Molybdenum Imido Alkylidene Metathesis Catalysts That Contain Electron-Withdrawing Biphenolates or Binaphtholates

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We have prepared new Mo(NR)(CHCMe$_2$Ph)(diolate) complexes (R = 2,6-*i*-Pr$_2$C$_6$H$_3$, 2,6-Me$_2$C$_6$H$_3$, 1-adamantyl, or 2-CF$_3$C$_6$H$_4$) that contain relatively electron-withdrawing binaphtholate (3,3′-bis(9-anthracenyl), 3,3′-bispentafluorophenyl, or 3,3′-bis(3,5-bis(trifluoromethyl)phenyl)) or biphenolate (3,3′-di-*tert*-butyl-5,5′-bistrifluoromethyl-6,6′-dimethyl-1,1′-biphenyl-2,2′-diolate) ligands. We also have prepared new monomeric Mo(NR)(CHCMe$_2$Ph)(2,5-dimethylpyrrolide)$_2$ complexes and have treated them with biphenols or binaphthols in order to prepare several Mo(NR)(CHCMe$_2$Ph)(diolate) species. In one case the new Mo(NR)(CHCMe$_2$Ph)(diolate) complexes could be prepared only through reaction of a binaphthol [3,3′-bis(pentafluorophenyl)binaphthol] with a bis(2,5-dimethylpyrrolide) complex. The pyrrolide approach can be employed either to isolate catalysts on a preparative scale or to generate catalysts *in situ*. Several simple preliminary ring-closing metathesis reactions show that the new complexes are catalytically competent.

Introduction

Complexes of the type M(NR)(CHR′)(OR″)$_2$ or M(NR)(CHR′)(diolate) (M = Mo or W) are established well-defined high oxidation state olefin metathesis catalysts[1] whose overall efficiencies depend dramatically upon the electronic and steric characteristics of the NR and OR″ or diolate groups. Operationally the most reactive M(NR)(CHR′)(OR″)$_2$ catalysts have been those with relatively strong electron-withdrawing alkoxides (e.g., hexafluoro-*tert*-butoxide) and sterically protected arylimido ligands (e.g., *N*-2,6-*i*-Pr$_2$C$_6$H$_3$). Catalysts that contain an enantiomerically pure diolate have been employed in a variety of asymmetric metathesis reactions in the last several years; examples are shown in Figure 1.[1a] Designing new homogeneous metathesis catalysts in the asymmetric family that contain new imido and alkoxide (or diolate) groups is a priority. Therefore, we decided to explore the possibility of preparing M(NR)(CHR′)(diolate) catalysts in which the biphenolate or binaphtholate ligands are more electron-withdrawing than those employed so far. In this paper we report several examples of new M(NR)(CHR′)(diolate) complexes of this type. In several cases syntheses involve addition of the biphenol or binaphthol to new, monomeric, bis(2,5-dimethylpyrrolide) complexes. The bis(2,5-dimethylpyrrolide) species should be compared with *dimeric* bispyrrolide species reported recently.[2] The use of bispyrrolide species as catalyst precursors avoids complications[3] in traditional catalyst syntheses in which triflate ligands are displaced by biphenolates or binaphtholates. In at least one synthesis reported here the bispyrrolide approach was the only one that was successful.

Results and Discussion

Synthesis of Electron-Withdrawing Binaphthols and Biphenols. The commercial availability of enantiopure binaphthol (BINOL) makes BINOL derivatives substituted in the 3 and 3′ positions an attractive class of enantiomerically pure diolate ligands.[4] The first ligand examined was a BINOL derivative with a 9-anthracenyl substituent in the 3 and 3′ positions. The 9-anthracenyl group combines a significant electron-withdrawing ability with significant steric bulk. In addition, we expected the low solubility of the ligand and catalysts that contain the ligand to facilitate isolation of Mo catalysts. Suzuki coupling of the known 3,3′-diiodo-2,2′-dimethoxy-1-binaphthyl[5] (**A**) and 9-anthracenylboronic acid (**B**),[6] followed by deprotection of the crude product using BBr_3 in CH_2Cl_2, afforded (*R*)-3,3′-bis-9-anthracenyl-BINOL (H_2[Binaph$_{Anth}$]) (Scheme 1). (All BINOL derivatives in this paper are enantiomerically pure and have the *R* configuration.) H_2[Binaph$_{Anth}$] has been claimed in a patent,[7] but no experimental details were provided.

The second ligand examined was a 3,3′-bis(pentafluorophenyl)-BINOL, (H_2[Binaph$_{C6F5}$]). Kumada- or Suzuki-type couplings are not applicable for the coupling reaction in this case since *ipso*-substitution on the electron-deficient aromatic system takes place instead. Therefore, we turned to fluoroborates as coupling partners in similar coupling reactions.[8] The coupling

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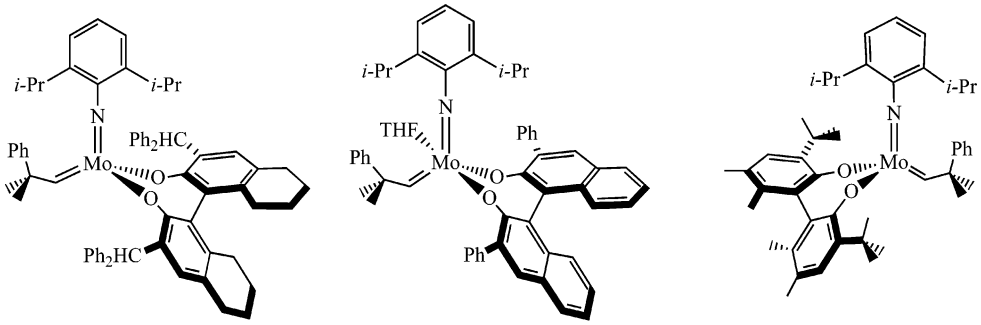
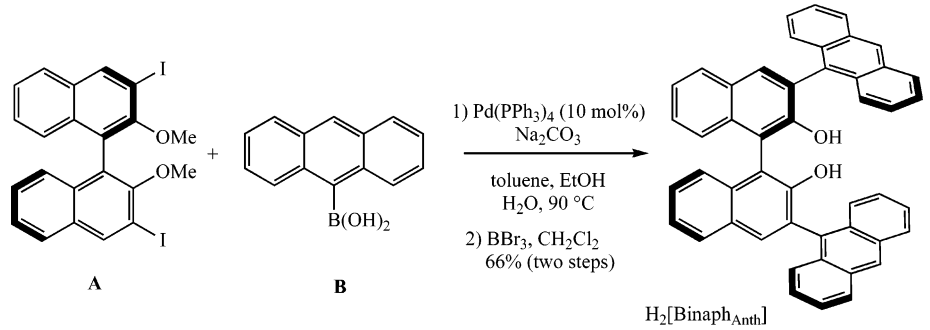
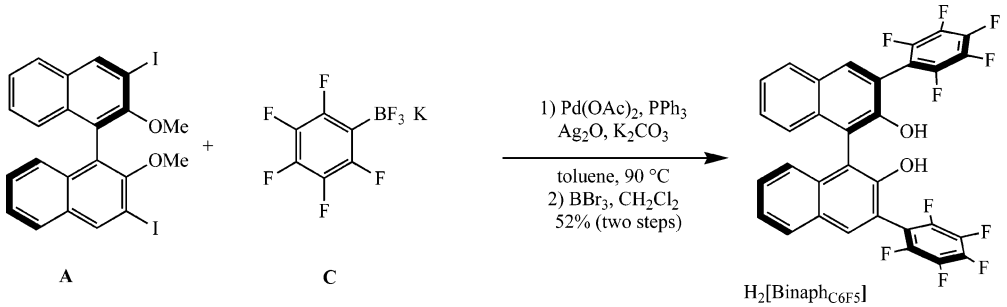


Figure 1. Examples of asymmetric molybdenum-based olefin metathesis catalysts.

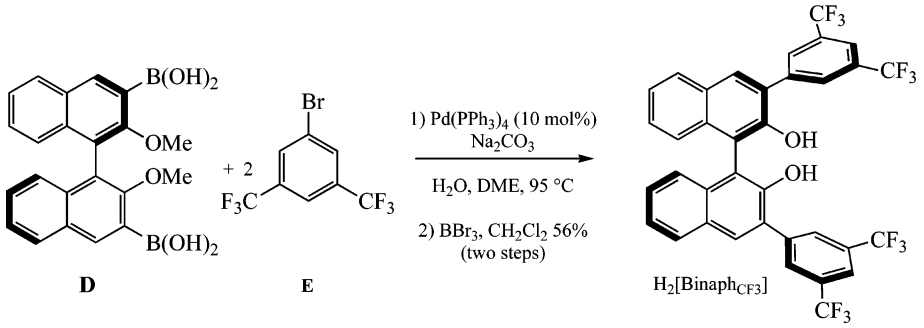
Scheme 1. Synthesis of (*R*)-3,3′-Bis-9-anthracenyl-BINOL (H_2[Binaph$_{Anth}$])



Scheme 2. Synthesis of (*R*)-3,3′-bis(pentafluorophenyl)-BINOL (H_2[Binaph$_{C6F5}$])



Scheme 3. Synthesis of (*R*)-3,3′-Bis(3,5-bis(trifluoromethyl)phenyl)-BINOL (H_2[Binaph$_{CF3}$])



of potassium trifluoro(pentafluorophenyl)borate (**C**) with 3,3′-diiodo-2,2′-dimethoxybinaphthyl catalyzed by palladium acetate in the presence of triphenyl phosphine afforded the desired H_2-[Binaph$_{C6F5}$] in 52% overall yield (Scheme 2). A report of the synthesis of this species appeared after we had completed our synthesis,[9] but no experimental details were provided.

The third BINOL derivative that we chose was 3,3′-bis(3,5-bis(trifluoromethyl)phenyl)-BINOL, H_2[Binaph$_{CF3}$].[10] Commercially available bromo-3,5-bis(trifluoromethyl)benzene (**E**) was treated with 2,2′-dimethoxybinaphthalene-3,3′-diboronic acid (**D**) under standard Suzuki conditions and deprotected *in situ* to give the desired ligand in 56% overall yield (Scheme 3). It was identical to the reported compound, which was prepared using a slightly different procedure.

A ligand that has yielded highly successful catalysts in ring-closing metathesis desymmetrizations has been the 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diolate ([Biphen]$^{2-}$) ligand. The synthesis of a related ligand having a trifluoromethyl group in the 5 and 5′ positions would provide the opportunity to study a significant electronic variation of the [Biphen]$^{2-}$ ligand with minimal change in the steric demands of the ligand.

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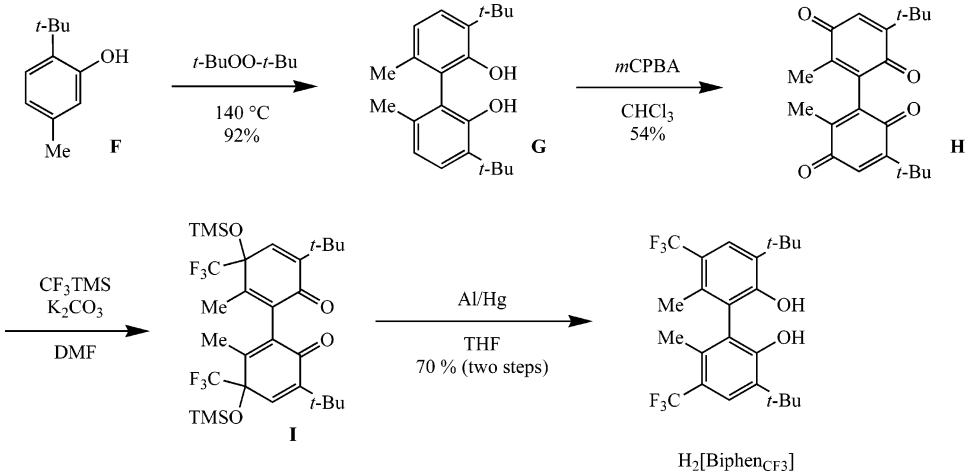
(10) Wu, T. R.; Shen, L.; Chong, J. M. *Org. Lett.* **2004**, *6*, 2701.

