Notes

Exchange Kinetics of Gold(I) Phosphine Complexes by Nuclear Magnetic Resonance Line Shape Analysis

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The ^{31}P-{^1H} n.m.r. spectra of $[NEt_4][AuBr_2]$ with various amounts of the ligands $PPhMe_2$ or PBu^n_3 were studied at different ratios in CD_2Cl_2 solutions. The solutions show the presence of species having one, two, and three co-ordinated phosphine ligands (four in the case of PBu^n_3), and these species exchange with one another at elevated temperatures. The entropies of activation ($\Delta S^\ddagger$) for these processes are negative and the mechanism of exchange is thus associative in all cases.

In recent years many studies have been conducted on the exchange kinetics of inorganic complexes *via* nuclear magnetic resonance.[1–4] Prior to the study reported here there has been mounting evidence of a rich co-ordination chemistry of gold(I) complexes with tertiary phosphines. It has been found that for many ligands (L) more species are capable of existence in solution than can be crystallized from solution. For example, for L = PEt_3 all the complexes $[AuL_n]^+$ (n = 2—4) could be observed, but Mays and Vergnano[5] were able to crystallize only $[Au(PEt_3)_2]PF_6$ even in the presence of a five-fold molar excess of the ligand. Similarly for L = PMe_3 Parish *et al.*[6] were able to isolate only $[Au(PMe_3)_2]NO_3$ from a solution with a 1:3 mol ratio of Au:L. However, the same system employing ClO_4^- as the counter ion yielded tris- and tetrakis-ligand complexes.

There are numerous examples to illustrate the fact that, although several species may be present in solution, the salts which crystallize out do not necessarily correspond to the major species. The trend appears to be that expected,[7] *viz.* that small anions favour the isolation of cations with low co-ordination numbers, whereas large anions stabilize the tetrakis-ligand complexes.

No studies on ligand-exchange kinetics have been reported, and we thus wish to report here the first study of the exchange kinetics of gold(I) complexes containing the phosphine ligands $PPhMe_2$ or PBu^n_3. These phosphines were chosen because their cone angles (*i.e.* their steric requirements) are different.

Results and Discussion

The typical behaviour of the ^{31}P-{^1H} n.m.r. spectra of $[NEt_4][AuBr_2]$ and $PPhMe_2$ at various temperatures is listed in Table 1. For low concentrations (L:Au = 0.5:1) a single species was observed at +6.4 p.p.m. The half width remained unchanged over the temperature range 14 to −110 °C indicating the presence of one species which is not exchanging with Br^- or $[AuBr_2]^-$. Addition of a further 0.5 mol equivalent of $PPhMe_2$ caused the appearance of a new species (+15.6 p.p.m. at −90 °C) at the expense of the species at +6.4 p.p.m. The relative areas were 7.0:1.0 for the +6.4 and +15.6 p.p.m. species respectively.† Thus since only two phosphorus species are obtained with sharp lines (no exchange) we can say that 0.0875 mmol of $[Au(PPhMe_2)Br]$ and 0.006 25 mmol of $[Au(PPhMe_2)_2Br]$ are present. Of course there must also be 0.006 25 mmol of $[AuBr_2]^-$ present (6.25%), as shown in the equation above.

	$PPhMe_2$ +	$[NEt_4][AuBr_2]$ $\longrightarrow$	$[Au(PPhMe_2)Br]$ +	$[Au(PPhMe_2)_2Br]$
Initial amount	0.1 mmol	0.1 mmol	0	0
Final amount	0.0 mmol	0.006 25 mmol	0.0875 mmol	0.006 25 mmol

On warming the solution to −40 °C the two peaks broadened and on further warming to −30 °C they collapsed to a single resonance. Upon addition of a further 0.5 mol equivalent of the ligand, the relative areas became 1.0:3.2 for the +6.4 and +15.6 p.p.m. species, respectively, and thus 0.0357 mmol of $[Au(PPhMe_2)Br]$ and 0.0571 mmol of $[Au(PPhMe_2)_2Br]$ were present. This accounts for 92.5% of the initial gold.

Whether some $[AuBr_2]^-$ is still present or the result is a function of experimental error is not clear. At a ligand:gold ratio of 2.0:1, a single peak was observed at −30 °C, and on cooling to −90 °C two peaks at +15.6 and −22.6 p.p.m. appeared at the expense of the species at +6.4 p.p.m., with relative areas 9.0:1.0 respectively {*i.e.* 0.009 mmol $[Au(PPhMe_2)_2Br]$ and 0.0067 mmol of $[Au(PPhMe_2)_3]Br$, indicating that 3.3% of $[AuBr_2]^-$ remained in solution}.

