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Organometallic Chemistry of Rhodium Tetraphenylporphyrin Derivatives: Formyl, Hydroxymethyl, and Alkyl Complexes

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Organometallic reactivity patterns of the rhodium tetraphenylporphyrin derivatives Rh(TPP)(H), Rh(TPP)$^-$, and (Rh(TPP))$_2$ are found to closely parallel those of the corresponding rhodium octaethylporphyrin species. Preparation and physical properties of the formyl, hydroxymethyl, and alkyl complexes of Rh(TPP) are described along with the photoinduced insertion of carbon monoxide into the Rh–CH$_3$ bond. Thermodynamic values for the reaction Rh(TPP)(H) + CO $\rightleftarrows$ Rh(TPP)(CHO) in C_6D_6 are $\Delta H° = -42$ kJ/mol and $\Delta S° = -89 \pm 15$ J/(K mol).

Organometallic reactions of rhodium octaethylporphyrin species have been used to imply that unusually strong Rh–C bonds (>50 kcal) are a dominant factor in this chemistry.[1-6] A primary purpose of this study was to determine whether changes in the electronic structure of the porphyrin macrocycle could be used in tuning the Rh–C bond energy over a sufficient range to alter the general reactivity patterns of the rhodium porphyrin species. Tetraphenylporphyrin, (TPP), and the *p*-methyl derivative, tetratolylporphyrin, (TTP), were chosen for comparison with octaethylporphyrin (OEP) complexes because these ligands represent extremes in the electronic properties of the porphyrins. The OEP and TPP dianions are respectively among the strongest and weakest porphyrin σ donors and metallo–TPP complexes are also more easily reduced than the corresponding OEP derivatives.[7] This paper reports on a comparison of the general organometallic reactivity patterns of Rh$^{\rm I}$(TPP)$^-$, (Rh$^{\rm II}$(TPP))$_2$, and Rh$^{\rm III}$(TPP)(H) species with the corresponding Rh(OEP) derivatives. Thermodynamic values for the reaction of Rh(TPP)(H) with CO to produce the metalloformyl complex, Rh(TPP)(CHO) are reported and compared with the corresponding values for the Rh(OEP) system.

Experimental Section

Proton NMR spectra were obtained with a Bruker Instruments WM250 NMR spectrophotometer with an Aspect 2000 computer. The variable-temperature and proton-decoupled spectra were obtained over a temperature range of 20–100 °C with an IBM Instruments SY200 NMR spectrophotometer interfaced to an Aspect 2000 computer with a Bruker Instruments BVT1000 variable-temperature controller. The temperature in the probe was calibrated with a sample of ethylene glycol. Electronic and IR spectra were obtained on a Cary recording spectrophotometer, Model 14. All solvents and gases were used without further purification except where noted. Benzene was dried over sodium metal and benzophenone. Deuterated benzene, C_6D_6, was degassed and then dried by refluxing over CaH_2 for several days. Chloroform was purified by washing with water and then drying by passing through a column of grade I alumina. The H_2 and CO gases used were grade 5.5 and 4.5, respectively. Proton NMR samples were prepared on a vacuum line, by using dried and degassed C_6D_6, and then sealed.

(TPP)(Rh(CO)$_2$)$_2$. The synthesis of (TPP)(Rh(CO)$_2$)$_2$ follows literature procedures.[8] ^{1}H NMR (δ in C_6D_6): 8.81 (d, 4 H, pyrrole), 8.70 (d, 4 H, pyrrole), 8.37 (m, 4 H, *o* phenyl), 8.05 (d, 4 H, *o'* phenyl), 7.52–7.25 (m, 12 H, *m* and *p* phenyl).

Rh(TPP)(I) and Rh(TTP)(I). The synthesis of Rh(TPP)(I) follows literature procedures.[9] ^{1}H NMR (δ in C_6D_6) of Rh(TTP)(I): 8.98 (s, 8 H, pyrrole), 8.25 (m, 4 H, *o* phenyl), 8.01 (d, 4 H, *o'* phenyl), 7.50–7.35 (m, 12 H, *m* and *p* phenyl). ^{1}H NMR (δ in C_6D_6) of Rh(TTP)(I): 9.09 (s, 8 H, pyrrole), 8.23 (d, 4 H, *o* phenyl), 7.98 (d, 4 H, *o'* phenyl), 7.35 (d, 4 H, *m* phenyl), 7.21 (d, 4 H, *m'* phenyl), 2.41 (s, 12 H, *p*-methyl).

