Experimental Section

The compound $Os_3H_2(CO)_{10}$ (**1**),[15] the adducts $Os_3H_2(CO)_{10}L$ (L = CO (**2a**), PPh_3 (**2b**), $AsPh_3$ (**2c**)),[2,3] and the substituted product $Os_3H_2(CO)_9PPh_3$[3] (**1b**) were synthesized according to literature procedures and their identities confirmed by IR and ^1H NMR spectroscopy on a Perkin-Elmer 580B and a Jeol GX-270-89 spectrometer, respectively. Elemental analysis of **1c**, namely $Os_3H_2(CO)_9(AsPh_3)$, has been obtained in our laboratories.

Compound **1c** has been obtained in almost quantitative yield by heating a *n*-hexane solution of **2c** at reflux for 2 h under nitrogen. Compound **1c** was crystallized from a hexane/dichloromethane (9:1) mixture.

Anal. Calcd for $C_{27}H_{17}O_9AsOs_3$: C, 28.66; H, 1.50; Os, 50.47. Found: C, 28.91; H, 1.65; Os, 50.34. IR (ν_{CO}, hexane): 2108 (m), 2070 (s), 2055 (s), 2028 (vs), 2020 (s), 2009 (s), 1999 (s), 1986 (m), 1975 (m) cm^{-1}. ^1H NMR (δ/ppm; $CDCl_3$): 7.50–7.39 (Ph, 15, m), −10.35 (hydrides, 2, s).

The ESR spectra were obtained from a Bruker 200 D-SCR instrument operating at 9.78 GHz (X-band) equipped with a variable-temperature ER 411 VT unit.

Voltammetric and polarographic measurements were performed with two sets of instrumentation: a PAR 273 electrochemical analyzer connected to an interfaced IBM microcomputer and a BAS 100 electrochemical analyzer.

A three-electrode cell was designed to allow the tip of the reference electrode (SCE) to closely approach the working electrode. Compensation for the *iR* drop was applied through a positive-feedback device. All measurements were carried out under nitrogen in anhydrous deoxygenated solvents. Solution concentrations were 1×10^{-3} M for the compounds under study and 1×10^{-1} M for the supporting electrolyte, $[Et_4N][ClO_4]$. The temperature of the solution was kept constant (±1 °C), by circulation of a thermostated water/ethanol mixture through a jacketed cell. The working electrode was a Pt-disk (area ca. 0.8 mm^2) or mercury dropping (DME) or hanging (HMDE) electrode. Potential data (vs SCE) were checked against the ferrocene (0/1+) couple, under the actual experimental conditions the ferrocene/ferrocenium couple is located at +0.51 in acetone and +0.49 V in dichloromethane.

The number of electrons transferred (n) was determined by controlled-potential coulometry at a Pt basket or at a mercury pool. The working potential (E_w) for the reduction process was 0.1 V negative of the corresponding electrode potential (E_p); all coulometric experiments were done in duplicate.

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[15] Knox, S. A. R.; Koepke, J. W.; Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3942.

Reactions of Molybdenum– and Tungsten–Propargyl Compounds with Iron and Ruthenium Carbonyls. Synthesis and Reactivity of Heteronuclear Metal–μ-Allenyl Complexes

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Reactions of transition-metal–propargyl complexes $L_nMCH_2C{\equiv}CR$ (L_nM = $(CO)_3CpMo$, R = Me (**1a**), Ph (**1b**); L_nM = $(CO)_3CpW$, R = Me (**1c**), Ph (**1d**), *p*-MeC_6H_4 (**1e**); L_nM = $(CO)_3Cp'W$ ($Cp' \equiv \eta^5$-C_5H_4Me), R = Ph (**1f**), *p*-MeC_6H_4 (**1g**); L_nM = $(CO)_3IndW$ ($Ind \equiv \eta^5$-C_9H_7), R = Ph (**1h**)) with $Fe_2(CO)_9$ or $M'_3(CO)_{12}$ provide the new heteronuclear metal μ-allenyls $(CO)_3Fe(\mu$-η^2,η^3-$RC{=}C{=}CH_2)MCp(or\ Ind)(CO)_2$ (**2**) and $(CO)_6M'_2(\mu_3$-η^1,η^2,η^2-$RC{=}C{=}CH_2)MCp(CO)_2$ (M′ = Fe (**3**), Ru (**4**)). These new products were characterized by a combination of elemental analysis, mass spectrometry, and IR and ^1H and ^{13}C NMR spectroscopy; the structures of **2e**, **3d**, and **4** were determined by single-crystal X-ray analysis. Crystallographic parameters are as follows: **2e** $P2_1/n$, a = 17.259 (5) Å, b = 8.184 (3) Å, c = 26.920 (7) Å, β = 90.65 (2)°, Z = 8, R = 0.030, R_w = 0.038 for 6533 independent reflections with $I > 3\sigma(I)$; **3d** $P2_1/c$, a = 12.185 (5) Å, b = 12.754 (7) Å, c = 15.418 (9) Å, β = 111.87 (4)°, Z = 4, R = 0.029, R_w = 0.041 for 4896 independent reflections with $I > 3\sigma(I)$; **4** $P2_1/n$, a = 9.936 (7) Å, b = 18.98 (2) Å, c = 11.752 (8) Å, β = 93.12 (6)°, Z = 4, R = 0.053, R_w = 0.061 for 2669 independent reflections with $I > 3\sigma(I)$. Compounds **2** represent rare examples of binuclear metal μ-η^2,η^3-allenyls, with **2e** featuring a remarkably sharp angle about the central allenyl carbon (128.9 (6)°). Compounds **3** and **4** are the first reported examples of heterotrinuclear metal–μ_3-η^1,η^2,η^2-allenyl clusters. Reactivity of **2**–**4** toward metal framework expansion, addition of unsaturated compounds, protonation, substitution of CO, and oxidation with I_2 is presented.

Introduction

While heteronuclear metal complexes containing μ-hydrocarbyl ligands represent an important and rapidly growing class of compounds,[1] the synthetic methodology used to prepare these compounds has not been well developed.[2] We have therefore investigated the use of

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[1] General reviews: (a) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Chapter 40. (b) Geoffroy, G. L. In *Metal Clusters in Catalysis*; Gates, B. C., Guczi, L., Knozinger, H., Eds.; Elsevier: New York, 1986; Chapter 1. (c) Vargas, M. D.; Nicholls, J. N. *Adv. Inorg. Chem. Radiochem.* **1987**, *30*, 123. (d) Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169.

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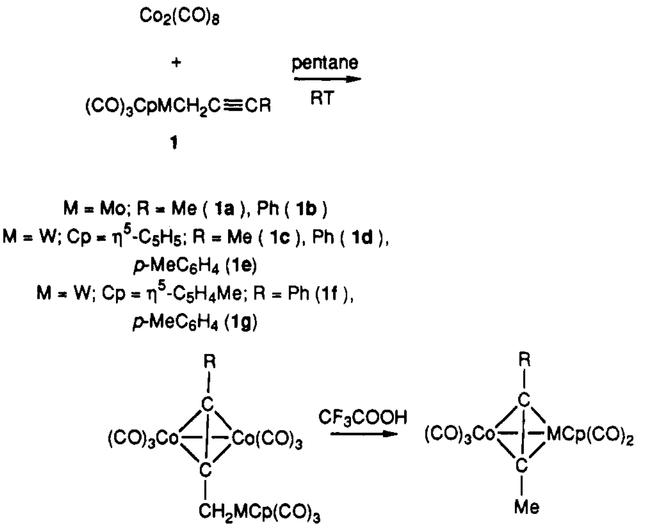
Scheme I



transition-metal–propargyl complexes, $L_nMCH_2C{\equiv}CR$ (1), as reagents for practical synthesis of various types of such heteronuclear organometallics.[3-6]

The crux of our synthetic strategy has been the use of the alkyne functionality of the propargyl complex as a molecular template to bring heterometallic nuclei into close proximity, thereby facilitating the formation of mixed metal–metal bonds. As an illustration, we recently reported[3] the synthesis of heterobinuclear CoMo and CoW μ-alkyne complexes by protonation of the alkyne-templated trinuclear Co_2Mo and Co_2W compounds, respectively (cf. Scheme I).

Described herein is the facile, one-step synthesis of the heterobinuclear and -trinuclear metal–μ-allenyl complexes $(CO)_3Fe(\mu$-η^2,η^3-$RC{=}C{=}CH_2)MCp(\text{or Ind})(CO)_2$ (2 M = Mo, W, Ind $\equiv$ η^5-C_9H_7) and $(CO)_6M'_2(\mu_3$-η^1,η^2,η^2-$RC{=}C{=}CH_2)MCp(CO)_2$ (3 M = Mo, W, M′ = Fe, 4 M = W, M′ = Ru), respectively, by the reactions of 1 with $Fe_2(CO)_9$ or $M'_3(CO)_{12}$ (M′ = Fe, Ru). The reactivity of 2–4 and the single-crystal X-ray structures of **2e**, **3d**, and **4** will be discussed. Parts of this study have been previously communicated.[4]

Experimental Section

General Procedures and Measurements. All reactions and manipulations of air-sensitive compounds were carried out under an atmosphere of Ar by using standard procedures.[7] Elemental analyses were performed by either Desert Analysis, Tucson, AZ, or M-H-W Laboratories, Phoenix, AZ. Chromatographic separations were effected on columns packed with Florisil (60-100 mesh). Melting points were measured on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared (IR) spectra were collected on a Perkin-Elmer Model 337 spectrophotometer and were calibrated with polystyrene. ^1H NMR spectra were recorded on a Bruker AM-250 spectrometer. ^{13}C NMR spectra were recorded by Mr. Carl Engelman on a Bruker AM-250 spectrometer or by Dr. Charles Cottrell on a Bruker AM-500 spectrometer. Electron impact (EI) and fast atom bombardment (FAB) mass spectra were recorded on Kratos MS-30 and VG70-250S spectrometers, respectively, by Mr. C. R. Wisenberger or Mr. David C. Chang.

Materials. All solvents were purified by distillation under an Ar atmosphere. Pentane was distilled from Na/K alloy, THF and diethyl ether were distilled from Na/K and benzophenone, and dichloromethane was distilled from P_4O_{10}.

Reagents were obtained from various commercial sources and used as received, except as noted below. Trimethylamine *N*-oxide (Me_3NO) was obtained from Aldrich and sublimed prior to use. The carbonyls $Fe_2(CO)_9$,[8] $Fe_3(CO)_{12}$,[9] and $Ru_3(CO)_{12}$[10] were synthesized according to the literature. The propargyl complexes $(CO)_3CpMoCH_2C{\equiv}CMe$ (**1a**),[11] $(CO)_3CpMoCH_2C{\equiv}CPh$ (**1b**),[11] $(CO)_3CpWCH_2C{\equiv}CMe$ (**1c**),[11] and $(CO)_3CpWCH_2C{\equiv}CPh$ (**1d**)[12] were prepared by literature procedures and $(CO)_3CpWCH_2C{\equiv}CC_6H_4Me$-$p$ (**1e**),[3b] $(CO)_3Cp'WCH_2C{\equiv}CPh$ (Cp′ ≡ C_5H_4Me) (**1f**),[3b] and $(CO)_3Cp'WCH_2C{\equiv}CC_6H_4Me$-$p$ (**1g**)[3b] by close adaptations of literature procedures using the reaction of either $CpW(CO)_3^-$ or $Cp'W(CO)_3^-$ with the appropriate propargyl bromide.

The previously unreported complex $(CO)_3IndWCH_2C{\equiv}CPh$ (Ind ≡ η^5-indenyl (C_9H_7)) (**1h**) was obtained in 36% yield as an orange-yellow solid, mp 80 °C dec, by reaction of $[IndW(CO)_3]_2Hg$[13] with Na/K in THF, followed by slow addition of phenylpropargyl bromide to the resulting solution of $IndW(CO)_3^-$ at −78 °C. IR (cm^{-1}, pentane): ν(CO) 2019 (s), 1946 (vs), 1937 (s). ^1H NMR ($CDCl_3$): δ 7.50–7.20 (m, 9 H, Ph and C_4H_4 of C_9H_7), 5.85 (d, J = 2.88 Hz, 2 H, C_3H_3 of C_9H_7), 5.60 (t, J = 2.88 Hz, 1 H, C_3H_3 of C_9H_7), 1.28 (s, 2 H, CH_2). Anal. Calcd for $C_{21}H_{14}O_3W$: C, 50.63; H, 2.83. Found: C, 50.75; H, 2.90.

Reactions of Transition-Metal–Propargyl Complexes with $Fe_2(CO)_9$. These reactions were carried out as room-temperature pentane or THF suspensions of $Fe_2(CO)_9$ with ca. 1:1, 2:1, or 2:3 molar ratios of the transition-metal–propargyl compound and the iron carbonyl. Unless otherwise noted, the reactions described below were conducted in pentane by using 1:1 relative amounts of reactants. A detailed description of the 1:1 molar ratio reaction between $(CO)_3CpWCH_2C{\equiv}CPh$ (**1d**) and $Fe_2(CO)_9$ is provided to illustrate the procedure. In those cases where a different ratio of reactants was used, the same procedure and workup were followed. Percent yields, physical properties, mass spectra, and analytical data for all isolated products are given below. The IR and NMR data for 2–4 are presented in Table I.

