Gold(I) Complexes of 1,2-Ditertiary phosphino-*o*-carborane Ligands: Two-, Three-, and Four-co-ordination

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Ditertiary phosphines (L) of the type $R_2P(C_2B_{10}H_{10})PR'_2$ (R = R' = Ph; R = R' = NMe_2; R = Ph, R' = NMe_2) react with tetraethylammonium dibromoaurate(I) to form the three-co-ordinate complexes [AuBrL], which have been isolated and characterized by elemental analyses, and i.r. and $^{31}P-\{^1H\}$ n.m.r. spectroscopy. A dimeric two-co-ordinate complex, $[(AuBr)_2\{Ph_2P(C_2B_{10}H_{10})PPh_2\}]$, has also been isolated and characterized. The $^{31}P-\{^1H\}$ n.m.r. spectra of $CD_3COCD_3-CH_2Cl_2$ (1 : 1) solutions of L and $[AuBr_2]^-$ show evidence for the formation of dimeric two-co-ordinate $[(AuBr)_2L]$, dimeric three-co-ordinate $[(AuBr)_2L_2]$, monomeric three-co-ordinate [AuBrL], and four-co-ordinate $[AuL_2]Br$ complexes. The unusual four-co-ordinate mixed-ligand complex $[Au\{Ph_2P(C_2B_{10}H_{10})PPh_2\}\{(Me_2N)_2P(C_2B_{10}H_{10})P(NMe_2)_2\}]Br$ is also observed. Phosphorus–phosphorus coupling constants decrease from three-co-ordinate to four-co-ordinate gold(I) complexes, as expected. The tertiary phosphine $H(C_2B_{10}H_{10})PPh_2$ also gives $[AuBr\{H(C_2B_{10}H_{10})PPh_2\}]$ two-co-ordinate complexes.

Gold, in spite of being the most noble of metals, manages to have an extensive and intriguing chemistry; its compounds have even found application in the treatment of the crippling disease rheumatoid arthritis.

The current upsurge of interest in gold(I) phosphine chemistry has centred around the stereochemistry and co-ordination number of these compounds. Two-, three-, and four-co-ordinate complexes are known and, in addition to ^{31}P n.m.r. investigations by Mays and Vergnano[1] and McAuliffe and co-workers,[2] ^{197}Au Mössbauer techniques have been elegantly applied[3–6] to structure elucidation.

A vast array of tertiary phosphine complexes of gold(I) exists;[7] the first, $[AuCl(PEt_3)]$, being prepared over a hundred years ago.[8] The majority are two-co-ordinate and are prepared either by reduction of gold(III) compounds or by substitution reactions on other gold(I) complexes.[2,4,7,9] For higher co-ordination numbers to be achieved the steric requirements of the tertiary phosphine (L) are important; for example, $P(C_6H_4Me-p)_3$ forms $[AuL_2]^+$, $[AuL_3]^+$, and $[AuL_4]^+$, but the bulkier $P(cyclo-C_6H_{11})_3$ forms only $[AuL_2]^+$.[2] The use of weakly co-ordinating anions such as $[BF_4]^-$ and $[ClO_4]^-$ makes it easier to isolate species with higher co-ordination numbers; $[AuL_4]^+$ is usually only achieved with these anions.[10] However, in addition to these ionic species, trigonal planar three-co-ordinate and pseudotetrahedral four-co-ordinate gold(I) complexes exist in neutral forms, such as $[Au(SCN)(PPh_3)_2]$,[11] $[Au(SCN)(PPh_3)_3]$,[12] and the presumably pseudotetrahedral $[Au(SnCl_3)(PPh_3)_3]$.[13] The trigonal species are nearly ideal with P–Au–P of 127.8°, but the pseudotetrahedral species usually have one long bond, making the structure more like a trigonal pyramid, [12–14] except for $[Au(PPh_2Me)_4]^+$ which has a geometry close to tetrahedral.[15]