Rh(TPP)(H) and Rh(TTP)(H). A 150-mg sample of Rh(TPP)(I) is dissolved in 50 mL of ethanol and warmed to 65 °C. A 6-mL aliquot of 0.5 M aqueous sodium hydroxide solution containing 30 mg of sodium borohydride is slowly added to the porphyrin solution. After several hours of stirring, 8 mL of glacial acetic acid is added to the solution. The solvent is removed under a steady stream of nitrogen yielding 79 mg of a reddish violet solid (yield 62%). Alternatively, Rh(TPP)(H) can be prepared by the reaction between Rh(TPP)(I) and sodium formate. A 200-mg sample of sodium formate and 200 mg of Rh(TPP)(I) were added to 100 mL of degassed methanol under a N_2 atmosphere; the solution was refluxed for 4 h. The solvent was driven off and the product extracted into dried degassed benzene. The solvent was removed under a steady stream of H_2. A 182-mg sample of reddish violet solid was recovered (yield 78%). ^{1}H NMR (δ in C_6D_6): 8.88 (s, 8 H, pyrrole), 8.25 (m, 4 H, *o* phenyl), 8.00 (d, 4 H, *o'* phenyl), 7.50–7.30 (m, 12 H, *m* and *p* phenyl), –40.19 (d, 1 H, hydride). The above procedures were also used to prepare Rh(TTP)(H). ^{1}H NMR (δ in C_6D_6) of Rh(TTP)(H): 9.01 (s, 8 H, pyrrole), 8.23 (d, 4 H *o* phenyl), 7.95 (d, 4 H, *o'* phenyl), 7.36 (d, 4 H, *m* phenyl), 7.20 (d, 4 H, *m'* phenyl), 2.42 (s, 12 H, *p*-methyl), –40.18 (d, 1 H, hydride).

Rh(TPP)$^-$ and Rh(TTP)$^-$. Dried and degassed C_6D_6 was vacuum-transferred into a NMR tube containing 3 mg of Rh(TPP)(H). a C_6D_6 solution of potassium hydroxide, solubilized by 18-crown-6-ether, was added, and the NMR tube was sealed. ^{1}H NMR (δ in C_6D_6) of Rh(TPP)$^-$: 8.46 (s, 8 H, pyrrole), 8.08 (d, 4 H, *o* phenyl), 8.05 (d, 4 H, *o'* phenyl), 7.46 (d, 8 H, *m* phenyl). The same procedure as for Rh(TPP)$^-$ was used to prepare Rh(TPP)$^-$. ^{1}H NMR (δ in C_6D_6) of Rh(TTP)$^-$: 8.55 (s, 8 H, pyrrole), 8.00 (d, 8 H, *o* phenyl), 7.29 (d, 8 H, *m* phenyl), 2.41 (s, 12 H, *p* phenyl).

(Rh(TPP))$_2$ and (Rh(TTP))$_2$. The synthesis of (Rh(TPP))$_2$ and (Rh(TTP))$_2$ follows literature methods.[10] A 3-mg sample of Rh(TPP)(H) and dried degassed C_6D_6 were placed in a NMR tube fitted with a septum cap. The solution is irradiated at $\lambda > 445$ nm while a stream of argon removes the evolved molecular hydrogen. ^{1}H NMR (δ in C_6D_6): 9.66 (d, 4 H, *o* phenyl), 8.49 (s, 8 H, pyrrole), 7.93 (d, 4 H, *o'* phenyl); *m*, *m'*, and *p* phenyl hydrogens are obscured by solvent resonance (7.15). The above procedure was also used in the preparation of (Rh(TTP))$_2$. ^{1}H NMR (δ in C_6D_6) of (Rh(TTP))$_2$: 9.64 (d, 4 H, *o* phenyl), 8.63 (s, 8 H, pyrrole), 7.75 (d, 4 H, *o'* phenyl), 2.50 (s, 12 H, *p*-methyl); *m*, *m'*, and *p* phenyl hydrogens are obscured by solvent (7.15).

Rh(TPP)(CHO) and Rh(TTP)(CHO). Dried and degassed C_6D_6 was vacuum distilled into an NMR tube containing 2 mg of Rh(TPP)(H). The NMR tube was pressurized with mixtures of hydrogen and carbon monoxide and sealed. ^{1}H NMR (δ in C_6D_6) of Rh(TPP)(CHO): 8.91 (s, 8 H, pyrrole), 8.22 (m, 4 H, *o* phenyl), 8.03 (d, 4 H, *o'* phenyl), 7.50–7.37 (m, 12 H, *m* and *p* phenyl), 3.18 (d, 1 H, formyl). The same procedure was utilized in the preparation of Rh(TPP)(CHO). ^{1}H NMR (δ in C_6D_6) of Rh(TTP)(CHO): 9.02 (s, 8 H, pyrrole, 8.19 (d, 4 H, *o* phenyl), 7.99 (d, 4 H, *o'* phenyl), 7.35 (d, 4 H, *m* phenyl), 7.23 (d, 4 H,

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m′ phenyl), 3.24 (d, 1 H, formyl), 2.42 (s, 12 H, *p*-methyl).

