

tetraanions at relatively low cathodic potentials. This highly electron accepting compound has redox properties close to the chemical derivatives used to generate charge-transfer complexes such as TCNQ ( $E_{1/2}^I = 0.17$  V;  $E_{1/2}^{II} = -0.37$  V;  $\Delta E = 0.54$  V) or TCNE ( $E_{1/2}^I = 0.15$  V;  $E_{1/2}^{II} = -0.57$  V;  $\Delta E_{1/2} = 0.72$  V)<sup>14</sup> and may allow their use in such complexes.

Studies are presently underway to examine the general chemical reactivity of (CN)<sub>8</sub>PcZn and other similar octacyano-substituted metal phthalocyanine complexes.

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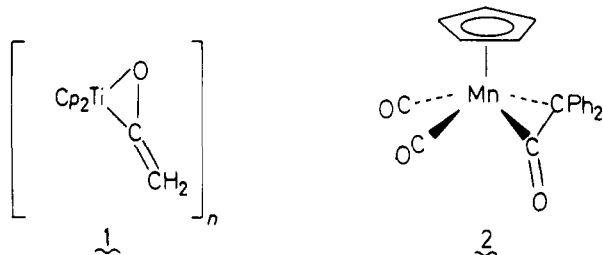
## Conversion of an $\eta^5$ -C<sub>5</sub>H<sub>5</sub> Complex into a Cyclopentadienylidene Ketene Complex

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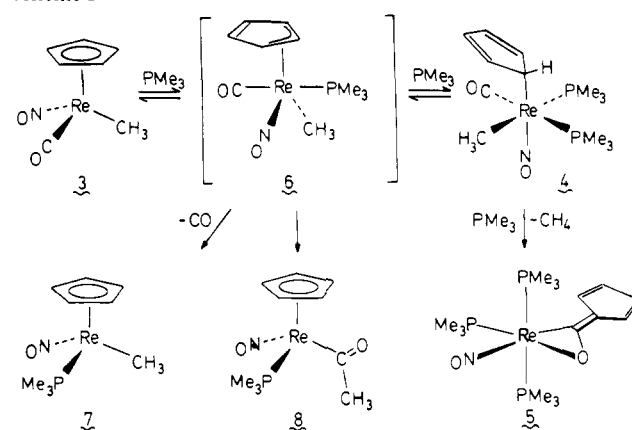
Transition-metal ketene complexes have been proposed as intermediates in CO reduction<sup>1</sup> and have been studied as models for CO<sub>2</sub> metal complexes.<sup>2a,b</sup> Two types of metal  $\eta^2$ -ketene complexes are known: early transition metals form  $\eta^2$ -CO complexes<sup>2</sup> such as **1** while later transition metals form  $\eta^2$ -CC com-



plexes such as **2**.<sup>3</sup> Previously, metal ketene complexes have been prepared by direct reaction of ketene with a coordinatively unsaturated metal complex,<sup>2a-d,3a</sup> by carbonylation of metal alkylidene complexes,<sup>3d</sup> and by deprotonation of metal acyl complexes.<sup>2e,4</sup> Here we report that ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Re(CO)(NO)(CH<sub>3</sub>) (**3**, Scheme I) reacts with high concentrations of PMe<sub>3</sub> to give an  $\eta^1$ -C<sub>5</sub>H<sub>5</sub> derivative, **4**, which is then converted to the novel cyclopentadienylidene ketene<sup>5</sup> complex **5**. This reaction further illustrates the reactivity of the normally unreactive C<sub>5</sub>H<sub>5</sub> ligand.

