

Reaction of Mo(CCMe₃)[OCH(CF₃)₂]₃(dimethoxyethane) with *tert*-Butylacetylene, an Aborted Acetylene Polymerization^{†1}

H. Strutz, J. C. Dewan, and R. R. Schrock*

Contribution from the Department of Chemistry, 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received April 1, 1985

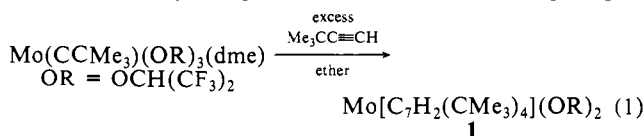
Abstract: The reaction between Mo(CCMe₃)[OCH(CF₃)₂]₃(dme) (dme = 1,2-dimethoxyethane) and excess Me₃CC≡CH yields green, crystalline Mo[C₇H₂(CMe₃)₄][OCH(CF₃)₂]₂ (**1**). Treatment of **1** with 2 equiv of RCO₂H yields the analogous complexes M[C₇H₂(CMe₃)₄](O₂CR)₂ (R = CH₃ (**2a**), CHMe₂ (**2b**), and CF₃ (**2c**)) and with 2 equiv of CF₃C(O)CH₂C(O)CF₃ yields the analogous complex Mo[C₇H₂(CMe₃)₄](hfac)₂ (**3**). Crystals of **2a** belong to the space group P2₁/n with *a* = 9.738 (2) Å, *b* = 16.026 (3) Å, *c* = 17.996 (3) Å, β = 104.71 (1)°, *V* = 2716.4 Å³, *Z* = 4, ρ(calcd) = 1.292 g cm⁻³. The compound is best described as an alkylidene complex of Mo(IV) (counting the alkylidene ligand as a dianion) with a *tert*-butyl group and an η³-2,4,6-tri-*tert*-butylphenyl group attached to the alkylidene carbon atom. It is proposed to form via sequential insertion of 2 equiv of Me₃CC≡CH into the Mo-C_α bond in a deprotonated molybdenacyclobutadiene complex. A proposed intermediate, a "deprotonated molybdenabenzene" complex, can be isolated as a monopyridine adduct, Mo[C₅H(CMe₃)₃][OCH(CF₃)₂]₂(C₅H₅N) (**5**). Crystals of **5** belong to the space group P2₁/c with *a* = 14.667 (2) Å, *b* = 11.913 (3) Å, *c* = 19.064 (6) Å, β = 102.43 (2)°, *V* = 3252.9 Å³, *Z* = 4, and ρ(calcd) = 1.514 g cm⁻³. The planar ring system in **5** is best described as a 1,3,5-tri-*tert*-butyl-substituted 2-ene-3-yne chain in which the first carbon atom is bound to Mo by a double bond. The Mo=C double bond reacts regioselectively with an additional equivalent of Me₃CC≡CH to form an analogous, expanded ring system in which the C≡C triple bond can now add to the Mo=C double bond to form the six-membered ring system in **1**. These proposals are supported by ¹H and ¹³C NMR studies and by the reaction between Mo[C₃(CMe₃)₂][OCH(CF₃)₂]₂(py)₂, a deprotonated molybdenacyclobutadiene complex, and Me₃SiC≡CH to give Mo[C₇H₂(CMe₃)₂(SiMe₃)₂][OCH(CF₃)₂]₂ regioselectively.

We have been studying the reactions of Mo(VI) and W(VI) alkylidene complexes with internal or terminal acetylenes.^{2,3} One of the possible reactions in the case of internal acetylenes is formation of a metallacyclobutadiene ring which subsequently breaks up to reform an alkylidene complex and an acetylene. In some cases, this catalytic acetylene metathesis reaction is quite rapid and virtually the only reaction observed. More often, however, other reactions compete or dominate, most commonly polymerization of the acetylene to give as yet unidentified polymers. In the process of studying reactions between complexes of the type Mo(CCMe₃)(OR)₃^{2b,3} and terminal acetylenes, we discovered what we believed might be a step in a polymerization process that consists of formation of larger and larger unsaturated MC_x ring systems (*x* odd), i.e., formation of a "molybdenabenzene" complex from a molybdenacyclobutadiene complex. Close examination of the system showed that not to be the case, however. A reduced molybdenum alkylidene complex is formed by a series of acetylene insertions into what can be viewed as a Mo=C bond followed by a related internal cyclization reaction. The solution of this puzzle, including the isolation and structural characterization of a reaction intermediate, is reported here. These findings help us to understand what may be a general mechanism of acetylene polymerization by alkylidene complexes and also shed some light on the nature of at least one type of reduced molybdenum alkylidene complex.

Results and Discussion

Synthesis and X-ray Structure of Mo[C₇H₂(CMe₃)₄](O₂CCH₃)₂

The reaction between Mo(CCMe₃)[OCH(CF₃)₂]₃(dme) (dme = 1,2-dimethoxyethane) and excess Me₃CC≡CH yields a green crystalline complex in high yield which contains a total of 3 equiv of Me₃CC≡CH plus the neopentylidene ligand, but only two of the original acetylenic protons and two alkoxide groups (eq 1).

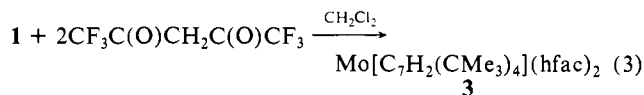
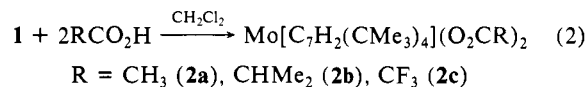


[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Table I. Selected Bond Distances (Å) and Angles (deg) for Mo[C₇H₂(CMe₃)₄](O₂CMe)₂ (**2a**) (See Figure 1).

Mo-O(1)	2.144 (2)	C(5)-C(6)	1.429 (4)
Mo-O(2)	2.190 (2)	C(6)-C(7)	1.482 (3)
Mo-O(3)	2.124 (2)	C(7)-C(8)	1.404 (3)
Mo-O(4)	2.264 (2)	C(8)-C(9)	1.435 (3)
Mo-C(5)	1.945 (3)	C(9)-C(23)	1.485 (3)
Mo-C(6)	2.178 (2)	C(14)-C(23)	1.332 (4)
Mo-C(7)	2.253 (2)	C(6)-C(14)	1.516 (3)
Mo-C(8)	2.300 (3)		
Mo-C(9)	2.355 (3)		
Mo-C(5)-C(10)	138.6 (2)	C(6)-C(7)-C(19)	125.3 (2)
Mo-C(5)-C(6)	78.8 (2)	C(6)-C(7)-C(8)	112.7 (2)
C(6)-C(5)-C(10)	141.7 (2)	C(8)-C(7)-C(19)	121.9 (2)
C(9)-C(23)-C(14)	119.9 (2)	C(5)-C(6)-C(7)	109.8 (2)
C(23)-C(14)-C(6)	110.1 (2)	C(5)-C(6)-C(14)	129.1 (2)
C(23)-C(14)-C(15)	124.9 (2)	C(7)-C(6)-C(14)	116.1 (2)
C(15)-C(14)-C(6)	124.7 (2)	C(7)-C(8)-C(9)	115.6 (2)
		C(8)-C(9)-C(23)	116.1 (2)

We felt that **1** might be a trigonal-bipyramidal tri-*tert*-butylmolybdenabenzene complex containing the MoC₅ ring and a *tert*-butylacetylidene ligand in the trigonal plane. Although crystals of **1** suitable for X-ray study could not be obtained, more suitable crystalline derivatives analogous to **1** (according to their ¹H and ¹³C NMR spectra; see later) could be prepared as shown in eq 2 and 3. Compounds **1** (green), **2a-c** (red), and **3** (green-black)



(1) Multiple Metal-Carbon Bonds. 40. For Part 39 see: Schrock, R. R.; Muzdzek, J. S.; Freudenberger, J. H.; Churchill, M. R.; Ziller, J. W. *Organometallics*, in press.

