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An Enantiomerically Pure Adamantylimido Molybdenum Alkylidene Complex. An Effective New Catalyst for Enantioselective Olefin Metathesis

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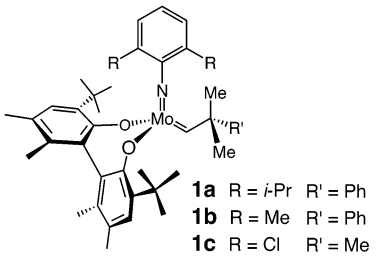
Abstract: An enantiomerically pure Mo-based complex that bears an alkylimido ligand is prepared and characterized through NMR spectroscopy and X-ray analysis. Mo complex **4** is the only reported chiral alkylimido catalyst; all previous chiral complexes are arylimido systems. These studies show that the chiral Mo catalyst exists exclusively as the syn isomer and that it offers unique reactivity and selectivity profiles in asymmetric olefin metathesis.

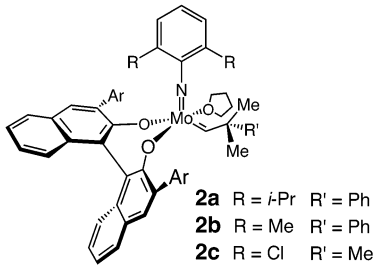
Introduction

During the past five years, research in these laboratories has focused on the synthesis, characterization, and development of optically pure chiral Mo-based arylimido alkylidene complexes that can be used to promote efficient enantioselective olefin metathesis.[1] Several representative examples are illustrated in Chart 1.[2,3] A collection of catalytic asymmetric ring-closing (ARCM)[4] and ring-opening metathesis (AROM)[5] transformations have thus been designed and developed. One underlying theme that has emerged from these investigations is that subtle variations in the structure of a chiral catalyst can lead to dramatic differences in reactivity and selectivity.[2b,4d,g,6] Since such

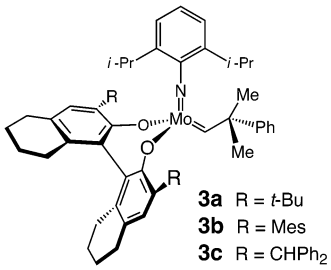
Chart 1. Representative Chiral Mo Arylimido Alkylidene Complexes



1a R = *i*-Pr R' = Ph
1b R = Me R' = Ph
1c R = Cl R' = Me



2a R = *i*-Pr R' = Ph
2b R = Me R' = Ph
2c R = Cl R' = Me
Ar = 2,4,6-(*i*-Pr)$_3$C$_6$H$_3$



3a R = *t*-Bu
3b R = Mes
3c R = CHPh$_2$

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[†] Massachusetts Institute of Technology.
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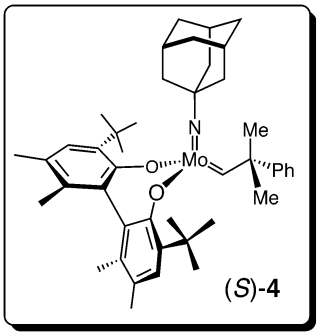
changes are typically based on nonobvious (particularly a priori) alterations of the energetics of the catalytic cycle that are also often unpredictable, we have adopted the strategy that involves the development of a class of potential catalysts that can be screened to achieve optimal results. This approach becomes especially attractive when the modular structure of the Mo-based alkylidenes is noted, an attribute that lends itself to the synthesis of an assortment of catalyst candidates. Thus far, we have been exclusively concerned with arylimido complexes, where the influence of changes in the diolate (e.g., **1a** vs **2a**) and substituents of the imido ligand (e.g., **1a** vs **1c**) on reactivity and stereoselectivity have been probed. More recently, to expand the structural diversity of available catalysts, we have set out to synthesize and examine the catalytic activity of chiral Mo catalysts in which the substituent in the imido ligand is an alkyl, not an aryl, group.

At the time we initiated our studies, only two non-aryl-substituted imido groups had been used to prepare imido alkylidene molybdenum complexes. These included a *tert*-butylimido and a 1-adamantylimido group. Osborn and co-workers disclosed the synthesis and characterization of Mo(N-*t*-Bu)(CHR)[OCH(CF$_3$)$_2$]$_2$ systems (R = CMe$_3$ or Ph) capable of initiating the slow but productive metathesis of internal olefins such as 2-pentene.[7] The synthesis route normally employed for the preparation of arylimido complexes[8] was utilized to access Mo(N-1-adamantyl)(CHCMe$_2$Ph)(OTf)$_2$(dme), from which Mo(N-1-adamantyl)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ was obtained (Ad = adamantyl).[9] Analogous complexes that contain hexafluoroisopropoxide ligands (e.g., Mo(NAd)(CHCMe$_2$Ph)[OCH(CF$_3$)$_2$]$_2$(2,4-lutidine)) have been synthesized and shown to promote living polymerization of *o*-trimethylsilylphenylacetylene.[10]



In this paper we report the synthesis and characterization of a chiral Mo-based complex (**4**) that bears an alkylimido ligand.

