Novel Ring Compounds of Bidentate Phosphines with Gold(I). Two-, Three-, and Four-co-ordination

Salam Al-Baker and William E. Hill *
Department of Chemistry, Auburn University, Auburn, AL 36849, U.S.A.
Charles A. McAuliffe *
Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

With n-butyldiphenylphosphine and gold(I), salts $[AuBr(PPh_2Bu^n)_x]$ (x = 1 or 2) and $[Au(PPh_2Bu^n)_x]^+$ (x = 2, 3, or 4) are formed in solution and in the solid state. A range of short-chain and long-chain diphosphines (L), $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2, 4, 6, 8, 10, or 12) have been employed to prepare the neutral complexes, $[(AuBr)_2L_x]$ (x = 1 or 2), in which the gold is two-, and three-co-ordinate, respectively, and the cationic compounds $[Au_2L_x][ClO_4]_2$ (x = 2, 3, or 4) in which the gold is two-, three-, and four-co-ordinate. However, it was only possible to isolate the novel $[Au_2L_4][ClO_4]_2$ complexes with the short-chain diphosphines, $Ph_2P(CH_2)_nPPh_2$ (n = 2, 3, or 4). A ^{31}P-{^1H} n.m.r. study employing $Ph_2P(CH_2)_6PPh_2$ and $AuBr_2^-$ at different ratios in CD_2Cl_2 shows the presence of two-, three-, and four-co-ordinate gold, and these species exchange with one another at temperatures > −50 °C. A similar study at −90 °C with the other diphosphines gave similar results, except that three- and four-co-ordination exist in the case of the short-chain ligands $Ph_2P(CH_2)_nPPh_2$ (n = 1 or 2) even at very low ligand:gold ratios.

There has been increasing interest in recent years in the phenomenon of *trans* chelation in square-planar metal complexes, with contributions from the groups of Venanzi[1–4] and Shaw[5–8] and ourselves.[9–13] Venanzi and co-workers[1–4] have shown that *trans* bonding is achieved if the ligand backbone is rigid and of suitable length; Shaw and co-workers[5–8] have concluded that bulky t-butyl groups induce favourable conformational and entropy effects which promote *trans* chelation in complexes such as $[MCl_2L]$ [M = Pd or Pt; L = $Bu^t_2P(CH_2)_nPBu^t_2$, n = 5—10] in which the ligand has a flexible backbone. However, we have shown that the formation of *cis* and *trans* isomers of long-chain flexible diphosphine ligands may be critically dependent on the choice of complex precursor: for example, the use of potassium tetrachloroplatinate gives *cis*-$[PtX_2L]$, while Zeise's salt, $K[PtCl_3(C_2H_4)]$, yields the *trans* analogue.[11]

We have extended our studies to gold(I) complexes. This allows the opportunity to study a metal ion for which two-co-ordination is common[14,15] but for which trigonal-planar three-co-ordination[16] and pseudotetrahedral[17–19] and tetrahedral[20] geometries are also known. Thus, the chemistry of the long-chain bis(phosphine) ligands can be extended to complexes of unusual co-ordination numbers and geometries other than square planar. Venanzi's group[21] have isolated the three-co-ordinate T-shaped complex [AuClL] {L = 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene}.

We report here our studies of the co-ordination of gold(I) to the bis(phosphine) ligands $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2, 4, 6, 8, 10, 12, or 16); we have also employed PPh_2Bu^n as a model unidentate ligand.

Results and Discussion

The diphosphine ligands employed in this study are of the type $Ph_2P(CH_2)_nPPh_2$ (n = 1, dppm; n = 2, dppe; n = 4, dppb; n = 6, dpphx; n = 8, dppo; n = 10, dppd; n = 12, dppdod; n = 16, dpphxd), and two main groups of complexes have been isolated. The complexes $[(AuBr)_2L_x]$ (L = diphosphine; x = 1, 2, or 3) are synthesized by the reaction of appropriate amounts of $[NEt_4][AuBr_2]$ and the ligand in ethanol–dichloromethane, and the complexes $[Au_2L_x][ClO_4]_2$ (x = 2, 3, or 4) are prepared by a similar reaction in the presence of excess lithium perchlorate. Although it was possible to isolate $[Au_2L_4][ClO_4]_2$ for the shorter chain diphosphines dppm, dppe, and dppb, with the other diphosphines only $[Au_2L_3][ClO_4]_2$ could be prepared, even in the presence of excess ligand. Elemental analysis, conductivity measurements, and i.r. data are given in Tables 1 and 2.

