Alternative Synthesis of Binuclear Gold(II) Ylide Complexes: Cationic Gold(II) Complexes. X-Ray Crystal Structures of $[\{Au(CH_2)_2PPh_2\}_2Br_2]$ and $[\{Au(CH_2)_2PPh_2\}_2(PPh_3)_2][ClO_4]_2$ *

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The complex $[\{Au(CH_2)_2PPh_2\}_2Cl_2]$ reacts with silver salts AgX to give the corresponding gold(II) derivatives $[\{Au(CH_2)_2PPh_2\}_2X_2]$ ($X = C_6F_5$, $C_6H_2F_3$-2,4,6, NO_3 or $MeCO_2$), whilst reaction with suitable silver complexes $[AgX'(L)]$ [$X' = ClO_4$, L = tetrahydrothiophene (tht) or PPh_3; $X' = NO_3$, $L = PMe_3$] gives cationic gold(II) derivatives $[\{Au(CH_2)_2PPh_2\}_2L_2]X'_2$, which either undergo metathetical reactions with MX [X = Br, SCN or $S_2CN(CH_2Ph)_2$] to give other neutral complexes inaccessible by the first procedure or react with neutral ligands L' to afford other cationic complexes [L' = pyridine (py), $AsPh_3$ or $SbPh_3$]. The structures of $[\{Au(CH_2)_2PPh_2\}_2Br_2]$ and $[\{Au(CH_2)_2PPh_2\}_2(PPh_3)_2][ClO_4]_2$ have been established by single-crystal X-ray diffraction studies.

Binuclear gold(II) complexes containing the bis(ylide) ligand $(CH_2)_2PPh_2$ have extensively been studied by Fackler and co-workers[1–4] who have reported the synthesis and structure of neutral complexes of the type $[\{Au(CH_2)_2PPh_2\}_2X(X')]$ (X,X' = anionic ligands). The synthetic approach used in most cases is a binuclear oxidative addition to the corresponding binuclear gold(I) complex and only the complexes $[\{Au(CH_2)_2PPh_2\}_2X(X')]$ with $X = X' = CF_3$,[5] S_4[6] or $X = S_4$, $X' = S_5$[6] have been obtained by metathetical reactions between the binuclear dichlorogold(II) precursor and $Cd(CF_3)_2$ or, respectively, the binuclear dibromogold(II) precursor and aqueous solutions of ammonium polysulphides.

In this paper, we describe the synthesis of neutral $[\{Au(CH_2)_2PPh_2\}_2X_2]$ [$X = C_6F_5$, $C_6H_2F_3$-2,4,6, NO_3, $MeCO_2$, Br, SCN or $S_2CN(CH_2Ph)_2$ or cationic $[\{Au(CH_2)_2PPh_2\}_2L_2]X'_2$ [$X' = ClO_4$, L = tetrahydrothiophene (tht) or PPh_3; $X' = NO_3$, $L = PMe_3$] and $[\{Au(CH_2)_2PPh_2\}_2L'_2]X'_2$ [$X' = ClO_4$, L' = pyridine (py), $AsPh_3$ or $SbPh_3$] gold(II) complexes. The molecular structures of the neutral complex with X = Br and of the cationic complex with $X' = ClO_4$, $L = PPh_3$ have been established by X-ray studies.

Results and Discussion

(*a*) *Reactions of* $[\{Au(CH_2)_2PPh_2\}_2Cl_2]$ *with Silver Salts.*—These reactions lead to precipitation of AgCl and from the CH_2Cl_2–OEt_2 solutions the neutral complexes $[\{Au(CH_2)_2PPh_2\}_2X_2]$ ($X = C_6F_5$ **1**, $C_6H_2F_3$-2,4,6 **2**, NO_3 **3** or $MeCO_2$ **4**) could be isolated. Complex **1** has previously been reported[5] and was obtained by a binuclear oxidative addition using $[Tl(C_6F_5)_2Cl]$ albeit in a lower yield (62%).

The complexes are air- and moisture-stable solids at room temperature and are yellow (**1**, **2**, **4**) or greenish yellow **3**. Their ^1H and ^{31}P-$\{^1H\}$ NMR spectra are as expected (Table 1). The acetone solutions of the complexes are non-conducting. The IR spectra show a band at 565m cm^{-1} due to $\nu(Au-C_{ylide})$.[7] The spectrum of **3** shows bands at 1483vs, 1272vs and 975s cm^{-1} confirming the presence of monodentate[8,9] ONO_2; the $\nu(Au-O)$ vibration appears at 250w cm^{-1}. The spectrum of **4** shows bands at 1604vs and 1580vs cm^{-1} [$\nu_{asym}(CO_2)$] and 1362vs and 1310vs cm^{-1} [$\nu_{sym}(CO_2)$], *i.e.* the acetato ligand is also monodentate.[9]

The use of other, less-soluble silver salts does not permit the preparation of the corresponding derivatives.