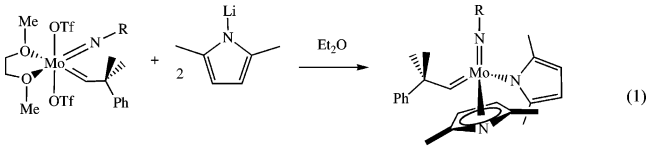
Scheme 4. Synthesis of *rac*-3,3′-Di-*tert*-butyl-5,5′-bistrifluoromethyl-6,6′-dimethyl-1,1′-biphenyl-2,2′-diol (H_2[Biphen$_{CF3}$])



The synthesis of 3,3′-di-*tert*-butyl-5,5′-bistrifluoromethyl-6,6′-dimethyl-1,1′-biphenyl-2,2′-diol (H_2[Biphen$_{CF3}$]) is depicted in Scheme 4. (The [Biphen$_{CF3}$]$^{2-}$ ligand is racemic in all procedures reported here.) The reaction between *tert*-butyl-*m*-cresol and di-*tert*-butyl peroxide afforded 3,3′-bis(*tert*-butyl)-6,6′-dimethylbiphenol (**G**), which was oxidized to the corresponding diquinone (**H**) using an excess of mCPBA. Treatment of **H** with Me_3SiCF_3 in DMF following a published procedure[11] produced the protected semiquinone (**I**). Upon treatment of **I** with amalgamated aluminum in a mixture of THF and water, 3,3′-di-*tert*-butyl-5,5′-bistrifluoromethyl-6,6′-dimethyl-1,1′-biphenyl-2,2′-diol (H_2[Biphen$_{CF3}$]) was obtained in 70% yield.

Synthesis of 2,5-Dimethylpyrrolide Complexes. We recently reported new [Mo(NR)(CHCMe$_2$R′)(C$_4$H$_4$N)$_2$]$_2$ species and noted that they react readily with various monoalcohols, binaphthols, and biphenols to yield Mo(NR)(CHCMe$_2$R′)(OR″)$_2$ or Mo(NR)(CHCMe$_2$R′)(diolate) complexes.[2] Preliminary experiments suggested that this method is a mild way to prepare a variety of catalysts from a single precursor through addition of a diol. However, the fact that 2 equiv of pyrrole are generated in the process leaves open the possibility that pyrrole may bind to the metal in the catalyst in question (although one might expect that it might be a relatively poor ligand) or otherwise complicate a subsequent metathesis reaction. Therefore, we became curious about the possibility of preparing what we expected would be monomeric 2,5-dimethylpyrrolide analogues and whether they too would serve as precursors to binaphtholate and biphenolate catalysts.

Addition of 2 equiv of lithium 2,5-dimethylpyrrolide to a diethyl ether solution of Mo(NR)(CHCMe$_2$Ph)(OTf)$_2$(DME) [R = 2,6-*i*-Pr$_2$C$_6$H$_3$ (Ar), 2,6-Me$_2$C$_6$H$_3$ (Ar′), 1-adamantyl (Ad), or 2-(CF$_3$)C$_6$H$_4$ (Ar$_F$)] produced Mo(NR)(CHCMe$_2$Ph)(2,5-Me$_2$NC$_4$H$_2$)$_2$ complexes in >80% yield (eq 1). Proton ^{1}H NMR spectra of **1a**−**1d** in C$_6$D$_6$ contain sharp alkylidene resonances at 13.30 ppm (**1a**), 13.19 ppm (**1b**), 12.94 ppm (**1c**), and 13.19 ppm (**1d**), but broad pyrrolide resonances at room temperature. At −80 °C, resonances were observed consistent with a molecule with no symmetry (two different pyrrolides) and a nonrotating diisopropyimido group; only one alkylidene resonance is observed. (See Supporting Information for variable-temperature NMR spectra.) We propose that the lowest energy species at this temperature is one in which one of the 2,5-pyrrolide ligands is bound in an η^5 fashion and the other is bound in an η^1 fashion, as shown in eq 1. The solid-state



(1)

structure of a related tungsten complex, W(NAr)(CHCMe$_3$)(2,5-Me$_2$NC$_4$H$_2$)$_2$,[12] shows it to have this structure. Carbon NMR spectra reveal alkylidene carbon resonances characteristic of *syn* isomers (J_{CH} = 120 Hz). We propose that at room temperature mirror symmetric Mo(NAr)(CHCMe$_2$Ph)(η^1-2,5-Me$_2$NC$_4$H$_2$)$_2$ is formed, which equilibrates the inequivalent pyrrolide ligands. Complexes **1a**−**1d** should be compared with the recently reported pseudotetrahedral bis(diphenylamido) species.[13]

Synthesis of Complexes That Contain *N*-2,6-*i*-Pr$_2$C$_6$H$_3$ (NAr), *N*-2,6-Me$_2$C$_6$H$_3$ (NAr′), *N*-(1-adamantyl) (NAd), or *N*-2-(CF$_3$)C$_6$H$_4$ (NAr$_F$) Ligands. Salt metathesis reactions between the dilithium salt of the ligands (generated *in situ* through deprotonation of the ligands with *n*-BuLi in THF) and Mo(NR)(CHCMe$_2$Ph)(OTf)$_2$(DME) (R = Ar, Ar′, Ad, Ar$_F$) in THF failed due to ligand decomposition (for H_2[Binaph$_{Anth}$]), formation of undesired products (for H_2[Binaph$_{C6F5}$]), and poor and inconsistent yields (for H_2[Biphen$_{CF3}$]). Therefore a related, but milder route that employs triethylamine as a base was pursued.

Mo(NAr)(CHCMe$_2$Ph)(Binaph$_{Anth}$)(THF) (**2a**; Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$) was synthesized in 90% yield through the reaction of Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME) with H_2[Binaph$_{Anth}$] in the presence of 10 equiv of triethylamine in THF (eq 2). The ^{1}H NMR spectrum of **2a** in C$_6$D$_6$ revealed two broad resonances at δ 13.21 ppm (80%) and 11.70 ppm (20%), which are assigned to *anti* and *syn* alkylidene isomers, respectively. The resonances are broad as a consequence of THF dissociation from the metal. In the presence of 10 equiv of THF sharp H_α resonances were observed at δ 13.20 and 12.34 ppm. Binding of THF to the metal is characteristic of binaphtholate compounds of this general type.[1a] The ^{1}H NMR spectrum of **2a** in CD$_2$Cl$_2$ displayed sharp resonances for both *syn* (δ 11.95 ppm, J_{CH} = 117 Hz) and *anti* (δ 12.89 ppm, J_{CH} = 145 Hz) isomers in the ratio of

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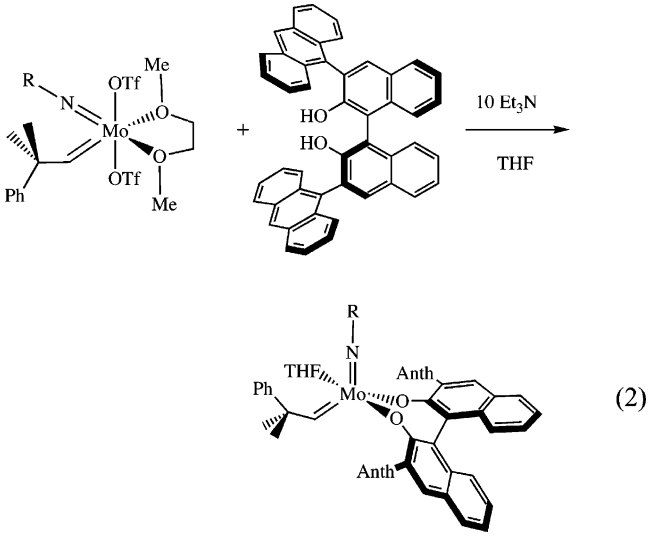
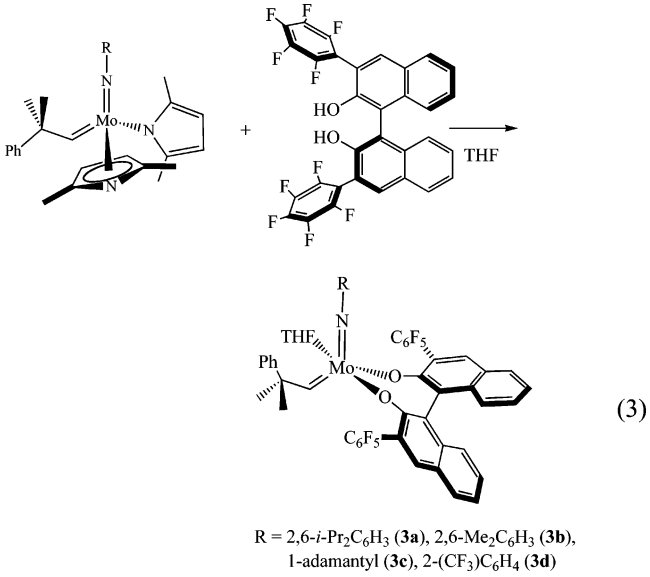


(2)

R = 2,6-*i*-$Pr_2C_6H_3$ (**2a**), 2,6-$Me_2C_6H_3$ (**2b**), 1-adamantyl (**2c**).



(3)

R = 2,6-*i*-$Pr_2C_6H_3$ (**3a**), 2,6-$Me_2C_6H_3$ (**3b**), 1-adamantyl (**3c**), 2-$(CF_3)C_6H_4$ (**3d**)

85(*anti*):15(*syn*). Mo(NR)($CHCMe_2Ph$)($Binaph_{Anth}$)(THF) compounds, where R = Ar′ (**2b**, 84%) or Ad (**2c**, 92%), were synthesized in a manner analogous to that described for **2a** (eq 2). Efforts to synthesize Mo[*N*-2-$(CF_3)C_6H_4$]($CHCMe_2Ph$)($Binaph_{Anth}$)(THF) (**2d**) in a similar manner resulted in formation of unknown products having multiple alkylidene resonances in their ^{1}H NMR spectra; apparently, therefore, **2d** could not be prepared using the method shown in eq 2.

Attempts to generate THF-free versions of **2a**−**2d** (**2a′**−**2d′**) in a reaction between $H_2[Binaph_{Anth}]$ and **1a**−**1d** in C_6D_6 resulted in <20% conversion after 12 h. Likewise, [Mo(NAr)($CHCMe_2Ph$)$(C_4H_4N)_2]_2$[2] did not react readily and cleanly with $H_2[Binaph_{Anth}]$ in C_6D_6. We ascribed these slow reactions to the sterically demanding characteristics of the $[Binaph_{Anth}]^{2-}$ ligand.

Single crystals of **2a** suitable for X-ray crystallography were obtained by slow diffusion of pentane into a THF solution at −30 °C (see Figure 2 and Table 1). The overall structure of **2a** is a trigonal bipyramid with the THF bound to a CNO face of the tetrahedral Mo(NAr)($CHCMe_3$)($Binaph_{Anth}$) core. This is the most often observed geometry of base adducts of this type.[1] The alkylidene displays an *anti* configuration with respect to the imido ligand, which is consistent with the observed room-temperature ^{1}H NMR spectrum in C_6D_6. The dihedral angle between the anthracenyl and the binaphthyl planes is 68.5°. All bond angles and bond distances observed are similar to bond angles and distances in other five-coordinate complexes of this type (see caption to Figure 2).[14]

Efforts to prepare **3a**−**3d** (eq 3) in a reaction between $H_2[Biphen_{C6F5}]$ and Mo(NR)($CHCMe_2Ph$)$(OTf)_2$(DME) [R = Ar, Ar′, Ad, and Ar_F] in the presence of 10 equiv of triethylamine in THF were not successful. The presence of doublet resonances in the alkylidene region was suggestive of some side product being formed in which an alkylidene proton is coupled to fluorine. However, complexes **3a**−**3d** could be prepared in >84% yield as THF adducts in reactions between the bispyrrolide complexes (**1a**−**1d**) and 1 equiv of $H_2[Binaph_{C6F5}]$ in THF (eq 3). The ^{1}H NMR spectra of **3a**, **3b**, and **3c** contain alkylidene resonances only for *anti* isomers in C_6D_6, which were assigned on the basis of their large J_{CH} (>140 Hz) values. The ^{1}H NMR spectrum of **3d** in C_6D_6 depicted two resonances in the alkylidene region at 14.08 ppm (*anti*, 60%) and 13.36 ppm (*syn*, 40%), which correlate with ^{13}C NMR resonances at 320.4 and 307.1 ppm. Compound **3a** should be compared with the previously reported *anti*-(*R*)-Mo(NAr)($CHCMe_2Ph$)($Binaph_{Ph}$)(THF) (δ 13.65 ppm in C_6D_6, J_{CH} = 150 Hz).[14] The ^{19}F NMR spectra of these complexes reveal 10 aryl fluoride resonances, consistent with pentafluorophenyl groups that do not rotate rapidly at room temperature.

