# Synthesis of Molybdenum Imido Alkylidene Complexes That Contain Siloxides

Keith M. Wampler, Richard R. Schrock,* and Adam S. Hock

*Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

*Received August 29, 2007*

Monosiloxide and disiloxide complexes have been prepared through the addition of silanols to Mo(NR)($CHCMe_2Ph$)(pyrrolyl)$_2$ species [R = 1-adamantyl (Ad) or 2,6-*i*-$Pr_2C_6H_3$ (Ar)]. The silanols employed include (*t*-Bu)$_3$SiOH (HSilox), (*i*-Pr)$_3$SiOH, ($Me_3Si$)$_3$SiOH, (*t*-Bu-O)$_3$SiOH, $Me_2$(*t*-Bu)SiOH, and $Ph_3SiOH$. The monoSilox complex, Mo(NAr)($CHCMe_2Ph$)(Silox)(pyrrolyl) (**2a**), could be isolated, while Mo(NAd)($CHCMe_2Ph$)(Silox)(pyrrolyl) was observed in situ but could not be crystallized. Disiloxides that could be crystallized include Mo(NAd)($CHCMe_2Ph$)(Silox)$_2$ (**1b**), Mo(NAd)($CHCMe_2Ph$)-[OSi($SiMe_3$)$_3$]$_2$ (**4**), Mo(NAd)($CHCMe_2Ph$)[OSi(O-*t*-Bu)$_3$]$_2$ (**5**), and Mo(NAr)($CHCMe_2Ph$)[OSi$Me_2$(*t*-Bu)]$_2$ (**6**); other disiloxide examples could be observed in situ but could not be crystallized. Compound **2a** reacts readily with ($CF_3$)$Me_2$COH, ($CF_3$)$_2$MeCOH, ($CF_3$)$_2$CHOH, ArOH, $C_6F_5OH$, (−)-menthol, and (−)-borneol to give compounds of the type Mo(NAr)($CHCMe_2Ph$)(Silox)(OR) (**3a**−**g**) in situ. No reaction was observed upon heating of **1b** under 5 atm of ethylene at 120 °C in toluene-$d_8$; only at 240 °C in *o*-dichlorobenzene-$d_4$ did **1b** react with ethylene to yield $CH_2{=}CHCMe_2Ph$, but the Mo-containing product could not be identified. Compound **2a** reacts with ethylene at 120 °C to give Mo(NAr)($CH_2$)(Silox)(pyr), while **3a**−**e** react with ethylene at ~60 °C; methylene species could be observed in several cases but could not be isolated. X-ray studies were carried out for **1b** and **2a**.

## Introduction

High-oxidation-state complexes of the type M(NR)(CHR′)-(OR″)$_2$ or M(NR)(CHR′)(diolate) (M = Mo or W) are established, well-defined catalysts for a variety of symmetric and asymmetric olefin metathesis reactions.[1] The vast majority of such species contain alkoxides or diolates. In comparison, M(NR)(CHR′)(OR″)$_2$ species, where OR″ is a siloxide, are relatively rare.[1b,d,2] Molybenum and tungsten imido alkylidene siloxide complexes, especially monosiloxide complexes, have become more relevant as a consequence of the synthesis of relatively well-defined catalysts attached to silica through one M−O−$Si_{surf}$ bond.[2,3] M(NR)(CHR′)(O$Si_{surf}$)X species have been prepared through the addition of a suitable M(NR)(CHR′)$X_2$ species (X = neopentyl, diphenylamido, or pyrrolyl) to dehydroxylated silica. M(NR)(CHR′)(pyr)$_2$ (pyr = pyrrolyl) species also have been employed as precursors to M(NR)(CHR′)(OR″)$_2$ species through the addition of 2 equiv of the appropriate alcohol or 1 equiv of a diol[4] or to M(NR)(CHR′)(OR″)(pyr) species through the addition of only 1 equiv of an alcohol.[5] M(NR)(CHR′)-(X)(Y) complexes also have become attractive targets in view of calculations that support a higher reactivity for compounds in which X is a donor and Y an acceptor.[6] For all of the above reasons, we became interested in preparing more homogeneous monosiloxide or disiloxide species.

In considering potential monosiloxide or disiloxide ligands for study, we became interested in tri-*tert*-butylsiloxide (Silox). Silox is a uniquely sterically demanding siloxide that has been used to prepare a large variety of unusual, highly unsaturated early-transition-metal species.[7,8] Examples include Ta(Silox)$_3$[9,10] [$TaH_2$(Silox)$_2$]$_2$,[11,12] and W(N-*t*-Bu)(Silox)$_2$.[13] We were interested in whether monoSilox or diSilox species could be prepared and whether they would have properties different from complexes that contain other types of bulky siloxides. We felt there was a possibility that some tri-*tert*-butylsiloxide alkylidene

---

* E-mail: rrs@mit.edu.

[1] (a) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4592. (b) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145. (c) Schrock, R. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 3748. (d) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1. (e) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158.

[2] Blanc, F.; Copéret, C.; Thivolle-Cazat, J.; Basset, J.-M.; Lesage, A.; Emsley, L.; Sinha, A.; Schrock, R. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 1216.

[3] (a) Rhers, B.; Salameh, A.; Baudouin, A.; Quadrelli, E. A.; Taoufik, M.; Copéret, C.; Lefebvre, F.; Basset, J.-M.; Solans-Monfort, X.; Eisenstein, O.; Lukens, W. W.; Lopez, L. P. H.; Sinha, A.; Schrock, R. R. *Organometallics* **2006**, *25*, 3554. (b) Blanc, F.; Copéret, C.; Thivolle-Cazat, J.; Basset, J.-M.; Lesage, A.; Emsley, L.; Sinha, A.; Schrock, R. R. *Inorg. Chem.* **2006**, *45*, 9587. (c) Rhers, B.; Quadrelli E. A.; Baudouin, A.; Taoufik, M.; Copéret, C.; Lefebvre, F.; Basset, J.-M.; Fenet, B.; Sinha, A.; Schrock, R. R. *J. Organomet. Chem.* **2006**, *691*, 5448. (d) Blanc, F.; Thivolle-Cazat, T.; Basset, J.-M.; Copéret, C.; Hock, A. S.; Tonzetich, Z. J.; Sinha, A.; Schrock, R. R. *J. Am. Chem. Soc.* **2007**, *129*, 1044. (e) Blanc, F.; Berthoud, R.; Salameh, A.; Basset, J.-M.; Copéret, C.; Singh, R.; Schrock, R. R. J. *Am. Chem. Soc.* **2007**, *129*, 8434.

[4] (a) Hock, A.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2006**, *128*, 16373. (b) Singh, R.; Czekelius, C.; Schrock, R. R.; Müller, P. *Organometallics* **2007**, *26*, 2528. (c) Kreickmann, T.; Arndt, S.; Schrock, R. R.; Müller, P. *Organometallics* **2007**, *26*, 5702.

[5] Singh, R.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2007**, *129*, 12655.

[6] Poater, A.; Solans-Monfort, X.; Clot, E.; Copéret, C.; Eisenstein, O. *J. Am. Chem. Soc.* **2007**, *129* (26), 8207.

[7] LaPointe, R. E.; Wolczanski, P. T.; Van Duyne, G. D. *Organometallics* **1985**, *4*, 1810.

[8] Wolczanski, P. T. *Polyhedron* **1995**, *14*, 3335.

[9] Neithamer, D. R.; LaPointe, R. E.; Wheeler, R. A.; Richeson, D. S.; Van Duyne, G. D.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1989**, *111*, 9056.

