Synthesis of Molybdenum Imido Alkylidene Complexes and Some Reactions Involving Acyclic Olefins

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Abstract: The reaction between Mo(C-*t*-Bu)(dme)Cl_3 (dme = 1,2-dimethoxyethane) and $Me_3SiNHAr$ (Ar = 2,6-diisopropylphenyl) yields Mo(C-*t*-Bu)(NHAr)Cl_2(dme) (**1**), which upon treatment with a catalytic amount of NEt_3 is transformed into Mo(CH-*t*-Bu)(NAr)Cl_2(dme) (**2**). Complexes of the type Mo(CH-*t*-Bu)(NAr)$(OR)_2$ (OR = $OCMe(CF_3)_2$, $OCMe_2(CF_3)$, O-*t*-Bu, or OAr) have been prepared from **2**. Complexes of the type Mo(C-*t*-Bu)(NHAr)$(OR)_2$ (OR = $OCMe(CF_3)_2$ or OAr) have been prepared from **1**, but they cannot be transformed into Mo(CH-*t*-Bu)(NAr)$(OR)_2$ complexes. A precursor to imido alkylidene complexes that is related to **2** has been prepared by the sequence $MoO_2 \rightarrow MoO_2Cl_2 \rightarrow Mo(NAr)_2Cl_2 \rightarrow Mo(NAr)_2(CH_2R')_2 \rightarrow Mo(CHR')(NAr)(OTf)_2(dme)$ (R' = *t*-Bu or CMe_2Ph; OTf = OSO_2CF_3). Mo(CH-*t*-Bu)(NAr)$(OTf)_2$(dme) crystallizes in the space group $P\bar{1}$ with a = 17.543 Å, b = 19.008 Å, c = 9.711 Å, α = 91.91°, β = 99.30°, γ = 87.27°, Z = 4, M_r = 729.60, V = 3191.1 Å^3, ρ(calcd) = 1.518 g cm^{-3}. It is a pseudooctahedral species in which the imido and alkylidene ligands are cis to one another, the triflate ligands are mutually trans, and the *tert*-butyl group points toward the imido ligand (syn orientation). Neophylidene complexes, Mo($CHCMe_2Ph$)(NAr)$(OR)_2$ (OR = O-*t*-Bu, OAr, or O-2-C_6H_4-*t*-Bu), have been prepared from Mo($CHCMe_2Ph$)(NAr)(triflate)$_2$(dme). Activity for the metathesis of *cis*-2-pentene by Mo(CHR')(NAr)$(OR)_2$ complexes roughly correlates with the electron-withdrawing ability of OR, being rapid when OR = $OCMe(CF_3)_2$ and slow to negligible when OR = O-*t*-Bu. In several cases it is clear from proton NMR studies that the alkylidene ligand can rotate on the NMR time scale; in Mo($CHSiMe_3$)(NAr)$(OAr)_2$ it has been shown that ΔG^*_{298} = 16.0 kcal mol^{-1} for this process. Mo[$CH(SiMe_3)CH(SiMe_3)CH_2$](NAr)[$OCMe_2(CF_3)$]$_2$ has been observed and found to be ~3 orders of magnitude less stable than the analogous tungsten complex. Trigonal-bipyramidal Mo($CH_2CH_2CH_2$)(NAr)[$OCMe(CF_3)_2$]$_2$ can be prepared at 25 °C in high yield, but it decomposes over a period of 12 h. Instability of $OCMe(CF_3)_2$ metallacyclobutane complexes has been traced to reduction by β-hydride rearrangement to give an olefin. In one case a complex containing the olefin product, Mo(NAr)($Me_3SiCH{=}CH_2$)[$OCMe(CF_3)_2$]$_2$, was isolated.

Tungsten, molybdenum, and rhenium are the three metals that are the most active for the metathesis of ordinary olefins in classical metathesis catalyst systems.[1] In the past several years well-characterized tungsten alkylidene complexes have been prepared that will metathesize olefins. Complexes of the type W(CH-*t*-Bu)(OCH_2-*t*-Bu)$_2X_2$ (X = a halide)[2] require a Lewis acid cocatalyst for high activity, probably in order to generate four-coordinate cationic species, [W(CH-*t*-Bu)(OCH_2-*t*-Bu)$_2$X]$^+$. Related complexes of the type W(CH-*t*-Bu)(OAryl)$_2X_2$ have been synthesized and used to metathesize olefins in the presence of alkyl tin reagents, but the nature of the active species is unproven.[3] Activity of W(CH-*t*-Bu)(OAryl)$_2X_2$ catalysts can be controlled to some extent by altering the nature of the OAryl ligand, more electron-withdrawing phenoxides giving more active catalysts. Perhaps the most versatile and controllable catalysts are those of the type W(CHR')(NAr)$(OR)_2$ (Ar = 2,6-diisopropylphenyl; OR = various alkoxides). They can now be prepared for a wide variety of alkoxides and phenoxides.[4] They react rapidly with ordinary internal olefins when OR is electron withdrawing (e.g., OR = $OCMe(CF_3)_2$) but only very slowly when OR = O-*t*-Bu. The relative inactivity of the *tert*-butoxide derivatives allows certain strained cyclic olefins to be ring-opened in a controlled way to give living homopolymers and block copolymers,[5] and recently it has been shown that acetylene also can be polymerized in a controlled manner by tungsten *tert*-butoxide catalysts of this type.[6] Transalkylidenation has been observed, as have tungstacyclobutane intermediates, in both the W(CH-*t*-Bu)(OCH_2-*t*-Bu)$_2X_2$[7] and W(CHR')(NAr)$(OR)_2$[4] catalyst systems. The structures of several tungstacyclobutane complexes prepared from W(CH-*t*-Bu)(NAr)$(OR)_2$ complexes have been determined,[4,8] most recently square-pyramidal species, e.g. W[CH_2CH(*t*-Bu)CH_2](NAr)[$OCMe_2(CF_3)$]$_2$.

Well-characterized catalysts of the type Mo(CHR')(NAr)$(OR)_2$ also should be preparable and may have certain advantages, namely a greater tolerance of functionalities than analogous tunsten catalysts. Likely disadvantages might include a greater tendency to be reduced (e.g., by rearrangement of a metallacyclobutane complex, a reaction that is common in related tantalum chemistry[9]) and (if qualitative results from classical metathesis systems are borne out for well-characterized species) a lower activity. Preliminary studies[10] showed that complexes of the type Mo(CH-*t*-Bu)(NAr)$(OR)_2$ could be prepared by routes analogous to those originally used to prepare the tungsten analogues. Recent studies have shown that molybdenum catalysts

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do outperform tungsten catalysts in selective ring-opening polymerization reactions when functionalities are present.[11,12] In this paper we outline the chemistry of molybdenum alkylidene complexes and metallacycles in detail, chemistry that is now readily accessible by a facile and high-yield synthesis of a versatile molybdenum catalyst precursor.

Results

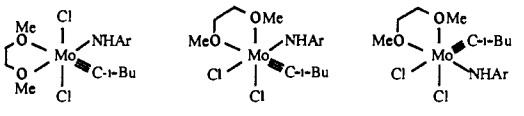
Synthesis of Molybdenum Imido Alkylidene Complexes. The synthesis of Mo(C-*t*-Bu)(CH_2-*t*-Bu)$_3$[13] created the possibility of preparing imido/neopentylidene complexes of molybdenum analogous to those of tungsten that could be prepared from W(C-*t*-Bu)(CH_2-*t*-Bu)$_3$,[4] although it was recognized at the outset that the low and irreproducible yield of Mo(C-*t*-Bu)(CH_2-*t*-Bu)$_3$ would limit the practicality of this synthesis. Mo(C-*t*-Bu)(CH_2-*t*-Bu)$_3$ is converted into blue Mo(C-*t*-Bu)Cl_3(dme) upon treatment with 3 equiv of HCl in the presence of ether. When 1 equiv of $Me_3SiNHAr$ (Ar = 2,6-diisopropylphenyl) is added to Mo(C-*t*-Bu)Cl_3(dme) in ether at −30 °C, orange Mo(C-*t*-Bu)(NHAr)Cl_2(dme) (**1**) is obtained upon warming the reaction to room temperature (eq 1). The infrared spectrum (Nujol mull) of **1** shows a strong N–H stretch at 3204 cm^{-1} and the proton NMR spectrum shows a fairly broad resonance for the N–H proton at 12.59 ppm in CD_2Cl_2 at room temperature. The resonance for the alkylidyne α-carbon atom appears as a singlet in the gated ^{13}C NMR spectrum at 321.2 ppm, a chemical shift that

$$\text{Mo(C-}t\text{-Bu)Cl}_3\text{(dme)} + \text{Me}_3\text{SiNHAr} \xrightarrow[\text{ether, } -30\ ^\circ\text{C}]{-\text{Me}_3\text{SiCl}} \text{Mo(C-}t\text{-Bu)(NHAr)Cl}_2\text{(dme)}\ (\mathbf{1}) \quad (1)$$

Ar = 2,6-diisopropylphenyl

is typical of alkylidyne ligands in "d^0" complexes,[14] but one that is not significantly larger than shifts in other alkylidene complexes reported here; in two cases (**2a** and **3**, see below) the alkylidene carbon atom chemical shift is greater than 321 ppm. Addition of another equivalent of $Me_3SiNHAr$ to **1** does not result in further substitution of the chloride ligands at 25 °C.

Although the resonances in the room temperature ^1H and ^{13}C NMR spectra of **1** are broad, at −60 °C all resonances are sharp. The methyl and methylene resonances for the dme ligand are not resolved into two sets in the ^1H NMR spectrum, but four carbon resonances can be resolved in the ^{13}C NMR spectrum. Two isopropyl methyl resonances and a single methine carbon resonance are observed. Since the neopentylidyne and the amido ligands must be mutually cis in order not to compete as π-bonding ligands,[15] three different octahedral geometries are possible (**1a–c**). If the structure were **1a**, rotation about the N–C_{ipso} bond would have to be slow on the NMR time scale. In less symmetric **1b**



1a **1b** **1c**

and **1c**, rotation about the N–C_{ipso} bond would have to be fast on the NMR time scale. We think **1a** is most likely on the basis of the structure of Mo(CH-*t*-Bu)(NAr)$(OTf)_2$(dme) to be described later, especially since rotation about the N–C_{ipso} bond in Mo(CH-*t*-Bu)(NAr)$(OTf)_2$(dme) is also slow on the NMR time scale.

When **1** is treated with 0.25 equiv of triethylamine in ether at −30 °C, the solution quickly darkens from orange to red-orange. If all solvents are removed in vacuo after 30 min, a 1:1 mixture of two alkylidene complexes is obtained. One has an H_α resonance at 12.91 ppm and a C_α resonance at 312.2 ppm (J_{CH} = 115 Hz), and the other has an H_α resonance at 14.10 ppm and a C_α resonance at 326.2 ppm (J_{CH} = 124 Hz). No N–H stretch is observed in the IR spectrum of the mixture. Recrystallization of the mixture from pentane at −40 °C yields the product that has its H_α resonance at 14.10 ppm. This species contains no dme, but it reacts with dme to give the compound that has its H_α resonance at 12.91 ppm. Therefore we formulate the dme-free species as $[Mo(CH\text{-}t\text{-Bu})(NAr)Cl_2]_x$ (**2a**), where x probably equals 2, and the species that contains dme as Mo(CH-*t*-Bu)(NAr)Cl_2(dme) (**2b**; eq 2). A dimeric (or possibly oligomeric) structure for **2a** would account for its lower solubility than **2b**. Unfortunately **2a** does not appear to be stable enough to obtain

$$\text{Mo(C-}t\text{-Bu)(NHAr)Cl}_2\text{(dme)} \xrightarrow[\text{ether, } -30\ ^\circ\text{C}]{0.25\ \text{NEt}_3} \underset{\mathbf{2a}}{[\text{Mo(CH-}t\text{-Bu)(NAr)Cl}_2]_x} + \underset{\mathbf{2b}}{\text{Mo(CH-}t\text{-Bu)(NAr)Cl}_2\text{(dme)}} \quad (2)$$

a satisfactory elemental analysis, and **2b** cannot be obtained free of **2a**. We feel that the structure for **2b** is most likely analogous to that of Mo(CH-*t*-Bu)(NAr)$(OTf)_2$(dme) (see below).

Our working hypothesis is that triethylamine deprotonates the amido ligand and the resulting ammonium ion reprotonates the neopentylidyne ligand to give the neopentylidene ligand. A variation would be dehydrohalogenation to give Mo(C-*t*-Bu)(NAr)Cl(dme) as an intermediate. Some evidence for actual dehydrohalogenation and reprotonation is that W(C-*t*-Bu)(NHPh)$(PEt_3)_2Cl_2$ can be dehydrohalogenated by $Ph_3P{=}CH_2$,[16] and alkylidyne ligands in related "d^0" systems have been protonated.[17] The formation of **1** and its conversion to **2** have exact analogues in the tungsten system.[4] However, W(CH-*t*-Bu)(NAr)Cl_2(dme) can be isolated in pure form, presumably since it does not lose dimethoxyethane as readily as Mo(CH-*t*-Bu)(NAr)Cl_2(dme) and allow a dimer to form.

α-Hydrogen atom migrations of the type shown in eq 2 are slow if alkoxides are present on the metal. Mo(C-*t*-Bu)(NHAr)Cl_2(dme) reacts with 2 equiv of LiOR to give the complexes shown in eq 3. Their IR and NMR spectra are unexceptional and unambiguous; for example, Mo(C-*t*-Bu)(NHAr)$(OAr)_2$ shows a strong N–H absorption at 3440 cm^{-1} in its infrared spectrum (Nujol mull), a broad N–H proton resonance at 11.59 ppm in its ^1H NMR spectrum, and an alkylidyne α-carbon resonance at 317.0 ppm in its ^{13}C NMR spectrum. We do not know at this

$$\text{Mo(C-}t\text{-Bu)(NHAr)Cl}_2\text{(dme)} + 2\text{LiOR} \xrightarrow[\text{ether, } -30\ ^\circ\text{C}]{-2\text{LiCl}} \text{Mo(C-}t\text{-Bu)(NHAr)(OR)}_2\text{(dme)}_x \quad (3)$$

OR = $OCMe(CF_3)_2$ (x = 0.5) or OAr (x = 0)

point whether one or both oxygens of dme in Mo(C-*t*-Bu)(NHAr)$[OCMe(CF_3)_2]_2(dme)_{0.5}$ is (are) bound to molybdenum, or whether dme is simply solvent of crystallization; it cannot be removed readily in vacuo. But the main point is that both complexes are relatively stable thermally; e.g., heating a sample of Mo(C-*t*-Bu)(NHAr)$(OAr)_2$ to 100 °C in toluene-d_8 for 10 min led to only minimal decomposition. We have seen no evidence that either complex rearranges thermally to an imido alkylidene complex, even in the presence of triethylamine, and even though those alkylidene complexes can be prepared from **2**. These results support the proposal that the amido ligand actually is deprotonated in the reaction shown in eq 2, since one would not expect the amido α proton to be as acidic in alkoxide complexes as in halide complexes.

The above preparative route to Mo(CH-*t*-Bu)(NAr)Cl_2(dme) suffers from three problems. Mo(C-*t*-Bu)(CH_2-*t*-Bu)$_3$ is tedious

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to prepare, its yield is poor (~35% at best), and the reaction resists scale-up to convenient quantities (10–20 g) without a further decrease in yield.[13] For some time we tried to perfect a synthesis beginning with $Mo(NAr)Cl_4$, which was modeled after an improved synthesis of $W(CH\text{-}t\text{-}Bu)(NAr)Cl_2(dme)$.[18] $Mo(NAr)Cl_4$ is not known, however. Although $Mo(Ntol)Cl_4(thf)$ has been prepared from $MoCl_4$ and tolyl azide,[19] we were not able to prepare $Mo(NAr)Cl_4(thf)$ in this manner, perhaps because of the greater steric demands of the 2,6-diisopropylphenyl group versus the tolyl group. We also had no success synthesizing $Mo(NAr)Cl_4$ from $Mo(O)Cl_4$ and ArNCO (analogous to the synthesis of $W(NAr)Cl_4$ from $W(O)Cl_4$[18]), in part, we believe, because $Mo(O)Cl_4$ is unstable toward reduction to $MoOCl_3$, and in part because the electrophilicity of Mo is lower than that of W (and therefore the reaction between $Mo(O)Cl_4$ and ArNCO is slower than that between $W(O)Cl_4$ and ArNCO). Therefore we turned to the synthesis and exploitation of $Mo(NAr)_2Cl_2$ as a route to imido alkylidene complexes based on the concept of an imido ligand as a protecting group.

