Ring Opening Metathesis Polymerization with Binaphtholate or Biphenolate Complexes of Molybdenum

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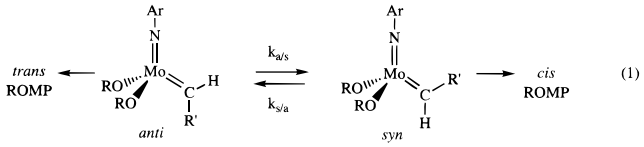
ABSTRACT: Several racemic or enantiomerically pure complexes of the general type Mo(CHR)(NR′)-(O_2R″) that contain binaphtholate or biphenolate (O_2R″) ligands have been prepared and employed to ring open several achiral, racemic, or enantiomerically pure norbornenes and norbornadienes. A bimodal molecular weight distribution sometimes results from polymerization of an enantiomerically pure monomer with a racemic initiator as a consequence of a different rate of chain growth from enantiomeric metal centers. The analogous polymerization of an enantiomerically pure monomer with an enantiomerically pure initiator yields only a single polymer chain, as expected. Evaluation of the *cis* content of the resulting polymers suggests that *cis* polymer results from polymerization via *syn* alkylidene propagating species and that accessibility of the *anti* rotamer on the polymerization time scale is determined by a subtle combination of steric bulk in the biphenoxide and imido ligands. All *cis* polymers were found to be highly isotactic. The X-ray structures of two catalytically active species are also described. One is a THF adduct of 3,3′-diphenyl-2,2′-diolate-1,1′-dinaphthyl (*anti* rotamer) while the other is a base-free *syn* species that contains the 6,6′-dimethyl-3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diolate ligand.

Introduction

We have been exploring the preparation of polymers from relatively symmetric norbornenes and norbornadienes using "well-defined" initiators,[1] most often complexes of the type Mo(NAryl)($CHCMe_2Ph$)($OR)_2$ (Aryl = a substituted aryl group such as 2,6-$Me_2C_6H_3$ (Ar′) or 2,6-i-$Pr_2C_6H_3$ (Ar); OR = O-t-Bu, $OCMe(CF_3)_2$, etc.).[2] *Syn* and *anti* rotamers of complexes of this type (eq 1)



(1)

appear to play a major role in determining whether polymers prepared from several norbornenes or norbornadienes contain *cis* or *trans* double bonds.[3] The *anti* rotamer was found to be significantly more reactive than the *syn* rotamer when OR = $OCMe(CF_3)_2$, and K_{eq} at 25 °C was found to be large (~10^3). However, the rate of interconversion of *anti* and *syn* rotamers was found to vary by up to 6 orders of magnitude. The rate of interconversion was estimated to be relatively rapid ($k_{s/a}$ = 1 s^{-1} at 25 °C) when OR = O-t-Bu, but shown to be relatively slow ($k_{s/a}$ = 10^{-5} s^{-1} at 25 °C) when OR = $OCMe(CF_3)_2$. This combination of circumstances led to the proposal that several 5,6-disubstituted norbornadienes were polymerized by Mo(NAr)($CHCMe_2Ph$)(O-t-$Bu)_2$ to give *trans* polymers via (unobservable) *anti* rotamers,[3] while they were polymerized by *syn*-Mo(NAr)($CHCMe_2Ph$)[$OCMe(CF_3)_2]_2$ as the initiator to give all *cis* polymers[4] via observable *syn* intermediates. Additional evidence for this proposal consists of the finding that a monomer that is too bulky to react with *syn*-Mo(NAr)($CHCMe_2Ph$)[$OCMe(CF_3)_2]_2$ is polymerized at a rate that is independent of the concentration of that monomer; i.e., the rate of conversion of *syn* to *anti* can become the rate-limiting step in the (now slow) polymerization reaction.[5,6] Although molybdenum alkylidene complexes that contain monophenoxide ligands have been relatively little studied, in those that have been studied both *syn* and *anti* rotamers are often observable, and they interconvert relatively easily with activation energies between 15 and 18 kcal mol^{-1}.[7,8]

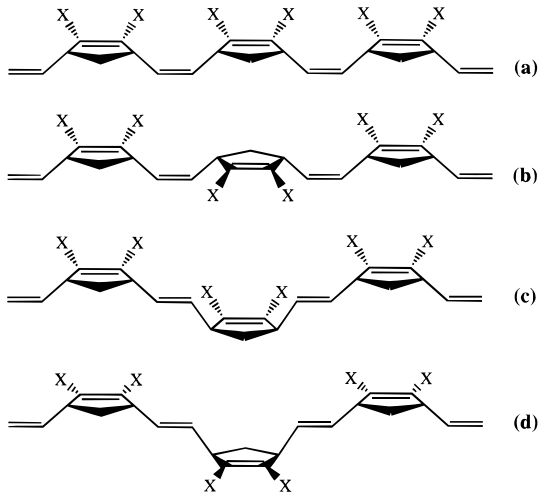


Figure 1. The four possible regular structures of 2,3-disubstituted norbornadienes: (a) cis, isotactic; (b) cis, syndiotactic; (c) trans, syndiotactic; (d) trans, isotactic.

Tacticity does not appear to be linked to the formation of *cis* or *trans* double bonds in the chain in polymer systems that have been explored so far. The four possible regular primary structures of a polymer made from a 2,3-disubstituted-norborna-2,5-diene (for purposes of illustration) are shown in Figure 1. It is believed that a molybdacyclobutane complex is formed when the monomer approaches one of the two CNO faces of the pseudotetrahedral catalyst. (The two CNO faces correspond to the two sides of the Mo=C bond.) If the monomer approaches the same CNO face in each step, an isotactic polymer is formed, while if the monomer approaches alternate CNO faces sequentially, a syndiotactic polymer is formed. Which face is approached in a living polymer made from an achiral

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initiator is determined by the chirality at the β carbon atom in the growing polymer chain (chain-end control). Several polymers containing all *trans* double bonds prepared with Mo(NAr)(CHCMe$_2$Ph)(O-t-Bu)$_2$ as the initiator were found to be highly tactic (>95%), while polymers containing all *cis* double bonds prepared with Mo(NAr)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ as the initiator were found to be biased toward one tacticity.[4,9]

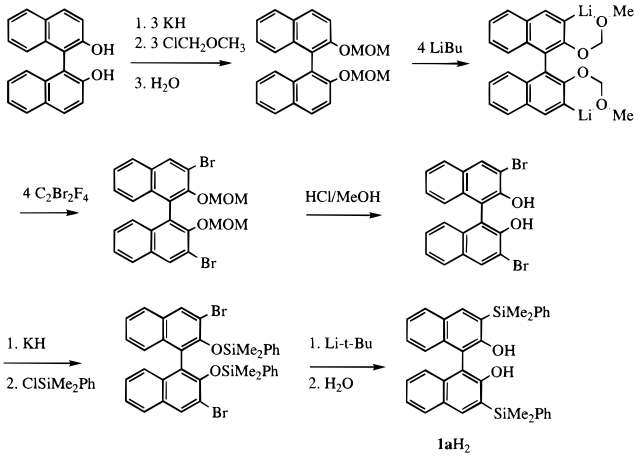
Highly tactic all *cis* polymers can be prepared using molybdenum initiators that contain a chiral (but racemic) binaphtholate ligand, presumably via enantiomorphic site control.[10] The potential advantages of enantiomorphic site control are the same here as in any polymerization; if the influence of the chirality at the metal center overwhelms that due to chirality of the chain-end, then "mistakes" will be corrected rather than propagated. In studies involving norbornadienes that contain an enantiomerically pure "tag" it was possible to prove that several all *cis* polymers are isotactic while all *trans* polymers are syndiotactic.[11] It was also shown that all *cis* polymers prepared from several enantiomerically pure 5,6-disubstituted norbornenes employing molybdenum binaphtholate initiators are isotactic.[11] It was noted that when a chiral, racemic initiator was used to polymerize enantiomerically pure disubstituted norbornenes and norbornadienes, a bimodal distribution of polymer chain lengths was sometimes observed. We speculated that the bimodality might be ascribed to the enantiomerically pure monomer reacting at different rates with the two chain propagating species that contain the two enantiomers of the binaphtholate ligand. All *cis*, isotactic polymers also were prepared using Mo(NAr)(CHCMe$_2$Ph)(BiphenoBu$_4$) (BiphenoBu$_4$ = 3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diolate)[12,13] as an initiator,[10] even though enantiomers of the *free* ligand interconvert readily, in contrast to the binaphthols. Recently, it was shown that the *cis* content of polymers prepared using Mo(N-2-t-Bu-C$_6$H$_4$)(CHCMe$_2$-Ph)(BiphenoBu$_4$) as an initiator in THF or toluene varied from ~40% to 60% and was highly temperature dependent, high *cis* polymers being formed at lower temperatures.[14] All findings were consistent with the proposal that *cis* double bonds are formed from *syn* rotamers of the chain propagating species when *syn*/*anti* conversion is slow and/or the *anti* rotamer is "poisoned" by a coordinating solvent.

In this paper we report additional studies of catalysts that contain substituted binaphtholate and biphenolate ligands. We had two immediate goals, the synthesis of stable racemic catalysts for preparing all *cis* isotactic polymers, and the synthesis of stable enantiomerically pure catalysts. Enantiomerically pure catalysts are not *required* in order to control polymer structure, but they may prove useful in reactions where consumption of one enantiomer in a racemic mixture is sought. A third goal was to determine whether the bimodality observed for certain polymers indeed could be ascribed to rate differences between one diastereomeric pathway and another, and if so, how general a phenomenon that might be.

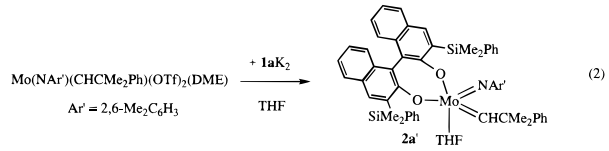
Results

Synthesis of Binaphtholate and Biphenolate Catalysts. Molybdenum complexes that contain the parent binaphtholate ligand did not appear to be monomeric species and were not investigated further.[15] In contrast, monomeric imido alkylidene complexes could be prepared if the binaphtholate ligand is substituted in the 3 and 3′ positions with SiMe$_2$Ph groups.[10] The

Scheme 1. Synthesis of the Silylated BINO ligand



synthesis of the substituted BINO ligand shown in Scheme 1 is based on a combination of reported reactions with some small improvements. (See Experimental Procedures.) Addition of the dipotassium salt of 3,3′-bis(dimethylphenylsilyl)-1,1′-binaphth-2,2′-diol (**1a**H$_2$) to Mo(NAr′)(CHCMe$_2$Ph)(OTf)$_2$(DME) yielded the THF adduct, **2a′** (eq 2). (Unless otherwise indicated, all chiral



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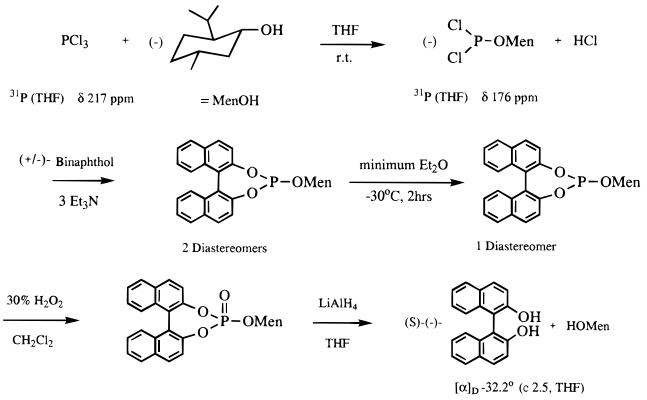
species are racemic.) Both *syn* and *anti* rotamers of **2a′** are observed in NMR spectra in amounts that depend on the amount of THF available and the temperature (cf. Figure 3 and later discussion of a thermally stable analog). The rotamer with the most downfield-shifted H$_\alpha$ resonance (δ 14.0 ppm) is believed to have a THF molecule coordinated to molybdenum on the basis of the fact that it is formed when THF is added or when samples containing at least 1 equiv of THF total are cooled. It is believed to be the *anti* rotamer on the basis of the relatively large value for J_{CH} (144 Hz).[3] We presume that in this species THF is bound in the apical position of a TBP structure as a consequence of attack on the CNO face of the pseudotetrahedral species on the basis of structures of other adducts of complexes of this type[2] and the X-ray structure of a closely related species (see below). An H$_\alpha$ resonance observed at δ 10.9 ppm is believed to be that in a *syn* rotamer in which THF is not bound. Unfortunately, we were not able to obtain crystals of **2a′** that were suitable for X-ray diffraction, in part because it appeared to decompose slowly (days) to unidentifiable products. We also could not obtain a stable THF-free version of **2a′**.

