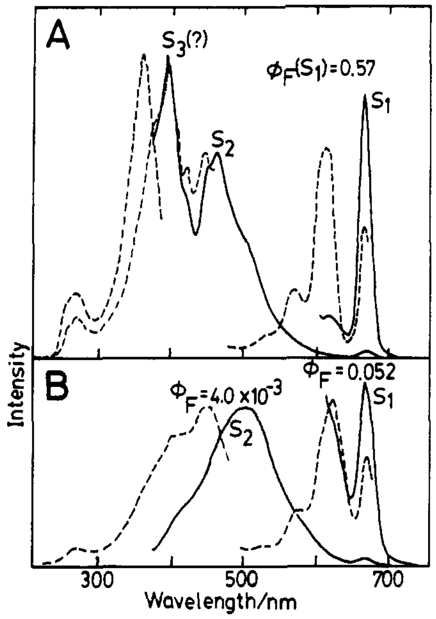

Figure 3. Emission (solid lines) and excitation spectra (broken lines) of (A) H_2TBP and (B) H_4TBPD in deaerated chloroform. Excitation was at 360 and 570 nm.

Figure 3 shows the emission and excitation spectra of H_2TBP and H_4TBPD. Both compounds show so-called S_1 and S_2 emissions, as has been detected in mononuclear ZnBP,[12b,c] and the quantum yield (Φ_F) of S_1 emission of H_4TBPD (0.052) is about 1 order smaller than that of H_2TBP (0.57). Such a weak emission in the dimer is an indication of intramolecular interaction of the two included units.[15a,20] In addition, the lifetime (τ) of the S_1 emission of the dimer in deaerated chloroform (9.80 ns) is shorter than that of the monomer (11.3 ns), as has been observed in porphyrin systems.[15a,20] Two S_2 emission τ values were obtained for both H_2TBP (τ_1 = 2.68 ns, 81.1%; τ_2 = 14.7 ns, 18.9%) and H_4TBPD (τ_1 = 3.17 ns, 71.6%; τ_2 = 11.6 ns, 28.4%). In addition, H_2TBP showed another emission at higher energy (S_3 emission?[12b]) (τ_1 = 1.87 ns, 94.7%; τ_2 = 7.14 ns, 5.3%). Since these fluorescence experiments were carried out at concentrations as low as 10^{-7} M, where aggregation phenomena may be neglected and all the excitation spectra were mirror images of the respective emission band, the presence of two components in the S_2 emission of H_2TBP and H_4TBPD suggests that the Soret region spectra of these porphyrins are not composed of a single pure transition.[21]

Binuclear Cu_2TBPD shows voltammetry similar to that of mononuclear CuTBP, although the waves are generally broader and weaker. However, well-defined peaks were obtained by differential pulse voltammetry (Figure 4). Cu_2TBPD exhibited broad peaks, roughly corresponding in potential to two one-electron oxidations and one one-electron reduction of the porphyrin ring of CuTBP. Since the shapes of the response are not much different between the two compounds, the broadening of the peaks suggests that the oxidation and reduction in Cu_2TBPD occur stepwise at closely located potentials and accordingly that the two CuTBP units in Cu_2TBPD are interacting. If we deconvolute the first reduction wave of Cu_2TBPD into two components using the bandwidth of the first reduction wave of CuTBP, their splitting energy is approximately 110–120 mV. The potential difference between the first oxidation and reduction in Cu_2TBPD (1.63 V) is slightly smaller than that in CuTBP (1.75 V), consistent with the longer wavelength shift of the absorption and MCD spectra. The difference of their potential differences (0.12 V = ca. 970 cm^{-1}) is very close to that calculated for edge-on porphyrin dimers (ca. 1000 cm^{-1}),[15a] however somewhat larger than the values expected from the Soret band absorption (Figure 1B, ca. 630 cm^{-1}) and MCD spectra (ca. 660 cm^{-1}). Electrochemical data are often slightly at variance with the spectroscopic data.[22]

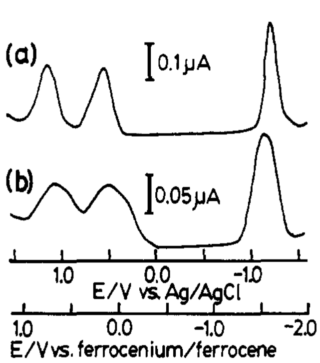

Figure 4. Differential pulse voltammograms of (a) CuTBP and (b) Cu_2TBPD in *o*-dichlorobenzene containing 0.3 M tetrabutylammonium perchlorate. Scan rate/(mV/s) = 5; [CuTBP] = [Cu_2TBPD]/mM = ca. 0.1; area of electrode/cm^2 = 0.07.

Thus, the above data consistently suggest that the two units rigidly constrained in a coplanar arrangement in H_4TBPD and Cu_2TBPD each retain independency and are interacting intramolecularly, as reported for several covalently linked relatively flexible binuclear porphyrin systems.[1,2,15,20] π-Conjugation of the two TBP units through the common benzene appears rather small.

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A Convenient Synthesis of the Manganese and Rhenium Alkoxides and Phenoxides *fac*-$(CO)_3$(dppe)MOR (R = CH_3, C_2H_5, C_6H_5; dppe = 1,2-Bis(diphenylphosphino)ethane). X-ray Structure of *fac*-$(CO)_3$(dppe)$ReOC_6H_5$

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Low-valent transition-metal alkoxides are reported to be likely intermediates in the carbalkoxylation of olefins[1] and in the catalytic hydrogenation of aldehydes and ketones,[2] and they continue to be the focus of much interest. However, relatively few of them have been fully characterized because not only are they frequently moisture and air sensitive but they are very labile as well, undergoing rapid spontaneous β-hydrogen elimination.[3] One of our interests in the synthesis and chemistry of transition-metal alkoxides stems from their presumed intermediacy in the conversion of acylmanganese complexes to the corresponding alkoxy carbonyl complexes when treated with synthesis gas (a formal insertion of formaldehyde).[4]

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In this article we report the synthesis, characterization, and reactions of *fac*-$(CO)_3(dppe)MOR$ (M = Mn, Re; R = CH_3, C_2H_5, C_6H_5; dppe = 1,2-bis(diphenylphosphino)ethane). Also included in this report is the X-ray structure determination of *fac*-$(CO)_3(dppe)ReOC_6H_5$.

