Organometallics 1983, 2, 1172-1178

Metal–Metal Multiple Bonds. 14. Synthesis, Stereochemistry, and Hydrogenation of Protonated Alkyne Adducts of $Cp_2Mo_2(CO)_4$

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Received March 21, 1983

$Cp_2Mo_2(CO)_4(Mo\equiv Mo)$ reacts with alkynes, $RC\equiv CR'$ (R, R′ = H, alkyl, $SnMe_3$, Ph), to form 1:1 adducts $Cp_2Mo_2(CO)_4(RC\equiv CR')$ in high yields. Protonation of these alkyne adducts by strong acids (such as CF_3COOH, $HBF_4{\cdot}Et_2O$, and HCl) yields compounds with a vinyl group both η^1 and η^2 bonded to the dimetal fragment. The protonation has been shown to occur in an anti-Markovnikov manner to give the (*E*)-alkene fragment. X-ray structural analysis of the protonated compounds shows a Mo–Mo single bond with the conjugate base of the acid (in the CF_3COOH case) coordinated to one of the molybdenum atoms. For $Cp_2Mo_2(CO)_4(PhC\equiv CH)$ plus $HBF_4{\cdot}Et_2O$, a H_2O adduct is formed upon addition of water. The water molecule was found to be coordinated to one of the molybdenums upon solution of the crystal structure. $Cp_2Mo_2(CO)_4(Ph(H)C\equiv CH)(H_2O)BF_4$: a = 14.095 (8) Å, b = 9.625 (6) Å, c = 18.176 (10) Å, β = 108.34 (4)°, V = 2341 (2) Å^3, Z = 4, space group $P2_1/a$. In the CF_3COOH adduct, the coordinated trifluoroacetate group is labilized in the presence of excess CF_3COOH, suggesting the possibility of facile displacement of coordinated TFA^- by groups such as H_2. This lability has been utilized in the hydrogenation of 1-hexyne and 1-hexene. The hydrogenation is quantitative when stoichiometric quantities of $Cp_2Mo_2(CO)_4$ and 1-hexyne are employed. When catalytic quantities of $Cp_2Mo_2(CO)_4$ and acid are used, then polymerization of the 1-hexyne becomes the favored reaction pathway.

Introduction

Since the first metal–metal multiply bonded compounds were recognized in 1965,[1] many comparisons have been made between organic multiple bonds and transition-metal multiple bonds.[2] A logical extension of these comparisons is to study the reactivity of these unsaturated systems toward one another. Since 1975, several groups[3-5] have studied the reactions of $Cp_2Mo_2(CO)_4$ (1) with acetylenes. It has been shown that alkynes will add across the metal–metal triple bond of 1 (eq 1) to form 1:1 adducts $Cp_2Mo_2(CO)_4(\mu\text{-}RCCR')$,[6] where R and R′ may be a wide range of groups including H,[2,8] Me,[4] Et,[7] Ph,[7,8] Me_3Sn, COOMe,[4] and Me_3Si.[9]

$$Cp_2Mo_2(CO)_4 + RCCR' \rightarrow Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}RCCR') \tag{1}$$

These acetylene adducts show interesting reactivities toward a variety of substrates. The $M_2(C_2H_2)$ (M = $Mo(CO)_2Cp$ throughout this paper) adduct reacts with silanes R_3SiH to give the silylacetylene complexes $M_2(R_3SiCCH)$ and hydrogen.[9] They also react further with acetylenes to give complexes containing ligands derived from sequentially linking two to four acetylene units.[9-12] The coordinated acetylene in $M_2(HCCH)$ also reacts with cyclic dienes to give a complex in which the formal Diels–Alder adduct of the acetylene and the diene is coordinated to the dinuclear center.[13] During the course of our investigations of the reactivity of the $M_2(\mu\text{-}RCCR)$ adducts, we discovered that strong acids, e.g., trifluoroacetic acid (HTFA), HCl, and HBF_4 react with the acetylene adducts to form M-η^1,η^2-vinyl complexes. Beck et al. independently discovered this reaction and have published the structure of the HTFA adduct.[5] We report here the synthesis of some new acetylene adducts, their reactions with strong acids, and some reactions of the protonated adducts with H_2 and acetylenes.

Experimental Section

All manipulations were carried out under an inert atmosphere of N_2 using standard Schlenk techniques. $Cp_2Mo_2(CO)_4$ was prepared by the literature method.[14] Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer. NMR spectra were recorded on Varian T-60A, JEOL FX900, or Bruker WM360 instruments. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

Preparation of $Cp_2Mo_2(CO)_4(RCCR')$. The $PhC\equiv CH$,[3,8] C_2H_2,[8] and $EtC\equiv CEt$[7] derivatives of 1 were prepared by the literature methods. The $EtC\equiv CH$ and $BuC\equiv CH$ derivatives were prepared by the same general procedure; outlined below in detail for $(BuC\equiv CH)Cp_2Mo_2(CO)_4$.

$Cp_2Mo_2(CO)_4$ (0.64 g, 1.48 mmol) was dissolved in CH_2Cl_2 (10 mL). 1-Hexyne (0.2 mL, 1.7 mmol) was syringed into the solution. The color changed from orange/red to deep red. After the solution was stirred for 1 h, the solvent and excess acetylene were removed under vacuum to leave a deep red powder that is spectroscopically pure. Recrystallization from CH_2Cl_2/hexane also affords pure samples in yields typically >90%. $M_2(BuC\equiv CH)$: mp 91–93 °C

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dec. Anal. Calcd for $C_{20}H_{20}Mo_2O_4$: C, 46.52; H, 3.87. Found: C, 46.41; H, 3.97. The $EtC{\equiv}CH$ adduct was prepared from 1.7 g of $Cp_2Mo_2(CO)_4$ in 20 mL of benzene and 100 mL of butyne gas. $M_2(EtC{\equiv}CH)$: mp 103–104 °C dec; ^{13}C NMR (C_6D_6, 90.55 MHz) δ 233.7, 228.2 (CO), 91.3 (Cp), 86.0 ($\equiv$CH), 60.9 ($\equiv$CEt), 29.4 (CH_2), 17.6 (CH_3). Anal. Calcd for $C_{18}H_{16}Mo_2O_4$: C, 44.26; H, 3.27. Found: C, 44.41; H, 3.31.

