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Reactions of a Dicarbenium Fulvalenyl Complex with Aromatic Nucleophiles and Synthesis of (μ-Alkyne)(fulvalenyl)tetracarbonyldimolybdenum Compounds: A Structure−Reactivity Relationship

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The compound [FvMo$_2$(CO)$_4$(μ-η^3:η^3-CH$_2$C≡CCH$_2$)][BF$_4$]$_2$ (**3**) reacts with weak nucleophiles to give the related carbenium complexes [FvMo$_2$(CO)$_4$(μ-η^2:η^3-CH$_2$C≡CCH$_2$Nu)][BF$_4$] (Nu = −C$_6$H$_4$OH, −C$_6$H$_4$OMe), where attack occurs exclusively on one carbenium center (−CH$_2^+$). Subsequent treatment by NaBH$_4$ reduces the second carbenium center (−CH$_2^+$) to yield the disubstituted alkyne fulvalenyl adducts. The difference in reactivity between **3** and the analogous dicarbenium Cp system [Cp$_2$Mo$_2$(CO)$_4$(μ-η^3:η^3-CH$_2$C≡CCH$_2$)][BF$_4$]$_2$ is attributed to the fulvalene effect.

Introduction

Propargylium ions coordinated to the dicobalt hexacarbonyl unit, Co$_2$(CO)$_6$, have been shown to be useful synthetic units in organic synthesis.[1] Nicholas and coworkers have elegantly demonstrated the large-scale synthesis of 2-(1-methyl-2-propynyl)cyclohexanone from the cobalt−carbenium ion complex [Co$_2$(CO)$_6${μ-η^2:η^3-HC≡CCH(Me)}][BF$_4$] and 1-(trimethylsiloxy)cyclohexene.[2] Lack of stability of these cobalt−carbenium ions precluded their X-ray structural determination. This difficulty was overcome by examining the chemistry of the analogous molybdenum species [Cp$_2$Mo$_2$(CO)$_4$(μ-η^2:η^3-R^{1}C≡CCR^{2}R^3)][BF$_4$],[3] which are stable and can be easily isolated; in addition, their X-ray structures can be determined. Our major goal was to study the influence of a bridging ligand (fulvalene) on the structure and reactivity of such molybdenum carbenium ions. It has been established that two directly bonded metal centers can be bridged by linked η^5-cyclopentadienyl rings, as in fulvalene.[4] Such an arrangement also maintains electronic interactions between the metals even when the direct bond is temporarily broken.[5]

We have prepared the first fulvalene carbenium ion complexes of the type [FvMo$_2$(CO)$_4$(μ-η^2:η^3-R^{1}C≡CCR^{2}R^3)]-[BF$_4$].[6] These fulvalene complexes are admirably suited for the study of fluxional behavior of the metal−hydrocarbyl interaction, while in the solid state they exhibit a different coordination mode in comparison to the analogous Cp systems.

In this paper we report on the reactivity of the dicarbenium fulvalenyl complex [FvMo$_2$(CO)$_4$(μ-η^3,η^3-CH$_2$C≡CCH$_2$)][BF$_4$]$_2$[7] (**3**) with weak aromatic nucleophiles (H−Nu = H−C$_6$H$_4$OH, H−C$_6$H$_4$OMe) to yield carbenium ions of the general formula [FvMo$_2$(CO)$_4$(μ-η^2:η^3-CH$_2$C≡CCH$_2$Nu][BF$_4$]. Subsequent treatment of the corresponding carbenium ions with NaBH$_4$ affords the neutral alkyne adduct [FvMo$_2$(CO)$_4$(μ-η^2:η^2-CH$_3$-C≡CCH$_2$Nu]. The influence of the fulvalene ligand on the reactivity of this dicarbenium fulvalenyl complex **3** is presented and shows that the nucleophile approaches the carbenium center in **3** in a regioselective manner, suggesting a structure−reactivity relationship. The

