orientation; at the internal ring, four C_2H_5 moieites of two adjacent pyrrole rings are directed to the first, the other four of the two other pyrrole rings to the second external macrocycle. The phenyl rings of the TCB solvates are planar within experimental error with C–C and C–Cl mean bond lengths of 1.358 (5) and 1.715 (5) Å, respectively, and C–C–C bond angles of 119.9 (4)°.

Conclusion. Besides a variety of phthalocyanine double-decker complexes $M(Pc)_2$, the lanthanoid derivative $Ce(OEP)_2$ (**2b**) is the first crystallographically identified porphyrin sandwich. Although Moskalev and Kirin[53] have already mentioned a phthalocyanine derivative of the molecular formula $Nd_2(Pc)_3$, they have suggested an ionic composition $Nd(Pc)^+Nd(Pc)_2^-$ for this material which may as well have been a triple-decker. Nonetheless, the triple-decker $Ce_2(OEP)_3$ (**2c**) seems to be the first of its kind which is fully characterized and its structure proven by crystal structure analysis. The chemistry and physics of the whole family of lanthanoid porphyrin double-decker and triple-decker systems is presently being explored in our laboratories.

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Registry No. 2b, 96383-13-0; **2c**, 96383-16-3; **2c**·2TCB, 96383-17-4; **2c**·4C_6H_6, 102233-38-5; **2e**, 102233-39-6; $Ce(acac)_3$, 15653-01-7.

Supplementary Material Available: Tables V and VI: positional and equivalent isotropic thermal parameters of all non-hydrogen atoms of **2b** and **2c**, respectively; Tables VII and VIII: anisotropic temperature factors for **2b** and **2c**; Tables IX and X: hydrogen atom coordinates for **2b** and **2c**; Tables XI and XII: complete sets of bond lengths for **2b** and **2c**; Tables XIII and XIV: complete sets of bond angles for **2b** and **2c**; Tables XV and XVI: observed and calculated structure factor amplitudes for **2b** (×10) and **2c** (78 pages). Ordering information is given on any current masthead page.

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Reactivity of Rhodium and Iridium Octaethylporphyrin Hydrides Toward Carbon Monoxide: Thermodynamic Studies of the Rhodium Formyl and Iridium Hydrido Carbonyl Complexes

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Abstract: Iridium octaethylporphyrin hydride, Ir(OEP)(H), reacts with carbon monoxide to form the carbonyl complex Ir(OEP)(H)(CO) at the same conditions where Rh(OEP)(H) reacts with CO to produce the metalloformyl complex Rh(OEP)(CHO). Thermodynamic studies for these reactions are reported and discussed in terms of differences in the M–H and M–C bond energies and the acceptor properties of the five-coordinate metalloporphyrin hydride complexes.

Metalloformyl species are important intermediates in the reactions of H_2 with CO to form organic oxygenates.[1] Formyl complexes are best known as kinetic products from reactions of metal carbonyls with hydride reducing agents.[2–6] Several metallohydrides are now known to react with CO to produce both η^1- and η^2-formyl species. Rhodium porphyrin hydrides[7–9] and $(\eta^5\text{-}C_5(CH_3)_5)_2V(H)$[10] react with CO to form carbon bonded η^1-formyl complexes, and $(\eta^5\text{-}C_5(CH_3)_5)_2Th(H)(OR)$ complexes produce compounds formulated as η^2-formyl species.[11] Rhodium

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octaethylporphyrin dimer, $[Rh(OEP)]_2$, is at present the only metallospecies that is known to utilize molecular H_2 and CO in forming observable concentrations of a carbon bonded η^1-metalloformyl complex (reactions 1,2). This paper reports on thermodynamic measurements for reaction 2 and on a comparative study for the reaction of Ir(OEP)(H) with CO.

$$[\mathrm{Rh(OEP)}]_2 + \mathrm{H}_2 \rightleftarrows 2\mathrm{Rh(OEP)(H)} \qquad (1)$$

$$\mathrm{Rh(OEP)(H)} + \mathrm{CO} \rightleftarrows \mathrm{Rh(OEP)(CHO)} \qquad (2)$$

Experimental Section

Proton NMR spectra were obtained with a Bruker WM 250 NMR spectrophotometer and an Aspect 2000 computer. The variable temperature spectra were obtained over a temperature range of -65 to 100 °C with an IBM instrument WP200SY NMR spectrophotometer interfaced to an Aspect 2000 computer with a Bruker Instruments BV-T1000 variable temperature controller. The temperature in the probe was calibrated with a capillary tube of ethylene glycol or methanol inside the NMR tube.[12] Electronic absorption spectra were obtained on a Model 14 Cary Recording spectrophotometer. The IR spectra were obtained on an IBM IR 97 with an Aspect 2000A data system. 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 and subsequently stored over sodium and benzophenone. For the low-temperature studies degassed dry deuterated toluene, $C_6D_5CD_3$, was the solvent of choice. The gases H_2 and CO were grade 5.5 and 4.5, respectively. Samples for NMR studies were prepared on a vacuum line with dried C_6D_6 and then sealed.

