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Two-Dimensional ^{1}H-NMR EXSY Study of the Fluxional Behavior of the Novel Carbenium Ion Complex [FvMo$_2$(CO)$_4$(μ,η^2,η^3-MeC$\equiv$CCH$_2$)][BF$_4$] (Fv = Fulvalene): Syntheses, Structures, and Reactivity

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Summary: The title compound [FvMo$_2$(CO)$_4$(μ,η^2,η^3-MeC$\equiv$CCH$_2$)][BF$_4$] (3) was obtained quantitatively by protonation of [FvMo$_2$(CO)$_4$(μ,η^2,η^2-MeC$\equiv$CCH$_2$OMe)] (2) in ether solution. In solution 3 was found to be fluxional. The mechanism of exchange was elucidated by 2-D ^{1}H NMR EXSY (exchange spectroscopy), and the rate constants were determined with $k_{int} = 35 \pm 4$ s^{-1}, $\Delta G^{\ddagger}_{70\,°C} = 17.7 \pm 0.4$ kcal/mol and $k_{rot} = 5 \pm 0.5$ s^{-1}, $\Delta G^{\ddagger}_{70\,°C} = 19.1 \pm 0.4$ kcal/mol (int = interconversion; rot = rotation). Consistent with this fluxional behavior the molecular structure of 3, ascertained by X-ray analysis, showed a dynamic disorder in the solid state for the bridged hydrocarbyl ligand as well as for the carbonyl groups. [FvMo$_2$(CO)$_4$(μ,η^2,η^3-MeC$\equiv$CCH$_2$)][BF$_4$] (3) crystallizes in the monoclinic space group $P2_1/n$ with Z = 4 and cell dimensions a = 8.546 (3), b = 26.4441 (14), and c = 8.619 (2) Å and β = 105.73 (2)°. The reactivity of this carbenium ion complex with respect to various nucleophiles is reported, including the X-ray molecular structure of the phosphonium derivative [FvMo$_2$(CO)$_4$(μ,η^2,η^2-MeC$\equiv$CCH$_2$PPh$_3$][BF$_4$] (6) obtained from phosphine addition to 3. Compound 6 crystallizes in the monoclinic space group $P2_1/c$ with Z = 8 and cell dimensions a = 13.243 (4), b = 13.243 (4), and c = 38.461 (4) Å and β = 93.92 (2)°; the structure was refined to R and R_w values of 4.3 and 5.0%, respectively, using 6606 reflections.

Introduction. The catalytic transformation of hydrocarbons on metallic surfaces has often been related to the mode of coordination of these organic substrates to the metal centers at the molecular level.[1] As a homogeneous model for understanding bonding and reactivity of unsaturated hydrocarbons on metal surfaces, we chose to prepare the novel carbenium ion complex [FvMo$_2$(CO)$_4$(μ,η^2,η^3-MeC$\equiv$CCH$_2$)][BF$_4$] (3) in which a hydrocarbyl ligand is bonded to a dimetal frame work. Although the analogous cyclopentadienyl derivative has been prepared and extensively studied by several groups,[2] no related investigations on a dimolybdenum carbenium ion stabilized by the Fv ligand have been reported. In this communication, we describe a high-yield synthesis for 3 as well as its fluxional behavior in solution and its relevance to the X-ray molecular structure, which also shows a dynamic disorder in the solid state consistent with the solution behavior. The reactivity of 3 toward various nucleophiles will be discussed and compared to that of the cyclopentadienyl analogue.

Results and Discussion. Treatment of FvMo$_2$(CO)$_6$ (1) with an excess of MeC$\equiv$CCH$_2$OMe in refluxing toluene gave [FvMo$_2$(CO)$_4$(μ,η^2,η^2-MeC$\equiv$CCH$_2$OMe)] (2) as the only product in 80% yield (based on reacted FvMo$_2$(CO)$_6$). Alkyne adducts of FvMo$_2$(CO)$_6$ (1) have been prepared previously on a small scale by photochemical substitution reactions where both the monosubstituted alkyne FvMo$_2$(CO)$_4$(alkyne) and the disubstituted alkyne FvMo$_2$(CO)$_3$(alkyne)$_2$ adducts were obtained.[3] Refluxing 1 in toluene in the absence of propargyl ether led to decomposition, giving rise to an intractable material. This result implies that unlike Cp$_2$Mo$_2$(CO)$_6$ the hexacarbonyl FvMo$_2$(CO)$_6$ reacts with MeC$\equiv$CCH$_2$OMe by following a selective substitution mode of the CO ligands and without formation of the tetracarbonyl "FvMo$_2$(CO)$_4$" intermediate (see Scheme I, path b). This is no doubt related to the rigidity of the Fv ligand, which fails to bend sufficiently to allow the formation of a short Mo$\equiv$Mo triple bond, as observed for the analogous Cp$_2$Mo$_2$(CO)$_4$ system.[4]

