

Governing the oxidative addition of iodine to gold(I) complexes by ligand tuning

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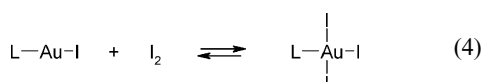
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While several gold(I) complexes of the type (L)AuX (X = Cl, Br) are known to undergo oxidative addition of elemental chlorine and bromine (X₂), respectively, to give the corresponding gold(III) complexes (L)AuX₃, the addition of iodine to (iodo)gold(I) compounds is strongly ligand-dependent, suggesting a crucial threshold in the oxidation potentials. A systematic investigation of this particular oxidative addition of iodine using a large series of tertiary phosphines as ligands L has shown that both electronic and steric effects influence the course of the reaction. The reactions were followed by ³¹P NMR spectroscopy and the products crystallized from dichloromethane–pentane solutions. Complexes with small trialkylphosphines (PMe₃, PEt₃) are readily oxidized, while those with more bulky ligands (P^tPr₃, P^tBu₃) are not. With L taken from the triarylphosphine series [PPh₃, P(2-Tol)₃, P(3-Tol)₃, P(4-Tol)₃] no oxidation takes place at all, but mixed alkyl/aryl-phosphines [PMe_nPh_{3-n}] induce oxidation for *n* = 3 and 2, but not for *n* = 1 and 0. However, in cases where no oxidation of the gold atoms is observed, the synthons may crystallize as adducts with molecular iodine of the polyiodide type instead, which have an iodine rich stoichiometry. This fact explains inconsistent reports in the literature. The metal atoms in (L)AuI coordination compounds with L representing a tri(heteroaryl)phosphine [P(2-C₄H₅E)₃, E = O, S], a phosphite [P(OR)₃] or a trialkenylphosphine [PVI₃] are all not subject to oxidative addition of iodine. The dinuclear complex of the ditertiary phosphine Ph₂PCH₂PPh₂, (dppm)(AuI)₂, gives an iodine adduct (without oxidation of the metal atoms), but with 1,2-Ph₂P(C₆H₄)PPh₂ (dppbe) an ionic complex [(dppbe)AuI₂]⁺I₃[−] with a chelated gold(III) centre is obtained. The gold(I) bromide complexes with tertiary phosphines are readily oxidized by bromine to give the corresponding gold(III) tribromide complexes, as demonstrated for (BzMePhP)AuBr and (Ph₃P)AuBr. With (dppm)(AuBr)₂ the primary product with mixed oxidation states was also isolated: (dppm)AuBr(AuBr₃). The crystal structures of the following representative examples and reference compounds have been determined: (Me₃P)AuI₃, (Me₂PhP)AuI₃, (P^tPrP)AuI·1.5I₂, (Ph₃P)AuI·I₂, [(2-Tol)₃P]AuI₂·I₂, [(2-Tol)₃P]AuI, (dppm)(AuX)₂ (with X = Br, I), (dppm)AuBr(AuBr₃) and [(dppbe)AuI₂]⁺I₃[−]. The structures are discussed focusing on the steric effects. It appears that *e.g.* the reluctance of (Ph₃P)AuI to add I₂ is an electronic effect, while that of (P^tPrP)AuI has its origin in the steric influence of the ligand.

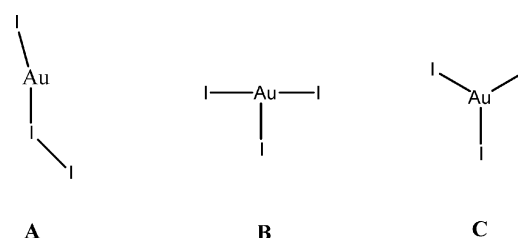
Introduction

Of the three coinage metals, only gold is readily oxidized to the oxidation state +III. This phenomenon is rationalized by relativistic effects which play only a minor role for copper (*Z* = 29) and silver (*Z* = 47), but are highly significant for the description of the properties of gold (*Z* = 79).^{1–4} However, in oxidation reactions with the halogens it is only for fluorine, chlorine and bromine that the pure binary AuX₃ compounds can be obtained.^{5–8} The oxidation potential of iodine appears to be not sufficient to make AuI₃ or its oligomers stable compounds. AuI is *not* oxidized by elemental iodine [eqn. (1)], and substitution reactions starting with AuCl₃ or AuBr₃ and iodide anions are associated with a redox process to give AuI and I₂ [e.g. eqn. (2)].^{9–11}



In recent quantum-chemical calculations the molecular geometries and electronic structures of AuI₃ and (AuI₃)₂ have been determined for the gas phase.^{12–14} It appears that AuI₃ could be expected to have an “L-shaped” structure (A) rather than the standard T-shaped or Y-shaped structures (B, C) calculated for AuF₃ or AuCl₃. In form A the gold atom is not in a higher oxidation state but rather acts as an acceptor centre

for an iodine molecule as a donor. There are no experimental data available in the literature on any of the monomeric AuX₃ molecules, except for an intercalate in the layer structure of the superconductor Bi₂Sr₂CaCu₂O₈,¹⁵ which may require further confirmation regarding the structure of the proposed AuI₃ unit.



For ternary or more complex phases with gold and iodine, the occurrence not only of the [AuI₂][−] anion with Au⁺, but also of the [AuI₄][−] anion with Au³⁺ is well documented.^{5,12,16,17} Apparently, there is a redox equilibrium connecting the anions [AuI₂][−] and [AuI₄][−] [eqn. (3)],¹⁸ but it represents a delicate balance depending on several parameters which decide if oxidative addition of iodine will occur or not. This is obvious from a few, at first sight, quite confusing observations: compounds of the type [H₃N(CH₂)_nNH₃]₂[AuI₂][AuI₄][I₃]₂ were shown to contain both [AuI₂][−] and the iodine carrier anions [I₃][−], and yet no redox reaction takes place.¹⁹ In other ammonium or sulfonium polyiodogold salts like [NH₄]₂[AuI₄][I₂], [Et₃S][AuI₄][I₂] and [Me₃S][AuI₄][I₃] all the gold is oxidized to Au³⁺ and the excess iodine is part of a triiodide or of a gold polyiodide network,^{12,20} while in Cs₂[AuI₂][AuI₄] the Au⁺ and Au³⁺ states coexist in separate anions.^{5,21} Finally, [Et₃S][AuI₂] and [Et₃S][AuI₄] are simple

reference compounds which contain solely $[\text{AuI}_2]^-$ and $[\text{AuI}_4]^-$ anions, respectively, of which the latter is perfectly stable.¹²

A similar complexity of results is documented for donor–acceptor complexes of the type $(\text{L})\text{AuI}_3$. A compound of this stoichiometry of the phosphine and arsine series, $(\text{Et}_3\text{P})\text{AuI}_3$, was first obtained as black needles (mp 77 °C) by addition of iodine to colourless $(\text{Et}_3\text{P})\text{AuI}$,²² but only elemental analysis data were used for identification [eqn. (4)]. $(\text{Me}_3\text{As})\text{AuI}_3$ was prepared by reacting gold powder with Me_3AsI_2 , and structurally characterized as a square-planar Au^{3+} complex.²³ In the analogous reaction with Me_3PI_2 only the 2 : 1 complex $(\text{Me}_3\text{P})_2\text{AuI}_3$ was obtained and shown to have a trigonal-bipyramidal structure. From ^{31}P NMR data it was concluded that this compound loses one of the two PMe_3 ligands in solution.²³ The ^{31}P NMR shifts given for $(\text{Me}_3\text{P})\text{AuI}_3$ (δ 30.1 ppm)²³ are not in agreement with the present results (δ –11.2 ppm, below). In another investigation²⁴ of the reaction between $(\text{Me}_3\text{P})\text{AuMe}$ with I_2 the 1 : 1 complex $(\text{Me}_3\text{P})\text{AuI}_3$ was not isolated. $(\text{Ph}_3\text{P})\text{AuI}$ was found to give only a black oily product on addition of I_2 , which showed a ^{31}P resonance identical with that of the starting material, indicating that no oxidative addition had taken place.²⁵ The same behaviour was observed for *P*-phenyldibenzophosphole.²⁵ However, in another study²⁴ a compound formulated as “ $(\text{Ph}_3\text{P})\text{AuI}_3$ ” was used as a substrate for the reaction with $\text{Cd}(\text{CF}_3)_2$ which led to the formation of the gold(I) complex $(\text{Ph}_3\text{P})\text{AuCF}_3$. The dinuclear gold(I) complex of bis(diphenylphosphino)methane (dppm) of the composition $(\text{dppm})(\text{AuI})_2$ was reacted with iodine and shown to yield a crystalline product of the stoichiometry $(\text{dppm})(\text{AuI}_2)_2$, but its ^{197}Au Mössbauer spectrum surprisingly suggested that the gold atoms in this tetraiodide were still in the oxidation state +1. In the absence of structural data, the formation of gold(I) polyiodides was proposed.²⁶

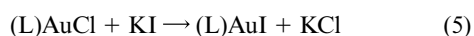
With sulfur ligands, stable complexes of the type $(\text{R}_2\text{S})\text{AuI}_3$ could only be prepared with chelating donor molecules such as $\text{MeSCH}_2\text{CH}_2\text{SMe}$, which are assumed to have an ionic structure $[(\text{CH}_2\text{SMe})_2\text{AuI}_2]\text{I}$.²⁷ Salts with iodide or triiodide anions associated with cyclic cations in which Au^{3+} is co-ordinated to two sulfur and two iodine atoms are also produced in the oxidation of gold with β -dithioketones and iodine.^{28,29}

From this collection of references it is obvious that the oxidative addition of iodine to AuI , $[\text{AuI}_2]^-$ and $(\text{L})\text{AuI}$ complexes [eqns. (1), (3) and (4)] is strongly dependent on the environment (gas, solvent, crystal packing) and on the qualities of ligands *L*. Because oxidation of gold metal and gold compounds with mild and environmentally benign oxidants like iodine is of great current interest in nanotechnology, we have initiated a systematic study of such processes and report herein a first set of our results.

Preparative studies

(Phosphine)gold(I) iodides

While a large number of 1 : 1 complexes of tertiary phosphines with AuCl and AuBr have been prepared and structurally characterized, the analogous coordination compounds of AuI are smaller in number. All of them have been prepared by metathesis reactions of the chloride complexes with alkali iodides [eqn. (5)]. In the present study this method – executed



in a two-phase system – was used for the new mononuclear compounds $(\text{Pr}_3\text{P})\text{AuI}$, $(\text{MePh}_2\text{P})\text{AuI}$, $[(2\text{-MeC}_6\text{H}_4)_3\text{P}]\text{AuI}$, $[(3\text{-MeC}_6\text{H}_4)_3\text{P}]\text{AuI}$, $[(4\text{-MeC}_6\text{H}_4)_3\text{P}]\text{AuI}$, $(\text{Vi}_3\text{P})\text{AuI}$, $[(2\text{-C}_4\text{H}_3\text{O})_3\text{P}]\text{AuI}$, $[(2\text{-C}_4\text{H}_3\text{S})_3\text{P}]\text{AuI}$, $[(\text{MeO})_3\text{P}]\text{AuI}$ and $[(\text{PhO})_3\text{P}]\text{AuI}$. The products were generally obtained in high yields as colourless crystalline solids. They were employed as substrates for the oxidative addition of iodine along with a series of known mononuclear compounds (Table 1).

