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Preliminary communication

THE MECHANISM OF DECOMPOSITION OF A PLATINUM—ACETYLENE COMPLEX

N. CHAUDHURY and R.J. PUDDEPHATT
Donnan Laboratories, The University of Liverpool, Liverpool L69 3BX (Great Britain)

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Summary

The complex PtClMe(2,2'-bipy)($MeO_2CC{\equiv}CCO_2Me$) decomposes to PtClMe(2,2'-bipy) and $MeO_2CC{\equiv}CCO_2Me$ by a complex mechanism involving preliminary ionisation of the chloride ligand, but the dissociation of $CF_3C{\equiv}CCF_3$ from PtIMe(2,2'-bipy)($CF_3C{\equiv}CCF_3$) takes place without ionisation of iodide.

It has been shown that insertion reactions of alkenes or alkynes (un) into the Pt—H or Pt—Me bonds of the complexes $PtHXL_2$ or $PtMeXL_2$ take place more readily if the group X is weakly coordinated (e.g., NO_3^-, acetone) and this has led to the suggestion that all such insertion reactions proceed by a dissociative mechanism [1], although no direct evidence that intermediates of the type $PtMe(un)L_2^+X^-$ are formed has been obtained when X is a good ligand (e.g., halide, cyanide) for platinum. We now present evidence that such intermediates can be formed in the decomposition of a 5 coordinate platinum- acetylene complex.

The complexes $PtXMeL_2$(RCCR) (I) where L_2 = 2,2'-bipyridyl (bipy), X = Cl, R = CO_2Me (Ia) or L_2 = 2,2'-bipy, X = I, R = CF_3 (Ib) decomposed to PtXMe(2,2'-bipy) and RCCR, the reactions following first-order kinetics in several organic solvents. However, the rate of decomposition of Ia was strongly dependent on the polarity of the solvent whereas that for Ib was not (Table 1). The values

TABLE 1

SOLVENT EFFECTS ON THE FIRST ORDER RATE CONSTANTS, *k*, FOR DECOMPOSITION OF PtXMe(2,2'-bipy)(RCCR) AT 40°

Solvent	E_T	$10^3 k$ (min^{-1}) X = Cl, R = CO_2Me	$10^3 k$ (min^{-1}) X = I, R = CF_3
Mesitylene			12.7
Benzene	34.1	4.8	
Tetrahydrofuran	37.4	11.7	
Acetone	42.2	191	13.9
Methyl cyanide	46.0	910	5

of log k for decomposition of Ia gave a linear correlation with the E_T values (measures of polarity) of the solvent, a behaviour reminiscent of S_N1 substitution reactions of t-butyl chloride, and suggesting an ionic intermediate [2].

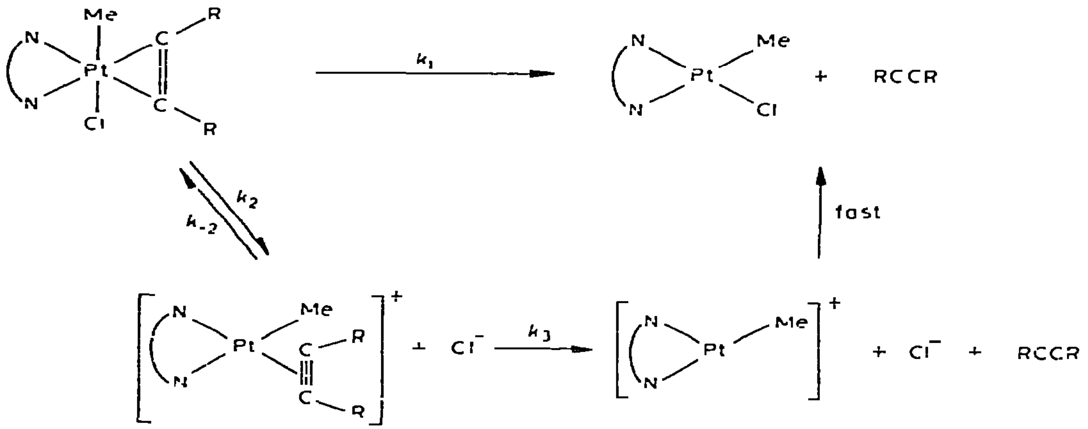
This was confirmed by studying the rate of reaction with added chloride ions in acetone solution. The reaction was strongly retarded by added chloride (Table 2), and the observed first-order rate constant was given by the expression $k = 0.0122 + 1/(9.2 \times 10^5 [Cl^-] + 5.59)$. The results are most readily explained according to the mechanism shown in Scheme 1, in which $k_1 = 0.0122$ min^{-1}, $k_2 = 0.179$ min^{-1} and $k_{-2}/k_3 = 16.5 \times 10^4$ l mol^{-1}.

TABLE 2

EFFECT OF ADDED CHLORIDE ON THE FIRST ORDER RATE CONSTANT, k, FOR DECOMPOSITION OF Ia IN ACETONE AT 40°C

10^4[LiCl] (M)	0	2.06	10.2	51.5	103
10^2k (min^{-1})	19.1	5.07	3.11	2.07	1.79

SCHEME 1 (NN = 2,2'-bipyridyl, R = CO_2Me)



Thus in acetone solution the dissociation of alkyne from Ia takes place very largely through the ionic intermediate, but the lack of solvent dependence on the rate of dissociation of alkyne from Ib indicates that no ionic intermediate is formed in this case. The platinum—acetylene bonds of complexes I are known to be strong from thermochemical studies [3], but in the ionic intermediate II the bond is expected to be considerably weakened since the contribution to the bond energy from back-bonding of electrons from filled platinum d-orbitals to vacant π^*-orbitals of the acetylene will be greatly diminished [4]. It is presumably this effect which makes the ionic mechanism favourable for Ia, but the ionisation process for Ib must require a higher activation energy so that a simple dissociation of the alkyne is preferred. Alkyne dissociation from I may be considered to be a reductive elimination reaction, and it has previously been shown that reductive elimination of ethane from the complexes $PtXMe_3L_2$ is accelerated by dissociation of a ligand X or L but that in some cases reductive elimination can take place without such dissociation (e.g., when X = I, $L_2 = Ph_2PCH_2CH_2PPh_2$)

[5]. The behaviour is thus similar to that for the alkyne dissociation reactions described above.

The rearrangement of complexes of type I to the insertion product PtX(CR=CRMe)L_2 can also be considered as a reductive elimination reaction [6], and the arguments presented above suggest that although the insertion reaction is expected to be accelerated by dissociation of a ligand X or L, if this is not easily achieved then insertion may take place by direct rearrangement of the intermediate I. Such a mechanism is certainly to be expected for insertion reactions into the methyl—platinum bonds of complexes *cis*-$PtMe_2(PR_3)_2$ or $PtMe_2$(2,2'-bipy) which takes place very readily in some cases although there is no ligand which can be displaced easily.

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