Gold(I) Complexes of Unidentate and Bidentate Phosphorus-, Arsenic-, Antimony-, and Sulphur-donor Ligands

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Complexes of gold(I) with a variety of unidentate and potentially chelating P-, As-, Sb-, and S-donor ligands have been characterised by analysis, ^{1}H n.m.r., i.r., and u.v.–visible spectroscopy, and electrical conductivity. In the majority of cases, the gold atom is two co-ordinate, [AuX(L)] or [XAu(L'–L')AuX] (L = unidentate ligand, L'–L' = bidentate ligand, X = Cl, Br, or SCN), but a few examples of probable three-co-ordination have been found, [AuXL$_2$] or [AuX(L'–L')]. With bidentate ligands, inflexibility of the backbone seems to be the key factor in promoting chelation. The ease of formation of cationic complexes [AuL$_2$]$^+$ is shown to depend on the polarity of the solvent.

In the majority of its complexes gold(I) is two-co-ordinate. Some examples of three- and even four-co-ordination have been reported,[1–12] but the factors which lead to the adoption of the higher co-ordination numbers are not understood. We have therefore undertaken a wide-ranging investigation of the co-ordination chemistry of gold(I) with a variety of uni- and bi-dentate ligands, and report here some complexes with Group 5 and S-donor ligands. We have recently published ^{197}Au Mössbauer data for some of these complexes.[9]

EXPERIMENTAL

Infrared, ^{1}H n.m.r., and electronic spectra were obtained using Perkin-Elmer 621, Hitachi–Perkin-Elmer R20, and Beckman Acta MIV spectrometers respectively. Microanalyses were carried out by the Analytical Laboratory of this Department; the results are presented in Table 1. Typical preparative procedures for the various types of complex are given below.

Chloro(triphenylphosphine)gold(I).—Sodium tetrachloroaurate(III) (3.97 g, 10 mmol) was dissolved in a 1 : 1 mixture of acetone and ethanol (30 cm^3) and triphenylphosphine (5.22 g, 20 mmol) in chloroform (30 cm^3) was added with stirring. The solution became warm, the yellow colour disappeared, and a white precipitate formed. After filtration, reduction in volume (to *ca.* 10 cm^3), and cooling in the refrigerator, white crystals were formed.

Complexes of this type were generally obtained in high yield (>90%) and were analytically pure. Metathesis with lithium bromide or potassium thiocyanate was carried out in hot ethanol.

Chloro(triphenylstibine)gold(I).—All manipulations of gold(I) solutions were carried out in darkened apparatus. Sodium tetrachloroaurate(III) (1.0 g, 2.5 mmol) in acetone (30 cm^3) was treated with sulphur dioxide until complete decolorisation had occurred. The solution was cooled to −78 °C, and triphenylstibine (0.88 g, 2.2 mmol) in chloroform (20 cm^3) was added dropwise. The solution was filtered and concentrated under reduced pressure, keeping the temperature below 0 °C, to give white crystals which were stored in the dark.

Chlorobis(triphenylphosphine)gold(I).—To [AuCl(PPh$_3$)] (0.5 g, 1 mmol) in acetone (20 cm^3) was added with stirring triphenylphosphine (1.05 g, 4.0 mmol) in acetone (30 cm^3). The solution was concentrated under reduced pressure to obtain white crystals of the product.

μ-[1,2-*Bis(diphenylphosphino)ethane*]-*bis*[*chlorogold*(I)].—Sodium tetrachloroaurate(III) (2.0 g, 5.0 mmol) in ethanol (30 cm^3) was treated with dppe (2.0 g, 5.0 mmol) in chloroform (20 cm^3). The solution became colourless and deposited a white solid which was filtered off. The filtrate was concentrated to *ca.* 10 cm^3 and cooled, when the white *complex* crystallised out.

Bromo- and thiocyanato-complexes were obtained by treating the gold(III) solution with 4—5 mol equivalents of lithium bromide or potassium thiocyanate before addition of the ligand.

Bis(methyldiphenylphosphine)gold(I) *Perchlorate.*—To a solution of the complex [AuCl(PMePh$_2$)] (0.43 g, 1.0 mmol) in acetonitrile (20 cm^3) was added silver perchlorate (0.21 g, 1.0 mmol) in acetone (15 cm^3) followed by PMePh$_2$ (0.20 g, 1.0 mmol) in acetonitrile (10 cm^3). The white precipitate which formed rapidly was filtered off and the filtrate was concentrated to obtain the *complex* as white crystals.

RESULTS

Unidentate Ligands.—In a minor variation of Levi Malvano's classical method,[13] sodium tetrachloroaurate(III) reacts with 2 mol equivalents of a tertiary phosphine or arsine to give the complexes [AuCl(L)] from which the corresponding bromo- and thiocyanato-complexes are obtained by metathesis. A previous report shows that gold(I) complexes of tertiary stibines are difficult to prepare by this method.[14] We find that a better procedure is to reduce the gold(III) starting material with sulphur dioxide before adding a slight deficiency of the ligand. The stibine complexes are all extremely light- and heat-sensitive.