At a ligand:gold ratio of 2.5:1 and at −90 °C again two peaks appeared at +15.6 and −22.6 p.p.m., but with relative areas 1.0:1.2, respectively {0.048 mmol of $[Au(PPhMe_2)_2Br]$ and 0.0513 mmol of $[Au(PPhMe_2)_3]Br$, *i.e.* 0.7% of $[AuBr_2]^-$ remained unreacted}. At a ligand:gold ratio of 3.5:1 a new peak appeared at −90 °C at −46.5 p.p.m. The ratio of $[Au(PPhMe_2)_2Br]$, $[Au(PPhMe_2)_3]Br$, and the free ligand was 1.0:2.5:1.1 respectively {*i.e.* 0.037 mmol of $[Au(PPhMe_2)_2Br]$ and 0.063

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† Proton decoupling can give a nuclear Overhauser effect (n.O.e.) which makes the areas unreliable. However, since all the species observed contain the same ligand the n.O.e. is expected to be constant. Indeed we have checked the relative areas with and without n.O.e. and do not find any significant differences.

Table 1. $^{31}P-\{^1H\}$ Chemical shifts (p.p.m.)[a] as a function of L:Au mol ratio and temperature, for $[NEt_4][AuBr_2]$ and L = $PPhMe_2$

	T/K						
L:Au	276	265	253	240	213	183[b]	Assignment for 183 K spectrum
1.0	+7.1	+7.0	+6.8	+6.7	+6.4	+6.4 (7.0)	$[Au(PPhMe_2)Br]$
					+15.7	+15.6 (1.0)	$[Au(PPhMe_2)_2Br]$
1.5	+12.8	+12.9	+13.5	+15.0	+7.0	+6.4 (1.0)	$[Au(PPhMe_2)Br]$
					+15.6	+15.6 (3.2)	$[Au(PPhMe_2)_2Br]$
2.0	+12.1	+12.1	+12.2	+12.3	+14.4	+15.6 (9.0)	$[Au(PPhMe_2)_2Br]$
						−22.6 (1.0)	$[Au(PPhMe_2)_3]Br$
2.5	+4.6	+4.4	+4.1	+3.8	+13.7	+15.6 (1.0)	$[Au(PPhMe_2)_2Br]$
						−22.6 (1.2)	$[Au(PPhMe_2)_3]Br$
3.5	−16.2	−16.4	−16.9	−17.2	−18.0	+15.6 (1.0)	$[Au(PPhMe_2)_2Br]$
						−22.6 (2.5)	$[Au(PPhMe_2)_3]Br$
						−46.5 (1.1)	Free ligand
4.5				−28.0		−22.6 (2.0)	$[Au(PPhMe_2)_3]Br$
						−46.5 (1.0)	Free ligand

[a] Relative to 85% H_3PO_4. [b] Relative intensities of peaks in parentheses.

Table 2. $^{31}P-\{^1H\}$ Chemical shifts (p.p.m.)[a] as a function of L:Au mol ratio and temperature for $[NEt_4][AuBr_2]$ and L = PBu^n_3

	T/K							
L:Au	280	248	227	206	190	173	160[b]	Assignment for 160 K spectrum
1.0	+29.4	+25.4	+25.1	+24.8	+24.5		+24.5 (1.0)	$[Au(PBu^n_3)Br]$
		+32.1	+32.3	+32.6			+32.6 (1.1)	$[Au(PBu^n_3)_2Br]$
2.0	+29.1	+30.5	+30.8		+32.4		+32.6 (3.2)	$[Au(PBu^n_3)_2Br]$
					+28.3		+28.3 (1.0)	$[Au(PBu^n_3)_3Br]$
3.5			+22.5	+21.2	+20.5		+28.3 (1.0)	$[Au(PBu^n_3)_3Br]$
							−13.3 (1.5)	$[Au(PBu^n_3)_4]Br$
5.0	+5.4				−7.8	−11.3	−13.3 (4.0)	$[Au(PBu^n_3)_4]Br$
						+14.7	−30.5 (1.0)	Free ligand

[a] Relative to 85% H_3PO_4. [b] Relative intensities of peaks in parentheses.

mmol of $[Au(PPhMe_2)_3]Br$ are present and 0.087 mmol of free ligand remained unreacted}. At a ligand:gold ratio of 4.5 the peak at +15.6 p.p.m. disappeared; the ratio of $[Au(PPhMe_2)_3]Br$ species to the free ligand was then 2.0:1.0 (*i.e.* 0.15 mmol of free ligand remained unreacted).

