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Heterobimetallic Compounds Linked by Heterodifunctional Ligands: Synthesis and X-ray Crystal Structure of $(CO)_4MnMo(CO)_3[\eta^5\text{-}C_5H_4P(C_6H_5)_2]$†

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Three new heterobimetallic compounds, $(CO)_4MnMo(CO)_3[\eta^5\text{-}C_5H_4P(C_6H_5)_2]$, **1**, $(CO)_4MnMo(CO)_3[\eta^5\text{-}C_5H_4P(C_6H_4\text{-}p\text{-}CH_3)_2]$, **2**, and $(CO)_4ReMo(CO)_3[\eta^5\text{-}C_5H_4P(C_6H_4\text{-}p\text{-}CH_3)_2]$, **3**, have been prepared. **1** was prepared by reaction of $Li^+[\eta^5\text{-}C_5H_4P(C_6H_5)_2]Mo(CO)_3^-$, **4**, with $[(CO)_4MnBr]_2$. Similarly, **2** was prepared by reacting $Li^+[\eta^5\text{-}C_5H_4P(C_6H_4\text{-}p\text{-}CH_3)_2]Mo(CO)_3^-$, **5**, with $[(CO)_4MnBr]_2$, and **3** was prepared from **5** and $[(CO)_4ReBr]_2$. **1** was structurally characterized by X-ray crystallography. **1** crystallizes in the space group $Pbca$ $[D_{2h}^{15}]$ with $Z = 8$ and orthorhombic unit cell dimensions of $a = 11.782$ (2) Å, $b = 17.215$ (3) Å, and $c = 23.129$ (6) Å. The Mo–Mn bond length is 3.054 (1) Å.

Introduction

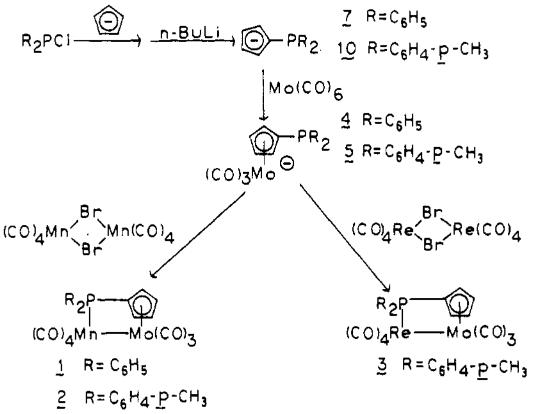
Binuclear transition-metal complexes have been known for many years, and they continue to be the focus of investigations of their synthesis and reactivity.[1] Of particular interest to us are heterobimetallic complexes. Complexes of this type include those which have two different metal fragments held together only through a metal–metal bond,[2] only through bridging ligands,[3] or through both bridging ligands and a metal–metal bond.[4] Our goal is to prepare heterobimetallic compounds which are held together through bridging ligands and metal–metal bonds and to investigate the reactivity of these compounds with hydrogen in an attempt to form heterobimetallic dihydrides which might be homogeneous catalysts for the reduction of carbon monoxide. Others have also explored the utility of heterobimetallic compounds for CO reduction.[5] In this paper we report the synthesis and characterization of $(CO)_4MnMo(CO)_3[\eta^5\text{-}C_5H_4PAr_2]$ (Ar = C_6H_5, **1**; Ar = $C_6H_4\text{-}p\text{-}CH_3$, **2**) and $(CO)_4ReMo(CO)_3[\eta^5\text{-}C_5H_4PAr_2]$ (Ar = $C_6H_4\text{-}p\text{-}CH_3$, **3**). In these heterobimetallic compounds, two different metal atoms are linked by a metal–metal bond as well as by a heterodifunctional ligand in which one metal is bonded to a cyclopentadienyl ring and the other metal is bonded to the phosphine portion of the bridging ligand. Schore and co-workers have prepared a similar heterodifunctional ligand which they used very successfully in the synthesis of a series of heterobimetallic compounds.[6]

Results and Discussion

Synthesis. The heterobimetallic compounds **1**–**3** in which molybdenum is linked to either manganese or rhenium both by a metal–metal bond and by a heterodifunctional (diarylphosphino)cyclopentadienyl ligand were synthesized in a logical stepwise fashion (Scheme I).

1-(Diphenylphosphino)cyclopentadiene,[7] **6**, was prepared by reaction of sodium cyclopentadienide with chlorodiphenylphosphine in THF as described by Davison et al.[8]

Scheme I



Since **6** slowly decomposes at room temperature, it was immediately converted to the corresponding lithium salt

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† This manuscript is dedicated to the fond memory of Rowland Pettit, one of the pioneers of transition-metal organometallic chemistry.

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7 by treatment with *n*-butyllithium. Lithium salt 7 was characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. The heterodifunctional ligand 7 had previously been used in situ for the synthesis of heterobimetallic compounds,[8] but it had not been isolated and characterized. Lithium (di-*p*-tolylphosphino)cyclopentadienide, **10**, was prepared by an analogous route and was used for the preparation of heterobimetallic complexes since the ^1H NMR spectra of its derivatives are greatly simplified compared with those of the related phenyl derivatives.

Reaction of **7** with $Mo(CO)_6$ in refluxing THF gave an impure solid that appeared by IR and ^1H NMR spectroscopy to be a 85:15 mixture of lithium [(diphenylphosphino)cyclopentadienyl]tricarbonylmolybdate, **4**, and $(CO)_5MoP(C_6H_5)_2C_5H_4^-$, **9**. The infrared spectrum of the mixture in THF had bands at 1911, 1812, 1788, and 1726 cm^{-1} assigned to **4**; for comparison, $Li^+(C_5H_5)Mo(CO)_3^-$ in THF has IR bands at 1905, 1807, 1780, and 1714 cm^{-1}.[9] In addition, the mixture had weaker IR bands at 2068, 1983, and 1947 cm^{-1} assigned to **9**; for comparison, $(CO)_5MoP(C_6H_5)_3$ in THF has IR bands at 2071, 1991, and 1948 cm^{-1}. Attempted purification of lithium salt **4** by crystallization from ethereal, aromatic, and aliphatic solvents failed. Cation exchange with $N(CH_3)_4^+Cl^-$ or $N(CH_2CH_3)_4^+Cl^-$ followed by attempted recrystallization also failed to give pure materials. Since we were unable to obtain pure salts of **4**, we attempted to characterize **4** by preparation of derivatives. However, attempts to prepare a halogenated derivative of **4** by treatment with CCl_4, *N*-bromosuccinimide, or 1,2-dibromoethane, a methylated derivative of **4** by treatment with CH_3I, or a protonated derivative of **4** by treatment with acetic acid gave complex reaction mixtures.

