Alkyl-exchange Reactions and their Catalysis in Platinum(II) Complexes

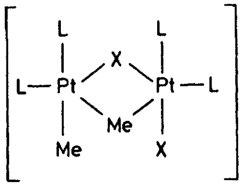
By **Richard J. Puddephatt** * and **Peter J. Thompson**, Donnan Laboratories, The University of Liverpool, Liverpool L69 3BX

A study of the symmetrisation reactions of $[PtR_2L_2]$ with $[PtX_2L_2]$ to give $[PtXRL_2]$ has been made (R = Me, Ph, or C≡CMe; L = PEt_3, PMe_3, PMe_2Ph, or $AsMe_3$; X = Cl, I, NCS, NO_2, or NO_3). The dependence of the reaction rate and stereochemistry on the substituents R, X, and L has been studied and the reaction mechanism is discussed. The reaction of *cis*-$[PtCl_2(PMe_2Ph)_2]$ with *cis*-$[PtMe_2(PMe_2Ph)_2]$ to give *cis*-$[PtClMe(PMe_2Ph)_2]$ is catalysed by $[Pt_2Cl_4(PMe_2Ph)_2]$, but the catalyst is destroyed in a competing reaction with *cis*-$[PtMe_2(PMe_2Ph)_2]$ to give *cis*-$[Pt_2(\mu\text{-}Cl)_2Me_2(PMe_2Ph)_2]$.

RECENT research indicates that alkyl transfer between transition-metal centres [equation (1); M,M′ = metal, R = alkyl, X = halogen] occurs readily in many cases [1-3] and that some unexpected reaction products can be rationalised on this basis. Examples include the reactions of $[AuMe(PMe_3)]$ with methyl iodide [4] or trifluoromethyl iodide [5] and of *cis*-$[PtMe_2(PMe_2Ph)_2]$ with nitrogen monoxide.[6] In some cases the reactions are sufficiently rapid that they might be expected to occur in catalytic sytems where transition-metal alkyls are implicated as intermediates.

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

Some methyl-for-halogen exchange reactions between platinum(II), palladium(II), gold(I), and gold(III) complexes have been reported previously, and an S_E2 (cyclic) mechanism was proposed.[1,2] The evidence was: (*i*) many of the reactions followed second-order kinetics; (*ii*) the reactivity could be correlated with the lability of both the metal alkyl and metal halide toward substitution reactions; and (*iii*) the reaction of *cis*-$[PtMe_2(PMe_2Ph)_2]$ with *cis*-$[PtX_2(PMe_2Ph)_2]$ took place with retention of stereochemistry at both platinum centres to give *cis*-$[PtXMe(PMe_2Ph)_2]$ as the product of kinetic control when X = Cl or NO_3. An intermediate or transition state of structure (1) was invoked.



(1) L = PMe_2Ph

The general symmetrisation reaction of equation (2) has now been studied in more detail, and in this paper the dependence of the rate and steric course of reaction are reported as a function of the organic group R, the inorganic group X, and the tertiary phosphine ligand L.

$$[PtR_2L_2] + [PtX_2L_2] \longrightarrow [PtXRL_2] \qquad (2)$$

Also reported is a remarkable catalysis of some symmetrisation reactions by the complex $[Pt_2Cl_4(PMe_2Ph)_2]$. A preliminary account of some of this work has been published.[7]

