

Asymmetric monocationic and dicationic gold(II) complexes: X-ray structure of $[\text{MePh}_2\text{PAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuOH}_2](\text{ClO}_4)_2 \cdot 2\text{CH}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$

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Abstract

The reaction of $[(\text{tht})\text{Au}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{Au}(\text{tht})](\text{ClO}_4)_2$ (tht = tetrahydrothiophene) with $[\text{Ag}(\text{OCIO}_3)\text{PR}_3]$ ($\text{PR}_3 = \text{PPh}_3$, PPh_2Me or $\text{P}(4\text{-MeOC}_6\text{H}_4)_3$) gives $[\text{R}_3\text{PAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{Au}(\text{tht})](\text{ClO}_4)_2$. Displacement of weakly coordinated ligands gives new dicationic $[\text{R}_3\text{PAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuL}](\text{ClO}_4)_2$ ($\text{L} = \text{py}$, AsPh_3 , PPh_2Me or OH_2) or monocationic complexes $[\text{R}_3\text{PAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuX}](\text{ClO}_4)$ ($\text{X} = \text{Cl}$, $\text{S}_2\text{CN}(\text{CH}_2\text{Ph})_2$ or OCIO_3). The structure of $[\text{MePh}_2\text{PAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{Au}(\text{OH}_2)](\text{ClO}_4)$ was confirmed by single-crystal X-ray diffraction analysis. The ^{197}Au Mössbauer spectra of $[\text{Ph}_3\text{PAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{Au}(\text{tht})](\text{ClO}_4)_2$ is reported and compared with other symmetric or asymmetric dinuclear gold(II) complexes.

Key words: Gold; X-ray structure; Mössbauer; Dinuclear; Ylide

1. Introduction

Most reported binuclear gold(II) complexes containing the bis(ylide) $[(\text{CH}_2)_2\text{PPh}_2]^-$ are neutral compounds of the type $[\text{XAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuX}]$ ($\text{X} =$ anionic ligand) [1–7], and only few examples of monocationic or dicationic complexes are known, e.g. $[\text{XAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuL}]^+$ ($\text{X} = \text{Br}$, I or C_6F_5 ; $\text{L} = \text{CH}_2\text{-PR}_3$, py , tht (tht = tetrahydrothiophene) or PR_3) [8,9], $[\text{LAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuL}]^{2+}$ ($\text{L} = \text{py}$, tht , PR_3 , AsPh_3 or SbPh_3) [10].

Here we describe the preparation of asymmetric cationic complexes $[\text{R}_3\text{PAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuL}]^{2+}$ ($\text{L} = \text{tht}$, OH_2 , py or PR_3) or $[\text{R}_3\text{PAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuX}]^+$ ($\text{X} = \text{Cl}$, $\text{S}_2\text{CN}(\text{CH}_2\text{Ph})_2$ or OCIO_3) by reaction of $[\text{LAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuL}]^{2+}$ ($\text{L} = \text{PPh}_3$ or tht) with mononuclear gold(I) or silver(I) complexes or with neutral or anionic ligands. The ^{197}Au Mössbauer spectra of some of these confirm the presence of two gold atoms with different chemical environments. The structure of $[\text{MePh}_2\text{PAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{Au}(\text{OH}_2)](\text{ClO}_4)_2$ has been established by single-crystal X-ray analysis. To the best of our knowledge, the only aqua complex of gold previously described is $[\text{AuMe}_2(\text{CF}_3\text{SO}_3)(\text{OH}_2)]$ [11].

$[\text{LAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuL}]^{2+}$ ($\text{L} = \text{PPh}_3$ or tht) with mononuclear gold(I) or silver(I) complexes or with neutral or anionic ligands. The ^{197}Au Mössbauer spectra of some of these confirm the presence of two gold atoms with different chemical environments. The structure of $[\text{MePh}_2\text{PAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{Au}(\text{OH}_2)](\text{ClO}_4)_2$ has been established by single-crystal X-ray analysis. To the best of our knowledge, the only aqua complex of gold previously described is $[\text{AuMe}_2(\text{CF}_3\text{SO}_3)(\text{OH}_2)]$ [11].

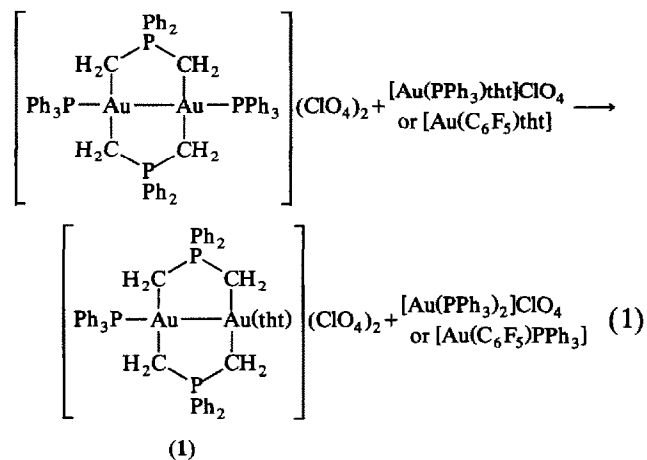
2. Results and discussion

The reaction of $[\text{Ag}(\text{OCIO}_3)\text{PR}_3]$ ($\text{PR}_3 = \text{PPh}_3$, PPh_2Me or $\text{P}(4\text{-MeOC}_6\text{H}_4)_3$) with $[(\text{tht})\text{Au}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{Au}(\text{tht})](\text{ClO}_4)_2$ in dichloromethane (1:1 molar

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ratio) leads to ligand exchange and precipitation of $[\text{Ag}(\text{OCIO}_3)(\text{tht})]$ and the asymmetric cationic complexes 1–3 can be isolated from the resulting solutions (see Scheme 1).