Optically pure binaphthol can be obtained commercially or can be prepared from racemic binaphthol by a method based on that reported by Brunel and Buono.[16] Experimental details were modified to a significant extent, as explained in the Experimental Procedures and summarized in Scheme 2. (*S*)-(−)-Binaphthol was isolated in enantiomerically pure form ([α]$^{25}_D$ −33° (*c* 2.5, THF)) and used to prepare (+)-**1a**H$_2$ ([α]$^{25}_D$ −148° (*c* 2.0, THF)) and the enantiomerically pure initiator, (+)-**2a′** ([α]$^{25}_D$ +47° (*c* 1.7, THF)). Unfortunately, (+)-**2a′** does not crystallize more readily than racemic **2a′**; we could not obtain suitable crystals of (+)-**2a′** or a THF-free version. (+)-**2a′** also decomposes slowly in solution or the solid state to unidentifiable products.

Scheme 2. Method of Resolving Binaphthol



It seemed likely that **2a′** was not indefinitely stable in solution. Under the assumption that reactions involving the silyl substituent were contributing to the instability of **2a′**, we turned to binaphthols that contained carbon-based substituents in the 3 and 3′ positions, in particular, phenyl groups. The parent, 3,3′-diphenyl-2,2′-dihydroxy-1,1′-dinaphthyl[17,18] (**1b**H_2), can be prepared via nickel catalyzed coupling between the MOM-protected dibromide (Scheme 1) and phenylmagnesium bromide.[19] The ether is then deprotected with BBr_3 and the diol converted to the dipotassium salt with a slight excess of potassium hydride. The dipotassium salt, **1b**K_2, is not soluble in THF and therefore was obtained as a precipitate that contained excess KH. Fortunately, KH does not react readily with Mo(NAr′)(CHCMe$_2$Ph)(OTf)$_2$(DME), so **1b**K_2 could be used as isolated (containing up to ∼20% KH) to prepare the desired complex as a THF adduct, Mo(NAr′)(CHCMe$_2$Ph)(**1b**)(THF) (**2b′**). Unlike **2a′**, **2b′** appears to be stable in solution, and X-ray quality crystals could be grown at room temperature by vapor diffusion of pentane into a toluene solution.

An X-ray study showed **2b′** to be a distorted trigonal bipyramid (Figure 2, Tables 1 and 2) with the binaphtholate ligand spanning axial and equatorial positions and the THF bound in an axial position. This is the species that would result from THF adding to the CNO face of the pseudotetrahedral catalyst, as proposed earlier and found for a variety of adducts of this general type.[2] Bond lengths and angles around the metal are not unusual. A significant fact is that the neophylidene ligand has the *anti* configuration in which the Mo−C(33)−C(34) angle is only 128.1(6)°. The THF adduct of the *anti* rotamer is the more stable relative to the THF adduct of the *syn* rotamer, on the basis of NMR spectra of **2b′** in solution (see below), and crystallizes selectively from solution. The phenyl ring of the imido ligand lies approximately in the O(1)−C(33)−Mo−N(1) plane; the Mo−N(1)−C(101) angle is 166.9(6)°, and the C(33)−Mo−N(1) angle is 100.3(3)°. Although O(2) is located approximately in an apical position, O(3) is tipped toward O(1). One phenyl ring on the BINO ligand is pointing more or less straight up (away from the C(33)-N(1)-O(1) face), while the other phenyl ring in the BINO ligand lies more or less beneath the Mo=N bond. The C(1)−C(2)−C(22)−C(17) dihedral angle is 65°, which is approximately what has been found in several W(6+) complexes that contain the parent binaphtholate ligand.[20−22]

Proton NMR spectra of **2b′** in toluene-d_8 show two alkylidene H_α resonances at low temperatures (Figure 3). The most downfield singlet (13.4 ppm) is assigned to *anti*-**2b′** (J_{CH} = 144 Hz), while that at 13.2 ppm is assigned to *syn*-**2b′**. The *anti* adduct predominates, and THF exchange is slow on the NMR time scale at −60 °C for both *syn* and *anti* forms. As the temperature is increased, *anti*-**2b′** becomes the more stable of the two until at 24 °C only the H_α resonance for *anti*-**2b′** can be observed. Above room temperature, THF begins to exchange rapidly on the NMR time scale in *anti*-**2b′**, leading to a broadening of its resonance, and a second broad H_α resonance is observed at 60 °C at ∼11 ppm. We assign the resonance at ∼11 ppm to the base-free *syn* rotamer, *syn*-**2b′**(-THF). (It is common for an H_α resonance to shift downfield by ∼2 ppm upon formation of an adduct.[2]) This temperature-dependent behavior is reversible, and there appears to be no decomposition of **2b′**. It is possible that the H_α resonances for *anti*-**2b′** and *syn*-**2b′**(-THF) are broadened also by direct interconversion of (unobservable) *anti*-**2b′**(-THF) and *syn*-**2b′**(-THF) via alkylidene rotation.[3] Interconversion of *anti* and *syn* alkylidene rotamers in *mono*phenoxide

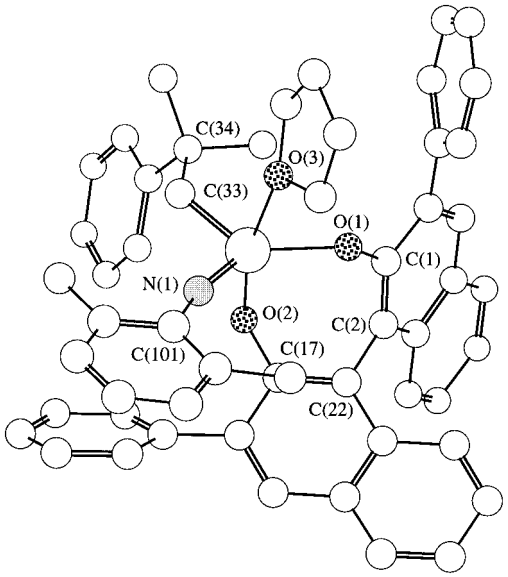


Figure 2. A Chem 3D view of Mo(N-2,6-$C_6H_3Me_2$)(CHCMe$_2$Ph)(3,3′-diphenyl-2,2′-diolate-1,1′-dinaphthyl)(THF) (**2b′**).

Table 1. Crystallographic Data, Collection Parameters, and Refinement Parameters for 2b′ and 4′

	2b′	**4′**
empirical formula	$C_{54}H_{49}NO_3Mo$	$C_{48}H_{65}NO_2Mo$
formula wt	855.93	783.99
cryst color, habit	orange, irregular	red, prism
cryst dimensions (mm)	0.28 × 0.18 × 0.38	0.28 × 0.24 × 0.18
cryst system	monoclinic	monoclinic
no. of reflns used for unit cell determination (2θ range)	25 (11.0−22.0)	na
a (Å)	21.151(3)	11.9205(7)
b (Å)	9.567(1)	18.4661(11)
c (Å)	21.203(3)	20.3925(12)
β (deg)	98.19(3)	96.0710 (10)
V (Å^3)	4247 (2)	4463.7 (5)
space group	$P2_1/a$	$P2_1/c$
Z	4	4
D_{calc} (g/cm^3)	1.340	1.166
F_{000}	1788	1672
μ(Mo Kα) (cm^{-1})	3.44	3.20
scan type	$\omega - 2\theta$	ω
temp (°C)	−86	18
total no. of unique reflns	5933	4150
no. of observations with $I > 3.00\sigma(I)$	3228	4106
no. of variables	532	470
R	0.058	0.0878
R_w	0.050	0.1128
GoF	1.54	1.372

Table 2. Selected Bond Distances (Å) and Angles (deg) in 2b′ and 4′

2b′		**4′**	
	Distances (Å)		
Mo−C(33)	1.927(9)	Mo−C(1)	1.868(9)
Mo−N(1)	1.732(7)	Mo−N(1)	1.731(8)
Mo−O(1)	1.988(5)	Mo−O(1)	1.990(6)
Mo−O(2)	2.012(5)	Mo−O(2)	2.003(6)
Mo−O(3)	2.195(5)		
	Angles (deg)		
Mo−C(33)−C(34)	128.1(6)	Mo−C(1)−C(2)	144.5(7)
Mo−N(1)−C(101)	166.9(6)	Mo−N(1)−C(11)	173.6(8)
Mo−O(1)−C(1)	130.0(5)	Mo−O(1)−C(31)	96.5(5)
Mo−O(2)−C(17)	112.8(5)	Mo−O(2)−C(21)	103.5(5)
C(33)−Mo−O(1)	127.4(3)	C(1)−Mo−O(1)	106.9(3)
C(33)−Mo−O(2)	92.5(3)	C(1)−Mo−O(2)	100.0(3)
C(33)−Mo−N(1)	100.3(3)	C(1)−Mo−N(1)	100.3(4)
N(1)−Mo−O(1)	131.3(3)	N(1)−Mo−O(1)	108.5(3)
N(1)−Mo−O(2)	100.4(3)	N(1)−Mo−O(2)	114.3(3)
O(1)−Mo−O(2)	87.8(2)	O(1)−Mo−O(2)	123.6(2)
O(1)−Mo−O(3)	78.4(2)		
N(1)−Mo−O(3)	88.8(3)		
O(2)−Mo−O(3)	166.2(2)		
C(33)−Mo−O(3)	96.1(3)		

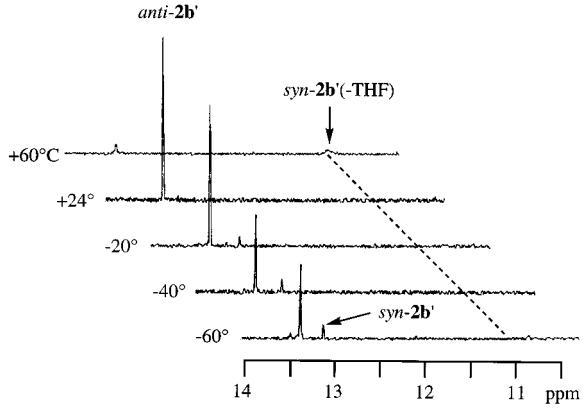


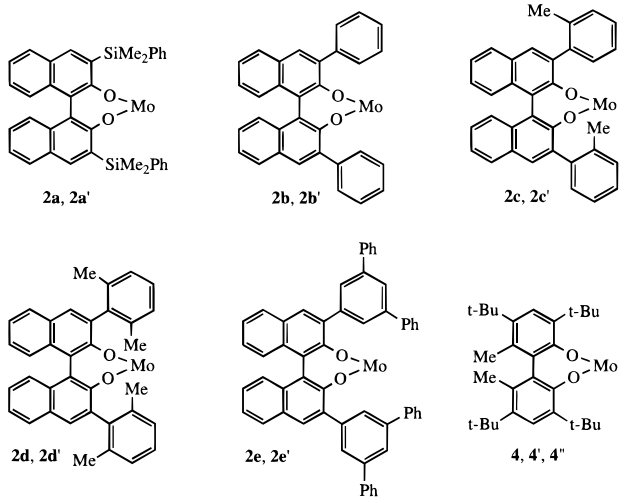
Figure 3. The alkylidene region of the variable temperature ^{1}H NMR spectrum of **2b′** in toluene-d_8.

complexes of this general type has been found to have barriers in the range of 15−18 kcal mol^{-1}.[7] There is no compelling reason to propose that "linked" phenoxide complexes will behave substantially differently than monophenoxide complexes, although at this stage we have no direct confirmation that that is the case.

Binaphtholates that have substituted phenyl groups in the 3,3′ positions were prepared by related methods. These include 2-methyl- (**1c**H_2), 2,6-dimethyl- (**1d**H_2), and 3,5-diphenyl- (**1e**H_2) derivatives. All were converted into dipotassium salts and added to Mo(NAr′)(CHCMe$_2$Ph)(OTf)$_2$(DME) to yield Mo(NAr′)(CHCMe$_2$Ph)(**1c**) (**2c′**), Mo(NAr′)(CHCMe$_2$Ph)(**1d**) (**2d′**), or Mo(NAr′)(CHCMe$_2$Ph)(**1e**) (**2e′**). All phenyl-substituted BINO ligands were added to Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME) to give the analogous complexes **2b**, **2c**, **2d**, and **2e**. All compounds that contain phenyl-substituted BINO ligands were obtained as THF adducts and have solution behavior analogous to that discussed for **2b′** above. All initiators are shown in Chart 1.