Table 1 $^{31}\text{P}\{^1\text{H}\}$ NMR data of $(\text{L})\text{AuI}$ complexes (*L* = tertiary phosphine) and the products obtained upon addition of equivalent quantities of elemental iodine in dichloromethane solution at 20 °C (δ values in ppm relative to the external 85% aqueous phosphoric acid standard). Bold face numbers indicate oxidation to gold(III), backslash refers to an equilibrium

Phosphine ligand <i>L</i>	$(\text{L})\text{AuI}$	$(\text{L})\text{AuI} + \text{I}_2$
Me_3P	2.6	–11.2
Et_3P	40.7	27.5
$^i\text{Pr}_3\text{P}$	71.1	71.8
$^t\text{Bu}_3\text{P}$	97.4	97.5
Me_2PhP	13.8	13.8/–10.3
MePh_2P	25.1	25.1
Ph_3P	39.4	39.3
$(2\text{-Tol})_3\text{P}$	19.2	19.5
$(3\text{-Tol})_3\text{P}$	39.5	39.6
$(4\text{-Tol})_3\text{P}$	37.9	38.3
Vi_3P	27.5	27.5/–12.1
$(2\text{-Fur})_3\text{P}$	–20.8	–20.7
$(2\text{-Thi})_3\text{P}$	2.6	2.9
$(\text{MeO})_3\text{P}$	132.3	132.3
$(\text{PhO})_3\text{P}$	119.9	119.8
dppm	28.0	28.1

Bis(diphenylphosphino)methane (dppm) was used for the preparation of the 1 : 2 complexes with AuBr and AuI . Both had been prepared previously.^{26,30}

The crystal and molecular structures of a few representative examples have been determined – intentionally or unintentionally – in order to identify the nature of a product or to have reference data for the corresponding addition products. Among others these include $(\text{dppm})(\text{AuI})_2$ and $(\text{dppm})(\text{AuBr})_2$ giving access to data of a complete set of complexes (together with the known structure of $(\text{dppm})(\text{AuCl})_2$)^{31a} as a reference. The $(\text{L})\text{AuX}$ (*X* = Br, I) structures show no anomalies. The complexes investigated bear large phosphine ligands which prevent aggregation *via* aurophilic or other closed-shell interactions⁴ (see below).

Attempted oxidative addition of iodine

As a rule, the substrates of the type $(\text{R}_3\text{P})\text{AuI}$ were initially treated with an equimolar quantity of elemental iodine in dichloromethane at –78 °C, and the reaction mixtures were then allowed to warm up slowly to room temperature. Violet to black solutions of the products were obtained which were investigated by ^{31}P NMR spectroscopy. The change in chemical shifts of the ligand resonance gave a first indication as to whether the oxidation was successful or not, since a transformation from $(\text{L})\text{AuI}$ to $(\text{L})\text{AuI}_3$ leads to an up-field shift of the ^{31}P signal. This upfield shift may seem to be unexpected, but similar results have been observed for complexes of tertiary phosphines with other metal(III) halides.^{31b}

As shown in Table 1, only very few mononuclear complexes were really undergoing oxidative addition of iodine to the metal centre, and certain rules emerge on inspection of the formulae and the data: The inductive effect of trialkylphosphines, which are potent σ -donor molecules, clearly favours iodine addition, as demonstrated for *L* = PMe_3 , PEt_3 . By contrast, the poorer triarylphosphine donors appear to have an adverse effect [*L* = PPh_3 , $\text{P}(4\text{-MeC}_6\text{H}_4)_3$ etc.]. This difference is due to electronic effects, and not to steric effects, since the cone angles of e.g. PEt_3 and PPh_3 differ only by about 10°.³²

As the donor strength of PR_3 is reduced by stepwise substitution of methyl by phenyl groups along the series PMe_3 – PMe_2Ph – PMePh_2 – PPh_3 , the oxidative addition is also gradually inhibited: With $(\text{Me}_3\text{P})\text{AuI}$ the oxidation with I_2 goes to completion in solution, and $(\text{Me}_3\text{P})\text{AuI}_3$ is isolated as a crystalline solid in quantitative yield. For $(\text{Me}_2\text{PhP})\text{AuI}$ and I_2 there is a temperature-dependent equilibrium between the species formulated in eqn. (4), which is easily followed in the

^{31}P NMR spectrum. Crystals of $(\text{Me}_2\text{PhP})\text{AuI}_3$ dissolved in CD_2Cl_2 at 20°C show again partial dissociation [eqn. (4)] as demonstrated by ^{31}P NMR spectroscopy. Both $(\text{MePh}_2\text{P})\text{AuI}$ and $(\text{Ph}_3\text{P})\text{AuI}$ undergo no oxidative addition of iodine.

Tri(heteroaryl)phosphines such as tri(2-furyl)- and tri(2-thienyl)phosphine have a similar ligand effect: Their AuI complexes are not oxidized by iodine. This result is in agreement with previous studies where both ligands were shown that their electronic and steric effects are comparable to that of PPh_3 .³³ The poor donors of the phosphite series, $\text{P}(\text{OMe})_3$ and $\text{P}(\text{OPh})_3$,³² also yield AuI complexes which do not undergo oxidative addition of I_2 .

Trivinylphosphine³⁴ with a cone angle in the region of that of triethylphosphine forms a gold(I) complex $(\text{Vi}_3\text{P})\text{AuI}$ which is partially transformed into the gold(III) complex $(\text{Vi}_3\text{P})\text{AuI}_3$ in CD_2Cl_2 at 20°C , indicating a lower donor character of PVi_3 as compared to PEt_3 . As the alkyl or alkenyl groups become larger, steric effects become important: both $[\text{Pr}_3\text{P}]\text{AuI}$ and $[\text{Bu}_3\text{P}]\text{AuI}$ are not oxidized by iodine.

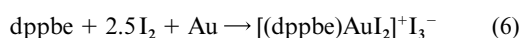
All the observations summarized in Table 1 relate to equilibria in solution, for which the results are unambiguous. The stoichiometry found for crystalline products has for some time been confusing, because the analytical composition seemed to indicate oxidation of gold(I) even in cases where the spectroscopic data (NMR, Mössbauer, ESCA) left no doubt that the oxidation state of the metal was unaltered after addition of iodine. The present studies have shown that crystals of all of these intriguing iodine-rich products are supramolecular aggregates of the gold(I) complexes with molecular iodine.

Single crystals of true gold(III) complexes of the type $(\text{L})\text{AuI}_3$ could only be obtained for $(\text{Me}_3\text{P})\text{AuI}_3$ and $(\text{Me}_2\text{PhP})\text{AuI}_3 \cdot 0.75\text{CH}_2\text{Cl}_2$. The molecules show the expected square planar mode of coordination (below). The structures of $(\text{Et}_3\text{P})\text{AuI}_3$ and $(\text{Vi}_3\text{P})\text{AuI}_3$, which also contain gold(III), could not yet be determined, but are expected to have similar geometries.

Iodo[tri(isopropyl)phosphine]gold(I) crystallizes with iodine in the molar ratio 2 : 3, i.e. $(\text{iPr}_3\text{P})\text{AuI} \cdot 1.5\text{I}_2$. The components form two-dimensional networks, with iodine molecules bridging an array of equivalent complex molecules. It is only in this case that the contacts of the iodine molecules are maintained side-on at the $\text{Au}-\text{I}$ bonds indicating an approach of the oxidant which comes to a premature standstill and does not lead to a full oxidative addition.

The compound of stoichiometry $(\text{Ph}_3\text{P})\text{AuI}_3$ already mentioned in the literature was shown to be an aggregate $(\text{Ph}_3\text{P})\text{AuI} \cdot \text{I}_2$ with I_2 molecules bridging the iodo ligands of neighbouring complexes in zigzag chains. For the crystals grown from solution containing equimolar quantities of $[(2\text{-MeC}_6\text{H}_4)_3\text{P}]\text{AuI}$ and I_2 the stoichiometry is $\{[(2\text{-MeC}_6\text{H}_4)_3\text{P}]\text{AuI}\}_2 \cdot \text{I}_2$ with each iodine molecule bridging a pair of complexes. All sub-van der Waals contacts are between iodine atoms. There is no evidence for an approach of iodine molecules towards the gold centres. Details of the structures are discussed below, together with those of the reference compounds $(\text{Ph}_3\text{P})\text{AuBr}_3$, $(\text{MeBzPhP})\text{AuBr}_3$, $(\text{dppm})(\text{AuX})_2$ ($\text{X} = \text{Br}, \text{I}$) and $(\text{dppm})\text{AuBr}(\text{AuBr}_3) \cdot 2\text{CH}_2\text{Cl}_2$.

The oxidation of gold with iodine in the presence of the dppbe ligand in dichloromethane gave a crystalline product of the composition $(\text{dppbe})\text{AuI}_3$ which was shown to have an ionic structure $[(\text{dppbe})\text{AuI}_2]^+ \text{I}_3^-$ [eqn. (6)]. This was the only product obtained directly from gold metal, the ligand and iodine. All other ligands were also found to assist the dissolution of gold metal in the presence of iodine, in agreement with results obtained earlier with polyhalides of tertiary phosphines and arsines.²³ These experiments will be described in a different context in future accounts.



Structural studies

Triiodo(trimethylphosphine)gold, $(\text{Me}_3\text{P})\text{AuI}_3$, forms black, solvent-free monoclinic crystals (from dichloromethane-*n*-pentane, space group $P2_1/c$, $Z = 4$) which are not isomorphous with the analogous arsine complex.²³ The molecules have the square-planar structure typical of a low-spin d^8 -complex of Au^{3+} (Fig. 1). The $\text{AuI}-\text{I3}$ distance (for the iodine atom *trans* to the ligand) is significantly longer than the $\text{AuI}-\text{I1/I2}$ distances (*cis* to the ligand). There are minor deviations of the *cis*- $\text{I}-\text{Au}-\text{I}$ angles from 90° , but the sum of these angles $[359.29^\circ]$ is almost exactly 360° .

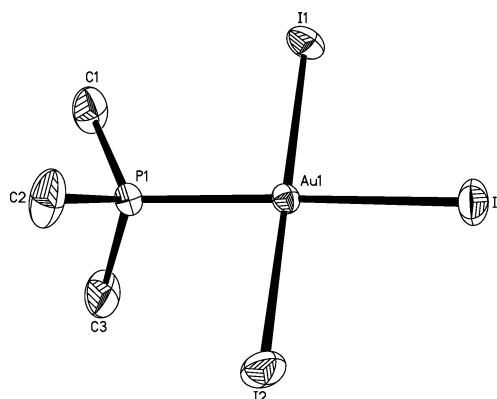


Fig. 1 Molecular structure of $(\text{Me}_3\text{P})\text{AuI}_3$ (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths (Å) and angles ($^\circ$): $\text{Au1}-\text{P1}$ 2.334(2), $\text{Au1}-\text{I1}$ 2.6235(5), $\text{Au1}-\text{I2}$ 2.6176(5), $\text{Au1}-\text{I3}$ 2.6572(5); $\text{P1}-\text{Au1}-\text{I1}$ 92.94(4), $\text{P1}-\text{Au1}-\text{I2}$ 87.61(4), $\text{P1}-\text{Au1}-\text{I3}$ 175.70(4), $\text{I1}-\text{Au1}-\text{I2}$ 175.95(2), $\text{I1}-\text{Au1}-\text{I3}$ 90.03(2), $\text{I2}-\text{Au1}-\text{I3}$ 89.21(2).