RESULTS AND DISCUSSION

cis-$[PtMe_2(PMe_2Ph)_2]$ *with* *cis*-$[Pt(NCS)_2(PMe_2Ph)_2]$ *and* *cis*-$[Pt(NO_2)_2(PMe_2Ph)_2]$.—The reactions of *cis*-$[PtMe_2(PMe_2Ph)_2]$ with *cis*-$[Pt(NCS)_2(PMe_2Ph)_2]$ and *cis*-$[Pt(NO_2)_2(PMe_2Ph)_2]$ were monitored by recording the n.m.r. spectra of reaction mixtures periodically. The aim was to study effects on the binding position of the ambidentate thiocyanato- and nitro-ligands during the exchange reaction. Both are *N*-bonded in *cis*-$[PtX_2(PMe_2Ph)_2]$ derivatives. If the cyclic intermediate of the exchange reaction involves Pt–NCS–Pt or Pt–N(O)O–Pt bridges, then one might expect the product to contain equimolar amounts of *trans*-$[Pt(NCS)Me(PMe_2Ph)_2]$ and *trans*-$[Pt(SCN)Me(PMe_2Ph)_2]$ or *trans*-$[Pt(NO_2)Me(PMe_2Ph)_2]$ and *trans*-$[Pt(ONO)Me(PMe_2Ph)_2]$ respectively. The reactions took place readily, being complete in 1 h at 33 °C with *cis*-$[Pt(NO_2)_2(PMe_2Ph)_2]$ and 4 d at 33 °C with *cis*-$[Pt(NCS)_2(PMe_2Ph)_2]$. However, the products were *trans*-$[Pt(NO_2)Me(PMe_2Ph)_2]$, with *N*-nitro-groups only, and an equilibrium mixture of *trans*-$[Pt(NCS)Me(PMe_2Ph)_2]$ (80%) and *trans*-$[Pt(SCN)Me(PMe_2Ph)_2]$ (20%) respectively. In the latter case the same ratio of isomers was obtained by methylation of *cis*-$[Pt(NCS)_2(PMe_2Ph)_2]$ by $[AuMe(PMe_2Ph)]$. It seems that isomerisation between the linkage isomers is faster than the exchange reactions, so that no evidence for or against nitro- or thiocyanato-bridge formation in the reaction was obtained. Combined with earlier work [1,2,8] the rate of reaction of *cis*-$[PtMe_2(PMe_2Ph)_2]$ with *cis*-

---

[1] R. J. Puddephatt and P. J. Thompson, *J.C.S. Dalton*, **1975**, 1810.

[2] P. J. Thompson and R. J. Puddephatt, *J.C.S. Chem. Comm.*, 1975, 841.

[3] J. P. Visser, W. W. Jager, and C. Masters, *Rec. Trav. chim.*, 1975, **94**, 61.

[4] A. Johnson and R. J. Puddephatt, *J. Organometallic Chem.*, 1975, **85**, 115.

[5] A. Johnson and R. J. Puddephatt, *J.C.S. Dalton*, **1976**, **1360**.

[6] R. J. Puddephatt and P. J. Thompson, *J.C.S. Dalton*, **1976**, 2091.

[7] R. J. Puddephatt and P. J. Thompson, *J. Organometallic Chem.*, 1976, **120**, C51.

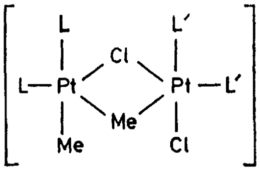
[8] R. J. Puddephatt and P. J. Thompson, *J. Organometallic Chem.*, 1976, **117**, 395.

$[Pt(NO_3)_2(PMe_2Ph)_2] \gg$ *cis*-$[Pt(NO_2)_2(PMe_2Ph)_2] >$ *trans*-$[Pt(SePh)_2(PMe_2Ph)_2] > [PtI_2(PMe_2Ph)_2]$ (*cis–trans* mixture) $>$ *cis*-$[Pt(NCS)_2(PMe_2Ph)_2] \gg$ *cis*-$[PtCl_2(PMe_2Ph)_2]$. The range of reactivity is very large. For example the reaction with *cis*-$[Pt(NO_3)_2(PMe_2Ph)_2]$ is too fast to measure by the n.m.r. technique but is certainly complete within 1 min, whereas the reaction with *cis*-$[PtCl_2(PMe_2Ph)_2]$ is only half-complete after 15 d at 34 °C.

cis-$[PtCl_2L_2]$ with *cis*-$[PtMe_2L_2']$.—The symmetrisation reactions of *cis*-$[PtCl_2L_2]$ with *cis*-$[PtMe_2L_2]$ to give $[PtClMeL_2]$ were studied for different tertiary phosphine ligands, L. The final product in each case was *trans*-$[PtClMeL_2]$ although the *cis* isomer could be identified at intermediate stages when $L = PMe_2Ph$, and in methanol but not in dichloromethane solution, when $L = PEt_3$, thus confirming the observations of Visser *et al.*[3] Little significance can be attached to the apparent solvent dependence since it is possible that the *cis* isomer is formed in the exchange reaction in each case but that the isomerisation to *trans*-$[PtClMe(PEt_3)_2]$ is faster in dichloromethane than in methanol. The rates followed the order $L = PEt_3$ ($t_{\frac{1}{2}}$ *ca.* 1 h) $\gg PMe_3$ (*ca.* 2 d) $\gg PMe_2Ph$ (*ca.* 15 d at 34 °C). Previous studies have established that similar exchange reactions take place as fast or faster for PMe_2Ph than for $PMePh_2$ complexes of Pt^{II}.[1]