(i) $(CO)_3CpWCH_2C{\equiv}CPh$ (1d). To a stirred, room-temperature solution of **1d** (0.302 g, 0.674 mmol) in pentane (50 mL) was added $Fe_2(CO)_9$ (0.245 g, 0.674 mmol) as a solid. The resulting suspension was stirred for 14 h, during which time the reaction mixture turned dark green and then orange. Stirring was then discontinued, and the mixture was allowed to settle. The orange solution was decanted away by cannula from a minor amount of a green-brown precipitate (0.038 g), which displayed no IR ν(CO) absorptions or ^1H NMR resonances and which was insoluble in common organic media. This precipitate is formed in all reactions of 1 with $Fe_2(CO)_9$. The decantate was concentrated in vacuo to provide a dark orange solid, which was dissolved in CH_2Cl_2 (2.5 mL) and introduced onto a Florisil column packed in pentane. Pentane elution provided a yellow band, which was concentrated to give a trace of $Fe(CO)_5$. Elution with a 2% solution of diethyl ether in pentane gave a large orange band, which was collected

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(2) Selected examples: (a) Stone, F. G. A.; Williams, M. L. *J. Chem. Soc., Dalton Trans.* **1988**, 2467 and cited papers by Stone et al. (b) Burn, M. J.; Kiel, G.-Y.; Seils, F.; Takats, J.; Washington, J. *J. Am. Chem. Soc.* **1989**, *111*, 6850. (c) Mackenzie, P. B.; Coots, R. J.; Grubbs, R. H. *Organometallics* **1989**, *8*, 8. (d) Seyferth, D.; Womack, G. B.; Archer, C. M.; Dewan, J. C. *Ibid.* **1989**, *8*, 430. (e) Ewing, P.; Farrugia, L. J. *Ibid.* **1989**, *8*, 1246. (f) Lukehart, C. M.; True, W. R. *Ibid.* **1988**, *7*, 2387. (g) Chetcuti, M. J.; Green, K. A. *Ibid.* **1988**, *7*, 2450. (h) Alvarez-Toledano, C.; Parlier, A.; Rose-Munch, F.; Rudler, H.; Daran, J. C.; Knobler, C.; Jeannin, Y. *J. Organomet. Chem.* **1987**, *323*, 371. (i) Jensen, S. D.; Robinson, B. H.; Simpson, *J. Organometallics* **1986**, *5*, 1690. (j) Jaouen, G.; Marinetti, A.; Mentzen, B.; Mutin, R.; Saillard, J.-Y.; Sayer, B. G.; McGlinchey, M. J. *Ibid.* **1982**, *1*, 753. (k) Aime, S.; Milone, L.; Osella, D.; Tiripicchio, A.; Lanfredi, A. M. *Inorg. Chem.* **1982**, *21*, 505.

(3) (a) Wido, T. M.; Young, G. H.; Wojcicki, A.; Calligaris, M.; Nardin, G. *Organometallics* **1988**, *7*, 452. (b) Young, G. H.; Wojcicki, A. *J. Organomet. Chem.* **1990**, *390*, 351.

(4) Young, G. H.; Wojcicki, A.; Calligaris, M.; Nardin, G.; Bresciani-Pahor, N. *J. Am. Chem. Soc.* **1989**, *111*, 6890.

(5) Shuchart, C. E.; Young, G. H.; Wojcicki, A.; Calligaris, M.; Nardin, G. *Organometallics* **1990**, *9*, 2417.

(6) Wojcicki, A.; Shuchart, C. E. *Coord. Chem. Rev.* **1990**, *105*, 35.

(7) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

(8) Braye, E. H.; Hübel, W. *Inorg. Synth.* **1966**, *8*, 178.

(9) McFarlane, W.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 181.

(10) Johnson, B. F. G.; Lewis, J. *Inorg. Synth.* **1972**, *13*, 92.

(11) Roustan, J.-L.; Charrier, C. *C.R. Seances Acad. Sci., Ser. C* **1969**, *268*, 2113.

(12) Kroll, J. O.; Wojcicki, A. *J. Organomet. Chem.* **1974**, *66*, 95.

(13) Nesmeyanov, A. N.; Ustynyuk, N. A.; Mararova, L. G.; Andre, S.; Ustynyuk, Yu. A.; Novikova, L. N.; Luzikov, Yu., N. *J. Organomet. Chem.* **1978**, *154*, 45.

Table I. IR and NMR Data for Heteronuclear Metal–μ-Allenyl Complexes 2–4[a]

complex	IR, ν(CO),[b] cm^{-1}	^{1}H NMR,[c] δ	^{13}C{^{1}H} NMR,[c,d] δ
2a	2036 (s), 2020 (m), 1995 (vs), 1972 (s), 1959 (vs), 1949 (m), 1938 (m), 1921 (w)	5.28 (s, 5 H, Cp), 4.48, 3.65 (2s, 2 H, =CH$_2$), 2.73 (s, 3 H, Me)	226.45, 225.48 (MoCO's), 212.00 (FeCO's), 93.08 (=*C*(Me)Fe), 92.07 (=C=), 90.60 (Cp), 67.24 (=CH$_2$), 20.78 (Me)
2b	2045 (br m), 1993 (vs), 1975 (s), 1965 (vs), 1951 (w)	7.28 (s, 5 H, Ph), 5.24 (s, 5 H, Cp), 4.73, 3.95 (2s, 2 H, =CH$_2$)	228.6, 226.4 (MoCO's), 214.0, 211.3, 206.3 (FeCO's), 142.7 (ipso-C of Ph), 129.5, 128.6, 126.6 (o-, m-, and p-C's of Ph), 120.1 (=C=), 92.4 (Cp), 83.1 (=*C*(Ph)Fe), 70.0 (=CH$_2$)
2c[e]	2033 (s), 1994 (vs), 1969 (s), 1955 (s), 1939 (m), 1913 (w)	5.28 (s, 5 H, Cp), 5.10, 3.65 (2s, 2 H, =CH$_2$), 2.95 (s, 3 H, Me)	212.98 (WCO), 212.30 (FeCO's), 209.49 (WCO), 112.3 (=C=), 87.51 (Cp), 84.58 (=*C*(Me)Fe), 67.88 (=CH$_2$, $J_{C\text{-}H}$ = 164 Hz), 19.61 (Me, $J_{C\text{-}H}$ = 130 Hz)
2d	2046 (m), 2036 (s), 1993 (vs), 1973 (s), 1960 (vs), 1946 (m)	7.25 (s, 5 H, Ph), 5.39 (d, J = 0.7 Hz, 1 H, =CH$_2$), 5.32 (s, 5 H, Cp), 3.99 (d, J = 0.7 Hz, 1 H, =CH$_2$)	213.30 (WCO, $J_{W\text{-}C}$ = 166 Hz[f]), 211.67 (FeCO's), 210.03 (WCO, $J_{W\text{-}C}$ = 173 Hz), 142.35 (ipso-C of Ph), 129.51, 128.83, 126.67 (o-, m-, and p-C's of Ph), 111.76 (=C=, $J_{W\text{-}C}$ = 34 Hz), 88.69 (Cp), 80.50 (=*C*(Ph)Fe), 70.53 (=CH$_2$)
2e	2054 (vs), 2012 (vs), 1997 (vs), 1983 (m), 1966 (m), 1952 (m), 1914 (w)	7.05 (s, 4 H, Ar), 5.36 (s, 1 H, =CH$_2$), 5.31 (s, 5 H, Cp), 3.46 (s, 1 H, =CH$_2$), 2.36 (s, 3 H, Me)	213.54 (WCO), 211.76 (FeCO's), 210.74 (WCO), 138.89, 136.56 (ipso-C's of Ar), 129.43, 129.06, (other C's of Ar), 111.80 (=C=), 88.61 (Cp), 81.24 (=*C*(Ar)Fe), 70.39 (=CH$_2$), 21.11 (Me)
2f	2054 (vs), 2010 (vs), 1996 (s) 1983 (m), 1967 (m), 1953 (m)	7.24–7.10 (m, 5 H, Ph), 5.38 (s, 1 H, =CH$_2$), 5.31–5.11 (m, 4 H, ring H's of Cp′), 4.01 (s, 1 H, =CH$_2$), 2.20 (s, 3 H, Me)	215.17, 214.68 (WCO's), 211.81 (FeCO's), 142.43 (ipso-C of Ph), 129.46, 128.26 126.50 (o-, m-, and p-C's of Ph), 111.78 (=C=), 106.5 (ipso-C of Cp′), 92.37, 90.47, 90.01, 89.19 (other C's of Cp′), 80.09 (=*C*(Ph)Fe), 70.07 (=CH$_2$), 14.33 (Me)
2g	2042 (m), 2031 (m), 1996 (vs), 1989 (s), 1969 (s), 1957 (s), 1941 (m), 1911 (w)	7.08 (s, 4 H, Ar), 5.27, 5.19, 5.15, 5.09 (4 m, 4 H, ring H's of Cp′), 5.34, 3.98 (2 s, 2 H, =CH$_2$), 2.36 (s, 3 H, Ar*Me*), 2.20 (s, 3 H, Cp*Me*)	214.78, 212.12 (WCO's), 211.86 (FeCO's), 139.02 (Ar C ipso to C=C), 136.36 (Ar C ipso to Me), 129.39, 129.01 (Ar ring C's), 111.83 (=C=), 106.06 (ipso C of Cp′), 92.35, 90.11, 89.25, 88.70 (other C's of Cp′), 80.77 (=*C*(Ar)Fe), 69.91 (=CH$_2$), 21.09 (Ar*Me*), 13.84 (Cp*Me*)
2h	2043 (s), 1996 (sh), 1988 (s), 1984 (sh), 1958 (m)	7.30–7.10 (m, 9 H, Ph and C_4H_4 of C_9H_7), 5.84 (d, J = 2.4 Hz, 2 H, C_3H_3 of C_9H_7), 5.46 (t, J = 2.4 Hz, 1 H, C_3H_3 of C_9H_7), 5.32, 4.01 (2 s, 2 H, =CH$_2$)	
3b	2085 (w), 2061 (s), 2049 (s), 2024 (m), 2002 (s), 1986 (vs), 1964 (s), 1945 (w), 1908 (w)	7.25–7.16 (m, 5 H, Ph), 5.64 (s, 5 H, Cp), 2.99, 2.38 (2 s, 2 H, =CH$_2$)	
3c	2071 (s), 2036 (s), 2001 (vs), 1989 (s), 1971 (s), 1950 (w)	5.57 (s, 5 H, Ph), 3.47, 3.00 (2 s, 2 H, =CH$_2$), 2.37 (s, 3 H, Me)	
3d	2052 (s), 2020 (vs), 1966 (s), 1984 (m), 1963 (m), 1951 (w)	7.75–7.71, 7.51–7.45, 7.36–7.26 (3 m, 5 H, Ph), 5.06 (s, 5 H, Cp), 3.44, 2.86 (2 d, J = 1.1 Hz, 2 H, =CH$_2$)	223.93, 221.10 (WCO's), 211.53 (FeCO's), 155.86 (=C=, $J_{W\text{-}C}$ = 43 Hz), 145.15 (ipso-C of Ph), 128.98, 128.58, 126.45 (o-, m-, and p-C's of Ph), (=*C*(Ph)Fe not seen), 91.50 (Cp), 27.80 (=CH$_2$)
3e	2053 (s), 2009 (vs), 1996 (s), 1985 (m), 1967 (m), 1951 (m)	7.63–7.61, 7.16–7.13 (2 m, 4 H, Ar), 5.05 (s, 5 H, Cp), 3.39, 2.84 (2 s, 2 H, =CH$_2$), 2.42 (s, 3 H, Me)	
3f	2053 (s), 2009 (vs), 1991 (s), 1973 (s), 1953 (s), 1945 (s)	7.74–7.69, 7.54–7.44, 7.36–7.30 (3 m, 5 H, Ph), 4.71–4.66, 4.27–4.20 (2 m, 4 H, ring H's of Cp′), 3.43, 2.81 (2 d, J = 0.4 Hz, 2 H, =CH$_2$), 2.19 (s, 3 H, Me)	223.91, 214.45 (WCO's), 211.63 (FeCO's), 156.68 (=C=), 145.04 (ipso-C of Ph), 136.36 (=*C*(Ph)Fe), 130.88, 130.24, 126.53 (o-, m-, and p-C's of Ph), 109.03 (ipso-C of Cp′), 92.51, 91.66, 90.44, 88.86 (other C's of Cp′), 26.99 (CH$_2$), 14.04 (Me)
3g	2052 (s), 2010 (s), 1996 (m), 1983 (m), 1966 (m), 1954 (m)	7.64–7.61, 7.25–7.13 (2 m, 4 H, ring H's of Ar), 5.50–4.89 (m, ring H's of Cp′), 3.17, 2.32 (2 s, 2 H, =CH$_2$), 2.36 (s, 3 H, Ar*Me*), 2.16 (s, 3 H, Cp*Me*)	
4	2067 (s), 2032 (s), 2005 (s), 1998 (m), 1981 (m), 1967 (m)	7.65–7.59, 7.44–7.38, 7.27–7.24 (3 m, 5 H, Ph), 5.03 (s, 5 H, Cp), 3.71 (s, $J_{W\text{-}H}$ = 6.5 Hz, 1 H, =CH$_2$), 3.26 (s, 1 H, =CH$_2$)	225.25, 222.28 (WCO's), 201.79, 198.74, 196.06, 195.13, 192.67 (RuCO's), 161.59 (=C=, $J_{W\text{-}C}$ = 45 Hz), 146.04 (ipso-C of Ph), 128.80, 128.00, 126.86 (o-, m-, and p-C's of Ph), 114.09 (=*C*(Ph)Ru), 90.92 (Cp), 26.99 (=CH$_2$)

[a] At room temperature. [b] In pentane (**2h**) or cyclohexane (other complexes) solution. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; br, broad. [c] In CDCl$_3$ solution. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. [d] Some assignments required the use of 2D ^{13}C{^{1}H}–^{1}H correlation NMR. [e] ^{13}C NMR (proton-coupled) spectrum. [f] ^{183}W isotope.

and concentrated to yield (CO)$_3$Fe(μ-η^2,η^3-PhC=C=CH$_2$)WCp(CO)$_2$ (**2d**) (0.101 g, 28%) as an air-stable orange solid: mp 144 °C; mass spectrum (EI), ^{184}W isotope, m/z (ion, relative intensity) 560 (M$^+$, 20), 532 (M$^+$ – CO, 40), 504 (M$^+$ – 2CO, 100), 476 (M$^+$ – 3CO, 58). Anal. Calcd for $C_{19}H_{12}FeO_5W$: C, 40.75; H, 2.16. Found: C, 41.04; H, 1.99. Elution with a 1:1 mixture of diethyl ether in pentane gave a yellow band, which was collected and concentrated to afford an uncharacterized yellow oil (0.021 g, 5% based on mass spectrum, M$^+$ = 672): IR ν(CO) (cm^{-1}, cyclohexane) 2052 (m), 2022 (s), 2005 (s), 1955 (m), 1942 (m); ^{1}H NMR (CDCl$_3$) δ 7.45–7.31, 7.18–7.14 (2 m, 5 H, Ph), 5.30 (s, 5 H, Cp), 2.50 (s, 2 H, CH$_2$); mass spectrum (FAB), ^{184}W isotope, m/z (ion, relative intensity) 673 (51), 644 (21), 617 (20), 589 (24), 561 (22), 532 (22), 505 (31), 476 (20), 448 (18), 420 (45). Elution with diethyl ether gave a purple band, which was concentrated, and the resulting solid was recrystallized from 1:1 CH$_2$Cl$_2$/pentane to yield (CO)$_6$Fe$_2$(μ_3-η^1,η^2,η^2-PhC=C=CH$_2$)WCp(CO)$_2$ (**3d**) (0.030 g, 5%) as dark purple air-stable plates: mp 177 °C dec; mass spectrum

(FAB), ^{184}W isotope, *m/z* (ion, relative intensity) 700 (M^+, 10), 672 (M^+ – CO, 11), 644 (M^+ – 2CO, 34), 616 (M^+ – 3CO, 28), 588 (M^+ – 4CO, 100), 560 (M^+ – 5CO, 81), 532 (M^+ – 6CO, 21), 504 (M^+ – 7CO, 15). Anal. Calcd for $C_{22}H_{12}O_8Fe_2W$: C, 37.75; H, 1.73. Found: C, 37.22; H, 1.51.

