Reactions of M(N-2,6-i-$Pr_2C_6H_3$)(CHR)(CH_2R')$_2$ (M = Mo, W) Complexes with Alcohols To Give Olefin Metathesis Catalysts of the Type M(N-2,6-i-$Pr_2C_6H_3$)(CHR)(CH_2R')(OR″)

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Received November 14, 2005

The reaction between M(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ (M = Mo, W, Ar = 2,6-i-$Pr_2C_6H_3$) and various alcohols (1-adamantyl-OH, t-BuOH, ArOH, $(CF_3)_2$CHOH, $(CF_3)_2$MeCOH, CF_3Me_2COH, $(CF_3)_3$COH, C_6F_5OH) in pentane or toluene yields either complexes of the type M(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR), through direct addition of ROH across a Mo−C bond, or complexes of the type M(NAr)(CH_2-t-Bu)$_3$(OR), through direct addition of ROH across a Mo=C bond. The trineopentyl species appear to be formed when the alcohol has a relatively low pK_a value. The outcome also can depend on whether the alcohol is employed neat or in benzene, and mixtures are observed in some circumstances. The conversion of M(NAr)(CH_2-t-Bu)$_3$(OR) into M(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) was shown to be unimolecular in several examples. Preliminary experiments have shown that M(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes are surprisingly active catalysts for various metathesis reactions, although conversion is sometimes limited by decomposition of intermediate alkylidenes to yield dimeric species that contain M=M bonds. In contrast, M(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ species are virtually inactive for metathesis. X-ray structures are reported for Mo(NAr)(CH_2-t-Bu)$_3$(OC_6F_5), Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)[OSi(O-t-Bu)$_3$], [Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)]$_2$, and Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)(PMe_3).

Introduction

We have been interested in olefin metathesis by imido alkylidene complexes of Mo and W,[1] most recently asymmetric metathesis reactions catalyzed by complexes of the type Mo(NR)(CHR′)(diolate) (R′ = CMe_3, CMe_2Ph) that contain an enantiomerically pure biphenolate or binaphtholate ligand.[2] As the number of catalyst variations increases, it would be highly desirable to prepare catalysts through protonation of two monoanionic ligands in an imido alkylidene precursor with an alcohol. Catalysts then could be prepared and evaluated in situ, a possibility that would create opportunities for rapid throughput or combinatorial screening of catalysts for activity, selectivity, enantioselectivity, etc., if other products that might be formed in such reactions are catalytically inactive. For this reason we began to explore reactions between alcohols and *dineopentyl* imido alkylidene species of the type M(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ (M = Mo, W, Ar = 2,6-i-$Pr_2C_6H_3$), in the hope that 2 equiv of neopentane would be lost and M(NAr)(CH-t-Bu)(OR)$_2$ species generated. This particular precursor also could be added to a silica surface (Si_{surf}OH) in order to create a relatively well-defined surface-supported catalyst.[3] Related reactions involving Ta(CH-t-Bu)(CH_2-t-Bu)$_3$,[4] W(C-t-Bu)(CH_2-t-Bu)$_3$,[5] and Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)$_2$[6] have been employed for this purpose so far.[3] It has been believed that the lifetime of surface-supported species would be greater than the lifetime of analogous species in solution as a consequence of slow bimolecular (in metal) decomposition at relatively low temperatures.[7,8]

In two preliminary communications we showed that addition of alcohols to M(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ did *not* lead to bis(alkoxide) species but to M(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) species.[9,10] Only one example of a complex of this general type had been reported[11] (prepared through addition of Ph_3SiOH to Mo(N-t-Bu)(CH-t-Bu)(CH_2-t-Bu)$_2$), although it was not characterized and its olefin metathesis activity was not explored. On the basis of what we know about 1-adamantylimido bis(alkoxide) complexes,[12,13] and the fact that Mo(NAd)(CH-t-Bu)(CH_2-t-Bu)$_2$ is unstable with respect to bimolecular decomposition to yield di-*tert*-butylethylene,[14] we suspect that the *tert*-butylimido ligand is "too small" to prevent bimolecular decomposition of Mo(N-t-Bu)(CH-t-Bu)(CH_2-t-Bu)($OSiPh_3$) and formation of products that prevent crystallization of these already highly soluble compounds. In this paper we present the full details of the reactions between M(NAr)(CHR)(CH_2R')$_2$ (M = Mo, W; R, R′ = CMe_3, CMe_2Ph) and selected alcohols. Some M(NAr)(CHR′)(CH_2-t-Bu)(OR) complexes decompose in a

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10.1021/om050978a CCC: $33.50
Publication on Web 02/16/2006

Table 1. Relevant Proton and Carbon NMR Data for Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(X) Compounds Reported in This Paper

X	Mo $\delta(H_\alpha)$	Mo $\delta(C_\alpha)$	W $\delta(H_\alpha)$ (J_{HW}, Hz)	W $\delta(C_\alpha)$ (J_{CH}, Hz)
CH_2-t-Bu	9.50	255.0	6.74 (15)	247.2 (102)
Cl	11.71[a]		8.83 (16)	261.0 (114)
OAd	11.71	275.7	8.86 (15)[c]	253.11 (110)
$OCMe_3$	11.63	275.9	8.80 (14)	253.6 (106)
OR_{F3}			8.88 (16)	256.0 (109)
OR_{F6}	11.90	283.6	9.00 (15)	259.2 (115)
$OCH(CF_3)_2$	11.80	284.5	8.96 (15)[b]	
OR_{F9}	12.21		9.39 (15)[c]	263.3 (107)[c]
OAr	11.99	277.7	9.37 (16)	255.1 (116)
OC_6F_5	12.07	286.5	9.29 (15)	260.5 (105)
$(OC_6F_5)(PMe_3)$	13.3 (anti)	309.7 (anti)		
	10.8 (syn)	278.7 (syn)		

[a] See ref 14. [b] Prepared in situ. [c] See ref 10.

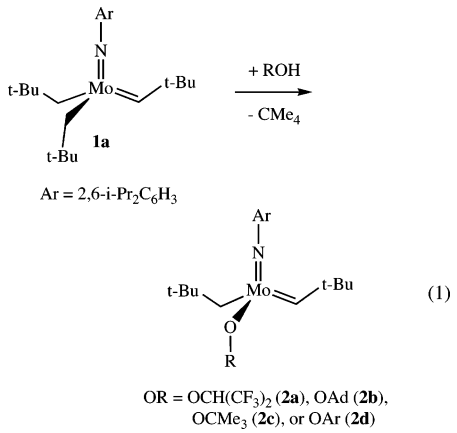
bimolecular fashion to yield species that contain a M═M bond that is not bridged by imido or alkoxide groups that are present.[10] These and other types of M═M species will be reported elsewhere. It should be noted that *N*-2,6-diisopropylphenyl (NAr) ligands are the most sterically demanding of the imido ligands available in compounds of this type today; three other imido ligands that have been reported in Mo(NR)(CHR′)(OR″)$_2$ compounds (inter alia) are *N*-2,6-dimethylphenyl, *N*-2,6-dichlorophenyl, and *N*-1-adamantyl.[2,15] Reactions analogous to those discussed here have not yet been carried out with complexes that contain these "smaller" imido ligands. Steric properties are so important that similar results could not be guaranteed, nor even expected.

Results

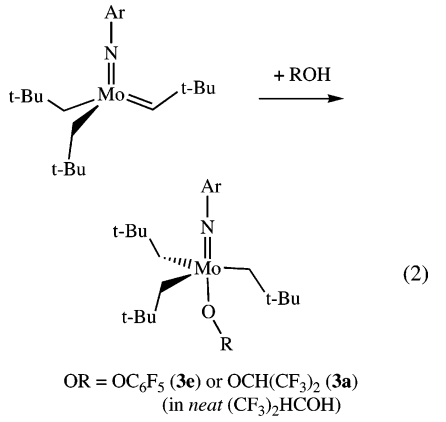
Syntheses of Molybdenum Complexes. Addition of 2 equiv of neopentylmagnesium chloride in ether to Mo(NAr)(CH-t-Bu)(triflate)$_2$(dme)[16] (Ar = 2,6-i-$Pr_2C_6H_3$, dme = 1,2-dimethoxyethane) in ether gives red-orange Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ (**1a**) in 93% isolated yield. Highly soluble **1a** can be prepared on a large scale and used in "crude" form for further reactions if pure Mo(NAr)(CH-t-Bu)(triflate)$_2$(dme) and accurately titrated Me_3CCH_2MgCl are employed. NMR spectra of **1a** in C_6D_6 show resonances for H_α at 9.50 ppm and for C_α at 255.0 ppm (J_{CH} = 108 Hz) for the alkylidene ligand and at 2.76 and 0.62 ppm ($\delta(CH_2)$; J_{HH} = 12 Hz) for the diastereotopic methylene protons in the neopentyl ligands. The neopentylidene chemical shifts are what one might expect for a high-oxidation-state syn alkylidene complex[1,17,18] and should be compared to $\delta(H_\alpha)$ 9.22 ppm and $\delta(C_\alpha)$ 249.3 ppm (J_{CH} = 106 Hz) in Mo(N-t-Bu)(CH-t-Bu)(CH_2-t-Bu)$_2$[11] and $\delta(H_\alpha)$ 6.74 ppm, $\delta(C_\alpha)$ 247.2 ppm (J_{CH} = 102 Hz), and $\delta(CH_2)$ 2.72 and 0.41 ppm in W(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$.[19] No alkylidene resonance for the anti isomer of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ could be found. Relevant proton and carbon NMR data for all compounds reported here are given in Table 1. Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ is relatively stable thermally. When a toluene solution is heated to 60 °C, 24% decomposition is observed after 1 day, 46% after 3 days, and 100% decomposition in 6 days. The nature of the decomposition product or products is (are) not known. Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ also has been prepared in 90% yield through addition of neopentyllithium to Mo(NAr)Np_3Cl at −30 °C.[14]

It is straightforward to prepare "mixed" alkyl/alkylidene compounds such as Mo(NAr)($CHCMe_2Ph$)(CH_2-t-Bu)$_2$ (**1b**) through alkylation of Mo(NAr)($CHCMe_2Ph$)(triflate)$_2$(dme) with neopentyl Grignard reagent and Mo(NAr)(CH-t-Bu)(CH_2CMe_2-Ph)$_2$ (**1c**) through alkylation of Mo(NAr)(CH-t-Bu)(triflate)$_2$-(dme) with neophyl Grignard reagent. There is no evidence for intramolecular α-proton migration that would lead to alkyl/alkylidene scrambling in any of these species in solution at room temperature. This type of intramolecular transfer or migration of an α-hydrogen from an alkyl α-carbon to an alkylidene α-carbon is known to be slow in all high-oxidation-state systems so far where it has been tested.[1,17,18] There is also no evidence that alkyl or alkylidene ligands transfer readily between metals.

Reactions between **1a** and the alcohols shown in eq 1 (Ad = 1-adamantyl) in benzene or toluene (22 °C, 0.1−0.2 M, up to 24 h reaction time) give isolable complexes of the type Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) (**2a**−**d**), which we will call the type **B** product. The product of a reaction between **1a** and (t-BuO)$_3$SiOH is also an isolable, crystalline species that has been reported elsewhere.[20] We can confirm that AdOH or t-BuOH adds across a Mo−C bond directly, since addition of ROH to **1b** gives Mo(NAr)($CHCMe_2Ph$)(CH_2-t-Bu)(OR) exclusively.



