4426 *Organometallics* **1994**, *13*, 4426−4430

A Comparative Study of the Structures and Fluxionality of the Carbenium Ion Complexes $[FvMo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}RC{\equiv}CCR'_2)]^+BF_4^-$ (R = H, Me; R′ = H, Me, Ph; Fv = Fulvalene): X-ray Crystal Structure of $[FvMo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCMe_2)]^+BF_4^-$

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Protonation of the fulvalene complexes $[FvMo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}RC{\equiv}CCR'_2OMe)]$, **1** (R = Me, R′ = H), **2** (R = H, R′ = Me), and **3** (R = H, R′ = Ph), yields the corresponding carbenium ion complexes $[FvMo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}RC{\equiv}CCR'_2)]^+$, **4**−**6**. The cluster $[FvMo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCMe_2)]^+BF_4^-$, **5**, crystallizes in the monoclinic space group $P2_1/c$, with $a = 10.509(4)$ Å, $b = 8.109(2)$ Å, $c = 23.137(6)$ Å, $\beta = 96.83°$, $V = 1958$ Å^3, and $Z = 4$. The Mo−C$^+$ distance of 2.75 Å is markedly longer than that found in the CH_2+ complex, **4**, where Mo−C$^+$ = 2.44 Å. Variable-temperature NMR measurements on **5** reveal that the barrier to rotation of the CMe_2^+ group and the energy for migration of the cation from one Mo to the other are both approximately 10 kcal mol^{-1}; this contrasts with the behavior for **4**. Finally, it is shown that in **6** the CPh_2^+ group interacts weakly with a molybdenum vertex. The structures and fluxional behavior of primary versus tertiary carbenium complexes of metal clusters are discussed.

Introduction

Bimetallic clusters containing such bridging hydrocarbyl ligands as vinylidene or allene continue to attract much interest. They provide models for reactive intermediates formed from surface carbides in catalytic heterogeneous carbon monoxide and alkyne conversion reactions.[1] In recent years, attention has been focused on metal-stabilized carbocations of the type $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}RC{\equiv}CCR_2)]^+$; numerous such molecules have been synthesized and characterized by X-ray crystallography.[2]

The low-temperature ^{13}C NMR spectra of these dimolybdenum cations are complicated by the asymmetric nature of the $Mo_2(CO)_4$ core, which generally possesses three terminal carbonyls and one semibridging CO ligand. The problems engendered by the differing orientations of the Cp rings relative to the Mo−Mo axis are largely overcome by use of the fulvalene ligand (Fv) in which the linked five-membered rings are much more restricted in their movements than are their monocyclopentadienyl analogues. Both homo- and heterobimetallic fulvalene complexes are known, and the presence of the conjugated π-system allows the two metals to maintain electronic communication regardless of the presence or absence of a direct metal−metal bond. These fulvalene complexes (and more recently the tercyclopentadienyl homologues) appear to present a closer analogy to the chemistry occurring on metal surfaces than do the bis(cyclopentadienyl) systems.[3]

The synthesis, X-ray crystallographic characterization, and dynamic NMR behavior of the primary carbocationic complex $[FvMo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}MeC{\equiv}CCH_2)]^+BF_4^-$, **4**, have recently been reported,[4] and we here describe synthetic, structural, and variable-temperature NMR studies on $[FvMo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCR_2)]^+BF_4^-$, where R = Me, **5**, and R = Ph, **6**. These data allow a comparison of the role played by the metal in the stabilization of primary carbocationic complexes relative to those in which the electron-deficient carbon atom is less dependent on anchimeric assistance from a metal center.

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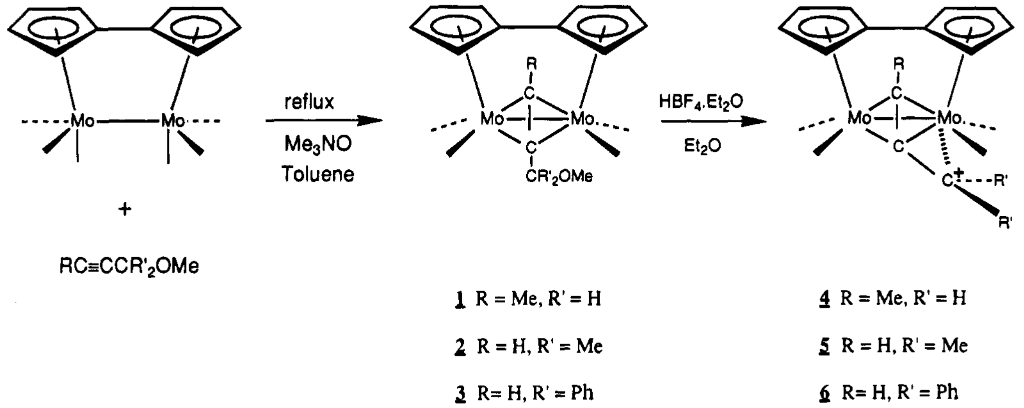
Scheme 1. Syntheses of the Cations of 4−6