Reaction of *cis*-$[PtMe_2(PEt_3)_2]$ with *cis*-$[PtCl_2(PMe_2Ph)_2]$ gave initially a 1 : 1 mixture of *trans*-$[PtClMe(PEt_3)_2]$ and *trans*-$[PtClMe(PMe_2Ph)_2]$, this reaction being half-complete in *ca.* 8 h at 20 °C. A much slower phosphine-exchange process then took place to give a mixture of the initial products and *trans*-$[PtClMe(PEt_3)(PMe_2Ph)]$ in the proportion *ca.* 1 : 1 : 2 as expected from statistical considerations only. This reaction was half-complete in *ca.* 10 d at 20 °C. The final product was characterised by the methylplatinum resonance in the ^1H n.m.r. spectrum which appeared as a doublet of doublets due to coupling with two non-equivalent phosphorus atoms.

In contrast, *cis*-$[PtMe_2(PMe_2Ph)_2]$ and *cis*-$[PtCl_2(PEt_3)_2]$ gave no detectable reaction after 1 week at 20 °C. Reaction is thermodynamically favourable since, in the presence of $[Pt_2Cl_4(PMe_2Ph)_2]$ as catalyst (see later), *cis*-$[PtClMe(PMe_2Ph)_2]$ and *trans*-$[PtClMe(PEt_3)_2]$ are formed. If a cyclic transition state is involved then steric interactions should be very similar in the intermediates (2) and (3) formed from *cis*-$[PtMe_2(PMe_2Ph)_2]$ and *cis*-$[PtCl_2(PEt_3)_2]$ and from *cis*-$[PtMe_2(PEt_3)_2]$ and *cis*-$[PtCl_2(PMe_2Ph)_2]$, so that the different rates of reaction must be attributed to electronic effects. The results are mostly readily explained if the basicity of the phosphine ligand L in *cis*-$[PtMe_2L_2]$ is the most important factor in determining the reactivity. In view of this strong dependence of the rate on the nature of the phosphine ligands, and of the catalysis of the exchange reactions by the phosphine scavenger $[Pt_2Cl_4(PMe_2Ph)_2]$ (see later), it might be argued that the rate-determining step in the exchange reactions involves dissociation of a tertiary phosphine ligand from *cis*-$[PtMe_2L_2]$ to give the three-co-ordinate $[PtMe_2L]$ which then rapidly reacts with *cis*-$[PtCl_2L_2]$. If this were the case, the exchange reactions would be expected to take place faster with complexes of tertiary arsine ligands since the ligand dissociation would then occur more readily.[9,10] The reaction when $L = AsMe_3$ followed overall second-order kinetics (using equal concentrations of starting materials) with a rate constant of 2.8×10^{-5} dm^3 mol^{-1} s^{-1} at 34 °C in dichloromethane solution. Under the conditions used the half-life was *ca.* 3 d when $L = AsMe_3$ compared with *ca.* 2 d for $L = PMe_3$ under similar conditions. Thus the dissociative mechanism is considered unlikely on this basis, and also since a mechanism involving slow ligand dissociation should give rise to a kinetic form which is first order in the complex from which the ligand is lost and zero'th order in the other complex. Thus the observation of overall second-order kinetics is not consistent with this mechanism.



(2) $L = PMe_2Ph$, $L' = PEt_3$
(3) $L = PEt_3$, $L' = PMe_2Ph$

$[PtI_2(PMe_2Ph)_2]$ *with* $[PtR_2(PMe_2Ph)_2]$.—It is interesting to compare the relative rates of reaction of $[PtI_2(PMe_2Ph)_2]$ with *cis*-$[PtMe_2(PMe_2Ph)_2]$ and with *trans*-$[PtPh_2(PMe_2Ph)_2]$ to give *trans*-$[PtIMe(PMe_2Ph)_2]$ and *trans*-$[PtIPh(PMe_2Ph)_2]$ respectively. The former reaction was complete in 1 d at 20 °C in dichloromethane solution, but the latter reaction required 2 weeks at 60 °C to reach completion. The complex *trans*-$[Pt(C{\equiv}CMe)_2(PMe_2Ph)_2]$ did not react with $[PtI_2(PMe_2Ph)_2]$ at 60 °C over a period of several weeks. The relatively low reactivity of the phenylplatinum complex is perhaps surprising since electrophilic attack is expected to take place more readily with aromatic than with aliphatic derivatives. For example, the symmetrisation reaction of HgI_2 with $HgPh_2$ is very much faster than with $HgMe_2$,[11] and reactions of $SnMe_3Ph$ with electrophiles invariably lead to cleavage of the phenyltin rather than a methyltin bond.[12] Various interpretations can be made for this difference. Thus steric hindrance to formation of the five-co-ordinate transition state could be greater in the phenylplatinum compared with the methylplatinum

