Removal of solvent and recrystallization from hexane gives the products as yellow **3a** or white **3b** powdery solids. Alternatively, the bis-benzyl **1** will react with HOAr′ (1 equiv) in toluene (120 °C) to give **3** directly. Anal. Calcd for $TiC_{42}H_{62}O_3$ (**3a**): C, 76.10; H, 9.43. Found: C, 76.36; H, 9.57. $ZrC_{42}H_{62}O_3$ (**3b**): C, 71.44; H, 8.85. Found: C, 67.88; H, 9.43. **3a**: ^{1}H NMR (30 °C, C_6D_6) δ 1.47 (s, $OC_6H_3Bu^t_2$), 1.57 (s, $OC_6H_3Bu^tCMe_2CH_2$), 1.35 (s, $OC_6H_3Bu^tCMe_2CH_2$), 3.09 (s, $OC_6H_3Bu^tCMe_2CH_2$), 7.75 (m, aromatics). **3b**: ^{1}H NMR (30 °C, C_6D_6) δ 1.47 (s, $OC_6H_3Bu^t_2$), 1.51 (s, $OC_6H_3Bu^tCMe_2CH_2$), 1.69 (s, $OC_6H_3Bu^tCMe_2CH_2$), 2.19 (s, $OC_6H_3Bu^tCMe_2CH_2$). **3a**: ^{13}C NMR (30 °C, C_6D_6) δ 111.7 (Ti–$OC_6H_3Bu^tCMe_2CH_2$), 47.3 (Ti–$OC_6H_3Bu^tCMe_2CH_2$), 37.8 (Ti–$OC_6H_3Bu^tCMe_2HC_2$). **3b**: ^{13}C NMR (30 °C, C_6D_6) δ 83.1 (Zr–$OC_6H_3Bu^tCMe_2CH_3$), 42.8 (Zr–$OC_6H_3Bu^tCMe_2CH_2$) 37.2 (Zr–$OC_6H_3Bu^tCMe_2CH_2$).

4. M($OC_6H_3Bu^tCMe_2CH_2$)(OAr′)(CH_2Ph)(py) (M = Ti, 4a; M = Zr, 4b). Hexane solutions of monometalated compounds **2** will react with pyridine (excess) to quantitatively give solutions containing **4**. Slow cooling to −15 °C gave the pyridine adducts as yellow **4a** and white **4b** powders. Anal. Calcd for $TiC_{40}H_{53}O_2N$ (**4a**): C, 77.31; H, 7.85; N, 2.20. Found C, 77.08; H, 8.29; N, 2.24. **4a**: ^{1}H NMR (30 °C, C_6D_6) δ 1.45 (s, $OC_6H_3Bu^t_2$), 1.63 (s, $OC_6H_3Bu^tCMe_2CH_2$), 1.32 (s), 1.27 (s, $OC_6H_3Bu^tCMe_2CH_2$), 3.51 (d), 2.49 (d, CH_2Ph), 2.30 (d), 1.78 (d, $OC_6H_3Bu^tCMe_2CH_2$), 8.71 (m, o-C_5H_5N), 6.5–7.5 (m, other aromatics). **4b**: ^{1}H NMR (30 °C, C_6D_6) δ 1.40 (s, $OC_6H_3Bu^t_2$), 1.59 (s, $OC_6H_3Bu^tCMe_2CH_2$), 1.42 (s), 1.68 (s, $OC_6H_3Bu^tCMe_2CH_2$), 2.85 (d), 2.31 (d, CH_2Ph), 1.85 (d, $OC_6H_3CMe_2CH_2$ – other half of AB obscured by Bu^t signals), 8.65 (m, o-C_5H_5N), 6.4–7.5 (m, other aromatics).

5. Ti($OC_6H_3Bu^tCMe_2CH_2$)(OAr′)(CH_2SiMe_3)(py) (4c). A mixture of $Ti(CH_2SiMe_3)_4$ (1.35 g) and 2.6-di-*tert*-butylphenol (1.4 g, 2 equiv) in toluene was heated at 120 °C for 12 h in a sealed Pyrex tube. The solvent was removed. The ^{1}H NMR spectrum of the resulting oil indicated the presence of Ti($OC_6H_3Bu^tCMe_2CH_2$)(OAr′)(CH_2SiMe_3) (**2c**). Addition of pyridine (excess) followed by cooling slowly to −15 °C gave the product as deep orange crystals. **2c**: ^{1}H NMR (30 °C, C_6D_6) δ 1.58 (s, $OC_6H_3Bu^t_2$), 1.69 (s, $OC_6H_3Bu^tCMe_2CH_2$), 1.11 (s), 1.39 (s, $OC_6H_3Bu^tCMe_2CH_2$), obscured ($OC_6H_3Bu^tCMe_2CH_2$), 6.9–7.5 (aromatics), 2.54 (d), 2.73 (d, CH_2SiMe_3), 0.08 (s, CH_2SiMe_3). **4c**: ^{1}H NMR (30 °C, C_6D_6) δ 1.59 (s, $OC_6H_3Bu^t_2$), 1.71 (s, $OC_6H_3Bu^tCMe_2Ch_2$), 1.20 (s), 1.41 (s, $OC_6H_3Bu^tCMe_2CH_2$), 1.95 (d), 1.80 (d, $OC_6H_3Bu^tCMe_2CH_2$), 2.79 (d), 1.41 (d, CH_2SiMe_3), 0.07 (s, CH_2SiMe_3), 8.87 (m, o-C_5H_5N), 6.5–7.4 (m, other aromatics).

6. X-ray Structure Determination of Ti($OC_6H_3Bu^tCMe_2CH_2$)(OAr′)(CH_2SiMe_3)(py) (4c). General operating procedures have been outlined previously.[26] A suitable yellow crystal was chosen and transferred to the goniostat with use of standard inert handling techniques and characterized with use of a reciprocal lattice search technique. The structure was solved by a combination of direct methods and Fourier techniques by using the 3372 data with $F_o > 2.33\delta(F)$. A final difference Fourier was featureless, the largest peak being 0.45 e/Å^3.

Acknowledgment. We thank the National Science Foundation (Grant CHE-821906 to I.P.R.) for support of this research.

Supplementary Material Available: Tables of fractional coordinates of hydrogen atoms, anisotropic thermal parameters, complete bond distances and angles, and observed and calculated structure factors for Ti($OC_6H_3Bu^tCMe_2CH_2$)(OAr′)(CH_2SiMe_3)(py) (**4c**) (30 pages). Ordering information is given on any current masthead page.

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Preparation of Trialkoxymolybdenum(VI) Alkylidyne Complexes, Their Reactions with Acetylenes, and the X-ray Structure of Mo[$C_3(CMe_3)_2$][$OCH(CF_3)_2$]$_2$(C_5H_5N)$_2$[1]

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Abstract: Mo($CCMe_3$)(CH_2CMe_3)$_3$ can be prepared in ~35% yield reproducibly and on a multigram scale by adding MoO_2Cl_2 in tetrahydrofuran to 6 equiv of Me_3CCH_2MgCl in ether. Mo($CCMe_3$)X_3(dme) complexes (X = Cl or Br) can be prepared by adding 3 equiv of HX to Mo($CCMe_3$)(CH_2CMe_3)$_3$ in the presence of 1,2-dimethoxyethane (dme). From Mo($CCMe_3$)Cl_3(dme), a wide variety of alkoxide complexes can be prepared of the type Mo($CCMe_3$)(OR)$_3$ (OR = $OCMe_3$, $OCHMe_2$, OCH_2CMe_3, $OCMe_2(CF_3)$, $OCMe(CF_3)_2$, and O-2,6-$C_6H_3(CHMe_2)_2$), Mo($CCMe_3$)(OR)$_3$(dme) (OR = $OCH(CF_3)_2$, $OCMe(CF_3)_2$, and $OC(CF_3)_3$), or Mo($CCMe_3$)(OR)$_2$Cl(dme) (OR = $OCH(CF_3)_2$, $OCMe(CF_3)_2$ and $OC(CF_3)_3$). Internal acetylenes do not react with Mo($CCMe_3$)($OCMe_3$)$_3$, they are largely polymerized by Mo($CCMe_3$)($OCHMe_2$)$_3$ and Mo($CCMe_3$)(OCH_2CMe_3)$_3$, and they react in an irreversible, apparently complex, and as yet unelucidated fashion with Mo($CCMe_3$)X_3(dme). Internal acetylenes react smoothly with all fluoroalkoxide complexes (most slowly with Mo($CCMe_3$)[$OCMe_2(CF_3)$]$_3$) and with Mo($CCMe_3$)[O-2,6-$C_6H_3(CHMe_2)_2$]$_3$ to give new, isolable alkylidyne complexes formed by loss of the *tert*-butyl-substituted acetylene from an intermediate molybdenacyclobutadiene complex. A molybdenacyclobutadiene complex, Mo(C_3Et_3)[O-2,6-$C_6H_3(CHMe_2)_2$]$_3$, can be isolated, although at room temperature in toluene-d_8 it is virtually totally dissociated into a mixture of Mo(CEt)[O-2,6-$C_6H_3(CHMe_2)_2$]$_3$ and 3-hexyne. Terminal acetylenes react with Mo($CCMe_3$)($OCMe_3$)$_3$ to produce $Me_3CC{\equiv}CH$ and Mo(CR)($OCMe_3$)$_3$. Reactions between terminal acetylenes and fluoroalkoxide complexes yield deprotiomolybdenacyclobutadiene complexes of the type Mo(C_3R_2)(OR′)$_2$, some of which can be isolated only as bis ligand adducts, Mo(C_3R_2)(OR′)$_2L_2$ (L = py, dme, etc.). Reactions between terminal acetylenes and Mo($CCMe_3$)[O-2,6-$C_6H_3(CHMe_2)_2$]$_3$ yield mixtures of Mo[$C_3(CMe_3)R$][O-2,6-$C_6H_3(CHMe_2)_2$]$_2$ and 2,6-$C_6H_3(CHMe_2)_2OH$ from which red crystalline Mo[$C_3(CMe_3)R$][O-2,6-$C_6H_3(CHMe_2)_2$]$_2$(py) complexes can be isolated upon addition of pyridine (R = CMe_3, Pr, and Ph). Mo[$C_3(CMe_3)_2$][$OCH(CF_3)_2$]$_2$(py)$_2$ crystallizes in the space group $C2/c$ with a = 18.367 (3) Å, b = 11.025 (2) Å, c = 16.641 (3) Å, β = 109.98 (1)°, V = 3166.9 Å^3, and Z = 4. It is a pseudooctahedron with the pyridine ligands trans to a planar MoC_3 ring in which Mo–C_α = 1.943 (3) Å and Mo···C_β = 2.005 (4) Å. The two oxygen atoms of the $OCH(CF_3)_2$ ligands are bent away from the ring system (O–Mo–O = 152.2 (1)°) and the α *tert*-butyl groups are bent away from the metal (Mo–C_α–C = 158.9 (2)°). The $OCMe(CF_3)_2$, $OC(CF_3)_3$, and O-2,6-$C_6H_3(CHMe_2)_2$ complexes are excellent catalysts for the metathesis of internal acetylenes. There is evidence for the formation of 4-octyne in the reaction between Mo(CPr)($OCMe_3$)$_3$ and 1-pentyne, presumably via a slow metathesis reaction to give unstable Mo(CH)($OCMe_3$)$_3$.

The first monomeric alkylidyne complexes, *trans*-X-$(CO)_4M{\equiv}CR$ (M = Mo and W), were prepared in 1973 by treating an alkylidene (or carbene) complex of the type M-$(CO)_5$[C(R)(OMe)] with BX_3.[2] In 1978, higher oxidation state

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species of the type $M(CCMe_3)(CH_2CMe_3)_3$ were prepared by treating $MoCl_5$ or WCl_6 with 5 or 6 equiv of neopentyllithium.[3] One can argue that the $M(CCMe_3)(CH_2CMe_3)_3$ species contain the metal in its highest possible oxidation state, i.e., that the alkylidyne ligand is a trianion, an analogue of the nitride ligand.

Interest in the d^0 alkylidyne complexes increased after it was discovered that d^0 alkylidene complexes of tungsten will metathesize olefins,[4] since there was then some reason to expect that d^0 alkylidyne complexes would metathesize acetylenes.[5] We now know that this is the case for tungsten complexes of the type $W(CR)(OR')_3$ and $W(CR)(OR')_3$(dme) (dme = dimethoxyethane) where OR' = $OCMe_3$,[6] $OCMe_x(CF_3)_{3-x}$,[7a] $OCH(CF_3)_2$,[7a] or O-2,6-$C_6H_3(CHMe_2)_2$.[7b] Intermediate tungstenacyclobutadiene complexes have been observed in several cases, their structures have been determined through X-ray studies, and the kinetics of their reactions with internal acetylenes have been explored in some detail.[7]

It is important to establish that d^0 molybdenum alkylidyne complexes will metathesize acetylenes since the only known classical homogeneous catalysts contain molybdenum, not tungsten.[8] It also should be possible to enhance and control the activity of isolable molybdenum acetylene metathesis catalysts through ligand variation, as has been achieved in the tungsten system.[7a,b] Unfortunately, however, the chemistry of molybdenum alkylidyne complexes has been relatively inaccessible because of the low and irreproducible yield of $Mo(CCMe_3)(CH_2CMe_3)_3$.[3a] We have now developed a route that produces adequate yields (35 ± 5%) of $Mo(CCMe_3)(CH_2CMe_3)_3$ on a moderate scale (6–7 g of product). Here we report some fundamental chemistry of molybdenum alkylidyne complexes aimed at exploring the question concerning the role of molybdenum alkylidyne complexes as acetylene metathesis catalysts. Some of these results were reported in a preliminary communication.[7c]

Results

Preparation of Neopentylidyne Complexes. $Mo(CCMe_3)(CH_2CMe_3)_3$ was first isolated from the reaction between 5 equiv of $LiCH_2CMe_3$ and $MoCl_5$ in diethyl ether at −78 °C.[3a] The yield was low (12–15%), irreproducible, and decreased upon scaling up the reaction beyond 1 g of $MoCl_5$. Consequently, we sought a better preparative route. Since one can argue that the metal is in its highest possible oxidation state in $Mo(CCMe_3)(CH_2CMe_3)_3$, it would seem advantageous to begin with Mo(VI) compounds. In general, reactions starting with Mo(VI) compounds have been the most successful, if the reactions are initiated at −78 °C in ether and if the molybdenum compound is added *to* 6 equiv of neopentylmagnesium chloride. Addition of Grignard to Mo invariably gives a lower yield of $Mo(CCMe_3)(CH_2CMe_3)_3$, at times only ~50% of that obtained by adding Mo to the Grignard. Reproducible yields between 30% and 40%, but occasionally 50%, are obtained starting with readily available and inexpensive MoO_2Cl_2. $MoOCl_4$ is also a suitable starting material. Low yields (5–15%) of $Mo(CCMe_3)(CH_2CMe_3)_3$ were obtained starting with $MoO_2(acac)_2$, MoO_2Br_2, or $MoOCl_2(OMe)_2$. Essentially no $Mo(CCMe_3)(CH_2CMe_3)_3$ was produced starting with $MoO_2(OCMe_3)_2$. Some $Mo(CCMe_3)(CH_2CMe_3)_3$ (~15%) could be obtained by employing $MoOCl_3$ and 5 equiv of Grignard. Other combinations ($MoOCl_4$/6$LiCH_2CMe_3$, $[Et_4N][MoNCl_4]$/6$LiCH_2CMe_3$, and $MoOCl_3$/2$Mg(CH_2CMe_3)_2$) gave essentially no $Mo(CCMe_3)(CH_2CMe_3)_3$. It has been noted that $Mo(CCMe_3)(CH_2CMe_3)_3$ is formed in the reaction between $MoOCl_4$ and $Mg(CH_2CMe_3)_2$(dioxane), although no yield was given.[9] $Mo(CCMe_3)(CH_2CMe_3)_3$ is yellow–orange, volatile, extremely sensitive to water, and perhaps somewhat light sensitive.

Halide derivatives can be prepared as shown in eq 1. Optimum

$$Mo(CCMe_3)(CH_2CMe_3)_3 + 3HX + \text{excess dme} \xrightarrow[0\ ^\circ C]{\text{ether}} Mo(CCMe_3)X_3(dme) \quad (1)$$

X = Cl, Br

dme = 1,2-dimethoxyethane

yields of blue $Mo(CCMe_3)Cl_3$(dme) and green $Mo(CCMe_3)Br_3$(dme) are approximately 75%. $Mo(CCMe_3)Br_3$(dme) also can be synthesized by treating $Mo(CCMe_3)Cl_3$(dme) with excess Me_3SiBr. Both complexes have the cis, *mer* geometry, judging from the fact that the two ends of the dme ligand are inequivalent. $Mo(CCMe_3)X_3$(dme) is stable in the presence of HX at 25 °C under the reaction conditions.