Rh(OEP)(H). The synthesis of Rh(OEP)(H) follows the procedures of Ogoshi et al.[13,14] $[Rh(CO)_2Cl]_2$ (111 mg) was dissolved in ethanol (34 mL) at room temperature and added to a flask containing sodium acetate (50 mg), octaethylporphyrin (117 mg), and glacial acetic acid (100 mL) (deep purple solution) under nitrogen. Addition of the $[Rh(CO)_2Cl]_2$ and ethanol resulted in a red-brown solution, after stirring and refluxing for 3 h. After the solution had cooled to room temperature, hydrogen gas was bubbled through the solution resulting in the immediate formation of a deep orange precipitate. The precipitate was filtered under H_2 and dried under nitrogen to give Rh(OEP)(H) in 85% yield: IR (KBr) 2220 cm^{-1} ν(RhH); ^{1}H NMR (C_6D_6) δ 10.15 (s, 4 H, methine), 3.95 (q, 16 H, CH_2CH_3), 1.87 (t, 24 H, CH_2CH_3), -41.28 (d, 1 H, Rh-*H*, $J_{^{103}\mathrm{Rh-H}}$ = 44 Hz). The methine peak temperature dependence for Rh(OEP)(H) in benzene follows the straight line expression δ H = 10.3117 - 62.61 (1/*T*).

Ir(OEP)(H). The synthesis of Ir(OEP)(H) follows the procedures of Ogoshi et al.:[15] IR (KBr) 2343 cm^{-1} ν(IrH); ^{1}H NMR (C_6D_6) δ 9.94 (s, 4 H, methine), 3.94 (m, 16 H, CH_2CH_3), 1.89 (t, 24 H, CH_2CH_3), -58.73 (s, 1 H, Ir-H); vis (C_6H_6) λ_{max} (log ϵ) 531 (4.41), 501 (3.97), and 392 nm (4.95).

Rh(OEP)(CHO). The synthesis of Rh(OEP)(CHO) follows the procedures reported previously.[7-9] Dried and degassed C_6D_6 was vacuum distilled into an NMR tube containing Rh(OEP)(H). Varying pressures of mixed hydrogen and carbon monoxide were added, and the NMR tube was sealed. A solid sample was isolated under a stream of CO: IR (Nujol mull) 1707 cm^{-1} ν(CO); ^{1}H NMR (C_6D_6) δ 10.27 (s, 4 H, methine), 3.96 (m, 16 H, CH_2CH_3), 2.82 (d, 1 H, C(O)-*H*, $J_{^{103}\mathrm{Rh-H}}$ = 1.90 Hz), 1.88 (t, 24 H CH_2CH_3).

Ir(OEP)(H)(CO). Dried and degassed C_6D_6 was vacuum distilled into an NMR tube containing Ir(OEP)(H). Varying pressures of carbon monoxide were added, and the NMR tube was sealed. Crystals of Ir(OEP)(H)(CO) were isolated by evaporation of the solvent under a CO atmosphere: IR (KBr) 2046 cm^{-1} ν(CO), 2105 cm^{-1} ν(IrH); ^{1}H NMR (C_6D_6) δ 10.20 (s, 4 H, methine),[16] -23.20 (s, 1 H, IrH),[16] vis (C_6D_6) λ_{max} 555, 545, 525, 405 nm.

Ir(OEP)(CH$_3$). An ethanol (25-mL) suspension of 19 mg of Ir(OEP)(Cl)(CO), prepared by the method of Ogoshi et al.,[15] is mixed with 4 mg of $NaBH_4$ in 1 mL of aqueous 1 N NaOH under nitrogen. The reaction mixture was stirred for 1 h at 50 °C. After having cooled to room temperature, 1 drop of methyl iodide was added to this solution containing Ir(OEP)$^-$. The solution was stirred for 5 h at ambient temperature. After removal of the solvent by evaporation, the residue was chromatographed on silica gel. The first eluate with benzene afforded bright orange crystals of Ir(OEP)(CH$_3$) in 85% yield: ^{1}H NMR (C_6D_6) δ 9.95 (s, 4 H, methine), 3.90 (m, 16 H, CH_2CH_3), 1.90 (t, 24 H, CH_2CH_3), and -6.36 (s, 3 H, IrCH_3).

Ir(OEP)(CH$_3$)(CO). Dried and degassed C_6D_6 was vacuum distilled into an NMR tube containing Ir(OEP)(CH$_3$). Varying pressures of carbon monoxide were added, and the NMR tube was sealed (proton NMR recorded at P_{CO} = 593 torr, *T* = 298 K): ^{1}H NMR (C_6D_6) δ 10.25 (s, 4 H, methine), 3.93 (q, 16 H, CH_2CH_3), 1.87 (t, 24 H, CH_2CH_3), and -7.01 (s, 3 H, IrCH_3).

