

Binuclear Ten-Membered Ring Cyclometallated Complexes of Digold(I) and their Reactions with Iodine and Bromine

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Z. Naturforsch. **59b**, 1563 – 1569 (2004); received September 7, 2004

Unserem Freund und Kollegen Herrn Professor Dr. Hubert Schmidbaur in Anerkennung seiner schönen Arbeiten auf dem Gebiet der Goldchemie zum 70. Geburtstag gewidmet

The cyclometallated digold(I) complexes [Au₂(μ-2-C₆H₄CH₂PPh₂)₂] (**10**) and [Au₂(μ-2-CH₂C₆H₄PPh₂)₂] (**11**) have been synthesized by the reaction of Li[2-C₆H₄CH₂PPh₂] and Li[2-CH₂C₆H₄PPh₂], respectively, with [AuBr(PEt₃)]. A single crystal X-ray structure analysis of **10** shows the linearly coordinated gold(I) atoms to be separated by 3.0035(9) Å in a puckered ten-membered ring. Both complexes add one mol equivalent of iodine to form initially gold(I)-gold(III) complexes [Au(μ-2-C₆H₄CH₂PPh₂)₂AuI₂] (**14a**) and [Au(μ-2-CH₂C₆H₄PPh₂)₂AuI₂] (**17**), which isomerize to the corresponding salts [Au(κ²-P,C-C₆H₄CH₂PPh₂)₂][AuI₂] (**13a**) and [Au(κ²-P,C-CH₂C₆H₄PPh₂)₂][AuI₂] (**16**). In **13a** the gold(III) cation is planar coordinated by a pair of chelate P-C donor ligands, the phosphorus and carbon atoms being, separately, mutually *cis*, as shown by X-ray structural analysis. From the reaction of **10** with 2 mol equivalents of bromine, the neutral chelate complex [AuBr₂(κ²-P,C-C₆H₄CH₂PPh₂)] (**15**) has been isolated and structurally characterized.

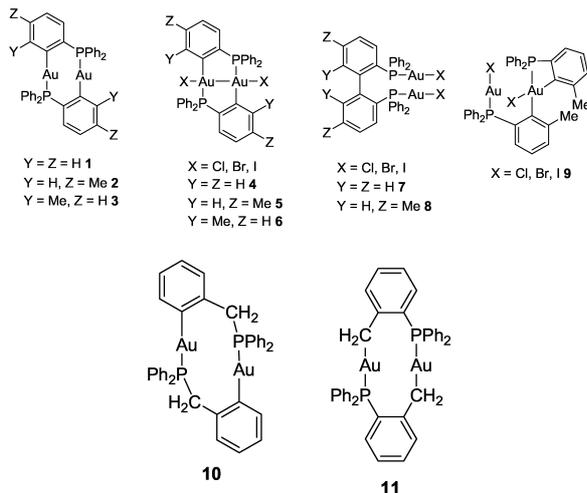
Key words: Gold(I), Cyclometallated Complexes, Phosphine Complexes

Introduction

We have shown that carbanions such as [2-C₆H₄PPh₂]⁻ and [2-C₆H₃-*n*-Me-PPh₂]⁻ (*n* = 5, 6) form dinuclear gold(I) complexes **1–3** in which the linearly coordinated metal atoms are separated by only *ca.* 2.86 Å, a distance that is comparable with the distance between the atoms in gold metal (2.88 Å) [1, 2]. Compounds **1–3** belong to an extensive family in whose members gold atoms are held in close contact by a pair of 1,3-bifunctional ligands, for example, 2-pyridyldimethylphosphine [3] and phosphorus bis(yliides) [R₂P(CH₂)₂] (R = Me, Et, Ph) [4] introduced by Schmidbaur and coworkers. The Au–Au separations are usually in the range of 2.80–3.10 Å suggestive of an attractive interaction (aurophilicity) between the 5d¹⁰ metal centres [5].