$Mo(CCMe_3)(CH_2CMe_3)_3$ also reacts with HCl in the presence of Et_4NCl to form $[Et_4N][Mo(CCMe_3)Cl_4]$ in good yield (eq 2).

$$Mo(CCMe_3)(CH_2CMe_3)_3 + 3HCl + Et_4NCl \xrightarrow[0\ ^\circ C]{CH_2Cl_2} [Et_4N][Mo(CCMe_3)Cl_4] \quad (2)$$

Again, excess HCl does not attack the neopentylidyne ligand under the reaction conditions. $Mo(CCMe_3)Cl_3$(dme) and $[Et_4N][Mo(CCMe_3)Cl_4]$ can be interconverted according to eq 3 and 4.

$$Mo(CCMe_3)Cl_3(dme) + Et_4NCl \xrightarrow{CH_2Cl_2} [Et_4N][Mo(CCMe_3)Cl_4] \quad (3)$$

$$[Et_4N][Mo(CCMe_3)Cl_4] + ZnCl_2(dioxane) \xrightarrow[\text{excess dme}]{CH_2Cl_2} Mo(CCMe_3)Cl_3(dme) \quad (4)$$

Complexes with the generic formula $Mo(CCMe_3)(OR)_3$ (OR = $OCHMe_2$, OCH_2CMe_3, and $OCMe_3$) can be prepared relatively straightforwardly from $Mo(CCMe_3)Cl_3$(dme) in ether at −40 °C. $Mo(CCMe_3)(OCMe_3)_3$ can also be prepared as shown in eq 5, although the yield is lower. We propose that these volatile,

$$Mo(CCMe_3)Cl_3(dme) + 3Me_3COH + 3NEt_3 \xrightarrow[-3Et_3NHCl]{\text{ether}} Mo(CCMe_3)(OCMe_3)_3 \quad (5)$$

pentane-soluble, nearly white complexes are monomers with a pseudotetrahedral geometry. There is some chance that they are weakly associated dimers with structures analogous to that of $[W(CMe)(OCMe_3)_3]_2$ in which one of the three equatorial *tert*-butoxide ligands on each W behave as a bridging ligand in the axial position trans to the neopentylidyne ligand.[10]

The preparation of molybdenum neopentylidyne tris(fluoroalkoxide) complexes is more problematic. Reaction conditions (solvent, length of reaction, concentration, etc.) must be finely balanced in order to avoid formation of bis(alkoxide) complexes

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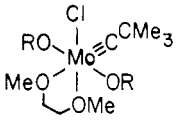
(see below). The syntheses of $Mo(CCMe_3)[OCH(CF_3)_2]_3(dme)$, $Mo(CCMe_3)[OCMe(CF_3)_2]_3(dme)$, and $Mo(CCMe_3)[OC(CF_3)_3]_3(dme)$ are summarized in eq 6. The two ends of the dme

$$Mo(CCMe_3)Cl_3(dme) + 3MOR_F \xrightarrow{\text{solvent}} Mo(CCMe_3)(OR_F)_3(dme) \quad (6)$$

MOR_F/solvent = $LiOCH(CF_3)_2/CH_2Cl_2$; $KOCMe(CF_3)_2$/ether; $KOC(CF_3)_3/CH_2Cl_2$

in $Mo(CCMe_3)[OC(CF_3)_3]_3(dme)$ are not exchanging rapidly on the NMR time scale in a molecule with the cis, *mer* geometry. However, the two ends of the coordinated 1,2-dimethoxyethane in $Mo(CCMe_3)[OCH(CF_3)_2]_3(dme)$ and $Mo(CCMe_3)[OCMe(CF_3)_2]_3(dme)$ are exchanging, and coordinated dme exchanges readily with free dme. We propose that the end of the dme ligand trans to the Mo≡C bond dissociates and, after some rearrangement of the five-coordinate molecule, reassociates to form the unobservable cis, *fac* isomer, thereby equilibrating the two ends of the dme ligand. Formation of intermediate $Mo(CCMe_3)[OCMe(CF_3)_2]_3(dme)_2$ in which each dme is coordinated to the metal through one oxygen atom is an alternative possibility. Since the dme ligand is lost completely from $Mo(CCMe_3)[OCMe(CF_3)_2]_3(dme)$ upon sublimation (see below), exchange of coordinated dme with free dme by complete dissociation of dme in solution cannot be ruled out as a possible bimolecular exchange pathway.

It is important to note that the reactions involving fluoroalkoxide ligands are relatively sensitive to solvent and the counterion of the alkoxide salt employed. For example, in ether (instead of dichloromethane), the reaction between $Mo(CCMe_3)Cl_3(dme)$ and $LiOCH(CF_3)_2$ yields $Mo(CCMe_3)[OCH(CF_3)_2]_2Cl(dme)$. Likewise, $Mo(CCMe_3)[OCMe(CF_3)_2]_2Cl(dme)$ is the product employing $LiOCMe(CF_3)_2$ in ether instead of $KOCMe(CF_3)_2$ in ether. Finally, use of $KOC(CF_3)_3$ in ether instead of in dichloromethane leads to $Mo(CCMe_3)[OC(CF_3)_3]_2Cl(dme)$ instead of $Mo(CCMe_3)[OC(CF_3)_3]_3(dme)$. The NMR data for all three are consistent with the structure



in which the two ends of the dme ligand do not exchange rapidly on the NMR time scale.

Two fluoroalkoxide complexes can be prepared that do not contain donor solvent ligands. The first is $Mo(CCMe_3)[OCMe_2(CF_3)]_3$, the product of the reaction between $Mo(CCMe_3)Cl_3(dme)$ and 3 equiv of $KOCMe_2(CF_3)$ in ether. Although it will not form a stable dme adduct, it will form an adduct with THF that crystallizes from pentane as $Mo(CCMe_3)[OCMe_2(CF_3)]_3(THF)$. The THF is lost again upon sublimation. The second solvent-free fluoroalkoxide complex can be obtained by sublimation of $Mo(CCMe_3)[OCMe(CF_3)_2]_3(dme)$; $Mo(CCMe_3)[OCMe(CF_3)_2]_3$ is probably the most electrophilic complex of Mo that we have isolated that does not contain coordinated solvent(s). $Mo(CCMe_3)[OC(CF_3)_3]_3(dme)$, in contrast, sublimes with the dme ligand intact. There is clearly a delicate balance between electronics and sterics in forming adducts of $Mo(CCMe_3)(OR)_3$ complexes. In general, complexes containing smaller and/or more electron-withdrawing alkoxide ligands form stronger adducts containing up to a maximum of two donor solvent ligands. As we shall see later, however, such details are relatively unimportant as far as reactions with acetylenes are concerned, since even $Mo(CCMe_3)[OC(CF_3)_3]_3(dme)$ reacts readily with acetylenes.

It is possible to prepare one tris(phenoxide) complex (eq 7).

$$Mo(CCMe_3)Cl_3(dme) + 3LiDIPP \xrightarrow[-40\ °C]{\text{ether}} Mo(CCMe_3)(DIPP)_3 \quad (7)$$

DIPP = O-2,6-$C_6H_3(CHMe_2)_2$

Although it does not appear to coordinate dme or THF, a yellow solution of it turns red upon addition of pyridine; we assume a monoadduct is formed, although we have not tried to isolate it. The 2,6-diisopropylphenoxide (DIPP) ligand appears to be a relatively special phenoxide ligand, since we have failed to prepare molybdenum complexes that contain several others. For example, the reaction between $Mo(CCMe_3)Cl_3(dme)$ or $[Et_4N][Mo(CCMe_3)Cl_4]$ and LiOPh produced only an intractable oil. Although NMR spectra suggest that $Mo(CCMe_3)(O\text{-}2,6\text{-}C_6H_3R_2)_3$ (R = Me or OMe) were formed in the reaction between $Mo(CCMe_3)Cl_3(dme)$ and Li-O-2,6-$C_3H_3R_2$, these complexes could not be isolated. We had no success at isolating a product from the reaction between $Mo(CCMe_3)Cl_3(dme)$ and Li-O-2,6-$C_6H_3(CMe_3)_2$. Similar results were obtained in the tungsten system; reaction between $W(CCMe_3)Cl_3(dme)$ and Li-O-2,6-$C_6H_3(CMe_3)_2$ produced an alkylidene complex by addition of a *tert*-butyl C–H bond across the W≡C bond.[7b]

The chemical shift of the neopentylidyne α-carbon atom in the above complexes varies from ~296 to 350 ppm. The greatest shift is for the tribromide complex and the least for the tri-*tert*-butoxide complex, with the fluoroalkoxide and phenoxide complexes falling between the two extremes. It is unclear at this time how much significance can be placed on the chemical shift as a measure of (e.g.) the electrophilicity of the metal.

Reactions of Neopentylidyne Complexes with Internal Acetylenes. Internal acetylenes (typically 3-hexyne) do not react readily at 25 °C with $Mo(CCMe_3)(OCMe_3)_3$ or $Mo(CCMe_3)(CH_2CMe_3)_3$. They do react with $Mo(CCMe_3)(OCHMe_2)_3$, $Mo(CCMe_3)(OCH_2CMe_3)_3$, and $Mo(CCMe_3)X_3(dme)$ (X = Cl and Br), but the reactions are relatively messy. In reactions involving $Mo(CCMe_3)(OCHMe_2)_3$ and $Mo(CCMe_3)(OCH_2CMe_3)_3$, small amounts of cleavage products ($Me_3CC{\equiv}CR$) are observed, but the main reaction pathway appears to be polymerization. Reactions involving $Mo(CCMe_3)X_3(dme)$ complexes yielded large quantities of relatively insoluble brown powders. Neither cleavage products nor molybdenacyclobutadiene compounds analogous to $W[C(CMe_3)C(R)C(R)]X_3$[11] were observed.

In contrast to the above reactions, those between the fluoroalkoxide or phenoxide complexes reported here and internal acetylenes are relatively well-behaved. $Mo(CCMe_3)[OCH(CF_3)_2]_3(dme)$ reacts with internal acetylenes to give the expected alkylidyne complexes formed by a metathetical reaction. The two complications are that an acetylene such as 3-hexyne is polymerized slowly and that the ability to isolate the product depends upon the size of the alkyl group in the dialkylacetylene. Addition of 2-butyne (10 equiv) to $Mo(CCMe_3)[OCH(CF_3)_2]_3(dme)$ in toluene followed by removing the solvent in vacuo produces a 1:15 mixture of $Mo(CCMe_3)[OCH(CF_3)_2]_3(dme)$ and $Mo(CMe)[OCH(CF_3)_2]_3(dme)$. 3-Hexyne produces relatively more product and 4-octyne even more; pure $Mo(CPr)[OCH(CF_3)_2]_3(dme)$ can be isolated as yellow crystals upon adding only 5 equiv of 4-octyne to $Mo(CCMe_3)[OCH(CF_3)_2]_3(dme)$. We ascribe formation of relatively more $Mo(CR)[OCH(CF_3)_2]_3(dme)$ in the reaction between $Mo(CCMe_3)[OCH(CF_3)_2]_3(dme)$ and RC≡CR when R is a longer chain alkyl group to a relatively slow back reaction between $Mo(CR)[OCH(CF_3)_2]_3(dme)$ and $Me_3CC{\equiv}CR$ and in part to the greater volatility of RC≡CR vs. $Me_3CC{\equiv}CR$ (up to the point where R = Pr). Formation of the thermodynamically more stable benzylidyne complex is favored in the reaction shown in eq 8 upon addition of only 1 equiv of PhC≡CEt.

$$Mo(CCMe_3)[OCH(CF_3)_2]_3(dme) \xrightarrow[-Me_3C{\equiv}CEt]{PhC{\equiv}CEt} Mo(CPh)[OCH(CF_3)_2]_3(dme) \quad (8)$$

Increasing the size of the alkoxide group from $OCH(CF_3)_2$ to $OCMe(CF_3)_2$ virtually eliminates both problems noted above. $Mo(CCMe_3)[OCMe(CF_3)_2]_3(dme)$ reacts with a slight excess of RC≡CR (R = Me, Et, and Pr) in ether to produce the new alkylidyne complexes, $Mo(CR)[OCMe(CF_3)_2]_3(dme)$, and with

(11) Schrock, R. R.; Pedersen, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1984**, *3*, 1574.

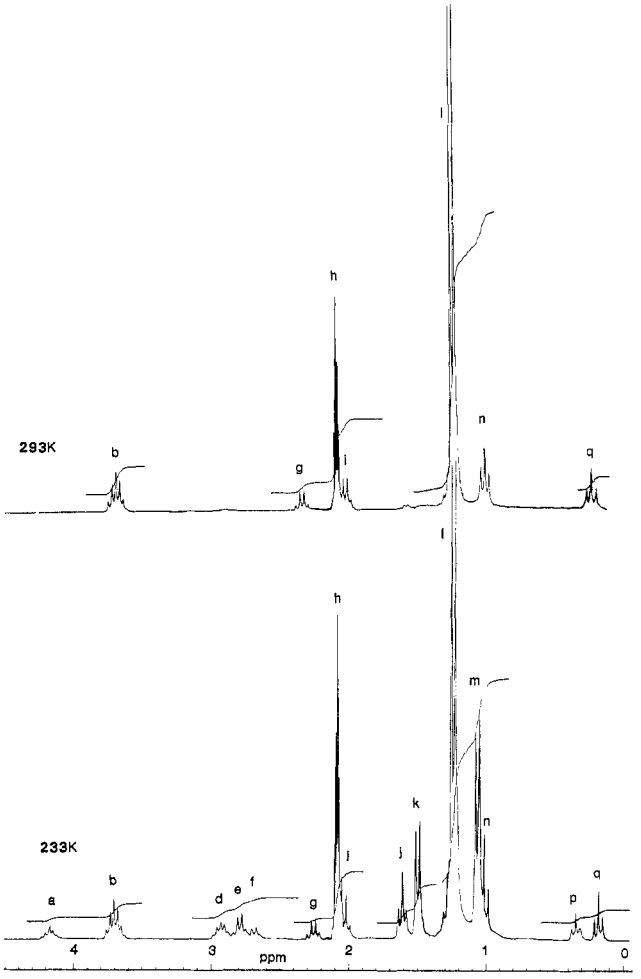


Figure 1. ^{1}H NMR spectrum of $Mo(C_3Et_3)[O\text{-}2,6\text{-}C_6H_3(CHMe_2)_2]_3$ in toluene-d_8 at 293 and 233 K. At 293 K, only $Mo(CEt)[O\text{-}2,6\text{-}C_6H_3(CHMe_2)_2]_3$ and 3-hexyne are observed: (a) equatorial $OC_6H_3(CHMe_2)_2$ of metallacycle, (b) $OC_6H_3(CHMe_2)_2$ of alkylidyne, (d) axial $OC_6H_3(CHMe_2)_2$ of metallacycle, (e) α-CH_2CH_3 of metallacycle, (f) β-CH_2CH_3 of metallacycle, (g) $MoCCH_2H_3$, (h) $C_6D_5CD_2H$, (i) $CH_3CH_2C{\equiv}CH_2CH_3$, (j) α-CH_2CH_3 of metallacycle, (k) equatorial $OC_6H_3(CHMe_2)_2$ of metallacycle, (l) $OC_6H_3(CHMe_2)_2$ of alkylidyne, (m) axial $OC_6H_3(CHMe_2)_2$ of metallacycle, (n) $CH_3CH_2C{\equiv}CCH_2CH_3$, (p) β-CH_2CH_3 of metallacycle, (q) $MoCCH_2CH_3$.

PhC≡CEt to produce $Mo(CPh)[OCMe(CF_3)_2]_3(dme)$, all in quantitative yield and without concomitant polymerization of the acetylene. Analogous reactions between $Mo(CCMe_3)[OCMe(CF_3)_2]_3$ and 3-hexyne or 4-octyne in toluene yield $Mo(CR)[OCMe(CF_3)_2]_3$ complexes quantitatively, again without concomitant polymerization of the acetylene. We believe that the increased steric requirements of the larger ligands prevent polymerization and select against the back reaction of $Mo(CR)(OR)_3(dme)$ with $Me_3CC{\equiv}CR$.

Reactions between $Mo(CCMe_3)[OCMe_2(CF_3)]_3$ and internal acetylenes are slower than those between $Mo(CCMe_3)[OCMe(CF_3)_2]_3$ and internal acetylenes. We have isolated $Mo(CPr)[OCMe_2(CF_3)]_3$ and have observed formation of $Mo(CPh)[OCMe_2(CF_3)]_3$ in situ.

In none of the above reactions have we observed formation of a molybdenacyclobutadiene complex analogous to $W(C_3Et_3)[OCH(CF_3)_2]_3$[7a] or $W(C_3Et_3)(DIPP)_3$.[7b] A reaction involving the 2,6-diisopropylphenoxide complex, however, is different. $Mo(CCMe_3)(DIPP)_3$ reacts with excess 3-hexyne in toluene to produce a yellow oil (after removal of toluene in vacuo) that by ^{1}H NMR is clearly pure $Mo(CEt)(DIPP)_3$. In ether, however, dark-red crystals can be obtained at low temperatures in the presence of excess 3-hexyne. An ^{1}H NMR spectrum of these red crystals in toluene-d_8 at 293 K shows only a 1:1 mixture of $Mo(CEt)(DIPP)_3$ and 3-hexyne (Figure 1). However, as the temperature is lowered, another set of signals appears that is similar to the set observed for $W(C_3Et_3)(DIPP)_3$;[7b] at 233 K, the solution contains approximately 50% of the new species, which we propose is $Mo(C_3Et_3)(DIPP)_3$ (Figure 1). This proposal is confirmed by elemental analysis and by the appearance of two signals in the low-temperature ^{13}C NMR spectrum at 328 and 260 ppm analogous to those observed in the spectrum of $W(C_3Et_3)(DIPP)_3$.[7b] The results obtained when using 4-octyne are very similar to those obtained with 3-hexyne, but addition of excess 2-butyne to $Mo(CCMe_3)(DIPP)_3$ in ether produces an intractable mixture, which we believe in part can be attributed to polymerization of 2-butyne.

