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PROTONOLYSIS OF THE Pt—C BOND IN *trans*-$[PtH(CH_2CN)(PPh_3)_2]$

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Summary

The protonolysis of the Pt—C bond in *trans*-$[PtH(CH_2CN)(PPh_3)_2]$ in methanol/1,2-dichloroethane is shown to take place by a two step mechanism involving oxidative addition to the metal center followed by reductive elimination of CH_3CN to give *trans*-$[PtHCl(PPh_3)_2]$.

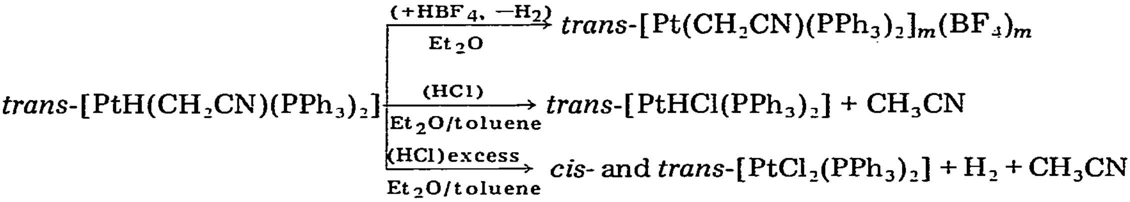
Introduction

The mechanism of electrophilic cleavage of metal—carbon σ bonds has been the subject of extensive investigations in the past few years. The picture is fairly clear for non-transition metal alkyl and/or aryl derivatives, for which a variety of mechanism operate depending on the polarity of the M—C bond, on the solvent, and on the electrophile [1]. When transition metals are involved, things are not so clear-cut. Here the presence of potentially available filled *d* orbitals makes it possible for the metal itself to participate in the activation process through prior oxidative addition of the electrophile to the substrate. Therefore the question arises as to which is the site of electrophilic attack, the metal atom or the carbon atom of the group being cleaved off [2]. For instance, in the protonolysis of Pt—C bonds of alkyl- and aryl-platinum(II) tertiary phosphine complexes in the presence of chloride ions in protic solvents, a single-step direct attack of the proton on the metal—carbon bond has been shown to occur for *trans*-$[Pt(PEt_3)_2(C_6H_5)_2]$ [3], *cis*-$[Pt(PEt_3)_2(\text{substituted aryl})_2]$ [4] and *trans*-$[Pt(PEt_3)_2(\text{substituted aryl})(CH_3)]$ [5], whereas the intermediacy of platinum(IV) hydride species has been invoked to explain a chloride-dependent third order term for *trans*-$[Pt(PEt_3)_2(CH_3)Cl]$ [6].

A reasonable basis for distinguishing between direct attack at the metal—carbond bond and oxidative addition to the platinum in these systems appears to be the presence of such an additional third order term, $k_3[H^+][Cl^-]$ in the rate law, along with a low solvent isotopic effect. As a matter of fact, its absence is accompanied by a very high isotope effect [4,5], which is near to the highest expected when the proton is half transferred and which provides compelling evidence that the rate-determining step of protonolysis is proton transfer to the substrate [7]. Therefore, the organotransition-metal systems span a whole range of mechanistic behaviour whose extremes are electrophilic attack on the metal centre on one side, and the processes typical of non-transition systems on the other. Whereas for the oxidative addition mechanism some diagnostic tools are available (isotopic effect and form of the rate law) the elucidation of the detailed mechanism when oxidative addition is unmistakably disproved becomes less easy on kinetic grounds alone. In the latter case a mechanism can only be assessed by exploiting also the effects of such structural factors as steric configuration of the substrate, *trans* and *cis* influence of ligands, π-bonding capabilities and low promotional energy to make oxidative addition at the metal center feasible, and solvent effects.

In the light of these considerations we have chosen the complex *trans*-$[PtH(CH_2CN)(PPh_3)_2]$ [8] as the substrate for protonolysis of the Pt—H and/or the Pt—C bond. Here the groups potentially cleaved by the electrophile exert a strong mutual *trans*-influence. Moreover the presence of the electron-withdrawing cyanide on the alkyl moiety raises the question of the selectivity of platinum—hydride vs. platinum—alkyl bond cleavage under the conditions of the kinetic studies.

