schemes. Time-resolved emission and excitation spectra could permit additional elaboration of the relaxation pathway and verification of the assignment of the broad and narrow emission bands.

References and Notes

(1) L. S. Forster in "Transition Metal Chemistry", Vol. 5, R. L. Carlin, Ed., Marcel Dekker, New York, 1969.
(2) L. S. Forster in "Concepts in Inorganic Photochemistry", A. Adamson and P. Fleischauer, Eds., Wiley, New York, 1975.
(3) P. D. Fleischauer, A. W. Adamson, and G. Sartori, *Prog. Inorg. Chem.*, **17**, 1 (1972).
(4) D. J. Robbins and A. J. Thomson, *Mol. Phys.*, **25**, 1103 (1973).
(5) M. K. DeArmond, *Acc. Chem. Res.*, **7**, 309 (1974).
(6) G. A. Crosby, *Acc. Chem. Res.*, **8**, 231 (1975).
(7) J. E. Hillis and M. K. DeArmond, *J. Lumin.* **4**, 273 (1971).
(8) Y. Ohashi, K. Yoshihora, and S. Nogukura, *J. Mol. Spectrosc.*, **38**, 43 (1971).
(9) W. Halper and M. K. DeArmond, *J. Lumin.*, **5**, 225 (1972).
(10) R. J. Watts, M. J. Brown, B. G. Griffith, and J. S. Harrington, *J. Am. Chem. Soc.*, **97**, 6029 (1975).
(11) R. J. Watts, B. G. Griffith, and J. S. Harrington, *J. Am. Chem. Soc.*, **98**, 674 (1976).
(12) R. J. Watts and D. Missimer, *J. Am. Chem. Soc.*, in press.
(13) P. J. Giordano, S. M. Fredericks, M. S. Wrighton, and D. L. Morse, *J. Am. Chem. Soc.*, **100**, 2257 (1978).
(14) C. K. Jorgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).
(15) J. E. Hillis and M. K. DeArmond, *Chem. Phys. Lett.*, **10**, 325 (1971).
(16) F. Weigert, *Verh. Dtsch. Phys. Ges.*, **1**, 100 (1920).
(17) S. I. Vavilov and V. L. Levshin, *Z. Phys.*, **16**, 136 (1923).
(18) F. Perrin, *J. Phys. Radium*, **7**, 390 (1926).
(19) A. Jablonski, *Z. Phys.*, **96**, 236 (1935).
(20) A. C. Albrecht and W. T. Simpson, *J. Am. Chem. Soc.*, **77**, 4454 (1955).
(21) A. C. Albrecht, *J. Mol. Spectrosc.*, **6**, 84 (1961).
(22) M. A. El-Sayed, *J. Chem. Phys.*, **38**, 2834 (1963).
(23) M. A. El-Sayed, *Acc. Chem. Res.*, **1**, 8 (1968).
(24) T. Pavlopoulos and M. A. El-Sayed, *J. Chem. Phys.*, **41**, 1082 (1964).
(25) M. A. El-Sayed, *J. Chem. Phys.*, **43**, 2864 (1965).
(26) Y. Kanda, J. Stanislaus, and E. C. Lim, *J. Am. Chem. Soc.*, **91**, 5085 (1969).
(27) Y. H. Li and E. C. Lim, *Chem. Phys. Lett.*, **7**, 15 (1970).
(28) M. E. Long and E. C. Lim, *Chem. Phys. Lett.* **20**, 413 (1973).
(29) I. Fujita and H. Kobayashi, *Inorg. Chem.*, **12**, 2758 (1973).
(30) W. H. Halper, Ph.D. Dissertation, North Carolina State University, 1973, p 12.
(31) L. F. Fieser, "Experiments in Organic Chemistry", D. C. Heath, Boston, Mass., 1957, pp 285–289.
(32) G. A. Heath and R. L. Martin, *Chem. Commun.*, 951 (1969).
(33) G. A. Heath and R. L. Martin, *Aust. J. Chem.*, **24**, 2061 (1957).
(34) K. Bechgaard, V. D. Parker, and C. T. Pedersen, *J. Am. Chem. Soc.*, **95**, 4373 (1973).
(35) C. A. Parker and W. T. Rees, *Analyst*, **85**, 587 (1960).
(36) H. V. Drushel, A. L. Sommers, and R. C. Cox, *Anal. Chem.*, **35**, 2166 (1963).
(37) W. H. Melhuish, *J. Opt. Soc. Am.*, **54**, 183 (1964).
(38) A. J. Barr, J. H. Goodnight, J. P. Sall, and J. T. Helwig, "A User's Guide to SAS 76", Sparks Press, Raleigh, N.C., 1976, pp 193–199.
(39) C. A. Parker, "Photoluminescence of Solutions", Elsevier, Amsterdam, 1968, p 438.
(40) A. Haber and R. P. Runyon, "General Statistics", Addison-Wesley, Reading, Mass., 1971, pp 181–218.
(41) T. J. Durnick and A. H. Kalantar, *J. Chem. Phys.*, **66**, 1914 (1977).
(42) J. R. Lombardi, J. W. Reynolds, and A. C. Albrecht, *J. Chem. Phys.*, **40**, 1148 (1964).
(43) J. N. Demas and G. A. Crosby, *Anal. Chem.*, **42**, 1010 (1970).
(44) G. A. van Salis and H. Labbert, *J. Phys. Chem.*, **72**, 752 (1968).
(45) P. F. Jones and S. Siegel in "Molecular Luminescence", E. C. Lim, Ed., W. A. Benjamin, New York, 1969, p 15.
(46) S. Kawanishi, A. Yokoyama, and H. Tanaka, *Chem. Pharm. Bull.*, **21**, 2653 (1973).
(47) T. J. Chuang and K. B. Eisenthal, *J. Chem. Phys.*, **57**, 5094 (1972).
(48) R. Beckett and B. F. Hoskins, *Inorg. Nucl. Chem. Lett.*, **8**, 683 (1972).
(49) W. C. Galley and R. M. Purkey, *Proc. Natl. Acad. Sci. U.S.A.*, **65**, 823 (1970).
(50) F. Castelli and L. S. Forster, *J. Am. Chem. Soc.*, **95**, 7223 (1973).
(51) F. Castelli and L. S. Forster, *J. Am. Chem. Soc.*, **97**, 6307 (1975).
(52) A. R. Henderson and R. L. Martin, *Aust. J. Chem.*, **25**, 257 (1972).
(53) A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968, p 224.
(54) C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes", Pergamon Press, Oxford, 1962, p 146.
(55) A. M. Bond, G. A. Heath, and R. L. Martin, *J. Electrochem. Soc.*, **117**, 1362 (1970).
(56) A. M. Bond, G. A. Heath, and R. L. Martin, *Inorg. Chem.*, **10**, 2026 (1971).
(57) T. Ohno and S. Kato, *Bull. Chem. Soc. Jpn.*, **47**, 1901 (1974).
(58) J. Wei and C. D. Prater, *Adv. Catal.*, **13**, 204 (1962).
(59) G. Gliemann and H. Yersin, *Ber. Bunsenges. Phys. Chem.*, **75**, 1257 (1971).
(60) F. Castelli and L. S. Forster, *J. Am. Chem. Soc.*, **97**, 6306 (1975).
(61) The Hamamatsu R955 photomultiplier tube used for detection weights light emitted from the blue edge of the emission spectrum most heavily.

Synthesis and Cyclization Reactions of Alkynyl(η^5-cyclopentadienyltricarbonylmolybdenum and -tungsten) Complexes

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Abstract: Cyclization of the organometallic complexes $CH_3C{\equiv}C(CH_2)_nM(C_5H_5)(CO)_3$ (n = 3, 4, 5; I, M = Mo; II, M = W) occurred under mild conditions to give cyclized products $M(C_5H_5)(CO)_2[C(CH_3){=}C(O)(CH_2)_n]$ (III, M = Mo; IV, M = W) derived from intramolecular insertion of the acetylenic function into a metal–acyl bond. Yields of III were high (>70%) for n = 3, moderate (~50%) for n = 4, and lower (<15%) for n = 5. No other isomers or products of insertion into metal–alkyl bonds were observed. Cleavage of the organic ligand from III (n = 4) under CO with CF_3COOH gave 2-ethylidenecyclohexanone and $CF_3CO_2Mo(C_5H_5)(CO)_3$ in >90% yield. Hydrogenation of III (n = 4) gave 2-ethylcyclohexanone and $[Mo(C_5H_5)(CO)_2]_2$ in >90% yield. Protonation of $CH_3C{\equiv}C(CH_2)_4W(C_5H_5)(CO)_3$ gave the bis acetylene complex, $W(C_5H_5)(CO)_2(\text{2-heptyne})_2^+$.

Introduction

Cyclization of acyclic ω-functionalized acetylenes A has been mediated by a number of metal reagents, yielding several kinds of products. Examples include RCuLi reagents[3a] (effective primarily for R = phenyl and n = 3, 4), which give products of type B and C, $PdI_2/CO/PBu_3$[3b,c] for X = OH, which give the compounds D, and $Ni(CO)_4/OR'^-$ [3d] for X = halide, which yield products of type E and F. Variation in ob-

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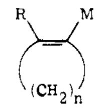
$\mathrm{R{-}C{\equiv}C(CH_2)_nX}$

A



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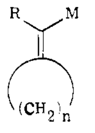

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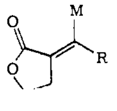
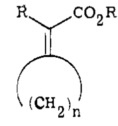


D



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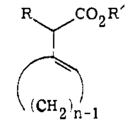
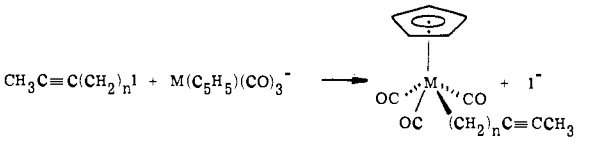


F

served products arises partly from the possibility of CO insertion into a σ-bonded intermediate either before or after acetylene insertion. This study describes the reactions of a series of acetylenes of type A ($\mathrm{R = CH_3}$; $n = 3, 4, 5$; X = I) with anions $\mathrm{M(C_5H_5)(CO)_3^-}$ (M = Mo, W) and characterization of the acyclic alkyl complexes (I and II) and of the products of cyclization (III and IV).