Complex 1 is also obtained from $[\text{Ph}_3\text{PAu}(\text{CH}_2\text{-PPh}_2\text{CH}_2)_2\text{AuPPh}_3](\text{ClO}_4)_2$ by reaction with $[\text{Au}(\text{PPh}_3)(\text{tht})]\text{ClO}_4$ or $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$, according to



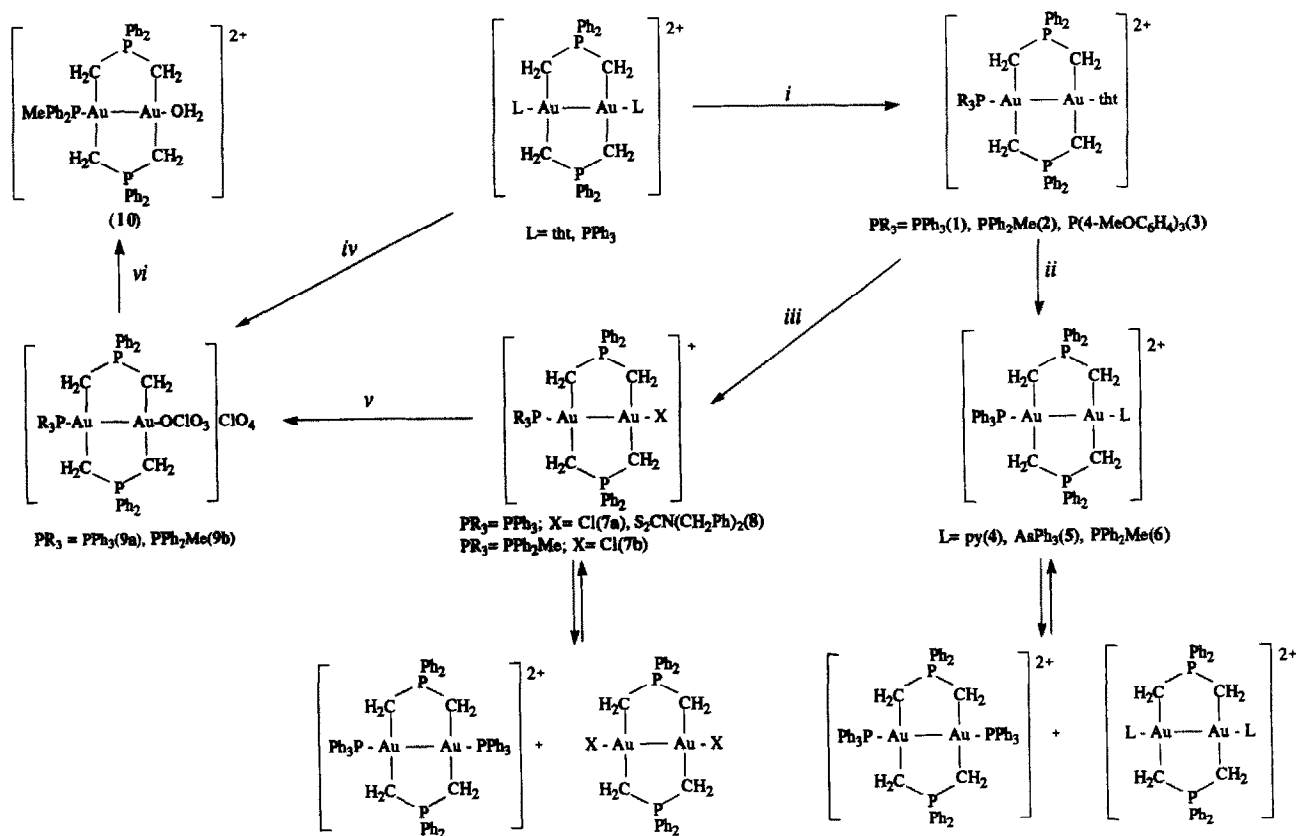
The isolation of 1 when mixed with $[\text{Au}(\text{C}_6\text{F}_5)(\text{PPh}_3)]$ is facile because the dinuclear complex is sparingly soluble in diethyl ether, but the solubilities in organic

solvents of 1 and $[\text{Au}(\text{PPh}_3)_2]\text{ClO}_4$ are similar and a mixture of both compounds is obtained.

Complexes 1–3 are air- and moisture-stable yellow solids. In acetone solutions they behave as 1:2 electrolytes (molar conductivity, about $190 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$). The IR spectra show bands at 1100 (s, br) and 620 (m) cm^{-1} which are characteristic of the ClO_4^- anion [12]. The $\nu(\text{Au}-\text{C}_{\text{ylide}})$ [13,14] appears at about 565 cm^{-1} .

The ylidic protons appear as an apparent doublet (CH_2 cis to tht) or as an apparent triplet (CH_2 cis to PR_3) (Table 1). Other resonances at $\delta = 3.3$ (m) and 2.02 (m) (1), 3.16 (m) and 1.94 (m) (2) and 3.23 (m) and 1.98 (m) (3) ppm are assigned to the tetrahydrothiophene ligand and at $\delta = 2.32$ (d, $J(\text{PH}) = 13.5 \text{ Hz}$) (2) and 3.86 (s) (3) ppm, to the methyl group of the phosphines. The ^{31}P $\{^1\text{H}\}$ NMR spectra of the ylidic phosphorus always appears as a doublet because of coupling to the phosphorus of the phosphine, which appears as a triplet (see Table 1).