Previously we have reported that ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Re(CO)(NO)(CH<sub>3</sub>) (**3**) reacts rapidly and reversibly with PMe<sub>3</sub> at room temperature

Scheme I



to give the  $\eta^1$ -C<sub>5</sub>H<sub>5</sub> bisphosphine complex **4** via the proposed  $\eta^3$ -C<sub>5</sub>H<sub>5</sub> monophosphine intermediate **6**. Upon being heated at 90 °C in benzene, the equilibrium mixture of **3** and **4** is slowly converted to a 4:1 mixture of phosphine-substituted methyl and acetyl complexes, **7** and **8**, probably via the same  $\eta^3$ -C<sub>5</sub>H<sub>5</sub> intermediate **6**.<sup>6</sup> We have now discovered that when conversion to **7** and **8** is inhibited by high concentrations of PMe<sub>3</sub>, another reaction leading to cyclopentadienylidene ketene complex **5** takes place.

When a toluene solution of **3** (0.986 mmol, 0.25 M) and PMe<sub>3</sub> (2.9 M) was heated for 17 h at 72 °C,<sup>7</sup> evolution of methane (44%) was detected. Removal of the excess PMe<sub>3</sub> and toluene under reduced pressure and recrystallization of the residue from THF-hexane gave a yellow solid identified as the  $\eta^2$ -CO-cyclopentadienylidene ketene complex **5** (150 mg, 28%).<sup>8</sup>

The <sup>1</sup>H NMR of **5** in benzene-*d*<sub>6</sub> establishes the presence of two equivalent *trans*-PMe<sub>3</sub> ligands ( $\delta$  1.05 (three-line pattern with  $J_{PH} + J_{PH} = 7$  Hz)), one unique PMe<sub>3</sub> ligand ( $\delta$  1.09 (d,  $J = 8.5$  Hz)), and four different coupled protons on the cyclopentadienylidene ketene ligand ( $\delta$  6.89 ( $J = 4.4, 1.8, 1.8$  Hz)), 7.03 ( $J = 4.4, 1.6, 1.8$  Hz)), 7.20 ( $J = 4.4, 2.4, 1.6$  Hz)), 7.30 ( $J = 4.4, 2.4, 1.8$  Hz)).<sup>9</sup> The observation of four different protons on the five-membered ring excludes a more symmetric  $\eta^2$ -CC-cyclopentadienylidene ketene complex for which only two different resonances would be possible.

The IR spectrum of **5** (Nujol) has a band at 1602 cm<sup>-1</sup> assigned to a linear nitrosyl ligand. A broad band at 1555 cm<sup>-1</sup> might be due to either the C—O or C=C stretch of the  $\eta^2$ -CO-cyclopentadienylidene ketene ligand. For comparison, the  $\eta^2$ -CO-complex **1** has a band at 1610 cm<sup>-1</sup><sup>2e</sup> while the  $\eta^2$ -CC-complex **2** has a band at 1787 cm<sup>-1</sup>.<sup>3b</sup>

In the <sup>13</sup>C[<sup>1</sup>H] NMR of **5** in CD<sub>2</sub>Cl<sub>2</sub>, the ketene carbon bonded to rhenium appears as a broad signal at  $\delta$  214.4<sup>10</sup> with  $\nu_{1/2} = 29$  Hz. The relatively narrow line width of this signal is consistent

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(7) The <sup>1</sup>H NMR of a similar benzene-*d*<sub>6</sub> solution at 72 °C shows that the  $\eta^1$ -C<sub>5</sub>H<sub>5</sub> complex **4** is the major species under these initial conditions.