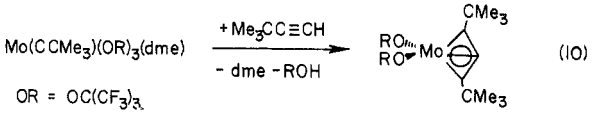
Reactions of Neopentylidyne Complexes with Terminal Acetylenes. We noted above that $Mo(CCMe_3)(OCMe_3)_3$ does not react with internal acetylenes. However, it *will* react cleanly with some *terminal* acetylenes. In ether, new alkylidyne complexes are formed as shown in eq 9. Only 1 equiv of RC≡CH is required

$$Mo(CCMe_3)(OCMe_3)_3 \xrightarrow[-Me_3CC{\equiv}CH]{RC{\equiv}CH} Mo(CR)(OCMe_3)_3 \quad (9)$$

R = Pr, $CHMe_2$, and Ph

to form $Mo(CR)(OCMe_3)_3$ (R = Pr, $CHMe_2$, and Ph), but a mixture of $Mo(CCMe_3)(OCMe_3)_3$ and $Mo(CSiMe_3)(OCMe_3)_3$ (1:4) is observed by ^{1}H NMR upon treatment of $Mo(CCMe_3)(OCMe_3)_3$ with 5 equiv of $Me_3SiC{\equiv}CH$.

Reactions between terminal acetylenes and neopentylidyne complexes containing fluoroalkoxide ligands are more complicated. For example, $Mo(CCMe_3)[OC(CF_3)_3]_3(dme)$ in ether reacts instantly with 1 equiv of $Me_3CC{\equiv}CH$ to give a bright-yellow solution from which violet crystals are obtained upon removing the ether in vacuo from a cold solution. The crystals turn yellow as they warm to room temperature in vacuo. They do not turn violet again upon being cooled to −78 °C in vacuo. The ^{1}H, ^{13}C, and ^{19}F NMR spectra of this product are consistent with a compound of the formula $Mo[C_3(CMe_3)_2][OC(CF_3)_3]_2$. In particular, we observe two resonances at 257 and 196 ppm that remain singlets in the gated spectrum. Similar signals have been observed in the ^{13}C NMR spectrum of the "deprotonated" tungstenacyclobutadiene complex, $W(\eta^5\text{-}C_5H_5)[C_3(CMe_3)_2]Cl$, at 220 and 197 ppm.[12] We conclude that $Mo[C_3(CMe_3)_2][OC(CF_3)_3]_2$ also is a "deprotio" metallacyclobutadiene complex, probably with pseudotetrahedral geometry (eq 10). Observations made on



(10)

related molecules (see below) suggest that the violet crystals are a dme adduct of $Mo[C_3(CMe_3)_2][OC(CF_3)_3]_2$ and that dme is lost in vacuo at room temperature.

The reaction between $Mo(CCMe_3)[OCMe(CF_3)_2]_3(dme)$ and $Me_3CC{\equiv}CH$ proceeds analogously, although several minutes are required to obtain the yellow solution. Red–violet crystals are obtained upon removing the ether in vacuo from a cold solution. These crystals turn into a low-melting yellow solid upon warming the flask to room temperature in vacuo. NMR spectra of the yellow solid are all consistent with its formulation as an analogous deprotiomolybdenacyclobutadiene complex, $Mo[C_3(CMe_3)_2][OCMe(CF_3)_2]_2$. If one warms the flask containing the red–violet crystals to room temperature under 1 atm of dinitrogen, they do not turn yellow. When they are dissolved in toluene-d_8, a yellow solution is obtained that by NMR contains a mixture of $Mo[C_3(CMe_3)_2][OCMe(CF_3)_2]_2$ and 1,2-dimethoxyethane. When this sample is cooled, the red–violet color returns and a new set of signals appear that are consistent with formation of a dme adduct (eq 11). A stable pyridine adduct can be obtained by addition of pyridine to $Mo[C_3(CMe_3)_2][OCMe(CF_3)_2]_2(dme)$ or $Mo[C_3(CMe_3)_2][OCMe(CF_3)_2]_2$ or by reaction of $Me_3CC{\equiv}CH$

(12) McCullough, L. G.; Listemann, M. L.; Schrock, R. R.; Churchill, M. R.; Ziller, J. W. *J. Am. Chem. Soc.* **1983**, *105*, 6729.

$$\underset{\text{purple}}{Mo[C_3(CMe_3)_2][OCMe(CF_3)_2]_2(dme)} \overset{-dme}{\rightleftharpoons} \underset{\text{yellow}}{Mo[C_3(CMe_3)_2][OCMe(CF_3)_2]_2} \quad (11)$$

with $Mo(CCMe_3)[OCMe(CF_3)_2]_3$ in the presence of pyridine (eq 12). The final piece to this puzzle is the finding that Mo-

$$Mo(CCMe_3)(OR)_3 \xrightarrow[-ROH]{+2py + Me_3CC{\equiv}CH} Mo[C_3(CMe_3)_2](OR)_2(py)_2$$

$$OR = OCMe(CF_3)_2 \quad (12)$$

$(CCMe_3)[OCMe(CF_3)_2]_3$ reacts with $Me_3CC{\equiv}CH$ to give yellow $Mo[C_3(CMe_3)_2][OCMe(CF_3)_2]_2$.

The reaction between $Mo(CCMe_3)[OCMe(CF_3)_2]_3(dme)$ in ether and an excess of a terminal alkyne having alkyl groups smaller than *tert*-butyl leads to the formation of deprotiomolybdenacyclobutadiene complexes that contain coordition dme, but no CMe_3 group (eq 13). The complexes in which

$$Mo(CCMe_3)(OR')_3(dme) \xrightarrow[-Me_3CC{\equiv}CH - R'OH]{\text{excess } RC{\equiv}CH} Mo(C_3R_2)(OR')_2(dme) \quad (13)$$

$$OR' = OCMe(CF_3)_2$$

R = Pr were observed by ^1H NMR only; those in which R = $CHMe_2$ or Ph could be isolated, albeit in lower yields than the $Mo[C_3(CMe_3)_2](OR')_2(dme)$ complexes. From this result, it is clear that loss of $Me_3CC{\equiv}CH$ from a presumed $Mo[C_3(CMe_3)(R)(H)](OR')_3$ complex must be fast relative to formtion of a $Mo[C_3(CMe_3)(R)](OR')_2$ complex by loss of R'OH from $Mo[C_3(CMe_3)(R)(H)](OR')_3$. Apparently the dme-free complexes, $Mo(C_3R_2)(OR')_2$, are not stable if $R \neq CMe_3$, or at least not as readily isolable, since the reaction between $Mo(CCMe_3)[OCMe(CF_3)_2]_3$ and $RC{\equiv}CH$ (R = Pr, $CHMe_2$, CH_2CHMe_2, and Ph) appeared to be relatively messy and no complexes of the type $Mo(C_3R_2)(OR')_2$ could be isolated. One possible reason why the reactions appear to be relatively complex is that both $Mo[C_3(CMe_3)(R)](OR')_2$ and $Mo(C_3R_2)(OR')_2$ are present. Another is that the terminal acetylene can react further with the deprotiocycle in the absence of dme (cf. the $OCH(CF_3)_2$ system below).

$Mo(CCMe_3)[OCH(CF_3)_2]_3(dme)$ reacts with $Me_3CC{\equiv}CH$ in the presence of pyridine to give $Mo[C_3(CMe_3)_2][OCH(CF_3)_2]_2(py)_2$. In the absence of pyridine, a complex with the empirical composition $Mo[OCH(CF_3)_2]_2[C_5H_2(CMe_3)_3](C_2CMe_3)$ is formed. This and analogous species will be reported separately.[13] The results of an X-ray study of $Mo[C_3(CMe_3)_2][OCH(CF_3)_2]_2(py)_2$ are reported below.

Reactions involving $Mo(CCMe_3)[OCMe_2(CF_3)]_3$ are relatively complex, as this molecule reacts with some terminal acetylenes to yield new alkylidyne complexes and with others to yield deprotiomolybdenacyclobutadiene complexes. A solution of $Mo(CCMe_3)[OCMe_2(CF_3)]_3$ turns light brown upon adding 1 equiv of $HC{\equiv}CCMe_3$, and a tan solid can be isolated after 1 h upon removing the solvent. A ^1H NMR spectrum of the crude brown solid shows it to be almost pure $Mo(CCMe_3)[OCMe_2(CF_3)]_3$ containing a small amount of what could be $Mo[C_3(CMe_3)_2][OCMe_2(CF_3)]_2$. Using a large excess of $HC{\equiv}CCMe_3$ and extending the reaction time to 1 day increases the yield of the "$Mo[C_3(CMe_3)_2][OCMe_2(CF_3)]_2$" to ~10%. 1-Pentyne, 3-methyl-1-butyne, and phenylacetylene react with $Mo(CCMe_3)[OCMe_2(CF_3)]_3$ to give new alkylidyne complexes (eq

$$Mo(CCMe_3)[OCMe_2(CF_3)]_3 \xrightarrow[\text{ether}]{x\,RC{\equiv}CH} Mo(CR)[OCMe_2(CF_3)]_3 \quad (14)$$

$$R = Pr, CHMe_2;\ x = 10$$

$$R = Ph,\ x = 1$$

(13) Strutz, H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* following paper in this issue.

14). If 2 equiv of $PhC{\equiv}CH$ is added, what appears to be $Mo[C_3Ph_2][OCMe_2(CF_3)]_2$ is found mixed with starting material upon removing the solvent. We propose that in this situation, $Mo(CPh)[OCMe_2(CF_3)]_3$ reacts with phenylacetylene to give a diphenylmolybdenacyclobutadiene complex in which the ring proton is significantly more acidic than it is in intermediate molybdenacyclobutadiene complexes containing only alkyl substituents on the ring.

Reactions are driven toward formation of deprotiomolybdenacyclobutadiene complexes upon addition of a nitrogenous base to the reaction mixture. For example, a green deprotiocomplex is formed in high yield as shown in eq 15 (cf. results immediately above). If $Me_3CC{\equiv}CH$ is employed in a

$$Mo(CCMe_3)[OCMe_2(CF_3)]_2 + 2PhC{\equiv}CH \xrightarrow[\text{ether}]{\text{excess py}} Mo(C_3Ph_2)[OCMe_2(CF_3)]_2(py)_2 \quad (15)$$

similar reaction, a purple solid can be isolated upon removing the solvent in vacuo. The solid turns yellow upon warming to room temperature in vacuo. A ^1H NMR spectrum of the solid shows it to be a mixture of approximately one-third unreacted $Mo(CCMe_3)[OCMe_2(CF_3)]_3$ and two-thirds $Mo[C_3(CMe_3)_2][OCMe_2(CF_3)]_2$. If quinuclidine (quin) is used instead of pyridine, then $Mo[C_3(CMe_3)_2][OCMe_2(CF_3)]_2$ can be prepared in pure form (eq 16). Presumably even 1 equiv of relatively bulky

$$Mo(CCMe_3)[OCMe_2(CF_3)]_3 \xrightarrow[\text{ether, quin}]{Me_3CC{\equiv}CH} Mo[C_3(CMe_3)_2][OCMe_2(CF_3)]_2 \quad (16)$$

quinuclidine cannot bind strongly to the metal in this deprotiocomplex. Similar reactions between $Mo(CCMe_3)(OCMe_3)_3$, quinuclidine, and $PhC{\equiv}CH$ yield mixtures that by ^1H NMR contain $Mo(CPh)(OCMe_3)_3(quin)$ and (most likely) $Mo(C_3Ph_2)(OCMe_3)_2$, although this deprotiocomplex could not be isolated in pure form.

Addition of 1 equiv of $RC{\equiv}CH$ (R = Pr, CMe_3, or Ph) to an ether solution of $Mo(CCMe_3)(DIPP)_3$ at −30 °C smoothly yields the deprotiometallacycle, $Mo[C_3(CMe_3)R](DIPP)_2$ (mixed with 1 equiv of 2,6-diisopropylphenol) in the form of an orange–yellow oil (eq 17). When more than 1 equiv of $RC{\equiv}CH$ is added to

$$Mo(CCMe_3)(DIPP)_3 \xrightarrow[\text{ether, } -30\ ^\circ C]{+RC{\equiv}CH} Mo[C_3(CMe_3)(R)](DIPP)_2 + DIPPH \quad (17)$$

R = Pr, CMe_3, and Ph

$Mo(CCMe_3)(DIPP)_3$, the results are the same as shown in eq 17, except that much of the excess acetylene is polymerized. We found no evidence for formation of a new alkylidyne complex, $Mo(CR)(DIPP)_3$, followed by reaction with a second equivalent of $RC{\equiv}CH$ to yield $Mo(C_3R_2)(DIPP)_2$. This result contrasts with those obtained in the analogous $OCMe(CF_3)_2$ system above (eq 13) where $Mo(C_3R_2)[OCMe(CF_3)_2]_2(dme)$ complexes are the only species isolated.

Monoadducts containing pyridine, $Mo[C_3(CMe_3)R](DIPP)_2(py)$, can be isolated as red–orange crystals by adding 1 or more equiv of pyridine to the mixture shown in eq 17 dissolved in ether or pentane. Alternatively, pyridine can be added to $Mo(CCMe_3)(DIPP)_3$ before the terminal acetylene; the pale-yellow solution of $Mo(CCMe_3)(DIPP)_3$ turns deep red when pyridine is added (probably the result of pyridine coordinating to Mo) and then slowly red–orange after the acetylene is added. The yield of $Mo[C_3(CMe_3)R](DIPP)_2(py)$ by either method is 75–80%. We assume that the failure to observe bis(pyridine) adducts (cf. bis(pyridine) adducts in eq 12) can be ascribed to the especially large steric requirements of the 2,6-diisopropoxide ligand.

The ^{13}C NMR chemical shifts of the ring carbon atoms in several of the deprotiomolybdenacyclobutadiene complexes described here are listed in Table I. We cannot be entirely certain of the assignments, although we feel confident that the resonance for C_α is normally downfield of that for C_β based on the data for the compounds containing two different ring substituents and the

Table I. ^{13}C NMR Chemical Shifts for Ring Carbon Atoms in Deprotiomolybdenacyclobutadiene Complexes[a]

compound	C_α	C_β
$Mo[C_3(CMe_3)_2][OCH(CF_3)_2]_2(py)_2$	235.4	208
$Mo[C_3(CMe_3)_2][OCMe_2(CF_3)]_2$	239.3	177.6
$Mo(C_3Ph_2)[OCMe_2(CF_3)]_2(py)_2$	203.3	201.1
$Mo[C_3(CMe_3)_2][OCMe(CF_3)_2]$	258.2	190.6
$Mo[C_3(CMe_3)_2][OCMe(CF_3)_2]_2(py)_2$	252.4	222.9
$Mo[C_3(CHMe_2)_2][OCMe(CF_3)_2]_2(dme)$	244.6	206.6
$Mo(C_3Ph_2)[OCMe(CF_3)_2]_2(dme)$	229.2	217.3
$Mo[C_3(CMe_3)_2][OC(CF_3)_3]_2$	257.4	196.2
$Mo[C_3(CMe_3)Ph][DIPP]_2$[b]	241.4/222.2	173.2
$Mo[C_3(CMe_3)Ph](DIPP)_2(py)$	233.2/209.0	187.5
$Mo[C_3(CMe_3)_2][DIPP]_2$[b]	243.6	171.4
$Mo[C_3(CMe_3)_2](DIPP)_2(py)$	232.4	185.9
$Mo[C_3(CMe_3)Pr][DIPP]_2$[b]	243.4/232.3	174.1
$Mo[C_3(CMe_3)Pr](DIPP)_2(py)$	233.5/219.6	186.7

[a] DIPP = O-2,6-$C_6H_3(CHMe_2)_2$. [b] Observed in situ only, mixed with DIPPH; see text and Experimental Section.

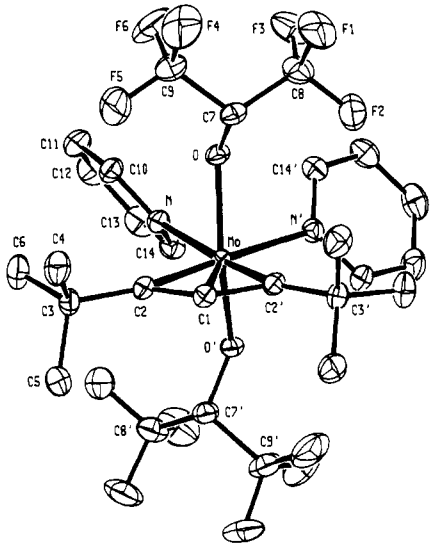


Figure 2. Geometry of $Mo[C_3(CMe_3)_2][OCH(CF_3)_2]_2(py)_2$ showing the atom labeling scheme and the 30% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Primed atoms are related to those unprimed by a crystallographically required 2-fold axis passing through Mo and C(1).

observed shorter Mo–C_α distance than Mo–C_β distance in $Mo[C_3(CMe_3)_2][OCH(CF_3)_2]_2(py)_2$ (see below). A possible exception is the third entry where the C_α resonance is shifted upfield substantially upon replacing the *tert*-butyl groups with a phenyl group. There are some interesting shifts incurred upon changing alkoxides or upon forming adducts. For example, the resonance for C_α shifts upfield and the resonance for C_β shifts downfield upon forming a bis(pyridine) adduct. These trends are consistent with the Mo–C_α bond length being shorter and the Mo–C_β bond length being longer in the donor ligand-free complexes than they are in the donor ligand adducts.

As we mentioned above, we believe the structures of the solvent-free compounds to be pseudotetrahedral. On the basis of the structure of $Mo[C_3(CMe_3)_2][OCH(CF_3)_2]_2(py)_2$ (see below), we expect all bis donor ligand adducts to be pseudooctahedra with donor ligands located trans to the MoC_3 ring. The mono donor ligand adducts we must assume for now are pseudotrigonal bipyramids with the donor ligand and MoC_3 ring in the equatorial plane.