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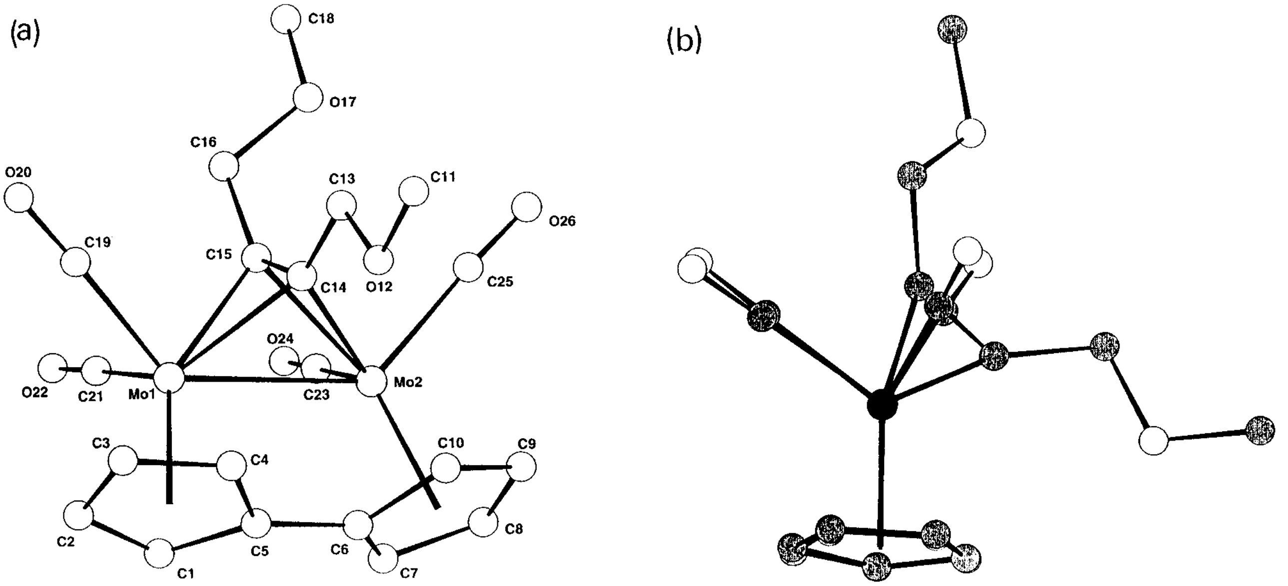

Figure 1. X-ray crystal structure of **2**: (a) Cameron view showing the atom-numbering system; (b) sidewise view showing the coordination mode of the alkyne to the dimolybdenum fulvalene cluster. Selected bond distances (Å) and angles (deg): Mo1−Mo2 = 2.892(3), Mo1−C1= 2.275(3), Mo1−C2 = 2.324(3), Mo1−C3 = 2.350(3), Mo1−C4 = 2.349(3), Mo1−C5 = 2.302(3), Mo2−C6 = 2.302(3), Mo2−C7 = 2.295(3), Mo2−C8 = 2.334(3), Mo2−C9 = 2.359(3), Mo2−C10 = 2.355(3), Mo1−C14 = 2.168(3), Mo2−C14 = 2.163(3), Mo1−C15 = 2.191(3), Mo2−C15 = 2.203(3), C14−C15 = 1.364(4), C13−C14 = 1.478(4), C15−C16 = 1.482(4), C1−C2 = 1.418(5), C2−C3 = 1.404(5), C3−C4 = 1.407(4), C4−C5 = 1.430(4), C5−C6 = 1.447(4), C−C7 = 1.431(4), C7−C8 = 1.409(4), C8−C9 = 1.410(4), C9−C10 = 1.420(4); C13−C14−C15 = 131.6(3), C14−C15−C16 = 137.1(3), Mo1−C14−Mo2 = 83.8(1), Mo1−C15−Mo2 = 82.3(1), C1−C5−C6−C7 = 1.8.

potential use of this dicarbenium complex in organic synthesis is briefly discussed.

Results and Discussion

Synthesis, NMR, Fluxional Behavior, and Structural Aspects. We reported recently the synthesis of the tetrahedral dimolybdenum alkyne cluster [FvMo$_2$(CO)$_4$(μ-η^2:η^2-MeOCH$_2$C≡CCH$_2$OMe)] (**2**) from FvMo$_2$(CO)$_6$ (**1**) and MeOCH$_2$C≡CCH$_2$OMe in refluxing toluene.[7] The ^{1}H NMR of **2** recorded at $T = 223$ K exhibits the expected four multiplets for the fulvalene protons in the area 2.7−5.0 ppm, but unexpectedly the symmetric alkyne displayed four singlets, suggesting unsymmetrical coordination to the bimetallic Mo- - -Mo cluster core. Moreover, the methylene and methoxy units of one side of the alkyne unit appeared downfield at 5.6 and 3.4 ppm while the other side showed two singlets upfield at 4.2 and 2.8 ppm. These results prompted us to establish the X-ray structure of **2**. Crystals of **2** were obtained from an Et$_2$O/hexane mixture. Cameron views of **2** are shown in Figure 1. Figure 1a shows that the alkyne unit MeOCH$_2$C≡CCH$_2$OMe is coordinated to the dimolybdenum cluster in a distorted manner, so that the two CH$_2$OMe moieties are not in the same plane. Further, one CH$_2$OMe moiety is perpendicular to the plane of the coordinated fulvalene unit while the other CH$_2$OMe group is almost parallel (Figure 1b). The Mo−Mo bond distance in **2** is 2.89 Å, typical for a single metal−metal bond in these alkyne−fulvalene complexes[6] but slightly shorter than those reported for alkyne−Cp systems, which lie in the range 2.90−3.1 Å.[8] Complex **2** shows the absence of a semibridging carbonyl, as is the case in the analogous alkyne−dimolybdenum adducts of the Cp systems [Cp$_2$Mo$_2$(CO)$_4$(μ-η^2:η^2-RC≡CR)].[8] We also note that the bending angle θ between the planes of the two connected cyclopentadienyls of the coordinated fulvalene ligand in **2** is 24.5°.

