

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

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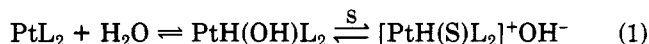
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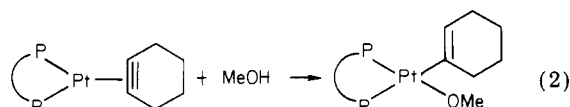
The complexes  $[\text{PtMe}_2(\text{N}\overline{\text{N}})]$ ,  $\text{N}\overline{\text{N}} = 2,2'$ -bipyridyl or 1,10-phenanthroline, react with alcohols (ROH, R = Me, Et, *i*-Pr) to give alkoxoplatinum complexes, characterized as  $[\text{PtMe}_2(\text{OR})(\text{N}\overline{\text{N}})(\text{OH}_2)]^+\text{OH}^-$ , while water gives similar hydroxoplatinum(IV) complexes  $[\text{PtMe}_2(\text{OH})(\text{N}\overline{\text{N}})(\text{OH}_2)]^+\text{OH}^-$ . The complexes are characterized by elemental analysis, by IR and NMR spectroscopy, by conductivity, and by conversion to derivatives  $[\text{PtMe}_2(\text{OR})(\text{N}\overline{\text{N}})(\text{OH}_2)]^+\text{X}^-$ , where X =  $\text{PF}_6$ ,  $\text{ClO}_4$ , or  $\text{BPh}_4$ , and to  $[\text{PtMe}_2(\text{OMe})\text{Cl}(\text{phen})]$ , when R = Me and  $\text{N}\overline{\text{N}} = \text{phen}$ . The alkoxoplatinum(IV) bond is inert to solvolysis with alcohols, water, and dilute perchloric acid.

## Introduction

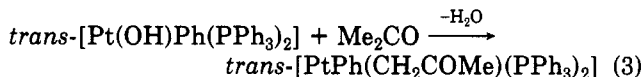
There has been much interest in the activation of alcohols and of water in catalysis by interaction with transition-metal complexes, and several approaches to this problem have been made.<sup>1-4</sup> One approach has involved oxidative addition.<sup>5-13</sup> Alcohols can react with low oxidation state complexes of tungsten, for example, by oxidative addition of the RO-H bond in both mononuclear and polynuclear compounds.<sup>5-7</sup> In addition, tungstocene can apparently insert into a C-H bond of methanol (or possibly the C-O bond) to give ultimately  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Me}(\text{OMe})]$ .<sup>5</sup> 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*-Pr<sub>3</sub>, S = solvent).<sup>8</sup>



With soft metal atoms, water thus protonates the metal center.<sup>9-14</sup> The first alkoxoplatinum(II) complexes were prepared by oxidative addition of methanol to a platinum(0) alkyne complex (eq 2,  $\text{P}\overline{\text{P}} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ).<sup>12,13</sup> The PtOMe grouping is reactive,



giving the corresponding hydroxo derivative with water and the methoxycarbonyl derivative with CO.<sup>12</sup> Both alkoxy and hydroxo derivatives of platinum(II) act as strong bases, as illustrated by reactions such as that of eq 3.<sup>8,15,16</sup>



Platinum(II) complexes with bridging alkoxy ligands are apparently less reactive, but  $\beta$ -hydride eliminations can lead to formation of platinum hydrides.<sup>17-21</sup>

In this article some reactions of the complexes  $[\text{PtMe}_2(\text{N}\overline{\text{N}})]$ , where  $\text{N}\overline{\text{N}} = 2,2'$ -bipyridyl or 1,10-phenanthroline, 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  $[\text{PtMe}_3(\text{OMe})_4]$ , which is air-sensitive and incompletely characterized,<sup>22</sup> whereas the new complexes reported here are remarkably robust. A preliminary account of parts of this work has been published.<sup>23</sup>

## Results and Discussion

**Reactions with Alcohols.** The complexes  $[\text{PtMe}_2(\text{bpy})]$  (I) and  $[\text{PtMe}_2(\text{phen})]$  (II) are red solids, the color being due to the presence of a metal to ligand charge-transfer band in the visible region of the spectrum.<sup>24</sup> The complexes are electron-rich and are among the most re-