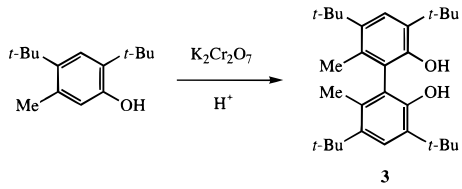
Although 3,3′-diphenylbinaphthol and related species are easier to prepare than silylated versions, some biphenols can be prepared even more simply by oxidative coupling,[23−25] e.g., of commercially available 2,4-di-*tert*-butylphenol. As mentioned in the Introduction, molybdenum catalysts that contain this biphenolate ligand appear to provide a substantial amount of enantiomorphic site control, even though enantiomers

Chart 1. Binaphtholate or Biphenolate Initiators Employed in This Work[a]



[a] All are neophylidene complexes; no prime = N-2,6-i-Pr$_2$C$_6$H$_3$ ligand; prime = N-2,6-Me$_2$C$_6$H$_3$ ligand; double prime = N-2-t-BuC$_6$H$_4$ ligand.

of the catalyst are likely to interconvert, at least on the chemical time scale. 2,4-Di-*tert*-butyl-5-methylphenol is also commercially available and can be coupled similarly to give a biphenol whose enantiomers cannot interconvert (eq 3). Mo(NAr)(CHCMe$_2$Ph)(**3**) (**4**), Mo-



(3)

((NAr′)CHCMe$_2$Ph)(**3**) (**4′**), and Mo(N-2-t-BuC$_6$H$_4$)(CHCMe$_2$Ph)(**3**) (**4″**) were prepared by methods analogous to those described so far. It should be noted that **4**, **4′**, and **4″** can be obtained free of THF and apparently are relatively stable in solution in the absence of THF, as was observed for the molybdenum catalyst that contained the parent Bipheno(t-Bu)$_4$ ligand.[14] The NMR behavior of **4**, **4′**, and **4″** is analogous to that of complexes that contain the parent Bipheno(t-Bu)$_4$ ligand;[14] i.e., in the absence of THF at room temperature only resonances for the *syn* rotamer are observed, while in the presence of THF H_α resonances for both *syn* and *anti* THF adducts (∼1:1) can be observed downfield of that for the *syn* rotamer at temperatures below 0 °C. It is clear that THF simply does not bind as strongly to **4**, **4′**, and **4″** as it does to binaphtholate complexes and that the *anti* and *syn* THF adducts are approximately of equal energy.

X-ray quality crystals of **4′** could be obtained and the structure determined (Figure 4; Tables 1 and 2). The complex is a pseudotetrahedral *syn* species, as expected on the basis of NMR spectra and by analogy with the behavior of binaphtholate complexes. The Mo−C, Mo−N, and two Mo−O bond lengths are statistically the same as they are in **2b′**. The Mo−C(1)−C(2) angle is relatively large in **4′** (144.5(7)°), as has been found for other pseudotetrahedral *syn* rotamers,[2] in contrast to the much smaller Mo−C(33)−C(34) angle (128.1(6)°) in *anti*-**2b′**. The Mo−N(1)−C angles are virtually the same in **2b′** and **4′**. One major difference between the two complexes is the degree to which the biphenolate ligand is twisted. In **4′** the dihedral angle C(31)−C(36)−C(26)−C(21) is 77.5°, while the analogous C(1)−C(2)−

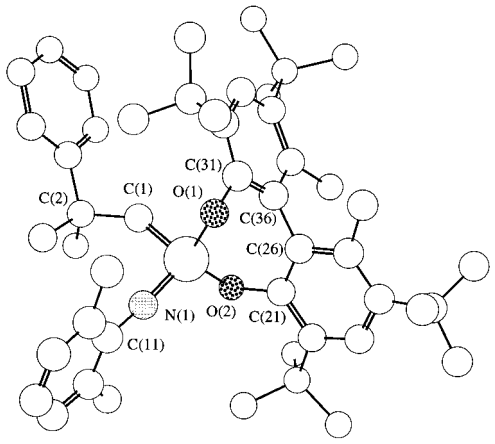


Figure 4. Chem 3D drawing of the structure of *syn*-Mo(CHCMe$_2$Ph)(N-2,6-Me$_2$C$_6$H$_3$)(6,6′-dimethyl-3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diolate) (**4′**).

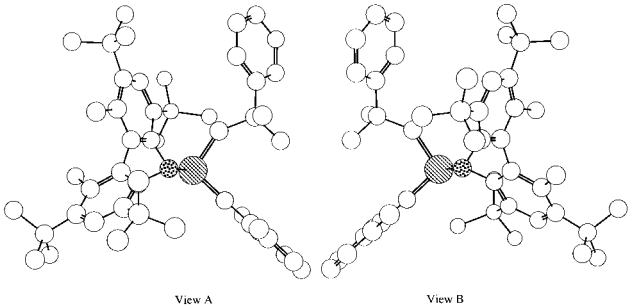


Figure 5. Chem 3D views of the two sides of the Mo=C bond in **4′**.

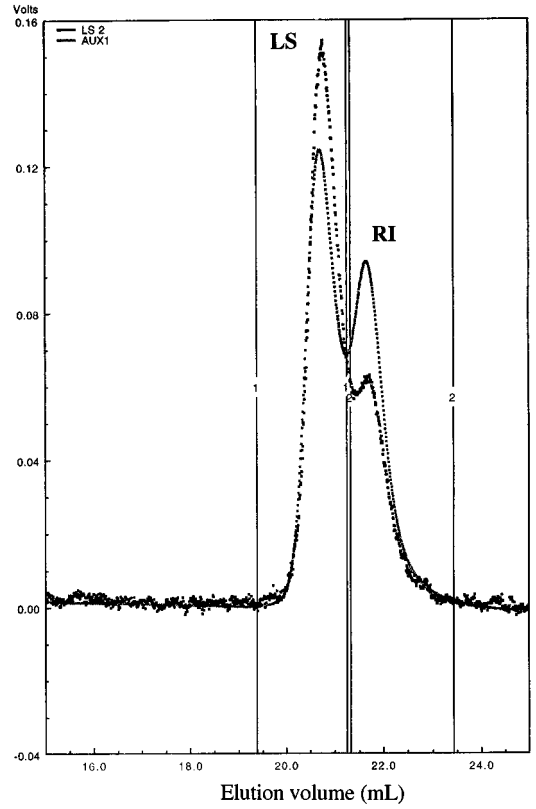


Figure 6. GPC trace (light scattering and refractive index detectors) of poly[(+)-2,3-bis[(pantalactonyloxy)carbonyl]-norbornadiene] made with initiator (±)-**2a′**.

C(22)−C(17) dihedral angle is 65.4° in **2b′**. A second major difference which perhaps arises in large part from the larger degree of twisting is that the Mo−O−C angles in **4′** (96.5°, 103.5°) are much smaller than they are in **2b′** (130.0°, 122.8°), and the Mo···C(31) distance (2.54 Å) and Mo···C(21) distance (2.68 Å) much shorter than the analogous distances in **2b′** (3.04 and 2.82 Å). Perhaps most of the features of the biphenolate ligand in **4′** can be attributed to a greater degree of steric congestion between the two phenyl rings compared to naphthyl rings in binaphtholate complexes. Greater steric congestion is also consistent with the relatively weak interaction between **4′** and THF. (The short Mo···C(31) and Mo···C(21) distances in **4′** may also lead to a decrease in the ability of the metal to bind an external base.) It should be noted that the ortho *tert*-butyl groups effectively distinguish one side of the Mo=C bond from the other. As shown in view B in Figure 5, a *tert*-butyl group appears to block access to the metal to a greater extent than in view A.

Ring Opening Metathesis Polymerization. We first showed that the initial observation[10] was correct; polymerization of (+)-2,3-bis[(pantalactonyloxy)carbonyl]norbornadiene with racemic **2a′** in dichloromethane yielded a polymer with a bimodal distribution of two unequal peaks (Figure 6). Therefore, it is unlikely that this result can be ascribed to an odd coincidence (partial catalyst decomposition, impure monomer, etc.). In this circumstance there are only two possible rates of chain growth, (+)Cat containing (+)monomer units in the growing chain reacting with a (+)monomer and (−)Cat containing (+)monomer units in the growing chain reacting with a (+)monomer. If the rates of these two reactions are significantly different, then two different chain length distributions should be produced in equimolar amounts. The higher molecular weight peak should have a larger area by refractive index detection because the change in refractive index of the sample stream is proportional to the mass of polymer in that stream. (The only assumption is that the change in refractive index per monomer unit in all polymer chains is essentially the same.[26]) Therefore, both the ratio of the M_n values and the relative areas should approximately equal the ratio of the two rates. The ratio of M_n values is 1.5. Light is scattered more efficiently by larger polymers in a nonlinear manner, so the disparity between the higher molecular weight peak and the lower molecular weight peak is exaggerated using light scattering detection (690 nm; Figure 6). It should be noted that the rate difference observed here would also be the hypothetical difference in rate between a (+)Cat containing (+)monomer units reacting with a (+)monomer and a (+)Cat containing (−)monomer units reacting with a (−)monomer. This is a circumstance that could in theory lead to polymerization of only one enantiomer of a racemic monomer by an enantiomerically pure initiator and is discussed in more detail later.

We then turned to the polymerization of (+)-(2*S*,3*S*)-2,3-bis(dimethoxymethyl)norborn-5-ene ((+)-DMMNBE; $[\alpha]^{25}_D$ 90.7° (*c* 3.0, $CHCl_3$)). Highly *cis* and isotactic poly(DMMNBE) is more soluble (especially in THF) than that prepared from a disubstituted norbornadiene such as 2,3-bis(trifluoromethyl)norbornadiene (NBDF6), and therefore is easier to analyze by GPC methods. Polymerization of (+)-DMMNBE with **2a′** in THF yielded polymers with a bimodal distribution of polymer chain lengths by GPC; an example is shown in Figure 7, and analytical data are listed in Table 3. As discussed above, a bimodal distribution with greater area for the higher molecular weight peak is to be expected, and the difference in areas is the same as the difference in M_n values. The rate difference (according to relative M_n values) between the two enantiomers of the initiator polymerizing the enantiomerically pure monomer in

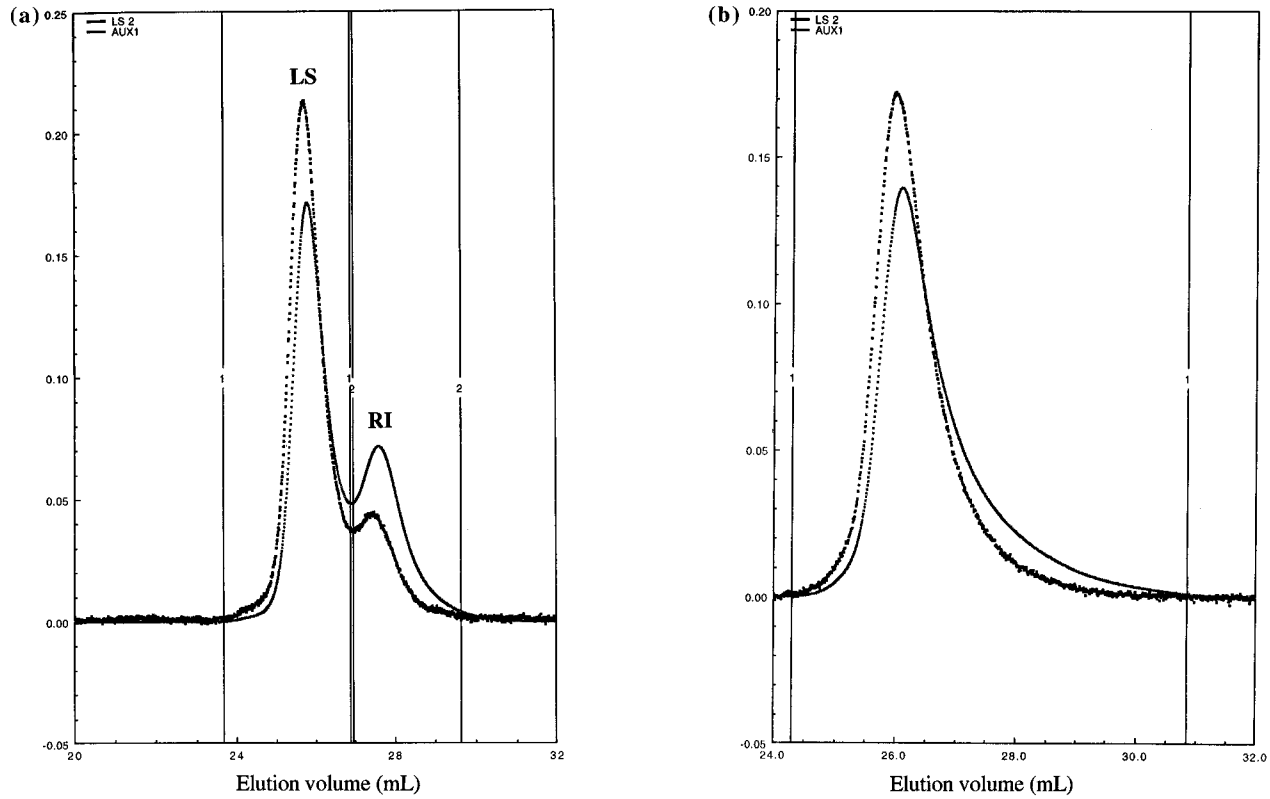


Figure 7. GPC traces (light scattering and refractive index detectors) of poly(5,6-dimethoxymethylnorbornene) made with initiators (a) (±)-**2a′** and (b) (−)-**2a′**.

