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Synthesis and Characterization of Binuclear Derivatives of Molybdenum–Manganese, Tungsten–Manganese, and Rhenium–Manganese Containing the Bridging $\eta^5:\eta^1$-Cyclopentadienyl Group[1,2]

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The treatment of $(\eta^5\text{-}C_5H_5)MH_2$ (M = Mo or W) with $CH_3Mn(CO)_5$ gives as principal products respectively the binuclear complexes $(\eta^5\text{-}C_5H_5)(CO)\overline{M(\mu\text{-}(\eta^5:\eta^1\text{-}C_5H_4))Mn}(CO)_4$, where M = Mo (**1a**) and M = W (**1b**), each accompanied by the evolution of methane and hydrogen; from $(\eta^5\text{-}C_5H_5)_2ReH$ and $CH_3Mn(CO)_5$ one obtains $(\eta^5\text{-}C_5H_5)(H)\overline{Re(\mu\text{-}(\eta^5:\eta^1\text{-}C_5H_4))Mn}(CO)_4$ (**2**), with evolution of methane and carbon monoxide. Studies with deuterium-labeled starting materials confirm that the methane in these reactions is formed from a hydrogen atom of a cyclopentadienyl ring of the metallocene hydride and the methyl group of $CH_3Mn(CO)_5$. The deuterium atom remaining in a sample of **2**-d_1, obtained from $(\eta^5\text{-}C_5H_5)_2ReD$ and $CD_3Mn(CO)_5$, is found to be randomly distributed over all positions indicating an intramolecular hydrogen tautomerism in this bimolecular metalation product. With H_2 at ambient temperatures, **1b** yields an unstable intermediate $(\eta^5\text{-}C_5H_5)_2(H)W\text{–}Mn(CO)_5$ which is converted at 80 °C in the presence of H_2 to $(\eta^5\text{-}C_5H_5)_2WH_2$ and $Mn_2(CO)_{10}$; with D_2 at 80 °C, the metallocene hydride obtained is found to contain extensive exchange of deuterium for hydrogen. The binuclear complex **2** is stable toward H_2 up to 80 °C but shows exchange of deuterium for hydrogen when treated with D_2 at that temperature. Treatment of **1b** with phosphorus-containing ligands gives substitution products with evolution of CO and no evidence of the formation of any acyl complexes.

Introduction

In view of the donor properties exhibited by the bis(η^5-cyclopentadienyl) hydrides of Mo, W, and Re[3] and our interests in the donor–acceptor interactions of low-valent complexes of the transition metals,[4] we were led to investigate the reactions of the aforementioned derivatives as potential donors with $CH_3Mn(CO)_5$, a potential acceptor.[5] We found no evidence of simple adducts at ambient temperatures, but, with passing of time, we observed a color change in solution accompanied by gas evolution and formation of novel binuclear complexes containing a bridging $\eta^5:\eta^1$-C_5H_4 ring. The isolation and characterization of such derivatives are described in the present and companion works.[6,7] In the time elapsed since submission of a preliminary communication of this work,[2] four further examples of complexes containing the bridging $\eta^5:\eta^1$-C_5H_4 ring have been reported, namely, $[(\eta^5\text{-}C_5H_5)(\mu\text{-}(\eta^5:\eta^1\text{-}C_5H_4))(H)Nb]_2$,[8a,b] $\overline{[(\eta^5\text{-}C_5H_5)_2(\mu\text{-}(\eta^5:\eta^1\text{-}C_5H_4))Th]}_2$,[8c] $(\eta^5\text{-}C_5H_5)(C_4H_8O)\overline{Ti(\mu\text{-}(\eta^5:\eta^1\text{-}C_5H_4))Ti}(\eta^5\text{-}C_5H_5)_2$,[8d] and $[(\eta^5\text{-}C_5H_5)\overline{Fe(\mu\text{-}(\eta^5:\eta^1\text{-}C_5H_4))Au_2}(PPh_3)_2][BF_4]$.[8e]

Results

The chemical transformations reported in this work and the derivatives isolated are summarized in Scheme I.

Scheme I

$$CH_3Mn(CO)_5 + (\eta^5\text{-}C_5H_5)_2MH_2 \xrightarrow[M\ =\ Mo\ or\ W]{} (\eta^5\text{-}C_5H_5)(CO)\overline{M(\mu\text{-}(\eta^5:\eta^1\text{-}C_5H_4))Mn}(CO)_4 + CH_4 + H_2 \qquad (1)$$

1a (M = Mo); **1b** (M = W)

$$\mathbf{1a}\ \text{or}\ \mathbf{1b} + 1.5H_2 \rightarrow (\eta^5\text{-}C_5H_5)_2MH_2 + 0.5Mn_2(CO)_{10} \qquad (2)$$

$$CH_3Mn(CO)_5 + (\eta^5\text{-}C_5H_5)_2ReH \rightarrow (\eta^5\text{-}C_5H_5)(H)\overline{Re(\mu\text{-}(\eta^5:\eta^1\text{-}C_5H_4))Mn}(CO)_4 + CH_4 + CO \qquad (3)$$

2

$$\mathbf{1b} + L \rightarrow (\eta^5\text{-}C_5H_5)(CO)\overline{W(\mu\text{-}(\eta^5:\eta^1\text{-}C_5H_4))Mn}(CO)_nL + (4 - n)CO \qquad (4)$$

3a or **3b**: L = R_3P or $(RO)_3P$, $n = 3$
4: L = 1,2-$(Ph_2P)_2C_2H_4$ (diphos), $n = 2$

The Systems W–Mn and Mo–Mn. Combination of $(\eta^5\text{-}C_5H_5)_2MH_2$, M = W or Mo, with $CH_3Mn(CO)_5$ under an inert atmosphere either in tetrahydrofuran at room temperature over a period of several days or in refluxing benzene over a period of 1 h results in a change of solution from yellow to red, accompanied by gas evolution. Following suitable workup the red crystalline complexes **1a** and **1b** are isolated in yields of 50% and 70%, respectively. Analytical data for the products and mass spectrometric analysis of both the products and the gases evolved (see Experimental Section) indicate that the principal reaction occurring in solution is that shown as eq 1 in Scheme I.

A structure has been determined for a single crystal of **1a**,[2,6] revealing a bridging $\eta^5:\eta^1$-C_5H_4 group between the molybdenum and manganese atoms which are also joined by a metal–metal bond. The mass spectra of compounds **1a** and **1b** show satisfactory parent ion peaks as well as the fragmentation pattern expected for the loss of each of five CO groups (see Experimental Section). Infrared and proton NMR data for the derivatives **1a** and **1b** as well as those of the homologous derivative **2** (discussed below) are given in Table I. Five principal bands in the carbonyl stretching region are observed each for **1a** and **1b**, reflecting the presence of the *cis*-$Mn(CO)_4$ group (four bands)[9] and the single CO group on the Mo or W atom. The carbonyl absorptions for **1b** are shown in the upper trace of Figure 1 (supplementary material) while the infrared spectrum in the region 4000–400 cm^{-1} is given as the upper trace in Figure 2 (supplementary material). The corresponding spectra for **1a** show similar features.

The ^1H NMR data in cyclohexane solution are listed in Table I. The actual spectra in two solvents of widely different character, pyridine and benzene, are shown in Figure 3 (supplementary material). These illustrate an unusual solvent effect on the resonances, which is discussed below. These spectra clearly indicate the presence of an η^5-C_5H_5 group by a sharp singlet of relative area 5 and a C_5H_4 group by the A_2B_2 pattern of relative area 4.[10] Without deuterium labeling we do not venture an assignment of the A_2B_2 group within the C_5H_4 ring at this time.[10] A remarkable dependence of the chemical shifts of these resonances on solvent is observed. This has been indicated in Figure 3 for two solvents and is shown schematically for a wider range of solvents in Figure 4; the chemical shift data represented by Figure 4 is listed in Table II (supplementary material). The origin of such large shifts

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Table I. Infrared and Proton Magnetic Resonance Data

complex	ν_{CO},[a] cm^{-1}	chem shift,[b] τ				
		H_A	H_B	$H_{C_5H_5}$	H_{M-H}	J_{AB}, Hz
$MoMnC_{15}O_5H_9$, **1a**	2033 s, 1963 s, 1950 m, 1928 s, 1919 s	5.57 t (2)	5.67 t (2)	5.84 s (5)		1.7
$WMnC_{15}O_5H_9$, **1b**	2038 s, 1973 s, 1944 m, 1935 s, 1924 s	5.56 t (2)	5.58 t (2)	5.83 s (5)		1.8
$ReMnC_{14}O_4H_{10}$, **2**	2043 s, 1960 s, 1946 s, 1925 s	5.20 t (2)	6.12 t (2)	5.97 s (5)	24.7 s (1)	2.0

[a] Cyclohexane solution. Relative intensities: s, strong; m, medium. [b] Benzene solution, relative to internal TMS standard; t = triplet, s = singlet; relative intensities of signals given in parentheses.

