Reaction Chemistry of Metal–η^1-Vinylpropargyl Ligands with Unsaturated Iron(0), Ruthenium(0), and Osmium(0) Carbonyl Clusters

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The reaction between $M—CH_2C{\equiv}CCH{=}CH_2$ (M = $CpW(CO)_3$ (1), $Mn(CO)_5$ (2)) and $Fe_2(CO)_9$ in hexane at 23 °C afforded $M—CH_2\underline{C(CO—Fe(CO)_4—CO)C}—CH{=}CH_2$ (M = $CpW(CO)_3$ (3), $Mn(CO)_5$ (4)), $MFe_2(CO)_6(\mu_3\text{-}\eta^1,\eta^3,\eta^3\text{-}CH_2CCCH{=}CH_2)$ (M = $CpW(CO)_3$ (5), $Mn(CO)_5$ (7)), and $CpWFe_2(CO)_8(\mu_3\text{-}\eta^1,\eta^2,\eta^2\text{-}CH_2CCCH{=}CH_2)$ (6). Under flowing CO, a similar reaction gave only 3 and 4 in high yields (>90%). Heating 1 with $Fe_3(CO)_{12}$ in refluxing hexane produced 5 and 6. Treatment of 1 with $Ru_3(CO)_{10}(CH_3CN)_2$ in CH_3CN afforded $CpWRu_2(CO)_8(\mu_3\text{-}\eta^1,\eta^2,\eta^2\text{-}CH_2CCCH{=}CH_2)$ (8). Stirring of 1 with $Os_3(CO)_{10}(CH_3CN)_2$ formed $CpWOs_3(CO)_{13}(\mu_4\text{-}\eta^1,\eta^1,\eta^1,\eta^2\text{-}CH_2CCCH{=}CH_2)$ (9) and an unusual tetranuclear cluster of which one W—CO has formally migrated to the ligand β-carbon. The molecular structures of 3, 5, 8, and 10 have been determined by X-ray diffraction study to have the following parameters: for 3 space group $P2_1/n$, a = 9.9947 (21) Å, b = 9.4773 (19) Å, c = 21.845 (3) Å, β = 93.635 (15)°, Z = 4, R = 0.030, and R_w = 0.023; for 5 space group triclinic, $P\bar{1}$, a = 9.6100 (24) Å, b = 13.654 (4) Å, c = 8.4220 (23) Å, α = 100.215 (21)°, β = 104.394 (21)°, γ = 92.978 (21)°, Z = 2, R = 0.024, and R_w = 0.022; for 8 space group monoclinic, C_2/c, a = 28.580 (5) Å, b = 9.285 (4) Å, c = 15.978 (4) Å, β = 110.062 (15)°, Z = 8, R = 0.046, and R_w = 0.034; for 10 space group $P2_1/n$, a = 11.825 (7) Å, b = 10.057 (7) Å, c = 22.889 (13) Å, β = 92.97 (6)°, Z = 4, R = 0.055, and R_w = 0.047 for 3060 reflections $>2\sigma(I)$ out of 4763 unique reflections and 362 parameters.

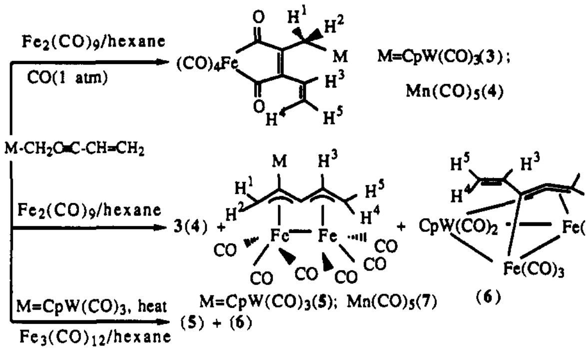
Introduction

Heteronuclear metal clusters[1] represent an important and rapidly expanding class of compounds. It is believed that clusters containing different metal centers can provide various active sites to facilitate the activation of hydrocarbon substrates in stoichiometric and catalytic reactions.[1] So far, a few synthetic methodologies[2] for compounds of this class have been developed. One example[3] is to use a metal–η^1-propargyl compound as a template for the construction of mixed metal–metal bonds. This synthetic approach has proven effective for the preparation of heteronuclear μ-η^2,η^3-allenyl, μ_3-η^1,η^2,η^2-allenyl, and μ-alkyne complexes. In this paper, we report the syntheses, characterizations, and molecular structures of polynuclear species derived from the related complexes $MCH_2C{\equiv}CCH{=}CH_2$ (M = $CpW(CO)_3$ (1), $Mn(CO)_5$ (2)). Notably, the complexes thus formed are quite different from those obtained from the corresponding η^1-propargyl complexes.[3a,b]

Results and Discussion

Synthesis and Characterization of Iron–Maleoyl Complexes. The complexes 1 and 2 were conveniently synthesized from the reaction between 2-pentyn-4-enyl-1-tosylate[4] and anions $NaMn(CO)_5$ or $NaCpW(CO)_3$ in THF at 0 °C. These two η^1 compounds were stable enough to be isolated in 50–60% yields and could be fully characterized. Their ^1H and ^{13}C NMR chemical shifts indicated an η^1 structure.

Scheme I



The reaction between 1 or 2 and $Fe_2(CO)_9$ was conducted in hexane at 23 °C; the results are summarized in Scheme I. Under flowing CO (1 atm), 1 and 2 undergo double carbonylation at the β,γ-carbons of its ligand to afford iron–maleoyl complexes 3 and 4 in yields >90%. In the absence of CO, the yield decreased to 30–40% along with formation of trinuclear μ_3-η^1,η^2,η^2 and μ_3-η^1,η^3,η^3 species (vide post). Purification of 3 and 4 was conducted by means of elution through a silica gel column. Single crystals of 3 suitable for X-ray analysis were grown from a saturated hexane solution cooled at −20 °C. An ORTEP drawing of 3 is shown in Figure 1, and selected bond distances and angles are provided in Table I. It is obvious that the η^1-2-pentyn-4-en-1-yl ligand has undergone double carbonylation and has become linked to the $Fe(CO)_4$ fragment to form a maleoyl ring. In this manner, this acyclic group can be viewed as a sickle-shaped *cis*-pentadienyl group with the C(16)–C(17) (1.350 (13) Å) and

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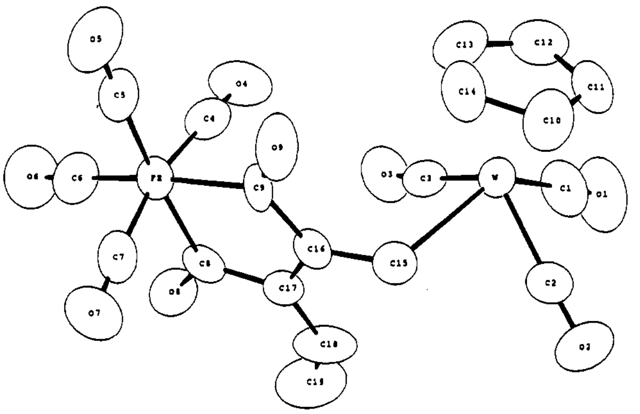

Figure 1. ORTEP drawing of the molecular structure of 3.

