Synthesis and Thermolysis of Neutral Metal Formyl Complexes of Molybdenum, Tungsten, Manganese, and Rhenium

Dorothy H. Gibson,* Kathryn Owens, Santosh K. Mandal, William E. Sattich, and Jaime O. Franco

Department of Chemistry, University of Louisville, Louisville, Kentucky 40292

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The synthesis and characterization of seven new formyl complexes are described, together with improved procedures for the preparation of four others. The compound types are $(\eta\text{-}C_5H_5)M(CO)_2(L)CHO$ [**2**: M = Mo, L = PPh_3 or $P(OPh)_3$; M = W, L = PPh_3], $(\eta\text{-}C_5Me_5)Mo(CO)_2(L)CHO$ [**4**: L = $P(OPh)_3$ or $P(OEt)_3$] and $M(CO)_3(L^1)(L^2)CHO$ [**6**: M = Mn, L^1 = CO, L^2 = PPh_3 or $P(OPh)_3$; M = Mn or Re, L^1 = L^2 = PPh_3 or $P(OPh)_3$]. All were prepared from the corresponding carbonyl cations (**1**, **3**, and **5**) by reductions with Et_4NBH_4 using procedures which allow the isolation of all except $Mn(CO)_4[P(OPh)_3]CHO$; yields averaged 89%. Thermolyses of compounds of types **2** and **4** occur with preferential loss of the phosphorus-containing ligand. Those of type **6** compounds occur with loss of CO, except for $Mn(CO)_3(PPh_3)_2CHO$ which loses one phosphine ligand.

Introduction

The possible intermediacy of catalyst-bound formyls in syngas transformations[1] has prompted efforts to prepare and study the chemistry of transition-metal formyl complexes over more than a decade. A number of anionic formyl complexes, somewhat fewer neutral compounds, and a very few cationic complexes have been prepared.[2] However, because of the lability of the compounds in solution, many of them were generated at low temperatures rather than being isolated and were characterized primarily by ^1H NMR spectroscopy.

As well as providing useful models for catalytic intermediates in CO reductions, it seemed to us that formyl complexes, especially the neutral compounds, might be developed as useful substrates for organometallic synthesis. In order to do this, we set out several years ago[3] to find synthetic methods which would not only provide good yields of neutral formyls but would allow their isolation; the latter task seemed particularly critical in efforts to use the compounds as reagents. Methods of synthesis for neutral formyls, some of which have been reported since our work began, are (a) hydride transfer to a metal carbonyl cation,[4] (b) oxidative addition of formaldehyde and/or rearrangement of an η^2-formaldehyde complex,[5] (c) hydrolysis of thiolato carbene cations,[6] (d) carbon monoxide "insertion" reactions of metal hydrides,[7] and (e) electrochemical reductions of metal carbonyl cations done in the presence of a tin hydride.[8] The first method has been the one most generally used. In most cases, main-group metal "super hydrides" have been used previously as the hydride source; recently, however, Nelson[9] demonstrated that a transition-metal hydride can be effective also. We have used a mild borohydride in our reactions with metal carbonyl cations and have introduced some variations into the syntheses which allow, in almost all cases, for the pure formyl complex to be precipitated from solution as it is formed. The formyl complexes and their cationic precursors are shown in Chart I. Seven of the formyls are new; improved procedures have been established for the other four. All but one of the compounds have been isolated.

Chart I. Metal Formyl Complexes and Cationic Precursors

cation	formyl complex
$(\eta\text{-}C_5H_5)M(CO)_3(L)^+BF_4^-$ **1a–c**	*trans*-$(\eta\text{-}C_5H_5)M(CO)_2(L)CHO$ **2a–c**
a: M = Mo, L = PPh_3	
b: M = Mo, L = $P(OPh)_3$	
c: M = W, L = PPh_3	
$(\eta\text{-}C_5Me_5)Mo(CO)_3(L)^+BF_4^-$ **3a,b**	*cis*- and *trans*-$(\eta\text{-}C_5Me_5)Mo(CO)_2(L)CHO$ **4a,b**
a: L = $P(OPh)_3$	
b: L = $P(OEt)_3$	
$M(CO)_4(L^1)(L^2)^+BF_4^-$ **5a–f**	$M(CO)_3(L^1)(L^2)CHO$[a] **6a–f**
a: M = Mn, L^1 = CO, L^2 = PPh_3[a]	
b: M = Mn, L^1 = L^2 = PPh_3[b]	
c: M = Mn, L^1 = CO, L^2 = $P(OPh)_3$[a]	
d: M = Mn, L^1 = L^2 = $P(OPh)_3$[b]	
e: M = Re, L^1 = L^2 = $P(OPh)_3$[b]	
f: M = Re, L^1 = L^2 = PPh_3[b]	

[a] Cis formyl isomer. [b] Mer, trans formyl isomer.

Results and Discussion

Synthesis and Characterization of Cations. All of the cations, except **1b** and **5c,e**, are new, although hexafluorophosphate or other analogues of some of them have been reported previously. Satisfactory elemental analyses have been obtained for all new compounds and for those which had not been fully characterized previously; IR carbonyl stretching frequencies, and ^1H and ^{13}C NMR spectral data are reported for all cations. Compounds **1b,c** and **3a,b** were prepared by hydride abstraction followed by addition of a phosphine or phosphite ligand to a coordinatively unsaturated cation as illustrated for **1b**:

$$(\eta\text{-}C_5H_5)Mo(CO)_3H \xrightarrow[CH_2Cl_2]{Ph_3C^+BF_4^-} [(\eta\text{-}C_5H_5)Mo(CO)_3{}^+BF_4^-] \xrightarrow{P(OPh)_3} (\eta\text{-}C_5H_5)Mo(CO)_3[P(OPh)_3]^+BF_4^-$$

1b

The others (**1a**, **5a–f**) were made by halide abstraction, using $AgBF_4$, followed by carbon monoxide addition; this

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route is illustrated below for **1a**:

$$(\eta\text{-}C_5H_5)Mo(CO)_2(PPh_3)Cl \xrightarrow[CO,\ CH_2Cl_2]{AgBF_4} (\eta\text{-}C_5H_5)Mo(CO)_3(PPh_3)^+BF_4^-$$

1a

Our procedure for **1a** is simpler and provides a higher product yield than the high-temperature, high-pressure technique reported by Treichel[10] for the corresponding hexafluorophosphate salt. The procedure used for **1b** was similar to the one described by Beck,[11] except that we did not isolate the coordinatively unsaturated cation; no product yield was reported previously. The procedure of Treichel[10] for the hexafluorophosphate analogue of **1c** gave a 23% yield of the cation by halide abstraction from $(\eta\text{-}C_5H_5)W(CO)_3Cl$; our method yields **1c** in 41% yield from $W(CO)_6$ and does not require isolation of intermediates in the synthesis. Our procedure for **5a** is simpler than the previous one[12] and proceeds in much higher yield. Similarly, **5b** was prepared in better yield and more easily than by the previous method.[13] Our procedure for **5c** is somewhat easier than the previous one,[12] and the product yield is improved as well. Our procedure for **5d** utilizes the same starting material as the one described by Berke;[14] it requires just one reaction sequence, but the product yield is not as high as that in the earlier procedure. The method of Berke[15] for **5e** uses the same starting material as ours and gives a higher product yield; the earlier method is somewhat less convenient since it requires high temperatures and pressures. The preparation of **5f** is much easier than the procedures for chlorometalate salts of this cation reported previously[16] and provides a much higher product yield. Compounds **3a,b** or other salts of these cations have not been reported previously.

Cations **5b,d–f** have trans geometry as evidenced[17] by their IR spectra which show a very intense band at 2033 ± 37 cm^{-1} together with one or two very weak bands at higher frequency. Also, their carbon spectra show the carbonyl resonances as one triplet except for **5d** which gives a broad singlet.

Synthesis of the Formyl Complexes. Reactions of the cations described above with Et_4NBH_4 have been used to prepare all of the formyl complexes; methanol was used as a solvent in most cases.[18] All of the formyls, except **4b** and **6c**, precipitated from solution in pure form as they were generated. It has not been necessary to rigorously purify solvents or to take special care in excluding air in these preparations. Although most of the formyl complexes are quite labile in solution, the dried solids can be manipulated in air for short periods of time without deterioration. Except in the synthesis of **6c**, reaction times were short, typically about 10 min, product yields were very high, averaging 89% for the compounds studied. The purified formyl complexes can be stored at −30 °C for several days without deterioration. Since our preliminary report of this method,[3a] with the preparation of compound

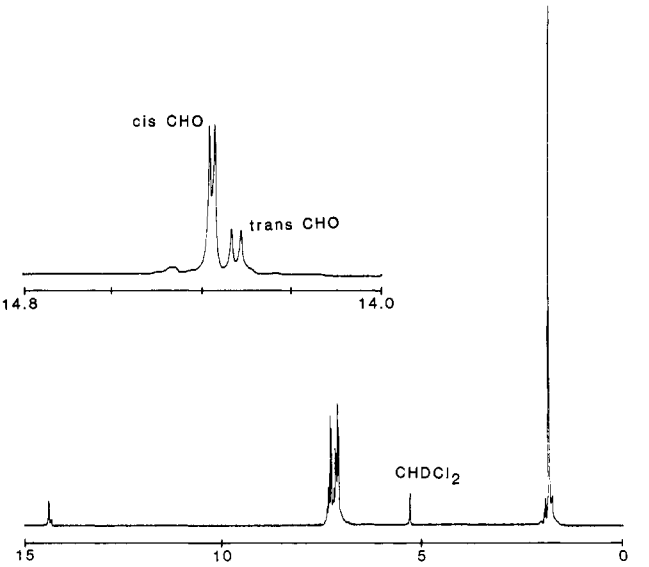

Figure 1. ^1H NMR spectrum of compound **4a** in CD_2Cl_2 at −30 °C.

