Evaluation of Enantiomerically Pure Binaphthol-Based Molybdenum Catalysts for Asymmetric Olefin Metathesis Reactions that Contain 3,3′-Diphenyl- or 3,3′-Dimesityl-Substituted Binaphtholate Ligands. Generation and Decomposition of Unsubstituted Molybdacyclobutane Complexes

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Enantiomerically pure molybdenum imido alkylidene complexes were prepared that contain binaphtholate ligands substituted in the 3 and 3′ positions with either phenyl (**4**; Mo(NAr)(CHCMe$_2$Ph)[Ph](THF)) or 2,4,6-trimethylphenyl groups (**5**; Mo(NAr)(CHCMe$_2$Ph)[Mes](THF); Ar = 2,6-i-Pr$_2$C$_6$H$_3$). Compound **5** was found to be an *anti* trigonal bipyramidal complex in an X-ray study. Asymmetric metatheses employing complex **5** were found to proceed to high conversion and to give high product % ee, while reactions that employed complex **4** were found to give lower conversion and lower % ee. One ring-closing reaction with **5** was shown to take place at a rate that was proportional to catalyst and substrate. Molybdacyclobutane complexes were observed in solution during ring-closing reactions. The molybdacyclobutane complex generated by treating **5** with ethylene was found to be a trigonal bipyramidal species which decomposed to yield some propylene; the metal-containing product or products of decomposition could not be identified. Molybdacyclobutane complexes were also formed upon adding ethylene to the analogous complex containing a 2,4,6-triisopropylphenyl-substituted binaphtholate ligand, or to **4**. The detection of propylene as a product of decomposition of the molybdacyclobutane complexes examined here suggests that a decomposition pathway that consists of β hydride rearrangement can compete with bimolecular decomposition of methylene complexes under some conditions.

Introduction

In the past decade it has become clear that well-defined, single-component olefin metathesis catalysts based on molybdenum (primarily Mo(N-2,6-i-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$)[1,2] or ruthenium (primarily Ru(CHPh)(PCy$_3$)$_2$Cl$_2$, Ru(CHPh)(IMes)(PCy$_3$)Cl$_2$, and related species)[3] offer some significant advantages over "classical" metathesis catalysts[4] in a variety of synthetic transformations of potential interest to synthetic organic chemists.[5−9] In the last three years the utility of olefin metathesis has been expanded through the synthesis of enantiomerically pure molybdenum imido alkylidene complexes.[10−23] Enantiomerically pure catalysts have been used for a variety of asymmetric olefin metathesis reactions that include kinetic resolutions, desymmetrization reactions, ring-opening/ring-closing reactions, and ring-opening/cross-coupling reactions.[18] Some of the most successful catalysts that have been employed in asymmetric reactions are **1**, **2**, and **3**. Catalysts of this type are attractive in terms of their modular nature, i.e., the ability to prepare variations by changing the diolate ligand and the imido ligand. With each new imido or diolate ligand the number of potential

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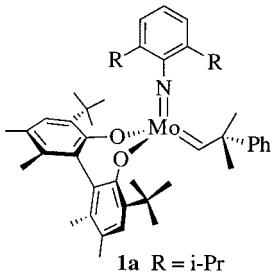
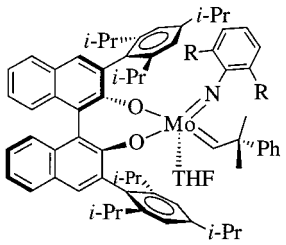
combinations expands markedly, thus ensuring that some variation will be found for optimum activity and % ee for a particular reaction of interest.



1a R = i-Pr
1b R = Me



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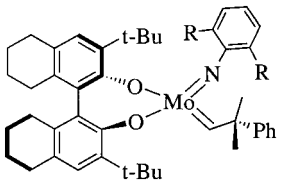
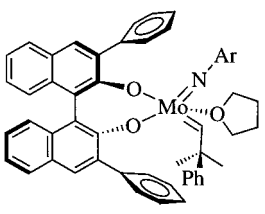


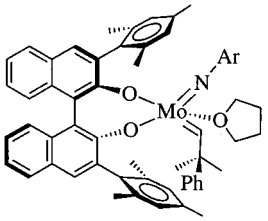
3a R = i-Pr

A relatively bulky group in the biphenolate or binaphtholate ligand in the 3 and 3′ positions apparently is required in order to prepare and isolate a stable neophylidene or neopentylidene initiator. Complexes of type **1** have been prepared in which adamantyl groups replace the *tert*-butyl groups in the biphenoxide ligand. Racemic complexes analogous to **2** have been prepared in which Ph, 2-MeC_6H_4, 2,6-$Me_2C_6H_3$, or 3,5-$Ph_2C_6H_3$ groups are present in the 3 and 3′ positions.[24] Not all such complexes were fully characterized, in part because some seemed to produce unstable intermediates in various ROMP reactions of interest at that time. Therefore we decided to attempt to prepare enantiomerically pure versions of catalysts of type **2** in which the 3,3′ substituents were either phenyl (**4**) or 2,4,6-trimethylphenyl (**5**) and to compare their fundamental characteristics and their efficiency in asymmetric metathesis reactions with the characteristics and efficiency of **2a**. This tack is attractive since species would be compared in which R = H (**4**), Me (**5**), or i-Pr (**2a**) in the 2,4,6-$R_3C_6H_2$ group of the binaphtholate ligand. In the process of a kinetic study of a ring-closing reaction in which ethylene is generated we discovered that the resting state of the species resulting from the reaction of **5** with ethylene is actually a relatively stable molybdacyclobutane complex and that one pathway by which this molybdacycle decomposes yields propylene. These are the first molybdenum systems of this general type in which issues concerning the catalyst resting state and modes of decomposition have been addressed.



4

(Ar = 2,6-i-$Pr_2C_6H_3$)



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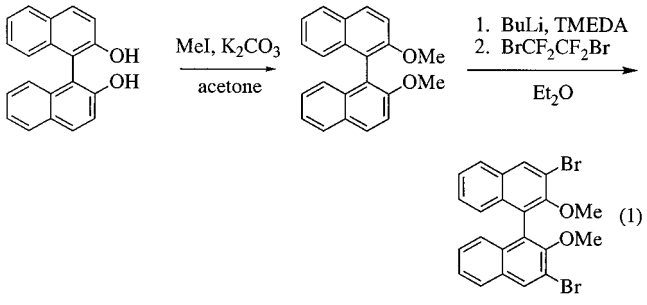
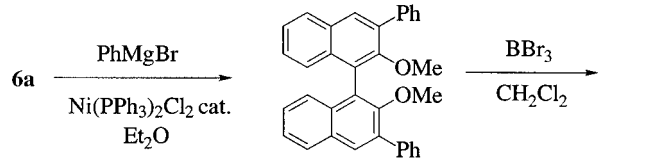
Results

Synthesis of Substituted Binaphthols and Molybdenum Imido Neophylidene Complexes. The synthesis of both *rac*- and (*R*)-3,3′-diphenyl-substituted binaphthol (H_2[Ph]) from the dibromide **6a** (prepared as shown in eq 1) was carried out in good yield using published procedures (eq 2).[25] Although Ni(PPh_3)$_2Cl_2$ is

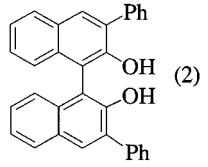


(1)

6a

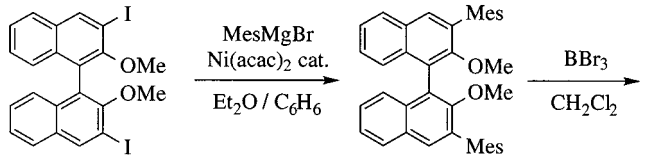


6b

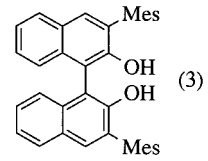


(2)

H_2[Ph]



7a **7b**



(3)

H_2[Mes]

an effective catalyst in the reaction between 2,4,6-triisopropylphenylmagnesium bromide and **6a**,[12] the yield of **7b** (eq 3) in the reaction between 2,4,6-trimethylphenylmagnesium bromide and **6a** was disappointingly low (23%), and no product was obtained using Ni(dppe)Cl_2 or Ni(dppp)Cl_2 as catalyst. Fortunately, the cross-coupling between the diiodo analogue of **6a**, (*rac* or *R*) **7a**, and MesMgBr was efficiently catalyzed by Ni(acac)$_2$ in refluxing 1:1 ether/benzene mixture. Diiodide

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7a was prepared in 80% yield on a 20 g scale by lithiation of methyl-protected binaphthol (LiBu/TMEDA), followed by dropwise addition of a freshly prepared solution of iodine in THF at −78 °C. Iodination attempts at room temperature or 0 °C on a scale of 20 g were unsuccessful, affording a mixture of starting material, product, and monoiodinated species. Deprotection of **7b** with BBr_3, followed by silica gel chromatography, gave a 62% yield of the desired H_2[Mes] on a 6 g scale.