Similarly, reaction of **10** with $Mo(CO)_6$ gave $Li^+[\eta^5\text{-}C_5H_4P(C_6H_4\text{-}p\text{-}CH_3)_2]Mo(CO)_3^-$, **5**, contaminated with $(CO)_5MoP(C_6H_4\text{-}p\text{-}CH_3)_2C_5H_4^-$. Attempted purification or derivatization of **5** was also unsuccessful.

We initially set out to synthesize anions **4** and **5** since we thought that their reactions with halogen-bridged metal dimers would provide an excellent route to a wide variety of heterobimetallic compounds linked by the heterodifunctional (diarylphosphino)cyclopentadienyl ligand. The anions **4** and **5** can be viewed as a difunctional chelate ligand with phosphine and metal anion donor groups. The reaction of **4** with the bromine-bridged dimanganese compound $[(CO)_4MnBr]_2$[10] gave the heterobimetallic complex **1** as an orange crystalline solid in 45% yield.

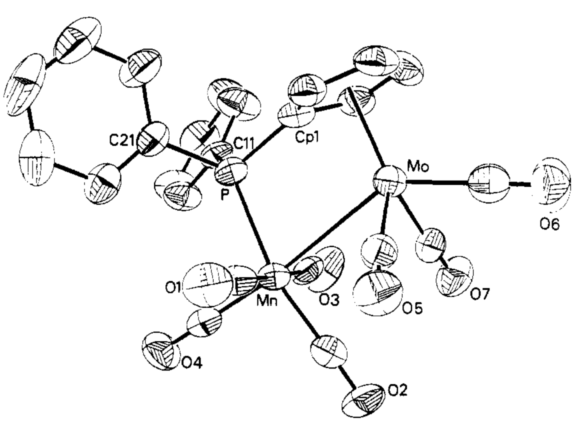

Figure 1.

The bimetallic compound **1** is simple and symmetric enough that its structure was readily determined spectroscopically. The IR spectrum of **1** in cyclohexane has seven CO bands for the seven CO ligands at 2056, 1994, 1980, 1976, 1941, 1921, and 1901 cm^{-1}. The ^1H NMR of **1** consists of multiplets at δ 8.1 for the ortho-phenyl hydrogens and at δ 7.6 for the meta- and para-phenyl hydrogens and four-line patterns at δ 5.8 and 4.7 for the two sets of protons on the cyclopentadiene coupled to each other and to phosphorus.

The ^{13}C NMR spectrum of **1** was particularly useful in structural characterization. In the room-temperature ^{13}C NMR of **1**, the molybdenum bound CO's give rise to two resonances at δ 236.8 and 227.0 in a 1:2 ratio, while the manganese bound CO's give rise to a ^{55}Mn quadrupole broadened resonance at δ 216. In the ^{13}C NMR at −40 °C, "thermal decoupling"[11] of the ^{55}Mn quadrupole results in the appearance of three peaks at δ 224.8, 222.9, and 216.2 in a 1:1:2 ratio assigned to the CO's bonded to manganese. The C_2 and C_3 carbons of the cyclopentadienyl ring appear at the normal positions of δ 91.0 and 89.2; however, the C_1 carbon bonded to the diarylphosphine group appears as a doublet (J_{PC} = 51.3 Hz) at δ 57.8. This ~32-ppm upfield shift of the C_1 carbon of the cyclopentadienyl group is undoubtedly related to the fact that it is held directly over the Mo–Mn bond.

Reaction of lithium [(di-*p*-tolylphosphino)cyclopentadienyl]tricarbonylmolybdate, **5**, with $[(CO)_4MnBr]_2$[10] similarly gave a 32% yield of the bridged bimetallic compound **2**. In the ^1H NMR of **2**, the protons ortho to phosphorus appear at δ 7.65 as a doublet of doublets (J_{PH} = 11.6 Hz, J_{HH} = 7.9 Hz), protons meta to phosphorus appear at δ 6.72 as a broad doublet and the tolyl methyl groups appear as a singlet at δ 1.84. The simplified ^1H NMR spectra of the *p*-tolyl derivatives have proven useful in studying the reactions of **2** and **3**.

Reaction of **5** with $[(CO)_4ReBr]_2$[12] gave the bridged molybdenum–rhenium compound **3** as a yellow solid in 31% yield. In the ^{13}C NMR at −50 °C, the molybdenum carbonyls give rise to two resonances in a 1:2 ratio at δ 230.7 and 223.9 and the rhenium carbonyls appear in 1:2:1 ratio at δ 192.4 (d, J_{PC} = 47 Hz, CO trans to P), 189.7 (d, J_{PC} = 9.2 Hz), and 187.4 (d, J_{PC} = 4.6 Hz). At 30 °C the ^{13}C resonances of the molybdenum carbonyls were broadened, and at 63 °C these resonances were not observable but the rhenium carbonyls remained sharp at all temperatures.

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Table I. Bond Distances and Bond Angles in $(CO)_4\overline{MnMo(CO)_3[\eta^5\text{-}C_5H_4P}(C_6H_5)_2]$[a]

Bond Distances (Å)