2a, Lapinte[19] and Leoni[20] have used similar procedures to isolate some related chromium and molybdenum formyl complexes in good yields also.

Compound **2a** was first prepared by Gladysz[4,21] by reaction of the hexafluorophosphate analogue of cation **1a** with $LiEt_3BH$; the formyl complex was generated in dichloromethane solution at low temperature and could not be isolated because of its extreme lability in solution. Our procedure allows **2a** to be isolated easily and in pure form. Compounds **2b,c** and **4a,b** are new formyl complexes closely related to **2a** and were prepared by almost identical procedures. Compound **4b** did not precipitate from solution as it was formed; however, it is particularly robust and could be purified by recrystallization. Among these formyls, only **4b** is crystalline; the others are always obtained as powders and never appear crystalline.

In the series **6a–f**, compounds **6b**,[22] **6d**,[23] and **6e**[15] have been reported previously, but our syntheses represent some improvements in product yields as well as in isolation and purification procedures. This is particularly evident with **6e**, since the previous method did not provide an analytically pure sample. Compounds **6a** and **6c** are more labile than the others in this series, and we have not yet isolated **6c**; the yield of this product has been estimated, based on its subsequent conversion to a metallacycle.[3b]

Characterization of Formyl Complexes. Acceptable elemental analyses have been obtained on **2a,c** and **6e**, but several of the formyl complexes darken after standing at room temperature for several hours so that spectral methods have been used, exclusively, for their characterization.

Evidence for the presence of a formyl ligand is most easily found from IR spectral data. The complexes which we have prepared show the carbonyl stretching frequency of the formyl group at 1575–1612 cm^{-1}; for compounds **2b**, **4a**, and **6c–e** the position of this band must be approxi-

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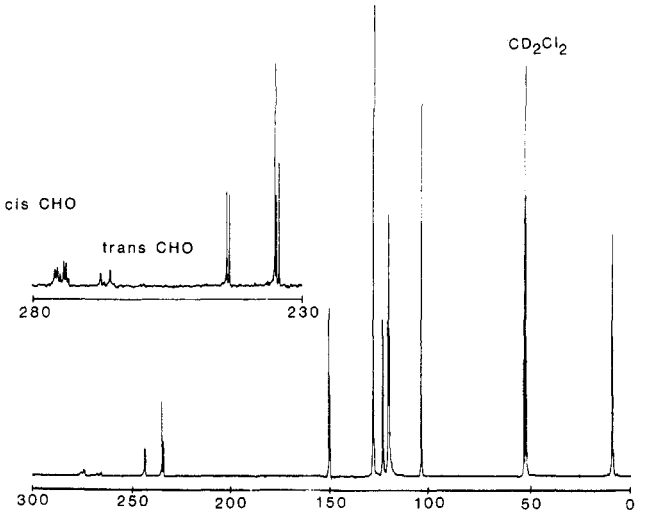

Figure 2. ^{13}C NMR spectrum of compound **4a** in CD_2Cl_2 at −30 °C.

mated because of the overlap, as noted previously,[24] with bands of the triphenyl phosphite ligands. The carbonyl stretching frequency position is sensitive to ancillary ligands on the metal; substitution of CO by more highly σ-donating ligands causes significant shifts to lower wavenumbers and suggests enhanced contributions of the carbenoid resonance form of the formyl complexes. IR DRIFTS spectra of all the compounds show two weak bands for the ν_{CH} of the formyl group at 2702 ± 50 and 2525 ± 50 cm^{-1}. These bands have also been reported[2] for some other formyl complexes, and Cole-Hamilton[25] has shown, through deuterium labeling of the formyl C–H bond, that these absorptions are due to the formyl group. Thus, it appears that they can be diagnostic for the presence of this ligand as the similar ones, at slightly higher frequencies, are diagnostic for the presence of carbon-bound aldehyde groups in organic compounds.

The ^1H NMR spectra of the formyl complexes show resonance signals for the formyl proton in the region δ 13.38–15.71 (see, for example, Figure 1). The tungsten complex **2c** has a lower field resonance for this proton than **2a**; similarly the rhenium complexes **6e** and **6f** have lower field resonances for this proton than their manganese analogues **6d** and **6b**. There seems to be little effect of the metals' ancillary ligands on the formyl proton resonances.

The formyl carbon resonances occurred in the region δ 247.5–283.2 (see, for example, Figure 2). The position within this range, for a given series of compounds, is dependent upon the metal center (tungsten raises the chemical shift relative to molybdenum, and rhenium raises it relative to manganese) and the ancillary ligands on the metal (a phosphite ligand raises the chemical shift when compared to the analogous phosphine and substitution of phosphine or phosphite for CO lowers the chemical shift).

Stereochemical assignments in the series **2a–c** and **4a,b** are determined from the pattern of resonances of the terminal carbonyl ligands; for reasons of symmetry, the trans isomers have equivalent carbonyl ligands and show a single doublet for this carbon due to coupling to the phosphorus atom. Cis isomers show two distinct resonances. The trans to cis ratios of the formyl carbonyl resonances were in good agreement with the ratios determined from their proton spectra. With compounds **2b,c** and **4a,b** there is evidence of conformational isomerism in the observed pattern of formyl carbon resonances; both trans and cis (where visible) isomers show two resonance signals for the formyl carbon. In the trans isomers, both signals are doublets, whereas the signals for the cis isomers are both multiplets. The proton spectra of the compounds show nothing unusual; a simple doublet is observed for each geometric isomer. There is also some temperature dependence of proton–phosphorus coupling constants as observed by Lapinte[19] for related systems (and attributed to the syn–anti isomerism about the metal–formyl carbon bond); however, this group did not report anything unusual about the carbon spectra of the compounds. Further work is in progress with our compounds to establish the nature of these conformational isomers.

Stereochemical assignments of compounds **6a–f** are based on the patterns of carbonyl stretching frequencies in the infrared spectra together with carbon spectral data for the compounds. Cis-disubstituted compounds (**6a,c**) show the characteristic weak, strong, very strong, and strong pattern of intensities for compounds having this geometry.[26] The mer,trans complexes (**6b,d–f**) show the characteristic weak, strong, and medium pattern of intensities for their stretching frequencies,[27] together with relative intensities of 2:1 for the ^{13}C NMR resonance signals of their terminal carbonyls. We have seen no evidence for the existence of conformational isomers in this series.

Thermolysis of Formyl Complexes. The thermal decomposition reactions of formyl complexes have received a great deal of attention,[2,4,9,19,20,28] and radical processes are indicated in a number of instances. We have studied the thermal decomposition reactions of **2a–c**, **4a,b**, and **6a–f** under very similar conditions in order to identify the thermolysis products and to try to establish whether these were primary products or compounds formed as a result of secondary reactions. All thermolyses have been conducted at relatively low temperatures, in CD_2Cl_2, for comparative purposes; in a few cases, other conditions have been used to provide additional comparisons.

Compounds **2a**, **2c**, and **4a** decompose with loss of the phosphorus-containing ligand, exclusively; this cannot be easily attributed to a labilizing effect of the formyl ligand on a particular site since **4a** is predominantly the cis isomer and the others are predominantly (**2c**) or exclusively (**2a**) trans. Also, the cis to trans ratio of **4a** isomers did not appear to change during thermolysis. When the thermolyses of **2a** and **4a** were conducted at higher temperatures, significant amounts of the corresponding phosphine or phosphite hydride complexes were formed. Compound **4b** is quite robust, and its thermolysis was very slow at room temperature; $(\eta\text{-}C_5Me_5)Mo(CO)_3H$ was visible in the early stages of decomposition (after 2 days at room temperature), but the phosphite hydride was present also. After $2^1/_2$ days additional time, at 40 °C, **4b** was converted to $(\eta\text{-}C_5Me_5)Mo(CO)_2[P(OEt)_3]H$ completely. The related molybdenum formyl complex prepared by Lapinte[19] also decomposes, preferentially, to the tricarbonyl hydride complex. The chromium and molybdenum complexes, $(\eta\text{-}C_5Me_5)M(CO)_2[P(OMe)_3]CHO$, prepared by Leoni[20] decompose very slowly, as does **4b**, so that only phosphite

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hydrides are observed as final products. Thus, it appears that, in every case in these two series, the formyl complexes decompose with preferential loss of the phosphorus-containing ligand, although this ligand may subsequently displace CO.

In the series **6a–e**, the preferential mode of thermal decomposition in CD_2Cl_2 involves loss of CO, except for **6b**, which decomposes slowly (12 h at room temperature) with loss of one phosphine ligand. In benzene, compound **6b** is even more stable, showing only slight decomposition after 12 h. Compound **6e** gives a small amount of the hydride containing one phosphite ligand, but the major product results from loss of CO. Thermolysis of **6f** in CD_2Cl_2 leads to $ClRe(CO)_4(PPh_3)$ and $ClRe(CO)_3(PPh_3)_2$, whereas thermolysis of solid **6f** in a sealed tube led, cleanly, to $HRe(CO)_3(PPh_3)_2$. Interestingly, this hydride was stable to CD_2Cl_2 under the conditions of the thermolysis of **6f**. Compound **6b** has a checkered history with regard to its decomposition reactions. Thus, Gladysz[4,21] found no known hydrides, halides, or dimers when the compound was allowed to decompose (presumably in the solution in which it was formed). Kochi[28d] reported that the compound decomposed, in the solution in which it was prepared (which also contained $(n\text{-}Bu)_3SnH$) to $HMn(CO)_3(PPh_3)_2$. In neither case were these investigators able to study the isolated formyl complex. Thus, the course of formyl decomposition reactions depends, very much, on the manner in which the reactions are performed and on the presence of other reagents.

