Gold(I) Complexes derived from Secondary Phosphines: $[\{Au(\mu\text{-}PR_2)\}_n]$, $[(AuBr)_2(\mu\text{-}PPh_2)]^-$, $[AuX(PHR_2)]$, and $[\{Au(PHR_2)_n\}]^+$. Crystal structure of $[AuBr(PHPh_2)]$†

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The interaction of secondary phosphines with a variety of gold(I) compounds has been studied. In the presence of bases or polar solvents, polymeric gold(I) phosphides $[\{Au(\mu\text{-}PR_2)\}_n]$ are formed. When these are obtained in the absence of additional ligands they are soluble, presumably with ring structures. More usually, insoluble forms are found, presumably with chain structures. The probable formation of these materials from complexes of the type $[AuX(PHR_2)]$ is discussed, and the isolation of the latter complexes (X = Cl or Br, R = Ph or *p*-tolyl) and of the novel monomeric phosphido-bridged anion $[(AuBr)_2(\mu\text{-}PPh_2)]^-$ is described. In non-polar solvents a series of secondary phosphine complexes is formed, $[Au(PHPh_2)_n]^+$ (n = 2—4), but that with n = 3 appears to be unstable to disproportionation. The compounds are characterised by ^{31}P n.m.r. and ^{197}Au Mössbauer spectroscopy, and *X*-ray crystallography in the case of $[AuBr(PHPh_2)]$.

Some gold(I) compounds have proved to be very useful in medicine. Good examples are the polymeric thiolates, $[\{Au(SR)\}_n]$, some of which are effective anti-arthritics.[1] However, in contrast to their silver analogues, the gold(I) thiolates do not crystallise and have proved very difficult to characterise. It is established that polymerisation occurs through bridging thiolate groups, $[\{Au(\mu\text{-}SR)\}_n]$, but it is still not known with certainty whether the structures are linear or cyclic, nor whether they depend on the physical state, *etc.*[2—5] In an effort to achieve some further understanding of the factors involved for compounds of this type, we undertook the preparation of the analogous gold(I) phosphides, $AuPR_2$. In such compounds it is possible, in principle at least, to probe every nucleus by appropriate techniques (^1H, ^{13}C, and ^{31}P n.m.r. and ^{197}Au Mössbauer spectroscopy).

Only one such material had been previously described: Puddephatt and Thompson[6] obtained a material analysing as $AuPPh_2$ by treatment of $[AuMe(PMe_2Ph)]$ with $PHPh_2$. This substance was insoluble and was not further characterised. Shortly after there was a brief report[7] of the reaction between $HAuCl_4$ and $PHBu^t_2$ which was thought to have given $[AuCl(PHBu^t_2)]$. This material was characterised by elemental analysis, molecular weight, and Au–Cl stretching frequency; however, the presence of the P–H group was not substantiated [no ν(P–H) could be seen in the i.r. spectrum, and the reported Raman frequency at 2 266 cm^{-1} corresponds to that of the free ligand; no n.m.r. data were given other than the ^1H signals of the t-butyl groups]. On the basis of our findings given below, it appears likely that the material first isolated was the secondary-phosphine complex which became a phosphide, $AuPBu^t_2$.

We now report various routes to compounds of the type $AuPR_2$ (R = phenyl, substituted phenyl, ethyl, or n-octyl), all of which involve reactions of gold(I) complexes with a secondary phosphine. During these studies it was also found possible to characterise novel series of complexes containing diphenylphosphine or ditolylphosphine ligands. Some of these data have been reported in preliminary communications.[8,9]

Table 1. Analytical data (%) with calculated values in parentheses

Complex	C	H	P	Au
$[\{Au(\mu\text{-}PPh_2)\}_n]$	37.8 (37.7)	2.6 (2.6)	8.4 (8.1)	51.5 (51.6)
$[\{Au[\mu\text{-}P(C_6H_4Me\text{-}p)_2]\}_n]$	41.0 (40.9)	3.5 (3.4)	7.6 (7.5)	48.0 (48.0)
$[\{Au[\mu\text{-}P(C_6H_4Bu^t\text{-}p)_2]\}_n]$	45.7 (48.6)	5.2 (5.3)	6.2 (6.3)	40.1 (39.8)
$[\{Au(\mu\text{-}PEt_2)\}_n]$	17.2 (16.8)	3.5 (3.5)	10.7 (10.8)	65.1 (68.9)
$[\{Au[\mu\text{-}P(C_8H_{17})_2]\}_n]$	42.3 (42.3)	7.9 (7.2)	6.7 (6.8)	43.4 (42.9)
$[AuBr(PHPh_2)]^a$	31.3 (31.1)	2.4 (2.4)	6.6 (6.7)	40.5 (42.5)
$[NBu_4][(AuBr)_2(\mu\text{-}PPh_2)]^b$	35.3 (34.2)	4.5 (4.6)		

^{a} Br 17.3 (17.3)%. ^{b} N 1.3 (1.4)%.

Experimental

Spectroscopic data were obtained with the following spectrometers: i.r., Perkin-Elmer 598 or Beckman IR720m; ^1H n.m.r. Perkin-Elmer R34 (220 MHz) or Bruker WP80 (80 MHz); ^{31}P n.m.r., Bruker WP80 (32.4 MHz); solid-state ^{31}P n.m.r., Bruker CXP200 (90.96 MHz) with cross polarisation (University of Oxford); ^{197}Au Mössbauer, Harwell 6000, with source and sample at 4.2 K.

All reactions involving secondary phosphines were carried out in carefully dried solvents under an atmosphere of nitrogen. Typical procedures are described. Analytical data are given in Tables 1 and 2.

Reactions of $[AuCl(tdg)]$ *with* PHR_2 (R = aryl).—A solution of sodium tetrachloroaurate(III) (199 mg, 0.5 mmol) in water (30 cm^3) was cooled in ice and thiodiglycol [tdg, $S(CH_2CH_2OH)_2$] (120 µl, 1.2 mmol) in water (5 cm^3) was added dropwise with stirring. The system was purged with nitrogen, and the appropriate amount of diarylphosphine dissolved in ethanol was added dropwise. There was an immediate white precipitate which increased in volume as the addition was continued. The

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† Bromo(diphenylphosphine)gold(I).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 2. Products from [AuCl(tdg)] and PHR_2

	P:Au	Yield[a] (%)	Colour	Analysis[b]/% C	H	Cl	P	Au	Mol ratio Au:Cl:P
(*a*) From $PHPh_2$									
(A)	0.5:1	45 (90)	White	34.3 (1.0)	2.4 (0.1)	5.7 (0.2)	7.5 (0.2)	48.8 (2.0)	3:2:3
(B)	1:1	90 (90)	White	37.9 (0.8)	2.7 (0.1)	3.3 (0.2)	8.2 (0.2)	46.1 (1.5)	3:1:3
(C)	2:1	80 (45)	Pale yellow	37.6 (0.5)	2.6 (0.1)	<0.1	8.2 *c*	48.8 *c*	3:0:3
(*b*) From $PH(C_6H_4Me\text{-}p)_2$									
(A)	0.5:1	45 (90)	White	39.0 (1.0)	3.5 (0.1)	5.6 (0.3)	7.2 (0.2)	41.5 (0.2)	3:2:3
(B)	1:1	90 (45)	White	41.4 *c*	3.4 *c*	3.5 *c*	7.4 *c*	44.5 *c*	3:1:3
(C)	2:1	75 (45)	Pale yellow	39.5 (0.5)	3.2 (0.1)	<0.1	7.5 (0.1)	47.5 (0.5)	3:0:3

[a] Average data, based on Au (figures in parentheses based on PHR_2). [b] Average data (figures in parentheses represent the range of values obtained). [c] Single sample only.

ice-bath was removed and stirring was continued for 10 min, after which the solid was filtered off, washed with water, and dried in vacuum over P_2O_5.

