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Reactions of Functionalized Metal–η^1-Propargyl Compounds with Unsaturated Cobalt(0) and Iron(0) Carbonyl Clusters

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The reactions between $M{-}CH_2C{\equiv}CCH{=}CH_2$ (M = $CpW(CO)_3$ (**1**), $Mn(CO)_5$ (**2**)) and $Co_2(CO)_8$ in THF at 0 °C afforded $Co(CO)_3[\mu_2\text{-}CpW(CO)_3CH_2C{\equiv}CCH{=}CH_2]Co(CO)_3$ (**3**) and $MnCo_2(CO)_{10}(\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^3\text{-}CH_2CCCHCH_2)$ (**4**), respectively. The dinuclear 2-butyne-1,4-di-yl compounds $M{-}CH_2C{\equiv}CCH_2{-}M$ (M = $CpW(CO)_3$ (**5**); $Cp^*W(CO)_3$ (**6**), Cp^* = C_5Me_5) have been prepared. Under flowing CO, the reactions of **5** and **6** with $Fe_2(CO)_9$ afforded the maleoyl compounds $M{-}CH_2\overline{C(CO{-}Fe(CO)_4{-}(CO)C}CH_2{-}M$ (M = $CpW(CO)_3$ (**7**), $Cp^*W(CO)_3$ (**8**)) in excellent yields. Under nitrogen, a similar reaction of **5** with $Fe_2(CO)_9$ produced two additional trinuclear clusters $Cp_2W_2Fe(CO)_8(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^3\text{-}CH_2CCCH_2)$ (**9**) and $CpWFe_2(CO)_8(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}CH_2CCCH_3)$ (**10**) in addition to **7**. In contrast, **6** reacted with $Fe_2(CO)_9$ in the absence of CO to give **8** as the only product. The reactions of **5** and **6** with $Co_2(CO)_8$ gave the tetranuclear compounds $\overline{Co(CO)_3(\mu\text{-}M{-}CH_2C{\equiv}CCH_2{-}M)C}oCO)_3$ (M = $CpW(CO)_3$ (**11**), $Cp^*W(CO)_3$ (**12**)). The molecular structures of **4**, **8**, **9**, and **12** were determined by X-ray diffraction study to have the following parameters: for **4**, space group $P\bar{1}$, a = 8.427 (3) Å, b = 9.326 (2) Å, c = 12.534 (4) Å, α = 97.31 (2)°, β = 87.76 (3)°, γ = 110.80 (2)°, Z = 2, R = 0.029 and R_w = 0.043; for **8**, space group $C2/c$, a = 47.984 (7) Å, b = 8.478 (2) Å, c = 19.883 (6) Å, β = 107.60 (2)°, Z = 8, R = 0.053, and R_w = 0.042; for **9**, space group $P\bar{1}$, a = 7.810 (2) Å, b = 10.889 (4) Å, c = 13.970 (5) Å, α = 110.96 (3)°, β = 95.20 (2)°, γ = 93.72 (2)°, Z = 2, R = 0.032, and R_w = 0.031; for **12**, space group $C2/c$, a = 20.267 (3) Å, b = 24.628 (3) Å, c = 8.816 (4) Å, β = 99.68 (2)°, Z = 4, R = 0.031, and R_w = 0.069.

Introduction

Heteronuclear metal–carbonyl clusters containing organic hydrocarbyl fragments are recognized to be an important and rapidly growing class of compounds.[1,2] The reactions of metal–propargyl complexes $L_nM{-}CH_2C{\equiv}CR$ (L_nM = $CpW(CO)_3$, $CpMo(CO)_3$, $CpRu(CO)_2$; R = Me, Ph) with metal carbonyls enable preparations of heteronuclear clusters with various bridging hydrocarbyl ligands such as dinuclear or trinuclear allenyl complexes.[3,4] Reactions of $CpFe(CO)_2CH_2C{\equiv}CPh$ with $Fe_2(CO)_9$ produced a binuclear η^4-allylcarbonyl product.[5] We[6] have studied the reactions of metal–η^1-vinylpropargyl compounds $M{-}CH_2C{\equiv}CCH{=}CH_2$ (M = $CpW(CO)_3$ (**1**), $CpMo(CO)_3$ (**2**)) with Fe(0), Ru(0), and Os(O) carbonyl clusters which gave heteronuclear maleoyl and trinuclear $\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^3$-divinylcarbene clusters. The fact that cluster formation depends strongly on both the type of metal and the functionality of propargyl ligands prompts us to investigate further the reaction chemistry of **1** and **2** with $Co_2(CO)_8$. Here we report syntheses of functionalized metal propargyl complexes $M{-}CH_2C{\equiv}CCH_2{-}M$ (M = $CpW(CO)_3$ (**5**) and $Cp^*W(CO)_3$ (**6**), Cp^* = C_5Me_5) and their reactions with Fe(0) and Co(0) carbonyl clusters.

Results and Discussion

Reaction of 1 and 2 with $Co_2(CO)_8$. The reaction between **1** and $Co_2(CO)_8$ conducted in THF solution at 0 °C was complete after 2 h. As shown in Scheme I, the product **3** isolated as an orange solid was purified through a silica gel column; the yield was only 10%. The characterization of this new trinuclear cluster was accomplished by appropriate physical methods. IR spectra in the ν(CO) region exhibited a marked similarity to those of related compounds $\overline{Co(CO)_3(\mu_2\text{-}CpW(CO)_3{-}CH_2C{\equiv}CR)C}o(CO)_3$ (R = Me, Ph).[3a] ^1H and ^{13}C NMR data are fully consistent with the proposed structure. The $W{-}CH_2$ protons resonate in ^1H NMR spectra at δ 2.40 ppm, and the free vinyl protons resonate at δ 5.14 (d), 5.20 (d), and 6.90 (dd) ppm. The methylene carbon $M{-}CH_2$ resonates in ^{13}C NMR spectra at δ 10.3 ppm and the two acetylide carbons resonate at δ 118.8 and 130.9 ppm. Elemental analyses and FAB mass data are consistent with the given formula.

A similar reaction between **2** and $Co_2(CO)_8$ was also performed which gave a dark red solid **4** in 82% yield after

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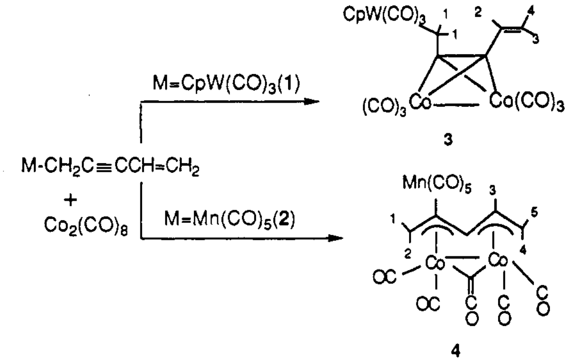
Scheme I



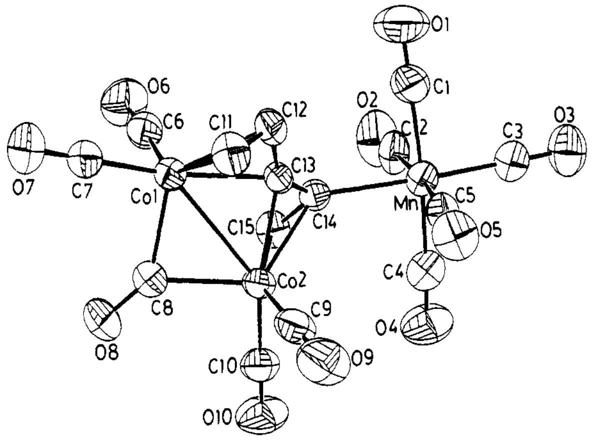


Figure 1. Perspective view and numbering scheme for complex 4.