In contrast, the reaction between **1a** and C_6F_5OH in benzene-d_6 or *neat* $(CF_3)_2CHOH$ at 22 °C gives the trineopentyl species **3e** or **3a** shown in eq 2 rapidly (minutes) and exclusively. We will call the trineopentyl species the type **A** product. (The results



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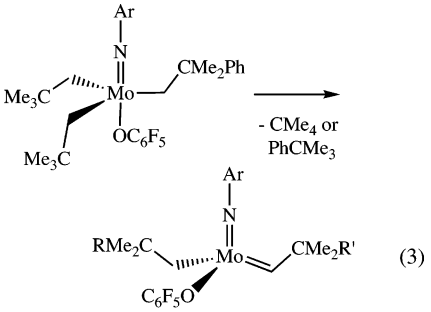
of alcohol addition are summarized in Table 2.) When solutions of **3e** or **3a** are heated to 60 °C over a period of hours, neopentane evolves smoothly to yield Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) species (OR = OC_6F_5 (**2e**), $OCH(CF_3)_2$ (**2a**)) quantitatively. The conversion of **3e** to **2e** was shown to be unimolecular with $k = 1.0 \times 10^{-4}$ s^{-1} in benzene-d_6 at 60 °C. (All rate constants for reactions of this type are gathered in Table 3.) Addition of C_6F_5OH to Mo(NAr)($CHCMe_2Ph$)(CH_2-t-Bu)$_2$ yields Mo(NAr)(CH_2CMe_2Ph)(CH_2-t-Bu)$_2$(OC_6F_5), which upon heating is transformed into a mixture of the expected three compounds (approximately 1:1:1) shown in eq 3, along with neopentane and *tert*-butylbenzene.



(3)

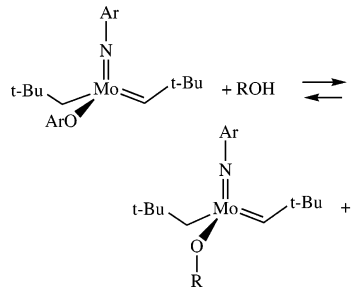
R = R' = Me; 36%
R = Ph; R' = Me; 31%
R = Me; R' = Ph; 33%

When $(CF_3)_3COH$ is added to **1a** in benzene-d_6, both Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)[$OC(CF_3)_3$] (**2f**) and Mo(NAr)(CH_2-t-Bu)$_3$[$OC(CF_3)_3$] (**3f**) are formed in a ratio of 1:1.2, while the reaction between Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ and *neat* $(CF_3)_3COH$ affords a mixture which contains >95% **3f** and <5% **2f**. Compound **3f** is converted into **2f** at 60 °C in benzene-d_6 with a rate constant of 7.2×10^{-4} s^{-1} (Table 3). Since the pK_a's of $HOC(CF_3)_3$ and HOC_6F_5 in water are similar (5.4 and 5.5**,** respectively),[21−23] these results demonstrate once again that α-hydrogen abstraction is accelerated in the electronically similar but sterically more crowded circumstance.[1,17,18] If $(CF_3)_3COH$ is added to Mo(NAr)($CHCMe_2Ph$)(CH_2-t-Bu)$_2$ in benzene-d_6, the alkylidene that is formed initially (~50% of the mixture) is only Mo(NAr)($CHCMe_2Ph$)(CH_2-t-Bu)[$OC(CF_3)_3$], thus confirming that in this case also a Mo−C bond is cleaved directly in competition with addition of $(CF_3)_3COH$ to the Mo=C bond to give Mo(NAr)(CH_2CMe_2Ph)(CH_2-t-Bu)$_2$[$OC(CF_3)_3$]. When Mo(NAr)(CH_2CMe_2Ph)(CH_2-t-Bu)$_2$[$OC(CF_3)_3$] decomposes, it yields all possible alkylidenes analogous to those shown in eq 3 in approximately a 1:1:1 ratio.

The complexes Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) (OR = OAd, $OCMe_3$, OAr) are relatively stable thermally. For example, when a 0.04 M solution of these complexes in toluene is heated at 60 °C for 11 days, less than 0.5% decomposition is observed. However, under identical conditions, Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) shows 54% decomposition in 11 days. The results of thermal decompositions of M(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) and related alkylidene complexes that lead to species that contain a M=M bond (M = Mo, W[24]) will be reported elsewhere.

Addition of 1.1 equiv of PMe_3 to Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) in benzene resulted in total disappearance of the parent alkylidene resonance. A proton NMR spectrum of the solution showed two new alkylidene resonances at 13.3 and 10.8 ppm in approximately a 1:1 ratio. On the basis of the chemical shift and coupling constant values, the resonance at 13.3 ppm (J_{CH} = 136.1 Hz) is assigned to the anti base adduct, while that at 10.8 ppm (J_{CH} = 107.7 Hz) is assigned to the syn base adduct.[25] The 13.3 ppm resonance is a doublet due to splitting by ^{31}P ($^3J_{HP}$ = 3.5 Hz). The ^{31}P NMR spectrum shows two resonances at −10.9 and −14.9 ppm that correspond to the phosphines in anti and syn base adducts. In the ^{13}C NMR spectrum in toluene, the alkylidene carbon resonance for the anti base adduct appears at 309.7 ppm and for the syn base adduct at 278.7 ppm. The anti to syn ratio does not change over a period of 3 days. When only 0.5 equiv of PMe_3 was added to Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) in benzene, a sharp anti base adduct resonance was observed along with a broad alkylidene proton resonance for the syn adduct and the base-free species at room temperature. Apparently trimethylphosphine is lost more readily from the syn adduct than from the anti adduct. A weaker coordination of a base to a syn isomer is a common finding for bis(alkoxide) imido alkylidene complexes.[2,15,17,18] The ready loss of trimethylphosphine from the syn isomer suggests that the constant ratio of anti to syn adducts is the result of ready equilibration of the two through loss of phosphine.

When Mo(NAr)(CH-*t*-Bu)(CH_2-*t*-Bu)(OAr) is treated with 1 equiv of ROH (OR = $OCMe_3$, OAd, OC_6F_5), a mixture containing both Mo(NAr)(CH-*t*-Bu)(CH_2-*t*-Bu)(OAr) and Mo(NAr)(CH-*t*-Bu)(CH_2-*t*-Bu)(OR) (and the expected alcohols) is obtained (eq 4). On the basis of the structure obtained for Mo-



(4)

Table 2. Formation of Complexes of the Types M(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) (B) and M(NAr)(CH_2-t-Bu)$_3$(OR) (A)

ROH	pK_a in H_2O[21−23]	Mo	W
Me_3COH	19.2	B	B
1-adamantanol	18	B	B
$Me_2(CF_3)COH$	12.6		B
2,6-i-$Pr_2C_6H_3OH$	11	B	B
$Me(CF_3)_2COH$	9.8	B	B
$(CF_3)_2CHOH$	9.3	A or B[a]	A + B
$(CF_3)_3COH$	5.4	A + B	A
C_6F_5OH	5.5	A	A

[a] Neat only.

Table 3. Rate Constants (10^{-5} s^{-1}) for Conversion of M(NAr)(CH_2-t-Bu)$_3$X into M(NAr)(CH_2-t-Bu)(CH-t-Bu)X in C_6D_6 at 60 °C (Except Where Noted)

	Mo	W
M(NAr)(CH_2-t-Bu)$_3$Cl	30[14]	11
M(NAr)(CH_2-t-Bu)$_3$(OR_{F9})	72	17
		43 (tol-d_8 at 80 °C)
M(NAr)(CH_2-t-Bu)$_3$(OC_6F_5)	10	7.0

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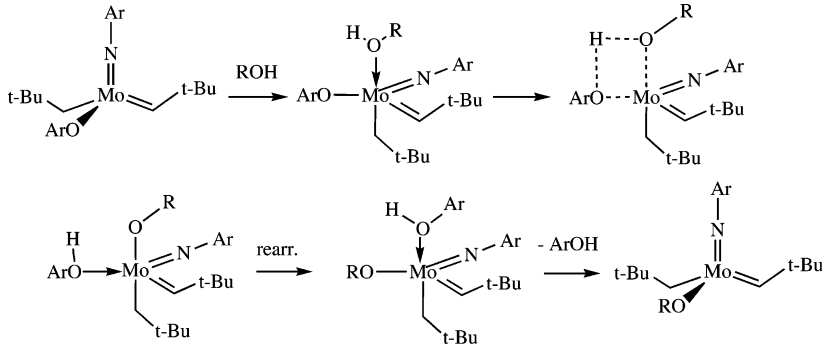
Scheme 1. Mechanism of Alkoxide Exchange at the Metal



(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)(PMe_3) (vide infra), we believe that the donor, in this case ROH, initially approaches the electrophilic metal center trans to the alkyl group: i.e., on the C_{ene}/N/O face (Scheme 1). The proton in theory could then migrate to the imido nitrogen, the alkylidene α-carbon atom, or the alkoxide oxygen. Reaction of Mo(NAr)($CHCMe_2Ph$)(CH_2CMe_3)$_2$ with ArOH in benzene-d_6 gave Mo(NAr)($CHCMe_2$-Ph)(CH_2CMe_3)(OAr) in situ, which upon treatment with 1 equiv of Me_3COH produced a mixture that contained Mo(NAr)-($CHCMe_2Ph$)(CH_2CMe_3)($OCMe_3$) and Mo(NAr)($CHCMe_2Ph$)-(CH_2CMe_3)(OAr) exclusively (along with ArOH and *tert*-butyl alcohol). If the proton were to migrate to the alkylidene α-carbon to give Mo(NAr)(CH_2-t-Bu)$_2$(OR)(OAr), that species either would be relatively stable toward loss of neopentane (W(NAr)-(O−t-Bu)$_2$(CH_2-t-Bu)$_2$ is known[19]) or would lose neopentane to yield Mo(NAr)(CHR′)(OR)(OAr), in which R′ would most likely be either t-Bu or CMe_2Ph. Migration of the proton to the imido group at a rate that is faster than migration to the alkoxide cannot be ruled out, although migration to the imido α-nitrogen would have to be readily reversible. (Proton migration to the imido group to give an amido complex has not been observed for NAr = *N*-2,6-diisopropylphenyl).[26] Rearrangement of the new five-coordinate species containing ArOH (Scheme 1), e.g., via a turnstile mechanism, would yield a ArOH adduct of the same type that was formed initially (or its enantiomer), from which ArOH would be lost to generate the new monoalkoxide species. (As we will show in the X-ray section below, the structure of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)(PMe_3) is highly distorted from any ideal; thus, a discussion of exchange in terms of ideal structures, rearrangements, etc. may not be valid.) The fact that even relatively acidic C_6F_5OH simply exchanges with OAr on the metal suggests that these catalysts may be "stable" in the presence of an alcohol functionality, at least if any mono(alkoxide) alkylidene that results from reaction with any alcohol in the system is itself reactive toward olefins.

When a 0.05 M solution Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)-(OC_6F_5) in benzene-d_6 was treated with 1 equiv of C_6F_5OH and the mixture was heated to 70 °C, what appears to be Mo(NAr)-(CH_2-t-Bu)(OC_6F_5)$_3$ (according to its proton NMR spectrum) is formed, along with unreacted Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)-(OC_6F_5). When 2 equiv of C_6F_5OH was employed in a similar experiment, Mo(NAr)(CH_2-t-Bu)(OC_6F_5)$_3$ was then formed in good yield. Therefore, we suspect that under forcing conditions, at least with a relatively small and acidic alcohol, Mo(NAr)-(CH-t-Bu)(OC_6F_5)$_2$ is formed either directly (through addition of C_6F_5OH to Mo−C) or indirectly (through addition of C_6F_5-OH to Mo=C followed by α abstraction) and that Mo(NAr)-(CH-t-Bu)(OC_6F_5)$_2$ reacts with C_6F_5OH rapidly to yield Mo-(NAr)(CH_2-t-Bu)(OC_6F_5)$_3$.

