Oxidation of Dimethylplatinum(II) Complexes with Alcohols: Synthesis and Characterization of Alkoxoplatinum(IV) Complexes

Patrick K. Monaghan and Richard J. Puddephatt*

Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7

Received August 11, 1983

The complexes $[PtMe_2(N N)]$, N N = 2,2'-bipyridyl or 1,10-phenanthroline, react with alcohols (ROH, R = Me, Et, i-Pr) to give alkoxoplatinum complexes, characterized as $[PtMe_2(OR)(N N)(OH_2)]^+OH^-$, while water gives similar hydroxoplatinum(IV) complexes [PtMe₂(OH)(N N)(OH₂)]⁺OH⁻. The complexes are characterized by elemental analysis, by IR and NMR spectroscopy, by conductivity, and by conversion to derivatives $[PtMe_2(OR)(N N)(OH_2)]^+X^-$, where $X = PF_6$, ClO_4 , or BPh_4 , and to $[PtMe_2(OMe)Cl(phen)]$, when R = Me and N = phen. The alkoxoplatinum(IV) bond is inert to solvolysis with alcohols, water, and dilute perchloric acid.

Introduction

There has been much interest in the activation of alcohols and of water in catalysis by interaction with transition-metal complexes, and several approaches to this problem have been made. 1-4 One approach has involved oxidative addition. 5-13 Alcohols can react with low oxidation state complexes of tungsten, for example, by oxidative addition of the RO-H bond in both mononuclear and polynuclear compounds.⁵⁻⁷ In addition, tungstenocene can apparently insert into a C-H bond of methanol (or possibly the C-O bond) to give ultimately $[W(\eta - C_5H_5)_2Me(OMe)].^5$ In oxidative addition of water to platinum(0) complexes, the hydroxide ligand in the product is weakly bonded to the "soft" metal center and is easily displaced (eq 1, L = P-i-Pr₃, S = solvent).8

$$PtL_2 + H_2O \rightleftharpoons PtH(OH)L_2 \stackrel{\underline{S}}{\rightleftharpoons} [PtH(S)L_2]^+OH^-$$
 (1)

With soft metal atoms, water thus protonates the metal center. $^{8-14}$ The first alkoxoplatinum(II) complexes were prepared by oxidative addition of methanol to a platialkyne complex (eq 2, PP Ph₂PCH₂CH₂PPh₂). ^{12,13} The PtOMe grouping is reactive,

giving the corresponding hydroxo derivative with water and the methoxycarbonyl derivative with CO.12 Both alkoxo and hydroxo derivatives of platinum(II) act as strong bases, as illustrated by reactions such as that of eq

$$trans-[Pt(OH)Ph(PPh_3)_2] + Me_2CO \xrightarrow{-H_2O} trans-[PtPh(CH_2COMe)(PPh_3)_2] (3)$$

Platinum(II) complexes with bridging alkoxo ligands are apparently less reactive, but β -hydride eliminations can lead to formation of platinum hydrides. 17-21

In this article some reactions of the complexes $[PtMe_2(N N)]$, where N N = 2,2'-bipyridyl or 1,10phenananthroline, with alcohols and with water are reported. The reactions with alcohols are of particular interest because they represent the first examples of oxidation of platinum(II) complexes with alcohols and because they give the first stable alkoxoplatinum(IV) complexes. The only simple platinum(IV) alkoxide reported previously is the complex [PtMe₃(OMe)]₄, which is air-sensitive and incompletely characterized,²² whereas the new complexes reported here are remarkably robust. A preliminary account of parts of this work has been published.²³

Results and Discussion

Reactions with Alcohols. The complexes [PtMe2-(bpy)] (I) and [PtMe2(phen)] (II) are red solids, the color being due to the presence of a metal to ligand chargetransfer band in the visible region of the spectrum.²⁴ The complexes are electron-rich and are among the most re-

⁽¹⁾ Isnard, P.; Denise, B.; Sneeden, R. P. A.; Cognion, J. M.; Durual, P. J. Organomet. Chem. 1982, 240, 169.

⁽²⁾ Drury, D. J.; Green, M. J.; Ray, D. J. M.; Stevenson, A. J. J. Organomet. Chem. 1982, 236, C23.
(3) Thompson, M. S.; Meyer, T. J. J. Am. Chem. Soc. 1982, 104, 4106.

Balzani, V.; Moggi, I.; Manfrin, M. F.; Bolletta, F.; Gleria, M. Science (Washington, D.C.) 1975, 189, 852.

 ⁽⁴⁾ Forster, D. Adv. Organomet. Chem. 1979, 17, 255.
 (5) Farrugia, L.; Green, M. L. H. J. Chem. Soc., Chem. Commun. 1975,

⁽⁶⁾ Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Abdul-Malik, K. M. J. Chem. Soc., Dalton Trans. 1981,

⁽⁷⁾ Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Leonelli, J.; Little, D. J. Am. Chem. Soc. 1981, 103, 779.
(8) Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. J. Am.

Chem. Soc. 1979, 101, 2027 (9) Yoshida, T.; Okano, T.; Ueda, Y.; Otsuka, S. J. Am. Chem. Soc.

^{1981, 103, 3411} (10) Yoshida, T.; Okano, T.; Saito, K.; Otsuka, S. Inorg. Chim. Scta

^{1980, 44,} L135 (11) Yoshida, T.; Okano, T.; Otsuka, S. J. Am. Chem. Soc. 1980, 102, 5966.

⁽¹²⁾ Bennett, M. A.; Yoshida, T. J. Am. Chem. Soc. 1978, 100, 1750. (13) Bennett, M. A.; Robertson, G. B.; Whimp, P. O.; Yoshida, T. J. Am. Chem. Soc. 1973, 95, 3028.

⁽¹⁴⁾ Gerlach, D. H.; Kane, A. R.; Parshall, G. W.; Jesson, J. P.; Muetterties, E. L. J. Am. Chem. Soc. 1971, 93, 3543.