Table I. Selected Bond Distances (Å) and Angles (deg) for 4

Mn–C(1)	1.863 (7)	Co(1)–C(13)	1.994 (5)
Mn–C(2)	1.839 (6)	Co(2)–C(8)	2.001 (6)
Mn–C(3)	1.832 (6)	Co(2)–C(9)	1.777 (6)
Mn–C(4)	1.866 (7)	Co(2)–C(10)	1.753 (6)
Mn–C(5)	1.869 (5)	Co(2)–C(13)	1.950 (5)
<n–C(14)	2.117 (5)	Co(2)–C(14)	2.118 (5)
Co(1)–Co(2)	2.6133 (12)	Co(2)–C(15)	2.096 (5)
Co(1)–C(6)	1.760 (6)	C(11)–C(12)	1.395 (8)
Co(1)–C(7)	1.768 (6)	C(12)–C(13)	1.406 (7)
Co(1)–C(8)	1.945 (6)	C(13)–C(14)	1.388 (7)
Co(1)–C(11)	2.112 (5)	C(14)–C(15)	1.433 (7)
Co(1)–C(12)	2.070 (5)	C(14)–C(15)	1.433 (7)
Co(2)–Co(1)–C(6)	109.56 (21)	C(8)–Co(2)–C(14)	122.71 (21)
Co(2)–Co(1)–C(7)	137.97 (18)	C(8)–Co(2)–C(15)	104.83 (23)
Co(2)–Co(1)–C(8)	49.44 (17)	C(9)–Co(2)–C(10)	93.6 (3)
Co(2)–Co(1)–C(11)	90.81 (16)	C(9)–Co(2)–C(13)	99.46 (23)
Co(2)–Co(1)–C(12)	81.41 (15)	C(9)–Co(2)–C(14)	115.99 (22)
Co(2)–Co(1)–C(13)	47.80 (14)	C(9)–Co(2)–C(15)	150.78 (25)
C(6)–Co(1)–C(7)	98.3 (3)	C(10)–Co(2)–C(13)	158.2 (3)
C(6)–Co(1)–C(8)	102.9 (3)	C(10)–Co(2)–C(14)	118.69 (25)
C(6)–Co(1)–C(11)	142.4 (3)	C(10)–Co(2)–C(15)	89.8 (3)
C(6)–Co(1)–C(12)	111.42 (25)	C(13)–Co(2)–C(14)	39.62 (20)
C(6)–Co(1)–C(13)	98.88 (24)	C(13)–Co(2)–C(15)	70.34 (21)
C(7)–Co(1)–C(8)	94.71 (25)	C(14)–Co(2)–C(15)	39.76 (21)
C(7)–Co(1)–C(11)	85.27 (24)	Co(1)–C(8)–Co(2)	82.93 (22)
C(7)–Co(1)–C(12)	117.37 (24)	Co(1)–C(11)–C(12)	68.9 (3)
C(7)–Co(1)–C(13)	156.43 (23)	Co(1)–C(12)–C(11)	72.2 (3)
C(8)–Co(1)–C(11)	114.19 (24)	Co(1)–C(12)–C(13)	66.9 (3)
C(8)–Co(1)–C(12)	127.42 (22)	C(11)–C(12)–C(13)	117.5 (5)
C(8)–Co(1)–C(13)	97.10 (22)	Co(1)–C(13)–Co(2)	82.99 (18)
C(11)–Co(1)–C(12)	38.97 (21)	Co(1)–C(13)–C(12)	72.7 (3)
C(11)–Co(1)–C(13)	71.28 (20)	Co(1)–C(13)–C(14)	134.8 (4)
C(12)–Co(1)–C(13)	40.43 (20)	Co(2)–C(13)–C(12)	132.6 (4)
Co(1)–Co(2)–C(8)	47.63 (16)	Co(2)–C(13)–C(14)	76.7 (3)
Co(1)–Co(2)–C(9)	104.47 (20)	C(12)–C(13)–C(14)	146.8 (5)
Co(1)–Co(2)–C(10)	142.95 (20)	Mn–C(14)–Co(2)	130.60 (23)
Co(1)–Co(2)–C(13)	49.22 (14)	Mn–C(14)–C(13)	123.4 (4)
Co(1)–Co(2)–C(14)	82.12 (14)	Mn–C(14)–C(15)	124.7 (4)
Co(1)–Co(2)–C(15)	89.59 (16)	Co(2)–C(14)–C(13)	63.7 (3)
C(8)–Co(2)–C(9)	103.5 (3)	Co(2)–C(14)–C(15)	69.3 (3)
C(8)–Co(2)–C(10)–	97.1 (3)	C(13)–C(14)–C(15)	111.6 (4)
C(8)–Co(2)–C(13)	96.70 (22)	Co(2)–C(15)–C(14)	71.0 (3)

work up. The characteristic features in the IR and NMR spectra of 4 differ greatly from those expected for (μ_2-alkyne)$Co_2(CO)_6$.[7] IR spectra in the ν(CO) region exhibited a broad absorption at 1845 cm^{-1}, characteristic of a bridging CO group. The methylene protons CH^4H^5 resonate in NMR spectra at δ 2.21 and 3.53 ppm, indicative of metal–olefin bonding. Single crystals of 4 suitable for X-ray structural analysis were grown from a saturated ether/hexane solution cooled to −20 °C. An ORTEP drawing of 4 appears in Figure 1, and the related bond distances, angles, and atomic coordinates are presented in Table I and II, respectively. Compound 4 consists of a core of two cobalt atoms, symmetrically bridged by the C(13) atom and C(8)–O(8) carbonyl group (Co(1)–C(13) = 1994 (5) Å vs Co(2)–C(13) = 1.950 (5) Å; Co(1)–C(8) = 1.945 (6) Å vs Co(2)–C(8) = 2.001 (6) Å). Notably the $Mn(CO)_5$ subunit migrated to the β-carbon with a normal length Mn–C(14) = 2.117 (5) Å. The Co(1)–Co(2) bond length 2.613 (1) Å is larger than that of a common Co–Co single bond 2.45 Å for structurally related cobalt μ_2-carbene complexes.[8] The acyclic hydrocarbyl ligand is W-shaped and nonplanar; it is twisted along C(12)–C(13) and C(13)–C(14) bonds, the dihedral angles between the planes C(11)–C(12)–C(13) and C(12)–C(13)–C(14), C(12)–C(13)–C(14) and C(13)–C(14)–C(15) are 24 (1)° and 27 (1)°. The C–C bond lengths are variable within a broad range, 1.388–1.433 (7) Å. Each cobalt is η^3-bonded to the ligand with Co–C lengths 1.950–2.118 (5) Å, comparable to those (2.01–2.05 Å) of other known Co(I)–allyl complexes.[9] The η^3-allyl bonding is also reflected by its ^1H NMR spectra which displays the two anti-proton resonances most upfield (δ 2.2–2.3 ppm), the two syn-proton H^1,H^5 resonances at δ 3.5–3.6 ppm, and the central H^3 proton resonance downfield at δ 5.50 ppm with J_{35} = 6.3 Hz and J_{34} = 9.5 Hz characteristic of a cis and trans coupling pattern for a metal–allyl bonding. The C(13)–C(14)–C(15) angle (111.6 (4)°) is smaller than the C(11)–C(12)–C(13) angle (117.5 (5)°) probably due to the steric hindrance of the bulky $Mn(CO)_5$. In contrast, the angle of the central carbon C(12)–C(13)–C(14) (146.8 (5)°) is rather large, owing to the μ_2-coordination. The Mn atom lies about 0.17 (2) Å above the plane defining by the C(13), C(14), C(15) atoms.

Monitoring the reactions by IR spectra, we detected no (μ_2-alkyne)$Co_2(CO)_6$ intermediate such as 3 before 4 was formed. There is no experimental evidences to support that 4 is derived from decarbonylation of a (μ_2-alkyne)$Co_2(CO)_6$ intermediate. We believe that the mechanism of formation of 4 involves a zwitterionic allene intermediate.[5,6] An uncommon feature of this mechanism is the 1,2-migration process of the metal fragment as shown in the structure of 4.

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Table II. Atomic Parameters *x*, *y*, and *z* for 4

	x	*y*	*z*	B_{iso}, Å^2
Mn	0.80322 (10)	0.68168 (9)	0.33467 (6)	3.22 (3)
Col	1.34369 (8)	1.07375 (8)	0.20789 (5)	3.02 (3)
Co2	1.22136 (9)	0.77193 (8)	0.17706 (5)	2.97 (3)
C1	0.7772 (8)	0.8728 (8)	0.3656 (5)	4.8 (3)
C2	0.8708 (7)	0.6943 (8)	0.4744 (5)	4.6 (3)
C3	0.5800 (8)	0.5810 (7)	0.3662 (4)	3.9 (3)
C4	0.8486 (8)	0.4993 (7)	0.3013 (5)	4.3 (3)
C5	0.7632 (6)	0.6797 (6)	0.1888 (4)	3.32 (23)
C6	1.4229 (8)	1.1360 (7)	0.3401 (5)	4.3 (3)
C7	1.4877 (7)	1.2270 (7)	0.1447 (5)	3.8 (3)
C8	1.4523 (7)	0.9262 (7)	0.1552 (5)	3.9 (3)
C9	1.1277 (7)	0.7267 (7)	0.0467 (5)	4.0 (3)
C10	1.2799 (8)	0.6080 (7)	0.1645 (5)	4.2 (3)
C11	1.1611 (7)	1.0845 (7)	0.1015 (4)	3.7 (3)
C12	1.0885 (6)	1.0424 (6)	0.2000 (4)	3.4 (3)
C13	1.1184 (6)	0.9201 (6)	0.2400 (4)	2.77 (21)
C14	1.0628 (6)	0.8036 (6)	0.3063 (4)	2.96 (22)
C15	1.2010 (7)	0.7676 (7)	0.3439 (4)	3.8 (3)
O1	0.7651 (8)	0.9897 (6)	0.3861 (5)	7.8 (3)
O2	0.9153 (7)	0.7028 (7)	0.5600 (4)	7.6 (3)
O3	0.4414 (6)	0.5194 (6)	0.3859 (4)	5.75 (24)
O4	0.8786 (8)	0.3906 (6)	0.2816 (4)	6.9 (3)
O5	0.7417 (6)	0.6783 (5)	0.1009 (3)	4.82 (23)
O6	1.4851 (7)	1.1877 (6)	0.4249 (4)	6.7 (3)
O7	1.5754 (6)	1.3248 (5)	0.1021 (4)	5.49 (23)
O8	1.5810 (5)	0.9241 (6)	0.1248 (4)	6.2 (3)
O9	1.0655 (6)	0.6861 (6)	−0.0372 (4)	6.1 (3)
O10	1.3151 (7)	0.5004 (6)	0.1573 (4)	6.7 (3)