Protonation of [FvMo$_2$(CO)$_4$(μ,η^2,η^2-MeC$\equiv$CCH$_2$OMe)] (2) by 1 equiv of aqueous HBF$_4$ (48%) in ether solution afforded a yellow orange precipitate, identified spectroscopically as [FvMo$_2$(CO)$_4$(μ,η^2,η^3-MeC$\equiv$CCH$_2$)][BF$_4$] (3). The IR absorption for the terminal carbonyls of 3 are shifted to higher wavenumbers by 50 cm^{-1}, as compared to the values of ν(CO) for 2. This can be attributed to an increase in the electrophilic character at the Mo centers due to the direct interaction between the Mo and the methylene CH$_2^+$ moiety at the α-position (vide infra), thus leading to a decrease in the d$\pi \rightarrow$ pπ^* CO back-donation as observed.

The structure of 3 was determined also by X-ray crystallography (Figure 1). Two similar molecular structures are shown due to the fact that the CO ligands and C1–C2 were found to be in a disordered fashion; nevertheless, the model refined satisfactorily. The observed disorder could be attributed to a dynamic behavior rather than a static one (vide infra).[5] The structures show that the alkyne (C2–C3) and/or (C′2–C3) bridges the two metal centers in a quasi symmetric fashion. Further, a direct Mo–CH$_2^+$ interaction is observed in both (a) *d*(Mo1–C1)

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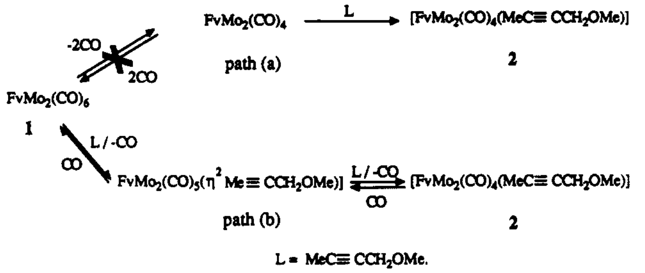
Scheme I



= 2.44 Å and (b) d(Mo2–C′1) = 2.55 Å. These distances are slightly longer than that reported for the analogous $[Cp_2Mo_2(CO)_4(\mu,\eta^2,\eta^3\text{-}HC\equiv CCH_2)][BF_4]$, where d (Mo–C) = 2.43 Å.[2a] The Mo–Mo distance in **3** is shorter than that of the cyclopentadienyl derivative by 0.09 Å. We also note the absence of semibridging carbonyls in contrast to that reported for $[Cp_2Mo_2(CO)_4(\mu,\eta^2,\eta^3\text{-}HC\equiv CCH_2)][BF_4]$.

Compound **3** was found to be fluxional in solution. The ^{1}H-NMR recorded at room temperature is consistent with the existence of a chiral molecule in the solid state and shows the presence of eight multiplet signals for the fulvalene protons and two singlets attributed to Ha and Hb at δ = 3.23 ppm and δ = 4.85 ppm, respectively. In contrast, the 2-D ^{1}H EXSY spectrum recorded at room temperature showed that the fulvalene protons and Ha and Hb are slowly exchanging (Figure 2). These results coincide with the molecular structure of **3** in the solid state, where CH_2^+ of the coordinated hydrocarbyl ligand is occupying two positions either on Mo1 or Mo2; thus, the X-ray structure is a stop-action picture of the observed dynamic process in solution. Similar behavior was reported for the $[Cp_2Mo_2(CO)_4(\mu\text{-}CN)][Et_4N]$ compound.[6]

The variable-temperature one-dimensional ^{1}H-NMR of **3** was recorded in CD_3CN. At elevated temperature the spectra show that the fulvalene signals broaden and coalesce into four peaks with $\Delta G^{\ddagger}_{92\,°C} = 18.2 \pm 0.4$ kcal/mol; at the coalescence in particular between the pair of resonances H2/H7, the Ha and Hb signals broaden but do not alter their positions. Furthermore, the Me group of the bridging alkyne appears as a sharp singlet even at 365 K. The variable-temperature ^{13}C spectra also show a similar behavior in which the four CO signals observed at room temperature coalesce into two peaks. These NMR studies show that a fluxional process is occurring fast at elevated temperature in which the fulvalene protons, the CO ligands, and Ha, Hb are equilibrating with respect to the NMR time scale.

An intramolecular dynamic process consistent with the above observation would be that **3a** interconverts into **3b** or **3b′** via intermediate **3c** or **3c′**, in which the "$MeC\equiv CCH_2$" group is perpendicular to the Mo–Mo bond (see Scheme II). During this process $-CH_2^+-$ swings from Mo1 to Mo2 concomitant with a rotation around the C1–C2 bond and a slight movement of the carbonyl ligands (vide infra).

