Use of Palladium-Catalyzed Coupling Reaction in Synthesis of Homobimetallic Dimers: Preparation of [Bis(cyclopentadienyl)acetylene]metal Complexes and Their Reaction with $Co_2(CO)_8$. Evidence for Formation of Dihydrido Species in Diiron Complexes

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The palladium-catalyzed coupling reaction of the η^5-iodocyclopentadienyl derivatives of Fe, W, Mo, Mn, and Re (**1–5**) with $Bu_3SnC{\equiv}CSnBu_3$ yields the dinuclear acetylene-bridged complexes of general formula $L_nM(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)ML_n$ (**6–10**). These compounds react readily and quantitatively with $Co_2(CO)_8$ to form the dicobalt adducts $L_nM(\eta^5\text{-}C_5H_4)C(OC)_3Co\text{–}Co(CO)_3C(\eta^5\text{-}C_5H_4)ML_n$ (**12–16**). The reaction of $CH_3(CO)_2Fe[(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)]Fe(CO)_2CH_3$ (**6**) with I_2 cleaved the iron–methyl bond to yield $I(CO)_2Fe[(\eta^5\text{-}C_5H_4)C{\equiv}C\text{-}(\eta^5\text{-}C_5H_4)]Fe(CO)_2I$ (**11**). Reaction of **11** with $Co_2(CO)_8$ also produced a bridged cobalt complex, $I(CO)_2Fe[(\eta^5\text{-}C_5H_4)C(CO)_3Co\text{–}Co(CO)_3C(\eta^5\text{-}C_5H_4)]Fe(CO)_2I$ (**12**), whose crystal structure was determined. Reaction of both **11** and **12** with $LiEt_3BH$ gave unstable complexes, which were assigned hydride structures on the basis of their ^1H NMR spectra.

Introduction

The preparation of transition-metal cluster carbonyl complexes has received increasing attention because of their potential for CO reduction. In a number of cases, the presence of different metal centers in the same molecular unit enhances the chemistry of the individual species as compared with their mononuclear analogues.[1] The presence of two or more metal centers may lead to unique reactive features as a result of metal–metal or metal–ligand–metal interactions that can readily accomplish otherwise difficult transformations, leading to new catalytic processes.[2]

Our attention in this area has been centered on the development of a convenient synthetic approach that would enable the construction of a multinuclear unit in which different metal centers could be easily introduced. The use of two covalently linked cyclopentadienyl units has attracted particular attention because of the ability of the cyclopentadiene to form strong bonds with a wide variety of metal nuclei, and its ability to maintain a stable framework under a variety of reaction conditions. A family of dinuclear organometallic complexes that uses the bis(cyclopentadienyl) unit as ligand has been reported, the most prevalent of which are bis(cyclopentadienyl)methane,[3] bis(cyclopentadienyl)ethane,[4] bis(cyclopentadienyl)dimethylsilane,[5] and fulvalene[6,7] in which the cyclopentadienyl rings are directly connected to one another. In one case, tris(cyclopentadienylmethyl)amine has been used as a ligand framework to assemble three metal centers.[8]

Recently, the preparation of bimetallic clusters using a bis(cyclopentadienyl)acetylene bridging ligand was reported.[9] These clusters are, in our opinion, of considerable interest since the unsaturated bridge linking the two cyclopentadienyl rings can be site of introduction of another metal unit. However, the method reported for the synthesis of these clusters containing cyclopentadienylmetal complexes linked by an acetylenic unit involves the preparation of the ligand in a five-step procedure, followed by the introduction of the two metal units, with an overall yield of 8%. Moreover only iron and nickel have been successfully introduced into this framework.

The palladium-catalyzed cross-coupling reaction between organostannanes and organoelectrophiles is one of the most effective synthetic methods for generating a new carbon–carbon bond under mild conditions.[10] In this

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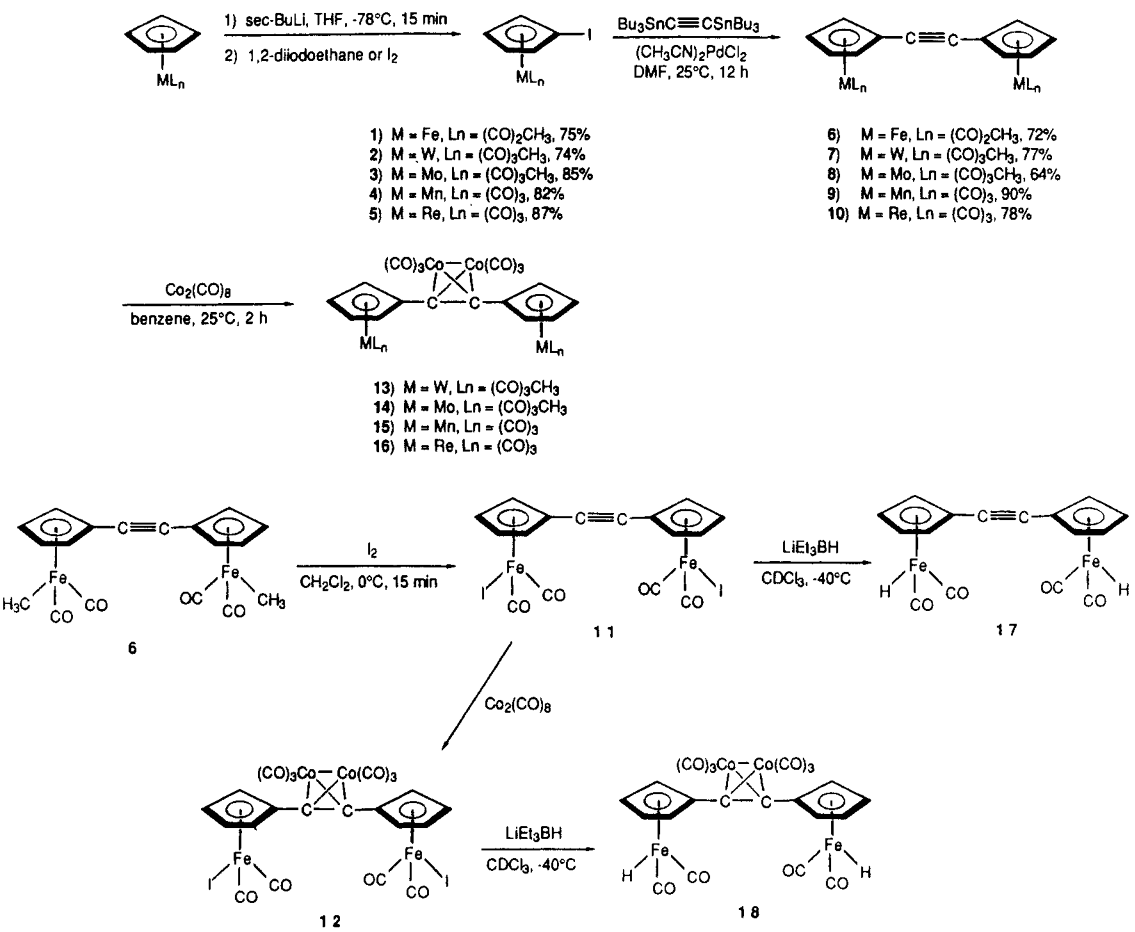
Scheme I



coupling reaction, a variety of sensitive functional groups can be tolerated on either coupling partner.