(*b*) *Reactions of* $[\{Au(CH_2)_2PPh_2\}_2Cl_2]$ *with Silver Complexes* $[AgX'(L)]$.—Although $AgClO_4$ is soluble in dichloromethane and reacts as the other silver salts in (*a*), the solution obtained undergoes successive changes in colour (green, yellow, red and yellow) and the final yellow solid gives a ^{31}P NMR spectrum with at least nine signals, indicative of a complex mixture.

By using silver complexes $[AgX'(L)]$ the reactions are clean and the abstraction of the chloride ligands, which precipitate as AgCl, leaves the neutral L and the anionic X' ligands competing for the vacant co-ordination sites. If the anion is weakly (ClO_4^-) or moderately strongly co-ordinating (NO_3^-), a strongly co-ordinating ligand (*e.g.* PMe_3) prevails and the cationic binuclear gold(II) complexes $[\{Au(CH_2)_2PPh_2\}_2L_2]X'_2$ ($X' = ClO_4$, L = tht **5** or PPh_3 **6**; $X' = NO_3$, $L = PMe_3$ **7**) can be isolated (see Scheme 1). Other cationic complexes have recently been reported,[10] albeit their structure has not been established.†

We have shown[11] that in the chemistry of gold-(I) and -(III) the tht ligand is very weakly co-ordinating and can therefore be readily displaced by a variety of both anionic and neutral ligands. The complex $[\{Au(CH_2)_2PPh_2\}_2(tht)_2][ClO_4]_2$ **5**

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* Bis(μ-2,2-diphenylphosphoniapropane-1,3-diyl-κC^1:κC^3)-bis[bromogold(II)](*Au–Au*) and -bis[(triphenylphosphine)gold(II)](*Au–Au*) diperchlorate.

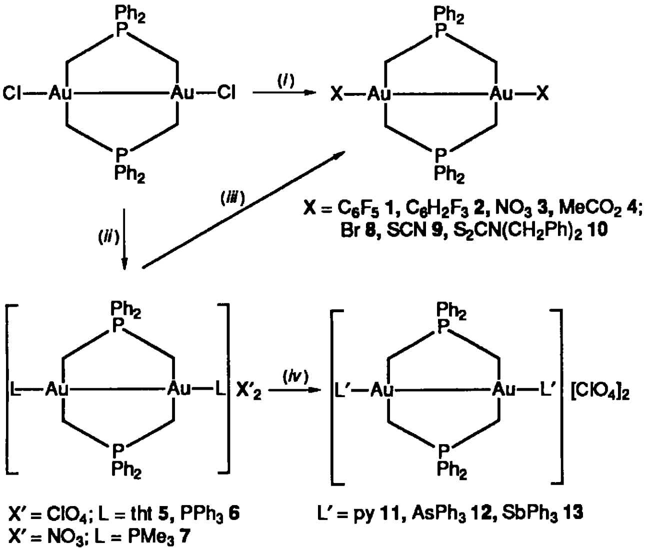
Supplementary data available: Complete bond lengths and angles, H-atom coordinates, structure factors and thermal parameters have been deposited at the Fachinformatioszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, FRG. Any request for this material should quote a full literature citation and the reference number CSD 54871.

† *Note added at proof.* We have recently reported some other cationic gold(II) complexes, R. Uson, A. Laguna, M. Laguna, J. Jimenez and P. G. Jones, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 198.