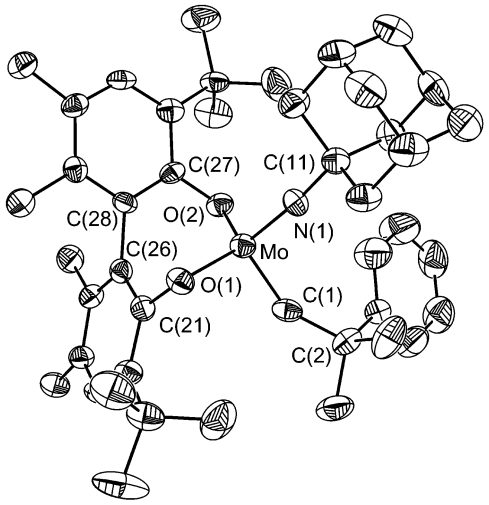
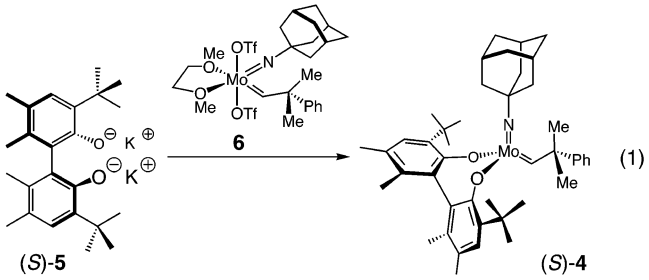


Figure 1. Thermal ellipsoid plot (50% probability level) of the structure of **4**.

Moreover, we present data clearly indicating that members of this new class of chiral Mo catalysts deliver reactivity and enantioselectivity levels that are not accessible by the complexes disclosed previously.

Results and Discussion

1. Synthesis and Characterization of Mo(NAd)(CHCMe$_2$Ph)(Biphen). a. Synthesis. The precursor to adamantylimido catalysts, Mo(NAd)(CHCMe$_2$Ph)(OTf)$_2$(dme) (**6**), is synthesized from (NH$_4$)$_2$Mo$_2$O$_7$ by previously reported methods.[9] Dipotassium salt **5** is easily prepared by addition of KH to 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diol. As depicted in eq 1, Mo(NAd)(CHCMe$_2$Ph)(biphen) (**4**) is prepared by dropwise addition of **5** to a THF solution of **6**. Chiral Mo complex **4** is isolated in 80% yield on a 2 g scale in racemic and enantiomerically pure forms (recrystallized from Et$_2$O).[11]



(1)

b. X-ray Crystal Structure. Yellow crystals suitable for X-ray diffraction were obtained from a concentrated solution of (*S*)-**4** at 20 °C; the ORTEP diagram is illustrated in Figure 1. Selected bond distances and angles are depicted in Table 1.[12] The overall structure is typical of a solvent-free tetrahedral imido alkylidene complex. The alkylidene has syn stereochemistry, the same isomer observed in compounds **1a**, **1c**, Mo(NAd)(CHCMe$_2$Ph)[OCH(CF$_3$)$_2$]$_3$[Li(dme)], and Mo(NAd)(CHCMe$_2$Ph)[OCH(CF$_3$)$_2$]$_2$(2,4-lutidine). The Mo−C(1) (Mo=C$_\alpha$) distance and Mo−C(1)−C(2) (Mo=C$_\alpha$−C$_\beta$) angle (1.867(4) Å and 149.3(3)°) are comparable to the bond distances and angles in

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(11) For simplicity we will use the *rac* or *S* label for the entire complex, although the label refers only to the biphenolate ligand in the complex.
(12) See the Supporting Information for crystal data and structure refinement parameters.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Chiral Complex **4**

Mo(1)−N(1)	1.709(3)
Mo(1)−C(1)	1.867(4)
Mo(1)−O(1)	1.986(3)
Mo(1)−O(2)	1.997(2)
Mo−C(1)−C(2)	149.3(3)
N(1)−Mo(1)−C(1)	105.37(17)
N(1)−Mo(1)−O(2)	106.66(13)
C(1)−Mo(1)−O(1)	107.54(14)
C(1)−Mo(1)−O(2)	100.34(15)
O(1)−Mo(1)−O(2)	123.54(1)
C(21)−C(26)−C(28)−C(27)	96.8(5)

