Bromination of (phosphine)gold(1) bromide complexes: stoichiometry and structure of products

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The course of the oxidative addition of elemental bromine to complexes of the type (L)AuBr is strongly influenced by the nature of the tertiary phosphine ligand L. Standard square planar gold(III) complexes (L)AuBr₃ are obtained not only with L = PMe₃ but also with P(ⁱPro)₃ for which the oxidative addition fails in the corresponding iodine system. Excess bromine is integrated into crystals of the products with the stoichiometry [(Me₃P)AuBr₃]·(Br₂) and {[(ⁱPro)₃P]AuBr₃}·(Br₂). Of the series of iodine analogues, an intercalate [(Me₃P)AuI₃]₂·(I₂) has been structurally characterized. [(ⁱBu)₃P]AuBr undergoes ligand redistribution upon treatment with bromine to give a complex reaction mixture, from which {[(ⁱBu)₃P]₂Au}+(Br₃)⁻·(Br₂) could be crystallized. It contains polymeric anions [(Br₅)⁻]_n as zig-zag chains. [(*o*-Tol)₃P]AuBr is readily brominated to give [(*o*-Tol)₃P]AuBr₃. Contrary to the situation in the gold(1) complex with its linear PAuBr unit, the square planar structure of the PAuBr₃ unit causes steric hindering of the rotation of the tolyl groups about the P–C bonds as demonstrated by solution NMR studies. (The corresponding reaction with iodine is known to give only polyiodides with the oxidation state of the gold atom unchanged.) The even more severe congestion in [(Mes)₃P]AuBr prevents oxidative addition not only of iodine but also of bromine. With the latter, P–Au cleavage occurs instead affording [(Mes)₃PBr]⁺[AuBr₄]⁻.

Introduction

The oxidative addition of elemental halogens X_2 to gold(I) halides AuX and their complexes (L)AuX and $[AuX_2]^-$ is of current interest because this process is an important step in the etching of metallic gold with various halogenating agents.¹⁻⁶ There are inconsistent reports on the nature and properties of the final products. A main issue is the stability of gold(III) complexes (L)AuX₃ with the two heavier halogens (X = Br, I) which strongly depends on the donor capabilities and the steric requirements of L.¹ If L is chosen from the series of tertiary phosphines or dithiones, the coordination chemistry can also be influenced by chelation using difunctional ligands.^{13,4}

$$2 \operatorname{Au} + X_2 \to 2 \operatorname{AuX} \tag{1}$$

$$2 \operatorname{AuX} + 2 \operatorname{L} \to 2 (\operatorname{L})\operatorname{AuX}$$
 (2a)

$$2 \operatorname{AuX} + 2 \operatorname{X}^{-} \to 2 [\operatorname{AuX}_2]^{-}$$
(2b)

2 (L)AuX + 2
$$X_2 \rightarrow 2$$
 (L)AuX₃ or 2 [(L)AuX]·(X₂) (3a)

$$2 [AuX_2]^- + 2 X_2 \rightarrow 2 [AuX_4]^- \text{ or } 2 [AuX_2]^- \cdot (X_2)$$
 (3b)

Following an account of our recent study of the chemistry of the iodo complexes with phosphine ligands,¹ we now present results on some bromo analogues. It should be noted that bromination of gold under standard conditions quite generally leads to gold(III) complexes which are thermodynamically stable in a square planar ground state structure (eqns. (3a) and (3b)).⁷⁻¹⁴ This is in contrast to the iodo compounds which are generally thermodynamically unstable unless small and powerful donor ligands shift the redox potential across a threshold to make oxidative addition of I₂ possible. With less potent ligands L the stoichiometry of the addition compounds may still feign an (L)AuI₃ state (eqn. (3a)), but the extra iodine is actually only associated to generate a gold(II) polyiodide instead of a gold(III) triiodide or tetraiodoaurate(III). The literature has been summarized in a preceding publication.¹

Preparative results

(*Trimethylphoshine*)gold(1) bromide $(Me_3P)AuBr$ (colourless) was shown to add one equivalent of elemental bromine to give the orange diamagnetic complex (Me₃P)AuBr₃ which has a square planar molecular structure.⁷ In this study it was noted that the crystals may trap excess bromine with a deep orange colour. When following up this observation using stoichiometric quantities of bromine, a new orange crystalline phase of the net composition (Me₃P)AuBr₅ was obtained. Solutions of this phase in dichloromethane showed NMR signals with chemical shifts similar to those of (Me₃P)AuBr₃ and had a significant vapour pressure of elemental bromine. These properties suggested a simple adduct, and a single crystal structure determination confirmed this assumption (below).

 $(Me_3P)AuBr_3 + Br_2 \rightarrow [(Me_3P)AuBr_3] \cdot (Br_2)$

 $(Me_3P)AuBr + 2 Br_2 \rightarrow [(Me_3P)AuBr_3] \cdot (Br_2)$

The same reaction in the iodine system affords an almost black crystalline 2 : 1 adduct, the decomposition temperature of which is 10 °C higher than that of the $(Me_3P)AuI_3$.¹ The compound also dissolves in dichloromethane to give the free components.