In this work, we report an interesting example of this coupling reaction with the one-step formation of [bis(cyclopentadienyl)acetylene]metal clusters via reaction of 2 equiv of an (η^5-iodocyclopentadienyl)metal complex with bis(tributyltin) acetylide in presence of a catalytic amount of bis(acetonitrile)dichloropalladium. This method is superior to the previously reported one, in both yield and variety of metals that can be incorporated. In fact, the yield of the product ranges from 64% to 90%, the only requirement for a given metal to form such a cluster being the availability of its η^5-cyclopentadienyl derivative.

Results and Discussion

Preparation of (η^5-Iodocyclopentadienyl)metal Carbonyl Complexes (1–5). Lithiation of the cyclopentadienyl ligand in the cyclopentadienyliron complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ or $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ (where R is a σ-bonded alkyl or aryl group) has been reported[11] to take place quite readily and specifically at −78 °C in THF, without deprotonating the alkyl or aryl group attached to the metal or attacking the carbonyl ligand. We have utilized this reaction with several cyclopentadienyl transition-metal complexes, such as $(\eta^5\text{-}C_5H_5)W(CO)_3CH_3$, $(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_3$, $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, and $(\eta^5\text{-}C_5H_5)Re(CO)_3$. Using *sec*-BuLi at −78 °C in THF the reaction takes place giving the corresponding intermediate lithium cyclopentadienide derivatives (Scheme I).

These derivatives have been converted to the corresponding iodides. Reaction of the iron complex with iodine yields 1 directly (75% yield), but a similar reaction with the W, Mo, Mn, and Re analogues yields a mixture of products. Reaction of these latter compounds with 1,2-diiodoethane, however, gives 2–5 cleanly in 74–87% yield. Chromatographic separation of the crude reaction mixture on silica with hexanes as the eluent gave pure product.

Palladium-Catalyzed Cross-Coupling Reactions of (η^5-Iodocyclopentadienyl)metal Carbonyl Complexes 1–5 with Bis(tributyltin) Acetylide. A wide variety of organic electrophiles and functionalized organostannanes undergo the cross-coupling reaction in presence of palladium catalysts, by a well-known multistep catalytic cycle.[10] In the oxidative addition step, the aromatic iodide is an efficient electrophile, and in the transmetallation step, the acetylenic stannanes undergo this reaction the fastest of the organostannanes. As the result of such a favorable combination, the coupling of (η^5-iodocyclopentadienyl)metal carbonyl complexes 1–5 with bis(tributyltin) acetylide proceeded smoothly in 12 h at room temperature by stirring the two reagents in *N,N*-dimethylformamide (DMF) in presence of 5 mol % of $(CH_3CN)_2Pd(Cl)_2$, giving high yields of product.

Removal of the tributyltin iodide formed as by product during the reaction required an aqueous potassium fluoride wash which produced the insoluble tributyltin fluoride.[12] Pure product (see Table I for spectra) was isolated by chromatographic separation followed by crystallization.

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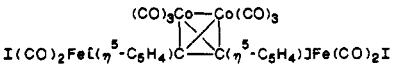
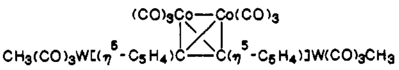
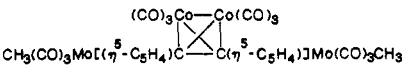
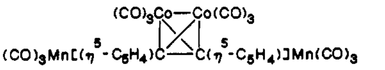
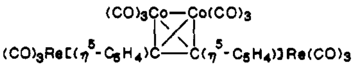
Table I. ^1H and ^{13}C NMR[a] and IR[b] Data for the Complexes 6–11

coupled products	^1H, δ	^{13}C, δ	IR, cm^{-1}
$CH_3(CO)_2Fe[(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)]Fe(CO)_2CH_3$ (6)	4.90, (t, 4 H, J = 1.9 Hz), 4.74 (t, 4 H, J = 1.9 Hz), 0.33 (s 6 H)	216.16, 98.55, 83.14, 83.09, 82.21, −18.78	2013, 1960
$CH_3(CO)_3W[(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)]W(CO)_3CH_3$ (7)	5.51 (t, 4 H, J = 2.3 Hz), 5.30 (t, 4 H, J = 2.3 Hz), 0.53 (s, 6 H)	214.71, 94.74, 91.21, 89.52, 82.32, −28.90	2019, 1930
$CH_3(CO)_3Mo[(\eta^5HC_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)]Mo(CO)_3CH_3$ (8)	5.44 (t, 4 H, J = 2.3 Hz), 5.23 (t, 4 H, J = 2.3 Hz), 0.49 (s, 6 H)	225.36, 95.94, 93.52, 90.42, 82.74, −15.21	2022, 1929
$(CO)_3Mn[(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)]Mn(CO)_3$ (9)	5.01 (t, 4 H, J = 2.2 Hz), 4.68 (t, 4 H, J = 2.2 Hz)	223.88, 86.60, 82.05, 81.22, 81.10	2026, 1945
$(CO)_3Re[(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)]Re(CO)_3$ (10)	5.62 (t, 4 H, J = 2.2 Hz), 5.28 (t, 4 H, J = 2.2 Hz)	198.85, 88.18, 84.01, 83.73, 80.42	2029, 1939
$I(CO)_2Fe[(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)]Fe(CO)_2]$ (11)	5.29 (t, 4 H, J = 1.9 Hz), 5.03 (t, 4 H, J = 1.9 Hz)	211.87, 89.03, 83.40, 83.11, 67.87	2045, 2007

[a] Recorded in $CDCl_3$. Abbreviation: t, triplet. [b] Recorded in CCl_4. Absorptions listed were very strong.

Table II. ^1H and ^{13}C NMR[a] and IR[b] Data for the Complexes 12–16

compound	^1H, δ	^{13}C, δ	IR, cm^{-1}
 12	5.58 (t, 4 H, J = 1.4 Hz), 5.06 (t, 4 H, J = 1.4 Hz)	212.97, 197.56, 98.46, 89.71, 81.57, 81.28	2097 s, 2067 vs, 2042 vs; 2001 s, 1998 s
 13	5.59 (t, 4 H, J = 2.3 Hz), 5.45 (t, 4 H, J = 2.3 Hz), 0.56 (s, 6 H)	215.05, 198.43, 108.86, 94.26, 91.13, 88.03, −33.03	2094 s, 2062 vs, 2033 vs, 2016 vs, 1930 vs
 14	5.56 (t, 4 H, J = 2.3 Hz), 5.35 (t, 4 H, J = 2.3 Hz), 0.52 (s, 6 H)	225.46, 198.15, 110.88, 94.93, 93.10, 87.77, −20.14	2093 s, 2061 vs, 2032 vs, 2022 vs, 1939 vs
 15	5.29 (t, 4 H, J = 2.1 Hz), 4.76 (t, 4 H, J = 2.1 Hz)	224.37, 198.15, 98.39, 87.88, 83.93, 81.15	2094 s, 2062 vs, 2033 vs, 2024 s, 1946 vs
 16	5.88 (t, 4 H, J = 1.9 Hz), 5.34 (t, 4 H, J = 1.9 Hz)	198.29, 193.41, 100.73, 89.05, 83.22, 82.05	2095 s, 2063 vs, 2033 vs, 2028 vs, 1938

[a] Recorded in $CDCl_3$. Abbreviation: t, triplet. [b] Recorded in CCl_4. Abbreviations: s, strong, vs, very strong.

