Organometallics **1996,** *15,* 1514−1517

An Unusual Dicarbenium Fulvalene Complex, $[FvMo_2(CO)_4(\mu\text{-}\eta^3{:}\eta^3\text{-}CH_2C{\equiv}CCH_2)][BF_4]_2$ (Fv = Fulvalene), Which Exhibits Reactivity toward Weak Nucleophiles

H. El Amouri* and Y. Besace

Ecole Nationale Supérieure de Chimie de Paris, URA CNRS 403,
11, rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

Received September 13, 1995[⊗]

Summary: The title compound was prepared and characterized by spectroscopic methods. The complex $[FvMo_2(CO)_4(\mu\text{-}\eta^3{:}\eta^3\text{-}CH_2C{\equiv}CCH_2)][BF_4]_2$ (**3**) *exhibits reactivity toward weak nucleophiles such as MeOH,* H_2O, *and PhOMe, affording the monocarbenium ions* $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}MeOCH_2C{\equiv}CCH_2)][BF_4]$ (**4**), $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}HOCH_2C{\equiv}CCH_2)][BF_4]$ (**5**), *and* $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}CH_2C{\equiv}CCH_2C_6H_4OMe)][BF_4]$ (**6a**,**b**; *para:ortho 55:45), respectively. When* **3** *was treated with strong nucleophiles such as pyridine and triphenylphosphine, double nucleophilic attack occurred, yielding the complexes* $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}C_5H_5NCH_2C{\equiv}CCH_2NC_5H_5))][BF_4]_2$ (**7**) *and* $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}PPh_3CH_2C{\equiv}CCH_2PPh_3)][BF_4]_2$ (**8**), *respectively. The reactivity of the fulvalenyl-bridged dimolybdenum propargyl dication complex* **3** *is compared to that of the related cyclopentadienyl system and discussed.*

Introduction

In our exploration of the organometallic chemistry of fulvalene propargylium complexes, we have prepared the first carbenium ion complexes of the type $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}R^1C{\equiv}CCR^2R^3)][BF_4]$ (R^1 = Me, $R^2 = R^3$ = H; R^1 = H, $R^2 = R^3$ = Me; R^1 = H, $R^2 = R^3$ = Ph).[1] These fulvalene complexes are admirably suited for the study of fluxional behavior of the metal−hydrocarbyl interaction, while in the solid state they exhibit different coordination modes when compared to their analogous Cp systems. The novel dicarbenium fulvalene complex $[FvMo_2(CO)_4(\mu\text{-}\eta^3{:}\eta^3\text{-}CH_2C{\equiv}CCH_2)][BF_4]_2$ (**3**) exhibits not only a different bonding structure but also a completely different reactivity when compared to the analogous dicationic Cp complex $[(CH_2C{\equiv}CCH_2)Cp_2Mo_2(CO)_6][BF_4]_2$ reported recently.[2]

In this paper we report the preparation and spectroscopic identification of an unusually reactive fulvalene dicarbenium propargylic complex, $[FvMo_2(CO)_4(\mu\text{-}\eta^3{:}\eta^3\text{-}CH_2C{\equiv}CCH_2)][BF_4]_2$ (**3**), exhibiting reactivity comparable to that of the Nicholas reagent $[Co_2(CO)_6(\mu\text{-}\eta^2{:}\eta^3\text{-}HC{\equiv}CCH_2)][BF_4]$.[3] This situation is a result of the unique and rigid coordination mode of the fulvalene ligand, which forces a steric crowding environment around the molybdenum centers and hence a weaker Mo- - -C$^+$ interaction. We show that the dicarbenium fulvalene complex **3** exhibits a different degree of reactivity; for instance, the first nucleophilic attack on the carbenium center proceeds rapidly with even mild carbon nucleophiles to give the corresponding stable monocarbenium complexes. These monocarbenium derivatives are less reactive, and only reactions with strong nucleophiles were observed. The molybdenum propargylium dicarbenium complex $[FvMo_2(CO)_4(\mu\text{-}\eta^3{:}\eta^3\text{-}CH_2C{\equiv}CCH_2)][BF_4]_2$ (**3**) is by far the most reactive among the propargyl cations stabilized by a dimolybdenum cluster ($FvMo_2(CO)_4$, $Cp_2Mo_2(CO)_6$).[1,4]