$$2 (Me_3P)AuI_3 + I_2 \rightarrow [(Me_3P)AuI_3]_2 \cdot (I_2)$$

$$2 (Me_3P)AuI + 3 I_2 \rightarrow [(Me_3P)AuI_3]_2 \cdot (I_2)$$

[*Tri*(*isopropy*])*phosphine*]*gold*(1) *iodide* was found to be reluctant to undergo oxidative addition of *iodine*, mainly for steric reasons. The product with the stoichiometry {[(^{1}Pro)₃P]AuI}₂·(I₂)₃ is a polyiodide and not a genuine gold(III) complex.¹ In the analogous reaction of colourless [(^{1}Pro)₃P]AuBr with an equimolar amount of *bromine* the red crystalline gold(III) complex is readily obtained in 90% yield. The product is stable to its mp (98 °C). With excess bromine a red 1 : 1 adduct {[(^{1}Pro)₃P]AuBr₃}·(Br₂) could be crystallized:

$$[(^{i}Pro)_{3}P]AuBr + Br_{2} \rightarrow [(^{i}Pro)_{3}P]AuBr_{3}$$

$$[(^{i}Pro)_{3}P]AuBr + 2 Br_{2} \rightarrow \{[(^{i}Pro)_{3}P]AuBr_{3}\} \cdot (Br_{2})$$

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[Tri(butyl)phosphine]gold(I) iodide has been shown to add no iodine. Neither a gold(III) complex nor a gold(I) polyiodide could be isolated.¹ The corresponding gold(I) bromide complex, [(^tBu)₃P]AuBr, appears to undergo reaction with equimolar quantities of Br2 in dichloromethane, but no product could be crystallized. The ¹H NMR spectrum of the reaction mixture shows a signal which has a chemical shift similar to that of the starting material, but its multiplicity has changed from a simple sharp doublet (A part of an A_nX spin systems) to a "filled in" doublet generally observed for $A_n XX'A'_n$ spin systems. This result suggested a ligand redistribution which leads to the formation of $\{[({}^{t}Bu)_{3}P]_{2}Au\}^{+}$ cations. And indeed, with an excess of bromine a crystalline solid of the composition $\{[(Bu)_3P]_2Au\}^+(Br_3)^-(Br_2) \text{ could be isolated and structurally}$ characterized (below). The by-products could not be identified, but it is very likely that the anions [AuBr₂]⁻ and [AuBr₄]⁻ required by the mass balance are among the counterions which remain in solution. The $\{[({}^{t}Bu)_{3}P]_{2}Au\}^{+}$ cation was also observed in the mass spectra of the products.

$$2 [({}^{\iota}Bu)_{3}P]AuBr + excess Br_{2} \rightarrow \{[({}^{\iota}Bu)_{3}P]_{2}Au\}^{+}(Br_{3})^{-}\cdot(Br_{2}) + by\text{-products}$$

This result shows that with the particularly bulky $P(^tBu)_3$ ligand even the smaller and more reactive Br_2 molecules (as compared to I_2 molecules) have no access to the gold(I) center of the complex and are hence unable to convert it into a gold(II) center.

[*Tri(ortho-tolyl)phosphine]gold(1) bromide* was found to readily undergo oxidative addition of a bromine molecule to give high yields of an orange gold(III) complex of high stability (mp 150 °C with decomposition).

$[(o-Tol)_3P]AuBr + Br_2 \rightarrow [(o-Tol)_3P]AuBr_3$

Although the reaction occurs readily and almost quantitatively, there is severe steric hindrance clearly discernible in the product: While the three o-tolyl groups have uninhibited rotational motion in the gold(I) complex, as indicated by their solution NMR-equivalence (in dichloromethane at 25 °C), these groups are NMR-inequivalent in the gold(III) complex (Fig. 1). Three separate signals are observed for the three methyl groups, and a temperature of ca. 80 °C is required (in a higher boiling solvent like chlorobenzene) to induce coalescence. Two of the three signals have a larger line-width than the third one already at room temperature, and as the temperature rises, these two are subject to coalescence first, before the third one also becomes involved. It is thus obvious that the rotation of the tolyl groups about the P-C bonds, and possibly even the rotation of the phosphine ligand about the Au-P bond are restricted by the *cis*-bromo substituents of the square planar gold(III) complex. The ground state conformation was determined by the crystal structure analysis (below). It shows that only a minor rotational barrier has to be overcome in order to make two of the three o-tolyl groups equivalent, the molecule attaining mirror symmetry. The third substituent is more strongly affected in its movement and therefore rotates freely only at higher temperature leading to virtual C_3 symmetry.



Fig. 1 ¹H NMR spectrum of [(o-Tol)₃P]AuBr₃ (CD₂Cl₂, 25 °C).

[Tri(mesityl)phosphine]gold(1) bromide was found to react with excess bromine in dichloromethane to give a product of Au–P cleavage, which was identified as bromotri(mesityl)phosphonium tetrabromoaurate(III). Red crystals were isolated in 87% yield (mp 217 °C with decomposition).

$[(Mes)_3P]AuBr + 2 Br_2 \rightarrow [(Mes)_3PBr]^+[AuBr_4]^-$

The $[(Mes)_3PBr]^+$ cation has been detected as the parent ion in the mass spectrum of the product. The compound is stable in air and readily soluble in polar solvents. The ¹H, ¹³C and ³¹P NMR signals appear in the expected shift regions. The rotation of the mesityl groups about their P–C bonds is hindered (in dichloromethane at 25 °C) rendering the 2,6-methyl groups and 3,5-hydrogen atoms inequivalent. This pattern suggests a propeller or paddlewheel structure.¹⁵

It appears that in the tri(mesityl)phosphine complex with three 2,4,6-trimethyl-phenyl groups instead of three 2methylphenyl groups in the tri(o-tolyl)phosphine complex—the gold(I) center is perfectly protected against oxidative addition of bromine. The situation resembles that of the tri('butyl)phosphine complex, but the reaction takes a different course. The cation [(Mes)₃P]₂Au}⁺ features a particularly severe steric conflict owing to the close proximity of two tri(mesityl)phosphine ligands.¹⁶ Therefore, any ligand redistribution giving this cation offers no relief for a crowded system, and in the presence of a strong oxidizing agent P–Au cleavage is thus the preferred alternative.