The tht ligand in 1 is very weakly coordinated and can therefore be readily displaced by a variety of neutral or anionic ligands. Complex 1 reacts with ligands L to give another series of dicationic derivatives $[\text{Ph}_3\text{PAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuL}](\text{ClO}_4)_2$ ($\text{L} = \text{py}$ (4),



Scheme 1. (i) ($\text{L} = \text{tht}$) $[\text{Ag}(\text{OCIO}_3)\text{PR}_3]$, $-\text{Ag}(\text{OCIO}_3)\text{tht}$; (ii) L , $-\text{tht}$; (iii) MX , $-(\text{tht} + \text{MClO}_4)$; (iv) ($\text{L} = \text{PPh}_3$) $[\text{Au}(\text{OCIO}_3)\text{PPh}_3]$, $-\text{Au}(\text{PPh}_3)_2\text{ClO}_4$; (v) ($\text{X} = \text{Cl}$) $\text{AgClO}_4 - \text{AgCl}$ (vi) OH_2 .

TABLE 1. NMR data

Compound	³¹ P{ ¹ H} NMR ^a		¹ H NMR ^b δ (CH ₂) ^d (ppm)
	δ (PPh ₂) (ppm)	δ (PR ₃) (ppm)	
1 [Ph ₃ PAu(CH ₂ PPh ₂ CH ₂) ₂ Au(tht)(ClO ₄) ₂	43.6 (d)	18.3 (t, ³ J(P-P) _{cis} 16.2 Hz)	1.84 ("d", N = 12.1 Hz), 1.57 (dd, N = 10.8, 8.4 Hz)
2 [Ph ₂ MePAu(CH ₂ PPh ₂ CH ₂) ₂ Au(tht)(ClO ₄) ₂	42.9 (d)	9.6 (t, ³ J(P-P) _{cis} 16.4 Hz)	1.78 ("d", N = 12.0 Hz); 1.55 ("t", N = 9.0 Hz)
3 [(4-MeOC ₆ H ₄) ₃ PAu(CH ₂ PPh ₂ CH ₂) ₂ Au(tht)(ClO ₄) ₂	43.0 (d)	16.8 (t, ³ J(P-P) _{cis} 14.1 Hz)	1.80 ("d", N = 12.0 Hz); 1.59 ("t", N = 10.3 Hz)
9a [Ph ₃ PAu(CH ₂ PPh ₂ CH ₂) ₂ AuOCIO ₃ ClO ₄	36.4 (s) ^c	13.1 (s) ^c	2.01 ("d", N = 11.4 Hz); 1.37 ("dd", N = 10.1, 6.3 Hz)
9b [Ph ₂ MePAu(CH ₂ PPh ₂ CH ₂) ₂ AuOCIO ₃ ClO ₄	34.9 (s) ^c	6.8 (s) ^c	1.83 ("d", N = 12.1 Hz); 1.34 (m)
10 [Ph ₂ MePAu(CH ₂ PPh ₂ CH ₂) ₂ AuOH ₂ (ClO ₄) ₂	34.6 (s) ^c	7.0 (s) ^c	

^a Recorded in CDCl₃ at 200 MHz referenced to external H₃PO₄. ^b Referred to internal tetramethylsilane. ^c Recorded in CD₂Cl₂. ^d N is the splitting between two consecutive lines.

AsPh₃ (**5**) or PPh₂Me (**6**) or with salts MX to give monocationic derivatives [Ph₃PAu(CH₂PPh₂CH₂)₂AuX](ClO₄) (X = Cl (**7a**) or S₂CN(CH₂Ph)₂ (**8**)) (see Scheme 1). In solution, the asymmetric complexes **4–8** are in equilibria with the corresponding symmetric derivatives (Scheme 1) and it is not possible to isolate them.

Similar equilibria are observed when an equimolar mixture of [Ph₃PAu(CH₂PPh₂CH₂)₂AuPPh₃](ClO₄)₂ and [MePh₂PAu(CH₂PPh₂CH₂)₂AuPPh₂Me](ClO₄)₂ or [Ph₃PAu(CH₂PPh₂CH₂)₂AuPPh₃](ClO₄)₂ and [ClAu(CH₂PPh₂CH₂)₂AuCl] in CDCl₃ are stirred at room temperature.

Consistent with these equilibria the ³¹P {¹H} NMR spectra show the resonances corresponding to the previously described symmetric derivatives [10] and the complexes **4–8**, which are in estimated proportions of 45% (**4**), 56% (**5**), 62% (**6**), 19% (**7**) or 36% (**8**).

The signals due to the asymmetric derivatives are a doublet for the ylidic phosphorus ($\delta = 42.6$ (**4**), 47.7 (**5**), 40.6 (**7a**) and 43.3 (**8**) ppm) and a triplet for PPh₃ ($\delta = 7.1$ ($J(\text{PP}) = 14.4$ Hz) (**4**), 26.4 ($J(\text{PP}) = 25.9$ Hz) (**5**), 15.0 ($J(\text{PP}) = 21.1$ Hz) (**7a**) and 17.3 ($J(\text{PP}) = 33.0$ Hz) (**8**) ppm). The ³J(P–P_{ylide}) values involving the ylide phosphorus are in the same range as those previously reported: about 17 Hz for [Au{C(SiMe₃)₂PMe₃}PMe₃]-Cl and related complexes [15,16] and 8.2–13 Hz for [Au₂(CH₂PR₂CH₂)(Ph₂PCHPPh₂)] (R = Me, Et or ^tBu) [17].

