Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research, to the Royal Society for a 1983 University Research Fellowship (to C.E.H.), and to the NSF for a grant toward the purchase of a diffractometer at the University of Delaware. Johnson-Matthey is thanked for generous loans of $RuCl_3$.

Supplementary Material Available: Tables of atomic coordinates, bond distances, bond angles, thermal parameters, and H atom coordinates (9 pages); a listing of structure factors (41 pages). Ordering information is given on any current masthead page.

Use of Palladium-Catalyzed Coupling Reactions in the Synthesis of Heterobimetallic Complexes. Preparation of Bis(cyclopentadienyl)acetylene Heterodinuclear Complexes

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The palladium-catalyzed coupling reactions of η^5-iodocyclopentadienyl complexes of Fe, W, Mn, and Re with $Bu_3SnC{\equiv}CH$ yield the corresponding η^5-ethynylcyclopentadienyl derivatives $(\eta^5\text{-}HC{\equiv}CC_5H_4)ML_n$ (M = Fe, W, Mn, Re). Upon reaction with Et_2NSnR_3 (R = Me, Bu), the acetylenic proton is replaced with a trialkyltin group, forming the η^5-[(trialkylstannyl)ethynyl]cyclopentadienyl derivatives $(\eta^5\text{-}R_3SnC{\equiv}CC_5H_4)ML_n$. A second palladium-catalyzed coupling reaction between these trialkyltin derivatives and (η^5-iodocyclopentadienyl)metal complexes affords the heterobimetallic complexes $L_nM(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)M'L_m$ (M and M' = Fe, W, Mo, Mn, Re). The crystal structure of $Ph_3P(CO)_2Mn(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)W(CO)_3CH_3$ confirmed the general structure of these heterobimetallic complexes and showed that the two metals attached to the cyclopentadienyl rings were pointed in opposite directions.

Introduction

One goal of research directed toward the efficient reduction of carbon monoxide by homogeneous catalysis has been the preparation of mixed-metal complexes containing both "early" and "late" transition metals.[1] Much of the interest in this chemistry is due to the expectation that the two metal centers will interact cooperatively in a catalytic process to affect novel reactions and increase the overall reaction rates under mild reaction conditions.[2] One approach to this goal has been to design an appropriate bridging ligand that holds the two metal centers in close proximity, thus allowing effective interaction (i.e., exchange of ligands) during the catalytic cycle. In such a dinuclear complex, either of the two metals may separately catalyze two consecutive reactions, or both metals may simultaneously perform some transformation through interaction with the substrate.

Most of the bidentate ligands used to bring two metal centers together are bridging ligands bearing two coordinating centers, P, As, N, S, or O, linked in the same molecule in various ways.[3] The limitation in the use of such ligands resides in the limited thermal stability of their metal complexes due to the relatively weak metal-ligand bond. By contrast, cyclopentadienyl ligands have much stronger ligand-metal bonds (60-70 kcal mol^{-1} for typical η^5-cyclopentadienyl-metal bonds versus 30-40 kcal mol^{-1} for a trialkylphosphine-metal bond).[4] However, general synthetic routes for the synthesis of heterobimetallic complexes held together by two covalently linked cyclopentadienide rings are difficult. While a number of homobimetallic structures in which two identical metal centers are complexed by the cyclopentadienyl rings of dicyclopentadienylmethane,[5] dicyclopentadienyldimethylsilane,[6] dicyclopentadienylacetylene,[7,8] and fulval-

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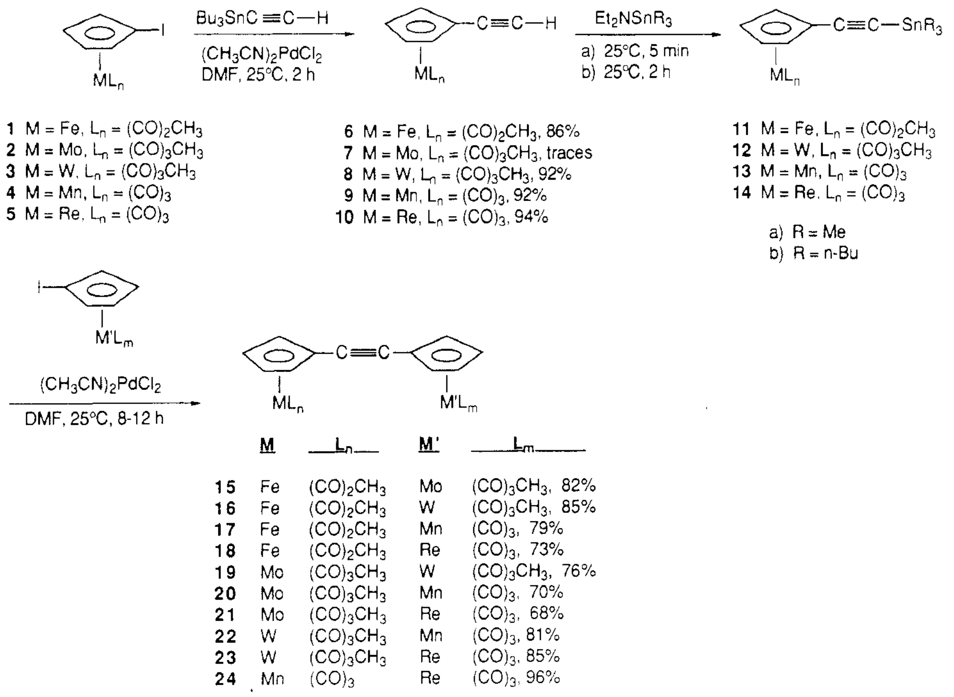
Scheme I



1 M = Fe, L_n = $(CO)_2CH_3$
2 M = Mo, L_n = $(CO)_3CH_3$
3 M = W, L_n = $(CO)_3CH_3$
4 M = Mn, L_n = $(CO)_3$
5 M = Re, L_n = $(CO)_3$

6 M = Fe, L_n = $(CO)_2CH_3$, 86%
7 M = Mo, L_n = $(CO)_3CH_3$, traces
8 M = W, L_n = $(CO)_3CH_3$, 92%
9 M = Mn, L_n = $(CO)_3$, 92%
10 M = Re, L_n = $(CO)_3$, 94%

11 M = Fe, L_n = $(CO)_2CH_3$
12 M = W, L_n = $(CO)_3CH_3$
13 M = Mn, L_n = $(CO)_3$
14 M = Re, L_n = $(CO)_3$

a) R = Me
b) R = n-Bu

	M	L_n	M'	L_m
15	Fe	$(CO)_2CH_3$	Mo	$(CO)_3CH_3$, 82%
16	Fe	$(CO)_2CH_3$	W	$(CO)_3CH_3$, 85%
17	Fe	$(CO)_2CH_3$	Mn	$(CO)_3$, 79%
18	Fe	$(CO)_2CH_3$	Re	$(CO)_3$, 73%
19	Mo	$(CO)_3CH_3$	W	$(CO)_3CH_3$, 76%
20	Mo	$(CO)_3CH_3$	Mn	$(CO)_3$, 70%
21	Mo	$(CO)_3CH_3$	Re	$(CO)_3$, 68%
22	W	$(CO)_3CH_3$	Mn	$(CO)_3$, 81%
23	W	$(CO)_3CH_3$	Re	$(CO)_3$, 85%
24	Mn	$(CO)_3$	Re	$(CO)_3$, 96%

ene[9] are known, few heterobimetallic structures have been reported. The reported examples of heterobimetallic complexes containing two cyclopentadienyl rings as "bidentate" ligands for the two metals are limited to those of the general formula $L_nM(\eta^5\text{-}C_5Et_4)CH_2CH_2(\eta^5\text{-}C_5Me_4)\text{-}M'L_m$ [M = W, L_n = $(O\text{-}tBu)O_2$, M' = Ru, Co; L_m = $(CO)_2$][10] as well as the heterobimetallic complexes containing the fulvalene ligand. The heterobimetallic complexes containing ethylene spacers were prepared by the reaction of a tungstacyclobutadiene derivative with ethynyl derivatives of (tetramethylcyclopentadienyl)rhodium or cobalt carbonyl complexes. The fulvalene heterobimetallic compounds were prepared in three different ways: (a) by reaction of dihydrofulvalene with a mixture of metal carbonyls;[11] (b) by partial decomplexation, via ring slippage, of a homobimetallic complex and subsequent recomplexation with a different metal carbonyl;[12,13] (c) by cyclization of an acylated cyclopentadienide to assemble a masked C_5 ring attached to an existing cyclopentadienylmetal system.[13] While the first method suffers from the reliance on statistics to form the heterobimetallic complex, the other two are more general, but several steps are required to obtain the final product and careful manipulation under an inert atmosphere is necessary. More recently, a heterobimetallic fulvalene complex containing Fe and W has been prepared[14] by the electrochemical reduction of bisferrocene and subsequent reaction of the monoanion with $W(CO)_3(PrCN)_3$. However, only one example is reported, and the yield is moderate (21%).