⁽¹⁵⁾ Arnold, D. P.; Bennett, M. A. J. Organomet. Chem. 1980, 199, 119.
(16) Michelin, R. A.; Napoli, M.; Ros, R. J. Organomet. Chem. 1979,

⁽¹⁷⁾ Clark, H. C.; Goel, A. B. J. Organomet. Chem. 1979, 178, C27. (18) Goel, A. B.; Goel, S. Transition Met. Chem. (Weinheim, Ger.)

^{1980, 5, 378.}

⁽¹⁹⁾ Siedle, A. R.; Pignolet, L. H. Inorg. Chem. 1982, 21, 3090.
(20) Giordano, F.; Vitagliano, A. Inorg. Chem. 1981, 20, 633.
(21) Goel, A. B.; Goel, S.; Vanderveer, D. G. Inorg. Chim. Acta 1981, 54, L169.

⁽²²⁾ Ivanova, O. M.; Gel'man, A. D. Zh. Neorg. Khim. 1958, 3, 1334. (23) Monaghan, P. K.; Puddephatt, R. J. Inorg. Chim. Acta 1982, 65, L59.

⁽²⁴⁾ Chaudhury, N.; Puddephatt, R. J. J. Organomet. Chem. 1975, 84,

Table I. 1H and 13C NMR Data

		Table I. 'H and 'C NMR Data				
	PtMe		PtOR a		ÑNь	
complex	δ	2 $J(PtH)/Hz$	δ	$J/{ m Hz}$	δ	$J/{ m Hz}$
Me Pr N 2 3	1.14	86			9.28 (H ₆) ^c 7.52 (H ₅) 8.02 (H ₄) 8.06 (H ₃)	$\begin{array}{c} 5.2 \; (J_{56}), 1.5 \; (J_{46}) \\ 7.2 \; (J_{45}), 1.5 \; (J_{34}) \\ 7.7 \; (J_{34}) \end{array}$
$[PtMe_2(OMe)(bpy)(OH_2)]^{+d}$	1.71	73	2.75	$41.0~(J_{\rm PtH})$	$9.04 (H_6)^e$ $7.67 (H_5)$ $8.06 (H_4)$ $8.20 (H_3)$	$\begin{array}{c} 5.0 \; (J_{sc}) \\ 8.0 \; (J_{4s}), 1.3 \; (J_{3s}) \\ 7.5 \; (J_{34}) \end{array}$
[PtMe2(OEt)(bpy)(OH2)]+ f	1.80	72.5	2.90 (CH ₂) 0.74 (CH ₃)	$rac{14\ (J_{ m PtH})}{7\ (J_{ m HH})}$	9.03 (H ₆) ^g 7.67 (H ₅) 8.05 (H ₄) 8.20 (H ₃)	$\begin{array}{c} 5 \ (J_{56}), \ 1.5 \ (J_{46}) \\ 8 \ (J_{45}), \ 1.3 \ (J_{35}) \\ 8 \ (J_{34}) \end{array}$
$[PtMe_2(O-i-Pr)(bpy)(OH_2)]^+$	1.82	73	2.84 (CH) 0.60 (CH ₃)	$6~(J_{\rm HH})$	9.04 (H ₆) 7.64 (H ₅) 8.05 (H ₄) 8.19 (H ₃)	$\begin{array}{ccc} 5 & (J_{56}) \\ 7 & (J_{45}) \\ 7 & (J_{34}) \end{array}$
$[PtMe_2(OH)(bpy)(OH_2)]^+$	1.84	70			9.02 (H ₆) ^h 7.90 (H ₅) 8.34 (H ₄) 8.72 (H ₃)	$\begin{array}{l} 5.5 \; (J_{56}), 1.5 \; (J_{46}) \\ 8.0 \; (J_{45}), 1.3 \; (J_{35}) \\ 8.1 \; (J_{34}) \end{array}$
Me Pt N 11 5	1.15	86.5			9.51 (H ₂) ⁱ 7.82 (H ₃) 8.63 (H ₄) 7.92 (H ₅)	$5.2 \ (J_{2,3}) \ 8.0 \ (J_{3,4}) \ 1.3 \ (J_{2,4})$
[PtMe ₂ (OMe)(phen)(OH ₂)] ⁺	1.80	72.5	2.65	$40~(J_{ m PtH})$	9.32 $(H_2)^j$ 8.03 (H_3) 8.62 (H_4) 8.07 (H_5)	$5.0 \ (J_{2,3}) \ 8.0 \ (J_{3,4}) \ 1.8 \ (J_{2,4})$
$[PtMe_2(OEt)(phen)(OH_2)]^+$	1.79	73	2.85 (CH ₂) 0.59 (CH ₃)	$rac{21\ (J_{ m PtH})}{7\ (J_{ m HH})}$	9.30 (H ₂) ^k 8.01 (H ₃) 8.60 (H ₄) 8.06 (H ₅)	$5 (J_{2,3}) 7 (J_{3,4}) 2 (J_{2,4})$
$[PtMe_2(O-i-Pr)(phen)(OH_2)]^{+l}$	1.84	73	2.89 (CH) 0.48 (CH ₃)	$^{40(J_{ m PtH})}_{6(J_{ m HH})}$	9.32 (H ₂) ^m 8.0 (H ₃) 8.51 (H ₄) 7.98 (H ₅)	$egin{array}{l} 5 \ (J_{2,3}) \ 8 \ (J_{3,4}) \ 1.5 \ (J_{2,4}) \end{array}$
$[PtMe_2(OH)(phen)(OH_2)]^+$	1.73	72.5			9.30 (H ₂) 8.0 (H ₃) 8.61 (H ₄) 8.05 (H ₅)	
[PtMe ₂ (OMe)Cl(phen)]	2.03	71	2.40	$58~(J_{ m PtH})$	9.40 (H ₂) ⁿ 8.28 (H ₃) 8.99 (H ₄) 8.33 (H ₅)	$\begin{array}{c} 5 \ (J_{2,3}) \\ 8 \ (J_{3,4}) \\ 1.5 \ (J_{2,4}) \end{array}$

