Table I. Summary of Labeling Experiment Observations for the Photolysis of 1[a]

expt	results
1. 1 + C_6D_6 + H_2	$C_6D_6 \rightarrow C_6D_5H$ PPh_3-$d_0 \rightarrow PPh_3$-d_n Re–H does not exchange for Re–D
2. 1 + C_6H_6 + D_2	$C_6H_6 \rightarrow C_6H_5D$ PPh_3 does not undergo H/D exchange Re–H → Re–D

[a] Based upon 16 mM 1 under 530 mm H_2 or D_2 gas, irradiated for 160 h.

into the Re–H bond of 1 is observed based upon a 6:1 ratio of the η^6-C_6H_6:Re-H resonances in the ^1H NMR. H/D exchange of the meta and para phosphine phenyl hydrogens does occur slowly (~10% after 40 h), and C_6D_5H is observed to grow in by ^1H NMR spectroscopy (~30 turnovers with respect to 1 after 40 h). The exchange of hydrogen into the benzene-d_6 solvent is qualitatively faster in the presence of hydrogen gas than in its absence. Table I summarizes the results of these reciprocal labeling experiments.

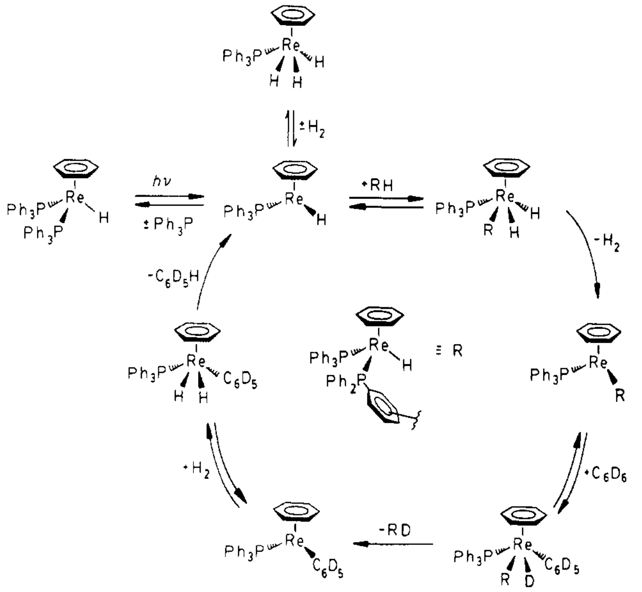
These observations require the following mechanistic features: (1) The hydrogens of the benzene solvent exchange only with the coordinated PPh_3 hydrogens, but not with the hydride ligand of 1. (2) D_2 gas exchanges with the hydride ligand of 1 and with the benzene solvent, but not with the hydrogens of the PPh_3 ligands of 1.

Scheme I shows a proposed mechanism in which three key features follow from the above requirements. First, if R–H (R = $(C_6H_4)Ph_2P$–Re) or benzene adds reversibly to the intermediate $[(\eta^6\text{-}C_6H_6)Re(PPh_3)H]$, it must do so regiospecifically (presumably cis) such that the hydrogen from the aryl group is not equilibrated with the hydride ligand. A similar argument has been made by Curtis for the addition of silanes to Cp_2TaH_3.[20] Second, H_2 addition to the intermediates $[(\eta^6\text{-}C_6H_6)Re(PPh_3)R]$ and $[(\eta^6\text{-}C_6H_6)Re(PPh_3)H]$ must be facile and $(\eta^6\text{-}C_6H_6)Re(PPh_3)H_3$ must also lose H_2 under the photochemical reaction conditions. Third, the benzene solvent must add to $[(\eta^6\text{-}C_6H_6)Re(PPh_3)R]$ faster than D_2 (at 530 mm); otherwise the phosphine ligand would have been deuterated during the photolysis of 1 in C_6H_6 under a D_2 atmosphere. This requirement is resonable since the benzene is ~12 M whereas the D_2 is <0.01 M.

Scheme I shows all steps as reversible except for the loss of H_2 from $[(\eta^6\text{-}C_6H_6)Re(PPh_3)RH_2]$ and those involving H/D exchange products, since the latter are initially present in small quantities. Also if benzene addition to $[(\eta^6\text{-}C_6H_6)Re(PPh_3)R]$ is rapid, then benzene addition to $[(\eta^6\text{-}C_6H_6)Re(PPh_3)(Ph)]$ should also be rapid, although only a degenerate exchange results. The possible presence of this type of degenerate aryl group exchange means that these experiments therefore serve only to provide a lower limit for the rate of oxidative addition of R–H bonds.