By use of the same ratio of reactants, procedure, and workup as above but with THF (60 mL) as solvent, the reaction of **1d** with $Fe_2(CO)_9$ provided $Fe(CO)_5$ (0.061 g), **2d** (0.109 g, 54%), and the same yellow compound as above (0.069 g, 14%), as ascertained by ^{1}H NMR spectroscopy.

Employing a 2:1 molar ratio of **1d** relative to $Fe_2(CO)_9$ at room temperature in THF solution (30 mL) gave $Fe(CO)_5$ (0.069 g), **2d** (0.086 g, 43%), and a trace amount of the yellow compound.

(ii) $(CO)_3$CpMoCH$_2$C≡CMe (1a). Product $(CO)_3Fe(\mu$-η^2,η^3-MeC=C=CH$_2$)MoCp$(CO)_2$ (**2a**) was obtained in 36% yield as a slightly air-sensitive light orange solid: mp 99 °C dec; mass spectrum (EI), ^{98}Mo isotope, *m/z* (ion, relative intensity) 412 (M^+, 4), 384 (M^+ – CO, 12), 356 (M^+ – 2CO, 23), 328 (M^+ – 3CO, 19), 298 (M^+ – 2 – 4CO, 46), 270 (M^+ – 2 – 5CO, 100). $(CO)_6Fe_2(\mu_3$-η^1,η^2,η^2-MeC=C=CH$_2$)MoCp$(CO)_2$ (**3a**) was obtained in 7% yield as a dark purple oil, which could not be induced to crystallize.

With the same reaction conditions and workup procedure, but with a 2:1 molar ratio of **1a** relative to $Fe_2(CO)_9$, **2a** was isolated in 93% yield as the sole product.

(iii) $(CO)_3$CpMoCH$_2$C≡CPh (1b). Product $(CO)_3Fe(\mu$-η^2,η^3-PhC=C=CH$_2$)MoCp$(CO)_2$ (**2b**) was isolated in 70% yield as a slightly air-sensitive light orange solid: mp 142 °C dec; mass spectrum (FAB), ^{98}Mo isotope, *m/z* (ion, relative intensity) 474 (M^+, 33), 446 (M^+ – CO, 50), 418 (M^+ – 2CO, 100), 390 (M^+ – 3CO, 68), 362 (M^+ – 4CO, 83), 334 (M^+ – 5CO, 83). $(CO)_6Fe_2(\mu_3$-η^1,η^2,η^2-PhC=C=CH$_2$)MoCp$(CO)_2$ (**3b**) was isolated in 2% yield as a dark purple air-sensitive oil, which could not be induced to crystallize.

(iv) $(CO)_3$CpWCH$_2$C≡CMe (1c). Product $(CO)_3Fe(\mu$-η^2,η^3-MeC=C=CH$_2$)WCp$(CO)_2$ (**2c**) was obtained in 15% yield as a slightly air-sensitive light orange solid: mp 118 °C; mass spectrum (EI), ^{184}W isotope, *m/e* (ion, relative intensity) 498 (M^+, 35), 470 (M^+ – CO, 62), 442 (M^+ – 2CO, 81), 416 (M^+ + 2 – 3CO, 48), 385 (M^+ – 1 – 4CO, 100), 358 (M^+ – 5CO, 51). $(CO)_6Fe_2(\mu_3$-η^1,η^2,η^2-PhC=C=CH$_2$)WCp$(CO)_2$ (**3c**) was isolated in 4% yield as a slightly air-sensitive purple solid.

(v) $(CO)_3$IndWCH$_2$C≡CPh (1h). Product $(CO)_3Fe(\mu$-η^2,η^3-PhC=C=CH$_2$)WInd$(CO)_2$ (**2h**) was isolated in 65% yield as an orange-red solid, mp 115–118 °C. Anal. Calcd for $C_{23}H_{14}FeO_5W$: C, 45.28; H, 2.31. Found: C, 45.45; C, 2.25. No trinuclear metal complex was obtained.

Reactions of Transition-Metal–Propargyl Complexes with $M'_3(CO)_{12}$ (M' = Fe, Ru). These reactions were carried out in benzene at reflux with a 1:1 molar ratio of the transition-metal–propargyl compound (1) and either $Fe_3(CO)_{12}$ or $Ru_3(CO)_{12}$. A detailed description of the reaction between $Fe_3(CO)_{12}$ and $(CO)_3$CpWCH$_2$C≡CPh (**1d**) is provided to illustrate the procedure. Other preparation and purification procedures were carried out in a strictly analogous fashion unless otherwise noted. Percent yields, physical properties, mass spectra, and analytical data for all isolated products not already listed are given below. The IR and NMR data for new compounds prepared in this manner are presented in Table I.

(i) $(CO)_3$CpWCH$_2$C≡CPh (1d) with $Fe_3(CO)_{12}$. A mixture of $Fe_3(CO)_{12}$ (0.504 g, 1.00 mmol) and $(CO)_3$CpWCH$_2$C≡CPh (**1d**) (0.448 g, 1.00 mmol) in benzene (50 mL) at reflux was stirred for 24 h. The solution was cooled to room temperature, and solvent was removed with the aid of a warm (35 °C) water bath. The resultant black residue was dissolved in CH_2Cl_2 (2 mL) and introduced onto a Florisil column (2 × 20 cm) packed with pentane. Elution with a 2% solution of diethyl ether in pentane gave a small orange band that provided $(CO)_3Fe(\mu$-η^2,η^3-PhC=C=CH$_2$)-WCp$(CO)_2$ (**2d**) (0.046 g, 5%) upon concentration. A large purple band collected with diethyl ether eluent afforded $(CO)_6Fe_2(\mu_3$-η^1,η^2,η^2-PhC=C=CH$_2$)WCp$(CO)_2$ (**3d**) (0.175 g, 25%) upon concentration.

(ii) $(CO)_3$CpWCH$_2$C≡CC$_6$H$_4$Me-*p* (1e) with $Fe_3(CO)_{12}$. Product $(CO)_3Fe(\mu$-η^2,η^3-*p*-MeC$_6$H$_4$C=C=CH$_2$)WCp$(CO)_2$ (**2e**) was obtained in 34% yield as orange air-stable needles upon recrystallization from a 1:1 mixture of CH_2Cl_2 and pentane: mp 148 °C; mass spectrum (EI), ^{184}W isotope, *m/z* (ion, relative intensity) 574 (M^+, 3), 546 (M^+ – CO, 9), 518 (M^+ – 2CO, 18), 490 (M^+ – 3CO, 16), 462 (M^+ – 4CO, 57), 434 (M^+ – 5CO, 61), 376 (M^+ – 2 – 5CO – Fe, 100). Product $(CO)_6Fe_2(\eta_3$-η^1,η^2,η^2-*p*-MeC$_6$H$_4$C=C=CH$_2$)WCp$(CO)_2$ (**3e**) was isolated in 12% yield as air-stable purple plates upon recrystallization from 1:1 CH_2Cl_2/pentane: mp 198 °C dec; mass spectrum (FAB), ^{184}W isotope, *m/z* (ion, relative intensity) 715 (M^+ + 1, 18), 686 (M^+ – CO, 26), 658 (M^+ – 2CO, 59), 630 (M^+ – 3CO, 50), 602 (M^+ – 4CO, 100), 574 (M^+ – 5CO, 50), 546 (M^+ – 6CO, 50), 518 (M^+ – 7CO, 55), 490 (M^+ – 8CO, 64).

(iii) $(CO)_3$Cp'WCH$_2$C≡CPh (1f) with $Fe_3(CO)_{12}$. Product $(CO)_3Fe(\mu$-η^2,η^3-PhC=C=CH$_2$)WCp'$(CO)_2$ (**2f**) was isolated in 27% yield as an orange air-stable solid: mp 123 °C. Anal. Calcd for $C_{20}H_{14}FeO_5W$: C, 41.85; H, 2.46. Found: C, 41.37; H, 2.31. Product $(CO)_6Fe_2(\mu_3$-η^1,η^2,η^2-PhC=C=CH$_2$)WCp'$(CO)_2$ (**3f**) was isolated in 7% yield as an air-stable purple solid: mp 152 °C dec; mass spectrum (FAB), ^{184}W isotope, *m/z* (ion, relative intensity) 714 (M^+, 7), 686 (M^+ – CO, 9), 658 (M^+ – 2CO, 21), 630 (M^+ – 3CO, 14), 602 (M^+ – 4CO, 29), 574 (M^+ – 5CO, 14), 546 (M^+ – 6CO, 7), 518 (M^+ – 7CO, 14), 490 (M^+ – 8CO, 100).

(iv) $(CO)_3$Cp'WCH$_2$C≡CC$_6$H$_4$Me-*p* (1g) with $Fe_3(CO)_{12}$. Product $(CO)_3Fe(\mu$-η^2,η^3-*p*-MeC$_6$H$_4$C=C=CH$_2$)WCp'$(CO)_2$ (**2g**) was obtained in 39% yield as an orange air-stable solid: mp 166 °C; mass spectrum (EI), ^{184}W isotope, *m/z* (ion, relative intensity) 588 (M^+, 3), 560 (M^+ – CO, 10), 532 (M^+ – 2CO, 23), 504 (M^+ – 3CO, 20), 476 (M^+ – 4CO, 68), 448 (M^+ – 5CO, 51), 392 (M^+ – 5CO – Fe, 100). Trinuclear $(CO)_6Fe_2(\mu_3$-η^1,η^2,η^2-*p*-MeC$_6$H$_4$C=C=CH$_2$)WCp'$(CO)_2$ (**3g**) was isolated in 4% yield as an air-stable purple solid: mp 178 °C dec; mass spectrum (FAB), ^{184}W isotope, *m/z* (ion, relative intensity) 729 (M^+ + 1, 11), 672 (M^+ – 2CO, 14), 644 (M^+ –3CO, 29), 616 (M^+ – 4CO, 71), 588 (M^+ – 5CO, 67), 503 (M^+ – 1 – 8CO, 100).

(v) $(CO)_3$CpMoCH$_2$C≡CMe (1a) with $Fe_3(CO)_{12}$. Chromatography of the crude reaction mixture on Florisil eluting with pentane gave a yellow band, which was concentrated to give a trace amount of an unidentified yellow solid: ^{1}H NMR ($CDCl_3$) δ 5.26, 4.16 (2 s, 2 H, CH$_2$), 5.23 (s, 5 H, Cp), 2.48 (s, 3 H, Me). Elution with a 2% solution of diethyl ether in pentane provided $Cp_2Mo_2(CO)_6$ (82%), which was identified by comparison of its IR and ^{1}H NMR spectra with those of an authentic sample.

(vi) $(CO)_3$CpMoCH$_2$C≡CPh (1b) with $Fe_3(CO)_{12}$. Product $(CO)_3Fe(\mu$-η^2,η^3-PhC=C=CH$_2$)MoCp$(CO)_2$ (**2b**) was obtained in 40% yield along with $Cp_2Mo_2(CO)_6$ (30%).

(vii) $(CO)_3$CpWCH$_2$C≡CPh (1d) with $Ru_3(CO)_{12}$. Pentane elution of the crude reaction mixture on Florisil gave an orange band, which was concentrated to give $Cp_2Ru_2(CO)_4$ (7%), identified by comparison of its IR and NMR spectra with the literature values.[14] Elution with 1:1 diethyl ether/pentane furnished a yellow band, which provided a yellow oil upon concentration. Crystallization of the oil from 1:1 $CHCl_3$/pentane afforded (21%) yellow needles of $(CO)_6Ru_2(\mu_3$-η^1,η^2,η^2-PhC=C=CH$_2$)WCp$(CO)_2$ (**4**): mp 202 °C dec; mass spectrum (FAB), ^{184}W isotope, *m/z* (ion, relative intensity) 790 (M^+ – 2, 14), 763 (M^+ – 1 – CO, 17), 735 (M^+ – 1 – 2CO, 28), 708 (M^+ – 3CO, 41), 680 (M^+ – 4CO, 100), 651 (M^+ – 1 – 5CO, 36), 625 (M^+ + 1 – 6CO, 33), 597 (M^+ + 1 – 7CO, 18), 567 (M^+ – 1 – 8CO, 42). Anal. Calcd for $C_{22}H_{12}O_8Ru_2W$: C, 33.43; H, 1.53. Found: C, 33.74; H, 1.60.

Reactions of $(CO)_3Fe(\mu$-η^2,η^3-RC=C=CH$_2$)MCp$(CO)_2$ (2). (i) With $Fe_2(CO)_9$ in Pentane. A mixture of $(CO)_3Fe(\mu$-η^2,η^3-*p*-MeC$_6$H$_4$C=C=CH$_2$)CpW$(CO)_2$ (**2e**) (0.453 g, 0.789 mmol) and $Fe_2(CO)_9$ (0.291 g, 0.800 mmol) in pentane (60 mL) was stirred at room temperature for 5 days. The resulting orange suspension was concentrated in vacuo to provide an orange solid. The solid was dissolved in CH_2Cl_2 (2 mL), and the solution was introduced onto a Florisil column packed in pentane. Elution with a 2% solution of diethyl ether in pentane gave **2e** (0.119 g, 26%). Elution of the column with diethyl ether afforded $(CO)_6Fe_2(\mu_3$-η^1,η^2,η^2-*p*-MeC$_6$H$_4$C=C=CH$_2$)WCp$(CO)_2$ (**3e**) (0.011 g, 2%).