Thermodynamic Studies of the Reactions of Rh(OEP)(H) and Ir(OEP)(H) with CO. 1. Rh(OEP)(CHO). Dried and degassed C_6D_6 was distilled into a 2-mg sample of Rh(OEP)(H) in an NMR tube attached to a vacuum line. Varying pressures of mixed carbon monoxide and hydrogen gases were added, and the tube was sealed. The samples were thermostated directly in the NMR probe, and spectra were recorded until equilibrium was achieved. The time required to reach equilibrium is approximately 2 h at 50 °C. The relative peak areas of the methine resonances of the Rh(OEP)(H) and Rh(OEP)(CHO) were measured by integration and used in conjugation with the CO concentration to calculate the equilibrium constant. The molar concentration of CO as a function of temperature and pressure is given by the following expression: $^{[\mathrm{CO}[}T,P = [7.078 \times 10^{-3} + 1.579 \times 10^{-5}\ (T(°\mathrm{C}))]\ [T(\mathrm{K})/300\ \mathrm{K})(P_{CO}/760\ \mathrm{torr/atm})]$.[17] A plot of the log of the equilibrium constant vs. the inverse of the temperature yielded the thermodynamic parameters.

2. Ir(OEP)(H)(CO). Dried and degassed C_6D_6 was distilled onto a 2-mg sample of Ir(OEP)(H) in a NMR tube attached to a vacuum line. Varying pressures of mixed carbon monoxide and hydrogen gases were added, and the tube was sealed. The methine resonances for the Ir(OEP)(H) and the Ir(OEP)(H)(CO) are in fast exchange. Temperature dependence of the exchange averaged methine peak position was utilized in determining the thermodynamic parameters.

$$\delta_{\mathrm{obsd}} = \delta_{\mathrm{H}} \frac{[\mathrm{H}]}{([\mathrm{H}] + [\mathrm{HCO}])} + \delta_{\mathrm{HCO}} \frac{[\mathrm{HCO}]}{([\mathrm{H}] + [\mathrm{HCO}])}$$

$$R = [\mathrm{H}]/[\mathrm{HCO}];\ \delta_{\mathrm{obsd}} = \delta_{\mathrm{H}} \frac{R}{R+1} + \delta_{\mathrm{HCO}} \frac{1}{R+1};\ R = \frac{\delta_{\mathrm{HCO}} - \delta_{\mathrm{obsd}}}{\delta_{\mathrm{obsd}} - \delta_{\mathrm{H}}}$$

$$K = \frac{[\mathrm{Ir(OEP)(H)(CO)}]}{[\mathrm{Ir(OEP)(H)}][\mathrm{CO}]}; \qquad K = \frac{1}{R[\mathrm{CO}]}$$

δ_{obsd} = observed proton NMR resonance for the methine peak at a given P_{CO} and *T*. δ_{HCO} = 10.2300 (determined experimentally by extrapolation to complete CO coordination.) δ_H = 54.83 (1/*T*) + 9.7638 (The methine peak temperature dependence for Ir(OEP)(H) in benzene follows this straight line expression). [H] = molar concentration of Ir(OEP)(H). [HCO] = molar concentration of Ir(OEP)(H)(CO). [CO] = molar concentration of CO in benzene at each given temperature. A plot of the log of the equilibrium constant vs. the inverse of the temperature yielded the thermodynamic parameters.

3. Low-Temperature Study of Rh(OEP)(H) + CO. Dried and degassed $C_6D_5CD_3$ was distilled onto a small sample of Rh(OEP)(H) in an NMR tube attached to a vacuum line at liquid nitrogen temperature. Varying pressures of mixed carbon monoxide and hydrogen gases were added, and then the tube was sealed. The NMR tube was kept in a dry ice/acetone bath to allow the $C_6D_5CD_3$ to thaw, but the temperature was not allowed to rise above -78 °C. The NMR sample was placed in the NMR probe that had been previously equilibrated at -70 °C. The sample was kept in the dark, and the only exposure to light was when it was placed in the NMR probe.

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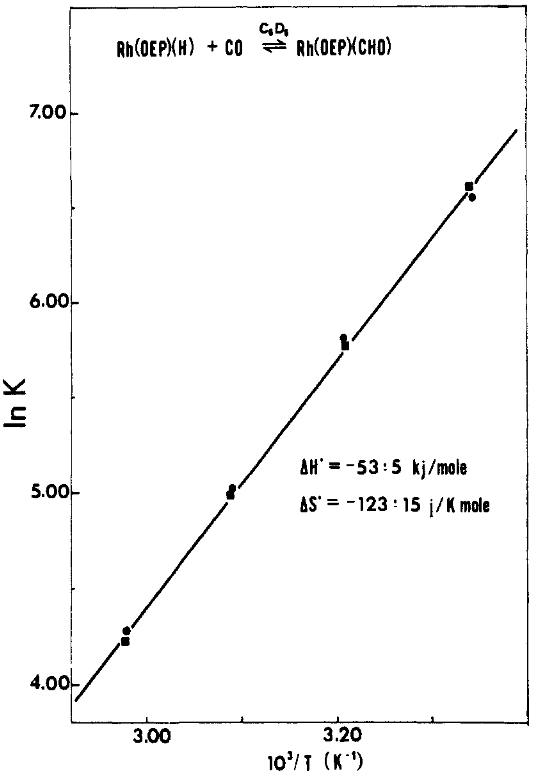

Figure 1. Temperature dependence of the equilibrium constant for reaction 2 ($Rh(OEP)(H) + CO \rightleftarrows Rh(OEP)(CHO)$). Initial pressure of CO for each experiment: ● = 392 torr and ■ = 467 torr.