The peaks at +6.4, +15.6, −22.6, and −46.5 p.p.m. are thus assigned to $[Au(PPhMe_2)Br]$, $[Au(PPhMe_2)_2Br]$, $[Au(PPhMe_2)_3Br]$, and free $PPhMe_2$, respectively.

The $^{31}P-\{^1H\}$ n.m.r. spectra of $[NEt_4][AuBr_2]$ as a function of added PBu^n_3 are given in Table 2. By analogous reasoning to that used for the $PPhMe_2$ experiments the peaks at +24.5, +32.6, +28.3, −13.3, and −30.5 p.p.m. are assigned to $[Au(PBu^n_3)Br]$, $[Au(PBu^n_3)_2Br]$, $[Au(PBu^n_3)_3Br]$, $[Au(PBu^n_3)_4]Br$, and PBu^n_3, respectively.

A pattern to the ^{31}P chemical shifts has emerged from our ^{31}P n.m.r. studies.[8] Addition of one phosphorus ligand (PR_3) to $[Au(PR_3)Br]$ to give $[Au(PR_3)_2Br]$ always results in deshielding (more positive chemical shift). Addition of another phosphorus ligand to $[Au(PR_3)_2Br]$ gives $Au(PR_3)_3Br$ which is more shielded than the $[Au(PR_3)_2Br]$ analogue. $[Au(PR_3)_4]^+$ species are further shielded. This pattern is observed for both phosphines reported here. It is interesting to note that the chemical shift difference between $[Au(PPhMe_2)_2Br]$ and $[Au(PPhMe_2)_3Br]$ is far greater than the difference between $[Au(PBu^n_3)_2Br]$ and $[Au(PBu^n_3)_3Br]$. Reasons for this difference are not clear, but of course PBu^n_3 has quite different steric and electronic properties compared to $PPhMe_2$.

Rate constants for the exchanging species at various temperatures, Figure, obtained from line shape analysis, are listed in Table 3, and some thermodynamic properties are listed in Table 4. It can be seen that the entropies of activation ($\Delta S^‡$) are negative, and therefore the mechanism of exchange must be associative in all cases.

The activation enthalpies ($\Delta H^‡$) for the $[Au(PR_3)Br]$ to $[Au(PR_3)_2Br]$ exchange reflect the greater steric demand of the

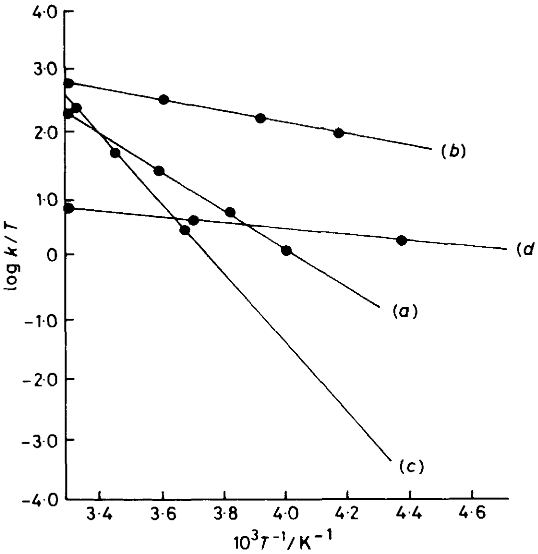


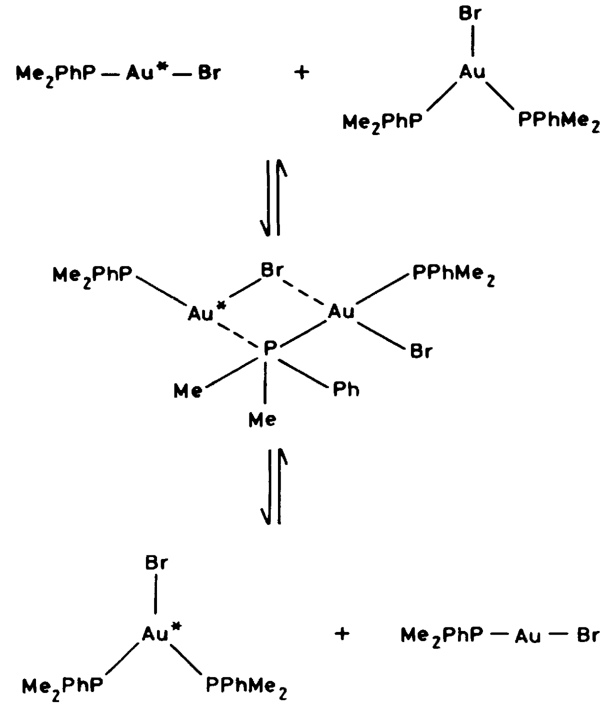
Figure. Log k/T as a function of temperature for an acetone–dichloromethane (1:1) solution with (*a*) $PPhMe_2:[AuBr_2]^-$ = 1.5:1, (*b*) $PPhMe_2:[AuBr_2]^-$ = 2.5:1, (*c*) $PBu^n_3:[AuBr_2]^-$ = 1.0:1, and (*d*) $PBu^n_3:[AuBr_2]^-$ = 2.0:1