The solid-state structure of **2** is in accord with the ^{1}H NMR data recorded at low temperature in toluene-d_8. We interpret the differences in chemical shifts $\Delta\delta = 1.5$ ppm for "CH$_2$" and to a lesser extent $\Delta\delta = 0.6$ ppm for "OMe" of the coordinated alkyne to result from the effect of the magnetic anisotropy of the fulvalene rings on the CH$_2$OMe group which lies in the equatorial position (parallel to the Fv plane) (Figure 1b). A simple precedent for our case is the chemical shift of the methyl group in toluene.[9] Evidently the other CH$_2$OMe group in the axial position (perpendicular to the Fv plane) is far away and is not affected by this anisotropy effect and, therefore, appears upfield.

When the sample tube of **2** was warmed to room temperature, the four multiplets of the fulvalene signals and the methylene and the methoxy groups of the alkyne unit became broad and eventually the two methoxy signals coalesced into one broad signal at $T = 333$ K. Due to experimental condition limitations, we were unable to see a complete coalescence of the fulvalene signals until 353 K. The activation free energy for this process $\Delta G^{\ddagger}_{333} = 15.7 \pm 0.5$ kcal/mol. This value is close to that reported by Vollhardt and co-workers for the fulvalene−alkyne adduct [FvMo$_2$(CO)$_4$(μ-η^2:η^2-PhC≡CPh)] with $\Delta G^{\ddagger} = 15 \pm 0.5$ kcal/mol. The authors have reported on its fluxional behavior.[4a] We feel that an alternative mechanism of exchange, but

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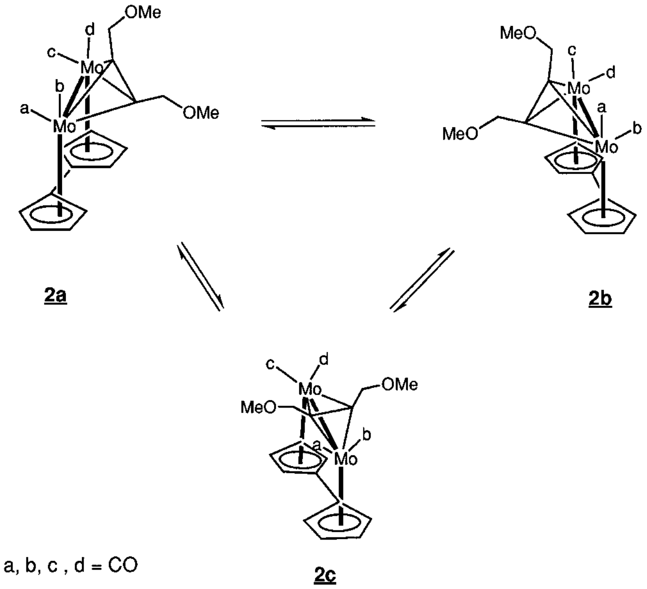
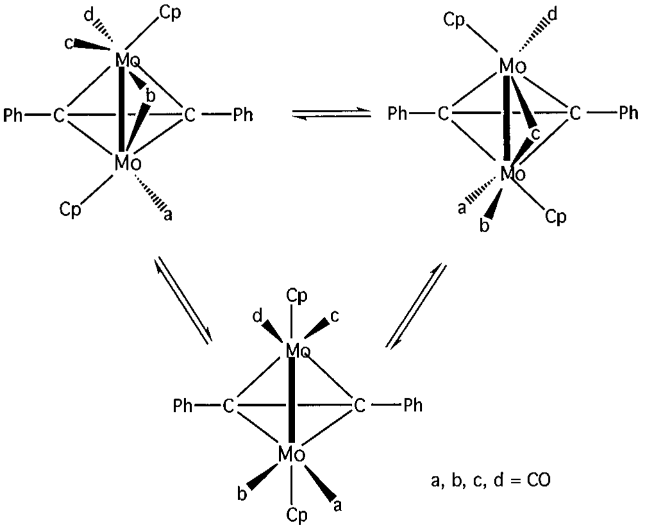
Scheme 1. Proposed Mechanism for the Exchange Process in the Fv System [FvMo$_2$(CO)$_4$(η^2:η^2-MeOCH$_2$C≡CCH$_2$OMe)] (2)