Fluxional behavior in solution of $[Cp_2Mo_2(CO)_4(\mu,\eta^2,\eta^3\text{-}RC\equiv CCR_2)][BF_4]$ carbenium ions have recently been studied extensively.[2,7] Curtis et al. have proposed a mechanism in which $-CH_2^+-$ migration is occurring in $[Cp_2Mo_2(CO)_4(\mu,\eta^2,\eta^3\text{-}HC\equiv CCH_2)][BF_4]$ but without rotation around the C1–C2 bond. Further investigations were carried out on analogous molecules but possessing two chiral centers such as $[Cp_2Mo_2(CO)_4(\mu,\eta^2,\eta^3\text{-}HC\equiv CCR^1R^2)][BF_4]$, where R^1 = Me, R^2 = H, or $HC\equiv CCR^1R^2$ = "mestranyl cation". The authors describe the presence of three mechanisms for the observed fluxional behavior: (a) simultaneous rotation/antrafacial migration (enantiomerization); (b) simultaneous rotation/suprafacial migration (diastereomerization); (c) simple carbon–carbon bond rotation about the CH_2^+–Mo bond (diastereomerization).[8] Due to the higher symmetry order in $[FvMo_2(CO)_4(\mu,\eta^2,\eta^3\text{-}MeC\equiv CCH_2)][BF_4]$ compared to that of the cyclopentadienyl analogue (absence of semibridging carbonyl, cis arrangement of cyclopentadienyls), we found that a simple migration of α-methylene group $-CH_2^+-$ from Mo1 to Mo2 and vice versa would equilibrate only the fulvalene protons and the CO ligands but not Ha and Hb. The EXSY experiments recorded at room temperature and at T = 343 K, however, show indeed that an exchange is occurring between Ha and Hb. This would imply that a rotation around C1–C2 bond is also taking place. We were able to determine the rate constants of these processes where $k_{int}/k_{rot} = 7$ and $\Delta G^{\ddagger}_{int} = 17.7 \pm 0.4$ kcal/mol and $\Delta G^{\ddagger}_{rot} = 19.1 \pm 0.4$ kcal/mol at T = 343 K[9] (int = interconversion; rot = rotation). This would imply that statistically CH_2^+ would migrate seven times between the two metal centers before allowing a rotation of 180° around C1–C2 bond (Scheme II). It is noteworthy that the rotation process may occur via intermediate **3c** or **3b**; nevertheless, in the first option a lower energy barrier is required.

It has been postulated that $\Delta G^{\ddagger}$ for the fluxional process in $[Cp_2Mo_2(CO)_4(\mu,\eta^2,\eta^3\text{-}RC\equiv CCR_2)][BF_4]$ systems increases from tertiary to primary carbenium cation and that such a trend is due to the stronger and shorter Mo–CH_2^+ bond in the primary ion, d(Mo–CH_2^+) = 2.43 and 2.74 Å, respectively.[7] It is of interest to compare $\Delta G^{\ddagger}$ of our primary cation $[FvMo_2(CO)_4(\mu,\eta^2,\eta^3\text{-}MeC\equiv CCH_2)][BF_4]$ (**3**) to that of the cyclopentadienyl analogue. Although the d(Mo–C_{av}) distance in **3** is 2.50 Å and longer than that of $[Cp_2Mo_2(CO)_4(\mu,\eta^2,\eta^3\text{-}HC\equiv CCH_2)][BF_4]$ (d(Mo–C) = 2.43 Å), the free energy ($\Delta G^{\ddagger}_{92\,°C} = 18.2 \pm 0.4$ kcal/mol) in **3** is higher than that reported for the analogous cyclopentadienyl derivative ($\Delta G^{\ddagger}_{65\,°C}$ = 16.9 kcal/mol).[2a] This result differs from the previous observation cited for the cyclopentadienyl carbenium ions. We feel that the high $\Delta G^{\ddagger}$ in our system may be related to the bending[12]

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(9) The rate constants $k_{int} = 35 \pm 4$ s^{-1} and $k_{rot} = 5 \pm 0.5$ s^{-1} were determined from three EXSY spectra recorded at T = 343 K but using different mixing times (t_m = 2, 5, and 10 ms) and assuming first approximation for short mixing time such that $I_{ij} \sim k_{ji}t_mM_j^0$, where I_{ij} is the integration intensity of the cross peak of the 2D-NMR contour plot, k_{ji} is the pseudo-first-order rate constant for exchange from site j to site i, t_m is the mixing time, and M_j^0 is the initial equilibrium z magnetization in site j.[10] The slopes of the straight lines obtained by plotting the intensity of the cross peak (I_{ij}) of the fulvalene protons and Ha and Hb as a function of the mixing time yielded respectively k_{int} and k_{rot}. The spectra were recorded twice under same t_m and same T as well as same t_m but different T. The ratio of k_{int}/k_{rot} is temperature dependent; for instance at T = 323 K, k_{int}/k_{rot} = 3. When the sealed tube was left for longer period of time, the older samples (containing some precipitate presumably due to decomposition) showed the rotation process to be slower relative to the interconversion one; after 2 weeks, at T = 343 K k_{int}/k_{rot} = 8.