Table I. Selected Bond Distances and Bond Angles for 3

W–C(1)	1.967 (12)	C(4)–O(4)	1.148 (13)
W–C(2)	1.952 (11)	C(5)–O(5)	1.131 (13)
W–C(3)	1.959 (11)	C(6)–O(6)	1.139 (13)
W–C(15)	2.354 (8)	C(7)–O(7)	1.140 (13)
Fe–C(4)	1.775 (11)	C(8)–C(17)	1.512 (13)
Fe–C(5)	1.832 (10)	C(8)–O(8)	1.216 (11)
Fe–C(6)	1.818 (10)	C(9)–C(16)	1.489 (13)
Fe–C(7)	1.789 (11)	C(9)–O(9)	1.195 (12)
Fe–C(8)	2.008 (9)	C(15)–C(16)	1.485 (13)
Fe–C(9)	2.023 (8)	C(16)–C(17)	1.350 (13)
C(1)–O(1)	1.148 (14)	C(17)–C(18)	1.466 (14)
C(2)–O(2)	1.158 (13)	C(18)–C(19)	1.153 (17)
C(3)–O(3)	1.169 (13)		
C(1)–W–C(2)	76.3 (5)	W–C(1)–O(1)	179.6 (11)
C(1)–W–C(3)	76.6 (4)	W–C(2)–O(2)	177.4 (9)
C(1)–W–C(15)	131.2 (4)	W–C(3)–O(3)	175.5 (8)
C(2)–W–C(3)	111.6 (4)	Fe–C(4)–O(4)	177.8 (9)
C(2)–W–C(15)	73.6 (4)	Fe–C(5)–O(5)	178.7 (11)
C(3)–W–C(15)	80.0 (4)	Fe–C(6)–O(6)	176.3 (10)
C(4)–Fe–C(5)	94.4 (5)	Fe–C(7)–O(7)	176.3 (9)
C(4)–Fe–C(6)	91.9 (5)	Fe–C(8)–C(17)	114.9 (6)
C(4)–Fe–C(7)	167.4 (4)	Fe–C(8)–O(8)	122.8 (7)
C(4)–Fe–C(8)	85.8 (4)	C(17)–C(8)–O(8)	122.4 (8)
C(4)–Fe–C(9)	85.8 (4)	Fe–C(9)–C(16)	114.1 (7)
C(5)–Fe–C(6)	95.8 (5)	Fe–C(9)–O(9)	124.0 (7)
C(5)–Fe–C(7)	95.2 (5)	C(16)–C(9)–O(9)	121.8 (8)
C(5)–Fe–C(8)	172.6 (4)	W–C(15)–C(16)	117.6 (6)
C(5)–Fe–C(9)	91.7 (4)	C(9)–C(16)–C(15)	118.9 (8)
C(6)–Fe–C(7)	95.2 (5)	C(9)–C(16)–C(17)	116.0 (8)
C(6)–Fe–C(8)	91.6 (5)	C(15)–C(16)–C(17)	125.0 (8)
C(6)–Fe–C(9)	172.4 (5)	C(8)–C(17)–C(16)	113.9 (8)
C(7)–Fe–C(8)	83.6 (4)	C(8)–C(17)–C(18)	121.7 (9)
C(7)–Fe–C(9)	85.7 (4)	C(16)–C(17)–C(18)	124.4 (9)
C(8)–Fe–C(9)	81.0 (4)	C(17)–C(18)–C(19)	136.0 (14)

C(18)–C(19) (1.153 (17) Å) lengths representing C–C double bonds. The extraordinarily short C(18)–C(19) bond is due to thermal motion of the C(19) atom. The Fe–C(9) (2.008 (9) Å) and Fe–C(8) (2.023 (8) Å)[5,6] lengths are reasonable according to the reported values for a normal Fe–C bond. The C(9)–O(9) (1.195 (12) Å) and C(8)–O(8) (1.1216 (11) Å) bonds have lengths close to that of a normal C–O double bond (1.21 Å).[7]

For 4, the mass, IR, and ^{1}H and ^{13}C NMR spectral data are consistent with the given structure. The β,γ-carbons of the η^1-dienyl ligand resonate at 155.5 and 185.0 ppm about 70–80 ppm downfield from those of 2. The maleoyl ketones are indicated by the infrared absorptions (Nujol) at 1658 (w) and 1640 (w) cm^{-1} as well as by the ^{13}C NMR resonances at δ 199.9 and 203.1 ppm. For 3, there are discrepancies in the NMR chemical chifts of the vinyl groups 3.22 (H^3, dd, J = 12.6, 8.7 Hz), 3.86 (H^4, d, J = 12.6 Hz), 2.25 (H^5, d, J = 8.7 Hz), and 34.9 (CH^{4}H^5) and 52.3 (CH^3). These values lie far upfield with respect to those of 4 and a normal vinyl group. The remaining ^{1}H and ^{13}C NMR resonances including the two ketone carbons and seven individual Fe–CO and W–CO carbons are normal. To assure no structural variations in solution, we have examined its solution IR spectrum (hexane) in the ν(CO) region, which was identical with that in the Nujol mull. Variable-temperature ^{1}H(–60 to +100 °C, toluene) NMR spectroscopy and spin-transfer techniques showed no signs of stereochemical nonrigidty. At present, we have no explanation of such abnormal NMR chemical shifts for the vinyl group of 3.

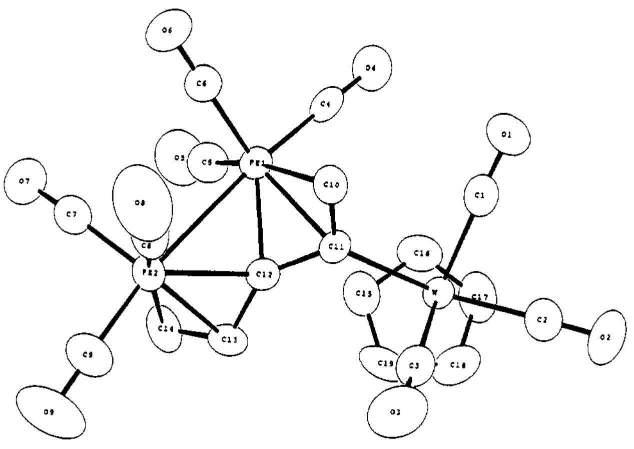

Figure 2. ORTEP drawing of the molecular structure of 5.

Complexes 1 and 2 are homologues of metal–η^1-propargyl complexes. The related complexes CpW(CO)$_3$(η^1-CH$_2$C≡CR) (R = Me, Ph)[3a] react with Fe$_2$(CO)$_9$ to give only heteronuclear μ-η^2,η^3- and μ_3-η^1,η^2,η^2-allenyl complexes.[3] Transition-metal maleoyls have been reported for iron[7] and cobalt.[8] The stable complexes CpCo(dimethylmaleoyl)(CO) and Fe(CO)$_4$(dicyclopropylmaleoyl) were prepared by the reaction involving alkynes and CpCo(CO)$_2$ and Fe(CO)$_5$, but the yields were low. An efficient synthesis was later developed involving the reaction between ClCo(PPh$_3$)$_3$ and cyclobutenedione.[9,10]

Synthesis and Structures of Trinuclear μ_3-η^1,η^2 and μ_3-η^1,η^3,η^3 Complexes. In the absence of CO, the reaction between Fe$_2$(CO)$_9$ and 1 afforded trinuclear CpWFe$_2$(CO)$_9$(μ_3-η^1,η^3,η^3-CH$_2$CCCH=CH$_2$) (5) (25%), CpWFe$_2$(CO)$_8$(μ_3-η^1,η^2,η^2-CH$_2$CCCH=CH$_2$) (6) (3%), and 3 (30%). The mixed products were separated by column chromatography. In an alternative preparation, heating 1 with Fe$_3$(CO)$_{12}$ in refluxing benzene only yielded 5 and 6 in respective yields of 5 and 7%. Allowing 2 to react with Fe$_2$(CO)$_9$ in hexane under argon at 25 °C yielded MnFe$_2$(CO)$_{11}$(μ_3-η^1,η^3,η^3-CH$_2$CCCHCH$_2$) (7) (14%) and 4 (32%). Irradiation or thermolysis of 3 or 4 alone in hexane

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Table II. Selected Bond Distances and Bond Angles for 5

