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Solution Studies of Gold(I) Complexes of n-Hexyldimethylphosphine, n-Butyldiphenylphosphine, 1-Dimethylphosphino-6-diphenylphosphinohexane, 1,6-Bis(dimethylphosphino)hexane and 1,6-Bis(diphenylphosphino)hexane

WILLIAM E. HILL*, MOHAMMED Q. ISLAM, THOMAS R. WEBB*
Department of Chemistry, Auburn University, Auburn, AL 36849, U.S.A.
and CHARLES A. McAULIFFE*
Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD, U.K.

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Abstract

The $^{31}P\{^1H\}$ NMR spectra of the monodentate phosphines PMe_2hex^n and PPh_2Bu^n in the presence of $Et_4N[AuBr_2]$ in $CDCl_3$ solution have been studied at various phosphine/gold ratios and temperatures. At *ca.* 195 K and a P/Au ratio of 1, only [BrAu(phosphine)] is present. Increasing the amount of phosphine leads to the formation of $[BrAu(phosphine)_2]$, $[Au(phosphine)_3]Br$ and $[Au(phosphine)_4]Br$. When $AuBr_2^-$, PMe_2hex^n and PPh_2Bu^n are mixed in a 1:1:1 ratio $[BrAu(PMe_2hex^n)]$, $[BrAu(PMe_2hex^n)_2]$, $[BrAu(PPh_2Bu^n)]$, $[BrAu(PPh_2Bu^n)_2]$ and the mixed ligand $[BrAu(PMe_2hex^n)(PPh_2Bu^n)]$ species are present. Addition of more PMe_2hex^n causes the disappearance of $[BrAu(PMe_2hex^n)]$ with formation of $[BrAu(PMe_2hex^n)_2]$; however this does not occur in the case of PPh_2Bu^n when $[BrAu(PPh_2Bu^n)]$ is still present even at a $Au:PMe_2hex^n:PPh_2Bu^n$ ratio of 1:1:2. Employing the unsymmetrical ditertiary phosphine $Ph_2P(CH_2)_6PMe_2$ enables the identification of the dimeric two-coordinate [BrAu(ligand)AuBr], the dimeric three-coordinate $[BrAu(ligand)_2AuBr]$ (two forms) and the monomeric three-coordinate [BrAu(ligand)]. Similar studies for the symmetrical ditertiary phosphines $Ph_2P(CH_2)_6PPh_2$ (dph) and $Me_2P(CH_2)_6PMe_2$ are reported. The rate constants for the exchange $BrAu(PMe_2hex^n) \rightleftharpoons BrAu(PMe_2hex^n)_2$, $BrAu(PPh_2Bu^n) \rightleftharpoons BrAu(PPh_2Bu^n)_2$ and $BrAu(dph)AuBr \rightleftharpoons BrAu(dph)_2AuBr$ have been determined from the $^{31}P\{^1H\}$ NMR spectra by line shape analysis. Activation parameters have been calculated by a least-squares method. The activation entropies for the exchange processes range from −1.1 to 13.9 cal(mol deg)$^{-1}$ depending on the ligand type. An associative mechanism is more probable although the possibility of a dissociative process cannot be ruled out. We also report here an improved synthetic method for unsymmetrical bisphosphines with chain length $> (CH_2)_4$.

Introduction

There is increasing interest in the chemistry of gold, and it is becoming ever clearer that this chemistry is both extensive and intriguing, despite the supremely noble nature of the metal. Moreover, not only have gold(I) phosphine complexes become established as anti-inflammatory agents, but they now are exhibiting antitumor activity [1].

A large number of tertiary phosphine complexes of gold(I) are known [2]; $[AuCl(PEt_3)]$ was prepared more than a century ago [3]. The dominant stereochemistry is linear two-coordinate, and such complexes are readily prepared by either reduction of gold(III) compounds or by substitution of other gold(I) complexes [2, 4–7]. Higher coordination numbers can be achieved, but here the steric properties of the ligand become important; for example $P(C_6H_4Me\text{-}p)_3$ [5] and PPh_2Bu^n [8] form $[AuL_2]^+$, $[AuL_3]^+$ and $[AuL_4]^+$, but the bulkier $P(cyclo\text{-}C_6H_{11})_3$ forms only $[AuL_2]^+$ [5]. Employing weakly coordinating anions such as BF_4^- or ClO_4^- also aids the isolation of species of higher coordination number and $[AuL_4]^+$ is usually only obtainable with these anions [9]. In addition to these cationic species, trigonal planar three-coordinate and pseudotetrahedral four-coordinate neutral gold(I) complexes are known, e.g. $[Au(SCN)(PPh_3)_2]$ [10], $[Au(SCN)(PPh_3)_3]$ [11] and $[Au(SnCl_3)(PPh_3)_3]$ [12]. The trigonal species have almost ideal geometries with P–Au–P bond angle of 128°, but the pseudotetrahedral species usually contain one long bond, resulting in what could be viewed as trigonal pyramidal [11–13] structures, although $[Au(PPh_2Me)_4]^+$ has a geometry very close to tetrahedral [14].

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*Authors to whom correspondence should be addressed.

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In contrast to the volume of work published on gold(I) complexes of tertiary phosphines there are few reports of complexes of ditertiary phosphines. For the ligands bis(diphenylphosphino)methane (dppm) [15], 1,2-bis(diphenylphosphino)ethane (dppe) [16] and *cis*-1,2-bis(diphenylphosphino)-ethylene [6], complexes of type $[AuX(dppm)_2]$ and $[(AuX)_2L]$ (X = halogen) are known; Venanzi's group [17] has characterized the T-shaped three-coordinate [AuClL] L = 2,11-bis(diphenylphosphinomethyl-benzo[C]phenanthrene; and Carty and Efraty [18] have prepared a number of complexes of bis-(diphenylphosphino)acetylene (dppa) including the interesting $[AuX(dppa)_2]$, a species whose structure is unknown.