Table III. Solvent Effect on ^1H NMR of Metallocene Hydrides

compd	solvent	$\tau(\eta^5\text{-}C_5H_5)$	τ(MH)
$(\eta^5\text{-}C_5H_5)_2MoH_2$	benzene	5.72	18.8
	THF[a]	5.46	17.7
$(\eta^5\text{-}C_5H_5)_2WH_2$	benzene	5.84	22.5
	THF	5.56	22.8
$(\eta^5\text{-}C_5H_5)_2ReH$	benzene	5.93	23.1
	THF	5.68	23.3

[a] Tetrahydrofuran.

undoubtedly is derived from some preferential solvent–solute orientation,[11] but the forces responsible for this do not lead to the formation of any isolable solvates. None of the solvents are retained upon evaporation and in mixed solvents and the position of the resonances are at the weighted average calculated from those observed in each of the solvents alone. A visual display of this for the solvent mixture benzene–pyridine is shown in Figure 5 (supplementary material) the data for which is also given in Table II. By contrast, the solvent effect on the resonances of the starting metallocene hydrides is relatively minor, see Table III.

The System Re–Mn. Combination of $(\eta^5\text{-}C_5H_5)_2ReH$ with $CH_3Mn(CO)_5$ in refluxing benzene over a period of several hours followed by suitable workup gives the red compound **2** in 40% yield (see Scheme I). By constrast to the formation of **1a** and **1b**, formation of **2** is accompanied by evolution of CH_4 and CO. The mass spectrum of **2** indicates this to be a tetracarbonyl hydride (see Experimental Section). Infrared and ^1H NMR data are summarized in Table I. Four carbonyl stretching modes are observed, as expected:[9] the absorptions in the carbonyl stretching region are shown as the lower trace of Figure 1. The infrared spectrum in the region 4000–400 cm^{-1} is given as the lower trace of Figure 2. ^1H NMR data indicate the presence of an unsubstituted $\eta^5\text{-}C_5H_5$ group, a C_5H_4 group, and a metal hydride. Reasoning by analogy to the known structure for **1b**[6] and taking into account the different electronic requirements of the metals, we find these data support the structure of **2** as indicated in Scheme I. A similar large dependence of the chemical shift of the ^1H NMR spectra for **2** is observed as seen for **1a** and **1b**; the data are listed in Table II and graphically represented in Figure 6. The spectrum of **2** in acetonitrile-d_3 shows the largest separation between the A_2 and B_2 resonances (3.11 ppm) observed in this work.

Deuterium-Labeling Studies. For identification of the source of hydrogen in the formation of CH_4 and H_2 in the syntheses of **1a** and **1b** and of CH_4 in the synthesis of **2**, the reactions described in the foregoing sections were repeated with isotopically labeled starting materials. On the basis of the earlier observations that the cyclopentadienyl hydrides of rhenium[3a] and of molybdenum and tungsten[3b] are protonated on the metal by mineral acids, we treated $(\eta^5\text{-}C_5H_5)_2WH_2$ and $(\eta^5\text{-}C_5H_5)_2ReH$ with deuterio acid under inert atmosphere followed by neutralization with deuterio base. We thus observed complexes which were completely deuterated at the metal (determined by ^1H NMR) but which also indicated a small amount of further deuterium incorporation into the rings (see discussion of the analysis of products). These materials were

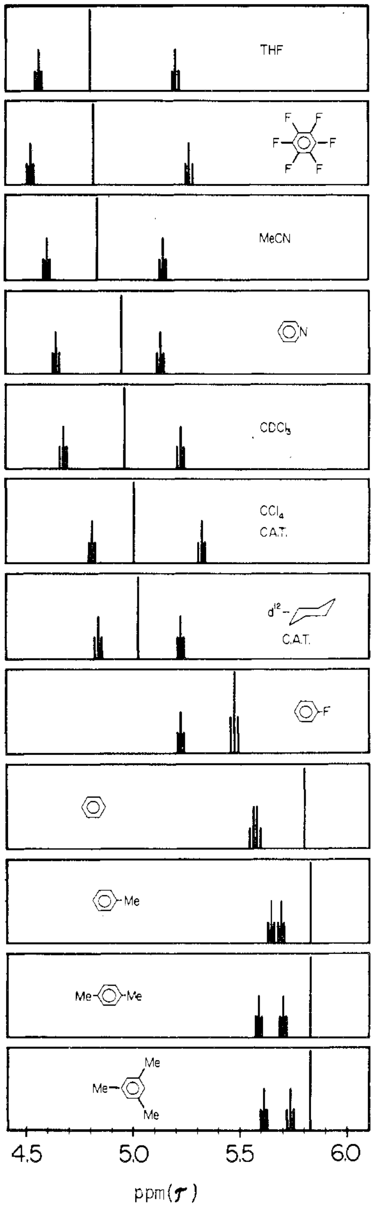


Figure 4. Schematic representation of solvent effect on ^1H NMR resonances of **1b**.

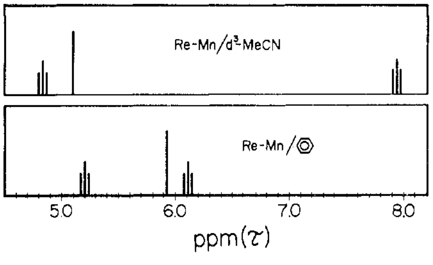


Figure 6. Schematic representation of solvent effect on C_5H_5 and C_5H_4 resonances of **2**.

Table IV. Calculated and Average Observed Peak Heights for Parent Ion Multiplet of **2** Obtained from the Reaction of $(\eta^5\text{-}C_5H_5)_2ReD$ + $CD_3Mn(CO)_5$ in Benzene-d_6

	peak heights		
mass	calcd[a]	av obsd[b]	diff
483	20.10	21.01	−0.91
484	11.04	11.16	−0.12
485	37.96	37.34	0.62
486	20.54	20.32	0.22
487	6.78	7.05	−0.27
488	3.08	3.12	−0.04
489	0.44	0.0	0.44
490	0.05	0.0	0.05
491	0.00	0.0	0.00
492	0.00	0.0	0.00
493	0.0	0.0	0.0
total	100.00	100.00	0.00

[a] Least-squares fit of data for **2** with isotopic distribution 0% d_{10}, 64% d_1h_9, 25% d_2h_8, 7% d_3h_7, and 4% d_4h_6; *R* factor 0.027. This distribution is equivalent to the isotopic content of 15.1% D. [b] Average of three measured spectra, each normalized to the total shown.

then combined with $CD_3Mn(CO)_5$ which was the labeled derivative employed to facilitate the mass spectrometric analysis of the gases (explained in the Experimental Section).

The methane obtained from $(\eta^5\text{-}C_5H_5)ReD$ and $CD_3Mn(CO)_5$ was found to consist of 0.5% CD_4 and 99.5% CD_3H, showing that the evolved methane arises from the methyl group of $CD_3Mn(CO)_5$ and a ring hydrogen of the cyclopentadienyl hydride. The product **2**-d_x isolated from this reaction was subjected to mass spectrometric analysis,[12] the results of which are shown in Table IV. These data indicate that the compound contains 15.1% D, significantly higher than expected if the starting materials were pure $(\eta^5\text{-}C_5H_5)_2ReD$. Deuteration with mineral acid must therefore result in some slow exchange of the ring protons.[13] This would also account for the small amount of CD_4 observed in the product gases, taking into account competition with the hydrogen atoms on the ring as well as possible deuterium isotope effect in the abstraction step. A proton NMR spectrum of product **2**-d_x clearly shows a resonance at τ 24.7 which integrates almost exactly 1.9 with that of the cyclopentadienyl ring protons. This indicates that the deuterium atom must have become statistically distributed over all 10 possible positions in the bimetallic product after evolution of CD_3H.

From the reaction of $(\eta^5\text{-}C_5H_5)_2WD_2$ and $CD_3Mn(CO)_5$, mass spectrometric analysis of the gases indicated the following (relative) percentages: for methane, 5.2% CD_4, 94.8% CD_3H, for hydrogen, 0.4% D_2, 6.1% HD, 93.5% H_2. Abstraction of the ring proton to give methane is thus again indicated. The presence of only a small amount of D_2 in the gas phase was at first puzzling. Separate experiments with **1b** and D_2 revealed a facile reaction at 80 °C and incorporation of deuterium (see equations under Scheme II, below). Mass spectral analysis of **1b**-d_x isolated from the reaction of $(\eta^5\text{-}C_5H_5)_2WD_2$ with $CD_3Mn(CO)_5$ is given in Table V. These data indicate 9.1% D content resulting at least in part from recycling of the deuterium (Scheme II). A deuterium balance on the products counting only the isotope introduced through $(\eta^5\text{-}C_5H_5)_2WD_2$ gives the following result: 9.1% (**1b**-d_x) + 5.2% (CD_4) + 0.8% (D_2) + 3.1% (HD) = 16.1%. This figure is in reasonably close agreement to 16.7%, the deuterium isotope content in $(\eta^5\text{-}C_5H_5)WD_2$, and indicates no additional deuterium was incorporated into the aromatic rings of the metallocene hydride in the deuterium exchange in mineral acid.

