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Generation of an (Alkoxycarbonyl)rhodium Complex in an Alcohol Analog of the Water-Gas Shift Reaction

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(Octaethylporphyrinato)rhodium(II) dimer ($(OEPRh)_2$, 1) reacts with CO and ethanol in CH_2Cl_2 to give (octaethylporphyrinato)rhodium(III) chloride (5), (ethoxycarbonyl)(octaethylporphyrinato)rhodium(III) (OEPRh(CO)OEt, 6), and formyl(octaethylporphyrinato)rhodium(III) (2). The structure of 6 was clarified by X-ray diffraction analysis. Complex 6 crystallized in the monoclinic space group $P2_1/n$ (No. 14) with $a = 14.581$ (1) Å, $b = 14.181$ (2) Å, $c = 17.4530$ (9) Å, $V = 3608.8$ (9) Å^3, $Z = 4$, $R = 0.046$, $R_w = 0.051$, and $T = 293$ K for 415 parameters and 4864 reflections. The ^1H and ^{13}C spectral properties of 2 and 6 in CD_2Cl_2 were determined and the behaviors of 1, 2, (octaethylporphyrinato)rhodium(III) hydride (3), and 6 in CH_2Cl_2 solvent were examined. Photolysis of 2 in CH_2Cl_2 at 300 nm afforded (octaethylporphyrinato)rhodium(III) chloride. Treatment of OEPCoNa with acetic anhydride in ethylene glycol dimethyl ether afforded acetyl(octaethylporphyrinato)cobalt(III) and an analogous experiment with acetic formic anhydride generated an acyl(octaethylporphyrinato)cobalt(III) complex.

In 1982, Wayland and co-workers[1] reported the fascinating reaction of (octaethylporphyrinato)rhodium(II) dimer ($(OEPRh)_2$, (1) with H_2O and CO to afford the formylrhodium compound formyl(octaethylporphyrinato)rhodium(III) (OEPRhCHO, 2). It was postulated that 2 was generated via reaction of CO with (octaethylporphyrinato)rhodium(III) hydride (OEPRhH, 3) formed in a water-gas shift reaction[2] by decarboxylation of the transient 4, eqs 1 and 2.

$$\underset{1}{(OEPRh)_2} + CO + H_2O \rightarrow \underset{4}{OEPRhCO_2H} + \underset{3}{OEPRhH} \quad (1)$$

$$OEPRhCO_2H \rightleftarrows (OEP)RhH + CO_2 \quad (2)$$

In our continuing study of the role of acyl transition-metal intermediates in catalysis,[3,4] we have conducted a number of experiments involving $(OEPRh)_2$, CO, and various substrates in dichloromethane and have been struck by the facility with which 2 is formed from traces of H_2O in this solvent. The phenomenon is mechanistically interesting because evidence in confirmation of the intervention of the transient 4 has not appeared. Since the apparent reactive nature of 4 contributes to the problem of its characterization, it seemed reasonable to investigate the behavior of a protic nucleophile other than H_2O in an attempt to generate an analog of 4 which would be kinetically stable. We wish to report the results of our study of the reaction of ethanol with 1 and CO in CH_2Cl_2 solvent and attempts to extend the study to the OEPCo system. We chose CH_2Cl_2 as a solvent for a number of reasons: (1) High molecular weight (octaethylporphyrinato)rhodium and -cobalt compounds are very soluble in this medium. (2) Aromatic solvents crystallize with these compounds, complicating interpretations of elemental analyses and affecting crystal structures. (3) This low boiling solvent is easily transferred in vacuo. (4) We wished to investigate the chemical behavior of 1 and hydrido- and acylmetal complexes in a chlorinated solvent.

Results and Discussion

Most of our experiments were conducted in dichloromethane solvent and solutions of 1, 2, and 3 in this medium had not previously been studied. We therefore examined the behavior of the compounds using ^1H and ^{13}C NMR as a probe.

Spectroscopic Characterization of 1 and 3 in Dichloromethane. The hydridorhodium complex 3[5] was synthesized by a slight modification of a literature procedure.[6] The ^1H NMR spectrum (CD_2Cl_2) exhibited a characteristic doublet at −41.61 ppm, $J_{Rh-H} = 44$ Hz, 10.05 (s) (4 H, methine), 4.04 (q) (16 H), 1.91 (t) (24 H). Compound 3 could be converted thermally to the dimer 1 in CD_2Cl_2 if small amounts of 1 were present in the initial reaction mixture. The product exhibited the characteristic[5] pair of methylene multiplets at 4.34 and 3.99 ppm, a methyl triplet at 1.60 ppm, and the methine singlet at 9.13 ppm. The identity could be confirmed by comparison of the C_6D_6 solution ^1H spectrum of the sample with that reported in the literature.[5]