Experimental Section

Materials and Methods. $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and 1,2-bis(diphenylphosphino)ethane were purchased from Pressure Chemical Co. and were used as received. All other reagents were purchased commercially and used without further purification. The solvents were refluxed and distilled from the appropriate reagents prior to use. $NaOC_6H_5$[5] and *fac*-$(CO)_3(dppe)MnH$[6] were prepared by the published procedures. All reactions and manipulations were conducted under an Ar atmosphere. The IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR instrument. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 250.133, 62.896, and 101.256 MHz, respectively, on a Bruker AC-250 FT spectrometer. H_3PO_4 (85%) was used as an external reference for ^{31}P NMR spectra. Mass spectra were obtained on an HP 5995C spectrometer. Melting points were recorded on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc. All high-pressure reactions were carried out in an Autoclave Engineers 300-mL magnedrive autoclave. In a typical reaction the autoclave was charged with the organometallic complex and with hexane (100 mL) and sealed. After appropriate flushing, the autoclave was pressurized with the desired gas. The mixture was heated to the required temperature for a specific period of time and cooled. The autoclave was then vented, and the contents were removed and examined.

Preparation of *fac*-$(CO)_3(dppe)ReH$ (1). A 1.0-g (1.53-mmol) sample of $Re_2(CO)_{10}$ was slurried with 1-propanol in the presence of dppe (1.21 g, 3.03 mmol), and the mixture was refluxed for 24 h. After cooling, the solvent was removed on a rotary evaporator and the residue was extracted with benzene (50 mL). Hexane was added to the solution, which was then cooled. The white precipitate that separated was collected by filtration, washed with hexane (3 × 15 mL), and dried under vacuum to give **1** (0.55 g, 0.8 mmol, 26%). This compound has been characterized previously.[7]

Preparation of *fac*-$(CO)_3(dppe)MnOTs$ (2). A 0.50-g (0.92-mmol) amount of *fac*-$(CO)_3(dppe)MnH$ in methylene chloride (100 mL) was treated with excess of *p*-toluenesulfonic acid. When hydrogen gas evolution ceased, the excess acid was removed by extraction with water. The methylene chloride solution was concentrated and mixed with hexane, and the resultant mixture was cooled. The orange microcrystals that separated were collected by filtration, washed with hexane (3 × 15 mL), and dried under vacuum to give **2** (0.61 g, 0.86 mmol, 93%), mp 195–198 °C dec. IR in CH_2Cl_2 ($\nu(C\equiv O)$, cm^{-1}): 2033 vs, 1965 s, 1920 s. ^{1}H NMR (CD_2Cl_2): δ 7.64–6.85 (m, 24 H, aromatic), 2.85 (d, J_{HP} = 17 Hz, 4 H, CH_2), 2.28 (s, 3 H, CH_3). ^{13}C NMR (CD_2Cl_2): δ 220.2 (t, J_{CP} = 19 Hz, CO), 217.9 (br, s, 2 CO), 140.6 (s, ipso, OC_6H_5), 133.3 (m, *m*, C_6H_5), 133.0/131.9 (t, J_{CP} = 4/5 Hz, *o*, C_6H_5), 131.5 (s, *o*, OC_6H_5), 131.1/130.8 (s, *p*, C_6H_5), 129.4/129.1 (t, J_{CP} = 5/4 Hz, *m*, C_6H_5), 128.6 (s, *o*, OC_6H_5), 126.5 (s, *p*, OC_6H_5), 25.9 (t, J_{CP} = 20 Hz, CH_2). ^{31}P NMR (CD_2Cl_2): δ 71.5 (s). Anal. Calcd for $C_{36}H_{31}MnO_6P_2S$: C, 61.0; H, 4.4. Found: C, 60.9; H, 4.5.

Preparation of *fac*-$(CO)_3(dppe)ReOTs$ (3). A procedure similar to that as described for the preparation of **2**, except for the use of **1** (0.5 g, 0.74 mmol) instead of *fac*-$(CO)_3(dppe)MnH$, was employed for this compound. White microcrystalline **3** (0.60 g, 0.71 mmol, 96%), mp 255–260 °C dec, was obtained. IR in CH_2Cl_2 ($\nu(C\equiv O)$, cm^{-1}): 2038 vs, 1961 s, 1912 s. ^{1}H NMR (CD_2Cl_2): δ 7.68–6.88 (m, 24 H, aromatic), 2.71 (m, 4 H, CH_2), 2.26 (s, 3 H, CH_3). ^{13}C NMR (CD_2Cl_2): δ 192.8 (dd, $J_{C(\alpha)P(\beta)}$ = 61 Hz, $J_{C(\alpha)P(\beta')}$ = 10 Hz, 2 CO), 191.5 (t, J_{CP} = 6 Hz, CO), 141.0 (s, ipso, OC_6H_5), 139.0 (m, ipso, C_6H_5), 133.0/132.2 (t, J_{CP} = 5/6 Hz, *o*, C_6H_5), 131.4/131.1 (s, *p*, C_6H_5), 129.5/129.2 (t, J_{CP} = 5/6 Hz, *m*, C_6H_5), 128.7 (s, *m*, OC_6H_5), 126.7 (s, *o*, OC_6H_5), 121.3 (s, *p*, OC_6H_5), 27.0 (m, CH_2), 21.3 (s, CH_3). ^{31}P NMR (CD_2Cl_2): δ 37.4 (s). Anal. Calcd for $C_{36}H_{31}O_6P_2ReS$: C, 51.5; H, 3.7. Found: C, 51.6; H, 3.7.