(Dimethylphenylphosphine)triiodogold is obtained from dichloromethane-*n*-pentane as black monoclinic crystals $(\text{Me}_2\text{PhP})\text{AuI}_3 \cdot 0.75\text{CH}_2\text{Cl}_2$, space group $C2/c$ with $Z = 16$. The asymmetric unit contains two independent molecules of the complex and 1.5 molecules of solvent. A superposition of the two complexes (one of which is presented in Fig. 2) has shown that their structures differ only in the conformation of the phenyl group, i.e. the dihedral angles $\text{Au1}-\text{P1}-\text{C111}-\text{C112}$ $[124.8(6)^\circ]$ and $\text{Au2}-\text{P2}-\text{C211}-\text{C212}$ $[89.9(6)^\circ]$. The gold atoms are in a square-planar coordination. Like for $(\text{Me}_3\text{P})\text{AuI}_3$, the distances $\text{Au1}-\text{I2}$ and $\text{Au2}-\text{I4}$ (*trans* to P) are slightly longer than the $\text{Au}-\text{I}$ (*cis*) distances, and the angles *cis*- $\text{I}-\text{Au}-\text{I}/\text{P}-\text{Au}-\text{I}$ are all close to 90° . An inspection of the structures of $(\text{Me}_3\text{P})\text{AuI}_3$ and $(\text{Me}_2\text{PhP})\text{AuI}_3$ shows that the ligands leave enough

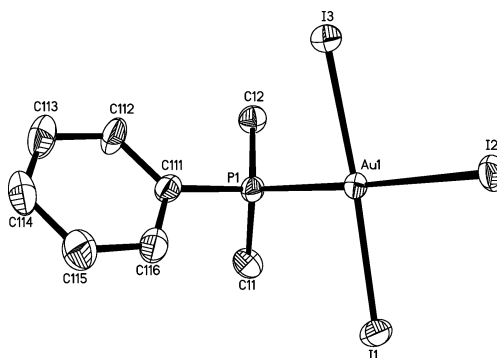


Fig. 2 Molecular structure of $(\text{Me}_2\text{PhP})\text{AuI}_3$ (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths (Å) and angles ($^\circ$) [the corresponding values of the second, crystallographically independent molecule are given in parentheses]: $\text{Au1}-\text{P1}$ 2.344(2) [2.345(2)], $\text{Au1}-\text{I1}$ 2.6231(5) [2.636(6)], $\text{Au1}-\text{I2}$ 2.6493(5) [2.6511(5)], $\text{Au1}-\text{I3}$ 2.6242(5) [2.6228(5)]; $\text{P1}-\text{Au1}-\text{I1}$ 92.95(5) [92.61(5)], $\text{P1}-\text{Au1}-\text{I2}$ 176.98(5) [175.44(5)], $\text{P1}-\text{Au1}-\text{I3}$ 88.81(5) [89.88(6)], $\text{I1}-\text{Au1}-\text{I2}$ 89.72(2) [89.30(2)], $\text{I1}-\text{Au1}-\text{I3}$ 171.51(2) [177.43(2)], $\text{I2}-\text{Au1}-\text{I3}$ 88.76(2) [88.17(2)].

room for two iodine atoms to approach the gold atoms at right angles to the molecular axis. For $(\text{Pr}_3\text{P})\text{AuI}$ this is no longer true:

Iodo[tri(isopropyl)phosphine]gold sesqui(diodine), $(\text{Pr}_3\text{P})\text{AuI} \cdot 1.5\text{I}_2$, precipitated from a solution of the components in dichloromethane upon slow diffusion of *n*-pentane, forms orthorhombic crystals (space group $C22_2$, $Z = 8$ formula units in the unit cell). The asymmetric unit contains one $(\text{Pr}_3\text{P})\text{AuI}$ complex, one complete iodine molecule and one iodine atom which is related to the other half of its I_2 molecule by symmetry.

The mode of supramolecular aggregation of the components makes this compound the most interesting example of the whole series: The iodine molecules are found to approach the $(\text{Pr}_3\text{P})\text{AuI}$ molecules end-on and midway between the AuI–I1 bond. This happens in two different ways, one of which produces a symmetrical I_2 bridge between two complexes with a twofold axis passing through the midpoint of the I_2 molecule (Fig. 3(a)). The second type of I_2 bridge has very similar distances and angles, but is unsymmetrical and connects two complexes which are inverted (head-to-tail, Fig. 3(b)). In both cases the AuI \cdots I3/I4/I5 and I1 \cdots I3/I4/I5 distances are of comparable lengths (in the range 3.556 to 3.861 Å).

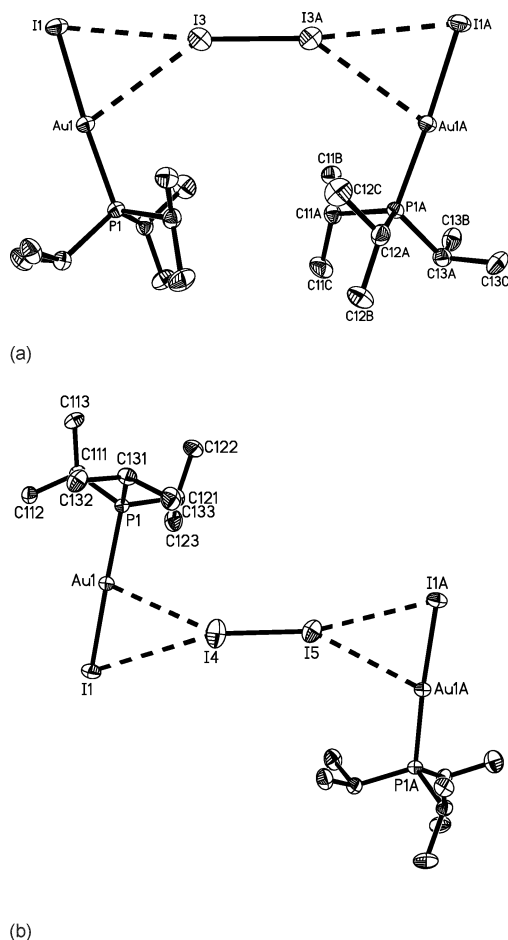


Fig. 3 Modes of supramolecular aggregation of the components in $(\text{Pr}_3\text{P})\text{AuI} \cdot 1.5\text{I}_2$ (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths (Å) and angles ($^\circ$): molecule (a): Au1–P1 2.271(1), Au1–I1 2.5776(3), I3–I3A 2.7470(7), I1 \cdots I3 3.647(1), Au1 \cdots I3 3.564(1); P1–Au1–I1 176.23(3); molecule (b): I4–I5 2.7078(5), I1 \cdots I4 3.863(1), I1A \cdots I5 3.614(1), Au1 \cdots I4 3.504(1), Au1A \cdots I5 3.556(1).

It appears that for steric reasons the iodine atoms cannot become attached to the gold atoms at right angles as required for a regular oxidative addition, but are kept at a distance where only weak bonding can be established. Accordingly, the I–I distances in the iodine molecules show no significant lengthening [I3–I3A 2.7470(7), I4–I5 2.7078(5) Å].

The aggregation of the components leads to the formation of two-dimensional arrays, in which zigzag chains $\cdots \text{AuI} \cdots \text{I4–I5} \cdots \text{Au1A} \cdots \text{I4A–I5A} \cdots \text{Au1B} \cdots$ can be recognized which are linked into corrugated sheets by the $\cdots \text{AuI} \cdots \text{I3–I3A} \cdots \text{Au1A} \cdots$ contacts (Fig. 4). These sheets are stacked in an –ABABAB– sequence, because in every second sheet the zigzag chains are inverted as related by a twofold axis.

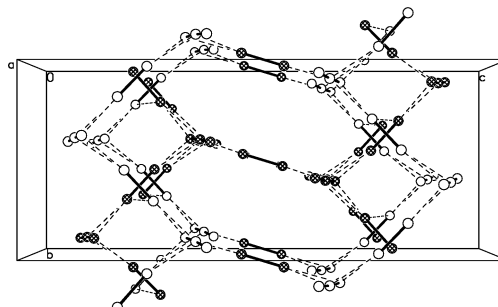


Fig. 4 View along the *a*-axis of the cell, showing the \cdots ABAB \cdots stacking of inverted zigzag chains (right and left side) formed by the components of $(\text{Pr}_3\text{P})\text{AuI} \cdot 1.5\text{I}_2$. These chains are linked by iodine molecules (centre) into sheets.

(Triphenylphosphine)gold “triiodide”, as crystallized from CH_2Cl_2 –*n*-pentane, is monoclinic, space group $P2_1/n$ with $Z = 4$, and is composed of equimolar amounts of the components, $(\text{Ph}_3\text{P})\text{AuI} \cdot \text{I}_2$. The iodine atoms form zigzag chains as shown in Fig. 5, the iodide atom I1 attached to the gold atom being in a bridging position between two iodine molecules with almost symmetrical contacts I1–I2A [3.4361(5) Å] and I1–I3 [3.5782(5) Å], and a large angle I2A–I1–I3 of $122.6(1)^\circ$ (Fig. 5). The iodine molecules approach the principal axis P1–Au1–I1 at the iodine atom I1 at approximately right angles and therefore there is no evidence for iodine coordination (and oxidation) of I2 and I3 to/of the metal atom. The I2–I3 distance of the I_2 molecule [2.7331(5) Å] deviates only marginally from the standard bond length in orthorhombic iodine [2.667(1) Å], suggesting weak intermolecular interactions.

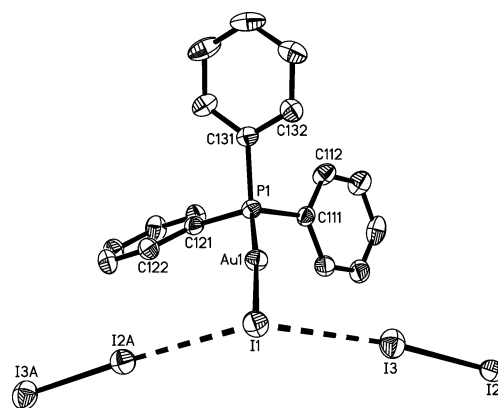


Fig. 5 The structure of $(\text{Ph}_3\text{P})\text{AuI} \cdot \text{I}_2$, with the $(\text{Ph}_3\text{P})\text{AuI}$ unit acting as a bridge between two I_2 molecules (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths (Å) and angles ($^\circ$): Au1–P1 2.258(2), Au–I1 2.5806(3), I1–I2a 3.4361(5), I1–I3 3.5782(5), I2–I3 2.7331(5); P1–Au1–I1 176.14(3), I1–I2a–I3a 176.9(1), I1–I3–I2 171.4(1), I2a–I1–I3 122.6(1).

It should be noted that the space around the metal atom in $(\text{Ph}_3\text{P})\text{AuI}$ is not very crowded and that there would be access of iodine atoms or molecules at right angles at the gold atom. That this is true can be deduced from the structure of $(\text{Ph}_3\text{P})\text{AuBr}_3$ which was determined as a reference.

The deep red crystals of tribromo(triphenylphosphine)gold are monoclinic, space group $P2_1$ with $Z = 2$, and contain molecules with a square-planar coordination geometry at the

gold atom (Fig. 6(a)). The Au1–Br3(*trans* to P) bond is longer than the Au1–Br1/Br2(*cis* to P) bonds and the angles Br–Au–Br are close to 90°. It is obvious from Fig. 6(a) that with iodine instead of bromine atoms there would still not be any significant steric hindrance for the tetracoordination of the gold atom. The failure of the oxidative addition of iodine to (Ph₃P)AuI is thus not a steric effect, but a consequence of the electronic influence of the PPh₃ ligand as compared to the PMe₃ or PET₃ ligands which have been found to support this addition. It should be noted that in a previous publication another monoclinic modification of (Ph₃P)AuBr₃ has been described (space group *P*2₁/*c*, *a* = 9.189, *b* = 26.703, *c* = 10.065 Å, β = 95.76°).³⁵ The molecular dimensions are similar.