(ii) With $Fe_2(CO)_9$ in THF. A mixture of $(CO)_3Fe(\mu$-η^2,η^3-*p*-MeC$_6$H$_4$C=C=CH$_2$)WCp$(CO)_2$ (**2e**) (0.219 g, 0.382 mmol) and $Fe_2(CO)_9$ (0.139 g, 0.382 mmol) in THF (30 mL) at reflux was stirred for 24 h. Cooling to room temperature and workup as described immediately above yielded **2e** (0.157 g, 73%) and

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[14] Humphries, A. P.; Knox, S. A. R. *J. Chem. Soc., Dalton Trans.* 1975, 1710.

$(CO)_6Fe_2(\mu_3-\eta^1,\eta^2,\eta^2-p-MeC_6H_4C{=}C{=}CH_2)WCp(CO)_2$ (**3e**) (0.011 g, 4%).

(iii) Photolysis in the Presence of $Fe(CO)_5$. A diethyl ether solution (30 mL) of $Fe(CO)_5$ (60 μL, 0.040 g, 0.42 mmol) and $(CO)_3Fe(\mu-\eta^2,\eta^3-PhC{=}C{=}CH_2)WCp(CO)_2$ (**2d**) (0.240 g, 0.42 mmol) was photolyzed for 5 h with a medium-pressure 450-W Hg lamp in a quartz reaction vessel. The reaction mixture was then concentrated in vacuo to give a gelatinous red solid. The solid was dissolved in CH_2Cl_2 and introduced onto a Florisil column (2 × 20 cm). Elution with a 2% solution of diethyl ether in pentane gave an orange band, which was concentrated to afford an orange tacky solid. A purple tacky solid was obtained by concentration of a purple band eluted from the column with a 9:1 mixture of diethyl ether and pentane. These solids were then washed separately with acetone (2 × 5 mL), affording a white polymeric or oligomeric solid (total mass = 0.009 g): ^1H NMR ($CDCl_3$) δ 7.4 (br s), 4.2 (br s). Separate concentration of the washings gave **2d** (0.140 g, 60%) and $(CO)_6Fe_2(\mu_3-\eta^1,\eta^2,\eta^2-PhC{=}C{=}CH_2)WCp(CO)_2$ (**3d**) (0.110 g, 37%).

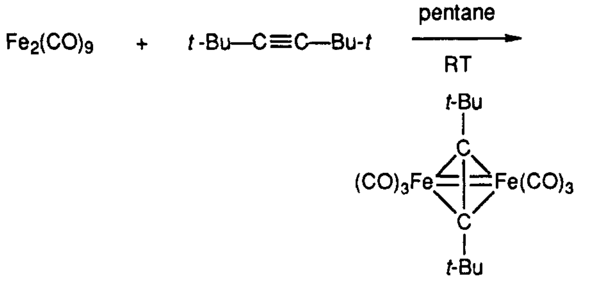
(iv) With Triphenylphosphine. Triphenylphosphine (0.241 g, 0.923 mmol) was added as a solid to a stirred, room-temperature solution of $(CO)_3Fe(\mu-\eta^2,\eta^3-p-MeC_6H_4C{=}C{=}CH_2)WCp(CO)_2$ (**2e**) (0.530 g, 0.923 mmol) and Me_3NO (0.140 g, 1.870 mmol) in THF (50 mL). After 14 h the reaction was complete, as ascertained by ^{31}P NMR spectroscopy. Solvent was removed to give a red oil, which was dissolved in CH_2Cl_2 (2 mL) and the resulting solution was introduced onto a Florisil column (2 × 15 cm) packed in pentane. Unreacted **2e** (0.102 g, 20%) was collected as an orange band with a 2% solution of diethyl ether in pentane as the eluent. Elution with a 3:1 mixture of diethyl ether and pentane gave a purple band, which was concentrated to give $(PPh_3)_2(CO)Fe(\mu-\eta^2,\eta^3-p-MeC_6H_4C{=}C{=}CH_2)WCp(CO)_2$ (**5**) (0.132 g, 27%) as an air-sensitive purple solid: IR ν(CO) (cyclohexane, cm^{-1}) 1996 (s), 1953 (s), 1929 (s), 1908 (m); ^1H NMR ($CDCl_3$) δ 7.64–7.57, 7.41–7.15, 7.09–6.81 (3 m, 34 H, 6 PPh_3, and C_6H_4), 5.24 (s, 5 H, Cp), 4.76 (d, J_{P-H} = 11.5 Hz, 1 H, CH_2), 4.28 (d, J_{P-H} = 2.2 Hz, 1 H, CH_2), 2.32 (s, 3 H, Me); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 81.5 (s), 66.1 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 219.26 (d, J_{P-C} = 16.8 Hz, WCO), 217.36, 216.57 (dd, J_{P-C} = 54.3, 45.2 Hz, FeCO), 214.27 (t, J_{P-C} = 34.0 Hz, WCO), 141.51 (s, ipso-C of C_6H_4), 137.19, 136.91, 136.59, 136.23, 135.62, 134.61 (6 s, ipso-C's of PPh_3), 133.85–127.84 (other C's of PPh_3 and C_6H_4), 113.90 (s, J_{W-C} = 6.2 Hz, =C=), 89.34 (s, Cp), 88.57 (s, =C(Ph)Fe), 70.39 (s, =CH_2), 21.11 (s, Me). Anal. Calcd for $C_{54}H_{44}FeO_3P_2W$: C, 62.21; H, 4.25. Found: C, 62.19; H, 3.99.

(v) With Iodine. A pentane solution (20 mL) of $(CO)_3Fe(\mu-\eta^2,\eta^3-MeC{=}C{=}CH_2)MoCp(CO)_2$ (**2a**) (0.11 g, 0.27 mmol) and sublimed I_2 (0.068 g, 0.27 mmol) was stirred at room temperature for 17 h. During this time the orange solution turned colorless and a black precipitate appeared. This precipitate showed no absorptions in the ν(CO) region of the IR spectrum and was not further investigated. The colorless solution was vacuum-transferred to a trap cooled to −78 °C, and solvent was distilled off at atmospheric pressure. After all the pentane had been removed, $Me(I)C{=}C{=}CH_2$ was obtained as a yellow oil (0.035 g, 72%). The identity of $Me(I)C{=}C{=}CH_2$ was confirmed by comparison of its IR and ^1H NMR spectra with those of an authentic sample prepared according to a literature method.[15]

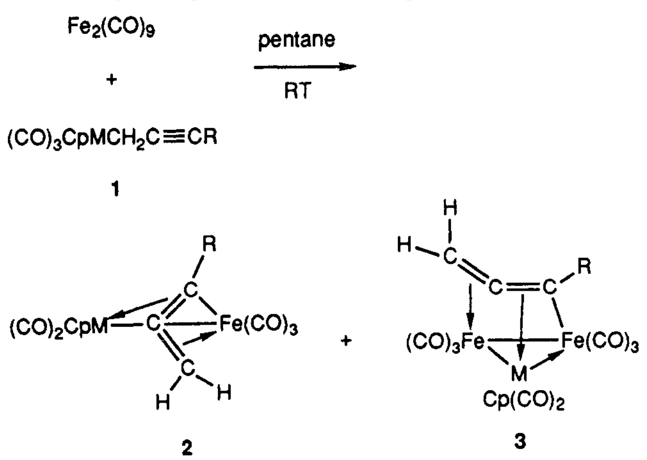
Crystallographic Analyses of $(CO)_3Fe(\mu-\eta^2,\eta^3-p-MeC_6H_4C{=}C{=}CH_2)WCp(CO)_2$ (2e), $(CO)_6Fe_2(\mu_3-\eta^1,\eta^2,\eta^2-PhC{=}C{=}CH_2)WCp(CO)_2$ (3d), and $(CO)_6Ru_2(\mu_3-\eta^1,\eta^2,\eta^2-PhC{=}C{=}CH_2)WCp(CO)_2$ (4). Crystals of **2e** were grown from 1:1 ethyl acetate/heptane at 0 °C, of **3d** from 1:1 CH_2Cl_2/pentane at 10 °C, and of **4** from 1:1 $CHCl_3$/pentane at 0 °C. They were mounted on an Enraf-Nonius CAD4 diffractometer, and lattice parameters were obtained by a least-squares refinement of 25 accurately centered reflections. A summary of the crystal data and the details of the intensity data collection and refinement for **2e**, **3d**, and **4** are provided in Table II. No significant change in intensities, due to crystal decay, was observed over the course of all data collections. All three structures were solved by the heavy-atom method. The hydrogen atoms of the CH_2 groups were located from the difference Fourier map after anisotropic refinement. The positions of all other hydrogen atoms were calculated and confirmed by the different Fourier map. Residual peaks were found only near the heavy atoms. Final full-matrix least-squares refinement, including extinction corrections for **2e** and **3d**, converged to R = 0.030, 0.029, and 0.053 for **2e**, **3d**, and **4**, respectively. The isotropic thermal factors of the hydrogen atoms were taken as 1.3 times the B_{eq} of the atom to which they are attached. They were included in the F_c calculations, but not refined. All the non-hydrogen atoms had anisotropic temperature factors. Scattering factors, anomalous dispersion terms and programs were taken from the Enraf-Nonius SDP library.[16] Final positional and equivalent thermal parameters are given in Tables III–V. Lists of anisotropic thermal parameters, hydrogen atom coordinates, and structure factors are available as supplementary material.[17]

Results and Discussion

Synthesis of Heteronuclear Metal-μ-Allenyl Complexes. The well-studied reactions of alkynes with iron carbonyls proceed to give numerous organometallic products, depending on reaction conditions.[18] Considering Cotton's characterization of $(CO)_3Fe(\mu-t-BuC{\equiv}C-t-Bu)Fe(CO)_3$,[19] obtained from t-BuC≡C-*t*-Bu and $Fe_2(CO)_9$[18] (eq 1), and envisioning a synthetic strategy similar to that used in our previous preparation of the heterobinuclear CoMo and CoW μ-alkyne complexes,[3] we anticipated that reactions of 1 with $Fe_2(CO)_9$ would provide a synthetic route to iron-containing analogues of the trinuclear Co_2Mo and Co_2W compounds in Scheme I. These products might then serve as precursors of new heteronuclear metal compounds. Instead, we find that the reactions of 1 with $Fe_2(CO)_9$ proceed, via cleavage of the M–CH_2 bond in 1 and concomitant rehybridization of the propargyl carbon (sp^3 → sp^2), to give directly the new heteronuclear metal-μ-allenyl compounds 2 and 3 (eq 2).



(1)



(2)

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[15] Baker, C. S. L.; Landor, P. D.; Landor, S. R.; Patel, A. N. *J. Chem. Soc.* **1965**, 4348.

[16] Frenz, B. A. and Associates, Inc. *Structure Determination Package*; Enraf-Nonius: Delft, Holland, 1985.

[17] See paragraph at end of paper regarding supplementary material.

[18] Hübel, W. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Interscience: New York, 1968; Vol. 1, pp 273–342.

[19] Cotton, F. A.; Jamerson, J. D.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 1774.

Table II. Crystal Data and Data Collection and Refinement for 2e, 3d, and 4

	2e	3d	4
	Crystal Data		
formula	$C_{20}H_{14}FeO_5W$	$C_{22}H_{12}Fe_2O_8W$	$C_{22}H_{12}O_8Ru_2W$
fw	754.0	699.9	790.3
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a, Å	17.259 (5)	12.185 (5)	9.936 (7)
b, Å	8.184 (3)	12.754 (7)	18.98 (2)
c, Å	26.920 (7)	15.418 (9)	11.752 (8)
β, deg	90.65 (2)	111.87 (4)	93.12 (6)
V, Å^3	3802 (2)	2224 (2)	2213 (3)
Z	8	4	4
D_{calcd}, g cm^{-3}	2.01	2.09	2.37
$F(000)$, e	2192	1336	1480
μ(Mo Kα), cm^{-1}	69.7	66.1	66.7
cryst size, mm	0.15 × 0.45 × 0.50	0.20 × 0.35 × 0.80	0.05 × 0.20 × 0.20
	Data Collection and Refinement		
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
temp, K	294 ± 1	294 ± 1	294 ± 1
λ(Mo Kα) radiatn, graphite monochromated, Å	0.71069	0.71069	0.71069
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
scan speed, deg min^{-1}	0.72–5	0.78–5	0.93–4
scan range, deg^{a}	$1.1 + 0.35 \tan\theta$	$1.2 + 0.35 \tan\theta$	$1.3 + 0.35 \tan\theta$
aperture width, mm	$1.1 + \tan\theta$	$1.1 + \tan\theta$	$1.2 + \tan\theta$
2θ range, deg	6–60	6–60	6–54
reflns measd	$\pm h,k,l$	$\pm h,k,l$	$\pm h,k,l$
orientatn monitors^{b}	3	3	3
intens monitors^{c}	3	3	2
no. of tot. measd data	12013	6955	5189
abs correcn	empirical from ψ scans of 3 close-to-axial reflns		
transm factors	0.358–0.999	0.439–0.999	0.522–0.998
no. of unique data with $I > 3\sigma(I)^{d}$	6533	4896	2669
no. of variables	488	299	298
minimized function	$\sum w\Delta^{2\,e}$	$\sum w\Delta^{2\,e}$	$\sum w\Delta^{2\,e}$
$R(\sum\Delta)/\sum\lvert F_o\rvert)^{e}$	0.030	0.029	0.053
$R_w([\sum w\Delta^2/\sum wF_o^2]^{1/2})^{e}$	0.038	0.041	0.061
w	$1/[\sigma(F_o)^2 + (0.02F_o)^2 + 1]$	$1/[\sigma(F_o)^2 + (0.02F_o)^2 + 1]$	$1/[\sigma(F_o)^2 + (0.02F_o)^2 + 1]$
extincn coeff	$3.2\ (3) \times 10^{-8}$	$2.3\ (1) \times 10^{-7}$	
goodness of fit	1.01	1.00	1.17
residuals in final diff map, e Å^{-3}	−0.92, +1.19	−1.28, +1.53	−2.13, +4.33

[a] Extended by 25% on both sides for background measurements. [b] Measured after each 400 reflections; new orientation matrix if angular change >0.12. [c] Measured after each 4000 s. [d] Standard deviation from counting statistics. [e] $\Delta = \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert$.