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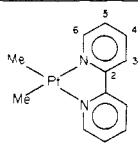
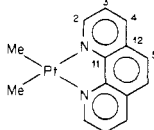
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Table I.  $^1\text{H}$  and  $^{13}\text{C}$  NMR Data

complex	PtMe		PtOR <sup>a</sup>		N $\bar{\text{N}}$ <sup>b</sup>	
	$\delta$	$^2J(\text{PtH})/\text{Hz}$	$\delta$	$J/\text{Hz}$	$\delta$	$J/\text{Hz}$
	1.14	86			9.28 (H <sub>6</sub> ) <sup>c</sup> 7.52 (H <sub>5</sub> ) 8.02 (H <sub>4</sub> ) 8.06 (H <sub>3</sub> )	5.2 ( $J_{56}$ ), 1.5 ( $J_{46}$ ) 7.2 ( $J_{45}$ ), 1.5 ( $J_{34}$ ) 7.7 ( $J_{34}$ )
[PtMe <sub>2</sub> (OMe)(bpy)(OH <sub>2</sub> )] <sup>+d</sup>	1.71	73	2.75	41.0 ( $J_{\text{PtH}}$ )	9.04 (H <sub>6</sub> ) <sup>e</sup> 7.67 (H <sub>5</sub> ) 8.06 (H <sub>4</sub> ) 8.20 (H <sub>3</sub> )	5.0 ( $J_{56}$ ) 8.0 ( $J_{45}$ ), 1.3 ( $J_{35}$ ) 7.5 ( $J_{34}$ )
[PtMe <sub>2</sub> (OEt)(bpy)(OH <sub>2</sub> )] <sup>+f</sup>	1.80	72.5	2.90 (CH <sub>2</sub> ) 0.74 (CH <sub>3</sub> )	14 ( $J_{\text{PtH}}$ ) 7 ( $J_{\text{HH}}$ )	9.03 (H <sub>6</sub> ) <sup>g</sup> 7.67 (H <sub>5</sub> ) 8.05 (H <sub>4</sub> ) 8.20 (H <sub>3</sub> )	5 ( $J_{56}$ ), 1.5 ( $J_{46}$ ) 8 ( $J_{45}$ ), 1.3 ( $J_{35}$ ) 8 ( $J_{34}$ )
[PtMe <sub>2</sub> (O- <i>i</i> -Pr)(bpy)(OH <sub>2</sub> )] <sup>+h</sup>	1.82	73	2.84 (CH) 0.60 (CH <sub>3</sub> )	6 ( $J_{\text{HH}}$ )	9.04 (H <sub>6</sub> ) 7.64 (H <sub>5</sub> ) 8.05 (H <sub>4</sub> ) 8.19 (H <sub>3</sub> )	5 ( $J_{56}$ ) 7 ( $J_{45}$ ) 7 ( $J_{34}$ )
[PtMe <sub>2</sub> (OH)(bpy)(OH <sub>2</sub> )] <sup>+i</sup>	1.84	70			9.02 (H <sub>6</sub> ) <sup>h</sup> 7.90 (H <sub>5</sub> ) 8.34 (H <sub>4</sub> ) 8.72 (H <sub>3</sub> )	5.5 ( $J_{56}$ ), 1.5 ( $J_{46}$ ) 8.0 ( $J_{45}$ ), 1.3 ( $J_{35}$ ) 8.1 ( $J_{34}$ )
	1.15	86.5			9.51 (H <sub>2</sub> ) <sup>i</sup> 7.82 (H <sub>3</sub> ) 8.63 (H <sub>4</sub> ) 7.92 (H <sub>5</sub> )	5.2 ( $J_{2,3}$ ) 8.0 ( $J_{3,4}$ ) 1.3 ( $J_{2,4}$ )
[PtMe <sub>2</sub> (OMe)(phen)(OH <sub>2</sub> )] <sup>+j</sup>	1.80	72.5	2.65	40 ( $J_{\text{PtH}}$ )	9.32 (H <sub>2</sub> ) <sup>j</sup> 8.03 (H <sub>3</sub> ) 8.62 (H <sub>4</sub> ) 8.07 (H <sub>5</sub> )	5.0 ( $J_{2,3}$ ) 8.0 ( $J_{3,4}$ ) 1.8 ( $J_{2,4}$ )
[PtMe <sub>2</sub> (OEt)(phen)(OH <sub>2</sub> )] <sup>+k</sup>	1.79	73	2.85 (CH <sub>2</sub> ) 0.59 (CH <sub>3</sub> )	21 ( $J_{\text{PtH}}$ ) 7 ( $J_{\text{HH}}$ )	9.30 (H <sub>2</sub> ) <sup>k</sup> 8.01 (H <sub>3</sub> ) 8.60 (H <sub>4</sub> ) 8.06 (H <sub>5</sub> )	5 ( $J_{2,3}$ ) 7 ( $J_{3,4}$ ) 2 ( $J_{2,4}$ )
[PtMe <sub>2</sub> (O- <i>i</i> -Pr)(phen)(OH <sub>2</sub> )] <sup>+l</sup>	1.84	73	2.89 (CH) 0.48 (CH <sub>3</sub> )	40 ( $J_{\text{PtH}}$ ) 6 ( $J_{\text{HH}}$ )	9.32 (H <sub>2</sub> ) <sup>m</sup> 8.0 (H <sub>3</sub> ) 8.51 (H <sub>4</sub> ) 7.98 (H <sub>5</sub> )	5 ( $J_{2,3}$ ) 8 ( $J_{3,4}$ ) 1.5 ( $J_{2,4}$ )
[PtMe <sub>2</sub> (OH)(phen)(OH <sub>2</sub> )] <sup>+n</sup>	1.73	72.5			9.30 (H <sub>2</sub> ) 8.0 (H <sub>3</sub> ) 8.61 (H <sub>4</sub> ) 8.05 (H <sub>5</sub> )	
[PtMe <sub>2</sub> (OMe)Cl(phen)]	2.03	71	2.40	58 ( $J_{\text{PtH}}$ )	9.40 (H <sub>2</sub> ) <sup>n</sup> 8.28 (H <sub>3</sub> ) 8.99 (H <sub>4</sub> ) 8.33 (H <sub>5</sub> )	5 ( $J_{2,3}$ ) 8 ( $J_{3,4}$ ) 1.5 ( $J_{2,4}$ )

