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OXIDATION OF COORDINATED OLEFINS: THE REACTION OF Cl_2 WITH TRICHLORO(ETHYLENE)PLATINATE(II)

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Summary

The oxidation of $[PtCl_3(C_2H_4)]^-$ by Cl_2 in aqueous solution, to yield CH_2ClCH_2OH and $[PtCl_4]^{2-}$, has been shown to proceed through the following sequence of steps:

$$[PtCl_3(C_2H_4)]^- \xrightarrow{Cl_2,Cl^-} [PtCl_5(CH_2CH_2Cl)]^{2-} \xrightarrow{H_2O(-HCl)}$$

$$[PtCl_5(CH_2CH_2OH)]^{2-} \rightarrow [PtCl_4]^{2-} + CH_2ClCH_2OH$$

Each of the steps and intermediates in this mechanistic sequence has been identified and characterized.

Introduction

Metal ions such as palladium(II) and thallium(III) are useful oxidants for olefins, particularly in view of the distinctive selectivities which they characteristically exhibit [1—5]. Mechanistic pathways for such oxidations have been postulated which involve both π- and σ-bonded organometallic intermediates as reflected, for example, in the widely accepted mechanism of the Wacker reaction, depicted by eq. 1 [1,2,6].

$$[PdCl_4]^{2-} \xrightarrow{CH_2=CH_2} [PdCl_3(CH_2=CH_2)]^- \xrightarrow{H_2O}$$

$$[PdCl_3(CH_2CH_2OH)]^{2-} \rightarrow Pd^0 + CH_3CHO \qquad (1)$$

The evidence upon which this mechanistic interpretation rests is inconclusive, particularly with regard to the involvement of the σ-bonded organometallic intermediate, $[PdCl_3(CH_2CH_2OH)]^{2-}$, for which there is only indirect evidence (although an analogous intermediate, i.e., $[Tl\lesssim C—C\lesssim OH]^{2+}$ has been detected

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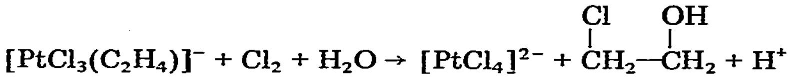
* Dedicated to Professor Joseph Chatt on the occasion of his 65th birthday.

[4] in the oxidation of certain olefins by thallium(III)). To the extent that initial coordination of the olefin to the metal ion is an important component of the oxidation pathway, such oxidations would appear to be constrained by the limited tendencies of olefins to coordinate to metal ions in high oxidation states. An objective of the study described in this paper, accordingly, was to examine the possibility of extending the scope of metal ion-oxidations of olefins by starting with stable olefin complexes of metals in low (i.e., non-oxidizing) oxidation states and oxidizing the pre-formed complex to a higher oxidation state (which would normally not complex the olefin) with an external oxidant. We have previously described a similar approach to the metal complex-catalyzed oxidation of CO [7].

Pursuing the above objective we have demonstrated that Cl_2 reacts stoichiometrically with Zeise's anion, $[PtCl_3(C_2H_4)]^-$, to oxidize the coordinated ethylene in accord with eq. 2. The present paper describes a study directed at elucidation of the mechanism of this reaction in which several component steps and organometallic intermediates were identified. The mechanistic insights gained from this study would also seem to have relevance for other reactions involving the oxidation of olefins by metal ions.

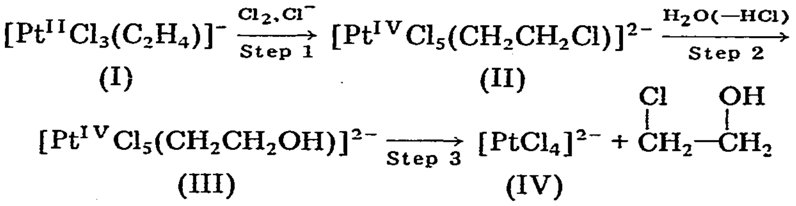


$$[PtCl_3(C_2H_4)]^- + Cl_2 + H_2O \rightarrow [PtCl_4]^{2-} + \overset{\mathrm{Cl}}{\mathrm{CH_2}}-\overset{\mathrm{OH}}{\mathrm{CH_2}} + H^+ \qquad (2)$$

Although not clearly pertinent to the present study, attention is directed to several earlier observations on the chemical and electrochemical oxidations of $[PtCl_3(C_2H_4)]^-$ [8,9].