Scheme II

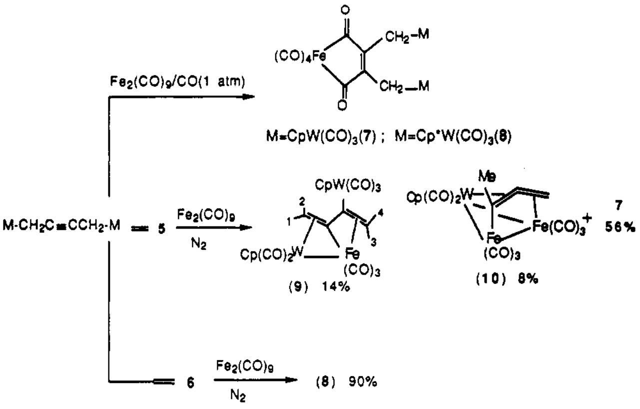

Table III. Selected Bond Distances (Å) and Angles (deg) for 8

W(1)–C(1)	1.867 (15)	Fe–C(10)	1.807 (14)
W(1)–C(2)	1.966 (13)	Fe–C(11)	2.027 (12)
W(1)–C(3)	1.960 (12)	Fe–C(12)	2.046 (11)
W(1)–C(13)	2.329 (11)	C(11)–C(14)	1.522 (15)
W(2)–C(4)	1.902 (14)	C(11)–O(11)	1.190 (15)
W(2)–C(5)	1.979 (13)	C(12)–C(15)	1.504 (16)
W(2)–C(6)	1.963 (14)	C(12)–O(12)	1.191 (15)
W(2)–C(16)	2.333 (11)	C(13)–C(14)	1.440 (7)
Fe–C(7)	1.807 (13)	C(14)–C(15)	1.372 (17)
Fe–C(8)	1.818 (15)	C(15)–C(16)	1.476 (15)
Fe–C(9)	1.846 (14)		

C(1)–W(1)–C(2)	114.2 (6)	C(11)–Fe–C(12)	81.9 (5)
C(1)–W(1)–C(3)	75.9 (6)	W(1)–C(1)–O(1)	174.1 (10)
C(1)–W(1)–C(13)	78.6 (5)	W(1)–C(2)–O(2)	168.7 (14)
C(2)–W(1)–C(3)	76.0 (5)	W(1)–C(3)–O(3)	179.3 (12)
C(2)–W(1)–C(13)	78.9 (5)	W(2)–C(4)–O(4)	176.8 (10)
C(3)–W(1)–C(13)	132.4 (5)	W(2)–C(5)–O(5)	176.8 (11)
C(4)–W(2)–C(5)	80.6 (7)	W(2)–C(6)–O(6)	173.6 (12)
C(4)–W(2)–C(6)	109.0 (6)	Fe–C(7)–O(7)	176.7 (11)
C(4)–W(2)–C(16)	77.8 (5)	Fe–C(8)–O(8)	175.4 (12)
C(5)–W(2)–C(6)	73.2 (6)	Fe–C(9)–O(9)	177.0 (15)
C(5)–W(2)–C(16)	138.4 (4)	Fe–C(10)–O(10)	176.6 (12)
C(6)–W(2)–C(16)	80.8 (5)	Fe–C(11)–C(14)	114.3 (8)
C(7)–Fe–C(8)	95.1 (6)	Fe–C(11)–O(11)	124.9 (9)
C(7)–Fe–C(9)	95.2 (6)	C(14)–C(11)–O(11)	120.6 (11)
C(7)–Fe–C(10)	164.9 (6)	Fe–C(12)–C(15)	112.1 (8)
C(7)–Fe–C(11)	85.4 (6)	Fe–C(12)–O(12)	124.4 (8)
C(7)–Fe–C(12)	84.6 (5)	C(15)–C(12)–O(12)	123.3 (10)
C(80–Fe–C(9)	99.5 (7)	W(1)–C(13)–C(14)	117.0 (7)
C(8)–Fe–C(10)	95.1 (7)	C(11)–C(14)–C(13)	120.5 (10)
C(8)–Fe–C(11)	169.7 (5)	C(11)–C(14)–C(15)	112.9 (10)
C(8)–Fe–C(12)	88.0 (5)	C(13)–C(14)–C(15)	126.5 (10)
C(9)–Fe–C(10)	94.0 (6)	C(12)–C(15)–C(14)	116.7 (10)
C(9)–Fe–C(11)	90.6 (6)	C(12)–C(15)–C(16)	117.4 (11)
C(9)–Fe–C(12)	172.5 (6)	C(14)–C(15)–C(16)	125.7 (11)
C(10)–Fe–C(11)	82.6 (6)	W(2)–C(16)–C(15)	120.8 (7)
C(10)–Fe–C(12)	84.7 (5)		

Reaction of Dinuclear Tungsten–η^1-Propargyl Complexes with $Fe_2(CO)_9$. Consistent with our previous results,[6] functionalized η^1-propargyl compounds 1 and 2 reacted with Fe(0) and Co(0) carbonyl culsters in a pathway which differs strongly from those of common metal-η^1-propargyl compounds.[3-5] The effect of a new functionalized ligand on its reaction chemistry is therefore of great interest. For this reason, we examined the reaction of the binuclear propargyl complex $M—CH_2C{\equiv}C—CH_2—M$ (M = $CpW(CO)_3$ (5), $Cp^*W(CO)_3$ (6)) with $Fe_2(CO)_9$. The complexes 5 and 6 were conveniently prepared in good yields from the reaction of $CpW(CO)_3Na$ (or $Cp^*W(CO)_3Na$) with 1,4-ditosylate-2-butyne in the molar ratio 2:1. The iron analogue $Fc—CH_2C{\equiv}CCH_2—F_c$ (F_c = $CpFe(CO)_2$) has been previously reported.[10] An interesting aspect of use of these complexes for cluster formation is that they may lead to the formation of heteronuclear clusters containing a hydrocarbyl fragment such as cumulene $CH_2{=}C{=}C{=}CH_2$. Along this direction, Iyoda et al. have recently reported a tetrairon poly-π-allyl complexes derived from zinc reduction of $ClCH_2C{\equiv}CC{\equiv}CCH_2Cl$ in the presence of $Fe_2(CO)_9$.[12] The reaction pathways of 5–6 with $Fe_2(CO)_9$ are illustrated in Scheme II. Treatment of 5–6 with 2 equimolar quantities of $Fe_2(CO)_9$ in THF at 23 °C under flowing CO generated the dinuclear maleoyl complexes 7 and 8 in excellent yields after workup. Single crystals of 8 suitable for X-ray structural analyses were grown from a saturated solution in diethyl ether/hexane cooled at −40 °C for 2 days. The selected bond distances, angles and atomic coordinates were given in Tables III and IV, respectively. According to the ORTEP drawing in Figure 2, the alkyne group of 8 has undergone double carbonylation and become symmetrically linked to the $Fe(CO)_4$ fragment to generate a five-membered maleoyl ring. The Fe–C(12) (2.046 (11) Å) and Fe–C(11) (2.027 (12) Å) distances are close to the values (2.05 Å) for a normal Fe(II)–C single bond. The C(12)–O(12) (1.191 (15) Å) and C(11)–O(11) (1.190 (15) Å) lengths represent a normal C–O double bond. In contrast, the C(15)–C(14) distance (1.372 (17) Å) exceeds a normal C–C double bond length (1.33 Å). The coordination geometry around Fe(II) atom approximates a distorted octahedron with a relatively small C(12)–Fe–C(11) angle, 81.9 (5)°. On the maleoyl ring, the C(14), C(12), Fe, and the two carbonyl groups nearly form a least-square plane within a mean deviation of 0.08 (1) Å.

The C_{2v} point group of 7–8 is reflected by its IR and ^1H and ^{13}C NMR spectra which show that the two tungsten fragments across the central symmetry plane are spectrally

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Table IV. Atomic Parameters *x*, *y*, and *z* for 8

