Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 7515–7522 **7515**
DOI: 10.1021/ma101375v

Z-Selective and Syndioselective Ring-Opening Metathesis Polymerization (ROMP) Initiated by Monoaryloxidepyrrolide (MAP) Catalysts

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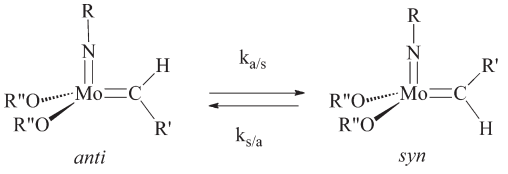
Received June 22, 2010; Revised Manuscript Received July 29, 2010

ABSTRACT: We report the *Z*-selective and syndioselective polymerization of 2,3-bis(trifluoromethyl)-bicyclo[2.2.1]hepta-2,5-diene (NBDF6) and 3-methyl-3-phenylcyclopropene (MPCP) by monoaryloxide monopyrrolide imido alkylidene (MAP) catalysts of Mo. The mechanism of polymerization with *syn*-Mo(NAd)($CHCMe_2Ph$)(Pyr)(OHIPT) (**1**; Ad = 1-adamantyl, OHIPT = O-2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3$) as the initiator is proposed to consist of addition of monomer to the *syn* initiator to yield a *syn* first insertion product and propagation via *syn* insertion products. In contrast, the mechanism of polymerization with *syn*-Mo(NAr)($CHCMe_2Ph$)(Pyr)(OTPP) (**4**; Ar = 2,6-*i*-$Pr_2C_6H_3$, OTPP = 2,3,5,6-Ph_4C_6H) as the initiator at −78 °C consists of addition of monomer to the *syn* initiator to yield an *anti* first insertion product and propagation via *anti* insertion products. Polymerizations of NBDF6 and MPCP at room temperature initiated by **4** led to polymers without a regular structure. We propose that the *syndiotacticity* of *cis* polymers is the consequence of the required inversion at the metal center with each insertion of monomer, i.e., *stereogenic metal control* of the polymer structure. We also propose that the two mechanisms for forming *cis, syndiotactic* polymers arise as a consequence of the relative steric bulk of the imido and phenoxide ligands.

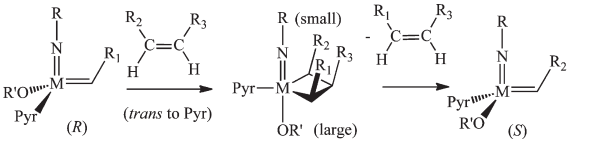
Introduction

The use of M(NR)(CHR′)(OR'')$_2$ (M = Mo or W)[1] olefin metathesis catalysts for ring-opening metathesis polymerization (ROMP)[2] has led to an increase in our understanding of how polymers that have a regular and long-range structure (in terms of *cis*/*trans* linkages and tacticities) can be formed from norbornenes or substituted norbornadienes.[3−5] *Syn* and *anti* alkylidene isomers of M(NR)(CHR′)(OR'')$_2$ catalysts (eq 1) are intimately involved in regulation of *cis* or *trans* linkages in ROMP polymers by initiators of this type,[6] while tacticities arise through either chain end control or enantiomorphic site control. For example, two of the four possible regular structures of poly-2,3-dicarbomethoxynorbornadiene (polyDCMNBD) have been prepared. *trans*,*syndiotactic*-PolyDCMNBD is formed through chain end control with Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$ (**2a**; Figure 1)[3c] as the initiator, while *cis*,*isotactic*-polyDCMNBD is formed through enantiomorphic site control with some initiators that contain a biphenolate or binaphtholate ligand.[7] Controlling polymer structures at the molecular level is key to the synthesis of polymers that have a single structure and therefore uniform and reproducible properties. *Syn* and *anti* isomers have not been found in Ru catalysts, and in general polymers prepared with Ru catalysts do not have regular structures.[2]



(1)

Recently, we discovered monoaryloxidepyrrolide (MAP) catalysts of the type M(NR)(CHR′)(OR'')(Pyr) (M = Mo or W) where Pyr is pyrrolide itself ($NC_4H_4^-$) or a substituted pyrrolide (e.g., 2,5-dimethylpyrrolide) and have been exploring their potential.[8] A key feature of a MAP catalyst is the presence of a stereogenic metal center. It has been demonstrated that MAP catalysts are especially reactive and useful for a variety of metathesis reactions, among them enantioselective reactions,[9] *Z*-selective ring-opening cross-metathesis reactions,[10] highly *Z*-selective coupling of terminal olefins,[11] and ethenolysis reactions.[12] *Z*-selectivity is possible when the olefin attacks the metal *trans* to the pyrrolide in a *syn* alkylidene isomer (one whose substituent points toward the imido group) to yield metallacyclobutane intermediates in which all substituents point toward the axial imido ligand and away from the axial OR′ group (eq 2). This version of *Z*-selectivity appears to be most efficient when the imido ligand is relatively "small" and the aryloxide ligand is relatively "large". Fundamental studies involving tungsten or molybdenum MAP species support the proposals that (i) intermediate trigonal-bipyramidal metallacyclobutanes contain axial imido and alkoxide ligands and (ii) the stereochemistry at the metal *inverts as a consequence of each forward metathesis step* (eq 2; R_1, R_2, R_3 = alkyl groups).[9c]



(2)

We suspected that new structures of polymers prepared through ROMP by MAP catalysts might be accessible as a consequence of the metal configuration at the metal inverting with each metathesis step. Our preliminary investigation[10b] revealed that polyDCMNBD$_1$ (produced employing Mo(NAd)(CHC-Me_2Ph)(OHIPT)(NC_4H_4), **1**, Figure 1; OHIPT = O-2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3$) as the initiator is *cis* and highly tactic, but it is

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Published on Web 08/31/2010

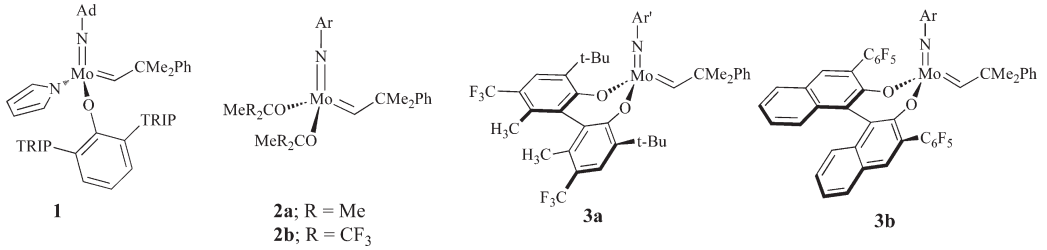
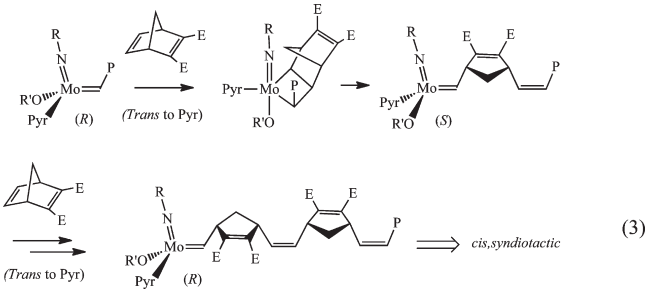


Figure 1. Ad = 1-adamantyl, Ar = 2,6-*i*-$Pr_2C_6H_3$, TRIP = 2,4,6-*i*-$Pr_3C_6H_2$, Ar′ = 2,6-$Me_2C_6H_3$.

not the known *cis,isotactic* structure. Since only two all *cis* regular structures are possible, polyDCMNBD$_1$ must be *cis,syndiotactic*. As expected, therefore, the analogous polymer produced from 2,3-dicarbomenthoxynorbornadiene (polyDCMenNBD) was proven[7] to be *cis,syndiotactic*. *Cis,syndiotactic*-PolyDCMNBD$_1$ is proposed to form as a consequence of coordination of the monomer to the CNO face of each enantiomer to give an "*all syn*" metallacyclobutane intermediate and inversion of the chirality at the metal with each step (eq 3). We call this new method of controlling polymer structure *stereogenic metal control*. As proposed byBrunner,[13] a stereogenic metal center should be a powerful determinant of which of the four approaches to the metal is most facile, since bonds are being formed *trans* to one of four significantly different ligands in the process. The fundamental feature of stereogenic metal (SM) control is distinct from chain end control or enantiomorphic site control. Chain-end and enantiomorphic site control are both primarily steric in origin and arise through steric interactions between the incoming monomer and the chiral polymer chain end in the last-inserted monomer unit or in a chiral ligand, respectively.