Results

The addition of a *stoichiometric* amount of Cl_2 to an aqueous solution of $[PtCl_3(C_2H_4)]^-$ containing *ca.* 1 mol HCl, resulted *ultimately* in the quantitative formation of $[PtCl_4]^{2-}$ and CH_2ClCH_2OH according to eq. 2. Completion of the *overall* reaction required a period of several weeks at room temperature, but only a few minutes under reflux conditions. As detailed below, evidence was deduced for the mechanistic scheme depicted by eq. 3, involving the following sequence of three distinct steps and the two organometallic intermediates II and III, which were intercepted and characterized both in solution and as stable salts.



$$\begin{aligned} &\underset{\text{(I)}}{[Pt^{II}Cl_3(C_2H_4)]^-} \xrightarrow[\text{Step 1}]{Cl_2,\,Cl^-} \underset{\text{(II)}}{[Pt^{IV}Cl_5(CH_2CH_2Cl)]^{2-}} \xrightarrow[\text{Step 2}]{H_2O(-HCl)} \\ &\underset{\text{(III)}}{[Pt^{IV}Cl_5(CH_2CH_2OH)]^{2-}} \xrightarrow[\text{Step 3}]{} \underset{\text{(IV)}}{[PtCl_4]^{2-}} + \overset{\mathrm{Cl}}{\mathrm{CH_2}}-\overset{\mathrm{OH}}{\mathrm{CH_2}} \qquad (3) \end{aligned}$$

Description of Step 1

The addition of a stoichiometric amount of Cl_2 to an aqueous solution of $[PtCl_3(C_2H_4)]^-$, containing *ca.* 1 mol HCl (or the equivalent procedure of passing

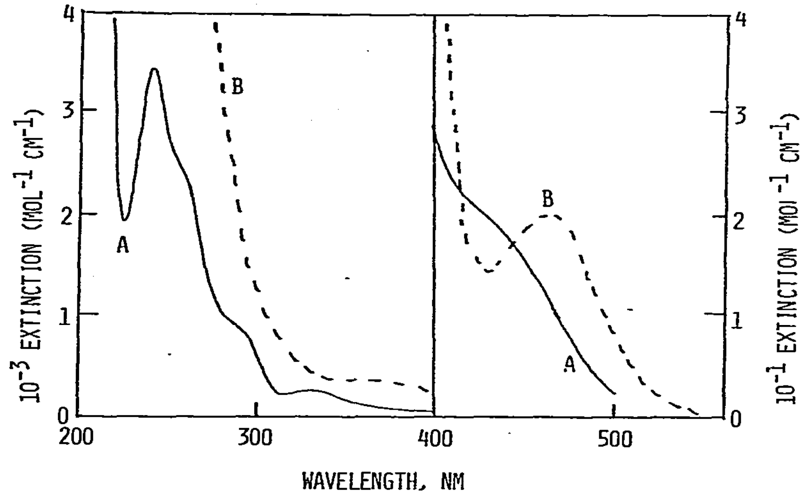


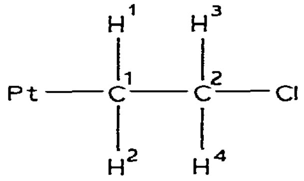
Fig. 1. Spectra of (A) $[PtCl_3(C_2H_4)]^-$ (I) and (B) $[PtCl_5(CH_2CH_2Cl)]^{2-}$ (II).