X-ray Structure of $Mo[C_3(CMe_3)_2][OCH(CF_3)_2]_2(py)$. The structure of $Mo[C_3(CMe_3)_2][OCH(CF_3)_2]_2(py)_2$ is illustrated in Figures 2 and 3. Final positional parameters are given in Table II and selected interatomic distances and angles in Table III. The molecule is a distorted octahedron that contains a 2-fold axis passing through Mo and C(1). The atoms N (N'), Mo, C(2) (C(2')), and C(1) all lie in a plane. The Mo–N distance is typical of that in a molecule in which pyridine bonds trans to a tightly

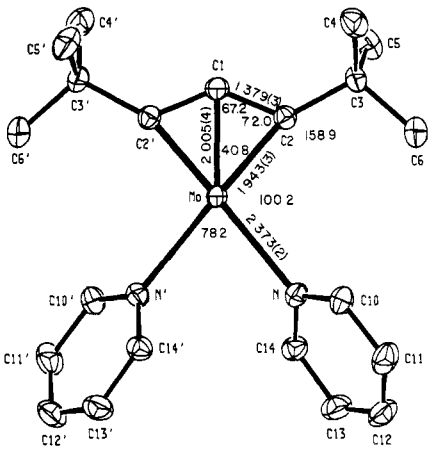


Figure 3. Projection of the structure onto the Mo, C(2), C(2') plane. The hexafluoroisopropoxide ligands have been omitted for clarity. Remaining details are the same as for Figure 2.

Table II. Final Positional Parameters for the Atoms of $Mo[C_3(CMe_3)_2][OCH(CF_3)_2]_2(py)_2$[a]

atom	x	y	z
Mo	0.0000	0.25496 (4)	0.2500
F(1)	−0.13306 (16)	0.2643 (3)	0.47843 (18)
F(2)	−0.15620 (13)	0.1951 (3)	0.35225 (16)
F(3)	−0.08445 (16)	0.0953 (2)	0.45968 (18)
F(4)	0.00830 (18)	0.3514 (4)	0.56160 (17)
F(5)	0.09142 (16)	0.3485 (3)	0.49835 (16)
F(6)	0.06079 (18)	0.1856 (3)	0.54410 (17)
O	−0.00193 (12)	0.21092 (18)	0.36714 (12)
N	0.08629 (14)	0.0879 (2)	0.29088 (15)
C(1)	0.0000	0.4368 (4)	0.2500
C(2)	0.07361 (17)	0.3883 (3)	0.27778 (18)
C(3)	0.15123 (17)	0.4531 (3)	0.3084 (2)
C(4)	0.1492 (2)	0.5502 (3)	0.3727 (2)
C(5)	0.1643 (2)	0.5145 (4)	0.2319 (2)
C(6)	0.21612 (19)	0.363 2 (3)	0.3496 (3)
C(7)	−0.03110 (18)	0.2726 (3)	0.42073 (18)
C(8)	−0.1006 (2)	0.2062 (4)	0.4292 (3)
C(9)	0.0323 (3)	0.2895 (4)	0.5070 (2)
C(10)	0.13508 (17)	0.0779 (3)	0.3713 (2)
C(11)	0.1826 (2)	−0.0217 (4)	0.3994 (2)
C(12)	0.1799 (2)	−0.1149 (3)	0.3435 (3)
C(13)	0.1296 (2)	−0.1051 (3)	0.2612 (3)
C(14)	0.08431 (18)	−0.0036 (3)	0.2368 (2)
H(41)	0.1975 (2)	0.5914 (3)	0.3923 (2)
H(42)	0.1397 (2)	0.5133 (3)	0.4198 (2)
H(43)	0.1090 (2)	0.6065 (3)	0.3460 (2)
H(51)	0.2128 (2)	0.5552 (4)	0.2505 (2)
H(52)	0.1240 (2)	0.5714 (4)	0.2070 (2)
H(53)	0.1642 (2)	0.4549 (4)	0.1906 (2)
H(61)	0.26433 (19)	0.4047 (3)	0.3685 (3)
H(62)	0.21686 (19)	0.3030 (3)	0.3090 (3)
H(63)	0.20770 (19)	0.3257 (3)	0.3971 (3)
H(71)	−0.04843 (18)	0.3504 (3)	0.39751 (18)
H(101)	0.13716 (17)	0.1416 (3)	0.4104 (2)
H(111)	0.2169 (2)	−0.0258 (4)	0.4569 (2)
H(121)	0.2121 (2)	−0.1843 (3)	0.3615 (3)
H(131)	0.1262 (2)	−0.1683 (3)	0.2212 (3)
H(141)	0.05011 (18)	0.0023 (3)	0.1793 (2)

[a] Atoms are labeled as shown in Figure 2. Estimated standard deviations, in parentheses, occur in the least significant figure(s) for each parameter. Hydrogen atoms are labeled according to the carbon atom to which they are bound.

bound carbon-based ligand (cf. $W[C_3Et_2(CMe_3)]Cl_3(Me_2NCH_2CH_2NMe_2)$);[11] the N–Mo–N' angle is only 78.2 (1)°. The $OCH(CF_3)_2$ ligands are bent away from the MoC_3 ring system so that O–Mo–O' = 152.2 (1)°. The Mo–O distance (2.021 (2) Å) and Mo–O–C(7) angle (130.5 (2)°) are close to those values found in $W(C_3Et_3)[OCH(CF_3)_2]_3$,[7b] and assumed to be characteristic of the relatively poor π-electron-donating, ionic $OCH(CF_3)_2$ ligand.

Table III. Selected Interatomic Distances (Å) and Angles (deg) for $Mo[C_3(CMe_3)_2][OCH(CF_3)_2]_2(py)_2$[a]

Mo-C(1)	2.005 (4)	C(1)-C(2)	1.379 (3)
Mo-C(2)	1.943 (3)	C(2)-C(3)	1.518 (4)
Mo-O	2.021 (2)	C(7)-C(8)	1.519 (5)
Mo-N	2.373 (2)	C(7)-C(9)	1.519 (5)
O-C(7)	1.368 (4)		
C(1)-Mo-C(2)	40.8 (1)	C(2)-Mo-N′	176.2 (1)
C(1)-Mo-N	140.9 (1)	C(2)-Mo-O	101.1 (1)
C(1)-Mo-O	103.9 (1)	N-Mo-O	76.5 (1)
C(2)-Mo-C(2′)	81.7 (1)	N-Mo-N′	78.2 (1)
C(2)-Mo-N	100.2 (1)	O-Mo-O′	152.2 (1)
Mo-C(1)-C(2)	67.2 (2)		
Mo-C(2)-C(1)	72.0 (2)		
Mo-C(2)-C(3)	158.9 (2)		
Mo-O-C(7)	130.5 (2)		
C(1)-C(2)-C(3)	129.1 (3)		

[a] See footnote a, Table II.

Table IV. Comparison of Distances (Å) and Angles (deg) in Two Complexes Containing $M[C_3(CMe_3)_2]$ Ring Systems

	$W(\eta^5\text{-}C_5H_5)\text{-}[C_3(CMe_3)_2]Cl$	$Mo[C_3(CMe_3)_2]\text{-}[OCH(CF_3)_2]_2(py)_2$
$M\text{-}C_\alpha$	1.929 (16)	1.943 (3)
	1.919 (8)	
$M\cdots C_\beta$	2.049 (8)	2.005 (4)
$C_\alpha\text{-}C_\beta$	1.311 (21)	1.379 (3)
	1.399 (11)	
$M\text{-}C_\alpha\text{-}C_\beta$	75.8 (7)	72.0 (2)
	74.5 (5)	
$C_\alpha\text{-}M\text{-}C'_\alpha$	79.4 (5)	81.7 (1)
$C_\alpha\text{-}C_\beta\text{-}C'_\alpha$	130.2 (9)	134.4 (4)
$M\text{-}C_\alpha\text{-}C_s$[a]	149.8 (9)	158.9 (1)
	155.0 (6)	

[a] C_s is the quaternary carbon atom of the *tert*-butyl group bound to C_α.

There are two features of the ligands' orientations that can be ascribed to steric crowding. The first is the twisting of the pyridine ligands out of the MoN_2C_3 plane by 57°. We suspect that the pyridine rings should lie *in* the MoN_2C_3 plane in order that their π systems can conjugate with the MoC_3 π system. But the N–Mo–N′ angle is only 78.2 (1)°. If they were to lie in the MoN_2C_3 plane, the hydrogen atoms on C(14) and C(14′) would probably be too close to each other. The second feature is that C(7) and C(7′) of the $OCH(CF_3)_2$ ligands lie over the MoC_3 ring, probably in order to avoid steric interactions with the pyridine ligands. The CF_3 group containing C(8) is tucked between the *tert*-butyl group containing C(3′) and the pyridine ligand containing N′. The CF_3 group that contains C(9) lies approximately above C(2) since it interacts with the proton on C(10) of the pyridine ligand tilted toward it. If the pyridine ligands were tilted toward one another (e.g., C(10) toward C(14′)) then although the $OCH(CF_3)_2$ group containing C(7), C(8), and C(9) could neatly be oriented so that C(7) would be above C(1), the other $OCH(CF_3)_2$ group would interact more strongly with both pyridine ligands now turned toward it.

The strictly planar MoC_3R_2 system is similar to that found in $W(\eta^5\text{-}C_5H_5)[C_3(CMe_3)_2]Cl$ (Table IV), the only other structurally characterized example.[12] (The differences could be ascribed solely to the rather different types of complexes involved.) The Mo–C(2) and Mo···C(1) distances are nearly the same, the Mo–C(2)–C(1) angle is only 72.0 (2)°, the C(2)–C(1)–C(2′) angle is 134.3 (4)°, and the C(2)–Mo–C(2′) angle is 81.7 (1)°. The two *tert*-butyl groups are bent away from the metal (Mo–C(2)–C(3) = 158.9 (2)°). One might have ascribed the latter to steric interaction between the *tert*-butyl groups and the pyridine ligands were it not for the relatively unhindered coordination sphere in $W(\eta^5\text{-}C_5H_5)[C_3(CMe_3)_2]Cl$ and similar large $M\text{-}C_\alpha\text{-}C_\beta$ angles in the tungstenacyclobutadiene complex, $W[C(CMe_3)C(Me)C(Me)]\text{-}Cl_3$,[11] a completely unhindered molecule that is related to the deprotiometallacyclobutadiene complexes.

Metathesis of Acetylenes. Several of the compounds reported here are good-to-excellent metathesis catalysts for internal acetylenes, roughly comparable to $W(CCMe_3)(OCMe_3)_3$.[6] The best appears to be $Mo(CCMe_3)[OCMe(CF_3)_2]_3$ or its dme adduct. $Mo(CCMe_3)[OCMe(CF_3)_2]_3$ reacts rapidly with 20 equiv of 3-heptyne to give high yields of cleavage products, and the 1:2:1 equilibrium mixture of 3-hexyne/3-heptyne/4-octyne is reached in less than 5 min at 25 °C (run 3, Table V). Little or no polymer is formed, even after long reaction times at high concentration of alkyne (e.g., 2 days, ~1.6 M 3-heptyne). $Mo(CCMe_3)\text{-}[OCMe(CF_3)_2]_3$(dme) qualitatively metathesizes 3-heptyne equally well (run 2, Table V). As we noted earlier, dimethoxyethane is lost from the metal under some circumstances; it must be at least partially and rapidly displaced by the acetylene in these metathesis reactions.

$Mo(CCMe_3)[OCMe_2(CF_3)]_3$ (run 4) also reacts smoothly with 3-heptyne to give high yields of cleavage products, but the rate of approach to equilibrium is clearly less than that for the more electrophilic catalysts containing the $OCMe(CF_3)_2$ ligand.

The most electrophilic catalyst should be $Mo(CCMe_3)[OC\text{-}(CF_3)_3]_3$(dme). Although the approach to equilibrium is rapid and little or no new polymer is formed, the yield of cleavage products is relatively low. We believe this result to be anomalous, perhaps ascribable to the starting material reacting with traces

Table V. Metathesis of 3-Heptyne by Molybdenum Alkylidyne Complexes

			cleavage prod (% yield)	
catalyst[a]	time, min	K[b]	tot	$PrC{\equiv}CCMe_3$/ $EtC{\equiv}CCMe_3$
1. $Mo(CCMe_3)[OC(CF_3)_3]_3$(dme)	5	0.22	63	1.42
	30	0.24	61	1.44
2. $Mo(CCMe_3)[OCMe(CF_3)_2]_3$(dme)	5	0.24	91	1.33
3. $Mo(CCMe_3)[OCMe(CF_3)_2]_3$	5	0.24	87	1.64
	30	0.24	90	1.65
4. $Mo(CCMe_3)[OCMe_2(CF_3)]_3$	5	0.08	94	1.61
	30	0.24	90	1.65
5. $Mo(CCMe_3)[OCH(CF_3)_2]_3$(dme)	5	0.20	90	1.31
	60	0.24	91	1.22
6. $Mo(CCMe_3)[OC(CF_3)_3]_2Cl$(dme)	5	0.15	84	1.90
	30	0.26	90	1.50
	60	0.24	89	1.54
7. $Mo(CCMe_3)[OCMe(CF_3)_2]_2Cl$(dme)	5	0.24	84	1.47
	120	0.24	87	1.29
8. $Mo(CCMe_3)[OCH(CF_3)_2]_2Cl$(dme)	5	0.24	78	1.23
	60	0.24	80	1.22
9. $Mo(CCMe_3)[O\text{-}2,6\text{-}C_6H_3(CHMe_2)]_3$	5	0.25	57	0.78
	120	0.24	84	1.15

[a] Typical reaction conditions are 30–50 mg of catalyst and 20 equiv of 3-heptyne in ether (5 mL) containing an internal standard (decane). [b] K = [3-hexyne][4-octyne]/[3-heptyne]^2.

of water. Unfortunately, the fact that only a small sample of $(CF_3)_3COH$ had been available prevented confirmation of this finding.

$Mo(CCMe_3)[OCH(CF_3)_2]_3(dme)$ and $Mo(CCMe_3)[OCH(CF_3)_2]_3(THF)_n$ (n = 1 and 2) are relatively fast acetylene metathesis catalysts, but these catalysts also polymerize acetylenes, as evidenced by the formation of insoluble solids and the decrease in the amounts of acetylenes (by GC) after 1 h. As we have noted before, the $OCH(CF_3)_2$ ligand is too small, thereby allowing more acetylene to react with intermediate molybdenacyclobutadiene complexes, perhaps to give larger and larger rings, or at least that is one possible interpretation of what appears to be a general trend toward polymer formation in the presence of relatively small alkoxide ligands.

The complexes containing one chloride ligand (runs 6, 7, and 8) will also metathesize acetylenes, but polymer formation is even more competitive in these cases. Therefore, the monochloro complexes would appear to be the least desirable as metathesis catalysts.

We briefly examined the metathesis of PhC≡CEt by $Mo(CCMe_3)[OCMe(CF_3)_2]_3(dme)$. The rate is significantly slower than the rate of metathesis of 3-heptyne. For 20 equiv of PhC≡CEt, $K = 2 \times 10^{-2}$ after 5 min and $K = 0.13$ after 210 min. Similar qualitative results were obtained for metathesis reactions involving $W(CCMe_3)(OCMe_3)_3$.[6b] In each case, the metal appears to react most rapidly with the more electron-rich dialkylacetylene. For acetylenes whose ends are significantly different electronically, there is also the likelihood that degenerate metathesis steps will be favored over productive metathesis steps. Here the benzylidyne complex should be the energetically favored species, and it should react with PhC≡CEt in a degenerate fashion.

Finally, we briefly explored the possibility that a terminal acetylene could be metathesized by the complex that is least likely to yield deprotiomolybdenacyclobutadiene complexes, namely a *tert*-butoxide complex. In fact, 1-pentyne reacts with $Mo(CPr)(OCMe_3)_3$ to produce a small amount of 4-octyne after 1 day, 0.36 equiv after 2 days, and 0.45 equiv after 3 days. No 4-octyne formed in the absence of 1-pentyne under the same conditions, thereby ruling out any bimolecular decomposition of $Mo(CPr)(OCMe_3)_3$. In the absence of confirmatory labeling studies, we can only say that the 4-octyne most likely is formed when 1-pentyne reacts with $Mo(CPr)(OCMe_3)_3$ to give $Mo(CH)(OCMe_3)_3$; $Mo(CH)(OCMe_3)_3$ is known to decompose in the absence of quinuclidine.[14]

Discussion

The mechanism of formation of $Mo(CCMe_3)(CH_2CMe_3)_3$ is obscure. Although the starting material contains Mo(VI), we cannot be certain that the metal is not reduced during the reaction. (Intermolecular decomposition of lower oxidation state neopentyl complexes to give $M(CCMe_3)(CH_2CMe_3)_3$ has been documented in the tungsten system.[3b]) Even if we could be certain the metal is not reduced along the pathway to $Mo(CCMe_3)(CH_2CMe_3)_3$, we simply do not have enough information to come up with any one mechanism that is more likely than any other. What we can say with some confidence, however, is that $Mo(CH_2CMe_3)_6$ is an unlikely precursor to $Mo(CCMe_3)(CH_2CMe_3)_3$. We also have argued against $W(CH_2CMe_3)_6$ being the precursor to $W(CCMe_3)(CH_2CMe_3)_3$.[3b]

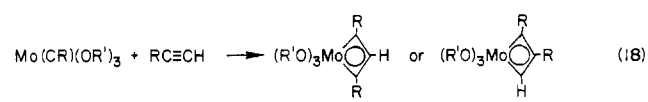
A relatively important finding is that the neopentylidyne ligand in $Mo(CCMe_3)(CH_2CMe_3)_3$ survives treatment with HCl. One might have naively expected the neopentylidyne α-carbon atom to be protonated to give a neopentylidene complex at some point and perhaps the neopentylidene complex to be protonated further to give a neopentyl complex. At least the first might indeed take place, but H_α^+ is then removed, either to give neopentane or to give HCl, and a neopentylidyne complex is reformed. Although we feel intuitively that formation of a significant amount of neopentyl complex is unlikely, the neopentylidyne complex could still reform in theory by loss of α protons. We believe that the reaction of $Mo(CCMe_3)(CH_2CMe_3)_3$ with HX in fact may proceed by initial monoprotonation of the neopentylidyne ligand. We are currently examining other protonation reactions in both the Mo and W systems.