In contrast to complexes of unidentate phosphines, few studies have been reported of gold(I) complexes of ditertiary phosphines. With bis(diphenylphosphino)methane (dppm),[16] and 1,2-bis(diethylphosphino)ethane[17] and *cis*-1,2-bis(diphenylphosphino)ethylene,[4] complexes of the type $[\{AuX(dppm)\}_2]$ and $[(AuX)_2L]$ respectively are known (X = halogen); Venanzi and co-workers[18] have isolated the three-co-ordinate T-shaped complex [AuClL] {L = 2,11-bis(diphenylphosphinomethylbenzo[*c*]phenanthrene};[18] and Carty and Efraty[19] have isolated several complexes containing bis(diphenylphosphino)acetylene (dppa), including the intriguing, but essentially uncharacterized, $[AuX(dppa)_2]$ species.[19]

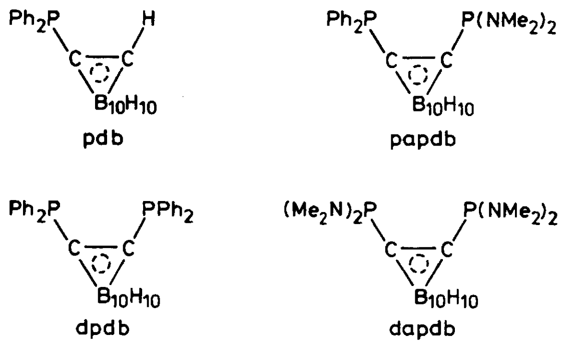


Figure 1. Structures of the ligands and their abbreviations

We have begun a program of work on gold(I) complexes of ditertiary phosphines,[20] an extension of our studies on platinum(II) complexes,[21,22] and here we report the isolation and structural characterization of gold(I) complexes of the unidentate tertiary phosphine decaborane ligand pdb (Figure 1) and the ditertiary phosphine decaborane ligands dpdb, papdb, and dapdb which contain the rigid '*o*-carborane' ($C_2B_{10}H_{10}$) backbone (this should encourage chelation).

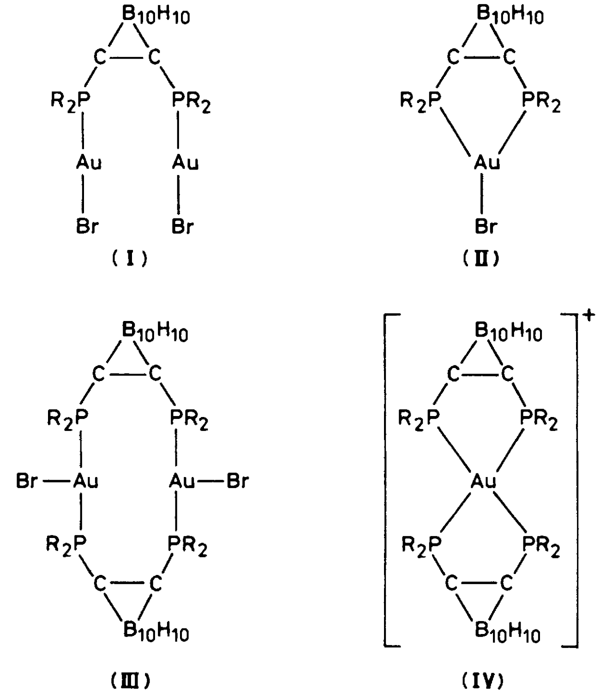
Results and Discussion

The ligands used in this study were synthesized by methods previously reported.[23,24] The structures of these compounds and their abbreviations are shown in Figure 1; the solid complexes isolated are listed in Table 1 and their proposed structures shown in Figure 2. The complex [AuBr(pdb)] was isolated from the reaction of $[NEt_4][AuBr_2]$ with the ligand pdb in a 1:1 ratio in acetone–ethanol solvent. Attempts to isolate $[AuBr(pdb)_2]$, $[AuBr(pdb)_3]$, and $[Au(pdb)_4]Br$ were unsuccessful. Complexes of the type [AuBr(dpdb)], [AuBr(papdb)], and [AuBr(dapdb)] were similarly prepared using a