Experimental Section

General Data. Reagent grade methanol and acetonitrile were dried over type 3A molecular sieves. Hexane was dried over concentrated H_2SO_4 and then fractionally distilled. Reagent grade anhydrous ether, acetone, and dichloromethane were used as received. Spectroscopic measurements were obtained on the following instruments: ^1H NMR, Varian XL-300, EM-390, and T-60; ^{13}C NMR, Varian XL-300; IR, Nicolet SX-170 FT-IR and Perkin-Elmer 599B. NMR chemical shifts are reported in parts per million downfield (+) or upfield (−) from tetramethylsilane. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Et_4NBH_4 was prepared by the method described previously.[29] $AgBF_4$, CD_2Cl_2, C_6D_6, pentamethylcyclopentadiene, triphenylphosphine, triphenyl phosphite, and triethyl phosphite were obtained from Aldrich and used directly. $Mo(CO)_6$, $W(CO)_6$, $[(\eta\text{-}C_5H_5)Mo(CO)_3]_2$, $Mn_2(CO)_{10}$, and $Re_2(CO)_{10}$ were obtained from Pressure Chemical Co. and used directly.

$(\eta\text{-}C_5H_5)Mo(CO)_3(PPh_3)^+BF_4^-$ (1a). $(\eta\text{-}C_5H_5)Mo(CO)_2(PPh_3)Cl$[10] (3.00 g, 5.83 mmol) was dissolved in 50 mL of CH_2Cl_2, and the resulting solution was maintained at 22–28 °C, with stirring, while CO was bubbled through it. $AgBF_4$ (0.308 g, 1.54 mmol) was added to the solution, and stirring was continued. After 1.5, 2.5, and 3.5 h, equivalent additional portions of $AgBF_4$ were added to the mixture. After 5 h, reaction was shown to be complete as evidenced by disappearance of the IR spectral bands of the chloride complex. The mixture was filtered through a Celite pad, and the resulting filtrate was concentrated to about 20 mL on a rotary evaporator. The resulting solution was then poured into 100 mL of hexane maintained at 0 °C to effect precipitation of the cation complex. The crude product was collected by filtration and recrystallized from CH_2Cl_2/hexane (activated charcoal is sometimes useful in removing residual silver salts). After the solution was chilled overnight at −30 °C, yellow crystals were obtained (1.88 g, 54% yield).

Anal. Calcd for $C_{26}H_{20}O_3PMoBF_4$: C, 52.56; H, 3.39; P, 5.21. Found: C, 52.72; H, 3.30; P, 5.02. IR: ν_{CO} (Nujol mull) 2055 (m), 1990 (m), 1960 (s) cm^{-1} [lit.[10] for the PF_6 salt: ν_{CO} 2025 (s), 1995 (m), 1955 (s) cm^{-1}]. ^1H NMR (acetone-d_6): δ 7.6 (m, phenyl), 6.1 (s, C_5H_5). ^{13}C NMR [acetone-d_6 with $Cr(acac)_3$]: δ 227.80 (s), 226.20 (d, J_{PC} = 29.9 Hz), 134.25 (d, J_{PC} = 10.6 Hz), 133.55 (d, J_{PC} = 2.8 Hz), 131.88 (d, J_{PC} = 51.0 Hz), 130.88 (d, J_{PC} = 11.1 Hz), 97.34 (s).

$(\eta\text{-}C_5H_5)Mo(CO)_3[P(OPh)_3]^+BF_4^-$ (1b). $Mo(CO)_6$ (1.50 g, 5.70 mmol) was added to 50 mL of CH_3CN, and the mixture was refluxed for 16 h; an IR spectrum of the yellow solution showed ν_{CO} at 1910 (s) and 1785 (s, br) cm^{-1}, indicating that conversion to $Mo(CO)_3(CH_3CN)_3$ was complete.[30] Solvent was removed on a rotary evaporator, 50 mL of methanol followed by 0.38 g (5.7 mmol) of cyclopentadiene was added, and the mixture was stirred for 5 h. An IR spectrum then showed bands at 2025 (m) and 1930 (s) cm^{-1}, indicating that conversion to $(\eta\text{-}C_5H_5)Mo(CO)_3H$ was complete. Solvent was removed, under vacuum on a Schlenk line, and the residue was triturated with hexane; the combined hexane extracts were filtered through $MgSO_4$, and then hexane was removed, leaving 0.84 g (3.40 mmol, 60% yield) of the hydride.[31] The hydride was added to 15 mL of CH_2Cl_2 chilled to −78 °C under nitrogen. $Ph_3C^+BF_4^-$ (1.06 g, 3.2 mmol) was added in small portions until IR spectra of the solution indicated that the hydride had been consumed (some dimerization of the hydride always occurs so that less than an equivalent amount of trityl cation is needed). $P(OPh)_3$ (1.09 g, 3.50 mmol) was dissolved in 5 mL of CH_2Cl_2 and the solution added, dropwise, to the violet solution; the reaction mixture was then allowed to warm to room temperature slowly. The red solution was then concentrated to 10 mL on a rotary evaporator and poured into 90 mL of cold anhydrous ether to effect precipitation of the cation complex.[32] The crude product was recrystallized from CH_3OH/ether (1:10); the yield was 0.70 g (32%).

IR: ν_{CO} (Nujol mull) 2077 (s), 2020 (m), 1980 (sh), 1970 (s) cm^{-1} [lit.[32] ν_{CO} 2083 (vs), 2026 (m), 1987 (sh), 1979 (vs), 1975 (sh) cm^{-1}]. ^1H NMR (CD_2Cl_2): δ 7.38 (m, phenyl), 5.61 (s, C_5H_5). ^{13}C NMR (CD_2Cl_2): δ 222.66 (d, J_{PC} = 40.9 Hz), 221.57 (d, J_{PC} = 3.2 Hz), 150.14 (d, J_{PC} = 9.7 Hz), 131.12 (d, J_{PC} = 1.3 Hz), 127.55 (d, J_{PC} = 1.8 Hz), 121.19 (d, J_{PC} = 4.4 Hz), 94.64 (s).

$(\eta\text{-}C_5H_5)W(CO)_3(PPh_3)^+BF_4^-$ (1c). $W(CO)_6$ (5.00 g, 14.2 mmol) was slurried in 375 mL of CH_3CN in a quartz vessel under nitrogen and then the mixture irradiated for 4 h with a 450-W mercury-arc lamp (Ace-Hanovia). After this time, solvent was removed on a rotary evaporator to yield a yellow-brown powder. An IR spectrum of the crude product indicated that it was primarily $W(CO)_3(CH_3CN)_3$ [ν_{CO} 1910 (s) and 1788 (s) cm^{-1}] with a small amount of $W(CO)_4(CH_3CN)_2$ [ν_{CO} 2020 (w), 1895 (s), and 1835 (m) cm^{-1}].[33] The mixture was taken up in 75 mL of THF, and 10 mL of freshly distilled cyclopentadiene was added to it under nitrogen. This mixture was then heated to 50–55 °C, with stirring, for an hour to give a dark red solution containing $(\eta\text{-}C_5H_5)W(CO)_3H$ [ν_{CO} 2020 (m) and 1920 (s) cm^{-1}]. Solvent was again removed on a rotary evaporator, and the resulting deep red oil was dissolved in 100 mL of CH_3CN. To the stirred acetonitrile solution, maintained under nitrogen, was added 5.00 g (19.1 mmol) of triphenylphosphine followed by $Ph_3C^+BF_4^-$ (3.00 g, 9.1 mmol) added in small portions during the next 5 h. After this time, IR spectra indicated complete conversion of the hydride to product. The solution was treated with activated charcoal and then filtered through Celite to give a yellow-brown solution which was concentrated to about 50 mL on a rotary evaporator. Ether (100 mL) was added to the solution to precipitate the crude product; the product was recrystallized from 1:1 acetone/ether to give 3.94 g [41% yield from $W(CO)_6$] of $(\eta\text{-}C_5H_5)W(CO)_3(PPh_3)^+BF_4^-$ as a yellow powder.

Anal. Calcd for $C_{26}H_{20}O_3PWBF_4$: C, 45.79; H, 2.95; P, 4.54. Found: C, 45.31; H, 3.02; P, 4.52. IR: ν_{CO} (Nujol) 2060 (s), 1970 (m), 1940 (s) cm^{-1} [lit.[10] for the PF_6 salt (Nujol): ν_{CO} 2040 (s), 1985 (m), 1945 (s) cm^{-1}]. ^1H NMR (CD_2Cl_2): δ 7.45 (m), 5.81 (s). ^{13}C NMR (CD_2Cl_2): δ 213.77 (d, J_{PC} = 23.1 Hz), 213.36 (d, J_{PC} = 3.4 Hz), 133.35 (d, J_{PC} = 10.4 Hz), 133.07 (d, J_{PC} = 3.3 Hz), 130.23 (s), 130.09 (s), 94.39 (s).