Under preparative conditions in aprotic solvents the complex *trans*-$[PtH(CH_2CN)(PPh_3)_2]$ undergoes cleavage of Pt—H and/or Pt—C bonds, depending on the electrophile:



$$trans\text{-}[PtH(CH_2CN)(PPh_3)_2] \begin{cases} \xrightarrow[Et_2O]{(+HBF_4,\ -H_2)} trans\text{-}[Pt(CH_2CN)(PPh_3)_2]_m(BF_4)_m \\ \xrightarrow[Et_2O/toluene]{(HCl)} trans\text{-}[PtHCl(PPh_3)_2] + CH_3CN \\ \xrightarrow[Et_2O/toluene]{(HCl)excess} cis\text{- and } trans\text{-}[PtCl_2(PPh_3)_2] + H_2 + CH_3CN \end{cases}$$

SCHEME 1

The reaction with Cl_2 in toluene leads to a mixture of *trans*-$[PtCl(CH_2CN)(PPh_3)_2]$, *trans*-$[PtHCl(PPh_3)_2]$ and *trans*-$[PtCl_2(PPh_3)_2]$. With CH_3I, *trans*-$[PtI(CH_2CN)(PPh_3)_2]$ is obtained [8].

Results and discussion

The protolytic cleavage of the Pt—C σ-bond in *trans*-$[PtH(CH_2CN)(PPh_3)_2]$ in a methanol/1,2-dichloroethane (9/1 v/v) solvent mixture takes place smoothly and quantitatively at temperatures in the range 20—60°C according to eq. 1.

$$\underset{(I)}{trans\text{-}[PtH(CH_2CN)(PPh_3)_2]} + H^+ + Cl^- \rightarrow \underset{(II)}{trans\text{-}[PtHCl(PPh_3)_2]} + CH_3CN \qquad (1)$$

The solvent was chosen such as to ensure the complete solubility of the metal substrate I while allowing extensive dissociation of electrolytes under the conditions used. In order to account for the small, variable amount of water introduced in the making up of reaction solutions for kinetic studies (see Experimental), appropriate quantities of water were deliberately added to each solution to make up for a total, constant water content of 0.54% in volume of the medium in all kinetic runs. Previous studies have shown that the rates of protolytic cleavage of Pt—alkyl bonds in protic solvents are exceedingly sensitive to the water content of the medium in the range 0—5% in volume, mostly because of reduction in free energy of the electrophile H^+ by solvation by the more polar solvent component [4—6].

Determination of rate constants

Reaction 1 appears to be first-order in the complex concentration when H^+ and Cl^- are present in excess, as shown by the dependence of absorbance values of the reaction mixture with time (A_t). For most experiments an infinite time measurement (A_∞) could be determined directly; however, an iterative non-linear least squares program was employed to determine the values of k_{obs}, A_o, A_∞ which best fit the A_t/t data within the first-order rate expression $A_t = A_\infty + (A_o - A_\infty) \exp(-k_{obs}t)$, the function minimized being $\Sigma_i(A_{calc} - A_{obs})^2$. The algorithm employs an undamped Gauss—Newton optimization procedure [9] and converges in a few cycles from an estimated starting vector of parameters. To maintain internal consistency, all kinetic data were treated by this nonlinear technique; where direct comparison was feasible, the optimized values of A_o and A_∞ agreed with the observed values to well within experimental error. Within each experiment, the values of A_t calculated from the expression above and the optimized values of A_o, A_∞, and k_{obs} always agreed with the observed values of A_t to a standard deviation of less than 0.002 absorbance unit and on the average to a standard deviation of less than 0.001 absorbance unit. Residuals were randomly scattered [10] and never greater than 0.0015 absorbance unit in absolute value.

The initial estimates necessary to start the iterative process were obtained by fitting a weighted least squares line, $\ln|A_i - A_\infty^{(J)}| = a_J + b_J t_i + \epsilon_{iJ}$ to the data points for a series of estimates $A_\infty^{(J)}$, and then minimizing the sum of squares of residuals $\Sigma w_{iJ}\epsilon_{iJ}^2$ as a function of $A_\infty^{(J)}$ by an accelerated unidimensional direct search procedure with step-doubling and final parabolic interpolation [11,12] (weighting scheme $w_{iJ} = (A_i - A_\infty^{(J)})^2$). Once the minimum is located, the corresponding $A_\infty^\star$ yields the best estimates of k_{obs} and A_o as functions of the intercept and slope of the line.

Estimated standard errors for k_{obs} were determined from the corresponding diagonal element of the variance/covariance matrix of parameters estimated at convergence of the non-linear least squares fitting [9a,10b]. The best fit k_{obs} values are listed in Table 1.