(3)

In this paper we expand our initial observations with studies that involve two additional monomers: 2,3-bis(trifluoromethyl)-bicyclo[2.2.1]hepta-2,5-diene (NBDF6) and 3-methyl-3-phenylcyclopropene (MPCP). Both polyNBDF6 and polyMPCP[14] have some issues that are unresolved. 2,3-Bis(trifluoromethyl)bicyclo-[2.2.1]hepta-2,5-diene (NBDF6) is an important member of the class of partially fluorinated monomers that can be polymerized through ROMP.[4] It has been found that **2a** (Figure 1) produces a high-*trans* (>98%) polymer (polyNBDF6$_{2a}$) that is 92% tactic while **2b** (Figure 1) produces a >98% *cis* polymer (polyNBDF6$_{2b}$) that is 75% tactic, both through chain end control.[4b] *Cis,* 100% tactic polymer can be formed when the initiator contains an enantiomerically pure biphenolate or binaphtholate;[7] that tacticity is the same as the major tacticity present in 75% tactic *cis*-polyNBDF6$_{2b}$. The tacticities of poly(2,3-dicarbomenthoxynorbornadiene)$_{2a}$ and poly(2,3-dicarbomenthoxynorbornadiene)$_{3a}$ could be proven[7] to be *trans,syndiotactic* and *cis,isotactic*, respectively; therefore, it is highly likely that polyNBDF6$_{2a}$ is *trans, syndiotactic* and polyNBDF6$_{3b}$ is *cis,isotactic*. However, it was suggested (on the basis of relaxed permittivity measurements) that the dominant (75%) tacticity of polyNBDF6$_{2b}$ (the same tacticity as polyDCMNBD$_{3b}$) was *cis,syndiotactic*, not *cis,isotactic*.[15] We felt that ROMP studies with the new MAP catalysts might resolve this issue. We were similarly optimistic about resolving issues concerning the structure of polyMPCP samples with a single microstructure that are formed with some initiators that contain a fluorinated biphenolate (**3a**) or binaphtholate (**3b**) ligand (Figure 1).[16]

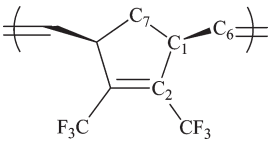
Results

ROMP of 2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (NBDF6). Addition of 100 equiv of NBDF6 to **1** in toluene led to formation of a white solid within minutes. In contrast to *cis,isotactic*-polyNBDF6,[7] polyNBDF6$_1$ was found to be essentially insoluble in common organic solvents, including halogenated solvents such as 1,2-dichlorobenzene and α,α,α-trifluorotoluene at their boiling points. Therefore, solution NMR techniques could not be employed in order to determine the degree of stereoregularity. However, a comparison of the IR spectrum of polyNBDF6$_1$ with the IR spectrum of what are proposed to be *trans,syndiotactic*-polyNBDF6$_{2a}$ and *cis,isotactic*-polyNBDF6$_{3b}$[3,7] (shown in Figure 1S of the Supporting Information) suggests that polyNBDF6$_1$ has predominantly a *cis* structure since it lacks a strong absorption around 970 cm^{-1} characteristic of *trans* olefins. An absorption between 950 and 1000 cm^{-1} corresponds to a C−H out-of-plane "wag"[17] in *trans* olefins and has been used for decades to assign *cis* or *trans* structures of ROMP polymers.[18]

The insolubility of polyNBDF6$_1$ could be ascribed to it having an ultrahigh molecular weight. However, a proton NMR spectrum of **1** in toluene-d_8 after addition of 5 equiv NBDF6 revealed that >98% **1** (with an alkylidene resonance at 11.9 ppm) was consumed, and several resonances for the alkylidenes formed upon insertion of NBDF6 into the M=C bond in **1** were observed at 11.2 and 12.1 ppm. Complete consumption of the initiator suggests that the insolubility of polyNBDF6$_1$ cannot be the consequence of a runaway polymerization (large k_p/k_i) by a small amount of initiator to give ultrahigh molecular weight material, but is a characteristic of the microstructure of polyNBDF6$_1$ itself. When 10 equiv of NBDF6 is added to **1** in toluene-d_8, ~40% of the polymer formed is insoluble. Therefore, we propose that polyNBDF6$_1$ begins to be insoluble when ~10 equiv has been incorporated. The ^{1}H NMR spectrum of the supernatant showed one major broad alkylidene peak at 11.2 ppm. Attempts to synthesize block copolymers containing NBDF6$_1$ with either MPCP or DCMNBD in order to obtain soluble polymers so far have yielded only insoluble polymers.

Since the insolubility of polyNBDF6$_1$ precluded solution NMR studies, a 900 MHz CPMAS ^{13}C NMR spectrum of polyNBDF6$_1$ was obtained in the solid state. The spectrum of this polymer can be found in the Supporting Information (Figure 2S). The ^{13}C NMR spectrum showed the five expected peaks corresponding to polyNBDF6, each with a line width from 2 to 7 ppm. For comparison, the ^{13}C NMR spectra of what are proposed to be *trans,syndiotactic*-polyNBDF6$_{2a}$ and *cis,isotactic*-polyNBDF6$_{3b}$ also were obtained in the solid state and are shown alongside the corresponding ^{13}C NMR

Table 1. Solid State and Solution ^{13}C NMR Spectra of PolyNBDF6[a]



		C1		C2		CF_3		C6		C7	
cat.	proposed structure	solid	soln	solid	soln	solid	soln	solid	soln	solid	soln
1	*cis,syndio*	44.2	N/A	139.3	N/A	121.7	N/A	131.4	N/A	35.8	36.5*
3b	*cis,iso*	44.6	44.7	140.7	140.2	122.1	121.9	132.0	131.9	38.3	38.3
2a	*trans,syndio*	49.5	49.8	139.1	140.0	121.6	122.0	132.0	133.5	34.5	37.1

[a] *Cis* or *trans* structure was determined through IR spectroscopy; tacticity is assigned on the basis of the proven tacticities of analogous polyDCMenNBD samples; solvent = acetone-d_6 for solution studies (*estimated as described in the text.).

solution spectra of each in acetone-d_6 (Figure 3S in the Supporting Information).

In the spectra displayed in Figure 3S one point for discussion is the splitting of the resonance around 50 ppm in *trans*, *syndiotactic*-polyNBDF6$_{\mathbf{2a}}$ in the solid state spectrum, but not in the solution spectrum of the same polymer. Splitting of a resonance in a solid state spectrum is not unexpected, as different local environments in the polymer chain in the solid state are known to give rise to different NMR resonances.[19] This unpredictable splitting and the breadth of the ^{13}C NMR resonances in general would appear to limit the use of solid state NMR for definitive proof of structures of regular NBDF6 polymers. However, in spite of this limitation, useful conclusions can be drawn. The chemical shifts (referenced to tetramethylsilane) of the major resonances in the solid state and solution ^{13}C NMR spectra of the three polymers are listed in Table 1. The chemical shift of C7 in *cis,syndiotactic*-polyNBDF6 in solution can be estimated as ~36.5 ppm on the basis of the chemical shifts of C7 resonances for mm (*isotactic*) triads, mr/rm (*atactic*) triads, and rr (*syndiotactic*) triads in all *cis* polymers with mixed tacticities.[20]

The chemical shifts of carbons in the three polymers in Table 1 suggest that three unique structures are present. The first evidence for three structures consists of the C1 chemical shifts. The C1 resonance in polyNBDF6$_{\mathbf{1}}$ and polyNBDF6$_{\mathbf{3b}}$ appears around 44 ppm, while the C1 resonance in polyNBDF6$_{\mathbf{2a}}$ appears around 50 ppm. A similar difference in chemical shifts is observed in the C1 resonances in the ^{13}C NMR spectra of polyNBDF6$_{\mathbf{3b}}$ and polyNBDF6$_{\mathbf{2a}}$ in solution. The chemical shift of C1 in polyNBDF6$_{\mathbf{1}}$ is close to that of polyNBDF6$_{\mathbf{3b}}$, suggesting that these two polymers have the same configuration about the double bond and therefore are both *cis*, as confirmed by IR spectroscopy.