A relatively important feature of molybdenum neopentylidyne complexes vs. tungsten neopentylidyne complexes is that molybdenum is less electrophilic. For example, $Mo(CCMe_3)(OCHMe_2)_3$ and $Mo(CCMe_3)(OCH_2CMe_3)_3$ appear to be monomers, while the analogous tungsten complexes appear to be dimers.[15a] Also, $Mo(CCMe_3)[OCMe(CF_3)_2]_3$ can be obtained by sublimation of $Mo(CCMe_3)[OCMe(CF_3)_2]_3(dme)$, whereas $W(CCMe_3)[OCMe(CF_3)_2]_3(dme)$ sublimes with the dme intact.[7a] The lower electrophilicity of Mo we feel is the primary reason why $Mo(CCMe_3)(OCMe_3)_3$ will not react with internal acetylenes while $W(CCMe_3)(OCMe_3)_3$ will. Changing the $OCMe_3$ ligand to $OCMe_2(CF_3)$ compensates for the inherently lower electrophilicity of Mo to the extent that $Mo(CCMe_3)[OCMe_2(CF_3)]_3$ now reacts readily with internal acetylenes. In keeping with this trend, $Mo(CCMe_3)[OCMe(CF_3)_2]_3$ reacts even more rapidly with internal acetylenes and is one of the best acetylene metathesis catalysts containing molybdenum that we have prepared. $Mo(CCMe_3)[OC(CF_3)_3]_3$ presumably would react most rapidly of all with internal acetylenes, but this species has not yet been obtained since $Mo(CCMe_3)[OC(CF_3)_3]_3(dme)$ does not lose dimethoxyethane upon sublimation.

Another important trend in the chemistry of $Mo(CR)(OR')_3$ complexes is the tendency to polymerize internal acetylenes when OR′ is small. When OR′ = OCH_2CMe_3, the rate of acetylene polymerization is significantly greater than the rate of metathesis. When OR′ = $OCHMe_2$, acetylenes are still polymerized, but more initial metathesis products (*tert*-butylacetylenes) and productive metathesis products are observed than in the OCH_2CMe_3 systems. Likewise, when OR′ = $OCH(CF_3)_2$, some polymerization of the acetylene is observed in addition to metathesis, but when OR′ = $OCMe(CF_3)_2$, no polymer is observed, even after long reaction times. These findings can be attributed to the larger OR′ groups, limiting access of more than 1 equiv of acetylene to the coordination sphere of the alkylidyne complex.

Observation of a molybdenacyclobutadiene complex only when O-2,6-$C_6H_3(CHMe_2)_2$ ligands are present is probably not of great significance since even it is rather unstable toward loss of an acetylene. What is more interesting, however, is the fact that $W(C_3Et_3)[O\text{-}2,6\text{-}C_6H_3(CHMe_2)_2]_3$,[7b] $W(C_3Et_3)[OCH(CF_3)_2]_3$,[7a] and $W(C_3Et_3)[OCMe(CF_3)_2]_3$[7a] are all relatively stable toward loss of 3-hexyne to give $W(CEt)(OR')_3$ complexes. (The O-2,6-$C_6H_3(CHMe_2)_2$ and $OCMe(CF_3)_2$ complexes will lose 3-hexyne, according to kinetic studies of 3-hexyne-d_{10} incorporation, but only the metallacycles have been observed.) The greater tendency for molybdenacyclobutadiene complexes to lose acetylene could be ascribed loosely to "the lower electrophilicity" of Mo vs. W toward an acetylene nucleophile. Unfortunately, it is not possible to pinpoint the difference between the two systems since the required thermodynamic data are lacking.

We believe that terminal acetylenes react readily with $Mo(CCMe_3)(OCMe_3)_3$ simply because of fewer steric problems than in the reaction between $Mo(CCMe_3)(OCMe_3)_3$ and internal acetylenes. But what is most important in reactions involving terminal acetylenes is the formation of deprotiomolybdenacyclobutadiene complexes. Almost certainly the first step is formation of either the α,α'- or α,β-disubstituted molybdenacyclobutadiene complex (eq 18). We have no evidence



(18)

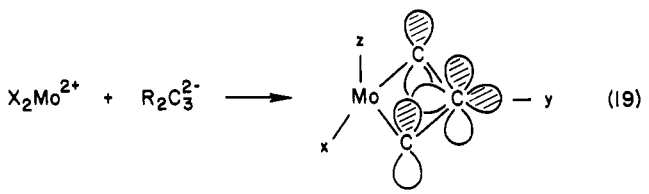
that either one is more favorable than the other, although steric interaction between the R groups in the α,β-disubstituted ring might cause the α,α'-disubstituted derivative to be favored. Removing a proton from the α,α'-disubstituted isomer is also the most logical and direct route to the deprotiometallacycles. If this is the case, then it is difficult to imagine how R′OH could be lost intramolecularly. Yet, interestingly, we have found this to be the

(14) Strutz, H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1600.

case for decomposition of analogous isolable tungsten complexes.[15b] We also have evidence that external base can remove the β proton directly in the tungsten complexes.[15b] Although we probably will never be able to study the formation of deprotiomolybdenacyclobutadiene complexes kinetically, we have no reason to suspect that the Mo chemistry differs substantially from that of analogous W systems.

The evidence gathered here suggests that electron-withdrawing alkoxide ligands markedly increase the acidity of a ring proton in putative molybdenacyclobutadiene complexes judging from the fact that the rate of formation of $Mo[C_3(CMe_3)_2](OR)_2$ increases in the order $OCMe_3 < OCMe_2(CF_3) < OCMe(CF_3)_2 < OC(CF_3)_3$, with the 2,6-diisopropylphenoxide ligand probably being roughly comparable to $OCMe(CF_3)_2$ or $OC(CF_3)_3$. Deprotiomolybdenacyclobutadiene complexes with phenyl substituents are also more rapidly formed than the corresponding complexes having alkyl substituents, as one would predict. Formation of deprotiomolybdenacyclobutadiene complexes does not augur well for successful metathesis of terminal acetylenes, even if all other problems such as adverse reactions involving the C_2H_2 product, or the instability of methylidyne complexes in general, could somehow be solved.

In attempting to understand what a deprotiometallacyclobutadiene complex is, it may be useful initially to view it as a MoX_2^{2+} complex containing the dianion, $R\bar{C}{=}C{=}\bar{C}R$ (eq 19).



In the process of forming the two Mo–C bonds to give a MoC_3 ring lying in the xy plane, the allenic character of the C_3 chain is necessarily destroyed. In an octahedral environment, three d orbitals can overlap with various combinations of the four p orbitals shown on the three carbon atoms. Two of these interactions, involving the d_{yz} and d_{xz} orbitals, were invoked to describe the bonding in a metallacyclobutadiene complex.[16] The third interaction between the $d_{x^2-y^2}$ orbital and the p orbital on C_β that lies in the $x-y$ plane is the one that most likely stabilizes the deprotio MC_3R_2 ring, since the resulting three bonding MO's now can accommmodate nicely the six total π electrons in the MC_3R_2 ring system.

An interesting question is whether the known acetylene metathesis systems based on Mo,[8] all of which qualitatively are much less active than those described here, contain active components that are analogous to the complexes described here. We believe the answer is likely to be yes. One feature of the known systems that is consistent with this proposal is that phenols or fluoroalcohols[8a] are required cocatalysts. However, while it is not difficult to imagine how a $Mo(CR)(OR')_3$ species could be formed in the $MoO_2(acac)_2/AlR_3$/phenol system,[8c,e] it is considerably less obvious how it would be formed from $Mo(CO)_6$, phenol, and an acetylene.[8a,b,d] Yet cluster complexes containing an alkylidyne ligand bound to a triangle of reduced metal atoms have been isolated from reactions between $Mo(CO)_6$ and acetic acid.[17] Disproportionation of related species in the presence of phenols or fluoroalcohols could result in formation of an adequate quantity of what might be an extremely active catalyst.

Molybdenum alkylidyne complexes could have certain advantages over tungsten complexes as acetylene metathesis catalysts. Perhaps the most important, at least as far as metathesis of functionalized acetylenes is concerned, is the apparent lower electrophilicity of molybdenum. Perhaps irreversible side reactions that are fast in a tungsten-based system could be minimized by employing molybdenum. We will turn to answering these and other questions concerning the application of molybdenum- and tungsten-based alkylidyne complexes to problems in catalysis in future publications.

Experimental Section

General Details. All experiments were performed under nitrogen by either standard Schlenk techniques or in a Vacuum Atmospheres drybox. Commercial grade pentane was extracted 3 times with H_2SO_4 containing 5% HNO_3 followed by washing with distilled water. It was then distilled from sodium/benzophenone ketyl. All other solvents (toluene, benzene, 1,2-dimethoxyethane, diethyl ether, tetrahydrofuran, acetonitrile, methylene chloride, and chloroform) were reagent grade and were rigorously purified and dried under N_2 by standard techniques and transferred into the drybox without exposure to air. Alkenes, alkynes, and deuterated solvents were deaerated with nitrogen and dried by passage through alumina prior to use. Alcohols were distilled from CaO under nitrogen unless otherwise noted. Amines were distilled from BaO under nitrogen.

^1H and ^{13}C NMR spectra are referenced to tetramethylsilane. ^{19}F spectra are referenced to C_6F_6 (162.9 ppm). ^{31}P spectra are referenced to 30% H_3PO_4. Coupling constants are quoted in hertz. Normal CH coupling constants and multiplicities are not listed specifically. Coupling constants quoted for one compound are not quoted later in another compound (e.g., carbon signals for $MeOCH_2CH_2OMe$) unless there are significant differences.

$LiCH_2CMe_3$,[18] $Mg(CH_2CMe_3)_2$,[19] $MoO_2Cl_2(THF)_2$,[20] and $MoOCl_3$[21] were prepared by published methods. $MoO_2(OCMe_3)_2$ was prepared from the unexceptional reaction of MoO_2Cl_2 with $LiOCMe_3$ in tetrahydrofuran. $MoOCl_2(OMe)_2$ was prepared from the unexceptional reaction of $MoOCl_4$ with Me_3SiOMe in dichloromethane.

Catalytic acetylene metathesis reactions were run in 5 mL of ether by using ~30 mg of catalyst and 20 equiv of 3-heptyne. Aliquots were periodically removed, quenched by shaking them with Al_2O_3, and analyzed by GLC methods. The internal standard was usually decane.

Crystallography. Data were collected at −20 °C on an Enraf-Nonius CAD4F-11 diffractometer equipped with a liquid nitrogen low-temperature device using Mo Kα radiation. The data collection, reduction, and refinement procedures used in this laboratory have been detailed elsewhere.[22] A total of 3629 reflections ($+h,+k,\pm l$) were collected in the range $3° \leq 2\theta \leq 55°$ with the 2761 having $F_o > 4\sigma(F_o)$ being used in the structure refinement which was by full-matrix least-squares techniques (203 variables) using SHELX-76. The final $R_1 = 0.037$ and $R_2 = 0.041$.

Hydrogen atoms were placed in geometrically calculated positions (C–H = 0.95 Å) and constrained to "ride" on their respective carbon atoms. There is no crystallographic evidence for a proton on C(1). With all the hydrogen atoms in the structure, the largest peak on the final difference Fourier map was 0.33 e/Å^3, and none of the peaks in this map were at a suitable distance from C(1) to be a proton. With H(101) left out of the calculation, this atom reappeared as the largest peak in a difference map at 0.84 e/Å^3. A similar situation occurred with H(71) which reappeared at 0.69 e/Å^3 and H(41)–H(43) which had peak heights of ca. 0.58 e/Å^3.

Crystal data are $a = 18.367$ (3) Å, $b = 11.025$ (2) Å, $c = 16.641$ (3) Å, $\beta = 109.98$ (1)°, $V = 3166.9$ Å^3, space group = $C2/c$, $Z = 4$, MW = 738.47, ρ(calcd) = 1.549 g cm^{-3}, and $\mu = 4.64$ cm^{-1} (absorption correction not applied). Final positional parameters appear in Table II and selected interatomic distances and angles in Table III. Figures 2 and 3 display the geometry of $Mo[C_3(CMe_3)_2][OCH(CF_3)_2]_2(py)_2$.

Preparations. MoO_2Cl_2. MoO_2Cl_2 was prepared in a glass apparatus consisting of a Schlenk tube (15 cm × 5 cm) and a 1-L two-neck flask. The tube and flask were connected by a glass tube (8 cm × 2 cm). The flask was fitted with a nitrogen outlet, and the Schlenk tube was fitted with a gas inlet tube extending to within 3 cm of the bottom. The Schlenk tube was heated in an oil bath, and the connecting tube was heated with a heating tape. MoO_2 (20 g, 160 mmol) was placed in the Schlenk tube and dried for 24 h at 160 °C in a stream of nitrogen. The nitrogen was then replaced by a stream of dry chlorine (passed through concentrated H_2SO_4). As the MoO_2Cl_2 formed, it sublimed out and was carried by the hot Cl_2 stream to the 2-L flask, where it crystallized as

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fluffy yellow–orange flakes. After ~2 h, 26 g (84%) of MoO_2Cl_2 had formed. It is helpful to place a magnetic stir bar in the collection flask in order to break up the MoO_2Cl_2 plug that sometimes threatens to block the entrance to the collection flask.

Mo(CCMe$_3$)(CH$_2$CMe$_3$)$_3$. A solution of MoO_2Cl_2 (10.0 g, 50.3 mmol) in THF (80 mL) was added dropwise to a solution of NpMgCl (~1 M, 301 mmol) in ether at −78 °C. The reaction mixture quickly turned red/brown, and a light-colored solid precipitated. The mixture was stirred for 1.5 h at −78 °C and was then allowed to warm to room temperature. After stirring the red reaction mixture for an additional 1.5 h, it was filtered and all solvents were removed from the filtrate in vacuo. The resulting dark solid was extracted with pentane (~300 mL total). The extracts were filtered and reduced in vacuo. Distillation of the resulting dark-brown oil at 60–80 °C and 0.1 μm through a short path distillation apparatus gave 6.45 g (34%) of yellow Mo(CCMe$_3$)-(CH$_2$CMe$_3$)$_3$. Alternatively, the product can be collected on a 0 °C probe in a sublimation apparatus; bumping can be minimized by placing a glass wool pad between the oil and the probe. The product so obtained is identical by ^{1}H and ^{13}C NMR with that previously reported: ^{1}H NMR (C_6D_6) δ 1.52 (CCMe$_3$), 1.39 (CH$_2$CMe$_3$), 1.15 (CH$_2$CMe$_3$); ^{13}C NMR (C_6D_6) δ 323.8 (CCMe$_3$), 88.1 (t, J = 111, CH$_2$CMe$_3$), 53.5 (CCMe$_3$), 34.0 (CH$_2$CMe$_3$), 33.5 (CH$_2$CMe$_3$), 30.2 (CCMe$_3$). We have tried 3 times to analyze Mo(CCMe$_3$)(CH$_2$CMe$_3$)$_3$. Each was unsuccessful (low in C by 1–2%). We can only guess that this compound might be sensitive to light.

Mo(CCMe$_3$)Cl$_3$(dme). A solution of HCl in ether (1.65 M, 30 mL, 49.5 mmol) was added slowly to a yellow solution of Mo(CCMe$_3$)-(CH$_2$CMe$_3$)$_3$ (6.00 g, 15.9 mmol) and 1,2-dimethoxyethane (4.9 mL, 47.1 mmol) in ether (50 mL) at 0 °C. The mixture slowly darkened to green–brown, and a brown precipitate formed. The mixture was allowed to warm to room temperature. After it had been stirred for 1 h, the now blue solution was filtered. The solvents were removed in vacuo and the residue was extracted with minimal ether. The combined extracts were filtered, concentrated in vacuo, and cooled to −40 °C to give 2.36 g of the blue crystals. Two additional crops were collected for a total yield of 4.20 g (73%): ^{1}H NMR (C_6D_6) δ 3.38 (MeOCH$_2$CH$_2$O*Me*), 3.30 (*Me*OCH$_2$CH$_2$OMe), 3.08 and 3.07 (br, four total, MeOC*H*$_2$C*H*$_2$OMe), 1.14 (CCMe$_3$); ^{13}C NMR (C_6D_6) δ 341.3 (*C*CMe$_3$), 77.4 (t, J = 151, MeO*C*H$_2$CH$_2$OMe), 72.5 (q, J = 147, *Me*OCH$_2$CH$_2$OMe), 69.5 (t, J = 145, MeOCH$_2$*C*H$_2$OMe), 59.1 (q, J = 145, MeOCH$_2$CH$_2$O*Me*), 53.4 (C*C*Me$_3$), 27.6 (CC*Me*$_3$). Anal. Calcd for $MoC_9H_{19}O_2Cl_3$: C, 29.90 H, 5.30. Found: C, 29.69; H, 5.18.