Complexes **1–3** undergo oxidative addition with halogens, even at –70 °C, to give initially the homovalent metal-metal bonded dihalodigold(II) com-

plexes [Au₂X₂(μ-2-C₆H₄PPh₂)₂] (X = Cl, Br, I; **4a–4c**) and [Au₂X₂(μ-2-C₆H₃-*n*-Me-PPh₂)₂] (X = Cl, Br, I, *n* = 5, **5a–5c**; *n* = 6, **6a–6c**), which, though isolable, are not thermodynamically stable [1b, 2, 6]. In the case of **4a–4c** and **5a–5c**, the rearrangement products are digold(I) complexes of the ditertiary phosphines 2,2'-Ph₂C₆H₄C₆H₄PPh₂ and 2,2'-Ph₂P(5,5'-Me₂C₆H₃C₆H₃)PPh₂, (**7a–7c**) and (**8a–8c**), respectively, derived from C-C coupling at the gold centres. In contrast, in the 6-methyl substituted series the products are the heterovalent gold(I)-gold(III) complexes **9a–9c** [2]. No C-C coupling is observed in the last case, presumably because of steric hindrance by the 6-methyl substituent, although in one instance in the 2-C₆H₄PPh₂ series (X = C₆F₅; Y = Z = H), a gold(I)-gold(III) species analogous to **9** has been detected as an intermediate in the C-C coupling process [7]. The observed behaviour has been rationalised on the basis of high-level *ab initio* calculations [8].



In the light of these results, it seemed worthwhile to examine the oxidative addition behaviour of digold(I) complexes analogous to **1–3** in which the metal atoms are held further apart by the interposition of a methylene group in the bridging carbanionic unit, *i.e.*, the complexes $[Au_2(\mu\text{-}2\text{-}C_6H_4CH_2PPh_2)_2]$ (**10**) or $[Au_2(\mu\text{-}2\text{-}CH_2C_6H_4PPh_2)_2]$ (**11**). We hoped to see whether digold(II) complexes analogous to **4–6** could be detected or isolated, and whether C–C coupling would occur. The results of this study are reported in this paper.

Results

As reported by Abicht and Issleib [9], the dinuclear complex **10** results in high yield as a colourless, microcrystalline solid from the reaction of (2-lithiobenzyl)diphenylphosphine, $Li[2\text{-}C_6H_4CH_2PPh_2]$, with $[AuX(PEt_3)]$ ($X = Cl, Br$). Complex **11** is obtained similarly from the reaction of $[AuBr(PEt_3)]$ with (2-diphenylphosphino) benzyl-lithium, $Li[2\text{-}CH_2C_6H_4PPh_2]$, which results from the lithiation of diphenyl(2-tolyl)phosphine [10]. Both complexes show parent ions in their EI mass spectra, singlet resonances at *ca.* $\delta = 36$ in their $^{31}P\{^1H\}$ NMR spectra and doublets due to the CH_2 groups in their 1H NMR spectra [$J = ca. 10$ Hz]. The structure of complex **10**, determined by single crystal X-ray analysis, is shown in Fig. 1; it contains two gold atoms bridged by a pair of $C_6H_4CH_2PPh_2$ ligands to give a puckered ten-membered ring similar to that found in $[Au_2(\mu\text{-}SCH_2CH_2PEt_2)_2]$ **12** [11].

The intramolecular $Au\cdots Au$ distance in **10**, 3.0035(9) Å, is significantly less than that in the ten-

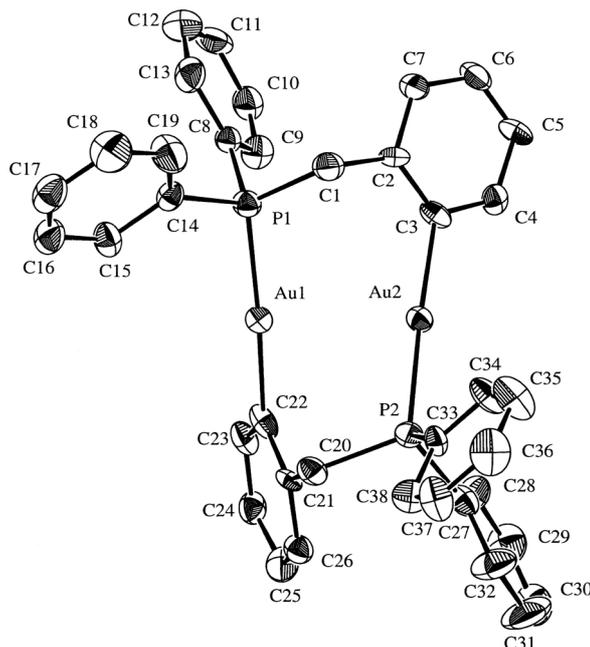
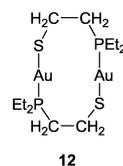
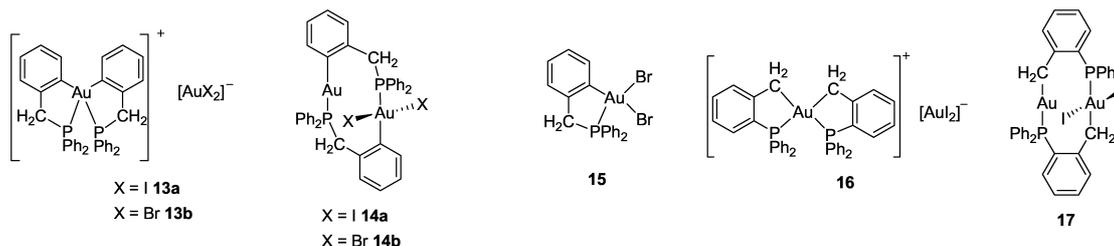