The conversion of the starting material was complete, and in all cases the product was isolated in good yield.

Reaction of Dimethyl Complex 6 with Iodine. Complexes 6, 7, and 8 each bearing a methyl group at both the metal centers were allowed to react with iodine in an effort to replace the alkyl group with the halogen. In the case of iron dimer 6, treatment with iodine at 0 °C in CH_2Cl_2 for 15 min leads to the replacement of the methyl group at both the iron centers with formation of 11.

Under the same reaction conditions, the W and Mo dimethyl analogues 7 and 8, respectively, were completely consumed, but in both cases no evidence of the iodo product was obtained. Product 11 was isolated in pure form by chromatographic separation followed by recrystallization.

Reaction of Dinuclear Complexes 7–11 with Dicobalt Octacarbonyl. The strong affinity that the dicobalt octacarbonyl $Co_2(CO)_8$ has for acetylene leads to the formation of stable complexes in which the two bridging carbonyls in $Co_2(CO)_8$ are replaced by the two carbons from the alkyne.[13] Complexes 7–11 react smoothly at room temperature with a slight excess of $Co_2(CO)_8$ in benzene to give quantitative yield of the expected tetranuclear clusters 12–16.

When the two reactants were mixed in benzene, evolution of gas was noted; after 2 h the solvent was evaporated, and the excess $Co_2(CO)_8$ was removed under reduced pressure leaving essentially pure product. Further purification can be achieved by either recrystallization or chromatographic separation. Compounds 12–16 are deep purple crystals that can be handled in air without decomposition. The infrared spectra (Table II) of these compounds contain a characteristic group of three sharp bands at 2093, 2061, and 2033 cm^{-1}, similar to the bands of the terminal carbonyls groups in $Co_2(CO)_8$, in addition to the

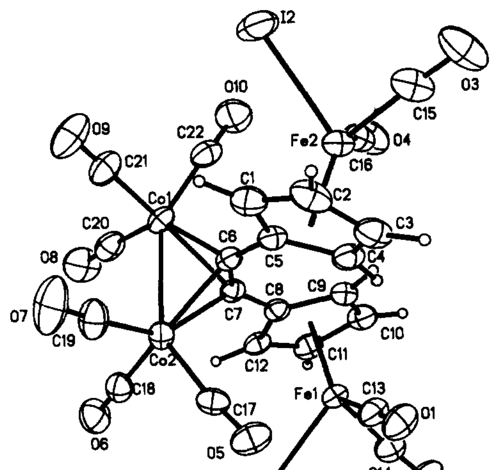


Figure 1. Crystal structure of $C_{22}H_8O_{10}Co_2Fe_2I_2$ (12).

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Table III. Details of the Crystallographic Experiment and Computations for 12

mol formula	$C_{22}H_8O_{10}Co_2Fe_2I_2$ (12)
fw, amu	915.66
cryst system	monoclinic
space group	$P2_1/c$
lattice constants	
a, Å	16.401 (4)
b, Å	14.895 (3)
c, Å	11.469 (2)
β, deg	106.83 (2)
V, Å^3	2681.8
temp, °C	−120
Z	4
F(000)	1728
ρ(calcd, g cm^{-3})	2.27
cryst dimens, mm	0.46 × 0.22 × 0.14
radiatn	Mo Kα (λ = 0.7107 Å)
monochromator	graphite
μ, cm^{-1}	47.3
scan type	$\theta/2\theta$
scan speed, deg min^{-1}	1.98–29.30 (variable)
2θ range, deg	4–50
indices collected	$+h,+k,+l$
total no. of reflections	5202 measured 4411 used ($I > 2.5\sigma(I)$)
no. of least-squares parameters	343
data/parameter ratio	12.9
R^a	0.031
R_w^a	0.034
GOF^a	1.508
g (refined)	4 × 10^{-4}
slope, normal probability plot^b	1.296

$^a R = (\sum |(F_o - F_c)|)/(\sum F_o)$; $R_w = \{(\sum w|F_o - F_c|^2)/(\sum w(F_o)^2)\}^{1/2}$; GOF = $\{(\sum w(|(F_o - F_c)|)^2/(N_{data} - N_{para})\}^{1/2}$. ^{b}Abrahams, S. C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, *B30*, 261–268.

Table IV. Bond Lengths (Å)^a for $C_{22}H_8O_{10}Co_2Fe_2I_2$ (12)

I1–Fe1	2.589 (1)	I2–Fe2	2.594 (1)
Fe1–C8	2.131 (4)	Fe1–C9	2.086 (4)
Fe1–C10	2.071 (4)	Fe1–C11	2.094 (3)
Fe1–C12	2.114 (3)	Fe1–C13	1.776 (4)
Fe1–C14	1.785 (5)	Fe2–C1	2.124 (4)
Fe2–C2	2.106 (4)	Fe2–C3	2.079 (4)
Fe2–C4	2.066 (4)	Fe2–C5	2.117 (4)
Fe2–C15	1.776 (4)	Fe2–C16	1.765 (4)
Co1–Co2	2.452 (1)	Co1–C6	1.939 (3)
Co1–C7	1.979 (3)	Co1–C20	1.819 (4)
Co1–C21	1.832 (5)	Co1–C22	1.804 (4)
Co2–C6	1.962 (3)	Co2–C7	1.944 (3)
Co2–C17	1.803 (3)	Co2–C18	1.839 (4)
Co2–C19	1.810 (5)	O1–C13	1.130 (4)
O2–C14	1.135 (6)	O3–C15	1.147 (6)
O4–C16	1.143 (5)	O5–C17	1.127 (4)
O6–C18	1.116 (5)	O7–C19	1.124 (6)
O8–C20	1.132 (5)	O9–C21	1.128 (6)
O10–C22	1.128 (5)	C1–C2	1.414 (5)
C1–C5	1.420 (6)	C2–C3	1.422 (6)
C3–C4	1.417 (6)	C4–C5	1.443 (5))
C5–C6	1.452 (5)	C6–C7	1.349 (5)
C7–C8	1.445 (5)	C8–C9	1.434 (5)
C8–C12	1.425 (5)	C9–C10	1.409 (6)
C10–C11	1.426 (6)	C11–C12	1.405 (6)

^{a}Estimated standard deviations in the least significant digits are given in parentheses.

characteristic band of the original homobimetallic cluster. The 1859 cm^{-1} band corresponding to the bridging carbonyls of $Co_2(CO)_8$ is absent. The ^{1}H NMR spectra of **12–16** show that the two apparent triplets due to the $H_{2,5}$ and $H_{3,4}$ protons in the cyclopentadienyl rings are systematically shifted downfield respect to the corresponding reactant complexes **7–11**.