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(η-C_5Me_5)Mo(CO)$_3$[P(OPh)$_3$]$^+$BF$_4^-$ (3a). (η-C_5Me_5)Mo(CO)$_3$H[34] (2.17 g, 6.86 mmol) was dissolved in 25 mL of CH_2Cl_2 and the solution cooled to −78 °C under nitrogen. $Ph_3C^+BF_4^-$ (2.49 g, 7.55 mmol) was added in small portions during 20 min. A solution containing $P(OPh)_3$ (2.34 g, 7.54 mmol) in 5 mL of CH_2Cl_2 was added to the violet solution, and the solution was gradually warmed to room temperature and stirred for 2 h. The red solution was concentrated to 10 mL, 90 mL of anhydrous ether was added, and the resulting solution was chilled to −30 °C overnight to effect precipitation. The crude product was recrystallized from CH_3OH/ether and afforded yellow crystals (yield 3.15 g, 64% based on the hydride).

Anal. Calcd for $C_{31}H_{30}O_6PMoBF_4$: C, 52.27; H, 4.24; P, 4.35. Found: C, 52.35; H, 4.19; P, 3.84. IR: ν_{CO} (Nujol mull) 2058 (s), 1990 (s), 1970 (vs) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.20 (m), 2.18 (d, J_{PH} = 1.1 Hz). ^{13}C NMR (CD_2Cl_2): δ 226.88 (d, J_{PC} = 40.5 Hz), 225.32 (s), 150.85 (d, J_{PC} = 12.5 Hz), 121.09 (d, J_{PC} = 4.0 Hz), 130.76 (s), 127.14 (s), 109.89 (s), 11.00 (s).

(η-C_5Me_5)Mo(CO)$_3$[P(OEt)$_3$]$^+$BF$_4^-$ (3b). (η-C_5Me_5)Mo(CO)$_3$H[34] (2.28 g, 7.2 mmol) was dissolved in 25 mL of CH_2Cl_2 maintained at −78 °C under nitrogen. Solid $Ph_3C^+BF_4^-$ (2.38 g, 7.2 mmol) was added to the solution slowly, with stirring, during 30 min. To the resulting violet solution was added 1.51 g (9.1 mmol) of $P(OEt)_3$, and the mixture was then allowed to warm to room temperature. After being stirred for an additional 2 h, the red solution was concentrated on a rotary evaporator to 10 mL, 90 mL of ether was added, and the mixture was chilled to −30 °C to precipitate the product. Recrystallization of the crude product from 1:9 CH_2Cl_2/ether afforded yellow crystals, 2.93 g, 72%.

Anal. Calcd for $C_{19}H_{30}O_6PMoBF_4$: C, 40.17; H, 5.32. Found: C, 39.98; H, 5.37. IR: ν_{CO} (Nujol) 2047 (m), 1974 (sh), 1957 (vs) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 4.14 (quintet), 2.07 (d, J_{PH} = 1.2 Hz), 1.38 (t, J = 7.1 Hz). ^{13}C NMR (CD_2Cl_2): δ 228.79 (d, J_{PC} = 1.7 Hz), 226.92 (d, J_{PC} = 41.2 Hz), 109.13 (s), 65.68 (d, J_{PC} = 9.0 Hz), 15.89 (d, J_{PC} = 7.2 Hz), 10.72 (s).

Mn(CO)$_5$(PPh$_3$)$^+$BF$_4^-$ (5a). *cis*-BrMn(CO)$_4$(PPh$_3$)[35] (5.00 g, 9.82 mmol) was dissolved in 100 mL of CH_2Cl_2 and the solution heated to reflux. CO was bubbled through the solution, and $AgBF_4$ (2.39 g, 12.28 mmol) was added slowly over 8 h; IR spectra then showed complete conversion of the bromide. The mixture was then cooled to room temperature and filtered through Celite, and 100 mL of ether was added to the filtrate. After the solution was cooled to 0 °C to complete precipitation of the product, a pale yellow powder was obtained (4.50 g, 84% yield).

Anal. Calcd for $C_{23}H_{15}O_5PMnBF_4$: C, 50.77; H, 2.78; P, 5.69. Found: C, 50.89; H, 2.80; P, 5.28. IR: ν_{CO} (CH_2Cl_2) 2140 (m), 2090 (sh), 2070 (sh), 2050 (vs) cm^{-1} [lit.[12] for the PF_6 salt: ν_{CO} 2142 (w), 2063 (sh), 2052 (vs) cm^{-1}]. ^{1}H NMR (CD_2Cl_2): δ 7.65 (m). ^{13}C NMR (CD_2Cl_2): δ 205.70 (m), 133.06 (s), 133.0 (d, J_{PC} = 9.7 Hz), 130.27 (d, J_{PC} = 10.4 Hz), 129.59 (d, J_{PC} = 49.5 Hz).

***trans*-Mn(CO)$_4$(PPh$_3$)$_2^+$BF$_4^-$ (5b).** *mer,trans*-BrMn(CO)$_3$(PPh$_3$)$_2$[36] (5.00 g, 6.73 mmol) was dissolved in 100 mL of CH_2Cl_2 and the solution heated to reflux. CO was bubbled through the stirred solution, and $AgBF_4$ (1.64 g, 8.41 mmol) was added slowly during 30 min. An IR spectrum indicated that the bromide had been consumed after this time. The mixture was then cooled to room temperature and filtered through Celite, and 100 mL of ether was added to the filtrate. After the solution was cooled to 0 °C, a pale yellow powder was obtained (4.80 g, 91% yield).

Anal. Calcd for $C_{40}H_{30}O_4P_2MnBF_4$: C, 61.72; H, 3.88; P, 7.96. Found: C, 61.72; H, 4.03; P, 8.04. IR: ν_{CO} (CH_2Cl_2) 2090 (vw), 2040 (w), 1996 (vs) cm^{-1} [lit.[37] for the PF_6 salt: ν_{CO} 2092 (vw), 2046 (w), 2001 (vs) cm^{-1}]. ^{1}H NMR (CD_2Cl_2): δ 7.63 (m). ^{13}C NMR (CD_2Cl_2): δ 221.97 (t, J_{PC} = 16.95 Hz), 132.90 (t, J_{PC} = 4.75 Hz), 132.45 (s), 131.45 (d, J_{PC} = 49.1 Hz), 129.96 (t, J_{PC} = 4.8 Hz).

Mn(CO)$_5$[P(OPh)$_3$]$^+$BF$_4^-$ (5c). *cis*-BrMn(CO)$_4$[P(OPh)$_3$][35] (3.00 g, 5.38 mmol) was dissolved in 50 mL of CH_2Cl_2 and the solution heated to reflux with stirring. CO was bubbled through the solution, and then $AgBF_4$ (0.30 g, 1.54 mmol) was added. Three additional equivalent portions of $AgBF_4$ were added after 3, 9, and 15 h of heating; heating was continued for an additional 5 h, until IR spectra indicated that the bromide had been consumed. The mixture was then cooled to room temperature and filtered through Celite. The filtrate was concentrated to about 5 mL and then added to 100 mL of ether/hexane (1:20) at 0 °C. The mixture was then agitated to effect solidification of the product. The crude product was redissolved in 10 mL of CH_2Cl_2 and then precipitated again by pouring this solution into 75 mL of ether at 0 °C. The partially purified product was then redissolved in CH_2Cl_2 and precipitated again with ether to afford white needles (0.73 g, 23% yield).

Anal. Calcd for $C_{23}H_{15}O_8PMnBF_4$: C, 46.66; H, 2.55; P, 5.23. Found: C, 46.15; H, 2.60; P, 5.37. IR: ν_{CO} (CH_2Cl_2) 2160 (w), 2095 (sh), 2070 (vs) cm^{-1} [lit.[12] (CH_3CN): ν_{CO} 2154 (w), 2084 (m), 2064 (vs) cm^{-1}]. ^{1}H NMR (acetone-d_6): δ 7.52 (m). ^{13}C NMR (CD_2Cl_2): 202.0 (s, br), 150.6 (d, J_{PC} = 12.3 Hz), 131.2 (d, J_{PC} = 1.4 Hz), 127.7 (s), 120.7 (d, J_{PC} = 4.5 Hz).

***trans*-Mn(CO)$_4$[P(OPh)$_3$]$_2^+$BF$_4^-$ (5d).** *mer,trans*-BrMn(CO)$_3$[P(OPh)$_3$]$_2$[36] (3.00 g, 3.57 mmol) was dissolved in 50 mL of CH_2Cl_2 and the solution heated to reflux. CO was bubbled through the solution, and $AgBF_4$ (0.30 g, 1.54 mmol) was added. Two more equivalent additions of $AgBF_4$ were made, after 7 and 14 h; heating of the mixture was continued for a total of 20 h. (More rapid addition of $AgBF_4$ results in a lower yield of cation and increased amounts of uncharacterized byproducts.) IR spectra then indicated that the starting bromide had disappeared. The mixture was cooled to room temperature and filtered through Celite, and the filtrate was concentrated to about 20 mL on a rotary evaporator. This solution was then poured into 100 mL of hexane/ether (3:1) maintained at 0 °C to precipitate the reaction products. The yellow precipitate was collected and redissolved in THF; ether (20 mL) was added and the cation crystallized from solution as white needles (1.60 g, 52% yield).

