initiate strand scission. The high yields of 3 obtained in the presence of DNA are in agreement with the belief that DNA promotes or acts as a template for the reactions of small molecules.[12] Thus the two strands of the DNA confine the diynene moiety in the minor groove in a manner that facilitates the aromatization of this moiety.

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Synthesis of Heteronuclear Metal–Allenyl Clusters: Transition-Metal–Propargyl Compounds as Templates for the Construction of Mixed Metal–Metal Bonds

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Heteronuclear metal clusters represent an important and rapidly growing class of compounds.[1] The presence of different metal centers in the same molecule can provide useful information concerning the activation of hydrocarbon substrates in stoichiometric and catalytic reactions. So far, however, synthetic methodology for this class of compounds is, in general, not well developed.[2] We now report a new, facile one-step preparation of heteronuclear metal complexes containing bridging allenyl ligands; these compounds had been essentially unknown for mixed metal systems.[3] Our method appears to be general and may be applicable to compounds with related bridging hydrocarbon groups. The heteronuclear μ-allenyl compounds described herein may be expected to undergo unusual transformations based on reactivity studies of homonuclear μ-allenyl compounds.[4]

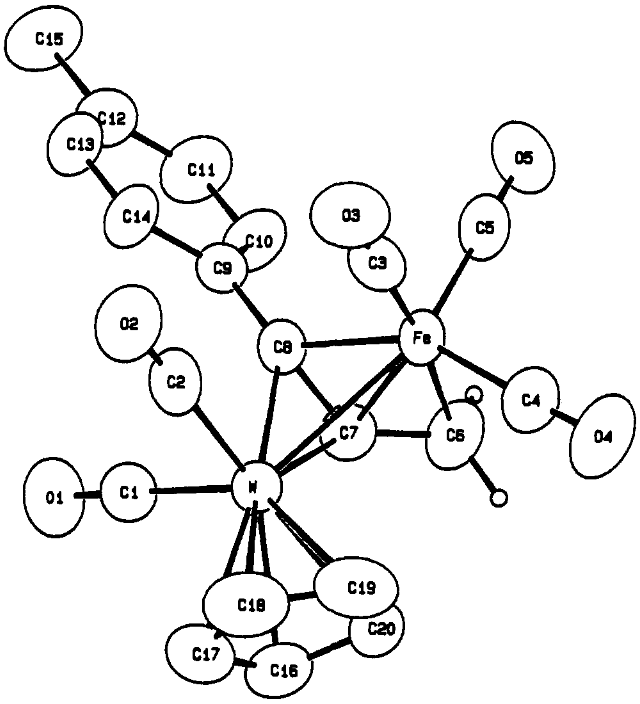


Figure 1. ORTEP plot of 2e showing atom numbering scheme. Only the CH_2 hydrogens are shown, drawn at an arbitrary radius. Non-hydrogen atoms are drawn at the 50% probability level.

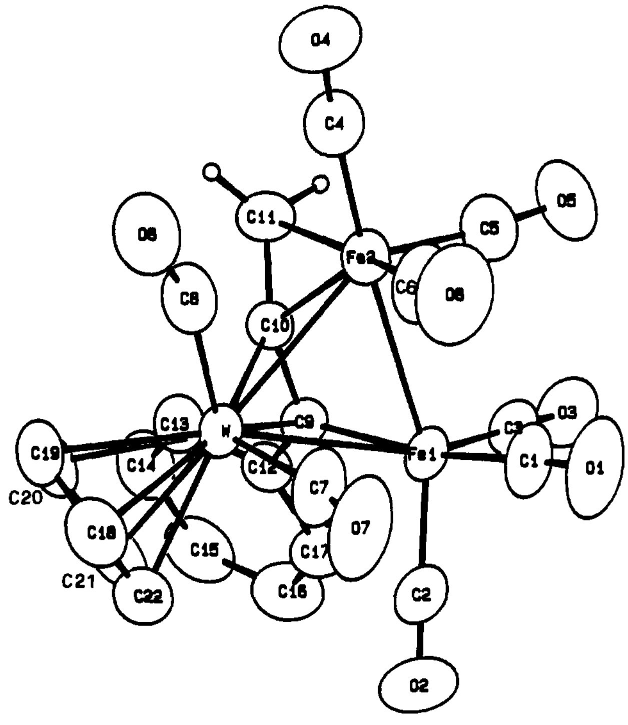
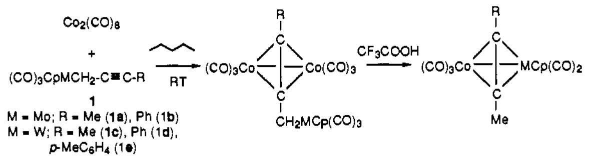