Results and Discussion

We have prepared complex **3** by direct protonation of the propargyl ether complex $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^2\text{-}MeOCH_2C{\equiv}CCH_2OMe)]$ (**2**) in CH_2Cl_2 at room temperature, which afforded a red oil-like compound (Scheme 1). Complex **2** was obtained by refluxing a toluene solution of $FvMo_2(CO)_6$ (**1**) with an excess of $MeOCH_2C{\equiv}CCH_2OMe$. The spectroscopic data (^1H, ^{13}C) of **2** recorded at low temperature showed the nonequivalence of the two method and methylene groups of the bridging alkyne "$\mu\text{-}\eta^2{:}\eta^2\text{-}MeOCH_2C{\equiv}CCH_2OMe$". Loss of symmetry is no doubt a result of the distortion of the fulvalene ligand, seen in several structures of metal−metal-bonded bimetallic derivatives. The ring centroids of a planar fulvalene are separated by 4 Å,[5] while most M−M bonds are less than 3.5 Z. Consequently, the fulvalene ligand acquires a pyramidalized structure to accommodate M−M bond lengths of 2.8−3.5 Å.

The dicarbenium compound **3** was identified by spectroscopic methods; the NMR spectra (^1H, ^{13}C) of **3** could only be recorded in a deuterated $TFA/HBF_4{\cdot}Et_2O$ mixture (TFA = CF_3COOD). The ^1H NMR spectrum shows the presence of four broad multiplets in the range 4.10−6.80 ppm, attributed to the fulvalene protons, while each metal-stabilized $-CH_2^+$ unit appears as a broad singlet at 4.80 and 6.34 ppm, respectively, where one resonance corresponds to the inside set of two protons $2H_a$ (one on each side of the $-CH_2$ groups) and the other is for the outside set $2H_b$ (see Scheme 1). Such an interpretation is suggested by comparison with the

---

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1996.

[1] (a) El Amouri, H.; Vaissermann, J.; Besace, Y.; Vollhardt, K. P. C.; Ball, G. E. *Organometallics* **1993**, *12*, 605. (b) El Amouri, H.; Besace, Y.; Vaissermann, J.; Jaouen, G.; McGlinchey, M. J. *Organometallics* **1994**, *13*, 4426.

[2] (a) McClain, M. D.; Hay, M. S.; Curtis, M. D.; Kampf, J. W. *Organometallics* **1994**, *13*, 4377. (b) Reutov, O. A.; Barinov, I. V.; Chertkov, V. A.; Sokolov, V. I. *J. Organomet. Chem.* **1985**, *297*, C25−C29. (c) Bennett, S. C.; Gelling, A.; Went, M. J. *J. Organomet. Chem.* **1992**, *439*, 189−199.

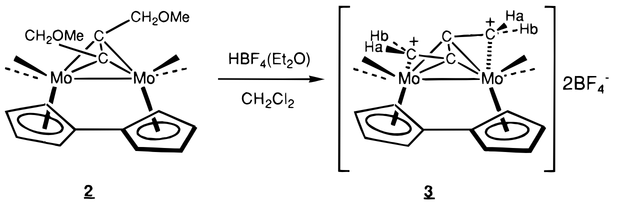
[3] (a) Nicholas, K. M. *Acc. Chem. Res.* **1987**, *20*, 207. (b) Padmanabhan, S.; Nicholas, K. M. *J. Organomet. Chem.* **1983**, *268*, C23. (b) Lockwood, R. F.; Nicholas, K. M. *Tetrahedron Lett.* **1977**, *48*, 4163.

