Organometallics 1989, 8, 950–955

Organometallic Reactions of Rhodium Octaethylporphyrin Species in Pyridine: Heterolytic Cleavage of $[(OEP)Rh]_2$ and Metalloanion Activation of CO

Bradford B. Wayland,* Kenneth J. Balkus, Jr., and Maria D. Farnos

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

Received July 28, 1988

The nature of the solution species and general organometallic reactivity for solutions resulting from dissolution of (octaethylporphyrin)rhodium(II) dimer, $[(OEP)Rh]_2$ (1), and (OEP)Rh–H (2) in pyridine have been investigated. The Rh–Rh bonded dimer $[(OEP)Rh]_2$ is found to dissociate and disproportionate in pyridine to form $[(OEP)Rh(py)_2]^+$ (3) and $[(OEP)Rh]^-$ (4). Dissolution of 2 in pyridine forms (OEP)Rh(H)(py) (5) which is found to react with CO and CH_3CHO to form metalloformyl, (OEP)RhCHO(py) (6), and α-hydroxyalkyl, $(OEP)RhCH(OH)CH_3$ (7), complexes. Pyridine solutions resulting from dissolution of 1 react with H_2 to form (OEP)Rh(H)(py) (5) and H_2/CO or CO/H_2O mixtures to produce a metalloformyl complex, (OEP)Rh(CHO)(py) (6). The metalloanion 4 is proposed to activate CO and in general to promote several reactions in pyridine that are ascribed to a metalloradical pathway in benzene.

Introduction

(Octaethylporphyrin)rhodium(II) dimer $[(OEP)Rh]_2$ (1) has a small dissociation energy (~16.5 kcal mol^{-1})[1] and functions as an effective source of the reactive metalloradical $[(OEP)Rh]^\bullet$ in hydrocarbon media. Reactions of 1 in benzene with carbon monoxide, alkenes, and alkylaromatics have been interpreted as occurring through the intermediacy of this metalloradical.[2-4] This paper reports on the nature and reactivity of solutions prepared by dissolving $[(OEP)Rh]_2$ (1) and (OEP)Rh–H (2) in the strong donor solvent pyridine. Reactivity and spectroscopic studies in pyridine suggest that the metalloanion $[(OEP)Rh]^-$ activates CO in a series of reactions that produce a metalloformyl species, (OEP)Rh(CHO)(py). The metalloanion $[(OEP)Rh]^-$ is proposed as the most reactive species in pyridine in contrast with benzene solutions where the metalloradical has this function.

Results

Species Resulting from Dissolution of $[(OEP)Rh]_2$ in Pyridine. ^1H NMR and electronic spectra for solutions prepared by dissolving $[(OEP)Rh]_2$ (1) in pyridine are found in Figures 1 and 2. Two equal intensity sets of rhodium porphyrin ^1H NMR peaks are compatable with the presence of equal amounts of $[(OEP)Rh(py)_2]^+$ (3) and $[(OEP)Rh]^-$ (4) (Figure 1). ^1H NMR spectra for $[(OEP)Rh]^-$ obtained by deprotonating (OEP)Rh–H with (K 18-crown-6-ether)OH and $[(OEP)Rh(py)_2]^+$ obtained by reacting a pyridine solution of (OEP)Rh–I with $AgClO_4$ are identical with those obtained for the two species that occur from dissolution of 1 in pyridine. Electronic spectra for solutions obtained by dissolving 1 in pyridine and benzene are illustrated in Figure 2. Interporphyrin π–π interaction in the Rh–Rh bonded dimer in benzene is reflected by the broadening in both the soret and visible bands. The broadening observed in benzene is absent in pyridine where the electronic spectra can be described as a superposition of spectra for 3 and 4. Mass spectra for these pyridine solutions using the FAB method have peaks consistent with the presence of 3 and 4. ^1H NMR, electronic spectra and mass spectral studies have failed to detect any Rh–Rh bonded species in pyridine.

(OEP)Rh–H in Pyridine. Dissolution of (OEP)Rh–H (2) in pyridine in contact with H_2 (0.17 atm) results in the ^1H NMR illustrated in Figure 3. The large downfield shift ($\delta_{Rh\text{-}H}$ (−32.95)) and reduction of $J_{^{103}Rh\text{-}H}$ (22 Hz) for the hydride resonance in pyridine compared to the values in benzene ($\delta_{Rh\text{-}H}$ (−41.3), $J_{^{103}Rh\text{-}H}$ (44 Hz)) are characteristic changes that occur for addition of a donor molecule trans to the hydride.[5,6] FAB mass spectra for these solutions gives a parent ion peak for the six-coordinate complex (OEP)Rh(H)(py) (5). In the absence of H_2 gas the ^1H NMR spectra for solutions of 5 in pyridine change over a period of hours due to the slow formation of $[(OEP)Rh(py)_2]^+$ and $[(OEP)Rh]^-$ with evolution of H_2.

(OEP)Rh(H)(py) (5) is not deprotonated to an observable extent in pyridine, which is consistent with the observation that $[(OEP)Rh]^-$ (4) deprotonates the pyridinium ion (pyH^+) to form (OEP)Rh–H(py) (5). Excess pyridinium ion oxidizes 4 to 3 with evolution of H_2. The anion 4 in pyridine does not deprotonate H_2O to an observable extent, and conversely 5 can be titrated with (K 18-crown-6)OH in pyridine to form 4.

Reactions of Hydrogen. Pyridine solutions of 3 and 4 that result from dissolution of 1 react reversibly with H_2 to form the hydride 5 with concomitant loss of both 3 and 4. Conversion of 3 and 4 (5×10^{-3} M) to 5 is virtually complete by ^1H NMR for H_2 pressures greater than 0.17 atm, while lower H_2 pressures produce an NMR observable equilibrium distribution of 3, 4, and 5. Neither 3 nor 4 reacts separately with dihydrogen in pyridine to form ^1H NMR observable quantities of 5.

Reactions of Carbon Monoxide. The ^1H NMR spectrum that results when CO and H_2 (P_{CO} = 270 Torr, P_{H_2} = 130 Torr) react with pyridine solutions of (OEP)Rh–H is shown in Figure 4. The ^1H NMR peaks are assigned to an equilibrium distribution of 5 with a metalloformyl complex, 6. Assignment of the ^1H NMR of 6 was assisted by observing solutions prepared by dissolving an independently prepared sample of (OEP)Rh–CHO in

---

[1] Wayland, B. B.; Farnos, M. D.; Coffin, V. L. *Inorg. Chem.* **1988**, *27*, 2745.