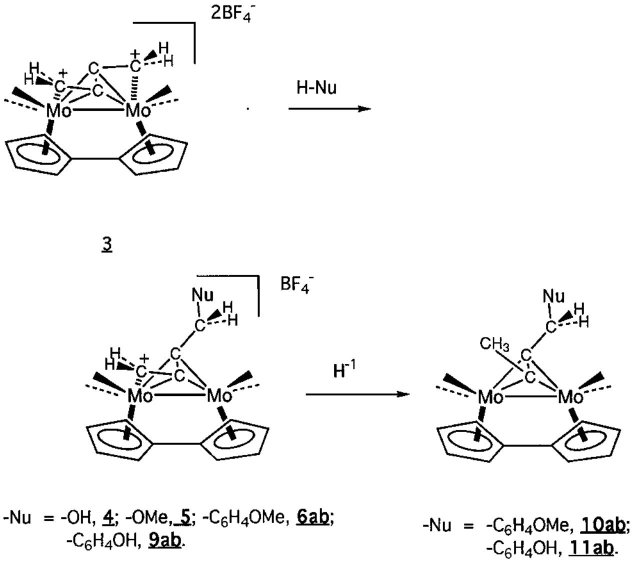


Scheme 2. Mechanisms of Exchange for the Cp System [Cp$_2$Mo$_2$(CO)$_4$(η^2:η^2-PhC≡CPh)]



a complementary one, in accord with the VT-NMR data would be that the two enantiomers **2a** and **2b** (Scheme 1) would exchange via the symmetrical species **2c**. In this exchange process the alkyne unit would swing from one side of the fulvalene to the other in a pendulum-like motion while the FvMo$_2$ unit was kept stationary. Cotton and co-workers[8] have elegantly demonstrated by variable-temperature NMR studies that the complex [Cp$_2$Mo$_2$(CO)$_4$(μ-η^2:η^2-PhC≡CPh)] is fluxional in solution. Two processes ($\Delta G^{\ddagger}$ = 8 and 10 kcal/mol) are observed: (i) first the carbonyl ligands switch between terminal and semibridging positions and (ii) then a higher energy process occurs where the metal vertex CpMo(CO)$_2$ rotates about the metal−metal bond. These two processes are depicted in Scheme 2. In summary, the fluxional behavior of the fulvalenyl alkyne system is substantially different from that of the Cp−alkyne one. The second question to answer is whether this particular coordination of the fulvalene ligand imposes a different reactivity as compared to the Cp system.

Scheme 3. Stepwise Reductions of the Carbenium Centers (−CH$_2^+$) of Complex 3



-Nu = -OH, 4; -OMe, 5; -C$_6$H$_4$OMe, 6ab; -C$_6$H$_4$OH, 9ab.

-Nu = -C$_6$H$_4$OMe, 10ab; -C$_6$H$_4$OH, 11ab.

Reactivity of the Dicarbenium Complex 3 with Nucleophiles and Structural Analysis. We have found that the action of HBF$_4$·Et$_2$O on [FvMo$_2$(CO)$_4$(μ-η^2:η^2-MeOCH$_2$C≡CCH$_2$OMe)] (**2**) in CH$_2$Cl$_2$ affords the dicationic complex [FvMo$_2$(CO)$_4$(μ-η^3:η^3-CH$_2$C≡CCH$_2$)][BF$_4$]$_2$ (**3**). A preliminary study on the reactivity of complex **2** with nucleophiles suggested that this species reacts with weak nucleophiles such as H$_2$O, MeOH, and PhOMe to give the corresponding carbenium complexes [FvMo$_2$(CO)$_4$(μ-η^2:η^3-CH$_2$C≡CCH$_2$R)][BF$_4$] (R = −OH (**4**), −OMe (**5**), −C$_6$H$_4$OMe (**6a**,**b**)), where attack occurs exclusively on one carbenium center (−CH$_2^+$) (Scheme 2), while with strong nucleophiles the disubstituted alkyne adducts were obtained.[7] This behavior is completely different from that displayed by analogous dicarbenium complexes coordinated to Co$_2$(CO)$_6$ and/or Cp$_2$Mo$_2$(CO)$_4$ moieties. In the latter systems nucleophilic attacks occur simultaneously on both carbenium centers.[10]

We extended our investigations to functionalization of phenols. To our knowledge only the Nicholas reagent [Co$_2$(CO)$_6$(μ-η^2:η^3-R^{1}C≡CCR^{2}R^3][BF$_4$][11] is known to react with carbon nucleophiles of activated arenes; those of the molybdenum analogs are inactive. Treatment of **3** with an excess of phenol afforded two complexes, [FvMo$_2$(CO)$_4$(μ-η^2:η^3-CH$_2$C≡CCH$_2$C$_6$H$_4$OH)][BF$_4$] (**9a**,**b**), in which the arene was alkylated at the ortho or para position in an almost 1:1 ratio (Scheme 3).

