Mechanism of Reductive Elimination of Ethane from some Halogenotrimethylbis(tertiary phosphine)platinum(IV) Complexes

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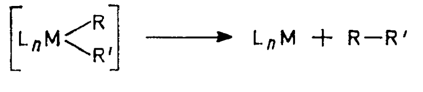
Specifically deuteriated complexes have been prepared by stereospecific oxidative addition of CD_3I to *cis*-$[PtMe_2(L)_2]$ (L = PMe_2Ph or $AsMe_2Ph$) and of MeX (X = Cl, Br, or I) to *cis*-$[Pt(CD_3)_2(PMe_2Ph)_2]$. These complexes undergo intramolecular scrambling of Me and CD_3 groups in solution at room temperature (L = $AsMe_2Ph$) or above (L = PMe_2Ph), and decompose by intramolecular reductive elimination of ethane. Kinetic studies of the decomposition of *fac*-$[PtX(Me)_3L_2]$ (I: X = Cl or Br, L = PMe_2Ph; X = I, L = PMe_3, PMe_2Ph, or $PMePh_2$) indicate that ethane is eliminated from a five-co-ordinate intermediate formed by dissociation of a phosphine ligand, but when L_2 = 1,2-bis(diphenylphosphino)ethane (dppe) ethane is eliminated without prior phosphine dissociation. In this case the activation energy (69 kJ mol^{-1}) for ethane elimination is considerably lower than the estimated methyl–platinum bond energy (144 kJ mol^{-1}) for (I; X = I, L = PMe_2Ph) obtained from a study of the ethane elimination by differential-scanning calorimetry. Methyl groups are eliminated from the platinum(IV) complexes more readily than $[^2H_3]$methyl groups, with a mean secondary kinetic-isotope effect $k(H)/k(D)$ of 1·07. The results are interpreted in terms of concerted reductive elimination, with the transition state resembling an ethane complex of platinum(II).

THERE has been considerable interest in oxidative-addition reactions with transition-metal complexes, for which ionic, free-radical, and concerted mechanisms have been established, but relatively little work on the mechanism of the reverse reductive-elimination reactions has been reported.[1,2] We were particularly interested in studying the mechanism of the elimination (1) (R,R′ = alkyl)



$$\left[L_nM\begin{matrix}R\\R'\end{matrix}\right] \longrightarrow L_nM + R{-}R' \qquad (1)$$

because reactions of this type form a necessary step in several catalytic systems and may provide a low-energy path[3,4] for decomposition of the transition-metal alkyl, $[L_nM(R)R']$. The reverse oxidative-addition reaction involving cleavage of a C–C σ-bond is known only in a few cases,[5-9] so that mechanistic information on this type of reaction is most readily obtained by studying the reductive-elimination reaction. We chose to study the mechanism of decomposition of complexes *fac*-$[PtX(Me)_3L_2]$ (I; X = halogen, L = tertiary phosphine or arsine) which have previously been shown to eliminate ethane cleanly on pyrolysis according to equation (2).[10]

$$fac\text{-}[PtX(Me)_3L_2] \longrightarrow trans\text{-}[PtX(Me)L_2] + C_2H_6 \qquad (2)$$

A preliminary account of this work has been published,[11] and we and other workers have also shown that ease of elimination of different alkyl groups from trialkylplatinum(IV) complexes is given by the series R = acetyl > allyl, ethyl > methyl > $[^2H_3]$methyl > benzyl > phenyl > trifluoromethyl.[12-14] The series follows roughly the expected order of increasing platinum–carbon bond strengths,[12,15] though there is some evidence that the acetyl–platinum bond may be stronger than the methyl–platinum bond.[11,12,16] The only mechanistic work on reductive-elimination reactions from platinum(IV) complexes appears to be that of Ettore who showed that elimination of iodobenzene from $[PtI_2(Ph)_2(PEt_3)_2]$ took place by an ionic mechanism [equation (3), S = solvent], the reverse of the mechanism often invoked for oxidative-addition reactions of alkyl and aryl halides.[17]

$$[PtI_2(Ph)_2(PEt_3)_2] \underset{-S}{\overset{S}{\rightleftharpoons}} [PtI(Ph)_2(PEt_3)_2S]I \xrightarrow{-S} [PtI(Ph)(PEt_3)_2] + PhI \qquad (3)$$

RESULTS

Preparation of fac-$[PtX(Me)_3L_2]$, (I).—In order to observe the effect of changing X(halogen) and L(tertiary phosphine or arsine) on the ease of elimination of ethane from the complexes *fac*-$[PtX(Me)_3L_2]$, we needed methods for preparing a variety of such complexes. Two methods were used. The first involves oxidative addition of a methyl halide to *cis*-$[Pt(Me)_2L_2]$.[18] In this way complexes (I: X = Cl, Br, I; L = PMe_2Ph or $AsMe_2Ph$) were prepared. The method is particularly useful for preparing selectively deuteriated derivatives. Thus reaction of CD_3I with *cis*-$[Pt(Me)_2L_2]$ (L = PMe_2Ph or $AsMe_2Ph$) gave complexes (II) arising from

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[1] A. J. Deeming in M.T.P. Internat. Rev. Sci., Inorganic Chemistry, series 1, vol. 9, Butterworths, 1972, ch. 4.

[2] J. Halpern, *Accounts Chem. Res.*, 1970, **3**, 386.

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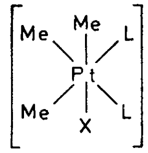
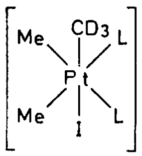
[18] J. D. Ruddick and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 2801, 2964.

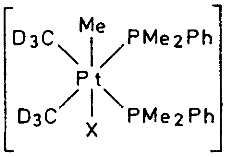
trans-addition of CD_3I, while reaction of MeI with *cis*-$[Pt(CD_3)_2(PMe_2Ph)_2]$ gave (III; X = I) only. The stereochemistry of the products was easily determined from the ^1H n.m.r. spectra (Table 1). Thus the n.m.r. spectrum in $CDCl_3$ of (I; X = I, L = PMe_2Ph) contained peaks due to methyl–platinum protons at τ 8·93 (*trans* to phosphine) and 9·33 (*trans* to iodide).[18] The former peak was absent in the spectrum of (III; X = I) while the latter was absent for (II; L = PMe_2Ph). We estimate that 5% of the alternative isomers could have been detected, so that the stereospecificity of the oxidative addition is at least 95% *trans*.