The second piece of evidence for three distinct structures lies in the chemical shifts of the C7 carbon atoms. A 2.5 ppm shift between the C7 resonances in the two *cis* polymers suggests that two different tacticities are present, namely *cis, isotactic* and *cis,syndiotactic*. Unfortunately, as a consequence of the breadth of the C7 resonance, it cannot be determined if polyNBDF6$_{\mathbf{1}}$ has a single tacticity or contains some material with the opposite tacticity.

Since both *cis,isotactic* and *cis,syndiotactic* polyDCMenNBD have been prepared, and by inference also both *cis,isotactic* and *cis,syndiotactic* polyDCMNBD, all data are consistent with the proposal that insoluble polyNBDF6$_{\mathbf{1}}$ has a *cis,syndiotactic* structure while the more soluble polyNBDF6$_{\mathbf{3b}}$ has a *cis, isotactic* structure. This proposal is also consistent with what appears to be a *required syndiotactic structure for cis polymers* formed with the appropriate MAP catalyst (eq 3). It seems unlikely that *cis*-polyNBDF6 polymers formed with catalysts analogous to those that yield *cis,isotactic* and *cis,syndiotactic* polyDCMenNBD in fact would have tacticities opposite to those expected.

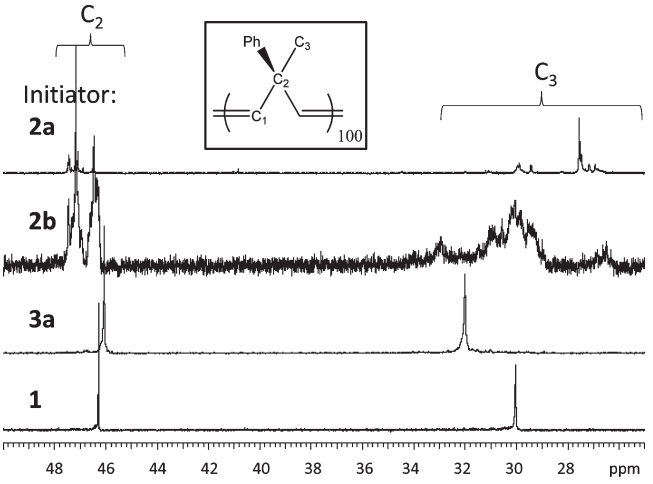


Figure 2. Partial ^{13}C NMR spectra of polyMPCP samples prepared from **1**, **2a**, **2b**, and **3a**.

ROMP of 3-Methyl-3-phenylcyclopropene (MPCP). Several years ago we reported the ROMP polymerization of 3-methyl-3-phenylcyclopropene (MPCP) by molybdenum imido alkylidene bisalkoxide initiators **2a** and **2b** (Figure 1).[14] If initiator **3a** or **3b** is employed for ROMP of MPCP, polyMPCP with a single microstructure can be formed.[16] It was proposed that *trans* linkages were formed between the repeat units on the basis of anticipated steric hindrance in the molybdacyclobutane intermediate, but *trans* linkages were not proven. We set out to investigate the structure of polyMPCP in more detail.

A proton NMR spectrum of a sample of **1** in toluene-d_8 after addition of 100 equiv of MPCP showed that both the monomer and the initiator were consumed within minutes. White polymer was isolated after addition of excess benzaldehyde and precipitation of the polymer in methanol. Proton and carbon NMR spectroscopy in CD_2Cl_2 revealed polyMPCP$_{\mathbf{1}}$ to have a highly regular structure. The aliphatic regions of the ^{13}C spectra of polyMPCP prepared using various initiators are displayed in Figure 2.

The resonances corresponding to C_2 and C_3 of polyMPCP prepared from initiators **1** and **3a** (polyMPCP$_{\mathbf{1}}$ and polyMPCP$_{\mathbf{3a}}$, respectively) are single peaks, suggesting that both are highly regular structures; however, the difference in chemical shifts for C_2 and C_3 suggests their structures are different. In contrast, polyMPCP$_{\mathbf{2a}}$ appears to be ~85% regular, and that structure is different from the structure of polyMPCP$_{\mathbf{1}}$ or polyMPCP$_{\mathbf{3a}}$. The structure of polyMPCP$_{\mathbf{2b}}$

is atactic, in agreement with previous results.[14] As shown in Table 2, the structures of the polymers obtained using molybdenum imido alkylidene initiators **1**, **2a**, and **3a** can be assigned on the basis of the presence or absence of an absorption around 980 cm^{-1} characteristic of *trans* olefins and the position of the olefinic carbon NMR resonance. PolyMPCP$_{2a}$ has an olefinic ^{13}C resonance at 136.7 ppm and exhibits a strong IR absorption at 980 cm^{-1} characteristic of *trans* olefins, while polyMPCP$_1$ and polyMPCP$_{3a}$ have olefinic ^{13}C resonances at 137.5 and 137.7 and do not exhibit a strong absorption at 980 cm^{-1}. A chemical shift difference of about 1 ppm is expected for *cis* vs *trans* olefins in ROMP polymers (such as polyDCMNBD[7b]). In a recent report, polyMPCP obtained with a ruthenium-based initiator was assigned to have the *trans* configuration on the basis of an absorption at ~980 cm^{-1} and an olefinic ^{13}C NMR resonance at 136 ppm.[21] Therefore, the structures of polyMPCP$_1$ and polyMPCP$_{3a}$ are assigned as *cis*, while polyMPCP$_{2a}$ is assigned to be *trans*. For steric reasons we propose that the C=C face in MPCP that adds to the Mo=C bond is the more accessible "methyl face".

As shown in Figure 2, *cis*-polyMPCP$_1$ and *cis*-polyMPCP$_{3a}$ have different microstructures on the basis of the methyl carbon resonance appearing at 30 ppm in the former and 32 ppm in the latter. Therefore, we propose that polyMPCP$_1$ has a *cis,syndiotactic* structure, while polyMPCP$_{3a}$ has a *cis,isotactic* structure.

If only 1 equiv of MPCP is added to **1** in benzene-d_6, the proton NMR spectrum reveals several new alkylidene resonances along with a resonance for remaining **1** (~30%). The olefinic region was complex, so we could not determine whether the first insertion product has the *cis* or *trans* configuration.

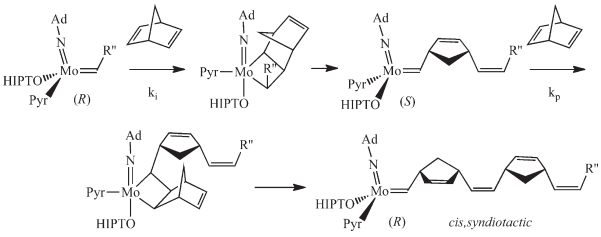
Table 2. Configuration of PolyMPCP Samples Prepared from Mo Imido Alkylidene Initiators[a]

initiator	olefinic resonance	assignment
2a	136.7 (major)	*trans*
2b	(135.0−138.1)	(irregular)
3a	137.5	*cis*
1	137.7	*cis*

[a] Carbon NMR spectra were recorded in CD_2Cl_2. *Cis* or *trans* structures are assigned on the basis of the presence or absence of ~980 cm^{-1} absorption for *trans*.

When 10 equiv of MPCP was added to **1** in benzene-d_6, the proton NMR spectrum revealed that all **1** had been consumed and only one new propagating alkylidene (H_α resonance at 11.68 ppm) was present. These results suggest that k_i and k_p are approximately the same magnitude. On the basis of the chemical shift of the propagating alkylidene alone, we propose that it has a *syn* configuration.

In summary, polymerization with **1** as the initiator takes place as shown in eq 4, where norbornadiene represents any of the four monomers (DCMNBD, DCMenNBD, NBDF6, or MPCP). *Cis,syndiotactic* structures are generated via *syn* initiation and propagation with the monomer approaching the metal *trans* to the pyrrolide and pointing toward the adamantylimido group (ene$_{syn}$) with $k_p \approx k_i$. We propose that only the methyl face of the C=C bond in MPCP adds to the metal. Syndiotacticity arises solely as a consequence of the monomers adding to alternating faces of the M=C bonds in a chiral, racemic catalyst.