(26) Schrock, R. R.; Jamieson, J. Y.; Araujo, J. P.; Bonitatebus, P. J. J.; Sinha, A.; Lopez, L. P. H. *J. Organomet. Chem.* **2003**, *684*, 56.

X-ray Structures. The structure of Mo(NAr)(CH_2-t-Bu)$_3$-(OC_6F_5) is shown in Figure 1. Crystallographic details are given in Table 4 and selected distances and angles in Table 5. Mo-(NAr)(CH_2-t-Bu)$_3$(OC_6F_5) is a pseudo trigonal bipyramid with the imido and phenoxide ligands in the axial positions. The three equatorial neopentyl ligands are approximately 120° apart. All Mo−ligand distances are normal. The Mo−N−C(21) bond angle is 169.9(3)°, but the Mo−O−C(11) bond angle (163.0-(3)°) seems large for a phenoxide. It is not clear whether steric factors or π bonding from oxygen to Mo, or both, are responsible for the large Mo−O−C(11) angle. The Mo−C(31)−C(32), Mo−C(41)−C(42), and Mo−C(51)−C(52) angles are all near 120°, with no evidence of an α agostic CH interaction with the metal in preparation for α-hydrogen abstraction. Almost certainly, this TBP species rearranges into another in order that neopentane can be lost and Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)-(OC_6F_5) generated. In the species from which neopentane is lost, one neopentyl ligand must be in a relatively more crowded environment, with another neopentyl ligand approximately 90° to it that behaves as the leaving group.

The structure of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)[OSi(O-t-Bu)$_3$][20] (Tables 4 and 6; Figure 2) is typical of pseudotetrahedral species of this type.[1,17] The structure shows extensive disorder, in which only the Mo atom is not involved. (See the Experimental Section for a discussion of the disorder.) Only the major component of the disorder is shown in Figure 2, although both sets of selected bond lengths and angles are listed in Table 6. The neopentylidene ligand in each molecule has a syn orientation in which the *tert*-butyl group points toward the imido nitrogen. The Mo−C(1) bond lengths (1.831(3) and 1.860(6) Å) and Mo−C(1)−C(2) bond angles (146.5(4) and 151.5(8)°) are typical for syn isomers. The neopentyl ligands appear to be normal, with Mo−C(6) distances of 2.144(5) and 2.259(6) Å and Mo−C(6)−C(7) angles of 118.1(5) and 116.6(6)°. Perhaps the largest differences between the two molecules are the Mo−

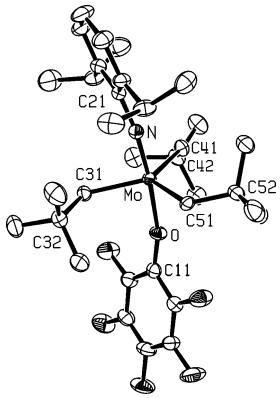


Figure 1. Thermal ellipsoid drawing of Mo(NAr)(CH_2-t-Bu)$_3$-(OC_6F_5).

Table 4. Crystal Data and Structure Refinement Details for Mo(NAr)(CH_2-t-Bu)$_3$(OC_6F_5), Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)[OSi(O-t-Bu)$_3$], [Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)]$_2$, and Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)(PMe_3)[a]

	Mo(NAr)(CH_2-t-Bu)$_3$(OC_6F_5)	Mo(NAr)(CH-t-Bu)-(CH_2-t-Bu)[OSi(O-t-Bu)$_3$]	[Mo(NAr)(CH-t-Bu)-(CH_2-t-Bu)(OC_6F_5)]$_2$	Mo(NAr)(CH-t-Bu)-(CH_2-t-Bu)(OC_6F_5)-(PMe_3)
identification code	03254	05165	04051	04088
empirical formula	$C_{33}H_{50}F_5MoNO$	$C_{34}H_{65}MoNO_4Si$	$C_{56}H_{76}F_{10}Mo_2N_2O_2$	$C_{31}H_{47}F_5MoNOP$
formula wt	667.68	675.90	1191.07	671.61
temp (K)	193(2)	100(2)	194(2)	194(2)
cryst syst	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
unit cell dimens				
a (Å)	10.2823(7)	9.7654(5)	11.0135(14)	11.0422(6)
b (Å)	17.4374(11)	11.4342(5)	11.2803(14)	17.2364(9)
c (Å)	18.7360(12)	18.8010(8)	13.7273(17)	18.4223(9)
α (deg)	90	97.7880(10)	106.623(2)	90
β (deg)	92.240(2)	97.465(2)	98.447(2)	105.176(2)
γ (deg)	90	108.6840(10)	111.854(2)	90
V (Å^3)	3356.7(4)	1936.44(15)	1453.8(3)	3484.0(3)
Z	4	2	1	4
calcd density (Mg/m^3)	1.321	1.159	1.360	1.318
abs coeff (mm^{-1})	0.443	0.402	0.503	0.485
F(000)	1400	728	616	1400
cryst size (mm^3)	0.26 × 0.21 × 0.16	0.20 × 0.20 × 0.07	0.20 × 0.16 × 0.12	0.16 × 0.13 × 0.13
θ range (deg)	1.60−27.48	1.11−29.13	1.62−28.26	1.65−25.68
index ranges	$-12 \le h \le 12$	$-13 \le h \le 13$	$-13 \le h \le 14$	$-13 \le h \le 12$
	$-20 \le k \le 20$	$-15 \le k \le 15$	$-14 \le k \le 12$	$-20 \le k \le 12$
	$-22 \le l \le 12$	$-25 \le l \le 25$	$-14 \le l \le 18$	$-21 \le l \le 21$
no. of rflns collected	20 925	42 470	9217	20 039
no. of indep rflns (R(int))	7666 (0.0689)	10 424 (0.0283)	6454 (0.0211)	6423 (0.0466)
completeness to $\theta = 29.13°$ (%)	99.5	99.8	89.6	99.9
abs cor	semiempirical	semiempirical	semiempirical	semiempirical
max and min transmission	0.9325 and 0.8934	0.9724 and 0.9239	0.9421 and 0.9061	0.9396 and 0.9264
no. of data/restraints/params	7666/19/401	10 424/1389/750	6454/3/344	6423/126/416
goodness of fit on F^2	1.122	1.106	1.062	1.042
final R indices ($I > 2\sigma(I)$)				
R1	0.0722	0.0442	0.0471	0.0575
wR2	0.1211	0.1133	0.1215	0.1535
R indices (all data)				
R1	0.1122	0.0485	0.0521	0.0703
wR2	0.1318	0.1165	0.1264	0.1630
largest diff peak and hole (e Å^{-3})	0.732 and −1.285	1.642 and −0.559	1.965 and −0.807	1.667 and −0.809

[a] In all cases the wavelength was 0.710 73 Å and the refinement method was full-matrix least squares on F^2.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Mo(NAr)(CH_2-t-Bu)$_3$(OC_6F_5)

Mo−N(1)	1.747(3)	Mo−C(41)	2.140(4)
Mo−O(1)	2.006(2)	Mo−C(51)	2.126(4)
Mo−C(31)	2.145(4)		
N(1)−Mo−O(1)	174.34(14)	C(51)−Mo−C(31)	121.33(16)
N(1)−Mo−C(31)	89.92(16)	C(51)−Mo−C(41)	116.75(17)
N(1)−Mo−C(41)	92.87(16)	Mo−N(1)−C(21)	169.9(3)
N(1)−Mo−C(51)	94.68(16)	Mo−O(1)−C(11)	163.0(2)
O(1)−Mo−C(31)	84.51(14)	Mo−C(31)−C(32)	121.3(3)
O(1)−Mo−C(41)	90.91(14)	Mo−C(41)−C(42)	126.1(3)
O(1)−Mo−C(51)	87.36(14)	Mo−C(51)−C(52)	121.5(3)
C(41)−Mo−C(31)	121.37(17)	Mo−O−C(11)	162.9(2)

Table 6. Selected Bond Lengths (Å) and Angles (deg) for Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)[OSi(O-t-Bu)$_3$]

	molecule 1	molecule 2
Mo−N(1)	1.725(5)	1.753(11)
Mo−C(1)	1.831(3)	1.860(6)
Mo−O(1)	1.973(3)	1.842(4)
Mo−C(6)	2.144(5)	2.259(6)
N(1)−Mo−C(1)	106.8(4)	109.5(8)
N(1)−Mo−O(1)	125.1(4)	126.3(8)
N(1)−Mo−C(6)	103.1(4)	98.1(8)
C(1)−Mo−O(1)	109.13(13)	114.3(3)
C(1)−Mo−C(6)	98.11(17)	92.7(3)
O(1)−Mo−C(6)	111.15(17)	109.0(2)
C(7)−C(6)−Mo	118.1(5)	116.6(6)
Mo−N(1)−C(11)	158.5(9)	165.4(18)
Mo−C(1)−C(2)	146.5(4)	151.5(8)
Mo−O(1)−Si(1)	134.5(2)	148.8(3)

O(1)−Si(1) angles of 134.5(2) and 148.8(3)°. We ascribe these variations to subtle differences in steric crowding in the two molecules.

An X-ray study of [Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)]$_2$ shows it to be a centrosymmetric dimeric species in which the phenoxide unsymmetrically bridges two metals (Tables 4 and 7; Figure 3). Each phenoxide is covalently bound to one metal and behaves as a donor toward the other. The donor interaction takes place roughly trans to the alkylidene ligand (C(1)−Mo−O(1A) = 158.76(10)°) at a typical distance (Mo−O(1A) = 2.3509(19) Å). Formation of an adduct in which the base is trans to the alkylidene ligand has been observed in various base adducts through NMR spectroscopy,[25] although structures of such species have been elucidated recently.[27] The neopentylidene has the syn orientation with normal bond lengths and angles (Mo−C(1) = 1.912(3) Å and Mo−C(1)−C(2) = 143.9(2)°). The imido ligand is normal. This is a rare example of a dimeric form of a pseudotetrahedral high-oxidation-state imido alkylidene species, although other species that contain a relatively small alkoxide and a neopentylidene or neophylidene ligand almost certainly could form analogous dimeric species in the

(27) Schrock, R. R.; Gabert, A. J.; Singh, R.; Hock, A. S. *Organometallics* **2005**, *24*, 5058.

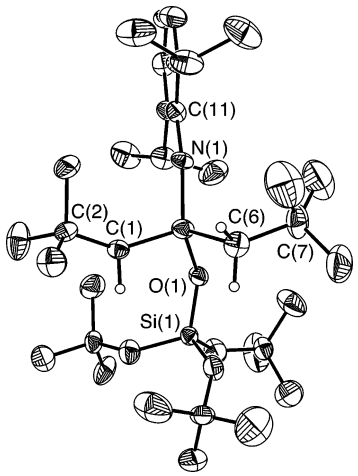


Figure 2. Thermal ellipsoid drawing of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)[OSi(O-t-Bu)$_3$].