Crystal and molecular structures

(Trimethylphosphine)gold(III) triiodide, (Me₃P)AuI₃, has recently been structurally characterized. Its gold atom is in a square planar environment with only minor differences in the details of bonding for the *cis*- and *trans* iodine atoms.¹

The same structure has now been found for the components of the new iodine adduct $[(Me_3P)AuI_3]_2 \cdot (I_2)$. Crystals of this phase are monoclinic, space group $P2_1/c$. The asymmetric unit contains two inequivalent (Me₃P)AuI₃ complexes and one I₂ molecule. The geometry of the two complexes is very similar, and in excellent agreement with that of molecules in the phase which contains no extra iodine. The molecules centered by Au2 have no contact with the I₂ molecule, and their conformation approaches quite closely the maximum attainable mirror symmetry: The dihedral angle I21–Au2–P2–C23 is only –1.3° (Fig. 2a).

A pair of molecules, each centered by Au1 is connected by two I₂ molecules as shown in Fig. 2b. Counting all I-I contacts, a 10membered ring is formed around a crystallographic center of inversion. The I-I-I-I bridges are not linear [I1-I2-I13 134.7(1)°, I2–I1–I12' 177.0(1)°], and the angles at the iodine atoms I12 and I13 are strongly different [Au1-I12-I1' 128.6(1)°, Au1-I2-I13 98.1(1)°]. The I1–I2 distance [2.729(1) Å] is significantly longer than in orthorhombic crystals of iodine [2.667(1) Å], and the distances I1-I12' = 3.360(1) and I2-I13 = 3.570(1) Å are shorter than the sum of two van der Waals radii [3.80 Å].17 The conformation of the molecules centered by Au1 deviates strongly from mirror symmetry [dihedral angle I13-Au1-P1- $C13 - 19.8(5)^{\circ}$], but it is interesting to note that the Au–I bond lengths are not affected by the contacts with the I_2 molecules as witnessed by the distances Au1-I11 2.620(1) and Au1-I13 2.623(3) Å.

(*Trimethylphosphine*)gold(III) tribromide, (Me₃P)AuBr₃, has already been structurally characterized.⁷ Crystals have now been grown for the 1 : 1 bromine adduct [(Me₃P)AuBr₃]·(Br₂) (orthorhombic, space group *Pnma*, Z = 4), in which the complex molecules are linked *via* bromine molecules into chains (Fig. 3). Mainly the two *cis*-bromine atoms (Br2–Br4', Br3–Br5) of the complexes are engaged in this aggregation, but there is also a sub-van der Waals contact to the *trans*-bromine atom (Br1– Br4'). Surprisingly, all atoms of a chain except for the C1/C1A atoms (and ignoring the hydrogen atoms) are accommodated on a crystallographically imposed mirror plane which is bisecting



Fig. 2 Crystal structure of $[(Me_3P)AuI]_2 \cdot (I_2)$. (a) One type of two independent complex molecules, not aggregated with intercalated I₂ molecules (ORTEP, 50% probability ellipsoids, H atoms omitted). (b) Cyclic assembly of $[(Me_3P)AuI]_2 \cdot (I_2)_2$ units containing the second type of two independent complex molecules. The components are related by a centre of inversion (arbitrary radii). Selected bond lengths [Å] and angles [°]: Au1–P1 2.330(3), Au1–I11 2.6196(9), Au1–I12 2.6617(8), Au1–I13 2.6231(9), Au2–P2 2.340(3), Au2–I21 2.6238(8), Au2–I22 2.6532(8), Au2–I23 2.6257(8); I1–I2 2.729(1), I1–I12' 3.360(1), I2–I13 3.570(1); I1–I2–I13 134.7(1), I2–I1–I12' 177.0(1), Au1–I12–I1' 128.6(1), Au1–I13–I2 98.1(1).



Fig. 3 Crystal structure of $[(Me_3P)AuBr_3]$ ·(Br₂) showing the connectivity pattern between the Br₂ molecules and the neighbouring (Me₃P)AuBr₃ complexes. All atoms except for C1 and C1A reside on a crystallographic mirror plane. Two neighbouring chains are related by centres of inversion (ORTEP, 50% probability ellipsoids, H atoms omitted). Selected bond lengths [Å] and angles [°]: Au1–P1 2.321(2), Au1–Br1 2.4815(8), Au1–Br2 2.4197(9), Au1–Br3 2.4296(8), Br4–Br5 2.3013(12); Br1–Br4' 3.7047(13), Br2–Br4' 3.2910(13), Br5–Br3 3.219; Br1–Br4'–Br5' 147.57(4), Br2–Br4'–Br5' 153.02(5), Br4–Br5–Br3 179.5.

the angles C1–P1–C1A and represents a common coordination plane for the gold atoms.