[2] (a) Wayland, B. B.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.* **1982**, *104*, 302. (b) Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1981**, 700.

[3] Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333.

[4] (a) Del Rossi, K. J.; Wayland, B. B. *J. Am. Chem. Soc.* **1985**, *107*, 7941. (b) Wayland, B. B.; Del Rossi, K. J. *J. Organomet. Chem.* **1984**, *276*, C27.

[5] Farnos, M. D.; Woods, B. A.; Wayland, B. B. *J. Am. Chem. Soc.* **1986**, *108*, 3659.

[6] Van Voorhees, S. L.; Wayland, B. B. *Organometallics* **1987**, *6*, 204.

0276-7333/89/2308-0950$01.50/0

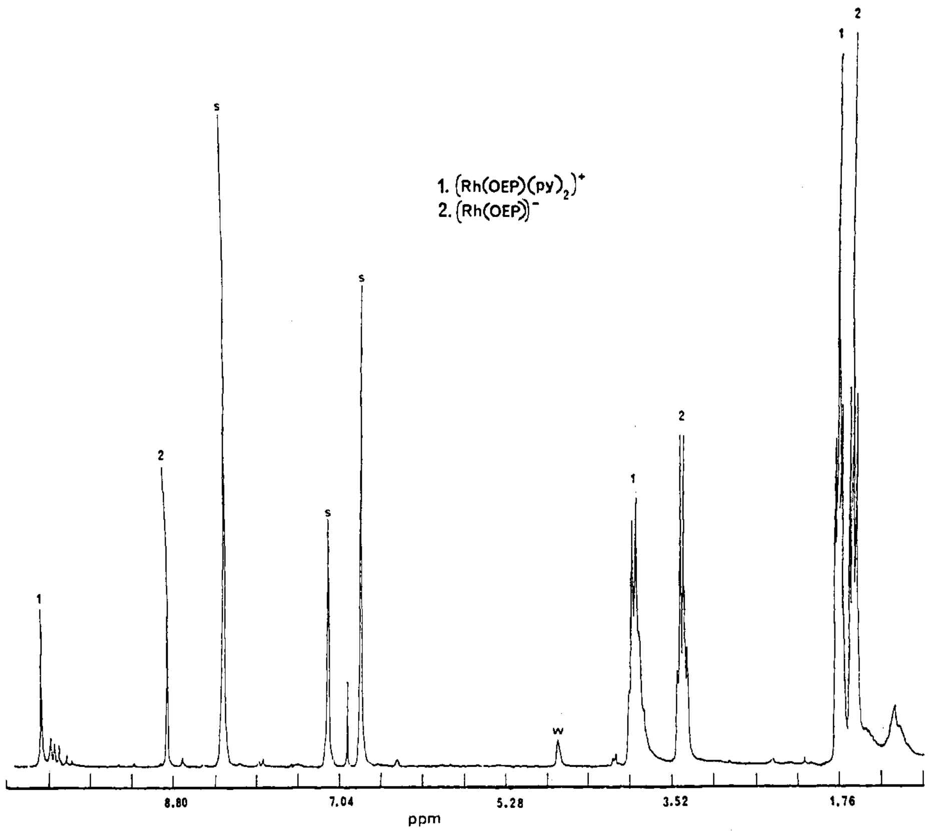


Figure 1. 250-MHz ^1H NMR spectrum of a solution prepared by dissolving $[(OEP)Rh]_2$ in pyridine-d_5: (1) $[(OEP)Rh(py)_2]^+$; (2) $[(OEP)Rh]^-$.

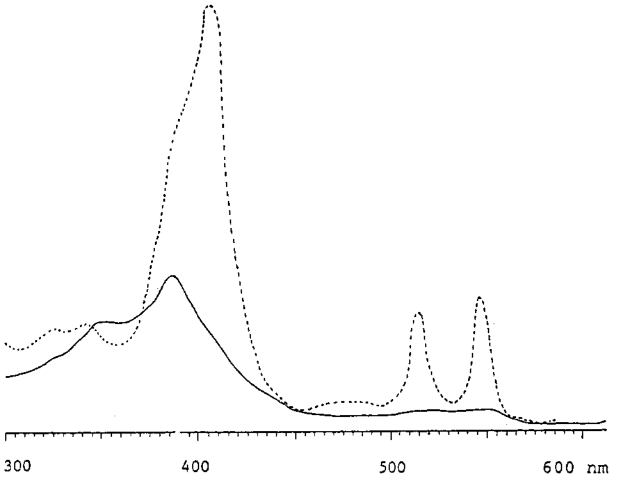


Figure 2. Electronic absorption spectra of solutions prepared by dissolving $[(OEP)Rh_2]$ in pyridine (···) and benzene (—).

pyridine. A doublet at $\delta = 4.51$ ($J_{^{103}Rh-CH}$ (3.95 Hz)), which splits into a doublet of doublets with ^{13}CO is used ($J_{^{13}C-H}$ (165 Hz), is assigned to the formyl hydrogen in an (OEP)Rh–CHO species. The ^{13}C NMR spectrum for a pyridine solution of the (OEP)Rh–^{13}CHO complex is a doublet of doublets ($\delta_{Rh-^{13}C}$ (213), $J_{^{103}Rh-^{13}C}$ (27.5 Hz), $J_{^{13}C-H}$ (165 Hz). Comparisons of the ^1H and ^{13}C NMR parameters for (OEP)Rh–CHO in pyridine and benzene are given in Table I. A parallel study of $H^{13}CHO$ and $CH_3{}^{13}CHO$ revealed that the ^1H and ^{13}C chemical shifts and ^{13}C–H coupling constants are not significantly different in benzene and pyridine.

Carbon monoxide is observed to react with **5** in pyridine to produce a well-defined equilibrium with **6** (Figure 4). Integration of the ^1H NMR spectrum gives a ratio of molar concentrations for the formyl, **6**, to the hydride, **5**, of 0.345 when $P_{CO} = 0.356$ atm and $T = 298$ K. Estimating the molar concentration of CO ($P_{CO} = 0.356$ atm, $T = 298$ K) in pyridine as 2.6×10^{-3} M gives an estimate of the molar equilibrium constant K (298) = 129 ($\Delta G°(298) \approx -2.9$ kcal mol^{-1}).