Rh(TPP)(alkyl). RhTPP(alkyl) compounds were synthesized by literature methods.[11] ^{1}H NMR (δ in $\mathrm{C_6D_6}$) of $\mathrm{Rh(TPP)(CH_3)}$: 8.88 (s, 8 H, pyrrole), 8.26 (m, 4 H, *o* phenyl), 8.05 (d, 4 H, *o′* phenyl), 7.50–7.40 (m, 12 H, *m* and *p* phenyl), −5.51 (d, 3 H, methyl). ^{1}H NMR (δ in $\mathrm{C_6D_6}$) of $\mathrm{Rh(TPP)(C_2H_5)}$: 8.86 (s, 8 H, pyrrole), 8.25 (m, 4 H, *o* phenyl), 8.07 (d, 4 H, *o′* phenyl), 7.50–7.40 (m, 12 H, *m* and *p* phenyl), −4.18 (t, 3 H, $\mathrm{CH_2{-}C}H_3$), −4.40 (q, 2 H, $\mathrm{C}H_2\mathrm{{-}CH_3}$). ^{1}H NMR ($\delta$ in $\mathrm{C_6D_6}$) of $\mathrm{Rh(TPP)(CH_2I)}$: 8.89 (s, 8 H, pyrrole), 8.26 (m, 4 H, *o* phenyl), 8.10 (d, 4 H, *o′* phenyl), 7.50–7.40 (m, 12 H, *m* and *p* phenyl), −3.30 (d, 2 H, $\mathrm{CH_2I}$).

$\mathbf{(Rh(TPP))_2(C_2H_4)}$. A dilute stock solution of 1,2-dibromoethane was slowly added to a solution of the rhodium porphyrin anion. ^{1}H NMR (δ in $\mathrm{C_6D_6}$): 8.42 (s, 8 H, pyrrole), 8.25 (m, 4 H, *o* phenyl), 8.09 (d, 4 H, *o′* phenyl), 7.50–7.40 (m, 12 H, *m* and *p* phenyl), −10.40 (s, 2 H, bridging $\mathrm{CH_2}$).

$\mathbf{Rh(TTP)(CH_2OH)}$. Monomeric formaldehyde was prepared by thermally cracking polymeric paraformaldehyde in previously dried and degassed deuterated benzene. This formaldehyde solution was vacuum-distilled into a sample tube containing 3 mg of Rh(TTP)(H). The NMR tube was pressurized with 500 Torr of hydrogen and then sealed. ^{1}H NMR (δ in $\mathrm{C_6D_6}$): 8.98 (s, 8 H, pyrrole), 8.20 (d, 4 H, *o* phenyl), 8.01 (d, 4 H, *o′* phenyl), 7.35 (d, 4 H, *m* phenyl), 7.25 (d, 4 H, *m′* phenyl), 2.43 (s, 12 H, *p*-methyl); ^{13}C NMR (δ in $\mathrm{C_6D_6}$) +55.81 (d, proton decoupled, ($J_{^{109}\mathrm{Rh}-^{13}\mathrm{C}}$ = 26.9 Hz). MS: *m/e*, 803 (experimental) vs. 802.9 (calculated) M$^+$.

$\mathbf{Rh(TTP)(C(O)CH_3)}$. Dried and degassed benzene was vacuum-transferred into a NMR tube containing $\mathrm{Rh(TTP)(CH_3)}$. This sample tube was pressurized with 500 Torr of carbon monoxide and sealed. The alkyl complex was irritated, with a band-path filter ($h\nu$ > 445 nm), at ice–water temperatures for 12 h until conversion of the $\mathrm{Rh(TTP)(CH_3)}$ compound to the methylacyl complex was complete. $\mathrm{Rh(TTP)(C(O)CH_3)}$ was identified by comparison with authentic samples prepared by published procedures.[12] ^{1}H NMR (δ in $\mathrm{C_6D_6}$): 8.96 (s, 8 H, pyrrole), 8.25 (d, 4 H, *o* phenyl), 8.00 (d, 4 H, *o′* phenyl), 7.46 (d, 4 H, *m* phenyl), 7.31 (d, 4 H, *m′* phenyl), 2.44 (s, 12 H, *p*-methyne), −2.73 (s, 3 H, acyl methyl).