In this paper, we describe the use of a palladium-catalyzed coupling reaction to prepare several different heterobimetallic complexes having the dicyclopentadienylethynyl framework as the bridging ligand. This novel route provides a straightforward synthetic entry to a variety of heterobimetallic complexes. The only requirement for a given transition metal to be introduced in this synthetic route is the availability of its cyclopentadienyl derivative. Because such derivatives are known for many transition metals, this procedure constitutes a powerful method for the assembly of heterobimetallic systems inaccessible in other ways.

Results and Discussion

Palladium-Catalyzed Cross-Coupling Reactions of (η^5-Iodocyclopentadienyl)metal Complexes (1–5) with Tributylethynylstannane. We have previously reported the preparation of (η^5-iodocyclopentadienyl)metal carbonyl complexes $(\eta^5\text{-}IC_5H_4)ML_n$ (M = Fe, W, Mo, Mn, Re) by metalation/iodination of the corresponding η^5-cyclopentadienyl derivatives.[8] Those cyclopentadienylhalometal complexes undergo reaction with $Bu_3SnC{\equiv}CSnBu_3$ in the presence of bis(acetonitrile)dichloropalladium to produce homobimetallic complexes of general formula $L_nM(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)ML_n$.[8] The synthetic pathway described herein relies on the stepwise construction of the dimer by sequential attachment of the two cyclopentadienylmetal units to each side of the alkyne bridge. In our synthetic strategy, the iodide complexes **1**–**5** are allowed to react with tributylethynylstannane in the presence of 5 mol % of $(CH_3CN)_2PdCl_2$, with DMF as the solvent, affording (with the exception of the molybdenum derivative **2**) the coupled products **6** and **8**–**10** in nearly quantitative yield (Scheme I).

This reaction takes place at room temperature and goes to completion in 2 h. Removal of the tributyltin iodide formed during the reaction was accomplished by an aqueous potassium fluoride wash, which produced the insoluble tributyltin fluoride.[15] Chromatographic separation of the crude reaction mixture, followed by vacuum dis-

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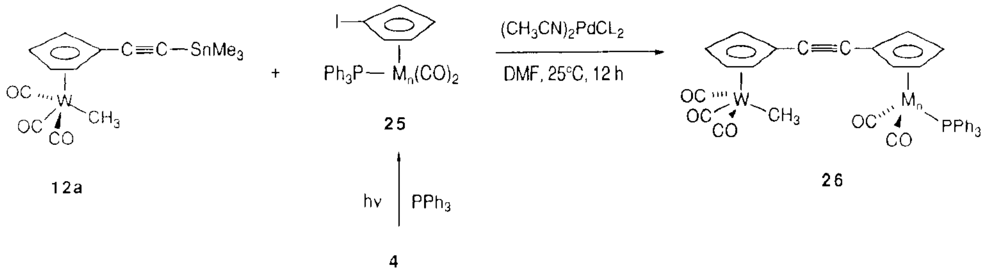
Scheme II



tillation or sublimation, gave the pure product.

Reactions of (η^5-Ethynylcyclopentadienyl)metal Complexes 6 and 8–10 with (Dimethylamino)trialkylstannane. Preparation of the two partners for the final palladium-catalyzed coupling reaction to yield a heterobimetallic complex requires the removal of the acetylenic proton in compounds and **6**, **8–10** and its replacement with a trialkyltin group. This reaction was carried out using either (dimethylamino)trimethylstannane or (dimethylamino)tributylstannane, in the absence of solvent. With both methods the yields were quantitative. When (diethylamino)trimethylstannane was used, the (η^5-ethynylcyclopentadienyl)metal complex was dissolved in an equimolar amount of tin reagent, and in a short period (5–10 min) the mixture solidified, indicating the completion of the reaction. When (dimethylamino)tributylstannane was used, a longer reaction time was required (2 h). In both cases, the dimethylamine formed during the reaction was removed in vacuo. Further purification was achieved by sublimation of the trimethyltin derivatives **11a–14a**, giving solid products. In contrast, the tributyltin derivatives **11b–14b** were liquids, and attempted purification by distillation, even under high vacuum, resulted in decomposition.

Formation of Heterobimetallic Complexes 15–24. The last step in the synthetic route was a second palladium-catalyzed coupling reaction in which the η^5{[(trialkylstannyl)ethynyl]cyclopentadienyl}metal complexes **11–14** were coupled with the (η^5-iodocyclopentadienyl)metal complexes **1–5**. As before, these reactions were carried out at room temperature, in DMF using 5 mol % of $(CH_3CN)_2PdCl_2$. The use of the trimethylethynylstannane derivatives was more convenient because the reaction was faster (8 h instead of 12 h), and the trimethyltin iodide formed during the reaction was removed by extraction with water, while removal of the corresponding tributyltin iodide required transformation to the insoluble fluoride.[15]

The crude product obtained from the reaction mixture after extraction was easily purified by chromatographic separation on silica gel with hexanes/benzene as the eluent. The yield was generally good, and the products **15–24** were solid, easy to crystallize, and stable at room temperature, even if exposed for a few hours to air.

In an effort to obtain crystals of a complex in which there was no disorder in the crystal (vide infra) and the two metals could be readily distinguished, it was necessary to substitute a phosphine ligand for a carbonyl at one of the metals. Accordingly, a coupling reaction was carried out between the acetylenic tin partner **12a** and a (η^5-iodocyclopentadienyl)manganese complex (**25**) in which one of the carbonyls in **4** had been replaced by triphenylphosphine (Scheme II).

Structure Determination of $(CO)_3Mn(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)Fe(CO)_2CH_3$ (17) and $CH_3(CO)_3W(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)Mn(CO)_2P(C_6H_5)_3$ (26). Single crystals of **17** were obtained as yellow needles by slow crystallization from a cold (−20 °C) mixture of chloroform/pentane. The ORTEP representation of the compound (Figure 1) reflects disorder in the crystal and the inability to distinguish the $Mn(CO)_3$ group from the $Fe(CO)_2CH_3$.

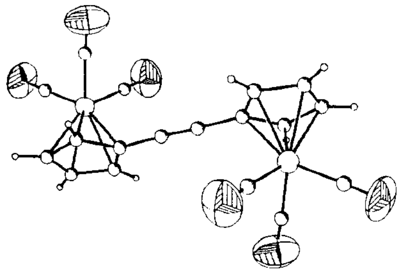


Figure 1. ORTEP plot of **17**.

The inability to assign the specific identity of the two metallic units is due to extensive disorder in the crystal packing. This random distribution creates an inversion center in the molecule, at the center of the triple bond, in such a way that only half of the molecular structure is crystallographically independent. Despite accurate reflection data, the disorder arising from this random distribution, in turn due to the slight difference in atomic number between Fe and Mn, results in the impossibility of assigning the exact nature of the ligands on the metals. Each one of the six ligands has a hybrid representation defined as $^5/_6$CO and $^1/_6CH_3$.

To circumvent this problem, the Mn–W complex (**26**) was prepared and its X-ray crystal structure was determined (Figure 2). Crystals of **26** were grown by the vapor diffusion of pentane into a tetrahydrofuran solution of the complex.

Crystallographic data for $C_{36}H_{26}O_5PMnW$ together with the details of the X-ray diffraction experiment and subsequent computations are given in Table I. The unit-cell dimensions were obtained from a least-squares fit to the setting angles for 25 reflections (2θ(av) = 25.25°) on a Nicolet R3m diffractometer.[16] The stability of the crystal was monitored by the measurement of the intensities of three reflections (200, 020, 004) every 100 data points. Due to the high average value of μ (44.07 cm^{-1}) an empirical[17] 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 0.844 to 0.399. Lorentz and polarization corrections were applied to the data.

The initial E map (using phases supplied by the direct methods routine SOLV[1]) revealed the positions of the P, Mn,

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[16] Software used for diffractometer operations was provided with the Nicolet R3m diffractometer. All crystallographic computations were carried out with the SHELXTL program library (G. M. Sheldrick, supplied by Nicolet XRD for the DG Eclipse S/140 computer in the crystallography laboratory at CSU).

