Chapter 3

Stereoselective Ring-Opening Metathesis Polymerization Using Cyclometalated Ruthenium Metathesis Catalysts

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Abstract

Using the sodium pivalate method outlined in *Chapter 2*, a series of previously inaccessible ruthenium alkylidene complexes containing a cyclometalated *N*-^tBu group was synthesized. These systems were shown to produce highly *cis*, highly tactic polymers (>95% *cis,syndiotactic* in some cases) via ring-opening metathesis polymerization (ROMP), marking the first time any norbornene- or norbornadiene-based polymer with >95% a single structure had been synthesized using a Ru-based olefin metathesis catalyst. Polymerization of an enantiomerically pure 2,3-dicarboalkoxynorbornadiene confirmed a syndiotactic microstructure. In order to elucidate the exact origin of tacticity in these and related cyclometalated ruthenium alkylidene initiators, experimental and computational methods were employed to develop a complete model of stereoselectivity in ROMP. Of the cyclometalated systems surveyed, most produced highly *cis,syndiotactic* polymers (>95% in many cases). Microstructural errors, when present, were generally in the form

of *trans,syndiotactic* or *cis,isotactic* dyads. These experimental data, in conjunction with computational analyses of the propagation transition states, strongly suggest that polymer stereoselectivity in these systems is a consequence of stereogenic metal control, while errors in the polymer structure primarily result from rotation about the ruthenium alkylidene bond.

Introduction

The precise control of polymer microstructures resulting from the ring-opening metathesis polymerization (ROMP) reactions of mono- and polycyclic olefins is critical for the development of polymers with well-defined characteristics.¹ With respect to norbornene- and norbornadiene-derived ROMP polymers in particular, these microstructures include *cis* or *trans* double bonds; isotactic (*m*) or syndiotactic (*r*) dyads; and, in the case of polymers derived from unsymmetrically substituted monomers, head-tail (HT) dyads or head–head (HH) and tail–tail (TT) dyads (Figure 3.1). These primary structural elements have a significant impact on the physical and mechanical properties of ROMP polymers.² For example, *cis,syndiotactic* poly(norbornene) is a crystalline polymer with a high melting point, while atactic *trans*-poly(norbornene) is amorphous and low-melting in comparison.³ Accordingly, the development of olefin metathesis catalysts capable of producing highly stereoregular polymers (comprised of >95% a single structure) via ROMP is of great interest.



Figure 3.1. (a) Structural possibilities of norbornene-derived ROMP polymers. (b) Head-head (HH), head-tail (HT), and tail-tail (TT) dyads resulting from polymerization of unsymmetrically substituted norbornenes.

Significant microstructural control of norbornene- and norbornadiene-based polymers was first achieved using classical, metal-salt type initiators (e.g., RuCl₃, ReCl₅, and OsCl₃), in which selectivity is usually a result of chain-end control.¹ However, because this type of control results from an influence of the polymer chain on the propagation step, whether through steric crowding or the coordination of recently formed double bonds to the metal center, the stereoselectivity of these systems can vary dramatically depending on the type of monomer and/or reaction conditions employed. As a result, examples of ROMP polymers composed predominately of a single structure produced by these systems are rare.

More recently, the development of molybdenum- and tungsten-based initiators with discrete ligand environments and mechanisms of action has led to the preparation of an increasing number of ROMP polymers with singular microstructures.^{4–7} Fully *cis,isotactic* polymers can be produced from a range of norbornene- and norbornadiene-based monomers using W and Mo biphenolate and binaphtholate initiators, which operate

through enantiomorphic site control, a primarily steric directing effect derived from the chirality of the biphenolate or binaphtholate ligand.⁵ Additionally, pure *cis,syndiotactic* microstructures are accessible through the use of monoaryloxide pyrrolide (MAP) alkylidene complexes as a result of stereogenic metal control, arising from the inversion of the absolute configuration of the metal center that occurs with each forward metathesis step.⁶ Finally, a few examples of predominantly *trans,syndiotactic* and *trans,isotactic* polymers have been prepared with certain Mo initiators as a consequence of chain-end control and a "turnstile-like" nonmetathesis-based polytopal rearrangement, respectivity.^{5b,6c,7}

In contrast, only limited control of *cis/trans* content and tacticity has been realized with discrete ruthenium alkylidenes, and, much like the classical initiators, this stereochemical control is generally dependent on the use of specialized monomers or reactions conditions.⁸ A prevailing theory for the overall lack of stereoselectivity in these systems is that the low calculated barriers of rotation for Ru alkylidenes result in the inability of the Ru=C bond to enforce the steric pressures necessary for the formation of tactic ROMP polymers.^{4a,6b,9} Recently, we reported the *Z*-selective ruthenium metathesis catalyst **3.4** (highlighted in *Chapter 1* of this thesis) containing a crucial cyclometalated *N*-heterocyclic carbene (NHC) ligand (Figure 3.2) in which the Ru–C bond is formed via C–H activation induced by the addition of silver pivalate (AgOPiv).¹⁰ This catalyst was shown to give on average 80-95% *cis* content in the ROMP of norbornene and norbornadiene derivatives, thus demonstrating for the first time the *cis*-selective ROMP of a wide range of monomers with a single Ru-based metathesis catalysts.¹¹ However, these polymers were originally thought to be atactic.



Figure 3.2. Catalysts **3.1–3.4**: Mes = 2,4,6-trimethylphenyl (**3.1**, **3.4**); MIPP = 2-methyl-6-isopropylphenyl (**3.2**, **3.3**).

In the first part of this chapter, a new series of cyclometalated catalysts (3.1–3.3) derived from the sodium pivalate (NaOPiv)-mediated C–H activation of an N-'Bu group is reported. These complexes display stereoselectivity in ROMP that is unprecedented for Ru-based metathesis catalysts, as they yield polymers that not only have generally higher *cis* contents that those obtained using 3.4 (>95% in many cases) but also are highly syndiotactic. This provides a further demonstration that like their W- and Mo-based counterparts, Ru-based metathesis catalysts are capable of producing polymers with singular microstructures *without* the use of specialized monomers or reaction conditions.

Because the stereochemical information contained in any given ROMP polymer represents a chronological "road map" of every catalytic cycle that took place over the course of the polymerization, careful microstructural analysis of the dyads and triads in a ROMP polymer can shed light on the exact nature of the propagation transitions state(s). ROMP, therefore, presents a powerful tool in which to gain additional insight into the mode-of-action of cyclometalated ruthenium catalysts in *cis*-selective metathesis transformations. To this end, we additionally conducted an experimental and computational study focused on elucidating the precise mechanisms responsible for *cis*selectivity and tacticity in Ru-based catalysts such as **3.1–3.3** and **3.4** by determining how variation of the cyclometalated group, *N*-aryl substituent, and X-type ligand affects the resulting polymer microstructure. The results of these mechanistic studies, along with a proposed general model for *cis*-selectivity and tacticity in cyclometalated Ru-based initiators, are detailed in the second part of this chapter. Overall, the results contained in both sections of this chapter provide a fundamental understanding of the mode-of-action of these catalysts and, as such, are generally applicable to other transformations mediated by cyclometalated Ru-based catalysts.