Table 1 Analytical data for products

Complex	Yield (%)	Analysis (%)[a] C	H	N	NMR[b] δ(PPh$_2$)(^{31}P)	δ(CH$_2$)(^{1}H)[c]
1 [{Au(CH$_2$)$_2$PPh$_2$}$_2$(C$_6$F$_5$)$_2$]	82	41.75 (41.6)	2.85 (2.45)		43.3(s)	1.64('d') [9.8]
2 [{Au(CH$_2$)$_2$PPh$_2$}$_2$(C$_6$H$_2$F$_3$)$_2$]	60	44.45 (44.4)	3.35 (3.0)		42.7(s)	1.66('d') [9.7]
3 [{Au(CH$_2$)$_2$PPh$_2$}$_2$(NO$_3$)$_2$]	70	35.2 (35.6)	2.95 (2.3)	2.95 (2.95)	35.4(s)	1.81('d') [10.1]
4 [{Au(CH$_2$)$_2$PPh$_2$}$_2$(MeCO$_2$)$_2$]	70	40.7 (40.95)	3.65 (3.65)		37.4(s)	1.68('d') [9.9]
5 [{Au(CH$_2$)$_2$PPh$_2$}$_2$(tht)$_2$][ClO$_4$]$_2$	75	36.6 (36.15)	3.85 (3.7)		41.7(s)	1.84('d') [11.5]
6 [{Au(CH$_2$)$_2$PPh$_2$}$_2$(PPh$_3$)$_2$][ClO$_4$]$_2$	78	49.8 (49.8)	3.95 (3.8)		48.8(t)	1.81(dm) [11.0]
7 [{Au(CH$_2$)$_2$PPh$_2$}$_2$(PMe$_3$)$_2$][NO$_3$]$_2$	75	37.0 (37.25)	4.2 (4.25)	2.4 (2.55)	44.6(t)	1.52(dm) [12.9]
9 [{Au(CH$_2$)$_2$PPh$_2$}$_2$(SCN)$_2$]	75	38.65 (38.45)	3.3 (3.0)	2.75 (3.0)	39.1(s)	1.62('d') [10.7]
10 [{Au(CH$_2$)$_2$PPh$_2$}$_2${S$_2$CN(CH$_2$Ph)$_2$}$_2$]	77	50.85 (51.0)	4.6 (4.15)	1.9 (2.05)	41.5(s)	2.07('d') [9.5]
11 [{Au(CH$_2$)$_2$PPh$_2$}$_2$(py)$_2$][ClO$_4$]$_2$	82	38.1 (38.75)	3.25 (3.25)	1.6 (1.4)	39.7(s)	1.87('d') [11.2]
12 [{Au(CH$_2$)$_2$PPh$_2$}$_2$(AsPh$_3$)$_2$][ClO$_4$]$_2$	82	47.45 (47.1)	3.8 (3.6)		47.3(s)	1.81('d') [11.7]
13 [{Au(CH$_2$)$_2$PPh$_2$}$_2$(SbPh$_3$)$_2$][ClO$_4$]$_2$	80	44.8 (44.55)	3.45 (3.4)		48.4(s)	2.05('d') [11.7]

[a] Calculated values are given in parentheses. [b] In CDCl$_3$, values in ppm; other data are in the Experimental section. [c] Values of N in Hz are given in square brackets.



Scheme 1 (*i*) AgX; (*ii*) [AgX'(L)]; (*iii*) MX; (*iv*) L'

behaves similarly and reacts with salts MX to give another series of neutral complexes [{Au(CH$_2$)$_2$PPh$_2$}$_2$X$_2$] [X = Br **8**, SCN **9** or S$_2$CN(CH$_2$Ph)$_2$ **10**] or with ligands L' to give a second series of cationic complexes [{Au(CH$_2$)$_2$PPh$_2$}$_2$L'$_2$][ClO$_4$]$_2$ (L' = py **11**, AsPh$_3$ **12** or SbPh$_3$ **13**). Complex **8** had previously been prepared[4] (with similar yield, 80%) by binuclear oxidative addition of Br$_2$ to the binuclear gold(I) derivative.

At room temperature the cationic complexes are air- and moisture-stable, orange (**5**, **6**, **12**), yellow (**7**, **11**) or greenish yellow (**13**) solids. Their acetone solutions show conductivities (*ca.* 200 S cm^2 mol^{-1}) which are characteristic for 1:2 electrolytes. Their ^{31}P NMR spectra present a signal between δ 39.7 and 48.8 from the P atom in the PPh$_2$ group which is normally a singlet but is a triplet for **6** and **7** because of coupling with neutral phosphine ligands [J(PP) 27.9 or 37.9 Hz]. The IR spectra of complexes **5**, **6** and **11**–**13** show a band at 565m cm^{-1}, corresponding to ν(Au–C$_{\text{ylide}}$) and two others at 1100vs (br) and 620m cm^{-1} from[12] ClO$_4^-$. In the spectrum of complex **9** the ν(C≡N) vibration is observed at 2090m cm^{-1} and the internal standard ratio[13] is 0.8, confirming the S-co-ordination of the ligand.

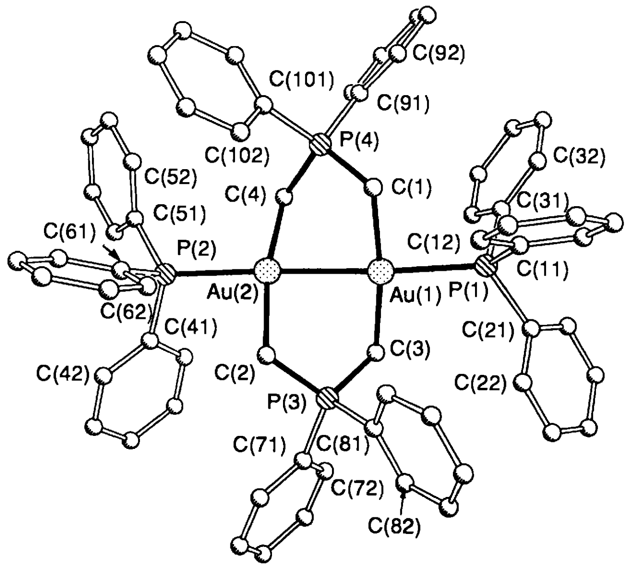


Fig. 1 The cation of complex **6** in the crystal, showing the atom numbering scheme. Hydrogen atoms are omitted for clarity; atom radii are arbitrary