(2) (a) Sancho, J.; Schrock, R. R. *J. Mol. Catal.* **1982**, *15*, 75-79. (b) McCullough, L. G.; Schrock, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 4067. (c) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554. (d) Freudenberger, J. H.; Schrock, R. R.; Churchill, M. R.; Rheingold, A. L.; Ziller, J. W. *Organometallics* **1984**, *3*, 1563. (e) Schrock, R. R.; Pedersen, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1984**, *3*, 1574.

(3) McCullough, L. G.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* previous paper in this issue.

Table II. Deviations (Å) from Mean Planes and Dihedral Angles (deg) between Planes in **2a**

plane 1	Deviations from Mean Planes ^a					
	Mo	C(5)	C(6)	C(10)		
	0.012	-0.055	0.018	0.025		
plane 2	C(6)	C(7)	C(8)	C(9)	C(24)	C(19)
	-0.009	0.017	-0.018	0.010	-0.081	0.172
plane 3	C(6)	C(14)	C(23)	C(9)	C(24)	C(15)
	-0.009	0.018	-0.019	0.010	-0.145	0.193
ext dihedral ang between planes 2 and 3	42.08°					
plane 4	Mo	O(1)	O(2)	C(1)	C(2)	
	-0.049	0.044	0.041	0.009	-0.045	
plane 5	Mo	O(3)	O(4)	C(4)	C(4)	
	-0.103	0.092	0.077	0.036	-0.102	
dihedral ang between planes 4 and 5	112.13°					

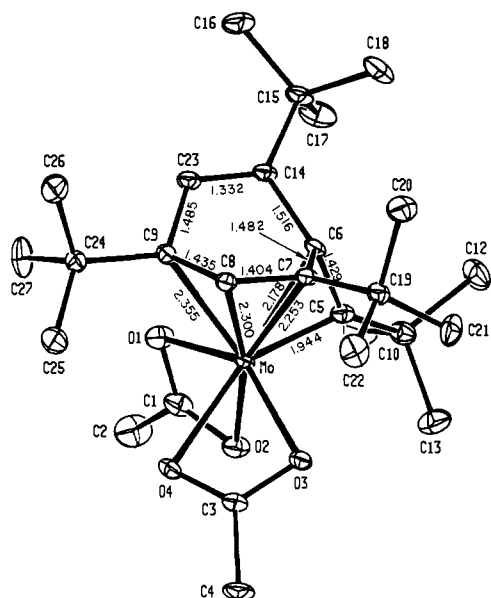
^aMean plane defined by first four atoms only.

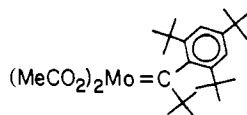
Table IV. ^{13}C NMR Shifts for the Ligand Carbon Atoms (Excluding *tert*-Butylmethyl Groups) in Compounds **1**, **2a-c**, **3**, and **4** at 298 K

compd	C(5)	C(7,14)	C(8,23) ^a	C(6,9)	C(15,19)	C(10)	C(24)
1 (C_6D_6)	297.4	129.5	102.2	98.1 66.7	35.0 ^b	46.8	32.6 ^b
2a (toluene- d_8)	309.7	153.5 111.2	136.1 98.4	113.4 73.1	37.9 35.0	47.0	36.3
2b (C_6D_6)	309.1	153.7 113.4	136.0 98.5	110.8 73.3	37.9 ~35	46.9	36.2
2c (C_6D_6)	322.2	133.7	113.8	118.5 71.5	36.3 ^b	48.5	36.1 ^b
3 (C_6D_6)	323.8	156.4 107.7	131.3 94.1	133.3 79.2	38.5 ^b 35.6 ^b	48.6	35.3 ^b
4 (C_6D_6)	296.8	133.7 104.8	117.2 ^c 106.2 ^c	80.9 73.1	34.8	46.4	

^a $J_{\text{CH}} = 158\text{--}165$ Hz. ^b Assignments arbitrary. ^c Assigned only on basis of relatively high intensity in $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum.

than 0.2 Å from plane 3. The external dihedral angle between planes 2 and 3 is 42.08°. The C(9)–C(23) and C(6)–C(14) bonds are close to being single bonds while C(14)–C(23) is essentially a double bond. All these data suggest that the C(7), C(8), C(9), C(23), C(14) ring system can best be described as a 2,5-diene with metal–carbon single bonds to C(6) and C(9) and one of the double bonds (C(7)–C(8)) strongly bound to the metal. Except for the strained configuration at C(6), the mode of bonding of the C_6 ring in **2a** is entirely analogous to that of η^4 -arene ligands in other complexes.⁵

The acetate ligand containing O(1) and O(2) is more or less symmetrically bonded to the metal in a manner such that the plane containing it roughly bisects the C(14)–C(23) and C(7)–C(8) bonds; O(1) occupies a position roughly beneath the C(14)–C(23) bond. The other acetate ligand is more asymmetrically bound to the metal with O(3) and O(4) roughly equidistant from plane 2. Our interpretation of the structure suggests that the compound in which the arene ring is not bound to the metal, viz. probably



would not exist as such and emphasizes that the relatively low electron count of the metal (14) in the hypothetical Mo(IV) alkylidene complex can be brought up to 18 by twisting the phenyl ring and binding it to the metal in an η^4 fashion. The *tert*-butyl groups are relatively important, we believe, in directing the assembly of the ligand system, as we shall see later, and probably to some extent in sterically blocking intermolecular decomposition during the assembly.

NMR Studies. The ^1H NMR spectrum of **2a** at 257 K is entirely consistent with the asymmetric structure found in the solid state; four different *tert*-butyl groups, two different protons on C(8) and C(23), and two different acetate methyl groups are observed. However, at 367 K, only three types of *tert*-butyl groups, one ring proton, and one acetate resonance are observed. Spectra at 367 and 298 K are shown in Figure 2. Since protons on C(8) and C(23) are interconverting rapidly on the NMR time scale at 367 K, we assume that the *tert*-butyl groups containing C(19) and C(15) are the two *tert*-butyl groups that interconvert at high temperature.

The ^{13}C NMR spectra of **2a** are consistent with the above results. At 298 K, the 11 resonances for the carbon atoms in the ligand (excluding *tert*-butyl methyl groups) can be clearly observed (Table IV). The one with the unusually low field shift at 309.7 ppm we assign to C(5) on the basis of the now well-known low field shift for alkylidene-like α -carbon atoms. The resonances at 153.5 and 111.2 are assigned to carbon atoms C(7,14) on the basis of the fact that they are singlets and the fact that they coalesce at higher temperatures. The doublets at 136.1 and 98.4 are assigned to carbon atoms C(8,23) on the same basis. The