Results and Discussion

Initial Discovery of cis, syndio-Selective Cyclometalated Ruthenium Complexes

As described in *Chapter 2*, the recent development of a milder method of effecting the salt metathesis and C–H activation of cyclometalated ruthenium metathesis catalysts using NaOPiv has enabled the synthesis of previously inaccessible complexes with significant alterations to the cyclometalated *N*-alkyl group of the NHC.¹² Using this new approach, we were able to prepare the less sterically encumbered *N*-^tBu catalysts **3.1–3.3** (Figure 3.2). While a nitrato ligand afforded increased activity, stability, and selectivity to **3.4** compared with other X-type ligands, catalysts **3.1–3.3** were significantly more stable in the pivalate form compared to the analogous nitrato species. It is also important to note that complexes **3.1–3.3** quickly decomposed upon exposure to terminal olefins and were therefore ineffective at mediating cross metathesis. As such, the focus of this investigation is on the effectiveness and stereoselectivity of **3.1–3.3** in ROMP. Single crystal X-ray diffraction of **3.2** confirmed the cyclometallation of the *N*-^tBu substituent as well as the bidentate coordination of the pivalate ligand and also revealed that the *N*-aryl

ring is positioned in such a way that the isopropyl substituent resides on the same face at the benzylidene (Figure 3.3). The structural parameters, including bond lengths and angles, were consistent with those for **3.4** and its pivalate derivative.¹⁰



Figure 3.3. Solid-state structure of **3.2** with thermal ellipsoids drawn at 50% probability. For clarity, H atoms have been omitted. Selected bond lengths (Å) for **3.2**: C1–Ru, 1.932; C5–Ru, 2.071; C18–Ru, 1.798; O1–Ru, 2.334; O2–Ru, 2.202; O3–Ru, 2.398.

We initiated our ROMP studies by adding **3.1** (1 mol %) to a solution of norbornene (NBE, **3.5**) in tetrahydrofuran (THF) (0.25 M) at room temperature (r.t.), upon which the resulting solution rapidly became viscous. Importantly, while catalyst solutions were prepared in the glovebox for convenience, **3.1** was determined to be relatively air-stable in the solid state, exhibiting minimal decomposition after exposure to air for 3 h. ¹H NMR spectroscopy revealed that the isolated **poly(3.5)** produced by **3.1** was almost exclusively *cis* ($\sigma_c = 0.97$; Table 3.1).¹³ While resolution of the *m/r* peaks is not observed in the NMR spectra of poly(NBE), a qualitative distinction between syndiotactic and atactic microstructures can be made in the case of highly *cis* poly(NBE)

(>90%) by looking at the relative peak heights of the signals corresponding to the $C_{1,4}$ and $C_{5,6}$ carbons: approximately equal heights and widths correspond to a highly syndiotactic polymer, while differing heights/widths suggest the presence of *m* dyads in the sample.¹⁴ A sample in which the $C_{1,4}$ line is half the height and twice the width of the $C_{5,6}$ peak is completely atactic. Examination of the $C_{1,4}$ and $C_{5,6}$ peaks in the ¹³C NMR spectrum of **poly(3.5)** prepared with **3.1** showed nearly equal heights and widths consistent with highly syndiotactic poly(NBE) (see Figure 3.14 in the Supporting Information [SI] section).

Table 3.1. Poly	vmerization	of Norbornene ((3.5)) with (Cataly	sts 3.1/	-3.3
•	•/		•	,	•/		

	cat. (1 mol %) THF (0.25 M), r.t.	>	€^_n
3.5			

catalyst	$\sigma_c{}^a$	$M_{\rm n} \left({ m kDa} ight)^b$	PDI^b
3.1	0.97	605^{c}	1.41
3.2	0.99	521 ^c	1.49
3.3	0.99	424^{c}	1.45

^{*a*}Fraction of double bonds having *cis* configuration; average of four values derived from C_{2,3}, C_{1,4}, C₇, and C_{5,6} resonances, with agreement generally within ±0.02. ^{*b*}Determined by gel-permeation chromatography (GPC) with a multiangle light scattering detector. ^{*c*}The specific refractive index increment (dn/dc) was determined to be 0.139 ± 0.005 mL/g.

In order to quantify the extent of tacticity in polymers produced by these initiators, we turned to the more complex monomer 2,3-dicarbomethoxynorbornadiene (DCMNBD, **3.6**). DCMNBD has been used extensively for this purpose, as the *cis* C_{1,4} peak displays m/r splitting that is sufficiently resolved for quantitative analysis.¹⁵ **Poly(3.6)** produced by catalyst **3.1** was found to be highly *cis* ($\sigma_c = 0.99$) and highly syndiotactic (the *cis* regions were comprised of 99% *r* dyads) (see Figure 3.7a in the second portion of this chapter) (Table 3.2).

MeO ₂ C MeO ₂ C 3.6	cat. (1 mol %) THF (0.25 M), r.t. ➤	$\begin{array}{c} \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$
catalyst	$\sigma_c{}^a$	$\% r (cis)^b$
3.1	0.99	99
3.2	>0.99	97
3.3	>0.99	98

 Table 3.2. Polymerization of Monomer 3.6 with Catalysts 3.1–3.3

^{*a*}Fraction of double bonds having *cis* configuration; average of two values derived from $C_{2,3}$ and $C_{1,4}$ resonances, with agreement generally within ±0.02. ^{*b*}Derived from *cis* $C_{1,4}$ peaks.

To probe the effect of the symmetry of the N-aryl group on cis content and tacticity, we next evaluated catalysts 3.2 and 3.3 containing a cyclometalated N^{-t} Bu group as in **3.1** but also an asymmetric *N*-aryl group (Figure 3.1). The geminal dimethyl backbone of **3.3** was installed to prevent any rotation of the *N*-aryl group that might occur in 3.2. Similar results to 3.1 were observed in the polymerization of 3.5 with catalysts 3.2 and 3.3; both produced poly(NBE) that was highly *cis* ($\sigma_c = 0.99$) and consistent with highly syndiotactic poly(NBE) by NMR (Table 3.1). Polymerization of **3.6** with catalysts **3.2** and **3.3** also yielded samples of **poly(3.6)** that were composed of almost exclusively cis, r dyads (97% and 98%, respectively) (Table 3.2).

As had previously been observed with 3.4, the experimental number-average molecular weights (M_n) for **poly(3.5)** prepared using catalysts **3.1–3.3** were significantly higher than the theoretical values (Table 3.1). This indicates that the propagation rate constant (k_p) of 3.5 exceeds the initiation rate constants (k_i) of 3.1–3.3, which would lead to the broad polydispersity indexes (PDIs) observed; this is likely a result of incomplete catalyst initiation. This might be expected on the basis of the relatively low k_i values of 3.1–3.3: The initiation rate constants of catalysts 3.1–3.3 at 25 °C were calculated to be

2.8 x 10⁻³, 4.1 x 10⁻⁴, and 1.1 x 10⁻⁴ s⁻¹, respectively. For comparison, $k_i = 8.4 \times 10^{-4} \text{ s}^{-1}$ for catalyst **3.4** and $k_i > 0.2 \text{ s}^{-1}$ for RuCl₂(C₅H₅N)₂(IMesH₂)(CHPh), the latter of which is the preferred catalyst for ROMP.¹⁶



Figure 3.4. Olefinic protons in (a) *cis,isotactic* and (b) *cis,syndiotactic* polymers made from an enantiomerically pure 2,3-disubstituted norbornadiene.