(*c*) *Crystal Structures of Complexes* **6** *and* **8**.—The X-ray structure analysis reveals that compound **6** (Fig. 1) possesses a general geometry typical of gold(II) complexes, the Au–Au bond lying across the eight-membered ring. The ring has a twisted conformation. The C–Au–C angles depart somewhat from linearity (170, 171°). The factors influencing Au$^{\text{II}}$–Au$^{\text{II}}$ bond

Table 2 Atomic coordinates ($\times 10^4$) for compound **6**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Au(1)	1 837.2(3)	4 232.2(4)	2 083.4(3)	C(61)	1355	8 059	3 113
Au(2)	1 520.4(3)	5 527.9(4)	2 705.1(3)	C(62)	1 711(6)	8 287(8)	2 794(6)
P(1)	2 057(2)	3 007(3)	1 473(2)	C(63)	1 827	9 316	2 697
P(2)	1 270(2)	6 727(3)	3 298(2)	C(64)	1 586	10 118	2 920
P(3)	3 011(2)	4 866(3)	3 288(2)	C(65)	1 230	9 890	3 240
P(4)	369(2)	5 020(3)	1 456(2)	C(66)	1 114	8 861	3 336
C(1)	1 053(8)	4 826(12)	1 307(7)	C(71)	3 487	4 707	4 085
C(2)	2 515(8)	5 981(12)	3 113(8)	C(72)	3 535(8)	3 734(9)	4 349(7)
C(3)	2 534(8)	3 743(11)	2 927(7)	C(73)	3 924	3 599	4 966
C(4)	592(8)	4 871(11)	2 224(7)	C(74)	4 265	4 438	5 319
C(11)	2 178	3 593	862	C(75)	4 217	5 411	5 056
C(12)	2 193(6)	4 671(7)	822(5)	C(76)	3 828	5 546	4 439
C(13)	2 302	5 131	363	C(81)	3 580	4 997	2 978
C(14)	2 396	4 513	−57	C(82)	4 177(5)	4 505(8)	3 257(4)
C(15)	2 381	3 436	−18	C(83)	4 594	4 515	2 983
C(16)	2 272	2 976	442	C(84)	4 413	5 017	2 430
C(21)	2 740	2 130	1 826	C(85)	3 815	5 509	2 151
C(22)	3 342(5)	2 598(5)	2 134(5)	C(86)	3 399	5 499	2 425
C(23)	3 893	1 988	2 420	C(91)	−237	4 104	1 010
C(24)	3 842	910	2 398	C(92)	−413(6)	4 012(8)	393(5)
C(25)	3 240	442	2 089	C(93)	−862	3 266	51
C(26)	2 689	1 052	1 803	C(94)	−1 136	2 611	325
C(31)	1 340	2 192	1 160	C(95)	−961	2 702	943
C(32)	987(6)	1 972(9)	546(4)	C(96)	−511	3 449	1 285
C(33)	420	1 395	347	C(101)	45	6 323	1 266
C(34)	206	1 036	763	C(102)	470(4)	7 155(8)	1 385(6)
C(35)	559	1 255	1 377	C(103)	240	8 169	1 330
C(36)	1 126	1 833	1 575	C(104)	−414	8 350	1 155
C(41)	1 821	6 526	4 083	C(105)	−838	7 518	1 036
C(42)	2 149(6)	7 333(6)	4 476(5)	C(106)	−608	6 504	1 091
C(43)	2 572	7 117	5 076	Cl(1)	7 344(2)	7 266(3)	1 529(2)
C(44)	2 667	6 096	5 283	O(1)	7 694(7)	6 941(10)	2 136(6)
C(45)	2 340	5 290	4 890	O(2)	7 775(8)	7 567(13)	1 293(8)
C(46)	1 917	5 505	4 290	O(3)	6 955(6)	8 145(9)	1 500(7)
C(51)	463	6 691	3 253	O(4)	6 949(9)	6 461(11)	1 191(7)
C(52)	−52(5)	6 995(8)	2 713(4)	Cl(2)	882(2)	2 839(3)	3 377(2)
C(53)	−679	6 977	2 660	O(5)	584(8)	2 428(9)	2 775(6)
C(54)	−791	6 657	3 147	O(6)	831(7)	2 112(9)	3 797(6)
C(55)	−276	6 354	3 687	O(7)	1 527(8)	3 095(13)	3 559(7)
C(56)	352	6 371	3 740	O(8)	561(9)	3 766(10)	3 393(7)