Our own program on gold(I) complexes of ditertiary phosphines is an extension of our studies on platinum(II) complexes [19, 20]. We have shown, for example, that for a series of ditertiary phosphines of the type, $Ph_2P(CH_2)_nPPh_2$ ($n = 1$, 2, 4, 6, 8, 10 or 12), neutral $[(AuBr)_2L_x]$ ($x = 1$ or 2) can form in which the gold is two-, and three-coordinate, respectively, and cationic compounds $[Au_2L_x](ClO_4)_2$ ($x = 2$, 3 or 4) in which the gold is two-, three- and four-coordinate. Novel $[Au_2L_4](ClO_4)_2$ complexes were isolable, but only with the short-chain ditertiary phosphines ($n = 2$, 3 or 4) [21]. A $^{31}P\{^1H\}$ NMR study using $Ph_2P(CH_2)_6PPh_2$ and $AuBr_2^-$ at different ratios in CD_2Cl_2 showed the presence of two-, three- and four-coordinate gold, and these species exchange with one another at temperatures >223 K [21]. Other ditertiary phosphines we have used (L) have been based on the rigid *o*-carborane $(C_2B_{10}H_{10})$ backbone, $R_2P(C_2B_{10}H_{10})PR_2'$ (R=R'=Ph; R=R'=NMe_2; R=Ph, R'=NMe_2), which react with $Et_4N[AuBr_2]$ to form the isolable three-coordinate [AuBrL], and the dimeric two-coordinate $[(AuBr)_2Ph_2P(C_2B_{10}H_{10})PPh_2]$. The $^{31}P\{^1H\}$ NMR spectra of CD_3COCD_3–CH_2Cl_2 solutions of L and $[AuBr_2]^-$ show evidence for the formation of dimeric two-coordinate $[(AuBr)_2L]$, dimeric three-coordinate $[(AuBr)_2L_2]$, monomeric three-coordinate [AuBrL], and four-coordinate $[AuL_2]Br$; the most unusual four-coordinate mixed ligand species, $[AuPh_2P(C_2B_{10}H_{10})PPh_2(Me_2N)_2P(C_2B_{10}H_{10})P(NMe)_2]Br$, is also observable [8].

In the study reported here we have extended the range of ditertiary phosphine ligands to the more basic unsymmetrical ligand $Ph_2P(CH_2)_6PMe_2$ and the symmetrical $Me_2P(CH_2)_6PMe_2$ ligand. Product distribution and kinetics of the reaction of gold(I) with model tertiary phosphines PPh_2Bu^n and PMe_2hex^n ($hex^n = -(CH_2)_5CH_3$) have been used to help elucidate the behavior of the ditertiary phosphine ligands.

Results and Discussion

The long-chain ditertiary phosphines were prepared by a modification of the method of Briggs and Dyer [22, 23]

$$Br(CH_2)_6Br + PR_2Ph \xrightarrow{R\,=\,Me,\ Ph} [R_2PhP(CH_2)_6Br]Br$$

$$[R_2PhP(CH_2)_6Br]Br + 2PPhMe_2 \xrightarrow{DMF} [R_2PhP(CH_2)_6PPhMe_2]Br_2$$

$$[R_2PhP(CH_2)_6PPhMe_2]Br_2 \xrightarrow{NaOH} R_2P(O)(CH_2)_6P(O)Me_2$$

$$R_2P(O)(CH_2)_6P(O)Me_2 \xrightarrow{SiHCl_3} R_2P(CH_2)_6PMe_2$$

In the published method [22] a large excess of the dibromoalkane in benzene was used and the monophosphonium salt precipitated from solution. However for a chain length where $n = 6$ or greater, the desired monophosphonium salt does not precipitate from the non-polar benzene medium. We find that reacting the neat dibromide with PR_2Ph (5:1 mole ratio) at 363 K for 5–6 h gives the monophosphonium salt as a sticky solid that floats on top of the liquid dibromide. Both temperature and time of reaction need to be controlled carefully; elevated temperatures lead to substantial disubstitution and reaction time < 5 h leaves unreacted PR_2Ph which is difficult to separate from the monophosphonium salt. The diphosphonium salt can be easily prepared by refluxing the monophosphonium salt and $PPhR_2$ in a polar solvent such as DMF. The diphosphonium salt is converted to the diphosphine dioxide by alkaline hydrolysis and subsequently to the free ligand by trichlorosilane reduction.

Gold(I)/Monodentate Phosphines in Solution

$Et_4N[AuBr_2]$ and the monodentate phosphine ligands at different mole ratios were mixed in CH_2Cl_2/CD_2Cl_2 and the $^{31}P\{^1H\}$ spectra of the solutions were recorded at different temperatures. The results are shown in Tables 1–3. Table 1 shows the $^{31}P\{^1H\}$ chemical shifts as a function of $PMe_2hex^n/[Et_4N][AuBr_2]$ ratio at 195 K, and Table 2 shows the $^{31}P\{^1H\}$ chemical shifts as a function of $PMe_2hex^n/[Et_4N][AuBr_2]$ ratio and temperature. It is clear from Table 2 that several species are exchanging at room temperature and a single NMR signal is observed. As the temperature is lowered, the exchange rate decreases, the signal broadens and splits into several peaks and the linewidth then narrows until all exchange has stopped. Assignments for the species have been made at a temperature where the linewidth and chemical shift do not change significantly with further decreases in temperature.

With one mole of PMe_2hex^n per mole of $[Et_4N][AuBr_2]$ the $^{31}P\{^1H\}$ NMR spectrum shows a sharp peak at 4.8 ppm. The chemical shift and linewidth do not change as the temperature is lowered to 195 K.