<sup>a</sup> R = H, Me, Et, or *i*-Pr; solvent CD<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> N $\bar{\text{N}}$  = bpy or phen. <sup>c</sup>  $J(\text{PtH}) = 22$  Hz. <sup>d</sup>  $^{13}\text{C}$  NMR in CD<sub>2</sub>Cl<sub>2</sub>: -2.30 (q,  $^1J(\text{PtC}) = 701$  Hz, MePt), 57.32 (q,  $^2J(\text{PtC}) = 18$  Hz, MeOPt), 155.0 (s, C<sup>2</sup>), 123.4 (d, C<sup>3</sup>), 139.1 (d, C<sup>4</sup>), 126.8 (d,  $^3J(\text{PtC}) = 12$  Hz, C<sup>5</sup>), 147.1 (d,  $^2J(\text{PtC}) = 10$  Hz, C<sup>6</sup>). <sup>e</sup>  $J(\text{PtH}) = 14$  Hz. <sup>f</sup>  $^{13}\text{C}$  NMR in CD<sub>2</sub>Cl<sub>2</sub>: -2.60 (q,  $^1J(\text{PtC}) = 700$  Hz, MePt), 64.0 (t,  $^2J(\text{PtC}) = 15$  Hz, CH<sub>2</sub>O); 19.7 (q,  $^3J(\text{PtC}) = 43$  Hz, CH<sub>3</sub>C), 153.3 (s, C<sup>2</sup>), 124.0 (d, C<sup>3</sup>), 139.6 (d, C<sup>4</sup>), 126.8 (d, C<sup>5</sup>). <sup>g</sup>  $J(\text{PtH}) = 13$  Hz. <sup>h</sup>  $J(\text{PtH}) = 16$  Hz. <sup>i</sup>  $J(\text{PtH}) = 21.5$  Hz. <sup>j</sup>  $J(\text{PtH}) = 12$  Hz. <sup>k</sup>  $J(\text{PtH}) = 15$  Hz. <sup>l</sup>  $^{13}\text{C}$  NMR in CD<sub>2</sub>Cl<sub>2</sub>: -2.9 ( $^1J(\text{PtC}) = 720$  Hz, MePt), 68.6 (CH), 27.4 (CH<sub>3</sub>C,  $^3J(\text{PtC}) = 20$  Hz), 147.2 (C<sup>2</sup>), 125.5 (C<sup>3</sup>), 138.6 (C<sup>4</sup>), 127.9 (C<sup>5</sup>), 147.1 (C<sup>11</sup>), 127.9 (C<sup>12</sup>). <sup>m</sup>  $J(\text{PtH}) = 16$  Hz. <sup>n</sup>  $J(\text{PtH}) = 12$  Hz.