All the complexes are non-conductors in nitromethane, and the i.r. spectra of the solids show bands due to the neutral ligands, Au–X stretching modes, and, for thiocyanates, C–N and C–S stretching modes (Table 2). In addition, for the phosphine complexes, bands appear in the region 350—390 cm^{-1} which are absent in the spectra of the corresponding arsine complexes; these are presumably Au–P stretching modes.[15,16] The Au–Cl stretching bands show shoulders to lower frequency (*ca.* 5 cm^{-1} from the main band) due to ^{37}Cl.[17] The spectra of the thiocyanates indicate bonding through the sulphur atom.[18,19] The electronic spectra show, in addition to bands due to the aromatic ligands, a single band presumably of the gold-to-ligand charge-transfer or 5*d*—6*s*(σ*) type.[20]

In several cases bis(ligand) complexes, [AuXL$_2$], were prepared by reaction of [AuX(L)] with an excess of the ligand in acetone. The i.r. spectra showed the gold–halogen stretching modes to be of lower frequency than those of [AuX(L)], suggesting three-co-ordination for the former. All the complexes were non-conductors in nitro-

TABLE 1

Analytical data (%)

Compound	C	H	Halogen	N(S)
$[AuCl(PPh_3)]$	43.5 (43.8)	3.0 (3.1)		
$[AuBr(PPh_3)]$	39.6 (40.1)	2.5 (2.8)		
$[AuCl(PMePh_2)]$	35.8 (36.1)	3.1 (3.0)	9.0 (8.2)	
$[AuBr(PMePh_2)]$	32.9 (32.7)	2.9 (2.7)	16.3 (16.8)	
$[Au(SCN)(PMePh_2)]$	37.0 (36.9)	2.6 (2.9)		2.9 (3.1)
$[AuCl(PEtPh_2)]$	38.0 (37.6)	3.4 (3.4)		
$[AuBr(PEtPh_2)]$	33.6 (34.2)	3.1 (3.0)	16.7 (16.3)	
$[Au(SCN)(PEtPh_2)]$	37.5 (38.4)	3.3 (3.2)		3.0 (3.0)
$[AuCl(PMe_2Ph)]$	25.8 (25.9)	3.3 (3.0)	9.6 (9.6)	
$[AuBr(PMe_2Ph)]$	22.9 (23.1)	2.3 (2.6)	18.6 (19.3)	
$[AuCl(PEt_2Ph)]$	30.4 (30.1)	3.7 (3.8)	9.0 (8.9)	
$[AuCl(PEt_3)]$	20.3 (20.5)	4.1 (4.3)	10.4 (10.1)	
$[AuCl\{P(C_6H_4Me\text{-}\mathit{p})_3\}]$	47.9 (47.0)	3.9 (3.9)	6.6 (6.7)	
$[AuBr\{P(C_6H_4Me\text{-}\mathit{p})_3\}]$	43.5 (43.4)	3.7 (3.6)	14.0 (13.8)	
$[AuCl\{P(CH_2Ph)_3\}]$	48.0 (47.2)	3.9 (3.4)	7.2 (6.7)	
$[AuCl(PPh_3)_2]$	57.0 (57.1)	4.0 (4.1)	4.7 (4.7)	
$[Au(SCN)(PPh_3)_2]$	56.4 (57.0)	4.0 (3.9)		2.0 (1.8)
$[AuCl(AsPh_3)]$	39.5 (40.1)	2.7 (2.8)	6.5 (6.6)	
$[AuBr(AsPh_3)]$	37.1 (37.1)	2.8 (2.6)	13.8 (13.7)	
$[Au(SCN)(AsPh_3)_2]$	51.5 (51.2)	4.1 (3.5)		1.7 (1.6)
$[AuCl(SbPh_3)]$	38.0 (37.0)	3.6 (2.7)	6.2 (6.1)	
$[(AuBr)_2(\mathit{cis}\text{-}Ph_2PCH{=}CHPPh_2)]$	31.7 (32.8)	2.6 (2.3)	16.3 (16.8)	
$[(AuBr)_2(\mathit{cis}\text{-}Ph_2AsCH{=}CHAsPh_2)]$	30.8 (30.1)	3.5 (2.1)	15.9 (15.4)	
$[AuBr(\mathit{cis}\text{-}Ph_2PCH{=}CHPPh_2)]$	46.8 (46.3)	3.5 (3.5)	11.1 (11.8)	
$[\{Au(SCN)\}_2(\mathit{cis}\text{-}Ph_2PCH{=}CHPPh_2)]$	36.6 (37.1)	2.5 (2.5)		3.0 (3.1)
$[Au(SCN)(\mathit{cis}\text{-}Ph_2AsCH{=}CHAsPh_2)]$	43.4 (43.8)	3.0 (3.0)		1.9 (1.6)
$[AuCl(\mathit{trans}\text{-}Ph_2PCH{=}CHPPh_2)]$	50.9 (49.7)	3.4 (3.5)	5.4 (5.7)	