Mo-Mn-P	3.054 (1)	Cp1-Cp2	1.423 (7)
Mn-P	2.278 (1)	Cp2-Cp3	1.394 (7)
Mn-C(1)	1.845 (5)	Cp3-Cp4	1.423 (7)
Mn-C(2)	1.833 (5)	Cp4-Cp5	1.392 (7)
Mn-C(3)	1.847 (5)	Cp5-Cp1	1.444 (6)
Mn-C(4)	1.792 (5)	Cp1-P	1.797 (5)
Mo-C(5)	2.004 (6)	C(11)-P	1.829 (5)
Mo-C(6)	1.957 (5)	C(21)-P	1.837 (5)
Mo-C(7)	1.970 (5)	C(11)-C(12)	1.388 (7)
O(1)-C(1)	1.139 (6)	C(12)-C(13)	1.365 (7)
O(2)-C(2)	1.151 (6)	C(13)-C(14)	1.356 (8)
O(3)-C(3)	1.137 (6)	C(14)-C(15)	1.361 (8)
O(4)-C(4)	1.151 (7)	C(15)-C(16)	1.389 (7)
O(5)-C(5)	1.137 (7)	C(16)-C(11)	1.375 (7)
O(6)-C(6)	1.162 (7)	C(21)-C(22)	1.388 (7)
O(7)-C(7)	1.149 (6)	C(22)-C(23)	1.369 (8)
Mo-Cp1	2.377 (5)	C(23)-C(24)	1.358 (9)
Mo-Cp2	2.333 (5)	C(24)-C(25)	1.370 (9)
Mo-Cp3	2.334 (5)	C(25)-C(26)	1.394 (8)
Mo-Cp4	2.335 (5)	C(26)-C(21)	1.367 (7)
Mo-Cp5	2.356 (5)	CENT-Mo	2.015 (3)

Bond Angles (deg)

Mo-Mn-P	77.3 (0)	C(5)-Mo-C(6)	77.9 (2)
C(1)-Mn-P	90.9 (1)	C(5)-Mo-C(7)	98.2 (2)
C(2)-Mn-P	165.7 (2)	C(6)-Mo-C(7)	81.2 (2)
C(3)-Mn-P	87.5 (2)	Mo-C(5)-O(5)	174.2 (5)
C(4)-Mn-P	97.3 (2)	Mo-C(6)-O(6)	179.2 (5)
Mn-C(1)-O(1)	176.5 (4)	Mo-C(7)-O(7)	175.4 (4)
Mn-C(2)-O(2)	178.5 (4)	C(1)-Mn-Mo	87.1 (2)
Mn-C(3)-O(3)	176.4 (5)	C(2)-Mn-Mo	88.6 (2)
Mn-C(4)-O(4)	179.5 (3)	C(3)-Mn-Mo	91.2 (2)
Mn-P-C(11)	116.4 (2)	C(4)-Mn-Mo	174.1 (2)
Mn-P-C(21)	121.1 (2)	C(5)-Mo-Mn	75.7 (2)
Mn-P-Cp1	103.6 (2)	C(6)-Mo-Mn	141.2 (2)
C(11)-P-C(21)	103.5 (2)	C(7)-Mo-Mn	75.0 (1)
P-Cp1-Cp2	128.2 (3)	P-C(11)-C(12)	119.1 (4)
P-Cp1-Cp5	122.0 (4)	P-C(11)-C(16)	123.3 (4)
Cp1-Cp2-Cp3	108.2 (4)	P-C(21)-C(22)	120.0 (4)
Cp2-Cp3-Cp4	108.8 (5)	P-C(21)-C(26)	120.7 (4)
Cp3-Cp4-Cp5	108.0 (4)	⟨av⟩ phenyl(1)	119.7 (5)
Cp4-Cp5-Cp1	108.1 (4)	⟨av⟩ phenyl(2)	120.0 (5)
Cp5-Cp1-Cp2	106.9 (4)	CENT-Cp1-P	165.1 (6)

[a] CENT = Cp ring centroid.

This broadening might be due to exchange between the two different types of molybdenum carbonyls.

X-ray Structure of 1. While the IR and NMR spectra of 1 established its overall structure, we were interested to see what distortions the heterodifunctional ligand caused in this cyclic bimetallic compound. Consequently, the X-ray crystal structure of 1 was determined. Bond lengths and angles are listed in Table I.

Table II. Least-Squares Planes for $(CO)_4\overline{MnMo(CO)_3[\eta^5\text{-}C_5H_4P}(C_6H_5)_2]$[a,b]

atoms	dev	atoms	dev
Plane I: $0.0593X + 0.5500Y + 0.8330Z = 7.3163$			
Cp1*	0.012 (7)	Cp4*	−0.004 (7)
Cp2*	−0.014 (7)	Cp5*	−0.005 (7)
Cp3*	0.011 (7)	P	−0.420 (4)
C(2)	−0.096		
Plane II: $0.5080X + 0.6931Y + 0.5114Z = 5.5900$			
Mo*	0.008 (1)	C(1)	1.835 (7)
Mn*	−0.007 (1)	C(2)	−0.096 (7)
P*	0.008 (4)	C(3)	−1.851 (7)
CENT*	−0.008 (7)	C(4)	0.057 (7)
C(11)	−1.417 (8)	C(5)	1.498 (7)
C(21)	1.455 (8)	C(6)	0.052 (7)
Cp(1)	−0.049 (7)	C(7)	−1.503 (7)

[a] Atoms marked with an asterisk were used in calculating the planes. [b] Dihedral angle (I/II) = 90.8 (4)°.

The ORTEP diagram of 1 (Figure 1) clearly demonstrates that the heterodifunctional (phosphino)cyclopentadienyl ligand links the manganese and molybdenum atoms. The manganese and molybdenum atoms are also linked by a single bond of 3.054 (1) Å. For comparison, the bond length of the metal–metal bond in $(C_5H_5)(CO)_3Mo\text{–}Mn(CO)_5$ is 3.08 Å,[13] and the average of the metal–metal bond lengths of $[(C_5H_5)Mo(CO)_3]_2$[14] (3.23 Å) and of $Mn_2(CO)_{10}$[15] (2.93 Å) is 3.08 Å. The molybdenum, manganese, phosphorous, and cyclopentadiene centroid form a nearly planar slightly strained ring system. Two carbonyls on manganese, two carbonyls on molybdenum, and the two phenyl rings are arranged nearly symmetrically on either side of this plane (Table II). The distance from molybdenum to the phosphine substituted cyclopentadiene carbon (Cp1) is ~0.04 Å longer than the distance to the other four cyclopentadiene carbons.