Table V. Calculated and Average Observed Peak Heights for Parent Ion Multiplet of **1a** Obtained from the Reaction of $(\eta^5\text{-}C_5H_5)_2WD_2$ + $CD_3Mn(CO)_5$ in Benzene-h_6

	peak heights		
mass	calcd[a]	av obsd[b]	diff
506	11.94	12.41	−0.47
507	15.82	15.52	0.30
508	22.20	22.40	−0.20
509	13.54	13.41	0.13
510	17.73	17.32	0.41
511	11.74	11.93	−0.19
512	4.43	4.73	−0.30
513	1.41	1.50	−0.09
514	0.68	0.78	−0.10
515	0.34	0.00	0.34
516	0.05	0.00	0.05
517	0.01	0.00	0.01
518	0.00	0.00	0.00
519	0.00	0.00	0.00
total	99.88	99.99	−0.11

[a] Least-squares fit of data for 3 with isotopic distribution 54% h_9, 33% d_1h_8, 8% d_2h_7, 2% d_3h_6, 2% d_4h_5, and 1% d_5h_4, equivalent to an isotopic content of 9.1% D. *R* factor is 0.026. [b] Average of four measured spectra, each normalized to the total shown.

Table VI. Calculated and Average Observed Peak Heights for Parent Ion Multiplet of **1a** Obtained from Reaction of $(\eta^5\text{-}C_5H_5)_2WH_2$ with $CH_3Mn(CO)_5$ in Benzene-d_6 (Experiment 2)[a]

	peak heights		
mass	calcd[a]	av obsd[b]	diff
504	0.12	0.00	0.12
505	0.02	0.00	0.02
506	22.07	22.86	−0.78
507	15.79	16.23	−0.43
508	28.18	28.31	−0.13
509	4.70	4.10	0.60
510	24.38	24.54	−0.15
511	4.11	3.27	0.83
512	0.57	0.69	−0.12
513	0.06	0.00	0.06
514	0.00	0.00	0.00
515	0.00	0.00	0.00
516	0.00	0.00	0.00
517	0.00	0.00	0.00
518	0.00	0.00	0.00
total	99.99	99.99	0.00

[a] Least-squares fit of data for **1a** with isotopic distribution 100% h_9. *R* factor is 0.033. [b] Average of three measured spectra, each normalized to the total shown.

The possibility of exchange of D_2 with solvent was considered in view of the observation by Klabunde and Parshall[14] of such exchange catalyzed by metallocene hydride species of niobium and tantalum. Two reactions were carried out in benzene-d_6. The first was the reaction of $(\eta^5\text{-}C_5H_5)_2WH_2$ with $CH_3Mn(CO)_5$ over a period of 2.5 h. Mass spectrometric analysis of the gases produced as well as of the product **1b** isolated (see Table VI) showed that within our experimental error *no* exchange with solvent occurred in this experiment. A second reaction in benzene-d_6 was carried out with $(\eta^5\text{-}C_5H_5)_2WH_2$ and $CD_3Mn(CO)_5$ for 2.5 h. In this case, CD_3H would be the principal gaseous product with the presence of CD_4 indicating possible exchange reactions with solvent. The ratio of these two gases could be measured by mass spectrometry which was not possible for the ratio of CH_4 to CH_3D for the previous experiment (see Experimental Section). Mass spectrometric analysis of the final gas mixture from the reaction revealed 4.8% CD_4, 95.2% CD_3H, 96.2% H_2, 3.5% HD, and 0.3% D_2. Analysis of **1b** recovered from this reaction is given in Table VII: these data indicate about 2% deuterium incorporation, a negligible amount from the point of view of our studies for the 2.5-h reaction time.

Treatment of $(\eta^5\text{-}C_5H_5)(CO)\overline{W(\mu\text{-}(\eta^5\text{:}\eta^1\text{-}C_5H_4))Mn}(CO)_4$

Table VII. Calculated and Average Observed Peak Heights for Parent Ion Multiplet of **1a** Obtained from the Reaction of $(\eta^5\text{-}C_5H_5)_2WH_2$ with $CD_3Mn(CO)_5$ in Benzene-d_6 (Experiment 3)[a]

mass	peak heights		
	calcd[a]	av obsd[b]	diff
504	0.10	0.00	0.10
505	0.03	0.00	0.03
506	18.55	18.71	−0.17
507	15.92	16.18	−0.27
508	26.23	26.17	0.06
509	8.02	7.87	0.15
510	22.05	21.72	0.33
511	6.80	6.74	0.06
512	1.75	1.97	−0.22
513	0.48	0.63	−0.15
514	0.07	0.00	0.07
515	0.01	0.00	0.01
516	0.00	0.00	0.00
517	0.00	0.00	0.00
total	99.99	99.99	0.00

[a] Least-squares fit of data for **1a** with isotopic distribution 84% h_9, 12% d_1h_8, 3% d_2h_7, and 1% d_3h_6. *R* factor is 0.016. [b] Average of three measured spectra, each normalized to the total shown.

(1b) with H_2 or D_2. Observation of the Transient Intermediate $(\eta^5\text{-}C_5H_5)_2(H)W\text{–}Mn(CO)_5$ (i-1). As discussed in the previous section, the complex **1b** isolated from the reaction of $(\eta^5\text{-}C_5H_5)_2WD_2$ with $CD_3Mn(CO)_5$ indicated considerable incorporation of deuterium. We were thus led to examine the reaction of **1b** first with H_2 and then with D_2.

At ambient temperature and pressure, a slow reaction is noted between H_2 and a solution of **1b** in benzene. The initial deep red color of the solution turned to a light red, accompanied by the appearance of a red precipitate. After 2 weeks this reaction was stopped and the benzene solution decanted from the precipitate. The supernatant liquid was found to contain traces of **1b**, identified by its infrared spectrum. The red precipitate was insoluble in benzene but quite soluble in acetone, in which its infrared spectrum was broad and featureless. This substance was insufficiently soluble in other less polar solvents to obtain a meaningful infrared spectrum. However an ^1H NMR spectrum in acetone-d_6 proved informative. Two resonances were observed at τ 4.73 and 20.8 with relative intensities of 10:1. A high amplitude scan of the high-field resonance revealed $^{183}W\text{–}H$ satellites with $J_{^{183}W\text{–}H} = 70$ Hz. These indicate that the high-field hydrogen atom is bonded to the tungsten atom. The ^1H NMR spectrum of this compound thus corresponds to an intermediate having two equivalent C_5H_5 rings and a W–H moiety such as $(\eta^5\text{-}C_5H_5)_2(H)W\text{–}Mn(CO)_5$ (**i-1**).

All attempts to isolate and/or crystallize this material were unsuccessful. In a tetrahydrofuran–hexane solution and under a nitrogen atmosphere this substance was found to evolve H_2, re-forming **1b** over a period of 5 weeks. A quantity of **1b** was then treated with H_2 at 3 atm pressure at 80 °C in benzene solution. Over a period of 3 h the initial red solution turned bright yellow. An ^1H NMR spectrum of the reaction residue in benzene displayed two resonances at τ 5.8 and 23.3 with relative intensities of 10:2. These correspond exactly to $(\eta^5\text{-}C_5H_5)_2WH_2$. An infrared spectrum of the reaction residue in cyclohexane indicated $Mn_2(CO)_{10}$ to be the only carbonyl species present. The result of the above observations can be summarized in Scheme II.

Scheme II

$$\mathbf{1b} + H_2 = \underset{\mathbf{i\text{-}1}}{(\eta^5\text{-}C_5H_5)_2(H)W\text{–}Mn(CO)_5}$$

$$\mathbf{i\text{-}1} + 0.5H_2 = (\eta^5\text{-}C_5H_5)_2WH_2 + 0.5Mn_2(CO)_{10}$$

A sample of **1b** was treated with D_2 at 3 atm pressure and 80 °C in benzene solution: after 3 h a gas sample was removed and examined by mass spectrometry. This indicated the presence of 5% H_2, 22% HD, and 73% D_2. $(\eta^5\text{-}C_5H_5)_2WH_2$ was isolated from this reaction in 84% yield and assayed for deuterium content by ^1H NMR. In this procedure, the cyclopentadienyl hydride is exposed to mineral acid followed by neutralization with NaOH; the metal-bonded deuterium is thus exchanged for proton, providing an internal reference for ^1H NMR assay of the ring deuteration. The first recovered product indicated 31% D in the rings. A further sample of **1b** was treated with D_2 at 10 atm at 80 °C, in benzene solution for 3 h. Cyclopentadienyl hydride recovered from this experiment was obtained in 78% yield and indicated 82% D. On the basis of these results we were able to develop a method for essentially complete exchange of dueterium for hydrogen in $(\eta^5\text{-}C_5H_5)_2WH_2$ using $Mn_2(CO)_{10}$ as a catalyst; this is described in a companion note.[7]

Reaction of $(\eta^5\text{-}C_5H_5)(CO)Mo(\mu\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))Mn(CO)_4$ (1a) with D_2. In view of the above results for the reaction of **1b**, a sample of **1a** was likewise treated with D_2 under the same conditions. The initial red color of the solution became yellow, and the gas above the solution after 3-h exposure at 80 °C was found, by mass spectrometry, to consist of 83% D_2, 14% HD, and 3% H_2. Workup of the reaction mixture indicated the presence of $Mn_2(CO)_{10}$, $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$, and a small quantity of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$.