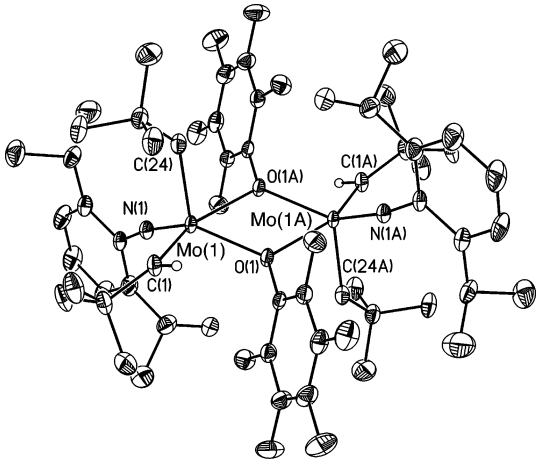


Figure 3. Thermal ellipsoid drawing of [Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)]$_2$.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for [Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)]$_2$

Mo(1)−N(1)	1.727(2)	Mo(1)−O(1)	2.1112(19)
Mo(1)−C(1)	1.912(3)	Mo(1)−O(1A)	2.3509(19)
Mo(1)−C(24)	2.139(3)		
C(1)−Mo(1)−O(1)	93.42(11)	N(1)−Mo(1)−O(1)	135.69(10)
O(1)−Mo(1)−C(24)	114.79(10)	C(6)−O(1)−Mo(1A)	119.31(16)
N(1)−Mo(1)−C(1)	100.63(12)	N(1)−Mo(1)−O(1A)	98.24(9)
C(12)−N(1)−Mo(1)	168.2(2)	Mo(1)−O(1)−Mo(1A)	113.89(8)
N(1)−Mo(1)−C(24)	104.00(12)	C(1)−Mo(1)−O(1A)	158.76(10)
Mo(1)−O(1)−C(6)	126.71(16)	O(1A)−Mo(1)−C(24)	85.02(10)
C(1)−Mo(1)−C(24)	99.69(13)	O(1)−Mo(1)−O(1A)	66.11(8)
C(2)−C(1)−Mo(1)	143.9(2)		

solid state but simply have not been crystallographically characterized. "Ate" species are also known when the alkoxide is small; for example, addition of 3 equiv of $LiOCH(CF_3)_2$ to Mo(NAd)($CHCMe_2Ph$)($OTf)_2$(DME)[28] (Ad = 1-adamantyl) in diethyl ether yields off-white, crystalline, pentane-soluble Li(DME)Mo(NAd)($CHCMe_2Ph$)[$OCH(CF_3)_2$]$_3$.[29]

The structure of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)(PMe_3) (Tables 4 and 8; Figure 4) is a distorted trigonal bipyramid in which trimethylphosphine is approximately trans to the neopentyl ligand (C(6)−Mo(1)−P(1) = 154.63(11)°); the neopentylidene, imido, and alkoxide ligands are all located in "equatorial" positions. The alkylidene ligand was found in two orientations (syn and anti) in a ratio of ~70:30, a circumstance not encountered in compounds of this type before. This disorder was refined with the help of restraints on the thermal parameters while setting the total occupancy to unity. The hydrogen atom on the major isomer was located in the difference map and refined using distance restraints. The H atom on the minor isomer was included on its geometrically calculated position and refined using a riding model. None of the bond lengths and angles is unusual, with one exception: The Mo(1)−P(1) bond length (2.5680(11) Å) is relatively long, which suggests that trimethylphosphine is relatively weakly bound and should be relatively labile, as found experimentally. In the syn form

Table 8. Selected Bond Lengths (Å) and Angles (deg) for Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)(PMe_3)

Mo(1)−N(1)	1.737(3)	Mo(1)−O(1)	2.051(3)
Mo(1)−C(1)	1.881(8)	Mo(1)−C(6)	2.199(4)
Mo(1)−C(1A)	1.96(3)	Mo(1)−P(1)	2.5680(10)
N(1)−Mo(1)−C(1)	113.0(3)	C(1)−Mo(1)−P(1)	93.8(3)
N(1)−Mo(1)−C(1A)	93.5(6)	C(1A)−Mo(1)−P(1)	93.8(7)
N(1)−Mo(1)−O(1)	134.93(15)	O(1)−Mo(1)−C(6)	81.76(13)
N(1)−Mo(1)−C(6)	102.37(13)	O(1)−Mo(1)−P(1)	73.84(9)
N(1)−Mo(1)−P(1)	90.34(10)	C(2)−Mo(1)−P(1)	154.63(11)
C(1)−Mo(1)−O(1)	110.0(3)	Mo(1)−N(1)−C(17)	162.5(3)
C(1)−Mo(1)−C(1A)	19.6(6)	Mo(1)−O(1)−C(11)	141.7(3)
C(1A)−Mo(1)−O(1)	128.7(6)	Mo(1)−C(6)−C(7)	126.1(3)
C(1)−Mo(1)−C(6)	101.0(3)	Mo(1)−C(1)−C(2)	149.6(7)
C(1A)−Mo(1)−C(6)	107.0(7)	Mo(1)−C(1A)−C(2A)	134(2)

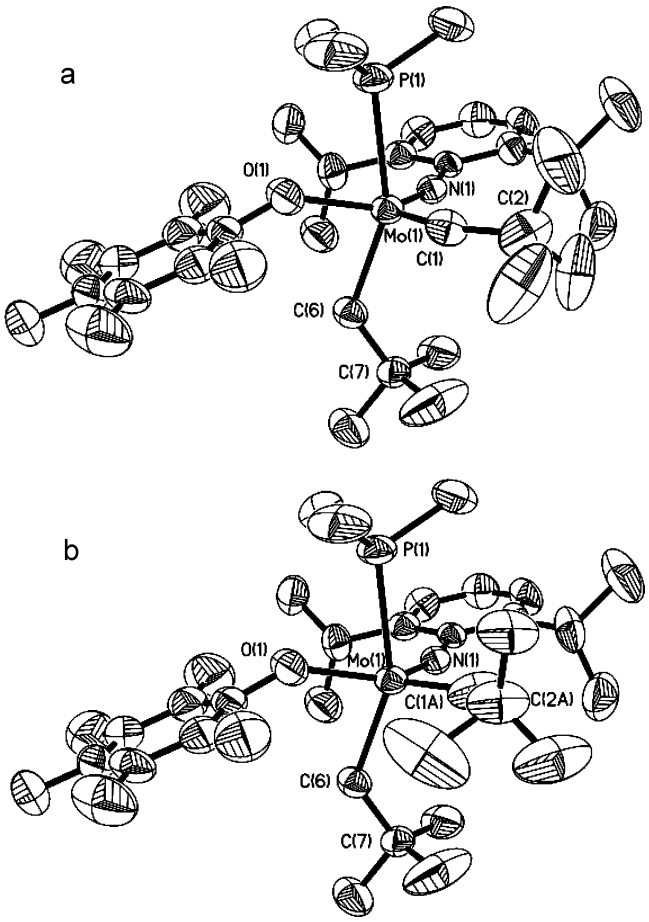


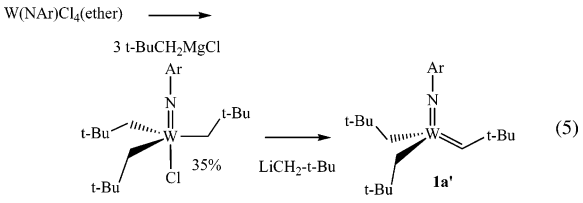
Figure 4. Thermal ellipsoid drawings of (A, top) *syn*-Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)(PMe_3) and (B, bottom) *anti*-Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)(PMe_3).

(28) Oskam, J. H.; Fox, H. H.; Yap, K. B.; McConville, D. H.; O'Dell, R.; Lichtenstein, B. J.; Schrock, R. R. *J. Organomet. Chem.* **1993**, *459*, 185.

(29) Schrock, R. R.; Luo, S.; Lee, J. C. J.; Zanetti, N. C.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3883.

the Mo−C(1) bond length is 1.881(8) Å and the Mo−C(1)−C(2) bond angle is 149.6(7)°. In the anti form the Mo−C(1A) bond length is 1.96(3) Å and the Mo−C(1A)−C(2A) bond angle is 137(2)°. Each is typical of a syn or anti isomer. The angle between the two α-carbon atoms in the two neopentylidene ligands in the two different isomers is 19.6(6)°. Therefore, angles at Mo for the two isomers differ slightly: e.g., N(1)−Mo−C(1) = 113.0(3)° (syn), while N(1)−Mo−C(1A) = 93.5(6)° (anti). It is striking that the structures of two species that differ so little are maintained in solution: i.e., distinct syn and anti adducts are observed in NMR spectra (vide supra).

Syntheses of Tungsten Complexes. W(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ is a known compound that has been synthesized in six steps from WCl_6 (WCl_6 → $WOCl_4$ → W(NAr)Cl_4(ether) → W(NAr)(O-t-Bu)$_2Cl_2$ → W(NAr)(O-t-Bu)$_2$(CH_2-t-Bu)$_2$ → W(NAr)(CH-t-Bu)Cl_2(dme) → W(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$).[19] W(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ also may be prepared through alkylation of W(NAr)(CH-t-Bu)(OTf)$_2$(dme).[19] A third method of synthesis is to treat W(NAr)Cl_4(ether) with 4 equiv of LiCH_2-t-Bu. So far, in our hands W(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ obtained by the third method has been isolated only as a red-brown oil, even though its proton NMR spectrum showed it to be essentially pure. Alkylation of W(NAr)Cl_4(ether) with 4 equiv of neopentylmagnesium chloride in ether led to a mixture of W(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ and W(NAr)(CH_2-t-Bu)$_3$Cl that could not be separated through recrystallization. However, if only 3 equiv of neopentylmagnesium chloride in ether are employed in pentane at −78 °C, then W(NAr)(CH_2-t-Bu)$_3$Cl can be isolated in pure form, but only in 35% yield (eq 5). The



(5)

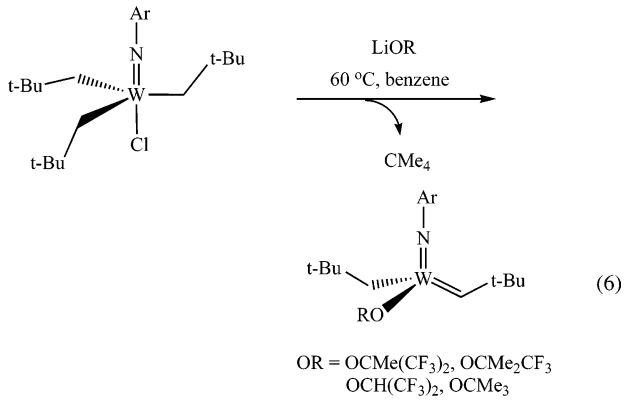
relatively low yield is largely a consequence of the high solubility of W(NAr)(CH_2-t-Bu)$_3$Cl in common organic solvents, which thereby complicates its separation from other highly soluble products of the reaction (e.g. W(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$). The proton NMR spectrum of W(NAr)(CH_2-t-Bu)$_3$Cl suggests a pseudo-trigonal-bipyramidal structure, with three equivalent equatorial neopentyl groups, analogous to the structure of W(NAr)(CH_2-t-Bu)$_3$(OC_6F_5) shown in Figure 1. Further alkylation of W(NAr)(CH_2-t-Bu)$_3$Cl with LiCH_2-t-Bu then gives the desired W(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ as a yellow-orange powder in quantitative yield (eq 5). Despite the low yield of isolated W(NAr)(CH_2-t-Bu)$_3$Cl prepared in this manner, and therefore the relatively high consumption of the neopentyl source (neopentyl chloride), this four-step synthesis (WCl_6 → $WOCl_4$ → W(NAr)Cl_4(ether) → W(NAr)(CH_2-t-Bu)$_3$Cl → W(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$) is relatively facile; the first two steps are essentially quantitative and can be carried out on a large scale. This synthesis is analogous to the reported synthesis of W(NPh)(CH-t-Bu)(CH_2-t-Bu)$_2$ from W(NPh)(CH_2-t-Bu)$_3$Cl.[30]

As found for the analogous molybdenum complex, W(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ reacts with 1 equiv of alcohol in pentane or benzene at room temperature to give two types of products, W(NAr)(CH_2-t-Bu)$_3$(OR) (type **A**) and W(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) (type **B**). As shown in Table 2, the nature of the product obtained correlates roughly with the acidity of the alcohol used and approximately mirrors the results obtained for Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$. Among the alcohols screened for this reaction, and under the conditions employed, only $(CF_3)_2$CHOH gave a mixture of products **A** and **B**.

