Organometallics **2007,** *26,* 831−837 831

New Enantiomerically Pure Alkylimido Molybdenum-Based Alkylidene Complexes. Synthesis, Characterization, and Activity as Chiral Olefin Metathesis Catalysts

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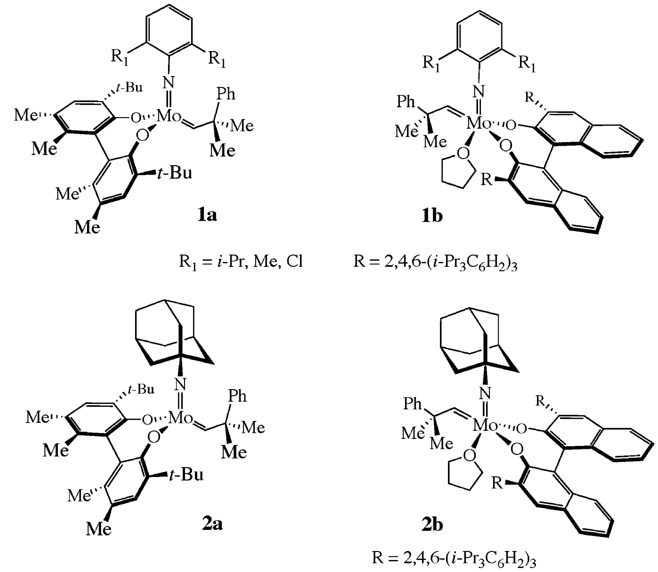
Received October 30, 2006

Molybdenum olefin metathesis catalysts that contain aliphatic 1-phenylcyclohexylimido (NPhCy) and 2-phenyl-2-adamantylimido (NPhAd) groups and (*S*)-Biphen or (*R*)-Trip ligands (Biphen = 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diolate; Trip = 3,3′-bis(2,4,6-triisopropylphenyl)-2,2′-binaphtholate) have been prepared. Their catalytic activity and enantioselectivity in desymmetrization reactions such as ring-closing metathesis of amines and lactams and ring-opening/cross-metathesis of substituted norborneols with styrene were compared to the results obtained with the only known alkylimido catalyst, Mo(NAd)(CHCMe$_2$Ph)[(*S*)-Biphen]. The activities and enantioselectivities provided by these new chiral complexes vary significantly, but in virtually all instances explored were not superior to the adamantylimido analogues.

Introduction

The first isolable (symmetric) olefin metathesis catalysts of the type Mo(NR)(CHR′)(OR″)$_2$[1] that contain an *alkyl*imido (adamantylimido) ligand, as opposed to an *aryl*imido ligand, were synthesized in 1993.[2] Adamantylimido complexes have been used for olefin cross-metathesis,[3] ring-opening polymerization (ROMP),[4] and living polymerization of substituted acetylenes.[5] In the last several years, we have designed and synthesized chiral, enantiomerically pure Mo-based imido alkylidene complexes that promote a variety of olefin metathesis reactions such as asymmetric ring-closing metathesis (ARCM) and asymmetric ring-opening/cross-metathesis (AROM/CM) with a high enantioselectivity (>90% ee).[6] The majority of these catalysts are four- or five-coordinate species that bear *aryl*imido functionalities and a chiral diolate (Scheme 1). In 2003, we disclosed the synthesis and selected enantioselective processes catalyzed by the first enantiomerically pure alkylimido catalyst, Mo(NAd)(CHCMe$_2$Ph)[(*S*)-Biphen] (Ad = 1-adamantyl; Biphen^{2-} = 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diolate; **2a**, Scheme 1).[7] We were surprised and pleased to find that this new chiral complex is often superior to the analogous arylimido alkylidenes, sometimes dramatically so, in terms of catalytic activity and selectivity. Therefore, we became interested in preparing other alkylimido catalysts and attempted to determine what property, if any, of alkylimido species is responsible for their effective promotion of asymmetric metathesis reactions. Herein, we report several new alkylimido species and evaluate their efficacy in a variety of catalytic ARCM and AROM/CM reactions that involve substrates that have proven challenging for arylimido-containing substrates.

Scheme 1. Chiral Mo Complexes Bearing Aryl- and Adamantylimido Ligands



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[†] Massachusetts Institute of Technology.

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[1] Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145−180.

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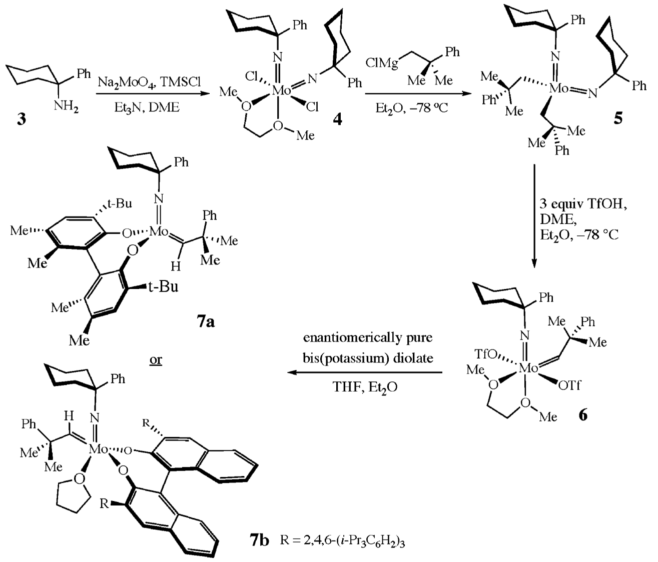
[6] (a) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4592−4633. (b) Schrock, R. R. *J. Mol. Cat. A: Chem.* **2004**, *213*, 21−30. (c) Schrock, R. R.; Jamieson, J. Y.; Dolman, S. J.; Miller, S. A.; Bonitatebus, P. J. Jr.; Hoveyda, A. H. H. *Organometallics* **2002**, *21*, 409−417. (d) Zhu, S. S.; Cefalo, D. R.; La, D. S.; Jamieson, J. Y.; Davis, W. M.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 8251−8259. (e) Dolman, S. J.; Hultzsch, K. C.; Pezet, F.; Teng, X.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **2004**, *126*, 10945−10953. (f) Alexander, J. B.; Schrock, R. R.; Davis, W. M.; Hultzsch, K. C.; Hoveyda, A. H.; Houser, J. H. *Organometallics* **2000**, *19*, 3700−3715.

[7] Tsang, W. C. P.; Jernelius, J. A.; Cortez, G. A.; Weatherhead, G. S.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 2591−2596.