To further verify the syndiotactic nature of the norbornene- and norbornadienebased polymers produced by catalysts **3.1–3.3**, we turned to chiral monomer **3.7**. Due to the lack of mirror planes relating the monomeric unit in polymers derived from monomer **3.7**, it is expected that if samples of **poly(3.7**) produced by **3.1–3.3** were *cis,isotactic*, then the olefinic protons would be inequivalent (Figure 3.4a), and a coupling characteristic of olefinic protons would be observed in a COSY NMR spectrum.^{5b} Conversely, in *cis,syndiotactic* **poly(3.7**), the *cis* olefinic protons are related by a C_2 axis passing through the midpoint of the double bond, meaning the protons would be equivalent and therefore uncoupled (Figure 3.4b). Samples of **poly(3.7**) produced by catalysts **3.1–3.3** were only moderately *cis* ($\sigma_c = 0.76-0.83$) (Table 3.3); however, no coupling was observed by COSY NMR between the *cis* olefinic protons (clearly resolved from the *trans* resonances in the COSY spectrum) confirming that the *cis* regions of **poly(3.7)** were syndiotactic in all cases (Figure 3.5). Furthermore, the *trans* olefinic protons were also uncoupled, similarly consistent with a syndiotactic microstructure.



Table 3.3. Polymerization of Monomer 3.7 with Catalysts 3.1–3.3

^{*a*}Fraction of double bonds having *cis* configuration; derived from olefinic proton resonances in ¹H NMR spectrum.



Figure 3.5. *Cis* olefinic proton region of the COSY spectrum of **poly(3.7)** prepared with catalyst **3.1**. The absence of olefinic coupling suggests that the *cis* regions of the polymer are predominantly syndiotactic.

Finally, we briefly explored the physical properties of the tactic ROMP polymers in comparison with their atactic counterparts using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The glass-transition temperature (T_g) of atactic *trans*-poly(NBE) is 37 °C.^{3a} As expected, the T_g of *cis,syndiotactic* **poly(3.5)** produced by catalyst **3.1** was significantly higher at ca. 70 °C, consistent with a higher packing order due to the increased stereoregularity of the polymer. Both the *trans,atactic* and *cis,syndiotactic* polymers decomposed at ca. 430 °C (see the SI).

Mechanistic Studies into cis, syndio-Selective ROMP Mediated by Cyclometalated Ruthenium Complexes

In order to elucidate the origin of tacticity in catalysts **3.1–3.3** and understand the enhanced stereoselectivity in these initiators relative to **3.4**, we undertook a combined experimental and computational study in collaboration with the Houk group at the University of California, Los Angeles (UCLA). Initial work focused on examining the microstructures of polymers produced by a selection of cyclometalated catalysts with varying NHC architectures and X-type ligands in order to gain a comprehensive view of activity and selectivity in this class of complexes. The information gained from this investigation then informed the computational work, which examined the propagation transition states of a select few cyclometalated complexes to better understand the role of alkylidene isomerization in ROMP stereoselectivity. Combined, these results have allowed us to develop a complete model for *cis*-selectivity and tacticity in cyclometalated Ru-based initiators such as **3.1–3.3** and **3.4**.

General Reactivity, *cis*-Selectivity, and Blockiness of ROMP Polymers Produced by Cyclometalated Ruthenium Metathesis Catalysts: Reactions of a variety of cyclometalated catalysts (3.1, 3.4, 3.8–3.13, Figure 3.6) with norbornene (3.5) were screened to study general reactivity and *cis*-selectivity.¹³ Consistent with previous ROMP reactions, all polymerizations were performed at r.t. in THF (0.25 M) at a ratio of [monomer]/[initiator] = 100 (1 mol %). In general, quantitative conversion of monomer to polymer was observed when using catalysts **3.1**, **3.4**, and **3.8–3.11**, whereas monodentate catalysts **3.12** and **3.13** were less active that their bidentate counterparts, giving only 20-50% yield. All of the catalysts were found to yield polymers with moderate to high *cis* contents ($\sigma_c > 0.95$ in many cases) (Table 3.4).



Figure 3.6. Catalysts 3.8–3.13: MIPP = 2,6-methylisopropylphenyl (3.8); DIPP = 2,6-diisopropylphenyl (3.9); Mes = 2,4,6-trimethylphenyl (3.10–3.13).

	3.5		•	
catalyst	$\sigma_c{}^a$	r_t^b	r_c^{b}	$r_t r_c$
3.1	0.97			
3.4	0.92	0.27	6.5	1.7
3.8	0.97			
3.9	0.99			
3.10	0.74	0.52	2.4	1.2
3.11	0.74	0.94	3.9	3.7
3.12	0.88	0.45	6.5	2.9
3.13	0.82	0.53	4.8	2.5

 Table 3.4. Polymerization of Norbornene (3.5) with Catalysts 3.1, 3.4, and 3.8–3.13

cat. (1 mol %) THF (0.25 M), rt. →

^{*a*}Fraction of double bonds having *cis* configuration; average of four values derived from C_{2,3}, C_{1,4}, C₇, and C_{5,6} resonances, with agreement generally within ± 0.02 . ^{*b*}Average of two values derived from C_{1,4} and C_{5,6} peaks.

In the case of poly(NBE) and related polymers, the distribution of *cis* and *trans* double bonds in a given chain can be readily determined from ¹³C NMR, which provides information on the proportions of double-bond dyads in the polymer.^{13b,17} This distribution, known as blockiness, is represented by the relationship $r_t r_c$, where $r_t = (tt)/(tc)$ and $r_c = (cc)/(ct)$. Understanding the nature of the double bond distribution in any ROMP polymer affords significant mechanistic insight: a random distribution, characterized by $r_t r_c = 1$, suggests that the formation of a *cis* double bond is independent of any previously formed double bonds, whereas a blocky distribution $(r_t r_c > 1)$ may indicate some influence of the polymer chain in the propagation step (i.e., chain-end control).

In general, predominantly *cis* ($\sigma_c > 0.50$) polymers of norbornene and related monomers formed by early generation ROMP catalysts are somewhat-to-highly blocky, with values of $r_t r_c$ ranging from 5 to 8 or more.^{17a} Significantly, r_t is almost always

greater that 1 (i.e., tt > tc), indicating a preference for *trans* double bonds to occur in pairs. One postulate for this observed behavior is the existence of multiple kinetically distinct propagating species each having a different selectivity for the formation of *cis* or trans double bonds. This is supported by careful examination of the proportions of double bond triads in the polymers (readily derived from the known proportions of dyads), from which it can be shown that in the classical systems, the probability of *cis* or *trans* double bond formation at any given propagation step varies greatly depending on the identity of the last- and/or second-to-last formed double bond; this is presumably due to some interaction of these recently formed double bonds with the metal center or alkylidene.¹⁸ Propagating species in which the most recently formed double bond is $cis(P_c)$ are highly cis-directing, whereas the selectivity of species in which the last-formed double bond is trans depends on whether the configuration of the penultimate double bond is cis (P_{tc} , highly *trans*-directing) or *trans* (P_{tt}, essentially nonselective) (Scheme 3.1).^{1b} These relative selectivities are ultimately responsible for the high incidence of *trans-trans* double bond pairs observed in poly(NBE) samples produced by many classical metathesis catalysts.