Table 1. Analyses, melting points, conductivities, and gold–bromine stretching frequencies for the complexes

Complex	M.p.^{a}/°C	Analysis^b(%) C	Analysis^b(%) H	Λ^c/S cm^2 mol^{-1}	ν(Au–Br)^d/cm^{-1}
[AuBr(pdb)]	303—305	26.3 (27.1)	3.4 (3.5)	—	226
[(AuBr)$_2$(dpdb)]	103—105	31.1 (29.3)	3.5 (2.8)	8.5	226
[AuBr(dpdb)]	181—183	40.1 (39.5)	3.8 (3.9)	11.5	238
[AuBr(papdb)]	121—123	28.9 (29.8)	4.6 (4.4)	15.2	226
[AuBr(dapdb)]	156—158	18.2 (18.0)	5.2 (5.2)	24.7 (28.2)^e	222

^{a} Uncorrected. ^{b} Calculated values are in parentheses. ^{c} Molar conductivities in nitromethane solution (10^{-3} mol dm^{-3}). ^{d} Nujol mull. ^{e} Conductivity for 10^{-4} mol dm^{-3} solution.



(I) (II) (III) (IV)

Figure 2. Proposed structures of the complexes

Table 2. ^{31}P-{^{1}H} N.m.r. spectra^a of solutions^b of [NEt$_4$][AuBr$_2$] and the ligands at −90 °C

Ligand (L)	Total mol L/ mol Au	Chemical shift (δ/p.p.m.)^c PPh$_2$	Chemical shift (δ/p.p.m.)^c P(NMe$_2$)$_2$	J_{PP}/Hz
dpdb	0.5	+49.0		
	1.0	+41.6, +39.2		
	1.5	+58.0, +41.6		
	2.5	+58.0, +41.6, +6.0		
papdb	0.5	+46.3 (d)	+99.7 (d)	40
	1.0	+16.9 (d)	+103.2 (d)	164
	2.5	+32.7 (m), +16.9 (d), +6.4 (d)	+123.0(m), +103.2 (d), +96.0 (d)	216,60^d 164 120
dapdb	0.5		+99.5	
	1.0		+105.8, +99.5	
	1.5		+127.4, +105.8	
	2.5		+127.4, +105.8, +95.0	
dpdb/ dapdb^e	1.0	+41.6, +39.2	+106.7, +100.0	
	2.0	+41.8 (t), +41.6, +6.0	+113.0 (t), +106.0, +95.0	58

^{a} Resonances are singlets unless stated otherwise. ^{b} CD$_3$COCD$_3$–CH$_2$Cl$_2$ solutions (50% each by volume). ^{c} Chemical shifts relative to 85% H$_3$PO$_4$. ^{d} J_{AX} = 216, $J_{AX'}$ = 60 Hz. ^{e} Equimolar amounts of dpdb and dapdb.

ligand (L):Au ratio of 1:1 (see Experimental section). Although a [(AuBr)$_2$L] complex was isolable for L = dpdb with a L:Au ratio of 0.5:1, no such complexes could be isolated for L = papdb or dapdb. Attempts to isolate [Au(dpdb)$_2$]X, [Au(dpdb)(papdb)]X, and [Au(dapdb)$_2$]X (X = ClO$_4$ or Br) were also unsuccessful

We have studied the ^{31}P-{^{1}H} n.m.r. spectra of CD$_3$COCD$_3$–CH$_2$Cl$_2$ solutions of [NEt$_4$][AuBr$_2$] with varying amounts of the ligands pdb, dpdb, papdb, and dapdb and mixed dpdb/dapdb, Table 2.