Thermodynamic Study of Rh(TPP)(CHO). Dried and degassed $\mathrm{C_6D_6}$ was distilled onto a 2 mg sample of solid Rh(TPP)(H) in an NMR tube attached to a vacuum line. Varying pressures of mixed carbon monoxide and hydrogen gases ranging from 150 to 600 torr were added, and the tube was sealed. The kinetics of this reaction are very slow at ~25 °C, and several days are required to reach an equilibrium position. Most experiments were conducted at elevated temperatures where the time to reach this equilibrium is more convenient (50 °C, 4 h; 80 °C, $^1/_2$ h). The relative pyrrole peak area of Rh(TPP)(H) and Rh(TPP)(CHO) was measured by integration of the proton NMR spectra and an equilibrium constant calculated. The solubility of carbon monoxide in benzene was taken as: $[\mathrm{CO}]_s = ((7.078 \pm 1.579) \times 10^{-5}\ (T\ (°\mathrm{C})))((T\ (\mathrm{K})/300\ \mathrm{K})(P_{\mathrm{CO}}/760\ \mathrm{Torr/atm}))$. Temperature dependence of the equilibrium constant yields the thermodynamic parameters for the reaction: $\mathrm{Rh(TPP)(H) + CO \rightleftarrows Rh(TPP)(CHO)}$; $\Delta H° = -42 \pm 4$ kJ/mol and $\Delta S° = -89 \pm 15$ J/(K mol). The conversion of the metallohydride to metalloformyl complex is greatly accelerated by the presence of $\mathrm{(Rh(TPP))_2}$. This reaction is much slower when the formation of $\mathrm{(Rh(TPP))_2}$ is suppressed by a overpressure of hydrogen gas. Interconversion of the metalloformyl and -hydride complexes is undoubtly catalyzed by $\mathrm{(Rh(TPP))_2}$, through a metallo-radical-chain process that has been previously observed by Halpern for the Rh(OEP) system.[3] Radical-initiated decomposition of a metalloformyl species has also been reported by Kochi.[14]

Results and Discussion

Rh(TPP)(H), $\mathrm{Rh(TPP)^-}$, and $\mathrm{(Rh(TPP))_2}$ were prepared in order to evaluate their patterns of organometallic reactivity. Each of these compounds has distinctive proton NMR features, which provide a convenient means for identifying and following the reactions of these species in benzene solution.

Rh(TPP)(H) (**1**) and Rh(TTP)(H) (**2**), which are prepared by borohydride or formate reduction of the corresponding iodide complexes, have proton NMR in spectra $\mathrm{C_6D_6}$ that contain highly broadened porphyrin peaks and fail to reveal hydride resonances. This severe NMR broadening was found to result from hydride exchange with $\mathrm{(Rh(TPP))_2}$, which is produced by loss of molecular hydrogen from Rh(TPP)(H). This exchange process probably occurs through the paramagnetic monomer, $\mathrm{Rh^{II}(TPP)^\bullet}$ (eq 1, 2). Solutions of Rh(TPP)(H) that are pressurized with $\mathrm{H_2}$ ($P_{\mathrm{H_2}}$

$$\mathrm{(Rh(TPP))_2 \rightleftarrows 2Rh^*(TPP)^\bullet} \quad (1)$$

$$\mathrm{Rh^*(TPP)^\bullet + Rh(TPP)(H) \rightarrow Rh^*(TPP)(H) + Rh(TPP)^\bullet} \quad (2)$$

= 400–600 Torr) produce sharp ^{1}H NMR spectra by repressing formation of $\mathrm{(Rh(TPP))_2}$ (eq 3). The hydride resonances for

$$\mathrm{(Rh(TPP))_2 + H_2 \rightleftarrows 2Rh(TPP)(H)} \quad (3)$$

1 and **2** are virtually indistinguishable ($\delta_{\mathrm{Rh-H}} = -40.2$, $J_{^{103}\mathrm{Rh}-^1\mathrm{H}} = 43.2$ Hz) and are comparable to that for Rh(OEP)(H) ($\delta_{\mathrm{Rh-H}} = -41.3$, $J_{^{103}\mathrm{Rh}-^1\mathrm{H}} = 44$ Hz). Inequivalence of the phenyl ortho hydrogens results from inhibition of phenyl rotation and is commonly observed for TPP complexes that lack a center of symmetry.[15]