1a (1.885(10) Å and 143.8(7)°),[2c] **1c** (1.872(7) Å and 150.3(6)°),[2g] Mo(NAd)(CHCMe$_2$Ph)[OCH(CF$_3$)$_2$]$_3$[Li(dme)] (1.87(2) Å and 152(2)°),[10] and Mo(NAd)(CHCMe$_2$Ph)[OCH(CF$_3$)$_2$]$_2$(2,4-lutidine) (1.880(4) Å and 145.5(3)°). The Mo−N(1) (Mo═N) bond distance and angle (1.709(3) Å and 172.8(3)°) are nearly the same as those observed in Mo(NAd)(CHCMe$_2$Ph)[OCH(CF$_3$)$_2$]$_3$-[Li(dme)] (1.67(1) Å and 165(1)°) and Mo(NAd)(CHCMe$_2$Ph)-[OCH(CF$_3$)$_2$]$_2$(2,4-lutidine) (1.729(3) Å and 166.1(3)°). The shorter Mo═N distance in **4** compared to that found in arylimido systems such as **1a** (1.738(6) Å) or **1c** (1.745(6) Å) may be attributed to a greater electron-donating ability (both σ and π) of the adamantylimido ligand.

c. ^{1}H NMR Studies. The ^{1}H NMR spectrum of **4** (in C$_6$D$_6$) reveals an alkylidene resonance at 10.88 ppm (J_{CH} = 119 Hz); the chemical shift and J_{CH} value are consistent with a syn solvent-free complex. The proton at 10.88 ppm is through-bond coupled to the alkylidene α carbon at 274 ppm in the ^{13}C NMR spectrum, according to a ^{1}H−^{13}C HMQC experiment. Spin saturation transfer (SST) experiments at 22 °C reveal that a weak anti alkylidene resonance is located at 13.48 ppm. (The two isomers are interconverting on the SST time scale at this temperature.) Collection of many transients showed that the syn/anti equilibrium constant at 22 °C is ∼200 (±20). Upon addition of pyridine to the NMR sample of **4**, two alkylidene resonances were observed in approximately a 1:1 ratio at 13.6 ($^1J_{CH}$ = 120 Hz) and 12.2 ($^1J_{CH}$ = 115 Hz) ppm. The downfield (δ 13.6) proton is coupled to a carbon at 302 ppm, while the upfield (δ 12.2) proton is coupled to another carbon at 293 ppm. On the basis of the $^1J_{CH}$ coupling values, both resonances were assigned as syn adducts with the pyridine bound complexes occupying the two diastereotopic CNO faces. Upon heating the sample to 80 °C, the two resonances at δ 13.6 and 12.2 broaden and merge presumably as a consequence of pyridine dissociating from each adduct at a rate on the order of the NMR time scale to give **4**. Upon cooling the sample back to 22 °C, the 1:1 diastereomeric mixture of syn pyridine adducts is regenerated. Unlike most arylimido alkylidenes, at no point in these studies was there any evidence for the formation of anti alkylidene pyridine adducts.

The Mo═CH resonances obtained from variable-temperature ^{1}H NMR spectra of **4** in toluene-d_8 from −80 to 90 °C in the presence of 10 equiv of THF are shown in Figure 2. The alkylidene proton resonance remains at 10.9 ppm upon addition of THF at 22 °C, suggesting that THF does not strongly bind to the metal center to any significant extent at ambient temperature. As the sample is chilled to −60 °C, the alkylidene resonance gradually moves downfield, broadens, and splits into two signals at ∼12.5 and 11.1 ppm. The resonance at 12.5 ppm

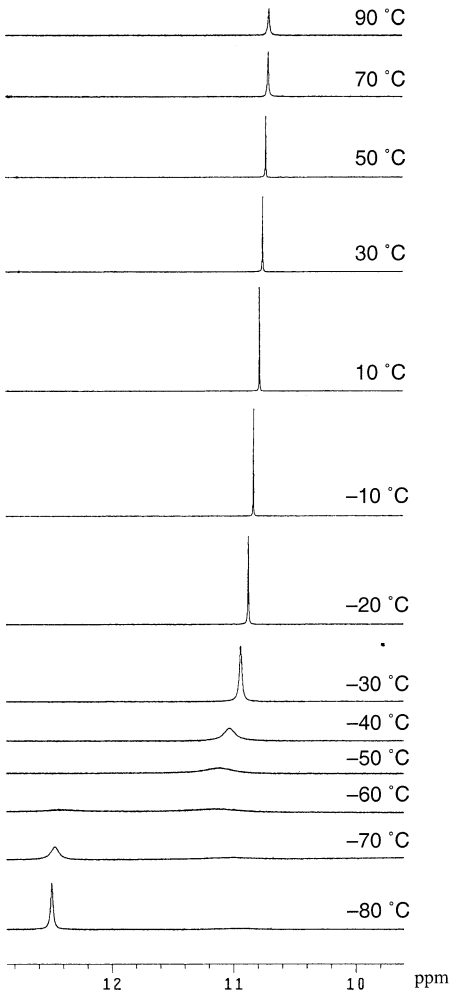


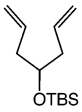
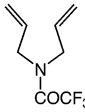
Figure 2. Alkylidene region (Mo-C*H*) from variable-temperature ^{1}H NMR experiments with **4**.