The spectrum of **6** shows an ABX₂ system, with $\delta\text{A}(\text{PPh}_3) = 28.6$ ppm, $\delta\text{B}(\text{PPh}_2\text{Me}) = 18.0$ ppm and $\delta\text{X}(\text{PPh}_2) = 47.1$ ppm; ³J(AX) = 35.0 Hz, ³J(BX) = 33.8 Hz and $J(\text{AB})$ [³J(P–Au–Au–P)] = 517.5 Hz. The value of the latter coupling constant is extremely high for two phosphine ligands across a gold–gold bond. This indicates that the gold–gold bond provides good electronic interaction between the two phosphine ligands presumably via the 6s orbitals of the two gold atoms. Such an interaction may also account for the variation in ³J(P–P_{ylide}) for the other complexes, where larger values are associated with complexes in which the second gold atom carries a soft ligand such as PPh₃, PPh₂Me, and AsPh₃. The soft ligand would increase the electron density on the gold atom to which it is directly bound, some of which would be transmitted through the gold–gold bond to the other gold atom, resulting in an increase in the coupling constant. The same trend is also seen in the Mössbauer data (see below).

The chloro complexes **7a** or **7b** react with AgClO₄ in dichloromethane with precipitation of AgCl and formation of green solutions from which the green complexes **9a** or **9b** are obtained. Complex **9a** can also be obtained by reaction of [Ph₃PAu(CH₂PPh₂CH₂)₂AuPPh₃](ClO₄)₂ with [Au(OCIO₃)PPh₃] (Scheme 1).

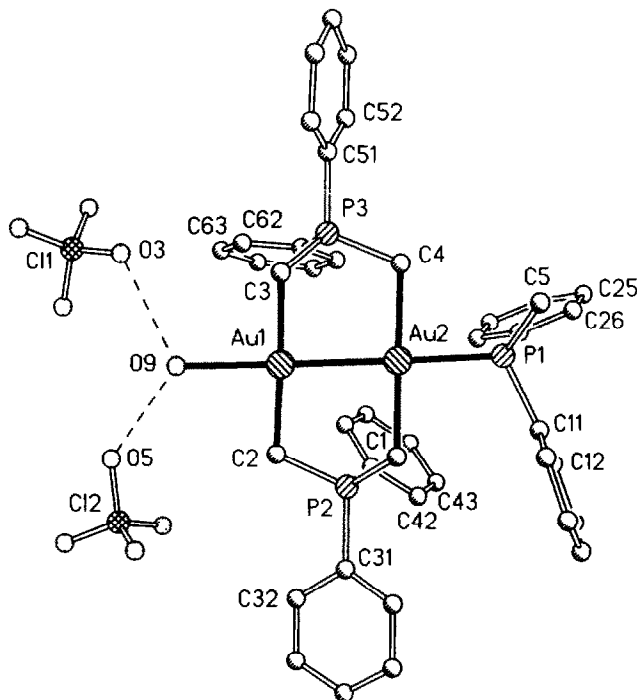


Fig. 1. Molecular structure of **10**, with the atom numbering scheme. Hydrogen atoms are omitted for clarity; atom sizes are arbitrary. H bonds are indicated by broken lines.

Complexes **9a** and **9b** are air- and moisture-stable green solids. It is not possible to confirm the presence of a coordinated perchlorate from the IR spectra, because their bands must overlap with those of the perchlorate anion at 1100 (s, br) and 620 (m) cm⁻¹ [12]. The ¹H NMR spectra are as expected (Table 1). For **9b** a signal at $\delta = 2.46$ (d, $J(\text{PH}) = 13.02$ Hz) ppm from the methyl group of the phosphine is observed. The ³¹P{¹H}NMR spectra show two resonances for the two different phosphorus atoms, but both appear as singlets. The ³J(P_{ylide}–P_{phosphine}) coupling constant changes from 35.0 Hz when the ligand *trans* to PPh₃ is PPh₂Me (**6**) to 0 Hz in the perchlorate complex **9a**. In [Ph₃PAu(CH₂PPh₂CH₂)₂AuR](ClO₄), ³J(P–P) is 59.1 Hz (R = C₆F₃H₂) or 54.5 Hz (R = C₆F₅) [9].

On cooling damp dichloromethane solutions of **9b** to –30°C, yellow crystals of **10** can be obtained (40% yield). The IR spectrum show bands at 3375 (w, br) ($\nu(\text{OH})$) and 1640 cm⁻¹ (w, br) ($\delta(\text{HOH})$) corresponding to coordinated OH₂.

The X-ray structure analysis reveals that **10** (Fig. 1) possesses a general geometry typical of gold(II) complexes, the Au–Au bond lying across the eight-membered ring. The Au–Au bond length is 2.601(1) Å, which is longer than that found in the symmetrical derivatives [Ph₃PAu(CH₂PPh₂CH₂)₂AuPPh₃](ClO₄)₂ [10] (2.579(3) Å) and [XAu(CH₂PPh₂CH₂)₂AuX] (X = PhCOO or CH₃COO) [18,19] where the distances lie

