New Chiral Molybdenum Catalysts for Asymmetric Olefin Metathesis that Contain 3,3′-Disubstituted Octahydrobinaphtholate or 2,6-Dichlorophenylimido Ligands

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Optically pure (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-bi-2-naphthol was derivatized with mesityl and benzhydryl groups in the 3 and 3′ positions to give R-H_2Mes$_2$Bitet and R-H_2-Benz$_2$Bitet, respectively. Addition of R-K_2Benz$_2$Bitet to Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(dme) yielded Mo(NAr)(CHCMe$_2$Ph)(R-Benz$_2$Bitet)(THF) (**7**), while addition of R-K_2Mes$_2$Bitet to Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(dme) in THF gave Mo(NAr)(CHCMe$_2$Ph)(R-Mes$_2$Bitet)(THF) (**8**). Four complexes that contained the 2,6-dichlorophenylimido ligand were prepared by similar procedures, namely, Mo(NAr$_{Cl}$)(CHCMe$_3$)(S-Biphen)(THF) (**9**), Mo(NAr$_{Cl}$)(CHCMe$_3$)(R-Trip$_2$-BINO)(THF) (**10**), Mo(NAr$_{Cl}$)(CHCMe$_3$)(R-Mes$_2$Bitet)(THF) (**11**), and Mo(NAr$_{Cl}$)(CHCMe$_3$)-(R-Benz$_2$Bitet)(THF) (**12**). X-ray studies of **8**, **9**, and **12** revealed them to be typical distorted trigonal bipyramids with THF and one biphenolate oxygen occupying axial positions. In **9** and **12** the alkylidene orientation was found to be *syn*, while in **8** the alkylidene orientation was found to be *anti*. Catalysts **7**, **8**, **9**, **10**, **11**, and **12** were all efficient in terms of both conversion and % ee for two standard desymmetrization reactions to form dihydrofurans.

Introduction

In the past decade the olefin metathesis reaction[1] has found a considerable number of applications in organic chemistry,[2−5] especially when well-characterized Mo[6] or Ru[7] catalysts are employed. During the last several years molybdenum imido alkylidene catalysts of the type Mo(NR)(CHR′)(Diolate) have been synthesized and employed for asymmetric metathesis reactions, where the diolate is optically pure.[8−21] Mo(NR)(CHR′)(Diolate) catalysts have a "modular" character since several imido groups and diolates are available. (The initial CHR′ group is usually neopentylidene or neophylidene.) The NR groups that have been employed most often are N-2,6-i-Pr$_2$C$_6$H$_3$ (NAr) and N-2,6-Me$_2$C$_6$H$_3$ (NAr′), while the most successful diolates have been Biphen^{2-} (as in **1**) or Trip$_2$BINO^{2-} (as in **2**). Recently we found that a ligand analogous to Biphen^{2-}, t-Bu$_2$Bitet^{2-} (as in **3**), could be prepared from enantiomerically pure octahydrobinaphthol and that **3** had some of the desirable characteristics of both catalysts **1** and **2** in various ring-closing reactions.[11] In this paper we report the preparation of complexes that contain two other variations of the octahydrobinaphtholate ligand, along with several that contain a new variation of imido ligand, N-2,6-Cl$_2$C$_6$H$_3$ (NAr$_{Cl}$).

Results and Discussion

Synthesis of H_2Mes$_2$Bitet, H_2Benz$_2$Bitet, and 2,6-Dichlorophenylimido Precursors. Optically pure (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-bi-2-naphthol is obtained readily by hydrogenation of commercially avail-

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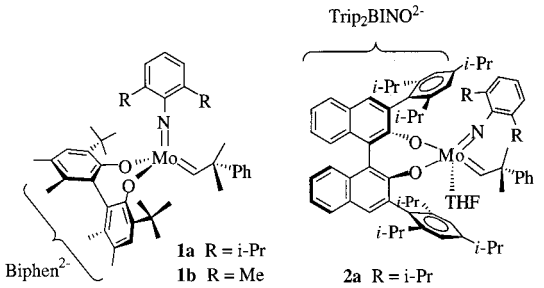
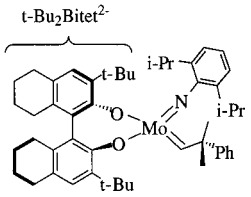
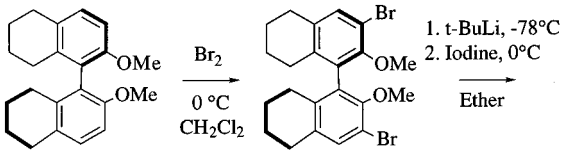


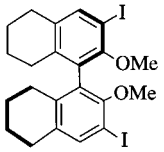


3

able (*R*)-1,1′-bi-2-naphthol.[11,22] It has the advantage over H_2Biphen of being easily prepared from commercially available enantiomerically pure binaphthol and the advantage over binaphthol of being reactive primarily at the 3 and 3′ positions. (Bulky substituents in the 3 and 3′ positions appear to be a requirement for a catalyst to be stable against bimolecular decomposition reactions.) After protection of the phenolic oxygens with a methyl group, addition of bromine gave the dibromide **4a** (eq 1). A diiodide (**4b**) was prepared by first lithiating



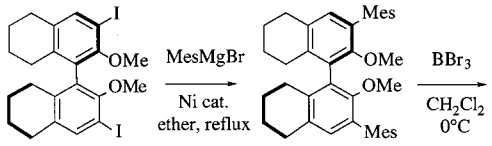
4a



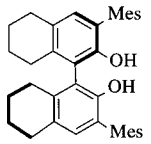
4b (1)

4a with *tert*-butyllithium followed by addition of iodine. Compound **4b** could be converted into the 3,3′-dimesityl derivative (**4c**) in a Ni(PPh_3)$_2$$Cl_2$-catalyzed coupling with MesitylMgBr in ether in ∼50% yield (eq 2). Compound **4c** was purified by column chromatography and then deprotected with boron tribromide to yield R-$H_2$$Mes_2$-Bitet (**5**). Compound **4a** performed significantly more poorly in the coupling reaction (yield ∼25%).

The synthesis of H_2(t-Bu)$_2$Bitet was accomplished via alkylation of (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-bi-2-naphthol with isobutylene and acid.[11] The benzhydryl group operationally has a steric influence approximately equal to a *tert*-butyl group in certain aspects of organometallic chemistry.[23] Therefore we chose to prepare the 3,3′-dibenzhydryl derivative as shown in eq 3. This

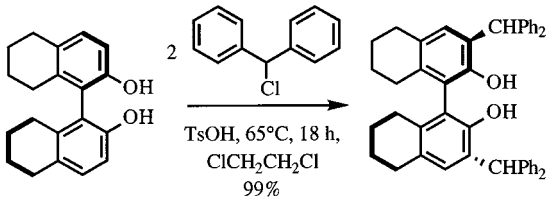


4b 4c



5 (R-$H_2$$Mes_2$Bitet) (2)

reaction proceeds cleanly and essentially quantitatively to afford (*R*)-3,3′-dibenzhydryl-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-bi-2-naphthol (**6**, R-$H_2$$Benz_2$Bitet) as a powdery solid. This reaction is performed readily on a 20 g scale.



6 (R-$H_2$$Benz_2$Bitet) (3)

The bisimido complex Mo(NAr_{Cl})$_2$$Cl_2$(dme) ($Ar_{Cl}$ = 2,6-$Cl_2C_6H_3$) was prepared from Na_2MoO_4, 2,6-dichloroaniline, triethylamine, and trimethylchlorosilane in dimethoxyethane in a manner that is analogous to syntheses of previously known Mo(NAryl)$_2$$Cl_2$(dme) complexes.[24] It could be obtained as dark red needles in 94% isolated yield on a multigram scale. Reaction of Mo(NAr_{Cl})$_2$$Cl_2$(dme) with 2 equiv of neopentylmagnesium chloride or neophylmagnesium chloride gave Mo(NAr_{Cl})$_2$(CH_2CMe_3)$_2$ or Mo(NAr_{Cl})$_2$(CH_2CMe_2Ph)$_2$, respectively, as orange-red powders in nearly quantitative yield.