continues to sharpen as the sample is further cooled to −80 °C, while the peak near 11.1 ppm decreases in intensity. On the basis of chemical shift, the resonance at 12.5 ppm can be attributed to syn-**4**·THF complex.[13] We ascribe the weak resonance at 11 ppm to that resulting from an equilibrium between the alternative syn-**4**·THF diastereomer and the unbound syn-**4**. The two signals are approximately the same distance apart as the two syn-pyridine adducts observed previously. When the sample is warmed from 20 to 50 °C, the singlet at 10.9 ppm remains sharp and moves slightly upfield. Above 50 °C, the resonance appears to broaden; the source of this apparent broadening is not clear at the present time.

It is important to note that the behavior of chiral complex **4** in solution is strikingly different from that of related Mo-based complexes that bear N-2,6-*i*-Pr$_2$C$_6$H$_3$ and N-2,6-Me$_2$C$_6$H$_3$ imido ligands (see **1a** and **1b**, Chart 1),[2c] where anti alkylidene isomers are observed spectroscopically, especially in the presence of THF or some other two-electron-donor ligand. This difference may be partly due to the smaller steric presence of the adamantyl unit in the proximity of the alkylidene substituent. Such a suggestion is consistent with the fact that ^{1}H NMR spectra of arylimido complexes bearing the smaller Cl atoms at the C2 and C6 position (vs Me and *i*-Pr; see **1c**, Chart 1) also do not

(13) The resonance was too broad for accurate J_{CH} determination.

Table 2. Catalytic Activity of **4** Relative to **1a**

entry	substrate	catalyst	time
1		**1a**	10 min
2		**4**	2 h
3		**1a**	0.5 h
4		**4**	0.5 h
5		**1a**	10 min
6		**4**	2 h

[a] All reactions performed in C_6D_6 at 22 °C with 5 mol % **1a** or **4**. [b] All reactions proceeded to >98% conv; % conv determined by analysis of 500 MHz ^{1}H NMR spectra of unpurified reactions mixtures.

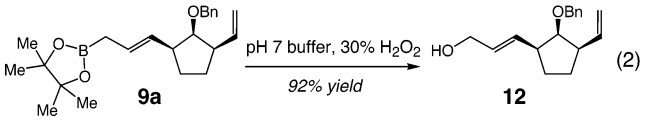
show the presence of the anti isomer.[2g] Both the N-2,6-$Cl_2C_6H_3$ (**1c**) and the NAd complex **4**, as will be discussed below, behave differently as chiral olefin metathesis catalysts compared to **1a** and **1b** (see Chart 1).

The relative stability and reactivity of the rotational isomers of Mo(NAd)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (Ad = adamantyl) have been studied and reported.[14] These investigations show that although both syn and anti alkylidenes are observed (12:1 syn:anti, toluene at 298 K), both isomers exhibit the same reactivity toward 2,3-bis(trifluoromethyl)norbornadiene. In contrast, the previously reported studies indicate that the anti alkylidene of Mo(NAr)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (Ar = 2,6-(*i*-Pr)$_2$C$_6$H$_3$) is nearly 100 times more reactive than its the corresponding syn isomer toward the same substrate. If syn and anti isomers of **4** and other alkylidenes derived from them also have approximately equal reactivity toward a range of olefins, the predominance of the syn form would suggest that the anti isomers may not play a significant role in the metathesis reactions described below.

2. Chiral Complex 4 as Olefin Metathesis Catalyst. a. Catalyst Activity. As the first step toward examination of the utility of **4** as an olefin metathesis catalysts, several catalytic RCM transformations were investigated. Representative data are summarized in Table 2; for comparison, the same set of reactions were screened with **1a**. Although all substrates undergo rapid RCM and reactions proceed to >98% conversion in less than 2 h (5 mol % loading), **1a** proves to be a somewhat more effective catalyst than **4**. Common functional groups such as ether, ester, amide, sulfonamide, CF_3, and siloxy groups are compatible with the new chiral complex.

b. Utility in Catalytic Asymmetric Olefin Metathesis. Initial studies clearly indicate that chiral Mo catalyst **4** offers reactivity and selectivity levels that are not available through any of the other arylimido-based complexes. The two examples discussed below are illustrative.