Table I. Comparison of ^1H and ^{13}C NMR Parameters for the Formyl Group of (OEP)Rh–CHO in Benzene and Pyridine Solvents

	pyridine-d_5	benzene-d_6
δ(C*H*O), ppm	4.51	2.90
J(^{103}Rh–C*H*O), Hz	3.95	1.75
δ(^{13}CHO), ppm	213	194
J(^{13}C*H*O), Hz	165	200
J(^{103}Rh–^{13}C), Hz	27.5	29.0

Solutions of $[(OEP)Rh(py)_2]^+$ (**3**) and $[(OEP)Rh]^-$ (**4**) resulting from dissolution of $[(OEP)Rh]_2$ in pyridine containing a small amount of H_2O also react with CO to produce the formyl complex **6**. In this reaction the anion **4** and the cation **3** react separately at different rates. $[(OEP)Rh]^-$ reacts rapidly (minutes) with CO and H_2O to produce the formyl complex **6**, and the cationic species $[(OEP)Rh(py)_2]^+$ is found to react slowly over a period of days with CO to also produce **6**.

Reactions of $CH_2{=}CH_2$, CH_3I, $CH_3C(O)Cl$, and CH_3CHO. Pyridine solutions of **3** and **4** resulting from dissolution of **1** fail to react with ethene, but when put in contact with methyl iodide or acetyl chloride, the anion **4** selectively reacts to form methyl and acyl derivatives, respectively, and **3** is left unchanged. Solutions of **3** and **4** that contain a small amount of water also give selective reaction of **4** with CH_3CHO to form an α-hydroxyalkyl complex, (OEP)Rh-CH(OH)CH_3 (**7**). Pyridine solutions of **5** also fail to react with ethene but add with acetaldehyde to form **7**. Identification of the methyl, acyl, and α-hydroxyalkyl derivatives of (OEP)Rh in solution was accomplished by comparisons of ^1H NMR and FAB mass

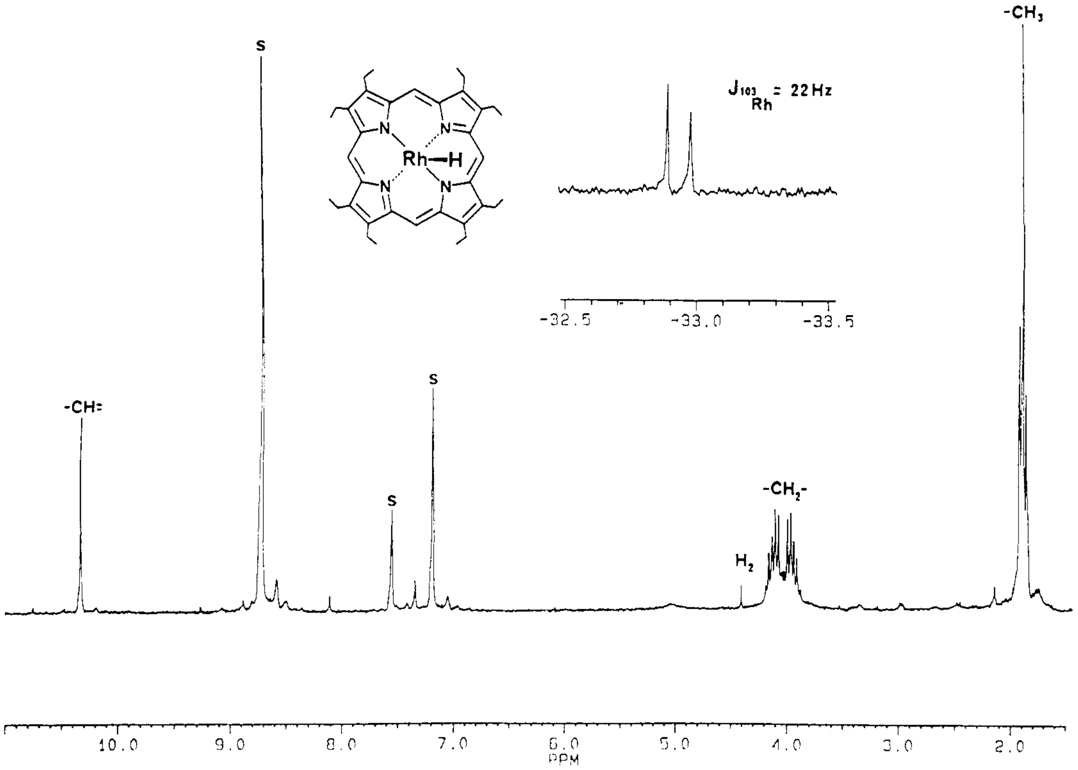


Figure 3. 250-MHz ^{1}H NMR spectrum that results from dissolving (OEP)Rh–H in C_5D_5N in contact with H_2 (0.17 atm).