Behavior of 1 and 3 in CD_2Cl_2. Solutions of 3 in CD_2Cl_2 exhibit an unusual stability in the absence of 1. The interconversion of 1 and 3 in benzene is well documented.[1,6,7] We have generated CD_2Cl_2 solutions of 3, via both

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photolysis and thermolysis, which contain no 1 detectable by ^{1}H NMR. These solutions have consistently contained (octaethylporphyrinato)rhodium(III) chloride (OEPRhCl, 5) as a product rhodium species. For example, a CD_2Cl_2 solution of 3 and 1 with a 5:1 δ 10.04:9.13 methine resonance ratio (10:1 mol ratio) in a sealed NMR tube when allowed to sit in the dark at room temperature for 27 h afforded a solution exhibiting a <2:1 δ 10.04:9.13 peak intensity ratio indicative of conversion of 3 to 1. On exposure of this sample for 29 min to the 532-nm laser line at 3.2 mJ/pulse, 1 was quantitatively and selectively converted to 5 as evidenced by the appearance of the methine resonance at δ 10.35 ppm. The resulting mixture of 3 and 5 was relatively stable, 3 converting slowly at room temperature to 5 to afford a 2:1 ratio of 5:3 after 1 month. No 1 was detected in the mixture during this period.

Exposure of a mixture of 3 and 1 in CD_2Cl_2 to the 416-nm laser line at 4.1 to 4.3 mJ/pulse for 27 min afforded a quantitative conversion of both reactants to 5.

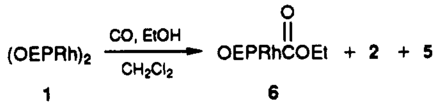
The above phenomena were not observed when conventional light sources were employed. For instance, irradiation of a CD_2Cl_2 solution of 1 with a medium pressure mercury-arc lamp with a chemical filter providing maximum transmittance at 542 nm afforded no 5 during 9 h. The aqueous filter solution was composed of $CuCl_2$, $CaCl_2$, and $Nd(NO_3)_3$ and the amount of light transmittance was detected by Ferrioxalate actinometry. The conversion of 1 to 5 was accomplished, however, when the filter was removed.

Characterization of OEPRhCHO (2) in CD_2Cl_2. Treatment of CD_2Cl_2 solutions of 1 with CO and H_2O in a sealed tube afforded a product with the following ^{1}H resonances: δ 10.15 (s) (methine), 4.05 (m) (methylene), 1.92 (t) (CH_3), and 2.59 (CHO). Employment of ^{13}CO as reactant gave a product with the following spectral properties: ^{13}C NMR δ 198.9 ppm (q) $J_{^{13}C-^{1}H} = 199$ Hz; $J_{^{13}C-^{103}Rh} = 30.5$ Hz. The ^{1}H resonance centered at δ 2.59 was split due to $^{13}C-^{1}H$ coupling in the enriched material. These data demonstrate unambiguously that the carbonyl carbon is bound to rhodium and bears one hydrogen atom. The disappearance of 1 was accompanied by the generation of 2, 3, and 5, the molar ratio of 1:2:3:5 in the mixture 3 days after CO introduction being 1.0:4.4:2.7:0.9 as determined from methine singlet peak intensities. Examination of the product mixture after 19 days showed the absence of 1 and a 2:3:5 mol ratio of 11.4:1.0:1.4. A resonance at 125.2 ppm confirmed the presence of $^{13}CO_2$.

On irradiation at 300 nm in a Rayonet reactor, 2 was converted to 5 as evidenced by the disappearance of the δ 10.15 methine singlet and the appearance of the peaks characteristic of 5 including δ 10.36.

Reaction of $(OEPRh)_2$ (1) with CO and Ethanol. Treatment of 1 with CO and ethanol in CD_2Cl_2 afforded during 6 h a mixture of OEPRhCHO (2), 5, and a new compound, 6, possessing the following spectral features: $\nu_{C=O}$ 1675 cm^{-1} (CH_2Cl_2), 1682 cm^{-1} (Nujol); ^{1}H NMR, 10.19 (s) 4 H, 4.11 (q) 16 H, 2.93 (t) 24 H, 0.89 (q) 2 H, −1.10 (t) 3 H. The infrared data along with the relative chemical shifts and multiplicities of the latter two resonances[8,9] are indicative of a carbethoxy group above the rhodium–porphyrin plane. The methine resonance chemical shift was somewhat concentration dependent. The ^{13}C NMR spectrum of 6 generated from ^{13}CO and ethanol exhibited in addition to resonances near 140 and 160 ppm due to natural abundance porphyrin ring carbons a doublet at 151.4 ppm, $J_{^{103}Rh-^{13}C} = 46$ Hz. We assign this unexpectedly high field resonance to a carbonyl carbon. It could be distinguished from that of a porphyrin ring carbon through the observation that other rhodium OEP complexes such as 2 and 5 do not absorb in the 150-ppm region. The close correspondence of the formyl ^{13}C chemical shift in 2 with values near 200 ppm reported for aldehydes[10] make the analogous ester carbonyl comparison of ca. 170 ppm[10] vs our 151.4 ppm value quite puzzling.