Variable-temperature ^{1}H NMR spectra of **3a** in toluene-d_8 from −80 to 90 °C are shown in Figure 3. At 20 °C, only the H_α resonance for the *anti* isomer (J_{CH} = 146 Hz) is observed at 13.81 ppm. Upon cooling the sample to −40 °C, only minor new alkylidene resonances (<5% total) are observed at 13.26 and 12.69 ppm, which are proposed to be two diastereomeric *syn* THF adducts. Warming the sample to 60 °C generates a broad upfield resonance that is the result of equilibration of *syn*-THF-free and *syn*-THF adducts on the NMR time scale. The resonance for the *anti*-THF adduct is broad for similar reasons, but does not shift upfield since relatively little THF-free *anti* isomer is present. At 90 °C broadening of the *anti* and the *syn* alkylidene resonances may also result from interconversion of *anti* and *syn* isomers through rotation about the Mo=C bond. After heating the sample to 90 °C in the variable-temperature experiment, some decomposition of **3a** was observed.

Mo(NAr)($CHCMe_2Ph$)($Binaph_{CF3}$)(THF) complexes can be prepared by treating the bispyrrolide precursors **1a**−**1d** with $H_2[Binaph_{CF3}]$ in THF (eq 4). For example, Mo(NAr)($CHCMe_2Ph$)($Binaph_{CF3}$)(THF) (**4a**) was isolated in 37% yield. The ^{1}H NMR spectrum of **4a** in C_6D_6 revealed alkylidene resonances at 13.77 ppm (J_{CH} = 140 Hz) for the *anti* isomer and at 12.23 ppm (5%) for the *syn* isomer. The presence of only two ^{19}F resonances for each isomer is the consequence of free rotation of the 3,5-bis(trifluoromethyl)phenyl groups on the NMR time scale at room temperature. Compounds **4b**, **4c**, and **4d** also could be observed to form cleanly in the reaction shown in eq 4. However, none could be isolated from solution. In C_6D_6 essentially one alkylidene resonance was found at 13.79 ppm for **4b**, 12.42 ppm for **4c**, and 13.91 ppm for **4d**. Generation of $Binaph_{CF3}^{2-}$-containing complexes through alcoholysis of Mo(NR)($CHCMe_2Ph$)$(OTf)_2$(DME) (R = Ar, Ar′, Ad, and Ar_F) with the ligand in the presence of 10 equiv of triethylamine resulted in clean conversion only in the case of the complex containing the 1-adamantyl imido ligand (δH_α = 13.18 ppm).

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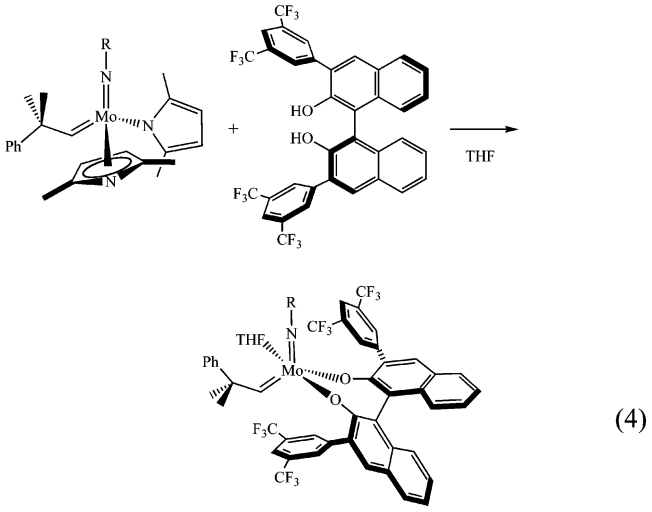
Table 1. Crystal Data and Structure Refinement for (*R*)-Mo(NAr)(CHCMe$_2$Ph)(Binaph$_{Anth}$)(THF) (06240) and *rac*-Mo(NAd)(CHCMe$_2$Ph)(Biphen$_{CF3}$)(THF) (06180).

	06240	06180
empirical formula	$C_{88.60}H_{94.18}MoNO_{6.65}$	$C_{48}H_{61}F_6MoNO_3$
fw	1375.31	909.92 g/mol
cryst syst	monoclinic	triclinic
space group	*P*2(1)	*P*$\bar{1}$
unit cell dimens	$a = 12.245(3)$ Å	$a = 12.7386(14)$ Å
	$b = 15.001(4)$ Å	$b = 12.9783(16)$ Å
	$c = 19.710(5)$ Å	$c = 15.7794(19)$ Å
	$\alpha = 90°$	$\alpha = 76.012(4)°$
	$\beta = 93.793(4)°$	$\beta = 80.948(3)°$
	$\gamma = 90°$	$\gamma = 61.683(3)°$
volume	3612.5(15) Å^3	2225.7(5) Å^3
Z	2	2
density (calcd)	1.264 g/cm^3	1.358 g/cm^3
absorp coeff	0.239 mm^{-1}	0.361 mm^{-1}
F(000)	1456	952
cryst size	0.25 × 0.15 × 0.15 mm^3	0.30 × 0.25 × 0.05 mm^3
θ range for data collection	1.71−29.08°	1.33−29.57°
index ranges	$-16 \le h \le 16$,	$-17 \le h \le 17$,
	$-20 \le k \le 20$,	$-17 \le k \le 18$,
	$-26 \le l \le 26$	$0 \le l \le 21$
no. of reflns collected	78 198	15 550
no. of indep reflns	19 293 [*R*(int) = 0.0721]	15 550[b]
completeness to $\theta = 29.08°$	100.0%	99.8%
max. and min. transmn	0.9651 and 0.9427	0.9822 and 0.8994
no. of data/restraints/params	19 293/1155/1066	15 550/1629/856
goodness-of-fit on F^2	1.036	1.026
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0461	R1 = 0.0403
	wR2 = 0.1203	wR2 = 0.0906
R indices (all data)	R1 = 0.0551	R1 = 0.0505
	wR2 = 0.1263	wR2 = 0.0942
largest diff peak and hole	0.768 and −0.825 e Å^{-3}	0.872 and −0.308 e Å^{-3}

[a] In each case the temperature was 100(2) K, the wavelength was 0.71073 Å, the absorption correction was semiempirical from equivalents, and the refinement method was full-matrix least-squares on F^2. [b] Nonmerohedral twin.



R = 2,6-*i*-Pr$_2$C$_6$H$_3$ (**4a**), 2,6-Me$_2$C$_6$H$_3$ (**4b**), 1-adamantyl (**4c**), 2-(CF$_3$)C$_6$H$_4$ (**4d**)

(4)

THF-free versions of **4a**−**4d** (**4a′**−**4d′**) could be prepared in C_6D_6. The reaction between **1a** and H$_2$[Binaph$_{CF3}$] proceeds in 15 min to yield "*syn*-Mo(NAr)(CHCMe$_2$Ph)(Binaph$_{CF3}$)" (**4a′**; $\delta H_\alpha = 10.86$ ppm). The 2,5-dimethylpyrrole resonances in the ^{1}H NMR spectrum are not shifted from where they are in free 2,5-dimethylpyrrole. This method of *in situ* catalyst generation also can be employed to prepare Mo(NR)(CHCMe$_2$Ph)(Binaph$_{CF3}$) species **4b′** (R = Ar), **4c′** (R = Ad), and **4d′** (R = Ar$_F$). Conversion was rapid (<15 min) in the case of **4b′** and **4c′**, but formation of **4d′** required 1 h for full conversion at 22 °C at a concentration of 23 mM. Compounds **4a′**, **4b′**, and **4c′** consisted of mostly the *syn* isomer ($\delta H_\alpha = 10.86$, 10.86, and 10.62 ppm, respectively), while **4d′** consisted of ap-

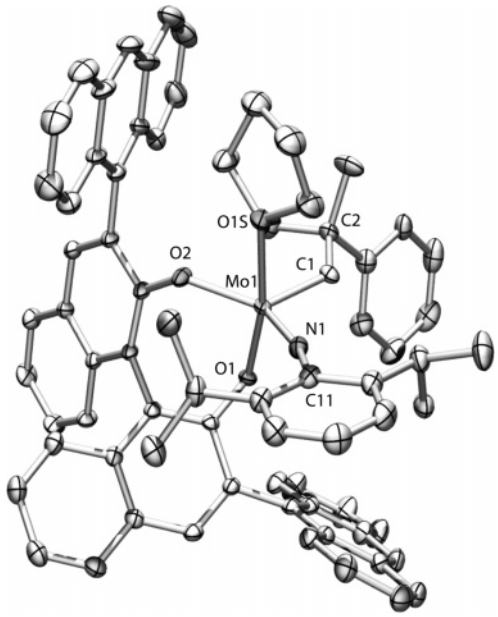
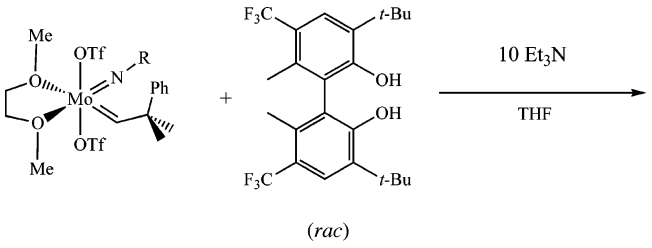


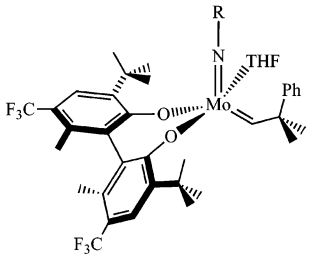
Figure 2. POV-ray diagram of Mo(NAr)(CHCMe$_2$Ph)(Binaph$_{Anth}$)(THF) (**2a**). Thermal ellipsoids are displayed at the 50% probability level. Hydrogen atoms and cocrystallized THF molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): Mo(1)−N(1) = 1.736(3), Mo(1)−C(1) = 1.941(4), Mo(1)−O(2) = 1.994(2), Mo(1)−O(1) = 2.025(2), Mo(1)−O(1S) = 2.235(2), N(1)−Mo(1)−C(1) = 96.94(18), N(1)−Mo(1)−O(2) = 131.98-(12), C(1)−Mo(1)−O(2) = 128.22(16), N(1)−Mo(1)−O(1) = 102.22(11), C(1)−Mo(1)−O(1) = 96.02(14), O(2)−Mo(1)−O(1) = 89.74(9), N(1)−Mo(1)−O(1S) = 85.39(11), C(1)−Mo(1)−O(1S) = 91.30(14), O(2)−Mo(1)−O(1S) = 78.95(9), O(1)−Mo(1)−O(1S) = 168.68(9), C(2)−C(1)−Mo(1) = 125.7(4), C(11)−N(1)−Mo-(1) = 159.8(2).

proximately an equal ratio of *syn* (δ 10.66 ppm) and *anti* (δ 13.71 ppm) isomers. Upon addition of THF (50 μL) to samples of **4a′**−**4d′** in C_6D_6, the THF adducts (**4a**−**4d**) are formed immediately.

Addition of H_2[Biphen$_{CF3}$] to a THF solution of Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME) in the presence of 10 equiv of triethylamine yielded *rac*-Mo(NAr)(CHCMe$_2$Ph)(Biphen$_{CF3}$)(THF) (**5a**) in 50% yield (eq 5). It should be noted that the



(*rac*)



(5)

R = 2,6-*i*-Pr$_2$C$_6$H$_3$ (**5a**), 2,6-Me$_2$C$_6$H$_3$ (**5b**), 1-adamantyl (**5c**)

analogous Mo(NAr)(CHCMe$_2$Ph)(Biphen) species does not crystallize with 1 equiv of THF bound to the metal.[15] In fact, the only other isolated THF adduct of a [Biphen]$^{2-}$ complex is Mo(*N*-2,6-Cl$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(Biphen)(THF), since the *N*-2,6-Cl$_2$C$_6$H$_3$ ligand creates a more electrophilic metal center.[16] Coordination of THF in **5a** is also consistent with a more electrophilic metal center than that in Mo(NAr)(CHCMe$_2$Ph)(Biphen).

Proton, carbon, and fluorine NMR spectra of **5a** in C_6D_6 at 20 °C are all consistent with a 70:30 mixture of *syn* and *anti* isomers being present. Temperature-dependent behavior of proton NMR spectra analogous to that for **3a** and a variety of previous biphenolate or binaphtholate complexes explored to date is observed (Figure 4).[17] Interestingly, at −60 °C four alkylidene proton resonances are observed for what we propose are four diastereomeric THF adducts of **5a**. During the entire cooling and heating of the sample, no decomposition of **5a** was observed.