(I) L = PMe_3, PMe_2Ph, $PMePh_2$, dppe, or $AsMe_2Ph$
X = Cl, Br, or I



(II) L = PMe_2Ph or $AsMe_2Ph$



(III) X = Cl, Br, or I

TABLE 1

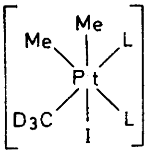
N.m.r. spectra of the methylplatinum complexes in deuteriochloroform

Complex	$\tau(CH_3P)$ [a] p.p.m.	$J(PH)$ [b] Hz	$J(PtH)$ Hz	$\tau(CH_3Pt)$ [a] p.p.m.	$J(PH)$ Hz	$J(PtH)$ Hz
(I; X = I, L = PMe_3)	8·46 (d)	10·2	8·4	8·97 (c) [c]		58
				9·18 (t) [d]	7·8	70
(I; X = I, L = PMe_2Ph)	8·25 (d)	9·0	11·5	8·93 (c) [c]		57
	8·33 (d)			9·33 (t) [d]	7·6	71
(II; L = PMe_2Ph)	8·25 (d)	9·0	11·5	8·93 (c) [c]		57
	8·33 (d)					
(III; X = I)	8·25 (d)	9·0	11·5	9·33 (t) [d]	7·6	71
	8·33 (d)					
(I; X = I, L = $PMePh_2$)	7·86 (d)	7·7	11·2	8·81 (c) [c]		58
				9·24 (t) [d]	7·0	72
(I; X = I, L = $AsMe_2Ph$)	8·40 (s) [e]		6·0	8·67 (s) [c]		64
	8·46 (s) [e]		6·4	9·11 (s) [d]		72
(II; L = $AsMe_2Ph$)	8·40 (s) [e]		6·0	8·67 (s) [c]		64
	8·46 (s) [e]		6·4			
(I; X = I, L = $\frac{1}{2}$dppe)	6·95 (c)			8·39 (t) [c]		58
	7·10 (c)			9·48 (t) [d]	7·5	67
trans-$[PtI(Me)(PMe_3)_2]$	7·91 (t)	6·6	29	8·93 (t)	7·8	80
cis-[PtI(Me)(dppe)]	7·66 (c)			9·31 (t)	7·2	72
	7·93 (c)					

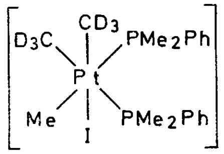
[a] s = Singlet, d = doublet, t = triplet, and c = complex. [b] $J(PH) = {}^2J + {}^4J(PH)$. [c] *trans* to Phosphorus. [d] *trans* to Halogen. [e] $\tau(CH_3As)$.

Methyl iodide did not react with *cis*-$[PtMe_2(PMePh_2)_2]$ so that an alternative route was needed for preparing (I; X = I, L = $PMePh_2$). This was achieved by reaction of the phosphine with tetrakis[iodotrimethylplatinum(IV)], a method which was also used to prepare [I; X = I, L = PMe_3 or $\frac{1}{2}$ 1,2-bis(diphenylphosphino)ethane (dppe)]. However, attempts to prepare the corresponding triphenylphosphine complex by this method were unsuccessful. The chief reaction in this case led to rapid formation of *cis*-$[PtMe_2(PPh_3)_2]$ with elimination of methyl iodide, but some ethane and *trans*-$[PtI(Me)(PPh_3)_2]$ were also formed. The methyl iodide formed reacted further with triphenylphosphine to give methyltriphenylphosphonium iodide. The low thermal stability of (I; X = I, L = PPh_3) is expected (see below), but it is surprising that methyl iodide rather than ethane is the chief product in the reductive-elimination reaction. Triphenylarsine did not cause elimination of ethane from $[\{Pt(I)Me_3\}_4]$ at room temperature, but at 60 °C elimination did take place. No (I; X = I, L = $AsPh_3$) could be isolated, and n.m.r. studies showed that even in the presence of excess of triphenylarsine a large proportion of the $[\{Pt(I)Me_3\}_4]$ remained unchanged.

Exchange and Scrambling Reactions.—Addition of CD_3I to *cis*-$[PtMe_2(AsMe_2Ph)_2]$ gave (II; L = $AsMe_2Ph$) by stereospecific *trans*-addition. However, in deuteriochloroform or benzene solution, subsequent scrambling of methyl and $[^2H_3]$methyl groups took place, as shown by growth of a peak in the n.m.r. spectrum due to the methylplatinum group *trans* to iodide [at τ 9·11, $^2J(^{195}PtCH_3)$ 72 Hz in $CDCl_3$]. The scrambling reaction was complete in 30 min at 33 °C, giving the statistical 1 : 2 mixture of (II) and (IV) (L = $AsMe_2Ph$). Complex (I; X = Br, L = $AsMe_2Ph$) underwent a ligand-exchange reaction with dimethylphenylphosphine to give (I; X = Br, L = PMe_2Ph), the reaction being complete in 40 min at 33 °C, and a similar reaction of dimethylphenylphosphine with (II; L = $AsMe_2Ph$) gave the statistical 1 : 2 mixture of (II) and (IV) (L = PMe_2Ph) so that complete scramblng of methyl and $[^2H_3]$methyl groups took place during the ligand-exchange reaction.



(IV) L = PMe_2Ph or $AsMe_2Ph$



(V)

The complexes (II; L = PMe_2Ph) and (III; X = I) did not scramble in benzene solution at 33 °C, but on heating to 68 °C slow intramolecular scrambling of methyl and $[^2H_3]$-

methyl groups took place to give the expected 1 : 2 ratios of (II) and (IV) (L = PMe_2Ph) or (III; X = I) and (V) respectively, as determined by integration of the relevant peaks in the n.m.r. spectra (see Table 1). The scrambling reaction was complete in 24 h at 68 °C. Heating benzene solutions of (I; X = I, L = PMe_2Ph) in sealed n.m.r. tubes at temperatures above 120 °C led to decomposition to ethane (τ 9·15) and *trans*-[PtI(Me)$(PMe_2Ph)_2$]. The decomposition was complete in 1·5 h at 130 °C. However, in the presence of free dimethylphenylphosphine (20 mol %), the complex did not decompose to any significant extent under these conditions or on heating to 145 °C for 1 h; it was necessary to heat the mixture to 170 °C for 1 h to bring about decomposition to ethane and *trans*-[PtI(Me)$(PMe_2Ph)_2$].

Decomposition of Solid Samples of Complexes (I).—The complexes were pyrolysed by heating solid samples until gas evolution ceased and the nature of the reactions was studied by the following methods. (*a*) The gases were identified by their mass spectra. When L = tertiary phosphine, the volatile products contained ethane only, with traces of free phosphine in some cases. However, when L = $AsMe_2Ph$ and X = Br, methyl bromide and dimethylphenylarsine were evolved also. (*b*) The volume of ethane evolved was measured. In all cases decomposition according to equation (2) was quantitative. (*c*) The platinum-containing products were identified. The product was *trans*-[PtX(Me)L_2] in all cases except when L_2 = dppe when the product necessarily had the *cis*-stereochemistry. The results are summarised in Table 2.

TABLE 2

Conditions and products of decomposition of the complexes *fac*-[PtX$(Me)_3L_2$], (I)

X	L	θ_c/°C	C_2H_6 (%)	Product	M.p. (θ_c/°C) [a]
I	PMe_3	155—160	98	*trans*-[PtI(Me)$(PMe_3)_2$]	157—160 (158—160) [b]
I	PMe_2Ph	150—160	100	*trans*-[PtI(Me)$(PMe_2Ph)_2$]	132—134 (133—135) [c]
I	$PMePh_2$	140—145	100	*trans*-[PtI(Me)$(PMePh_2)_2$]	171—172 (170—172) [c]
I	dppe	215—220	96	*cis*-[PtI(Me)(dppe)]	243—245 (243—245) [d]
Br	PMe_2Ph	155—160	100	*trans*-[PtBr(Me)$(PMe_2Ph)_2$]	144—147 (147·5—149·5) [c]
Cl	PMe_2Ph	155—160	100	*trans*-[PtCl(Me)$(PMe_2Ph)_2$]	144—148 (146—148) [c]

[a] Literature values are given in parentheses. D. M. Adams, J. Chatt, and B. L. Shaw, *J. Chem. Soc.*, 1960, 2047. [c] Ref. 18. [d] K. A. Hooton, *J. Chem. Soc.* (*A*), 1970, 1896.