Cl_2 gas through the solution for about one minute and then removing the excess Cl_2 by purging with N_2) resulted in an immediate spectral change, depicted in Fig. 1, which could be identified with Step 1 of the above sequence, i.e., with the reaction:

$$\underset{\text{(I)}}{[PtCl_3(C_2H_4)]^-} + Cl_2 + Cl^- \rightarrow \underset{\text{(II)}}{[PtCl_5(CH_2CH_2Cl)]^{2-}} \quad (4)$$

Confirmation of the 1/1 stoichiometry of the reaction is provided by the results of spectral titrations such as that depicted by Fig. 2. The species II, whose spectrum is depicted in Fig. 1, was stable in concentrated aqueous HCl (*ca.* 12 mol) for a period of at least a week and could be isolated from such solutions as the stable cesium salt, $Cs_2[PtCl_5(CH_2CH_2Cl)]$, which was characterized analytically (C, H, Cl).

$[PtCl_5(CH_2CH_2Cl)]^{2-}$ was characterized in concentrated aqueous HCl solution by ^{13}C and ^1H NMR spectroscopy, the spectra (Figs. 3 and 4) being assignable to the structural unit V. ^{13}C NMR: δ(C(1)) 29.4 (accompanied by ^{195}Pt satellites), J(Pt—C(1)) 444 Hz, J(H(1,2)—C(1)) 150 Hz. δ(C(2)) 46.3 (expectedly close to δ 45.6 for CH_2ClCH_2Cl), J(H(3,4)—C(2)) 159 Hz. ^1H NMR (in D_2O): Two broad multiplets which could be simulated (Fig. 4) for the AA′BB′ structure V using the values, δ(H(1)) = δ(H(2)) = 4.11, δ(H(3)) = δ(H(4)) = 3.92, J(H(1)—H(2)) —7.4 Hz, J(H(3)—H(4)) —10 Hz, J(H(1)—H(4)) = J(H(2)—H(3)) = 12.9 Hz, J(H(1)—H(3)) = J(H(2)—H(4)) = 4.3 Hz, J(Pt—H(1)) = J(Pt—H(2)) = 82 Hz. (These assignments are based on the assumption that the large coupling to Pt is associated with the α-protons, H(1) and H(2).



(V)

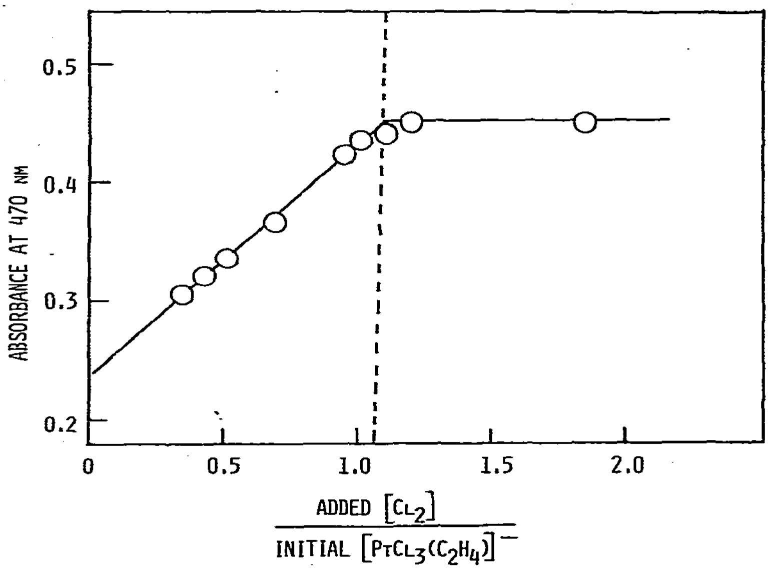
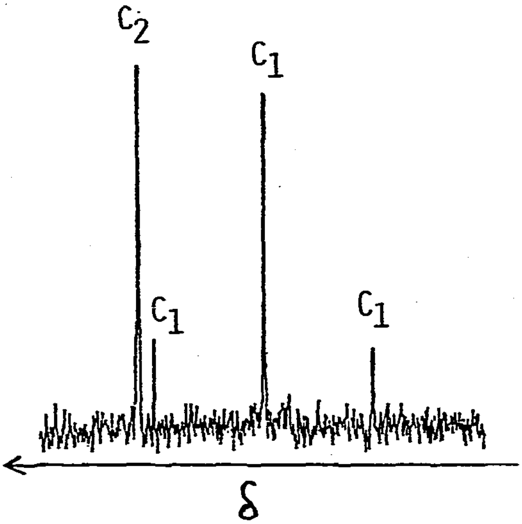