Fig. 1. Molecular structure of **10**. Displacement ellipsoids show 30% probability levels; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Au(1)–Au(2) 3.0035(9), Au(1)–P(1) 2.296(4), Au(2)–P(2) 2.297(4), Au(1)–C(22) 2.02(2), Au(2)–C(3) 2.07(2). Selected bond angles ($^\circ$) P(1)–Au(1)–C(22) 176.9(5), C(3)–Au(2)–P(2) 176.0(4), P(1)–C(1)–C(2) 113(1), P(2)–C(20)–C(21) 110(1).



membered ring complex $[Au_2(\mu\text{-}SCH_2CH_2PEt_2)_2]$ (**12**) (3.104 Å), but is *ca.* 0.14 Å greater than those in the eight-membered ring complexes **1** and **2** [1a, 2]. The Au–P and Au–C distances in **10** [2.296(4), 2.297(4) Å and 2.02(2), 2.07(4) Å, respectively] are similar to those in **1** and **2**. The coordination about each gold atom is close to linear and there are no unusual bond lengths or angles that would indicate strain. The P–Au–C units are not coplanar, the dihedral angle between the planes Au(1)–Au(2)–P(1)–C(22) and Au(1)–Au(2)–P(2)–C(3) being 40.7 $^\circ$.

Treatment of complex **10** with one mol equiv. of iodine in CH_2Cl_2 or toluene at -70 $^\circ C$ gives an orange solution whose $^{31}P\{^1H\}$ NMR spectrum contains a pair of doublets at $\delta = 42.5$ and 33.2 ($^2J_{PP} = 2.3$ Hz), the singlet due to **10** being absent. The species



responsible for this spectrum can be isolated as an orange-yellow solid in a fairly pure state, as judged by ^{31}P NMR spectroscopy, by evaporating the solution below 0°C , but it isomerizes above this temperature to a second species, which shows a ^{31}P NMR singlet at $\delta = 52.5$. The two species apparently co-exist in the almost colourless solution at room temperature, but only the second compound precipitates as a colourless solid, which has been shown by single-crystal X-ray analysis (Fig. 2) to be the gold(III)-gold(I) salt $[\text{Au}(\kappa^2\text{-}P, C\text{-}C_6H_4CH_2PPh_2)_2][\text{Au}_2]^-$ (**13a**). The gold(III) centre in the cation is planar coordinated by a pair of five-membered chelate $C_6H_4CH_2PPh_2$ groups, while the anion is the well-known, linear $[\text{Au}_2]^-$ species. The formulation has been confirmed by elemental analysis and by FAB mass spectrometry, which shows a parent ion peak at m/z 747.2 due to the cation in positive ion mode, and a parent ion peak at m/z 450.8 due to the anion in negative ion mode.