The two-carbon acetylenic bridge in the homobimetallic dimers **7–11** places the cyclopentadienyl rings at a distance that eliminates any possibility of a direct metal–metal bond. In order to allow cooperative interaction between the two metal centers in the dimer and provide the possibility of catalytic behavior by cooperative interaction, not only should the two metals be chosen appropriately, but also even more importantly they should be properly oriented in the molecular frame in a way that effective interaction can take place. In order to determine whether complexation of the acetylenic linkage with cobalt carbonyl and forming the butterfly array would allow interaction of the two metals, a single-crystal X-ray diffraction study of iron–cobalt cluster **12** containing four metal centers was carried out.

Crystals of **12** suitable for X-ray structural determination were obtained by crystallization from a chloroform-/pentane solution at −20 °C. Details of the data collection are summarized in Table III; bond lengths and bond angles are given in Tables IV and V.

Although the acetylenic bond is lengthened to 1.349 (5) Å, the linear array of the two cyclopentadienyl rings at the ends of the acetylenic link is now bent, providing C_5–C_6–C_7 and C_6–C_7–C_8 bond angles of 142.3 (3)° and 144.8 (3)°, respectively. Consequently, this places the cyclopentadienyl centroids at a distance of 5.693 Å. The Fe–Cp centroid distances, at 1.721 (Fe_1) and 1.716 Å (Fe_2), are usual for iron cyclopentadienyl compounds.[14] The ligand bond angles around the iron centers C–Fe–C and C–Fe–I average 94.45 and 88.95°, respectively, and are close to the ideal C_{3v} symmetry angles of 90°. The structure of **12** can be described with respect to the plane determined by carbon atoms C_5, C_6, C_7, and C_8. The two cyclopentadienyl rings bearing the $Fe(CO)_2I$ units are in a transoid configuration. However the two cyclopentadienyl rings are not coplanar but are twisted with a dihedral angle between the two planes described by C_5–C_6–C_7 and C_6–C_7–C_8 of 16.2°. The dicobalt hexacarbonyl unit is perpendicular to and bisects the C_6–C_7 bond.

A remarkable feature in this complex is the orientation of the $Fe(CO)_2I$ groups. Although they adopt the transoid configuration, the iodo substituents are oriented in such a way that they each face one of the carbonyl groups on each cobalt, iodine atoms 1 and 2 being 3.65 and 4.08 Å, respectively, from the carbonyl carbons C_{17} and C_{22}. The iodine distances to oxygen atoms (O_5 and O_{10}) on those carbonyls are 3.75 and 4.11 Å, respectively. This feature is especially noteworthy considering that in the reaction of **12** with $LiEt_3BH$, replacement of the iodines with hydrides places the hydride closest to one of the carbonyls on cobalt, which could allow the attack of hydride on the electrophilic carbon of the cobalt carbonyl.

Even though in the crystal, the two iron atoms are pointed generally in opposite directions, in solution, this does not preclude rotation of the cyclopentadienyl rings about the C_5–C_6 or C_7–C_8 bonds to place the two metals within bonding distance.

Reaction of Complexes 11 and 12 with Lithium Triethylborohydride (Super Hydride). Observation of the Metal Dihydrides. The general class of transition-metal hydrides, (η^5-cyclopentadienyl)M(CO)$_n$H, is known to include a number of transition-metal centers (M = Fe,[15] Ru,[16] Os,[17] Cr,[18] Mo,[18] W[18]). However, examples

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Table V. Bond Angles (deg)[a] for $C_{22}H_8O_{10}Co_2Fe_2I_2$ (12)