Results

Rh(OEP)(H). Proton NMR of Rh(OEP)(H) in C_6D_6 shows a characteristic doublet hydride resonance ($\delta_{RhH} = -41.28$ ppm, $J_{^{103}Rh-H} = 44$ Hz). An overpressure of H_2 gas ($P_{H_2} > 200$ torr) is used in order to repress the slow conversion of Rh(OEP)(H) into the metal-metal bonded dimer $[(Rh(OEP)]_2$ (reaction 1). Traces of $[Rh(OEP)]_2$ result in exchange broadening of the Rh(OEP)(H) hydride resonance (reaction 3). This exchange process probably occurs through dissociation of $[Rh(OEP)]_2$ into the metalloradical monomers (reaction 4, 5).[18]

$$Rh^*(OEP)(H) + [Rh(OEP)]_2 \rightleftarrows Rh(OEP)(H) + (OEP)Rh^*Rh(OEP) \quad (3)$$

$$[Rh(OEP)]_2 \rightleftarrows 2Rh(OEP)^{\bullet} \quad (4)$$

$$Rh(OEP)^{\bullet} + Rh^*(OEP)(H) \rightleftarrows Rh(OEP)(H) + Rh^*(OEP)^{\bullet} \quad (5)$$

Rh(OEP)(H) with Donor Molecules. The rhodium center in Rh(OEP)(H) functions as a relatively weak acceptor toward donor molecules such as pyridine, *n*-butyl isonitrile, and triphenylphosphine. Six-coordinate adduct formation can be conveniently observed by large changes in the Rh*H* resonance in the ^1H NMR spectrum. [Rh(OEP)(H) $\delta_{RhH} = -41.28$ ppm, $J_{^{103}Rh-H} = 44$ Hz; Rh(OEP)(H)(Py) $\delta_{RhH} = -32.92$ ppm, $J_{^{103}Rh-H} = 22$ Hz; Rh(OEP)(H)(nBuNC) $\delta_{RhH} = -29.50$ ppm, $J_{^{103}Rh-H} = 18.2$ Hz]. Each of these donor adducts is found to manifest limiting fast ligand exchange at 295 K. The large shift in the hydride resonance that accompanies six-coordinate adduct formation provides a sensitive probe for the interaction of Rh(OEP)(H) with donors.

Rh(OEP)(H) with CO. When a toluene solution of Rh(OEP)(H) at 220 K is in contact with CO ($P_{CO} = 700$ torr) there is no detectable change in the hydride resonance position or the $^{103}Rh-H$ coupling constant which indicates the absence of a detectable quantity of the six-coordinate CO complex at -50 °C.

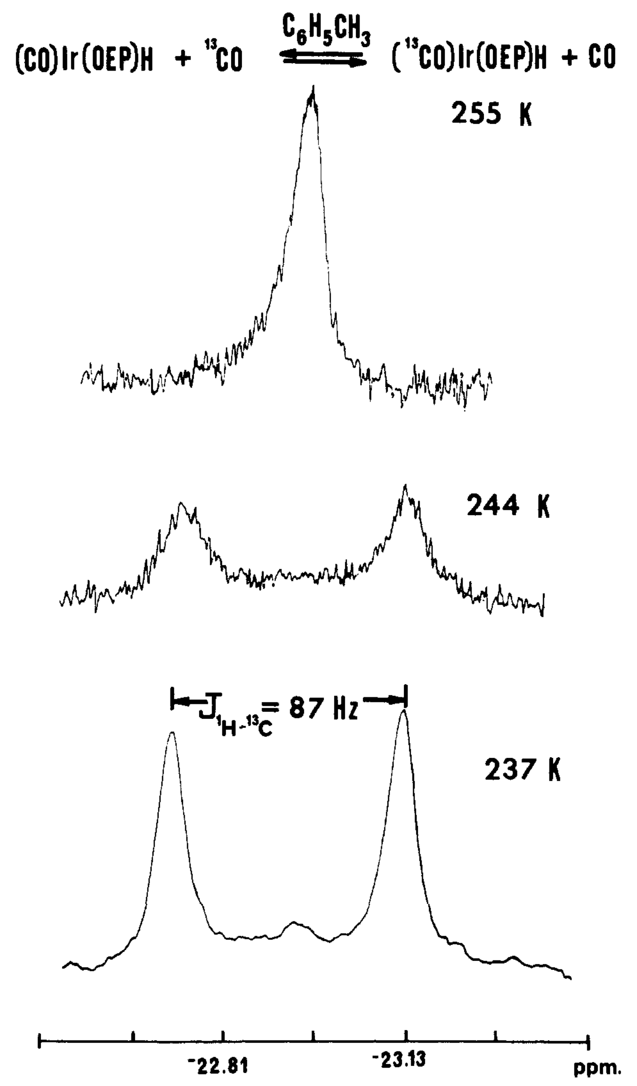

Figure 2. Temperature dependence of the ^1H NMR for the hydride peak of $Ir(OEP)(H)(^{13}CO)$ in contact with ^{13}CO.

Cooling the solution to 200 K results in disappearance of the hydride resonance which could result from adduct formation, but direct observation of Rh(OEP)(H)(CO) has not been achieved. Warming the sample to 273 K resulted in initiating the formation of Rh(OEP)(CHO).