	x	*y*	*z*	B_{iso}, Å^2
W1	0.805317 (13)	0.05665 (6)	0.13966 (3)	3.254 (25)
W2	0.938414 (13)	0.23376 (6)	0.33400 (3)	3.446 (24)
Fe	0.88193 (4)	0.43930 (22)	0.05214 (9)	3.02 (10)
C1	0.8399 (3)	–0.0222 (14)	0.1278 (6)	4.8 (7)
C2	0.7900 (4)	0.2449 (16)	0.0828 (6)	6.1 (10)
C3	0.7936 (3)	–0.0210 (15)	0.0423 (6)	5.4 (8)
C4	0.9049 (3)	0.3568 (15)	0.3308 (6)	4.5 (7)
C5	0.9577 (4)	0.4384 (15)	0.3663 (7)	7.5 (10)
C6	0.9548 (3)	0.3072 (15)	0.2601 (7)	5.7 (8)
C7	0.9019 (3)	0.5702 (15)	0.1218 (6)	4.9 (7)
C8	0.9109 (3)	0.4234 (16)	0.0110 (7)	5.9 (9)
C9	0.8598 (4)	0.5963 (17)	–0.0033 (7)	7.0 (10)
C10	0.8601 (3)	0.2815 (16)	0.0016 (6)	5.8 (8)
C11	0.8529 (3)	0.4221 (13)	0.1077 (6)	3.7 (6)
C12	0.9023 (3)	0.2637 (13)	0.1198 (5)	3.6 (6)
C13	0.8390 (3)	0.2465 (13)	0.1981 (6)	3.5 (6)
C14	0.8604 (3)	0.2958 (12)	0.1647 (5)	3.2 (6)
C15	0.8878 (3)	0.2338 (12)	0.1760 (5)	3.1 (6)
C16	0.9033 (3)	0.1309 (13)	0.2355 (6)	3.7 (6)
C17	0.7733 (3)	0.0902 (14)	0.2053 (7)	5.5 (8)
C18	0.7630 (3)	–0.0239 (14)	0.1538 (6)	4.0 (7)
C19	0.7819 (3)	–0.1535 (14)	0.1703 (6)	4.3 (7)
C20	0.8048 (3)	–0.1230 (15)	0.2302 (7)	5.1 (8)
C21	0.7992 (3)	0.0302 (15)	0.2539 (6)	5.6 (8)
C22	0.7605 (4)	0.2408 (17)	0.2177 (9)	10.0 (14)
C23	0.7328 (4)	–0.0200 (18)	0.1022 (8)	7.7 (11)
C24	0.7762 (4)	–0.3121 (15)	0.1337 (8)	7.0 (10)
C25	0.8285 (4)	–0.2341 (20)	0.2676 (8)	8.7 (11)
C26	0.8183 (5)	0.1002 (20)	0.3224 (7)	10.8 (14)
C27	0.93743 (24)	–0.0331 (12)	0.3679 (5)	2.9 (5)
C28	0.9359 (3)	0.0631 (14)	0.4253 (6)	4.5 (7)
C29	0.9622 (3)	0.1476 (14)	0.4485 (6)	5.3 (8)
C30	0.9799 (3)	0.1102 (15)	0.4055 (7)	5.7 (8)
C31	0.9655 (3)	–0.0019 (14)	0.3557 (7)	4.6 (7)
C32	0.9150 (4)	–0.1590 (15)	0.3384 (7)	7.6 (12)
C33	0.9133 (5)	0.0645 (18)	0.4627 (8)	9.5 (13)
C34	0.9718 (5)	0.2547 (18)	0.5126 (7)	11.5 (15)
C35	1.0103 (4)	0.1632 (20)	0.4168 (10)	11.2 (12)
C36	0.9746 (4)	–0.0895 (19)	0.3016 (8)	8.5 (12)
O1	0.86098 (22)	–0.0858 (11)	0.1174 (5)	6.4 (6)
O2	0.7766 (3)	0.3493 (11)	0.0506 (5)	8.4 (7)
O3	0.7868 (3)	–0.0658 (13)	–0.0156 (5)	8.4 (7)
O4	0.88433 (23)	0.4359 (11)	0.3322 (5)	7.0 (6)
O5	0.96939 (24)	0.5529 (10)	0.3978 (5)	7.5 (6)
O6	0.9668 (3)	0.3521 (13)	0.2215 (5)	8.5 (7)
O7	0.9146 (3)	0.6465 (11)	0.1678 (5)	8.1 (7)
O8	0.9298 (3)	0.4057 (12)	–0.0115 (5)	8.2 (8)
O9	0.8454 (3)	0.6922 (12)	–0.0355 (6)	10.3 (9)
O10	0.8460 (3)	0.1789 (12)	–0.0274 (5)	8.8 (7)
O11	0.83267 (21)	0.5080 (10)	0.1014 (5)	6.1 (6)
O12	0.92192 (20)	0.1859 (10)	0.1131 (4)	5.0 (5)

equivalent. Only one ^{1}H NMR signal for both W–CH$_2$ and Cp groups was observed at δ 2.14 and 5.33 ppm, respectively. Likewise, the three W–*C*H$_2$–*C*–*C*O carbons in ^{13}C NMR spectra exhibit three signals at δ –18.8, 168.2, and 178.2 ppm, respectively; only two Fe–CO signals were observed at δ 201.1 and 203.8 ppm.

In the absence of CO, a similar reaction between **5** and Fe$_2$(CO)$_9$ in the molar ratio 1:2 under nitrogen produced two additional clusters Cp$_2$W$_2$Fe(CO)$_8$(μ_3-η^1:η^2:η^3-CH$_2$CCCH$_2$) (**9**, 14%) and CpWFe$_2$(CO)$_8$(μ_3-η^1:η^2:η^3-CH$_2$CCMe) (**10**, 8%) in addition to **7** (56%). The yields of **9** and **10** increased to 18% and 12%, respectively, when less Fe$_2$(CO)$_9$ than 1 equimolar quantity was used, which however decreased the yield of **7** (40%). In contrast with **5**, under flowing nitrogen, only **8** was obtained in good yield despite that various ratios of Fe$_2$(CO)$_9$ to **6** (1/1 and 1/2 molar ratio) were used in the reaction. Separation of **7**, **9**, and **10** was conducted by a combination of Florisil column chromatography and preparative SiO$_2$ TLC plate. The spectral data of **10** are identical to those of an authentic compound previously reported.[3a] Structural characterization of **9** relies on an X-ray diffraction measurement. The molecular structure and its atomic numbering scheme are given in Figure 3; the selected bond distances, angles, and atomic coordinates are given in Tables V and VI respectively. According to the ORTEP drawing, the acyclic hydrocarbyl moiety is twisted into an S-shape with the C(11) atom asymmetrically bridged to the Fe and W(2) atoms with a long Fe–W single bond (2.946 (2) Å). The Fe–W lengths reported for CpWFe(CO)$_5$(μ-η^2:η^3:CH$_2$CCC$_6$H$_4$Me) and CpWFe$_2$(CO)$_8$(μ_3-η^1:η^2:η^3-CH$_2$CCPh) are 2.767 (1) Å, 2.7418 (5) and 2.8373 (7) Å, respectively.[4b] The hydrocarbyl ligand is η^2-coordinate to W and η^3-coordinated to Fe atom in an asymmetric fashion with the bridging Fe–C(11) (1.965 (9) Å) and W(2)–C(11) (2.126 (10) Å) lengths being particularly small relative to analogous bonds Fe–C(9) = 2.113 (10) Å, Fe–C(10) = 2.112 (9) Å, and W(2)–C(2) = 2.312 (12) Å. Similarly, the C(9)–C(10) length (1.467 (14) Å) of this hydrocarbyl moiety is appreciably greater than those of the other three C–C lengths (1.40–1.41 (1) Å). Neglecting the CpW(1)(CO)$_3$ fragment, we view the S-shaped hydrocarbyl moiety as a η^2:η^3-butadienylidene fragment, which is similar to that found for Ru$_3$(CO)$_7$(μ_3-η^1:η^2:η^3-CH$_2$CC(*i*-pr)CH)(μ-PPh$_2$).[13] Analogous to **4**, the CpW(CO)$_3$ fragment has undergone 1,2-migration and linked to the C(10) carbon with a normal W(1)–C distance 2.282 (10) Å. Owing to the steric

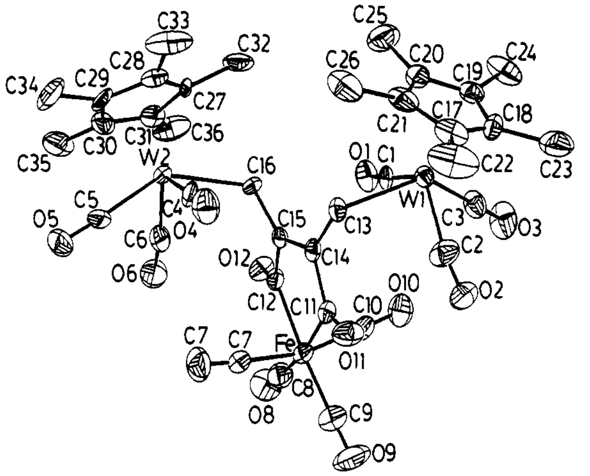

Figure 2. ORTEP drawing of the trinuclear maleoyl complex **8**.

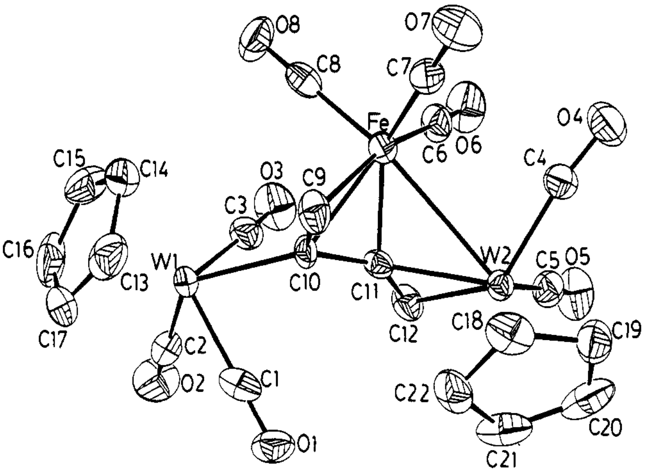

Figure 3. ORTEP drawing of the molecular structure of **9**.