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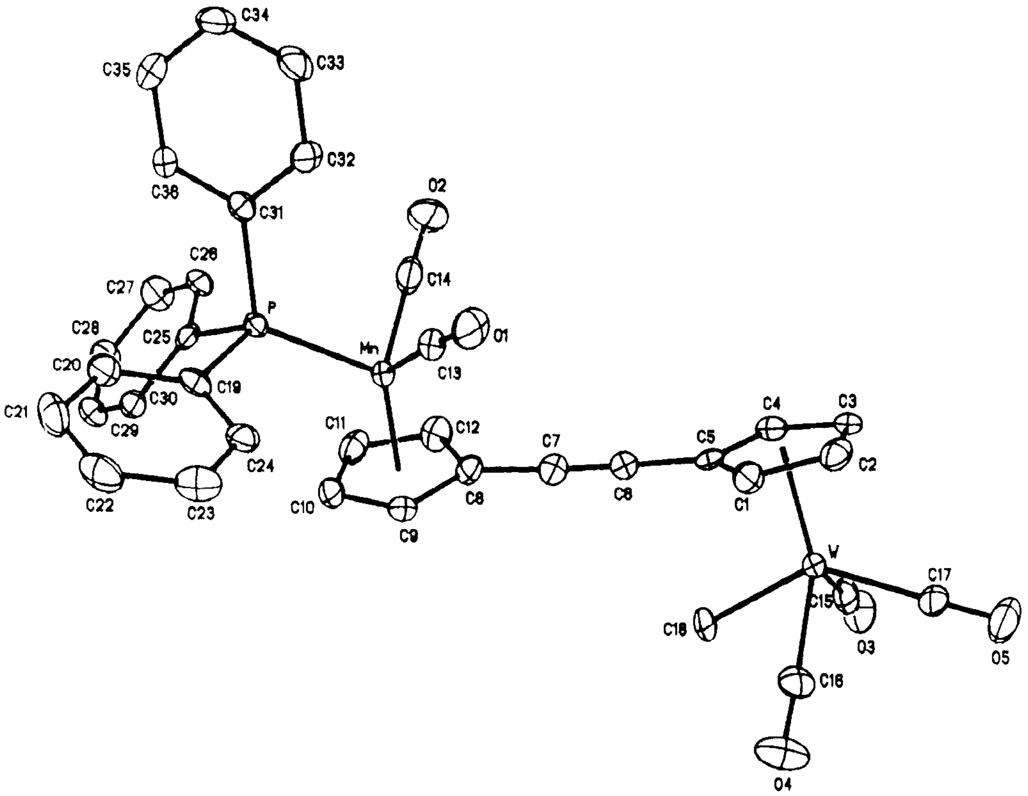

Figure 2. Crystal structure of $C_{36}H_{26}O_5PMnW$ (**26**).

and W atoms. Neutral-atom scattering factors[18] and anomalous scattering contributions[18] 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 of F, (shift/esd) < 0.015 over the last three cycles) the ΔF map exhibited a maximum of 1.05 e Å^{-3} in the immediate vicinity of W (0.99 Å) and a minimum of -1.31 e Å^{-3}.

Final fractional atomic coordinates for all non-hydrogen atoms are listed in Table II. Metric parameters relevent to the discussion in this paper are listed in Tables III and IV.

The metal-cyclopentadienyl centroid distances for tungsten and manganese are 2.007 and 1.775 Å, respectively, and are usual for tungsten[19] and manganese[20] cyclopentadienyl complexes. The methyl group on tungsten is located directly under a cyclopentadienyl carbon as is generally the case in the parent complexes. It is aligned along the acetylenic group connecting the two cyclopentadienyl rings in the direction of the cyclopentadienyl ring coordinated to manganese. The slight distortion of the idealized square-pyramidal geometry about tungsten leads to a wider angle of 136.2° between the carbonyl group and the methyl group trans to it and a smaller angle of 101.9° about tungsten and the two carbonyl groups trans to each other.

Table I. Details of the Crystallographic Experiment and Computations for $C_{36}H_{26}O_5PMnW$ (26)

mol formula	$C_{36}H_{26}O_5PMnW$
formula wt	808
cryst syst	monoclinic
space group	$P2_1/c$
lattice constants	
a, Å	12.582 (5)
b, Å	10.199 (3)
c, Å	24.440 (3)
β, deg	99.07 (2)
V, Å^3	3096.9
temp, °C	-120
Z	4
F(000)	1584
ρ(calcd), g cm^{-3}	1.73
cryst dimens, mm	0.20 × 0.25 × 0.54
radiation	Mo Kα (λ = 0.71 07 Å)
monochromator	graphite
μ, cm^{-1}	44.07
scan type	ω (Wyckoff)
scan speed, deg min^{-1}	5.98-29.30 (variable)
2θ range, deg	4-50
indexes collected	$\pm h,+k,+l$
total no. of reflns	5927 measd 4527 used ($I < 2.5\sigma(I)$)
no. of least-squares parameters	400
data/parameter ratio	11.32
R^a	0.037
$R_w{}^a$	0.034
GOF^a	1.298
g (refined)^c	3 × 10^{-4}
slope, normal probability plot^b	1.088

[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 = $\{(\sum w|(F_o - F_c)|)^2/(N_{data} - N_{params})\}^{1/2}$. [b] Abrahams, S. C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, *B30*, 261-268. [c] g downweights intense reflections ($w = [\sigma^2(F) + |g|F^2]^{-1}$). Values between 1 × 10^{-4} and 1 × 10^{-2} are normal; values much outside this range are unrealistic.

The two carbonyl and the phosphine ligands on manganese form a nearly perfect triagonal array, the bond angles between the ligands varying from 92.2° to 94.2°. The phosphine ligand is directed away from the ethynyl bridge. A Newman-type projection of this portion of the molecule shows that the angle between the two carbonyls is not bisected by the C_8–C_7 bond of the acetylenic link but instead places the C_{13} carbonyl closer to C_8 then the

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Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)[a] for $C_{36}H_{26}O_5PMnW$

atom	*x*	*y*	*z*	U_{iso}[b]
W	12512 (1)	15663 (1)	6071 (1)	18 (1)
Mn	8818 (1)	9817 (1)	6148 (1)	18 (1)
P	7293 (1)	8736 (1)	6178 (1)	16 (1)
O1	7810 (4)	12100 (4)	5546 (2)	38 (2)
O2	9206 (4)	8483 (5)	5133 (2)	49 (2)
O3	14951 (4)	14981 (5)	6362 (2)	38 (2)
O4	12058 (4)	17135 (5)	7126 (2)	46 (2)
O5	13313 (4)	18461 (4)	5816 (2)	48 (2)
C1	10714 (5)	15278 (6)	5677 (3)	26 (2)
C2	11206 (5)	16041 (6)	5308 (3)	27 (2)
C3	12029 (5)	15285 (6)	5133 (2)	25 (2)
C4	12047 (5)	14052 (6)	5398 (2)	25 (2)
C5	11215 (5)	14037 (6)	5726 (2)	23 (2)
C6	10882 (5)	12938 (6)	6019 (2)	27 (2)
C7	10587 (5)	12021 (6)	6256 (3)	27 (2)
C8	10198 (5)	10903 (6)	6513 (3)	25 (2)
C9	9418 (5)	10937 (6)	6883 (2)	25 (2)
C10	9240 (5)	9626 (6)	7036 (2)	27 (2)
C11	9891 (5)	8791 (6)	6774 (3)	31 (2)
C12	10489 (5)	9575 (6)	6452 (3)	30 (2)
C13	8167 (5)	11173 (6)	5776 (2)	24 (2)
C14	9022 (5)	9005 (6)	5527 (3)	31 (2)
C15	14069 (5)	15271 (6)	6253 (3)	28 (2)
C16	12242 (5)	16613 (6)	6734 (2)	28 (2)
C17	13052 (5)	17424 (6)	5917 (2)	26 (2)
C18	12789 (5)	14188 (6)	6797 (3)	28 (2)
C19	6313 (5)	9509 (5)	6570 (2)	21 (2)
C20	5456 (5)	8826 (6)	6715 (2)	25 (2)
C21	4705 (5)	9458 (7)	6995 (3)	33 (2)
C22	4844 (5)	10766 (7)	7125 (3)	35 (2)
C23	5699 (5)	11444 (7)	6978 (3)	31 (2)
C24	6429 (5)	10824 (5)	6705 (2)	24 (2)
C25	7561 (4)	7129 (5)	6505 (2)	19 (2)
C26	7976 (5)	6146 (6)	6209 (2)	23 (2)
C27	8264 (5)	4954 (6)	6454 (3)	31 (2)
C28	8187 (5)	4734 (6)	7010 (3)	30 (2)
C29	7795 (5)	5718 (6)	7308 (2)	26 (2)
C30	7482 (5)	6910 (5)	7064 (2)	21 (2)
C31	6434 (5)	8296 (5)	5523 (2)	20 (2)
C32	6385 (5)	9081 (5)	5057 (2)	26 (2)
C33	5715 (5)	8773 (6)	4570 (3)	31 (2)
C34	5065 (6)	7684 (6)	4543 (3)	31 (2)
C35	5104 (6)	6898 (6)	4999 (3)	35 (2)
C36	5780 (5)	7188 (6)	5485 (2)	26 (2)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] The equivalent isotropic *U* is defined as one third of the trace of the U_{ii} tensor.