W–C(1)	1.955 (7)	Fe(2)–C(13)	2.069 (6)
W–C(2)	1.971 (6)	Fe(2)–C(14)	2.110 (6)
W–C(3)	1.991 (6)	C(1)–O(1)	1.169 (8)
W–C(11)	2.279 (5)	C(2)–O(2)	1.159 (8)
Fe(1)–Fe(2)	2.7537 (13)	C(3)–O(3)	1.141 (8)
Fe(1)–C(4)	1.784 (6)	C(4)–O(4)	1.151 (7)
Fe(1)–C(5)	1.770 (7)	C(5)–O(5)	1.146 (8)
Fe(1)–C(6)	1.809 (6)	C(6)–O(6)	1.127 (8)
Fe(1)–C(10)	2.114 (5)	C(7)–O(7)	1.138 (9)
Fe(1)–C(11)	2.129 (5)	C(8)–O(8)	1.152 (8)
Fe(1)–C(12)	1.971 (5)	C(9)–O(9)	1.143 (8)
Fe(2)–C(7)	1.801 (7)	C(10)–C(11)	1.414 (8)
Fe(2)–C(8)	1.776 (7)	C(11)–C(12)	1.392 (7)
Fe(2)–C(9)	1.747 (7)	C(12)–C(13)	1.394 (8)
Fe(2)–C(12)	2.018 (5)	C(13)–C(14)	1.414 (9)
C(1)–W–C(2)	75.32 (24)	C(7)–Fe(2)–C(14)	90.9 (3)
C(1)–W–C(3)	109.87 (24)	C(8)–Fe(2)–C(9)	88.9 (3)
C(1)–W–C(11)	79.89 (21)	C(8)–Fe(2)–C(12)	101.20 (24)
C(2)–W–C(3)	78.81 (24)	C(8)–Fe(2)–C(13)	129.6 (3)
C(2)–W–C(11)	129.90 (21)	C(8)–Fe(2)–C(14)	168.7 (3)
C(3)–W–C(11)	69.76 (21)	C(9)–Fe(2)–C(12)	126.8 (3)
Fe(2)–Fe(1)–C(4)	172.89 (19)	C(9)–Fe(2)–C(13)	95.2 (3)
Fe(2)–Fe(1)–C(5)	87.91 (21)	C(9)–Fe(2)–C(14)	89.4 (3)
Fe(2)–Fe(1)–C(6)	90.03 (18)	C(12)–Fe(2)–C(13)	39.86 (22)
Fe(2)–Fe(1)–C(10)	90.22 (14)	C(12)–Fe(2)–C(14)	71.14 (21)
Fe(2)–Fe(1)–C(11)	81.22 (14)	C(13)–Fe(2)–C(14)	39.53 (25)
Fe(2)–Fe(1)–C(12)	47.05 (14)	W–C(1)–O(1)	178.2 (5)
C(4)–Fe(1)–C(5)	91.2 (3)	W–C(2)–O(2)	178.6 (5)
C(4)–Fe(1)–C(6)	97.1 (3)	W–C(3)–O(3)	177.0 (5)
C(4)–Fe(1)–C(10)	89.26 (23)	Fe(1)–C(4)–O(4)	178.3 (5)
C(4)–Fe(1)–C(11)	93.97 (22)	Fe(1)–C(5)–O(5)	175.5 (6)
C(4)–Fe(1)–C(12)	126.45 (23)	Fe(1)–C(6)–O(6)	179.5 (5)
C(5)–Fe(1)–C(6)	99.9 (3)	Fe(2)–C(7)–O(7)	178.1 (6)
C(5)–Fe(1)–C(10)	168.3 (3)	Fe(2)–C(8)–O(8)	174.1 (5)
C(5)–Fe(1)–C(11)	129.4 (3)	Fe(2)–C(9)–O(9)	178.0 (7)
C(5)–Fe(1)–C(12)	101.5 (3)	Fe(1)–C(10)–C(11)	71.1 (3)
C(6)–Fe(1)–C(10)	91.72 (24)	W–C(11)–Fe(1)	130.82 (23)
C(6)–Fe(1)–C(11)	129.20 (24)	W–C(11)–C(10)	128.4 (4)
C(6)–Fe(1)–C(12)	130.44 (23)	W–C(11)–C(12)	120.0 (4)
C(10)–Fe(1)–C(11)	38.93 (21)	Fe(1)–C(11)–C(10)	70.0 (3)
C(10)–Fe(1)–C(12)	69.11 (22)	Fe(1)–C(11)–C(12)	64.2 (3)
C(11)–Fe(1)–C(12)	39.47 (21)	C(10)–C(11)–C(12)	111.5 (4)
Fe(1)–Fe(2)–C(7)	90.58 (20)	Fe(1)–C(12)–Fe(2)	87.30 (21)
Fe(1)–Fe(2)–C(8)	88.33 (20)	Fe(1)–C(12)–C(11)	76.4 (3)
Fe(1)–Fe(2)–C(9)	171.0 (3)	Fe(1)–C(12)–C(13)	137.7 (4)
Fe(1)–Fe(2)–C(12)	45.65 (15)	Fe(2)–C(12)–C(11)	140.1 (4)
Fe(1)–Fe(2)–C(13)	80.06 (16)	Fe(2)–C(12)–C(13)	72.1 (3)
Fe(1)–Fe(2)–C(14)	91.67 (17)	C(11)–C(12)–C(13)	141.1 (5)
C(7)–Fe(2)–C(8)	100.3 (3)	Fe(2)–C(13)–C(12)	68.1 (3)
C(7)–Fe(2)–C(9)	98.4 (3)	Fe(2)–C(13)–C(14)	71.8 (3)
C(7)–Fe(2)–C(12)	129.8 (3)	C(12)–C(13)–C(14)	117.6 (5)
C(7)–Fe(2)–C(13)	128.3 (3)	Fe(2)–C(14)–C(13)	68.7 (3)

Table III. Selected Bond Distances and Bond Angles for 8

W–Ru(1)	2.9152 (13)	Ru(2)–C(14)	2.478 (15)
W–Ru(2)	2.9179 (13)	Ru(2)–C(15)	2.160 (11)
W–C(1)	2.008 (13)	C(1)–O(1)	1.137 (15)
W–C(2)	1.964 (11)	C(2)–O(2)	1.161 (13)
W–C(15)	2.118 (11)	C(3)–O(3)	1.133 (16)
W–C(16)	2.274 (13)	C(4)–O(4)	1.170 (17)
Ru(1)–Ru(2)	2.8148 (18)	C(5)–O(5)	1.127 (18)
Ru(1)–C(3)	1.872 (13)	C(6)–O(6)	1.137 (16)
Ru(1)–C(4)	1.878 (15)	C(7)–O(7)	1.157 (21)
Ru(1)–C(5)	1.926 (15)	C(8)–O(8)	1.112 (16)
Ru(1)–C(16)	2.039 (11)	C(14)–C(15)	1.395 (18)
Ru(2)–C(6)	1.875 (14)	C(15)–C(16)	1.315 (15)
Ru(2)–C(7)	1.888 (18)	C(16)–C(17)	1.452 (21)
Ru(2)–C(8)	1.926 (14)	C(17)–C(18)	1.268 (21)
Ru(1)–W–Ru(2)	57.70 (4)	Ru(1)–Ru(2)–C(7)	87.3 (4)
Ru(1)–W–C(1)	73.3 (3)	Ru(1)–Ru(2)–C(8)	159.4 (4)
Ru(1)–W–C(2)	69.6 (4)	Ru(1)–Ru(2)–C(14)	94.9 (3)
Ru(1)–W–C(15)	63.8 (3)	Ru(1)–Ru(2)–C(15)	65.4 (3)
Ru(1)–W–C(16)	44.2 (3)	C(6)–Ru(2)–C(7)	91.2 (6)
Ru(2)–W–C(1)	72.7 (3)	C(6)–Ru(2)–C(8)	102.1 (6)
Ru(2)–W–C(2)	127.2 (4)	C(6)–Ru(2)–C(14)	88.5 (5)
Ru(2)–W–C(15)	47.6 (3)	C(6)–Ru(2)–C(15)	108.8 (5)
Ru(2)–W–C(16)	67.8 (3)	C(7)–Ru(2)–C(8)	92.1 (6)
C(1)–W–C(2)	90.3 (5)	C(7)–Ru(2)–C(14)	177.7 (6)
C(1)–W–C(15)	118.4 (4)	C(7)–Ru(2)–C(15)	147.8 (5)
C(1)–W–C(16)	116.9 (4)	C(8)–Ru(2)–C(14)	85.7 (5)
C(2)–W–C(15)	111.9 (4)	C(8)–Ru(2)–C(15)	107.3 (5)
C(2)–W–C(16)	77.4 (4)	C(14)–Ru(2)–C(15)	34.1 (4)
C(15)–W–C(16)	34.6 (4)	W–C(1)–O(1)	169.3 (10)
W–Ru(1)–Ru(2)	61.20 (4)	W–C(2)–O(2)	171.6 (11)
W–Ru(1)–C(3)	138.9 (4)	Ru(1)–C(3)–O(3)	178.8 (11)
W–Ru(1)–C(4)	112.9 (4)	Ru(1)–C(4)–O(4)	174.6 (13)
W–Ru(1)–C(5)	111.7 (5)	Ru(1)–C(5)–O(5)	177.8 (16)
W–Ru(1)–C(16)	51.0 (4)	Ru(2)–C(6)–O(6)	178.5 (12)
Ru(2)–Ru(1)–C(3)	88.8 (4)	Ru(2)–C(7)–O(7)	175.4 (12)
Ru(2)–Ru(1)–C(4)	173.8 (4)	Ru(2)–C(8)–O(8)	178.7 (13)
Ru(2)–Ru(1)–C(5)	95.8 (5)	Ru(2)–C(14)–C(15)	60.3 (7)
Ru(2)–Ru(1)–C(16)	72.8 (3)	W–C(15)–Ru(2)	86.0 (4)
C(3)–Ru(1)–C(4)	95.3 (6)	W–C(15)–C(14)	139.1 (9)
C(3)–Ru(1)–C(5)	97.8 (7)	W–C(15)–C(16)	79.2 (7)
C(3)–Ru(1)–C(16)	95.6 (5)	Ru(2)–C(15)–C(14)	85.6 (8)
C(4)–Ru(1)–C(5)	88.3 (7)	Ru(2)–C(15)–C(16)	113.8 (8)
C(4)–Ru(1)–C(16)	102.1 (6)	C(14)–C(15)–C(16)	140.0 (12)
C(5)–Ru(1)–C(16)	162.2 (6)	W–C(16)–Ru(1)	84.9 (4)
W–Ru(2)–Ru(1)	61.10 (4)	W–C(16)–C(15)	66.2 (7)
W–Ru(2)–C(6)	151.6 (4)	W–C(16)–C(17)	126.8 (10)
W–Ru(2)–C(7)	106.2 (4)	Ru(1)–C(16)–C(15)	107.8 (8)
W–Ru(2)–C(8)	99.5 (4)	Ru(1)–C(16)–C(17)	121.4 (10)
W–Ru(2)–C(14)	74.9 (3)	C(15)–C(16)–C(17)	129.1 (12)
W–Ru(2)–C(15)	46.4 (3)	C(16)–C(17)–C(18)	140.6 (19)
Ru(1)–Ru(2)–C(6)	98.5 (4)		