The reactions of 1 with $Fe_2(CO)_9$ were usually conducted as a pentane slurry at room temperature. They experience an induction period of ca. 30 min and reach completion within 24 h, as determined by IR and ^1H NMR spectroscopy. The occurrence of induction leads us to believe that the species reacting with 1 is a coordinately unsaturated iron carbonyl, $Fe(CO)_x$(x = 3 or 4), formed by decomposition of $Fe_2(CO)_9$. Coincident with the start of reaction, the mixture rather abruptly turns dark green and then gradually changes to orange.

All reactions of cyclopentadienyl-group-containing 1 with $Fe_2(CO)_9$ gave the heterobinuclear metal–μ-allenyl compounds, 2, as the major product and the heterotrinuclear metal–μ-allenyl compounds, 3, as the minor product. The indenyl-ligand-containing 1 (i.e. **1h**) afforded the heterobinuclear **2h** as the only isolable product. The isolated yields of 2 and 3 varied greatly depending on the nature of 1 and the ratio 1:$Fe_2(CO)_9$ employed in the reaction. Use of a 1:1 molar ratio of reactants led to the isolation of 2 in yields between 28% (**2d**) and 70% (**2b**) and of 3 in yields ca. 5%. When a 2:1 molar ratio of 1 to $Fe_2(CO)_9$ was used, only complexes 2 (up to 95% yield) were produced. Although still obtained as the minor product, 3 was isolated in higher yields (ca. 20%) if a 2:3 ratio of 1 to $Fe_2(CO)_9$ was employed. The reaction between **1d** and $Fe_2(CO)_9$ in THF solution provided **2d** (ca. 50%) as the sole metal–μ-allenyl product regardless of the relative amounts of reactants (1:1 or 2:1).

Compounds 2 and 3 were also obtained by reacting 1 with $Fe_3(CO)_{12}$ in benzene at reflux for 24 h. The yields of products obtained in this way were also dependent on the identity of 1. For example, whereas the reaction of **1d** with $Fe_3(CO)_{12}$ gave 3 as the major product (25%) along with a minor amount of **2d** (5%), **1b** provided only **2b** (40%) and $Cp_2Mo_2(CO)_6$ (30%). Neither **2a** nor **3a** was produced from the reaction of **1a** with $Fe_3(CO)_{12}$, and the only organometallic product isolated was $Cp_2Mo_2(CO)_6$ (82%). Apparently, **1a** is not stable at this high temperature, decomposing more rapidly than it can react with $Fe_3(CO)_{12}$. In support of this supposition, attempted reactions of all compounds 1 with $Fe_3(CO)_{12}$ in higher boiling solvents, such as toluene, at reflux gave only $Cp_2M_2(CO)_6$ (M = Mo, W).

Although no discrete intermediates were observed in the foregoing reactions—largely because of the inherent difficulties in spectroscopically monitoring changes in composition of these heterogeneous mixtures—it is nevertheless worthwhile to consider how such processes might proceed. The occurrence of a propargyl-to-allenyl ligand rearrangement and the attachment of the terminal propargylic carbon (i.e. CR) to iron, both suggest that the mechanism is perhaps similar to that of the well-studied reactions of transition-metal–propargyl complexes with neutral electrophiles, such as SO_2, $(CN)_2C{=}C(CN)_2$, $ClSO_2NCO$, etc.[20] Accordingly, we propose a pathway

Table III. Positional and Equivalent Thermal Parameters for 2e

	molecule I				molecule II			
atom	*x*	*y*	*z*	B,[a] Å^2	*x*	*y*	*z*	B,[a] Å^2
W	0.68625 (1)	0.30749 (3)	0.38615 (1)	3.357 (4)	0.17270 (1)	0.46377 (3)	0.36525 (1)	3.374 (4)
Fe	0.60394 (5)	0.5466 (1)	0.33542 (3)	3.49 (2)	0.04960 (5)	0.4442 (1)	0.29895 (3)	3.74 (2)
O(1)	0.6954 (4)	0.2723 (8)	0.5014 (2)	6.7 (1)	0.1598 (3)	0.4354 (7)	0.4804 (2)	5.7 (1)
O(2)	0.8283 (3)	0.5474 (7)	0.3950 (2)	6.2 (1)	0.1862 (4)	0.0833 (7)	0.3686 (3)	7.4 (2)
O(3)	0.7427 (3)	0.7301 (7)	0.3110 (2)	6.0 (1)	0.0965 (4)	0.1229 (7)	0.2644 (2)	6.9 (1)
O(4)	0.5854 (4)	0.4137 (8)	0.2352 (2)	7.8 (2)	0.1075 (4)	0.6309 (9)	0.2145 (2)	8.9 (2)
O(5)	0.4987 (3)	0.8266 (7)	0.3350 (2)	6.5 (1)	−0.1142 (3)	0.3878 (9)	0.2751 (2)	7.1 (1)
C(1)	0.6916 (4)	0.2871 (8)	0.4594 (2)	4.5 (1)	0.1636 (3)	0.4456 (8)	0.4386 (2)	4.01 (1)
C(2)	0.7763 (4)	0.4623 (9)	0.3918 (2)	4.4 (1)	0.1812 (4)	0.2223 (8)	0.3669 (3)	4.9 (2)
C(3)	0.6887 (4)	0.6587 (8)	0.3213 (2)	4.1 (1)	0.0790 (4)	0.248 (1)	0.2780 (2)	4.8 (1)
C(4)	0.5938 (5)	0.4625 (9)	0.2743 (3)	5.2 (2)	0.0851 (5)	0.559 (1)	0.2473 (3)	5.5 (2)
C(5)	0.5398 (4)	0.7182 (9)	0.3347 (2)	4.5 (1)	−0.0501 (4)	0.4135 (9)	0.2841 (2)	4.6 (1)
C(6)	0.5071 (4)	0.399 (1)	0.3623 (3)	5.1 (2)	0.0173 (4)	0.6694 (8)	0.3382 (3)	4.6 (1)
C(7)	0.5746 (3)	0.3953 (8)	0.3910 (2)	3.6 (1)	0.0607 (3)	0.5575 (7)	0.3656 (2)	3.4 (1)
C(8)	0.6181 (3)	0.5207 (7)	0.4104 (2)	3.2 (1)	0.0471 (3)	0.3927 (7)	0.3709 (2)	3.2 (1)
C(9)	0.6123 (3)	0.6343 (7)	0.4516 (2)	3.2 (1)	0.0038 (3)	0.2835 (7)	0.4022 (2)	3.4 (1)
C(10)	0.5397 (4)	0.6763 (9)	0.4706 (3)	4.7 (1)	−0.0281 (4)	0.3406 (8)	0.4465 (2)	4.0 (1)
C(11)	0.5333 (4)	0.7786 (9)	0.5105 (3)	5.0 (2)	−0.0690 (4)	0.234 (1)	0.4768 (3)	4.9 (1)
C(12)	0.5972 (4)	0.8499 (8)	0.5330 (2)	4.4 (1)	−0.0807 (4)	0.0752 (9)	0.4651 (3)	4.6 (1)
C(13)	0.6686 (4)	0.8092 (9)	0.5141 (2)	4.3 (1)	−0.0507 (5)	0.0192 (9)	0.4209 (3)	5.2 (2)
C(14)	0.6765 (3)	0.7055 (8)	0.4743 (2)	3.9 (1)	−0.0094 (4)	0.1212 (8)	0.3904 (2)	4.3 (1)
C(15)	0.5896 (5)	0.965 (1)	0.5761 (3)	6.1 (2)	−0.1251 (4)	−0.037 (1)	0.4987 (3)	6.8 (2)
C(16)	0.6628 (5)	0.0315 (9)	0.3791 (3)	5.3 (2)	0.2516 (4)	0.6898 (9)	0.3775 (3)	5.6 (2)
C(17)	0.7427 (5)	0.0513 (9)	0.3855 (3)	5.7 (2)	0.2983 (4)	0.549 (1)	0.3809 (3)	6.0 (2)
C(18)	0.7715 (5)	0.131 (1)	0.3453 (4)	7.0 (2)	0.2980 (4)	0.474 (1)	0.3334 (3)	6.3 (2)
C(19)	0.7097 (6)	0.164 (1)	0.3125 (3)	7.2 (2)	0.2512 (5)	0.571 (1)	0.3022 (3)	6.4 (2)
C(20)	0.6421 (5)	0.1027 (9)	0.3336 (3)	5.7 (2)	0.2221 (4)	0.7017 (9)	0.3299 (3)	5.9 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table IV. Positional and Equivalent Thermal Parameters for 3d

atom	*x*	*y*	*z*	B,[a] Å^2
W	0.26503 (1)	0.04441 (1)	0.13732 (1)	2.919 (3)
Fe(1)	0.31846 (5)	0.11351 (5)	0.31681 (3)	3.06 (1)
Fe(2)	0.17828 (5)	0.23772 (5)	0.17692 (4)	3.45 (1)
O(1)	0.1374 (4)	0.0862 (5)	0.3975 (3)	7.9 (1)
O(2)	0.4312 (4)	−0.0809 (3)	0.4046 (3)	6.6 (1)
O(3)	0.4638 (4)	0.2631 (3)	0.4549 (2)	5.48 (9)
O(4)	0.0222 (4)	0.3817 (4)	0.0393 (3)	8.0 (1)
O(5)	0.2301 (5)	0.3864 (4)	0.3309 (3)	8.0 (1)
O(6)	−0.0324 (3)	0.1472 (5)	0.1941 (3)	8.5 (1)
O(7)	0.1028 (4)	−0.0710 (4)	0.2238 (3)	7.7 (1)
O(8)	0.0600 (4)	0.1381 (4)	−0.0308 (3)	8.0 (1)
C(1)	0.2052 (4)	0.0977 (5)	0.3644 (3)	4.8 (1)
C(2)	0.3882 (5)	−0.0044 (4)	0.3700 (3)	4.2 (1)
C(3)	0.4055 (4)	0.2054 (4)	0.4011 (3)	3.79 (9)
C(4)	0.0848 (4)	0.3258 (5)	0.0903 (3)	5.2 (1)
C(5)	0.2139 (5)	0.3248 (5)	0.2742 (4)	5.2 (1)
C(6)	0.0532 (4)	0.1808 (6)	0.1904 (4)	5.7 (1)
C(7)	0.1623 (5)	−0.0199 (5)	0.1983 (3)	5.1 (1)
C(8)	0.1329 (4)	0.1164 (5)	0.0395 (3)	4.8 (1)
C(9)	0.4127 (3)	0.1417 (3)	0.2411 (2)	2.64 (6)
C(10)	0.3376 (3)	0.1989 (3)	0.1676 (2)	2.68 (7)
C(11)	0.3136 (4)	0.2982 (4)	0.1288 (3)	3.89 (9)
C(12)	0.5407 (3)	0.1331 (3)	0.2619 (3)	2.95 (7)
C(13)	0.5884 (3)	0.1656 (4)	0.1962 (3)	3.54 (8)
C(14)	0.7084 (4)	0.1593 (5)	0.2162 (3)	4.7 (1)
C(15)	0.7842 (4)	0.1220 (5)	0.3022 (4)	5.1 (1)
C(16)	0.7379 (4)	0.0919 (5)	0.3674 (4)	4.9 (1)
C(17)	0.6195 (4)	0.0968 (4)	0.3477 (3)	3.71 (9)
C(18)	0.2333 (5)	−0.1158 (4)	0.0600 (4)	5.1 (1)
C(19)	0.2586 (6)	−0.0442 (4)	0.0029 (3)	5.4 (1)
C(20)	0.3699 (5)	−0.0066 (4)	0.0462 (3)	5.3 (1)
C(21)	0.4201 (5)	−0.0563 (4)	0.1335 (4)	5.7 (1)
C(22)	0.3364 (6)	−0.1234 (4)	0.1422 (4)	5.8 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

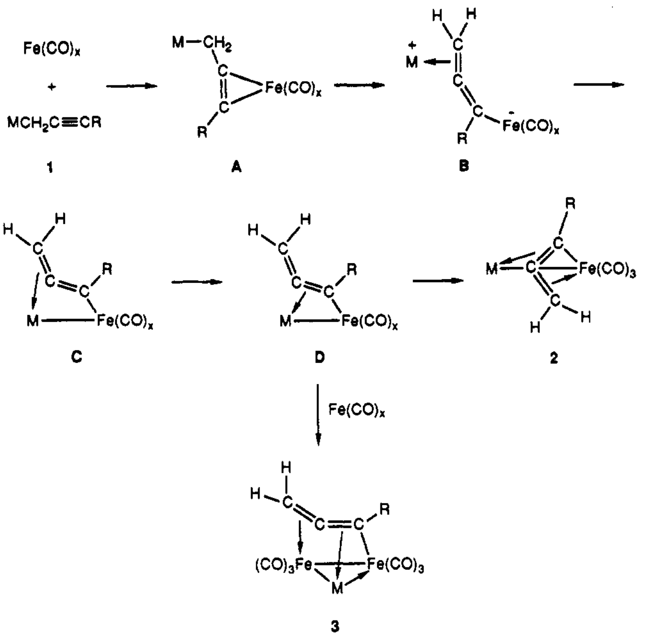
Table V. Positional and Equivalent Thermal Parameters for 4