TABLE 1. The $^{31}P\{^1H\}$ NMR Spectra of $[Et_4N][AuBr_2]$ and PMe_2hex^n in Different Mole Ratios at 195 K

Mol L/mol Au	Chemical shift (ppm)[a]	Assignment
1.0/1.0	4.8	$[BrAu(PMe_2hex^n)]$
2.0/1.0	4.8(1.0)[b] 13.8(4.8)	$[BrAu(PMe_2hex^n)]$ $[BrAu(PMe_2hex^n)_2]$
3.0/1.0	11.5(1.0)br[c] 13.6(3.5)br –27.3(3.0)	$[Au(PMe_2hex^n)_3]Br$ $[BrAu(PMe_2)hex^n)_2]$ $[Au(PMe_2hex^n)_4]Br$
4.0/1.0	11.5(1.0)br 13.6(1.0)br –27.3(7.0)	$[Au(PMe_2hex^n)_3]Br$ $[BrAu(PMe_2hex^n)_2]$ $[Au(PMe_2hex^n)_4]Br$
5.0/1.0	–26.5(5.1) –51.6(1.0)br	$[Au(PMe_2hex^n)_4]Br$ free ligand

[a] Relative to external 85% H_3PO_4. [b] Relative area of NMR peaks in parentheses. [c] br = broad.

TABLE 2. $^{31}P\{^1H\}$ Chemical Shifts[a] (ppm) as a Function of $PMe^2hex^n/[Et_4N][AuBr_2]$ Ratio and Temperature[a]

Mol of PMe_2hex^n/ Et_4NAuBr_2	Temperature (K)							Assignments for 184 K spectrum
	295	273	243	223	213	200	184	
1.5/1.0	12.2br[b]	5.2(1.0)[c] 13.9(2.0)	5.2(1.0) 13.9(2.0)	5.2(1.0) 13.9(2.0)	5.1(1.0) 13.9(2.0)		5.1(1.0) 13.9(2.0)	$BrAu(PMe_2hex^n)$ $BrAu(PMe_2hex^n)_2$
2.5/1.0	–7.6	–9.1	–10.5	11.7 –26.5	13.0(1.0) –27.0(2.0)		14.1(3.5) 11.8(1.0) 27.0(8.0)	$BrAu(PMe_2hex^n)_2$ $[Au(PMe_2hex^n)_3]Br$ $[Au(PMe_2hex^n)_4]Br$
5.0/1.0	–25.5	–28.6	–29.6	–26.5(5) –51.4(1)br	–26.5(8.0) –51.6(1.0)		–26.6(5.3) –51.8(1)	$[Au(PMe_2hex^n)_4]Br$ free ligand
8.0/1.0	–23.3		–29.6	–27.3br		–27.1(5.2) –52.1(1.0)	–27.1(5.0) –52.1(1.0)	$[Au(PMe_2hex^n)_4]Br$ free ligand

[a] Chemical shifts in ppm relative to 85% H_3PO_4. [b] br = broad. [c] Relative areas of NMR peaks in parentheses.

This species has been assigned to the complex, $BrAu(PMe_2hex^n)$. Addition of a further mole of ligand (*i.e.* ligand/Au = 2/1) results in the appearance of two sharp lines (195 K) at 4.8 and 13.8 ppm (relative area = 1:4.8). Since the 4.8 ppm peak corresponds to $[BrAu(PMe_2hex^n)]$, the 13.8 ppm peak has been assigned to $[BrAu(PMe_2hex^n)_2]$, an assignment consistent with the fact that 2P/Au species appear at lower field than 1P/Au species [5, 24]. The relative areas of these two peaks suggest that there must also be some unreacted $AuBr_2^-$ or a third species which is not detectable at this temperature. At a P:Au ratio of 3:1, three signals at 11.5, 13.6 and –27.3 ppm, with relative areas 1:3.5:3 are observed at 195 K. Of these, two (at 11.5 and 13.6 ppm) are still broad but the one at –27.3 ppm is sharp. The 13.6 ppm peak is assigned to $[Au(PMe_2hex^n)_2Br]$ and the 11.5 ppm peak is assigned to $[Au(PMe_2hex^n)_3]Br$. Such assignments are again consistent with the observation that the addition of a third ligand or fourth ligand to gold moves the chemical shift progressively upfield [5, 24] toward the free ligand value. The –27.3 ppm peak is assigned to $[Au(PMe_2hex^n)_4]Br$. Here again, the relative areas suggest that some unreacted $AuBr_2^-$ or other undetected species must be present. With 4 mol of ligand per mole of gold salt the peak at 13.6 ppm decreases with a corresponding increase in intensity of the –27.3 ppm peak. Both the 11.5 and 13.6 ppm peaks are still broad at 195 K, suggesting these species are still exchanging. At a P:Au of 5:1, two peaks are observed at –26.6 and –51.6 ppm in the ratio of 5.1:1 indicating that trace amounts of other species are present. The observed peaks are broad, so the free ligand exchange with $[Au(PMe_2hex^n)_4]Br$ still continues at 195 K. Since no species containing two or three ligands are observed, $[Au(PMe_2hex^n{}_4]Br$ must be favored under

TABLE 3. The $^{31}P\{^1H\}$ NMR Data of $[Et_4N][AuBr_2]$ and PPh_2Bu^n in Different Mole Ratios at 200 K

Mol L/mol Au	Chemical shifts (ppm)[a]	Assignment[b]
1.0/1.0	31.6	$[BrAu(PPh_2Bu^n)]$
2.0/1.0	31.9 (1.0) 36.4 (4.0)	$[BrAu(PPh_2Bu^n)]$ $[BrAu(PPh_2Bu^n)_2]$
3.0/1.0	31.9 (1.0) 36.4 (3.2) 33.6 (3.0)	$[BrAu(PPh_2Bu^n)]$ $[BrAu(PPh_2Bu^n)_2]$ $[Au(PPh_2Bu^n)_3]Br$
5.0/1.0	19.2 (5.4) –17.3 (1.0)	$[Au(PPh_2Bu^n)_4]Br$ free ligand

[a] Relative to 85% H_3PO_4 external. [b] Assignments agree well with values for independently prepared compounds.

these conditions. As with the lower P:Au ratios, the relative areas for P:Au ratios of 4 and 5 suggest that some $AuBr_2^-$ or other undetected species must be present.