Determination of rate law

To determine the dependence of pseudo-first-order rate constants on the proton and chloride concentrations, it was necessary to detect which variables or

TABLE 1

PSEUDO-FIRST-ORDER RATE CONSTANTS, k_{obs}, FOR THE REACTION:
trans-$[PtH(CH_2CN)(PPh_3)_2] + H^+ + Cl^- \rightarrow$ *trans*-$[PtHCl(PPh_3)_2] + CH_3CN$
IN METHANOL/1,2-DICHLOROETHANE (9/1 v/v with 0.54% H_2O. *I* 0.3 *M*

Temperature (°C)	$10^2[H^+]$ (*M*)	$10^2[Cl^-]$ (*M*)	10^4k_{obs} (sec^{-1})	Temperature (°C)	10^2 $[H^+]$ (*M*)	10^2 $[Cl^-]$ (*M*)	10^4 obs (sec^{-1})
25	5.20	1.00	0.27	40	5.72	1.00	1.24
25	10.60	1.00	0.50	40	10.60	1.00	2.25
25	15.00	1.00	0.65	40	15.10	1.00	3.33
25	20.00	1.00	0.85	40	19.90	1.00	4.28
25	15.10	5.00	1.08	40	1510	5.00	5.08
25	15.00	10.00	1.50	40	15.10	10.00	7.83
25	15.10	14.90	2.07	40	15.10	14.90	10.42
30	5.60	1.00	0.46	45	5.20	1.00	1.66
30	10.60	1.00	0.82	45	10.15	1.00	3.37
30	15.10	1.00	1.17	45	15.30	1.00	5.02
30	17.30	1.00	1.30	45	20.00	1.00	6.52
30	20.90	1.00	1.57	45	15.30	5.00	8.90
30	15.10	5.00	1.85	45	15.30	10.00	13.92
30	15.10	10.00	2.88				
30	15.10	14.90	3.77				

groups of variables significantly influence the analytic form of rate law. This was achieved by multivariate linear regression analysis through the backward elimination procedure [10a,13]. The basic steps in the procedure were the following: a regression equation containing "all" variables was computed:

$$k_{obs} = k_1 + k_2[H^+] + k_3[H^+][Cl^-] + \ldots$$

A partial F-test value was calculated for every variable treated as though it were the last variable to enter the regression equation. The lowest partial F-test value F_L was compared with a preselected significance level F_o (95% confidence level). If $F_L < F_o$, the variable which gave rise to F_L was removed from consideration and the regression equation was recomputed in the remaining variables. Then the procedure was re-entered at the second step. If $F_L > F_o$, the regression equation as calculated was adopted. The resulting rate law is a two-term expression:

$$k_{obs} = k_2[H^+] + k_3[H^+][Cl^-] \qquad (2)$$

with the contribution of other reasonably expected terms being (statistically) insignificant at the 95% confidence level. The best fit values of k_2 and k_3 terms are listed in Table 2 along with their standard errors of estimate computed from diagonal elements of the variance/covariance matrix.

Activation parameters

The determination of activation parameters from the temperature dependence of rate constants is a little more difficult than one commonly thinks. According to the theory of absolute reaction rates [14] a second-order rate parameter, k, is related to the absolute temperature by the expression:

$$k/T = \exp(23.76)\exp(\Delta S^{\neq}/R - \Delta H^{\neq}/RT) \qquad (3)$$

TABLE 2

RATE AND ACTIVATION PARAMETERS FOR THE REACTION
trans-$[PtH(CH_2CN)(PPh_3)_2] + H^+ + Cl^- \rightarrow$ *trans*-$[PtHCl(PPh_3)_2] + CH_3CN$
IN METHANOL/1,2-DICHLOROETHANE (9/1 v/v) WITH 0.54% H_2O; I 0.3 M.

Temperature (°C)	$10^3 k_2$ [b] (M^{-1} sec^{-1})	$10^2 k_3$ [b] (M^{-2} sec^{-1})	$\Delta H_2^{\neq}$ [a] (kcal/mol)	$\Delta S_2^{\neq}$ [a] (e.u.)	$\Delta H_3^{\neq}$ [a] (kcal/mol)	$\Delta S_3^{\neq}$ [a] (e.u.)
25	0.37 ± 0.03	0.66 ± 0.02	17.5 ± 0.5	—15 ± 2	20.5 ± 0.7	0.5 ± 2
30	0.63 ± 0.01	1.26 ± 0.02				
40	1.79 ± 0.04	3.39 ± 0.05				
45	2.62 ± 0.02	6.46 ± 0.04				

[a] Uncertainties quoted are standard errors estimated from diagonal elements of variance/covariance matrix of non-linear regression analysis of (k/T) vs. T (see text). [b] From the rate law $k_{obs} = k_2[H^+] + k_3[H^+][Cl^-]$.