in the range 2.561(2)–2.592(1) Å. The factors influencing Au(II)–Au(II) bond lengths are not clearly understood; however, it seems that the *trans* influence or the structural *trans* effect of the ligands joined to gold act through, rather than on, the Au(II)–Au(II) bond [4,20]. The Au–P bond length is 2.326(2) Å which is shorter than in $[\text{Ph}_3\text{PAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuPPh}_3](\text{ClO}_4)_2$ (2.365(6) and 2.384(6) Å) and in the asymmetric $[(\text{C}_6\text{F}_5)\text{Au}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuPPh}_3]\text{ClO}_4$ [9] (2.43(3) Å), consented with the weaker *trans* influence of oxygen ligands. However, the Au–O distance of 2.300(6) Å is longer than in other gold(II) derivatives with oxygen ligands $[\text{XAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuX}]$ (X = PhCOO or CH₃COO), where the distances fall in the range 2.117(13)–2.144(12) Å and in the only aqua-complex reported $[\text{AuMe}_2(\text{CF}_3\text{SO}_3)(\text{OH}_2)]$, where Au–OH₂ is 2.157(6) Å. This is probably caused by the strong *trans* influence of phosphine ligands and to the expected weakness of a gold–water bond.

The gold atoms exhibit a square-planar geometry (maximum deviation, 5.0°). There are no significant differences between the Au–CH₂ distances and those in the symmetric or asymmetric complexes above mentioned.

Mössbauer data for **1** and related complexes are shown in Table 2. For the asymmetric complexes the spectra were too broad and the peaks were too asymmetric to allow fitting with a simple doublet. However, the two doublets expected overlapped heavily. It was not possible from the spectra alone to decide how the lines should be paired because both nested and overlapping pairs of doublets gave similar statistics. Choices were therefore made to give best agreement with the symmetrical compounds containing the same groups, but it should be noted that the errors on the values given are greater than normal.

The data show the transmission of electronic effects across the gold–gold bond which was postulated above from the NMR coupling-constant data. That is, a soft ligand on one gold atom produces an increase in s-electron density on the second atom which is reflected

in the isomer shift. For instance the isomer shifts values for the gold atom bearing the tht ligand in $[(\text{tht})\text{Au}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuL}](\text{ClO}_4)_2$ are 4.17 mm s^{−1} (L = tht) and 4.65 mm s^{−1} (L = PPh₃). The same effect is seen in $[\text{Ph}_3\text{PAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuL}](\text{ClO}_4)_2$ and $[(\text{C}_6\text{F}_5)\text{Au}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuL}]\text{ClO}_4$. On this basis, PPh₃ is a slightly better donor than C₆F₅.

3. Experimental section

Instrumentation and general experimental techniques were as described earlier [9]. Mössbauer spectra were obtained with source (¹⁹⁷Pt) and sample immersed in liquid helium. Isomer shifts are quoted relative to gold foil. The spectra were fitted with pairs of Lorentzian lines; for two-doublet spectra, it was necessary to constrain each doublet to be symmetrical. All the reactions were performed at room temperature.

3.1. $[\text{R}_3\text{PAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{Au}(\text{tht})](\text{ClO}_4)_2$ (PR₃ = PPh₃ (**1**), PPh₂Me (**2**), or P(4-MeOC₆H₄)₃ (**3**))

(a) To a solution of $[\text{Ph}_3\text{PAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuPPh}_3](\text{ClO}_4)_2$ [10] (0.154 g, 0.1 mmol) in dichloromethane (20 cm³) was added $[\text{Au}(\text{PPh}_3)\text{tht}]\text{ClO}_4$ [21] (0.064 g, 0.1 mmol) and the mixture was stirred for 30 min. Concentration of the solution to about 5 cm³ and addition of diethyl ether (20 cm³) led to the precipitation of a mixture of complex **1** and $[\text{Au}(\text{PPh}_3)_2]\text{ClO}_4$.

(b) To a solution of $[\text{Ph}_3\text{PAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuPPh}_3](\text{ClO}_4)_2$ [10] (0.154 g, 0.1 mmol) in dichloromethane (20 cm³) was added $[\text{Au}(\text{C}_6\text{F}_5)\text{tht}]$ [22] (0.045 g, 0.1 mmol) and the mixture was stirred for 3 h. Concentration of the solution to about 5 cm³ and addition of diethyl ether (20 cm³) led to the precipitation of **1**. By concentration of the diethyl ether solution to about 5 cm³ and addition of hexane, $[\text{Au}(\text{C}_6\text{F}_5)\text{PPh}_3]$ was obtained.

(c) To a solution of $[(\text{tht})\text{Au}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{Au}(\text{tht})](\text{ClO}_4)_2$ [10] (0.120 g, 0.1 mmol) in dichloromethane (20 cm³) was added $[\text{Ag}(\text{OCIO}_3)\text{PR}_3]$ [23] [0.1 mmol, PR₃ = PPh₃ (0.047 g), PPh₂Me (0.041 g) or

TABLE 2. ¹⁹⁷Au Mössbauer data for $[\text{LAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuL'}](\text{ClO}_4)_n$

L	L'	n	Au–C ₆ F ₅		Au–PPh ₃		Au–tht	
			IS ^{a,b} (mm s ^{−1})	QS (mm s ^{−1})	IS ^{a,b} (mm s ^{−1})	QS ^b (mm s ^{−1})	IS ^{a,b} (mm s ^{−1})	QS ^b (mm s ^{−1})
tht	tht	2					4.17	6.72
PPh ₃	PPh ₃	2			4.97	7.41		
C ₆ F ₅	tht	1	4.55	7.60			4.65	6.50
C ₆ F ₅	PPh ₃	1	4.85	6.90	4.85	7.90		
PPh ₃	tht	2			4.75	7.80	4.60	6.64

IS, isomer shift; QS, quadrupole splitting. ^a Relative to gold metal. ^b Errors are ±0.03 mm s^{−1} for doublets, and about ±0.06 mm s^{−1} for overlapping doublets.

