One-Electron Activation of CO by a Rhodium(II) Porphyrin Bimetalloradical Complex and Concerted Reactions of Two (RhCO)• Units

Xiao-Xiang Zhang, Gregory F. Parks, and Bradford B. Wayland*

Contribution from the Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

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Abstract: A rhodium(II) porphyrin bimetalloradical complex, •Rh(CH$_2$)$_6$Rh• (**1**) reacts with CO and ethene to form an ethanedionyl reductive coupling product, Rh(CH$_2$)$_6$Rh(μ-C(O)C(O)) (**2**), and an ethylene-bridged complex, Rh(CH$_2$)$_6$Rh(μ-CH$_2$CH$_2$) (**4**), respectively. Reaction of **1** with 1,3-butadiene proceeds by a 1,4-addition to yield a four-carbon-bridged complex, Rh(CH$_2$)$_6$Rh(μ-CH$_2$CH=CHCH$_2$) (**5**). ^{1}H NMR spectra of **2** and **4** manifest the inherent chirality of two-carbon-bridged tethered diporphyrin complexes. Solutions of **1** and CO react with H$_2$O, CH$_3$CH$_2$OH, and H$_2$ to produce multifunctionalized formyl complexes H—Rh(CH$_2$)$_6$Rh—CHO (**6**), H(O)C—Rh(CH$_2$)$_6$Rh—C(O)-OCH$_2$CH$_3$ (**7**), and H(O)C—Rh(CH$_2$)$_6$Rh—CHO (**8**), respectively, but fail to react to an observable extent with methane. Reactivity studies indicate that solutions of **1** and CO function as a source of a species that contains two carbonyl groups (•[OCRh(CH$_2$)$_6$RhCO]•) (**3**) that are activated toward one-electron reactions at the carbonyl carbon. Reactions of **3** with substrates (H$_2$O, C$_2$H$_5$OH, H$_2$) are discussed in terms of a proposed pathway where two metalloformyl radicals ([MCO]•) and the substrate occur in a four-centered transition state (Rh—C(O)•···A···B···•(O)C—Rh).

Introduction

Rhodium(II) porphyrins have previously been shown to form carbon monoxide complexes (((por)RhCO)•) where CO is activated toward one-electron reactions at the carbonyl carbon.[1,2] Reactions of [(por)RhCO]• with sources of X• that form (por)-Rh—C(O)X complexes illustrate the formal relationship of [(por)RhCO]• species with the formyl radical (HC(O)•).[1] Prominent examples include dimerization through —(O)C—C(O)— bonding to form 1,2-ethanedionyl complexes, (por)Rh—C(O)—C(O)—Rh(por),[2] and reactions with H atom sources that produce formyl complexes, (por)Rh—CHO.[3] Samarium(II) complexes which are exceptionally strong reducing agents also produce carbon monoxide coupling through one-electron activation of CO.[4] Diporphyrin complexes of rhodium(II) (•Rh(CH$_2$)$_6$Rh•) (**1**) have recently been reported to accomplish relatively fast methane C—H bond activation by the concerted reaction of the two metalloradical centers.[5] In this paper we report on reactivity studies of •Rh(CH$_2$)$_6$Rh• (**1**) and CO with a series of substrates (H$_2$O, C$_2$H$_5$OH, H$_2$) where the observed products are consistent with reactions of two one-electron-activated CO fragments in a diradical molecular unit, •[OCRh(CH$_2$)$_6$RhCO]• (**3**).

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Scheme 1

Results

Preparation of a Rhodium(II) Porphyrin Bimetalloradical Complex. A diporphyrin ligand where the porphyrin units are tethered by a diether (—O(CH$_2$)$_6$O—) spacer was prepared and converted to the dirhodium(II) derivative by procedures outlined in Scheme 1.[5–8] The dimethyl derivative photolyzes in benzene to form a dirhodium(II) complex (•Rh(CH$_2$)$_6$Rh•) (**1**) which is

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Figure 1. ^{1}H NMR for the pyrrole of Rh(CH$_2$)$_6$Rh(μ-C(O)C(O)) (**2**) in C$_6$D$_6$ (296 K).

shown to be a persistent bimetalloradical through observation of Curie behavior for the porphyrin pyrrole contact shifts (350–200 K). EPR parameters for **1** in toluene glass (90 K) ($g_{||}$ = 1.93, $g_\perp$ = 2.66; $A(^{103}$Rh)($g_{||}$)= 159 MHz)[1] are characteristic of a low-spin rhodium(II) species with a $(d_{xy})^2(d_{xz}d_{yz})^4d_{z^2}{}^1$ electron configuration. The steric requirements of the diporphyrin ligand that contains six mesityl groups precludes intra- and intermolecular Rh–Rh bonding and provides a stable rhodium(II) porphyrin bimetalloradical complex, $^\bullet$Rh(CH$_2$)$_6$Rh$^\bullet$ (**1**)[5] (Scheme 1).

Reaction of $^\bullet$Rh(CH$_2$)$_6$Rh$^\bullet$ (1) with CO, CH$_2$=CH$_2$, and CH$_2$=CHCH=CH$_2$. (a) Reaction of 1 with CO. Benzene solutions of **1** react with CO (P_{CO} = 0.3–0.9 atm, T = 295 K) to produce an equilibrium distribution of species containing CO where the 1,2-ethanedione complex (Rh(CH$_2$)$_6$Rh(μ-C(O)C(O)) (**2**) (eq 1) greatly predominates. Compound **2** is the only

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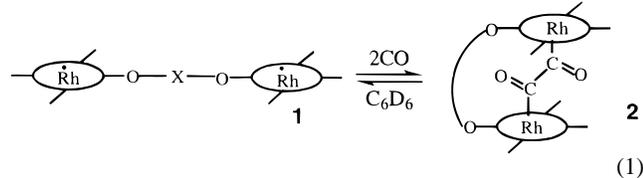
rhodium porphyrin species observed in the ^{1}H NMR for solutions of **1** and CO when the CO pressure is greater than 0.2 atm (T = 295 K). Several prominent features in the ^{1}H NMR of **2** include eight chemically inequivalent pyrrole hydrogen resonances (Figure 1) and diastereotopic CH$_2$ groups in the diether tether ($-$O(CH$_2$)$_6$O$-$). The ^{13}C NMR of the ^{13}C(O) derivative of **2** displays an AA'XX' pattern characteristic of the ^{103}Rh$-^{13}$C(O)^{13}C(O)$-$Rh^{103} unit that is closely related to analogous ((por)Rh)$_2$(μ-^{13}C(O)^{13}C(O)) complexes.[1,2] The AA'XX' pattern for **2** is simulated by using the following parameters: δ^{13}C = 164.5, $^1J_{^{103}\text{Rh}-^{13}\text{C}}$ = 40 Hz, $^2J_{^{103}\text{Rh}-^{13}\text{C}}$ = 9 Hz, $^3J_{^{103}\text{Rh}-^{103}\text{Rh}}$ = 4 Hz, $^1J_{^{13}\text{C}-^{13}\text{C}}$ = 20 Hz.

Solvent evaporation from a frozen benzene solution of **2** produces a yellow-orange solid which as a Nujol mull displays two bands in the CO stretching region ($\nu_{CO} \approx$ 1780, 1769 cm^{-1}; $\nu_{^{13}\text{CO}} \approx$ 1736, 1725 cm^{-1}) which are very similar to those observed for (TXP)Rh$-$C(O)C(O)$-$Rh(TXP) ($\nu_{CO} \approx$ 1778, 1767 cm^{-1}; $\nu_{^{13}\text{CO}} \approx$ 1738, 1727 cm^{-1})[1] and (TMP)Rh$-$C(O)-C(O)$-$Rh(TMP) ($\nu_{CO} \approx$ 1782, 1770 cm^{-1})[1] (TXP = tetra-xylylporphyrin; TMP = tetramesitylporphyrin). The ν_{CO} bands in the Nujol mull of **2** decline in intensity and disappear over a period of hours due to loss of CO. FAB MS for benzene solutions of **2** yields the parent ion for **1** as the highest mass species, indicating facile loss of CO from **2**. Attempts to grow single crystals of **2** for X-ray diffraction study have not yet been successful.