Table 3. Rate constants of the exchanging species at various temperatures

T/K	[Au(PPhMe$_2$)Br] ⇌ [Au(PPhMe$_2$)$_2$Br] k/s^{-1}	[Au(PPhMe$_2$)$_2$Br] ⇌ [Au(PPhMe$_2$)$_3$]Br k/s^{-1}	[Au(PBu$^n_3$)Br] ⇌ [Au(PBu$^n_3$)$_2$Br] k/s^{-1}	[Au(PBu$^n_3$)$_2$Br] ⇌ [Au(PBu$^n_3$)$_3$Br] k/s^{-1}
309			76 200	
303	6 478	138 500	30 300	2 195
298			16 640	
278	5 635	80 180	790	1 460
266	1 790			1 205
250	465	38 720	6	840
238	75	27 075	0.5	655
216				370
206				280
184				136

Table 4. Thermodynamic parameters for the exchange process (cal = 4.184 J)

	[Au(PPhMe$_2$)Br] ⇌ [Au(PPhMe$_2$)$_2$Br]	[Au(PPhMe$_2$)$_2$Br] ⇌ [Au(PPhMe$_2$)$_3$]Br	[Au(PBu$^n_3$)Br] ⇌ [Au(PBu$^n_3$)$_2$Br]	[Au(PBu$^n_3$)$_2$Br] ⇌ [Au(PBu$^n_3$)$_3$Br]
$\Delta G^{\ddagger}$/kcal mol^{-1}	20.42	13.1	22.75	12.47
E_a/kcal mol^{-1}	14.89	7.65	23.76	2.59
$\Delta H^{\ddagger}$/kcal mol^{-1}	14.37 ± 0.31	3.08 ± 0.43	23.63 ± 1.0	2.1 ± 0.23
$\Delta S^{\ddagger}$/kcal K^{-1} mol^{-1}	−22.71 ± 0.34	−37.53 ± 0.48	−8.0 ± 1.2	−42.5 ± 0.92



Scheme 1. Proposed mechanism for exchange between [Au(PPhMe$_2$)Br] and [Au(PPhMe$_2$)$_2$Br]

PBu$^n_3$ ligand. Therefore, based on the fact that $\Delta S^{\ddagger}$ is highly negative and that $\Delta H^{\ddagger}$ is greater for the more basic phosphine (PBu$^n_3$) we suggest the mechanism shown in Scheme 1.

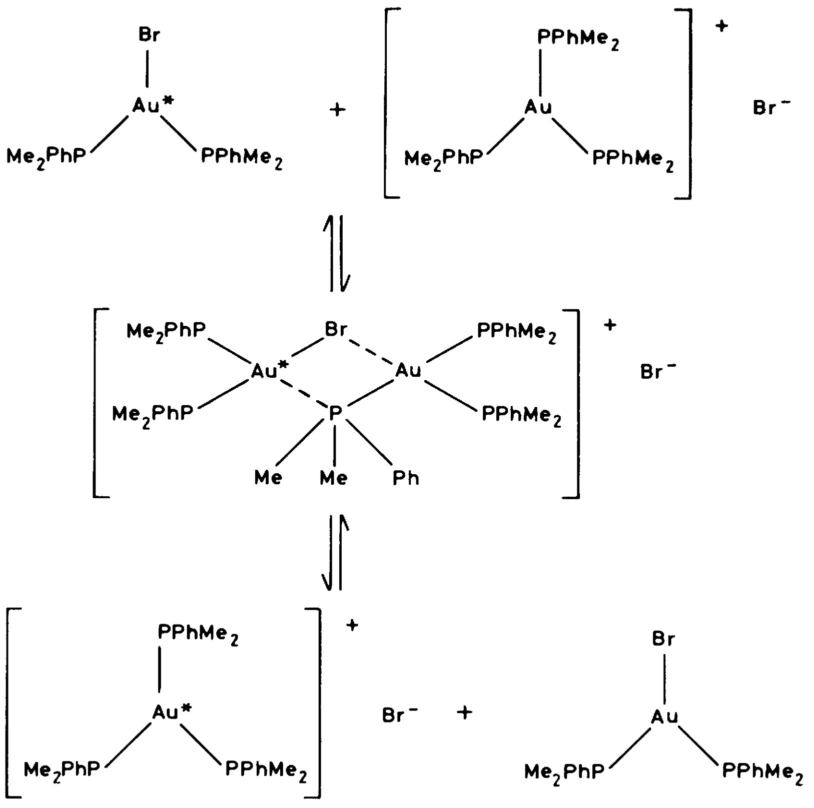
The values of $\Delta H^{\ddagger}$ for the [Au(PR$_3$)$_2$Br] to Au(PR$_3$)$_3$Br exchange are much smaller than those for the [Au(PR$_3$)Br] to [Au(PR$_3$)$_2$Br] exchange, suggesting a different mechanism. In fact conductivity measurements of Au(PR$_3$)$_3$Br in nitromethane have shown the complex to have appreciable conductivity while [Au(PR$_3$)$_2$Br] is essentially non-conducting.[8] Therefore we propose the mechanism shown in Scheme 2 for this exchange.