produced only **1** (or **2**) in 20–30%. We have also prepared the Ru analogue of **3**, $CpWRu_2(CO)_8(\mu_3\text{-}\eta^1,\eta^2,\eta^2\text{-}CH_2CCCH{=}CH_2)$ (**8**) (42% yield) from the reaction between **1** and $Ru_3(CO)_{10}(CH_3CN)_2$. The structures of these two trinuclear μ_3-η^1,η^3,η^3 and μ_3-η^1,η^2,η^2 complexes were unambiguously confirmed by X-ray diffraction as the representative compounds **5** and **8**.

The ORTEP drawing of **5** (Figure 2) confirms the above formulation. Selected bond distances and angles are given in Table II. Complex **5** consists of a core of two iron atoms with a large Fe(1)–Fe(2) (2.7537 (13) Å) distance, symmetrically bridged by the C(12) atom in a μ_2-η^3,η^3 fashion (Fe(1)–C(12) = 1.971 (5) Å, Fe(2)–C(12) = 2.018 (5) Å). Notably, $CpW(CO)_3$ has migrated to the β-carbon with a normal W–C(11) (2.279 (5) Å) single bond. The acyclic five-carbon chain is W-shaped; the C–C bond lengths are quite similar, 1.392–1.414 (9) Å. Each iron is bonded to the ligand in a η^3-allylic fashion within the close distances 1.971 (5)–2.129 (5) Å. The η^3-allyl bonding is shown by the ^1H and ^{13}C NMR chemical shifts of the ligand. On the basis of the data above, complex **5** is best described as a divinylcarbene complex.[11] The C(10)–C(11)–C(12) angle (111.5 (4)°) is highly strained, probably due to the steric effect of the bulky $CpW(CO)_3$ unit, and is even smaller than the C(12)–C(13)–C(14) angle 117.6 (5)°. The angle at the central carbon (C(11)–C(12)–C(13) = 141.5 (5)°) is less strained. The Fe(1)–Fe(2) length herein is larger than that of a normal Fe–Fe single bond (2.50–2.65 Å) of the related μ-carbene.[12]

On the basis of its ORTEP drawing (Figure 3), complex **8** can be viewed as a μ_3-η^1,η^2,η^2-allenyl complex and its structure is essentially equivalent to that of the recently reported $CpWFe_2(CO)_8(CH_2CCR)$.[3a] The complex consists of a W–Ru(1)–Ru(2) triangular core with the lengths Ru(1)–Ru(2) (2.8148 (18) Å), W–Ru(1) (2.9179 (13) Å), and W–Ru(2) (2.9152 (13) Å). From the bond lengths in Table III, the distances of metal to allenyl carbon are dissimilar. The lengths Ru(2)–C(15) (2.160 (11) Å) and W–C(15)

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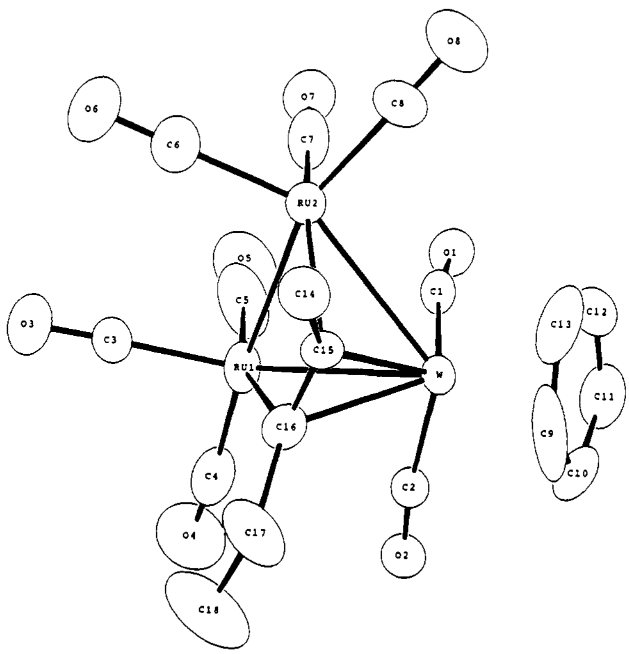
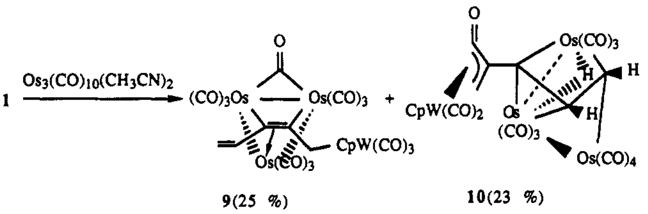


Figure 3. ORTEP drawing of the molecular structure of 8.

(2.118 (11) Å) are smaller than those of Ru(2)–C(14) (2.478 (15) Å) and W–C(16) (2.274 (13) Å). Obviously, the C(15) atom lies closer to the triangular faces relative to the C(14) and C(16) atoms, and the allenyl ligand has similar C–C bond lengths C(14)–C(15) = 1.395 (8) Å, C(15)–C(16) = 1.315 (8) Å. In contrast to **5**, the angles around the central allene atom C(14)–C(15)–C(16) are less strained, 140.0 (12)°, owing to the μ_3 coordination. A dative bond is indicated between Fe and W to meet the 18-electron requirement.

Reaction of $Os_3(CO)_{10}(CH_3CN)_2$ with 1. As depicted in the equation, stirring of **1** with an equimolar amount of $Os_3(CO)_{10}(CH_3CN)_2$(23 °C, CH_3CN, 4 h) produced air-stable complexes **9** and **10** in 25 and 23% yields, respectively. The two compounds were obviously produced from two independent pathways, since heating each alone in refluxing hexane for 1 h does not produce mutual exchange; in each case, the compounds were recovered exclusively. Structural assignment of **9** is straightforward upon comparison of its spectroscopic data with those of the related known compounds $Os_3(CO)_{10}$(alkyne).[13] The μ_2-CO is indicated by its IR ν(CO) absorption at 1846 (w) cm^{-1}. Its ^{13}C NMR spectra at −60 °C exhibited ten Os–CO carbon resonances (174–185 ppm) which begin to broaden and eventually coalesce to one broad resonance (177 ppm) as the temperature is warmed to 23 °C, consistent with the carbonyl exchange between the three Os cores.[13b] An X-ray structure of **10** has been determined. Figure 4 shows the ORTEP drawing of **10** which reveals that one tungsten carbonyl has migrated to the β-carbon of the vinylpropargyl ligand to form an η^3-vinylacyl complex. The Os(2)–Os(3) bond (Os–Os = 3.776 (3) Å) has been cleaved, into which the doubly bridged C(14) atom has inserted to form an L-shaped triosmium core. The hydride is presumably located between Os(1) and Os(2), as indicated by the large angles C(3)–Os(1)–Os(2) = 117.8 (8)° and C(16)–Os(2)–Os(1) = 114.4 (8)°. On the tungsten–vinyl moiety, the W–C(13) length (2.07 (3) Å) is considerably shorter than those of the W–C(17) (2.38 (3) Å) and W–C(18) (2.33 (3) Å) bonds.