Scheme I



$$\underset{1}{(OEPRh)_2} \xrightarrow[CH_2Cl_2]{CO,\ EtOH} \underset{6}{OEPRh\overset{O}{\overset{\|}{C}}OEt} + 2 + 5$$

Although the OEP ligand proton chemical shifts were almost identical in CD_2Cl_2, the molar ratio of 2:6 in the product mixtures could be determined by integration of the 2.59-ppm formyl proton resonance in 2 and the −1.10 ppm methyl triplet in 6. Pure 6 could be isolated by exploiting the photochemistry of 2. The product mixture could be irradiated at 300 nm, affording a mixture composed primarily of 5 and 6, both of which were found to be relatively stable in air. The compounds were separated by flash chromatography on silica gel.

The generation of 2 could conceivably derive from traces of H_2O in the system since the NMR experiments were conducted on a very small molar scale and the 125.2-ppm resonance of $^{13}CO_2$ was present in monitoring spectra. However, the rate of formation of 2 at 25 °C was *lower* when 1 was actually treated with CO and H_2O than when 1 was treated with CO and EtOH containing only traces of H_2O impurity. This suggests that the generation of some of the 2 is associated with that of 6, Scheme I.

Removal of CO from the CD_2Cl_2 product solution of 2 and 6 caused the disappearance of 2 with the coincident appearance of 3, the resulting mixture of 3 and 6 being stable for days. Reintroduction of CO caused regeneration of 2 at the expense of 3. No 1 was detected during this series of operations.

In view of our method of preparation of 1 from 3 in dichloromethane containing ethanol, the observed stability of 3 in the absence of 1 is quite remarkable. These results and those from the laser photolysis experiments suggest that 1 promotes the conversion of 3 into 1. Under conditions in dichloromethane where traces of 1 are removed, 3 is stable for days. The absence of any trace of 1 in some of these product solutions may be due to abstraction of a chlorine atom from the solvent by the OEPRh$^\bullet$ radical derived from 1 or 2[11] to generate 5, thus affecting the equilibria among rhodium species.[6,7]

Crystal Structure of 6. The seemingly anomalous carbonyl ^{13}C chemical shift assignment and the consequent question of whether the carbethoxy carbonyl carbon is

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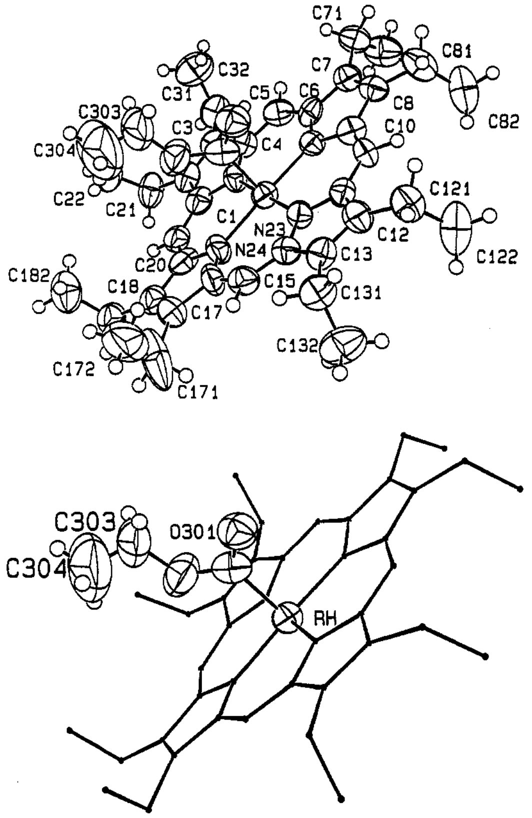

Figure 1. ORTEP view of OEPRh(CO)OEt (**6**). Ellipsoids are drawn at the 50% probability level.

Table I. Crystal Data and Data Collection Parameters

formula	$RhO_2N_4C_{39}H_{49}$
formula weight	708.76
space group	$P2_1/n$ (No. 14)
a, Å	14.581 (1)
b, Å	14.181 (2)
c, Å	17.4530 (9)
β, deg	90.072 (5)
V, Å^3	3608.8 (9)
Z	4
D_{calc}, g cm^{-3}	1.304
cryst dimensns, mm	0.25 × 0.15 × 0.10
temp, K	293.0
radtn (wavelength)	Cu Kα (1.54184 Å)
monochromator	none
linear abs coeff, cm^{-1}	41.82
absorptn corrctn applied	empirical[a]
transmission factors: min, max	0.61, 1.00
diffractometer	Enraf-Nonius CAD4
scan method	ω–2θ
h, k, l limits	−15 to 15, 0 to 15, 0 to 18
2θ range, deg	4.00–112.00
scan width, deg	0.89 + 0.15 tan θ
take-off angle, deg	6.00
programs used	Enraf-Nonius MolEN
$F(000)$	1488.0
p-factor used in weighting	0.040
data collected	4864
unique data	4864
data with $I > 3.0\sigma(I)$	2360
no. of variables	415
largest shift/esd in final cycle	0.20
R	0.046
R_w	0.051
goodness of fit	1.234