TABLE 3. Atomic coordinates and equivalent isotropic displacement parameters for **10** where U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	U_{eq} ($\text{\AA}^2 \times 10^3$)
Au(1)	6245.2(3)	5712.6(2)	4999.0(2)	23.8(1)
Au(2)	6606.2(3)	5939.1(2)	6371.9(2)	22.5(1)
P(1)	6927(2)	6150.6(10)	7593.6(12)	23.4(5)
P(2)	7063(2)	4558.3(10)	6000.5(12)	24.3(5)
P(3)	6875(2)	7063.9(10)	5294.7(12)	24.9(5)
Cl(1)	6736(2)	6486.6(11)	2259.8(12)	36.6(5)
Cl(2)	6762(2)	3804.5(11)	3316.2(13)	37.3(5)
O(1)	7136(8)	5876(4)	2202(5)	70(3)
O(2)	7617(7)	6910(4)	2294(5)	65(2)
O(3)	6205(7)	6538(4)	2915(4)	54(2)
O(4)	5974(7)	6625(4)	1673(4)	62(2)
O(5)	6655(12)	4439(5)	3124(6)	113(4)
O(6)	7713(6)	3757(5)	3794(4)	66(2)
O(7)	5830(8)	3649(7)	3641(6)	113(4)
O(8)	6866(8)	3477(5)	2681(5)	82(3)
O(9)	6204(6)	5525(3)	3777(3)	38(2)
O(10)	3865(29)	7211(17)	1188(20)	366(18)
C(1)	6279(7)	5009(4)	6538(5)	27(2)
C(2)	6743(8)	4783(4)	5100(5)	29(2)
C(3)	5838(7)	6624(4)	4857(5)	26(2)
C(4)	6847(8)	6891(4)	6224(5)	30(2)
C(5)	6059(8)	6753(4)	7878(5)	35(2)
C(11)	6688(8)	5489(4)	8145(5)	32(2)
C(12)	7556(9)	5128(4)	8425(5)	39(2)
C(13)	7344(11)	4596(5)	8778(6)	50(3)
C(14)	6289(11)	4413(5)	8835(6)	54(3)
C(15)	5425(11)	4756(5)	8558(6)	51(3)
C(16)	5620(9)	5301(5)	8212(5)	38(2)
C(21)	8342(7)	6368(4)	7795(5)	27(2)
C(22)	9115(8)	6210(4)	7325(5)	35(2)
C(23)	10194(9)	6369(5)	7480(6)	46(2)
C(24)	10491(10)	6691(5)	8117(7)	53(3)
C(25)	9736(9)	6845(5)	8583(6)	50(3)
C(26)	8659(9)	6683(5)	8418(6)	42(2)
C(31)	6842(7)	3750(4)	6143(5)	29(2)
C(32)	7068(8)	3334(4)	5607(5)	35(2)
C(33)	6942(8)	2710(4)	5721(6)	39(2)
C(34)	6594(7)	2522(5)	6361(5)	34(2)
C(35)	6333(9)	2908(4)	6883(6)	43(2)
C(36)	6453(8)	3534(4)	6774(5)	37(2)
C(41)	8482(7)	4698(4)	6260(5)	29(2)
C(42)	8939(8)	4445(4)	6904(5)	34(2)
C(43)	10034(8)	4540(5)	7129(6)	42(2)
C(44)	10674(8)	4873(5)	6717(6)	42(2)
C(45)	10233(8)	5131(4)	6083(6)	39(2)
C(46)	9129(8)	5047(4)	5841(5)	33(2)
C(51)	6744(8)	7872(4)	5144(5)	31(2)
C(52)	7663(9)	8252(5)	5273(6)	42(2)
C(53)	7518(11)	8884(5)	5176(7)	57(3)
C(54)	6519(11)	9155(4)	4968(5)	45(2)
C(55)	5651(11)	8773(5)	4856(5)	48(3)
C(56)	5731(9)	8126(5)	4930(5)	40(2)
C(61)	8160(7)	6862(4)	4965(5)	30(2)
C(62)	8178(8)	6809(4)	4228(5)	35(2)
C(63)	9134(9)	6677(5)	3919(6)	42(2)
C(64)	10073(9)	6594(5)	4362(6)	45(2)
C(65)	10065(8)	6629(5)	5099(7)	46(2)
C(66)	9096(8)	6777(5)	5403(6)	39(2)

TABLE 3. (continued)

	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	U_{eq} ($\text{\AA}^2 \times 10^3$)
Cl(6)	8190(11)	281(6)	6352(7)	65(4)
Cl(3)	7233(4)	740(2)	5858(2)	90.1(12)
Cl(4)	9358(3)	177(2)	5919(3)	91.4(13)
Cl(7)	8605(16)	2125(10)	3533(11)	116(7)
Cl(5)	9826(5)	1966(2)	3157(3)	106(2)
Cl(6)	8724(6)	1851(3)	4436(4)	167(3)

P(4-MeOC₆H₄)₃ (0.056 g)]. After stirring for 20 min at room temperature in the dark, the precipitated [Ag(OClO₃)tht] was filtered off and washed with dichloromethane (3 × 5 cm³). Concentration of the filtrate to about 5 cm³ and addition of diethyl ether (20 cm³) gave **1–3** as yellow solids.

1: yield, 95%. Anal. Found: C, 43.5; H, 3.55. C₅₀H₅₁Au₂Cl₂O₈P₃S calc.: C, 43.85; H, 3.75%.