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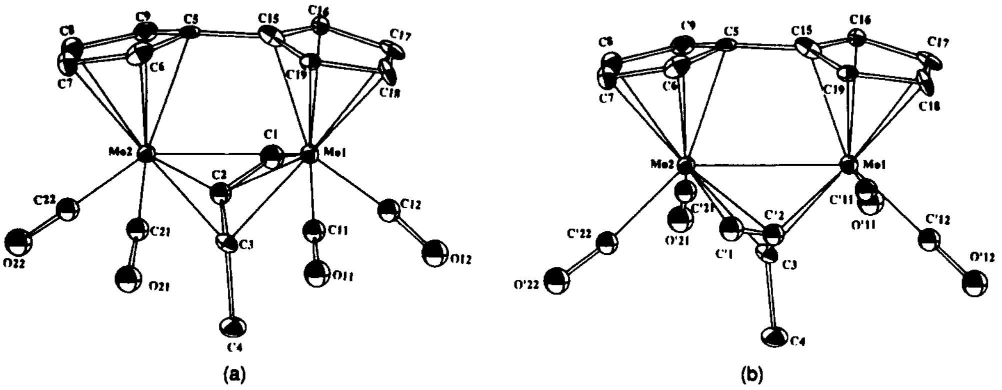


Figure 1. Molecular structure of the cationic part of molecule **3** (hydrogen atoms omitted). Two limited structures a and b are drawn showing different orientations for the carbenium (–CH$_2^+$) of the bridging hydrocarbyl ligand either bound to Mo1 or Mo2, their occupancy factor being one-half. The disorder is observed for the carbonyl groups and C1, C′1, C2, and C′2, while Mo1 and Mo2 were identically placed in both forms a and b. Selected bond lengths (Å) and angles (deg) are given for (a) and (b), respectively: Mo1–Mo2 = 2.926 (2), Mo1–C1 = 2.44 (5), Mo1–C2 = 2.20 (5), Mo1–C3 = 2.21 (2), Mo1–C15 = 2.26 (3), Mo1–C16 = 2.33 (2), Mo1–C17 = 2.33 (2), Mo1–C18 = 2.34 (2), Mo1–C19 = 2.30 (2), Mo1–C11 = 2.03 (5), Mo1–C12 = 1.91 (5), Mo2–C2 = 2.00 (4), Mo2–C3 = 2.20 (2), Mo2–C5 = 2.32 (2), Mo2–C6 = 2.25 (2), Mo2–C7 = 2.30 (3), Mo2–C8 = 2.33 (3), Mo2–C9 = 2.33 (3), Mo2–C21 = 2.03 (5), Mo2–C22 = 1.92 (6), C2–C3 = 1.38, C1–C2–Mo1 = 80.6 (29), C3–C2–C1 = 131.5 (xx), C4–C3–C2 = 121.9 (30), C3–C2–Mo1 = 72.0 (19), C4–C3–Mo1 = 134.5 (22), C3–C2–Mo2 = 79.1 (18), C4–C3–Mo2 = 142.4 (22), Mo2–C′1 = 2.55 (5), Mo2–C′2 = 2.19 (5), Mo2–C′21 = 1.96 (5), Mo2–C′22 = 1.98 (5), Mo1–C′2 = 2.02 (4), Mo1–C′11 = 2.04 (5), Mo1–C′12 = 1.98 (6), C′2–C3 = 1.38 (2), C′1–C′2–Mo1 = 85.7 (28), C3–C′2–C′1 = 140.6 (38), C4–C3–C′2 = 119.5 (30), C3–C′2–Mo1 = 78.5 (18), C3–C′2–Mo2 = 72.1 (19).

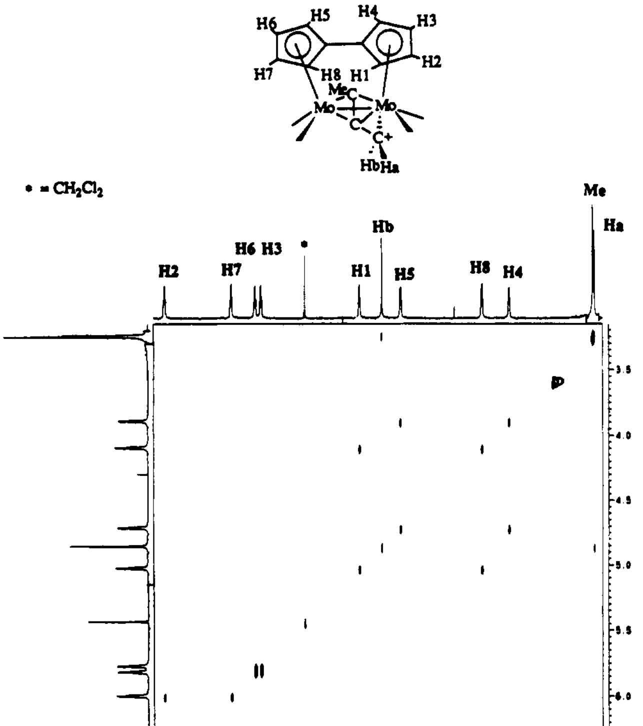
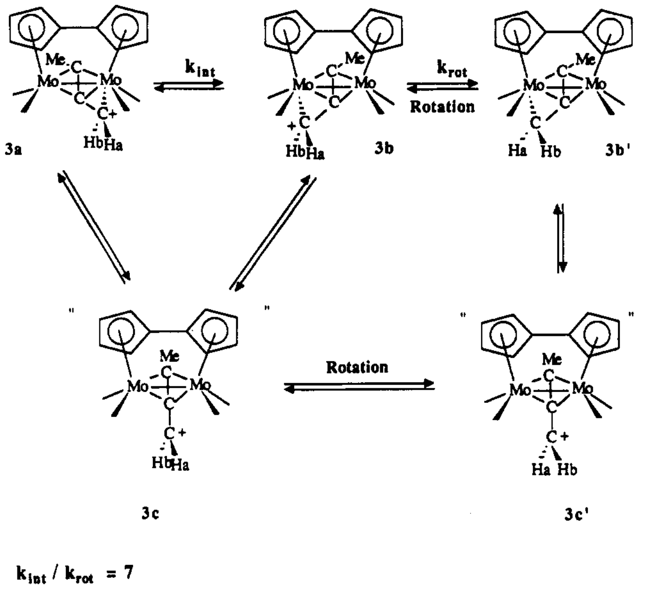