The adduct **$M_2(Me_3SnC{\equiv}CPh)$** was prepared by adding 0.870 g (2.0 mmol) of $Cp_2Mo_2(CO)_4$ to 20 mL of toluene containing 0.535 g (2.02 mmol) of $Me_3SnC{\equiv}CPh$. The reaction was complete after 1 h at which time the solution was filtered and the volume of the filtrate reduced to ca. 3 mL. After the mixture was left standing at -20 °C overnight, 0.96 g of crystalline product, mp 184–197 °C dec, was collected. Anal. Calcd for $C_{25}H_{24}Mo_2O_4Sn$: C, 42.93; H, 3.46. Found: C, 43.07; H, 3.56.

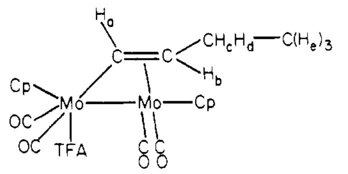
$M_2(Ph_3SnCCSnPh_3)$ was prepared in an analogous fashion from 0.318 g of $Cp_2Mo_2(CO)_4$ and 0.516 g of $Ph_3SnCCSnPh_3$ in 20 mL of toluene for 3 days at room temperature. The resulting solid was collected and recrystallized from CH_2Cl_2 to give maroon crystals: mp 185–187 °C dec; yield ~50%; ^{13}C NMR ($CDCl_3$, 90.55 MHz) δ 230.6 (CO), 128.1, 128.8 (Ph), 137.3, 140.4 (PhC(ipso) and $\equiv$C), 91.6 (Cp). Anal. Calcd for $C_{52}H_{40}Mo_2O_4Sn_2$: C, 53.90; H, 3.48. Found: C, 53.81; H, 3.53.

Reactions of $Cp_2Mo_2(CO)_4(RCCR')$ with Strong Acids. (i) $Cp_2Mo_2(CO)_4(HC{\equiv}CH)$ with CF_3COOH. Typically $Cp_2Mo_2(CO)_4(HC{\equiv}CH)$ (0.236 g, 0.44 mmol) was dissolved in toluene (or CH_2Cl_2) (10 mL). The CF_3COOH (0.032 mL, 0.44 mmol) was then syringed into the solution at room temperature. The cherry red solution immediately becomes red/purple upon addition of the acid. The product was crystallized from a concentrated toluene solution. The yield is essentially quantitative: IR ν_{CO} (KBr) 2021 (s), 1953 (s), 1901 (m, sh), 1892 (m), 1870 (s), ν_{CO} (TFA) 1681 (m) cm^{-1}; ^1H NMR (60 MHz, toluene-d_8) δ 8.60 (dd, J_{MX} = 8.8 Hz, J_{AX} = 12.3 Hz, 1 H), 4.52 (s, Cp), 4.48 (s, Cp), 3.59 (dd, J_{MX} = 8.8 Hz, $J_{MA} \approx$ 1.2 Hz, 1 H), 3.04 (dd, $J_{MA} \approx$ 1.2 Hz, J_{AX} = 12.3 Hz, 1 H); ^{13}C NMR (90.55 MHz, $(CD_3)_2CO$) δ 231.0 (CO), 165.1 (C=O), 62.4 and 59.4 (C$\equiv$C), 94.7 and 93.6 (Cp). The signal due to the CF_3 carbon was not observed. Anal. Calcd for $C_{18}H_{13}F_3O_6Mo_2$: C, 37.65; H, 2.28; F, 9.93. Found: C, 37.48; H, 2.38; F, 10.03.

(ii) $Cp_2Mo_2(CO)_4(HC{\equiv}CPh)$ with $HBF_4{\cdot}Et_2O$. $Cp_2Mo_2(CO)_4(HC{\equiv}CPh)$ (0.51 g, 0.95 mmol) was dissolved in CH_2Cl_2 (30 mL). $HBF_4{\cdot}EtO$ (0.14 mL, 1 mmol) in CH_2Cl_2 (2 mL) was added to the solution. An immediate violet coloration was observed. Slow cooling over several days in a refrigerator (4 °C) caused a red crystalline product to precipitate. An X-ray analysis shows this product to be the water adduct $Cp_2Mo_2(CO)_4(\mu\text{-}CH{=}CHPh)(OH_2)BF_4$: IR ν_{CO} (Nujol) 2005 (m-s), 1957 (s), 1880 (br, m-s), ν_{B-F} 1020 (br, m) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$, -60 °C) δ 9.24 (d, $J_{HH} \approx$ 12.6 Hz, 1 H), 5.63 (s, Cp), 5.14 (s, Cp), 4.90 (d, $J_{HH} \approx$ 12.6 Hz, 1 H), 7.30 (m, Ph). Anal. Calcd for $C_{22}H_{19}BF_4O_5Mo_2$: C, 41.14; H, 2.96; Mo, 29.90; F, 11.84. Found: C, 41.08; H, 3.02; Mo, 32.74; F, 11.22. The yield of the H_2O adduct is ca. 50% when a stoichiometric quantity of water in THF is added.

(iii) $Cp_2Mo_2(CO)_4(HC{\equiv}CH)$ with HCl. $Cp_2Mo_2(CO)_4(HC{\equiv}CH)$ (0.3 g, 0.69 mmol) was dissolved in toluene (10 mL). HCl was then bubbled through the solution at room temperature (10 min). A solution infrared spectrum (2010 (m), 1960 (vs), 1910 (vs) cm^{-1}) indicated that the desired product $M_2(Cl)(\mu\text{-}CHCH_2)$[5] had been obtained; yield >95%.

(iv) $Cp_2Mo_2(CO)_4(HC{\equiv}CEt)$ with CF_3CO_2H. CF_3CO_2H (0.154 mL, 2.0 mmol) was added to $Cp_2Mo_2(CO)_4(HC{\equiv}CEt)$ (0.98 g, 2.0 mmol) in 15 mL of toluene. Concentration of the solution under vacuum and cooling give the red solid: mp 78–80 °C dec; yield >95%; ^1H NMR (360 MHz, C_6D_6) (see Figure 2 and below for labeling scheme)



δ 8.34 (d, H_a), 4.54 and 4.46 (s, Cp), 3.88 (ddd, H_b), 1.95 (ddq, H_c or H_d), 1.15 (ddq, H_d or H_c), 1.04 (dd, H_e), coupling constants (J, Hz) H_a–H_b, 11.7, H_c,H_d–H_b, 8.5 and 4.4, H_c,H_d–H_e, 7.1 and 7.3, H_c–H_d ~13.2; ^{13}C NMR (22.6 MHz, gated decoupled, C_6D_6) δ 237.7, 236.0, 231.4 (CO), 162.9 (C=O, TFA), 161.4 (C_1, J = 142 Hz), 97.4 and 89.3 (Cp), 90.2 (C_2, J = 153 Hz), 35.9 (CH_2, J = 127 Hz), 17.7 (CH_3, J = 124 Hz). Anal. Calcd for $C_{20}H_{17}F_3Mo_2O_6$: C, 39.89; H, 2.82. Found: C, 39.44; H, 2.45.