10.1021/om061001o CCC: $37.00

Scheme 2. Synthesis of Chiral Mo-Based Complexes 7a and 7b



Results and Discussion

Synthesis of Alkylimido Mo-Based Olefin Metathesis Catalysts. New imido groups were chosen on the basis of the requirement that an imido group be sufficiently bulky to prevent bimolecular decomposition of at least the initial neopentylidene or neophylidene. Therefore, we judged that the imido group should contain a quaternary carbon bound to the imido nitrogen. Two imido groups that fulfill these requirements, and can be readily prepared, are 1-phenylcyclohexylimido (NPhCy) and 2-phenyl-2-adamantylimido (NPhAd). We employed phenyl groups in the hope that catalysts that contain these imido groups would be more crystalline and therefore could be isolated more readily. We selected (*S*)-Biphen and (*R*)-Trip ligands (Biphen^{2-} = 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diolate; Trip^{2-} = 3,3′-bis(2,4,6-triisopropylphenyl)-2,2′-binaphtholate) from the pool of available chiral chelating diolates since these ligands have been utilized successfully in previous asymmetric metathesis studies.[6a]

The sequence leading to the Mo(NR)(CHCMe$_2$Ph)(diolate*) catalysts (R = NPhCy, NPhAd; diolate* = (*S*)-Biphen, (*R*)-Trip) is the one that has been employed for all imido alkylidene compounds.[8] As illustrated in Scheme 2, 1-phenylcyclohexyl amine **3**, easily prepared in two steps from 1-phenylcyclohexanol,[9] and sodium molybdate react to produce the bis(imido)-dichloride complex **4** (>98% conv, 90 °C, 24 h); the product is isolated as a 1,2-dimethoxyethane adduct, which is typical of bis(imido) dichloride complexes of this type. Alkylation yields the dineophyl bisimido complex **5**, which upon treatment with 3 equiv of triflic acid in cold diethyl ether in the presence of DME is converted into **6**, which is then converted into Mo(NR)(CHCMe$_2$Ph)(diolate*) complexes **7a** and **7b**. Contrary to our expectations, **7a** and **7b** are highly soluble in all common solvents, but can be isolated as crystalline solids from concentrated pentane solutions at −20 to −30 °C.

In the 500 MHz ^{1}H NMR spectrum of compound **7a** in C_6D_6 the alkylidene resonance at 10.7 ppm can be attributed to a *syn* alkylidene on the basis of the value for the CH coupling constant (121 Hz). ^{1}H NMR spectra of a sample of **7a** in toluene-d_8 remain unchanged in the range −80 to 100 °C; there is no evidence for any significant amount of the *anti* isomer in this temperature interval.

Table 1. Crystal Data and Structure Refinement for Complex 7a

empirical formula	$C_{46}H_{59}MoNO_2$
fw	753.88
temperature	100(2) K
wavelength	0.71073 Å
cryst syst	orthorhombic
space group	*P*2(1)2(1)2(1)
unit cell dimens	$a = 12.9341(10)$ Å, $\alpha = 90°$
	$b = 16.5919(16)$ Å, $\beta = 90°$
	$c = 19.2463(18)$ Å, $\gamma = 90°$
volume	4130.3(6) Å^3
Z	4
density (calcd)	1.212 Mg/m^3
absorp coeff	0.354 mm^{-1}
F(000)	1600
cryst size	0.15 × 0.05 × 0.04 mm^3
θ range for data collection	1.90 to 29.57°
index ranges	$-17 \le h \le 17, 0 \le k \le 23, 0 \le l \le 26$
no. of reflns collected	93 372
no. of indep reflns	11 592 [*R*(int) = 0.0647]
completeness to $\theta = 29.57°$	100.0%
absorp corr	semiempirical from equivalents
max. and min. transmn	0.9860 and 0.9489
refinement method	full-matrix least-squares on F^2
no. of data/restraints/ params	11 592/0/463
goodness-of-fit on F^2	1.095
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0365, wR2 = 0.0828
R indices (all data)	R1 = 0.0416, wR2 = 0.0856
absolute struct param	−0.01(2)
largest diff peak and hole	1.443 and −0.315 e Å^{-3}

An X-ray crystallographic analysis of **7a** (Table 1) shows it to have the expected structure (Figure 2). Structural parameters for **7a** lie within the range of values observed for similar molybdenum complexes. The Mo−C(1) bond distance (1.889(2) Å) and Mo−C(1)−C(2) bond angle (144.51(16)°) are comparable to the analogous distance and angle in **2a** (1.867(4) Å and 149.3(3)°). The Mo(1)−N(1) distance (1.7185(18) Å) is also approximately the same as in **2a** (1.709(3) Å).

Chiral complex **7b** is obtained as a THF adduct, which is typical of complexes that contain binaphtholate ligands.[6a] Only one alkylidene resonance is observed in the ^{1}H NMR spectrum of **7b** (at 14.0 ppm, 22 °C), while the alkylidene carbon resonance in the ^{13}C NMR spectrum is found at 308 ppm (J_{CH} = 145 Hz); the large value for J_{CH} suggests that the alkylidene ligand is in the *anti* configuration with the alkyl substituent pointing away from the imido group. The spectrum does not change upon heating a toluene-d_8 sample of **7b** to 100 °C. However, when the solution is cooled to −70 °C, two alkylidene resonances are observed (Figure 2). We propose that these two resonances correspond to the diastereomeric THF adducts. It is not clear which resonance corresponds to which Mo complex diastereomer and what the precise identity of each diastereomer (i.e., the stereochemistry of THF binding) is. The intensities of the alkylidene resonances suggest that the two species are approximately equal energetically at −70 °C. In Figure 2 we show THF binding to the two CNO faces *trans* to one of the binaphtholate oxygens. Addition of 10 equiv of THF yields the same variable-temperature ^{1}H NMR spectra between 10 and −70 °C. This finding suggests that the two diastereomers interconvert *without* dissociation of THF by a mechanism that is unclear at the present time. A good possibility is successive “turnstile” operations in which three ligands rotate with respect to the other two. Mo complex **7b** is analogous to **2b** (Scheme

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[8] Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O’Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875−3886.