Results

A. $\mathrm{CH_3C{\equiv}C(CH_2)_nM(C_5H_5)(CO)_3}$ (M = Mo, W; n = 3, 4, 5). Alkylation of $\mathrm{Na^+[Mo(C_6H_5)(CO)_3]^-}$[4] with 1 equiv of $\mathrm{I(CH_2)_nC{\equiv}CCH_3}$ (n = 3, 4, 5) to give the alkyl complexes $\mathrm{CH_3C{\equiv}C(CH_2)_nMo(C_5H_5)(CO)_3}$ (I) and NaI occurred slowly at 20 °C in a variety of polar solvents (THF, acetone, acetonitrile) (eq 1). At reactant concentrations of ~0.5 M in THF, alkylation was complete after 1 week at 20 °C. At reactant concentrations of 0.03 M, alkylation was complete within 0.5 h at 65 °C. The molybdenum alkyl species Ib,c were identified in solution by IR and NMR but subsequent reaction hindered their convenient isolation. However, *solutions* of Ib free of starting materials or secondary products were obtained by alkylation of the very soluble $(n\text{-}\mathrm{Bu})_4\mathrm{N^+[Mo(C_5H_5)(CO)_3]^-}$ salt in excess with $\mathrm{CH_3C{\equiv}C(CH_2)_4I}$ in THF. Owing to increased nucleophilicity of the anion with a less coordinating cation, plus an excess of the anion (to consume all the alkyl iodide) in concentrated solution, the rate of the bimolecular alkylation reaction was increased relative to the rate of subsequent reactions of Ib. Removal of the solvent from solutions of Ib gave the complex as an orange oil which decomposed over 1-2 h at 20 °C, possibly by *inter*molecular reactions of the acetylenic moieties with molybdenum centers. The complexes Ia-c did not undergo β-hydrogen elimination. Carbonyl stretching bands of Ib appeared at 2010 and 1920 cm^{-1} in the IR, consistent with IR data for $\mathrm{CH_3Mo(C_5H_5)(CO)_3}$[5] (2020 and 1925 cm^{-1}). Although dilute solutions of Ib were considerably more stable than the neat material, after 12 h at 20 °C at least 25% of the complex could not be accounted for as a total of Ib and cyclization product (vide infra) when monitored by NMR. This decomposition led to no isolable or NMR-observable products. The rate of alkylation of $\mathrm{Na^+[MO(C_5H_5)(CO_3]^-}$ with $\mathrm{CH_3C{\equiv}C(CH_2)_4Y}$ decreased in the order Y = I > Br ~ OTs, with the iodo alkyl at least twice as reactive (at 65 °C in THF). Spectral properties of Ic [IR carbonyl bands at 2010 and 1920 cm^{-1} in benzene; NMR δ 4.66 (s, $\mathrm{C_5H_5}$) and 1.75 (m, $\mathrm{(CH_2)_5C{\equiv}CCH_3}$) in benzene-$d_6$] were similar to those of Ib. The complex Ia was not *observed* as the initial product of reaction between $\mathrm{Mo(C_5H_5)(CO)_3^-}$ and $\mathrm{CH_3C{\equiv}C(CH_2)_3I}$.



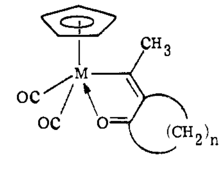
(1)

I, M = Mo
II, M = W
(a, n = 3; b, n = 4; c, n = 5)

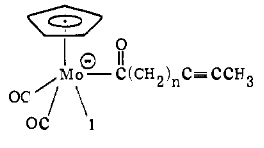
The tungsten complexes II, obtained by alkylation of $\mathrm{Na^+[W(C_5H_5)(CO)_3]^-}$ with $\mathrm{CH_3C{\equiv}C(CH_2)_nI}$ (n = 3, 4, 5) in THF at 20 °C, were isolated, fully characterized species. IR spectra of IIa-c showed carbonyl stretching modes at 2010 and 1910 cm^{-1}. The compounds IIa-c showed high thermal stability and underwent slow decomposition to uncharacterizable materials above 120 °C.

B. Cyclization of $\mathrm{CH_3C{\equiv}C(CH_2)_nM(C_5H_5)(CO)_3}$ (I and II). Thermal reaction of $\mathrm{CH_3C{\equiv}C(CH_2)_nMo(C_5H_5)(CO)_3}$ (n = 3, 4, 5) generated in situ by alkylation of $\mathrm{X^+[Mo(C_5H_5)(CO)_3]^-}$ ($\mathrm{X^+ = Na^+, PPN^+}$) with $\mathrm{I(CH_2)_nC{\equiv}CCH_3}$ gave the products (IIIa-c) of intramolecular cyclization of the acetylenic bond across the metal-*acyl* bond. Use of the $\mathrm{PPN^+}$ salt, rather than the $\mathrm{Na^+}$ salt, of $\mathrm{[Mo(C_5H_5)(CO)_3]^-}$ gave somewhat cleaner reaction mixtures. Both the rate of cyclization and the yield were greatest for n = 3 and decreased progressively with n = 4 and n = 5. Cyclization of Ia to IIIa was sufficiently rapid that Ia was not observed during reaction of $\mathrm{PPN[Mo(C_5H_5)(CO)_3]}$ and $\mathrm{CH_3C{\equiv}C(CH_2)_3I}$. Isolated yields of IIIa after 0.5 h at 65 °C (0.03 M reactant concentrations) were 70-80%. Reaction of $\mathrm{PPN[Mo(C_5H_5)(CO)_3]}$ with $\mathrm{CH_3C{\equiv}C(CH_2)_4I}$ and $\mathrm{CH_3C{\equiv}C(CH_2)_5I}$ under identical conditions with the above yielded IIIb and IIIc after ~4 and 48 h, respectively, in isolated yields of 50 and 15%. While the intermediate Ib was observed to build up in solution during cyclization to IIIb, the intermediate Ic was completely formed before any cyclization had occurred. The low yields of IIIb and IIIc were a consequence of thermal decomposition (or polymerization) of the intermediate complexes Ib and Ic, both at a rate about half of the rate of cyclization of Ib. Attempted isolation of Ic by removal of solvent under vacuum at 25 °C (after removing $\mathrm{PPN^+I^-}$ by filtration) gave only brown, solid residues which could not be redissolved in THF, methylene chloride, or acetonitrile.

The bright orange complexes III showed carbonyl stretching absorptions in the IR at 1960 and 1875 cm^{-1} similar to those observed by Green[6] and by Alt[7] for products obtained by reaction of $\mathrm{CH_3M(C_5H_5)(CO)_3}$ (M = Mo, W) with acetylenes. The ketonic C=O stretch was lowered to 1540 cm^{-1} by complexation (KBr disk). The methyl groups of IIIa-c appeared as characteristic singlets in the NMR at δ 2.9-3.0.



III, M = Mo
IV, M = W
(a, n = 3; b, n = 4; c, n = 5)



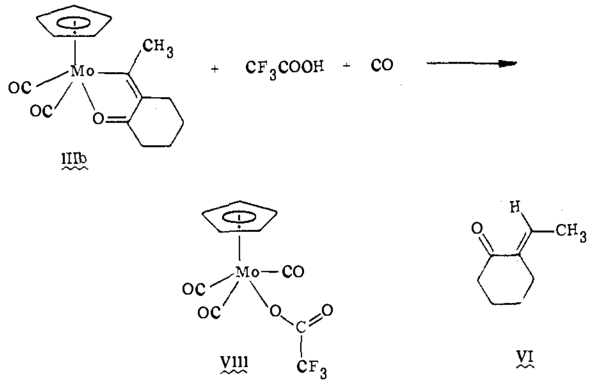
V
(a, n = 3; b, n = 4; c, n = 5)

In solutions more concentrated than ~0.05 M, formation of an additional complex was observed in the b and c (but not a) series. These materials exhibited carbonyl bands of equal intensity in the IR spectrum at 1865 and 1665 cm^{-1}; structure V is tentatively assigned to them. The compounds could not be obtained pure, and were difficult to redissolve after attempted isolation. Variable relative yields of III and V were observed, depending on concentration and countercation. Addition of excess $\mathrm{I^-}$ ($\mathrm{PPN^+}$ or $\mathrm{Na^+}$) during synthesis of IIIB increased the amount of Vb formed, supporting assignment as an $\mathrm{I^-}$ complex. Variability in yield was rationalized on the basis of a unimolecular, first-order rate-determining step leading to formation of III from I, vs. a bimolecular process leading to V. Thus formation of III was favored under conditions of greater dilution and lower solubility of the iodide salt (formed in situ during alkylation). Yields of V decreased in the order X = $(n\text{-Bu})_4N^+ > Na^+ > PPN^+$ using $X^+[Mo(C_5H_5)(CO)_3]^-$ as reactant.

The rate of formation of IIIa from $Na^+[Mo(C_5H_5)(CO)_3]^-$ and $CH_3C{\equiv}C(CH_2)_3I$ was not affected by the addition of more than 1 equiv of CO at 1-2 atm pressure, and the expected intermediate, Ia, was still not observed under these conditions. The effect of CO pressure on the rate of cyclization of IIb could not be studied, owing to decomposition of IIb under 1-2 atm pressure at a rate faster than the rate of cyclization.

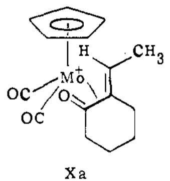
The tungsten complexes II did not undergo the cyclization reaction thermally. However, the complexes IVa-c were obtained in 30-40% yields when ~0.2 M solutions of IIa-c in THF were irradiated under an atmosphere of CO using a low-pressure mercury lamp. Yields were lower (~20%) when the irradiation was conducted in the absence of CO, presumably because the product was also photochemically labile. The rate of cyclization was slowed by a factor of at least 2 when carried out under CO.