---

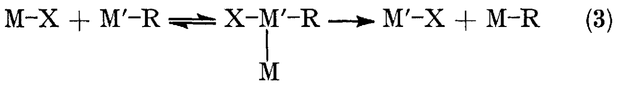
[9] J. D. Ruddick and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 2964.

[10] M. P. Brown, R. J. Puddephatt, and C. E. E. Upton, *J.C.S. Dalton*, 1974, 2457.

[11] R. E. Dessy and I. K. Lee, *J. Amer. Chem. Soc.*, 1961, **82**, 689.

[12] R. C. Poller, 'The Chemistry of Organotin Compounds,' Logos, London, 1970.

complexes. Steric effects would be expected to be much greater than in the linear mercury(II) derivatives. There also appears to be a larger difference between the phenyl- and methyl-metal bond energies for platinum than for mercury derivatives. Thus M–C bond energies are 250 kJ mol^{-1} for *trans*-[$\mathrm{PtPh_2(PEt_3)_2}$],[13] 144 kJ mol^{-1} for *fac*-[$\mathrm{PtIMe_3(PMe_2Ph)_2}$],[10] 136 kJ mol^{-1} for $\mathrm{HgPh_2}$, and 122 kJ mol^{-1} for $\mathrm{HgMe_2}$.[14] The high Pt–Ph bond energy may thus be partially responsible for the low reactivity of the phenylplatinum complex. The dependence of the rate of reaction on the nature of R and L in [$\mathrm{PtR_2L_2}$]

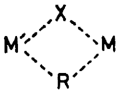


$$\mathrm{M{-}X + M'{-}R \rightleftharpoons X{-}\underset{\displaystyle M}{\underset{|}{M'}}{-}R \longrightarrow M'{-}X + M{-}R} \qquad (3)$$

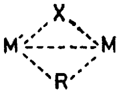
gives R = Me > Ph > C≡CMe and L = $\mathrm{PEt_3 > PMe_3 > PMe_2Ph > PMePh_2}$. This is also the order of expected electron-donor ability of the groups R and L, and the order would be expected if the exchange reactions took place by an oxidative-addition–reductive-elimination mechanism [equation (3)].

The mechanism merits consideration since cleavage of the phenylplatinum bond in *trans*-[$\mathrm{PtPh_2(PEt_3)_2}$] by HCl has been shown to take place *via* a hydridoplatinum(IV) intermediate,[15] and oxidative addition of a platinum–halogen bond to the platinum(0) complex [$\mathrm{Pt(PPh_3)_4}$] has been reported.[16] This mechanism cannot be expected to operate in cleavage of methylgold bonds in [$\mathrm{AuMe_3(PMe_3)}$] since $\mathrm{Au^{III}}$ cannot readily undergo oxidative-addition reactions, but could play a part in reactions of gold(I) or platinum(II) alkyls where oxidation occurs readily. The transition states for the oxidative-addition and $S_\mathrm{E}2$ (cyclic) mechanisms may be represented

(4)



(5)



(6)

as (4) and (5) respectively. These are not dissimilar and an attractive hypothesis is that intermediate mechanisms between these extremes are possible involving some metal–metal bond formation as shown in structure (6). Whether the transition state resembled (4) or (5) most closely would then depend on the reactivity of the metal alkyl, MR, towards oxidative addition.