Anal. Calcd for $C_{40}H_{30}O_{10}P_2MnBF_4$: C, 54.95; H, 3.46; P, 7.08. Found: C, 54.60; H, 3.40; P, 6.85. IR: ν_{CO} (CH_2Cl_2) 2115 (vw), 2070 (w), 2040 (s) cm^{-1} [lit.[14] for the PF_6 salt: 2120 (vw), 2075 (w), 2040 (s) cm^{-1}]. ^{1}H NMR (acetone-d_6): δ 7.4 (m). ^{13}C NMR (CD_2Cl_2): δ 204.7 (s, br), 150.5 (t, J_{PC} = 5.6 Hz), 130.9 (s), 127.2 (s), 120.6 (t, J_{PC} = 2.1 Hz).

***trans*-Re(CO)$_4$[P(OPh)$_3$]$_2^+$BF$_4^-$ (5e).** *fac*-BrRe(CO)$_3$[P(OPh)$_3$]$_2$[38] (2.56 g, 2.63 mmol) was dissolved in 75 mL of CH_2Cl_2 and the solution was heated to reflux. $AgBF_4$ (0.78 g, 4.01 mmol) was added to the mixture, and CO was bubbled through the heated mixture for 12 h. After this time, the CO addition was discontinued, the mixture was cooled to room temperature, and stirring was continued for another 12 h. A small amount of activated charcoal was then added to the mixture, and it was filtered through Celite. Solvent was removed from the filtrate on a rotary evaporator to leave a colorless oil. Ether (50 mL) was added, and the mixture was stirred for a few minutes to effect precipitation of the solid product. The crude product was then taken up in 1:10 CH_2Cl_2/ether and then chilled to −30 °C to afford white crystals (0.72 g, 27% yield).

IR: ν_{CO} (CH_2Cl_2) 2080 (w), 2038 (s) cm^{-1} [lit.[15] ν_{CO} 2068 (w), 2028 (s) cm^{-1}]. ^{1}H NMR (CD_2Cl_2): δ 7.34 (m). ^{13}C NMR (CD_2Cl_2): δ 179.19 (t, J_{PC} = 12.0 Hz), 150.50 (s, br), 131.12 (s), 127.30 (s), 120.94 (s, br).

***trans*-Re(CO)$_4$(PPh$_3$)$_2^+$BF$_4^-$ (5f).** *mer,trans*-BrRe(CO)$_3$(PPh$_3$)$_2$[36] (3.00 g, 3.43 mmol) was slurried in 50 mL of CH_2Cl_2, and the mixture was heated to reflux. After reflux temperature was attained, $AgBF_4$ (0.30 g, 1.5 mmol) was added to the mixture as CO was bubbled into it; equivalent quantities of $AgBF_4$ were added to the mixture after 2 and 5 h of reaction and CO addition was continued. After a total of 8 h, the reaction was complete and the mixture was cooled to room temperature and then filtered through Celite. The filtrate was concentrated to 40 mL and 20 mL of ether was added; the product (2.9 g, 94% yield) precipitated as white crystals.

Anal. Calcd for $C_{40}H_{30}O_4P_2ReBF_4$: C, 52.82; H, 3.32; P, 6.81. Found: C, 52.47; H, 3.07; P, 6.76. IR: ν_{CO} (CH_2Cl_2) 2000 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.52 (m). ^{13}C NMR (CD_2Cl_2): δ 185.81 (t,

(34) A procedure similar to that described above for (η-C_5H_5)Mo(CO)$_3$H was used to prepare this hydride.

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J_{PC} = 7.5 Hz), 132.95 (t, J_{PC} = 5.8 Hz), 132.41 (s), 132.03 (t, J_{PC} = 27.0 Hz), 129.84 (t, J_{PC} = 5.3 Hz).

***trans*-(η-C_5H_5)Mo(CO)$_2$(PPh$_3$)CHO (2a).** (η-C_5H_5)Mo(CO)$_3$(PPh$_3$)$^+BF_4^-$ (0.20 g, 0.34 mmol) was slurried in 20 mL of methanol and the solution chilled to 0 °C under a nitrogen atmosphere. Et_4NBH_4 (0.10 g, 0.69 mmol) was added during 15 min. The mixture was stirred an additional 10 min; during this time, the yellow product precipitated. The product was collected by filtration under nitrogen, washed with cold methanol, and then dried, in vacuo (yield 0.15 g, 89%). The product had a melting point of 155–160 °C dec.

Anal. Calcd for $C_{26}H_{21}O_3PMo$: C, 61.43; H, 4.16; P, 6.09. Found: C, 61.37; H, 4.18; P, 5.89. IR: ν_{CO} (Nujol mull) 1945 (m), 1854 (s), 1596 (m) cm^{-1}; ν_{CHO} (neat, DRIFTS) 2700, 2550 (wm) cm^{-1}. ^{1}H NMR (CD_2Cl_2 with added Et_4NBH_4): δ 14.89 (d, J_{PH} = 4.0 Hz, CHO), 7.31 (m, phenyl), 5.10 (d, J_{PH} = 1.0 Hz, C_5H_5) [lit.[4] (CH_2Cl_2, −41 °C): δ 14.70 (d, J_{PH} = 4 Hz)]. ^{13}C NMR (CH_2Cl_2/CD_2Cl_2, −12 °C, with added Et_4NBH_4): δ 263.40 (s, br, CHO), 232.67 (d, J_{PC} = 24.9 Hz), 132.31 (s), 129.85 (s), 127.92 (s), 127.81 (s), 95.15 (s).

A solution of **2a** in CD_2Cl_2 was allowed to stand at room temperature, under nitrogen, for a few minutes, and then its IR spectrum was recorded. The spectrum showed ν_{CO} bands at 2030 (s) and 1930 (s) cm^{-1} [lit.[39] for (η-C_5H_5)Mo(CO)$_3$H (CS_2): ν_{CO} 2030 (s), 1949 (s) cm^{-1}] and no longer showed any evidence of the formyl ν_{CHO} band at 1580 cm^{-1}. A ^{1}H NMR spectrum of the solution showed signals at δ 5.1 (s, 5 H) and −5.7 (s, 1 H) as well as the resonance for free PPh_3 [lit.[39] for (η-C_5H_5)Mo(CO)$_3$H (toluene): δ 5.4 (s) and −5.4 (s)]. Reactions conducted at higher temperatures showed substantial amounts of (η-C_5H_5)Mo(CO)$_2$(PPh$_3$)H (primarily the cis isomer) as evidenced by the cyclopentadienyl resonance at δ 5.1 (d, J_{PH} = 0.6 Hz) and the hydride resonance at −5.7 (d, J_{PH} = 48.0 Hz) [lit.[40] δ 5.03 (d, J_{PH} = 0.5 Hz) and −5.6 (d, J_{PH} = 48.6 Hz)]. The tricarbonyl hydride slowly converts to the phosphine hydride over 2 days.

***trans*-(η-C_5H_5)Mo(CO)$_2$[P(OPh)$_3$]CHO (2b).** (η-C_5H_5)Mo(CO)$_3$[P(OPh)$_3$]$^+BF_4^-$ (0.50 g, 0.78 mmol) was dissolved in 25 mL of methanol and the solution chilled to 0 °C under a nitrogen atmosphere. Et_4NBH_4 (0.14 g, 0.96 mmol) was then added, in small portions, to the stirred solution during about 5 min. The mixture was allowed to stir for an additional 5 min; during this time, the formyl product precipitated. The yellow product was collected by filtration under nitrogen, washed with cold methanol, and then dried, in vacuo (yield 0.39 g, 89%); the product had a melting point of 65.5–67.5 °C dec.

IR: ν_{CO} (Nujol mull) 1965 (s), 1945 (sh), 1885 (s, br), 1655 (vw), 1610 (s) cm^{-1}; ν_{CHO} (neat, DRIFTS) 2706 (w), 2565 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, −57 °C): δ 14.75 (d, J_{PH} = 6.2 Hz, CHO), 7.36 (m), 4.74 (s). ^{13}C NMR (CD_2Cl_2, −57 °C): δ 259.15, 257.22 (both doublets; CHO, J_{PC} = 7.6 and 9.1 Hz, respectively; relative ratio approximately 53:47, respectively), 229.23 (d, J_{PC} = 34.6 Hz), 150.04 (d, J_{PC} = 6.2 Hz), 129.77 (s), 125.51 (s), 121.57 (s), 94.47 (d, J_{PC} = 18.6 Hz). A small amount of the cis isomer (<10%) is partially observable: ^{1}H NMR: δ 15.10 (d, J_{PH} = 5.3 Hz), 7.36 (m), 4.98 (s). ^{13}C NMR: δ 238.11 (d, J_{PC} = 36.2 Hz), 230.58 (d, J_{PC} = 6.0 Hz); the formyl, phenyl, and cyclopentadienyl resonances are not visible.

A sample of (η-C_5H_5)Mo(CO)$_2$[P(OPh)$_3$]CHO was dissolved in CD_2Cl_2 at −78 °C in an NMR tube under nitrogen. The tube was placed in the NMR probe (−6 °C), and the spectrum was recorded; a small amount of decomposition had occurred by this time and the high-field singlet for (η-C_5H_5)Mo(CO)$_3$H was already visible. The sample was allowed to remain at −6 °C for an additional 20 min and the spectrum recorded again; about 40% conversion of the formyl complex had occurred, and both the carbonyl hydride and phosphite hydride were present in approximately equal amounts. The sample was allowed to warm to room temperature and allowed to stand for 2 h; after this time, decomposition of **2b** was complete and the spectrum of the product mixture showed singlets at δ 5.19 and −5.62 [lit.[39] for (η-C_5H_5)Mo(CO)$_3$H: δ 5.4 (s), −5.4 (s)] and also showed resonances at δ 7.27 (m), 4.82 (s), and −6.73 (d, J_{PH} = 71.8 Hz) [lit.[40] for *cis*-(η-C_5H_5)Mo(CO)$_2$[P(OPh)$_3$]H: δ 4.84 (s), −6.62 (d, J_{PH} = 73.0 Hz)]. The relative ratio of the two compounds was 1:6, respectively.