I1–Fe1–C8	106.8 (1)	I1–Fe1–C9	145.9 (1)
C8–Fe1–C9	39.8 (1)	I1–Fe1–C10	151.3 (1)
C8–Fe1–C10	66.7 (1)	C9–Fe1–C10	39.6 (2)
I1–Fe1–C11	111.3 (1)	C8–Fe1–C11	66.0 (1)
C9–Fe1–C11	66.5 (2)	C10–Fe1–C11	40.0 (2)
I1–Fe1–C12	90.7 (1)	C8–Fe1–C12	39.2 (1)
C9–Fe1–C12	66.1 (1)	C10–Fe1–C12	66.4 (1)
C11–Fe1–C12	39.0 (1)	I1–Fe1–C13	88.2 (1)
C8–Fe1–C13	102.0 (2)	C9–Fe1–C13	93.2 (2)
C10–Fe1–C13	120.3 (2)	C11–Fe1–C13	159.1 (2)
C12–Fe1–C13	138.3 (2)	I1–Fe1–C14	88.9 (1)
C8–Fe1–C14	158.1 (2)	C9–Fe1–C14	124.9 (2)
C10–Fe1–C14	92.3 (2)	C11–Fe1–C14	94.3 (2)
C12–Fe1–C14	128.1 (2)	C13–Fe1–C14	93.5 (2)
I2–Fe2–C1	90.6 (1)	I2–Fe2–C2	108.0 (1)
C1–Fe2–C2	39.1 (1)	I2–Fe2–C3	147.3 (1)
C1–Fe2–C3	66.1 (2)	C2–Fe2–C3	39.7 (2)
I2–Fe2–C4	149.9 (1)	C1–Fe2–C4	66.5 (2)
C2–Fe2–C4	66.9 (2)	C3–Fe2–C4	40.0 (2)
I2–Fe2–C5	109.7 (1)	C1–Fe2–C5	39.1 (2)
C2–Fe2–C5	66.3 (1)	C3–Fe2–C5	67.0 (1)
C4–Fe2–C5	40.3 (1)	I2–Fe2–C15	89.1 (1)
C1–Fe2–C15	134.3 (2)	C2–Fe2–C15	98.5 (2)
C3–Fe2–C15	91.5 (2)	C4–Fe2–C15	120.8 (2)
C5–Fe2–C15	158.4 (2)	I2–Fe2–C16	89.2 (1)
C1–Fe2–C16	130.3 (2)	C2–Fe2–C16	158.0 (2)
C3–Fe2–C16	123.3 (2)	C4–Fe2–C16	91.3 (2)
C5–Fe2–C16	95.3 (2)	C15–Fe2–C16	95.4 (2)
Co2–Co1–C6	51.5 (1)	Co2–Co1–C7	50.7 (1)
C6–Co1–C7	40.3 (1)	Co2–Co1–C20	94.3 (1)
C6–Co1–C20	139.7 (2)	C7–Co1–C20	103.5 (2)
Co2–Co1–C21	101.3 (1)	C6–Co1–C21	101.6 (2)
C7–Co1–C21	140.4 (1)	C20–Co1–C21	106.4 (2)
Co2–Co1–C22	149.5 (1)	C6–Co1–C22	103.3 (2)
C7–Co1–C22	99.4 (2)	C20–Co1–C22	99.4 (2)
C21–Co1–C22	100.7 (2)	Co1–Co2–C6	50.6 (1)
Co1–Co2–C7	52.0 (1)	C6–Co2–C7	40.4 (1)
Co1–Co2–C17	144.8 (1)	C6–Co2–C17	94.7 (1)
C7–Co2–C17	99.4 (1)	Co1–Co2–C18	103.9 (1)
C6–Co2–C18	142.6 (1)	C7–Co2–C18	103.4 (2)
C17–Co2–C18	102.6 (2)	Co1–Co2–C19	97.2 (1)
C6–Co2–C19	105.1 (2)	C7–Co2–C19	142.4 (2)
C17–Co2–C19	97.8 (2)	C18–Co2–C19	105.1 (2)
Fe2–C1–C2	69.8 (2)	Fe2–C1–C5	70.2 (2)
C2–C1–C5	109.1 (4)	Fe2–C2–C1	71.1 (2)
Fe2–C2–C3	69.1 (2)	C1–C2–C3	107.8 (4)
Fe2–C3–C2	71.2 (2)	Fe2–C3–C4	69.5 (2)
C2–C3–C4	108.2 (3)	Fe2–C4–C3	70.5 (2)
Fe2–C4–C5	71.7 (2)	C3–C4–C5	108.1 (4)
Fe2–C5–C1	70.7 (2)	Fe2–C5–C4	68.0 (2)
C1–C5–C4	106.8 (3)	Fe2–C5–C6	131.0 (2)
C1–C5–C6	127.1 (3)	C4–C5–C6	125.9 (3)
Co1–C6–Co2	77.9 (1)	Co1–C6–C5	139.7 (3)
Co2–C6–C5	127.4 (2)	Co1–C6–C7	71.5 (2)
Co2–C6–C7	69.1 (2)	C5–C6–C7	142.2 (3)
Co1–C7–Co2	77.4 (1)	Co1–C7–C6	68.2 (2)
Co2–C7–C6	70.5 (2)	Co1–C7–C8	130.7 (2)
Co2–C7–C8	136.1 (3)	C6–C7–C8	144.8 (3)
Fe1–C8–C7	130.7 (2)	Fe1–C8–C9	68.4 (2)
C7–C8–C9	127.6 (3)	Fe1–C8–C12	69.7 (2)
C7–C8–C12	125.6 (3)	C9–C8–C12	106.6 (3)
Fe1–C9–C8	71.8 (2)	Fe1–C9–C10	69.6 (2)
C8–C9–C10	108.6 (3)	Fe1–C10–C9	70.8 (2)
Fe1–C10–C11	70.9 (2)	C9–C10–C11	107.8 (3)
Fe1–C11–C10	69.1 (2)	Fe1–C11–C12	71.3 (2)
C10–C11–C12	108.1 (3)	Fe1–C12–C8	71.0 (2)
Fe1–C12–C11	69.7 (2)	C8–C12–C11	109.0 (3)
Fe1–C13–O1	178.5 (4)	Fe1–C14–O2	177.4 (4)
Fe2–C15–O3	178.1 (4)	Fe2–C16–O4	176.7 (4)
Co2–C17–O5	173.3 (4)	Co2–C18–O6	178.5 (3)
Co2–C19–O7	175.7 (4)	Co1–C20–O8	176.1 (4)
Co1–C21–O9	176.7 (3)	Co1–C22–O10	176.8 (4)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

of dihydride complexes in which the two hydride ligands are terminally bonded to two separate metal centers within the same dimer are restricted to tungsten[19] and molybdenum.[7e] These compounds are important because their hydridic character could lead to reactions at the carbonyl carbons, particularly those of the late transition metals.[20] These transformations could provide information concerning the mechanism of carbon monoxide reduction. Preliminary experiments conducted on an NMR time scale at low temperature (−40 °C) were carried out on **11** and **12** to explore the possibility of generating an hydrido complex. The addition of lithium triethylborohydride to a deuteriochloroform solution of complex **11** produced a new peak at −12.04 ppm while the cyclopentadienyl protons were shifted from 5.34 and 5.05 ppm to 5.13 and 4.73 ppm. For **12**, a new peak appeared at −11.85 ppm and the cyclopentadienyl resonances were shifted from 5.67 and 5.03 ppm to 5.55 and 5.09 ppm. By comparison, the hydride singlet for $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ appears at −11.91 ppm (C_6D_{12}).[15]

At −40 °C the spectra of these new species remained unchanged for several hours. However, on warming to 0 °C the resonance due to the hydride disappeared along with the related signal for the cyclopentadienyl protons and decomposition occurred in the NMR tube. These reactions were repeated on a preparative scale in order to attempt the isolation of the dihydrido species **17** and **18**, but the products were very unstable and could not be isolated.

Experimental Section

All manipulations were carried out under a protective atmosphere of argon in carefully dried equipment. Conventional vacuum line and/or Schlenk tube techniques were used. Liquids were transferred by syringe or cannula. Infrared spectra were recorded on Perkin-Elmer 983 grating infrared spectrometer, attached to a Perkin-Elmer 3600 Data Station. Abbreviations: v, very; s, strong; w, weak; m, medium; sh, shoulder. The ^1H NMR spectra and the broad-band proton-decoupled ^{13}C NMR spectra were recorded in the Fourier transform mode on a Bruker AC 300 P spectrometer, operating at 300 MHz for proton and at 75 MHz for carbon, and on a Bruker WP-200 spectrometer, operating at 200 MHz for proton and 50 MHz for carbon. The NMR chemical shifts are reported in parts per million vs Me_4Si by assigning the ^1H impurity in the solvent $(CDCl_3)$ at 7.24 ppm. The ^{13}C spectral chemical shifts are reported relative to the ^{13}C triplet $(CDCl_3)$ at 77.00 ppm. Elemental analyses were carried out by Atlantic Microlab, Norcross, GA. High-resolution mass spectra (HRMS) were obtained from the Midwest Center for Mass Spectrometry at the University of Nebraska, Lincoln, NE. Melting points were determined with a Mel-Temp apparatus and are uncorrected.