[10] LaPointe, R. E.; Wolczanski, P. T.; Mitchell, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 6382.

[11] LaPointe, R. E.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1986**, *108*, 3535.

[12] Miller, R. L.; Toreki, R.; LaPointe, R. E.; Wolczanski, P. T.; Van Duyne, G. D.; Roe, D. C. *J. Am. Chem. Soc.* **1993**, *115*, 5570.

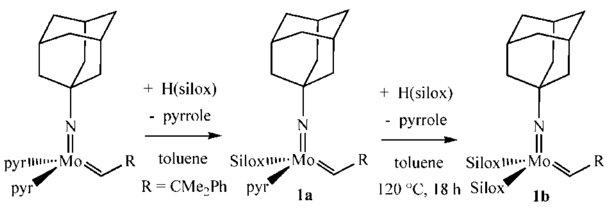
[13] Eppley, D. F.; Wolczanski, P. T.; Van Duyne, G. D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 584.

10.1021/om700864u CCC: $37.00

species would be relatively stable to bimolecular decomposition reactions yet still be reactive toward olefins, thereby increasing the lifetime of a Silox catalyst in solution and the overall metathesis turnover. We report here the results of this preliminary foray into mono- and disiloxide molybdenum species.

## Results

**Syntheses.** The addition of 1 equiv of H(Silox) (H(Silox) = ($t$-Bu)$_3$SiOH) to Mo(NAd)(CHCMe$_2$Ph)(pyr)$_2$[4a] (Ad = 1-adamantyl; 59 mM in toluene-$d_8$) at 23 °C results in the formation of 1 equiv of pyrrole and a species having $C_1$ symmetry that we assign as Mo(NAd)(CHCMe$_2$Ph)(Silox)(pyr) (**1a**; eq 11; $\delta$H$_\alpha$ = 12.24 ppm). Conversion of Mo(NAd)(CHCMe$_2$Ph)(pyr)$_2$ into **1a** is complete in 15 min at a concentration of 59 mM.



(1)

Unfortunately, **1a** is highly soluble and has not yet been isolated in crystalline form. Compound **1a** is formed even in the presence of 2 equiv of H(Silox); i.e., at 23 °C displacement of the remaining pyrrolyl in Mo(NAd)(CHCMe$_2$Ph)(Silox)(pyr) by a second 1 equiv of H(Silox) is extremely slow. However, if a mixture of Mo(NAd)(CHCMe$_2$Ph)(pyr)$_2$ (59 mM) and ($t$-Bu)$_3$SiOH is heated to 120 °C for 18 h, 2 equiv of pyrrole and Mo(NAd)(CHCMe$_2$Ph)(Silox)$_2$ (**1b**) are formed (eq 11). Compound **1b** can be isolated as yellow-orange blocks in 66% yield from a saturated pentane solution at −30 °C. $^1$H, $^{13}$C, and $^{29}$Si NMR spectra are all consistent with a $C_s$-symmetric structure in which rotation about the N−C and Si−C bonds is rapid on the NMR time scale at room temperature. The alkylidene proton resonance in **1b** was found at 11.08 ppm in benzene-$d_6$; a $J_{CH}$ of 119 Hz is consistent with a syn orientation of the alkylidene, as shown in eq 11. Compound **1b** is relatively stable to air, moisture, and temperature. An $o$-dichlorobenzene-$d_4$ solution of **1b** was heated to 240 °C for 12 hours, with no change being observed.

Crystals of **1b** suitable for a single-crystal X-ray study were grown from a saturated pentane solution at −30 °C over the course of 12 h. The structure of **1b** is shown in Figure 1, and X-ray details can be found in Table 1. (A rotational disorder about the O(1)−Si(1) bond was observed, but the disorder was effectively modeled.) Molybdenum adopts a tetrahedral coordination geometry with bond lengths and angles that are typical of related crystallographically characterized compounds.[1] The Mo−O−Si angles are large [Mo−O(1)−Si(1) = 169.66(10)°], as is commonly found in Silox complexes. Large M−O−Si bond angles are believed to result from steric interactions between the *tert*-butyl groups and the remaining coordination environment. The N(1)−Mo−O(1) [114.30(9)°] and N(1)−Mo−O(2) [116.06(9)°] angles are relatively large compared to other angles at Mo; for example, O(1)−Mo−O(2) is only 108.72(7)°.

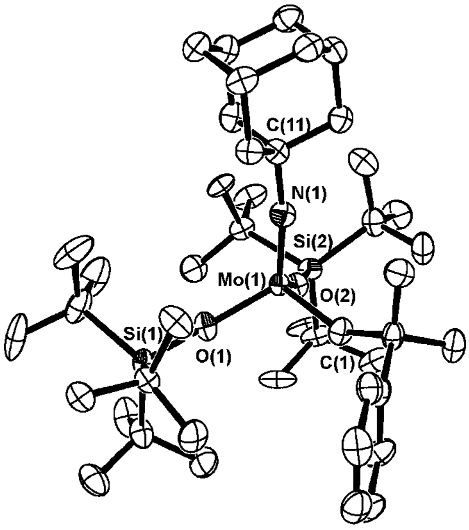
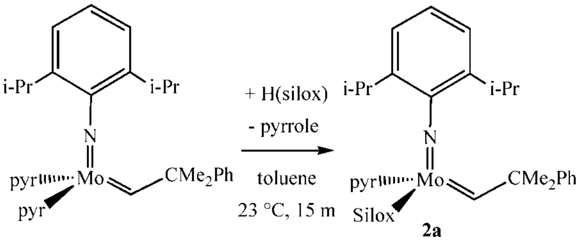


**Figure 1.** Thermal ellipsoid drawing of **1b** (ellipsoids at 50%; minor disorder and H atoms omitted). Selected bond distances (Å) and angles (deg): Mo−C(1) = 1.885(2), Mo−N(1) = 1.707(2), Mo−O(1) = 1.8906(16), Mo−C(1)−C(2) = 147.7(2), Mo−N(1)−C(11) = 171.18(18), Mo−O(1)−Si(1) = 169.66(10), O(1)−Mo−O(2) = 108.72(7), N(1)−Mo−C(1) = 104.73(11), N(1)−Mo−O(1) = 114.30(9), N(1)−Mo−O(2) = 116.06(9), C(1)−Mo−O(1) = 105.86(9), C(1)−Mo−O(2) = 106.27(9).

The reaction between 1 equiv of H(Silox) and Mo(NAr)(CHCMe$_2$Ph)(pyr)$_2$ (Ar = 2,6-$i$-Pr$_2$C$_6$H$_3$) in toluene for 30 min produced the monoSilox compound **2a** (eq 2), which could be isolated as yellow crystals from pentane at −30 °C in 74% yield. $^1$H and $^{13}$C NMR spectra of **2a** in C$_6$D$_6$ at 22 °C are consistent with rapid rotation about the N$_{\text{imido}}$−C$_{\text{ipso}}$ bond. The pyrrolyl α-H and $\beta$-H resonances in **2a** are found as two poorly resolved resonances at 7.07 and 6.47 ppm, respectively. The alkylidene proton resonance is found at 12.69 ppm in C$_6$D$_6$ ($J_{CH}$ = 118 Hz), which should be compared with $\delta$H$_\alpha$ = 12.24 ppm for the alkylidene proton in **1a**.