$[(AuCl)_2\{MeS(CH_2)_2SMe\}]$	8.5 (8.2)	1.9 (1.7)	12.1 (12.3)	11.2 (10.9) S
$[(AuCl)_2\{MeS(CH_2)_3SMe\}]$	10.2 (10.0)	2.1 (2.0)	11.9 (11.8)	10.5 (10.6) S
$[(AuCl)_2\{EtS(CH_2)_2SEt\}]$	12.0 (11.7)	2.3 (2.3)	11.8 (11.5)	10.4 (10.4) S
$[(AuCl)_2\{PhS(CH_2)_2SPh\}]$	23.0 (23.6)	2.0 (2.0)	10.2 (10.0)	8.4 (9.0) S
$[(AuCl)_2\{PhS(CH_2)_5SPh\}]$	27.4 (27.1)	2.9 (2.7)		8.5 (8.5) S
$[(AuCl)_2\{PhS(CH_2)_8SPh\}]$	30.7 (30.2)	3.5 (3.3)	8.6 (8.9)	8.0 (8.0) S
$[(AuCl)_2\{PhS(CH_2)_{10}SPh\}]$	31.7 (32.1)	3.9 (3.7)	8.1 (8.6)	7.5 (7.8) S
$[AuCl_3(PPh_3)]$	37.4 (38.2)	3.0 (2.7)		
$[AuBr_3(PPh_3)]$	31.1 (30.9)	2.3 (2.2)	34.4 (34.3)	
$[AuCl_2Br(PPh_3)]$	34.8 (35.4)	2.7 (2.5)	11.0 (11.6) Cl 13.8 (13.1) Br	
$[AuClBr_2(PPh_3)]$	32.9 (33.0)	2.4 (2.3)	4.9 (5.4) Cl 23.9 (24.4) Br	
$[AuCl_3(PMePh_2)]$	30.4 (31.0)	2.6 (2.6)	21.8 (21.2)	
$[AuBr_3(PMePh_2)]$	24.6 (24.5)	2.1 (2.0)	37.4 (37.7)	
$[AuCl_3(PEtPh_2)]$	32.0 (32.5)	3.0 (2.9)	20.9 (20.6)	
$[AuBr_3(PEtPh_2)]$	25.7 (25.8)	2.5 (2.3)	36.3 (36.9)	
$[AuBr_3(PMe_2Ph)]$	17.0 (16.7)	2.0 (1.9)	41.1 (41.7)	
$[AuCl_3(PEt_2Ph)]$	25.5 (25.6)	3.5 (3.2)	22.6 (22.7)	
$[AuBr_3(PEt_2Ph)]$	19.9 (20.1)	2.5 (2.5)	38.4 (39.8)	
$[AuCl\{Sb(C_6H_4Me\text{-}\mathit{o})_3\}]$	40.8 (40.2)	3.6 (3.4)	5.6 (5.6)	
$[AuBr\{Sb(C_6H_4Me\text{-}\mathit{m})_3\}_2]$	47.5 (47.3)	4.1 (3.9)	7.7 (7.5)	
$[AuCl\{P(CH_2Ph)_3\}_2]$	59.3 (60.4)	5.0 (4.3)	4.7 (4.3)	
$[Au(PPh_3)_2][ClO_4]$	52.6 (52.7)	4.0 (3.7)	4.5 (4.3)	
$[Au(PMePh_2)_2][ClO_4]$	44.1 (44.8)	3.8 (4.3)	5.6 (5.1)	
$[Au(PEtPh_2)_2][ClO_4]$	47.3 (46.4)	4.2 (4.2)	5.3 (4.9)	
$[Au(PEt_2Ph)_2][ClO_4]$	38.9 (38.2)	4.8 (4.8)	5.3 (5.6)	
$[Au(PMePh_2)(PMe_2Ph)][ClO_4]$	40.1 (39.7)	4.1 (4.1)	5.6 (5.6)	
$[(AuBr)_2(Ph_2PCH_2PPh_2)]$	32.0 (32.0)	2.6 (2.4)	16.8 (17.1)	
$[\{Au(SCN)\}_2(Ph_2PCH_2PPh_2)]$	36.5 (36.2)	2.5 (2.5)		2.9 (3.1)
$[(AuCl)_2\{Ph_2P(CH_2)_2PPh_2\}]$	35.4 (36.1)	2.7 (2.8)	8.4 (8.2)	
$[\{Au(SCN)\}_2\{Ph_2P(CH_2)_2PPh_2\}]$	37.0 (37.0)	2.6 (2.6)		2.8 (3.1)
$[(AuCl)_2\{Ph_2P(CH_2)_6PPh_2\}]$	40.4 (39.2)	3.7 (3.5)	7.8 (7.7)	
$[(AuBr)_2\{Ph_2P(CH_2)_6PPh_2\}]$	36.5 (35.7)	3.4 (3.2)	15.1 (15.9)	
$[(AuCl)_2\{Ph_2P(CH_2)_8PPh_2\}]$	40.7 (40.6)	3.8 (3.8)	7.6 (7.5)	
$[(AuBr)_2\{Ph_2P(CH_2)_8PPh_2\}]$	37.2 (37.1)	3.9 (3.5)	14.6 (15.4)	
$[(AuCl)_2\{Ph_2P(CH_2)_{10}PPh_2\}]$	42.0 (41.9)	4.2 (4.1)	7.4 (7.3)	
$[(AuCl)_2\{Ph_2P(CH_2)_{12}PPh_2\}]$	43.8 (43.1)	4.4 (4.4)	7.0 (7.1)	
$[(AuBr)_2\{Ph_2P(CH_2)_{12}PPh_2\}]$	39.6 (39.6)	3.8 (4.0)	14.2 (14.6)	
$[(AuCl)_2(\mathit{cis}\text{-}Ph_2PCH{=}CHPPh_2)]$	35.6 (36.2)	2.7 (2.6)	8.4 (8.3)	
$[(AuCl)_2(\mathit{cis}\text{-}Ph_2AsCH{=}CHAsPh_2)]$	33.2 (32.9)	2.4 (2.3)	8.1 (7.5)	
$[AuCl_3\{P(C_6H_4Me\text{-}\mathit{p})_3\}]$	41.7 (41.5)	2.9 (3.5)	16.3 (17.5)	
$[AuBr_3\{P(C_6H_4Me\text{-}\mathit{p})_3\}]$	34.6 (34.0)	3.0 (2.8)	30.7 (32.4)	
$[AuCl_3(AsPh_3)]$	34.9 (35.4)	2.6 (2.5)	17.9 (17.5)	
$[AuBr_3(AsPh_3)]$	29.9 (29.1)	2.5 (2.0)	26.0 (32.3)	