2: yield, 93%. Anal. Found: C, 41.55; H, 3.6. C₄₅H₄₉Au₂Cl₂O₈P₃S calc.: C, 41.35; H, 3.8%.

3: yield: 95%. Anal. Found: C, 43.75; H, 3.8. C₅₃H₅₇Au₂Cl₂O₁₁P₃S calc.: C, 43.6; H, 3.95%.

3.2. [Ph₃PAu(CH₂PPh₂CH₂)₂AuL](ClO₄)₂ (L = py (**4**), AsPh₃ (**5**) or PPh₂Me (**6**))

(a) To a solution of **1** (0.137 g, 0.1 mmol) in dichloromethane (20 cm³) was added py (1 cm³ of a solution 0.1 mol dm⁻³ in hexane), AsPh₃ (0.031 g, 0.1 mmol) or PPh₂Me (1 cm³ of a solution 0.1 mol dm⁻³ in hexane) and the mixture was stirred for 15 min. The solution was evaporated to about 5 cm³ and addition of diethyl ether (20 cm³) led to precipitation of a mixture of the symmetrical derivatives, [Ph₃PAu(CH₂PPh₂CH₂)₂AuPPh₃](ClO₄)₂ and [LAu(CH₂PPh₂CH₂)₂AuL](ClO₄)₂ (L = py, AsPh₃ or PPh₂Me), and **4–6**.

3.3. [R₃PAu(CH₂PPh₂CH₂)₂AuX]ClO₄ (PR₃ = PPh₃; X = Cl (**7a**) or S₂CN(CH₂Ph)₂ (**8**); PR₃ = PPh₂Me; X = Cl (**7b**))

(a) To a solution of **1** (0.137 g, 0.1 mmol) in dichloromethane (20 cm³) was added a solution of NaCl (0.006 g, 0.1 mmol) or NaS₂CN(CH₂Ph)₂ (0.029, 0.1 mmol) in water (10 cm³) and the mixture was stirred for 15 min. The dichloromethane layer was removed using a separating funnel and dried with anhydrous magnesium sulphate (1–2 g). The filtered solution was evaporated to about 5 cm³ and addition of diethyl ether (20 cm³) led to the precipitation of a mixture of **7a** or **8** and the symmetrical derivatives [Ph₃PAu-

$(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuPPh}_3](\text{ClO}_4)_2$ and $[\text{XAu}(\text{CH}_2\text{-PPh}_2\text{CH}_2)_2\text{AuX}]$ ($\text{X} = \text{Cl}$ or $\text{S}_2\text{CN}(\text{CH}_2\text{Ph})_2$).

(b) To a solution of $[\text{ClAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuCl}]$ [4] (0.045 g, 0.05 mmol) in dichloromethane (20 cm³) was added $[\text{R}_3\text{PAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuPR}_3](\text{ClO}_4)_2$ [10] ($\text{PR}_3 = \text{PPh}_3$ (0.077 g, 0.05 mmol) or PPh_2Me (0.071 g, 0.05 mmol)) and the mixture was stirred for 15 min. Evaporation of the solution to about 2 cm³ and addition of diethyl ether (20 cm³) led to the precipitation of a mixture of **7a**, **7b** and the symmetrical derivatives $[\text{R}_3\text{PAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuPR}_3](\text{ClO}_4)_2$ ($\text{PR}_3 = \text{PPh}_3$ or PPh_2Me) and $[\text{XAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuX}]$.

3.4. $[\text{R}_3\text{PAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuOClO}_3](\text{ClO}_4)$ ($\text{PR}_3 = \text{PPh}_3$ (**9a**) or PPh_2Me (**9b**))

(a) To a solution of **1** (0.137 g, 0.1 mmol) in dichloromethane (20 cm³) was added a solution of $[\text{Au}(\text{OClO}_3)\text{PPh}_3]$ [24] (0.1 mmol in 10 cm³ of dichloromethane). After 30 min, the solution was evaporated to about 20 cm³ and addition of diethyl ether (20 cm³) led to the precipitation of a green solid (**9a**) which was washed with a mixture of 40% dichloromethane–60% diethyl ether to remove $[\text{Au}(\text{PPh}_3)_2]\text{ClO}_4$.

(b) To a solution of $[\text{ClAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuCl}]$ [4] (0.045 g, 0.05 mmol) in dichloromethane (20 cm³) was added $[\text{R}_3\text{PAu}(\text{CH}_2\text{PPh}_2\text{CH}_2)_2\text{AuPR}_3](\text{ClO}_4)_2$ [10] ($\text{PR}_3 = \text{PPh}_3$ (0.077 g, 0.05 mmol) or PPh_2Me (0.071 g, 0.05 mmol) and AgClO_4 (0.021 g, 0.1 mmol)).

The mixture was stirred for 90 min in the dark. The precipitated AgCl was filtered off and washed with dichloromethane (3 × 5 cm³). Concentration of the filtrate to about 5 cm³ and addition of diethyl ether (20 cm³) led to the precipitation of **9a** and **9b** as green solids.

9a: yield, 89%. Anal. Found: C, 43.45; H, 3.7. $\text{C}_{46}\text{H}_{43}\text{-Au}_2\text{Cl}_2\text{O}_8\text{P}_3$ calc.: C, 43.1; H, 3.4%.

9b: yield, 83%. Anal. Found: C, 40.1; H, 3.15. $\text{C}_{41}\text{-H}_{41}\text{Au}_2\text{Cl}_2\text{O}_8\text{P}_3$ calc.: C, 40.4; H, 3.4%.