The pyrrole ^{1}H NMR resonances for **2** are relatively narrow below 295 K but broaden substantially as the temperature is elevated (300–350 K) ($\Delta\nu_{1/2}$(ex) = $\Delta\nu_{1/2}$(obs) $-$ $\Delta\nu_{1/2}$(nat); $\Delta\nu_{1/2}$(ex) (**2**) = 0.75 ± 0.15 Hz (300 K); 2.30 ± 0.25 Hz (310

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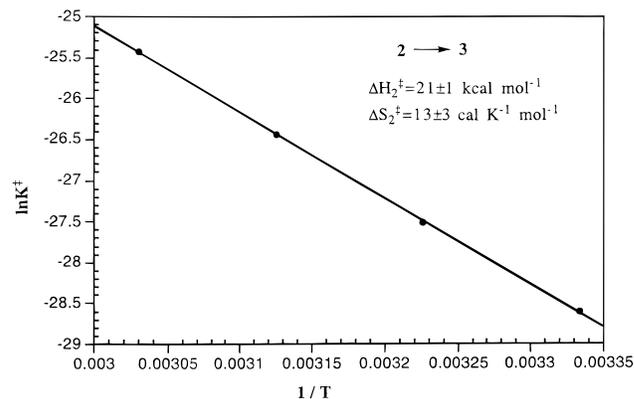
Figure 2. Determination of the activation parameters for the dissociation of Rh(CH$_2$)$_6$Rh(μ-C(O)C(O)) (**2**) into $^\bullet$[OCRh(CH$_2$)$_6$RhCO]$^\bullet$ (**3**) using proton NMR line broadening of **2** as the observable ($k_f = \tau_d^{-1}$; $K^\ddagger = k_f(h/kT)$.

K); 7.0 ± 0.8 Hz (320 K); 20 ± 2 Hz (330 K)). The pyrrole hydrogen line broadening is ascribed to dissociation of **2** into the paramagnetic dicarbonyl diradical unit $^\bullet$[OCRh(CH$_2$)$_6$-RhCO]$^\bullet$ (**3**) (eq 2) by (O)C$-$C(O) bond homolysis in analogy

$$(2)$$
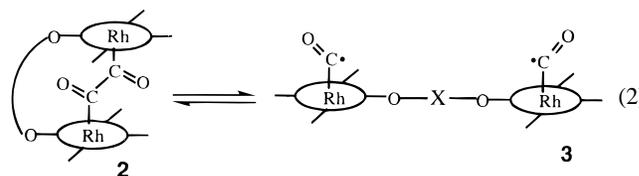
with the previously reported dissociation of ((TMP)Rh)$_2$(μ-C(O)C(O)) into [(TMP)Rh$-$CO]$^\bullet$ monomer fragments.[1] The contribution of exchange to the line width at half-height ($\Delta\nu_{1/2}$; T_2^{-1}(ex) = $\pi\Delta\nu_{1/2}$) is given by the general expression T_2^{-1}(ex) = $\tau_d^{-1}[(A\tau_p/2)^2][1 + (A\tau_p/2)^2]^{-1}$, where τ_d and τ_p are the lifetimes of the nuclear spin states in the diamagnetic and paramagnetic species and A is the electron$-$nuclear coupling constant for the nucleus being observed.[9] When $(A\tau_p/2)^2 \gg 1$, T_2^{-1}(ex) = τ_d^{-1} = k_f, where k_f is the rate constant for dissociation.[7,10] A relatively long electron spin relaxation time (τ_p >10^{-5} s^{-1}) and moderate pyrrole hydrogen$-$electron coupling constant (A > 10^6 s^{-1}) fulfill these limiting conditions so that T_2^{-1}(ex) equals the rate constant for dissociation. Evaluation of the activation parameters for reaction 2 gives $\Delta H_2^\ddagger$ = 21 ± 1 kcal mol^{-1} and $\Delta S_2^\ddagger$ = 13 ± 3 cal K^{-1} mol^{-1} (Figure 2). $\Delta H_2^\ddagger$ is effectively equal to and $\Delta S_2^\ddagger$ smaller than the corresponding values for ((TMP)Rh)$_2$(μ-C(O)C(O)) ($\Delta H^\ddagger$ = 21.3 ± 0.8 kcal mol^{-1} and $\Delta S^\ddagger$ = 22 ± 3 cal K^{-1} mol^{-1}).[1]

(b) Reaction of 1 with Ethene. Benzene solutions of $^\bullet$Rh(CH$_2$)$_6$Rh$^\bullet$ (**1**) react with ethene ($P_{CH_2=CH_2} \approx$ 0.4 atm, T = 295 K) to generate an ethylene-bridged complex, Rh(CH$_2$)$_6$Rh-(μ-CH$_2$CH$_2$) (**4**), as the exclusive observed product (eq 3). Prominent features in the ^{1}H NMR of **4** include eight pyrrole resonances, diasteriotopic CH$_2$ groups in the diether ($-$O(CH$_2$)$_6$O$-$) tether, and distinctive high-field multiplets associated with diasteriotopic CH$_2$ groups in the bridging ethylene unit ($\delta_{CH(A)}$ = $-$7.81, $\delta_{CH(B)}$ = $-$8.24). Repeating this experiment with ^{13}CH$_2$=^{13}CH$_2$ results in ^{13}C splitting of

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(3)
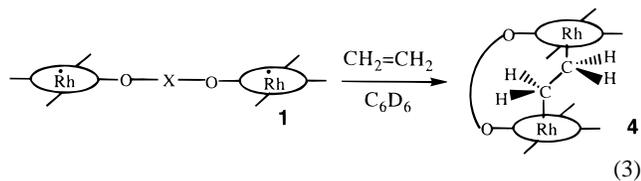
the two high-field multiplets ($^1J_{^{13}C-H}$ = 144 Hz) (Figure 3). The ^{1}H-decoupled ^{13}C NMR of the ethylene bridge in the ($^{13}CH_2)_2$ derivative of **4** appears as an AA′XX′ pattern (Figure 4) that is simulated by using the following parameters: $\delta_{^{13}C}$ = 19.34 ppm, $^1J_{^{103}Rh-^{13}C}$ = 30.2 Hz, $^2J_{^{103}Rh-^{13}C}$ = −3.2 Hz, $^1J_{^{13}C-^{13}C}$ = 32.4 Hz, $^3J_{^{103}Rh-^{103}Rh}$ ≈ 0.2 Hz.

   (c) Reaction of 1 with 1,3-Butadiene. Benzene solutions of **1** react with 1,3-butadiene ($P_{C_4H_6}$ ≈ 0.4 atm) to produce a four-carbon-bridged complex, $Rh(CH_2)_6Rh(\mu\text{-}CH_2CH{=}CHCH_2)$ (**5**) (eq 4). The ^{1}H NMR of **5** shows only three resolved pyrrole

(4)
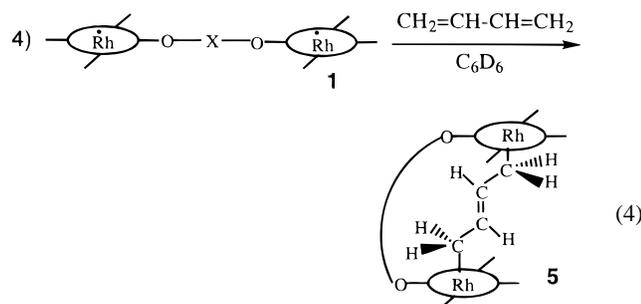
resonances with intensity ratios of 1:1:2, chemically equivalent CH_2 groups in the diether ($-O(CH_2)_6O-$) tether, and high-field resonances for the CH_2(dd, −5.32) and CH (t, −2.24) groups in the bridging $-CH_2CH{=}CHCH_2-$ unit.