Benzene solutions of Rh(OEP)(H) when in contact with CO ($P_{CO} = 100$–700 torr; $T = 295$ K) react in a period of hours to produce equilibrium distributions with the metalloformyl complex Rh(OEP)(CHO) (reaction 2; $Rh(OEP)(H) + CO \rightleftarrows Rh(OEP)(CHO)$). The formyl complex can be conveniently identified in solution by ^1H and ^{13}C NMR of the metal bonded formyl unit ($\delta_{CHO} = 2.82$ ppm, $J_{^{103}Rh-^{13}CHO} = 29$ Hz, $J_{^{13}CHO} = 200$ Hz).[7] Reaction 2 is shown to be a well-behaved equilibrium through varying both the CO pressure and the reaction temperature. Equilibrium constants have been determined by NMR methods at a series of temperatures and used in deriving thermodynamic values for reaction 2 (Figure 1) ($\Delta H°_2 = -13 \pm 1$ kcal mol^{-1} (-53 ± 5 kJ mol^{-1}); $\Delta S°_2 = -29.4 \pm 3.6$ eu (-123 ± 15 J K^{-1} mol^{-1}); $\Delta G°_2$ (298) = -3.8 ± 1.2 kcal mol^{-1} (-16 ± 5 kJ mol^{-1}); K_2 (298) = 733 ± 55).

The only previous equilibrium studies for a metalloformyl system pertain to the η^2-formyl formed from $(\eta^5\text{-}C_5(CH_3)_5)_2Th(OR)(H)$ and CO ($\Delta H° = 4.5 \pm 9$ kcal/mol; $\Delta S° = -23.9$ eu).[11]

Ir(OEP)(H) with Donor Molecules. Ir(OEP)(H) in C_6D_6 exhibits a very high field Ir*H* hydride NMR resonance ($\delta_{IrH} = -58.73$ ppm). Ir(OEP)(H) readily forms six-coordinate adducts with donor molecules (pyridine, $(C_6H_5)_3P$, RNC) which can be detected in solution by significant shifts in the characteristic hydride ^1H NMR peak position [Ir(OEP)(H)(pyridine) δ_{IrH} =

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[18] Metalloradical reactivity of $[Rh(OEP)]_2$ has been previously recognized. (a) Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333. (b) Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1981**, 475.

−40.73 ppm; Ir(OEP)(H)(($C_6H_5)_3$P) $\delta_{\mathrm{Ir}H}$ = −32.95 ppm, $J_{^{31}\mathrm{P-Ir}H}$ = 259 Hz].

When a benzene solution of Ir(OEP)(H) is put in contact with CO ($P_{\mathrm{CO}} > 600$ torr), the Ir*H* resonance shifts to −23.20 ppm which is consistent with formation of the six-coordinate adduct Ir(OEP)(H)(CO) (reaction 6).

$$\mathrm{Ir(OEP)(H) + CO \rightleftarrows Ir(OEP)(H)(CO)} \qquad (6)$$

Toluene solutions of Ir(OEP)(H) in contact with ^{13}CO (P_{CO} ~500 torr) have a singlet hydride peak at 295 K which resolves into a doublet ($J_{^{13}\mathrm{C}-^{1}\mathrm{H}}$ = 87 Hz) at temperatures below 240 K where CO exchange becomes slow (Figure 2). The ^{13}C–Ir–^{1}H coupling constant of 87 Hz in Ir(OEP)(H)(CO) is unusually large and approaches values observed for agostic C–H bonds ($J_{^{13}\mathrm{C-H}}$ = 74–101 Hz)[19] and η^2-formyl species ($J_{^{13}\mathrm{C-H}}$ = 113–117 Hz).[11] Observation of a very large ^{31}P–Ir–^{1}H coupling constant in the triphenylphosphine adduct, Ir(OEP)(H)(P($C_6H_5)_3$) ($J_{^{31}\mathrm{P}-^{1}\mathrm{H}}$ = 259 Hz), illustrates that a ^{13}C–^{1}H coupling of 87 Hz in Ir(OEP)(H)(^{13}CO) is not inconsistent with simple adduct formation. The rigid porphyrin macrocycle requires the axial ligands to be in trans positions and to compete for the same metal valence orbitals ($5d_z{}^2(6p_z, 6s)$) which contributes to the efficient transmission of coupling effects between the trans ligand nuclei.

Observation of two IR bands (2105, 2046 cm^{-1}) in the ν_{IrH} and ν_{CO} regions is also consistent with the adduct formulation, Ir(OEP)(H)(CO). Ir(OEP)(D)(CO) has a single band in this region (ν_{CO} = 2079 cm^{-1}) which is comparable to the value observed in Ir(OEP)(Cl)(CO) (ν_{CO} = 2050 cm^{-1}). The ν_{CO} observed in Ir(OEP)(D)(CO) is substantially different from either of the bands in Ir(OEP)(H)(CO) which is a manifestation of effective coupling of the ν_{IrH} and ν_{CO} stretching modes.[20] The $\nu_{\mathrm{Ir-D}}$ band which occurs at ~1480 cm^{-1} is obscured by more intense porphyrin bands. Large reduction in the iridium–hydrogen stretching frequency ($\Delta\nu_{\mathrm{IrH}}$ = 238 cm^{-1}) in forming the six-coordinate CO adduct results from the competition of the trans ligands for the same metal valence orbitals.