Mo-Catalyzed Asymmetric Ring-Opening/Cross Metathesis (AROM/CM) Reactions Involving Allylboronates. Allylboronates are synthetically useful partners in catalytic AROM/CM reactions, as the resulting functionalized chiral nonracemic products may be readily functionalized further to afford a variety of additional synthetically useful molecules.[15] Toward this end, we examined the Mo-catalyzed AROM/CM between norbornyl ethers **7a**−**c** and allylboronate **8**. As illustrated in Scheme 1, for reactions between **7a** and **8**, chiral arylimido Mo complexes either deliver a mixture of cis and trans olefin products **9** and **10** that are formed along with substantial amounts (up to ~50%) of achiral **11** or afford highly inefficient transformations (5 mol % catalyst, C_6H_6, 22 °C, 6 h). In contrast, *under identical conditions, adamantylimido complex **4** efficiently and selectively delivers **9a** in 90% ee and 78% isolated yield (>13:1 trans:cis*). As also shown in Scheme 1, similar results are obtained with substrates **7b**,**c**. It should be noted that the resulting enantioenriched allylboronate can be converted to the derived alcohols in 72% overall isolated yield (after metathesis and oxidation). For example, as depicted in eq 2, **9a** is transformed to the corresponding alcohol in 92% yield upon oxidation with 30% aqueous H_2O_2.



(2)

Mo-Catalyzed AROM/RCM Reactions. Another set of metathesis reactions that have proved to be inefficient with various arylimido ligands are AROM/RCM[4c,5c] of norbornyl trienes such as **13** in Scheme 2. The desired product is the chiral spirocyclic **14**. However, a typical achiral byproduct is meso **15**, arising from RCM between the two terminal alkenes. As the chart in Scheme 2 illustrates, reactions promoted by various arylimido Mo complexes suffer from formation of significant amounts of **15**, low enantioselectivities, or low overall conversion (5 mol % catalyst, C_6H_6, 22 °C, 3 h). However, as depicted in Scheme 2, under identical conditions, but with 5 mol % **4**, the desired product **14** is obtained with significantly superior levels of reactivity and selectivity (96% ee, 82% isolated yield, 4:1 **14**:**15**).

Conclusions

We report a chiral Mo-based catalyst for enantioselective olefin metathesis (**4**) that bears an *alkyl*imido rather than an arylimido ligand. Spectroscopic analysis of **4** suggests that, unlike most arylimido systems reported previously, anti metal alkylidene isomer is present only to the extent of ~0.5%. Our studies illustrate that chiral complex **4** can offer catalytic activity that is not available by any other chiral metathesis catalyst, including the related arylimido systems (Schemes 1 and 2). Mechanistic studies aimed to determine whether the unique reactivity of **4** is related to the predominance of its syn isomer are underway. Synthesis and development of additional chiral Mo-based catalysts for enantioselective synthesis continue in these laboratories as well.

Experimental Section

General Procedures. Infrared (IR) spectra were recorded on a ThermoNicolet Avatar 360 or Nicolet 210 spectrophotometer, ν_{max} in cm^{-1}. Bands were characterized as broad (br), strong (s), medium (m), and weak (w). ^{1}H NMR spectra are recorded on a Varian INOVA 500 (500 MHz) or INOVA 400 (400 MHz). Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ 7.26; C_6D_6, δ 7.16). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and