Preparation of *fac*-$(CO)_3(dppe)MnOCH_3$ (4). A 0.50-g (0.70-mmol) sample of **2** was slurried with 100 mL of methanol, and the mixture was stirred at room temperature with 1.65 mL of 0.43 M solution of $NaOCH_3$ (0.70 mmol, 0.038 g) (freshly prepared from the reaction of Na with methanol). The reaction was monitored with IR spectroscopy and was complete in 6 h. The solution was evaporated to dryness, the solids were extracted with benzene (15 mL), and the benzene solution, diluted with hexane (30 mL), was cooled. The resulting yellow microcrystals were collected by filtration, washed with hexane (3 × 15 mL), and dried under vacuum to give **4** (0.33 g, 0.58 mmol, 83%), mp 105–107 °C dec. IR in C_6H_6 ($\nu(C\equiv O)$, cm^{-1}): 2008 vs, 1931 s, 1894 s. IR in KBr pellet ($\nu(O-H)$, cm^{-1}): 3110–3050 br. ^{1}H NMR (C_6D_6): δ 7.81–6.90 (m, 20 H, C_6H_5), 3.51 (s, 3 H, OCH_3), 3.21 (s, 3 H, $C\mathit{H}_3OH$), 2.92–2.61 (m, 2 H, CH_2), 2.32–2.01 (m, 2 H, CH_2). ^{13}C NMR (C_6D_6): δ 219.4 (br, CO), 135.5/134.4 (t, J_{CP} = 16/21 Hz, ipso, C_6H_5), 133.4/132.5 (t, J_{CP} = 4/5 Hz, *o*, C_6H_5), 130.3/130.0 (s, *p*, C_6H_5), 128.9/128.3 (t, J_{CP} = 4/5 Hz, *m*, C_6H_5), 63.9 (t, J_{CP} = 5 Hz, OCH_3), 49.5 (s, CH_3OH), 26.4 (t, J_{CP} = 20 Hz, CH_2). ^{31}P NMR (C_6D_6): δ 71.7 (s, br). Anal. Calcd for $C_{30}H_{27}MnO_4P_2\cdot CH_3OH$: C, 62.0; H, 5.2. Found: C, 61.4; H, 5.0.

Preparation of *fac*-$(CO)_3(dppe)MnOC_2H_5$ (5). A 0.50-g (0.70-mmol) sample of **2** was treated with 1.85 mL of a 0.38 M solution of $NaOC_2H_5$ (0.70 mmol, 0.047 g) in ethanol (100 mL) in a manner similar to that described for the preparation of **4**. The reaction was complete in about 8 h. Yellow microcrystals of **5** (0.33 g, 0.56 mmol, 81%) were obtained. This complex has been synthesized and characterized previously.[6]

Preparation of *fac*-$(CO)_3(dppe)MnOC_6H_5$ (6). A 0.50-g (0.70-mmol) amount of **2** was slurried with THF (100 mL), and the mixture was stirred at room temperature with $NaOC_6H_5$ (0.08 g, 0.72 mmol). The reaction was complete in about 2 days. The solution was evaporated to dryness, the residue was extracted with benzene (15 mL), and the benzene solution, diluted with hexane (20 mL), was cooled. The yellow crystals that separated were collected by filtration, washed with hexane (3 × 15 mL), and dried under vacuum to give **6** (0.34 g, 0.54 mmol, 77%), mp 166–168 °C dec. IR in C_6H_6 ($\nu(C\equiv O)$, cm^{-1}): 2015 vs, 1940 s, 1906 s. ^{1}H NMR (C_6D_6): δ 7.65–7.00 (m, 20 H, C_6H_5), 6.85–6.60 (m, 5 H, OC_6H_5), 2.85–2.55 (m, 2 H, CH_2), 2.45–2.15 (m, 2 H, CH_2). ^{13}C NMR (C_6D_6): δ not observed (CO), 169.8 (s, ipso, OC_6H_5), 134.4/132.8 (t, J_{CP} = 17/20 Hz, ipso, C_6H_5), 133.2/132.0 (t, J_{CP} = 5/4 Hz, *o*, C_6H_5), 130.4/130.3 (s, *p*, C_6H_5), 129.1/128.5 (t, J_{CP} = 6/5 Hz, *m*, C_6H_5), 127.7 (s, *m*, OC_6H_5), 120.8 (s, *o*, OC_6H_5), 113.6 (s, *p*, OC_6H_5), 26.2 (t, J_{CP} = 20 Hz, CH_2). ^{31}P NMR (C_6D_6): δ 71.6 (s, br). Anal. Calcd for $C_{35}H_{29}MnO_4P_2$: C, 66.7; H, 4.6. Found: C, 66.8; H, 4.8.

Preparation of *fac*-$(CO)_3(dppe)ReOCH_3$ (7). A 0.50-g (0.59-mmol) sample of **3** was treated with $NaOCH_3$ (0.59 mmol) in methanol (100 mL) in a manner similar to that described for the preparation of **6**. The reaction was complete in about 5 days. **7** was obtained as a white solid (0.37 g, 0.53 mmol, 90%) mp 108–109 °C dec. IR in C_6H_6 ($\nu(C\equiv O)$, cm^{-1}): 2012 vs, 1927 s, 1884 s. IR in KBr pellet ($\nu(O-H)$, cm^{-1}): 3100–3040 m. ^{1}H NMR (C_6D_6): δ 7.75–6.85 (m, 20 H, C_6H_5), 4.15 (s, 3 H, CH_3), 3.21 (s, 3 H, $C\mathit{H}_3OH$), 3.05–2.61 (m, 2 H, CH_2), 2.32–2.03 (m, 2 H, CH_2). ^{13}C NMR (C_6D_6): δ 196.4 (dd, $J_{C(\alpha)P(\beta)}$ = 61 Hz, $J_{C(\alpha)P(\beta')}$ = 10 Hz, 2 CO), 192.8 (t, J_{CP} = 6 Hz, CO), 133.9–128.4 (m, C_6H_5), 67.2 (t, J_{CP} = 5 Hz, OCH_3), 50.0 (s, CH_3OH), 26.4 (m, CH_2). ^{31}P NMR (C_6D_6): δ 32.7 (s). Anal. Calcd for $C_{30}H_{27}O_4P_2Re\cdot CH_3OH$: C, 50.9, H, 4.2. Found: C, 50.0; H, 4.1.