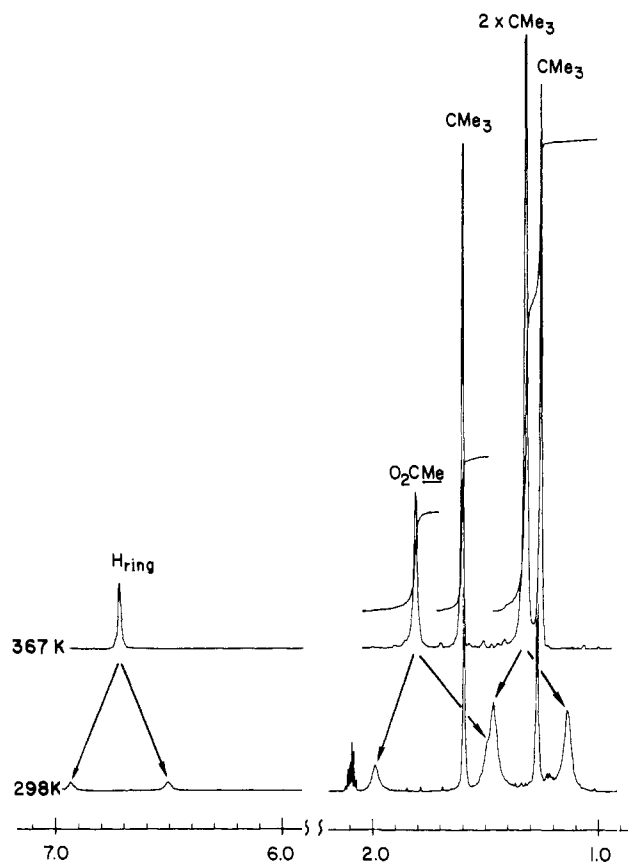


Figure 2. ^1H NMR spectrum of $\text{Mo}[\text{C}_7\text{H}_2(\text{CMe}_3)_4](\text{O}_2\text{CMe})_2$ (**2a**) in toluene- d_8 at 367 and 298 K showing fluxional behavior of η^4 -arene ring.

singlets that do not coalesce at 113.4 and 73.1 are assigned to C(6) and C(9) (or vice versa). The signals at 37.9 and 35.0 are assigned to C(15) and C(19) (or vice versa), since they are in the region where quaternary carbon atom signals are normally found, and the signals coalesce at high temperatures. The noncoalescing signals at 47.0 and 36.3 are assigned to carbon atoms C(10) and C(24), respectively, on the basis of the fact that quaternary carbon atoms in neopentylidene and neopentylidyne complexes are usually shifted downfield from where they are observed in more ordinary *tert*-butyl groups.⁶ Signals for C(1) and C(3) (at 185.8 and 189.3) and for C(4) and C(2) (at 22.8 and 23.4) also coalesce at high temperature.

The NMR data suggest that the C_6 ring is "flipping" so as to produce the equivalent species with C(14) and C(23) bound to the metal and C(7) and C(8) free. We do not know from these data alone whether the acetate ligands physically exchange or

(5) (a) Hull, J. W., Jr.; Gladfelter, W. L. *Organometallics* **1984**, *3*, 605. (b) Huttner, G.; Lange, S. *Acta Crystallogr., Sect. B* **1972**, *28B*, 2019. (c) Churchill, M. R.; Mason, R. *Proc. R. Soc. London* **1966**, *292*, 61.

(6) (a) In $\text{W}(\text{CCMe}_3)(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)(\text{dmpe})$,^{6b} for example, the quaternary carbon resonances for the neopentylidyne, neopentylidene, and neopentyl ligands are found at 51.7, 47.7, and 34.0 ppm, respectively. (b) Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774.

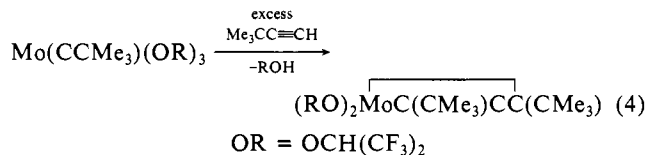
whether they exchange only by virtue of the ring flipping process. We also do not know whether C(6) and C(9) remain bound to the metal during the flipping process, although data we will present later suggest that they do. If the acetate ligands do not physically exchange, as C(14) and C(23) move toward Mo, the first acetate ligand must twist out of the way; as the C(7) and C(8) dissociate, the second acetate twists so that O(3) or O(4) roughly points toward the space created when C(7) and C(8) dissociate.

The ^1H and ^{13}C NMR spectra of **2b** are entirely analogous to those of **2a**. (See Table IV for ^{13}C NMR data.)

We believe the structure of **1** and **2c** to be virtually the same as that of **2a** in the solid state. In solution, however, the process of flipping the C_6 ring is relatively fast on the NMR time scale at room temperature and readily accessible lower temperatures. The ^{13}C resonance at 133.7 in the spectrum of **2c** is assigned to the average of C(7) and C(14), that at 113.8 to the average of C(8) and C(23), and that at 36.3 (or 36.1) to the average of C(15) and C(19); all three peaks fall approximately where the average analogous resonances in the high-temperature spectra of **2a** and **2b** fall. The analogous resonances in the ^{13}C NMR spectrum of **1**, the parent compound, are very similar to those in the other compounds. The greatest variation seems to be in the chemical shifts of C(5), C(6), and C(9).

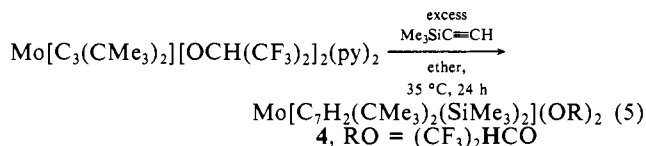
The NMR spectra of **3** suggest that it has essentially the same structure as the other compounds, but the rate of the fluxional process is relatively slow (see Table IV). All carbon atoms in the two $\text{CF}_3\text{C}(\text{O})\text{CHC}(\text{O})\text{CF}_3$ ligands are inequivalent. Only at >370 K is the rate of ring flipping sufficiently fast to cause some broadening of the appropriate signals as observed in the above complexes.

Preparation of a Compound Containing a $\text{C}_7\text{H}_2(\text{CMe}_3)_2(\text{SiMe}_3)_2$ Ligand System. We know that in the presence of pyridine $\text{Mo}(\text{CCMe}_3)[\text{OCH}(\text{CF}_3)_2]_3(\text{dme})$ reacts with excess $\text{Me}_3\text{CC}\equiv\text{CH}$ to give the deprotiomolybdenacyclobutadiene complex $\text{Mo}[\text{C}_3(\text{CMe}_3)_2][\text{OCH}(\text{CF}_3)_2]_2(\text{py})_2$, whose structure has been determined.³ We find that isolated $\text{Mo}[\text{C}_3(\text{CMe}_3)_2][\text{OCH}(\text{CF}_3)_2]_2(\text{py})_2$ reacts with excess $\text{Me}_3\text{CC}\equiv\text{CH}$ in 16 h at 40°C to give largely **1** by ^1H NMR, plus some decomposition products. Therefore, we propose that $\text{Mo}[\text{C}_3(\text{CMe}_3)_2][\text{OCH}(\text{CF}_3)_2]_2$ is the first product formed in the reaction between $\text{Mo}[\text{CCMe}_3][\text{OCH}(\text{CF}_3)_2]_3(\text{dme})$ and excess $\text{Me}_3\text{CC}\equiv\text{CH}$ (eq 4). Com-



pounds analogous to that shown in eq 4 can be isolated from reactions between neopentylidyne complexes containing relatively bulky electron-withdrawing alkoxide ligands (e.g., $\text{OC}(\text{CF}_3)_3$ or $\text{OCMe}(\text{CF}_3)_2$) and excess $\text{Me}_3\text{CC}\equiv\text{CH}$.³

An analogous reaction between $\text{Mo}[\text{C}_3(\text{CMe}_3)_2][\text{OCH}(\text{CF}_3)_2]_2(\text{py})_2$ and $\text{Me}_3\text{SiC}\equiv\text{CH}$ proceeds smoothly as shown in eq 5. The ^1H and ^{13}C NMR spectra of **4** show it to be a "nonfluxional" molecule of a type analogous to **1**, **2**, and **3** (Table IV). However, we believe that the ring system is still flipping



rapidly; i.e., that **4** is "nonfluxional" only by virtue of an unsymmetric substitution of CMe_3 and SiMe_3 groups on the C_6 ring. Also note that the $\text{OCH}(\text{CF}_3)_2$ ligands do not physically exchange; i.e., they are inequivalent also by virtue of the unsymmetric substitution pattern.