   Reaction of 1 and CO with H$_2$O, C$_2$H$_5$OH, H$_2$, and CH$_4$. (a) Reaction of 1 and CO with Water. Addition of H_2O to a benzene solution of **1** and CO (P_{CO} = 0.4 atm; T = 295 K) results in the formation of a single species observed in the ^{1}H NMR that is assigned as the hydrido−formyl complex $H-Rh(CH_2)_6Rh-CHO$ (**6**) (eq 5). When ^{13}CO is used,

(5)
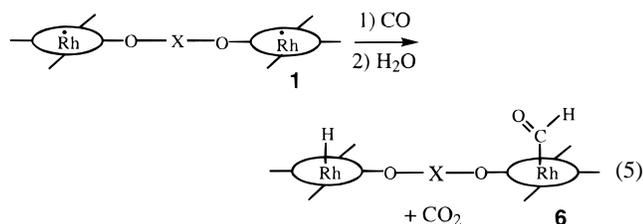
concomitant formation of **6** and $^{13}CO_2$ ($\delta_{^{13}CO_2}$ = 124 ppm) with the disappearance of **2** is observed in the ^{13}C NMR. The ^{1}H NMR spectrum of **6** has characteristic resonances for a rhodium formyl unit (δ_{CHO} = 3.66; $^2J_{^{103}Rh-CHO}$ = 1.3 Hz) and a rhodium hydride fragment (δ_{Rh-H} = −40.07; $^1J_{^{103}Rh-H}$ = 44.5 Hz) (Figure 5a), as well as chemically inequivalent methylene groups in the diether tether ($\delta_{OCH_2(CH_2)_4CH_2O}$ = 3.92, 3.90). Repeating this experiment with ^{13}CO in toluene results in ^{13}C splitting of the formyl hydrogen into a doublet of doublets ($^1J_{^{13}CHO}$ = 197.5 Hz). The ^{1}H-coupled ^{13}C NMR spectrum of the formyl units in the ^{13}CO derivative of **6** appears as a doublet of doublets from ^{103}Rh and ^{1}H coupling ($\delta_{^{13}CHO}$ = 193.7; $^1J_{^{103}Rh-^{13}C}$ = 30.2 Hz; $^1J_{H-^{13}C}$ = 197.5 Hz) (Figure 5b).

   (b) Reaction of 1 and CO with Ethanol. Addition of ethanol to a benzene solution of **1** and CO (P_{CO} = 0.45 atm)
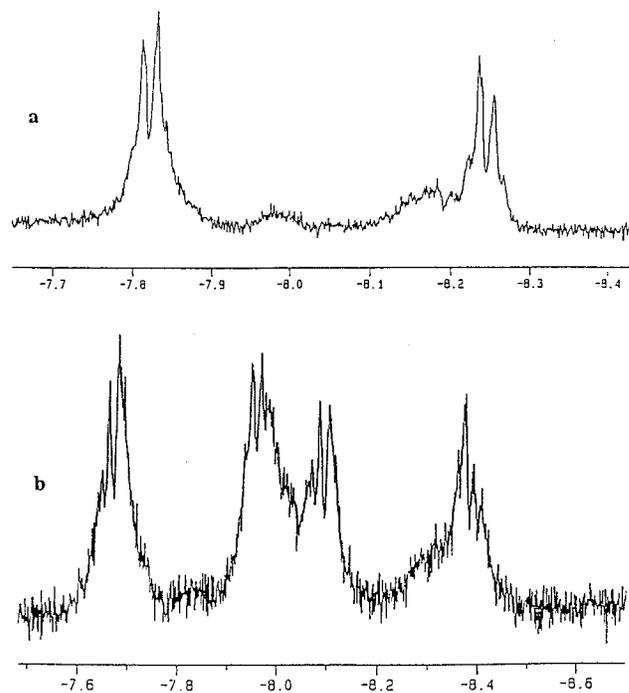
Figure 3. (a) ^{1}H NMR of the $Rh-CH_2-CH_2-Rh$ unit of **4** in C_6D_6 (296 K). (b) ^{1}H NMR for the carbon-13 derivative of **4**.
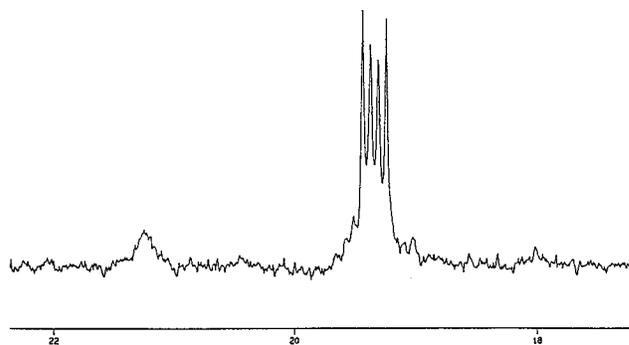
Figure 4. Proton-decoupled ^{13}C NMR spectrum of the ethylene-bridged ($Rh-^{13}CH_2-^{13}CH_2-Rh$) unit in the carbon-13 derivative of **4** in C_6D_6 (296 K) (AA′XX′; $\delta_{^{13}C}$ = 19.34 ppm; $^1J_{^{103}Rh-^{13}C}$ = 30.2 Hz, $^2J_{^{103}Rh-^{13}C}$ = −3.2 Hz, $^1J_{^{13}C-^{13}C}$ = 32.4 Hz, $^3J_{^{103}Rh-^{103}Rh}$ = 0.2 Hz).

results exclusively in the formation of a formyl−ester complex, $H(O)C-Rh(CH_2)_6Rh-C(O)OCH_2CH_3$ (**7**) (eq 6). The ^{1}H NMR

(6)
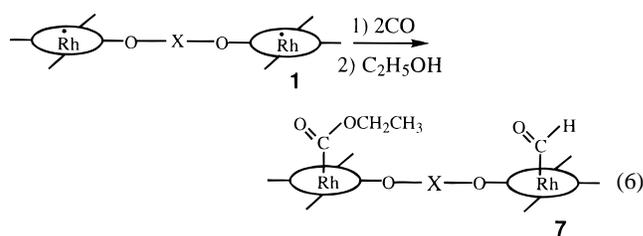
spectrum of **7** displays a characteristic formyl resonance (δ_{CHO} = 3.66; $^2J_{^{103}Rh-CHO}$ = 1.6 Hz), quartet and triplet resonances for the organometallic ester group ($Rh-C(O)OCH_2CH_3$) (δ_{CH_2} = 1.38; δ_{CH_3} = −1.04; $^3J_{H-H}$ = 6.8 Hz), and chemically inequivalent methylene groups in the diether tether ($\delta_{OCH_2(CH_2)_4CH_2O}$ = 3.92, 3.90). Repeating this experiment with ^{13}CO results in ^{13}C splitting of the formyl peak ($^1J_{H-^{13}C}$ = 197.5 Hz) and the CH_2 group of the organometallic ester unit ($^3J_{C(O)OCH_2}$ = 4.4 Hz). The ^{1}H-coupled ^{13}C NMR spectrum of the ^{13}CO derivative of **7** shows a doublet of doublets ($\delta_{^{13}CHO}$ = 194.51; $^1J_{^{103}Rh-^{13}C}$
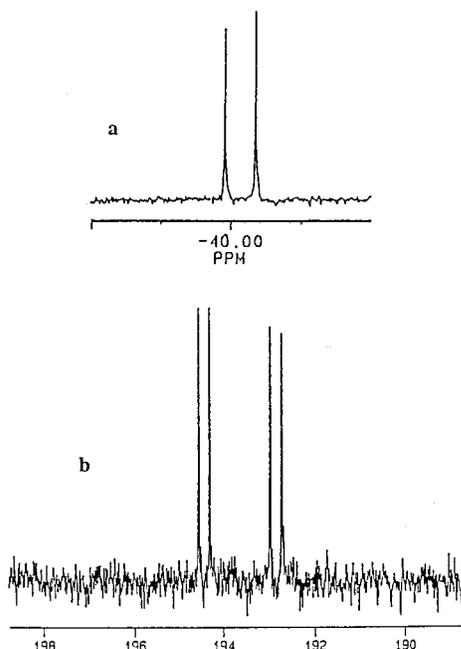
Figure 5. NMR spectra for the ^{13}C derivative of **6** (H$-$Rh(CH$_2$)$_6$Rh$-$^{13}CHO) in CD$_3$C$_6$D$_5$ (296 K): (a) ^{1}H NMR of the rhodium hydride group, Rh$-$H ($\delta = -40.07$ ppm; $^1J_{^{103}\text{Rh}-\text{H}} = 43.4$ Hz); (b) proton-coupled ^{13}C NMR of the formyl group, Rh$-$^{13}CHO ($\delta = 193.7$ ppm; $^1J_{^{103}\text{Rh}-^{13}\text{C}} = 30.2$ Hz, $^1J_{\text{H}-^{13}\text{C}} = 197.5$ Hz).