The slight strain of the ring system gives rise to several distortions from the geometry expected for acyclic systems. The P–Mn–Mo angle is contracted to 77.3° and is the only major distortion from idealized octahedral geometry about manganese. The phosphorous atom is bent down 0.42 Å (Table II) from the plane of the cyclopentadiene ring toward the manganese atom. The angle between the centroid of the cyclopentadiene ring, molybdenum, and manganese is contracted to 102.0°; for comparison the Cp–Mo–Mo angle in $[C_5H_5Mo(CO)_3]_2$ is 117.6°,[16] and the Cp–Mo–Hg angle in $(C_5H_5)(CO)_3Mo\text{–}HgCl$ is 111.95°.[17] This distortion of the idealized four-legged piano stool geometry about molybdenum in 1 leads to a wider angle of 141.2° between manganese–molybdenum and the CO "trans" to manganese [Mn–Mo–C(6)] and a smaller angle of 98.2° about molybdenum and the CO's "trans" to one another [C(5)–Mo–C(7)]. For comparison, the corresponding Mo–Mo–CO angle is 128.2° and the CO–Mo–CO angle between "trans" CO's is 105.9° in $[(C_5H_5)Mo(CO)_3]_2$.[14] There are no significant interactions between manganese and the carbonyls on molybdenum (C–Mn distances ≥3.17 Å) or between molybdenum and the carbonyls on manganese (C–Mo distances ≥3.49). Moreover, the carbonyl ligands are not significantly bent; the most distorted carbonyl is a molybdenum carbonyl cis to manganese (<Mo–C(5)–O(5) = 174.2°).

Stability of 1 under H_2. In our continuing search for heterobimetallic dihydrides, we have looked for interaction between 1 and H_2. Cyclohexane solutions of 1 under high pressure of H_2 were examined by high-pressure IR spectroscopy as a function of temperature. No change in the IR spectrum of 1 was seen even upon heating to 145 °C under 1200 psi of H_2. Slow decomposition of 1 occurs above 170 °C, and the integrated intensities of the metal carbonyl bands decrease. The major band in the IR spectrum of decomposed 1 is seen at ~1960 cm^{-1}.

The stability of rhenium–molybdenum compound 3 under H_2 was studied by heating THF solutions of 3 under high hydrogen pressure, cooling the solutions, and exam-

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ining samples of the solutions at room temperature and atmospheric pressure. No change in the IR spectrum of **3** was noted upon heating at 90 °C for 4 h under 1400 psi of H_2. Further heating at 120 °C for 14 h led to 10% decomposition. Complete decomposition to nonmetal carbonyl-containing material occurred when **3** was heated at 150 °C for 24 h under 1400 psi of H_2.

Thus **1** and **3** thermally decompose when heated under H_2, and no evidence was obtained for formation of a bimetallic dihydride resulting from addition of hydrogen across the metal–metal bond.

In the hope that a catalytic, undetectable amount of heterobimetallic dihydride might be in equilibrium with **1** and that it might act as a CO hydrogenation catalyst, we heated **1** under high pressure of synthesis gas. When a toluene solution of **1** (6 mM) was heated at 180 °C for 22 h under 1400 psi of a 1:1 CO/H_2 mixture, a small amount of decomposition of **8** was noted by IR spectroscopy but no CH_4 or CH_3OH were detected by gas chromatography (detection limit 0.1%). Similarly, when a toluene solution of rhenium–molybdenum compound **3** (5 mM) was heated at 205 °C for 16 h under 1200 psi of 1:1 CO/H_2, a small amount of decomposition of **3** occurred but no CH_4 or CH_3OH were observed.

An attempt to intercept heterobimetallic dihydrides in equilibrium with **1** or **3** by reaction with cyclohexene was made but no hydrogenation of cyclohexene was observed. When a toluene solution of **1** (3.3 mM) and cyclohexene (20 mM) was heated at 165 °C under 1400 psi of H_2 for 27 h, about 50% decomposition of **1** was observed by IR, but no cyclohexane was detected by gas chromatography (detection limit 0.1%). Similarly, when a toluene solution of **3** (2.6 mM) and cyclohexene (25 mM) was heated at 170 °C under 1200 psi of H_2 for 20 h, no decomposition of **3** or formation of cyclohexane was observed.

The reaction of heterobimetallic compounds **1–3** with H_2 might be expected to require prior metal–metal bond cleavage or ligand dissociation to generate a site for the activation of hydrogen. Their failure to react with hydrogen may reflect the difficulty of generating such reactive sites in these molecules. We are now synthesizing heterobimetallic compounds in which one of the metals is a coordinatively unsaturated d^8 metal capable of oxidatively adding H_2 without prior ligand dissociation or metal–metal bond cleavage.

Experimental Section

General Data. Solvents were distilled from sodium benzophenone ketyl prior to use. All reactions were run under dry nitrogen, except where indicated. ^1H NMR spectra were recorded on a Bruker WH-270 (270 MHz) spectrometer; ^{13}C NMR (50.10 MHz) and ^{31}P NMR (80.76 MHz) spectra were recorded on a JEOL FX-200 spectrometer. ^{31}P chemical shifts are referenced in parts per million from 85% H_3PO_4; downfield chemical shifts are recorded as positive. Infrared spectra were recorded on either a Beckman 4230 infrared spectrometer or a Digilab FTS-20 interferometer. Elemental analyses were performed by Schwarzkopf Microanalytical Labs (Woodside, N.Y.).

1-(Diphenylphosphino)cyclopentadiene (6) was prepared by a modification of the method of Mathey and Lampin.[7] Freshly distilled chlorodiphenylphosphine (19.5 g, 88.2 mmol) was added by cannula to a solution of $Na(C_5H_5)\cdot DME$[18] (15.70 g, 88.2 mmol) in THF (180 mL) at −78 °C and then stirred for 30 min at room temperature. The solution was filtered through Celite in a drybox, and the solvent was evaporated on a vacuum line to give a pale orange oil (17.9 g, 81% yield). The ^1H NMR of **6** was in agreement with the reported spectrum.[7]

1- and 2-(Di-*p*-tolylphosphino)cyclopentadiene (8A and 8B). Reaction of $Na(C_5H_5)\cdot DME$[18] (10.1 g, 57 mmol) with freshly distilled $P(C_6H_4\text{-}p\text{-}CH_3)_2Cl$[19] (14.1 g, 57 mmol) following the procedure used in the preparation of **6** gave a 2:1 mixture of **8A/8B** (14.4 g, 91%) as a red-brown oil: ^1H NMR (270 MHz, $CDCl_3$) δ 7.26 (t, $J_{HH} \approx J_{PH} \approx 7.2$ Hz, ortho), 7.13 (d, $J = 8.3$ Hz, meta), 6.38–6.60 (m, 3 H of C_5H_5P), 3.09 (s, 0.7 H, CH_2 of **8B**), 3.0 (s, 1.3 H, CH_2 of **8A**), 2.32 (s, CH_3).