The ^{1}H NMR data of the starting material **2**, the dicarbenium complex **3**, and the resulting carbenium complexes **4**, **5**, **6a**,**b**, and **9a**,**b** provide us with valuable information about the structure of these fulvalene complexes. (a) The −CH$_2^+$ center in **3** that reacts with the weak nucleophile exhibits an AB system, because it lies in the α-position relative to the chiral cluster (see

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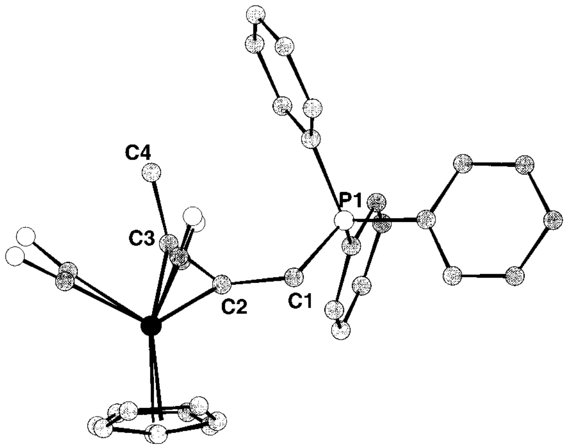
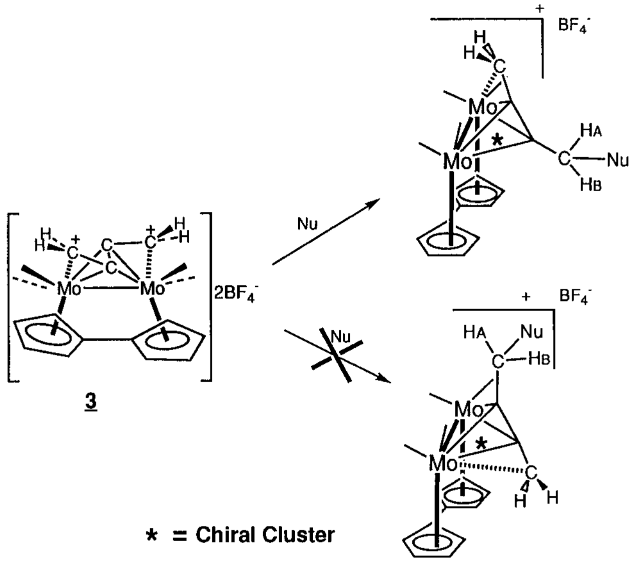


Figure 2. Sidewise view of the structure of $[FvMo_2(CO)_4(\eta^2{:}\eta^2\text{-}CH_3C{\equiv}CCH_2PPh_3)]^+$.

Scheme 4



Scheme 4). (b) The second important observation is that only the $-CH_2$ group whose signal is downfield and appears in the area 4.75 −5.3 ppm reacts with the nucleophile. If this were not so, every reaction of **3** with a weak nucleophile should have produced two isomers, i.e. (i) with the incoming nucleophile in the axial position and (ii) with the incoming nucleophile in the equatorial position.

In order to explain the NMR data and to better understand the reactivity of a fulvalene dicarbenium ion complex such as **3**, we examined the X-ray molecular structures of the phosphonium complex $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^2\text{-}CH_3C{\equiv}CCH_2PPh_3)][BF_4]$ as a model system and of the starting material **2**.

Unlike **2**, the other species possesses two different groups on the coordinated alkyne unit ($R_s = -CH_3$, $R_b = -CH_2PPh_3$). The side view of the phosphonium complex is shown in Figure 2. The X-ray structure of each complex (Figures 1b and 2) shows that (a) the alkyne unit coordinates the dimolybdenum unit in an unsymmetrical, sidewise manner and (b) the smaller group ($-CH_3$) is always axial (i.e. perpendicular) to the Mo−Mo metal while the larger one ($-CH_2PPh_3$) occupies the equatorial position and is closer to the $\eta^5{:}\eta^5$-fulvalene moiety. Combining the NMR and the structural data on these fulvalene complexes, we therefore conclude that the attack of a weak nucleophile on **3** should occur regioselectively at the less sterically hindered $-CH_2^+$ carbenium center (Scheme 4). Evidently, it is the one that lies in the equatorial position parallel to the fulvalene unit.