The first successful synthesis of $Mo(NAr)_2Cl_2$ is a variation of some syntheses of imido complexes reported by Nugent.[20] MoO_2Cl_2 can be prepared virtually quantitatively by treating commercially available MoO_2 with chlorine gas at ~160 °C in a glass flow reactor. (Commercially available MoO_2Cl_2 in our hands gave poorer yields in subsequent reactions reported here.) $MoO_2Cl_2(thf)_2$ is prepared readily and is easier to handle than fluffy MoO_2Cl_2. From it brick-red $Mo(NAr)_2Cl_2(dme)$ can be prepared in dimethoxyethane at 25 °C quantitatively as shown in eq 4. If trimethylchlorosilane is left out of the reaction then the yield of $Mo(NAr)_2Cl_2(dme)$ is halved (~45%) and an un-

$$MoO_2Cl_2(thf)_2 + 2ArNH(SiMe_3) \xrightarrow[4Me_3SiCl]{+2\ 2,6\text{-lutidine}} Mo(NAr)_2Cl_2(dme) + 2\ 2,6\text{-lutidine}\cdot HCl \quad (4)$$

identified precipitate that contains the remaining molybdenum is formed. We speculate that the role of trimethylchlorosilane is to convert any oxo or $OSiMe_3$ ligands to hexamethyldisiloxane and replace them with chlorides. Intermediates can be observed, but the mixtures are complex, and none has yet been identified. A variation of the reaction shown in eq 4 is now the preferred method of synthesizing $Mo(NAr)_2Cl_2(dme)$, since it avoids preparing $ArNH(SiMe_3)$; addition of 4 equiv of 2,6-lutidine, 10 equiv of Me_3SiCl, and 2 equiv of $ArNH_2$ to $MoO_2Cl_2(thf)_2$ gives $Mo(NAr)_2Cl_2(dme)$ in high yield after heating the mixture to 50 °C for 5 h.

Once $Mo(NAr)_2Cl_2(dme)$ had been characterized we showed that it was present in reactions in which MoO_2Cl_2 was treated with 2–3 equiv of ArNCO in toluene at 25 °C for 4–5 days followed by addition of dimethoxyethane. However, it is clear that such reactions are incomplete, the product cannot be separated readily from starting materials, and heating leads to decomposition. We also were not able to prepare $Mo(NAr)_2Cl_2$ from $MoO_2Cl_2(MeCN)_2$ and ArNCO, an approach that has been used to prepare $[Mo(O)(N\text{-}t\text{-}Bu)Cl_2(MeCN)]_3$ and $Mo(N\text{-}t\text{-}Bu)_2Cl_2$.[21] Reactions involving *t*-BuNCO probably are faster and separation of unreacted isocyanate and purification of $Mo(N\text{-}t\text{-}Bu)_2Cl_2$ easier.[21b]

$Mo(NAr)_2Cl_2(dme)$ reacts smoothly with $R'CH_2MgCl$ (R' = *t*-Bu or $PhMe_2C$) as shown in eq 5. Neophyl is advantageous for several reasons: (i) neophyl chloride is inexpensive (~1/50th the cost of neopentyl chloride) and easy to purify; (ii) the neophyl

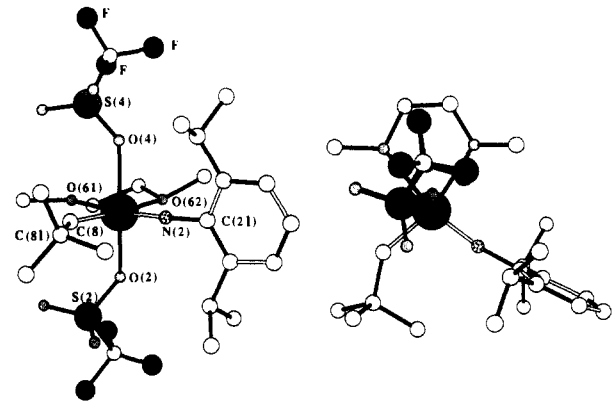

Figure 1. Two views of $Mo(CH\text{-}t\text{-}Bu)(NAr)(OSO_2CF_3)_2(dme)$.

Grignard is easier to prepare than the temperamental neopentyl Grignard; (iii) neophyl complexes tend to be slightly more

$$Mo(NAr)_2Cl_2(dme) + 2R'CH_2MgCl \xrightarrow{-dme} Mo(NAr)_2(CH_2R')_2 \quad (5)$$

$$R' = t\text{-Bu or } PhMe_2C$$

crystalline than neopentyl complexes; and (iv) the methyl groups of the neophyl or neophylidene ligand offer an additional stereochemical NMR probe. Both $Mo(NAr)_2(CH_2R')_2$ complexes are formed in high yield and are nicely crystalline. Dimethoxyethane must be lost in the process for steric reasons.

The final step in the four-step sequence to a versatile catalyst precursor is the reaction involving triflic acid shown in eq 6. The most logical intermediate in this reaction is $Mo(NAr)$-

$$Mo(NAr)_2(CH_2R')_2 + 3TfOH \rightarrow Mo(CHR')(NAr)(OTf)_2(dme) + ArNH_3OTf + R'CH_3 \quad (6)$$

$$R' = t\text{-Bu (3a) or } PhMe_2C \text{ (3b)}$$

$(CH_2R')_2(OTf)_2$, formed by multiple protonation of an imido ligand and removal of it as the anilinium salt. $Mo(NAr)$-$(CH_2R')_2(OTf)_2$ should be quite unstable with respect to loss of alkane to generate "$Mo(CHR')(NAr)(OTf)_2$", given the ionic nature of the triflate ligand[22] and the instability of dineopentyl complexes when electronegative, poor π-bonding ligands are present.[9] A key to the success of this reaction is that Mo-$(CHR')(NAr)(OTf)_2(dme)$ is relatively stable to triflic acid, in spite of the potential for protonating either the alkylidene or the imido ligand, perhaps largely because of the still relatively high partial positive charge on the metal. NMR studies suggest that dme does not exchange on the NMR time scale, consistent with the proposal that the metal is electron-poor and that the dme therefore is tightly bound. Although the isopropyl methine protons are equivalent in **3**, the isopropyl methyl groups are not, i.e., the phenyl ring does not rotate rapidly about the N–C bond. An analogous reaction between $Mo(NAr)_2(CH_2R')_2$ and HCl is complex, although some $Mo(CHR')(NAr)Cl_2(dme)$ can be observed in the crude product (by proton NMR). The same property that makes $Mo(CHR')(NAr)(OTf)_2(dme)$ relatively stable to triflic acid also makes it reactive toward a wide variety of alkoxides, as we shall see below.

An X-ray study of $Mo(CH\text{-}t\text{-}Bu)(NAr)(OTf)_2(dme)$ confirmed that it is a pseudooctahedral species in which the imido and alkylidene ligands are cis to one another and the triflate ligands are mutually trans. Two views of one of the two independent molecules in the unit cell are shown in Figure 1. Important bond distances and angles for the two independent molecules in the unit cell are listed in Table I, and crystal data are listed in Table III. The two molecules in the unit cell do not differ appreciably and only the second is discussed here.

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Table I. Selected Bond Distances (Å) and Angles (deg) in Mo(CH-*t*-Bu)(NAr)(OSO_2CF_3)$_2$(dme)

molecule 1		molecule 2	
Mo(1)–N(1)	1.72 (1)	Mo(2)–N(2)	1.72 (1)
Mo(1)–C(7)	1.90 (1)	Mo(2)–C(8)	1.93 (1)
Mo(1)–O(3)	2.085 (8)	Mo(2)–O(4)	2.100 (8)
Mo(1)–O(1)	2.101 (8)	Mo(2)–O(2)	2.105 (8)
Mo(1)–O(5)	2.299 (8)	Mo(2)–O(61)	2.317 (9)
Mo(1)–O(51)	2.325 (8)	Mo(2)–O(62)	2.333 (8)
Mo(1)–O(1)–S(1)	135.5 (5)	Mo(2)–O(2)–S(2)	136.6 (5)
Mo(1)–O(3)–S(3)	132.5 (5)	Mo(2)–O(4)–S(4)	132.6 (5)
Mo(1)–N(1)–C(11)	171.0 (8)	Mo(2)–N(2)–C(21)	173.7 (8)
Mo(1)–C(7)–C(71)	142.0 (1)	Mo(2)–C(8)–C(81)	141 (1)
N(1)–Mo(1)–C(7)	101.4 (5)	N(2)–Mo(2)–C(8)	99.6 (5)
N(1)–Mo(1)–O(3)	98.4 (4)	N(2)–Mo(2)–O(4)	97.1 (4)
N(1)–Mo(1)–O(1)	96.8 (4)	N(2)–Mo(2)–O(2)	99.3 (4)
N(1)–Mo(1)–O(5)	165.6 (4)	N(2)–Mo(2)–O(61)	167.4 (4)
N(1)–Mo(1)–O(51)	95.2 (4)	N(2)–Mo(2)–O(62)	97.5 (4)
C(7)–Mo(1)–O(3)	97.6 (4)	C(8)–Mo(2)–O(4)	99.5 (4)
C(7)–Mo(1)–O(1)	100.1 (4)	C(8)–Mo(2)–O(2)	97.7 (4)
C(7)–Mo(1)–O(5)	92.9 (4)	C(8)–Mo(2)–O(61)	92.9 (4)
C(7)–Mo(1)–O(51)	163.3 (4)	C(8)–Mo(2)–O(62)	163.0 (4)
O(3)–Mo(1)–O(1)	153.8 (3)	O(4)–Mo(2)–O(2)	153.8 (3)
O(3)–Mo(1)–O(5)	79.9 (3)	O(4)–Mo(2)–O(61)	79.2 (3)
O(3)–Mo(1)–O(51)	78.0 (3)	O(4)–Mo(2)–O(62)	78.7 (3)
O(1)–Mo(1)–O(5)	80.0 (3)	O(2)–Mo(2)–O(61)	80.3 (3)
O(1)–Mo(1)–O(51)	79.5 (3)	O(2)–Mo(2)–O(62)	79.0 (3)
O(5)–Mo(1)–O(51)	70.5 (3)	O(61)–Mo(2)–O(62)	70.1 (3)

There are several features of Mo(CH-*t*-Bu)(NAr)(OTf)$_2$(dme) worth pointing out that are analogous to features of structurally characterized pseudotetrahedral tungsten complexes.[4] The essentially linear imido and neopentylidene ligands are cis to one another, the *tert*-butyl group points toward the imido ligand (syn orientation; Mo–C(8)–C(81) = 141°), and the Mo–N(2) (1.72 (1) Å) and Mo–C(8) (1.93 (1) Å) bond lengths are in the expected range. The diisopropylphenyl ring of the imido ligand is oriented perpendicular to the C(21)–N(2)–Mo–C(8)–C(81) plane; it must not be able to rotate past the *tert*-butyl group of the syn neopentylidene ligand for steric reasons. Note how O(62), O(4), C(8), and O(2) are all tipped away from the imido ligand (Figure 1, right), so much so that the structure alternatively could be described as a distorted square pyramid in which the imido ligand occupies the axial position. The two oxygen atoms of the triflate ligands are tipped away from the Mo=C and Mo=N multiple bonds (O(4)–Mo–O(2) = 153.8 (3)°), as has been observed in other species that contain two multiply bound ligands cis to one another.[9] The Mo–triflate bond lengths are relatively long and the Mo–O–S bond angles relatively small compared to those of typical alkoxide Mo–O bonds, as one would expect for relatively ionic ligands with poor π-bonding abilities. These bond lengths and bond angles are similar to values found in other transition-metal triflate complexes[22] and in two other triflate complexes of Mo.[23] Note how the tiflate ligands are oriented (Figure 1, right) so that the CF_3 groups seem to take up the best compromise position sterically, and the position of a given SO_2 unit is then determined by a combination of steric interactions involving the imido isopropyl group, the *tert*-butyl group, and the CF_3 group. Any rotation of the OSO_2CF_3 group about the Mo–O bond would bring either the SO_2 group or the CF_3 group closer to one of the isopropyl substituents of the imido ligand.

Synthesis of Alkoxide and Phenoxide Alkylidene Complexes. Either the mixture of Mo(CH-*t*-Bu)(NAr)Cl_2(dme) and [Mo(CH-*t*-Bu)(NAr)Cl_2]$_x$ (**2a**/**2b**) or Mo(CH-*t*-Bu)(NAr)(OTf)$_2$(dme) (**3a**) can be treated with 2 equiv of LiOR in ether at −30 °C to yield complexes of the type Mo(CH-*t*-Bu)(NAr)(OR)$_2$ (**4**) (eq 7). All of the complexes **4** are yellow-orange, crystalline and extremely soluble in pentane. None contains dme, either coordinated or as a molecule of crystallization. (In contrast, W(CH-*t*-Bu)(NAr)[$OCMe(CF_3)_2$]$_2$ crystallizes with 1 equiv of dme that can be removed under high vacuum.[4a]) Yields of crude reaction products are high, but yields of recrystallized compounds are often in the 75% range on a scale of 1–2 g because of their high solubility in pentane. All complexes **4** are presumed to be pseudotetrahedral molecules in which Mo, N, C_α, and H_α all lie in a plane and in which the *tert*-butyl group points toward the imido ligand. This is the basic structure of W(CHPh)(NAr)[$OCMe(CF_3)_2$]$_2$[4a] and W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$,[4b] and Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ has been shown to have the same unit cell parameters as W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and therefore presumably is isostructural.[24] Compounds **4** are relatively robust; for example, Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ sublimes at 70 °C and 0.01 μm with little decomposition. In another experiment less than 5% of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (~0.01 M, measured against an internal standard) decomposed over a period of 2 weeks in C_6D_6 in a sealed NMR tube. Neophylidene complexes **5a–c** (eq 8) have been prepared from **3b** straightforwardly. They are entirely analogous species that are stable for long periods in solution in a sealed NMR tube.

$$\mathbf{2a/2b}\ \text{or}\ \mathbf{3a} + 2\text{LiOR} \xrightarrow{\text{ether, } -30\ ^\circ\text{C}} \text{Mo(CH-}t\text{-Bu)(NAr)(OR)}_2 \quad (7)$$

OR = $OCMe(CF_3)_2$ (**4a**), $OCMe_2(CF_3)$ (**4b**), O-*t*-Bu (**4c**), OAr (**4d**)

$$\mathbf{3b} + 2\text{LiOR} \xrightarrow[-30\ ^\circ\text{C}]{\text{ether}} \underset{\mathbf{5}}{\text{Mo(CHCMe}_2\text{Ph)(NAr)(OR)}_2} \quad (8)$$

OR = O-*t*-Bu (**5a**), OAr (**5b**), O-2-C_6H_4-*t*-Bu (**5c**)

NMR data (Table II) are all consistent with the proposed pseudotetrahedral structures of **4** and **5**. Note that both δH_α and δC_α increase as the alkoxide ligands become more electron withdrawing. Similar trends have been noted for W(CH-*t*-Bu)(NAr)(OR)$_2$ complexes.[4] It is interesting also to note that the H_α shifts are all larger by ~3 ppm than they are in the

Table II. ^{1}H and ^{13}C NMR Data for Molybdenum(VI) Alkylidene Complexes[a]