atom	*x*	*y*	*z*	B,[a] Å^2
W	0.75116 (6)	0.82447 (4)	0.83471 (5)	2.10 (1)
Ru(1)	1.0014 (1)	0.89563 (7)	0.7871 (1)	2.71 (3)
Ru(2)	0.7819 (1)	0.90752 (8)	0.6261 (1)	2.75 (3)
O(1)	1.014 (1)	1.0523 (7)	0.861 (1)	5.0 (3)
O(2)	1.210 (1)	0.8654 (8)	0.978 (1)	4.8 (3)
O(3)	1.202 (1)	0.9050 (9)	0.608 (1)	5.5 (4)
O(4)	0.496 (2)	0.913 (1)	0.515 (1)	6.8 (5)
O(5)	0.945 (1)	0.9372 (8)	0.423 (1)	4.6 (3)
O(6)	0.770 (1)	1.0622 (7)	0.694 (1)	4.7 (3)
O(7)	0.736 (1)	0.9762 (8)	0.931 (1)	4.9 (3)
O(8)	0.952 (1)	0.776 (1)	1.031 (1)	5.8 (4)
C(1)	1.008 (2)	0.994 (1)	0.831 (2)	3.7 (4)
C(2)	1.131 (2)	0.876 (1)	0.908 (1)	3.4 (4)
C(3)	1.127 (2)	0.904 (1)	0.675 (1)	3.0 (3)
C(4)	0.602 (2)	0.909 (1)	0.557 (2)	3.4 (4)
C(5)	0.885 (2)	0.9278 (9)	0.500 (1)	2.7 (3)
C(6)	0.777 (2)	1.003 (1)	0.671 (2)	3.1 (4)
C(7)	0.756 (1)	0.920 (1)	0.886 (2)	3.2 (4)
C(8)	0.881 (2)	0.797 (1)	0.959 (1)	3.4 (4)
C(9)	0.949 (2)	0.7931 (9)	0.745 (1)	2.0 (3)
C(10)	0.830 (2)	0.8023 (9)	0.677 (1)	2.4 (3)
C(11)	0.786 (2)	0.7939 (9)	0.565 (1)	2.7 (3)
C(12)	1.022 (2)	0.7252 (9)	0.751 (1)	2.4 (3)
C(13)	0.959 (2)	0.663 (1)	0.720 (2)	3.9 (4)
C(14)	1.032 (2)	0.600 (1)	0.713 (2)	5.1 (5)
C(15)	1.169 (2)	0.599 (1)	0.733 (2)	4.4 (5)
C(16)	1.232 (2)	0.661 (1)	0.762 (2)	4.0 (4)
C(17)	1.163 (2)	0.724 (1)	0.771 (2)	3.4 (4)
C(18)	0.598 (2)	0.784 (1)	0.958 (2)	4.4 (5)
C(19)	0.530 (2)	0.828 (1)	0.882 (2)	4.5 (5)
C(20)	0.529 (2)	0.801 (1)	0.773 (2)	3.9 (4)
C(21)	0.597 (2)	0.736 (1)	0.778 (2)	4.1 (4)
C(22)	0.638 (2)	0.726 (1)	0.893 (2)	4.4 (5)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

(Scheme II) based on this assumption. Initially, the propargylic C≡C coordinates to the iron in Fe(CO)$_x$ (x = 3 or 4), a behavior which has ample precedence in the reactions of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ with alkynes.[21] The

Scheme II

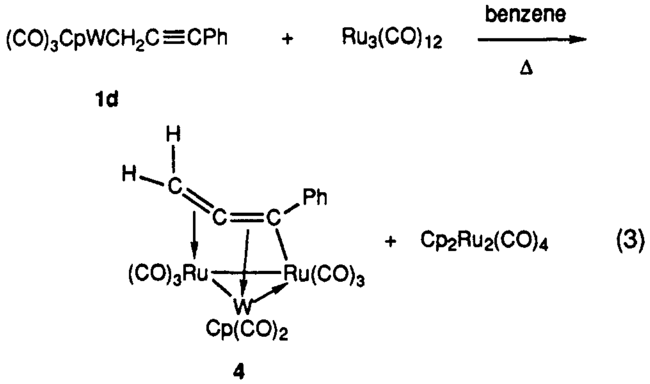


resultant binuclear metal–propargyl complex (A) rearranges to a dipolar metal–η^2-(metal–η^1-allenyl) species (B), which then rapidly converts to a heterobinuclear metal–μ-η^1,η^2-allenyl compound, C. The latter isomerizes to D, which either combines with an additional $Fe(CO)_x$ fragment to yield **3** or undergoes intramolecular coordination of the free C=C to Fe to afford **2**. A RuPt μ-allenyl complex analogous to D has been recently characterized.[22] Alternatively, the binuclear metal–propargyl intermediate A may rearrange with insertion of a CO ligand to give a dipolar metal–η^2-(metal–η^1-allenylcarbonyl) species,[5] which at some point of continued reaction loses the acyl CO to account for the formation of **2** and **3**.

This proposal of the reaction pathway is consistent with the isolation of **2** as the sole product when a 2:1 molar ratio of **1** to $Fe_2(CO)_9$ is employed, since under these conditions a 1:1 ratio of **1** to $Fe(CO)_x$ obtains. When excess $Fe(CO)_x$ is present, reaction with intermediate C may afford the heterotrinuclear product **3**. Compound **3** is probably not formed from $Fe(CO)_x$ and **2**, since **2** does not react with $Fe_3(CO)_{12}$ and furnishes only minor amounts of **3** (<5%) when reacted with $Fe_2(CO)_9$. The reactivity of **2** toward iron carbonyls is considered again later in the paper.

When $Ru_3(CO)_{12}$ and **1d** were reacted under the same conditions as in the reactions involving $Fe_3(CO)_{12}$, the ruthenium analogue of **3d**, **4** was formed along with a small quantity of $Cp_2Ru_2(CO)_4$ (eq 3). No heterobinuclear metal–allenyl complex was isolated, and neither could one be prepared via reaction of **1d** with $Ru(CO)_5$ or $Ru(CO)_4(C_2H_4)$.

Characterization of Heteronuclear Metal–μ-Allenyl Complexes. The orange heterobinuclear metal–μ-allenyl complexes (**2**) are indefinitely stable to air in the solid state and stable over several hours in solution. However, the deep purple or yellow-brown heterotrinuclear metal–μ_3-allenyl compounds **3** and **4**, respectively, decompose upon



exposure to air within several hours as solids and immediately as solutions. Characterization of **2**–**4** was accomplished through a combination of elemental analysis, mass spectrometry, and IR and ^{1}H and ^{13}C NMR spectroscopies. Unequivocal confirmation of the structures of **2e**, **3d**, and **4** was obtained by X-ray diffraction analysis.

(i) Heterobinuclear Metal-μ-η^2,η^3-Allenyl Complexes (2). The IR spectra of **2** in the ν(CO) region generally exhibit more than the five absorptions expected for their C_1 symmetry, suggesting that isomers may be present in solution. The carbonyl ligands bonded to iron give rise to three absorptions between ca. 2055 and 1990 cm^{-1}, whereas those attached to molybdenum or tungsten absorb at lower energy (1985–1935 cm^{-1}). Frequently, a weak absorption is noted at ca. 1915 cm^{-1}, which may arise from the presence of an isomer containing a semibridging[23] carbonyl ligand.

The sp^2 hybridization at the CH_2 carbon of the bridging hydrocarbyl ligand in **2** is readily apparent upon inspection of the ^{1}H and ^{13}C{^{1}H} NMR spectra. The CH_2 protons appear as singlets or two weakly split ($J \leq 0.7$ Hz) doublets of equal intensity and with considerably different chemical shifts (δ 3.5–4.0 and 4.5–5.4 ppm). The proton nearest the group VI metal (H_a) can be differentiated from the one closer to Fe (H_b) by comparison of the chemical shifts of the more downfield CH_2 resonances in **2a** and **2c**. The chemical shift of H_a is significantly affected when the metal is changed from Mo (**2a**: δ 4.48 ppm) to W (**2c**: δ 5.10 ppm), while there is no change in δ for H_B (**2a** = **2c**: δ 3.65 ppm). The 2D ^{13}C{^{1}H}–^{1}H correlation NMR spectrum of **2a** confirms that H_a and H_b are attached to the same carbon atom.

The magnitude of the J_{C-H} coupling constant observed in the ^{13}C NMR spectrum of **2** (**2c**: $J_{C-H} = 164$ Hz) provides further evidence for the sp^2 hybridization at the CH_2 carbon,[24] and the downfield chemical shift (δ ca. 70 ppm) of this atom indicates that the M–CH_2 bond is no longer intact. The assignment of resonances due to the quaternary allenyl carbons (**2b**–**2g**: =C=, δ 110–120 ppm; *C*(R)Fe, δ 80–90 ppm) was made on the basis of the tendency of the carbon atoms that are σ-bonded to metal to resonate upfield relative to those that are π-bonded. However, some σ interaction is suggested between the Mo or W atom and the central allenyl carbon (=C=), since spin–spin coupling of the ^{183}W and ^{13}C nuclei (**2d**: $J_{W-C} = 34$ Hz) is about the same as that in **1**.

Although the spectroscopic data provided valuable structural information, the unequivocal formulation of **2** required an X-ray structural analysis owing to the paucity of analogous compounds. Crystals of **2e** contain two

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[20] Wojcicki, A. In *Fundamental Research in Organometallic Chemistry*; Tsutsui, M., Ishii, Y., Huang, Y., Eds.; Van Nostrand-Reinhold: New York, 1982; pp 569–597.

[21] (a) Davison, A.; McFarlane, W.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 3653. (b) Clifford, A. F.; Mukerjee, A. K. *Inorg. Chem.* **1963**, *2*, 151. (c) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 3438.

[22] Shuchart, C. E.; Rheingold, A. L.; Wojcicki, A. To be submitted for publication.

[23] Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1.

[24] Cooper, J. W. *Spectroscopic Techniques for Organic Chemists*; Wiley-Interscience: New York, 1980; p 87.

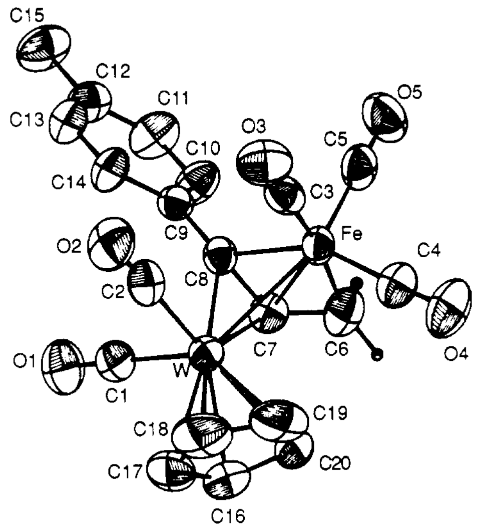
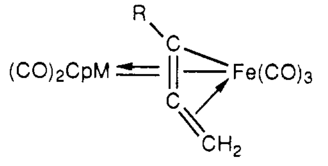


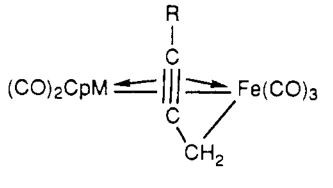
Figure 1. ORTEP plot of **2e** showing atom-numbering scheme. For clarity, only the hydrogen atoms of the CH_2 group are given, with an arbitrary radius. Non-hydrogen atoms are drawn at the 50% probability level.

crystallographically independent molecules (I and II) with normal van der Waals contacts. Molecules I and II have essentially the same structure, shown in Figure 1 with the atom-numbering scheme. Selected bond distances and angles are given in Table VI.

On the basis of the normal bond lengths between the carbon atoms of the bridging hydrocarbyl ligand (C(6)–C(7) = 1.390 (9) Å, C(7)–C(8) = 1.375 (8) Å) and the sp^2 hybridization at C(6) (J_{C-H} = 164 Hz, vide supra), we believe that **2e** is best formulated as a rare example of a heteronuclear metal–μ-allenyl compound[25-27] (cf. representation X). This formulation is further supported by the essentially trigonal environment of C(6) provided by C(7) and the two methylene H's (located in the X-ray analysis). Significantly however, the angle about the central allenyl carbon atom (C(6)–C(7)–C(8) = 128.9 (6)°) is the smallest yet reported for molecules of this type and suggests possible contribution to the structure of representation Y. Resonance contribution of representations analogous to X and Y was previously discussed in the structural description of the related cationic homobinuclear molybdenum–μ-allenyl complex $(CO)_2Cp'Mo(\mu\text{-}\eta^2,\eta^3\text{-}HC{=}C{=}CH_2)MoCp'(CO)_2^+$ ($Cp' \equiv C_5H_4Me$).[28]



X



Y

Table VI. Selected Bond Distances (Å) and Angles (deg) for 2e

	molecule I	molecule II
	Bond Distances	
W-Fe	2.7695 (9)	2.7638 (9)
W-C(1)	1.981 (7)	1.988 (6)
W-C(2)	2.010 (7)	1.983 (7)
W-C(7)	2.063 (6)	2.080 (6)
W-C(8)	2.208 (6)	2.251 (6)
W-C(16)	2.302 (7)	2.318 (8)
W-C(17)	2.312 (7)	2.310 (8)
W-C(18)	2.345 (9)	2.336 (8)
W-C(19)	2.342 (8)	2.354 (8)
W-C(20)	2.316 (7)	2.333 (8)
Fe-C(3)	1.771 (7)	1.774 (8)
Fe-C(4)	1.791 (7)	1.791 (8)
Fe-C(5)	1.787 (7)	1.780 (7)
Fe-C(6)	2.191 (7)	2.199 (7)
Fe-C(7)	2.012 (6)	2.026 (6)
Fe-C(8)	2.042 (6)	1.983 (6)
C(6)-C(7)	1.390 (9)	1.390 (9)
C(7)-C(8)	1.372 (8)	1.377 (8)
C(8)-C(9)	1.451 (8)	1.443 (8)
C-O(av)	1.136 (9)	1.13 (1)
	Bond Angles	
Fe-W-C(1)	124.6 (2)	124.7 (2)
Fe-W-C(2)	89.1 (2)	90.7 (2)
Fe-W-C(7)	46.4 (2)	46.9 (2)
Fe-W-C(8)	46.8 (2)	45.2 (1)
C(1)-W-C(2)	87.2 (3)	84.8 (3)
C(1)-W-C(7)	90.0 (3)	86.6 (2)
C(1)-W-C(8)	77.9 (2)	80.0 (2)
C(2)-W-C(7)	119.9 (3)	115.8 (3)
C(2)-W-C(8)	83.9 (2)	79.1 (3)
W-Fe-C(3)	93.0 (2)	92.1 (2)
W-Fe-C(4)	103.0 (3)	101.8 (3)
W-Fe-C(5)	151.0 (2)	152.5 (2)
W-Fe-C(6)	80.6 (2)	80.7 (2)
W-Fe-C(7)	48.0 (2)	48.5 (2)
W-Fe-C(8)	52.0 (2)	53.6 (2)
Fe-C(6)-C(7)	63.8 (4)	64.2 (4)
Fe-C(7)-C(6)	77.8 (4)	77.7 (4)
Fe-C(7)-C(8)	71.4 (4)	68.2 (3)
Fe-C(7)-W	85.6 (2)	84.6 (2)
C(6)-C(7)-C(8)	130.2 (6)	127.6 (6)
Fe-C(8)-W	81.2 (2)	81.2 (2)
Fe-C(8)-C(7)	69.0 (3)	71.6 (3)
C(7)-C(8)-C(9)	136.7 (5)	139.2 (5)
W-C-O(av)	178.6 (6)	179.0 (7)
Fe-C-O(av)	178.2 (7)	179 (1)