Fig. 2. Spectral titration of 5.0×10^{-3} mol $[PtCl_3(C_2H_4)]^-$ with Cl_2 in aqueous 1 mol HCl (5 cm path length).



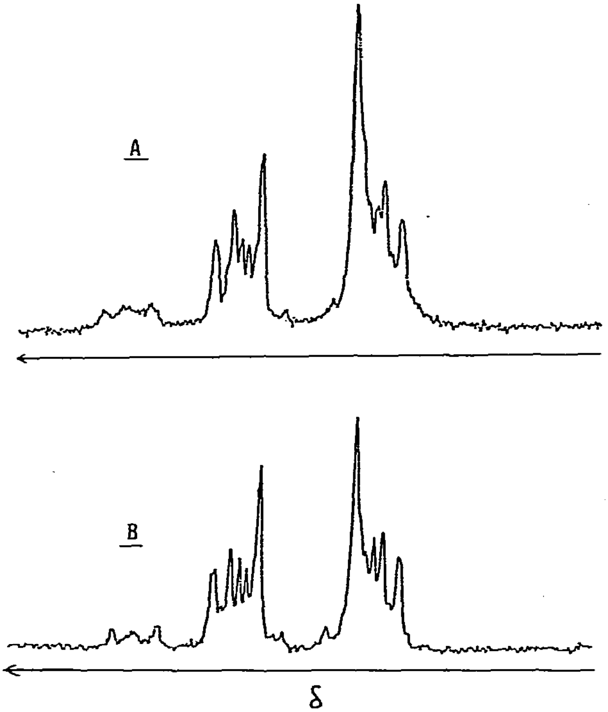


Fig. 3. ^{13}C NMR spectrum of $[PtCl_5(CH_2CH_2Cl)]^{2-}$ (see text for interpretation and parameters).

Fig. 4. ^1H NMR (270 MHz) spectra of $[PtCl_5(CH_2CH_2Cl)]^{2-}$ in D_2O. (A) Experimental. (B) Simulated (see text for explanation and parameters).

Reaction 4 proved too fast for reliable kinetic measurements even by the stopped flow method.

Description of Step 2

The second stage of the reaction sequence, depicted by eq. 5, proceeded over a period of *ca.* 48 h at room temperature. As expected, no significant change in the UV-visible spectrum accompanied this reaction which could, however, readily be monitored by ^1H NMR. At very low Cl^- concentrations, reaction 5 went essentially to completion and III could be isolated as the stable cesium salt, $Cs_2[PtCl_5(CH_2CH_2OH)]$, which was characterized analytically (C, H, Cl).

$$\underset{\text{(II)}}{[PtCl_5(CH_2CH_2Cl)]^{2-}} + H_2O \rightarrow \underset{\text{(III)}}{[PtCl_5(CH_2CH_2OH)]^{2-}} + H^+ + Cl^- \qquad (5)$$

$[PtCl_5(CH_2CH_2OH)]^{2-}$ was characterized in aqueous solution by ^{13}C and ^1H NMR spectroscopy, the spectra (Figs. 5 and 6) being consistent with the structure VI. ^{13}C NMR: $\delta(C(1))$ 24.8 (accompanied by ^{195}Pt satellites), $J(Pt—C(1))$ 477 Hz, $J(H(1)—C(1))$ 144 Hz. $\delta(C(2))$ 64.0 (expectedly close to δ 63.5 for CH_2OHCH_2OH), $J(H(2)—C(2))$ 148 Hz. ^1H NMR (in D_2O): $\delta(H(1))$ 3.99 (t,