Preparation of *fac*-$(CO)_3(dppe)ReOC_2H_5$ (8). A 0.50-g (0.59-mmol) amount of **3** was treated with a freshly prepared solution of $NaOC_2H_5$ (0.04 g, 1.75 mL of 0.34 M, 0.59 mmol) in ethanol in a manner similar to that described for the preparation of **6**. The reaction was complete in about 10 days. **8** was obtained as a white material (0.35 g, 0.49 mmol, 83%), mp 95–97 °C dec. IR in C_6H_6 ($\nu(C\equiv O)$, cm^{-1}): 2011 vs, 1926 s, 1882 s. ^{1}H NMR (C_6D_6): δ 7.89–6.93 (m, 20 H, C_6H_5), 3.71 (q, 2 H, $C\mathit{H}_2CH_3$), 2.88–2.62 (m, 2 H, CH_2), 2.22–1.98 (m, 2 H, CH_2), 0.95 (t, 3 H, $CH_2C\mathit{H}_3$). ^{13}C NMR (C_6D_6): δ 196.5 (dd, $J_{C(\alpha)P(\beta)}$ = 61 Hz, $J_{C(\alpha)P(\beta')}$ = 10 Hz, 2 CO), 192.9 (t, J_{CP} = 6 Hz, CO), 133.5/133.2 (t, J_{CP} = 5/5 Hz, *o*, C_6H_5), 133.0 (m, ipso, C_6H_5), 130.7/130.2 (s, *p*, C_6H_5), 129.1/128.3 (t, J_{CP} = 5/6 Hz, *m*, C_6H_5), 74.3 (t, J_{CP} = 6 Hz, $O\mathit{C}H_2CH_3$), 26.3 (m, $-\mathit{C}H_2\mathit{C}H_2-$), 23.1 (s, CH_3). ^{31}P NMR (C_6D_6): δ 31.9 (s). Anal. Calcd for $C_{31}H_{29}O_4P_2Re$: C, 52.1; H, 4.1. Found: C, 51.6; H, 4.2.

Preparation of *fac*-$(CO)_3(dppe)ReOC_6H_5$ (9). A 0.50-g (0.59-mmol) sample of **3** was treated with $NaOC_6H_5$ (0.07 g, 0.60 mmol) in a manner similar to that described for the preparation of **6**. The reaction was complete in about 2 weeks. The white crystals that separated were collected by filtration, washed with hexane (3 × 15 mL), and dried under vacuum to give **9** (0.41 g, 0.54 mmol, 92%), mp 178–180 °C dec. IR in C_6H_6 ($\nu(C\equiv O)$, cm^{-1}): 2019 vs, 1936 s, 1897 s. ^{1}H NMR (C_6D_6): δ 7.56–6.88 (m, 20 H, C_6H_5), 6.72–6.65 (m, 5 H, OC_6H_5), 2.66–2.42 (m, 2 H, CH_2), 2.24–2.00 (m, 2 H, CH_2). ^{13}C NMR (C_6D_6): 195.2 (dd, $J_{C(\alpha)P(\beta)}$ = 61 Hz, $J_{C(\alpha)P(\beta')}$ = 10 Hz, 2 CO), 192.5 (t, J_{CP} = 6 Hz, CO), 168.5 (s, ipso, OC_6H_5), 133.3/132.4 (t, J_{CP} = 5/5 Hz, *o*, C_6H_5), 132.6

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Table I. Crystallographic Data for *fac*-$(CO)_3(dppe)ReOC_6H_5$ (**9**)

$C_{35}H_{29}O_4P_2Re$	fw = 761.78
cryst syst: monoclinic	space group: $P2_1/c$ (No. 14)
$a = 16.183$ (2) Å	$T = 294$ K
$b = 11.735$ (1) Å	radiation (λ): Mo Kα (0.71073 Å)
$c = 16.358$ (2) Å	$\rho_{calcd} = 1.63$ g cm^{-3}
$\beta = 92.692$ (9)°	$\mu = 41.06$ cm^{-1}
$V = 3103.0$ (6) Å^3	$R(F) = 0.0397$
$Z = 4$	$R_w(F) = 0.0401$

(m, ipso, C_6H_5), 130.7/130.6 (s, *p* C_6H_5), 129.2/128.8 (t, $J_{CP} = 5/5$ Hz, *m*, C_6H_5), 127.8 (s, *m*, OC_6H_5), 120.4 (s, *o*, OC_6H_5), 114.5 (s, *p*, OC_6H_5), 26.6 (m, CH_2). ^{31}P NMR (C_6D_6): δ 34.7 (s).

Crystal Structure Determination of *fac*-$(CO)_3(dppe)ReOC_6H_5$ (9). Examination and data collection, using a colorless needle (0.08 × 0.22 × 0.55) sealed in a glass capillary, were performed on a Siemens R3m/V four-circle diffractometer. Data were collected for $4.0° \leq 2\theta \leq 55.0°$ ($-21 \leq h \leq +21$, $0 \leq k \leq +15$, $0 \leq l \leq +21$). Lorenz–polarization corrections were applied to 7272 reflections. A semiempirical absorption correction was applied ($T_{max} = 0.9229$, $T_{min} = 0.5686$). A total of 4913 reflections ($R_{int} = 0.0211$) with $F > 3\sigma(F)$ were used in further calculations. The structure was solved by direct methods (XF:TREF, SHELXTL-PLUS program package[8]) and refined by full-matrix least-squares techniques (XLS). The non-hydrogen atoms were refined with anisotropic temperature parameters; hydrogen atoms were allowed to ride on their perspective carbons [C–H = 0.96 Å, U(H) = 0.08 Å^2]. The quantity minimized was $\sum w(F_o - F_c)^2$; $w = [\sigma^2(F) + |g|F^2]^{-1}$, $g = 0.000374$. Crystal data are given in Table I, and atomic coordinates and equivalent isotropic displacement parameters are given in Table II.