Reactions (i)–(iii) are general for all the acetylenes we have studied except for the case of $HCCSnMe_3$. In this case, treatment of the adduct $M_2(\mu\text{-}HCCSnMe_3)$ with strong acid HX cleaves the Me_3SnX group to give $M_2(HCCH)$ which is further protonated to $M_2(\mu\text{-}HCCH_2)X$. Beck et al.[9] have also observed that strong acids cleave the Me_3Si group from the adducts $M_2(\mu\text{-}Me_3SiCCR)$.

(v) $Cp_2Mo_2(CO)_4(PhCCH)$ with 2 Equiv of CF_3COOH. When 2 equiv of CF_3COOH are added to $Cp_2Mo_2(CO)_4(PhCCH)$, the Cp region of the ^1H NMR spectrum exhibits two broad resonances consistent with the fluxional species of the type $[Cp_2Mo_2(CO)_4(Ph(H)CCH]^+[H(TFA)_2]^-$. Removal of the excess acid regenerates the original spectrum (see Figure 3). This result is general for all the HTFA adducts studied.

(vi) $Cp_2Mo_2(CO)_4(RCCR)$ with CH_3COOH. No protonation of the acetylene was observed spectroscopically when CH_3COOH was used as the proton source.

Attempted Hydrogenation of Acetylenes. (i) Low Pressure. Typically $Cp_2Mo_2(CO)_4$(1-hexyne) was prepared in situ in a glass tube apparatus capable of holding pressures of 45 psig by addition of $BuC{\equiv}CH$ to **1** dissolved in toluene. (For stoichiometric hydrogenation reactions, $Cp_2Mo_2(CO)_4(BuC{\equiv}CH)$ was prepared as described above and isolated before use.) The CF_3COOH (a 0.1–0.6-fold excess) was added and the solution frozen. Three freeze–pump–thaw cycles were employed to ensure complete degassing of the system before the final evacuation. Then H_2 (30 psig) was admitted to the reactor. The various reaction times and temperatures are outlined in Table V. The workup procedure consisted of transferring the solution to a Schlenk flask followed by trap-to-trap distillation of the volatile fraction which was then analyzed by GC/MS methods. The involatile residue was then characterized by NMR and IR spectroscopy.

In several cases where CH_3COOH was used as both the solvent and protonating acid the experimental procedure was identical with that outlined above except that **1** was dissolved in the CH_3COOH instead of toluene. The results obtained are summarized in Table V.

(ii) High Pressure. Samples for high-pressure hydrogenation reactions (100–270 atm) were prepared in a Schlenk flask by addition of CF_3COOH to $Cp_2Mo_2(CO)_4(BuC{\equiv}CH)$ in toluene (~6 mL). The sample was then transferred to a high-pressure reaction vessel that had been thoroughly flushed with N_2. The reaction vessels were pressurized immediately. Sample workup was as described for the low-pressure reactions. The results are collected in Table V.

Structure Determination. Crystals of $[M_2(\mu\text{-}CH{=}CHPh)(OH_2)][BF_4]$ were grown from methylene chloride as red plates. Initial rotation photographs and counter data indicated the crystal to be monoclinic of space group $P2_1/a$ with Z = 4. The positions of the molybdenums were located from a Patterson map. All other non-hydrogen atoms were located in subsequent difference maps.[15] Refinement with the molybdenums and oxygens anisotropic and all other atoms isotropic lead to final convergence at R_1 = 6.0 and R_2 = 7.4. The BF_4^- anion was found to be disordered. A suitable model of the BF_4 disorder is represented by a rotation about the B–F1 bond. During the final cycles of refinement and positional and thermal parameters of the disordered BF_4 were kept constant. Table II lists the pertinent crystallographic data, Table III the fractional atomic coordinates, and Table IV a selection of bond distances and angles.

Results and Discussion

Acetylenes react readily with **1** (eq 1) to form 1:1 adducts $Cp_2Mo_2(CO)_4(RCCR)$ (see Table I). These acetylene ad-

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[15] A description of the computer programs has been given previously: Curtis, M. D.; Greene, J.; Butler, W. M. *J. Organomet. Chem.* **1979**, *164*, 371.

Table I. New $Cp_2Mo_2(CO)_4$(acetylene) Complexes

acetylene	IR, cm^{-1}	^1H NMR, δ	mp, °C
EtC≡CH	1980 (s), 1920–1900 (vs), 1835 (s)[a]	5.58 (HC≡), 4.90 (Cp), 2.56 (q, CH_2), 0.88 (t, CH_3) (*J* = 7 Hz)	103–104 dec
BuC≡CH	1975 (s), 1910–1900 (vs), 1830[c]	5.97 (HC≡), 5.30 Cp), 2.60 (q, ≡C-CH), 1.30 (m, $CH_2(CH_2)_2$), 0.94 (t, CH_3)[d]	91–93 dec
$Me_3SnC≡CPh$	1979 (s), 1915 (vs), 1829 (m)[e]	7.15 (Ph), 5.13 (Cp), 0.28 (Me)[b]	184–187
$Ph_3SnC≡CSnPh_3$	1928 (s), 1915 (vs), 1830 (m)[e]	7.20 (Ph), 4.90 (Cp)[b]	185–187

[a] Benzene solvent. [b] Benzene-d_6 solvent. [c] Nujol. [d] $CDCl_3$ solvent. [e] CH_2Cl_2 solvent.