In contrast to $CpRe(PPh_3)_2H_2$,[11] alkanes (methane, propane) do not exchange hydrogen for deuterium in C_6D_6 under these conditions. Other arenes such as toluene do show H/D exchange with C_6D_6. The exchange is limited to only the aromatic hydrogens of the ring, with no benzylic exchange being observed by ^2H NMR.

Scheme I



This system is unique in that all other complexes reported to catalyze arene H/D exchange also exchange deuterium into the metal hydride position.[21] Parshall noted previously that $Ta(dmpe)_2H_5$ also catalyzes deuterium exchange from C_6D_6 into the meta and para positions of PPh_3.[22] Other derivatives of this system are under investigation.

Acknowledgment is made to the U.S. Department of Energy (83ER13095) and to the Camille and Henry Dreyfus and Alfred P. Sloan Foundations for their support of this work. We also thank Prof. R. Eisenberg for helpful discussions.

Registry No. 1, 101519-31-7; $[(\eta^6\text{-}C_6H_6)Re(PPh_3)H]$, 101519-32-8.

---

[20] Curtis, M. D.; Bell, L. G.; Butler, W. M. *Organometallics* **1985**, *4*, 701-707.

[21] Chatt, J.; Coffey, R. S. *J. Chem. Soc., Chem. Commun.* **1966**, 545-546. Chatt, J.; Coffey, R. S. *J. Chem. Soc. A* **1969**, 1963-1972. Klaubunde, U.; Parshall, G. W. *J. Am. Chem. Soc.* **1972**, *94*, 9081-9087. Seiwell, L. P. *J. Am. Chem. Soc.* **1974**, *96*, 1734-7135. Roberts, D. A.; Geoffroy, G. L. *J. Organomet. Chem.* **1981**, *214*, 221-231. Grebenik, P. D.; Green, M. L. H.; Izquierdo, A. *J. Chem. Soc., Chem. Commun.* **1981**, 186-187. Adams, G. S. B.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1981**, 353-356. Bradley, M. G.; Roberts, D. A.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 379-384. Green, M. A.; Huffman, J. C.; Caulton, K. G.; Rybak, W. K.; Ziolkowski, J. J. *J. Organomet. Chem.* **1981**, *218*, C39-C43. Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Organomet. Chem.* **1983**, *243*, C78-C82. Fisher, B. J.; Eisenberg, R. *Organometallics* **1983**, *2*, 764-767. Zeiher, E. H. K.; DeWit, D. G.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 7006-7011.

[22] Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113-117.

Evidence for a Metallo Ketone Complex in the Reactions of Rhodium Octaethylporphyrin Dimer with Carbon Monoxide: Solution Equilibria and Spectroscopic Studies

Bradford B. Wayland,* Bruce A. Woods, and Virginia L. Coffin

Department of Chemistry and the Laboratory for Research on the Structure of Matter, University of Pennsylvania Philadelphia, Pennsylvania 19104

Received July 17, 1985

Summary: Proton NMR studies of toluene solutions of rhodium octaethylporphyrin dimer and CO (P_{CO} = 0.2–22 atm) demonstrate the presence of equilibria involving two species with the same stoichiometry (2:1 RhOEP/CO), assigned to an adduct, $(RhOEP)_2(CO)$, and a metallo ke-

tone, (OEPRh)-C(O)-(RhOEP). The metallo ketone structure is supported by IR spectra (ν_{CO} = 1733 cm^{-1}) and a triplet in the ^{13}C NMR ($\delta_{^{13}C}$ 116 ($J_{^{13}C-^{103}Rh}$ = 44 Hz)).

Metallo ketone complexes,[1] which contain a bridging carbonyl unit without a supporting metal–metal bond, have at present only been characterized for the "A-frame" complexes of Pd, Pt, and Rh where other ligand bridges may help to promote the unusual electronic and geometric structure.[2] Spectroscopic evidence exists for an unsupported bridging carbonyl as a transient intermediate in the photoreaction of $[CpFe(CO)_2]_2$ with phosphines and phosphites.[3] Species of this type also have been proposed but not yet observed as intermediates in the decomposition of dionyl-bridged metallo complexes[4] and in the dicobalt octacarbonyl catalyzed hydrogenation of CO to methanol.[5] We wish to report the observation of a metallo ketone species in the equilibrium reactions of rhodium octaethylporphyrin dimer, $(RhOEP)_2$, with CO.[6]

The ^{1}H NMR of $(RhOEP)_2$ ($\sim 10^{-3}$ M) in toluene-d_8 when exposed to CO exhibits an immediate upfield shift of the porphyrin methyne protons (spectrum I) and slower evolution of a second species, (spectrum II) (Figure 1A). Removal of CO by freeze, pump, and thaw cycles results in reversion to $(RhOEP)_2$, demonstrating complete reversibility.