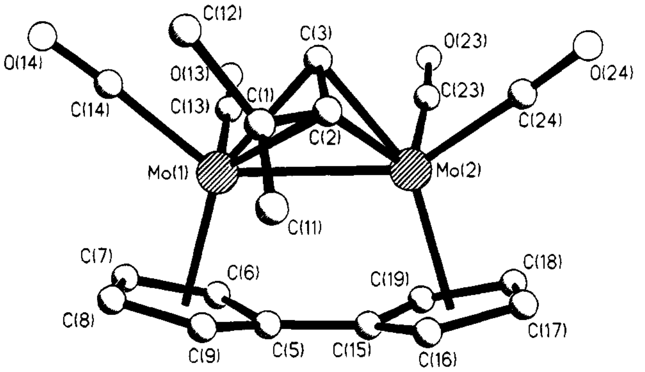


Figure 1. View of the cation in $[FvMo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCMe_2)]^+BF_4^-$, **5**, showing the atom-numbering system.

Results and Discussion

Synthetic and Structural Aspects. Reaction of $FvMo_2(CO)_6$ with alkynes ($RC{\equiv}CCR'_2OMe$) in refluxing toluene provides a convenient route to the alkyne−dimolybdenum tetrahedral clusters $FvMo_2(CO)_4(RC{\equiv}CCR'_2OMe)$, **1**−**3**. Interestingly, addition of 1 equiv of Me_3NO to the reaction mixture improves the overall efficiency such that the complexes **1** (R = Me, R′ = H), **2** (R = H, R′ = Me), and **3** (R = H, R′ = Ph) are available as red crystals in yields of 80%, 60%, and 55%, respectively. Moreover, we have observed that it is better to use the methyl propargyl ethers, $RC{\equiv}CCR'_2OMe$, rather than the corresponding alcohols, $RC{\equiv}CCR'_2OH$, which often result in inseparable mixtures. The complexes **1**−**3** each display four ν_{CO} vibrations in the region 1890−2000 cm^{-1}, thus precluding structures possessing a semibridging carbonyl such as are generally found for the analogous bis(cyclopentadienyl) systems.

As shown in Scheme 1, protonation of the clusters **1**−**3** with HBF_4 etherate yields the cationic clusters **4**−**6**. We have already reported the X-ray crystal structure of the primary cation complex $[FvMo_2(CO)_4(MeC{\equiv}CCH_2)]^+BF_4^-$, **4**, which adopts two slightly different structures in the solid state; these have $Mo\cdot\cdot CH_2^+$ distances of 2.44 and 2.55 Å.[4]

Recrystallization of $[FvMo_2(CO)_4(HC{\equiv}CCMe_2)]^+BF_4^-$, **5**, from CH_2Cl_2/hexane gave a sample suitable for an X-ray crystallographic diffraction study. Figure 1 shows a view of the cation of **5**, and crystallographic data collection parameters and selected bond lengths and angles are listed in Tables 1−3. The cation of **5** possesses a tetrahedral Mo_2C_2 core, and the carbocationic center is oriented such that the Mo(1)−C(1) distance is 2.75 Å. This compares favorably with the $Mo\cdot\cdot C^+$ distances in the bis(cyclopentadienyl) analogues $[Cp_2M_2(CO)_4(HC{\equiv}CCMe_2)]^+$, M = Mo, 2.75 Å,[2b] and M = W, 2.83 Å.[5] In **5**, the Mo(1)−Mo(2) bond length is 2.874(3) Å, considerably shorter than the metal−metal distance in $[Cp_2Mo_2(CO)_4(HC{\equiv}CCMe_2)]^+$, cation of **7**, for which Mo−Mo is 3.021(1) Å.[2b] This shortening of the metal−metal bond, together with the lack of a semibridging carbonyl, is a characteristic feature of these bridged-cyclopentadienyl M_2C_2 clusters. In the propargyl fragment of **5**, the cationic carbon, C(1), is in an almost idealized trigonal planar geometry and the C(1)−C(2) and C(2)−C(3) distances are 1.36(3) and 1.43(3) Å, respectively. We note, however, that it was not possible to obtain a single crystal of the cationic **5** of the very highest quality and so the errors in the bond distances