The gases evolved on pyrolysis of the selectively deuteriated derivatives (II; L = PMe_2Ph) and (III; X = I), and of the products obtained by scrambling the methyl and [$^2H_3$]methyl groups in these complexes, were analysed by mass spectrometry. The results are given in Table 3, and may be summarised as follows. (*i*) The gases formed are those expected for *intramolecular* elimination of ethane. Thus (II; L = PMe_2Ph) gave no C_2D_6 and (III) gave no C_2H_6. (*ii*) In the samples in which the methyl and [$^2H_3$]-methyl groups had been scrambled prior to pyrolysis, the only chemical effect which can influence the product ratio is the deuterium-isotope effect. Thus the 1 : 2 mixture of (II) and (IV) (L = PMe_2Ph) gave a product ratio $MeCD_3 : C_2H_6$ = 1·90 : 1, while the 1 : 2 mixture of (III; X = I) and (V) gave a ratio $MeCD_3 : C_2D_6$ = 2·14 : 1. In each case the product ratio expected from statistical considerations only is 2·00 : 1. Clearly [$^2H_3$]methyl groups are eliminated less readily than methyl groups. The former result above gives a secondary deuterium-isotope effect $k(C_2H_6)/k(MeCD_3)$ = 1·05, while the latter gives $k(MeCD_3)/k(C_2D_6)$ = 1·07. (*iii*) Complex (II; L = PMe_2Ph) and the product obtained by scrambling the methyl and [$^2H_3$]methyl groups gave different ratios of $C_2H_6 : MeCD_3$. The results can be explained if the groups *trans* to phosphine in this complex are eliminated more readily than the group *trans* to iodide. In turn this suggests that scrambling of methyl and [$^2H_3$]methyl groups is not complete before reductive elimination from the solid samples takes place (in contrast to the behaviour in solution). The somewhat smaller difference in product ratio obtained from (III; X = I) and the 1 : 2 mixture of this complex and (V) can be interpreted in the same way.

TABLE 3

Composition of gases formed on decomposition of the deuteriated complexes

	Amount of gaseous products/%		
Complex	C_2H_6	$MeCD_3$	C_2D_6
(I; X = I, L = PMe_2Ph)	100		
(II; L = PMe_2Ph)	40·7	59·3	0
(II; L = PMe_2Ph)–(IV; L = PMe_2Ph) (1 : 2)	34·5	65·5	0
(III; X = I)	0	67·7	32·3
(III; X = I)–(V) (1 : 2)	0	68·2	31·8
(III; X = Cl)	0	67·3	32·7
(III; X = Br)	0	68·7	31·3
fac-[PtI$(CD_3)_3(PMe_2Ph)_2$]			100

The decomposition of crystalline (I; X = I, L = PMe_2Ph) was studied by differential-scanning calorimetry (d.s.c.). An endothermic change due to melting of the complex was observed followed by an exothermic process as ethane is eliminated. The following enthalpy changes were measured:

$$fac\text{-}[\mathrm{PtI(Me)_3(PMe_2Ph)_2}](\mathrm{c}) \longrightarrow trans\text{-}[\mathrm{PtI(Me)(PMe_2Ph)_2}](\mathrm{l}) + \mathrm{C_2H_6};$$

$$\Delta H = -29{\cdot}2 \pm 8\ \mathrm{kJ\ mol^{-1}}$$

$$trans\text{-}[\mathrm{PtI(Me)(PMe_2Ph)_2}](\mathrm{c}) \longrightarrow trans\text{-}[\mathrm{PtI(Me)(PMe_2Ph)_2}](\mathrm{l});$$

$$\Delta H = +34{\cdot}0 \pm 2\ \mathrm{kJ\ mol^{-1}}$$

Hence the enthalpy change for the following reaction may be calculated:

$$fac\text{-}[\mathrm{PtI(Me)_3(PMe_2Ph)_2}](\mathrm{c}) \longrightarrow trans\text{-}[\mathrm{PtI(Me)(PMe_2Ph)_2}](\mathrm{c}) + \mathrm{C_2H_6};$$

$$\Delta H = -63{\cdot}2 \pm 10\ \mathrm{kJ\ mol^{-1}}$$

If it is assumed that this enthalpy change arises from cleavage of two methyl–platinum σ-bonds and formation of the carbon–carbon σ-bond of ethane, for which the bond energy is 351 kJ mol^{-1},[19] a mean value of the methyl–platinum

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[19] T. L. Cottrell, 'The Strengths of Chemical Bonds,' Butterworths, London, 1958.

bond energy can be calculated to be ½(351 − 63) = 144 kJ mol^{-1}. Several assumptions, whose validity have not been tested, have to be made in calculating bond energies by this method.[12,20] Nevertheless, the bond energy determined lies close to the value of E(Pt–Me) of 160 kJ mol^{-1} determined by Eggar[21] for the complex [$PtMe_3$(cp)] (cp = η-cyclopentadienyl), and with the average σ-bond energy for the Me–Pt and MeCO–Pt bonds in [PtCl(Me)$_2$(COMe)(PMe$_2$Ph)$_2$] of 158 kJ mol^{-1} determined by d.s.c.[12] The great advantage of using d.s.c. to estimate bond energies in these complexes is the relative ease with which enthalpy changes can be determined. To estimate the bond energies by more conventional calorimetric methods would be very difficult indeed.

Kinetic Studies.—Complex (I; X = I, L = PMe$_2$Ph) decomposed at a rate suitable for kinetic measurements in the temperature range 60—90 °C in the solvent 1,4-dioxan. The reaction was followed by studying the decrease in absorbance in the u.v. spectrum at 280 nm, and the product was identified as *trans*-[PtI(Me)(PMe$_2$Ph)$_2$] by comparing its u.v. spectrum with that of an authentic sample. There was an isosbestic point at 306 nm. At all temperatures the reaction followed first-order kinetics, as indicated by the plots shown in Figure 1. The decomposition was inhibited in the presence of free dimethylphenylphosphine. Thus at 90 °C the first-order rate constant was 0·2 min^{-1}, but in the presence of free dimethylphenylphosphine (0·02M) no decomposition occurred at this temperature (in these cases the reaction was followed by studying the increase in absorbance at 316 nm since the free phosphine absorbed strongly at 280 nm).*