Table 3. Polymerization of (+)-5,6-Dimethoxymethylnorbornene[a]

initiator	solvent	equiv	time (h)	MW (theory)	M_n (found)	PDI
(±)-**2a′**	THF	50	16	9340	30 500	1.08(3)[b]
					14 800	1.07(14)
(±)-**2a′**	THF	50	0.75	9340	35 000	1.07(7)[c]
					13 000	1.10(33)
(±)-**2a′**	benzene	50	15	9340	19 100	1.20(19)
(±)-**2a′**	CH_2Cl_2	50	15	9340	13 500	1.13(21)
	CH_2Cl_2	50	17	9340	25 100	1.19(8)
(+)-**2a′**	THF	51	3	9520	27 000	1.16(14)[d]
(±)-**2b**	THF	110	0.75	20300	20 000	1.01(6)[e]

[a] All polymers were obtained in >95% yield. 5.67 μmol of catalyst was employed except where noted. M_n (found) was determine using a light scattering detector operating at 690 nm. [b] Approximate relative area 66:34. [c] Approximate relative area 56:44. [d] Results were essentially identical in a repeated experiment. [e] 2.48 μmol of catalyst was employed.

Table 4. The Structures of Poly(NBDF6) and Poly(DCMNBD) Prepared Using Mo(NAr′)(CHCMe$_2$Ph)(O$_2$R″) Initiators in THF

initiator	O_2R''	monomer	equiv	% yield	% cis	PDI
2a′ [a]	**1a**	NBDF6	200	97	>99	*b*
2a′ [a]	**1a**	DCMNBD	100	97	>99	1.28
2b′	**1b**	NBDF6	100	70	95	*b*
2b′	**1b**	DCMNBD	52	90	70	1.02
2c′	**1c**	NBDF6	55	94	93	*b*
2c′	**1c**	DCMNBD	60	65	83	1.41
2d′	**1d**	NBDF6	42	95	99	*b*
2d′	**1d**	DCMNBD	46	99	91	1.18
2e′	**1e**	NBDF6	51	70	93	*b*
2e′	**1e**	DCMNBD	55	85	84	1.04

[a] See refs 10 and 11. [b] Polymers are insoluble in CH_2Cl_2 and THF.

THF was found to be 2.1 in one experiment and 2.7 in a second. The M_n values for these and other polymers prepared using **2a′** as the initiator are higher than theory (cf. (±)-**2b**); the reason is not yet known. If methylene chloride or benzene is used as the polymerization solvent, only *one* peak is observed by GPC. We believe that two molecular weight distributions are actually present, but now have nearly equal M_n values, and simply cannot be resolved. The possible role of solvent in determining the rate difference is discussed later.

Only one chain growth should be possible in the polymerization of (+)-DMMNBE with (+)-**2a′** in THF. The two polymers that were prepared indeed have a *unimodal* distribution of chain lengths (Figure 7b and Table 3) with PDI values of 1.16.

Polymerization of 110 equiv of DMMNBE with **2b** in THF (last entry in Table 3) produced a polymer with a very low polydispersity, even though two chains should again be produced by polymerization at the two enantiomeric metal centers. Apparently the 3,3′-diphenyl-substituted binaphtholate catalyst is relatively inefficient in producing polymers with different chain length distributions. A possible explanation is that a phenyl substituent is simply not bulky enough.

The stereoselectivity of the new ROMP initiators was tested by polymerizing 2,3-bis(trifluoromethyl)norbornadiene (NBDF6) and 2,3-bis(dicarbomethoxy)norbornadiene (DCMNBD), monomers that have been employed in previous studies. The results are shown in Tables 4 and 5. Results obtained previously with initiators **2a** and **2a′** are listed for comparison. It had previously been observed that **2a′** was vastly superior to **2a** in terms of yielding highly *cis*, isotactic polymers for a variety of substituted norbornenes and norbornadienes.[10] However, when the BINO ligand is substituted by a phenyl group instead of a SiMe$_2$Ph group, the *cis* content drops dramatically for poly(DCMNBD), from >99% for **2a′** to 70% for **2b′**. Increasing the size of the phenyl substituent in initiator **2c′** or **2d′** produces poly(DCMNBD) having progressively higher *cis* contents (83% and 91%, respectively), while an initiator containing the 3,5-diphenylphenyl-substituted BINO ligand

Table 5. The Structures of Poly(NBDF6) and Poly(DCMNBD) Prepared Using Mo(NAr)(CHCMe$_2$Ph)(O$_2$R″) Initiators in THF

initiator	O_2R''	monomer	equiv	% yield	% cis	PDI
2a[a]	**1a**	NBDF6	100	87	71	*b*
2a[a]	**1a**	DCMNBD	100	94	93	1.84
2b	**1b**	NBDF6	50	78	>99	*b*
2b	**1b**	DCMNBD	50	80	>99	1.02
2c	**1c**	NBDF6		95	99	*b*
2c	**1c**	DCMNBD		99	98	1.07
2d	**1d**	NBDF6	49	99	98	*b*
2d	**1d**	DCMNBD	55	85	99	1.18
2e	**1e**	NBDF6	55	58[c]	98	*b*
2e	**1e**	DCMNBD	55	94	>99	1.04

[a] See refs 10 and 11. [b] Polymers are insoluble in CH_2Cl_2 and THF. [c] Incomplete precipitation.

Table 6. Poly(NBDF6) and Poly(DCMNBD) Prepared with Initiators 4′ and 4″[a]

initiator	monomer	solvent	cis (%)	isotacticity (%)	PDI
4′	NBDF6	toluene	96	>99	*b*
4″	DCMNBD	THF	54		1.29
4″	NBDF6	THF	44		

[a] All yields were >95%. [b] Polymer was insoluble in CH_2Cl_2.

(**2e′**) produces poly(DCMNBD) that has a *cis* content of 84%. The latter results suggest that substituents in the 3 and 5 positions are less effective than ortho substituents at creating the appropriate steric bulk relatively near the metal. The *cis* content in poly(NBDF6) does not decrease to the same degree in a similar series of experiments (95%, 93%, 99%, 93%), the poly(NBDF6) prepared from **2d′** having the highest *cis* content (99%). When NAr catalysts are employed, the *cis* content *rises* for *all* polymers prepared with *phenyl*-substituted BINO ligands to a level of 98% or greater (Table 5). This result is somewhat surprising since it was found previously that the *cis* content drops dramatically upon replacing the NAr′ ligand with the NAr ligand when the dimethylphenylsilyl-substituted binaphtholate ligand is present.[10] These results suggest that there is an additivity effect of the imido and BINO substituents, i.e., the "smaller effective size" of the various phenyl-substituted BINO ligands relative to SiMe$_2$Ph-substituted BINO ligands can be compensated by increasing the size of the imido ligand from NAr′ to NAr. These results also demonstrate clearly that *cis* content depends sensitively on monomer type as a consequence of different monomer reactivities with *syn* and *anti* rotamers.

The results of polymerizing NBDF6 and DCMNBD with catalysts containing the chiral Bipheno(t-Bu)$_4$Me$_2$ ligand, **4′** (NAr′ ligand) and **4″** (N-2-t-BuC$_6$H$_4$ ligand), are shown in Table 6. These results are analogous to what was found previously for catalysts that contain the Bipheno(t-Bu)$_4$ ligand, which in the free state is not chiral as a consequence of ready rotation of the two naphthyl groups relative to each other. Polymerization of 250 equiv of DCMNBD with Mo(NAr)(CH-t-Bu)-[Bipheno(t-Bu)$_4$] in THF[10] or 100 equiv of NBDF6 with Mo(NAr)(CHCMe$_2$Ph)[Bipheno(t-Bu)$_4$] in THF[14] yielded polymers with a *cis* content of >99%. The *cis* content using Bipheno(t-Bu)$_4$ catalysts[14] was found not to be especially sensitive to temperature. In contrast, poly(NBDF6) and poly(DCMNBD) prepared using **4″** as the initiator yielded polymer with a dramatically lower *cis* content (~40−60%; Table 6), and the *cis* content was highly temperature dependent. Lower *cis* content appears to be characteristic of catalysts that contain the 2-*tert*-butylphenylimido ligand, as the *anti* rotamer, which is believed to be the source of *trans* linkages, becomes more accessible on the polymerization time scale as a consequence of more facile rotation of the alkylidene about the Mo=C bond and conversion of the *syn* rotamer to the *anti* rotamer.

Discussion

The theory concerning the origin of *cis* polymers from *syn* rotamers and *trans* polymers from *anti* rotamers remains intact, although we have done nothing specifically to prove or disprove that theory here. We believe we have shown here that if this theory is correct, then the steric factors that determine the relative reactivity of the base-free *syn* and *anti* rotamers must be exceedingly finely balanced and that therefore each combination of alkoxide, imido group, and monomer must be evaluated separately. It is gratifying that catalysts that contain the phenyl-substituted BINO ligands not only do not decompose readily in solution, but give essentially all *cis* polymers of NBDF6 and DCMNBD if the NAr ligand is present. For the two monomers tested here, the SiMe$_2$Ph substituted BINO ligand in combination with the NAr ligand as well as the phenyl-substituted BINO ligands in combination with the NAr′ ligand are both unsatisfactory; the first is "too crowded" and the last is "not crowded enough". Quantification will not be possible in the absence of relatively sophisticated molecular mechanics calculations, which at this stage does not seem likely for transition metal complexes of the complexity of those discussed here.

We believe the results reported here lend strong support to the proposal[11] that racemic initiators can polymerize enantiomerically pure monomers to give two polymer distributions, owing to the two diastereomeric polymerization pathways. The difference in rate is only approximately a factor of 2 at best, and in many circumstances (even upon changing solvent), essentially zero. The low diastereoselectivity might be ascribed in part to the fact that the chiral groups in the monomers investigated here are not close to where the metal adds to the norbornene-like double bond. The greater rate difference in THF versus benzene or dichloromethane could be ascribed to the coordinating ability of THF. The fact that (+)Cat propagating species containing (+)monomer and (−)Cat propagating species containing (+)monomer are not enantiomers makes it likely that THF binds with different strengths to the (+)Cat/(+)monomer and (−)Cat/(+)monomer propagating species, thereby selectively inhibiting polymerization at either the (+)Cat or (−)Cat center. It seems plausible that some base could be found that would lead to a more dramatic difference in polymerization activity by (+)Cat/(+)monomer/base versus (−)Cat/(+)monomer/base, and thereby a greater difference in molecular weights of the resulting polymers prepared from an enantiomerically pure monomer.

Ultimately it would be desirable to polymerize selectively one enantiomer of a racemic monomer ((±)M) with an enantiomerically pure initiator (e.g., (+)Cat). The difference in the rate of reaction of (+)Cat/(+)M with (+)M relative to (−)Cat/(+)M with (+)M can be used as a first approximation of whether this is likely to be successful. If the configuration of the catalyst itself (not the configuration of any monomer that has been incorporated in the chain) is the major factor that governs the rate at which (+)M is polymerized, then this difference in rate should be equivalent to the difference in rate between (+)Cat reacting with (+)M and (+)Cat reacting with (−)M. We know that this rate difference to be no greater than approximately 2 in the systems examined so far. A selective polymerization of one enantiomer in a racemic mixture to give at least a 50mer

would be possible only if this rate difference were a factor of ~50 or more. But this rate difference is only an approximation, as in general either (+)M or (−)M can be incorporated to varying degrees in any polymer chain, although the last monomer to be incorporated will probably influence the rate of the next step most strongly. Therefore, the reaction steps that are most likely to have significantly different rates are (+)Cat/(+)M_{last} with (+)M, (+)Cat/(+)M_{last} with (−)M, (+)Cat/(−)M_{last} with (+)M, and (+)Cat/(−)M_{last} with (−)M. It is impossible at this stage to say to what extent these four rates would differ on the basis of the rate difference between (+)Cat reacting with (+)M and (+)Cat reacting with (−)M.

Finally, stable, enantiomerically pure catalysts could be useful in the long run in other types of asymmetric metathesis reactions. For example, some success at ring closing one enantiomer of a diene in a ring closing metathesis reaction with an enantiomerically pure catalyst has been realized recently.[27,28] However, relatively few enantiomerically pure well-defined catalysts have been reported.[10,27,28] Future studies will be directed toward expanding this pool of enantiomerically pure catalysts, and determining their effectiveness in enantioselective metathesis reactions.