***cis*- and *trans*-(η-C_5H_5)W(CO)$_2$(PPh$_3$)CHO (2c).** (η-C_5H_5)W(CO)$_3$(PPh$_3$)$^+BF_4^-$ (0.268 g, 0.392 mmol) was slurried in 10 mL of methanol under nitrogen. Et_4NBH_4 (0.075 g, 0.517 mmol) was added in several portions, with stirring, to the mixture. Stirring was continued for 20 min; during this time, the product precipitated as a yellow powder. The product was collected by filtration under nitrogen, washed with methanol and dried, in vacuo (yield, 0.213 g, 91%); the melting point was 98–101 °C dec.

Anal. Calcd for $C_{26}H_{21}O_3PW$: C, 52.37; H, 3.55; P, 5.19. Found: C, 51.68; H, 3.75; P, 5.13. IR: ν_{CO} (Nujol mull) 1925 (m), 1840 (s), 1590 (m) cm^{-1}; ν_{CHO} (neat, DRIFTS) 2727 (w), 2564 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2, −25 °C, Et_4NBH_4 added): trans isomer, δ 15.71 (d, J_{PH} = 2.6 Hz, CHO), 7.45 (m), 5.22 (s); cis isomer, δ 15.61 (d, J_{PH} = 15.6 Hz, CHO), 7.45 (m), 5.38 (s). The relative intensities of the formyl protons (or cyclopentadienyl ring protons) were 5:1, respectively. ^{13}C NMR (CD_2Cl_2, −25 °C, Et_4NBH_4 added): trans isomer, δ 247.50 (d, J_{PC} = 10.7 Hz, CHO), 247.36 (d, J_{PC} = 10.1 Hz, CHO), 225.60 (d, J_{PC} = 18.2 Hz), 133.20 (m), 130.76 (s), 128.73 (s), 128.59 (s), 94.50 (s); cis isomer (carbonyl signals not visible), δ 133.20 (m), 130.76 (s), 128.79 (s), 128.65 (s), 94.67 (s). At −60 °C, the carbonyl resonances were further separated: trans isomer, δ 249.53 (m, CHO), 247.55 (m, CHO), 225.04 (d, J_{PC} = 18.4 Hz); cis isomer, 249.53 (m, CHO), 238.40 (d, J_{PC} = 20.9 Hz), 230.95 (s). Also, the proton spectrum at this temperature showed a 4:1 distribution of trans:cis isomers, and the J values for the formyl protons were changed to 4.5 and 14.4 Hz, respectively.

A saturated solution of **2c** in CD_2Cl_2 was sealed in an NMR tube under nitrogen at room temperature, and its ^{1}H NMR spectrum was monitored periodically. After 2 h, the resonance signal of the formyl proton had disappeared and the spectrum consisted of a singlet at δ 5.52 and a triplet at δ −7.32 (J_{WH} = 37.0 Hz). The spectral data compare favorably with those reported[41] for (η-C_5H_5)W(CO)$_3$H. ^{1}H NMR (CS_2): δ 5.47 (s), −7.30 (t, J_{WH} = 36.0 Hz).

***cis*- and *trans*-(η-C_5Me_5)Mo(CO)$_2$[P(OPh)$_3$]CHO (4a).** (η-C_5Me_5)Mo(CO)$_3$[P(OPh)$_3$]$^+BF_4^-$ (0.10 g, 0.14 mmol) was dissolved in 5 mL of methanol and the solution chilled to 0 °C, with stirring, under nitrogen. Et_4NBH_4 (0.04 g, 0.28 mmol) was added in several small portions, and the mixture was allowed to stir an additional 2–3 min; during this time the product precipitated from solution. The yellow solid was collected by filtration, washed with cold methanol, and dried, in vacuo (yield 0.07 g, 80%); the melting point was 63–65 °C dec.

IR: ν_{CO} (Nujol mull) 1947 (s, br), 1865 (s, br), 1612 (m), 1603 (m) cm^{-1}; ν_{CHO} (neat, DRIFTS) 2652 (w), 2527 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, −35 °C): cis isomer, δ 14.36 (d, J_{PH} = 3.6 Hz, CHO), 7.22 (m), 1.85 (s); trans isomer, 14.31 (d, J_{PH} = 6.4 Hz, CHO), 7.22 (m), 1.86 (s). The integration of the formyl proton signals indicated a cis to trans ratio of 2:1. ^{13}C NMR (CD_2Cl_2, −35 °C): cis isomer, δ 275.24 (m, CHO), 273.66 (m, CHO) (integrated area ratio of these two multiplets was 1:1), 243.53 (d, J_{PC} = 35.9 Hz), 234.80 (s), 151.46 (d, J_{PC} = 10.7 Hz), 121.95 (d, J_{PC} = 17.7 Hz), 129.47 (s), 124.84 (s), 105.58 (s), 10.23 (d, J_{PC} = 12.7 Hz); trans isomer, δ 267.23 (d, J_{PC} = 8.3 Hz, CHO), 265.45 (d, J_{PC} = 9.1 Hz, CHO) (integrated area ratio of these two doublets was 1:1), 234.28 (d, J_{PC} = 36.6 Hz), 151.01 (d, J_{PC} = 10.7 Hz), 121.43 (d, J_{PC} = 13.9 Hz), 129.64 (s), 124.62 (s), 105.81 (s), and 9.96 (d, J_{PC} = 12.9 Hz). Integration of the two low-field signals of the cis isomer and the two low-field signals of the trans isomer (or of their respective C_5Me_5 signals) again indicated a cis to trans ratio of 2:1.

A freshly prepared sample of the isomeric formyl complexes was dissolved in CD_2Cl_2 in an NMR tube at −78 °C under nitrogen. The proton spectrum was recorded at −35 °C, then the probe temperature was raised to +20 °C, and the sample was maintained at this temperature until decomposition of the formyl complex was complete (2.5 h). After this time, the spectrum showed singlets at δ 2.10 and −5.33 [lit.[42] for (η-C_5Me_5)Mo(CO)$_3$H ($CDCl_3$): δ 2.11 and −5.41]. Reactions conducted at higher temperatures showed significant amounts of a second hydride. ^{1}H NMR: δ 7.24 (m), 1.95 (s), −6.26 (d, J_{PH} = 79.8 Hz). ^{13}C NMR: a doublet at δ 239.44

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(J_{PC}= 7.7 Hz) and a singlet at δ 236.84 in agreement with its assignment as *cis*-(η-C_5Me_5)Mo(CO)$_2$[P(OPh)$_3$]H.

***cis*- and *trans*-(η-C_5Me_5)Mo(CO)$_2$[P(OEt)$_3$]CHO (4b).** (η-C_5Me_5)Mo(CO)$_3$[P(OEt)$_3$]$^+BF_4^-$ (0.30 g, 0.53 mmol) was dissolved in 10 mL of methanol and the solution cooled to 0 °C, with stirring, under nitrogen. Solid Et_4NBH_4 (0.08 g, 0.58 mmol) was then added, and the mixture was allowed to stir for 15 min. Solvent was removed, in vacuo, and the yellow solid was triturated with 2 × 20 mL of ether/hexane (1:19); the combined hexane extracts were concentrated to 10 mL and chilled to −35 °C to effect crystallization of the yellow product, yield 0.14 g (77%). The product does not have a discrete melting point; it begins to decompose at 45 °C. Although the solid is relatively stable in air, it darkens upon exposure to light.

IR: ν_{CO} (Nujol) 1935 (s), 1858 (vs), 1597 (m) cm^{-1}; ν_{CHO} (DRIFTS) 2657 (w), 2536 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, −57 °C): trans isomer, δ 14.61 (d, J_{PH} = 6.1 Hz, CHO), 3.85 (quintet), 1.88 (s), 1.22 (t, J = 6.8 Hz); cis isomer, δ 14.46 (s, CHO), 3.76 (quintet), 1.86 (s), 1.18 (t, J = 7.2 Hz). ^{13}C NMR (CD_2Cl_2, −57 °C): trans isomer, δ 274.63 (d, J_{PC} = 12.9 Hz, CHO), 272.93 (d, J_{PC} = 9.8 Hz, CHO), 234.46 (d, J_{PC} = 37.3 Hz), 105.16 (s), 61.52 (d, J_{PC} = 5.3 Hz), 15.74 (d, J_{PC} = 6.6 Hz), 9.84 (d, J_{PC} = 5.0 Hz); cis isomer, 279.56 (m, CHO), 277.97 (m, CHO), 246.32 (d, J_{PC} = 37.3 Hz), 238.92 (s), 105.27 (s), 61.49 (d, J_{PC} = 5.7 Hz), 15.82 (d, J_{PC} = 4.5 Hz), 10.15 (d, J_{PC} = 5.0 Hz). The trans to cis distribution of isomers was 70:30 as determined by integration.