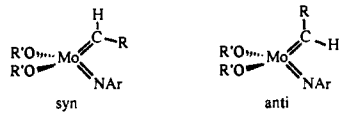
compd	δH_α (ppm)	δC_α (ppm)	J_{CH} (Hz)
[Mo(CH-*t*-Bu)(NAr)Cl_2]$_x$ (**2a**)[b]	14.10	326.2	124
Mo(CH-*t*-Bu)(NAr)Cl_2(dme) (**2b**)[b]	12.91	312.2	115
Mo(CH-*t*-Bu)(NAr)(OTf)$_2$(dme) (**3a**)	14.29	331.9	121
Mo(CHCMe$_2$Ph)(NAr)(OTf)$_2$(dme) (**3b**)	14.45	328.4	
Mo(CH-*t*-Bu)(NAr)[$OCMe(CF_3)_2$]$_2$ (**4a**)	12.06	288.2	117
Mo(CH-*t*-Bu)(NAr)[$OCMe_2(CF_3)$]$_2$ (**4b**)	11.61	276.8	118
Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (**4c**)	11.23	265.8	117
Mo(CH-*t*-Bu)(NAr)(OAr)$_2$ (**4d**)	11.42 (94%)	277.0	116
	12.64		
Mo(CHCMe$_2$Ph)(NAr)(O-*t*-Bu)$_2$ (**5a**)	11.34		
Mo(CHCMe$_2$Ph)(NAr)(OAr)$_2$ (**5b**)	11.77 (92%)	276.0	125
	12.74		
Mo(CHCMe$_2$Ph)(NAr)(O-2-C_6H_4-*t*-Bu)$_2$ (**5c**)	11.79 (94%)	276.5	121
	13.36		
Mo(CHSiMe$_3$)(NAr)[$OCMe(CF_3)_2$]$_2$ (**6a**)	13.86	289.8	113
Mo(CHSiMe$_3$)(NAr)[$OCMe_2(CF_3)$]$_2$ (**6b**)	13.25	274.5	111
Mo(CHSiMe$_3$)(NAr)(O-*t*-Bu)$_2$ (**6c**)	12.83 (90%)[c]		
	12.20		
Mo(CHSiMe$_3$)(NAr)(OAr)$_2$ (**6d**)	13.10 (35%)	268.8	117
	13.02	267.0	145
Mo(CHEt)(NAr)[$OCMe(CF_3)_2$]$_2$[d]	12.44[e]		
Mo(CHEt)(NAr)[$OCMe_2(CF_3)$]$_2$[d]	11.95[f]		
Mo(CHPh)(NAr)[$OCMe_2(CF_3)$]$_2$[d]	12.44		

[a] All spectra obtained in C_6D_6 unless otherwise noted. [b] Solvent = CD_2Cl_2. [c] At −60 °C in toluene-d_8. [d] Observed in situ. [e] Triplet, $^3J_{HH}$ = 6.2 Hz. [f] Triplet, $^3J_{HH}$ = 6.3 Hz.

(23) (a) The Mo–OTf distance in *cis*-[$Mo_2(O_2CCH_3)_2(CH_3CN)_4(O_3SCF_3)$][$HO_3SCF_3$)$_2$(THF) is 2.575 (15) Å and the bonding described is ionic.[23b] Covalently bound triflate can be found in Mo(CO)$_2$(L)$_2$(OSO_2CF_3) (L = 1,3-diethylimidazolidin-2-ylidene) where the Mo–OTf distance is 2.181 (4) Å.[23c] (b) Cotton, F. A.; Reid, A. H.; Schwotzer, W. *Inorg. Chem.* **1985**, *24*, 3965. (c) Anderson, D. M.; Bristow, G. S.; Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F.; Skelton, B. W. *J. Chem. Soc., Dalton Trans.* **1987**, 2843.

(24) Davis, W. M. Unpublished results. The structure could not be solved satisfactorily because of poor crystal quality.

analogous tungsten complexes. But the most interesting finding is that in several instances two alkylidene resonances are observed. In **5b**, for example, the two H_α resonances differ by approximately 1 ppm, the major resonance comprising 92% of the mixture at 22 °C. Similar results are found for **4d** and **5c**. The most sensible proposal is that these resonances can be ascribed to syn and anti alkylidene rotamers. Unfortunately, the small amount of each minor rotamer prevented full confirmation of this proposal by



carbon NMR. However, we have shown that upon raising the temperature of samples of **4d**, **5b**, and **5c**, resonances for each rotamer broaden and coalesce, consistent with a process that interconverts them, most likely by rotation about the Mo=C bond. Related observations involving Mo=CHSiMe$_3$ species (see below) more clearly demonstrate that such resonances can be ascribed to rotamers, and that the syn rotamer is that which most likely gives rise to the dominant H_α resonance. It should be noted that small amounts of the minor rotamer in other cases reported here may have escaped detection in the initial stages of this work, or that a system in which only one rotamer is apparent in one solvent may also display a resonance for the other in another solvent. Detailed studies of alkylidene rotation for a wide variety of alkylidene complexes of both Mo and W will be reported in due course.

Other Alkylidene Complexes Produced by Stoichiometric Reactions between Mo(CH-*t*-Bu)(NAr)(OR)$_2$ and Olefins. Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ reacts with a slight excess of vinyltrimethylsilane in pentane at −30 °C to yield Mo(CHSiMe$_3$)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (**6a**) and neohexene (eq 9). Although **6a** appears to form in good yield in an NMR experiment in C_6D_6, it is difficult to isolate on a preparative scale since decomposition is significant in the presence of any excess vinyl-

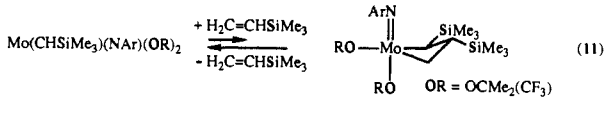
$$\underset{\textbf{4a}}{\text{Mo(CH-}t\text{-Bu)(NAr)[OCMe(CF}_3)_2]_2} \xrightarrow[-CH_2=CH(t\text{-Bu})]{+CH_2=CHSiMe_3} \underset{\textbf{6a}}{\text{Mo(CHSiMe}_3)(NAr)[OCMe(CF}_3)_2]_2 \quad (9)$$

trimethylsilane. This behavior contrasts with that for W(CHSiMe$_3$)(NAr)[OCMe(CF$_3$)$_2$]$_2$, which has been shown to form W[CH(SiMe$_3$)CH(SiMe$_3$)CH$_2$](NAr)[OCMe(CF$_3$)$_2$]$_2$ reversibly in the presence of vinyltrimethylsilane.[4a] Studies to be described below suggest that it is not Mo(CHSiMe$_3$)(NAr)[OCMe(CF$_3$)$_2$]$_2$ that is unstable, but Mo[CH(SiMe$_3$)CH$_2$CH(SiMe$_3$)](NAr)[OCMe(CF$_3$)$_2$]$_2$, formed by reaction of it with vinyltrimethylsilane.

The reaction between Mo(CH-*t*-Bu)(NAr)[OCMe$_2$(CF$_3$)]$_2$ and excess vinyltrimethylsilane proceeds readily to yield Mo(CHSiMe$_3$)(NAr)[OCMe$_2$(CF$_3$)]$_2$ (**6b**; eq 10). In contrast to **6a**, **6b** does not decompose in the presence of excess vinyltrimethylsilane. Furthermore, when **6b** and several equivalents of

$$\underset{\textbf{4b}}{\text{Mo(CH-}t\text{-Bu)(NAr)[OCMe}_2(CF_3)]_2} \xrightarrow[-CH_2=CH(t\text{-Bu})]{+CH_2=CHSiMe_3} \underset{\textbf{6b}}{\text{Mo(CHSiMe}_3)(NAr)[OCMe}_2(CF_3)]_2 \quad (10)$$

vinyltrimethylsilane are dissolved in toluene-d_8 and the solution is cooled to −40 °C, resonances characteristic of a trigonal-bipyramidal metallacyclobutane complex analogous to W[CH(SiMe$_3$)CH(SiMe$_3$)CH$_2$](NAr)[OCMe$_2$(CF$_3$)]$_2$[4a] are observed in the ^{1}H NMR spectrum at −0.56 (m, H_β), 4.26 (br d, H_α), 4.54 (m, $H_{\alpha'}$(a)), and 5.89 ppm (m, $H_{\alpha'}$(b); eq 11). Metallacycle formation is completely reversible. By integrating the multiplet for the isopropyl methine protons in the metallacycle at 4.11 ppm versus that for the methine protons in **6b** at 3.68 ppm, K_{eq} for



(11)

formation of the metallacycle was determined to be 5.1×10^{-1} M^{-1} at −40 °C in one experiment and 4.0×10^{-1} M^{-1} in another. Comparison with the value for the analogous tungsten complex (3.3×10^2 M^{-1} at −38 °C[4a]) demonstrates that the molybdacyclobutane complex is approximately three orders of magnitude in K_{eq} less stable relative to vinyltrimethylsilane and the trimethylsilylmethylene complex than is W[CH(SiMe$_3$)CH(SiMe$_3$)CH$_2$](NAr)[OCMe$_2$(CF$_3$)]$_2$. The fact that metallacycles such as Mo[CH(SiMe$_3$)CH$_2$CH(SiMe$_3$)](NAr)[OCMe$_2$(CF$_3$)]$_2$ and W[CH(SiMe$_3$)CH$_2$CH(SiMe$_3$)](NAr)[OCMe(CF$_3$)$_2$]$_2$ do not decompose readily is consistent with a greater stability of a complex containing the less electron withdrawing OCMe$_2$(CF$_3$) ligand (in the first case) and the less reducible tungsten (in the second case).

Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ reacts with excess vinyltrimethylsilane (17 equiv) to yield Mo(CHSiMe$_3$)(NAr)(O-*t*-Bu)$_2$ (**6c**; eq 12). The ^{1}H NMR spectrum of **6c** differs from that of **6a** or **6b** in that the resonances are somewhat broad at room temperature in toluene-d_8. The resonance for the alkylidene α

$$\underset{\textbf{4c}}{\text{Mo(CH-}t\text{-Bu)(NAr)(O-}t\text{-Bu)}_2} \xrightarrow[-CH_2=CH(t\text{-Bu})]{+CH_2=CHSiMe_3} \underset{\textbf{6c}}{\text{Mo(CHSiMe}_3)(NAr)(O\text{-}t\text{-Bu})_2} \quad (12)$$

proton, in particular, is a broad singlet at 12.65 ppm. Above room temperature all resonances begin to sharpen until at 80 °C the alkylidene α-proton resonance appears as a sharp singlet at 12.55 ppm. All resonances also sharpen as the sample is cooled. Most importantly beginning at −20 °C a second alkylidene α-proton resonance can be observed at 12.20 ppm, and at −60 °C the two alkylidene α-proton resonances are sharp. The major resonance (~90%) appears at 12.83 ppm and the minor resonance (~10%) at 12.20 ppm. (Other resonances cannot be assigned unambiguously.) This temperature-dependent behavior is totally reversible. This appears to be another case where syn and anti rotamers are both present, and one where rotation about the Mo=C bond appears to be slightly faster on the NMR time scale than in the case of **5b** and **5c** discussed above.

Mo(CH-*t*-Bu)(NAr)(OAr)$_2$ reacts with excess vinyltrimethylsilane (~10 equiv) at room temperature to yield Mo(CHSiMe$_3$)(NAr)(OAr)$_2$ (**6d**; eq 13). The variable-temperature proton and carbon NMR spectra most clearly illustrate the presence of syn and anti rotamers (Figure 2). Two sharp alkylidene α-proton resonances are found at 13.10 and 13.02 ppm in C_6D_6 in a ratio of ~1:2 at 25 °C (Table II). These resonances (at 13.03 and 12.96 ppm in toluene-d_8; Figure 2) coalesce into a single sharp resonance at 13.00 ppm at 70 °C. One resonance can be assigned to the α-hydrogen atom in the syn rotamer and

$$\underset{\textbf{4d}}{\text{Mo(CH-}t\text{-Bu)(NAr)(OAr)}_2} \xrightarrow[-CH_2=CH(t\text{-Bu})]{+CH_2=CHSiMe_3} \underset{\textbf{6d}}{\text{Mo(CHSiMe}_3)(NAr)(OAr)_2} \quad (13)$$

the other resonance to the α-hydrogen atom in the anti rotamer. Interconversion of the syn and anti rotamers is totally reversible. Simulation of the proton NMR spectra by complete band shape analysis revealed that $\Delta H^\ddagger$ = 16.5 kcal mol^{-1}, $\Delta S^\ddagger$ = 1.5 eu, and $\Delta G^\ddagger_{298}$ = 16.0 kcal mol^{-1}.

The room temperature carbon NMR spectrum of **6d** shows two resonances for C_α at 268.8 (J_{CH} = 117 Hz) and 267.0 ppm (J_{CH} = 145 Hz) that we assign to syn and anti rotamers, respectively. The difference in coupling constants is significant and we believe characteristic of syn (low J_{CH}) and anti (high J_{CH}) conformations.[25] This proposal is being explored in detail along with studies of alkylidene ligand rotation in a variety of Mo and W complexes.

Propylidene complexes can be prepared by treating neopentylidene complexes with 3-hexene, but they are not isolable. For example, in a sealed ^{1}H NMR sample containing Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (~0.05 M), 10 equiv of *cis*-3-hexene,

(25) We thank Dr. W. E. Crowe for this suggestion.

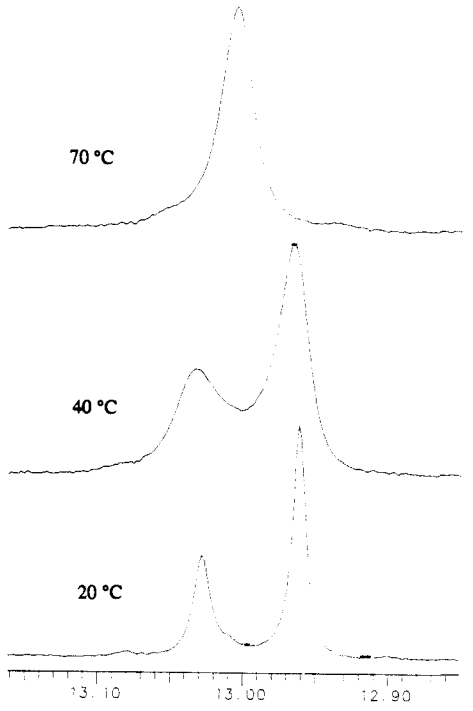


Figure 2. The alkylidene region of the variable-temperature proton NMR spectrum of $Mo(CHSiMe_3)(NAr)(OAr)_2$.

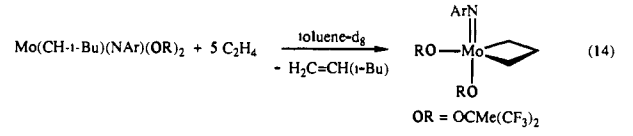
and an internal mesitylene standard in C_6D_6, the *cis*-3-hexene is isomerized to 84% *trans*-3-hexene before any other significant change is observed in the ^1H NMR spectrum. This rapid isomerization suggests that a small amount of $Mo(CHEt)(NAr)[OCMe(CF_3)_2]_2$ forms, and that it isomerizes the olefin (via a metathesis mechanism) before much more $Mo(CH\text{-}t\text{-}Bu)(NAr)[OCMe(CF_3)_2]_2$ reacts. After 15 h 50% of the neopentylidene complex was converted to what we propose is the analogous propylidene complex with little decomposition. The alkylidene α-proton resonance in $Mo(CHEt)(NAr)[OCMe(CF_3)_2]_2$ appears as a triplet ($^3J_{HH}$ = 6.2 Hz) at 12.42 ppm (Table II). After 24 h 80% of the neopentylidene complex was converted to the propylidene complex with no more than 10% decomposition. After 39 h no neopentylidene complex remained, but little propylidene complex did either. We can conclude that some component of this system largely decomposes over a period of ~24 h at a concentration of ~0.05 M. These observations are analogous to those made for $W(CHEt)(NAr)[OCMe(CF_3)_2]_2$.[4a] At this time we assume that $Mo(CHEt)(NAr)[OCMe(CF_3)_2]_2$ decomposes biomolecularly. An alternative explanation is that $Mo(CHEtCHEtCHEt)(NAr)[OCMe(CF_3)_2]_2$ is actually the species that decomposes by rearrangement of the MoC_3 ring to the olefin.