Methylation of [$\mathrm{Pt_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2}$].—*cis*-[$\mathrm{PtMe_2(PMe_2Ph)_2}$] and [$\mathrm{Pt_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2}$] (probably *trans*) reacted rapidly according to equation (4), the reaction being complete within 5 min at room temperature. The dimeric complex *cis*-[$\mathrm{Pt_2(\mu\text{-}Cl)_2Me_2(PMe_2Ph)_2}$] could not be isolated from this reaction mixture in pure form, but was prepared independently by methylation of [$\mathrm{Pt_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2}$] with tetramethyltin. In this case the product was easily separated from excess of $\mathrm{SnMe_4}$ and from the trimethyltin chloride formed in the reaction. Consistent with the proposed formulation is the ^{13}C n.m.r. spectrum which contains two resonances due to the $\mathrm{PCH_3}$ and $\mathrm{PtCH_3}$ groups, each appearing as a 1 : 1 doublet due to coupling with the adjacent ^{31}P and

$$2\,cis\text{-}[\mathrm{PtMe_2(PMe_2Ph)_2}] + [\mathrm{Pt_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2}] \longrightarrow 2\,trans\text{-}[\mathrm{PtClMe(PMe_2Ph)_2}] + cis\text{-}[\mathrm{Pt_2(\mu\text{-}Cl)_2Me_2(PMe_2Ph)_2}] \qquad (4)$$

with satellites of 0.25 intensity due to coupling with ^{195}Pt. The ^{1}H n.m.r. spectrum also contained a 1 : 1 doublet due to the $\mathrm{PCH_3}$ groups, but the $\mathrm{PtCH_3}$ resonance appeared as a broad triplet at 35 °C and as a doublet of doublets at low temperature. Again satellites due to coupling with ^{195}Pt of intensity 0.25 were observed. The low-temperature spectrum is surprising since in similar complexes *cis*-[$\mathrm{Pt_2Me_2(\mu\text{-}SMe)_2(PMe_2Ph)_2}$] the methylplatinum resonance appears as a 1 : 1 doublet due to coupling with the adjacent phosphorus atom only,[17] and in the ^{13}C n.m.r. spectra no coupling of the $\mathrm{PtCH_3}$ carbon atom to the distant ^{31}P nucleus is observed in either *cis*-[$\mathrm{Pt_2(\mu\text{-}Cl)_2Me_2(PMe_2Ph)_2}$] or *cis*-[$\mathrm{Pt_2Me_2(\mu\text{-}SMe)_2(PMe_2Ph)_2}$]. The further splitting of the $\mathrm{PtCH_3}$ resonance in the ^{1}H n.m.r. spectrum, presumably due to coupling with the remote ^{31}P, is therefore anomalous. {The ^{31}P nuclei and $\mathrm{PtCH_3}$ protons should actually give a second-order $[\mathrm{AX_3}]_2$ splitting pattern, the form of which depends on the magnitude of ^4J(PP) relative to ^3J(PH) + ^5J(PH).} The *cis* configuration is deduced from the dipole moment of 4.4 ± 0.2 D in toluene solution.* This is very similar to the value for *cis*-[$\mathrm{Pt_2(\mu\text{-}Br)_2Ph_2(PPr_3)_2}$] of 4.05 D.[18] The complex reacted immediately with 2 mol equiv. of dimethylphenylphosphine to give a mixture of *cis*- and *trans*-[$\mathrm{PtClMe(PMe_2Ph)_2}$] in the ratio *ca.* 2 : 3, followed by slower isomerisation of the *cis* to the more stable *trans* isomer.

Catalysis of Exchange Reactions by [$\mathrm{Pt_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2}$].—The symmetrisation reaction between *cis*-[$\mathrm{PtMe_2(PMe_2Ph)_2}$] and *cis*-[$\mathrm{PtCl_2(PMe_2Ph)_2}$] was catalysed by [$\mathrm{Pt_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2}$]. The nature of the catalysis is illustrated in Figures 1 and 2, and the chief results are summarised briefly.

(1) In general, a rapid catalytic effect was observed followed by a plateau region in which the reaction proceeded slowly as in the uncatalysed process. The extent of conversion in the rapid catalytic process was approximately proportional to the catalyst concentration up to a catalyst concentration of 2 mol% (at which >70% con-

---

* Throughout this paper: 1 D ≈ 3.33×10^{-30} Cm.

[13] S. J. Ashcroft and C. T. Mortimer, *J. Chem. Soc.* (*A*), 1967, 930.

[14] J. D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds,' Academic Press, New York, 1970.

[15] R. Romeo, D. Minniti, S. Lanza, P. Uguagliati, and U. Belluco, *Inorg. Chim. Acta*, 1976, **19**, L55.

[16] A. J. Layton, R. S. Nyholm, G. A. Pneumaticakis, and M. L. Tobe, *Chem. and Ind.*, 1967, 465.

[17] M. P. Brown, R. J. Puddephatt, and C. E. E. Upton, *J.C.S. Dalton*, 1976, 2490.