The PPh_2Bu^n *System*.—The ^{31}P-{^1H} n.m.r. spectra of CD_2Cl_2 solutions of $[NEt_4][AuBr_2]$ with varying amounts of the unidentate PPh_2Bu^n were studied as a model for the bidentate system. For low phosphine concentrations (0.5—1.0 mol per mol of Au) a single species is observed at +31.9 p.p.m. The spectrum is identical to that of an independently prepared sample of $[AuBr(PPh_2Bu^n)]$. Solutions of $[AuBr(PPh_2Bu^n)]$ are non-conducting and the solid-state i.r. spectrum exhibits ν(Au–Br) at *ca.* 225 cm^{-1}; both of these results indicate a two-co-ordinate P–Au–Br arrangement. Addition of more PPh_2Bu^n (to give total concentrations of 1.5—2.0 mol per mol of Au) results in the appearance of a new species at +36.1 p.p.m., with a corresponding decrease in the peak due to $[AuBr(PPh_2Bu^n)]$. The new species exchanges with $[AuBr(PPh_2Bu^n)]$ at temperatures above −50 °C, but at −90 °C resonances for each species are very sharp, indicating that the exchange is slow on the n.m.r. time-scale. Independently prepared $[AuBr(PPh_2Bu^n)_2]$ exhibits ν(Au–Br) at 229 cm^{-1} in the solid state and is non-conducting in nitromethane.

Further addition of ligand (2.5—3.0 mol per mol of total Au) resulted in a decrease in the intensity of the +36.1 p.p.m. species and a new species appeared at +33.6 p.p.m. At temperatures above −90 °C exchange between these species occurred. At ligand:Au ratios >4:1, two broad resonances appeared at +9.2 and −17.3 p.p.m. The latter represents free ligand, while the former must be due to a new species. The species represented by the peak at +36.1 p.p.m. is thus assigned to $[AuBr(PPh_2Bu^n)_2]$, that at +33.6 p.p.m. to $[Au(PPh_2Bu^n)_3]Br$, and that at +9.2 p.p.m. to $[Au(PPh_2Bu^n)_4]Br$. Independently prepared samples of $[Au(PPh_2Bu^n)_2]ClO_4$, $[Au(PPh_2Bu^n)_3]ClO_4$, and $[Au(PPh_2Bu^n)_4]ClO_4$ exhibit single resonances in CD_2Cl_2 solution at +41.3, +33.1, and +9.2 p.p.m., respectively. Thus, clearly, in solution the AuL_3 and AuL_4 species must be cationic while the AuL_2 species must have co-ordinated Br.

Table 1. Elemental analyses, conductivities, and i.r. data (cm^{-1}) for the gold(I) bromide complexes

	Analysis^a (%)				
Complex	C	H	Λ^b	ν(Au–P)	ν(Au–Br)
$[(AuBr)_2(dppm)]$	32.8 (32.0)	2.3 (2.3)		362s	224s
$[(AuBr)_2(dppe)]$	32.6 (32.8)	2.6 (2.5)		342s	225s
$[(AuBr)_2(dppb)]$	33.9 (34.3)	3.0 (2.9)	(8.0)	387m	228s
$[(AuBr)_2(dpphx)]$	35.5 (35.7)	3.2 (3.2)	(9.0)	350w	228s
$[(AuBr)_2(dppo)]$	37.0 (37.0)	3.5 (3.5)		381m	225s
$[(AuBr)_2(dppd)]$	38.4 (38.3)	3.8 (3.8)		385m	227s
$[(AuBr)_2(dppdod)]$	39.7 (39.6)	4.1 (4.0)	(10.0)	378m	228s
$[(AuBr)_2(dpphxd)]$	42.1 (41.8)	4.6 (4.5)		377m	228s
$[(AuBr)_2(dppm)_2]$	44.9 (45.4)	3.4 (3.3)	68.0 (69.3)	359m	226m
$[(AuBr)_2(dppe)_2]$	45.7 (46.2)	3.7 (3.6)	64.0 (68.0)	343s	224m
$[(AuBr)_2(dppb)_2]$	47.7 (47.9)	4.0 (3.8)		360s	227m
$[(AuBr)_2(dpphx)_2]$	49.2 (49.4)	4.6 (4.4)	50.0 (53.0)	368w	220m
$[(AuBr)_2(dppo)_2]$	50.1 (50.7)	4.5 (4.8)	43.0 (48.0)	360w	218m
$[(AuBr)_2(dppd)_2]$	51.9 (51.8)	5.2 (5.1)		360w	226m
$[(AuBr)_2(dppdod)_2]$	52.4 (53.0)	5.4 (5.4)	40.0 (45.0)	360w	220m
$[(AuBr)_2(dpphxd)_2]$	54.7 (55.2)	5.8 (6.0)		360w	218m
$[(AuBr)_2(dppm)_3]$	52.4 (52.9)	4.2 (3.9)	112 (145)	372m	
$[(AuBr)_2(dppe)_3]$	53.1 (53.7)	4.3 (4.1)		355m	
$[(AuBr)_2(dppb)_3]$	54.0 (55.0)	4.7 (4.6)		305w	
$[(AuBr)_2(dpphx)_3]$	54.7 (56.5)	5.2 (5.0)	105 (150)	340w	
$[(AuBr)_2(dppo)_3]$	56.9 (57.7)	5.3 (5.4)		360w	
$[(AuBr)_2(dppd)_3]$	58.8 (58.9)	6.2 (5.8)		360w	
$[(AuBr)_2(dppdod)_3]$	59.6 (59.9)	5.8 (6.1)	126 (150)	360w	
$[(AuBr)_2(dpphxd)_3]$	60.9 (61.8)	6.8 (6.7)		360w	