active of noble-metal complexes in oxidative addition reactions.<sup>25-28</sup> A solution of [PtMe<sub>2</sub>(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 CH<sub>2</sub>Cl<sub>2</sub> solution with

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 [PtMe<sub>2</sub>(phen)] reacted in the same way. The complexes were not easy to characterize, and the evidence for the structure proposed, [PtMe<sub>2</sub>(OR)(N $\bar{\text{N}}$ )(OH<sub>2</sub>)]<sup>+OH<sup>-</sup></sup>, 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.<sup>31</sup>

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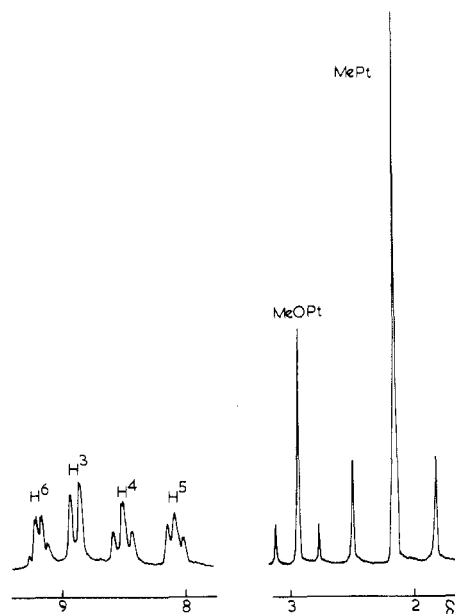
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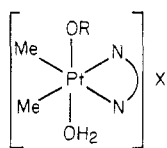
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**Figure 1.**  $^1\text{H}$  NMR spectrum (100 MHz) of  $[\text{PtMe}_2(\text{OMe})(\text{bpy})(\text{OH}_2)]$  in  $\text{CD}_3\text{OD}$ . For labeling of bpy protons see Table I.

2. The stereochemistry at platinum (except the presence of the  $\text{OH}_2$  ligand) was established by NMR spectroscopy. For example, the  $^1\text{H}$  NMR spectrum of IIIa (Table I,



III,  $\text{N}\widehat{\text{N}} = \text{bpy}$

IIIa, R = Me, X = OH

b, R = Et, X = OH

c, R = *i*-Pr, X = OH

d, R = Me, X =  $\text{PF}_6^-$

e, R = Me, X =  $\text{BPh}_4^-$

f, R = Me, X =  $\text{ClO}_4^-$

IV,  $\text{N}\widehat{\text{N}} = \text{phen}$

IVa, R = Me, X = OH

b, R = Et, X = OH

c, R = *i*-Pr, X = OH

Figure 1) gave resonances due to MePt, MeO, and bpy protons in the ratio 6:3:8 as expected. The coupling constant  $^2J(\text{PtH})$  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).<sup>26</sup> The spectra show that the two MePt groups and the two aromatic rings of the bpy ligand are equivalent and hence that the *cis*- $[\text{PtMe}_2\text{N}_2]$  structure is retained in IIIa. The assignments of bpy protons (Table I) were straightforward, using literature precedents on similar compounds,<sup>32-37</sup> and were confirmed by homonuclear decoupling experiments.