When $Mo(CH\text{-}t\text{-}Bu)(NAr)[OCMe_2(CF_3)]_2$ is treated with 10 equiv of *cis*-3-hexene in C_6D_6 in a sealed NMR tube, all of the *cis*-3-hexene is isomerized to ~85% *trans*-3-hexene before any of what we presume to be $Mo(CHEt)(NAr)[OCMe_2(CF_3)]_2$ can be detected. After ~23 h ~10% of the neopentylidene complex (δH_α = 11.61 ppm) has been converted to the propylidene complex (δH_α = 11.95 ppm). Spectra recorded periodically over the next 6 days showed ~40% total decomposition during this time, with only 10–15% of the neopentylidene complex remaining. We conclude that $Mo(CH\text{-}t\text{-}Bu)(NAr)[OCMe_2(CF_3)]_2$ reacts significantly more slowly with *cis*-3-hexene than does $Mo(CH\text{-}t\text{-}Bu)(NAr)[OCMe(CF_3)_2]_2$, and that some component of this system also is unstable in solution at concentrations of ~0.05 M over a period of several days.

No $Mo(CHEt)(NAr)(O\text{-}t\text{-}Bu)_2$ is observed over the course of 2 weeks in a sample containing $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ and 10 equiv of *cis*-3-hexene in C_6D_6 in a sealed NMR tube. The propylidene complex most likely is formed in small amounts, however, because *cis*-3-hexene is isomerized to ~80% trans during this period. These observations are consistent with a reactivity toward internal olefins that is even more attenuated than that of the analogous $OCMe_2(CF_3)$ complex.

When 3 equiv of styrene are added to $Mo(CH\text{-}t\text{-}Bu)(NAr)[OCMe(CF_3)_2]_2$ at room temperature in C_6D_6 most of the neopentylidene complex is converted into a new alkylidene complex (δH_α = 12.44) in 5–6 h, presumably $Mo(CHPh)(NAr)[OCMe(CF_3)_2]_2$. Only a trace of $Mo(CHPh)(NAr)[OCMe(CF_3)_2]_2$ remains after this solution is left for 3 days at room temperature.

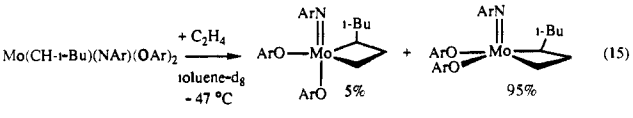
When 5 equiv of ethylene and $Mo(CH\text{-}t\text{-}Bu)(NAr)[OCMe(CF_3)_2]_2$ in toluene-d_8 were sealed in an NMR tube, the room temperature proton NMR spectrum showed that all of the neopentylidene complex had reacted with ethylene to give neohexene and what appeared to be largely trigonal-bipyramidal $Mo(CH_2CH_2CH_2)(NAr)[OCMe(CF_3)_2]_2$ by comparison with NMR data for $W(CH_2CH_2CH_2)(NAr)[OCMe(CF_3)_2]_2$[4a] (eq 14). Broad resonances at −0.26 and −1.15 ppm are characteristic of



the β protons in such a trigonal-bipyramidal metallacyclobutane ring. One α-proton resonance of area 2 can be observed as a broad doublet at ~4.8 ppm, and the other at ~5.0 ppm. $Mo(CH_2CH_2CH_2)(NAr)[OCMe(CF_3)_2]_2$ is stable at 25 °C in the presence of excess ethylene but decomposes over a period of ~12 h to as yet unidentified species. These observations contrast with those made for $W(CH_2CH_2CH_2)(NAr)[OCMe(CF_3)_2]_2$,[4a] one of the most readily formed and stable of the tungstacyclobutane complexes.

Experiments employing $^{13}C_2H_4$ and ^{13}C NMR as a probe helped to characterize $Mo(CH_2CH_2CH_2)(NAr)[OCMe(CF_3)_2]_2$ more completely. At −60 °C the β protons of $Mo(CH_2CH_2CH_2)(NAr)[OCMe(CF_3)_2]_2$ appear as two broad doublets centered at −0.26 ($^1J_{CH}$ = 158 Hz) and −1.13 ppm ($^1J_{CH}$ = 155 Hz), and the α protons give rise to two doublets of doublets at 5.01 (J_{HH} = 10.3 Hz, $^1J_{HC}$ = 159 Hz) and 4.82 ppm (J_{HH} = 10.6 Hz, $^1J_{HC}$ = 162 Hz). In the proton-decoupled ^{13}C NMR spectrum at −60 °C (Figure 3), the β-carbon atom of the metallacyclobutane complex appears at −2.28 ppm (t), and the α-carbon atom resonance appears at 104.1 ppm (d, $^1J_{CC}$ = 11 Hz). These chemical shifts and coupling constant are very similar to those of trigonal-bipyramidal $W(CH_2CH_2CH_2)(NAr)[OCMe(CF_3)_2]_2$.[4a] We conclude that $Mo(CH_2CH_2CH_2)(NAr)[OCMe(CF_3)_2]_2$ can be formed and is a trigonal-bipyramidal species, but it is significantly less stable than the analogous tungsten complex.

Analogous reactions in which $^{13}C_2H_4$ was added to $Mo(CH\text{-}t\text{-}Bu)(NAr)(OAr)_2$ were followed at low temperature by ^{13}C NMR. At −47 °C α-*tert*-butyl-substituted TBP and SP metallacycles (eq 15) were observed in the ratio of 5:95, along with a small amount of $Mo(CH_2CH_2CH_2)(NAr)(OAr)_2$. The SP



isomer has characteristic resonances at δ 44.5 (d, $J_{CC} \approx$ 53 Hz) for C_α and δ 29.7 (d, $J_{CC} \approx$ 49 Hz) for C_β, while the TBP isomer has resonances at δ 97.8 (d, $J_{CC} \approx$ 22 Hz) for C_α and δ −0.7 (br s) for C_β. After 20 min at −47 °C, only a trace of the α-*tert*-butyl SP metallacycle was observable. Warming the sample to −17.5 °C led to complete formation of SP $Mo(CH_2CH_2CH_2)(NAr)(OAr)_2$ [95%; δ 39.9 (C_α), 26.5 C_β] mixed with 5% of TBP $Mo(CH_2CH_2CH_2)(NAr)(OAr)_2$ [δ 100.1 (C_α), −0.7 (C_β)] and a trace of SP $Mo[CH_2CH(t\text{-}Bu)CH_2](NAr)(OAr)_2$ (δ 45.2 for C_α). A spectrum acquired at room temperature showed broadened resonances at 40 and 26 ppm characteristic of interconverting TBP and SP forms of $Mo(CH_2CH_2CH_2)(NAr)(OAr)_2$. This behavior is entirely analogous to that observed for the mixture of analogous tungsten complexes, except that approximately equal amounts of

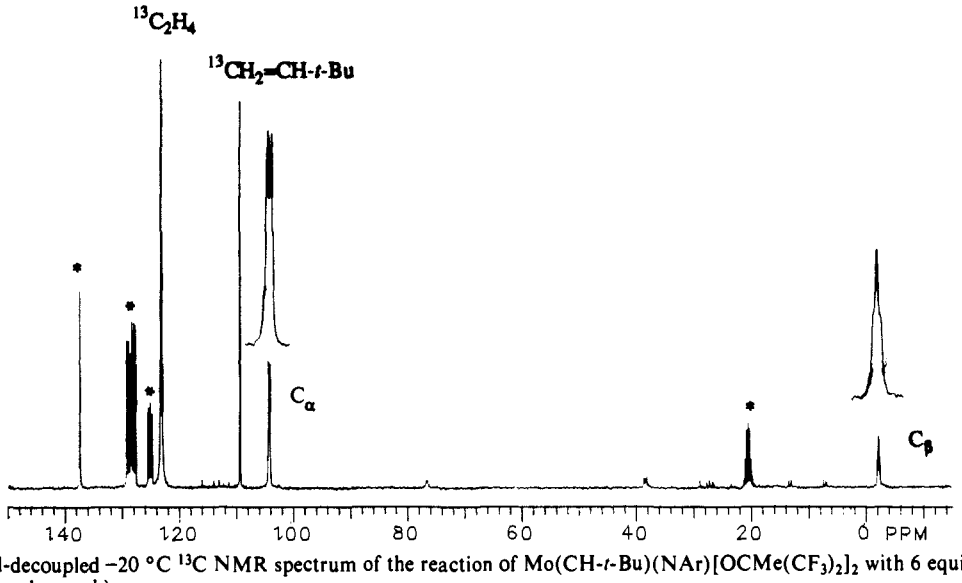
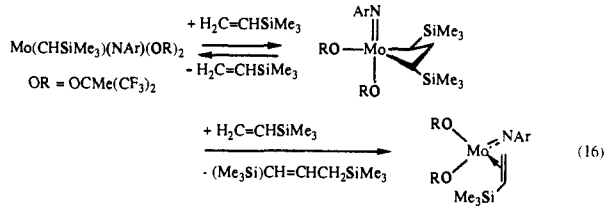


Figure 3. Broadband-decoupled −20 °C ^{13}C NMR spectrum of the reaction of Mo(CH-*t*-Bu)(NAr)[OCMe$(CF_3)_2]_2$ with 6 equiv of $^{13}C_2H_4$ at 25 °C (an asterisk indicates toluene-d_8).

TBP and SP tungsten complexes are present.[8b]

Decomposition of Molybdacyclobutane Complexes To Give Reduced Species. The apparent instability of Mo(CHSiMe_3)(NAr)[OCMe$(CF_3)_2]_2$ has been traced to the reaction shown in eq 16. No α,α'-disubstituted metallacycle in systems of this type has ever been observed, so its geometry is uncertain; the TBP geometry shown is for convenience only. $(Me_3Si)CH$=



$CHCH_2(SiMe_3)$ has been identified as the high-yield product of β-hydride rearrangement of the metallacycle by ^1H NMR, and a complex with the formula Mo(NAr)[$(Me_3Si)CH$=CH_2]-[OCMe$(CF_3)_2]_2$ can be isolated. It is apparently thermally unstable in the solid state, however, and so has been characterized only by NMR methods. Its ^{13}C NMR spectrum shows an olefinic CH resonance at 67.4 ppm (J_{CH} = 129 Hz) and an olefinic CH_2 resonance at 63.6 ppm (J_{CH} = 157 Hz), and the alkoxide ligands are inequivalent. One might predict that the structure of Mo-(NAr)[$(Me_3Si)CH$=CH_2][OCMe$(CF_3)_2]_2$ is one in which the C=C axis is oriented perpendicular to the N/Mo/(olefin centroid) plane in its lowest energy conformation. Mo(NAr)[(Me_3Si)-CH=CH_2][OCMe$(CF_3)_2]_2$ has been transformed into other complexes (e.g., acetylene adducts) that have been more thoroughly characterized.[26] Since such formally "reduced" molybdenum species are not directly relevant to the subject of alkylidene complexes and olefin metathesis, their preparation and chemistry will be presented in due course elsewhere.

On the basis of the above finding we might propose that the instability of Mo$(CH_2CH_2CH_2)$(NAr)[OCMe$(CF_3)_2]_2$ can be attributed to reduction of the metal by a β-hydride rearrangement analogous to that shown in eq 16. If that were the case, then propylene would be formed. But propylene is *not* observed in NMR samples after Mo$(CH_2CH_2CH_2)$(NAr)[OCMe$(CF_3)_2]_2$ has decomposed. Either the proposal is incorrect, or propylene is consumed as it is formed. This aspect is still under active investigation and will be reported along with the preparation and chemistry of other formally "reduced" molybdenum complexes.

Reactions of Mo(CH-*t*-Bu)(NAr)$(OR)_2$ with Olefins: Qualitative Observations. Mo(CH-*t*-Bu)(NAr)[OCMe$(CF_3)_2]_2$ metathesizes 500 equiv of *cis*-2-pentene in toluene to an equilibrium mixture of *cis*- and *trans*-2-butenes, 2-pentenes, and 3-hexenes within 2 min at 25 °C. If this reaction mixture is treated with an additional 500 equiv of *cis*-2-pentene 6 h later, equilibrium is again reached in less than 2 min. A rate of ~250 turnovers per minute appears to be the approximate upper limit, because when 1000 equiv of *cis*-2-pentene is added all at once to a sample of fresh catalyst, 5–10 min are required to reach equilibrium at 25 °C. The system is no longer active after approximately 1 day. It is not known the extent to which the catalyst is deactivated by traces of impurities or water in the olefin feed, although we know that the required chain carrying alkylidene complexes (or metallacycles, or both) are not stable indefinitely. It should be noted that W(CH-*t*-Bu)(NAr)[OCMe$(CF_3)_2]_2$ has been reported to metathesize at least 3700 equiv of *cis*-2-pentene to equilibrium in less than 5 min at 25 °C (lower limit ~1000 turnovers per minute).[4a] Therefore to a first approximation the tungsten catalyst may be as much as an order of magnitude faster than the analogous molybdenum catalyst for the metathesis of *cis*-2-pentene.

Mo(CH-*t*-Bu)(NAr)[OCMe$(CF_3)_2]_2$ also will metathesize some terminal acyclic olefins. For instance, it metathesizes 20 equiv of styrene to equilibrium in 1.5–2 h at 25 °C in toluene. W-(CH-*t*-Bu)(NAr)[OCMe$(CF_3)_2]_2$ under identical conditions requires at least 2.5 h.[4a] The molybdenum systems are not long-lived, however. For example, when Mo(CH-*t*-Bu)(NAr)[OCMe-$(CF_3)_2]_2$ is treated with 200 equiv of styrene in toluene, the reaction proceeds only about one-third of the way to equilibrium after 2 h, and it does not proceed much further during the next 24 h. We presume that the OCMe$(CF_3)_2$ system is deactived by rearrangement of metallacycles, perhaps most readily the unsubstituted metallacycle formed from the intermediate methylene complex and ethylene.

The rate of olefin metathesis is significantly slower when the alkoxide ligands are more electron donating. For example, when Mo(CH-*t*-Bu)(NAr)[OCMe$_2(CF_3)]_2$ in toluene is treated with 50 equiv of *cis*-2-pentene equilibrium is not reached for ~10 h. This corresponds to a rate of ~5 turnovers per hour, ~10^3 times slower than Mo(CH-*t*-Bu)(NAr)[OCMe$(CF_3)_2]_2$. Metathesis of 200 equiv of styrene with Mo(CH-*t*-Bu)(NAr)[OCMe$_2(CF_3)]_2$ is also relatively slow. After 4 h at room temperature in toluene the reaction proceeded only ~5% of the way to equilibrium. After 42 h the reaction had stopped, but it had proceeded only ~10% of the way to equilibrium.

When Mo(CH-*t*-Bu)(NAr)$(O$-*t*-$Bu)_2$ is treated with 50 equiv of *cis*-2-pentene at 25 °C in toluene, metathesis products (2-butenes and 3-hexenes) are barely detectable by GLC. After 2 days the reaction had proceeded ~10% of the way to equilibrium. This corresponds to 1–2 turnovers per day, which is ~10^2 times slower than Mo(CH-*t*-Bu)(NAr)[OCMe$_2(CF_3)]_2$ and ~10^5 times slower than Mo(CH-*t*-Bu)(NAr)[OCMe$(CF_3)_2]_2$. In a separate

(26) Robbins, J. Unpublished results.

experiment, Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ in toluene was treated with 50 equiv of *cis*-3-heptene. No metathesis was detected by GLC after 3 days. The reaction of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ with 50 equiv of 1-pentene proceeds at a rate of less than one turnover per day, and no metathesis was detected after 3 days in a reaction between Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and 50 equiv of styrene.

Although uncertainties are inherent in these experiments because a neopentylidene complex reacts much more slowly than an *n*-alkylidene (e.g., propylidene) complex, it is clear nevertheless that the trend in reactivity is $OCMe(CF_3)_2 > OCMe_2(CF_3) >> O$-*t*-Bu for a given olefin. This is the trend that has been shown semiquantitatively to be the case in the analogous tungsten system.[4a] It is also clear that metathesis activity employing molybdenum catalysts is significantly lower than that employing tungsten catalysts.

