

**GOLD(I) AND GOLD(III) *ortho*-NITROPHENYL COMPLEXES.
 CRYSTAL AND MOLECULAR STRUCTURE OF
ortho-NITROPHENYLTRIPHENYLARSINEGOLD(I) ***

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Summary

The reaction between $[\text{Au}(o\text{-C}_6\text{H}_4\text{NO}_2)\text{Cl}]^-$ and tetrahydrothiophene (tht) in the presence of NaClO_4 gives a solution (probably containing $[\text{Au}(o\text{-C}_6\text{H}_4\text{NO}_2)(\text{tht})]$) that can be used to prepare neutral $[\text{Au}(o\text{-C}_6\text{H}_4\text{NO}_2)\text{L}_n]$ ($\text{L} = \text{AsPh}_3$, $n = 1$; $\text{L} = \text{SbPh}_3$, $n = 2$; $\text{L} = 1,10\text{-phenanthroline}$, $n = 1$) or anionic $[\text{Au}(o\text{-C}_6\text{H}_4\text{NO}_2)(\text{CN})]^-$ complexes. Treatment of $[\text{Au}(o\text{-C}_6\text{H}_4\text{NO}_2)(\text{PPh}_3)]$ with chlorine or PhICl_2 gives *trans*- or *cis*- $[\text{Au}(o\text{-C}_6\text{H}_4\text{NO}_2)\text{Cl}_2(\text{PPh}_3)]$. Isomerizations occur when the *cis*-isomer is treated with concentrated solutions of chlorine or when the *trans*-isomer is heated.

An X-ray diffraction study of $[\text{Au}(o\text{-C}_6\text{H}_4\text{NO}_2)(\text{AsPh}_3)]$ has revealed an almost linear coordination around the gold atom (As-Au-C mean value $177(2)^\circ$). The Au–O distance is too long (mean value $2.80(3)$ Å) for intramolecular coordination.

Introduction

We recently reported the synthesis of gold(I) and gold(III) complexes containing *ortho*-nitrophenyl groups by use of bis(*ortho*-nitrophenyl)mercury as an arylating agent [1–3]. We now describe some new types of *ortho*-nitrophenyl-gold(I) and -gold(III) complexes.

Reactions of $[\text{BzPPh}_3][\text{Au}(\text{R})\text{Cl}]$ ($\text{Bz} = \text{benzyl}$, $\text{R} = o\text{-C}_6\text{H}_4\text{NO}_2$) with anionic (Br^- , I^-) or neutral monodentate (PPh_3 , AsPh_3) or bidentate [1,2-bis(diphenylphosphino)ethane(dppe)] ligands gave complexes of the types $[\text{Au}(\text{R})\text{X}]^-$, $[\text{Au}(\text{R})\text{L}]$, and

* Dedicated to Prof. Rafael Usón on the occasion of his 60th birthday.

$[\text{Au}_2(\text{R})_2(\text{dppe})]$, respectively [3]. We tried unsuccessfully to replace the chloride ligand by SbPh_3 or 1,10-phenanthroline (phen). We were interested in these reactions because one of us some time ago obtained tetra- and tri-coordinate gold(I) complexes ($[\text{Au}(\text{SbPh}_3)_4][\text{Au}(\text{C}_6\text{F}_5)_2]$ and $[\text{Au}(\text{C}_6\text{F}_5)(\text{phen})]$) containing such ligands [4,5] by starting from $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ (tht = tetrahydrothiophene). It is well established that most gold(I) complexes are two-coordinate. We present the results of attempts to prepare $[\text{Au}(\text{R})(\text{tht})]$ and describe its reactions with AsPh_3 , SbPh_3 , phen and CN^- .

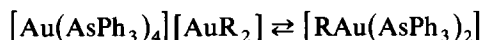
By treating $[\text{AuCl}_4]^-$ with R_2Hg we obtained only $[\text{Au}(\text{R})_2\text{Cl}_2]^-$ even when a 1/1 molar ratio was used [2]. We describe here a route to monoarylgold(III) derivatives containing the *ortho*-nitrogen group.

On the basis of the IR spectra we have suggested that in all the reported *ortho*-nitrophenylgold complexes there is no Au–O bonding. We report here the molecular structure of the complex $[\text{Au}(\text{R})\text{AsPh}_3]$ which is in accord with this view.