Table III. Bond Lengths (Å)[a] for $C_{36}H_{26}O_5PMnW$

W–C1	2.347 (6)	W–C2	2.315 (6)
W–C3	2.310 (5)	W–C4	2.333 (6)
W–C5	2.385 (6)	W–C15	1.979 (7)
W–C16	1.964 (6)	W–C17	1.977 (6)
W–C18	2.310 (6)	Mn–P	2.224 (2)
Mn–C8	2.133 (6)	Mn–C9	2.163 (6)
Mn–C10	2.161 (6)	Mn–C11	2.147 (6)
Mn–C12	2.131 (6)	Mn–C13	1.780 (6)
Mn–C14	1.782 (7)	P–C19	1.853 (6)
P–C25	1.832 (6)	P–C31	1.840 (5)
O1–C13	1.155 (7)	O2–C14	1.155 (9)
O3–C15	1.139 (8)	O4–C16	1.152 (8)
O5–C17	1.146 (8)	C1–C2	1.406 (9)
C1–C5	1.410 (8)	C2–C3	1.411 (9)
C3–C4	1.413 (8)	C4–C5	1.417 (9)
C5–C6	1.427 (9)	C6–C7	1.190 (9)
C7–C8	1.424 (9)	C8–C9	1.437 (9)
C8–C12	1.417 (8)	C9–C10	1.415 (8)
C10–C11	1.404 (9)	C11–C12	1.417 (10)
C19–C20	1.375 (9)	C19–C24	1.384 (8)
Ci0–C21	1.408 (10)	C21–C22	1.376 (10)
C22–C23	1.374 (10)	C23–C24	1.371 (9)
C25–C26	1.385 (8)	C25–C30	1.405 (8)
C26–C27	1.379 (8)	C27–C28	1.396 (9)
C28–C29	1.375 (9)	C29–C30	1.383 (8)
C31–C32	1.385 (8)	C31–C36	1.392 (8)
C32–C33	1.382 (8)	C33–C34	1.375 (9)
C34–C35	1.368 (9)	C35–C36	1.378 (8)

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

C_{14} carbonyl, the angles in this projection being 37.3° and 82.4°, respectively. This unsymmetrical placement of the carbonyls with respect to the cyclopentadienyl ring is seen in the parent complex.[20]

The two metals are pointed generally in opposite directions, but the two cyclopentadienyl rings are not coplanar. The dihedral angle between the C_1, C_2, C_3, C_4, C_5 plane and the C_8, C_9, C_{10}, C_{11}, C_{12} plane is 15.6°. This places the two metals at a distance of 7.597 Å from each other. This distance as is present in the crystal is too great for any interaction. Rotation of one of the cyclopentadienyl rings about 165° about the C_5–C_4 or C_7–C_8 bonds produces a conformation in which the metals are a little less than 6.4 Å, the distance between the centroids of the two cyclopentadienyl rings.

Experimental Section

All manipulations were carried out under an 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 a Perkin-Elmer 983 grating infrared spectrometer, attached to a Perkin-Elmer 3600 data station; abbrevations: v, very; s, strong; w, weak; m, medium; sh, shoulder. The ^{1}H 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 ppm vs Me_4Si, assigning the ^{1}H impurity in the solvent ($CDCl_3$) at 7.24 ppm. ^{13}C spectra chemical shifts are reported relative to the ^{13}C triplet ($CDCl_3$) at 77.00 ppm. Elemental analyses were performed 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. Cyclopentadienyl complexes and reagents prepared by known methods: $(\eta^5\text{-IC}_5H_4)Fe(CO)_2CH_3$,[8] $(\eta^5\text{-IC}_5H_4)Mo(CO)_3CH_3$,[8] $(\eta^5\text{-IC}_5H_4)W(CO)_3CH_3$,[8f] $(\eta^5\text{-IC}_5H_4)Mn(CO)_3$,[8] $(\eta^5\text{-IC}_5H_4)Re(CO)_3$,[8] $[CH_3(CH_2)_3]_3SnC{\equiv}CH$,[21] $(CH_3CN)_2PdCl_2$,[22] $(CH_3CH_2)_2NSn(CH_3)_3$,[23] $(CH_3CH_2)_2NSn[(CH_2)_3CH_3]_3$.[23]

General Procedure for the Palladium-Catalyzed Coupling Reaction of (η^5-Iodocyclopentadienyl)metal Complexes 1–5 and Tributylethynylstannane. $(\eta^5\text{-HC}{\equiv}CC_5H_4)Fe(CO)_2CH_3$ (6). An argon-purged flask was charged with 3.04 g (9.56 mmol) of $(\eta^5\text{-IC}_5H_4)Fe(CO)_2CH_3$ (3), 3.01 g (9.56 mmol) of tributylethynylstannane, and 150 mL of DMF. To the stirred solution, 0.124 g (0.47 mmol) of $(CH_3CN)_2PdCl_2$ dissolved in 20 mL of DMF was added by syringe. Stirring was continued at room temperature for 2 h, and then 200 mL of ether was added to the reaction mixture, followed by addition of 100 mL of a 50% solution of KF in water. The mixture was rapidly stirred for 1 h while argon was bubbled through the solution, and then the solution was transferred to 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 ethyl ether. The organic phases were collected and dried over magnesium sulfate. Filtration and removal of the solvent yielded

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Table IV. Bond Angles (deg)[a] for $C_{36}H_{26}O_5PMnW$