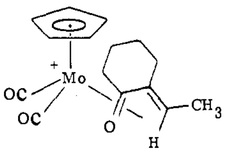
C. Protonation of $(C_8H_{11}O)M(C_5H_5)(CO)_2$ (IIIb and IVb). Protonation of $(C_8H_{11}O)Mo(C_5H_5)(CO)_3$ (IIIb) under CO with CF_3COOH (eq 2) gave 2-ethylidenecyclohexanone in 90-100% yield (by GC; isolated yields starting with 150 mg of IIIb were 60%). The organic product was specifically the anti isomer VI, shown by the position of the olefinic quartet of triplets at δ 6.92 in the NMR spectrum. The syn isomer of VI (VII) (olefinic proton absorption at δ 5.46 in the NMR spectrum) was not observed.[8] The organometallic product VIII was also isolated in over 90% yield.



(2)

In the absence of excess CO, protonation of IIIb with CF_3COOH yielded less than 20% free 2-ethylidenecyclohexanone. Two complexes, intermediates in eq 2, were observed by NMR. These are proposed to be isomers of the ionic π complex $(C_8H_{11}O)Mo(C_5H_5)(CO)_2{}^+CF_3COO^-$, Xa and Xb. Protonation of IIIb occurred instantly at 0 °C to yield initially only one of the isomers. That this complex contained a π-bound, α,β-unsaturated ketone moiety was suggested by the NMR spectrum: δ 5.88 (s, C_5H_5, 5 H), 3.51 (q, J_{HH} = 6 Hz, terminal olefinic H, 1 H), 2.91 (t, methylenes α to ethylidene and ketone, 4 H), and 2.11, 1.91 (m and d, J_{HH} of d = 6 Hz, interior methylenes of ring and CH_3, 7 H). [For comparison, the terminal vinyl protons in tris(methyl vinyl ketone) tungsten were reported[9a] to have a chemical shift of δ 1.6, and in (cinnamaldehyde) iron tricarbonyl[9b] the proton cis to the aldehyde was reported at δ 5.95.] Assignment of the proton and methyl of the ethylidene group was supported by protonation with CF_3COOD, which gave an NMR spectrum lacking the quartet at δ 3.51 and in which the doublet at δ 1.91 had collapsed to a singlet. The IR spectrum showed absorptions at 2050 and 2010 cm^{-1}. Over a period of 30 min, 70% of this complex (as the CF_3COO^- salt in methylene chloride) had converted to a mixture (~1:1) of VIII and an isomer of this complex (C_5H_5 resonance at δ 5.75 and doublet of the methyl group at δ 1.51 in the NMR spectrum). Under 1 atm CO, formation of VIII from the first-formed isomer (Xa or Xb) was moderately fast, but the second isomer reacted only slowly (~30% gone in 24 h).

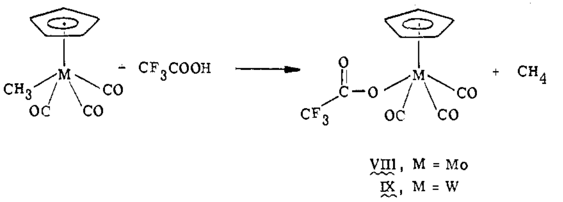

Xa


Xb

The first-formed isomer (Xa or Xb) was isolated and characterized as the PF_6^- salt. This salt, in the absence of CF_3COO^- or coordinating solvents, was quite stable (e.g., as a solid under nitrogen) and in methylene chloride solution showed slow isomerization plus ~50% decomposition over a period of several weeks at 30 °C.

Protonation of $(C_8H_{11}O)W(C_5H_5)(CO)_2$ (IVb), with CF_3COOH in the absence of CO gave complexes, the NMR data for which indicated formation of the tungsten analogues of Xa and Xb. However, the tungsten intermediates did not decompose cleanly under CO to yield uncomplexed 2-ethylidenecyclohexanone.

The previously unreported red, crystalline trifluoroacetate complexes, generated as the final organometallic product in the above protonation reactions (VIII, M = Mo; IX, M = W), were prepared independently by reaction of $CH_3M(C_5H_5)(CO)_3$ (M = Mo, W) with CF_3COOH (eq 3). The complexes showed carbonyl stretching modes at 2060 and 1975 (VIII) and 2060 and 1955 (IX) cm^{-1}. The carbonyl stretch of the complexed trifluoroacetate appeared at 1710 (VIII) and 1715 (IX) cm^{-1}. That the complexes VIII and IX contained a monodentate rather than a bidentate (e.g., as in complex XI) trifluoroacetate ligand was verified by elemental analysis and by quantitative measurement of evolved gases in the reaction described by eq 3 (M = Mo). Only 1 equiv of gas (CH_4, with no CO) was liberated during reaction of CF_3COOH with $CH_3Mo(C_5H_5)(CO)_3$. Reduction of VIII and IX occurred readily when THF solutions of the complexes were stirred with dilute Na(Hg), quantitatively generating the anions, $[M(C_5H_5)(CO)_3]^-$ (M = Mo, W).



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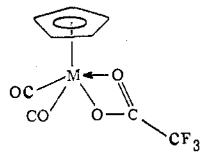
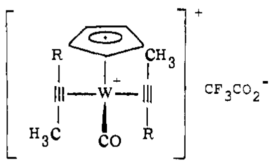

XI

D. Hydrogenation of $(C_8H_{11}O)M(C_5H_5)(CO)_2$ (IIIb and IV). The saturated ketone, 2-ethylcyclohexanone, was the major product (>90% yield) obtained from the reaction of IIIb with hydrogen (1-2 atm) at 90 °C. Trace amounts (<5%) of 2-ethylidenecyclohexanone (VI) were observed by NMR during the reaction, indicating that an initial hydrogenolysis of the molybdenum-vinyl bond of IIIb could precede reduction of the olefinic bond. Catalytic hydrogenation of VI (2 equiv) added to reaction mixtures of IIIb and hydrogen did in fact occur, yielding 2-ethylcyclohexanone as product. The initial organometallic product from the reaction of IIIb with hydrogen was the binuclear, coordinately unsaturated dimer $[Mo(C_5H_5)(CO)_2]_2$. This species was the catalyst, or catalyst precursor, for hydrogenation of VI. Extended heating at 90 °C also resulted in some formation of the saturated complex $[Mo(C_5H_5)(CO)_3]_2$, the carbon monoxide presumably arising from partial decomposition of $[Mo(C_5H_5)(CO)_2]_2$.

Hydrogenation of IIIa gave results completely analogous to those for IIIb. The product, 2-ethylcyclopentanone, was obtained in >90% yield. When a deficiency of hydrogen was used 2-ethylidenecyclopentanone accounted for 12% of the product, again indicating that hydrogenation of the olefinic bond proceeded at a rate slightly slower than the rate of hydrogenolysis of the molybdenum-vinyl bond.

Under 1-2 atm hydrogen, the tungsten complex IVb remained unchanged (in benzene at 100 °C). Photolysis of a solution of IVb under hydrogen did not result in any reaction.

E. Protonation of the Alkyl Complex $CH_3C{\equiv}C(CH_2)_4W(C_5H_5)(CO)_3$ (IIb). The complex $CH_3C{\equiv}C(CH_2)_4W(C_5H_5)(CO)_3$ was protonated using CF_3COOH, initially for confirmatory evidence that the alkyl chain was uncyclized as formulated. The reaction did not lead cleanly to the expected products, 2-heptyne and IX. By GC, only about 30% of the stoichiometrically expected yield of 2-heptyne was observed. Two organometallic products were identified, the expected trifluoroacetate complex IX and a complex containing the elements of *two* 2-heptyne molecules, XII (as the CF_3COO^- salt). The ratio of IX to XII formed was ≈1.8:1.



XII (R = n-C_4H_9)

The trifluoroacetate IX was independently synthesized by reaction of CF_3COOH with $CH_3W(C_5H_5)(CO)_3$. The salt XII was also prepared by heating an acetonitrile solution of IX with excess 2-heptyne at 65 °C. The NMR spectrum of XII in benzene showed a singlet (C_5H_5) resonance and two singlets due to the two sets of nonequivalent methyl groups. The ^{13}C NMR spectrum showed four nonequivalent acetylene carbons and the IR spectrum showed a single carbonyl stretch at 2045 cm^{-1}. These data are consistent[10] with the structure assigned to XII.

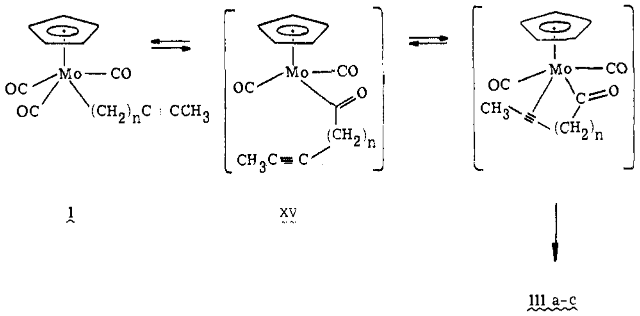
Discussion

Mechanism of Cyclization. The coordinatively unsaturated acyl intermediate (XV), shown in Scheme I, could reasonably be expected to exist in solution in equilibrium with Ia-c, based on evidence for such intermediates in reactions of Lewis bases with (σ-alkyl)$Mo(C_5H_5)(CO)_3$ complexes.[11]

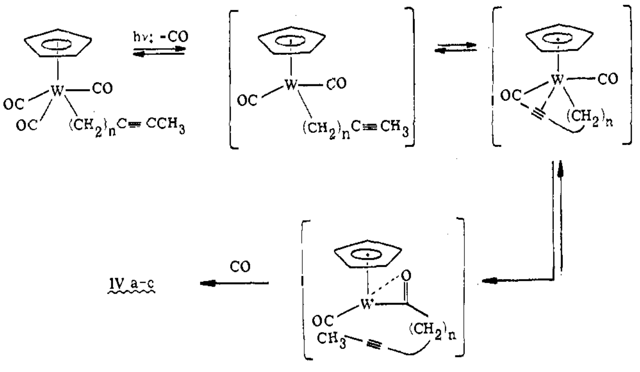
Coordination of the acetylene followed by insertion of the acetylene into the molybdenum-acyl bond provides a plausible mechanism for formation of IIIa-c. Preference for this mechanism over an initial CO dissociation was supported by the lack of any inhibition of cyclization of IIIa under an atmosphere of CO. Thus, a vacant coordination site is required for acetylene insertion to occur, but this vacant site is apparently always provided by alkyl migration rather than CO dissociation. It also seems clear that the efficiency of insertion decreases through the series n = 3, 4, and 5, presumably owing to the increasingly negative entropy associated with intramolecular complexation of the triple bond.