With fractional ratios of ligand/Au, Table 2, the observation is similar to that of the even mole ratio cases in that at room temperature a single peak is observed. The resonance broadens and splits into several peaks at low temperature. Thus, at a P/Au ratio of 1.5, a broad single resonance is observed at 295 K. Below 295 K, two resonances centered at 5.1 and 13.9 ppm (relative areas 1:2) are observed. With a P/Au ratio of 2.5, a single resonance is observed to 243 K. At 233 K, broad peaks are observed at 11.7 and −26.5 ppm. On further cooling to 184 K, peaks at 14.1, 11.8 and −27.0 ppm are observed in the ratio of 3.5:1:8. Since the 13.0 ppm peak splits into two peaks at 14.1 and 11.8 ppm at 184 K, $[BrAu(PMe_2hex^n)_2]$ exchanges with $[Au(PMe_2hex^n)_3]Br$ at a faster rate than either $[BrAu(PMe_2hex^n)_2]$ and $[Au(PMe_2hex^n)_4]Br$ or $[Au(PMe_2hex^n)_3]Br$ and $[Au(PMe_2hex^n)_4]Br$. The linewidth of the −27.0 ppm peak does not change below 213 K. No $[BrAu(PMe_2hex^n)]$ exists at P/Au ratios greater than 2.0. At a higher ratio (>4.0) $[Au(PMe_2hex^n)_4]Br$ is the only species and it exchanges with the free ligand.

Table 3 shows the $^{31}P\{^1H\}$ chemical shifts of a solution of PPh_2Bu^n and $[Et_4N][AuBr_2]$ at 200 K for different P:Au ratios. For a low phosphine concentration (1 mol ligand/mol Au), a single species is observed at 31.6 ppm. Addition of more ligand to give P:Au = 2 results in the appearance of a new species at 36.4 ppm with a corresponding decrease in the peak at 31.6 ppm. The relative area of these peaks is 4:1. The 31.6 ppm peak is assigned to $[BrAu(PPh_2Bu^n)]$ and that at 36.4 ppm to $[BrAu(PPh_2Bu^n)_2]$. At 203 K, the peaks are quite sharp, indicating that exchange is slow on the NMR time scale, but at temperatures above 223 K these two species exchange. Further addition of ligand (P:Au = 3) results in a decrease in the intensity of the peak at 36.4 ppm while a new peak appears at 33.6 ppm, assignable to the $[Au(PPh_2Bu^n)_3]Br$ complex. The ratio of the areas of the three peaks is 1:3.2:3.

At a P:Au ratio of 5:1, two resonances appear at 19.2 and −17.1 ppm in a 5.4:1 ratio, and both peaks are slightly broadened even at 200 K. The latter resonance is due to free ligand, and the peak at 19.2 ppm is assigned to $[Au(PPh_2Bu^n)_4]Br$. These assignments agree well with those made [21] for independently prepared and isolated complexes. It may be noted that a comparison of the previously reported cationic perchlorate complexes [21] with these bromide complexes for the P:Au = 3 and P:Au = 4 ratios indicate identical cationic structures for each. As with the PMe_2hex^n results, the $^{31}P\{^1H\}$ NMR integrals indicate that some $AuBr_2^-$ or other undetected species must be present at all ligand/gold ratios.

TABLE 4. The $^{31}P\{^1H\}$ NMR of a 1:1:1 Molar Mixture of $[Et_4N][AuBr_2]$, PMe_2hex^n and PPh_2Bu^n at 195 K

Chemical shift (ppm)[a]	Assignment
36.1(2)[b]	$[BrAu(PPh_2Bu^n)_2]$
13.7(2)	$[BrAu(PMe_2hex^n)_2]$
31.6(1)	$[BrAu(PPh_2Bu^n)]$
4.8(1)	$[BrAu(PMe_2hex^n)]$
37.1(2)d[c] 13.8(2)d	$[BrAu(PMe_2hex^n)(PPh_2Bu^n)]$

[a] Relative to external 85% H_3PO_4. [b] Relative area from ^{31}P NMR peaks. [c] d = doublet (J_{PP} = 322 Hz); 37.1 peak is assigned to PPh_2Bu^n and the 13.8 peak to PMe_2hex^n.

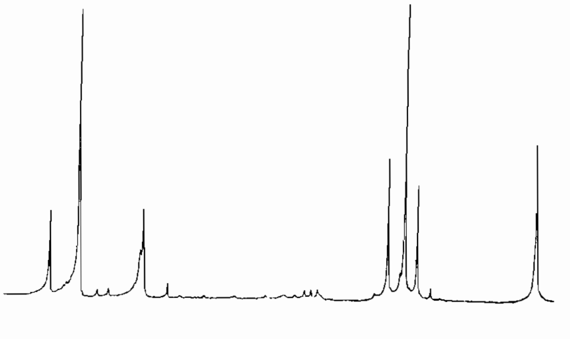

Fig. 1. The $^{31}P\{^1H\}$ NMR spectrum of a 1:1:1 molar mixture of PMe_2hex^n, PPh_2Bu^n and $[Et_4N][AuBr_2]$ at 195 K.