[a] Calculated values are given in parentheses. [b] Molar conductance (S cm^2 mol^{-1}), concentrations 10^{-3} mol dm^{-3}; values for 10^{-4} mol dm^{-3} given in parentheses.

Table 2. Elemental analyses, conductivities, and i.r. data for the gold(I) perchlorate complexes

	Analysis^a (%)				
Complex	C	H	Λ^b	ν(Au–P)	ν(Cl–O)
$[Au_2(dppm)_2][ClO_4]_2$	43.8 (44.1)	3.4 (3.2)	143	360m	1 100br, 622s
$[Au_2(dppe)_2][ClO_4]_2$	44.9 (44.9)	3.6 (3.5)		345m	1 090br, 622s
$[Au_2(dppb)_2][ClO_4]_2$	46.4 (46.5)	3.9 (3.9)	140	360w	1 100br, 621s
$[Au_2(dpphx)_2][ClO_4]_2$	47.8 (48.0)	4.3 (4.4)		360w	1 100br, 622s
$[Au_2(dppo)_2][ClO_4]_2$	48.8 (49.3)	4.9 (4.6)	149	340w	1 100br, 620s
$[Au_2(dppd)_2][ClO_4]_2$	50.0 (50.6)	5.1 (5.0)	158 (178)	388s	1 090br, 622s
$[Au_2(dppdod)_2][ClO_4]_2$	51.5 (51.6)	5.4 (5.3)	186 (210)	360w	1 120br, 622s
$[Au_2(dpphxd)_2][ClO_4]_2$	53.6 (53.9)	6.1 (5.8)		365w	1 115br, 622s
$[Au_2(dppm)_3][ClO_4]_2$	50.9 (51.5)	3.9 (3.8)	174	367w	1 120br, 622s
$[Au_2(dppe)_3][ClO_4]_2$	52.9 (52.4)	4.4 (4.1)	165	340w	1 090br, 622s
$[Au_2(dppb)_3][ClO_4]_2$	54.0 (53.8)	4.6 (4.5)		360w	1 100br, 622s
$[Au_2(dpphx)_3][ClO_4]_2$	54.7 (55.2)	5.1 (4.9)	164 (189)	367w	1 110br, 622s
$[Au_2(dppo)_3][ClO_4]_2$	56.3 (56.5)	5.4 (5.3)	170 (197)	340w	1 100br, 622s
$[Au_2(dppd)_3][ClO_4]_2$	57.7 (57.7)	5.7 (5.7)	197	360w	1 090br, 622s
$[Au_2(dppdod)_3][ClO_4]_2$	58.7 (58.7)	6.1 (6.0)	209	360w	1 090br, 622s
$[Au_2(dpphxd)_3][ClO_4]_2$	59.9 (60.6)	6.7 (6.6)	215	365w	1 110br, 622s
$[Au_2(dppm)_4][ClO_4]_2$	56.8 (56.5)	4.3 (4.1)	162	360m	1 100br, 622s
$[Au_2(dppe)_4][ClO_4]_2$	57.5 (57.1)	4.3 (4.4)	160	330w	1 090br, 622s
$[Au_2(dppb)_4][ClO_4]_2$	57.9 (58.5)	5.1 (4.9)	149	350w	1 094br, 621s

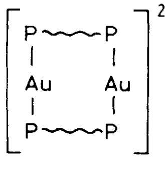
[a] Calculated values are given in parentheses. [b] Molar conductance (S cm^2 mol^{-1}), concentration 10^{-3} mol dm^{-3}; values for 10^{-4} mol dm^{-3} given in parentheses.