The species that produce the NMR resonances labeled I and II (Figure 1) all have relatively high-field methyne and methyl proton NMR resonances and widely split AB patterns for the methylene hydrogens, CH_2CH_3. These features have been previously observed only when there are two porphyrin units in close proximity as in $(RhOEP)_2$[8] and $(LRuOEP)_2O$.[9] Proton NMR studies have been used in evaluating the solution equilibria and the stoichiometry of the species that contain CO. The methyne proton peak designated as I in Figure 1B shifts to higher field with increasing CO pressure and approaches a limiting value (δ 9.11) when the CO pressure exceeds $\sim$13 atm (T = 297 K). The observed shifts were fitted to a general expression derived for the case of $(RhOEP)_2$ in fast exchange with mono and bis CO adducts.[10] Results from this study indicate that only the mono CO complex $(RhOEP)_2(CO)$ is present in significant amounts in the range of conditions studied (T = 297 K, P_{CO} = 0.2–22 atm)[11] (Figure 2).

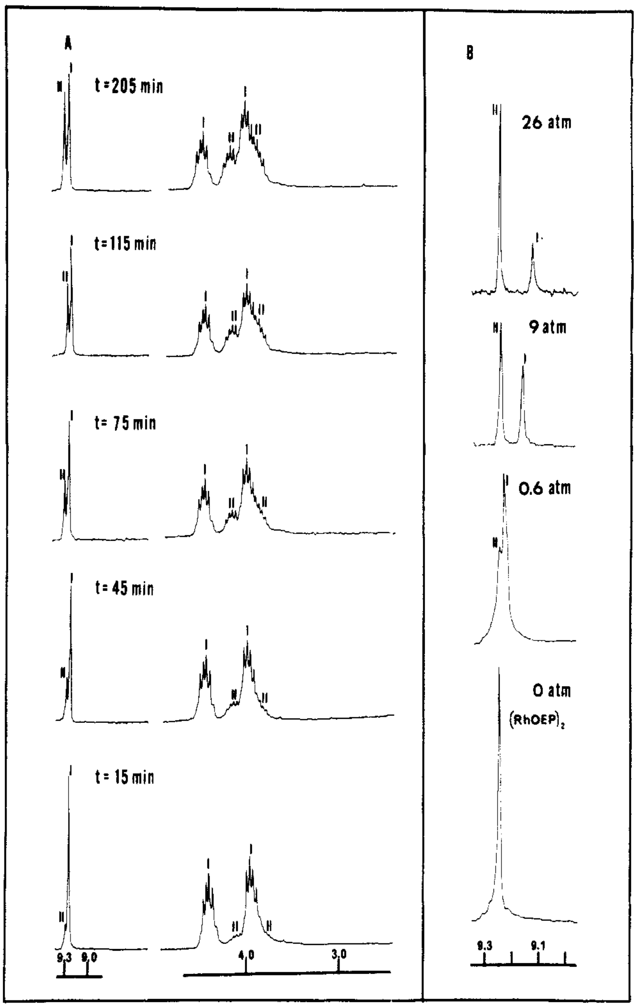


Figure 1. A. Time evolution of II, (OEPRh)–C(O)–(RhOEP), at P_{CO} = 650 torr as shown by the 200-MHz ^{1}H NMR spectra.[7] B. CO pressure dependence of the $(RhOEP)_2$ + CO system at equilibrium (297 K) as seen in the 250-MHz NMR spectra: I, $(RhOEP)_2 + CO \rightleftarrows (RhOEP)_2(CO)$; II, (OEPRh)–C(O)–(RhOEP). All spectra recorded in toluene-d_8 referenced downfield from Me_4Si.

In the higher pressure regime, where the concentration of $(RhOEP)_2$ becomes negligible (P_{CO} > 13 atm), the ratio of the areas (A_{II}/A_I) asymptotically approaches the ratio of the concentration of CO species II to the concentration of the CO adduct $(RhOEP)_2(CO)$ (CO species I).[13] The ratio of areas is observed to approach a limit (A_{II}/A_I = 2.2) in the same range of pressures that the shift in spectrum

---

(1) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980; p 84.