Results and discussion

Reaction of $[\text{BzPPh}_3][\text{Au}(\text{R})\text{Cl}]$ ($\text{Bz} = \text{C}_6\text{H}_5\text{CH}_2$, $\text{R} = o\text{-C}_6\text{H}_4\text{NO}_2$) with an excess of tetrahydrothiophene (tht) and NaClO_4 in tetrahydrofuran (thf), followed by removal of NaCl and $[\text{BzPPh}_3]\text{ClO}_4$ by addition of diethyl ether (Et_2O), gave a solution from which a yellow solid separated on cooling (-60°C). This compound (probably $[\text{Au}(\text{R})(\text{tht})]$) is unstable at room temperature in the solid state, and could not be characterized. Fortunately the (ca. 1/10) thf/ Et_2O solution obtained from the reaction is stable enough to be handled. Owing to the high proportion of Et_2O in the solvent addition of different ligands leads to clean reactions because of the precipitation of the products.

The complex $[\text{Au}(\text{R})(\text{AsPh}_3)]$ has been prepared before [3] by treating $[\text{Au}(\text{R})\text{Cl}]^-$ with AsPh_3 in the presence of NaClO_4 but the yield was only 51%. We tried to improve the yield by treating “ $\text{RAu}(\text{tht})$ ” with AsPh_3 in 1/3.3 ratio. The reaction took place as expected to give the yellow complex $[\text{Au}(\text{R})(\text{AsPh}_3)]$, but the yield was not improved (41%) and furthermore a white product was also obtained in very low yield. The elemental analysis of this compound points to the stoichiometry $\text{RAu}(\text{AsPh}_3)_2$; if the product is formulated as $[\text{Au}(\text{AsPh}_3)_4][\text{AuR}_2]$ its molar conductivity in acetone ($54 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$) is lower than that expected for a 1/1 electrolyte, probably owing to the equilibrium:

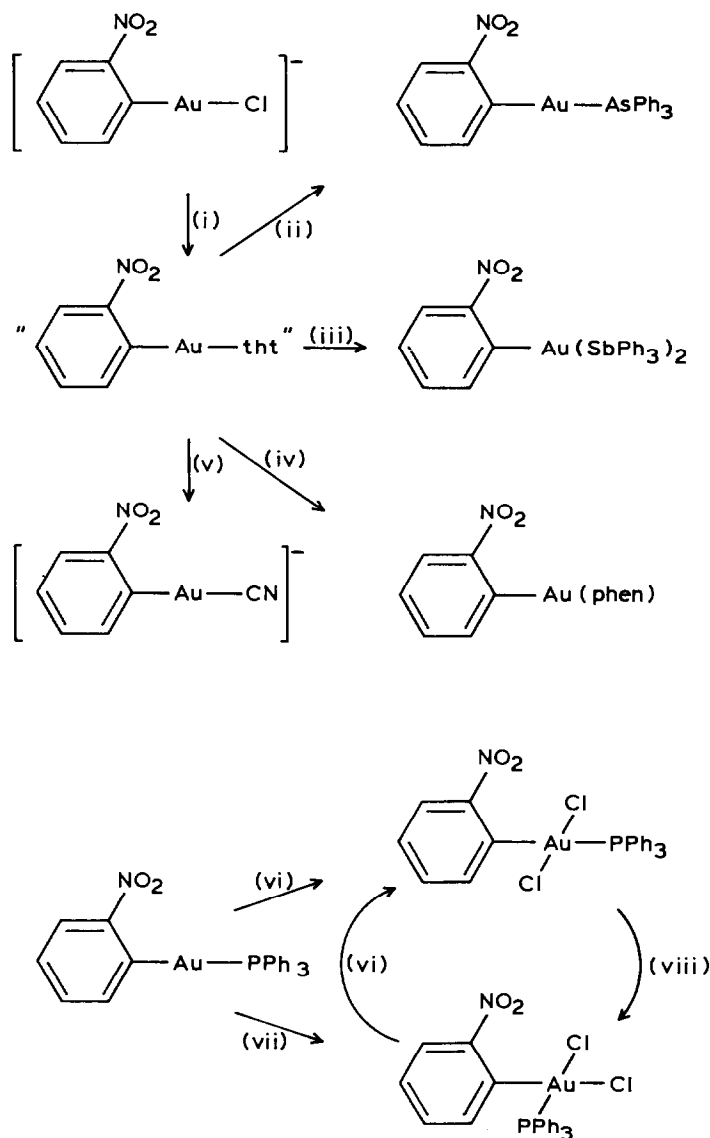


Similar behaviour has been reported [6] for the complexes $[\text{AuL}_4][\text{AuR}'_2]$ where $\text{R}' = 4,4'\text{-HC}_6\text{F}_4\text{C}_6\text{F}_4$ and $\text{L} = \text{SbPh}_3$ or $\text{L}_2 = o\text{-phenylenebis}(\text{dimethylarsine})$. If NaClO_4 is added after the addition of AsPh_3 to the “ $\text{RAu}(\text{tht})$ ” solution, the previously unreported complex $[\text{Au}(\text{AsPh}_3)_4]\text{ClO}_4$ can be isolated.

Similarly the reaction between “ $\text{RAu}(\text{tht})$ ” and SbPh_3 (1/2.7) gives a white precipitate and from the resulting solution a yellow complex can be isolated. The white solid turns pale yellow in a few minutes. Both the yellow and pale yellow compounds give elemental analyses corresponding to the stoichiometry “ $\text{RAu}(\text{SbPh}_3)_2$ ”, but the pale yellow one has a conductivity in acetone which suggests the presence of $[\text{Au}(\text{SbPh}_3)_4][\text{AuR}_2]$ (Λ_M $33 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$), containing a tetracoordinate cation [4,5]. All attempts to isolate this compound pure by recrystallization

caused further conversion into the yellow complex. This is a non-conducting complex and must be formulated as $[\text{Au}(\text{R})(\text{SbPh}_3)_2]$. It decomposes slowly to metallic gold in solution and the solid state at room temperature, preventing the growing of crystals for an X-ray structural study.

The addition of a solution of "RAu(tht)" to phen (1/1.2) in Et_2O causes immediate precipitation of a white solid that cannot be isolated because it changes to an orange species within a few minutes. This orange complex analyses as



SCHEME 1. (i) + tht + $\text{NaClO}_4 - \text{ClO}_4^- - \text{NaCl}$; (ii) + AsPh_3 ; (iii) + SbPh_3 ; (iv) + phen; (v) + KCN ; (vi) + Cl_2/CCl_4 ; (vii) + Cl_2IPh ; (viii) refluxing in CH_3CN .

[Au(R)(phen)], is non-conducting in acetone, and decomposes rapidly in the air at room temperature.

Starting from [Au(R)Cl]⁻ we were able [3] to replace Cl by Br or I, but reactions with NaCN or KCN gave complex mixtures that we were unable to resolve. However, reaction of the "RAu(tht)" solution with KCN and [BzPPh₃]Cl gave the yellow complex BzPh₃P[Au(R)(CN)] showing $\nu(\text{CN})$ at 2134 cm⁻¹.

The *trans*- or *cis*-isomers of [Au(R)Cl₂(PPh₃)] can be obtained by treating [Au(R)(PPh₃)] [3] with a saturated solution of chlorine in CCl₄ or with PhICl₂. The *trans*-isomer is a yellow compound, and has a strong band at 365 cm⁻¹ in its IR spectrum assignable to $\nu(\text{Cl}-\text{Au}-\text{Cl})$ [7], whereas the *cis*-isomer is white and gives two strong bands, at 322 and 307 cm⁻¹, assignable to $\nu(\text{AuCl})$ *trans* to PPh₃ [7] and to $\nu(\text{AuCl})$ *trans* to the *o*-C₆H₄NO₂ group, respectively, the aryl ligand having the higher *trans*-influence.

As previously observed, some *trans*-dihaloarylgold(III) complexes isomerize to their *cis*-isomers in solution at room temperature [8] or on heating [9]. In our case the *trans*-isomer is converted into the *cis*-isomer when its solution in acetonitrile is refluxed. The reverse process can be brought about by treating the solid *cis*-isomer with a saturated solution of chlorine in CCl₄. As far as we know the latter type of isomerization has not been observed previously for gold complexes.