Heating solutions of W(NAr)(CH_2-t-Bu)$_3$OR (OR = OC(CF_3)$_3$, OC_6F_5) at 60 °C in benzene or toluene gave W(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) species, a process that is analogous to that shown for the Mo species in eq 2. It should be noted that W(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) was obtained in good yields only by heating *dilute* solutions (<0.05 M) of W(NAr)(CH_2-t-Bu)$_3$(OC_6F_5). Attempts to isolate W(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) by heating progressively more concentrated solutions of W(NAr)(CH_2-t-Bu)$_3$(OC_6F_5) gave progressively higher percentages of [W(NAr)(CH_2-t-Bu)(OC_6F_5)]$_2$, the bimolecular decomposition product of W(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5).[10]

Interestingly, heating a solution of W(NAr)(CH_2-t-Bu)$_3$Cl gave W(NAr)(CH-t-Bu)(CH_2-t-Bu)Cl, which has been obtained only as an oil. Its ^{1}H and ^{13}C NMR spectra in C_6D_6 show a singlet at 8.83 ppm (J_{HW} = 16 Hz) and a doublet at 261.0 ppm (J_{CH} = 114 Hz, J_{CW} = 171 Hz), respectively.

With the synthesis of W(NAr)(CH_2-t-Bu)$_3$Cl, a third route to W(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) became accessible, e.g., the reaction between W(NAr)(CH_2-t-Bu)$_3$Cl and a lithium alkoxide to give W(NAr)(CH_2-t-Bu)$_3$(OR) followed by heating to give W(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) (eq 6). In this manner



(6)

W(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes with OR = $OCMe_2CF_3$, $OCMe(CF_3)_2$, $OCH(CF_3)_2$, $OCMe_3$ were prepared. W(NAr)(CH-t-Bu)(CH_2-t-Bu)($OCMe_3$), W(NAr)(CH-t-Bu)(CH_2-t-Bu)($OCMe_2CF_3$), and W(NAr)(CH-t-Bu)(CH_2-t-Bu)[$OCMe(CF_3)_2$] were isolated as yellow powders, while W(NAr)(CH-t-Bu)(CH_2-t-Bu)[$OC(H)(CF_3)_2$] was obtained only as a red oil. The W(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes prepared using this method are identical in all respects with those of the samples obtained from the reaction between W(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ and ROH.

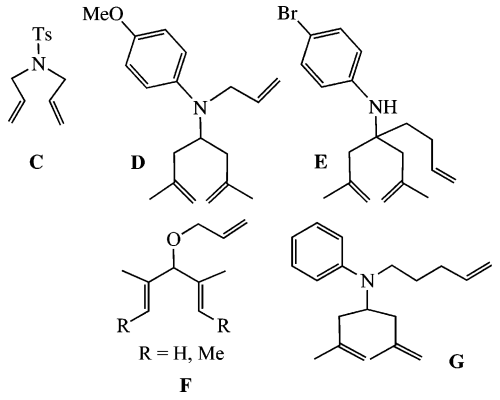
Metathesis Activity. We were interested in whether M(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) species would metathesize olefins. We now know that many M(NAr)(CHR′)(CH_2-t-Bu)(OR) species that are formed when M(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) reacts with an internal olefin such as 3-hexene are unstable toward bimolecular decomposition to yield M═M-bonded species in which the neopentyl group is intact.[10] Therefore, we felt that the neopentyl group should survive at least some metathesis reactions. Although this initial exploration of metathesis activity is relatively qualitative, it is important to establish some initial benchmarks.

Complexes of the type Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) (**2b**−**e**) are catalysts for various ring-closing metathesis reac-

(30) Pedersen, S. F.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 7483.

tions. Ring-closing of diallyl ether with either **2b** or **2c** is slow and incomplete. However, both **2d** (OR = OAr) and **2e** (OR = OC_6F_5) are relatively efficient, with 92% conversion in 6 min with 5% loading at 13.6 mM concentration of catalyst in C_6D_6. However, **2e** appears to be relatively short-lived; a second 20 equiv was not metathesized rapidly when added to the first reaction mixture. However, when an additional 20 equiv was added after 15 min to the first reaction mixture involving 5% **2d**, it was converted to product in 91% yield in ~1 h. Therefore, **2d** appears to be the most efficient catalyst for diallyl ether under these conditions.

Ring-closings of the amine substrates **C**, **D**,[31] and **E**[32] by **2d** and **2e** (3.0−4.2 M (5%) in C_6D_6) were also fast, being complete in 5−30 min in C_6D_6 at room temperature. However, the



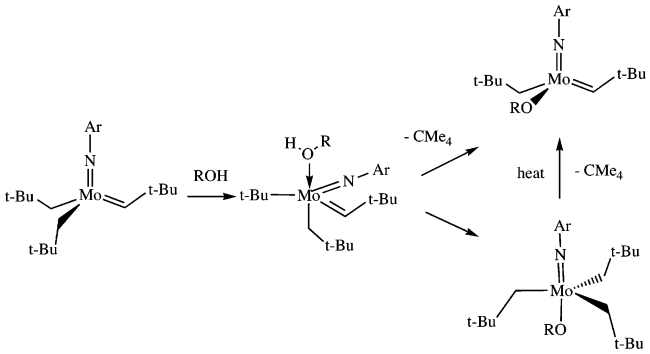
reaction involving substrate **E** in the case of **2e** went to only 85% completion, presumably as a consequence of decomposition of intermediates.

Similar results were observed with analogous tungsten catalysts. Only the $OC(CF_3)_3$ and OAr catalysts ring-closed diallyl ether efficiently in 20 min (5 mol % loading) in C_6D_6 (0.01 M; 5%); the yields are 24% when OR = $OCMe_3$, 35% for OR = $OCMe_2CF_3$, 57% for OR = $OCMe(CF_3)_2$, 95% for OR = $OC(CF_3)_3$, 43% for OR = OC_6F_5, and 96% for OR = OAr. W(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ is virtually inactive, while W(NAr)(CH-t-Bu)(CH_2-t-Bu)Cl (10% loading) yielded only 5% product in 20 min. The pentafluorophenoxide system again apparently is highly active, but intermediates also decompose rapidly in a bimolecular fashion to yield [W(NAr)(CH_2-t-Bu)-(OC_6F_5)]$_2$,[10] according to proton NMR spectra.

W(NAr)(CH-t-Bu)(CH_2-t-Bu)[$OC(CF_3)_3$] and W(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAr) were employed in ring closings of substrates **C**, **D**, **F**,[33] and **G**[31] (5% in benzene). The reactions were >95% complete in 20 min at room temperature. In all cases an additional 20 equiv of substrate was not metathesized when added to the first completed reaction, even upon heating.

The same general trend in reactivity was observed for the metathesis of *cis*-2-pentene by tungsten catalysts (5 mol % in benzene). Catalyst activity varied in the order OR = OAr ≈ $OC(CF_3)_3$ > $OCMe(CF_3)_2$ > $OCMe_2CF_3$ > $OCMe_3$. Using 5 mol % catalyst, equilibrium was achieved within 20 min at room temperature when OR = OAr, $OC(CF_3)_3$ and 120 min when OR = $OCMe(CF_3)_2$. Equilibrium was not established within a period of 1 day at 25 °C using catalysts where OR = $OCMe_2$-CF_3, $OCMe_3$, only 50% and 30% conversion being observed,

Scheme 2. Mechanism of Alcohol Addition to Dineopentyl Alkylidene Imido Species



respectively. Again, bimolecular decomposition of the intermediate alkylidenes is a likely problem, although that remains to be proven.

Discussion

The results reported here suggest that alcohols can add cleanly to M(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ and related species (M = Mo, W) to yield either M(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) or M(NAr)(CH_2-t-Bu)$_3$(OR) and that the latter can be transformed into the former upon heating (Scheme 2). Whether the alcohol adds to the M=C or M−C bond varies dramatically with the size and pK_a value of the alcohol and the conditions under which the reaction is run (e.g., in benzene or neat alcohol). In general, the higher the pK_a value of the alcohol, the more readily it adds to the M−C bond. It is not clear to us why this should be the case, nor can we assume that the imido group is innocent in such reactions. This selectivity recently has allowed the synthesis of well-defined analogues of Mo(NAr)(CH_2-t-Bu)(CH_2-t-Bu)-(OR) species on the surface of silica in which the silanols (Si_{surf}-OH) are relatively isolated from one another: i.e., Mo(NAr)-(CH_2-t-Bu)(CH_2-t-Bu)(OSi_{surf}).[20] These surface-supported species show olefin metathesis activities that appear to be higher than those of a homogeneous analogue.

There are some parallels between the reactions reported here and those that involve Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)$_2$.[6] The reaction between Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)$_2$ and a silica surface produces a Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)(OSi_{surf}) species that has been deduced to form via addition of Si_{surf}OH to both the Re−C and Re=C bonds (followed by rapid α abstraction under the conditions employed);[3,34] no addition of Si_{surf}OH to the neopentylidyne ligand took place. The Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)(OSi_{surf}) species is an active olefin metathesis catalyst at room temperature. In solution Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)$_2$ was shown to react with Ph_3SiOH over a period of 12 h at room temperature to yield Re(C-t-Bu)-(CH-t-Bu)(CH_2-t-Bu)($OSiPh_3$) as a 10:1 mixture of syn and anti isomers.[34] It is also known that HX (X^- = $C_6F_5O^-$, $CF_3SO_3^-$, BF_4^-) reacts with Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)$_2$ rapidly in solution to give Re(C-t-Bu)(CH_2-t-Bu)$_3$X species, which upon subsequent treatment with L (L = py, CH_3CN, CD_3OD, THF) yield neopentane and Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(L)$_n$X (*n* = 1−3) species.[35]

The preliminary metathesis results by catalysts of this type are encouraging. It is especially striking to note that M(NAr)-(CH-t-Bu)(CH_2-t-Bu)$_2$ species are virtually inactive for metath-

(31) Dolman, S. J.; Sattely, E. S.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **2002**, *124*, 6991.
(32) Dolman, S. J.; Schrock, R. R.; Hoveyda, A. H. *Org. Lett.* **2003**, *5*, 4899.
(33) Alexander, J. B.; La, D. S.; Cefalo, D. R.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1998**, *120*, 4041.
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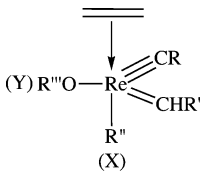
esis, while M(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) species can be highly active (OR = OAr, $OC(CF_3)_3$, OC_6F_5), although they also can be short-lived, especially for OR = OC_6F_5. Detailed investigations of the various steps in the metathesis reactions, as well as the stability of intermediates, clearly must be carried out in order to establish (inter alia) how stable the intermediate alkylidenes and metallacyclobutanes are. We already know that several of these neopentylidene species react readily with internal olefins to yield homochiral or heterochiral dimeric species of the type $[M(NAr)(CH_2\text{-t-Bu})(OR)]_2$. At this stage we presume that dimers form through bimolecular decomposition of new and relatively small alkylidenes (e.g., propylidene).[10] However, we cannot discount at this stage that metallacyclobutane[17] rearrangement to an olefin is at least a competitive mode of "reduction" of the metal. We aim to establish the stability of metallacyclobutane species in future studies.