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

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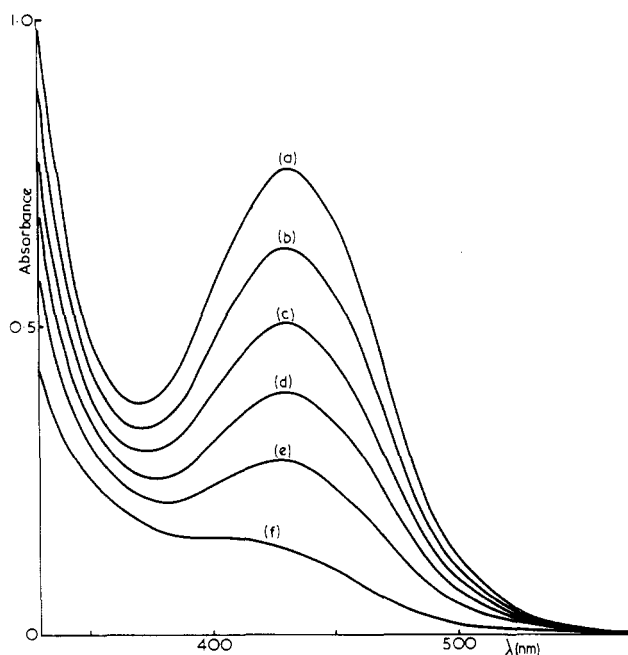
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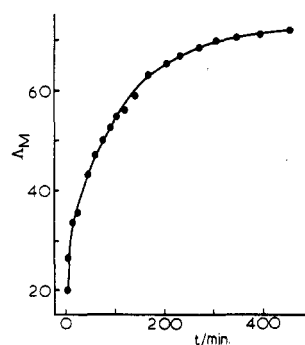
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**Figure 2.** UV-visible spectra of  $[\text{PtMe}_2(\text{bpy})]$  ( $10^{-4}$  M) in ethanol at  $21^\circ\text{C}$ : (a)  $t = 0$ , (b)  $t = 23$  min, (c)  $t = 48$  min, (d)  $t = 78$  min, (e)  $t = 119$  min, (f)  $t = 280$  min.



**Figure 3.** Molar conductivity ( $\Lambda_M$ ,  $\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$ ) of a solution of  $[\text{PtMe}_2(\text{bpy})]$  ( $10^{-3}$  M) in methanol as a function of time.

The presence of the methoxy ligand in IIIa was demonstrated by the observation of  $^{195}\text{Pt}$  coupling in both the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra [ $\delta(\text{CH}_3\text{OPt})$  2.75 ( $^3J(\text{PtH}) = 41$  Hz),  $\delta(\text{CH}_3\text{OPt})$  57.3 ( $^2J(\text{PtC}) = 18$  Hz)]. No exchange was observed when the complex was dissolved in  $\text{CD}_3\text{OD}$  or in  $\text{D}_2\text{O}$ , since the methoxy signal with  $^{195}\text{Pt}$  coupling was still observed in the  $^1\text{H}$  NMR spectrum. Remarkably, the  $\text{D}_2\text{O}$  solution could be made 0.1 M in  $\text{HClO}_4$ , and the MeOPt group was still present as evidenced by an unchanged  $^1\text{H}$  NMR spectrum.

$^1\text{H}$  NMR data for complexes III and IV are given in Table I, which also contains  $^{13}\text{C}\{^1\text{H}\}$  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  $^1\text{H}$  NMR spectra of solutions in  $\text{CDCl}_3$  or  $\text{CD}_2\text{Cl}_2$ , but these gave no structural information. In  $\text{CD}_3\text{OD}$  or  $\text{D}_2\text{O}$  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  $^1\text{H}$  NMR spectra (or the  $^2\text{H}$  NMR spectra on the product of reaction of I with  $\text{CH}_3\text{OD}$ ).