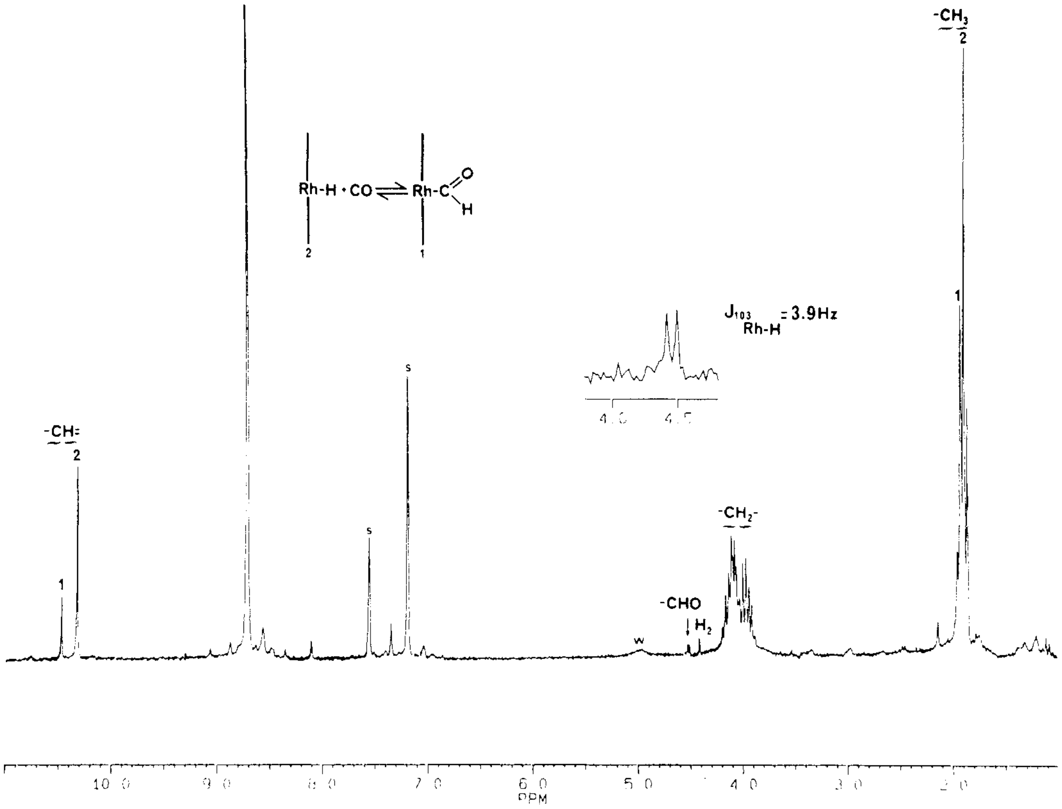


Figure 4. 250-MHz ^{1}H NMR spectrum that results from dissolving (OEP)Rh–H in C_5D_5N in contact with CO (0.35 atm) and H_2 (0.171 atm) (T = 296 K): (1) (OEP)Rh(H)(py); (2) (OEP)Rh-CHO.

spectra with independently prepared samples of these complexes dissolved in pyridine.

Discussion

When $[(OEP)Rh]_2$ (1) is dissolved in pyridine, the Rh–Rh bond is cleaved and a solution containing equal concentrations of $[(OEP)Rh(py)_2]^+$ (3) and $[(OEP)Rh]^-$ (4) is produced (eq 1). Heterolytic cleavage of the Rh–Rh bond

$$[(OEP)Rh]_2 + 2py \overset{py}{\rightleftharpoons} [(OEP)Rh(py)_2]^+ + [(OEP)Rh]^- \quad (1)$$

is thermodynamically justified by coordination of pyridine to the cationic Rh(III) species $[(OEP)Rh]^+$. Dissolution of $[(OEP)Ru]_2$ in pyridine has been previously reported to result in homolytic clevage of the Ru–Ru double bond to form $(OEP)Ru(py)_2$ which is isoelectronic with $[(OEP)Rh(py)_2]^+$.[7] Disproprotionation of metal carbonyl species in pyridine provide further precedents for reactions similar to eq 1.[8-10] Pyridine coordinates or solvates all of the (OEP)Rh species, but the specific coordination of pyridine to $[(OEP)Rh]^+$ is undoubtedly the dominant interaction that drives the heterolylic bond cleavage. Observation of reaction 1 implies that the energy associated with binding two pyridines to $[(OEP)Rh]^+$ is sufficient to compensate for breaking the Rh–Rh bond and the difference between the ionization potential and electron affinity for $[(OEP)Rh]^\bullet$.

Heterolytic cleavage of the Rh–Rh bond in pyridine produces a nucleophile, $[(OEP)Rh]^-$, and an electrophile, $[(OEP)Rh(py)_2]^+$. The Rh(I) anion has a filled dz^2 orbital and should not bind pyridine very strongly. The nucleophilic character of **4** observed in benzene and alcohols[11,12] is retained in pyridine, as evidenced by the reactions of **4** in pyridine with alkyl halides to form alkyl complexes (eq 2). The strong electrophilic character of $[(OEP)Rh]^+$

$$[(OEP)Rh]^- + RBr \xrightarrow{py} (OEP)Rh{-}R + Br^- \quad (2)$$

observed in hydrocarbon solvents[13,14] is substantially repressed in pyridine by formation of the bis(pyridinate) complex. Strong binding of pyridine to $Rh(III)^+$ also adversely affects the thermodynamics of addition reactions. Solutions resulting from dissolution of **1** in pyridine fail to react with ethene which contrasts with the reaction of **1** in benzene to produce a bridged ethylene complex, $(OEP)Rh{-}CH_2CH_2{-}Rh(OEP)$.[3,15]

Reaction of H_2. Heterolytic addition of hydrogen to the ionic fragments **3** and **4** that result from dissolution of $[(OEP)Rh]_2$ in pyridine is an important feature of the reactivity for this system (eq 3). Pyridine solutions of

$$[(OEP)Rh]^- + [(OEP)Rh(py)_2]^+ + H_2 \underset{py}{\overset{py}{\rightleftharpoons}} 2(OEP)Rh(H)(py) \quad (3)$$

$[(OEP)Rh(py)_2]^+$ do not react with H_2 (P_{H_2} 0.2–0.4 atm, T = 296 K) to produce NMR observable concentrations of the metallohydride **5** by eq 4. The metalloanion **4** is

$$[(OEP)Rh(py)_2]^+ + H_2 \overset{py}{\rightleftharpoons} (OEP)Rh(H)(py) + pyH^+ \quad (4)$$

$$[(OEP)Rh]^- + pyH^+ \overset{py}{\rightleftharpoons} (OEP)Rh(H)(py) \quad (5)$$

independently observed to deprotonate pyridinium ion (eq 5), and thus reaction 3, which is the sum of reactions 4 and 5, is thermodynamically favored over reaction 4. Observable reaction of H_2 with $[(OEP)Rh(py)_2]^+$ in pyridine apparently requires the presence of a base that can deprotonate the pyridinium ion. Heterolytic additions of hydrogen are well precedented,[16] but reaction 3 is unusual in that both the hydride and proton fragments of dihydrogen add to metal centers.

The analogue of reaction 3 in benzene is the reaction of $[(OEP)Rh]_2$ (**1**) with H_2 to form (OEP)Rh–H (**2**) (eq 6).

$$[(OEP)Rh]_2 + H_2 \overset{C_6D_6}{\rightleftharpoons} 2(OEP)Rh{-}H \quad (6)$$

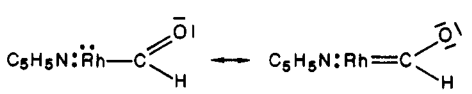
Observation of reaction 3 in pyridine requires that the energetics associated with dissociating the Rh–Rh bond of $[(OEP)Rh]_2$ along with pyridine coordination and solvation of $[(OEP)Rh]^+$ and $(OEP)Rh^-$ must be nearly balanced by the interactions of pyridine with (OEP)Rh–H.