Poly[μ-*diphenylphosphido-gold*(I)].—(*a*) *From* [AuMe(PMe$_2$Ph)].[6] Bromo(dimethylphosphine)gold(I) (315 mg, 0.76 mmol), suspended in diethyl ether, was cooled to −80 °C and treated with methyl-lithium (0.75 mmol) in ether. The mixture was stirred for 4 h, allowed to warm to room temperature, and hydrolysed with water (20 μl). After being dried over $MgSO_4$, the solution was evaporated to give a crystalline residue of [AuMe(PMe$_2$Ph)] which was dissolved in dichloromethane. Diphenylphosphine (0.7 mmol) was added dropwise. A fine precipitate gradually formed, which was centrifuged, washed with diethyl ether, and dried under vacuum. Yield 60 mg (20%).

(*b*) *From* [AuCl(PPh$_3$)]. Diphenylphosphine (90 μl, 0.5 mmol) was added dropwise to a stirred solution of chloro(triphenylphosphine)gold(I) (247 mg, 0.5 mmol) in pyridine (10 cm^3). The rapidly formed fine white precipitate was isolated by centrifugation, washed with ether, and dried under vacuum. Yield 160 mg (85%).

(*c*) *From* AuCN. Diphenylphosphine (190 μl, 1.1 mmol) was added dropwise with constant stirring to a slurry of gold(I) cyanide (225 mg, 1.0 mmol) in ethanol (10 cm^3) at 30—40 °C. The suspended solid slowly changed from yellow to white during the addition. The mixture was stirred for a further 15 min, while cooling to room temperature, and centrifuged. The product was washed with ether and dried under vacuum. Yield 340 mg(90%).

Bromo(*diphenylphosphine*)*gold*(I).—Diphenylphosphine (180 μl, 1.0 mmol) was added to a solution of tetra(n-butyl)ammonium dibromoaurate[10] (599 mg, 1.0 mmol) in dichloromethane (5 cm^3). The colourless solution was stirred for 10 min and the solvent was removed under reduced pressure. The resulting oil was dissolved in chloroform from which colourless crystals were recovered by slow diffusion of light petroleum with cooling. Yield 250 mg (55%).

Tetra(*n-butyl*)*ammonium* μ-*diphenylphosphido-bis*[*bromogold*(I)].—The oil obtained by the above procedure was shaken with light petroleum for 2 d and then recrystallised from chloroform by slow addition of light petroleum. Attempts to repeat this preparation always gave the diphenylphosphine complex.

Reaction of [AuBr(PHPh$_2$)] *with Pyridine.*—Bromo(diphenylphosphine)gold(I) (98 mg, 0.21 mmol) was dissolved in dichloromethane (3 cm^3) and pyridine (18 μl, 0.21 mmol) was added dropwise with stirring. A white precipitate formed over 5 min and was recovered by centrifugation and washed with ether. It was identified by analysis and i.r. spectroscopy as [{Au(μ-PPh$_2$)}$_n$]. Yield 60 mg (80%).

X-*Ray Structure Analysis of* [AuBr(PHPh$_2$)].—*Crystal data.* $C_{12}H_{11}AuBrP$, $M = 463.07$, triclinic, space group $P\bar{1}$, $a = 10.235(4)$, $b = 10.444(4)$, $c = 14.407(6)$ Å, $\alpha = 70.03(3)$, $\beta = 68.52(3)$, $\gamma = 66.47(3)°$, $U = 1\,279.0$ Å^3, $Z = 4$ (2 crystallographically unique molecules), $D_c = 2.40$ g cm^{-3}, $F(000) = 848$, $w = 1.8520/[\sigma^2(F) + 0.0014F^2]$, $\mu(\text{Mo-}K_\alpha) = 142.13$ cm^{-1}.

Data were measured on a CAD4 diffractometer with graphite-monochromatised Mo-K_α radiation using $\omega/2\theta$ scans. The structure was solved by normal heavy-atom techniques followed by full-matrix least-squares refinement (SHELX[11]). The unit cell consists of the two molecules shown in the PLUTO[12] plot (Figure 1) together with two more generated by the centre of symmetry. One pair of symmetry-related molecules showed a small degree of disorder: 3.2(2)% of the molecules occupy alternative packing positions, so that the Au(2B) atoms appear to occupy sites between the phosphorus atom of one normal molecule and the bromine of the other. In terms of the environment of the phosphorus atom, this is equivalent to an exchange of positions between the unique hydrogen atom and the gold atom. This exchange is associated with only one of the two conformers which form the asymmetric unit. A final $R = 0.054$ and $R' = 0.065$ were obtained for 3 118 observed independent reflections [$|F_o| > 3\sigma(|F_o|)$, $\theta < 25°$], with all non-hydrogen atoms being refined anisotropically and hydrogen atoms constrained to chemically reasonable positions with a common isotropic thermal parameter, except for those attached to phosphorus, which were ignored.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results

(*a*) *Products obtained from* $[AuCl(tdg)]$.—A convenient route to gold(I) complexes of the type $[AuCl(L)]$ (where L is a neutral unidentate ligand) is by reduction of $[AuCl_4]^-$ with thiodiglycol.[13] The resulting complex, $[AuCl(tdg)]$, is very labile, and tdg is readily displaced [equation (1)]. If the ligand L

$$[AuCl(tdg)] + L \longrightarrow [AuCl(L)] + tdg \qquad (1)$$

has a replaceable proton, HCl may be eliminated, and we have prepared a range of gold(I) thiolates by this method [equation (2)].[14] We have therefore investigated the interaction of

$$[AuCl(tdg)] + HSR \longrightarrow \tfrac{1}{n}[\{Au(\mu\text{-}SR)\}_n] + HCl \qquad (2)$$

$[AuCl(tdg)]$ with the secondary phosphines PHR_2 (R = phenyl or *p*-tolyl).