Both *rac*-H_2[Mes] and (*R*)-H_2[Mes] were treated with (−)-menthyldichlorophosphite (Men*PCl_2), and ^{31}P NMR spectra were recorded. Within the NMR detection limit, only (*R*)-[Mes]PMen* (δ ^{31}P = 153.60 ppm) was observed in the sample prepared from (*R*)-H_2[Mes]; the resonance for (*S*)-[Mes]PMen* was found at 150.83 ppm in the sample prepared from *rac*-H_2[Mes].

Binaphthol H_2[Ph] can be deprotonated by benzyl potassium[26,27] or by potassium hydride to form K_2[Ph]. Addition of K_2[Ph] to Mo(NAr)(Neo)$(OTf)_2$(DME) (Ar = 2,6-i-$Pr_2C_6H_3$; Neo = $CHCMe_2Ph$) in THF produced the molybdenum imido alkylidene complex, Mo(NAr)(Neo)[Ph](THF) (**4**; eq 4), in high yield, according to NMR

$$K_2[Ar'] + Mo(NAr)(Neo)(OTf)_2(DME) \xrightarrow[THF]{} \text{Ar' = Ph (4) or Mes (5)} \quad (4)$$

spectra, in either *rac* or *R* forms. (For simplicity we will use the *R* label for the entire complex, even though it refers to the configuration of the ligand within that complex.) Use of KH for deprotonation appeared to yield a purer product. At −30 °C, we observed formation of crystals of (*R*)-**4** in a mixture of THF and pentane, but the crystals redissolved before they could be isolated at room temperature. Isolation of *rac*-**4** has been reported in the literature,[24] but we have not been able to recrystallize (*R*)-**4** consistently on a practical scale (>1 g).

rac- and (*R*)-H_2[Mes] both can be cleanly deprotonated with KH. Addition of K_2[Mes] to a THF solution of Mo(NAr)(Neo)$(OTf)_2$(DME) led to *rac*- and (*R*)-**5**. Complex (*R*)-**5** was isolated in 75% yield on a 750 mg scale from pentane that contained a small amount of THF. If desired, (*R*)-K_2[Mes] can be isolated as a bright yellow powder in virtually quantitative yield.

Potassium hexamethyldisilazide (KHMDS) also can be employed to deprotonate H_2[Mes]. Excess KHMDS and $(TMS)_2NH$ can be removed by triturating the isolated dipotassium salt with small portions of chilled diethyl ether. A virtually quantitative yield of *rac*-K_2[Mes] was obtained. However, since (*R*)-K_2[Mes] is more soluble in diethyl ether, this procedure afforded only a 44−50% yield of (*R*)-K_2[Mes].

Crystals of *rac*-**5** suitable for X-ray crystallography were obtained by slow diffusion of pentane into a THF solution. (See Tables 1 and 2 and Figure 1; two uncoordinated molecules of THF were found in the crystal lattice.) The overall structure of **5** is typical of a trigonal bipyramidal base adduct of a Mo or W imido alkylidene complex;[24,28] the alkylidene and imido ligands are located in equatorial positions, and the THF is bound to one of the two CNO faces of pseudotetrahedral Mo(NAr)(Neo)[Mes]. The alkylidene has the *anti* configuration, similar to the configuration in *anti*-Mo(N-2,6-$Me_2C_6H_3$)(Neo)[Ph](THF),[24] and in contrast to the *syn* orientation found for *syn*-Mo(NAr)(Neo)[Trip](py) (where [Trip] is the binaphtholate found in **2a**).[12] (Whether the *syn* or the *anti* adduct is isolated depends

Table 1. Crystal Data and Structure Refinement for *rac*-5

empirical formula	$MoC_{72}H_{85}NO_5$
fw	1140.35
temperature	183(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	*P*2(1)/*n*
unit cell dimens	a = 15.2983(19) Å, α= 90° b = 17.319(2) Å, β = 104.868(2)° c = 24.100(3) Å, γ= 90°
volume, Z	6171.5(13) Å^3, 4
density(calcd)	1.227 Mg/m^3
abs coeff	0.263 mm^{-1}
F(000)	2424
cryst size	0.5 × 0.3 × 0.3 mm^3
θ range for data collection	2.26−22.50°
index ranges	$-9 \le h \le 16$, $-18 \le k \le 17$, $-25 \le l \le 25$
no. of reflns collected	23 072
no. of ind reflns	8032 [*R*(int) = 0.0959]
abs corr	empirical
max. and min. transmn	0.3287 and 0.2822
refinement method	full-matrix least-squares on F^2
data/restraints/params	8032/0/713
goodness-of-fit on F^2	1.055
final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0721, wR_2 = 0.1386
R indices (all data)	R_1 = 0.1224, wR_2 = 0.1569
extinction coeff	0.0000(3)
largest diff peak and hole	0.467 and −0.337 e Å^{-3}

Table 2. Selected Bond Distances (Å) and Angles (deg) in *anti*-Mo(NAr′)(Neo)[Ph](THF)[24] (Ar′ = 2,6-$Me_2C_6H_3$), *anti*-5, and *syn*-Mo(NAr)(Neo)[Trip](py)[12] [a]

	anti-Mo(NAr′)(Neo)-[Ph](THF)	*anti*-**5**	*syn*-Mo(NAr)-(Neo)[Trip](py)
Mo−N(1)	1.732(7)	1.734(5)	1.715(10)
Mo−C(1)	1.927(9)	1.909(7)	1.840(12)
Mo−O(1)	1.988(5)	1.991(4)	1.988(7)
Mo−O(2)	2.012(5)	2.017(4)	2.018(7)
Mo−O(3)	2.195(5)	2.223(4)	2.251(10)
Mo−C(1)−C(2)	128.1(6)	130.6(5)	149.5(10)
Mo−N(1)−C(49)	166.9(6)	165.5(4)	158.6(8)
Mo−O(2)−C(17)	112.8(5)	113.6(3)	122.3(6)
C(1)−Mo−O(1)	127.4(3)	128.2(3)	117.8(4)
C(1)−Mo−O(2)	92.5(3)	94.6(2)	86.1(4)
N(1)−Mo−C(1)	100.3(3)	97.0(3)	110.8(5)
N(1)−Mo−O(1)	131.3(3)	132.67(19)	130.6(4)
N(1)−Mo−O(2)	100.4(3)	102.18(18)	105.8(3)
O(1)−Mo−O(2)	87.8(2)	88.94(15)	86.5(3)
O(1)−Mo−O(3)	78.4(2)	77.95(14)	78.5(3)
N(1)−Mo−O(3)	88.8(3)	89.50(18)	87.9(4)
O(2)−Mo−O(3)	166.2(2)	166.41(14)	164.2(3)
C(1)−Mo−O(3)	96.1(3)	90.8(2)	96.5(4)

[a] Atom numbers in other structures were changed to correspond to the atom labels in *anti*-**5**.

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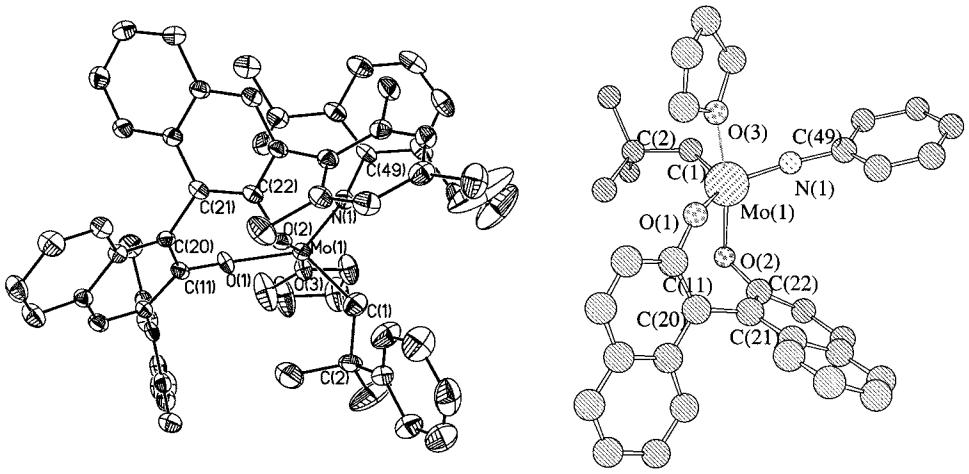

Figure 1. ORTEP diagram and simplified drawing of pseudo-trigonal bipyramidal core of Mo(NAr)(Neo)[Mes](THF), **5**. Thermal ellipsoids are displayed at 30% probability level. Selected groups (Mes, i-Pr, Ph) and hydrogen atoms were omitted for clarity in the structure on the right.

on crystallization conditions and upon the identity of the base; at present the outcome is not entirely predictable.) The Mo−C(1) (Mo=C_α) bond distance (1.909(7) Å) and Mo−C(1)−C(2) (Mo=C_α−C_β) bond angle (130.6(5)°) are typical of *anti* isomers in this class of transition metal complexes; they are comparable to the distance (1.927(9) Å) and angle (128.1(6)°) observed in *anti*-Mo(N-2,6-$Me_2C_6H_3$)(Neo)[Ph](THF).[24] The Mo−C_α bond lengths in *syn* isomers are usually shorter than in *anti* isomers as a consequence of some agostic interaction[29] between the *syn* C−H_α bond and the metal center, which gives the M=C bond some triple-bond character.[28,30−36]

