

Preliminary communication

MECHANISM OF ELECTROPHILIC CLEAVAGE OF THE Pt—C (ALKYL) BOND IN *trans*-[Pt(PET₃)₂(YC₆H₄)(CH₃)] COMPLEXES

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Summary

Protonolysis of the complexes *trans*-[Pt(PET₃)₂(R)(Me)] (R = C₆H₅; *m*-MeC₆H₄; *o*-MeC₆H₄; *m*-FC₆H₄; *p*-FC₆H₄; *m*-CF₃C₆H₄ and C₆F₅) by hydrogen chloride in methanol/water (90/10 v/v) selectively cleaves the alkyl group yielding *trans*-[Pt(PET₃)₂(R)Cl] and methane. A kinetic study of these reactions suggests that the primary step involves a proton transfer to the carbon—metal σ -bond with release of CH₄ in a three-center transition state.

There is debate on whether reactions of electrophiles with σ -bonded organoplatinum(II) complexes occur by attack on the carbon—metal bond or by oxidative addition to the metal. [1]. The selectivity between alkyl— or aryl—metal bond cleavage in mixed methyl-arylplatinum(II) complexes has been suggested as a criterion to distinguish between these two mechanisms [2]. Thus the preferential cleavage of the alkyl rather than the aryl group in the complex *cis*-[PtMe(*p*-MeC₆H₄)(PMe₂Ph)₂] was interpreted as evidence for an oxidative addition—reductive elimination mechanism.

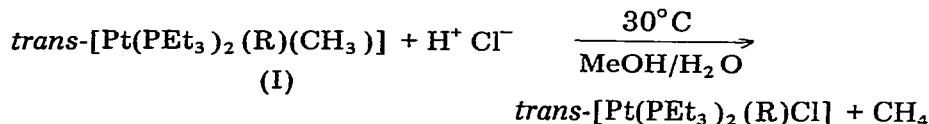
In this context we considered it of interest to undertake a kinetic study of the acid cleavage of the Pt—C(alkyl) bond in *trans*-[Pt(PET₃)₂(YC₆H₄)(Me)] with the aim of shedding light on the mechanism and of determining the effect of electron donation by substituents on the *trans* aromatic ring.

Kinetics

The reactions of *trans*-[Pt(PET₃)₂(C₆F₅)(Me)] with HCl in aqueous methanol or DCl in MeOD/D₂O were followed by usual spectrophotometric methods. The other reactions all faster, were followed by means of a Durrum Gibson D110 stopped-flow apparatus.

Results

The reactions examined were:



(R = C₆H₅; *m*-MeC₆H₄; *o*-MeC₆H₄; *m*-FC₆H₄; *p*-FC₆H₄; *m*-CF₃C₆H₄; C₆F₅)

The cleavage of the Pt—C(aryl) bond was extremely slow under the conditions used and the final spectra were identical with those of the corresponding *trans*-chloroaryl complexes.

The pseudo-first-order rate constants $k_{\text{obsd.}}(\text{s}^{-1})$ were linearly dependent on acid concentration (in the range 0.001–0.04 *M*) but independent of chloride concentration at constant ionic strength (0.05 *M*, LiClO₄), i.e. $k_{\text{obsd.}} = k_2 [\text{H}^+]$. The values of k_2 are listed in Table 1. The rate of protonolysis of *trans*-[Pt(PEt₃)₂(C₆F₅)(Me)] is seven times faster with H⁺ in MeOH/H₂O than with D⁺ in MeOD/D₂O (Table 1). Increasing electron withdrawing from *meta* and *para* substituents on the aryl ring decreases the rate of reaction (Table 1), and the effect is especially large for the pentafluorophenyl complex. Steric hindrance causes a decrease in rate, as shown by the comparison between the phenyl and the *o*-tolyl complex.

TABLE 1

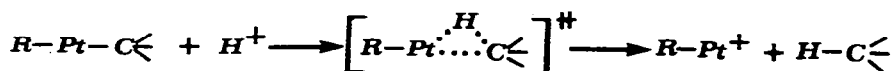
SECOND ORDER RATE CONSTANTS FOR THE REACTIONS:
 $\text{trans-[Pt(PEt}_3)_2(\text{YC}_6\text{H}_4)(\text{CH}_3)] + \text{H}^+ + \text{Cl}^- \rightarrow \text{trans-[Pt(PEt}_3)_2(\text{YC}_6\text{H}_4)\text{Cl}] + \text{CH}_4$
 IN 90% AQUEOUS METHANOL AT 30°C^a

Complex	$k_2 (\text{M}^{-1} \text{s}^{-1})^b$	Complex	$k_2 (\text{M}^{-1} \text{s}^{-1})^b$
[PtL ₂ (<i>m</i> -MeC ₆ H ₄)Me]	28100	[PtL ₂ (<i>m</i> -FC ₆ H ₄)Me]	4016
[PtL ₂ (<i>o</i> -MeC ₆ H ₄)Me]	5700	[PtL ₂ (<i>m</i> -CF ₃ C ₆ H ₄)Me]	2180
[PtL ₂ (C ₆ H ₅)Me]	20300	[PtL ₂ (C ₆ F ₅)Me]	1.19
[PtL ₂ (<i>p</i> -FC ₆ H ₄)Me]	7540	[PtL ₂ (C ₆ F ₅)Me]	0.17 ^c

^aIonic strength 0.05 *M* (LiClO₄). ^bSlopes of plots of $k_{\text{obsd.}}(\text{s}^{-1})$ vs. [H⁺]. ^cDCl in MeOD/D₂O (90/10 v/v).

The mechanism of protonolysis

The fairly large value of $k_{\text{H}}/k_{\text{D}}$ argues against the formation of a hydrido-platinum(IV) intermediate, as required by the multistep oxidative addition mechanism, and indicates that there is a rate-determining proton transfer to the substrate [3]. As suggested for the protonolysis of *cis*-[Pt(PEt₃)₂(YC₆H₄)₂] complexes [4], the attack of the electrophile probably occurs at the carbon—metal bond with formation of a three-center transition state which would be susceptible to steric hindrance. The absence of an observable effect of added chloride ion shows that no nucleophilic assistance by the anion is required.



The rate of proton transfer will thus depend on the extent of electron release to the Pt—C bond. A plot of $\log k_2$ vs. the Hammett's σ constants for the substituents on the aryl ring is satisfactorily. Further studies with other *meta* and *para* substituents on *trans*-[Pt(PEt₃)₂(YC₆H₄)(Me)] are in progress, and these should permit an assessment of the relative importance of inductive and resonance effects within the reaction considered.

It is noteworthy that the above findings contradict the prediction [2] that in these systems the preferred position of attack of the electrophile may be the metal. Consideration of the nature of the group being displaced only may not be sufficient to determine the reaction course. At this stage it appears that each system must be separately investigated before its mechanism can be stated with confidence.

Acknowledgment

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References

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