Experimental Procedures

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques unless otherwise specified. Pentane was washed with sulfuric acid/nitric acid (95/5 v/v), sodium bicarbonate, and water, stored over calcium chloride, and distilled from sodium benzophenone ketyl under nitrogen. Reagent grade diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl under nitrogen. Toluene was distilled from sodium, and CH_2Cl_2 was distilled from CaH_2. Polymerization grade solvents were stored over activated molecular sieves, and a small amount was tested with a THF solution of sodium benzophenone ketyl prior to use. Benzene-d_6 and toluene-d_8 were pre-dried with calcium hydride, vacuum transferred onto sodium and benzophenone, stirred under vacuum for 2 days, and then vacuum transferred into small storage flasks.

All chemicals were reagent grade and were purified by standard methods. Potassium hydride was purchased from Aldrich as a suspension in oil and was washed with pentane prior to use. $Pd(PPh_3)_4$ was purchased from Strem Chemicals, Inc., and used as received. Benzaldehyde was purchased from Aldrich, and was distilled over Na and passed over alumina before use. BBr_3 (1 M in CH_2Cl_2), (2-methylphenyl)magnesium bromide (1 M in THF), and $NiCl_2(PPh_3)_2$ were purchased from Aldrich and used as received. (2,6-Dimethylphenyl)magnesium bromide,[29] 3,3′-diphenyl-2,2′-dihydroxy-1,1′-dinaphthyl,[17] 3,3′-dibromo-2,2′-dimethoxy-1,1′-dinaphthyl,[17] NBDF6,[30] DCMNBD,[31] (+)-(2*S*,3*S*)-2,3-(dimethoxymethyl)norborn-5-ene,[11,32,33] Mo(CHCMe$_2$Ph)(N-2,6-Me$_2$C$_6$H$_3$)(OTf)$_2$(DME),[34] Mo(CHCMe$_2$Ph)(N-2,6-i-Pr$_2$C$_6$H$_3$)(OTf)$_2$(DME),[8] Mo(CHCMe$_2$Ph)(N-2-t-BuC$_6$H$_4$)(OTf)$_2$(DME),[34] (±)-**1a**H_2,[11] and (+)-2,3-bis-[(pantalactonyloxy)carbonyl]norbornadiene[11] were prepared as described in the literature.

NMR data were obtained at 300 MHz (^{1}H), 75.4 MHz (^{13}C), and 121.4 MHz (^{31}P) or 500 MHz (^{1}H) and 125.7 MHz (^{13}C) and are listed in parts per million downfield from tetramethylsilane for proton and carbon and 85% H_3PO_4 for phosphorus. Coupling constants are listed in hertz. Spectra were obtained at 25 °C unless otherwise noted. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN analyzer. Optical rotations were measured with a Perkin-Elmer 243B polarimeter using a sodium lamp set at 589 nm (cell length = 0.1 dm).

GPC analyses were done on a system equipped with two Alltech columns (Jordi-Gell DVB mixed bed; 250 mm × 10 mm (i.d.)). The solvent was supplied to the columns at a flow rate of 1.0 mL/min with a Knauer HPLC pump 64. HPLC grade CH_2Cl_2 was continuously dried and distilled from CaH_2. Detection was effected using a Wyatt Technology mini Dawn light scattering detector coupled to a Knauer differential refractometer assuming that the differential refractive index increment, d*n*/d*c*, is a constant for homopolymers of identical structure.[35] The total mass method was used to measure d*n*/d*c* and was calculated to be 0.096 mL/g for *cis*,isotactic poly(DCMNBD), 0.093 mL/g for *cis*,isotactic poly[(+)-2,3-bis-[(pantalactonyloxy)carbonyl]norbornadiene], and 0.114 mL/g for *cis*,isotactic poly(DMMNBE) in the molecular weight range studied; the error in each of these values is approximately ±0.005. (A referee cautioned that an "outside" measurement of d*n*/d*c* is desirable before the absolute molecular weights can be assumed to be correct.)

(±)-1aK$_2$(THF). KH (74 mg, 1.85 mmol) was added slowly as a solid to a stirred THF (50 mL) solution of (±)-**1a**H_2 (420 mg, 0.716 mmol) at room temperature. The colorless solution turned canary yellow. The reaction mixture was allowed to stir for 2 h, after which the excess KH was removed by filtration through Celite. The THF was removed in vacuo to yield 513 mg (0.698 mmol, 97%) of (±)-**1a**K_2(THF), which was sufficiently pure for subsequent reactions. (−)-**1a**K_2(THF) was prepared similarly from (−)-**1a**H_2.

Mo(CHCMe$_2$Ph)(NAr)(1a)(THF) (2a).[10] To a stirred THF (5 mL) solution of Mo(CH-t-Bu)(NAr)(OTf)$_2$(DME) (66 mg, 0.090 mmol) was added a THF (1 mL) solution of **1a**K_2 (57 mg, 0.090 mmol). The solution was stirred for 1 h and the THF removed under vacuum. The product was extracted with pentane and filtered through a pad of Celite. Concentrating and cooling this solution to −40 °C gave a canary yellow solid; yield 70%: ^{1}H NMR (C_6D_6, 2:1 *syn*/*anti* ratio) δ 13.31 (s, C*H*-t-Bu, *anti*), 10.71 (s, C*H*-t-Bu, *syn*), 8.21 (s, *H*^{4}, *syn*), 8.19 (s, *H*^{4}, *anti*), 8.04 (s, *H*^{4}, *syn*), 7.99 (s, *H*^{4}, *anti*), 7.84−6.80 (m, aromatic *H*), 3.92 (sept, C*H*Me$_2$, *syn*), 3.53 (br, THF), 3.32 (sept, C*H*Me$_2$, *anti*), 1.34 (br, THF), 1.16−0.60 (CHC*Me*$_3$, CH*Me*$_2$, Si*Me*); Partial ^{13}C{^{1}H} NMR (C_7D_8) δ 281.4 ($^1J_{CH}$ = 118, *syn*), 293.7 ($^1J_{CH}$ = 146, *anti*). Anal. Calcd for $C_{57}H_{67}NO_3Si_2Mo$: C, 70.85; H, 6.99; N, 1.45. Found: C, 70.54; H, 7.09; N, 1.14.

Mo(CHCMe$_2$Ph)(NAr′)(1a)(THF) (2a′).[10] The preparation of **2a′** is identical to that for **2a** except that Mo(CHCMe$_2$Ph)(NAr′)(OTf)$_2$(DME) was used; the yield was 65%: ^{1}H NMR (C_6D_6, 1:1 *syn*/*anti* ratio) δ 14.10 (s, C*H*-t-Bu, *anti*), 10.95 (s, C*H*-t-Bu, *syn*), 8.27 (s, *H*^{4}, *anti*), 8.22 (s, *H*^{4}, *syn*), 8.10 (s, *H*^{4}, *syn*), 7.95 (s, *H*^{4}, *anti*), 7.80−6.60 (m, aromatic *H*), 3.43 (br, THF), 2.17 (s, Ar*Me*, *syn* and *anti*), 1.80 (s, CHC*Me*$_2$Ph, *anti*), 1.72 (s, CHC*Me*$_2$Ph, *anti*), 1.53 (s, CHC*Me*$_2$Ph, *syn*), 1.27 (s, CHC*Me*$_2$Ph, *syn*), 1.17 (br, THF), 0.89−0.66 (Si*Me*, *syn* and *anti*); Partial ^{13}C{^{1}H} NMR (C_7D_8) δ 281.4 (*C*HCMe$_2$Ph, $^1J_{CH}$ = 119, *syn*), 296.7 (*C*HCMe$_2$Ph, $^1J_{CH}$ = 147, *anti*). Anal. Calcd for $C_{58}H_{61}NO_3Si_2Mo$: C, 71.65; H, 6.32; N, 1.44. Found: C, 71.28; H, 6.77; N, 1.51.

Resolution of 1,1′-Bi-2-naphthol.[16] **(i) Preparation of (−)-Menthyl Phosphorodichloridite.** A solution of phosphorus trichloride (5.77 g, 42 mmol) in dry THF (~100 mL) was added dropwise under N_2 to a stirred solution of (1*R*,2*S*,5*R*)-(−)-menthol (6.56 g, 42 mmol) in dry THF (~400 mL). The mixture was stirred at room temperature for 1 h. The phosphorodichloridite was used in solution without further purification; ^{31}P NMR (THF) δ 175.6 ppm.

(ii) Preparation of Diastereomerically Pure Phosphites. The phosphorodichloridite solution was cooled to −78 °C. To this mixture, triethylamine (20.5 mL, 147 mmol) was added slowly through a dropping funnel. After addition was complete, the solution was allowed to stir at room temperature for 15 min, following which, racemic 1,1′-bi-2-naphthol (12.0 g, 42 mmol) was added as a solid under a positive pressure of argon. The mixture was stirred for 12 h, and the reaction was then transferred to a glovebox. The triethylamine hydrochloride salts were removed by filtration through a pad of Celite. THF was removed from the filtrate, yielding a white foam. The diastereomeric mixture was redissolved in a minimum amount of diethyl ether (~100 mL), and the solution was cooled to −30 °C for approximately 3 h. After 3 h at −30 °C, a white precipitate formed and was isolated by filtration. ^{31}P NMR (THF δ 151 ppm) verified that it was a single diastereomer; yield 6.89 g, 14.6 mmol, 70%. The other diastereomer has a ^{31}P NMR resonance in THF at 157 ppm.

(iii) Oxidation of Phosphite to Phosphate. The optically pure phosphite (12.15 g, 25.8 mmol) was dissolved in CH_2Cl_2 (200 mL) in air. The solution was stirred while an aqueous solution of H_2O_2 (30%) was added. The resulting biphasic solution was allowed to stir for 3 h. The layers were separated, and the aqueous layer was extracted with diethyl ether. The combined organic fractions were dried over Na_2SO_4, and the solution was filtered. The solvent was removed in vacuo to yield 12.3 g (25.2 mmol, 98%) of the phosphate: ^{31}P NMR (THF) δ 3.3 ppm.

(iv) Reduction to (*S*)-(−)-1,1′-Bi-2-naphthol. Excess $LiAlH_4$ (5.1 g, 134 mmol) was added as a solid slowly to a stirred THF (500 mL, −30 °C) solution of the phosphate. The reaction mixture was stirred at room temperature for 20 h. The reaction mixture was quenched by the very slow addition of water (**Caution**). A dilute solution of NaOH (2 N) was added to make the mixture slightly basic. The aqueous layers were extracted with CH_2Cl_2, and the combined organic layers were washed with brine. The organic extracts were dried with Na_2SO_4 and filtered. The solvent was removed in vacuo, and the product was isolated by washing the residue with benzene and removing the binaphthol from the soluble byproducts by filtration; yield 4.91 g, 17.2 mmol, 64%; $[\alpha]^{25}_D$ −33° (*c* 2.5, THF).

(*S*)-(−)-3,3′-Bis(dimethylphenylsilyl)-1,1′-binaphth-2,2′-diol. (*S*)-(−)-Bi-2-naphthol (4.9 g, 17 mmol) was dissolved in THF (150−200 mL), and KH (2.0 g, 51 mmol) was added. After stirring the mixture for 1.5 h, chloromethyl methyl ether (4.1 g, 51 mmol) was added and the reaction was allowed to stir for 21 h. The flask was then taken from the box and the solvent removed in vacuo. Water and CH_2Cl_2 were added and the organic compounds extracted with CH_2Cl_2 (3 × 100 mL). The combined CH_2Cl_2 fractions were dried over Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. The product was isolated by recrystallization from diethyl ether; yield 5.8 g, 15.5 mmol, 91%: ^{1}H NMR ($CDCl_3$) δ 7.95 (d, 2, Ar*H*), 7.87 (d, 2, Ar*H*), 7.57 (d, 2, Ar*H*), 7.34 (td, 2, Ar*H*), 7.20 (m, 4, Ar*H*), 5.51 (dd, 4, CH_2), 3.11 (s, 6, OCH_3).

The methoxymethyl ether protected binaphthol (5.8 g, 15.5 mmol) was partially dissolved in diethyl ether (150 mL), and the solution was cooled to −35 °C. A 2.5 M n-BuLi solution (in hexane) was concentrated in vacuo to remove most of the hexane solvent. The concentrated n-BuLi (62 mmol) was dissolved in diethyl ether (∼20 mL) at −35 °C, and the solution was slowly added to the precooled solution of the protected binaphthol. After the addition was complete, the clear solution turned cloudy and changed to light brown. This mixture was allowed to stir for 4 h. Bromination was effected by the slow addition of dibromotetrafluoroethane (16.2 g, 62 mmol, 7.4 mL). During addition, gas evolved vigorously. Near the end of the addition, the cloudy solution turned clear and reddish. This mixture was allowed to stir in the drybox for 15−20 min. The reaction mixture was worked up in air by quenching with water and extracting the organics with CH_2Cl_2. The dichloromethane extracts were dried over Na_2SO_4, and dichloromethane was removed in vacuo. The dibromide was recrystallized from diethyl ether; yield 5.32 g, 10.0 mmol, 65%: ^{1}H NMR ($CDCl_3$) δ 8.28 (s, 2, Ar*H*), 7.80 (d, 2, Ar*H*), 7.44 (td, 2, Ar*H*), 7.25 (m, 4, Ar*H*), 4.80 (s, 4, CH_2), 2.52 (s, 6, OCH_3).