Scheme 3.1. Probabilities of forming *cis* or *trans* double bonds in the $W(CO)_6/hv$ catalyzed ROMP of norbornene (**3.5**). P_c refers to a propagating species that has just
formed a *cis* double bond, while P_{tc} and P_{tt} describe species that have just formed a *trans*double bond but have different penultimate double bonds (*cis* and *trans*, respectively).
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Values of $r_t r_c$ calculated for the poly(NBE)s produced by catalysts **3.1**, **3.4**, and **3.8–3.13** ranged from 1.2 to 3.7 (Table 3.4), indicating only modest deviations from

randomness in the *cis/trans* double bond distributions of the polymers. Moreover, all of the highly *cis* polymers produced by catalysts **3.1**, **3.4**, and **3.8–3.13** had r_t values that were less than unity; in conjunction with the overall low values of $r_t r_c$, these low r_t values suggest that *trans* double bonds occur as single, random errors throughout the polymers rather than in pairs as observed with the classical systems. Furthermore, calculation of the probabilities of forming a *cis* or *trans* double bond according to the identity of the last- or last-but-one double bond revealed no significant dependence of *cis*-selectivity on the configurations of these previously formed double bonds in the polymerization of norbornene (Scheme 3.2). This suggests that chain-end control is most likely *not* the driving force behind the stereoselectivity in ROMP observed with initiators **3.1**, **3.4**, and **3.8–3.13**.



Scheme 3.2. Probabilities of forming *cis* or *trans* double bonds in the ROMP of norbornene (3.5) by catalyst 3.10 ($\sigma_c = 0.74$).

Tacticity and Head–Tail Bias of ROMP Polymers Produced by Catalysts 3.1, 3.4, and 3.8–3.13: To fully understand the origins of selectivity in cyclometalated catalysts 3.1, 3.4, and 3.8–3.13, a complete microstructural picture, taking into account not only *cis/trans* content but also tacticity and, in some cases, head–tail selectivity across dyads and triads, is essential. As such, we once again turned to DCMNBD (3.6) in order to quantify tacticity in the polymers produced by these systems. For polymerizations of 3.6 with catalysts 3.1, 3.4, and 3.8–3.13, the fraction of *cis, r* dyads in each highly *cis* polymer was easily determined using the *m/r* splitting displayed by the *cis* C_{1.4} peak (Table 3.5; Figure 3.7). Surprisingly, the *cis* portions of the polymers produced by catalysts **3.4** and **3.8–3.13** were found to be highly syndiotactic and not atactic as previously thought. In fact, monodentate catalysts **3.12** and **3.13** yielded polymers that were almost exclusively *cis,syndiotactic*.

Table 3.5. Pol	ymerization	of Monomer	3.6 with	Catalysts	3.1, 3.4,	and 3.8–3.13
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MeO ₂ C MeO ₂ C 3.6	cat. (1 mol %) THF (0.25 M), r.t. ➤	$ \begin{array}{c} $
catalyst	$\sigma_c{}^a$	$\% r (cis)^b$
3.1	0.99	99
3.4	0.87	85
3.8	0.84	84
3.9	0.91	85
3.10	0.72	68
3.11	0.65	68
3.12	0.98	96
3.13	0.94	96

^{*a*}Fraction of double bonds having *cis* configuration; average of two values derived from $C_{2,3}$ and $C_{1,4}$ resonances, with agreement generally within ±0.02. ^{*b*}Derived from *cis* $C_{1,4}$ peaks.



Figure 3.7. ¹³C NMR spectra of (a) *cis,syndiotactic* **poly(3.6)** produced by catalyst 3.1 and (b) 72% *cis*, 68% syndiotactic (*cis* regions) **poly(3.6)** produced by catalyst 3.10.

We next probed the effects of temperature and dilution on the polymerization of **3.6** by initiator **3.4**. If the propagation reaction is in competition with other processes occurring at the catalyst center, such as alkylidene isomerization, changes in *cis* content and/or tacticity can result from variations in temperature or monomer concentration.^{1b} Decreasing monomer concentration in particular presents a simple method in which to slow propagation relative to these other processes. However, we found that the concentration of **3.6** had very little appreciable effect on the microstructures of the polymers produced by catalyst **3.4** (Table 3.6). Increasing the temperature from 25 to 40 °C, on the other hand, resulted in an approximately 5% decrease in both the *cis* content and the tacticity of **poly(3.6)/3.4**, while decreasing the temperature to 0 °C had the opposite effect. These results suggest that alkylidene isomerization might indeed be

occurring at a rate comparable to (or faster than) that of propagation and could therefore

feasibly be a major contributor in the resulting stereoselectivity of the polymerization.

Table 3.6. Temperature and Concentration Effects on the Polymerization ofMonomer 3.6 with Catalyst 3.4

temp (°C)	conc (M)	$\sigma_c{}^a$	$\% r (cis)^b$
25	0.25	0.87	85
0	0.25	0.92	90
40	0.25	0.83	81
25	0.05	0.90	88
25	1.25	0.88	85

^{*a*}Fraction of double bonds having *cis* configuration; average of two values derived from $C_{2,3}$ and $C_{1,4}$ resonances, with agreement generally within ±0.02. ^{*b*}Derived from *cis* $C_{1,4}$ peaks.

As catalysts **3.1**, **3.4**, and **3.9** were found to cover the general range of microstructures produced by **3.1**, **3.4**, and **3.8–3.13**, further polymerizations were performed using only these three systems. Results similar to monomer **3.6** were obtained when 2,3-bis(trifluoromethyl)-norbornadiene (**3.14**) was polymerized using catalysts **3.1**, **3.4**, and **3.9** (Table 3.7);¹⁹ the resulting polymers were also *cis*-biased with highly syndiotactic *cis* regions.

Table 3.7. Polymerization of Monomer 3.14 with Catalysts 3.1, 3.4, and 3.9



catalyst	$\sigma_c{}^a$	$\% r (cis)^b$
3.1	0.79	99
3.4	0.63	99
3.9	0.55	>99

^{*a*}Fraction of double bonds having *cis* configuration; average of three values derived from $C_{2,3}$, $C_{1,4}$, and C_7 resonances, with agreement generally within ±0.02. ^{*b*}Derived from *cis* C_7 peaks.