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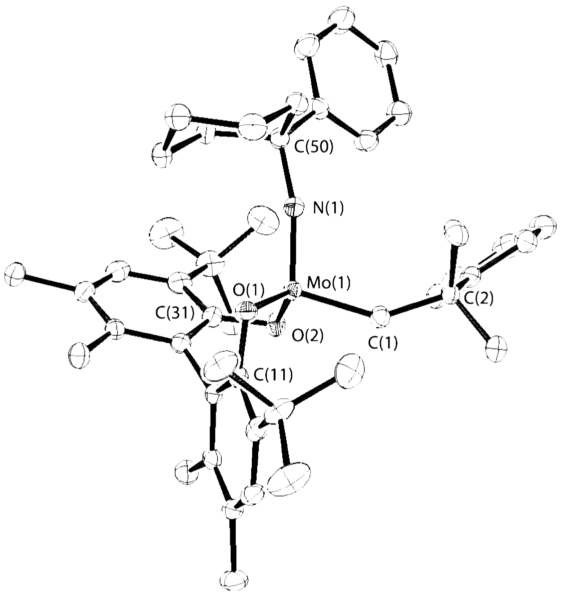


Figure 1. Thermal ellipsoid drawing of the structure of **7a**. Selected distances (Å) and angles (deg): Mo−N(1) = 1.7185(18), Mo−C(1) = 1.889(2), Mo−O(1) = 2.0070(15), Mo−O(2) = 2.0140(16), O(1)−Mo−O(2) = 129.45(6), N(1)−Mo−C(1) = 105.97(9), Mo−C(1)−C(2) = 144.51(16), Mo−N(1)−C(50) = 167.18(15).

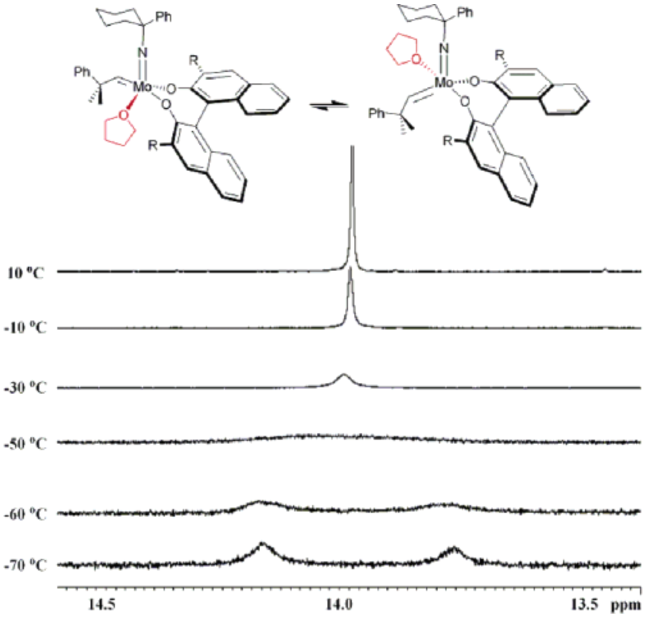
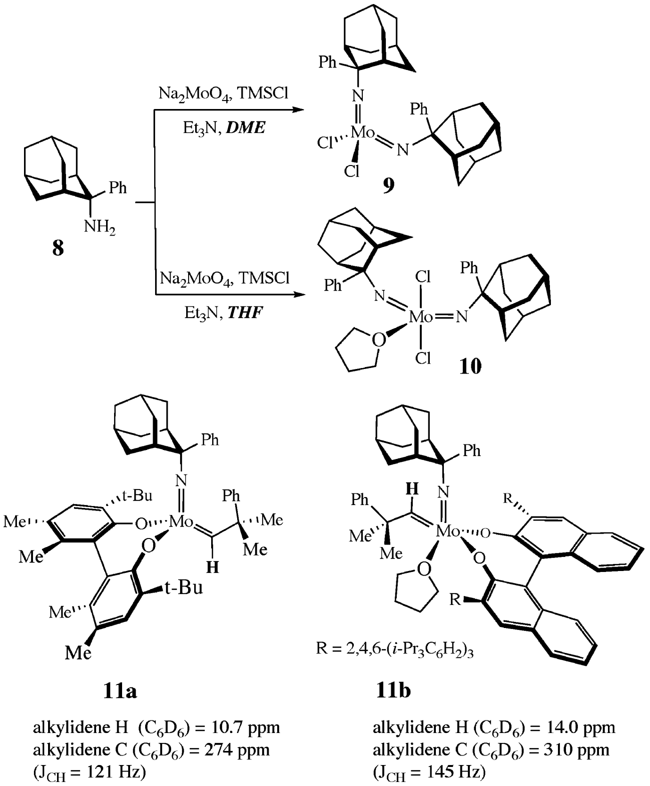


Figure 2. Variable-temperature ^{1}H NMR spectrum of a sample of **7b** in toluene-d_8. Two alkylidene resonances at −70 °C correspond to the two diastereomers of the *anti* THF adduct.

1);[10] **2b** also is exclusively an *anti* alkylidene THF adduct (δH_α = 13.8 ppm in toluene-d_8, J_{CH} = 145 Hz). In stark contrast to the new alkylidene **7b**, however, cooling the sample of **2b** to −70 °C does not lead to splitting of the alkylidene resonance.[10] Therefore, either only one diastereomer is present under these conditions or two are present whose interconversion is too facile for their alkylidene resonances to be resolved.

Chiral Mo complexes **11a** and **11b** (Scheme 3) were also synthesized. The requisite 2-phenyl-2-adamantylamine (**8**) is prepared in a three-step sequence from 2-adamantanone.[11] Bis(imido) dichloride complexes (**9** and **10**, Scheme 3) are synthesized as described previously. However, **9** does not contain coordinated dimethoxyethane. The yields of Mo(NPhAd)$_2$Cl$_2$ are atypically low (20−40%), and the reaction is not easily reproduced. We ascribe the absence of DME to the significant steric bulk of the imido ligand. If the same reaction is performed in THF, a five-coordinate complex is obtained in which one molecule of THF is bound in the coordination sphere (**10** in Scheme 3).

Scheme 3. Synthesis of Mo Bisimido Complexes 9 and 10 and Chiral Mo-Based Complexes 11a and 11b



The NMR characteristics of **11a** and **11b** are analogous to those of **7a** and **7b**, respectively; that is, **11a** exists predominantly as a *syn* alkylidene, while the alkylidene in **11b** is *anti*. However, the ^{1}H NMR spectrum of **11b** (δH_α = 14.06 ppm), like that of **2b** (Scheme 1), does not change upon cooling to −80 °C (toluene-d_8). As a result, it is not known with certainty whether compound **11b** exists as a mixture of diastereomeric THF adducts, as with **7b**, and interconversion is too facile for the alkylidene resonances to be resolved at −80 °C, or whether only one diastereomeric adduct is present.