When an ethanolic solution of PHR_2 was added to an aqueous solution of $[AuCl(tdg)]$ there was immediate precipitation of a white solid. If addition was continued beyond P:Au = 1:1 the solid became pale yellow. The compositions of the solid products were reasonably reproducible, and varied according to the final P:Au ratio (Table 2). In every case the product had a P:Au mol ratio which was accurately unity, but the amount of chlorine decreased as the amount of secondary phosphine added was increased, suggesting the formation of mixtures of products. The final product [(**C**), Table 2] corresponded to $Au(PR_2)$. Its ^{197}Au Mössbauer spectrum was a simple doublet [isomer shift (i.s.) (Au) = 4.9 mm s^{-1}, quadrupole splitting (q.s.) = 8.7 mm s^{-1}] similar to those of the other products of this composition described below.

The Mössbauer spectra of the mixed products contained the doublet for $AuPR_2$ together with a second doublet with smaller parameters: i.s.(Au) = 3.8 mm s^{-1}, q.s. = 6.9 mm s^{-1}. These values are similar to those for a wide range of complexes of the type $[AuCl(PR_3)]$,[15] suggesting the presence of $[AuCl(PHR_2)]$. The relative intensities of the two doublets were in reasonable agreement with the P:Au:Cl ratios found by analysis. The i.r. spectra of these products showed a broad weak band at 2 340 cm^{-1} due to P–H stretching [ν(P–H) for free PHR_2 is 2 280 cm^{-1}], and another band at 320 cm^{-1} corresponding to ν(Au–Cl). Product (**C**), $Au(PR_2)$, showed neither of these features.

The products obtained at the lowest ratios of PHR_2 to $[AuCl(tdg)]$ [(**A**), Table 2] were sufficiently soluble for n.m.r. measurements. The ^{31}P spectra (Table 5) support the above assignment, showing resonances at *ca.* −1 and *ca.* +90 p.p.m., only the first of which showed one-bond coupling to hydrogen [^1J(P–H) = 402 Hz]. These signals thus confirm the presence of $AuPR_2$ and $[AuCl(PHR_2)]$. There was a marked decrease in the relative intensity of the latter signal on removal of decoupling, suggesting the operation of the Overhauser effect.

The solid-state ^{31}P n.m.r. data (Table 5) are also in agreement with these assignments (slight shifts to high frequency of the corresponding solution data are not unusual). The mixed product [(**A**)(Ph)] showed an additional signal at +38 p.p.m. which might be due to a product of oxidative degradation: $Ph_2P(O)OH$ gives a signal at +27.5 p.p.m. in CD_2Cl_2 (see below). However, it is more likely that this signal is the same as that seen for an aged solution of the mixed product (**A**). When the solution was allowed to stand, the signal for $[AuCl(PHPh_2)]$ decreased while that of $AuPPh_2$ increased. After 3 d there was some decomposition with precipitation of dark solids presumed to be elemental gold and $AuPPh_2$: simultaneously, a new signal of low intensity appeared at +33.4 p.p.m. The solid-state spectrum of $AuPPh_2$ [(**C**), which is not soluble] showed only a strong signal at +45 p.p.m. Given that chemical shifts for solid-state data are accurate only to *ca.* ±5 p.p.m., it is likely that these signals are all due to the same, or closely related, species. The soluble and insoluble forms of the phosphido-bridged polymer presumably have different structures and hence different ^{31}P chemical shifts.

(*b*) *Products obtained from* $[AuX(PR_3)]$ *or* AuX.—The reaction of $[AuMe(PMe_2Ph)]$ with $PHPh_2$, first described by Puddephatt and Thompson,[6] yielded material analysing as $AuPPh_2$. Apparently analogous materials were also obtained from the reaction of PHR_2 (R = Ph, *p*-MeC_6H_4, *p*-$Bu^tC_6H_4$, or Et) with $[AuX(PR'_3)]$ (X = Cl, Br, or NO_3; R′ = Ph) or $[AuBr(PMePh_2)]$. In all these cases, however, no reaction appeared to occur unless an additional base was present; we normally employed pyridine (py) [equation (3)]. In most cases,

$$[AuX(PR'_3)] + PHR_2 + py \longrightarrow AuPR_2 + PR'_3 + [Hpy]X \qquad (3)$$

the gold phosphide precipitated, but for R = *p*-$Bu^tC_6H_4$ it was necessary to remove the solvent and triturate the residue with diethyl ether. The resulting solid was found to be soluble in pyridine and other common solvents.

More conveniently, it was found that gold(I) cyanide reacts with secondary phosphines simply by warming in ethanol or dichloromethane. For the aromatic phosphines, PHR_2 (R = Ph or *p*-MeC_6H_4), solid products were obtained directly in ethanol, while for R = Ph in CH_2Cl_2 a solution was obtained which deposited $AuPPh_2$ over 5—10 min. Aliphatic secondary phosphines PHR_2 (R = Et or octyl) gave products which were soluble in ethanol, which solidified on removal of the solvent and addition of ether or methanol. The solubility trends are similar to those of the corresponding thiolates,[14] except that the n-octyl derivative shows good solubility.

The i.r. spectra of these materials showed no absorption in the P–H or Au–Cl stretching regions. The ^{197}Au Mössbauer spectra are slightly asymmetric doublets, whose parameters are consistent with P–Au–P co-ordination[15] and vary systematically with the nature of the organic group, increasing with increasing inductive effect (Table 6).

For R = n-octyl or *p*-$Bu^tC_6H_4$ the products were soluble enough to allow the ^{31}P-$\{^1H\}$ n.m.r. spectra to be obtained. For R = n-octyl a slightly broadened signal at +16.8 p.p.m. was seen, which broadened further on removal of proton decoupling. Concentrated solutions in $CDCl_3$ or CD_2Cl_2 deposited cream coloured solids over 15—30 min, making it difficult to obtain well defined spectra. For R = *p*-$Bu^tC_6H_4$ only a very broad (20 p.p.m.) resonance centred on +40 p.p.m. was observed. The width of both spectra suggests that some type of exchange process is occurring, which may be a fluxional process involving flexing of a ring structure, as we suggested for $[\{Au(\mu\text{-}SR)\}_n]$.[14] The ^1H n.m.r. spectrum of the t-butylphenylphosphide showed three broad methyl resonances at δ 1.1, 1.3, and 1.8. The combined area of the first two peaks was about four times that of the third. This behaviour is also reminiscent of the thiolate, which shows three such resonances with intensity ratio 2:2:1. On lowering the temperature the signal at δ 1.3 became dominant and the other two appeared to merge beneath it, but no well resolved pattern could be obtained (down to 180 K). It is therefore not possible to distinguish between a mixture of species and a set of signals from non-equivalent positions within a single polymeric structure, although we favour the latter.

(*c*) *Products from* $[AuBr_2]^-$.—(*i*) 1:1 *Mole ratio.* Treatment of a dichloromethane solution of $[NBu_4][AuBr_2]$ with 1 mol equivalent of $PHPh_2$ gave an oily product which could be crystallised by slow diffusion of light petroleum into a solution in chloroform. Analytical data (Table 1) suggested the formulation $[AuBr(PHPh_2)]$, which is confirmed by n.m.r. and Mössbauer spectroscopy, and *X*-ray crystallography.