Since none of the three- or four-co-ordinate complexes is observed until the diphosphine: gold ratio is greater than 2:1 or 3:1 respectively the relative magnitudes of the stability constants vary as $\beta_2 > \beta_3 > \beta_4$; the same order as that observed by Mays and Vergnano[22] for the PEt_3 system.

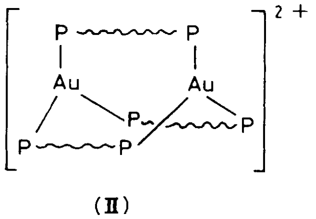
The AuBr–*Diphosphine System.*—Analytical results and solid-state i.r. data for the isolated gold(I) bromide–bidentate phosphine complexes are reported in Table 1. The existence of ν(Au–Br) for the complexes indicates that bromine is co-ordinated in the solid state. The BrAu(μ-L)AuBr complexes are non-conducting in nitromethane, but some conductivity occurs for the $BrAu(\mu\text{-}L)_2AuBr$ compounds in this solvent, presumably due to solvolysis.

Analytical data, conductivities, and solid-state i.r. data for the gold(I) perchlorate complexes are in Table 2. The conductivities are clearly indicative of 1:2 electrolytes in all cases, and they may be formulated as $[Au_2L_x][ClO_4]_2$ (x = 2 or 3), structures (**I**) and (**II**). Complexes containing four phosphorus atoms per gold were only preparable with the short-chain diphosphines dppm, dppe, and dppb. Solubilities of these, $[Au_2L_4][ClO_4]_2$, were very low compared to those for $[Au_2L_x][ClO_4]_2$ (x = 2 or 3) and this suggests a polymeric structure, (**III**). The solid-state i.r. spectra show only unco-ordinated perchlorate groups. The fact that the longer chain diphosphines did not form such a complex may indicate that the structure (**III**) is highly ordered and does not lend itself to formation with the diphosphines having very flexible backbones. It is worth pointing out that no $[AuL_4]Br$ complexes could be prepared, indicating that a co-ordinating anion binds in preference to a fourth phosphine.

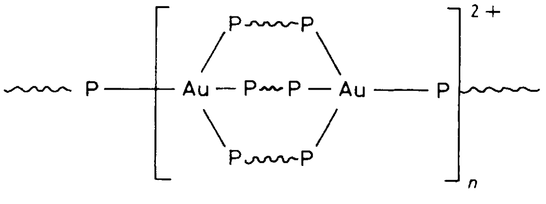
The ^{31}P-{^1H} n.m.r. spectra of the perchlorate complexes at −90 °C in CD_2Cl_2 are presented in Table 3. The chemical shifts and co-ordination chemical shifts of the two-co-ordinated complexes are virtually identical except for the complex of the short-chain dppe. A similar observation may be made for the three-co-ordinate $[Au_2L_3][ClO_4]_2$ complexes. The increased shielding of the three-co-ordinate species is expected. Further shielding is observed for the four-co-ordinate complex $[Au_2(dppe)_4][ClO_4]_2$. Interestingly, solutions containing $[Au(PPh_2Bu^n)_3]^+$ always exhibit some $[AuBr(PPh_2Bu^n)_2]$, suggesting that the three-co-ordinate complexes of the bidentate phosphine are more stable than their unidentate counterparts.



(I)



(II)



(III)

Table 3. ^{31}P-{^1H} N.m.r. spectra of isolated perchlorate complexes at −90 °C

Complex	$\delta(^{31}P)$/p.p.m.[a] (Δ/p.p.m.)[b]
$[Au_2(dppe)_2][ClO_4]_2$	+44.6 (+59.3)
$[Au_2(dpphx)_2][ClO_4]_2$	+39.6 (+57.5)
$[Au_2(dppo)_2][ClO_4]_2$	+40.0 (+57.9)
$[Au_2(dppd)_2][ClO_4]_2$	+40.4 (+58.1)
$[Au_2(dppod)_2][ClO_4]_2$	+40.7 (+58.4)
$[Au_2(dpphxd)_2][ClO_4]_2$	+40.7 (+58.4)
$[Au_2(dppe)_3][ClO_4]_2$	+37.0 (+51.7)
$[Au_2(dpphx)_3][ClO_4]_2$	+36.1 (+54.0)
$[Au_2(dppo)_3][ClO_4]_2$	+36.0 (+53.9)
$[Au_2(dppd)_3][ClO_4]_2$	+36.1 (+53.5)
$[Au_2(dppdod)_3][ClO_4]_2$	+36.1 (+53.8)
$[Au_2(dppdhx)_3][ClO_4]_2$	+36.2 (+53.7)
$[Au_2(dppe)_4][ClO_4]_2$	+21.4 (+36.2)

[a] Relative to 85% H_3PO_4; CD_2Cl_2 solutions. [b] Co-ordination chemical shifts.

