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; ΔE = 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)[14] and may allow their use in such complexes.

Studies are presently underway to examine the general chemical reactivity of $(CN)_8PcZn$ and other similar octacyano-substituted metal phthalocyanine complexes.

Acknowledgment. K.M.K. acknowledges the support of the National Science Foundation (Grant CHE-792156).

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Conversion of an η^5-C_5H_5 Complex into a Cyclopentadienylidene Ketene Complex

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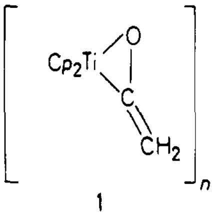
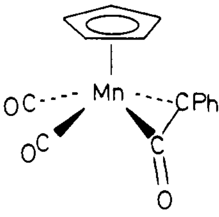
Received January 10, 1983

Transition-metal ketene complexes have been proposed as intermediates in CO reduction[1] and have been studied as models for CO_2 metal complexes.[2a,b] Two types of metal η^2-ketene complexes are known: early transition metals form η^2-CO complexes[2] such as **1** while later transition metals form η^2-CC complexes such as **2**.[3] Previously, metal ketene complexes have been prepared by direct reaction of ketene with a coordinatively unsaturated metal complex,[2a-d,3a] by carbonylation of metal alkylidene complexes,[3d] and by deprotonation of metal acyl complexes.[2e,4] Here we report that $(\eta^5\text{-}C_5H_5)Re(CO)(NO)(CH_3)$ (**3**, Scheme I) reacts with high concentrations of PMe_3 to give an η^1-C_5H_5 derivative, **4**, which is then converted to the novel cyclopentadienylidene ketene[5] complex **5**. This reaction further illustrates the reactivity of the normally unreactive C_5H_5 ligand.



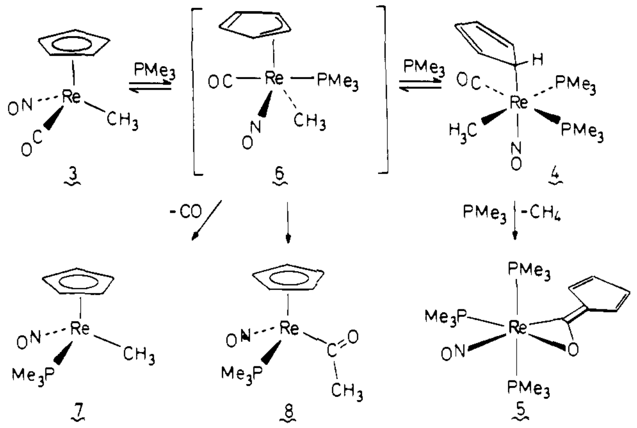
1



2

Previously we have reported that $(\eta^5\text{-}C_5H_5)Re(CO)(NO)(CH_3)$ (**3**) reacts rapidly and reversibly with PMe_3 at room temperature to give the η^1-C_5H_5 bisphosphine complex **4** via the proposed η^3-C_5H_5 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 η^3-C_5H_5 intermediate **6**.[6] We have now discovered that when conversion to **7** and **8** is inhibited by high concentrations of PMe_3, another reaction leading to cyclopentadienylidene ketene complex **5** takes place.

Scheme I



When a toluene solution of **3** (0.986 mmol, 0.25 M) and PMe_3 (2.9 M) was heated for 17 h at 72 °C,[7] evolution of methane (44%) was detected. Removal of the excess PMe_3 and toluene under reduced pressure and recrystallization of the residue from THF-hexane gave a yellow solid identified as the η^2-CO-cyclopentadienylidene ketene complex **5** (150 mg, 28%).[8]

The ^1H NMR of **5** in benzene-d_6 establishes the presence of two equivalent *trans*-PMe_3 ligands (δ 1.05 (three-line pattern with $J_{PH} + J_{P'H}$ = 7 Hz)), one unique PMe_3 ligand (δ 1.09 (d, J = 8.5 Hz)), and four different coupled protons on the cyclopentadienylidene ketene ligand (δ 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)).[9] The observation of four different protons on the five-membered ring excludes a more symmetric η^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^{-1} assigned to a linear nitrosyl ligand. A broad band at 1555 cm^{-1} might be due to either the C-O or C=C stretch of the η^2-CO-cyclopentadienylidene ketene ligand. For comparison, the η^2-CO-complex **1** has a band at 1610 cm^{-1} [2e] while the η^2-CC-complex **2** has a band at 1787 cm^{-1}.[3b]

In the $^{13}C\{^1H\}$ NMR of **5** in CD_2Cl_2, the ketene carbon bonded to rhenium appears as a broad signal at δ 214.4[10] with $\nu_{1/2}$ = 29 Hz. The relatively narrow line width of this signal is consistent

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[4] Lappert[2f] has reported that carbonylation of $Cp_2Zr(CHPh_2)R$ gives the η^2-CO complex $\{Cp_2Zr(COCPh_2)\}_2$. Grubbs[2e] has suggested that the reaction may proceed by deprotontation of an intermediate $Cp_2Zr(COCHPh_2)R$ species.