^a R = H, Me, Et, or *i*·Pr; solvent CD₂Cl₂. ^b N N = bpy or phen. ^c J(PtH) = 22 Hz. ^d ¹³C NMR in CD₂Cl₂: -2.30 (q, ¹J(PtC) = 701 Hz, MePt), 57.32 (q, ²J(PtC) = 18 Hz, MeOPt), 155.0 (s, C²), 123.4 (d, C³), 139.1 (d, C⁴), 126.8 (d, ³J(PtC) = 12 Hz, C⁵), 147.1 (d, ²J(PtC) = 10 Hz, C⁶). ^e J(PtH) = 14 Hz. ^f ¹³C NMR in CD₂Cl₂: -2.60 (q, ¹J(PtC) = 700 Hz, MePt), 64.0 (t, ²J(PtC) = 15 Hz, CH₂O); 19.7 (q, ³J(PtC) = 43 Hz, CH₂O, 153.3 (s, C²), 124.0 (d, C³), 139.6 (d, C⁴), 126.8 (d, C⁵). ^g J(PtH) = 13 Hz. ^h J(PtH) = 16 Hz. ⁱ J(PtH) = 12 Hz. ^k J(PtH) = 15 Hz. ^l ¹³C NMR in CD₂Cl₂: 2.0 (Hz) 2.7 (CH) 2.7 (CH) 2.3 (PtC) = 20 \text{ Hz} 1.47 2 (C³), 125.5 (C³), 128.6 (CC), 127.9 (C⁵) $-2.9 (^{1}J(PtC) = 720 \text{ Hz}, MePt), 68.6 (CH), 27.4 (CH₃C, ^{3}J(PtC) = 20 \text{ Hz}), 147.2 (C²), 125.5 (C³), 138.6 (C⁴), 127.9 (C⁵), 147.1 (C¹¹), 127.9 (C¹²). <math>^{m}J(PtH) = 16 \text{ Hz}.$ $^{n}J(PtH) = 12 \text{ Hz}.$

active of noble-metal complexes in oxidative addition reactions. 25-28 A solution of [PtMe2(bpy)] in methanol was initially yellow-orange in color, but the color slowly faded to very pale yellow. Evaporation of the solution gave a pale yellow oil, from which a tan solid could be obtained, with difficulty, by precipitation from CH₂Cl₂ solution with

(25) Jawad, J. K.; Puddephatt, R. J. J. Organomet. Chem. 1976, 117,

pentane. The complex was hygroscopic, and we have been unable to grow crystals, despite many attempts. Similar compounds were formed in ethanol and 2-propanol as solvents, and [PtMe₂(phen)] reacted in the same way. The complexes were not easy to characterize, and the evidence for the structure proposed, $[PtMe_2(OR)(N N)(OH_2)]^+OH^-$, is summarized below.

1. Elemental analysis (Experimental Section) was consistent with this formula. In some cases, a better agreement was obtained by including extra water of crystallization. Formulas giving the best fit with experimental analyses are given in the Experimental Section, but the number of water molecules present is difficult to determine unambiguously, given the hygroscopic nature of the compounds.31

^{297.} (26) Jawad, J. K.; Puddephatt, R. J. J. Chem. Soc., Dalton Trans.

⁽²⁷⁾ Monaghan, P. K.; Puddephatt, R. J. Inorg. Chim. Acta 1983, 76, L237.

⁽²⁸⁾ Ferguson, G.; Parvez, M.; Monaghan, P. K.; Puddephatt, R. J. J. Chem. Soc., Chem. Commun. 1983, 267.
(29) Kuyper, J. Inorg. Chem. 1977, 16, 2171; 1978, 17, 77, 1458

⁽³⁰⁾ Jawad, J. K.; Puddephatt, R. J. Inorg. Chim. Acta 1978, 31, L391.

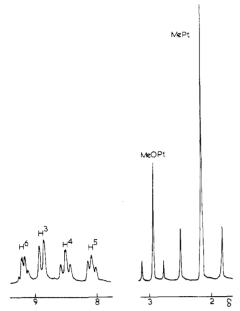


Figure 1. 1H NMR spectrum (100 MHz) of [PtMe2(OMe)-(bpy)(OH₂)][OH] in CD₃OD. For labeling of bpy protons see Table I.

2. The stereochemistry at platinum (except the presence of the OH₂ ligand) was established by NMR spectroscopy. For example, the ¹H NMR spectrum of IIIa (Table I,

III,
$$\stackrel{\frown}{N}N = bpy$$
IIIa, $\stackrel{\frown}{R} = Me$, $\stackrel{\frown}{X} = OH$
 $\stackrel{\frown}{b}$, $\stackrel{\frown}{R} = Et$, $\stackrel{\frown}{X} = OH$
 $\stackrel{\frown}{c}$, $\stackrel{\frown}{R} = i.Pr$, $\stackrel{\frown}{X} = OH$
 $\stackrel{\frown}{d}$, $\stackrel{\frown}{R} = Me$, $\stackrel{\frown}{X} = PF$
 $\stackrel{\frown}{e}$, $\stackrel{\frown}{R} = Me$, $\stackrel{\frown}{X} = PF$
 $\stackrel{\frown}{e}$, $\stackrel{\frown}{R} = Me$, $\stackrel{\frown}{X} = PF$

 $f, R = Me, X = ClO_A$

Figure 1) gave resonances due to MePt, MeO, and bpy protons in the ratio 6:3:8 as expected. The coupling constant ²J(PtH) for the MePt groups decreased from 86 Hz in I to 73 Hz in IIIa, as expected on oxidation from Pt(II) to Pt(IV).²⁶ The spectra show that the two MePt groups and the two aromatic rings of the bpy ligand are equivalent and hence that the cis-[PtMe₂N₂] structure is retained in IIIa. The assignments of bpy protons (Table I) were straightforward, using literature precedents on similar compounds, 32-37 and were confirmed by homonuclear decoupling experiments.