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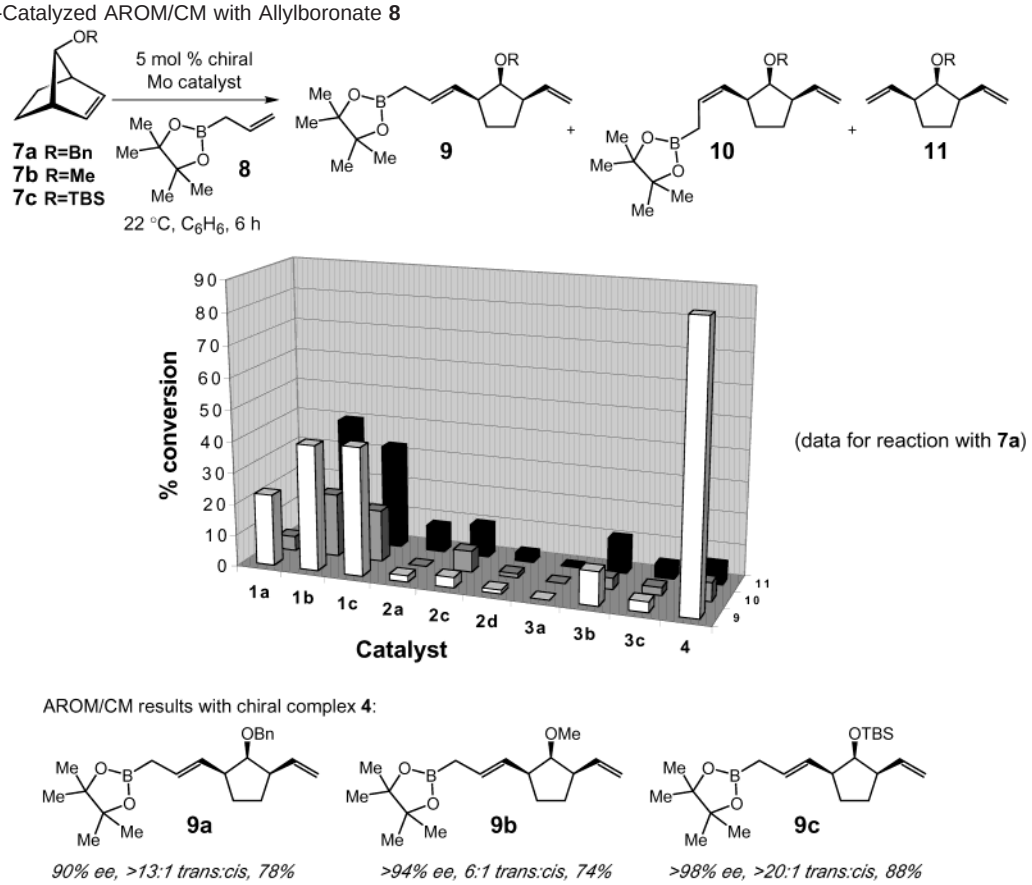
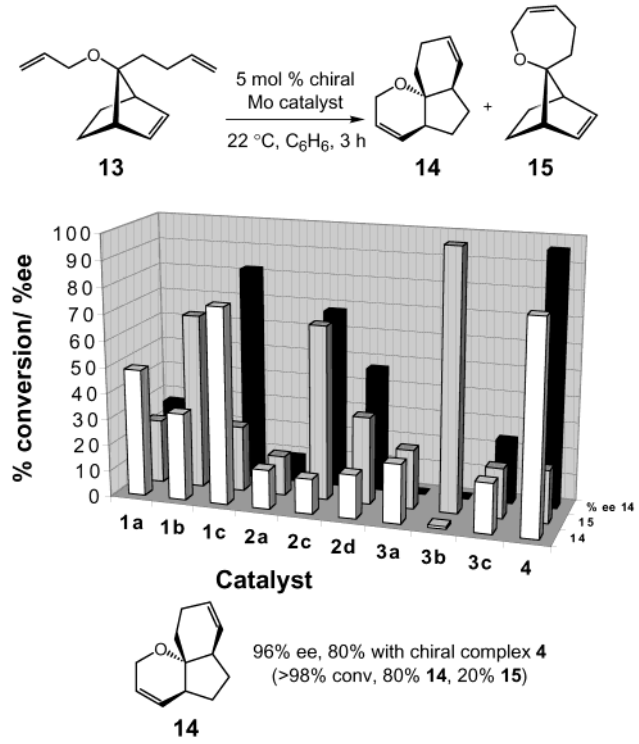
Scheme 1. Mo-Catalyzed AROM/CM with Allylboronate **8**



Scheme 2. Mo-Catalyzed AROM/RCM with Triene **13**



integration. ^{13}C NMR spectra are recorded on a Varian Unity INOVA 500 (125 MHz) or Varian INOVA 400 (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ 77.1; C_6D_6, δ 128.1). Enantiomer ratios were determined by chiral GLC analysis (Alltech Associates Chiraldex GTA column (30 m × 0.25 mm) or BETADEX 120 column (30 m × 0.25 mm)) in comparison with authentic racemic materials. Elemental analyses were performed by Robertson Microlit Laboratories (Madison, NJ) or by Kolbe Microanalytical Laboratories (Mülheim an der Ruhr, Germany). High-resolution mass spectrometry was performed by the University of Illinois Mass Spectrometry Laboratories (Urbana, IL). Absolute stereochemistry was determined by optical rotation on a Rudolph Research Analytical Autopol IV polarimeter.