(8) <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 0.09 M Cr(acac)<sub>3</sub>)  $\delta$  214.1 ( $\nu_{1/2} = 29$  Hz), 125.0 (d,  $J_{CH} = 162$  Hz), 120.3, 119.0 (d,  $J_{CH} = 156$  Hz), 118.0 (d,  $J_{CH} = 159$  Hz), 112.3 (d,  $J_{CH} = 165$  Hz), 16.16 (q, t,  $J_{CH} = 127$  Hz,  $J_{PC} + J_{PC} = 27.9$  Hz), 21.1 (q, d,  $J_{CH} = 127$  Hz,  $J_{PC} = 27.8$  Hz); <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  -26.6 (d,  $J_{PP} = 7.9$  Hz), -32.9 (t,  $J_{PP} = 7.9$  Hz) relative to external H<sub>3</sub>PO<sub>4</sub>. Anal. Calcd for C<sub>15</sub>H<sub>31</sub>NO<sub>2</sub>P<sub>3</sub>Re: C, 33.59; H, 5.83; N, 2.61. Found: C, 33.63; H, 5.83; N, 2.80. *m/e* calcd for C<sub>15</sub>H<sub>31</sub>NO<sub>2</sub>P<sub>3</sub>Re, 537.1121; obsd 537.1130. Molecular weight by osmometry in dichloroethane 502, calcd 536.

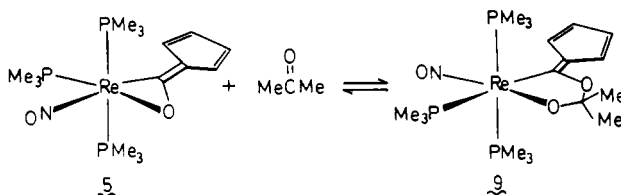
(9) The magnitudes of these coupling constants are similar to those observed for fulvene derivatives: Hollenstein, R.; von Philipsborn, W.; Vögeli, R.; Neuenschwander, M. *Helv. Chim. Acta* **1973**, *56*, 847-859.

(10) For comparison, the ketene carbon bonded to oxygen in **1** comes at  $\delta$  220<sup>2e</sup> and for **2** at  $\delta$  201.3.<sup>3b</sup> Additional resonances of **5** were observed for the carbons of the five-membered ring at  $\delta$  125.0, 120.3, 119.0, 118.0, and 112.3; for the unique PMe<sub>3</sub> ligand at  $\delta$  21.1 (d,  $J_{PC} = 27.8$  Hz) and for the equivalent *trans* PMe<sub>3</sub> ligands at  $\delta$  16.2 (three-line pattern with  $J_{PC} + J_{PC} = 27.9$  Hz).

with structure **5** in which the ketene carbon is cis to all three phosphorus ligands.<sup>11</sup>

Significantly higher yields of **5** were obtained from photolysis of **3** and  $\text{PMe}_3$  than were obtained from thermal reaction. When a toluene solution of **3** (2.64 mmol, 0.31 M) and  $\text{PMe}_3$  (34.4 mmol, 4.05 M) was photolyzed in a Rayonet photochemical reactor at 366 nm for 112 h, at 59% yield of ketene complex **5** was isolated. Methane (66%) was also observed.<sup>12</sup>

The ketene complex **5** reacts with acetone solvent over the course



of 48 h at 25 °C to form a high yield of the 1:1 adduct **9**<sup>13</sup> resulting from insertion of acetone into the Re–O bond of **5**. The reaction is analogous to the addition of  $(\text{C}_6\text{H}_5)_2\text{C}=\text{C}=\text{O}$  to  $\{(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{Ph}_2\text{C}_2\text{O})_2\}$ , which leads to insertion of the C=O bond of the ketene into the Ti–O bond.<sup>2a</sup>