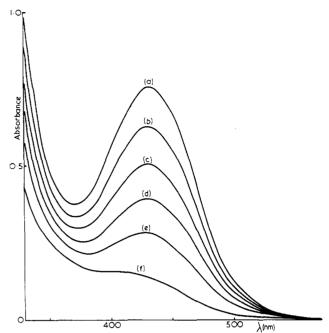


Figure 2. UV-visible spectra of [PtMe₂(bpy)] (10⁻⁴ M) in ethhanol at 21 °C: (a) t = 0, (b) $t = 23 \min$, (c) $t = 48 \min$, (d) t= 78 min, (e) t = 119 min, (f) t = 280 min.

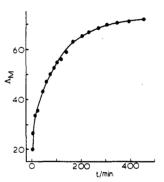


Figure 3. Molar conductivity $(\Lambda_M, \, cm^2 \, \Omega^{-1} \, mol^{-1})$ of a solution of [PtMe₂(bpy)] (10⁻³ M) in methanol as a function of time.

The presence of the methoxo ligand in IIIa was demonstrated by the observation of ¹⁹⁵Pt coupling in both the ¹H and ¹³C(¹H) NMR spectra [δ (CH₃OPt) 2.75 (³J(PtH) = 41 Hz), $\delta(CH_3OPt)$ 57.3 ($^2J(PtC)$ = 18 Hz)]. No exchange was observed when the complex was dissolved in CD_3OD or in D_2O , since the methoxo signal with ¹⁹⁵Pt coupling was still observed in the ¹H NMR spectrum. Remarkably, the D₂O solution could be made 0.1 M in HClO₄, and the MeOPt group was still present as evidenced by an unchanged ¹H NMR spectrum.

¹H NMR data for complexes III and IV are given in Table I, which also contains 13C{1H} NMR data for complexes IIIa, IIIb, and IVc. The assignments are straightforward and confirm the structural conclusions discussed above for the particular case of IIIa.

The presence of OH groups in the products was indicated by broad resonances of varying chemical shift in the ¹H NMR spectra of solutions in CDCl₃ or CD₂Cl₂, but these gave no structural information. In CD₃OD or D₂O solutions, the presence of OH groups was demonstrated by increased intensity of the solvent OH resonances, indicating H for D exchange with solvent.

A simple oxidative addition of alcohol RO-H groups should lead to formation of Pt-H groups, but no high-field resonances were seen in the ¹H NMR spectra (or the ²H NMR spectra on the product of reaction of I with CH₃OD).

⁽³¹⁾ Repeat analyses on samples from different syntheses gave carbon analyses that differed by up to 1%

⁽³²⁾ Castellano, S.; Günther, H.; Ebersole, S. J. Phys. Chem. 1965, 69,

⁽³³⁾ Saito, T.; Ariki, M.; Uchida, Y.; Misono, A. J. Phys. Chem. 1967,

 ⁽³⁴⁾ Gillard, R. D.; Lyons, J. R. J. Chem. Soc., Chem. Commun. 1973,
 585. Bielli, E.; Gillard, R. D.; James, D. W. J. Chem. Soc., Dalton Trans.
 1976, 1837. Bielli, E.; Gidney, P. M.; Gillard, R. D.; Heaton, B. T. Ibid.
 1974, 2133. Gillard, R. D. Coord. Chem. Rev. 1975, 16, 67. Al-Obaidi, K. H.; Gillard, R. D.; Kane-Maguire, L. A. P.; Williams, P. A. Transition Met. Chem. (Weinheim, Ger.) 1977, 2, 64. (35) Farver, O.; Monsted, O.; Nord, G. J. Am. Chem. Soc. 1979, 101,

⁽³⁶⁾ Wernberg, O.; Hazell, A. J. Chem. Soc., Dalton Trans. 1980, 973. (37) Könnecke, A.; Lippmann, E.; Mlochowski, J.; Sliwa, W. Org. Magn. Rescn. 1979, 12, 696.

The absence of Pt-H groups was also indicated by the IR spectra that contained no peaks in the 2000 cm⁻¹ region.

- 3. The UV-visible spectra (see Figure 2) of III and IV contain no MLCT band in the region 350-500 nm, confirming that oxidation of Pt(II) to Pt(IV) has occurred.²⁴⁻²⁶
- 4. The ionic nature of the products was first demonstrated by conductivity measurements. The conductivity of a 10^{-3} M solution of I in methanol increased as reaction occurred (Figure 3) to a limiting value of $\Lambda_{\rm M}=76.5$ cm² Ω^{-1} mol⁻¹, in the range (though toward the low end) expected for a 1:1 electrolyte.³⁸ For example, LiCl (10^{-3} M) gave $\Lambda_{\rm M}=88$ cm² Ω^{-1} mol⁻¹ in methanol.

Confirmation of the ionic nature was obtained by isolation of the complexes IIId-f with noncoordinating anions. The ¹H NMR spectra of these complexes were identical with those of IIIa, indicating that the cation was the same.

An equilibrium of the form shown in eq 4 might be expected, but the isomeric form IIIa must be favored.

If VI were formed, exchange of coordinated MeOH with CD_3OD or D_2O would be expected in IIIa but was not observed. However, the equilibrium IIIA \rightleftharpoons V may explain why the conductivity is somewhat lower than a typical 1:1 electrolyte. It follows from the proposed equilibrium III or IV \rightleftharpoons V that complexes IIIa-c or IVa-c should act as bases. This was confirmed. A 10^{-2} M solution of IVb in ethanol had a pH of 10.3, indicating that it is a somewhat stronger base than sodium acetate (pH 9.3 at 10^{-2} M). The solution of IVb could be titrated in a 1:1 molar ratio with dilute HCl solution.