C1–W–C2	35.1 (2)	C1–W–C3	58.6 (2)
C2–W–C3	35.5 (2)	C1–W–C4	58.3 (2)
C2–W–C4	58.8 (2)	C3–W–C4	35.4 (2)
C1–W–C5	34.7 (2)	C2–W–C5	58.2 (2)
C3–W–C5	58.4 (2)	C4–W–C5	34.9 (2)
C1–W–C15	156.0 (2)	C2–W–C15	140.1 (3)
C3–W–C15	106.6 (2)	C4–W–C15	98.4 (2)
C5–W–C15	122.5 (2)	C1–W–C16	98.1 (2)
C2–W–C16	112.9 (2)	C3–W–C16	148.1 (2)
C4–W–C16	150.8 (2)	C5–W–C16	115.9 (2)
C15–W–C16	101.9 (3)	C1–W–C17	114.3 (2)
C2–W–C17	85.3 (2)	C3–W–C17	90.5 (2)
C4–W–C17	124.2 (2)	C5–W–C17	143.3 (2)
C15–W–C17	82.5 (2)	C16–W–C17	79.5 (3)
C1–W–C18	103.0 (2)	C2–W–C18	136.8 (2)
C3–W–C18	129.6 (2)	C4–W–C18	94.2 (2)
C5–W–C18	80.2 (2)	C15–W–C18	70.8 (3)
C16–W–C18	73.3 (2)	C17–W–C18	136.2 (2)
P–Mn–C8	153.3 (2)	P–Mn–C9	115.1 (2)
C8–Mn–C9	39.1 (2)	P–Mn–C10	89.9 (2)
C8–Mn–C10	64.6 (2)	C9–Mn–C10	38.2 (2)
P–Mn–C11	100.6 (2)	C8–Mn–C11	64.9 (2)
C9–Mn–C11	64.3 (2)	C10–Mn–C11	38.0 (2)
P–Mn–C12	137.7 (2)	C8–Mn–C12	38.8 (2)
C9–Mn–C12	64.9 (2)	C10–Mn–C12	64.3 (3)
C11–Mn–C12	38.7 (3)	P–Mn–C13	94.2 (2)
C8–Mn–C13	95.1 (2)	C9–Mn–C13	94.9 (2)
C10–Mn–C13	127.1 (3)	C11–Mn–C13	158.2 (3)
C12–Mn–C13	128.1 (3)	P–Mn–C14	92.2 (2)
C8–Mn–C14	112.3 (3)	C9–Mn–C14	151.0 (3)
C10–Mn–C14	140.1 (3)	C11–Mn–C14	102.7 (3)
C12–Mn–C14	88.6 (3)	C13–Mn–C14	92.5 (3)
Mn–P–C19	117.0 (2)	Mn–P–C25	111.0 (2)
C19–P–C25	104.3 (3)	Mn–P–C31	118.9 (2)
C19–P–C31	101.9 (3)	C25–P–C31	101.7 (2)
W–C1–C2	71.2 (3)	W–C1–C5	74.1 (3)
C2–C1–C5	108.4 (6)	W–C2–C1	73.7 (3)
W–C2–C3	72.1 (3)	C1–C2–C3	108.1 (5)
W–C3–C2	72.4 (3)	W–C3–C4	73.2 (3)
C2–C3–C4	107.9 (6)	W–C4–C3	71.4 (3)
W–C4–C5	74.5 (3)	C3–C4–C5	108.0 (5)
W–C5–C1	71.2 (3)	W–C5–C4	70.5 (3)
C1–C5–C4	107.6 (5)	W–C5–C6	127.4 (4)
C1–C5–C6	125.9 (6)	C4–C5–C6	126.4 (5)
C5–C6–C7	178.8 (6)	C6–C7–C8	176.9 (6)
Mn–C8–C7	123.0 (4)	Mn–C8–C9	71.6 (3)
C7–C8–C9	125.0 (5)	Mn–C8–C12	70.5 (3)
C7–C8–C12	127.4 (6)	C9–C8–C12	107.6 (5)
Mn–C9–C8	69.3 (3)	Mn–C9–C10	70.8 (3)
C8–C9–C10	107.2 (5)	Mn–C10–C9	71.0 (3)
Mn–C10–C11	70.4 (3)	C9–C10–C11	109.0 (6)
Mn–C11–C10	71.5 (3)	Mn–C11–C12	70.1 (4)
C10–C11–C12	108.1 (6)	Mn–C12–C8	70.7 (3)
Mn–C12–C11	71.2 (4)	C8–C12–C11	108.2 (6)
Mn–C13–O1	175.3 (6)	Mn–C14–O2	176.8 (6)
W–C15–O3	176.5 (5)	W–C16–O4	177.5 (6)
W–C17–O5	176.5 (5)	P–C19–C20	122.0 (4)
P–C19–C24	118.8 (5)	C20–C19–C24	119.2 (6)
C19–C20–C21	120.5 (6)	C20–C21–C22	119.0 (6)
C21–C22–C23	120.3 (7)	C22–C23–C24	120.5 (6)
C19–C24–C23	120.6 (6)	P–C25–C26	118.6 (4)
P–C25–C30	122.0 (4)	C26–C25–C30	118.9 (5)
C25–C26–C27	120.4 (6)	C26–C27–C28	120.7 (6)
C27–C28–C29	118.9 (6)	C28–C29–C30	121.1 (6)
C25–C30–C29	119.9 (5)	P–C31–C32	121.2 (4)
P–C31–C36	121.1 (4)	C32–C31–C36	117.7 (5)
C31–C32–C33	121.2 (5)	C32–C33–C34	120.2 (6)
C33–C34–C35	119.3 (6)	C34–C35–C36	120.9 (6)
C31–C36–C35	121		

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

an orange oil. Pure product was obtained by a Kugelrohr distillation at 70 °C/0.02 mmHg by cooling the receiver flask to 0 °C, to give 1.77 g (86%) of red oil. An analytical sample was obtained by fractional distillation at 45–46 °C/0.04 mmHg: ^{1}H NMR (CDCl$_3$) δ 4.90 (t, 2 H, J = 2.1 Hz), 4.71 (t, 2 H, J = 2.1 Hz), 2.04 (s, 2 H), 0.32 (s, 3 H); ^{13}C NMR (CDCl$_3$) δ 216.1, 89.9, 83.1, 82.2, 77.3, 76.1, −19.1; IR (film, NaCl) 3310 m, 2005 vs, 1955 vs cm^{-1}; HRMS calcd for $C_{10}H_8FeO_2$ 215.9871, found 215.9874.

(η^5-HC≡CC$_5$H$_4$)Mo(CO)$_3$CH$_3$ (7). This compound was prepared from 0.787 g (2.03 mmol) of (η^5-IC$_5$H$_4$)Mo(CO)$_3$CH$_3$ (4), 0.641 g (2.03 mmol) of tributylethynylstannane, and 0.026 g (0.1 mmol) of (CH$_3$CN)$_2$PdCl$_2$ as described for **8**. Chromatographic separation of the reaction mixture over silica using hexanes as eluent gave only traces of the desired product.

(η^5-HC≡CC$_5$H$_4$)W(CO)$_3$CH$_3$ (8). This compound was prepared from 10.79 g (22.7 mmol) of (η^5-IC$_5$H$_4$)W(CO)$_3$CH$_3$ (3), 7.14 g (22.7 mmol) of tributylethynylstannane, and 0.295 g (1.13 mmol) of (CH$_3$CN)$_2$PdCl$_2$, as described for **6**. From the crude reaction mixture, the pure product was isolated as yellow crystals by sublimation at 40 °C/0.05 mmHg to yield 7.76 g (92%): mp 34–35 °C; ^{1}H NMR (CDCl$_3$) δ 5.52 (t, 2 H, J = 2.2 Hz), 5.27 (t, 2 H, J = 2.2 Hz), 2.93 (s, 1 H), 0.52 (s, 3 H); ^{13}C NMR (CDCl$_3$) δ 215.52, 94.91, 91.31, 89.14, 79.01, 75.14, −28.66; IR (CCl$_4$) 3302 s, 2003 vs, 1932 vs cm^{-1}. Anal. Calcd for $C_{11}H_8O_3W$: C, 35.51; H, 2.16. Found: C, 35.43; H, 2.27.

(η^5-HC≡CC$_5$H$_4$)Mn(CO)$_3$ (9). This compound was prepared from 2.84 g (8.6 mmol) of (η^5-IC$_5$H$_4$)Mn(CO)$_3$ (4), 2.70 g (8.6 mmol) of tributylethynylstannane, and 0.111 g of (CH$_3$CN)$_2$PdCl$_2$ as described for **6**. Chromatographic separation over silica using hexanes as eluent gave after evaporation of solvent a yellow oil that was further purified by Kugelrohr distillation at 50 °C/0.05 mmHg to give 1.80 g (92%). An analytical sample was obtained by fractional distillation at 45.5–46 °C/0.05 mmHg: ^{1}H NMR (CDCl$_3$) δ 5.02 (t, 2 H, J = 2.1 Hz), 4.66 (t, 2 H, J = 2.1 Hz), 2.79 (s, 1 H); ^{13}C NMR (CDCl$_3$) δ 223.83, 87.01, 81.91, 80.53, 77.10, 76.10; IR (film, NaCl) 3300 w, 2015 vs, 1935 vs cm^{-1}; LRMS, m/e 228 (M$^+$), 200 (M$^+$ − CO), 172 (M$^+$ − 2CO), 144 (M$^+$ − 3CO); HRMS calcd for $C_{10}H_5MnO_3$ 227.9627, found 227.9618.

(η^5-HC≡CC$_5$H$_4$)Re(CO)$_3$ (10). This compound was prepared from 3.66 g (7.93 mmol) of (η^5-IC$_5$H$_4$)Re(CO)$_3$ (7), 2.49 g (7.93 mmol) of tributylethynylstannane, and 0.102 g (0.39 mmol) of (CH$_3$CN)$_2$PdCl$_2$ as described for **8**. Chromatographic separation over silica using hexanes as eluent gave, after removal of solvent, a beige solid. Sublimation at 60 °C/0.005 mmHg gave 2.67 g (94%) of pure product as a white solid: mp 57–58 °C; ^{1}H NMR (CDCl$_3$) δ 5.63 (t, 2 H, J = 2.2 Hz), 5.26 (t, 2 H, J = 2.2 Hz), 2.80 (s, 2 H); ^{13}C NMR (CDCl$_3$) δ 192.83, 88.42, 83.82, 83.55, 77.44, 74.72; IR (CCl$_4$) 2023 vs, 1945 vs cm^{-1}. Anal. Calcd for $C_{10}H_5O_3Re$: C, 33.42; H, 1.40. Found: C, 33.40; H, 1.45.