Table II. Summary of Crystallographic Statistics

a, Å	14.095 (8)
b, Å	9.625 (6)
c, Å	18.176 (10)
β, deg	108.34 (4)
V, $Å^3$	2341 (2)
Z	4
ρ_{calcd}, g cm^{-3}	1.82
space group	$P2_1/a$
cryst dimens, mm	0.02 × 0.22 × 0.18
radiatn	Mo Kα (monochromatized from graphite)
takeoff angle, deg	4
μ, cm^{-1}	11.0
scan speed, deg/min	1.5–12.0 (variable)
scan range	Mo $K\alpha_1$ − 0.8° to Mo $K\alpha_2$ + 0.8
bkgd/scan time	0.8
2θ limit, deg	40
reflctns	1481 ($I > 3\sigma(I)$)
R_1	6.0
R_2	7.4
$[\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/NO - NV]^{1/2}$	2.37
residuals ρ_{max} and ρ_{min}	0.8 and −1.0

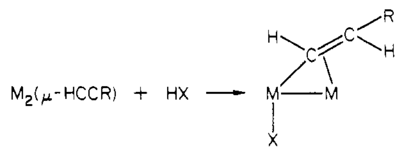
Table III. Final Positional Parameters for $[(Ph(H)CCH)(H_2O)Cp_2Mo_2(CO)_4^+](BF_4^-)$

atom	*x*[a]	*y*	*z*
Mo1	0.4325 (1)	0.5166 (2)	0.3036 (1)
Mo2	0.2474 (1)	0.4746 (2)	0.1653 (1)
O	0.3254 (9)	0.6262 (12)	0.1088 (7)
C1	0.0855 (13)	0.4563 (19)	0.1579 (11)
C2	0.1034 (13)	0.3468 (19)	0.1125 (11)
C3	0.1253 (14)	0.4077 (20)	0.0490 (11)
C4	0.1185 (14)	0.5526 (20)	0.0552 (11)
C5	0.0929 (14)	0.5860 (20)	0.1224 (11)
C6	0.5038 (14)	0.7261 (19)	0.2779 (12)
C7	0.5413 (14)	0.6934 (20)	0.3593 (12)
C8	0.5970 (14)	0.5694 (20)	0.3669 (12)
C9	0.5931 (13)	0.5249 (19)	0.2945 (11)
C10	0.5377 (14)	0.6179 (19)	0.2378 (12)
C11	0.4490 (13)	0.3192 (21)	0.2902 (11)
C12	0.4223 (13)	0.4390 (20)	0.3982 (12)
C13	0.2532 (13)	0.3449 (19)	0.2520 (11)
C14	0.3383 (15)	0.3393 (20)	0.1332 (12)
O11	0.4661 (11)	0.2006 (15)	0.2867 (9)
O12	0.4156 (9)	0.3878 (14)	0.4547 (7)
O13	0.2379 (9)	0.2675 (13)	0.2949 (7)
O14	0.3843 (10)	0.2625 (16)	0.1122 (9)
C15	0.2897 (12)	0.6326 (16)	0.2525 (10)
C16	0.2876 (12)	0.6237 (16)	0.3276 (10)
C17	0.3120 (12)	0.7401 (16)	0.3843 (10)
C18	0.3369 (13)	0.8715 (18)	0.3672 (10)
C19	0.3610 (14)	0.9801 (20)	0.4244 (12)
C20	0.3640 (15)	0.9445 (21)	0.4980 (12)
C21	0.3376 (15)	0.8167 (21)	0.5185 (12)
C22	0.3111 (13)	0.7143 (18)	0.4603 (11)
B	0.7231 (0)	0.5342 (0)	0.1030 (0)
F1	0.7089 (0)	0.4260 (0)	0.0463 (0)
F2	0.7172 (0)	0.4665 (0)	0.1664 (0)
F3	0.8163 (0)	0.5872 (0)	0.1216 (0)
F4	0.6517 (0)	0.6227 (0)	0.0813 (0)
F24	0.7276 (0)	0.6337 (0)	0.0661 (0)
F34	0.6505 (0)	0.5093 (0)	0.1306 (0)
F43	0.8134 (0)	0.5067 (0)	0.1610 (0)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses. Note: esd's for the disordered BF_4^- are 0 since the positional parameters of the anion were not varied in final cycles of refinement.

ducts have several features in common. The solution infrared spectra show three strong carbonyl stretching modes. The low-frequency band is indicative of a "semibridging" carbonyl.[4] Bulky substituents, e.g., Me_3Si, cause a rotation of the $Cp(CO)_2Mo$ groups with respect to one another so that the semibridging carbonyl feature is lost.[9] At room temperature the ^1H NMR spectra exhibit a single cyclopentadienyl resonance,[4,8] even when the acetylene is asymmetric. Bailey et al.[4] have shown that these adducts are fluxional on the NMR time scale, and Beck et al.[9] have commented on the mechanism. The structural parameters of the acetylene adducts are all similar.[2a,4,9,16] The Mo_2C_2 core consists of a tetrahedrane-like arrangement of atoms. The Mo–Mo bond lengths are ca. 2.98 Å (a single bond), Mo–C(acetylene) 2.18 Å, and C–C(acetylene) 1.33 Å.

We have been interested in the use of 1 and the HX adducts (X = halogen) $M_2(\mu\text{-}H)(\mu\text{-}X)$,[2a,8,17] as possible catalysts for the anti-Markovnikov addition of HX to terminal olefins and acetylenes. This interest led us to investigate the reactions of the adducts $M_2(\mu\text{-}RCCR')$ with strong protic acids. We have found that these adducts react directly with HX to give the adducts shown in eq 2



(2)

3

(M = $Mo(CO)_2Cp$, X = e.g., $CF_3CO_2^-$, Cl^-, BF_4^-). During the course of this work, Beck et al.[5] independently discovered this reaction with HBF_4 and showed that the BF_4^- could be replaced by nucleophiles, e.g., TFA^- ($CF_3CO_2^-$), Cl^-, and acetate ions. The ^1H NMR spectra are as expected for a μ-η^1,η^2-vinyl group.[18]

In donor solvents, e.g., Me_2CO, complex 3 is in equilibrium with 2 and the acid (eq 3) as evidenced by the appearance in the ^1H NMR of the signals due to 2 and an increase in the conductivity of the solution. The rate at which equilibrium is achieved depends upon the substit-

$$\underset{\mathbf{3}}{M_2(\mu\text{-}CHCH_2)(TFA)} \rightleftarrows \underset{\mathbf{2}}{M_2(HCCH)} + H(Me_2CO)_n{}^+TFA^- \quad (3)$$

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(16) Fotinos, N. A. Ph.D. Thesis, The University of Michigan, 1981.

(17) Curtis, M. D.; Fotinos, N. A.; Han, K. R.; Butler, W. M. *J. Am. Chem. Soc.* **1983**, *105*, 2686.

(18) Maddox, M. L.; Stafford, S. L.; Kaesz, H. D. *Adv. Organomet. Chem.* **1965**, *3*, 1–180 (see especially p 37).