5. The chief problem in characterization at this stage was to confirm the presence of the H_2O or HO^- ligand on platinum. This is difficult to do directly, as already shown by others.⁸⁻¹³ The most direct evidence came from a reaction of IVa in methanol with an equimolar amount of anhydrous HCl, giving the reaction of eq 5.

$$\begin{bmatrix}
Me & N \\
Me & N
\end{bmatrix} + HCI \longrightarrow \begin{bmatrix}
Me & N \\
Me & N
\end{bmatrix}, VII (5)$$

The product VII was sufficiently volatile to give a parent ion in the electron-impact mass spectrum (see Experimental Section for details), whereas the ionic complexes III and IV failed to give platinum-containing species in their mass spectra. The 1H NMR spectrum of VII (Table I) was very similar to that of IVa except that the coupling constant $^3J(PtH) = 58$ Hz associated with the MeOPt group was higher than that for IVa, with $^3J(PtH) = 41$ Hz, due to the lower trans influence of chloride. 15

Treatment of IIIa or IVa with lithium chloride in methanol or with aqueous HCl solution gave mixtures of complexes that could not be separated.

Since the chloride ligand in VII is definitely present, it follows that there must be a ligand, OH_2 or OH^- , trans to the methoxo group in complexes III and IV.

6. The stoichiometry of the reaction requires that hydrogen should be formed, and this was confirmed for the

Table II. Observed First-Order Rate Constants for Reaction of I or II with Alcohols at 21 °C a

complex	alcohol	λ/nm b	104kobsd/s-1 c
Ī	MeOH	430	3.3
I	EtOH	430	1.6
I	i PrOH	430	0.45
II	MeOH	416	3.85
II	EtOH	423	1.8

^a Using alcohols as solvent. ^b Wavelength used to monitor reactions. ^c Observed first-order rate constants.

reaction of II with methanol by GC analysis. Thus the initial reactions are described by eq 6.

$$[PtMe2(NN)] + 3MeOH \xrightarrow{-H2} [PtMe2(OMe)(NN)(MeOH)][MeO] (6)$$

¹H NMR spectra of products, obtained by removing solvent from crude reaction mixtures, show additional methoxy resonances that are not present after purification by repeated precipitations. We suggest that the coordinated MeOH and free methoxide undergo rapid exchange with adventitious water to give complexes IIIa or IVa, during the workup procedure.

Rates of Reaction with Alcohols. Rates of reaction of I or II with alcohols were easily determined, using the pure alcohols as solvent, by monitoring the decay of the MLCT band in the UV-visible spectra due to I or II as the reactions progressed (Figure 2). Results are given in Table II. It can be seen that complexes I and II are very similar in reactivity and that the reactivity of the alcohols follows the series MeOH > EtOH > i-PrOH. This is the same as the series of acidities, p K_a , of the alcohols.³⁹ The rate of reaction of [PtMe₂(bpy)] with methanol was not affected by the presence of NaI (4 × 10⁻² M) or LiCl (2 × 10⁻² M).

Reactions with Water. When a solution of I or II in acetone was treated with water, the color of the solution became pale yellow and pale yellow products were obtained by evaporation of the solvents. The complexes analyzed as $[PtMe_2(OH)(N N)(OH_2)][OH]$, (VIII, N N = bpy; IX, N N = phen] and, by analogy with the alcohol reactions described above, they are formulated in this way. The ¹H NMR spectra (Table I) and UV-visible spectra were very similar to those of III or IV except for the absence of alkoxide resonances in the NMR, and a derivative, $[PtMe_2(OH)(NN)(OH_2)][PF_6]$ (X), was prepared when N N = phen. This indicates that the platinum is largely present in the form of a monocationic complex, as for the alkoxo derivatives. The ¹H NMR spectrum of IV in CD₂Cl₂ contained a broad resonance due to OH groups at δ 1.0, and the analogous product formed from II and D_2O gave a broad resonance in the ²H NMR spectrum at δ 1.1. In neither case was coupling to 195Pt observed, and we assume that rapid exchange of protons occurs.

Conclusions

The reactions of alcohols with I or II to give III or IV have several unusual features. They differ remarkably from oxidative addition to platinum(0) complexes, in which protonation of the metal occurs and the alkoxide is either weakly bonded or remains as a counterion. It is possible that the reactions are mechanistically related, since oxidative addition of RO-H to I or II could occur to give $[PtMe_2(OR)H(NN)]$ followed by rapid reaction of the Pt-H group with protic solvent. However, there is an

⁽³⁹⁾ Lowry, T. H.; Richardson, K. S., "Mechanism and Theory in Organic Chemistry"; Harper and Row: New York, 1981; pp 262-267. Hine, J.; Hine, M. J. Am. Chem. Soc. 1952, 74, 5266.

obvious parallel with the reactions of alkali- and alkaline-earth metals with alcohols (e.g., eq 7), and it is also possible that a similar electron-transfer mechanism operates.41

$$Ca + 2ROH \rightarrow Ca(OR)_2 + H_2 \tag{7}$$

Perhaps most remarkable is the inertness of the Pt-OR bond in the products III and IV. This group fails to undergo exchange with free alcohol and is also inert to hydrolysis by water or by dilute perchloric acid. These properties are extremely unusual in metal alkoxides and must be attributed to the general kinetic inertness of platinum(IV) complexes. 42,43

Experimental Section

¹H and ¹³C{¹H} NMR spectra were recorded by using a Varian XL 100 spectrometer, using CDCl₃ or CD₂Cl₂ as solvent, unless otherwise stated. IR spectra and UV-visible spectra were recorded by using Beckman 4250 and Cary 118 spectrophotometers.