Table 1. Crystallographic Data for $[FvMo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCMe_2)]^+BF_4^-$, 5

chem formula	$Mo_2C_{19}H_{15}O_4BF_4$
fw	586.0
cryst system	monoclinic
space group	$P2_1/c$
Z	4
a, Å	10.509(4)
b, Å	8.109(2)
c, Å	23.137(6)
β, deg	96.83(3)
V, Å^3	1958(6)
F(000)	1144
ϱ(calcd), g·cm^{-3}	1.99
μ(Mo Kα) cm^{-1}	13.10
diffractometer	CAD4
monochromator	graphite
radiation (λ, Å)	Mo Kα (0.710 70)
temp, °C	20
scan type	$\omega/2\theta$
scan range θ, deg	$1.0 + 0.34 \tan\theta$
2θ range, deg	2−46
reflcns collcd	2714
reflcns used (criteria)	1145 ($I > 3\sigma(I)$)
R	0.058
R_w[a]	0.067
abs corr[b]	min 0.84, max 1.53
secondary ext	no
weighting scheme	unit weights
rms (shift/esd) (last ref)	0.32
ls params	183

[a] $R_w = [\sum_i W_i(F_o - F_c)^2/\sum_i W_i F_o^2]^{1/2}$. [b] DIFABS: Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 159.

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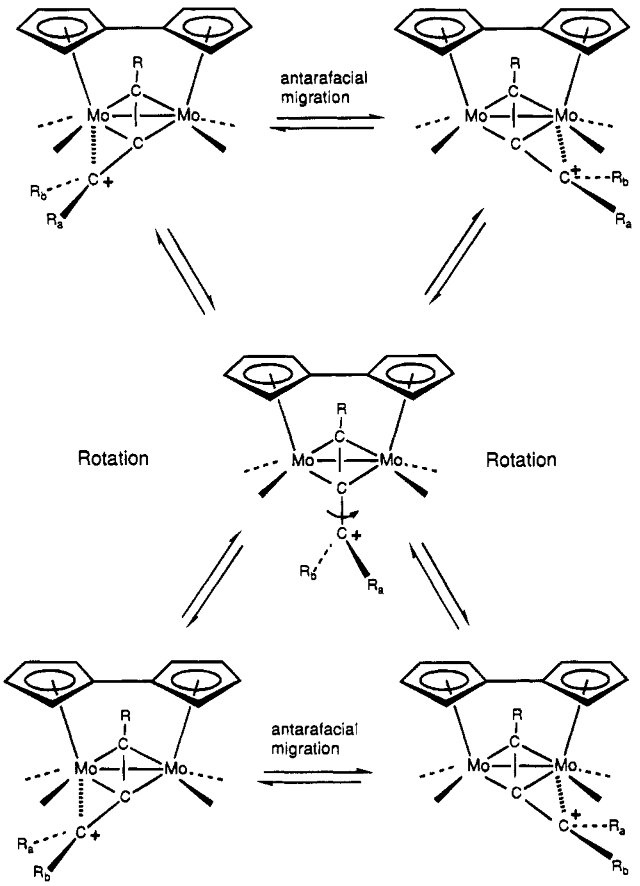
Table 2. Fractional Coordinates and U Values (Å^2) for $[FvMo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCMe_2)]^+BF_4^-$, 5