Addition of 3 equiv of triflic acid to Mo(NAr_{Cl})$_2$(CH_2-CMe_3)$_2$ in dme at −30 °C yielded Mo(NAr_{Cl})(CHCMe_3)-(OTf)$_2$(dme) as a yellow solid in 56% yield. The proton NMR spectrum suggested that the product is a 1:4 mixture of *anti* and *syn* isomers with the *anti* alkylidene proton resonance at 14.98 ppm and the *syn* resonance at 14.08 ppm (J_{CH} = 121 Hz). (In a *syn* isomer the alkylidene's alkyl group is pointed toward the imido ligand; in the *anti* isomer it is pointed away from the imido ligand.) If THF is employed in the workup procedure, then a mixture of THF and dme adducts is obtained, as judged by the presence of two *syn* alkylidene resonances at 14.66 ppm (J_{CH} = 124 Hz, THF adduct) and 14.08 ppm (J_{CH} = 121 Hz, dme adduct) in the ^{1}H NMR spectrum. The ratio of the two species differed from sample to sample, as did the ratio of coordinated THF and dme. The presence of two species was also confirmed in the ^{19}F NMR spectrum by the observation of two singlets at −78.58 and −79.95 for each adduct's CF_3 group.

To our surprise, the synthesis of Mo(NAr_{Cl})(CHCMe_2-Ph)(OTf)$_2$(dme) or related THF adducts has not yet been

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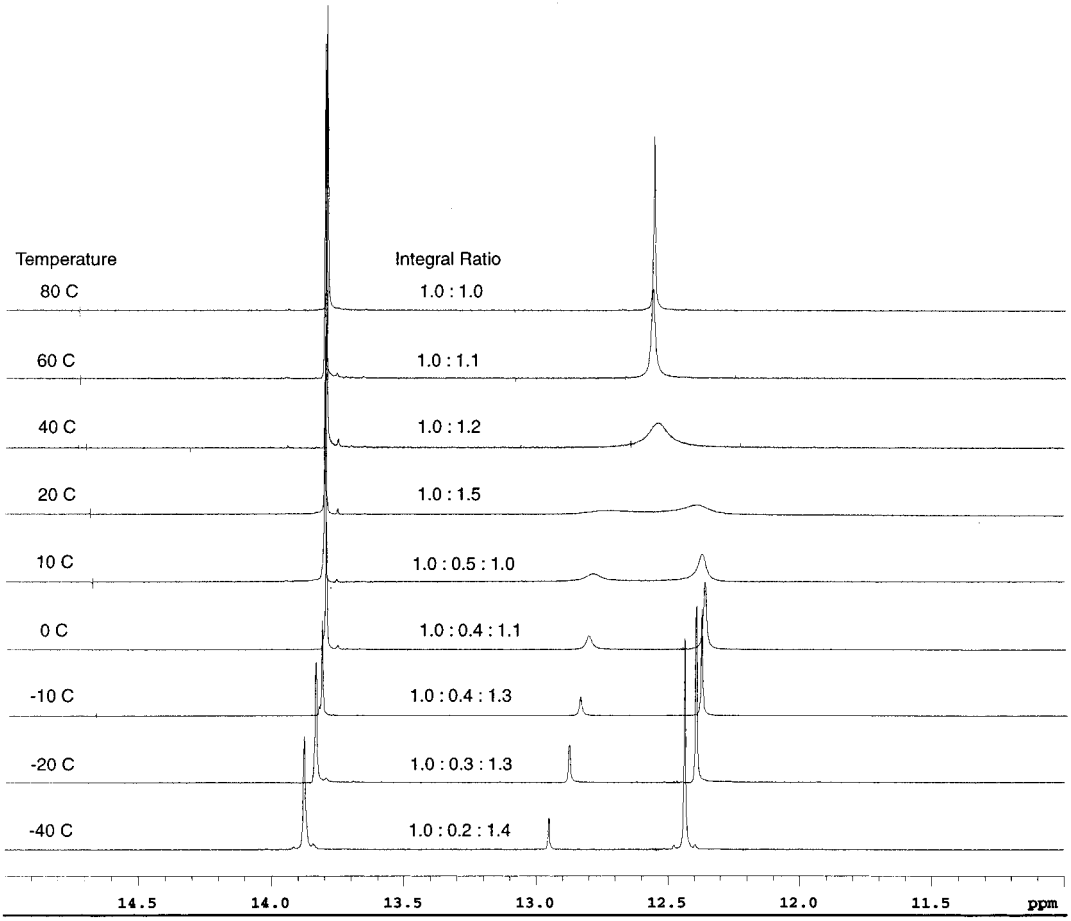

Figure 1. Variable-temperature ^{1}H NMR spectra (500 MHz, toluene-d_8) in the alkylidene region of Mo(NAr)(CHCMe$_2$Ph)(R-Mes$_2$Bitet)(THF) plus 10 equiv of DMF.

reproducible and does not take place in good yield, perhaps in part because of subtle solubility differences that prevent purification. Therefore we will only describe neopentylidene 2,6-dichlorophenylimido complexes in this paper. This is the first instance where there is a difference between neopentylidene and neophylidene complexes that is significant enough to warrant choosing one alkylidene over the other.

Synthesis of New Mo(NAryl)(CHCMe$_2$R)(Diolate) Complexes. Addition of R-K$_2$Benz$_2$Bitet (generated by deprotonation of R-H$_2$Benz$_2$Bitet with KH in THF) to Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(dme) yielded Mo(NAr)(CHCMe$_2$Ph)(R-Benz$_2$Bitet)(THF) (**7**), which is highly crystalline and readily isolated by recrystallization from diethyl ether. The ratio of *syn* to *anti* alkylidene proton resonances (at 11.16 and 14.07 ppm, respectively) was found to be 2.0 by ^{1}H NMR at 22 °C in C_6D_6. The presence of THF contrasts with the THF-free nature of **1a** or **3**, which suggests that the coordination sphere in the Benz$_2$Bitet^{2-} derivative is less sterically congested. The *syn*/*anti* ratio of ~2 (versus a *syn*/*anti* ratio of ~13 at 22 °C for Mo(NAr)(CHCMe$_2$Ph)(t-Bu$_2$Bitet)[11]) is also consistent with less steric interaction between the *anti* alkylidene substituent and the bisphenoxide ligand in the Benz$_2$Bitet^{2-} derivative.

Addition of a suspension of R-K$_2$Mes$_2$Bitet in THF to Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(dme) in THF led to formation of Mo(NAr)(CHCMe$_2$Ph)(R-Mes$_2$Bitet)(THF) (**8**), which could be isolated from pentane as a yellow powder in 69% yield. A proton NMR spectrum of **8** at room temperature showed alkylidene resonances for both *syn* and *anti* isomers at 11.6 and 13.8 ppm in a ratio of 3:4, respectively. As the sample was cooled to −70 °C the *syn* resonance shifted downfield, while the *anti* resonance shifted only slightly; at −70 °C the *syn* resonance was found at 12.55 ppm while the *anti* resonance was found at 13.80 ppm and the *syn*/*anti* ratio was 1:5. This temperature-dependent behavior is similar to what was observed for **3** in THF-d_8.[11] The presence of THF bound to the metal suggests that the Mes$_2$Bitet^{2-} ligand is less sterically demanding than the t-Bu$_2$Bitet^{2-} ligand.

In the process of exploring the functionality tolerance of **8** we obtained the temperature-dependent spectrum of **8** in toluene-d_8 in the presence of 10 equiv of acetonitrile or dimethylformamide (DMF). The spectra in the presence of DMF are shown in Figure 1. At −40 °C it is clear that DMF is bound to the metal on the NMR time scale to give primarily one *anti* adduct with an alkylidene resonance at ~13.9 ppm and two *syn* adducts with resonances at 12.95 and 12.43 ppm. Upon warming the sample to 80 °C the two diastereomeric *syn* adducts interconvert via loss of DMF. However, little or no DMF-free alkylidene is present, judging from the position of the *syn* adduct average resonance at ~12.6 ppm and the fact that **8** is inactive for metathesis of a test substrate at room temperature (vide infra). Although spectra in the presence of acetonitrile are roughly analogous to those shown in Figure 1, the average resonance for the two interconverting *syn* adducts moves upfield with increasing temperature,