Reactions of CO. Solutions of (OEP)Rh(H)(py) (**5**) in pyridine react reversibly with CO and CH_3CHO to produce equilibrium distributions of metalloformyl (OEP)Rh(CHO)(py) (**6**) and α-hydroxyalkyl complexes (eq 7, 8).

$$[(OEP)Rh(H)(py)] + CO \overset{py}{\rightleftharpoons} (OEP)Rh(CHO)(py) \quad (7)$$

$$(OEP)Rh(H)(py) + CH_3CHO \overset{py}{\rightleftharpoons} (OEP)Rh(CH(OH)CH_3)(py) \quad (8)$$

The difference in $\Delta G°(298\ K)$ for producing the metalloformyl in benzene ($\Delta G°(298\ K) = -3.8\ kcal\ mol^{-1}$)[5] and pyridine ($\Delta G°(298\ K) = -2.9\ kcal\ mol^{-1}$) is only ~1 kcal which indicates that the interactions of pyridine with (OEP)Rh–H and CO are virtually cancelled by the interactions with (OEP)Rh–CHO. Changes in the NMR parameters for (OEP)Rh–CHO in pyridine compared with benzene, Table I ($\Delta_{^{13}C} = +29$ ppm, $\Delta J_{^{13}C-H} = -35$ Hz, $\Delta\delta_{C-H} = 1.61$ ppm, $\Delta J_{^{103}Rh-CH} = 2.2$ Hz), provide clear evidence that pyridine interactions significantly perturb the Rh–CHO unit. Comparison of the ^1H and ^{13}C NMR parameters for formaldehyde and acetaldehyde in pyridine and benzene indicates that pyridine produces very little perturbation of the formyl unit in organic aldehydes, which suggests that the perturbation of the Rh–CHO unit in **6** results from coordination of pyridine with the rhodium center. Binding of pyridine to rhodium could make the formyl unit more carbene like in character



and account for the changes in the formyl NMR parameters.

Combining eq 4, 5, and 7 produces eq 9 which describes

$$[(OEP)Rh(py)_2]^+ + [(OEP)Rh]^- + H_2 + 2CO \rightleftharpoons 2(OEP)Rh{-}CHO(py) \quad (9)$$

the reactions for a solution of **3** and **4** in pyridine with H_2 and CO to produce the metalloformyl complex **6**. Reactions 7–9 are analogues of previously observed reactions in benzene (eq 10–12). Even though the nature of the

---

(7) Collman, J. P.; Brothers, P. J.; McElwee-White, L.; Rose, E.; Wright, L. J. *J. Am. Chem. Soc.* **1985**, *107*, 4570.

(8) (a) Stiegman, A. E.; Tyler, D. R. *Inorg. Chem.* **1984**, *23*, 527. (b) Stiegman, A. E.; Tyler, D. R. *Acc. Chem. Res.* **1984**, *17*, 61. (c) Stiegman, A. E.; Tyler, D. R. *J. Photochem.* **1984**, *24*, 311.

(9) McCullen, S. B.; Brown, T. L. *Inorg. Chem.* **1981**, *20*, 0000.

(10) Lacombe, D. A.; Anderson, J. E.; Kadish, K. M. *Inorg. Chem.* **1986**, *25*, 2074.

(11) (a) Ogoshi, H.; Setsune, J.; Yoshida, Z. *J. Organomet. Chem.* **1980**, *185*, 95. (b) Ogoshi, H.; Setsune, J.; Omura, T.; Yoshida, Z. *J. Am. Chem. Soc.* **1975**, *97*, 6461. (c) Setsune, J.; Yoshida, Z.; Ogoshi, H. *J. Chem. Soc., Perkins Trans. 1* **1982**, 983.

(12) (a) Ogoshi, H.; Setsune, J.; Yoshida, Z. *J. Chem. Soc., Chem. Commun.* **1975**, 572. (b) James, B. R.; Stynes, D. V. *J. Chem. Soc., Chem. Commun.* **1972**, 1261.

(13) (a) Aoyama, Y.; Yoshida, T.; Sakurai, K.; Ogoshi, H. *Organometallics* **1986**, *5*, 168. (b) Aoyama, Y.; Yoshida, T.; Sakurai, K.; Ogoshi, H. *J. Chem. Soc., Chem. Commun.* **1983**, 478.

(14) (a) Setsune, J.; Yazawa, T.; Ogoshi, H.; Yoshida, Z. *J. Chem. Soc., Perkins Trans. 1* **1980**, 1641. (b) Ogoshi, H.; Setsune, J.; Nanbo, Y.; Yoshida, Z. *J. Organomet. Chem.* **1978**, *159*, 329.

(15) Del Rossi, K. J. Ph.D. Dissertation, University of Pennsylvania, 1986.

(16) Brothers, P. J. *Prog. Inorg. Chem.* **1980**, *28*, 1.

(17) (a) Van Voorhees, S. L.; Wayland, B. B. *Organometallics* **1985**, *4*, 1887. (b) Wayland, B. B.; Woods, B. A.; Minda, V. M. *J. Chem. Soc., Chem. Commun.* **1982**, 634.

(18) Wayland, B. B.; Woods, B. A.; Coffin, V. L. *Organometallics* **1986**, *5*, 1059.

$$\text{(OEP)Rh–H} + \text{CO} \xrightleftharpoons{C_6H_6} \text{(OEP)Rh–(CHO)} \quad (10)$$

$$\text{(OEP)Rh–H} + \text{CH}_3\text{CHO} \xrightleftharpoons{C_6H_6} \text{(OEP)Rh–CH(OH)CH}_3 \quad (11)$$

$$[\text{(OEP)Rh}]_2 + 2\text{CO} + \text{H}_2 \xrightleftharpoons{C_6H_6} 2\text{(OEP)Rh–CHO} \quad (12)$$

species in pyridine and benzene solutions are quite different, similar reactivity occurs because the thermodynamic consequences of pyridine interactions with the reactants and products virtually cancel.