(2)

Crystallographic quality crystals of **2a** were grown from a saturated pentane solution at –30 °C over the course of 36 h. A drawing of the structure can be found in Figure 2 and crystallographic details in Table 1. The alkylidene is found in the syn orientation with Mo−C(1) = 1.876(2) Å and Mo−C(1)−C(2) = 145.62(15)°. The pyrrolyl ligand is bound in an $\eta^1$ fashion with Mo−N(2) = 2.0238(17) Å, which is typical of pyrrolyl complexes of Mo(6+)[4a] or W(6+).[4c] The commanding steric properties of the Silox ligand are reflected in the larger N(1)−Mo−O(1) [119.86(7)°], C(1)−Mo−O(1) [110.17(8)°], and N(2)−Mo−O(1) [113.77(7)°] angles compared to N(1)−Mo−N(2) [108.61(8)°], C(1)−Mo−N(2) [98.73(8)°], and N(1)−Mo−C(1) [103.11(8)°].

A toluene-$d_8$ solution of Mo(NAr)(CHCMe$_2$Ph)(pyr)$_2$ (55 mM) and 2 equiv of H(Silox) was heated to 160 °C in a sealed NMR tube for 18 h. Compound **2a** was formed first, but only ~45% of **2a** was converted into Mo(NAr)(CHCMe$_2$Ph)(Silox)$_2$ (**2b**) under these conditions; no change was observed upon heating samples for longer periods of time, while heating samples to higher temperatures led to decomposition. The alkylidene resonance for Mo(NAr)(CHCMe$_2$Ph)(Silox)$_2$ was observed at 11.66 ppm (cf. 11.08 ppm for **1b**). We propose that the greater steric demands of the 2,6-diisopropylphenylimido ligand prevent complete conversion of **2a** into **2b** under these

**Table 1. Crystal Data and Structure Refinement for 2a and 1b**[a]

| | 2a | 1b |
|---|---|---|
| empirical formula | $C_{38}H_{60}MoN_2OSi$ | $C_{44}H_{81}MoNO_2Si_2$ |
| fw | 684.91 | 808.22 |
| $T$ (K) | 110(2) | 100(2) |
| cryst syst | triclinic | monoclinic |
| space group | $P\bar{1}$ | $C2/c$ |
| unit cell dimens | | |
| $a$ (Å) | 12.038(2) | 30.5622(9) |
| $b$ (Å) | 12.567(3) | 18.2552(6) |
| $c$ (Å) | 12.897(3) | 22.2579(7) |
| α (deg) | 81.45(3) | 90 |
| $\beta$ (deg) | 86.62(3) | 132.7510(10) |
| $\gamma$ (deg) | 87.79(3) | 90 |
| $V$ (Å$^3$) | 1925.1(7) | 9118.7(5) |
| $Z$ | 2 | 8 |
| density (calcd) (Mg/m$^3$) | 1.182 | 1.177 |
| abs coeff (mm$^{-1}$) | 0.401 | 0.374 |
| $F$(000) | 732 | 3504 |
| cryst size (mm$^3$) | 0.25 × 0.15 × 0,10 | 0.30 × 0.25 × 0.11 |
| $\theta$ range for data collection (deg) | 1.60−29.57 | 1.44−28.46 |
| index ranges | $-16 \leq h \leq +16$, $-17 \leq k \leq +17$, $-17 \leq l \leq +17$ | $-40 \leq h \leq +40$, $-24 \leq k \leq +24$, $-29 \leq l \leq +29$ |
| reflns collected | 43 269 | 94 706 |
| indep reflns | 10 721 [$R$(int) = 0.0338] | 11 458 [$R$(int) = 0.0973] |
| completeness to $\theta = 29.57°$ (%) | 99.2 | 99.5 |
| abs corrn | semiempirical | semiempirical |
| max and min transmission | 0.9610 and 0.9065 | 0.9600 and 0.8961 |
| data/restraints/param | 10 721/40/388 | 11 458/100/560 |
| GOF on $F^2$ | 1.055 | 1.016 |
| final $R$ indices [$I > 2\sigma(I)$] | R1 = 0.0352, wR2 = 0.0955 | R1 = 0.0425, wR2 = 0.0917 |
| $R$ indices (all data) | R1 = 0.0418, wR2 = 0.1021 | R1 = 0.0690, wR2 = 0.1044 |
| largest diff peak and hole (e/Å$^3$) | 1.250 and −0.336 | 0.732 and −0.306 |

[a] In each case, the wavelength was 0.710 73 Å and the refinement method was full-matrix least squares on $F^2$.

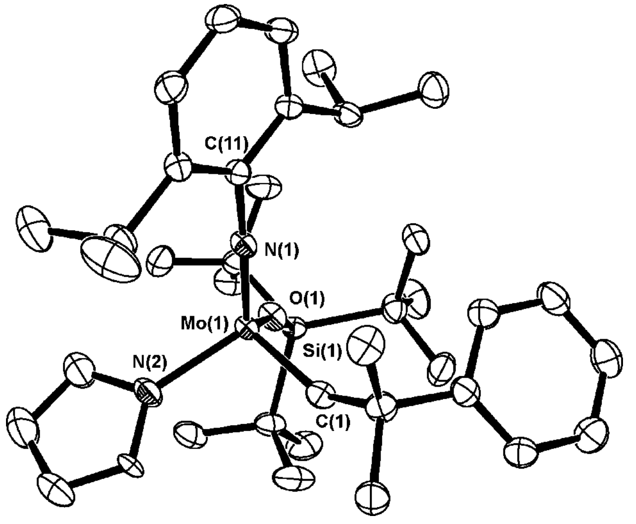
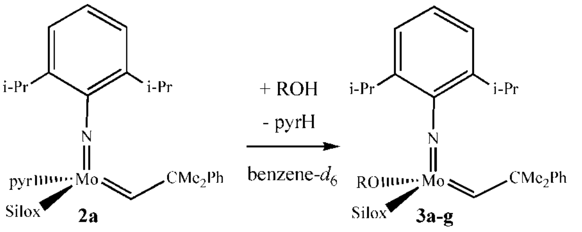


**Figure 2.** Thermal ellipsoid drawing of **2a** (ellipsoids at 50%; H atoms omitted). Selected bond distances (Å) and angles (deg): Mo−C(1) = 1.876(2), Mo−N(1) = 1.7299(16), Mo−N(2) = 2.0238(17), Mo−O(1) = 1.88677(14), Mo−C(1)−C(2) = 145.62(15), Mo−N(1)−C(11) = 177.22(14), Mo−O(1)−Si(1) = 166.72(9), N(1)−Mo−O(1) = 119.86(7), C(1)−Mo−O(1) = 110.17(8), N(2)−Mo−O(1) = 113.77(7), N(1)−Mo−N(2) = 108.61(8), C(1)−Mo−N(2) = 98.73(8), N(1)−Mo−C(1) = 103.11(8).

conditions, although the possibility remains that **2a** and **2b** have reached equilibrium under these conditions.

Compound **2a** reacts readily with alcohols that are smaller than H(Silox) to yield pyrrole and Mo(NAr)($CHCMe_2Ph$)(Silox)(OR) complexes [eq 3; ROH = $(CF_3)Me_2COH$, **3a**, $\delta H_\alpha$ = 11.77 ppm; $(CF_3)_2MeCOH$, **3b**, $\delta H_\alpha$ = 12.14 ppm; $(CF_3)_2CHOH$, **3c**, $\delta H_\alpha$ = 12.57 ppm; ArOH, **3d**, $\delta H_\alpha$ = 11.68 ppm; $C_6F_5OH$, **3e**, $\delta H_\alpha$ = 12.43 ppm; (−)-menthol, **3f**, $\delta H_\alpha$ = 11.48 (62%) and 11.42 (38%); (−)-borneol, **3g**, $\delta H_\alpha$ = 11.47 (59%) and 11.46 (41%)]. Although **3a–g** are formed virtually quantitatively according to $^1H$ NMR spectra, attempts to crystallize these complexes on a preparative scale were not successful. The enantiopure alcohols (−)-menthol and (−)-borneol yielded a mixture of diastereomers of **3f** and **3g** when the reaction was carried out in either benzene-$d_6$ at 23 °C or toluene-$d_8$ at −30 °C. The ratio of diastereomers remained unchanged after the solutions had been stored at 23 °C for 1 week.