(2) (a) Cowie, M.; Southern, T. G. *J. Organomet. Chem.* **1980**, *193*, C46. Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2500. (b) Colton, R.; McCormick, M. J.; Pannan, C. D. *Aust. J. Chem.* **1978**, *32*, 1425; *J. Chem. Soc., Chem. Commun.* **1977**, 823. (c) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1978**, 1540. Brown, M. P.; Keith, A. N.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chim. Acta* **1979**, *34*, L223. (d) Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1982**, *21*, 2119; *J. Am. Chem. Soc.* **1980**, *102*, 8637.

(3) Tyler, D. R.; Schmidt, M. A.; Gray, H. B. *J. Am. Chem. Soc.* **1979**, *101*, 2753. *J. Am. Chem. Soc.* **1983**, *105*, 6018.

(4) deBoer, E. J. M.; DeWith, J.; Meijboom, N.; Orpen, A. G. *Organometallics* **1985**, *4*, 259.

(5) Daroda, R. J.; Blackborrow, J. R.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1980**, 1098.

(6) The metallo ketone species may also have been observed in the $(RhOEP)_2$-catalyzed reaction of (RhOEP)H with CO to form (RhOEP)-CHO. Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333, footnote 12.

(7) (OEPRh)-C(O)-(RhOEP): ^{1}H NMR $\delta_{methyne}$ 9.25 (s); $\delta_{CH_2CH_3}$ 4.18 (m), 3.83 (m); $\delta_{CH_2CH_3}$ 1.70 (t); $J_{HaHb}(CH_2CH_3)$ = 15 Hz, $J_{CH_2CH_3}$ = 7 Hz; recorded in toluene-d_8 solution internally referenced to toluene.

(8) $(RhOEP)_2$: ^{1}H NMR $\delta_{methyne}$ 9.25 (s); $\delta_{CH_2CH_3}$ 4.45 (m), 3.98 (m); $\delta_{CH_2CH_3}$ 1.70 (t); $J_{H_aH_b}(CH_2\text{-}CH_3)$ = 14.5 Hz, $J_{CH_2CH_3}$ = 7 Hz; recorded in toluene-d_8 internally referenced to toluene.

(9) Collman J. P.; Barnes, C. E.; Brothers, P. J.; Collins, T. J.; Ozawa, T.; Gallucci, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 5151; *J. Am. Chem. Soc.* **1981**, *103*, 7030.

(10) For a fast-exchange process $\delta_{obsd} = \delta_a X_a + \delta_b X_b + ...$, where δ_n is the chemical shift of the observed peak in species n. For $K_1 = [(RhOEP)_2(CO)]/[(RhOEP)_2][CO] = X_{(RhOEP)_2(CO)}/X_{(RhOEP)_2}[CO]$, $K'_1 = [(RhOEP)_2(CO)_2]/[(RhOEP)_2][CO]^2 = X_{(RhEOP)_2(CO)}/X_{(RhOEP)_2}[CO]^2$, and $\delta_{obsd} = \delta_{(RhOEP)_2} + K_1\delta_{(RhOEP)_2(CO)}[CO] + K_1'\,\delta_{(RhOEP)_2(CO)_2}/1 + K_1[CO] + K_1'[CO]^2$ When only a mono CO adduct is present, K_1' = O and the function depicted in Figure 2 is obtained.

(11) Samples in excess of atmospheric pressure were prepared by condensing a measured pressure of CO out of a known volume into an NMR tube equipped with a Teflon stopcock for connection to the vacuum line at liquid N_2 temperature. The tube is then sealed and thawed. Heavy walled tubes such as Wilmad 502-PP are recommended for pressures above $\sim$5 atm, and we recommend thawing the tubes behind a shock shield.

(12) Solubility calculations are based on data obtained from: Gjaldbeck, J. C.; Andersen, E. *Acta Chem. Scand.* **1954**, 1396. Brunner, R. F.; Van Bibber, K. *International Critical Tables*, 1st ed.; Washburn, E. W., Ed.; McGraw-Hill: New York, 1930; Vol. III, p 27. Decombe, L.; Décombe, J. *International Critical Tables* 1st ed.; Washburn, E. W., Ed.; McGraw-Hill: New York, 1930; Vol. III, p 35. Field, L. R.; Wilhelm, E.; Battino, R. *J. Chem. Thermodyn.* **1974**, *6*, 237. Calculated solubilities were checked qualitatively by ^{13}C NMR.