Figure 2. ORTEP plot of 3d showing atom numbering scheme (drawn as described in Figure 1).

We recently used the alkyne functionality of transition-metal–propargyl compounds as a template for the two-step synthesis of the heteronuclear μ-alkyne complexes $(CO)_3Co(\mu\text{-}RC{\equiv}CMe)MCp(CO)_2$[5] (eq 1). An extension of the chemistry



(1)

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(3) Exceptions are $PPh_4[Fe_3Rh_2(CO)_{10}(\mu\text{-}CO)_3(\mu_4\text{-}\eta^3\text{-}MeC{=}C{=}CH_2)]$ (Attali, S.; Dahan, F.; Mathieu, R. *Organometallics* **1986**, *5*, 1376) and $FeCo(CO)_5L(\mu\text{-}\eta^3\text{-}R'C{=}C{=}CR_2)$ (L = CO, PPh_3; R_2 = H_2, HMe, Me_2; R' = Me, Et, CH_2OH) (Aime, S.; Osella, D.; Milone, L.; Tiripicchio, A. *Polyhedron* **1983**, *2*, 77); however, the FeCo complexes could not be accurately characterized by X-ray crystallography.

(4) (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. *Organometallics* **1988**, *7*, 118. (c) Nucciarone, D.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Organometallics* **1988**, *7*, 106. (d) Randall, S. M.; Taylor, N. J.; Carty, A. J.; Haddah, T. B.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1988**, 870.

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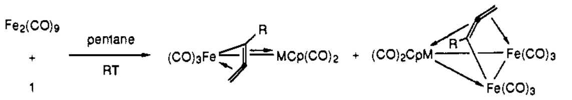
of step 1 to reactions of **1** with group VIII metal carbonyls has afforded allenyl-bridged heteronuclear compounds. Accordingly, stirring (24 h) equimolar quantities of $Fe_2(CO)_9$ and **1** as a room-temperature pentane suspension, followed by chromatography of the reaction mixture on Florisil, provides **2** and **3** (eq 2).[6] The reaction occurs with cleavage of the M–CH_2 bond in **1** and concomitant rehybridization of the propargyl carbon ($sp^3 \rightarrow sp^2$). Refluxing (18 h) $Fe_3(CO)_{12}$ and **1** in benzene gives the reverse product distribution of **2** and **3**.



(2)

major minor

2
M = Mo; R = Me (**2a**), Ph (**2b**)
M = W; R = Me (**2c**), Ph (**2d**),
p-MeC_6H_4 (**2e**)

3
M = Mo; R = Me (**3a**), Ph (**3b**)
M = W; R = Me (**3c**), Ph (**3d**),
p-MeC_6H_4 (**3e**)

The structures of **2e** and **3d** were unambiguously confirmed by X-ray crystallography (Figures 1 and 2).[7] On the basis of the normal bond lengths of the bridging carbons (C_6–C_7 = 1.390 (9) Å, C_7–C_8 = 1.375 (8) Å) and the sp^2 hybridization at C_6($J_{^{13}C-^{1}H}$ = 164 Hz), **2e** is best formulated as a rare example of a heterobinuclear μ-η^2,η^3-allenyl compound.[3] The angle about the central allenyl carbon (C_6–C_7–C_8 = 128.9 (6)°) is even more acute than that observed in the structurally similar $(Mo(CO)_2Cp')_2(\mu$-η^2,η^3-$HC{=}C{=}CH_2)^+$ (Cp′ = C_5H_4Me)[8] and may reflect the contribution of resonance stabilization from other structures.