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.<sup>41</sup>



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.<sup>42,43</sup>

### Experimental Section

<sup>1</sup>H and <sup>13</sup>C[<sup>1</sup>H] NMR spectra were recorded by using a Varian XL 100 spectrometer, using CDCl<sub>3</sub> or CD<sub>2</sub>Cl<sub>2</sub> 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 O by Canadian Microanalytical Service, Vancouver. Samples were dried under high vacuum prior to analysis.

[PtMe<sub>2</sub>(bpy)]. To a solution of [Pt<sub>2</sub>Me<sub>4</sub>(μ-SMe<sub>2</sub>)<sub>2</sub>]<sup>44</sup> (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%.

[PtMe<sub>2</sub>(phen)] was prepared by the same method, and the complexes were characterized by comparison with authentic samples.<sup>24</sup> This synthesis is considerably easier than the initial method.<sup>24</sup>

[PtMe<sub>2</sub>(OMe)(bpy)(OH<sub>2</sub>)] [OH]. An orange-red solution of [PtMe<sub>2</sub>(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 CH<sub>2</sub>Cl<sub>2</sub> (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 ν(OH) 3450. Anal. Calcd for C<sub>13</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>Pt: C, 34.9; H, 4.5; N, 6.3. Found: C, 35.1; H, 4.3; N, 5.7. Adducts with CD<sub>3</sub>OD [IR ν(CD<sub>3</sub>) 2025, 2160] and CH<sub>3</sub>OD were prepared similarly. The following similarly were prepared [PtMe<sub>2</sub>(OEt)(bpy)(OH<sub>2</sub>)] [OH]·H<sub>2</sub>O [IR ν(OH) 3400. Anal. Calcd for C<sub>14</sub>H<sub>24</sub>N<sub>2</sub>O<sub>3</sub>Pt: C, 35.1; H, 5.0; N, 5.9. Found: C, 34.7; H, 4.6; N, 5.9]; [PtMe<sub>2</sub>(O-i-Pr)(bpy)(OH<sub>2</sub>)] [OH] [Anal. Calcd for C<sub>15</sub>H<sub>24</sub>N<sub>2</sub>O<sub>3</sub>Pt: C, 37.9; H, 5.1; N, 5.9. Found: C, 37.5; H, 5.1; N, 5.4.]; [PtMe<sub>2</sub>(OMe)(phen)(OH<sub>2</sub>)] [OH] [mp 140 °C dec. Anal. Calcd for C<sub>15</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>Pt: C, 38.2; H, 4.2; N, 5.9. Found: C, 38.0; H, 4.3; N, 5.65.]; [PtMe<sub>2</sub>(OEt)(phen)(OH<sub>2</sub>)] [OH]·H<sub>2</sub>O [mp 110 °C dec. Anal. Calcd for C<sub>16</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub>Pt: C, 38.2; H, 4.8; N, 5.6; O, 11.3. Found: C, 38.0; H, 5.1; N, 5.8; O, 11.3.]; [PtMe<sub>2</sub>(O-i-Pr)(OH)(phen)] [decomp pt 70 °C. Anal. Calcd for

C<sub>17</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>Pt: C, 39.9; H, 4.6; N, 5.8. Found: C, 40.0; H, 4.6; N, 5.7.].

[PtMe<sub>2</sub>(OH)(phen)(OH<sub>2</sub>)] [OH]. To a solution of [PtMe<sub>2</sub>(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 CH<sub>2</sub>Cl<sub>2</sub> and was then precipitated by addition of pentane: yield 82%. Anal. Calcd for C<sub>14</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>Pt: 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<sub>2</sub>(OH)(bpy)(OH<sub>2</sub>)] [OH]. similarly was prepared. Anal. Calcd for C<sub>12</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>Pt: C, 33.3; H, 4.2; N, 6.5. Found: C, 32.9; H, 4.3; N, 6.2.