A sample of **4b** was dissolved in CD_2Cl_2 at −78 °C in an NMR tube, and the tube was sealed, in vacuo. The tube was allowed to warm to room temperature, and its ^{1}H NMR spectrum showed only the resonances of the formyl complex. After the solution was left standing for 2 days at room temperature, slight (<10%) decomposition to (η-C_5Me_5)Mo(CO)$_3$H and (η-C_5Me_5)Mo(CO)$_2$-[P(OEt)$_3$]H was evident. The sample was then heated to 40 °C, and its NMR spectrum monitored periodically; after 2.5 days, conversion to the phosphite hydride was complete as evidenced by disappearance of the formyl resonances and appearance of a singlet at δ 1.84 and a doublet (J_{PH} = 68.0 Hz) at δ −6.41. On the basis of comparison with the product from **4a**, this hydride is tentatively assigned cis stereochemistry. The trans:cis distribution of formyl isomers appeared to remain approximately the same during the thermolysis.

***cis*-Mn(CO)$_4$(PPh$_3$)CHO (6a).** Mn(CO)$_5$(PPh$_3$)$^+BF_4^-$ (0.50 g, 0.92 mmol) was slurried with 10 mL of methanol and chilled to −40 °C under nitrogen. A molar equivalent of Et_4NBH_4 was added rapidly, and precipitation of the product was complete after about 1 min. The mixture was immediately transferred, under nitrogen, to a low-temperature crystallizer[43] maintained at −40 °C; the pale yellow product was collected, washed with cold methanol, and then dried, in vacuo (yield 0.36 g, 88%). The product had a melting point of 134–135 °C dec.

IR: ν_{CO} (Nujol mull) 2065 (m), 1975 (s), 1965 (s), 1945 (s), 1605 (m) cm^{-1}; ν_{CHO} (neat, DRIFTS) 2720, 2575 (w-m) cm^{-1}. ^{1}H NMR (C_6D_6, 3 °C): 14.26 (s, br, CHO), 7.50 (m, phenyl). ^{13}C NMR (CD_2Cl_2, −50 °C): 273.0 (d, J_{PC} = 40.0 Hz, CHO), 216.2 (s, br), 215.1 (d, J_{PC} = 27.9 Hz), 213.7 (d, J_{PC} = 20.4 Hz), 133.0 (d, J_{PC} = 9.5 Hz), 133.2 (d, J_{PC} = 42.2 Hz), 130.9 (s), 129.0 (d, J_{PC} = 9.1 Hz). The relative ratio of the terminal carbonyls was 1:2:1, respectively.

A sample of the formyl complex **6a** was dissolved in cold (0 °C) CD_2Cl_2 under nitrogen, then the sample was allowed to warm to 20 °C, and the progress of its decomposition was monitored by ^{1}H NMR. Decomposition was complete after 3 h, and the spectrum showed the following resonances: δ 7.45 (m) and −6.64 (d, J_{PH} = 33.5 Hz). The spectral data are consistent with those reported[44] for *cis*-HMn(CO)$_4$PPh$_3$.

***mer,trans*-Mn(CO)$_3$(PPh$_3$)$_2$CHO (6b).** *trans*-Mn(CO)$_4$-(PPh$_3$)$_2$$^+BF_4^-$ (0.100 g, 0.128 mmol) was dissolved in 15 mL of a 1:1 mixture of methanol and acetonitrile and the solution chilled to 0 °C under nitrogen. Et_4NBH_4 (0.025 g, 0.172 mmol) was added to this stirred solution; the reaction was complete after 2 min and the product precipitated from solution. The mixture was transferred to a low-temperature crystallizer[43] maintained at 0 °C under nitrogen, and the product was collected on the frit, washed with cold CH_3CN/CH_3OH and dried, in vacuo (yield 0.086 g, 97%). The product had a melting point of 99–102 °C dec.

IR: ν_{CO} (Nujol mull) 2010 (w), 1920 (s), 1900 (s), 1590 (m) cm^{-1} [lit.[22] ν_{CO} (CH_2Cl_2) 2010, 1930, 1900, 1590 cm^{-1}]; ν_{CHO} (neat, DRIFTS) 2715, 2520 (w-m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 13.38 (t, J_{PH} = 3.0 Hz, CHO), 7.61 (m, phenyl). ^{13}C NMR (CD_2Cl_2, −40 °C): δ 283.2 (t, J_{PC} = 15.4 Hz, CHO), 222.6 (t, J_{PC} = 14.8 Hz), 220.5 (t, J_{PC} = 20.5 Hz), 135.5 (d, J_{PC} = 40.8 Hz), 133.5 (d, J_{PC} = 9.9 Hz), 130.4 (s), 128.6 (d, J_{PC} = 9.0 Hz). The relative ratio of the terminal carbonyls was 2:1, respectively.

A solution of the formyl complex **6b** in CD_2Cl_2 and under nitrogen was allowed to stand at 20 °C, and its decomposition was monitored by ^{1}H NMR. Complete decomposition required 12 h, and the spectrum showed a multiplet at δ 7.41 and a doublet at δ −6.88 (J_{PH} = 33.7 Hz), indicating that only *cis*-HMn(CO)$_4$-(PPh$_3$) had been formed [lit.[44] δ −6.94 (d, J_{PH} = 34 Hz)]. Thermolysis of the formyl complex in benzene-d_6 is much slower; only slight decomposition, to the same hydride, was evidenced after a sample of **6b** was allowed to stand overnight at room temperature.

***cis*-Mn(CO)$_4$[P(OPh)$_3$]CHO (6c).** Mn(CO)$_5$[P(OPh)$_3$]$^+BF_4^-$ (0.40 g, 0.68 mmol) was dissolved in 6 mL of CH_2Cl_2 under nitrogen; 6 mL of hexane was added, and the solution was chilled, with stirring, to −40 °C. Et_4NBH_4 (0.10 g, 0.68 mmol) was added to the solution, and stirring was continued; after 45 min, an IR spectrum of the solution indicated that the cation had been consumed and showed new bands as follows: ν_{CO} 2070 (w), 2000 (sh, m), 1980 (s), 1960 (sh, m), and 1590 (m) cm^{-1} consistent with those expected for the formyl complex. The yield of formyl complex prepared in this way is estimated to be at least 82%, based on subsequent conversion of the formyl product to the corresponding metallacycle.[3b] Efforts were made to do the reduction in both methanol and acetonitrile in hopes that the formyl complex might precipitate from these solvents. From IR spectra the reductions were successful, but the formyl complex was soluble in these solvents also.

^{1}H NMR (CD_2Cl_2, −16 °C): δ 14.0 (s, br, CHO), 7.2 (m). ^{13}C NMR (CD_2Cl_2, −16 °C): 272.4 (s, CHO), 214.3 (s, br), 150.8 (d, J_{PC} = 10.0 Hz), 130.9 (s), 125.6 (s), 121.1 (d, J_{PC} = 3.8 Hz).

A mixture containing the formyl complex, prepared in the manner described above, was filtered, the filtrate was concentrated to dryness, and the residue was redissolved in CD_2Cl_2 and placed in an NMR tube. The ^{1}H NMR spectrum showed a multiplet at δ 7.4 and a doublet at δ −8.4 (J_{PH} = 54.0 Hz) [lit.[44] for HMn-(CO)$_4$[P(OPh)$_3$]: Mn–H at δ −7.95 (d, J_{PH} = 55 Hz)]; there was no evidence of the formyl proton.

***mer,trans*-Mn(CO)$_3$[P(OPh)$_3$]$_2$CHO (6d).** *trans*-Mn-(CO)$_4$[P(OPh)$_3$]$_2$$^+BF_4^-$ (0.20 g, 0.23 mmol) was dissolved in 20 mL of acetonitrile and the solution cooled to 0 °C under nitrogen. To this stirred solution was added Et_4NBH_4 (0.033 g, 0.230 mmol) during 5 min. Stirring was continued for an additional 2 min to complete the precipitation of the product. The white product was then collected by filtration under nitrogen, washed with cold CH_3CN, and dried, in vacuo (yield 0.169 g, 95%). The product had a melting point of 107–109 °C dec.

IR: ν_{CO} (CH_2Cl_2) 2020 (w), 1970 (vs), 1950 (s), 1580 (s) cm^{-1} [lit.[23] same]; ν_{CHO} (neat, DRIFTS) 2720, 2530 (w-m) cm^{-1}. ^{1}H NMR (acetone-d_6): δ 14.21 (s, br, CHO), 7.26 (m, phenyl) [lit.[23] δ 14.19 (s), 7.27 (m)]. ^{13}C NMR (CD_2Cl_2, −30 °C): δ 274.58 (m, CHO), 214.26 (t, J_{PC} = 30.1 Hz), 213.98 (t, J_{PC} = 31.1 Hz), 151.04 (s), 129.83 (s), 125.23 (s), 121.04 (s).

A sample of **6d** was dissolved in CD_2Cl_2 and the solution placed in an NMR tube under nitrogen. ^{1}H NMR spectra were recorded periodically over 5 h; the decomposition was complete after this time as evidenced by disappearance of the formyl proton signal. The spectrum showed a multiplet at δ 6.90–7.60 and a triplet (J_{PH} = 48.0 Hz) at δ −8.70 [lit.[14] δ 6.96–7.40 and −8.52 (t, J_{PH} = 48 Hz)]; an IR spectrum showed ν_{CO} at 2040 (w) and 1950 (s) cm^{-1} [lit.[14] same]. Both are consistent with the thermolysis product being *mer,trans*-HMn(CO)$_3$[P(OPh)$_3$]$_2$.