Carbonylation of *fac*-$(CO)_3(dppe)MnOCH_3$ (4). A 0.95-g (1.67-mmol) sample of **4** suspended in hexane (100 mL) was placed in the autoclave and pressurized with 4000 psi of CO at 88 °C for 24 h. The mixture was cooled, and the contents were transferred to a flask by rinsing with benzene (50 mL). The solvents were removed on a rotary evaporator, and the solid was recrystallized from benzene/hexane at −5 °C to give *fac*-$(CO)_3(dppe)MnC(O)OCH_3$ (0.71 g, 1.19 mmol, 71%), mp 123–125 °C dec. IR in hexane (ν(C≡O), cm^{-1}): 2015 vs, 1946 s, 1924 s. IR (ν(C=O), cm^{-1}): 1610 m. ^1H NMR (C_6D_6): δ 7.65–6.95 (m, 20 H, C_6H_5), 3.15 (s, 3 H, CH_3), 3.10–2.85 (m, 2 H, CH_2), 2.35–2.15 (m, 2 H, CH_2). ^{13}C NMR (C_6D_6): δ 223.0 (t, $J_{CP} = 7$ Hz, 2 C≡O), 218.6 (t, $J_{CP} = 15$ Hz, C≡O), 216.1 (t, $J_{CP} = 25$ Hz, C=O), 137.1 (m, ipso, C_6H_5), 132.4/131.4 (t, $J_{CP} = 5/4$ Hz, *o*, C_6H_5), 129.8/129.7 (s, *p*, C_6H_5), 128.9/128.4 (t, $J_{CP} = 4/5$ Hz, *m*, C_6H_5), 49.2 (s, CH_3) 27.0 (t, $J_{CP} = 21$ Hz, CH_2). ^{31}P NMR (C_6D_6): δ 83.6 (s). Similar spectral properties are also observed for samples of *fac*-$(CO)_3(dppe)MnC(O)OCH_3$ prepared by an alternate procedure.[9]

Carbonylation of *fac*-$(CO)_3(dppe)MnOC_2H_5$ (5). A 0.75-g (1.29-mmol) amount of **5** was carbonylated as described above. The IR spectrum of the mixture in hexane showed an absorption at 1606 (m) cm^{-1} due to ν(C=O) of the $C(O)OC_2H_5$ group. The ^1H NMR spectrum of the mixture in C_6D_6 gave resonances (δ 3.55 q, 0.76 t) characteristic of the ethyl protons. Similar spectral properties were also observed for the samples of *fac*-$(CO)_3(dppe)MnC(O)OC_2H_5$ prepared by an alternate procedure.[9] Attempts to separate *fac*-$(CO)_3(dppe)MnC(O)OC_2H_5$ from an impurity were unsuccessful.

Attempted Insertion of C_2H_4 into *fac*-$(CO)_3(dppe)MnOCH_3$ (4). A 0.90-g (1.58-mmol) sample of **4** suspended in hexane (100 mL) in the autoclave was pressurized with C_2H_4 to 1000 psi followed by CO until a total pressure of 2000 psi was reached. The mixture was heated to 85 °C for 24 h and cooled, and the autoclave was then vented. The solution was filtered, the residue was triturated with benzene (2 × 50 mL), and a white solid was recovered. The white solid was polyethylene. Polyethylene was also deposited on the wall of the reactor. The identity of the organometallic compound is under investigation.

Reaction of *fac*-$(CO)_3(dppe)MnOCH_3$ (4) with *p*-Anisoyl Chloride. A 1.0-g (1.76-mmol) quantity of **4** was dissolved in benzene (25 mL), and the mixture was stirred in the presence of *p*-anisoyl chloride (0.31 g, 0.25 mL, 1.83 mmol) at room temperature for 4 h. The solvent was then removed on a rotary evaporator, and the residues was triturated with hexane (2 × 50 mL). The hexane extract was concentrated on a rotary evaporator. The mass spectrum of the residual oil (*m/z* 166) confirmed the presence of methyl *p*-anisate. The organometallic compound proved to be *fac*-$(CO)_3(dppe)MnCl$ on the basis of comparison of its IR spectrum to that of an authentic sample prepared from the reaction of *fac*-$(CO)_3(dppe)MnH$ with HCl.

Table II. Atomic Coordinators (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for *fac*-$(CO)_3(dppe)ReOC_6H_5$ (**9**)

atom	x	y	z	U_{eq},[a] Å^2
Re	2631 (1)	39 (1)	2051 (1)	34 (1)
P(1)	4022 (1)	−451 (1)	2663 (1)	33 (1)
P(2)	2253 (1)	−1724 (1)	2776 (1)	37 (1)
O(1)	3063 (3)	−1174 (4)	465 (3)	61 (2)
O(2)	892 (3)	158 (5)	1198 (4)	82 (2)
O(3)	3189 (3)	2291 (4)	1288 (3)	69 (2)
O(4)	2406 (3)	783 (3)	3206 (2)	45 (1)
C(1)	2900 (4)	−717 (5)	1076 (4)	42 (2)
C(2)	1517 (4)	167 (5)	1555 (4)	48 (2)
C(3)	2983 (4)	1464 (5)	1583 (3)	42 (2)
C(4)	3929 (4)	−1866 (5)	3141 (3)	41 (2)
C(5)	3103 (4)	−1982 (5)	3542 (3)	44 (2)
C(6)	4517 (4)	422 (5)	3470 (3)	38 (2)
C(7)	5334 (4)	793 (5)	3423 (4)	49 (2)
C(8)	5701 (5)	1473 (6)	4035 (4)	59 (3)
C(9)	5272 (5)	1776 (6)	4688 (4)	61 (3)
C(10)	4471 (5)	1411 (6)	4759 (4)	57 (3)
C(11)	4092 (4)	727 (5)	4159 (3)	46 (2)
C(12)	4858 (3)	−627 (5)	1968 (3)	38 (2)
C(13)	5462 (4)	−1458 (5)	2109 (4)	46 (2)
C(14)	6143 (4)	−1518 (6)	1621 (4)	55 (2)
C(15)	6230 (4)	−719 (7)	1003 (4)	59 (3)
C(16)	5626 (4)	102 (6)	860 (4)	58 (2)
C(17)	4947 (4)	147 (6)	1332 (3)	47 (2)
C(18)	1333 (4)	−1752 (5)	3377 (4)	45 (2)
C(19)	1127 (5)	−2730 (6)	2788 (5)	67 (3)
C(20)	443 (6)	−2726 (8)	4267 (5)	82 (3)
C(21)	−23 (5)	−1758 (9)	4345 (5)	83 (4)
C(22)	181 (5)	−804 (8)	3930 (5)	73 (3)
C(23)	861 (4)	−785 (6)	3444 (4)	55 (2)
C(24)	2186 (4)	−3012 (5)	2152 (4)	43 (2)
C(25)	2531 (4)	−4038 (6)	2409 (4)	55 (2)
C(26)	2467 (5)	−4983 (6)	1905 (5)	71 (3)
C(27)	2075 (5)	−4928 (7)	1155 (5)	73 (3)
C(28)	1727 (5)	−3917 (7)	888 (4)	68 (3)
C(29)	1783 (4)	−2954 (6)	1389 (4)	54 (2)
C(30)	1990 (4)	1717 (5)	3401 (4)	44 (2)
C(31)	1489 (5)	2348 (6)	2868 (5)	67 (3)
C(32)	1081 (6)	3295 (7)	3135 (6)	86 (4)
C(33)	1157 (6)	3667 (7)	3929 (6)	83 (4)
C(34)	1648 (5)	3053 (6)	4468 (5)	65 (3)
C(35)	2060 (4)	2094 (6)	4225 (4)	54 (2)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j U_{ij}$.