Variable-temperature ^{1}H NMR spectra of (*R*)-**4** in toluene-d_8 from −30 to 80 °C in the presence of 2 to 3 equiv of THF are shown in Figure 2. Two primary alkylidene resonances were observed. That furthest downfield (δ 13.7) could be assigned as an *anti* isomer at −30 °C on the basis of a value for J_{CH} = 150 Hz, while that at 12.2 ppm was identified as a *syn* isomer on the basis of a value for J_{CH} = 122 Hz.[37−39] Both are assumed to be THF adducts. At 20 °C both resonances are broadened. Below 20 °C, the *anti* resonance sharpens as another tiny H_α resonance appears at 13.4 ppm that we ascribe to a second diastereomer of the *anti* THF adduct. The resonance for the *syn* isomer also eventually sharpens at low temperature, but a resonance for the second diastereomer of the *syn* THF adduct did not appear. Upon warming the sample the resonance for the observed *syn* THF adduct broadens, sharpens, and then

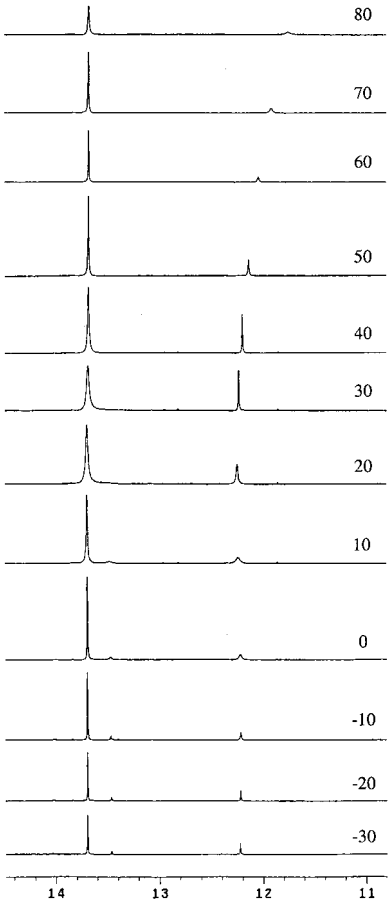

Figure 2. Variable-temperature 500 MHz ^{1}H NMR spectra of (*R*)-**4** in toluene-d_8 in the presence of 2−3 equiv of THF. (Units are ppm; all temperatures are reported in °C.)

begins to shift upfield as more of the THF-free *syn* species is generated that is in rapid equilibrium with the *syn* THF adduct. The resonance for the *anti* THF adduct does not shift upfield at higher temperatures, as little THF is lost from the *anti* THF adduct. Base-free *syn* and *anti* isomers of compounds of type **1** begin to interconvert on the NMR time scale near 80 °C.[15] The same is likely to be true for binaphtholate complexes, although alkylidene interconversion in base-free species

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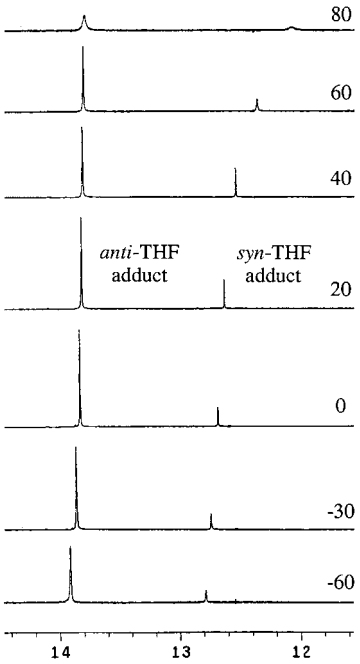


Figure 3. Variable-temperature 500 MHz ^{1}H NMR spectra of recrystallized **5** in toluene-d_8 in the presence of 5 equiv of THF. (Units are ppm; all temperatures are reported in °C.)

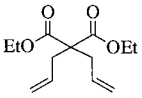
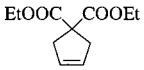
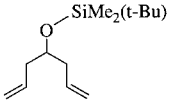
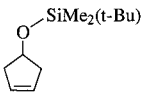
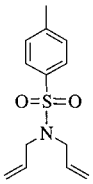
is masked by processes involving dissociation of THF. This behavior is similar to what has been observed in the variable-temperature ^{1}H NMR studies of **2a**.[12]

Similar NMR experiments were carried out for **5**. In the presence of 5 equiv of THF, both the *anti*- and *syn*-THF adducts can be observed (Figure 3; $J_{CH} = 145$ and 115 Hz, respectively, at 20 °C). A ^{1}H−^{13}C heteronuclear multiple quantum correlation (HMQC) experiment suggested through-bond coupling of the protons with resonances at 13.8 and 12.6 ppm to their respective alkylidene carbons with resonances at 315 and 298 ppm. Broadening of the alkylidene proton resonances was observed at temperatures above 60 °C, but the catalyst was relatively stable in the presence of THF. Upon cooling the sample from 100 °C to room temperature, the initial spectra were reproduced and the solution remained bright yellow, indicating little or no decomposition. In the absence of excess THF at 40 °C both *syn* and *anti* resonances were broad, and above 60 °C, the solution turned from bright yellow to dark red as **5** began to decompose.

It should be noted that the *anti* isomer is favored for both **4** and **5**, whereas the *syn* isomer is favored for **2a**.[12] Generally in complexes of this type the *syn* isomer becomes more favorable when the substituents in the imido ligand are small and/or those in the 3 and 3′ positions of the binaphtholate ligand are large, while the opposite is true for the *anti* isomer. The greater stability of the *anti* isomer in **4** and **5** is consistent with the presence of smaller groups in the 3 and 3′ positions of the binaphtholate ligand.

Ring-Closing Metathesis. Some simple ring-closing metathesis reactions catalyzed by **5** are shown in Table 3. (The reactions were carried out under dinitrogen in loosely capped vials, as described in the Experimental Section.) Ether, ester, amide, sulfonamide, CF_3, and siloxy groups under these circumstances are all compatible with the catalyst. Reaction times can be significantly shortened by raising the temperature to 54 °C. A low conversion (16% at 54 °C) was observed when ring-closing of benzyl diallylamine was attempted, although **11** and **12** could be ring-closed successfully. Compound **2a** also could be used for ring-closing reactions at 60 °C.

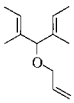
Table 3. Some Simple Ring-Closing Reactions Catalyzed by Mo(NAr)(Neo)[Mes] (5) and 2a[a]

Entry	Substrate	Product	Catalyst	Temp (°C)	Time (h)[a]
1	 **8**		**5**	22	3
			5	54	1
			2a	60	0.5
2	 **9**		**5**	22	3
			5	54	1
			2a	60	0.5
3	 **10**		**5**	22	8
			5	54	1
			2a	60	0.5
4	 **11**		**5**	22	3
			5	54	0.5
			2a	60	0.5
5	 **12**		**5**	22	3
			5	54	0.5
			2a	60	0.5

[a] Solvent = benzene-d_6; 5% catalyst loading (0.005 M). The reaction time was that required for full conversion as determined by the analysis of the 500 MHz ^{1}H NMR spectrum.

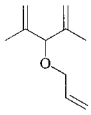
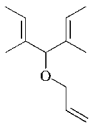
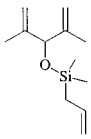
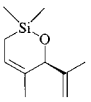
We first examined asymmetric metathesis reactions with crude (*R*)-**4**. The results are shown in Table 4. The potential of (*R*)-**4** in effecting kinetic resolution did not look promising. As shown in entry 1, only 56% of the ring-closed product was obtained from **13** and the % ee of the product was only 32%. Raising the reaction temperature to 40 °C (entry 2) increased the yield slightly, but depressed the % ee. The results of catalytic desymmetrization of trienes **14** and **15** were more encouraging, but still not impressive. Complex (*R*)-**4** ring-closed substrates **14** and **15** at room temperature to give products with 75% and 60% ee, respectively. It should be noted that substrate **15** was found to be unreactive toward catalyst **2a**.[12] Warming the reaction mixture to 40 °C did not enhance the enantioselectivity but reduced the conversion of **15** from 90% to 41%. Cumulatively, these data suggest that **4** is more reactive than **2a**, but also less enantioselective. The incomplete conversion of **13** and the persistence of homocoupled product can be ascribed to catalyst decomposition.

Table 4. Catalytic ARCM Screening Results Using (*R*)-4

Entry	Substrate	Product	Temp (°C)	Time (h)	Product (%)[a]	Product ee (%)[b]	Unreacted sub. ee (%)[b]	"Dimer" (%)[a]
1			22	7	56	32	10	20
2			40	7	67	22	26	13
	13							
3			22	0.5	90	75	-	10
	14							
4			22	0.5	90	60	-	10
5			40	0.5	41	54	-	-
	15							

[a] Solvent = benzene-d_6; 5% catalyst loading (0.01 M). Conversion determined by the analysis of the 500 MHz ^{1}H NMR spectrum of the unpurified mixture. The "dimer" is the product of homocoupling of the substrate. [b] Enantioselectivity determined by GLC analysis (Chiraldex-GTA by Alltech).