The variable-temperature ^{31}P-{^1H} n.m.r. spectra for species having varying amounts of dpphx and $[NEt_4][AuBr_2]$ are given in Table 4. At a ratio of 0.5 mol of L per mol of Au, a single species at *ca.* +31 p.p.m. from +10 to −90 °C is observed and no variation in linewidth over the temperature range occurs. The chemical shift is almost identical to that found for $[AuBr(PPh_2Bu^n)]$, and thus we assign this species to [BrAu(dpphx)AuBr]. At a L:Au ratio of 0.75:1, a single sharp peak is observed at +10 °C. This peak broadens as the temperature is decreased and at −50 °C two peaks are observed at +35.3 and +31.9 p.p.m., with relative intensities 2:1. Thus, the peak at +31.9 p.p.m. is assigned to [BrAu(dpphx)AuBr] and that at +35.3 p.p.m. to $[\{AuBr(dpphx)\}_x]$ (x = 1 or 2). Upon further cooling this latter peak splits into two peaks at +36.1 and +35.5 p.p.m. The relative intensities at −90 °C are 2:3. The peak at +36.1 p.p.m. is identical to that observed for the three-co-ordinate $[AuBr(PPh_2Bu^n)_2]$. While the structure of this complex cannot be assigned with certainty, it is clearly not $[Au(dpphx)_2Au]^{2+}$, since a chemical shift of +39.6 p.p.m. (see Table 3) is characteristic of this cation. The existence of two peaks (+36.1, +35.5 p.p.m.) with such close chemical shifts suggests similar environments and exchange between these environments occurs about −70 °C. Since the peak at +36.1 p.p.m. has the same chemical shift as the $[AuBr(PPh_2Bu^n)_2]$ complex, it is reasonable to believe that this species is the $[BrAu(dpphx)_2AuBr]$ ring compound which would have very little ring strain. Thus we assign the peak at +35.5 p.p.m. to the monomeric [AuBr(dpphx)].

At a dpphx:$AuBr_2$ ratio of 1:1, a single peak (+33.2 p.p.m.) is observed, again at +10 °C. This peak broadens as the temperature decreases, and at −50 °C peaks at +35.2 and +18.8 p.p.m. are observed. Cooling to −90 °C further splits the former into two peaks at +36.1 and +33.4 p.p.m. The peak at +33.4 p.p.m. is easily assignable to a species containing three phosphorus atoms per gold, based on the the n.m.r. peak due to $[Au(PPh_2Bu^n)_3]Br$, and the peak at +18.6 p.p.m. is assignable to a complex with four phosphorus atoms per gold. Of course the peak at +36.1 p.p.m. is assignable to the species $[BrAu(dpphx)_2AuBr]$ based on the PPh_2Bu^n study.

Thus, at a dpphx:Au ratio of 1:1 at −90 °C the two-co-ordinate, three-co-ordinate, and four-co-ordinate gold com-

Table 4. Variable-temperature (°C) ^{31}P-{^1H} n.m.r. spectra for $[NEt_4][AuBr_2]$ and dpphx[a]

Mol L/mol Au	+10	−30	−50	−70	−90
0.5	+31.6	+31.4	+31.3	+31.1	+31.0
0.75	+34.5	+34.7	+35.3 (2.0)	+36.1 (1.0)	+36.1 (1.0)
			+31.9 (1.0)	+35.5 (3.0)	+35.5 (1.5)
				+31.0 (2.5)	+31.0 (1.5)
1.0	+33.2	+36.0	+35.2 (5.0)	+36.1 (1.75)	+36.1 (1.75)
			+18.8 (1.0)	+34.9 (5.0)	+33.4 (5.0)
				+19.0 (1.0)	+18.6 (1.0)
1.25	+26.4	+35.3 (1.0)		+34.5 (1.0)	+36.8 (1.0)
		+19.5 (1.6)		+18.4 (2.3)	+34.4 (2.2)
					+18.5 (4.3)
2.5	+11.5		+19.3 (1.0)	+19.3 (1.0)	+19.2 (1.0)
			−17.2 (2.0)[b]	−17.2 (2.0)[b]	−17.3 (2.0)[b]

[a] Relative amounts estimated from n.m.r. are given in parentheses. [b] Free ligand.