Mo(CCMe$_3$)Br$_3$(dme). Mo(CCMe$_3$)Br$_3$(dme) was prepared from Mo(CCMe$_3$)(CH$_2$CMe$_3$)$_3$ (2.88 g, 7.61 mmol), 1,2-dimethoxyethane (2.37 mL, 22.8 mmol), and HBr (0.83 M, 30 mL, 24.9 mmol) in a manner analogous to the preparation of Mo(CCMe$_3$)Cl$_3$(dme). Green needles (2.82 g, 75%) were collected in three crops: ^{1}H NMR (C_6D_6) δ 3.46 (*Me*OCH$_2$CH$_2$OMe), 3.06 (br, 5, *Me*OC*H*$_2$CH$_2$OMe), 2.89 (br, 2, MeOC*H*$_2$CH$_2$OMe), 1.29 (CCMe$_3$); ^{13}C NMR (C_6D_6) δ 350.6 (*C*CMe$_3$), 77.5 (MeO*C*H$_2$CH$_2$OMe), 72.4 (*Me*OCH$_2$CH$_2$OMe), 69.6 (MeO*C*H$_2$CH$_2$OMe), 59.8 (*Me*OCH$_2$CH$_2$OMe), 53.0 (C*C*Me$_3$), 28.5 (CC*Me*$_3$). Anal. Calcd for $MoC_9H_{19}O_2Br_3$: C, 21.84; H, 3.87. Found: C, 21.78; H, 3.71.

[Et$_4$N][Mo(CCMe$_3$)Cl$_4$]. A solution of HCl in ether (2.61 M, 29.4 mL, 76.7 mmol) was added dropwise to a solution of Mo(CCMe$_3$)-(CH$_2$CMe$_3$)$_3$ (9.50 g, 25.1 mmol) and Et$_4$NCl (4.16 g, 25.1 mmol) in dichloromethane (50 mL) at 0 °C. The solution quickly darkened to a muddy green. After the addition of the HCl was complete, the reaction was allowed to warm to room temperature and stir for 20 min. The solvents were removed in vacuo, and the residue was extracted with minimal THF. The extracts were combined and filtered. The THF was removed from the filtrate in vacuo, leaving a green solid. This solid was recrystallized from dichloromethane by adding ether and cooling the mixture to −40 °C overnight: yield 7.80 g (71%); ^{1}H NMR (CD_2Cl_2) δ 3.21 (NC*H*$_2$CH$_3$), 1.32 (br, NCH$_2$C*H*$_3$), 1.21 (CCMe$_3$); ^{13}C NMR (CD_2Cl_2) δ 338.8 (*C*CMe$_3$), 55.2 (br, N*C*H$_2$CH$_3$), 52.3 (C*C*Me$_3$), 26.6 (CC*Me*$_3$), 8.7 (NCH$_2$*C*H$_3$). Anal. Calcd for $MoC_{13}H_{29}NCl_4$: C, 35.72; H, 6.69. Found: C, 35.91; H, 6.71.

Mo(CCMe$_3$)(OCMe$_3$)$_3$. Solid Mo(CCMe$_3$)Cl$_3$(dme) (2.45 g, 6.8 mmol) was added in portions to a solution of LiOCMe$_3$ (1.63 g, 20.4 mmol) in ether (150 mL) at −40 °C. After stirring the pale brown solution for 2 h, it was filtered and the solvent was removed in vacuo. The brown residue was sublimed at 40 °C and 0.01 μm to give 2.38 g (91%) of product. The compound can also be crystallized from minimal ether by adding acetonitrile and cooling: ^{1}H NMR (C_6D_6) δ 1.45 (OCMe$_3$), 1.28 (CCMe$_3$); ^{13}C NMR (C_6D_6) δ 296.1 (*C*CMe$_3$), 78.0 (OCMe$_3$), 51.4 (C*C*Me$_3$), 32.6 (OC*Me*$_3$), 31.3 (CC*Me*$_3$). Anal. Calcd for $MoC_{17}H_{36}O_3$: C, 53.12; H, 9.44. Found: C, 52.72; H, 9.30.

Mo(CCMe$_3$)(OCHMe$_2$)$_3$. Mo(CCMe$_3$)(OCHMe$_2$)$_3$ was prepared from Mo(CCMe$_3$)Cl$_3$(dme) (0.71 g, 1.96 mmol) and LiOCHMe$_2$ (0.39 g, 5.91 mmol) in a manner analogous to the preparation of Mo-(CCMe$_3$)(OCMe$_3$)$_3$: yield 0.54 g (80%); ^{1}H NMR (C_6D_6) δ 5.44 (m, OC*H*Me$_2$), 1.48 (d, J = 6, OCH*Me*$_2$), 1.15 (CCMe$_3$); ^{13}C NMR (C_6D_6) δ 299.5 (*C*CMe$_3$), 86.5 (d, J_{CH} = 140, O*C*HMe$_2$), 51.3 (C*C*Me$_3$), 31.8 (OCH*Me*$_2$), 27.2 (CC*Me*$_3$).

Mo(CCMe$_3$)(OCH$_2$CMe$_3$)$_3$. Mo(CCMe$_3$)(OCH$_2$CMe$_3$)$_3$ was prepared from Mo(CCMe$_3$)Cl$_3$(dme) (1.12 g, 3.13 mmol) and LiOCH$_2$CMe$_3$ (0.88 g, 9.35 mmol) in a manner similar to the preparation of Mo(CCMe$_3$)(OCMe$_3$)$_3$. The product was recrystallized from ether by addition of acetonitrile: yield 1.15 g (86%); ^{1}H NMR (C_6D_6) δ 5.00 (OC*H*$_2$CMe$_3$), 1.19 (CCMe$_3$), 1.14 (OCH$_2$C*Me*$_3$); ^{13}C NMR (C_6D_6) δ 304.6 (*C*CMe$_3$), 96.5 (t, J = 141, O*C*H$_2$CMe$_3$), 52.5 (C*C*Me$_3$), 34.6 (OCH$_2$*C*Me$_3$), 32.4 (CC*Me*$_3$), 27.1 (OCH$_2$C*Me*$_3$).

Mo(CCMe$_3$)[O-2,6-C$_6$H$_3$(CHMe$_2$)$_2$]$_3$. Mo(CCMe$_3$)Cl$_3$(dme) (1.00 g, 2.77 mmol) was added in portions to a solution of LiO-2,6-C$_6$H$_3$-(CHMe$_2$)$_2$(OEt$_2$) (2.14 g, 8.28 mmol) in ether (15 mL) at −40 °C. The mixture turned yellow and then slowly red–orange. The reaction was allowed to warm to room temperature and was stirred for 90 min. The solvent was removed in vacuo and the residue was extracted with pentane. The extracts were combined, filtered, and concentrated. Cooling the concentrate to −40 °C afforded 1.55 g (80%) of yellow cubes: ^{1}H NMR (C_6D_6) δ 7.28 (d, *m*-C$_6$H$_3$(CHMe$_2$)$_2$), 7.15 (t, *p*-C$_6$H$_3$(CHMe$_2$)$_2$), 3.79 (m, C*H*Me$_2$), 1.43 (d, CH*Me*$_2$), 0.72 (CMe$_3$); ^{13}C NMR (C_6D_6) δ 337.2 (*C*CMe$_3$), 165.9 (*ipso*-C), 137.5 (*o*-C), 123.0 (*m*-C), 122.8 (*p*-C), 50.6 (C*C*Me$_3$), 21.1 (CC*Me*$_3$), 20.0 (*C*HMe$_2$), 15.0 (CH*Me*$_2$). Anal. Calcd for $MoC_{41}H_{60}O_3$: C, 70.67; H, 8.68. Found: C, 70.46; H, 8.70.

Mo(CCMe$_3$)[OCMe$_2$(CF$_3$)]$_3$. Mo(CCMe$_3$)Cl$_3$(dme) (1.00 g, 2.77 mmol) was added in portions to a solution of KOCMe$_2$(CF$_3$) (1.11 g, 8.28 mmol) in ether (20 mL) at −40 °C. The solution turned orange first, and then yellow–brown. The mixture was allowed to warm to room temperature and stirred for 3 h. The solvent was removed in vacuo, and the residue was extracted with pentane. The pentane extracts were filtered, concentrated, and cooled to −40 °C. Fluffy white needles (1.24 g, 82%) were isolated in two crops: ^{1}H NMR (C_6D_6) δ 1.45 (OC*Me*$_2$-(CF$_3$)), 1.03 (CC*Me*$_3$); ^{13}C NMR (C_6D_6) δ 309.7 (*C*CMe$_3$), 126.8 (q, J_{CF} = 285, (OCMe$_2$(*C*F$_3$)), 80.7 (q, $^2J_{CF}$ = 29, O*C*Me$_2$(CF$_3$)), 53.5 (C*C*Me$_3$), 30.3 (CC*Me*$_3$), 25.3 (CC*Me*$_2$(CF$_3$)); ^{19}F NMR (C_6D_6) δ 246.6. Anal. Calcd for $MoC_{17}H_{27}O_3F_9$: C, 37.37; H, 4.98. Found: C, 37.22; H, 5.07.

Mo(CCMe$_3$)[OCMe(CF$_3$)$_2$]$_3$(dme). Mo(CCMe$_3$)Cl$_3$(dme) (2.00 g, 5.53 mmol) was added in portions to a solution of KOCMe(CF$_3$)$_2$ (3.75 g, 17.0 mmol) in ether (35 mL). The solution quickly turned orange. After 16 h, the solvent was removed in vacuo, and the residue was extracted with pentane. The extracts were combined, filtered, and concentrated. Cooling the concentrate to −40 °C afforded 3.50 g (79%) of orange–red crystals: ^{1}H NMR (C_6D_6) δ 3.20 (*Me*OCH$_2$CH$_2$O*Me*), 3.05 (MeOC*H*$_2$C*H*$_2$OMe), 1.79 (OCMe(CF$_3$)$_2$), 0.86 (CCMe$_3$); ^{13}C NMR (C_6D_6) δ 318.8 (*C*CMe$_3$), 124.6 (q, J_{CF} = 289, OCMe(*C*F$_3$)$_2$), 82.9 (m, $^2J_{CF}$ = 29, O*C*Me(CF$_3$)$_2$), 71.8 (MeO*C*H$_2$CH$_2$OMe), 63.2 (*Me*OCH$_2$CH$_2$O*Me*), 53.6 (C*C*Me$_3$), 30.4 (CC*Me*$_3$), 19.3 (OC*Me*-(CF$_3$)$_2$); ^{19}F NMR (C_6D_6) δ 252.1. Anal. Calcd for $MoC_{21}H_{24}O_5F_{18}$: C, 31.75; H, 3.05. Found: C, 31.34; H, 3.50.

Mo(CCMe$_3$)[OCMe(CF$_3$)$_2$]$_3$. Mo(CCMe$_3$)[OCMe(CF$_3$)$_2$]$_3$(dme) (2.00 g, 2.51 mmol) was sublimed at 50 °C and 10^{-2} μm. The resulting solid was recrystallized from pentane to give 1.62 g (91%) of fluffy yellow needles: ^{1}H NMR (C_6D_6) δ 1.60 (OCMe(CF$_3$)$_2$), 0.82 (CCMe$_3$); ^{13}C NMR (C_6D_6) δ 325.2 (*C*CMe$_3$), 123.2 (q, J_{CF} = 287, OCMe(*C*F$_3$)$_2$), 83.1 (m, J_{CF} = 30, O*C*Me(CF$_3$)$_2$), 56.0 (C*C*Me$_3$), 29.2 (CC*Me*$_3$), 19.4 (OC*Me*(CF$_3$)$_2$); ^{19}F NMR (C_6D_6) δ 250.9. Anal. Calcd for $MoC_{17}H_{18}O_3F_{18}$: C, 28.83; H, 2.56. Found: C, 28.40; H, 2.61.

Mo(CCMe$_3$)[OCH(CF$_3$)$_2$]$_3$(dme). Mo(CCMe$_3$)Cl$_3$(dme) (1.00 g, 2.77 mmol) was added in portions to a suspension of LiOCH(CF$_3$)$_2$ (1.45 g, 8.33 mmol) in dichloromethane (30 mL). The reaction first turned muddy green and then lightened to yellow. After stirring the mixture for 24 h, the solvent was removed in vacuo. The residue was extracted with pentane. The extracts were combined, filtered, and concentrated. Cooling the concentrate to −40 °C yielded 1.79 g (86%) of yellow crystals: ^{1}H NMR (C_6D_6) δ 5.67 (m, OCH(CF$_3$)$_2$), 3.11 (br s, *Me*OCH$_2$CH$_2$O*Me*), 2.81 (br s, MeOC*H*$_2$C*H*$_2$OMe), 0.74 (CMe$_3$); ^{13}C NMR (C_6D_6) δ 318.2 (*C*CMe$_3$), 123.2 (q, J_{CF} = 288, OCH(*C*F$_3$)$_2$), 85.9 (dm, $^2J_{CF}$ = 32, O*C*H(CF$_3$)$_2$), 71.7 (MeO*C*H$_2$CH$_2$OMe), 63.8 (*Me*OCH$_2$CH$_2$O*Me*), 54.2 (C*C*Me$_3$), 30.3 (CC*Me*$_3$); ^{19}F NMR (C_6D_6) δ 254.6. Anal. Calcd for $MoC_{18}H_{22}O_5F_{18}$: C, 28.59; H, 2.93. Found: C, 28.25; H, 2.85.

Mo(CCMe$_3$)[OC(CF$_3$)$_3$]$_3$(dme). Mo(CCMe$_3$)Cl$_3$(dme) (0.20 g, 0.55 mmol) was added all at once to a suspension of KOC(CF$_3$)$_3$ (0.47 g, 1.71 mmol) in dichloromethane (5 mL). The mixture turned blue and then slowly violet. After 20 h, the solvent was removed in vacuo. The residue was extracted with pentane and the extracts were filtered. This *yellow* solution was concentrated in vacuo, and the concentrate was cooled to

−40 °C to give a purple powder. The purple solid was sublimed at 50 °C and 0.01 μm to give purple crystals (0.37 g; 70%): ^{1}H NMR (C_6D_6) δ 3.15 (br s, *Me*OCH$_2$CH$_2$O*Me*), 2.90 (br s, MeOC*H*$_2$C*H*$_2$OMe), 0.80 (CCMe$_3$); partial ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 121.3 (q, J_{CF} = 293, OC(*C*F$_3$)), 78.9 (MeO*C*H$_2$CH$_2$OMe), 71.6 (*Me*O*C*H$_2$CH$_2$OMe), 69.2 (*Me*OCH$_2$CH$_2$OMe), 29.1 (C*C*Me$_3$). Other signals were not seen due to poor solubility of the compound. ^{19}F NMR (C_6D_6) δ 257.1, 256.8. We have never been able to obtain satisfactory elemental analyses of any Mo or W[7a] compound containing three OC(CF$_3$)$_3$ ligands. The reason is unknown.

Mo(CCMe$_3$)[OCH(CF$_3$)$_2$]$_2$Cl(dme). LiOCH(CF$_3$)$_2$ (0.25 g, 1.44 mmol) was added to a solution of Mo(CCMe$_3$)Cl$_3$(dme) (0.26 g, 0.72 mmol) in ether (25 mL). The solution quickly turned orange, and a white precipitate formed. After the mixture was stirred for 2.5 h, the solvent was removed in vacuo and the residue was extracted with dichloromethane. The extracts were combined, filtered, and then evaporated to dryness in vacuo. The solid was dissolved in a minimum of ether, and the resulting solution was cooled to −40 °C to give orange crystals (0.29 g, 65%): ^{1}H NMR (C_6D_6) δ 5.80 (m, CH(CF$_3$)$_2$), 3.3–2.8 (br, 10, dme) 0.86 (CC*Me*$_3$); ^{13}C NMR (CD_2Cl_2) δ 323.6 (*C*CMe$_3$), 123.1 (q, J_{CF} = 284, OCH(*C*F$_3$)$_2$), 122.9 (q, J_{CF} = 284, OCH(*C*F$_3$)$_2$), 88.3 (dm, $^2J_{CF}$ = 33, O*C*H(CF$_3$)$_2$), 75.4 (MeOCH$_2$*C*H$_2$OMe), 69.4 (br m, MeOCH$_2$*C*H$_2$O*Me*), 59.0 (*Me*OCH$_2$CH$_2$OMe), 53.9 (C*C*Me$_3$), 29.2 (CC*Me*$_3$); ^{19}F NMR (C_6D_6) δ 255.3, 254.4.