[18] J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 1964, 2433.

version took place) but then tailed off at higher catalyst concentrations (Figure 2). Addition of more catalyst to a system in which reaction was incomplete caused a further rapid reaction to occur.

(2) The product of reaction was *cis*-[PtClMe$(PMe_2Ph)_2$] which is thermodynamically less stable than the *trans* isomer.

(3) In order to observe the catalytic effect it was necessary to add the catalyst to *cis*-[$PtCl_2(PMe_2Ph)_2$] followed by addition of *cis*-[$PtMe_2(PMe_2Ph)_2$]. If the catalyst was added to *cis*-[$PtMe_2(PMe_2Ph)_2$], reaction to give *cis*-[$Pt_2(\mu\text{-}Cl)_2Me_2(PMe_2Ph)_2$] occurred and no catalytic effect was observed. The complex *cis*-[$Pt_2(\mu\text{-}Cl)_2Me_2(PMe_2Ph)_2$] did not catalyse the symmetrisation reaction and did not react with *cis*-[$PtCl_2(PMe_2Ph)_2$].

(4) The catalysed reaction of *cis*-[$PtMe_2(PMe_2Ph)_2$] with *cis*-[$PtCl_2(PEt_3)_2$] took place without scrambling of the phosphine groups.

We have considered two mechanisms for this catalytic effect. In the first mechanism the catalyst could act by abstracting a phosphine ligand from *cis*-[$PtMe_2(PMe_2Ph)_2$] to give three-co-ordinate [$PtMe_2(PMe_2Ph)$] which is the active methylating agent. Precedents for [$Pt_2Cl_4L_2$] acting as phosphine scavengers are known.[10] However, a T-shaped three-co-ordinate species would not be stereochemically rigid and would be expected to give at least some *trans*-[PtClMe$(PMe_2Ph)_2$] after exchange and recombination with phosphine. Also scrambling of phosphine groups during the exchange process would be expected but was not observed.

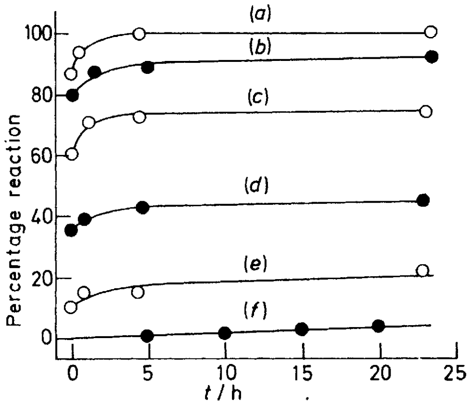


FIGURE 1 Percentage of *cis*-[$PtMe_2(PMe_2Ph)_2$] reacted in the catalysed reaction with *cis*-[$PtCl_2(PMe_2Ph)_2$] against time. Initial concentration of *cis*-[$PtMe_2(PMe_2Ph)_2$] and of *cis*-[$PtCl_2(PMe_2Ph)_2$] was 0.116 4 mol dm^{-3}. Concentration of catalyst [$Pt_2Cl_4(PMe_2Ph)_2$]: (*a*) 1.01×10^{-2}, (*b*) 8.08×10^{-3}, (*c*) 2.12×10^{-3}, (*d*) 1.21×10^{-3}, (*e*) 4.04×10^{-4} mol dm^{-3}, and (*f*) no catalyst

In the second mechanism the catalyst is methylated by *cis*-[$PtMe_2(PMe_2Ph)_2$] and then, in turn, methylates *cis*-[$PtCl_2(PMe_2Ph)_2$] with regeneration of the catalyst. This mechanism is consistent with all the available data. However, the nature of the reactive intermediate is not known. It is clear that it is not *cis*-[$Pt_2(\mu\text{-}Cl)_2Me_2(PMe_2Ph)_2$] since this does not catalyse the reaction. Indeed it is formation of this species by reaction (4) which destroys the catalyst. We think it likely that a reactive species with a bridging methyl group, [$Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}Me)(PMe_2Ph)_2$], or possibly monomeric [PtClMe(PMe_2Ph)], is the active intermediate, but further kinetic studies, which are not possible by the n.m.r. technique, are needed to settle this point.

In view of this remarkable catalytic effect it is obviously necessary to check very carefully the purity of complexes [$PtCl_2L_2$] used in studies of methyl-exchange reactions, since a trace amount of [$Pt_2Cl_4L_2$] impurity could obviously greatly affect the reaction rate.