[4] Meyer, A.; McCabe, D. J.; Curtis, M. D. *Organometallics* **1987**, *6*, 1491.

[5] Churchill, M. R.; Wormald, J. *Inorg. Chem.* **1969**, *8*, 1970.

0276-7333/96/2315-1514$12.00/0

Scheme 1



data obtained previously for the monocarbenium ion $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}MeC\equiv CCH_2)][BF_4]$, where the two protons on the $-CH_2$ group do have different chemical shifts.[1]

The spectroscopic data suggest an increase of symmetry in molecule **3** with the bridging C_4H_4 ligand adopting a $\mu\text{-}\eta^3{:}\eta^3$ coordination mode. The dicarbenium propargylium complex **3** is moisture sensitive and transforms rapidly to the hydrolyzed monocarbenium complex $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}HOCH_2C\equiv CCH_2)][BF_4]$ (**5**), owing to the very reactive stabilized carbenium centers. It is well-established that monocarbenium ion complexes stabilized by a dimolybdenum cluster are usually stable toward hydrolysis; this is due to the strong Mo- - -C$^+$ interaction.[1,4] This interaction is stronger than that of the isolobal cobalt complexes $[Co_2(CO)_6(\mu\text{-}\eta^2{:}\eta^3\text{-}R^1C\equiv C\text{-}CR^2R^3)][BF_4]$. Furthermore, in mixed-metal systems (M_2L_6 = CoMoCp(CO)$_5$) the monocarbenium ions are preferentially stabilized by the Mo center.[6,7]

Scheme 2 shows the reactivity of **3** with various nucleophiles;[8] thus, treatment of **3** with neat anisole for 1 h afforded an orange microcrystalline solid which was identified by spectroscopic methods as a mixture of para- and ortho-substituted anisole derivatives of the monocation propargylium complexes $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}CH_2C\equiv CCH_2C_6H_4OMe)][BF_4]$ (**6a**,**b**) (para:ortho 55:45). When **3** was treated with strong nucleophiles such as pyridine and triphenylphosphine, a double nucleophilic attack took place on both carbenium centers, affording the corresponding dipyridinium complex $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^2\text{-}C_5H_5NCH_2C{=}CCH_2NC_5H_5)][BF_4]_2$ (**7**) and $[FvMo_2(CO)_4(\mu\text{-}\eta^2L\eta^2\text{-}PPh_3H_2CC{=}CCH_2PPh_3)][BF_4]_2$ (**8**), respectively.

Unlike the dicarbenium Cp complexes $[(CH_2C\equiv CCH_2)Cp_2Mo_2(CO)_6][BF_4]_2$,[9] our compound $[FvMo_2(CO)_4(\mu\text{-}\eta^3{:}\eta^3\text{-}CH_2C\equiv CCH_2)][BF_4]_2$ (**3**) reacts with dry MeOH to give the monocarbenium ion $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}MeOCH_2C\equiv CCH_2)][BF_4]$ (**4**). The latter can be also obtained by direct protonation of the propargyl ether complex $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^2\text{-}MeOCH_2C\equiv CCH_2OMe)]$ (**2**) in diethyl ether solution (Scheme 3). The monocation species $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}MeOCH_2C\equiv CCH_2)][BF_4]$ (**4**) is air and moisture stable and soluble in CH_2Cl_2. It can be further protonated in CH_2Cl_2 to yield the dicarbenium complex **3**.