Table 5. Enantioselective Catalytic Desymmetrization by (*R*)-5

Entry	Substrate	Product	Solvent	[Cat.] (M)	Temp (°C)	Time (h)	Product (%)[a]	Product ee (%)[b]
1			C_6D_6	0.005	22	1	92	86
2			C_6D_6	0.01	22	3	90	92
3			tol-d_8	0.01	22	3	93	88
4			C_6D_6	0.01	54	1	96	96
	14							
5			C_6D_6	0.005	22	0.75	95	90
6			C_6D_6	0.01	22	3	95	94
7			tol-d_8	0.01	22	2.5	94	93
8			C_6D_6	0.01	54	0.5	94	94
	15							
9			C_6D_6	0.01	22	4	27	71
10			C_6D_6	0.01	54	8	> 99	> 99
	16	**16′**						

[a] Catalyst loading was 5%. Conversion was determined by analysis of the 500 MHz ^{1}H NMR spectrum of the unpurified mixture. [b] Enantioselectivity determined by GLC analysis (Chiraldex-GTA by Alltech for entries 1−8, Betadex-120 for entries 9 and 10) in comparison to authentic racemic ring-closed product.

In contrast, as shown in Table 5, (*R*)-**5** would ring-close **14** and **15** with >90% conversion to give products with >90% ee under a variety of conditions, while **16** was quantitatively converted to **16′** with >99% ee at 54 °C. The beneficial effect of higher temperature was also observed in the desymmetrization of substrate **14**, raising both the conversion and product ee to 96% at 54 °C. Although catalyst **1a** also ring-closed **14** and **15** with high conversion and enantioselectivity, only a 50% yield of the product (**16′**) was obtained (65% ee), along with 32% of the corresponding homocoupled product ("dimer").[11] Catalyst **2a** ring-closed **14** and **16** efficiently and enantioselectively, but was unreactive toward **15**.[12]

Changes in the conversion and product % ee were relatively minor when the solvent was switched from C_6D_6 to toluene-d_8. Other differences were observed when concentrations were changed. For example, doubling the amount of C_6D_6 used in ring-closing **15** reduced the reaction time from 3 h to 45 min with only a minor decrease in product ee. A similar observation was made with substrate **14**. In view of the results soon to be described below, an attempt to explain concentration effects is premature. We did find, not unexpectedly, that the rate of ring-closing is dramatically attenuated in THF-d_8, consistent with competitive binding of THF to the metal.

Substrate **16** and the ring-closed product **16′** have characteristics that allowed the desymmetrization of **16** by (*R*)-**5** to be followed in a kinetic study. Opening of six-membered rings containing a trisubstituted double bond, as in **16′**, which would lead to some decrease of product ee, is apparently not facile, as judged by the >99% ee obtained at 54 °C. Formation of the homometathesis product ("dimer") also was not observed throughout the course of the ring-closing reaction; the only organic species present were **16**, **16′**, and the 3-methyl-3-phenyl-1-butene, the initial metathesis product generated in 5% (stoichiometric) yield. Although substrate **16** was readily ring-closed at 54 °C, ring-closing was slow at room temperature. Therefore the reaction at 54 °C could be sampled after quickly cooling the reaction.

Removal of ethylene was found to be crucial in obtaining consistent results and in driving the reaction to completion. In fact, ring-closure of **16** by (*R*)-**5** was extremely slow when the reaction was carried out in a sealed NMR tube at 54 °C. Consequently, the 54 °C reaction was carried out in a J-Young tube on a Schlenk line with a stream of dinitrogen passing rapidly by the opening of the tube. The J-Young tube was periodically chilled and closed, and its ^{1}H NMR spectrum recorded at room temperature. A smooth and quantitative conversion of **16** to **16′** was observed over a period of 8 h with no observable catalyst decomposition. A plot of the log of the substrate concentration vs time over a period of 400 min yielded a straight line with $R = 0.99552$ and an observed rate constant $k_{obs} = 1.1 \times 10^{-4}$ s^{-1}. If we assume that d[**16**] $= -k$[catalyst][**16**]dt, then $k = 0.0110(8)$ M^{-1} s^{-1}.

Observation of Unsubstituted Molybdacyclobutane Complexes. Several well-defined and reproducible resonances were observed in two regions (3.7 to 4.4 ppm and −0.4 to −0.8 ppm) while monitoring the ring-closure of **16** with (*R*)-**5**. The same resonances were observed (along with those for CH_2=$CHCMe_2Ph$) when ethylene gas was passed into a sample of (*R*)-**5** in C_6D_6. The relative intensities of the five sets of protons centered at 4.3 (a), 4.1−4.2 (b+c), 3.9 (d+e), −0.5 (f), and −0.7 ppm (g) were 1:2:2:1:1 (Figure 4). When doubly ^{13}C-labeled ethylene was employed, resonances a, b+c, e, f, and g were split into two, while one (d in Figure 4) was not. The resonance that was not split by coupling to ^{13}C was assigned to one of the methine protons in a nonrotating NAr ring. We propose that resonances a, b+c (area 2), e, f, and g can be ascribed to the six protons in an unsubstituted molybdacyclobutane complex, Mo-

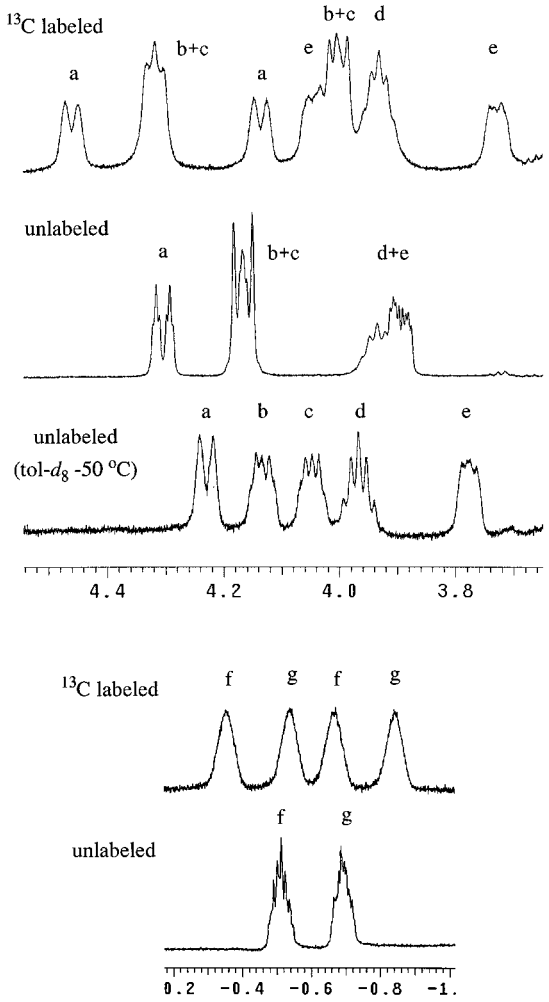
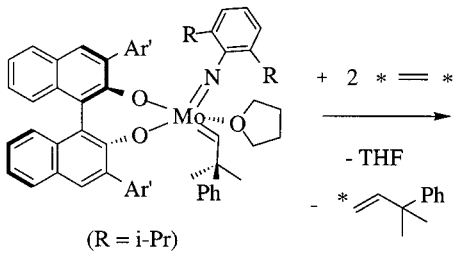
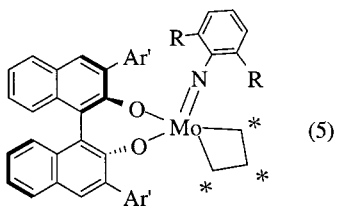


Figure 4. ^{1}H NMR spectra of unlabeled and ^{13}C-labeled Mo(NAr)(C_3H_6)[Mes] (Spectra are in C_6D_6 at 20 °C, unless otherwise noted, and units are ppm.)

(NAr)(C_3H_6)[Mes] (**17**; eq 5). At −50 °C all six inequivalent protons and the methine proton were fully separated from one another, with the chemical shifts for the four metallacycle protons and methine proton in the 3.7−4.4 ppm region being 4.23, 4.13, 4.05, 3.96 (methine), and 3.78 ppm (Figure 4). As the temperature was increased from −50 to 0 °C, the two resonances at 4.13 and 4.05 ppm merged to form the multiplet centered at approximately 4.16 ppm at 20 °C. Between 50 and 60 °C the methine proton resonance (at 3.94 ppm at 20 °C in Figure 4) broadened and shifted upfield as it coalesced with the other methine resonance to give an average at ∼2.7 ppm as rotation of the Ar ring became rapid on the NMR time scale. The metallacycle appeared to be relatively stable at 60 °C under an atmosphere of ethylene, and any exchange of free ethylene with the metallacycle was too slow to lead to significant broadening of the metallacycle resonances. Integration of the resonances in the 3.7−4.3 ppm region versus the olefinic resonances for CH_2=$CHCMe_2Ph$ in the experiment in which (*R*)-**5** in C_6D_6 was treated with ethylene suggested that the molybdacyclobutane was formed quantitatively.