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bonded directly to the rhodium atom[12] induced us to determine the molecular structure of **6**. An ORTEP drawing and a representation highlighting the atoms of the carbethoxy group relative to the rhodium–porphyrin plane are shown in Figure 1. Tables I–III present details of data collection, positional parameters, and selected bond distances and angles. The results confirm that the ethoxycarbonyl carbon is bonded directly to rhodium as a monohapto ligand. The remarkably short[12c] Rh–C bond distance of 1.92 Å may be compared to the 1.90 Å value reported for the formyl analog.[1] The C–O bond distance of 1.16 Å is substantially shorter than the 1.22–1.23 Å average carbonyl distances in organic esters[2] but similar to the 1.175 value for **2**.[1] The structure features four equivalent molecules per unit cell with an absence of solvent. Four contiguous OEP ethyl groups project anti to the alkoxycarbonyl ligand while four are syn. The Rh atom projects slightly above the porphyrin plane in the direction of the carbethoxy ligand as evident by the 177° N–Rh–N bond angle.

Descriptions of alkoxycarbonyl[13] rhodium porphyrin compounds have been reported in the literature.[14] Structure assignments were based solely on ^{1}H NMR and infrared data and it was not demonstrated that the carbalkoxy carbonyl was bonded to the metal. The only other example of which we are aware is an incidental reference to a coupling constant.[15] We believe, therefore, that our results provide the first report of the complete characterization in terms of composition and structure of this class of rhodium compound.

Behavior of Cobalt Analogs. We have found that OEPCo[16] (**7**) is unreactive toward CO/H_2O and CO/EtOH under conditions in which $(OEPRh)_2$ (**1**) is readily converted to acylrhodium products. A literature search revealed that the cobalt analogs of **2**, **3**, and **6** have not been characterized. We have investigated a potential alternate synthesis of the cobalt analog of **2** to determine if it is capable of existence and detection under our reaction conditions. Precedent exists for the preparation of acylcobalt compounds[17] and a formyliron complex[4,18] via reactions of transition-metal anions with acyl transfer agents. We have attempted to use this independent route for the preparation of OEPCoCHO.

Treatment of $OEPCo^-Na^+$ in ethylene glycol dimethyl ether with acetic anhydride afforded an isolated 68% yield of the acetylcobalt complex $OEPCo(CO)CH_3$ (**8**): IR ν_{CO} 1734 cm^{-1} (KBr); ^{1}H NMR (C_6D_6) 10.24 (s) 4 H, 3.91 (m) 16 H, 1.83 (t) 24 H, −2.60 (s) 3 H. The bright red crystalline product was moderately light and heat sensitive and was isolated by chromatography in the dark on a cold water-cooled column.

The $OEPCo^-Na^+$ reacted with acetic formic anhydride under a CO atmosphere to afford a marginally stable red solid product which was isolated by removal of the reaction

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Table II. Positional Parameters for 6[a]