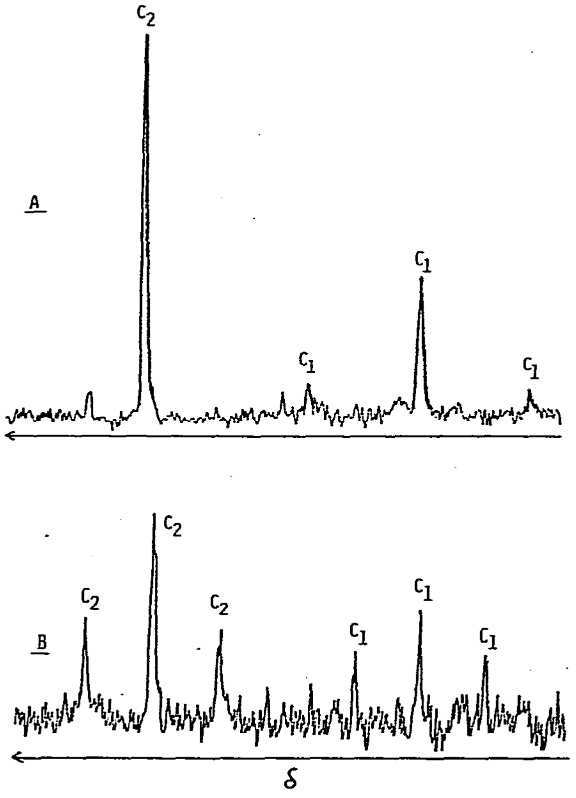


Fig. 5. ^{13}C NMR spectrum of $[PtCl_5(CH_2CH_2OH)]^{2-}$ (A) Proton decoupled. (B) Proton coupled. (See text for interpretation and parameters. ^{195}Pt satellites are not discernable in the proton coupled spectrum.)

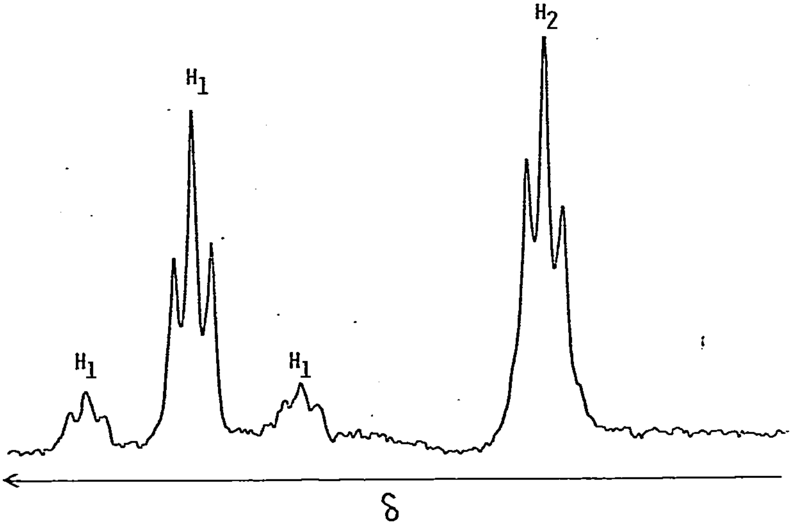
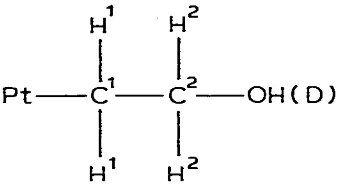


Fig. 6. ^{1}H NMR (270 MHz) spectrum of $[PtCl_5(CH_2CH_2OD)]^{2-}$ in D_2O. (See text for explanation and parameters.)