(3)

We then turned to other reactions that would yield species of the type Mo(NR)($CHCMe_2Ph$)(siloxide)$_2$ (R = Ad or Ar). Reactions between Mo(NR)($CHCMe_2Ph$)(pyr)$_2$ and 2 equiv of $(i\text{-}Pr)_3SiOH$, $(SiMe_3)_3SiOH$, $(t\text{-}Bu\text{-}O)_3SiOH$, $Me_2(t\text{-}Bu)SiOH$, and $Ph_3SiOH$ produced Mo(NR)($CHCMe_2Ph$)(siloxide)$_2$ species (**4**−**7**). Mo(NR)($CHCMe_2Ph$)(siloxide)$_2$ species that could be crystallized included Mo(NAd)($CHCMe_2Ph$)[$OSi(SiMe_3)_3$]$_2$ (**4**), Mo(NAd)($CHCMe_2Ph$)[$OSi(O\text{-}t\text{-}Bu)_3$]$_2$ (**5**), and Mo(NAr)($CHCMe_2Ph$)[$OSiMe_2(t\text{-}Bu)$]$_2$ (**6**). Unlike reactions between Mo(NR)($CHCMe_2Ph$)(pyr)$_2$ and 2 equiv of H(Silox), in all cases little or no Mo(NR)($CHCMe_2Ph$)(pyr)(siloxide) complex could be observed as a consequence of a rapid reaction of presumed intermediate Mo(NR)($CHCMe_2Ph$)(siloxide)(pyr) with the second 1 equiv of silanol. Reactions involving $(i\text{-}Pr)_3SiOH$ and $Ph_3SiOH$ led to impure oils, although the desired products could be observed in $^1H$ NMR spectra of the crude product. Pure Mo(NAr)($CHCMe_2Ph$)($OSiPh_3$)$_2$ (**7**) was best prepared (in 91%

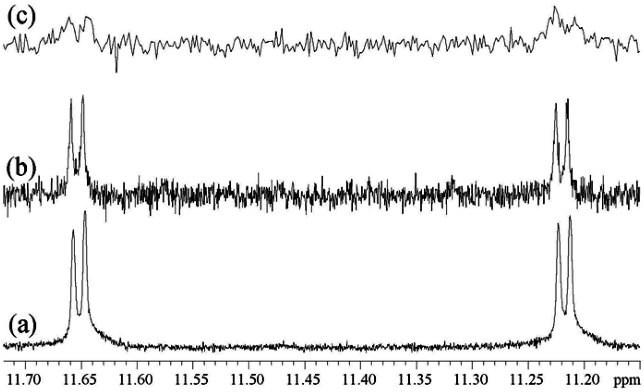


**Figure 3.** $^1$H NMR monitoring of the reaction between **2a** in benzene-$d_6$ and ethylene (1 atm) after heating the solutions to (a) 55 °C, (b) 80 °C, and (c) 120 °C.

yield) in a reaction between Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME) and 2 equiv of KOSiPh$_3$.

**Reactions with Olefins.** When an *o*-dichlorobenzene-$d_4$ solution (55 mM) of **1b** was heated to 240 °C for 12 h under 1 atm of ethylene, **1b** was consumed and the expected first metathesis product (3-methyl-3-phenylbutene) was observed in the $^1$H NMR spectrum of the reaction mixture. Compound **1b** did not decompose at 240 °C in the absence of ethylene, as noted earlier. A similar reaction was performed with a toluene solution of **1b** under 5 atm of ethylene at 120 °C; no reaction was observed. Heating solutions of **1b** in neat 1-hexene, 1-octene, or 3-hexene up to 120 °C also led to less than 5% consumption of **1b**. However, complex **1b** does initiate the polymerization of 100 equiv of norbornene, producing a 56% yield of polynorbornene at 23 °C in dichloromethane in 1 h.

In contrast, compound **2a** in C$_6$D$_6$ under 1 atm of ethylene was completely consumed after heating the solution for 12 h at 120 °C. When the reaction at 55 °C was monitored by $^1$H NMR spectroscopy, a pair of doublets could be observed at 11.15 and 11.85 ppm, which we assign to inequivalent methylene protons in Mo(NAr)(CH$_2$)(Silox)(pyr). This compound comprises a maximum of ~10% of the reaction mixture under these conditions. A $J_{HH}$ value of 6.0 Hz was observed for the alkylidene protons, a value that is typical for high-oxidation-state methylene complexes. The resonance at 11.85 ppm is analogous to what is observed in an *anti*-M=CHR species; i.e., the proton is syn with respect to the imido group, with no agostic CH$_\alpha$ interaction with the metal.1 The resonance at 11.15 ppm is analogous to what is observed in an *syn*-M=CHR species; i.e., the proton is anti with respect to the imido group and has a weak agostic CH$_\alpha$ interaction with the metal.1 (It should be noted that the reaction between W(NAr)(CH-*t*-Bu)(2,5-dimethylpyrrolyl)$_2$ and ethylene at 60 °C over a period of 24 h yields the isolable and crystallographically characterized methylene complex W(NAr)(CH$_2$)(2,5-dimethylpyrrolyl)$_2$, which has H$_\alpha$ resonances at 12.12 and 11.10 ppm ($J_{HH}$ = 7.3 Hz) in its $^1$H NMR spectrum in CD$_2$Cl$_2$.[4c] Mo(NAr)(CH$_2$)(Silox)(pyr) decomposes upon heating C$_6$D$_6$ solutions of it to 80 or 120 °C (Figure 3). Compound **2a** also reacts with 1-hexene and 3-hexene at 120 °C and is an initiator for ring-opening metathesis polymerization of 100 equiv of norbornene, producing a 78% yield of polynorbornene at 23 °C in dichloromethane in 1 h.

Compounds **3a–e** react more readily than does **2a** with ethylene (1atm). The starting material in benzene-$d_6$ is fully consumed at ~60 °C after 4 h. Two cases warrant special mention. First, the reaction between **3a** and ethylene produces Mo(NAr)(CH$_2$)(Silox)[OCMe$_2$(CF$_3$)], as shown in Figure 4 ($J_{HH}$ = 6.0 Hz). The proposed methylidene species comprises up to ~70% of the reaction mixture if the reaction is carried out at 55 °C. Second, **3e** reacts with ethylene at room temperature to produce what appears to be the dimeric species [Mo(NAr)(Silox)(OC$_6$F$_5$)]$_2$, according to NMR spectra; it presumably is formed through facile bimolecular decomposition of unobservable intermediate Mo(NAr)(CH$_2$)(Silox)(OC$_6$F$_5$). Attempts to crystallize [Mo(NAr)(Silox)(OC$_6$F$_5$)]$_2$ on a preparative scale were unsuccessful. The facile reaction of **3e** with ethylene at room temperature compared with the relatively slow reaction between **2a** and ethylene can be attributed to the replacement of a relatively electron-donating pyrrolyl ligand with a relatively small and more electron-withdrawing perfluorophenoxide ligand.