General Procedure for the Reaction of (η^5-Ethynylcyclopentadienyl)metal Complexes 6 and 8–10 with (Dimethylamino)trialkylstannane. The following procedure is a general method for the preparation of compounds **11–14**.

[η^5-(CH$_3$)$_3$SnC≡CC$_5$H$_4$]Fe(CO)$_2$CH$_3$ (11a). Into an argon-purged 100-mL Schlenk tube equipped with a magnetic stirrer, mineral oil overpressure valve, and rubber septum was introduced 0.495 g (2.29 mmol) of (η^5-HC≡CC$_5$H$_4$)Fe(CO)$_2$CH$_3$ (6). To this complex 0.540 g (2.29 mmol) of (CH$_3$CH$_2$)$_2$NSn(CH$_3$)$_3$ was added by syringe, and the mixture was stirred at room temperature for 10 min. After this time, the tube was connected to a vacuum line, and the diethylamine formed during the reaction was removed. The product was isolated in quantitative yield as a brown oil. An analytical sample was obtained by Kugelrohr distillation at 75 °C/0.005 mmHg: ^{1}H NMR (CDCl$_3$) δ 4.82 (t, 2 H, J = 2.1 Hz), 4.67 (t, 2 H, J = 2.1 Hz), 0.31 (s, 9 H), 0.29 (s, 3 H); ^{13}C NMR (CDCl$_3$) δ 216.49, 101.10, 94.54, 88.98, 85.24, 82.92, −7.62, −18.43; IR (film, NaCl), 2000 vs, 1960 vs cm^{-1}; HRMS calcd for $C_{13}H_{16}FeO_2Sn$ 379.9516, found 379.9590.

[η^5-(CH$_3$)$_3$SnC≡CC$_5$H$_4$]W(CO)$_3$CH$_3$ (12a). Equimolar amounts of (η^5-HC≡CC$_5$H$_4$)W(CO)$_3$CH$_3$ (10) and (CH$_3$CH$_2$)$_2$N-Sn(CH$_3$)$_3$ were stirred for 5 min. After evacuation of diethylamine, the product was recovered as a yellow solid in quantitative yield. An analytical sample was obtained by sublimation at 80 °C/0.005 mmHg: yellow solid; mp 66–68 °C; ^{1}H NMR (CDCl$_3$) δ 5.45 (t, 2 H, J = 2.1 Hz), 5.20 (t, 2 H, J = 2.1 Hz), 0.50 (s, 3 H), 0.32 (s, 9 H); ^{13}C NMR (CDCl$_3$) δ 215.33, 99.25, 96.51, 94.39, 91.16, 87.99, −7.56, −26.91; IR (CCl$_4$) 2008 vs, 1934 vs cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_3SnW$: C, 31.44; H, 3.01. Found: C, 31.40; H, 3.02.

[η^5-(CH$_3$)$_3$SnC≡CC$_5$H$_4$]Mn(CO)$_3$ (13a). This compound was prepared from an equimolar amount of (η^5-HC≡CC$_5$H$_4$)Mn(CO)$_3$ (9) and (CH$_3$CH$_2$)$_2$NSn(CH$_3$)$_3$ by stirring the mixture for 5 min. Evacuation of diethylamine under vacuum gave the product as a yellow solid in quantitative yield: mp 48–49 °C; ^{1}H NMR ($CDCl_3$) δ 4.93 (t, 2 H, J = 2.1 Hz), 4.62 (t, 2 H, J = 2.1 Hz), 0.30 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 224.39, 100.30, 94.60, 86.03, 83.81, 81.75, −7.77; IR (CCl_4), 2020 vs, 1955 vs cm^{-1}. Anal. Calcd for $C_{13}H_{13}MnO_3Sn$: C, 39.94; H, 3.35. Found: C, 39.79; H, 3.40.

[η^5-$(CH_3)_3SnC{\equiv}CC_5H_4$]$Re(CO)_3$ (14a). As described for **11a**, equimolar amounts of (η^5-$HC{\equiv}CC_5H_4$)$Re(CO)_3$ (**10**) and $(CH_3CH_2)_2NSn(CH_3)_3$ were mixed and stirred for 5 min. Evacuation of diethylamine under vacuum gave the product as a white solid in quantitative yield. An analytical sample was obtained by sublimation at 80 °C/0.002 mmHg: mp 85–87 °C; ^{1}H NMR ($CDCl_3$) δ 5.54 (t, 2 H, J = 2.2 Hz), 5.22 (t, 2 H, J = 2.2 Hz), 0.30 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 192.37, 98.63, 95.44, 87.41, 87.14, 83.63, −7.77; IR (CCl_4) 2020 vs, 1943 vs cm^{-1}. Anal. Calcd for $C_{13}H_{13}O_3ReSn$: C, 29.90; H, 2.51. Found: C, 29.93; H, 2.56.

(η^5-$nBu_3SnC{\equiv}CC_5H_4$)$Fe(CO)_2CH_3$ (11b). The procedure was the same as described for **11a**, but instead $(CH_3CH_2)_2NSn[(CH_2)_3CH_3]_3$ was used. Stirring equimolar amounts of this tin reagent and (η^5-$HC{\equiv}CC_5H_4$)$Fe(CO)_2CH_3$ (**6**) for 2 h gave a quantitative yield of product. It was recovered as a red oil after evacuation of the dimethylamine formed during the reaction under vacuum: ^{1}H NMR ($CDCl_3$) δ 4.81 (t, 2 H, J = 2.0 Hz), 4.66 (t, 2 H, J = 2.0 Hz), 1.55 (q, 6 H, J = 7.4 Hz), 1.33 (q, 6 H, J = 7.4 Hz), 1.00 (t, 6 H, J = 7.4 Hz), 0.39 (t, 9 H, J = 7.4 Hz), 0.31 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 217.11, 102.72, 94.43, 98.62, 85.55, 82.74, 29.27, 27.27, 13.19, 11.47, −18.13; IR (film, NaCl) 2960 s, 2920 s, 2870 m, 2850 m, 2005 vs, 1963 vs cm^{-1}; LMRS, m/e 505 (M^+).

(η^5-$nBu_3SnC{\equiv}CC_5H_4$)$W(CO)_3CH_3$ (12b). Equimolar amounts of (η^5-$HC{\equiv}CC_5H_4$)$W(CO)_3CH_3$ (**8**) and $(CH_3CH_2)_2NSn[(CH_2)_3CH_3]_3$ were stirred for 2 h. Evaporation of the dimethylamine formed during the reaction gave the pure product as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 5.44 (t, 2 H, J = 2.2 Hz), 5.19 (t, 2 H, J = 2.2 Hz), 1.54 (q, 6 H, J = 7.6 Hz), 1.32 (q, 6 H, J = 7.6 Hz), 1.00 (t, 6 H, J = 7.6 Hz), 0.69 (t, 9 H, J = 7.6 Hz), 0.51 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 215.43, 100.70, 96.61, 95.18, 94.33, 87.99, 28.84, 26.94, 13.61, 11.35, −27.01; IR (CCl_4) 2955 s, 2910 s, 2865 s, 2845 s, 2005 vs, 1930 vs cm^{-1}; HMRS calcd for $C_{23}H_{34}O_3SnW$ 662.1040, found 662.1040.

(η^5-$nBu_3SnC{\equiv}CC_5H_4$)$Mn(CO)_3$ (13b). This product was obtained by stirring for 2 h equimolar amounts of (η^5-$HC{\equiv}CC_5H_4$)$Mn(CO)_3$ (**9**) and $(CH_3CH_2)_2NSn[(CH_2)_3CH_3]_3$. Dimethylamine was removed under vacuum, and the product was recovered quantitatively as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 4.93 (t, 2 H, J = 2.0 Hz), 4.61 (t, 2 H, J = 2.0 Hz), 1.54 (q, 6 H, J = 7.2 Hz), 1.32 (q, 6 H, J = 7.2 Hz), 0.99 (t, 6 H, J = 7.2 Hz), 0.89 (t, 9 H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 224.30, 101.26, 94.49, 86.19, 81.49, 83.92, 28.79, 26.84, 13.57, 11.19; IR (film, NaCl) 2960 vs, 2930 vs, 2870 vs, 2850 vs, 2140 w, 2015 vs, 1935 vs; HRMS calcd for $C_{22}H_{31}MnO_3Sn$ 518.0667, found 518.0676.