atom	*x*	*y*	*z*	*B* (Å^2)
Rh	0.08760(5)	0.02160(5)	0.38827(4)	4.29(1)
O(301)	0.1176(4)	0.0198(5)	0.2307(3)	6.3(2)
O(302)	–0.0249(4)	–0.0019(6)	0.2640(3)	8.5(2)
N(21)	0.0138(4)	–0.0967(5)	0.4081(4)	4.3(2)
N(22)	0.2021(4)	–0.0594(5)	0.3775(3)	4.2(2)
N(23)	0.1633(4)	0.1404(4)	0.3737(4)	4.0(2)
N(24)	–0.0250(4)	0.1009(5)	0.4045(4)	4.7(2)
C(1)	–0.0778(6)	–0.0922(6)	0.4241(4)	4.8(2)
C(2)	–0.1075(6)	–0.1988(6)	0.4282(5)	5.1(2)
C(3)	–0.0333(6)	–0.2502(6)	0.4135(5)	5.4(2)
C(4)	0.0443(6)	–0.1879(6)	0.4023(5)	4.8(2)
C(5)	0.1328(6)	–0.2145(6)	0.3850(5)	5.1(2)
C(6)	0.2063(6)	–0.1550(6)	0.3750(4)	4.3(2)
C(7)	0.2995(6)	–0.1845(6)	0.3580(5)	4.8(2)
C(8)	0.3507(6)	–0.1061(6)	0.3533(5)	4.8(2)
C(9)	0.2899(5)	–0.0277(6)	0.3646(4)	4.5(2)
C(10)	0.3134(5)	0.0651(6)	0.3579(5)	4.5(2)
C(11)	0.2563(6)	0.1431(6)	0.3622(5)	4.5(2)
C(12)	0.2837(6)	0.2413(7)	0.3501(5)	5.2(2)
C(13)	0.2068(6)	0.2952(6)	0.3523(5)	4.6(2)
C(14)	0.1330(6)	0.2301(6)	0.3684(4)	4.3(2)
C(15)	0.0419(6)	0.2542(6)	0.3756(5)	5.1(2)
C(16)	–0.0316(5)	0.1946(7)	0.3936(5)	5.3(2)
C(17)	–0.1248(6)	0.2245(7)	0.4041(5)	5.7(3)
C(18)	–0.1765(6)	0.1488(7)	0.4201(5)	5.3(2)
C(19)	–0.1109(6)	0.0723(7)	0.4205(5)	5.2(2)
C(20)	–0.1342(5)	–0.0219(7)	0.4326(4)	5.3(2)
C(21)	–0.2043(6)	–0.2278(7)	0.4419(6)	6.8(3)
C(22)	–0.2601(7)	–0.2279(9)	0.3697(7)	9.6(4)
C(31)	–0.0272(7)	0.3576(7)	0.4109(6)	7.0(3)
C(32)	–0.0258(9)	–0.3961(8)	0.3312(7)	9.3(4)
C(71)	0.3298(6)	–0.2856(6)	0.3493(5)	5.7(2)
C(72)	0.3615(8)	–0.3319(7)	0.4215(6)	8.0(3)
C(81)	0.4520(6)	–0.0986(7)	0.3412(6)	6.5(3)
C(82)	0.5050(7)	–0.088(1)	0.4138(7)	9.9(4)
C(121)	0.3804(6)	0.2737(7)	0.3392(5)	5.8(3)
C(122)	0.4330(7)	0.2801(9)	0.4131(7)	9.2(4)
C(131)	0.1980(6)	0.3998(6)	0.3421(5)	5.9(3)
C(132)	0.2002(8)	0.4536(7)	0.4143(6)	8.6(4)
C(171)	–0.1555(7)	0.332(1)	0.4034(6)	12.3(4)
C(172)	–0.1680(9)	0.3539(9)	0.332(1)	13.8(5)
C(181)	–0.2776(6)	0.1388(8)	0.4310(5)	6.7(3)
C(182)	–0.3273(7)	0.1167(9)	0.3587(7)	8.8(4)
C(301)	0.0645(6)	0.0142(6)	0.2802(5)	5.2(2)
C(303)	–0.0532(8)	–0.003(1)	0.1867(7)	12.2(5)
C(304)	–0.123(1)	0.035(2)	0.174(1)	29(1)

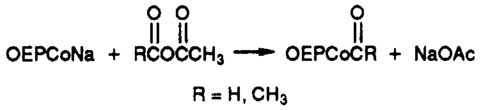
[a] Anisotropically refined atoms are given in the form of the isotropic equivalent temperature factor defined as $(^4/_3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table III. Selected Bond Distances (Å) and Angles (deg) for 6[a]

Rh–N(21)	2.023(8)	O(301)–C(301)	1.163(9)
Rh–N(22)	2.035(7)	O(302)–C(301)	1.35(1)
Rh–N(23)	2.030(8)	O(302)–C(303)	1.41(1)
Rh–N(24)	2.010(8)	C(303)–C(304)	1.18(2)
Rh–C(301)	1.918(9)		
N(21)–Rh–N(22)	89.1(3)	N(23)–Rh–C(301)	91.0(4)
N(21)–Rh–N(23)	177.3(3)	N(24)–Rh–C(301)	91.6(4)
N(21)–Rh–N(24)	90.3(4)	C(301)–O(302)–C(303)	118.9(9)
N(21)–Rh–C(301)	91.7(4)	Rh–C(301)–O(301)	127.6(9)
N(22)–Rh–N(23)	90.6(3)	Rh–C(301)–O(302)	112.5(7)
N(22)–Rh–N(24)	117.2(3)	O(301)–C(301)–O(302)	119.9(9)
N(22)–Rh–C(301)	91.2(4)	O(302)–C(303)–C(304)	115(2)
N(23)–Rh–N(24)	89.9(4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

solvent in vacuo followed by trituration with C_6D_6: IR ν_{CO} 1738 cm^{-1} (C_6D_6); ^{1}H NMR (C_6D_6) 10.16 (s) 4 H, 3.85 (m) 16 H, 1.81 (t) 24 H. Solutions of the product in C_6D_6 decomposed with the evolution of gas to generate OEPCo. The sensitive nature of the compound precluded is further characterization. Although we have not unambiguously established the identity of the product, several factors suggest that the material is a formyl cobalt complex, eq 3: (1) its mode of preparation which has been demonstrated to produce acyl transition-metal complexes; (2) the ^{1}H NMR spectrum which demonstrates the formation of a cobalt(III) octaethylporphyrin complex and the absence of 8. [It is reasonable to suggest that the formyl proton resonance (present at δ 2.90 ppm in the rhodium analog) is masked by the δ 3.85 ethyl CH_2 proton multiplet. Compare the −2.60 CH_3 resonance in 8 with the −3.18 resonance in the acetylrhodium analog.[19] One expects a larger difference for the formyl proton which is one bond closer to the metal atom.[8,9]]; (3) the infrared absorption at 1738 cm^{-1}.



