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"Mechanism and Stereochemistry for Nucleophilic Attack at Carbon of Platinum (IV) alkyls: Model Reactions for Hydrocarbon Oxidation with Aqueous Platinum Chlorides"

by

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13. ABSTRACT (Maximum 200 words) Reactions of $[PtCl_4]^{2-}$ with RI (R = CH ₃ , CH ₂ CH ₂ OH) in water yield $[PtCl_5R]^{2-}$ which were isolated as their NMe ₄ salts. They decompose in aqueous chloride solution to give ROH and RCl. <i>erythro</i> - and <i>threo</i> - $[PtCl_5(CHDCHDOH)]^{2-}$ are obtained by oxidation of $[PtCl_3(cis\text{- and } trans\text{-CHD=CHD)]^-$ respectively. Kinetic rate laws and stereochemistry support S _N 2 displacement by Cl ⁻ or H ₂ O as the mechanism of the decomposition reactions.					
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Mechanism and Stereochemistry for Nucleophilic Attack at Carbon of Platinum(IV) Alkyls: Model Reactions for Hydrocarbon Oxidation with Aqueous Platinum Chlorides.

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Abstract

Reactions of $[\text{PtCl}_4]^{2-}$ with RI (R = CH₃, CH₂CH₂OH) in water yield $[\text{PtCl}_5\text{R}]^{2-}$ which were isolated as their NMe₄ salts. They decompose in aqueous chloride solution to give ROH and RCl. *erythro*- and *threo*- $[\text{PtCl}_5(\text{CHDCHDOH})]^{2-}$ are obtained by oxidation of $[\text{PtCl}_3(\text{cis- and trans-CHD=CHD})]^{-}$ respectively. Kinetic rate laws and stereochemistry support S_N2 displacement by Cl⁻ or H₂O as the mechanism of the decomposition reactions.

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Mechanism and Stereochemistry for Nucleophilic Attack at Carbon of Platinum(IV) Alkyls: Model Reactions for Hydrocarbon Oxidation with Aqueous Platinum Chlorides.

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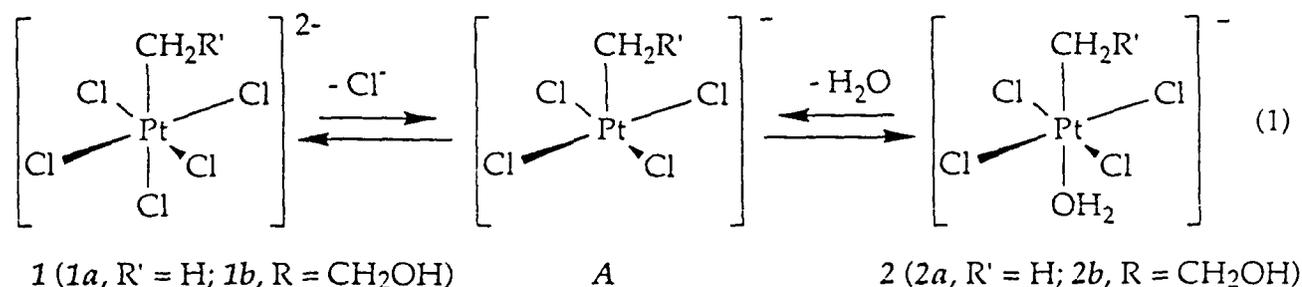
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We¹ and others² have recently confirmed the original reports by Shilov³ that aqueous solutions of a mixture of $[\text{PtCl}_4]^{2-}$ and $[\text{PtCl}_6]^{2-}$ are capable of functionalizing the C-H bonds of substrates including methane, initially producing a mixture of alcohols and alkyl chlorides. The working mechanistic scheme invokes the following general features: (1) electrophilic C-H activation to generate a platinum(II) alkyl, (2) oxidation to a platinum(IV) alkyl and (3) nucleophilic attack by water or chloride displacing platinum(II) and generating the product alcohol or alkyl chloride. In this article we report the preparation, isolation and characterization of methyl and β -hydroxyethyl derivatives of chloroplatinum(IV) along with the results of our investigations of the mechanism for nucleophilic attack by water or chloride. The rates and stereochemistry provide some of the first firm support for the latter stages of this working mechanistic scheme.