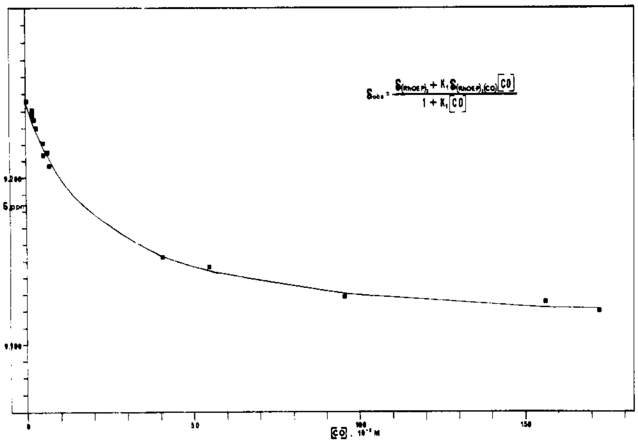


Figure 2. Observed chemical shift of the methyne protons of I vs. CO concentration.[12] The best fit is obtained for K_1 = [(RhOEP)$_2$(CO)]/[(RhOEP)$_2$][CO] = 49 ± 3 M^{-1} and $\delta_{\mathrm{methyne}}$ (RhOEP)$_2$(CO) 9.11: ■, measured data points; —, calculated function.[10]

I approaches a limit (Figure 3). This behavior clearly demonstrates that CO species I and II have the same stoichiometry (2:1 RhOEP/CO). The solution equilibria that occur when (RhOEP)$_2$ is in contact with CO are modeled by reactions 1 and 2. Analysis of the methyne shift data yields K_1 = 49 ± 3 M^{-1} while the area measurements give K_1 = 47 ± 22 M^{-1} and K_2 = 103 ± 30 M^{-1} (Figures 2 and 3).

$$\mathrm{(RhOEP)_2 + CO \rightleftarrows (RhOEP)_2(CO)} \qquad (1)$$

$$K_1 = \mathrm{[(RhOEP)_2(CO)]/[(RhOEP)_2][CO]}$$

$$\mathrm{(RhOEP)_2 + CO \rightleftarrows OEPRh{-}C(O){-}RhOEP} \qquad (2)$$

$$K_2 = \mathrm{[OEPRh{-}C(O){-}RhOEP]/[(RhOEP)_2][CO]}$$

Solution IR spectra and ^{13}C NMR were used to assign the structures of CO species I and II. Benzene solutions of (RhOEP)$_2$ with CO (P_{CO} = 650 torr) have two new bands (2094, 1733 cm^{-1}) in the ν_{CO} region. The 2094 cm^{-1} band is assigned to the terminal CO adduct (RhOEP)$_2$CO, while the 1733 cm^{-1} band is associated with a bridged CO complex. Carbon-13 NMR for solutions of (RhOEP)$_2$ with ^{13}CO show a broad intense peak centered at ~180 ppm and a sharp triplet at 116 ppm, which are unaffected by proton decoupling. The broad ^{13}C resonance is assigned to free CO exchanging with a terminal CO adduct [(RhOEP)$_2$CO].[14] The triplet resulting from the coupling of two equivalent ^{103}Rh nuclei with ^{13}C (J = 44 Hz) and an anomalously high-field chemical shift[15] suggest that the carbonyl carbon is symmetrically bound between two porphyrin rings. Most of the known symmetric carbonyl bridges have bond angles (M–C–M) ≈ 90° and are believed to be supported by metal–metal bonds.[16] This type of structure is virtually eliminated in this case due to the rigidly planar porphyrin macrocycle and electronic structure of the metal in the Rh^{II}OEP unit ($d_{xy}{}^2$, $d_{xz}{}^2$, $d_{yz}{}^2$, $d_{z^2}{}^1$ configuration) which preclude the occurrence of cis-coordination sites for the Rh–C and Rh–Rh bonds. Therefore, the structure of CO species II is assigned as a symmetric metallo ketone, with normal covalent bonds between two RhOEP units and an sp^2-hybridized carbonyl carbon.