The ether protected brominated binaphthol (5.32 g, 10.0 mmol) was dissolved in diethyl ether (200 mL), and a methanol/HCl solution (150 mL of MeOH, 50 mL of conc HCl) was added. The biphasic mixture was stirred vigorously at room temperature overnight. The phases were separated, and the combined diethyl ether layers were neutralized with a saturated $NaHCO_3$ solution. The aqueous layer was further extracted with CH_2Cl_2, and the organic fractions were combined and dried over Na_2SO_4 and filtered. The solvent was removed in vacuo, and the white solid was washed with CH_2Cl_2 (100 mL); yield 4.0 g, 9.7 mmol, 97%: ^{1}H NMR ($CDCl_3$) δ 8.20 (s, 2, Ar*H*), 7.75 (d, 2, Ar*H*), 7.25 (m, 4, Ar*H*), 7.02 (d, 2, Ar*H*), 5.5 (s, 2, O*H*).

3,3′-Dibromo-1,1′-binaphth-2,2′-diol (2.0 g, 4.5 mmol) was dissolved in THF (40 mL). KH (450 mg, 11.3 mmol) was added slowly in order to allow hydrogen to evolve. The mixture was stirred at room temperature for 30 min and $ClSiMe_2Ph$ (1.41 g, 8.30 mmol) added dropwise. This reaction mixture was allowed to stir at room temperature for 2.5 h. It was filtered through Celite, and all solvent was removed from the filtrate under reduced pressure to yield a yellowish colored foam. The product was redissolved in THF (80 mL), and the solution was cooled to −30 °C. A precooled solution of t-BuLi (1.7 M, 18 mmol, 10.6 mL) was added slowly by syringe. Upon completion of the addition, the solution turned dark green. The reaction mixture was stirred for 2 h and then removed from the box and quenched with a saturated solution of NH_4Cl. Chromatography of the crude product on a 2 cm × 20 cm silica column with hexane as the eluent produced a white, foamy solid; yield 1.18 g (2.13 mmol, 47%) of (*S*)-(−)-3,3′-bis-(dimethylphenylsilyl)-1,1′-binaphth-2,2′-diol: ^{1}H NMR ($CDCl_3$) δ 7.95 (s, 2, Ar*H*), 7.80 (d, 2, Ar*H*), 7.63 (m, 4, Ar*H*), 7.50 (m, 2, Ar*H*), 7.30 (m, 8, Ar*H*), 7.08 (d, 2, Ar*H*), 5.21 (s, 2, O*H*), 0.68 (s, 12, CH_3). $[\alpha]^{25}_D$ −148° (*c* 2.0, THF).

(+)-Mo(CHCMe$_2$Ph)(NAr′)[(−)-1a](THF) [(+)-2a′]. Mo(CHCMe$_2$Ph)(NAr′)(OTf)$_2$(DME) (117 mg, 0.159 mmol) was dissolved in THF (8 mL), and the solution was cooled to −30 °C. (−)-**1a**K$_2$(THF) (137 mg, 0.195 mmol) was added quickly to the cold solution, and the reaction was returned to the freezer. The reaction mixture was allowed to react at −30 °C for 13 h. The clear orange solution was stirred at room temperature for an additional hour, and the THF was removed in vacuo. The residue was extracted with pentane, and the filtrate was passed through Celite. The solvent was removed from the filtrate to give crude **2a′**, which was recrystallized from diethyl ether at −35 °C; yield 143 mg, 0.147 mmol, 92%. The specific rotation in degrees was measured as a function of concentration (mg/mL) to give a straight line characterized by the equation $y = 66.5 + -0.839x$, with $R = 0.999$; $[\alpha]^{25}_D$ +47° (*c* 1.7, THF).

1bK$_2$(THF). (±)-3,3′-Diphenyl-2,2′-dihydroxy-1,1′-dinaphthyl[17] (380 mg, 0.867 mmol) was dissolved in THF (10 mL), and KH (76 mg, 1.9 mmol) was slowly added to this mixture. The reaction mixture was stirred for 5 h, during which time the dipotassium salt precipitated from the solution. The THF was removed in vacuo, and the solid was washed with pentane until a constant dried weight was achieved. The total weight was 516 mg (508 mg of the dipotassium salt and 8 mg of the excess KH). Further purification of the salt was not necessary as the small contamination of the KH does not interfere with the following reactions.

Mo(CHCMe$_2$Ph)(NAr′)(1b)(THF) (2b′). Mo(CHCMe$_2$Ph)(NAr′)(OTf)$_2$(DME) (209 mg, 0.284 mmol) was dissolved in THF (10 mL) at room temperature, and solid **1b**K$_2$(THF) (200 mg, 0.341 mmol) was added all at once. The reaction mixture was stirred for 15 min, after which the THF was removed in vacuo and the residue was extracted with toluene. The filtrate was passed through Celite and the solvent removed from the filtrate to yield the desired product. The crude product was recrystallized from a mixture of toluene and diethyl ether; yield 240 mg, 0.271 mmol: ^{1}H NMR (toluene-d_8, −20 °C) δ 13.48 (s, C*H*CMe$_2$Ph, *anti*/THF adduct), 13.14 (s, C*H*CMe$_2$Ph, *syn*/THF adduct), 10.89 (s, C*H*CMe$_2$Ph, *syn*/THF free), 7.88 (s, Ar*H*), 7.81 (s, Ar*H*), 7.74 (t, Ar*H*), 7.58 (d, Ar*H*), 7.38 (d, Ar*H*), 7.2−6.8 (m, Ar*H*), 6.81 (m, Ar*H*), 6.66 (m, Ar*H*), 6.61 (m, Ar*H*), 3.11 (m, THF), 2.68 (m, THF), 1.91 (s, Ar*Me*), 1.55 (s, CHC*Me*$_2$-Ph), 1.48 (s, CHC*Me*$_2$Ph), 1.38 (s, Ar*Me*), 0.66 (m, THF); (toluene-d_8, +40 °C) δ 13.52 (s, C*H*CMe$_2$Ph, *anti*/THF adduct), 11.3 (very broad, C*H*CMe$_2$Ph, *syn*/THF free), 8.09 (s, Ar*H*), 7.90 (s, Ar*H*), 7.87 (d, Ar*H*), 7.81 (s, Ar*H*), 7.74 (m, Ar*H*), 7.67 (d, Ar*H*), 7.58 (d, Ar*H*), 7.48 (d, Ar*H*), 7.40 (d, Ar*H*), 7.35 (d, Ar*H*), 7.3−6.8 (m, Ar*H*), 6.7 (m, Ar*H*); ^{13}C NMR (toluene-d_8, room temperature) δ 314 (d, *C*HC(Me)$_2$Ph, J_{CH} = 144, *anti*).

Mo(CHCMe$_2$Ph)(NAr)(1b)(THF) (2b). Mo(CHCMe$_2$Ph)(NAr)(OTf)$_2$(DME) (245 mg, 0.310 mmol) was dissolved in THF (50 mL) at room temperature, and (−)-**1b**K$_2$(THF) (200 mg, 0.341 mmol) was added all at once. The reaction mixture was allowed to stir at room temperature for 45 min. All THF was removed in vacuo, and the residue was extracted with toluene. The mixture was filtered through Celite, and all toluene was removed from the filtrate in vacuo. The product was recrystallized by cooling a diethyl ether solution to −35 °C; yield 153 mg, 0.168 mmol: ^{1}H NMR (toluene-d_8) δ 13.65 (br s, C*H*CMe$_2$Ph, *anti*), 10.85 (br s, C*H*CMe$_2$Ph, *syn*); ^{13}C{^{1}H} NMR

(toluene-d_8, −20 °C) δ 315 (d, $CHCMe_2Ph$, J_{CH} = 149 Hz, *anti*), 280 (d, $CHCMe_2Ph$, J_{CH} = 120 Hz, *syn*).

3,3′-Bis(2-methylphenyl)-2,2′-dimethoxy-1,1′-dinaphthyl. A solution of 2-MeC_6H_4Br (18.0 mL, 1 M in THF) was added dropwise over the course of 20 min to a stirred solution of 3,3′-dibromo-2,2′-dimethoxy-1,1′-dinaphthyl (3.00 g, 6.36 mmol) and $NiCl_2(PPh_3)_2$ (0.244g, 0.373 mmol) in ether (50 mL). The mixture was heated to reflux for 24 h and allowed to cool to room temperature. Aqueous HCl (300 mL, 1 N) was then added, and the mixture was extracted with $CHCl_3$ (4 × 250 mL). The combined chloroform extracts were dried over $MgSO_4$ and filtered, and the chloroform was removed from the filtrate in vacuo. By ^{1}H NMR ($CDCl_3$) the resulting yellow foam was 90% pure. It was used in the next step without further purification.

3,3′-Bis(2-methylphenyl)-2,2′-dihydroxy-1,1′-dinaphthyl (1cH_2) and Its Dipotassium Salt. BBr_3 (35.0 mL, 1 M in CH_2Cl_2) was added dropwise via syringe to a stirred solution of crude 3,3′-bis(2-methylphenyl)-2,2′-dimethoxy-1,1′-dinaphthyl (5.73 mmol) in CH_2Cl_2 (250 mL) at 0 °C. The ice bath was removed when the addition was complete, and the reaction was stirred for 1 h. Proton NMR showed the reaction to be complete (no methoxy CH_3 protons at 3.15 ppm). The reaction mixture was quenched with water (100 mL) at 0 °C and extracted with CH_2Cl_2 (3 × 100 mL). The combined extracts were dried over $MgSO_4$, and the solvents were removed from the filtrate in vacuo, leaving a yellow-brown oil. The crude product was recrystallized from a mixture of CH_2Cl_2 and pentane to give 1.46 g of off-white product (in two crops); yield 54.5%: ^{1}H NMR ($CDCl_3$) δ 7.86 (d, 2, Ar*H*), 7.82 (s, 2, Ar*H*), 7.38−7.22 (m, 14, Ar*H*), 5.07 (br, 2, O*H*), 2.23 (br, 6, Ar*Me*).

1cK_2(THF) was prepared by adding KH (42 mg, 1.1 mmol) to a stirred solution of **1c**H_2 (0.182 g, 0.390 mmol) in THF (15 mL). After 5 h the mixture had become bright yellow. Some yellow precipitate had formed, but most of the product stayed in solution. This THF mixture was used directly in the next step.

Mo(CHCMe$_2$Ph)(NAr′)(1c)(THF) (2c′). Mo($CHCMe_2Ph$)(NAr′)$(OTf)_2$(DME) (0.190 g, 0.258 mmol) was added to a stirred THF mixture of **1c**K_2 (0.390 mmol) prepared as described above. After stirring the mixture at room temperature for 15 min, the solvent was removed and the dark residue was extracted with 2 mL of toluene. The dark solution was filtered through a pad of Celite, and the filtrate was concentrated to 0.5 mL. Diethyl ether (5 mL) was added, and the mixture was cooled to −40 °C to give 0.096 g (42%) of bright yellow-orange crystals: ^{1}H NMR (C_6D_6, 0.35:1 *syn*/*anti* ratio) δ 13.62 (s, C*H*CMe_2Ph, *anti*), 12.51 (br, C*H*CMe_2Ph, *syn*), 7.75, 7.72, 7.71, 7.69, 7.66, 7.63, 7.60, 7.42, 7.41, 7.38, 7.35, 7.32, 7.22, 7.18, 7.16, 7.13, 7.125, 7.11, 7.10, 7.07, 7.04, 7.01, 7.00, 6.98, 6.96, 6.94, 6.92, 6.89, 6.83, 6.81, 6.78, 6.72, 6.66, 6.39, 2.98 (br, THF), 2.5−1.4 (m, Ar*Me* and CHC*Me*$_2$Ph, *syn* and *anti*), 0.82 (br, THF); ^{13}C{^{1}H} NMR (C_6D_6) δ 314.981 (*C*$HCMe_2$-Ph, $^1J_{CH}$ = 149, *anti*; *syn* not observed), 160.24, 158.13, 151.24, 142.97, 140.43, 138.76, 138.54, 137.09, 136.51, 135.35, 134.99, 72.18 (OCH_2CH_2), 52.14, 34.20, 33.38, 31.44, 29.54, 28.08, 25.22, 20.74, 20.13, 19.04.