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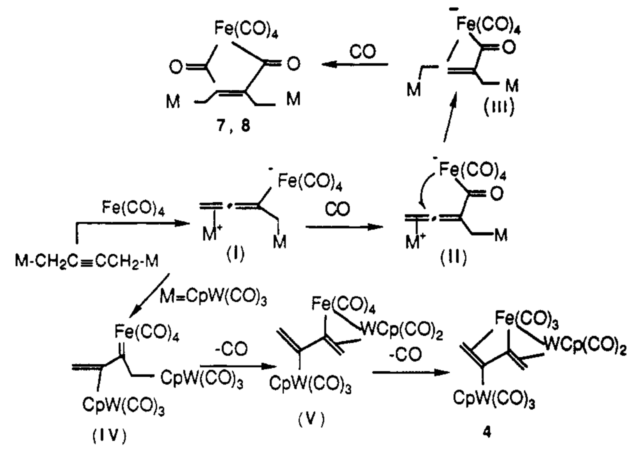
Table V. Selected Bond Distances (Å) and Angles (deg) for 9

W(1)–C(1)	1.965 (11)	Fe–C(6)	1.783 (10)
W(1)–C(2)	2.025 (14)	Fe–C(7)	1.803 (12)
W(1)–C(3)	1.994 (11)	Fe–C(8)	1.803 (11)
W(1)–C(10)	2.282 (10)	Fe–C(9)	2.113 (10)
W(2)–Fe	2.9462 (19)	Fe–C(10)	2.122 (9)
W(2)–C(4)	1.932 (10)	Fe–C(11)	1.965 (9)
W(2)–C(5)	1.927 (11)	C(9)–C(10)	1.467 (14)
W(2)–C(11)	2.126 (10)	C(10)–C(11)	1.405 (13)
W(2)–C(12)	2.312 (110	C(11)–C(12)	1.410 (14)
C(1)–W(1)–C(2)	76.4 (4)	C(6)–Fe–C(11)	94.1 (4)
C(1)–W(1)–C(3)	106.8 (4)	C(7)–Fe–C(8)	95.5 (5)
C(1)–W(1)–C(10)	71.3 (4)	C(7)–Fe–C(9)	88.6 (5)
C(2)–W(1)–C(3)	76.8 (4)	C(7)–Fe–C(10)	128.9 (4)
C(2)–W(1)–C(10)	129.4 (4)	C(7)–Fe–C(11)	138.9 (4)
C(3)–W(1)–C(10)	76.5 (4)	C(8)–Fe–C(9)	95.3 (4)
Fe–W(2)–C(4)	71.9 (3)	C(8)–Fe–C(10)	93.8 (4)
Fe–W(2)–C(5)	110.9 (3)	C(8)–Fe–C(11)	121.2 (5)
Fe–W(2)–C(11)	41.81 (24)	C(9)–Fe–C(10)	40.5 (4)
Fe–W(2)–C(12)	70.77 (25)	C(9)–Fe–C(11)	71.5 (4)
C(4)–W(2)–C(5)	79.5 (4)	C(10)–Fe–C(11)	40.0 (4)
C(4)–W(2)–C(11)	111.0 (4)	Fe–C(9)–C(10)	70.1 (5)
C(4)–W(2)–C(12)	118.9 (4)	W(1)–C(10)–Fe	134.9 (4)
C(5)–W(2)–C(11)	104.1 (4)	W(1)–C(10)–C(9)	121.4 (6)
C(5)–W(2)–C(12)	71.1 (4)	W(1)–C(10)–C(11)	126.2 (7)
C(11)–W(2)–C(12)	36.8 (4)	Fe–C(10)–C(9)	69.4 (5)
W(2)–Fe–C(6)	83.0 (3)	Fe–C(10)–C(11)	64.0 (5)
W(2)–Fe–C(7)	98.9 (3)	C(9)–C(10)–C(11)	112.4 (9)
W(2)–Fe–C(8)	165.5 (3)	W(2)–C(11)–Fe	92.0 (4)
W(2)–Fe–C(9)	86.9 (3)	W(2)–C(11)–C(10)	134.8 (7)
W(2)–Fe–C(10)	78.56 (24)	W(2)–C(11)–C(12)	78.8 (6)
W(2)–Fe–C(11)	46.1 (3)	Fe–C(11)–C(10)	76.0 (5)
C(6)–Fe–C(7)	103.0 (5)	Fe–C(11)–C(12)	131.7 (7)
C96)–Fe–C(8)	92.0 (5)	C(10)–C(11)–C(12)	140.4 (10)
C(6)–Fe–C(9)	165.7 (4)	W(2)–C(12)–C(11)	64.4 (6)
C(6)–Fe–C(10)	126.7 (4)		

Table VI. Atomic Parameters *x*, *y*, and *z* for 9

	x	*y*	*z*	B_{iso}, Å^2
W1	0.76105 (5)	0.24679 (4)	0.32176 (3)	2.136 (20)
W2	0.81411 (5)	–0.25754 (4)	0.08821 (3)	1.850 (19)
Fe	0.71638 (18)	–0.13762 (15)	0.29808 (11)	2.19 (7)
C1	0.7790 (12)	0.1951 (11)	0.1734 (8)	2.8 (6)
C2	0.9662 (17)	0.3671 (13)	0.3169 (8)	3.8 (7)
C3	0.9605 (15)	0.1810 (11)	0.3816 (8)	3.0 (6)
C4	0.7916 (13)	–0.3941 (11)	0.1456 (7)	2.6 (5)
C5	1.0485 (15)	–0.3026 (11)	0.0929 (7)	3.1 (6)
C6	0.9059 (14)	–0.2027 (11)	0.3328 (8)	3.1 (6)
C7	0.5454 (14)	–0.2612 (11)	0.2908 (8)	3.0 (6)
C8	0.7040 (13)	–0.0353 (11)	0.4307 (8)	2.8 (6)
C9	0.5327 (13)	–0.0448 (11)	0.2346 (8)	2.8 (5)
C10	0.7064 (12)	0.0224 (10)	0.2455 (7)	2.0 (4)
C11	0.8276 (12)	–0.0666 (10)	0.2054 (7)	2.0 (5)
C12	0.9975 (13)	–0.0676 (11)	0.1787 (8)	2.9 (6)
C13	0.4688 (15)	0.2747 (14)	0.3251 (9)	4.1 (7)
C14	0.5250 (15)	0.2471 (12)	0.4147 (8)	3.3 (6)
C15	0.6441 (18)	0.3510 (15)	0.4744 (9)	4.8 (8)
C16	0.6658 (19)	0.4416 (12)	0.4283 (12)	5.3 (8)
C17	0.5591 (20)	0.3976 (15)	0.3363 (10)	5.1 (9)
C18	0.5501 (13)	–0.2919 (12)	–0.0158 (8)	3.3 (6)
C19	0.6450 (16)	–0.3976 (12)	–0.0634 (8)	3.5 (6)
C20	0.7839 (17)	–0.3512 (16)	–0.0923 (8)	4.7 (8)
C21	0.7904 (16)	–0.2125 (15)	–0.0634 (9)	4.3 (8)
C22	0.6433 (15)	–0.1727 (12)	–0.0155 (8)	3.4 (6)
O1	0.7855 (9)	0.1632 (8)	0.0852 (5)	3.6 (4)
O2	1.0826 (11)	0.4348 (9)	0.3183 (6)	5.0 (5)
O3	1.0738 (10)	0.1481 (9)	0.4198 (6)	4.9 (5)
O4	0.7820 (11)	–0.4885 (8)	0.1682 (6)	4.4 (5)
O5	1.1944 (9)	–0.3287 (9)	0.0932 (6)	4.5 (5)
O6	1.0249 (11)	–0.2419 (9)	0.3580 (6)	5.0 (5)
O7	0.4372 (11)	–0.3382 (9)	0.2851 (6)	4.6 (5)
O8	0.6975 (10)	0.0282 (8)	0.5135 (5)	4.1 (4)

Scheme III



hindrance of the bulky $CpW(CO)_3$ fragment, the C(9)–C(10)–C(11) angle (112.4 (9)°) is much smaller than the C(10)–C(11)–C(12) angle (140.4 (10)°). The W(1) atom lies only (+0.02 (5) Å) above the plane defined by the three C(11), C(10), and C(9) atoms (+ sign indicates toward the Fe atom). Consistent with its solid state structure, the ^1H NMR resonances of the CH^1H^2 and CH^3H^4 groups are inequivalent and split into four sets as two singlets at δ 1.56 (H^1), 2.75 (H^2) ppm and two doublets at δ 2.54 (H^3) and 2.82 (H^4) ppm with geminal coupling J = 6.0 H. On the basis of 2-D $^{13}C\{H\}$–H NMR spectra, the corresponding carbons in ^{13}C NMR spectra resonate at δ 54.0 (CH^1H^2) and 12.1 (CH^3H^4) ppm with $J_{^{13}C-H}$ = 160 and 138 Hz, respectively. The two central quaternary carbons resonate at δ 188.5 and 199.0 ppm. No ^{183}W–^{13}C nuclei coupling was observed for the two methylene carbons. We assign the AB pattern in the proton NMR resonances to the CH^3H^4 protons because its geminal coupling constant J = 6.0 Hz is indicative of sp^3 hybridization. This character is more consistent with the geometry around the C(9) atom which has a long C(9)–C(10) bond. Moreover the two H(9B) and H(9A) atoms of which the positions were located on the difference Fourier map are distorted from a trigonal plane including C(9) and C(10) atoms. The dihedral angle between the H(9B)–C(12)–C(11) and H(9A)–C(12)–C(11) is 26.7 (15)°. In contrast, the dihedral angle between the H(12B)–C(12)–C(11) and H(12A)–C(12)–C(11) plane is 16.4 (16)°, more characteristic of sp^2 hybridization.