At low concentration of dpdb (0.5 mol per mol [AuBr$_2$]$^-$), a single peak at +49.0 p.p.m. is present and the linewidth does not vary from +10 to −90 °C. The spectrum is identical to that exhibited by an independently prepared sample of [(AuBr)$_2$(dpdb)]. Solutions of the latter complex are non-conducting in nitromethane and the solid-state i.r. spectrum exhibits a ν(Au–Br) band at 226 cm^{-1}. We thus assign two-co-ordination, structure (**I**), to this ligand-bridged complex, formed at low L:Au concentrations. Upon addition of more ligand (1.0 mol dpdb per mol [AuBr$_2$]$^-$) two new peaks, at +41.6 and +39.2 p.p.m., appear at −90 °C at the expense of that at +49.0 p.p.m. due to [(AuBr)$_2$(dpdb)]. These new species exchange with each other and with [(AuBr)$_2$(dpdb)] at temperatures above −40 °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. The existence of two peaks with close chemical shifts (+41.6 and +39.2 p.p.m.) suggests very similar environments. Further addition of ligand, to give 1.5 mol dpdb per mol Au, at temperatures below −50 °C resulted in a decrease in the intensity of the species at +39.2 p.p.m. and the appearance of a new species at +58.0 p.p.m. Interestingly, the intensity of the species at +41.6 p.p.m. did not decrease, suggesting that the stability of the species with this peak is greater than that giving the resonance at +39.2 p.p.m. At higher ligand:gold ratios (>1.5:1) the species at +41.6 p.p.m. decreases, but never disappears, even at ligand:gold ratios >2.5:1. Although it is not possible to assign structures to either the species at +41.6 p.p.m. or that at +39.2 p.p.m., we feel that they are both likely to be three-co-ordinate gold(I), structures (**II**) or (**III**), containing two phosphorus and one bromine about each gold. At ligand:$[AuBr_2]^-$ ratios >1.5:1 and temperatures below −50 °C, three peaks appear at +58.0, +41.6, and +6.0 p.p.m. The last is clearly assignable to free ligand, that at +41.6 p.p.m. to [AuBr(dpdb)] or [{AuBr(dpdb)}$_2$], and that at +58.0 p.p.m. is assigned to [Au(dpdb)$_2$]Br, structure (**IV**).

It is interesting to note that at high ligand:gold ratios (2.0—2.5:1) some three-co-ordinate species remain and free ligand is observed along with the four-co-ordinate species. This phenomenon is observed for all the ligands studied here, and this suggests that the order of stability constants for the complexes is $K_1 > K_2$. Similar observations have been found for complexes with other bidentate phosphines.[20]

Similar experiments with the ligand papdb at a ligand: $[AuBr_2]^-$ ratio of 0.5:1 showed a single species over a wide temperature range exhibiting resonances at +99.7 (d) and +46.3 p.p.m. (d), $^3J_{P-P}$ = 40 Hz. This is thus assigned as the ligand-bridged two-co-ordinate complex [(AuBr)$_2$(papdb)], structure (**I**). Upon addition of more ligand, 1.0 mol papdb per mol Au, and at temperatures below −50 °C, a new species is observed at the expense of the first, exhibiting resonances at +103.2 (d) and at +16.9 p.p.m. (d), J_{P-P} = 164 Hz. An independently isolated sample of [AuBr(papdb)] shows the same spectrum and since this complex is non-conducting in nitromethane and exhibits ν(Au–Br) at 226 cm^{-1} in the solid-state i.r. spectrum, then three-co-ordination, structures (**II**) or (**III**), may be confidently assigned to the species resonating at +103.2 and +16.9 p.p.m.