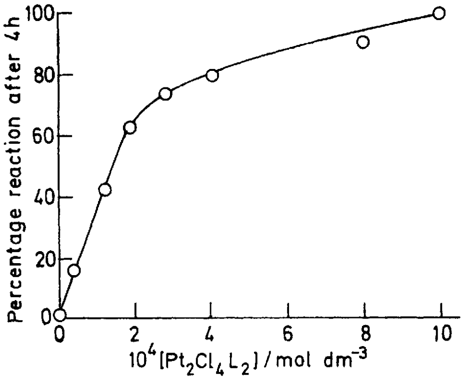


FIGURE 2 Percentage of *cis*-[$PtMe_2(PMe_2Ph)_2$] reacted after 4 h in the reaction with *cis*-[$PtCl_2(PMe_2Ph)_2$] against the concentration of catalyst

EXPERIMENTAL

Preparations of starting materials were by literature methods unless given below. Methyl-exchange reactions were carried out in dichloromethane solution (*ca.* 0.1 mol dm^{-3} in each reagent) and were monitored by n.m.r. as described previously.[1] Dipole moments were measured in toluene solvent.

cis-[$Pt(NO_3)_2(PMe_2Ph)_2$].—To a solution of *cis*-[$PtCl_2(PMe_2Ph)_2$] (0.31 g, 0.58 mmol) in dichloromethane (4 cm^3) was added Ag[NO_3] (0.195 g, 1.15 mmol) dissolved in hot methanol (8 cm^3). The mixture was stirred for 2 h then filtered to remove AgCl and the solvent was evaporated to give the *product* as white crystals, which were recrystallised from methanol, yield 0.22 g, m.p. 200—203 °C; n.m.r. in CH_2Cl_2 $\delta(PCH_3)$ 1.56 (d) [$^2J(PH) + {}^4J(PH)$ 11.6, $^3J(PtH)$ 36.4 Hz] (Found: C, 32.2; H, 4.7; N, 4.7. Calc. for $C_{16}H_{22}N_2O_6Pt$: C, 32.3; H, 3.7; N, 4.7%).

trans-[$Pt(C{\equiv}CMe)_2(PMe_2Ph)_2$].—The complex *cis*-[$PtCl_2(PMe_2Ph)_2$] (1.0 g, 1.9 mmol) was added to a solution of Li(CCMe) [from LiMe (13 mmol) and excess of propyne in diethyl ether (100 cm^3)] cooled to −78 °C. The mixture was allowed to warm to room temperature and was stirred for 2 h. The mixture was hydrolysed and the *product* was obtained by evaporation of the dried ether layer. It was purified by chromatography through a column of silica eluting with dichloromethane, yield 0.6 g, m.p. 173 °C, n.m.r. in CH_2Cl_2 $\delta(PCH_3)$ 2.01 (t) [$^2J(PH) + {}^4J(PH)$ 6.8, $^3J(PtH)$ 31 Hz], $\delta(CCH_3)$ 1.83 (t) [$^5J(PH)$ 4.2 Hz], i.r. $\nu(C{\equiv}C)$ at 2 116 cm^{-1} (Found: C, 47.6; H, 4.85. Calc. for $C_{22}H_{28}P_2Pt$: C, 48.1; H, 5.1%).

cis-[$PtMe_2(PMe_2Ph)_2$] *with* *cis*-[$Pt(NCS)_2(PMe_2Ph)_2$].—

The complexes *cis*-$[PtMe_2(PMe_2Ph)_2]$ (0.05 g, 0.1 mmol) and *cis*-$[Pt(NCS)_2(PMe_2Ph)_2]$ (0.06 g, 0.1 mmol) were mixed in dichloromethane (0.7 cm^3) in an n.m.r. tube. The products, identified by the n.m.r. spectra after 4 d at 20 °C, were: *trans*-$[Pt(NCS)Me(PMe_2Ph)_2]$ (0.16 mmol), n.m.r. δ(PtMe) 0.04 (t) [^3J(PH) 7.2, ^2J(PtH) 78.5 Hz], δ(PMe) 1.74 (t) [^2J(PH) + ^4J(PH) 6.9, ^3J(PtH) 30.3 Hz], i.r. ν(CN) at 2 092vs, ν(CS) at 820m and 816m cm^{-1}; and *trans*-$[Pt(SCN)Me(PMe_2Ph)_2]$ (0.04 mmol), n.m.r. δ(PtMe) 0.21 (t) [^3J(PH) 7.1, ^2J(PtH) 75.0 Hz], δ(PMe) 1.81 (t) [^2J(PH) + ^4J(PH) 6.8, ^3J(PtH) 29.5 Hz], i.r. ν(CN) at 2 210m cm^{-1}. The mixture of isomers had m.p. 104—105 °C (Found: C, 38.9; H, 4.4; N, 2.4. Calc. for $C_{18}H_{25}NP_2PtS$: C, 39.7; H,4.6; N, 2.6%).