The $^{31}P\{^1H\}$ NMR of a 1:1:1 mixture of $[Et_4N][AuBr_2]$, PMe_2hex^n and PPh_2Bu^n was run in order to identify the type of solution species present in this mixture (Table 4 and Fig. 1). All peaks can be assigned by comparison with the chemical shift values obtained when PMe_2hex^n and PPh_2Bu^n are separately mixed with $Et_4N[AuBr_2]$ at different mole ratios (Tables 1 and 3).

The 4.8 ppm peak is thus assigned to $[BrAuPMe_2hex^n]$, and the 31.6 ppm peak to $[BrAuPPh_2Bu^n]$. These peaks are in a 1:1 ratio, suggesting that these complexes are present in equal concentration. The 13.7 ppm peak is assigned to $[BrAu(PMe_2hex^n)]_2]$ and the 36.1 ppm peak to $[BrAu(PPh_2Bu^n)_2]$, and these species again exist in a 1:1 ratio. The doublets at 13.8 ppm (J_{PP} = 322 Hz) and 37.1 ppm (J_{PP} = 322 Hz) are assigned to the mixed ligand complex, $[BrAu(PMe_2hex^n)(PPh_2Bu^n)$; the 13.8 peak is assigned to free PMe_2hex^n and the 37.1 peak for free PPh_2Bu^n lies under the 36.1 ppm peak due to $[BrAu(PPh_2Bu^n)_2]$. The P–P coupling constants are large, which is to be expected for linearly coordinated gold(I) [25]. From the relative intensities in Table 4, the molar concentration of this mixed ligand complex is twice that of any other detectable species, which is the statistically expected ratio. Since complexes containing 1P/Au are detected, some other undetected species must also be present containing more than two phosphorus atoms per gold.

Addition of a further mole of PMe_2hex^n to the above 1:1:1 mixture of $[Et_4N][AuBr_2]$, PMe_2hex^n, and PPh_2Bu^n at 195 K (giving 2 mol PMe_2hex^n/Au) causes the disappearance of the 4.8 ppm peak $[BrAuPMe_2hex^n]$ with an increase in the intensity of the 13.7 ppm peak, $BrAu(PMe_2hex^n)_2$, and this becomes the major species in this mixture. A number of other species are present but cannot be assigned because of signal overlap. Presumably some $[Au(PMe_2hex^n)_2(PPh_2Bu^n)]Br$, $[Au(PMe_2hex^n)(PPh_2Bu^n)_2]Br$, $[Au(PMe_2hex^n)_3]Br$ and $[Au(PPh_2Bu^n)_3]Br$ are present, as may be some 4P/Au complexes. Surprisingly, when a mole of PPh_2Bu^n is added to a 1:1:1 mixture of $[Et_4N][AuBr_2]$, PMe_2hex^n, and PPh_2Bu^n (giving 2 mol of PPh_2Bu^nAu), the 31.9 ppm peak assigned to $[BrAuPPh_2Bu^n]$ does not disappear. However $[BrAu(PPh_2Bu^n)_2]$ (13.7 ppm) and $[Au(PPh_2Bu^n)_3]Br$ (33.7 ppm) become the major species in this mixture. Furthermore $[BrAu(PMe_2hex^n)_2]$ is also present in substantial amounts. The mixed-ligand species, $[BrAu(PMe_2hex^n)(PPh_2Bu^n)]$ (J_{PP} = 322 Hz), can be identified in both cases (with increased PMe_2hex^n or PPh_2Bu^n) but it is not present in substantial amounts.

Solution Species from $[Et_4N][AuBr_2]$ and the Unsymmetrical Bidentate Ligand, $Me_2P(CH_2)_6PPh_2$

The $^{31}P\{^1H\}$ NMR spectra of 1:0.5 and 1:1 ratios of ligand:Au were run with the hope that the species in solution could be identified by comparison with the $^{31}P\{^1H\}$ NMR of a 1:1:1 mixture of PMe_2hex^n:PPh_2Bu^n:Au. The bidentate phosphine ligands separated by six methylene groups may be considered as equivalent to the two monodentate phosphine ligands.

For a ligand/Au ratio of 0.5, two peaks are observed at 4.6 and 32.1 ppm at room temperature. The linewidth of these peaks remains unchanged to 233 K, indicating that no exchange is occurring on the NMR time scale. This species has been assigned to $[BrAu(Me_2P(CH_2)_6PPh_2)AuBr]$ by comparison with the results obtained with PPh_2Bu^n and PMe_2hex^n. For a ligand/Au ratio of 1.0, at room temperature two broad peaks are observed at 36.3 and 12.4 ppm, with a small peak at 32.7 ppm. These peaks correspond to 2 phosphorus/Au and 1 phosphorus/Au containing species as seen previously, but no mixed species are observed. These peaks are broad, suggesting that the species are exchanging. Lowering the temperature to 253 K causes the appearance of new peaks at 39.2, 14.5, 13.0 and 5.0 ppm, but lowering the temperature further to 223 K gives a spectrum with sharp peaks, Fig. 2. By comparing this spectrum with that of a 1:1:1 mixture of Au and monodentate ligands, all the peaks can be assigned, as shown in Fig. 3.