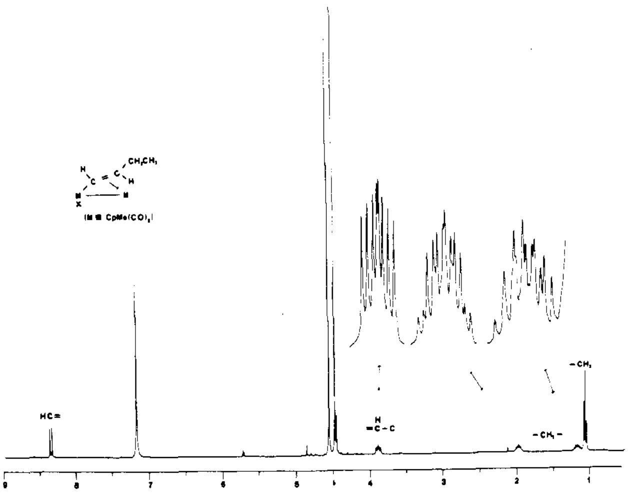
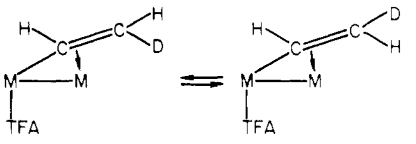


Figure 1. ^1H NMR spectrum (360 MHz, C_6D_6) of $Cp_2Mo_2(CO)_4(HCC(H)Et)(TFA)$. The multiplets corresponding to the =C(H)—C and methylene protons are shown as blowups (X = coordinated TFA anion).

uents on the acetylene, with bulkier groups giving the slowest rates. Beck et al. observed that 3 is deprotonated with strong bases.[5]

The ^1H NMR spectra (cf. Figure 1) clearly show that protonation of terminal alkynes coordinated to the M_2 fragment occurs in an anti-Markovnikov manner as shown in eq 2. Furthermore, the J_{HCCH} coupling across the C=C double bond reveals that the resulting vinyl group has the *E* configuration as shown. J_{HCCH} values of ca. 12 Hz are typical of trans HCCH coupling, while cis HCCH couplings are typically around 8–9 Hz. The observed, trans couplings for the complexes 3 are 12.3 (R = H), 12.6 (R = Ph), and 11.7 Hz (R = Et). In the case of the adduct $M_2(\mu\text{-}CH{=}CHPh)(OH_2)^+BF_4^-$, the stereochemistry was confirmed by an X-ray structure analysis (see below).

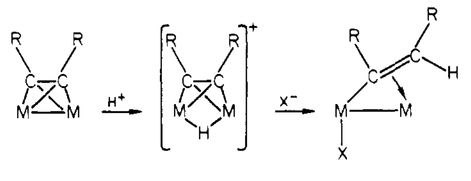
Addition of deuterated trifluoroacetic acid, DTFA, to the acetylene adduct gives the deuterated adduct $M_2(\mu\text{-}CH{=}CHD)(TFA)$, in which the deuterium is equally distributed over the positions shown in eq 4. This finding



(4)

is consistent with an isomerization which is slow on the NMR time scale at 25 °C but which is chemically rapid. The more ionic adduct $M_2(\mu\text{-}CH{=}CH_2)^+BF_4^-$ is fluxional on the NMR time scale, and the fluxional process averages the inequivalent Cp environments as well as the syn and anti protons on the $=CH_2$ group.[5]

Since the *E* configuration is observed upon protonation of all the substituted acetylene complexes and since this stereochemistry brings the proton up from the side toward the metal–metal bond, we suggest that the metal–metal bond is first protonated, followed by coordination of X^- and subsequent migration of the proton to the coordinated alkyne (eq 5). The protonation of metal–metal bonds opposite coordinated carbide and nitride ligands in Fe_4 clusters has been observed.[19,20]



(5)

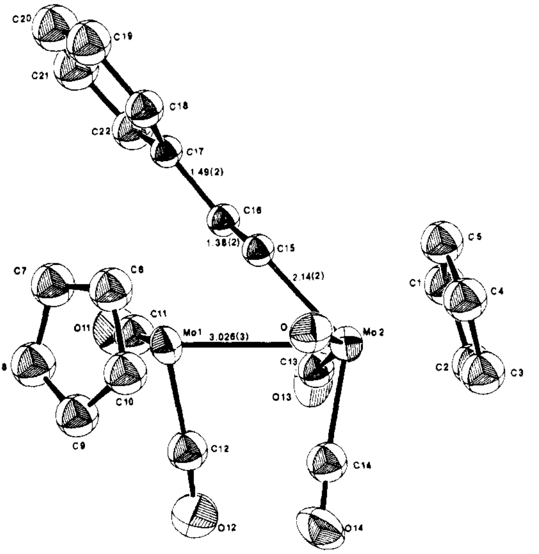


Figure 2. An *ORTEP* drawing of $[Cp_2Mo_2(CO)_4(Ph(H)CCH)H_2O^+][BF_4^-]$. The BF_4^- is omitted for clarity.

Structure of $[M_2(\mu\text{-}CH{=}CHPh)(OH_2)]BF_4$. A structure with a Mo=Mo double bond has been proposed for the $M_2(\mu\text{-}CH{=}CH_2)(BF_4)$ adduct. Since there are no structurally characterized adducts of 1 which contain a Mo=Mo double bond[2a,21] and since we desired to confirm the *E* configuration of the coordinated vinyl group in the protonated adducts, we undertook an X-ray structure determination of the adduct $M_2(\mu\text{-}CH{=}CHPh)(BF_4)$. However, only small crystals of marginal suitability could be obtained. Furthermore, upon solution of the structure, a water molecule was found to be incorporated and coordinated to one molybdenum. The presence of the coordinated water in the X-ray sample was confirmed by IR (ν_{OH} = 3400 cm^{-1}). Apparently, water vapor found its way into the sample container during the slow crystallization process in the refrigerator. We have also shown that this compound may be prepared by deliberately adding an equivalent of H_2O to a solution of freshly prepared $M_2(\mu\text{-}CH{=}CHPh)(BF_4)$.

The essential features of the structure of the water adduct are illustrated in Figure 2. (See Table IV for selected bond lengths and angles.) The Mo–Mo bond length is 3.02 Å, corresponding to a single bond. The presence of the coordinated water molecule precludes the existence of a metal–metal double bond since each Mo acquires an 18-electron configuration. The structure is thus similar to that with the TFA coordinated to a molybdenum.[5] The Mo–C(15) distance, 2.14 Å, is in the range expected for a Mo–C(sp^2) single bond, and the C(15)–C(16) distance, 1.38 Å, is about 0.05 Å longer than a normal C=C double bond, reflecting the loss of π bonding upon coordination to Mo(1). The Mo(2)–C(15)–C(16) and C(15)–C(16)–C(17) angles are 127° and 124°, respectively, compared to the angle of ca. 120° expected for sp^2 carbon.