cis-$[PtMe_2(PEt_3)_2]$ with *cis*-$[PtCl_2(PMe_2Ph)_2]$.—Reaction carried out as above gave, after 1 d at 33 °C, *trans*-$[PtClMe(PEt_3)_2]$ and *trans*-$[PtClMe(PMe_2Ph)_2]$ identified by the n.m.r. spectra. After 7 d the major product was $[PtCl^aMe^c(PMe_2Ph)^b(PEt_3)^d]$; n.m.r. in CH_2Cl_2 δ(PtMe) 0.24 (d, d) [^3J(PH) 6.2, 7.0, ^2J(PtH) 84.6 Hz].

trans-$[PtPh_2(PMe_2Ph)_2]$ with $[PtI_2(PMe_2Ph)_2]$.—A solution of *trans*-$[PtPh_2(PMe_2Ph)_2]$ (0.06 g, 0.1 mmol) and $[PtI_2(PMe_2Ph)_2]$ (0.07 g, 0.1 mmol) in dichloromethane (0.9 cm^3) was placed in an n.m.r. tube and the tube was sealed *in vacuo*. After 14 d at 60 °C reaction to give *trans*-$[PtIPh(PMe_2Ph)_2]$ was complete, and the product was isolated by evaporation of the solvent, m.p. 111—116 °C, n.m.r. in CH_2Cl_2 δ(PMe) 1.14 (t) [^2J(PH) + ^4J(PH) 7.0, ^3J(PtH) 32.1 Hz] (Found: C, 39.3; H, 4.0. Calc. for $C_{22}H_{27}IP_2Pt$: C, 39.1; H, 4.0%).

cis-$[Pt_2(\mu\text{-}Cl)_2Me_2(PMe_2Ph)_2]$.—Excess of $SnMe_4$ (0.4 g, 2.7 mmol) was added to a solution of $[Pt_2Cl_4(PMe_2Ph)_2]$ (0.4 g, 0.5 mmol) in dichloromethane (10 cm^3). After 24 h at room temperature the solvent was evaporated, the *product* was washed with diethyl ether, and recrystallised from dichloromethane–light petroleum to give brown crystals (0.13 g), m.p. 132—135 °C. N.m.r. spectra: ^{1}H in CH_2Cl_2 at 25 °C, δ(PtMe) 0.39 (t) [J(PH) 6.0, ^2J(PtH) 81.6 Hz], δ(PMe) 1.64 (d) [^2J(PH) 11.4, ^3J(PtH) 51 Hz], at -25 °C δ(PtMe) 0.36 (d, d) [J(PH) 3.6, 4.2, J(PtH) 84 Hz]; ^{13}C in $CDCl_3$, $\delta(PtCH_3)$ -13.65 (d) [^2J(PC) 30, ^1J(PtC) 708 Hz], $\delta(PCH_3)$ 13.47 (d) [^1J(PC) 44, ^2J(PtC) 52.4 Hz] (Found: C, 28.5; H, 3.8. Calc. for $C_{18}H_{28}Cl_2P_2Pt_2$: C, 28.2; H, 3.65%).

Catalysis by $[Pt_2Cl_4(PMe_2Ph)_2]$.—The required volume of a standard solution of $[Pt_2Cl_4(PMe_2Ph)_2]$ (0.024 mol dm^{-3} in dichloromethane) was added to *cis*-$[PtCl_2(PMe_2Ph)_2]$ (0.038 g, 0.07 mmol) and the volume was made up to 0.6 cm^3 with dichloromethane. The solution was then added to *cis*-$[PtMe_2(PMe_2Ph)_2]$ (0.035 g, 0.07 mmol) and the n.m.r. spectrum of the resulting solution was recorded at intervals to monitor the course of reaction.

[6/2240 *Received, 7th December*, 1976]