To obtain a comprehensive understanding of the origins of *cis*-selectivity and tacticity in cyclometalated catalysts 3.1, 3.4, and 3.8–3.13, it is necessary to also determine the tacticity of the *trans* regions of polymers produced by these systems. However, the *trans* peaks in polymers derived from monomers **3.6** and **3.14** are too small and not sufficiently resolved for meaningful analysis. Thus, we next turned our attention toward polymers with more easily analyzable *trans* regions, specifically *exo,exo*-7-oxa-5norbornene-2,3-dicarboxylic acid (3.15) and 7-methylnorbornene (7-MNBE, 3.16).^{15,20} Polymers produced from 3.15 had generally lower *cis* contents ($\sigma_c = 0.73-0.94$) (Table 3.8), allowing for facile qualitative analysis of the *trans* portions via the *trans* $C_{1,4}$ peak, which displays m/r tacticity splitting (the signals were still too small to allow for accurate integration, however). Although the *cis* peaks are not sensitive to tacticity splitting, a tacticity bias can be determined on the basis of comparison with data from catalyst 3.1, shown to consistently produce predominantly syndiotactic polymers. All of the polymers produced by catalysts 3.1, 3.4, and 3.9 contained syndiotactic-biased *cis* regions. The tacticities of the *trans* regions, however, were found to differ somewhat depending on the specific catalyst/monomer combination being studied. Catalysts 3.1 and 3.9 produced polymers with *trans* regions that were largely syndiotactic, while **poly(3.15)** produced by catalyst **3.4** appeared to have negligible bias for either m or r dyads in the trans regions (Figure 3.8).

Table 3.8. Polymerization of Monomer 3.15 with Catalysts 3.1, 3.4, and 3.9

MeO ₂ C MeO ₂ C 3.15	$\begin{array}{c} \textbf{cat. (1 mol \%)} \\ \hline \textbf{THF (0.25 M), r.t.} \end{array} \xrightarrow{\textbf{R}} \overbrace{\textbf{Q}}^{\textbf{R}} \overbrace{\textbf{Me}}^{\textbf{R}} \\ R = CO_2 Me \end{array}$
catalyst	$\sigma_c{}^a$
3.1	0.94
3.4	0.73
3.9	0.93

^{*a*}Fraction of double bonds having *cis* configuration; average of three values derived from CO₂Me, C_{2,3}, and C_{1,4} resonances, with agreement generally within ± 0.03 .



Figure 3.8. ¹³C NMR spectra highlighting the *trans* $C_{1,4}$ regions of (a) 94% *cis* **poly(3.15)** produced by catalyst 3.1, (b) 73% *cis* **poly(3.15)** produced by catalyst 3.4, and (c) 93% *cis* **poly(3.15)** produced by catalyst 3.9.

Next, we exposed catalysts **3.1**, **3.4**, and **3.9** to a 1.2:1 *syn/anti* mixture of **3.16**. It is generally accepted that norbornene and related compounds react at the less-hindered *exo* face in ROMP.²¹ This was confirmed for catalysts **3.1** and **3.4** by the polymerization of **3.16**; both polymerized the *anti* monomer almost exclusively (<2% *syn*-derived

polymer was observed by ¹³C NMR). This occurs because the 7-methyl group in the *syn* monomer is positioned directly over the *exo* face of the double bond; as a result, polymerization via *exo* attack is prohibitively high in energy, whereas this is avoided in the *anti* monomer. Gratifyingly, quantitative determination of tacticity was achieved for both the *cis* and the *trans* regions by analyzing polymers of *anti-3.16*, in which all of the carbons with the exception of C₇ are sensitive to tacticity. Samples of poly(*anti-7-MNBE*) produced by catalysts **3.1** and **3.4** were highly *cis* ($\sigma_c = 0.97$ and 0.87, respectively) with highly syndiotactic *cis* regions (90-95% *r*) and highly syndiotactic *trans* regions (>99% *r*) (Table 3.9). No appreciable amount of polymer was formed with initiator **3.9**; this is likely a result of the increased steric bulk associated with the *N*-2,6-diisopropylphenyl group of this catalyst.

Table 3.9. Polymerization of a 1.2:1 syn/anti Mixture of 7-Methylnorbornene (3.16)with Catalysts 3.1, 3.4, and 3.9



catalyst	$\sigma_c{}^a$	tacticity ^b
3.1	0.97	<i>cis</i> regions, 95% <i>r</i> ; <i>trans</i> , >99% <i>r</i>
3.4	0.87	<i>cis</i> , 90% <i>r</i> ; <i>trans</i> , >99% <i>r</i>
3.9 ^c		

^{*a*}Fraction of double bonds having *cis* configuration; derived from $C_{1,4}$ resonances. ^{*b*}Derived from *cis* and *trans* $C_{1,4}$ peaks. ^{*c*}No reaction.

Finally, we probed the extent of head-to-tail (HT) selectivity exhibited by catalysts **3.1**, **3.4**, and **3.9** in the polymerization of racemic unsymmetrically substituted norbornenes. HT bias is measured by determining the ratios of head-head/head-tail (HH/HT) and tail-tail/tail-head (TT/TH) dyads in both the *cis* and the *trans* regions of a

The degree of HT bias in polymers derived from substituted norbornenes is delicately related to electronic and steric effects associated with both the monomer substituent(s) and the catalyst.^{1b} Additionally, any catalyst relaxation or isomerization processes occurring on the same time scale as propagation may also contribute to HT bias, as different propagating species can exhibit different levels of HT discrimination. One way to probe the role of the catalyst in HT selectivity is via the polymerization of norbornene monomers substituted at the C_5 or C_6 position. These substituents are sufficiently remote from the double bond that they generally do not exert any intrinsic head-to-tail bias resulting from steric effects; thus, any observed bias with these monomers is likely catalyst-dependent. An HT bias in the polymerization of C_5 - and C_6 -substituted norbornene monomers with a given catalyst, then, particularly one that increases with decreasing rate of polymerization (or increasing dilution), may point toward the existence of two or more distinct propagating species with distinctive HT biases.

no bias is present) when these values are equal to unity.

To test for HT-bias, catalysts **3.1**, **3.4**, and **3.9** were used to polymerize the unsymmetrically substituted racemic monomers 5-methylene-2-norbornene (**3.17**) and 5,5-dimethylnorbornene (DMNBE, **3.18**).^{22,23} Although all of the catalysts were found to be essentially bias-free in the polymerization of monomer **3.17** (*cis* TT/TH ratios = 0.93– 1.04), initiators **3.1** and **3.4** displayed more significant biases in the polymerization of **3.18** (*cis* TT/TH ratios = 1.11–1.51; *trans* TT/TH ratios = 0.20–1.00) (Table 3.10). Notably, the rate of polymerization of monomer **3.18** by initiators **3.1** and **3.4** was

significantly lower than that of **3.17** (1–4 h to full conversion vs minutes); additionally, as seen with monomer **3.16** no appreciable amount of **poly(3.18)** was formed using catalyst **3.9**. Both of these results are likely a consequence of the increased steric hindrance imparted by the *endo* substitution in monomer **3.18**. The increase in HT bias with decreasing rate suggests that there are multiple propagating species (perhaps resulting from alkylidene isomerization or a similar process), each with a different inherent HT bias.