9(25 %) 10(23 %)

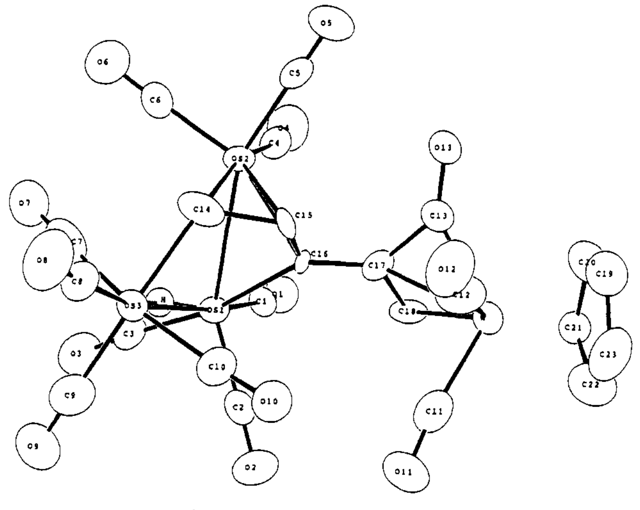
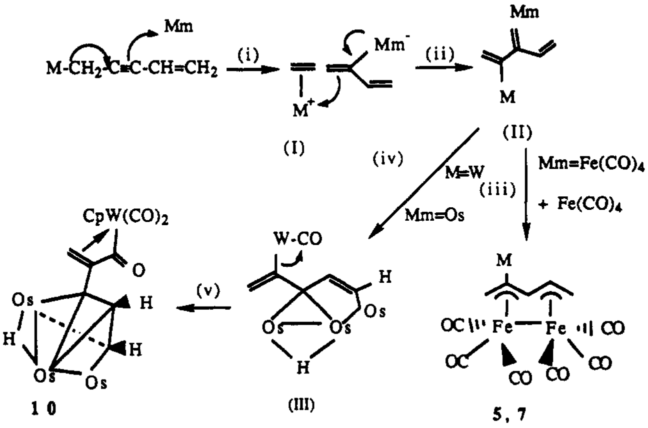


Figure 4. ORTEP drawing of the molecular structure of **10**.

Scheme II[a]



[a] M = $CpW(CO)_3$, $Mn(CO)_5$.

We have performed a seperate labeling experiment involving the use of $Os_3(^{13}CO)_{10}(CH_3CN)_2$ (^{13}CO content = 50%). The ^{13}C NMR spectrum of **10** thus formed revealed that only the 10 Os–CO resonances (168–186 ppm) are ^{13}CO-enriched whereas the other resonances including the η^3-acyl carbon (243.1 ppm) stilled remained naturally abundant. For a sample in the Nujol mull, no new infrared absorption due to the η^3-acyl ν(^{13}CO) mode was observed; from these results we concluded that the η^3-acyl CO is derived from the W–CO group.

1,2-Migration Mechanism. Complex **10** represents an interesting case in which the W–CO group forms a bond to the β-carbon of the η^1-organic moiety. In CO migratory insertion, only the "α-insertion mode" is operative and no exceptional case appears to have been reported.[15] On the

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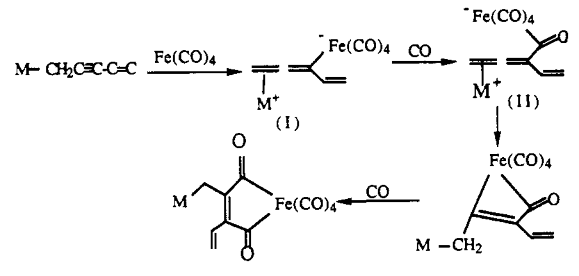
Table IV. Selected Bond Distances and Bond Angles for 10

Os(1)–Os(2)	2.9291 (24)	W–C(13)	2.07 (3)
Os(1)–Os(3)	2.8717 (23)	W–C(17)	2.38 (3)
Os(1)–C(1)	1.92 (3)	W–C(18)	2.33 (3)
Os(1)–C(2)	1.90 (3)	C(1)–O(1)	1.10 (3)
Os(1)–C(3)	1.87 (3)	C(2)–O(2)	1.16 (3)
Os(1)–C(16)	2.163 (23)	C(3)–O(3)	1.20 (4)
Os(1)–H	1.2041	C(4)–O(4)	1.11 (3)
Os(2)–C(4)	1.98 (3)	C(5)–O(5)	1.11 (3)
Os(2)–C(5)	1.95 (3)	C(6)–O(6)	1.16 (4)
Os(2)–C(6)	1.88 (3)	C(7)–O(7)	1.17 (4)
Os(2)–C(14)	2.332 (25)	C(8)–O(8)	1.13 (3)
Os(2)–C(15)	2.259 (22)	C(9)–O(9)	1.14 (4)
Os(2)–C(16)	2.302 (22)	C(10)–O(10)	1.16 (4)
Os(3)–C(7)	1.90 (3)	C(11)–O(11)	1.17 (4)
Os(3)–C(8)	1.93 (3)	C(12)–O(12)	1.20 (3)
Os(3)–C(9)	1.94 (3)	C(13)–C(17)	1.52 (4)
Os(3)–C(10)	1.91 (3)	C(13)–O(13)	1.25 (3)
Os(3)–C(14)	2.07 (3)	C(14)–C(15)	1.55 (4)
Os(3)–H	1.9168	C(15)–C(16)	1.42 (3)
W–C(11)	1.95 (3)	C(16)–C(17)	1.52 (4)
W–C(12)	1.90 (3)	C(17)–C(18)	1.40 (4)

Os(2)–Os(1)–Os(3)	81.22 (5)	C(8)–Os(3)–C(10)	98.7 (12)
Os(2)–Os(1)–C(1)	92.4 (7)	C(8)–Os(3)–C(14)	89.8 (11)
Os(2)–Os(1)–C(2)	148.2 (8)	C(8)–Os(3)–H	161.8
Os(2)–Os(1)–C(3)	117.8 (8)	C(9)–Os(3)–C(10)	93.1 (13)
Os(2)–Os(1)–C(16)	51.1 (6)	C(9)–Os(3)–C(14)	174.5 (12)
Os(2)–Os(1)–H	84.25	C(9)–Os(3)–H	88.7
Os(3)–Os(1)–C(1)	173.5 (7)	C(10)–Os(3)–C(14)	87.5 (12)
Os(3)–Os(1)–C(2)	93.1 (9)	C(10)–Os(3)–H	98.8
Os(3)–Os(1)–C(3)	84.4 (9)	C(14)–Os(3)–H	85.8
Os(3)–Os(1)–C(16)	85.0 (6)	C(11)–W–C(12)	81.7 (12)
Os(3)–Os(1)–H	29.45	C(11)–W–C(13)	124.0 (12)
C(1)–Os(1)–C(2)	93.0 (12)	C(11)–W–C(17)	89.7 (11)
C(1)–Os(1)–C(3)	97.5 (13)	C(11)–W–C(18)	83.7 (10)
C(1)–Os(1)–C(16)	92.0 (10)	C(12)–W–C(13)	79.2 (11)
C(1)–Os(1)–H	149.1	C(12)–W–C(17)	91.2 (12)
C(2)–Os(1)–C(3)	92.4 (12)	C(12)–W–C(18)	123.7 (12)
C(2)–Os(1)–C(16)	97.4 (10)	C(13)–W–C(17)	39.2 (10)
C(2)–Os(1)–H	105.9	C(13)–W–C(18)	65.3 (9)
C(3)–Os(1)–C(16)	165.9 (11)	C(17)–W–C(18)	34.7 (9)
C(3)–Os(1)–H	58.2	Os(1)–C(1)–O(1)	170 (3)
C(16)–Os(1)–H	109.0	Os(1)–C(2)–O(2)	178.5 (24)
Os(1)–Os(2)–C(4)	94.0 (7)	Os(1)–C(3)–O(3)	174.9 (24)
Os(1)–Os(2)–C(5)	153.1 (7)	Os(2)–C(4)–O(4)	170 (3)
Os(1)–Os(2)–C(6)	114.4 (8)	Os(2)–C(5)–O(5)	178.3 (22)
Os(1)–Os(2)–C(14)	73.5 (6)	Os(2)–C(6)–O(6)	176.9 (24)
Os(1)–Os(2)–C(15)	71.2 (6)	Os(3)–C(7)–O(7)	177 (3)
Os(1)–Os(2)–C(16)	47.0 (6)	Os(3)–C(8)–O(8)	175 (3)
C(4)–Os(2)–C(5)	90.1 (11)	Os(3)–C(9)–O(9)	178 (3)
C(4)–Os(2)–C(6)	99.1 (12)	Os(3)–C(10)–O(10)	176.7 (25)
C(4)–Os(2)–C(14)	166.1 (10)	W–C(11)–O(11)	172 (3)
C(4)–Os(2)–C(15)	131.3 (10)	W–C(12)–O(12)	170 (3)
C(4)–Os(2)–C(16)	100.3 (10)	W–C(13)–C(17)	81.3 (14)
C(5)–Os(2)–C(6)	91.1 (11)	W–C(13)–O(13)	143.4 (20)
C(5)–Os(2)–C(14)	98.3 (10)	C(17)–C(13)–O(13)	135.2 (25)
C(5)–Os(2)–C(15)	86.2 (9)	Os(2)–C(14)–Os(3)	118.1 (12)
C(5)–Os(2)–C(16)	106.1 (9)	Os(2)–C(14)–C(15)	67.8 (12)
C(6)–Os(2)–C(14)	91.8 (12)	Os(3)–C(14)–C(15)	115.2 (17)
C(6)–Os(2)–C(15)	129.5 (11)	Os(2)–C(15)–C(14)	72.9 (13)
C(6)–Os(2)–C(16)	153.9 (10)	Os(2)–C(15)–C(16)	73.5 (12)
C(14)–Os(2)–C(15)	39.4 (10)	C(14)–C(15)–C(16)	118.5 (20)
C(14)–Os(2)–C(16)	66.8 (10)	Os(1)–C(16)–Os(2)	81.9 (8)
C(15)–Os(2)–C(16)	36.3 (8)	Os(1)–C(16)–C(15)	116.3 (17)
Os(1)–Os(3)–C(7)	87.6 (10)	Os(1)–C(16)–C(17)	121.6 (16)
Os(1)–Os(3)–C(8)	168.2 (9)	Os(2)–C(16)–C(15)	70.2 (13)
Os(1)–Os(3)–C(9)	96.2 (10)	Os(2)–C(16)–C(17)	116.4 (15)
Os(1)–Os(3)–C(10)	82.1 (8)	C(15)–C(16)–C(17)	122.1 (21)
Os(1)–Os(3)–C(14)	78.4 (7)	W–C(17)–C(13)	59.5 (13)
Os(1)–Os(3)–H	17.99	W–C(17)–C(16)	127.5 (16)
C(7)–Os(3)–C(8)	90.5 (13)	W–C(17)–C(18)	70.8 (15)
C(7)–Os(3)–C(9)	92.4 (14)	C(13)–C(17)–C(16)	117.1 (21)
C(7)–Os(3)–C(10)	168.7 (13)	C(13)–C(17)–C(18)	109.4 (24)
C(7)–Os(3)–C(14)	86.1 (13)	C(16)–C(17)–C(18)	132.8 (24)
C(7)–Os(3)–H	71.6	W–C(18)–C(17)	74.5 (14)
C(8)–Os(3)–C(9)	95.5 (13)	Os(1)–H–Os(3)	132.57