Lithium (Diphenylphosphino)cyclopentadienide (7). Since **6** decomposes if left standing at room temperature for several hours, it is imperative that the deprotonation be carried out on freshly prepared samples of **6**. At −78 °C *n*-BuLi (31 mL, 1.51 M in hexane, 46.6 mmol, 1.2 equiv) was added to a solution of **6** (9.70 g, 38.8 mmol) in toluene (100 mL). When the solution was vigorously stirred at room temperature for 15 min, a yellow precipitate formed. The precipitate was collected by filtration in a drybox and washed with hexane to give **7** as a yellow powder (9.47 g, 95% yield): mp 167–170 °C dec; ^1H NMR (270 MHz, THF-d_8) δ 7.15 (m, meta and para) 7.34 (m, ortho), 5.95–5.91 (m, C_5H_4); ^{13}C NMR (50.1 MHz, THF-d_8) δ 145.6 (d, $J_{PC} = 12.2$ Hz, ipso), 133.8 (d, $J_{PC} = 18.3$ Hz, ortho), 128.0 (d, $J_{PC} = 6.1$ Hz, meta), 127.1 (s, para), 113.0 (d, $J_{PC} = 20.8$ Hz, C_2 of C_5H_4P), 107.3 (d, $J_{PC} = 9.8$ Hz, C_3 of C_5H_4P), 105.8 (s, C_1 of C_5H_4P); ^{31}P NMR (80.76 MHz, THF) δ −18.1 (s).

Lithium (Di-*p*-tolylphosphino)cyclopentadienide (10). Reaction of **8** (8.90 g, 32 mmol) with *n*-BuLi (35 mL, 1.35 M in hexane, 47.6 mmol, 1.5 equiv) following a procedure similar to that described for **7** gave **10** as a pale yellow solid (8.70 g, 78% yield): mp 175–178 °C dec; ^1H NMR (270 MHz, THF-d_8) δ 7.20 (t, $J_{HH} \approx J_{PH} \approx 7.3$ Hz, ortho), 6.97 (d, $J = 7.7$ Hz, meta), 5.95–5.91 (m, C_5H_4), 2.25 (s, CH_3); ^1H NMR (270 MHz, C_6D_6) δ 7.51 (t, $J_{HH} \approx J_{PH} \approx 7.2$ Hz, ortho), 7.04 (d, $J = 7.5$ Hz, meta), 5.65 and 5.37 (2 br s, C_5H_4P), 2.13 (s, CH_3); ^{13}C NMR (50.10 MHz, THF-d_8) δ 136.6 (s, para), 133.9 (d, $J_{PC} = 18.3$ Hz, ortho), 128.8 (d, $J_{PC} = 6.1$ Hz, meta), 112.9 (d, $J = 20.7$ Hz, C_2 of C_5H_4P), 107.0 (d, $J = 8.6$ Hz, C_3 of C_5H_4P), 21.2 (s, CH_3), ipso carbon and C_1 of C_5H_4P not observed; ^{31}P NMR (80.76 MHz, THF-d_8) δ −19.0 (s).

Lithium [(Diphenylphosphino)cyclopentadienyl]tricarbonylmolybdate (4). A solution of $Mo(CO)_6$ (3.50 g, 13.3 mmol) and **7** (3.40 g, 13.3 mmol) in THF (100 mL) was refluxed for 19 h. The solvent was removed on a vacuum line to give 5.62 g of a tan solid. The IR in THF consisted of bands (cm^{-1}, relative absorption) assigned to **4** at 1911 (1.0), 1812 (0.88) 1788 (0.70) and 1726 (0.59); bands assigned to $Li^+(CO)_5MoP(C_6H_5)_2(C_5H_4)^-$ were at 2068 (0.08), 1983 (0.21), and 1947 (0.53). NMR indicated that the ratio of **4**:Li^+ $(CO)_5MoP(C_6H_5)_2(C_5H_4)^-$ was about 85:15. ^1H NMR indicated that the solid was a THF solvate of **4** containing ~1.6 molecules of THF/Mo: ^1H NMR (270 MHz, C_6D_6) δ 7.60 (m, ortho), 7.13 (m, meta and para), 5.40 (br s, C_5H_4P). Also observed in this spectrum were resonances from THF at δ 3.73 and 1.56 and low intensity broad singlets at δ 5.50 and 5.31 which are probably due to $Li^+(CO)_5MoP(C_6H_5)_2(C_5H_4)^-$: ^1H NMR (270 MHz, THF-d_8 δ 7.32 (m, ortho), 7.15 (m, meta and para), 5.09 and 4.94 (2 m, C_5H_4P); ^{13}C NMR (50.10 MHz, THF-d_8, 0.07 M $Cr(acac)_3$) δ 235.4 (s, $Mo(CO)_3$) 141.3 (d, $J_{PC} = 12.8$ Hz, ipso), 133.9 (d, $J_{PC} = 18.3$ Hz, ortho), 128.1 (s, meta and para), 96.4 (br s, C_1 of C_5H_4P), 94.3 (d, $J_{PC} = 14.6$ Hz, C_2 of C_5H_4P), 88.8 (s, C_3 of C_5H_4P); ^{31}P NMR (80.76 MHz, THF) δ −16.3 (s).