Reactivity of the Carbenium Ions $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}CH_2C{\equiv}CCH_2R)][BF_4]$ (6a,b and 9a,b) with $NaBH_4$. The fulvalenylmolybdenum carbenium ions $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}CH_2C{\equiv}CCH_2C_6H_4OR)][BF_4]$ (R = −Me (**6a**,**b**), H (**9a**,**b**)) react smoothly with $NaBH_4$ in CH_2Cl_2 to give quantitatively the corresponding fulvalenyl−alkyne adducts $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^2\text{-}CH_3C{\equiv}CCH_2C_6H_4OR)]$ (Scheme 3). Similar reactivity was reported for the Cp−carbenium ions. Thus, Kergoat and co-workers reported the reduction of the Cp−carbenium complex $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}HC{\equiv}CCH(Me)][BF_4]$ by $NaBH_4$ to give the corresponding alkyne complex $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^2\text{-}HC{\equiv}CCH_2Me)]$.

It should be borne in mind that the novelty of our work lies in the fact that the dicarbenium complex **3** reacts first with a weak nucleophile (phenol, anisole) on one carbenium center (CH_2^+); subsequent treatment with a hydride source reduces the second carbenium center, yielding the methyl unit (Scheme 3). Evidently, in the Cp system only reactions of one carbenium center with $NaBH_4$ or other hydride sources were reported.[12]

Overall, we have succeeded in preparing disubstituted alkynes coordinated to a dimolybdenum fulvalene framework using the dicarbenium complex **3** as the reactive species. However, the true potential of our approach for functionalization of alkynes will not be realized until a high-yield synthesis on the gram scale is achieved. Further detachment of the alkyne from the molybdenum centers has not so far been successful under mild conditions.

In conclusion, the fulvalene ligand coordinates to the dimolybdenum carbonyl cluster and forces the alkyne unit to occupy a specific coordination mode. Consequently, the related dicarbenium fulvalene complex **3** shows a completely different reactivity relative to that reported for the analogous Cp system.

Experimental Section

General Procedures. All manipulations were carried out under an argon atmosphere using Schlenk techniques. Solvents were purified and dried prior to use by conventional distillation techniques. All reagents were distilled prior to use; pyridine and MeOH were distilled twice, to avoid side reactions with H_2O. ^1H and ^{13}C NMR were recorded on a Bruker AM 250 MHz instrument. ^1H NMR chemical shifts are reported in δ (ppm) and referenced to residual solvent peaks: CHD_2CN, 1.93; $(CHD_2)_2CO$, 2.05; $CHDCl_2$, 5.27. Infrared spectra were obtained on an FT Bruker IR45 spectrometer from samples prepared either as KBr disks or in CH_2Cl_2 solutions. All absorptions are expressed in wavenumbers (cm^{-1}). The syntheses of **2**, **3**, **4**, **5**, and **6a**,**b** were performed according to published procedures.[7]

Synthesis of $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}CH_2C{\equiv}CCH_2C_6H_4OH)][BF_4]$ (9a,b). A 70 mg (0.74 mmol) amount of phenol was introduced into a Schlenk tube containing $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^2\text{-}MeOCH_2C{\equiv}CCH_2OMe)]$ (**2**; 60 mg, 0.105 mmol) in CH_2Cl_2 (10 mL). To this mixture was added an excess of $HBF_4{\cdot}Et_2O$ (200 μL), and the reaction mixture was stirred for 4 h. The supernatant phase was filtered and concentrated under vacuum.

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Addition of Et_2O (20 mL) gave an orange-pink precipitate. The precipitate was washed several times with Et_2O, dried under vacuum, and identified as an inseparable mixture of the two isomers **9a**,**b**. The residue of this reaction was extracted by acetone (10 mL) and filtered through a column packed with Celite. The solvent was concentrated under vacuum followed by addition of Et_2O (20 mL) to yield a second batch of **9a**,**b**, which was separated and dried under vacuum. Overall yield: 60 mg, 83%.

9a: ^{1}H NMR (250 MHz, acetone-d_6) δ 3.41 (s, 1H, $-CH_2$), 4.37 (m, 1H, fulvalene), 4.51 (m, 1H), 4.56 (s, 1H, $-CH_2$), 4.77 (dd, AB system, 2H, $-CH_2Ph$), 5.15 (m, 1H, fulvalene), 5.41 (m, 1H, fulvalene), 6.07 (m, 2H, fulvalene), 6.21 (m, 1H, fulvalene), 6.71 (m, 1H, fulvalene), 6.90 (d, 2H, $-C_6H_4-$, aromatic protons), 7.10 (d, 2H, $-C_6H_4-$, aromatic protons), 8.90 (s, 1H, $-OH$).