Water soluble platinum(IV) alkyls have been prepared using a modification of the method described by Zamashchikov *et al.*⁴ Oxidative addition of ICH_3 or $\text{ICH}_2\text{CH}_2\text{OH}$ to $\text{K}_2[\text{PtCl}_4]$ in water yields a complex mixture of insoluble $[\text{PtI}_2]_x$, KCl and platinum(IV) alkyls, from which orange or yellow $[\text{NMe}_4]_2[\text{PtCl}_5\text{R}]$ ($\text{R} = \text{CH}_3; \text{CH}_2\text{CH}_2\text{OH}$) may be isolated. These platinum alkyls are the postulated intermediates in the oxidation of methane (to CH_3OH and CH_3Cl) and ethanol (to $\text{HOCH}_2\text{CH}_2\text{OH}$ and $\text{ClCH}_2\text{CH}_2\text{OH}$), respectively.¹

^1H and ^{195}Pt NMR data and electrospray ionization mass spectrometry⁵ indicate an equilibrium ($K^a = 0.9 \text{ M}$ at 25°)⁶ mixture of $[\text{PtCl}_5\text{R}]^{2-}$ and $[\text{PtCl}_4(\text{H}_2\text{O})\text{R}]^-$ for aqueous solutions containing excess chloride (eq 1). As shown, it is most likely that the ligand trans to the alkyl substituent of these low spin d^6 complexes undergoes rapid dissociative exchange via five coordinate intermediate A.



Over a period of several hours at 25° in water $[\text{PtCl}_5\text{R}]^{2-}$ decomposes to $[\text{PtCl}_{4-x}(\text{H}_2\text{O})_x]^{(2-x)-}$ and a mixture of either methanol and methyl chloride or ethylene glycol and 2-chloroethanol. Addition of sodium chloride increases the rate of decomposition as well as the relative amount of alkyl chloride product, suggesting competitive (H_2O vs. Cl^-) nucleophilic attack at carbon of the platinum(IV) alkyl. At $[\text{Cl}^-] > 0.5 \text{ M}$, $>95\%$ methyl chloride formation from $[\text{PtCl}_5(\text{CH}_3)]^{2-}$ is observed. Reaction kinetics for nucleophilic displacement of Pt(II) by water and chloride, followed by both ^1H NMR spectrometry and uv-visible spectroscopy ($\lambda_{\text{max}} = 364 \text{ nm}$ for $[\text{PtCl}_5(\text{CH}_3)]^{2-}$; 366 nm for $[\text{PtCl}_5(\text{CH}_2\text{CH}_2\text{OH})]^{2-}$), are well behaved, and a rate law of the form shown in equation 3 has been established.⁷



$$\frac{d[1+2]}{dt} = k_{\text{obs}}[1+2], \quad k_{\text{obs}} = \frac{k_1[\text{Cl}^-] + k_2[\text{H}_2\text{O}]}{1 + K^{-1}[\text{Cl}^-]} \quad (3)$$

The value of K for the methyl complex **1a** determined from the kinetics at 45° is $1.0 M$, in good agreement with the spectroscopic value. The kinetics do not distinguish between nucleophilic attack at intermediate **A** or aquo complex **2**. Since the first possibility corresponds to the microscopic reverse of the accepted mechanism for oxidative addition of methyl halides to square planar d^8 complexes, it is therefore perhaps more reasonable. The ratio of the second order rate constants for attack at methyl for chloride and water at 45° , $[k_1/k_2]_{1a} = 4.5 \times 10^3$ may be compared to that for S_N2 displacement on methyl bromide (600).⁸ The corresponding ratio for attack at β -hydroxyethyl, $[k_1/k_2]_{1b} = 9.0 \times 10^2$.

The most definitive supporting evidence for an S_N2 mechanism is inversion of stereochemistry at carbon. Oxidation of Zeise's salt, $[\text{PtCl}_3(\text{CH}_2=\text{CH}_2)]^-$, with $[\text{PtCl}_6]^{2-}$ in water cleanly affords a mixture of **1b** and **2b**.⁹ Similar oxidation of $[\text{PtCl}_3(\textit{trans-}$ and $\textit{cis-}$ $\text{CHD}=\text{CHD})]^-$ give primarily¹⁰ *erythro*- and *threo*- $[\text{PtCl}_5\text{CHDCHDOH}]^{2-}$ respectively. This stereochemistry is as expected for external attack by water at ethylene subsequent to oxidation of Zeise's salt, as observed with olefin complexes of palladium.¹¹ Treatment of the *erythro* isomer with chloride affords primarily *threo*- ClCHDCHDOH ($^3J_{\text{HH}} = 5 \text{ Hz}$), which on conversion to 2,3-dideuteroethylene oxide gives $85 \pm 5\%$ *cis*-isomer¹² (Scheme); again the opposite results are obtained from *threo*. The stereochemistry for the overall oxidation of *trans*-1,2-dideuteroethylene to *cis*-2,3-dideuteroethylene oxide has also been demonstrated under Wacker conditions using $\text{CuCl}/\text{PdCl}_2$ systems;¹³ however, in the present study the stereochemistry of each intermediate in the sequence of three reactions, each proceeding with inversion, may be examined.