The reaction of complex **10** with 1 mol equiv. of bromine in CH_2Cl_2 appears to be very similar to that with iodine. At -70°C a pair of doublets appears in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at $\delta = 43.7$ and 30.2 ($^2J_{\text{PP}} = 2.3$ Hz). On warming to room temperature, the solution turns almost colourless and the main species present shows a singlet ^{31}P resonance at $\delta = 51.4$ assignable to $[\text{Au}(\kappa^2\text{-}P, C\text{-}C_6H_4CH_2PPh_2)_2][\text{AuBr}_2]$ (**13b**). The initial products in both halogenation reactions are clearly not digold(II) complexes analogous to **4–6**, but are most reasonably formulated on the basis of their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra as gold(I)-gold(III) complexes $[\text{Au}(\mu\text{-}C_6H_4CH_2PPh_2)_2\text{AuX}_2]$ [$X = \text{I}$ (**14a**), Br (**14b**)].

The reaction of 2 mol equiv. of bromine with a solution of **10** in CH_2Cl_2 has also been investigated briefly on an NMR scale. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the solution is complex, containing a singlet at $\delta = 59.7$ together with resonances in the region of $\delta = 33–37$, one or more of which could correspond to the orange complex $[\text{Au}_2\text{Br}_4(\mu\text{-}C_6H_4CH_2PPh_2)_2]$ isolated by Abicht and Issleib [9]. The yellow, crystalline solid that deposited from the solution was shown by X-ray

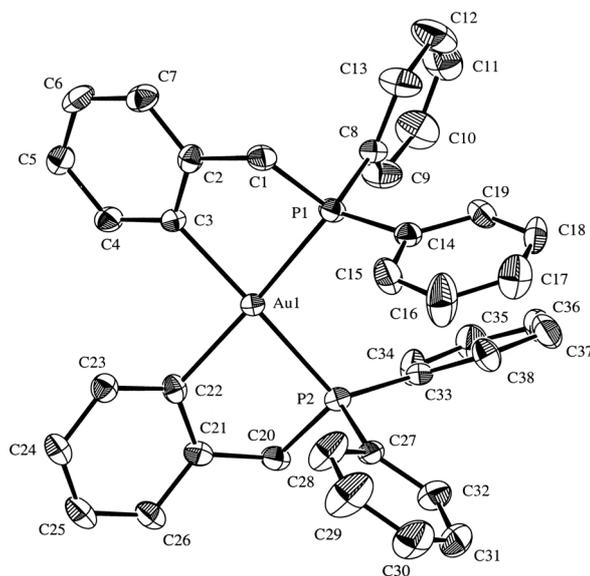


Fig. 2. Molecular structure of the cation of **13a**. Displacement ellipsoids show 30% probability levels; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Au(1)-P(1) 2.350(2), Au(1)-P(2) 2.347(2), Au(1)-C(3) 2.089(9), Au(1)-C(22) 2.076(9). Selected bond angles ($^\circ$): P(1)-Au(1)-P(2) 103.46(9), C(3)-Au(1)-C(22) 96.6(4), P(2)-Au(1)-C(3) 170.2(3), P(1)-Au(1)-C(22) 167.3(3), P(2)-Au(1)-C(22) 81.4(3), P(1)-Au(1)-C(3) 80.5(3).

analysis (Fig. 3) to be the monomeric, planar gold(III) complex $[\text{AuBr}_2(\kappa^2\text{-}P, C\text{-}C_6H_4CH_2PPh_2)]$ (**15**), which contains the same five-membered chelate ring system as **13a**. It is noteworthy that the ^{31}P chemical shifts of **14a** and **15** are *ca.* 20 ppm deshielded relative to those of **10**, **13a** and **13b** containing $\mu\text{-}C_6H_4CH_2PPh_2$, as expected for five-membered ring chelate complexes [12].

The reaction of complex **11** with 1 mol equiv. of iodine in CH_2Cl_2 resembles that of **10**. The brown solid isolated after reaction at -70°C shows in its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum a pair of equally intense singlets at $\delta = 31.7$ and 48.1 , together with a singlet at $\delta = 52.3$, the latter increasing at the expense of the first two over time. The elemental analysis of the pale yellow solid that was obtained by crystallisation at room temperature corresponded to the