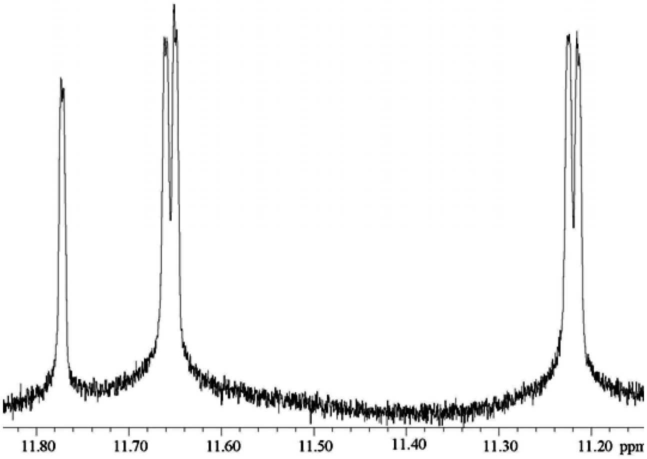


**Figure 4.** $^1$H NMR spectrum of **3a** in benzene-$d_6$ under 1 atm of ethylene after heating to 60 °C. (The singlet is the alkylidene H$_\alpha$ resonance in **3a**.)

Compounds **4** and **5** failed to react completely with ethylene or 1-hexene unless temperatures above 120 °C were employed. At these temperatures, both started to decompose, giving rise to several new aliphatic resonances. Compounds **7** and **8** react completely with ethylene or 1-hexene in a C$_6$D$_6$ solution (46 mM) over the course of 12 h at 22 °C, but no attempt was made to characterize the metal-containing products of these reactions.

## Discussion and Conclusions

The object of this investigation was to prepare and explore various Mo(NR)(CHR′)(siloxide)$_2$ or Mo(NR)(CHR′)(siloxide)(X) complexes in the hope that some not only would react readily with olefins but also would yield relatively stable intermediates, especially methylene species. A secondary goal was to compare reactions of alkylidene complexes that contain one or two Silox ligands with similar reactions of analogous complexes that contain other siloxides. On the basis of what we have observed, it appears that siloxides (except Silox) do not seem to be unusual compared to alkoxide or aryloxide analogues. Second, as we suspected, Silox complexes have reactivities that are dramatically different from those of other siloxide analogues. Two results are especially dramatic. One is that Silox is large enough to allow Mo(NR)(CHR′)(Silox)(NC$_4$H$_4$) species to be prepared highly selectively. In contrast, it has not been possible to prepare other siloxide/pyrrolyl analogues, and it also has not yet been possible to prepare alkoxide/pyrrolyl analogues relatively selectively unless 2,5-dimethylpyrrolyl is employed. A successful synthesis of monosiloxide/monopyrrolyl or monoalkoxide/monopyrrolyl species through protonation of bispyrrolyls is likely to depend dramatically upon a complex interplay between the steric demands of all four ligands in the Mo(NR)(CHR′)(OR″)(pyrrolyl) species; we have explored only a small fraction of the possibilities. The second dramatic result is that Mo(NAd)(CHCMe$_2$Ph)(Silox)$_2$ is virtually unreactive toward ethylene, an olefin that we assume provides a relatively accurate measure of alkylidene reactivity. Either that assumption is incorrect or the Mo(NAd)(CHCMe$_2$Ph)(Silox)$_2$(C$_2$H$_4$) transition state simply cannot be reached readily when *two* Silox ligands are present. The latter makes the most sense on the basis of what is known about the transition state in metathesis with complexes of this general type; i.e., one Silox would be axial and trans to the incoming ethylene, but the second (equatorial) Silox would be cis to the incoming ethylene.[1e,4] The steric problems associated with two Silox ligands ~90° to one another would seem to be too significant to overcome. (Another example of a dramatic slowing of a reaction involving complexes that contain two Silox ligands is the failure of trigonal-planar W(N-*t*-Bu)(Silox)$_2$[13] to dimerize to give W$_2$ species,[14] i.e., (*t*-BuN)(Silox)$_2$W=W(N-*t*-Bu)(Silox)$_2$.) Unfortunately, on the basis of what we have found here, it seems unlikely that reactive alkylidenes can be prepared that at the same time are relatively stable toward bimolecular decomposition of (especially) intermediate methylene complexes.

Perhaps the most interesting of the compounds we have encountered here are the Mo(NR)(CHR′)(Silox)(pyrrolyl) species because they are members of a class of Mo(NR)(CHR′)(OR″)(pyrrolyl) species that have been shown to have unusual reactivities and selectivities for enyne metathesis reactions.[5] They also are members of a larger M(NR)(CHR′)(X)(Y) class in which X and Y are a “donor” and an “acceptor”, respectively, which a recent theory suggests are especially efficient catalysts when the acceptor is in an equatorial position in a distorted trigonal bipyramid as an olefin approaches Mo.[4] However, it is not clear what the *steric* preference for various combinations of Silox and substituted pyrrolyls will be and whether the steric preference coincides with the electronic preference. In future studies, we look forward to preparing a variety of Mo(NR)(CHR′)(siloxide)(pyrrolyl) complexes and comparing them with Mo(NR)(CHR′)(alkoxide)(pyrrolyl) species.

## Experimental Section

**General Procedures.** All manipulations were performed in oven-dried (200 °C) glassware under an atmosphere of nitrogen on a Schlenk line or in a Vacuum Atmospheres glovebox. HPLC-grade organic solvents were sparged with nitrogen, passed through activated alumina, and stored over 4 Å Linde-type molecular sieves prior to use. Benzene-$d_6$ and toluene-$d_8$ were dried over sodium benzophenone ketyl and distilled in vacuo prior to use. *o*-Dichlorobenzene-$d_4$ was dried over CaH$_2$ and vacuum-distilled prior to use. NMR spectra were recorded on Varian Mercury and Varian INOVA spectrometers operating at 300 and 500 MHz ($^1$H NMR), respectively. Chemical shifts for $^1$H and $^{13}$C NMR spectra were referenced to the residual $^1$H/$^{13}$C NMR resonances of the deuterated solvent and are reported as parts per million relative to tetramethylsilane. $^{19}$F and $^{29}$Si NMR spectra were referenced externally to fluorobenzene ($\delta = -113.15$ ppm upfield of CFCl$_3$) and tetramethylsilane ($\delta = 0.00$ ppm). Elemental analyses were performed by H. Kolbe Microanalytics Laboratory, Mülheim an der Ruhr, Germany. Mo(NR)(CHCMe$_2$R′)(OTf)$_2$(DME) and Mo(NR)(CHCMe$_2$R′)(pyr)$_2$ complexes were prepared according to published procedures cited in the text. H(Silox) was a generous donation from the Wolczanski group (Cornell University, Ithaca, NY). (Me$_3$Si)$_3$SiOH and Me$_2$(*t*-Bu)SiOH were synthesized from the corresponding silyl chloride via two-phase hydrolysis using NEt$_3$ as an acid scavenger.[15] Triisopropylsilanol was prepared as reported by Wolczanski et al.[16] (*t*-BuO)$_3$SiOH, Ph$_3$SiOH, 1-hexene, 3-hexene, Me$_3$COH, Me$_2$(CF$_3$)COH, Me(CF$_3$)$_2$COH, (CF$_3$)$_3$COH, 2,6-diisopropylphenol, and C$_6$F$_5$OH were purchased from Sigma-Aldrich Co. (St. Louis, MO) and either were degassed via successive freeze–pump–thaw cycles (liquids) or left under high vacuum (0.005 mmHg) for 18 h and finally dried via storage of the neat liquid or a toluene solution over activated sieves. Ph$_3$SiOK was produced via the reaction of Ph$_3$SiOH with KH in tetrahydrofuran. Ethylene was purchased from Airgas East (Hingham, MA) and dried via passage through a 20 cm × 5 cm column of anhydrous CaSO$_4$.