methane, but $[AuCl(PPh_3)_2]$ and $[AuCl\{P(CH_2Ph)_3\}_2]$ showed considerable conductivity in acetonitrile.

The low conductivities in nitromethane could be due either to lack of ionic dissociation or strong ion-pair formation [equation (1)] or to loss of ligand and reversion to the non-ionic two-co-ordinate complex [equation (2)]. The latter explanation has been suggested for the low conductivity of triphenylphosphine derivatives.[5] To distinguish between these possibilities and to obtain more information on the

$$[AuL_2]^+ + Cl^- \rightleftharpoons [AuClL_2] \qquad (1)$$

$$[AuL_2]Cl \rightleftharpoons [AuCl(L)] + L \qquad (2)$$

occurrence of cationic complexes, the effect of adding the ligand to solutions of $[AuCl(L)]$ in various solvents was examined. With the complex $[AuCl(PMe_2Ph)]$ in methanol, ethanol, acetone, or nitromethane, the addition of dimethylphenylphosphine gave only slight increases in conductivity. When 1 mol equivalent of the phosphine had been added the conductivity had risen to 10—15% of the value expected for 1 : 1 electrolytes. The conductivity continued to rise slowly as more ligand was added, but even after the addition of 5 mol equivalents the conductivities were only 20—40% of the value for a 1 : 1 electrolyte, except in the case in acetone for which there was a steady rise in conductivity to the full-dissociation value. However, when acetonitrile was used the conductivity increased linearly as the ligand was added, reaching a constant value after the addition of 1 mol equivalent which corrresponded to that for a 1 : 1 electrolyte. Thus, in this case, a clean stoicheiometric reaction occurs, suggesting that acetonitrile might be a suitable solvent for preparative work (see below). Similar results were found when the ligand added was different from that already bonded to the gold, suggesting that mixed-ligand complexes might be obtainable. In acetonitrile, the addition of 1 mol equivalent of ligand always gave highly conducting solutions, although whenever triphenylphosphine was used the conductivities were significantly lower.

TABLE 2

Physical data for gold(I) complexes of unidentate ligands

	I.r. spectra [a] (cm^{-1})					
Complex	ν(Au–X)	ν(Au–P)	ν(C–N)	ν(C–S)	$10^{-3}E$ [b] / cm^{-1}	$\Lambda(MeNO_2)$ / $ohm^{-1}\ cm^2\ mol^{-1}$
$[AuCl(PPh_3)]$	325				40.1	3
$[AuCl(PPh_3)_2]$	321	365			39.4	10 [c]
$[AuCl(PMePh_2)]$	314	359			40.3	6
$[AuCl(PEtPh_2)]$	319	361			39.9	4
$[AuCl(PMe_2Ph)]$	310	370			40.6	5
$[AuCl(PEt_2Ph)]$	307	381			40.3	4
$[AuCl(PEt_3)]$	302					6
$[AuCl\{P(C_6H_4Me\text{-}p)_3\}]$	321					5
$[AuCl\{P(CH_2Ph)_3\}]$	317					7
$[AuCl\{P(CH_2Ph)_3\}_2]$	315	371				12 [d]
$[AuCl(PMe_2Ph)(PPh_3)_2]$	302					8
$[AuCl(AsPh_3)]$	319				40.6	4
$[AuCl\{Sb(C_6H_4Me\text{-}o)_3\}]$	321				41.2, 40.6	4
$[AuBr(PPh_3)]$	229				39.9	3
$[AuBr(PMePh_2)]$	211	363			40.1	5
$[AuBr(PEtPh_2)]$	215				40.0	5
$[AuBr(PMe_2Ph)]$	209				40.3	6
$[AuBr(PEt_2Ph)]$	210				40.4	
$[AuBr\{PC_6H_4Me\text{-}p)_3\}]$	219					4
$[AuBr(AsPh_3)]$	225				40.4	6
$[AuBr\{Sb(C_6H_4Me\text{-}o)_3\}]$	214					7
$[Au(SCN)(PPh_3)_2]$	303		2 117	730		5 [e]
$[Au(SCN)(PMePh_2)]$	291		2 115	721		7
$[Au(SCN)(PEtPh_2)]$	292	367	2 117	723		7
$[Au(SCN)(PMe_2Ph)]$	291		2 111	720		
$[Au(SCN)(PEt_2Ph)_2]$	304	368	2 118	726		6 [f]
$[Au(SCN)(AsPh_3)_2]$	302		2 119	736		9