Thermal insertion of coordinated CO into the alkyl-W bond of complexes such as II is known to be difficult.[12] Alt[7] has shown that the reactions in Scheme III may be induced thermally, and this provides a model for the photolytically initiated mechanism for the cyclization reaction shown in Scheme II. Photolytically induced formation of an acyl complex cannot arbitrarily be ruled out.

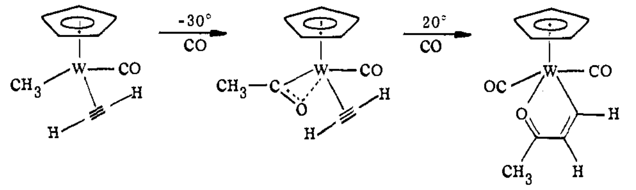
Scheme I



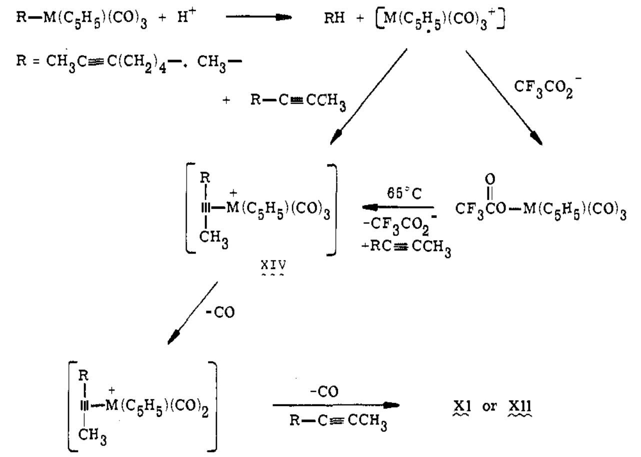
Scheme II



Scheme III



Scheme IV



Protonolysis Reactions. A reasonable mechanism for the formation of the species XI or XII is shown in Scheme IV. Apparently the intermediate complex XIV proposed in Scheme IV is very reactive toward loss of CO. No complexes of type XIV were isolated or even observed during formation of XI and XII. Formation of XIV would not have been unexpected considering a report in the literature of the ethylene complex $(C_2H_4)Mo(C_5H_5)(CO)_3^+$.[13] Loss of CF_3COO^- leading to formation of XI and XII from VIII and IX, respectively, may also be contrasted with reports[14,15] of the reactions of acetylenes with $XMo(C_5H_5)(CO)_3$ (X = Cl, CF_3) yielding 16-

electron *neutral* complexes such as $XMo(C_5H_5)(CO)$(acetylene) and $XMo(C_5H_5)$(acetylene)$_2$.

Experimental Section

Unless otherwise indicated, all reactions were carried out at 20 °C under a nitrogen atmosphere in a Vacuum Atmospheres 553-2 Dri-Lab with attached M6-40-1H Dri-Train. Routine manipulations such as suction filtration and column chromatography were also carried out in the Dri-Lab. Removal of solvent from reaction mixtures, preparation of sealed NMR tube samples, and the manipulation of gaseous reactants such as H_2 were usually accomplished using conventional vacuum line techniques.

Tetrahydrofuran (THF), benzene, and diethyl ether were dried and degassed by vacuum distillation from Na/benzophenone. Petroleum ether was stirred with concentrated H_2SO_4 for several hours, washed with H_2O, then refluxed over CaH_2 for several days under nitrogen before distillation under vacuum. Methanol and methylene chloride were stirred for several days over CaH_2, under nitrogen, then vacuum distilled. Acetonitrile was dried over CaH_2, then P_2O_5.

Infrared (IR) spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer. Solid samples were recorded in THF solution using 0.10- or 0.05-mm sodium chloride cells. Liquid samples were run either in THF solution or as a thin film between sodium chloride plates.

Proton nuclear magnetic resonance (NMR) spectra were measured on a Varian A60A or Varian EM-390 spectrometer using benzene or THF as the internal reference in benzene-d_6 or THF-d_8 solutions, respectively. Resonances are expressed in units of δ (ppm downfield from tetramethylsilane). ^{13}C NMR spectra were recorded on a Varian XL-100 spectrometer.

Column chromatographic separations were carried out on alumina (Woelm neutral, activity 1) without further treatment, or silica gel 60 (EM reagents).

Analytical gas-phase chromatography (GC) was performed using a Varian Aerograph (Model 90-P) gas chromatograph or a Hewlett-Packard 5750 research chromatograph with attached Spectra-Physics Autolabs computing integrator. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Materials. $[Mo(C_5H_5)(CO)_3]_2$ and $W(CO)_6$ were purchased from Alfa, stored under nitrogen, and used without further purification. Deuterated solvents (benzene-d_6, acetonitrile-d_3, acetone-d_6, methanol-d_4, and tetrahydrofuran-d_8) were purchased from Aldrich. Typically these solvents were not dried before use but were opened and stored under nitrogen.

Organic reagents such as 1-bromo-4-chlorobutane (Aldrich), 1-bromo-3-chloropropane (Aldrich), 1-iodo-5-chloropentane (Columbia Organics), and *p*-toluenesulfonic acid (Matheson Coleman and Bell) were purchased in their purest commercially available form and used as obtained. Trifluoroacetic acid (Matheson Coleman and Bell) was stored over and vacuum transferred from 4Å molecular sieves.

The inorganic reagents such as sodium iodide (Allied Chemical) and silver nitrate (J. T. Baker) were used as obtained. Tetra(*n*-butyl)ammonium chloride (Eastman) was dried at 50 °C under vacuum for 8 h before use. Bis(triphenylphosphine)iminium chloride (Alfa) was dried at 100 °C under vacuum for 4 h prior to use.

The gases, hydrogen and carbon monoxide, were purchased in the purest available forms from Matheson Gas Products and were used without further purification. Technical grade propyne was purchased from Linde division of Union Carbide and was used as obtained.

$Na[Mo(C_5H_5)(CO)_3]$.[4] A solution of $[Mo(C_5H_5)(CO)_3]_2$ in THF (40 mL) was stirred with excess sodium amalgam (about 3 mL of amalgam containing 0.021 mol of sodium) for 45 min. The color of the solution changed from deep red to yellow. The THF solution was decanted from the residual amalgam and was suction filtered through a fine frit. The clear yellow filtrate was concentrated to dryness under vacuum, leaving yellow solids. These solids were redissolved in a minimum of THF (~2 mL) and then diethyl ether (15 mL) was added to precipitate the product as pale yellow, microcrystalline solids. The product was collected by filtration and dried under vacuum: yield 3.4 g (100%); IR (THF) 1900 (s), 1795 (s), 1740 (s) cm^{-1}; ^1H NMR (THF) δ 4.95 (s) ppm.

Anal. Calcd for $C_8H_5MoNaO_3$: C, 35.84; H, 1.88; Mo, 35.79; Na, 8.58. Found: C, 35.94; H, 1.94; Mo, 35.62; Na, 8.53.

$PPN[Mo(C_5H_5)(CO)_3]$. To a solution of $Na[Mo(C_5H_5)(CO)_3]$ (generated in situ by reduction of $[Mo(Cp)(CO)_3]_2$ (5.0 g, 0.0102 mol) in THF (300 mL) with excess Na(Hg) followed by filtration through a fine frit) was added PPN^+Cl^- (11.6 g, 0.0204 mol). The solution was stirred at 20 °C for 9 h, then suction filtered. The filtrate was concentrated under vacuum to a volume of 30 mL and the precipitated product was then collected by filtration (8 g). Solids from the first filtration (of the crude reaction mixture) were extracted with THF (200 mL) and filtered, and the filtrate was concentrated to a volume of 30 mL. The precipitated product was collected by filtration (5.0 g): total yield 14.0 g (81%); mp 214–216 °C; IR (THF) 1900 (s), 1780 (s) cm^{-1}; ^1H NMR (THF-d_8) δ 7.46–7.75 (m, phenyl), 4.90 (s, C_5H_5) ppm.

Anal. Calcd for $C_{44}H_{35}MoNO_3P_2$: C, 67.41; H, 4.50; Mo, 12.25. Found: C, 67.42; H, 4.56; Mo, 11.87.

$(n\text{-}Bu)_4N[Mo(C_5H_5)(CO)_3]$. A solution of $Na[(Mo(C_5H_5)(CO)_3]$ (2.5 g, 0.0102 mol) and $(n\text{-}Bu)_4N^+Cl^-$ (2.8 g, 0.0101 mol) in THF (100 mL) was stirred at 20 °C for 12 h. The volume of the solution was reduced under vacuum to 40 mL. Petroleum ether (10 mL) was added to the solution, which was then filtered. To the filtrate was added more petroleum ether (~100 mL) inducing further precipitation. The solids were collected by filtration and dried under vacuum: yield 3.5 g (70%); mp 111–113 °C; IR (THF) 1894 (s), 1780 (s), 1760 (s) cm^{-1}; ^1H NMR (THF-d_8) δ 5.03 (s, C_5H_5), 3.50–3.16 (m, NCH), 1.85–0.88 (m, CH) ppm.

Anal. Calcd for $C_{24}H_{41}MoNO_3$: C, 59.10; H, 8.48; Mo, 19.69; N, 2.87. Found: C, 59.05; H, 8.67; Mo, 20.22; N, 2.97.