Lithium [(Di-*p*-tolylphosphino)cyclopentadienyl]tricarbonylmolybdate (5). A solution of $Mo(CO)_6$ (4.63 g, 17.5 mmol) and **10** (5.00 g, 17.5 mmol) in THF (130 mL) was refluxed for 22 h. The solvent was evaporated on a vacuum line to give 9.09 g of a golden yellow solid. ^1H NMR indicated the solid was a nearly pure THF solvate of **5** containing ~2.5 molecules of THF/Mo: ^1H NMR (270 MHz, C_6D_6) δ 7.61 (t, $J_{HH} \approx J_{PH} \approx 7.5$ Hz, ortho), 7.04 (d, $J = 9.2$ Hz, meta), 5.46 (pseudotriplet, $J = 1.8$ Hz, 2 H of C_5H_4P), 5.43 (pseudodoublet, $J = 1.8$ Hz, 2 H of C_5H_4P), 2.09 (s, CH_3), resonances for THF at δ 3.72 and 1.57; ^{13}C (50.10 MHz, THF-d_8, 0.07 M ($Cr(acac)_3$) δ 235.7 (s, $Mo(CO)_3$), 137.6 (s, para), 133.9 (d, $J_{PC} = 18.3$ Hz, ortho), 129.1 (br s, meta), 21.5 (s, CH_3). Other observed resonances and tentative assignments include (1) a singlet at δ 128.3 which we believe is the upfield resonance of a doublet due to the ipso carbon; the downfield portion of the doublet is probably obscured by the peak at δ 129.1, (2) δ 97.7 (br s, C_1 of C_5H_4P), (3) δ 94.1 (d, $J_{PC} = 11.0$ Hz, C_2 of

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Table III. Crystallographic Data and Nicolet R3 Data Collection Parameters (24 °C)

formula	$MnMoC_{24}H_{14}PO_7$
cryst system	orthorhombic
space group	*Pbca* [D_{2h}^{15} (No. 61)]
a, Å	11.782 (2)
b, Å	17.215 (3)
c, Å	23.129 (6)
V, Å^3	4691.3 (2.3)
Z	8
d_{calcd}, g/cm^3	1.6921 (2)
crystal size, mm	0.20 × 0.25 × 0.35
radiation	graphite monochromated Mo Kα (λ = 0.710 73 Å)
μ, cm^{-1}	10.22
scan type	ω
2θ units	$3° \leqslant 2\theta \leqslant 42°$, $\pm h,k,l$
scan range, deg	$1.9 + \Delta\ (\alpha_1 - \alpha_2)$
no. of rflns measd	5404
no. of unique data, ($F^2 \geqslant 2.0\sigma(F)^2$)	2431
std reflns	3/141 (no decay observed)
$R(F_o)$	0.034
$Rw(F_o)$	0.028
esd of unit weight	1.200
largest shift/error on final cycle	0.093
largest peak in final diff map, e/Å^3	0.29

C_5H_4P), and (4) δ 88.8 (s, C_3 of C_5H_4P). IR (THF): 1912 (s), 1813 (s), 1790 (m), 1723 (s) cm^{-1}.

In various preparations, the purity of **5** varied from 95% to 80%; the major impurity is probably $Li^+(CO)_5MoP(C_6H_4\text{-}p\text{-}CH_3)_2C_5H_4^-$.

$(CO)_4MnMo(CO)_3[\eta^5\text{-}C_5H_4P(C_6H_5)_2]$ (1). A solution of **4** (3.00 g) in THF (75 mL) was added by cannula to a suspension of $[(CO)_4MnBr]_2$[10] (150 g, 3.0 mmol) in THF at 0 °C. The solution was stirred at 0 °C for 3 h, and the solvent was evaporated on a vacuum line. The residue was purified by column chromatography (silica gel, 9:1 hexane/ether) to give **1** as an orange solid (1.62 g, 45% based on $[(CO)_4MnBr]_2$, mp 184–187 °C dec): ^1H NMR (270 MHz, acetone-d_6) δ 8.1 (m, ortho), 7.57 (m, meta and para), 5.77 (pseudoquartet, $J \approx 2.1$ Hz, 2 H, C_5H_4P), 4.70 (pseudoquartet, $J \approx 2.0$ Hz, 2 H, C_5H_4P); ^1H NMR (270 MHz, C_6D_6) δ 7.72–7.63 (m, ortho), 6.84 (m, meta and para), 4.53 (pseudoquartet, $J \approx 2.1$ Hz, 2 H, C_5H_4P), 3.80 (pseudoquartet, $J \approx 2.1$ Hz, 2 H, C_5H_4P); ^{13}C NMR (50.10 MHz, acetone-d_6, 0.07 M $Cr(acac)_3$, 25 °C) δ 236.8 (s, Mo(CO)), 227.0 (s, $Mo(CO)_2$), 215.9 (quadrupole broadened $^{55}Mn(CO)_4$), 134.2 (d, $J_{PC} = 42.2$ Hz, ipso), 132.7 (s, para), 132.3 (d, $J_{PC} = 12.8$ Hz, ortho), 130.3 (d, $J_{PC} = 10.9$ Hz, meta), 91.0 (br s, C_2 or C_3 of C_5H_4P), 89.2 (d, $J = 9.2$ Hz, C_2 or C_3 of C_5H_4P), 57.8 (d, $J = 51.3$ Hz, C_1 of C_5H_4P). A ^{13}C NMR spectrum obtained at −40 °C caused "thermal decoupling"[11] of the ^{55}Mn quadrupole, and the $Mn(CO)_4$ resonances appeared at δ 224.8, 222.9, and 216.2 (relative intensities 1:1:2) in addition to the other resonances described above: IR (cyclohexane): 2056 (m), 1994 (m), 1980 (s), 1976 (s), 1941 (m), 1921 (m), 1901 (m) cm^{-1}. Anal. Calcd for $C_{24}H_{14}MnMoO_7P$: C, 48.35; H, 2.37. Found: C, 48.47; H, 2.35.

$(CO)_4MnMo(CO)_3[\eta^5\text{-}C_5H_4P(C_6H_4\text{-}p\text{-}CH_3)_2]$ (2). Reaction of molybdenum anion **5** (3.30 g) with $[(CO)_4MnBr]_2$[10] (1.25 g, 2.52 mmol) using the procedures used in the preparation of **1** gave **2** (1.00 g, 32% yield) as an orange solid: mp 169–170 °C dec; ^1H NMR (270 MHz, C_6D_6) δ 7.65 (dd, $J_{PH} = 11.6$ Hz, $J_{HH} = 7.9$ Hz, ortho), 6.72 (br d, peak separation 7 Hz), 4.55 (m, 2 H, C_5H_4P), 3.93 (m, 2 H, C_5H_4P), 1.84 (s, CH_3); ^{13}C NMR (50.10 MHz, CD_2Cl_2, 0.07 M $Cr(acac)_3$) δ 231.4 (s, Mo(CO)), 225.0 (s, $Mo(CO)_2$), 215.8 (quadrupole broadened $^{55}Mn(CO)_4$), 142.3 (s, para), 131.2 (d, $J_{PC} = 12.2$ Hz, ortho), 129.9 (d, $J_{PC} = 10.7$ Hz, meta), 130.6 (tentatively assigned as one resonance of the ipso tolyl doublet; other resonance