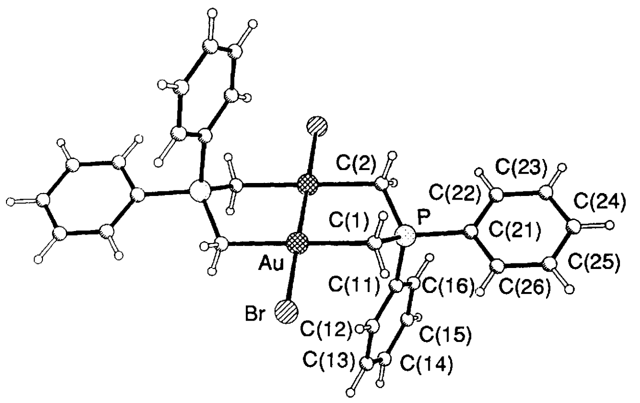


Fig. 2 The molecule of complex **8** in the crystal, showing the numbering scheme of the asymmetric unit. Radii are arbitrary

lengths are not yet clearly understood. Here the Au–Au bond is very short (2.579 Å) despite the presence of phosphine ligands, which one might naively expect through the usual strong *trans* influence to lengthen the Au^{II}–Au^{II} bond; oxygen ligands, which have little affinity for gold, produce short Au^{II}–Au^{II} bonds (< 2.6 Å).[14] However, the *trans* influence may act through, rather than on, the Au^{II}–Au^{II} bond.[4,15] The Au–P bond lengths (2.365, 2.384 Å) are longer than in [$AuCl_3(PPh_3)$] (2.335 Å),[16] which may reflect such an extended *trans* influence. In [$AuMe_3(PPh_3)$][17] the Au–P bond lengths of 2.350 and 2.347 Å (two independent molecules) were regarded as lengthened by steric effects. There are not many data for Au^{III}–P bond lengths, perhaps because of the reducing properties of phosphine ligands.

The structure of complex **8** is shown in Fig. 2 (Fackler and co-workers[4] have already mentioned the structure in a footnote, but it has to the best of our knowledge never been published in full; their cell constants are essentially the same as ours)*. The molecule possesses crystallographic inversion symmetry and the ring thus displays the chair conformation. The Au–Au bond length is 2.614 Å, which lies neatly between the 2.600 Å for the chloro analogue[18] (2.579 Å with the diethylphosphonium ylide[19]) and 2.654 Å for the iodo analogue.[15] The Au–Br bond length is 2.516 Å; no other disorder-free values are available for Au^{II}–Br, but Au^{III}–Br bond lengths are usually *ca.* 2.41 Å.[20] Similarly, Au^{II}–Cl bonds are usually *ca.* 0.1 Å longer than Au^{III}–Cl (typical values 2.37, 2.27 Å).[18–20]

Experimental

Instrumentation and general experimental techniques were as described earlier.[21] The yields, C, H and N analyses, proton and $^{31}P-\{^1H\}$ NMR data are listed in Table 1. All the reactions were performed at room temperature.

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* *Note added at proof.* We are grateful to Professor J. P. Fackler, jun., for his comments on the 'amplified structural *trans* effect' in complex **8** (his earlier determination of the structure appeared in the Ph.D. Thesis of D. Dudis, Case Western Reserve University, 1984) and for pointing out that similar effects have been observed for Pt–Pt systems (S. M. Sanson and R. J. Puddephatt, *Polyhedron*, 1986, **5**, 1423).