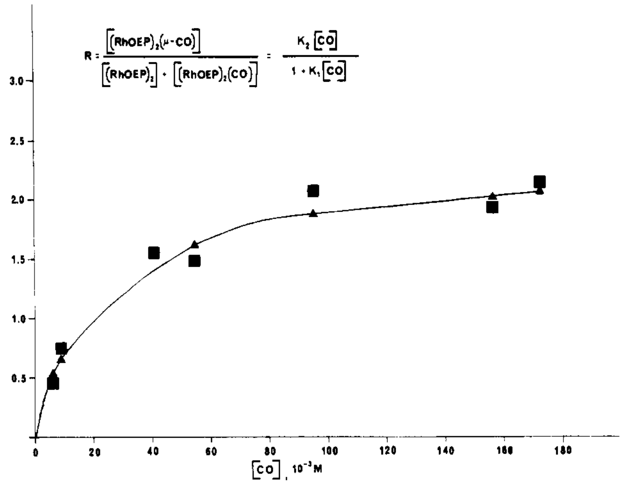


Figure 3. Observed ratio of the areas of the methyne peaks (R = $A_{\mathrm{II}}/A_{\mathrm{I}}$) as a function of CO concentration.[12] The best fit is obtained with the molar equilibrium constants K_1 = 49 ± 22 M^{-1} and K_2 = 103 ± 30 M^{-1}: ■, measured data points; ▲, calculated data points; —, calculated function. No fit can be obtained for an analogous function assuming that CO species II contains two CO units.[13]

Formation of metallo ketone species by a generalized reaction 3 is unusual because the M–C bond energy must be sufficiently large (≥50 kcal/mol) to compensate for cleavage of the M–M bond, reduction of the CO bond order [(C≡O) - (C=O); $\Delta H \simeq$ 72 kcal], and entropy losses ($\Delta S \simeq$ 25 eu; $T\Delta S$ (298 K) ≈ 7.5 kcal).[17] Rh–C bond energies

$$\mathrm{M{-}M + C{\equiv}O \rightleftarrows M{-}C(O){-}M} \qquad (3)$$

in excess of 50 kcal have been previously implied by the unusual organometallic chemistry of rhodium porphyrins.[18] The occurrence of reaction 3 for Rh, Pt, and Pd "A-frame" complexes[2] indicates that these metallo species also form unusually strong M–C bonds.[19] Continuing investigations in this area include more complete thermodynamic and

---

(13) $A_{\mathrm{II}} \propto$ [OEPRh)-C(O)-RhOEP] = K_2[(RhOEP)$_2$][CO]. $A_{\mathrm{I}} \propto$ [(RhOEP$_2$] + [(RhOEP)$_2$CO] = [(RhOEP)$_2$] + K_1[(RhOEP)$_2$][CO]. $A_{\mathrm{II}}/A_{\mathrm{I}} = K_2[\mathrm{CO}]/(1 + K_1[\mathrm{CO}])$. If CO species II had the stoichiometry 2:2 RhOEP/CO as for a bis CO adduct, the ratio of areas would approach a line of positive slope. $A_{\mathrm{II}}'/A_{\mathrm{I}} = K_2'[\mathrm{CO}]^2/(1 + K_1[\mathrm{CO}])$.

(14) Free ^{13}CO appears at δ 184.

(15) ^{13}C chemical shifts for bridging carbonyls generally appear ~200–240 ppm. Mann, B. E.; Taylor, B. B. *^{13}C NMR Data for Organometallic Compounds*, Academic Press: New York, 1981; Table 2.8. One exception is Rh$_2$(dpm)$_2$(Cl)$_2$(μ-CO)(μ-DMA) which appears at δ 181 and which has a metallo ketone structure.[2a]

(16) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; pp 1052–1055.

(17) The estimate of the difference in (C≡O) - (C=O) is obtained from considering the thermodynamic data for reaction a and using an aldehyde CH bond of energy 88 kcal and an H-H bond energy of 104 kcal.

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

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

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

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

$$\mathrm{CO + M{-}M \rightleftarrows M{-}C(O){-}M} \qquad (b)$$

$$\Delta H_{\mathrm{b}} = \mathrm{(C{\equiv}O) + (M{-}M) - 2(M{-}C) - (C{=}O)}$$

$$\mathrm{(M{-}M) - 2(M{-}C)} \simeq \Delta H_{\mathrm{b}} - 72\ \mathrm{kcal/mol}$$

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. (c) Allen, T. L.; Keefer, R. M. *Chemistry Experiment and Theory*, 2nd ed.; Harper and Row: New York, 1982.