Mo(NR)(CHCMe$_2$Ph)(Biphen$_{CF3}$)(THF) complexes (R = Ar′ (**5b**) or R = Ad (**5c**); eq 5) were prepared in a manner analogous to the synthesis of **5a**. The ^{1}H NMR spectrum of **5b** in C_6D_6 showed it to be a mixture of *anti* (14.10 ppm, J_{CH} = 146 Hz, ∼75%) and *syn* isomers (12.41 ppm, J_{CH} = 117 Hz, ∼25%). The ^{1}H NMR spectrum of **5c** in C_6D_6 revealed only one broad alkylidene resonance at 12.14 ppm.

Single crystals of **5c** suitable for X-ray crystallography were grown from a diethyl ether solution at −30 °C (Table 1 and Figure 5). The overall structure is analogous to that shown in Figure 2, and all bond angles and bond distances observed are

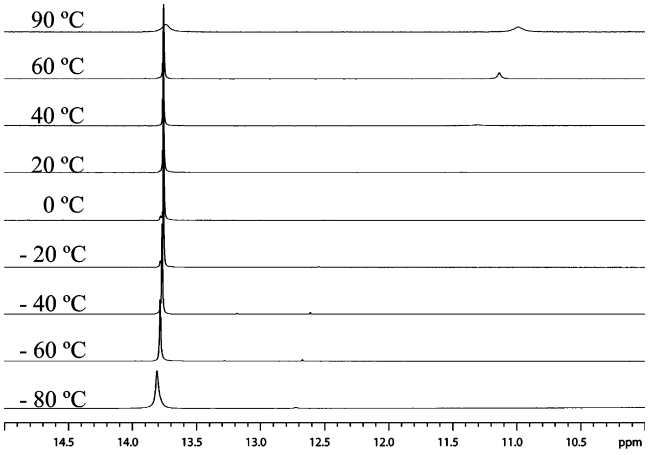


Figure 3. Variable-temperature ^{1}H NMR spectra of Mo(NAr)(CHCMe$_2$Ph)(Binaph$_{C6F5}$)(THF) (**3a**) in toluene-d_8 (500 MHz).

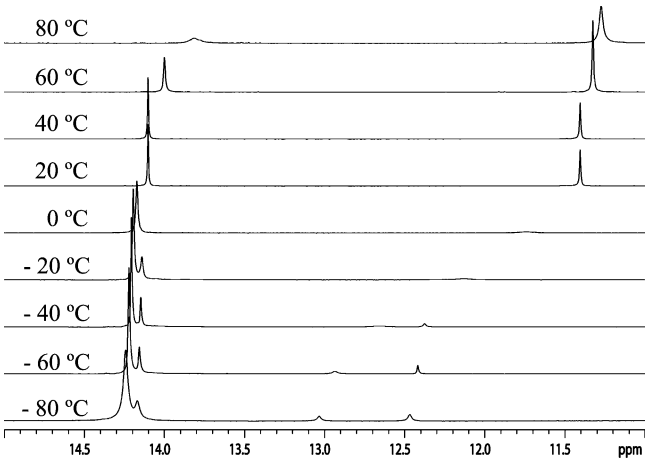


Figure 4. Variable-temperature ^{1}H NMR spectra of Mo(NAr)(CHCMe$_2$Ph)(Biphen$_{CF3}$)(THF) (**5a**) in toluene-d_8 (500 MHz).

typical for five-coordinate complexes of this type (see caption to Figure 5).[16]

Reactions between **1a**−**1c** and H_2[Biphen$_{CF3}$] showed <10% conversion at room temperature in 12 h in C_6D_6 at concentrations of ∼0.25 M. Upon heating the samples to 70 °C, complete conversion to compounds having a single alkylidene (**5a′** δH_α = 11.33 ppm; **5b′** δH_α = 11.28 ppm; **5c′** δH_α = 11.18 ppm) was achieved in 18 h. (The rates of conversion were similar when the reaction was performed in CD_2Cl_2.) Upon addition of one or more equivalents of THF to samples of **5a′**, **5b′**, and **5c′**, primarily one alkylidene resonance was observed for **5a** at 14.24 ppm, **5b** at 14.34 ppm, and **5c** at 12.26 ppm, respectively. (These chemical shifts depend slightly upon how many equivalents of THF are added.) A reaction between Mo(NAr$_F$)(CHCMe$_2$Ph)(OTf)$_2$(DME) and H_2[Biphen$_{CF3}$] in the presence of 10 equiv of triethylamine in C_6D_6 showed clean conversion to THF-free "Mo(NAr$_F$)(CHCMe$_2$Ph)(Biphen$_{CF3}$)" (**5d′**; δH_α = 12.86 ppm), although attempts to isolate this species as a solid also were not successful.

Preliminary Metathesis Reactions. Ring-closing metatheses of diallyl ether were carried out in C_6D_6 with ∼4% catalyst loading (14 mM), and product yield was determined through ^{1}H NMR studies. (See Experimental Section for details.) Of the compounds examined (**2a**−**2c**, **3a**−**3d**, **4a**, **5a**−**5c**), only Biphen$_{CF3}^{2-}$ complexes (**5**) were successful. In 15 min **5a** afforded the ring-closed product dihydrofuran in essentially 100% yield, while **5b** and **5c** yielded 80% and 50% ring-closed product, respectively, in the same time period. No BINOL-based

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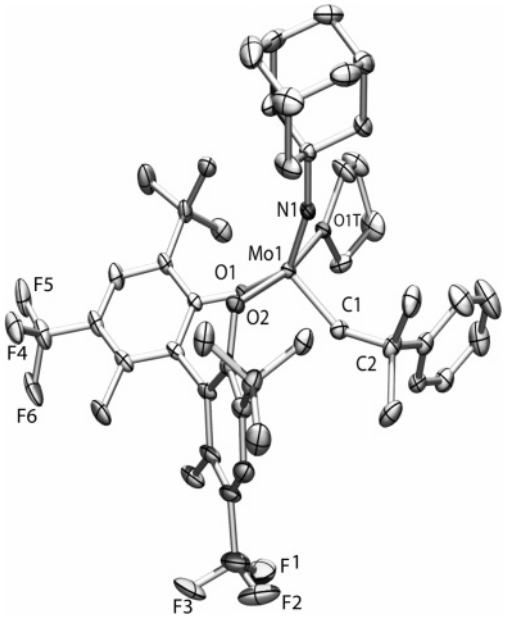

Figure 5. POV-ray diagram of Mo(NAd)($CHCMe_2Ph$)($Biphen_{CF3}$)(THF) (**5c**). Thermal ellipsoids are displayed at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Mo−C(1) = 1.8825(19), Mo−N(1) = 1.7280(16), Mo−O(1) = 1.987(2), Mo−O(2) = 2.027(2), Mo−O(1T) = 2.2206(13), Mo−C(1)−C(2) = 146.73(15), Mo−N(1)−C(11) = 162.04(13), C(1)−Mo−N(1) = 105.19(8), C(1)−Mo−O(1) = 109.13(14), C(1)−Mo−O(2) = 102.14(17), N(1)−Mo−O(1T) = 92.62(6), N(1)−Mo−O(1) = 144.54(14), N(1)−Mo−O(2) = 95.06(12), N(1)−Mo−O(1T) = 92.62(6), O(1)−Mo−O(2) = 86.35(14), O(1)−Mo−O(1T) = 78.15(12), O(2)−Mo−O(1T) = 162.21(17).

catalyst (**2**, **3**, or **4**) produced any significant amount of product (<1% based on ^1H NMR) in 12 h, even though resonances for the first metathesis product (3,3-dimethyl-3-phenyl-1-propene) were observed in the ^1H NMR spectra. No product was observed upon heating reactions to 60 °C.

In contrast, diallyltosylamine can be ring-closed with BINOL-based catalysts to yield the product in good yields. Catalysts **2a**, **2b**, and **2c** produced 15%, 65%, and 6% product after 15 min, and 90%, 100%, and 50%, respectively, at 40 °C in 3 h. Catalyst **3a** completely ring-closed diallyltosylamine in 3 h, while **3b**−**3d** produced 86%, 29%, and 25%, respectively, of the ring-closed product after 3 h. Interestingly, "*in situ*" catalysts **4a′**−**4d′** in C_6D_6 produced 77%, 60%, 43%, and 20%, respectively, of the ring-closed product in 15 min. Therefore we can conclude that 2,5-dimethylpyrrole that is liberated in reactions between **1a**−**1d** and $H_2[Binaph_{CF3}]$ does not block metathesis activity.

We ascribe the inability of BINOL-based catalysts to ring-close diallyl ether to coordination of the oxygen atom of the ring-closed product to the more accessible metal center, thereby slowing metathesis significantly. The ether oxygen can coordinate in either diallyl ether itself or a $Mo{=}CHCH_2OCH_2CHCH_2$ intermediate. The biphenolate-based diolates provide more steric hindrance at the metal center compared to the BINOL-based diolates, which could be the reason for complete ring-closing metathesis of diallyl ether by **5a**. In the case of diallyltosylamine, the nitrogen does not coordinate strongly enough to inhibit metathesis to any significant degree.

In depth evaluations of both isolated and *in situ*-generated new catalysts will be reported in future publications.

Conclusions

We have shown that new Mo(NR)($CHCMe_2Ph$)(diolate) complexes can be prepared that contain relatively electron-withdrawing biphenolate or binaphtholate ligands. New Mo(NR)($CHCMe_2Ph$)(2,5-$Me_2NC_4H_2$)$_2$ complexes also can be prepared in excellent yields and can serve as precursors to several of the new catalysts upon addition of the diol. In fact, new Mo(NR)($CHCMe_2Ph$)[3,3′-bis(pentafluorophenyl)binaphtholate] complexes could be prepared and isolated only through reactions between 3,3′-bis(pentafluorophenyl)binaphthol and bispyrrolide complexes. Several simple preliminary ring-closing metathesis reactions show that the new catalysts are catalytically competent. It has also been demonstrated that the 2,5-dimethylpyrrole that is liberated when $[Binaph_{CF3}]^{2-}$ catalysts are prepared *in situ* does not inhibit metathesis activity.

Experimental Section

General Comments. All manipulations were conducted under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using Schlenk techniques. All glassware was oven-dried prior to use. Ether, pentane, toluene, dichloromethane, toluene, and benzene were degassed with dinitrogen and passed through activated alumina columns. Dimethoxyethane was distilled *in vacuo* from a dark purple solution of sodium benzophenone ketyl and degassed three times through freeze−pump−thaw techniques. All dried and deoxygenated solvents were stored over molecular sieves in a nitrogen-filled glovebox.

C_6D_6, CD_2Cl_2, and $C_6D_5CD_3$ were dried over 4 Å Linde-type molecular sieves. $CDCl_3$ was used as received. NMR spectra were recorded on a Varian 300 MHz or 500 MHz spectrometer at room temperature unless otherwise noted. Chemical shifts for ^1H and ^{13}C spectra were referenced to the residual $^1H/^{13}C$ resonances of the deuterated solvent (^1H: $CDCl_3$, δ 7.26; C_6D_6, δ 7.16; CD_2Cl_2, δ 5.32; $C_6D_5CD_3$, δ 2.01 (methyl); ^{13}C: $CDCl_3$, δ 77.23; C_6D_6, δ 128.39; CD_2Cl_2, δ 54.00) and are reported as parts per million relative to tetramethylsilane. The following abbreviations refer to the multiplicity: s = singlet, d = doublet, t = triplet, sept = septet, q = quartet, m = multiplet, br = broad signal. Elemental analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

Evaporation of organic solutions was carried out through rotary evaporation on a water bath below 40 °C. Product purification by flash column chromatography was accomplished using silica gel 60 (32−63 μm particle size from EMD chemicals) at 0.1−0.3 bar pressure. Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} glass plates. Visualization was achieved by either fluorescence quenching or by staining with aqueous potassium permanganate solution.

Mo(NAr)($CHCMe_2Ph$)$(OTf)_2$(DME), Mo(NAr′)($CHCMe_2Ph$)$(OTf)_2$(DME), Mo(NAd)($CHCMe_2Ph$)$(OTf)_2$(DME), and Mo(NAr_F)($CHCMe_2Ph$)$(OTf)_2$(DME) were prepared as described in the literature.[18] Li-2,5-$Me_2NC_4H_2$ was prepared by treating the respective pyrrole with Li-*n*-Bu in diethyl ether. 2,5-Dimethylpyrrole was purchased from Aldrich. All binaphthols in the syntheses below have the *R* configuation; all biphenols are racemic.