$$\mathrm{OEPCoNa} + \mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3} \longrightarrow \mathrm{OEPCo}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R} + \mathrm{NaOAc} \quad (3)$$

$$\mathrm{R = H, CH_3}$$

Conclusions

We have demonstrated the generation of an (alkoxycarbonyl)rhodium complex under reaction conditions which are consistent with the operation of the alcohol analog of the water-gas shift (WGS) reaction. The results support the proposed[1] intervention of 4 in a WGS route to 2. Hydrido- and acylrhodium OEP complexes show very little thermal reactivity toward CH_2Cl_2 solvent at 25 °C but may react via chlorine atom abstracton by the intermediate OEPRh$^\bullet$ on photolysis. Evidence is presented for the synthesis of a labile formylcobalt complex.

Experimental Section

General Comments. All manipulations were performed under prepurified nitrogen using Schlenk/vacuum line techniques unless otherwise indicated. Solvents were distilled and dried prior to use and were deoxygenated by three evacuation/nitrogen purge cycles. Sample tubes for NMR experiments were prepared using an Ace Glass tip-off manifold in conjunction with a flame seal or by use of a J. Young Valve resealable tube. ^{1}H and ^{13}C NMR spectra were recorded on a Chemagnetics A-200 spectrometer. ^{1}H chemical shifts are in ppm relative to tetramethylsilane as measured from the 5.32-ppm resonance of residual proton in the CD_2Cl_2 solvent. The peak intensity of this signal was used as an internal reference to monitor material balance in the reaction mixtures. ^{13}C chemical shifts were measured from the natural abundance CD_2Cl_2 ^{13}C δ 53.8 resonance. Either a Perkin-Elmer Model 457 or a 1320 instrument was used to record infrared spectra, and electronic spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer. The laser photolysis experiments employed a Nd:YAG infrared pulsed laser with a natural lasing wavelength of 1064 nm, operated at 10 pulses/s at a power of 3–5 mJ/pulse.

Microanalyses were performed by the Purdue University Department of Chemistry Microanalytical Laboratory and by Galbraith Laboratories, Inc., Knoxville, TN.

Materials. Silica gel for flash chromatography was either Merck 60 Å or J.T. Baker 40 Å material. Dichloromethane, hexane, tetrahydrofuran, and ethylene glycol dimethyl either were Aldrich Sureseal products. THF was distilled from sodium–benzophenone and CH_2Cl_2 was distilled and then passed through a column of basic alumina prior to use. $[Rh(CO)_2Cl]_2$, 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine (OEPH$_2$), and OEPCo were supplied by Aldrich. C_6D_6 and CD_2Cl_2 were

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(19) Wayland, B. B.; Balkus, K. J., Jr.; Farnos, M. D. *Organometallics* 1989, *8*, 950.

purchased in glass ampules from Aldrich and were stored over molecular sieves prior to tube-to-tube distillation in the NMR tube tip-off manifold. Acetic formic anhydride was prepared by a literature method[20] and its purity after distillation under N_2 was confirmed by ^{1}H NMR. Acetic anhydride was distilled prior to use. CO was Matheson purity (99.99% minimum) and ^{13}CO was purchased from Aldrich.

Preparation of OEPRhH (3). The compound[5] was prepared by a modification of the reagent ratio used in Wayland's procedure.[6] From 0.222 g (0.572 mmol) of $[Rh(CO)_2Cl]_2$ and 0.612 g (1.14 mmol) of $OEPH_2$ in 50 mL acetic acid and 20 mL of ethanol containing 0.100 g of sodium acetate were afforded 0.433 g of deep red-orange crystals of **3** after filtration under H_2. The material, ν_{Rh-H} (KBr) 2220 cm^{-1}, which exhibited the ^{1}H NMR spectral properties described in the text, was stored under N_2 at 0 °C. Samples prepared in the above fashion were contaminated with small amounts of **1**.