**Crystallography.** Low-temperature diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.710\ 73$ Å), performing $\varphi$ and $\omega$ scans. All structures were solved by direct methods using *SHELXS*[17] and refined against $F^2$ on all data by full-matrix least squares with *SHELXL-97*.[18] All non-H atoms were refined anisotropically. Unless described otherwise, all H atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all H atoms were fixed to 1.2 times the $U$ value of the atoms they are linked to (1.5 times for methyl groups). See the Supporting Information for a full discussion of each structure.

**Mo(NAd)(CHCMe$_2$Ph)(Silox)$_2$ (1b).** Mo(NAd)(CHCMe$_2$Ph)(pyr)$_2$ (300 mg, 0.59 mmol) and H(Silox) (254 mg, 1.2 mmol, 2.02 equiv) were weighed and transferred to a 50 mL solvent bulb style flask equipped with a Teflon stopcock. Toluene (10 mL) was added, and the solution was degassed three times. The sealed flask was then submerged in a silicon oil bath and heated to 120 °C for 18 h, over which time the solution became dark orange. The solution was then allowed to cool to room temperature, and all volatiles were removed in vacuo. The resulting yellow-orange solid was heated to 60 °C under a high vacuum for 4 h in order to remove all toluene and pyrrole. The product was crystallized from pentane at −30 °C to give **1b** as yellow-orange blocks (319 mg, 0.39 mmol, 66% yield): $^1$H NMR (C$_6$D$_6$) $\delta$ 11.08 (s, 1H, $J_{CH} = 119$ Hz, Mo=C*H*), 7.46 (d, 2H, CMe$_2$*Ph*), 7.21 (m, 2H, CMe$_2$*Ph*), 7.07 (t, 1H, CMe$_2$*Ph*), 2.25 (br, 6H, N*Ad*), 1.95 (br, 3H, N*Ad*), 1.89 (s, 6H, C*Me*$_2$Ph), 1.51 (m, 6H, N*Ad*), 1.24 (s, 54H, Silox); $^{13}$C{$^1$H} NMR (C$_6$D$_6$) $\delta$ 257.6 (Mo=C), 150.7 (CMe$_2$*Ph*), 128.8 (CMe$_2$*Ph*), 126.2 (CMe$_2$*Ph*), 75.8 (N*C*Ad), 50.2 (*C*Me$_2$Ph), 45.7 (Ad), 36.6 (Ad), 32.9 (Ad), 30.8 (SiC*Me*$_3$), 24.3 (Si*C*Me$_3$); $^{29}$Si{$^1$H} NMR (C$_6$D$_6$) $\delta$ 8.14. Anal. Calcd for C$_{44}$H$_{81}$NO$_2$Si$_2$Mo: C, 65.39; H, 10.10; N, 1.73. Found: C, 65.48; H, 10.06; N, 1.70.

**Mo(NAr)(CHCMe$_2$Ph)(Silox)(pyr) (2a).** Mo(NAr)(CHCMe$_2$Ph)(pyr)$_2$ (500 mg, 0.93 mmol) and H(Silox) (204 mg, 0.94 mmol, 1.01 equiv) were weighed and transferred to a 50 mL solvent bulb style flask equipped with a Teflon stopcock. Toluene (15 mL) was added, and the reaction was allowed to stir at room temperature. After 4 h, all volatiles were removed in vacuo to give a dark-yellow oil. Pentane (10 mL) was then condensed into the flask, and all volatiles were removed again after 15 min. This procedure was repeated three times. The resulting solid was dried at 60 °C under a high vacuum for 4 h in order to remove all volatile components. The product was crystallized from pentane at −30 °C to give two crops of **2a** as yellow blocks (446 mg, 0.65 mmol, 70% yield): $^1$H NMR (C$_6$D$_6$) $\delta$ 12.69 (s, 1H, $J_{CH} = 118$ Hz, Mo=C*H*), 7.37 (d, 2H),

---

[14] (a) Lopez, L. P. H.; Schrock, R. R. *J. Am. Chem. Soc.* **2004**, *126*, 9526. (b) Lopez, L. P. H.; Schrock, R. R.; Müller, P. *Organometallics.* **2006**, *25*, 1978.

[15] Cella, J. A.; Carpenter, J. C. *J. Organomet. Chem.* **1994**, *480*, 23.

[16] Chadeayne, A. R.; Wolczanski, P. T.; Lobkovsky, E. B. *Inorg. Chem.* **2004**, *43*, 3421.

[17] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

[18] Sheldrick, G. M. *SHELXL 97*; University of Göttingen: Göttingen, Germany, 1997.

7.19 (m, 1H), 7.07 (m, 2H, pyr-αH), 7.00 (m, 4H), 6.96 (t, 1H), 6.47 (m, 2H, pyr-*β*H), 3.79 (septet, 2H, C*H*Me$_2$), 1.74 (s, 3H, C*Me*$_2$Ph), 1.65 (s, 3H, C*Me*$_2$Ph), 1.22 (d, 6H, CH*Me*$_2$), 1.15 (d, 6H, CH*Me*$_2$), 1.23 (s, 27H, Silox); $^{13}C\{^1H\}$ NMR ($C_6D_6$) δ 285.3 (Mo=C), 154.0, 148.9, 147.2, 132.4, 129.0, 128.5, 126.9, 123.5, 123.8, 111.4, 55.9 (*C*Me$_2$Ph), 31.6 (C*Me*$_2$Ph), 30.9 (C*Me*$_2$Ph), 30.3 (SiC*Me*$_3$), 29.2 (*C*HMe$_2$), 25.4 (Si*C*Me$_3$), 23.9 (CH*Me*$_2$), 23.7 (CH*Me*$_2$); $^{29}Si\{^1H\}$ NMR ($C_6D_6$) δ 13.67. Anal. Calcd for $C_{38}H_{60}N_2OSiMo$: C, 66.64; H, 8.83; N, 4.09. Found: C, 66.48; H, 8.72; N, 4.01.

**In Situ Preparation of Mo(NAr)(CHCMe$_2$Ph)(Silox)[OCMe$_2$(CF$_3$)] (3a).** Mo(NAr)(CHCMe$_2$Ph)(Silox)(pyr) (25 mg, 0.037 mmol) was weighed and transferred to a 5 mm NMR tube equipped a Teflon stopcock (J. Young, Berkshire, U.K.). The solid was dissolved in 0.7 mL of $C_6D_6$, and 4 μL of HOCMe$_2$(CF$_3$) (0.038 mmol, 1.05 equiv) was added via syringe. The tube was then heated to 60 °C for 12 h via an oil bath. After 4 h at 60 °C, Mo(NAr)(CHCMe$_2$Ph)(Silox)[OCMe$_2$(CF$_3$)] was formed in 95% yield according to $^1H$ NMR studies: $^1H$ NMR ($C_6D_6$) δ 11.77 (s, 1H, $J_{CH}$ = 121 Hz, Mo=C*H*), 7.36 (d, 2H, CMe$_2$*Ph*), 7.12 (m, 4H, CMe$_2$*Ph* + Ar), 7.01 (m, 2H, CMe$_2$*Ph* + Ar), 3.80 (septet, 2H, C*H*Me$_2$), 1.75 (s, 3H, C*Me*$_2$Ph), 1.65 (s, 3H, C*Me*$_2$Ph), 1.22 (m, 9H, CH*Me*$_2$ + OC*Me*$_2$(CF$_3$)), 1.15 (m, 9H, CH*Me*$_2$ + OC*Me*$_2$(CF$_3$)), 1.11 (s, 27H, Silox); $^{19}F$ NMR ($C_6D_6$) δ −74.62.

