Methyl for Halogen Exchange Reactions Between Palladium(II), Platinum(II), Gold(I), and Gold(III) Complexes

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A series of reactions in which methyl and halogen groups are exchanged between gold(I), gold(III), palladium(II), and platinum(II) centres has been studied. It is proposed that the exchange reactions proceed by the S_E2(cyclic) mechanism, in order to rationalise the observations that cleavage of the Pt–Me bond in *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] by various metal halides follows the reactivity series [AuI(PMe$_2$Ph)] > [AuBr(PMe$_2$Ph)] > [AuCl(PMe$_2$Ph)]; [PtI$_2$(PMe$_2$Ph)$_2$] ⩾ [PtCl$_2$(PMe$_2$Ph)$_2$]; [AuCl(PMe$_2$Ph)] > *cis*-[PdCl$_2$(PMe$_2$Ph)$_2$] ⩾ *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$], that the rate of methylation reactions using [MeAu(PMe$_2$Ph)] as methylating agent is much greater than for *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$], and that the reaction of *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] with *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] gives *cis*-[PtCl(Me)(PMe$_2$Ph)$_2$] as the product of kinetic control. The methylating power of various methylmetal complexes follows the series *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$], [AuMe(PMe$_2$Ph)] > [AuMe$_3$(PMe$_2$Ph)] ⩾ *trans*-[MCl(Me)-(PMe$_2$Ph)$_2$] (M = Pd or Pt), *cis*-[AuX(Me)$_2$(PMe$_2$Ph)] (X = halogen).

DURING recent studies [1-3] in which attempts were made to determine the relative reactivity of several methylplatinum(II) and methylgold-(I) and -(III) complexes towards cleavage of the methyl–metal bond by benzenethiol or benzeneselenol it became apparent that the results were complicated by exchange of methyl and phenylthio- or phenylseleno-groups after the initial cleavage [equation (1); X = SPh or SePh; M,M′ =

$$\text{M–X} + \text{M}'\text{–Me} \longrightarrow \text{M–Me} + \text{M}'\text{–X} \qquad (1)$$

Au^{I}, Au^{III}, or Pt^{II}]. Exchange reactions such as this where an alkyl group is transferred from one transition-metal centre to another have been studied very little. One other reaction has been shown to take place with exchange of a methyl group from Au^{I} to Au^{III} [equation (2); L = PPh$_3$ or PMe$_3$].[4,5] Methyl groups can also be transferred from cobalt to rhodium.[6]

$$cis\text{-[AuI(Me)}_2\text{L]} + \text{[MeAuL]} \longrightarrow \text{[AuMe}_3\text{L]} + \text{[AuIL]} \qquad (2)$$

Cleavage of methyl–transition-metal bonds by main-group metal halides has been examined more closely.[7] Thus Chatt and Shaw showed that methyl–platinum bonds could be cleaved with magnesium iodide,[8] and Gregory and Ingold, in a detailed kinetic investigation, showed that reactions (3) and (4) proceed at similar rates

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[1] A. Johnson and R. J. Puddephatt, *J.C.S. Dalton*, 1975, 115.

[2] R. J. Puddephatt and P. J. Thompson, unpublished work.

[3] N. G. Hargreaves, A. Johnson, R. J. Puddephatt, and L. H. Sutcliffe, *J. Organometallic Chem.*, 1974, **69**, C21.

[4] A. Tamaki and J. K. Kochi, *J. Organometallic Chem.*, 1974, **64**, 411.

[5] A. Johnson and R. J. Puddephatt, *J. Organometallic Chem.*, 1975, **85**, 115; *Inorg. Nuclear Chem. Letters*, 1973, **9**, 1175.

[6] D. Dodd and M. D. Johnson, *Chem. Comm.*, 1971, 1371.

[7] M. H. Abraham in 'Comprehensive Chemical Kinetics,' vol. 12, eds. C. H. Bamford and C. F. H. Tipper, Elsevier, 1973, ch. 3.

