

Mechanism of Cleavage of the Pt-C Bond in *Cis*-[Pt(PEt₃)₂(C₆H₄Y)₂] upon Electrophilic Attack

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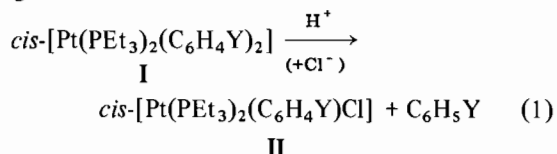
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Received June 23, 1976

The cleavage of Pt-C σ bonds through electrophilic attack by the proton on complexes of type *trans*-[Pt(PEt₃)₂Ph₂]¹ and *trans*-[Pt(PEt₃)₂(Me)X] (X = Cl, I)² in protic solvents was shown to take place via a rapid preequilibrium between the complex substrate and H⁺ leading to a Pt(IV) hydrido intermediate, followed by slow elimination of benzene or methane and rearrangement to *trans*-[Pt(PEt₃)₂PhCl] or *trans*-[Pt(PEt₃)₂XCl], respectively.

We have now extended these mechanistic studies on electrophilic attack to include bis(substituted aryl) complexes of Pt(II) in *cis* configuration, according to the reaction:



(Y = *p*-OMe, *p*-Me, H, *p*-F, *m*-F)

We report herein on preliminary results of these studies.

Results

The kinetics were followed by customary spectrophotometric methods in the 250–350 nm range in anhydrous methanol or aqueous methanol (up to 10% v/v water content) under pseudo-first-order conditions, at a constant ionic strength of 0.3 M (LiClO₄) at 30 °C. The concentration of H⁺ was in the range 5 × 10⁻³–2.5 × 10⁻¹ M, whereas the concentration of Cl⁻ ranged between 5 × 10⁻³ and 10⁻¹ M. The cleavage of the second Pt-C σ bond was sufficiently slow under these conditions to allow the rates of cleavage of the first one to be easily followed.

The pseudo-first-order rate constants for the cleavage of the first Pt-C bond (eq. 1), k_{obs}/sec⁻¹, are linearly dependent on the proton concentration

and independent of chloride concentration. Addition of water to the solvent (methanol) effectively depresses the rates which level off to a constant value at a water content of about 5% in volume. Second order rate constants, k_Y/M⁻¹ sec⁻¹ are listed in the Table.

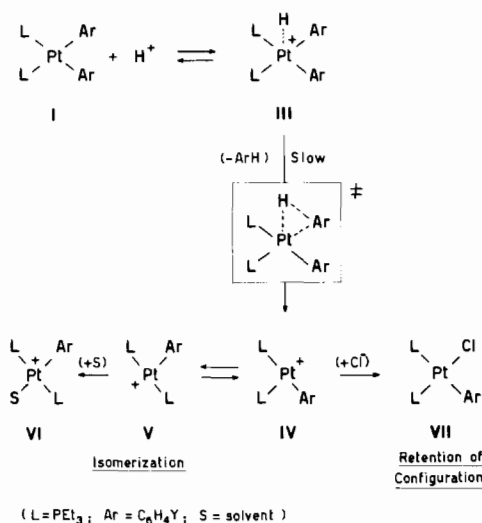
TABLE. Second-order Rate Constants, k_Y(M⁻¹ Sec⁻¹), for Reaction (1) in Methanol and 90% Aqueous Methanol at 30 °C. [Cl⁻] = 5 × 10⁻² M, ionic strength = 0.3 M(LiClO₄).

Substituent	10 ² k _Y , M ⁻¹ sec ⁻¹	
	Methanol	90% Aqueous Methanol
<i>p</i> -OMe	—	11.2
<i>p</i> -Me	35	4.3
H	5.8	0.8
<i>p</i> -F	1.7	0.3
<i>m</i> -F	—	0.03

The values of log (k_Y/k_H) fit a linear relationship with Hammett's parameters of the Y substituents in the platinum-bonded aromatic rings of the substrates. The rates of electrophilic attack increase markedly with increasing electron-donating ability of the Y substituent both in methanol and aqueous methanol (ρ ~ -4.6 in either type of solvent). Further, reaction 1 proceeds with retention of configuration in the presence of Cl⁻. In the absence of chloride ion, *cis*→*trans* isomerization takes also place leading to *trans*-[Pt(PEt₃)₂(C₆H₄Y(S))ClO₄ (S = solvent).

Discussion

All these experimental findings are easily accommodated by the following mechanism of Pt-C bond electrophilic cleavage:



Cleavage of the Pt-C σ bond takes place by electrophilic attack by the proton on the central metal in a preliminary reversible protonation step, followed by ArH release *via* a slow three-center interaction. Of course, the alternative possibility of a direct, electrophilic attack by the proton on the aryl carbon linked to the platinum atom cannot be ruled out on the basis of available kinetic evidence. The question of the protonation site in these electrophilic metal-carbon bond cleavage reactions (*i.e.* the transition metal *vs.* the carbon group) seems rather semantic in nature. In either case, the rate will increase with increasing electron density on the Pt-C axis, as dictated by the electron donating ability of the aryl substituent Y. Also, increasing proportions of the more polar water in the methanol solvent are expected to depress the rate of attack through stabilization of the electrophile H⁺ by solvation, as observed. The lack of any dependence of the rates on chloride concentration is also in accord with the mechanism.

As can be seen, a key intermediate resulting from the electrophilic attack is assumed to be a 14-electron, 3-coordinate "cis-like" species (IV), the fate of which is governed by the presence of nucleophilic groups in the system. When chloride is present, the vacant coordination site in IV is blocked before the intermediate isomerizes to its "trans-like" counterpart (V), thereby leading to retention of configuration in the resulting mono-aryl platinum product (VII); in the absence of good nucleophiles (*i.e.* when only perchlorate ion is present) *cis*→*trans* isomerization (IV→V) can take place and the mono-aryl product has

trans-configuration. This picture is in agreement with the well established mechanism of uncatalyzed *cis*→*trans* isomerization in Pt(II) complexes,³ which has been shown to involve dissociation in the platinum substrate to give a 3-coordinate species in the rate-determining step. As a matter of fact, the overall sequence I→IV in the present mechanism of Pt-C bond cleavage may be looked upon as a "dissociation" of an aryl group providing a pathway for the final mono-aryl product. The rate will be markedly sensitive to the changes in the electron density at the coordinated carbon atom produced by substituents on the aromatic ring. The highly negative value for ρ in the Hammett relationship observed fits perfectly into this interpretation.

It may be interesting to mention in this context that the occurrence of 14-electron, 3-coordinate species in d^8 metal complexes appears to be much more frequent than expected on the basis of Tolman's 18-electron rule.⁴

References

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