Preparation of OEPRhCl (5). A ca. 5:1 mixture of **3**:**1**, 0.053 g, in 20 mL of oxygen-free CH_2Cl_2 was irradiated at 350 nm in a Rayonet reactor for 4 h. After removal of solvent in vacuo, the residue was flash chromatographed in air on a 1.5- × 10.5-cm column of 60-Å silica gel prepared in 1:1 CH_2Cl_2:hexane (by volume). An orange fraction eluted with CH_2Cl_2 afforded 0.021 g of **5**, ^{1}H NMR (CD_2Cl_2): δ 10.38 (s) 4 H, 4.20 (apparent symmetric 9 peak multiplet) 16 H, 2.01 (t) 24 H. IR (KBr): 2970, 2938, 2875, 1464, 1449, 1381, 1271, 1230, 1151, 1110, 1056, 1018, 992, 960, 835, 744, 705, 390 cm^{-1}. The analytical sample was recrystallized from cold EtOH/CH_2Cl_2. Anal. Calcd for $C_{36}H_{46}N_4OClRh$ (OEPRhCl·H_2O): C, 62.82; H, 6.72; N, 8.13; Cl, 5.14. Found: C, 62.30; H, 7.11; N, 7.86; Cl, 5.57. Visible absorption (CH_2Cl_2): λ_{max} 416, 518, 552 nm.

A deep red solid material eluted with 1:1 CH_2Cl_2:hexane was a minor product which was not detected in the NMR tube photolysis experiments. It was characterized by ^{1}H NMR (CD_2Cl_2): 10.15 (s), 4.13 (q), 1.93 (t), −3.87 (s). We were unable to obtain satisfactory microanalyses of this compound.

Compound **5** was also synthesized by a literature route[21] from reaction of 0.150 g of $[Rh(CO)_2Cl]_2$ with 0.125 g of $OEPH_2$ in 100 mL of C_6H_6. Flash chromatography of the product mixture on silica gel as described above afforded, on elution with CH_2Cl_2, the same orange product which exhibited an identical ^{1}H NMR spectrum: δ 10.37, 4.20, 2.01 ppm.

Reaction of 1 with CO and Ethanol. A resealable NMR tube containing 5 mg of **3** was connected to the right arm of an ACE tip-off manifold, evacuated, and filled with N_2. A standard NMR tube containing 7 μL of absolute ethanol in 1 mL of CD_2Cl_2 was placed in the left arm. After three evacuation/nitrogen purge cycles at −40 °C, the CD_2Cl_2–ethanol mixture at 35–40 °C was distilled in vacuo into the resealable tube containing **3** and cooled to −40 °C, the tube was sealed, and the tube and contents were allowed to sit at room temperature. The reaction mixture was monitored at 25 °C by ^{1}H NMR until **3** was completely converted to **1**, ca. 12 h. The tube was then evacuated, ca. 1 atm of CO was introduced, the tube was sealed, and the reaction was monitored at 25 °C by NMR. The 9.13-ppm methine singlet of **1** shifted to lower field on coordination of CO.[15] The −1.12-ppm triplet of **6** was evident within an hour after CO introduction and the conversion of **1** to **6** was complete in 6 h. Resonances associated with byproduct **2** were present and the **6**:**2** mol ratio was generally 3:1 or greater. The 10.0-ppm resonance of **3** was not evident during the early stages of the reaction but could be detected after 24 h, **6**:**3** mol ratio = 21. Product mixtures consistently contained 10–14% of **5** as determined from methine resonance intensities.

The CO was then removed by evacuation of the NMR tube and the reaction was monitored. During 3 days, **2** disappeared with the coincident formation of **3**. No trace of dimer **1** could be detected during a 6-day period. Reintroduction of CO caused the regeneration of **2** at the expense of **3**. Finally the mixture was photolyzed for 135 min at 300 nm selectively converting **2** to **5**. The amount of product **6** remained constant, as did the total number of moles of rhodium species in solution during the evacuation, CO addition, photolysis sequence.

Reaction of 1 with CO and H_2O. An analogous experiment at 25 °C employing the technique described above with 5 mg of **1** and 2 μL of H_2O per 1 mL of CD_2Cl_2 in the absence of ethanol afforded only a ca. 50% conversion of **1** to **2** during 24 h and was not complete after 48 h.

This same experimental technique was employed for the laser photolysis experiments with the exception that the NMR tube was cooled in liquid N_2 for the degassing procedure and the tube was flame-sealed prior to photolysis and NMR monitoring.

Isolation of 6. In a typical preparative-scale experiment, 0.097 g of **1** in 25 mL of CH_2Cl_2 containing 30 μL of ethanol was stirred under a CO atmosphere for 3 days. Then, the mixture was irradiated at 300 nm in a Rayonet reactor for 3 h. After removal of solvent in vacuo, the residue was flash chromatographed under N_2 pressure on a 20 × 1 cm column of silica gel (60 Å) prepared in 1:1 CH_2Cl_2:hexane. Five fractions were collected in air, fractions 2 and 3 with eluant compositions ranging from 1:1 CH_2Cl_2:hexane to pure CH_2Cl_2, containing 0.031 g of fairly pure **6**. Recrystallization from hexane/CH_2Cl_2 at −50 °C afforded an analytical sample which was used for the X-ray analysis. Anal. Calcd for $C_{39}H_{49}N_4O_2Rh$: C, 66.09; H, 6.97; N, 7.91. Found: C, 65.97; H, 7.22; N, 7.64. A later fraction contained **5**: ^{1}H NMR (CD_2Cl_2) δ 10.38 (s), 4.20 (m), 2.01 (t).