Pyridine solutions of **3** and **4** resulting from dissolution of $[(OEP)Rh]_2$ react with CO and H_2O to produce the stoichiometry depicted by eq 13. The overall reaction may

$$[\text{(OEP)Rh(py)}_2]^+ + [\text{(OEP)Rh}]^- + 3\text{CO} + \text{H}_2\text{O} \xrightarrow{py} 2\text{(OEP)Rh–(CHO)(py)} + \text{CO}_2 \quad (13)$$

be better described as separate reactions of **3** and **4** because the anion $[(OEP)Rh]^-$ reacts much more rapidly than the cation $[(OEP)Rh](py)_2]^+$ in the overall process (eq 14, 15).

$$[\text{(OEP)Rh}]^- + \text{CO} + \text{H}_2\text{O} \xrightarrow[py]{fast} \text{(OEP)Rh–CHO(py)} + \text{OH}^- \quad (14)$$

$$[\text{(OEP)Rh(py)}_2]^+ + 2\text{CO} + \text{OH}^- \xrightarrow[py]{slow} \text{(OEP)Rh–CHO(py)} + \text{CO}_2 + \text{py} \quad (15)$$

Observation of independent reactions for **3** and **4** provides compelling evidence that trace amounts of the metalloradical $[(OEP)Rh]^•$ in equillibrium with **3** and **4** cannot be involved in reaction 13.

In benzene solution where $[(OEP)Rh_2$ and $[(OEP)Rh]^•$ are viable species, a metalloradical chain reaction has been shown by Halpern to provide an effective pathway for CO activation in producing the formyl complex (eq 16–18). In

$$[\text{(OEP)Rh}]_2 \xrightleftharpoons{C_6H_6} 2[\text{(OEP)Rh}]^• \quad (16)$$

$$[\text{(OEP)Rh}]^• + \text{CO} \xrightleftharpoons{C_6H_6} [\text{(OEP)RhCO}]^• \quad (17)$$

$$[\text{(OEP)RhCO}]^• + \text{(OEP)Rh–H} \xrightarrow{C_6H_6} \text{(OEP)Rh–CHO} + [\text{(OEP)Rh}]^• \quad (18)$$

pyridine solution where $[(OEP)Rh]^•$ disproportionates into **3** and **4**, interaction of the metalloanion $[(OEP)Rh]^-$ with CO may provide the most effective pathway for reactions that produce the metalloformyl species (eq 19–21). The

$$[\text{(OEP)Rh}]^- + \text{CO} \xrightleftharpoons{py} [\text{(OEP)RhCO}]^- \quad (19)$$

$$[\text{(OEP)RhCO}]^- + \text{(OEP)Rh–(H)(py)} \xrightarrow{py} \text{(OEP)Rh–CHO(py)} + [\text{(OEP)Rh}]^- \quad (20)$$

$$[\text{(OEP)Rh(CO)}]^- + \text{H}_2\text{O} \xrightarrow{py} \text{(OEP)Rh–CHO} + \text{OH}^- \quad (21)$$

Rh(I) anion could potentially activate CO by inducing carbanion character ($[(OEP)Rh:]^- + CO \rightarrow [(OEP)Rh{:}\ddot{C}{=}O]^-$) which facilitates the rehybridization and protonation that would occur in the product-forming step. This proposed utilization of the nucleophilic property of a metalloanion to activate CO is at present based only on reactivity studies, but more detailed kinetic–mechanistic studies are in progress.

Experimental Section

Procedures. Proton NMR spectra were recorded with Bruker 250 and IBM WP200SY NMR spectrometers interfaced with an Aspect 2000 computer. NMR samples were prepared by using vacuum line techniques and sealed. Spectra were internally referenced to the residual proton resonances in C_5D_5N or C_6D_6. Electronic spectra were obtained with a Cary Model 14 spectrophotometer and a Hewlett-Packard HP8452 diode array spectrophotometer interfaced to an IBM XT computer. Cells for electronic spectra were adapted to allow solvent and gas transfer on a vacuum line. Low-resolution fast-atom bombardment mass spectra (FABMS) were recorded on a VG ZAB-E spectrometer.

Reagents. Pyridine and pyridine-d_5 (99.9 atom %) were dried with calcium hydride and molecular sieves. All solvents were degassed by repeated freeze, pump, and thaw cycles. All other reagents were used without further purification unless otherwise specified. Hydrogen (grade 5.5) and carbon monoxide (grade 4.5) were purchased from Matheson. A mixture of CO (grade 4), 67.6%, and H_2 (grade 5.5), 32.4%, was purchased from AIRCO.

(OEP)Rh–H. (Octaethylporphyrin)rhodium hydride was prepared by a published procedure.[11b] A solution containing 20 mg of $NaBH_4$ in 2 mL of 1 N NaOH was added dropwise to a solution of 113 mg of (OEP)Rh–I in 50 mL of degassed ethanol. This solution was gently heated (320 K) until the color changed from dark red to yellow-brown which indicates the presence of $[(OEP)Rh]^-$. Glacial acetic acid was added slowly to the solution of $[(OEP)Rh]^-$ which resulted in precipitation of (OEP)Rh–H as a brick red solid. ^1H NMR (C_5D_5N): δ 10.32 (s, CH, 4 H), 4.16 (m, CH_2CH_3, 8 H) 3.96 (m, CH_2CH_3, 8 H), 1.88 (t, CH_2CH_3, 24 H), –32.95 (d, Rh–*H*, 1 H), $J_{^{103}Rh-H}$ = 22 Hz. LR FABMS (C_5H_5N): (OEP)Rh(H)(py) *m/e* = 714. ^1H NMR (C_6D_6): δ 10.15 (s, CH, 4 H), 3.95 (q, CH_2CH_3, 16 H), 1.87 (t, CH_2CH_3, 24 H), –41.28 (d, Rh*H*, 1 H), $J_{^{103}Rh-H}$ = 44 Hz. LR FABMS (C_6H_6): (OEP)Rh–H *m/e* = 635.