Equilibrium constants for reaction 6 were determined at several pressures of CO at a series of temperatures. Results from this thermodynamic study are summarized in Figure 3 ($\Delta H^\circ_6 = -8.1 \pm 1.2$ kcal mol^{-1} (-34 ± 5 kJ mol^{-1}); $\Delta S^\circ_6 = -12 \pm 3.6$ eu (-49 ± 15 J K^{-1} mol^{-1}); ΔG°_6 (298) = -4.5 ± 1.2 kcal mol^{-1} (-19 ± 5 kJ mol^{-1}); K_6 (298) = 2.5×10^3). The observed entropy change is unusually small for 1:1 complex formation, which suggests that reaction 6 actually involves the displacement of benzene by CO. The only observed product from reaction of Ir(OEP)(H) with CO is six-coordinate adduct Ir(OEP)(H)(CO). There is no evidence for a metalloformyl complex.

Discussion

The discovery and characterization of metallohydrides that initiate the reduction of CO by transfer of hydrogen to the carbon center is a major aspect of organometallic catalysis studies. This general reaction has been accomplished by several types of transition metal species including Cp$_2$*VH,[10] Cp$_2$*ZrH$_2$,[21] Rh(porphyrin)(H),[7–9] and actinide complexes of the form Cp$_2$*Th(OR)(H)[11] [Cp* = η^5-C$_5$(CH$_3$)$_5$].

An η^1-carbon bonded formyl group is observed in Rh(OEP)(CHO)[8] and is also formulated in the reaction product of Cp$_2$*VH with CO (ν_{CO} = 1690 cm^{-1}).[7] Both Cp$_2$*Th(OR)(H) and Cp$_2$*ZrH$_2$ react with CO to produce η^2-formyl species or react further to produce metalloenediolates and alkoxides. Metal-catalyzed hydrogenation of CO requires that the metallohydride be formed from reaction with dihydrogen, and this feature is presently available only to the rhodium porphyrin systems. Another important feature of the rhodium porphyrin formyls[7–9] is that the physical properties of the Rh–CHO unit (ν_{CO} = 1707 cm^{-1}, $J_{^{13}\mathrm{C-H}}$ = 200 Hz) are more closely related to organic aldehydes (ν_{CO} = 1740–1660 cm^{-1}, $J_{^{13}\mathrm{C-H}}$ = 170–180 Hz) or amides (ν_{CO} = 1770–1630 cm^{-1}, $J_{^{13}\mathrm{C-H}}$ = 180–190 Hz)[22] than other reported η^1-formyls (ν_{CO} = 1550–1650 cm^{-1}, $J_{^{13}\mathrm{C-H}}$ ~120–150 Hz)[10] and distinctly different from η^2-formyl species (ν_{CO} = 1469 cm^{-1}, $J_{^{13}\mathrm{C-H}}$ = 113–117 Hz).[11] Benzene solutions of Rh(OEP)(H) react with CO to achieve well-behaved equilibria with Rh(OEP)(CHO) which are not complicated by coordination of CO to either Rh(OEP)(H) or Rh(OEP)(CHO) for the reaction conditions ($P_{\mathrm{CO}} < 1$ atm, $T > 293$ K). This system thus provides an unusual opportunity to determine thermodynamic values for an overall reaction corresponding to the insertion of CO into the Rh–H bond (reaction 2).

The general reaction of a metal hydride with CO to form a carbon bonded formyl complex is given by reaction 7. Equation 7i expresses ΔH° for reaction 7 in terms of a set of bond dissociation energies. Similarity of the M–CHO to an organic formyl group provides justification for approximating the sum of the last three terms in (7i) as 16 kcal from bond energies derived from thermodynamic studies of organic molecules.[23] Reaction 7 is thus exothermic when the M–H bond energy exceeds the M–C bond energy by no more than 16 kcal. Reaction 7 is entropy unfavorable, and using ΔS°_2 (−29 cal K^{-1} mol^{-1}) as an estimate for the general reaction 7 ($\Delta S^\circ_7 \simeq -29$ cal/Kmol) suggests the ΔG° (298 K) will be negative when the M–H is no more than 7 kcal stronger than the M–C bond.[24] In the few systems where both M–H and M–C bond energies are available, the M–H bond energy ranges from 14 to 30 kcal stronger than the M–C, and none of these systems have been reported to produce observable equilibrium concentrations of metalloformyl by reaction 7.[25,26] Several specific examples include (CO)$_4$Mn–X (X = H, C(O)CH$_3$) and [(CO)$_4$Fe–X]$^-$ (X = H, CHO) where (M–H)–(M–C) values are +20 and +27 kcal, respectively.[25b,27] In the specific case of Rh(OEP)(H), the observed ΔH° for reaction 7 is −13 kcal. Substituting the observed ΔH°_7 (−13 kcal) and approximate bond

$$\mathrm{M{-}H + CO \rightleftarrows M{-}CHO} \qquad (7)$$

$$\Delta H^\circ_7 = (\mathrm{M{-}H}) - (\mathrm{M{-}C}) + (\mathrm{C{\equiv}O}) - (\mathrm{C{=}O}) - (\mathrm{C{-}H}) \qquad (7i)$$