The magnitude of J_{P-P} overall can be thought of as the sum of the coupling through the backbone, $^BJ_{P-P}$, and coupling through the metal atom, $^MJ_{P-P}$. If an estimate of $^BJ_{P-P}$ is made from the coupling observed for [(AuBr)$_2$(papdb)], where only through-backbone coupling is likely, then the magnitude of $^MJ_{P-P}$ can be calculated. Thus $^BJ_{P-P}$ = 40 Hz and J_P(overall) = $^BJ_{P-P} + {}^MJ_{P-P}$, giving $^MJ_{P-P}$ = 124 or 204 Hz, depending on the relative signs of $^MJ_{P-P}$ and $^BJ_{P-P}$.

Further addition of ligand (1.5—2.0 mol per mol Au) at −50 °C causes the appearance of another species resonating at +123.0 (m) and +32.7 p.p.m. (m), assigned to the four-co-ordinate species, structure (**IV**), as well as peaks due to the free ligand at +96.0 (d) and +6.4 p.p.m. (d). The multiplets at +123.0 and +32.7 p.p.m. are symmetrical about the centre and easily assignable to an AXA′X′ spin system, where the ratio J/δ is 10. Analysis of the system gives $J_{AX'}$ = 60 and J_{AX} = 216 Hz.

An inspection of Table 2 shows that similar observations were made with the dapdb ligand, *i.e.* dimeric two-co-ordination at very low ligand:gold ratios (δ_P +99.5 p.p.m.). Addition of more ligand shows the appearance of a new species at +105.8 p.p.m. at the expense of the peak at +99.5 p.p.m. These species exchange at temperatures above −30 °C, but at −90 °C the resonances are quite sharp. The new species has the same resonance as that of an independently prepared sample of the three-co-ordinate complex [AuBr(dapdb)]. Further addition of ligand (1.5—2.5 mol per mol Au) causes a further decrease in the intensity of the peak at +99.5 p.p.m. and two new peaks appear at +127.4 and +95.0 p.p.m. The former is assigned to the four-co-ordinate cation $[Au(dapdb)_2]^+$, and the latter is due to free ligand.

When a mixture of dpdb (0.5 mol) and dapdb (0.5 mol) was added to a molar equivalent of $[AuBr_2]^-$ in CD_3COCD_3–CH_2Cl_2 at −50 °C the ^{31}P n.m.r. shows four resonances at +106.7, +100.0, +41.6, and +39.2 p.p.m. These have been assigned to structures (**II**) (R = NMe$_2$), (**I**) (R = NMe$_2$), (**II**) (R = Ph), and (**III**) (R = Ph), respectively. Further addition (0.5 mol dpdb +0.5 mol dapdb per mol Au) results in the appearance of a new species at +113.0 (t) and +41.8 p.p.m. (t) $^3J_{P-P}$ = 58 Hz, while the two peaks at +39.2 and +100.0 p.p.m. disappeared; the two new peaks are assigned to a four-co-ordinate complex of type (**IV**) but with mixed ligands. The magnitude of $^2J_{P-P}$ for the four-co-ordinate complex $[Au(dpdb)(dapdb)]^+$ compares quite favourably with the value for $J_{AX'}$ in $[Au(papdb)_2]^+$, as expected, since both coupling constants reflect coupling through gold only. The magnitudes of $^2J_{P-P}$ and $J_{AX'}$ for the four-co-ordinate complexes are smaller than the value of $^2J_{P-P}$ observed for the three-co-ordinate complex, in accordance with the greater *s* character in the bonds in the sp^2-hybridized three-co-ordinate complex.

Experimental

The ligands were prepared as described previously.[24]

Preparation of [AuBr(pdb)].—A solution of [NEt$_4$][AuBr$_2$] (0.51 mmol, 0.25 g) in ethanol (15 cm^3) was added to a solution of the ligand pdb (0.51 mmol, 0.17 g) in dichloromethane (10 cm^3) under nitrogen and stirred for 10 min. The colourless solution was concentrated to *ca.* 5 cm^3, by gentle warming, and the white precipitate which formed was filtered off, washed with distilled water (5 × 10 cm^3) and dried *in vacuo* over P_4O_{10} for 1 d at 110 °C. Yield 0.2 g, 78% based on ligand.