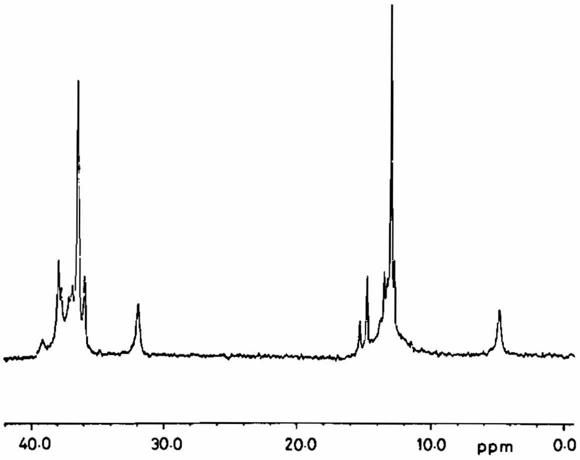

Fig. 2. The $^{31}P\{^1H\}$ NMR spectrum of a 1:1 molar mixture of $Ph_2P(CH_2)_6PMe_2$ and $[Et_4N][AuBr_2]$ at 233 K.

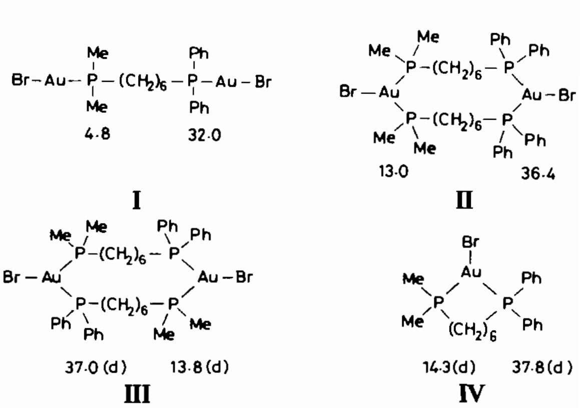

Fig. 3. Proposed structures of the solution species of a 1:1 molar mixture of $Ph_2P(CH_2)_6PMe_2$ and $[Et_4N][AuBr_2]$ at 233 K. $^{31}P\{^1H\}$ NMR assignnments are given in ppm for each environment (d = doublet).

Solution Species from $[Et_4N][AuBr_2]$ and the Symmetrical Bidentate Ligand, $Me_2P(CH_2)_6PMe_2$

For $[Et_4N][AuBr_2]$ and $Me_2P(CH_2)_6PMe_2$ a single peak is observed at 5.1 ppm for a ligand/Au ratio of 0.5. The linewidth of this peak remains unchanged over the temperature range 293 to 200 K. For a ligand/Au ratio of 1.25/1.0 two broad peaks are observed at room temperature at 4.1 and 13.0 ppm in the ratio 2:1. At 253 K a new species appears at 13.1 ppm. All the peaks are quite sharp indicating no significant exchange at this temperature. At 213 K there are three peaks (Fig. 4) at 14.1, 13.3 and 5.1 ppm in the ratio of 1:2:6. Comparing the chemical shifts of this bidentate system with the monodentate PMe_2hex^n system, the 5.1 ppm peak can be assigned to a 1P/Au species. Since there is no peak corresponding to free phosphine, this species (1P/Au) must be

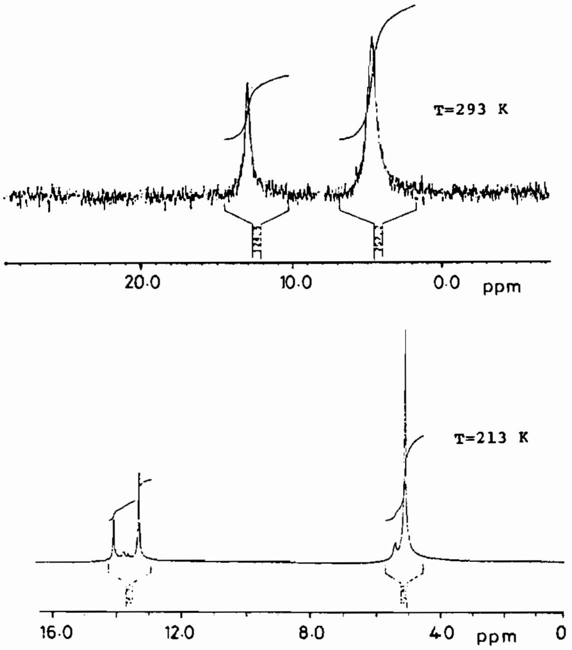

Fig. 4. The $^{31}P\{^1H\}$ NMR spectra of a 1.25/1.0 molar mixture of $PMe_2(CH_2)_6PMe_2$ and $[Et_4N][AuBr_2]$.

dimeric, *i.e.* $[BrAu(P{-}P)_2AuBr]$. The 14.1 ppm peak can be assigned to a 2P/Au species also by comparison with the monodentate system, Table 2. No 3P/Au species is observed since that would appear at 11.3 ppm, Table 3. Therefore the peak at 13.3 ppm can be assigned to another species containing 2P/Au. Two possible structures exist for the 2P/Au species – the bridged dimer $[BrAu(Me_2P(CH_2)_6PMe_2)_2AuBr]$ species and the chelated monomer $[BrAu(Me_2P(CH_2)_6PMe_2)]$. Due to the small difference in chemical shifts of the two 2P/Au species, it is not possible to assign a particular species to a particular peak.

Rate Constants for Ligand Exchange

Rate constants for the exchange between 1 ligand/Au and 2 ligand/Au species {ligand = PMe_2hex^n, PPh_2Bu^n, $Ph_2P(CH_2)_6PPh_2$} have been determined at different temperatures from line shape analysis. These are listed in Table 5. $\Delta G^{\neq}$ and $\Delta S^{\neq}$ have been calculated by least-squares analyses and are reported in Table 6. Al-Baker *et al.* [26] have found that $PPhMe_2$ and $PBu^n{}_3$ form one-, two-, and three-coordinate (four-coordinate in the case of $PBu^n{}_3$) species which exchange with one another at room temperature. This exchange can be stopped below 213 K. The $\Delta S^{\neq}$ values for the exchange between BrAuL and $BrAuL_2$ (L = $PPhMe_2$, $PBu^n{}_3$) are −22 eu for $PPhMe_2$ and −8 eu for $PBu^n{}_3$. This has been cited as evidence for exchange via an associative mechanism. In this study, the value of −1.1 eu found for exchange between $BrAu(PPh_2Bu^n)$ and $BrAu(PPh_2Bu^n)_2$ as well as the value of 1.9 eu for the BrAu(dph)AuBr with $BrAu(dph)_2AuBr$ exchange are in a range that inference about the mechanism of exchange cannot be made.