atom	x/a	y/b	z/c	U(eq)	U(iso)
Mo(1)	0.6823(2)	0.2355(3)	0.42257(9)	0.0329	
Mo(2)	0.8427(2)	0.0391(3)	0.35733(9)	0.0331	
O(13)	0.784(2)	0.052(2)	0.5351(8)	0.0619	
O(14)	0.427(2)	0.216(2)	0.4802(8)	0.0581	
O(23)	0.940(2)	−0.195(2)	0.4622(8)	0.0614	
O(24)	0.804(2)	−0.280(2)	0.2800(7)	0.0521	
C(1)	0.531(2)	0.147(3)	0.322(1)	0.0364	
C(2)	0.639(2)	0.065(3)	0.3440(9)	0.0346	
C(3)	0.671(2)	−0.024(3)	0.3973(9)	0.0208	
C(5)	0.833(2)	0.406(3)	0.388(1)		0.038(6)
C(6)	0.846(2)	0.417(3)	0.451(1)		0.051(7)
C(7)	0.726(2)	0.486(3)	0.466(1)		0.050(7)
C(8)	0.649(2)	0.522(3)	0.416(1)		0.036(6)
C(9)	0.709(2)	0.470(3)	0.367(1)		0.043(6)
C(11)	0.523(2)	0.249(4)	0.269(1)		0.059(7)
C(12)	0.399(2)	0.098(3)	0.340(1)		0.057(7)
C(13)	0.748(3)	0.117(3)	0.492(1)	0.0446	
C(14)	0.518(2)	0.218(3)	0.458(1)	0.0387	
C(15)	0.913(2)	0.305(3)	0.354(1)		0.047(7)
C(16)	0.882(2)	0.260(3)	0.295(1)		0.046(6)
C(17)	0.964(2)	0.126(3)	0.281(1)		0.045(6)
C(18)	1.050(2)	0.090(3)	0.335(1)		0.057(8)
C(19)	1.021(2)	0.207(3)	0.380(1)		0.046(7)
C(23)	0.907(2)	−0.113(3)	0.424(1)	0.0394	
C(24)	0.818(2)	−0.164(3)	0.3090(9)	0.0297	
B(1)	0.742(2)	0.115(2)	0.1344(8)		0.13(1)
F(1)	0.787(2)	0.249(3)	0.1653(9)		0.178(5)
F(2)	0.640(2)	0.159(3)	0.0947(9)		0.178(5)
F(3)	0.837(2)	0.054(3)	0.1063(9)		0.178(5)
F(4)	0.706(2)	0.003(3)	0.1735(9)		0.178(5)

Table 3. Interatomic Distances (Å) in $[FvMo_2(CO)_4(\eta\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCMe_2)]^+BF_4^-$, 5

	Mo(1)—Mo(2)	2.874(3)	
Mo(1)—C(2)	2.29(2)	Mo(2)—C(2)	2.13(2)
Mo(1)—C(3)	2.19(2)	Mo(2)—C(3)	2.19(2)
Mo(1)—C(5)	2.31(2)	Mo(2)—C(15)	2.28(2)
Mo(1)—C(6)	2.30(3)	Mo(2)—C(16)	2.37(2)
Mo(1)—C(7)	2.29(3)	Mo(2)—C(17)	2.40(2)
Mo(1)—C(8)	2.35(2)	Mo(2)—C(18)	2.34(3)
Mo(1)—C(9)	2.33(2)	Mo(2)—C(19)	2.33(2)
Mo(1)—C(13)	1.93(3)	Mo(2)—C(23)	2.02(3)
Mo(1)—C(14)	2.00(2)	Mo(2)—C(24)	1.99(2)
O(13)—C(13)	1.15(3)	O(23)—C(23)	1.13(3)
O(14)—C(14)	1.14(2)	O(24)—C(24)	1.16(2)
C(1)—C(2)	1.36(3)	C(1)—C(11)	1.48(3)
C(1)—C(12)	1.55(3)	C(2)—C(3)	1.43(3)
C(5)—C(6)	1.43(3)	C(5)—C(9)	1.44(3)
C(5)—C(15)	1.48(3)	C(6)—C(7)	1.46(3)
C(7)—C(8)	1.37(3)	C(8)—C(9)	1.42(3)
C(15)—C(16)	1.42(3)	C(15)—C(19)	1.46(3)
C(16)—C(17)	1.44(3)	C(17)—C(18)	1.47(3)
C(18)—C(19)	1.48(3)		
B(1)—F(1)	1.36(2)	B(1)—F(2)	1.37(2)
B(1)—F(3)	1.35(2)	B(1)—F(4)	1.37(2)

Scheme 2. Stereochemical Consequences of the Antarafacial Shift Process and of Rotation about the C—CR$_2$$^+$ Bond



must be borne in mind when such comparisons are made. In the bis(cyclopentadienyl) analogue, **7**, the corresponding values are 1.34 and 1.35 Å.[2b]