Mo(CCMe$_3$)[OCMe(CF$_3$)$_2$]$_2$Cl(dme). Mo(CCMe$_3$)[OCMe(CF$_3$)$_2$]$_2$Cl(dme) was prepared from Mo(CCMe$_3$)Cl$_3$(dme) (1.00 g, 2.77 mmol) and LiOCMe(CF$_3$)$_2$ (1.04 g, 5.53 mmol) in a manner analogous to the preparation of Mo(CCMe$_3$)[OCH(CF$_3$)$_2$]$_2$Cl(dme): yield 1.53 g (85%) of red flakes in two crops; ^{1}H NMR (C_6D_6) δ 3.3–2.8 (br, 10, MeOCH$_2$CH$_2$OMe), 1.90 (OCMe(CF$_3$)$_2$), 0.97 (CCMe$_3$); ^{13}C NMR (CD_2Cl_2) δ 323.0 (*C*CMe$_3$), 124.3 and 124.1 (q, J_{CF} = 288, OCMe(*C*F$_3$)$_2$), 83.1 (O*C*Me(CF$_3$)$_2$), 77.0 (MeO*C*H$_2$CH$_2$OMe), 70.8 (*Me*OCH$_2$CH$_2$OMe), 69..7 (MeO*C*H$_2$CH$_2$OMe), 59.1 (*Me*OCH$_2$CH$_2$OMe), 53.7 (C*C*Me$_3$), 29.4 (CC*Me*$_3$), 19.2 (OC*Me*(CF$_3$)$_2$; ^{19}F NMR (C_6D_6) δ 252.7, 251.8. Anal. Calcd for MoC$_{17}$H$_{25}$O$_4$F$_{12}$Cl: C, 31.28; H, 3.86; Cl, 5.43. Found: C, 31.26; H, 3.86; Cl, 5.43.

Mo(CCMe$_3$)[OC(CF$_3$)$_3$]$_2$Cl(dme). KOC(CF$_3$)$_3$ (3.03 g, 11.1 mmol) was added to a solution of Mo(CCMe$_3$)Cl$_3$(dme) (2.00 g, 5.53 mmol) in ether (60 mL). The reaction mixture turned red-purple and then violet; a white precipitate of KCl was present. After 5 h, the solvents were removed in vacuo, and the residue was extracted with pentane. The extracts were combined, filtered, and concentrated, and the concentrate was cooled to −40 °C to give 3.37 g (80%) of purple flakes: ^{1}H NMR (C_6D_6) δ 3.4–2.3 (br, 10, dme) 0.97 (CCMe$_3$); ^{13}C NMR (CD_2Cl_2) δ 335.7 (*C*CMe$_3$), 121.6 (q, J_{CF} = 190, OC(*C*F$_3$)$_3$), 85.6 (m, O*C*(CF$_3$)$_3$), 78.9 (MeO*C*H$_2$CH$_2$OMe), 73.8 (*Me*O*C*H$_2$CH$_2$OMe), 69.2 (MeOCH$_2$CH$_2$OMe), 59.1 (*Me*OCH$_2$CH$_2$OMe), 55.8 (C*C*Me$_3$), 28.9 (CC*Me*$_3$); ^{19}F NMR (C_6D_6) δ 257.4. Anal. Calcd for MoC$_{17}$H$_{19}$O$_4$F$_{18}$Cl: C, 26.84; H, 2.52; Cl, 4.66. Found: C, 26.81; H, 2.77; Cl, 5.25.

Mo(CR)(OCMe$_3$)$_3$. Excess RC≡CH (∼10 equiv) was added to Mo(CCMe$_3$)(OCMe$_3$)$_3$ in ether. After 30 min, the solvent was removed in vacuo, leaving yellow crystals that were pure Mo(CR)(OCMe$_3$)$_3$ by ^{1}H NMR.

R = Pr: ^{1}H NMR (C_6D_6) δ 2.95 (m, C*H*$_2$CH$_2$CH$_3$), 1.66 (m, CH$_2$*C*H$_2$CH$_3$), 1.45 (OCMe$_3$), 0.74 (t, CH$_2$CH$_2$*C*H$_3$); ^{13}C NMR (C_6D_6) δ 286.6 (*C*Pr), 78.7 (O*C*Me$_3$), 52.1 (CC*H*$_2$CH$_2$CH$_3$), 32.8 (OC*Me*$_3$), 23.5 (CCH$_2$*C*H$_2$CH$_3$), 14.1 (CCH$_2$CH$_2$*C*H$_3$).

R = CHMe$_2$: ^{1}H NMR (C_6D_6) δ 3.11 (hept, CC*H*Me$_2$), 1.44 (OCMe$_3$), 1.16 (CCH*Me*$_2$); ^{13}C{^{1}H} NMR (C_6D_6) δ 292.7 (*C*CHMe$_2$), 78.3 (O*C*Me$_3$), 48.3 (*C*CHMe$_2$), 32.8 (OC*Me*$_3$), 23.4 (CCH*Me*$_2$).

R = Ph: ^{1}H NMR (C_6D_6) δ 7.49 (d, 2, Ph), 7.09 (t, 4, Ph), 6.87 (t, 2, Ph), 1.48 (OCMe$_3$); ^{13}C{^{1}H} NMR (C_6D_6) δ 276.6 (*C*Ph), 146.7 (*ipso*-Ph), 129.7 (Ph), 127.7 (Ph), 126.9 (Ph), 80.2 (O*C*Me$_3$), 32.8 (OC*Me*$_3$).

Mo(CPr)[OMe$_2$(CF$_3$)]$_3$. Excess 4-octyne (125 μL, 0.85 mmol) was added to Mo(CCMe$_3$)[OCH(CF$_3$)$_2$]$_3$ (0.09 g, 0.16 mmol) dissolved in ether (3 mL). After 30 min, the solvent was removed in vacuo, leaving white needles that were pure by NMR: ^{1}H NMR (C_6D_6) δ 2.66 (m, CC*H*$_2$CH$_2$CH$_3$), 1.39 (OC*Me*$_2$(CF$_3$)), 1.35 (CCH$_2$C*H*$_2$CH$_3$), 0.60 (CCH$_2$CH$_2$C*H*$_3$); ^{13}C NMR (C_6D_6) δ 299.3 (*C*Pr), 126.8 (q, J_{CF} = 285, OCMe$_2$(*C*F$_3$)), 81.3 (q, J_{CF} = 29, O*C*Me$_2$(CF$_3$)), 52.8 (*C*CH$_2$CH$_2$CH$_3$), 25.3 (OC*Me*$_2$(CF$_3$)), 22.5 (CCH$_2$*C*H$_2$CH$_3$), 13.7 (CCH$_2$CH$_2$*C*H$_3$); ^{19}F NMR (C_6D_6) δ 246.7.

Mo(CR)[OCMe(CF$_3$)$_2$]$_3$. Excess RC≡CR (∼10 times) was added to a solution of Mo(CCMe$_3$)[OCMe(CF$_3$)$_2$]$_3$ dissolved in toluene. After 30 min, the toluene was removed in vacuo and the residue recrystallized from pentane to give pale yellow needles of Mo(CR)[OCMe(CF$_3$)$_2$]$_3$ (R = Me, Et, and Pr).

R = Me: ^{1}H NMR (C_6D_6) δ 1.98 (CMe), 1.41 (OCMe(CF$_3$)$_2$); ^{13}C NMR (CD_2Cl_2) δ 313.8 (*C*Me), 124.5 (q, J_{CF} = 290, OCMe(*C*F$_3$)$_2$), 83.9 (m, J_{CF} = 29, O*C*Me(CF$_3$)$_2$), 35.9 (C*Me*), 19.4 (OC*Me*(CF$_3$)$_2$); ^{19}F NMR (CD_2Cl_2) δ 252.2.

R = Et: ^{1}H NMR (C_6D_6) δ 2.52 (CC*H*$_2$CH$_3$), 1.62 (OCMe(CF$_3$)$_2$), 0.64 (CCH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR (C_6D_6) δ 312.1 (*C*Et), 123.6 (q, J_{CF} = 289, OCMe(*C*F$_3$)$_2$), 83.8 (m, J_{CF} = 29, O*C*Me(CF$_3$)$_2$), 45.0 (C*C*H$_2$CH$_3$), 19.3 (OC*Me*(CF$_3$)$_2$), 13.6 (CCH$_2$*C*H$_3$); ^{19}F NMR (C_6D_6) δ 250.8.

R = Pr: ^{1}H NMR (C_6D_6) δ 2.57 (CC*H*$_2$CH$_2$CH$_3$), 1.56 (OCMe(CF$_3$)$_2$), 1.20 (CCH$_2$C*H*$_2$CH$_3$), 0.50 (CCH$_2$CH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR (C_6D_6) δ 313.4 (*C*Pr), 123.4 (q, J_{CF} = 287, OCMe(*C*F$_3$)$_2$), 83.7 (O*C*Me(CF$_3$)$_2$), 54.0 (C*C*H$_2$CH$_2$CH$_3$), 21.5 (CCH$_2$*C*H$_2$CH$_3$), 19.3 (OC*Me*(CF$_3$)$_2$), 7.2 (CCH$_2$CH$_2$*C*H$_3$); ^{19}F NMR (C_6D_6) δ 250.8.

Mo(CR)[OCMe(CF$_3$)$_2$]$_3$(dme). Excess RC≡CR (∼10 times) was added to a solution of Mo(CCMe$_3$)[OCMe(CF$_3$)$_2$]$_3$(dme) in ether. After 15 min, the ether was removed in vacuo and the residue was recrystallized from minimal pentane by cooling to −40 °C (yields 80–90%).

R = Me: ^{1}H NMR (C_6D_6) δ 3.13 (s, 6, dme), 3.03 (s, 4, dme), 2.24 (CMe), 1.65 (OCMe(CF$_3$)$_2$); ^{13}C{^{1}H} NMR (C_6D_6) δ 302.9 (*C*Me), 124.6 (q, J_{CF} = 289, OCMe(*C*F$_3$)$_2$), 83.4 (m, J_{CF} = 28, O*C*Me(CF$_3$)$_2$), 71.4 (MeOCH$_2$CH$_2$OMe), 62.7 (*Me*OCH$_2$CH$_2$O*Me*), 34.8 (C*Me*), 19.0 (OC*Me*(CF$_3$)$_2$); ^{19}F NMR (C_6D_6) δ 252.0.

R = Et: ^{1}H NMR (C_6D_6) δ 3.16 (s, 6, dme), 3.00 (s, 4, dme), 2.63 (CC*H*$_2$CH$_3$), 1.68 (OCMe(CF$_3$)$_2$), 0.58 (CCH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR (C_6D_6) δ 310.1 (*C*Et), 124.6 (q, J_{CF} = 288, OCMe(*C*F$_3$)$_2$), 83.5 (m, J_{CF} = 28, O*C*Me(CF$_3$)$_2$), 71.6 (MeO*C*H$_2$*C*H$_2$OMe), 63.5 (*Me*OCH$_2$CH$_2$O*Me*), 43.2 (C*C*H$_2$CH$_3$), 18.9 (OC*Me*(CF$_3$)$_2$), 12.4 (CCH$_2$*C*H$_3$); ^{19}F NMR (C_{D6}) δ 252.2.

R = Pr: ^{1}H NMR (C_6D_6) δ 3.19 (s, 6, dme), 3.05 (s, 4, dme), 2.80 (CC*H*$_2$CH$_2$CH$_3$), 1.74 (OCMe(CF$_3$)$_2$), 1.24 (CCH$_2$C*H*$_2$CH$_3$), 0.52 (CCH$_2$CH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR (C_6D_6) δ 309.0 (*C*Pr), 124.7 (q, J_{CF} = 289, OCMe(*C*F$_3$)$_2$), 83.5 (m, J_{CF} = 30, O*C*Me(CF$_3$)$_2$), 71.6 (MeO*C*H$_2$*C*H$_2$OMe), 63.7 (*Me*OCH$_2$CH$_2$O*Me*), 52.5 (C*C*H$_2$CH$_2$CH$_3$), 21.8 (CCH$_2$*C*H$_2$CH$_3$), 18.9 (OC*Me*(CF$_3$)$_2$), 13.5 (CCH$_2$CH$_2$*C*H$_3$); ^{19}F NMR (C_6D_6) δ 252.1.

R = Ph: ^{1}H NMR (C_6D_6) δ 7.20 (d, 2, Ph), 7.01 (t, 2, Ph), 6.81 (t, 1, Ph), 3.31 (s, 6, dme), 3.09 (s, 4, dme), 1.86 (OCMe(CF$_3$)$_2$); ^{13}C{^{1}H} NMR (C_6D_6) δ 295.2 (*C*Ph), 131.9 (ipso), 30.2 (Ph), 129.5 (Ph), 128.1 (Ph), 124.6 (q, J_{CF} = 289, OCMe(*C*F$_3$)$_2$), 83.7 (O*C*Me(CF$_3$)$_2$), 71.6 (MeO*C*H$_2$*C*H$_2$OMe), 63.7 (*Me*OCH$_2$CH$_2$O*Me*), 24.8 (OC*Me*(CF$_3$)$_2$); ^{19}F NMR (C_6D_6) δ 252.3.

Mo(CR)[OCH(CF$_3$)$_2$]$_3$(dme). R = Pr. Excess 4-octyne (100 μL, 0.68 mmol) was added to Mo(CCMe$_3$)[OCH(CF$_3$)$_2$]$_3$(dme) (0.10 g, 0.13 mmol) dissolved in toluene (6 mL). After 15 min, the reaction was filtered and the solvent was removed in vacuo, leaving yellow crystals that were pure by NMR: ^{1}H NMR (C_6D_6) δ 5.51 (m, OC*H*(CF$_3$)$_2$), 3.03 (s, 6, dme), 2.75 (s, 4, dme), 2.41 (CC*H*$_2$CH$_2$CH$_3$), 1.05 (CCH$_2$C*H*$_2$CH$_3$), 0.46 (CCH$_2$CH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR (C_6D_6) δ 311.6 (*C*Pr), 123.4 (q, J_{CF} = 284, OCH(*C*F$_3$)$_2$), 85.1 (m, J_{CF} = 31, O*C*H(CF$_3$)$_2$), 71.7 (MeO*C*H$_2$*C*H$_2$OMe), 63.7 (*Me*OCH$_2$CH$_2$O*Me*), 58.7 (C*C*H$_2$CH$_2$CH$_3$), 22.7 (CCH$_2$*C*H$_2$CH$_3$), 13.4 (CCH$_2$CH$_2$*C*H$_3$); ^{19}F NMR (C_6D_6) δ 254.2.

R = Ph. PhC≡CEt (25 μL, 0.18 mmol) was added to a solution of Mo(CCMe$_3$)[OCH(CF$_3$)$_2$]$_3$(dme) (0.13 g, 0.17 mmol) in ether (4 mL). The solution turned orange. After 30 min, the ether was removed in vacuo until a saturated solution was obtained. Addition of pentane and cooling the solution to −40 °C afforded 0.11 g (82%) of orange flakes: ^{1}H NMR (C_6D_6) δ 7.01 (d, 2, Ph), 6.88 (t, 2, Ph), 6.72 (t, 1, Ph), 5.76 (m, 3, OCH(CF$_3$)$_2$), 3.15 (s, 6, dme), 2.84 (s, 4, dme); ^{13}C{^{1}H} NMR (C_6D_6) δ 297.0 (*C*Ph), 142.0 (*ipso*-Ph), 130.3 (Ph), 130.1 (Ph), 128.5 (Ph), 123.3 (q, J_{CF} = 284, OCH(*C*F$_3$)$_2$), 85.0 (m, J_{CF} = 32, O*C*H(CF$_3$)$_2$), 71.8 (MeO*C*H$_2$*C*H$_2$OMe), 63.9 (*Me*OCH$_2$CH$_2$O*Me*); ^{19}F NMR (C_6D_6) δ 254.5.

Mo(C$_3$Et$_3$)[O-2,6-C$_6$H$_3$(CHMe$_2$)$_2$]$_3$. Excess 3-hexyne (330 μL, 2.90 mmol) was added to a solution of Mo(CCMe$_3$)[O-2,6-C$_6$H$_3$(CHMe$_2$)$_2$]$_3$ (0.40 g, 0.57 mmol) in ether (10 mL). The solution quickly darkened to red. After 30 min, the ether was removed in vacuo and the cold solid residue was extracted with pentane. The extracts were combined, filtered, concentrated, and cooled to −40 °C, yielding 0.37 g (86%) of dark red crystals: partial ^{1}H NMR (toluene-d_8 233 K) δ 4.17 (m, 2, O-2,6-C$_6$H$_3$(C*H*Me$_2$)$_2$), 2.93 (m, 4, O-2,6-C$_6$H$_3$(C*H*Me$_2$)$_2$), 2.79 (C$_\alpha$C*H*$_2$CH$_3$), 2.69 (C$_\beta$CH$_2$CH$_3$), 1.61 (C$_\alpha$CH$_2$C*H*$_3$), 1.50 (O-2,6-C$_6$H$_3$(CH*Me*$_2$)$_2$), 1.07 (O-2,6-C$_6$H$_3$(CH*Me*$_2$)$_2$), 0.34 (C$_\beta$CH$_2$C*H*$_3$). Anal. Calcd for MoC$_{45}$H$_{66}$O$_3$: C, 71.97; H, 8.86. Found: C, 71.88; H, 9.14.

Mo[C$_3$(CMe$_3$)$_2$][OCH(CF$_3$)$_2$]$_2$(py)$_2$. Excess Me$_3$CC≡CH (250 μL, 2.04 mmol) was added to Mo(CCMe$_3$)[OCH(CF$_3$)$_2$]$_3$(py)$_2$ (0.33 g, 0.40 mmol) prepared in situ in ether (20 mL) from the dme adduct. The solution slowly turned purple. After 1 h, the solvent was removed in vacuo and the resulting solid was dissolved in a minimum of pentane. Cooling the solution to −40 °C yielded 0.27 g (91%) of purple flakes in two crops: ^{1}H NMR (C_6D_6) δ 8.97 (m, 4, py), 6.94 (m, 2, py), 6.67 (m,

4, py), 3.51 (m, 2, OC*H*$(CF_3)_2$), 1.58 (CMe_3); ^{13}C NMR (C_6D_6) δ 235.4 (C_α), 208.0 (C_β), 151.3 (py), 138.3 (py), 124.8 (py), 123.0 (q, J_{CF} = 286, OCH(CF_3)$_2$), 82.5 (dm, J_{CF} = 32, OCH(CF_3)$_2$), 44.9 (CMe_3), 32.3 (q, CMe_3); ^{19}F NMR (C_6D_6) δ 254.6. A crystal for the X-ray study was selected from a sample that was pure by high-field ^1H NMR.