(18) Wayland, B. B.; Del Rossi, K. J. *J. Organomet. Chem.* **1984**, *276*, C27. Wayland, B. B.; Woods, B. A.; Pierce, R. *J .Am. Chem. Soc.* **1982**, *104*, 302. Wayland, B. B.; Woods, B. A.; Minda, V. M. *J. Chem. Soc., Chem. Commun.* **1982**, 634.

kinetic studies of reactions 1 and 2, exploration of the range of metallo species capable of accomplishing reaction 3, and an evaluation of the potential role of metallo ketones as reactive intermediates.

Acknowledgment. This work was supported by the National Science Foundation and the Office of Basic Energy Sciences, DOE Grant No. DE-AC02-83-Er13133.

Registry No. $(RhOEP)_2$, 63439-10-1; $(RhOEP)_2(CO)$, 101403-89-8; OEPRh-C(O)-RhOEP, 101403-90-1.

---

[19] (a) On the basis of the thermodynamic parameters obtained for the Pd A-frame system[19b] where ΔH is measured to be between −11 kcal and −15 kcal, we estimate[14] that the M–C bond energies must be at least 49 kcal: (M–M) − 2(M–C) = −83 kcal (−87 kcal). Assuming that (M–M) ≥ 15 kcal, or there would be appreciable dissociation: (M–C) ≥ 49 kcal (51 kcal). (b) Lee, C.; James, B. R.; Nelson, D. A.; Hallen, R. T. *Organometallics* **1984**, *3*, 1360.

Asymmetric Carbon–Carbon Bond Formation Using Optically Active (η-C_5H_5)Fe(CO)$_2$–Vinyl Ether Complexes. Asymmetric Control at Two Adjacent Carbon Centers

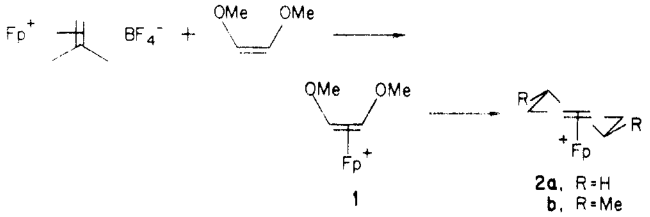
Myron Rosenblum,* Mark M. Turnbull, and Bruce M. Foxman

Department of Chemistry, Brandeis University
Waltham, Massachusetts 02254

Received November 26, 1985

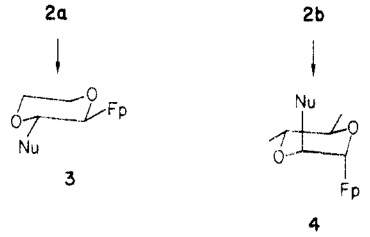
Summary: The dihydrodioxin–Fp complex **2b** (Fp = (η-C_5H_5)Fe(CO)$_2$) adds a broad range of nucleophiles to give optically active adducts **4** in which nucleophile and Fp group are diaxial. These may be converted to optically active Fp(η^2-vinyl ether) or Fp(η^2-alkene) cations of defined absolute configuration.

Optically active metal–olefin complexes, in which the olefin *itself* is a center of asymmetry, provide unique substrates for asymmetric carbon–carbon bond formation.[1] We wish now to report the preparation of optically active complex **2b**, which serves both as a unique platform for asymmetric C–C bond formation and for the preparation of optically active alkyl vinyl ether–iron complexes in which the *exclusive* locus of asymmetry is the olefin center. Both the achiral parent complex **2a** as well as **2b** are readily available from **1** by exchange etherification with ethylene glycol (CH_2Cl_2, 0 °C, 0.25 h; Et_2O, 94%) or with (R,R)-2,3-butanediol[2] (CH_2Cl_2, 0 °C, 1.5 h; Et_2O, 89%). Like **1**, which is available in multigram quanitities by exchange complexation of *cis*-1,2-dimethoxyethylene[3] with



Fp(isobutylene)BF_4, **2a** and **2b** are moderately air stable, storable solids.