X-ray 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 Kα radiation (λ = 0.71073 Å), performing φ- and ω-scans. All structures were solved by direct methods using SHELXS[19] and refined against F^2 on all data by full-matrix least-

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squares with SHELXL-97.[20] All non-hydrogen atoms were refined anisotropically. Except for the hydrogen atoms on carbon atoms binding directly to molybdenum, which were taken from the difference Fourier synthesis and refined semifreely with the help of distance restraints, all hydrogen atoms were included in 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 to which they are linked (1.5 times for methyl groups). Details of the data quality and a summary of the residual values of the refinements are listed in Table 1.

Compound **2a** crystallizes in the monoclinic space group $P2_1$ with one molecule in the asymmetric unit. The entire alkylidene ligand shows disorder over two positions. Again, the atomic positions of the two components of the disorder were found to be relatively close to one another, suggesting flexibility in coordination geometry rather than two alternative conformations. The disorder was 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 ratio was refined freely, while the total occupancies of both components were constrained to unity; the occupancies of the main component converged at 0.781(7). Including the THF molecule coordinating to the molybdenum atom, the molecule cocrystallized with five crystallographically independent molecules of THF, all of which show at least some disorder. One of the THF molecules is only partially occupied and collides with the minor component of a fully occupied, but nevertheless disordered, THF molecule. Therefore the occupancy of the partially occupied THF molecule was coupled to that of the major component of the one creating the collision. A second component for the partially occupied molecule could not be found. Consequently noninteger values for the elements C, H, and O in the calculated empirical formula of the structure of **2a** result.

Complex **5c** crystallizes in the triclinic space group $P\bar{1}$ with one molecule in the asymmetric unit. Both the coordinated THF and the $[Biphen_{CF3}]^{2-}$ ligand show disorder. The atomic positions of the two components of the disorders are relatively close to one another, suggesting that the disorder can be understood as flexibility in coordination geometry rather than as two alternative conformations. The disorders 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 constraining the total occupancy of both components to unity; the occupancies of the main components converged at 0.806(8) for the $[Biphen_{CF3}]^{2-}$ ligand and 0.849(7) for the THF. In addition to challenges arising from the disorders, the crystal on which this analysis is based was nonmerohedrally twinned. Two independent orientation matrixes for the unit cell were found using the program CELL_NOW,[21] and data reduction taking into account the twinning was performed with SAINT.[22] The program TWINABS[23] was used to perform absorption correction and to set up the HKLF5 format file for structure refinement. The twin ratio was refined freely and converged at a value of 0.2143(5). To counteract correlation effects between otherwise uncorrelated parameters that could be traced to twinning, mild similarity restraints on displacement parameters as well as rigid bond restraints for anisotropic displacement parameters were applied to all atoms in the structure. Nonmerohedral twinning results in a partial overlap of some reflections in a way that is not related to the Laue symmetry of the crystal. Therefore symmetry equivalent reflections must not be merged and it impossible to calculate a merging *R*-value. Consequently a merging *R*-value is not listed in Table 1.

3,3′-Bis(9-anthracenyl)-BINOL ($H_2[Binaph_{Anth}]$). In a 100 mL pressure flask 3,3′-diiodo-2,2′-dimethoxy-1-binapthyl (**A**) (2.15 g, 3.81 mmol) and 9-anthracenylboronic acid[24] (**B**) (3.50 g, 15.8 mmol) were suspended in a mixture of toluene (30 mL), ethanol (15 mL), and aqueous Na_2CO_3 solution (2 M, 15 mL). The suspension was purged with nitrogen for 30 min, tetrakis(triphenylphosphine)-palladium (441 mg, 0.381 mmol) was added, and the mixture was heated to 90 °C for 14 h. After cooling the mixture to room temperature it was filtered and dichloromethane and water were added to the filtrate. The reaction mixture was dried over $MgSO_4$ and the solvent was removed *in vacuo*. The residue was dissolved in methylene chloride (50 mL), and boron tribromide (1.0 M in CH_2Cl_2, 10 mL, 10 mmol) was added. After stirring the mixture for 12 h at 22 °C, it was cooled to 0 °C and water was added. The mixture was extracted with dichloromethane, the dichloromethane solution was dried over $MgSO_4$, and the solvent was evaporated. Flash column chromatography (silica gel, toluene/hexane/ethyl acetate, 25:25:1) gave 3,3′-bis(9-anthracenyl)-BINOL, $H_2[Binaph_{Anth}]$, as an off-white solid (1.68 g, 66%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.24 (s, 2, *Ar*), 8.03 (m, 2, *Ar*), 7.86 (m, 2, *Ar*), 7.80 (d, $J = 8.3$ Hz, *Ar*), 7.63−7.75 (m, 8, *Ar*), 7.10−7.30 (m, 12, *Ar*), 6.94 (m, 2, *Ar*), 5.10 (s, 2, O*H*); ^{13}C NMR ($CDCl_3$, 75 MHz, 23 °C) δ 151.0, 133.9, 133.0, 131.4, 131.4, 130.8, 130.7, 130.7, 129.2, 128.9, 128.5, 128.4, 128.3, 127.8, 127.4, 127.1, 126.2, 126.1, 126.1, 126.1, 125.3, 124.8, 124.2, 113.4; IR (thin film) ν 3530, 3051, 1623, 1497, 1436, 1246, 1147, 905, 729 cm^{-1}; HRMS (EI, [M + Na]) calcd for $C_{48}H_{30}O_2Na$ 661.2138, found 661.2159.

3,3′-Bis(pentafluorophenyl)-BINOL ($H_2[Binaph_{C6F5}]$). In a 100 mL pressure flask 3,3′-diiodo-2,2′-dimethoxy-1-binapthyl (**A**) (3.36 g, 5.93 mmol), potassium (pentafluorophenyl)trifluoro borate (6.50 g, 23.7 mmol), palladium acetate (220 mg, 1.00 mmol), triphenylphosphine (520 mg, 2.00 mmol), silver oxide (5.50 g, 23.7 mmol), and potassium carbonate (5.45 g, 39.5 mmol) were suspended in toluene (50 mL), and the mixture was heated to 110 °C for 48 h. The mixture was filtered and water was added. The mixture was extracted with chloroform. The chloroform solution was separated and dried over $MgSO_4$, and the solvent was evaporated *in vacuo*. The residue was dissolved in methylene chloride (100 mL), and boron tribromide (1 M in CH_2Cl_2, 20.0 mL, 20.0 mmol) was added at 0 °C. The mixture was stirred for 14 h. Water was added at 0 °C, and the mixture was extracted with dichloromethane. The dichloromethane solution was separated and dried with $MgSO_4$, and the solvent was evaporated *in vacuo*. Flash column chromatography (silica gel, hexane/ethyl acetate, 30:1) gave 3,3′-bis(pentafluorophenyl)-BINOL, $H_2[Binaph_{C6F5}]$, as a glassy, colorless solid (1.90 g, 52%): ^{1}H NMR ($CDCl_3$, 300 MHz,) δ 8.04 (s, 2, *Ar*), 7.95 (m, 2, *Ar*), 7.40−7.51 (m, 4, *Ar*), 7.25 (m, 2, *Ar*), 5.28 (s, 2 O*H*); ^{19}F NMR ($CDCl_3$, 282 MHz, 23 °C) δ −140.03 (dd, $J = 22.2$, 8.2 Hz, 2F), −140.51 (dd, 25.0, 8.2 Hz, 2F), −155.16 (t, $J = 19.4$ Hz, 2F), −162.91 (m, 4F); ^{13}C NMR ($CDCl_3$, 75 MHz, 23 °C) δ 150.4, [146.3 (m), 143.0 (m), 142.7 (m), 139.3 (m), 136.0 (m), C_6F_5], 134.1, 133.6, 129.0, 128.9, 128.8, 125.0, 124.0, 115.7, 111.9 (m, C_6F_5), 111.3; IR (thin film) ν 3532, 3065, 1625, 1520, 1495, 1443, 1360, 1212, 1047, 989, 906, 735; HRMS (ESI, [M − H]) calcd for $C_{32}H_{11}F_{10}O_2$ 617.0594, found 617.0603.

3,3′-Bis(3,5-bis(trifluoromethyl)phenyl)-BINOL ($H_2[Binaph_{CF3}]$). In a 100 mL pressure flask 2,2′-dimethoxy-1-binapthyl-3,3′-diboronic acid (4.02 g, 10.0 mmol), 3,5-bis(trifluoromethyl)-bromobenzene (8.79 g, 30.0 mmol), and sodium carbonate (2.65 g, 25.0 mmol) were dissolved in a mixture of dimethoxy ethane (50 mL) and water (12 mL). The solution was purged with

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nitrogen for 15 min and tetrakis(triphenylphosphine)palladium (578 mg, 0.500 mmol) added. The mixture was heated to 95 °C for 36 h. The mixture was cooled to room temperature and filtered. The filtrate was extracted with dichloromethane after addition of water. The dichloromethane layer was dried over $MgSO_4$, and the solvent was evaporated *in vacuo*. The residue was dissolved in methylene chloride (50 mL), and boron tribromide (1.0 M in CH_2Cl_2, 30 mL, 30 mmol) was added at room temperature. The mixture was stirred for 6 h and cooled to 0 °C, and water was added. The mixture was extracted with dichloromethane. The dichloromethane layer was dried over $MgSO_4$, and the solvent evaporated *in vacuo*. Flash column chromatography (silica gel, hexane/ethyl acetate, 30:1) gave 3,3′-bis(3,5-bis(trifluoromethyl)-phenyl)-BINOL, $H_2[Binaph_{CF3}]$, as a white solid (4.00 g, 56%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.31 (s, 4, *Ar*), 8.18 (s, 2, *Ar*), 8.05 (d, J = 7.4 Hz, 2, *Ar*), 7.98 (s, 2, *Ar*), 7.42−7.58 9M, 4, *Ar*), 7.30 (d, J = 8.0 Hz, 2, *Ar*), 5.45 (br s, 2, O*H*); ^{19}F NMR ($CDCl_3$, 282 MHz, 23 °C) δ −63.1; ^{13}C NMR ($CDCl_3$, 75 MHz, 23 °C) δ 149.87, 139.47, 133.24, 132.38, 131.57 (q, J = 33.4 Hz), 129.89, 129.46, 128.9, 128.67, 127.71, 125.22, 123.99, 123.44 (q, J = 272.7 Hz), 121.34, 111.72; IR (thin film) ν 3527, 3063, 1622, 1502, 1378, 1358, 1279, 1174, 1135, 895, 682 cm^{-1}; HRMS (EI, [M+]) calcd for $C_{36}H_{18}F_{12}O_2$ 710.1110, found 710.1126.

3,3′-Bis(*tert*-butyl)-6,6′-dimethylbiphenol (G). In a 250 mL three-necked round-bottom flask with reflux condenser 2-*tert*-butyl-5-methylphenol (89.7 g, 546 mmol) and *tert*-butyl peroxide (7.98 g, 54.6 mmol) were mixed and heated to 140 °C for 36 h. The mixture was cooled to room temperature, and residual phenol was distilled off *in vacuo*. The residue was purified by flash column chromatography (silica gel, hexanes) to give the product as a white solid (16.4 g, 50.2 mmol, 92%): ^{1}H NMR ($CDCl_3$, 300 MHz, 23 °C) δ 7.26 (d, J = 8.0 Hz, 2H, Ar), 6.86 (d, J = 8.0 Hz, 2H, Ar), 5.00 (s, 2H, O*H*), 1.93 (s, 6H, *Me*), 1.41 (s, 18H, *t*-Bu); ^{13}C NMR ($CDCl_3$, 75 MHz, 23 °C) δ 152.44, 136.17, 133.84, 127.35, 121.79, 120.05, 34.62, 29.47, 19.16; IR (thin film) ν 3515, 2959, 2914, 2870, 1606, 1485, 1414, 1384, 1270, 1185, 1136, 812 cm^{-1}; HRMS (ESI, [M + H]) calcd for $C_{22}H_{31}O_2$ 327.2319, found 327.2328.