$Na[W(CP)(CO)_3]$.[4] A solution of $Na^+C_5H_5^-$ (3.72 g, 0.04 mol) and $W(CO)_6$ (14.1 g, 0.04 mol) in THF (100 mL) was stirred at reflux under argon (with slow argon purge) for 4 days. When cool, the solution was filtered to remove insoluble impurities. Solvent was removed under vacuum from the filtrate and the residues were slurried in diethyl ether (50 mL) to remove soluble impurities. The product was collected by suction filtration and dried under vacuum: yield 15 g (100%); IR (THF) 1935 (w), 1895 (s), 1790 (s), 1740 (s) cm^{-1}; NMR (THF-d_8) δ 5.03 (s, Cp) ppm.

6-Chloro-2-hexyne.[16] The procedure described in the literature was followed, using sodium (7.2 g, 0.31 mol), propyne (20 mL at −78 °C, 0.33 mol), and $Cl(CH_2)_3Br$ (42.4 g, 0.27 mol), yield 17.2 g (62.4%). Analysis by gas chromatography (4% SE-30, ⅜ in. × 12 ft on Chromosorb W, column 95 °C) showed no residual $Cl(CH_2)_3Br$: NMR benzene-d_6 δ 1.61 (m, 5 H, $C\mathit{H}_3C{\equiv}CCH_2$, CH_2, CH_2Cl), 2.14 (m, 2 H, $CH_3C{\equiv}CC\mathit{H}_2$, $(CH_2)_2Cl$), 3.34 (t, 2 H, $CH_3C{\equiv}C$, $(CH_2)_2$, CH_2Cl) ppm; bp 35–38 °C (~0.5 mm) [lit.[16] bp 86–88 °C (90 mm); lit.[17] bp 146–158 °C (760 mm)].

6-Iodo-2-hexyne.[16] The procedure described in the literature was followed, using 6-chloro-2-hexyne (10 g 0.086 mol): yield (after distillation at 35–40 °C (~0.4 mm) [lit.[16] bp 99–104 °C (35 mm)]) 8 g, 45%. Analysis by gas chromatography (4% SE-30, ⅜ in. × 12 ft on Chromosorb W, column 105 °C) showed ~98% purity. NMR (benzene-d_6): δ 1.59 (t, J = 2.5 Hz, $C\mathit{H}_3C{\equiv}C(CH_2)_3I$), overlapping with δ 1.67 (quintet, J = 6 Hz, $CH_3C{\equiv}C\text{-}CH_2C\mathit{H}_2CH_2I$) (together, 5 H), 2.07 (m, 2 H, $CH_3C{\equiv}CC\mathit{H}_2(CH_2)_2I$), 2.97 (t, J = 6 Hz, 2 H, $CH_3C{\equiv}C(CH_2)_2C\mathit{H}_2I$).

7-Chloro-2-heptyne.[18] A procedure analogous to that described[16] in the literature for preparation of 6-chloro-2-hexyne was followed, using sodium (4.8 g, 0.21 mol), propyne (12 mL at −78 °C, 0.21 mol), and $Cl(CH_2)_4Br$ (20.6 mL, 0.18 mol), yield 19.9 g (85%), bp 40–42 °C (0.5–0.7 mm). Analysis by gas chromatography (4% SE-30, ⅜ in. × 12 ft on Chromosorb W, column 120 °C, detector 140 °C, injector 160 °C) showed no tetramethylene chlorobromide to be present and other trace impurities amounted to less than 1%. NMR (neat): δ 1.72 (t, J = 2.5 Hz, $C\mathit{H}_3C{\equiv}C(CH_2)_4Cl$), 2.13 (m, $CH_3C{\equiv}C(C\mathit{H}_2)_3CH_2Cl$) (region δ 1.6–2.4, J 9 Hz), 3.53 (t, J = 6 Hz, 2 H, $CH_3C{\equiv}C(CH_2)_3C\mathit{H}_2Cl$) ppm.

7-Iodo-2-heptyne.[18] 7-Chloro-2-heptyne (6.4 g, 0.049 mol) and sodium iodide (14.7 g, 0.098 mol, i.e., excess) were refluxed in acetone (100 mL) for 48 h. On addition of water (250 mL), 7-iodo-2-heptyne separated from the less dense water–acetone phase. The water–acetone solution was carefully decanted from the product. A solution of the crude product in diethyl ether (200 mL) was washed with water (2 × 200 mL) and dried over $MgSO_4$. Diethyl ether was removed under vacuum at 20 °C, leaving a pale yellow oil which was vacuum distilled: bp 42–45 °C (0.5–0.7 mm) [lit.[18] bp 88–95 °C (5 mm)]; yield 9.4 g (86%); NMR (neat) δ 1.75 (t, J = 2.5 Hz, $C\mathit{H}_3C{\equiv}C(CH_2)_4I$), 1.30–2.35 (m, 9 H, $C\mathit{H}_3C{\equiv}C(C\mathit{H}_2)_3CH_2I$), 3.23 (t, J = 6.5 Hz, 2 H, $CH_3C{\equiv}C(CH_2)_3C\mathit{H}_2I$) ppm.

8-Chloro-2-octyne. The procedure described for preparation of 6-chloro-2-hexyne was followed, using sodium (10 g, 0.43 mol), propyne (26 mL at −78 °C, 0.45 mol), and $I(CH_2)_5Cl$ (90 g, 0.39 mol), yield (42.4 g, 75%. Analysis by gas chromatography (4% SE-30, $^3/_8$ in. × 12 ft on Chromosorb W, column 115 °C) showed 5% impurity of $Cl(CH_2)_5Cl$ which was present in the reagent $I(CH_2)_5Cl$.

8-Iodo-2-octyne. The procedure described for preparation of 6-iodo-2-hexyne was followed, using 8-chloro-2-octyne (42.4 g, 0.29 mol): yield (after distillation, 80–95 °C at 1 mm, followed by redistillation through a glass helices packed column, 12 × 1.5 cm at 0.1 mm collecting the fraction which boiled at 63 °C) 16 g, 23%; ^1H NMR δ 2.85 (tr, J_{HH} = 6.5 Hz, 2 H, CH_2I), 2.04 (m, 2 H, $CH_2C{\equiv}C$), 1.67 (tr, J_{HH} = 3 Hz, $CH_3C{\equiv}C$), 1.54 and 1.37 (m, $(CH_2)_3$) (total for 1.67, 1.54, and 1.37 = 9 H).

$CH_3C{\equiv}C(CH_2)_4OSO_2C_6H_4CH_3$ [$CH_3C{\equiv}C(CH_2)_4OTs$]. A solution of $CH_3C{\equiv}C(CH_2)_4I$ (11.1 g, 0.05 mol) and $AgOSO_2C_6H_4CH_3$ (14.9 g, 0.05 mol) in CH_3CN was stirred overnight at 20 °C. Solvent was removed on the rotary evaporator and the oily residues were redissolved in diethyl ether (120 mL) and pentane (70 mL). This solution was filtered to remove AgI. The filtrate was cooled to −78 °C for 3 h and the supernatant was decanted leaving the product as an oil. This oil was again "precipitated" from diethyl ether (120 mL) and pentane (70 mL) at −78 °C. The product was redissolved in diethyl ether (80 mL) and dried over Na_2SO_4 for 12 h: ^1H NMR (benzene-d_6) δ 7.84, 7.69, 7.09, 6.96 (m, 4 H, aromatic H), 3.96 (t, J_{HH} = 6 Hz, 2 H, CH_2O), 2.15 (s, 3 H, CH_3), 1.97, 1.66, 1.47 (m, 9 H, $(CH_2)_4$-$C{\equiv}CCH_3$, J_{HH} of CH_3 triplet at 1.66 (2.5 Hz).

$CH_3C{\equiv}C(CH_2)_4Mo(C_5H_5)(CO)_3$. A solution of $(n\text{-}Bu)_4N$-$[Mo(C_5H_5)(CO)_3]$ (0.26 g, 0.00 53 mol) and $I(CH_2)_4C{\equiv}CCH_3$ (0.092 g, 0.000 41 mol) in THF-d_8 (0.8 mL) was observed by NMR. After 30 min at 20 °C the solution contained $[Mo(C_5H_5)(CO)_3]^-$ (30%, C_5H_5 resonance at δ 5.03), $CH_3C{\equiv}C(CH_2)_4Mo(C_5H_5)(CO)_3$ (54%, δ 5.46), and Vb (16%, δ 4.89). After 1 h the solution contained $[Mo(C_5H_5)(CO)_3]^-$ (22%), $CH_3C{\equiv}C(CH_2)_4Mo(C_5H_5)(CO)_3$ (45%), and Vb (33%). Petroleum ether (2 mL) was added to the solution to precipitate the ionic species $[Mo(C_5H_5(CO)_3]^-$ and Vb, and the reaction mixture was then filtered. The filtrate was concentrated under vacuum to an orange oil. The oil was immediately redissolved in benzene-d_6 to take the NMR spectrum: δ 4.65 (s, C_5H_5) and 1.74 (m, $(CH_2)_4C{\equiv}CCH_3$); IR (benzene) 2010 (m) and 1920 (s) cm^{-1}. If left as the solvent-free oil for ≈1 h at 20 °C, $CH_3C{\equiv}C$-$(CH_2)_4Mo(C_5H_5)(CO)_3$ could not be redissolved. The compound also decomposed on alumina.

Cyclization of $CH_3C{\equiv}C(CH_2)_4Mo(C_5H_5)(CO)_3$. A solution of $CH_3C{\equiv}C(CH_2)_4Mo(C_5H_5)(CO)_3$ in benzene-d_6 (prepared as above), approximately 0.05 M, was diluted so that two samples were obtained, one exactly half the concentration of the other. The samples were monitored by NMR. After 12 h, approximately 25% of the *total* C_5H_5 resonances in both samples had disappeared (evidenced by integration against $C_6H_1D_5$) and the mode of this decomposition was undetermined. Conversion of $CH_3C{\equiv}C(CH_2)_4Mo(C_5H_5)(CO)_3$ to $(C_8H_{11}O)Mo(C_5H_5)(CO)_2$ (IIb) (the only observable reaction) occurred at the same rate in both samples. After 14 h at 25 °C, 35% conversion to IIb had occurred.