2 H, accompanied by ^{195}Pt satellites), J(Pt—H(1)) 85 Hz, J(H(2)—H(1)) 7.1 Hz. δ(H(2)) 3.48 (t, 2 H).



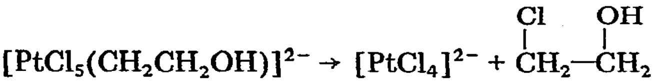
$$Pt-\overset{H^1}{\underset{H^1}{C^1}}-\overset{H^2}{\underset{H^2}{C^2}}-OH(D)$$

(VI)

The reversibility of reaction 5 was demonstrated by redissolving some precipitated $Cs_2[PtCl_5(CH_2CH_2OH)]$ in concentrated aqueous HCl and observing the back-conversion of $[PtCl_5(CH_2CH_2OH)]^{2-}$ to $[PtCl_5(CH_2CH_2Cl)]^{2-}$ by ^{1}H NMR.

Description of Step 3

The final stage of the reaction sequence, i.e., the "reductive-elimination" step depicted by eq. 6, required several weeks to go to completion at room temperature in *ca.* 1 mol HCl, but was accelerated markedly by warming the solution (half-life approximately 3 h at 50°C and a few minutes at 100°C). The final conversion to $[PtCl_4]^{2-}$ (identified and estimated spectrophotometrically) and CH_2ClCH_2OH (identified and estimated by ^{1}H NMR and GLC) was essentially quantitative (yields >85% and >95%, respectively). No CH_2ClCH_2Cl (a minor product of the direct oxidation of C_2H_4 by Cl_2 under comparable conditions) could be detected by either ^{1}H NMR or GLC, demonstrating that the reaction did not proceed *via* elimination of C_2H_4 and Cl_2-oxidation of the latter. At very high concentrations of $[PtCl_5(CH_2CH_2OH)]^{2-}$ and very low Cl^- concentrations (no excess Cl^-) the formation of CH_2ClCH_2OH was accompanied by formation of some CH_2OHCH_2OH.



$$[PtCl_5(CH_2CH_2OH)]^{2-} \rightarrow [PtCl_4]^{2-} + \overset{Cl}{\overset{|}{CH_2}}—\overset{OH}{\overset{|}{CH_2}} \qquad (6)$$

Preliminary kinetic measurements on the "reductive elimination" reaction (eq. 6) suggest that the principal path, at least at relatively high Cl^- concentrations ($\gtrsim 0.5$ mol), is Cl^--dependent according to the second-order rate-law of eq. 7 with $k_7 \approx 6 \times 10^{-5}$ mol^{-1} sec^{-1} at 50°C (independent of $[H^+]$).

$$-d[PtCl_5(CH_2CH_2OH)^{2-}]/dt \approx k_7[PtCl_5(CH_2CH_2OH)^{2-}][Cl^-] \qquad (7)$$

Other observations

The addition of excess NaOH to an aqueous solution containing $[PtCl_5(CH_2CH_2OH)]^{2-}$ (or a mixture of the latter and $[PtCl_5(CH_2CH_2Cl)]^{2-}$, resulted in the formation of ethylene oxide in >80% yield along with an unidentified platinum(II) compound. This reaction appeared to be faster than the formation of ethylene oxide by addition of NaOH to a solution of CH_2ClCH_2OH; hence it is concluded that the latter is not an intermediate in the reaction.

The reaction of Cl_2 with $[PtCl_3(C_2H_4)]^-$ also was examined in anhydrous methanol. The formation of $[PtCl_5(CH_2CH_2Cl)]^{2-}$ was confirmed by ^1H NMR but no further reaction occurred for several days. Thus, water appears to be required to induce the further steps leading to oxidation of the coordinated C_2H_4. (This is consistent with an earlier report pertaining to attempts to oxidize $[PtCl_3(C_2H_4)]^-$ with Cl_2 in chloroform or nitrobenzene [9].) The original stoichiometric reaction of Cl_2 with $[PtCl_3(C_2H_4)]^-$ in anhydrous methanol (i.e., that corresponding to eq. 4) appears to be reversible since, upon standing for about a month, the resulting solution of $[PtCl_5(CH_2CH_2Cl)]^{2-}$ reverted to $[PtCl_3(C_2H_4)]^{2-}$, presumably by loss of Cl_2.