Let us use a numbering scheme in discussing **4** that is analogous to that we used for **2a** (Figure 1). We can first say that a CMe_3 group is bound to C(5) on the basis of the relatively unique shift for the quaternary carbon atom (46.4 ppm; Table IV). The second

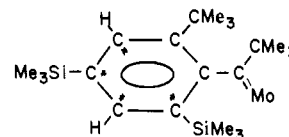


Figure 3. Proposed substitution pattern in the $\text{C}_7\text{H}_2(\text{CMe}_3)_2(\text{SiMe}_3)_2$ ligand in **4**.

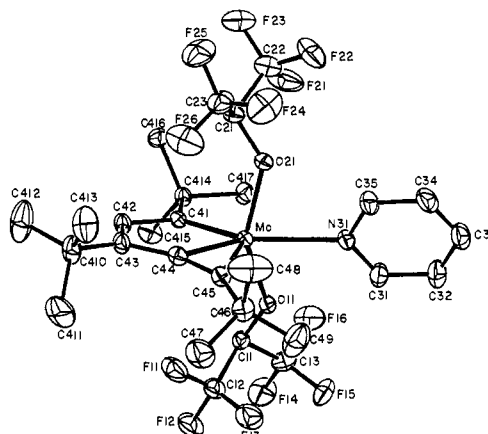


Figure 4. ORTEP drawing of $\text{Mo}[\text{C}_3\text{H}(\text{CMe}_3)_3][\text{OCH}(\text{CF}_3)_2]_2(\text{py})$ (**5**) (30% probability ellipsoids; hydrogen atoms omitted).

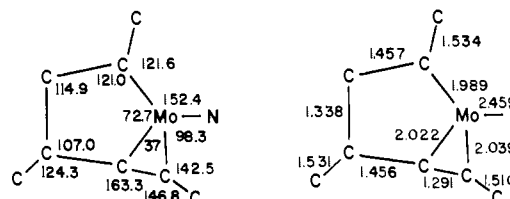
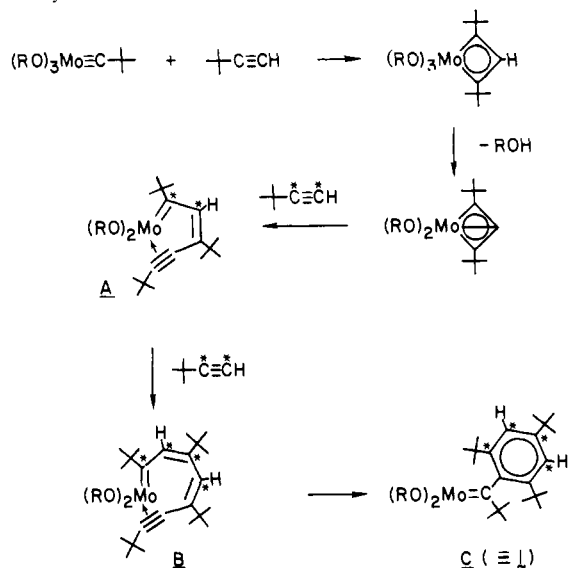


Figure 5. Schematic drawings of the ring system in **5** showing relevant bond lengths (angstroms) and angles (degrees).

CMe_3 group and two SiMe_3 groups are attached to C(5), C(9), and C(14). The CMe_3 group cannot be bound to C(9), or a relatively symmetric structure would result. Therefore, a SiMe_3 group is bound to C(9) and the second CMe_3 group and SiMe_3 group are bound to C(7) and C(14). The signal for the quaternary carbon atom of the CMe_3 group bound to C(7) or C(14) is then an average of where it would be found in the static structure if it were C(19) and where it would be if it were C(15). Two signals are found for C(8) and C(23) since different groups are bound to C(7) and C(14). Each signal (that for C(8) and that for C(23)) is an average due to the fluxional process that exchanges C(8) and C(23). The same is true of the signals for C(7) and C(14). Interestingly, one of the signals assigned to C(7) or C(14) occurs well upfield (at 104.8) from where the other does (at 133.7). The latter is characteristic of a carbon atom substituted by a CMe_3 group (129.5 in **1**). The upfield shift is most likely caused by the presence of the Me_3Si group. Therefore, we can say with some confidence that the organic system is substituted as shown (in arene form) in Figure 3. The starred carbon atoms are those in the $\text{Me}_3\text{SiC}\equiv\text{CH}$ that was added.

Isolation and X-ray Structure of an Intermediate in the Reaction between $\text{Mo}[\text{C}_3(\text{CMe}_3)_2][\text{OCH}(\text{CF}_3)_2]_2(\text{py})_2$ and $\text{Me}_3\text{CC}\equiv\text{CH}$. We noted above that the reaction between $\text{Mo}[\text{C}_3(\text{CMe}_3)_2][\text{OCH}(\text{CF}_3)_2]_2(\text{py})_2$ and excess $\text{Me}_3\text{CC}\equiv\text{CH}$ for 16 h at 40°C yields **1**. If the reaction mixture is examined after ~ 3 h, however, relatively little **1** is present. In addition to primarily starting material, an intermediate is observed. Fortunately, it (**5**) can be isolated from the mixture as green crystals by careful fractional crystallization.

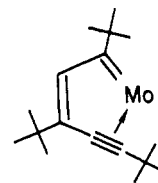
An ORTEP drawing of **5** is shown in Figure 4 and schematic drawings in Figure 5. The geometry of **5** is roughly trigonal bipyramidal with the metallacyclic ring and the nitrogen of the pyridine ligand lying in the equatorial plane. The axial ligands' oxygen atoms are bent back from the ring system so that O-

Scheme I. Proposed Mechanism of Forming the $\text{C}_7\text{H}_2(\text{CMe}_3)_4$ Ligand System

(21)–Mo–O(11) is only $145.9 (1)^\circ$. This should be compared with an O–Mo–O angle of $152.2 (1)^\circ$ in $\text{Mo}[\text{C}_3(\text{CMe}_3)_2][\text{OCH}(\text{CF}_3)_2]_2(\text{py})_2$,³ a distorted octahedral deprotonated molybdenacyclobutadiene complex, and $157.6 (4)^\circ$ in $\text{W}(\text{C}_3\text{Et}_3)[\text{OCH}(\text{CF}_3)_2]_3$,^{2d} a triethyltungstenacyclobutadiene complex. The Mo–O(21) and Mo–O(11) bond lengths are similar to what they are in the other two complexes, as are the relatively large Mo–O(21)–C(21) and Mo–O(11)–C(11) bond angles of $134.5 (2)^\circ$ and $135.3 (2)^\circ$, characteristic of relatively ionic, poor π -bonding fluoroalkoxide ligands. The two $\text{OCH}(\text{CF}_3)_2$ ligands are turned so that the $\text{CH}(\text{CF}_3)_2$ groups lie over the Mo–C(41)–C(42)–C(43)–C(44)–C(45) ring system, perhaps because the plane of the pyridine ligand is essentially perpendicular to the plane of the metallacyclic ring system (108° ; Table VI). A CF_3 group appears to occupy the “hole” between two *tert*-butyl groups or between a *tert*-butyl group and the pyridine ring.