Table 3 Selected bond lengths (Å) and angles (°) for compound **6**

Au(1)–Au(2)	2.579(3)	Au(1)–P(1)	2.384(6)
Au(1)–C(1)	2.117(14)	Au(1)–C(3)	2.089(13)
Au(2)–P(2)	2.365(6)	Au(2)–C(2)	2.143(17)
Au(2)–C(4)	2.117(15)	P(1)–C(11)	1.809(14)
P(1)–C(21)	1.821(9)	P(1)–C(31)	1.822(12)
P(2)–C(41)	1.806(11)	P(2)–C(51)	1.816(13)
P(2)–C(61)	1.811(11)	P(3)–C(2)	1.771(17)
P(3)–C(3)	1.800(14)	P(3)–C(71)	1.791(15)
P(3)–C(81)	1.790(14)	P(4)–C(1)	1.788(21)
P(4)–C(4)	1.736(17)	P(4)–C(91)	1.792(11)
P(4)–C(101)	1.816(10)		
Au(2)–Au(1)–P(1)	176.3(1)	Au(2)–Au(1)–C(1)	87.1(5)
P(1)–Au(1)–C(1)	90.3(5)	Au(2)–Au(1)–C(3)	84.4(5)
P(1)–Au(1)–C(3)	98.1(5)	C(1)–Au(1)–C(3)	170.8(8)
Au(1)–Au(2)–P(2)	177.9(1)	Au(1)–Au(2)–C(2)	86.0(5)
P(2)–Au(2)–C(2)	91.9(5)	Au(1)–Au(2)–C(4)	83.6(5)
P(2)–Au(2)–C(4)	98.4(5)	C(2)–Au(2)–C(4)	169.6(7)
Au(1)–P(1)–C(11)	113.5(4)	Au(1)–P(1)–C(21)	119.3(4)
C(11)–P(1)–C(21)	103.9(6)	Au(1)–P(1)–C(31)	104.1(5)
C(11)–P(1)–C(31)	109.4(5)	C(21)–P(1)–C(31)	106.1(5)
Au(2)–P(2)–C(41)	108.5(4)	Au(2)–P(2)–C(51)	117.9(4)
C(41)–P(2)–C(51)	106.5(7)	Au(2)–P(2)–C(61)	112.6(5)
C(41)–P(2)–C(61)	107.5(5)	C(51)–P(2)–C(61)	103.3(6)
C(2)–P(3)–C(3)	110.1(7)	C(2)–P(3)–C(71)	112.2(8)
C(3)–P(3)–C(71)	113.4(7)	C(2)–P(3)–C(81)	109.7(8)
C(3)–P(3)–C(81)	105.6(8)	C(71)–P(3)–C(81)	105.4(7)
C(1)–P(4)–C(4)	109.9(8)	C(1)–P(4)–C(91)	107.7(7)
C(4)–P(4)–C(91)	111.9(7)	C(1)–P(4)–C(101)	112.1(7)
C(4)–P(4)–C(101)	106.0(7)	C(91)–P(4)–C(101)	109.3(5)
Au(1)–C(1)–P(4)	110.3(9)	Au(2)–C(2)–P(3)	109.7(8)
Au(1)–C(3)–P(3)	106.5(7)	Au(2)–C(4)–P(4)	108.1(10)

Table 4 Atomic coordinates (× 10^4) for compound **8**

Atom	*x*	*y*	*z*
Au	3342.7(1)	3051.8(1)	306.7(1)
Br	4893.8(4)	4127.0(5)	1026.3(4)
P	3478(1)	560(1)	803.0(8)
C(1)	4230(4)	1618(4)	581(3)
C(2)	2380(4)	445(4)	−6(3)
C(11)	3076(3)	841(4)	1706(3)
C(12)	3435(4)	1745(4)	2168(3)
C(13)	3107(5)	1937(5)	2864(3)
C(14)	2436(5)	1229(5)	3102(4)
C(15)	2069(5)	308(5)	2650(4)
C(16)	2394(4)	114(5)	1946(3)
C(21)	4186(4)	−702(4)	985(3)
C(22)	3787(4)	−1677(4)	616(3)
C(23)	4335(4)	−2630(4)	768(4)
C(24)	5287(5)	−2654(5)	1292(4)
C(25)	5713(5)	−1702(5)	1660(4)
C(26)	5165(4)	−729(5)	1507(3)

Preparation.—$[\{Au(CH_2)_2PPh_2\}_2X_2]$ (X = C_6F_5 **1**, $C_6H_2F_3$-2,4,6 **2**, NO_3 **3** *or* $MeCO_2$ **4**). To a solution of $[\{Au(CH_2)_2PPh_2\}_2Cl_2]$[4] (0.0891 g, 0.1 mmol) in dichloromethane (20 cm^3) was added a solution of $Ag(C_6F_5)$[22] (0.22 mmol) in diethyl ether (20 cm^3), a solution of $Ag(C_6H_2F_3$-2,4,6)[23] (0.22 mmol) in diethyl ether (20 cm^3), solid $AgNO_3$ (0.0679 g, 0.4 mmol) or solid $Ag(O_2CMe)$ (0.0668 g, 0.4 mmol). The mixture was stirred for 2 (**1** and **2**) or 10 h (**3** and **4**). The precipitated AgCl was filtered off and washed with dichloromethane (3 × 5 cm^3). Concentration to *ca.* 5 cm^3 and addition of diethyl ether (20 cm^3) led to the precipitation of complexes **1**–**4**. NMR (see also Table 1): **1**, ^{1}H, δ 7.46–7.32 (m, 20 H, Ph); ^{19}F, δ −121.17 (m, 4 F, *o*-F), −160.96 [t, 2 F, *p*-F, *J*(FF) 20.7 Hz] and −161.79 (m, 4 F, *m*-F); **2**, ^{1}H, δ 7.60–6.50 (m, 24 H, Ph); ^{19}F, −90.98 (m, 4 F, *o*-F) and −118.26 (m, 2 F, *p*-F); **3**, ^{1}H, δ 7.57–7.41 (m, 20 H, Ph); **4**, ^{1}H, δ 7.68–7.37 (m, 20 H, Ph) and 2.07 (s, 6 H, Me).