Ettore showed that the decomposition of [PtI$_2$(Ph)$_2$(PEt$_3$)$_2$] was inhibited by added iodide,[17] and we wished to check the effect of added iodide on the rate of decomposition of (I; X = I, L = PMe$_2$Ph). Since sodium iodide is virtually insoluble in 1,4-dioxan we used 2-methoxyethanol as solvent. In this solvent the decomposition reaction again gave *trans*-[PtI(Me)(PMe$_2$Ph)$_2$] as product, but the reaction was not first order in substrate. The change in absorbance at 280 nm with time at 90 °C is shown in Figure 2, and it can be seen that in the early stages the order of the reaction is almost zero. Addition of 0·02M-iodide to the solution had no effect on the rate or order of the reaction (Figure 2). However, addition of *trans*-[PtI(Me)(PMe$_2$Ph)$_2$] (1·0 × 10^{-4}M) to the solution of (I) (2·5 × 10^{-4}M) did affect the rate. The decomposition was faster and the order of the

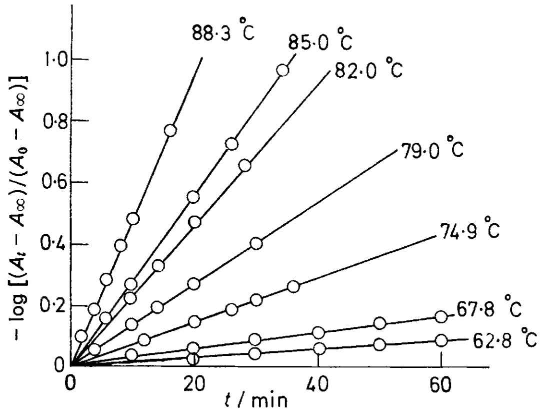

FIGURE 1 First-order plots for the decomposition of *fac*-[PtI(Me)$_3$(PMe$_2$Ph)$_2$] in 1,4-dioxan

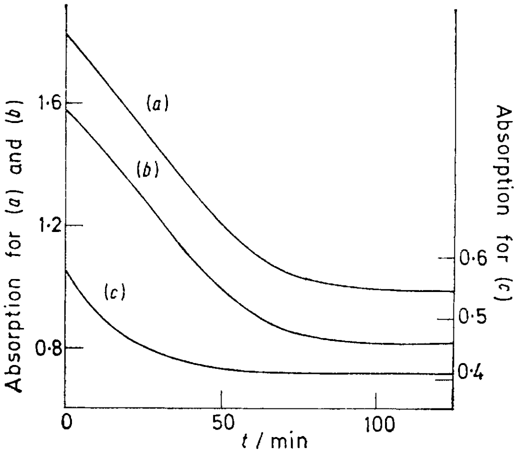

FIGURE 2 Optical density against time plots for decomposition of *fac*-[PtI(Me)$_3$(PMe$_2$Ph)$_2$] in 2-methoxyethanol: (*a*), with no additives; (*b*), with added I$^-$ (0·02M); and (*c*) with added *trans*-[PtI(Me)(PMe$_2$Ph)$_2$]

TABLE 4

Apparent first-order rate constants, k_1, for decomposition of the complexes *fac*-[PtX(R)$_3$L$_2$] in 1,4-dioxan

X	R	L	θ_c/°C	10^4k_1/s^{-1}
I	Me	PMe$_2$Ph	62·9	0·57
			67·8	1·03
			75·0	2·8
			79·0	5·2
			82·0	9·2
			83·3	10·2
			83·6	10·7
			85·0	11·2
			85·9	13·2
			88·3	18·8
			92·0	33·7
I	CD$_3$	PMe$_2$Ph	79·0	4·8
			83·6	9·8
			85·0	10·0
			88·3	17·2
Br	Me	PMe$_2$Ph	63·9	0·62
			76·0	3·2
			77·6	3·5
			93·7	25·7
			93·8	27·0
Cl	Me	PMe$_2$Ph	67·1	0·82
			68·7	1·15
			76·1	1·53
			81·4	5·0
			81·9	5·7
			94·2	15·8
I	Me	PMePh$_2$	25·6	0·83
			30·3	5·0
			35·2	9·5
			35·5	12·3
			37·2	20·8
			41·3	35·5
			42·0	37·7
I	Me	½dppe	70·2	0·90
			78·9	1·57
			80·3	2·0
			85·2	2·83
			90·0	3·0
			105·0	8·0

* 1M = 1 mol dm^{-3}.

[20] C. T. Mortimer, J. L. McNaughton, and R. J. Puddephatt, *J.C.S. Dalton*, 1972, 1265.

[21] K. W. Eggar, *J. Organometallic Chem.*, 1970, **24**, 501.

reaction was close to one in the early stages, as shown in Figure 2.

In order to confirm that a deuterium-isotope effect was important in determining the products obtained on pyrolysis of (II)—(V), we compared the first-order rate constants for decomposition of *fac*-[PtI(Me)$_3$(PMe$_2$Ph)$_2$] and *fac*-[PtI(CD$_3$)$_3$(PMe$_2$Ph)$_2$] in 1,4-dioxan at various temperatures. The results are shown in Table 4; they give a mean secondary deuterium-isotope effect $k_1(C_2H_6)/k_1(C_2D_6) = 1{\cdot}09 \pm 0{\cdot}02$, and confirm that methyl groups are eliminated more readily than [^{2}H$_3$]methyl groups.[11,14]

Further kinetic studies were carried out to determine the effect of varying X and L on the decomposition rate of complexes (I). In most cases the decomposition followed first-order kinetics in 1,4-dioxan and the resulting rate constants are shown in Table 4. The following trends may be noted. (*i*) The rates for (I; L = PMe$_2$Ph) varied only slightly when X = Cl, Br, or I. (*ii*) The rate of decomposition of (I; X = I) was much greater when L = PMePh$_2$ than when L = PMe$_2$Ph. Decomposition of (I; X = I, L = PMe$_3$) did not follow first-order kinetics in 1,4-dioxan, but qualitative experiments showed that it decomposed only slowly at 106 °C ($t_{\frac{1}{2}}$ *ca.* 100 min) whereas the corresponding PMe$_2$Ph complex decomposed immeasurably quickly at this temperature. Complex (I; X = I, L = PPh$_3$) could not be prepared and evidently decomposes rapidly at room temperature, albeit with formation of iodomethane as well as ethane. Clearly then, as more phenyl groups are substituted for methyl groups in the phosphine ligand, the rate of decomposition increases very markedly. (*iii*) The rate of decomposition of (I; X = I) was much greater when L = PMePh$_2$ than when L$_2$ = dppe. The chelating ligand obviously makes the platinum(IV) complex more inert to reductive elimination, an effect which has been observed in several related systems.[22-24] (*iv*) The decomposition of (I; X = Br, L = AsMe$_2$Ph) did not follow first-order kinetics in 1,4-dioxan, possibly due to the occurrence of the side reactions discussed earlier. The overall rate of decomposition at 77 °C was slightly faster than for the corresponding phosphine complex however. (*v*) Complex (I; X = I, L = PMe$_2$Ph) decomposed more rapidly than [PtI(Me)$_2$(CF$_3$)(PMe$_2$Ph)$_2$] (for which $k_1 = 3 \times 10^{-4}$ s^{-1} at 91 °C for decomposition in 1,4-dioxan). Decomposition of [PtI(Me)$_2$(CF$_3$)(PMe$_2$Ph)$_2$] was also retarded by added PMe$_2$Ph. The lower decomposition rate for the (trifluoromethyl)platinum(IV) complex is surprising in view of the greater electronegativity and bulk of the CF$_3$ group compared with the methyl group.