Figure 2. Excerpt from 500-MHz EXSY spectrum of [FvMo$_2$(CO)$_4$(μ,η^2,η^3-MeC≡CCH$_2$)][BF$_4$] (**3**) at 298 K showing exchange-related hydrogen nuclei of the fulvalene ligand as well as Ha and Hb. Only negative cross peaks due to exchange are being shown.

of the Fv ligand during the intramolecular process, which needs high energy to take place. The rigidity of the fulvalene ligand as well as the electronic delocalization

Scheme II



between its two connected Cp groups remains the main reason for the difference in stability and chemical reactivity between the two systems.

As expected, compound **3** reacts with various nucleophiles with attack taking place on the electrophilic methylene group –CH$_2^+$– at the α-position of the dimolybdenum cluster (see Scheme III), a result similar to that observed for the analogous cyclopentadienyl derivative.[2]

The novel compounds **4**–**6** were completely identified by spectroscopic methods; in addition the structure of **6** was confirmed by X-ray analysis. The ORTEP view of the cation with the labeling scheme, as well as selected interatomic distances and angles, is presented in Figure 3. The cation part of **6** exists in two independent molecular structures due to the difference in orientation of the phenyl groups on the phosphorus atom. The Mo–Mo distance is 2.86 (2) Å, slightly shorter than that observed in **3**. We note the absence of any direct stabilizing interaction

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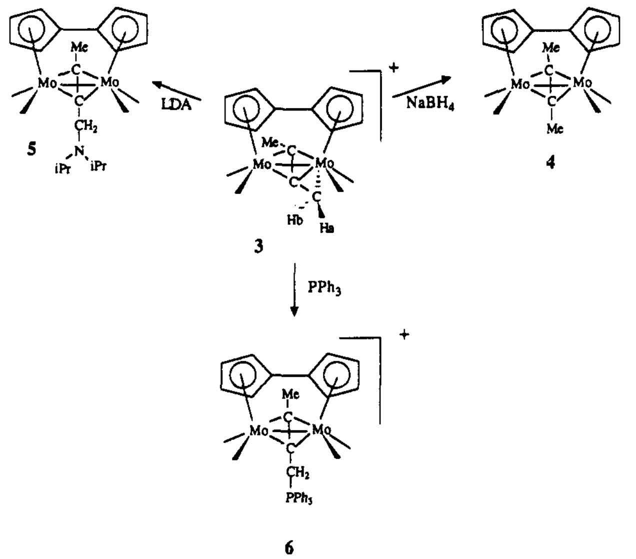
(12) Rigidity in fulvalene systems is often related to the dihedral angle θ between the two planes of the connected Cp (for instance θ = 155° in **3**). During the dynamic process the two connected Cp's may acquire a planar geometry; i.e., θ = 180° in the **3c** transition state. This requires high energy to take place.

Scheme III



between the molybdenum centers and the α-methylene group in contrast to that observed for the carbenium ion **3** (vide supra).

It appears from the above studies that the rigidity of the fulvalene ligand does not alter the reactivity of **3** toward nucleophilic addition. Furthermore, it is worth emphasizing that reduction of **3** to give **4** by NaBH$_4$ was achieved completely within 30 min, while the analogous reaction performed on the cyclopentadienyl analogue was reported to take 18 h.[2b]

Currently we are investigating the reactivity of higher oligomers involving three metal centers such as Mo$_2$W and/or Ru$_2$W. The results of these studies will be reported in a forthcoming publication.