Compounds **3** represent the first examples of heterotrinuclear μ_3-η^1,η^2,η^2-allenyl complexes.[9] The allenyl ligand in **3d** has similar bond distances (C_9–C_{10} = 1.371 (5) Å, C_{10}–C_{11} = 1.385 (6) Å) to those in **2e**; however, the angle about the central allene carbon atom is less strained (C_9–C_{10}–C_{11} = 144.3 (3)°) owing to the μ_3 coordination. A dative bond is shown between Fe and W to satisfy the $18e^-$ requirement at each metal.

Complexes **2** afford no detectable **3** when heated or irradiated alone in solution. However, conversion of **2** to **3** by reaction with $Fe_2(CO)_9$ in pentane or by photolysis with $Fe(CO)_5$ does occur but only in minor yields (<20%). Moreover, only **2** is isolated (up to 95%) when a 1:2 molar ratio of $Fe_2(CO)_9$ and **1** is employed. We suggest that these reactions may occur via transition-metal-assisted electrophilic attack on the alkyne moiety of **1** by a coordinatively unsaturated $Fe(CO)_x$ (x = 3 or 4) fragment in a manner similar to that proposed for reactions of **1** with organic electrophiles.[10]

When $Ru_3(CO)_{12}$ and **1** are reacted under similar conditions to those used in the reaction of $Fe_3(CO)_{12}$, the Ru analogue of **3d**, **4a**,[11] is formed along with a minor amount of $Ru_2Cp_2(CO)_4$. No heterobinuclear allenyl species was isolated. The crystal structure of **4a**[7] confirms the allenyl coordination (C_9–C_{10}–C_{11} = 138 (2)°; C_9–C_{10} = 1.40 (2) Å, C_{10}–C_{11} = 1.37 (2) Å). Interestingly, the configurations of the tungsten atoms in **4a** and **3d** differ. In **3d** C_4 and C_8 are nearly eclipsed (C_8–W–Fe_2–C_4 = −15.3°), whereas in **4a** they are trans to each other (C_8–W–Ru_2–C_4 = −179.1°).

We are currently investigating the generality of this methodology, including extensions to reactions of mononuclear metal-η^1-allenyl complexes with metal carbonyls.

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation (through Grant CHE-8420806 to A.W.) and Ministero Pubblica Istruzione (Rome). High field NMR and mass spectra were obtained at The Ohio State University Chemical Instrument Center (funded in part by National Science Foundation Grant 79-10019)).

Supplementary Material Available: Spectroscopic and analytical data for metal–allenyl complexes **2** and **3** (except **2d** and **3d**) and details of the structure determinations of **2e**, **3d**, and **4a** as listed in ref 7 (24 pages). Ordering information is given on any current masthead page.

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(5) Wido, T. G.; Young, G. H.; Wojcicki, A.; Calligaris, M.; Nardin, G. *Organometallics* **1988**, *7*, 452.