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[23] An estimate of difference in (C≡O) − (C=O) bond energies is obtained from considering the thermodynamic data for reaction a and using an aldehyde CH bond energy of 88 kcal and an H–H bond energy for 104

$$\text{(a)} \qquad \mathrm{CO_{(g)} + H_{2(g)} \rightleftarrows H_2CO_{(g)}} \qquad \Delta H_a = 0.5 \text{ kcal}$$

kcal.

$$\Delta H_a = (\mathrm{C{\equiv}0}) + (\mathrm{H{-}H}) - (\mathrm{C{=}O}) - 2(\mathrm{C{-}H}) \text{ (aldehyde)}$$

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

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

$$\text{(b)} \qquad \mathrm{CO + MH \rightleftarrows MCHO}$$

$$\Delta H_b = (\mathrm{C{\equiv}O}) + (\mathrm{M{-}H}) - (\mathrm{M{-}C}) - (\mathrm{C{=}O}) - (\mathrm{C{-}H}) \text{ (aldehyde)}$$

$$(\mathrm{C{\equiv}O}) - (\mathrm{C{=}O}) - (\mathrm{C{-}H}) \text{ (aldehyde)} \simeq -16 \text{ kcal}$$

$$(\mathrm{M{-}H}) - (\mathrm{M{-}C}) \simeq \Delta H_b + 16 \text{ kcal}$$

Thermodynamic values are taken from (a) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465. (b) Benson, S. W. *Thermochemical Kinetics*; *Methods for the Estimation of Thermochemical Data and Rate Parameters*; Wiley: New York, 1968; p 21.

[24] In order for ΔG°_7 to be negative at 298 K the difference in the M–H and M–C energies must not exceed ~7 kcal.

$$\Delta H^\circ_7 = (\mathrm{M{-}H}) - (\mathrm{M{-}C}) + (\mathrm{C{=}O}) - (\mathrm{C{-}H}) \text{ (aldehyde)}$$

$$\Delta H^\circ_7 = (\mathrm{M{-}H}) - (\mathrm{M{-}C}) - 16 \text{ kcal} \qquad \Delta S^\circ \sim -29 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$\Delta G^\circ_7 \simeq \Delta H^\circ_7 - T\Delta S^\circ = \Delta S^\circ_7 = (\mathrm{M{-}H}) - (\mathrm{M{-}C}) - 16 \text{ kcal} - T\Delta S^\circ$$

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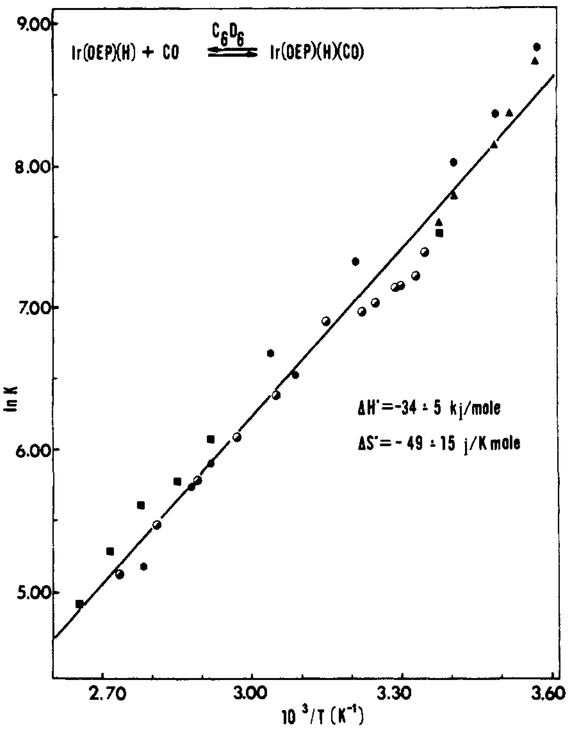

Figure 3. Temperature dependence of the equilibrium constant for reaction 6 (Ir(OEP)(H) + CO $\rightleftarrows$ Ir(OEP)(H)(CO)). Initial pressure of CO for each experiment: ▲, ⬢, ■ = 409 torr; ● = 298 torr; ◑ = 702 torr.

energies ((C≡O) - (C═O) - (C—H) = -16 kcal) into expression 7i reveals that the difference in the (OEP)Rh-H and (OEP)-Rh-CHO bond energies is very small (~3 kcal). The near convergence of the Rh-H and Rh-C bond energies could result from either an usually small Rh-H or an unusually large Rh-C bond energy. An average Rh-H bond energy of 57.9 kcal has been determined for *cis*-Rh(Cl)(P(tolyl)$_3$)$_3$(H)$_2$.[28] The Rh-H stretching frequency in Rh(OEP)(H) ($\nu_{\text{Rh-H}}$ = 2220 cm^{-1}) is among the highest values reported (ν_{RhH} = 1900-2200 cm^{-1})[20] and substantially larger than the value for *cis*-Rh(Cl)(P(tolyl)$_3$)$_3$(H)$_2$ ($\nu_{\text{Rh-H}}$ = 2034 cm^{-1}). The Rh-H bond in the five-coordinate species Rh(OEP)(H) thus appears to fall in the normal range for M-H bond energies (Rh-H ~60 kcal). The spontaneous reaction of [Rh(OEP)]$_2$ with H$_2$ to form Rh(OEP)(H) is also compatible with a 60-kcal Rh-H bond energy. We believe that an unusually strong Rh-C bond energy (Rh-C > 55 kcal) in Rh(OEP)(CHO) is responsible for obtaining the metalloformyl as the thermodynamic product of reaction 2. π-Bonding in the Rh-CHO fragment undoubtedly makes a contribution to the Rh-C bond strength, but the relatively high carbonyl stretching frequency (ν_{CO} = 1707 cm^{-1}) and associated short C-O bond distance (1.175 (5) Å)[8] in Rh(OEP)(CHO) argue against large π-bonding effects. Rh-C bond energies must be quite large (Rh-C > 50 kcal) even in the absence of π-bonding. Observed reactions of [Rh(OEP)]$_2$ with the alkyl C-H bonds in alkylaromatics and addition reactions with alkenes are compatible with this conclusion.[29,30]