Table 3. Fractional atomic co-ordinates ($\times 10^4$) for non-hydrogen atoms of the complex [AuBr(PHPh$_2$)]

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Au(1)	3 893(1)	737(1)	7 643(1)
Au(2A)	3 779(1)	3 996(1)	6 342(1)
Au(2B)	5 909(34)	5 501(35)	5 735(25)
Br(1)	1 863(2)	2 019(2)	8 819(1)
Br(2)	2 407(2)	3 567(2)	5 503(1)
P(1)	5 812(4)	−639(4)	6 681(3)
P(2)	4 984(4)	4 587(5)	7 061(3)
C(1)	7 022(15)	−2 098(15)	7 390(11)
C(2)	8 132(17)	−3 138(16)	6 931(13)
C(3)	9 042(18)	−4 268(18)	7 478(15)
C(4)	8 816(19)	−4 377(21)	8 506(17)
C(5)	7 755(19)	−3 290(20)	8 964(13)
C(6)	6 855(17)	−2 178(17)	8 411(13)
C(7)	6 956(16)	272(15)	5 580(12)
C(8)	7 245(20)	119(19)	4 587(14)
C(9)	8 093(25)	844(25)	3 783(16)
C(10)	8 752(26)	1 640(27)	3 934(15)
C(11)	8 471(26)	1 768(27)	4 911(19)
C(12)	7 583(18)	1 118(17)	5 723(13)
C(13)	6 431(16)	3 159(17)	7 616(11)
C(14)	6 040(19)	2 094(18)	8 460(12)
C(15)	7 142(23)	997(19)	8 890(15)
C(16)	8 547(24)	1 017(25)	4 453(21)
C(17)	8 952(21)	2 048(25)	7 591(21)
C(18)	7 862(19)	3 111(20)	7 201(15)
C(19)	3 809(14)	5 576(14)	8 027(10)
C(20)	2 311(16)	5 997(17)	8 261(12)
C(21)	1 416(19)	6 847(21)	8 952(15)
C(22)	2 048(19)	7 262(17)	9 436(12)
C(23)	3 545(20)	6 852(23)	9 224(15)
C(24)	4 452(18)	5 954(20)	8 545(13)

The i.r. spectrum showed a broad P–H stretching band centred at 2 340 cm^{-1}, which is the same as that for [AuCl(PHPh$_2$)] described above. The corresponding Au–Br modes were observed at 231 and 226 cm^{-1} (^{79}Br, ^{81}Br), and are close to the value of 229 cm^{-1} reported for [AuBr(PPh$_3$)].[16] N.m.r. parameters are also similar to those of the corresponding chloro complex: ^{31}P, +3.2, d, 420 (at 180 K); +1.7 p.p.m., 402 Hz (ambient); ^{1}H, δ 6.9, d, 404(4) Hz (ambient). The small diminution in ^{31}P parameters at the higher temperature may indicate slight dissociation.

The ^{197}Au Mössbauer spectrum showed a simple doublet with parameters in the normal range for P–Au–X co-ordination (X = halide):[15] i.s.(Au) = 3.53 mm s^{-1}, q.s. = 6.98 mm s^{-1}. These values are similar to those of the corresponding chloro complex found as a component of the mixtures described above, and fit the previously defined correlations with bond lengths.[17]

A crystal-structure determination confirmed linear two-co-ordination for the gold, with diphenylphosphine acting as a conventional neutral ligand (Figure 1). The bond distances are normal and there is only slight deviation from linearity (Table 4). The Au–Au distance of 3.256(1) Å is within the range[18] normally defined as 'short' (*i.e.* <350 pm), but probably does not indicate an important interaction.

On one occasion, when the oil obtained from a solution containing a 1 : 1 molar mixture of [NBu$_4$][AuBr$_2$] and PHPh$_2$ was shaken with light petroleum for 2 d before recrystallisation from chloroform–light petroleum, white crystals were obtained which were identified by *X*-ray crystallography[8] as the novel monomeric phosphide [NBu$_4$][(AuBr)$_2$(μ-PPh$_2$)]. The ^{31}P-{^{1}H} n.m.r. spectrum of this complex (CD$_2$Cl$_2$) showed a single strong resonance at +0.8 p.p.m. This value is considerably lower than for any of the other bridging phosphido groups described earlier, and is discussed further below.

Table 4. Selected bond lengths (Å) and angles (°)

Au(1)–P(1)	2.226(4)	Au(1)–Br(1)	2.395(2)
Au(2A)–Br(2)	2.398(2)	Au(2A)–P(2)	2.225(4)
Au(2B)–P(2)	1.90(3)	Au(2B)–Br(2′)	2.24(2)
Au(1) ··· Au(2A)	3.256(1)	P(2)–C(19)	1.79(1)
P(1)–C(1)	1.80(1)	P(2)–C(13)	1.83(2)
P(1)–C(7)	1.81(2)		
P(1)–Au(1)–Br(1)	174.3(1)	C(13)–P(2)–Au(2A)	118.3(5)
P(2)–Au(2A)–Br(2)	175.2(1)	C(19)–P(2)–Au(2A)	114.3(5)
C(1)–P(1)–Au(1)	113.9(5)	C(19)–P(2)–C(13)	106.0(6)
C(7)–P(1)–C(1)	107.5(7)	C(7)–P(1)–Au(1)	116.4(5)

The prime denotes an atom generated by 1 − *x*, 1 − *y*, 1 − *z*.

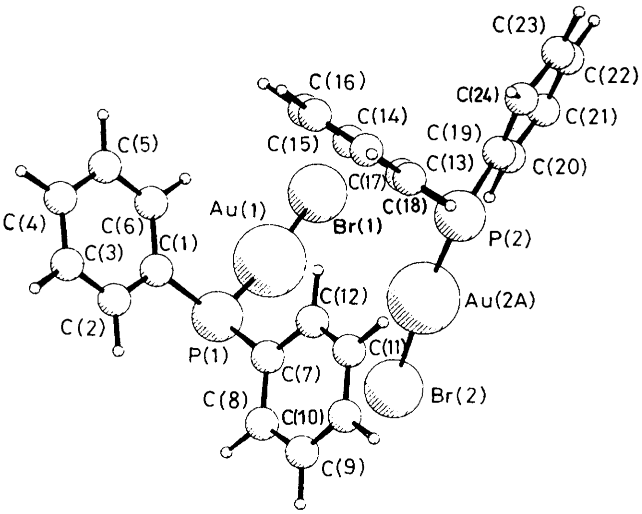


Figure 1. The structure of [AuBr(PHPh$_2$)]. Hydrogen atoms are omitted for convenience, those bound to phosphorus were not located. The two molecules shown form an asymmetric unit which, together with another such unit generated by a centre of symmetry, constitute the unit cell

When 1 mol equivalent of pyridine is added to a dichloromethane solution of [AuBr(PHPh$_2$)] there is rapid precipitation of the insoluble phosphide [{Au(PPh$_2$)}$_n$].