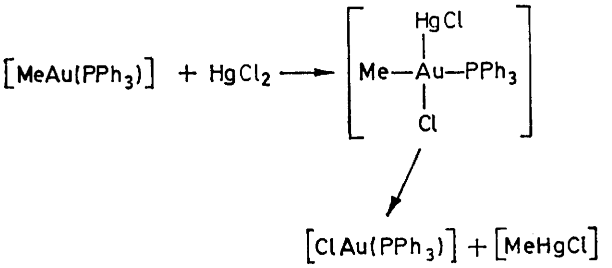
[8] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 705.

by an S_E2 mechanism.[9] More recently it has been suggested that these reactions proceed by a mechanism

$$[MeAu(PPh_3)] + HgCl_2 \longrightarrow [ClAu(PPh_3)] + [MeHgCl] \quad (3)$$

$$[Me_3Au(PPh_3)] + HgCl_2 \longrightarrow cis\text{-}[Me_2AuCl(PPh_3)] + [MeHgCl] \quad (4)$$

involving oxidative addition–reductive elimination processes [*e.g.* equation (5)],[10] but this seems unlikely in


(5)

$$[MeAu(PPh_3)] + HgCl_2 \longrightarrow \left[\begin{array}{c} HgCl \\ | \\ Me\text{—}Au\text{—}PPh_3 \\ | \\ Cl \end{array}\right] \longrightarrow [ClAu(PPh_3)] + [MeHgCl] \quad (5)$$

view of the great difference in reactivity between Au^I and Au^{III} towards oxidative addition.

RESULTS AND DISCUSSION

Reactions of cis-$[PtMe_2(PMe_2Ph)_2]$.—Many of the features of the exchange reactions are seen in reaction (6)

$$cis\text{-}[PtMe_2(PMe_2Ph)_2] + [AuX(PMe_2Ph)] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans\text{-}[PtX(Me)(PMe_2Ph)_2] + [AuMe(PMe_2Ph)] \quad (6)$$

(X = Cl, Br, or I). Both starting materials and products have characteristic n.m.r. spectra (Table)[5,11] and the reactions were followed by monitoring the n.m.r. spectra periodically. If the reactions proceed with retention of configuration at platinum, *cis*-$[PtCl(Me)(PMe_2Ph)_2]$ is expected as the product when X = Cl. This was not observed, but no stereochemical deductions can be made since a separate experiment showed that methyl(dimethylphenylphosphine)gold(I) catalyses the isomerisation of *cis*-$[PtCl(Me)(PMe_2Ph)_2]$ to the thermodynamically more stable[12] *trans* isomer at a rate considerably faster than the exchange reactions.

The equilibrium constants for reaction (6) in dichloromethane solution at 20 °C were dependent on the halogen X, being $K = 0.3$ (X = I), 1.0 (Br), and 5.4 (Cl).