$[(OEP)Rh]_2$. (Octaethylporphyrin)rhodium(II) dimer was prepared according to literature procedures.[11c] (OEP)Rh–H was dissolved in dried and degassed benzene. (OEP)Rh–H in benzene slowly converts to an equilibrium distribution with the metal–metal bonded dimer, and periodic removal of hydrogen by freeze, pump, and thaw cycles shifts the equilibrium in favor of the dimer. Both heat and light accelerate conversion of the hydride to $[(OEP)Rh]_2$. ^1H NMR (C_5D_5N): δ 10.74 (s, CH, 4 H), 9.30 (s, CH, 4 H), 4.16 (q, CH_2CH_3, 16 H), 3.64 (q, CH_2CH_3, 16 H), 1.92 (t, J = 2 Hz, CH_3, 24 H), 1.76 (t, CH_2 CH_2CH_3, 24 H). LR FABMS (C_5H_5N): $[(OEP)Rh(py)_2]^+$ *m/e* = 793. ^1H NMR (C_6D_6): δ 9.29 (s, CH, 4 H), 4.45 (m, CH_2CH_3, 8 H), 3.96 (m, CH_2CH_3, 8 H), 1.71 (t, CH_2CH_3, 24 H). LR FABMS (C_6H_6): *m/e* = 1270.

(OEP)Rh–CHO. (Octaethylporphyrin) rhodium formyl was prepared by a previously reported procedure.[2] A benzene solution of (OEP)Rh–H was pressurized with CO (1 atm) for 18 h followed by evaporation of the solvent in a stream of CO. ^1H NMR (C_5D_5N): δ 10.46 (s, CH, 4 H), 4.06 (q, CH_2CH_3, 16 H), 1.91 (t, CH_2CH_3, 24 H), 4.51 (d, C*H*O, 1 H), $J_{^{103}Rh-CHO}$ = 3.95 Hz. LR FABMS (C_5H_5)N: (OEP)Rh(CHO)(C_5D_5N) *m/e* = 753. ^1H NMR (C_6D_6): δ 10.27 (s, CH, 4 H), 3.96 (m, CH_2CH_3, 16 H), 1.88 (t, CH_2CH_3, 24 H), 2.82 (d, C*H*O, 1 H), $J_{^{103}Rh-CHO}$ = 1.9 Hz. LR FABMS (C_6H_6): (OEP)Rh–CHO *m/e* = 664.

$[(OEP)Rh(py)_2]^+$. A pyridine solution of (octaethylporphyrin)rhodium(II) cation was prepared by reacting (OEP)-Rh–I with $AgClO_4$ in pyridine. ^1H NMR (C_5D_5N): δ 10.74 (s, CH, 4 H), 4.16 (q, CH_2CH_3, 16 H), 1.92 (t, CH_2CH_3, 24 H). LR FABMS: $[(OEP)Rh(C_5H_5N)_2]^+$ *m/e* = 793. Electronic spectra: λ_{max} 404, 518, 548 nm.

$[(OEP)Rh]^-$. Complexes containing (octaethylporphyrin)-rhodium(I) anion were prepared by $NaBH_4$ reduction of (OEP)Rh–I and by deprotonation of (OEP)Rh–H with an excess of [K 18-crown-6]OH. ^1H NMR (C_5D_5N): δ 9.30 (s, CH, 4 H), 3.64 (q, CH_2CH_3, 16 H), 1.76 (t, CH_2CH_3, 24 H). LR FABMS (C_5H_5N): $[(OEP)Rh]^-$ *m/e* = 635. Electronic spectra (C_5H_5N): λ_{max} 380, 480, 520 nm. ^1H NMR (C_6D_6): δ 9.43 (s, CH, 4 H), 3.54 (q, CH_2CH_3, 16 H), 1.77 (t, CH_2CH_3, 24 H).

(OEP)Rh–CH(OH)CH_3. (Octaethylporphyrin)rhodium α-hydroxyethyl was prepared by a reported method.[17b] ^1H NMR (C_5D_5N): δ 10.35 (s, CH, 4 H), 4.03 (q, CH_2CH_3, 16 H), 1.88 (t, CH_2CH_3, 24 H), –2.62 (m, C*H*(CH_3)OH, 1 H), –3.90 (d, CH(C*H*$_3$)OH, 3 H), –4.12 (d, CH(CH_3)O*H*, 1 H), J_{CH-OH} = 4.87, $J_{^{103}Rh-CH}$ = 3.4 Hz. ^1H NMR (C_6D_6): δ 10.15 (s, CH, 4 H), 3.97 (m, CH_2CH_3, 16 H), 1.90 (t, CH_2CH_3, 24 H), –2.56 (m, C*H*(CH_3)OH, 1 H), –4.30 (d, CH(CH_3)OH, 3 H), –4.40 (d, CH(CH_3)O*H*, 1 H), J_{CH-OH} = 4.75 Hz, $J_{^{103}Rh-CH}$ = 3.5 Hz.

(OEP)Rh–CH_3. (Octaethylporphyrin)rhodium methyl was prepared by literature methods.[11b] ^1H NMR (C_5D_5N): δ 10.35

(s, CH, 4 H), 4.0 (q, CH_2CH_3, 16 H), 1.93 (t, CH_2CH_3, 24 H), –6.61 (d, CH_3, 3 H), $J_{^{103}Rh-CH}$ = 3.0 Hz. LR FABMS (C_5H_5N): OEPRh–CH_3 *m/e* = 650. ^1H NMR (C_6D_6): δ 10.21 (s, CH, 4 H), 3.97 (q, CH_2CH_3, 16 H), 1.92 (t, CH_2CH_3, 24 H), –6.01 (d, CH_3, 3 H), $J_{^{103}Rh-CH}$ = 3.0 Hz).

(OEP)Rh–C(O)CH_3. (Octaethylporphyrin)rhodium acyl was prepared by literature procedures.[11b] ^1H NMR (C_5D_5N): δ 10.43 (s, CH, 4 H), 4.07 (m, CH_2CH_3, 16 H), 1.91 (t, CH_2CH_3, 24 H), –3.14 (s, C(O)CH_3, 3 H). LR FABMS (C_5H_5N): (OEP)Rh–C(O)CH_3 *m/e* = 678. ^1H NMR (C_6D_6): δ 10.30 (s, CH, 4 H), 3.98 (m, CH_2CH_3, 16 H), 1.90 (t, CH_2CH_3, 24 H), –3.16 (s, C(O)CH_3, 3 H).

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation and the Department of Energy, Division of Chemical Sciences, Offices of Basic Energy Sciences, through Grant DE-FG02-86ER13615.