The other complexes were prepared in a similar manner using appropriate quantities of the ligands and [NEt$_4$][AuBr$_2$].

Physical Measurements.—The phosphorus-31 n.m.r. experiments were performed on a Varian CFT-20 Fourier-transform spectrometer at 32.1 MHz. I.r. spectra were recorded on a Perkin-Elmer 580 spectrometer using polyethylene plates for the region 600—200 cm^{-1} in Nujol mulls. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tennessee.

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References

1 M. J. Mays and P. A. Vergnano, *J. Chem. Soc., Dalton Trans.*, 1979, 1112.
2 C. B. Colburn, W. E. Hill, C. A. McAuliffe, and R. V. Parish, *J. Chem. Soc., Chem. Commun.*, 1979, 218.
3 R. V. Parish and J. D. Rush, *Chem. Phys. Lett.*, 1979, **63**, 37.
4 C. A. McAuliffe, R. V. Parish, and P. D. Randall, *J. Chem. Soc., Dalton Trans.*, 1977, 1426.
5 R. V. Parish, O. Parry, and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, 1981, 2098.
6 G. C. H. Jones, P. G. Jones, A. G. Maddock, M. J. Mays, P. A. Vergnano, and A. F. Williams, *J. Chem. Soc., Dalton Trans.*, 1977, 1440.
7 C. A. McAuliffe and W. Levason, 'Phosphine, Arsine and Stibine Complexes of the Transition Elements,' Elsevier, Amsterdam, 1979.
8 A. Cahour and H. Gal, *C.R. Acad. Sci.* (*Paris*), 1876, **70**, 1380.
9 F. G. Mann, A. F. Wells, and D. Purdie, *J. Chem. Soc.*, 1937, 1828.
10 L. Malatesta, L. Naldini, G. Simonetta, and F. Cariati, *Coord. Chem. Rev.*, 1966, **1**, 255.
11 J. A. Muir, M. M. Muir, and S. Arias, *Acta Crystallogr., Sect. B*, 1982, **38**, 1318.
12 J. A. Muir, M. M. Muir, S. Arias, C. F. Campana, and S. K. Dwight, *Acta Crystallogr., Sect. B.*, 1982, **38**, 2047.
13 J. A. Dills and M. P. Johnston, *Inorg. Chem.*, 1966, **5**, 2079.
14 P. G. Jones, *J. Chem. Soc., Chem. Commun.*, 1980, 1031.
15 R. C. Elder, E. H. Kelle-Zeiher, M. Onady, and R. R. Whittle, *J. Chem. Soc., Chem. Commun.*, 1981, 900.
16 H. Schmidbaur, A. Wohlleben, U. Schubert, A. Frank, and G. Huttner, *Chem. Ber.*, 1977, **110**, 2751.
17 C. E. Wymore and J. C. Bailar, *J. Inorg. Nucl. Chem.*, 1960, **14**, 42.

18 M. Barron, H. B. Buergi, D. K. Johnson, and L. M. Venanzi, *J. Am. Chem. Soc.*, 1982, **98**, 2356.
19 A. J. Carty and A. Efraty, *Inorg. Chem.*, 1969, **8**, 543.
20 S. Al-Baker, W. E. Hill, and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, in the press.
21 W. E. Hill, D. M. A. Minahan, J. G. Taylor, and C. A. McAuliffe, *J. Am. Chem. Soc.*, 1982, **104**, 6001.
22 J. C. Briggs, C. A. McAuliffe, W. E. Hill, D. M. A. Minahan, J. G. Taylor, and G. Dyer, *Inorg. Chem.*, 1982, **21**, 4204.
23 R. Alexander and F. Rohrscheid, *J. Organomet. Chem.*, 1965, **4**, 335.
24 W. E. Hill and L. M. Silva-Trivino, *Inorg. Chem.*, 1978, **17**, 2495.

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