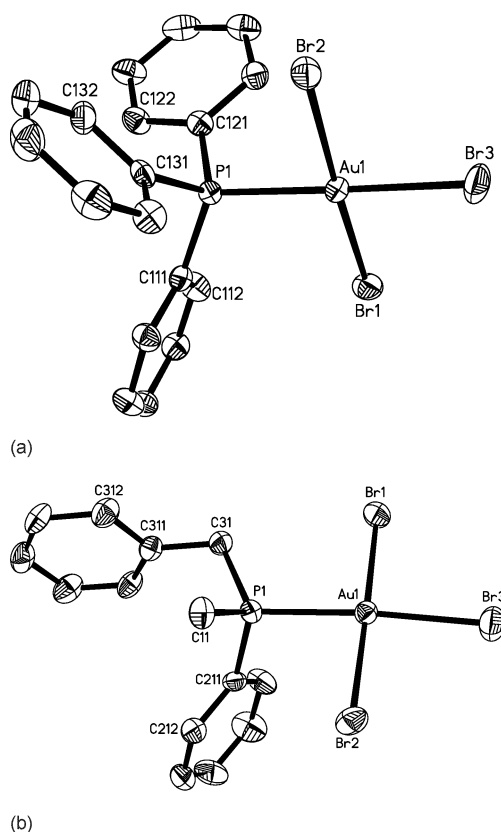


Fig. 6 (a) Molecular structure of (Ph₃P)AuBr₃ (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Au1–P1 2.3282(9), Au–Br1 2.4170(4), Au–Br2 2.4251(4), Au–Br3 2.4554(4); P1–Au1–Br1 92.19(3), P1–Au1–Br2 88.18(3), P1–Au1–Br3 177.48(3), Br1–Au1–Br2 175.11(2), Br1–Au1–Br3 90.18(2), Br2–Au1–Br3 89.54(2). (b) Molecular structure of (BzMePhP)AuBr₃ (one enantiomer, ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Au1–P1 2.312(2), Au1–Br1 2.4124(9), Au1–Br2 2.4240(9), Au1–Br3 2.468(1); P1–Au1–Br1 92.19(5), P1–Au1–Br2 86.73(5), P1–Au1–Br3 174.49(5), Br1–Au1–Br2 178.91(3), Br1–Au1–Br3 89.97(4), Br2–Au1–Br3 91.13(4).

As a model AuBr₃ complex with a *mixed alkyl-aryl*-substituted phosphine, the structure of (benzyl(methyl)phenylphosphine)tribromogold was structurally characterized. The molecules in crystalline (BzMePhP)AuBr₃ (monoclinic, space group *P*2₁/*c*, *Z* = 4) are square-planar complexes (Fig. 6(b)) with dimensions very similar to those of (Ph₃P)AuBr₃ (above). The molecules are chiral and the crystal contains both enantiomers.

Iodo[tri(2-tolyl)phosphine]gold crystallizes from dichloromethane–*n*-pentane as colourless needles (orthorhombic, space group *Pbca*, *Z* = 16). The asymmetric unit contains two independent molecules with very similar bond lengths and angles but different conformations of the phosphine ligands (Fig. 7). In both cases a propeller configuration is observed with all methyl groups oriented towards the gold atoms which

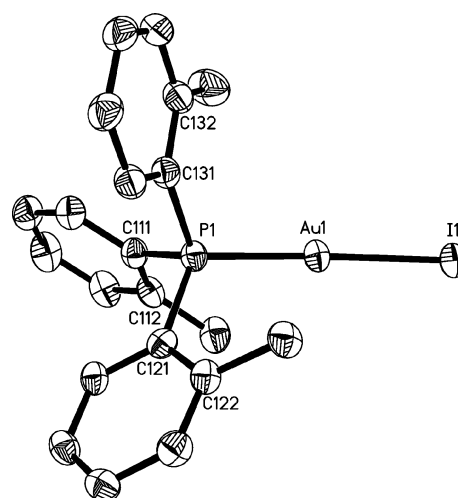


Fig. 7 Molecular structure of [(2-Tol)₃P]AuI (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths (Å) and angles (°), [the corresponding values of the second, crystallographically independent molecule are given in parentheses]: Au1–P1 2.271(1) [2.264(1)], Au1–I1 2.5681(4) [2.5544(5)]; P1–Au1–I1 176.35(4) [175.19(4)].

clearly pose steric hindrance to large atoms approaching the gold atom.

From solutions in dichloromethane containing iodine the same compound crystallizes as the orange 2 : 1 solvate, {[(2-MeC₆H₄)₃P]AuI₂·I₂} (triclinic, space group *P* $\bar{1}$, *Z* = 2). The components are arranged in groups consisting of one iodine molecule flanked by two complex molecules with a centre of inversion located at the mid-point of the I₂ molecule (Fig. 8). The iodine molecule shows no major change of its interatomic distance [2.7389(6) Å] and the contacts I1–I2 are long at 3.441(1) Å. The axis I1–I2–I2A–I1A is almost linear and the angles Au1–I1–I2 are small at only 68.1°. These trimolecular units are further aggregated through even longer I1–I1A contacts [4.189(1) Å] to give zigzag chains along the *a* axis of the crystal. The supramolecular aggregate thus shows the features of typical metal iodide/iodine adducts as recently reviewed.^{12b}

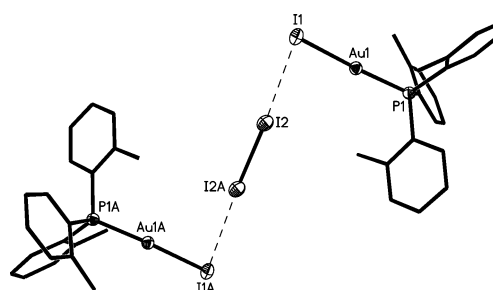


Fig. 8 Structure of {[(2-Tol)₃P]AuI₂·I₂}, with the I₂ molecule bridging two [(2-Tol)₃P]AuI units (ORTEP drawing with 50% probability ellipsoids for the heavy atoms, H-atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Au1–P1 2.2662(9), Au1–I1 2.5591(3), I2–I2a 2.7389(6), I1–I2 3.441(1); P1–Au1–I1 176.81(2), I1–I2–I2a 176.11(1).

Crystals of (dppm)(AuBr)₂ and (dppm)(AuI)₂ are isomorphous together with those of the chloro analogue, (dppm)(AuCl)₂ (monoclinic, space group *C*2/*c*, *Z* = 4).³¹ Only the iodide is shown in Fig. 9. A crystallographic twofold axis passing through the methylene carbon atoms and bisecting the P–C–P angles relates the two halves of the molecules. The conformational twist holds the gold atoms at a distance of 3.444(1) Å for the AuBr complex and of 3.575(1) Å for the AuI complex. This indicates only very weak auriphilic interactions in both cases. Any closer approach would obviously lead to steric hindrance in other parts of the molecule. The 1 : 1 addition compound with I₂ described previously²⁶ could not be crystal-

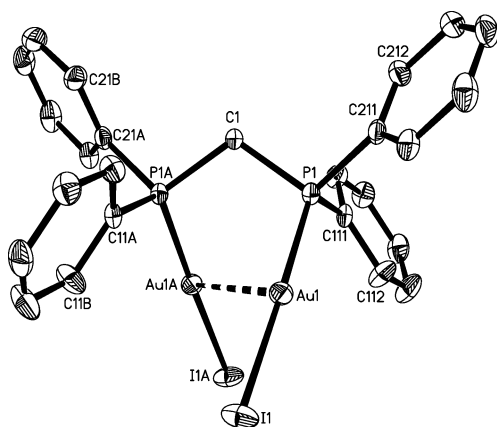


Fig. 9 Molecular structure of (dppm)(AuI)₂ (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Au1–P1 2.253(1), Au1–I1 2.5604(4), Au1...Au1A 3.575(1); P1–Au1–I1 178.29(3).

lized. It is expected to have an inclusion type structure similar to that of the triarylphosphine complexes (above).

However, the product of the 1 : 1 oxidative addition of bromine to (dppm)(AuBr)₂ of the formula (dppm)AuBr(AuBr₃) was obtained as red crystals of the bis-dichloromethane solvate (monoclinic, space group *P*2₁/*n*, *Z* = 4). This complex has one linearly two-coordinate Au⁺ centre while the other is a square-planar tetracoordinate Au³⁺ (Fig. 10). The geometrical details of the two parts resemble quite closely those of (Ph₃P)AuBr and (Ph₃P)AuBr₃ (above). The product of complete bromination of the composition (dppm)(AuBr₃)₂ was not crystallized. ¹⁹⁷Au Mössbauer spectra obtained for a related mixed chloro/bromo compound of this type have shown that the product has two equivalent gold(III) centres.²⁶

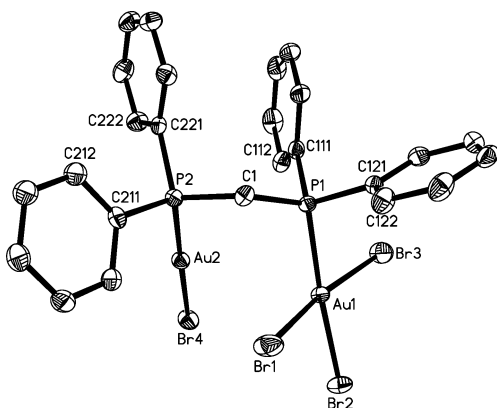


Fig. 10 Molecular structure of (dppm)AuBr(AuBr₃) (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Au1–P1 2.317(1), Au1–Br1 2.4319(6), Au1–Br2 2.4555(5), Au1–Br3 2.4240(6), Au2–P2 2.241(1), Au2–Br4 2.4040(5); P1–Au1–Br1 93.06(3), P1–Au1–Br2 176.38(3), P1–Au1–Br3 88.00(3), Br1–Au1–Br2 88.83(2), Br1–Au1–Br3 169.78(2), Br2–Au1–Br3 89.59(2), P2–Au2–Br4 178.95(3).

The compound obtained from the reaction of metallic gold with iodine and dppbe has the composition [(dppbe)AuI₂]⁺[I₃][−]. The crystals are monoclinic, space group *P*2₁/*n* with *Z* = 4 formula units in the unit cell. In the cation the gold(III) centre is chelated by the ligand and its square-planar coordination sphere is complemented by two iodide anions (Fig. 11). The structure of the cation approaches mirror symmetry quite closely, but point group *C*_s is not imposed crystallographically. The triiodide anion is linear [I3–I4–I5 179.23(2)°] with slightly different bond lengths: I3–I4 2.8811(6), I4–I5 2.9420(6) Å. There are interionic contacts I1...I3 of 3.773(1) and I2...I4A of 4.069(1) Å which indicate only weak association (Fig. 12). Geometrical details are given in the caption to Fig. 11.

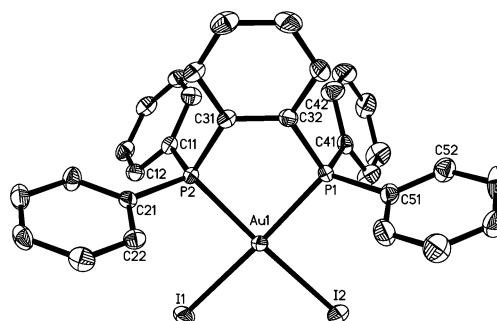


Fig. 11 Structure of the cation of [(dppbe)AuI₂]⁺[I₃][−] (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Au1–P1 2.329(2), Au1–P2 2.334(1), Au1–I1 2.6342(4), Au1–I2 2.6248(4), P1–Au1–P2 85.71(5), P1–Au1–I1 176.68(4), P2–Au1–I1 91.91(4), P1–Au1–I2 91.75(4), P2–Au1–I2 177.36(4), I1–Au1–I2 90.60(2).

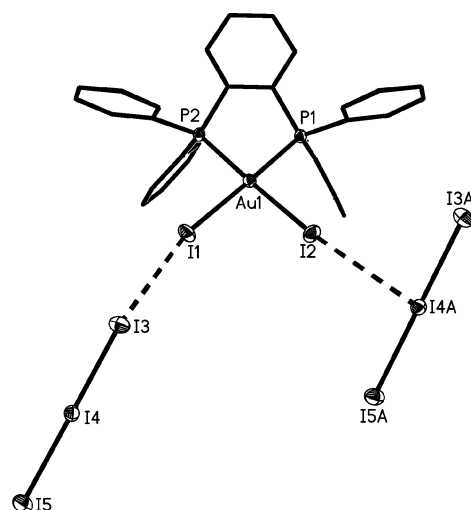


Fig. 12 Interionic contacts in the structure of [(dppbe)AuI₂]⁺[I₃][−] (ORTEP drawing with 50% probability ellipsoids for the heavy atoms, H-atoms omitted for clarity). Selected bond lengths (Å) and angles (°): I3–I4 2.8811(6), I4–I5 2.9420(6), I1...I3 3.773(1), I2...I4A 4.069(1); I3–I4–I5 179.23(2).