NMR and Fluxionality of 4–6. The variable-temperature NMR spectra of a variety of $[Cp_2Mo_2(CO)_4(RC{\equiv}CCR'R'')]^+$ clusters have been interpreted in terms of several independent fluxional mechanisms. Normally, the process with the lowest barrier involves the interconversion of terminal and semibridging carbonyls. Concomitantly, there is a swiveling motion of the entire $CpMo(CO)_2$ vertex, and it is the presence of these "CpMo—MoCp" rotamers which complicates the NMR spectra at low temperatures.[6] At higher temperatures, two fluxional phenomena become apparent. The initially different Cp resonances (in either the ^{1}H or ^{13}C regimes) are seen to coalesce; clearly, the molecule has time-averaged mirror symmetry as a result of the migration of the CR_2^+ moiety from one molybdenum vertex to the other. However, this latter process does not equilibrate the *exo* and *endo* substituents within the CR_2^+ unit, thus demonstrating the antarafacial nature of the migration step. Subsequently, rotation about the C(2)—CR_2 bond interconverts the *exo* and *endo* environments.

An advantage of studying the complexes **4–6** is that the relatively rigid nature of the bridging fulvalene ligand obviates the spectral complications attributable to the presence of "CpMo—MoCp" rotamers. Indeed, these systems are admirably suited to a study of the relative energetics of the antarafacial migration process versus the rotational barrier to exchanging the *exo* and *endo* substituents. The former barrier can be monitored by the coalescence of symmetry-related protons in the fulvalene rings; the energetics of the latter process can be evaluated from the behavior of the CH_2^+ and CMe_2^+ moieties in **4** and **5**, respectively. A 2D-EXSY study on **4** yielded $\Delta G^{\ddagger}_{343}$ values of 17.7 ± 0.4 kcal mol^{-1} for the migration process and 19.1 ± 0.4 kcal mol^{-1} for the rotational barrier about the C(2)—CH_2 linkage. This can be restated in terms of seeing only one rotation of the CH_2 fragment for every seven migrations of the methylene from Mo to Mo, at 343 K (see Scheme 2).

The coalescence behavior of the fulvalene protons and of the two methyl groups in the tertiary cation complex

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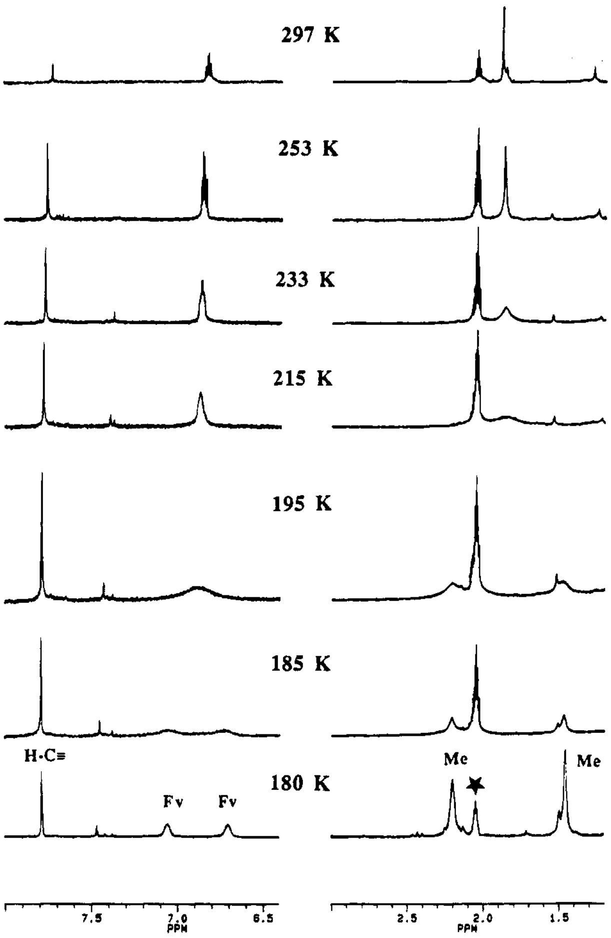

Figure 2. Variable-temperature 250 MHz ^{1}H NMR spectra of $[\mathrm{FvMo_2(CO)_4}(\mu\text{-}\eta^2,\eta^3\text{-HC{\equiv}CCMe_2})]^+\mathrm{BF_4}^-$, **5**, showing the coalescence of fulvalene protons and of the methyl groups. (An asterisk marks the acetone peak.)