All the complexes show $\nu_{\text{asym}}(\text{NO}_2)$ and $\nu_{\text{sym}}(\text{NO}_2)$ vibrations at ca. 1500 and 1330 cm⁻¹, respectively, as observed for other Au^I and Au^{III} complexes [1-3], suggesting that there is no coordination of the nitro group. When it does $\nu_{\text{sym}}(\text{NO}_2)$ is observed [10] at around 1270 cm⁻¹.

Scheme 1 illustrates the methods used to prepare the complexes.

X-Ray crystal structure of [Au(R)(AsPh₃)]

The unit cell contains two significantly different molecules (see Figs. 1 and 2 and Table 1) each with almost linear coordination around the gold atoms. The Au-As bond distance (mean value 2.384(1) Å) is longer than that in [Au(Br)AsPh₃] [11] (2.342(5) Å) owing to the greater *trans*-influence of the nitrophenyl group. One of the Au-C bond distances [2.051(4) Å; molecule 2] is similar to those reported for other in arylgold(I) complexes [4,12] but the other one (1.977(5) Å; molecule 1) is the shortest so far observed.

Both of the Au-O distances (2.775(5) and 2.821(5) Å) are too long to permit assumption of intramolecular coordination. The Au-O distances in [(Ph₃PAu)₃O]⁺ are in the range 1.93(8)-2.04(7) Å [13], but an even longer Au-O distance [12a] (2.961(4) Å in [Au(R)(PPh₃)] (R = 2,6-dimethoxyphenyl)) has been taken to reflect a weak interaction.

The differences between the two molecules can be interpreted by assuming that a weak interaction occurs through a small $sp^3 \sigma(\text{O}) \rightarrow p\sigma(\text{Au})$ overlap that should leave the $p_z(\text{N})$ more accessible to a $p_z\pi(\text{C}) \rightarrow p_z\pi(\text{N})$ bonding. Although such O...Au interaction is weak, its effect on the nitrophenyl group is strong enough to give rise to observable lengthening of the N-O(Au) and C(1)-C(2) distances and shortening of the N-O, C-N and Au-C distances when the interaction is stronger (i.e. in molecule 1) (see Scheme 2). The suggested O...Au overlap also accounts for the linearity of the complex because it does not modify the type of hybrid (*sp*) used by the gold atom.

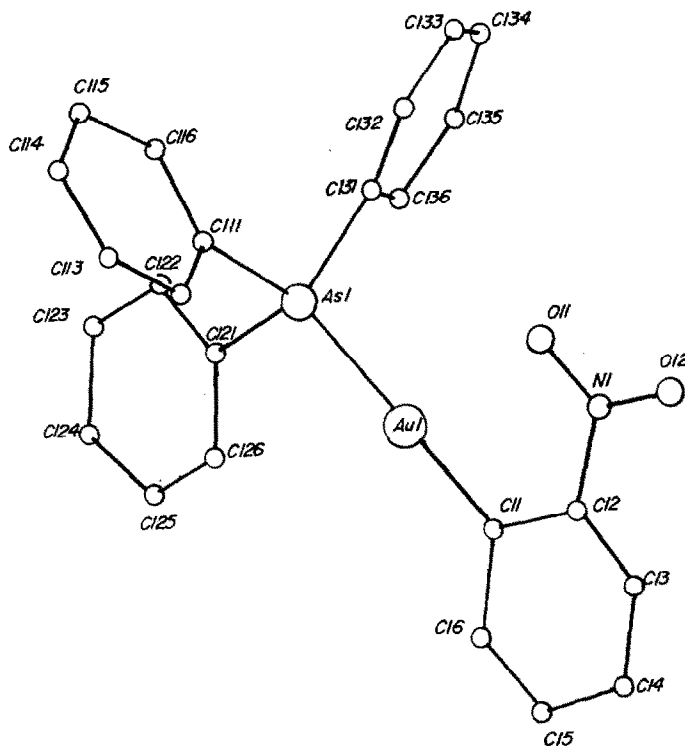
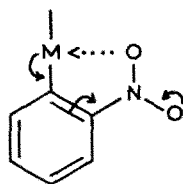


Fig. 1. View of the molecule 1 of complex $[\text{Au}(\text{R})(\text{AsPh}_3)]$ showing the atom numbering.