Mo[C_3(CMe_3)$_2$][$OCMe_2(CF_3)$]$_2$. Excess $Me_3CC{\equiv}CH$ (90 μL, 0.73 mmol) was added to an ether solution (5 mL) of Mo($CCMe_3$)-[$OCMe_2(CF_3)$]$_3$ (0.20 g, 0.37 mmol) and quinuclidine (0.04 g, 0.36 mmol). The solution turned bright yellow first and then green. After 1 h, the solvents were removed in vacuo, leaving small green crystals that were pure by NMR (0.16 g, 87%): ^1H NMR (C_6D_6) δ 1.57 (CMe_3), 0.82 ($OCMe_2(CF_3)$); ^{13}C NMR (C_6D_6) δ 239.3 (C_α), 177.6 (C_β), 128.4 (q, J_{CF} = 288, $OCMe_2(CF_3)$), 78.1 (q, J_{CF} = 29, $OCMe_2(CF_3)$), 43.1 (CMe_3), 31.3 (q, CMe_3), 25.1 (q, $OCMe_2(CF_3)$); ^{19}F NMR (C_6D_6) δ 245.7.

Mo(C_3Ph_2)[$OCMe_2(CF_3)$]$_2$(py)$_2$. PhC≡CH (82 μL, 0.75 mmol) was added to an ether solution (5 mL) of Mo($CCMe_3$)[$OCMe_2(CF_3)$]$_3$ (0.20 g, 0.37 mmol) and pyridine (70 μL, 0.86 mmol). The solution quickly turned dark green. After 15 min, the solvent was removed in vacuo, leaving a green solid. The solid was dissolved in a minimum of pentane, and the solution was cooled to −40 °C to give 0.20 g (88%) of green crystals: ^1H NMR (C_6D_6) δ 9.20 (d, 4, py) 8.20 (d, 4, Ph), 7.35 (t, 4, (Ph), 7.00 (overlapping m, 4, py and Ph), 6.76 (t, 4, py), 0.57 ($OCMe_2(CF_3)$); ^{13}C NMR (C_6D_6) δ 203.3 (C_α), 201.1 (C_β), 151.4 (py), 139.9 (ipso), 137.6 (py or Ph), 132.2 (py or Ph), 129.0 (py or Ph), 129.1 (q, J_{CF} = 287, $OCMe_2(CF_3)$), 127.4 (py or Ph), 123.7 (py or Ph), 77.7 (q, J_{CF} = 27, $OCMe_2(CF_3)$), 21.5 ($OCMe_2(CF_3)$); ^{19}F NMR (C_6D_6) δ 246.9. Anal. Calcd for $MoC_{33}H_{32}N_2O_2F_6$: C, 56.74; H, 4.62. Found: C, 57.36; H, 4.96.

Mo[C_3(CMe_3)$_2$][$OCMe(CF_3)_2$]$_2$. Excess $Me_3CC{\equiv}CH$ (230 μL, 1.88 mmol) was added to a solution of Mo($CCMe_3$)[$OCMe(CF_3)_2$]$_3$(dme) (0.50 g, 0.63 mmol) in ether (10 mL). The solution lightened to yellow. The solvent was removed after 15 min, leaving a red solid. On warming to room temperature in vacuo, the solid turned to a yellow oil that was pure by NMR (yield 0.36 g; 94%): ^1H NMR (C_6D_6) δ 1.51 (CMe_3), 0.88 ($OCMe(CF_3)_2$); ^{13}C NMR (C_6D_6) δ 258.2 (C_α), 190.6 (C_β), 122.8 (q, J_{CF} = 288, $OCMe(CF_3)_2$), 76.9 (m, J_{CF} = 30, $OCMe(CF_3)_2$), 37.5 (CMe_3), 22.9 (CMe_3), 10.5 ($OCMe(CF_3)_2$); ^{19}F NMR (C_6D_6) δ 250.0. The pyridine adduct was analyzed (see next preparation).

Mo[C_3(CMe_3)$_2$][$OCMe(CF_3)_2$]$_2$(py)$_2$. Pyridine (65 μL, 0.80 mmol) was added to a solution of Mo[C_3(CMe_3)$_2$][$OCMe(CF_3)_2$]$_2$ (0.23 g, 0.38 mmol) in ether (5 mL). The solution turned red-purple. After 5 min, the ether was removed in vacuo and the residue was recrystallized from a minimum amount of pentane to give 0.23 g (80%) of purple flakes: ^1H NMR (C_6D_6) δ 8.94 (py), 6.96 (py), 6.71 (py), 1.67 (CMe_3), 0.63 ($OCMe(CF_3)_2$)); ^{13}C NMR (CD_2Cl_2) δ 252.4 (C_α), 222.9 (C_β), 159.8 (py), 144.6 (py), 130.1 (m, J_{CF} = 290, $OCMe(CF_3)_2$), 129.5 (py), 81.1 (m, J_{CF} = 28, $OCMe(CF_3)_2$), 44.7 (CMe_3), 30.3 (CMe_3), 14.3 ($OCMe(CF_3)_2$); ^{19}F NMR (CD_2Cl_2) δ 252.2. Anal. Calcd for $MoC_{29}H_{34}O_2N_2F_{12}$: C, 45.44; H, 4.47. Found: C, 45.18; H, 4.48.

Mo[C_3($CHMe_2$)$_2$][$OCMe(CF_3)_2$]$_2$(dme). Excess $Me_2CHC{\equiv}CH$ (320 μL, 3.13 mmol) was added to a solution of Mo($CCMe_3$)[$OCMe(CF_3)_2$]$_3$(dme) (0.50 g, 0.63 mmol) in ether (10 mL) at −40 °C. The solution initially turned lighter orange and then darkened to red after ~1 min. The ether was removed in vacuo, and the resulting solid was recrystallized from a minimum amount of pentane to yield 0.24 g (57%) of red cubes: ^1H NMR (C_6D_6) δ 4.18 ($CHMe_2$), 3.63 ($MeOCH_2CH_2OMe$), 3.36 ($MeOCH_2CH_2OMe$), 1.44 ($CHMe_2$), 0.60 ($OCMe(CF_3)_2$)); ^{13}C NMR (C_6D_6) δ 244.6 (C_α), 206.6 (C_β), 124.0 (q, J_{CF} = 289, $OCMe(CF_3)_2$)), 74.9 (m, J_{CF} = 26, $CMe(CF_3)_2$), 67.2 ($MeOCH_2CH_2OMe$), 56.2 ($MeOCH_2CH_2OMe$), 32.6 ($CHMe_2$), 15.0 ($CHMe_2$), 7.7 ($OCMe(CF_3)_2$); ^{19}F NMR (C_6D_6) δ 251.3.

Mo(C_3Ph_2)[$OCMe(CF_3)_2$]$_2$(dme). PhC≡CH (90 μL, 0.82 mmol) was added to a solution of Mo[$C_3(Ph)_2$][$OCMe(CF_3)_2$]$_3$(dme) (0.30 g, 0.38 mmol) in ether (10 mL). The solution's color slowly changed to red-purple. After 30 min, the solvent was removed in vacuo and the resulting solid was dissolved in a minimum of pentane. Cooling the pentane solution to −40 °C afforded 0.24 g (86%) of purple flakes: ^1H NMR (C_6D_6) δ 8.28 (d, 4, Ph), 7.40 (t, 4, Ph), 7.06 (t, 2, (Ph), 3.71 (s, 6, dme), 3.42 (s, 4, dme), 0.39 ($OCMe(CF_3)_2$); ^{13}C NMR (CD_2Cl_2) δ 229.2 (C_α), 217.3 (C_β), 146.6 (*ipso*-Ph), 138.3 (Ph), 135.4 (Ph), 135.2 (Ph), 129.6 (q, J_{CF} = 290, $OCMe(CF_3)_2$), 82.3 (m, J_{CF} = 28, $OCMe(CF_3)_2$), 74.0 ($MeOCH_2CH_2OMe$), 64.2 ($MeOCH_2CH_2OMe$), 13.9 ($OCMe(CF_3)_2$); ^{19}F NMR (CD_2Cl_2) δ 251.4. Anal. Calcd for $MoC_{27}H_{26}O_4F_{12}$: C, 43.92; H, 3.55. Found: C, 43.87; H, 3.85.

Mo[C_3(CMe_3)$_2$][$OC(CF_3)_3$]$_2$. Excess $Me_3CC{\equiv}CH$ (50 μL, 0.41 mmol) was added to a solution of Mo($CCMe_3$)[$OC(CF_3)_3$]$_3$(dme) (0.10 g, 0.10 mmol) in ether (5 mL). The reaction's color immediately turned bright yellow. The solvent was removed in vacuo, leaving violet crystals which upon warming to room temperature in vacuo turned bright yellow. The resulting yellow solid (0.07, 80%) was pure by NMR: ^1H NMR (C_6D_6) δ 1.47 (CMe_3); ^{13}C NMR (C_6D_6) δ 257.4 (C_α), 196.2 (C_β), 120.6 (q, J_{CF} = 292, $OC(CF_3)$), 45.6 ($CCMe_3$), 30.2 (CMe_3). We did not observe a signal for $OC(CF_3)_3$ in this spectrum; ^{19}F NMR (C_6D_6) δ 254.0.

Mo[C_3(CMe_3)R][O-2,6-$C_6H_3(CHMe_2)_2$]$_2$(py). Excess RC≡CH (2 equiv) and pyridine (3 equiv) were added to a yellow ether solution of Mo($CCMe_3$)[O-2,6-$C_6H_3(CHMe_2)_2$]$_3$ at −30 °C. The resulting red-orange solution was allowed to warm to room temperature over the next 3 h. The solvents were removed in vacuo, and the yellow-orange residue was recrystallized from a minimum amount of pentane by cooling the solution to −40 °C. Red-orange crystals were obtained in three crops (75–80%). In the description of the NMR data below, DIPP = diisopropylphenoxide.

R = Pr: ^1H NMR (C_6D_6) δ 9.32 (*o*-py), 7.03 (*p*-py), 6.95 (*m*-DIPP), 6.84 *p*-DIPP), 6.80 (*m*-py), 3.63 ($CH_2CH_2CH_3$), 2.65 (br, 4, $CHMe_2$), 1.84 ($CH_2CH_2CH_3$), 1.22 (CMe_3), 1.18 ($CHMe_2$), 1.11 ($CHMe_2$), 1.01 ($CH_2CH_2CH_3$); ^{13}C NMR (CD_2Cl_2) δ 235.5 ($CCMe_3$), 219.6 (CPr), 186.7 (C_β), 162.4 (*ipso*-C), 150.5 (*o*-py), 138.5 (*p*-py), 136.0 (*o*-DIPP), 124.8 (*m*-py), 122.6 (*m*-DIPP), 120.4 (*p*-DIPP), 43.6 (CMe_3), 40.8 ($CH_2CH_2CH_3$), 31.1 (CMe_3), 26.9 ($CHMe_2$), 24.7 ($CH_2CH_2CH_3$), 23.2 ($CHMe_2$), 23.0 ($CHMe_2$), 14.4 ($CH_2CH_2CH_3$). Anal. Calcd for $MoC_{39}H_{55}O_2N$: C, 70.35; H, 8.33. Found: C, 70.33; H, 8.39.

R = CMe_3: ^1H NMR (CD_2Cl_2) δ 9.33 (*o*-py), 8.00 (*p*-py), 7.57 (*m*-py), 6.84 (4, *m*-DIPP), 6.70 (*p*-DIPP), 2.37 (br, 4, $CHMe_2$), 1.16 (CMe_3), 1.01 ($CHMe_2$); ^{13}C NMR (CD_2Cl_2) δ 232.4 ($CCMe_3$), 185.9 (C_β), 163.0 (*ipso*-C), 150.7 (*o*-py), 138.6 (*p*-py), 136.0 (*o*-DIPP), 124.7 (*p*-py), 122.6 (*m*-DIPP), 120.5 (*p*-DIPP), 43.5 (CMe_3), 31.6 (CMe_3), 26.9 ($CHMe_2$) 23.15, ($CHMe_2$). Anal. Calcd for $MoC_{40}H_{57}O_2N$: C, 70.67; H, 8.45. Found: C, 70.66; H, 8.49.

R = Ph: ^1H NMR (CD_2Cl_2) δ 9.39 (*o*-py), 8.07 (*p*-py), 7.65 (*o*-Ph), 7.64 (*m*-py), 7.37 (*m*-Ph), 7.19 (*p*-Ph), 6.83 (*m*-DIPP), 6.70 (*p*-DIPP), 2.51 (br, 4, $CHMe_3$), 1.10 (s, 9, CMe_3), 1.02 (br, 12, $CHMe_2$), 0.95 (d, 12, $CHMe_2$); ^{13}C NMR (CD_2Cl_2) δ 233.2 ($CCMe_3$), 209.0 (CPh), 187.5 (C_β), 162.6 (*ipso*-DIPP), 150.6 (*o*-py), 139.0 (*p*-py), 138.8 (*ipso*-Ph), 135.9 (*o*-DIPP), 130.6 (*o*-Ph), 128.7 (*m*-Ph), 127.6 (*p*-Ph), 125.1 (d, *J* = 167, *m*-py), 122.7 (*m*-DIPP), 120.7 (*p*-DIPP), 43.7 (CMe_3), 31.2 (CMe_3), 27.0 ($CHMe_2$), 23.2 ($CHMe_2$), 23.0 ($CHMe_2$). Anal. Calcd for $MoC_{42}H_{53}O_2N$: C, 72.08; H, 7.63. Found: C, 71.87; H, 7.54.

In Situ Characterization of Mo[C_3(CMe_3)(R)][O-2,6-$C_6H_3(CHMe_2)_2$]$_2$. RC≡CH (1–2 equiv for R = CMe_3, Ph, or Pr) was added to a yellow ether solution (10 mL) of Mo($CCMe_3$)[O-2,6-$C_6H_3(CHMe_2)_2$]$_3$ (0.10 g, 0.142 mmol). The resulting yellow-orange solution was allowed to warm to room temperature over the next 2 h. Solvents were removed in vacuo, yielding a yellow-orange oil, a mixture of Mo[C_3(CMe_3)(R)][O-2,6-$C_6H_3(CHMe_2)_2$]$_2$, and 1 equiv of HO-2,6-$C_6H_3(CHMe_2)_2$, virtually quantitatively.

R = Pr: ^1H NMR (CD_2Cl_2) δ 6.95 (H_m), 6.87 (H_p), 3.88 ($CH_2CH_2CH_3$), 2.74 ($CHMe_2$), 1.97 ($CH_2CH_2CH_3$), 1.45 (CMe_3), 1.18 ($CHMe_2$), 1.16 ($CHMe_2$), 1.10 ($CH_2CH_2CH_3$); ^{13}C NMR (CD_2Cl_2) δ 243.3 ($CCMe_3$), 232.3 (CPr), 174.1 (C_β), 157.5 (C_{ipso}), 136.9 (C_o), 123.2 (C_m), 122.3 (d, C_p), 44.4 (CMe_3), 43.0 ($CH_2CH_2CH_3$), 31.4 (CMe_3), 27.5 ($CHMe_2$), 24.3 ($CH_2CH_2CH_3$), 23.4 ($CHMe_2$), 23.2 ($CHMe_2$), 14.3 ($CH_2CH_2CH_3$).

R = CMe_3: ^1H NMR (CD_2Cl_2), δ 6.94 (H_m), 6.86 (H_p), 2.59 ($CHMe_2$), 1.42 (CMe_3), 1.15 ($CHMe_2$); ^{13}C NMR (CD_2Cl_2) δ 243.6 ($CCMe_3$), 171.4 (C_β), 157.3 (C_{ipso}), 136.8 (C_o), 123.1 (C_m, 122.3 (C_p), 44.3 (CMe_3), 31.4 (CMe_3), 27.4 ($CHMe_2$), 23.3 ($CHMe_2$).

R = Ph: ^1H NMR (CD_2Cl_2) δ 8.12 (H_o-Ph), 7.58 (H_m-Ph), 7.34 (H_p-Ph), 6.94 (H_m-DIPP), 6.86 (H_p-DIPP), 2.83 ($CHMe_2$), 1.55 (CMe_3), 1.12 ($CHMe_2$); ^{13}C NMR (CD_2Cl_2) δ 241.4 ($CCMe_3$), 222.2 (CPh), 173.2 (C_β), 157.3 (C_{ipso}-DIPP), 138.9 (C_{ips3}-Ph), 137.0 (C_o-Ph), 131.2 (C_m-Ph), 129.2 (C_p-Ph), 123.2 (C_m-DIPP), 122.5 (C_p-DIPP), 44.4 ($CHMe_3$), 31.5 (CMe_3), 27.5 ($CHMe_2$), 27.4 ($CHMe_2$), 23.3 ($CHMe_2$), 23.2 ($CHMe_2$).

Acknowledgment. We thank the National Science Foundation for support (CHE84-02892) and the Biomedical Research Support Shared Instrumentation Grant Program, Division of Research Resources, for funds to purchase the X-ray diffraction equipment (NIH Grant S10RR02243-01). L.G.M. thanks the Dow Central Research Department for a predoctoral fellowship. R.R.S. thanks E. I. du Pont de Nemours and Co. for a gift of a sample of $(CF_3)_3COH$.

Supplementary Material Available: Tables S1 and S2 listing final thermal parameters and final observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.