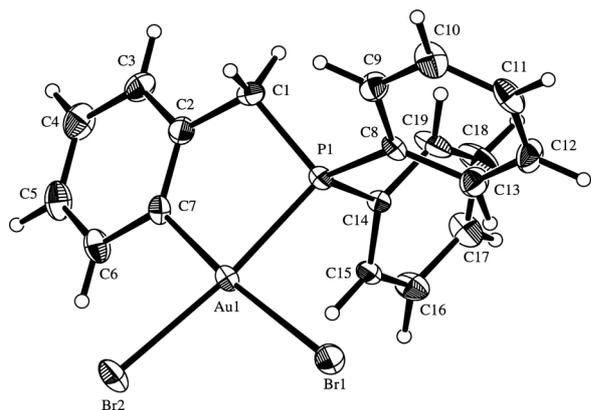


Fig. 3. Molecular structure of **15**. Displacement ellipsoids show 30% probability levels; hydrogen atoms are shown as spheres of arbitrary radius. Selected bond distances (Å): Au(1)-P(1) 2.273(2), Au(1)-Br(1) 2.491(1), Au(1)-Br(2) 2.4670(9), Au(1)-C(7) 2.072(8). Selected bond angles (°) Br(1)-Au(1)-Br(2) 92.55(3), Br(1)-Au(1)-P(1) 92.66(6), Br(1)-Au(1)-C(7) 169.2(2), P(1)-Au(1)-C(7) 80.3(2).

empirical formula $\text{AuI}(\text{CH}_2\text{C}_6\text{H}_4\text{PPh}_2)$ and the FAB-MS spectrum showed parent ion peaks due to the cation $[\text{Au}(\text{CH}_2\text{C}_6\text{H}_4\text{PPh}_2)_2]^+$ and the anion $[\text{AuI}_2]^-$. An X-ray structural analysis to be reported elsewhere has confirmed the formulation $[\text{Au}(\kappa^2\text{-P,C-CH}_2\text{C}_6\text{H}_4\text{PPh}_2)_2][\text{AuI}_2]$ (**16**) analogous to **13a**. The species responsible for the pair of singlets is presumably $[\text{Au}(\mu\text{-2-CH}_2\text{C}_6\text{H}_4\text{PPh}_2)_2\text{AuI}_2]$ (**17**), analogous to **14a**.

The molecular structures of **13a** (cation only) and **15** are shown in Figs 2 and 3, together with atom labelling.

In the cation of **13a**, the phosphorus and carbon atoms of the *P,C*-chelate groups are, separately, mutually *cis*. The envelope-shaped five-membered rings in **13a** and **15** subtend angles of 80–85° at the gold atoms, causing the P-Au-P angles in **13a** to open out to *ca.* 105°. The Au-C distances fall in the range 2.07–2.12 Å, similar to the Au-C bond length of 2.10(4) Å in $[\text{AuBr}_2\{\kappa\text{-P,C-CH}(\text{CH}_2\text{Br})\text{C}_6\text{H}_4\text{PPh}_2\}]$ [13], and significantly greater than those in *C,N*-cycloaurated complexes containing 2- $\text{C}_6\text{H}_4\text{N}=\text{N}$ or 2- $\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2$, which are in the range of 1.99–2.03 Å [14, 15]. This may be a consequence of the larger size of phosphorus relative to nitrogen. The Au-P distances in **13** and **15**, and the Au-Br distances in the latter, are also close to the corresponding distances in $[\text{AuBr}_2\{\kappa\text{-P,C-CH}(\text{CH}_2\text{Br})\text{C}_6\text{H}_4\text{PPh}_2\}]$ [13]. The Au-I distance in the $[\text{AuI}_2]^-$ ion of **13a** [2.5276(9) Å] is almost identical to that reported for $[n\text{-Bu}_4\text{N}][\text{AuI}_2]$ [2.529(1) Å] [16].

Discussion

The main effect of the increased separation of the gold atoms in the ten-membered ring complexes **10** and **11** (*ca.* 3.0 Å) relative to that in their eight-membered ring analogues **1–3** (*ca.* 2.9 Å) is that the first detectable product of reaction of iodine or bromine arises from oxidative addition at only one of the metal centres, leading to the gold(I)-gold(III) complexes **14** and **17**, respectively. In contrast, in the eight-membered ring series a halogen adds initially to each gold atom, giving metal-metal bonded digold(II) complexes which, as summarised in the Introduction, then undergo further change *via* gold(I)-gold(III) complexes such as **9**. In the latter, only one of the two *P-C* groups acts as a bidentate chelate to the gold(III) atom, whereas in **13** and **16** both *P-C* ligands chelate to the gold(III) atom, leading to the salts $[\text{Au}(\text{P-C})_2][\text{AuX}_2]$. This difference in behaviour probably stems from the greater flexibility imparted to the system by the additional methylene groups and the greater stability of the five-membered chelate rings relative to their four-membered counterpart. In further contrast to the eight-membered ring series, we have found no evidence for C-C coupling in the ten-membered systems, which may also reflect the reduced strain in the five-membered rings in **13** and **16**.