9b: ^{1}H NMR (250 MHz, acetone-d_6) δ 3.52 (s, 1H, $-CH_2$), 4.37 (m, 1H, fulvalene), 4.51 (m, 1H, fulvalene), 4.83 (s, 1H, $-CH_2$), 4.95 (dd, AB system, 2H, $-CH_2Ph$), 5.15 (m, 1H, fulvalene), 5.45 (m, 1H, fulvalene), 6.08 (m, 2H, fulvalene), 6.21 (m, 1H, fulvalene), 6.75 (m, 1H, fulvalene), 7.14 (m, 2H, $-C_6H_4-$, aromatic protons), 7.28 (d, 2H, $-C_6H_4-$, aromatic protons).

9a,b: $^{13}C\{^1H\}$ NMR (62.87 MHz, acetone-d_6) δ, 69.30, 69.5 ($-CH_2$), 70.5, 70.7 ($-CH_2C_6H_4OH$), 82.30, 82.50, 85.90, 86.0, 86.30, 86.70, 90.68, 91.1, 93.50, 94.10, 94.3, 98.30, 98.84 (fulvalene C$-$H), 89.50, 93.17, 93.50 (fulvalene C_{ipso}'s), 114.1, 114.3 (s, $-C\equiv$), 116.80 (s, two superimposed signals, $\equiv C-$), 123.4, 126.5, 127.30, 130.2, 132.0, 132.2, 133.5 (aromatic C$-$H), 156.2 (two superimposed signals, aromatic C$-$OH), 212.50, 212.9, 215.70, 215.89, 222.20, 224.25, 224.60 (Mo carbonyls); IR (KBr disk) v(CO) 2043 (s), 2009 (s), 1979 (b) cm^{-1}. Anal. Calcd for **9a**,**b**, $C_{24}H_{17}BF_4Mo_2O_5$: C, 43.30; H, 2.70. Found: C, 43.18; H, 2.73.

Synthesis of [$FvMo_2(CO)_4(\mu$-η^2:η^2-$CH_3C\equiv CCH_2C_6H_4$-OMe)] (10a,b). An excess of $NaBH_4$ (100 mg, 2.63 mmol) was added to a solution of [$FvMo_2(CO)_4(\eta^2$:η^3-$CH_2C\equiv CCH_2C_6H_4$-OMe)][BF_4] (**6a**,**b**; 50 mg, 0.075 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 12 h, the solvent was removed, and the residue was eluted on silica gel plates (20 cm × 20 cm) using CH_2Cl_2/hexane (1:1) as eluent. The first band was separated and identified as the ortho isomer **10a**. A second orange band afforded the para isomer **10b**. Overall yield: 45 mg, 90% (para/ortho = 55/45).

10a: ^{1}H NMR (250 MHz, CD_2Cl_2) δ 3.10 (s, 3H, $-CH_3$), 3.15-(m, 2H, fulvalene), 3.25 (s, 2H, $-CH_2-$), 3.70 (s, 3H, $-OMe$), 3.81 (m, 2H, fulvalene), 5.71 (m, 2H, fulvalene), 5.52 (m, 2H, fulvalene), 6.7$-$7.15 (m, 4H, aromatic protons); $^{13}C\{^1H\}$ NMR (62.87 MHz, CD_2Cl_2) δ 19.54 ($-CH_3$), 37.37 ($-CH_2$), 54.36 ($-OMe$), 75.83, 81.72, 83.97, 91.55 (fulvalene C$-$H), 92.31 (C_{ipso} fulvalene), 109.54, 119.55, 127.18, 131.16, 156.6 (aromatic C's), 221.56, 232.34 (Mo carbonyls); IR (KBr disk) ν(CO) 1971 (s), 1942 (s), 1898 (vs) cm^{-1}.

10b: ^{1}H NMR (250 MHz, CD_2Cl_2) δ 3.10 (s, 2H, $-CH_2-$), 3.25 (s, 3H, $-CH_3$), 3.72 (s, 3H, $-OMe$), 3.75 (m, 4H, fulvalene, almost obscured), 5.70 (m, 2H, fulvalene), 5.55 (m, 2H, fulvalene), 6.70 (dd, AB system, 4H, aromatic protons); $^{13}C\{^1H\}$ NMR (62.87 MHz, CD_2Cl_2) δ 19.66 ($-CH_3$), 43.04 ($-CH_2$), 54.89 ($-OMe$), 75.91, 81.73, 83.50, 91.57 (fulvalene C$-$H), 92.22 (C_{ipso} fulvalene), 113.00, 130.09, 133.50, 158.3 (aromatic C's), 221.60, 232.4 (Mo carbonyls); IR (KBr disk) ν(CO) 1991 (s), 1948 (s), 1902 (vs), 1859 (vw) cm^{-1}.