Alcohols were purified by heating under reflux with magnesium and then distilling from the resulting magnesium alkoxide solution under nitrogen. Precautions were taken to exclude moisture from reactions, but the starting materials and products were stable to oxygen and so rigorous inert-atmosphere techniques were not used.

Elemental analyses for C, H, and N were performed by Guelph Chemical Laboratories and for 0 by Canadian Microanalytical Service, Vancouver. Samples were dried under high vacuum prior to analysis.

[PtMe₂(bpy)]. To a solution of [Pt₂Me₄(μ -SMe₂)₂]⁴⁴ (0.46 g) in dry benzene (20 mL) was added 2,2'-bipyridine (0.56 g) in dry ether (15 mL). An immediate red coloration was observed. The solution was cooled to 5 °C for 16 h. The red crystals that formed were filtered off, washed with ether, and dried under vacuum; yield 80%.

[PtMe2(phen)] was prepared by the same method, and the complexes were characterized by comparison with authentic samples.24 This synthesis is considerably easier than the initial method.²⁴

 $[PtMe_2(OMe)(bpy)(OH_2)][OH]$. An orange-red solution of [PtMe₂(bpy)] (0.10 g) in dry methanol (20 mL) was stirred at room temperature until the color became yellow (5 h). The solvent was removed under vacuum to leave an oily solid. This was dissolved in CH₂Cl₂ (3 mL), pentane (10 mL) was added, and the mixture was left at 0 °C for 16 h. The product precipitated as a pale yellow-brown solid: yield 73%; mp 160 °C dec; IR $\nu(OH)$ 3450. Anal. Calcd for $C_{13}H_{20}N_2O_3Pt$: C, 34.9; H, 4.5; N, 6.3. Found: C, 35.1; H, 4.3; N, 5.7. Adducts with CD₃OD [IR ν (CD₃) 2025, 2160] and CH₃OD were prepared similarly. The following similarly were prepared [PtMe₂(OEt)(bpy)(OH₂)][OH]H₂O [IR ν (OH) 3400. Anal. Calcd for $C_{14}H_{24}N_2O_4Pt$: C, 35.1; H, 5.0; N, 5.9. Found: C, 34.7; H, 4.6; N, 5.9]; $[PtMe_2(O-i-Pr)(bpy)(OH_2)][OH]$ [Anal. Calcd for C₁₅H₂₄N₂O₃Pt: C, 37.9; H, 5.1; N, 5.9. Found: C, 37.5; H, 5.1; N, 5.4.]; $[PtMe_2(OMe)(phen)(OH_2)][OH]$ [mp 140 °C dec. Anal. Calcd for $C_{15}H_{20}N_2O_3Pt$: C, 38.2; H, 4.2; N, 5.9. Found: C, 38.0; H, 4.3; N, 5.65.]; $[PtMe_2(OEt)(phen)(OH_2)][OH]H_2O[mp]$ 110 °C dec. Anal. Calcd for $\hat{C}_{16}H_{24}\hat{N}_2O_4Pt$: C, 38.2; H, 4.8; N, 5.6; 0, 11.3. Found: C, 38.0; H, 5.1; N, 5.8; 0, 11.3.]; [PtMe₂(O-i-Pr)(OH)(phen)] [decomp pt 70 °C. Anal. Calcd for

(41) Hughes, G.; Lobb, C. R., "Comprehensive Chemical Kinetics"; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1976; Vol.

 $C_{17}H_{22}N_2O_2Pt$: C, 39.9; H, 4.6; N, 5.8. Found: C, 40.0; H, 4.6; N, 5.7.].

 $[PtMe_2(OH)(phen)(OH_2)][OH]$. To a solution of $[PtMe_2-$ (phen)] (0.03 g) in acetone (15 mL) was added distilled water (15 mL). The mixture was allowed to stand at room temperature for 5 h, and then the solvents were removed under vacuum. The residue was dissolved in the minimum volume of CH2Cl2 and was then precipitated by addition of pentane: yield 82%. Anal. Calcd for C₁₄H₁₈N₂O₃Pt: C, 36.8; H, 3.9; N, 6.1; O, 10.5. Found: C, 37.8; H, 3.7; N, 5.6; O, 10.8.

 $[PtMe_2(OH)(bpy)(OH_2)][OH]$. similarly was prepared. Anal. Calcd for C₁₂H₁₈N₂O₃Pt: C, 33.3; H, 4.2; N, 6.5. Found: C, 32.9; H, 4.3; N, 6.2.

 $[PtMe_2(OMe)(bpy)(OH_2)][PF_6]$. A solution of $[PtMe_2(bpy)]$ (0.10 g) in methanol (20 mL) was allowed to react for 5 h at room temperature. The volume was reduced to ~ 3 mL, and a solution of [NH₄][PF₆] (0.09 g) in MeOH (5 mL) was added. The product precipitated as a pale yellow solid. It was filtered off and dried under vacuum: yield 53%; mp 180 °C dec; IR ν (OH) 3450, ν (PF₆) 845, 555 cm⁻¹. Anal. Calcd for $C_{13}H_{19}F_6N_2O_2PPt$: C, 27.1; H, 3.3; N, 4.9; F, 19.8. Found: C, 26.5; H, 3.4; N, 4.7; F, 18.5.

 $[PtMe_2(OMe)(bpy)(OH_2)][BPh_4] \cdot H_2O$ similarly was prepared (from NaBPh₄); mp 153 °C dec. Anal. Calcd for C₃₇H₄₁BN₂Pt: C, 57.9; H, 5.3; N, 3.65. Found, C, 58.0; H, 4.9; N, 3.8. These materials were purified by precipitation from CH₂Cl₂ solution using n-pentane. Attempts to grow single crystals were unsuccessful by using several techniques.