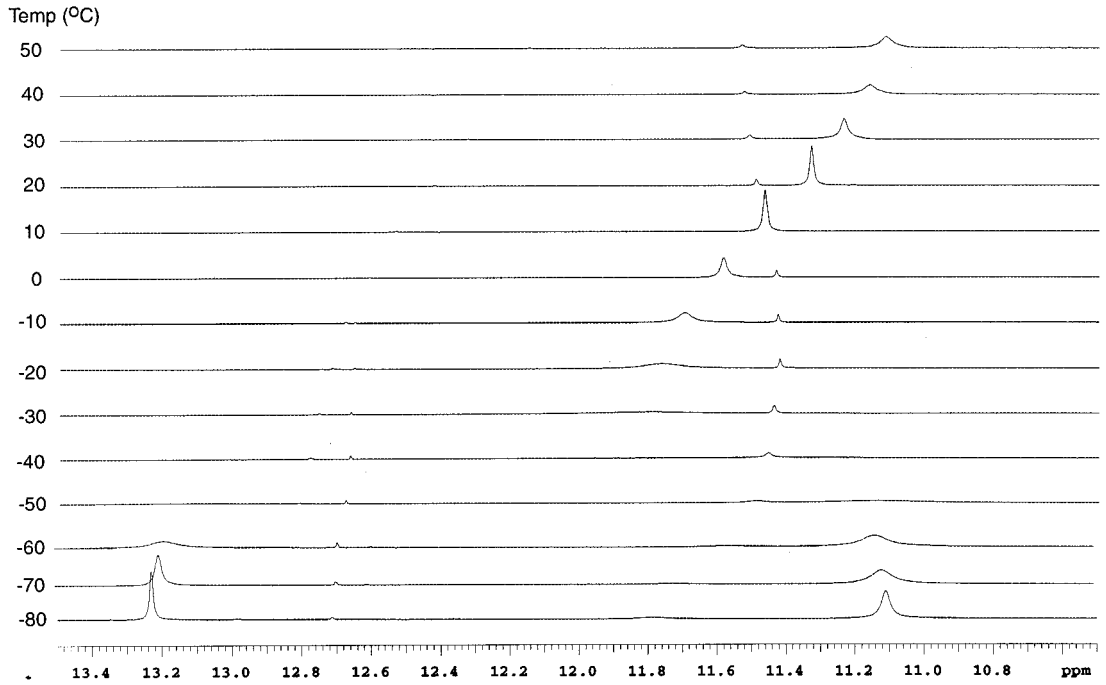

Figure 2. Variable-temperature ^{1}H NMR spectra (500 MHz, toluene-d_8) of the alkylidene proton region of Mo(NAr$_{Cl}$)(CHCMe$_3$)(S-Biphen)(THF).

consistent with some loss of acetonitrile to yield a base-free species. Consistent with this observation is the fact that **8** is active for metathesis in the presence of acetonitrile (vide infra). All evidence suggests that loss of a coordinated base is a prerequisite for metathesis activity.[25]

Four complexes were prepared by similar procedures that contained the 2,6-dichlorophenylimido ligand; they are Mo(NAr$_{Cl}$)(CHCMe$_3$)(S-Biphen)(THF) (**9**; 55% yield), Mo(NAr$_{Cl}$)(CHCMe$_3$)(R-Trip$_2$BINO)(THF) (**10**; 49% yield), Mo(NAr$_{Cl}$)(CHCMe$_3$)(R-Mes$_2$Bitet)(THF) (**11**; 41% yield), and Mo(NAr$_{Cl}$)(CHCMe$_3$)(R-Benz$_2$Bitet)(THF) (**12**; 49% yield). In all cases 1 equiv of THF is present. The proton NMR spectrum of **9** in toluene-d_8 at room temperature reveals primarily one alkylidene proton resonance at 11.31 ppm with J_{CH} = 120 Hz. Upon cooling this sample (Figure 2), this resonance shifts downfield and at −80 °C is resolved into two at 13.24 and 11.12 ppm. The resonance at 13.24 ppm has a value for J_{CH} = 120 Hz, characteristic of a *syn* alkylidene. A J_{CH} value could not be obtained for the resonance at 11.12 ppm because of its breadth, but that must also be ∼120 Hz in view of the average value being 120 Hz at 20 °C. These arguments, along with the position of the 11.12 ppm resonance, suggest that the high-field resonance can be ascribed to a THF-free *syn* species in equilibrium with the *syn* THF adduct under these conditions (∼1:1 at −80 °C). At +50 °C the high-field position of the average resonance suggests that the complex is largely free of THF. The proton NMR spectrum of **10** in toluene-d_8 at 20 °C shows a *syn* THF adduct resonance at 13.15 ppm (J_{CH} = 121 Hz) and an *anti* THF adduct resonance at 13.90 ppm with a *syn*/*anti* ratio of 16. No THF-free *syn* species is observed. The proton NMR spectra of **9**, **10**, and **12** in THF-d_8 show largely a resonance for the *syn* THF adduct, although a small resonance for the *anti* THF adduct is also observed, at both 20 and −40 °C. (See Experimental Section for chemical shifts and *syn*/*anti* ratios.) These data suggest that little *anti* isomer is formed for 2,6-dichlorophenylimido complexes, even in neat THF-d_8. We should note that in most spectra (e.g., in Figure 2) tiny additional alkylidene resonances (one or more) appear that we ascribe to trace alkylidene impurities. The species responsible for the resonances could not be identified.

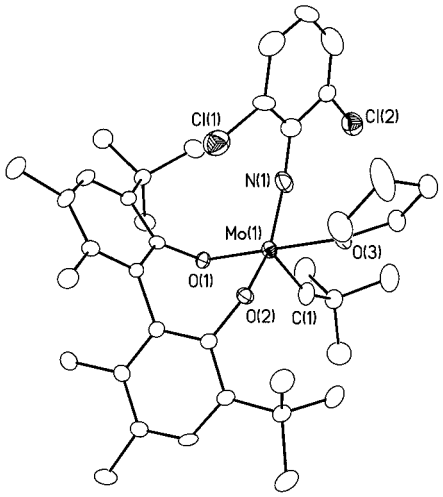

Figure 3. ORTEP representation of *syn*-Mo(NAr$_{Cl}$)(CHCMe$_3$)(S-Biphen)(THF) (**9**).

X-ray Studies of Three Mo(NAryl)(CHCMe$_2$R)(diolate) Complexes. X-ray studies were carried out on **9** (Table 1; Figure 3), **8** (Table 1; Figure 4), and **12** (Table 1; Figure 5). All are typical distorted trigonal bipyramids with THF (O(3)) and one biphenolate oxygen (O(1)) occupying axial positions. Pertinent bond lengths and angles are listed in Table 2. In **9** and **12** the alkylidene orientation was found to be *syn*, while in **8** the alkylidene orientation was found to be *anti*. The

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Table 1. Crystallographic Data, Collection Parameters, and Refinement Parameters for *syn*-Mo(NAr$_{Cl}$)(CHCMe$_3$)(S-Biphen)(THF) (9), *anti*-Mo(NAr)(CHCMe$_2$Ph)(R-Mes$_2$Bitet)(THF) (8), and *syn*-Mo(NAr$_{Cl}$)(CHCMe$_3$)(R-Benz$_2$Bitet)(THF) (12)[a]

	9	8	12
empirical formula	$MoC_{39}H_{53}NO_3Cl_2$	$C_{68}H_{87}MoNO_4$	$C_{61}H_{61}Cl_2MoNO_3$
fw	750.66	1078.33	1022.95
temperature	293(2) K	183(2) K	183(2) K
cryst syst, space group	orthorhombic, $P2_12_12_1$	orthorhombic, $P2_12_12_1$	orthorhombic, $P2_12_12_1$
unit cell dimens	a = 10.5365(6) Å b = 18.3753(11) Å c = 19.7029(12) Å $\alpha = \beta = \gamma = 90°$	a = 13.755(5) Å b = 20.578(7) Å c = 21.263(7) Å $\alpha = \beta = \gamma = 90°$	a = 13.773(5) Å b = 17.182(6) Å c = 21.696(8) Å $\alpha = \beta = \gamma = 90°$
volume	3814.7(4) Å^3	6018(4) Å^3	5134(3) Å^3
Z, calcd density	4, 1.307 Mg/m^3	4, 1.190 Mg/m^3	4, 1.323 Mg/m^3
abs coeff	0.520 mm^{-1}	0.265 mm^{-1}	0.406 mm^{-1}
F(000)	1576	2304	2136
θ range for data	2.19−23.29°	2.02−20.00°	2.11−23.30°
limiting indices	$-11 \le h \le 11$, $-20 \le k \le 15$, $-21 \le l \le 21$	$-13 \le h \le 11$, $-19 \le k \le 10$, $-17 \le l \le 19$	$-6 \le h \le 15$, $-18 \le k \le 19$, $-24 \le l \le 24$
no. of reflns collected/unique	15643/5473 [R(int) = 0.0387]	8503/5333 [R(int) = 0.0861]	21131/7382 [R(int) = 0.0552]
max. and min. transmn	0.2670 and 0.2316	0.2662 and 0.2041	0.9760 and 0.9342
no. of data/restraints/params	5473/0/415	5333/0/658	7382/0/613
goodness-of-fit on F^2	1.044	1.028	1.027
final R indices [$I>2\sigma(I)$]	R1 = 0.0502, wR2 = 0.1243	R1 = 0.0663, wR2 = 0.1101	R1 = 0.0435, wR2 = 0.0994
R indices (all data)	R1 = 0.0567, wR2 = 0.1280	R1 = 0.1126, wR2 = 0.1261	R1 = 0.0520, wR2 = 0.1034
abs structure param	0.01(6)	−0.08(7)	−0.06(4)
largest diff peak and hole	0.838 and −0.551 e Å^{-3}	0.394 and −0.287 e Å^{-3}	0.492 and −0.322 e Å^{-3}

[a] For all structures λ was 0.71073 Å, the refinement method was full-matrix least-squares on F^2, and the absorption correction was empirical.