The interaction of Ir(OEP)(H) (reaction 6) with CO in benzene results in the six-coordinate complex, Ir(OEP)(H)(CO), but fails to produce observable quantities of a metalloformyl species, Ir(OEP)(CHO) or Ir(OEP)(CHO)(CO) (reactions 8, 9). Unfavorable kinetic factors cannot yet be excluded as the origin for not observing reactions 8 and 9, but attempts to catalyze these reactions by using hydride sources and [Ir(OEP)]$_2$ as well as photopromotion have not yet produced an Ir(OEP)(formyl) species. We believe that thermodynamic factors prohibit formation of observable equilibrium concentrations of Ir(OEP)(formyl) complexes at the condition of these studies (P_{CO} ~ 1 atm, T = 270-350 K). An increse in the difference between the Ir-H and Ir-C bond energies and differences in the enthalpy of CO adduct formation with Ir(OEP)(H) and Ir(OEP)(CHO) could provide unfavorable contribution to the thermodynamics of producing an Ir(OEP)(formyl) species.

$$\text{Ir(OEP)(H)} + \text{CO} \rightleftarrows \text{Ir(OEP)(CHO)} \qquad (8)$$

$$\text{Ir(OEP)(H)(CO)} + \text{CO} \rightleftarrows \text{Ir(OEP)(CHO)(CO)} \qquad (9)$$

$$\text{Ir(OEP)(CHO)} + \text{CO} \rightleftarrows \text{Ir(OEP)(CHO)(CO)} \qquad (10)$$

Adduct formation between Rh(OEP)(X) (X = H, CHO) and CO does not occur to a measurable extent (P_{CO} ~ 1 atm, T = 250-350 K) and is not a complicating factor in the thermodynamic of producing Rh(OEP)(CHO) (P_{CO} = 1 atm, T = 220-300 K). In contrast with Rh(OEP)(H), Ir(OEP)(H) forms a six-coordinate CO adduct in benzene [reaction 6: $\Delta H°_6$ = -34 kJ mol^{-1}; K_6 (298) = 2.5 × 10^3] which complicates this system. Ir(OEP)(CH$_3$) has been examined as representative of an Ir-C bonded complex and found to readily bond CO to form Ir(OEP)(CH$_3$)(CO). Preliminary studies indicate that Ir(OEP)(CH$_3$) is comparable to Ir(OEP)(H) in binding CO. The influence of CO adduct formation cannot be quantitatively obtained at this time because Ir(OEP)(CHO) is not available for the study of reaction 10. It seems clear, however, that the potentially unfavorable contribution from CO adduct formation with Ir(OEP)(H) should be largely compensated by CO adduct formation with Ir(OEP)(CHO). We presently believe that the difference in bond energies (Ir-H) - (Ir-C) must be larger than the corresponding value in the Rh-(OEP) system ((Rh-H) - (Rh-C) ≃ 3 kcal) and that this effect is largely responsible for lack of observation of iridium formyl species.

IR data suggest that the Ir-H bond in Ir(OEP)(H) (ν_{IrH} = 2343 cm^{-1}) is stronger than the Rh-H bond in Rh(OEP)(H) (ν_{RhH} = 2220 cm^{-1}) and this increase in the M-H bond energy (Ir-H > Rh-H) may not be compensated by an equivalent increase in the Ir-C bond energy. The thermodynamic criteria for producing a metalloformyl from reaction of a metallohydride with CO are stringent, and unfavorable changes in thermodynamic factors of only 4-5 kcal from the Rh(OEP) system would prohibit observation of an Ir(OEP) formyl species.

A more complete understanding of these systems is dependent on quantitative evaluation of the acceptor properties of Ir(OEP)(X) (X = H, CH$_3$, C(O)CH$_3$) species toward CO and thermodynamic studies that relate directly to the M-M, M-H, and M-C (M = Rh(OEP), Ir(OEP)) bond energies.

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Registry No. Rh(OEP)(H), 63372-77-0; Ir(OEP)(H), 68332-06-9; Rh(OEP)(CHO), 79666-16-3; Ir(OEP)(H)(CO), 102261-41-6; Ir(OEP)(CH$_3$), 68357-02-8; Ir(OEP)(Cl)(CO), 68324-58-3; Ir(OEP)(CH$_3$)(CO), 83582-10-9.

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