Reaction of $(\eta^5\text{-}C_5H_5)(H)Re(\mu\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))Mn(CO)_4$ (2) with D_2. The reaction was carried out as given above for **1b**. No color change was observed even after 24 h. At that point the gas phase consisted of 94% D_2, 4% HD, and 2% H_2. The reaction was then stopped and solvent removed; an infrared spectrum of the solids indicated that the major constituent was **2**, with trace quantities of $(\eta^5\text{-}C_5H_5)Re(CO)_3$ and $Mn_2(CO)_{10}$. The mass spectrum of **2** recovered from the reaction showed that deuterium exchange has occurred, represented by derivatives of **2** containing d_1h_9. No attempts were made to pursue this exchange reaction further.

Reaction of $(\eta^5\text{-}C_5H_5)(CO)W(\mu\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))Mn(CO)_4$ (1b) with Phosphorus Ligands. It was of interest to explore the reactions of **1b** with some typical phosphorus ligands in order to see whether acyl derivatives would be formed by C_5H_4-group migration or whether simple substitution products would be obtained. The results, surprisingly in our opinion, indicated the latter. We treated **1b** separately with three different types of phosphorus-containing ligands: a phosphite, a phosphine, and a chelating diphosphine. The reactions of **1b** with the three ligands are clean and quantitative, although high yields of crystals were obtained only for the $P(OCH_3)_3$ derivative.

Analytical data on the resulting complexes as well as mass spectrometric data on these and the evolved gases are given in the Experimental Section. These data clearly indicate that, in each case, substitution is accompanied by CO evolution. Spectroscopic data for the three complexes isolated are given in Table VIII. The carbonyl stretching region in the infrared spectra of each of the recrystallized products reveals more absorptions than carbonyl groups contained in the complex, indicating the presence of more than one species. The infrared spectrum of the $P(OCH_3)_3$ derivatives is shown in Figure 1. This spectrum exhibits a shift in the maximum and a doubling of three of the four bands observed for the unsubstituted derivative **1b**. The doubling is characteristic of isomer pairs such as the rotamers observed in $(\eta^5\text{-}C_5H_5)Fe(CO)_2Si(CH_3)Cl_2$[15] or cis,trans isomers observed in $(\eta^5\text{-}C_5H_5)M(X)(CO)_2L$ (M = Mo or W).[16] Significantly, no bridging carbonyl absorptions were observed.

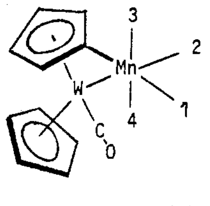
Table VIII. Spectroscopic Data for (η^5-C_5H_5)(CO)W(μ-(η^5:η^1-C_5H_4))Mn(CO)$_3$L (3) and (η^5-C_5H_5)(CO)W(μ-(η^5:η^1-C_5H_4))Mn(CO)$_2$(diphos) (4)

		^{1}H NMR				
		η^5-C_5H_5 region τ^b			ligand protons	
complex	IR ν_{CO},^{a} cm^{-1}	H_A	H_B	$H_{C_5H_5}$	τ^b	assignt
3a (L = P(OCH$_3$)$_3$)	1995 sh, 1993 m, 1953 vs, 1903 sh, 1899 s, 1892 sh, 1882 sh	4.46^c b (2)	5.38 b (2)	4.79 s (5)	6.48 d (9)	CH_3 (J_{P-H} = 12 Hz)
3b (L = P(CH$_3$)$_2$(C$_6$H$_5$))	1989 sh, 1980 m, 1946 vs, 1882 vs, 1872 s	4.72^d b (2)	5.55 b (2)	5.06 s (5)	2.54 mult 8.38 d (6)	C_6H_5 CH_3 (J_{P-H} = 8 Hz)
4	2025 s, 2019 sh, 1940 vs, 1932 s, 1921 m, 1868 w, 1849 w, 1827 m	5.95^e b (2)	6.26 b (2)	4.64 s (5)	2.72 mult (5) 7.5–9.2^f mult (4)	C_6H_5 CH_2

^{a} Hexane solution, **3a**; cyclohexane, **3b** and **4**. Relative intensities: vs, very strong; s, strong; sh, shoulder; m, medium; w, weak; vw, very weak. ^{b} Relative to internal TMS standard; relative intensities of signals given in parentheses. ^{c} Me$_3$SO-d_6 solution. ^{d} Acetone-d_6 solution. ^{e} CDCl$_3$ solution. ^{f} These resonances were unresolved.

An ^{1}H NMR spectrum of the P(OCH$_3$)$_3$ derivatives was obtained; the spectrum in acetone-d_6 is shown in Figure 7 (supplementary material), and the chemical shifts are listed in Table VIII. At 40 °C the protons of the C_5H_4 ring appear as two broad A_2B_2 resonances at τ 4.46 and 5.38, respectively, each of relative area 2. The protons on the unsubstituted ring appear as a sharp singlet at τ 4.79 (relative area 5). The methyl groups on the ligand appear as a doublet (J_{P-CH_3} = 12 Hz) of relative area 9. These results suggest that the P(OCH$_3$)$_3$ group is on the manganese rather than the tungsten atom. Substitution on tungsten can give rise to a doublet for the η^5-C_5H_5 resonance as observed for *trans*-(η^5-C_5H_5)M(X)(CO)$_2$L derivatives.[16] However, since no ^{31}*P*M-η^5-C_5*H*$_5$ coupling is observed for the cis isomers, absence of such coupling in the derivative **3a** or **3b** cannot be taken as conclusive evidence for the location of the phosphorus ligand.

A variable-temperature ^{1}H NMR study of the P(OCH$_3$)$_3$ complex was undertaken in an attempt to resolve the broad features observed near room temperature. The spectra of **3a** in acetone-d_6 solution at various temperatures are shown in Figure 7. Upon cooling of the solution, the two broad A_2B_2 signals each separate into two new peaks. The higher field C_5H_4 resonance coalesces and then reappears as two separate resonances. The lower field C_5H_4 resonance also splits into two separate resonances, but at a lower temperature (1 °C). As the temperature is further decreased to −73 °C, no change is observed except broadening due to solvent viscosity. These results indicate that the product is a rapidly interconverting equilibrium mixture of two of the four possible isomers where the ligand, L, may be in positions 1, 2, 3, or 4:



At the highest temperature examined (50 °C) the resonances appear at the average position of the limiting low-temperature peaks.

The energy barrier for the interconversion of the two isomers was determined by standard methods;[17] a plot of log k vs. $1/T$ is shown in Figure 8 (supplementary material). The rate of interconversion at 25 °C is 98 s^{-1}. The Arrhenius activation energy for the interconversion is 7.7 (±1.1) kcal mol^{-1}. From an Eyring plot of the data the following activation parameters are extracted: $\Delta G^{\ddagger}_{298}$ = 14.7 ± 0.4 kcal mol^{-1}; $\Delta H^{\ddagger}_{298}$ = 7.0 ± 1.0 kcal mol^{-1}; $\Delta S^{\ddagger}_{298}$ = −25 ± 4 eu.

Similar observations were made for the derivative **3b**; variable-temperature ^{1}H NMR spectra are shown in Figures 9A and 9B (supplementary material). The methyl and phenyl resonances integrate to their expected values; the phenyl resonance appears as a complex multiplet in the range τ 2.24–2.85. Both the high- and low-field C_5H_4 resonances coalesce and split into two separate resonances as the temperature is lowered. The high-field C_5H_4 resonance coalesces at a higher temperature than in **3a**. As the temperature is lowered from +50 to −8 °C, the C_5H_5 resonance also broadens and then sharpens again below −8 °C. Simultaneously, a new resonance appears between the split high-field C_5H_4 peaks at −8 °C. Below −8 °C, this peak sharpens until at −78 °C two new small resonances in the proximity of the new peak are detected. The methyl doublet also broadens with decreasing temperature until at −78 °C some fine structure appears under the methyl resonance. The freezing-out process is reversible. For this derivative the Arrhenius activation energy is 7.0 (±1.0) kcal mol^{-1} with an interconversion rate of 2.1 × 10^3 s^{-1} at 25 °C. Activation parameters are $\Delta G^{\ddagger}_{298}$ = 12.9 ± 0.4 kcal mol^{-1}, $\Delta H^{\ddagger}_{298}$ = 6.9 ± 0.9 kcal mol^{-1}, and $\Delta S^{\ddagger}_{298}$ = −22 ± 4 eu.

A red crystalline complex was isolated from the reaction of **1** with diphos which analyzed for a chelate complex with loss of two CO ligands. As shown in Table VIII, the terminal carbonyl stretch infrared spectrum exhibited a multiplicity of bands indicating the presence of several isomers. However, ^{1}H NMR results indicate that tautomerism had been quenched. The resonances in the CDCl$_3$ spectrum, presented in Table VIII, underwent no change from +45 to −20 °C. Therefore, isomers of the chelate compound, with high-energy barriers, are present which do not interconvert at temperatures below 45 °C.

A P(CH$_2$CH$_3$)$_3$ derivative of **1b** was synthesized but not isolated due to its failure to crystallize from a number of solvents. The carbonyl stretching region of the infrared spectrum of the reaction solution (given in the Experimental Section), however, indicated that starting material had been completely consumed. The spectrum of the product bore a striking similarity to that of the P(CH$_3$)$_2$(C$_6$H$_5$) derivative. The corresponding isomers may also be present in this derivative, but the characteristic pairing or broadening of the infrared absorptions was less apparent. Either the separation between infrared isomer peaks is small or the equilibrium of isomers at room temperature may favor one isomer more than the other such that the infrared peaks would represent a more prevalent isomer.