Scheme III[a]



[a] M = CpW(CO)$_3$, Mn(CO)$_5$.

basis of the characterization of 5 and 7 where the metal fragment has formally undergone 1,2-migration, the formation mechanism of **10** is proposed in Scheme II. The key step involves a nucleophilic attack of the C_3-acetylide carbon at the unsaturated metal carbonyls to generate a zwitterionic intermediate (I),[16] which then rearranges to a dinuclear divinylcarbene species. Recombination of this carbene intermediate with additional reactive Fe(CO)$_4$ leads to the formation of **5** and **7** after a loss of two CO. In the case of the osmium congener, the vinyl C–H bond of this carbene intermediate was oxidatively cleaved by the triosmium core to give II. The bulky triosmiun core possibly exerts strong steric hinderance on the CpW(CO)$_3$ fragment and weakens the W–vinyl σ bond of II to facilitate the CO insertion to produce **10**.

The high yield of **3** and **4** at ambient conditions is particularly noticeable, and it is well documented that maleoyl formation from alkynes and metal carbonyls,[7,8] including Fe$_2$(CO)$_9$, is severely plagued by its low selectivity. We believe their formation is closely associated with that of **5**, **7**, and **10** rather than an isolated case. As demonstrated in Scheme III, we believe that the zwitterionic intermediate I undergoes further carbonylation to give the intermediate II. Further intramolecular cyclization of II, followed by recarbonylation is expected to give the observed products. This proposed mechanism is supported by the feasible nature of the key step (II), which has been demonstrated by the recent work of Wojcicki.[16]

Experimental Section

All operations were carried out under argon or in a Schlenk apparatus. The solvents Et$_2$O, hexane, and THF were dried with sodium/benzophenone and distilled before use. Dichloromethane was dried over P$_2$O$_5$ and distilled. Os$_3$(CO)$_{12}$, Fe$_2$(CO)$_9$, Ru$_3$(CO)$_{12}$, and W(CO)$_6$ (Strem Chemicals) were used without further purification. NaMn(CO)$_5$,[18] NaWCp(CO)$_3$,[18] Fe$_2$(CO)$_9$,[18] Fe$_3$(CO)$_{12}$,[19] Ru$_3$(CO)$_{10}$(CH$_3$CN)$_2$,[20] Os$_3$(CO)$_{10}$(CH$_3$CN)$_2$,[18] and 2-pentyn-4-enyl-1-tosylate[4] were prepared according to the procedures in the literature.

All ^{1}H (400 MHz, 300 MHz) and ^{13}C (100 MHz, 75 MHz) NMR spectra were recorded on either a Bruker AM-400 instrument or a Varian Gemini-300 spectrometer; IR spectra were measured on a Bomem MB-100 spectrophotometer; and FAB mass spectra were recorded on a Jeol JMX-HX110 mass spectrometer. Microanalyses were performed in the Microanalytic Laboratory at the National Taiwain University.

(a) Synthesis of CpW(CO)$_3$(η^1-CH$_2$CCCH=CH$_2$) (1). A THF solution (50 mL) of NaWCp(CO)$_3$ (4.04 g, 11.4 mmol) was added with 2-pentyn-4-enyl-1-tosylate (2.70 g, 11.4 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

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Table V. Summary of Crystal Data and Data Collection for **3**, **5**, **8**, and **10**

	3	5	8	10
emp formula	$C_{19}H_{10}O_9WFe$	$C_{19}H_{10}O_9WFe_2$	$C_{18}H_{11}O_8WRu_2$	$C_{23}H_{10}O_{13}WOs_3$
cryst size, mm	0.06 × 0.12 × 0.40	0.20 × 0.25 × 0.40	0.08 × 0.12 × 0.40	0.25 × 0.30 × 0.50
space group	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$	monoclinic, $C2/c$	monoclinic, $P2_1/n$
cell dimens				
α, Å	9.995 (2)	9.610 (2)	28.580 (5)	11.825 (7)
b, Å	9.477 (2)	13.654 (4)	9.286 (4)	10.057 (7)
c, Å	21.845 (3)	8.422 (2)	15.978 (4)	22.89 (1)
α, deg		100.22 (2)		
β, deg	93.65 (2)	104.39 (2)	110.06 (2)	92.97 (6)
γ, deg		92.98 (2)		
vol. Å^3	2065.0 (7)	1048.1 (5)	3983 (2)	2718 (3)
Z	4	2	8	4
fw	619.95	677.83	738.24	1249.77
dens (calcd), μg/m^3	1.994	2.148	2.462	3.054
abs coeff, mm^{-1}	6.43	7.01	7.40	18.37
F(000)	1183.68	643.82	2767.38	2211.12
diffractometer	Enraf-Nonius, CAD4	same	same	same
radiation	Mo Kα (0.7093 Å)	same	same	same
monochromator	highly oriented graphite crystal	same	same	same
2θ range, deg	2.0–45.0	2.0–50.0	2.0–50.0	2.0–50.0
scan type	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
scan speed, deg/min	1.83–8.24	1.65–8.24	1.65–8.24	1.37–8.24
scan range, deg	$0.70 + 0.35 \tan \theta$	$0.65 + 0.35 \tan \theta$	$0.80 + 0.35 \tan \theta$	$0.75 + 0.35 \tan \theta$
std reflns (variation)	3 measured/1 h (<4%)	3 measured/2 h (<2%)	3 measured/2 h (<6%)	3 measured/1 h (<5%)
index ranges	$-10 \le h \le 10$	$-11 \le h \le 11$	$-33 \le h \le 31$	$-14 \le h \le 14$
	$0 \le k \le 10$	$0 \le k \le 16$	$0 \le k \le 11$	$0 \le k \le 11$
	$0 \le l \le 23$	$-10 \le l \le 9$	$0 \le l \le 18$	$0 \le l \le 27$
no. of ind reflns ($I > 2\sigma(I)$)	2693, 1917	3682, 3272	3502, 2566	4763, 3060
T_{min}/T_{max} (ϕ scan abs)	0.766/1.000	0.608/1.000	0.623/1.000	0.346/1.000
soln	Patterson methods	same	same	same
extinction corrn (g)		0.75 (3)^a	0.14 (1)	0.79 (2)
hydrogen atom	fixed, isotropic U	same	same	same
weighting scheme	$w^{-1} = \sigma^2(F)$	$w^{-1} = \sigma^2(F)$	$w^{-1} = \sigma^2(F)$	$w^{-1} = \sigma^2(F)$
final R indices (include unobs ref)	R = 3.0%, R_w = 2.3% (R = 5.9%, R_2 = 2.5%)	R = 2.4%, R_w = 2.2% (R = 3.1%, R_w = 2.3%)	R = 4.6%, R_w = 3.4% (R = 7.0%, R_w = 3.5%)	R = 5.4%, R_w = 4.6% (R = 10.1%, R_w = 4.8%)
goodness-of-fit	1.36	2.22	2.44	2.44
no. of variables	271	281	263	362
data-to-param ratio	7.07:1	11.64:1	9.76:1	8.45:1
largest diff peak, e/Å^3	0.72	0.66	3.52	3.87
largest diff hole, e/Å^3	−0.60	−0.95	−2.00	−2.96