Tetrahydrofuran (THF) was distilled under argon from potassium prior to use; *N,N*-dimethylformamide (DMF) was distilled under vacuum from CaH_2. The active organometallic content of the organolithium reagents was checked periodically by titration with 2,5-dimethoxybenzyl alcohol.[21] The following compounds were prepared according to literature methods: $CpFe(CO)_2CH_3$[17] using the modified procedure,[22] $CpMo(CO)_3CH_3$,[23] CpW-

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$(CO)_3CH_3$,[24] $CpMn(CO)_3$,[25] $CpRe(CO)_3$,[26] $Bu_3SnC{\equiv}CSnBu_3$,[27] $(CH_3CN)_2PdCl_2$.[28]

General Procedure for the Preparation of (η^5-Iodocyclopentadienyl)metal Complexes 1–5. (η^5-IC_5H_4)$Fe(CO)_2CH_3$ (1). Into an argon-purged flask equipped with an argon inlet, a mineral oil overpressure valve, a pressure-equalizing dropping funnel, and a magnetic stirrer was placed 7.3 g (38.0 mmol) of $CpFe(CO)_2CH_3$. The flask was evacuated, and 100 mL of THF, freshly distilled from sodium/benzophenone ketyl, was transferred by cannula. The solution was cooled to −78 °C and treated dropwise with 30.91 mL (38.0 mmol) of *sec*-BuLi (1.23 M solution in hexane) over 10 min. Upon completion of the addition, stirring was continued at low temperature for 20 min and then 9.65 g (38.0 mmol) of iodine, dissolved in 50 mL of THF, was added rapidly to the purple solution. At the end of the addition, the reaction mixture was allowed to warm to room temperature and stirring was continued for 30 min. Removal of the solvent in vacuo gave a gummy brown oil. The oil was mixed with Celite in CH_2Cl_2, the solvent was removed, and the coated product was placed on a chromatographic column packed with silica. By elution with hexanes, a broad orange band could be isolated. Removal of the solvent left a brown oil, its ^1H NMR spectrum showing one product contaminated with 6% of starting material. Kugelrohr distillation of this mixture at 70 °C (0.05 mmHg) gave 9.05 g (75%) of pure product as a brown oil.

IR (film, NaCl): 2010 vs, 1960 vs cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.88 (t, 2 H, J = 2.0 Hz), 4.69 (t, 2 H, J = 2.0 Hz), 0.29 (t, 3 H). ^{13}C NMR ($CDCl_3$): δ 216.38, 93.58, 84.08, 48.14, −17.38. An analytical sample was obtained by fractional distillation at 76.5 °C/0.15 mmHg. Anal. Calcd for $C_8H_7FeIO_2$: C, 30.22; H, 2.21. Found: C, 30.05; H, 2.26.

(η^5-IC_5H_4)$W(CO)_3CH_3$ (2). This compound was prepared from 5.0 g (14.35 mmol) of $CpW(CO)_3CH_3$ and 11.68 mL (14.35 mmol) of *sec*-BuLi (1.23 M solution in hexane) as described for **1** except that 4.04 g (14.35 mmol) of 1,2-diiodoethane was added instead of iodine. Pure product was isolated by chromatographic separation over silica using hexanes as the eluent. Evaporation of solvent gave 5.78 g (85%) of pure product as yellow solid: mp 47–48 °C; IR (CCl_4) 2008 vs, 1933 vs cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.51 (t, 2 H, J = 2.2 Hz), 5.28 (t, 2 H, J = 2.2 Hz), 0.51 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 214.82, 99.61, 91.56, 49.10, −29.58; HRMS calcd for $C_9H_7IO_3W$ 473.8947, found 473.8965.

(η^5-IC_5H_4)$Mo(CO)_3CH_3$ (3). This product was prepared from 2.8 g (10.7 mmol) of $CpMo(CO)_3CH_3$ dissolved in 100 mL of THF which was treated at −78 °C with 8.75 mL (10.7 mmol) of *sec*-BuLi (1.23 M solution in hexane) followed by 3.01 g (10.7 mmol) of 1,2-diiodoethane. The product was isolated by chromatographic separation over silica using benzene/hexanes (1/1) as the eluent. Evaporation of the solvent gave 3.05 g, (74%) of pure product as a green solid: mp 30–31 °C; IR (CCl_4) 2000 vs, 1955 vs cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.43 (t, 2 H, J = 2.3 Hz), 5.20 (t, 2 H, J = 2.3 Hz), 0.47 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 225.50, 100.76, 92.47, 52.22, −16.00. HRMS calcd for $C_9H_7IMnO_3$ 387.8486, no molecular peak found; $C_8H_7O_2IMo$ (M^+ − CO), calcd 359.8537, found 359.8536; C_7H_7OIMo (M^+ − 2CO), calcd 329.8577, found 329.8586; C_6H_7IMo (M^+ − 3CO), calcd 300.8649; found 300.8655.

(η^5-IC_5H_4)$Mn(CO)_3$ (4). This compound was prepared from 8.84 g (43.32 mmol) of $CpMn(CO)_3$, 35.22 mL (43.32 mmol) of *sec*-BuLi (1.23 M solution in hexane), and 12.21 g (43.32 mmol) of 1,2-diiodoethane as described above. Chromatographic separation over silica using hexanes as the eluent gave, after evaporation of solvent, 11.72 g (82%) of pure product as a brown solid: IR (CCl_4) 2000 vs, 1930 vs cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.98 (t, 2 H, J = 1.8 Hz), 4.65 (t, 2 H, J = 1.8 Hz); ^{13}C NMR ($CDCl_3$) δ 224.30, 90.41, 83.21, 43.21. The spectra matched the published data.[29]

(η^5-IC_5H_4)$Re(CO)_3$ (5). This compound was prepared from 3.05 g (9.09 mmol) of $CpRe(CO)_3$, 7.39 mL (9.09 mmol) of *sec*-BuLi (1.23 M solution in hexane), and 2.56 g (9.09 mmol) of 1,2-diiodoethane as described above. The product was isolated by chromatographic separation over silica using hexanes/benzene (1/1) as the eluent. Evaporation of solvent gave 3.64 g (87%) of pure product as light green solid: IR (CCl_4) 2020 vs, 1945 vs cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.58 (t, 2 H, J = 1.9 Hz), 5.25 (t, 2 H, J = 1.9 Hz); ^{13}C NMR ($CDCl_3$) δ 193.26, 91.48, 86.41, 41.00. The spectra matched the published data.[30]

$CH_3(CO)_2Fe[(\eta^5$-$C_5H_4)C{\equiv}C(\eta^5$-$C_5H_4)]Fe(CO)_2CH_3$ (6). To a solution of (η^5-C_5H_4I)$Fe(CO)_2CH_3$ (1) (7.17 g, 22.5 mmol) and $(CH_3CN)_2PdCl_2$ (0.29 g, 1.25 mmol) in DMF (200 mL) was added 6.81 g (11.7 mmol) of $Bu_3SnC{\equiv}CSnBu_3$. The mixture was stirred at room temperature for 12 h; then 200 mL of ether was added to the reaction mixture, followed by the addition of 100 mL of a 50% solution of KF in water. The mixture was rapidly stirred for 30 min while argon was bubbled through the solution and then transferred into a separatory funnel. The ether solution was washed three times with 100-mL portions of water, and the combined aqueous solutions were extracted twice with 50-mL portions of ether. The organic phases were collected and dried over magnesium sulfate. Filtration and removal of the solvent gave a brown solid. Chromatographic separation over silica using a mixture of hexanes/EtOAc (9/1) gave pure product as an orange solid (3.28 g, 72%). Recrystallization from pentane/chloroform by vapor diffusion at −20 °C gave analytically pure product as orange plates, mp 124–125 °C (chloroform–pentane). Anal. Calcd for $C_{18}H_{14}Fe_2O_4$: C, 53.25; H, 3.47. Found: C, 53.36; H, 3.49.