We recently reported that in complex $[\text{Rh}\{2\text{-C}_6\text{H}_4\text{N}(\text{O})\text{O}\}_2\text{Cl}(\text{CO})]$ the nitro groups act as strong π -acceptors of the ring π -HOMO electronic density as a consequence of their chelating nature [10]. The stronger $\text{O} \rightarrow \text{Rh}$ bonding leads to shorter C–N (1.378(5) and 1.362(5) Å) and longer N–O(Rh) (1.283(5) and 1.375(5) Å) distances than those in molecule 1, in accord with the above arguments. Similarly in $[\text{Pt}(2\text{-C}_6\text{H}_4\text{N}(\text{O})\text{O})(2\text{-C}_6\text{H}_4\text{NO}_2)(\text{PPh}_3)]$ [14] the N–O(Pt) distance is also longer than the corresponding distance in molecule 1. However other parameters in these Rh and Pt complexes do not show the expected changes, probably because the nature of the metal and/or the other ligands have an important influence on the electronic distribution in the *ortho*-nitrophenyl moieties. Thus the N–O bond distance (1.321(4) Å) in one of the nitrophenyl groups and the C(1)–C(2) (1.286(6) Å) in the other one both in the rhodium complex are longer and shorter, respec-

(Continued on p. 376)



SCHEME 2

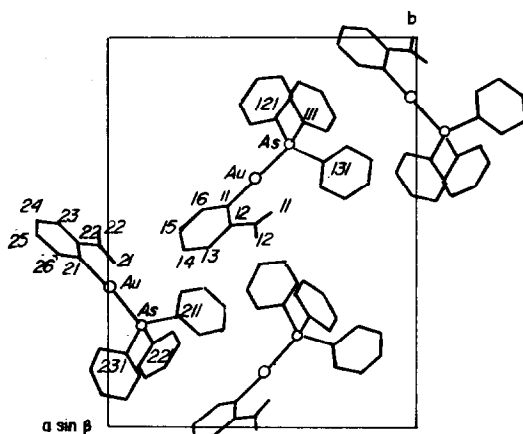


Fig. 2. Projection down the [001]-axis of an half of the unit-cell content.

TABLE 2

ATOMIC COORDINATES ($\times 10^4$; Au and As $\times 10^5$) FOR NON-HYDROGEN ATOMS AND EQUIVALENT TEMPERATURE COEFFICIENT $B_{eq} = 8\pi^2/3\sum U_j a_j^* a_j^* a_j$ OF $[\text{Au}(\text{R})(\text{AsPh}_3)]$