Organometallic complexes containing coordinated water are extremely rare, especially if a M–C σ bond is also present in the molecule. The only other examples known

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(19) Holt, E. M.; Whitmire, K. H.; Shriver, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 5621.

(20) Fjare, D. E.; Gladfelter, W. L. *Inorg. Chem.* **1981**, *20*, 3533.

(21) Since submission of this manuscript, we have succeeded in synthesizing a μ-fluorenylidene complex, $M_2(\mu\text{-}C_{13}H_8)$, which contains a Mo=Mo double bond (d(Mo=Mo) = 2.798 (1) Å). EHMO calculations show that, depending on the relative orientation of the bridging alkylidene group, a low-energy acceptor orbital is generated. Hence, certain configurations of the $M_2(\mu\text{-}CR_2)$ structure do act as strong Lewis acids. D'Errico, J. J.; Curtis, M. D. *J. Am. Chem. Soc.* **1983**, *105*, 4479.

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) for $[Cp_2Mo_2(CO)_4(\mu\text{-CHCHPh})(H_2O)^+][BF_4^-]$

Bond Lengths

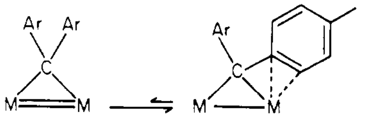
Mo1-Mo2	3.026 (3)	C16-C17	1.49 (2)	Mo2-C14	2.04 (2)
Mo1-C(Cp)	2.30 (2)-2.38 (2)	C11-O11	1.17 (2)	Mo2-C15	2.14 (2)
Mo1-C11	1.92 (2)	C12-O12	1.17 (2)	Mo2-C16	3.17 (2)
Mo2-C12	1.94 (2)	C15-C16	1.38 (2)	Mo2-O	2.26 (1)
Mo1-C15	2.23 (2)	Mo2-C(Cp)	2.25 (2)-2.36 (2)	C13-O13	1.15 (2)
Mo1-C16	2.44 (2)	Mo2-C13	1.99 (2)	C14-O14	1.13 (2)
C1-C2	1.41 (2)	C6-C7	1.44 (3)	C17-C18	1.37 (2)
C2-C3	1.41 (2)	C7-C8	1.41 (2)	C18-C19	1.44 (2)
C3-C4	1.40 (2)	C8-C9	1.37 (2)	C19-C20	1.37 (2)
C4-C5	1.41 (2)	C9-C10	1.40 (2)	C20-C21	1.37 (3)
C5-C1	1.42 (2)	C10-C6	1.43 (2)	C21-C22	1.41 (3)
				C22-C17	1.40 (2)

Bond Angles

Mo1-Mo2-C15	47.4 (4)	Mo1-C12-O12	178 (2)	Mo2-C14-O14	176 (2)
C15-C16-C17	124 (1)	Mo2-C15-C16	127 (1)		
Mo1-C11-O11	174 (2)	Mo2-C13-O13	167 (2)		
C1-C2-C3	107 (2)	C4-C5-C1	105 (2)	C8-C9-C10	110 (2)
C2-C3-C4	108 (2)	C5-C1-C2	110 (2)	C9-C10-C6	106 (2)
C3-C4-C5	110 (2)	C6-C7-C8	107 (2)	C10-C6-C7	107 (2)
		C7-C8-C9	108 (2)		
C17-C18-C19	121 (2)	C21-C22-C17	122 (2)	C20-C21-C22	117 (2)
C19-C20-C21	124 (2)	C18-C19-C20	117 (2)	C22-C17-C18	118 (2)

to the authors are the $Me_2Au(OH_2)(O_3SCF_3)$,[22] $[(Me_3P)(CO)_3Cr(CMe)(H_2O)][BF_4]$,[23] aquomethylcobalamins and related species,[24] and the cluster compounds $Mo_3(CMe)_2(OAc)_6(H_2O)_3$[25] and $Mo_3(O)(CMe)(OAc)_6(H_2O)_3$.[26] The Mo–C(vinyl) bond in the $M_2(\mu\text{-CH=CHR})X$ complexes are extremely resistant to cleavage, even in excess acid (see below), possibly due to the $\mu\text{-}\eta^1,\eta^2$-bonding mode present. Therefore, it is not unreasonable to find in the structure of $M_2(\mu\text{-CH=CHPh})(OH_2)^+$ a Mo–C σ bond adjacent to the potentially acidic O–H bonds of the coordinated H_2O.

Evidently, any structure requiring a Mo=Mo double bond to reach saturation in the $Cp_2Mo_2(CO)_4$ fragment is unstable and these species act as extremely strong Lewis acids.[21] Corroboration for this view is found in the structure of $M_2(\mu\text{-CAr}_2)$ (Ar = *p*-tolyl),[27] in which it is found that one of the *p*-tolyl groups is coordinated to a Mo atom, so that the Ar_2C: group behaves as a four-electron donor, thus reducing the Mo–Mo bond order from 3 to 1 (eq 6). In fact, in most adducts of 1 the added ligand(s) donates a total of four electrons so as to displace both π bonds, leaving a Mo–Mo singly bonded dimer.[2a]



(6)

M ≡ $Mo(CO_2)Cp$; Ar ≡ *p*-tolyl

Hydrogenation of $M_2(\mu\text{-CR=CHR})$(TFA) Adducts. The HTFA complex 3 becomes fluxional at room temperature in the presence of excess HTFA. As Figure 3 shows, the Cp resonances of the complex collapse to broad humps but are restored to sharp singlets when the excess acid is removed. We interpret these results to mean that the coordinated trifluoroacetate is protonated, giving a species resembling the more ionic BF_4^- salt which is known to be fluxional.[5] The process shown in eq 7 would give rise