3.5. Crystal structure determination of compound **10**

Crystal data: $\text{C}_{43}\text{H}_{49}\text{Au}_2\text{Cl}_6\text{O}_{10}\text{P}_3$; M_r 1407.3; monoclinic, space group, $P2_1/c$; $a = 12.283(3)$, $b = 21.789(6)$ and $c = 18.653(4)$ Å, $\beta = 94.81(2)^\circ$; $V = 4974(2)$ Å³; $Z = 4$; $D_{\text{calc}} = 1.88$ Mg m⁻³; $F(000) = 2728$; λ (Mo $K\alpha$) = 0.71073 Å; $\mu = 6.4$ mm⁻¹; $T = -95^\circ\text{C}$.

3.6. Data collection and reduction

A yellow tablet 0.5 × 0.4 × 0.2 mm, obtained by cooling a concentrated damp dichloromethane solution of **9b** at -30°C , was mounted on a glass fibre in inert oil. 11080 intensities were measured on a Siemens R3 diffractometer with an LT-2 low temperature attachment using monochromated Mo $K\alpha$ radiation ($2\theta_{\text{max}} = 50^\circ$). An absorption correction based on Ψ scans was applied, with transmission factors 0.39–0.55. Merging equivalents gave 8791 reflections ($R_{\text{int}} = 0.038$), which were used for all calculations (program system SHELXL-92 [25]). Ccell constants were refined from setting angles of 50 reflections in the 2θ range 20–23°.

3.7. Structure solution and refinement

The structure was solved by the heavy-atom method and refined on F^2 . The coordinated oxygen atom O(9), initially unexpected, was identified on the basis of peak height and short contacts to perchlorate oxygen atoms (O(9)...O(3), 2.73 Å; O(9)...O(5), 2.74 Å), although the water H could not be identified (one peak at a suitable position was rather large for a hydrogen atom, at 2 electrons Å⁻³). A further oxygen atom, O(10), was tentatively identified as water because it too makes an H bonding contact to perchlorate (O(10)...O(4), 2.96 Å), although the high displacement parameter may indicate partial occupation. Two ordered dichloromethane molecules were also identified. Anisotropic refinement (except O(10) and dichloromethane carbon) with riding H atoms proceeded to $wR(F^2) = 0.108$ (all reflections), $R(F > 4\sigma(F)) = 0.042$. The weighting scheme was $w^{-1} = \sigma^2(F_o^2) + (0.0286P)^2 + 65.71P$, where $P = (F_o^2 + 2F_c^2)/3563$ parameters, $S = 1.09$,

TABLE 4. Selected bond lengths (Å) and angles (°) for **10**

Bond lengths			
Au(1)–C(2)	2.088(9)	Au(1)–C(3)	2.090(8)
Au(1)–O(9)	2.308(7)	Au(1)–Au(2)	2.6013(7)
Au(2)–C(1)	2.095(8)	Au(2)–C(4)	2.116(9)
Au(2)–P(1)	2.326(2)	P(1)–C(5)	1.799(9)
P(1)–C(11)	1.809(9)	P(1)–C(21)	1.810(9)
P(2)–C(1)	1.749(9)	P(2)–C(2)	1.762(9)
P(2)–C(41)	1.795(9)	P(2)–C(31)	1.805(9)
P(3)–C(3)	1.742(10)	P(3)–C(4)	1.777(9)
P(3)–C(51)	1.789(9)	P(3)–C(61)	1.796(9)
Bond angles			
C(2)–Au(1)–C(3)	175.8(4)	C(2)–Au(1)–O(9)	85.1(3)
C(3)–Au(1)–O(9)	92.7(3)	C(2)–Au(1)–Au(2)	95.0(2)
C(3)–Au(1)–Au(2)	87.4(2)	O(9)–Au(1)–Au(2)	177.1(2)
C(1)–Au(2)–C(4)	176.7(4)	C(1)–Au(2)–P(1)	93.7(2)
C(4)–Au(2)–P(1)	85.4(2)	C(1)–Au(2)–Au(1)	87.3(2)
C(4)–Au(2)–Au(1)	93.7(2)	P(1)–Au(2)–Au(1)	177.26(6)
C(5)–P(1)–C(11)	106.5(4)	C(5)–P(1)–C(21)	109.3(5)
C(11)–P(1)–C(21)	106.8(4)	C(5)–P(1)–Au(2)	112.2(3)
C(11)–P(1)–Au(2)	112.2(3)	C(21)–P(1)–Au(2)	109.6(3)
C(1)–P(2)–C(2)	107.5(4)	C(1)–P(2)–C(41)	108.6(4)
C(2)–P(2)–C(41)	110.1(4)	C(1)–P(2)–C(31)	111.5(4)
C(2)–P(2)–C(31)	112.8(4)	C(41)–P(2)–C(31)	106.3(4)
C(3)–P(3)–C(4)	105.5(4)	C(3)–P(3)–C(51)	114.6(4)
C(4)–P(3)–C(51)	110.7(4)	C(3)–P(3)–C(61)	109.5(4)
C(4)–P(3)–C(61)	111.8(5)	C(51)–P(3)–C(61)	104.9(4)

maximum $\Delta/\sigma = 0.06$; maximum $\Delta\rho = 2.2$ electrons \AA^{-3} .

Atomic positional parameters for **10** are listed in Table 3 and Table 4 contains selected bond lengths and angles. All data have been deposited at the Cambridge Crystallographic Data Centre.

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