$= 30.2$ Hz; $^1J_{\text{H}-^{13}\text{C}} = 197.5$ Hz) for the Rh$-$^{13}CHO unit and a doublet of triplets ($\delta_{^{13}\text{C}} = 148.29$; $^1J_{^{103}\text{Rh}-^{13}\text{C}} = 46.5$ Hz; $^3J_{\text{H}-^{13}\text{C}} = 4.4$ Hz) for the Rh$-$^{13}C(O)OCH$_2$CH$_3$ unit (Figure 6).

(c) Sequential Reaction of 1 with CO and H$_2$. When benzene solutions of •Rh(CH$_2$)$_6$Rh• (**1**) are pressurized sequentially with carbon monoxide ($P_{\text{CO}} = 0.52$ atm) and then H$_2$ ($P_{\text{H}_2} = 0.22$ atm, $P_{\text{CO}} = 0.52$ atm; $T = 295$ K) compound **2** forms initially and then reacts away to produce a diformyl complex, H(O)C$-$Rh(CH$_2$)$_6$Rh$-$CHO (**8**) (eq 7), as the only species
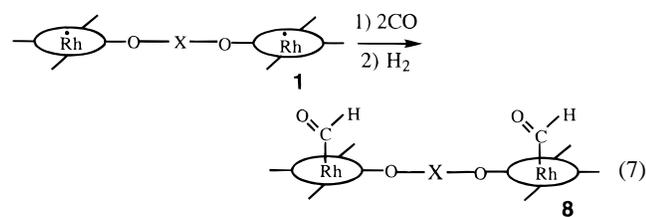
observed by NMR. The ^{1}H NMR spectrum of **8** gives a characteristic Rh$-$CHO resonance ($\delta_{^{13}\text{CHO}} = 3.66$; $^2J_{^{103}\text{Rh}-\text{CHO}} = 1.4$ Hz) which becomes a doublet of doublets in the ^{13}CO derivative of **8** ($^1J_{^{13}\text{C}-\text{H}} = 197.5$ Hz) (Figure 7a). The ^{1}H-coupled ^{13}C NMR spectrum in toluene of the formyl units in the ^{13}CO derivative of **8** appears as a doublet of doublets from ^{103}Rh and ^{1}H coupling ($\delta_{^{13}\text{CHO}} = 193.65$; $^1J_{^{103}\text{Rh}-^{13}\text{C}} = 30.2$ Hz; $^1J_{\text{H}-^{13}\text{C}} = 197.5$ Hz) (Figure 7b).

(d) Sequential Reaction of 1 with H$_2$ and CO. Benzene solutions of **1** react rapidly with H$_2$ ($P_{\text{H}_2} = 0.3$ atm) to form the dihydrido complex H$-$Rh(CH$_2$)$_6$Rh$-$H (**9**) (eq 8),[5] which when subsequently pressurized with CO ($P_{\text{CO}} = 0.5$ atm; $P_{\text{H}_2} = 0.3$ atm; $T = 295$ K) fails to produce observable quantities of formyl complexes **6** and **8** over a period of weeks.

(e) Reaction of 1 and CO with Methane. When benzene solutions of **1** were sequentially pressurized with carbon monoxide ($P_{\text{CO}} = 0.37$ atm) and then CH$_4$ ($P_{\text{CH}_4} = 0.53$ atm), the dionyl complex **2** formed and persisted. Neither the desired
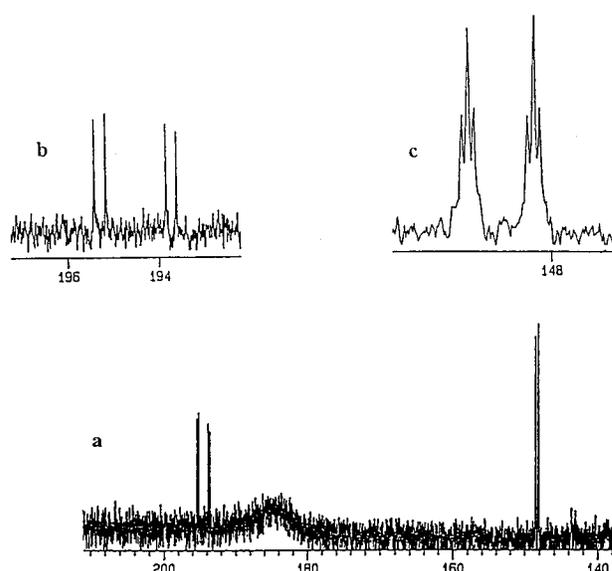
Figure 6. (a) Proton-coupled ^{13}C NMR spectrum of the formyl and ester groups in the carbon-13 derivative of H(O)^{13}C$-$Rh(CH$_2$)$_6$Rh$-$^{13}C(O)OCH$_2$CH$_3$ (**7**) in C$_6$D$_6$ (296 K). (b) Expanded ^{13}C NMR spectrum of the Rh$-$^{13}CHO unit ($\delta_{^{13}\text{CHO}} = 194.51$, $^1J_{^{103}\text{Rh}-^{13}\text{C}} = 30.2$ Hz, $^1J_{\text{H}-^{13}\text{C}} = 197.5$ Hz). (c) Expanded ^{13}C NMR of the Rh$-$^{13}C(O)OCH$_2$CH$_3$ unit ($\delta_{^{13}\text{C(O)OCH}_2\text{CH}_3} = 148.29$, $^1J_{^{103}\text{Rh}-^{13}\text{C}} = 46.5$ Hz, $^3J_{\text{H}-^{13}\text{C}} = 4.4$ Hz).
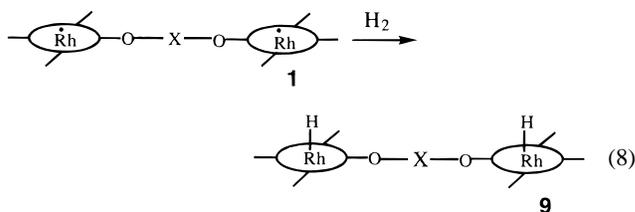
product of CH$_4$ activation, H(O)C$-$Rh(CH$_2$)$_6$Rh$-$C(O)CH$_3$ (**10**) (eq 9), nor any other products containing Rh$-$CHO or Rh$-$
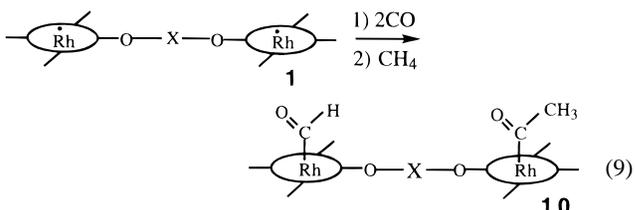
C(O)CH$_3$ units were detected by ^{1}H NMR. A very slow reaction ($\sim$2 weeks) ultimately results in formation of the hydrido$-$methyl complex, H$-$Rh(CH$_2$)$_6$Rh$-$CH$_3$ (**11**)[4] (eq 10). The ^{1}H
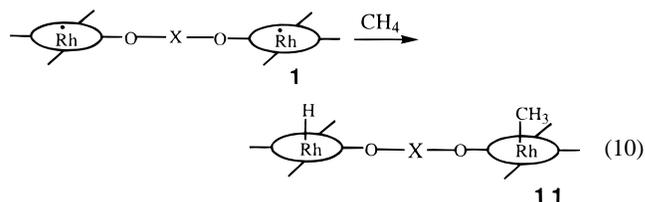
NMR spectrum of **11** displays a high-field doublet ($\delta_{\text{Rh}-\text{CH}_3} = -5.29$; $^2J_{^{103}\text{Rh}-\text{H}} = 3.0$ Hz) for the Rh$-$CH$_3$ unit and a high-field doublet ($\delta_{\text{Rh}-\text{H}} = -40.07$; $^1J_{^{103}\text{Rh}-\text{H}} = 43.4$ Hz) for the rhodium hydride fragment. Compound **11** presumably forms from reaction of CH$_4$ with the small concentration of **1** (eq 10)[5] in equilibrium with **2** (eq 1).