Both kinetics and stereochemistry thus support an S_N2 mechanism for the last step in the sequence leading to functionalization (hydroxylation or chlorination) of alkanes by aqueous platinum systems. Studies aimed at extending these reactions to other types of functionalization, and to making these reactions catalytic in platinum, are in progress.

Acknowledgment. This work was supported by the Office of Naval Research. We thank Dr. A.P. Bruins at the University of Groningen for measuring the electrospray ionization mass spectra.

Supplementary Material: Experimental details describing the syntheses of 1a and 1b and their precursors, details of the measurements of reaction kinetics and derivation of rate laws (5 pages). Ordering information is given on any current masthead page.

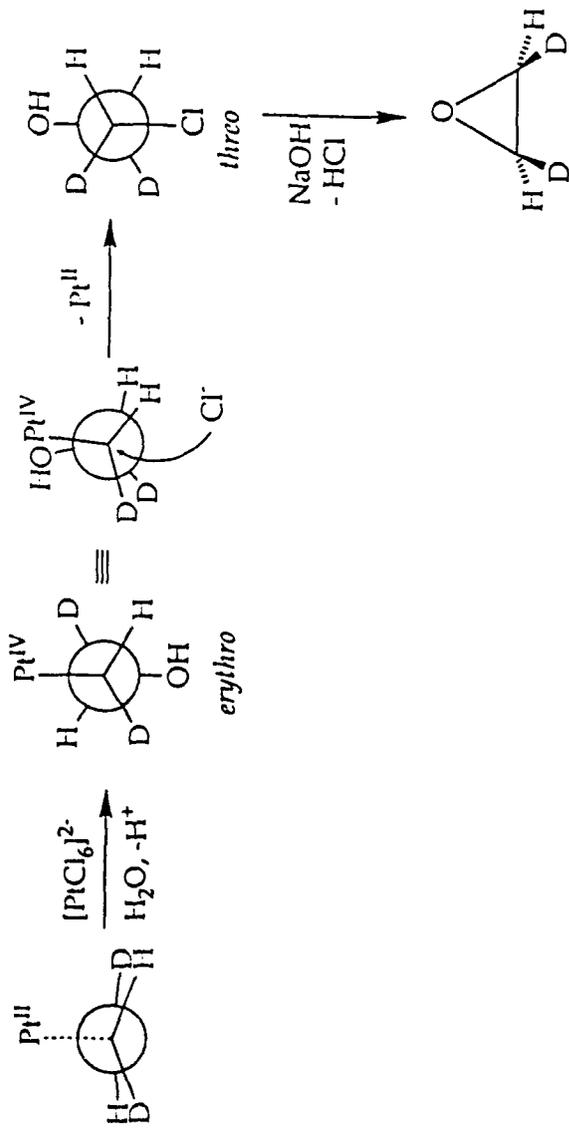
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6. ^{195}Pt NMR gives a value of $K^b \approx 0.7 M$; however, the ratio of signals observed in the ^1H spectrum appears to depend upon concentration and ionic strength in a complex manner.
7. Reaction of Cl^- with 1a was previously reported ((a) Zamashchikov, V. V.; Mitchenko, S. A.; Rudakov, E. S.; Pekhtereva, T. M. *Koord. Khim.* 1985, 11, 69. (b) Zamashchikov, V. V.; Mitchenko, S. A. *Kinet. Katal.* 1983, 24, 254.). The rate law and rate agrees approximately with our findings, but the competitive attack by water and our mechanistic

interpretation were not found in the earlier work. Our results for attack of Cl^- and H_2O at **1b** are in accord with the preliminary, qualitative results reported by Halpern and Jewsbury (ref. 8).

