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

Gerrit A. Luinstra, Jay A. Labinger,* and John E. Bercaw*

Arnold and Mabel Beckman
Laboratories of Chemical Synthesis
California Institute of Technology
Pasadena, California 91125

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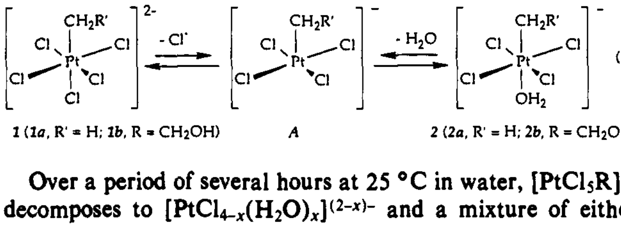
We[1] and others[2] have recently confirmed the original reports by Shilov[3] that aqueous solutions of a mixture of $[PtCl_4]^{2-}$ and $[PtCl_6]^{2-}$ are capable of functionalizing the C–H bonds of substrates including methane, initially producing a mixture of alcohols and alkyl chlorides. The working 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 ICH_2CH_2OH to $K_2[PtCl_4]$ in water yields a complex mixture of insoluble $[PtI_2]_x$, KCl, and platinum(IV) alkyls, from which orange $[NMe_4]_2[PtCl_5R]$ (R = CH_3; CH_2CH_2OH) may be isolated. These platinum alkyls are the postulated intermediates in the oxidation of methane (to CH_3OH and CH_3Cl) and ethanol (to $HOCH_2CH_2OH$ and $ClCH_2CH_2OH$), respectively.[1]

^1H and ^{195}Pt NMR data and electrospray ionization mass spectrometry[5] indicate an equilibrium (K_a = 0.9 M at 25 °C)[6] mixture of $[PtCl_5R]^{2-}$ and $[PtCl_4(H_2O)R]^-$ for aqueous solutions containing excess chloride (eq 1). As shown, it is most likely that the ligand trans to the alkyl substituents of these low-spin d^6 complexes undergoes rapid dissociative exchange via five-coordinate intermediate **A**.



(1)

1 (*1a*, R' = H; *1b*, R = CH₂OH) *A* *2* (*2a*, R' = H; *2b*, R = CH₂OH)

Over a period of several hours at 25 °C in water, $[PtCl_5R]^{2-}$ decomposes to $[PtCl_{4-x}(H_2O)_x]^{(2-x)-}$ 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 $[Cl^-] > 0.5$ M, >95% methyl chloride formation from $[PtCl_5(CH_3)]^{2-}$ is observed. Reaction kinetics for nucleophilic displacement of Pt(II) by water and chloride, followed by both ^1H NMR spectrometry and UV-visible spectroscopy (λ_{max} = 364 nm for $[PtCl_5(CH_3)]^{2-}$, 366 nm for $[PtCl_5(CH_2CH_2OH)]^{2-}$), are well behaved, and a rate law of the form shown in eq 3 has been established.[7]

$$1 \underset{H_2O}{\overset{K}{\rightleftarrows}} 2 + Cl^- \qquad (2)$$

$$\frac{d[1+2]}{dt} = k_{obs}[1+2], \quad k_{obs} = \frac{k_1[Cl^-] + k_2[H_2O]}{1 + K^{-1}[Cl^-]} \qquad (3)$$

The value of K for the methyl complex **1a** determined from the kinetics at 45 °C 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 °C, $[k_1/k_2]_{1a} = 4.5 \times 10^3$, may be compared to that for S_N2 displacement on methyl bromide (600).[8] The corresponding ratio for attack at β-hydroxyethyl is $[k_1/k_2]_{1b} = 9.0 \times 10^2$.