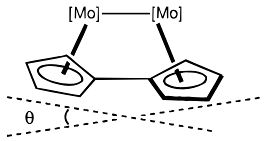
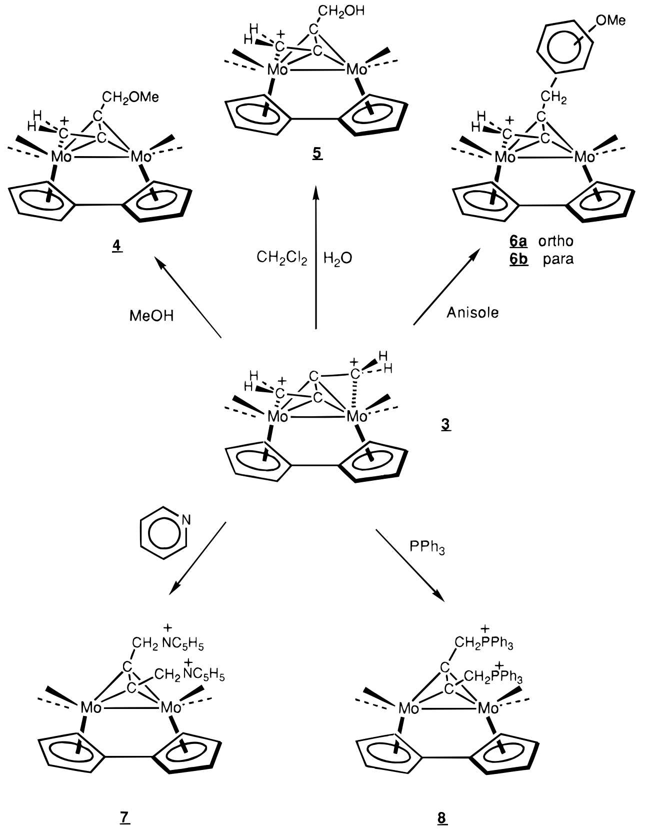
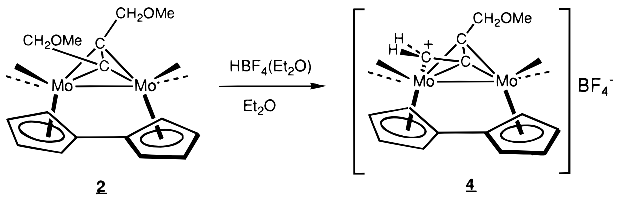


Figure 1.

Scheme 2



Scheme 3



We consider that the Mo- - -CH$_2^+$ interaction is weaker in the case of the dicarbenium ion $[FvMo_2(CO)_4(\mu\text{-}\eta^3{:}\eta^3\text{-}CH_2C\equiv CCH_2)][BF_4]_2$ (**3**), with respect to those of the analogous fulvalene monocarbenium adducts. This explains why **3** is only stable in strongly acidic medium. We note that the analogous cyclopentadienyl system $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^3{:}\eta^3\text{-}CH_2C\equiv CCH_2)][BF_4]_2$ was recently reported, and its X-ray structure was determined.[2a] Both carbenium ions are equally stabilized via a Mo- - -CH$_2^+$ interaction, at least in the solid state (d(Mo- - -Cl$^+$) = 2.456 Å; d(Mo- - -Cl$^+$) = 2.464 Å) and only reactivity toward strong nucleophiles was observed with both carbenium centers.[2a] At this stage a brief comment on the nature and coordination mode of the fulvalene ligand is required. It is well-known that the fulvalene ligand allows electronic communication between metal centers even if the metal–metal bond is temporarily

---

(6) (a) Gruselle, M.; Philomin, V.; Chaminant, F.; Jaouen, G.; Nicholas, K. M. *J. Organomet. Chem.* **1990**, *399*, 317. (b) Barinov, I. V.; Chertkov, V. A.; Reutov, O. A. *J. Organomet. Chem.* **1993**, *455*, C9.

(7) Gruselle, M.; El Hafa, H.; Nikolski, M.; Jaouen, G.; Vaissermann, J.; Li, L.; McGlinchey, M. J. *Organometallics* **1993**, *12*, 4917–4925.