The reaction chemistry of 5 and 6 with $Fe_2(CO)_9$ closely resembles that of metal–η^1-vinylpropargyl compounds 1 and 2 because their alkyne groups readily undergo double carbonylation to produce maleoyl compounds. It is well documented that maleoyl formation from alkyne and metal carbonyls including $Fe_2(CO)_9$ is severely plagued by its low selectivity.[14,15] Scheme III shows the formation mechanism of 7 and 8 which involves a zwitterionic mechanism (I) generated from electrophilic attack of $Fe(CO)_4$ on the acetylide carbon. This mechanism is similar to that of [3 + 2] cycloaddition of the metal–η^1-propargyl complex with SO_2, $(CN)_2C{=}C(CN)_2$.[16] The intermediate I undergoes a further CO insertion to give the allene acyl species II. A subsequent intramolecular cyclization of II, followed by a second CO insertion is

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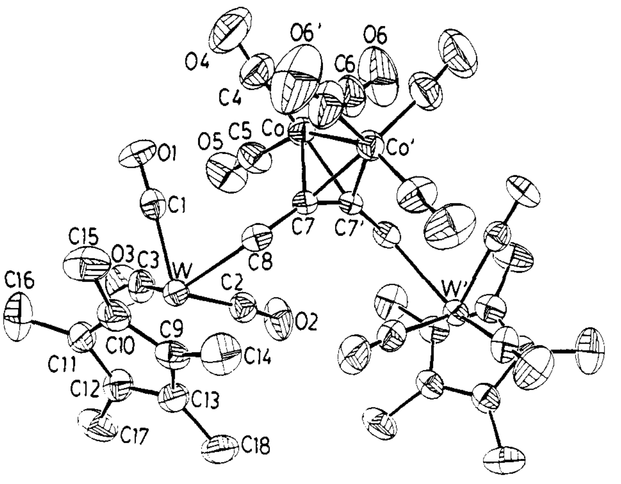

Figure 4. ORTEP view of the molecular structure of 12.

expected to give the observed products 7 and 8. The formation mechanism may be closely related to that of 4 because of a common 1,2-migration of the metal fragment. We suggest in Scheme III a mechanism based on that given for 4 and other μ_3-η^1:η^3:η^3-divinylcarbene[6] compounds, which like the maleoyl complexes 7 and 8 have a common intermediate (I). The rearrangement of negative charge on the $Fe(CO)_4^-$ center is expected to give the μ_2-carbene intermediate IV, of which one $CpW(CO)_3$ fragment has migrated to the β-carbon of hydrocarbyl moiety. The loss of two successive CO of (IV) is expected to give 9.

Reaction of 5 and 6 with $Co_2(CO)_8$. In the reaction of dinuclear complexes 5 and 6 with $Ru_3(CO)_{10}(CH_3CN)_2$, we were unable to isolate new polynuclear compounds. Their reactions with $Co_2(CO)_8$ in THF at 0 °C afford the μ_2-alkyne compounds $Co(CO)_3(\mu\text{-}M\text{-}CH_2C{\equiv}CCH_2\text{-}M)Co(CO)_3$ 11 (M = $CpW(CO)_3$) and 12 (M = $Cp^*W(CO)_3$) in 48% and 75% yields, respectively. In contrast with the great stability of 12 in solution, cooling a THF/hexane solution of 11 for 3 days slowly deposited a dark black microcrystalline solid. Its FAB mass spectra and elemental analyses show that the newly formed crystals have a molar mass which corresponds to loss of one CO from 11. We were unable to deduce clearly its structure from NMR and IR spectra. Attempts to grow better crystals for X-ray structural analyses were not successful partly due to its instability during recrystallization. An X-ray structural analysis of 12 has been performed; the ORTEP drawing, selected bond distances, angles, and atomic coordinates are given in Figure 4 and Tables VII and VIII respectively. Similar to F_c—C≡C—F_c[18] (F_c = $CpFe(CO)_2$), the alkyne fragment of 12 is bonded to a $Co_2(CO)_6$ fragment in a pseudotetrahedral structure with the two C(7) and two Co atoms occupying the four vertices. The molecule has a C_2 symmetry axis which is perpendicular to both the C(7)–C(7)′ and Co–Co′ bonds. The molecular fragments related by this symmetry axis are crystallographically equivalent. The lengths of Co–Co (2.462 (5) Å) and Co–C(7) (1.985 (15) Å) are near the values (2.46–2.50 and 1.92–2.00 Å) of several (μ_2-alkyne)$Co_2(CO)_6$ complexes.[18] The C(7)–C(7)′ (1.28 (3) Å) bond represents a normal C–C double bond, also indicated by IR spectra that showed the ν(C=C) vibration frequency at 1652 (w) cm^{-1}. The C(8)–C(7)–C(7)′ angle (149.9 (14)°) is large to minimize the steric hindrance between the two bulky $CpW(CO)_3$ fragments.

Table VII. Selected Bond Distances (Å) and Angles (deg) for 12

W–C(1)	1.973 (18)	Co–C(6)	1.784 (22)
W–C(2)	1.964 (19)	Co–C(7)	1.989 (15)
W–C(3)	1.968 (18)	Co–C(7)	1.981 (15)
W–C(8)	2.364 (16)	C(7)–Co	1.981 (15)
W–C(9)	2.394 (15)	C(7)–C(7)	1.28 (3)
W–C(10)	2.346 (16)	C(7)–C(8)	1.483 (21)
W–C(11)	2.208 (17)	C(9)–C(10)	1.42 (3)
W–C(12)	2.300 (17)	C(9)–C(13)	1.440 (24)
W–C(13)	2.354 (17)	C(10)–C(11)	1.42 (3)
Co–Coa	2.462 (5)	C(11)–C(12)	1.417 (24)
Co–C(4)	1.753 (21)	C(12)–C(13)	1.41 (3)
Co–C(5)	1.738 (21)		
C(1)–W–C(2)	111.0 (7)	C(4)–Co–C(7)	141.5 (8)
C(1)–W–C(3)	80.3 (7)	C(5)–Co–C(6)	96.4 (10)
C(1)–W–C(8)	73.1 (6)	C(5)–Co–C(7)	101.0 (8)
C(2)–W–C(3)	76.8 (7)	C(5)–Co–C(7)	103.6 (8)
C(2)–W–C(8)	77.8 (6)	C(6)–Co–C(7)	136.0 (8)
C(3)–W–C(8)	133.2 (6)	C(6)–Co–C(7)	99.0 (8)
Co–Co–C(4)	95.2 (7)	C(7)–Co–C(7)	37.7 (6)
Co–Co–C(5)	151.8 (6)	Co–C(7)–Co	76.6 (5)
Co–Co–C(6)	100.7 (7)	Co–C(7)–C(7)	70.8 (9)
Co–Co–C(7)	51.5 (5)	Co–C(7)–C(8)	133.6 (11)
Co–Co–C(7)	51.8 (5)	Co–C(7)–C(7)	71.5 (9)
C(4)–Co–C(5)	100.8 (10)	Co–C(7)–C(8)	125.3 (11)
C(4)–Co–C(6)	107.5 (11)	C(7)–C(7)–C(8)	149.9 (14)
C(4)–Co–C(7)	108.3 (8)	W–C(8)–C(7)	125.2 (10)

Table VIII. Atomic Parameters *x*, *y*, and *z* for 12

	x	*y*	*z*	B_{iso}, Å^2
W	0.84231 (4)	0.13828 (3)	0.23721 (8)	2.52 (3)
Co	0.96459 (12)	0.28592 (9)	0.1221 (3)	3.22 (11)
C1	0.8087 (8)	0.2126 (7)	0.1895 (19)	3.1 (8)
C2	0.9182 (9)	0.1220 (7)	0.1324 (20)	3.5 (8)
C3	0.7997 (9)	0.1282 (8)	0.0214 (21)	3.9 (9)
C4	0.9083 (11)	0.3349 (9)	0.1678 (25)	5.2 (11)
C5	0.9152 (11)	0.2530 (8)	–0.0308 (22)	4.5 (10)
C6	1.1088 (11)	0.3187 (10)	0.011 (3)	5.9 (12)
C7	0.9739 (8)	0.2283 (6)	0.2824 (18)	2.5 (7)
C8	0.9254 (8)	0.1985 (6)	0.3598 (17)	2.9 (8)
C9	0.8492 (9)	0.1040 (7)	0.4935 (19)	3.1 (8)
C10	0.7866 (9)	0.1304 (7)	0.4489 (21)	3.7 (9)
C11	0.7410 (9)	0.1005 (7)	0.3227 (20)	3.5 (8)
C12	0.7922 (9)	0.0578 (7)	0.2855 (20)	3.4 (8)
C13	0.8530 (9)	0.0593 (7)	0.3988 (20)	3.4 (8)
C14	0.8991 (10)	0.1182 (8)	0.6320 (20)	4.8 (11)
C15	0.7588 (11)	0.1767 (7)	0.5328 (22)	5.2 (11)
C16	0.6785 (10)	0.1100 (9)	0.2520 (24)	5.8 (13)
C17	0.7706 (11)	0.0111 (7)	0.1758 (23)	5.1 (11)
C18	0.9077 (10)	0.0180 (7)	0.4046 (24)	5.0 (11)
O1	0.7868 (7)	0.2553 (5)	0.1671 (15)	4.7 (7)
O2	0.9602 (7)	0.1088 (2)	0.0663 (16)	5.4 (7)
O3	0.7764 (7)	0.1195 (6)	–0.1042 (15)	5.7 (8)
O4	0.8746 (8)	0.3681 (7)	0.2030 (20)	8.4 (10)
O5	0.8837 (9)	0.2334 (6)	–0.1362 (16)	6.8 (9)
O6	1.0526 (9)	0.3378 (8)	–0.0625 (21)	10.5 (13)

Experimental Section

All operations were carried out under argon or in a Schlenk apparatus. The solvents Et_2O, hexane, and THF were dried with sodium benzophenone and distilled before use. Dichloromethane was dried over P_2O_5 and distilled. $Fe_2(CO)_9$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, and $Co_2(CO)_8$ (Strem Chemicals) were used without further purification. 2-Butyn-1,4-ditosylate was prepared from 2-butyn-1,2-diol and tosylate chloride according to a standard procedure.[19] $CpW(CO)_3Na$[20] and $Cp^*W(CO)_3Na$[21] were prepared according to published procedures. The synthesis of 1 and 2 was reported.[6]

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All ^{1}H (400, 300 MHz) and ^{13}C (100, 75 MHz) NMR spectra were recorded on either a Bruker AM-400 instrument or a Varian Gemini-300 spectrometer; IR spectra were recorded on a Bomem MB-100 spectrophotometer; FAB mass spectra were recorded on a JEOL JMX-HX-110 mass spectrometer. Microanalyses were performed in the Microanalytic Laboratory at National Cheng Kung University, Tainan, Taiwan.