TABLE 5

Activation parameters for decomposition of the complexes *fac*-[PtX(Me)$_3$L$_2$] in 1,4-dioxan at 353 K

X	L	$E^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J K^{-1} mol^{-1}	$\Delta G^{\ddagger}$ / kJ mol^{-1}
Cl	PMe$_2$Ph	116 ± 5	15 ± 10	108
Br	PMe$_2$Ph	125 ± 5	46 ± 5	106
I	PMe$_2$Ph	132 ± 5	68 ± 5	105
I	PMePh$_2$	150 ± 5	185 ± 15	82
I	$\frac{1}{2}$dppe	69 ± 5	−125 ± 5	109

For the complexes whose decomposition followed first-order kinetics, Arrhenius parameters were determined and are shown in Table 5. It can be seen that as the bulk of the substituents X and L in (I) increased, the activation energy $E^{\ddagger}$ actually increased and the increase in rate of decomposition with the size of X and L is due to the larger increase in the apparent entropy of activation term, $\Delta S^{\ddagger}$, counterbalancing this effect. For complex (I; X = I, L$_2$ = dppe) the activation energy was lower than that for any of the complexes with unidentate phosphine ligands, and the relatively low rate of decomposition can be attributed to the large negative value of $\Delta S^{\ddagger}$. The domination of the activation-entropy term in determining the rate strongly suggests that it is the steric rather than electronic effects of the ligand which influence the reactivity series.

DISCUSSION

The rate of reductive elimination of ethane from (I; X = I, L = PMe$_2$Ph) was greatly retarded in the presence of excess of phosphine in benzene or 1,4-dioxan solutions, but was not affected by added iodide ions in 2-methoxyethanol. This suggests strongly that the reaction proceeds by dissociation of a phosphine ligand followed by rate-determining elimination of ethane from the five-co-ordinate intermediate formed [equation (4), L = PMe$_2$Ph]. Independent evidence for the initial dissociation step was obtained. Thus complex (II; L = AsMe$_2$Ph), formed by addition of CD$_3$I to *cis*-[PtMe$_2$(AsMe$_2$Ph)$_2$], undergoes a reaction in which methyl and [^{2}H$_3$]methyl groups on platinum are scrambled. The reaction takes place at a similar rate to the ligand-exchange reaction in which dimethylphenylphosphine displaces the arsine ligands from (II; L = AsMe$_2$Ph) with concurrent scrambling of methyl and [^{2}H$_3$]methyl groups. This suggests that these reactions take place *via* a common intermediate formed by loss of an arsine ligand to give a five-co-ordinate species in which rapid scrambling of methyl and [^{2}H$_3$]methyl groups occurs. The intermediate can then recombine with arsine ligand or, if the better donor dimethylphenylphosphine is present, with this [equations (5) and (6)].

$$fac\text{-}[\mathrm{PtI(Me)_3L_2}] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{L} + [\mathrm{PtI(Me)_3L}] \xrightarrow{k_1} trans\text{-}[\mathrm{PtI(Me)L_2}] + \mathrm{C_2H_6} \quad (4)$$

As expected in view of the stronger metal–ligand bond in the phosphine complexes, (II; L = PMe$_2$Ph) and (III; X = I) did not undergo scrambling of methyl and [^{2}H$_3$]methyl groups at room temperature, but scrambling did take place at 68 °C in benzene solution again presumably by a mechanism involving dissociation of a phosphine ligand. This scrambling reaction, and hence the rate of phosphine dissociation, is clearly rapid with respect to the elimination reaction which does not take place in benzene solution at temperatures less than 120 °C. Further support for the conclusion that the ligand dissociation and recombination is fast with respect to the ethane-elimination reaction, comes from the observation that complex (I; X = Br, L = AsMe$_2$Ph) undergoes

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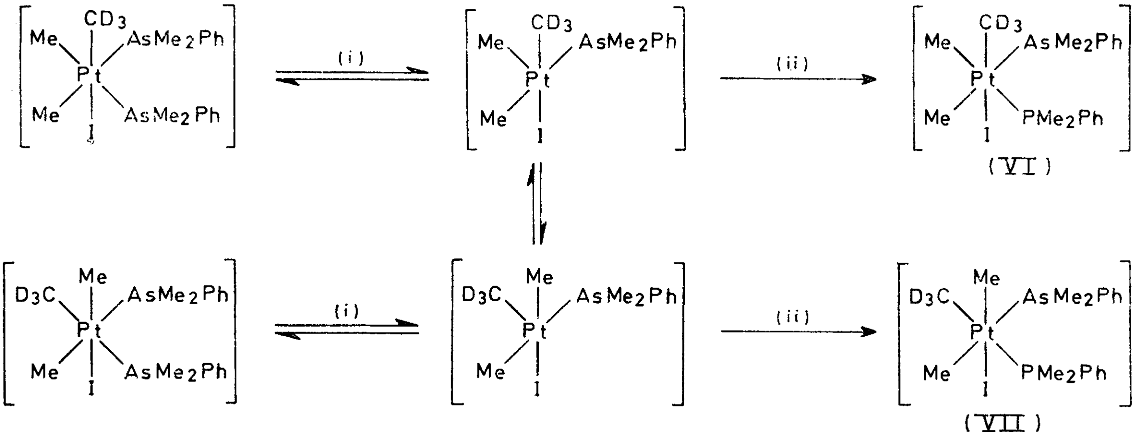
[22] L. Vaska, L. S. Chen, and W. V. Miller, *J. Amer. Chem. Soc.*, 1971, **93**, 6671.

[23] G. R. Clark, C. A. Reed, W. R. Roper, B. W. Skelton, and T. N. Waters, *Chem. Comm.*, 1971, 758.

[24] T. E. Nappier, D. W. Meek, R. M. Kirchner, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1973, **95**, 4194.

ethane elimination only slightly faster than the analogous phosphine complex, although the rate of arsine dissociation is an order of magnitude greater than that for phosphine (as shown above).