The  $^1\text{H}$  NMR of acetone adduct **9** in benzene- $d_6$  consists of multiplets at  $\delta$  7.36 (2 H), 6.96 (1 H), and 6.90 (1 H) assigned to the four protons of the cyclopentadiene ring, a singlet at  $\delta$  1.36 assigned to the *gem*-dimethyl protons, a doublet at  $\delta$  1.02 ( $J = 7.9$  Hz) assigned to the unique  $\text{PMe}_3$  ligand, and a three-line pattern ( $J_{\text{PH}} + J_{\text{PH}} = 6.8$  Hz) at  $\delta$  1.19 assigned to the equivalent *trans*- $\text{PMe}_3$  ligands. In the related 1:1 adduct of **5** with 2-butanone, the *trans*- $\text{PMe}_3$  ligands are no longer equivalent and resonances due to three different  $\text{PMe}_3$  ligands are seen as  $\delta$  1.50 (three lines,  $J_{\text{PH}} + J_{\text{PH}} = 6.8$  Hz), 1.47 (three lines,  $J_{\text{PH}} + J_{\text{PH}} = 6.8$  Hz), and 1.61 (d,  $J = 8.1$  Hz).<sup>14</sup> In the  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) of **9**, there is a doublet ( $J_{\text{PC}} = 55$  Hz) at  $\delta$  238.2 assigned to the carbon bonded to rhenium, which is *trans* to the unique  $\text{PMe}_3$  ligand.<sup>11,13</sup>

The formation of **9** from **5** and acetone was shown to be reversible by heating a 0.036 M benzene- $d_6$  solution of **9** at 80 °C for 4 h. Periodic observation by  $^1\text{H}$  NMR indicated the clean conversion of **9** to **5** and free acetone with a half-life of  $\sim 60$  min at 80 °C.

The conversion of  $\eta^5\text{-C}_5\text{H}_5$  complex **3** into the cyclopentadienylidene ketene complex **5** probably proceeds via the observed intermediate  $\eta^1\text{-C}_5\text{H}_5$  bisphosphine adduct **4**. The mechanism for formation of **5** is necessarily complex due to the large number of bonds that must be broken or formed in the

process. Cleavage of the Re–CH<sub>3</sub> bond and formation of methane might occur either by protonation of the Re–CH<sub>3</sub> bond or by reductive elimination from an intermediate  $\text{CH}_3\text{ReH}$  species. Cleavage of the C–H bond of the cyclopentadiene unit could occur either by base abstraction or insertion of Re into the  $\alpha\text{-CH}$  bond of an  $\eta^1\text{-C}_5\text{H}_5\text{Re}$  species; alternatively, migration of the  $\eta^1\text{-C}_5\text{H}_5$  unit to CO might precede C–H cleavage by either base abstraction or Re  $\beta\text{-H}$  elimination from a Re–CO– $\text{C}_5\text{H}_5$  species. Formation of the new carbon–carbon bond of the ketene complex could occur either by migration of an  $\eta^1\text{-C}_5\text{H}_5$  ligand to CO or by coupling of an intermediate cyclopentadienylidene ligand with coordinated CO.<sup>1b,3d</sup> Whatever the mechanism, it is becoming clear that a great deal of interesting chemistry is resulting from  $\text{PMe}_3$ -induced  $\eta^5\text{-C}_5\text{H}_5 \rightleftharpoons \eta^3\text{-C}_5\text{H}_5 \rightleftharpoons \eta^1\text{-C}_5\text{H}_5$  transformations.

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**Registry No.** **3**, 38814-45-8; **5**, 85283-03-0; **9**, 85283-04-1.

### Synthesis, Characterization, and Reaction Chemistry of a Bis(iodosylbenzene)–Metalloporphyrin Complex, $[\text{PhI}(\text{OAc})\text{O}]_2\text{Mn}^{\text{IV}}\text{TPP}$ . A Complex Possessing a Five-Electron Oxidation Capability