(8) The fulvalene protons of the monocarbenium ions were assigned without ambiguity by comparing with analogous species $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}R^1C\equiv CCR^2R^3)][BF_4]$ (R^1 = Me, R^2 = R^3 = H; R^1 = H, R^2 = R^3 = Me) having known X-ray structures.[1]

(9) We have investigated the reactivity of the dicarbenium cyclopentadienyl system $[(CH_2C\equiv CCH_2)Cp_2Mo_2(CO)_6][BF_4]_2$ with dry MeOH and in neat anisole, i.e. under the same experimental conditions as for the dicarbenium fulvalene complex $[FvMo_2(CO)_4(\mu\text{-}\eta^3{:}\eta^3\text{-}CH_2C\equiv CCH_2)][BF_4]_2$ (**3**). The dicarbenium Cp complex failed to react with MeOH or with anisole.

broken.[10] Another important feature is the bending or strain angle θ, which is defined by the angle between the two planes of the connected Cp rings in the solid state (Figure 1). This angle increases from 15.3°[11] in $FvMo_2(CO)_6$ to 25°[1a] for the monocation $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}CH_2C{\equiv}CCH_2)][BF_4]$. The angle change is accompanied by a shortening of the metal−metal bond. For the dicarbenium ion **3**, the strain angle should be even greater than 25°. The rigid coordination mode of the fulvalene ligand forces a steric crowding around the metal centers and, hence, a weak metal- - -C^+ interaction with both carbenium centers. This perhaps explains the reactivity of **3** toward weak nucleophiles.

Another important factor is the charge differences between the mono- and dicarbenium ions. It is well-known that in the Cp system the bicationic species are more reactive toward nucleophiles than their monocationic counterparts. In this respect the dicarbenium complex $[FvMo_2(CO)_4(\mu\text{-}\eta^3{:}\eta^3\text{-}CH_2C{\equiv}CCH_2)][BF_4]_2$ (**3**) should be more electrophilic than the corresponding monocarbenium ion.

The selectivity of **3** toward weak nucleophiles allows the preparation of different substituted alkyne−$FvMo_2(CO)_4$ adducts and hence it shows the potential utility of complex **3** for organic synthesis, providing that the release of the organic ligand after substitution is not a difficult process. Evidently the monocarbenium ions $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}CH_2C{\equiv}CCH_2R)][BF_4]$ can be reduced by $NaBH_4$[1,4] to give the corresponding alkyne adducts $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^2\text{-}CH_3C{\equiv}CCH_2R)][BF_4]$.

Our future objectives are currently directed toward the preparation of these disubstituted alkyne fulvalene adducts as well as the X-ray structural determination of monosubstituted and disubstituted cationic derivatives. These results will be reported in a forthcoming paper.

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 a FT Bruker IR45 spectrometer from samples prepared either as KBr disks or CH_2Cl_2 solutions. All absorptions are expressed in wavenumbers (cm^{-1}). Elemental analyses were performed by the Microanalytical Laboratory of the CNRS of the University of Paris VI.

Synthesis of $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^2\text{-}MeOCH_2C{\equiv}CCH_2OMe)]$ (2). $MeOCH_2C{\equiv}CCH_2OMe$ (1.5 mL, 12 mmol) was added to a pink solution of $FvMo_2(CO)_6$ (**1**) (488 mg, 1 mmol) in toluene (25 mL), and the mixture was refluxed for 12 h. The purple suspension was filtered, and unreacted $FvMo_2(CO)_6$ (260 mg, 0.53 mmol) was recovered. After removal of solvent, the residue was chromatographed on silica gel and eluted with acetone/hexane (1:3) to give a red band which afforded orange-red crystals of **2** (240 mg, 91%) based on unrecovered $FvMo_2(CO)_6$ (**1**).