In practice the straightforward least squares fitting (non-linear) of eq. 3 is complicated by the high correlation between the activation parameters, which implies that if the value of a parameter is approximately assessed, this value is balanced in the fitting procedure by a compensating wrong value of the other parameter. Hence, the knowledge of the standard error of estimate is not sufficient to characterize the confidence region because the joint confidence region based on individual confidence limits does not take the correlation into account [15,16]. In this situation the contours of the sum-of-squares surface in the region of the minimum appear as thin, badly elongated, banana-like ellipses (ill-conditioned): convergence of the iterative procedure becomes a problem and the guessing of initial parameter estimates is critical. One way of circumventing this difficulty is to reparametrize the model equation to be fitted by a transformation of the independent variable [10a, 13,15] that improves the conditioning of the response surface. We have found the following transformation of eq. 3 quite satisfactory:

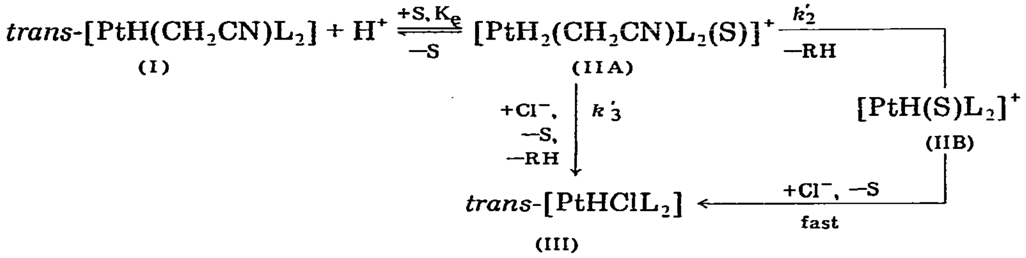
$$k' = A \exp(-B/T^*) \qquad (4)$$

where: $k' = (k/T)\exp(-23.76)$, $A = \exp(\Delta S^{\neq}/R - \Delta H^{\neq}/RT_o)$, $B = \Delta H^{\neq}/R$, $1/T^* = 1/T - 1/T_o$ and T_o = average value of absolute temperature.

The parameter correlation coefficients from a weighted nonlinear least squares fit of rate constants k_2 and k_3 in Table 2 to eq. 4 with A and B to be optimized have dropped to ca. 0.6. Each rate constant was weighted as $w_i = 1/\sigma_i^2$. At convergence, the standard error of estimate for $\Delta H^{\neq}$ was computed directly from the corresponding diagonal element of the variance/covariance matrix of estimates, whereas for $\Delta S^{\neq}$ use was also made of the off-diagonal element (which is related to the parameter correlation coefficient) since $\Delta S^{\neq}$ in eq. 4 is expressed as a function of A and B [9a]. Initial guesses were obtained from weighted linear least-squares fits of $\ln(k/T)$ to T (weighting scheme $w_i = k_i^2/\sigma_i^2$ to maintain the original distribution of errors). The resulting activation parameters are listed in Table 2.

Rate law 2 is consistent with a stepwise mechanism involving prior oxidative addition of the proton to give an unstable platinum(IV) hydride intermediate

(IIA), followed by slow reductive-elimination of CH_3CN (Scheme 2).



(L = PPh_3; S = solvent; R = CH_2CN)

SCHEME 2

The reductive-elimination takes place both intramolecularly (chloride-independent path) and under the influence of an entering chloride ion. The activation parameters for the single steps in this mechanism are composite quantities of pre-equilibrium and rate-determing components, each one depending on structural features of activated states and solvent participation. It would be hard to detail precisely each single contribution to the overall activation parameters, since only the overall rate constants ($K_e \times k'_2$ and $K_e \times k'_3$) are available. Moreover, the presence of three well defined isosbestic points in the spectral changes which accompany the conversion of substrate I to product III indicates that the platinum(IV) dihydride intermediate IIA is present in the system at kinetically significant but undetectable concentrations; this prevents even an indirect kinetic measurement of the pre-equilibrium protonation constant, K_e.