(*ii*) *Various mol ratios.* The interaction between PHPh$_2$ and [NBu$_4$][AuBr$_2$] was also followed by ^{31}P n.m.r. spectroscopy by recording the spectra at 180 K after successive additions of the phosphine. The spectra are shown in Figure 2, and the assignments in Table 7. For P:Au ratios up to 1 : 1 only a single species is seen, with a chemical shift corresponding to that of [AuBr(PHPh$_2$)]. On addition of a further 0.5 mol equivalent of the phosphine this signal disappears and is replaced by three. Peaks labelled 2 and 3 are almost equally intense, while 4 is very weak. The most logical assignment for peak 2 (at highest frequency) is as [Au(PHPh$_2$)$_2$]$^+$; with tertiary phosphine ligands such species always give higher chemical shifts than the corresponding 1 : 1 complexes.[19] Peak 3 appears to be due to [AuBr(PHPh$_2$)] (see discussion of undecoupled spectra below); the slight difference in chemical shift from that found at low P:Au ratios is due to the changes in concentration, viscosity, *etc.* Peak 4 is presumably due to a complex containing more than two phosphine ligands. With a further 0.5 mol equivalent of PHPh$_2$, this peak becomes the strongest, peak 3 has diminished considerably, and an extra very weak peak (5) is seen between peaks 2 and 4. For P:Au >3 : 1, peak 4 remains,

Table 5. N.m.r. data for products (**A**)

		[{Au(μ-PR$_2$)}$_n$]	[AuCl(PHR$_2$)]			
		δ[a]	δ[a]	^1J(P–H)/Hz	Solvent	Temperature
(*a*) R = Ph						
	^{31}P	+90.1	−1.0	402	CDCl$_3$	Ambient
		+88.7	+0.6	*b*	CD$_2$Cl$_2$	180 K
		+88[c]	+7[c]		None[d]	Ambient
	^{1}H		6.9	400	CDCl$_3$	Ambient
(*b*) R = C$_6$H$_4$Me-*p*						
	^{31}P	+90.2	−2.8	402	CDCl$_3$	Ambient
	^{1}H		6.8	400	CDCl$_3$	Ambient

[a] Chemical shift to high frequency of H$_3$PO$_4$. [b] Not measured. [c] ±5 p.p.m. [d] Solid state. Another signal was observed at +38 p.p.m.

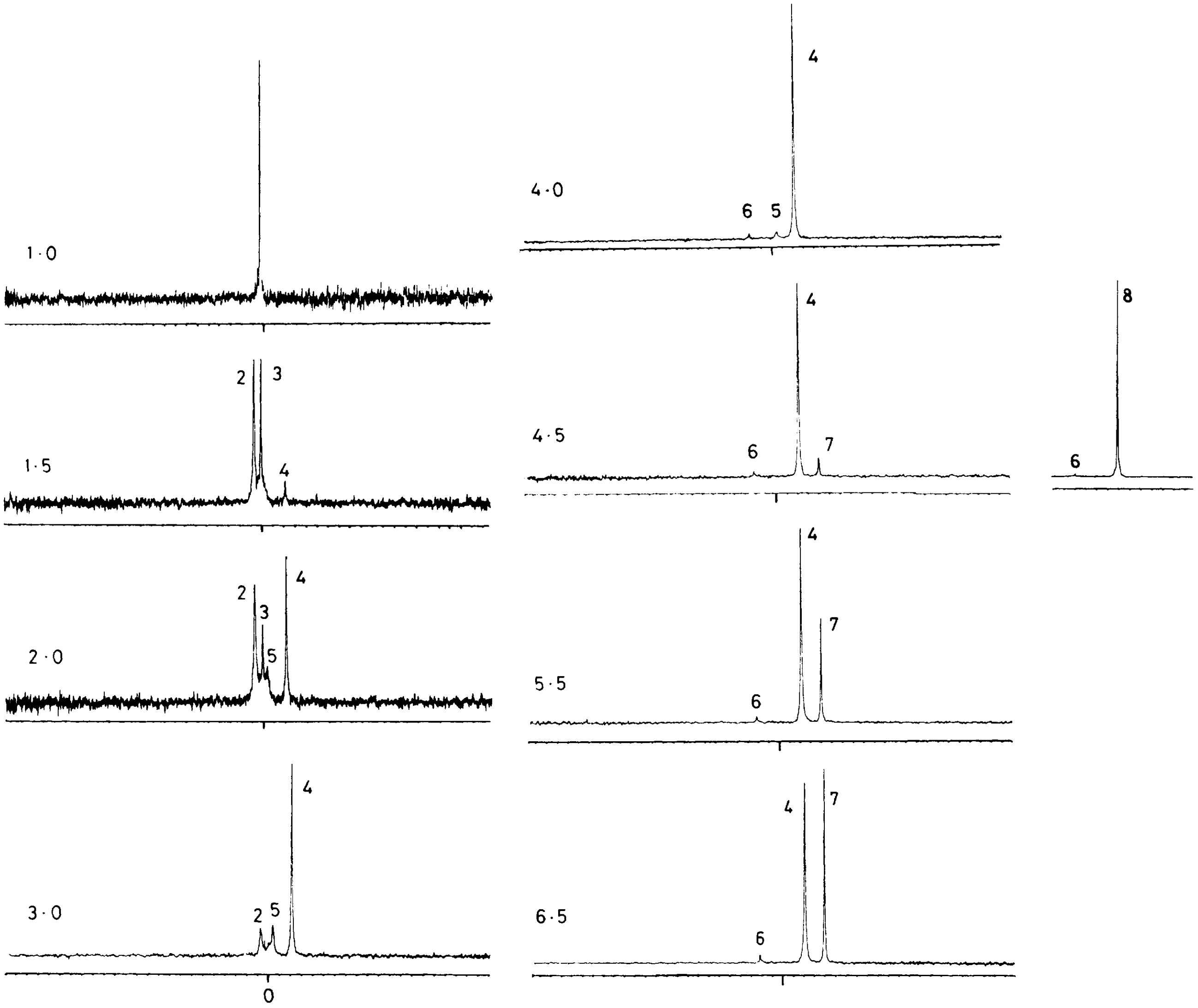


Figure 2. ^{31}P-{^{1}H} N.m.r. spectra of solutions of [AuBr$_2$]$^-$ containing different amounts of PHPh$_2$ (at 180 K, except for the insert at P:Au = 4.5 which is at ambient temperature)

peak 2 disappears, peak 3 diminishes rapidly, but peak 5 persists until P:Au becomes greater than 4:1. Beyond 4.5:1, free PHPh$_2$ is seen (peak 7) at −40.3 p.p.m. A weak peak (6) present at high P:Au ratios is thought to be due to a trace of an oxidation product of the phosphine, probably Ph$_2$P(O)H; a similar signal was found for some samples of the free phosphine.