There is a significant *trans* influence of the phosphine ligand which lengthens the Au1–Br1 bond to 2.4815(8) Å as compared to 2.41979(1) for Au1–Br2 and 2.4296(8) Å for Au1–Br3, even though the latter include the bromine atoms functioning as bridging atoms for the bromine molecules. Nevertheless, the Br4–Br5 distance in the bromine molecule [2.3013(12) Å] is somewhat lengthened as compared to the value for "free" Br₂ [2.284 Å], and the contacts Br2–Br4′ 3.2910(13) and Br3–Br5 3.219 Å are shorter than the sum of two van der Waals radii [3.60 Å].

Neigbouring chains of the structure run in opposite directions, referring *e.g.* to the orientation of the unique bonds P1–C2, and are related by centers of inversion located between the chains.

[*Tri(isopropyl)phosphine*]gold(III) tribromide, [($^{\circ}Pro$)₃P]Au-Br₃, was crystallized as the 1 : 1 adduct with bromine, {[($^{\circ}Pro$)₃-P]AuBr₃}·(Br₂) (monoclinic, space group *Cc*, *Z* = 4). As in the PMe₃ complex (above), the coordination compounds are also aggregated into chains *via* the bromine molecules, but the connectivity pattern is significantly different. As shown in Fig. 4, together with the *trans*-Au-Br bond (Au1-Br2), only one of the two *cis*-Au-Br bonds (Au1-Br1) becomes involved, and the approach of the Br₂ molecules is not strictly to the terminal



Fig. 4 Chain structure of { $[(^{h}Pro)_{3}P]AuBr_{3}$ } (Br₂) (arbitrary radii, hydrogen atoms omitted). Selected bond lengths [Å] and angles [°]: Au1–P1 2.351(2), Au1–Br1 2.422(1), Au1–Br2 2.500(1), Au1–Br3 2.412(1), Br4–Br5 2.333(2), Au1–Br5' 3.534(1), Au1–Br4 3.857(7), Br1–Br4 3.308(2), Br2–Br5' 3.098(2); Br1–Br4–Br5 128.7(1), Br2–Br5'–Br4' 125.0(1), Br4–Br1–Au1 110.6(1), Au1–Br5'–Br2 73.4(1) (Au1': 1 + x, y, z; Au2'': -1 + x, y, z).



Fig. 5 Molecular structures of the two independent molecules in crystals of $[(o-Tol)_3P]AuBr_3$ (ORTEP, 50% probability ellipsoids, H atoms omitted). Note, that the tolyl groups C111–C117 and C211–C217 are roughly perpendicular to the coordination plane of the gold atoms, with their methyl groups oriented away, but with the H-atoms on C112 and C212 orientated towards the metal atoms. Selected bond lengths [Å] and angles [°]: Au1–P1 2.3481(14), Au1–Br11 2.4348(6), Au1–Br12 2.4573(7), Au1–Br13 2.4273(7), Au2–P2 2.3537(14), Au2–Br21 2.4225(6), Au2–Br22 2.4652(6), Au2–Br23 2.4269(6).

bromine atoms but about midway between a gold and a bromine atom. The angles Br4–Br1'–Au1' and Br5–Br2–Au1 are $110.6(1)^{\circ}$ and $73.4(1)^{\circ}$. However, with the Br–Br contacts shorter than the Br–Au contacts in both cases, the bonding is clearly stronger for the former. The distance Br4–Br5 = 2.333(2) Å in the Br₂ molecule shows that this bond is also lengthened considerably as compared to "free" bromine.

The conformation of the $P(^{i}Pro)_{3}$ ligand does not approach any standard symmetry (point groups C_{3} or C_{s}) and it is obvious that there should be no restricted rotation of the substituents about the P–C bonds or of the ligand about the Au–P bond in solution. This is in agreement with the NMR findings in $CD_{2}Cl_{2}$ as a solvent, where all six methyl groups are equivalent on the NMR time-scale at 25 °C. In the mass spectrum (FAB) only the products of the reductive elimination of Br₂ and ligand redistribution were observed, including also the dinuclear cation of the type {[($^{i}Pro_{3}P$)Au]₂Br}⁺, for which there are precedents in the literature.^{18,19}

[*Tri*(*o*-toly1)phosphine]gold(111) tribromide, [(*o*-Tol)₃P]AuBr₃, forms red monoclinic crystals (space group $P2_1/c$, Z = 8) with two independent complex molecules in the asymmetric unit together with some disordered dichloromethane solvent, which could not be modeled successfully (see Experimental). The geometry of the PAuBr₃ units is very similar to that of the other two (R₃P)AuBr₃ complexes (above) and therefore not discussed any further (Fig. 5).

The conformation of the $P(o-Tol)_3$ ligands has no symmetry leaving all *o*-tolyl groups inequivalent. It should be noted that only a C_3 propeller or a $C_{3\nu}$ paddlewheel symmetry would lead to equivalence. In each of the two ligands (with P1 and P2) the methyl group of one *o*-tolyl substituent (C117 and C217) is oriented away from the gold atom, while the other two are closer to the metal atom. The dihedral angles Au1–P1–C111–C116 = $172.2(4)^{\circ}$ and Au2–P2–C211–C216 = $171.2(4)^{\circ}$ are clear indicators for this *E* (entgegen, "single-*trans*") orientation. Rotation of the aryl groups about the P–C bonds appears to be restricted as already demonstrated in solution NMR experiments (Fig. 1).