(5)

17 (Ar' = Mes); **18** (Ar' = Trip); **19** (Ar' = C_6H_5)

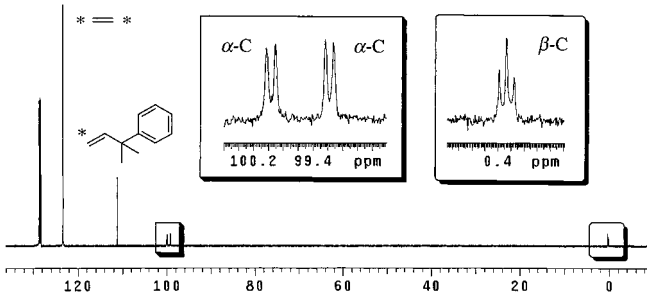


Figure 5. ^{13}C NMR spectrum of Mo(NAr)($^{13}CH_2{}^{13}CH_2{}^{13}CH_2$)[Mes] prepared from Mo(NAr)($CHCMe_2Ph$)[Mes] and doubly labeled ethylene. (Units are ppm.).

In the experiment that employed ^{13}C-labeled ethylene the ^{13}C spectrum showed (in addition to resonances for ethylene and the ^{13}C-labeled initial metathesis product) two doublets centered at 99.9 (J_{CC} = 14.4 Hz) and 99.2 ppm (J_{CC} = 14.0 Hz; Figure 5). The carbons giving rise to the doublets were coupled to a carbon that produced the pseudo-triplet at 0.25 ppm (J_{CC} = 14.4, 14.0 Hz). On the basis of the spin−spin coupling and subsequent information from multidimensional NMR experiments, we assigned the 99.9 and 99.2 ppm resonances to the two α-carbons of the unsubstituted metallacycle. The 0.25 ppm peak was assigned to the *β*-carbon. The J_{CH} values were determined from the ^{1}H-coupled ^{13}C NMR spectrum. The three J_{CH} values were found to be 162 Hz (*δ* 99.9), 159 Hz (*δ* 99.2), and 152 Hz (*δ* 0.25).

The assignment of **17** as an unsubstituted molybdacyclobutane was further confirmed by a series of multidimensional NMR experiments. A ^{1}H−^{13}C HMQC experiment showed that the protons with resonances at 4.3 and 3.9 ppm were coupled to the α-carbon whose resonance was found at 99.9 ppm. The two protons giving rise to the resonance at 4.1 ppm were coupled to the α-carbon whose resonance was found at 99.2 ppm. The protons with resonances at −0.4 and −0.7 ppm were coupled to the *β*-carbon whose resonance was found at 0.25 ppm. A gCOSY experiment suggested that all α-protons were through-bond coupled to the *β*-protons, while the cross-peaks in the α-proton range suggested that the two protons on one of the α-carbons were through-bond coupled to each other. A homonuclear ^{13}C gCOSY experiment suggested that the α-carbons were

Table 6. Coupling Values for Unsubstituted Molybdacyclobutanes 17, 18, and 19

	13C δ (ppm)	1H δ (ppm)	$^1J_{CC}$ (Hz)	$^1J_{CH}$ (Hz)
Mo(NAr)[Ph](C_3H_6), **19**	100.8	4.35	12.8	160
		4.26		
	99.2	4.31	13.8	160
		4.22		
	−0.3	−0.17	13.8	154
		−0.87	12.8	
Mo(NAr)[Mes](C_3H_6), **17**	99.9	4.27	14.4	162
		3.86		
	99.2	4.13	14.0	159
		4.13		
	0.25	−0.54	14.4	152
		−0.72	14.0	
Mo(NAr)[Trip](C_3H_6), **18**	103.4	4.47	15.3	160
		3.96		
	102.4	4.49	13.4	158
		4.42		
	0.2	−0.43	15.3	152
		−0.68	13.4	

not through-bond coupled to each other, which was further confirmed in a $^{13}C-^{13}C$ INADEQUATE experiment.

Since complex **2a** has been employed in many asymmetric metathesis reactions in the literature,[18] we were curious whether a molybdacyclobutane complex would be formed when **2a** is treated with ethylene. We found that an analogous unsubstituted molybdacyclobutane complex (**18**, eq 5) was formed essentially quantitatively and that its ^{1}H NMR spectrum displayed four resonances centered at approximately 4.45, 3.95, −0.4, and −0.7 ppm with relative areas of 3:1:1:1. The four sets of resonances were each split when doubly ^{13}C-labeled ethylene was used. (In this case an imido methine resonance is not found in the 3.8−4.4 ppm region.) In the ^{13}C spectrum, two sets of doublets were located at 103.4 and 102.4 ppm, and the carbons responsible for them were found to be coupled to the carbon giving rise to a pseudo-triplet at 0.2 ppm. The J_{CC} and J_{CH} values of metallacycle **18**, summarized in Table 6, were similar to the values found for **17**. Although the six protons did not separate in a low-temperature proton NMR spectrum in this case, they could be observed as discrete contour circles in the expanded $^1H-^{13}C$ HMQC spectra. Correlational data obtained from homonuclear ^{1}H and ^{13}C gCOSY experiments were similar to those obtained with metallacycle **17**.

When ethylene gas was passed into a sample of in situ generated (*R*)-**4** in C_6D_6, a third molybdacyclobutane (**19**, eq 5) was formed quantitatively. Three sets of protons centered at 4.3, −0.2, and −0.9 ppm were observed with relative areas of 4:1:1. Each of the three resonances was split into two when labeled ethylene was employed. In the ^{13}C spectrum, two sets of doublets were located at 100.8 and 99.2 ppm; both were coupled to the pseudo-triplet at −0.3 ppm. The J_{CH} and J_{CC} values of metallacycle **19** are similar to those found for **17** and **18** (Table 6). The C−H connectivity was established in an $^1H-^{13}C$ HMQC experiment; each carbon was coupled to two protons. All six protons of **19** were observed as discrete contour circles. Correlational data obtained from homonuclear ^{1}H and ^{13}C gCOSY experiments were similar to those obtained with **17** and **18**.

The following results suggest that the molybdacyclobutane complexes **17** and **18** are THF-free species. An NMR sample of **17** (along with the initial metathesis product) was prepared under 1 atm of ethylene. All solvent was subsequently removed in vacuo, and fresh C_6D_6 was added to the sample. Although the initial metathesis product was still present in the sample, THF was not present, and the chemical shifts of the metallacycle resonances in the absence of THF were identical to the resonances observed in the presence of THF (i.e., when made from the THF-adduct (*R*)-**5**). A similar experiment was performed on **18**, which was also confirmed to be a THF-free species. It should be noted that after removing all readily volatile components from a sample of **17** or **18** the resulting glassy solid changed color from a dark yellow to a dark red. Although ^{13}C NMR spectra of these samples still showed a substantial amount of **17** or **18** to be present, we believe that some decomposition takes place to give metal-containing products that do not contain a ^{13}C label. We have not been able to isolate **17** or **18** in pure form.

The observation of **17** at room temperature throughout the course of desymmetrization of **16** suggests that the resting state of the catalyst is actually the molybdacyclobutane complex, at least under the conditions employed in these experiments, and that catalyst turnover is only possible when ethylene is lost from **17** to yield (undoubtedly highly reactive and unstable) Mo(NAr)(CH_2)[Mes]. Therefore slow turnover at room temperature or in a sealed vessel might be expected. In fact ring-closing of **11** in an NMR tube in the presence of **17** was relatively slow at 54 °C under ethylene, only a 42% conversion being observed in 1 h. However, when a similar sample was fully degassed immediately after the addition of **11**, the reaction was complete in 0.5 h at 54 °C. A reaction time of 0.5 h was found when substrate **11** was ring-closed by (*R*)-**5** (Table 3, entry 4). Therefore **17** is a catalytically competent resting state in a catalytic cycle in which ethylene is present or generated, at least under conditions where no ligand is present that binds more strongly to Mo(NAr)(CH_2)[Mes] than does ethylene.

Samples of **17** and **18** were prepared at a concentration of 0.01 M in C_6D_6 under ethylene, and their decompositions were followed over a period of ∼12 days at ∼22 °C (Figure 6). Under 1 atm ethylene, only ∼15% of **17** decomposed over that time period, while all of **18** decomposed. The shape of the decomposition curve for **18** suggests that it is not a simple first- or second-order process. Decomposition of both metallacycles was slower when the atmosphere was half dinitrogen (0.5 atm C_2H_4, 0.5 atm N_2). Interestingly, the rate of decomposition of **18** *increased* again under a mixture of 0.25 atm of ethylene and 0.75 atm of dinitrogen. These data suggest that at least two decomposition pathways are operative, one of which is faster in the presence of ethylene and a second that is faster in the absence of ethylene, assuming that dinitrogen is not involved at any stage of the decomposition.