Table 3.10. Polymerization of Monomers 3.17 and 3.18 with Catalysts 3.1, 3.4, and3.9

R	cat. (1 mol 9 THF (0.25 M)	%) , r.t. +	$R = -CH_2$ $n = -(CH_3)$	(3.17) ₃) ₂ (3.18)
catalyst	monomer	$\sigma_{c}{}^{a}$	$cis TT/TH^b$	<i>trans</i> TT/TH ^c
3.1	3.17	0.98	0.93	^d
3.4	3.17	0.87	0.95	
3.9	3.17	0.94	1.0	
3.1	3.18	0.78	1.1	0.20
3.4	3.18	0.77	1.5	0.50
3.9 ^e	3.18			

^{*a*}Fraction of double bonds having *cis* configuration; derived from C₆ resonances (**3.17**) and C₂ resonances (**3.18**). ^{*b*}Derived from *cis* TT and TH C_{2,3} peaks (**3.17**) and *cis* TT and TH C₂ peaks (**3.18**). ^{*c*}Derived from *trans* TT and TH C₂ peaks (**3.18**). ^{*d*}Here and below: overlap of *trans* TT and HH C_{2,3} peaks in **poly(3.17**) precluded *trans* TT/TH or HH/HT analysis. ^{*e*}No reaction.

Computational Investigations of Reaction Pathways and Proposed Model for *cis*-**Selectivity and Tacticity in Catalysts 3.1, 3.4, and 3.8–3.13:** The selectivity for *cis,syndiotactic* polymers exhibited by catalysts **3.1, 3.4**, and **3.8–3.13** is hypothesized to be due in large part to stereogenic metal control, as in the case of the Mo- and W-based MAP alkylidene complexes described earlier. Because initiators **3.1, 3.4**, and **3.8–3.13** are stereogenic-at-Ru, the absolute configuration of the metal center is inverted with each

propagation step to generate enantiomeric (in the case of **3.1**) or diastereomeric (**3.4** and **3.8–3.13**) carbenes (Figure 3.9), resulting in the addition of incoming monomers to alternating sides of the Ru=C bond.



Figure 3.9. Enantiomeric (**3.1**) and diastereomeric (**3.4**) alkylidenes generated by the stereochemical inversion of the Ru metal center that occurs with each forward metathesis step.

Previous computational and experimental work has shown that *cis*-selectivity in cross metathesis reactions mediated by cyclometalated catalysts similar to **3.1** and **3.4** stems from the steric influence of the bulky *N*-aryl group positioned directly over the side-bound metallacycle, which results in the destabilization of the transition state leading to the formation of *trans* olefins (described in further detail in *Chapter 1* of this thesis).²⁴ It is likely that monomer approach in ROMP is similarly influenced by the presence of the *N*-aryl group, in that norbornene and related monomers would be expected to react at the less hindered *exo* face with the methylene bridge pointed away from the *N*-aryl "cap."²⁵ In the terminology employed by Schrock and co-workers in regards to well-defined Mo and W initiators, this approach is designated *anti*, in that the bulk of the monomer points away from the *N*-aryl group; the opposite approach is *syn*.^{5c} Likewise, *syn* and *anti* Ru=CHR isomers are defined according to whether the R group of the alkylidene points towards or away from the *N*-aryl group, respectively. A consistently

anti monomer approach to alternate sides of an *anti* alkylidene as a result of stereogenic metal control leads to the formation of a *cis,syndiotactic* polymer (Scheme 3.3). However, if the incoming monomer were to occasionally adopt a *syn* approach to the *anti* alkylidene, a single *trans,isotactic* "error" would be produced (Scheme 3.4).



Scheme 3.3. Proposed mechanism for forming *cis,syndiotactic* polymers using cyclometalated catalyst 3.1. Mes = 2,4,6-trimethylphenyl, R = *o*-isopropoxyphenyl.



Scheme 3.4. Formation of a *trans,isotactic* dyad in a predominantly *cis,syndiotactic* polymer following a *syn* approach of the monomer to an *anti* alkylidene. R = o-isopropoxyphenyl.

Mixed tacticities (i.e., *cis,isotactic* and *trans,syndiotactic* dyads) would result if isomerization of the *anti* alkylidene were to occur between propagation steps, either through rotation about the M=C double bond to adopt a *syn* configuration or via a nonmetathesis-based polytopal rearrangement²⁶ between the stereoisomeric metal alkylidenes (i.e., (*R*)-**3.1** and (*S*)-**3.1**). Moreover, the degree to which these "errors" occur would be related to the barrier to these processes, with an increase in regions of mixed tacticity being observed when the rate of alkylidene isomerization occurs on a time scale that is comparable to the time scale for propagation. Competition between alkylidene isomerization and propagation would also provide a reasonable explanation for the HT bias detected in catalysts **3.1** and **3.4** as well as the temperature effect observed in the polymerization of **3.6** with catalyst **3.4**, as outlined previously.

To explore these possible alkylidene isomerization processes, as well as to better understand how they may lead to a loss in *cis*-selectivity and tacticity in some of these cyclometalated ruthenium-based systems, DFT calculations on polymerization reactions involving catalysts **3.1** and **3.4** were performed by the Houk group at UCLA.²⁷ All calculations were performed with Gaussian 09^{28} at the M06/SDD-6-311+G(d,p)/SMD(THF)//B3LYP/SDD-6-31G(d) level of theory. See the SI for computational details.

We first investigated the likelihood of alkylidene isomerization through a nonmetathesis-based polytopal rearrangement pathway. The computed energy profile of the polytopal rearrangement of *N*-^{*i*}Bu-cyclometalated ruthenium alkylidene **3.19** to form its diastereomer **3.20** (using a 3-cyclopentenyl group as a model of the polymer chain) is shown in Figure 3.10. This multistep rearrangement process starts from alkylidene *anti* to *syn* isomerization via rotation (**3.21-TS**), which requires a relatively low barrier to form the *syn* alkylidene intermediate **3.22**. Isomerization of the alkylidene to the position *trans* to the NHC leads to highly unstable intermediate **3.24**. Complex **3.24** subsequently undergoes ring flip of the five-membered chelate (**3.25-TS**) and a very unfavorable rearrangement of the pivalate ligand (**3.27-TS**) to form complex **3.28**, which then



Figure 3.10. Nonmetathesis-based polytopal rearrangement of ruthenium alkylidene 3.19 to its diastereomer 3.20.

We next explored the possibility of isomerization via rotation about the alkylidene Ru=C double bond. The computed rotational barriers for catalysts **3.1** and **3.4** are summarized in Table 3.11. Because of steric repulsions between the alkylidene R group and the *N*-aryl group, the *syn* alkylidene is less stable than the *anti* isomer. The alkylidene rotational barrier is only slightly affected by the steric bulk of the substituent on the alkylidene and the cyclometalated group on the catalyst. In general, the barrier to alkylidene rotation is comparable to the barrier for monomer addition (see below).



Table 3.11. Computed Alkylidene Rotational Barriers

^{*a*}Alkylidene rotational barrier with respect to the *anti* alkylidene. ^{*b*}Energy difference between *syn* and *anti* alkylidene isomers. All energies are in kcal/mol.