$[Ag(OClO_3)(tht)]$. To a solution of $AgClO_4$ (0.207 g, 1 mmol) in diethyl ether was added tetrahydrothiophene (0.088 cm^3, 1 mmol). A white precipitate was formed and the mixture was stirred for 15 min. The white solid was filtered off and washed with diethyl ether (3 × 5 cm^3) (95% yield).

Table 5 Bond lengths (Å) and angles (°) for compound **8**

Au–Br	2.516(1)	Au–C(1)	2.110(5)
Au–Au^{I}	2.614(1)	Au–C(2^{I})	2.092(5)
P–C(1)	1.732(5)	P–C(2)	1.778(5)
P–C(11)	1.798(5)	P–C(21)	1.801(5)
C(11)–C(12)	1.391(7)	C(11)–C(16)	1.396(7)
C(12)–C(13)	1.391(9)	C(13)–C(14)	1.371(10)
C(14)–C(15)	1.399(9)	C(15)–C(16)	1.405(9)
C(21)–C(22)	1.404(7)	C(21)–C(26)	1.398(7)
C(22)–C(23)	1.371(8)	C(23)–C(24)	1.373(8)
C(24)–C(25)	1.391(8)	C(25)–C(26)	1.392(8)
Br–Au–C(1)	88.9(1)	Br–Au–Au^{I}	174.0(1)
C(1)–Au–Au^{I}	91.9(1)	Br–Au–C(2^{I})	86.1(1)
C(1)–Au–C(2^{I})	173.3(2)	Au^{I}–Au–C(2^{I})	93.5(1)
C(1)–P–C(2)	106.7(2)	C(1)–P–C(11)	110.2(3)
C(2)–P–C(11)	110.9(2)	C(1)–P–C(21)	112.8(2)
C(2)–P–C(21)	111.5(2)	C(11)–P–C(21)	104.8(2)
Au–C(1)–P	111.3(3)	P–C(2)–Au^{I}	111.7(2)
P–C(11)–C(12)	121.9(4)	P–C(11)–C(16)	118.2(4)
C(12)–C(11)–C(16)	119.9(5)	C(11)–C(12)–C(13)	120.3(5)
C(12)–C(13)–C(14)	120.2(5)	C(13)–C(14)–C(15)	120.6(6)
C(14)–C(15)–C(16)	119.4(6)	C(11)–C(16)–C(15)	119.6(5)
P–C(21)–C(22)	122.0(4)	P–C(21)–C(26)	120.0(4)
C(22)–C(21)–C(26)	118.0(5)	C(21)–C(22)–C(23)	121.1(5)
C(22)–C(23)–C(24)	120.5(5)	C(23)–C(24)–C(25)	120.0(5)
C(24)–C(25)–C(26)	119.9(5)	C(21)–C(26)–C(25)	120.5(5)

Symmetry operator: I 0.5 − *x*, 0.5 − *y*, −*z*.

$[\{Au(CH_2)_2PPh_2\}_2L_2]X'_2$ (X′ = ClO_4, L = tht **5** *or* PPh_3 **6**; X′ = NO_3, L = PMe_3 **7**). To a solution of $[\{Au(CH_2)_2PPh_2\}_2Cl_2]$[4] (0.0891 g, 0.1 mmol) in dichloromethane (20 cm^3) was added $[Ag(OClO_3)(tht)]$ (0.0591 g, 0.2 mmol), $[Ag(OClO_3)(PPh_3)]$[24] (0.0939 g, 0.2 mmol) or $[Ag(ONO_2)(PMe_3)]$ (0.0492 g, 0.2 mmol) and the mixture was stirred for 2 h. The AgCl was filtered off and the solution was evaporated to *ca.* 5 cm^3; addition of diethyl ether (20 cm^3) gave complexes **5**–**7**. NMR (see also Table 1): **5**, ^{1}H, δ 7.7–7.31 (m, 20 H, Ph), 2.99 (m, 8 H, SCH_2) and 1.96 (m, 8 H, CH_2); **6**, ^{1}H, δ 7.5–7.3 (m, 50 H, Ph); ^{31}P, δ 31.6 [t, PPh_3, *J*(PP) 27.9 Hz]; **7**, ^{1}H, δ 7.75–7.51 (m, 20 H, Ph) and 1.40 ('t', 18 H, Me, separation of outer peaks 7.8 Hz); ^{31}P, δ −1.18 [t, PMe_3, *J*(PP) 37.9 Hz].