Table 5. ^{31}P-{^{1}H} N.m.r. spectra[a] of solutions of $[NEt_4][AuBr_2]$ and ligands at −90 °C

Mol L/mol $AuBr_2$	^{31}P Chemical shifts[b]					
	dppm	dppe	dppo	dppd	dppdod	dpphxd
0.50	+28.2 (+53.8)	+31.4 (+46.1)	+31.6 (+49.6)	+31.2 (+48.9)	+31.5 (+49.2)	+31.8 (+49.5)
0.75	+33.2 (+58.8)	+41.2 (+55.9)	+36.8 (+54.7)	+38.2 (+55.9)	+36.0 (+53.7)	+36.2 (+53.9)
	+30.8 (+56.4)	+35.0 (+49.7)	+35.6 (+49.5)	+36.4 (+54.1)	+31.5 (+49.3)	+31.1 (+48.8)
	+28.2 (+53.7)	+21.3 (+36.0)	+31.6 (+49.6)	+31.3 (+49.0)		
1.00	+33.0 (+58.6)	+41.4 (+56.2)	+36.8 (+54.7)	+37.8 (+55.5)	+36.1 (+53.76)	+36.8 (+54.5)
	+30.7 (+56.3)	+35.1 (+49.9)	+35.7 (+53.6)	+36.1 (+53.8)		
		+21.5 (+36.2)				
1.25	+30.5 (+56.1)	+41.5 (+56.3)	+36.2 (+54.1)	+36.1 (+53.8)	+36.1 (+53.8)	+36.6 (+54.3)
		+21.6 (+36.3)	+31.0 (+49.0)	+31.8 (+49.5)	+33.3 (+51.0)	+34.6 (+52.3)
1.50		+21.4 (+36.1)	+29.4 (+47.4) (broad)		+33.3 (+51.0)	
2.50	+35.6 (+61.2)	+21.5 (+36.2)	+21.0 (+38.9)	+21.2 (+38.9)	+19.7 (+37.4)	+18.0 (+35.7)
	+29.4 (+55.0)	−14.7[c]	−17.1[c]	−17.3[c]	−17.7[c]	−17.7[c]
	+23.2 (+48.8)					
	−25.5[c]					

[a] In CD_2Cl_2 solution. [b] Co-ordination chemical shifts given in parentheses. [c] Free ligand.

plexes are present, and, of course this implies that $AuBr_2^-$ is also present due to the stoicheiometry. Since the four-co-ordinate species appears at lower temperatures than the three- and two-co-ordinate species, then this suggests that exchange between the two- and three-co-ordinate complexes is faster than exchange between the two- and four-co-ordinate gold complexes of dpphx. Exchange between the four-co-ordinate complex and free ligand is observed at dpphx:Au ratios >2:1. However, cooling to −50 °C slows the exchange and both free ligand and the four-co-ordinate complex can be observed. Nevertheless, the lines are still relatively broad at −90 °C indicating that exchange is still relatively fast.

The ^{31}P-{^{1}H} n.m.r. species at −90 °C of the other diphosphines as a function of added ligand are given in Table 5. Even a casual comparison with Table 4 indicates the close similarity of dpphxd, dppdod, dppd, and dppo with the dpphx system. Of interest is the fact that none of the species seen at *ca.* +35.5 p.p.m. (three-co-ordination) is observed for the L:Au ratios of 0.75—1.00:1 for the ligand dppdod and dpphxd. This suggests that the length of the ligand backbone influences the formation of this species. The absence of the species seen at *ca.* 35.5 p.p.m. for the longer chain ligands is further evidence for assigning this peak to the monomer for dpphx, if we assume that the longer backbone chains would have more steric interaction in the monomer. The spectra of the CD_2Cl_2 solutions of the shorter chain ligands dppm, dppe, and dpphx reveal that three- and four-co-ordinate complexes are formed even at L:Au ratios of 1:1. Thus, the complexes containing high co-ordination numbers are favoured for shorter chain ligands, suggesting that steric or entropy factors are important.

Experimental

Materials.—Tetraethylammonium dibromoaurate(I) was prepared as previously described[23] and the solvents employed were used without further purification. The ligands dppm, dppe, dppb, dpphx, dppo, dppd, dppdod, and dpphxd were prepared and characterized as described previously.[10]

Preparation of the Complexes.—μ-[*Bis(diphenylphosphino)methane*]-*dibromodigold*(I), $[(AuBr)_2(\mu\text{-dppm})]$. An ethanol solution (10 cm^3) of $[NEt_4][AuBr_2]$ (0.25 g, 0.51 mol) was added to a dichloromethane solution (15 cm^3) of dppm (0.098 g, 0.25 mmol) under nitrogen and stirred for 15 min. The solution was then concentrated to 5 cm^3 by gentle warming and n-pentane (100 cm^3) was added. The resulting precipitate was filtered off, washed with water (5 × 25 cm^3) to remove any unreacted ammonium salt, and dried *in vacuo* over P_2O_5 at 100 °C for 1 d.