5-*tert*-Butyl-3-(5-*tert*-butyl-2-methyl-3,6-dioxocyclohexa-1,4-dienyl)-2-methylcyclohexa-2,5-diene-1,4-dione (H). In a 50 mL flask 3,3′-bis(*tert*-butyl)-6,6′-dimethylbiphenol (500 mg, 1.53 mmol) was dissolved in chloroform (25 mL), and mCPBA (660 mg, 3.83 mmol) was added. The mixture was stirred at room temperature for 48 h. After addition of more chloroform the mixture was washed with aqueous sodium thiosulfate and sodium hydrogen carbonate solution. The chloroform layer was dried over Na_2SO_4, and the solvent was evaporated *in vacuo*. Flash column chromatography (silica gel, hexane/ethyl acetate, 20:1) and recrystallization from diethyl ether gave the product as a yellow solid (292 mg, 54%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.63 (s, 2, *Ar*), 1.79 (s, 6, *Me*), 1.24 (s, 18, C*Me*$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz, 23 °C) δ 187.41, 185.29, 156.15, 141.61, 140.01, 131.44, 35.24, 29.04, 13.14; IR (thin film) ν 2963, 1653, 1635, 1457, 1317, 1251, 1189, 897 cm^{-1}; HRMS (ESI, [M + H]) calcd for $C_{22}H_{27}O_4$ 355.1904, found 355.1918.

3,3′-Bis(*tert*-butyl)-5,5′-bis(trifluoromethyl)-6,6′-dimethylbiphenol (I). In a 25 mL flask the dienone **H** (200 mg, 0.564 mmol) and potassium carbonate (20.0 mg, 0.145 mmol) were dissolved in DMF (1 mL), and trifluoromethyltrimethylsilane (241 mg, 1.69 mmol) was added. The orange mixture turned dark and was stirred for 12 h at room temperature. After addition of water, the mixture was extracted with ether and the ether layer was dried over sodium sulfate. The solvent was evaporated *in vacuo*, and the residue was dissolved in a mixture of THF and water (9:1, 15 mL). Aluminum foil (152 mg, 5.64 mmol) was amalgamated by dipping it in an aqueous mercuric chloride solution (2%) for 15 s, followed by dipping in ethanol and then in ether. The foil was cut into fine pieces and added to the quinone solution. The mixture evolved hydrogen and was heated to reflux for 2 h. The gray suspension was filtered and washed with THF (200 mL). The solution was concentrated *in vacuo* and extracted with diethyl ether. The ether layer was dried over Na_2SO_4, and the solvent was evaporated *in vacuo*. Flash column chromatography (silica gel, hexane/ethyl acetate, 30:1) gave the product as white crystals (183 mg, 70%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.82 (s, 2, *Ar*), 4.59 (s, 2, O*H*), 1.90 (s, 6, *Me*), 1.30 (s, 18, C*Me*$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz, 23 °C) δ 154.82, 135.56, 134.44, 128.88, 126.25 (q, J = 5.9 Hz), 124.8 (q, J = 272.9 Hz), 122.0 (q, J = 29.5 Hz), 121.20, 34.91, 29.19, 15.56; ^{19}F NMR ($CDCl_3$, 282 MHz, 23 °C) δ −59.6; IR (thin film) ν 3520, 2965, 2917, 1611, 1576, 1473, 1365, 1327, 1304, 1259, 1185, 1095, 908, 737, 674, 669, 608 cm^{-1}; HRMS (ESI, [M − H]) calcd for $C_{24}H_{27}F_6O_2$ 461.1910, found 461.1926.

3-*tert*-Butyl-3-(3-*tert*-butyl-2-hydroxy-6-methylphenyl)-5-methyl-4-trifluoromethylphenol ($H_2[Biphen_{CF3}]$). In a 100 mL flask semiquinone **I** (6.00, 17.6 mmol) and potassium carbonate (205 mg, 3.52 mmol) were dissolved in DMF (20 mL), and trifluoromethyltrimethylsilane (3.00 g, 21.1 mmol) was added. The orange mixture turned dark and was stirred for 12 h at room temperature. Water was added, and the mixture was extracted with ether. The ether layer was dried over sodium sulfate and the solvent evaporated *in vacuo*. The residue was dissolved in a THF/water mixture (9:1, 200 mL). Aluminum foil (4.75 g, 176 mmol) was amalgamated by dipping in an aqueous mercuric chloride solution (2%) for 15 s, then in ethanol and ether. The foil was cut into fine pieces and added to the quinone solution. The mixture evolved hydrogen and was heated to reflux for 2 h. The gray suspension was filtered and washed with THF (400 mL). The solution was concentrated *in vacuo* and extracted with diethyl ether. The ether layer was dried over Na_2SO_4, and the solvent was evaporated. Flash column chromatography (silica gel, hexane/ethyl acetate, 30:1) gave the product as a white powder (2.85 g, 41%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.68 (s, 1, *Ar*), 7.34 (d, J = 8.0 Hz, 1, *Ar*), 6.92 (d, J = 8.0 Hz, 1, *Ar*), 5.39 (s, 1, O*H*), 4.88 (s, 1, O*H*), 2.08 (m, 3, *Me*), 1.93 (s, 3, *Me*), 1.45 (m, 18, C*Me*$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz, 23 °C) δ 154.91, 152.44, 136.14, 134.47, 133.81, 128.85, 128.06, 125.61, 125.54, 122.44, 122.29, 118.92, 34.82, 34.68, 30.29, 29.45, 29.19, 19.11; ^{19}F NMR ($CDCl_3$, 282 MHz, 23 °C) δ −59.9; IR (thin film) ν 3529, 3495, 2961, 2915, 2872, 1576, 1330, 1259, 1188, 1118, 1090, 907, 846, 675 cm^{-1}; HRMS (EI, [M+]) calcd for $C_{23}H_{29}F_3O_2$ 394.2114, found 394.2121.

Mo(*N*-2,6-*i*-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(2,5-$Me_2NC_4H_2$)$_2$ (1a). Lithium 2,5-dimethylpyrrolide (103 mg, 1.01 mmol) was added to a chilled (−30 °C) solution of Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME) (400 mg, 0.511 mmol) in Et_2O (30 mL), and the reaction was warmed to room temperature, during which time the solution's color changed from yellow to red. After 3 h, the volatiles were removed *in vacuo* and the crude solid was extracted with toluene (40 mL). Removal of the volatiles *in vacuo* yielded a dark red solid. Addition of pentane and filtration produced the product as a yellow solid (270 mg, 90%): ^{1}H NMR (C_6D_6, 300 MHz) δ 13.30 (s, 1, *syn* Mo=C*H*, J_{CH} = 120 Hz), 7.37 (d, 2, *Ar*), 7.7.14 (m, 3, *Ar*), 7.03 (d, 1, *Ar*), 6.97 (d, 2, *Ar*), 5.94 (br s, 2, NC$_4H_2$) 3.54 (sept, 2, MeC*H*Me), 2.02 (s, 12, *Me*$_2$NC$_4H_2$), 1.72 (s, 6, HC*Me*$_2$), 1.69 (br, 12, *Me*CH*Me*); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 315.16, 151.88, 149.32, 128.72, 127.83, 126.85, 126.44, 124.13, 105.64, 70.77, 58.22, 31.61, 27.99, 25.19, 24.13, 22.79, 18.17. Anal. Calcd for $C_{34}H_{45}MoN_3$: C, 69.02; H, 7.67; N, 7.10. Found: C, 69.01; H, 7.60; N, 7.14.

Mo(*N*-2,6-$Me_2C_6H_3$)(CHCMe$_2$Ph)(2,5-$Me_2NC_4H_2$)$_2$ (1b). The synthesis was analogous to that for **1a**; yield 83%: ^{1}H NMR (C_6D_6, 300 MHz) δ 13.19 (s, 1, *syn* Mo=C*H*, J_{CH} = 120 Hz), 7.29 (d, 2, *Ar*), 7.07 (t, 3, *Ar*), 7.03 (d, 1, *Ar*), 6.77 (s, 2, *Ar*), 5.94 (br s, 2, NC$_4H_2$) 2.16 (s, 6, *Me*$_2$C$_6$H$_3$), 2.02 (s, 12, *Me*$_2$NC$_4$H$_2$), 1.61 (s, 6, HC*Me*$_2$); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 314.41, 154.34, 149.20, 136.61, 128.76, 128.70, 128.60, 126.96, 126.88, 126.29, 105.91,

57.53, 31.03, 19.64, 17.90. Anal. Calcd for $C_{30}H_{37}MoN_3$: C, 67.28; H, 6.96; N, 7.85. Found: C, 67.34; H, 7.08; N, 7.74.

Mo(*N*-1-adamantyl)(CHCMe$_2$Ph)(2,5-Me$_2$NC$_4$H$_2$)$_2$ (1c). The synthesis was analogous to that for **1a**; yield 86%: ^{1}H NMR (C_6D_6, 300 MHz) δ 12.94 (s, 1, *syn* Mo=C*H*, J_{CH} = 120 Hz), 7.38 (d, 2, *Ar*), 7.10 (t, 3, *Ar*), 6.98 (d, 1, *Ar*), 5.96 (br s, 2, NC$_4$*H*$_2$), 2.22 (br s, 12, *Me*$_2$NC$_4$*H*$_2$), 1.77 (s, 3, adamantyl), 1.53 (s, 6, HC*Me*$_2$), 1.45 (s, 6, adamantyl), 1.34 (s, 6, adamantyl); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 306.87, 151.05, 128.47, 127.81, 126.10, 74.40, 54.91, 44.45, 36.13, 30.16, 30.10. Anal. Calcd for $C_{32}H_{43}MoN_3$: C, 67.95; H, 7.66; N, 7.43. Found: C, 68.09; H, 7.60; N, 7.28.

Mo(*N*-2-(CF$_3$)C$_6$H$_4$)(CHCMe$_2$Ph)(2,5-Me$_2$NC$_4$H$_2$)$_2$ (1d). The synthesis was analogous to that for **1a**; yield 82%: ^{1}H NMR (C_6D_6, 300 MHz) δ 13.19 (s, 1, *syn* Mo=C*H*, J_{CH} = 120 Hz), 7.30 (d, 2, *Ar*), 7.20−6.85 (m, 5, *Ar*), 6.64 (t, 1, *Ar*), 6.44 (t, 1, *Ar*), 6.02 (br s, 2, NC$_4$*H*$_2$), 2.08 (br s, 12, *Me*$_2$NC$_4$*H*$_2$), 1.59 (s, 6, HC*Me*$_2$); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 317.76, 152.73, 149.45, 132.85, 132.05, 128.63, 127.15, 126.59, 126.39, 126.16, 125.20, 123.04, 122.83, 120.86, 59.12, 31.33, 27.99; ^{19}F NMR (C_6D_6, 471 MHz) δ −60.42. Anal. Calcd for $C_{29}H_{32}F_3MoN_3$: C, 60.52; H, 5.60; N, 7.30. Found: C, 60.46; H, 5.52; N, 7.24.

Mo(*N*-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(Binaph$_{Anth}$)(THF) (2a). A 50 mL round-bottom flask was charged with Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME) (200 mg, 0.252 mmol), H$_2$[Binaph$_{Anth}$] (162 mg, 0.252 mmol), THF (15 mL), and Et$_3$N (0.175 mL, 1.26 mmol), and the reaction was stirred at room temperature for 12 h. The volatiles were removed *in vacuo*. Addition of pentane to the crude solid yielded a yellow powder. The yellow powder was isolated by filtration and recrystallized from a mixture of THF and pentane (2:4) to yield yellow crystals (250 mg, 90%): ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 12.89 (s, 1, *anti* Mo=C*H*, J_{CH} = 147 Hz), 11.95 (s, 1, *syn* Mo=C*H*, J_{CH} = 116 Hz), *anti isomer* 8.47−8.38 (m, 3, *Ar*), 8.11−7.85 (m, 10, *Ar*), 7.58−7.50 (m, 3, *Ar*), 7.42−7.22 (m, 10, *Ar*), 7.15−7.11 (m, 2, *Ar*), 7.04−6.86 (m, 3, *Ar*), 6.76 (t, 2, *Ar*), 6.41 (d, 2, *Ar*), 6.16 (t, 1, *Ar*), 3.66 (br, 4, C*H*$_2$OC*H*$_2$), 3.12 (sept, 2, MeC*H*Me), 1.34 (s, 3, HC(*Me*)Me), 1.35 (s, 3, HC(Me)*Me*), 0.81 (d, 3, inequivalent *Me* of *i*-Pr), 0.65 (d, 3, inequivalent *Me* of *i*-Pr), 0.62 (s, 4, C*H*$_2$C*H*$_2$) 0.34 (d, 3, inequivalent *Me* of *i*-Pr), 0.05 (d, 3, inequivalent *Me* of *i*-Pr); ^{13}C NMR *one isomer* (CD_2Cl_2, 125 MHz) δ 317.15, 164.77, 162.07, 155.16, 150.45, 145.83, 143.16, 137.29, 136.42, 135.83, 135.58, 133.54. 132.49, 132.43, 132.13, 131.82, 131.69, 131.40, 131.29, 131.02, 130.67, 130.54, 130.28, 130.16, 129.34, 129.04, 128.77, 128.72, 128.67, 128.51, 128.46, 128.44, 128.37, 128.33, 128.26, 127.56, 127.23, 127.18, 126.49, 126.45, 126.39, 126.02, 125.97, 125.84, 125.81, 125.76, 125.71, 125.52, 125.33, 125.20, 125.06, 124.09, 123.07, 123.04, 122.62, 122.13, 119.90, 68.60, 51.03, 47.38, 29.12, 28.07, 27.34, 27.18, 25.76, 24.75, 22.35, 21.99, 21.89, 21.81. Anal. Calcd for $C_{74}H_{65}MoNO_3$: C, 79.91; H, 5.89; N, 1.26. Found: C, 80.09; H, 5.81; N, 1.24.