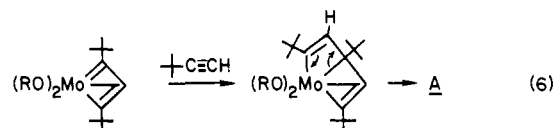
The atoms Mo, C(41), C(42), C(43), C(44), and C(45) form a plane from which C(46), C(410), and C(414) deviate little (Table VI). The plane of the pyridine ligand is essentially perpendicular to the plane of the metallacyclic ring, and the Mo–N bond length is relatively long, as one would expect for pyridine bound trans to a relatively strongly bound carbocyclic system (cf. Mo–N = $2.373 (2) \text{ \AA}$ in $\text{Mo}[\text{C}_3(\text{CMe}_3)_2][\text{OCH}(\text{CF}_3)_2]_2(\text{py})_2$ ³ or $2.492 (6) \text{ \AA}$ in $\text{Mo}[\text{C}_3\text{Me}_2(\text{CMe}_3)]\text{Cl}_3(\text{tmeda})$ ^{2e}). The various angles in the equatorial ring system are relatively uninformative compared to the bond distances. The shortest C–C bond length (C(44)–C(45)) is $1.291 (5) \text{ \AA}$, consistent with it being a metal-bound C–C triple bond. The lengths of the C(43)–C(44) and C(41)–C(42) bonds are consistent with each being somewhere between a double and a single bond, while the C(42)–C(43) bond length ($1.338 (5) \text{ \AA}$) is consistent with it being a double bond. Of the Mo–C bonds, Mo–C(41) is approximately a double bond at $1.989 (3) \text{ \AA}$, with Mo–C(44) and Mo–C(45) being somewhat longer ($2.022 (4)$ and $2.039 (4) \text{ \AA}$, respectively). The latter are approximately what are found in acetylene complexes of group 6 metals in higher oxidation states (e.g., $2.053 (13)$, $2.063 (14)$, $2.032 (15)$, and $2.050 (14) \text{ \AA}$ in $[\text{W}(\text{PhC}\equiv\text{CPh})\text{Cl}_2(\text{dimethoxyethane})]_2(\mu\text{-N}_2)$).^{7b} Therefore, the Mo–C(41) bond is best regarded as a double bond. Overall, then, the best valence bond description of the ring system is

The ^{13}C NMR spectra of **5** are consistent with the above valence bond description. Resonances for the five-ring carbon atoms are found at 307.5, 202.9, 194.1 (d, $J_{\text{CH}} = 16 \text{ Hz}$), 163.0, and 156.6 (d, $J_{\text{CH}} = 150 \text{ Hz}$). The 307, 157, and 194 ppm resonances can

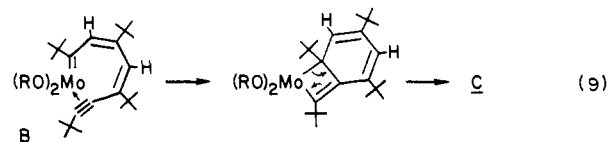
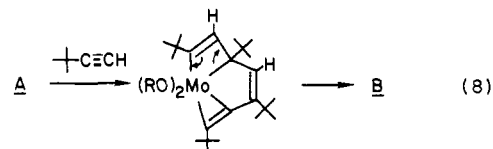
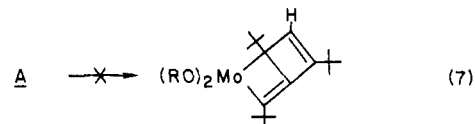


be assigned readily to C(41), C(42), and C(43), respectively. The assignment of the 203 and 163 ppm resonances is uncertain. We prefer that the 203 ppm resonance be assigned to C(45) on the basis of the fact that the resonance for a *tert*-butyl-substituted α -carbon atom in a deprotonated molybdenacyclobutadiene complex always is found downfield of the resonance for the β -carbon atom.³

Mechanism of Formation of $\text{Mo}[\text{C}_7\text{H}_2(\text{CMe}_3)_4][\text{OCH}(\text{CF}_3)_2]_2(\text{py})$ (1**).** We can now propose how the $\text{C}_7\text{H}_2(\text{CMe}_3)_4$ system in **1** might be assembled (Scheme I). *tert*-Butylacetylene adds to $\text{Mo}(\text{CCMe}_3)[\text{OCH}(\text{CF}_3)_2]_3(\text{dme})$ to give a molybdenacyclobutadiene complex from which alcohol is lost to give a “deprotonated” version. The deprotonated metallacyclobutadiene reacts regioselectively (presumably for steric reasons) with a second equivalent of $\text{Me}_3\text{CC}\equiv\text{CH}$ to give **A** (Scheme I), a reaction that can be viewed as an addition of the acetylene to a $\text{Mo}=\text{C}$ double bond followed by rearrangement (eq 6). **A** is the species that is trapped



by pyridine to give **5**. If the acetylenic bond in **A** were to add to the $\text{Mo}=\text{C}$ bond, the resulting system (eq 7) would be able to rearrange only to a cyclopentadienylydene- or cyclobutadiene-substituted alkylidene complex; evidently neither is



favored (if the intermediate actually forms) relative to the back equation to give **A**. **A** then reacts readily and regioselectively with another molecule of $\text{Me}_3\text{CC}\equiv\text{CH}$ to give **B**, most likely as shown in eq 8. The $\text{Mo}=\text{C}$ bond in **B** now can react with the $\text{C}\equiv\text{C}$ bond at the end of the chain to give **C** as shown in eq 9.

The key to the mechanism shown in Scheme I is the selective reaction of a $\text{C}\equiv\text{C}$ bond with a molybdenum–carbon double bond, first in the deprotonated molybdenacyclobutadiene complex (eq 6), then in **A** (eq 8), and then (intramolecularly) in **B** (eq 9). The addition of an acetylene to a $\text{M}=\text{C}$ bond was first noted by Dötz in a low oxidation state complex.⁸ More recently, several variations of this reaction have found application in acetylene polymerization and in organic transformations.⁹ The first example of a reaction

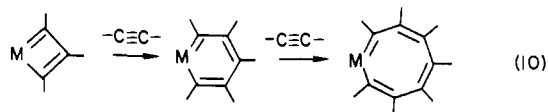
(8) (a) Dötz, K. H.; Kreiter, C. G. *J. Organomet. Chem.* **1975**, *99*, 309. (b) Dötz, K. H.; Kreiter, C. G. *Chem. Ber.* **1976**, *109*, 2026.

(9) (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587 and references therein. (b) Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737. (c) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422. (d) Wulff, W. D.; Kaesler, R. W.; Petersen, G. A.; Tang, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 1060.

(7) (a) Iteľ, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33. (b) Churchill, M. R.; Li, Y.-J.; Theopold, K. H.; Schrock, R. R. *Inorg. Chem.* **1984**, *23*, 4472.

between a high oxidation state alkylidene complex ($\text{Ta}(\eta^5\text{-C}_5\text{H}_5)(\text{CHCMe}_3)\text{Cl}_2$) and an acetylene ($\text{PhC}\equiv\text{CPh}$) was noted in 1979.¹⁰ Although there has been no other unambiguous example involving a high oxidation state alkylidene complex, there is considerable circumstantial evidence that this type of reaction may be quite general.

We believe that the observations reported here lend support to the proposition that MC_x (x odd) rings can continue to grow via sequential insertions into $\text{M}=\text{C}$ bonds³ and that this may be an important mechanism of what we mentioned in the introduction as a fairly commonly observed polymerization of acetylenes by Mo(VI) and W(VI) trialkoxyalkylidene complexes (eq 10). This



proposition may be especially difficult to prove, as one can argue that the rate of reaction of the metallacyclobutadiene complex with additional acetylene is the slowest step; larger rings probably are going to be relatively more reactive because they are floppier, they are less sterically crowded, and the bonds are more localized. But since we know also that alkylidene complexes of tungsten can be protonated to give alkylidene complexes,¹¹ acetylenes could be polymerized by trace quantities of reactive alkylidene complexes formed by the reaction of alkylidyne complexes with traces of water. Therefore, we cannot be certain how general the "ring expansion" mechanism of acetylene polymerization (eq 10) actually is.