Results and Discussion

The reaction sequence for the synthesis of the manganese and rhenium alkoxide and phenoxide complexes is summarized in eqs 1–3. The hydrides were synthesized from the reaction of the metal

$$\mathrm{M_2(CO)_{10} + dppe + 1\text{-}C_3H_7OH \rightarrow \textit{fac}\text{-}(CO)_3(dppe)MH + ?} \quad (1)$$

$$\mathrm{\textit{fac}\text{-}(CO)_3(dppe)MH + HOTs \rightarrow \textit{fac}\text{-}(CO)_3(dppe)MOTs + H_2} \quad (2)$$

$$\mathrm{\textit{fac}\text{-}(CO)_3(dppe)MOTs + NaOR \rightarrow \textit{fac}\text{-}(CO)_3(dppe)MOR + NaOTs} \quad (3)$$

carbonyls with dppe in the presence of 1-propanol (eq 1). The oxidation products of the latter were not isolated. In the second step (eq 2) tosylates were obtained from the reaction of hydrides in methylene chloride with *p*-toluenesulfonic acid. Finally, the alkoxides and phenoxides were formed from the metathetical reaction between the tosylates with NaOR (eq 3). This three-step procedure proved to be a convenient and general route to the respective alkoxides and phenoxides. All these complexes have been characterized by analytical methods. **4** proved to be solvated with methanol as deduced from the IR (ν(O–H) at 3110–3050

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(8) SHELXTL-PLUS 3.43 for R3/V and R3m/V crystallographic systems: G. M. Sheldrick, University of Goettingen, FRG, and Siemens/Nicolet Analytical X-ray instruments, Inc., Madison, WI, 1988.

(9) Reaction of $[(CO)_4(dppe)M]^+BF_4^-$ with NaOR in ROH at 0 °C yielded *fac*-$(CO)_3(dppe)MC(O)OR$ in high yield. IR of *fac*-$(CO)_3(dppe)$-$MnC(O)OC_2H_5$ in hexane cm^{-1}): ν(C≡O) 2014 vs, 1946 s, 1928 s; ν(C=O) 1606 m. ^1H NMR in C_6D_6: δ 7.69–6.91 (m, 20 H, C_6H_5), 3.55 (q, 2 H, CH_2CH_3), 2.99 (m, 2 H, $-CH_2CH_2-$), 2.21 (m, 2 H, $-CH_2CH_2-$), 0.76 (t, 3 H, CH_3).