Despite these differences, the chemistry reported here shows similarities to systems that are based on digold(I) complexes containing eight membered rings. Thus, treatment of dialkyldithiocarbamato digold(I), $[\text{Au}_2(\mu\text{-S}_2\text{CNR}_2)_2]$ ($\text{R} = n\text{-Bu}$), with halogens at room temperature gives the salts $[\text{Au}(\kappa^2\text{-S}_2\text{CNR}_2)_2][\text{AuX}_2]$ [17], analogous to **13a** and **16**, and, in the case of $\text{R} = \text{Et}$, intermediate digold(II) complexes $[\text{Au}_2\text{X}_2(\mu\text{-S}_2\text{CNEt}_2)_2]$ have been isolated [18]. In this series, the formation of dibromogold(III) complexes $[\text{AuBr}_2(\kappa^2\text{-S}_2\text{CNEt}_2)]$ by the addition of bromine (2 mol. equiv.) on the digold(I) precursors has also been reported [19], which parallels the formation of the chelate complex **15** in our system. Depending on the solvent, the action of iodine on the digold(I) methylenethiophosphinate complex $[\text{Au}_2\{\mu\text{-Ph}_2\text{P}(\text{S})\text{CH}_2\}_2]$ can give either a homonuclear digold(II) complex $[\text{Au}_2\text{I}_2\{\mu\text{-Ph}_2\text{P}(\text{S})\text{CH}_2\}_2]$ or a heterodinuclear gold(I)-gold(III) complex $[\text{Au}\{\mu\text{-Ph}_2\text{P}(\text{S})\text{CH}_2\}_2\text{AuI}_2]$ [20], the latter being analogous to complexes **14a** and **17** in our systems.

Experimental Section

All manipulations were performed in an atmosphere of dry nitrogen using standard Schlenk techniques, although the solid gold complexes, once isolated, were air-stable. Solvents were dried by standard methods, distilled and stored under nitrogen. The following instruments were used for spectroscopic measurements: Varian XL-200E (^1H at 200 MHz, ^{31}P at 80.96 MHz), Varian Gemini (^1H at 300 MHz), Bruker Aspect 2000 (^{31}P at 80.96 MHz) and VG ZAB-2SEQ (high resolution EI and FAB mass spectra). The NMR chemical shifts (δ) are given in ppm relative to TMS (^1H) and 85% H_3PO_4 (^{31}P), referenced either to residual solvent signals (^1H) or externally (^{31}P). Coupling constants are given in Hz. Elemental analyses were carried out by staff of the Microanalytical Laboratory of the Australian National University. The compounds (2-tolyl)diphenylphosphine [21], (2-bromobenzyl)diphenylphosphine [22] and $[\text{AuBr}(\text{PEt}_3)]$ [23] were prepared as described in the literature.

Bis(2-diphenylphosphinomethyl)phenyldigold(I) (**10**): To a solution of (2-bromobenzyl)diphenylphosphine (1.0 g, 2.8 mmol) in ether (15 ml) was added dropwise a 1.4 M solution of *n*-butyllithium in hexane (2.0 ml, 2.8 mmol) and the mixture was stirred for 2 h at room temperature. The red supernatant was removed by cannulation from the precipitated colourless solid and the latter was washed with hexane (3×5 ml). The solid was suspended in ether and the slurry was added by cannula to a stirred solution of $[\text{AuBr}(\text{PEt}_3)]$ (0.99 g, 2.5 mmol) in ether (15 ml), the temperature being maintained below -65 °C. The mixture was stirred at low temperature for 2 h, then at room temperature for 1.5 h, the flask being shielded from light. After removal of the solvent by cannulation, the solid was washed with methanol (10 ml), ether (3×15 ml) and hexane (3×15 ml) and dried *in vacuo*. For final purification the solid was dissolved in CH_2Cl_2 (*ca.* 50 ml) and the solution was filtered through Celite. Evaporation *in vacuo* gave **10** (0.82 g, 69%) as a colourless solid. M.p. 210 °C. – MS (EI, 70 eV): *m/z* 944 [M^+] – ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.7–7.8 (m, 8H), 7.4–7.6 (m, 14H), 7.0 (t, 2H), 6.7 (t, 2H), 6.6 (d, 2H) (PPh_2 , C_6H_4), 4.0 (d, J = 11 Hz, 4H, CH_2) – $^{31}\text{P}\{^1\text{H}\}$ NMR (80.96 MHz, CD_2Cl_2): δ = 37.0 – $\text{C}_{38}\text{H}_{32}\text{Au}_2\text{P}_2$ (944.5): calcd. C 48.3, H 3.4, P 6.6; found C 48.4, H 3.5, P 6.3. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a dichloromethane solution of **10**.