[PtMe<sub>2</sub>(OMe)(bpy)(OH<sub>2</sub>)] [PF<sub>6</sub>]. A solution of [PtMe<sub>2</sub>(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 [NH<sub>4</sub>][PF<sub>6</sub>] (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(PF<sub>6</sub>) 845, 555 cm<sup>-1</sup>. Anal. Calcd for C<sub>13</sub>H<sub>19</sub>F<sub>6</sub>N<sub>2</sub>O<sub>2</sub>Pt: 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<sub>2</sub>(OMe)(bpy)(OH<sub>2</sub>)] [BPh<sub>4</sub>]·H<sub>2</sub>O similarly was prepared (from NaBPh<sub>4</sub>); mp 153 °C dec. Anal. Calcd for C<sub>37</sub>H<sub>41</sub>BN<sub>2</sub>Pt: 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 CH<sub>2</sub>Cl<sub>2</sub> solution using *n*-pentane. Attempts to grow single crystals were unsuccessful by using several techniques.

[PtMe<sub>2</sub>(OMe)(bpy)(OH<sub>2</sub>)] [ClO<sub>4</sub>]<sub>2</sub>·2H<sub>2</sub>O. A solution of [PtMe<sub>2</sub>(bpy)] (0.12 g) in methanol (20 mL) was allowed to react for 16 h at room temperature. A solution of HClO<sub>4</sub> (0.1 mL) in methanol (2 mL) was added, and the solution was evaporated under vacuum. The residue was washed with ether, dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and precipitated with pentane: yield 0.07 g; decomp pt 206 °C; IR ν(OH) 3450, ν(ClO<sub>4</sub>) 1070–1130 cm<sup>-1</sup>. Anal. Calcd for C<sub>13</sub>H<sub>20</sub>ClN<sub>2</sub>O<sub>3</sub>Pt: C, 27.7; H, 3.55; N, 5.0. Found: C, 26.8; H, 3.5; N, 5.1.

[PtMe<sub>2</sub>(OH)(bpy)(OH<sub>2</sub>)] [PF<sub>6</sub>]. A solution of [PtMe<sub>2</sub>(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. [NH<sub>4</sub>][PF<sub>6</sub>] (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, ν(PF<sub>6</sub>) 848, 560. Anal. Calcd for C<sub>12</sub>H<sub>17</sub>F<sub>6</sub>N<sub>2</sub>O<sub>2</sub>Pt: 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.

[PtMe<sub>2</sub>(OMe)Cl(phen)]. A solution of [PtMe<sub>2</sub>(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 recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/pentane to give the product: mp 180–200 °C dec; mass spectrum (reporting only *m/e* values for <sup>195</sup>Pt, <sup>35</sup>Cl 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 [<sup>35</sup>Cl:<sup>37</sup>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 C<sub>15</sub>H<sub>17</sub>ClN<sub>2</sub>O<sub>2</sub>Pt: C, 38.2; H, 3.6; N, 5.9. Found: C, 37.7; H, 3.9; N, 5.7.

**Kinetic Studies.** A solution of [PtMe<sub>2</sub>(phen)] in methanol (10<sup>-4</sup> 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 ln(A<sub>t</sub> - A<sub>∞</sub>) vs. time gave a good straight line plot, from which the observed rate constant, *k*<sub>obsd</sub> (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 [PtMe<sub>2</sub>(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 × 1/8 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 [PtMe<sub>2</sub>(N<sup>-</sup>N)] with acids leads to formation of methane from an intermediate thought to be formed by oxidative addition.<sup>30</sup> [PtMe<sub>2</sub>H(N<sup>-</sup>N)]<sup>+</sup>. In the alcohol reactions very little or no methane is detected.

(41) Hughes, G.; Lobb, C. R., "Comprehensive Chemical Kinetics"; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1976; Vol. 18, Chapter 7.