Mo(CHCMe$_2$Ph)(NAr)(1c)(THF) (2c). This compound was prepared and isolated as described for **2c′** from Mo($CHCMe_2Ph$)(NAr)$(OTf)_2$(DME) (0.170 g, 0.215 mmol) and a solution of **1c**K_2 (0.214 mmol) prepared as described above; yield 0.092 g (44%) of bright yellow-orange crystals: ^{1}H NMR (C_6D_6, 0.092:1 *syn*/*anti* ratio) δ 13.74 (s, $CHCMe_2Ph$, *anti*), 11.30 (br, $CHCMe_2Ph$, *syn*), 7.78, 7.76, 7.74, 7.17, 7.69, 7.67, 7.42 (d, 1 H, ArH), 7.30 (d, 1H, ArH), 7.18, 7.165, 7.16, 7.155, 7.12, 7.09, 7.08, 7.07, 7.04, 70.3, 6.99, 6.96, 6.94, 6.91, 6.89, 6.86, 6.83, 6.81, 6.66, 2.97 (br, THF), 2.48 (m, $NArCHMe_2$), 2.43 (s, BINOMe), 2.31 (s, BINOMe), 0.93 (br, $NArCHMe_2$), 0.82 (br, THF); ^{13}C{^{1}H} NMR (C_6D_6) δ 315.80 (*C*$HCMe_2Ph$, $^1J_{CH}$ = 145, *anti*), 284.29 (*C*$HCMe_2Ph$, *syn*), 162.33, 160.55, 155.15, 151.34, 145.28, 143.47, 140.82, 139.15, 138.20, 136.06, 135.71, 135.57, 135.20, 133.83, 133.44, 131.26, 130.98, 130.81, 130.65, 130.43, 130.26, 129.90, 129.76, 129.44, 129.24, 128.80, 128.18, 127.85, 127.72, 127.47, 127.35, 127.18, 126.66, 126.52, 126.38, 126.31, 126.12, 126.05, 125.85, 125.46, 124.73, 123.45, 123.26, 122.53, 119.89, 73.73 (OCH_2CH_2), 66.24, 52.37, 29.72, 29.45, 28.21, 25.41, 24.42, 23.84, 23.77, 22.96, 20.82, 20.41, 15.91.

3,3′-Bis(2,6-dimethylphenyl)-2,2′-dimethoxy-1,1′-dinaphthyl. A solution of (2,6-dimethylphenyl)magnesium chloride (20.0 mL, 0.66 M in Et_2O) was added dropwise over the course of 60 min to a stirred solution of 3,3′-dibromo-2,2′-dimethoxy-1,1′-dinaphthyl (2.198g, 4.655 mmol) and $NiCl_2(PPh_3)_2$ (0.166 g, 0.254 mmol) in ether (50 mL). The mixture was heated to reflux for 24 h, and an additional amount of Grignard reagent (10 mL) was added. After refluxing for another 4 h, the mixture was allowed to cool to room temperature and aqueous HCl (200 mL, 1 N) was added. The mixture was extracted with $CHCl_3$ (3 × 200 mL). The combined extracts were dried over $MgSO_4$, and the solvent was removed in vacuo, leaving a yellow foam. By ^{1}H NMR ($CDCl_3$) the yellow foam was 90% pure (^{1}H NMR methoxy group resonance of starting material at δ 3.5 was absent and a major resonance was observed at δ 3.08). All of this crude product was used in the next step without further purification.

Preparation of 3,3′-Bis(2,6-dimethylphenyl)-2,2′-dihydroxy-1,1′-dinaphthyl (1dH_2) and Its Dipotassium Salt. BBr_3 (28.5 mL, 1 M in CH_2Cl_2) was added dropwise through an addition funnel to a stirred solution of crude 3,3′-bis(2-methylphenyl)-2,2′-dimethoxy-1,1′-dinaphthyl (4.190 mmol) in CH_2Cl_2 (150 mL) at 0 °C. The ice bath was removed when addition was complete, and the reaction was stirred for 1 h. The reaction was quenched with water (100 mL) at 0 °C and extracted with CH_2Cl_2 (3 × 100 mL). The combined extracts were dried over $MgSO_4$, and the solvent was removed in vacuo, leaving a yellow-brown oil. Pure product was isolated by recrystallization from a mixture of CH_2Cl_2 and pentane to give 1.06 g (46%) of a white powder in two crops: ^{1}H NMR ($CDCl_3$) δ 7.87 (d, 2, Ar*H*), 7.47 (s, 2, Ar*H*), 7.38−7.15 (12, m, Ar*H*), 4.96 (s, 2, O*H*), 2.17 (s, 6, Ar*Me*), 2.09 (s, 6, Ar*Me*); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 150.09, 137.50, 137.43, 136.17, 133.63, 130.73, 129.66, 128.52, 128.35, 127.89, 127.81, 127.15, 124.71, 124.17, 113.14, 20.88 (Ar*Me*), 20.78 (Ar*Me*).

KH (26 mg, 0.66 mmol) was added to a stirred solution of **1d**H_2 (0.125 g, 0.253 mmol) in THF (10 mL). After 1 h, gas evolution had ceased and a bright yellow precipitate had formed. This entire mixture was used in the next step.

Mo(CHCMe$_2$Ph)(NAr′)(1d)(THF) (2d′). Mo($CHCMe_2Ph$)(NAr′)$(OTf)_2$(DME) (0.190 g, 0.258 mmol) was added to a stirred THF mixture of **1d**K_2 (0.253 mmol) prepared as described above. After stirring the mixture at room temperature for 15 min, the solvent was removed in vacuo and the dark residue was extracted with 2 mL of toluene. The dark solution was filtered through a pad of Celite and the solvent removed from the filtrate in vacuo. Diethyl ether (5 mL) was added and the reaction mixture was cooled to −40 °C to give 67 mg (27%) of bright yellow-orange crystals: ^{1}H NMR (C_6D_6, 1:0.25 *syn*/*anti* ratio) δ 13.74 (s, C*H*CMe_2Ph, *anti*), 11.74 (s, C*H*CMe_2Ph, *syn*), 7.77−7.52 (m, 4H, Ar*H*, *syn* and *anti*), 7.33−7.27 (m, 2H, Ar*H*), 7.24−6.68 (m, 13, Ar*H*), 6.6 (s, 3, Ar*H*), 3.03 (br, THF), 2.59 (BINOAr*Me*, *anti*), 2.55 (BINOAr*Me*, *syn*), 2.51 (BINOAr*Me*, *anti*), 2.48 (BINOAr*Me*, *syn*), 2.32 (BINOAr*Me*, *anti*), 2.09 (BINOAr*Me*, *syn*), 1.90 (NAr*Me*, *syn* and *anti*), 1.70 (BINOAr*Me*, *syn*), 1.64 (BINOAr*Me*, *anti*), 1.59 (CHC*Me*$_2$Ph, *anti*), 1.56 (CHC*Me*$_2$Ph, *anti*), 1.35 (CHC*Me*$_2$Ph, *syn*), 1.33 (CHC*Me*$_2$Ph, *syn*), 0.921 (br, THF); ^{13}C{^{1}H} NMR (C_6D_6) δ 315.15 (*C*$HCMe_2Ph$, $^1J_{CH}$ = 141, *anti*) , 291.28, (*C*$HCMe_2Ph$, *syn*), 158.48, 156.24, 150.69, 139.22, 139.09, 139.02, 138.90, 138.77, 137.10, 136.90, 136.70, 136.31, 135.82, 135.41, 133.97, 133.60, 133.08, 132.93, 132.52, 132.00, 131.19, 130.58, 130.12, 129.88, 129.81, 129.73, 128.97, 128.86, 128.57, 128.30, 128.26, 128.19, 127.95, 127.85, 127.68, 127.60, 127.55, 127.36, 127.11, 126.93, 126.83, 126.77, 126.60, 126.51, 126.45, 126.31, 126.21, 126.05, 124.37, 124.18, 123.38, 123.21, 123.14, 72.36 (OCH_2CH_2), 54.06, 51.77, 32.99, 31.06, 29.52, 28.46, 25.53, 22.79, 22.31, 21.73, 21.53, 21.46, 21.43, 21.32, 21.28, 21.16, 20.16, 19.42.

Mo(CHCMe$_2$Ph)(NAr)(1d)(THF) (2d). Mo($CHCMe_2Ph$)(NAr)$(OTf)_2$(DME) (0.118 g, 0.149 mmol) was added to a stirred THF mixture of **1d**K_2 (0.15 mmol) prepared as described above, and the product was isolated as described for **2d′**; yield 0.092 g (64%) of large star-shaped yellow crystals: ^{1}H NMR (C_6D_6, 0.35:1 *syn*/*anti* ratio) δ 13.86 (C*H*CMe_2Ph, *anti*), 11.87 (C*H*CMe_2-

Ph, *syn*), 7.68−6.80 (m, 24 Ar*H*), 3.36 (br, 2, NArC*H*Me$_2$), 3.11 (br, THF), 2.51−0.63 (m, 30, Ar*Me*, NArCH*Me*$_2$, and CHC*Me*$_2$-Ph, *syn* and *anti*), 1.99 (br, THF); ^{13}C{^{1}H} NMR (C_6D_6) δ 315.94 (*C*HCMe$_2$Ph, *anti*), 290.55 (*C*HCMe$_3$Ph, *syn*), 163.61, 161.12, 155.25, 151.61, 150.88, 142.00, 139.63, 139.35, 138.93, 138.86, 138.81, 136.97, 136.42, 136.05, 135.99, 135.87, 133.32, 132.82, 132.54, 132.26, 131.04, 130.71, 130.51, 130.43, 129.71, 129.31, 129.06, 128.94, 128.59, 128.56, 128.26, 127.87, 127.77, 127.68, 127.30, 127.20, 127.10, 126.83, 126.78, 126.63, 126.59, 126.49, 126.27, 126.07, 124.52, 124.21, 123.53, 123.39, 123.26, 73.08, 54.61, 51.89, 34.84, 33.30, 30.68, 30.11, 29.85, 29.27, 28.73, 25.54, 24.76, 23.52, 23.12, 22.60, 22.33, 21.67, 21.46, 21.19, 21.11, 14.67.

Mo(CHCMe$_2$Ph)(NAr)(1d)(pyridine) could be prepared by recrystallization of Mo(CHCMe$_2$Ph)(NAr)(**1d**)(THF) in the presence of pyridine. Calcd for $C_{63}H_{62}N_2O_2Mo$: C, 77.60; H, 6.41; N, 2.87. Found: C, 77.93; H, 6.46; N, 2.55.

3,3′-Bis(3,5-diphenylphenyl)dimethoxy-1,1′-dinaphthyl. A Schlenk flask, equipped with a stirring bar and condenser, was charged with 3,3′-dibromo-2,2′-dimethoxy-1,1′-dinaphthyl[17] (2.2 g, 4.6 mmol) and Pd(PPh$_3$)$_4$ (265 mg, 0.23 mmol). 3,5-Dibromo-1-(trimethylsilyl)benzene[36] (2.8 g, 10.2 mmol) was dissolved in a mixture of ethanol and THF (100 mL, 1:5). The solution was concentrated to 20 mL in vacuo, deoxygenated with a stream of Ar, and added to the Schlenk reaction flask. A solution containing 2 M Na_2CO_3 (9 mL) and 20 mL of toluene were also degassed with Ar and added to the Schlenk reaction flask. The reaction mixture was heated to reflux for 1 day, cooled to room temperature, and poured into a flask containing a mixture of CH_2Cl_2 and water. The phases were separated, and the aqueous phase was washed with CH_2Cl_2. The dichloromethane extracts were washed with brine and dried over $MgSO_4$. The dichloromethane was removed in vacuo to give a black oil which was chromatographed on silica (2.5 cm × 20 cm) using a gradient mobile phase of CH_2Cl_2 and hexane (0−50%). The product was eluted in pure form with 15% CH_2Cl_2/hexane; yield 1.2 g (1.6 mmol, (36%). (After 1.2 g of product had eluted from the column, the remaining product began to elute along with the monobrominated dinaphthyl.) ^{1}H NMR ($CDCl_3$) δ 8.11 (s, Ar*H*), 8.00 (d, Ar*H*), 7.89 (d, Ar*H*), 7.83 (s, Ar*H*), 7.72 (d, Ar*H*), 7.49−7.28 (m, Ar*H*), 3.32 (s, OC*H*$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 154.8, 142.5, 141.7, 140.5, 135.5, 134.4, 131.5, 131.3, 129.5, 128.8, 128.1, 128.0, 127.8, 127.1, 126.7, 126.5, 125.8, 125.7 (ArH), 61.4 (O*C*H$_3$). Anal. Calcd for $C_{58}H_{42}O_2$: C, 90.36; H, 5.49. Found: C, 89.31; H, 5.85. MS (EI) *m*/*e* 770 (M$^+$).