$[\mathrm{FvMo_2(CO)_4(HC{\equiv}CCMe_2)}]^+$, **5**, is shown in Figure 2. These data yield a *migration* barrier, $\Delta G^{\ddagger}_{195}$, of 9.5 ± 0.5 kcal mol^{-1}; the *rotational* barrier, $\Delta G^{\ddagger}_{215}$, is 10.3 ± 0.5 kcal mol^{-1}. Evidently, there is no significant difference between these $\Delta G^{\ddagger}$ values suggesting that both processes occur via a common pathway such that the cationic carbon is no longer receiving anchimeric assistance from an electron-rich metal and is free to rotate about the C(2)—CMe$_2$ bond. The increased $\mathrm{Mo}\cdots\mathrm{C}^+$ distance and greatly reduced barrier to both migration and rotation in the tertiary cation of **5** relative to the primary cation of **4** provide compelling evidence of decreased involvement in cationic stabilization by the metal in **5**.

We have previously used a combined theoretical and crystallographic approach to determine the trajectory followed by a CH$_2$ group as it migrates between the molybdenum vertices in $[\mathrm{FvMo_2(CO)_4(HC{\equiv}CCH_2)}]^+$. The minimum energy trajectory obtained from an EHMO study is remarkably well paralleled by a series of X-ray crystal structures of cations $[\mathrm{Cp_2Mo_2(CO)_4(RC{\equiv}CCR'R'')}]^+$, where the groups R′ and R″ range from H, Me, and ferrocenyl to terpenoid and steroidal substituents.[7] These data reveal that, at the bottom of the potential energy well, the primary cations lie directly above the molybdenum vertices, while, for secondary and tertiary cationic complexes, the $\mathrm{Mo}\cdots\mathrm{C}^+$ distances have lengthened and the $\mathrm{CR'R''}^+$ fragment has in effect "climbed the wall" of the potential well and is aligned closer to the plane bisecting the molybdenum vertices.

These data parallel closely the NMR results of Nicholas[8] and of Schreiber[9] on the isolobal $[\mathrm{Co_2(CO)_6(RC{\equiv}CCR'R'')}]^+$ clusters where, again, the antarafacial migration barrier falls markedly as one proceeds from primary through secondary to tertiary cationic systems.

One might envisage that a particularly stable carbocation might be situated in the molecular mirror plane, equidistant from the two molybdenum atoms. The known stability of the trityl cation, and trigonal planar character of its central carbon, suggest that the cluster $[\mathrm{FvMo_2(CO)_4(HC{\equiv}CCPh_2)}]^+\mathrm{BF_4}^-$, **6**, might provide an example of a cation which has no need of anchimeric assistance from a metal. Despite repeated attempts, it has not been possible to obtain an X-ray-quality crystal of **6**; however, the variable-temperature NMR spectra do provide considerable insight into the structure of this cation. At room temperature, the ^{1}H NMR spectrum in acetone-d_6 exhibits four multiplets for the fulvalene rings, each representing a pair of protons, and these resonances are unchanged at 190 K. However, the ^{13}C absorptions of the two carbons which link the five-membered rings appear as a single peak at 102 ppm but, upon cooling, these split to give signals at 104 and 99 ppm. Furthermore, the molybdenum carbonyl ligands yield two room-temperature ^{13}CO resonances (at 224 and 213 ppm) which broaden and split at 190 K. We note also that the carbocationic center, to which the two phenyls are bonded, resonates at 153 ppm. This value is remarkably similar to the chemical shift of 150 ppm previously found for the corresponding C$^+$ center in $[\mathrm{FvMo_2(CO)_4(HC{\equiv}CCMe_2)}]^+\mathrm{BF_4}^-$, **5**. Finally, one can see small splittings in the phenyl ring carbons, again indicating the two rings are no longer equivalent.