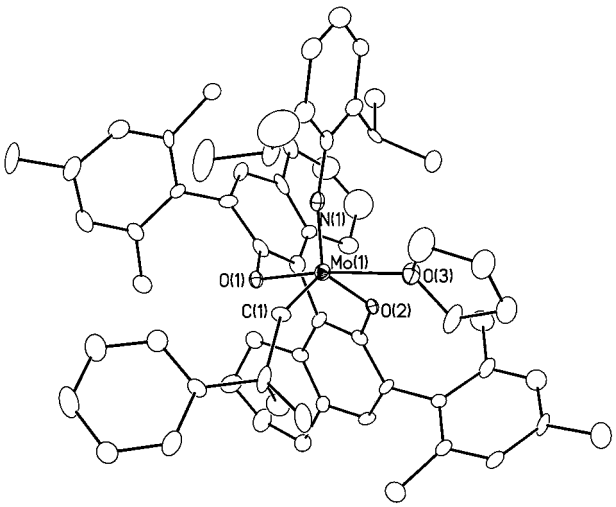


Figure 4. ORTEP representation of *anti*-Mo(NAr)(CHCMe$_2$-Ph)(R-Mes$_2$Bitet)(THF) (**8**).

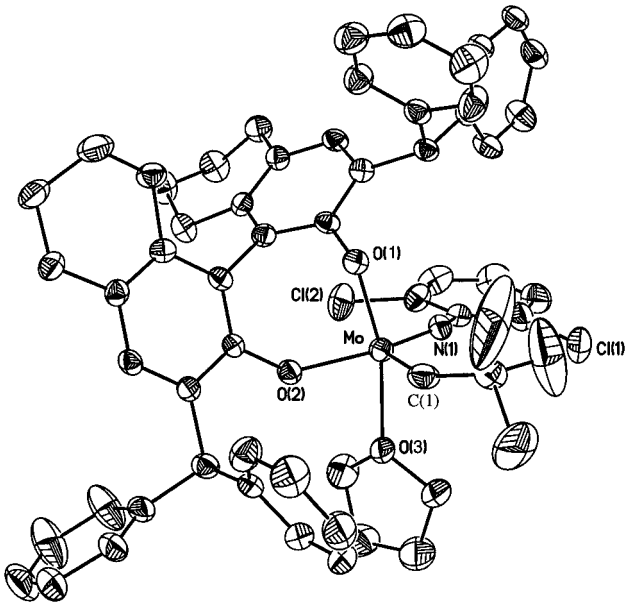


Figure 5. ORTEP representation of *syn*-Mo(NAr$_{Cl}$)-(CHCMe$_3$)(R-Benz$_2$Bitet)(THF) (**12**).

Mo−C(1)−C(2) angles are larger for the *syn* structures (150.3(6)°, 143.5(4)°) than for the *anti* structure (128.4-(9)°), which is the typical consequence of some agostic interaction of the *syn* CH$_\alpha$ bond with the metal.[25] The largest Mo−N(1)−C(30) angle is found in **8** (164.2(8)°), perhaps as a consequence of the NAr group being most resistant to bending (for steric as well as electronic reasons) compared to the NAr$_{Cl}$ group. Accordingly the Mo−N(1) bond length is significantly shorter in **8** (1.721-(9) Å versus 1.745(6) Å in **9** and 1.757(4) Å) in **12**. In **12** the Mo−Cl(2) distance (3.456 Å) is too long to be considered a true bond, although the chloride has the capacity to donate to the metal in a position *trans* to C(1). The observed circumstance may be the result of steric circumstances that force Cl(2) into that position.

These structures should be compared with three others in this general class in the literature, namely, Mo(NAr)(CHCMe$_2$Ph)(S-Ph$_2$BINO)(THF) (the crystal used in the X-ray study was of the racemic compound),[26] Mo(NAr)(CHCMe$_2$Ph)(R-Trip$_2$BINO)(pyridine),[21] and Mo-(N-2-CF$_3$C$_6$H$_4$)(CHCMe$_3$)(S-Biad)(pyridine) (Biad^{2-} = 3,3′-bis-1-adamantyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diolate).[13] The structures of these three compounds along with the three structures described in this paper are shown in Figure 6. Each is oriented with the base coming out of the page, the CNO equatorial plane approximately in the plane of the paper, and the alkylidene pointing down. Each compound that contains a diolate with the *S* configuration reveals a clockwise C/O/N arrangement of the alkylidene α carbon, diolate oxygen, and imido nitrogen lying in the plane of the

(26) Totland, K. M.; Boyd, T. J.; Lavoie, G. G.; Davis, W. M.; Schrock, R. R. *Macromolecules* **1996**, *29*, 6114.

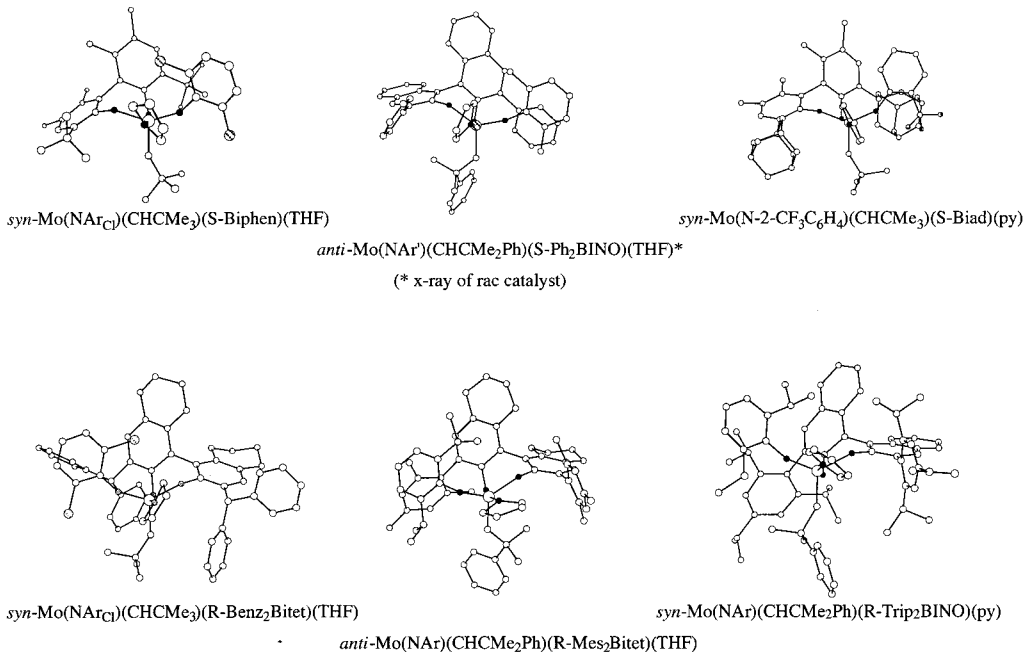


Figure 6. Comparison of structures of various adducts.