[a] $F_{c'} = kF_c/(1 + g\beta F_c^2)^{1/4}$.

column with Et_2O/hexane (1:1) gave an orange-yellow fraction, which was collected and brought to dryness to give a yellow solid (2.49 g, 6.26 mmol). The yield was 55%. IR (Nujol): ν(CO) 2021 (s), 1930 (vs) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.08 (d, 2 H, H^1), 5.23 (dd, 1 H, H^4), 5.36 (dd, 1 H, H^3), 5.47 (s, 5 H), 5.80 (ddt, 1 H, H^2), J_{12} = 2.7 Hz, J_{24} = 10.8 Hz, J_{23} = 11.4 Hz, J_{34} = 2.32 Hz. ^{13}C NMR (100 MHz, $CDCl_3$): δ −3.4 (CH^1), 80.1, 100.8 (C≡C), 92.5 (Cp), 118.4 (CH^2), 123.2 (CH^{3}H^4), 216.4, 228.8 (W—CO), MS (12 eV) (^{184}W): m/z 398 (M)$^+$. Anal. Calcd for $C_{13}H_{10}WO_3$: C, 39.20; H, 2.51. Found: C, 39.30; H, 2.70.

(b) Synthesis of $Mn(CO)_5(\eta^1\text{-}CH_2CCCH{=}CH_2)$ (2). This complex was prepared similarly by the reaction between Na-$Mn(CO)_5$ (2.80 g, 12.8 mmol) and 2-pentyn-4-enyl-1-tosylate (3.02 g, 12.8 mmol) in THF at 0 °C; the yield of **2** was 83% (2.79 g, 10.61 mmol). IR (Nujol): ν(CO) 2110 (w), 2035 (vs), 1990 (vs) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.48 (s, 2 H, H^1), 5.23 (d, 1 H, H^4), 5.40 (d, 1 H, H^3), 5.79 (dd, 1 H, H^2), J_{23} = 17.4 Hz, J_{24} = 10.7 Hz. ^{13}C NMR (100 MHz, $CDCl_3$): δ −14.8 (CH^1), 80.3, 99.8 (C≡C), 118.2 (CH^2), 123.3 (CH^{3}H^4), 209.3, 211.1 (Mn—CO). MS (12 eV): m/z 260 (M)$^+$. Anal. Calcd for $C_{10}H_5MnO_5$: C, 46.15; H, 1.92. Found: C, 46.28; H, 1.95.

(c) Synthesis of $CpW(CO)_3\text{—}CH_2\text{—}\underline{C[CO\text{—}Fe(CO)_4\text{—}CO]C}CH{=}CH_2$ (3). A hexane solution (50 mL) of **1** (0.22 g, 0.55 mmol) was added to $Fe_2(CO)_9$ (0.40 g, 1.1 mmol). CO was bubbled through this solution at 23 °C for 10 h, and the solution gradually turned orange. After removal of the solvent to dryness, the residues were chromatographed through a silica column. Elution with a mixture of Et_2O/hexane (1:1) produced an orange band, which was collected and evaporated to dryness. Further recrystallization from Et_2O gave orange crystals of **3** (0.33 g, 0.52 mmol), in 95% yield. IR (Nujol): ν(CO) 2100 (w), 2085 (w), 2045 (s), 2030 (vs), 1970 (s), 1930 (vs), 1658 (w), 1640 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.25 (d, 1 H, H^5), 2.57 (d, 1 H, H^1), 2.78 (d, 1 H, H^2), 3.29 (dd, 1 H, H^3), 3.86 (d, 1 H, H^4), J_{12} = 8.5 Hz, J_{34} = 12.6 Hz, J_{35} = 8.7 Hz. ^{13}C NMR (100 MHz, $CDCl_3$): δ −19.9 (CH^{1}H^2), 35.0 (CH^{4}H^5), 52.3 (CH^3), 165.4, 182.2 (C=C), 199.4, 199.9, 202.6, 202.8, 217.6, 218.5, 226.5, 239.3, 241.2 (M—CO). MS (FAB): m/z 622 (M)$^+$. Anal. Calcd for $C_{19}H_{10}FeWO_9$: C, 36.66; H, 1.61. Found: C, 36.82; H, 1.72.

(d) Synthesis of $Mn(CO)_5\text{—}CH_2\text{—}\underline{C[CO\text{—}Fe(CO)_4\text{—}CO]C}CH{=}CH_2$ (4). This complex was prepared similarly from the reaction between $Fe_2(CO)_9$ (1.25 g, 3.13 mmol) and **2** (0.40 g, 1.54 mmol) in a mixed solvent of hexane (40 mL) and THF (10 mL). CO was bubbled through the solution for 12 h. The yield of **4** was 81% (0.64 g, 1.32 mmol). IR (Nujol): ν(CO) 2110 (w), 2080 (vw), 2030 (vs), 1995 (s), 1658 (w), 1640 (w) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.94 (s, 2 H, H^{1}H^2), 5.58 (d, 1 H, H^5), 6.21 (d, 1 H, H^4), 6.45 (dd, 1 H, H^3), J_{34} = 17.3 Hz, J_{35} = 11.4 Hz. ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.5 (CH^{1}H^2), 123.9 (CH^{4}H^5), 127.3 (CH^3), 155.5, 185.0 (C=C), 200.0, 203.1, 210.2, 211.0, 244.7 (W—CO, Fe—CO). MS (FAB): m/z 485 (M + 1)$^+$. Anal. Calcd for $C_{16}H_5MnFeO_{11}$: C, 39.67; H, 1.03. Found: C, 39.81; H, 1.05.

(e) Synthesis of $CpWFe_2(CO)_9(\mu_3\text{-}\eta^1,\eta^3,\eta^3\text{-}CH_2CCCHCH_2)$ (5) and $CpWFe_2(CO)_8(\mu_3\text{-}\eta^1,\eta^2,\eta^2\text{-}CH_2CCCHCH_2)$ (6). (i) Method A. Complex **1** (0.10 g, 0.25 mmol) and $Fe_3(CO)_{12}$ (0.13 g, 0.25 mmol) were heated under reflux for 1.5–2 h. The solution was evaporated to dryness, and the residues were eluted through a long Florisil column with Et_2O/hexane as the eluant. The first purple band off the column was identified as **5**, which produced purple block crystals (8 mg, 0.012 mmol) after recrystallization from Et_2O. Collection of the second purple band produced purple crystals of **6** (11 mg, 0.017 mmol) after recrystallization from Et_2O. Complex **5**: IR (Nujol) ν(CO) 2057 (s), 2027 (s), 2014 (vs), 1985 (s), 1939 (s), 1905 (w) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.84 (dd, 1 H, H^4), 1.93 (dd, 1 H, H^1), 2.65 (d, 1 H, H^5), 3.16 (d, 1 H, H^2), 5.28 (dd, 1 H, H^3), 5.62 (s, 5 H, Cp), J_{12} = 1.4 Hz, J_{34} = 8.6 Hz, J_{35} = 6.4 Hz, J_{45} = 1.3 Hz; ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.64 (CH^{1}H^2), 58.48 (CH^{4}H^5), 65.28 (CH^3), 66.2, 90.7 (C–C), 211.3, 211.5, 211.6, 218.1, 218.6, 226.3 (W–CO, Fe–CO); MS (FAB) *m/z* 678 (M)$^+$. Anal. Calcd for $C_{19}H_{10}WFe_2O_9$: C, 33.63; H, 1.47. Found: C, 33.52; H, 1.60. Complex **6**: IR (Nujol) ν(CO) 2055 (s), 2021 (vs), 1995 (vs), 1965 (s), 1958 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.80 (s, 1 H, H^1), 3.49 (s, 1 H, H^2), 5.22 (d, 1 H, H^5), 5.26 (s, 5 H), 5.57 (d, 1 H, H^4), 6.79 (dd, 1 H, H^3), J_{34} = 16.5 Hz, J_{35} = 10.0 Hz, J_{45} = 0.5 Hz; MS (FAB) *m/z* 650 (M)$^+$. Anal. Calcd for $C_{18}H_{10}WFe_2O_8$: C, 33.23; H, 1.54. Found: C, 33.42; H, 1.60.