Another factor that could prove to be important in the long run is that most of the (possibly interconverting) metallacyclobutane intermediates that one can imagine as intermediates in these reactions are "electronically" unsymmetric at the metal: i.e., unsymmetric as a consequence of different elements being present in α positions, not unsymmetric merely as a consequence of asymmetry in the ligands themselves, as in a chiral diolate derivative. This stands in contrast to both trigonal-bipyramidal (TBP) and square-pyramidal (SP) metallacyclobutane complexes derived from bis(alkoxide) species.[17] An electronically unsymmetric metallacyclobutane may more rapidly eject an olefin than one that is not electronically unsymmetric.

Relevant to the results described here are some recent DFT-(B3PW91) calculations on systems of the type Re(C-t-Bu)(CH-t-Bu)(X)(Y), which are isoelectronic with Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) species when X = alkyl and Y = alkoxide.[36] A key step in the reaction of Re(CR)(CHR′)(alkyl)(alkoxide) species with an olefin is a distortion toward a trigonal monopyramid in which the alkyl ligand is in the axial position. This distortion prepares the metal for a weak interaction with an olefin (see **H**, where the incoming olefin is ethylene), and facile



H

formation of a heavily distorted TBP metallacyclobutane intermediate with an "axial" alkylidyne and "axial" alkoxide. When both X and Y are alkoxides, then the barrier for addition of the olefin and conversion to the metallacycle is higher by several kilocalories. When both X and Y are alkyls, the barrier is higher still. These calculations help explain why addition of Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)$_2$ to silica(700) yielded a well-defined Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)(OSi_{surf}) species, which has an unusually high metathesis activity,[7,37] while homogeneous Re(C-t-Bu)(CH-t-Bu)$(OR)_2$ species are relatively poor metathesis catalysts.[38,39] Although bimolecular decomposition reactions are essentially eliminated on the surface at the mild temperatures employed, it seems plausible that there is not a linear relationship between the electron-withdrawing ability of the two atoms attached to the metal and reactivity and that "distorted" and, in particular, *unsymmetric* (at the metal) species have shallower energy surfaces leading to and from a metallacyclobutane intermediate. This is potentially an important new insight in olefin metathesis reactions with well-defined species.

Experimental Section

General Considerations. All operations were performed under a nitrogen atmosphere in the absence of oxygen and moisture in a Vacuum Atmospheres glovebox or using standard Schlenk procedures. The glassware, including NMR tubes, were flame- and/or oven-dried prior to use. Ether, pentane, toluene, and benzene were degassed with dinitrogen and passed through activated alumina columns. Dimethoxyethane was distilled from a dark purple solution of sodium benzophenone ketyl and degassed three times by freeze−pump−thaw techniques. Dichloromethane was distilled from CaH_2 under N_2. All dried and deoxygenated solvents were stored over 4 Å molecular sieves in a nitrogen-filled glovebox. ^{1}H, ^{13}C, and ^{19}F NMR spectra were acquired at room temperature (unless otherwise noted) using Varian Mercury (^{1}H, 300 MHz; ^{13}C, 75 MHz; ^{19}F, 282 MHz) and Varian Inova (^{1}H, 500 MHz; ^{13}C, 125 MHz) spectrometers and referenced to the residual protio solvent resonances or external C_6F_6 (−163.0 ppm). Elemental analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. Mo(NAr)(CH-*t*-Bu)$(OTf)_2$(dme) was prepared as described in the literature.[16] Neopentylmagnesium chloride and neophylmagnesium chloride were titrated against propanol in a THF solution using 1,10-phenanthroline as an indicator immediately prior to use. All other chemicals were procured from commercial sources and used as received. W(NAr)$Cl_4(Et_2O)$, W(NAr)(CH_2-t-Bu)$_3$(OC_6F_5), W(NAr)(CH_2-t-Bu)$_3$Cl, W(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$, W(NAr)(CH-t-Bu)(CH_2-t-Bu)[$OC(CF_3)_3$], and W(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAd) were prepared as described in the literature.[10,19]

Mo(NAr)(CH-*t*-Bu)(CH_2-*t*-Bu)$_2$ (1a). A solution (23.5 mL) of 1.85 M neopentylmagnesium chloride solution in ether was added dropwise to a prechilled solution of 15.88 g (21.76 mmol) of Mo(NAr)(CH-*t*-Bu)$(OTf)_2$(dme) in 270 mL of ether. The color changed from yellow to deep red-orange as a precipitate formed. The mixture was stirred for 12 h, ether was removed in vacuo, and the residue was extracted with pentane. The pentane extract was filtered through Celite, and the pentane was removed in vacuo to afford 9.75 g of a red powder (93% yield) that was pure enough for further reactions: ^{1}H NMR (C_6D_6) δ 9.50 (s, 1, C*H*CMe$_3$, J_{CH} = 108 Hz), 7.05 (br s, 3, Ar *H*), 3.99 (sept, 2, C*H*Me$_2$), 2.76 (d, 2, CH*H*CMe$_3$), 1.30 (d, 12, CH*Me*$_2$), 1.22 (s, 18, CH_2C*Me*$_3$), 1.17 (s, 9, CHC*Me*$_3$), 0.62 (d, 2, C*H*HCMe$_3$); ^{13}C NMR (C_6D_6) δ 255.0 (*C*HCMe$_3$), 154.2 (C_{ipso}), 144.8 (C_{ortho}), 127.2 (C_{para}), 123.5 (C_{meta}), 77.9 (*C*H_2CMe$_3$), 47.1 (CH*C*Me$_3$), 34.8 (CH_2C*Me*$_3$), 34.1 (CH_2*C*Me$_3$), 32.7 (CHC*Me*$_3$), 29.2 (*C*HMe$_2$), 24.9 (CH*Me*$_2$). Anal. Calcd for $C_{27}H_{49}$NMo: C, 67.05; H, 10.21; N, 2.90; Mo, 19.84. Found: C, 66.79; H, 10.08; N, 3.18; Mo, 20.04.

Mo(NAr)(CHMe$_2$Ph)(CH_2-*t*-Bu)$_2$ (1b). A 4.27 mmol reaction was carried out in a manner virtually identical with that above for **1** to give 1.52 g (65%) of the product as a red-orange powder: ^{1}H NMR (C_6D_6) δ 9.69 (s, 1, C*H*CMe$_2$Ph), 7.44 (d, 2, CHCMe$_2$*Ph*), 7.16 (m, 2, CHCMe$_2$*Ph*), 7.05 (br s, 3, Ar *H*), 3.97 (sept, 2, C*H*Me$_2$), 2.71 (d, 2, CH*H*CMe$_3$), 1.54 (s, 6, CHC*Me*$_2$Ph), 1.26 (d, 12, CH*Me*$_2$), 1.14 (s, 18, CH_2C*Me*$_3$), 0.74 (d, 2, C*H*HCMe$_3$); ^{13}C NMR (C_6D_6) δ 252.8, 154.2, 149.5, 145.0, 128.7, 127.4, 126.6, 126.5, 123.6, 78.3, 52.9, 34.5, 33.9, 32.1, 28.8, 24.5. Anal. Calcd for $C_{32}H_{51}$NMo: C, 70.43; H, 9.42; N, 2.57. Found: C, 70.25; H, 9.27; N, 2.56.

Mo(NAr)(CH-*t*-Bu)(CH_2CMe$_2$Ph)$_2$ (1c). This complex was obtained as a deep red oil from the reaction between Mo(NAr)(CH-*t*-Bu)$(OTf)_2$(dme) and neophylmagnesium chloride in a pro-

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cedure analogous to the preparation of **1a**: ^{1}H NMR (C_6D_6) δ 8.85 (s, 1, C*H*CMe$_3$), 7.38−7.16 (overlapping resonances, 10, CHCMe$_2$*Ph*), 7.07 (br s, 3, Ar *H*), 4.00 (sept, 2, C*H*Me$_2$), 2.65 (d, 2, CH*H*CMe$_2$Ph), 1.44−0.99 (33, CHC*Me*$_2$Ph, CH*Me*$_2$, CH$_2$C*Me*$_3$), 0.63 (d, 2, C*H*HCMe$_2$Ph); ^{13}C NMR (C_6D_6) δ 259.4, 154.2, 152.8, 149.7, 145.1, 129.1, 127.3, 126.6, 126.4, 123.7, 77.1, 46.6, 40.6, 34.7, 34.1, 32.9, 32.1, 31.8, 29.6, 28.6, 24.6, 24.1.

Mo(NAr)(CH-*t*-Bu)(CH$_2$-*t*-Bu)[OCH(CF$_3$)$_2$] (2a). Perfluoro-2-propanol (97 μl, 0.91 mmol, 2.2 equiv) was added to a solution of 200 mg (0.41 mmol) of Mo(NAr)(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_2$ in 5 mL of toluene. The reaction mixture was stirred for 16 h and stored at −20 °C to afford red-orange crystals in 52% yield (124 mg): ^{1}H NMR (C_6D_6) δ 11.80 (s, 1, C*H*CMe$_3$, J_{CH} = 116 Hz), 6.99 (m, 3, Ar *H*), 4.55 (sept, 1, (CF$_3$)$_2$C*H*O), 3.73 (sept, 2, C*H*Me$_2$), 2.42 (d, 1, CH*H*CMe$_3$, J_{CH} = 13 Hz), 2.16 (d, 1, C*H*HCMe$_3$), 1.27 (d, 6, CH*Me*$_2$), 1.24 (d, 6, CH*Me*$_2$), 1.18 (s, 9, CH$_2$C*Me*$_3$), 1.11 (s, 9, CHC*Me*$_3$); ^{13}C NMR (C_7D_8) δ 284.5, 153.2, 146.5, 123.7, 58.7, 48.1, 33.7, 32.7, 31.9, 31.4, 30.5, 28.4, 24.6, 23.8; ^{19}F NMR (C_6D_6) δ −74.97 (CF$_3$), −75.17 (CF$_3$). Anal. Calcd for $C_{25}H_{39}NOF_6Mo$: C, 51.81; H, 6.78; N, 2.42. Found: C, 51.64; H, 6.79; N, 2.36.

Mo(NAr)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(OAd) (2b). Mo(NAr)(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_2$ (520 mg, 1.07 mmol) was placed in a 25 mL scintillation vial, and 1-adamantanol (163 mg, 1.07 mmol) and 6 mL of pentane were added. The reaction mixture was stirred overnight at room temperature. Removing the volatiles in vacuo afforded an orange-yellow powder that could be washed with cold pentane to obtain a fine yellow powder, yield 502 mg (83%): ^{1}H NMR (C_6D_6) δ 11.71 (s, 1, C*H*CMe$_3$, J_{CH} = 115 Hz), 7.07 (br s, 3, Ar *H*), 3.99 (sept, 2, C*H*Me$_2$), 2.38 (d, 1, CH*H*CMe$_3$, J_{CH} = 13 Hz), 2.12 (d, 1, C*H*HCMe$_3$), 2.05 (br s, 3, C*H*), 1.92 (m, 6, C*H*$_2$), 1.51 (s, 6, C*H*$_2$), 1.29 (m, 30, CH*Me*$_2$, CH$_2$C*Me*$_3$, CHC*Me*$_3$); ^{13}C NMR (C_6D_6) δ 275.7, 153.2, 145.3, 126.6, 123.6, 79.0, 52.7, 46.7, 36.7, 34.5, 32.2, 31.9, 29.2, 24.9, 24.1. Anal. Calcd for $C_{32}H_{53}NOMo$: C, 68.18; H, 9.48; N, 2.48. Found: C, 68.03; H, 9.32; N, 2.55.