Some preliminary experiments also were attempted on the oxidation of other platinum(II)-olefin complexes by Cl_2. Under conditions comparable to those for $[PtCl_3(C_2H_4)]^-$, the reaction of $[PtCl_3(CH_3CH{=}CH_2)]^-$ yielded acetone as the principal organic oxidation product, apparently through organometallic intermediates analogous to II and/or III which were, however, only qualitatively characterized.

Discussion

The results described above conclusively demonstrate that the oxidation of $[PtCl_3(C_2H_4)]^-$ by Cl_2 in aqueous solution to yield $[PtCl_4]^{2-}$ and CH_2ClCH_2OH (eq. 2) proceeds according to the mechanistic sequence depicted by eq. 3, with the formation of the remarkably stable organometallic intermediates II and III which have been intercepted and characterized.

Since it is known that C_2H_4 reacts directly with $[PtCl_4]^{2-}$ to regenerate $[PtCl_3(C_2H_4)]^-$ (eq. 8), the combination of reactions 4, 5, 6 and 8 are, accordingly, demonstrated to constitute a *catalytic cycle* for the highly selective oxidation of C_2H_4 by Cl_2 to CH_2ClCH_2OH (eq. 9).

$$[PtCl_4]^{2-} + CH_2{=}CH_2 \rightarrow [PtCl_3(CH_2{=}CH_2)]^- + Cl^- \quad (8)$$

$$CH_2{=}CH_2 + Cl_2 + H_2O \rightarrow CH_2ClCH_2OH + H^+ + Cl^- \quad (9)$$

Several points arising from our observations warrant further comment, notably:

1. A *plausible* mechanism for reaction 4 involves the oxidative-addition of Cl_2, followed by nucleophilic attack of Cl^- on the resulting platinum(IV)-olefin complex, as depicted by eq. 10. Unfortunately, this reaction proved to be too fast for reliable kinetic measurements.

$$[Pt^{II}Cl_3(CH_2{=}CH_2)]^- \xrightarrow{Cl_2} [Pt^{IV}Cl_5(CH_2{=}CH_2)]^- \xrightarrow{Cl^-} [Pt^{IV}Cl_5(CH_2CH_2Cl)]^{2-} \quad (10)$$

2. Step 2 of the reaction sequence 3 (i.e., reaction 5) proceeds at a much higher rate than solvolysis of a simple organic primary alkyl chloride under comparable conditions. While this reaction could conceivably proceed through an indirect olefin "elimination-reinsertion" sequence it seems likely that the mechanism involves a simple solvolytic nucleophilic displacement whose rate is enhanced by the β-Pt substituent. Unfortunately, reaction 5 is insufficiently rapid compared with the final decomposition step (reaction 6) to permit either its equilibrium or kinetics to be examined quantitatively.

3. The difference between the ^1H NMR patterns of $[PtCl_5(CH_2CH_2Cl)]^{2-}$ and $[PtCl_5(CH_2CH_2OH)]^{2-}$ (i.e., $AA'BB'$ *vs.* A_2B_2) implies a higher degree of restriction of rotation about the C—C bond in the former case. While such $AA'BB'$ patterns are not uncommon among compounds of the type CH_2XCH_2Y, the reasons for the differences between these two closely related cases are unclear. It is unlikely that steric factors alone are responsible. A possible explanation may be that the more hydrophilic character of the CH_2CH_2OH group (relative to CH_2CH_2Cl) confers greater freedom of motion on the former in the aqueous medium.