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The current interest in high-valent manganese porphyrin complexes derives from the ability of these materials to activate hydrocarbons<sup>1</sup> and water<sup>2</sup> under very mild conditions. Rigorous investigation of these activation processes has been hindered by the lack of availability of purified forms of these highly reactive complexes. Recently, we reported the preparation, purification, and characterization of a monomeric manganese(IV) complex,  $\text{Mn}^{\text{IV}}\text{TPP}(\text{OCH}_3)_2$ ,<sup>3,4</sup> two types of dimeric manganese(IV) complexes,  $[\text{XMn}^{\text{IV}}\text{TPP}]_2\text{O}$ , **1**,  $\text{X} = \text{N}_3^-$  and  $\text{OCN}^-$ ,<sup>5</sup> and  $[\text{YMn}^{\text{IV}}\text{TPP}(\text{OIPh})]_2\text{O}$ , **2**,  $\text{Y} = \text{Cl}^-$  and  $\text{Br}^-$ ,<sup>6</sup> and a manganese(V) complex,  $\text{NMn}^{\text{V}}\text{TpMPP}$ .<sup>7</sup> The dimeric manganese(IV) complexes enabled us to establish a detailed mechanism for alkane functionalization by **1** and **2**.<sup>8</sup> We report here the synthesis, characterization, and reaction chemistry of a new type of manganese(IV) complex,  $[\text{PhI}(\text{OAc})\text{O}]_2\text{Mn}^{\text{IV}}\text{TPP}$ , **3**, which hydroxylates alkanes and epoxidizes olefins. This complex contains both a transition metal (Mn) and a nonmetal ion (I) in unusual oxidation states. The high-valent iodine and manganese atoms provide this complex with a five-electron oxidation capability.

(Tetraphenylporphinato)manganese(III) acetate,  $\text{Mn}^{\text{III}}\text{TPP}(\text{OAc})$ , was dissolved in chlorobenzene and oxidized in the presence of 6 equiv of glacial acetic acid with 3 equiv of iodosylbenzene. A slight excess of iodosylbenzene above the 2.5

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(12) In a related experiment in benzene- $d_6$ , the  $^1\text{H}$  NMR before photolysis indicated complete conversion of **3** to **4**, which was indefinitely stable at 32 °C in the dark. Photolysis at 366 nm and 32 °C for 80 h led to formation of 67% **5**. In addition, equal intensity multiplets at  $\delta$  6.44, 6.27, and 2.71 were observed and are assigned to cyclopentadiene (30%).

(13)  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $-45^\circ\text{C}$ , 0.09 M  $\text{Cr}(\text{acac})_3$ )  $\delta$  238.3 (d,  $J_{\text{PC}} = 55$  Hz), 135.8, 122.5, 117.1, 116.4, 115.9, 109.3, 29.8, 18.0 (d,  $J_{\text{PC}} = 23.2$  Hz), 15.0 (three-line pattern,  $J_{\text{PC}} + J_{\text{PC}} = 27.8$  Hz);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $-40^\circ\text{C}$ , 0.09 M  $\text{Cr}(\text{acac})_3$ )  $\delta$  –34.1 (three-line pattern with  $J_{\text{PP}} + J_{\text{PP}} = 31.2$  Hz), –38.9 (d,  $J = 15.6$  Hz) relative to external  $\text{H}_3\text{PO}_4$ ; IR (Nujol) 1647 (s), 1494 (s), 1350 (m), 1253 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{18}\text{H}_{17}\text{O}_3\text{NP}_3\text{Re}$ : C, 36.36; H, 6.27; N, 2.36. Found: C, 36.26; H, 6.27; N, 2.35. *m/e* calcd 595.1538, obsd 595.1548.

(14) A referee suggested that **9** might be a simple adduct with a coordinated acetone ligand and a bent NO ligand. However, this structure is inconsistent with our new data on the 2-butanone adduct of **5**. Moreover, our earlier NMR data for **9** showed an upfield shift of the *gem*-dimethyl protons relative to free acetone in benzene ( $\delta$  1.36 vs. 1.54); for comparison, a downfield shift has been seen for the methyl groups of coordinated acetone in  $(\text{C}_5\text{H}_5)_2\text{Re}(\text{CO})(\text{NO})(\text{O}=\text{C}(\text{CH}_3)_2)^+$ .<sup>15</sup> In addition, the large upfield shift of the acetone carbonyl from  $\delta$  206 in acetone to  $\delta$  135.8 in the  $^{13}\text{C}$  NMR of **9** is most consistent with our proposed formulation.

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