 $[PtMe_2(OMe)(bpy)(OH_2)][ClO_4] \cdot 2H_2O$. A solution of [PtMe₂(bpy)] (0.12 g) in methanol (20 mL) was allowed to react for 16 h at room temperature. A solution of HClO₄ (0.1 mL) in methanol (2 mL) was added, and the solution was evaporated under vacuum. The residue was washed with ether, dissolved in CH₂Cl₂, and precipitated with pentane: yield 0.07 g; decomp pt 206 °C; IR ν (OH) 3450, ν (ClO₄) 1070–1130 cm⁻¹. Anal. Calcd for C₁₃H₂₀ClN₂O₈Pt: C, 27.7; H, 3.55; N, 5.0. Found: C, 26.8; H, 3.5;

 $[PtMe_2(OH)(bpy)(OH_2)][PF_6]$. A solution of $[PtMe_2(bpy)]$ (0.17 g, 0.4 mmol) in acetone (25 mL) and water (25 mL) was allowed to react at room temperature for 16 h. [NH₄][PF₆] (0.4 mmol) in the minimum volume of water was added to precipitate the product as a pale yellow solid: mp 195 °C dec; IR ν (OH) 3550, $\nu(PF_6)$ 848, 560. Anal. Calcd for $C_{12}H_{17}F_6N_2O_2Pt$: C, 25.7; H, 3.0; N, 5.0; P, 5.5. Found: C, 26.4; H, 3.3; N, 5.0; P, 5.35.

[PtMe₂(OMe)Cl(phen)]. A solution of [PtMe₂(phen)] (0.081 g) in methanol (35 mL) was allowed to react for 16 h at room temperature. Next, a solution of HCl in ether (0.32 mL, 0.63 M, 1:1 mol ratio) was added. After 30 min, the solvent was evaporated and the residue was recrystallised from CH₂Cl₂/pentane to give the product: mp 180-200 °C dec; mass spectrum (reporting only m/e values for ¹⁹⁵Pt, ³⁵Cl isotopomers): m/e 471 (P), 456 (P – Me), 440 (P - MeO), 425 (P - Me - MeO), 420 (P - Me - Cl), 410 (P - 2Me - MeO). The peaks at m/e 471, 456, 440, 425, and 410 all gave the expected isotope pattern, thus proving the presence of the PtCl group [35 Cl: 37 Cl = 3:1] e.g., m/e, intensity found (calcd): 468, 0.02 (0.02); 470, 0.82 (0.78); 471, 0.94 (0.94); 472, 1.00 (1.00); 473, 0.41 (0.42); 474, 0.42 (0.42); 475, 0.07 (0.07); 476, 0.06 (0.06); 477, 0.01 (0.01). Anal. Calcd for C₁₅H₁₇ClN₂OPt: C, 38.2; H, 3.6; N, 5.9. Found: C, 37.7; H, 3.9; N, 5.7.

Kinetic Studies. A solution of [PtMe2(phen)] in methanol (10⁻⁴ M) was prepared, and part of the solution was immediately transferred to a 1-cm quartz cuvette held in the cell compartment of a Cary 118 spectrophotometer at 21 °C. The decay of the absorption at 416 nm was measured with time. A graph of 1n $(A_t - A_{\infty})$ vs. time gave a good straight line plot, from which the observed rate constant, k_{obsd} (Table II), was calculated. The same method was used to obtain the results given in Table II.

Detection of Hydrogen. Methanol (5 mL) was added to [PtMe₂(phen)] (0.01 g) in a reaction vessel (10 mL) fitted with a stopcock. The mixture was frozen in liquid nitrogen, and the flask was evacuated, allowed to warm to room temperature and left for 1 day. Gaseous samples were withdrawn through a septum by using a gas-tight syringe and analyzed by GC using a 6 ft × s in. column of molecular sieve 5A on a Varian Aerograph 1400 GC. Hydrogen was detected by comparison of the retention time and from the negative response using a thermal conductivity detector with helium carrier gas.

⁽⁴⁰⁾ Note that treatment of [PtMe₂(NN)] with acids leads to formation of methane from an intermediate thought to be formed by oxidative addition, ³⁰ [PtMe₂H(N N)]⁺. In the alcohol reactions very little or no methane is detected.

⁽⁴²⁾ We considered the possibility that alcohol attack at the N N ligand, rather than at the metal, might have occurred as suggested by Gillard, 34 but challenged by others, 35,36 in related systems. However, the NMR data in particular (Table I) are not consistent with this formulation. The presence of a direct Pt-OR bond is definitely established. In reactions with CD₃OD, no H-D exchange between the bpy or phen ligand and alcohol was observed. Constable, E.C.; Seddon, K. R. J. Chem. Soc., Chem. Commun. 1982, 34.

⁽⁴³⁾ Alkylperoxoplatinum(IV) complexes have been reported recently and they are also inert.28

⁽⁴⁴⁾ Scott, J. D.; Puddephatt, R. J. Organometallics 1983, 2, 1643.

Acknowledgment. We thank NSERC (Canada) and the University of Western Ontario for financial support and Ms. J. R. McCulloch and Mr. R. H. Hill for valuable experimental assistance.

Registry No. I, 52594-52-2; II, 52594-55-5; III (R = Me), 88036-59-3; III (R = Et), 88036-60-6; III (R = I-Pr), 88036-61-7;

III (R = H), 88036-62-8; III (R = H, X = PF₆), 88036-79-7; IIIa, 88036-68-4; IIIb, 88036-69-5; IIIc, 88036-70-8; IIId, 88036-76-4; IIIe, 88036-77-5; IIIf, 88036-78-6; IV (R = Me), 88036-63-9; IV (R = Et), 88036-64-0; IV (R = i-Pr), 88036-65-1; IV (R = H), 88036-66-2; IVa, 88036-71-9; IVb, 88036-72-0; VII, 88036-67-3; VIII, 88036-75-3; IX, 88036-74-2; [PtMe₂(O-i-Pr)(OH)(phen)], 88036-73-1; [Pt₂Me₄(μ -SMe₂)₂], 79870-64-7.