Compounds **1** and **2** function as weak acids and are deprotonated by a 10-fold molar excess of KOH, solubilized by 18-crown-6 ether, to form benzene solutions of the anions $\mathrm{Rh(TPP)^-}$ (**3**) and $\mathrm{Rh(TTP)^-}$ (**4**), (reaction 4). Equivalence of the two

$$\mathrm{Rh(TPP)(H) + OH^- \rightleftarrows Rh(TPP)^- + H_2O} \quad (4)$$

phenyl ortho hydrogens is a distinctive feature in the proton NMR spectra of **3** and **4** and is associated with the presence of an effective center of symmetry in these anionic Rh(I) species. The pyrrole hydrogens for **3** and **4** are shifted to high field (δ = 8.46 and 8.55, respectively) compared to Rh(TPP)(H) (δ = 8.88) and other related five-coordinated Rh(III) species [Rh(TPP)(I), δ = 9.16; Rh(TPP)(CHO), δ = 8.91; $\mathrm{Rh(TPP)(CH_3)}$ δ = 8.88; $\mathrm{Rh(TPP)(CH_2OH)}$, δ = 8.98; $\mathrm{Rh(TPP)(C(O)CH_3)}$, δ = 8.96]. Increased charge density at the Rh(I) center and the concomitant increase in the porphyrin π-electron population can account for these chemical shift effects. The reactivity of **3** and **4** is dominated by nucleophilic displacement reactions as illustrated by reactions with alkyl halides (reactions 5 and 6). High-field ^{1}H NMR shifts

$$\mathrm{Rh(TPP)^- + CH_3Br \rightarrow Rh(TPP)(CH_3) + Br^-} \quad (5)$$

$$\mathrm{2Rh(TPP)^- + BrCH_2CH_2Br \rightarrow (Rh(TPP))_2(CH_2CH_2) + 2Br^-} \quad (6)$$

for the alkyl hydrogens in Rh(TPP)(R) complexes ($\mathrm{CH_3}$, δ = −5.5; $\mathrm{CH_2{-}CH_2}$ δ = −10.4) primarily result from the porphyrin ring current effects on the axially metal bound substituents.[11]

The TPP and TTP analogues of the Rh–Rh-bonded dimer, $\mathrm{(Rh(OEP))_2}$, can be conveniently prepared in benzene solution by photolysis ($h\nu$ > 450 nm) of the hydrides. $\mathrm{(Rh(TPP))_2}$ has been previously observed as a product from sublimation of $\mathrm{Rh^{III}(TPP)}$ compounds,[16] photolysis of $\mathrm{(Rh(CO)_2)_2TPP}$[17] and through electrochemical reduction of $\mathrm{Rh(TPP)[NH(CH_3)_2]Cl}$.[18] The proton NMR spectra of $\mathrm{(Rh(TPP))_2}$ and $\mathrm{(Rh(TTP))_2}$ are very distinctive because of the mutual ring current effects of the two porphyrin macrocycles. A relatively high-field position for the pyrrole hydrogens and an extraordinarily low field position for one of the phenyl ortho hydrogens of $\mathrm{(Rh(TPP))_2}$ and $\mathrm{(Rh(TTP))_2}$ are features that have only been previously reported for

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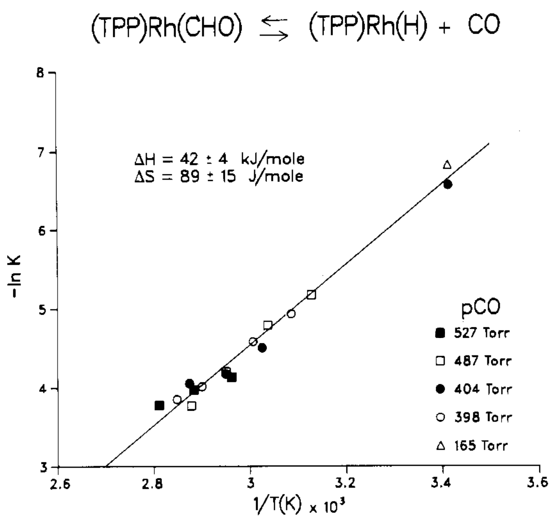

Figure 1. Temperature dependence for the equilibrium between Rh(TTP)(CHO), Rh(TTP)(H) and CO in benzene.

$(\mathrm{Mo(TTP)})_2$,[10] and can be considered diagnostic of a diamagnetic M–M-bonded TPP or TTP complex.

Rh(TPP)(CHO). Benzene solutions of Rh(TPP)(H) and Rh(TTP)(H) are found to react reversibly with CO to produce an equilibrium distribution with the metalloformyl complexes Rh(TPP)(CHO) (**5**) and Rh(TTP)(CHO) (**6**) (eq 7). The formyl complex can be alternately prepared by the reaction of $\mathrm{Rh(TPP)}_2$ with H_2 and CO (eq 8). NMR and IR parameters of the formyl unit in Rh(TPP)(CHO) ($\delta_{\mathrm{CHO}} = 3.18$, $J_{^{103}\mathrm{Rh-CHO}} = 1.8$ Hz; $J_{^{13}\mathrm{CHO}} = 200$ Hz, $\delta_{^{13}\mathrm{CHO}} = 194$, $J_{^{103}\mathrm{Rh}-^{13}\mathrm{CHO}} = 30$ Hz) are comparable to those for the structurally characterized formyl species, Rh(OEP)(CHO).[4,6]