Anal. Calcd for **10a**,**b**, $C_{25}H_{20}Mo_2O_5$: C, 50.60; H, 3.37. Found: C, 49.83; H, 3.88.

Synthesis of [$FvMo_2(CO)_4(\mu$-η^2:η^2-$CH_3C\equiv CCH_2C_6H_4OH$)] (11a,b). These compounds **11a**,**b** were prepared in a way similar to that described for **10a**,**b** using the same amount of starting material [$FvMo_2(CO)_4(\mu$-η^2:η^3-$CH_2C\equiv CCH_2C_6H_4OH$)]-[$BF_4$] (**9a**,**b**; 50 mg, 0.075 mmol). The isomers **11a**,**b** were separated on silica gel using CH_2Cl_2 as eluent. Overall yield: 40 mg, 93% (para/ortho = 55/45).

11a: ^{1}H NMR (250 MHz, CD_2Cl_2) δ 3.20 (s, 3H, $-CH_3$), 3.30 (s, 2H, $-CH_2-$), 3.70 (m, 2H, fulvalene), 3.85 (m, 2H, fulvalene), 4.55 (s, 1H, $-OH$), 5.20 (m, 2H, fulvalene), 5.60 (m, 2H, fulvalene), 6.7, 6.80, 7.1 (t, dd, dt, 2H, 1H, 1H, aromatic protons); $^{13}C\{^1H\}$ NMR (62.87 MHz, CD_2Cl_2) δ 19.61 ($-CH_3$), 37.79 ($-CH_2$), 76.01, 81.98, 83.61, 91.83 (fulvalene C$-$H), 92.16 (C_{ipso} fulvalene), 121.14 ($-C\equiv$), 115.11, 120.15, 127.15, 127.49, 131.34, 156.6 (aromatic C's), 221.58, 231.72 (Mo carbonyls); IR (KBr disk) ν(CO) 1993 (s), 1933 (s), 1914 (vs), 1891 (sh) cm^{-1}. Anal. Calcd for **11a**, $C_{24}H_{18}Mo_2O_5\cdot CH_2Cl_2$: C, 45.20; H, 3.01. Found: C, 45.41; H, 3.27.

11b: ^{1}H NMR (250 MHz, CD_2Cl_2) δ 3.10 (s, 2H, $-CH_2-$), 3.22 (s, 3H, $-CH_3$), 3.70 (m, 2H, fulvalene), 3.79 (m, 2H, fulvalene), 4.85 (s, 1H, $-OH$), 5.20 (m, 2H, fulvalene), 5.58 (m, 2H, fulvalene), 6.65 (dd, AB system, 4H, aromatic protons); $^{13}C\{^1H\}$ NMR (62.87 MHz, CD_2Cl_2) δ 19.66 ($-CH_3$), 43.09 ($-CH_2$), 75.91, 81.80, 83.51, 91.56 (fulvalene C$-$H), 92.22 (C_{ipso} fulvalene), 114.37, 130.25, 133.50, 153.85 (aromatic C$-$H), 221.59, 231.85 (Mo carbonyls); IR (KBr disk) ν(CO) 1984 (s), 1941 (s), 1931 (s), 1903 (vs) cm^{-1}.

X-ray Structural Determination of [$FvMo_2(CO)_4(\mu$-η^2:η^2-$MeOCH_2C\equiv CCH_2OMe$)] (2). Crystals of **2** were grown from a solution of Et_2O/hexane. Data were collected at -150 ± 0.5 °C on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation ($\lambda = 0.710\ 73$ Å) and a graphite monochromator. The crystal structure was solved and refined using the Enraf-Nonius MOLEN package. The compound crystallizes in space group $P2_1/c$ (No. 14), with $a = 12.949(1)$ Å, $b = 7.948(1)$ Å, $c = 19.278(2)$ Å, $\beta = 91.65(1)°$, $V = 1983.05(61)$ Å^3, $Z = 4$, $d_{calc} = 1.830$ g/cm^3, $\mu = 12.7$ cm^{-1}, and $F(000) = 1080$. A total of 6386 unique reflections were recorded in the range $2° \le 2\theta \le 60.0°$, of which 1521 were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 4865 for solution and refinement. Direct methods yielded a solution for all atoms. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement, while anisotropic temperature factors were used for all other atoms. A non-Poisson weighting scheme was applied with a p factor equal to 0.08. The final agreement factors were $R = 0.041$, $R_w = 0.082$, GOF = 1.66.

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Supporting Information Available: A figure giving variable-temperature 250 MHz ^{1}H NMR spectra of **2** and complete lists of crystal data (Table S1), bond lengths and angles (Table S2), anisotropic displacement parameters (Table S3), and fractional parameters (Table S4) for **2** (10 pages). Ordering information is given on any current masthead page.

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