TABLE 5. Rate Constants of the Exchanging Species at Different Temperatures

T (K)	$BrAu(PMe_2hex^n)$ ⇅ $BrAu(PMe_2hex^n)_2$ k (s^{-1})	$BrAu(PPh_2Bu^n)$ ⇅ $BrAu(PPh_2Bu^n)_2$ k (s^{-1})	BrAu(dph)AuBr [a] ⇅ $BrAu(dph)_2AuBr$ k (s^{-1})
310			13897
305	7655		
292			3560
280	574		1330
273	273	4600	
260		1600	
215		15	

[a] dph = 1,6-Bis(diphenylphosphino)hexane.

TABLE 6. Thermodynamic Parameters for the Exchange Between Gold Complexes in Solution

	$BrAu(PMe_2hex^n)$ ⇅ $BrAu(PMe_2hex^n)_2$	$BrAu(PPh_2Bu^n)$ ⇅ $BrAu(PPh_2Bu^n)_2$	BrAu(dph)AuBr [a] ⇅ $BrAu(dph)_2AuBr$
$\Delta G^{\neq}$ (kcal/mol)	12.4	11.3	12.3
$\Delta H^{\neq}$ (kcal/mol)	16.7	11.0	12.9
$\Delta S^{\neq}$ (cal/mol-deg)	13.9	−1.1	1.86
E_a (kcal/mol)	17.3	11.7	13.5

[a] dph = 1,6-Bis(diphenylphosphino)hexane.

Furthermore the value of 13.9 eu for $BrAu(PMe_2hex^n)$ and $BrAu(PMe_2hex^n)_2$ exchange could be explained in terms of a dissociative mechanism. However, with very basic phosphines, ionization of $BrAuL_2$ in solution would in all likelihood increase $\Delta S^{\neq}$ even if exchange of phosphine was associative. Furthermore, ionization producing AuL_2^+ and Br^- would be favored in dilute solutions. In fact, in the present study, the concentrations were approximately one half those of the previous study [26] which perhaps accounts for the larger numbers measured for PPh_2Bu^n and PMe_2hex^n compared to $PPhMe_2$ and PBu^n_3. In conclusion, the $\Delta S^{\neq}$ values obtained here do not rule out an associative mechanism such as that postulated earlier especially if ionization of the complexes is occurring at low concentrations and is favoured by the more basic phosphines.

Experimental

Preparation of 1-Bromo-6-triphenylphosphonium-hexyl Bromide, [Br(CH₂)₆PPh₃]Br

Triphenylphosphine (17.5 g; 0.067 mol) and 1,6-dibromohexane (84.0 g; 0.34 mol) were mixed in a 250 cm^3 round-bottom flask fitted with a reflux condenser, and heated in an oil bath at 90 °C for 5–6 h. On cooling for 3 h two layers were obtained. The monophosphonium salt formed a sticky solid on the top, and excess liquid dibromide remained at the bottom. The dibromide was decanted off, and the monophosphonium salt was washed three times with dry benzene (50 cm^3) to remove any unreacted triphenylphosphine. Finally the paste-like solid was washed with ether and dried *in vacuo*. The monophosphonium salt was obtained as a white solid in almost quantitative yield, 98%.

Preparation of 1-Dimethylphenylphosphonium-6-triphenylphosphonium Hexyl Dibromide, $[Me_2PhP(CH_2)_6PPh_3]Br_2$

The monophosphonium salt $[Br(CH_2)_6PPh_3]Br$ (12.7 g; 0.025 mol) was dissolved in dimethylformamide (125 cm^3) and the mixture was placed in a 250 cm^3 three-necked round-bottom flask fitted with a water-cooled reflux condenser, a nitrogen inlet, and a dropping funnel. N_2 was passed through the reaction vessel for 15 min and $PPhMe_2$ (3.5 g; 0.025 mol) was added dropwise to the solution. After refluxing for 4 h under N_2 and cooling to room temperature, the liquid was transferred to a beaker. Dry toluene (400 cm^3) was added slowly with stirring; an oily semi-solid precipitated. After decanting the solvent, the sticky solid in the beaker was washed once with dry toluene (50 cm^3) and twice with anhydrous ether (30 cm^3). The diphosphonium salt was obtained as a white sticky solid in almost quantitative yield, 99%.

Preparation of 1-Dimethylphosphoryl-6-diphenylphosphorylhexane, $[Me_2P(O)(CH_2)_6P(O)Ph_2]$

The unsymmetrical diphosphonium salt $[PhMe_2P(CH_2)_6PPh_3]Br_2$ (16.1 g; 0.025 mol) was placed in a 100 cm^3 beaker with 20 cm^3 25% aqueous sodium hydroxide. The mixture was stirred rapidly and heated to boiling for 1 h. As the reaction proceeded the solid diphosphonium salt gradually disappeared and a viscous oil formed, which floated on the surface of the solution. Benzene produced during the reaction boiled off. The mixture was allowed to cool and the oil was separated using a separatory funnel. The diphosphine oxide was purified by dissolving in a mixture of hot toluene (40 cm^3) and ethanol (2:1 by volume. The undissolved solid was filtered off. The solution was boiled at 110 °C and cooled; the diphosphine oxide was precipitated by adding dry diethyl ether. The solid was dried *in vacuo*. Yield 92%.