The dppe, dppb, dpphx, dppo, dppd, dppdod, and dpphxd complexes were prepared in a similar manner.

Bis[μ-*bis(diphenylphosphino)methane*]-*dibromodigold*(I), $[(AuBr)_2(\mu\text{-dppm})_2]$. This was prepared by a method similar to that above as were the dppe, dppb, dpphx, dppo, dppd, dppdod, and dpphxd analogues.

Tris[μ-*bis(diphenylphosphino)methane*]-*dibromodigold*(I), $[(AuBr)_2(\mu\text{-dppm})_3]$. This complex and the analogous complex containing the ligands dppe, dppb, dppo, dppd, dppdod, and dpphxd were prepared in a manner similar to that used for $[(AuBr)_2(\mu\text{-dppm})_2]$.

Bis[μ-*bis(diphenylphosphino)methane*]-*digold*(I) *perchlorate*, $[Au_2(\mu\text{-dppm})_2][ClO_4]_2$. An ethanolic solution of lithium perchlorate (5 cm^3, 1 mol dm^{-3}) was added to a solution of tetraethylammonium dibromoaurate(I) (0.2 g, 0.41 mmol) in ethanol (10 cm^3) and the mixture was added to a solution of dppm (0.61 g, 0.41 mmol) in dichloromethane (15 cm^3) under nitrogen and stirred for 30 min. The colourless solution was concentrated by gentle warming to 5 cm^3 and the white precipitate which formed was filtered off, washed with ethanol (5 × 10 cm^3), water (10 cm^3) and dried *in vacuo* over P_2O_5 at 110 °C for 1 d.

The dppe, dppb, dpphx, dppo, dppd, dppdod, and dpphxd complexes were prepared in an analogous manner.

Tris[μ-*bis(diphenylphosphino)methane*]-*digold*(I) *perchlorate*, $[Au_2(\mu\text{-dppm})_3][ClO_4]_2$. This complex and the analogous complexes of dppe, dppb, dpphx, dppo, dppd, dppdod, and dpphxd were prepared by the method used to prepare $[Au_2(\mu\text{-dppm})_2][ClO_4]_2$ using appropriate quantities of reactants.

Tetrakis[μ-*bis(diphenylphosphino)methane*]-*digold*(I) *perchlorate*, $[Au_2(\mu\text{-dppm})_4][ClO_4]_2$. This complex and the analogous complexes of dppe and dppb were prepared by the method used to prepare $[Au_2(\mu\text{-dppm})_2][ClO_4]_2$ using appropriate quantities of reactants. Attempts to isolate $[Au(\mu\text{-L})_4][ClO_4]_2$ (L = dpphx, dppo, dppd, dppdod, or dpphxd) gave only the $[Au_2(\mu\text{-L})_3][ClO_4]_2$ complexes, even in the presence of excess ligand.

Bis(n-butyldiphenylphosphine)gold(I) *perchlorate*, $[Au(PPh_2Bu^n)_2]ClO_4$. An ethanol solution of lithium perchlorate (5 cm^3, 1 mol dm^{-3}) was added to a solution of $[NEt_4][AuBr_2]$ (0.15 g, 0.31 mmol) in ethanol (10 cm^3) and this mixture was added to a solution of the phosphine (0.62 mmol) in acetone (5 cm^3) under nitrogen and stirred for 1 h. The colourless solution was concentrated by gentle warming to 10 cm^3 and the white precipitate which formed was filtered off, washed with ethanol (5 × 10 cm^3) and dried *in vacuo* over P_4O_{10} at 110 °C for 1 d. The yield was 0.2 g, 85% based on $[NEt_4][AuBr_2]$. The analogous tris- and tetrakis-phosphine complexes were isolated, each in 70% yield, using a similar method employing appropriate quantities of reactants.