Mo(*N*-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(Binaph$_{Anth}$)(THF) (2b). Compound **2b** was prepared in a manner similar to **2a** and isolated in 84% yield: ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 12.73 (s, 1, *anti* Mo=CH) 12.05 (s, 1, *syn* Mo=CH), *one isomer* 8.47−8.40 (m, 3, *Ar*), 8.10−7.87 (m, 10, *Ar*), 7.52−7.24 (br m, 13, *Ar*), 7.11 (br s, 2, *Ar*), 7.01−6.93 (m, 3, *Ar*), 6.60 (t, 2, *Ar*), 6.42 (d, 2, *Ar*), 6.22 (br, 1, *Ar*), 3.12 (br s, C*H*$_2$OC*H*$_2$), 1.37 (br s, 3, *Me*), 1.34 (br s, 3, *Me*), 0.91 (m, 4, C*H*$_2$C*H*$_2$), 0.74 (s, 3, HC(*Me*)Me), 0.66 (s, 3, HC(Me)*Me*); ^{13}C NMR *one isomer* (CD_2Cl_2, 125 MHz) δ 315.15, 168.90, 168.77, 164.30, 164.09, 162.57, 162.25, 156.32, 155.37, 151.73. 150.29, 150.11, 137.11, 135.95, 135.68, 135.49, 135.12, 134.99, 134.44, 133.70, 133.57, 133.31, 132.51, 132.27, 132.08, 131.97, 131.93, 131.77, 131.67, 131.54, 131.37, 131.26, 130.94, 130.74, 129.85, 129.64, 129.47, 129.19, 129.06, 128.98, 128.90, 128.62, 128.54, 128.49, 128.44, 128.34, 128.22, 128.08, 127.90, 127.79, 127.73, 127.70, 127.62, 126.82, 126.66, 126.50, 126.45, 126.30, 126.22, 126.08, 126.00, 125.93, 125.89, 125.83, 125.74, 125.66, 125.57, 125.15, 125.05, 124.84, 124.75, 124.17, 123.36, 123.16, 123.03, 122.93, 122.36, 119.89, 50.85, 47.36, 32.55, 28.46, 25.11, 19.99. Anal. Calcd for $C_{70}H_{57}MoNO_3$: C, 79.61; H, 5.44; N, 1.33. Found: C, 79.47; H, 5.37; N, 1.31.

Mo(*N*-1-adamantyl)(CHCMe$_2$Ph)(Binaph$_{Anth}$)(THF) (2c). Compound **2c** was prepared in a manner similar to **2a** and isolated in 92% yield: ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 12.60 (br s, 1, Mo=CH), 8.44 (br s, 4, *Ar*), 8.01−7.69 (m, 13, *Ar*), 7.44−7.10 (m, 12, *Ar*), 6.92 (br s, 2, *Ar*), 6.75 (br s, 2, *Ar*), 3.13 (t, 4, C*H*$_2$OC*H*$_2$), 2.08 (br s, 1, adamantyl), 1.87(br s, 1, adamantyl), 1.72 (br s, 2, adamantyl), 1.42 (br s, 4, adamantyl), 1.34 (br s, 6, HC*Me*$_2$), 1.09 (s, 2, adamantyl), 0.49 (br s, 4, C*H*$_2$C*H*$_2$); ^{13}C NMR *one isomer* (CD_2Cl_2, 125 MHz) δ 291.73, 178.08, 166.48, 160.38, 150.09, 137.53, 136.64, 135.87, 135.28, 133.67. 132.69, 131.98, 131.87, 131.44, 131.12, 130.71, 129.93, 129.31, 129.05, 128.81, 128.43, 128.38, 128.32, 128.23, 128.17, 127.92, 127.28, 126.65, 126.38, 125.80, 125.66, 125.38, 122.99, 122.57, 122.22, 122.15, 121.28, 120.64, 119.68, 117.15, 113.99, 76.74, 72.93, 49.93, 47.43, 43.55, 36.07, 32.19, 29.81, 25.86, 24.31, 22.89.

Mo(*N*-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(Binaph$_{C6F5}$)(THF) (3a). H$_2$-[Binaph$_{C6F5}$] (209 mg, 0.340 mmol) dissolved in THF (2 mL) was added dropwise to a stirred solution (−30 °C) of **1a** (200 mg, 0.340 mmol) in THF (20 mL). The solution was allowed to come to room temperature and was stirred for 2 h. The volatiles were removed *in vacuo*, and addition of pentane afforded a yellow powder (310 mg, 84%): ^{1}H NMR (C_6D_6, 300 MHz) δ 13.81 (s, 1, *anti* Mo=C*H*, J_{CH} = 140 Hz), 7.80 (s, 1, *Ar*), 7.76 (s, 1, *Ar*), 7.73 (s, 1, *Ar*), 6.70 (s, 1, *Ar*), 7.41 (d, 1, *Ar*), 7.15−7.06 (m, 6, *Ar*), 6.99−6.80 (m, 7, *Ar*), 3.78 (br s, 1, Me*CH*Me), 3.10 (d, 4, *CH*$_2$O*CH*$_2$), 1.72 (s, 3, HC(*Me*)MePh), 1.46 (s, 3, HC(Me)MePh), 0.95−0.78 (br, 12, HC*Me*$_2$), 0.42 (br, 4, C*H*$_2$C*H*$_2$); ^{19}F NMR (C_6D_6, 282 MHz) δ −133.14, −136.40, −139.28, −142.21, −157.80, −158.21, −162.19, −162.99, −163.88, −165.17; ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 319.64, 161.83, 160.07, 154.29, 150.47, 146.57, 146.17, 145.62, 144.60, 144.21, 143.66, 141.70, 139.55, 138.90, 137.50, 136.92, 136.20, 135.61, 132.55, 131.88, 132.55, 131.88, 129.53, 128.94, 128.85, 128.73, 128.57, 127.91, 127.19, 126.93, 126.68, 126.29, 125.85, 123.64, 123.44, 121.88, 119.68, 117.08, 114.36, 106.22, 75.66, 52.13, 29.57, 28.77, 27.98, 27.10, 26.40, 25.64, 22.96. Anal. Calcd for $C_{58}H_{47}F_{10}MoNO_3$: C, 63.80; H, 4.34; N, 1.28. Found: C, 63.65; H, 4.36; N, 1.23.

(*R*)-Mo(*N*-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(Binaph$_{C6F5}$)(THF) (3b). Compound **3b** was prepared using the same protocol as that employed for **3a** and was isolated in a yield of 86%: ^{1}H NMR (C_6D_6, 500 MHz) δ 13.65 (s, 1, *anti* Mo=C*H*, J_{CH} = 140 Hz), 7.87−7.76 (m, 4, *Ar*), 7.46 (d, 1, *Ar*), 7.32 (d, 1, *Ar*), 7.19−7.12 (m, 6, *Ar*), 6.98 (t, 2, *Ar*), 6.89 (t, 1, *Ar*), 6.84 (br s, 1, *Ar*), 6.72 − 6.61 (m, 2, *Ar*), 3.31 (br s, 2, CH$_2$OC*H*$_2$), 2.91 (br s, 2, C*H*$_2$OCH$_2$), 2.24 (s, 3, *Me*), 1.70 (s, 3, *Me*), 1.49 (s, 3, HC(*Me*)Me), 1.42 (s, 3, HC(Me)*Me*), 0.77 (br s, 2, C*H*$_2$CH$_2$), 0.69 (br s, 2, CH$_2$C*H*$_2$); ^{19}F NMR (C_6D_6, 282 MHz) δ −130.49, −134.11, −137.29, −140.40, −156.41, −157.09, −161.30, −162.59, −162.79 −163.53; ^{13}C NMR *one isomer* (CD_2Cl_2, 125 MHz) δ 318.99, 161.27, 159.94, 155.90, 154.59, 150.34, 149.47, 146.36, 145.47, 144.39, 143.50, 141.67, 141.34, 139.49, 138.71, 136.76, 135.50, 135.22, 133.16, 132.49, 131.91, 129.17, 128.87, 128.82, 128.68, 128.34, 128.20, 128.02, 127.18, 126.95, 126.77, 126.67, 126.43, 126.34, 125.95, 124.01, 123.68, 122.22, 120.08, 119.71, 119.65, 116.63, 113.98, 76.44, 52.08, 28.60, 27.40, 25.32, 19.39, 17.74. Anal. Calcd for $C_{54}H_{39}F_{10}MoNO_3$: C, 62.62; H, 3.80; N, 1.35. Found: C, 62.80; H, 3.73; N, 1.28.

(*R*)-Mo(*N*-1-adamantyl)(CHCMe$_2$Ph)(Binaph$_{C6F5}$)(THF) (3c). Compound **3c** was prepared using the same protocol as that employed for **3a**, and the yield was 85%: ^{1}H NMR (C_6D_6, 500 MHz) δ 12.59 (s, 1, Mo=CH), 7.99 (br s, 1, *Ar*), 7.84 (br s, 1, *Ar*), 7.76 (br s, 1, *Ar*), 7.71 (d, 2, *Ar*), 7.55 (br s, 1, *Ar*), 7.27 (d, 2, *Ar*), 7.08 (t, 1, *Ar*), 6.98 (br, 2, *Ar*), 6.87 (t, 1, *Ar*), 6.82−6.72 (br, 3,

Ar), 2.85 (br, 4, CH_2OCH_2), 1.94−1.83 (br, 6, adamantyl), 1.46 (br s, 3, adamantyl), 1.44 (br s, 3, adamantyl), 1.18 (br s, 3, adamantyl), 0.64 (br, 4, CH_2CH_2); ^{19}F NMR (C_6D_6, 282 MHz) δ −130.49, −134.11, −137.29, −140.40, −156.41, −157.09, −161.30, −162.59, −162.79, −163.53; ^{13}C NMR *one isomer* (CD_2Cl_2, 125 MHz) δ 294.06, 166.26, 159.40, 149.57, 146.64, 146.23, 145.69, 144.59, 144.26, 143.75, 141.41, 139.36, 137.39, 136.00, 135.40, 132.25, 131.72, 128.89, 128.76, 126.89, 126.80, 126.48, 123.56, 123.16, 121.73, 121.07, 119.91, 118.90, 116.31, 115.51, 77.95, 73.61, 49.97, 44.23, 36.35, 30.08, 24.81, 22.93. Anal. Calcd for $C_{56}H_{45}F_{10}MoNO_3$: C, 63.10; H, 4.26; N, 1.31. Found: C, 62.88; H, 4.18; N, 1.26.