At the end of one week, two small sets of doublets centered at 116 and 20 ppm were observed in the ^{13}C NMR spectrum of the sample of **17**. Compared to the metallacycle resonances, the new doublets accounted for less than 10% of the labeled material. A proton NMR spectrum suggested that ∼5% of the propylene that could be formed was present in solution (relative to the

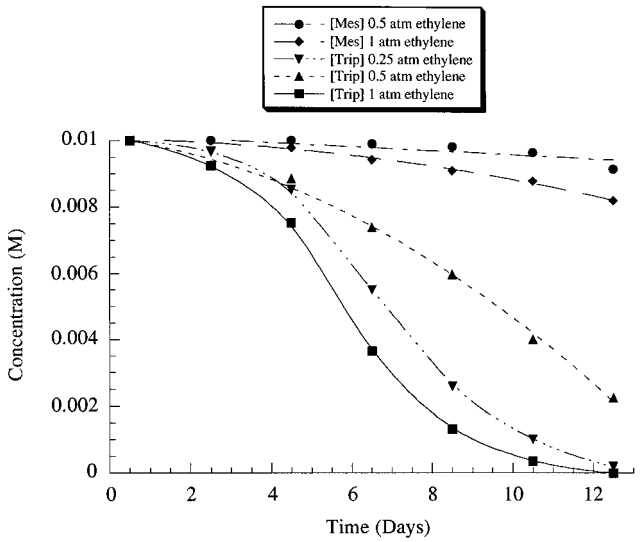


Figure 6. Comparison of the decomposition of Mo(NAr)-$(CH_2CH_2CH_2)$[Mes] and Mo(NAr)$(CH_2CH_2CH_2)$[Trip] in C_6D_6 at 22 °C.

initial cleavage product). The same resonances were observed in the sample of **18**, although the doublets accounted for much more of the labeled material at the end of the week. Proton NMR suggested that 30−40% of the propylene that could be formed was present in solution (relative to the initial cleavage product). The carbons giving rise to the two new doublets were shown to be through-bond coupled to a carbon whose doublet of doublet resonance is centered at around 134 ppm in the homonuclear ^{13}C gCOSY experiment. Observed J_{CC} values (69.7 and 42.2 Hz) were close to those published for fully ^{13}C-labeled propylene (70.0 and 41.9 Hz),[40] while the J_{CH} values (151.7, 153.2, 125.8 Hz) were also identical to those for propylene within three significant figures.[41] A $^1H-^{13}C$ HMQC experiment suggested that the corresponding ^1H chemical shifts were approximately at 5.7, 5.0, and 1.5 ppm, also consistent with unbound propylene being present as the major organic decomposition product. Therefore we propose that one mode of decomposition of **17** and **18** under ethylene is "rearrangement" of the metallacycle to give propylene and some metal-containing product that does not react with propylene or ethylene under the conditions employed. Unfortunately, all attempts to observe or isolate these final decomposition products have failed. The amount of propylene formed during the decomposition of **18** is not consistent with decomposition of **18** solely by a β hydride rearrangement process. Unfortunately, the amount is difficult to quantify in view of the presence of a substantial headspace above the solution in the NMR tube.

Discussion

We have confirmed that use of **4** in several asymmetric metathesis reactions results in low conversion and low % ee. In contrast, use of **5** leads to high conversion and relatively high % ee's. Steric hindrance is clearly crucial to the success of these catalysts, both in terms of efficient enantioselectivity and in terms of catalyst longevity. We still believe that steric hindrance prevents decomposition of intermediate methylene complexes and, therefore, that sterically more hindered systems in general are longer lived for that reason. However, we now know that relatively stable unsubstituted molybdacyclobutane complexes are observable in these reactions in the presence of ethylene and that the sterically more crowded molybdacyclobutane complex (**18**) decomposes *more* rapidly over a period of days than the less sterically crowded molybdacyclobutane complex (**17**) *under an atmosphere of ethylene.* Both species decompose more slowly under 0.5 atm of ethylene, but **18** again decomposes more rapidly under 0.25 atm of ethylene. We hypothesize that decomposition consists of either loss of ethylene to give a methylene complex, which decomposes bimolecularly, or rearrangement of the unsubstituted molybdacyclobutane complex to give propylene. The peculiarity is that formation of propylene appears to be *accelerated* under 1 atm of ethylene. Therefore it would appear that catalyst longevity under some conditions might depend critically upon the amount of ethylene that is present, if no other modes of catalyst decomposition are competitive.

It was originally believed that coordination of THF or some other functionality during the metathesis reaction was the main reason elevated temperatures often are required in order to observe rapid turnover in some asymmetric metathesis reactions catalyzed by **2a**[12,42] in which ethylene is generated. While coordination of an ether oxygen or some other base to the metal certainly can inhibit the rate of metathesis, and probably also inhibit the rate of bimolecular decomposition of methylene species, the reason elevated temperatures are sometimes required in reactions catalyzed by **2a** may be to eject ethylene from the molybdacyclobutane complex and from solution.

Tungstacyclobutane complexes are stable enough to be characterized crystallographically.[28] Several other molybdacyclobutane complexes have been observed, but they are not stable enough to isolate.[43,44] The molybdacycle generated by treating Mo(NAr)(CH-t-Bu)[OCMe-$(CF_3)_2]_2$ with ethylene is stable at 25 °C under ethylene for hours, but decomposes over a period of ~12 h under ethylene to yield a molybdacyclopentane complex, Mo-(NAr)[OCMe$(CF_3)_2]_2(C_4H_8)$ (δ C_α = 76.8 ppm, δ C_β = 38.6 ppm, $J_{C\alpha C\beta}$ = 32 Hz, $J_{C\alpha H}$ = 128 Hz, $J_{C\beta H}$ = 141 Hz).[43] (An example of an imido molybdacyclopentane complex that contains a bisamido system has been reported recently.[45]) On the basis of the chemical shifts for the α carbon atoms at 104.1 ppm and the β carbon atom at −2.28 ppm, and by analogy with crystallographically characterized tungstacyclobutane complexes,[28] Mo(NAr)[OCMe$(CF_3)_2]_2(C_3H_6)$ was proposed to have a trigonal bipyramidal structure. Treatment of Mo-(NAr)(CH-t-Bu)$(OAr)_2$ (Ar = 2,6-i-$Pr_2C_6H_3$) with ethylene yields primarily (95%) square pyramidal Mo(NAr)-$(OAr)_2(C_3H_6)$ (δ C_α = 39.9 ppm, δ C_β = 26.5 ppm) mixed

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with 5% TBP Mo(NAr)$(OAr)_2(C_3H_6)$ (δ C_α = 100.1 ppm, δ C_β = −0.7 ppm). Addition of ethylene to Mo(NAr)(CH-t-Bu)(O-t-Bu)$_2$ was proposed to yield a third molybdacyclobutane complex, square pyramidal Mo(NAr)(O-t-Bu)$_2(C_3H_6)$ (δ C_α = 34.9 ppm, δ C_β = 29.1 ppm, J_{CC} = 32 Hz, J_{CH} = 140 and 129 Hz) in low yield (~25%).[44] Mo(NAr)(O-t-Bu)$_2(C_3H_6)$ decomposed to yield crystallographically characterized [Mo(NAr)(O-t-Bu)$_2$]$_2$, in which the imido ligands bridge symmetrically between the metals. On the basis of NMR data, the molybdacyclobutane complexes reported here appear to have a trigonal bipyramidal structure, rather than a square pyramidal structure (cf. Mo(NAr)$(OAr)_2(C_3H_6)$), possibly because of a preferred O−Mo−O angle close to 90° (see Table 2).

Propylene has been detected here for the first time as a product of decomposition of molybdacyclobutane complexes. To what extent rearrangement competes with intermolecular decomposition of methylene complexes is likely to depend strongly upon conditions, including the concentration of ethylene in solution. Decomposition pathways also could change with the nature of any coordinating functionalities that might be present. Clearly more studies will be required. We plan to examine reactions between ethylene and other alkylidene complexes that have been used in asymmetric metathesis reactions. We are particularly interested in discovering circumstances under which formation of a bimetallic complex that contains two bridging imido ligands can be sterically prevented, and circumstances under which molybdacyclopentane or even olefin complexes[45] might be observed.

Experimental Section

General Procedures. All reactions were conducted in oven- or flame-dried glassware under an atmosphere of nitrogen or argon. Commercially available chemicals were obtained from Aldrich Co. or Lancaster Synthesis and were used without further purification. Liquids were degassed before use. Toluene and THF were distilled from sodium benzophenone ketyl. Dichloromethane was distilled from calcium hydride. Benzyl potassium and Mo(NAr)$(CHCMe_2Ph)(OTf)_2$(DME) were synthesized according to published procedures.[26,27,43]

Conversions were determined by ^{1}H NMR of the unpurified reaction mixtures. Enantiomeric ratios were determined by chiral GLC analyses with an Alltech Associates Chiraldex GTA column (30 m × 0.25 mm) or Betadex 120 column (30 m × 0.25 mm) in comparison with authentic samples. Microanalyses were performed by Kolbe Laboratories (Mülheim, Germany).

Representative Procedures for Ring-Closing Reactions at 22 °C. Complex **5** (10 mg) and benzene-d_6 (1 mL) were added to a 5 mL scintillation vial in order to obtain a 0.01 M catalyst solution. Half of the 0.01 M catalyst solution was added to **16** (21 mg, 0.10 mmol) via syringe, and the reaction mixture was stirred vigorously with the scintillation vial loosely capped. The reaction was periodically monitored by ^{1}H NMR spectroscopy. The product ee was determined by standard chiral GLC.