Given the high barrier and the unstable intermediates in the polytopal rearrangement process, we conclude that a nonmetathesis isomerization of the ruthenium alkylidene is highly unlikely to occur under the reaction conditions, and a pathway involving bond rotation about the Ru=C alkylidene is much more likely to be responsible for alkylidene isomerization. With this in mind, we can now complete our model for *cis*-selectivity and tacticity in catalysts **3.1**, **3.4**, and **3.8–3.13** by factoring in the effects of alkylidene rotation on the final polymer microstructure. In a predominantly *cis,syndiotactic* polymer resulting from stereogenic metal control, rotation of the alkylidene from *anti* to *syn* followed by monomer approach in either an *anti* or *syn*

fashion results in the formation of a *trans,syndiotactic* or *cis,isotactic* dyad, respectively (Scheme 3.5).



Scheme 3.5. Formation of a *trans,syndiotactic* or *cis,isotactic* dyad resulting from an *anti* or *syn* monomer approach, respectively, to a *syn* alkylidene following alkylidene rotation (*anti* to *syn*) in a predominantly *cis,syndiotactic* polymer. R = o-isopropoxyphenyl.

We next set out to explore the possible pathways leading to the formation of each type of dyad in more depth. We focused on the [2 + 2] cycloaddition step, as in reactions with norbornene and norbornadienc derivatives, the [2 + 2] cycloaddition step requires a significantly higher barrier than the [2 + 2] cycloelimination, and thus the [2 + 2] cycloaddition is effectively irreversible.^{27b,29} Importantly, *cis/trans*-selectivity and tacticity are both determined in the [2 + 2] cycloaddition step. The four possible transition states derived for the [2 + 2] cycloaddition of monomer **3.6** at the *exo* face to ruthenium alkylidene **3.30**, a model of the propagating species of the *N*-'Bucyclometalated catalyst **3.1**, are shown in Figure 3.11. Because isomerization between the *anti* and *syn* alkylidenes via rotation of the Ru=C bond occurs with a barrier comparable to that of propagation, monomer addition to both *anti* and *syn* alkylidenes was computed

(3.31-TS-A/B and 3.31-TS-C/D, respectively). In these transition states, the olefin approaches the catalyst from the side, that is, *cis* to the NHC ligand, in line with previous computational studies of olefin cross-metathesis with cyclometalated *cis*-selective ruthenium catalysts.²⁴ The bottom-bound pathway, i.e., olefin approaching *trans* to the NHC, and the addition to the *endo* face of the norbornadiene both require much higher activation energies (15–21 kcal/mol, see the SI for details).



Figure 3.11. [2 + 2] cycloaddition transition states for the polymerization of monomer 3.6 with catalyst 3.30. Energies are with respect to the separated ruthenium alkylidene and monomer 3.6.

The most favorable [2 + 2] cycloaddition transition state is the one leading to the formation of a *cis,syndiotactic* dyad, **3.31-TS-A**, in which the *anti* alkylidene reacts with a monomer approaching in an *anti* fashion. The ligand–substrate steric repulsions in this *anti/anti* approach are minimized due to the bulk of the monomer and the alkylidene both

being directed away from the *N*-aryl group. The next lowest energy transition state leads to the formation of a *trans,syndiotactic* arrangement (**3.31-TS-C**), in which the *syn* alkylidene reacts with a monomer approaching in an *anti* fashion. This *anti/syn* approach (**3.31-TS-C**) is 2.1 kcal/mol higher in energy than the *anti/anti* approach (**3.31-TS-A**), which is consistent with the high *cis*-selectivity observed experimentally. Both *trans,isotactic* and *cis,isotactic* dyads result when the monomer approaches in a *syn* fashion (**3.31-TS-B** and **3.31-TS-D**, respectively), which requires much higher activation energies due to the repulsion of the methylene bridge with the *N*-aryl group. This is in agreement with the high syndiotacticity of both the *cis* and the *trans* regions observed experimentally.

Experimentally, the polymerization of monomer **3.6** with *N*-adamantyl cyclometalated ruthenium catalysts (**3.4**, **3.8–3.13**) is both less *cis*-selective and less syndioselective than that with the *N*-'Bu cyclometalated catalyst **3.1** (Table 3.5). Interestingly, when the total content of *cis* double bonds in **poly**(**3.6**) is plotted against the percentage of *cis* double bonds in *cis*, *r* dyads for catalysts **3.1**, **3.4**, and **3.8–3.13**, a linear relationship is observed (Figure 3.12). Because the barriers to alkylidene rotation in catalysts **3.1** and **3.4** with monomer **3.6** are comparable (Table 3.11), this relationship is likely a result of the relative differences in the energetics of the propagation transition states for each catalyst (which also determine both *cis*- and syndioselectivity). Thus, the [2 + 2] cycloaddition transition states with monomer **3.6** and alkylidene **3.32**, a model of the propagating species of catalyst **3.4**, were calculated to further investigate the connection between *cis*-selectivity and tacticity in these systems.



Figure 3.12. Linear relationship between *cis* content and tacticity of the *cis* regions in poly(DCMNBD) [**poly(3.6**)] for catalysts **3.1**, **3.4**, and **3.8–3.13** (data obtained from Table 3.5).

With the asymmetric *N*-adamantyl-cyclometalated group on catalyst **3.4**, an additional set of alkylidene diastereomers is possible, resulting in eight total propagation transition states (Figure 3.13). In the more stable alkylidene diastereomer (R,R)-**3.32**, the Ru=C bond is *anti* to the alpha C–H bond on the cyclometalated carbon atom. In (R,S)-**3.32**, the Ru=C bond is *syn* to the alpha C–H bond. As discussed above, direct isomerization between (R,R)-**3.32** and (R,S)-**3.32** via polytopal rearrangement is not possible. Instead, the configuration of ruthenium alternates between (R,R)-**3.32** and (R,S)-**3.32** after each monomer addition.



Figure 3.13. [2 + 2] cycloaddition transition states for the polymerization of monomer 3.6 with catalyst 3.32. Energies are with respect to the separated ruthenium alkylidene and monomer 3.6.

Similar to the reaction with catalyst **3.1**, the *cis,syndio*-selective *anti/anti* approach is the most favorable with catalyst **3.4** (**3.33-TS-A** and **3.34-TS-A** for the addition to alkylidenes (*R*,*R*)-**3.32** and (*R*,*S*)-**3.32**, respectively). However, the corresponding *trans,syndio*-selective transition states **3.33-TS-C** and **3.34-TS-C** are only 0.7 and 2.0 kcal/mol less stable, respectively. Similarly, the transition states leading to the formation of *trans,isotactic* and *cis,isotactic* dyads (**3.33-TS-B/D** and **3.34-TS-B/D**, respectively), while still highly unfavorable, are also less destabilized relative to *cis,syndio*-selective **3.33-TS-A** and **3.34-TS-A**. The lower selectivity for *cis,syndiotactic* dyads is attributed to the increased steric repulsion between the alkylidene R group and the bulkier cyclometalated *N*-adamantyl group in the *cis,syndio*-selective transition states, in particular in **3.34-TS-A**. These results likely extend to the other cyclometalated *N*-adamantyl initiators **3.8–3.13**.

Conclusions and Future Outlook

In spite of expectations to the contrary, we have demonstrated the ability of Rubased olefin metathesis catalysts to generate norbornene- and norbornadiene-based polymers with singular microstructures via ROMP. Using the recently developed sodium pivalate method (detailed in *Chapter 2*), a series of ruthenium alkylidene initiators containing a cyclometalated *N*-^{*t*}Bu group were synthesized. All of these complexes yielded highly *cis,syndiotactic* ROMP polymers (>95% in some cases).