Preparation of 1-Dimethylphosphino-6-diphenylphosphinohexane, $[Me_2P(CH_2)_6PPh_2]$

Trichlorosilane (10.8 g; 0.08 mol) was pipetted into a 250 cm^3 three-necked flask fitted with a reflux condenser, a dropping funnel, and a N_2 inlet. Triethylamine (8.0 g; 0.08 mol) (dried over NaOH) in 100 cm^3 of sodium-dried toluene was added carefully to the silane through the dropping funnel, while cooling the flask with an ice-water bath. The unsymmetrical diphosphine oxide, $Me_2P(O)(CH_2)_6P(O)PPh_2$, 7.2 g (0.02 mol) in 75 cm^3 of dry warm toluene, was added to the mixture in the flask over 5 min, and refluxed for 5 h under a slow stream of N_2. (A rapid flow of N_2 removes silane (b.p. 32 °C) from the flask.) The flask was then cooled in ice, and 50% aqueous sodium hydroxide (75 cm^3) was added dropwise cautiously. The mixture was then stirred for 1 h during which most of the solid in the toluene layer had dissolved. The top toluene layer was pipetted out under N_2. The aqueous layer was washed with 25 cm^3 of toluene, which was added to the toluene fraction previously separated. The toluene fraction was filtered under N_2 through a Buchner funnel, and the solvent (toluene) was removed *in vacuo*. The product, $Me_2P(CH_2)_6PPh_2$, was obtained as a white semi-solid and was dried on the vacuum line for several days to remove toluene. Yield 82%. The ^{31}P chemical shifts are −16.00 (PPh_2) and −51.8 ($(-PMe_2)_2$) ppm, for the two phosphorus atoms. A product of incomplete reduction due to less trichlorosilane or shorter reflux period or air exposure shows phosphine oxide peaks at 32.9 ($-P(O)Ph_2$) and 43.0 ($-P(O)Me_2$) ppm respectively for the phosphorus atoms in the ^{31}P NMR.

Materials

Tetraethylammonium dibromoaurrate(I) was prepared as previously described [27] and the solvents employed were used without further purification.

NMR Experiments

NMR and other physical measurements were carried out as previously described [8, 21].

References

1 C. F. Shaw III, R. Beery and G. C. Stocco, *Inorg. Chim. Acta, 123* (1986) 213.
2 C. A. McAuliffe and W. Levason, *Phosphine, Arsine and Stibine Complexes of the Transition Elements,* Elsevier, Amsterdam, 1979.
3 A. Cahour and H. Gal, *C.R. Acad. Sci. (Paris), 70* (1876) 1380.
4 A. K. Al-Sa'ady, C. A. McAuliffe, R. V. Parish and J. A. Sandbank, *Inorg. Synth., 23* (1985) 191.
5 C. B. Colburn, W. E. Hill, C. A. McAuliffe and R. V. Parish, *J. Chem. Soc., Chem. Commun.,* (1979) 218.
6 C. A. McAuliffe, R. V. Parish and P. D. Randall, *J. Chem. Soc., Dalton Trans.,* (1977) 1426.
7 F. G. Mann, A. F. Wells and D. Purdie, *J. Chem. Soc.,* (1937) 1828.
8 S. Al-Baker, W. E. Hill and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.,* (1985) 1387.
9 L. Malatesta, L. Naldini, G. Simonetta and F. Cariati, *Coord. Chem. Rev., 1* (1966) 255.
10 J. A. Muir, M. M. Muir and S. Arias, *Acta Crystallogr., Sect. B, 38* (1982) 1318.
11 J. A. Muir, M. M. Muir, S. Arias, C. F. Campana and S. K. D. Dwight, *Acta Crystallogr., Sect. B, 38* (1982) 2047.
12 J. A. Dills and M. P. Johnson, *Inorg. Chem., 5* (1966) 2079.
13 P. G. Jones, *J. Chem. Soc., Chem. Commun.,* (1980) 1031.
14 R. C. Elder, E. H. Kelle-Zeiher, M. Onady and R. R. Whittle, *J. Chem. Soc., Chem. Commun.,* (1981) 900.
15 H. Schmidbaur, A. Wohlleben, U. Schubert, A. Frank and G. Huttner, *Chem. Ber., 110* (1977) 2751.
16 C. E. Wymore and J. C. Bailar, *J. Inorg. Nucl. Chem., 14* (1960) 42.
17 M. Barron, H. B. Buergi, D. K. Johnson and L. M. Venanzi, *J. Am. Chem. Soc., 98* (1982) 2356.
18 A. J. Carty and A. Efraty, *Inorg. Chem., 8* (1969) 543.
19 W. E. Hill, D. M. A. Minahan, J. G. Taylor and C. A. McAuliffe, *J. Am. Chem. Soc., 104* (1982) 6001.
20 J. C. Briggs, C. A. McAuliffe, W. E. Hill, D. M. A. Minahan, J. G. Taylor and G. Dyer, *Inorg. Chem., 21* (1982) 4204.
21 S. Al-Baker, W. E. Hill and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.,* (1985) 2655.
22 J. C. Briggs and G. Dyer, *Chem. Ind.,* (1982) 163.
23 F. R. Benn, J. C. Briggs and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.,* (1984) 293.
24 R. V. Parish, O. Parry and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.,* (1981) 2102.
25 P. S. Pregosin and R. W. Kunz, *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes,* Springer, West Berlin, 1979.
26 S. Al-Baker, W. E. Hill and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.,* (1986) 1297.
27 P. Braunstein and R. J. H. Clark, *J. Chem. Soc., Dalton Trans.,* (1973) 1845.