Asymmetric Olefin Metathesis Reactions. Initial studies, involving representative substrates, indicate that the new alkylimido complexes can effectively promote enantioselective olefin metathesis reactions. The results of these are summarized in Tables 2−6. We have previously demonstrated that complex **2a** exhibits a different profile of reactivity and selectivity than analogous arylimido complexes when applied to certain classes of metathesis substrates. One of the reactions in which **2a** is a significantly better catalyst (versus arylimido complexes) is tandem asymmetric ring-opening metathesis/cross-metathesis (AROM/CM) of norbornene derivatives with monosubstituted olefins. The results for the AROM/CM reaction between *syn*-7-(benzyloxy)bicyclo[2.2.1]hept-2-ene (**12**) and styrene[12] are

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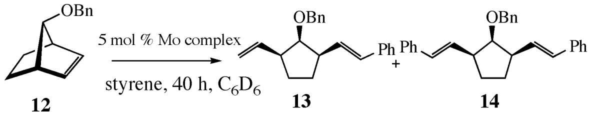
[10] Tsang, W. C. P. Ph.D. Thesis, Massachusetts Institute of Technology, 2003.

[11] Kalir, A.; Balderman, D. *Org. Synth.* **1981**, *60*, 104−108.

[12] La, D. S.; Sattely, E. S.; Ford, J. G.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2001**, *123*, 7767−7778.

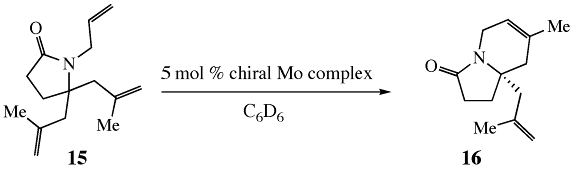
Table 2. Mo-Catalyzed AROM/CM Reactions



entry	chiral complex	temp (°C)	yield (%) **13**^{b}	yield (%) **14**^{b}	ee (%) **13**^{c}
1	**2a**	25	56	36	91
2	**7a**	25	36	42	80
3	**11a**	25	<2^{a}	<2	n.d.
4	**2b**	25	64	24	96^{d}
5	**7b**	75	61	14	98^{d}
6	**11b**	75	57	14	98^{d}

^{a} Only ROMP of norbornyl substrate was observed. ^{b}Isolated yields of purified products. ^{c}Determined by chiral GLC analysis. ^{d}Opposite configuration.

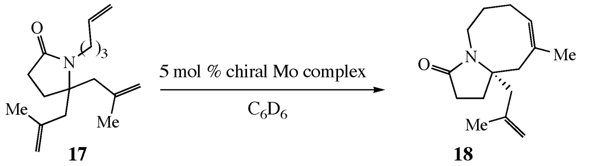
Table 3. Mo-Catalyzed ARCM Reactions of Cyclic Amide 15



entry	chiral complex	temp (°C)	time (h)	yield (%)^{a}	ee (%)^{b}
1	**2a**	25	60	84	83
2	**7a**	25	20	96	82
3	**11a**	25	60	86	79
4	**2b**	65	48	97	97^{c}
5	**7b**	65	20	<2	n.d.
6	**11b**	65	20	<2	n.d.

^{a} Isolated yields of purified products. ^{b}Determined by chiral GLC analysis. ^{c}Opposite configuration.

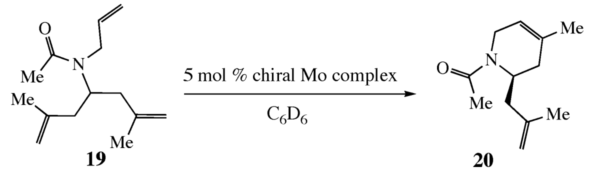
Table 4. Mo-Catalyzed ARCM Reactions of Cyclic Amide 17



entry	chiral complex	temp (°C)	time (h)	yield (%)^{a}	ee (%)^{c}
1	**2a**	25	44	62	>98
2	**7a**	25	44	69	>98
3	**11a**	257	20	23^{c}	n.d.
4	**2b**	0	48	37^{c}	n.d.
5	**7b**	70	48	<5^{c}	n.d.
6	**11b**	70	48	20^{c}	n.d.

^{a} Isolated yields of purified products. ^{b}Determined by chiral GLC analysis. ^{c}Yield based on ^{1}H NMR analysis.

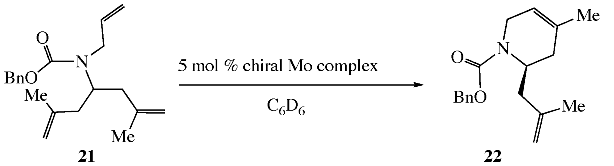
Table 5. Mo-Catalyzed ARCM Reactions of Amide 19



entry	chiral complex	temp (°C)	time (h)	yield (%)^{a}	ee (%)^{b}
1	**2a**	25	24	84	96
2	**7a**	25	24	84	96
3	**11a**	25	24	69	94
4	**2b**	70	48	33^{c}	n.d.
5	**7b**	70	48	34^{c}	n.d.
6	**11b**	70	48	<2^{c}	n.d.

^{a} Isolated yields of purified products. ^{b}Determined by chiral GLC analysis. ^{c}Yield determined by ^{1}H NMR analysis.

Table 6. Mo-Catalyzed ARCM Reactions of Amide 21



entry	chiral complex	temp (°C)	time (h)	yield (%)^{a}	ee (%)^{b}
1	**1a**	25	48	90	96
2	**7a**	25	48	86	94
3	**11a**	25	48	81	83
4	**1b**	80	60	66	81^{d}
5	**7b**	80	60	15^{c}	n.d.
6	**11b**	80	60	42	90^{d}

^{a} Isolated yields of purified products. ^{b}Determined by chiral GLC analysis. ^{c}Yield determined by ^{1}H NMR analysis. ^{d}Opposite configuration.

listed in Table 2. Mo complexes **2a** and **7a** efficiently convert the starting materials into **13** and **14**. However, the yields of the desired product (**13**) are low to moderate in spite of the fact that only 1 equiv of styrene is used. The formation of a significant quantity of **14** suggests that the catalysts are too reactive, which thereby leads to impaired selectivity for **13**. The enantioselectivities in entries 1 and 2 are high, but not outstanding. In contrast, **2b**, **7b**, and **11b** provide a much higher ratio of **13** to **14** product ratios and high enantiomeric purities for **13**. (It is not surprising to find that the other enantiomer of **13** is observed since the (*R*)-Trip ligand is present in catalysts **2b**, **7b**, and **11b**.) Reactions performed in the presence of **7b** or **11b** (but not **2b**) must be run at 75 °C; at 22 °C transformations do not proceed to >98% conversion. It should be noted that **11a** does not yield any **13** or **14**; instead **12** apparently is polymerized in a ROMP process. At present, we cannot explain the drastic difference in the reactivity of **11a** in this circumstance relative to other catalysts we examined.