***mer,trans*-Re(CO)$_3$[P(OPh)$_3$]$_2$CHO (6e).** *trans*-Re(CO)$_4$-[P(OPh)$_3$]$_2$$^+BF_4^-$ (0.415 g, 0.413 mmol) was slurried in 4 mL of CH_3OH and the solution chilled to 0 °C under nitrogen. Et_4NBH_4 (0.076 g, 0.524 mmol) was added, during 1 min, to the stirred solution, and stirring was continued for an additional 2 min; during

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this time, the pale yellow product precipitated. The product was collected by filtration under nitrogen, washed with methanol, and dried, in vacuo (yield 0.361 g, 95%). The product had a melting point of 110–111 °C dec.

Anal. Calcd for $C_{40}H_{31}O_{10}P_2Re$: C, 52.23; H, 3.40; P, 6.74. Found: C, 52.19; H, 3.65; P, 6.95. IR: ν_{CO} (CH_2Cl_2) 2065 (w), 1970 (s), 1955 (s), 1575 (m) cm^{-1} [lit.[15] ν_{CO} 2062, 1963, 1943, 1578 cm^{-1}]; ν_{CHO} (neat, DRIFTS) 2752, 2511 (w-m) cm^{-1}. ^1H NMR (CD_2Cl_2, −20 °C): δ 14.90 (s, CHO), 7.20 (m, phenyl) [lit.[15] (acetone-d_6, 23 °C): δ 15.12 (s), 7.22 (m)]. ^{13}C NMR (CD_2Cl_2, −20 °C): δ 259.78 (d, J_{PC} = 16.0 Hz, CHO), 189.31 (t, J_{PC} = 13.5 Hz), 189.13 (t, J_{PC} = 8.7 Hz), 150.80 (s), 129.99 (s), 125.43 (s), 121.24 (s).

A saturated solution of **6e** in CD_2Cl_2 was sealed in an NMR tube under nitrogen at room temperature, and its ^1H NMR spectrum was monitored periodically. After 3 h, the formyl proton signal had disappeared and the spectrum consisted of a multiplet at δ 7.24, a doublet at δ −6.18 (J_{PH} = 32.0 Hz), and a triplet at δ −6.71 (J_{PH} = 27.0 Hz). The integrated intensities of the high field signals were 3:20, respectively. The ^1H NMR spectrum reported[45] for *cis*-$HRe(CO)_4[P(OPh)_3]$ (in C_6D_6) indicated the hydride resonance as a doublet at δ −5.86 (J_{PH} = 32.5 Hz) whereas the spectrum (in C_6D_6) reported[46] for *mer,trans*-$HRe(CO)_3[P(OPh)_3]_2$ shows the hydride resonance at δ −6.67 (triplet, J_{PH} = 28.1 Hz). The formyl complex, therefore, decomposes preferentially to the bis-phosphite hydride.

***mer,trans*-$Re(CO)_3(PPh_3)_2CHO$ (6f).** *trans*-$Re(CO)_4(PPh_3)_2^+BF_4^-$ (0.30 g, 0.33 mmol) was slurried in 20 mL of methanol, under nitrogen, at room temperature. Solid Et_4NBH_4 (0.24 g, 1.6 mmol) was added to the stirred mixture, and stirring was continued until gas evolution ceased (5–10 min); the yellow product precipitated during this time. The product was collected on a filtering funnel under a blanket of nitrogen and washed with 5 × 10 mL of methanol and then dried, in vacuo; yield 0.25 g (93%). The product did not have a discrete melting point; it changed from yellow to white, beginning at 125 °C.

IR: ν_{CO} (Nujol) 2030 (w), 1925 (s), 1900 (s), 1575 (m) cm^{-1}; ν_{CHO} (DRIFTS) 2746, 2507, 2474 (w, br) cm^{-1}. ^1H NMR (CD_2Cl_2, −40 °C): δ 14.31 (s, CHO), 7.45 (m). ^{13}C NMR (CD_2Cl_2, −40 °C): δ 268.7 (s, br, CHO), 197.6 (t, J_{PC} = 6.4 Hz), 195.3 (t, J_{PC} = 8.8 Hz) (the integrated areas of these two triplets was 1:2, respectively), 134.8 (t, J_{PC} = 24.3 Hz), 133.0 (t, J_{PC} = 5.9 Hz), 130.1 (s), 128.3 (t, J_{PC} = 4.9 Hz).

A sample of **6f**, dissolved in CH_2Cl_2 and under nitrogen, was allowed to stand at room temperature for 15 min; an IR spectrum showed that the formyl complex had disappeared. Solvent was removed on a rotary evaporator, and the residue was triturated with ether. Ether was removed, and the residual solid was dissolved in CH_2Cl_2 and its IR spectrum recorded: ν_{CO} at 2110 (m), 2018 (s, sh), 2000 (vs), and 1943 (s) cm^{-1} were in agreement with those reported for *cis*-$ClRe(CO)_4(PPh_3)$.[47] The ether-insoluble residue was dissolved in CH_2Cl_2, and its IR spectrum showed ν_{CO} at 1945 (s) and 1895 (m) cm^{-1} which were in agreement with those reported for *mer,trans*-$ClRe(CO)_3(PPh_3)_2$.[36]

Because of the limited solubility of the formyl complex in many common solvents (acetonitrile, methanol, THF, and benzene) and its reactivity toward CH_2Cl_2, thermolysis of the solid compound was accomplished. A sample of **6f** was sealed in a glass tube, in vacuo, and heated at 120 °C for 4 days. The spectral properties of the product are consistent with its formulation as *mer,trans*-$HRe(CO)_3(PPh_3)_2$. IR: ν_{CO} (CH_2Cl_2) 1998 (vw), 1935 (vs) cm^{-1} [lit.[45] (benzene): ν_{CO} 1931 (br) cm^{-1}]. ^1H NMR (CD_2Cl_2, 0 °C): δ 7.52 (m), −5.12 (t, J_{PH} = 18.1 Hz) [lit.[45] (benzene) δ −4.48 (t, J_{PH} = 18.0 Hz)]. A solution of this hydride in CH_2Cl_2 was allowed to stand for 22 h; no conversion of the compound to chlorinated products occurred as evidenced by ^1H NMR and IR spectroscopy.

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Registry No. **1a**, 67251-60-9; **1b**, 78803-21-1; **1c**, 62866-72-2; **2a**, 88642-96-0; *trans*-**2b**, 118228-18-5; *cis*-**2b**, 118332-78-8; *cis*-**2c**, 118228-19-6; *trans*-**2c**, 118332-76-6; **3a**, 118247-00-0; **3b**, 118228-15-2; *cis*-**4a**, 118333-34-9; *trans*-**4a**, 118228-20-9; *cis*-**4b**, 118228-21-0; *trans*-**4b**, 118332-77-7; **5a**, 54039-46-2; **5b**, 118228-16-3; **5c**, 54039-50-8; **5d**, 117686-85-8; **5e**, 106232-69-3; **5f**, 118228-17-4; **6a**, 111635-36-0; **6b**, 110351-58-1; **6c**, 111035-35-9; **6d**, 92397-63-2; **6e**, 106232-74-0; **6f**, 118228-22-1; $(\eta\text{-}C_5H_5)Mo(CO)_2(PPh_3)Cl$, 12115-01-4; $Mo(CO)_6$, 13939-06-5; $Mo(CO)_3(CH_3Cn)_3$, 15038-48-9; $(\eta\text{-}C_5H_5)Mo(CO)_3H$, 12176-06-6; $W(CO)_6$, 14040-11-0; $W(CO)_3(CH_3CN)_3$, 16800-47-8; $W(CO)_4(CH_3CN)_2$, 16800-45-6; $(\eta\text{-}C_5H_5)W(CO)_3H$, 12128-26-6; $(\eta\text{-}C_5Me_5)Mo(CO)_3H$, 78003-92-6; *cis*-$BrMn(CO)_4(PPh_3)$, 57693-96-6; *mer,trans*-$BrMn(CO)_3(PPh_3)_2$, 15662-31-4; *cis*-$BrMn(CO)_3(PPh_3)_2$, 59818-97-2; *mer,trans*-$BrMn(CO)_3[P(OPh)_3]_2$, 15614-85-4; *fac*-$BrRe(CO)_3[P(OPh)_3]_2$, 49742-38-3; *mer,-trans*-$BrRe(CO)_3(PPh_3)_2$, 51446-58-3; $(\eta\text{-}C_5H_5)Mo(CO)_2(PPh_3)H$, 32011-66-8; *cis*-$(\eta\text{-}C_5H_5)Mo(CO)_2[P(OPh)_3]H$, 32011-65-7; *cis*-$(\eta\text{-}C_5Me_5)Mo(CO)_2[P(OPh)_3]H$, 118332-79-9; $(\eta\text{-}C_5Me_5)Mo(CO)_2[P(OEt)_3]H$, 118228-23-2; *cis*-$HMn(CO)_4PPh_3$, 39796-96-8; $HMn(CO)_4[P(OPh)_3]$, 105228-19-1; *mer,trans*-$HMn(CO)_3[P(OPh)_3]_2$, 17250-37-2; *cis*-$HRe(CO)_4[P(OPh)_3]$, 25734-50-3; *mer,trans*-$HRe(CO)_3[P(OPh)_3]_2$, 97485-58-0; *cis*-$ClRe(CO)_4(PPh_3)$, 15189-56-7; *mer,trans*-$ClRe(CO)_3(PPh_3)_2$, 19394-85-5; *mer,trans*-$HRe(CO)_3(PPh_3)_2$, 25734-54-7.

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