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> _{eq} | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> _{eq} | |
|--------|----------|----------|----------|------------------------|----------|----------|----------|------------------------|----------|
| Au(1) | 35769(1) | 49309(1) | 26878(1) | 4.30(1) | Au(2) | 64273(1) | 2621(1) | 19838(1) | 3.95(1) |
| As(1) | 26895(2) | 60200(3) | 27928(3) | 3.92(2) | As(2) | 73758(2) | 13164(3) | 20584(3) | 3.84(2) |
| C(11) | 4306(2) | 4024(3) | 2591(3) | 4.46(21) | C(21) | 5683(2) | -719(3) | 2019(3) | 4.80(21) |
| C(12) | 4585(3) | 4104(3) | 2048(3) | 4.71(23) | C(22) | 5280(2) | -808(3) | 2595(3) | 3.67(19) |
| C(13) | 5345(3) | 3458(3) | 2037(4) | 5.26(25) | C(23) | 4798(2) | -1479(3) | 2670(4) | 5.36(24) |
| C(14) | 5422(3) | 2652(4) | 2490(4) | 6.40(31) | C(24) | 4722(2) | -2161(4) | 2070(4) | 6.36(31) |
| C(15) | 4914(3) | 2494(4) | 3036(4) | 7.01(32) | C(25) | 5100(3) | -2135(3) | 1362(5) | 7.45(33) |
| C(16) | 4416(2) | 3152(3) | 3088(3) | 5.50(25) | C(26) | 5580(2) | -1434(4) | 1340(4) | 6.20(28) |
| N(1) | 4771(3) | 4901(3) | 1522(3) | 5.56(24) | N(2) | 5354(3) | -90(3) | 3304(4) | 6.51(28) |
| O(11) | 4417(3) | 5563(3) | 1629(4) | 9.60(31) | O(21) | 5844(3) | 440(3) | 3441(3) | 9.73(32) |
| O(12) | 5156(3) | 4939(3) | 1051(3) | 9.03(32) | O(22) | 4928(2) | -124(3) | 3749(3) | 8.65(28) |
| C(111) | 2112(2) | 6457(3) | 1682(3) | 3.46(18) | C(211) | 7141(2) | 2448(3) | 1417(3) | 3.59(18) |
| C(112) | 1449(3) | 5976(3) | 1291(3) | 4.97(24) | C(212) | 7655(3) | 3205(3) | 1613(3) | 5.37(26) |
| C(113) | 1047(3) | 6276(4) | 459(3) | 5.36(25) | C(213) | 7451(3) | 4006(3) | 1098(4) | 5.44(26) |
| C(114) | 1304(3) | 7029(4) | 39(3) | 6.12(29) | C(214) | 6894(3) | 3985(3) | 405(3) | 5.68(28) |
| C(115) | 1942(3) | 7460(4) | 435(3) | 6.03(29) | C(215) | 6419(3) | 3319(4) | 244(3) | 5.53(27) |
| C(116) | 2381(3) | 7185(3) | 1232(3) | 5.17(26) | C(216) | 6547(2) | 2536(3) | 728(3) | 4.17(21) |
| C(121) | 2006(2) | 5555(3) | 3391(3) | 4.50(22) | C(221) | 7859(2) | 1655(3) | 3263(3) | 3.63(18) |
| C(122) | 1412(2) | 6094(3) | 3389(3) | 4.83(24) | C(222) | 7501(3) | 2321(4) | 3644(3) | 5.05(25) |
| C(123) | 909(2) | 5757(4) | 3885(4) | 5.91(29) | C(223) | 2844(3) | 2475(4) | 9463(5) | 7.36(36) |
| C(124) | 1053(3) | 4895(4) | 4328(4) | 6.46(33) | C(224) | 8459(3) | 2055(4) | 4956(3) | 5.76(28) |
| C(125) | 1657(3) | 4402(4) | 4224(4) | 7.48(35) | C(225) | 8758(3) | 1406(3) | 4572(3) | 5.10(26) |
| C(126) | 2163(3) | 4723(4) | 3794(4) | 6.32(29) | C(226) | 8436(2) | 1203(3) | 3717(3) | 4.93(24) |
| C(131) | 3106(2) | 7103(3) | 3459(3) | 4.45(22) | C(231) | 8144(2) | 808(3) | 1611(3) | 4.21(20) |
| C(132) | 2679(3) | 7885(3) | 3354(4) | 6.11(29) | C(232) | 8014(2) | -12(3) | 1187(4) | 5.63(26) |
| C(133) | 3001(4) | 8652(4) | 3918(5) | 8.17(40) | C(233) | 8559(3) | -359(5) | 854(4) | 7.62(37) |
| C(134) | 3696(3) | 8547(5) | 4503(4) | 7.24(36) | C(234) | 9170(3) | 2(4) | 933(4) | 5.83(30) |
| C(135) | 4096(3) | 7779(5) | 4542(4) | 8.00(38) | C(235) | 9271(3) | 819(5) | 1291(4) | 7.25(34) |
| C(136) | 3746(2) | 7016(4) | 4014(3) | 5.32(25) | C(236) | 8729(2) | 1285(3) | 1673(4) | 4.96(24) |

tively, than those in molecule 1. In the platinum complex the C–N (1.446(11) Å) and C(1)–C(2) (1.403(12) Å) bond distances in the chelating ligand are respectively marginally longer and significantly shorter than those in molecule 1. More structural data for other *ortho*-nitrophenyl complexes are necessary to enable understanding of this type of metal–ligand bonding.

Experimental

IR spectra were recorded on a Perkin–Elmer 457 or a Nicolet MX-1 spectrophotometer. Conductivities were measured on 5×10^{-4} M solutions in acetone with a Philips 9501 conductimeter. Melting points were determined on a Reichert apparatus and are uncorrected. C, H and N analyses were determined with a Perkin–Elmer 240C microanalyzer; Au was determined by ashing the samples with an aqueous solution of hydrazine. Solvents were distilled before use. Unless otherwise stated, the reactions were carried out at room temperature with magnetic stirring. Molar conductivities (Λ_M) are given in $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

“RAu(tht)” solutions

To solid $[\text{BzPPh}_3][\text{Au}(\text{R})\text{Cl}]$ (81 mg, 0.11 mmol) were added a solution of tht (0.16 mmol) in tetrahydrofuran (0.8 ml) and solid NaClO_4 (20 mg, 0.16 mmol). After a few minutes the yellow insoluble gold complex changed to a mixture of white solids. Addition of diethyl ether (8 ml) and filtration gives a yellow solution of “RAu(tht)”.