N.m.r. spectra of the complexes in dichloromethane

Complex	δ(MeP)[a] p.p.m.	^2J(PH) Hz	^3J(PtH) Hz	δ(MeM)[a] p.p.m.	^3J(PH) Hz	^2J(PtH) Hz
$[AuMe(PMe_2Ph)]$	1.64 (d)	8.3		0.26 (d)	8.1	
$[AuCl(PMe_2Ph)]$	1.94 (d)	10.8				
$[AuBr(PMe_2Ph)]$	1.79 (d)	11.0				
$[AuI(PMe_2Ph)]$	1.81 (d)	10.4				
$[AuMe(PMePh_2)]$						
$[AuI(PMePh_2)]$	2.08 (d)	10.6				
$[AuCl_3(PMe_2Ph]$	2.24 (d)	13.6				
$[AuBr_3(PMe_2Ph)]$	2.39 (d)	13.3				
$[AuMe_3(PMe_2Ph)]$	1.71 (d)	9.4		0.78d,[b] 0.01d[c]	9.1,[b] 7.4[c]	
cis-$[AuCl(Me)_2(PMe_2Ph)]$	1.80 (d)	10.5		0.97 (d),[b] 0.86 (d)[d]	9.5,[b] 8.9[d]	
cis-$[AuBr(Me)_2(PMe_2Ph)]$	1.88 (d)	10.4		1.08 (d),[b] 0.99 (d)[d]	9.6,[b] 8.7[d]	
cis-$[PtCl_2(PMe_2Ph)_2]$	1.71 (d)	11.0	34.5			
cis-$[PtI_2(PMe_2Ph)_2]$	1.89 (d)	10.6	36.3			
trans-$[PtI_2(PMe_2Ph)_2]$	2.15 (t)	7.4	25.0			
trans-$[PtCl(Me)(PMe_2Ph)_2]$	1.96 (t)	7.2	30.2	0.13 (t)	7.1	83.2
trans-$[PtBr(Me)(PMe_2Ph)_2]$	1.78 (t)	7.0	30.0	0.17 (t)	7.0	82
trans-$[PtI(Me)(PMe_2Ph)_2]$	1.90 (t)	7.1	30.3	0.26 (t)	7.9	80.6
cis-$[PtCl(Me)(PMe_2Ph)_2]$	1.51 (d), 1.54 (d)	10.8, 8.5	46, 16.3	0.59 (dd)	4.5, 7.3	54.4
cis-$[PtMe_2(PMe_2Ph)_2]$	1.44 (d)	7.8	20.1	0.39 (c)		67.2
cis-$[PtCl_2(PMePh_2)_2]$	1.89 (d)	11.4	36.4			
cis-$[PtI_2(PMePh_2)_2]$	2.12 (d)	10.3	37.8			
trans-$[PtI_2(PMePh_2)_2]$	2.52 (t)	6.9	26.4			
trans-$[PtI(Me)(PMePh_2)_2]$	2.42 (t)	7.0	31.4	−0.01 (t)	7.0	79.2
cis-$[PtMe_2(PMePh_2)_2]$	1.59 (d)	7.2	20.4	0.26 (c)		68.5
$[PtBr_2(Me)_2(PMe_2Ph)_2]$	1.67 (d)	9.6	11.1	1.34 (c)		58.2
mer-$[PtBr_3Me(PMe_2Ph)_2]$	2.29 (t)	8.4	16.6	0.98 (t)	5.3	68.2
cis-$[PdCl_2(PMe_2Ph)_2]$	1.67 (d)	11.3				
trans-$[PdCl(Me)(PMe_2Ph)_2]$	1.64 (t)	6.7		0.03 (t)	6.5	

[a] d = Doublet, t = triplet, dd = doublet of doublets, and c = complex multiplet. [b] Methyl group *trans* to phosphorus. [c] Methyl group *trans* to carbon. [d] Methyl group *trans* to halogen.

We now report some reactions involving transfer of methyl groups between palladium(II), platinum(II), gold(I), and gold(III) centres, with particular emphasis on determining which methylmetal complexes are the stronger methylating agents and what factors influence the rates and stereochemistry.

The equilibrium position could be reached by starting with reagents on either side of equation (6).

The rate of reaction of *cis*-$[PtMe_2(PMe_2Ph)_2]$ with $[AuBr(PMe_2Ph)]$ was solvent dependent. Thus equilibrium was reached in 10 d in benzene solvent, in 4 d in acetone, and in 1 d in dichloromethane. In order to eliminate solvent effects all other reactions were carried out in dichloromethane. The reaction rate was also

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[9] B. J. Gregory and C. K. Ingold, *J. Chem. Soc.* (*B*), 1969, 276.

[10] A. Shiotani and H. Schmidbaur, *J. Organometallic Chem.*, 1972, **37**, C24.

[11] J. D. Ruddick and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 2801.

[12] M. P. Brown, R. J. Puddephatt, C. E. E. Upton, and S. W. Lavington, *J.C.S. Dalton*, 1974, 1613.

strongly dependent on the halogen, X; the reaction was complete in 1 h when X = I, 1 d when X = Br, and 2 d when X = Cl. When X = Cl the approach to equilibrium followed second-order kinetics at 20 °C in dichloromethane with rate constant $k_1 = 2.0 \times 10^{-4}$ l mol^{-1} s^{-1}.