We recently reported the enantioselective synthesis of cyclic amides and amines through Mo-catalyzed ring-closing metathesis.[13] Certain compounds studied in this project proved to be challenging substrates for ARCM reactions in the presence of arylimido catalysts. The results of ARCM of lactams **15** and **17** in the presence of the six catalysts are listed in Tables 3 and 4. Lactams **15** and **17** exhibit notably different reactivity profiles under the conditions of the ARCM reaction. Compound **15** undergoes olefin metathesis efficiently at 22 °C in the presence of **2a**, **7a**, and **11a**. Complex **7a** provides >98% conversion (22 °C, 20 h), while reactions that involve **2a** and **11a** require longer reaction times. All three reactions yield **16** with similar modest enantioselectivities. Catalysts **7b** and **11b** do not lead to conversion of **15** to the desired ARCM products even if the mixture is heated to 65 °C for 20 h. Reactions involving **2b**, however, afford **16** in high yield and with 97% ee when the transformation is performed at 65 °C for 48 h.

Catalytic ARCM of cyclic amide **17** (Table 4), on the other hand, turns out to be challenging for all catalysts except **2a** and

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[13] Sattely, E. S.; Cortez, G. A.; Moebius, D. C.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2005**, *127*, 8526−8533.

7a, which provide **18** in good yields and excellent enantioselectivities. It is worth noting that catalyst **11a** exhibits drastically diminished reactivity toward **17**. We presume that the decreased reactivity is a consequence of the steric bulk of the 2-phenyl-2-adamantylimido ligand, which prevents an olefin from interacting efficiently with the Mo center. The remaining catalysts give moderate and low yields of the desired product, predominantly converting **17** into a dimer formed through cross-metathesis of the 1-pentene fragment of the molecule. These results are not especially surprising since formation of the corresponding dimer instead of the bicyclic compound **18** has been observed before in the catalytic ARCM of **17** in the presence of arylimido complexes. We expected that higher temperatures or conditions that allow ethylene to escape the reaction mixture would improve the yield of the desired product. However, experiments showed that the yield of **18** does not depend on the temperature of the reaction mixture or on the volume of the reaction vessel.[14]

Two additional substrates (**19** and **21**) were explored (Tables 5 and 6, respectively). These last two substrates differ only in the nature of the protecting group on the nitrogen atom. Mo-catalyzed ARCM of the unprotected amine is not successful. In the case of **19**, catalysts in entries 1−3 afford heterocycle **20** in high yields and enantioselectivities. Similar to the examples discussed above, chiral complex **11a** exhibits a relatively lower reactivity under identical conditions compared to catalysts **2a** and **7a**. Complexes **2b** and **7b** require higher temperatures in order to convert **19** to **21**, although even after 48 h, the yields of product are relatively low. Catalyst **11b** is inactive toward catalytic ARCM of amide **19**. Heterocycle **22** (Table 6) is somewhat easier to obtain than **20**. Complexes **2a** and **7a** provide **22** in good yield and with high enantioselectivities. However, Mo complexes **11a**, **2b**, and **11b**, even at 80 °C, show lower conversions and more moderate enantioselectivities. With catalyst **7b** only a 15% conversion was realized over the course of 36 h and the starting material was isolated from the reaction mixture.

Conclusions

Chiral complexes **7a**, **7b**, **11a**, and **11b** have been prepared and, along with **2b**, compared with the only previously known alkylimido catalyst (**2a**) in ring-closing and ring-opening/cross-metathesis reactions of a variety of amides and a protected norborneol. Complex **7a** provides reactivity and enantioselectivity in all reactions that is approximately equal or superior to **2a**. Catalysts containing the (*R*)-Trip ligand (**2b**, **7b**, and **11b**) are generally less reactive, but provide products in moderate to high yields and enantioselectivities at higher temperatures. Complexes containing 2-phenyl-2-adamantylimido groups (**11a** and **11b**) exhibit diminished reactivity, probably as a consequence of the size of the imido substituent. These results suggest that activities and enantioselectivities are not comparable for all alkylimido ligands explored. Aside from steric factors, it is not known to what these differences can be ascribed. It is important now to generate catalysts from dipyrrolyl precursors[15] in order to attempt to understand more about the role of solvent,[16] especially in reactions that employ binaphtholates, a variation that has been largely unexplored to date.

Experimental Section

General Procedures. All reactions were conducted in oven-dried (at 135 °C) and flame-dried glassware under an inert atmosphere of dry nitrogen employing standard Schlenk and glovebox techniques. Toluene, diethyl ether, and THF were degassed and passed through a column of activated alumina. DME was distilled from sodium/benzophenone under nitrogen atmosphere. *n*-Pentane was washed with H_2SO_4 and water, dried over $CaCl_2$, degassed, and then passed through a column of activated alumina. Deuturated benzene and toluene were dried over CaH_2. Chemical shifts in ^1H and ^{13}C NMR spectra are reported in ppm from tetramethylsilane with the solvent as an internal standard. Elemental analyses were performed by H. Kolbe Analytical Laboratories, Mülheim an der Ruhr, Germany.

1-Phenylcyclohexylamine ($PhCyNH_2$),[9] 2-phenyl-2-adamantylamine ($PhAdNH_2$),[11] **2a** and **2b**,[10] substrates **12**,[12] **15**, **17**, **19**, and **21**,[13] and diolates (*S*)-BiphenK_2[17] and (*R*)-TripK_2[18] were prepared according to literature procedures. Compounds **13**, **14**, **16**, **18**, **20**, and **22** were isolated, purified, and analyzed according to published procedures.[12,13]

$Mo(NPhCy)_2Cl_2(dme)$ (4). $PhCyNH_2$ (20.0 g, 0.11 mol), Na_2MoO_4 (11.3 g, 0.06 mol), Et_3N (38 mL, 0.27 mol), and trimethylsilyl chloride (76 mL, 0.6 mol) were dissolved in 300 mL of dry DME. The mixture became bright yellow after being stirred at 90 °C for 18 h. The solids were filtered off and the solvent was removed from the filtrate *in vacuo* to give a yellow powder. The powder was triturated with 100 mL of pentane, isolated via filtration, and dried *in vacuo*; yield 30.8 g (0.05 mol, 85%): ^1H NMR (C_6D_6) δ 7.58 (d, $J_{HH} = 7.5$ Hz, 4H), 7.28 (t, $J_{HH} = 7.5$ Hz, 4H), 7.11 (t, $J_{HH} = 7.5$ Hz, 2H), 3.34 (s, 6H), 3.19 (s, 4H), 2.21 (m, 4H), 2.07 (m, 4H), 1.85 (m, 4H), 1.58 (br s, 2H), 1.37 (m, 4H), 1.14 (m, 2H). Anal. Calcd for $C_{28}H_{40}MoO_2Cl_2N_2$: C, 55.73; H, 6.68; N, 4.64; Cl, 11.75. Found: C, 55.61; H, 6.64; N, 4.63; Cl, 11.80.