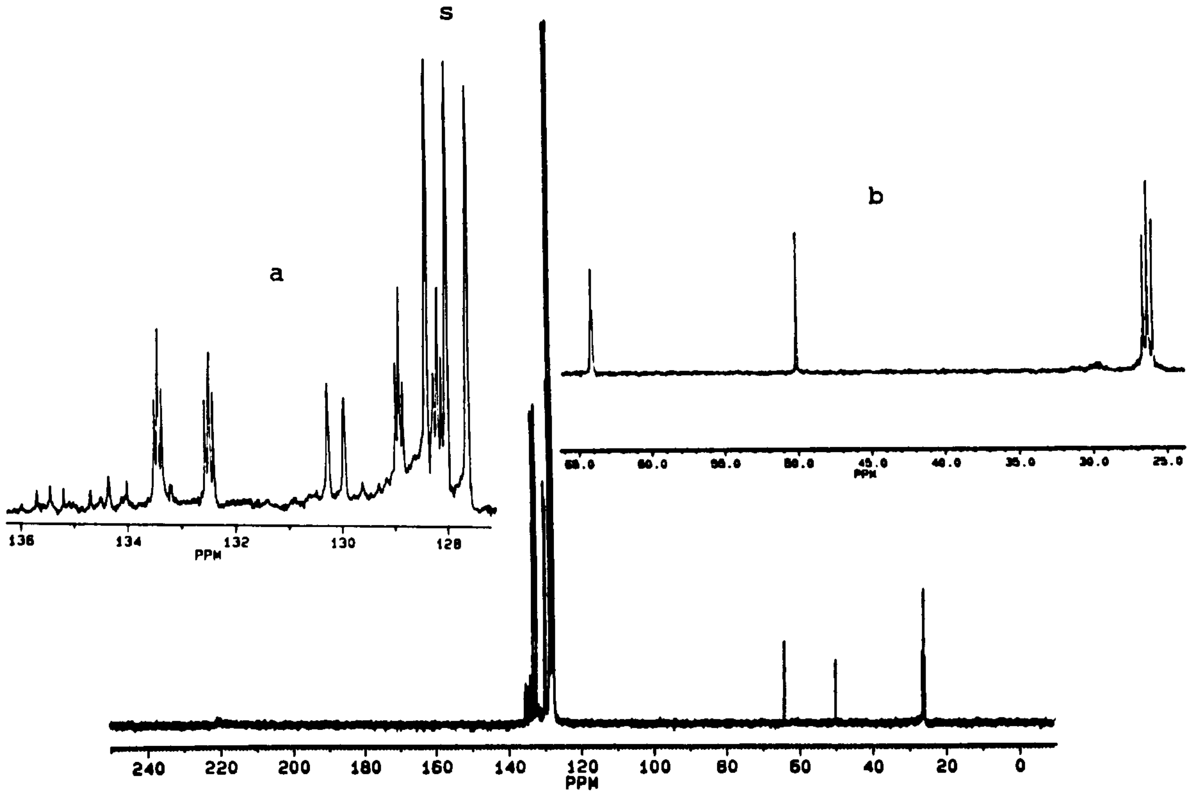

Figure 1. ^{13}C NMR spectrum of *fac*-$(CO)_3$(dppe)$MnOCH_3$ (4) in C_6D_6: (a) expanded phenyl region, 120–136 ppm; (b) expanded methyl–methylene region, 25–65 ppm.

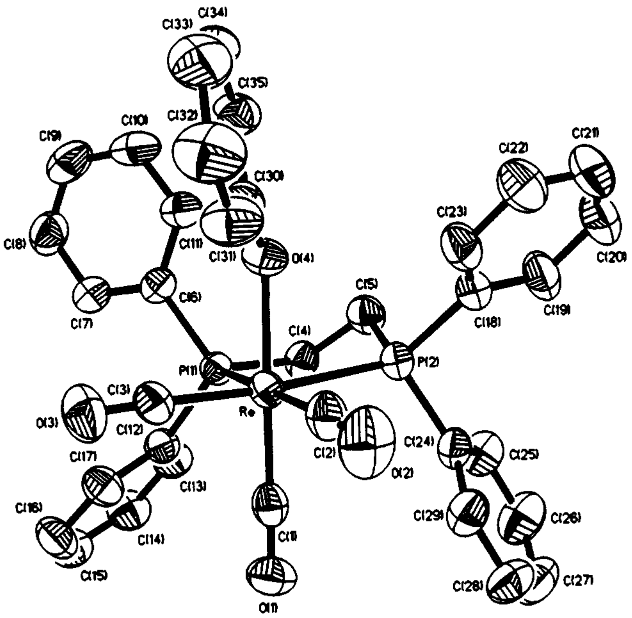

Figure 2. Perspective drawing of *fac*-$(CO)_3$(dppe)$ReOC_6H_5$ (9).

br cm^{-1}), ^1H NMR (two methyl proton resonances), and ^{13}C NMR spectra (two methyl carbon resonances). The solvation is a result of hydrogen bonding, as has been shown previously both in solution and in the solid state.[10] Phenyl resonances in the ^{13}C NMR spectra of some of the alkoxides or phenoxides in the series *fac*-$(CO)_3$(dppe)MOR were well resolved. The diastereotopic $P(C_6H_5)_2$ groups in 4, for example, appear as sharp triplets virtually coupled to two ^{31}P atoms (see Figure 1).[11] The manganese and rhenium alkoxides slowly decompose in solution.[12] The rhenium phenoxide 9 is the most stable of the *fac*-$(CO)_3$-

Table III. Selected Bond Distances and Angles for *fac*-$(CO)_3$(dppe)$ReOC_6H_5$ (9)

Bond Distances (Å)			
Re–P(1)	2.488 (2)	P(2)–C(5)	1.841 (6)
Re–P(2)	2.475 (2)	P(2)–C(18)	1.823 (7)
Re–O(4)	2.127 (4)	P(2)–C(24)	1.825 (6)
Re–C(1)	1.894 (6)	O(1)–C(1)	1.174 (8)
Re–C(2)	1.947 (6)	O(2)–C(2)	1.143 (8)
Re–C(3)	1.936 (6)	O(3)–C(3)	1.141 (8)
P(1)–C(4)	1.844 (6)	O(4)–C(30)	1.332 (7)
P(1)–C(6)	1.825 (6)	C(4)–C(5)	1.523 (9)
P(1)–C(12)	1.820 (6)		
Bond Angles (deg)			
P(1)–Re–P(2)	81.5 (1)	C(4)–P(1)–C(6)	103.9 (3)
P(1)–Re–O(4)	85.8 (1)	Re–P(1)–C(12)	117.4 (2)
P(2)–Re–O(4)	82.0 (1)	C(4)–P(1)–C(12)	103.8 (3)
P(1)–Re–C(1)	89.5 (2)	C(6)–P(1)–C(12)	101.6 (3)
P(2)–Re–C(1)	94.8 (2)	Re–P(2)–C(5)	105.7 (2)
O(4)–Re–C(1)	174.6 (2)	Re–P(2)–C(18)	120.0 (2)
P(1)–Re–C(2)	171.7 (2)	C(5)–P(2)–C(18)	103.5 (3)
P(2)–Re–C(2)	91.2 (2)	Re–P(2)–C(24)	115.7 (2)
O(4)–Re–C(2)	98.4 (2)	C(5)–P(2)–C(24)	105.5 (3)
C(1)–Re–C(2)	86.0 (3)	C(18)–P(2)–C(24)	104.9 (3)
P(1)–Re–C(3)	94.7 (2)	Re–O(4)–C(30)	131.2 (4)
P(2)–Re–C(3)	174.4 (2)	Re–C(1)–O(1)	179.1 (5)
O(4)–Re–C(3)	93.6 (2)	Re–C(2)–O(2)	172.2 (6)
C(1)–Re–C(3)	89.3 (3)	Re–C(3)–O(3)	178.2 (5)
C(2)–Re–C(3)	93.0 (3)	P(1)–C(4)–C(5)	110.7 (4)
Re–P(1)–C(4)	106.8 (2)	P(2)–C(5)–C(4)	109.6 (4)
Re–P(1)–C(6)	121.3 (2)		

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[10] (a) Kegley, S. E.; Schaverien, C. J.; Freudenberger, J. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 6563. (b) Braga, C.; Sabatino, P.; Bugno, C. D.; Leoni, P.; Pasquali, M. *J. Organomet. Chem.* **1987**, *34*, C46. (c) Kim, Y.-J.; Osakada, K.; Takenaka, A.; Yamamoto, A. *J. Am. Chem. Soc.* **1990**, *112*, 1096. (d) Kim, Y.-J.; Osakada, K.; Sugita, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1988**, *7*, 2182. (e) Osakada, K.; Kim, Y.-J.; Tanaka, M.; Ishiguro, S.; Yamamoto, A. *Inorg. Chem.* **1991**, *30*, 197.

