCl) precipitated immediately. After 1 h the orange solution was filtered and the solvents were removed. The product was obtained as an orange solid. Orange crystals were obtained by recrystallisation from dichloromethane–diethyl ether. Yield: 87%, mp 310 °C (decomp.) (Found: C, 52.35; H, 3.34; P, 9.8. Calc. for $\text{C}_{84}\text{H}_{66}\text{Au}_2\text{B}_2\text{F}_8\text{P}_6\cdot 2\text{CH}_2\text{Cl}_2$: C, 51.68; H, 3.53; P, 9.3%). MS (FAB): m/z 1655.1 $[\text{M}^+]$ and 827.1 $[\text{M}^{2+}]$. ^1H NMR (CD_2Cl_2 , 20 °C): δ 5.8, 6.09, 6.39, 6.8–7.44 and 7.8 (all m, C_6H_4 , C_6H_5). ^{31}P - $\{^1\text{H}\}$ NMR: (CD_2Cl_2 , 20 °C) δ 16.4 (pseudo-qt, 1 P) and 26.2 (br, 2 P); (CD_2Cl_2 , -60 °C) δ 15.6 (m, 1 P), 19.4 (m, 1 P) and 33.8 (pseudo-t, 1 P); (*o*-dichlorobenzene–DMSO- d_6 , 125 °C) δ 16.9 (broad pseudo-qt, 1 P) and 25.6 (pseudo-t, 2 P). ^{19}F NMR (CD_2Cl_2 , 20 °C): δ 73.6 (s, BF_4^-).

[Ag₂(TP)₂][BF₄]₂ 4. A mixture of AgBF_4 (31 mg, 0.16 mmol) and TP (100 mg, 0.16 mmol) in dichloromethane was stirred for 96 h. From the homogeneous colourless solution the product could be isolated as a white solid by removing the solvent. Diethyl ether was allowed to diffuse into a dichloromethane solution of compound **4** to precipitate colourless needle-like crystals. Yield: 74%, mp 215 °C (decomp.) (Found: C, 59.9; H, 4.32. Calc. for $\text{C}_{42}\text{H}_{33}\text{Ag}_2\text{BF}_4\text{P}_3$: C, 61.12; H, 4.03%). MS (FAB): 737.7 $[\text{M}^{2+}]$. ^1H NMR (CD_2Cl_2 , 20 °C): δ 6.62, 6.96 and 7.18–7.48 (all m, C_6H_4 , C_6H_5). ^{31}P - $\{^1\text{H}\}$ NMR (CD_2Cl_2 , 20 °C): δ -0.6 (pseudo-qt, 2 P) and -14.8 (m, 1 P).

Crystal structure determinations

Specimens of suitable quality and size of compounds **1–4** were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection on an Enraf Nonius CAD4 diffractometer (Mo- $K\alpha$ radiation, $\lambda = 0.71073$ Å). During data collection three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. Lorentz-polarization correction was applied, and the data of **1**, **3** and **4**

Table 1 Crystal data, data collection, and structure refinement

	[Au(TP)Cl] 1	[Ag(TP)Cl] 2	[Au ₂ (TP) ₂][BF ₄] ₂ ·2 CH ₂ Cl ₂ 3	[Ag ₂ (TP) ₂][BF ₄] ₂ 4
Formula	C ₄₂ H ₃₃ AuClP ₃	C ₄₂ H ₃₃ AgClP ₃	C ₈₆ H ₇₀ Au ₂ B ₂ Cl ₄ F ₈ P ₆	C ₄₂ H ₃₃ AgBF ₄ P ₃
<i>M_r</i>	863.01	773.91	1998.59	825.27
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	13.586(1)	13.606(1)	12.794(2)	21.129(3)
<i>b</i> /Å	18.422(1)	18.609(1)	25.383(1)	17.005(2)
<i>c</i> /Å	13.773(1)	13.731	24.788(3)	21.876(3)
β/°	96.71(1)	96.06(1)	91.69(1)	104.83(1)
<i>V</i> /Å ³	3419.0(4)	3457.2(4)	8043(3)	7598(2)
<i>D_c</i> /g cm ⁻³	1.677	1.487	1.650	1.443
<i>Z</i>	4	4	4	8
<i>F</i> (000)	1704	1576	3936	3344
μ(Mo-Kα)/cm ⁻¹	73.24	8.30	39.60	7.06
<i>T</i> /°C	-85	-78	-78	-70
Measured reflections	6802	7848	16458	13606
Unique reflections	6691 [<i>R</i> _{int} = 0.0225]	7539 [<i>R</i> _{int} = 0.0348]	15748 [<i>R</i> _{int} = 0.0250]	8260 [<i>R</i> _{int} = 0.0325]
Reflections used for refinement	6103	7155	14177	7325
Refined parameters	424	424	893	460
Final <i>R</i> values [<i>I</i> > 2σ(<i>I</i>)]				
<i>R</i> 1	0.0245	0.0237	0.0423	0.0545
<i>wR</i> 2	0.0563	0.0609	0.1048	0.1554
ρ _{hm} (max./min.)/e Å ⁻³	0.545/-0.574	0.545/-0.574	3.321/-1.728 ^a	3.248/-0.970 ^b

^a Residual electron densities are located around BF₄⁻ and CH₂Cl₂. ^b Residual electron densities are located at Ag.

were corrected for absorption (DIFABS³²). The structures of **1**, **3**, and **4** were solved with direct methods (SHELXS 86³³) and completed by full-matrix least squares techniques against *F*² (SHELXL 93³⁴). The coordinates of the solution of **1** were used for the refinement of the isomorphous compound **2**. The thermal motion of all non-hydrogen atoms was treated anisotropically, except for those of the solvent CH₂Cl₂ and the BF₄ anion in the lattice of **3**, which were refined isotropically. All hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions [*U*_{iso(fix)} = 1.5 × *U*_{eq} of the attached C atom]. Crystal data, data collection and structure refinement are summarized in Table 1. Important interatomic distances and angles are shown in the corresponding Figure Captions.

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