Bromo(*n-butyldiphenylphosphine*)*gold*(I), $[AuBr(PPh_2Bu^n)]$. A solution of $[NEt_4][AuBr_2]$ (0.15 g, 0.31 mmol) in dichloromethane (10 cm^3) was added to a solution of the phosphine (0.93 mmol) in acetone (5 cm^3) under nitrogen and stirred for 15 min. A white precipitate formed and was filtered off, washed with water (5 × 25 cm^3), and dried *in vacuo* over P_4O_{10} in an Abderhalden apparatus at 100 °C for 1 d. The yield was 0.1 g, 65% based on $[NEt_4][AuBr_2]$. The bis- and tris-phosphine complexes were prepared in a similar manner (60% yields) using appropriate quantities of reactants.

Physical Measurements.—The ^{31}P n.m.r. spectra of the complexes were recorded on a Varian CFT-20 Fourier-transform spectrometer at 32.1 MHz. Infrared spectra were recorded on a Perkin-Elmer 580 spectrometer using polyethylene plates for the region 600—200 cm^{-1} in Nujol mull. Conductivity measurements were made using a platinum electrode dipping cell and a conductivity bridge. Elemental analyses were carried out by Atlantic Microlabs Inc., Atlanta, or by the Microanalytical Laboratory at U.M.I.S.T.

References

1 N. J. DeStefano, D. K. Johnson, R. M. Lane, and L. M. Venanzi, *Helv. Chim. Acta*, 1976, **59**, 2674.
2 N. J. DeStefano, D. K. Johnson, and L. M. Venanzi, *Helv. Chim. Acta*, 1976, **59**, 2683.
3 F. J. S. Reed and L. M. Venanzi, *Helv. Chim. Acta*, 1977, **60**, 2804.
4 F. Bachechi, L. Zambonelli, and L. M. Venanzi, *Helv. Chim. Acta*, 1977, **60**, 2815.
5 A. Pryde, B. L. Shaw, and B. J. Weeks, *J. Chem. Soc., Dalton Trans.*, 1976, 322.
6 N. A. Al-Salem, H. D. Empsall, R. Markham, B. L. Shaw, and B. J. Weeks, *J. Chem. Soc., Dalton Trans.*, 1979, 1972.
7 C. Crocker, R. J. Errington, R. Markham, C. J. Moulton, K. J. Odell, and B. L. Shaw, *J. Am. Chem. Soc.*, 1980, **102**, 4373.
8 B. L. Shaw, *J. Am. Chem. Soc.*, 1975, **97**, 3856.
9 W. E. Hill, J. G. Taylor, C. A. McAuliffe, K. W. Muir, and L. Manojlovic-Muir, *J. Chem. Soc., Dalton Trans.*, 1982, 833.
10 W. E. Hill, C. A. McAuliffe, I. E. Niven, and R. V. Parish, *Inorg. Chim. Acta*, 1979, **38**, 273.
11 W. E. Hill, D. M. A. Minahan, J. G. Taylor, and C. A. McAuliffe, *J. Am. Chem. Soc.*, 1982, **104**, 6001.
12 J. C. Briggs, C. A. McAuliffe, W. E. Hill, D. M. A. Minaham, J. G. Taylor, and G. Dyer, *Inorg. Chem.*, 1982, **21**, 4204.
13 W. Levason, C. A. McAuliffe, and S. G. Murray, *J. Organomet. Chem.*, 1976, **110**, C25.
14 C. B. Colburn, W. E. Hill, C. A. McAuliffe, and R. V. Parish, *J. Chem. Soc., Chem. Commun.*, 1979, 218.
15 C. A. McAuliffe, R. V. Parish, and P. D. Randall, *J. Chem. Soc., Dalton Trans.*, 1977, 1426.
16 J. A. Muir, M. M. Muir, and S. Arias, *Acta Crystallogr., Sect. B*, 1982, **38**, 1318.
17 J. A. Muir, M. M. Muir, S. Arias, C. F. Campana, and S. K. Dwight, *Acta Crystallogr., Sect. B*, 1982, **38**, 2047.
18 J. A. Dills and M. P. Johnson, *Inorg. Chem.*, 1966, **5**, 2079.
19 P. G. Jones, *J. Chem. Soc., Chem. Commun.*, 1980, 1031.
20 R. C. Elder, E. H. Kelle-Zeiher, M. Onady, and R. R. Whittle, *J. Chem. Soc., Chem. Commun.*, 1981, 900.
21 M. Barron, H. B. Buergi, D. K. Johnson, and L. M. Venanzi, *J. Am. Chem. Soc.*, 1976, **98**, 2356.
22 M. J. Mays and P. Vergnano, *J. Chem. Soc., Dalton Trans.*, 1979, 1112.
23 P. Braunstein and R. J. H. Clark, *J. Chem. Soc., Dalton Trans.*, 1973, 1845.

Received 1*st February* 1985; *Paper* 5/182