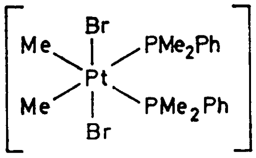
The complex *cis*-$[PtMe_2(PMe_2Ph)_2]$ also methylated *cis*-$[AuBr(Me)_2(PMe_2Ph)]$ according to equation (7).

$$cis\text{-}[PtMe_2(PMe_2Ph)_2] + cis\text{-}[AuBr(Me)_2(PMe_2Ph)] \longrightarrow trans\text{-}[PtBr(Me)(PMe_2Ph)_2] + [AuMe_3(PMe_2Ph)] \quad (7)$$

The reaction was complete in 2 d at 20 °C in dichloromethane solution. However, with $[AuBr_3(PMe_2Ph)]$ a different reaction took place involving reduction of Au^{III} to Au^{I} and oxidation of Pt^{II} to Pt^{IV} [equation (8)].

$$cis\text{-}[PtMe_2(PMe_2Ph)_2] + [AuBr_3(PMe_2Ph)] \longrightarrow [PtBr_2(Me)_2(PMe_2Ph)_2] + [AuBr(PMe_2Ph)] \quad (8)$$

This was a rapid exothermic reaction. The configuration of $[PtBr_2(Me)_2(PMe_2Ph)_2]$ was as in (I), as confirmed by its characteristic n.m.r. spectrum.[11] This product has been obtained previously [11] by reaction of bromine with *cis*-$[PtMe_2(PMe_2Ph)_2]$, but it is unlikely that free bromine is the effective reagent in reaction (8); direct stereospecific transfer of the elements of Br_2 from Au^{III} to Pt^{II} seems more likely.



(I)

The complex *cis*-$[PtMe_2(PMe_2Ph)_2]$ methylated *cis*-$[PdCl_2(PMe_2Ph)_2]$ according to equation (9), reaction

$$cis\text{-}[PtMe_2(PMe_2Ph)_2] + cis\text{-}[PdCl_2(PMe_2Ph)_2] \longrightarrow trans\text{-}[PtCl(Me)(PMe_2Ph)_2] + trans\text{-}[PdCl(Me)(PMe_2Ph)_2] \quad (9)$$

being complete in 4 d at 20 °C, but the product *trans*-$[PdCl(Me)(PMe_2Ph)_2]$ could not be further methylated to $[PdMe_2(PMe_2Ph)_2]$. The reaction with a *cis–trans* mixture of $[PtI_2(PMe_2Ph)_2]$ [equation (10)] was complete

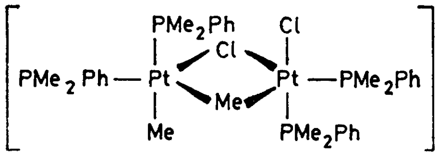
$$cis\text{-}[PtMe_2(PMe_2Ph)_2] + [PtI_2(PMe_2Ph)_2] \longrightarrow 2\ trans\text{-}[PtI(Me)(PMe_2Ph)_2] \quad (10)$$

in 1 d and gives a useful preparative route to *trans*-$[PtI(Me)(PMe_2Ph)_2]$.

The symmetrisation reaction of *cis*-$[PtMe_2(PMe_2Ph)_2]$ with *cis*-$[PtCl_2(PMe_2Ph)_2]$ was particularly interesting. This was a very slow reaction, being half complete in 3 weeks at 20 °C. The reaction followed overall second-order kinetics with a rate constant $k = 5.5 \times 10^{-6}$ l mol^{-1} s^{-1} at 34 °C. After 2 d the only product was *cis*-$[PtCl(Me)(PMe_2Ph)_2]$, but after this the concentration of *cis*-$[PtCl(Me)(PMe_2Ph)_2]$ remained approximately constant and some *trans*-$[PtCl(Me)(PMe_2Ph)_2]$ could be detected and this was the final product. It seems that the initial exchange reaction gives only *cis*-$[PtCl(Me)(PMe_2Ph)_2]$ [equation (11)] which then slowly isomerises to the more stable [12] *trans* isomer.

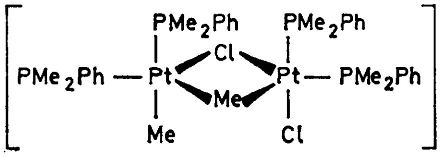
$$cis\text{-}[PtMe_2(PMe_2Ph)_2] + cis\text{-}[PtCl_2(PMe_2Ph)_2] \longrightarrow 2\ cis\text{-}[PtCl(Me)(PMe_2Ph)] \longrightarrow 2\ trans\text{-}[PtCl(Me)(PMe_2Ph)_2] \quad (11)$$