Upon solvation in dichloromethane the two complex molecules (with Au1 and Au2) become equivalent and only three methyl signals are observed (instead of six). It is further conceivable that upon heating more extended rotational movements of the aryl groups originally bearing methyl carbon atoms designated as C127/C137 and C227/C237, respectively, make these methyl groups equivalent first (leading to a virtual mirror symmetry of the ligand), as observed in the temperaturedependent NMR measurements. Full equivalence is achieved as the third aryl group becomes freely rotating at higher temperature. Unfortunately, temperature-dependent NMR studies are not straightforward owing to solubility/stability problems. Most common polar solvents (dimethylsulfoxide, dimethylformamide, chloroform, tetrahydrofuran, *etc.*) are readily brominated at elevated temperatures by the increasingly aggressive gold(III) tribromide complex, while others (benzene, chlorobenzene, dioxane, *etc.*) feature only limited solubility. Therefore no quantitative data (based on a line shape analysis) could be collected over a sufficiently large temperature interval to allow determination of the energy parameters of the dynamic processes involved.

There is another minor detail in the room temperature ¹H NMR spectrum of $[(o-Tol)_3P]AuBr_3$ concerning the resonance of an aryl proton. Its chemical shift [dd, δ 8.70 ppm (³J_{H,H} 7.2, ⁴J_{P,H} 18.2 Hz), 1H] is well separated from that of the resonances of the other aryl protons (m, δ 7.20–7.70 ppm, 11H) suggesting exposure of this H atom to the influence of the gold atom (Fig. 1). The likely candidates are those at C-atoms originally designated C112 and C212 in the crystal structure (Fig. 5) which have the right *Z* (zusammen, "single-*cis*") orientation as indicated by the dihedral angles Au1–P1–C111–C112 = 3.1(5)° and Au2–P2–C211–C212 = -5.2(5)°.

 ${Bis{[tri('butyl)phosphine]gold(1)} tribromide crystallizes as}$ the 1 : 1 adduct with bromine, ${[['Bu)_3P]_2Au}^+(Br_3)^-(Br_2)$. The red crystals are triclinic (space group $P\overline{1}$, Z = 1) with half of the cation, half of the tribromide anion and half of the bromine molecule in the asymmetric unit, the other halves being generated by centres of inversion (Fig. 6). The structure of the cation has been determined previously in salts with Cl⁻ and



Fig. 6 Molecular structure of the components of $\{[({}^{1}Bu_{3})P]_{2}-Au\}^{+}(Br_{3})^{-}(Br_{2})(ORTEP, 50\% \text{ probability ellipsoids, H atoms omitted}).$ Selected bond lengths [Å]: Au1–P1 2.3213(17), Br1–Br2 2.5494(9), Br3–Br3' 2.353(2) (P1': 1 – x, -y, -z; Br1": -x, 1 - y, 1 - z).

 BF_4^- counterions and requires no discussion.^{20,21} The Br_3^- and Br_2 units form zig-zag chains as shown in Fig. 7 for which there is also precedent in the literature.^{22,23} Some details are given in the figure caption.



Fig. 7 Unit cell of the crystal structure of $\{[({}^{t}Bu)_{3}P]_{2}Au\}^{+}(Br_{3})^{-}(Br_{2})$ (arbitrary radii, hydrogen atoms omitted). Zig-zag chain anions $[(Br_{2})\cdot(Br_{3})^{-}]_{n}$ separate layers of cations. All three components reside on centres of inversion. Selected bond lengths [Å] and angles [°]: Br1–Br3 3.124(2); Br2–Br1–Br3 113.4(1).

Bromo-tri(mesityl)phosphonium tetrabromoaurate(III), [(Mes)₃-PBr]⁺[AuBr₄]⁻, was isolated as triclinic crystals (space group $P\overline{1}$, Z = 2) with one cation and two halves of anions in the asymmetric unit, the other two halves being generated by centers of inversion (Fig. 8). The geometry of the cation approaches propeller symmetry (point group C_3) with the P–Br bond as the main axis. The dimensions compare well with reference compounds.²⁴ Both anions are almost ideally square planar. The packing of the components in the crystal shows no anomalies.



Fig. 8 Structures of the components of the compound $[(Mes)_{3}-PBr]^{+}[AuBr_{4}]^{-}$ (ORTEP, 50% probability ellipsoids, H atoms omitted). The gold atoms of the two anions reside on centres of inversion. The geometry of the cation approaches propeller symmetry (C_{3}). Selected bond lengths [Å]: P1–Br1 2.2032(15), Au1–Br11 2.4241(6), Au1–Br12 2.4121(6), Au2–Br21 2.4281(6), Au2–Br22 2.4255(6).

Conclusions

In the present study it has been demonstrated that oxidative addition of elemental bromine to gold(I) complexes of the type (L)AuBr is a facile process for complexes with small and medium-sized tertiary phosphines L giving quantitative yields of square planar gold(III) complexes (L)AuBr₃. In the tri*alkyl*phosphine series, the limit is reached with L = P ('Bu)₃, for which only a ligand redistribution is induced by bromine to give salts of the cation {[[('Bu)₃P]₂Au}⁺, of which a tribromide has been crystallized as the adduct with bromine. A salt with the gold-containing anion $[AuBr_4]^-$ required to balance the stoichiometry could not be crystallized.