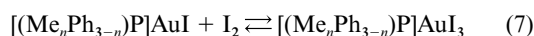
Conclusions

From the results of the present study it appears that the oxidative addition of iodine to gold(I) complexes of the formula (L)AuI is strongly dependent on the nature of the ligand L:

Gold(I) centres conditioned by a strong σ-donor ligand of the trialkylphosphine series undergo rapid and quantitative conversion to (L)AuI₃ complexes (L = PMe₃, PEt₃). With these ligands the oxidation potential of the complexes is clearly shifted beyond the threshold determined by the oxidation potential of elemental iodine. As the steric bulk of the substituents is growing, the addition of iodine leads to adducts in which the approach of the I₂ molecules to the gold centre does not quite reach the standard Au–I bonding distance {(Pr₃P)AuI·1.5I₂} and no oxidation of the gold atom can occur.

Gold(I) centres with poorer σ-donor ligands taken from the triaryl- or triheteroaryl-phosphine series do not undergo oxidative addition of iodine as demonstrated for triphenylphosphine, the three isomeric tritolylphosphines, as well as tri(2-furyl)- and tri(2-thienyl)phosphine. Trimethyl- and triphenylphosphite are in the same category. These ligands are thus not shifting the oxidation potential beyond the said threshold, but following the series (Me_nPh_{3−n})P with *n* = 3, 2, 1, 0, there is complete addition for *n* = 3, an equilibrium for *n* = 2, and no reaction at all for *n* = 1 and 0 [eqn. (7)], indicating a stepwise shift towards and across the borderline of the electrochemical potential of the reaction partner. With the

simplest trialkenylphosphine, Vi_3P , the addition of iodine is also incomplete.



The dinuclear complex $(\text{dppm})(\text{AuI})_2$, derived from the dppm ligand which has a substitution pattern like MePh_2P and poor chelating properties (owing to the formation of strained four-membered rings), is also not oxidized by iodine. By contrast, the more powerful oxidant *bromine* is readily added to $(\text{dppm})(\text{AuBr})_2$ to give first $(\text{dppm})\text{AuBr}(\text{AuBr}_3)$ and finally $(\text{dppm})(\text{AuBr}_3)_2$. This result indicates that the failure of oxidative addition of iodine to $(\text{Ph}_3\text{P})\text{AuI}$, $(\text{MePh}_2\text{P})\text{AuI}$ and $(\text{dppm})(\text{AuI})_2$ is not a steric effect but is due to the poor donor qualities of the *aryl*/phosphine ligands, and this reasoning is supported by the results of the structural studies.

The ligand dppbe with a rigid skeleton predisposed to chelation forms a stable mononuclear gold(III) complex with an ionic structure $[(\text{dppbe})\text{AuI}_3]^+\text{I}_3^-$. Chelation of gold cations by phosphine thus is found to assist in the oxidation process even with fully aryl-substituted ligands.

The structures of the gold(I) and gold(III) complexes of the types $(\text{L})\text{AuI}$ and $(\text{L})\text{AuI}_3$ determined in this study have standard linear and square-planar geometries, respectively. There are only minor variations *e.g.* induced by the *trans*-influence of the ligands.

The adducts of the type $(\text{LAuI})_m \cdot n\text{I}_2$ have supramolecular structures with long $\text{I} \cdots \text{I}$ contacts between the iodine atoms of the components. The patterns of their island-, chain- or layer-structures generally conform to motifs previously found for many adducts of iodine and metal iodides as recently summarized in a pertinent review,^{12b} but the fascinating details originating from steric effects and delicately balanced intermolecular forces are still largely unpredictable.

Experimental

General

All experiments were routinely carried out in an atmosphere of dry nitrogen. Solvents and glassware were dried and saturated/filled with nitrogen. Standard equipment was used throughout. NMR spectra were obtained at room temperature on JEOL-400 or JEOL-270 spectrometers. Chemical shifts are reported in δ values relative to the residual solvent resonances (^1H , ^{13}C). $^{31}\text{P}\{^1\text{H}\}$ NMR spectra are referenced to external aqueous H_3PO_4 (85%). The following complexes were prepared by published methods: $(\text{MePh}_2\text{P})\text{AuCl}$,³⁰ $[(2\text{-MeC}_6\text{H}_4)_3\text{P}]\text{AuCl}$,³⁶ $[(3\text{-MeC}_6\text{H}_4)_3\text{P}]\text{AuCl}$,³⁷ $[(4\text{-MeC}_6\text{H}_4)_3\text{P}]\text{AuCl}$,³⁸ $(^i\text{Pr}_3\text{P})\text{AuCl}$,³⁹ $(\text{Vi}_3\text{P})\text{AuCl}$,³⁴ $[(2\text{-Fur})_3\text{P}]\text{AuCl}$,⁴⁰ $[(2\text{-Thi})_3\text{P}]\text{AuCl}$,⁴⁰ $[(\text{MeO})_3\text{P}]\text{AuCl}$,⁴¹ $[(\text{PhO})_3\text{P}]\text{AuCl}$,⁴² $(\text{dppm})(\text{AuCl})_2$,³¹ $(\text{Me}_3\text{P})\text{AuI}$,⁴³ $(\text{Me}_2\text{PhP})\text{AuI}$,⁴⁴ $(\text{Ph}_3\text{P})\text{AuI}$,⁴⁵ $(t\text{-Bu}_3\text{P})\text{AuI}$.⁴⁶ A sample of $(\text{BzMePhP})\text{AuBr}_3$ was provided by Dr A. Bayler.

Synthesis of (phosphine)gold(I) bromides and iodides

All syntheses were carried out in a dichloromethane/water two-phase system. One equivalent of (phosphine)gold(I) chloride was dissolved in 20 ml of dichloromethane, and five equivalents of potassium bromide or potassium iodide, respectively, dissolved in 15 ml water was added and the reaction mixture stirred for 3 h. The aqueous phase was then separated from the organic phase and extracted three times with 5 ml portions of CH_2Cl_2 . The combined organic phases were washed three times with 5 ml portions of water and dried over MgSO_4 . After evaporation of the solvent in a vacuum to a volume of about 2 ml, the white product was precipitated with about 50 ml of pentane. After filtration and drying in vacuum the product was recrystallized from dichloromethane/pentane.

Iodo(methyldiphenylphosphine)gold(I). 300 mg (0.70 mmol, 1 eq.) $(\text{MePh}_2\text{P})\text{AuCl}$ and 581 mg (3.5 mmol, 5 eq.) KI; 298 mg (81% yield), mp 147 °C (Found: C, 29.86; H, 2.46; I, 24.3. Calc. for $\text{C}_{13}\text{H}_{13}\text{AuIP}$: C, 29.79; H, 2.50; I, 24.2%). NMR (CD_2Cl_2), ^1H : δ 7.69–7.49 (m, 10 H, Ph); 2.14 (d, $J_{\text{HP}} = 10.4$ Hz, 3 H, Me). $^{31}\text{P}\{^1\text{H}\}$: δ 25.1 (s).

Iodo[tri(2-tolyl)phosphine]gold(I). 300 mg (0.56 mmol, 1 eq.) $[(2\text{-MeC}_6\text{H}_4)_3\text{P}]\text{AuCl}$ and 465 mg (2.8 mmol, 5 eq.) KI; 316 mg (90% yield), mp 279–282 °C with decomposition (Found: C, 39.91; H, 3.28; I, 20.2. Calc. for $\text{C}_{21}\text{H}_{21}\text{AuIP}$: C, 40.15; H, 3.37; I, 20.2%). NMR (CD_2Cl_2), ^1H : δ 7.64–6.92 (m, 12 H, C_6H_4); 2.69 (s, 9 H, Me). $^{31}\text{P}\{^1\text{H}\}$: δ 19.2 (s).

Iodo[tri(3-tolyl)phosphine]gold(I). 300 mg (0.56 mmol, 1 eq.) $[(3\text{-MeC}_6\text{H}_4)_3\text{P}]\text{AuCl}$ and 465 mg (2.8 mmol, 5 eq.) KI; 300 mg (85% yield), mp 173–175 °C with decomposition (Found: C, 40.13; H, 3.23; I, 19.6. Calc. for $\text{C}_{21}\text{H}_{21}\text{AuIP}$: C, 40.15; H, 3.37; I, 20.2%). NMR (CD_2Cl_2), ^1H : δ 7.51–7.13 (m, 12 H, C_6H_4); 2.36 (s, 9 H, Me). $^{31}\text{P}\{^1\text{H}\}$: δ 39.5 (s).

Iodo[tri(4-tolyl)phosphine]gold(I). 300 mg (0.56 mmol, 1 eq.) $[(4\text{-MeC}_6\text{H}_4)_3\text{P}]\text{AuCl}$ and 465 mg (2.8 mmol, 5 eq.) KI; 309 mg (88% yield), mp 340–341 °C with decomposition (Found: C, 39.96; H, 3.32; I, 19.9. Calc. for $\text{C}_{21}\text{H}_{21}\text{AuIP}$: C, 40.15; H, 3.37; I, 20.2%). NMR (CD_2Cl_2), ^1H : δ 7.44–7.15 (m, 12 H, C_6H_4); 2.40 (s, 9 H, Me). $^{31}\text{P}\{^1\text{H}\}$: δ 37.9 (s).

Iodo(trivinylphosphine)gold(I). 200 mg (0.58 mmol, 1 eq.) $(\text{Vi}_3\text{P})\text{AuCl}$ and 480 mg (2.9 mmol, 5 eq.) KI; 220 mg (87% yield), mp 37–40 °C with decomposition (Found: C, 16.59; H, 2.13; I, 28.4. Calc. for $\text{C}_6\text{H}_9\text{AuIP}$: C, 16.53; H, 2.08; I, 29.1%). NMR (CD_2Cl_2), ^1H : δ 6.42–6.06 (m, ABCX-spin system). $^{31}\text{P}\{^1\text{H}\}$: δ 27.5 (s).

Iodo[tri(2-furyl)phosphine]gold(I). 250 mg (0.54 mmol, 1 eq.) $[(2\text{-Fur})_3\text{P}]\text{AuCl}$ and 448 mg (2.7 mmol, 5 eq.) KI; 267 mg (89% yield), mp 153–155 °C with decomposition (Found: C, 25.94; H, 1.65; I, 22.2. Calc. for $\text{C}_{12}\text{H}_9\text{AuIPO}_3$: C, 25.92; H, 1.63; I, 22.8%). NMR (CD_2Cl_2), ^1H : δ 7.81–6.58 (m, ABCX-spin system). $^{31}\text{P}\{^1\text{H}\}$: δ –20.8 (s).

Iodo[tri(2-thienyl)phosphine]gold(I). 250 mg (0.41 mmol, 1 eq.) $[(2\text{-Thi})_3\text{P}]\text{AuCl}$ and 350 mg (2.1 mmol, 5 eq.) KI; 220 mg (89% yield), mp 172–173 °C (Found: C, 23.91; H, 1.54; I, 20.4. Calc. for $\text{C}_{12}\text{H}_9\text{AuIPS}_3$: C, 23.85; H, 1.50; I, 21.0%). NMR (CD_2Cl_2), ^1H : δ 7.81–7.23 (m, ABCX-spin system). $^{31}\text{P}\{^1\text{H}\}$: δ 2.6 (s).

Iodo[tri(isopropyl)phosphine]gold(I). 200 mg (0.51 mmol, 1 eq.) $(^i\text{Pr}_3\text{P})\text{AuCl}$ and 415 mg (2.5 mmol, 5 eq.) KI; 209 mg (84% yield), mp 181 °C with decomposition (Found: C, 22.01; H, 4.45; I, 25.9. Calc. for $\text{C}_9\text{H}_{21}\text{AuIP}$: C, 22.33; H, 4.37; I, 26.2%). NMR (CD_2Cl_2), ^1H : δ 2.38 (d/sept, $J_{\text{HP}} = 9.1$ Hz, $J_{\text{HH}} = 7.3$ Hz, 3H, CH); 1.33 (d/d, $J_{\text{HP}} = 16.1$ Hz, $J_{\text{HH}} = 7.3$ Hz, 18 H, Me). $^{31}\text{P}\{^1\text{H}\}$: δ 71.1 (s).