(5)

$$(\mathrm{VI}) + (\mathrm{VII}) + 2\,PMe_2Ph \longrightarrow (\mathrm{II};\ L = PMe_2Ph) + (\mathrm{IV};\ L = PMe_2Ph) + 2\,AsMe_2Ph \qquad (6)$$

(i) $-AsMe_2Ph$; (ii) PMe_2Ph

If the steady-state approximation for $[PtI(Me)_3L]$ is made, then the rate of reaction (4) is predicted to be as in (7). This expression accounts for the strong retardation effect of added ligand, L, and also for the first-order

$$\text{Rate} = k_1[PtI(Me)_3L] = k_1k_2[PtI(Me)_3L_2]/(k_{-2}[L] + k_1) \qquad (7)$$

kinetics in 1,4-dioxan in the absence of added ligand, if $k_1 \gg k_{-2}[L]$ under these conditions. However, the arguments presented above strongly suggest that this is not the case and that $k_{-2}[L] \gg k_1$ even in the absence of added ligand. Under these conditions, first-order kinetics should be observed only if [L] remains constant throughout the reaction, and hence if the equilibrium constants for formation of L from (I; X = I) and the product *trans*-$[PtI(Me)L_2]$ are equal. This is not inconceivable, however, in view of the similarity of metal–ligand bond strengths in comparable platinum(II) and platinum(IV) complexes.[25] Our attempts to study the dependence of the observed rate constant on the concentration of added ligand were unsuccessful. The most promising results were obtained from the reaction of (I; X = I, L = $PMePh_2$) in the presence of added $PMePh_2$ at 45 °C in 1,4-dioxan; the reaction took place at a measurable rate using added phosphine concentrations of 10^{-5}—10^{-7}M. The reaction was retarded under these conditions but no longer followed first-order kinetics, the rate increasing markedly as the reaction progressed. This suggests that the free ligand is reacting with the reaction product *trans*-$[PtI(Me)(PMePh_2)_2]$ according to equation (8)

$$trans\text{-}[PtI(Me)L_2] + L \longrightarrow [Pt(Me)L_3]^+ + I^- \qquad (8)$$

(L = $PMePh_2$). This reaction is known to take place readily in polar solvents,[26] and since free ligand is removed the overall effect will be to accelerate the elimination reaction. Attempts to study the elimination reaction using higher concentrations of free ligand, so that its effective concentration would not be altered greatly by the above reaction, were unsuccessful since using phosphine concentrations greater than 10^{-4}M the elimination reaction was too slow for kinetic studies. The decomposition of (I; X = I, L = PMe_2Ph) in 2-methoxyethanol was not first order, perhaps because reaction (8) is important even in the absence of added ligand in the more polar, alcoholic, solvent. The observation that the reaction became almost first order in the presence of added *trans*-$[PtI(Me)(PMe_2Ph)_2]$ is consistent with this conclusion.

Deuterium-isotope Effect.—The average value of the secondary kinetic-isotope effect for the elimination reaction, obtained by analysis of the gases formed on pyrolysis of the partially deuteriated complexes and by comparing the rates of decomposition of *fac*-$[PtI(Me)_3(PMe_2Ph)_2]$ and *fac*-$[PtI(CD_3)_3(PMe_2Ph)_2]$, is $k(H)/k(D) = 1{\cdot}07$. It should be noted that the precise effects being measured are different in each of the above experimental methods, but we take this average value as the basis for further discussion.

It has been noted previously[14,27] that the Pt–C stretching frequencies in methyl and $[^2H_3]$methyl derivatives of platinum can be interpreted by considering that these groups vibrate as rigid groups with masses 15 and 18 atomic units respectively, and by assuming that the methyl–platinum stretching vibrations are not significantly coupled to other vibrational modes of the molecules. This treatment predicts the ratio $\nu(PtCH_3)$:

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[25] F. R. Hartley, ' The Chemistry of Platinum and Palladium,' Applied Science Publishers, London, 1973.

[26] H. C. Clark and J. D. Ruddick, *Inorg. Chem.*, 1970, **9**, 1226.

[27] D. M. Adams, *J. Chem. Soc.*, 1962, 1220.

$\nu(PtCD_3)$ to be 1·088 : 1, which compares favourably with the average value of 1·083 : 1 found for vibrations in the complexes shown in Table 6.

TABLE 6

Platinum–carbon stretching wavenumbers (cm^{-1}) from Raman spectra of some methyl and [$^2H_3$]methyl derivatives of platinum(IV)

Complex	$\bar{\nu}(PtCH_3)$ *trans*-I	$\bar{\nu}(PtCH_3)$ *trans*-P	$\bar{\nu}(PtCD_3)$ *trans*-I	$\bar{\nu}(PtCD_3)$ *trans*-P
(I; X = I, L = PMe_2Ph)	541	529, 519		
(II; L = PMe_2Ph)		530, 518	500	
(III; X = I)	540			489, 477
fac-[$PtI(CD_3)_3$-$(PMe_2Ph)_2$]			502	488, 477

If the same model can be used to interpret the secondary kinetic-isotope effect,[28,29] a maximum value of $k(H)/k(D)$ of 1·088 is expected if the transition state is formed by complete cleavage of a Pt–C bond. Clearly the observed value of 1·07 suggests considerable weakening of the Pt–C bonds in the transition state. It is interesting that the primary deuterium-isotope effect, $k(H_2)/k(D_2) = 1{\cdot}22$, for oxidative addition [30] of hydrogen to Ir^I is smaller than that for reductive elimination [31] of hydrogen from Ir^{III} for which $k(H_2)/k(D_2) = 2{\cdot}1$, suggesting that the transition state resembles more closely the reduced species. The elimination of hydrogen from Ir^{III} and of ethane from Pt^{IV} appear to take place by similar mechanisms, therefore, with the transition states being closer to the reduced species than to the starting materials in each case.

Further Consideration of the Arrhenius Parameters.—Since the observed first-order rate constant is given by $k_{obs} = Kk_1/[L]$, where K is the equilibrium constant for the ligand-dissociation reaction, the simple interpretation of the apparent activation energy which we used previously [11] is not justified. The observed activation energy will be the sum of the activation energy for ethane elimination and the enthalpy of dissociation of the phosphine ligand, the latter term being modified by a smaller term arising from the expected increase in concentration of free ligand L with increasing temperature. Now since the phosphine dissociation will almost certainly be endothermic,[25,32] the activation energy for ethane elimination should be significantly lower than the observed value. Since the apparent activation energies (Table 5) were similar to or lower than the estimated methyl–platinum bond energy of 144 kJ mol^{-1}, it seems clear that the elimination reaction must be a concerted process in which cleavage of the methyl–platinum bonds is accompanied by carbon–carbon bond formation. In contrast, the thermal decomposition of main-group metal alkyls, which usually take place by homolysis of the metal–carbon bonds, generally requires an activation energy for homolysis somewhat higher than the metal–carbon bond energy.[33]

It is interesting that the higher rate of decomposition of the complexes having bulkier ligands is caused by the higher apparent entropies of activation for these complexes. Molecular models indicate that, especially with methyldiphenylphosphine ligand, rotation about the platinum–phosphorus and phosphorus–carbon bonds is severely limited in the complexes (I) due to steric constraints. Both the ligand-dissociation and ethane-elimination steps relieve these steric constraints and more vibrational degrees of freedom are then possible for the remaining co-ordinated ligand (and for the dissociated ligand of course). Thus as the bulk of the ligands increases a greater contribution to the apparent entropy of activation from the phosphine-dissociation and ethane-elimination steps is expected. It is presumably this reinforcement effect which leads to the large range of entropies of activation observed. The tendency of bulky ligands to stabilise low co-ordination numbers and oxidation states has been established in some related systems.[34-36]

The activation parameters (Table 5) for decomposition of (I; X = I, L = $\frac{1}{2}$dppe) are in marked contrast to those for the complexes with unidentate ligands. A change in the apparent entropy of activation is expected in view of the chelate effect, but the large negative value observed coupled with the very low activation energy suggests that in this case ethane elimination may take place without prior cleavage of a platinum–phosphorus bond. Some support for this is given by the observation that the decomposition of this complex in 1,4-dioxan at 95 °C was not retarded by added dppe (0·02M), though the reaction did not follow strict first-order kinetics. It is interesting that the activation energy for ethane elimination, 69 kJ mol^{-1}, is less than half the expected methyl–platinum bond energy.