Thus the configuration at *both* platinum centres is retained during the exchange reactions. Substitution reactions at Pt^{II} generally proceed by an S_N2 mechanism with retention of configuration at platinum.[13] The intermediate is thought to have trigonal bipyramidal geometry, with the entering and leaving groups and the *trans* ligand in the equatorial plane. The methyl-exchange reaction can be considered to involve a bimolecular electrophilic-substitution reaction at the methyl group, generally known as an S_E2 reaction.[7] Cyclic transition states or intermediates are thought to be involved in many S_E2 reactions.[7] These pictures can be combined to explain the stereochemistry of reaction (11), if the cyclic dimer (II) is involved. Thus the reaction can be considered to involve S_N2 substitution with retention of configuration at each platinum centre, and S_E2 substitution at the saturated carbon atom of the methyl group. If (II) is the actual transition state the reaction is designated S_E2 (cyclic), though it is also possible that (II) is an intermediate. The distinction between these pictures is very tenuous and has been discussed at length by Abraham.[7]



(IIa)

or



(IIb)

In order to see if the reaction rates were dependent on steric factors, we examined the reactions of *cis*-$[PtMe_2(PMePh_2)_2]$ with $[AuI(PMePh_2)]$ and $[PtI_2(PMePh_2)_2]$. The nature and rate of each reaction were very similar to those when the ligand was PMe_2Ph, indicating that steric effects of the ligand are not dominant in determining the reaction rates.

Reactions of $[AuMe_3(PMe_2Ph)]$.—This complex is not

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[13] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Wiley–Interscience, 1972, pp. 665—667.

a powerful methylating agent. It reacted with *cis*-[MCl$_2$(PMe$_2$Ph)$_2$] (M = Pd or Pt) according to equation (12). When M = Pd the reaction was complete in 4 d at

$$[\mathrm{AuMe_3(PMe_2Ph)}] + \textit{cis}\text{-}[\mathrm{MCl_2(PMe_2Ph)_2}] \longrightarrow \textit{cis}\text{-}[\mathrm{AuCl(Me)_2(PMe_2Ph)}] + \textit{trans}\text{-}[\mathrm{MCl(Me)(PMe_2Ph)_2}] \tag{12}$$

20 °C and gave second-order kinetics with $k = 2.1 \times 10^{-4}$ l mol^{-1} s^{-1}, and when M = Pt the reaction was half complete in 1 week. The complex did not react with *trans*-[MCl(Me)(PMe$_2$Ph)$_2$] (M = Pd or Pt) nor with [AuX(PMe$_2$Ph)] (X = I or Br); it is therefore a weaker methylating agent than *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] or [AuMe(PMe$_2$Ph)].

The complex [AuMe$_3$(PMe$_2$Ph)] reacted with [AuBr$_3$(PMe$_2$Ph)] according to equation (13) and this reaction,

$$2[\mathrm{AuMe_3(PMe_2Ph)}] + [\mathrm{AuBr_3(PMe_2Ph)}] \longrightarrow 3\ \textit{cis}\text{-}[\mathrm{AuBr(Me)_2(PMe_2Ph)}] \tag{13}$$

which is complete in 1 h at 20 °C, gives a useful synthesis of *cis*-[AuBr(Me)$_2$(PMe$_2$Ph)]. The reaction presumably takes place in two steps according to equations (14) and (15), but the presumed intermediate [AuBr$_2$(Me)(PMe$_2$Ph)] could not be detected during the reaction by n.m.r. spectroscopy and so must react very rapidly with [AuMe$_3$(PMe$_2$Ph)] [equation (15)]. This high reactivity explains why all attempts to prepare monoalkylgold(III) complexes have been unsuccessful.

$$[\mathrm{AuMe_3(PMe_2Ph)}] + [\mathrm{AuBr_3(PMe_2Ph)}] \longrightarrow \textit{cis}\text{-}[\mathrm{AuBr(Me)_2(PMe_2Ph)}] + [\mathrm{AuBr_2(Me)(PMe_2Ph)}] \tag{14}$$

$$[\mathrm{AuBr_2(Me)(PMe_2Ph)}] + [\mathrm{AuMe_3(PMe_2Ph)}] \longrightarrow 2\ \textit{cis}\text{-}[\mathrm{AuBr(Me)_2(PMe_2Ph)}] \tag{15}$$