Attempted Reaction of 1b with CO. A CO insertion reaction was attempted with **1b** to check whether this would occur with CO under pressure. Treatment of **1b** with up to 6.9 atm of CO and at 80 °C did not afford any acyl derivatives as monitored by the absence of any perceptible absorptions in the CO bridging region in the products after their return to atmospheric pressure and room temperature. Instead, reaction products consisted of some starting material, some $Mn_2(CO)_{10}$, some $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, and an unidentified carbonyl-containing species with a weak infrared absorption at 1873 cm^{-1}. Thus, decomposition or rearrangement, rather than CO insertion, is observed in the reaction with CO.

Treatment of 3a with H_2. This reaction gave the products $(\eta^5\text{-}C_5H_5)_2WH_2$ and, in order of elution from a silica gel column, $Mn_2(CO)_{10}$ (14% based on Mn), 1-$Mn_2(CO)_9P(OCH_3)_3$ (30%), and 1,10-$Mn_2(CO)_8[P(OCH_3)_3]_2$ (50%), where 1 and 10 represent the axial positions on the manganese dimer. $(\eta^5\text{-}C_5H_5)_2WH_2$ was identified from its ^1H NMR spectrum and $Mn_2(CO)_{10}$ from its infrared spectrum in the carbonyl stretching region. The mono- and disubstituted manganese carbonyl complexes were characterized by infrared, ^1H NMR, and mass spectra as described in the Experimental Section.

The hydrogenolysis products are consistent with $(\eta^5\text{-}C_5H_5)_2WH_2$ and $Mn_2(CO)_{10}$ obtained from the hydrogenolysis of **1b**. The presence of unsubstituted $Mn_2(CO)_{10}$ along with mono- and disubstituted $Mn_2(CO)_{10}$ indicates that some type of rearrangement process occurs in solution accompanying the cleavage of the tungsten–manganese and cyclopentadienyl–manganese bonds.

Experimental Section

General Procedures. All reactions were performed in standard Schlenk-type flasks under an inert atmosphere of nitrogen or argon. Reactions under greater than ambient pressure were run in sealed Carius tubes. All solvents were distilled from CaH_2 except for halogenated solvents, which were dried over molecular sieves (4A) and deoxygenated by bubbling nitrogen through them for 5–10 min.

Reagents. The following materials were obtained from the indicated sources: $MoCl_5$, WCl_6, and $ReCl_5$, Alfa Inorganics, Beverly, Mass.; $Mn_2(CO)_{10}$, Pressure Chemical Co., Pittsburgh, Pa.; D_2, Liquid Carbonics; CD_3I, Aldrich Chemical Co., Milwaukee, Wis.; CD_3H and CD_4, Merck Laboratory Chemicals, Rahway, N.J.; $P(CH_3)_2(C_6H_5)$, Pressure Chemical Co., Pittsburgh, Pa. All other reagents and solvents are those available from general chemical vendors.

The syntheses employed for $(\eta^5\text{-}C_5H_5)_2WH_2$ and $CH_3Mn(CO)_5$ are those described by King.[18] The synthesis of $CH_3Mn(CO)_5$ was altered by using a 0.4% sodium amalgam in anhydrous ether in place of a methanolic solution of sodium hydroxide or metallic sodium. CD_3I was used in place of CH_3I in the synthesis of $CD_3Mn(CO)_5$.

Instrumentation. Mass spectra of gases were taken on a Consolidated Engineering Corp. Model 21-620 mass spectrometer with an ionizing current of 20 μA. Mass spectra of solids were obtained on an AEI MS9 spectrometer. Infrared spectra in the region 4000–400 cm^{-1} either for solids or for solutions in various appropriate solvents were obtained on a Perkin-Elmer 421 grating spectrophotometer. Spectra in the carbonyl stretching region (2100–1800 cm^{-1}) were obtained on a Beckman IR-4 spectrophotometer equipped with LiF prism; spectra were calibrated either with the absorption of cyclohexane at 2138.6 cm^{-1} or, by using the spectrophotometer in the single-beam mode, against the absorption of water in air at 1988 cm^{-1}. Well-known carbonyl derivatives observed in this work were identified through their carbonyl stretching absorptions by comparison with those of authentic samples. Our measured values for the principal absorptions (only the strong or medium-intensity bands) in cyclohexane solution are given as follows (cm^{-1}):[19] $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$, 2032, 1948;[20a] $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$, 1962, 1918;[20b] $Mn_2(CO)_{10}$, 2044, 2013, 1983;[20c] $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, 2028, 1945;[20d] $(\eta^5\text{-}C_5H_5)Re(CO)_3$, 2031, 1941.[20a]

Proton magnetic resonance spectra were obtained on Varian A-60D or HA-100 spectrometers using tetramethylsilane as internal reference. The low temperatures employed in the studies were estimated to ±2 °C from the observed chemical shift differences between the doublet and quintet resonances of methanol.

Calibration of Gas Mixtures by Mass Spectrometry. The gas mass spectra for mixtures of CD_4 and CD_3H were calibrated with a series of mixtures of these gases of known composition. Gas compositions were obtained by successive pressure–volume readings of CD_4 and CD_3H by using a Toepler pump and collection into evacuated bulbs. The gas mixtures were stirred with Teflon paddles fitted inside the bulbs, and the CD_3H^+/CD_4^+ ratios were obtained directly from the heights of the CD_3H and CD_4 parent ion peaks at *m/e* 19 and 20, respectively (see Table IX, supplementary material). The plot of experimental CD_3H^+/CD_4^+ vs. calculated CD_3H/CD_4 is shown in Figure 10 (supplementary material). A least-squares straight line is drawn through the experimental points indicating either a greater ionization efficiency of CD_4 relative to CD_3H or the greater probability of loss of a H atom from CD_3H than a D atom from CD_4 as previously suggested for deuterated methanes.[21] The scatter of points demonstrates possible errors in the assumed minimum isotopic purities of the gases.

The mass spectrometer was also calibrated with known mixtures of H_2 and D_2 by Hoel[22] and was found to exhibit no isotope effect for these gases within experimental error.

All mass spectra were taken with the same ionizing current and at the same gas pressure as used in the analysis of the gas mixtures from the kinetic experiments. To cancel changes in the height due to pressure loss inside the ionizing chamber, we performed all measurements at identical time intervals after injection of the gas mixture.

Synthesis of 1b. A solution of $(\eta^5\text{-}C_5H_5)_2WH_2$ (1 g, 3 mmol) and $CH_3Mn(CO)_5$ (1 g, 5 mmol) in 30 mL of benzene was refluxed under N_2. The initial yellow solution turned deep red in several minutes with copious gas evolution, monitored by use of a mercury-filled buret. When gas evolution ceased (about 1 h), the gas was sampled in an evacuated bulb and solvent removed under vacuum. Excess $CH_3Mn(CO)_5$ was removed by pumping overnight at 10^{-3} mmHg. The residue was dissolved in 1:1 hexane/diethyl ether; the solution was then filtered under N_2 and cooled slowly to −20 °C. The resulting dark red crystals of **1b** were washed with hexane; further crops were grown from the mother liquor. Total yield was 1.1 g (70% based on W). The crystals are air stable for several weeks, but the compound is air-sensitive in solution. Anal. Calcd for $C_{15}H_9MnO_5W$: C, 35.46; H, 1.79; Mn, 10.81; O, 15.74, W, 36.19. Found:[23] C, 35.23; H, 2.25; Mn, 10.71; O, 15.61; W, 35.98. The mass spectrum of **1b** displayed a tungsten isotope pattern typical of a compound with one tungsten atom per molecule with a parent peak at *m/e* 508 (^{184}W). This corresponds exactly to the molecular formula indicated above. The spectrum also showed fragments corresponding to successive loss of five CO groups from the parent ion peak and a principal fragment at $C_{10}H_{10}W(CO)^+$.

Reaction of $(\eta^5\text{-}C_5H_5)_2WH_2$ and $CH_3Mn(CO)_5$ at Room Temperature. $(\eta^5\text{-}C_5H_5)_2WH_2$ (0.3 g, 1 mmol) and $CH_3Mn(CO)_5$ (0.3 g, 1.5 mmol) were dissolved in 20 mL of THF in a Schlenk flask which was connected to a Hg bubbler under an N_2 atmosphere. This solution was stirred at room temperature for 1 week. Infrared spectra of the solution were taken periodically to obtain evidence of an intermediate metal–metal adduct with negative results. Instead, slow gas evolution was observed and, after a few hours, the solution turned red. After 1 week of reaction at room temperature, gas evolution ceased and an infrared spectrum of the solution showed only the presence of **1b**.