Mechanism of Reaction.—It has been established that elimination of ethane from the complexes (I) takes place by intramolecular elimination from the five-co-ordinate complex formed by dissociation of a phosphine (or arsine) ligand, at least for unidentate ligands L. A similar result has been reported by Kochi and his co-workers [37] for the elimination of ethane from methylgold(III) complexes [equation (9)]. The mechanisms are evidently

$$[Me_3AuL] \rightleftharpoons L + [Me_3Au] \longrightarrow [MeAuL] + C_2H_6 \quad (9)$$

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[28] 'Isotope Effects in Chemical Reactions,' eds. C. J. Collins and N. S. Bowman, Amer. Chem. Soc. Monograph 167, Van Nostrand, New York, 1970.

[29] W. H. Saunders in 'Technique of Organic Chemistry,' vol. VIII, part I, Interscience, 1961, ch. IX.

[30] P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, 1966, **88**, 3511.

[31] M. J. Mays, R. N. F. Simpson, and F. P. Stefanini, *J. Chem. Soc.* (*A*), 1970, 3000.

[32] W. Partenheimer and E. F. Hoy, *Inorg. Chem.*, 1973, **12**, 2805.

[33] S. J. W. Price in 'Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, 1972, ch. 4.

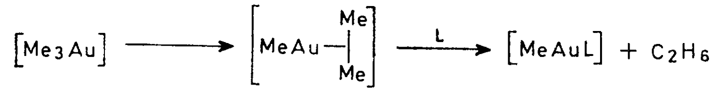
[34] C. Masters, B. L. Shaw, and R. E. Stainbank, *Chem. Comm.*, 1971, 209.

[35] C. Masters, W. S. McDonald, and B. L. Shaw, *Chem. Comm.*, 1971, 210.

[36] B. L. Shaw and R. E. Stainbank, *J.C.S. Dalton*, 1972, 223.

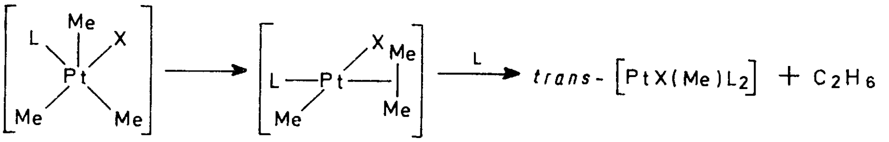
[37] A. Tamaki, S. A. Magennis, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1973, **95**, 6487.

essentially the same, and it is clear that phosphine dissociation lowers the activation energy for the reductive-elimination reaction. There are two possible contributory factors. First, the dissociation is expected to reduce the electron density at the metal centre. It has been amply demonstrated that the reactivity of a complex towards oxidative addition reactions is decreased by factors which decrease electron density at the metal centre [1,38,39] and the corollary is clearly that reactivity towards reductive-elimination reactions should be enhanced by such factors.



$$[\mathrm{Me_3Au}] \longrightarrow \left[\mathrm{MeAu}-\begin{array}{c}\mathrm{Me}\\ |\\ \mathrm{Me}\end{array}\right] \xrightarrow{L} [\mathrm{MeAuL}] + \mathrm{C_2H_6}$$

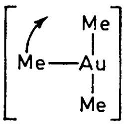
(10)



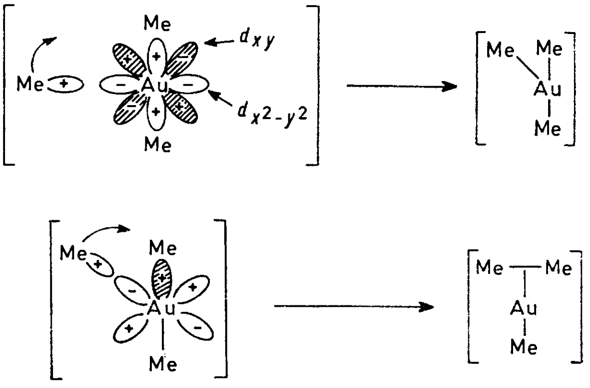
(11)

The second likely contributory factor is related to the preferred co-ordination number of the reduced metal complex. It is reasonable to assume that if the ethane elimination is a concerted process the reaction will proceed through a stage in which C–C bond formation occurs but the ethane so formed is still co-ordinated to the metal. The metal–ethane bond is expected to have σ- and π-components using respectively the filled σ- and vacant σ*-orbitals associated with the C–C bond. Such a bond is expected to be weak and the ethane would be rapidly displaced by free ligand.[40] Nevertheless, prior dissociation of a phosphine ligand would allow the ethane complex to be formed with the preferred co-ordination number of gold(I) or platinum(II) of two or four respectively as shown in equations (10) and (11), thus stabilising this predicted intermediate. It is interesting that reductive elimination of dihydrogen from $[\mathrm{IrH_2(CO)_2(PR_3)_2}]^+$ takes place without prior dissociation of a neutral ligand.[31] The intermediate 'dihydrogen complex' is thus a five-co-ordinate $\mathrm{Ir^I}$ complex, again the preferred co-ordination number.

Further insight into the nature of the transition state may be gained by consideration of orbital-symmetry arguments. We consider elimination from the d^8 complex $[\mathrm{Me_3Au}]$ since it has higher symmetry (C_{2v} for a T-shaped molecule) than the d^6 complex $[\mathrm{Me_3Pt(X)L}]$, but the basic factors are very similar in either case. The supposed initial product $[\mathrm{MeAu(C_2H_6)}]$ also has C_{2v} symmetry, and the transformation involves the electron configuration change at gold, $d^8 \longrightarrow d^{10}$. Since the elimination of two mutually *cis*-methyl groups is known to occur, the reaction is likely to be initiated by a vibrational mode of the molecule which brings the methyl groups closer together. Since the distance between two *cis*-methyl groups is estimated as 3 Å (based on an average methyl–gold bond distance of 2·12 Å), and considerable C–C bond formation is assumed in the transition state by analogy with the platinum(IV) reaction, such a vibrational mode is clearly necessary to reduce the C–C distance. The most likely vibrational mode is in-plane deformation of B_{1u} symmetry.



Since the orbital $d_{x^2-y^2}$ (vacant in the starting material but filled in the product) has A_1 symmetry in both product and starting material, the reaction appears to be orbitally forbidden. However, if the methyl group migrates first on to the filled d_{xy} orbital which has B_{1u} symmetry, the reaction is allowed. This is illustrated using the frontier-orbital approach popularised by Pearson for reactions of transition-metal complexes.[41-43]



In the first stage, the orbitals involved are the filled d_{xy} and the vacant σ-antibonding combination $d_{x^2-y^2}{}^*$. The B_{1u} deformation shown leads to cleavage of the initial Me–Au bond by occupying the σ* orbital, and

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[38] L. Vaska, *Inorg. Chim. Acta*, 1971, **5**, 295.