Reactions of [AuMe(PMe$_2$Ph)].—The complex reacted with *cis*-[MCl$_2$(PMe$_2$Ph)$_2$] (M = Pd or Pt) according to equation (16), the reactions being complete in 10 min

$$[\mathrm{AuMe(PMe_2Ph)}] + \textit{cis}\text{-}[\mathrm{MCl_2(PMe_2Ph)_2}] \longrightarrow [\mathrm{AuCl(PMe_2Ph)}] + \textit{trans}\text{-}[\mathrm{MCl(Me)(PMe_2Ph)_2}] \tag{16}$$

and 3 d respectively. It also reacted with *cis*-[AuX(Me)$_2$(PMe$_2$Ph)] (X = Br or I) to give [AuMe$_3$(PMe$_2$Ph)], the reactions being complete in 1 h and 15 min respectively.

An exothermic reaction took place with [AuBr$_3$(PMe$_2$Ph)] according to equation (17). This reaction

$$2[\mathrm{AuMe(PMe_2Ph)}] + [\mathrm{AuBr_3(PMe_2Ph)}] \longrightarrow 2[\mathrm{AuBr(PMe_2Ph)}] + \textit{cis}\text{-}[\mathrm{AuBr(Me)_2(PMe_2Ph)}] \tag{17}$$

presumably takes place in two stages with [AuBr$_2$(Me)(PMe$_2$Ph)] being formed as a reactive intermediate. In turn this could be formed in two ways, either by methyl–bromo-exchange between [AuMe(PMe$_2$Ph)] and [AuBr$_3$(PMe$_2$Ph)] or by transfer of the elements of dibromine from [AuBr$_3$(PMe$_2$Ph)] to [AuMe(PMe$_2$Ph)]. The latter mechanism is perhaps the more likely in view of the exothermic reactions of [AuBr$_3$(PMe$_2$Ph)] with *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] and *trans*-[PtBr(Me)(PMe$_2$Ph)$_2$] which certainly involve this mechanism. The reaction of [AuBr$_3$(PMe$_2$Ph)] with [AuMe$_3$(PMe$_2$Ph)], which can only reasonably take place by simple exchange, was considerably slower.

Reaction of trans-[PtBr(Me)(PMe$_2$Ph)$_2$] *with* [AuBr$_3$(PMe$_2$Ph)].—An exothermic reaction took place between *trans*-[PtBr(Me)(PMe$_2$Ph)$_2$] and [AuBr$_3$(PMe$_2$Ph)] according to equation (18). The configuration of the product

$$\textit{trans}\text{-}[\mathrm{PtBr(Me)(PMe_2Ph)_2}] + [\mathrm{AuBr_3(PMe_2Ph)}] \longrightarrow \textit{mer}\text{-}[\mathrm{PtBr_3(Me)(PMe_2Ph)_2}] + [\mathrm{AuBr(PMe_2Ph)}] \tag{18}$$

was deduced from its n.m.r. spectrum, and confirms that *trans* addition of bromine has taken place, as with *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$].

Other Reactions of Trihalogenogold(III) *Complexes.*—Reaction of equimolar quantities of bromine and chloro(dimethylphenylphosphine)gold(I) gave orange crystals which melted sharply at 116—117 °C and analysed as [AuCl(Br)$_2$(PMe$_2$Ph)]. However, the n.m.r. spectrum showed that the product contained at least three different species. Thus there were three doublets due to methylphosphorus protons each with the characteristic coupling constant of 13—14 Hz typical of trihalogenogold(III) complexes of PMe$_2$Ph; halogenogold(I) complexes have a coupling constant $^2J(\mathrm{PCH_3})$ in the region 10.5—11.5 Hz. Similar mixtures are obtained by oxidising [AuBr(PMe$_2$Ph)] with chlorine or by mixing [AuCl$_3$(PMe$_2$Ph)] and [AuBr$_3$(PMe$_2$Ph)], though this latter reaction is considerably slower. The mixture of products is easily explained if reactions (19)—(21) take place.