[5] Cyclopentadienylidene ketene has been observed by IR (2133 (vs), 2130 (s), 1445 (m), 1325 (m) cm^{-1}), UV and photoelectron spectroscopy in low-temperature matrices: Torres, M.; Clement, A.; Strausz, O. P. *J. Org. Chem.* **1980**, *45*, 2273-2274 and references therein.

[6] Casey, C. P.; Jones, W. D. *J. Am. Chem. Soc.* **1980**, *102*, 6154-6156. Casey, C. P.; Jones, W. D.; Harsy, S. G. *J. Organomet. Chem.* **1981**, *206*, C38-C42. Casey, C. P.; O'Connor, J. M.; Jones, W. D.; Haller, K. J. *Organometallics*, in press.

[7] The ^1H NMR of a similar benzene-d_6 solution at 72 °C shows that the η^1-C_5H_5 complex **4** is the major species under these initial conditions.

[8] **5**: ^{13}C NMR (CD_2Cl_2, 0.09 M $Cr(acac)_3$) δ 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, $J_{PC} + J_{P'C}$ = 27.9 Hz), 21.1 (q, d, J_{CH} = 127 Hz, J_{PC} = 27.8 Hz); ^{31}P NMR (C_6D_6) δ -26.6 (d, J_{PP} = 7.9 Hz), -32.9 (t, J_{PP} = 7.9 Hz) relative to external H_3PO_4. Anal. Calcd for $C_{15}H_{31}NO_2P_3Re$: C, 33.59; H, 5.83; N, 2.61. Found: C, 33.63; H, 5.83; N, 2.80. *m/e* calcd for $C_{15}H_{31}NO_2P_3Re$, 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 δ 220[2e] and for **2** at δ 201.3.[3b] Additional resonances of **5** were observed for the carbons of the five-membered ring at δ 125.0, 120.3, 119.0, 118.0, and 112.3; for the unique PMe_3 ligand at δ 21.1 (d, J_{PC} = 27.8 Hz) and for the equivalent trans PMe_3 ligands at δ 16.2 (three-line pattern with $J_{PC} + J_{P'C}$ = 27.9 Hz).

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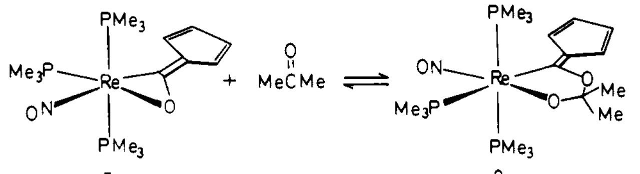
with structure **5** in which the ketene carbon is cis to all three phosphorus ligands.[11]

Significantly higher yields of **5** were obtained from photolysis of **3** and PMe_3 than were obtained from thermal reaction. When a toluene solution of **3** (2.64 mmol, 0.31 M) and 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.[12]

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**[13] resulting from insertion of acetone into the Re–O bond of **5**. The reaction is analogous to the addition of $(C_6H_5)_2C{=}C{=}O$ to $\{(\eta^5\text{-}C_5H_5)_2Ti(Ph_2C_2O)\}_2$, which leads to insertion of the C=O bond of the ketene into the Ti–O bond.[2a]



The ^1H NMR of acetone adduct **9** in benzene-d_6 consists of multiplets at δ 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 δ 1.36 assigned to the *gem*-dimethyl protons, a doublet at δ 1.02 (J = 7.9 Hz) assigned to the unique PMe_3 ligand, and a three-line pattern ($J_{PH} + J_{P'H}$ = 6.8 Hz) at δ 1.19 assigned to the equivalent *trans*-PMe_3 ligands. In the related 1:1 adduct of **5** with 2-butanone, the *trans*-PMe_3 ligands are no longer equivalent and resonances due to three different PMe_3 ligands are seen as δ 1.50 (three lines, $J_{PH} + J_{P'H}$ = 6.8 Hz), 1.47 (three lines, $J_{PH} + J_{P'H}$ = 6.8 Hz), and 1.61 (d, J = 8.1 Hz).[14] In the $^{13}C\{^1H\}$ NMR (CD_2Cl_2) of **9**, there is a doublet (J_{PC} = 55 Hz) at δ 238.2 assigned to the carbon bonded to rhenium, which is trans to the unique PMe_3 ligand.[11,13]

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 ^1H NMR indicated the clean conversion of **9** to **5** and free acetone with a half-life of ~60 min at 80 °C.