For tertiary phosphines, species [Au(PR$_3$)$_n$]$^+$ appear at successively lower chemical shifts as *n* increases from 2 to 4.[19]

Table 6. ^{197}Au Mössbauer data for $[\{Au(\mu\text{-}PR_2)\}_n]$

R	I.s.^{a,b}	Q.s.^{b}	Width^{c}
		mm s^{-1}	
Ph	4.83	8.50	2.0, 1.8
C_6H_4Me-*p*	4.93	8.55	2.2, 2.2
$C_6H_4Bu^t$-*p*	4.95	8.61	2.1, 2.4
Et	5.23	9.02	1.6, 2.0
n-Octyl	5.33	9.59	1.9, 1.9

^{a} Relative to gold metal. ^{b} ±0.05 mm s^{-1}. ^{c} ±0.1 mm s^{-1}

Table 7. Phosphorus-31 n.m.r. data for various $[AuBr_2]^-$–$PHPh_2$ mixtures at 180 K

Peak	Chemical shift	Assignment
1	+2.8^{a}	$[AuBr(PHPh_2)]$
2	+7.7^{b}	$[Au(PHPh_2)_2]^+$
3	+0.7^{a}	$[AuBr(PHPh_2)]$
4	−21.4^{c}	$[Au(PHPh_2)_4]^+$
5	−4.1	$[Au(PHPh_2)_3]^+$
6	+21.4	$Ph_2P(O)OH$
7	−40.3	$PHPh_2$
8	−21.7^{d}	Exchange (ambient)

^{a} ^1J(P–H) = 420 Hz. ^{b} Second-order spectrum, ^1J(P–H) = 392 Hz. ^{c} Second-order spectrum, ^1J(P–H) $\leqslant$365 Hz. ^{d} ^1J(P–H) = 218 Hz.

Thus, the species with the lowest chemical shift (−21.4 p.p.m.) is likely to be the tetrakis(ligand) complex $[Au(PHPh_2)_4]^+$, since there is no steric constraint on the co-ordination number of the gold. This assignment is confirmed by the Mössbauer spectrum (see below). It is then likely that peak 5 corresponds to the tris(ligand) complex $[Au(PHPh_2)_3]^+$, even though it never attains a very high intensity.

These assignments were confirmed by removal of the proton decoupling. For P:Au = 1.0 a single doublet is observed with a coupling constant of 420 Hz (at 180 K). This spectrum was identical to that of a solution of independently prepared $[AuBr(PHPh_2)]$. At P:Au = 1.5 the two major peaks (2 and 3) of the decoupled spectrum split into six intense peaks and three or four minor peaks (Figure 3). When the spectrum was re-run at a higher operating frequency [Figure 3(*b*)] it was plain that peak 3 had become a doublet, ^1J(P–H) = 420 Hz, *i.e.* corresponding to $[AuBr(PHPh_2)]$. The remaining peaks constitute the second-order pattern expected for $[Au(PHPh_2)_2]^+$, in which the P–H groups are not magnetically equivalent. Analysis of the spectrum gives ^1J(P–H) = 392, ^3J(P–H) = *ca.* 1.7, ^2J(P–P) = 291 Hz, and ^4J(H–H) = *ca.* 0.

For P:Au = 4.0, peak 4 (−21.4 p.p.m.) splits into a complex doublet on removal of decoupling; signals originating from peaks 5 and 6 were too weak to be detected. Partially resolved fine structure on the inner edges of the two main signals indicates that this is also a second-order pattern, which we have been unable to analyse. The splitting places an upper limit on ^1J(P–H) of about 365 Hz, and indicates that ^2J(P–P) is small. As confirmed below, this corresponds to the tetrakis(ligand) complex $[Au(PHPh_2)_4]^+$. At higher P:Au ratios, this signal persists and is joined by signals due to $PHPh_2$ [−40.3 p.p.m., ^1J(P–H) = 218 Hz].

Attempts to isolate the complexes $[Au(PHPh_2)_n]^+$ were unsuccessful, presumably because they are in labile equilibrium. Ambient-temperature $^{31}P\text{-}\{^1H\}$ n.m.r. spectra showed only single signals at average chemical shifts. Removal of the solvent from a 4:1 mixture of $PHPh_2$ and $[NBu_4][AuBr_2]$ gave an oil which rapidly congealed in air to a sticky white solid. The $^{31}P\text{-}\{^1H\}$ (180 K) n.m.r. spectrum of a CD_2Cl_2 solution of this material showed that the principal gold-containing species was still $[Au(PHPh_2)_4]^+$ (peak 4) together with traces of the other complexes (peaks 2, 3, and 5) and oxidation products of the phosphine, $Ph_2P(O)H$ [+21.7 p.p.m., ^1J(P–H) = 489 Hz] and $Ph_2P(O)OH$ (+27.5 p.p.m.). On warming the solution to room temperature the signals for the gold-containing species coalesced to a single peak, but those for the phosphorus oxy species remained distinct. The latter were also observed in a deliberately oxidised sample of diphenylphosphine. The ^{197}Au Mössbauer spectrum of the solid showed a rather broad (2.6 mm s^{-1}) single line, with an i.s. of 1.49 mm s^{-1}. The absence of resolvable quadrupole splitting is consistent only with a tetrahedral structure, $[Au(PHPh_2)_4]^+$. The four-co-ordinate $[AuBr(PHPh_2)_3]$ and three-co-ordinate $[Au(PHPh_2)_3]^+$ would be expected [15,19,20] to show q.s. values of 3—5 and 7—9 mm s^{-1}, respectively, both of which would be clearly resolvable. The i.s. value is similar to that found [19] for $[Au(PMePh_2)_4]^+$.

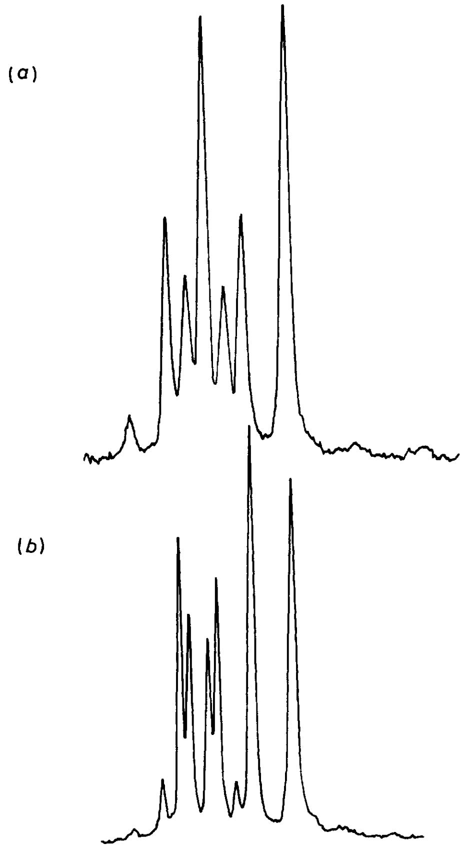


Figure 3. Phosphorus-31 n.m.r. spectra (without decoupling) of $[AuBr_2]^-$ + 1.5 $PHPh_2$ at 180 K, (*a*) at 32.4 MHz, (*b*) at 121.5 MHz

When the solid product mentioned above was triturated with diethyl ether in the presence of air a free-flowing white solid was obtained. Analysis showed this to have a P:Au ratio of 1.1:1. The i.r. spectrum indicated the presence of the Bu_4N^+ cation, but showed no trace of any P–H stretching band. The ^{31}P n.m.r. spectrum was a sharp singlet at +89 p.p.m., which was only slightly broadened on removal of proton decoupling. This material is evidently the soluble form of $[\{Au(\mu\text{-}PPh_2)\}_n]$ described above.