Iodo(trimethylphosphite)gold(I). 250 mg (0.70 mmol, 1 eq.) $[(\text{MeO})_3\text{P}]\text{AuCl}$ and 581 mg (3.5 mmol, 5 eq.) KI; 248 mg (79% yield), mp 55–57 °C with decomposition (Found: C, 8.07; H, 1.98; I, 28.1. Calc. for $\text{C}_3\text{H}_9\text{AuIO}_3\text{P}$: C, 8.04; H, 2.03; I, 28.3%). NMR (CD_2Cl_2), ^1H : δ 3.83 (d, $^3J_{\text{CP}} = 13.9$ Hz, Me). $^{31}\text{P}\{^1\text{H}\}$: δ 132.3 (s).

Iodo(triphenylphosphite)gold(I). 300 mg (0.55 mmol, 1 eq.) $[(\text{PhO})_3\text{P}]\text{AuCl}$ and 464 mg (2.8 mmol, 5 eq.) KI; 288 mg (83% yield), mp 119 °C with decomposition (Found: C, 34.18; H, 2.33; I, 19.6. Calc. for $\text{C}_{18}\text{H}_{15}\text{AuIPO}_3$: C, 34.09; H, 2.38; I, 20.0%). NMR (CD_2Cl_2), ^1H : δ 7.47–7.27 (m, Ph). $^{31}\text{P}\{^1\text{H}\}$: δ 119.9 (s).

(Bis(diphenylphosphino)methane)bis(bromogold(I))³⁰. 400 mg (0.47 mmol, 1 eq.) (dppm)(AuCl)₂ and 560 mg (4.7 mmol, 10 eq.) KBr; 379 mg (86% yield), mp 274 °C with decomposition (Found: C, 31.78; H, 2.40; Br, 16.6. Calc. for C₂₅H₂₂Au₂Br₂P₂: C, 32.01; H, 2.36; Br, 17.0%). NMR (CD₂Cl₂), ¹H: δ 7.71–7.49 (m, 20 H, Ph); 3.70 (t, *J*_{HP} = 11.4 Hz, 2 H, CH₂). ³¹P{¹H}: δ 26.8 (s).

(Bis(diphenylphosphino)methane)bis(iodogold(I))²⁶. 400 mg (0.47 mmol, 1 eq.) (dppm)(AuCl)₂ and 780 mg (4.7 mmol, 10 eq.) KI; 386 mg (80% yield), mp 250 °C (Found: C, 29.57; H, 2.26; I, 24.2. Calc. for C₂₅H₂₂Au₂I₂P₂: C, 29.09; H, 2.15; I, 24.6%). NMR (CD₂Cl₂), ¹H: δ 7.85–7.35 (m, 20 H, Ph); 3.71 (t, *J*_{HP} = 11.2 Hz, 2 H, CH₂). ³¹P{¹H}: δ 28.0 (s).

Tribromo(triphenylphosphine)gold(III) (prepared by Dr. P. Roembke). 119 mg (0.22 mmol, 1 eq.) bromo(triphenylphosphine)gold(I) and 70 mg (0.44 mmol, 2 eq.) bromine were reacted in 10 ml chloroform as previously published.²⁵ Red crystals suitable for XRD could be grown by slow diffusion of *n*-pentane into the reaction mixture at –30 °C, 160 mg (91% yield), mp 148 °C (Found: C, 30.43; H, 2.27. Calc. for C₁₈H₁₅AuBr₃P: C, 30.93; H, 2.16%). NMR (CDCl₃), ¹H: δ 7.73–7.24 (m, Ph). ³¹P{¹H}: δ 31.4 (s). ¹³C{¹H}: δ 135.1 (d, *J*_{CP} = 10.4 Hz); 133.3 (d, *J*_{CP} = 3.1 Hz); 128.9 (d, *J*_{CP} = 13.0 Hz); 125.3 (d, *J*_{CP} = 68.0 Hz).

(Bis(diphenylphosphino)methane)bromogold(I)–tribromogold(III). 300 mg (0.32 mmol, 1 eq.) of (dppm)(AuBr)₂ was dissolved in 20 ml of dichloromethane and 51 mg (0.32 mmol, 1 eq.) of bromine, dissolved in 10 ml dichloromethane, was added dropwise. After 2 h the solvent was evaporated under reduced pressure to about 5 ml and an orange solid was precipitated with 50 ml *n*-pentane. After recrystallisation from the same solvents crystals suitable for XRD were obtained, 275 mg (78% yield), mp 164 °C with decomposition (Found: C, 27.44; H, 2.11; Br, 28.1. Calc. for C₂₅H₂₂Au₂Br₄P₂: C, 27.35; H, 2.02; Br, 29.1%). NMR (d⁶-DMSO), ¹H: δ 7.62–7.13 (m, 20 H, Ph); 3.75 (m, 2 H, CH₂). ³¹P{¹H}: δ 25.9 (d, *J*_{PP} = 20.7 Hz, PAu(I)); 25.1 (d, *J*_{PP} = 20.7 Hz, PAu(III)).

Reactions with iodine

Triiodo(trimethylphosphine)gold(III). 100 mg (0.25 mmol) of iodo(trimethylphosphine)gold(I) was dissolved in 25 ml of dichloromethane at –78 °C and 64 mg (0.25 mmol) of iodine was added. After 30 min the reaction mixture was allowed to warm slowly to room temperature. The colour of the solution changed from dark violet to black. After 2 h the solvent was evaporated under reduced pressure to a volume of 2 ml and 50 ml of *n*-pentane was added to precipitate the black product. Crystals were obtained by slow diffusion of *n*-pentane vapour into the reaction mixture in the course of several weeks. The product is air- and light-stable but decomposes at room temperature within a few days. It can be stored for a few months in the refrigerator. 114 mg (70% yield), mp 115 °C with decomposition (Found: C, 5.57; H, 1.30; I, 58.8. Calc. for C₃H₉AuI₃P: C, 5.51; H, 1.39; I, 58.2%). NMR (CD₂Cl₂), ¹H: δ 2.26 (d, *J*_{HP} = 13.6 Hz, Me). ³¹P{¹H}: δ –11.2 (s). ¹³C{¹H}: δ 19.6 (d, *J*_{CP} = 32.7 Hz, Me).

(Triethylphosphine)triiodogold(III)²². Following the same procedure (above), using 200 mg (0.45 mmol) of (triethylphosphine)iodogold(I) and 115 mg (0.45 mmol) of iodine. The product was purified by recrystallisation from dichloromethane–*n*-pentane. The black crystals decompose within a few weeks even when kept at –30 °C. 248 mg (80% yield), mp 75 °C with decomposition (lit.²² 77 °C) (Found: C, 10.13; H, 2.26; I, 53.4. Calc. for C₆H₁₅AuI₃P: C, 10.36; H, 2.17; I, 54.7%). NMR (CD₂Cl₂), ¹H: δ 2.68 (m, 6H, CH₂); 1.23 (d/t, *J*_{HH} = 7.7 Hz, *J*_{HP} = 19.4 Hz, 9H, Me). ³¹P{¹H}: δ 27.5 (s).

Triiodo(dimethylphenylphosphine)gold(III). Following the same procedure, using 116 mg (0.25 mmol) of (dimethylphenylphosphine)iodogold(I) and 64 mg (0.25 mmol) of iodine in 25 ml of dichloromethane. An equilibrium of the gold(I) and gold(III) species was observed in solution by ³¹P NMR spectroscopy. The product was isolated as black crystals after diffusion of *n*-pentane into the reaction mixture. The crystals are stable to air and light but decompose after a few weeks even when kept at low temperatures (–30 °C). 116 mg (61% yield), mp 72 °C with decomposition (Found: C, 13.49; H, 1.54; I, 53.3. Calc. for C₈H₁₁AuI₃P: C, 13.42; H, 1.55; I, 53.2%). NMR (CD₂Cl₂), ¹H: δ 7.87–7.49 (m, 5 H, Ph Au(I)/Au(III)); 2.60 (br s, 6 H, Me Au(I)/Au(III)). ³¹P{¹H}: δ 13.8, (br s, PAu(I)); –10.3 (br s, PAu(III)).

Iodo(triphenylphosphine)gold(I)–diiodine (1 : 1). 124 mg (0.25 mmol) of iodo(triphenylphosphine)gold(I) and 64 mg (0.25 mmol) of iodine were dissolved in 10 ml of dichloromethane at room temperature. The red–brown reaction mixture was set aside for crystallisation by slow diffusion of *n*-pentane at –30 °C. After several weeks red crystals were isolated. The product is air and light stable, but decomposes at room temperature within one week. It can be stored in the refrigerator (–30 °C) for several months. 136 mg (65% yield), mp 110 °C with decomposition (Found: C, 25.81; H, 1.89; I, 46.4. Calc. for C₁₈H₁₅AuI₃P: C, 25.74; H, 1.80; I, 45.3%). NMR (CD₂Cl₂), ¹H: δ 7.88–7.43 (m, Ph). ³¹P{¹H}: δ 39.3 (s, PAu(I)).

Iodo[tri(2-tolyl)phosphine]gold(I)–diiodine (2 : 1). Following the same procedure, using 157 mg (0.25 mmol, 1 eq.) of iodo[tri(2-tolyl)phosphine]gold(I) and 32 mg (0.125 mmol, 0.5 eq) of iodine. Orange crystals of [(2-Tol)₃P]AuI·0.5I₂ were obtained in low yield after several weeks by slow diffusion of *n*-pentane into the reaction mixture. The product is stable to air and moisture but decomposes within a few weeks when kept in the refrigerator. 66 mg (35% yield), mp 78 °C with decomposition (Found: C, 33.95; H, 2.93; I, 32.4. Calc. for C₂₁H₂₁AuI₃P: C, 33.40; H, 2.80; I, 33.6%). NMR (CD₂Cl₂), ¹H: δ 7.64–6.92 (m, 12 H, C₆H₄); 2.69, s, 9 H, Me). ³¹P{¹H}: δ 19.5 (s, PAu(I)).

Iodo[tri(isopropyl)phosphine]gold(I)–diiodine (2 : 3). Following the same procedure, using 121 mg (0.25 mmol, 1 eq.) of iodo[tri(isopropyl)phosphine]gold(I) and 95 mg (0.375 mmol, 1.5 eq) of iodine. Black crystals of [iPr₃P]AuI·1.5 I₂ were isolated after several weeks on slow diffusion of *n*-pentane into the reaction mixture. The stability of the product is similar to that of [(2-Tol)₃P]AuI·0.5I₂. 166 mg (77% yield), mp 67 °C with decomposition (Found: C, 12.34; H, 2.56; I, 57.2. Calc. for C₉H₂₁AuI₄P: C, 12.50; H, 2.45; I, 58.7%). NMR (CD₂Cl₂), ¹H: δ 2.39 (d/sept, *J*_{HP} = 9.1 Hz, *J*_{HH} = 7.3 Hz, 3H, CH); 1.33 (d/d, *J*_{HP} = 16.5 Hz, *J*_{HH} = 7.3 Hz, 18H, Me). ³¹P{¹H}: δ 71.8 (s, PAu(I)).

Iodo[tri(2-thienyl)phosphine]gold(I)–diiodine (2 : 3). 151 mg (0.25 mmol, 1 eq.) of iodo[tri(2-thienyl)phosphine]gold(I) and 95 mg (0.375 mmol, 1.5 eq) of iodine were dissolved in 15 ml of dichloromethane, and the brown solution stirred for 2 h at 20 °C. Black crystals of [(2-thienyl)₃P]AuI·1.5 I₂ were obtained by slow diffusion of *n*-pentane into the reaction mixture at –30 °C. The stability of the compound is the same as that of [(2-Tol)₃P]AuI·0.5I₂. 132 mg (54% yield), mp 59 °C with decomposition (Found: C, 15.64; H, 1.14; I, 49.2. Calc. for C₁₂H₆AuI₄PS₃: C, 14.63; H, 0.92; I, 51.5%). NMR (CD₂Cl₂), ¹H: δ 7.73–7.21 (m, ABCX-spin system). ³¹P{¹H}: δ 2.9 (s, PAu(I)).