All reactions were conducted in oven (135 °C) and flame-dried glassware under an inert atmosphere of dry nitrogen. Solvents were purified under a positive pressure of dry Ar by a modified Innovative Technologies purification system. Benzene and toluene were sparged with argon and passed through activated copper and alumina columns. Tetrahydrofuran, diethyl ether, and dichloromethane were purged with argon and passed through activated alumina columns. Olefin-free pentane was generated by stirring commercial grade pentane over concentrated sulfuric acid for 24 h. The pentane was then poured over fresh concentrated sulfuric acid. This process was repeated until the acid layer remained colorless for 48 h. The pentane layer was separated, washed with water, dried over Na_2SO_4, filtered, purged with argon, and then passed successively through activated alumina and activated copper columns. All catalyst preparations and metathesis reactions were performed in a glovebox under a nitrogen atmosphere. All substrates for Mo-catalyzed asymmetric metathesis were rigorously dried by azeotropic distillation with anhydrous benzene (3×) prior to use. Commercially available materials were obtained from Aldrich Chemical Co., Strem Chemicals, Inc., or Lancaster Synthesis and purified by appropriate methods prior to use.

Dipotassium Salt of *rac*- *and* (*S*)-3,3′-Di-*tert*-butyl-5,5′,6,6′-tetramethyl-2,2′-dihydroxy-1,1′-biphenyl (*rac*- and (*S*)-K_2(biphen)) (5). A 50 mL round-bottomed flask was charged with 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-2,2′-dihydroxy-1,1′-biphenyl (0.50 g, 1.4 mmol)

and dry THF (25 mL). Potassium hydride (0.17 g, 4.2 mmol) was slowly added in several portions to a stirring homogeneous biphenol solution at 22 °C. After 0.5 h, a white suspension formed. The mixture was allowed to stir for an additional 12 h. Subsequently, excess KH was removed by filtration through Celite. The filtered dipotassium salt solution was immediately used in the synthesis of **4**.

***rac*- and (*S*)-Mo(NAd)(CHCMe$_2$Ph)(biphen) (4).** A 100 mL round-bottomed flask was charged with Mo(NAd)(CHCMe$_2$Ph)(OTf)$_2$(DME) (**6**)[9] (1.1 g, 1.4 mmol) and dry THF (30 mL). The solution was allowed to stir for 10 min or until it turned homogeneous. The dipotassium salt solution of the ligand (**5**) was added dropwise to the stirring bistriflate solution at 22 °C, and the mixture was allowed to stir for an additional 8 h. All volatiles were removed in vacuo. The resulting residue was taken up in cold (−30 °C) toluene, and the washings were filtered through Celite. The filtrate was concentrated by rotary evaporation, and the resulting residue was recrystallized from diethyl ether at −30 °C. The resulting yellow powder obtained after 12 h was rinsed with cold pentane (−30 °C) and dried in vacuo to afford **4** in 81% yield (0.84 g, 1.1 mmol). ^{1}H NMR (C_6D_6): δ 10.88 (s, 1H, J_{CH} = 119.24(7) Hz), 7.52 (d, J = 7.5 Hz, 2H), 7.42 (s, 1H), 7.36 (s, 1H), 7.23 (t, J = 7.7 Hz, 2H), 7.05 (t, J = 7.3 Hz, 1H), 2.14 (s, 3H), 2.12 (s, 3H), 1.84 (s, 3H), 1.74 (s, 9H), 1.72 (s, 3H), 1.68 (s, 3H), 1.86−1.68 (m, 9H), 1.66 (s, 9H), 1.35 (s, 3H), 1.26 (m, 6H). ^{13}C NMR (125 MHz, C_6D_6): δ 273.8, 154.8, 154.4, 151.7, 139.4, 139.1, 136.4, 136.2, 131.7, 130.8, 130.7, 129.8, 129.0, 128.9, 128.7, 128.7, 128.0, 127.7, 126.3, 77.1, 51.9, 44.7, 36.2, 36.1, 36.0, 33.5, 32.3, 31.0, 30.6, 30.2, 20.9, 20.8, 17.1, 17.0. Anal. Calcd for $MoC_{44}H_{59}NO_2$: C, 72.19; H, 8.13; N, 1.91. Found: C, 72.06; H, 8.10; N, 1.92. The corresponding diastereotopic CNO face pyridine adducts were observed by adding 2 equiv of neat pyridine to a solution of Mo(NAd)(CHCMe$_2$Ph)(Biphen) (**4**) in C_6D_6. ^{1}H NMR (C_6D_6): δ 13.6 (s, 1, syn Mo=CH, J_{CH} = 120 Hz), 12.2 (s, 1, syn Mo=CH, J_{CH} = 115 Hz). ^{13}C NMR (125 MHz, C_6D_6): δ 302.0, 293.0.