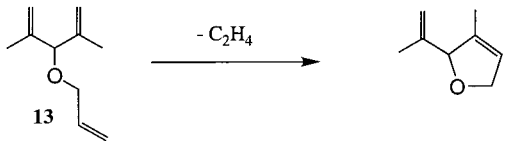
Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Non-Hydrogen Atoms of *syn*-Mo(NAr$_{Cl}$)(CHCMe$_3$)(S-Biphen)(THF) (9), *anti*-Mo(NAr)(CHCMe$_2$Ph)(R-Mes$_2$Bitet)(THF) (8), and *syn*-Mo(NAr$_{Cl}$)(CHCMe$_3$)(R-Benz$_2$Bitet)(THF) (12)

	9	8	12
Mo−N(1)	1.745(6)	1.721(9)	1.757(4)
Mo−C(1)	1.872(7)	1.882(1)	1.898(5)
Mo−O(1)	1.998(3)	2.005(5)	2.006(3)
Mo−O(2)	1.961(3)	2.000(7)	1.950(3)
Mo−O(3)	2.266(4)	2.263(7)	2.232(3)
Mo−C(1)−C(2)	150.3(6)	128.4(9)	143.5(4)
Mo−N(1)−C(30)	149.8(8)	164.2(8)	152.1(3)
Mo−O(1)−C(6)	114.0(3)	114.2(6)	112.4(2)
Mo−O(2)−C(17)	122.8(3)	131.2(6)	131.9(3)
N(1)−Mo−C(1)	107.0(3)	100.5(4)	108.6(2)
N(1)−Mo−O(1)	99.5(2)	103.8(4)	102.61(16)
N(1)−Mo−O(2)	140.5(3)	131.9(3)	134.62(16)
N(1)−Mo−O(3)	83.9(2)	85.1(3)	89.07(16)
C(1)−Mo−O(1)	90.6(2)	89.8(3)	90.27(18)
C(1)−Mo−O(2)	109.1(3)	125.4(4)	115.2(2)
C(1)−Mo−O(3)	95.3(2)	95.3(4)	93.91(18)
O(1)−Mo−O(2)	95.58(16)	91.1(3)	88.89(12)
O(1)−Mo−O(3)	172.03(15)	168.8(3)	165.64(12)
O(2)−Mo−O(3)	77.44(15)	77.8(3)	76.89(12)

page. Each compound that contains a diolate with the *R* configuration reveals a counterclockwise C/O/N arrangement. In short, all structures are the same type of diastereomer, regardless of the diolate, imido group, base, or alkylidene orientation (*syn* or *anti*). Therefore it seems likely that this type of diastereomer binds the base most strongly of the two that are possible for any compound that contains an enantiomerically pure form of the diolate and an alkylidene with a given orientation (*syn* or *anti*), and the one that is dominant in solution. Although we cannot conclude that this type of diastereomer is analogous to that formed upon reaction with an olefin in some catalytic pathway that produces a product with high % ee, that currently is our working hypothesis.

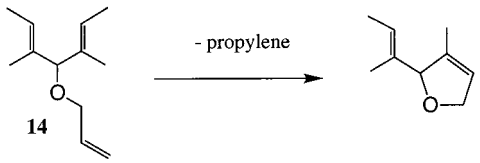
Asymmetric Metathesis Reactions. Several of the new catalysts were employed with the "test" desymmetrization substrates **13** and **14**, as shown in Tables 3 and 4. (The % ee is arbitrarily assigned as negative for the S-Biphen catalyst.) Catalysts **7**, **8**, **9**, **10**, **11**, and **12** were all relatively effective in terms of both conversion to the product and % ee, and virtually no homocoupled product derived from either substrate was observed. Catalysts **9** and **10** already have been employed in other types of asymmetric metathesis reactions and have shown superior activity and high product % ee in several circumstances.[14,20] In the future we will be exploring

Table 3. Desymmetrization of 13 with Mo Catalysts at Room Temperature



catalyst	time (h)	mol %	conv (%)	prod % ee
Mo(NAr)(CHCMe$_2$Ph)(R-Benz$_2$Bitet)(THF) (**7**)	2	5	>95	93
Mo(NAr)(CHCMe$_2$Ph)(R-Mes$_2$Bitet)(THF) (**8**)	3	5	84	93
Mo(NAr$_{Cl}$)(CHCMe$_3$)(S-Biphen)(THF) (**9**)	1	5	>99	−90
Mo(NAr$_{Cl}$)(CHCMe$_3$)(R-Trip$_2$BINO)(THF) (**10**)	1	5	>99	86
Mo(NAr$_{Cl}$)(CHCMe$_3$)(R-Mes$_2$Bitet)(THF) (**11**)	1	5	>99	90
Mo(NAr$_{Cl}$)(CHCMe$_3$)(R-Benz$_2$Bitet)(THF) (**12**)	1	5	>99	95

Table 4. Desymmetrization of 14 with Mo Catalysts at Room Temperature



catalyst	time (h)	mol %	conv (%)	prod % ee
Mo(NAr)(CHCMe$_2$Ph)(R-Mes$_2$Bitet)(THF) (**8**)	3	5	83	98
Mo(NAr$_{Cl}$)(CHCMe$_3$)(S-Biphen)(THF) (**9**)	1	5	99	−97
Mo(NAr$_{Cl}$)(CHCMe$_3$)(R-Trip$_2$BINO)(THF) (**10**)	1	5	>99	91
Mo(NAr$_{Cl}$)(CHCMe$_3$)(R-Mes$_2$Bitet)(THF) (**11**)	1	5	>95	96
Mo(NAr$_{Cl}$)(CHCMe$_3$)(R-Benz$_2$Bitet)(THF) (**12**)	1	5	>95	91

other catalysts that have been prepared here in asymmetric metathesis reactions.

One issue that will arise in future applications is the effect of various functionalities on rate and % ee. We have explored the use of **8** for desymmetrizing substrate **13** in the presence of 1 equiv (per equivalent of **13**) of diethyl ether, THF, dioxane, tetrahydrothiazole, 2,6-lutidine, 2-methylpyridine, pyridine, acetonitrile, and DMF. The reaction failed in the presence of pyridine and DMF, the first as a consequence of an unknown type of reaction with the catalyst, and the second because DMF coordinates strongly to the catalyst (vide supra). All other added bases lengthened the time required for ring-closure to 12−20 h at 22 °C (2−6 h at 50 °C), but conversion and % ee remained high.

Conclusion

We have shown that new Mo(NAryl)($CHCMe_2R$)(diolate) complexes can be prepared in which the aryl group is 2,6-dichlorophenyl and/or the diolate is (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-bi-2-naphtholate substituted in the 3 and 3′ positions with mesityl or benzhydryl groups and that they all are less crowded around the metal than closely related analogues, judging by their tendency to crystallize with 1 equiv of bound THF. Preliminary results with two test substrates show them to be highly active as well as efficient asymmetric metathesis catalysts. Catalysts that contain these new ligands therefore are likely to find utility in future asymmetric metathesis applications.

Experimental Section

General Details. All experiments were conducted under nitrogen in a Vacuum Atmospheres drybox or using standard Schlenk techniques. THF, ether, toluene, and pentane were sparged with nitrogen and passed through alumina columns under dinitrogen. Benzene and dme were distilled from sodium benzophenone ketyl. Anhydrous Et_3N, HOTf, $ClSiMe_3$, and 2,6-$Cl_2C_6H_3NH_2$ were purchased from Aldrich, while Na_2MoO_4 was purchased from Strem. Neophylmagnesium chloride and neopentylmagnesium chloride were prepared in ether by standard procedures. Benzyl potassium,[27] R-Trip$_2$BINO,[21] and S-Biphen[13] were synthesized as described in the literature. Benzene-d_6, THF-d_8, and toluene-d_8 were sparged with nitrogen and stored over 4 Å molecular sieves. ^{1}H and ^{13}C NMR data are listed in parts per million downfield from tetramethylsilane and referenced using the residual protonated solvent peak. ^{19}F NMR data were referenced externally using C_6F_6 in $CHCl_3$ as a standard (−164 ppm). Elemental analyses were performed by H. Kolbe Laboratories, Mülheim an der Ruhr, Germany.

(+)-(*R*)-2,2′-Dimethoxy-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl. A three-neck flask, equipped with a condenser, was charged with R-H_2Bitet (10 g, 34 mmol), K_2CO_3 (23.5 g, 170 mmol), and acetone (300 mL). Methyl iodide (8 mL, 128 mmol) was added, and the mixture was heated to 70 °C. After 20 h, more methyl iodide was added (7 mL, 112 mmol), and the mixture was held at 70 °C for another 14 h. The reaction mixture was cooled to room temperature and then poured into water (300 mL) to produce a white slurry. The white solid was filtered off and dried in vacuo; yield 10.54 g (96%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.1 (d, 2, aryl H), 6.8 (d, 2, aryl H), 3.7 (s, 6, OCH_3), 2.8 (br t, 4), 2.2 (m, 4), 1.75 (m, 8); HRMS (EI$^+$) calcd 322.1927, found 322.1903. This material was pure enough to be used in the next step.

(27) Lochmann, L.; Trekoval, J. *J. Organomet. Chem.* **1987**, *326*, 1.