Reaction between “RAu(tht)” and AsPh_3

A solution of “RAu(tht)” (from 0.18 mmol of $[\text{Au}(\text{R})\text{Cl}]^-$) was added to a solution of AsPh_3 (182 mg, 0.60 mmol) in dichloromethane (3 ml). The resulting yellow solution was evaporated to dryness and the residue dissolved in dichloromethane (1 ml). Addition of *n*-pentane (3 ml) and cooling (-4°C) gave a white solid (2.8 mg; m.p. 207°C ; Λ_M 54 (in acetone). Analytical data: C, 53.80; H, 3.86; $[\text{Au}(\text{AsPh}_3)_4][\text{AuR}_2]$ calcd.: C, 54.15; H, 3.67%). *n*-Pentane was added to the resulting solution until no more yellow solid separated, and this solid was filtered off and washed with a mixture of diethyl ether/*n*-pentane (1/3) to give $[\text{Au}(\text{R})(\text{AsPh}_3)]$ (41% yield) identified by m.p. and IR spectrum [3].

In a separate experiment (starting from 0.086 mmol of $[\text{BzPPh}_3][\text{Au}(\text{R})\text{Cl}]$ and 0.29 mmol of AsPh_3) the residue after evaporation to dryness was dissolved in acetone (2 ml) and NaClO_4 (Au/ ClO_4 0.8) was added. After 14 h the precipitate was filtered off and washed with acetone (0.5 ml) then diethyl ether to give $[\text{Au}(\text{AsPh}_3)_4]\text{ClO}_4$ (7 mg) (m.p. 220°C ; Λ_M 102°C . Analytical data: C, 56.81; H, 3.91. $[\text{Au}(\text{AsPh}_3)_4]\text{ClO}_4$ calcd.: C, 56.84; H, 3.97%.)

$[\text{Au}(\text{R})(\text{SbPh}_3)_2]$

A solution of “RAu(tht)” (from 0.18 mmol of $[\text{Au}(\text{R})\text{Cl}]^-$) was added to a solution of SbPh_3 (171 mg, 0.48 mmol) in diethyl ether (5 ml). A white solid immediately separated, but during 15 min stirring it became yellow. The suspension was concentrated (2 ml) and filtered. The yellow solid obtained was washed with diethyl ether (4 ml) and *n*-pentane (76% yield; m.p. 120°C (d); Λ_M 3. Analytical data: C, 49.48; H, 3.44; N, 1.43; Au, 20.70. $[\text{Au}(\text{R})(\text{SbPh}_3)_2]$ calcd.: C, 49.21; H, 3.44; N, 1.37; Au, 19.21%.)

[Au(R)(phen)]

A solution of 'RAu(tht)' (from 0.12 mmol of $[\text{Au}(\text{R})\text{Cl}]^-$) was added under nitrogen to a solution of phen (31 mg; 0.15 mmol) in diethyl ether (6 ml). A white solid immediately separated, but then rapidly turned orange. The precipitate was filtered off under nitrogen and washed with diethyl ether (73% yield: m.p. 100°C (d); Λ_M 4. Analytical data: C, 42.82; H, 2.49; N, 7.79; Au, 38.46. $[\text{Au}(\text{R})(\text{phen})]$ calcd.: C, 43.30; H, 2.42; N, 8.42; Au, 39.45%.)