Reactions of Alkylidene Complexes with the Carbonyl Group. Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ and Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ react with 3–4 equiv of benzaldehyde (6.8×10^{-2} M) in C_6D_6 in less than 10 min to yield Mo(O)(NAr)(OR)$_2$ and PhCH=CH(*t*-Bu) essentially quantitatively relative to an internal mesitylene standard (eq 17). Proton NMR and GLC coinjection

$$\text{Mo(CH-}t\text{-Bu)(NAr)(OR)}_2 + \text{PhCHO} \rightarrow \text{Mo(O)(NAr)(OR)}_2 + \text{PhCH=CH(}t\text{-Bu)} \quad (17)$$

$$\text{OR} = \text{OCMe(CF}_3)_2 \text{ or O-}t\text{-Bu}$$

confirmed that the Wittig product was solely *trans*-PhCH=CH(*t*-Bu). Although Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ and Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ react with 3 equiv of acetone (6.8×10^{-2} M) in C_6D_6 in a sealed NMR tube, the products could not be identified. Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ did not react to a measurable extent (by ^{1}H NMR spectroscopy) with 3.5 equiv of ethyl acetate (6.8×10^{-2} M) in C_6D_6 at room temperature in a sealed NMR tube over the course of 2 weeks, or with 3.8 equiv of *N*,*N*-dimethylformamide (6.8×10^{-2} M) in C_6D_6 in a sealed NMR tube at room temperature over a period of 8 days. The neopentylidene complex should react significantly more slowly with the carbonyl functionality than a complex containing a relatively small alkylidene ligand (e.g., propylidene), so it is difficult to make predictions concerning the reactivity of (e.g.) propylidene complexes. It is also likely that syn and anti rotamers will react with a carbonyl group at different rates, although at this stage it is unclear how significant that difference might be.

Discussion

The synthetic route to molybdenum catalysts reported here allows one to prepare significant amounts of any of the known alkoxide or phenoxide derivatives, and therefore to control the reactivity of the metal to a maximum extent. The key to the synthesis is the use of an imido ligand as a protecting group. This approach has been used in rhenium(VII) chemistry, the imido ligand ultimately being replaced by two chlorides upon protonation by HCl and removal of the imido ligand as the ammonium salt.[27] It has been equally successful in preparing tungsten imido alkylidene complexes analogous to those reported here.[4b] It remains to be determined whether the approach can be used to prepare other M(NR)(alkylidene)(triflate)$_2$(dme) complexes (M = Mo or W; e.g., R = *t*-Bu), since the NAr ligand has some highly desirable steric properties that might make it unique as an ancillary ligand among the readily available, bulky, imido ligands.

A recently reported synthesis of Mo(CH-*t*-Bu)(N-*t*-Bu)[OCH(CF$_3$)$_2$]$_2$[21b] consists of a series of steps in which the *tert*-butylimido ligand is used as a protecting group and $(CF_3)_2CHOH$ as the "acid" in the last step ($MoO_2Cl_2 \rightarrow$ Mo(N-*t*-Bu)$_2$Cl$_2$ $\rightarrow$ Mo(N-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$ $\rightarrow$ Mo(CH-*t*-Bu)(N-*t*-Bu)[OCH(CF$_3$)$_2$]$_2$). Since α-abstraction and related proton-transfer reactions are most successful when highly electron-withdrawing halide (or triflate) ligands are present,[9] the reaction should not be successful for a wide variety of alcohols. In fact, hexafluoro-2-propanol was the only successful one of several alcohols (including phenols) that were tried. To what extent these results are slanted by the presence of a N-*t*-Bu ligand instead of a NAr ligand is not known. Although it ultimately may be possible to prepare some usable catalysts directly using some alcohols, synthesis via a catalyst precursor (if possible) is the cleanest, least-ambiguous method.

A new aspect of complexes of this general type, or at least now a more visible one, is the existence of rotamers. Alkylidene rotation in high oxidation state complexes was observed over 10 years ago for some tantalum complexes.[28] More recently a fluxional process consistent with alkylidene ligand rotation has been observed in five-coordinate tungsten alkylidene complexes of the general type W(CHR)(OCH$_2$-*t*-Bu)$_2$X$_2$ in which the alkylidene ligand is coordinated in an equatorial position and lies in the trigonal plane, and X (halide) ligands are located in axial positions.[29] Our findings here add to the evidence that alkylidene ligand rotation is a general phenomenon. In four-coordinate imido/alkylidene complexes it is in fact somewhat surprising that both rotamers are observable in certain circumstances, since that implies $< \sim 2$ kcal mol^{-1} difference in their energies. It is interesting to note that the values for J_{CH} for the syn and anti isomers in the best-defined case are significantly different. A possibility that is under consideration is that there is a significant electronic stabilization of the syn form as a result of a donation of electron density from its CH_α bond to the metal.[25] More detailed discussion and evidence for stabilization of syn and anti forms will be presented in due course.

Much more data that allow a direct comparison of stabilities of W and Mo alkylidene complexes that contain β protons are needed. The evidence presented here suggests that molybdenum alkylidene complexes that contain one or more β protons are not significantly more stable (in the absence of functionalities) than analogous tungsten complexes,[4a] although the evidence is weak and relatively unconvincing. Although one important practical difference between Mo and W catalysts is what could be called a greater tolerance of functionalities by Mo,[11,12] an inherently greater stability of a variety of intermediate Mo alkylidene complexes toward decomposition would yield the same result.

The nature of the initial reaction between an alkylidene complex of the general type described here and an olefin can be described as electrophilic attack by the metal, the greatest activity being observed for hexafluoro-*tert*-butoxide complexes. Since the activity of a given molybdenum catalyst is probably lower by approximately an order of magnitude compared to the activity of the analogous tungsten catalyst, we might conclude that tungsten is "more electrophilic" than molybdenum. Although these statements may be qualitatively correct, there are still large gaps in our knowledge of the detailed mechanism of metathesis by well-characterized complexes that prevent a more quantitative, scientifically satisfying explanation. For example, it is not known whether attack on the olefin is rate-limiting, or to what extent rearrangement of intermediate metallacyclobutane complexes may be a crucial feature of the mechanism. Fortunately, it should now be possible to probe for detailed answers to such questions.

Molybdacyclobutane complexes appear to differ from the analogous tungstacyclobutane complexes in two ways. First, a molybdacycle loses an olefin more readily than the analogous tungstacycle. This has been documented quantitatively in one case here (when OR = OCMe$_2$(CF$_3$)) and qualitatively appears to be the case also when OR = OAr. Second, the ratio of SP to TBP geometries for Mo and W metallacyclobutane complexes differs. When OR = OAr, the SP geometry predominates for molybdenum, while for tungsten,[8b] SP and TBP complexes are approximately of equal energy. The preference for formation of square-pyramidal molybdacycles could be a factor in the lower

(27) (a) Schrock, R. R.; Weinstock, I. A.; Horton, A. H.; Liu, A. H.; Schofield, M. H. *J. Am. Chem. Soc.* **1988**, *110*, 2686. (b) Toreki, R.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2448.

(28) Schrock, R. R.; Guggenberger, L. J.; Messerle, L. W.; Wood, C. D. *J. Am. Chem. Soc.* **1978**, *100*, 3793.

(29) Kress, J.; Osborn, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 3953.

activity of molybdenum versus tungsten catalysts for the metathesis of olefins, although in our opinion kinetic considerations will likely be at least as important if not more important than thermodynamic considerations.

We have uncovered one clear-cut example of reduction of molybdenum as a result of rearrangement of a molybdacyclobutane complex that contrasts strongly with the analogous tungsten system, where reduction is not observed. This is what one might have expected on the basis of periodic trends for Mo vs W. Slower β-hydride rearrangement when more electron-donating alkoxide ligands are used is also consistent with what one might view as the overall tendency for relatively electron rich metals to be reduced less readily. These findings correlate with what has been observed for tantalacyclobutane complexes;[9] when halides are replaced by alkoxides then the rate of tantalacyclobutane rearrangement to an olefin slows significantly relative to the rate of metathesis. It was this finding that pointed the way toward the use of alkoxides as ligands in order to prepare well-behaved, relatively stable metathesis catalysts.[30] Reactions between complexes of the type M(CH-*t*-Bu)(NAr)X_2(dme) (X = Cl or OTf) and olefins remain to be explored, but it seems likely that if they do react, then the metal probably will be reduced relatively easily by rearrangement of intermediate metallacyclobutane complexes.[31]

Overall the results reported here establish trends in high oxidation state alkylidene chemistry more firmly, and also establish molybdenum as a potentially important metal for metathesis of olefins. Future studies will be aimed toward understanding the metathesis reaction by molybdenum catalysts in more detail, the role of rotamers, reduction via rearrangement of metallacyclobutane rings, and the role of simple donor ligands.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques. Reagent grade ether, tetrahydrofuran, and toluene were distilled from sodium benzophenone ketyl under nitrogen. Pentane was washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled from calcium hydride under nitrogen. All deuterated NMR solvents were passed through a column of activated alumina.

Mo(C-*t*-Bu)Cl_3(dme)[13] was prepared as described in the literature. $Me_3SiNHAr$ (Ar = 2,6-C_6H_3-*i*-Pr_2) was prepared from Me_3SiCl and LiNHAr in ether at room temperature and was distilled prior to use. $MoO_2Cl_2(thf)_2$[32] was prepared by adding solid MoO_2Cl_2 slowly to THF at −30 °C. In our experience addition of THF to MoO_2Cl_2 is too exothermic to control. All other reagents were purchased from commercial sources and purified by standard techniques.

NMR data are listed in parts per million downfield from TMS for proton and carbon, and downfield from external $CFCl_3$ for fluorine. Coupling constants are quoted in hertz. Obvious multiplicities and routine coupling constants usually are not listed. Spectra were obtained in benzene-d_6 at 25 °C unless otherwise noted.

Preparation of Compounds. Mo(C-*t*-Bu)(NHAr)Cl_2(dme) [Ar = 2,6-C_6H_3-*i*-Pr_2] (1). A solution of $Me_3SiNHAr$ (0.69 g, 2.77 mmol) in ether (6.0 mL) was added dropwise over 5 min to a stirred blue solution of Mo(C-*t*-Bu)Cl_3(dme) (1.00 g, 2.77 mmol) in 45 mL of ether at −30 °C. The resulting orange-red solution was allowed to warm to room temperature over 90 min and solvents were removed in vacuo. The orange residue thus obtained was pure enough for subsequent reactions. Recrystallization from a minimum amount of ether at −40 °C yielded analytically pure material as yellow-orange needles (1.06 g, 76%, 3 crops): ^{1}H NMR (CD_2Cl_2) δ 12.49 (br s, 1, N*H*Ar), 7.12 (s, 3, NH-2,6-C_6H_3-*i*-Pr_2), 3.78 (br s, 4, MeOCH_2CH_2OMe), 3.62 (br s, 6, *Me*OCH_2CH_2O*Me*), 1.17 (br d, 12, CHMe_2), 0.77 (s, 9, MoCCMe_3). The resonance for NH-2,6-C_6H_3(C*H*Me_2)$_2$ was not found; ^{1}H NMR (CD_2Cl_2, 213 K) δ 12.59 (s, 1, N*H*Ar), 7.09 (s, 3, NH-2,6-C_6H_3-*i*-Pr_2), 3.89 (s, 6, *Me*OCH_2CH_2O*Me*), 3.63 (s, 4, MeOCH_2CH_2OMe), 1.23 (d, 6, CHMe_2), 0.95 (d, 6, CHMe_2), 0.65 (s, 9, MoCCMe_3). The resonance for NH-2,6-C_6H_3(C*H*Me_2)$_2$ was not found; ^{13}C NMR (CD_2Cl_2) δ 321.2 (MoCCMe$_3$), 156.1 (C_{ipso}), 142.9 (C_o), 127.0 (C_p), 123.3 (C_m), 72.5 (MeO*C*H_2*C*H_2OMe), 61.7 (*Me*OCH_2CH_2O*Me*), 27.8 (q and d, MoC*C*Me_3 and *C*HMe$_2$), 23.8 (CH*Me*$_2$). The peak for MoC*C*Me_3 was not found; ^{13}C NMR (CD_2Cl_2, 213 K) δ 320.4 (MoCCMe$_3$), 153.5 (C_{ipso}), 141.9 (C_o), 126.3 (C_p), 122.8 (C_m), 72.8 (*Me*OCH_2CH_2OMe), 71.0 (MeO*C*H_2*C*H_2OMe), 67.4 (MeOCH_2*C*H_2OMe), 59.6 (MeOCH_2CH_2O*Me*), 52.6 (MoC*C*Me$_3$), 27.0 (q and d, MoC*Me*$_3$ and *C*HMe$_2$), 24.0 (CH*Me*$_2$), 22.6 (CH*Me*$_2$); IR (Nujol) 3204 cm^{-1} (s, NH). Anal. Calcd for $MoC_{21}H_{37}O_2Cl_2N$: C, 50.21; H, 7.42. Found: C, 49.88; H, 7.35.

Mo(C-*t*-Bu)(NHAr)(OAr)$_2$. LiOAr (0.22 g, 1.19 mmol) was dissolved in ether (25 mL) and the solution was stirred at −30 °C as Mo(C-*t*-Bu)(NHAr)Cl_2(dme) (0.30 g, 0.60 mmol) was added in small portions as a solid. The solution turned bright yellow and LiCl precipitated as the reaction was allowed to warm to room temperature over the next 90 min. Solvents were then removed in vacuo. The yellow residue was extracted with pentane, the extracts were filtered through Celite, and the filtrate was evaporated to dryness in vacuo. Recrystallization of the crude product from a minimum amount of pentane at −40 °C yielded large yellow cubes (0.23 g, 55%) in two crops: ^{1}H NMR (CD_2Cl_2) δ 11.59 (br s, 1, N*H*Ar), 7.23 (d, 2, H_m, NHAr), 7.11 (d, 4, H_m, OAr), 7.03 (t, 1, H_p, NHAr), 6.93 (t, 2, H_p, OAr), 3.48 (septet, 4, O-2,6-C_6H_3(C*H*Me_2)$_2$), 3.01 (septet, 2, NH-2,6-C_6H_3(C*H*Me_2)$_2$), 1.47 (d, 12, NH-2,6-C_6H_3(CH*Me*$_2$)$_2$), 1.29 and 1.13 (d, 12 each, O-2,6-C_6H_3-(CH*Me*$_2$)$_2$), 0.65 (s, 9, MoCC*Me*$_3$); ^{13}C NMR (CD_2Cl_2) δ 317.0 (MoCCMe$_3$), 164.4 (C_{ipso}, OAr), 146.8 (C_{ipso}, NHAr), 136.6 (C_o, OAr), 135.1 (C_o, NHAr), 124.2 (C_m, NHAr), 123.0 (C_m, OAr), 122.9 (C_p, NHAr), 121.7 (C_p, OAr), 55.6 (MoC*C*Me$_3$), 31.3 (NH-2,6-C_6H_3-(*C*HMe$_2$)$_2$), 28.3 (MoCC*Me*$_3$), 27.6 (O-2,6-C_6H_3(*C*HMe$_2$)$_2$), 24.2 (NH-2,6-C_6H_3(CH*Me*$_2$)$_2$), 23.4 and 23.3 (O-2,6-C_6H_3(CH*Me*$_2$)$_2$); IR (Nujol) 3440 cm^{-1} (NH). Anal. Calcd for $MoC_{41}H_{61}O_2N$: C, 70.77; H, 8.84. Found: C, 70.65; H, 8.62.