Discussion

The interaction of secondary phosphines with gold(I) complexes leads either to a series of complexes $[AuX(PHR_2)]$, [Au-

$(PHR_2)_n]^+$ (n = 2—4), or to the polymer $[\{Au(\mu\text{-}PR_2)\}_n]$ depending on the nature of X, the solvent used, and the presence or absence of additional base.

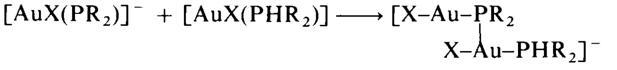
A common intermediate in many of the reactions is the complex $[AuX(PHR_2)]$ (*e.g.* X = Cl, Br, or CN). For X = Br this complex can be readily isolated from non-polar solvents. However, in the presence of a base deprotonation occurs to give the polymer [equations (4)—(6)]. Polymerisation presumably

$$AuCN + PHR_2 \longrightarrow [Au(CN)(PHR_2)] \quad (4)$$

$$[AuBr_2]^- + PHPh_2 \longrightarrow [AuBr(PHPh_2)] \quad (5)$$

$$[AuX(PHR_2)] + B \longrightarrow \tfrac{1}{n}[\{Au(\mu\text{-}PR_2)\}_n] \quad (6)$$

occurs *via* attack by the phosphorus atom of the deprotonated form $[AuX(PR_2)]^-$ on an undeprotonated complex [equation (7)], followed by displacement of either the phosphine or the anion, X [equations (8a) and (8b)]. On one occasion, we serendipitously isolated the product of equation (8a).



$$[AuX(PR_2)]^- + [AuX(PHR_2)] \longrightarrow [X\text{-}Au\text{-}PR_2(\text{-}Au(X)\text{-}PHR_2)]^- \quad (7)$$

$$[XAu(\mu\text{-}PR_2)AuX(PHR_2)]^- \longrightarrow [(AuX)_2(\mu\text{-}PR_2)]^- \quad (8a)$$

$$[XAu(\mu\text{-}PR_2)AuX(PHR_2)]^- \longrightarrow [XAu(\mu\text{-}PR_2)Au(PHR_2)] \quad (8b)$$

It is also likely that three-co-ordinate intermediates $[AuX(L)(PHR_2)]$ are formed in reactions of $[AuMe(PMe_2Ph)]$ or AuCN with PHR_2 in non-polar solvents. In these cases, intramolecular elimination of HX (CH_4 or HCN) seems more likely than deprotonation, especially as it is evident from the n.m.r. studies that $PHPh_2$ is not a strong enough base to deprotonate the co-ordinated ligand, at least in a non-polar solvent. On the other hand, in ethanol $PHPh_2$ does appear to be able to effect some deprotonation, since [AuCl(tdg)] reacts with an excess of the phosphine to give high yields of the polymer. It may be that solvation of the phosphonium cation $H_2PPh_2^+$ is important.

There appear to be (at least) two forms of the phosphido polymer, soluble and insoluble. For diarylphosphides the insoluble form is normally obtained, presumably an infinite chain structure. The dialkylphosphide derivatives are all soluble when first obtained, in contrast to the corresponding thiolates, although insoluble forms tend to deposit slowly if solutions are allowed to stand. The formation of an insoluble chain structure may be aided by π interactions between phenyl rings on adjacent chains, as we have suggested for the corresponding thiolates.[14] As with the thiolates, the introduction of large substituents on the rings imparts solubility, possibly by inhibiting the close approach of adjacent rings. In these cases, intertwined double-ribbon structures may be present as found for $[\{Ag(\mu\text{-}SCMeEt_2)\}_n]$:[21] such a structure allows ready interconvertibility of chains to rings.

Even for the diarylphosphides, soluble polymers are possible. In the preparation of $[\{Au(\mu\text{-}PPh_2)\}_n]$ from AuCN in dichloromethane, clear solutions were obtained which persisted for several minutes before the insoluble polymer precipitated. Similar observations were made in the preparation of $[\{Au(\mu\text{-}SPh)\}_n]$ from [AuCl(tdg)] and HSPh.[22] When $PHPh_2$ was added to [AuCl(tdg)], soluble products were obtained when the P:Au ratio of the mixture was not greater than 1:1. The soluble form is also obtained by aerial oxidation of $[Au(PHPh_2)_4]^+$. The key feature in all these preparations seems to be the absence of any additional ligand. It seems likely that the soluble form is a small-ring polymer, and that conversion into an insoluble long-chain form occurs when a ligand is present which can cleave the ring. This would produce a terminal phosphido group, the lone pair of which could attack another ring and initiate chain growth [equations (9) and (10)]. In this way, a trace of ligand could catalyse the precipitation of the chain form.

$$[\{Au(\mu\text{-}PR_2)\}_n] + L \longrightarrow L\text{-}[Au(\mu\text{-}PR_2)]_{n-1}\text{-}AuPR_2 \quad (9)$$

$$L\text{-}[Au(\mu\text{-}PR_2)]_{n-1}\text{-}AuPR_2 + [\{Au(\mu\text{-}PR_2)\}_n] \longrightarrow L\text{-}[Au(\mu\text{-}PR_2)]_{2n-1}\text{-}AuPR_2 \quad (10)$$

The solid-state ^{31}P n.m.r. data for $[\{Au(\mu\text{-}PR_2)\}_n]$ indicate that the soluble and insoluble forms are quite different, since they exhibit substantially different chemical shifts, +90 and *ca.* +40 p.p.m. respectively. The monomeric digold anion $[(AuBr)_2(\mu\text{-}PPh_2)]^-$ has a chemical shift of +0.8 p.p.m. (CD_2Cl_2). Phosphorus-31 chemical shifts normally cover quite wide ranges, but those for bridging phosphido groups are unusually variable. Values have been recorded from −180 to +289 p.p.m., and seem to depend on the M–P–M bond angle and the presence or absence of M–M bonds.[23–27] Large positive values are associated with metal–metal bonded structures.[24] On this basis, it would seem that the ring polymers embody a degree of intramolecular gold–gold interaction which is greater than that for the chain structure. Consistently with this, the monomeric phosphido-bridged anion has the lowest chemical shift. Chemical shifts of +33 to +54 p.p.m. have been observed for the insoluble forms. It is not clear whether this range represents different structures or simply the lower inherent accuracy of solid-state n.m.r. data.