(ii) Method B. A hexane solution (50 mL) of **1** (0.20 g, 0.50 mmol) and $Fe_2(CO)_9$ (0.38 g, 1.0 mmol) was stirred at room temperature for 20 h, and the solution gradually turned brown. After removal of the solvent to dryness, the residues were chromatographed through a long Florisil column with Et_2O/hexane (1:10) as the eluting solvent. Three bands were developed, which were identified as **3** (the first band), **5**, and **6**, respectively. The yields of **3**, **5**, and **6** were 30, 25, and 3%.

(f) Synthesis of $MnFe_2(CO)_{11}(\mu_3\text{-}\eta^1,\eta^3,\eta^3\text{-}CH_2CCCHCH_2)$ (7). Complex **2** (0.401 g, 1.54 mmol) and $Fe_2(CO)_9$ (1.25 g, 3.43 mmol) were stirred at 23 °C for 15 h; during this period the solution gradually turned brown. After removal of the solvent to dryness, the residues were chromatographed through a Florisil column with Et_2O/hexane as the elution solvent. The first orange band off the column was identified as **4**, collected, and concentrated to produce orange solids (0.24 g, 0.50 mmol). The second dark band was further eluted off, to produce dark red block crystals of **7** (0.18 g, 0.33 mmol) after removal of the solvent. IR (Nujol): ν(CO) 2105 (w), 2050 (s), 2025 (vs), 1980 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.87 (dd, 1 H, H^4), 2.29 (d, 1 H, H^1), 2.70 (dd, 1 H, H^5), 2.94 (d, 1 H, H^2), 5.49 (dd, 1 H, H^3), J_{12} = 1.6 Hz, J_{34} = 8.7 Hz, J_{35} = 6.6 Hz, J_{45} = 1.5 Hz. ^{13}C NMR (75 MHz, $CDCl_3$): δ 42.8 (CH^{1}H^2), 57.2 (CH^{4}H^5), 63.8 (CH^3), 73.1, 86.1 (C–C), 208.7, 210.6 (Mn–CO, Fe–CO). MS (FAB): *m/z* 540 (M)$^+$. Anal. Calcd for $C_{16}H_5MnFe_2O_{11}$: C, 35.56; H, 0.93. Found: C, 35.70; H, 1.00.

(g) Synthesis of $CpWRu_2(CO)_8(\mu_3\text{-}\eta^1,\eta^2,\eta^2\text{-}CH_2CCCH{=}CH_2)$ (8). $Ru_3(CO)_{10}(CH_3CN)_2$ (0.35 g, 0.53 mmol) and **1** (0.21 g, 0.53 mmol) were stirred at 23 °C in 10 mL of CH_3CN for 9 h; during this period the mixture gradually turned red. The solution was concentrated and eluted through a silica column with CH_2Cl_2/cyclohexane (3:7) as the eluant. An orange band was collected and evaporated to dryness to afford an orange solid. The residue was purified by using a preparative TLC plate with 10% Et_2O/hexane as the eluant. The crude product was recrystallized from hexane/Et_2O to give orange-red block crystals (0.30 g, 0.35 mmol). IR (Nujol): ν(CO) 2065 (s), 2041 (vs), 2005 (vs), 1995 (vs), 1980 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.17 (s, 1 H, H^1), 3.74 (s, 1 H, H^2), 4.82 (d, 1 H, H^5), 5.02 (d, 1 H, H^4), 5.44 (s, 5 H), 6.55 (dd, 1 H, H^3), J_{34} = 16.4 Hz, J_{35} = 10.5 Hz. ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.1 (CH^{1}H^2), 90.5 (Cp), 112.5 (CH^{4}H^5), 110.8 (R—C=), 143.4 (CH^3), 161.7 (=C=), 194.3, 199.7, 223.3, 225.0, 227.7 (W—CO, Ru—CO). MS (FAB): *m/z* 740 (M)$^+$. Anal. Calcd for $C_{18}H_{10}Ru_2O_8$: C, 29.19; H, 1.35. Found: C, 29.20; H, 1.44.

(h) Synthesis of 9 and 10. $Os_3(CO)_{10}(CH_3CN)_2$ (100 mg, 0.11 mmol) and **1** was stirred in 20 mL of CH_3CN for 4 h; during this period the solution turned dark yellow. After removal of the solvent, the residues were chromatographed through a preparative TLC plate to afford two orange bands of **10** and **12**, respectively. Further recrystallization from CH_2Cl_2/hexane (volume 1:1) produced orange crystals of **9** (40 mg, 0.024 mmol) and **10** (16 mg, 0.013 mmol). Complex **9**: IR (Nujol) ν(CO) 2093 (m), 2058 (vs), 2043 (vs), 2014 (vs), 1997 (s), 1939 (m), 1926 (s), 1846 (w) cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6, 233 K) δ 2.71 (d, 1 H, H^1), 4.70 (d, 1 H, H^5), 4.85 (d, 1 H, H^4), 5.81 (s, Cp), 5.88 (d, 1 H, H^2), 6.60 (dd, 1 H, H^3), J_{12} = 9.1 Hz, J_{34} = 16.4 Hz, J_{35} = 10.2 Hz; ^{13}C NMR (100 MHz, acetone-d_6) δ 11.1 (CH^{1}CH^2), 113.8 (CH^{3}H^5), 121.7, 171.4 (C—C), 145.3 (CH^4), 222.6, 225.5 (W—CO), 212.3 (C=O), 174.0, 175.1, 176.5, 178.0, 178.1, 178.2, 180.8, 181.6, 184.6 (Os—CO); MS (FAB) *m/z* 1251 (M + 1)$^+$. Anal. Calcd for $C_{23}H_{10}WOs_3O_{13}$: C, 22.08; H, 0.80. Found: C, 22.19; H, 0.86. Complex **10**: IR (Nujol) ν(CO) 2111 (w), 2083 (vs), 2055 (vs), 2028 (vs), 2008 (vs), 2001 (vs), 1986 (s), 1924 (s), 1716 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.62 (d, 1 H, H^4), 2.91 (s, 1 H, H^1), 2.99 (s, 1 H, H^2), 5.37 (s, 5 H), 8.02 (d, 1 H, H^3), −18.25 (sattelite, H^5), J_{34} = 6.6 Hz, $J_{Os\text{-}H^5}$ = 37 Hz; ^{13}C NMR (100 MHz, $CDCl_3$) δ −9.1 (CH^4), 26.0 (CH^{1}H^2), 57.8, 109.8 (C—C), 122.2 (CH^3), 216.2, 217.8 (W—CO), 166.7, 167.7, 169.8, 170.3, 173.1, 178.3, 178.9, 185.6, 187.7 (Os—CO), 243.1 (W—(C=O)–); MS (FAB) *m/z* 1251 (M + 1)$^+$. Anal. Calcd for $C_{23}H_{10}WOs_3O_{13}$: C, 22.08; H, 0.80. Found: C, 22.20; H, 0.87.

(i) X-ray Diffraction. A single crystal of each **3**, **5**, **8**, and **10** 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 method; all data reduction and structure refinements were performed with the NRCCSDP package. Crystal data and details of the data collection and structure analysis are summarized in Table V. 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.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond distances and angles, and crystal data and labeled diagrams for **3**, **5**, **8**, and **10** (23 pages); listings of structure factors for **3**, **5**, **8**, and **10** (53 pages). Ordering information is given on any current masthead page.