$$[\mathrm{AuCl(PMe_2Ph)}] + \mathrm{Br_2} \longrightarrow [\mathrm{AuCl(Br)_2(PMe_2Ph)}] \tag{19}$$

$$[\mathrm{AuCl(PMe_2Ph)}] + [\mathrm{AuCl(Br)_2(PMe_2Ph)}] \longrightarrow [\mathrm{AuCl_2(Br)(PMe_2Ph)}] + [\mathrm{AuBr(PMe_2Ph)}] \tag{20}$$

$$[\mathrm{AuBr(PMe_2Ph)}] + \mathrm{Br_2} \longrightarrow [\mathrm{AuBr_3(PMe_2Ph)}] \tag{21}$$

If reaction (20) and similar reactions are rapid then scrambling of the initial adduct [AuCl(Br)$_2$(PMe$_2$Ph)] to complexes [AuCl$_n$(Br)$_{3-n}$(PMe$_2$Ph)] will be catalysed by the presence of the Au$^{\mathrm{I}}$ complex. A similar type of reaction has been demonstrated for the analogous Pt$^{\mathrm{II}}$–Pt$^{\mathrm{IV}}$ system. Complexes such as '[AuCl(Br)$_2$(PMe$_2$Ph)]' obtained by this type of reaction have in the past been assumed to contain a single species, and the products certainly appear pure on the basis of the sharp m.p.s and highly crystalline homogeneous form. The complexes [AuCl$_n$Br$_{3-n}$(PMe$_2$Ph)] are presumably sufficiently similar to pack together in the same crystal lattice.

Conclusions.—The mechanism of the methyl–halogen exchange reactions is most likely the $S_{\mathrm{E}}2$(cyclic) mechanism of electrophilic substitution at a saturated carbon atom. Thus preliminary kinetic data have shown that several of the reactions follow second-order kinetics. The evidence for a cyclic intermediate is based on the reaction of *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] with *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] which gave as the product of kinetic control *cis*-[PtCl(Me)(PMe$_2$Ph)$_2$] which subsequently isomerised to the thermodynamically more stable *trans* isomer. No evidence about the stereochemistry of the other reactions was obtained, and so there is no direct evidence for a cyclic intermediate in these reactions. The rates of cleavage by various reagents of the methyl-platinum bond in *cis*-[$PtMe_2(PMe_2Ph)_2$] followed the series [$AuI(PMe_2Ph)$] $\gg$ [$AuBr(PMe_2Ph)$] $\gg$ [$AuCl(PMe_2Ph)$] and [$PtI_2(PMe_2Ph)_2$] $\gg$ [$PtCl_2(PMe_2Ph)_2$]. If a cyclic intermediate is involved this is consistent with the greater ability of iodide to bridge between metal atoms in this region of the Periodic Table.[14] The reaction rates also correlate with the reactivity towards nucleophilic substitution of *both* the methyl-donating and -accepting metal centre, again supporting a cyclic intermediate. Thus the reactivity towards *cis*-[$PtMe_2(PMe_2Ph)_2$], for a given halogen X, follows the series [$AuX(PMe_2Ph)$] > *cis*-[$PdX_2(PMe_2Ph)_2$] $\gg$ *cis*-[$PtX_2(PMe_2Ph)_2$] consistent with known reactivity towards substitution reactions. Similarly [$AuMe(PMe_2Ph)$] reacted with *cis*-[$PdCl_2(PMe_2Ph)_2$] or *cis*-[$PtCl_2(PMe_2Ph)_2$] much faster than did *cis*-[$PtMe_2(PMe_2Ph)_2$]. The Au^{III} complexes are rather more difficult to place in the reactivity series. Thus [$AuMe_3(PMe_2Ph)$] reacted with *cis*-[$PdCl_2(PMe_2Ph)_2$] or *cis*-[$PtCl_2(PMe_2Ph)_2$] at about the same rate as did *cis*-[$PtMe_2(PMe_2Ph)_2$], although substitution reactions at Au^{III} usually take place more rapidly than at Pt^{II}. The result is also surprising in view of the similarity in rate for reaction of [$AuMe(PPh_3)$] and [$AuMe_3(PPh_3)$] by mercury(II) halides,[9] though other substitution reactions are known to take place more rapidly at Au^{I} than Au^{III}.[15] The reactivity of Au^{III} halides towards methylation reactions appears to depend strongly on the particular complex. From a variety of reactions, the reactivity series [$AuBr_2(Me)(PMe_2Ph)$] > [$AuBr_3(PMe_2Ph)$] $\gg$ [$AuBr(Me)_2(PMe_2Ph)$] can be deduced but is difficult to rationalise.