Stabilization of **2** via contribution from Y may be significant, since the C(7)—C(8) bond of the μ-hydrocarbyl ligand of **2e** transversely bridges the Fe and W atoms, joined by a single bond (average Fe—W = 2.767 (1) Å), at an angle (86.4° (I), 96.8° (II)) comparable to that in the μ-alkyne complexes $(CO)_3Co(\mu\text{-}PhC{\equiv}CMe)WCp(CO)_2$ (87.7°)[3a] and $(CO)_3Co(\mu\text{-}CF_3C{\equiv}CCF_3)MoCp(CO)_2$ (88.5°).[29] Furthermore, the average W—C(7,8) bond distances in **2e** (average W—C(7) = 2.07 (6) Å, average W—C(8) = 2.23 (3) Å) are similar to the W—C(μ-alkyne) distances in $(CO)_3Co(\mu\text{-}PhC{\equiv}CMe)WCp(CO)_2$ (2.14 (2) Å). Also suggestive of representation Y is the value of the angle C(7)—C(8)—C(9) (average 138.0 (5)°), which is only ca. 9° greater than that of the angle C(6)—C(7)—C(8). On balance, however, X-ray diffraction and, especially, NMR

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(25) Other examples are $PPh_4[Fe_3Rh_2(CO)_{10}(\mu\text{-}CO)_3(\mu_4\text{-}MeC{=}C{=}CH_2)]$[26] and $FeCo(CO)_5L(\mu\text{-}R'C{=}C{=}CR_2)$ (L = CO, PPh_3; R_2 = H_2, HMe, Me_2; R' = Me, Et, CH_2OH);[27] however, the latter could not be accurately characterized by X-ray crystallography.

(26) Attali, S.; Dahan, F.; Mathieu, R. *Organometallics* **1986**, *5*, 1376.

(27) Aime, S.; Osella, D.; Milone, L.; Tiripicchio, A. *Polyhedron* **1983**, *2*, 77.

(28) Meyer, A.; McCabe, D. J.; Curtis, M. D. *Organometallics* **1987**, *6*, 1491.

(29) Jensen, S. D.; Robinson, B. H.; Simpson, J. *Organometallics* **1986**, *5*, 1690.

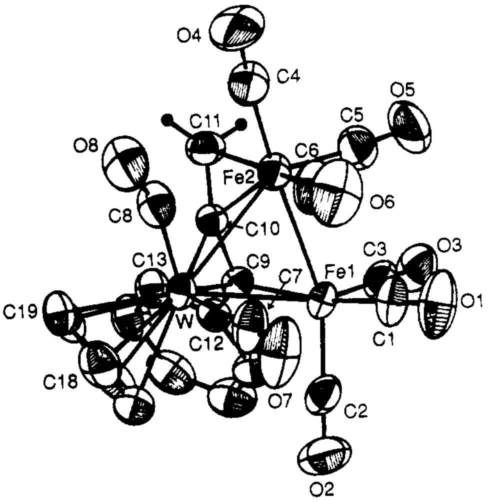

Figure 2. ORTEP plot of **3d** showing atom-numbering scheme. For clarity, only the hydrogen atoms of the CH_2 group are given, with an arbitrary radius. Non-hydrogen atoms are drawn at the 50% probability level.

data favor representation X,[30] which we use throughout this paper.

(ii) Heterotrinuclear Metal-μ_3-η^1,η^2,η^2-Allenyl Complexes (3, 4). The spectroscopic data of the heterotrinuclear complexes **3** and **4** exhibit many similarities and several diagnostic differences when compared with those of **2**. The IR spectra generally display six ν(CO) absorptions of varying intensity between 2070 and 1945 cm^{-1}. Again, the higher energy bands are attributed to FeCO, and the lower energy ones to MoCO or WCO. The mass spectra of **3** and **4**, obtained by the FAB method owing to low volatility of these complexes, show peaks corresponding to loss of eight CO's with the (M^+ - 4CO) peak generally being the most intense.

As with **2**, the hydrogens of the CH_2 group in **3** and **4** are inequivalent and appear in the ^1H NMR spectra as singlets or weakly split doublets ($J \leq 1.1$ Hz) as a result of geminal coupling. The chemical shift difference of H_a and H_b is smaller, and the resonances appear farther upfield, than for the corresponding protons of **2**. The assignments for H_a and H_b were made as for **2**, by taking into account the influence of the group VI metal on the shift and with the help of a 2D $^{13}C\{^1H\}$–^1H correlation NMR spectrum. In the case of **4**, additional, long-range coupling ($^4J_{W-H}$ = 6.5 Hz) is observed between one of the CH_2 protons and the ^{183}W nucleus; this will be considered later in connection with the X-ray crystallographic analysis.

The carbon atoms of the μ_3-allenyl ligand of **3** and **4** resonate at diagnostic chemical shifts in the $^{13}C\{^1H\}$ NMR spectra. The signals due to the central allenyl carbon ($=C=$, δ 156–162 ppm) and the carbon σ-bonded to metal ($=C(R)M$, δ 114–136 ppm) occur ca. 45–55 ppm downfield from the corresponding signals of **2**, whereas the resonance of the methylene carbon ($=CH_2$, δ 27 ppm) is observed ca. 45 ppm upfield from that of **2**. Complex **3d** also shows coupling between the $=C=$ carbon and ^{183}W (J_{W-C} = 43 Hz) that is approximately of the same magnitude as that observed for **2d**.

Table VII. Selected Bond Distances (Å) and Angles (deg) for 3d

	Bond Distances		
W–Fe(1)	2.7418 (5)	Fe(1)–C(2)	1.772 (5)
W–Fe(2)	2.8373 (7)	Fe(1)–C(3)	1.777 (4)
W–C(7)	2.000 (7)	Fe(1)–C(9)	1.952 (4)
W–C(8)	1.975 (5)	Fe(2)–C(4)	1.792 (5)
W–C(9)	2.279 (3)	Fe(2)–C(5)	1.786 (6)
W–C(10)	2.139 (4)	Fe(2)–C(6)	1.769 (6)
W–C(18)	2.325 (5)	Fe(2)–C(10)	2.060 (4)
W–C(19)	2.336 (6)	Fe(2)–C(11)	2.185 (5)
W–C(20)	2.316 (6)	C(9)–C(10)	1.371 (5)
W–C(21)	2.304 (6)	C(9)–C(12)	1.475 (5)
W–C(22)	2.301 (6)	C(10)–C(11)	1.385 (6)
Fe(1)–Fe(2)	2.7082 (8)	C–O(av)	1.140 (8)
Fe(1)–C(1)	1.800 (6)		
	Bond Angles		
Fe(1)–W–C(7)	67.2 (1)	C(3)–Fe(1)–C(9)	89.6 (2)
Fe(2)–W–C(7)	84.6 (2)	Fe(1)–Fe(2)–C(4)	176.1 (2)
C(7)–W–C(8)	94.3 (2)	Fe(1)–Fe(2)–C(5)	79.1 (2)
C(7)–W–C(9)	111.2 (2)	Fe(1)–Fe(2)–C(6)	89.0 (2)
C(7)–W–C(10)	123.8 (2)	Fe(1)–Fe(2)–C(10)	65.4 (1)
Fe(1)–W–C(8)	116.2 (2)	Fe(1)–Fe(2)–C(11)	98.4 (1)
Fe(2)–W–C(8)	59.8 (2)	W–C(9)–Fe(1)	80.4 (1)
C(8)–W–C(9)	119.3 (2)	W–C(9)–C(10)	66.4 (2)
C(8)–W–C(10)	83.8 (2)	W–C(9)–C(12)	127.3 (3)
W–Fe(1)–Fe(2)	62.74 (2)	Fe(1)–C(9)–C(10)	103.5 (3)
W–Fe(1)–C(1)	116.5 (1)	Fe(1)–C(9)–C(12)	131.8 (3)
W–Fe(1)–C(2)	95.0 (2)	C(10)–C(9)–C(12)	123.0 (4)
W–Fe(1)–C(3)	143.4 (2)	W–C(10)–Fe(2)	85.0 (1)
Fe(2)–Fe(1)–C(1)	92.2 (2)	W–C(10)–C(9)	77.6 (2)
C(1)–Fe(1)–C(2)	91.4 (3)	W–C(10)–C(11)	138.2 (2)
C(1)–Fe(1)–C(3)	96.6 (2)	Fe(2)–C(10)–C(9)	115.2 (3)
C(1)–Fe(1)–C(9)	167.4 (2)	Fe(2)–C(10)–C(11)	75.9 (3)
Fe(2)–Fe(1)–C(2)	156.5 (1)	C(9)–C(10)–C(11)	144.3 (3)
C(2)–Fe(1)–C(3)	99.7 (2)	Fe(2)–C(11)–C(10)	66.2 (3)
C(2)–Fe(1)–C(9)	98.4 (2)	Fe–C–O(av)	176.6 (6)
Fe(2)–Fe(1)–C(3)	103.0 (1)	W–C–O(av)	165.6 (5)

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

	Bond Distances		
W–Ru(1)	2.910 (2)	Ru(1)–C(2)	1.90 (2)
W–Ru(2)	2.945 (2)	Ru(1)–C(3)	1.87 (2)
W–C(7)	1.92 (2)	Ru(1)–C(9)	2.07 (2)
W–C(8)	1.96 (2)	Ru(2)–C(4)	1.93 (2)
W–C(9)	2.36 (2)	Ru(2)–C(5)	1.89 (2)
W–C(10)	2.09 (2)	Ru(2)–C(6)	1.89 (2)
W–C(18)	2.29 (2)	Ru(2)–C(10)	2.13 (2)
W–C(19)	2.30 (2)	Ru(2)–C(11)	2.27 (2)
W–C(20)	2.34 (2)	C(9)–C(10)	1.40 (2)
W–C(21)	2.34 (2)	C(9)–C(12)	1.48 (2)
W–C(22)	2.30 (2)	C(10)–C(11)	1.37 (2)
Ru(1)–Ru(2)	2.818 (2)	C–O(av)	1.14 (2)
Ru(1)–C(1)	1.94 (2)		
	Bond Angles		
Ru(1)–W–C(7)	67.4 (5)	C(3)–Ru(1)–C(9)	94.6 (7)
Ru(2)–W–C(7)	75.8 (6)	Ru(1)–Ru(2)–C(4)	162.2 (6)
C(7)–W–C(8)	90.8 (8)	Ru(1)–Ru(2)–C(5)	96.4 (5)
C(7)–W–C(9)	112.1 (6)	Ru(1)–Ru(2)–C(6)	85.6 (5)
C(7)–W–C(10)	117.9 (7)	Ru(1)–Ru(2)–C(10)	65.4 (4)
Ru(1)–W–C(8)	74.4 (6)	Ru(1)–Ru(2)–C(11)	96.2 (4)
Ru(2)–W–C(8)	131.8 (5)	W–C(9)–Ru(1)	81.9 (5)
C(8)–W–C(9)	74.6 (6)	W–C(9)–C(10)	61.5 (8)
C(8)–W–C(10)	110.0 (7)	W–C(9)–C(12)	128 (1)
W–Ru(1)–Ru(2)	61.84 (4)	Ru(1)–C(9)–C(10)	102 (1)
W–Ru(1)–C(1)	114.4 (5)	Ru(1)–C(9)–C(12)	134 (1)
W–Ru(1)–C(2)	108.5 (6)	C(10)–C(9)–C(12)	122 (1)
W–Ru(1)–C(3)	141.7 (5)	W–C(10)–Ru(2)	88.4 (6)
Ru(2)–Ru(1)–C(1)	96.8 (5)	W–C(10)–C(9)	82.4 (9)
C(1)–Ru(1)–C(2)	88.8 (8)	W–C(10)–C(11)	140 (1)
C(1)–Ru(1)–C(3)	95.2 (8)	Ru(2)–C(10)–C(9)	116 (1)
C(1)–Ru(1)–C(9)	167.3 (7)	Ru(2)–C(10)–C(11)	78 (1)
Ru(2)–Ru(1)–C(2)	170.2 (6)	C(9)–C(10)–C(11)	138 (2)
C(2)–Ru(1)–C(3)	95.4 (7)	Ru(2)–C(11)–C(10)	66 (1)
C(2)–Ru(1)–C(9)	98.3 (7)	Ru–C–O(av)	177 (2)
Ru(2)–Ru(1)–C(3)	92.2 (5)	W–C–O(av)	170 (2)

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(30) A reviewer suggested that formulation Y may be more important than X, since the bond distance Fe–C(6) (average 2.195 (7) Å) is appreciably longer than the distances Fe–C(7) (average 2.019 (6) Å) and Fe–C(8) (average 2.012 (6) Å), rather than Fe–C(8) > Fe–C(6), Fe–C(7). However, the last-mentioned relationship does not even hold for the trinuclear Fe_2W μ_3-allenyl complex **3d** (Fe(1)–C(9) (i.e., σ) = 1.952 (4) Å, Fe(2)–C(10) (i.e., π central) = 2.060 (4) Å, Fe(2)–C(11) (i.e., π terminal) = 2.185 (5) Å; cf. Table VII; note a different numbering system) where an alkyne representation would appear to be less important than with **2e**.

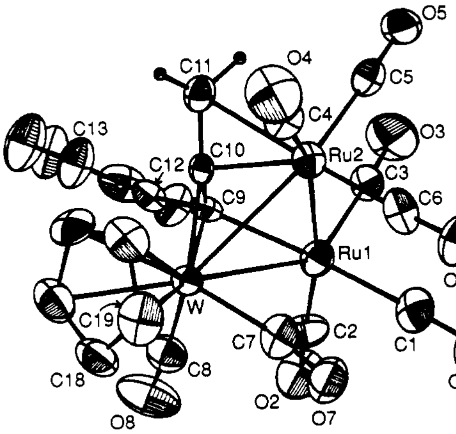

Figure 3. ORTEP plot of 4 showing atom-numbering scheme. For clarity, only the hydrogen atoms of the CH_2 group are given, with an arbitrary radius. Non-hydrogen atoms are drawn at the 50% probability level.