8. Swain, C. G.; Scott, C. B. *J. Am. Chem. Soc.* 1953, 75, 141.
9. Halpern and Jewsbury have also reported conversion of Zeise's salt to a mixture of $[\text{PtCl}_5(\text{CH}_2\text{CH}_2\text{X})]^{2-}$ ($\text{X} = \text{Cl}, \text{OH}$), employing chlorine as oxidant: Halpern, J.; Jewsbury, R. A. *J. Organomet. Chem.* 1979, 181, 223. We find other oxidants (e.g. ClO_3^- , H_2O_2) are other effective oxidizing reagents. On the other hand, $[\text{PtCl}_4]^{2-}$ appears to react with Zeise's salt only slowly, eventually producing a mixture of acetic acid and acetaldehyde. $[\text{PtCl}_5(\text{CH}_2\text{CH}_2\text{Cl})]^{2-}$ does not undergo nucleophilic attack under these conditions; the large vicinal coupling constant of $[\text{PtCl}_5(\text{CHDCH}_2\text{DCl})]^{2-}$ (14 Hz) indicates that the rotamer proposed in the Scheme as the reactive state is much less accessible.
10. ^1H NMR indicates roughly 90% *erythro* ($^3J_{\text{HH}} = 8$ Hz) and 10% *threo* ($^3J_{\text{HH}} = 6$ Hz) from the *trans* isomer, and the opposite distribution from *cis*. The coupling constants agree with those extracted from the AA'XX' patterns of the all-protio complexes⁹ within experimental accuracy.
11. (a) Stille, J.K.; James, D.E. *J. Am. Chem. Soc.* 1975, 97, 674. (b) Stille, J.K.; Divakaruni, R. *J. Organomet. Chem.* 1979, 169, 239. (c) Henry, P.M. *Adv. Organomet. Chem.* 1975, 13, 363.
12. Determined by infrared spectroscopy as described in Whinnery, Jr., L. L.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* 1991, 113, 7575.
13. Bäckvall, J. E.; Åkermark, B.; Ljunggren, S.O. *J. Am. Chem. Soc.* 1979, 101, 2411.

Scheme



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Supplementary Material

General. NMR spectra were recorded on GE300, Jeol FNM400, and Bruker AM500 spectrometers. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer. UV-Vis spectra were recorded on a HP 8452A spectrophotometer, the cuvet holder was electronically thermostated with a HP 89090A instrument. Platinum salts were obtained from Aldrich (with the exception of Na_2PtCl_4 , which was obtained from Aesar). All other reagents were obtained commercially and used without further purification. Micro analysis were performed by Galbraith Laboratories or Fenton Harvey of this department. Given values are the average of two independent determinations.

Ion exchange. All ion exchange experiments were performed on a column prepared as described below. A chromatography column (\varnothing 1 cm) was charged with 5 g of cationic resin (Bio-Rad AG 50W-X2, 50-100 mesh, 5.2 meq/g, hydrogen form) and treated with a solution prepared from 6 g NMe_4OH in 150 mL of water. Subsequently, the column was washed with deionized water until the eluant had $\text{pH} = 7$.

Synthesis of $\text{K}_x\text{Cl}_y\text{Pt}(\text{CH}_3)$. K_2PtCl_4 , 4.0 g (9.6 mmol) was suspended in 50 mL water. CH_3I (500 mL, 8 mmol) was added, and soon a brownish-black precipitate formed. After stirring for 6 h the water was removed in vacuum and residue extracted with methanol until washings were colorless (approx 500 mL). After evaporation to dryness of the methanolic solution, 1.9 g of a dark yellow powder remained. AgNO_3

(3.0 g) was dissolved in water and treated with 5 mL conc. HCl. The solid AgCl so formed was thoroughly washed with water to remove excess chloride. The yellow powder was dissolved in 40 mL water and added to the freshly prepared AgCl. The slurry was stirred, and a sample was taken periodically for analysis by uv-visible spectroscopy. After approximately 4 h the absorption at 430 nm had disappeared. The mixture was filtered, and the filtrate was evaporated to dryness. The yellow residue was extracted with methanol and evaporated to dryness. Yield 1.3 g of yellow powder. IR (cm^{-1}): 1400 (bm), 1230 (s), 1020 (w), 803 (w), 570 (w). ^1H NMR (D_2O): 3.08 ppm (s, $^2J(\text{Pt-H})$ 78 Hz). ^{13}C NMR (D_2O): 3.67 ppm (q, $^1J(\text{C-H})$ 145 Hz, $^1J(\text{C-Pt})$ 462 Hz). ^{195}Pt NMR (D_2O): -780 ppm. Anal. Calc. for $\text{PtKCl}_4(\text{CH}_3)(\text{H}_2\text{O})\cdot(\text{KCl})_{3.7}$: Pt, 29.38; K, 27.68; Cl, 41.11; C 1.8. Found: Pt, 29.38; K, 27.64; Cl, 38.38; C, 1.65.