Reaction of $(\eta^5\text{-}C_5H_5)_2WH_2$ with $P(CH_3)_2(C_6H_5)$. $(\eta^5\text{-}C_5H_5)_2WH_2$ (0.3 g, 1 mmol) and $P(CH_3)_2(C_6H_5)$ (0.14 g, 1 mmol) were dissolved in 20 mL of benzene, and the mixture was refluxed overnight under N_2 with a slow stream of N_2 bubbled continuously through the solution. A ^1H NMR spectrum of this solution showed only free $P(CH_3)_2(C_6H_5)$ and $(\eta^5\text{-}C_5H_5)_2WH_2$ with no evidence of reaction. Furthermore, no reaction was observed in refluxing toluene for 12 h. However, the same reaction at 160 °C in decalin for 12 h indicated that the $(\eta^5\text{-}C_5H_5)WH_2$ was consumed, but no attempt was made to characterize the products.

Synthesis of 1a. $(\eta^5\text{-}C_5H_5)_2MoH_2$ (1 g, 4 mmol) and $CH_3Mn(CO)_5$ (1.5 g, 6 mmol) were dissolved in 30 mL of benzene under N_2, and the solution was brought to reflux. Gas evolution was monitored and was quite rapid as the yellow solution became red during the first 10 min. After 3 h, gas evolution leveled off to a slow, constant rate, and the reaction was stopped. The constant rate of gas evolution near the end of the reaction was probably due to the slow decomposition of the new compound to $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$, which was identified as a minor product by its terminal carbonyl absorptions in the infrared spectrum in solution. The gas was collected and the reaction mixture worked up as in the synthesis of **1b**. Total yield of **1a** was 0.84 g, 50% based on $(\eta^5\text{-}C_5H_5)_2MoH_2$. Red crystals of **1a** are stable in air for several days; the compound is however very air sensitive in solution. The mass spectrum of **1a** is analogous in every feature to that of **1b**; its parent peak is observed at *m/e* 422 (^{98}Mo) corresponding exactly to the molecular formula $MoMnC_{15}H_9O_5$.

Synthesis of 2. $(\eta^5\text{-}C_5H_5)_2ReH$ (1 g, 3 mmol) and $CH_3Mn(CO)_5$ (1 g, 5 mmol) were dissolved in 30 mL of benzene under N_2, and the solution was brought to reflux. Slow gas evolution was observed as the solution turned red after 1 h. Gas evolution was monitored and ceased after 16 h. The gas was collected and the reaction mixture was worked up as in the reaction of (η^5-C_5H_5)WH_2 with $CH_3Mn(CO)_5$. Total yield of the red crystals of **2** was 0.58 g (40% based on Re). The crystals were contaminated with small quantities of (η^5-C_5H_5)$Re(CO)_3$ which was indentified by its infrared spectrum. The (η^5-C_5H_5)$Re(CO)_3$ could be removed by pumping under high vacuum for several days at room temperature. The red crystals are stable in air for several hours, but the compound is quite air sensitive in solution. Anal. Calcd for $C_{14}H_{10}MnO_4Re$: C, 34.93; H, 2.09. Found:[24] C, 36.27; H, 2.44. The mass spectrum of **2** exhibits a parent ion peak at *m/e* 484 (^{187}Re) which corresponds to the formula indicated above. This also corresponds to the loss of CH_4 and CO from the hypothetical adduct (η^5-C_5H_5)$_2$ReH·MnC(O)$CH_3(CO)_4$. The mass spectrum of **2** displays *m/e* fragments corresponding to the successive loss of four CO groups from the parent ion and a principal peak at $C_{10}H_{11}Re^+$.

Synthesis of (η^5-C_5H_5)$_2WD_2$ and (η^5-C_5H_5)ReD and Reaction with $CD_3Mn(CO)_5$. Each of the respective hydrides (1 g, 3 mmol) was dissolved in 20 mL of 6 N DCl in D_2O, and the mixture was stirred under N_2 for 48 h. The solutions were then neutralized with 6 N NaOD in D_2O. Upon neutralization, the yellow metal deuterides precipitated from solution. The precipitates were collected on a filter under N_2, pumped to dryness, and dissolved in benzene. The benzene solutions were then dried by stirring with anhydrous $MgSO_4$ for 1 h and filtered. The filtrate was evaporated to dryness under vacuum, leaving pure (η^5-C_5H_5)$_2$ReD and (C_5H_5)$_2WD_2$, respectively, in the flask. ^{1}H NMR spectra of the products were obtained; they showed only the C_5H_5 resonance at low field. The high-field M–H resonance was not observed, indicating essentially complete exchange. (Note: When the metal hydrides were stirred for only 24 h in 6 N DCl, exchange was not complete.)

The reactions of these derivatives each with $CD_3Mn(CO)_5$ were performed exactly like those of undeuterated derivatives as described above. Evolved gases were collected and products analyzed as described below. Mass spectra were obtained on a gas-inlet mass spectrometer equipped with a pen recorder. Relative quantities of CD_4 and CD_3H and of D_2, HD and H_2 were calculated from the heights of the parent ion peaks at *m/e* 20 and 19, respectively. $CD_3Mn(CO)_5$ was used in the above two experiments for the following reasons. Use of $CH_3Mn(CO)_5$ would have led to formation of CH_3D and CH_4 with parent ion peaks at *m/e* 17 and 16, respectively. The fragment CH_2D^+ resulting from the loss of a H atom from CH_3D would also have an *m/e* value of 16, thus making it difficult if not impossible to calculate the true quantity of CH_4. This is not a problem with $CD_3Mn(CO)_5$ which would lead to formation of CD_4 and CD_3H with parent ions at *m/e* 20 and 19, respectively. The first fragment from CD_4 will be CD_3^+ with *m/e* 18 and thus will not interfere with the parent ion of CD_3H at *m/e* 19.

The mass spectrum of the gas from reaction of (η^5-C_5H_5)$_2$ReD with $CD_3Mn(CO)_5$ indicated a ratio of CD_4 to CD_3H of 0.4% to 99.6%. Mass spectral analysis also showed large quantities of CO but only a trace of D_2, HD, or H_2. The mass spectrum of the gas from reaction of (η^5-C_5H_5)$_2WD_2$ with $CD_3Mn(CO)_5$ indicated 5.2% CD_4 and 94.8% CD_3H and, in the low-mass region, 0.4% D_2, 6.1% HD, and 93.5% H_2.

Deuterium Assay of Complexes 2 and 1a Obtained from Reactions of (η^5-C_5H_5)$_2$ReD and (η^5-C_5H_5)$_2WD_2$ with $CD_3Mn(CO)_5$. The deuterium content of complexes **2** and **1a** was determined from the mass spectrum. The mass spectra were obtained at source temperatures of 100–140 °C and at 12–15-eV ionizing voltages (direct-inlet probe). Analyses of the parent ion multiplets were based on the average of several measured spectra because of pressure variations which caused small fluctuations in peak heights within the multiplets. A least-squares fit allowing for hydrogen loss or varying deuterium content in the present ion multiplets was also carried out on the UCLA IBM 360/91 computer with MASPAN, a program written in Fortran IV.[12] No hydrogen loss in **2** or **1a** was observed. A conventional *R* factor, $R = \sum \langle |I_{obsd} - I_{calcd}|/I_{calcd} \rangle$, was calculated to give a measure of the fit between the calculated and observed spectra. Tables IV–VI exhibit the results of analyses on complexes **2** and **1a**, respectively, obtained from the above-mentioned reactions with varying deuterium content by using MASPAN. With use of Table IV as an example, the average of three measured spectra of **1a** normalized to a total intensity of 100 is given in the third column. The fourth column lists the differences between the calculated and observed peaks. These results are standardized: a 50:50 mixture of an analyzed 78.8% deuterated sample of **1a** and 0% deuterated sample of **1a** analyzed to the exact hydrogen and deuterium content as was put in. However, a very slight shift in distribution in the deuterated species occurred. The important fact is, however, that the proton and deuterium compounds ionize similarly in the mass spectrometer at the conditions used.

Reaction of 1a with H_2. **1a** (0.2 g, 0.4 mmol) was dissolved in 10 mL of benzene, and the mixture was reacted with 3 atm of H_2 at 80 °C for 3 h. The initial red solution turned yellow over this period of time. The reaction was stopped, the solution was filtered under N_2, and the solvent was removed under vacuum. An infrared spectrum of the reaction residue showed $Mn_2(CO)_{10}$ to be the only carbonyl-containing species present. ^{1}H NMR spectrum of the yellow residues in benzene showed two resonances at τ 5.8 and 23.3 of relative intensity 10:2.

Reaction of 1a with D_2. A solution of **1a** (0.2 g, 0.4 mmol) in 10 mL of benzene was treated with 3 atm of D_2 for 3 h at 80 °C. A mass spectrum of the final gas mixture showed the presence of 74% D_2, 22% HD, and 5% H_2 plus a trace of CO. The solid products were isolated in the same manner as in the reaction of **1a** with H_2. A ^{1}H NMR spectrum of the residue in benzene showed resonances at τ 5.8 and 23.3 of relative intensities 5:2.

Reaction of (η^5-C_5H_5)$_2WH_2$ with D_2 in C_6H_6. (η^5-C_5H_5)$_2WH_2$ (0.15 g, 0.47 mmol) was reacted with 3 atm of D_2 in 10 mL of benzene at 80 °C for 3 h. The reaction was stopped and the gas collected. The solution was filtered under N_2 and solvent removed under vacuum. A ^{1}H NMR spectrum of the reaction residue in benzene displayed two resonances at τ 5.8 and 23.3 of relative intensities of 10:2. A mass spectrum of the gas showed 98% D_2 and about 1% HD and 1% H_2, corresponding approximately to the 99% isotopically pure D_2 starting reagent.