Mo(NAr)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(OCMe$_3$) (2c). Mo(NAr)(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_2$ (1 g, 2.07 mmol) was placed in a 100 mL heavy-walled pressure vessel along with a magnetic stirrer, and 1.1 equiv of t-BuOH (169 mg, 2.28 mmol) and 10 mL of toluene were added to it. Stirring the reaction mixture at 80 °C for 2 h caused the color of the solution to change from red to dark yellow-orange. Removing toluene in vacuo resulted in a dark orange oil that was dissolved in a minimum amount of pentane and stored at −20 °C to give 0.97 g (96%) of a yellow-brown powder: ^{1}H NMR (C_6D_6) δ 11.63 (s, 1, C*H*CMe$_3$, J_{CH} = 115 Hz), 7.05 (br s, 3, Ar *H*), 3.96 (sept, 2, C*H*Me$_2$), 2.38 (d, 1, CH*H*CMe$_3$, J_{CH} = 13 Hz), 2.09 (d, 1, C*H*HCMe$_3$), 1.35 (s, 9, OC*Me*$_3$), 1.29 (d, 12, CH*Me*$_2$), 1.26 (s, 9, CH$_2$C*Me*$_3$), 1.21 (s, 9, CHC*Me*$_3$); ^{13}C NMR (C_6D_6): δ 275.9, 153.1, 145.3, 126.6, 123.5, 79.8, 52.7, 46.7, 34.5, 32.9, 32.2, 29.2, 24.9, 24.1. Anal. Calcd for $C_{26}H_{47}NOMo$: C, 64.31; H, 9.76; N, 2.88. Found: C, 64.38; H, 9.69; N, 2.81.

Alternatively, when a pentane solution of **1a** and 1.1 equiv of t-BuOH is stirred for 12 h, the product is obtained quantitatively as an orange powder.

Mo(NAr)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(OAr) (2d). To Mo(NAr)(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_2$ (500 mg, 1.03 mmol) in 5 mL of pentane was added 210 μL (203 mg, 1.13 mmol) of 2,6-diisopropylphenol, and the reaction mixture was stirred for 12 h at room temperature. After the solvent was removed, a red waxy material was obtained. This waxy material was dissolved in a minimum amount of pentane, and the solution was stored at −20 °C; a red-orange solid (575 mg) was filtered off (95% yield): ^{1}H NMR (C_6D_6) δ 11.99 (s, 1, C*H*CMe$_3$, J_{CH} = 116 Hz), 7.07 (d, 2, Ar *H*), 7.00 (t, 1, Ar *H*), 6.97 (br s, 3, Ar *H*), 3.55 (sept, 4, C*H*Me$_2$), 2.72 (d, 1, CH*H*CMe$_3$, J_{CH} = 13 Hz), 2.35 (d, 1, C*H*HCMe$_3$), 1.34−1.13 (overlapping signals, 42, CH*Me*$_2$, CH$_2$C*Me*$_3$, CHC*Me*$_3$); ^{13}C NMR (C_6D_6): δ 277.7, 159.1, 153.4, 145.6, 137.2, 127.3, 123.8, 123.5, 122.4, 59.5, 47.7, 33.9, 32.2, 30.0, 28.4, 24.7, 24.0, 23.2. Anal. Calcd for $C_{34}H_{55}NOMo$: C, 69.24; H, 9.40; N, 2.37. Found: C, 69.26; H, 9.29; N, 2.32.

Mo(NAr)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(OC$_6$F$_5$) (2e). A solution of Mo(NAr)(CH$_2$-*t*-Bu)$_3$(OC$_6$F$_5$) (1.4 g, 2.10 mmol) in 11 mL of toluene was stirred and heated at 60 °C for 8 h in a heavy-walled pressure vessel. The light yellow color of the solution darkened. Toluene was removed in vacuo to leave an orange-yellow solid. Washing this solid with cold pentane over a fine-porosity frit gave 1.01 g (81%) of a pale yellow powder: ^{1}H NMR (C_6D_6) δ 12.07 (s, 1, C*H*CMe$_3$, J_{CH} = 116 Hz)), 6.99 (m, 3, Ar *H*), 3.75 (sept, 2, C*H*Me$_2$), 2.61 (d, 1, CH*H*CMe$_3$, J_{CH} = 13 Hz), 2.22 (d, 1, C*H*HCMe$_3$), 1.24 (d, 12, CH*Me*$_2$), 1.22 (s, 9, CH$_2$C*Me*$_3$), 1.08 (s, 9, CHC*Me*$_3$); ^{13}C NMR (C_6D_6) δ 286.5, 153.3, 146.5, 123.8, 60.4, 48.2, 33.6, 32.8, 31.2, 30.7, 29.9, 24.5, 23.8; ^{19}F NMR (C_6D_6) δ −160.83 (d, 2), −165.07 (t, 2), −169.83 (t, 1). Anal. Calcd for $C_{28}H_{38}NOF_5Mo$: C, 56.47; H, 6.43; N, 2.35. Found: C, 56.28; H, 6.28; N, 2.40.

Mo(NAr)(CH$_2$-*t*-Bu)$_3$[OCH(CF$_3$)$_2$] (3a). A few drops of neat (CF$_3$)$_2$CHOH were added to 20 mg (0.04 mmol) of Mo(NAr)(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_2$; a yellow suspension formed immediately. The reaction mixture was stirred for 10 min and the excess alcohol removed in vacuo to yield the product quantitatively: ^{1}H NMR (C_6D_6) δ 6.98 (m, 3, Ar *H*), 5.22 (sept, 1, (CF$_3$)$_2$C*H*O), 4.06 (sept, 2, C*H*Me$_2$), 2.51 (s, 6, C*H*$_2$CMe$_3$), 1.24 (d, 12, CH*Me*$_2$), 1.13 (s, 27, CH$_2$C*Me*$_3$); ^{13}C NMR (C_6D_6) δ 146.4, 124.6, 123.7, 82.9, 58.6, 47.9, 37.1, 33.7, 31.9, 31.3, 30.4, 29.7, 25.6, 24.6, 23.8.

Mo(NAr)(CH$_2$-*t*-Bu)$_3$(OC$_6$F$_5$) (3e). Pentafluorophenol (761 mg, 4.14 mmol) was added all at once to a solution of Mo(NAr)(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_2$ (2 g, 4.14 mmol) in 10 mL of pentane. Stirring the reaction mixture for 6 h and removing the volatile components in vacuo afforded an orange-brown solid, which was washed with cold pentane to get a bright yellow solid (1.80 g, 66%). Alternatively, the orange-brown solid can be dissolved in a minimum amount of pentane and the solution stored at −20 °C for 24 h to afford a yellow crystalline material in 75% yield: ^{1}H NMR (C_6D_6) δ 6.99 (br s, 3, Ar *H*), 4.14 (sept, 2, C*H*Me$_2$), 2.73 (s, 6, C*H*$_2$CMe$_3$), 1.28 (d, 12, CH*Me*$_2$), 1.14 (s, 27, CH$_2$C*Me*$_3$); ^{13}C NMR (C_6D_6) δ 150.5, 128.7, 124.9, 123.8, 84.5, 36.9, 33.7, 31.9, 29.9, 28.9, 25.7, 24.5, 23.7; ^{19}F NMR (C_6D_6) δ −157.39 (d, 2), −165.53 (t, 2), −171.94 (t, 1). Anal. Calcd for $C_{33}H_{50}NOF_5Mo$: C, 59.36; H, 7.55; N, 2.10; Mo, 14.37; F, 14.23. Found C, 59.40; H, 7.42; N, 2.12; Mo, 14.40; F, 14.16.

Mo(NAr)(CH$_2$-*t*-Bu)$_3$[OC(CF$_3$)$_3$] (3f). Neat (CF$_3$)$_3$COH was added to 20 mg (0.04 mmol) of Mo(NAr)(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_2$ to obtain a yellow-orange suspension immediately. Stirring the reaction mixture for 10 min and removing the excess alcohol yielded a yellow-orange solid almost quantitatively that contains <5% of **2f**: ^{1}H NMR (C_6D_6) δ 7.03 (m, 3, Ar *H*), 4.21 (sept, 1, C*H*Me$_2$), 2.84 (s, 6, C*H*$_2$CMe$_3$), 1.35 (d, 12, CH*Me*$_2$), 1.24 (s, 27, CH$_2$C*Me*$_3$); ^{13}C NMR (C_6D_6): δ 151.2, 150.3, 128.7, 125.1, 83.9, 37.9, 33.8, 31.1, 28.7, 25.5. 22.9.

Conversion of Mo(NAr)(CH$_2$-*t*-Bu)$_3$[OCH(CF$_3$)$_2$] (3a) into Mo(NAr)(CH-*t*-Bu)(CH$_2$-*t*-Bu)[OCH(CF$_3$)$_2$] (2a). Mo(NAr)(CH$_2$-*t*-Bu)$_3$[OCH(CF$_3$)$_2$] (20 mg) was dissolved in 0.6 mL of C_6D_6 in a J. Young NMR tube to give a yellow solution. Heating the tube to 60 °C overnight resulted in darkening of the color of the solution. The ^{1}H NMR spectrum showed that **3a** had been converted quantitatively into **2a**.

Mo(NAr)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(OC$_6$F$_5$)(PMe$_3$). Mo(NAr)(CH$_2$-*t*-Bu)$_3$(OC$_6$F$_5$) (200 mg, 0.34 mmol) was taken up in 2 mL of pentane, and 5 equiv of PMe$_3$ (174 μL, 1.68 mmol) was added to it via a microsyringe. Stirring for 2 h afforded a green suspension, from which volatiles were removed in vacuo to obtain a lime-lemon (green-yellow) solid in almost quantitative yield. Recrystallization in a minimum amount of pentane at −20 °C overnight afforded yellow crystals in 72% yield (162 mg): ^{1}H NMR (C_6D_6) δ 13.3 (d, J_{CH} = 136.1 Hz, $^3J_{HP}$ = 3.5 Hz, 1, *anti*-C*H*CMe$_3$), 10.8 (s, J_{CH}

= 107.7 Hz, 1, *syn*-C*H*CMe$_3$); ^{13}C NMR (toluene-d_8) δ 309.7, 278.7; ^{31}P NMR (C_6D_6) δ −10.9, −14.9.

Conversion of Mo(NAr)(CH$_2$-*t*-Bu)$_3$[OC(CF$_3$)$_3$] (3f) into Mo(NAr)(CH-*t*-Bu)(CH$_2$-*t*-Bu)[OC(CF$_3$)$_3$] (2f). A yellow solution was obtained when 20 mg of **3f** was dissolved in 0.6 mL of C_6D_6 in a J. Young NMR tube. Heating the tube to 60 °C overnight produced a darker solution whose ^{1}H NMR spectrum (C_6D_6) was consistent with the formation of **2f**: δ 12.21 (s, 1, C*H*CMe$_3$, J_{CH} = 116 Hz), 6.98 (m, 3, Ar *H*), 3.71 (sept, 2, C*H*Me$_2$), 2.54 (d, 1, CH*H*CMe$_3$, J_{CH} = 13 Hz), 2.18 (d, 1, C*H*HCMe$_3$), 1.21 (d, 6, CH*Me*$_2$), 1.24 (d, 6, CH*Me*$_2$), 1.15 (s, 9, CH$_2$C*Me*$_3$), 1.07 (s, 9, CHC*Me*$_3$).

General Method Employed for Metathesis Reactions. In all reactions involving diallyl ether, a ∼0.3 M solution of diallyl ether in C_6D_6 and 10 μL of anisole (an internal standard) were placed in a J. Young NMR tube and 5 mol % of the catalyst was then added. The tube was capped, and the solution was allowed to stand at room temperature. In other cases, 10 mg of the substrate was taken up in 0.5 mL of C_6D_6 followed by addition of 5 mol % of catalyst. Conversions were determined by ^{1}H NMR spectroscopy (500 MHz).