While the spectroscopic data clearly indicate the allenyl nature of the coordinated hydrocarbyl ligand, accurate structural characterization of 3 and 4 required X-ray crystallographic analyses. The structures of **3d** and 4 with the atom-numbering schemes are shown in Figures 2 and 3, respectively. Selected bond distances and angles are presented in Tables VII (for **3d**) and VIII (for 4).

Compounds 3 and 4 represent the first examples of heterotrinuclear metal–μ_3-η^1,η^2,η^2-allenyl complexes, and the first such trinuclear allenyls of any constitution that are nonionic and lack ancillary bridging ligands. Several homotrinuclear ruthenium- and osmium–μ_3-η^1,η^2,η^2-allenyl complexes, all possessing additional bridging ligands (H, PR_2, CH_2), have been previously prepared.[31-33] An anionic triiron–μ_3-η^1,η^2,η^2-allenyl complex is known as well.[34]

The iron and tungsten atoms in **3d** are joined together in a triangular array by single metal—metal bonds (Fe(1)—W = 2.7418 (5) Å, Fe(2)—W = 2.8373 (7) Å, Fe(1)—Fe(2) = 2.7082 (8) Å). The Fe—Fe bond distance is essentially equal to the corresponding Fe—Fe bond distance in $PPh_4[Fe_3(CO)_9(\mu_3\text{-}\eta^1,\eta^2,\eta^2\text{-}C(OEt){=}C{=}CHC(O)Me)]$ (2.7460 (6) Å).[33] A W-to-Fe(1) donor–acceptor bond in **3d** is necessary to satisfy the 18-electron requirement at each metal. The allenyl ligand shows carbon—carbon bond distances (C(9)—C(10) = 1.371 (5) Å, C(10)—C(11) = 1.385 (6) Å) that are very similar to those in **2e** and in the reported homotrinuclear metal–μ_3-η^1,η^2,η^2-allenyl complexes.[31,32b,34] The angle about the central allenyl carbon is substantially wider (C(9)—C(10)—C(11) = 144.3 (3)°) than that in **2e** owing to the μ_3 coordination; however, it is comparable with that found in the structurally similar Fe_3 and Ru_3 μ_3-allenyl complexes (140.6 (2)–146.8 (4)°).[31,32b,34] The W—C(9) and W—C(10) bond lengths of 2.279 (3) and 2.139 (4) Å, respectively, compare well with analogous distances in $(CO)_3Co(\mu\text{-}PhC{\equiv}CMe)WCp(CO)_2$ (2.120 (3) and 2.151 (3) Å)[3a] and **2e**.

The X-ray crystallographic analysis of 4 reveals the same μ_3-η^1,η^2,η^2-allenyl coordination of the hydrocarbyl ligand as in **3d**. In both **3d** and 4 the W atom binds the internal C=C of the allenyl fragment while Fe or Ru is attached to the terminal C=C. This mode of coordination is to be contrasted with that recently found in $(CO)_6Fe_2(\mu_3\text{-}\eta^1,\eta^2,\eta^2\text{-}PhC{=}C{=}CH_2)RuCp(CO)$, where the metal derived from the reactant propargyl complex, i.e. Ru, binds the terminal allenyl C=C.[5] The reason for this difference in connectivity may lie in the mechanism of formation of such μ_3-allenyl compounds; this is considered in some detail elsewhere.[6]

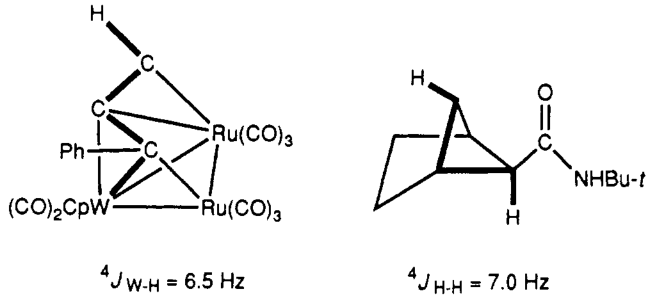

Figure 4. Comparison of the structural features of 4 and $C_6H_9C(O)NH$-*t*-Bu that emphasize the positions of the atoms involved in the ^1H NMR "W-effect".

The important bond distances and angles of the allenyl ligand of 4 (C(9)–C(10) = 1.40 (2) Å, C(10)–C(11) = 1.37 (2) Å, C(9)–C(10)–C(11) = 138 (2)°) are comparable with those of **3d**. These data, as well as the Ru(1)–Ru(2) (2.818 (2) Å), Ru(1)–C(9) (2.09 (2) Å), Ru(2)–C(10) (2.13 (2) Å), and Ru(2)–C(11) (2.27 (2) Å) bond distances, are also very similar to the corresponding distances reported for the Ru_3 μ_3-η^1,η^2,η^2-allenyl complexes.[31,32b] Interestingly, the configuration of the tungsten atom in 4 differs from that in **3d**. Whereas in **3d** the carbons C(4) and C(8) are nearly eclipsed (C(8)–W–Fe(2)–C(4) = −15.3°), in 4 they appear in trans positions (C(8)–W–Ru(2)–C(4) = −179.1°). The different arrangement of ligands around tungsten in 4 causes slight changes, compared to **3d**, in the positions of the ruthenium carbonyls and in some bond angles (cf. Tables VII and VIII), owing to intramolecular steric interactions. The crystal structure of 4 also provides a clue as to the origin of the previously mentioned long-range coupling between one of the CH_2 hydrogens and the W atom. The relative positions of the H and W atoms in 4 are similar to those of the two highlighted hydrogens in the bicyclic organic amide $C_6H_9C(O)NH$-*t*-Bu (Figure 4), for which coupling occurs via a through-space interaction, termed the "W-effect".[35]

Reactions of Heteronuclear Metal-μ-Allenyl Complexes. Although only a limited number of reactions have been tried to date, complexes 2–4 appear to be much less reactive than the triruthenium μ_3-allenyls investigated by Carty.[32b,36] For example, **2d** and **3d** do not react with diazomethane in diethyl ether at room temperature over 24 h. Likewise, there is no observable reaction between **2d** and $MeO_2CC{\equiv}CCO_2Me$ in THF at ca. 25 °C or in benzene at reflux over 36 h or longer. Photolysis of THF solutions of **2d** or 4 and $MeO_2CC{\equiv}CCO_2Me$ for at least 8 h leads only to slight decomposition of the metal allenyl. Lack of reactivity toward 2 extends to $Me_3SiC{\equiv}CH$ (no reaction other than decomposition of **2b** in THF at reflux in 38 h) and SO_2 (no reaction with **2e** in pentane at ambient temperatures in 4.5 h). Protonation of **2d** with $HBF_4{\cdot}Et_2O$ or CF_3CO_2H in diethyl ether at ca. 25 °C also leads to no observable reaction for 36 h and neither does

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(31) Gervasio, G.; Osella, D.; Valle, M. *Inorg. Chem.* **1976**, *15*, 1221.

(32) (a) Nucciarone, D.; Taylor, N. J.; Carty, A. J. *Organometallics* **1984**, *3*, 177. (b) Nucciarone, D.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Ibid.* **1988**, *7*, 106.

(33) Deeming, A. J.; Arce, A. J.; De Sanctis, Y.; Bates, P. A.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 2935.

(34) Suades, J.; Dahan, F.; Mathieu, R. *Organometallics* **1988**, *7*, 47.

(35) Reference 24, p 84.

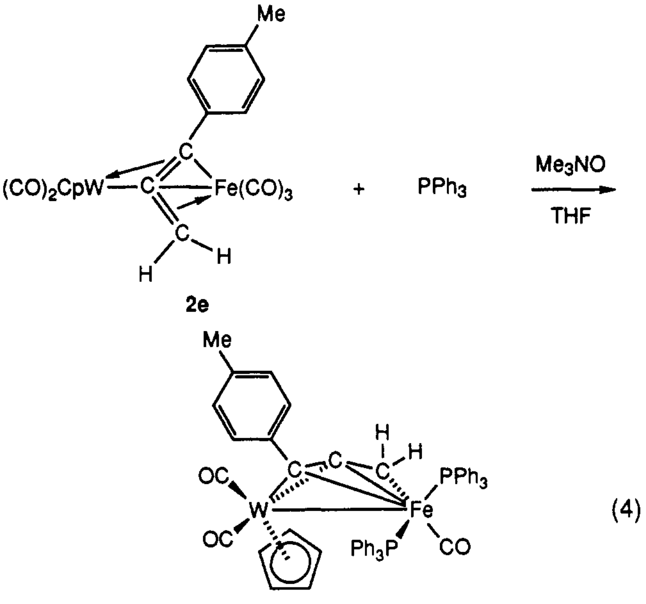
(36) (a) Nucciarone, D.; Taylor, N. J.; Carty, A. J. *Organometallics* **1988**, *7*, 127. (b) Nucciarone, D.; Taylor, N. J.; Carty, A. J.; Tiripicchio, A.; Tiripicchio, M. T.; Sappa, E. *Ibid.* **1988**, *7*, 118. (c) Randall, S. M.; Taylor, N. J.; Carty, A. J.; Haddah, T. B.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1988**, 870.

treatment of **2d** with $K[B(s\text{-}Bu)_3H]$ in pentane at ca. 25 °C for 48 h.

Attempts were made to convert **2** to **3** by action of iron carbonyls. Thus, **2e** was treated with $Fe_2(CO)_9$ in pentane or THF (cf. Experimental Section), and **2d** was reacted with $Fe_3(CO)_{12}$ in benzene. Whereas the former reactions afforded trace amounts of **3e**, the latter gave no observable **3d**. By contrast, photolysis of **2d** and $Fe(CO)_5$ in diethyl ether provided a reasonable yield (37%) of **3d** along with a small amount of a white tacky solid, which appears to be a low molecular weight organic polymer or an oligomer. The relatively effective conversion of **2** to **3** with $Fe(CO)_5$ under photochemical conditions may indicate that both a coordinately unsaturated $Fe(CO)_x$ and an "activated **2**" are necessary to form the trinuclear metal–μ_3-allenyl product.

The allenyl ligand in **2** can be removed as $R(I)C{=}C{=}CH_2$ by treatment with iodine. In this manner $Me(I)C{=}C{=}CH_2$ was obtained (in 72% yield) from **2a**; however, this reaction is not synthetically important since allenyl iodides are readily prepared in high yield by more convenient methods.[15,37]

Complex **2e** reacts with 1 equiv of PPh_3 in the presence of 2 equiv of Me_3NO[38] in THF at room temperature to afford only the disubstituted derivative **5** (eq 4). Surprisingly, no reaction occurs when 1 equiv of Me_3NO is employed. Also, there is no substitution when **2e** and PPh_3 react in THF solution at reflux in the absence of Me_3NO.



2e

5

(4)

The structure of **5** may be assigned with confidence from the IR and NMR data. Since only one IR absorption attributable to $\nu(CO)$ of FeCO is noted (at 1996 cm^{-1}), it follows that both PPh_3 ligands are bonded to iron. This is confirmed by the absence of J_{W-P} satellites associated with the two $^{31}P\{^1H\}$ NMR resonances at δ 81.5 and 66.1. The lack of observable J_{P-P} indicates that the PPh_3 ligands are mutually cis.[39] In the $^{13}C\{^1H\}$ NMR spectrum, the lowest field signal (at δ 219.26), assigned to a WCO, is split by only one P nucleus (d, J_{P-C} = 29.1 Hz), indicating that this CO must be nearly eclipsed relative to the other PPh_3. The appearance of the second WCO resonance (at δ 214.25) as a triplet (J_{P-C} = 29.1 Hz) shows that this carbonyl occupies an equivalent position with respect to both phosphines. Likewise, the iron-bound CO is located in a similar environment relative to each PPh_3, since the FeCO resonance (at δ 216.93) is split nearly equivalently (J_{P-C} = 54.3, 45.2 Hz) by the two P nuclei. The structure of **5** depicted in eq 4 accords with the foregoing data.

Conclusion

Molybdenum- and tungsten-propargyl complexes of the general formula $(CO)_3CpMCH_2C{\equiv}CR$ (**1**) react with $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, and $Ru_3(CO)_{12}$ to afford heterobinuclear and -trinuclear metal–μ-allenyl complexes, $(CO)_3Fe(\mu\text{-}\eta^2,\eta^3\text{-}RC{=}C{=}CH_2)MCp(CO)_2$ (**2**) and $(CO)_6M'_2(\mu_3\text{-}\eta^1,\eta^2,\eta^2\text{-}RC{=}C{=}CH_2)MCp(CO)_2$ (M′ = Fe (**3**), Ru (**4**), respectively. Reaction conditions have been developed to optimize yields of each **2** and **3**. There appears to be no interconversion between the binuclear and trinuclear complexes, and this behavior accords with a proposed mechanism of their formation. The present study suggests that reactions of transition-metal propargyls may provide a useful general synthetic approach to heteronuclear metal–μ-allenyl complexes; subsequent work in our laboratory furnishes additional support for this claim.[5,6]

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Supplementary Material Available: Listings of anisotropic thermal parameters and hydrogen atom coordinates for complexes **2e**, **3d**, and **4** and selected torsion angles for complexes **3d** and **4** (12 pages); tables of structure factors for **2e**, **3d**, and **4** (58 pages). Ordering information is given on any current masthead page.

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[37] Flood, T.; Peterson, P. E. *J. Org. Chem.* **1980**, *45*, 5006.

[38] Me_3NO is used as a decarbonylation reagent; see, e.g.: (a) Albers, M. O.; Coville, N. J. *Coord. Chem. Rev.* **1984**, *53*, 227. (b) Luh, T.-Y. *Ibid.* **1984**, *60*, 255.

[39] Generally, small coupling can be observed, although in some cases no coupling was detected; see, e.g.: (a) Nixon, J. F.; Pidcock, A. *Annu. Rev. NMR Spectrsc.* **1969**, *2*, 345. (b) Pregosin, P. S.; Kunz, R. W. *Phosphorus-31 and Carbon-13 NMR of Transition-Metal Complexes*; Springer Verlag: New York, 1979.