[11] For example: (a) Jablonski, C.; Bellachioma, G.; Cardaci, G.; Reichenbach, G. *J. Am. Chem. Soc.* **1990**, *112*, 1632. (b) Schumann, H. *J. Organomet. Chem.* **1987**, *323*, 193.

[12] The rhenium alkoxides 7 and 8 appear to form the same bridging carbonate on long standing in benzene solution. Characterization of this complex will be reported elsewhere.

(dppe)MOR complexes synthesized, and an X-ray diffraction study on a suitable crystal of it was carried out. The conformation and atomic numbering scheme for **9** are shown in Figure 2. Selected bond distances and angles are found in Table III. The Re–O distance of 2.127 (4) Å in this complex is similar to the corresponding distance of 2.143 (4) Å in $[P(CH_3)_2C_6H_5]_2(CO)_2ReO(o\text{-}C_6H_4CH{=}NC_6H_5)$[13] and the mean distance of 2.153 (8) Å in $[Re(CO)_3C_6H_4(O)N{=}NC_6H_5]_2$[14] but appreciably longer than the average distance of 1.965 Å reported for *trans*-$[P(CH_3)_3]_2Re(OC_6H_5)_4$[15] due in part to the higher oxidation state of the rhenium atom in the latter. The geometry at the metal center is essentially octahedral. The Re–O–C (phenyl) angle is 131.2 (4)°, and the P(1)–Re–P(2) angle is 81.5 (1)°; the latter is similar to the corresponding angle of 82.2 (8)° in *fac*-$(CO)_3(dppe)ReC(O)Si(C_6H_5)_3$.[16]

Insertion of CO into the metal–oxygen bond of **4** and **5** in hexane under high pressure afforded *fac*-$(CO)_3(dppe)MnC(O)OCH_3$ and *fac*-$(CO)_3(dppe)MnC(O)OC_2H_5$, respectively. To the best our knowledge, this is a rare example of CO insertion into an octahedral alkoxide complex of known structure.[17] Both associative[18] and ionic[19] mechanisms have been proposed for analogous CO insertion reactions of 4- and 5-coordinated complexes, respectively. There have been no similar studies in the octahedral case, and we have not attempted to demonstrate a mechanism for our reactions. However, it is important to note that the manganese and rhenium alkoxy carbonyl complexes *fac*-$(CO)_3(dppe)MC(O)OR$[9] slowly ionize in polar solvents to produce the relatively unstable $[(CO)_4(dppe)M]^+[OR]^-$ during workup, and accordingly, polar solvents should be avoided in carrying out CO insertion reactions with these materials. Similar treatment of rhenium alkoxides **7** and **8** did not yield any rhenium alkoxy carbonyl complexes. Attempted insertion of C_2H_4 into the metal–alkoxide bond of **4** in hexane under high pressure afforded only polyethylene. Reaction of **4** with *p*-anisoyl chloride produced methyl *p*-anisate and *fac*-$(CO)_3(dppe)MnCl$. Similar reactions of alkoxides and aryloxides with acid chlorides to produce esters have been also observed by others.[20]

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Supplementary Material Available: For **9**, tables of anisotropic displacement parameters, H atom coordinates, and bond distances and angles (8 pages); a listing of observed and calculated structure factor amplitudes (25 pages). Ordering information is given on any current masthead page.

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(13) Bertolasi, V.; Ferretti, V.; Gilli, G.; Duatti, A.; Marchi, A.; Magon, L. *J. Chem. Soc., Dalton Trans.* **1987**, 613.

(14) Aleksandrov, G. G.; Derunov, V. V.; Johansson, A. A.; Struchkov, Y. T. *J. Organomet. Chem.* **1980**, *188*, 367.

(15) Edwards, P. G.; Wilkinson, G.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 2467.

(16) Anglin, J. R.; Calhoun, H. P.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 2281.

(17) For CO insertion into the metal–alkoxide bond of an octahedral tungsten–methoxide complex, see: Kundel, P.; Berke, H. *J. Organomet. Chem.* **1988**, *339*, 103.

(18) Bryndza, H. E. *Organometallics* **1985**, *4*, 1686.

(19) Rees, W. M.; Churchill, M. R.; Fettinger, J. C.; Atwood, J. D. *Organometallics* **1985**, *4*, 2179.

(20) (a) Garner, C. M.; Fernandez, J. M.; Gladysz, J. A. *Tetrahedron Lett.* **1989**, *30*, 3931. (b) Professor R. G. Bergman and co-workers of the University of California recently synthesized *fac,cis*-$(CO)_3(PPh_3)_2Re(OC_6H_4CH_3\text{-}p)$, and reaction of this with CH_3COCl gave methyl *p*-toluate (personal communication from R.G.B.).

Additions and Corrections

1991, Volume 30

R. Guilard,* N. Jagerovic, A. Tabard, P. Richard, L. Courthaudon, A. Louati, C. Lecomte,* and K. M. Kadish*: Metalloporphyrins Containing σ-Bonded Nitrogen Axial Ligands. 1. Synthesis and Characterization of Indium(III) Porphyrin Complexes. Molecular Structures of (4-Phenyltetrazolato)- and (5-Methyltetrazolato)-(2,3,7,8,12,13,17,18-octaethylporphinato)indium(III).

Page 26. Reference 64 in Table XIV was accidentally deleted and is as follows: Cornillon, J.-L.; Anderson, J. E.; Kadish, K. M. *Inorg. Chem.* **1986**, *25*, 2611.—K. M. Kadish