What we have documented here is one of the many possible reactions that will compete with acetylene polymerization under certain circumstances. We have documented some other possibilities, e.g., formation of cyclopentadienyl rings, most likely from MC_5R_5 "metallabenzene" ring systems, or ejection of an acetylene from an MC_3R_3 , or possibly, also, an MC_3R_5 ring system, i.e., acetylene metathesis.^{2c,d} Each possibility, including that reported here, depends critically on the identity and size of the anionic ligands. We are continuing to explore the factors that determine which reaction pathway will be taken under a given set of circumstances.

Experimental Section

General experimental methods may be found elsewhere.³ $\text{Mo}(\text{CCMe}_3)[\text{OCH}(\text{CF}_3)_2]_3(\text{dme})$ was prepared as reported in the literature.³ NMR chemical shifts are reported relative to TMS. Expected intensities, multiplicities, and coupling constants (in hertz) are usually omitted. Most ¹³C NMR data are listed in Table I.

Preparations. $\text{Mo}[\text{C}_7\text{H}_2(\text{CMe}_3)_4][\text{OCH}(\text{CF}_3)_2]_2$ (**1**). Excess $\text{Me}_3\text{CC}\equiv\text{CH}$ (500 μL , 4.08 mmol) was added to $\text{Mo}(\text{CCMe}_3)[\text{OCH}(\text{CF}_3)_2]_3(\text{dme})$ in ether (10 mL). The solution quickly turned red and then slowly changed to green. After stirring the reaction for 2 h, the solvent and excess $\text{Me}_3\text{CC}\equiv\text{CH}$ were removed in vacuo and the residue was extracted with pentane. The extracts were filtered, concentrated, and cooled to -40°C to give 0.45 g (91%) of dark-green crystals in three crops: ¹H NMR (C_6D_6) δ 6.52 (s, 2, H_{ring}), 5.26 (sept, $J_{\text{HF}} = 6.3$, 2, $\text{OCH}(\text{CF}_3)_2$), 1.58 (s, 9, CMe_3), 1.14 (s, 9, CMe_3), 1.06 (s, 18, CMe_3); ¹³C NMR (C_6D_6) δ 123.7 (q, $J_{\text{CF}} = 291$, $\text{OCH}(\text{CF}_3)_2$), 77.9 (d sept, $J_{\text{CH}} = 146$, $J_{\text{CF}} = 31$, $\text{OCH}(\text{CF}_3)_2$), 33.4, 32.9, 30.9 (CMe_3). Anal. Calcd for $\text{MoC}_{29}\text{H}_{40}\text{O}_2\text{F}_{12}$: C, 46.78; H, 5.42. Found: C, 46.90; H, 5.56.

$\text{Mo}[\text{C}_7\text{H}_2(\text{CMe}_3)_4](\text{O}_2\text{CMe})_2$ (**2a**). $\text{Mo}[\text{C}_7\text{H}_2(\text{CMe}_3)_4][\text{OCH}(\text{CF}_3)_2]_2$ (600 mg, 0.81 mmol) was dissolved in ~ 10 mL of dichloromethane, and 1.0 mmol of glacial acetic acid was added. After 2 h, the dichloromethane, excess acetic acid, and $(\text{CF}_3)_2\text{CHOH}$ were removed in vacuo, leaving a red solid. Recrystallization of the red solid from pentane at -40°C yielded red crystals in 78% yield. The analytical sample was prepared by recrystallizing again from pentane: ¹H NMR (toluene- d_8 , 257 K) δ 6.97 (H_{ring}), 6.53 (H_{ring}), 1.97 (CH_3CO_2), 1.62 (CMe_3), 1.48 (CMe_3 and one CH_3CO_2), 1.32 (CMe_3), 1.15 (CMe_3); see Figure 1; ¹³C NMR (C_6D_6) δ 189.3 (CH_3CO_2), 185.8 (CH_3CO_2), 32.3, 31.3, 30.8 (overlapping CMe_3 signals), 23.4 (CH_3CO_2), 22.8 (CH_3CO_2); see Table I. Anal. Calcd for $\text{MoC}_{27}\text{H}_{44}\text{O}_4$: C, 61.35; H, 8.39. Found: C, 61.48; H, 8.49.

Table V. Selected Bond Distances (\AA) and Angles (deg) in $\text{Mo}[\text{C}_7\text{H}_2(\text{CMe}_3)_4][\text{OCH}(\text{CF}_3)_2]_2(\text{py})$ (**5**) (See Figure 4)

Mo-C(41)	1.989 (3)	C(43)-C(44)	1.456 (5)
Mo-C(44)	2.022 (4)	C(44)-C(45)	1.291 (5)
Mo-C(45)	2.039 (4)	C(41)-C(414)	1.534 (5)
Mo-N(31)	2.459 (3)	C(43)-C(410)	1.531 (5)
Mo-O(11)	1.965 (2)	C(45)-C(46)	1.510 (5)
Mo-O(21)	1.974 (2)	O(21)-C(21)	1.371 (4)
C(41)-C(42)	1.457 (5)	O(11)-C(11)	1.379 (4)
C(42)-C(43)	1.338 (5)		
N(31)-Mo-C(41)	152.4 (1)	C(42)-C(43)-C(44)	107.0 (3)
N(31)-Mo-C(44)	134.4 (1)	C(43)-C(44)-C(45)	163.3 (4)
N(31)-Mo-C(45)	98.3 (1)	C(44)-C(45)-C(46)	146.8 (4)
C(44)-Mo-C(41)	72.7 (1)	C(410)-C(43)-C(44)	124.3 (3)
C(45)-Mo-C(44)	37.1 (1)	O(21)-Mo-O(11)	145.9 (1)
Mo-C(41)-C(414)	121.6 (2)	N(31)-Mo-O(11)	78.3 (1)
Mo-C(44)-C(43)	124.1 (3)	N(31)-Mo-O(21)	75.3 (1)
Mo-C(41)-C(42)	121.0 (2)	Mo-O(21)-C(21)	134.5 (2)
Mo-C(45)-C(46)	142.5 (3)	Mo-O(11)-C(11)	135.3 (2)
C(41)-C(42)-C(43)	114.9 (3)	Mo-C(45)-C(44)	70.7 (2)
		Mo-C(44)-C(45)	72.2 (2)

$\text{Mo}[\text{C}_7\text{H}_2(\text{CMe}_3)_4](\text{O}_2\text{CHMe}_2)_2$ (**2b**). The preparation of **2b** is analogous to that for **2a**. It is isolated by sublimation (55°C , 0.001 μm) as a waxy red solid in 83% yield: ¹H NMR (toluene- d_8) δ 6.92 (H_{ring}), 6.53 (H_{ring}), 2.60 (CHMe_2), ~ 2.1 (CHMe_2), 1.62 (CMe_3), 1.49 (CMe_3), 1.30 (br s, CMe_3 and CHMe_2), 1.16 (CMe_3), 0.95 (CHMe_2); ¹³C NMR (C_6D_6) see Table I. Anal. Calcd for $\text{MoC}_{31}\text{H}_{52}\text{O}_4$: C, 63.68; H, 8.96. Found: C, 64.09; H, 9.00.