Reaction of (η^5-C_5H_5)$_2WH_2$ with H_2 in C_6D_6. (η^5-C_5H_5)$_2WH_2$ (0.15 g, 0.47 mmol) was treated with H_2 in C_6D_6 under the conditions described above; products were isolated also as described above. A ^{1}H NMR spectrum of the yellow reaction residue in benzene showed two resonances at τ 5.8 and 23.3 of relative intensities 10:2. A mass spectrum of the gas showed only H_2 to be present.

Reaction of 1a with H_2 in C_6D_6 at 80 °C. **1a** (0.20 g, 0.39 mmol) was reacted, as described above, with H_2 in C_6D_6. After 3 h the red solution became yellow. After isolation of the products described above, a ^{1}H NMR spectrum of the residue in benzene showed two resonances at τ 5.8 and 23.3 of relative intensities 10:2. A mass spectrum of the gas showed the presence only of H_2.

^{1}H NMR Estimation of Deuteration in (η^5-C_5H_5)$_2WH_2$. The method for determination of the extent of dueterium incorporation into the products from the reaction of **1a** with D_2 is described below. After reaction, the Carius tube or Hoke cylinder was opened, the solution was filtered under N_2, and the solvent was removed under vacuum, leaving a yellow residue. This residue, containing $Mn_2(CO)_{10}$ and (η^5-$C_5H_{5-n}D_n$)$_2WH_{2-m}D_m$, was stirred with three 5-mL portions of deoxygenated 6 N HCl and each portion filtered into the same Schlenk tube under N_2. The $Mn_2(CO)_{10}$ remained on the frit, and the resulting 15-mL solution contained (η^5-$C_5H_{5-n}D_n$)$_2WH_{3-m}D_m^+$ ($m \leq 2$). The HCl solution was allowed to exchange for 48 h, giving a solution of (η^5-$C_5H_{5-n}D_n$)$_2WH_3^+$. This solution was then cooled in an ice bath and neutralized by adding a solution of 6 N NaOH under N_2, resulting in a flocculent yellow precipitate, which was collected on a frit under N_2 and dried under vacuum. The yellow precipitate was then sublimed at 80 °C, collected into a Schlenk tube, and weighed. The residue was then dissolved in benzene and a ^{1}H NMR spectrum obtained. The spectrum was integrated and the relative intensities of the two peaks at τ 5.8 and 23.3 were compared by using the high-field resonance which had been reprotonated in the acid exchange to measure the extent of deuterium exchange in the C_5H_5 ring. Thus, in deuterated samples the integration will be $(10 - n)$:2 where $n/10$ represents the extent of deuteration in the original exchange with D_2.

Reaction of 1a with 10 Atm of D_2 with Determination of Deuterium Incorporation in the Product. A 20-mL benzene solution of **1a** (0.34 g, 0.67 mmol) was reacted with D_2 (10 atm) at 80 °C for 3 h in a 310-mL Hoke cylinder. The ratio of D_2 in the gas phase to hydrogen in **1a** was about 98:2. Complete exchange should give 98% (η^5-C_5D_5)$_2WD_2$ in this case. After the reaction was stopped, the products were isolated, exchanged with HCl, and purified as described above to give 0.15 g of (η^5-$C_5H_{5-n}D_n$)$_2WH_2$ (78% yield based on **1a**). A ^{1}H NMR spectrum in benzene showed resonances at τ 5.8 and 23.3

of relative intensities 1.8:2, corresponding to $(\eta^5\text{-}C_5H_{0.9}D_{4.1})_2WH_2$ or 82% enrichment in deuterium.

Reaction of 1a with H_2 at Room Temperature. A sample of **1a** (0.3 g, 0.6 mmol) was dissolved in 20 mL of benzene, and the solution was placed in a Carius tube with H_2 gas (3 atm). This solution was stirred for 2 weeks at room temperature, during which time the initial deep red solution turned light red. This color change was accompanied by the appearance of large quantities of a red precipitate. After 2 weeks the reaction was stopped, the Carius tube opened, the benzene decanted, and the red precipitate washed twice with 10-mL portions of benzene to remove any residual **1a**. The residue was then dissolved in 1 mL of acetone-d_6 and the solution was filtered under N_2 into an NMR tube which was then sealed under vacuum. The ^1H NMR spectrum of this solution showed two resonances at τ 4.73 and 20.8 of relative intensities 10:1. A high-amplitude spectrum of the high-field resonance displayed ^{183}WH satellites with $J_{^{183}WH} = 70$ Hz. The red precipitate was insoluble in cyclohexane; infrared spectra in THF or acetone were broad and featureless.

Reaction of 1a with D_2 at Room Temperature. A 20-mL benzene solution of **1a** (0.28 g, 0.57 mmol) was treated with D_2 (3 atm) at room temperature as described above for the corresponding H_2 reaction. After 2 weeks the reaction was stopped and the gas collected for a mass spectrum which indicated the presence of 76% D_2, 21% HD, and 4% H_2. Thus, exchange with D_2 occurs even at room temperature.

Reaction of $(\eta^5\text{-}C_5H_5)_2WH_2$ with $CH_3Mn(CO)_5$ at Room Temperature under Vacuum. A ^1H NMR Experiment. $(\eta^5\text{-}C_5H_5)_2WH_2$ (0.1 g, 0.3 mmol) and $CH_3Mn(CO)_5$ (0.07 g, 0.3 mmol) were dissolved in 1 mL of acetone-d_6 and the solution was filtered into an NMR tube, which was then sealed under vacuum. A spectrum of this yellow solution was recorded immediately and showed only free $(\eta^5\text{-}C_5H_5)_2WH_2$ and free $CH_3Mn(CO)_5$ with no evidence of adduct formation. After 16 h at room temperature the solution started to turn red, and a small singlet started to grow at τ 4.73. This singlet was about 20% as intense as the cyclopentadienyl resonance of $(\eta^5\text{-}C_5H_5)_2WH_2$. Over a period of days the signal at τ 4.73 continued to grow while the signals due to free $(\eta^5\text{-}C_5H_5)_2WH_2$ and $CH_3Mn(CO)_5$ diminished in intensity. After 5 days a second new signal was found at τ 20.8. After 16 days at room temperature all of the $(\eta^5\text{-}C_5H_5)_2WH_2$ and $CH_3Mn(CO)_5$ had been consumed and the only resonances in the ^1H NMR spectrum were the two new ones at τ 4.73 and 20.8. The relative intensities of these two signals were 10:1. A high-amplitude spectrum of the high-field signal displayed ^{183}WH satellites with $J_{^{183}WH} = 70$ Hz. This spectrum appears to be identical with that obtained for the red precipitate **i-1** (Scheme II) from the reaction of **1b** with H_2 at room temperature. At no time in this reaction was there any evidence either of adduct formation or of **1b** in the ^1H NMR spectra recorded during the 16-day reaction. After the reaction was complete, the NMR tube was opened on a vacuum line and the gas collected. Its mass spectrum showed almost entirely CH_4 with only a trace of CO and H_2.

The reaction residue was insoluble in hexane, and attempts to crystallize the product from THF, diethyl ether, or THF–hexane mixtures were unsuccessful. An attempts was also made to grow crystals by solvent diffusion. After 5 weeks at room temperature and under N_2, the diffusion of hexane into the THF solution of the product appeared to be complete. However, no crystals were obtained. The solvent was stripped off, and an infrared spectrum of the red residue in cyclohexane showed that is consisted almost entirely of **1b** with a trace of $Mn_2(CO)_{10}$ present. Thus, over a period of 5 weeks at room temperature, intermediate **i-1** under an N_2 atmosphere is transformed to **1b** and H_2, a reverse of the first equation in Scheme II.

Reaction of 1a with D_2. A 0.25-g sample (0.6 mmol) of **1a** was dissolved in benzene (10 mL) and the mixture was treated with D_2 (3 atm) at 80 °C for 3 h. Over this period of time, the initial red solution turned yellow. The reaction was stopped and the gas was collected. The mass spectrum of the gas showed 83% D_2, 14.5% HD, and 2.5% H_2 plus a large quantity of CO. An infrared spectrum of the reaction residue in cyclohexane showed the presence of $Mn_2(CO)_{10}$ and $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ and a small quantity of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$. The ^1H NMR spectrum of the reaction residue in benzene showed four $\eta^5\text{-}C_5H_5$ resonances and one Mo–H resonance.

Reaction of 2 with D_2. A 20-mg sample of **2** (0.04 mmol) was dissolved in benzene (5 mL), and the mixture was reacted with 3 atm of D_2 at 80 °C. After 24 h the initial red color of the solution persisted. The reaction was stopped and the gas collected. A mass spectrum of the gas indicated 93.9% D_2, 4.1% HD, and 2.0% H_2. An infrared spectrum of the reaction residue in cyclohexane showed a predominance of **2** with trace quantities of $Mn_2(CO)_{10}$ and $(\eta^5\text{-}C_5H_5)Re(CO)_3$. After the reaction, **2** was recrystallized from hexane–diethyl ether solution, and the crystals were submitted for a mass spectrum. An analysis of the parent ion in the mass spectrum showed that **2** had been enriched with deuterium with species ranging from d_1 to d_7.