$(C_7H_9O)Mo(C_5H_5)(CO)_2$. A solution of PPN$[Mo(C_5H_5)(CO)_3]$ (4.0 g, 0.0051 mol) and $CH_3C{\equiv}C(CH_2)_3I$ (1.4 g, 0.0068 mol) in THF (150 mL) was heated at reflux with stirring for 1 h under nitrogen. The solution was cooled, then filtered. Solvent was removed from the filtrate under vacuum and the residues were column chromatographed (alumina 6 × 2 cm, benzene) twice, collecting the orange fraction. Solvent was removed from this fraction under vacuum, leaving the product as an orange powder which was washed quickly with petroleum ether (2 × 2 mL) and dried again under vacuum. A sample for analysis was recrystallized from benzene by addition of petroleum ether: yield 1.3 g (72%); mp 124–126 °C; IR (benzene) ν_{CO} 1960 (s), 1870 (s) cm^{-1}; ^1H NMR (benzene-d_6) δ 4.82 (s, 5 H, C_5H_5), 2.81 (s, 3 H, CH_3), 2.41–1.71 (m, 6 H, $(CH_2)_3$) ppm; $^{13}C\{^1H\}$ 100-MHz NMR (C_6D_6) 34.3, 36.8, 43.6, 43.8 ($(CH_2)_3$ and CH_3), 93.0 (C_5H_5), 127.2 ($MoC{=}C$), 145.4 ($C{=}O$), 212.6 ($MoC{=}C$), 251.8 and 251.9 ($C{\equiv}O$).

Anal. Calcd for $C_{14}H_{14}MoO_3$: C, 51.69; H, 4.31; Mo, 29.32. Found: C, 51.86; H, 4.44; Mo, 29.08.

$(C_8H_{11}O)Mo(C_5H_5)(CO)_2$. A solution of PPN$[Mo(C_5H_5)(CO)_3]$ (4.0 g, 0.0051 mol) and $CH_3C{\equiv}C(CH_2)_4I$ (1.2 g, 0.0054 mol) in THF (75 mL) was heated at reflux for 3 h under N_2 in a 250-mL round-bottom flask equipped with a reflux condenser. The reaction was maintained with a slow purge of CO (at 1 atm) across the top of the condenser. After the solution was cooled, petroleum ether (50 mL) was added and the solution was filtered. Solvent was removed from the filtrate under vacuum, and the residues were column chromatographed (alumina, 2 × 6 cm, benzene) under nitrogen, collecting the orange eluate. Solvent was removed from this fraction under vacuum, leaving the product as an orange powder. The product was washed with diethyl ether (2 × 3 mL) and dried under vacuum: yield 0.6 g (35%); mp 163–164 °C dec; IR (THF) ν_{CO} 1965 (s), 1875 (s) cm^{-1}; ^1H NMR (benzene-d_6) δ 4.84 (s, 5 H, C_5H_5), 2.92 (s, 3 H, CH_3), 2.44 (m, 4 H, CH_2), 1.44 (m, 4 H, CH_2) ppm.

Anal. Calcd for $C_{15}H_{16}O_3Mo$: C, 52.95; H, 4.74; Mo, 28.20. Found: C, 53.05; H, 4.79; Mo, 28.14.

Reaction of $Na[Mo(C_5H_5)(CO)_3]$ and $CH_3C{\equiv}C(CH_2)_3I$. Effect of CO. A solution of $Na[Mo(C_5H_5)(CO)_3]$ (0.05 g, 0.000 186 mol) and $CH_3C{\equiv}C(CH_2)_3I$ (0.05 g, 0.000 24 mol) in CD_3CN (0.6 mL) was prepared. Half was sealed in an NMR tube under N_2, and the other half was sealed in an NMR tube under 1–1.5 atm CO (0.0001–0.000 15 mol). The rates of formation of $(C_7H_9O)MO(C_5H_5)(CO)_2$ were monitored by NMR, and were exactly the same for both samples. At 34 °C the reaction was complete in ~8 h. *No* resonances due to the intermediate alkyl complex, $CH_3C{\equiv}C(CH_2)_3Mo(C_5H_5)(CO)_3$, were observed in the sample.

$CH_3C{\equiv}C(CH_2)_3W(C_5H_5)(CO)_3$. $Na[W(C_5H_5)(CO)_3]$ (3.56 g, 0.01 mol) and $CH_3C{\equiv}C(CH_2)_3I$ (2.06 g, 0.01 mol) were stirred in THF (80 mL) at 20 °C under nitrogen for 48 h. THF was removed from the reaction mixture under vacuum. The residues were dissolved in diethyl ether (5 mL) and filtered to remove NaI. The filtrate was concentrated and chromatographed using an alumina (neutral, activity 1, 16 × 1.5 cm) column, eluting with a mixture of petroleum ether and THF (96:4). The yellow, fastest moving fraction was collected. Solvent was removed from this fraction under vacuum and residues were redissolved in petroleum ether (20 mL). This solution was crystallized at −78 °C and the crystalline product was collected by filtration at −78 °C, then dried under high vacuum at 20 °C for several hours: yield 2.6 g (63%); mp 68–70 °C; IR (THF) 2010 (m) and 1910 (s) cm^{-1}; NMR (benzene-d_6) δ 4.59 (s, C_5H_5, 5 H), 2.21 (m, $CH_3C{\equiv}CCH_2$), 2.04–1.44 (m), 1.67 (6, J_{HH} = 2.4 Hz, CH_3) (integration for δ 2.21–1.44 = 9.2 H) ppm.

Anal. Calcd for $C_{14}H_{44}O_3W$: C, 40.60; H, 3.41; W, 44.40. Found: C, 40.79; H, 3.33; W, 44.67.

$CH_3C{\equiv}C(CH_2)_4W(C_5H_5)(CO)_3$. $Na[W(C_5H_5)(CO)_3]$ (3.6 g, 0.0101 mol) and $CH_3C{\equiv}C(CH_2)_4I$ (2.25 g, 0.0101 mol) were stirred in THF (50 mL) under nitrogen for 14 h. THF was then removed under vacuum and residues from the reaction mixture were redissolved in petroleum ether (5 mL). The petroleum ether solution was suction filtered to remove NaI and the filtrate was concentrated under vacuum, then chromatographed using an alumina (neutral, activity 1) column, eluting with a mixture of petroleum ether and THF (95:5). The light yellow, fastest moving fraction was collected. This fraction was immediately crystallized at −78 °C, and the crystalline product was collected at −78 °C by filtration. The product was then dried under vacuum for several hours at 20 °C: yield 2.7 g (62%); mp 68–70 °C; IR (THF) 2010 (m) and 1910 (s) cm^{-1}; NMR (benzene-d_6) δ 4.64 (s, C_5H_5, 5 H), 1.2–2.6 (m, alkyl, 11.4 H) ppm.

Anal. Calcd for $C_{15}H_{16}O_3W$: C, 42.08; H, 3.77; W, 42.94. Found: C, 42.12; H, 3.83; W, 43.05.

$CH_3C{\equiv}C(CH_2)_5W(C_5H_5)(CO)_3$. $Na[W(C_5H_5)(CO)_3]$ (2.6 g, 0.0073 mol) and $CH_3C{\equiv}C(CH_2)_5I$ (1.7 g, 0.0072 mol) were stirred under nitrogen in acetonitrile (50 mL) for 48 h at 20 °C. Solvent was removed from the reaction mixture under vacuum. The residues were dissolved in diethyl ether (10 mL) and filtered to remove NaI. The filtrate was concentrated and chromatographed (silica gel, 8 × 2 cm, eluting with diethyl ether). The yellow, fastest moving fraction was collected. Solvent was removed from this fraction under vacuum leaving yellow solids, yield 2.4 g (75.4%). The product was recrystallized by dissolving 1 g in petroleum ether (25 mL), filtering this solution twice through a fine frit, and then cooling the solution to −78 °C. Crystalline material was collected by filtration at −78 °C and dried at 20 °C under high vacuum for several hours: mp 84–85 °C; IR (THF) 2010 (m) and 1910 (s) cm^{-1}; NMR (benzene-d_6) δ 4.56 (s, C_5H_5, 5 H), 2.22 (m), 1.69 (t, J_{HH} = 2.4 Hz, CH_3), 1.61 (m) (integration for δ 2.22–1.61 = 13 H) ppm.

Anal. Calcd for $C_{16}H_{18}O_3W$: C, 42.08; H, 4.10. W, 42.94. Found: C, 42.42; H, 3.95; W, 42.68.

$(C_7H_9O)W(C_5H_5)(CO)_2$. A solution of $CH_3C{\equiv}C(CH_2)_3W$-

$(C_5H_5)(CO)_3$ (1.0 g, 0.0024 mol) in THF (100 mL) in a 400-mL capacity quartz vessel under CO (1 atm) was irradiated for 80 h using a low-pressure mercury lamp. Solvent was removed from the reaction solution under vacuum. Residues were column chromatographed (alumina, 4 × 2 cm, benzene) twice. The orange eluate was collected and solvent was removed from this fraction under vacuum, leaving the product as an orange powder: yield 0.40 g (40%); mp 138–139 °C; IR (THF) ν_{CO} 1950 (s), 1860 (s) cm^{-1}; ^1H NMR (benzene-d_6) δ 4.87 (s, 5 H, C_5H_5), 2.90 (s, 3 H, CH_3), 2.47–1.87 (m, 6 H, $(CH_2)_3$) ppm.

Anal. Calcd for $C_{14}H_{14}O_3W$: C, 40.60; H, 3.41; W, 44.40. Found: C, 40.40; H, 3.48; W, 44.90.