[a] As Nujol mulls. [b] Electronic spectra for 10^{-4} mol dm^{-3} solutions in CH_2Cl_2 or $CHCl_3$. [c] 91 $ohm^{-1}\ cm^2\ mol^{-1}$ in MeCN. [d] 80 $ohm^{-1}\ cm^2\ mol^{-1}$ in MeCN. [e] 11 $ohm^{-1}\ cm^2\ mol^{-1}$ in MeCN. [f] 9 $ohm^{-1}\ cm^2\ mol^{-1}$ in MeCN.

Using acetonitrile as solvent, it was possible to prepare bis(ligand) complexes by stoicheiometric reaction between the mono(ligand) complex and the ligand, but attempts to obtain mixed-ligand complexes met with some difficulty. Frequently the product obtained was an oil which was difficult to crystallise. Treatment with ethanol and diethyl ether yielded solid products, but these were not mixed-ligand complexes. For example, when $[AuCl(PMePh_2)]$ was treated with PMe_2Ph in acetonitrile, followed by precipitation with ether, the precipitate was $[Au(PMePh_2)_2]Cl$, and $[Au(PMe_2Ph)_2]Cl$ was left in solution. When $[AuCl(PPh_3)]$ was the starting material, the product isolated was the uncharged substitution derivative, in which the phosphine had been replaced rather than the chloride ion [equation (3)]. The conductivity measurements showed that ionic species were being formed in solution and their isolation was attempted by precipitation with a suitable anion. Use of tetraphenylborate and hexafluorophosphate

$$[AuCl(PPh_3)] + PMe_2Ph \longrightarrow [AuCl(PMe_2Ph)] + PPh_3 \qquad (3)$$

was unsuccessful but perchlorate, added as the ammonium or silver salt, gave clean products. With silver perchlorate it was necessary to exclude light to prevent decomposition of silver chloride and, subsequently, of the gold complex. The best procedure was to mix acetonitrile solutions of the starting complex and silver perchlorate and then to add a slight excess of the appropriate ligand. Precipitation of silver chloride did not begin until the ligand was added. In this way several cationic complexes were prepared, some containing two different ligands. Conductivity measurements indicated that these compounds were ionised in acetonitrile solution, and the i.r. spectra of the solids (Table 3) showed that the perchlorate anions were not coordinated. The spectra of the symmetrical complexes

TABLE 3

Infrared and conductivity data for ionic gold(I) complexes

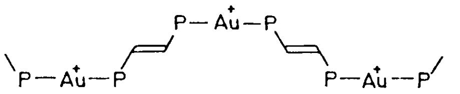
Complex	I.r. spectra (cm^{-1}) ν(Au–P)	ν(Cl–O)	ν(Cl–O)	Λ(MeCN) * ohm^{-1} cm^2 mol^{-1}
[Au(PPh$_3$)$_2$][ClO$_4$]	365	1 075	620	136
[Au(PMePh$_2$)$_2$][ClO$_4$]	350	1 066	621	158
[Au(PEtPh$_2$)$_2$][ClO$_4$]	373	1 081	622	161
[Au(PEt$_2$Ph)$_2$][ClO$_4$]	381	1 072	619	161
[Au(PMe$_2$Ph)(PMePh$_2$)][ClO$_4$]	355, 341	1 076	621	162

* For 10^{-4} mol dm^{-3} solutions.

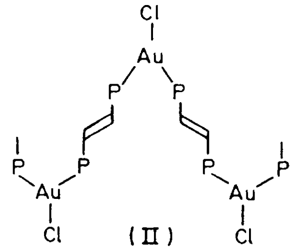
showed a single Au–P stretching mode, as expected for a linear P–Au–P arrangement, while the mixed-ligand complexes showed two such bands. Two-co-ordination by phosphine ligands was confirmed by the ^{197}Au Mössbauer spectra.[9]

Bidentate Ligands.—Reaction between equimolar amounts of [AuX$_4$]$^-$ (X = Cl, Br, or SCN) and bidentate phosphines or thioethers gave, in most instances, white complexes containing two AuX units per ligand. The i.r. spectra (Table 4) indicated that P=O or As=O groups were absent, and that the SCN groups were *S*-bonded. Bands assigned to Au–X, Au–P, and Au–S stretching modes were visible. All the diphosphine complexes were non-conductors in nitromethane. These materials can only be formulated as conventional, linear, two-co-ordinate gold(I) complexes with the bidentate ligand bridging between the gold atoms: [XAu(L'–L')AuX].