Although the experimental findings do not disprove other alternative mechanisms, we can confidently assume that the oxidative addition path as sketched in the scheme is favoured by the small size and high donor ability of the hydride ligand while the electronegative cyanomethyl group helps in stabilizing the platinum(II) substrate toward reductive elimination to platinum(0) species and CH_3CN. When the alkyl group *trans* to the hydride is not electronegatively substituted (i.e., CH_3) the corresponding alkylplatinum(II) hydride species decomposes to phosphineplatinum(0) complexes with liberation of methane, even at low temperature [17]. We note at this point that the stability of platinum(II) hydride derivatives seems hardly to be related to the overall charge of the complex [18]. Oxidative addition of platinum(II) complexes as a pathway for electrophilic cleavage of Pt—C bonds is not unprecedented, and it is sometimes possible even to isolate the platinum(IV) intermediate adduct [cf. the reaction of [Pt(bipy)Me_2] with $HgCl_2$ [19]). The choice between oxidative addition and direct electrophilic attack at the metal—carbon bond is also related to the question of the selectivity of cleavage when the substrate is a mixed alkyl—arylplatinum(II) species. Chemical tests have been proposed to distinguish between these mechanisms by studying the competitive electrophilic cleavage of methyl— vs. aryl—metal bonds [20]. It was assumed that preferential cleavage of a methyl—platinum bond is an evidence for the oxidative addition/reductive elimination mechanism. However, the selective cleavage of the methyl group from *trans*-[PtL_2-(substituted aryl)Me] by the proton has been recently reported to take place by direct proton attack on the metal—carbon bond [21]. Moreover, the selectivity of cleavage appears to be strictly related to the type of electrophile and experimental conditions employed; the substrate *trans*-[$PtH(CH_2CN)(PPh_3)_2$] undergoes cleavage of the Pt—CH_2CN bond by hydrogen chloride in ether, whereas the Pt—H bond is involved in the cleavage when HBF_4 in ether is used as the electrophile. Therefore it appears that both the particular mechanism which is operative and the selectivity of attack are the result of many factors (electronic and steric properties of the groups to be cleaved and of ancillary ligands. steric configuration of the substrate, nature of the electrophile and solvation properties of the medium). Care must thus be exercised in extrapolating mechanistic features of general validity from particular systems.

Experimental

Materials

Anhydrous methanol was obtained by distillation of the reagent grade solvent over $Mg(OCH_3)_2$ · $LiClO_4$ "anhydrous" (99.8%) was purchased from K&K Fine and Rare Chemicals. All other reagents were used without purification.

The starting substrate, *trans*-[$PtH(CH_2CN)(PPh_3)_2$] was prepared as described elsewhere [8].

The final product of protonolysis, *trans*-[$PtHCl(PPh_3)_2$], was prepared by literature methods [22].

Product identification

trans-[$PtH(CH_2CN)(PPh_3)_2$] (125 mg, 0.164 mmol) was dissolved in 250 ml of a methanol/1,2-dichloroethane mixture (8/2 v/v) containing $LiClO_4$ (2.13 g, 20 mmol). 1.25 ml of a solution of HCl in water (2.83 *M*) was added with stirring under nitrogen at room temperature. After 24 h the solution was evaporated under vacuum to dryness and treated with water (25 ml). The white material was filtered off and recrystallized from methanol. Yield 109 mg of *trans*-[$PtHCl(PPh_3)_2$] · CH_3OH identified by comparison of IR and proton NMR spectra with those of an authentic sample which was prepared independently [22].

Kinetics

The progress of the reaction was followed spectrophotometrically in a methanol/1,2-dichloroethane solvent mixture (9/1 v/v) containing a total constant amount of water (0.54%, vide supra) under pseudo-first-order conditions at a constant ionic strength of 0.3 *M* ($LiClO_4$). The desired proton and chloride concentrations were varied independently of one another by mixing in a volumetric flask the appropriate amounts of standardized solutions of dry hydrogen chloride or perchloric acid, LiCl, anhydrous (99.8%) $LiClO_4$ and water in the solvent mixture. The complex concentration was ca. 10^{-4} *M*.

The reactions were carried out in a silica cell in the thermostatted cell compartment of a double-beam Shimadzu—Bausch & Lomb Spectronic 210UV spectrophotometer equipped with a Houston Instrument Omnigraphic Recorder. The cell temperature was controlled to within ±0.05°C. The pre-thermostatted reactant solutions were rapidly mixed in the reaction cell to start kinetic runs.

Spectral changes were monitored in the 300—250 nm range and featured three isosbestic points, at 297, 283 and 257.5 nm. The final spectrum after completion of kinetic runs was identical with that of an authentic sample of *trans*-[$PtHCl(PPh_3)_2$] independently prepared [22].

Data reduction and analysis

The statistical treatment of absorbance and rate data (see Results) was carried out by algorithms which were especially implemented by one of us (P.U.) on a Hewlett—Packard 9815A Desktop Computer with 2008-step extended memory. Annotated program listings and sample outputs are available from this author on request.

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