These data suggest very strongly that, at low temperature, the exchange of the CPh$_2$$^+$ moiety between the two molybdenum sites can become slow on the NMR time scale. That is, the diphenylmethyl cation in **6** does indeed interact with a molybdenum center, albeit rather weakly. This result is in accord with the crystallographically determined structure of the α,α-(diphenylmethyl)ferrocenyl cation, $[\mathrm{(C_5H_5)Fe(C_5H_4CPh_2)}]^+$, **8**, in which the carbocation center leans through 22° toward the iron atom.[10] However, since in the ferrocenyl—tropylium system $[\mathrm{(C_5H_5)Fe(C_5H_4{-}C_7H_6)}]^+$, **9**, the seven-membered ring and the ferrocenyl unit are coplanar,[11] one might be able to isolate and characterize the analogous dimolybdenum complex $[\mathrm{FvMo_2(CO)_4(HC{\equiv}CC_7H_6)}]^+$, **10**, as a symmetrical species. We are currently directing our synthetic efforts toward this goal.

Experimental Section

All manipulations were carried out under an argon atmosphere using Schlenk techniques, and all solvents were dried

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by conventional methods. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 250 instrument operating at 250 and 62.86 MHz, respectively. Infrared spectra were obtained on Perkin-Elmer 681 instrument. Elemental analyses were performed by the Microanalytical Laboratory of the Université de Paris VI. The methyl propargyl ethers $HC\equiv CCMe_2OMe$ and $HC\equiv CCPh_2OMe$ were prepared by literature methods.[12,13]

$FvMo_2(CO)_4(HC\equiv CCMe_2OMe)$, 2. $HC\equiv CCMe_2OMe$ (0.7 mL, 7.5 mmol) was added to a pink solution of $FvMo_2(CO)_6$ (370 mg, 0.76 mmol) in toluene (40 mL) in the presence of Me_3NO (75 mg, 1.0 mmol), and the mixture was heated under reflux for 12 h. The purple suspension was filtered, and unreacted $FvMo_2(CO)_6$ (125 mg, 0.25 mmol) was recovered. After removal of solvent, the residue was chromatographed on silica gel and eluted with acetone/hexane (1:4) to give a red band which afforded orange-red crystals of **2** (150 mg, 0.29 mmol; 58%). ^1H NMR (250 MHz, acetone-d_6) (δ): 7.30 (s, 1H, $\equiv$CH); 5.71 (m, 2H), 5.39 (m, 2H), 5.20 (m, 2H), 4.10 (m, 2H) (fulvalene ring H's); 2.95 (s, 3H, OMe); 0.99 (s, 6H, Me's). ^{13}C NMR (62.86 MHz, acetone-d_6) (δ): 231.5, 224.8 (CO's); 104.6 (alkyne C); 93.0 (fulvalene ring C's); 91.6, 83.8, 82.6, 77.7 (fulvalene ring CH's); 79.6 (*C*Me$_2$); 57.5 (alkyne CH); 48.9 (OMe); 28.7 (Me's). IR (CH_2Cl_2) (cm^{-1}) ν_{CO} at 1996 vs, 1957 vs, 1925 vs, 1890 sh. Anal. Calcd for $C_{20}H_{18}O_5Mo_2$: C, 45.30; H, 3.42. Found: C, 46.78; H, 3.59.

$[FvMo_2(CO)_4(HC\equiv CCMe_2)]^+BF_4^-$, 5. An excess of $HBF_4\cdot Et_2O$ was added to a red solution of **2** (150 mg, 0.28 mmol) in Et_2O (15 mL) to give an orange precipitate. After removal of the mother liquor, the precipitate was washed several times with diethyl ether and recrystallized from CH_2Cl_2/hexane to give orange-red crystals of **5** (150 mg, 0.25 mmol; 91%). ^1H NMR (250 MHz, acetone-d_6) (δ): 7.80 (s, 1H, $\equiv$CH); 6.70 (m, 2H), 6.00 (m, 2H), 4.90 (m, 2H), 4.55 (m, 2H) (fulvalene ring H's); 1.85 (s, 6H, Me's). ^{13}C NMR (62.86 MHz, acetone-d_6) δ 224.4, 215.5 (CO's); 153.6 (*C*Me$_2$); 99.9 (fulvalene ring C's); 97.1, 96.1, 85.9, 82.1 (fulvalene ring CH's); 92.1 (alkyne C); 60.0 (alkyne CH); 33.3 (Me's). IR (CH_2Cl_2) (cm^{-1}) ν_{CO} at 2048 vs, 2020 vs, 1989 vs, 1920 vw. Anal. Calcd for $C_{19}H_{15}O_4Mo_2BF_4$: C, 39.94; H, 2.58. Found: C, 39.14; H, 3.08.