(+)-(*R*)-3,3′-Dibromo-2,2′-dimethoxy-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl (4a). Bromine (6.75 mL, 131 mmol) was added to a solution of (+)-(*R*)-2,2′-dimethoxy-5,5′,6,6′,7,7′,-8,8′-octahydro-1,1′-binaphthyl (16.9 g, 52 mmol) in dichloromethane (500 mL) at 0 °C. After 1 h, the red solution was poured into a solution of $NaHSO_3$ (600 mL), and the mixture was stirred for 1 h. The resultant biphasic mixture was extracted three times with dichloromethane (600 mL). The dichloromethane layer was dried over $MgSO_4$, and the mixture was filtered. The solvent was removed from the filtrate in vacuo to give 22.1 g (88%) of white, crystalline product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.4 (s, 2, aryl H), 3.6 (s, 6, OCH_3), 2.8 (br t, 4), 2.2 (m, 4), 1.75 (m, 8); ^{13}C{H} NMR (75 MHz, $CDCl_3$) δ 151.50, 135.93, 134.71, 132.91, 131.94, 113.81, 60.44, 29.25, 27.41, 22.74, 22.71; HRMS (EI$^+$) calcd 478.0138, found 478.0112.

(+)-(*R*)-3,3′-Diiodo-2,2′-dimethoxy-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl (4b). *tert*-BuLi (25 mL, 1.7 M in hexanes) was added at −78 °C to a colorless solution of **4a** (5 g, 10 mmol) in ether (250 mL) under N_2. The orange mixture was warmed to 0 °C for 30 min, then a solution of iodine (5.8 g, 23 mmol) in ether (50 mL) was added to the reaction mixture via cannula. The reaction mixture turned pale yellow, then brown, and was left to warm to room temperature overnight. The reaction was poured into a $NaHSO_3$ solution. The solution was stirred for 2 h, then extracted twice with ether (300 mL). The extract was dried over $MgSO_4$ and the solvent removed in vacuo to give 5.04 g (84% yield) of a pale yellow foam, which was used without further purification: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.6 (s, 2, aryl H), 3.5 (s, 6, OCH_3), 2.8 (br t, 4), 2.2 (m, 4), 1.75 (m, 8); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 154.22, 139.11, 137.19, 135.50, 131.36, 88.28, 60.42, 29.01, 27.39, 25.65, 22.63, 22.61; HRMS (EI$^+$) calcd 573.9860, found 573.9861.

(+)-(*R*)-3,3′-Bis-2″,4″,6″-trimethylphenyl-2,2′-dimethoxy-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl (4c). To a dark green mixture of **4b** (4 g, 6.97 mmol) and bistriphenylphosphinenickel(II) chloride (1.7 g, 2.6 mmol) in ether (500 mL) was added mesitylmagnesium bromide (60 mL, 1.3 M) under N_2. The black mixture was heated to reflux overnight, then quenched with 10% HCl (300 mL). The red, biphasic mixture was stirred for 20 min. This mixture was extracted three times with ether (400 mL). The ether layer was washed with a solution of $NaHCO_3$ and then brine. The ether solution was dried over $MgSO_4$, and after filtration, the ether was removed in vacuo to give an orange solid. The product was purified via column chromatography, eluting with 750 mL of toluene/hexanes (1:4). The off-white solid was washed with pentane; yield 6.77 g of white powder (46%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (s, 2, aryl H), 6.92 (s, 2, aryl H), 6.76 (s, 2, aryl H), 3.13 (s, 6, OCH_3), 2.78 (br t, 4), 2.32 (m, 4), 2.32 (s, 6), 2.13 (s, 6), 2.10 (s, 6), 1.77 (m, 8); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 152.45, 136.48, 136.37, 136.18, 135.32, 132.13, 130.92, 130.74, 130.28, 127.89, 127.84, 59.23, 29.40, 27.43, 25.35, 23.24, 23.10, 21.07, 20.82, 20.77; HRMS (EI$^+$) calcd 558.3492, found 558.3461.

(+)-(*R*)-3,3′-Bis-2″,4″,6″-trimethylphenyl-2,2′-dihydroxy-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl (5). To a solution of **4c** (6.77 g, 12.0 mmol) in dry CH_2Cl_2 (250 mL) at 0 °C was added tribromoborane (36 mL, 1.0 M). The dark red mixture was stirred for 2 h and warmed to room temperature. The reaction was quenched with water (400 mL). The mixture was extracted three times with CH_2Cl_2 (400 mL). The dichloromethane solution was dried over $MgSO_4$, and the solvent was removed in vacuo to give a brown, crystalline solid. The crude product was dissolved in pentane, and the solution was passed through a short Celite layer to obtain 5.25 g of **5** as an off-white foam (82% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 (s, 2), 6.99 (s, 2), 6.87 (s, 2), 4.53 (s, 2, OH), 2.82 (br t, 4), 2.40 (m, 4), 2.36 (s, 6), 2.15 (s, 6), 2.08 (s, 6), 1.82 (m, 8); ^{13}C{H} NMR (75 MHz, $CDCl_3$) δ 147.83, 136.99, 136.92, 135.86, 133.60, 131.11, 129.62, 128.28, 128.15, 124.53, 120.23, 29.18,

27.02, 23.17, 23.05, 21.06, 20.52, 20.44; HRMS (EI^+) calcd 530.3179, found 530.3179.

(+)-(*R*)-3,3′-Dibenzhydryl-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-bi-2-naphthol (6). A 500 mL flask was charged with (*R*)-octahydrobinaphthol (10.00 g, 33.97 mmol), $TsOH\cdot H_2O$ (10.00 g, 52.6 mmol), and 100 mL of 1,2-dichloroethane. This mixture was warmed to 65 °C, and a solution of benzhydryl chloride (13.77 g, 67.93 mmol, 2.0 equiv) in 100 mL of 1,2-dichloroethane was added dropwise via an addition funnel over 50 min. After 18 h, the reaction was cooled to room temperature and combined with 300 mL of CH_2Cl_2. The organic layer was extracted with H_2O (2 × 100 mL) and with 5% aqueous KOH (1 × 100 mL). The organic layer was dried over $MgSO_4$. The mixture was filtered, and the solvent was removed from the filtrate in vacuo to provide the product in quantitative yield (21.29 g): ^{1}H NMR ($CDCl_3$) δ 7.12−7.40 (m, 20, aryl H), 6.58 (s, 2, OH), 5.83 (s, 2, phenol-C*H*Ph_2), 4.64 (s, 2, OH), 2.60 (m, 16, C*H*$_2$), 2.19, 1.68; ^{13}C NMR ($CDCl_3$) δ 23.24, 23.18, 27.04, 29.48 (−*C*H_2), 50.39 (*C*HPh_2), 126.33, 126.41, 128.12, 128.37, 128.37, 128.48, 128.48, 128.56, 129.45, 129.45, 129.63, 129.63, 129.75, 131.80, 135.38, 143.73, 143.97, 149.14 (aryl). Anal. Calcd for $C_{46}H_{42}O_2$: C, 88.14; H, 6.75. Found: C, 88.25; H, 6.76.

Mo(NAr$_{Cl}$)$_2$Cl$_2$(dme). This procedure has appeared in the Supporting Information of a previous publication.[14] It is repeated for convenience here.

Na_2MoO_4 (20.00 g, 97.13 mmol), Me_3SiCl (148 mL, 1170 mmol), Et_3N (39.32 g, 388.5 mmol), 2,6-$Cl_2C_6H_3NH_2$ (31.47 g, 194.3 mmol), and dme (500 mL) were mixed in a 1 L flask, and the mixture was heated to 65 °C for 4 days to give a red suspension. All solvents were then removed in vacuo, leaving a pink solid that was extracted with a Soxhlet apparatus using dme as a solvent. The dme was removed in vacuo, and the resulting red solid was dried in vacuo to yield Mo(N-2,6-$Cl_2C_6H_3)_2Cl_2$(dme) as a red solid (52.6 g, 94%). If necessary, the product can be recrystallized from ether to remove trace impurities: ^{1}H NMR (500 MHz, C_6D_6) 6.79 (d, 4, aryl H), 6.11 (t, 2, aryl H), 3.61 (br s, 4, OC*H*$_2$), 3.21 (br s, 6, OC*H*$_3$); ^{13}C NMR (125 MHz, C_6D_6) δ 152.44, 132.38, 127.87, 118.40, 30.56, 23.07. Anal. Calcd for $MoC_{16}H_{16}Cl_6N_2O_2$: C, 33.31; H, 2.80; N, 4.86; Cl, 36.87. Found: C, 33.18; H, 2.88; N, 4.90; Cl, 36.78.