^1H NMR (250 MHz, acetone-d_6): $T = 243$ K, δ 3.06 (s, 3H, $-OCH_3$), 3.50 (s, 3H, $-OCH_3$), 3.86 (s, 2H, $-CH_2O-$), 4.24 (m, 2H), 4.93 (m, 2H), 5.28 (s, 2H, $-CH_2O-$), 5.47 (m, 2H), 5.81 (m, 2H). $^{13}C\{^1H\}$ NMR (62.87 MHz, acetone-d_6): $T = 243$ K, δ 58.07 (s, $-OCH_3$), 59.09 (s, $-OCH_3$), 76.11 (s, $-CH_2O-$), 81.13 (s, $-CH_2O-$), 77.88, 82.57, 83.71, 93.00 (four singlets, C−H), 87.74 (s, C ipso), 85.20 (s, $-C{\equiv}$), 117.96 (s, ${\equiv}C-$), 222.46, 232.20 (Mo carbonyls). IR (KBr): δ(CO) 1997 (s), 1947 (s), 1925 (b) cm^{-1}. Anal. Calcd for **2** ($C_{20}H_{18}O_6Mo_2$): C, 43.95; H, 3.29. Found: C, 44.27; H, 3.47.

Synthesis of $[FvMo_2(CO)_4(\mu\text{-}\eta^3{:}\eta^3\text{-}CH_2C{\equiv}CCH_2)][BF_4]_2$ (3). An excess of $HBF_4{\cdot}Et_2O$ was added to a red solution of **2** (50 mg, 0.088 mmol) in CH_2Cl_2 (15 mL) to give a red oil-like precipitate. After removal of the supernatant solution the residue was washed with CH_2Cl_2 and dried under vacuum; yield 50 mg (83%). The dicarbenium propargylium complex **3** is moisture sensitive and is hydrolyzed rapidly to the monocarbenium complex $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}HOCH_2C{\equiv}CCH_2)][BF_4]$ (**5**).

3: ^1H NMR (250 MHz, TFA-d_1/$HBF_4{\cdot}Et_2O$) δ 4.20 (m, 2H), 4.80 (b, 2H, $-CH_2$), 5.35 (m, 2H), 6.26 (m, 2H), 6.34 (b, 2H, $-CH_2$), 6.65 (m, 2H); $^{13}C\{^1H\}$ NMR (250 MHz, TFA-d_1/$HBF_4{\cdot}Et_2O$) δ 79.72 (s, $-CH_2$), 80.05 (s, $-CH_2$), 84.13, 85.43, 88.19, 88.62 (four singlets, C−H), 92.13 (s, C ipso), 128.63 (s, $-C{\equiv}C-$),198.21, 202.27 (Mo carbonyls).

Synthesis of $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}MeOCH_2C{\equiv}CCH_2)][BF_4]$ (4). This compound was prepared by two different routes.

Method A. An excess of $HBF_4{\cdot}Et_2O$ was added to a red solution of **2** (50 mg, 0.088 mmol) in Et_2O (15 mL) to give an orange-red precipitate. After removal of the supernatant solution, the residue was washed with Et_2O and dried under vacuum to quantitatively yield **4** as a stable complex.

Method B. To the dicarbenium species **3** was added 10 mL of MeOH, and the mixture was stirred for 1 h. Addition of Et_2O (20 mL) to the red solution afforded an orange-red precipitate, which was separated, washed with Et_2O several times, and identified as complex **4**.