$\text{Mo}[\text{C}_7\text{H}_2(\text{CMe}_3)_4](\text{O}_2\text{CCF}_3)_2$ (**2c**). The preparation of **2c** is analogous to that of **2a** (yield 80%). An analytical sample was prepared by crystallization followed by sublimation (55°C , 0.001 μm): ¹H NMR (C_6D_6) δ 6.65 (2, H_{ring}), 1.45 (CMe_3), 1.11 (18, CMe_3), 1.09 (CMe_3); ¹³C NMR (C_6D_6) δ 169.4 (q, $J_{\text{CF}} = 41$, O_2CCF_3), 114.3 (q, $J_{\text{CF}} = 285$, O_2CCF_3), 30.3, 30.9, 31.6 (overlapping CMe_3 peaks); see Table I. Anal. Calcd for $\text{MoC}_{27}\text{H}_{38}\text{O}_4\text{F}_6$: C, 50.95; H, 6.02. Found: C, 50.63; H, 5.89.

$\text{Mo}[\text{C}_7\text{H}_2(\text{CMe}_3)_4][\text{CF}_3\text{C}(\text{O})\text{CHC}(\text{O})\text{CF}_3]_2$ (**3**). The preparation of **3** is analogous to that of **2a**. It was isolated as green-black microcrystals after two sublimations (65°C , 0.001 μm): yield 70%; ¹H NMR (C_6D_6) δ 7.07 (H_{ring}), 6.82 (H_{ring}), 6.27 ($\text{CF}_3\text{C}(\text{O})\text{CHC}(\text{O})\text{CF}_3$), 6.06 ($\text{CF}_3\text{C}(\text{O})\text{CHC}(\text{O})\text{CF}_3$), 1.43, 1.36, 1.10, 0.74 (CMe_3 groups); ¹³C NMR (C_6D_6) δ 178.0 (q, $J_{\text{CF}} = 38$, $\text{CF}_3\text{C}(\text{O})$), 176.0 (q, $J_{\text{CF}} = 36$, $\text{CF}_3\text{C}(\text{O})$), 171.4 (overlapping quartets, $J_{\text{CF}} = 37$, $\text{CF}_3\text{C}(\text{O})$), 118.5, 118.0, 117.3, 117.1 (each a q, $J_{\text{CF}} = 284$, $\text{CF}_3\text{C}(\text{O})$), 93.4, 91.5 (each a d, $J_{\text{CH}} = 166$, 170, $\text{CF}_3\text{C}(\text{O})\text{CHC}(\text{O})\text{CF}_3$). Anal. Calcd for $\text{MoC}_{33}\text{H}_{44}\text{O}_4\text{F}_{12}$: C, 48.07; H, 4.89. Found: C, 48.57; H, 5.26.

$\text{Mo}[\text{C}_7\text{H}_2(\text{CMe}_3)_2(\text{SiMe}_3)_2][\text{OCH}(\text{CF}_3)_2]_2$ (**4**). A solution of $\text{Mo}[\text{C}_3(\text{CMe}_3)_2][\text{OCH}(\text{CF}_3)_2]_2(\text{py})_2$ (0.60 g, 0.81 mmol), 1,2-dimethoxyethane (340 μL , 3.3 mmol), and 1.16 mL (8.03 mmol) of $\text{Me}_3\text{SiC}\equiv\text{CH}$ dissolved in ether was heated to reflux for 20 h. The ether was removed in vacuo, and the oily green solid was recrystallized from minimum pentane by cooling the solution of -40°C over a period of 2 days to give 607 mg (75%) of green-black crystals: ¹H NMR (C_6D_6) δ 6.40 (H_{ring}), 6.36 (H_{ring}), 5.34, 5.23 (each a m, $J_{\text{HF}} = 6.4$, $\text{OCH}(\text{CF}_3)_2$), 1.56 (CMe_3), 1.01 (CMe_3), 0.21 (SiMe_3), 0.18 (SiMe_3); ¹³C{¹H} NMR (C_6D_6) δ 123.5 (q, $J_{\text{CF}} = 287$, CF_3 groups), 79.6, 77.2 (each a sept, $J_{\text{CF}} = 30$, $\text{OCH}(\text{CF}_3)_2$), 33.0 (CMe_3), -0.8 (SiMe_3), -1.6 (SiMe_3); see Table I. Anal. Calcd for $\text{MoC}_{27}\text{H}_{38}\text{O}_2\text{Si}_2\text{F}_{12}$: C, 41.86; H, 4.94. Found: C, 41.72; H, 4.75.

$\text{Mo}[\text{C}_5\text{H}(\text{CMe}_3)_3][\text{OCH}(\text{CF}_3)_2]_2(\text{py})$ (**5**). A solution of $\text{Mo}[\text{C}_3(\text{CMe}_3)_2][\text{OCH}(\text{CF}_3)_2]_2(\text{py})_2$ (0.60 g, 0.81 mmol), 340 μL (2.44 mmol) of 1,2-dimethoxyethane, and 1.0 mL (8.1 mmol) of $\text{Me}_3\text{CC}\equiv\text{CH}$ was heated to 40°C for $3\frac{1}{4}$ h. The solvents and excess $\text{Me}_3\text{CC}\equiv\text{CH}$ were removed in vacuo, and the residue was dissolved in 20 mL of pentane. Starting material crystallizes out upon cooling this solution to -40°C for 16 h. The filtrate was concentrated to 2-3 mL and again cooled to -40°C to yield green-black crystals that were recrystallized several times from pentane to give green-black cubes of pure **5**: ¹H NMR (toluene- d_8 , 325 K) δ 9.16, 6.74 (each a m, 2, H_α and H_β), 5.08 (sept, $J_{\text{HF}} = 6.2$, $\text{OCH}(\text{CF}_3)_2$), 1.26 (CMe_3), 1.20 (CMe_3), 1.09 (CMe_3); ¹³C NMR (C_6D_6) δ 307.5 (s), 202.9 (s), 194.1 (d, $J_{\text{CH}} = 16$), 163.0 (s), 156.6 (d, $J_{\text{CH}} = 150$), 124 (q, $J_{\text{CF}} = 286$), 85.7 (d sept, $J_{\text{CH}} = 147$, $J_{\text{CF}} = 30$), 45.3 (s), 38.6 (s), 34.3 (s), 31.7, 30.5, 30.3 (overlapping CMe_3 peaks).

Crystallographic Procedures for $\text{Mo}[\text{C}_7\text{H}_2(\text{CMe}_3)_4](\text{O}_2\text{CMe})_2$ (2a**).** The crystal data for **2a** are the following: $a = 9.738$ (2) \AA , $b = 16.026$ (3) \AA , $c = 17.996$ (3) \AA , $\beta = 104.71$ (1)°, $V = 2716.4$ \AA^3 , space group = $P2_1/n$, $Z = 4$, $\text{MW} = 528.6$, $\rho(\text{calcd}) = 1.292$ g cm^{-3} , $\mu = 4.72$ cm^{-1} (empirical absorption correction applied). Data were collected at -50°C on an Enraf-Nonius CAD4F-11 diffractometer equipped with a liquid

(10) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210.

(11) Freudenberg, J. H.; Schrock, R. R. *Organometallics*, in press.