Discussion

Reactions of 1 with CO, CH$_2$=CH$_2$, and CH$_2$=CH-CH=CH$_2$. The dirhodium(II) diporphyrin bimetallo-
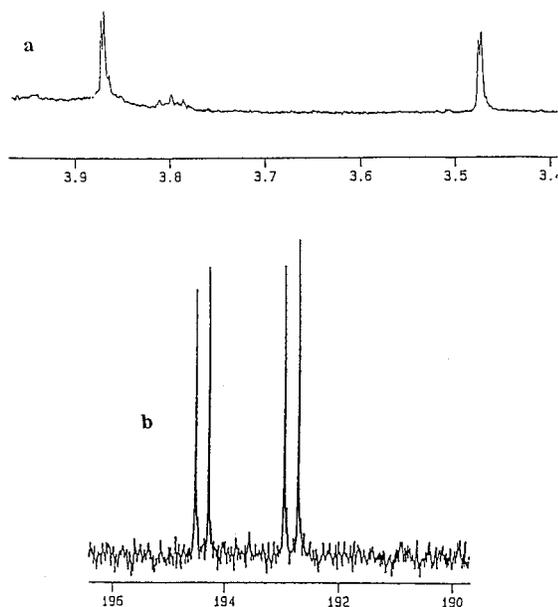
Figure 7. NMR spectra of the formyl unit in the carbon-13 derivative of H(O)^{13}C$-$Rh(CH$_2$)$_6$Rh$-$^{13}CHO (**8**) in CD$_3$C$_6$D$_5$ (296 K): (a) ^{1}H NMR ($\delta_{^{13}CHO}$ = 3.66 ppm; $^1J_{^{13}C-H}$ = 197.5 Hz, $^2J_{^{103}Rh-CHO}$ = 1.4 Hz); (b) proton-coupled ^{13}C NMR ($\delta_{^{13}CHO}$ = 193.65 ppm; $^1J_{^{103}Rh-^{13}C}$ = 30.2 Hz, $^1J_{H-^{13}C}$ = 197.5 Hz).

radical, $^\bullet$Rh(CH$_2$)Rh$^\bullet$ (**1**), reacts with CO, CH$_2$=CH$_2$, and CH$_2$=CHCH=CH$_2$ to form complexes where reduced substrate units bridge two rhodium centers, Rh(CH$_2$)$_6$ Rh(μ-C(O)$-$C(O)) (**2**), Rh(CH$_2$)$_6$Rh(μ-CH$_2$CH$_2$) (**4**), and Rh(CH$_2$)$_6$Rh(μ-CH$_2$-CH=CHCH$_2$) (**5**), respectively. There is no evidence for a dirhodium ketone (Rh$-$C(O)$-$Rh) which is a prominent species in the reaction of [(OEP)Rh]$_2$ with CO (OEP = octaethyl-porphyrin).[2] The bent Rh$-$C(O)$-$Rh unit causes steric interactions between mesityl groups on adjacent porphyrin units that inhibit formation of the one-carbon-bridged dimetal ketone (M$-$C(O)$-$M) in a manner similar to that previously observed for the (TMP)Rh system.[1] ^{1}H NMR spectra of **2**, **4**, and **5** show that these molecules appear to have two chemically equivalent units consisting of the porphyrin and half of the diether tether and bridging substrate. The chemical equivalencies presumably result from the dynamic molecular structure passing through a conformation with a C_2 axis that bisects the diether tether and bridging substrate units.
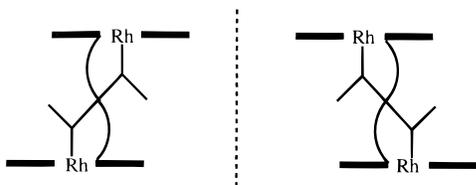
Observation of eight pyrrole hydrogen doublets from four diastereotopic pyrrole H$-$C$-$C$-$H AB patterns and diastereo-topic CH$_2$ AB patterns for the diether tether ($-$OCH$_2$(CH$_2$)$_4$-CH$_2$O$-$) are manifestations in the ^{1}H NMR of the inherent chirality of **2** and **4**. The dynamic structural changes for **2** and **4** must not pass through a conformation that contains an improper axis of rotation on the NMR time scale. Rotation of the substrate bridges of **2** and **4** (Rh$-$C(O)C(O)$-$Rh, Rh$-$CH$_2$CH$_2$$-$Rh) would interconvert the enantiomers by passing through a conformation with an effective plane of symmetry (S_1). This rotation in **2** and **4** must be inhibited by the constraints of the tightly packed diporphyrin pocket contain-ing the two-carbon-bridged substrates. Inhibition of motions

for the bridging substrate sandwiched between two porphyrins has previously been proposed as the reason for observing geometric isomers for (OEP)Rh$-$CH$_2$CH(CO$_2$CH$_3$)$-$Rh(OEP) and related complexes.[11] Chemical equivalence of the CH$_2$ groups in both the diether tether and the substrate bridge ($-$CH$_2$CH$-$CHCH$_2$$-$) as well as several pyrrole hydrogen equivalencies in Rh(CH$_2$)$_6$Rh(μ-CH$_2$CH=CHCH$_2$) (**5**) indicate that the inherent chirality for the static molecule is not manifested by the NMR spectra (T = 270$-$295 K). Introduction of the four-carbon-bridged substrate in **5** apparently opens the diporphyrin pocket enough to permit sufficiently fast rotation of the bridging substrate such that the enantiomers are rapidly interconverted on the NMR time scale.

Reactions of 1 and CO with H$_2$O, C$_2$H$_5$OH, H$_2$, and CH$_4$. Rhodium(II) porphyrins have previously been observed to react with CO to produce 17-electron [Rh$-$CO]$^\bullet$ units that have reactivity patterns similar to that of the formyl radical [HCO]$^\bullet$.[1,2,4] Hydrogen atom abstractions from (por)Rh$-$H and HSnR$_3$ that produce formyl complexes ((por)Rh$-$CHO),[1,4] reaction with (por)Rh$^\bullet$ to form dimetal ketone complexes ((por)Rh$-$C(O)$-$Rh(por)),[2] and dimerization by RhC(O)$-$C(O)Rh bond forma-tion[2] illustrate the activation of the [(por)Rh$-$CO]$^\bullet$ unit toward one-electron reactions at the carbonyl carbon.