(4)

Polymerizations Employing Mo(NAr)(CHCMe$_2$Ph)(OTPP)(Pyr) as the Initiator. We then turned to exploration of a catalyst variation for ROMP of MPCP in which the imido ligand is larger than adamantylimido and the phenoxide ligand smaller than OHIPT, namely Mo(NAr)(CHCMe$_2$Ph)(OTPP)(Pyr) (**4**, Ar = 2,6-diisopropylphenyl, Pyr = pyrrolide, OTPP = 2,3,5,6-tetraphenylphenoxide). Polymerization of MPCP at 20 °C with **4** led to a polymer with no regular structure. Surprisingly, however, polyMPCP can be formed at −78 °C employing **4** as the initiator, and the polyMPCP$_4$ thus formed has a regular structure that is identical with the *cis,syndiotactic*-polyMPCP$_1$ described above. As the temperature of polymerization is increased from −78 to 46 °C in separate experiments, the regularity of the polymer decreases steadily, as shown in Figure 3.

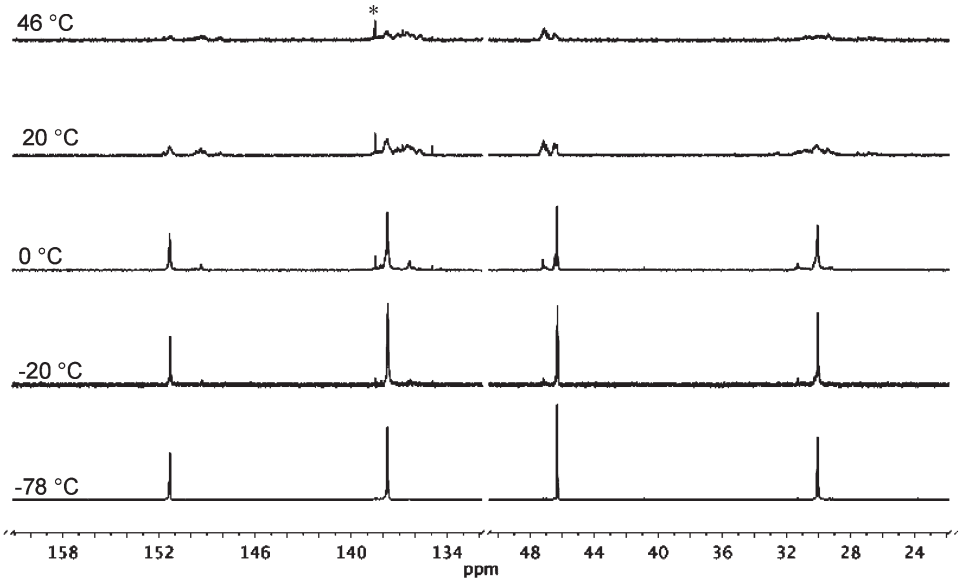


Figure 3. Partial $^{13}C\{^1H\}$ NMR spectra (CD_2Cl_2, 125 MHz) of polyMPCP synthesized at various temperatures (t = 6 h for runs at −78, 0, and 20 °C; t = 2 h for 46 and −20 °C; *residual toluene).

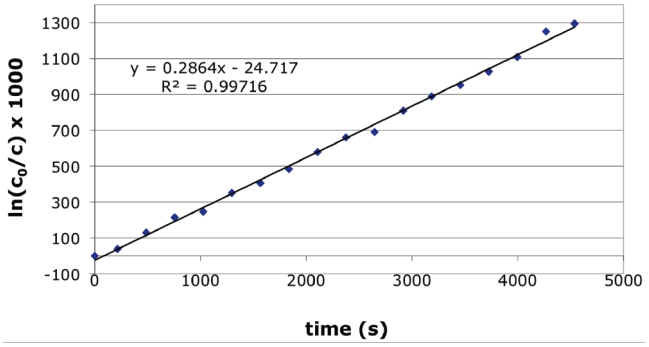


Figure 4. First-order plot for the conversion of *anti*-**4**+**1**$_{trans}$ to *syn*-**4**+**1**$_{trans}$ at −30 °C.

Addition of 1 equiv of MPCP to **4** in toluene at −78 °C, followed by warming the sample to 22 °C, leads to formation of a mixture that contains a relatively large fraction (> 80%) of the first insertion product (*syn*-**4**+**1**) whose alkylidene resonance is found at 12.1 ppm ($^1J_{CH}$ = 124 Hz). The $^3J_{HH}$ coupling constant of the olefinic protons in the ^{1}H NMR spectrum of *syn*-**4**+**1** was found to be 16 Hz, characteristic of a *trans* C=C bond; i.e., the first insertion product after warming a sample to 22 °C is *syn*-**4**+**1**$_{trans}$. Some *syn*-**4** remains even upon addition of more MPCP at −78 °C followed by warming the sample to 22 °C. Therefore, it appears that some *syn*-**4**+**1**$_{trans}$ reacts further to give higher insertion products before all **4** is initiated. Perhaps for this reason it has not yet been possible to isolate *syn*-**4**+**1**$_{trans}$ from the mixture as a pure compound. Observation of a *trans* C=C bond in the first insertion product when MPCP is added at −78 °C suggests that a *trans* double bond is formed upon polymer *initiation* at −78 °C, even though *cis* double bonds are formed upon *propagation* at −78 °C.

If 0.8 equiv of MPCP is added to **4** at −78 °C and the sample is *kept* at −78 °C, then *anti*-**4**+**1**$_{trans}$ is observed. The ^{1}H NMR spectrum of *anti*-**4**+**1**$_{trans}$ displays an alkylidene singlet at 14.1 ppm and two olefin proton doublets at 6.19 and 5.79 ppm with $^3J_{HH}$ = 16 Hz, indicative of a *trans* double bond. In order to confirm the *anti* assignment, partially ^{13}C-labeled MPCP (see Experimental Section) was added to *syn*-**4** at −70 °C; the $^1J_{CH}$ value for the proposed *anti*-**4**+**1**$_{trans}$ was found to be 144 Hz, which confirms the *anti* proposal. Upon raising the temperature to −30 °C, *anti*-**4**+**1**$_{trans}$ decays with first-order kinetics to *syn*-**4**+**1**$_{trans}$ (k = 2.86(0.04) × 10^{-4} s^{-1} at −30 °C; see Figure 4). In the experiment that employed partially ^{13}C-labeled MPCP the $^1J_{CH}$ value for *syn*-**4**+**1**$_{trans}$ was confirmed to be 124 Hz. When 3 equiv of MPCP was added to **4** at −70 °C, several new resonances are observed in the *anti* region (13.6−14.3 ppm), but none in the *syn* region (11.4−12.2 ppm), which suggests that further *anti* insertion products are formed at −70 °C, but *syn* species are *not* formed, either directly or from *anti* species through M=C bond rotation. Upon raising the temperature of the sample to 20 °C, the alkylidene resonances of the *anti* insertion product decay rapidly through M=C bond rotation to yield alkylidene resonances in the *syn* region (11.4−12.2 ppm).

We became curious as to whether an *anti* isomer also could be observed for **4**. Since it has been shown that irradiation of *syn* imido alkylidene bisalkoxide complexes at low temperature results in formation of some *anti* isomer,[6] **4** was photolyzed at 366 nm at −78 °C for 3 h. The NMR spectrum observed at −70 °C after photolysis of **4** at −78 °C shows a new resonance (~5−20% of the total) at 13.6 ppm, which is downfield of the alkylidene resonance for *syn*-**4** (12.1 ppm, $^1J_{CH}$ = 122 Hz; Figure 5, top). The value of J_{CH} for the

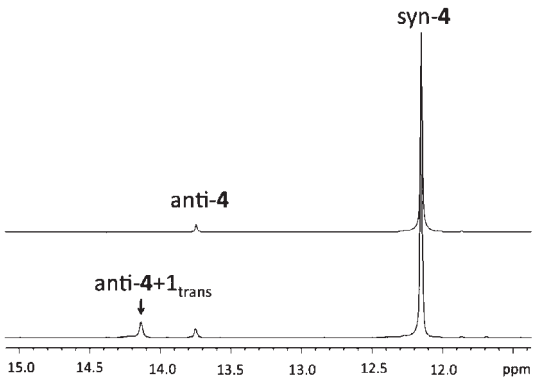


Figure 5. ^{1}H NMR spectra at −60 °C of (top) *syn*-**4** after irradiation at −78 °C in toluene-d_8 with 360 nm light and (bottom) after addition of MPCP (~0.1 equiv) to the mixture of *syn*-**4** plus *anti*-**4**.