Registry No. 1, 63439-10-1; 2, 63372-77-0; (OEP)Rh–CHO, 79666-16-3; [(OEP)Rh(py)$_2$]ClO_4, 118977-41-6; (OEP)Rh–I, 69509-36-0; Na[(OEP)Rh], 118977-42-7; (OEP)Rh–CH(OH)CH_3, 83691-20-7; (OEP)Rh–CH_3, 36643-85-3; (OEP)Rh–C(O)CH_3, 83691-22-9; CO, 110-86-1; H_2, 1333-74-0; $CH_2{=}CH_2$, 74-85-1; CH_3I, 74-88-4; $CH_3C(O)Cl$, 75-36-5; CH_3CHO, 75-07-0; pyridine, 110-86-1.

Synthesis, Optical, Photophysical, and Redox Properties of a Ligand-Bridged Heteronuclear $(OC)_5W(pyz)Re(CO)_4Cl$ (pyz = Pyrazine) Complex

Mthembeni M. Zulu and Alistair J. Lees*

Department of Chemistry, University Center at Binghamton, State University of New York, Binghamton, New York 13901

Received August 1, 1988

The heteronuclear ligand-bridged complex $(OC)_5W(pyz)Re(CO)_4Cl$ (pyz = pyrazine) has been prepared by thermal reaction of $ClRe(CO)_4(pyz)$ with photochemically generated $W(CO)_5(THF)$ (THF = tetrahydrofuran). Infrared, electronic absorption, photophysical, and redox data have been obtained from this complex, the corresponding mononuclear derivatives, and the homonuclear dimer complexes $(OC)_5W(pyz)W(CO)_5$ and $Cl(OC)_4Re(pyz)Re(CO)_4Cl$. Infrared spectra illustrate that the carbonyl ligands in the $W(CO)_5$ and $ClRe(CO)_4$ groups of these compounds have approximately C_{4v} and C_s local symmetries, respectively. Electronic absorption spectra reveal the presence of $^1A_1 \rightarrow {}^1E$ ligand field (LF) and M $\rightarrow$ π^*(pyz) metal to ligand charge-transfer (MLCT) transitions for all species. In each case the MLCT bands are attributed to be at lowest energy; these transitions are substantially lowered in the binuclear molecules and reflect the perturbation of the pyz π^*-acceptor system. The absorption spectra indicate that the chromophores' LF transitions are relatively unaffected on binucleation, whereas the energy of the ligand π^*-system is influenced by both metals. Emission spectra, lifetimes, quantum yields, and excitation spectra recorded from the complexes in 283–298 K solution are consistent with the lowest lying MLCT excited state model. No evidence has been obtained from the electronic spectra for a metal to metal charge-transfer (MMCT) transition in the heteronuclear $(OC)_5W(pyz)Re(CO)_4Cl$ complex. Cyclic voltammetry data have been obtained from each complex; oxidation potentials are in accordance with the $^1A_1$ HOMO assignment, and first reduction potentials are further illustrative of the energy stabilization of the pyz π^*-acceptor system. Comparisons of redox potential differences with MLCT transition energies indicate appreciable Franck–Condon reorganization energies in the binuclear Re complexes. Calculated conproportionation constants are also representative of strong electronic perturbations of the binucleating pyz ligands in these complexes.

Introduction

In the past few years there has been great interest in the electronic spectra[1] and photochemical properties[2] of ligand-bridged zerovalent group 6 metal carbonyl dimer complexes. Extensive studies have been carried out on binuclear complexes that are linked between two $M(CO)_5$ groups with the formula $(OC)_5M{-}L{-}M'(CO)_5$ and between two $M(CO)_4$ fragments with the formula $(OC)_4M{-}L{-}M'(CO)_4$ (M, M′ = Cr, Mo, W). One aspect of research in our laboratory has been concerned with the excited-state properties of the $(OC)_5M{-}L{-}M'(CO)_5$ system. In particular, we have sought to understand the substantial photophysical and photochemical changes that occur to these molecules on forming dimers and on varying the binucleating ligand.[3] Additionally, the extraordinary solvent dependence exhibited by several of these binuclear complexes has been rationalized in terms of the bridging ligands' electronic characteristics and the nature of the lowest energy excited states in these molecules.[4]

This paper reports a further development in our investigation of this system with the now successful synthesis

---

[1] (a) Pannell, K. H.; Guadalupe de la Paz Saenz Gonzalez, M.; Leano, H.; Iglesias, R. *Inorg. Chem.* **1978**, *17*, 1093. (b) Pannell, K. H.; Iglesias, R. *Inorg. Chim. Acta* **1979**, *33*, L161. (c) Daamen, H.; Stufkens, D. J.; Oskam, A. *Inorg. Chim. Acta* **1980**, *39*, 75. (d) Gaus, P. L.; Boncella, J. M.; Rosengren, K. S.; Funk, M. O. *Inorg. Chem.* **1982**, *21*, 2174. (e) Garber, L. L. *Inorg. Chem.* **1982**, *21*, 3244. (f) Kaim, W. *Inorg. Chem.* **1984**, *23*, 3365. (g) Ernst, S.; Kaim, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 430. (h) Kohlmann, S.; Ernst, S.; Kaim, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 684. (i) Kaim, W.; Kohlmann, S. *Inorg. Chim. Acta* **1985**, *101*, L21. (j) Haga, M.-A.; Koizumi, K. *Inorg. Chim. Acta* **1985**, *104*, 47. (k) Gross, R.; Kaim, W. *Inorg. Chem.* **1986**, *25*, 498. (l) Ernst, S.; Kaim, W. *J. Am. Chem. Soc.* **1986**, *108*, 3578. (m) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1987**, *26*, 68.

[2] (a) Moore, K. J.; Petersen, J. D. *Polyhedron* **1983**, *2*, 279. (b) Chun, S.; Palmer, D. C.; Mattimore, E. F.; Lees, A. J. *Inorg. Chim. Acta* **1983**, *77*, L119. (c) Lees, A. J.; Fobare, J. M.; Mattimore, E. F. *Inorg. Chem.* **1984**, *23*, 2709.

[3] Zulu, M. M.; Lees, A. J. *Inorg. Chem.* **1988**, *27*, 1139.

[4] (a) Zulu, M. M.; Lees, A. J. *Inorg. Chem.* **1988**, *27*, 3325. (b) Zulu, M. M.; Lees, A. J. *Inorg. Chem.* **1989**, *28*, 85.

0276-7333/89/2308-0955$01.50/0