(42) We considered the possibility that alcohol attack at the N<sup>-</sup>N ligand, rather than at the metal, might have occurred as suggested by Gillard,<sup>34</sup> but challenged by others,<sup>35,36</sup> 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 CD<sub>3</sub>OD, 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.<sup>28</sup>

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

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**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 = PF<sub>6</sub>), 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; [PtMe<sub>2</sub>(O-*i*-Pr)(OH)(phen)], 88036-73-1; [Pt<sub>2</sub>Me<sub>4</sub>(μ-SMe<sub>2</sub>)<sub>2</sub>], 79870-64-7.

## Mechanism of the Photochemical Oxidation of Fe(CO)<sub>5</sub> and CpW(CO)<sub>3</sub>Cl (Cp = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) by Chlorocarbons

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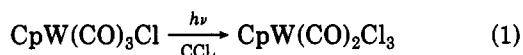
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The photochemical oxidation of CpW(CO)<sub>3</sub>Cl (Cp = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) by carbon tetrachloride and other polychlorocarbons affords CpW(CO)<sub>2</sub>Cl<sub>3</sub>. The sole photoprocess is dissociation of CO from the complex to give CpW(CO)<sub>2</sub>Cl. 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)<sub>5</sub> in carbon tetrachloride gives FeCl<sub>2</sub>, tetrachloroethylene, tar, and minor amounts of hexachloroethane. As in the CpW(CO)<sub>3</sub>Cl 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)<sub>4</sub>, followed by α-chlorine elimination. Degradation of the complex can then result in either dimerization or telomerization of the dichlorocarbene moiety. The CpW(CO)<sub>3</sub>Cl system is believed to follow an analogous pathway.

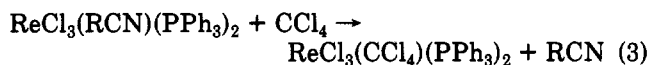
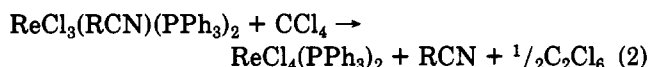
### Introduction

We recently reported that CpW(CO)<sub>3</sub>Cl reacts photochemically with CCl<sub>4</sub> to give CpW(CO)<sub>2</sub>Cl<sub>3</sub> (eq 1).<sup>1</sup> Be-

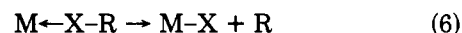


cause of our interest in the synthesis of high oxidation state organometallic complexes, we investigated the mechanism of this reaction. Mechanistic studies of halocarbon oxidations of organometallic complexes have been reported by several research groups.<sup>2</sup> Broadly speaking, three different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

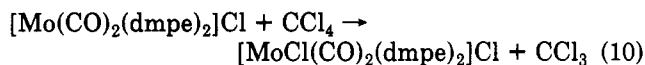
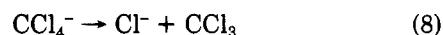
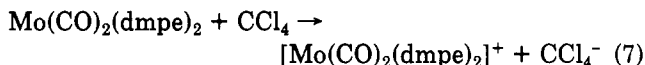
In the first type of mechanism, the initiating step is coordination of the halocarbon to the metal complex.<sup>3</sup> An example is the oxidation of ReCl<sub>3</sub>(RCN)(PPh<sub>3</sub>)<sub>2</sub> reported by Wilkinson<sup>4</sup> (eq 2). He suggested the mechanism shown



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:



A second type of pathway proposed in halocarbon oxidation mechanisms is the electron-transfer mechanism<sup>5</sup> invoked, for example, in the oxidation of Mo(CO)<sub>2</sub>(dmpe)<sub>2</sub> (dmpe = Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>) by CCl<sub>4</sub>. Connor<sup>6</sup> 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.



The third type of mechanism proposed in halocarbon oxidation reactions is the radical pathway, exemplified by the photochemical oxidation of Mn<sub>2</sub>(CO)<sub>10</sub> in CCl<sub>4</sub> 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.

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(5) Bellachioma, G.; Cardaci, G.; Reichenbach, G. *J. Organomet. Chem.* 1981, 291-299.

(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.