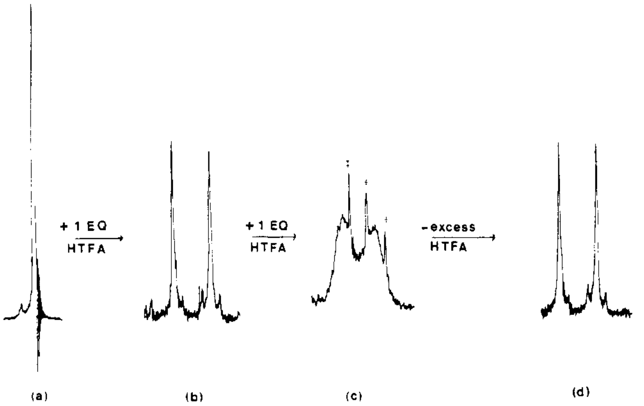
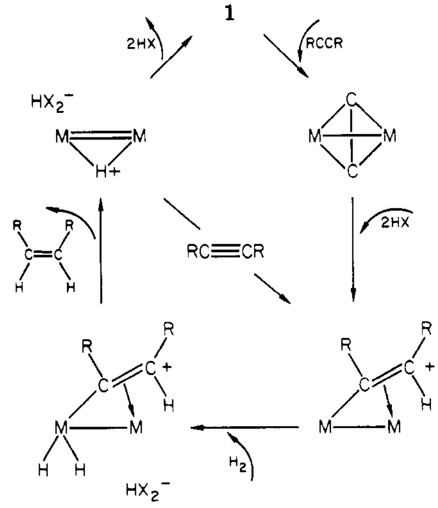


Figure 3. ^{1}H NMR reaction of $Cp_2Mo_2(CO)_4(PhCCH)$ with excess CF_3COOH: (a) $M_2(PhCCH)$ in $CDCl_3$; (b) $M_2(PhCCH)$ plus 1 equiv of HTFA; (c) $M_2(Ph(H)CCH)(TFA)$ plus a second equivalent of HTFA; (d) resulting spectrum after the excess HTFA has been pumped off. Double dagger (‡) and dagger (†) correspond to $Cp_2Mo_2(CO)_6$ and a secondary product (the nature of this product is unknown) produced by a side reaction during protonation, respectively. Only the Cp resonances are shown.

Scheme I



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[25] Ardon, M.; Bino, A.; Cotton, F. A.; Dori, Z.; Kaftory, M.; Kolthammer, B. W. S.; Kapon, M.; Reisner, G. *Inorg. Chem.* **1981**, *20*, 4083.

[26] Bino, A.; Cotton, F. A.; Dori, Z.; Kolthammer, B. W. S. *J. Am. Chem. Soc.* **1981**, *103*, 5779.

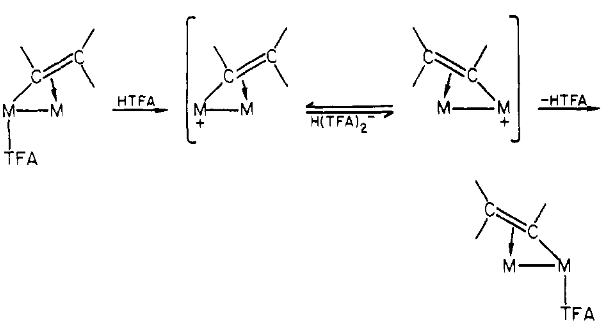
[27] Messerle, L.; Curtis, M. D. *J. Am. Chem. Soc.* **1980**, *101*, 7789.

Table V. Hydrogenation of Acetylenes Catalyzed by Complexes 3

reactn	ratio of $Cp_2Mo_2(CO)_4$ to acetylene: $Cp_2Mo_2(CO)_4$	acetylene	no. of equiv of CF_3COOH	conditns[a]	yield of alkene,[c] %	alkyne remaining, %
			1-hexyne			
A	0	1	1.2	18 h/45 °C/100 atm	4	80
B	1	1	1	18 h/45 °C/30 psig	26	
C	1	1	1.2	15 h/45 °C/30 psig	56	
D	1	1	1.1	3 days/25 °C/30 psig	100	
E	1	10	1.6	18 h/45 °C/30 psig	1.3	19.5
F	1	10	1.1	18 h/45 °C/100 atm	4	4.5
G	1	10	1.2	18 h/45 °C/270 atm	10	0
H	1	10	CH_3COOH	18 h/45 °C/30 psig	3	14
I	1	10	CH_3COOH	12 h/45 °C[b]	0	36
J	1	1	CH_3COOH	18 h/45 °C/30 psig	41	
			3-hexyne			
K	1	10	1.6	18 h/45 °C/30 psig		68

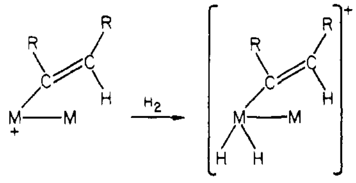
[a] Reactions in toluene, except where CH_3COOH is both solvent and proton source. [b] No H_2 atmosphere. [c] Taken from the GC chromatagrams.

to the simultaneous collapse of both Cp signals, as observed.



(7)

The intermediate (shown in brackets in eq 7) is coordinatively unsaturated and one metal, marked (+), has only a 16-electron count. We reasoned that such an electron-deficient intermediate might oxidatively add H_2 to give the complex 4 (eq 8). If intermediate 4 were to



(8)

4

eliminate an alkene, RHC=CHR, the catalytic cycle shown in Scheme I could be established. Since it has already been shown that 1 does not react with alkenes,[2a,8] the catalysis should be specific for the reduction of alkynes to *cis*-alkenes. In fact, Slater and Muetterties have demonstrated that the alkyne adducts $M_2(\mu\text{-RCCR})$ catalyze the hydrogenation of alkynes to *cis*-alkenes at 150–170 °C.[28] These authors postulate a CO-dissociation step in the catalytic cycle to open up a vacant coordination site for uptake of H_2. In the cycle shown in Scheme I, the vacant site is opened up by the proton-assisted dissociation of an anionic group and should be operative at much lower temperatures.

The results from the attempted hydrogenation reactions are shown in Table V. When the $Cp_2Mo_2(CO)_4$ to 1-hexyne ratio was 1:1, then yields of between 26% and 100% of 1-hexene may be obtained depending on the specific reaction conditions (reactions B, C, D). Longer reaction times with a small excess of CF_3COOH (~1.1–1.2×) give higher yields of 1-hexene than in reactions in which no excess CF_3COOH is present. However, as can be seen from reaction E when a 10-fold excess of 1-hexyne was used, only traces of 1-hexene were obtained and a limited amount of starting acetylene was recovered.