W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OC$_6$F$_5$). A solution of 2.00 g of W(NAr)(CH$_2$-t-Bu)$_3$(OC$_6$F$_5$) in ∼150 mL of benzene was heated at 60 °C for 12 h. After this time, the solution was concentrated to dryness. The product was then taken up in pentane and the solution filtered. Removal of volatiles in vacuo from the filtrate gave a yellow powder, which was collected on a frit, washed with cold pentane, and dried in vacuo to give 1.5 g (88% yield) of the product: ^{1}H NMR (C_6D_6) δ 9.29 (s, 1, J_{HW} = 15 Hz), 7.10 (m, 3), 3.76 (m, 2), 2.80 (d, 1, J_{HH} = 15 Hz), 2.34 (d, 1, J_{HH} = 15 Hz), 1.28 (d, 6), 1.26 (d, 6), 1.21 (s, 9), 1.14 (s, 9); ^{19}F NMR (C_6D_6) δ −160.0 (d, 2), −164.2 (t, 2), −167.3 (td, 1); ^{13}C NMR (C_6D_6) δ 260.5 (J_{CH} = 105 Hz, J_{CW} = 178 Hz), 152.5, 145.8, 145.2, 141.4, 139.5, 137.4, 135.3, 127.3, 123.5, 61.8 (J_{CW} = 123 Hz), 46.8, 34.0, 32.9, 29.6, 24.4, 23.7. Anal. Calcd for WNOC$_{28}$H$_{38}$F$_5$: C, 49.21; H, 5.60; N, 2.05. Found: C, 49.09, H, 5.51, N, 1.97.

W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)Cl. W(NAr)(CH$_2$-t-Bu)$_3$Cl (500 mg, 0.822 mmol) was dissolved in a minimum amount of benzene and heated at 60 °C for 8 h. The volatiles were then removed in vacuo to give a red oil which was pure by NMR: ^{1}H NMR (toluene-d_8, 500 MHz) δ 8.83 (s, 1, J_{HW} = 16 Hz), 7.05 (m, 3), 3.74 (m, 2), 2.84 (d, 1, J_{HH} = 15 Hz), 1.87 (d, 1, J_{HH} = 15 Hz), 1.26 (d, 6), 1.24 (d, 6), 1.19 (s, 9), 1.09 (s, 9); ^{13}C NMR (C_6D_6) δ 261.0 (J_{CH} = 114 Hz, J_{CW} = 171 Hz), 145.05, 127.55, 123.43, 71.84 (t) (J_{CW} = 117 Hz), 62.33, 47.32, 35.04, 33.90, 32.75, 29.35, 24.26, 23.98. Anal. Calcd for WNC$_{22}$H$_{38}$Cl: C, 49.31; H, 7.15; Cl, 6.62; N, 2.61. Found: C, 49.24, H, 7.09, Cl, 6.71; N, 2.68.

Representative Procedure for the Reaction between W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)$_2$ and ROH To Give the Corresponding W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OR). One equivalent of the alcohol was added to a solution of W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)$_2$ in pentane, and the resulting mixture was stirred for 8 h at room temperature. Removal of the solvent in vacuo gave the crude product, which may be recrystallized from pentane to give the pure compound.

Representative Procedure for the Reaction between W(NAr)(CH$_2$-t-Bu)$_3$Cl and LiOR To Give W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OR). To a solution of W(NAr)(CH$_2$-t-Bu)$_3$Cl in benzene was added as a solid 1 equiv of LiOR. The reaction mixture was stirred and heated at 60 °C overnight as it was being stirred. It was filtered through a bed of Celite, and the filtrate was concentrated to dryness to give the desired product.

W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OCMe$_3$). The product was obtained as a yellow powder in quantitative yield: ^{1}H NMR (C_6D_6, 500 MHz) δ 8.80 (s, 1, J_{HW} = 14 Hz), 7.17 (d, 2), 7.12 (t, 1), 3.95 (m, 2), 2.53 (d, 1, J_{HH} = 15 Hz), 2.16 (d, 1, J_{HH} = 15 Hz), 1.36 (s, 27), 1.34 (d, 6), 1.28 (d, 6); ^{13}C NMR (C_6D_6) δ 253.6 (J_{CH} = 106 Hz), 152.95, 144.28, 128.68, 125.63, 123.31, 82.10, 56.37 (J_{CW} = 122 Hz), 50.07, 45.74, 34.62, 33.81, 32.49, 32.35, 28.85, 24.67, 24.01. Anal. Calcd for C$_{26}$H$_{47}$NOW: C, 54.45; H, 8.26; N, 2.44. Found: C, 54.36, H, 8.18, N, 2.41.

W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)[OCMe$_2$(CF$_3$)]. The product was obtained as a yellow powder in quantitative yield: ^{1}H NMR (C_6D_6, 500 MHz) δ 8.88 (s, 1, J_{HW} = 16 Hz), 7.17 (d, 2), 7.13 (t, 1), 3.89 (m, 2), 2.59 (d, 1, J_{HH} = 15 Hz), 2.19 (d, 1, J_{HH} = 15 Hz), 1.43 (s, 3), 1.40 (s, 3), 1.35 (d, 6), 1.34 (d, 6), 1.26 (s, 9), 1.25 (s, 9); ^{19}F NMR (C_6D_6) −82.1 (s); ^{13}C NMR (C_6D_6) δ 256.05 (J_{CH} = 109 Hz, J_{CW} = 180 Hz), 152.64, 144.80, 128.68, 126.40, 126.13, 123.40, 81.91, 58.79 (J_{CW} = 122 Hz), 46.17, 34.81, 34.33, 33.42, 32.55, 28.95, 26.78, 25.56, 25.14, 24.74, 23.89. Anal. Calcd for C$_{26}$H$_{44}$F$_3$NOW: C, 49.77; H, 7.07; N, 2.23. Found: C, 49.62, H, 7.16, N, 2.27.

W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)[OCMe(CF$_3$)$_2$]. The product was obtained as a yellow powder in quantitative yield: ^{1}H NMR (C_6D_6, 500 MHz) δ 9.00 (s, 1, J_{HW} = 15 Hz), 7.08 (d, 2), 7.05 (t, 1), 3.75 (m, 2), 2.59 (d, 1, J_{HH} = 15 Hz), 2.16 (d, 1, J_{HH} = 15 Hz), 1.46 (s, 3), 1.28 (d, 6), 1.25 (d, 6), 1.16 (s, 9), 1.13 (s, 9); ^{19}F NMR (C_6D_6) δ −77.3 (q, 3) and −77.9 (q, 3); ^{13}C NMR (C_6D_6) δ 259.15 (J_{CH} = 115 Hz, J_{CW} = 180 Hz), 152.42, 145.23, 128.69, 127.05, 125.39, 123.50, 61.17 (J_{CW} = 123 Hz), 46.61, 34.80, 34.07, 33.07, 32.81, 29.05, 24.85, 23.81, 19.86. Anal. Calcd for C$_{26}$H$_{41}$F$_6$NOW: C, 45.83; H, 6.06; N, 2.06. Found: C, 46.04, H, 6.15, N, 2.18.

W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)[OC(H)(CF$_3$)$_2$]. The product was obtained as a red oil in quantitative yield: ^{1}H NMR (C_6D_6) δ 8.96 (s, 1, J_{HW} = 15 Hz), 7.05 (m, 3), 4.50 (m, 1), 3.70 (m, 2), 2.58 (d, 1, J_{HH} = 15 Hz), 2.13 (d, 1, J_{HH} = 15 Hz), 1.28 (d, 6), 1.26 (d, 6), 1.14 (s, 9), 1.12 (s, 9); ^{19}F NMR (C_6D_6) δ −74.0 (q, 3) and −74.3 (q, 3).

W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OAr). The product was obtained as a yellow-orange powder: ^{1}H NMR (C_6D_6, 500 MHz) δ 9.37 (s, 1, J_{HW} = 15 Hz), 7.06 (d, 2), 7.02 (t, 1), 6.97 (m, 3), 3.58 (m, 2), 3.52 (m, 2), 2.96 (d, 1), 2.31 (d, 1), 1.34 (s, 9), 1.30 (s, 9), 1.26 (d, 6), 1.21 (d, 6), 1.20 (d, 6), 1.03 (d, 6); ^{13}C NMR (C_6D_6) δ 255.15 (J_{CH} = 116 Hz), 158.44, 152.83, 150.80, 144.46, 137.52, 134.13, 126.33, 124.16, 123.82, 123.34, 123.21, 121.47, 117.91, 62.12 (J_{CW} = 123), 46.60, 34.13, 33.90, 29.68, 29.31, 25.56, 24.50, 23.10. Anal. Calcd for C$_{35}$H$_{59}$NOW: C, 60.60; H, 8.57; N, 2.02. Found: C, 60.48, H, 8.51, N, 2.04.

X-ray Structures. 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 Kα radiation (λ = 0.710 73 Å), performing φ- and ω-scans. All structures were solved by direct methods using SHELXS[40] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[41] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms (except the hydrogen atoms on carbon that binds directly to molybdenum in the structures of Mo(NAr)(CH$_2$-t-Bu)$_3$(OC$_6$F$_5$), Mo(NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OC$_6$F$_5$), and (NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OC$_6$F$_5$)(PMe$_3$), which have been taken from the difference Fourier synthesis and refined semi-freely with the help of distance restraints) were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups). Details of the data quality and a summary of the residual values of the refinements are given in Table 4.

The structure of Mo(NAr)(CH-t-Bu)(CH$_2$-t-Bu)[OSi(O-t-Bu)$_3$] shows extensive disorder, in which only the Mo atom is not involved. The NAr ligand displays a 64:36 disorder, corresponding to an approximate rotation about the Mo−N axis. All other nonmetal atoms are involved in a 56:44 disorder, also corresponding to an approximate rotation about the Mo−N axis. It would seem most

(40) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
(41) Sheldrick, G. M. SHELXL-97; Universität Göttingen, Göttingen, Germany, 1997.

likely that the nitrogen atom should not be disordered at all. However, the model improved significantly (both in the geometry and in the residual factors of the refinement) when the nitrogen position was split. The Mo atom may also be disordered (relatively high displacement parameters), but the fact that the two relative occupancies of the described disorders are refined to significantly different values speaks against a whole-molecule disorder. Thus, the Mo atom was refined as not disordered and the two disorders were treated as independent. They were refined with the help of similarity restraints on 1−2 and 1−3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. The ratios were refined freely, while the total occupancy of both components was constrained to unity. The hydrogen atoms on the carbon atoms that bind directly to the Mo atom (C1, C1A, C6, and C6A) have all been located in the difference Fourier synthesis and were refined semi-freely with the help of distance restraints.

Acknowledgment. We thank Dr. William M. Davis for collecting data for **3e**, members of the group of A. H. Hoveyda for gifts of metathesis substrates, and the National Science Foundation (Grant Nos. CHE-9988766 and CHE-0138495) for supporting this research.

Supporting Information Available: Tables and figures giving crystal data and structure refinement details, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters and additional views for Mo(NAr)(CH_2-*t*-Bu)$_3$(OC_6F_5), [Mo(NAr)(CH-*t*-Bu)(CH_2-*t*-Bu)(OC_6F_5)]$_2$, Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)[OSi(O-t-Bu)$_3$], and Mo(NAr)(CH-*t*-Bu)(CH_2-*t*-Bu)(OC_6F_5)(PMe_3). This material is available free of charge via the Internet at http://pubs.acs.org. Data for the four structures are also available to the public at http://www.reciprocalnet.org/. The identification code in Table 4 identifies each structure at this site.

OM050978A