$FvMo_2(CO)_4(HC\equiv CCPh_2OMe)$, 3. In an analogous fashion to the preparation of **2**, $HC\equiv CCPh_2OMe$ and $FvMo_2(CO)_6$ gave **3** in 53% yield after chromatography on silica gel and elution with acetone/hexane (1:10). The product was washed with pentane to remove unreacted alkyne. ^1H NMR (250 MHz, acetone-d_6) (δ): 7.51 (s, 1H, $\equiv$CH); 7.3–7.1 (m, 10H, phenyl H's); 5.70 (m, 2H), 5.32 (m, 2H), 4.97 (m, 2H), 3.97 (m, 2H) (fulvalene ring H's); 2.66 (s, 3H, OMe). ^{13}C NMR (62.86 MHz, acetone-d_6) (δ): 233.0, 221.3 (CO's); 143.6 (alkyne C); 133.2 (*C*Ph$_2$); 132.2, 128.4, 127.3 (phenyl CH's); 107.1 (fulvalene ring C's); 93.1, 85.6, 82.6, 77.5 (fulvalene ring CH's); 52.8 (OMe). IR (CH_2Cl_2) (cm^{-1}) ν_{CO} at 1990 vs, 1955 vs, 1920 vs, 1895 sh.

$[FvMo_2(CO)_4(HC\equiv CCPh_2)]^+BF_4^-$, 6. In an analogous fashion to the preparation of **5**, $HBF_4\cdot Et_2O$ and **3** gave a tan precipitate of **6** in 50% isolated yield. ^1H NMR (250 MHz, acetone-d_6) (δ): 8.60 (s, 1H, $\equiv$CH); 7.5–7.3 (m, 10H, phenyl H's); 7.00 (m, 2H), 6.05 (m, 2H), 4.55 (m, 2H), 3.60 (m, 2H) (fulvalene ring H's). ^{13}C NMR (62.86 MHz, acetone-d_6) at 300 K (δ): 224.1, 213.9 (CO's); 152.5 (*C*Ph$_2$); 143.6 (phenyl C's); 129.9, 129.1 (phenyl CH's); 101.7 (fulvalene ring C's); 99.1, 96.2, 85.7, 82.7 (fulvalene ring CH's); 92.2 (alkyne C); 68.2 (alkyne CH). ^{13}C NMR (62.86 MHz, acetone-d_6) at 193 K (δ): 224.5 (broad), 214.5, 212.5 (CO's); 148.5 (*C*Ph$_2$); 146.6, 142.3 (phenyl C's); 129.6, 129.4, 129.0 (phenyl CH's); 104.2, 99.0 (fulvalene ring C's); 100.4, 95.6, 85.6, 82.3 (broadened peaks, fulvalene ring CH's); 92.4 (alkyne C); 68.1 (alkyne CH). IR (CH_2Cl_2) (cm^{-1}) ν_{CO} at 2053 vs, 2023 vs, 2000 vs, 1984 vw. Anal. Calcd for $C_{29}H_{19}O_4Mo_2BF_4$: C, 49.05; H, 2.70. Found: C, 49.19; H, 2.76.

X-ray Crystallography. Suitable crystals of $[FvMo_2(CO)_4(HC\equiv CCMe_2)]^+BF_4^-$, **5**, were obtained by recrystallization from dichloromethane/hexane. Crystallographic data are collected in Table 1. Accurate cell dimensions and orientation matrices were obtained by least-squares refinement of 25 accurately centered reflections on Nonius CAD4 diffractometer equipped with graphite-monochromated Mo Kα radiation. No significant variations were observed in the two check reflections during data collection. The data were corrected for Lorentz and polarization effects; an empirical absorption correction (DIFABS)[14] was applied. Computations were performed by using CRYSTALS[15] modified locally for a Microvax II computer. Scattering factors and corrections for anomalous absorption were taken from ref 16. The structure was solved by direct methods (SHELXS)[17] and refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were then located on a difference Fourier map and their coordinates refined with an isotropic thermal parameter. The structure was refined to $R = 0.058$ and $R_w = 0.067$ with use of 1145 reflections for 183 least-squares parameters. Final atomic coordinates and selected bond distances are listed in Tables 2 and 3.

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Supplementary Material Available: Tables of anisotropic displacement parameters (Table S1) and bond angles (Table S2) and an NMR spectrum (Figure S1) (4 pages). Ordering information is given on any current masthead page.

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