Experimental Section. General Procedures. All manipulations were carried out under argon atmosphere by using Schlenk techniques. Solvents were purified and dried prior to use by conventional distillation techniques. All reagents obtained from commercial sources were used without further purification. Melting points are uncorrected. ^{1}H and ^{13}C NMR were recorded on Bruker AM 250, AM 500, and AMX 400 MHz instruments. ^{1}H-NMR chemical shifts are reported in parts per million referenced to residual solvent proton resonance. All 2D-NMR spectra were recorded in the phase-sensitive mode. At T = 233 K no dynamic process is occurring and the observed cross peaks are due to ^{1}H–^{1}H relaxation (NOESY experiment). At room temperature cross peaks due to ^{1}H–^{1}H relaxation (NOESY) and exchange cross peaks were observed (EXSY = exchange spectroscopy). At T = 343 K only cross peaks due to dynamic process were observed (EXSY) because short mixing times were used; those related to ^{1}H–^{1}H relaxation (NOESY) are insignificant.[10] Infrared spectra were obtained on a Perkin-Elmer 681 instrument, and all absorptions are expressed in wavenumbers (cm^{-1}). Elemental analyses were performed by the Microanalytical Laboratory of the University of California, Berkeley, CA. FvMo$_2$(CO)$_6$ was prepared according to ref 3, and MeC$\equiv$CCH$_2$OMe was prepared from 2-butyne-1-ol following Brandsma's procedure[11] (bp = 86–91 °C; yield 59%).

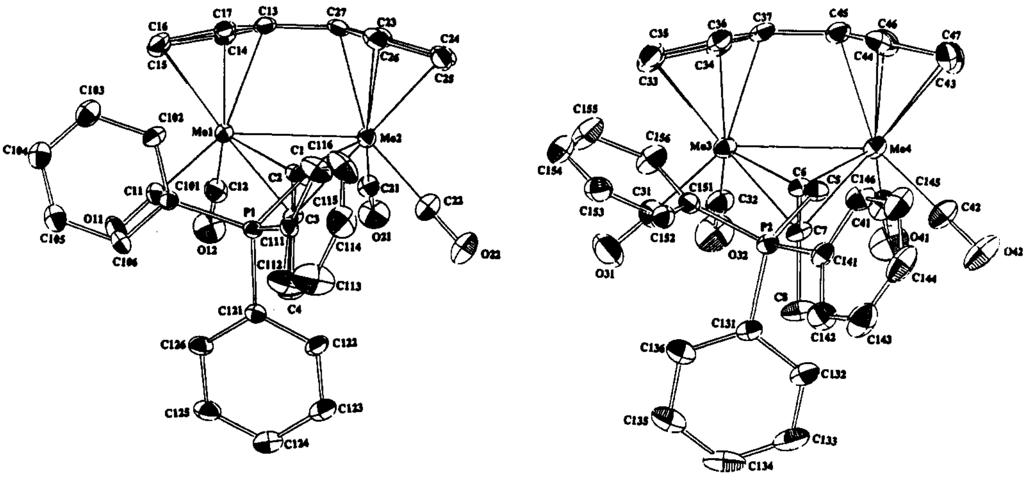
Synthesis of [FvMo$_2$(CO)$_4$(μ,η^2,η^2-MeC$\equiv$CCH$_2$OMe)] (2). A 10-fold molar excess of MeC$\equiv$CCH$_2$OMe was added to a suspension of FvMo$_2$(CO)$_6$ (**1**) (550 mg, 1.12 mmol) in 50 mL of toluene, and the mixture was refluxed for 12 h. The reaction was cooled to room temperature, the suspension filtered, and the precipitate washed with THF. The precipitate was identified as starting material (280 mg recovered). The combined filtrate was concentrated under vacuum, and **2** was purifed by column chromatography over silica gel using acetone/hexanes (1/9) as eluant. The first orange band was collected, and solvent was removed under vacuum yielding orange crystals (236 mg), 80% yield based on reacted FvMo$_2$(CO)$_6$. Data for **2**: orange-red crystals, mp 128–129 °C dec; ^{1}H-NMR (250 MHz, CD$_3$CN; T = 243 K) δ 5.68 (ddd, 2H), 5.32 (ddd, 2H), 4.72 (dt, 2H), 4.02 (dt, 2H), 3.76 (s, 2H, –CH$_2$–), 3.18 (s, 3H, –OMe), 3.07 (s, 3H, –Me); IR (CH$_2$Cl$_2$) ν(CO) = 1992 (s), 1920 (s) cm^{-1}. Anal. Calcd for C$_{19}$H$_{16}$O$_5$Mo$_2$: C, 44.18; H, 3.10. Found: C, 44.37; H, 3.24.