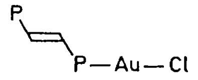
In four cases 1 : 1 complexes were obtained, for which several structures are possible. Unfortunately, none of the complexes was sufficiently soluble for molecular-weight determination. For [AuCl(*trans*-Ph$_2$PCH=CHPPh$_2$)] an i.r. band at 331 cm^{-1} shows the presence of an Au–Cl bond, eliminating the polymeric ionic structure (I). (In this and the following structures, phenyl groups on the phosphorus atoms are omitted for clarity.) The similarity of this value to that of the 1 : 1 complexes of ligands with comparable donor groups suggests that the three-co-ordinate polymeric structure (II) is unlikely and that the most probable configuration is a monomeric two-co-ordinate structure, (III), in which one phosphine group is unco-ordinated. The ^{1}H n.m.r. spectrum showed only a single vinylic proton resonance group close to the much stronger broad signal for the phenyl groups; it is possible that another resonance could have been obscured. For complexes involving ligands with *cis*-E–CH=CH–E groups (E = PPh$_2$ or AsPh$_2$) several structures are also possible. In addition to poly-



(I)



(II)



(III)

TABLE 4

Physical data for gold(I) complexes of bidentate ligands

Complex	I.r. spectra (cm^{-1}) ν(Au–X)	ν(Au–L)	ν(C–N)	ν(C–S)	10^{-3}$E_{max.}$ cm^{-1}	Λ(MeNO$_2$) ohm^{-1} cm^2 mol^{-1}
[(AuBr)$_2$(Ph$_2$PCH$_2$PPh$_2$)]	231	365			40.5	4
[{Au(SCN)}$_2$(Ph$_2$PCH$_2$PPh$_2$)]	292	361	2 115	711		7
[(AuCl)$_2${Ph$_2$P(CH$_2$)$_2$PPh$_2$}]	321				41.0	6
[{Au(SCN)}$_2${Ph$_2$P(CH$_2$)$_2$PPh$_2$}]	288		2 117	709	40.3	5
[AuCl(*trans*-Ph$_2$PCH=CHPPh$_2$)]	331	360			39.8	5
[(AuCl)$_2$(*cis*-Ph$_2$PCH=CHPPh$_2$)]	329	371			41.3	3
[AuBr(*cis*-Ph$_2$PCH=CHPPh$_2$)]	218				40.2	3
[(AuBr)$_2$(*cis*-Ph$_2$PCH=CHPPh$_2$)]	231	366				7
[{Au(SCN)}$_2$(*cis*-Ph$_2$PCH=CHPPh$_2$)]	291	362	2 112	714		6
[(AuCl)$_2$(*cis*-Ph$_2$AsCH=CHAsPh$_2$)]	325				41.5	6
[(AuBr)$_2$(*cis*-Ph$_2$AsCH=CHAsPh$_2$)]	229					6
[{Au(SCN)}$_2$(*cis*-Ph$_2$AsCH=CHAsPh$_2$)]	303		2 115	711	40.2	4
[(AuCl)$_2${Ph$_2$P(CH$_2$)$_6$PPh$_2$}]	325	375			40.8	4
[(AuBr)$_2${Ph$_2$P(CH$_2$)$_6$PPh$_2$}]	231	369			40.5	7
[(AuCl)$_2${Ph$_2$P(CH$_2$)$_8$PPh$_2$}]	323	371				6
[(AuBr)$_2${Ph$_2$P(CH$_2$)$_8$PPh$_2$}]	233	370				5
[(AuCl)$_2${Ph$_2$P(CH$_2$)$_{10}$PPh$_2$}]	327	371				5
[(AuCl)$_2${Ph$_2$P(CH$_2$)$_{12}$PPh$_2$}]	322	375				6
[(AuBr)$_2${Ph$_2$P(CH$_2$)$_{12}$PPh$_2$}]	228	368				5
[AuCl{*o*-C$_6$H$_4$(PPh$_2$)$_2$}]	325					7
[(AuCl)$_2${PhS(CH$_2$)$_5$SPh}]	329	343				
[(AuCl)$_2${PhS(CH$_2$)$_8$SPh}]	331	341				
[(AuCl)$_2${PhS(CH$_2$)$_{10}$SPh}]	328	343				
[(AuCl)$_2${MeS(CH$_2$)$_2$SMe}]	327	341				
[(AuCl)$_2${MeS(CH$_2$)$_3$SMe}]	329	339				
[(AuCl)$_2${EtS(CH$_2$)$_2$SEt}]	324	340				
[(AuCl)$_2$(*cis*-EtSCH=CHSEt)]	321	339				