3,3′-Bis(3,5-diphenylphenyl)dihydroxy-1,1′-dinaphthyl (1eH_2) and Its Dipotassium Salt. 3,3′-Bis(3,5-diphenylphenyl)dimethoxy-1,1′-dinaphthyl (1.1 g, 1.4 mmol) was dissolved in CH_2Cl_2 (100 mL), and the solution was cooled to 0 °C. A solution containing BBr_3 (9.36 mL, 1 M in CH_2Cl_2, 9.36 mmol) was slowly added dropwise by syringe. After the addition was complete, the ice bath was removed and the mixture was allowed to warm to room temperature and was stirred overnight. The reaction mixture was then recooled to 0 °C, and water (50 mL) was added slowly using a pipet. The biphasic mixture was poured into a beaker containing a solution of CH_2Cl_2/H_2O (50/50), and the aqueous layer was further extracted with CH_2Cl_2. The combined organic fractions were dried with $MgSO_4$, and the solvent was removed in vacuo. The crude product was recrystallized from a mixture of CH_2Cl_2 and hexane to yield the pure product as a white powder; yield 850 mg (1.15 mmol, 82%): ^{1}H NMR ($CDCl_3$) δ 8.17 (s, Ar*H*), 7.97 (d, Ar*H*), 7.95 (s, Ar*H*), 7.85 (m, Ar*H*), 7.73 (m, Ar*H*), 7.50−7.36 (m, Ar*H*), 5.49 (s, O*H*); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 150.4, 142.3, 141.2, 138.6, 138.0, 133.3, 131.8, 130.7, 129.7, 129.0, 128.7, 127.7, 127.6, 125.8, 124.7, 124.5 (ArH).

3,3′-Bis(3,5-diphenylphenyl)dihydroxy-1,1′-dinaphthyl (500 mg, 0.674 mmol) was dissolved in THF (10 mL), and KH (59 mg, 1.48 mmol) was slowly added. The mixture was stirred at room temperature for 19 h. All solvent was then removed in vacuo, and the resulting yellow solid was then extracted into toluene. The toluene solution was filtered through Celite and the toluene was removed in vacuo to give a yellow powder; yield 551 mg (0.620 mmol, 92%). The dipotassium salt is sufficiently pure for subsequent reactions.

Mo(CHCMe$_2$Ph)(NAr′)(1e)(THF) (2e′). To a solution of Mo(CHCMe$_2$Ph)(NAr′)(OTf)$_2$(DME) (100 mg, 0.131 mmol) in toluene (10 mL) at room temperature was added solid **1e**K_2(THF) (128 mg, 0.157 mmol) all at once. The solution changed from yellow to orange and became clear immediately as the dipotassium salt reacted with the Mo bis-triflate and went into solution. After 20−30 min, the solution became slightly cloudy as the potassium triflate precipitated. The reaction mixture was allowed to stir for an additional 50 min. The solution was filtered through Celite and the toluene removed in vacuo. The complex was isolated as an orange powder in 88% yield (134 mg, 0.115 mmol).

Mo(CHCMe$_2$Ph)(NAr)(1e)(THF) (2e). The synthesis and isolation of **2e** was analogous to that described for **2e′** from Mo(CHCMe$_2$Ph)(NAr)(OTf)$_2$(DME)[8] (100 mg, 0.126 mmol) dissolved in THF (10 mL) and **1e**K_2(THF) (114 mg, 0.139 mmol); yield 85 mg, 0.070; ^{1}H NMR (toluene-d_8) δ 13.64 (br s, C*H*CMe$_2$Ph, *anti*), 10.86 (br s, C*H*CMe$_2$Ph, *syn*).

Synthesis of 6,6′-Dimethyl-3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diol (3H_2)[24] and Its Dipotassium Salt. 3-Methyl-4,6-di-*tert*-butylphenol (5.00 g, 22.7 mmol) was dissolved in 23 mL of glacial acetic acid. Concentrated sulfuric acid (4.5 mL) was added to a solution of $K_2Cr_2O_7$ (2.27 g, 7.72 mmol) in 24 mL of water. This solution was added dropwise to the solution of the phenol over 30 min at 55 °C. The orange solution turned green and a precipitate appeared. The mixture was filtered and the solid was washed with methanol to give 3.57 g (72%) of the product, which can be further purified by recrystallization from a mixture of dioxane and methanol.

Potassium hydride (3.65g, 91.0 mmol) was added by portion to a solution of **3**H_2 (1.00 g, 22.6 mmol) in 40 mL of THF at −30 °C. The reaction was stirred at room temperature for 24 h and was filtered to give 1.25 g (94%) of pure **3**K_2(THF): ^{1}H NMR ($CDCl_3$) δ 7.35 (s, 2, aromatic), 3.72 (br t, 2, THF), 1.99 (s, 6, Me), 1.83 (br t, 2, THF), 1.40 (s, 18, 2 t-Bu), 1.38 (s, 18, 2 t-Bu).

Mo(CHCMe$_2$Ph)(NAr)(3) (4). Mo(CHCMe$_2$Ph)(NAr)(OTf)$_2$(DME) (50 mg, 0.632 mmol) was dissolved in 50 mL of THF, and **3**K_2(THF) (600 mg, 1.00 mmol) was then added rapidly. The yellow solution turned dark red. The reaction was stirred for 2.25 h, and the solvent was removed in vacuo. The residue was extracted into pentane and the mixture was filtered in order to remove the potassium triflate. The pentane was removed from the filtrate in vacuo and the product was recrystallized from ether at −30 °C; yield 460 mg (0.554 mmol, 88%): ^{1}H NMR (C_6D_6) δ 11.14 (s, 1, alkylidene), 8.04 (s, 1, biphenoxide Ar), 7.82 (s, 1, biphenoxide Ar), 7.60 (d, 2, J = 8, imido Ar), 7.37 (s, 5, neophyl Ar), 7.23 (t, 1, J = 8, imido Ar), 4.08 (sept, 2, J = 7, i-Pr), 2.38 (s, 3, biphenoxide Me), 2.19 (s, 3, biphenoxide Me), 2.03 (s, 3, neophyl Me), 1.83 (s, 9, t-Bu), 1.81 (s, 9, t-Bu), 1.59 (s, 9, t-Bu), 1.56 (s, 9, t-Bu), 1.43 (s, 3, neophyl Me), 1.40 (d, 6, J = 7, i-Pr), 1.14 (6, J = 7, i-Pr).

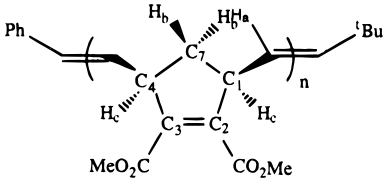
Mo(CHCMe$_2$Ph)(NAr′)(3) (4′). Mo(CHCMe$_2$Ph)(NAr′)(OTf)$_2$(DME) (507 mg, 0.688 mmol) was dissolved in 10 mL of THF, and the solution was cooled to −30 °C. **3**K_2(THF) (497 mg, 0.847 mmol) was then rapidly added. The yellow solution immediately turned dark red. The reaction was stored at −30 °C for 18 h, and the solvent was removed in vacuo. The solid was dissolved in a minimum amount of ether, and the solution was cooled to −30 °C to yield the orange-red catalyst; yield 488 mg (90%): ^{1}H NMR (toluene-d_8) δ 10.79 (s, 1, alkylidene), 7.80 (s, 1, biphenoxide), 7.55 (s, 1, biphenoxide), 7.28 (d, J = 8, 2, Ar), 7.09 (t, J = 8, 2, Ar), 6.90−7.02 (4, Ar), 6.67 (s, 2, Ar), 2.25 (s, 6, N-2,6-C$_6$H$_3$-Me$_2$), 2.11 (s, 3, biphenoxide Me), 1.92 (s, 3, biphenoxide Me), 1.56 (s, 18, 2 biphenoxide t-Bu), 1.42 (s, 12, biphenoxide t-Bu and CMe$_2$Ph), 1.30 (s, 9, biphenoxide t-Bu), 1.25 (s, 3, CMe$_2$Ph); ^{13}C{^{1}H} NMR (toluene-d_8) δ 277.9 (CHCMe$_2$Ph), 156.4, 154.3, 153.5,150.6, 142.6, 142.0, 139.2, 137.0, 136.8, 136.7, 135.3, 132.3, 131.9, 128.2, 127.0, 126.7, 125.9 (C Ar), 53.6 (CMe$_2$Ph), 36.2, 36.1, 35.9, 32.6, 31.6, 31.5, 31.4, 30.5 (CMe$_2$Ph), 30.1 (CMe$_2$Ph), 19.7, 19.4, 19.1. Calcd for $C_{48}H_{65}NO_2Mo$: C, 73.54; H, 8.36; N, 1.79. Found: C, 73.31; H, 8.22; N, 1.60.

Mo(CHCMe$_2$Ph)(N-2-t-BuC_6H_4)(3) (4″). Mo(CHCMe$_2$Ph)(N-2-C$_6$H$_4$-t-Bu)(OTf)$_2$(DME) (143 mg, 0.187 mmol) was dissolved in 10 mL of THF and chilled to −30 °C. The potassium salt (121 mg; 0.206 mmol) was then rapidly added to the above

solution. The yellow solution immediately turned dark red. The solution was stored at −30 °C for 18 h. The solvent was removed under reduced pressure, and the solid was extracted with cold pentane. Toluene was added to the pentane solution, and the solvents were evaporated in vacuo; yield 138 mg (91%): ^{1}H NMR (toluene-d_8) δ 10.97 (s, 1, alkylidene), 7.84 (s, 1, biphenoxide), 7.52 (s, 1, biphenoxide), 7.44 (d, J = 8, 2, Ar), 6.72−7.24 (8, Ar), 2.07 (s, 3, biphenoxide methyl), 2.00 (s, 3, biphenoxide methyl), 1.77 (s, 3, CHMe_2), 1.64 (s, 9, *t-Bu*), 1.50 (s, 9, *t-Bu*), 1.37 (s, 9, *t-Bu*), 1.33 (s, 9, *t-Bu*), 1.32 (s, 9, *t-Bu*), 1.16 (s, 3, CHMe_2); ^{13}C{^{1}H} NMR (toluene-d_8) δ 275.4 (*C*HCMe$_2$Ph, $^1J_{CH}$ = 120) 123.9−155.5 (*C* Ar), 54.4 (*C*Me$_2$Ph), 36.4, 36.3, 36.1, 35.6, 33.1, 32.5, 30.7 (C*Me*$_2$Ph), 30.3 (C*Me*$_2$Ph), 21.8, 19.9, 19.5, 19.2.

Typical Procedure for Polymerization of 5,6-Dimethoxymethylnorbornene (Racemic or Enantiomerically Pure). A 189 μL aliquot of a 0.030 M stock solution of **2a′** in CH_2Cl_2 (previously stored on activated molecular sieves and passed through activated alumina prior to use) was diluted to approximately 10 mL. (+)-5,6-Dimethoxymethylnorbornene (51.0 mg, 0.280 mmol, 50 equiv) was mixed with ∼1 mL of CH_2Cl_2, and the solution was added in one portion to the stirred solution of the initiator. The mixture was stirred for a period of 1−17 h. Two drops of benzaldehyde (previously passed through alumina) was added, and the solution was stirred for an additional 12 h. The polymer was precipitated by adding the reaction mixture to methanol, and the resulting fine white powder was isolated by centrifugation and dried overnight in vacuo.

Typical Procedure for the Polymerization of 2,3-Dicarbomethoxynorbornadiene. To a rapidly stirred solution of **2b′** (8.2 mg, 9.61 μmol) in THF (∼7 mL) the monomer (100 mg, 0.481 mmol, 50 equiv) was diluted in approximately 1 mL of THF and added in one portion to the stirred solution of the initiator. The mixture was stirred for 4 h before being capped with benzaldehyde (2 drops) followed by stirring for 12 h. Following precipitation from MeOH, the resulting fine white polymer (94 mg, 91%) was isolated by centrifugation and dried overnight under high vacuum. ^{1}H NMR ($CDCl_3$) δ 5.4 (m, olefinic, cis and trans), 3.9 (m, allylic, cis), 3.7 (s, CO_2Me), 3.6 (m, allylic, trans), 2.5 (m, bridgehead), 1.4 (m, bridgehead); ^{13}C{^{1}H} NMR($CDCl_3$) δ 165.7 (CO_2CH_3), 142.7 ($C_{2,3}$), 131.9 ($C_{5,6}$), 52.5 ($COCH_3$), 44.47($C_{1,4}$), 39.2 (C_7).



(+)2,3-Bis[(pantalactonyloxy)carbonyl]norbornadiene was polymerized in an analogous fashion, as was 2,3-bis(trifluoromethyl)norbornadiene.

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Supporting Information Available: A detailed description of X-ray data collection, structure solution and refinement, labeled ORTEP diagrams, tables of fractional coordinates, and isotropic and anisotropic thermal parameters for **2b′** and **4′** (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm edition of this journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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