$[\{Au(CH_2)_2PPh_2\}_2X_2]$ [X = Br **8**, SCN **9** *or* $S_2CN(CH_2Ph)_2$ **10**]. To a solution of complex **5** (0.1196 g, 0.1 mmol) in dichloromethane (20 cm^3) was added a solution of KBr (0.0357 g, 0.3 mmol), KSCN (0.0292 g, 0.3 mmol) or $Na[S_2CN(CH_2Ph)_2]$ (0.0886 g, 0.3 mmol) in water (20 cm^3) and the mixture was stirred for 15 min. The dichloromethane layer was removed by using a separating funnel and dried with anhydrous magnesium sulphate (1–2 g). The filtered solution was evaporated to *ca.* 5 cm^3 and addition of hexane (20 cm^3) led to the precipitation of complexes **8**–**10**. Proton NMR (see also Table 1): **9**, δ 7.56–7.38 (m, 20 H, Ph); **10**, δ 7.63–7.23 (m, 40 H, Ph) and 5.21 (s, 8 H, CH_2).

$[\{Au(CH_2)_2PPh_2\}_2L'_2][ClO_4]_2$ (L′ = py **11**, $AsPh_3$ **12** *or* $SbPh_3$ **13**). A mixture of complex **5** (0.1196 g, 0.1 mmol) and L′ [L′ = py (2 cm^3 of a solution 0.1 mol dm^{-3} in hexane), $AsPh_3$ (0.0612 g, 0.2 mmol) or $SbPh_3$ (0.0706 g, 0.2 mmol)] in dichloromethane (20 cm^3) was stirred for 15 min. Partial concentration of the solution to *ca.* 5 cm^3 and addition of diethyl ether (20 cm^3) led to precipitation of complexes **11**–**13**. Proton NMR (see also Table 1): **11**, δ 8.17–7.4 (m, 30 H, Ph and py); **12**, δ 7.55–7.19 (m, 50 H, Ph); **13**, δ 7.55–7.28 (m, 50 H, Ph).

X-Ray Structure Determination of Compound **6**.—*Crystal data.* $C_{64}H_{58}Au_2Cl_2O_8P_4$, *M* = 1543.8, monoclinic, space group $P2_1/a$, *a* = 23.07(2), *b* = 12.90(1), *c* = 24.61(1) Å, β =

116.01(6)°, U = 6588 Å^3, Z = 4, D_c = 1.56 Mg m^{-3}, F(000) = 3032, λ(Mo-Kα) = 0.710 69 Å, μ = 4.7 mm^{-1}, T = −95 °C.

Data collection and reduction. A Siemens R3 diffractometer with monochromated Mo-Kα radiation and an LT-2 low-temperature attachment was used. A yellow prism 0.55 × 0.45 × 0.25 mm was mounted in inert oil and transferred to the cold gas stream. 11 339 Intensities were registered to $2\theta_{max}$ 50°. Averaging equivalents gave 11 069 unique reflections, of which 7589 with $F > 4\sigma(F)$ were used for all calculations (program system Siemens SHELXTL PLUS). Cell constants were refined from setting angles of 46 reflections in the range 2θ 20–22°. An absorption correction was applied using DIFABS[25] (transmissions 0.85–1.21).

Structure solution and refinement. The structure was solved by direct methods and extended by difference syntheses. Atoms Au, P, Cl and O were refined anisotropically. The phenyl groups were refined isotropically with idealised geometry. Methylene hydrogens were included using a riding model. The final R value was 0.064, with R' 0.066. The weighting scheme was $w^{-1} = \sigma^2(F) + gF^2$, with g 0.001; 281 parameters, S 2.1; maximum $\Delta/\sigma < 0.001$, maximum Δρ 3.5 e Å^{-3}. Final atomic coordinates are given in Table 2, with derived bond lengths and angles in Table 3.

X-Ray Structure Determination of Compound **8**.—*Crystal data.* $C_{28}H_{28}Au_2Br_2P_2$, M = 980.2, monoclinic, space group $C2/c$, a = 13.173(4), b = 12.302(4), c = 17.359(5) Å, β = 103.09(2)°, U = 2740 Å^3, Z = 4, D_c = 2.38 Mg m^{-3}, F(000) = 1816, μ(Mo-Kα) = 13.7 mm^{-1}, T = −95 °C.

Data collection and reduction. As for compound **6**, with the following differences: orange prism 0.7 × 0.3 × 0.2 mm; 4845 reflections, 2420 independent (R_{int} 0.024), 2152 with $F > 4\sigma(F)$; transmission 0.86 − 1.32.

Structure solution and refinement. Heavy-atom method with subsequent anisotropic refinement of all non-H atoms; H atoms with riding model. R 0.023, R' 0.023, g 0.0002, 154 parameters, S 1.2, maximum Δ/σ 0.001, maximum Δρ 1 e Å^{-3}. Final atom coordinates are given in Table 4, with derived bond lengths and angles in Table 5.

Additional material for both structures available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the Direccion General de Investigación Científica y Técnica (no. PB88-0075) and the Fonds der Chemischen Industrie for financial support.

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Received 30*th July* 1990; *Paper* 0/03474F