Reaction of iodo(trivinylphosphine)gold(I) with iodine. 109 mg (0.25 mmol) of iodo(trivinylphosphine)gold(I) and 64 mg (0.25 mmol) of iodine were dissolved in 15 ml of dichloro-

Table 2 Crystal data, data collection, and structure refinement

	(Me ₃ P)AuI ₃	(Me ₂ Ph P)AuI ₃ ·0.75CH ₂ Cl ₂	(ⁱ Pr ₃ P)AuI·1.5I ₂	(Ph ₃ P)AuI·I ₂
<i>Crystal data</i>				
Formula	C ₃ H ₉ AuI ₃ P	C _{8.75} H _{12.50} AuCl _{1.5} I ₃ P	C ₉ H ₂₁ AuI ₄ P	C ₁₈ H ₁₅ AuI ₃ P
<i>M_r</i>	653.74	779.50	864.79	839.94
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 222 ₁	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	7.6198(1)	35.9785(4)	9.8516(1)	10.2140(1)
<i>b</i> /Å	12.1910(2)	8.3066(1)	12.4681(2)	12.5045(1)
<i>c</i> /Å	12.1256(2)	25.1157(4)	30.3821(4)	16.7349(2)
<i>α</i> /°	90	90	90	90
<i>β</i> /°	96.967(1)	116.494(1)	90	105.354(1)
<i>γ</i> /°	90	90	90	90
<i>V</i> /Å ³	1118.1(1)	6717.7(1)	3731.9(1)	2061.1(1)
<i>D_c</i> /g cm ^{−3}	3.884	3.083	3.078	2.707
<i>Z</i>	4	16	8	4
<i>F</i> (000)	1120	5496	3048	1504
<i>μ</i> (Mo-Kα)/cm ^{−1}	215.16	145.82	145.66	117.06
<i>Data collection</i>				
<i>T</i> /°C	−130	−130	−130	−130
Measured reflections	28524	101645	51743	53934
Unique reflections (<i>R_{int}</i>)	2483 (0.059)	7357 (0.057)	3386 (0.062)	4557 (0.042)
Absorption correction	DELABS	DELABS	DELABS	DELABS
<i>T_{min}</i> / <i>T_{max}</i>	0.390/0.774	0.348/0.787	0.553/0.863	0.465/0.826
<i>Refinement</i>				
Refined parameters	73	276	136	208
Final <i>R</i> values [<i>I</i> ≥ 2σ(<i>I</i>)]				
<i>R</i> 1	0.0323	0.0336	0.0156	0.0258
<i>wR</i> 2 ^a	0.0834	0.0837	0.0446	0.0636
Absolute structure parameter	—	—	0.051(3)	—
<i>ρ_{int}</i> (max./min.)/e Å ^{−3}	2.864/−2.532	3.499/−3.515	0.539/−0.611	1.972/−0.822

^a *wR*2 = {Σ[w(*F_o*² − *F_c*²)]/Σ[w(*F_o*²)]}^{1/2}; *w* = 1/[σ(*F_o*²) + (*ap*)² + *bp*]; *p* = (*F_o*² + 2*F_c*²)/3; *a* = 0.0362 [(Me₃P)AuI₃], 0.0053 [(Me₂PhP)AuI₃·0.75CH₂Cl₂], 0.0000 [(ⁱPr₃P)AuI·1.5I₂], 0.0198 [(Ph₃P)AuI·I₂]; *b* = 8.86 [(Me₃P)AuI₃], 116.68 [(Me₂PhP)AuI₃·0.75CH₂Cl₂], 2.80 [(ⁱPr₃P)AuI·1.5I₂], 5.44 [(Ph₃P)AuI·I₂].

methane. After 1 h the solvent was removed under reduced pressure to yield a brown oil. The NMR-spectra of the solution indicate an equilibrium between the gold(i) and gold(iii) complexes. Neither a gold(i) intercalation compound nor a gold(iii) iodide could be isolated. NMR (CD₂Cl₂), ¹H: δ 6.42–6.06 (m, PAu(i)/PAu(iii)). ³¹P{¹H} 27.5 (br s, Au(i)); −12.1 (br s, PAu(iii)).

Reaction of iodo[tri(*tert*-butyl)phosphine]gold(i) with iodine. 132 mg (0.25 mmol) of iodo[tri(*tert*-butyl)phosphine]gold(i) and 64 mg (0.25 mmol) of iodine 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), ¹H: δ 1.58 (t, ³*J*_{HP} = 7.05 Hz, Me). ³¹P{¹H} 97.5 (s, PAu(i)).

Reaction of iodo(methyldiphenylphosphine)gold(i) with iodine. Following the same procedure, using 131 mg (0.25 mmol) of iodo(methyldiphenylphosphine)gold(i) and 64 mg (0.25 mmol) of iodine. In solution only the gold(i) species is observed. It was not possible to crystallize an intercalation compound for further characterisation. NMR (CD₂Cl₂), ¹H: δ 7.72–7.35 (m, 10 H, Ph); 2.13 (d, *J*_{HP} = 10.7 Hz, 3 H). ³¹P{¹H} 25.1 (s, PAu(i)).

Reaction of iodo[tri(3-tolyl)phosphine]gold(i) or iodo[tri(4-tolyl)phosphine]gold(i) with iodine. Following the same procedure, using 157 mg (0.25 mmol) of iodo[tri(3-tolyl)phosphine]gold(i) or iodo[tri(4-tolyl)phosphine]gold(i), respectively, and 64 mg (0.25 mmol) of iodine for each reaction. In both cases no reaction occurs and only the starting materials exist in solution. No solid products could be crystallized. 3-Tolyl: NMR (CD₂Cl₂), ¹H: δ 7.60–7.11 (m, 12 H, C₆H₄); 2.35 (s, 9 H,

Me). ³¹P{¹H} 39.6 (s, PAu(i)). 4-Tolyl: NMR (CD₂Cl₂), ¹H: δ 7.45–7.19 (m, 12 H, C₆H₄); ³¹P{¹H} 38.3 (s, PAu(i)).

Reaction of iodo[tri(2-furyl)phosphine]gold(i) with iodine. Following the same procedure, using 139 mg (0.25 mmol) of iodo[tri(2-furyl)phosphine]gold(i) and 64 mg (0.25 mmol) of iodine. The NMR spectra showed no changes which would indicate oxidation. No solid product could be isolated. NMR (CD₂Cl₂), ¹H: δ 7.91–6.52 (m, ABCX-spin system); 2.41 (s, 9 H, Me). ³¹P{¹H} −20.7 (s, PAu(i)).

Reaction of iodo(trimethylphosphite)gold(i) or iodo(triphenylphosphite)gold(i) with iodine. Following the same procedure, using 115 mg (0.25 mmol) of iodo(trimethylphosphite)gold(i) or 159 mg (0.25 mmol) iodo(triphenylphosphite)gold(i) and 64 mg (0.25 mmol) of iodine. The NMR-spectra showed that in both cases no reaction had occurred. A crystallisation of products was not possible. *I*(*MeO*)₃*P*/*AuI*: NMR (CD₂Cl₂), ¹H: δ 3.79 (d, *J*_{HP} = 13.9 Hz, Me). ³¹P{¹H} 132.3 (s, PAu(i)). *I*(*PhO*)₃*P*/*AuI*: NMR (CD₂Cl₂), ¹H: δ 7.51–7.30 (m, Ph). ³¹P{¹H} 119.8 (s, PAu(i)).

Reaction of (dppm)(AuI)₂ with iodine²⁶. Following the same procedure, 248 mg (0.25 mmol) of (dppm)(AuI)₂ and 64 mg (0.25 mmol) of iodine. The NMR analysis of the reaction mixture showed that no oxidation of the gold centres took place. NMR (CD₂Cl₂), ¹H: δ 7.87–7.39 (m, 20 H, Ph); 3.71 (t, *J*_{HP} = 11.1 Hz, 2 H, CH₂). ³¹P{¹H}: δ 28.1 (s, PAu(i)).

[1,2-Bis(diphenylphosphino)benzene]diiodogold(iii) triiodide. 90.6 mg (0.20 mmol, 1 eq.) of 1,2-bis(diphenylphosphino)benzene (dppbe) and 127 mg (0.50 mmol, 2.5 eq.) of iodine were dissolved in 30 ml of dichloromethane. After 15 min 40 mg

Table 3 Crystal data, data collection, and structure refinement

	[(2-Tol) ₃ P]AuI	[(2-Tol) ₃ P]AuI·0.5I ₂	(dppm)(AuBr) ₂	(dppm)(AuI) ₂
<i>Crystal data</i>				
Formula	C ₂₁ H ₂₁ AuIP	C ₂₁ H ₂₁ AuI ₂ P	C ₂₅ H ₂₂ Au ₂ Br ₂ P ₂	C ₂₅ H ₂₂ Au ₂ I ₂ P ₂
<i>M_r</i>	628.21	755.11	938.12	1032.10
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	<i>Pbca</i>	<i>P</i> $\bar{1}$	<i>C</i> /2 <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	14.0151(2)	8.9024(1)	22.3812(3)	22.4894(2)
<i>b</i> /Å	20.1112(2)	11.6435(2)	7.3201(1)	7.5585(1)
<i>c</i> /Å	28.2688(4)	11.7222(2)	18.3499(3)	18.7126(3)
<i>a</i> °	90	105.877(1)	90	90
<i>β</i> °	90	95.169(1)	122.226(1)	123.579(1)
<i>γ</i> °	90	103.724(1)	90	90
<i>V</i> /Å ³	7967.9(2)	1119.6(1)	2543.15(6)	2650.07(6)
<i>D_x</i> /g cm ^{−3}	2.095	2.240	2.450	2.587
<i>Z</i>	16	2	4	4
<i>F</i> (000)	4704	694	1720	1864
<i>μ</i> (Mo-Kα)	90.15	94.00	148.04	135.21
<i>Data collection</i>				
<i>T</i> /°C	−130	−130	−130	−130
Measured reflections	208102	29379	32750	35673
Unique reflections (<i>R_{int}</i>)	8431 (0.062)	4650 (0.039)	2823 (0.055)	2939 (0.059)
Absorption correction	DELABS	DELABS	DELABS	DELABS
<i>T_{min}</i> / <i>T_{max}</i>	0.526/0.852	0.386/0.788	0.488/0.836	0.323/0.754
<i>Refinement</i>				
Refined parameters	439	229	144	144
Final <i>R</i> values [<i>I</i> ≥ 2σ(<i>I</i>)]				
<i>R</i> 1	0.0330	0.0254	0.0311	0.0260
<i>wR</i> 2 ^a	0.0696	0.0681	0.0687	0.0670
Absolute structure parameter	—	—	—	—
<i>ρ_{hkl}</i> (max./min.) e Å ^{−3}	3.864/−3.306	1.321/−1.772	1.348/−1.423	1.917/−1.925

^a *wR*2 = {[Σ(*w*(*F_o*² − *F_c*²)/Σ(*w*(*F_o*²))]^{1/2}}; *w* = 1/[σ²(*F_o*²) + (*ap*)² + *bp*]; *p* = (*F_o*² + 2*F_c*²)/3; *a* = 0.0254 [(2-Tol)₃P]AuI], 0.0250 [(2-Tol)₃P]AuI·0.5I₂], 0.0319 [(dppm)(AuBr)₂], 0.0249 [(dppm)(AuI)₂]; *b* = 45.20 [(2-Tol)₃P]AuI], 1.05 [(2-Tol)₃P]AuI·0.5I₂], 28.65 [(dppm)(AuBr)₂], 23.37 [(dppm)(AuI)₂].