Bis(2-diphenylphosphinobenzyl)digold(I) (**11**): To a stirred solution of *n*-butyllithium (1.85 ml, 2.96 mmol) in hexane (30 ml) containing TMEDA (0.45 ml) was added slowly at room temperature a solution of diphenyl(2-tolyl)phosphine (0.80 g, 2.88 mmol). The mixture was stirred for 2 h and the bright yellow, crystalline solid was separated by filtration and dried *in vacuo*. It was then suspended in hexane (*ca.* 25 ml) and added slowly to a

stirred suspension of $[\text{AuBr}(\text{PEt}_3)]$ (1.0 g, 2.6 mmol) in ether (30 ml) at -70 °C. The mixture was stirred overnight. Solvents were removed by cannulation and the residue was stirred with methanol (10 ml) for 15 min and filtered. The resulting colourless, crystalline solid was washed with ether and hexane. For final purification the solid was dissolved in CH_2Cl_2 (*ca.* 400 ml) and the solution was filtered through Celite. Evaporation *in vacuo* gave **11** (0.85 g, 72%) as a colourless solid. M.p. 230 °C. – MS (EI, 70 eV): *m/z* 944 [M^+] – ^1H NMR (300 MHz, CDCl_3): δ = 7.3–7.6 (m, 24H), 6.7 (t, 2H), 6.5 (t, 2H), (PPh_2 , C_6H_4), 2.6 (d, J = 10 Hz, 4H, CH_2) – $^{31}\text{P}\{^1\text{H}\}$ NMR (80.96 MHz, CDCl_3): δ = 36.2 – $\text{C}_{38}\text{H}_{32}\text{Au}_2\text{P}_2 \cdot \text{CH}_2\text{Cl}_2$ (1029.5): calcd. C 45.5, H 3.3, P 6.0, Cl 6.9; found C 46.0, H 3.3, P 5.9, Cl 6.6.

Bis{bis(2-diphenylphosphinomethyl)phenyl}gold(III) diiodoaurate(I) (**13a**) and *bis{bis(2-diphenylphosphinobenzyl)gold(III) diiodoaurate(I)}* (**16**): A suspension of **10** or **11** (50 mg, 0.053 mmol) in toluene or dichloromethane (*ca.* 10 ml) was cooled to -70 °C and treated with a slight molar excess of iodine in the same solvent. The solution was stirred for 30 min at low temperature, then allowed to come to room temperature and stirred for a further 30 min. The solution had changed colour from brown to yellow and some precipitate had formed. The solution was concentrated *in vacuo* and the solid was filtered off, washed with toluene, and air-dried. Yields were *ca.* 50%. Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into dichloromethane solutions. ^{31}P NMR data are reported in the text. **13a**: MS (FAB, NBA matrix, positive ion mode): 747.2 [cation M^+] – MS (FAB, NBA matrix, negative ion mode): 450.8 [anion M^-] – $\text{C}_{38}\text{H}_{32}\text{Au}_2\text{I}_2\text{P}_2$ (1198.4): calcd. C 38.1, H 2.7, P 5.2; found C 38.1, H 3.0, P 5.4. – **16**: MS (FAB, NBA matrix, positive ion mode): 747.2 [cation M^+] – MS (FAB, NBA matrix, negative ion mode): 450.8 [anion M^-] – $\text{C}_{38}\text{H}_{32}\text{Au}_2\text{I}_2\text{P}_2$ (1198.4): calcd. C 38.1, H 2.7, I 21.2; found C 38.2, H 2.5, I 21.2.