Representative Procedure for Mo-Catalyzed AROM/CM. Benzyl ether **7a** (40.0 mg, 0.200 mmol) and allylboronate **8**[16] (33.6 mg, 0.200 mmol) were weighed into a 4 mL vial containing a stir bar; the mixture was then diluted with 1.00 mL of benzene. Chiral complex **4** (7.20 mg, 0.010 mmol) was added, and the vial was fitted with a Teflon-lined cap. The reaction was allowed to stir at 22 °C for 6 h. The vessel was removed from the glovebox and the reaction quenched by exposure to air. Volatiles were removed to give a viscous black oil. Purification by silica gel chromatography (2% Et_2O in pentane) afforded **9a** as a colorless oil in 72% yield (53.0 mg, 0.144 mmol).

2-[3-(2-Benzyloxy-3-vinylcyclopentyl)allyl]-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (9a). IR (neat): 3074 (w), 2974 (m), 2930 (m), 2867 (m), 1463 (m), 1319 (s), 1142 (s), 1097 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.20 (m, 1H), 6.02−5.94 (m, 1H), 5.59−5.48 (m, 2H), 5.06−4.95 (m, 2H), 4.58−4.48 (ABq, J = 11.9 Hz, 2H), 3.71−3.69 (t, J = 4.0 Hz, 1H), 2.60−2.50 (br m, 2H), 1.80−1.67 (m, 4H), 1.66−1.64 (d, J = 6.2 Hz, 2H), 1.21 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.0, 131.7, 128.3, 127.9, 127.7, 127.4, 125.4, 114.5, 87.5, 83.3, 77.4, 73.6, 50.0, 49.2, 29.4, 29.0, 25.0. HRMS of **9a** calcd for derived alcohol $C_{17}H_{22}O_2$: 258.1619, found 258.1617.

Representative Procedure for Tandem Mo-Catalyzed ARCM/RCM. Triene **13** (25.0 mg, 0.122 mmol) was weighed into a 4 mL vial containing a stir bar and then diluted with 1.20 mL of benzene. Chiral complex **4** (4.40 mg, 0.0061 mmol, 5 mol %) was then added, and the vial was fitted with a Teflon-lined cap. The mixture was allowed to stir at 22 °C for 3 h. The vessel was then removed from the glovebox, and the reaction was quenched by exposure to air. Volatiles were removed in vacuo to afford a viscous black oil. Purification by silica gel chromatography (40:1 pentane/Et_2O) afforded **14** in 82% yield (17.7 mg, 0.100 mmol).

Product of Catalytic AROM/CM (14). IR (neat): 3024 (m), 2955 (m), 1465 (w), 1440 (w), 1095 (m). ^{1}H NMR (400 MHz, C_6D_6): δ 5.88−5.82 (dq, J = 10.0, 2.4 Hz, 1H), 5.78−5.70 (m, 2H), 5.62−5.56 (dq, J = 9.2, 2.4 Hz, 1H), 4.36−4.22 (m, 2H), 2.64−2.54 (m, 1H), 2.24−2.06 (m, 3H), 2.02−1.86 (m, 2H), 1.84−1.74 (dq, J = 18.4, 8.4 Hz), 1.40−1.30 (m, 2H), 1.22−1.12 (dt, J = 12.8, 5.6 Hz, 1H). ^{13}C NMR (100 MHz, C_6D_6): δ 129.4, 126.2, 126.0, 77.3, 63.7, 45.5, 43.3, 29.2, 23.2, 21.9, 19.4. Anal. Calcd for **14** $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.84; H, 9.26.

15. IR (neat): 3054 (w), 3024 (w), 2961 (m), 2936 (m), 2861 (w), 2842 (w), 1309 (m). ^{1}H NMR (400 MHz, C_6D_6): δ 6.02−5.98 (t, J = 2.2 Hz, 2H), 5.80−5.70 (m, 1H), 5.58−5.52 (m, 1H), 4.10−4.07 (dq, J = 6.0, 2.0 Hz, 2H), 2.62−2.60 (m, 2H), 2.15−2.05 (m, 4H), 1.98−1.92 (m, 2H), 1.34−1.20 (m, 2H). ^{13}C NMR (100 MHz, C_6D_6): δ 135.3, 131.9, 129.2, 97.6, 63.0, 47.4, 29.4, 25.9, 23.7. HRMS of **15** calcd for $C_{12}H_{16}O$: 176.1201, found 176.1199.

Acknowledgment. This paper is dedicated to the memory of the late Professor John A. Osborn, a pioneer in the fields of catalysis and organometallic chemistry. We thank the National Institutes of Health (GM-59426 to R.R.S. and A.H.H.) and the National Science Foundation (CHE-9988766 to R.R.S. and CHE-0213009 to A.H.H.) for support. We acknowledge the generous assistance of Dr. Jeffrey H. Simpson in multidimensional NMR experiments.

Supporting Information Available: Fully labeled ORTEP drawing, crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **4** as well as full characterization data for **9b**, **9c**, and **12** are available free of charge via the Internet at http://pubs.acs.org.

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