$CH_3(CO)_3W[(\eta^5$-$C_5H_4)C{\equiv}C(\eta^5$-$C_5H_4)]W(CO)_3CH_3$ (7). This product was prepared as described for **6**. (η^5-C_5H_4I)$W(CO)_3CH_3$ (2) (5.26 g, 11.09 mmol) and $Bu_3SnC{\equiv}CSnBu_3$ (3.68 g, 6.10 mmol) were allowed to react in DMF (60 mL) in the presence of $(CH_3CN)_2PdCl_2$ (0.143 g, 0.55 mmol). After workup and chromatographic separation, pure product was recovered as an orange solid (3.06 g, 77%). An analytical sample was obtained by recrystallization from chloroform/pentane by vapor diffusion at −20 °C to give orange needles, mp 185–187 °C (chloroform–pentane). Anal. Calcd for $C_{20}H_{14}O_6W_2$: C, 33.45; H, 1.96. Found: C, 33.47; H, 1.96.

$CH_3(CO)_3Mo[(\eta^5$-$C_5H_4)C{\equiv}C(\eta^5$-$C_5H_4)]Mo(CO)_3CH_3$ (8). As described for **6**, (η^5-C_5H_4I)$Mo(CO)_3CH_3$ (3) (2.66 g, 6.89 mmol) and $Bu_3SnC{\equiv}CSnBu_3$ (2.28 g, 3.79 mmol) were allowed to react in DMF (35 mL) in the presence of $(CH_3CN)_2PdCl_2$ (0.08 g, 0.34 mmol). After workup and chromatographic separation, 1.19 g (64%) of product was recovered as a yellow solid. Recrystallization from pentane/chloroform by vapor diffusion at −20 °C gave analytically pure product as yellow needles, mp decomp above 138 °C. Anal. Calcd for $C_{20}H_{14}Mo_2O_6$: C, 44.30; H, 2.60. Found: C, 44.32; H, 2.63.

$(CO)_3Mn[(\eta^5$-$C_5H_4)C{\equiv}C(\eta^5$-$C_5H_4)]Mn(CO)_3$ (9). This product was prepared as described for **6**. (η^5-C_5H_4I)$Mn(CO)_3$ (4) (2.45 g, 7.42 mmol) and $Bu_3SnC{\equiv}CSnBu_3$ (2.69 g, 4.45 mmol) were allowed to react in DMF (100 mL) in the presence of $(CH_3CN)_2PdCl_2$ (0.057 g, 0.222 mmol). After workup and chromatographic separation, pure product was recovered as a pale yellow solid (1.434 g, 90%). Recrystallization from pentane/chloroform by vapor diffusion at −20 °C gave analytically pure product as yellow needles, mp 178–179 °C (chloroform–pentane). Anal. Calcd for $C_{18}H_8Mn_2O_4$: C, 50.26; H, 1.87. Found: C, 50.20; H, 1.89.

$(CO)_3Re[(\eta^5$-$C_5H_4)C{\equiv}C(\eta^5$-$C_5H_4)]Re(CO)_3$ (10). As described for **6**, (η^5-C_5H_4I)$Re(CO)_3$ (5) (0.36 g, 0.706 mmol) and $Bu_3SnC{\equiv}CSnBu_3$ (0.234 g, 0.388 mmol) were allowed to react in DMF (10 mL) in the presence of $(CH_3CN)_2PdCl_2$ (0.009 g, 0.035 mmol). After workup and chromatographic separation, 0.191 g (78%) of product was recovered as a tan solid. Recrystallization from pentane/chloroform by vapor diffusion at −20 °C gave analytically pure product as yellow crystals, mp 204–206 °C (chloroform–pentane). Anal. Calcd for $C_{18}H_8O_6Re_2$: C, 31.21; H, 1.16. Found: C, 31.23; H, 1.16.

Preparation of $I(CO)_2Fe[(\eta^5$-$C_5H_4)C{\equiv}C(\eta^5$-$C_5H_4)]Fe(CO)_2I$ (11). $CH_3(CO)_2Fe[(\eta^5$-$C_5H_4)C{\equiv}C(\eta^5$-$C_5H_4)]Fe(CO)_2CH_3$ (6) (0.40

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g, 0.99 mmol) was dissolved in dichloromethane (50 mL), and the solution was cooled to 0 °C. Iodine (0.50 g, 1.98 mmol) dissolved in dichloromethane (50 mL) was added, the mixture was stirred, and after 15 min, the solvent was removed in vacuo. The residue was dissolved in a minimum amount of THF and flash-chromatographed over silica, using hexanes/EtOAc, 4/1. A first pink fraction was eluted; a second one was collected by decreasing the hexanes/EtOAc ratio to 2/1. Finally a large brown band was eluted with hexanes/EtOAc, 1/1. Evaporation of the solvent from the last fraction gave pure product (1.23 g, 49%) as a dark solid. Recrystallization by vapor diffusion at −20 °C from THF/pentane gave black crystals, mp decomp above 142 °C. Satisfactory C and H analytical determination could not be obtained because of the sensitivity of the product. LRMS: 630 (M^+), 574 (M^+ − 2CO), 518 (M^+ − 4CO).

Preparation of 12 from $I(CO)_2Fe[(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)]Fe(CO)_2I$ (11) and $Co_2(CO)_8$. $I(CO)_2Fe[(\eta^5\text{-}C_5H_5)C{\equiv}C(\eta^5\text{-}C_5H_4)]Fe(CO)_2I$ (0.36 g, 0.57 mmol) was dissolved in benzene (60 mL) and stirred at room temperature. To this solution was added $Co_2(CO)_8$ (0.24 g, 0.63 mmol), which was accompanied by the evolution of gas from the stirred solution. After 2 h the solvent was removed in vacuo. The crude product was redissolved in chloroform and chromatographed over silica using chloroform as the eluent. Pure product was recovered (0.4 g, 78%) as a dark red solid. Recrystallization from chloroform/pentane at −20 °C gave black crystals, mp decomp above 135 °C. Anal. Calcd for $C_{22}H_8Co_2Fe_2I_2O_{10}$: C, 28.85; H, 0.88. Found: C, 28.88; H, 0.95.

Formation of 13 by Reaction of $CH_3(CO)_3W(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)W(CO)_3CH_3$ and $Co_2(CO)_8$. $CH_3(CO)_3W(\eta^5\text{-}C_5H_4)\text{-}C{\equiv}C(\eta^5\text{-}C_5H_4)W(CO)_3CH_3$ (1.43 g, 1.99 mmol) and $Co_2(CO)_8$ (0.75 g, 2.19 mmol) were mixed in benzene (20 mL) and stirred at room temperature for 2 h. The solvent was removed, and the flask was connected to the high vacuum line to remove the excess $Co_2(CO)_8$ giving 2.0? g (100%) of product recovered as a black solid. This solid was recrystallized by vapor diffusion from THF/pentane at −20 °C; mp decomp above 175 °C. Anal. Calcd for $C_{26}H_{14}Co_2O_{12}W_2$: C, 31.10; H, 1.40. Found: C, 30.99; H, 1.46.