Solutions of **1** and CO primarily contain the dionyl-bridged complex **2**, but small equilibrium concentrations of **1**, along with the mono- and bis-CO complexes of **1** must also be present. ^{1}H NMR line broadening for **2** associated with RhC(O)$-$C(O)-Rh bond homolysis indicates that the system resulting from **1** and CO is a thermal source for a dirhodium dicarbonyl diradical, $^\bullet$[OCRh(CH$_2$)$_6$RhCO]$^\bullet$ (**3**). An objective of this study was to evaluate the potential of diradical species like **3** to activate substrates (A, B) through reaction with two metalloformyl radical units in analogy with the reported reaction of the dimetalloradical $^\bullet$Rh(CH$_2$)$_6$Rh$^\bullet$ (**1**) with CH$_4$ and H$_2$.[5]
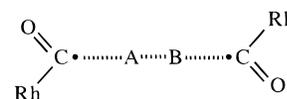
Solutions of **1** and CO which contain **2** as the predominant species react with H$_2$O exclusively to produce a hydrido$-$formyl complex (H-Rh(CH$_2$)$_6$Rh$-$CHO (**6**)) which does not react further with CO at a finite rate to yield the diformyl complex H(O)C$-$Rh(CH$_2$)$_6$Rh$-$CHO (**8**). Observation that **6** forms as the exclusive product simultaneously with disappearance of **2** is compatible with a rate-limiting reaction of **3** with water to form an intermediate formyl$-$carboxylic acid complex (HO(O)C$-$Rh(CH$_2$)$_6$Rh$-$CHO (**12**)) that rapidly loses CO$_2$ to form **6**. Elimination of CO$_2$ is a general reaction of metallo carboxylic acid complexes[12] and was previously observed for rhodium porphyrin derivatives.[4b,13]

Additional evidence for a dominant concerted reaction of two metalloformyl radical units ((RhCO)$^\bullet$) in **3** is obtained from the reaction of **1** and CO with ethanol (eq 6) that yields the formyl$-$ester complex CH$_3$CH$_2$OC(O)$-$Rh(CH$_2$)$_6$Rh$-$CHO (**7**) as the predominant product observed in the ^{1}H NMR. Reaction of ethanol with (Rh$-$CO)$^\bullet$ units in different molecules of **3** would yield symmetrically derivatized carbonyl products (H(O)C$-$Rh(CH$_2$)$_6$Rh$-$CHO, CH$_3$CH$_2$O(O)C$-$Rh(CH$_2$)$_6$Rh$-$C(O)OCH$_2$-

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CH_3) in addition to **7**. While it is not possible to distinguish between symmetrically derivatized carbonyl products in the ^1H NMR, we believe that the lack of any intermediates suggests the predominance of compound **7**. In addition, nonconcerted reaction of ethanol with a monocarbonyl complex (•Rh(CH$_2$)$_6$-RhCO•) would form species containing Rh—H units. Since these Rh—H units are readily distinguished by ^1H NMR and are not present at any time during the reaction, we conclude that the most probable pathway involves reaction of two (RhCO)• units from the same dionyl complex. Reaction 6 is envisioned to occur through a four-centered transition state[7,14–16] that produces concerted formation of the rhodium ester and formyl units in **7**.

Reaction of H_2 with **1** and CO produces a diformyl complex, H(O)C—Rh(CH$_2$)$_6$Rh—CHO (**8**) (eq 7), as the exclusive rhodium porphyrin species observed by ^1H NMR. Reaction 7 does not proceed through rhodium hydride intermediates because both H—Rh(CH$_2$)$_6$Rh—H (**9**) and H—Rh(CH$_2$)$_6$Rh—CHO (**6**) have been independently shown to not react at a finite rate with any species present in a solution of **1** and CO (**2**, **3**, CO) to produce **8**. The sterically demanding porphyrin ligands prohibit achieving the transition state for hydrogen atom transfer from the Rh—H unit to the (RhCO)• fragment which inhibits formation of metalloformyl species by the pathway that operates in the (OEP)Rh system.[4c] The apparent simultaneous formation of two formyl units in **8** implies that this process occurs in concert with cleavage of the H—H bond through a four-centered transition state.[14]

When solutions of **1** and CO are put in contact with CH_4, no products with either formyl or acyl groups are observed to form. The potential reaction with CH_4 to produce CH$_3$(O)C—Rh(CH$_2$)$_6$-Rh—CHO (**10**) is expected to be thermodynamically less favorable than that for H_2 by ∼6–8 kcal mol^{-1},[17] and this may account for the absence of observable concentrations of **10**; however, this negative result could have its origin in either or both kinetic and thermodynamic factors.

The overall reactions of **1** and CO with C_2H_5OH, H_2, and CH_4 to form **7**, **8**, and **10**, respectively (eqs 6, 7, and 9) are all highly thermodynamically favorable.[17b] In these reactions an intermediate dionyl complex (**2**) forms, and it is the equilibrium of **2** with the products of reactions 6, 7, and 9 that actually determines the equilibrium distribution of rhodium porphyrin complexes in solution (eqs 11–13). Thermochemical estimates

$$2 + C_2H_5OH \rightleftharpoons H(O)C—Rh(CH_2)_6—C(O)OC_2H_5 \quad (11)$$

$$2 + H_2 \rightleftharpoons H(O)C—Rh(CH_2)_6Rh—C(O)H \quad (12)$$

$$2 + CH_4 \rightleftharpoons H(O)C—Rh(CH_2)_6Rh—C(O)CH_3 \quad (13)$$
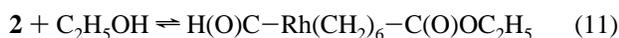
indicate that the ethanol reaction with **2** is highly favorable ($\Delta H^\circ_{11} \approx -21$ kcal mol^{-1} , ΔG°_{11}(298 K) ≈ -13 kcal mol^{-1}), the H_2 reaction is slightly favorable ($\Delta H^\circ_{12} \approx -11$ kcal mol^{-1}, ΔG°_{12}(298 K) ≈ -3 kcal mol^{-1}), and the reaction of CH_4 is

probably unfavorable ($\Delta H^\circ_{13} \approx -5$ kcal mol^{-1}, ΔG°_{13}(298 K) $\approx +3$ kcal mol^{-1}).[17–19] In order to obtain clearly favorable thermodynamics for methane C—H bond reactions like that depicted in reactions 9 and 13, the dionyl (O)C—C(O) bond must be weakened or eliminated.

Any of a set of related pathways where the H and X (X = OH, OR, H) units from H—X add to the carbonyl carbon centers of the dionyl **2** could account for the observed reaction products. The observations are most easily reconciled by pathways that involve four-centered transition states that direct a concerted cleavage of the H—X and formation of Rh—C(O)H and Rh—C(O)X units. Polar substrates (H_2O, CH_3CH_2OH) could involve interaction with a carbonyl carbon of **2** to preorganize formation of the Rh—C(O)OR unit prior to (O)C—C(O) homolysis and hydrogen transfer. However, this form of preorganization is not readily envisioned for the H_2 reaction (eq 12). Reaction of CH_4 may be kinetically inhibited by requiring a more restrictive near linear four-centered transition state which is not demanded by the other substrates. Incorporating more sterically demanding substituents on the tethered diporphyrin complexes such that the dionyl (O)C—C(O) bond is weakened can be expected to reveal whether or not a facile pathway is available for simultaneous activation of CO and methane.

Experimental Section

General Considerations. All manipulations were performed on a high-vacuum line equipped with a Welch Duo-Seal vacuum pump or in an inert atmosphere box unless otherwise noted. All reagents were purchased from Aldrich or Strem Chemicals. Pyrrole was distilled and [Rh(CO)$_2$Cl]$_2$ was sublimed prior to use. Deuterated NMR solvents such as benzene and toluene were degassed by freeze—pump—thaw cycles to remove oxygen and then refluxed over sodium/benzophenone ketyl until the indicator turned purple to remove water. Chloroform, methylene chloride, and 1,2-dichloroethane used in synthetic procedures were purified by washing three times with water followed by chromatography on grade 1 alumina for the removal of ethanol and water. Substrates were degassed by freeze—pump—thaw cycles and stored over molecular sieves. Research grade hydrogen, methane, ethene, 1,3-butadiene and carbon monoxide were purchased from Matheson Gas Products or Aldrich and used without further purification. Carbon-13-labeled carbon monoxide was purchased from Cambridge Isotope Laboratories, Inc. Prepurified nitrogen and argon gases used for the inert atmosphere box were purchased from Airco or MG Industries.