(*R*)-Mo(*N*-2-(CF_3)C_6H_4)(CHCMe$_2$Ph)(Binaph$_{C6F5}$)(THF) (3d). Compound **3d** was prepared using the same protocol as that employed for **3a**, and the yield was 84%: ^{1}H NMR (C_6D_6, 500 MHz) δ 14.08 (s, 1, *anti* Mo=CH), 13.36 (br s, 1, *syn* Mo=CH), *one isomer* 7.86 (s, 1, *Ar*), 7.78 − 7.69 (m, 4, *Ar*), 7.46 (t, 1, *Ar*), 7.34 (d, 1, *Ar*), 7.24−7.06 (m, 6, *Ar*), 6.55 (t, 2, *Ar*), 6.53 (t, 1, *Ar*), 6.40 (br s, 1, *Ar*), 6.02 (d, 2, *Ar*), 3.41 (q, 2, CH_2OCH$_2$), 2.84 (q, 2, CH$_2$OCH_2), 1.59 (s, 3, HC(*Me*)Me), 1.37 (s, 3, HC(Me)*Me*), 0.88 (q, 4, CH_2CH_2); ^{19}F NMR *one isomer* (C_6D_6, 282 MHz) δ −60.61, −132.57, −136.45, 139.07, −143.09, −158.10, −158.96, −163.01, −164.80, −165.34; ^{13}C NMR *one isomer* (CD_2Cl_2, 125 MHz) δ 320.44 (*anti* C_α), 307.09 (*syn* C_α). Anal. Calcd for $C_{53}H_{34}F_{13}MoNO_3$: C, 59.17; H, 3.19; N, 1.30. Found: C, 59.32; H, 3.26; N, 1.32.

Mo(*N*-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(Binaph$_{CF3}$)(THF) (4a). A solution of H$_2$[Binaph$_{CF3}$] (240 mg, 0.338 mmol) in THF (2 mL) was added to a stirred solution of **1a** (200 mg, 0.338 mmol) in THF (20 mL) and the reaction stirred at room temperature for 1 h. Removal of the volatiles *in vacuo* afforded a yellow residue, which dissolved in pentane (2 mL). Cooling the pentane solution to −30 °C yielded **4a** as a yellow powder (150 mg, 37%): ^{1}H NMR (C_6D_6, 300 MHz) δ 13.77 (s, 1, *anti* Mo=CH), 12.23 (s, 1, *syn* Mo=CH), 8.13 (s, 1, *Ar*), 8.12 (s, 1, *Ar*), 7.90 (s, 1, *Ar*), 7.82−7.71 (m, 3, *Ar*), 7.64−7.47 (m, 4, *Ar*), 7.29 (d, 1, *Ar*), 7.23−7.02 (m, 10 *Ar*), 6.90 (t, 1, *Ar*), 6.81 (d, 2, *Ar*), 3.29 (br, 2, MeC*H*Me), 3.25 (br, 4, CH_2OCH_2), 1.85 (s, 3, HC(*Me*)Me), 1.34 (s, 3, HC(Me)*Me*), 1.12 (d, 6, *Me*CH*Me*), 1.09 (d, 6, *Me*CH*Me*), 0.70 (br, 4, CH$_2$CH$_2$); ^{19}F NMR (C_6D_6, 282 MHz) δ −61.92, −62.19 (*anti*), −61.99, −62.30 (*syn*); ^{13}C NMR *one isomer* (CD_2Cl_2, 125 MHz) δ 317.90 (C_α). Anal. Calcd for $C_{62}H_{53}F_{12}MoNO_3$: C, 62.89; H, 4.51; N, 1.81. Found: C, 62.76; H, 4.61; N, 1.09.

***In Situ* Generation of Mo(*N*-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)-(Binaph$_{CF3}$) (4b′).** H$_2$[Binaph$_{CF3}$] (9 mg, 0.013 mmol) was added as a solid to the solution of **1b** (10 mg, 0.013 mmol, 0.024 M) in C_6D_6 in a J-Young NMR tube. Conversion to **4b′** was complete after 15 min according to ^{1}H NMR: ^{1}H NMR (C_6D_6, 500 MHz) δ 10.86 (s, 1, base-free *syn* Mo=CH), 7.65 (s, 1, *Ar*), 7.62 (s, 1, *Ar*), 7.60 (s, 1, *Ar*), 7.45−6.54 (m, 21, *Ar*), 6.23 (br, 2, N$_{pyr}$*H*), 5.91 (d, 4, C*H*CH$_{pyr}$), 1.70 (s, 6, *Me*$_2$C$_6$H$_3$), 1.18 (s, 12, *Me*$_2$NC$_4$H$_2$), 0.79 (s, 6, HC*Me*$_2$).

Mo(*N*-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(Binaph$_{CF3}$) (**4a′**), (C_6D_6, 500 MHz) δ 10.86 (s, 1, base-free *syn* Mo=CH); Mo(*N*-1-adamantyl)-(CHCMe$_2$Ph)(Binaph$_{CF3}$) (**4c′**), (C_6D_6, 500 MHz) δ 10.62 (s, 1, base-free *syn* Mo=CH); and Mo(*N*-2-$CF_3C_6H_4$)(CHCMe$_2$Ph)-(Binaph$_{CF3}$) (**4d′**), (C_6D_6, 500 MHz) δ 13.71 (s, 1, *anti* Mo=CH), 10.66 (s, 1, *syn* Mo=CH), were generated *in situ* in a similar manner.

Mo(*N*-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(Biphen$_{CF3}$)(THF) (5a). To a 100 mL round-bottom flask charged with Mo(NAr)(CHCMe$_2$-Ph)(OTf)$_2$(DME) (500 mg, 0.632 mmol), H$_2$[Biphen$_{CF3}$] (292 mg, 0.632 mmol), and THF (60 mL) was added Et$_3$N (0.890 mL, 6.32 mmol) via a syringe. The reaction was stirred at room temperature for 12 h. The volatiles were removed *in vacuo*, and the residue was extracted with pentane (60 mL). Concentration of the pentane solution resulted in formation of a yellow solid, which was isolated by filtration (300 mg, 50%): ^{1}H NMR (C_6D_6, 500 MHz) δ 14.17 (s, 1, *anti* Mo=C*H*), 11.46 (br s, 1, *syn* Mo=CH), 7.90 (s, 1, *Ar*), 7.78 (s, 1, *Ar*), 7.28 (br s, 2, *Ar*), 7.12 (t, 2, *Ar*), 7.00 (t, 1, *Ar*), 6.91 (m, 3, *Ar*), 3.62 (br, 2, MeC*H*Me), 3.48 (br, 4, CH_2OCH_2), 2.13 (s, 6, C*Me*$_2$), 1.68 (s, 3, Biphen*Me*), 1.57 (s, 3, Biphen*Me*), 1.43 (s, 9, Biphen-*t-Bu*), 1.37 (s, 9, Biphen-*t-Bu*), 1.20 (br, 4, CH_2CH_2), 1.11 (d, 12, *Me*CH*Me*); ^{19}F NMR (C_6D_6, 282 MHz) δ −58.21, −58.40, −58.77, −58.90; ^{13}C NMR (CD_2Cl_2, 125 MHz) *both isomers* δ 322.00 (*anti*, C_α), 290.30 (*syn*, C_α), 154.54, 154.00, 150.61, 149.81, 136.08, 135.28, 134.99, 131.38, 131.07, 130.17, 128.92, 128.88, 128.83, 128.65, 127.95, 126.78, 126.74, 126.70, 126.67, 126.64, 123.85, 123.56, 35.96, 35.87, 35.52, 35.49, 30.96, 30.81, 30.48, 30.38, 30.03, 29.48, 29.43, 25.91, 24.54, 24.45, 23.44, 16.00, 15.89. Anal. Calcd for $C_{50}H_{63}F_6MoNO_3$: C, 64.16; H, 6.78; N, 1.50. Found: C, 64.04; H, 6.85; N, 1.48.

Mo(*N*-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(Biphen$_{CF3}$)(THF) (5b). Complex **5b** was prepared in a manner analogous to **5a** and isolated in 60% yield: ^{1}H NMR (C_6D_6, 500 MHz) δ 14.10 (s, 1, *anti* Mo=C*H*, J_{CH} = 146 Hz), 12.41 (br, 1, *syn* Mo=C*H*, J_{CH} = 117 Hz), 7.93 (s, 1, *Ar*), 7.72 (s, 1, *Ar*), 7.39 (d, 2, *Ar*), 7.18 (t, 1, *Ar*), 7.10−6.96 (m, 2, *Ar*), 6.71 (d, 2, *Ar*), 6.63 (t, 1, *Ar*), 3.45 (br s, 4, CH$_2$-OCH$_2$), 2.16 (s, 3, C*Me*$_2$Ph), 2.15 (s, 3, Ar*Me*) 2.08 (s, 3, C*Me*$_2$Ph), 2.05 (s, 3, Ar*Me*), 1.66 (s, 3, Biphen*Me*), 1.53 (s, 3, Biphen*Me*), 1.47 (s, 8, Biphen-*t-Bu*), 1.33 (s, 9, Biphen-*t-Bu*), 0.98 (br s, 4, CH_2CH_2); ^{19}F NMR (C_6D_6, 282 MHz) δ −58.2, −58.3, −58.8; ^{13}C NMR (C_6D_6, 125 MHz) *both isomers* δ 320.48, 168.31, 165.48, 156.67, 156.21, 150.76, 149.46, 136.50, 135.45, 134.92, 132.22, 131.99, 131.15, 129.87, 128.99, 128.92, 127.42, 127.28, 126.96, 126.68, 126.32, 126.11, 126.01, 125.70, 124.84, 124.03, 120.83, 75.40, 55.21, 53.72, 35.85, 35.74, 35.69, 34.80, 32.33, 31.16, 30.98, 30.79, 30.68, 30.63, 28.60, 27.22, 25.21, 23.10, 20.11, 19.03, 16.76, 16.60, 16.15, 15.66. Anal. Calcd for $C_{46}H_{55}F_6MoNO_3$: C, 62.79; H, 6.30; N, 1.59. Found: C, 62.88; H, 6.38; N, 1.62.

Mo(*N*-1-adamantyl)(CHCMe$_2$Ph)(Biphen$_{CF3}$)(THF) (5c). Complex **5c** was prepared in a manner analogous to **5a** and isolated in 71% yield: ^{1}H NMR (C_6D_6, 500 MHz) δ 12.14 (br, 1, *syn* Mo=C*H*), 7.92 (s, 1, *Ar*), 7.86 (s, 1, *Ar*), 7.26 (d, 2, *Ar*), 7.15 (t, 2, *Ar*), 7.01 (t, 1, *Ar*), 3.42 (br s, 4, CH_2OCH_2), 2.11 (s, 3, C*Me*$_2$Ph), 2.08 (s, 3, C*Me*$_2$Ph), 1.78 (br s, 6, *adamantyl*), 1.71 (br s, 3, *adamantyl*), 1.66 (s, 3, Biphen*Me*), 1.59 (s, 3, Biphen*Me*), 1.47 (s, 9, Biphen-*t-Bu*), 1.42 (s, 9, Biphen-*t-Bu*), 1.33(br s, 6, *adamantyl*), 1.23 (m, 4, CH_2CH_2); ^{19}F NMR (C_6D_6, 282 MHz) δ −58.36, −58.52; ^{13}C NMR (CD_2Cl_2, 125 MHz, −40 °C) *both diastereomers* δ 309.11, 295.71, 171.06, 168.30, 165.96, 165.39, 148.92, 147.95, 135.02, 134.32, 134.10, 133.91, 132.55, 131.26, 130.70, 130.01, 129.72, 128.35, 126.50, 126.98, 126.22, 126.14, 125.96, 125.86, 124.81, 124.70, 123.84, 123.34, 123.15, 118.46, 117.33, 77.42, 76.93, 74.97, 73.83, 51.13, 50.37, 44.24, 44.08, 35.68, 35.57, 35.12, 34.84, 34.37, 32.47, 31.78, 30.80, 30.32, 30.15, 29.83, 29.69, 29.52, 29.42, 29.28, 25.88, 25.65, 22.77, 15.98, 15.75, 15.62, 15.30. Anal. Calcd for $C_{48}H_{61}F_6MoNO_3$: C, 63.36; H, 6.76; N, 1.54. Found: C, 63.26; H, 6.71; N, 1.47.

Preliminary Ring-Closing Metathesis Reactions. Diallyl ether (0.225 mmol, 28 μL) was added to a solution of **2a** (10 mg, 0.009 mmol) in C_6D_6. The solution was transferred to a J. Young NMR tube, and ^{1}H NMR spectra were recorded after the stated time interval at the stated temperature. A similar procedure was employed for ring-closing diallyltosylamine.

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Supporting Information Available: Crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters for Mo(NAr)(CHCMe$_2$Ph)(Binaph$_{Anth}$)(THF) (06240) and Mo(NAd)(CHCMe$_2$Ph)(Biphen$_{CF3}$)(THF) (06180). This information is available free of charge via the Internet at http://pubs.acs.org. Data for the structures are also available to the public at http://www.reciprocalnet.org/.

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