BzPPh₃[Au(R)(CN)]

Solid KCN (0.41 mmol) was added to a solution of "RAu(tht)" (from 0.12 mmol of $[\text{Au}(\text{R})\text{Cl}]^-$). The suspension was evaporated to dryness and acetone (2 ml) was added. After 10 min stirring the solution was evaporated to dryness and a solution of $[\text{BzPPh}_3]\text{Cl}$ (0.12 mmol) in dichloromethane (5 ml) was added. The suspension was stirred for 10 min then filtered. The solution was concentrated (to 2 ml) and diethyl ether was added to precipitate a yellow solid; the suspension was cooled (-4°C) then filtered to give the product (64% yield; m.p. 133; Λ_M 91. Analytical data: C, 54.53; H, 3.62; N, 4.42; Au, 28.47. $\text{BzPPh}_3[\text{Au}(\text{R})(\text{CN})]$ calcd.: C, 55.02; H, 3.75; N, 4.01; Au, 28.20%.)

trans-[Au(R)Cl₂PPh₃]

A saturated solution of Cl_2 in CCl_4 (0.6 ml) was added to solid $[\text{Au}(\text{R})(\text{PPh}_3)]$ (81 mg; 0.14 mmol). After 15 min stirring 10 ml of diethyl ether was added. The yellow solid was filtered off and washed with diethyl ether then recrystallized from dichloromethane/diethyl ether (53% yield: m.p. 144; Λ_M 0. Analytical data: C, 44.18; H, 2.93; N, 2.13; Au, 30.57. $[\text{Au}(\text{R})\text{Cl}_2(\text{PPh}_3)]$ calcd.: C, 44.19; H, 2.94; N, 2.15; Au, 30.20%.)

From *cis*- $[\text{Au}(\text{R})\text{Cl}_2(\text{PPh}_3)]$. A saturated solution of Cl_2 in CCl_4 (0.5 ml) was added to a solid sample of the *cis* complex (37 mg). After 1 h stirring diethyl ether was added and the solid was filtered off and identified as the *trans*-isomer.

cis-[Au(R)Cl₂(PPh₃)]

A solution of PhICl_2 (13 mg; 0.05 mmol) in CCl_4 (10 ml) was added to a solid $[\text{Au}(\text{R})(\text{PPh}_3)]$ (29 mg; 0.05 mmol). After 45 min stirring diethyl ether was added, and the white solid formed filtered off washed with diethyl ether, and recrystallized from dichloromethane/diethyl ether (79% yield; m.p. 218; Λ_M 0. Analytical data: C, 43.38; H, 2.81; N, 2.06; Au, 30.87%.)

From *trans*- $[\text{Au}(\text{R})\text{Cl}_2(\text{PPh}_3)]$. A solution of this complex in acetonitrile was refluxed until a colourless solution was obtained. Concentration of this solution and addition of diethyl ether gave the *cis*-isomer.

Crystal data for [Au(R)(AsPh₃)]. $\text{C}_{24}\text{H}_{19}\text{NO}_2\text{AsAu}$, F_w 625.3, monoclinic, a 19.336(3), b 14.736(3), c 15.754(3) Å; β 105.09(2)°, V 4334(2) Å³, $P2_1/n$, D_x 1.91 g cm⁻³, $Z = 8$, $F(000) = 2384$, $\mu(\text{Mo-K}\alpha)$ 45.0 cm⁻¹; transmission factor 0.97. Yellow crystals were obtained by cooling (-4°C) of a diethyl ether/*n*-pentane solution.

Data collection, structure solution and refinement

A crystal was mounted on a Philips PW-1100 four-circle diffractometer. The unit-cell was determined from 25 reflections ($4 < \theta < 12^\circ$). Intensities were collected with monochromatized Mo- K_α radiation using the ω -scan technique, scan width 1°,

scan speed $0.03^\circ \text{ s}^{-1}$. 5017 reflections were collected in the range $2 \leq \theta \leq 25^\circ$, 4641 of which, those with $I \geq 2.5\sigma(I)$ were taken as "observed".

The Au and As atoms were located by direct methods using MULTAN system of computer programs [15]. The remaining non-hydrogen atoms were located with the DIRDIF system [16]. Full-matrix least-squares refinement were carried out using the SHELX 76 program [17]. The final R was 0.036 ($R_w = 0.039$) for all observed reflections. The function minimized was $W\{|F_o| - |F_c|\}^2$, where $W^{-1} = \sigma^2|F_o| + 0.00089|F_o|^2$, f , f' and f'' were from International Tables of X-Ray Crystallography [18]. Table 1 gives the main bond distances and angles and Table 2 the atomic coordinates for non-hydrogen atoms. Lists of anisotropic thermal parameters and structure factors are available from the authors (X.S.).

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