$(C_8H_{11}O)W(C_5H_5)(CO)_2$. A solution of $CH_3C{\equiv}C(CH_2)_4W(C_5H_5)(CO)_3$ (1.0 g, 0.002 34 mol) in THF (120 mL) in a 400-mL capacity quartz vessel under CO (at 1 atm) was irradiated for 80–90 h using a low-pressure mercury lamp. Solvent was then removed under vacuum, the orange eluate was collected from the column, and solvent was removed from this fraction under vacuum leaving the product as an orange powder. This powder was washed with diethyl ether (2 × 2 mL) to remove any uncyclized starting material and was then dried thoroughly under vacuum: yield 0.35 g (35%); mp 167–168 °C; IR (benzene) ν_{CO} 1950 (s), 1860 (s) cm^{-1}; ^1H NMR (benzene-d_6) δ 4.86 (s, 5 H, C_5H_5), 3.00 (s, 3 H, CH_3), 2.57 (m, 2 H), 2.40 (m, 2 H), 1.46 (m, 4 H) ppm.

Anal. Calcd for $C_{15}H_{16}O_3W$: C, 42.08; H, 3.77; W, 42.94. Found: C, 42.42; H, 3.95; W, 42.68.

Protonation of $(C_8H_{11}O)Mo(C_5H_5)(CO)_2$ with CF_3COOH under CO. $(C_8H_{11}O)Mo(C_5H_5)(CO)_2)$ (0.13 g, 0.000 382 mol) was dissolved in benzene (2 mL) in a 50-mL round-bottom flask with septum sealed side arm, under a slow flow of CO (1 atm). CF_3COOH (0.06 mL, 0.000 76 mol) was added via syringe through the septum. The solution changed in color from orange to deep red. After 30 min, 2-ethylidenecyclohexanone was present in 90% yield in the solution (using GC detection, 5% SE-30, 20 ft × 1/4 in. on Chromosorb W at 130 °C, with dodecane as internal standard). Benzene was removed under vacuum leaving a red oil. Addition of petroleum ether (3 mL) caused the organometallic product, $Mo(C_5H_5)(CO)_3OC(O)CF_3$, to precipitate as red microcrystals. 2-Ethylidenecyclohexanone (0.034 g, 57%) was recovered from the supernatant hexane solution by stirring the solution in air for 1 h to decompose a small amount of $Mo(C_5H_5)(CO)_3OC(O)CF_3$, followed by elution with benzene from a short silica gel column (2 × 0.5 cm) and removal of the solvent on a rotary evaporator at 20 °C. 2-Ethylidenecyclohexanone was identified by comparison of the NMR, IR, mass spectrum, and GC retention time with the corresponding data from an authentic sample (Chemical Samples Co.).

$Mo(C_8H_{12}O)(C_5H_5)(CO)_2{}^+PF_6{}^-$. CF_3COOH (0.2 mL, 0.0026 mol) was condensed under vacuum onto a solution of $Mo(C_8H_{11}O)(C_5H_5)(CO)_2$ (0.179 g, 0.000 53 mol) and $NH_4{}^+PF_6{}^-$ (0.1 g, 0.000 61 mol) in CH_3OH (4 mL) and CH_2Cl_2 (2 mL), at 196 K. The solution was warmed to 0 °C (ice bath) and stirred for 1–5 h. An orange precipitate formed which was collected by filtration at 0 °C, washed with CH_3OH, and dried under vacuum: yield 0.13 g (50%); mp 183–186 °C dec (the compound darkened above 170 °C); IR (CH_2Cl_2) ν_{CO} 2050 (s), 2010 (s) cm^{-1}; NMR (CH_2Cl_2) δ 5.91 (s, 5 H, C_5H_5), 3.51 (q, J_{HH} = 6.5 Hz, 1 H, olefinic H), 2.88, 2.71 (m, 4 H, methylenes α to ethylidene and ketone functions), 2.11 (m, internal ring methylenes), 1.91 (d, J_{HH} = 6.5 Hz, CH_3) (total integration δ 2.11 and 1.91 = 7 H).

Anal. Calcd for $C_8H_{12}F_5MoO_3P$: C, 37.05; H, 3.52. Found: C, 36.65; H, 3.52.

Protonation of $(C_8H_{11}O)W(C_5H_5)(CO)_2$ with CF_3COOH under CO. $(C_8H_{11}O)W(C_5H_5)(CO)_2$ (0.06 g, 0.0014 mol) in benzene-d_6 was placed in a septum-sealed NMR tube under 1 atm CO at 20 °C. CF_3COOH (20 μL, 0.000 26 mol) was added via syringe. The solution turned dark red and separated into two phases. After 10 min the starting material was gone and a new complex (A) was presented. After 15 h, the solution was homogeneous and contained three major components: A (39%), B (33%), and IX (28%) (correspondingly, 2-ethylidenecyclohexanone was present in 30% yield, calculated using the solvent as reference). A, assigned as one isomer of $(C_8H_{12}O)W(C_5H_5)(CO)_2{}^+CF_3COO^-$, had a C_5H_5 resonance at δ 5.24 and doublet due to methyl group at δ 2.44 (J_{HH} = 6 Hz). B, the other isomer, had a C_5H_5 resonance at δ 4.84 and doublet at δ 2.24 (J_{HH} = 6 Hz). The C_5H_5 resonance of IX appeared at δ 4.77. Several other resonances, comprising 25% total absorptions in the δ 3–6 region, were observed. After 3 days the yield of 2-ethylidenecyclohexanone was 35%.

$Mo(C_5H_5)(CO)_3OC(O)CF_3$. To a solution of $CH_3Mo(C_5H_5)(CO)_3$ (0.23 g, 0.000 885 mol) in benzene (0.4 mL) under nitrogen was added CF_3COOH (0.25 ml, 0.003 29 mol). After 20 min, solvent and excess CF_3COOH were removed under vacuum leaving a red oil. This oil was crystallized from diethyl ether (3 mL) by the addition of petroleum ether (2 mL), followed by slow evaporation of the solvent. Red, crystalline solids were collected by filtration and dried under vacuum: yield 0.21 g (66%); mp 86–88 °C; IR (THF) 2060 (m), 2075 (s), 1710 (m) cm^{-1}; ^1H NMR (benzene-d_6) δ 4.67 (methylene-d_2 chloride), 5.61 (s, C_5H_5) ppm.

Anal. Calcd for $C_{10}H_5F_3MoO_5$: C, 33.54; H, 1.41; F, 15.92; Mo, 26.79. Calcd for $C_9H_5F_3MoO_4$: C, 32.74; H, 1.53; F, 17.26; Mo, 29.07. Found: C, 33.70; H, 1.57; F, 16.20; Mo, 26.19.

$W(C_5H_5)(CO)_3OC(O)CF_3$. To a solution of $CH_3W(C_5H_5)(CO)_3$ (0.225 g, 0.000 646 mol) in benzene (0.4 mL) under nitrogen was added CF_3COOH (0.20 ml, 0.002 63 mol). After 30 min, solvent and excess CF_3COOH were removed under vacuum leaving a red oil. The oil was crystallized from diethyl ether (3 mL) by addition of petroleum ether (3 mL), three times. The red, crystalline product was collected by filtration and dried under vacuum: yield 0.153 g (52%); mp 90–91 °C; IR (THF) 2058 (m), 1955 (s), 1712 (m) cm^{-1}; ^1H NMR (benzene-d_6) δ 4.69 (s, C_5H_5) ppm.

Anal. Calcd for $C_{10}H_5F_3MoO_5$: C, 26.93; H, 1.13; F, 12.78; W, 41.22. Calcd for $C_9H_5F_3MoO_4$: C, 25.86; H, 1.21; F, 13.64; W, 43.98. Found: C, 27.20; H, 1.20; F, 13.10; W, 41.55.

Stoichiometry of Reaction of CF_3COOH with $CH_3Mo(C_5H_5)(CO)_3$. A solution of $CH_3Mo(C_5H_5)(CO)_3$ (16 g, 0.000 615 mol) in benzene (3 mL) was degassed under vacuum. CF_3COOH (0.3 mL, 0.003 95 mol) was distilled onto the solution, which was then stirred at 20 °C for 6 h. Evolved gases were collected by Toepler pump after freezing the solution with dry ice/acetone traps; 0.000 615 mol (1 equiv based on Mo) of gas was collected, which was shown by IR to be only methane. No CO was present in the evolved gases, indicating the formula of the organometallic product to be $Mo(C_5H_5)(CO)_3OC(O)CF_3$.

Reduction of $Mo(C_5H_5)(CO)_3OC(O)CF_3$. A. $Mo(C_5H_5)(CO)_3OC(O)CF_3$ (0.067 g, 0.000 187 mol) was dissolved in THF (3 mL) and the solution was stirred over excess 1.6 M Na(Hg). After 10 min the red color had changed to yellow, and the IR spectrum showed bands only at 1900, 1790, and 1740 cm^{-1} due to $Mo(C_5H_5)(CO)_3{}^-$ and at 1700 cm^{-1} due to CF_3COO^-.

B. $Mo(C_5H_5)(CO)_3OC(O)CF_3$ (0.067 g, 0.000 187 mol) in THF-d_8 (0.4 mL) was shaken with excess 1.6 M Na(Hg). The initial C_5H_5 resonance at δ 5.93 converted quantitatively to a resonance at δ 5.13 due to $Mo(C_5H_5)(CO)_3{}^-$.