(η^5-$nBu_3SnC{\equiv}CC_5H_4$)$Re(CO)_3$ (14b). An equimolar amount of (η^5-$HC{\equiv}CC_5H_4$)$Re(CO)_3$ (**12**) and $(CH_3CH_2)_2NSn[(CH_2)_3CH_3]_3$ were stirred for 2 h, and then evacuation of the diethylamine gave the pure product as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 5.54 (t, 2 H, J = 2.1 Hz), 5.21 (t, 2 H, J = 2.1 Hz), 1.54 (q, 6 H, J = 7.4 Hz), 1.32 (q, 6 H, J = 7.4 Hz), 0.99 (t, 6 H, J = 7.4 Hz), 0.88 (t, 9 H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$) δ 193.33, 99.57, 95.44, 87.46, 83.44, 27.21, 26.84, 13.57, 11.19; IR (film, NaCl) 2955 vs, 2920 vs, 2865 vs, 2845 vs, 2020 vs, 1930 vs cm^{-1}; HRMS calcd for $C_{22}H_{31}O_3ReSn$ 650.0846, found 650.0872.

(η^5-IC_5H_4)$Mn(CO)_2P(C_6H_5)_3$ (25). A mixture of 4.87 g (14.75 mmol) of (η^5-IC_5H_4)$Mn(CO)_3$ (**4**) and 5.806 g (22.13 mmol) of $P(C_6H_5)_3$ in 100 mL of cyclohexane was exposed for 5 h to the ultraviolet irradiation from a 125-W mercury lamp. Solvent was removed from the reaction mixture at 25 °C/30 mmHg. The residue was absorbed on Celite and placed on a silica column. Elution with 3/1 hexane/dichloromethane and evaporation of solvent afforded 4.31 g (52%) of pure product as a yellow solid. An analytical sample was recrystallized from chloroform/pentane at 25 °C: mp 141–143 °C; ^{1}H NMR ($CDCl_3$) δ 7.36 (m, 15 H), 4.55 (t, 2 H, J = 1.91 Hz), 3.99 (t, 2 H, J = 1.91 Hz); ^{13}C NMR ($CDCl_3$) δ 242.40, 137.27, 139.97, 132.83, 129.67, 129.64, 128.28, 128.16, 88.46, 84.75, 45.18; IR (CCl_4), 1946 vs, 1886 vs cm^{-1}. Anal. Calcd for $C_{25}H_{19}IMnO_2P$: C, 53.21; H, 3.39. Found: C, 53.30; H, 3.64.

General Procedure for Palladium-Catalyzed Coupling Reactions of [η^5-[(Trialkylstannyl)ethynyl]cyclopentadienyl]metal Complexes 11–14 and (η^5-Iodocyclopentadienyl)metal Complexes 1–5. Under an argon atmosphere, a 100-mL Schlenk flask was charged with a magnetic stirring bar, an equimolar amount of the two coupling partners (usually 2–4 mmol), and 50 mL of DMF. While stirring, 5 mol % of $(CH_3CN)_2PdCl_2$ dissolved in 5–10 mL of DMF was added by a syringe to the flask. The color of the mixture immediately turned dark, but no formation of a precipitate was observed. The stirring was continued at room temperature for 8 or 12 h (the longer times were used for the tributyltin derivative), and then the mixture was diluted with 200 mL of Et_2O, transferred to a 500-mL separatory funnel, and washed three times with 100-mL portions of water. When tributyltin derivatives were used, the ether extracts were stirred vigorously for 30 min with 100 mL of a 50% solution of KF while argon was bubbled through the solution. The solution was then filtered through a plug of glass wool. The filtrate was washed twice with 100-mL portions of water. In both cases, the organic layers were dried over magnesium sulfate and filtered. Evaporation of the solvent gave the crude product, which was purified by chromatographic separation over silica by using 5/1 hexanes/benzene as eluent, followed by sublimation at 100 °C/10-5 mmHg.

$CH_3(CO)_2Fe(\eta^5$-$C_5H_4)C{\equiv}C(\eta^5$-$C_5H_4)Mo(CO)_3CH_3$ (15). Orange crystals; mp dec above 150 °C (chloroform–pentane; IR (CCl_4) 2018 vs, 2008 vs, 1968 vs, 1945 vs cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.75 (t, 2 H, J = 2.0 Hz), 4.90 (t, 2 H, J = 2.0 Hz), 5.22 (t, 2 H, J = 2.1 Hz), 5.44 (t, 2 H, J = 2.1 Hz), 0.33 (s, 3 H), 0.49 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 225.42, 216.00, 95.81, 94.17, 90.16, 89.86, 83.97, 83.18, 82.38, 81.01, −15.07, −19.14. Anal. Calcd for $C_{19}H_{14}FeMoO_5$: C, 48.13; H, 2.97. Found: C, 48.30; H, 3.04.

$CH_3(CO)_2Fe(\eta^5$-$C_5H_4)C{\equiv}C(\eta^5$-$C_5H_4)W(CO)_3CH_3$ (16). Yellow crystals; mp 115–117 °C (chloroform–pentane); IR (CCl_4) 2005 vs, 1970 vs, 1935 vs cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.75 (t, 2 H, J = 2.1 Hz), 4.91 (t, 2 H, J = 2.1 Hz), 5.28 (t, 2 H, J = 2.2 Hz), 5.52 (t, 2 H, J = 2.2 Hz), 0.33 (s, 3 H), 0.54 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 215.96, 214.84, 94.49, 92.46, 89.95, 88.99, 84.13, 83.18, 81.91, 80.43, −19.09, −28.38. Anal. Calcd for $C_{19}H_{14}FeO_5W$: C, 40.60; H, 2.51. Found: C, 40.63; H, 2.52.

$CH_3(CO)_2Fe(\eta^5$-$C_5H_4)C{\equiv}C(\eta^5$-$C_5H_4)Mn(CO)_3$ (17). Yellow crystals; mp dec above 130 °C (chloroform–pentane); IR (CCl_4) 2018 vs, 2002 vs, 1965 sh, 1950 vs cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.74 (t, 2 H, J = 2.1 Hz), 4.90 (t, 2 H, J = 2.1 Hz), 4.68 (t, 2 H, J = 2.1 Hz), 5.02 (t, 2 H, J = 2.1 Hz), 0.32 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 224.02, 216.06, 89.48, 86.62, 83.27, 82.77, 82.22, 82.02, 81.59, 81.11, −19.14. Anal. Calcd for $C_{18}H_{11}FeMnO_5$: C, 51.71; H, 2.65. Found: C, 51.86; H, 2.83.

$CH_3(CO)_2Fe(\eta^5$-$C_5H_4)C{\equiv}C(\eta^5$-$C_5H_4)Re(CO)_3$ (18). Yellow crystals; mp 140–141 °C (chloroform–pentane); IR (CCl_4) 2020 vs, 2005 vs, 1968 vs, 1945 vs cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.74 (t, 2 H, J = 2.0 Hz), 4.89 (t, 2 H, J = 2.0 Hz), 5.28 (t, 2 H, J = 2.1 Hz), 5.63 (t, 2 H, J = 2.1 Hz), 0.32 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 216.00, 192.93, 89.50, 88.04, 84.02, 83.92, 83.38, 82.55, 82.34, 80.17, −19.19. Anal. Calcd for $C_{18}H_{11}FeO_5Re$: C, 39.35; H, 2.01. Found: C, 39.11; H, 2.08.

$CH_3(CO)_3Mo(\eta^5$-$C_5H_4)C{\equiv}C(\eta^5$-$C_5H_4)W(CO)_3CH_3$ (19). Yellow crystals; mp dec above 150 °C (chloroform–pentane); IR (CCl_4) 2015 vs, 1940 vs cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.23 (t, 2 H, J = 2.3 Hz), 5.44 (t, 2 H, J = 2.3 Hz), 5.29 (t, 2 H, J = 2.4 Hz), 5.51 (t, 2 H, J = 2.4 Hz), 0.49 (s, 3 H), 0.53 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 225.31, 214.81, 96.02, 95.49, 94.60, 93.05, 91.69, 90.53, 89.35, 82.86, −15.87, −28.69. Anal. Calcd for $C_{20}H_{14}MoO_6W$: C, 38.12; H, 2.23. Found: C, 38.04; H, 2.30.