Table IV. Final Positional and Thermal Parameters[a] and Their Esd's for Non-Hydrogen Atoms of $(CO)_4MnMo(CO)_3[\eta^5\text{-}C_5H_4P(C_6H_5)_2]$

atom	x[b]	y[b]	z[b]	U_{11}[c]	U_{22}[c]	U_{33}[c]	U_{12}[c]	U_{13}[c]	U_{23}[c]
Mo(1)	2894 (1)	3943 (1)	709 (1)	44 (1)	40 (1)	40 (1)	3 (1)	1 (1)	−1 (1)
Mn(1)	5018 (1)	2930 (1)	775 (1)	46 (1)	34 (1)	30 (1)	2 (1)	3 (1)	−2 (1)
P(1)	5160 (1)	3675 (1)	1586 (1)	49 (1)	36 (1)	31 (1)	−1 (1)	0 (1)	−2 (1)
O(1)	6236 (3)	4128 (3)	80 (2)	85 (3)	55 (2)	60 (2)	−14 (2)	16 (2)	8 (2)
O(2)	4270 (3)	2114 (2)	−297 (1)	85 (3)	86 (3)	39 (2)	5 (2)	−10 (2)	−23 (2)
O(3)	3851 (4)	1734 (2)	1494 (2)	96 (3)	63 (3)	66 (3)	−38 (2)	−12 (3)	20 (2)
O(4)	7165 (3)	2076 (2)	912 (2)	57 (3)	77 (3)	72 (3)	24 (2)	−4 (2)	−2 (2)
O(5)	3946 (3)	4158 (2)	−527 (2)	76 (3)	72 (3)	45 (3)	−4 (2)	10 (2)	10 (2)
O(6)	810 (3)	4272 (2)	−86 (2)	75 (3)	89 (3)	102 (3)	9 (3)	−30 (3)	4 (3)
O(7)	1954 (3)	2258 (2)	595 (2)	69 (3)	58 (2)	76 (3)	−16 (2)	−9 (2)	−6 (2)
C(1)	5740 (4)	3684 (3)	343 (2)	61 (4)	39 (3)	37 (3)	1 (3)	7 (3)	−6 (3)
C(2)	4549 (4)	2437 (3)	115 (2)	50 (4)	47 (3)	44 (3)	9 (3)	6 (3)	3 (3)
C(3)	4265 (4)	2204 (3)	1221 (2)	57 (4)	46 (4)	37 (4)	−2 (3)	−12 (3)	−12 (3)
C(4)	6327 (5)	2412 (3)	860 (2)	58 (4)	38 (3)	35 (3)	−6 (3)	2 (3)	−5 (3)
C(5)	3615 (4)	4057 (3)	−71 (3)	49 (4)	37 (3)	53 (4)	4 (3)	−6 (3)	−1 (3)
C(6)	1581 (5)	4147 (3)	213 (2)	65 (4)	52 (4)	65 (4)	2 (3)	0 (3)	−4 (3)
C(7)	2340 (4)	2869 (3)	624 (2)	47 (3)	54 (3)	42 (3)	2 (3)	−9 (3)	−2 (3)
C(11)	5179 (4)	3157 (3)	2276 (2)	55 (4)	41 (3)	26 (3)	−6 (3)	1 (3)	−4 (2)
C(12)	5946 (4)	2554 (3)	2355 (2)	69 (4)	60 (4)	35 (3)	13 (3)	5 (3)	−1 (3)
C(13)	5963 (5)	2135 (3)	2856 (2)	95 (5)	59 (4)	46 (4)	22 (3)	−5 (4)	6 (3)
C(14)	5213 (5)	2293 (3)	3285 (2)	95 (5)	78 (4)	47 (4)	−7 (4)	−5 (4)	15 (3)
C(15)	4473 (5)	2897 (3)	3235 (2)	90 (5)	114 (5)	40 (4)	28 (4)	19 (3)	19 (4)
C(16)	4461 (5)	3329 (3)	2727 (2)	90 (5)	78 (4)	36 (4)	29 (4)	7 (3)	5 (3)
C(21)	6297 (4)	4397 (3)	1666 (2)	50 (3)	38 (3)	38 (3)	−7 (3)	−8 (3)	4 (3)
C(22)	6154 (5)	5024 (3)	2036 (3)	82 (5)	59 (4)	72 (4)	−18 (4)	−4 (4)	−16 (4)
C(23)	7010 (5)	5554 (3)	2104 (3)	110 (5)	58 (4)	94 (5)	−22 (4)	−27 (5)	−13 (4)
C(24)	8002 (5)	5471 (3)	1812 (3)	100 (5)	61 (4)	116 (6)	−44 (4)	−49 (5)	27 (4)
C(25)	8163 (5)	4860 (4)	1440 (3)	53 (5)	87 (5)	86 (5)	−18 (4)	−10 (4)	23 (4)
C(26)	7294 (4)	4319 (3)	1370 (2)	60 (4)	47 (3)	57 (4)	−6 (3)	−11 (3)	5 (3)
Cp(1)	3889 (4)	4252 (2)	1573 (2)	58 (4)	34 (3)	37 (3)	1 (3)	3 (3)	−8 (3)
Cp(2)	2764 (4)	4021 (3)	1714 (2)	55 (3)	56 (3)	39 (3)	−3 (3)	13 (3)	−8 (3)
Cp(3)	2017 (4)	4568 (3)	1485 (2)	52 (4)	77 (4)	52 (4)	17 (3)	13 (3)	−8 (3)
Cp(4)	2653 (5)	5134 (3)	1176 (2)	79 (5)	40 (3)	51 (4)	17 (3)	−0 (3)	−7 (3)
Cp(5)	3798 (4)	4947 (3)	1226 (2)	57 (4)	40 (3)	45 (3)	4 (3)	−3 (3)	−4 (3)

[a] The form of the expression defining the thermal ellipsoids is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [b] ×10^4. [c] ×10^3.

is obscured by either the δ 131.2 or the δ 129.9 peak), 89.4 (d, J_{PC} = 9.1 Hz, C_3 of C_5H_4P), 88.0 (d, J_{PC} = 18.1 Hz, C_2 of C_5H_4P), 57.3 (d, J_{PC} = 50.5 Hz, C_1 of C_5H_4P), 21.0 (s, CH_3); IR (cyclohexane) 2059 (m), 1996 (m), 1978 (s), 1973 (s), 1939 (m), 1919 (m), 1900 (m) cm^{-1}. Anal. Calcd for $C_{26}H_{18}MnMoO_7P$: C, 50.02; H, 2.91. Found: C, 50.45; H, 3.25.