$Mo(NPhCy)_2(CH_2CMe_2Ph)_2$ (5). A suspension of $Mo(NPhCy)_2Cl_2(dme)$ (9.5 g, 0.15 mol) in 100 mL of diethyl ether was cooled to −78 °C. A solution of $PhCMe_2CH_2MgCl$ (0.31 mol) in 50 mL of ether was added dropwise. The mixture was stirred at −78 °C for 3 h and then at room temperature for 12 h. The solvent was removed *in vacuo*, and the solid residue was dissolved in 50 mL of toluene. 1,4-Dioxane (4 mL) was added, the mixture was stirred for 1 h, and the white precipitate was removed by filtration. The solvents were removed from the filtrate *in vacuo*, and the solids were triturated with pentane overnight. The product was filtered off, and the pentane washes were reduced to 10 mL and left at −35 °C for 12 h. The crystallized material was collected and combined with the solid obtained from trituration to give 9.2 g of a bright yellow crystalline product (0.013 mol, 81%): ^1H NMR (C_6D_6) δ 7.34−7.29 (m, 8H), 7.22−7.17 (m, 8H), 7.11−7.05 (m, 4H), 1.85 (m, 12H), 1.76 (s, 4H), 1.52 (m, 4H), 1.42 (s, 12H), 1.22 (m, 4H). Anal. Calcd for $C_{44}H_{56}MoN_2$: C, 74.55; H, 7.96; N, 3.95. Found: C, 74.46; H, 7.94; N, 3.87.

$Mo(NPhCy)(CHCMe_2Ph)(OTf)_2(DME)$ (6). $Mo(NCyPh)_2(CH_2CMe_2Ph)_2$ (5.2 g, 7.3 mmol) was dissolved in 200 mL of ether, and 5 mL of DME was added. The mixture was cooled to −78 °C, and a solution of TfOH (3.3 g, 21.9 mmol) in 15 mL of ether was added slowly. The mixture was stirred at −78 °C for 1 h and then warmed to room temperature and stirred for 2 h. Solvents were removed *in vacuo*, and the resulting brown oil was dissolved in 15 mL of toluene. Addition of an equal volume of pentane caused a

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(14) The conditions were as follows: (a) 22 °C, 20 mL vessel, 2 mL reaction volume; (b) 70 °C, 20 mL vessel, 2 mL reaction volume; (c) 70 °C, 200 mL vessel, 2 mL reaction volume.

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precipitate to form, which was filtered off. The solution volume was reduced to 1 mL, and ether was layered on top. The mixture was left at −30 °C overnight, and the white crystalline material was filtered off. Two more crops were collected in a similar manner to give 2.9 g of white crystals (3.7 mmol, 51%): ^{1}H NMR (C_6D_6) δ 13.96 (s, 1H), 7.57 (d, 2H, J_{HH} = 8.5 Hz), 7.51 (d, 2H, J_{HH} = 8.5 Hz), 7.28 − 7.00 (m, 6H), 3.32 (s, 4H), 2.68 (m, 2H), 2.46 (s, 6H), 2.12 (m, 2H), 1.84 (s, 6H), 1.59−1.14 (m, 6H). Anal. Calcd for $C_{28}H_{37}F_6MoS_2NO_8$: C, 42.59; H, 4.72; N, 1.77. Found: C, 42.68; H, 4.79; N, 1.77.

Mo(NPhCy)(CHCMe$_2$Ph)[(S)-Biphen] (7a). (*S*)-BiphenH$_2$ (99.3 mg, 0.28 mmol) was dissolved in 10 mL of THF, and the solution was cooled to −35 °C. Benzyl potassium (74.2 mg, 0.57 mmol) was added, and the mixture was stirred for 1 h. The mixture was added to a solution of Mo(NPhCy)(CHCMe$_2$Ph)(OTf)$_2$(dme) (240 mg, 0.28 mmol) in 20 mL of ether that had been cooled to −35 °C, and the mixture was stirred for 5 h. The solvent was removed *in vacuo*, and the resulting solid was extracted with 50 mL of pentane. The white precipitate was filtered off, and the resulting yellow-orange solution was taken to dryness *in vacuo* to give an orange powder (180 mg, 0.22 mmol, 79%): ^{1}H NMR (C_6D_6) δ 10.95 (s, 1H), 7.41 (m, 1H), 7.39 (m, 2H), 7.37 (m, 2H), 7.22−7.19 (m, 2H), 7.13 (br s, 1H), 7.08−7.04 (m, 1H), 7.00−6.95 (m, 3H), 2.27 (m, 1H), 2.18 (m, 1H), 2.09 (s, 3H), 2.07 (s, 3H), 1.75 (s, 3H), 1.71 (s, 3H), 1.68 (s, 3H), 1.62 (m, 2H), 1.59 (s, 9H), 1.55−1.49 (m, 4H), 1.45 (s, 9H), 1.16 (s, 3H), 1.03 (m, 2H); ^{13}C NMR (C_6D_6) δ 273.6 (d, J_{CH} = 119.8 Hz). Anal. Calcd for $C_{46}H_{59}MoNO_2$: C, 73.28; H, 7.89; N, 1.86. Found: C, 73.20; H, 8.05; N, 1.84.