**In Situ Preparation of Mo(NAr)(CHCMe$_2$Ph)(Silox)[OCMe(CF$_3$)$_2$] (3b).** A procedure analogous to the preparation of **3a** employing 25 mg of Mo(NAr)(CHCMe$_2$Ph)(Silox)(pyr) (0.037 mmol) and 4.5 μL of HOCMe(CF$_3$)$_2$ (0.038 mmol, 1.05 equiv) produced a 100% yield of **3b**: $^1H$ NMR ($C_6D_6$) δ 12.14 (s, 1H, $J_{CH}$ = 122 Hz, Mo=C*H*), 7.28 (d, 2H, CMe$_2$*Ph*), 7.15 (m, 4H, CMe$_2$*Ph* + Ar), 6.99 (m, 2H, CMe$_2$*Ph* + Ar), 3.78 (septet, 2H, C*H*Me$_2$), 1.77 (s, 3H, C*Me*$_2$Ph), 1.44 (s, 3H, C*Me*$_2$Ph), 1.34 (m, 3H, OC*Me*(CF$_3$)$_2$), 1.23 (d, 6H, CH*Me*$_2$), 1.20 (s, 27H, Silox), 1.15 (d, 6H, CH*Me*$_2$); $^{19}F$ NMR ($C_6D_6$): δ −76.74 (q, 3F), −77.91 (q, 3F).

**In Situ Preparation of Mo(NAr)(CHCMe$_2$Ph)(Silox)[OC(CF$_3$)$_3$] (3c).** A procedure analogous to the preparation of **3a** employing 25 mg of Mo(NAr)(CHCMe$_2$Ph)(Silox)(pyr) (0.037 mmol) and 5.1 μL of HOC(CF$_3$)$_3$ (0.038 mmol, 1.05 equiv) yielded **3c** in 95% yield: $^1H$ NMR ($C_6D_6$) δ 12.57 (s, 1H, $J_{CH}$ = 122 Hz, Mo=C*H*), 7.25 (d, 2H, CMe$_2$*Ph*), 7.10 (m, 4H, CMe$_2$*Ph* + Ar), 7.07 (m, 2H, CMe$_2$*Ph* + Ar), 3.68 (septet, 2H, C*H*Me$_2$), 1.94 (s, 3H, C*Me*$_2$Ph), 1.26 (s, 3H, C*Me*$_2$Ph), 1.18 (s, 27H, Silox), 1.14 (d, 6H, CH*Me*$_2$), 1.07 (d, 6H, CH*Me*$_2$); $^{19}F$ NMR ($C_6D_6$) δ −73.26.

**In Situ Preparation of Mo(NAr)(CHCMe$_2$Ph)(Silox)(OAr) (3d).** A procedure analogous to the preparation of **3a** employing 25 mg of Mo(NAr)(CHCMe$_2$Ph)(Silox)(pyr) (0.037 mmol) and 8.5 μL of HOAr (0.038 mmol, 1.05 eq) yielded **3d** in 95% yield: $^1H$ NMR ($C_6D_6$) δ 11.68 (s, 1H, $J_{CH}$ = 123 Hz, Mo=C*H*), 7.38 (d, 2H, OAr), 7.19 (m, 2H, CMe$_2$*Ph*), 7.02 (m, 4H, CMe$_2$*Ph* + Ar), 6.94 (m, 3H, CMe$_2$*Ph* + Ar + OAr), 3.44 (septet, 4H, ArC*H* + OArC*H*), 1.79 (s, 3H, C*Me*$_2$Ph), 1.76 (s, 3H, C*Me*$_2$Ph), 1.27 (s, 27H, Silox), 1.21 (overlapping d, 12H, ArCH*Me*$_2$ + OArCH*Me*$_2$), 1.14 (d, 6H, OArCH*Me*$_2$), 0.91 (d, 6H, ArCH*Me*$_2$).

**In Situ Preparation of Mo(NAr)(CHCMe$_2$Ph)(Silox)(OC$_6$F$_5$) (3e).** Mo(NAr)(CHCMe$_2$Ph)(Silox)(pyr) (25 mg, 0.037 mmol) and HOC$_6$F$_5$ (6.8 mg, 0.038 mmol, 1.05 equiv) were combined in a procedure analogous to that for **3a**; yield 100%; $^1H$ NMR ($C_6D_6$) δ 12.43 (s, 1H, $J_{CH}$ = 120 Hz, Mo=C*H*), 7.07 (m, 8H, CMe$_2$*Ph* + Ar), 3.87 (septet, 2H, C*H*Me$_2$), 1.77 (s, 3H, C*Me*$_2$Ph), 1.44 (s, 3H, C*Me*$_2$Ph), 1.34 (m, 3H, OC*Me*(CF$_3$)$_2$), 1.27 (m, 12H, CH*Me*$_2$), 1.22 (s, 27H, Silox); $^{19}F$ NMR ($C_6D_6$): δ −160.09 (d, 2F), −166.16 (t, 2F), −166.16 (t, 1F).

**In Situ Preparation of Mo(NAr)(CHCMe$_2$Ph)(Silox)[(−)-menthoxide] (3f). 3f** was obtained from 15 mg of Mo(NAr)(CHCMe$_2$Ph)(Silox)(pyr) (0.022 mmol) and 3.6 mg of (−)-menthol (0.023 mmol, 1.05 equiv) similarly to **3a**: yield 100% according to $^1H$ NMR.

**In Situ Preparation of Mo(NAr)(CHCMe$_2$Ph)(Silox)[(−)-borneoxide] (3g). 3g** was obtained from 15 mg of Mo(NAr)(CHCMe$_2$Ph)(Silox)(pyr) (0.022 mmol) and 3.5 mg of (−)-borneol (0.023 mmol, 1.05 equiv) similarly to **3a**: yield 100% according to $^1H$ NMR.

**Mo(NAd)(CHCMe$_2$Ph)[OSi(TMS)$_3$]$_2$ (4).** This complex was prepared by treating 300 mg of Mo(NAd)(CHCMe$_2$Ph)(pyr)$_2$ (0.59 mmol) with 314 mg of HOSi(TMS)$_3$ (1.2 mmol, 2.02 equiv) in a manner analogous to that of complex **2a**. The product can be crystallized via slow evaporation in vacuo of a −30 °C pentane solution to yield orange microcrystals (517 mg, 0.57 mmol, 97% yield): $^1H$ NMR ($C_6D_6$) δ 10.88 (s, 1H, $J_{CH}$ = 120 Hz, Mo=C*H*), 7.47 (d, 2H, CMe$_2$*Ph*), 7.25 (t, 2H, CMe$_2$*Ph*), 7.09 (t, 1H, CMe$_2$*Ph*), 2.16 (br, 6H, N*Ad*), 1.98 (br, 3H, N*Ad*), 1.87 (s, 6H, C*Me*$_2$Ph), 1.53 (m, 6H, N*Ad*), 0.31 (s, 54H, TMS); $^{13}C\{^1H\}$ NMR ($C_6D_6$) δ 254.2 (Mo=C), 151.5 (CMe$_2$*Ph*), 128.9 (CMe$_2$*Ph*), 126.8 (CMe$_2$*Ph*), 74.6 (N*C*Ad), 49.8 (*C*Me$_2$Ph), 46.0 (Ad), 36.6 (Ad), 33.7 (Ad), 30.5 (C*Me*$_2$Ph), 0.55 (Si*Me*$_3$); $^{29}Si\{^1H\}$ NMR ($C_6D_6$) δ 9.59 (*β*-Si), −16.42 (α-Si). Anal. Calcd for $C_{38}H_{81}MoNO_2Si_8$: C, 50.45; H, 9.02; N, 1.55. Found: C, 50.65; H, 8.96; N, 1.48.