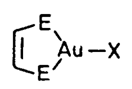
TABLE 5

Physical data for gold(III) complexes

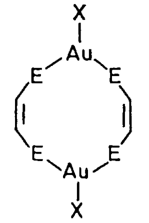
Complex	I.r. spectra (cm^{-1}) ν(LAu–X)	ν(XAu–X)$_{asym}$	ν(Au–P)	$10^{-3}E_{max.}$ [a] cm^{-1}	ε [a] dm^3 mol^{-1} cm^{-1}	$10^{-3}E_{max.}$ [b] cm^{-1}	Λ(MeNO$_2$) ohm^{-1} cm^2 mol^{-1}
[AuCl$_3$(PPh$_3$)]	300	361	370	30.4	1 167	24.3	7
[AuBr$_3$(PPh$_3$)]	215	258		23.7, 29.2	4 313	22.1	6
[AuClBr$_2$(PPh$_3$)]	301	255	371	24.4, 29.1	1 783	22.3	4
[AuCl$_2$Br(PPh$_3$)]	210	360	371				6
[AuCl$_3$(PMePh$_2$)]	298	360	372	30.2	873	24.4	5
[AuBr$_3$(PMePh$_2$)]	208	258	379	27.0, 30.8	5 196	22.4	7
[AuCl$_3$(PEtPh$_2$)]	298	358	371	30.3	1 077	24.6	3
[AuBr$_3$(PEtPh$_2$)]	213	255	369	29.4, 30.1	4 860	22.6	6
[AuCl$_3$(PMe$_2$Ph)]	297	361	370	31.1	1 286	24.9	
[AuBr$_3$(PMe$_2$Ph)]	211	261	367	25.9, 30.9	4 742	23.1	7
[AuCl$_3$(PEt$_2$Ph)]	298	363	371	31.4	1 161	25.2	5
[AuBr$_3$(PEt$_2$Ph)]	210	253	369	26.4, 30.8	4 395	23.8	4
[AuCl$_3${P(C$_6$H$_4$Me-*p*)$_3$}]	301	361	372	29.2	4 182	21.7	6
[AuBr$_3${P(C$_6$H$_4$Me-*p*)$_3$}]	209	259	371	21.1, 23.3	1 421	23.9	7
[AuCl$_3$(AsPh$_3$)]	302	362		29.1	4 411	20.9	6
[AuBr$_3$(AsPh$_3$)]	208	256		25.6, 21.6			

[a] In CHCl$_3$. [c] Reflectance spectrum.

meric and monomeric structures analogous to those for the *trans* ligand, there are monomeric (IV) and dimeric (V) structures involving three-co-ordinate gold. All the complexes show some solubility, albeit small, which suggests that fully polymeric structures analogous to (I) and (II) are not correct. The i.r. spectra show Au–X stretching modes indicating co-ordination of the anion, which also eliminates the ionic structure. The Au–X frequencies are different from those of similar two-co-ordinate complexes but are similar to those of the three-co-ordinate complexes. The ^{1}H n.m.r. spectrum of [Au(SCN)(*cis*-Ph$_2$AsCH=CHAsPh$_2$)] shows only a single vinylic resonance, 0.22 p.p.m. to high field of that for the free ligand. In this case, the signal is well removed from that of the single, sharp phenyl resonance, and there is unlikely to be a further, undetected signal. These observations rule out the unidentate structure but, in the absence of molecular-weight data, we are unable to distinguish between (IV) and (V).



(IV)



(V)

Gold(III) *Complexes*.—The complexes [AuX(L)] (X = Cl or Br) were oxidised in chloroform solution with the stoicheiometric quantity of chlorine or bromine to give the corresponding complexes [AuX$_3$L]. These complexes are nonconductors in nitromethane and are presumably conventional square-planar gold(III) complexes. The far-i.r. spectra (Table 3) show two bands assignable as Au–X stretching modes, separated by 50—60 cm^{-1}. The lower-frequency band in each case corresponds to the stretching of the Au–X bond *trans* to the neutral ligand, and the higher-frequency band to the asymmetric stretching mode of the linear X–Au–X system. The symmetric mode is generally not visible.[21] When attempts were made to oxidise [AuCl(L)] with bromine or [AuBr(L)] with chlorine, the products isolated were usually mixtures of the trichloro- and tribromo-complexes in appropriate proportions. Only when L = PPh$_3$ were mixed halogeno-complexes isolated, the i.r. spectra of which clearly indicated *trans* configuration. Mann and Purdie[22] report stereospecific *trans* addition, but Williamson and Baird[17] obtained *cis–trans* mixtures and also found ready halogen exchange.

DISCUSSION

Gold(III) reacts with tertiary phosphines or with thioethers to give gold(I) complexes and the ligand oxide. With bidentate ligands there was no evidence of 1 : 1 complexes with half-oxidised ligands, *i.e.* reaction (4) occurs in preference to (5).