Mo(NAr$_{Cl}$)$_2$(CH$_2$CMe$_3$)$_2$. This procedure has appeared in the Supporting Information of a previous publication.[14] It is repeated for convenience here.

Mo(NAr$_{Cl}$)$_2$Cl$_2$(dme) (15.82 g, 27.42 mmol) was dissolved in ether (150 mL), and Me_3CCH_2MgCl (1.46 M in ether, 42.0 mL, 60.3 mmol) was added dropwise. The mixture was stirred for 18 h and filtered through Celite. The solvent was removed from the filtrate in vacuo to give the product as a red powder that was recrystallized from pentane; yield 15.20 g (99%): ^{1}H NMR (500 MHz, C_6D_6) δ 6.88 (d, 4, aryl H), 6.21 (t, 2, aryl H), 2.55 (s, 4, C*H*$_2$), 1.23 (s, 18, C*H*$_3$); ^{13}C NMR (125 MHz, C_6D_6) 151.81, 130.79, 128.37, 125.56, 87.69, 35.30, 33.73. Anal. Calcd for $MoC_{22}H_{28}Cl_4N_2$: C, 47.34; H 5.06; N, 5.02; Cl, 25.40. Found: C, 47.30; H, 5.11; N, 5.00; Cl, 25.27.

Mo(NAr$_{Cl}$)$_2$(CH$_2$CMe$_2$Ph)$_2$. Neophylmagnesium chloride (0.62 M in ether, 31.0 mL, 19.1 mmol) was added dropwise to a solution of Mo(NAr$_{Cl}$)$_2$Cl$_2$(dme) (5.00 g, 8.67 mmol) in ether (100 mL). After stirring for 19 h, the mixture was filtered through Celite. The ether was removed from the filtrate in vacuo to give Mo(NAr$_{Cl}$)$_2$(CH$_2$CMe$_2$Ph)$_2$ as a brown-orange solid; yield 5.91 g (quantitative): ^{1}H NMR (500 MHz, C_6D_6) δ 7.41 (d, 4, aryl H), 7.16 (t, 4, aryl H), 7.01 (t, 2, aryl H), 6.85 (d, 2, aryl H), 6.19 (t, 2, aryl H), 2.10 (s, 4, MoC*H*$_2$), 1.47 (s, 12, C*H*$_3$); ^{13}C NMR (125 MHz, C_6D_6) 150.51, 130.73, 129.09, 128.26, 126.95, 126.66, 125.37, 84.73, 40.66, 32.50. Anal. Calcd for $MoC_{32}H_{32}Cl_4N_2$: C, 56.33; H, 4.73; N, 4.11; Cl, 20.78. Found: C, 56.46; H, 4.72; N, 3.75; Cl, 20.78.

Mo(NAr$_{Cl}$)(CHCMe$_3$)(OTf)$_2$(dme). This procedure has appeared in the Supporting Information of a previous publication.[14] It is repeated for convenience here.

A solution of Mo(N-2,6-$Cl_2C_6H_3)_2$(CH$_2$CMe$_3$)$_2$ (13.52 g, 24.22 mmol) in dme (150 mL) was placed in a 500 mL flask. This solution was cooled to −30 °C, and HOTf (10.90 g, 72.65 mmol) was added in a dropwise fashion to yield a dark brown solution. The resulting mixture was allowed to warm gradually to room temperature and allowed to stir for 18 h. At this time, the volatile components were removed in vacuo to leave behind a brown foam that was then dissolved in toluene and filtered through Celite. Toluene was evaporated, leaving a brown solid that was dissolved in a mixture of ether and pentane and stored at −30 °C to give a brown powder. The brown powder was isolated by filtration and washed with cold ether to give Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(OTf)$_2$(dme) as a yellow solid (9.64 g, 55.7%): ^{1}H NMR (500 MHz, C_6D_6) (1:4 mixture of *anti* and *syn*) δ 14.98 (s, *anti*-CH), 14.08 (s, *syn*-CH, J_{CH} = 120.6 Hz). Anal. Calcd for $MoC_{17}H_{23}NCl_2F_6S_2O_8$: C, 28.58; H, 3.25; N, 1.96; Cl, 9.93. Found: C, 28.67; H, 3.26; N, 2.10; Cl, 9.86.

Pure and dry starting materials and solvents are imperative to the success of this procedure. Purification requires *complete* evaporation of solvent. If an oil or gummy solid is obtained from the various extractions, further removal of solvent is *required* (lyophilization with benzene is suggested) in order to obtain pure materials in good yield.

Mo(NAr$_{Cl}$)(CHCMe$_3$)(OTf)$_2$(dme)$_x$(THF)$_y$. Triflic acid (2.58 g, 17.20 mmol) was added dropwise to a solution of Mo(NAr$_{Cl}$)$_2$(CH$_2$CMe$_3$)$_2$ in dme (50 mL) at −30 °C. The solution turned dark brown. It was allowed to warm gradually to room temperature and stirred for 18 h. The solvent was removed in vacuo, leaving a brown foam that was then dissolved in benzene. The mixture was filtered through Celite and the benzene was removed in vacuo, leaving a brown, gummy solid. Addition of THF gave a fine yellow powder in a brown solution. The yellow powder was filtered off and shown by ^{1}H NMR spectroscopy to be a mixture of dme and THF adducts; yield 1.99 g (49%): ^{1}H NMR (500 MHz, C_6D_6) (∼1:1 mix of THF/dme adducts) δ 14.66 (s, *syn*-CH, THF adduct, J_{CH} = 123.6 Hz), 14.08 (s, *syn*-CH, dme adduct, J_{CH} = 120.6 Hz). Anal. Calcd for Mo(NAr$_{Cl}$)(CHCMe$_3$)(OTf)$_2$(dme)$_{0.37}$(THF)$_{0.63}$ (solvent ratios confirmed by ^{1}H NMR spectrum of sample) $MoC_{17}H_{21.74}NCl_2F_6S_2O_6$: C, 31.74; H, 3.66; N, 1.86; Cl, 9.41. Found: C, 32.22; H, 3.76; N, 1.78; Cl, 9.47.

Mo(NAr)(CHCMe$_2$Ph)(R-Mes$_2$Bitet)(THF) (8). Solid potassium hydride (362 mg, 9.0 mmol) was added portionwise to a solution of R-H_2(Mes$_2$Bitet) (2.4 g, 4.5 mmol) in THF (30 mL). The resultant white suspension was stirred for 40 min at room temperature, then filtered over a fine frit to isolate an off-white powder, which was dried under vacuum to 1.5 g (56% yield) and used without further purification.

R-K_2Mes$_2$Bitet (500 mg, 0.8 mmol) was added portionwise to a cold solution of Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(dme) (652 mg, 0.8 mmol) in THF (15 mL) at −30 °C. The reaction mixture turned deep red after 15 min and was stirred another 4 h. THF was then removed in vacuo, and the resultant yellow-brown solid was dissolved in toluene. The solution was filtered through Celite and solvent removed once more. The crude product was then taken up in pentane, whereupon a yellow powder precipitated. The powder was isolated by filtration and washed with cold pentane. The filtrate was concentrated to half the original volume and cooled to produce a second crop of product; total yield 570 mg (69%): ^{1}H NMR (400 MHz, C_6D_6) δ 13.8 (s, *anti*-CH, 56% of total) 11.6 (s, *syn*-CH, 44% of total). Anal. Calcd for $MoC_{64}H_{77}O_3N$: C, 76.54; H, 7.73; N, 1.39. Found: C, 76.63; H, 7.67; N, 1.33.

Mo(NAr)(CHCMe$_2$Ph)(THF)(R-Benz$_2$Bitet) (7). A 100 mL flask was charged with (*R*)-3,3′-dibenzhydryl-5,5′,6,6′,7,7′,-8,8′-octahydro-1,1′-bi-2-naphthol (1.690 g, 2.70 mmol) and potassium hydride (0.270 g, 6.73 mmol, 2.5 equiv). THF (30 mL) was condensed in at −78 °C, and the reaction was allowed to warm slowly. After 21 h, all solvent was removed and Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(dme) was added. THF (30 mL) was condensed in at −78 °C, and the reaction was allowed to warm

slowly. After 18 h, solvent was removed and benzene (30 mL) was condensed in and then removed by lyophilization to remove trace amounts of THF. Benzene (20 mL) was added, and the mixture was filtered. The benzene was removed in vacuo, and diethyl ether (20 mL) was added to give a yellow slurry, from which the solid was collected by filtration; yield 1.040 g. A second crop was obtained by reducing the volume of the filtrate and standing the filtrate at −30 °C; yield 0.423 g (49% total yield): ^{1}H NMR (C_6D_6) 14.07 (s, *anti*-CH), 11.16 (s, *syn*-CH). Anal. Calcd for $C_{72}H_{77}NO_3Mo$: C, 78.59; H, 7.05; N, 1.27. Found: C, 78.44, H, 6.97, N, 1.23.