Formation of 14 by Reaction of $CH_3(CO)_3Mo(\eta^5\text{-}C_5H_4)\text{-}C{\equiv}C(\eta^5\text{-}C_5H_4)Mo(CO)_3CH_3$ and $Co_2(CO)_8$. As described for 13, $CH_3(CO)_3Mo(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)Mo(CO)_3CH_3$ (0.41 g, 0.75 mmol) and $Co_2(CO)_8$ (0.28 g, 0.83 mmol) were allowed to react in benzene (20 mL) at room temperature for 2 h to give 0.64 g (100%) of product. Recrystallization from THF/pentane at −20 °C gave black crystals, mp decomp above 155 °C. Anal. Calcd for $C_{26}H_{14}Co_2Mo_2O_{12}$: C, 37.70; H, 1.70. Found: C, 37.68; H, 1.71.

Formation of 15 by Reaction of $(CO)_3Mn(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)Mn(CO)_3$ and $Co_2(CO)_8$. With the same procedure described for 13, $(CO)_3Mn(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)Mn(CO)_3$ (0.42 g, 0.976 mmol) and $Co_2(CO)_8$ (0.400 g, 1.171 mmol) were allowed to react in benzene (40 mL) at room temperature for 2 h to yield 0.698 g (100%) of product that was recovered as a black solid. Recrystallization from $CHCl_3$/pentane at −20 °C gave black crystals, mp 145–147 °C (chloroform–pentane). Anal. Calcd for $C_{24}H_8Co_2Mn_2O_{12}$: C, 40.25; H, 1.12. Found: C, 40.21; H, 1.15.

Formation of 16 by Reaction of $(CO)_3Re(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)Re(CO)_3$ and $Co_2(CO)_8$. As described for 13, $(CO)_3Re(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)Re(CO)_3$ (0.150 g, 0.216 mmol) and $Co_2(CO)_8$ (0.088 g, 0.259 mmol) were allowed to react in benzene (20 mL) at room temperature for 2 h to yield 0.211 g (100%) of product recovered as a black solid. Recrystallization from $CHCl_3$/pentane at −20 °C gave black crystals, mp >280 °C. Anal. Calcd for $C_{24}H_8Co_2O_{12}Re_2$: C, 29.45; H, 0.82. Found: C, 29.34; H, 0.83.

Reaction of 11 and 12 with $LiEt_3BH$. A weighted amount of 11 or 12 (20–30 mg) was loaded in an NMR tube, and deuteriochloroform was vacuum transferred into the tube to dissolve the complex. The tube was then transferred into the NMR magnet previously cooled to −40 °C, and the spectra were recorded. The same NMR tube was quickly extracted from the magnet, and a stoichiometric amount of lithium triethylborohydride was syringed in. New spectra were recorded at −40 °C, and the immediate appearance of new peaks was observed. In the case of 11, a new peak at δ −12.04 was observed, while for 12 the new resonance appeared at δ −11.85. A blank experiment was carried out to determine if those new adsorbances could be determined by reaction of the super hydride with the solvent, but no peaks were found in the regions where the previously observed signals were recorded.

Structure Determination for $I(CO)_2Fe[(\eta^5\text{-}C_5H_4)C(CO)_3Co\text{–}Co(CO)_3C(\eta^5\text{-}C_5H_4)]Fe(CO)_2I$ (12). Crystallographic data for $I(CO)_2Fe[(\eta^5\text{-}C_5H_4)C(CO)_3Co\text{–}Co(CO)_3C(\eta^5\text{-}C_5H_4)]Fe(CO)_2I$ together with the details of the X-ray diffraction experiment and subsequent computations are given in Table III. The unit cell dimensions were obtained from a least-squares fit to the setting angles for 25 reflections (2θ(av) = 22.0°) on a Nicolet R3m diffractometer.[31] The stability of the crystal was monitored by measurement of the intensities of three reflections (200, 020, 002) every 100 data points. Due to the high average value of μ (47.3 cm^{-1}) an empirical absorption correction was performed by utilizing the intensity profiles obtained for 15 reflections as a function of Ψ ($\Delta\Psi$ = 15°). The transmission factors ranged from 0.031 to 0.046. Lorentz and polarization corrections were applied to the data.

The initial E map (using phases supplied by the direct methods routine SOLV[31]) revealed the positions of the Fe atoms. Neutral atom scattering factors[32] and anomalous scattering contributions[32] were used for all atoms. Subsequent Fourier difference electron density maps revealed all non-hydrogen atoms. In the final structure model, all non-hydrogen atoms were given anisotropic thermal parameters. At convergence (weighted least-squares refinement on F, (shift/esd) < 0.011 over the last three cycles) the ΔF map exhibited a maximum of 1.03 e $Å^{-3}$ in the immediate vicinity of I1 and a minimum of −0.79 e $Å^{-3}$.

Final fractional atomic coordinates for all non-hydrogen atoms of 12 are listed in Table S-1. Metric parameters relevent to the discussion in this paper are listed in Tables IV and V.

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Registry No. 1, 68148-25-4; 2, 122236-43-5; 3, 122236-44-6; 4, 12079-63-9; 5, 51508-36-2; 6, 122236-45-7; 7, 122269-69-6; 8, 122269-70-9; 9, 122269-71-0; 10, 122269-72-1; 11, 122269-73-2; 12, 122269-74-3; 13, 122269-75-4; 14, 122269-76-5; 15, 122269-77-6; 16, 122269-78-7; 17, 122269-79-?; 18, 122269-80-1; $CpFe(CO)_2CH_3$, 12080-06-7; $CpW(CO)_3CH_3$, 12082-27-8; $CpMo(CO)_3CH_3$, 12082-25-6; $CpMn(CO)_3$, 12079-65-1; $CpRe(CO)_3$, 12079-73-1; $(CH_3CN)_2PdCl_2$, 14592-56-4; $Bu_3SnC{\equiv}CSnBu_3$, 994-71-8; $CO_2(CO)_8$, 10210-68-1; 1,2-diiodoethane, 624-73-7.

Supplementary Material Available: Table S-1, atomic coordinates and isotropic thermal parameters, and Table S-2, anisotropic thermal parameters for $C_{22}H_8O_{10}Co_2Fe_2I_2$ (12) (3 pages); Table S-3, observed and calculated structure factors for $C_{22}H_8O_{10}Co_2Fe_2I_2$ (12) (26 pages). Ordering information is given on any current masthead page.

(31) Software used for diffractometer operations and data collection was provided with the Nicolet R3m diffractometer. Crystallographic computations were carried out with the SHELXTL program library, written by G. M. Sheldrick and supplied by Nicolet XRD for the Data General Eclipse S/140 computer in the Crystallography Laboratory at Colorado State University.

(32) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 99.