The ring polymers show only a single ^{31}P resonance, even at 180 K. It is unlikely that all positions in a ring would be equivalent, and this is confirmed by the slight asymmetry of the Mössbauer spectra. There is, therefore, a rapid exchange process occurring in solution. For the phenyl- and *p*-tolyl-phosphides the signal is sharp at room temperature, but for the *p*-t-butylphenyl and n-octyl derivatives the room temperature spectra are very broad. It was not possible to investigate the effect of raising the temperature. The ^1H n.m.r. spectrum of the *p*-t-butylphenyl compound shows three broad resonances at and below ambient temperature. Presumably the higher frequency employed (220 *vs.* 32.4 MHz for ^{31}P) allows observation of non-equivalent t-butyl groups. Similar observations were made for $[\{Au(\mu\text{-}SC_6H_4Bu^t)\}_n]$.[14] There is, however, one major difference between these two systems. While both can show fluxional behaviour by ring flexing, only the thiolate can undergo intermolecular exchange processes. This is because, in the phosphides, there is no lone pair available on the bridging ligand to attack a gold atom in a neighbouring molecule.

The complex $[AuBr(PHPh_2)]$ reacts readily with $PHPh_2$ in dichloromethane to form a series of complexes $[Au(PHPh_2)_n]^+$ (n = 2—4). This behaviour is similar to that found with tertiary phosphines,[19] and the n.m.r. data follow the same pattern. The chemical shift at low temperature decreases in the order $[Au(PHPh_2)_2]^+ < [AuBr(PHPh_2)] < [Au(PHPh_2)_3]^+ < [Au(PHPh_2)_4]^+$. At ambient temperature the spectra collapse to single average signals. There is a difference from the tertiary phosphine case, however, in that the three complexes $[Au(PHPh_2)_n]^+$ ($n = 2$—4) co-exist at P:Au ratios between 1.5 and 3.0:1, and $[Au(PHPh_2)_n]^+$ ($n = 3$) is still present at 4.0:1. With tertiary phosphines no more than two signals are seen for any given ratio. It is also noticeable that $[Au(PHPh_2)_n]^+$ ($n = 3$) is only ever present in low concentrations, suggesting that it is unstable to disproportionation, like the tris PMe_2Ph complex.[20] This observation indicates that, for these ligands, the tetrakis(ligand) complexes have formation constants greater than the normal trends would suggest.

The coupling constants ^1J(P–H) are all greater than those for free $PHPh_2$, as would be expected, and show systematic variations. The value for $[AuBr(PHPh_2)]$ is slightly larger than for $[Au(PHPh_2)_2]^+$ (420 *vs.* 392 Hz), consistent with the *trans* influence of the phosphine being greater than that of the bromide ligand. Further reduction occurs in $[Au(PHPh_2)_4]^+$ (< 365 Hz), showing a slight rehybridisation of the P–H bond as the co-ordination number increases. The bis(ligand) complex shows strong P–P coupling (291 Hz), consistent with linear geometry. The only other values which appear to be available for comparison are for the four-co-ordinate mixed-ligand complexes $[Au(PEt_3)_n\{P(OEt)_3\}_{4-n}]^+$, which range from 77 ($n = 1$) to 100 Hz ($n = 3$).[28] Although we have not been able to analyse the second-order spectrum of $[Au(PHPh_2)_4]^+$, ^1J(P–P) is undoubtedly small, and certainly less than 77 Hz. However, coupling between a tertiary phosphine and a phosphite would presumably be greater than between two phosphines, owing to the different hybridisation of the phosphite, in the same way that the phosphorus to metal coupling changes.

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References

1 R. V. Parish, *Gold Bull.*, 1987, **20**, 3.
2 M. A. Mazid, M. T. Razi, G. N. Greaves, S. J. Gurman, M. H. J. Koch, J. C. Phillips, and P. J. Sadler, *J. Chem. Soc., Chem. Commun.*, 1980, 1261.
3 K. Brown, R. V. Parish, and C. A. McAuliffe, *J. Am. Chem. Soc.*, 1981, **103**, 4943.
4 P. J. Salder and M. Grootveld, *J. Inorg. Biochem.*, 1983, **19**, 51.
5 R. C. Elder, K. Ludwig, J. N. Cooper, and K. M. Eidsness, *J. Am. Chem. Soc.*, 1985, **107**, 5024.
6 R. J. Puddephatt and P. J. Thompson, *J. Organomet. Chem.*, 1976, **117**, 395.
7 H. Schmidbaur and A. A. M. Aly, *Z. Naturforsch., Teil B*, 1979, **34**, 23.
8 R. G. Pritchard, D. B. Dyson, R. V. Parish, C. A. McAuliffe, and B. Beagley, *J. Chem. Soc., Chem. Commun.*, 1987, 371.
9 R. V. Parish, D. B. Dyson, C. A. McAuliffe, and R. Fields, *Hyperfine Interact.*, 1988, **40**, 327.
10 P. Braunstein and R. J. H. Clark, *J. Chem. Soc., Dalton Trans.*, 1973, 1845.
11 G. M. Sheldrick, SHELX 76, Program for crystal structure determination, University of Cambridge, 1976.
12 W. D. S. Motherwell and W. Clegg, PLUTO, Program for plotting molecular and crystal structures, University of Cambridge, 1978.
13 A. K. H. Al-Sa'ady, C. A. McAuliffe, R. V. Parish, and J. A. Sandbank, *Inorg. Synth.*, 1985, **23**, 191.
14 A. K. H. Al-Sa'ady, K. Moss, C. A. McAuliffe, and R. V. Parish, *J. Chem. Soc., Dalton Trans.*, 1984, 1609.
15 R. V. Parish, in 'Mössbauer Spectroscopy Applied to Inorganic Chemistry,' ed. G. J. Long, Plenum, New York, 1984, vol. 1, p. 577; *Gold Bull.*, 1982, **15**, 51.
16 D. R. Williamson and M. C. Baird, *J. Inorg. Nucl. Chem.*, 1972, **34**, 3393.
17 M. Melnik and R. V. Parish, *Co-ord. Chem. Rev.*, 1986, **70**, 157.
18 P. G. Jones, *Gold Bull.*, 1981, **14**, 102.
19 R. V. Parish, O. Parry, and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, 1981, 2098.
20 A. K. H. Al-Sa'ady, C. A. McAuliffe, K. Moss, R. V. Parish, and R. Fields, *J. Chem. Soc., Dalton Trans.*, 1984, 491.
21 I. G. Dance, L. J. Fitzpatrick, A. D. Rae, and M. L. Scudder, *Inorg. Chem.*, 1983, **22**, 3785.
22 L. S. Moore, R. V. Parish, and C. A. McAuliffe, unpublished work.
23 G. W. Bushnell, K. R. Dixon, P. M. Moroney, A. D. Rattray, and Ch'eng Wang, *J. Chem. Soc., Chem. Commun.*, 1977, 709.
24 P. E. Kreter and D. W. Meek, *Inorg. Chem.*, 1983, **22**, 319.
25 N. J. Taylor, P. C. Chieh, and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 1975, 448.
26 J. B. Brandon and D. R. Dixon, *Can. J. Chem.*, 1981, **59**, 1188.
27 A. M. Arif, D. E. Heaton, R. A. Jones, and C. M. Nunn, *Inorg. Chem.*, 1987, **26**, 4228.
28 M. J. Mays and P. Vergnano, *J. Chem. Soc., Dalton Trans.*, 1979, 1112.

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