Complex **2b**, like the parent **2a** and its acylic analogue **1**, adds nucleophiles of a broad range of basicities, yielding a *single* optically active adduct (Table I). The structures of these products **4** are supported by their proton NMR spectra ($J_{2,3}$ = 1 Hz), which contrast with the spectra of all similar products **3** derived from the parent complex **2a** ($J_{2,3}$ = 8 Hz). Their ^{13}C spectra shows each of these to be a single diastereomer.[4] These structural assignments are further supported by a single-crystal X-ray structure determination of the cyano adduct **4e** shown in Figure 1.[5,6]



The high regioselectivity observed in the reaction of **2b** with nucleophiles may be due to stereoelectronic control, which would be expected to favor the chair transition state associated with nucleophile addition to C-3, but other factors may be operative.[7]

Complex **2b** serves as a valuable starting material for the synthesis of optically active Fp(alkyl vinyl ether) and Fp(alkene) cations of defined absolute configuration and high optical purity. Thus, **4a** is quantitatively converted to (R)-**5a** (ϵ_{480} = +1.34 $M^{-1}\cdot cm^{-1}$, 0°) on treatment with Me_3Si triflate and CH_2Cl_2–Et_2O at −78 °C for 10 min. ^{13}C NMR measurements at 0 °C show it to be a single diastereomer. Epimerization of the asymmetric olefin center in **5** occurs slowly at room temperature, through rotation about the putative double bond, to give a mixture of diastereomers.[8]

---

[1] For the use of optically active tricarbonyl (η^5-cyclohexadienyl)iron complexes in asymmetric synthesis, see: Birch, A. J.; Kelly, L. F. *J. Organomet. Chem.* **1985**, *285*, 267 and references therein. Assymetric C–C bond formation has more commonly been achieved through addition to unsaturated ligands of transition-metal complexes in which either the metal or another ligand are optically active centers. See for example: Faller, J. W.; Chao, K.-H. *J. Am. Chem. Soc.* **1983**, *105*, 3893. Faller, J. W.; Chao, K.-H. *Organometallics* **1984**, *3*, 927. Trost, B. M.; Dietsche, T. *J. Am. Chem. Soc.* **1973**, *95*, 8200. Trost, B. M.; Strege, P. E. *J. Am. Chem. Soc.* **1977**, *99*, 1649. Fiaud, J. C.; De Gournay, A. H.; Larcheveque, M.; Kagan, H. B. *J. Organomet. Chem.* **1978**, *154*, 175. Consiglio, G.; Botteghi, C. *Helv. Chim. Acta* **1973**, *56*, 460. Bosnich, B.; Mackenzie, P. B. *Pure Appl. Chem.* **1982**, *54*, 189.

[2] Strem Chemicals, Inc., Newburyport, MA.

[3] Marsi, M.; Rosenblum, M. *J. Am. Chem. Soc.* **1984**, *106*, 7264.

[4] Full ^1H and ^{13}C NMR data and elemental analyses are included in the supplementary material.

[5] Crystal data: monoclinic, space group $P2_1$; a = 7.859 (2) Å, b = 7.625 (2) Å, c = 12.212 (3) Å; β = 99.54 (3)°. Refinement by full-matrix least squares, with anisotropic temperature factors assigned to Fe, C, and O atoms and with H atoms in calculated positions led to R = 0.022 and R_w = 0.032 (using 2104 data) for which $|F_o| > 3.92\sigma(|F_o|)$. The absolute configuration was established by known stereochemistry at C-10 and C-11 as well as by using a Hamilton R factor test.

[6] The low conformation energy for an axial Fp group in **4**, despite the large size of this group, is no doubt due to the long Fe–C bond in Fp–R complexes (2.07 Å in **4e**, for example). The conformational energy for an axial Fp group in **4a** is estimated as no more than 0.1 kcal/mol, based on a minimum equilibrium value of 80% axial conformer in solution and a value of 0.9 kcal/mol for the conformational energy of an axial methyl group in **4a** and for the gauche methyl interaction in the corresponding diequatorial conformer.

[7] Electronic effects, associated with unsymmetrical coordination of the Fp cation to the olefin in **2b**, cannot be ruled out as contributing to the observed regioselectivity. The chemical shift for C-2,3 in **2a** is δ 102.7 (CD_3NO_2), but for **2b** these centers show resonance at δ 95.5 and 108.6, suggestive of unsymmetrical bonding and hence unsymmetrical charge distribution in this complex.

[8] At 25 °C, in CH_2Cl_2 solution, conversion of **5** to an equilibrium mixture of diasteromers may be followed in its CD spectrum. An equilibrium value of ϵ_{480} = +0.003 (±0.0006) $M^{-1}\cdot cm^{-1}$ is reached at the end of 19 h, at room temperature. For rotational barriers in Fp(vinyl ether)BF_4 complexes, see: Chang, T. C. T.; Foxman, B. M.; Rosenblum, M.; stockman, C. *J. Am. Chem. Soc.* **1981**, *103*, 7361 and ref 3.