Mo(C-*t*-Bu)(NHAr)[OCMe(CF$_3$)$_2$]$_2$(dme)$_{0.5}$. Mo(C-*t*-Bu)(NHAr)-Cl_2(dme) (0.30 g, 0.60 mmol) was added slowly as a solid to a stirred ether solution (30 mL) of LiOCMe(CF$_3$)$_2$ (0.23 g, 1.20 mmol) at −30 °C. The solution immediately darkened to orange-red and then lightened. LiCl precipitated as the reaction was allowed to warm to room temperature over the next 2 h. Removing the solvents in vacuo yielded an off-white solid. This residue was extracted with pentane, the extracts were filtered through Celite, and filtrate was concentrated to a white solid. Recrystallization from a minimum amount of pentane at −40 °C yielded white cubes (0.31 g, 69%) in two crops: ^{1}H NMR (CD_2Cl_2) δ 10.92 (br s, 1, N*H*Ar), 7.17 (s, 3, NH-2,6-C_6H_3-*i*-Pr_2), 3.65 (s, 2, MeOCH_2CH_2OMe), 3.37 (s, 3, *Me*OCH_2CH_2O*Me*), 3.26 (septet, 2, C*H*Me$_2$), 1.84 (s, 6, OC*Me*(CF$_3$)$_2$), 1.30 and 1.03 (d, 6 each, CH*Me*$_2$), 0.74 (s, 9, MoCC*Me*$_3$); ^{13}C NMR (CD_2Cl_2) δ 316.3 (MoCCMe$_3$), 154.7 (C_{ipso}), 142.8 (C_o), 126.6 (C_p), 124.5 and 124.1 (q, $^1J_{CF}$ = 286 and 287, respectively, OCMe(*C*F$_3$)$_2$), 122.9 (C_m), 81.3 (septet, $^2J_{CF}$ = 29, O*C*Me(CF$_3$)$_2$), 71.4 (MeO*C*H_2*C*H_2OMe), 58.8 (*Me*OCH_2CH_2O*Me*), 54.1 (MoC*C*Me$_3$), 29.7 (MoCC*Me*$_3$), 28.6 (*C*HMe$_2$), 24.6 and 21.3 (CH*Me*$_2$), 20.4 (OC*Me*(CF$_3$)$_2$); ^{19}F NMR (CD_2Cl_2) δ −78.3 and −79.2 (s, 6 each, OCMe(C*F*$_3$)$_2$); IR (Nujol) 3276 cm^{-1} (NH). Anal. Calcd for $MoC_{27}H_{38}O_3F_{12}N$: C, 43.33; H, 5.12. Found: C, 42.86; H, 5.13.

Mo(CH-*t*-Bu)(NAr)Cl_2(dme) (2b). Crude Mo(C-*t*-Bu)(NHAr)Cl_2-(dme), prepared from 0.24 g (0.66 mmol) of Mo(C-*t*-Bu)Cl_3(dme) as described above, was dissolved in ether (20 mL) and the solution was stirred at −30 °C as first dme (70 μL, 0.67 mmol) and then NEt_3 (25 μL, 0.18 mmol) were added via syringe. The solution was allowed to warm to room temperature over the next 20 min. Solvents were then removed in vacuo, leaving an orange-red residue that was pure enough for subsequent reactions. ^{1}H and ^{13}C NMR spectra of this residue showed the presence of two alkylidene complexes, one containing dme (δ$H_α$ = 12.91 ppm, δ$C_α$ = 312.2 ppm, J_{CH} = 115 Hz) and one not containing dme (δ$H_α$ = 14.10 ppm, δ$C_α$ = 326.2 ppm, J_{CH} = 124 Hz). The dme-free complex could be crystallized selectively from the mixture as an orange solid (0.15 g, 45%) from a minimum amount of pentane at −40 °C. It was not stable enough to be analyzed and the complex containing dme could not be obtained free of the dme-free complex: ^{1}H NMR (CD_2Cl_2) δ 14.10 (s, 1, MoC*H*CMe$_3$), 7.20 (m, 3, N-2,6-C_6H_3-*i*-Pr_2), 4.26 (br, 2, C*H*Me$_2$), 1.26 (br, 12, CH*Me*$_2$), 1.22 (s, 9, MoCHC*Me*$_3$); ^{13}C NMR (CD_2Cl_2) δ 326.2 (d, J = 124, MoCHCMe$_3$), 151.4 (C_{ipso}), 149.8 (C_o), 127.7 (C_p), 123.0 (C_m), 49.7 (MoCHC*Me*$_3$), 29.4 (MoCHC*Me*$_3$), 27.5 (*C*HMe$_2$), 24.1 (CH*Me*$_2$); IR (Nujol) no $ν_{NH}$ absorption was observed.

MoO_2Cl_2. MoO_2 (40.0 g, 0.313 mol) was dried for 12 h at 140 °C under argon in the apparatus shown in Figure 4. The temperature of the tube containing the MoO_2 was raised to 160 °C with an oil bath and a stream of chlorine gas was passed through two sulfuric acid traps and then over the MoO_2 for 10 h. The connecting tube to the collection flask

(30) Schrock, R. R. *J. Organomet. Chem.* **1986**, *300*, 249.

(31) Preliminary studies suggest that Mo(CH-*t*-Bu)(NAr)(OTf)$_2$(dme) does not react readily even with norbornene in benzene, probably because the dme is so firmly bound.

(32) Krauss, H.; Huber, W. *Chem. Ber.* **1961**, *94*, 2864.

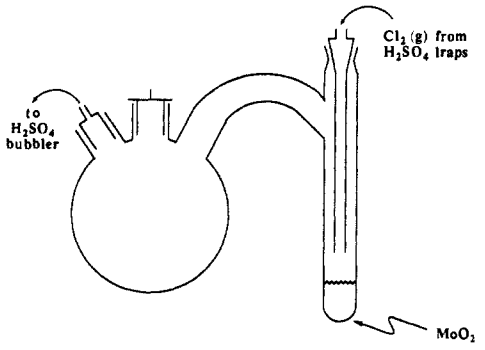


Figure 4. A drawing of the apparatus used to prepare MoO_2Cl_2.

was wrapped with heating tape in order to encourage the MoO_2Cl_2 to sublime into the round-bottom collection flask as it formed. MoO_2Cl_2 is obtained as ivory flakes and can be used without further purification.

Mo(NAr)$_2$Cl$_2$(dme). (a) To a rapidly stirred solution of $MoO_2Cl_2(thf)_2$ (10.0 g, 29.0 mmol) in dme (100 mL, −30 °C), the following were added in succession: a solution of 2,6-lutidine (6.2 g, 58 mmol) in dme (5 mL, −30 °C) over a period of 3–5 min, a solution of chlorotrimethylsilane (12.6 g, 116 mmol) in dme (25 mL, −30 °C) over a period of 5–10 min, and a solution of *N*-(trimethylsilyl)-2,6-diisopropylaniline (14.6 g, 58 mmol) in dme (25 mL, −30 °C) over a period of 5–10 min. The color changed from slightly yellow to bright red-orange to deep red-orange as a precipitate formed. The mixture was allowed to stir and warm to room temperature over a period of 6 h. The reaction mixture was then filtered through Celite to remove lutidine hydrochloride, which was then washed with diethyl ether until the washings ran through colorless. Solvents were removed from the filtrate in vacuo to yield 16.7 g (27.5 mmol, 95%) of brick-red product that need not be purified further: ^{1}H NMR δ 7.01 (d, 4, H_m), 6.89 (t, 2, H_p), 4.29 (sept, 4, C*H*Me$_2$), 3.44 (s, 6, *Me*OCH$_2$CH$_2$O*Me*), 3.18 (s, 4, MeO*CH*$_2$CH$_2$OMe), 1.25 (d, 24, CH*Me*$_2$); ^{13}C NMR δ 154.2 (C_{ipso}), 145.5 (C_p), 128.0 (C_m), 123.9 (C_o), 71.3 (*Me*OCH$_2$CH$_2$OMe), 62.8 (MeO*CH*$_2$CH$_2$OMe), 28.2 (*C*HMe$_2$), 25.2 (CH*Me*$_2$). Anal. Calcd for $MoC_{28}H_{44}Cl_4NO_2$: C, 55.35; H, 7.30; N, 4.61; Cl, 11.67. Found: C, 55.18; H, 7.23; N, 4.72; Cl, 11.61.

(b) The preferred method is to add to a rapidly stirred solution of $MoO_2Cl_2(thf)_2$ (10.0 g, 29.0 mmol) in dimethoxyethane (200 mL, −30 °C) (i) a solution of 2,6-lutidine (12.4 g, 116 mmol) in dme (10 mL, −30 °C) over a period of 3–5 min, (ii) a solution of trimethylchlorosilane (31.5 g, 0.290 mol) in dme (40 mL, −30 °C) over a period of 3–5 min, and (iii) a solution of 2,6-diisopropylaniline (10.3 g, 58.0 mmol) in dme (15 mL, −30 °C) over a period of 15 min. The color changed from slightly yellow to bright red-orange to deep red-orange as a precipitate formed. The mixture was then heated to 50 °C for 5 h. The 2,6-lutidine hydrochloride was filtered off and washed with diethyl ether until the washings ran clear. Solvents were removed from the filtrate in vacuo to yield 16.7 g (27.5 mmol, 95%) of brick-red Mo(NAr)$_2$(dme)Cl$_2$ that was pure enough for alkylation.

Mo(NAr)$_2$(CH$_2$-*t*-Bu)$_2$. An ether solution of neopentylmagnesium chloride (98.7 mL, 1.00 M, 98.7 mmol) was added dropwise to a stirred solution of Mo(NAr)$_2$(dme)Cl$_2$ (30 g, 49.3 mmol) in ether (500 mL) at −30 °C. All Mo(NAr)$_2$(dme)Cl$_2$ need not be dissolved. The color of the reaction changes from red to orange as $MgCl_2$ precipitates. The reaction mixture was allowed to warm to 25 °C and was stirred for 3 h. The resulting mixture was filtered through Celite, and the filtrate was concentrated in vacuo and kept at −40 °C to yield several crops (usually three) of orange crystals: yield 20.2 g (70%); ^{1}H NMR δ 6.96 (m, 6, H_m and H_p), 3.72 (sept, 4, C*H*Me$_2$), 2.28 (s, 4, CH_2CMe$_3$), 1.26 (s, 18, CH$_2$C*Me*$_3$), 1.21 (d, 24, CH*Me*$_2$); ^{13}C NMR δ 153.2 (C_{ipso}), 141.4 (C_p), 124.5 (C_o), 122.7 (C_m), 79.9 (*C*H$_2$CMe$_3$), 33.7 (*C*HMe$_2$), 33.5 (CH$_2$*C*Me$_3$), 28.3 (*C*HMe$_2$), 23.3 (CH$_2$*C*Me$_3$). Anal. Calcd for $MoC_{34}H_{23}N_2$: C, 69.36; H, 9.59; N, 4.76. Found: C, 69.23; H, 9.59; N, 4.86.

Mo(NAr)$_2$(CH$_2$CMe$_2$Ph)$_2$. A 25-mmol reaction was carried out in a manner virtually identical with that above for Mo(NAr)$_2$(CH$_2$-*t*-Bu)$_2$ to give 14.92 g (80%) of product: ^{1}H NMR δ 7.45 (d, 4, aromatic), 7.24 (t, 4, aromatic), 7.10 (t, 2, aromatic), 7.00–6.92 (m, 6, aromatic), 3.65 (sept, 4, C*H*Me$_2$), 1.72 (s, 4, CH_2CMe$_2$Ph), 1.49 (s, 12, CH$_2$C*Me*$_2$Ph), 1.11 (d, 24, CH*Me*$_2$); ^{13}C NMR δ 153.3, 142.7, 128.6, 126.8, 126.4, 126.0, 123.2, 78.6, 39.5, 32.0, 27.9, 23.5. Anal. Calcd for $C_{44}H_{60}MoN_2$: C, 74.13; H, 8.48; N, 3.93. Found: C, 74.45; H, 8.60; N, 3.84.

Mo(CH-*t*-Bu)(NAr)(OSO$_2$CF$_3$)$_2$(dme) (3a). A prechilled solution of triflic acid (3.15 mL, 35.5 mmol, 3 equiv) in dme (20 mL) was added dropwise to a solution of Mo(NAr)$_2$(CH$_2$-*t*-Bu)$_2$ (7.00 g, 11.8 mmol) in dme (200 mL) at −30 °C over a period of 10 min. It is important in this step that the solution be homogeneous and cold. It is best to grind the Mo(NAr)$_2$(CH$_2$-*t*-Bu)$_2$ crystals to a fine powder to aid dissolution; some pentane (15–30 mL) may be added. The solution was allowed to warm up to room temperature and stirred for 3 h. During this period the color changed from orange to dark yellow. The solvent was evaporated in vacuo to yield a yellow solid, which was then extracted with cold toluene (100–150 mL). The extract was filtered through a bed of Celite and the toluene removed from the filtrate in vacuo to give 5.9 g (65%) of the product as yellow flakes, which can be used without further purification. The product should be checked by NMR for contamination by anilinium triflate, which is slightly soluble in toluene: ^{1}H NMR δ 14.29 (s, 1, C*H*-*t*-Bu), 6.90 (m, 3, H_m and H_p), 3.91 (sept, 2, C*H*Me$_2$), 3.85 (s, 3, MeOCH$_2$CH$_2$O*Me*), 3.13 (m, 2, MeOCH$_2$C*H*$_2$OMe), 2.76 (s, 3, *Me*OCH$_2$CH$_2$OMe), 2.72 (m, 2, MeOC*H*$_2$CH$_2$OMe), 1.44 (s, 9, CH-*t*-Bu), 1.40 (d, 3, CH*Me*$_2$), 1.24 (d, 3, CH*Me*$_2$); ^{13}C NMR δ 331.9 (C_α, J_{CH} = 121), 151.2, 141.6, 130.6, 125.6, 121.4, 115.5, 72.5, 70.1, 65.3, 61.5, 31.0, 28.3, 25.2, 22.7; ^{19}F δ −77.0. Anal. Calcd for $MoC_{23}H_{37}F_6NO_8S_2$: C, 37.86; H, 5.11; N, 1.92. Found: C, 37.99; H, 5.33; N, 1.85.

Mo(CHCMe$_2$Ph)(NAr)(OSO$_2$CF$_3$)$_2$(dme) (3b). A −30 °C solution of triflic acid (4.42 g, 29.45 mmol) in 15 mL of dimethoxyethane was added in a dropwise manner to an orange solution of Mo(NAr)$_2$(CH$_2$CMe$_2$Ph)$_2$ (prepared as described above) in 150 mL of dimethoxyethane at −30 °C. The solution was allowed to warm and was stirred overnight (16 h) to give a dark yellow solution, which was concentrated in vacuo. The resulting yellow solid was then extracted with approximately 100 mL of chilled (0 °C) toluene and filtered. The filtrate was itself concentrated in vacuo, and the resulting dark yellow solid was recrystallized from cold diethyl ether. Three crops gave 5.94 g of the product (76%): ^{1}H NMR δ 14.45 (s, 1, C*H*CMe$_2$Ph), 7.57 (d, 2, aromatic), 7.18 (t, 2, aromatic), 6.97–6.89 (m, 4, aromatic), 3.84 (sept, 2, C*H*Me$_2$), 3.73 (s, 3, OCH_3), 3.18 (m, 2, OCH_2), 2.84–2.78 (m, 5, OCH_3, OCH_2), 1.91 (s, 6, CHC*Me*$_2$Ph), 1.37 (d, 6, CH*Me*$_2$), 1.21 (d, 6, CH*Me*$_2$); ^{13}C NMR δ 328.4, 152.1, 151.8, 148.7, 130.6, 128.7, 126.6, 124.3, 72.8, 70.0, 65.7, 61.9, 58.8, 31.1, 28.3, 25.6, 22.8. Anal. Calcd for $C_{28}H_{39}F_6MoNO_8S_2$: C, 42.48; H, 4.97; N, 1.77. Found: C, 42.82; H, 5.06; N, 1.57.

Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (4a). Crude Mo(CH-*t*-Bu)(NAr)Cl$_2$(dme), prepared from 1.00 g (2.76 mmol) of Mo(C-*t*-Bu)Cl$_3$(dme) as described above, was dissolved in ether (60 mL) and the solution was stirred at −30 °C as LiOCMe(CF$_3$)$_2$ (1.04 g, 5.53 mmol) was added as a solid over a period of 5 min. The solution lightened slightly from red-orange to yellow-orange and LiCl precipitated as the reaction was allowed to warm to room temperature over the next 3 h. Solvents were then removed in vacuo and the residue was extracted with pentane. The extracts were filtered through Celite and the filtrate was evaporated to dryness in vacuo. The residue thus obtained was virtually pure according to its ^{1}H NMR spectrum. Recrystallization from a minimum amount of pentane at −40 °C gave a yellow-orange solid in three crops (1.49 g, 77% from Mo(C-*t*-Bu)Cl$_3$(dme)): ^{1}H NMR δ 12.06 (s, 1, MoC*H*CMe$_3$), 6.94 (m, 3, NAr), 3.54 (sept, 2, C*H*Me$_2$), 1.37 (s, 6, OC*Me*(CF$_3$)$_2$), 1.16 (d, 12, CH*Me*$_2$), 1.04 (s, 9, MoCHC*Me*$_3$); ^{13}C NMR δ 288.2 (d, J = 117, MoCHCMe$_3$), 154.0 (C_{ipso}), 147.8 (C_o), 129.5 (C_p), 124.2 (q, $^1J_{CF}$ = 288, OCMe(*C*F$_3$)$_2$), 124.1 (q, $^1J_{CF}$ = 288, OCMe(*C*F$_3$)$_2$), 123.5 (C_m), 81.2 (sept, $^2J_{CF}$ = 29, O*C*Me(CF$_3$)$_2$), 49.4 (MoCH*C*Me$_3$), 31.3 (MoCHC*Me*$_3$), 28.6 (*C*HMe$_2$), 23.7 (CH*Me*$_2$), 18.9 (OC*Me*(CF$_3$)$_2$); ^{19}F NMR δ −78.0 (OCMe(C*F*$_3$)$_2$). Anal. Calcd for $MoC_{25}H_{33}O_2NF_{12}$: C, 42.69; H, 4.73. Found: C, 42.87; H, 4.55.

Mo(CH-*t*-Bu)(NAr)[OCMe$_2$(CF$_3$)]$_2$ (4b). A procedure analogous to that described above for the preparation of Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ employing crude Mo(CH-*t*-Bu)(NAr)Cl$_2$(dme) prepared from 0.55 g (1.52 mmol) of Mo(C-*t*-Bu)Cl$_3$(dme) and LiOCMe$_2$(CF$_3$) (0.41 g, 3.04 mmol) gave 0.88 g (97%) of virtually pure product as an orange solid. Recrystallization from a minimum amount of pentane at −40 °C gave 57% of pure product: ^{1}H NMR δ 11.61 (s, 1, MoC*H*CMe$_3$), 6.99 (s, 3, NAr), 3.74 (sept, C*H*Me$_2$), 1.35 and 1.28 (s, 6 each, OC*Me*$_2$(CF$_3$)), 1.20 (d, 1, CH*Me*$_2$), 1.12 (s, 9, MoCHC*Me*$_3$); ^{13}C NMR δ 276.8 (d, J = 118, MoCHCMe$_3$), 153.4 (C_{ipso}), 146.9 (C_o), 128.3 (C_p), 127.4 (q, $^1J_{CF}$ = 287, OCMe$_2$(*C*F$_3$)), 123.3 (C_m), 78.5 (q, $^2J_{CF}$ = 30, O*C*Me$_2$(CF$_3$)), 47.7 (MoCH*C*Me$_3$), 28.5 (MoCHC*Me*$_3$), 24.8 (*C*HMe$_2$), 24.7 (CH*Me*$_2$), 23.7 (OC*Me*$_2$(CF$_3$)); ^{19}F NMR δ −82.3 (OCMe$_2$(C*F*$_3$)). Anal. Calcd for $MoC_{25}H_{39}F_6O_2N$: C, 50.42; H, 6.60. Found: C, 50.50; H, 6.82.

Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (4c). This complex was prepared from crude Mo(CH-*t*-Bu)(NAr)Cl$_2$(dme) [prepared from 1.00 g (2.76 mmol) of Mo(C-*t*-Bu)Cl$_3$(dme) as described above] and LiO-*t*-Bu (0.67 g, 8.37 mmol) in a manner analogous to the preparation of Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ described above. The residue was recrystallized from a minimum amount of pentane at −40 °C to yield an orange microcrystalline solid (0.94 g, 70%) in three crops. It can be purified by recrystallization from a minimum amount of pentane (extremely soluble)

or by sublimation at high vacuum (60 °C and 0.1 μm): ^{1}H NMR δ 11.23 (s, 1, MoC*H*CMe$_3$), 7.04 (m, 3, NAr), 3.96 (sept, 2, C*H*Me$_2$), 1.33 (s, 18, OC*Me*$_3$), 1.26 (d, 12, CH*Me*$_2$), 1.23 (s, 9, MoCHC*Me*$_3$); ^{13}C NMR δ 265.8 (d, J = 117, MoCHCMe$_3$), 153.2 (C$_{ipso}$), 146.1 (C$_o$), 127.0 (C$_p$), 123.1 (C$_m$), 76.6 (OCMe$_3$), 46.3 (MoCHC*M*e$_3$), 32.5 and 32.1 (OC*Me*$_3$ and MoCHC*Me*$_3$), 28.2 (*C*HMe$_2$), 24.0 (CH*Me*$_2$). Anal. Calcd for $MoC_{25}H_{45}O_2N$: C, 61.59; H, 9.30. Found: C, 61.84; H, 9.16.

Alternatively **4c** can be prepared from **3a**. Lithium *tert*-butoxide (0.95 g, 11.8 mmol) was slowly added as a solid to a solution of **3a** (4.00 g, 5.5 mmol) in a mixture of ether (200 mL, −30 °C) and dme (20 mL, −30 °C) over a period of 10 min. The reaction mixture was allowed to warm to room temperature, stirred for 2 h, and evaporated to dryness. The dark orange solid was extracted with a minimum amount pentane (~50 mL) and filtered through a bed of Celite. Evaporation of the solvent gave 2.54 g (95%) of the product.

Mo(CH-*t*-Bu)(NAr)(OAr)$_2$ (4d). This complex was prepared from crude Mo(CH-*t*-Bu)(NAr)Cl$_2$(dme) (prepared from 0.70 g of Mo(C-*t*-Bu)(dme)Cl$_3$ as described above) and LiOAr(ether) (1.00 g, 3.87 mmol) in a manner analogous to the preparation of Mo(CH-*t*-Bu)(NAr)-[OCMe(CF$_3$)$_2$]$_2$ described above. This residue was recrystallized from a minimum amount of pentane at −40 °C to yield an orange-red microcrystalline solid (0.83 g, 62%) in two crops: ^{1}H NMR δ 11.42 (s, 1, MoC*H*CMe$_3$), 7.11 (d, 4, H$_m$, OAr), 6.98 (t, 2, H$_p$, OAr), 6.93 (m, 3, NAr), 3.67 (sept, 4, C*H*Me$_2$), 3.53 (sept, 2, C*H*Me$_2$), 1.34 (d, 12, CH*Me*$_2$), 1.28 (d, 12, CH*Me*$_2$), 1.07 (s, 9, MoCHC*Me*$_3$), 1.05 (d, 12, CH*Me*$_2$); ^{1}H NMR (minor isomer, 6%) δ 12.64 (s, 1, MoC*H*CMe$_3$); ^{13}C NMR δ 277.0 (d, J = 116, MoCHCMe$_3$), 161.7 (C$_{ipso}$, OAr), 153.8 (C$_{ipso}$, NAr), 146.6 (C$_o$, NAr), 137.4 (C$_o$, OAr), 128.5 (C$_p$, NAr), 123.6 (C$_m$, OAr), 123.3 (C$_p$, OAr), 122.4 (C$_m$, NAr), 48.5 (MoCH*C*Me$_3$), 31.7 (MoCHC*Me*$_3$), 29.3 (N-*C*HMe$_2$), 27.5 (O-*C*HMe$_2$), 24.0, 23.8, and 23.5 (O-CH*Me*$_2$ and N-CH*Me*$_2$). Anal. Calcd for $MoC_{41}H_{61}O_2N$: C, 70.77; H, 8.84. Found: C, 70.97; H, 8.93.

Mo(CHCMe$_2$Ph)(NAr)(O-*t*-Bu)$_2$ (5a). A cold (−30 °C) solution of Mo(CHCMe$_2$Ph)(NAr)(OSO$_2$CF$_3$)$_2$(dme) (203 mg, 0.256 mmol) in 10 mL of diethyl ether was treated with solid lithium *tert*-butoxide in one portion (41 mg, 0.513 mmol). The reaction was allowed to warm to room temperature while it was stirred. After 1 h, the solvent was removed in vacuo, and the resulting solids were extracted with pentane. Pentane was removed in vacuo from the filtered pentane extracts to give a solid, which was recrystallized from a minimal volume of pentane to afford 101 mg (72%) of **5a**: ^{1}H NMR δ 11.34 (s, 1 C*H*CMe$_2$Ph), 7.45 (d, 2, aromatic), 7.21–7.00 (m, 6, aromatic), 4.00 (sept, 2, C*H*Me$_2$), 1.71 (s, 3, CHC*Me*$_2$Ph), 1.32 (s, 3, CHC*Me*$_2$Ph), 1.28 (s, 18, OC*Me*$_3$).

Mo(CHCMe$_2$Ph)(NAr)(OAr)$_2$ (5b). A cold (−30 °C) solution of Mo(CHCMe$_2$Ph)(NAr)(OSO$_2$CF$_3$)$_2$(dme) (503 mg, 0.535 mmol) in 50 mL of diethyl ether was treated with solid lithium 2,6-diisopropylphenoxide etherate in one portion (328 mg, 1.271 mmol). The reaction was allowed to warm to room temperature. After 2.5 h, the reaction mixture was concentrated to dryness, and the resulting solids were extracted with pentane. The filtered pentane extracts were concentrated to approximately 5 mL. Chilling this solution afforded 359 mg (64%) of the product as orange cubes. ^{1}H NMR spectroscopy revealed a 12:1 mixture of isomers. Only selected resonances are reported for the minor isomer (integrals are internally consistent with the individual isomers): ^{1}H NMR (C$_6$D$_6$, major isomer) δ 11.77 (s, 1, C*H*CMe$_2$Ph), 7.11–6.90 (m, 14, aromatic), 3.69–3.64 (m, 6, C*H*Me$_2$), 1.30 (d, 12, CH*Me*$_2$), 1.22 (d, 12, CH*Me*$_2$), 1.08 (d, 12, CH*Me*$_2$); ^{1}H NMR (C$_6$D$_6$, selected resonances of minor isomer) δ 12.74 (s, C*H*CMe$_2$Ph), 1.67 (s, 6, CHC*Me*$_2$Ph), 1.17 (d, 12, CH*Me*$_2$); ^{13}C NMR δ 276.0 (d, J_{CH} = 125 Hz, *C*HCMe$_2$Ph), 154.0, 149.5, 146.8, 137.5, 128.6, 128.5, 126.1, 125.7, 123.6, 123.4, 122.6, 54.3 (CHCMe$_2$Ph), 31.4 (CHC*Me*$_2$Ph), 28.8 (*C*HMe$_2$), 27.3 (*C*HMe$_2$), 23.44 (CH*Me*$_2$), 23.36 (CH*Me*$_2$), 23.0 (CH*Me*$_2$). Anal. Calcd for $MoC_{46}H_{63}NO_2$: C, 72.89; H, 8.38; N, 1.85. Found: C, 72.84; H, 8.46; N, 1.95.

Mo(CHCMe$_2$Ph)(NAr)(O-2-C$_6$H$_4$-*t*-Bu)$_2$ (5c). A cold (−30 °C) solution of Mo(CH-*t*-Bu)(NAr)(OSO$_2$CF$_3$)$_2$(dme) (600 mg, 0.758 mmol) in 50 mL of diethyl ether was treated with solid lithium 2-*tert*-butylphenoxide in one portion (237 mg, 1.52 mmol). The reaction was allowed to warm to room temperature. After 1 h, the reaction was concentrated, and the resulting solids were extracted with pentane. The pentane extracts were filtered and concentrated to approximately 5 mL. Chilling this solution afforded 266 mg (50%) of the product as orange cubes. ^{1}H NMR spectroscopy revealed a 15:1 mixture of apparently isomeric compounds (integrals are internally consistent with the individual isomers): ^{1}H NMR (major isomer) δ 11.79 (s, 1, C*H*CMe$_2$Ph), 7.50–7.00 (m, 9, aromatic), 6.70 (dd, J = 1.7, 7.3, 2, phenoxide), 3.85 (sept, 2, C*H*Me$_2$), 1.89 (s, 6, CHC*Me*$_2$Ph), 1.76 (s, 18, C$_{ar}$C*Me*$_3$), 1.21 (d, 12, CH*Me*$_2$); ^{1}H NMR (minor isomer) δ 13.36 (s, 1, C*H*CMe$_2$Ph), 6.79 (dd, J = 1.3, 6.9, 2, phenoxide), 3.96 (sept, 2, C*H*Me$_2$), 2.00 (s, 6, CHC*Me*$_2$Ph), 1.78 (s, 18, C$_{ar}$C*Me*$_3$), 1.25 (d, 12, CH*Me*$_2$); ^{13}C NMR (major isomer) δ 276.5 (d, J_{CH} = 121, *C*HCMe$_2$Ph), 162.9, 154.0, 148.3, 147.1, 138.3, 128.9, 128.6, 127.4, 126.6, 126.3, 126.2, 123.2, 121.7, 121.5, 54.3, 35.3, 31.1, 30.3, 29.2, 23.4. Anal. Calcd for $MoC_{42}H_{55}NO_2$: C, 71.88; H, 7.90; N, 1.10. Found: C, 71.98; H, 8.07; N, 1.86.

Mo(CHSiMe$_3$)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (6a). Vinyltrimethylsilane (62 μL, 0.43 mmol) was added all at once to a yellow-orange pentane solution (20 mL) of Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (0.10 g, 0.14 mmol) at −30 °C. The solution was allowed to warm to room temperature over the next 2.5 h during which time the solution darkened to green. Removing solvents in vacuo yielded a dark solid. Recrystallization of the residue from a minimum amount of pentane at −40 °C yielded a greenish-yellow solid (0.08 g, 74%): ^{1}H NMR δ 13.86 (s, 1, MoC*H*SiMe$_3$), 6.94 (m, 3, NAr), 3.49 (sept, 2, C*H*Me$_2$), 1.31 (s, 6, OC*Me*(CF$_3$)$_2$), 1.15 (d, 12, CH*Me*$_2$), 0.01 (s, 9, MoCHSi*Me*$_3$); ^{13}C NMR δ 289.8 (d, J = 113, MoCHSiMe$_3$), 154.9 (C$_{ipso}$), 146.9 (C$_o$), 129.3 (C$_p$), 124.1 (q, $^1J_{CF}$ = 290, OCMe(*C*F$_3$)$_2$), 124.0 (q, $^1J_{CF}$ = 288, OCMe(*C*F$_3$)$_2$), 123.4 (C$_m$), 81.2 (m, $^2J_{CF}$ = 45, O*C*Me(CF$_3$)$_2$), 28.6 (*C*HMe$_2$), 23.7 (CH*Me*$_2$), 18.4 (OC*Me*(CF$_3$)$_2$), 0.4 (MoCHSi*Me*$_3$). This compound could not be isolated in analytically pure form due to its decomposition in the presence of vinyltrimethylsilane.