$CH_3(CO)_3Mo(\eta^5$-$C_5H_4)C{\equiv}C(\eta^5$-$C_5H_4)Mn(CO)_3$ (20). Yellow crystals; mp 92–93 °C (chloroform–pentane); IR (CCl_4) 2023 vs, 2018 vs, 1950 vs cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.22 (t, 2 H, J = 2.2 Hz), 5.44 (t , 2 H, J = 2.2 Hz), 4.69 (t, 2 H, J = 2.1 Hz), 5.03 (t, 2 H, J = 2.1 Hz), 0.49 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 225.37, 223.90, 95.81, 93.70, 90.28, 88.10, 86.97, 83.23, 82.03, 80.73, −15.27. Anal. Calcd for $C_{19}H_{11}MoMnO_6$: C, 46.94; H, 2.28. Found: C, 47.08; H, 2.31.

$CH_3(CO)_3Mo(\eta^5$-$C_5H_4)C{\equiv}C(\eta^5$-$C_5H_4)Re(CO)_3$ (21). Yellow crystals; mp 118–120 °C (chloroform–pentane); IR (CCl_4) 2022 vs, 2018 vs, 1945 vs cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.22 (t, 2 H, J = 2.3 Hz), 5.44 (t, 2 H, J = 2.3 Hz), 5.28 (t, 2 H, J = 2.1 Hz), 5.64 (t, 2 H, J = 2.1 Hz), 0.49 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 225.30, 192.83, 95.88, 93.21, 90.44, 88.39, 87.83, 83.90, 83.59, 81.40, −15.56.

Anal. Calcd for $C_{19}H_{11}MoO_6Re$: C, 36.96; H, 1.79. Found: C, 37.03; H, 1.81.

$CH_3(CO)_3W(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)Mn(CO)_3$ (22). Yellow crystals; mp 113–115 °C (chloroform–pentane); IR (CCl_4) 2025 vs, 2015 vs, 1955 vs, 1937 vs cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.28 (t, 2 H, J = 1.9 Hz), 5.52 (t, 2 H, J = 1.9 Hz), 4.69 (t, 2 H, J = 1.8 Hz), 5.03 (t, 2 H, J = 1.8 Hz), 0.53 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 223.83, 214.87, 94.48, 92.06, 89.11, 87.06, 83.39, 82.06, 81.03, 80.18, −28.54. Anal. Calcd for $C_{19}H_{11}MnO_6W$: C, 39.75; H, 1.93. Found: C, 39.71; H, 1.98.

$CH_3(CO)_3W(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)Re(CO)_3$ (23). Yellow crystals; mp 143–145 °C (chloroform–pentane); IR (CCl_4) 2025 vs, 2015 vs, 1940 vs cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.29 (t, 2 H, J = 2.2 Hz), 5.51 (t, 2 H, J = 2.2 Hz), 5.29 (t, 2 H, J = 2.2 Hz), 5.44 (t, 2 H, J = 2.2 Hz), 0.53 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 214.73, 192.76, 94.57, 94.49, 89.33, 88.50, 83.95, 83.49, 82.02, 80.83, −28.87. Anal. Calcd for $C_{19}H_{11}O_6ReW$: C, 32.35; H, 1.57. Found: C, 32.49; H, 1.62.

$(CO)_3Mn(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)Re(CO)_3$ (24). Orange crystals; mp 196–198 °C (chloroform–pentane); IR (CCl_4) 2020 vs, 1950 vs cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.69 (t, 2 H, J = 2.0 Hz), 5.00 (t, 2 H, J = 2.0 Hz), 5.28 (t, 2 H, J = 2.1 Hz), 5.62 (t, 2 H, J = 2.1 Hz); ^{13}C NMR ($CDCl_3$) δ 223.84, 192.89, 88.06, 86.62, 84.27, 83.93, 82.11, 81.80, 80.69, 79.86. Anal. Calcd for $C_{18}H_8O_6MnRe$: C, 38.51; H, 1.43. Found: C, 38.35; H, 1.48.

$CH_3(CO)_3W(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)Mn(CO)_2P(C_6H_5)_3$ (26). Yellow crystals; mp 158–160 °C (chloroform–pentane); IR (CCl_4) 2019 vs, 1946 vs, 1930 vs, 1886 vs cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45–7.35 (15 H), 5.48 (2 H), 4.26 (2 H), 4.61 (2 H), 4.09 (2 H), 0.54 (3 H); ^{13}C NMR ($CDCl_3$) δ 231.42, 228.23, 215.09, 137.69, 137.15, 132.95, 132.81, 129.57, 128.19, 128.07, 94.5, 94.14, 88.22, 86.65, 86.12, 83.14, 78.95, 77.89, 77.43, 77.00, 76.58, −27.34. Anal. Calcd for $C_{36}H_{26}MnO_5PW$: C, 53.40; H, 3.42. Found: C, 52.83; H, 3.35.

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Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen coordinates, and thermal parameters for **26** (2 pages); a listing of observed and calculated structure factors for complex **26** (27 pages). Ordering information is given on any current masthead page.

Multiple-Bond Character in $Cp_3U{=}CHPMe_3$: First Low-Temperature Neutron Diffraction Analysis of a Uranium Organometallic Complex

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The structure of $Cp_3U{=}CHPMe_3$ has been determined from neutron diffraction data at 20 K. Crystal data: space group $P\bar{1}$, a = 10.352 (2) Å, b = 11.326 (2) Å, c = 8.235 (1) Å, α = 91.23 (1)°, β = 93.14 (1)°, and γ = 64.291 (9)°; V = 869.5 Å^3; Z = 2. Data were collected at the Brookhaven High Flux Beam Reactor, with a single-crystal specimen of approximate dimensions 4.3 × 1.4 × 1.2 mm. Final agreement factors are $R(F^2)$ = 0.029 and $R(wF^2)$ = 0.038 for 2227 independent reflections and 421 parameters varied. The neutron diffraction study was undertaken to investigate a possible metal–hydrogen interaction and the metal–carbon–phosphorus geometry. Bond distances and angles of interest include U–C = 2.293 (1)Å, C–H = 1.082 (2)Å, C–P = 1.692 (2)Å, U···H = 2.859 (3)Å, U–C–P = 141.49 (7)°, and U–C–H = 110.6 (2)°. The α-hydrogen atom is not agostic, and the short U–C bond distance and large U–C–P bond angle indicate multiple-bond character.

Introduction

The compounds $Cp_3U{=}CHPR_3$ have a rich insertion chemistry, and the products from the insertion of CO, RCN, RNC, RNCO, and several metal carbonyls into the uranium–carbon bond have been reported.[1] On the basis of short U–C bond distances and large U–C–P bond angles found in the X-ray structures of $Cp_3U{=}CHPMe_2Ph$ and $Cp_3U{=}CHPMe_3$, it has been suggested that the U–C bonds in these molecules possess multiple-bond character.[2–5] This assignment, which implies a two-electron, three-center π bond between the Cp_3U and $CHPR_3$

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(1) (a) Gilje, J. W.; Cramer, R. E. *Inorg. Chim. Acta* **1987**, *139*, 177. (b) Gilje, J. W.; Cramer, R. E.; Bruck, M. A.; Higa, K. T.; Panchanatheswaran, K. *Inorg. Chim. Acta* **1985**, *110*, 139.

(2) In saturated alkyluranium(IV) complexes the U–C(alkyl) distances are 2.43 (3) Å in $Cp_3U(n\text{–}C_4H_9)$ (Perego, G.; Cesari, M.; Farina, F.; Lugli, G. *Acta Crystallogr.* **1976**, *B32*, 3034.), 2.43 (2) Å in $Cp^*{}_2UMe_2$ ((a) Roth, S. Ph.D. Dissertation, University of Hawaii, 1988. (b) Marks, T. J.; Day, V. W., private communication), and 2.41 (1) Å in $(dmpe)_2(CH_2C_6H_5)_3UMe$ (Edwards, P. G.; Andersen, R. A.; Zalkin, A. *Organometallics* **1984**, *3*, 293). U–C multiple bond lengths obtained from X-ray structures are 2.274 (8) Å for $Cp_3U{=}CHPMe_3$ and 2.29 (3) Å for $Cp_3U{=}CHPMe_2Ph$.[3,4] The significance of these and other distances to the nature of the U–C bond has been discussed (ref 3–6 and; Cramer, R. E.; Mori, A. L.; Maynard, R. B.; Gilje, J. W.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1984**, *106*, 5920.)

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