$(CO)_4ReMo(CO)_3[\eta^5\text{-}C_5H_4P(C_6H_4\text{-}p\text{-}CH_3)]$ (3). A solution of 5 (183 mg) in THF (30 mL) was added by cannula to a suspension of $[(CO)_4ReBr]$[12] (80 gm, 0.10 mmol) in 10 mL of THF at −78 °C and stirred for 1 h at −78 °C and 10 min at room temperature. The solvent was removed by rotary evaporation, and the residue was purified by preparative TLC (silica gel, 1:1 hexane/ether) which gave **10** (50 mg, 31% based on $[(CO)_4ReBr]_2$, $R_f \approx 0.4$, lower yellow band) as a yellow solid: mp 167–169 °C dec; ^1H NMR (270 MHz, C_6D_6) δ 7.58 (dd, J_{PH} = 12.0 Hz, J_{HH} = 8.4 Hz, ortho), 6.70 (dd, J_{HH} = 8.0 Hz, J_{PH} = 2.0 Hz, meta), 4.66 (pseudoquartet, $J \approx 2.1$ Hz, 2 H, C_5H_4P), 4.02 (pseudoquartet, $J \approx 2.1$ Hz, 2 H, C_5H_4P), 1.84 (s, CH_3); ^{13}C NMR (50.10 MHz, CD_2Cl_2, 0.07 M $Cr(acac)_3$, 25 °C) δ 224.2 (br s, $Mo(CO)_3$), 192.4 (d, J_{PC} = 47.7 Hz, Re(CO) trans to P), 189.7 (d, J_{PC} = 9.2 Hz, $Re(CO)_2$), 187.4 (d, J_{PC} = 4.6 Hz, Re(CO) cis to P), 142.7 (s, para), 131.8 (d, J_{PC} = 13.8 Hz, ortho), 130.0 (d, J_{PC} = 12.2 Hz, meta), 128.0 (d, J_{PC} = 49.0 Hz, ipso), 89.7 (d, J_{PC} = 7.6 Hz, C_2 or C_3 of C_5H_4P), 89.2 (d, J_{PC} = 9.2 Hz, C_2 or C_3 of C_5H_4P), 61.6 (d, J_{PC} = 59.7 Hz, C_1 of C_5H_4P), 21.1 (s, CH_3). At −50 °C, the Mo carbonyls appeared in a 1:2 ratio at δ 230.7 and 223.9. IR (cyclohexane): 2081 (m), 2006 (m), 1992 (s), 1974 (s), 1939 (m), 1910 (m), 1886 (m) cm^{-1}. Anal. Calcd for $C_{26}H_{18}MoO_7PRe$: C, 41.33; H, 2.40. Found: C, 41.35; H, 2.22.

High-pressure reactions under H_2 and H_2/CO mixtures were carried out in a stainless-steel bomb; details of the experimental procedure have been published elsewhere.[20] The stability of 1 under 950–1420 psi of H_2 at 25–190 °C was measured by using a high-pressure infrared cell. We thank Dr. Stanley W. Polichnowski and Ms. Norma Lafferty of the Tennessee Eastman Co. for carrying out the high pressure infrared experiments.

X-ray Data Collection and Structure Determination. Crystals of $(CO)_4MnMo[\eta^5\text{-}C_5H_4P(C_6H_5)_2]$ suitable for diffraction measurements were obtained by slow cooling of a hot toluene solution. The crystals were mounted in thin-walled glass capillaries, immobilized on an aluminum pin with beeswax, and fixed in a eucentric goniometer head. Unit-cell dimensions were determined and refined from the angular settings of 25 reflections, $20 \leq 2\theta \leq 30°$, chosen to sample all regions of reciprocal space. The space group *Pbca* was uniquely determined from the systematic absences observed in the data. Crystal data and data collection parameters are listed in Table III. All data processing was performed on a Data General Nova 4 using the Nicolet SHELXTL program library (version 3.0). An empirical absorption correction was performed by using the azimuthal data from four ψ-scan reflections collected in 10° increments, maximum/minimum intensity ratio was 1.16 ± 0.01. Neutral atom scattering factors were calculated by the standard procedures, and anomolous dispersion corrections were applied to all non-hydrogen atoms.

The structure was solved by direct methods, and all non-hydrogen atoms were located by subsequent difference Fourier syntheses phased by the metal atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom locations were calculated and not refined by using a "riding" model with *d*(C–H) = 0.96 Å and isotropic thermal parameters of 1.2 times the isotropic equivalent for the carbon atom to which it was attached. A correction for extinction was applied to the data. The largest peak found on the final difference Fourier map, 0.29 e/Å^3, was located equidistant from C(6) and O(6). A table of calculated vs. observed structure factors is available as supplementary material. Final positional and thermal Parameters and their esd's are listed in Table IV.

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Registry No. **1**, 83334-33-2; **2**, 83334-34-3; **3**, 83334-35-4; **4**, 83334-36-5; **5**, 83334-37-6; **6**, 83334-39-8; **7**, 83272-80-4; **8A**, 83334-40-1; **8B**, 83334-41-2; **9**, 83334-38-7; **10**, 83334-42-3; Ph_2PCl, 1079-66-9; $Na(C_5H_5)$, 4984-82-1; $P(C_6H_4\text{-}p\text{-}CH_3)_2Cl$, 1019-17-2; $Mo(CO)_6$, 13939-06-5; $[(CO)_4Mnbr]_2$, 18535-44-9; $[(Co)_4ReBr]_2$, 15189-54-5.

Supplementary Material Available: A table of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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[20] Casey, C. P.; Bullock, R. M. *J. Mol. Catal.* **1982**, *14*, 283–292.