[39] M. Kubota, G. W. Kiefer, R. M. Ishikawa, and K. E. Bencala, *Inorg. Chim. Acta*, 1973, **7**, 195.

[40] R. J. Hodges, D. E. Webster, and P. B. Wells, *J.C.S. Dalton*, 1972, 2571, 2577.

[41] R. G. Pearson, *Theor. Chim. Acta*, 1970, **16**, 107; *J. Amer. Chem. Soc.*, 1972, **94**, 8287; *Accounts Chem. Res.*, 1971, **4**, 152.

[42] R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, 1970, **92**, 5519.

[43] C. F. Shaw, J. W. Lundeen, and R. S. Tobias, *J. Organometallic Chem.*, 1973, **51**, 365.

formation of a new and presumably weaker Me–Au bond at 45° to the original bond. In the second step the frontier orbitals are the filled Me–Au σ-bonding orbital (presumably *sp* hybrid) and the vacant σ-antibonding orbital d_{xy}* associated with the newly formed Me–Au bond. This leads to cleavage of both Me–Au bonds, formation of a C–C σ-bond and a gold–ethane bond, and reduction to gold(I). Participation of the d_{xy} orbital is not necessary if decomposition is initiated by the A_1 stretching vibration,[43] but since this lengthens the C–C bond distance it is considered less likely. A similar mechanism of elimination from the trimethylplatinum(IV) complexes is fully consistent with all the mechanistic data available.

EXPERIMENTAL

General methods of preparation of the complexes have been described previously;[12] *fac*-[PtX(Me)$_3$(PMe$_2$Ph)$_2$] (I; X = Cl, Br, or I) and specifically deuteriated derivatives were prepared by the method of Ruddick and Shaw;[18] [{Pt(I)Me$_3$}$_4$] was prepared by an adaptation of the method of Clark and Manzer[44] by heating [PtMe$_2$(cod)] (cod = η-cyclo-octa-1,5-diene) under reflux in methyl iodide for 48 h, and precipitating the *product* with acetone (yield 70%).

fac-*Iodotrimethylbis*(*methyldiphenylphosphine*)*platinum*(IV).—This complex was prepared by adding PMePh$_2$ (0·22 g) to a solution of [{Pt(I)Me$_3$}$_4$] (0·23 g) in benzene (10 cm^3). After 15 min at room temperature the *product* was precipitated by addition of pentane, filtered off, washed thoroughly with diethyl ether, and dried *in vacuo*, yield 0·41 g (86%), m.p. 132—135 °C (decomp.) (Found: C, 45·25; H, 4·40. Calc. for $C_{29}H_{35}IP_2Pt$: C, 45·4; H, 4·55%).

The complex *fac*-[PtI(Me)$_3$(dppe)] was prepared similarly, yield 88%, m.p. 208—212 °C (decomp.) (Found: C, 45·9; H, 4·50. Calc. for $C_{29}H_{33}IP_2Pt$: C, 45·35; H, 4·30%). The complex *fac*-[PtI(Me)$_3$(PMe$_3$)$_2$] was prepared similarly, yield 60%, m.p. 154—157 °C (decomp.) (Found: C, 20·9; H, 5·45. Calc. for $C_9H_{27}IP_2Pt$: C, 20·8; H, 5·20%).

Reaction of [{Pt(I)Me$_3$}$_4$] *with* PPh$_3$.—To a solution of [{Pt(I)Me$_3$}$_4$] in CHCl$_3$ in an n.m.r. tube was added PPh$_3$ (2 mol). The peak due to [{Pt(I)Me$_3$}$_4$] [τ 8·28, ^2J(PtH) 76 Hz] disappeared and new peaks due to *cis*-[PtMe$_2$(PPh$_3$)$_2$] [τ (CH$_3$Pt) 9·65, ^2J(PtH) 69 Hz; lit.[45] τ 9·63, ^2J(PtH) 69 Hz] and MeI (τ 7·93) appeared. Smaller peaks due to ethane (τ 9·26) and *trans*-[PtI(Me)(PPh$_3$)$_2$] [τ (CH$_3$Pt) 9·98; ^3J(PH) 6·5 Hz; lit.[46] τ 9·91, ^3J(PH) 6·5 Hz] were also observed. The latter product crystallised from solution, m.p. 273—274 °C (lit.[47] 270—275 °C). Addition of more PPh$_3$ to the solution caused the peak due to MeI to decay and a new peak due to Ph$_3$MePI appeared [τ (CH$_3$P) 6·88, doublet, ^2J(PH) 14 Hz] identical with that from an authentic sample.

Kinetics.—Reactions were monitored by following changes in the absorbance of the solutions (*ca*. 10^{-4}M) in 1,4-dioxan (freshly distilled from calcium hydride) or 2-methoxyethanol using a Unicam SP 1800 spectrophotometer, with an electrically heated cell compartment thermostatted to ±0·2 °C. For temperatures of 95 °C or higher, solutions were heated in sealed tubes in a thermostatted oil-bath for various times and the absorbance measured subsequently. The two methods gave identical results. The wavelengths used for monitoring reactions were 300 (I; X = Cl, L = PMe$_2$Ph; X = I, L = ½dppe), 290 (I; X = I, L = PMePh$_2$), and 280 nm for (I; X = Br or I, L = PMe$_2$Ph). In each case the identity of the product was confirmed by comparing its u.v. spectrum with that of an authentic sample. The kinetic data for (I; X = Cl, L = PMe$_2$Ph) were less accurate than for the other complexes due to a much lower difference in absorbance between starting material and product.

Analysis of Deuterioethanes.—Deuteriated platinum complexes were pyrolysed on the inlet system of a Micromass 601 mass spectrometer. The identity and composition of C_2D_6, MeCD$_3$, and C_2H_6 mixtures were confirmed from the mass spectra, in particular from the intensities of the peaks at *m*/*e* 36, 33, and 30. Measurements at 13·5 and 20·0 eV (and at 70·0 eV for C_2D_6–MeCD$_3$ mixtures) gave identical results.*

Decompositions.—fac-[PtI(Me)$_3$(dppe)]. The complex (6·0 × 10^{-5} mol) was heated in a side-arm of the vacuum line. Ethane was evolved at 215—220 °C, immediately above the m.p. point of the complex. The ethane (5·8 × 10^{-5} mol, 96%) was collected and identified by its mass spectrum. The residue was identified as pure *cis*-[PtI(Me)-(dppe)] by its m.p. and n.m.r. spectrum.

fac-[PtI(Me)$_3$(PMe$_2$Ph)$_2$]. The enthalpy change on decomposition was determined by heating weighed samples in the sample chamber of a Perkin-Elmer DSC 1B differential scanning calorimeter as described earlier.[12,20] Quoted values are the average of five results. Frothing on decomposition led to spurious results in several runs; consistent results were obtained only using crimped sample pans.

We thank Drs. C. F. H. Tipper and K. R. Seddon for valuable discussions, Engelhard Ltd. for a gift of platinum complexes, and the S.R.C. for a research grant (to C. E. E. U.).

[4/759 *Received*, 17*th April*, 1974]

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* 1 eV ≈ 1·60 × 10^{-19} J.

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