Table VI. Deviations from Mean Planes (Å) and Dihedral Angles (deg) between Planes in Mo[C₅H(CMe₃)₃][OCH(CF₃)₂]₂(py) (5)

	Deviations from Mean Planes					
	Mo	C(41)	C(42)	C(43)	C(44)	C(45)
plane 1	-0.204	0.032	0.072	-0.015	-0.069	-0.007
plane 2		-0.020	0.069	-0.005	0.099	-0.063
	C(46)	C(410)	C(414)			
plane 1	0.156	-0.056	0.091			
plane 2	0.095	0.002	0.021			
	N(31)	C(31)	C(32)	C(33)	C(34)	C(35)
plane 3	0.002	-0.005	0.000	0.006	-0.008	0.004
dihedral ang between planes 1 and 3	108.02°					

Table VII. Final Positional Parameters for the Non-Hydrogen Atoms in Mo[C₅H(CMe₃)₃][OCH(CF₃)₂]₂(py) (5)

atom	x	y	z
Mo(1)	0.785 79 (2)	0.118 93 (2)	0.697 11 (2)
O(11)	0.849 28 (17)	0.136 9 (2)	0.616 95 (12)
C(11)	0.912 7 (3)	0.211 9 (3)	0.599 87 (19)
C(12)	0.864 5 (3)	0.313 1 (4)	0.560 2 (2)
C(13)	0.971 9 (3)	0.149 4 (4)	0.556 5 (2)
F(11)	0.818 7 (2)	0.370 2 (2)	0.601 17 (16)
F(12)	0.925 8 (2)	0.383 5 (2)	0.541 11 (15)
F(13)	0.803 1 (2)	0.286 2 (2)	0.500 71 (15)
F(14)	1.043 17 (18)	0.209 8 (3)	0.544 07 (15)
F(15)	0.923 69 (19)	0.116 9 (2)	0.492 73 (13)
F(16)	1.008 0 (2)	0.057 6 (3)	0.591 04 (15)
O(21)	0.750 15 (18)	0.013 3 (2)	0.766 36 (13)
C(21)	0.751 1 (3)	0.017 3 (3)	0.838 4 (2)
C(22)	0.788 9 (5)	-0.093 6 (4)	0.873 4 (3)
C(23)	0.654 1 (4)	0.042 6 (5)	0.849 6 (3)
F(21)	0.867 1 (3)	-0.121 5 (3)	0.855 35 (19)
F(22)	0.729 8 (3)	-0.176 6 (3)	0.854 1 (2)
F(23)	0.804 3 (3)	-0.088 8 (3)	0.944 04 (16)
F(24)	0.589 7 (2)	-0.023 1 (4)	0.811 76 (19)
F(25)	0.647 6 (2)	0.033 1 (3)	0.917 66 (16)
F(26)	0.629 3 (3)	0.145 9 (3)	0.828 8 (2)
N(31)	0.737 5 (2)	-0.052 5 (3)	0.627 07 (17)
C(31)	0.774 6 (3)	-0.082 1 (4)	0.571 9 (2)
C(32)	0.753 7 (3)	-0.180 8 (4)	0.534 3 (3)
C(33)	0.691 3 (4)	-0.252 5 (4)	0.554 1 (3)
C(34)	0.651 3 (4)	-0.223 8 (4)	0.609 4 (3)
C(35)	0.676 4 (3)	-0.123 7 (4)	0.645 4 (2)
C(41)	0.874 9 (2)	0.207 1 (3)	0.769 88 (18)
C(42)	0.846 9 (3)	0.312 5 (3)	0.797 76 (19)
C(43)	0.759 5 (3)	0.345 1 (3)	0.768 9 (2)
C(44)	0.720 5 (3)	0.262 7 (3)	0.714 27 (19)
C(45)	0.669 6 (3)	0.213 2 (3)	0.659 3 (2)
C(46)	0.582 2 (3)	0.217 7 (4)	0.600 5 (2)
C(47)	0.561 5 (4)	0.337 7 (5)	0.576 7 (3)
C(48)	0.504 2 (4)	0.173 1 (7)	0.629 8 (4)
C(49)	0.594 1 (4)	0.151 7 (6)	0.535 5 (3)
C(410)	0.706 6 (3)	0.448 0 (4)	0.787 3 (3)
C(411)	0.694 7 (5)	0.531 6 (5)	0.727 1 (3)
C(412)	0.758 2 (4)	0.501 5 (5)	0.855 7 (3)
C(413)	0.610 0 (4)	0.410 0 (5)	0.796 9 (3)
C(414)	0.973 5 (3)	0.163 8 (3)	0.802 33 (18)
C(415)	1.048 1 (3)	0.248 8 (4)	0.791 2 (2)
C(416)	0.986 7 (3)	0.148 1 (3)	0.883 78 (19)
C(417)	0.991 4 (3)	0.051 1 (3)	0.768 9 (2)

nitrogen low-temperature device and using Mo K α radiation. Data collection, reduction, and refinement procedures have been described elsewhere.¹² A total of 6221 reflections (+*h*,+*k*, \pm *l*) were collected in the range $3^\circ \leq 2\theta \leq 55^\circ$ with the 5203 having $F_o > 4\sigma(F_o)$ being used

(12) Silverman, L. D.; Dewan, J. C.; Giandomenico, C. M.; Lippard, S. *J. Inorg. Chem.* **1980**, *19*, 3379.

in the structure refinement which was by full-matrix least-squares techniques (337 variables) using SHELX-76. The final $R_1 = 0.037$ and $R_2 = 0.046$. All non-hydrogen atoms were refined anisotropically. Methyl group hydrogen atoms were placed in calculated positions (C-H = 0.95 Å; H-C-H = 109.5°) and constrained to ride on their respective carbon atoms. Toward the final stages of refinement, a difference Fourier map, with all methyl hydrogens in position, showed only two peaks of significance. One of these was 0.95 Å from C(8); the other was 0.98 Å from C(23), and these were included in the refinement as invariant hydrogen atoms.

An ORTEP drawing of **2a** can be found in Figure 1. Selected bond distances and angles can be found in Table I, and deviations from mean planes and dihedral angles between planes can be found in Table II. Final thermal parameters can be found in Table S1, observed and calculated structure factors in Table S2, and final positional parameters for hydrogen atoms in Table S5 of the supplementary material.

Crystallographic Procedures for Mo[C₅H(CMe₃)₃][OCH(CF₃)₂]₂(py) (5). The crystal data for **5** are the following: $a = 14.667$ (2) Å, $b = 11.913$ (3) Å, $c = 19.064$ (6) Å, $\beta = 102.43$ (2)°, $V = 3252.9$ Å³, space group = $P2_1/c$, $Z = 4$, $MW = 741.5$ g, $\rho(\text{calcd}) = 1.514$ g cm⁻³, $\mu = 4.51$ cm⁻¹ (empirical absorption correction applied). Data were collected at -50 °C on a Enraf-nonius CAD4F-11 diffractometer equipped with a liquid nitrogen low-temperature device and using MoK α radiation. Data collection, reduction, and refinement procedures have been described elsewhere.¹¹ A total of 7461 reflections (+*h*,+*k*, \pm *l*) were collected in the range $3^\circ \leq 2\theta \leq 55^\circ$ with the 4939 having $F_o > 6\sigma(F_o)$ being used in the structure refinement by full-matrix least-squares techniques (398 variables) using SHELX-76. The final $R_1 = 0.043$ and $R_2 = 0.048$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions (C-H = 0.95 Å) and were constrained to ride on their respective carbon atoms. A final difference Fourier map showed no significant features.

An ORTEP drawing of **5** can be found in Figure 4. Selected bond distances and angles can be found in Table V and deviations from mean planes can be found in Table VI. Final thermal parameters can be found in Table S3, observed and calculated structure factors in Table S4, and final positional parameters for the hydrogen atoms in Table S6 of the supplementary material.

Acknowledgment. R.R.S. thanks the National Science Foundation for support through Grant CHE84-02892, and H. S. thanks NATO for a postdoctoral fellowship. We also thank the Biomedical Research Support Shared Instrumentation Grant Program, Division of Research Resources, for funds to purchase the X-ray diffraction equipment under NIH Grant S10RR02243-01.

Supplementary Material Available: Final thermal parameters, observed and calculated structure factors, and final positional parameters for hydrogen atoms for Mo[C₇H₂(CMe₃)₄](O₂CCH₃)₂ (**2a**) and Mo[C₅H(CMe₃)₃][OCH(CF₃)₂]₂(C₅H₅N) (**5**) (47 pages). Ordering information is given on any current masthead page.