Dibromo{(2-diphenylphosphinomethyl)phenyl}gold(III) (**15**): A solution of **10** (*ca.* 10 mg) in CD_2Cl_2 (*ca.* 0.5 ml) in an NMR tube was cooled in dry ice/acetone and treated with 2 mol equiv. of bromine. The mixture was then allowed to warm slowly to room temperature. Above -20 °C the main feature of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was a singlet at δ = 59.4 due to **15**. The solution was evaporated to dryness *in vacuo*, the residue was dissolved in toluene, and the solution was layered with hexane. On standing at room temperature, a pale yellow, crystalline solid deposited that was identified as a 1:1 toluene solvate of **15** by single-crystal X-ray structural analysis.

X-Ray crystallography: The crystal and refinement data for compounds **10**, **13a** and **15** are summarised in Table 1. All three structures were solved by direct methods (SIR 92) [24]. Hydrogen atoms were included at geometrically determined

Compound	10	13a	15
Formula	C ₃₈ H ₃₂ Au ₂ P ₂	C ₃₈ H ₃₂ Au ₂ I ₂ P ₂	C ₁₉ H ₁₆ AuBr ₂ P·C ₇ H ₈
<i>M_r</i> [g/mol]	944.55	1198.36	724.22
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>a</i> (# 14)	<i>P</i> 1̄ (# 2)	<i>C</i> 2/ <i>c</i> (# 15)
<i>a</i> [Å]	18.922(3)	10.204(3)	31.738(5)
<i>b</i> [Å]	10.163(5)	11.548(2)	9.568(3)
<i>c</i> [Å]	19.786(3)	18.056(2)	18.450(4)
α [°]	90	107.22	90
β [°]	113.19(1)	94.35	118.31(1)
γ [°]	90	11.29(2)	90
<i>V</i> [Å ³]	3498(2)	1853.2(8)	4933(2)
<i>Z</i>	4	2	8
Crystal habit	colourless needle	colourless plate	pale yellow block
Crystal size [mm ³]	0.30 × 0.12 × 0.03	0.32 × 0.13 × 0.07	0.40 × 0.20 × 0.20
<i>D</i> _{calcd.} [g/cm ³]	1.794	2.147	1.950
θ Range [°]	4.35 to 60.07	2.02 to 27.55	2.02 to 27.55
Diffractometer	Rigaku AFC6R	Rigaku AFC6S	Rigaku AFC6S
μ [mm ⁻¹]	16.32 (Cu-Kα)	9.642 (Mo-Kα)	9.31 (Mo-Kα)
λ [Å]	1.5418	0.7107	0.7107
Temperature [K]	293	296	293
Absorption correction	analytical	analytical	empirical
<i>T</i> _{max} / <i>T</i> _{min}	0.692 / 0.190	0.538 / 0.278	1.00 / 0.67
Measured reffs	4857 [<i>I</i> > 2σ(<i>I</i>)]	8539 [<i>I</i> > 3σ(<i>I</i>)]	6037 [<i>I</i> > 3σ(<i>I</i>)]
Independent reffs	2918	5096	3234
<i>R</i> _{int}	0.073	0.0212	0.020
<i>F</i> (000)	1792	1108	2752
Parameters	379	401	271
<i>S</i>	1.537	1.249	1.56
<i>R</i> ₁	0.0485	0.0353	0.035
<i>wR</i> ₂	0.0572	0.0362	0.038
Δρ _{max} /Δρ _{min} [eÅ ⁻³]	1.30 / -2.08	1.45 / -0.92	1.19 / -0.82

Table 1. Crystallographic details for complexes **10**, **13a**, and **15**.

positions, which were periodically recalculated but not refined. Analytical absorption corrections [25] were applied for complexes **10** and **13a**. All calculations were performed using the teXsan crystallographic software package [26]. The crystal of **15** contained a disordered toluene molecule having two possible orientations. The atom sites corresponding to the two images of the molecule were refined, with individual isotropic displacement parameters and appropriate restraints, employing the CRYSTALS program [27].

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Cen-

tre, deposition codes CCDC 250220 (**15**), 250221 (**10**) and 250222 (**13a**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgement

We wish to thank Mr. Michael Migliorisi (RMIT University) for experimental assistance and FM is grateful to the Australian Government for the award of an Australian Post-graduate Scholarship.

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