^1H NMR (250 MHz, acetone-d_6): δ 3.50 (s, 3H, $-OCH_3$), 3.58 (s, 1H, $-CH_2$), 4.44 (m, 1H), 4.52 (m, 1H), 5.17 (m, 1H), 5.55 (m, 1H), 5.31 (dd, AB system, 2H, $-CH_2OMe$), 6.15 (m, 1H), 6.18 (m, 1H), 6.31 (m, 1H), 6.88 (m, 1H). $^{13}C\{^1H\}$ NMR (62.87 MHz, acetone-d_6): δ 59.33 (s, $-OCH_3$), 72.00 (s, $-CH_2$), 74.12 (s, $-CH_2OMe$), 82.63, 82.71, 86.61, 86.77, 90.68, 93.32, 94.18, 97.84 (8 singlets, C−H), 89.17, 93.87 (two singlets, C ipso), 112.97 (s, $-C{\equiv}$), 118.41 (s, ${\equiv}C-$), 212.31, 215.89, 221.23, 223.37 (Mo carbonyls). IR (KBr): ν(CO) 2047 (s), 2014 (s), 1985 (b) cm^{-1}. Anal. Calcd for **4** ($C_{19}H_{15}O_5BF_4Mo_2$): C, 37.87; H, 2.49. Found: C, 37.88; H, 2.43.

Synthesis of $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}HOCH_2C{\equiv}CCH_2)][BF_4]$ (5). To the dicarbenium species **3** was added 10 mL of CH_2Cl_2/H_2O (10:1), and the mixture was stirred for 1 h. Addition of Et_2O (20 mL) gave quantitatively an orange precipitate identified as compound **5**.

^1H NMR (250 MHz, $CDCl_2$): δ 3.35 (s, 1H, $-CH_2$), 3.67 (b, 1H, $-OH$), 4.20 (m, 1H), 4.55 (m, 1H), 4.85 (s, 1H, $-CH_2$), 5.15 (s, 2H, $-CH_2O$), 5.25 (m, 1H), 5.30 (m, 1H, mostly obscured by CD_2Cl_2 signal), 5.60 (m, 1H), 5.70 (m, 1H), 5.85 (m, 1H), 6.45 (m, 1H). IR (KBr): ν(CO) 2045 (s), 2013 (s), 1984 (b) cm^{-1}.

Synthesis of $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}CH_2C{\equiv}CCH_2C_6H_4\text{-}OMe)][BF_4]$ (6a,b). One milliliter of anisole was added to the dicarbenium complex **3**, prepared in situ from $[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^2\text{-}MeOCH_2C{\equiv}CCH_2OMe)]$ (**2**; 50 mg, 0.088 mmol), and the reaction mixture was stirred for 1 h. Addition of Et_2O (10 mL) gave an orange precipitate. The precipitate was washed several times with Et_2O, dried under vacuum, and identified as an inseparable mixture of the two isomers **6a**,**b**; yield 55 mg (83%).

6a: ^1H NMR (250 MHz, acetone-d_6) δ 3.41 (s, 1H, $-CH_2$), 3.77 (s, 3H, CH_3OPh), 4.39 (m, 1H), 4.49 (s, 1H, $-CH_2$), 4.52 (m, 1H), 4.82 (dd, AB system, 2H, $-CH_2Ph$), 5.16 (m, 1H), 5.49 (m, 1H), 5.60 (s, 2H, solvated CH_2Cl_2), 6.09 (m, 1H), 6.23 (m, 1H), 6.76 (m, 1H), 6.92 (d, 2H, $-C_6H_4-$, aromatic protons),

---

(10) Connelly, N. G.; Lucy, A. R.; Payne, J. D.; Galas, A. M. R.; Geiger, W. E. *J. Chem. Soc., Dalton Trans.* **1983**, 1879.

(11) Drage, J. S.; Vollhardt, K. P. C. *Organometallics* **1986**, *5*, 280.

7.30 (d, 2H, $-C_6H_4-$, aromatic protons); IR (KBr) ν(CO) 2045 (s), 2011 (s), 1982 (b) cm^{-1}.