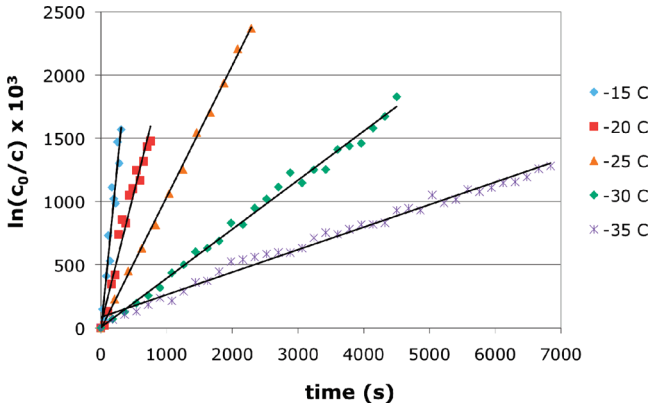


Figure 6. Decay of *anti*-**4** to *syn*-**4**; k = 5.2(0.5) × 10^{-3} s^{-1} at −15 °C, 2.1(0.1) × 10^{-3} s^{-1} at −20 °C, 1.07(0.01) × 10^{-3} s^{-1} at −25 °C, 4.1(0.1) × 10^{-4} s^{-1} at −30 °C, and 1.84(0.09) × 10^{-4} s^{-1} at −35 °C.

alkylidene resonance at 13.6 ppm was determined to be 143 Hz by measuring the ^{13}C satellites, which is characteristic of an *anti* alkylidene. The *anti*-**4** resonance decays upon warming the sample to room temperature. At several temperatures over a 20 °C range the decay was found to be first order (Figure 6), consistent with an intramolecular process. Rate constants for the conversion of *anti*-**4** to *syn*-**4** ($k_{a/s}$ as defined in eq 1) were obtained at several temperatures (Figure 6). An Eyring plot (Figure 7) revealed $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ to be 19.9 ± 0.5 kcal/mol and 8 ± 2 eu, respectively.[22]

Addition of ~0.1 equiv of MPCP to a mixture of *syn*-**4** and *anti*-**4** obtained through photolysis of *syn*-**4** (Figure 5 top) leads to formation of a mixture of *syn*-**4**, *anti*-**4**, and *anti*-**4**+**1**$_{trans}$ (Figure 5, bottom). This experiment confirms that *anti*-**4**+1$_{trans}$ is formed from *syn*-**4**, not from *anti*-**4**, and that *anti*-**4**+**1**$_{trans}$ does not react with added MPCP in the presence of a relatively large amount of *syn*-**4**. These results also suggest that at −78 °C *syn*-**4** is the most reactive species and that $k_p < k_i$.

Values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were employed to calculate $\Delta G^{\ddagger}$ at 298 K (17.5 ± 0.8 kcal/mol) and the rate constant for conversion of *anti*-**4** to *syn*-**4** at 298 K ($k_{a/s}$ = 1 s^{-1}). The value for $k_{a/s}$ should be compared with those for Mo(NAr)(CHCMe$_2$Ph)[OCMe$_2$(CF$_3$)]$_2$ ($k_{a/s}$ = 6.8 s^{-1}) and Mo(NAr)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ ($k_{a/s}$ = 0.10 s^{-1}) at 298 K obtained in previous studies.[6] At −30 °C the rate constant for conversion of *anti*-**4** to *syn*-**4** ((4.0 ± 0.1) × 10^{-4} s^{-1}) is essentially the same as $k_{a/s}$ (2.84(0.04) × 10^{-4} s^{-1} at −30 °C) for conversion of *anti*-**4**+**1**$_{trans}$ to *syn*-**4**+**1**$_{trans}$.

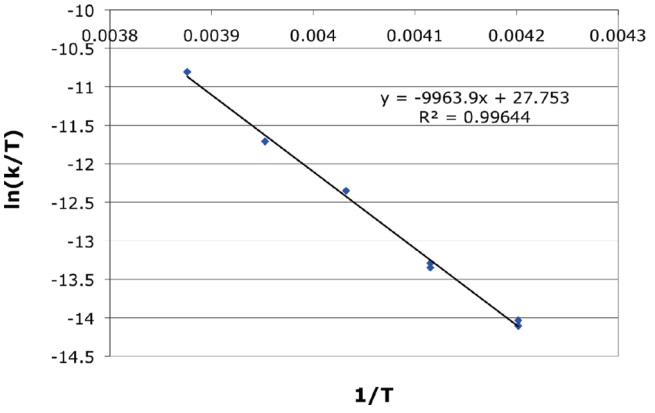
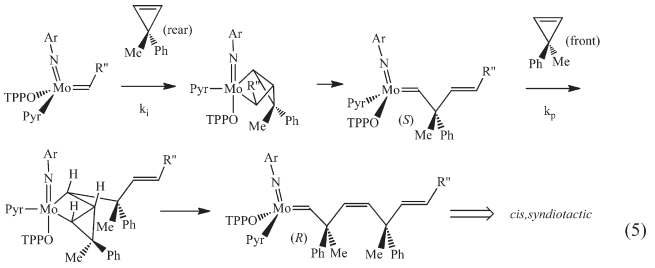


Figure 7. Eyring plot for the decay of *anti*-**4**$_{trans}$ to *syn*-**4**$_{trans}$. $\Delta H^{\ddagger} = 19.9 \pm 0.5$ kcal/mol and $\Delta S^{\ddagger} = 8 \pm 2$ eu.

On the basis of these experiments, it appears that *anti* species form in the reaction between MPCP and the *syn* initiator at low temperatures and the *anti* alkylidene insertion products do not readily convert to *syn* species at low temperature. (Since $k = 1.84(0.09) \times 10^{-4}\ s^{-1}$ at −35 °C, the calculated half-life of *anti*-**4** at −35 °C is 1 h.) Therefore, *cis*, *syndiotactic*-polyMPCP (except for the first C=C bond) is formed as shown in eq 5. *cis,syndiotactic*-PolyMPCP is obtained at low temperatures since only *anti* species are available on the time scale of the polymerization at low temperature. It is assumed that the methyl face of the C=C bond adds to the metal in the propagation step. In eq 5 the methyl face is also shown adding to the M=C bond in the initiation step. Whether that is the case or not does not affect the conclusions that the *syndiotacticity* arises as a consequence of MPCP adding to alternating faces of *anti*-M=C bonds selectively through one C=C face of MPCP.



(5)

Polymerizations of 100 equiv of NBDF6 were carried out at −78, −20, 0, and 22 °C. Polymers synthesized at −78, −20, and 0 °C were insoluble in dichloromethane or chloroform. Not all of the polymer synthesized at 22 °C dissolved in $CHCl_3$, but what did dissolve has a *cis* content of 38%, according to NMR spectra. IR spectra of the polyNBDF6 show that the 970 cm^{-1} absorption is stronger in the polymers synthesized at higher temperatures than at −78 °C, consistent with higher *trans* content at higher temperatures, although the precise cis/trans content cannot be determined accurately by IR methods. Therefore, on the basis of insolubility of polyNBDF6$_4$, we propose that polyNBDF6$_4$ formed at low temperatures is predominantly *cis,syndiotactic* and that the structure degrades when the polymerization temperature is increased.

The reaction between **4** with 1 equiv of NBDF6 at −78 °C produced several new alkylidene peaks, although two major alkylidene doublet resonances appeared (at 12.06 and 11.81 ppm), which we assign to the first and second insertion product, respectively, in addition to the alkylidene singlet for **4**. The two olefinic doublet resonances correlate with the first and second insertion products and can be assigned to *trans* C=C bonds on the basis of $^1J_{CH} = 16$ Hz. Therefore, initiation yields a *trans* C=C bond, although propagation again proceeds at low temperature to yield *cis, syndiotactic* polymer. Therefore, the polymerization of NBDF6 by **4** appears to proceed via a mechanism analogous to that for polymerization of MPCP by **4** (eq 5).