The methylating power of the various methyl transition-metal complexes studied follows the series *cis*-[$PtMe_2(PMe_2Ph)_2$], [$AuMe(PMe_2Ph)$] > [$AuMe_3(PMe_2Ph)$] $\gg$ *trans*-[$MCl(Me)(PMe_2Ph)_2$] (M = Pd or Pt), *cis*-[$AuX(Me)_2(PMe_2Ph)$] (X = halogen). From the inability of *cis*-[$PtMe_2(PMe_2Ph)_2$] or [$AuMe(PMe_2Ph)$] to methylate *trans*-[$PdCl(Me)(PMe_2Ph)_2$] it seems likely that [$PdMe_2(PMe_2Ph)_2$] is a stronger methylating agent than either, but it is too unstable to be studied directly. The driving force for the methyl–halogen exchange reactions presumably arises from differences in the metal–methyl and –halogen bond strengths in the different complexes, and the dependence of the equilibrium constant for reaction (6) on the halogen, X, must arise as a result of differences in the Pt–X and Au–X bond strengths.

EXPERIMENTAL

Methyl-platinum [11] and -gold [1,5] complexes were prepared by known methods. All reactions were studied by dissolving the reagents in the required proportions in dichloromethane (0.5 cm³) in an n.m.r. tube and monitoring the course of the reactions by n.m.r. spectroscopy. Products were usually identified by their n.m.r. spectra by comparison with authentic specimens.[1,5,11,16–19] Concentrations of reagents were determined by measuring peak heights of the methyl-gold or -platinum resonance, using the height of the high-field ^{13}C satellite peak of dichloromethane solvent as internal reference. A previous calibration was made with known concentrations of the methyl-gold or -platinum complex in dichloromethane.

N.m.r. spectra were recorded using a Perkin-Elmer R12B spectrometer. Chemical shifts are given in p.p.m. downfield from $SiMe_4$, using dichloromethane as internal reference.

(Dimethylphenylphosphine)trimethylgold(III).—The following method gives higher yields than that reported earlier.[5] The complex [$AuBr(PMe_2Ph)$] (0.68 g) was suspended in diethyl ether (20 cm³) and iodomethane (2 cm³) under dry nitrogen at −78 °C. Methyl-lithium (4 cm³, 2.3M) was added slowly and the solution allowed to warm to room temperature and stirred for 1.5 h. The mixture was hydrolysed with water and the *product* obtained by evaporating the dried ether layer *in vacuo*. It was identical (n.m.r. and i.r.) with an authentic specimen.

cis-*Bromo(dimethylphenylphosphine)dimethylgold*(III).—Solutions of (dimethylphenylphosphine)methylgold(I) (0.20 mmol) and tribromo(dimethylphenylphosphine)gold(III) (0.10 mmol) in dichloromethane (1 cm³) were mixed. After 30 min the solvent was evaporated and the product was extracted with diethyl ether. Cooling the ether solution gave colourless crystals of the *product*, m.p. 85—88 °C (Found: C, 26.5; H, 3.85. Calc. for $C_{10}H_{17}AuBrP$: C, 26.95; H, 3.80%). Alternatively the product was obtained in quantitative yield by reaction of [$AuMe_3(PMe_2Ph)$] (2 mol) with [$AuBr_3(PMe_2Ph)$] (1 mol) in dichloromethane for 2 h, followed by recrystallisation from diethyl ether.

Dibromochloro(dimethylphenylphosphine)gold(III).— This was obtained as orange crystals by adding a solution of bromine in carbon tetrachloride (0.3 cm³, 0.546M) to chloro(dimethylphenylphosphine)gold(I) (0.06 g) in dichloromethane (0.8 cm³). The product crystallised from the solution and was filtered off and dried *in vacuo*, m.p. 116—117 °C (Found: C, 18.05; H, 2.25. Calc. for $C_8H_{11}AuBr_2ClP$: C, 18.1; H, 2.10%).

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