Mo(NPhCy)(CHCMe$_2$Ph)[(R)-Trip](thf) (7b). (*R*)-TripK$_2$ (214 mg, 0.25 mmol) was dissolved in 10 mL of THF. The solution was cooled to −35 °C and added to a cold solution of Mo(NPhCy)(CHCMe$_2$Ph)(OTf)$_2$(dme) (200 mg, 0.25 mmol) in 15 mL of THF. The mixture was stirred for 5 h, and the solvent was removed *in vacuo*. The solid was extracted with 50 mL of pentane, and the white precipitate was filtered off. The resulting yellow solution was taken to dryness to give a yellow powder (294 mg, 0.24 mmol, 99%): ^{1}H NMR (C_6D_6) δ 14.02 (s, 1H), 7.73 (s, 1H), 7.71−7.61 (m, 3H), 7.58 (s, 1H), 7.49 (m, 1H), 7.46 (s, 1H), 7.37 (m, 1H), 7.24−7.17 (m, 3H), 7.13 (br s, 1H), 7.12−6.58 (m, 13H), 3.53 (m, 2H), 3.25 (septet, J_{HH} = 7 Hz, 1H), 3.07 (septet, J_{HH} = 7 Hz, 1H), 2.95 (septet, J_{HH} = 7 Hz, 1H), 2.78 (septet, J_{HH} = 7 Hz, 1H), 2.56 (br d, J_{HH} = 8 Hz, 1H), 2.32 (br d, J_{HH} = 8 Hz), 2.14 (br s, 4H), 1.85 (d, J_{HH} = 6.6 Hz, 6H), 1.77 (s, 3H), 1.64 (br s, 1H), 1.51 (d, J_{HH} = 6.6 Hz, 6H), 1.42 (d, J_{HH} = 6.9 Hz, 6H), 1.37 (d, J_{HH} = 6.9 Hz, 12H), 1.34−1.20 (m, 3H), 1.24 (s, 3H), 1.17 (d, J_{HH} = 6.9 Hz, 6H), 1.08−1.04 (m, 4H), 0.69 (br s, 4H); ^{13}C NMR (C_6D_6, ppm) δ 308.6 (d, J_{CH} = 145 Hz). Anal. Calcd for $C_{77}H_{93}MoNO_3$: C, 78.61; H, 7.97; N, 1.19. Found: C, 78.47; H, 8.09; N, 1.14.

Mo(NPhAd)$_2$Cl$_2$ (9). PhAdNH$_2$ (5.0 g, 0.22 mol) was dissolved in 150 mL of DME, and Na_2MoO_4 (2.3 g, 0.011 mol), Et_3N (6.1 mL, 0.044 mol), and Me_3SiCl (13.9 mL, 0.11 mol) were added. The mixture was stirred at 60 °C for 18 h. The solids were filtered off, and the solvent was removed *in vacuo* to give a yellow oil. Treatment of the oil with pentane gave a white powder, which was removed by filtration. The resulting yellow solution was reduced to 20 mL and cooled to −30 °C. The yellow product was filtered off 48 h later; yield 3.0 g (0.05 mol, 44%): ^{1}H NMR (C_6D_6) δ 7.44 (d, 2H, J_{HH} = 7.5 Hz), 7.25 (t, 2H, J_{HH} = 8 Hz), 7.13 (t, 1H, J_{HH} = 8 Hz), 2.66 (s, 2H), 2.61 (d, 2H, J_{HH} = 13 Hz), 1.89 (s, 1H), 1.71 (d, 2H, J_{HH} = 12.5 Hz), 1.63−1.54 (m, 7H). Anal. Calcd for $C_{32}H_{38}Cl_2MoN_2$: C, 62.24; H, 6.20; N, 4.54. Found: C, 62.14; H, 6.16; N, 4.38.

Mo(NPhAd)$_2$Cl$_2$(thf) (10). PhAdNH$_2$ (3.2 g, 0.14 mol) was dissolved in 100 mL of THF, and Na_2MoO_4 (1.4 g, 0.07 mol), Et_3N (3.9 mL, 0.28 mol), and trimethylchlorosilane (8.8 mL, 0.69 mol) were added. The mixture was stirred at 85 °C for 48 h. The solids were filtered off, and the solvent was removed *in vacuo* to give a yellow solid. The solid was triturated with pentane to give a pale yellow powder; yield 4.6 g (0.07 mmol, 97%): ^{1}H NMR (C_6D_6) δ 7.40 (br s, 4H), 7.30 (br s, 6H), 3.80 (s, 4H), 2.86 (s, 4H), 1.99 (s, 2H), 1.68−1.57 (m, 18H), 1.32 (s, 4H). Anal. Calcd for $C_{36}H_{46}Cl_2MoN_2O$: C, 62.70; H, 6.72; N, 4.06; Cl, 10.28. Found: C, 62.86; H, 6.65; N, 4.14; Cl, 10.34.

Mo(NPhAd)$_2$(CH$_2$CMe$_2$Ph)$_2$. Procedure A. Mo(NPhAd)$_2$Cl$_2$ (3.0 g, 4.8 mmol) was dissolved in 100 mL of ether, and the solution was cooled to −78 °C. A solution of PhMe$_2$CCH$_2$MgCl in ether (10.2 mmol) was added dropwise to the reaction mixture. The mixture was stirred at −78 °C for 30 min and then stirred at room temperature overnight. The solution was diluted with 10 mL of 1,4-dioxane and stirred for 1 h. The solids were filtered off, and the solvents were removed from the filtrate to give a brown oil. The oil was dissolved in 10 mL of pentane. This solution was cooled to −30 °C, and two crops of bright yellow crystals were collected; yield 1.7 g (2.0 mmol, 42%): ^{1}H NMR (C_6D_6) δ 7.44 (d, J_{HH} = 7.5 Hz, 4H), 7.33 (d?, J_{HH} = 7.5 Hz, 4H), 7.24 (m, 8H), 7.10 (m, 4H), 2.62 (s, 4H), 2.48 (d, 2H, J_{HH} = 12 Hz), 1.82 (d, 4H, J_{HH} = 12 Hz), 1.78 (s, 2H), 1.66−1.58 (m, 22H), 1.26 (s, 12H). Anal. Calcd for $C_{52}H_{64}N_2Mo$: C, 76.82; H, 7.93; N, 3.45. Found: C, 76.88; H, 8.02; N, 3.54.

Procedure B. Mo(NPhAd)$_2$Cl$_2$(thf) (4.4 g, 6.4 mmol) was dissolved in 50 mL of ether, and the solution was cooled to −78 °C. A solution of PhMe$_2$CCH$_2$MgCl in ether (11.8 mmol) was added dropwise to the reaction mixture. The mixture was stirred at −78 °C for 30 min, then stirred at room temperature overnight. The solvents were removed *in vacuo*, and the resulting solid was extracted with toluene. The white precipitate was filtered off, and the toluene was removed *in vacuo* to give a yellow solid. The solid was triturated with pentane and isolated via filtration. The filtrate was reduced to 5 mL *in vacuo* and the solution cooled to −30 °C overnight. A crop of yellow solid was collected and combined with the triturated powder to give 2.7 g of the product (3.3 mmol, 52%). The spectral data and elemental analysis results of this material match the data obtained for the product synthesized via method A.