Discussion

In previous studies with a limited number of bisalkoxide (or biphenolate or binaphtholate) catalysts and a limited number of monomers (often DCMNBD or NBDF6), it has been proposed that the monomer approaches the metal pointed toward the imido group ("ene$_{syn}$"), even when the imido group is the relatively sterically demanding diisopropylphenylimido group. For each step of this type, a *cis* double bond is formed from a *syn* isomer (and the insertion product is *syn*) and a *trans* double bond is formed from an *anti* isomer (and the insertion product is *syn*).[6] Therefore, key issues are whether *syn* and *anti* isomers of the growing polymer chain can interconvert readily under the conditions of the polymerization and which isomer is more reactive toward a given monomer. Four insertion steps are possible if a C=C bond adds to *one* side of the M=C bond (*syn* or *anti*, ene$_{syn}$ or ene$_{anti}$). Since the monomer can approach either side of the M=C bond, eight propagation steps are possible if the monomer adds only through one (the same) C=C face in each step. If the faces of the C=C bond in the monomer are different (as is the case for MPCP) and either C=C face can add to the M=C bond, then a total of 16 propagation steps are possible. For MAP species these 16 potential propagating steps are diastereomeric for a given configuration at the metal center. However, if the monomer always adds *trans* to a pyrrolide in a MAP species, then only eight propagating steps are possible. If only one C=C face adds to the M=C bond, then only four propagation steps are possible. In the reactions described here where *cis* polymers are formed the only two possible pathways are *syn*+ene$_{syn}$ and *anti*+ene$_{anti}$. It makes sense that the *syn*+ene$_{syn}$ situation would most likely arise when the imido ligand is "small" and the *anti*+ene$_{anti}$ situation when the imido ligand is "large" with respect to the aryloxide. Any circumstance in which competitive propagation steps are accessible (e.g., conversion of *syn* to *anti* alkylidenes or loss of ene$_{syn}$ and ene$_{anti}$ specificity) would lead to a loss of *cis* specificity and tacticity in the resulting polymer. Nevertheless, it was surprising to us that MPCP can be polymerized by **4** at −78 °C.

A correlation between *cis* or *trans* C=C bond formation and temperature in polyNBDF6 and polyDCMNBD (and polymers prepared from related ester derivatives) has been observed for a variety of bisalkoxide initiators of molybdenum.[20] At low temperatures (−35 °C) *cis* polymers were formed, and at high temperatures (65 °C) up to 90% *trans* polymers were formed. These results were proposed to be consistent with formation of *cis* polymers from *syn* alkylidenes and *trans* polymers from *anti* alkylidenes in circumstances where *syn* and *anti* isomers can interconvert through rotation about the M=C bond. Several all *cis* polymers were found to be biased toward iso- or syndiotacticity. The bisalkoxide systems that were explored are essentially the same as those explored in an earlier paper in which it was proposed that *anti* alkylidenes are more reactive than *syn* alkylidenes *in general*.[6] Several other examples of an apparent higher reactivity of *anti* alkylidenes versus *syn* alkylidenes have been published.[4]

The alkylidene isomer observed for MAP species that have been explored in some detail so far is *syn*.[8] Observation of a significant amount of *anti*-**4**+**1**$_{trans}$ upon addition of MPCP to *syn*-**4** suggests that the rate of addition of MPCP$_{anti}$ to *syn*-**4** is greater than the rate of "ene$_{anti}$" addition of MPCP to *anti*-**4**+**1**$_{trans}$.

As expected, therefore, addition of MPCP to the mixture of *syn*-**4** and *anti*-**4**+**1**$_{trans}$ does not lead to consumption of *anti*-**4**+**1**$_{trans}$. Although the (initial) alkylidene in *syn*-**4** is different from that in *anti*-**4**+**1**$_{trans}$, this is the first evidence that suggests that a *syn* alkylidene can be more reactive than an *anti* alkylidene, but now in a MAP catalyst, not a bisalkoxide catalyst.

Measurement of the rates of conversion of *anti*-**4**+**1**$_{trans}$ to *syn*-**4**+**1**$_{trans}$ and of *anti*-**4** to *syn*-**4** are the first for any MAP species that contains a monosubstituted alkylidene. Generation of *anti*-**4** from *syn*-**4** through photolysis is also a first for a MAP species. On the basis of what we know now, we do not expect MAP species to be wildly different from bisalkoxides in terms of interconversion of *syn* and *anti* species and the role of *syn* and *anti* species in forming *cis* versus *trans* C=C bonds or (in polymer chemistry) in generating tactic polymers. But rates of interconversion of *syn* and *anti* alkylidenes in bisalkoxide species, as well as relative reactivities of *syn* and *anti* alkylidenes in bisalkoxide species, can vary by orders of magnitude, with the electronics of the alkoxide being the primary determining factor.[6] Therefore, it will prove informative to compare MAP species with bisalkoxides in a wide variety of metathesis reactions.

Interconversion of the two methylidene protons in methylidene MAP species have now been observed in several cases. In Mo(NAr)(CH_2)(OHIPT)(Pyr) and Mo(NAr)(CH_2)(OBitet)(Pyr) (OBitet is the anion derived from (*R*)-3,3′-dibromo-2′-(*tert*-butyldimethylsilyloxy)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2-ol) at 20 °C the methylidene rotates at a rate of < 0.2 s^{-1},[8e] while rates of methylidene rotation at 20 °C have been found to be 230 s^{-1} in W(NAr$^{t\text{-Bu}}$)(CH_2)(OTPP)(Me_2Pyr) (Ar$^{t\text{-Bu}}$ = 2-t-butylC_6H_4), 90 s^{-1} in W(NAr)(CH_2)(OTPP)(Me_2Pyr),[8d] 5.1 s^{-1} in (*S*)-W(NAr)(CH_2)(OBitet)(Me_2Pyr),[8d] and 3.6 s^{-1} in (*R*)-W(NAr)(CH_2)(OBitet)(Me_2Pyr).[8d] At 298 K the rate constant for conversion of *anti*-**4** to *syn*-**4** determined here ($k_{a/s}$) is 3 s^{-1}, compared with those for Mo(NAr)(CHCMe_2Ph)[OCMe_2-(CF_3)]$_2$ ($k_{a/s}$ = 6.8 s^{-1}) and Mo(NAr)(CHCMe_2Ph)[OCMe-(CF_3)$_2$]$_2$ ($k_{a/s}$ = 0.10 s^{-1}) at 298 K obtained in previous studies.[6] Typically, rate constants for conversion of *syn* to *anti* bisalkoxide species ($k_{s/a}$) have been orders of magnitude smaller than those for $k_{a/s}$ with the equilibrium between the two therefore lying toward the *syn* isomer. At this early stage we can say that rates of rotation of MAP methylidenes and interconversion of *syn* and *anti* MAP species appear to vary widely, as have the rates of interconversion of *syn* and *anti* bisalkoxide species.

Finally, it should be noted that the *Z*-selective polymerizations discussed here turn out to be relatively simple compared with situations in which *trans* C=C bonds are formed, largely since *syn* and *anti* isomers are formed from one another when a *trans* C=C bond is formed. Therefore, while it seems promising that *Z*-selectivity employing MAP species can be controlled in a variety of reactions involving acyclic or cyclic olefins, it is not yet clear how to form C=C bonds with *kinetic E*-selectively employing MAP species.

Conclusions

We have shown that *Z*-selective reactions in ROMP have some generality and that syndiotacticity (for *cis* polymers) is predictable as a consequence of the mechanism through which MAP catalysts operate, i.e., inversion of configuration at the metal center with each forward metathesis step (stereogenic metal control). Two mechanisms of forming the same *cis,syndiotactic* ROMP polymer have resulted from inverting the relative sterics of the imido and phenoxide ligands. MAP species that contain an *anti* alkylidene can be observed, either as intermediates in a ROMP reaction or upon photolysis of *syn* alkylidenes.