4. The Cl^- dependence of the rate of the final step (i.e., eq. 6) suggests that this "reductive-elimination" reaction actually proceeds through nucleophilic displacement at the Pt-bonded alkyl group by an external Cl^- ion (eq. 11,12). This is consistent with earlier suggestions [10,11] that the mechanism of the reverse reaction, i.e., of "oxidative-addition" of organic halides to low-valent d^8 metals such as iridium(I), also involves nucleophilic displacement. Susceptibility to nucleophilic attack apparently is a common feature of alkyl groups bonded to high-valent metal ions [12,13].

$$[Pt^{IV}Cl_5(CH_2CH_2OH)]^{2-} + Cl^- \rightarrow [Pt^{II}Cl_5]^{3-} + CH_2ClCH_2OH \quad (11)$$

$$[Pt^{II}Cl_5]^{3-} \rightarrow [Pt^{II}Cl_4]^{2-} + Cl^- \quad (12)$$

In view of the occurrence of reaction 6 the failure to observe comparable reactivity for $[PtCl_5(CH_2CH_2Cl)]^{2-}$ (i.e., according to eq. 13) is somewhat surprising, although the direction of the reactivity difference is consistent with the expected greater activating influence of an OH substitutent (relative to Cl) on a nucleophilic displacement such as reaction 11.

$$[PtCl_5(CH_2CH_2Cl)]^{2-} \rightarrow [PtCl_4]^{2-} + CH_2ClCH_2Cl \quad (13)$$

Experimental

Materials. $K[PtCl_3(C_2H_4)] \cdot H_2O$ was prepared by reacting $[PtCl_4]^{2-}$ with C_2H_4 in the presence of a catalytic amount of $SnCl_2$ as described elsewhere [14]. Solutions of Cl_2 were prepared by passing Cl_2 gas through aqueous 1 mol HCl for a few minutes, and were subsequently analyzed at frequent intervals by titration against $Na_2S_2O_3$.

Spectra. UV-visible spectra were recorded with a Cary 14 spectrophotometer. ^1H NMR spectra (both continuous wave and Fourier transform) were determined with a Bruker HS270 spectrometer. ^1H chemical shifts (δ, ppm) are reported relative to $(CH_3)_3SiC_2H_4COONa$ (1% w/v) as an internal reference. ^{13}C NMR spectra were determined with a Transform Technology TT14 spectrometer. ^{13}C chemical shifts were measured relative to CH_2OHCH_2OH (δ 63.5) and are reported relative to TMS.

Analyses. Elemental analyses were performed by Galbraith Laboratories, Inc. GLC analyses were performed on a Varian Aerograph 14 chromatograph using a flame ionization detector and a Poropak Q column (80/100 mesh, 4 ft. by 1/8 in.).

Isolation of intermediates. $Cs_2[PtCl_5(CH_2CH_2Cl)]$ was prepared by suspending $K[PtCl_3(C_2H_4)] \cdot H_2O$ (0.2 g) in concentrated HCl (0.5 ml) into which Cl_2 was passed for about 30 s. The salt dissolved completely and, after a few minutes, the excess Cl_2 was removed by passing a stream of N_2 through the solution. The product was precipitated by dropwise addition of a saturated solution of CsCl in concentrated HCl.

$Cs_2[PtCl_5(CH_2CH_2OH)]$ was prepared by suspending $K[PtCl_3(C_2H_4)] \cdot 2\ H_2O$ (0.6 g) in D_2O (1.5—2.0 ml) and passing Cl_2 into the solution for about 15 s. The salt dissolved and the solution took on a deeper yellow colour. After two minutes Cl_2 was again passed into the solution to ensure completion of the reaction and excess Cl_2 was removed with a stream of N_2. When the ^1H NMR spectrum of the solution showed that all the $[PtCl_5(CH_2CH_2Cl)]^{2-}$ had been consumed (after 36—48 h at toom temperature) a saturated solution of CsCl was added dropwise until no further precipitation occurred. The precipitate was filtered, washed sparingly with a sequence of ice-cold water, ethanol and ether, and dried in air or under vacuum.

Acknowledgements

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