Synthesis of [FvMo$_2$(CO)$_4$(μ,η^2,η^3-MeC$\equiv$CCH$_2$)][BF$_4$] (3). A 150-mg amount (0.29 mmol) of **2** was dissolved in 20 mL of degassed diethyl ether. To the resulting orange-red solution was added 50 μL of aqueous HBF$_4$ (48%). The reaction was stirred for 15 min, and then the orange precipitate was collected by filtration. The precipitate was washed twice with 15 mL of diethyl ether and then dried under vacuum (150 mg, 90%). Data for **3**: orange crystals, mp 184 °C dec. Assignment of the fulvalene protons was done without ambiguity by 2D ^{1}H-NMR (NOESY) (500 MHz, CD$_3$CN) at T = 233 K: δ 6.49 (m, 1 H), 5.99 (m, 1 H), 5.81 (m, 1H), 5.77 (m, 1H) 5.01 (m, 1H), 4.85 (s, 1H, –Hb), 4.71 (m, 1H), 4.09 (m, 1H), 3.88 (m, 1H), 3.25 (s, 3H, –Me) 3.23 (s, H, –Ha). ^{13}C{^{1}H}-NMR (62 MHz, CD$_3$CN): δ 224.30, 222.60, 216.43, 212.90, 120.24, 113.84, 98.0, 94.31, 93.79, 92.95, 90.54, 89.34, 86.47, 82.59, 69.57, 20.51. IR (CH$_2$Cl$_2$): ν(CO) = 2049 (s), 2022 (vs), 1995 (vs), 1950 (s) cm^{-1}. Anal. Calcd for C$_{18}$H$_{13}$O$_4$Mo$_2$BF$_4$: C, 37.76; H, 2.27. Found: C, 38.25; H, 2.41.

Synthesis of [FvMo$_2$(CO)$_4$(μ,η^2,η^2-MeC$\equiv$CMe)] (4). A 40-mg amount (0.07 mmol) of **3** was introduced into a Schlenk tube containing 10 mL of THF, and then 7 mg (0.18 mmol) of NaBH$_4$ was added to the orange suspension. The mixture was stirred for 30 min, during which time the solution became a clear purple. The solvent was removed, and product was separated by column chromatography with silica gel using acetone/hexane (1/3) to give quantitatively **4** as microcrystalline substance. Data for **4**: deep red crystals, mp 140 °C dec; ^{1}H-NMR (250 MHz, CD$_3$CN; T = 243 K) δ 5.75 (m, 2H), 5.35 (m, 2H), 4.25 (m, 2H), 4.05 (m, 2H), 3.15 (s, 3H, –Me(a)), 1.70 (s, 3H, –Me(b)). Anal. Calcd for C$_{18}$H$_{14}$O$_4$Mo$_2$: C, 44.44; H, 2.88. Found: C, 44.35; H, 3.29.

Synthesis of [FvMo$_2$(CO)$_4$(μ,η^2,η^2-MeC$\equiv$CCH$_2$N(iPr)$_2$] (5). A 0.28-mL volume of 0.25 M solution of LiN(iPr)$_2$ (prepared in situ) was added to a suspension of 40 mg (0.07 mmol) of **3** in 10 mL of THF, causing a rapid color change to purple, and the solution became clear. After 1 h the solvent was removed under vacuum and compound **5** was separated by column chromatography with silica gel using acetone/hexane to yield an oily product (20 mg, 50%). Data for **5**: brown oil; ^{1}H-NMR (500 MHz, CD$_3$COCD$_3$) δ 5.75 (m, 2H), 5.40 (m, 2H), 4.60 (m, 2H), 4.18 (m, 2H), 3.20 (s, 2H, –CH$_2$–), 3.10 (s, 3H, –Me), 2.95 (sep, 2H, –*CH*[CH$_3$]$_2$), 0.90 (d, 12 H, [*CH$_3$*]$_2$CH–).

Synthesis of [FvMo$_2$(CO)$_4$(μ,η^2,η^2-MeC$\equiv$CCH$_2$PPh$_3$][BF$_4$] (6). A 30-mg amount (0.11 mmol) of PPh$_3$ in 2 mL of CH$_2$Cl$_2$ was added to a solution of 50 mg (0.09 mmol) of **3** in 10 mL of CH$_2$Cl$_2$, resulting in a sudden color change from orange to red. The reaction was stirred for 30 min,



(a) (b)