**Mo(NAd)(CHCMe$_2$Ph)[OSi(O-t-Bu)$_3$]$_2$ (5).** This complex was prepared from 300 mg of Mo(NAd)(CHCMe$_2$Ph)(pyr)$_2$ (0.59 mmol) and 314 mg of HOSi(O-*t*-Bu)$_3$ (1.2 mmol, 2.02 equiv) in a manner analogous to that of complex **2a**. Crystallization of the crude product from pentane at −30 °C produced yellow fibrous needles (429 mg, 0.51 mmol) in 87% yield: $^1H$ NMR ($C_6D_6$) δ 12.63 (s, 1H, $J_{CH}$ = 154 Hz, *anti*-Mo=C*H* ~11%), 11.44 (s, 1H, $J_{CH}$ = 121 Hz, *syn*-Mo=C*H* ~89%), 7.59 (d, 2H, CMe$_2$*Ph*), 7.31 (m, 2H, CMe$_2$*Ph*), 7.12 (t, 1H, CMe$_2$*Ph*), 2.14 (br, 6H, N*Ad*), 1.95(br, 3H, N*Ad*), 1.85 (s, 6H, C*Me*$_2$Ph), 1.53 (m, 6H, N*Ad*), 1.48 (s, 54H, t-Bu); $^{13}C\{^1H\}$ NMR ($C_6D_6$) δ 262.5 (Mo=C), 152.2 (CMe$_2$*Ph*), 127.5 (CMe$_2$*Ph*), 126.2 (CMe$_2$*Ph*), 72.7 (N*C*Ad), 50.9 (*C*Me$_2$Ph), 45.6 (Ad), 36.5 (Ad), 33.6 (Ad), 32.3 (SiOC*Me*$_3$), 30.4 (SiO*C*Me$_3$); $^{29}Si\{^1H\}$ NMR ($C_6D_6$) δ −92.21. Anal. Calcd for $C_{44}H_{81}MoNO_8Si_2$: C, 58.44; H, 9.03; N, 1.55. Found: C, 58.29; H, 9.06; N, 1.48.

**Mo(NAr)(CHCMe$_2$Ph)[OSiMe$_2$(*t*-Bu)]$_2$ (6).** This complex was prepared from 300 mg of Mo(NAr)(CHCMe$_2$Ph)(pyr)$_2$ (0.59 mmol) and 159 mg of HOSiMe$_2$(*t*-Bu) (1.2 mmol, 2.02 equiv) in a manner analogous to that of complex **2a**. Crystallization of the crude product from pentane at −30 °C gave **7** as orange blocks (358 mg, 0.54 mmol) in 91% yield: $^1H$ NMR ($C_6D_6$) δ 11.13 (s, 1H, $J_{CH}$ = 120 Hz, Mo=C*H*), 7.36 (m, 4H, CMe$_2$*Ph* + N*Ar*), 7.19 (m, 4H, CMe$_2$*Ph* + N*Ar*), 3.83 (septet, 2H, C*H*Me$_2$), 1.67 (s, 6H, C*Me*$_2$Ph), 1.25 (d, 12H, CH*Me*$_2$), 1.05 (s, 9H, OSiMe$_2$(*t*-Bu)), 0.17 (s, 6H, OSi*Me*$_2$(*t*-Bu)), 0.12 (s, 6H, OSi*Me*$_2$(*t*-Bu)); $^{13}C\{^1H\}$ NMR ($C_6D_6$) δ 261.7 (Mo=C), 153.6, 150.5, 146.9, 128.8, 126.6, 126.4, 126.2, 123.7, 53.7, 32.0, 28.9, 26.6, 24.3, 19.8, −2.3, −2.7; $^{29}Si\{^1H\}$ NMR ($C_6D_6$) δ 19.95. Anal. Calcd for $C_{34}H_{59}MoNO_2Si_2$: C, 61.32; H, 8.93; N, 2.10. Found: C, 61.18; H, 8.85; N, 2.05.

**Mo(NAr)(CHCMe$_2$Ph)(OSiPh$_3$)$_2$ (7).** Mo(NAr)(CHCMe$_2$Ph)](OTf)(DME) (250 mg, 0.32 mmol) was weighed and dissolved in 10 mL of diethyl ether, and the solution was cooled to −30 °C. K(OSiPh$_3$) (204 mg, 0.65 mmol, 2.02 equiv) was added in portions to the rapidly stirred solution over the course of 5 min. The solution was then allowed to come to room temperature and was stirred for 4 h, during which time the color of the solution changed from translucent yellow to dark yellow, concomitant with the formation of KOTf. All volatile components were removed in vacuo, and the resulting dark-yellow oil was extracted with 20 mL of toluene. The extract was filtered through a fine-porosity glass frit. The toluene was removed from the filtrate to yield a dark-yellow oil, which was triturated with pentane to yield a yellow microcrystalline solid and a brown mother liquor. The solid was collected via filtration and recrystallized from hot pentane (~35 °C) to yield **7** as yellow microcrystals (238 mg, 0.25 mmol) in 79% yield: $^1H$ NMR ($C_6D_6$) δ 11.18 (s, 1H, $J_{CH}$ = 123 Hz, Mo=C*H*), 7.75 (d, 1H, CMe$_2$*Ph*), 7.69 (d, 12 H, OSi*Ph*$_3$), 7.18 (t, 6H, OSi*Ph*$_3$), 7.15 (m, 4H, CMe$_2$*Ph*

+ Ar), 7.10 (t, 12H, OSi*Ph*$_3$), 7.06 (m, 2H, CMe$_2$*Ph*), 6.98 (t, 1H, CMe$_2$*Ph*), 3.69 (septet, 2H, C*H*Me$_2$), 1.51 (s, 6H, C*Me*$_2$Ph), 1.00 (d, 12H, CH*Me*$_2$). $^{13}$C{$^1$H} NMR ($C_6D_6$) $\delta$ 267.9 (Mo═C), 154.0, 150.0, 147.4, 137.1, 136.1, 135.8, 130.3, 128.5, 126.5, 126.3, 123.6, 54.0 (*C*Me$_2$Ph), 32.1 (C*Me*$_2$Ph), 29.4 (*C*HMe$_2$), 23.9 (CH*Me*$_2$); $^{29}$Si{$^1$H} NMR ($C_6D_6$) $\delta$ −11.62 Anal. Calcd for $C_{58}H_{59}MoNO_2Si_2$: C, 73.01; H, 6.23; N, 1.47. Found: C, 72.88; H, 6.20; N, 1.45.

**Acknowledgment.** R.R.S. and K.M.W. thank Prof. Peter T. Wolczanski and David S. Kuiper (Cornell University, Ithaca, NY) for helpful conversations as well as a generous gift of H(Silox). R.R.S. thanks the National Science Foundation (Grant CHE-0554734) for supporting this research.

**Supporting Information Available:** Crystallographic information files in CIF format and fully labeled thermal ellipsoids drawings. This material is available free of charge via the Internet at http://pubs.acs.org. X-ray crystallographic data for **1b** (06162) and **2a** (06199) are also available to the public at http://reciprocal.mit.edu.

OM700864U