Proton NMR spectra were obtained on a Bruker WP200SY, a Bruker AC-250, or a Bruker AMX-500 interfaced to an Aspect 300 computer at ambient temperature. All spectra were referenced using the residual solvent peak as an internal standard (benzene-d_6, $\delta = 7.155$; toluene-d_8, $\delta = 2.09$). Carbon-13 NMR spectra were obtained on the AMX-500 instrument equipped with a carbon-13 probe. Variable-temperature ^1H NMR spectra were obtained on an IBM-Bruker AF200SY or IBM Bruker WP200SY spectrometer equipped with a Bruker VT-1000 temperature controller or boil-off from liquid nitrogen when the temperature needed is below 220 K. The probe was cooled with an FTS systems refrigerator unit equipped with a temperature controller. The temperatures in the probe were referenced against an external sample of methanol (below ambient) and ethylene glycol (above ambient). The samples were kept away from light prior to and during the experiments. Fast atom bombardment mass spectrometry (FAB-MS) data were recorded on a VG-ZAB-E spectrometer with a cesium

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(17) (a) Thermochemical estimates are obtained by using standard organic bond enthalpies (kcal mol^{-1}),[18] H—H (104), H$_3$C—H (105), (O)C—H (87), (O)C—CH$_3$ (82), (C≡O)—(C=O) (70), RO—H (104), (O)C—OR (97), using (por)Rh—C(O)X (X = H, CH$_3$, OR) (59) and (por)Rh—H (60) and estimating ΔH°_7(37) (**1** + 2CO → **2**) from prior thermodynamic results for ((por)Rh)$_2$(μ-C(O)C(O)) complexes.[19] (b) $\Delta H^\circ_6 \approx -58$ kcal mol^{-1}, ΔG°_6-(298 K) ≈ -34 kcal mol^{-1}, $\Delta H^\circ_7 \approx -48$ kcal mol^{-1}, ΔG°_7(298 K) ≈ -24 kcal mol^{-1}, $\Delta H^\circ_9 \approx -42$ kcal mol^{-1}, ΔG°_9(298 K) ≈ -18 kcal mol^{-1}.[17–19]

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ion gun. Electronic spectra were recorded with a Hewlett-Packard UV 8452 instrument interfaced to an IBM PC. Fourier transform infrared (FT-IR) spectra were taken on an IBM 97 instrument interfaced to an Aspect 2000 computer, or with a Perkin-Elmer 1760 FT-IR spectrometer. Samples were prepared as either KBr pellets or Nujol mulls. Electron paramagnetic resonance spectra were obtained by use of an ER 100 D X-band spectrometer. Temperature measurements were calibrated with a Bruker Model VT unit using N_2 as the cooling source (283−90 K). All EPR experiments were performed at 90 K unless otherwise noted and calibrated using diphenylpicrylhydrazine (DPPH, $\langle g \rangle = 2.0036$) as an external standard.

Rh(CH₂)₆Rh(μ-C(O)C(O)) (2). The dirhodium α-diketone complex Rh(CH₂)₆Rh(μ-C(O)C(O)) (2) was formed from the reaction of carbon monoxide with the rhodium(II) porphyrin bimetalloradical complex •Rh(CH₂)₆Rh• (1): ¹H NMR (C₆D₆) δ 8.85, 8.65, 8.62, 8.39, 8.36, 8.26, 8.22, 8.19 (each a doublet of 2H, $^3J_{H-H}$ = 4.7 Hz, pyrrole); 7.76, 7.38 (dd, 2H each, $^3J_{H-H}$ = 8.2 Hz, $^4J_{H-H}$ = 2.2 Hz, *o*-phenyl); 7.17 (dd, 2H, $^3J_{H-H}$ = 8.2 Hz, $^4J_{H-H}$ = 2.6 Hz, *m*-phenyl), 7.05 (dd, 2H, $^3J_{H-H}$ = 8.4 Hz, $^4J_{H-H}$ = 2.6 Hz, *m*-phenyl), 7.32, 7.24, 7.12, 7.04, 6.98, 6.87 (s, 2H each, *m*-phenyl); 3.99 (m, 2H, $^3J_{H-H}$ = 5.0 Hz, −OCH_aH_b−), 3.94 (m, 2H, $^3J_{H-H}$ = 5.0 Hz, −OCH$_aH_b$); 2.46, 2.41, 2.40 (s, 6H each, *p*-CH₃); 1.62, 1.49, 1.48, 1.35, 1.27, 1.16 (s, 6H each, *o*-CH₃); 1.78 (m, 4H, −OCH₂CH_2−), 1.54 (m, 4H, −CCH₂CH₂C−); ¹³C NMR (CD₃C₆D₅) δ 164.47 (AA′XX′ m, 2¹³C, Rh(CH₂)₆Rh(μ-¹³C(O)−¹³C(O)), six transitions observed at ±12, ±18, and ±27 Hz relative to the center of δ 164.47 ppm); IR (Nujol mull) $\nu_{CO} \approx$ 1780, 1769 cm⁻¹; $\nu^{13}_{CO} \approx$ 1736, 1725 cm⁻¹.

Rh(CH₂)₆Rh(μ-CH₂CH₂) (4). The dirhodium ethylene-bridged complex Rh(CH₂)₆Rh(μ-CH₂CH₂) (4) was formed from the reaction of ethene with the rhodium(II) porphyrin bimetalloradical complex •Rh(CH₂)₆Rh• (1): ¹H NMR (C₆D₆) δ 8.77, 8.52, 8.43, 8.36, 8.35, 8.20, 8.12, 8.06 (each a doublet of 2H, $^3J_{H-H}$ = 4.7 Hz, pyrrole); 7.89, 7.69 (dd, 2H each, $^3J_{H-H}$ = 8.3 Hz, $^4J_{H-H}$ = 2.2 Hz, *o*-phenyl); 7.47, 7.06 (dd, 2H each, $^3J_{H-H}$ = 8.3 Hz, $^4J_{H-H}$ = 2.6 Hz, *m*-phenyl), 7.25, 7.19, 7.12, 6.97, 6.94, 6.88 (s, 2H each, *m*-phenyl); 3.96 (m, 2H, $^3J_{H-H}$ = 5.0 Hz, −OCH_aH_b−), 3.91 (m, 2H, $^3J_{H-H}$ = 5.0 Hz, −OCH$_aH_b$); 2.44, 2.42, 2.41 (s, 6H each, *p*-CH₃); 2.39, 1.78, 1.54, 1.40, 1.20, 1.10 (s, 6H each, *o*-CH₃); 1.78 (m, 4H, −OCH₂CH_2−), 1.49 (m, 4H, −CCH₂CH₂C−); −7.81 (dm, 2H, $^1J_{13C-H}$ = 144 Hz, Rh(CH₂)₆Rh(μ-¹³CH_aH$_b$−¹³CH_aH$_b$)), −8.24 (dm, 2H, $^1J_{13C-H}$ = 144 Hz, Rh(CH₂)₆Rh(μ-¹³CH$_a$H$_b$−¹³CH$_a$H$_b$)); ¹³C NMR (C₆D₆) δ 19.34 (AA′XX′ m, 2 ¹³C, $^1J_{103Rh-13C}$ = 30.2 Hz, $^2J_{103Rh-13C}$ = −3.2 Hz, $^1J_{13C-13C}$ = 32.4 Hz, $^3J_{103Rh-103Rh} \approx$ 0.2 Hz, Rh(CH₂)₆Rh(μ-¹³CH₂−¹³CH₂)).