Mechanism of the Photochemical Oxidation of Fe(CO)₅ and CpW(CO)₃Cl (Cp = η^5 -C₅H₅) by Chlorocarbons

Alan S. Goldman and David R. Tyler*

Department of Chemistry, Columbia University, New York, New York 10027

Received August 10, 1983

The photochemical oxidation of $CpW(CO)_3Cl$ ($Cp = \eta^5 - C_5H_5$) by carbon tetrachloride and other polychlorocarbons affords $CpW(CO)_2Cl_3$. The sole photoprocess is dissociation of CO from the complex to give $CpW(CO)_2Cl$. The major pathway of the oxidation involves the net transfer of two halogen atoms from one halocarbon molecule to the unsaturated metal complex. Pathways involving the formation of trichloromethyl radical were shown to be unimportant. In a related reaction, the photooxidation of $Fe(CO)_5$ in carbon tetrachloride gives $FeCl_2$, tetrachloroethylene, tar, and minor amounts of hexachloroethane. As in the $CpW(CO)_3Cl$ system, trichloromethyl radical is produced in, at most, only minor amounts. The reaction proceeds through an iron dichlorocarbene intermediate. Evidence for such an intermediate includes formation of isocyanides, phosgene, and thiophosgene when the oxidation is carried out in the presence of primary amines, dioxygen, and sulfur, respectively. In addition, tetrachloroethylene forms in neat carbon tetrachloride. Various alternative explanations for the above phenomena are considered and found unsatisfactory. The iron carbene species is proposed to arise via oxidative addition of carbon tetrachloride to photolytically generated $Fe(CO)_4$, followed by α -chlorine elimination. Degradation of the complex can then result in either dimerization or telomerization of the dichlorocarbene moiety. The $CpW(CO)_3Cl$ system is believed to follow an analogous pathway.

Introduction

We recently reported that $CpW(CO)_3Cl$ reacts photochemically with CCl_4 to give $CpW(CO)_2Cl_3$ (eq 1).¹ Be-

$$CpW(CO)_3Cl \xrightarrow[CCl_4]{h\nu} CpW(CO)_2Cl_3$$
 (1)

cause of our interest in the synthesis of high oxidation state organometallic complexes, we investigated the mechanism of this reaction. Mechanistic studies of halocarbon oxidations of organometallic complexes have been reported by several research groups.² Broadly speaking, three different fundamental mechanisms have been proposed.

In the first type of mechanism, the initiating step is coordination of the halocarbon to the metal complex.³ An example is the oxidation of ReCl₃(RCN)(PPh₃)₂ reported by Wilkinson⁴ (eq 2). He suggested the mechanism shown

$$ReCl_3(RCN)(PPh_3)_2 + CCl_4 \rightarrow$$

$$ReCl_4(PPh_3)_2 + RCN + \frac{1}{2}C_2Cl_6$$
 (2)

 $ReCl_3(RCN)(PPh_3)_2 + CCl_4 \rightarrow$

$$ReCl_3(CCl_4)(PPh_3)_2 + RCN$$
 (3)

$$ReCl_3(CCl_4)(PPh_3)_2 \rightarrow ReCl_4(PPh_3)_2 + CCl_3$$
 (4)

$$2CCl_3 \rightarrow C_2Cl_6 \tag{5}$$

in eq 3-5. The essence of this and related mechanisms is the coordination of RX to a vacant coordination site followed by R-X bond cleavage:

$$\mathbf{M} \leftarrow \mathbf{X} - \mathbf{R} \to \mathbf{M} - \mathbf{X} + \mathbf{R} \tag{6}$$

A second type of pathway proposed in halocarbon oxidation mechanisms is the electron-transfer mechanism⁵ invoked, for example, in the oxidation of Mo(CO)₂(dmpe)₂ (dmpe = Me₂PCH₂CH₂PMe₂) by CCl₄. Connor⁶ has proposed that this reaction proceeds as shown in eq 7–10. The key feature of this and related reactions is the initial step in which the metal complex is oxidized by the alkyl halide.

$$Mo(CO)_2(dmpe)_2 + CCl_4 \rightarrow$$

$$[Mo(CO)2(dmpe)2]+ + CCl4- (7)$$

$$CCl_4^- \to Cl^- + CCl_3 \tag{8}$$

$$[Mo(CO)_2(dmpe)_2]^+ + Cl^- \rightarrow [Mo(CO)_2(dmpe)_2]Cl \quad (9)$$

$$[Mo(CO)_2(dmpe)_2]Cl + CCl_4 \rightarrow \\ [MoCl(CO)_2(dmpe)_2]Cl + CCl_3 (10)$$

The third type of mechanism proposed in halocarbon oxidation reactions is the radical pathway, exemplified by the photochemical oxidation of Mn₂(CO)₁₀ in CCl₄ to form

⁽¹⁾ Tyler, D. R. *Inorg. Chem.* 1981, 20, 2257-2261. (2) A good general introduction to this topic is: Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978: pp. 139-212.

^{1978;} pp 139-212.
(3) Chatt, J.; Head, R. A.; Leigh, G. J.; Pickett, C. J. J. Chem. Soc., Dalton Trans. 1978, 1638-1647.

⁽⁴⁾ Rouschias, G.; Wilkinson, G. J. Chem. Soc. A 1967, 993-1000. (5) Bellachioma, G.; Cardaci, G.; Reichenbach, G. J. Organomet.

^{(6) (}a) Connor, J. A.; Riley, P. I. J. Chem. Soc., Chem. Commun. 1976, 634-635. (b) Connor, J. A.; Riley, P. I. Ibid. 1976, 149-150.