The conversion of η^5-C_5H_5 complex **3** into the cyclopentadienylidene ketene complex **5** probably proceeds via the observed intermediate η^1-C_5H_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_3 bond and formation of methane might occur either by protonation of the Re–CH_3 bond or by reductive elimination from an intermediate CH_3ReH species. Cleavage of the C–H bond of the cyclopentadiene unit could occur either by base abstraction or insertion of Re into the α-CH bond of an η^1-C_5H_5Re species; alternatively, migration of the η^1-C_5H_5 unit to CO might preceed C–H cleavage by either base abstraction or Re β-H elimination from a Re–CO–C_5H_5 species. Formation of the new carbon–carbon bond of the ketene complex could occur either by migration of an η^1-C_5H_5 ligand to CO or by coupling of an intermediate cyclopentadienylidene ligand with coordinated CO.[1b,3d] Whatever the mechanism, it is becoming clear that a great deal of interesting chemistry is resulting from PMe_3-induced $\eta^5\text{-}C_5H_5 \rightleftarrows \eta^3\text{-}C_5H_5 \rightleftarrows \eta^1\text{-}C_5H_5$ transformations.

Acknowledgment. Support from the Department of Energy, Division of Basic Energy Sciences, is gratefully acknowledged.

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

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[11] For rhenium compounds, trans J_{PC} is typically 40–60 Hz and cis J_{PC} is typically 5–10 Hz: Anglin, J. R.; Calhoun, H. P.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 2281–2289. However, we are unable to definitively assign the configuration of **5** since cases are known in which cis J_{PC} is greater than trans J_{PC}: Flood, T. C.; Jensen, J. E.; Statler, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4410–4414.

[12] In a related experiment in benzene-d_6, the ^1H 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 δ 6.44, 6.27, and 2.71 were observed and are assigned to cyclopentadiene (30%).

[13] 9: $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −45 °C, 0.09 M $Cr(acac)_3$) δ 238.3 (d, J_{PC} = 55 Hz), 135.8, 122.5, 117.1, 116.4, 115.9 109.3, 29.8, 18.0 (d, J_{PC} = 23.2 Hz), 15.0 (three-line pattern, $J_{P'C} + J_{PC}$ = 27.8 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40 °C, 0.09 M $Cr(acac)_3$) δ −34.1 (three-line pattern with $J_{PP'} + J_{PP''}$ = 31.2 Hz), −38.9 (d, J = 15.6 Hz) relative to external H_3PO_4; IR (Nujol) 1647 (s), 1494 (s), 1350 (m), 1253 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{37}O_3NP_3Re$: 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 coordinaged 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 (δ 1.36 vs. 1.54); for comparison, a downfield shift has been seen for the methyl groups of coordinated acetone in $(C_5H_5)Re(CO)(NO)(O{=}C(CH_3)_2)^+$.[15] In addition, the large upfield shift of the acetone carbonyl from δ 206 in acetone to δ 135.8 in the ^{13}C NMR of **9** is most consistent with our proposed formulation.

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Synthesis, Characterization, and Reaction Chemistry of a Bis(iodosylbenzene)–Metalloporphyrin Complex, $[PhI(OAc)O]_2Mn^{IV}TPP$. 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[1] and water[2] 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, $Mn^{IV}TPP(OCH_3)_2$,[3,4] two types of dimeric manganese(IV) complexes, $[XMn^{IV}TPP]_2O$, **1**, X = N_3^- and OCN^-,[5] and $[YMn^{IV}TPP(OIPh)]_2O$, **2**, Y = Cl^- and Br^-,[6] and a manganese(V) complex, $NMn^{V}T$*p*MPP.[7] The dimeric manganese(IV) complexes enabled us to establish a detailed mechanism for alkane functionalization by **1** and **2**.[8] We report here the synthesis, characterization, and reaction chemistry of a new type of manganese(IV) complex, $[PhI(OAc)O]_2Mn^{IV}TPP$, **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, $Mn^{III}TPP(OAc)$, 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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[3] Abbreviations: TPP, TpMPP are the tetraphenylporphinato and the tetrakis(*p*-methoxyphenyl)porphinato dianion ligands, respectively.

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