In the tri*aryl* phosphine series, tri(*o*-tolyl)phosphine still permits addition of bromine, but in the product $[(o-Tol)_3P]AuBr_3$ there is severe steric hindrance of intramolecular dynamics rendering the three tolyl groups inequivalent as shown by solution NMR experiments. In $[(Mes)_3P]AuBr$ addition of bromine to the gold centre is sterically prohibited and P–Au bond cleavage occurs instead to give a bromo-phosphonium salt $[(Mes)_3PBr]^+[AuBr_4]^-$.

Experimental

All experiments were carried out in an atmosphere of pure and dry nitrogen. Glassware was oven-dried and filled with nitrogen, solvents were dried, distilled and saturated with nitrogen. Standard equipment was used throughout. Mass spectra were recorded on a Finnigan MAT 90 spectrometer using FAB as an ionization method. NMR spectra were obtained at room temperature on JEOL-400 or JEOL-270 spectrometers. Chemical shifts are reported in δ values [ppm] relative to the residual solvent resonances (¹H, ¹³C). ³¹P{¹H} NMR spectra are referenced to external aqueous H₃PO₄ (85%). Coupling constants J and N = $J_{AX} + J_{AX'}$ (for AXX' spin systems) are given in Hz. Low halogen contents in the microanalysis data are due to loss of elemental halogen during manipulation of the crystals. The reagents were commercially available or prepared following literature procedures: (Me₃P)AuBr₃,⁷ (Me₃P)AuI₃,¹ [(ⁱPro)₃P]AuBr,¹⁵ [(o-Tol)₃P]AuBr,¹⁵ [('Bu)₃P]AuBr,²⁵ and [(Mes)₃P]AuBr.¹⁵

[(Me₃P)AuBr₃]·(Br₂)

(Me₃P)AuBr₃ (153 mg, 0.30 mmol) was dissolved in 5 ml of dichloromethane and bromine (48 mg, 0.30 mmol) was added slowly. The mixture was used for crystallisation by slow diffusion of pentane at -30 °C. After a few weeks orange crystals were collected; 161 mg (80% yield), mp 124 °C with decomposition. C₃H₉AuBr₃P (672.6), calcd. C 5.36, H 1.35, Br 59.4; found C 5.42, H 1.38, Br 58.0%. NMR (CD₂Cl₂, 25 °C), ³¹P{¹H}: 21.3 (s); ¹³C{¹H}: 17.3 (d, *J* 44.6 Hz); ¹H: 2.24 (d, *J* 13.3 Hz).

$[(Me_3P)AuI_3]_2 \cdot (I_2)$

(Me₃P)AuI (196 mg, 0.30 mmol) and I₂ (38 mg, 0.15 mmol) were dissolved in dichloromethane (5 ml). Pentane vapour was allowed to condense into the solution at -30 °C. Black crystals were filtered off and dried in a light vacuum; 172 mg (74% yield), mp 124 °C with decomposition. C₃H₉AuI₄P (780.64), calcd. C 4.62, H 1.16, I 65.0; found C 4.48, H 1.30, I 63.8%. NMR (CD₂Cl₂, 25 °C), ³¹P{¹H}: -10.8 (s); ¹³C{¹H}: 19.6 (d, *J* 32.4 Hz); ¹H: 2.27 (d, *J* 13.4 Hz).

[(ⁱPro)₃P]AuBr₃

[(¹Pro)₃P]AuBr (400 mg, 0.92 mmol) was dissolved in dichloromethane (20 ml) and a solution of Br₂ (147 mg, 0.92 mmol) in 10 ml of the same solvent was added slowly with stirring at 20 °C. After 1 h the solvent was evaporated in a vacuum to leave a red solid, which was crystallized from dichloromethane/pentane; 496 mg (90% yield), mp 98 °C with decomposition. C₉H₂₁AuBr₃P (596.92), calcd. C 18.11, H 3.55, Br 40.2; found C 17.98, H 3.45, Br 39.6%. MS (FAB): m/z 793.4 {[(¹Pro₃P)Au]₂Br]⁺, 517.5 [(¹Pro₃P)₂Au]⁺. NMR (CD₂Cl₂, 25 °C), ³¹P{¹H}: 77.4 (s); ¹³C{¹H}: 28.0 (d, *J* 26.0, CH), 19.8 (d, *J* 2.6, Me); ¹H: 3.40 (dsept, *J* 12.2 and 7.4, 3H, CH), 1.33 (dd, *J* 9.7 and 7.2, 18H, Me).

$\{[(^{i}Pro)_{3}PAuBr_{3}]\cdot(Br_{2})\}$

 $[({}^{i}Pro)_{3}P]AuBr_{3}$ (150 mg, 0.25 mmol) and Br_{2} (50 mg, 0.31 mmol) were dissolved in dichloromethane (10 ml). Red crystals could be grown by slow diffusion of *n*-pentane into the reaction mixture at

-30 °C; 125 mg (66% yield), mp 39–41 °C with decomposition. C₉H₂₁AuBr₃P (756.73), calcd. C 14.29, H 2.80, Br 52.8; found C 14.65, H 2.69, Br 51.2%. NMR (CD₂Cl₂, 25 °C), ³¹P{¹H}: 77.4 (s); ¹³C{¹H}: 27.9 (d, *J* 26.1, CH), 19.8 (s, Me); ¹H: 3.41 (dsept, *J* 14.4 and 7.4, 3H, CH), 1.34 (dd, *J* 17.1 and 7.4, 18H, Me).