$$\mathrm{Rh(TPP)(H) + CO \xrightleftharpoons{C_6D_6} Rh(TPP)(CHO)} \qquad (7)$$

$$\mathrm{(Rh(TPP))_2 + H_2 + 2CO \rightleftarrows 2Rh(TPP)(CHO)} \qquad (8)$$

Reaction 7 is found to achieve an equilibrium position in benzene that is observable by NMR methods under convenient conditions (P_{CO} 200–700 Torr; $T = 292$–350 K). Temperature dependence of the equilibrium constants provide thermodynamic values for reaction 7 ($\Delta H^\circ = -42 \pm 4$ kJ, $\Delta S^\circ = -87 \pm 15$ J/(mol K)) (Figure 1). Assuming that the bond energies in the Rh(TPP) unit are constant, ΔH° for reaction 7 can be expressed in terms of bond dissociation energies pertinent to the formation of the formyl unit; $\Delta H^\circ{}_7 = (\mathrm{Rh{-}H}) - (\mathrm{Rh{-}C}) + [(\mathrm{C{\equiv}O}) - (\mathrm{C{=}O}) - (\mathrm{C{-}H})] = -10$ kcal (-42 kJ). The similarity of the metalloformyl unit to an organic formyl group provides justification for approximating the last three terms of $\Delta H^\circ{}_7$ as -16 kcal on the basis of thermodynamic studies of organic molecules.[19] These approximations result in an estimate of ~6 kcal for the difference in the Rh-H and Rh-C bond energies.

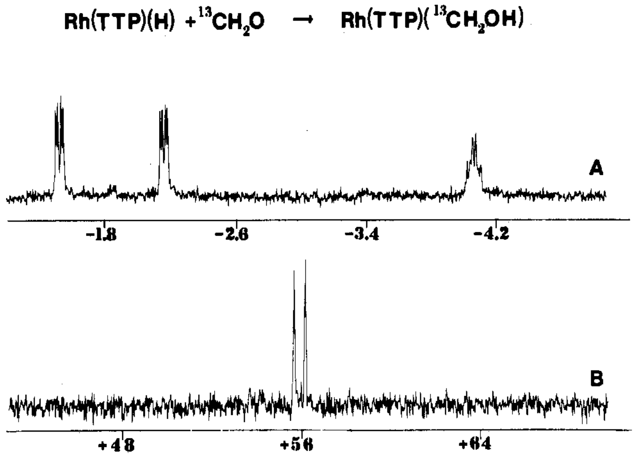

Figure 2. NMR spectra of the hydroxymethyl group in Rh(TPP)(CH$_2$OH): (A) ^{1}H NMR spectrum in C_6D_6 ($J_{^{13}\mathrm{C}-^1\mathrm{H}} = 163.0$ Hz, $J_{^{13}\mathrm{C-OH}} = 2.45$ Hz); (B) ^{13}C NMR spectrum in C_6D_6 with selective methylene proton decoupling ($J_{^{103}\mathrm{Rh}-^{13}\mathrm{C}} = 26.8$ Hz).

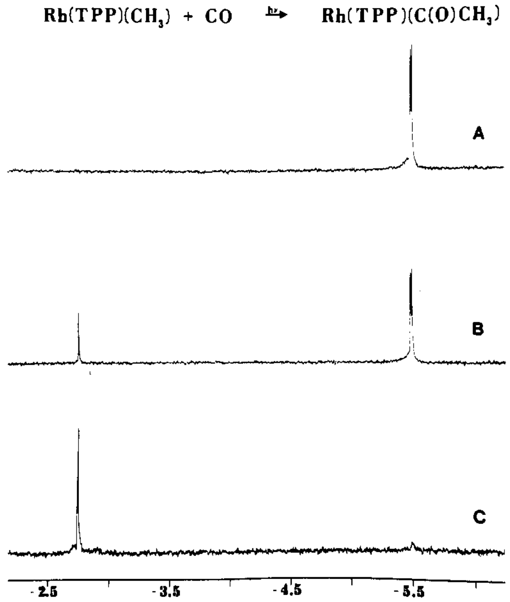

Figure 3. ^{1}H NMR spectra illustrating the conversion of Rh(TTP)(CH$_3$) to Rh(TTP)(C(O)CH$_3$) in the presence of carbon monoxide ($P = 500$ Torr): (A) pure Rh(TTP)(CH$_3$) in the presence of CO prior to irradiation; (B) mixture of Rh(TTP)(CH$_3$) and Rh(TTP)(C(O)CH$_3$) after irradiation; ($\lambda > 445$ nm) for 2 h; (C) complete conversion to Rh(TTP)(C(O)CH$_3$) after irradiation for 12 h.