Representative Procedures for Ring-Closing Reactions at 54 °C. In this case **16** was loaded in a J-Young tube. The 0.01 M catalyst solution was added and the J-Young tube was sealed, attached to a dinitrogen line, and immersed into a 54 °C oil bath. Ethylene was vented to a fast flowing stream of N_2 orthogonal to the tube by slightly opening the J-Young seal. Periodically, the tube was resealed and the reaction monitored by ^{1}H NMR at room temperature.

***(R)*-2,2′-Dimethoxy-1,1′-dinaphthyl.** To a 1000 mL round-bottomed flask were charged (*R*)-(+)-2,2′-dihydroxy-1,1′-dinaphthyl (60 g, 0.212 mol) and acetone (800 mL). The mixture was stirred until homogeneous before anhydrous potassium carbonate (110 g, 0.80 mol) was added. The heterogeneous mixture was then refluxed under nitrogen. Methyl iodide (80 mL, 1.28 mol) was added to the refluxing solution via syringe. The mixture was stirred and refluxed for a minimum of 4 h, when a second portion of methyl iodide (40 mL, 0.64 mol) was added to ensure complete protection of the binaphthol. After 18 h the volatile components were removed by rotary evaporation, and the resulting light yellow residue was dissolved in distilled water (1 L). This mixture was stirred for 8 h to ensure that all potassium carbonate was removed from the solid. The white flaky powder was filtered off and dried in vacuo: yield 66 g (99%); ^{1}H NMR ($CDCl_3$) δ 7.99 (d, 2, Aryl), 7.88 (d, 2, Aryl), 7.47 (d, 2, Aryl), 7.33 (td, 2, Aryl), 7.22 (td, 2, Aryl), 7.12 (d, 2, Aryl), 3.78 (s, 6, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.16, 134.19, 129.61, 129.40, 128.13, 126.51, 125.45, 123.71, 119.75, 114.42, 57.11.

***rac*- and (*R*)-3,3′-Dibromo-2,2′-dimethoxy-1,1′-dinaphthyl (6a).** A solution of BuLi (28 mL, 2.5 M in hexanes, 70 mmol) and TMEDA (7.8 g, 67 mmol) was added to diethyl ether (500 mL). After 15 min solid (*R*)-2,2′-dimethoxy-1,1′-dinaphthyl (10 g, 31.8 mmol) was added to this solution. The brown dilithium salt precipitated from solution after 4 h. The reaction mixture was cooled to −30 °C, and 1,2-dibromotetrafluoroethane (16.8 g, 65.3 mmol) was added over a period of 0.5 h. The white suspension was warmed to room temperature and stirred for 2 h. Distilled water (50 mL) was added slowly to the mixture at 0 °C. The ether layer was separated, dried over $MgSO_4$, and concentrated in vacuo. The product precipitated from the ether solution as a white powder, yield 9.9 g (66%). The ^{1}H NMR spectrum is the same as that reported in the literature.[25] $[\alpha]_D$ = +71.4, (*c* 1.4, THF).

***rac*- and (*R*)-3,3′-Diiodo-2,2′-dimethoxy-1,1′-dinaphthyl (7a).** Butyllithium (48 mL, 2.5 M, 120 mmol), TMEDA (10 mL, 66 mmol), and 500 mL of diethyl ether were added to a 1000 mL round-bottomed flask under nitrogen. The homogeneous solution was stirred for 20 min before 2,2′-dimethoxy-1,1′-dinaphthyl (15 g, 48 mmol) was added. The mixture was stirred overnight at room temperature. The flask was cooled to −78 °C in a dry ice/acetone bath. Molecular iodine (30.2 g, 120 mmol) in the form of iodine chips was dissolved in dry THF (60 mL) and added to the chilled solution dropwise via syringe. The mixture was stirred for 1 h at −78 °C. The solution was warmed to room temperature and allowed to stir for another 12 h to ensure complete ortho-iodination. Some deep red sticky material may be observed at the bottom of the flask as the mixture warms. Approximately 400 mL of water was added slowly. More THF (50 mL) was added to afford clearer solution phases. Stirring was continued for another 2 h. The organic layer was separated, and the aqueous layer was extracted by 1:1 diethyl ether/THF (3 × 150 mL). The combined organic solution was washed with 10% aqueous Na_2SO_3 solutions (3 × 100 mL), followed by a wash of distilled water (200 mL). The separated organic solution was dried over anhydrous $MgSO_4$ and filtered. All solvents were removed by rotary evaporation. Diethyl ether (40 mL) was added to the residue, and the mixture was stirred vigorously for 1 h. The light yellow to off-white powder was filtered off, yield 21.6 g (80%). The lightly colored compound can be further purified by recrystallization from methylene chloride. Even without the recrystallization, the crude compound was pure by NMR spectroscopy: ^{1}H NMR ($CDCl_3$) δ 8.60 (s, 2, Aryl), 7.81 (d, 2, Aryl), 7.42 (t, 2, Aryl), 7.28 (t, 2, Aryl), 7.09 (d, 2, Aryl), 3.428 (s, 6, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.66, 140.09, 134.03, 132.37, 127.29, 127.18, 125.97, 125.87, 125.57,

92.59, 61.34; HRMS (EI, 70 eV) *m/z* calcd for $C_{22}H_{16}I_2O_2$ 565.9240, found 565.9248.

***rac*- and (*R*)-3,3′-Diphenyl-2,2′-dihydroxy-1,1′-dinaphthyl (6b).** This compound was prepared following literature procedures using **6a**, PhMgBr, and $Ni(PPh_3)_2Cl_2$.[25] A higher-yield Suzuki cross-coupling procedure has been reported.[46]

***rac*- and (*R*)-3,3′-Bis(mesityl)-2,2′-dimethoxy-1,1′-dinaphthyl (7b).** In a 250 mL round-bottomed flask were charged 3,3′-diiodo-2,2′-dimethoxy-1,1′-dinaphthyl (11.3 g, 20 mmol), $Ni(acac)_2$ (0.51 g, 1.98 mmol), and benzene (100 mL). The mixture was stirred for 20 min. Commercially available mesitylmagnesium bromide (80 mL, 1 M in diethyl ether, 80 mmol) was added slowly to the mixture. The solution immediately turned dark. Stirring was continued for 30 min at room temperature, and the dark solution was then refluxed under nitrogen for 12 h. The mixture was quenched with aqueous HCl (120 mL, 1 M, 120 mmol) and stirred for 1 h. The organic phase was separated, and the aqueous layer was extracted with diethyl ether (3 × 50 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and filtered, and the solvents were removed from the filtrate by rotary evaporation. The greenish brown sticky material was chromatographed on a silica gel column using 90:10 hexanes/ethyl acetate. All the chromatographed material was used in the deprotection to afford the final ligand: yield 7.05 g (64%); ^{1}H NMR ($CDCl_3$) δ 7.83 (d, 2, Aryl), 7.68 (s, 2, Aryl), 7.38 (m, 2, Aryl), 7.25 (d, 4, Aryl), 6.96 (s, 4, Aryl), 3.08 (s, 6, OCH_3), 2.33 (s, 6, $ArCH_3$), 2.16 (s, 6, $ArCH_3$), 2.12 (s, 6, $ArCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) 136.99, 136.89, 136.58, 134.52, 130.74, 128.31, 128.06, 126.02, 125.94, 124.82, 99.86, 60.13, 21.34, 21.06, 20.93. Anal. Calcd for $C_{40}H_{38}O_2$: C, 87.24; H, 6.95. Found: C, 86.50; H, 7.10.

***rac*- and (*R*)-H$_2$[Mes].** The 3,3′-bis(trimethylphenyl)-2,2′-dimethoxy-1,1′-dinaphthyl from the previous step (7.05 g, 12.8 mmol) was dissolved in CH_2Cl_2 (100 mL) under nitrogen in a 500 mL flask. The solution was chilled to 0 °C, and BBr_3 (80 mL, 1 M in CH_2Cl_2, 80 mmol) was added slowly. After addition was complete, the mixture was left to stir at room temperature for a period of 12 h. The solution was cooled to 0 °C, and distilled H_2O (150 mL) was added slowly to quench the excess BBr_3. Stirring was continued for another half hour. The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 100 mL). All organic fractions were combined and dried over anhydrous $MgSO_4$. The solvents were removed from the filtrate by rotary evaporation, and the residue was chromatographed on a silica gel column with 65:35 hexanes/CH_2Cl_2. A light yellow to off-white powder was obtained, yield 6.5 g (97%); ^{1}H NMR ($CDCl_3$) δ 7.89 (d, 2, Aryl), 7.75 (s, 2, Aryl), 7.39 (t, 2, Aryl), 7.33 (t, 2, Aryl), 7.25 (d, 2, Aryl), 7.02 (s, 4, Aryl), 5.00 (s, 2, OH), 2.35 (s, 6, $ArCH_3$), 2.15 (s, 6, $ArCH_3$), 2.08 (s, 6, $ArCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.06, 137.65, 137.11, 133.50, 132.98, 130.58, 129.54, 129.50, 128.62, 128.52, 128.31, 126.86, 124.58, 123.90, 113.29, 77.44, 21.21, 20.59, 20.53; HRMS (EI, 70 eV) *m/z* calcd for $C_{38}H_{34}O_2$ 522.2559. found 522.2573. $[\alpha]_D = +70°$, (*c* 1, THF).