[(o-Tol)₃P]AuBr₃

[(*o*-Tol)₃P]AuBr (200 mg, 0.34 mmol) was dissolved in dichloromethane (20 ml), bromine (55 mg, 0.34 mmol) was added and the mixture was stirred for 1 h at 20 °C. The solvent was evaporated to leave a red solid, which was redissolved in dichloromethane and precipitated by slow condensation of pentane; 216 mg (86% yield), mp 150 °C with decomposition. $C_{21}H_{21}AuBr_3P$ (741.04), calcd. C 34.04, H 2.86, Br 32.4; found C 33.12, H 2.69, Br 31.2%. MS (FAB): m/z 501.5 [(*o*-Tol)₃PAu]⁺. NMR (CD₂Cl₂, 25 °C), ³¹P{¹H}: 32.0 (s); ¹³C{¹H}: 143.1, 133.3, 126.9, 123.1 (three sets of poorly resolved resonances, C_6H_4), 24.8 (2C) and 23.1 (1C) (broad singlets, Me); ¹H: 8.69 (dd, J 18.2 and 7.2, 1H, see text), 7.64–7.32 (m, 11H, aryl); 2.93, 1.96 and 1.65 (3 × s, 3 × 3H, Me).

$\{[(^{t}Bu)_{3}P]_{2}Au\}^{+}(Br_{3})^{-}\cdot(Br_{2})$

[(${}^{1}Bu$)₃P]AuBr (200 mg, 0.42 mmol) was dissolved in dichloromethane (10 ml) and treated with a solution of Br₂ (67 mg, 0.42 mmol) in 5 ml of the same solvent at -78 °C with stirring. Subsequently the reaction mixture was warmed to 20 °C and stirring continued for 3 h. The solvent was removed in a vacuum to leave a red solid. Solutions in CD₂Cl₂ showed only ¹H and ³¹P NMR signals indicative of {[(${}^{1}Bu$)₃P]₂Au}+

Table 1 Crystal data, data collection and structure refinement

cations. The former has a "filled-in doublet" multiplicity with N = 14.8 Hz (A'_nXX'A'_n). Crystals of the tribromide were obtained as the 1 : 1 adduct with bromine upon reacting [('Bu)₃P]AuBr with bromine in the molar ratio 1 : 4 and allowing pentane vapour to condense into the solution of the product in tetrahydrofuran at 4°C; 145 mg (34% yield). The red crystals give off bromine vapour slowly upon storage at 20 °C and rapidly on heating. C₂₄H₅₄AuBr₅P₂ (1001.13) calcd. C 28.79, H 5.44; found C 28.13, H 5.37%. MS (FAB): *m/z* 879.5 {[[('Bu₃P)Au]₂Br]⁺, 606 [('Bu₃P)₂Au]⁺. NMR (CD₂Cl₂, 25 °C), ³¹P{¹H}: 96.8 (s); ¹³C{¹H}: 40.7 (m, AXX', N = 16.6, CP), 32.8 (s, Me); ¹H: 1.57 (m, A₂₇XX'A'₂₇, N = 15.6, Me).

[(Mes)₃PBr]⁺[AuBr₄]⁻

 $[(Mes)_3 P]$ AuBr (200 mg, 0.30 mmol) was reacted with Br₂ (96 mg, 0.60 mmol) in a total of 15 ml of dichloromethane at 20 °C with stirring. After 2 h, the volume of the reaction mixture was reduced to a few ml and the product precipitated by addition of pentane. Red crystals could be grown upon condensing pentane vapour into a solution in dichloromethane at -30 °C; 256 mg (87% yield), mp 217 °C with decomposition. C₂₇H₃₃AuBr₅P (985.02), calcd. C 32.92, H 3.38, Br 40.56; found C 32.75, H 3.24, Br 40.86%. MS (FAB): m/z 468.5 [(Mes)₃PBr]⁺; m/z 515.7 $[AuBr_4]^-$. NMR (CD₂Cl₂, 25 °C), ³¹P{¹H}: 39.1 (s); ¹³C{¹H}: 148.0 (d, J 3.6, C4), 146.0 (d, J 10.4, C3/5), 144.2 (d, J 15.1, C5/3), 134.2 (d, J 12.5, C2/6), 133.6 (d, J 13.5, C6/2), C1 not detected, 25.3 (d, J 6.2, Me2/6), 24.6 (d, J 7.8, Me6/2), 21.5 (s, Me4); ¹H: 7.25 (d, J 4,7, 1H, HC3/5), 7.05 (d, J 7.2, 1H, HC5/3), 2.45 and 2.43 (2 \times s, 2 \times 3H, Me2/6), 2.01 (s, 3H, Me4).