Experimental Section

General Details. All air-sensitive manipulations were performed under nitrogen in a drybox or using Schlenk techniques. All glassware was oven-dried and allowed to cool under vacuum or nitrogen before use. Ether, pentane, and toluene were sparged with nitrogen and passed through activated alumina. Anhydrous DMSO was dried over molecular sieves before use. All solvents were stored over molecular sieves in a nitrogen atmosphere. Deuterated solvents were degassed and passed through activated alumina before use and stored over molecular sieves. **1**,[10b] **2a**,**b**,[23] **3a**,[24] **3b**,[24] DCMNBD,[25] MPCP,[26] and NBDF6,[27] 2,3,5,6-Ph_4C_6HOH (TPPOH),[28] and Mo(NAr)(CHCMe_2Ph)-(Pyr)$_2$[8b] were prepared according to the literature. (1-^{13}C)-2-Phenylpropene[29] and (1-^{13}C)-MPCP were prepared in ways analogous to literature procedures for unlabeled species. Benzaldehyde was distilled and stored under nitrogen. All other reagents were used as received. NMR spectra were obtained on Varian 300 MHz, Varian 500 MHz, Bruker 400 MHz, or Bruker 600 MHz spectrometers, reported in δ (parts per million) relative to tetramethylsilane, and referenced directly to a tetramethylsilane internal standard or to residual ^{1}H/^{13}C signals of the deuterated solvent (^{1}H (δ) benzene 7.16, chloroform 7.27, methylene chloride 5.32, toluene 2.09; ^{13}C (δ) benzene 128.39, chloroform 77.23, methylene chloride 54.00, toluene 20.40).

ROMP of MPCP. This description is representative for ROMP of MPCP with other initiators and at other temperatures. 3-Methyl-3-phenylcyclopropene (101 mg, 0.776 mmol, 100 equiv) was dissolved in 0.5 mL of toluene, and the solution was added to a 1 mL toluene solution of **1** (0.00776 mmol) in one portion. The mixture was stirred for 1 h, and then 500 μL of benzaldehyde was added. The reaction mixture became brown within 5 min and was stirred for 1 h. The entire mixture was added dropwise to 100 mL of vigorously stirred methanol. A fine white solid formed immediately, and the mixture was stirred for 12 h. The white polymer was filtered off employing a glass frit, rinsed with methanol, and dried *in vacuo*. ^{1}H NMR (CD_2Cl_2) δ: 7.09 (s, 5H, Ar), 5.48 (s, 2H, C=C), 1.33 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ: 151.3 (C_{ipso}), 137.8 (C=C), 128.4 (Ar), 127.2 (Ar), 126.0 (Ar), 46.2 (C_{quat}), 30.0 (CH_3).

Mo(NAr)(CHCMe_2Ph)(OTPP)(Pyr) (4). Mo(NAr)(CHCMe_2Ph)(Pyr)$_2$ (0.489 g, 0.913 mmol) was dissolved in 8 mL of diethyl ether in a scintillation vial. TPPOH was added as a solid, and a yellow precipitate formed. The mixture was stirred for 1.5 h, and the yellow solid was collected on a frit and dried *in vacuo*. The solution was left in the freezer at −25 °C overnight, and a second crop was collected; total yield 0.668 g (84%). ^{1}H NMR (benzene-d_6) δ: 11.96 (s, 1H, $^1J_{CH}$ = 125 Hz, MoC*H*), 7.32−6.89 (overlapping, Ar−*H*), 6.84 (t, J_{HH} = 7.5 Hz, 2H, Ar−H_{para}), 6.44 (d, J_{HH} = 2 Hz, 2H, pyr), 6.42 (d, J_{HH} = 2 Hz, 2H, pyr), 3.25 (septet, J_{HH} = 7 Hz, 2H, C*H*Me_2), 1.48 (s, 3H, C(CH_3)$_2$(Ph)), 1.31 (s, 3H, C(CH_3)$_2$(Ph)), 1.06 (d, J_{HH} = 7 Hz, 6H, CH(CH_3)$_2$), 1.02 (d, J_{HH} = 7 Hz, 6H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (benzene-d_6) δ: 291.6, 159.4, 153.8, 148.5, 146.9, 142.7, 142.2, 138.3, 133.0, 131.9, 131.3, 130.4, 129.1, 128.9, 128.4, 127.5, 127.1, 126.9, 126.8, 126.6, 123.5, 110.6, 55.6, 31.8, 30.9, 29.1, 24.9, 23.7. Anal. Calcd for $C_{56}H_{54}MoN_2O$: C, 77.38; H, 6.27; N, 3.20. Found: C, 77.58; H, 6.28; N, 3.23.

Kinetic Studies of Conversion of *anti*-4 to *syn*-4. After photolysis at 350 nm for 3 h at −78 °C the samples were kept at −78 °C until placed in the preequilibrated 500 MHz ^{1}H NMR probe. Data were collected over at least two half-lives by observing the disappearance of the *anti*-**4** resonance with respect to an internal standard (anthracene, poly(dimethylsiloxane), or tetramethylsilane).

Observation of Mo(NAr)[CH(Me)(Ph)(CH)$_2$CMe_2Ph]-(OTPP)(Pyr) (*syn*-4+1$_{trans}$). Mo(NAr)(CHCMe_2Ph)(OTPP)-(Pyr) (0.188 g, 0.217 mmol) was dissolved in 4 mL of toluene in a 10 mL Schlenk tube, and the solution was cooled to −78 °C. A solution of MPCP (27.7 μL, 0.217 mmol) in 0.5 mL of toluene was added. The yellow solution turned dark orange. The reaction was stirred 15 min at −78 °C and 2 h at room temperature. The volatiles were removed *in vacuo*. ^{1}H NMR (benzene-d_6, 293 K) δ: 12.14 (s, 1H, MoC*H*), 7.35−6.72 (overlapping Ar−H, pyr), 6.55 (t, J_{HH} = 2 Hz, 2H, pyr), 5.65 (d, J_{HH} = 16 Hz, 1H,

olefinic C*H*), 5.43 (d, J_{HH} = 16 Hz, 1H, olefinic C*H*), 3.25 (septet, J_{HH} = 6.5 Hz, C*H*Me$_2$), 1.89 (s, 3H, MoCHC(CH_3)), 1.31 (d, J_{HH} = 12 Hz, 6H, terminal C(Ph)(CH_3)$_2$), 0.99 (d, J_{HH} = 6.5 Hz, 6H, CHC(CH_3)$_2$), 0.96 (d, J_{HH} = 6.5 Hz, 6H, CHC(CH_3)$_2$).

Observation of Mo(NAr)[^{13}CHC(Me)(Ph)^{13}CH=CHCMe$_2$Ph](OTPP)(Pyr). A solution of MPCP (66% ^{13}C-labeled at one olefinic position) in 0.3 mL of toluene was added to a −78 °C solution of **4** in 2 mL of toluene. The mixture was stirred 1.5 h at −78 °C and then 1 h at RT. The volatiles were removed *in vacuo*. ^{1}H NMR (benzene-d_6, 293 K) δ: 12.14 (1/3 d, $^1J_{CH}$ = 124 Hz, Mo=^{13}CH), 5.43 (1/3 dd, $^1J_{CH}$ = 154 Hz, $^3J_{HH}$ = 16 Hz, ^{13}CH=CH); all other resonances the same as in unlabeled species. ^{13}C NMR (benzene-d_6, 293 K) δ: 290.4 (d, $^1J_{CH}$ = 125 Hz, Mo=^{13}CH), 133.2 (d, $^1J_{CH}$ = 154 Hz, ^{13}CH=CH).

Observation of *anti*-(Mo)(NAr)[CHC(Me)(Ph)(CH)$_2$CMe$_2$Ph](OTPP)(Pyr) (*anti*-4+1$_{trans}$). An NMR sample of **4** (20.5 mg, 22.6 μmol) in toluene-d_8 in a screw-capped NMR tube with a septum top was cooled to −70 °C in the NMR probe. ^{13}C-labeled (33%) MPCP (3 μL, 23 μmol) was added by syringe, the tube inverted once to mix and returned to the probe. ^{1}H NMR (toluene-d_8, characteristic resonances, 203 K) δ: 14.15 ($^1J_{CH}$ = 144 Hz, Mo=CH), 6.29 (d, $^3J_{HH}$ = 16 Hz, CH=CH), 5.79 (d, $^3J_{HH}$ = 16 Hz, CH=CH).