Mo(CHSiMe$_3$)(NAr)[OCMe$_2$(CF$_3$)]$_2$ (6b). Vinyltrimethylsilane (1.24 mL, 8.55 mmol) was added all at once to a pentane solution (60 mL) of Mo(CH-*t*-Bu)(NAr)[OCMe$_2$(CF$_3$)]$_2$ (1.70 g, 2.85 mmol) with stirring at ambient temperature. After 4 h the solvents were removed in vacuo. The yellow-orange residue thus obtained was dissolved in a minimum amount of pentane and stored at −40 °C. Yellow-orange needles (1.15 g, 66%) were isolated in two crops by filtration and dried in vacuo: ^{1}H NMR δ 13.25 (s, 1, MoC*H*SiMe$_3$), 7.00 (s, 3, NAr), 3.68 (sept, 2, C*H*Me$_2$), 1.33 and 1.25 (s, 6 each, OC*Me*$_2$(CF$_3$)), 1.20 (d, 12, CH*Me*$_2$), 0.09 (s, 9, MoCHSi*Me*$_3$); ^{13}C NMR δ 274.5 (d, J = 111, MoCHSiMe$_3$), 154.3 (C$_{ipso}$), 145.8 (C$_o$), 128.2 (C$_m$ or C$_p$), 127.3 (q, $^1J_{CF}$ = 286, OCMe$_2$(*C*F$_3$)), 123.2 (C$_m$ or C$_p$), 78.6 (q, $^2J_{CF}$ = 29, O*C*Me$_2$(CF$_3$)), 28.5 (*C*HMe$_2$), 24.4 and 24.3 (OC*Me*$_2$)(CF$_3$)), 23.8 (CH*Me*$_2$), 0.9 (MoCHSi*Me*$_3$); ^{19}F NMR δ −82.4 (OCMe$_2$(C*F*$_3$)). Anal. Calcd for $MoC_{24}H_{39}F_6O_2NSi$: C, 47.13; H, 6.43. Found: C, 47.47; H, 6.82.

Mo(CHSiMe$_3$)(NAr)(O-*t*-Bu)$_2$ (6c). Vinyltrimethylsilane (3.00 mL, 20.7 mmol) was added to a stirred yellow pentane solution (5 mL) of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (0.60 g, 1.23 mmol) at 25 °C. After 16 h all solvents were removed in vacuo. The yellow-orange oily residue thus obtained was pure by ^{1}H and ^{13}C NMR spectroscopy. A crystalline sample for analysis was obtained from a minimum amount of pentane at −40 °C, but recovery was low (0.33 g, 53%) because of the compound's high solubility: ^{1}H NMR (toluene-d_8) δ 12.65 (br, 1, MoC*H*SiMe$_3$), 7.03 (s, 3, NAr), 3.91 (br, 2, C*H*Me$_2$), 1.32 (s, 18, OC*Me*$_3$), 1.28 (d, 12, CH*Me*$_2$), 0.27 (br, 9, MoCHSi*Me*$_3$); ^{1}H NMR (toluene-d_8, 333 K) δ 12.57 (br s, 1, MoC*H*SiMe$_3$), 7.03 (s, 3, NAr), 3.93 (br sept, 2, C*H*Me$_2$), 1.31 (s, 18, OC*Me*$_3$), 1.27 (d, 12, CH*Me*$_2$), 0.21 (s, 9, MoCHSi*Me*$_3$); ^{1}H NMR (toluene-d_8, 233 K) δ 12.79 (s, 1, MoC*H*SiMe$_3$, major isomer), 7.03 (s, 3, NAr), 3.94 (sept, 2, C*H*Me$_2$), 1.34 (s, 18, OC*Me*$_3$), 1.30 (d, 12, CH*Me*$_2$), 0.24 (s, 9, MoCHSi*Me*$_3$); ^{1}H NMR (toluene-d_8, 215 K) δ 12.83 and 12.20 (9:1). Anal. Calcd for $MoC_{24}H_{45}O_2NSi$: C, 57.23; H, 9.01. Found: C, 57.36; H, 9.13.

Mo(CHSiMe$_3$)(NAr)(OAr)$_2$ (6d). Vinyltrimethylsilane (315 μL, 2.17 mmol) was added to an orange solution of Mo(CH-*t*-Bu)(NAr)(OAr)$_2$ (0.15 g, 0.22 mmol) in pentane (15 mL) at room temperature. The resulting solution was stirred overnight at 25 °C, concentrated in vacuo, and stood at −40 °C to give orange crystals in 66% yield: ^{1}H NMR δ 13.10 (s, MoC*H*SiMe$_3$, minor isomer, ~33%), 13.02 (s, MoC*H*SiMe$_3$, major isomer, ~67%), 7.15–6.90 (multiplets, OAr and NAr), 3.88 and 3.60 (sept, O-2,6-C$_6$H$_3$(C*H*Me$_2$)$_2$, minor and major isomers, respectively), 3.24 and 2.94 (sept, N-2,6-C$_6$H$_3$(C*H*Me$_2$)$_2$, major and minor isomers, respectively), 1.33 and 1.25 (d, O-2,6-C$_6$H$_3$(CH*Me*$_2$)$_2$, minor and major isomers, respectively), 1.14 and 0.94 (d, N-2,6-C$_6$H$_3$(CH*Me*$_2$)$_2$, minor and major isomers, respectively), 0.17 and 0.12 (s, MoCHSi*Me*$_3$, minor and major isomers, respectively); ^{1}H NMR (toluene-d_8, 363 K) δ 13.00 (s, 1, MoC*H*SiMe$_3$), 7.03–6.91 (multiplets, 9, O-2,6-C$_6$*H*$_3$-*i*-Pr$_2$ and N-2,6-C$_6$*H*$_3$-*i*-Pr$_2$), 3.54 (sept, 6, O-2,6-C$_6$H$_3$(C*H*Me$_2$)$_2$ and N-2,6-C$_6$H$_3$(C*H*Me$_2$)$_2$), 1.21 (d, 36, O-2,6-C$_6$H$_3$(CH*Me*$_2$)$_2$ and N-2,6-C$_6$H$_3$-(CH*Me*$_2$)$_2$), 0.10 (s, 9, MoCHSi*Me*$_3$); ^{13}C NMR δ 268.8 (d, J = 117, MoCHSiMe$_3$, major isomer), 267.0 (d, J = 145, MoCHSiMe$_3$, minor isomer), 160.3, 160.2, 154.4, 145.8, 144.0, 137.7, 136.4, and 133.8 (C$_{ipso}$ and C$_o$, OAr and NAr), 123.7, 123.5, 123.3, 123.1, 122.8, 122.7, 122.1, and 121.1 (C$_m$ and C$_p$, OAr and NAr), 29.7, 29.2, 27.3, and 27.1 (*C*HMe$_2$, OAr, and NAr), 24.0, 23.8, 23.5, and 23.3 (CH*Me*$_2$), OAr, and NAr), 1.4 and 0.5 (MoCHSi*Me*$_3$, major and minor isomers, respectively). Anal. Calcd for $MoC_{40}H_{61}NO_2Si$: C, 67.48; H, 8.64; N, 1.97. Found: C, 67.39; H, 8.60; N, 2.02.

Observation of Mo[CH(SiMe$_3$)CH(SiMe$_3$)CH$_2$](NAr)[OCMe$_2$(CF$_3$)]$_2$. Vinyltrimethylsilane (35 μL, 0.24 mmol) was added to a solution of Mo(CHSiMe$_3$)(NAr)[OCMe$_2$(CF$_3$)]$_2$ (0.030 g, 0.049 mmol) in 600 μL

Table III. Crystal Data for Mo(NAr)(CHCMe$_3$)(OTf)$_2$(dme)

empirical formula	$MoC_{23}H_{37}NF_6S_2O_8$
formula weight	729.60
crystal system	triclinic
a, Å	17.543 (7)
b, Å	19.008 (6)
c, Å	9.711 (3)
α, deg	91.91 (2)
β, deg	99.30 (3)
γ, deg	87.27 (3)
V, Å^3	3191 (2)
space group	$P\bar{1}$
Z	4
ρ(calcd), g/cm^3	1.518
$\mu_{(Mo K\alpha)}$, cm^{-1}	6.0
final R; R_w	0.054; 0.070

of toluene-d_8 in an NMR tube. The sample was cooled to −40 °C in the NMR probe: ^{1}H NMR δ 5.89 and 4.54 (m, 1 each, C$_\alpha H_A$, and C$_\alpha H_B$), 4.26 (br d, 1, C$_\alpha H$SiMe$_3$), 4.11 (m, 2, CHMe$_2$), −0.56 (m, 1, C$_\beta H$SiMe$_3$). The resonances of the remaining protons were obscured by those for Mo[CH(SiMe$_3$)](NAr)[OCMe$_2$(CF$_3$)]$_2$.

The equilibrium constant for the above reaction was determined by integrating the multiplet at 4.11 ppm versus the isopropyl methine resonance of the alkylidene complex at 3.68 ppm; $K_{eq} = 4.0 \times 10^{-1}$ M^{-1}. The reaction was also carried out with a solution about one-third the concentration of each reagent; $K_{eq} = 5.1 \times 10^{-1}$ M^{-1}. Volumes were assumed to be additive in both cases.

Observation of Mo(CH$_2$CH$_2$CH$_2$)(NAr)[OC(CH$_3$)(CF$_3$)$_2$]$_2$. Mo(NAr)(CH-*t*-Bu)[OC(CH$_3$)(CF$_3$)$_2$]$_2$ (14 mg, 0.020 mmol) was dissolved in toluene-d_8 (0.40 mL) on an NMR tube, which was then frozen on the high-vacuum line. Ethylene (5.6 equiv, 0.011 mmol) was condensed and the tube was sealed under vacuum. The solution was thawed to room temperature, and a proton NMR spectrum after 30 min showed that the alkylidene complex had reacted completely with ethylene to give CH$_2$=CH(*t*-Bu) and Mo(CH$_2$CH$_2$CH$_2$)(NAr)[OC(CH$_3$)(CF$_3$)$_2$]$_2$: ^{1}H NMR (toluene-d_8) δ 6.75 (br m, 3, N-2,6-C$_6H_3$(CHMe$_2$)$_2$), 5.02 (br m, 2, C$_\alpha H_2$), 4.83 (br m, 2, C$_\alpha H_2$), 3.88 (sept, 2, CHMe$_3$), 1.67 br s, 3, OC(CH_3)(CF$_3$)$_2$), 1.50 (s, 3, OC(CH_3)(CF$_3$)$_2$), 1.09 (d, 6, CHMe_2) 1.00 (d, 6, CHMe_2), −0.20 (br m, 1, C$_\beta H_2$), −0.95 (br m, 1, C$_\beta H_2$). An analogous reaction was done with ^{13}C$_2$H$_4$ for a carbon NMR spectrum: ^{13}C NMR (toluene-d_8, 213 K) δ 104.1 (td, $^1J_{CC}$ = 11, $^1J_{CH}$ = 161, C_αH$_2$), −2.28 (tt, $^1J_{CC}$ = 13, $^1J_{CH}$ = 155, C_βH$_2$).

Observation of Mo[CH(*t*-Bu)CH$_2$CH$_2$](NAr)(OAr)$_2$ and Mo[CH$_2$CH$_2$CH$_2$](NAr)(OAr)$_2$. Partial ^{13}C NMR spectra of Mo[CH(*t*-Bu)CH$_2$CH$_2$](NAr)(OAr)$_2$ and Mo[CH$_2$CH$_2$CH$_2$](NAr)(OAr)$_2$ were obtained as follows. To a frozen solution of Mo(CH-*t*-Bu)(NAr)(OAr)$_2$ (20 mg, 0.023 mmol) in 600 μL of toluene-d_8 was added 0.12 mmol of ^{13}C$_2$H$_4$ by vacuum transfer. The tube was then sealed and solution thawed and quickly placed inside a precooled (−47 °C) 125-MHz carbon NMR probe. The initial spectrum showed a mixture of Mo[CH(*t*-Bu)CH$_2$CH$_2$](NAr)(OAr)$_2$ and Mo[CH$_2$CH$_2$CH$_2$](NAr)(OAr)$_2$. For both metallacycles the SP geometry predominates (SP/TBP 95:5).

^{13}C NMR (*α-tert*-butyl metallacycle, toluene-d_8, −47 °C): SP isomer, δ 44.5 (d, J_{CC} = 53, C$_\alpha$), 29.7 (d, J_{CC} = 49, C$_\beta$); TBP isomer, δ 97.8 (d, J_{CC} = 22, C$_\alpha$), −0.7 (br s, C$_\beta$). ^{13}C NMR (unsubstituted metallacycle, toluene-d_8, −47 °C): SP isomer, δ 39.9 (d, J_{CC} = 53, C$_\alpha$), 26.5 (t, J_{CC} = 53, C$_\beta$); TBP isomer, δ 100.1 (d, J_{CC} = 22, C$_\alpha$), −0.7 (br s, C$_\beta$).

After 20 min at −47 °C, only a trace of the *α-tert*-butyl metallacycle was observable. Warming the sample to −17.5 °C led to the complete consumption of the *α-tert*-butyl metallacycle, leaving only the unsubstituted metallacycle. With time a singlet appeared at δ 45.2, assignable to the C$_\alpha$ resonance of the *β-tert*-butyl-substituted metallacycle. At room temperature the spectrum consisted of two broad resonances at 40 and 26 ppm.

Mo(NAr)[CH$_2$=CH(SiMe$_3$)][OCMe(CF$_3$)$_2$]$_2$. Vinyltrimethylsilane (0.400 mL, 2.75 mmol) was added to a solution of Mo(CH-*t*-Bu)(NAr)(OR)$_2$ (0.400 g, 0.568 mmol) in pentane (25 mL, −40 °C). Within 10 min the orange solution had turned deep green and within 30 min the solution had turned deep red. The solution was allowed to stir for another 30 min, after which time the solvents were removed leaving behind a red solid (0.350 g, 85%): ^{1}H NMR δ 6.91 (m, 3, N-2,6-C$_6H_3$(CHMe$_2$)$_2$), 3.72 (sept, 2, CHMe$_2$), 2.77 (dd, 1, CH_2CHSiMe$_3$, J = 18.0, 4.5), 2.65 (dd, 1, CH_2CHSiMe$_3$, J = 18.0, 4.5), 1.96 (dd, 1, CH$_2$CHSiMe$_3$, J = 18.0), 1.46 (s, 3, OC(CH_3)(CF$_3$)$_2$), 1.38 (s, 3, OC(CH_3)(CF$_3$)$_2$), 1.17 (d, 12, CHMe_2), −0.03 (s, 9, SiMe$_3$); the fact that only one isopropyl methyl resonance is observed is ascribed to an accidental degeneracy; ^{13}C NMR (toluene-d_8) δ 155.2 (C$_{ipso}$), 148.2 (C$_o$), 129.7 (C$_p$), 124.0 (C$_m$), 124.5 (q, $^1J_{CF}$ = 288, CF_3), 83.5 (sept, $^2J_{CF}$ = 30, OC(CF$_3$)$_2$(CH$_3$)), 82.8 (sept, $^2J_{CF}$ = 30, OC(CF$_3$)$_2$Me), 67.4 (d, J_{CH} = 129, CH$_2$=CHSiMe$_3$), 63.6 nt, J_{CH} = 157, CH_2=CHSiMe$_3$), 29.5 (CHMe), 29.2 (CHMe), 24.5 (OC(CF$_3$)$_2$(CH_3)), 8.0 (SiMe$_3$).

X-ray Structure of Mo(CH-*t*-Bu)(NAr)(OSO$_2$CF$_3$)$_2$(dme). Data were collected at −65 °C on a Rigaku AFC6 diffractometer equipped with a liquid-nitrogen low-temperature device and using graphite monochromated Mo Kα radiation (λ = 0.71069 Å) and a 12 kW rotating anode generator. A total of 11 646 reflections were collected, 11 239 of which were unique. The intensities of three representative reflections that were measured after every 150 reflections remained constant throughout data collection, indicating crystal and electronic stability. The structure was solved by direct methods.[33] Refinement was by full-matrix least squares with TEXAN from Molecular Structure Corporation. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions (d_{C-H} = 0.95 Å). Final R = 0.054 and R_w = 0.070. Crystal data can be found in Table III.

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Supplementary Material Available: Labeled drawing of Mo(NAr)(CHCMe$_3$)(OTf)$_2$(dme), ORTEP drawing, and tables of final positional parameters and anisotropic thermal parameters (6 pages); listing of final observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

(33) (a) Gilmore, C. J. *J. Appl. Cryst.* **1984**, *17*, 42. (b) Beurskens, P. T. Technical Report 1984/1 Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, Netherlands.