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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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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. Microanalyses 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 columm prepared as described below. A chromatography columm (Ø 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 columm was washed with deionized water until the eluant had pH = 7.

Synthesis of $K_xCl_yPt(CH_3)$. K_2PtCl_4, 4.0 g (9.6 mmol) was suspended in 50 mL water. CH_3I (500 μL, 8 mmol) was added, and soon a brownish-black precipitate formed. After stirring for 6 h the water was removed in vacuum and the 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(Pt-H) 78 Hz). ^{13}C NMR (D_2O): 3.67 ppm (q, ^1J(C-H) 145 Hz, ^1J(C-Pt) 462 Hz). ^{195}Pt NMR (D_2O): -780 ppm ($[PtCl_4(CH_3)(H_2O)]^-$), -822 ppm ($[PtCl_5(CH_3)]^{2-}$), relative to $[PtCl_6]^{2-}$ = 0. Anal. Calc. for $PtKCl_4(CH_3)(H_2O)\cdot(KCl)_{3.7}$: 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 $[NMe_4]_2[PtCl_5(CH_3)]$ (1a). $K_xCl_yPt(CH_3)$ (200 mg) was dissolved in 4 mL of water and loaded on an ion exchange columm 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 °C): λ_{max} = 364, ε_{mol} = 142 (4) L/mol(cm); λ_{max} = 462, ε_{mol} = 25 (2) L/mol(cm). Anal. Calc. for $PtCl_5(CH_3)(N(CH_3)_4)_2$: C, 20.18; H, 5.08; N, 5.23. Found: C, 20.03; H, 4.82; N, 4.99.

Synthesis of $K_xCl_yPt(CH_2CH_2OH)$. 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 [$PtCH_2CH_2OH$] 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 $[NMe_4]_2[PtCl_5(CH_2CH_2OH)]$ (1b). $K_xCl_yPt(CH_2CH_2OH)$ (300 mg) was dissolved in approximately 5 mL water and loaded onto an ion exchange columm 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 sample was further purified by dissolving in methanol, adding a saturated solution of $[NMe_4]Cl$ in methanol, and adding ethanol to precipitate an orange powder, which was filtered off and dried. The ^1H NMR spectrum (D_2O) corresponds to the one reported in *ref.* 9. ^{195}Pt NMR (D_2O): -731 ppm ($[PtCl_4(CH_2CH_2OH)(H_2O)]^-$), -750 ppm ($[PtCl_5(CH_2CH_2OH)]^{2-}$), relative to $[PtCl_6]^{2-}$ = 0. 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°): λ_{max} = 364, ε_{mol} = 150 (5) L/mol(cm); λ_{max} = 468, ε_{mol} = 20 (3) L/mol(cm). Anal. Calc. for $PtCl_5(CH_2CH_2OH)(N(CH_3)_4)_2$: C, 21.23; H, 5.17; N, 4.95. Found: C, 20.90; H, 4.99; N, 5.07.

Conditions for Kinetic Measurements by Uv-Vis Spectroscopy. Kinetic measurements were performed in 1 cm glass cuvets 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.

Derivation of Rate Laws. We have:

$$\mathbf{1} \underset{}{\overset{K_1}{\rightleftharpoons}} \mathbf{A} + Cl^- \overset{K_2}{\rightleftharpoons} \mathbf{2} + Cl^-$$

where **1**, **2** and **A** are as defined in eq 1 of the main text.

Disappearance of starting complex, as monitored by UV-visible spectroscopy, follows:

$$d[Pt_{total}]/dt = - k_{obs}[Pt_{total}]$$

In case 1, [**A**] is negligible, and products are formed from **2** according to:

$$\mathbf{2} + Cl^- \xrightarrow{k_1} RCl + Pt^{II}$$

$$\mathbf{2} + H_2O \xrightarrow{k_2} ROH + Pt^{II}$$

$$d[Pt_{total}]/dt = - (k_1[Cl^-] + k_2)[\mathbf{2}]$$

$$[\mathbf{2}][Cl^-]/[\mathbf{1}] = K_1K_2 \qquad [\mathbf{1}] = [\mathbf{2}][Cl^-]/K_1K_2$$

$$[Pt_{total}] = [\mathbf{1}] + [\mathbf{2}] = [\mathbf{2}]([Cl^-]/K_1K_2 + 1)$$

$$d[Pt_{total}]/dt = - \frac{(k_1[Cl^-] + k_2)[Pt_{total}]}{[Cl^-]/K_1K_2 + 1}$$

$$k_{obs} = \frac{k_1[Cl^-] + k_2}{[Cl^-]/K_1K_2 + 1}$$

In case 2, products are formed from **A** according to

$$\mathbf{A} + Cl^- \xrightarrow{k_1} RCl + Pt^{II}$$

$$\mathbf{A} + H_2O \xrightarrow{k_2} ROH + Pt^{II}$$

$$d[Pt_{total}]/dt = - (k_1[Cl^-] + k_2)[\mathbf{A}]$$

$$[\mathbf{A}][Cl^-]/[\mathbf{1}] = K_1 \qquad [\mathbf{1}] = [\mathbf{A}][Cl^-]/K_1$$

$$[\mathbf{2}]/[\mathbf{A}] = K_2 \qquad [\mathbf{2}] = K_2[\mathbf{A}]$$

$$[Pt_{total}] = [1] + [2] + [A] = [A]([Cl^-]/K_1 + K_2 + 1)$$

$$d[Pt_{total}]/dt = -\frac{(k_1[Cl^-] + k_2)[Pt_{total}]}{[Cl^-]/K_1 + K_2 + 1}$$

$$k_{obs} = \frac{k_1[Cl^-] + k_2}{[Cl^-]/K_1 + K_2 + 1}$$

But if [**A**] is very small, then $K_2 >> 1$, so

$$k_{obs} \approx \frac{k_1[Cl^-] + k_2}{[Cl^-]/K_1 + K_2}$$

$$= \frac{(k_1[Cl^-] + k_2)/K_2}{[Cl^-]/K_1K_2 + 1}$$

which has the same form as that derived for case 1: the apparent equilibrium constant extracted from kinetic data will be equal to K_1K_2, the macroscopic constant relating [**1**] and [**2**], in either case, while the apparent individual rate constants will be either the actual rate constants or $1/K_2$ times those values for cases 1 and 2 respectively.

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