Synthesis of Co(CO)$_3$(μ_2-CpW(CO)$_3$CH$_2$C≡CCHCH$_2$)Co(CO)$_3$ (3). A THF solution (40 mL) of 1 (0.30 g, 0.75 mmol) and Co$_2$(CO)$_8$ (0.26 g, 0.76 mmol) was stirred at 0 °C for 2 h. The resulting brown solution was evaporated to dryness. A hexane solution (10 mL) was added to extract the residues. The extract was stripped onto a silica column and eluted with diethyl ether (5%) in hexane. An orange band was developed, collected and evaporated to dryness to give analytically pure orange solid (50 mg, 0.71 mmol) in 10% yield. IR (Nujol, cm^{-1}): ν(CO) 2082 (s), 2056 (s), 2016 (s), 1958 (s), 1952 (s); ν(C=C) 1590 (s); ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.40 (s, 2 H, H^1), 5.14 (d, 1 H, H^4), 5.20 (d, 1 H, H^3), 5.48 (s, 5 H, C$_5$H$_5$), 6.90 (dd, 1 H, H^2), J_{23} = 16.6 Hz, J_{24} = 9.5 Hz, ^{13}C NMR (75 MHz, CDCl$_3$): δ 10.3 (W–CH^1), 92.5 (C$_5$H$_5$), 117.1 (CH^{3}H^4), 118.8, 130.9 (CH^1–C–C), 138.0 (CH^2), 211.2, 213.5 (Co–CO), 228.1, 229.8 (W–CO). Mass (FAB, ^{184}W): *m/z* 684 (M$^+$). Anal. Calcd for C$_{19}$H$_{10}$WCo$_2$O$_9$: C, 33.33; H, 1.46%. Found: C, 33.48; H, 1.56%.

Synthesis of MnCO$_2$(CO)$_{10}$(μ_3-η^1:η^2:η^3-CH$_2$CCCHCH$_2$) (4). A THF solution (40 mL) of 2 (0.53 g, 1.60 mmol) and Co$_2$(CO)$_8$ (0.26 g, 1.60 mmol) was stirred at 0 °C for 2 h. The resulting brown solution was evaporated to dryness. An aliquot (10 mL) of hexane was added to extract the residue. The extract was chromatographed on a silica column with diethyl ether (20 mL) in hexane. A red band was developed, collected, and evaporated to dryness to give a red solid 4 (0.66 g, 1.32 mmol). Recrystallization from a saturated solution gave dark red block-shaped crystals. IR (Nujol, cm^{-1}): ν(CO) 2110 (w), 2055 (vs), 1990 (s), 1960 (s), 1845 (m). ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.21 (d, 1 H, H^4), 2.33 (S, 1 H, H^2), 3.53 (d, 1 H, H^5), 3.62 (s, 1 H, H^1), 5.50 (dd, 1 H, H^3), J_{34} = 9.5 Hz, J_{35} = 6.3. ^{13}C NMR (75 MHz, CDCl$_3$): 57.5, 70.4 (CH^{1}H^2 + CH^{3}H^4), 75.0 (CH$_3$), 96.5, 96.9 (C–C), 192.8, 208.8 (Fe–CO + Mn–CO). Mass (FAB): *m/z* 518 (M$^+$). Anal. Calcd for C$_{15}$H$_5$MnCo$_2$O$_{10}$: C, 34.74; H, 0.96%. Found: C, 34.84; H, 1.05%.

Synthesis of CpW(CO)$_3$CH$_2$C≡CCH$_2$CpW(CO)$_3$ (5). To a THF solution (50 mL) of NaWCp(CO)$_3$ (5.52 g, 15.6 mmol) was added 1,4-ditosylate-2-butyne (3.00 g, 7.61 mmol) and stirred at 0 °C for 6 h. The solvent was removed under reduced pressure, leaving a yellow residue. The residue was extracted with Et$_2$O, filtered, and evaporated to dryness. Elution on a silica column with Et$_2$O/hexane (1:1) gave an orange-yellow fraction, which was collected and brought to dryness to give a yellow solid 5 (3.80 g, 5.30 mmol); the yield is 69%. IR (Nujol, cm^{-1}) ν(C≡C) 2280; ν(CO) 2004 (vs), 1914 (vs). ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.15 (s, 4 H), 5.47 (s, 5 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ −29.8 (W–CH$_2$), 89.1 (C≡C), 92.6 (C$_5$H$_5$), 216.9, 229.3 (W–CO). Mass (FAB, ^{184}W): *m/z* 718 (M$^+$). Anal. Calcd for C$_{20}$H$_{14}$W$_2$O$_6$: C, 33.42; H, 1.95%. Found: C, 33.54; H, 2.12%.

Synthesis of Cp*W(CO)$_3$CH$_2$C≡CCH$_2$Cp*W(CO)$_3$ (6). This complex was prepared similarly by the reaction between Cp*W(CO)$_3$Na (4.68 g, 11.40 mmol) and 1,4-ditosylate-2-butyne (2.20 g, 5.58 mmol) in THF at 0 °C; the yield of 6 (3.52 g, 4.10 mmol) was 73%. IR (Nujol, cm^{-1}): ν(C≡C) 2280; ν(CO) 1998 (vs), 1907 (vs). ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.69 (s, 4 H, W–CH$_2$), 2.01 (s, 3 H, C$_5$Me$_5$). ^{13}C NMR (75 MHz, CDCl$_3$): δ −22.9 (W–CH$_2$), 10.1 (s, Me$_5$), 86.0 (s, C≡C), 103.7 (C$_5$Me$_5$), 216.9, 229.3 (W–CO). Mass (FAB, ^{184}W): *m/z* 858 (M$^+$). Anal. Calcd for C$_{30}$H$_{34}$W$_2$O$_6$: C, 41.96; H, 3.96%. Found: C, 42.02; H, 4.04%.

Synthesis of CpW(CO)$_3$CH$_2$C[CO–Fe(CO)$_4$–CO]CCH$_2$-CpW(CO)$_3$ (7). To a THF solution (50 mL) of 5 (0.53 g, 0.74 mmol) was added Fe$_2$(CO)$_9$ (0.55 g, 1.50 mmol), and CO was bubbled through the solution for 12 h. The resulting dark orange solution was evaporated to dryness and the residues were chromatographed through a Florisil column with diethyl ether/hexane (1:9) as the eluant. After an unwanted brown band was eluted off, a diethyl ether/hexane mixed solvent (1:1) was used as eluant. An orange band was developed, collected and brought to dryness to give 7 as an orange solid (0.60 g, 0.64 mmol); the yield was 88%. IR (Nujol, cm^{-1}): ν(CO), 2104 (s), 2015 (s), 1955 (s), 1913 (m), 1685 (w); ν(C=C) 1605 (w). ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.14 (s, 4 H, W–CH$_2$), 5.53 (s, 10 H, Cp). ^{13}C NMR (100 MHz, CDCl$_3$): δ −18.8 (W–CH$_2$), 91.9 (Cp), 168.2 (s, C=C), 178.2 (*C*O—C=), 201.1, 203.8 (Fe–CO), 218.5, 228.8 (W–2CO). Mass (FAB, ^{184}W): *m/z* 942 (M$^+$). Anal. Calcd for C$_{26}$H$_{14}$W$_2$FeO$_{12}$: C, 33.12; H, 1.48%. Found: C, 33.29; H, 1.56%.

Synthesis of Cp*W(CO)$_3$CH$_2$C[CO-Fe(CO)$_4$-CO]C-CH$_2$WCp(CO)$_3$ (8). This compound was prepared similarly by the reaction between 6 (0.25 g, 0.29 mmol) and Fe$_2$(CO)$_9$ (0.21 g, 0.60 mmol) in THF under flowing CO; the yield of 8 (0.29 g, 0.26 mmol) was 90%. IR (Nujol, cm^{-1}): ν(CO) 2100 (s), 2022 (vs), 1905 (vs), 1644 (w) cm^{-1}. ^{1}H NMR (300, CDCl$_3$): δ 1.94 (s, 4 H, W–CH$_2$), 2.02 (s, 30 H, C$_5$Me$_5$). ^{13}C NMR (75 MHz, CDCl$_3$): δ −6.9 (W–CH$_2$), 10.5 (C$_5$*Me*$_5$), 104.2 (*C*$_5$Me$_5$), 160.1 (C=C), 179.3 (*C*O—C=C), 201.7, 203.9 (Fe–CO), 224.8, 234.4 (W–CO). Mass (FAB, ^{184}W): *m/z* 1083 (M$^+$ + 1). Anal. Calcd for C$_{36}$H$_{34}$W$_2$FeO$_{12}$: C, 39.92; H, 3.14%. Found: C, 40.04; H, 3.30%.