The most definitive supporting evidence for an S_N2 mechanism is inversion of stereochemistry at carbon. Oxidation of Zeise's salt, $[PtCl_3(CH_2{=}CH_2)]^-$, with $[PtCl_6]^{2-}$ in water cleanly affords a mixture of **1b** and **2b**.[9] Similar oxidation of $[PtCl_3$(*trans-* and *cis*-CHD=CHD)$]^-$ give primarily[10] *erythro-* and *threo-*$[PtCl_5CHDCHDOH]^{2-}$, 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 ($^3J_{HH}$ = 6 Hz), which on conversion to 2,3-dideuterioethylene oxide gives 85 ± 5% cis-isomer[12] (Scheme I); again the opposite results are obtained from threo. The stereochemistry for the overall oxidation of *trans*-1,2-dideuterioethylene to *cis*-2,3-dideuterioethylene oxide has also been demonstrated under Wacker conditions using $CuCl/PdCl_2$

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† Contribution No. 8750.

(1) (a) Labinger, J. A.; Herring, A. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 5628. (b) Labinger, J. A.; Herring, A. M.; Lyon, D. K.; Luinstra, G. A.; Bercaw, J. E.; Horváth, I. T.; Eller, K. *Organometallics*, submitted for publication.

(2) Sen, A.; Lin, M.; Kao, L.-C.; Hutson, A. C. *J. Am. Chem. Soc.* **1992**, *114*, 6385.

(3) Kushch, K. A.; Lavrushko, V. V.; Misharin, Yu. S.; Moravsky, A. P.; Shilov, A. E. *New J. Chem.* **1983**, *7*, 729.

(4) (a) Zamashchikov, V. V.; Kitaigorodskii, A. N.; Litvinenko, S. L.; Rudakov, E. S.; Uzhik, O. N.; Shilov, A. E. *Izv. Akad. Nauk. SSSR, Ser. Khim* **1985**, *8*, 1730. (b) Zamashchikov, V. V.; Litvinenko, S. L.; Shologon, V. I. *Kinet. Katal.* **1987**, *28*, 1059 and references cited therein.

(5) Katta, V.; Chowdhury, S. K.; Chait, B. T. *J. Am. Chem. Soc.* **1990**, *112*, 5348.

(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 agree 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 9).

(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 $[PtCl_5(CH_2CH_2X)]^{2-}$ (X = Cl, OH), employing chlorine as oxidant: Halpern, J.; Jewsbury, R. A. *J. Organomet. Chem.* **1979**, *181*, 223. We find that other oxidants (e.g., ClO_3^-, H_2O_2) are also effective oxidizing reagents. On the other hand, $[PtCl_4]^{2-}$ appears to react with Zeise's salt only slowly. $[PtCl_5(CH_2CH_2Cl)]^{2-}$ does not undergo nucleophilic attack under these conditions; the large vicinal coupling constant of $[PtCl_5(CHDCHDCl)]^{2-}$ (14 Hz) indicates that the rotamer proposed in Scheme I as the reactive state is much less accessible.

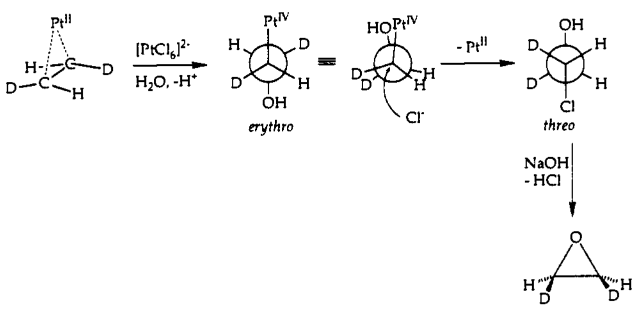
(10) ^1H NMR indicates roughly 90% erythro ($^3J_{HH}$ = 8 Hz) and 10% threo ($^3J_{HH}$ = 6 Hz) from the trans isomer and the opposite distribution from the cis. The coupling constants agree with those extracted from the AA'XX' patterns of the all-protio complexes[9] within experimental accuracy.

(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, L. L., Jr.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 7575.

0002-7863/93/1515-3004$04.00/0

Scheme I



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.

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Supplementary Material Available: 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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(13) Bäckvall, J. E.; Akermark, B.; Ljunggren, S. O. *J. Am. Chem. Soc.* **1979**, *101*, 2411.