Mo(NPhAd)(CHCMe$_2$Ph)(OTf)$_2$(DME). Mo(NPhAd)$_2$(CH$_2$CMe$_2$Ph)$_2$ (1.0 g, 1.2 mmol) was dissolved in 50 mL of ether, and 2 mL of DME was added. The mixture was cooled to −35 °C, and a cold solution of freshly distilled TfOH (0.56 g, 3.7 mmol) in 10 mL of ether was added to it slowly. The mixture was stirred for 5 h. The solvents were removed *in vacuo*, and the resulting brown oil was extracted with toluene. The solids were filtered off, and the toluene solution was reduced to 5 mL. The white solid was filtered after 48 h at −30 °C; yield 461 mg (0.55 mmol, 54%): ^{1}H NMR (C_6D_6) δ 15.65 (s, 0.6 H), 14.89 (s, 0.4H), 14.11 (s, 1H), 7.54 (d, 2H, J_{HH} = 7 Hz), 7.47−7.18 (m, 8H), 7.14−6.88 (m, 12H), 3.32 (s, 4H), 3.12 (s, 3.6H), 3.31−2.34 (m, 10H), 2.28 (s, 6H), 2.20−1.96 (m, 4H), 1.86 (s, 6H), 1.82−1.22 (m, 24H), 1.64 (s, 2.4 H). Anal. Calcd for $C_{32}H_{41}F_6MoNO_8S_2$: C, 45.66; H, 4.91; N, 1.66. Found: C, 45.32; H, 5.02; N, 1.78.

Mo(NPhAd)(CHCMe$_2$Ph)[(S)-Biphen] (11a). (*S*)-BiphenK$_2$ (136 mg, 0.31 mmol) was dissolved in 10 mL of ether, and the solution was cooled to −35 °C. The solution was added to a solution of Mo(NPhAd)(CHCMe$_2$Ph)(OTf)$_2$(dme) (266 mg, 0.31 mmol) in 20 mL of ether that had been cooled to −35 °C. The solution was stirred for 10 h. The solvent was removed *in vacuo*, and the resulting solid was extracted with 50 mL of pentane. The white precipitate was filtered off, and the resulting orange solution was taken to dryness to give an orange powder (210 mg, 0.26 mmol, 84%): ^{1}H NMR (C_6D_6) δ 10.72 (s, 1H), 7.49 (d, J_{HH} = 7.2 Hz, 1H), 7.32 (d, J_{HH} = 7.2 Hz, 1H), 7.26 (s, 1H), 7.23−6.98 (m, 8H), 2.89 (br s, 1H), 2.54 (br s, 1H), 2.46 (br s, 1H), 2.22 (br s, 1H), 2.16 (s, 1H), 2.09 (s, 3H), 2.08 (s, 1H), 1.88 (br s, 1H), 1.85 (br s, 1H), 1.82 (br s, 1H), 1.79 (br s, 1H), 1.77 (s, 3H), 1.75 (s, 1H), 1.70 (s, 1H), 1.62 (s, 6H), 1.59 (s, 6H), 1.53 (s, 18H), 1.33 (s, 1H), 1.26 (s, 1H);

^{13}C NMR (C_6D_6) δ 274.0 (d, J_{CH} = 121.0 Hz). Anal. Calcd for $C_{50}H_{63}MoNO_2$: C, 74.51; H, 7.88; N, 1.74. Found: C, 74.38; H, 8.08; N, 1.79.

Mo(NPhAd)(CHCMe$_2$Ph)[(R)-Trip](thf) (11b). (*R*)-TripK$_2$ (181 mg, 0.23 mmol) was dissolved in 10 mL of THF, and the solution was cooled to −35 °C. It was added to a solution of Mo(NPhAd)(CHCMe$_2$Ph)(OTf)$_2$(dme) (198 mg, 0.23 mmol) in 10 mL of THF that had been cooled to −35 °C. The reaction was stirred for 10 h at room temperature. The solvent was removed *in vacuo*, and the resulting solid was extracted with 50 mL of pentane. The white precipitate was filtered off, and the resulting orange solution was taken to dryness to give an orange powder (261 mg, 0.22 mmol, 98%): ^{1}H NMR (C_6D_6) δ 14.06 (s, 1H), 7.70 (s, 1H), 7.69−7.62 (m, 4H), 7.59 (s, 1H), 7.52−7.37(m, 5H), 7.34−7.18 (m, 7H), 7.15−6.76 (m, 6H), 5.34 (br s, 4H), 3.66 (septet, J_{HH} = 7 Hz, 1H), 3.52 (septet, J_{HH} = 7 Hz, 1H), 3.07 (m, 2H), 2.84 (m, 2H), 2.60 (s, 1H), 2.33−2.16 (m, 2H), 2.03 (m, 1H), 1.79 (br m, 4H), 1.46 (m, 4H), 1.32−1.21 (m, 30H), 1.16 (d, J_{HH} = 7 Hz, 6H), 1.12 (d, J_{HH} = 7 Hz, 6H), 1.03 (m, 2H), 0.69 (br s, 4H); ^{13}C NMR (C_6D_6, ppm) δ 310.4 (d, J_{CH} = 145.0 Hz). Anal. Calcd for $C_{81}H_{97}MoNO_3$: C, 79.19; H, 7.96; N, 1.14. Found: C, 79.26; H, 8.09; N, 1.18.

A Representative Procedure for AROM/CM. Styrene (19.0 mg, 0.18 mmol) and compound **12** (36.6 mg, 0.18 mmol) were dissolved in 1 mL of C_6D_6 in a 20 mL vial, and 0.36 mL of 0.026 M solution of catalyst **7a** in C_6D_6 (7.2 mg, 9.5 × 10^{-3} mmol) was added to the solution. The reaction mixture was stirred in a nitrogen-filled glovebox at room temperature for 40 h, then reduced to 0.5 mL and separated on a silica gel column using a mixture of hexanes and ether (10:1) as an eluent to give products **13** (20.6 mg, 0.068 mmol, 36%) and **14** (14.7 mg, 0.038 mmol, 42%) as colorless oils. The spectral data for the products match the published results.

A Representative Procedure for ARCM. In a nitrogen-filled glovebox lactam **15** (67.3 mg, 0.26 mmol) was dissolved in 1 mL of C_6D_6 in a 20 mL vial, and 0.74 mL of a 0.017 M solution of catalyst **2b** in C_6D_6 (14.8 mg, 12.9 × 10^{-3} mmol) was added to the mixture. The vial was sealed and taken out of the glovebox. The mixture was stirred at 65 °C for 48 h, then the solution was reduced to 0.5 mL and separated on a silica gel column using ether as an eluent to give 52.0 mg of **16** as a colorless oil (0.25 mmol, 97%). The spectral data for the product match the published results.

Acknowledgment. We thank the NIH (GM-59426 to R.R.S. and A.H.H.) for supporting this research.

Supporting Information Available: Crystallographic data for **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM061001O