Synthesis of $(\eta^5\text{-}C_5H_5)(CO)\overline{W(\mu\text{-}C_5H_4)Mn}(CO)_3P(OCH_3)_3$ (3a). To a 20-mL benzene solution of **1b** (0.570 g, 1.12 mmol) was added dropwise $P(OCH_3)_3$ (0.185 g, 1.49 mmol) in 10 mL of benzene over a 10-min period under an atmosphere of argon. After 3 h at 80 °C, gas evolution ceased and the red solution had turned darker red. The benzene was removed under vacuum, and 0.43 g of dark red crystals was recovered from ether at −20 °C (64% yield based on **1b**). As shown by the mass spectrum, the gas evolved was nearly 100% CO and its yield, based on 1, was 76%. Anal. Calcd for $C_{17}H_{18}MnO_7PW$: C, 33.81; H, 3.00. Found:[24] C, 34.35; H, 3.00. Temperatures of 600–700 °C were required for complete combustion of this and other phosphorus derivatives. A parent ion peak for this complex was observed at *m/e* 604 below 80 °C, at 70 eV. This is in good agreement with *m/e* calculated for the above given formula (604). The mass spectrum was found to be temperature sensitive. Below 80 °C a clean CO fragmentation pattern of up to four CO groups is observed. Above 80 °C, however, lower peaks of rearrangement and/or pyrolysis products are seen.

Synthesis of $(\eta^5\text{-}C_5H_5)(CO)\overline{W(\mu\text{-}(C_5H_4)Mn}(CO)_3P(CH_3)_2(C_6H_5)$ (3b). $P(CH_3)_2(C_6H_5)$ (0.543 g, 0.394 mmol) in 65 mL of benzene was added dropwise to a 9-mL benzene solution of **1b** (0.182 g, 0.358 mmol), and the mixture was heated at 80 °C for 2.5 h. After removal of solvent under vacuum, dark red crystals were obtained from a filtered benzene–ether solution (1:1) at 5 °C. Anal. Calcd for $C_{22}H_{20}MnO_4PW$: C, 42.74; H, 3.26. Found:[24] C, 42.36; H, 3.56. A parent ion peak at *m/e* 618 and a clear fragmentation pattern of four CO's are observed for the phosphine complex at 130 °C source temperature and 70 eV; the calculated molecular weight is 618.

Synthesis of $(\eta^5\text{-}C_5H_5)(CO)\overline{W(\mu\text{-}(C_5H_4)Mn}(CO)_2$(diphos) (4). An 8-mL benzene solution of **1b** (0.100 g, 0.197 mmol) and diphos (0.095 g, 0.239 mmol) was reacted at 80 °C for 2.0 h. The solvent was removed under vacuum, the residue was dissolved in a benzene–ether mixture (1:1), and bright red crystals were obtained at 5 °C in a yield of 34 mg (20% based on **1b**). Anal. Calcd for $C_{39}H_{33}P_2O_3MnW$: C, 55.09; H, 3.91. Found:[24] C, 54.80; H, 4.22. A mass spectrum of this derivative was not attempted due to its low volatility.

Synthesis of $(\eta^5\text{-}C_5H_5)(CO)\overline{W(\mu\text{-}C_5H_4)Mn}(CO)_3P(CH_2CH_3)_3$. a 12-mL benzene solution of **1b** (0.243 g, 0.478 mmol) was added dropwise $P(CH_2CH_3)_3$ (0.074 g, 0.626 mmol) in 8 mL of benzene under an atmosphere of argon. After 2.2 h at reflux temperature, reaction was complete, and the solution had become darker red. A mass spectrum determined the evolved gas to be pure CO. After removal of the benzene under vacuum, all attempts to crystallize the air-sensitive product failed. A cyclohexane infrared spectrum showed the following absorptions in the carbonyl stretching region (cm^{-1}): 1997 (sh), 1977 (s), 1944 (s), 1877 (vs), 1866 (vs).

Reaction of 1b with CO. CO was bubbled for 5 h into a solution of **1b** (0.102 g, 0.201 mmol) in 30 mL of benzene at 80 °C. No change in the infrared spectrum was observed. At 80 °C, a 10 mL benzene solution of **1b** (0.206 g, 0.405 mmol) was exposed to CO (6.9 atm, 85 mmol) in a sealed Carius tube for 3.6 days. A hexane infrared spectrum of the carbonyl stretching region showed the presence of **1b**, $Mn_2(CO)_{10}$, $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, and an unidentified weak absorption at 1873 cm^{-1}.

Reaction of $(\eta^5\text{-}C_5H_5)(CO)\overline{W(\mu\text{-}C_5H_4)Mn}(CO)_3P(OCH_3)_3$ (3a) with H_2. A 20-mL benzene solution of **3a** (0.291 g, 0.482 mmol) was reacted at 80 °C with H_2 (0.92 atm, 1.7 mmol) for 12 h in a Carius tube, sealed under vacuum. The reaction mixture turned from clear red to a clear yellow. The Carius tube was opened, the solution filtered through anhydrous magnesium sulfate, and the benzene removed under vacuum. The residue was chromatographed on a silica gel column, eluting initially with pure hexane and then hexane–benzene mixtures, with up to 60% benzene. $Mn_2(CO)_{10}$ (13 mg, 14% based on Mn), 1-$Mn_2(CO)_9P(OCH_3)_3$ (35 mg, 30%), and 1,10-$Mn_2(CO)_8[P(OCH_3)_3]_2$ (70 mg, 50%) were eluted in the above sequence.

Attempts at crystallization of 1-$Mn_2(CO)_9P(OCH_3)_3$ failed. Its hexane infrared spectrum displayed the following absorptions (cm^{-1}): 2094 (w), 2018 (m), 1977 (vs), 1975 (m), 1970 (sh), 1955 (m), 1943 (sh); see Figure 11 (supplementary material). This is in good agreement with the analogous spectrum for $Mn_2(CO)_9PPh_3$.[25] The ^{1}H NMR spectrum of the yellow oil in benzene gave a doublet centered at τ 7.20 (external Me_4Si in CH_3OH; J_{P-CH_3} = 12 Hz). In the mass spectrum a parent ion peak of m/e 486 and a clean CO fragmentation pattern were observed at 70 eV and source temperatures of 90–100 °C.

1,10-$Mn_2(CO)_8[P(OCH_3)_3]_2$ was crystallized from an ether–hexane mixture at 20 °C. Its cyclohexane infrared spectrum (see Figure 11) showed the following absorptions (cm^{-1}): 2068 (vw), 2061 (sh), 1998 (m), 1988 (sh), 1983 (sh), 1970 (vs), 1949 (w), 1930 (vw), 1891 (vw), in good agreement with that reported by Lewis, Manning, and Miller.[26] The ^{1}H NMR spectrum in benzene showed a doublet centered at τ 6.93 (external Me_4Si in $CHCl_3$; J_{P-CH_3} = 12 Hz). A mass spectrum at 80 °C source temperature and 70 eV gave a parent ion at m/e 582. Anal. Calcd for $C_{14}H_{18}Mn_2O_{14}P_2$: C, 28.88; H, 3.12. Found:[24] C, 28.67; H, 3.35.

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Registry No. **1a**, 71411-08-0; **1b**, 71433-81-3; **2**, 71486-19-6; **3a**, 71433-82-4; **3b**, 71486-20-9; **4**, 71433-83-5; (η^5-C_5H_5)(CO)W(μ-C_5H_4)$Mn(CO)_3P(CH_2CH_3)_3$, 71486-18-5; 1-$Mn_2(CO)_9P(OCH_3)_3$, 19652-77-8; 1,10-$Mn_2(CO)_8[P(OCH_3)_3]_2$, 15529-61-0; $Mn_2(CO)_{10}$, 10170-69-1; (η^5-C_5H_5)$_2WH_2$, 1271-33-6; (η^5-C_5H_5)$_2MoH_2$, 1291-40-3; (η^5-C_5H_5)$_2ReH$, 1271-32-5; $CH_3Mn(CO)_5$, 13601-24-6; (η^5-C_5H_5)$_2WD_2$, 11082-26-1; (η^5-C_5H_5)$_2ReD$, 71426-01-2; $CD_3Mn(CO)_5$, 15653-52-8.

Supplementary Material Available: Figures 1–3, 5, and 7–11 (IR and NMR spectra, an Arrhenius plot of rate data, and a mass spectrometric calibration curve) and Tables II and IX (effect of solvent on chemical shift and calibration data for the mass spectrometer) (12 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) The present work has been taken in part from the Ph.D. dissertation of R. J. Hoxmeier, UCLA, 1972, and the M.S. and Ph.D. dissertations of J. R. Blickensderfer, UCLA, 1971 and 1974, respectively. This is part 14 of a series of papers on metalation reactions. (b) Part 13: S. S. Crawford, C. B. Knobler, and H. D. Kaesz, *Inorg. Chem.*, **16**, 3201 (1977).

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