$$2\mathrm{L'{-}L'} + 2[\mathrm{AuX_4}]^- \longrightarrow [\mathrm{XAu(L'{-}L')AuX}] + \mathrm{X_2L'{-}L'X_2} \quad (4)$$

$$\not\longrightarrow 2[\mathrm{AuX(L'{-}L'X_2)}] \quad (5)$$

In the majority of cases, with uni- or bi-dentate ligands, the complexes obtained here are conventional two-co-ordinate gold(I) complexes of the types [AuX(L)], [AuX(L′–L′)], or [XAu(L′–L′)AuX]. For X = Cl or Br the i.r. data show the normal *trans*-influence series. The Au–X stretching mode seems not to be coupled with the Au–L mode, since the frequencies are insensitive to changes in the mass of L. When X = SCN the anion is bonded through sulphur, as would be expected for a soft metal with no steric constraints from *cis* ligands.[19] With unidentate ligands some 1 : 2 complexes have been obtained most of which appear to contain two-co-ordinate gold, especially when the anion is not a good ligand (*e.g.* ClO$_4^-$). These complexes appear to be ionic in solution and in the solid state. When one of the ligands is PPh$_3$ the electrical conductivities of the solutions are somewhat lower than normal for 1 : 1 electrolytes. This could be due to the size of the ligand, but is more probably caused by disproportionation reactions of the type observed by Muetterties with tri-*p*-tolylphosphine [equation (6)].[6] The perchlorates [AuL(PPh$_3$)][ClO$_4$] (L = PPh$_3$ or PMe$_2$Ph) gave the normal,

$$2[\mathrm{AuL_2}]\mathrm{Cl} \rightleftharpoons [\mathrm{AuL_3}]\mathrm{Cl} + [\mathrm{AuCl(L)}] \quad (6)$$

higher, values. The ^{197}Au Mössbauer spectrum shows that $[Au(PPh_3)_2][ClO_4]$ is ionic in the solid state.

No chloride is liberated from [AuCl(L)] until free ligand is added, when the conductivity rises, but only in acetonitrile solution does a stoicheiometric reaction occur to give the ionic complexes. With the less polar solvents the low conductivity does not necessarily imply lack of co-ordination of the added ligand, since equilibria of the type (7) could be set up. It seems significant, however,

$$[AuClL_2] \rightleftharpoons [AuL_2]Cl \qquad (7)$$

that in order to isolate the compounds $[AuClL_2]$ in these solvents it is necessary to use a 4–5-fold excess of the ligand,[4] which is also necessary to achieve complete ionisation of the chloride. It is likely that the major equilibrium is that of equation (2) which is displaced towards $[AuL_2]Cl$ by strongly solvating media. In acetonitrile, equilibria of type (8) must be rather mobile since, when mixtures of ligands are employed, the product isolated seems to reflect differential solubilities rather than thermodynamic stabilities.

$$2[AuL(L')]^+ \rightleftharpoons [AuL_2]^+ + [AuL'_2]^+ \qquad (8)$$

When the anion is a better ligand than perchlorate, *e.g.* halide or thiocyanate, three-co-ordination may be possible, and several of the complexes $[AuXL_2]$ gave non-conducting solutions. In the absence of molecular-weight data this does not establish a higher co-ordination number, since dissociation may be occurring, but the i.r. spectra demonstrate that the anion is co-ordinated in the solid state. The benzene solvate of $[AuCl(PPh_3)_2]$ is known to be three-co-ordinate in the solid [7] and ^{197}Au Mössbauer data confirm the higher co-ordination number for $[AuX(PPh_3)_2]$ (X = Cl, I, or SCN).[9,10] The Au–X stretching frequency (X = Cl or Br) is slightly lower than for $[AuX(PPh_3)]$, in line with the increase in bond length, *e.g.* the Au–Cl bond distance is 250 pm in $[AuCl(PPh_3)_2]$ but 229 pm in $[AuCl(PPh_3)]$.[7]

Bidentate ligands usually co-ordinate to two separate gold atoms [23-27] but with some ligands 1 : 1 complexes were obtained even in the presence of an excess of gold. In view of the geometry of the ligands involved, these complexes are almost certainly chelated, since all have rigid vinylic or *o*-phenylene backbones which would be conducive to chelation. This geometry would also give a relatively small bond angle at the gold atom, allowing the co-ordination of the anion, as observed. With o-$C_6H_4(ER_2)_2$ (E = P or As), four-co-ordination is reported.[1-3] Similar effects are seen when the bidentate ligand is 2,2′-bipyridyl or 1,10-phenanthroline, when an additional neutral ligand can be co-ordinated to give a three-co-ordinate cation.[10] In the one case where strict comparison can be made, *cis*-$Ph_2AsCH{=}CHAsPh_2$, the chelated three-co-ordinate complex shows the lower Au–Br stretching frequency.

The gold(III) complexes all appear to be conventional square-planar four-co-ordinate complexes. The *trans* influence of the phosphines and arsines is evident in the i.r. data, the gold–halogen stretching frequencies being lower where the halogen is *trans* to the neutral ligand than when *trans* to another halogen. This lower frequency is also lower than that in the corresponding gold(I) complexes, which would not normally be expected. For the triphenylphosphine complexes this observation is in line with the Au–Cl bond lengths: 229 pm in $[AuCl(PPh_3)]$ [7] and 235 pm in $[AuCl_3(PPh_3)]$ (the *trans* Au–Cl bonds are 227 and 228 pm).[28] These observations imply that the *trans* influence is stronger in gold(III) complexes than in gold(I) complexes, which might be expected from the greater covalency anticipated for bonds to the metal in the higher oxidation state. The trend is also consistent with the recent suggestion [29] that *d* orbitals are significant in transmitting the *trans* influence.

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