6b: ^{1}H NMR (250 MHz, acetone-d_6) δ 3.54 (s, 1H, $-CH_2$), 3.84 (s, 3H, CH_3OPh), 4.39 (m, 1H), 4.50 (m, 1H), 4.87 (s, 1H, $-CH_2$), 4.90 (dd, Ab system, 2H, $-CH_2Ph$), 5.16 (m, 1H), 5.45 (m, 1H), 6.09 (m, 1H), 6.23 (m, 1H), 6.70 (m, 1H), 6.90 (m, 1H, $-C_6H_4-$, aromatic proton), 7.00 (m, 1H, $-C_6H_4-$, aromatic proton), 7.29 (m, 2H, $-C_6H_4-$, aromatic protons). IR (KBr): ν(CO) 2045 (s), 2011 (s), 1982 (b) cm^{-1}. Anal. Calcd for **6a**,**b** ($C_{25}H_{19}O_5BF_4Mo_2 \cdot CH_2Cl_2$): C, 40.89; H, 2.75. Found: C, 40.61; H, 3.01.

Synthesis of [FvMo$_2$(CO)$_4$(μ-η^2:η^2-C$_5$H$_5$NCH$_2$C≡CCH$_2$NC$_5$H$_5$)][BF$_4$]$_2$ (7). An excess of pyridine was distilled directly into a Schlenk tube containing the dicarbenium species **3** prepared in situ from [FvMo$_2$(CO)$_4$(μ-η^2:η^2-MeOCH$_2$C≡CCH$_2$OMe)] (**2**; 50 mg, 0.088 mmol). The reaction mixture was stirred for 1 h. Addition of Et_2O gave an orange-red precipitate. After removal of the supernatant solution, the precipitate was washed several times with Et_2O and dried under vacuum. The compound was first identified with two molecules of solvated pyridine (**7**·2py). Further recrystallization from CH_2Cl_2/Et_2O gave red crystals identified as **7**, yield 55 mg (80%).

^{1}H NMR (250 MHz, acetone-d_6): δ 4.41 (m, 2H), 4.75 (m, 2H), 5.37 (s, 2H, $-CH_2N$), 5.60 (m, 2H), 6.15 (m, 2H), 6.81 (s, 2H, $-CH_2N$), 8.08, 8.75, 9.33 (t, t, d, 5H, C_5H_5N-), 8.50, 8.78, 8.88 (t, d, t, 5H, C_5H_5N-). IR (KBr): ν(CO) 2001 (s), 1963 (s), 1928 (s), 1903 (sh) cm^{-1}. Anal. Calcd for **7** ($C_{28}H_{22}O_4N_2B_2F_8Mo_2$): C, 41.17; H, 2.69; N, 3.43. Found: C, 41.55; H, 2.93; N, 3.65.

Synthesis of [FvMo$_2$(CO)$_4$(μ-η^2:η^2-PPh$_3$H$_2$CC≡CCH$_2$PPh$_3$)][BF$_4$]$_2$ (8). A CH_2Cl_2 solution (5 mL) of triphenylphosphine (60 mg, 0.23 mmol) was added to a Schlenk tube containing the dicarbenium species **3**, prepared in situ from [FvMo$_2$(CO)$_4$(μ-η^2:η^2-MeOCH$_2$C≡CCH$_2$OMe)] (**2**; 50 mg, 0.088 mmol). The reaction mixture was stirred for 1 h. Addition of Et_2O gave an orange precipitate. After removal of the supernatant solution, the precipitate was washed several times with Et_2O and dried under vacuum; yield 60 mg (50%).

8: ^{1}H NMR (250 MHz, acetone-d_6) δ 3.45, (m, 2H), 3.85 (m, 2H), 4.35 (d, 2H, $-CH_2$-P, $J_{P-H} = 12$ Hz), 5.25 (m, 2H), 5.58 (m, 2H), 5.70 (s, 2H, $-CH_2-$P, $J_{P-H} = 0$ Hz), 7.30−7.90 (m, 30H, C_6H_5). IR (KBr): ν(CO) 1994 (s), 1958 (s), 1921 (s), 1900 (sh) cm^{-1}.

Acknowledgment. We gratefully acknowledge the CNRS for supporting this work and the reviewers for their perceptive comments.

OM950730T