	$[(Me_3P)AuI]_2 \cdot (I_2)$	$[(Me_3P)AuBr_3] \cdot (Br_2)$	$\{[(^{i}Pro)_{3}P]AuBr_{3}\}\cdot(Br_{2})$
Crystal data			
Formula	C ₃ H ₉ AuI₄P	C ₃ H ₉ AuBr ₅ P	C ₉ H ₂₁ AuBr ₅ P
M.	780.64	672.59	756.72
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	Pnma	Cc
a/Å	7.7199(1)	13.9842(3)	8.5738(2)
b/Å	23.7025(4)	7.2404(1)	15.1158(3)
c/Å	15.9063(2)	12.2119(2)	14.0133(3)
$a/^{\circ}$	90	90	90
$\beta/^{\circ}$	116.2520(9)	90	96.6076(8)
γ/°	90	90	90
$V/Å^3$	2610.35(6)	1235.8(2)	1804.06(7)
$\rho_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	3.973	3.615	2.775
Z		8	4
F(000)	2664	1184	1364
μ (Mo-K α)/cm ⁻¹	208.00	281.43	192.95
Data collection			
T/°C	-130	-130	-130
Measured reflections	59562	283745	20615
Unique reflections	$4522 [R_{int} = 0.045]$	$1224 [R_{int} = 0.053]$	$3294 [R_{int} = 0.064]$
Absorption correction	DELABS	DELABS	DELABS
T_{\min}/T_{\max}	0.340/0.763	0.828/1.572	0.410/0.800
Refinement			
Refined parameters	169	67	151
Final <i>R</i> values $[I \ge 2\sigma(I)]$			
<i>R</i> 1	0.0398	0.0254	0.0276
$wR2^a$	0.1076	0.0612	0.0686
Absolute structure parameter	—	_	0.011(11)
Weighting scheme	a = 0.0502	a = 0.0252	a = 0.0306
8	b = 49.8084	b = 7.2641	b = 15.1740
$a (max/min)/a \Lambda^{-3}$	2 0/11/ 2 212	1 201 / 1 567	1 701 / 1 420

 ${}^{a} wR2 = \{ \sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{o}^{2})^{2}] \}^{1/2}; w = 1 / [\sigma^{2}(F_{o}^{2}) + (ap)^{2} + bp]; p = (F_{o}^{2} + 2F_{c}^{2}) / 3.$

Table 2 Crystal data, data collection and structure refinement

	[(o-Tol) ₃ P]AuBr ₃	${[({}^{t}Bu)_{3}P]_{2}Au}^{+}(Br_{3})^{-}\cdot(Br_{2})$	$[(Mes)_3PBr]^+[AuBr_4]$
Crystal data			
Formula	$C_{21}H_{21}AuBr_3P$	$C_{24}H_{54}AuBr_5P_2$	C ₂₇ H ₃₃ AuBr ₅ P
\mathbf{M}_r	741.04	1001.13	985.02
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\overline{1}$	PĪ
a/Å	8.5107(1)	8.6524(3)	8.2777(2)
b/Å	35.9228(4)	8.9391(3)	8.6329(2)
c/Å	15.5325(2)	11.6377(4)	21.4606(5)
a/°	90	82.4755(13)	82.4809(10)
β/°	95.2154(4)	74.3263(17)	88.8961(11)
y/°	90	88.7371(14)	85.9632(8)
$V/Å^3$	4729.06(10=	859.10(5)	1516.55(6)
$ ho_{ m calc}/ m g~cm^{-3}$	2.082	1.935	2.157
Z	8	1	2
F(000)	2768	482	928
μ (Mo-K α)/cm ⁻¹	113.62	102.00	115.05
Data collection			
T/°C	-130	-130	-130
Measured reflections	85564	19895	34935
Unique reflections	$8397 [R_{int} = 0.061]$	2848 [$R_{\rm int} = 0.074$]	5187 [$R_{\rm int} = 0.047$]
Absorption correction	DELABS	DELABS	DELABS
$T_{\rm min}/T_{\rm max}$	0.765/1.755	0.266/0.689	0.545/0.859
Refinement			
Refined parameters	475	157	319
Final R values $[I \ge 2\sigma(I)]$			
	0.0347	0.0448	0.0317
R1		0 1 2 9 1	0.0780
$\frac{R1}{wR2^a}$	0.0832	0.1281	0.0789
R1 wR2 ^a Weighting scheme	$ \begin{array}{l} 0.0832 \\ a = 0.0402 \end{array} $	a = 0.0824	a = 0.0348
R1 wR2 ^a Weighting scheme	0.0832 a = 0.0402 b = 18.4634	a = 0.0824 b = 2.8662	a = 0.0348 b = 4.4526

Reaction of (Mes₃P)AuI with iodine

178 mg (0.25 mmol) of [(Mes)₃P]AuI and 64 mg (0.25 mmol) of I₂ were dissolved in 15 ml of dichloromethane. After 1 h, the solvent was removed under reduced pressure to yield a brown liquid. In solution only the gold(I) species is observed. It was not possible to crystallize a product for further characterisation. NMR (CD₂Cl₂), ³¹P{¹H}: 5.6 (s, PAu(I)); ¹H: δ 7.01 (broad singlet, 2H, aryl), 2.76 (s, 6H, *o*-Me), 1.87 (s, 3H, *p*-Me).

Crystal structure determinations

Specimens of suitable quality and size were mounted on the ends of quartz fibers in F06206R oil and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo-K α radiation. Intensity data were corrected for absorption effects (DELABS from PLATON). The structures were solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full matrix least-squares calculations on F^2 (SHELXL-97).²⁶ The thermal motion was treated anisotropically for all non-hydrogen atoms. All hydrogen atoms were calculated and allowed to ride on their parent atoms with fixed isotropic contributions. During the structure refinement of $[(o-Tol)_3P]AuBr_3$, the atoms of a dichloromethane molecule were observed but could not be modelled satisfactorily. The SQUEEZE routine in PLATON was used to modify the *hkl* file.

Further information on crystal data, data collection and structure refinement are summarized in Tables 1 and 2. Important interatomic distances and angles are shown in the corresponding figure captions.

CCDC reference numbers 264733–264738.

See http://www.rsc.org/suppdata/dt/b5/b502861b/ for crystallographic data in CIF or other electronic format.

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