***rac*-3,3′-Bis(mesityl)-2,2′-dihydroxo-1,1′-dinaphthyl Menthyl Phosphite.** In a 25 mL scintillation vial was added Men*PCl_2 (14.8 mg, 58 μmol) and 2 mL of dry THF in a nitrogen atmosphere. Triethylamine (0.08 mL, 0.57 mmol) was added, and the mixture was stirred for 30 min. *rac*-3,3′-Bis(trimethylphenyl)-2,2′-dihydroxy-1,1′-dinaphthyl (30 mg, 58 μmol) was then added, and the whole mixture was stirred for 12 h. The cloudy solution was filtered through Celite, and the filtrate was examined by phosphorus NMR: ^{31}P NMR (THF) δ 153.60, 150.83.

(*R*)-3,3′-Bis(mesityl)-2,2′-dihydroxo-1,1′-dinaphthyl Menthyl Phosphite ((*R*)-[Mes]PMen*). A similar procedure was employed as that described above using (*R*)-(+)-3,3′-bis(trimethylphenyl)-2,2′-dihydroxy-1,1′-dinaphthyl: ^{31}P NMR (THF) δ 153.60.

Dipotassium Salt of *rac*-3,3′-Bis(mesityl)-2,2′-dihydroxy-1,1′-dinaphthyl (*rac*-K$_2$[Mes]). To a 100 mL round-bottomed flask were charged 3,3′-bis(trimethylphenyl)-2,2′-dihydroxy-1,1′-dinaphthyl (1 g, 1.92 mmol) and dry THF (40 mL) under nitrogen. The solution was stirred for 10 min, and potassium hexamethyldisilazide (0.85 g, 5 mmol) was added. A yellow powder was observed to form after 0.5 h. The mixture was allowed to stir for an additional 5 h. Volatile components were removed by rotary evaporation in the glovebox. Diethyl ether (25 mL) was added to the residue, and the mixture was stirred vigorously for 1 h in order to remove any excess hexamethyldisilazide and the corresponding amine formed in the deprotonation. The suspension was then filtered through a fine frit. The yellow powder was washed with diethyl ether (2 × 10 mL), collected in a scintillation vial, and dried under oil-pump vacuum in the glovebox for 1 h to obtain 1.17 g (quantitative yield) of the desired product. The dipotassium salt was checked by reaction with MeI. As suggested by ^{1}H NMR, 3,3′-bis(trimethylphenyl)-2,2′-dimethoxy-1,1′-dinaphthyl was obtained.

Dipotassium Salt of (*R*)-3,3′-Bis(mesityl)-2,2′-dihydroxy-1,1′-dinaphthyl ((*R*)-K$_2$[Mes]). To a 100 mL round-bottomed flask were charged 3,3′-bis(trimethylphenyl)-2,2′-dihydroxy-1,1′-dinaphthyl (1 g, 1.92 mmol) and dry THF (40 mL) under nitrogen. The solution was stirred for 10 min or until homogeneous. Potassium hydride (0.23 g, 5.7 mmol) was added to the THF solution. A yellow solution of the desired dipotassium salt was observed to form after 0.5 h. The mixture was allowed to stir for an additional 12 h. The excess KH was removed by filtration through Celite. The solvents were removed from the filtrate in vacuo to afford 1.13 g of the desired product, yield 99%.

(*R*)-Mo(NAr)(CHCMe$_2$Ph)[Ph](THF) (4). To a 100 mL round-bottomed flask were charged 3,3′-diphenyl-2,2′-dihydroxy-1,1′-dinaphthyl (0.8 g, 1.82 mmol) and dry THF (40 mL) in a nitrogen glovebox. Potassium hydride (0.22 g, 5.47 mmol) was added slowly in small portions, and the mixture was stirred for 5 h. In a separate 250 mL round-bottomed flask, Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME) (1.45 g, 1.82 mmol) was dissolved in dry THF (100 mL). The freshly prepared dipotassium salt solution was filtered through Celite and added dropwise to the triflate solution. The mixture was stirred in the glovebox for a minimum of 2 h. Solvents were removed in vacuo, and the residue was extracted with cold toluene (−30 °C). All solvents were removed by rotary evaporation. A reddish, foamy material was obtained, yield 1.2 g (70%). Within the NMR detection limit, no free ligand was observed at 5.4 ppm. In one experiment, a very small amount of yellow microcrystals was formed at −30 °C in a mixture of THF and pentane. The crystals readily redissolved before isolation at room temperature was possible: ^{1}H NMR (tol-d_8) δ 13.65 (s, br, Mo=CH, *anti*-THF, J_{CH} = 150 Hz), 10.85 (s, br, Mo=CH, syn); ^{13}C NMR (125 MHz, tol-d_8) δ 315.

***rac*- and (*R*)-Mo(NAr)(CHCMe$_2$Ph)[Mes](THF) (5).** To a 100 mL round-bottomed flask was charged Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME) (0.60 g, 0.76 mmol) and dry THF (50 mL) in a nitrogen glovebox. After 5 min the dipotassium salt of the ligand (0.46 g, 0.77 mmol) was added to the triflate solution, and the mixture was stirred in the glovebox for 4 h. Solvents were removed in vacuo, and the residue was extracted with dry benzene and filtered through Celite under nitrogen. All benzene was removed by rotary evaporation. The residue was taken up in pentane (10−15 mL), and all solvents were removed in vacuo. A minimum amount of THF was then added dropwise. The viscous oil dissolves in the supernatant, and the THF adduct falls out of solution as a yellow powder, which can be trituated with chilled ether to afford 0.58 g of bright yellow powder, yield 75%. Single crystals were grown from a mixture of THF and pentane: ^{1}H NMR (C_6D_6) δ 13.87 (s, Mo=

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CH, *anti*-THF), 12.07 (s, br, Mo=CH, *syn*), 7.75 (d, 2, Aryl), 7.71−7.61 (m, 6, Aryl), 7.58 (s, 2, Aryl), 7.38 (d, 2, Aryl), 7.32 (d, 2, Aryl), 7.24−6.85 (complicated multiplet, Aryl), 6.65 (s, 4, Aryl), 3.96 (m, br, 1 Me_2CH), 3.67 (m, br, 1, Me_2CH), 3.32 (s, br, THF), 2.51 (s, 3, Ar-CH_3), 2.50 (s, 3, Ar-CH_3), 2.48 (s, 3, Ar-CH_3), 2.41 (s, 3, Ar-CH_3), 2.33 (s, 3, Ar-CH_3), 2.32 (s, 3, Ar-CH_3), 2.28 (s, 3, Ar-CH_3), 2.23 (s, 3, Ar-CH_3), 2.17 (s, 3, Ar-CH_3), 2.14 (s, 3, Ar-CH_3), 1.74 (s, 3, Ar-CH_3), 1.68 (s, 6, Ar-CH_3 and $CHC(CH_3)_2Ph$), 1.52 (s, 3, $CHC(CH_3)_2Ph$), 1.49 (s, 3, $CHC(CH_3)_2Ph$), 1.38 (s, 3, $CHC(CH_3)_2Ph$), 1.36−0.97 (m, br, $CH(CH_3)_2$ and THF); ^{13}C NMR (125 MHz, tol-d_8) δ 315.38, 163.23, 160.81, 154.79, 153.46, 151.29, 150.58, 146.59, 142.94, 139.18, 138.77, 138.63, 138.43, 138.27, 137.20, 136.79, 136.36, 136.28, 136.18, 136.03, 135.84, 135.78, 135.64, 135.46, 135.38, 135.36, 135.10, 134.89, 133.07, 132.86, 132.79, 132.34, 130.76, 130.26, 130.07, 129.97, 129.55, 129.49, 129.15, 128.53, 128.41, 128.34, 128.23, 128.17, 127.60, 127.40, 127.17, 126.95, 126.86, 126.42, 126.21, 126.17, 126.07, 125.83, 125.60, 125.45, 125.38, 123.96, 123.24 (br), 123.02, 122.89, 122.83, 122.72, 122.53 (br), 122.05, 121.99, 120.08, 119.85, 70.94, 53.69, 51.47, 32.45, 29.76, 29.57, 29.31, 28.36, 25.30, 24.79, 24.61, 23.93, 23.21, 22.52, 21.87, 21.77, 21.18, 21.08, 21.03, 21.01, 20.96, 20.50. Anal. Calcd for $MoC_{64}H_{69}NO_3$: C, 77.00; H, 6.97; N, 1.40. Found: C, 77.12; H, 6.82; N, 1.29.

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Supporting Information Available: Fully labeled ORTEP drawing, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **5** are available free of charge via the Internet at http://pubs.acs.org.

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