Rh(TPP)(CH₂OH). Rh(TPP)(H) reacts with formaldehyde in benzene to produce the hydroxymethyl complex Rh(TPP)(CH$_2$OH) (**7**) (reaction 9). Formation of compound **7** is followed in benzene solution by the appearance of the hydroxymethyl group (^{1}H NMR: $\delta_{\mathrm{CH_2}} = -1.84$, $J_{^{103}\mathrm{Rh-CH}} = 3.58$ Hz; $\delta_{\mathrm{OH}} = -4.15$, $J_{\mathrm{CH_2-OH}} = 8.61$ Hz. ^{13}C NMR: $\delta_{\mathrm{CH_2}} = 55.81$, $J_{^{13}\mathrm{C}-^1\mathrm{H}} = 163.0$ Hz, $J_{^{13}\mathrm{CH_2O}H} = 2.45$ Hz, $J_{^{103}\mathrm{Rh}-^{13}\mathrm{C}} = 26.8$ Hz). Addition of D_2O to a benzene solution of **7** results in disappearance of the proton resinance at $\delta = -4.15$, which provides further evidence for the assignment of the OH functionality. Two molecules of compound **7** undergo a slow self-condensation to produce an equilibrium with the symmetrically bridged ether complex $(\mathrm{Rh(TPP)(CH_2{-})})_2\mathrm{O}$ (**8**) (reaction 10). Compound **8** is characterized by the following NMR parameters ($\delta_{\mathrm{CH_2}} = -1.87$, $J_{^{103}\mathrm{Rh-CH_2}} = 2.86$ Hz, $J_{^{13}\mathrm{C}-^1\mathrm{H}} = 163.0$ Hz, $J_{^{13}\mathrm{CH_2-OC}H_2} = 5.9$ Hz).

$$\mathrm{Rh(TPP)(H) + CH_2O \rightleftarrows Rh(TPP)(CH_2OH)} \qquad (9)$$

$$\mathrm{2Rh(TPP)(CH_2OH) \rightleftarrows (Rh(TPP)(CH_2{-}))_2O + H_2O} \qquad (10)$$

Rh(TPP)(C(O)CH₃). Benzene solutions of Rh(TPP)(CH$_3$) fail to react thermally with CO at temperatures up to 350 K, but CO readily inserts into the Rh–CH$_3$ bond by a photoinduced process (eq 11, Figure 3). The photoinduced insertion of CO

$$\mathrm{Rh(TPP)(CH_3) + CO \xrightarrow[\lambda > 445\ nm]{h\nu} Rh(TPP)(C(O)CH_3)} \qquad (11)$$

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(19) An estimate of difference in (C≡O) – (C═O) bond energies is obtained by considering the thermodynamic data for the following reaction, using an aldehyde C—H bond energy of 88 kcal and an H—H bond energy of 104 kcal:

$$\mathrm{CO(g) + H_2(g) \rightleftarrows H_2CO(g)} \quad \Delta H_{\mathrm{a}} = 0.5\ \mathrm{kcal}$$

$$\Delta H_{\mathrm{a}} = (\mathrm{C{\equiv}O}) + (\mathrm{H{-}H}) - (\mathrm{C{=}O}) - 2(\mathrm{C{-}H})(\mathrm{aldehyde})$$

$$(\mathrm{C{\equiv}O}) - (\mathrm{C{=}O}) = \Delta H_{\mathrm{a}} - (\mathrm{H{-}H}) + 2(\mathrm{C{-}H})(\mathrm{aldehyde})$$

$$(\mathrm{C{\equiv}O}) - (\mathrm{C{=}O}) = 0.5 - 104 + 176 = 72\ \mathrm{kcal}$$

Thermodynamic values are taken from: Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465.

into the Rh–CH_3 bond probably occurs through the reaction of a geminate radical pair[20] that is trapped in the benzene solvent cage.

Conclusion

The physical properties and reactivity patterns of the Rh(TPP) species Rh(TPP)(H), $Rh(TPP)^-$, and $(Rh(TPP))_2$ are shown to be closely analogous to those of the more fully characterized Rh(OEP) species. Reactions of Rh(TPP)(H) with CO and H_2CO to produce the metalloformyl (Rh(TPP)(CHO)) and the hydroxymethyl ($Rh(TPP)(CH_2OH)$) complexes, respectively, are particularly important parallels with the reported Rh(OEP) system. The similarity in reactivity patterns for these electronically extreme types of porphyrin ligands (TPP, OEP) indicates that changing the electronic properties by substituent effects results in only minor changes at the rhodium center. We believe that the unusual organometallic chemistry presently observed only for rhodium porphyrins should occur for many sets of strong σ-donor ligands that produce planar low-spin rhodium(III) complexes.