Synthesis of Cp$_2$W$_2$Fe(CO)$_8$(μ_3-η^1:η^2:η^3-CH$_2$CCCH$_2$) (9) and CpWFe$_2$(CO)$_8$(μ_3-η^1:η^2:η^2-CH$_2$CCMe) (10). To a THF solution (50 mL) of 5 (0.53 g, 0.74 mmol) was added Fe$_2$(CO)$_9$ (0.55 g, 1.50 mmol); and the mixture was stirred for 10 h at 23 °C under nitrogen atmosphere. The resulting brown solution was brought to dryness and stripped onto a Florisil column and eluted with diethyl ether/hexane (1:9) eluant to remove an unwanted brown red band. Further elution with diethyl ether/hexane (1:1) produced an orange band which gave 7 as an orange solid (0.39 g, 0.41 mmol). The top immobile part on the column was eluted with diethyl ether/hexane, and a brown band containing a mixture of 9 and 10 was developed, collected, and evaporated to dryness. Further elution of the residues on a preparative SiO$_2$ plate (20 cm × 20 cm × 1 mm) with diethyl ether/hexane (1:1) eluant allowed separation of the two compounds: 9 (a brown band, 91 mg, 0.10 mmol) and 10 (a red band, 42 mg 0.060 mmol). The mass (FAB), IR (Nujol), and NMR data of 10 were identical to those of the authentic sample.[4a] Complex 9, IR (Nujol, cm^{-1}): ν(CO) 2082 (w), 2035 (s), 2013 (s), 1961 (vs), 1936 (s), 1907 (vs), 1847 (m). ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.56 (s, 1 H, H^1), 2.54 (d, 1 H, H^3), 2.75 (s, 1 H, H^2), 282 (d, 1 H, H^4), 5.12 (s, 5 H, C$_5$H$_5$), J_{34} = 6.0 Hz. ^{13}C NMR (75 MHz, CDCl$_3$): δ 12.1 (CH^{3}H^4), 54.0 (CH^{1}H^2), 90.4, 94.1 (2Cp), 185.5, 199.0 (CH^{1}H^2*C*C), 210.1, 211.0, 214.8, 218.1, 219.4, 223.5, 226.0, 226.5 (W–CO + Fe–CO). Mass (FAB, ^{184}W): *m/z* 830 (M$^+$). Anal. Calcd for C$_{22}$H$_{14}$W$_2$FeO$_8$: C, 31.80; H, 1.69%. Found C, 31.92; H, 1.82%.

Synthesis of (CO)$_3$Co[μ_2-CpW(CO)$_3$CH$_2$C≡CCH$_2$-CpW(CO)$_3$]Co(CO)$_3$ (11). To a THF solution (20 mL) of 5 (0.34 g, 0.47 mmol) was added Co$_2$(CO)$_8$ (0.16 g, 0.47 mmol), the mixture was evaporated to dryness, and the residues were stripped onto a short silica column with diethyl ether/hexane as extract. The column was first eluted with diethyl ether/hexane (1:19) to remove unwanted compounds. Further elution with ether/hexane (1:8) produced a brown band, which gave 11 as brown solid in 48% yield (0.23 g, 0.23 mmol). IR (Nujol, cm^{-1}). ν(CO) 2072 (s), 2034 (vs), 2001 (vs), 1963 (s), 1917 (m), 1892 (s); ν(C=C) 1650 (w). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 3.55 (br s, 4 H, W–CH$_2$), 4.47 (br s, 5 H, Cp). A ^{13}C NMR spectrum was not obtained because of its broad signal. Mass (FAB, ^{184}W), *m/z* 1004 (M$^+$). Anal. Calcd for C$_{26}$H$_{14}$W$_2$Co$_2$O$_{12}$: C, 31.08; H, 1.39. Found: C, 30.94; H, 1.43. Attempts to recrystallize this complex in diethyl ether/hexane at −10 °C for 4 days gave dark block crystals of unknown structure. Its spectral data are as follows: IR (Nujol): ν(CO) 2047 (s), 2013 (s), 1995 (s), 1975 (s), 1899 (vs), 1866 (vs), 1821 (vs). ^{1}H NMR

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Table IX. Crystal Data for X-ray Structural Studies of 4, 8, 9, and 12

compd	**4**	**8**	**8**	**12**
empirical formula	$MnCo_2C_{15}H_6O_{10}$	$W_2FeC_{36}H_{34}O_{12}$	$W_2FeC_{22}H_{14}O_8$	$W_2Co_2C_{36}H_{34}O_{12}$
formula mass	518.90	1082.33	830.03	1144.23
cell dimens				
a, Å	8.427 (3)	47.984 (7)	7.810 (2)	20.267 (3)
b, Å	9.326 (2)	8.478 (2)	10.889 (4)	24.628 (3)
c, Å	12.534 (4)	19.883 (6)	13.970 (5)	8.816 (4)
α, deg	97.31 (2)		110.96 (3)	
β, deg	87.76 (3)	107.60 (2)	95.20 (2)	99.68 (2)
γ, deg	110.80 (2)		93.72 (2)	
vol, Å^3	913.3 (4)	7710 (3)	1098.9 (6)	4338 (2)
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$C2/c$
Z	2	8	2	4
D(calcd), mg/m^3	1.888	1.866	2.509	1.753
μ, cm^{-1}	25.0	65.1	113.7	62.0
cryst dimens, mm	0.30 × 0.40 × 0.50	0.15 × 0.50 × 0.50	0.15 × 0.30 × 0.50	0.20 × 0.20 × 0.20
collection range	$2\theta_{max} = 50°$, $\pm hk\pm l$	$2\theta_{max} = 50°$, $hk\pm l$	$2\theta_{max} = 50°$, $\pm hk\pm l$	$2\theta_{max} = 50°$ $hk\pm l$
scan mode; scan speed, deg min^{-1}	$\omega/2\theta$; 1.83–8.24	$\omega/2\theta$; 1.65–8.24	$\omega/2\theta$; 1.65–8.24	$\omega/2\theta$; 1.50–8.24
scan width, deg	$0.60 = 0.35 \tan\theta$	$0.65 = 0.35 \tan\theta$	$0.70 = 0.35 \tan\theta$	$0.65 = 0.35 \tan\theta$
collection T, K	298	298	298	298
decay correction	no (<3%)	yes (7%)	no (<2%)	no (<4%)
absorption correction (min–max transmission)	yes (0.90–1.00)	yes (0.30–1.00)	yes (0.41–1.00)	yes (0.83–1.00)
indep reflns	3189	6748	3860	3818
obsd reflns, m	2721 ($I > 2\sigma(I)$)	5004 ($I > 2\sigma(I)$)	3327 ($I > 2\sigma(I)$)	2807 ($I > 2\sigma(I)$)
no. of params, p	254	461	315	236
R_F[a] (all reflns)	0.030 (0.039)	0.053 (0.075)	0.032 (0.039)	0.031 (0.055)
R_{wF}[a] (all reflns)	0.045 (0.061)	0.042 (0.043)	0.031 (0.031)	0.069 (0.069)
weighting scheme	unit weights	$w^{-1} = \sigma^2(F)$	$w^{-1} = \sigma^2(F)$	$w^{-1} = \sigma^2(F)$
S[a]	1.41	3.21	3.35	4.27
residual extremes in final difference map, e/Å^3	–0.720, +0.380	–2.270, +2.250	–1.680, +1.500	–0.500, +1.010

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. $S = [\sum w(|F_o| - |F_c|)^2/(m - p)]^{1/2}$.

(300 MHz, $CDCl_3$): δ 0.25 (s, 1 H), 2.01 (s, 1 H), 3.14 (s, 1 H), 4.92 (s, 1 H), 5.14 (s, 5 H, Cp), 5.22 (s, 5 H, Cp). Mass (FAB, ^{184}W): m/z 976 (M^+). Anal. Calcd for $C_{25}H_{14}W_2Co_2O_{11}$: C, 30.73; H, 1.43%. Found: C, 30.82; H, 1.56%.

Synthesis of $(CO)_3Co[\mu_2$-Cp*W$(CO)_3CH_2C{\equiv}CCH_2$-Cp*W$(CO)_3]Co(CO)_3$ (12). This compound was prepared similarly from the reaction of **6** (0.40 g, 0.47 mmol) and $Co_2(CO)_8$ (0.16 g, 0.47 mmol) in THF at 0 °C for 2 h. The yield of **12** was 75%. IR (Nujol): ν(CO) 2072 (s), 2069 (vs), 1963 (s), 1917 (m) and 1892 (s) cm^{-1}; ν(C=C) 1652 (w) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 1.95 (s, 3 H, C_5Me_5), 2.84 (s, 4 H, W–CH_2), 113.8 (CC), 202.1, 203.0 (Co–CO), 227.2, 234.6 (W–CO). Mass (FAB, ^{184}W): m/z 116 (M^+ – CO). Anal. Calcd for $C_{36}H_{34}W_2Co_2O_{12}$: C, 37.76; H, 2.90%. Found: C, 37.84; H, 3.10%.

X-ray Diffraction Measurement. A single crystal of each of **4**, **8**, **9**, and **12** was sealed in a glass capillary under an inert atmosphere. Data were collected on a Enraf-Nonius CAD-4 diffractometer, using graphite-monochromated Mo Kα radiation, and the structures were solved by the heavy-atom methods; all data reduction and structural refinement were performed with the NRCCSDP package. Crystal data and details of the data collection and structural analysis are summarized in Table IX. For all structures, all non-hydrogen atoms were refined with anisotropic parameters. All hydrogen atoms included in the structure factor calculations were placed in idealized positions except for H(9A) H(9B), H(12A), H(12B) of compound **9** and H(11A), H(11B), H(15A), H(15B) of compound **4** which were located on the difference Fourier map.

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Supplementary Material Available: Listings of calculated atomic coordinates, anisotropic thermal parameters, and bond distances and angles of compounds **4**, **8**, **9**, and **12** (16 pages). Ordering information is given on any current masthead page.

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