Synthesis of $[\text{NMe}_4]_2[\text{PtCl}_5(\text{CH}_3)]$ (1a). $\text{K}_x\text{Cl}_y\text{Pt}(\text{CH}_3)$ (200 mg) was dissolved in 4 mL of water and loaded on an ion exchange column charged with NMe_4^+ ions as described above. A yellow band, following a orange band, was collected after elution with water. The solution was evaporated to dryness in vacuum leaving an orange colored solid. The solid was repeatedly washed with ethanol to remove excess NMe_4Cl . The residue was dissolved in methanol (30 mL) and filtered. Approx 2 mL of a saturated solution of NMe_4Cl in methanol was added and the resulting pale orange precipitate collected on a filter. Yield 34 mg. IR (KBr, cm^{-1}): 3448 (b,m), 3021 (vs), 2927 (m), 1488 (vs), 1460 (w), 1420 (w), 1291 (s), 1215 (m), 953 (s). Uv-vis (water, 25 $^\circ\text{C}$): $\lambda_{\text{max}} = 364$, $\epsilon_{\text{mol}} = 142$ (4) L/mol(cm); $\lambda_{\text{max}} = 462$, $\epsilon_{\text{mol}} = 25$ (2) L/mol(cm). Anal. Calc. for $\text{PtCl}_5(\text{CH}_3)(\text{N}(\text{CH}_3)_4)_2$: C, 20.18; H, 5.08; N, 5.23. Found: C, 20.03; H, 4.82; N, 4.99.

Synthesis of $\text{K}_x\text{Cl}_y\text{Pt}(\text{CH}_2\text{CH}_2\text{OH})$. K_2PtCl_4 (3.42 g, 8.24 mmol) was dissolved in 20 mL of water and 2-iodoethanol (430 μL , 5.5 mmol) was added. After approx. 0.5 h the solutions darkened, and a dark precipitate was formed. The mixture was left overnight and filtered. The red filtrate was evaporated to dryness in vacuum, and the residue was extracted with methanol (2 x 25 mL). From the residue 2.24 g (5.4 mmol) of K_2PtCl_4 was re-isolated. The yellow methanol fraction was evaporated to dryness, yielding a yellow powder with NMR spectra (in D_2O) indicative of the $[\text{PtCH}_2\text{CH}_2\text{OH}]$ moiety. The powder was dissolved in 20 mL of water and added to freshly precipitated AgCl. The slurry was stirred for 2 h, filtered and the filtrate evaporated to dryness. Yield 332 mg yellow powder. The compound was stored at

-60°. IR (KBr, cm^{-1}): 3450 (b), 2978 (w), 2929 (m), 1414 (s), 1384 (s), 1242 (m), 1167 (m), 1071 (m), 968 (w), 917 (s), 825 (w), 788 (w), 550 (w,b).

Synthesis of $[\text{NMe}_4]_2[\text{PtCl}_5(\text{CH}_2\text{CH}_2\text{OH})]$ (1b). $\text{K}_x\text{Cl}_y\text{Pt}(\text{CH}_2\text{CH}_2\text{OH})$ (300 mg) was dissolved in approximately 5 mL water and loaded onto an ion exchange column charged with NMe_4^+ ions as described above. A yellow band was collected (20 mL) after elution with deionized water. The solution was concentrated to approximately 3 mL. During this process a yellow precipitate was formed which was collected on a filter. Yield 111 mg. The ^1H NMR spectrum (D_2O) corresponds to the one reported in *ref* 9. IR (KBr, cm^{-1}): 3048 (m), 3575 (b,s), 3020 (m), 2937 (m), 1482 (vs), 1439 (w), 1403 (w), 1384 (s), 1261 (w), 1170 (s), 1071 (s), 990 (m), 950 (vs), 913 (vs), 797 (m), 654 (w), 473 (w). Uv-vis (water, 25°): $\lambda_{\text{max}} = 366$, $\epsilon_{\text{mol}} = 190$ (5) L/mol(cm); $\lambda_{\text{max}} = 464$, $\epsilon_{\text{mol}} = 22$ (3) L/mol(cm). Anal. Calc. for $\text{PtCl}_5(\text{CH}_2\text{CH}_2\text{OH})(\text{N}(\text{CH}_3)_4)_2$: C, 21.23; H, 5.17; N, 4.95. Found: C, 16.30; H, 3.79; N, 3.65. The C:H:N ratios agree exactly with expected values, but all are too low, suggesting the compound is contaminated with an as-yet-unidentified species that contains none of those elements.

Conditions for Kinetic Measurements by Uv-Vis Spectroscopy. Kinetic measurements were performed in 1 cm glass cuvetts in the thermostated cuvet holder of the spectrophotometer. Spectra were recorded at preset intervals in the wavelength region between 250 and 500 nm, using the HP 89531A software packet. In all cases isosbestic points were observed at approximately 395, 440 and 490 nm.