Obviously a mechanism is operative which funnels off the 1-hexyne. The most probable mechanism is that of polymerization of the alkyne, with the alkyne competing with the H_2 for the vacant coordination site. The formation of a polymer was confirmed by the isolation of a yellow oil which gave ^1H NMR and mass spectral data consistent with the oil being a polyacetylene. The mass spectrum of the neat oil derived from 1-hexyne shows peaks up to *m/e* 935 (the mass limit of the instrument used is 1000), corresponding to $P - 1^+$ of Bu(H)C=C(H) $(BuC{=}CH)_n$-$(BuC{=}CH_2)$, $n = 10$. The NMR of this oil shows a broad hump for the olefinic protons at δ 6.4 and a complex set of broad peaks in the aliphatic region, δ 1–3. The intensities of these peaks are in the ratio 1:7.8, corresponding to an average degree of polymerization, $\overline{DP} = 12.4$, assuming the above structure for the polymer. It was felt that if a competitive mechanism were operative, then increased H_2 concentration may make the formation of the alkene a more favorable pathway. But as can be seen from reactions F and G the 50–100-fold increase in H_2 pressure does not lead to a similar increase in formation of 1-hexene. In going from 2 to 270 atm only a 10-fold increase in production of 1-hexene was observed, but the proportion of lower oligomers in the polyacetylene fraction increased. Thus, an increase in H_2 pressure increases the rate of the chain termination step in the polymerization. Some tributylbenzene was detected also (GC/MS, *m/e* 246) under these conditions.

Interestingly, similar results were observed in neat CH_3COOH, where the CH_3COOH is both the proton source and solvent, even though no protonated species are observed spectroscopically when $M_2(\mu\text{-RCCR})$ is dissolved in CH_3COOH. Apparently a limited amount of protonation does take place, but the similarity of the results from the two reaction systems (CF_3COOH/toluene and CH_3COOH) suggest that the protonation of the acetylene is not the rate-determining step in either the polymerization or hydrogenation.

If an internal acetylene, 3-hexyne, rather than the terminal acetylene, 1-hexyne, is used, then no 3-hexene formation is observed and 68% of the 3-hexyne is recovered. This result suggests that steric factors are controlling the polymerization step. Also 3-hexyne competes with H_2 for

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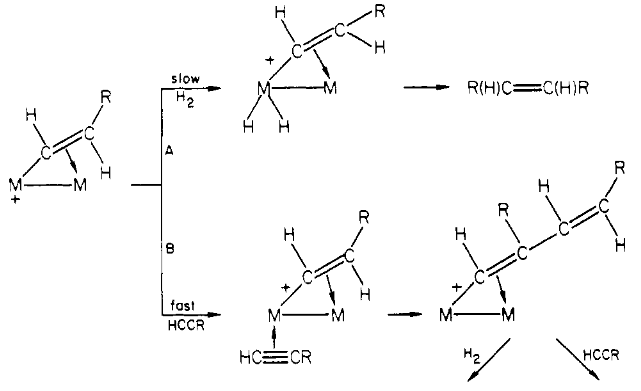
[28] Slater, S.; Muetterties, E. *Inorg. Chem.* **1980**, *19*, 3337.

the vacant coordination site but because of steric interactions cannot then continue to react by a polymerization pathway.

A reaction scheme consistent with these observations is given in eq 9. The two possible reaction pathways involve



(9)

addition of H_2 followed by elimination of an alkene (path A) or addition of an alkyne followed by insertion of the alkyne (path B) with path B being faster than path A for terminal acetylenes.

Attempts to isolate the molybdenum-containing species after completion of the reactions were unsuccessful. Only in the case of reaction B, when stoichiometric amounts of $Cp_2Mo_2(CO)_4$, 1-hexyne, and CF_3COOH were used, could the molybdenum-containing compounds be identified. These were unreacted $M_2(HCC(H)Bu)^+TFA^-$ and $Cp_2Mo_2(CO)_4$. In all other reactions the molybdenum-containing products could not be identified although one possibility is that any $Cp_2Mo_2(CO)_4$ formed will react with CF_3COOH to form $CpMo(CO)_3H$ and a species derived from the acetate group, since it has been shown independently that CF_3COOH will react slowly with $Cp_2Mo_2(CO)_4$ to give $CpMo(CO)_3H$ and dark solids.

Summary

Acetylene adducts of 1 undergo rapid protonation by strong acids to yield μ-vinyl complexes. The protonation has been shown (by NMR and X-ray methods) to proceed in an anti-Markovnikov manner to yield the (*E*)-alkene. The conjugate base of the protonating acid (Cl^-, TFA^-) coordinates to one of the molybdenums of the dimetallic center to produce Mo–Mo single-bonded species.

The coordinated base (in the TFA^- case) is labile in the presence of excess acid. The adducts $M_2(\mu\text{-}RCC(H)R)TFA$ are hydrogenated stoichiometrically to alkenes under very mild conditions (30 psig H_2, 30 °C). However the possible use of these protonated species as catalysts for the hydrogenation of acetylenes to olefins is negated by the competition of excess alkyne for the coordination site which, in the case of terminal alkynes, leads to alkyne polymerization.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE79-07748-02) and the AMAX Foundation for support of this work. We also thank Dr. L. Messerle for assistance in obtaining 360-MHz NMR spectra and Dr. W. Gustavson for assistance in obtaining GC/MS data.

Registry No. $Cp_2Mo_2(CO)_4(EtC{\equiv}CH)$, 86365-86-8; $Cp_2Mo_2(CO)_4(BuC{\equiv}CH)$, 74482-82-9; $Cp_2Mo_2(CO)_4(Me_3SnC{\equiv}CPh)$, 86365-87-9; $Cp_2Mo_2(CO)_4(Ph_3SnC{\equiv}CSnPh_3)$, 86365-88-0; $Cp_2Mo_2(CO)_4(\mu\text{-}CH{=}CHPh)(OH_2)BF_4$, 86372-80-7; $Cp_2Mo_2(CO)_4(PhC{\equiv}CH)$, 56200-30-7; Mo, 7439-98-7; $Cp_2Mo_2(CO)_4(HC{\equiv}CH)$, 86391-51-7; $Cp_2Mo_2(CO)_4(\mu\text{-}CH{=}CH_2)(TFA)$, 86372-81-8; $Cp_2Mo_2(CO)_4(Cl)(\mu\text{-}CH{=}CH_2)$, 86372-82-9; $Cp_2Mo_2(CO)_4(\mu\text{-}CH{=}CHCH_2CH_3)(TFA)$, 86372-83-0; $[Cp_2Mo_2(CO)_4(Ph(H)CCH]^+[H(TFA)_2]^-$, 86372-85-2; 1-hexyne, 693-02-7; 3-hexyne, 928-49-4.

Supplementary Material Available: Tables VI and VII, listings of the thermal parameters and observed and calculated structure factors (F_o, F_c), respectively (7 pages). Ordering information is given on any current masthead page.