X-ray Structure Determination of 6. A red chunk of $C_{39}H_{49}N_4O_2Rh$ having approximate dimensions of 0.25 × 0.15 × 0.10 mm was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Cu Kα radiation (λ = 1.54184 Å) on an Enraf-Nonius CAD4 computer controlled κ axis diffractometer equipped with a graphite crystal, incident beam monochromator.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $24 < \theta < 32°$, measured by the computer-controlled diagonal slit method of centering. The monoclinic cell parameters and calculated volume are given in Table I. From the systematic absences of $h01$ $h + 1 = 2n$, $0k0$ $k = 2n$ and from subsequent least-squares refinement, the space group was determined to be $P2_1/n$ (No. 14).

The data were collected at a temperature of 293 ± 1 K using the ω–2θ scan technique. The scan rate varied from 2 to 16°/min (in ω). The variable scan rate allows rapid data collection for intense reflections where a fast scan rate is used and assures good counting statistics for weak reflections where a slow scan rate is used. Data were collected to a maximum 2θ of 112.0°. The scan range (in deg) was determined as a function of θ to correct for the separation of the Kα doublet.[22] The scan width was calculated as follows: ω scan width = $0.89 + 0.150 \tan\theta$. Moving-crystal moving-counter background counts were made by scanning an additional 25% above and below this range. Thus the ratio of peak counting time to background time was 2:1. The counter aperture was also adjusted as a function of θ. The horizontal aperture width ranged from 2.2 to 2.8 mm; the vertical aperture was set at 4.0 mm. The diameter of the incident beam collimator was 0.7 mm and the crystal to detector distance was 21 cm. For intense reflections an attenuator was automically inserted in front of the detector; the attenuator factor was 25.6. A total of 4864 reflections were collected, of which 4864 were unique.

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 41.8/cm for Cu Kα radiation. An empirical absorption correction based on the method of Walker and Stuart[23] was applied. Relative transmission coefficients ranged from 0.612 to 1.000 with an average value of 0.827.

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Structure Solution and Refinement. The structure was solved using the Patterson heavy-atom method which revealed the position of the Rh atom. The remaining atoms were located using DIRDIF[24] and in succeeding difference Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculations but their positions were not refined. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma\omega(|F_o| - |F_c|)^2$ and the weight w is defined as per the Killean and Lawrence method with terms of 0.020 and 1.0.[25]

All calculations were performed on a VAX computer. Refinement was done using MolEN.[26]

Synthesis of 8. The general procedure of Johnson[17] was followed. OEPCo, 100 mg, and sodium amalgam (1.5%), 5.0 g, in 35 mL of ethylene glycol dimethyl either were stirred in one side of a two-sided Schlenk under a N_2 atmosphere for 18 h. The resulting brick red solution was filtered to the other side and then treated in darkness with 1.5 mL of acetic anhydride. The mixture was stirred for 15 min and then treated with 150 mL of a deoxygenated 2:1 H_2O:CH_2Cl_2 mixture. The CH_2Cl_2 layer was dried over $MgSO_4$ and filtered and the solvent was removed in vacuo. Chromatography of the residue under N_2 on a water-cooled silica gel column constructed from two water condensers in series afforded fractions eluted with 3:1 hexane:benzene which contained 80 mg (68% yield) of red crystals of 8 which were recrystallized from cold CH_2Cl_2/petroleum ether: λ_{max} nm (log E) 248 (4.45), 391 (4.91), 411 (4.73), 555 (4.23). Anal. Calcd for $C_{38}H_{47}N_4OCo$: C, 71.91; H, 7.46; N, 8.83; Co, 9.28. Found: C, 71.93; H, 7.53; N, 8.84; Co, 9.44.

Reaction of OEPCoNa with Acetic Formic Anhydride. The procedure was very similar to that employed in the preparation of 8. Either THF or ethylene glycol dimethyl ether could be used as solvent. Typically, the solution of OEPCoNa, prepared as described above, was added to 3.0 mL of very pure CO-saturated acetic formic anhydride.[20] The mixture was stirred in the dark under a CO atmosphere for 20 min after which the solvent was removed in vacuo. The solid red residue was treated with 2 mL of CO-saturated C_6D_6 and was analyzed under a CO atmosphere.

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Supplementary Material Available: Full listings of bond distances, bond angles, anisotropic thermal parameters for non-hydrogen atoms, positional parameters for hydrogen atoms, and torsional angles (14 pages). Ordering information is given on any current masthead page.

OM920588L

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