Rh(CH₂)₆Rh(μ-CH₂CH=CHCH₂) (5). The dirhodium four-carbon-bridged complex Rh(CH₂)₆Rh(μ-CH₂CH=CHCH₂) (5) was formed from the reaction of 1,3-butadiene with the rhodium(II) porphyrin bimetalloradical complex •Rh(CH₂)₆Rh• (1): ¹H NMR (C₆D₆) δ 8.35, 8.27 (each a doublet of 4H, $^3J_{H-H}$ = 4.8 Hz, pyrrole), 8.32 (s, 8H, pyrrole); 7.71, 7.39 (dd, 2H each, $^3J_{H-H}$ = 8.3 Hz, $^4J_{H-H}$ = 2.2 Hz, *o*-phenyl); 7.17, 7.01 (dd, 2H each, $^3J_{H-H}$ = 8.3 Hz, $^4J_{H-H}$ = 2.6 Hz, *m*-phenyl), 7.26, 7.12 (s, 4H each, *m*-phenyl), 7.02, 7.00 (s, 2H each, *m*-phenyl); 4.00 (t, 4H, $^3J_{H-H}$ = 5.5 Hz, −OCH₂−), 2.55 (s, 12H, p-CH₃), 2.39 (s, 6H, *p*-CH₃); 1.94, 1.50 (s, 12H, *o*-CH₃), 1.61, 1.57 (s, 6H, *o*-CH₃); 1.91 (m, 4H, −OCH₂CH_2−), 1.70 (m, 4H, −CCH₂CH₂C−) −2.24 (t, 2H, Rh(CH₂)₆Rh(μ-CH₂CH=CHCH₂)), −5.32 (dd, 4H, Rh(CH₂)₆Rh(μ-CH_2CH=CHCH_2)).

H−Rh(CH₂)₆Rh−CHO (6). The rhodium(III) diformyl complex H−Rh(CH₂)₆Rh−CHO (6) was formed from the reaction of water with the dirhodium α-diketone complex Rh(CH₂)₆Rh(μ-C(O)C(O)) (2): ¹H NMR (C₆D₆) δ 9.03, 8.97, 8.88, 8.86, 8.85, 8.84, 8.82, 8.81 (each a doublet of 2H, $^3J_{H-H}$ = 4.9 Hz, pyrrole); 8.16, 8.14, 8.02, 8.00 (dd, 1H each, $^3J_{H-H}$ = 8.3 Hz, $^4J_{H-H}$ = 2.2 Hz, *o*-phenyl); 7.31, 7.29, 7.13, 7.10 (dd, 1H each, $^3J_{H-H}$ = 8.3 Hz, $^4J_{H-H}$ = 2.6 Hz, *m*-phenyl), 7.24, 7.07 (s, 4H each, *m*-phenyl), 7.18, 7.11 (s, 2H each, *m*-phenyl); 3.92 (t, 2H, $^3J_{H-H}$ = 6.1 Hz, −OCH₂−), 3.90 (t, 2H, $^3J_{H-H}$ = 6.1 Hz, −OCH₂−); 2.45 (s, 12H, *p*-CH₃), 2.43 (s, 6H, *p*-CH₃); 2.29, 1.76 (s, 12H each, *o*-CH₃), 2.16, 1.79(s, 6H each, *o*-CH₃); 1.86 (m, 4H, −OCH₂CH_2−), 1.58 (m, 4H, −CCH₂CH₂C−); 3.66 (d, 1H, $^2J_{103Rh-CHO}$ = 1.3 Hz, Rh−CHO), −40.07 (d, 1H, $^1J_{103Rh-H}$ = 44.5 Hz, Rh−H); ¹³C NMR (CD₃C₆D₅) δ 193.7 (dd, 1¹³C, $^1J_{103Rh-13C}$ = 30.2 Hz, $^1J_{H-13C}$ = 197.5 Hz, Rh−¹³CHO).

H(O)C−Rh(CH₂)₆Rh−C(O)OCH₂CH₃ (7). The rhodium(III) diformyl complex H(O)C−Rh(CH₂)₆Rh−C(O)OCH₂CH₃ (7) was formed from the reaction of ethanol with the dirhodium α-diketone complex Rh(CH₂)₆Rh(μ-C(O)C(O)) (2): ¹H NMR (C₆D₆) δ 9.02, 8.95, 8.89, 8.86, 8.83, 8.81, 8.80, 8.79 (each a doublet of 2H, $^3J_{H-H}$ = 4.9 Hz, pyrrole); 8.18, 8.14, 8.01, 7.89 (dd, 1H each, $^3J_{H-H}$ = 8.3 Hz, $^4J_{H-H}$ = 2.2 Hz, *o*-phenyl); 7.26, 7.22, 7.10, 7.08 (dd, 1H each, $^3J_{H-H}$ = 8.3 Hz, $^4J_{H-H}$ = 2.6 Hz, *m*-phenyl), 7.20, 7.10 (s, 4H each, *m*-phenyl), 7.18, 7.14 (s, 2H each, *m*-phenyl); 3.92 (t, 2H, $^3J_{H-H}$ = 6.1 Hz, −OCH₂−), 3.90(t, 2H, $^3J_{H-H}$ = 6.1 Hz, −OCH₂−); 2.45 (s, 12H, *p*-CH₃), 2.39 (s, 6H, *p*-CH₃); 2.26 (s, 12H, *o*-CH₃), 1.93, 1.87, 1.77, 1.42 (s, 6H each, *o*-CH₃); 1.87 (m, 4H, −OCH₂CH_2−), 1.57 (m, 4H, −CCH₂CH₂C−), 3.66 (dd, 1H, $^1J_{13C-H}$ = 197.6 Hz, $^2J_{103Rh-CHO}$ = 1.6 Hz, Rh−¹³CHO), 1.38 (qd, 2H, $^3J_{13C-H}$ = 4.4 Hz, $^3J_{H-H}$ = 6.8 Hz, Rh−¹³C(O)OCH₂CH₃), −1.04 (t, 3H, $^3J_{H-H}$ = 6.8 Hz, Rh−¹³C(O)-OCH₂CH_3); ¹³C NMR (C₆D₆) δ 148.29 (dt, 1¹³C, $^1J_{103Rh-13C}$ = 46.5 Hz, $^3J_{H-13C}$ = 4.4 Hz, Rh−¹³C(O)OCH₂CH₃), 194.51 (dd, 1¹³C, $^1J_{103Rh-13C}$ = 30.2 Hz, $^1J_{H-13C}$ = 197.5 Hz, Rh−¹³CHO).

H(O)C-Rh(CH₂)₆Rh-CHO (8). The rhodium(III) diformyl complex H(O)C−Rh(CH₂)₆Rh−CHO (8) was formed from the reaction of hydrogen with the dirhodium α-diketone complex Rh(CH₂)₆Rh(μ-C(O)C(O)) (2): ¹H NMR (C₆D₆) δ 9.02, 8.87, 8.86, 8.85 (each a doublet of 2H, $^3J_{H-H}$ = 4.9 Hz, pyrrole); 8.16, 7.94 (dd, 1H each, $^3J_{H-H}$ = 8.4 Hz, $^4J_{H-H}$ = 2.1 Hz, *o*-phenyl); 7.30, 7.12 (dd, 1H each, $^3J_{H-H}$ = 8.4 Hz, $^4J_{H-H}$ = 2.6 Hz, *m*-phenyl), 7.24 (s, 4H, *m*-phenyl), 7.20 (s, 2H, *m*-phenyl), 7.12 (s, 6H, *m*-phenyl); 3.91 (t, 4H, $^3J_{H-H}$ = 6.1 Hz, −OCH₂−); 2.45 (s, 12H, *p*-CH₃), 2.43 (s, 6H, *p*-CH₃); 2.28, 1.76 (s, 12H each, *o*-CH₃), 2.05, 1.87 (s, 6H each, *o*-CH₃); 1.85 (m, 4H, −OCH₂CH_2−), 1.58 (m, 4H, −CCH₂CH₂C−); 3.66 (d, 1H, $^2J_{103Rh-CHO}$ = 1.3 Hz, Rh−CHO), −40.07 (d, 1H, $^1J_{103Rh-H}$ = 44.5 Hz, Rh−H); ¹³C NMR (CD₃C₆D₅) δ 193.65 (dd, 1¹³C, $^1J_{103Rh-13C}$ = 30.2 Hz, $^1J_{H-13C}$ = 197.5 Hz, Rh−¹³CHO).