Hydrogenation of IIIa. A. $(C_7H_9O)Mo(C_5H_5)(CO)_2$ (IIIa, 0.19 g, 0.000 582 mmol) in benzene (2 mL) was sealed under hydrogen (~10-mL volume at ≈1.5 atm, i.e., estimated 0.0006–0.0008 mol). After heating at 90 °C for 4 days the tube was opened under nitrogen and volatiles were transferred off under vacuum. An NMR spectrum of the involatile residues showed IIIa (48%), $[Mo(C_5H_5)(CO)_3]_2$ (5%), and $[Mo(C_5H_5)(CO)_2]_2$ (47%). Volatiles were examined by GC (20% SE-30 on Chromosorb W, 20 ft × 5/16 in., 140 °C; dodecane as internal standard), and contained 2-ethylcyclopentanone (87% yield based on 50% conversion of IIIa to product) and 2-ethylidenecyclopentanone (12%). 2-Ethylcyclopentanone was identified by IR (ν_{CO} 1740 cm^{-1}), NMR in C_6D_6 [δ 0.87 (t, 3 H, J_{HH} = 7.5 Hz) and 1.07–2.07 (m, 9 H)], and mass spectrum (parent *m/e* 112). 2-Ethylidenecyclopentanone was identified by IR (ν_{CO} 1720, $\nu_{C=C}$ 1650 cm^{-1}) and mass spectrum (parent *m/e* 110).

B. IIIa (0.1 g, 0.000 31 mol) in benzene (2 mL) was sealed under hydrogen (20-mL volume at ≈1.5 atm, i.e., estimated 0.0015 mol) and heated for 4 days at 90 °C. The volatiles contained 2-ethylcyclopentanone (95% yield) when examined by GC (as above).

Hydrogenation of IIIb. $(C_8H_{11}O)Mo(C_5H_5)(CO)_2$ (IIIb, 0.08 g, 0.000 23 mol) in C_6D_6 (0.3 mL) was sealed under hydrogen (≈1.5 atm) in an NMR tube. After heating at 90 °C for 1 day the solution contained IIIb (73%, C_5H_5 proton resonance at δ 4.84), $[Mo(C_5H_5)(CO)_3]_2$ (4%, C_5H_5 at δ 4.78), and $[Mo(C_5H_5)(CO)_2]_2$ (22%, C_5H_5 at δ 4.74). After 4 days, the solution contained $[Mo(C_5H_5)(CO)_3]$ (10%) and $[Mo(C_5H_5)(CO)_2]_2$ (90%). Integration against C_5HD_5 showed that 91% total C_5H_5 originally in the reaction mixture could be accounted for as the two dimers. Volatiles were removed from the reaction mixture under vacuum and were shown by GC (20% SE-30 on Chromosorb W, 20 ft × $^{5}/_{16}$ in., 140 °C, dodecane as internal standard) to contain 2-ethylcyclohexanone (87% yield). 2-Ethylcyclohexanone was identified by comparison with an authentic sample obtained from Chemical Samples Co.: IR (ν_{CO} 1715 cm^{-1}), NMR in C_6D_6 [δ 0.96 (t, 3 H, J_{HH} = 7.5 Hz) and 1.10–2.44 (m, 11 H)], and mass spectrum (parent *m/e* 126).

Hydrogenation of *cis*- and *trans*-2-Ethylidenecyclohexanone (VII) and VI) with IIIb. A solution of IIIb (0.015 g, 0.000 044 mol), VI (0.010 g, 0.000 08 mol), and VII (0.004 g, 0.000 03 mol) in C_6D_6 (0.2 mL) was heated under hydrogen (≈1.5 atm) in a sealed NMR tube at 90 °C. After 2 days, all VII and 50% of VI had been hydrogenated (indicated by loss of vinyl resonances in the NMR); 75% of IIIb had been hydrogenated. After 6 days, the solution contained 0.019 g (95% yield from IIIb, VI, and VII) of 2-ethylcyclohexanone (by GC).

Attempted Hydrogenation of $(C_8H_{11}O)W(C_5H_5)(CO)_2$. A solution of $(C_8H_{11}O)W(C_5H_5)(CO)_2$ (0.044 g, 0.0001 mol) in benzene (0.3 mL) was sealed under 1 atm H_2 in an NMR tube (approximately 0.0001 mol of H_2) and was heated at 100 °C. After 23 h no reaction was observed (by NMR) to have taken place.

Photolysis of $(C_8H_{11}O)W(C_5H_5)(CO)_2$ under H_2. A sample identical with that described above was irradiated for 1 h using a high-pressure mercury lamp. Although the solution turned dark brown, no reaction products were observed in the NMR spectrum.

Protonation of $CH_3C\equiv C(CH_2)_4W(C_5H_5)(CO)_3$. A. To a solution of $CH_3C\equiv C(CH_2)_4W(C_5H_5)(CO)_3$ (0.05 g, 0.000 12 mol) in benzene-d_6 (0.3 mL) in a septum-capped NMR tube under N_2 was added CF_3COOH (0.025 mL, 0.000 33 mol). After 1.5 h, 72% (by NMR) of the $CH_3C\equiv C(CH_2)_4W(C_5H_5)(CO)_3$ (C_5H_5 at δ 4.63) had been converted to a mixture of IX (C_5H_5 at δ 4.85) and XII (C_5H_5 at δ 5.32) in a ratio of 1.8:1. The reaction went to completion over 2 days with the ratio of products staying approximately the same (in comparable reactions, ratios of IX:XII of 1.5–1.8:1 were observed).

B. To a solution of $CH_3C\equiv C(CH_2)_4W(C_5H_5)(CO)_3$ (0.07 g, 0.000 16 mol) in THF (0.4 mL) in a septum-capped NMR tube under N_2 was added CF_3COOH (0.015 mL, 0.000 18 mol). After 4 days less than 5% reaction had occurred, and the observed product was IX (only).

$W(C_5H_5)(CO)(2\text{-heptyne})_2^+PF_6^-$. Excess CF_3COOH (0.46 g, 0.004 mol, freshly distilled from a minimum of P_2O_5) was condensed onto a solution of $CH_3W(C_5H_5)(CO)_3$ (0.45 g, 0.0013 mol) in benzene (5 mL) at −196 °C, under vacuum in a 100-mL flask. The solution was warmed to 20 °C, and was stirred for 2 h. All volatiles were then transferred from the reaction mixture under vacuum, leaving red solid $CF_3CO_2W(C_5H_5)(CO)_3$. These residues were dissolved in acetonitrile (15 mL) with 2-heptyne (1 mL, 0.0078 mol), and the solution was heated at 65 °C under vacuum in the closed vessel for 3 days until the solution turned pale yellow-brown. The solution was cooled and gases were pumped off once, after the first day. Solvent was removed from the reaction mixture and $NH_4^+PF_6^-$ (0.22 g, 0.001 34 mol) was added to the residues in methanol (5 mL). This solution was filtered and then cooled to −78 °C to precipitate the product as white crystals: yield 0.28 g (41%); mp 77.0–77.5 °C; IR (CH_2Cl_2) ν_{CO} 2045 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.93 (s, 5 H, C_5H_5), 3.53–2.9 (m) and 3.07, 2.83 (both s) (total 10 H, $CH_3C\equiv CCH_2$), 1.83–0.70 (m, 14 H, $(CH_2)_2CH_3$) ppm; ^{13}C NMR {^1H} (CD_3CN) δ 11.9, 14.79, 19.09, 20.99, 29.58, 30.29, 34.11, 34.59 (CH_3, $(CH_2)_3CH_3$), 99.25 (C_5H_5), 141.45, 144.75, 159.38, 162.21 ($C\equiv C$).

Anal. Calcd for $C_{20}H_{29}F_6OPW$: C, 39.10; H, 4.76; W, 29.93. Found: C, 38.85; H, 4.75; W, 29.70.

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References and Notes

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(3) (a) J. Crandall et al., *J. Am. Chem. Soc.*, **97**, 7171 (1975); (b) J. Norton, K. Shenton, and J. Schwartz, *Tetrahedron Lett.*, 51 (1975); (c) T. F. Murray, V. Varma, and J. R. Norton, *J. Org. Chem.*, **43**, 353 (1978); (d) W. Michaely, Ph.D. Thesis, Indiana University, Bloomington, Ind., 1971.

(4) (a) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956); (b) E. O. Fischer, *Inorg. Synth.*, **7**, 136 (1963); (c) R. B. King and F. G. A. Stone, *ibid.*, **7**, 99 (1963); (d) J. J. Eisch and R. B. King, "Organometallic Syntheses", Vol. 1, Academic Press, New York, 1965, pp 145, 156.

(5) W. Jolly, *Inorg. Synth.*, **11**, 116 (1968); ref 4d, p 145.

(6) J. L. Davidson, M. Green, J. Z. Nyathi, C. Scott, F. G. A. Stone, A. J. Welch, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 714 (1976).

(7) H. G. Alt, *J. Organomet. Chem.*, **127**, 349 (1977).

(8) Authentic samples of *cis*- and *trans*-2-ethylidenecyclohexanone were obtained from Chemical Samples Co. and were separated by GC.

(9) (a) R. B. King and A. Fronzaglia, *Chem. Commun.*, 274 (1966); (b) K. Stark et al., *Z. Naturforsch. B*, **19**, 284 (1964).

(10) For related complexes, see (a) J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 738 (1976); (b) M. L. H. Green, J. Knight, and J. A. Segal, *ibid.*, 2189 (1977). We have obtained further evidence for the bisalkyne structure of complexes such as XII by correlating them chemically with certain of the substances reported in ref 10b; these results will be reported shortly (P. L. Watson and R. G. Bergman, manuscript in preparation).

(11) P. J. Craig and M. Green, *J. Chem. Soc. A*, 1978 (1968).

(12) A. Wojcicki, *Adv. Organomet. Chem.*, **11**, 87 (1973).

(13) W. H. Knoth, *Inorg. Chem.*, **14**, 1566 (1975).

(14) J. L. Davidson, M. Green, J. Z. Nyathi, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 2246 (1977).

(15) (a) J. L. Davidson, M. Green, D. W. A. Sharp, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 706 (1974); (b) J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 738 (1976).

(16) P. E. Peterson, R. J. Bopp, and M. M. Ajo, *J. Am. Chem. Soc.*, **92**, 2834 (1970).

(17) A. Hatanaka, M. Hamada, and M. Ono, *Sci. Insect Control (Kyoto)*, **24**, 151 (1959); *Chem. Zentralbl.*, **132**, 9745 (1961).

(18) M. S. Newman and J. H. Wotiz, *J. Am. Chem. Soc.*, **71**, 1292 (1949).