Observation of Labeled *syn*-4+1$_{trans}$ at 203 K Generated from *anti*-4+1$_{trans}$. After observation of *anti*-**4**+1$_{trans}$ by ^{1}H NMR spectroscopy (see above), the sample was removed from the probe and allowed to warm to room temperature before being reinserted into the cold probe. ^{1}H NMR (toluene-d_8, characteristic peaks, 203 K) δ: 12.55 ($^1J_{CH}$ = 124 Hz, Mo=CH), 5.66 (d, $^3J_{HH}$ = 16 Hz, CH=CH), 5.38 (d, $^3J_{HH}$ = 16 Hz, CH=CH).

Observation of First and Second Insertion Products of NBDF6. Mo(NAr)(CHCMe$_2$Ph)(Pyr)(OTPP) (**1**) (20 mg, 0.023 mmol) was dissolved in 2 mL of toluene and cooled to −78 °C. NBDF6 (between 0.5 and 2 equiv) were added as a solution in 0.3 mL of toluene. The mixtures were stirred for 30 min at −78 °C and warmed to 22 °C and stirred for 2 h. The volatiles were removed *in vacuo*, and ^{1}H NMR used to assign the first and second insertion products based on the relative ratios. First insertion product: ^{1}H NMR (benzene-d_6, 294 K) δ: 12.06 (d, J_{HH} = 8 Hz, 1H, Mo=CH), 5.61 (d, J_{HH} = 16 Hz, 1H, C*H*CMe$_2$Ph), 5.24 (dd, J_{HH} = 16 Hz, J_{HH} = 9 Hz, 1H, C*H*CHCMe$_2$Ph). Second insertion product: ^{1}H NMR (benzene-d_6, 294 K) δ: 11.81 (d, J_{HH} = 8 Hz, Mo=CH), 5.66 (d, J_{HH} = 16 Hz, C*H*CMe$_2$Ph), 5.31 (dd, J_{HH} = 16 Hz, J_{HH} = 9 Hz, C*H*CHCMe$_2$Ph).

Acknowledgment. We are grateful to the U.S. Army (Institute for Soldier Nanotechnology, under Contract DAAD-19-02-D-0002 with the U.S. Army Research Office) and to the Department of Energy (DE-FG02-86ER13564) for research support. The Department of Chemistry thanks the NSF (CHE-9808061) for funds to purchase a Varian 500 NMR instrument. We are indebted to Professor R. G. Griffin for use of the high-field NMR facilities and to Marvin J. Bayro for technical advice. R.G.G. thanks the National Institutes of Health for funding (GM066360 and EB002026).

Supporting Information Available: Solid state carbon NMR spectra and IR spectra of polymer samples. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1. (b) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145.
(2) *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, 2003; Vol *3*.
(3) (a) Bazan, G. C.; Schrock, R. R.; Cho, H.-N.; Gibson, V. C. *Macromolecules* **1991**, *24*, 4495. (b) Bazan, G. C.; Oskam, J. H.; Cho, H.-N.; Park, L. Y.; Schrock, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 6899. (c) Bazan, G.; Schrock, R. R.; Khosravi, E.; Feast, W. J.; Gibson, V. C. *Polym. Commun.* **1989**, *30*, 258. (d) Bazan, G.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378.
(4) (a) Feast, W. J.; Gibson, V. C.; Ivin, K. J.; Kenwright, A. M.; Khosravi, E. *J. Mol. Catal.* **1994**, *90*, 87. (b) Feast, W. J.; Gibson, V. C.; Marshall, E. L. *J. Chem. Soc., Chem. Commun.* **1992**, 1157. (c) Davies, G. R.; Hubbard, H. V. S. A.; Ward, I. M.; Feast, W. J.; Gibson, V. C.; Khosravi, E.; Marshall, E. L. *Polymer* **1995**, *36*, 235. (d) Feast, W. J.; Gibson, V. C.; Khosravi, E.; Marshall, E. L. *J. Chem. Soc., Chem. Commun.* **1994**, 9. (e) Feast, W. J.; Gibson, V. C.; Ivin, K. J.; Kenwright, A. M.; Khosravi, E. *J. Chem. Soc., Chem. Commun.* **1994**, 1399. (f) Feast, W. J.; Khosravi, E. *J. Fluorine Chem.* **1999**, *100*, 117. (g) Broeders, J.; Feast, W. J.; Gibson, V. C.; Khosravi, E. *Chem. Commun.* **1996**, 343. (h) Feast, W. J.; Khosravi, E. *New Methods Polym. Synth.* **1995**, 69. (i) Davies, G. R.; Feast, W. J.; Gibson, V. C.; Hubbard, H. V. S. A.; Ivin, K. J.; Kenwright, A. M.; Khosravi, E.; Marshall, E. L.; Mitchell, J. P.; Ward, I. M.; Wilson, B. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 289. (j) Feast, W. J.; Gibson, V. C.; Ivin, K. J.; Khosravi, E.; Kenwright, A. M.; Marshall, E. L.; Mitchell, J. P. *Makromol. Chem.* **1992**, *193*, 2103.
(5) (a) Schrock, R. R. In *Ring-Opening Polymerization*; Brunelle, D. J., Ed.; Hanser: Munich, 1993; p 129. (b) Black, G.; Maher, D.; Risse, W. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, 2003; Vol. *3*, p 2.
(6) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11831.
(7) (a) McConville, D. H.; Wolf, J. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 4413. (b) O'Dell, R.; McConville, D. H.; Hofmeister, G. E.; Schrock, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 3414.
(8) (a) Schrock, R. R. *Chem. Rev.* **2009**, *109*, 3211. (b) Hock, A.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2006**, *128*, 16373. (c) Singh, R.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2007**, *129*, 12654. (d) Jiang, A. J.; Simpson, J. H.; Müller, P.; Schrock, R. R. *J. Am. Chem. Soc.* **2009**, *131*, 7770. (e) Schrock, R. R.; Jiang, A. J.; Marinescu, S. C.; Simpson, J. H.; Müller, P. *Organometallics* **2010**, in press.
(9) (a) Malcolmson, S. J.; Meek, S. J.; Sattely, E. S.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2008**, *456*, 933. (b) Sattely, E. S.; Meek, S. J.; Malcolmson, S. J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 943. (c) Meek, S. J.; Malcolmson, S. J.; Li, B.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 16407.
(10) (a) Ibrahem, I.; Yu, M.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 3844. (b) Flook, M. M.; Jiang, A. J.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 7962.
(11) King, A. J.; Zhao, Y.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 16630.
(12) Marinescu, S. C.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 10840.
(13) Brunner, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1194.
(14) Singh, R.; Czekelius, C.; Schrock, R. R. *Macromolecules* **2006**, *39*, 1316.
(15) Davies, G. R.; Hubbard, H. V. S. A.; Ward, I. M.; Feast, W. J.; Gibson, V. C.; Khosravi, E.; Marshall, E. L. *Polymer* **1995**, *36*, 235.
(16) Singh, R.; Schrock, R. R. *Macromolecules* **2008**, *41*, 2990.
(17) Colthup, N. B.; Daly, L. H.; Wiberly, S. E. *Introduction to Infrared and Raman Spectroscopy*; Academic Press: San Diego, CA, 1990.
(18) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, CA, 1997.
(19) Mathias, L. J. *Solid State NMR of Polymers*; Plenum Press: New York, 1988.
(20) Schrock, R. R.; Lee, J.-K.; O'Dell, R.; Oskam, J. H. *Macromolecules* **1995**, *28*, 5933.
(21) Binder, W. H.; Kurzhals, S.; Pulamagatta, B.; Decker, U.; Manohar Pawar, G.; Wang, D.; Kuhnel, C.; Buchmeiser, M. R. *Macromolecules* **2008**, *41*, 8405.
(22) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*; John Wiley & Sons: New York, 1981.
(23) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.
(24) Singh, R.; Czekelius, C.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *Organometallics* **2007**, *26*, 2528.
(25) Tabor, D. C.; White, F. H.; Collier, L. W.; Evans, S. A. *J. Org. Chem.* **1983**, *48*, 1638.
(26) Rubin, M.; Gevorgyan, V. *Synthesis* **2004**, *5*, 796.
(27) Alimuniar, A. B.; Blackmore, P. M.; Edwards, J. H.; Feast, W. J.; Wilson, B. *Polymer* **1986**, *27*, 1281.
(28) Yates, P.; Hyre, J. E. *J. Org. Chem.* **1962**, *27*, 4101.
(29) Pine, S. H.; Shen, G. S.; Hoang, H. *Synthesis* **1991**, 165–167.