Experimental

Preparation of Tetraethylammonium Tetrabromoaurate(III), [NEt$_4$][AuBr$_4$].—An ethanolic solution (100 cm^3) of HAuCl$_4$·3H$_2$O (2.0 g, 5.1 mmol) was treated at 60 °C with an eight-fold (8.6 g, 0.32 mol) excess of tetraethylammonium bromide in ethanol (30 cm^3). Substitution of bromide for chloride took place immediately to give a deep maroon precipitate. After collecting the precipitate by filtration, recrystallization from absolute ethanol gave 3.0 g (91% yield based on HAuCl$_4$·3H$_2$O) of [NEt$_4$][AuBr$_4$], m.p. 157—159 °C.

Preparation of Tetraethylammonium Dibromoaurate(I), [NEt$_4$][AuBr$_2$].—Tetraethylammonium tetrabromoaurate(III) (1.8 g, 2.8 mmol) was partly dissolved in absolute ethanol (15 cm^3) and acetone (1 cm^3). The slurry was then heated to 70 °C on a water-bath in a hood until the initially red solution became colourless. During this time a lachrymatory substance was evolved (bromoacetone). The final colourless solution was allowed to cool to room temperature and then placed in a refrigerator for 5 h. Long colourless needles precipitated. These were filtered off, rapidly washed with diethyl ether, and stored *in vacuo* (yield: 1.14 g, 84%). Addition of diethyl ether to the filtrate gave an additional 0.21 g of tetraethylammonium dibromoaurate(I) for an overall yield of 99% [based on tetraethylammonium tetrabromoaurate(III)] (m.p. 88—89 °C).

Kinetic Studies.—Apparatus. The ^{31}P n.m.r. spectra were obtained on a CFT-20 n.m.r. spectrometer in 8-mm tubes. The temperature was monitored either with a standard (Minneapolis-Honeywell model 126w2 Brown) portable potentiometer calibrated in degrees centigrade from −110 to +20 °C, or with an iron–constantin thermocouple and a



Scheme 2. Proposed mechanism for exchange between $[Au(PPhMe_2)_2Br]$ and $[Au(PPhMe_2)_3]Br$

Keithley millivolt voltmeter. At least 10 min was allowed for temperature equilibration. Temperatures were measured by inserting an open tube containing acetone–dichloromethane 1:1) into the probe and measuring the voltage after equilibrium. In most cases the ^{31}P n.m.r. spectra were measured every 10 °C from the freezing point to *ca.* 10 °C above the boiling point of the solvent.

^{31}P-$\{^1H\}$ *N.m.r. spectra at various temperatures for* $[NEt_4][AuBr_2]$ *and monophosphine ligands* ($PPhMe_2$ *or* $PBu^n{}_3$). The ^{31}P-$\{^1H\}$ n.m.r. spectra of CH_2Cl_2 solutions of $[NEt_4][AuBr_2]$ with various amounts of $PBu^n{}_3$ were taken as an example for kinetic studies. The tetraethylammonium dibromoaurate(I) (0.0487 g, 0.1 mmol) was weighed into an 8-mm n.m.r. tube. Deuterodichloromethane (1.50 cm^3) was added, and $PBu^n{}_3$ (12.0 µl, 0.05 mmol) was added under a nitrogen blanket. The chemical shifts of the species were measured at various temperatures starting from room temperature to the freezing point of the solvent in 10 °C intervals.

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