(6) E.g., reaction mixture of $Fe_2(CO)_9$ and **1d** was eluted with 2% ether in pentane to give **2d** (58%) as an orange solid upon concentration: IR (C_6H_{12}) ν_{CO} 2046 m, 2036 s, 1993 vs, 1973 s, 1960 vs, 1946 m cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 213.30 (W–CO, $J_{^{183}W-^{13}C}$ = 166 Hz), 211.67 (Fe–CO), 210.63 (W–CO, $J_{^{183}W-^{13}C}$ = 173 Hz), 111.76 (=C=, $J_{^{183}W-^{13}C}$ = 34 Hz), 80.50 (=CPh), 70.53 (=CH_2); ^{1}H NMR ($CDCl_3$) δ 5.39, 3.99 (2 d, J = 0.7 Hz, =CH_2); mass spectrum (^{184}W) m/z (rel intensity) 560 (M^+, 5.53) followed by five successive peaks due to CO loss (M^+ − 4CO, 100). Anal. Calcd for $C_{19}H_{12}FeO_5W$: C, 40.75; H, 2.16. Found: C, 41.04; H, 1.99. Elution with ether gave **3d** (5.3%) as purple plates upon recrystallization from 1:1 CH_2Cl_2/pentane: IR (C_6H_{12}) ν_{CO} 2052 s, 2020 vs, 1996 s, 1984 m, 1963 m, 1951 w cm^{-1}; ^{13}C NMR ($CDCl_3$) 223.93, 221.10 (W–CO), 211.53 (Fe–CO), 155.86 (=C=), 27.80 (=CH_2); ^{1}H NMR ($CDCl_3$) δ 3.44, 2.86 (2d, J = 1.1 Hz, =CH_2); mass spectrum (^{184}W) m/z (rel intensity) 700 (M^+, 0.89) followed by eight successive peaks due to CO loss (M^+ − 4CO, 100). Anal. Calcd for $C_{22}H_{12}Fe_2O_8W$: C, 37.75; H, 1.73. Found: C, 37.22; H, 1.51.

(7) Details of the structure determination, including crystal data, data collection and refinement, positional parameters and their standard deviations, temperature factor expressions (B's), and selected bond distances and angles are available in Supplementary Material.

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

(11) **4a** was isolated (21%) as orange needles by recrystallization from 1:1 $CHCl_3$/pentane: IR (C_6H_{12}) ν_{CO} 2067 s, 2032 s, 1998 m, 1981 m, 1967 m cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 225.25, 222.28 (W–CO), 201.79, 198.74, 196.06, 195.13, 192.67 (Ru–CO), 161.59 (=C=, $J_{^{183}W-^{13}C}$ = 45 Hz), 114.09 (=CPh), 26.99 (=CH_2); mass spectrum (^{184}W) m/z (rel intensity) 790 (M^+, 0.5) followed by eight successive peaks due to loss of CO (M^+ − 3CO, 100). Anal. Calcd for $C_{22}H_{12}O_8Ru_2W$: C, 33.43; H, 1.53. Found: C, 33.45; H, 1.46.

$RhCl(PPh_3)_3$-Catalyzed Hydrosilation of Organoiron Acyl Complexes

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Two general procedures currently are available for reducing acyl ligands on organotransition-metal complexes.[1,2] (1) Carbocationic activation of acyl L_xM–C(O)R and hydride transfer from a borohydride affords α-alkoxyalkyl compounds L_xM–CH(OR′)R,[3] and (2) borane (BH_3) typically reduces acyl complexes to saturated alkyl compounds L_xM–CH_2R.[4] The established

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(1) Cutler, A. R.; Hanna, P. K.; Vites, J. C. *Chem. Rev.* **1988**, *88*, 1363.

(2) Intermolecular reduction of electron-deficient η^2-acyl complexes [e.g., $Cp_2Zr(X)(COR)$] by metal hydrides,[2a] *i*-Bu_2AlH, aluminum alkyls AlR_3,[2b] zirconocene alkyl complexes,[2c] and Lewis bases[2d] has been documented. (a) Marsella, J. A.; Huffman, J. C.; Folting, K.; Caulton, K. G. *Inorg. Chim. Acta* **1985**, *96*, 161. Gell, K. I.; Posin, P.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846. Erker, G.; Kropp, K. *Chem. Ber.* **1982**, *115*, 2437. Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. Katahira, D. A.; Moloy, K. G.; Marks, T. J. *Organometallics* **1982**, *1*, 1723. (b) Waymouth, R. M.; Grubbs, R. H. *Organometallics* **1988**, *7*, 1631. (c) Martin, B. D.; Matchett, S. A.; Norton, J. R.; Anderson, O. P. *J. Am. Chem. Soc.* **1985**, *107*, 7952. Matchett, S. A.; Norton, J. R.; Anderson, O. P. *Organometallics* **1988**, *7*, 2228. (d) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J.; Arif, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 149 and references cited.

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