Mo(NAr$_{Cl}$)(CHCMe$_3$)(S-Biphen)(THF) (9). Benzyl potassium (182 mg, 1.40 mmol) in THF (1 mL) was added to S-Biphen (248 mg, 0.70 mmol) in THF (1 mL) until a slight orange color persisted. This solution was then added to Mo(NAr$_{Cl}$)(CHCMe$_3$)(OTf)$_2$(dme) (500 mg, 0.70 mmol) in THF (2 mL). The dark red mixture was stirred for 17 h. The solvent was evaporated, and the resulting residue was extracted with benzene. The extract was filtered through Celite, and the benzene was removed in vacuo to give a red foam. The red foam was dissolved in a small amount of ether, and the solution was stored at −30 °C to yield Mo(NAr$_{Cl}$)(CHCMe$_3$)(S-Biphen)(THF) as ruby red crystals; yield 287 mg (55%): ^{1}H NMR (500 MHz, toluene-d_8, 20 °C) δ 11.33 (*syn*-CH, J_{CH} = 120.1 Hz) (see Figure 1); ^{1}H NMR (500 MHz, THF-d_8, 20 °C) δ 14.12 (*anti*-CH, THF adduct), 12.91 (*syn*-CH, THF adduct, J_{CH} = 120.5), *syn*/*anti* ratio = 7.4; ^{1}H NMR (500 MHz, THF-d_8, −40 °C) δ 14.18 (*anti*-CH, THF adduct), 12.96 (*syn*-CH, THF adduct, J_{CH} = 119.4), *syn*/*anti* ratio = 10. Anal. Calcd for $MoC_{39}H_{53}Cl_2NO_3$: C, 62.40; H, 7.12; N, 1.87; Cl, 9.45. Found: C, 62.29; H, 7.19; N, 1.94; Cl, 9.41.

Mo(NAr$_{Cl}$)(CHCMe$_3$)(R-Trip$_2$BINO)(THF) (10). This procedure has appeared in the Supporting Information of a previous publication.[14] It is repeated for convenience here.

A solution of benzyl potassium (340 mg, 2.60 mmol) in THF (5 mL) was added to R-Trip$_2$BINO (899 mg, 1.30 mmol) in THF (20 mL) until the endpoint was reached. This solution was then added to a solution of Mo(NAr$_{Cl}$)(CHCMe$_3$)(OTf)$_2$(dme) (929 mg, 1.30 mmol) in THF (40 mL) at −30 °C, and the mixture was stirred for 20 h. The THF was then removed in vacuo and the residue dissolved in toluene. The mixture was filtered through Celite and the toluene evaporated from the filtrate in vacuo. The resulting residue was then dissolved in a minimal amount of ether. An equal volume of $Me_3SiOSiMe_3$ was then added, along with 2 drops of THF, and the solution was stored at −30 °C for 24 h, at which point a brownish yellow solid had formed. The solid was filtered off and rinsed with cold $Me_3SiOSiMe_3$ and ether to give Mo(NAr$_{Cl}$)(CHCMe$_3$)(R-Trip$_2$BINO)(THF) as a dark yellow solid; yield 690 mg (49%): ^{1}H NMR (500 MHz, toluene-d_8, 20 °C) δ 13.90 (*anti*-CH, THF adduct), 13.15 (*syn*-CH, THF adduct, J_{CH} = 120.8 Hz), *syn*/*anti* ratio = 16; (−40 °C) δ 13.92 (*anti*-CH, THF adduct), 13.26 (*syn*-CH, THF adduct), *syn*/*anti* ratio = 26; ^{1}H NMR (500 MHz, THF-d_8, 20 °C) δ 13.15 (*syn*-CH, THF adduct); (−40 °C) δ 13.29 (*syn*-CH, THF adduct). Anal. Calcd for $MoC_{65}H_{77}NO_3Cl_2$: C, 71.81; H, 7.14; N, 1.29; Cl, 6.52. Found: C, 71.80; H, 7.20; N, 1.21; Cl, 6.62.

Mo(NAr$_{Cl}$)(CHCMe$_3$)(R-Mes$_2$Bitet)(THF) (11). K_2Mes_2-Bitet (327 mg, 0.54 mmol) was added to Mo(NAr$_{Cl}$)(CHCMe$_3$)(OTf)$_2$(dme) (385 mg, 0.54 mmol) in THF (3 mL), and the mixture was stirred for 17 h. The solvent was evaporated to give a dry residue that was dissolved in toluene. The solution was filtered through Celite, and the solvent was removed in vacuo. The resulting solid was dissolved in minimal ether, and a drop of THF was added. After storing the solution at −30 °C for several days, the product was isolated in several crops as orange-yellow crystals; total yield 205 mg (41%): ^{1}H NMR (500 MHz, C_6D_6, 20 °C) 12.89 (s, 1, Mo=C*H*, J_{CH} = 120.8 Hz). Anal. Calcd for $MoC_{53}H_{61}NO_3Cl_2$: C, 68.68; H, 6.63; N, 1.51; Cl, 7.65. Found: C, 68.78; H, 6.71; N, 1.57; Cl, 7.54.

Mo(NAr$_{Cl}$)(CHCMe$_3$)(R-Benz$_2$Bitet)(THF) (12). KH (43 mg, 1.06 mmol) was added to **6** (303 mg, 0.48 mmol) in THF (8 mL). After 1.5 h the solution was added to Mo(NAr$_{Cl}$)(CHCMe$_3$)(OTf)$_2$(dme) (345 mg, 0.48 mmol), and the mixture was stirred for 16 h. The solvent was removed in vacuo, and the resulting solid was dissolved in toluene. The mixture was filtered through Celite, and the toluene was removed from the filtrate in vacuo. The residue was suspended in minimal ether and isolated by filtration as a golden yellow powder. Further crops were obtained by concentrating and cooling the filtrates; total yield 234 mg (47%): ^{1}H NMR (500 MHz, C_6D_6, 20 °C) δ 12.51 (s, Mo=C*H*, J_{CH} = 123.3 Hz); ^{1}H NMR (500 MHz, THF-d_8, 20 °C) δ 14.27 (*anti*-CH, THF adduct), 12.28 (*syn*-CH, THF adduct, J_{CH} = 121.2), *syn*/*anti* ratio = 17; ^{1}H NMR (500 MHz, THF-d_8, −40 °C) δ 14.29 (*anti*-CH, THF adduct), 12.08 (*syn*-CH, THF adduct, J_{CH} = 122.2), *syn*/*anti* ratio = 17. Anal. Calcd for $MoC_{62}H_{61}NO_3Cl_2$: C, 71.95; H, 5.94; N, 1.35; Cl, 6.85. Found: C, 72.09; H, 6.05; N, 1.31; Cl, 6.81.

X-ray Study of Mo(NAr)(CHCMe$_2$Ph)(R-Mes$_2$Bitet)(THF) (8). X-ray diffraction quality crystals were obtained by dissolving a small sample in ether and storing the solution at −30 °C for 3 days. The crystals appeared as red rods when viewed under a microscope, although they appeared yellow to the naked eye.

X-ray Study of Mo(NAr$_{Cl}$)(CHCMe$_3$)(S-Biphen)(THF) (9). X-ray diffraction quality red blocks were obtained by dissolving a small sample in a minimum amount of ether and storing the solution at −30 °C for several days.

X-ray Study of Mo(NAr$_{Cl}$)(CHCMe$_3$)(R-Benz$_2$Bitet)(THF) (12). Crystals of Mo(NAr$_{Cl}$)(CHCMe$_3$)(R-Benz$_2$Bitet)(THF) were grown over several days from a concentrated mixture of ether and THF solution at −30 °C. The crystals were square, pale yellow plates.

Desymmetrization Reactions. In all cases, the substrates were diluted in C_6D_6 to give a ∼0.2 M solution to which 5 mol % catalyst was then added. The solutions were stirred for ∼1 h at room temperature under dinitrogen in loosely capped vials, and the conversions were then determined by ^{1}H NMR spectroscopy (500 MHz). The % ee was determined by gas chromatography on chiral columns.

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Supporting Information Available: Complete NMR data along with a fully labeled ORTEP drawing, crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **8**, **9**, and **12** are available free of charge via the Internet at http://pubs.acs.org.

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