Figure 3. ORTEP plot of the cationic part of molecule 6. The two independent molecules are shown as well as the different orientation of the phenyl groups on the phosphorus atom. Selected bond lengths (Å) and angles (deg): Mo1–Mo2 = 2.865 (1), Mo3–Mo4 = 2.865 (1), Mo1–C2 = 2.183 (8), Mo3–C6 = 2.178 (8), Mo1–C3 = 2.222 (8), Mo3–C7 = 2.189 (8), Mo1–C13 = 2.302 (8), Mo1–C14 = 2.354 (8), Mo1–C15 = 2.352 (8), Mo1–C16 = 2.332 (9), Mo1–C17 = 2.291 (8), Mo3–C33 = 2.309 (9), Mo3–C34 = 2.294 (9), Mo3–C35 = 2.350 (1), Mo3–C36 = 2.336 (9), Mo3–C37 = 2.302 (8), Mo2–C2 = 2.197 (2), Mo4–C6 = 2.187 (8), Mo2–C3 = 2.215 (8), Mo4–C7 = 2.212 (9), Mo2–C23 = 2.295 (9), Mo2–C24 = 2.322 (9), Mo2–C25 = 2.351 (9), Mo2–C26 = 2.341 (8), Mo2–C27 = 2.291 (8), Mo4–C43 = 2.33 (1), Mo4–C44 = 2.27 (1), Mo4–C45 = 2.283 (9), Mo4–C46 = 2.341 (9), Mo4–C47 = 2.37 (1), C2–C3 = 1.36 (1), C6–C7 = 1.33 (1), C1–C2–C3 = 136.1 (7), C5–C6–C7 = 136.3 (7), Mo1–C2–C3 = 73.8 (5), Mo3–C6–C7 = 72.7 (5), Mo1–C3–C4 = 133.8 (6), Mo3–C7–C8 = 133.6 (7), C2–C1–P1 = 122.0 (5), C6–C5–P2 = 123.9 (6), Mo2–C2–C3 = 72.8 (5), Mo4–C6–C7 = 73.5 (4), Mo2–C3–C4 = 132.9 (6), Mo4–C7–C8 = 133.3 (7).

and then ether was added to give a red precipitate. The solid was filtered out, washed twice by 15 mL of diethyl ether, and recrystallized from CH_2Cl_2/diethyl ether (60 mg, 83%). Data for 6: red crystals, mp 180 °C dec; ^{1}H-NMR (500 MHz, CD_2Cl_2) δ 7.74–7.62 (m, 15H), 5.66 (m, 2H), 5.18 (m, 2H), 4.76 (m, 2H), 4.17 (d, 2H, ^2J(P–H) = 12 Hz, $-CH_2-$), 3.73 (m, 2H), 2.43 (s, 3H, –Me); $^{13}C\{^1H\}$ (125 MHz, CD_3CN) δ 222.35, 214.44, 135.26, 134.11, 130.64, 120.03, 119.03, 93.80, 88.34, 82.96, 77.51, (36.2 d, ^2J(P–C) = 41 Hz), 20.71. IR (CH_2Cl_2) ν(CO) = 1999 (s), 1960 (s), 1931 (s) cm^{-1}. Anal. Calcd for $C_{35}H_{28}O_4PMo_2BF_4$: C, 51.79; H, 3.35. Found: C, 52.05; H, 3.30.

X-ray Structural Determination of $[FvMo_2(CO)_4(\mu,\eta^2,\eta^3\text{-MeC}{\equiv}CCH_2)][BF_4]$ (3) and of $[FvMo_2(CO)_4(\mu,\eta^2,\eta^2\text{-MeC}{\equiv}CCH_2PPh_3][BF_4]$ (6). Intensity data were collected at room temperature on a Nonius CAD4 diffractometer using Mo Kα radiation. The accurate cell dimensions and orientation matrices were obtained from least-squares refinements of the setting angles of 25 well-defined reflections. No decays in the intensities of two standard reflections were observed during the courses of data collections. Compound 3 crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ and cell dimensions $a = 8.546$ (3), $b = 26.4441$ (14), and $c = 8.619$ (2) Å and $\beta = 105.73$ (2)°. Compound 6 crystallizes in the monoclinic space group $P2_1/c$ with $Z = 8$ and cell dimensions $a = 13.243$ (4), $b = 13.243$ (4), and $c = 38.461$ (4) Å and $\beta = 93.92$ (2)°. The usual corrections for Lorentz and polarization effects were applied. An empirical absorption correction (DIFABS)[13] was applied. Complete crystal data and crystal data parameters are included in the supplementary material. Computations were performed by using CRYSTAL[14] adapted to a Microvax-II computer. Scattering factors and corrections for anomalous dispersion were from ref 15. The structures were resolved by direct methods (SHELXS).[16] For compound 3 the asymmetric unit consists of one disordered cationic molecule as shown in Figure 2 and one BF_4^- anion. The structure was refined by least squares with anisotropic thermal parameters for all non-disordered atoms, the disordered carbonyl ligand as well as C(1), C(1′), C(2), and C(2′) atoms being left isotropic and in half-occupation. The hydrogen atoms linked to nondisordered carbon atoms were introduced as fixed contributors in theoretical positions (with u(iso) = 1.2u(eq) of the related carbon atom) and their coordinates recalculated after each refinement cycle. The structure was refined to $R = 0.059$ and $R_w = 0.062$ with use of 1332 reflections for 237 least-squares parameters. For compound 6 the asymmetric unit consists of two independent cationic molecules as shown on Figure 3 and two BF_4^- anions. The structure was refined by least squares with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were introduced in the same way as for compound 3. The structure was refined to $R = 0.043$ and $R_w = 0.050$ with the use of 6606 reflections for 867 least-squares parameters.

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Supplementary Material Available: Tables of crystallographic parameters, positional and thermal parameters, and complete bond distances and angles of 3 and 6 (15 pages). Ordering information is given on any current masthead page.

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