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Registry No. $(TPP)[Rh(CO)_2]_2$, 88083-36-7; Rh(TPP)(I), 69509-35-9; Rh(TTP)(I), 103533-53-5; Rh(TPP)(H), 103533-54-6; Rh(TTP)(H), 103562-44-3; $Rh(TPP)^-$, 103533-55-7; $Rh(TTP)^-$, 103533-56-8; $[Rh(TPP)]_2$, 88083-37-8; $[Rh(TTP)]_2$, 103533-57-9; Rh(TPP)(CHO), 86412-76-2; Rh(TTP)(CHO), 86399-35-1; $Rh(TPP)(CH_3)$, 103562-25-0; $Rh(TPP)(C_2H_5)$, 103533-58-0; $Rh(TPP)(CH_2I)$, 69509-26-8; $[Rh(TPP)]_2(C_2H_4)$, 103533-59-1; $Rh(TTP)(CH_2OH)$, 103562-26-1; $Rh(TTP)[C(O)CH_3]$, 103533-60-4; $Rh(TTP)(CH_3)$, 103533-61-5; 1,2-dibromoethane, 106-93-4; formaldehyde, 50-00-0.

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Redox Properties of Polypyridyl–Aqua Complexes of Osmium

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The electrochemical properties of the *trans*-dioxoosmium(VI) complexes $[(trpy)Os(O)_2(OH)]^+$ and $[(phen)Os(O)_2(OH)_2]$ (trpy = 2,2′:6′2″-terpyridine and phen = 1,10-phenanthroline) have been studied in aqueous solutions over the pH range 0–14. Multiple electron, proton coupled redox steps are observed with the formation of lower oxidation state Os(III) and Os(II) hydroxo or aqua complexes upon reduction. Acid dissociation constants for aqua and hydroxo complexes and pH-dependent potential values for the redox couples that appear between Os(VI) and Os(II) were determined from pH-dependent electrochemical data. From the data available here and from data in earlier studies, variations in K_a values and redox potentials as pyridyl groups are replaced by aqua groups are discussed as to the role of the oxo group in stabilizing higher oxidation states.

There is an extensive, still emerging polypyridyl–oxo chemistry of Ru and Os based on the higher oxidation states VI, V, and IV.[1-6] Examples include $[(bpy)_2(py)Ru^{IV}{=}O]^{2+}$ (bpy = 2,2′-bipyridine; py = pyridine),[1] $[(trpy)Os^{VI}(O)_2(OH)]^+$ (trpy = 2,2′:6′,2″-terpyridine),[3] and *cis*- and *trans*-$[(bpy)_2M^{VI}(O)_2]^{2+}$ (M = Ru, Os).[4,5] A key to the formation of the high oxidation state complexes is the loss of protons and stabilization by electron donation from bound hydroxo or oxo groups. The accessibility of the higher oxidation states and the existence of a series of oxidation states within a narrow potential range enable the oxo complexes to act as effective stoichiometric and/or catalytic oxidants toward a variety of inorganic and organic substrates.[7-10]

The results of electrochemical studies on polypyridyl aqua–oxo complexes of Os, $[(trpy)(bpy)Os^{II}(OH_2)]^{2+}$[2] and *cis*- and *trans*-$[(bpy)_2Os^{VI}(O)_2]^{2+}$, have been reported.[4] We have extended that work to include a series of mixed aqua–oxo, polypyridyl complexes of Os and report here the results of the study and of the systematic variations in redox and acid–base properties that occur through the series.

Experimental Section

Materials. OsO_4 (>99%), 1,10 phenanthroline (gold label), and deuterium-labeled water were obtained from Aldrich Chemical Co. 2,2′:6′,2″-Terpyridine was obtained from G. F. Smith, Inc. Water was distilled over $KMnO_4$ before use. All other chemicals were reagent grade and used without further purification.

Measurements. Routine UV–vis spectra were obtained on a Bausch & Lomb 210 UV–vis 2000 spectrophotometer in 1-cm quartz cells. Spectroelectrochemical experiments were carried out in a three-compartment cell, where the working-electrode compartment was a quartz cell. Infrared spectra were obtained as KBr pellets on a Nicolet 20DX FTIR spectrometer. Proton NMR spectra were obtained in D_2O on a Bruker 250-MHz NMR spectrometer. Cyclic voltammetric experiments

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