(0.20 mmol, 1 eq.) of gold wire was added to the solution. After 3 d of stirring the gold was completely dissolved and the colour of the reaction mixture had changed to black. The solvent was evaporated under reduced pressure to a volume of about 5 ml and the solution used for crystallisation by slow diffusion of *n*-pentane. After two weeks the product was obtained as black crystals, which are air- and moisture-stable but decompose at room temperature after a few days. 132 mg (54% yield), mp 125 °C with decomposition (Found: C, 27.38; H, 1.82; I, 48.4. Calc. for C₃₀H₂₄AuI₅P₂: C, 28.20; H, 1.89; I, 49.6%). NMR (CD₂Cl₂), ¹H: δ 8.28 (m, 2H, C₆H₄); 7.72–7.16 (m, 20 H, Ph); 7.52–7.40 (m, 2H, C₆H₄). ³¹P{¹H}: δ 50.2 (s). ¹³C{¹H}: δ C₆H₄: 137.6 (m); 137.3 (s); 136.6 (m); Ph: 134.9 (t, *J*_{CP} = 5.4 Hz); 132.9 (s); 130.5 (t, *J*_{CP} = 6.9 Hz); 123.5 (d, *J*_{CP} = 68.4 Hz).

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 or an Enraf Nonius CAD 4 [(BzMePhP)AuBr₃] diffractometer, employing graphite-monochromated Mo-Kα 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). 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. Further information on crystal data, data collection and structure refinement are summarized in Tables 2–4.

CCDC reference numbers 232528–232539.

See <http://www.rsc.org/suppdata/dt/b4/b403005b/> for crystallographic data in CIF or other electronic format.

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References

- P. Pykkö, *Chem. Rev.*, 1988, **88**, 563.
- (a) W. H. E. Schwarz, *Fundamentals of Relativistic Effects in Chemistry, in Theoretical Models of Chemical Bonding*, ed. Z. M. Maksic, Springer, Heidelberg, 1989, vol. 2, p. 593; (b) S.-G. Wang and W. H. E. Schwarz, *J. Am. Chem. Soc.*, 2004, **126**, 1266.
- (a) P. Schwerdtfeger, M. Dolg, W. H. E. Schwarz, G. A. Bowmaker and P. D. W. Boyd, *J. Chem. Phys.*, 1989, **91**, 1762; (b) P. Schwerdtfeger and G. A. Bowmaker, *J. Chem. Phys.*, 1994, **100**, 4487; (c) P. Schwerdtfeger, *J. Am. Chem. Soc.*, 1989, **111**, 7261.
- (a) H. Schmidbaur, *Gold. Bull.*, 1990, **23**, 11; (b) H. Schmidbaur, *Interdisc. Sci. Rev.*, 1992, **17**, 213; (c) H. Schmidbaur, *Chem. Soc. Rev.*, 1995, **24**, 391.
- H. G. Raubenheimer and S. Cronje, in *Gold: Progress in Chemistry, Biochemistry and Technology*, ed. H. Schmidbaur, Wiley, Chichester, 1999, p. 557 ff.
- M. C. Gimeno and A. Laguna, *Chem. Rev.*, 1997, **97**, 511.
- R. J. Puddephatt, in *Comprehensive Coordination Chemistry*, Pergamon, Oxford, 1987, vol. 5, p. 861.
- M. Melnik and R. V. Parish, *Coord. Chem. Rev.*, 1986, **70**, 157.
- M. Hargittai, A. Schulz, B. Reffy and M. Kolonits, *J. Am. Chem. Soc.*, 2001, **123**, 1449.
- M. Teicher and R. Weil, *Phys. Rev. B*, 1978, **38**, 7134.
- (a) L. I. Elding and L. H. Skibsted, *Inorg. Chem.*, 1986, **25**, 4084; (b) L. I. Elding and L. F. Olsson, *Inorg. Chem.*, 1982, **21**, 779.

Table 4 Crystal data, data collection, and structure refinement

	(Ph ₃ P)AuBr ₃	(BzMePhP)AuBr ₃	(dppm)AuBr(AuBr ₃)·2CH ₂ Cl ₂	[(dppbe)AuI ₂] ⁺ I ₃ [−]
<i>Crystal data</i>				
Formula	C ₁₈ H ₁₅ AuBr ₃ P	C ₁₄ H ₁₅ AuBr ₃ P	C ₂₇ H ₂₆ Au ₂ Br ₄ Cl ₄ P ₂	C ₃₀ H ₂₄ AuI ₃ P ₂
<i>M_r</i>	698.97	650.93	1267.79	1277.90
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	7.9533(1)	9.573(1)	11.1186(1)	9.8050(1)
<i>b</i> /Å	14.0747(2)	14.264(1)	15.8399(1)	14.3361(2)
<i>c</i> /Å	9.3338(1)	12.973(1)	19.7887(2)	24.5570(3)
<i>a</i> /°	90	90	90	90
<i>β</i> /°	112.967(1)	104.10(1)	96.162(1)	101.442(1)
<i>γ</i> /°	90	90	90	90
<i>V</i> /Å ³	962.0(1)	1718.1(3)	3465.0(1)	3383.3(1)
<i>D_c</i> /g cm ^{−3}	2.413	2.517	3.078	2.509
<i>Z</i>	2	4	4	4
<i>F</i> (000)	644	1192	2336	2312
<i>μ</i> (Mo-Kα)	139.56	156.17	134.90	90.24
<i>Data collection</i>				
<i>T</i> /°C	−130	−73	−130	−130
Measured reflections	23415	3943	85839	76016
Unique reflections (<i>R</i> _{int})	4196 (0.057)	3720 (0.036)	7114 (0.047)	6208 (0.056)
Absorption correction	DELABS	DIFABS	DELABS	DELABS
<i>T</i> _{min} / <i>T</i> _{max}	0.491/0.837	0.129/1.000	0.603/0.881	0.532/0.854
<i>Refinement</i>				
Refined parameters	208	172	352	343
Final <i>R</i> values [<i>I</i> ≥ 2σ(<i>I</i>)]				
<i>R</i> 1	0.0196	0.0405	0.0270	0.0312
<i>wR</i> 2 ^a	0.0510	0.1133	0.0632	0.0782
Absolute structure parameter	0.022(5)	—	—	—
<i>ρ</i> _{max} (max./min.)/e Å ^{−3}	0.929/−0.732	1.704/−1.727	1.064/−1.094	1.338/−1.469

^a *wR*2 = {Σ[w(*F*_o² − *F*_c²)]/Σ[w(*F*_o²)]}^{1/2}; *w* = 1/[σ²(*F*_o²) + (*ap*)² + *bp*]; *p* = (*F*_o² + 2*F*_c²)/3; *a* = 0.0000 [(Ph₃P)AuBr₃], 0.0814 [(BzMePhP)AuBr₃], 0.0120 [(dppm)AuBr(AuBr₃)·2CH₂Cl₂], 0.0340 [(dppbe)AuI₂]⁺I₃[−]; *b* = 0.00 [(Ph₃P)AuBr₃], 8.25 [(BzMePhP)AuBr₃], 16.34 [(dppm)AuBr(AuBr₃)·2CH₂Cl₂], 19.92 [(dppbe)AuI₂]⁺I₃[−].

- 12 (a) P. H. Svensson, J. Rosdahl and L. Kloo, *Chem. Eur. J.*, 1999, **5**, 305; (b) P. H. Svensson and L. Kloo, *Chem. Rev.*, 2003, **103**, 1649.
- 13 T. Sönnel, R. Brown, L. Kloo and P. Schwerdtfeger, *Chem. Eur. J.*, 2001, **7**, 3167.
- 14 A. Schulz and M. Hargittai, *Chem. Eur. J.*, 2001, **7**, 3657.
- 15 J.-H. Choy, Y.-H. Kim, S.-J. Hwang and P. V. Huong, *J. Phys. Chem. B*, 2000, **104**, 7273.
- 16 J. L. Ryan, *Inorg. Chem.*, 1969, **8**, 2058.
- 17 J. Strähle, J. Gelinek, M. Kolmel and A. M. Nemecek, *Z. Naturforsch., Teil B*, 1979, **34**, 952.
- 18 A. Hakansson and L. Johansson, *Chem. Scr.*, 1975, **7**, 201.
- 19 L. M. Castro-Castro and A. M. Guloy, *Angew. Chem., Int. Ed.*, 2003, **42**, 2771.
- 20 E. S. Lang and J. Strähle, *Z. Anorg. Allg. Chem.*, 1996, **622**, 981.
- 21 J. Strähle, J. Gelinek and M. Koelmel, *Z. Anorg. Allg. Chem.*, 1979, **456**, 241.
- 22 F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1940, 1235.
- 23 S. M. Godfrey, N. Ho, C. A. McAuliffe and R. G. Pritchard, *Angew. Chem., Int. Ed.*, 1996, **35**, 2344.
- 24 R. D. Sanner, J. H. Satcher Jr. and M. W. Droegge, *Organometallics*, 1989, **8**, 1498.
- 25 S. Attar, J. H. Nelson, W. H. Bearden, N. W. Alcock, L. Solujic and E. B. Milosavljevic, *Polyhedron*, 1991, **10**, 1939.
- 26 H. Schmidbaur, A. Wohlleben, F. E. Wagner, D. F. Van de Vondel and G. P. van der Kelen, *Chem. Ber.*, 1977, **110**, 2758.
- 27 K. C. Dash and H. Schmidbaur, *Chem. Ber.*, 1973, **106**, 1221.
- 28 F. Bigoli, P. Deplano, M. L. Mercuri, M. A. Pellinghelli, G. Pintus, A. Serpe and E. F. Trogu, *Chem. Commun.*, 1998, 2351.
- 29 L. Cau, P. Deplano, L. Marchio, L. Mercuri, L. Pilia, A. Serpe and E. F. Trogu, *Dalton Trans.*, 2003, 1969.
- 30 C. A. McAuliffe, R. V. Parish and P. D. Randall, *Dalton Trans.*, 1979, 1730.
- 31 (a) H. Schmidbaur, A. Wohlleben, F. E. Wagner, O. Orama and G. Huttner, *Chem. Ber.*, 1977, **110**, 1748; (b) M. Sigl, A. Schier and H. Schmidbaur, *Eur. J. Inorg. Chem.*, 1998, 203.
- 32 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.
- 33 N. G. Andersen and B. A. Keay, *Chem. Rev.*, 2001, **101**, 997.
- 34 U. Monkowius, S. Nogai and H. Schmidbaur, *Organometallics*, 2003, **22**, 145.
- 35 L. G. Kuz'mina, *Zh. Neorg. Khim.*, 1993, **38**, 640.
- 36 A. K. Al-Saady, C. A. McAuliffe, R. V. Parish and J. A. Sandbank, *Inorg. Synth.*, 1985, **23**, 191.
- 37 C. S. W. Harker and E. R. T. Tiekink, *Acta Crystallogr., Sect. C*, 1991, **47**, 878.
- 38 P. D. Cookson and E. R. T. Tiekink, *Acta Crystallogr., Sect. C*, 1994, **50**, 1896.
- 39 H. Schmidbaur, B. Brachthäuser, O. Steigelmann and H. Beruda, *Chem. Ber.*, 1992, **125**, 2705.
- 40 U. Monkowius, S. Nogai and H. Schmidbaur, *Z. Naturforsch., Teil B*, 2003, **58**, 751.
- 41 D. R. Williamson and M. C. Baird, *J. Inorg. Nucl. Chem.*, 1972, **34**, 3393.
- 42 P. B. Hitchcock and P. Pye, *J. Chem. Soc., Dalton Trans.*, 1977, 1457.
- 43 S. Ahrlund, K. Dreisch, B. Norén and Å. Oskarsson, *Acta Chem. Scand., Ser. A*, 1987, **41**, 173.
- 44 D. V. Toronto, B. Weissbart, D. S. Tinti and A. L. Balch, *Inorg. Chem.*, 1996, **35**, 2482.
- 45 P. F. Barron, L. M. Engelhardt, P. C. Healy, J. Oddy and A. H. White, *Aust. J. Chem.*, 1987, **40**, 1545.
- 46 H. Schmidbaur and A. A. M. Aly, *Z. Naturforsch., Teil B*, 1979, **34**, 23.