Using experimental and computational insights, a model was subsequently developed to explain the pattern of stereoselectivity exhibited in these and related cyclometalated ruthenium metathesis catalysts. A series of Ru-based initiators containing differing cyclometalated groups, N-aryl substituents, and X-type ligands were evaluated in the ROMP of various norbornene- and norbornadiene-derived monomers. Highly cis, syndiotactic polymers were generated in many cases. In polymers with an imperfect microstructure, the major errors were in the form of *cis,isotactic* and *trans,syndiotactic* regions. Additionally, hypothetical reaction intermediates and propagation transition states were analyzed computationally. Combined experimental and computational data suggests that the near-perfect *cis,syndio*-selectivity of these systems arises from the inversion of configuration at the metal center that occurs with each propagation step (i.e., stereogenic metal control) in conjunction with an almost exclusive approach of the monomer in an *anti* fashion to the energetically preferred *anti* alkylidene. The majority of microstructural errors are likely a result of interconversion between syn and anti alkylidene isomers in the propagating catalytic species: Addition of the monomer in an anti or syn fashion to the higher energy syn alkylidene leads to the formation of a *trans,syndiotactic* or *cis,isotactic* dyad, respectively. Furthermore, the comparatively high *cis,syndio*-selectivity of the cyclometalated-*N*-^{*i*}Bu initiators was determined to originate from the decreased steric environment in these catalysts relative to the N-adamantylcyclometalated systems, as increased substitution close to the metal center was shown to minimize the differences in energy between transition states. The mechanistic insights gained in this study will not only aid in the development of new and improved cisselective Ru-based catalysts, but also provide increased predictive power in synthetic transformations mediated by these systems.
Since the two papers comprising this chapter were published in the *Journal of the* American Chemical Society, an additional example of Ru-mediated stereoselective ROMP has been reported. Mikus et al. found that certain Ru catechothiolate systems generated polynorbornenes and -norbornadienes with all-cis controllable syndioselectivity, ranging from \sim 50% to >95%, also as a result of stereogenic metal control.³⁰ Higher syndioselectivities, resulting from lower rates of non-metathesis-based polytopal isomerization relative to monomer propagation, could be selected for by adjusting the monomer concentration and/or the catalyst's steric and electronic characteristics via substitution of the dithiolate ligand. Despite these recent advances in the area of Ru-mediated stereoselective ROMP, however, norborneneand norbornadiene-based polymer architectures other than *cis,syndiotactic*, namely *cis,isotactic, trans,syndiotactic,* and *trans,isotactic,* remain elusive. Using the progress made in stereoselective ROMP mediated by W- and Mo-based complexes as a model, it is reasonable to expect that highly *cis,isotactic* polynorbornenes and –norbornadienes may be accessible through the design of a catalyst that operates via enantiomorphic site control, while the synthesis of a catalyst capable of generating *trans,syndiotactic* and *trans,isotactic* polymers will likely be significantly more challenging. Regardless, the insights gained in the studies presented in this chapter provide a platform for the development of new Ru-based systems capable of producing interesting and varied architectures via ring-opening metathesis polymerization.

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Supporting Information

General Information: All reactions were carried out in dry glassware under an argon atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres Glovebox under a nitrogen atmosphere, unless otherwise specified. All solvents were purified by passage through solvent purification columns and further degassed by bubbling argon. C_6D_6 was purified by passage through a solvent purification column. CDCl₃, CD₂Cl₂, THF-d₈, and (CD₃)₂CO were used as received. Monomers **3.6**,³¹ **3.7**,^{5b,32} **3.14**,³³ **3.15**,³⁴ **3.16**,^{13a} and **3.18**³⁵ were synthesized according to literature procedure, while monomers **3.5** and **3.17** were purchased from Sigma Aldrich and either used as received (**3.5**) or distilled over CaH₂ prior to use (**3.17**). Catalysts **3.4** and **3.9**, as well as RuCl₂(PCy₃)(=CH-*o*-O[′]PrC₆H₄) (**3.36**), were obtained from Materia, Inc. Catalysts **3.10**, **3.11**, **3.12**,^{10b} and **3.13**,³⁶ as well as 2-bromo-*N*-(2-*iso*-propyl-6-methylphenyl)acetamide $(3.38)^{12}$ and *N*-heterocyclic carbenes (NHCs) 3.35^{37} and 3.47,^{10b} were synthesized according to literature procedures.

¹H NMR spectra were acquired at 500 MHz and ¹³C NMR spectra at 100 or 126 MHz as CDCl₃ or C_6D_6 solutions unless otherwise noted. Chemical shifts are reported in ppm downfield from Me₄Si by using the residual solvent peak as an internal standard. Spectra were analyzed and processed using MestReNova Versions 7.1 and 9.0.

High-resolution mass spectra (HRMS) were provided by the California Institute of Technology Mass Spectrometry Facility using a JEOL JMS-600H High Resolution Mass Spectrometer. All HRMS were by FAB+ ionization, except where specified.

Polymer molecular weights were determined by multi-angle light scattering (MALS) gel permeation chromatography (GPC) using a miniDAWN TREOS light scattering detector, a Viscostar viscometer, and an OptilabRex refractive index detector, all from Wyatt Technology. An Agilent 1200 UV-Vis detector was also present in the detector stack. Absolute molecular weights were determined using *dn/dc* values calculated by assuming 100% mass recovery of the polymer sample injected into the GPC. No internal standards were used. DSC was performed using a Perkin Elmer DSC 7 at a nitrogen flow rate of 40 mL/min and a heating rate of 2 K/min from 0 °C to 200 °C. TGA was performed using a TA Instruments O5000 TGA at a nitrogen flow rate of 10 mL/min (sample) and 25 mL/min (balance).

Computational Details: Geometries were optimized with B3LYP and a mixed basis set of LANL2DZ for ruthenium and 6-31G(d) for other atoms. Single point calculations were performed with M06 and a mixed basis set of SDD for ruthenium and 6-311+G(d,p) for

other atoms. The SMD solvation model with THF as solvent was used in the single point energy calculations. This is the same level of theory used in the Houk group's previous calculations on ruthenium metathesis catalysts.



Preparation of 3.37: In a glovebox, a solution of **3.35** (0.19 g, 0.66 mmol) in hexanes (20 mL) was treated with KCOMe₂Et (88 mg, 0.69 mmol), and the mixture was allowed to stir at r.t. for 2 h. To the reaction mixture was then added **3.36** (0.38 g, 0.64 mmol), upon which the mixture was removed from the glove box and allowed to stir at 65 °C overnight (12 h). The precipitated solids were filtered and washed well with warm hexanes and pentane and then collected with CH₂Cl₂ and concentrated. The crude mixture was further purified by flash column chromatography (SiO₂, eluent pentane to 20% Et₂O in pentane to CH₂Cl₂) to provide **3.37** (0.24 g, 68%) as a green powder. ¹H NMR (500 MHz, CDCl₃) δ 16.87 (s, 1H), 7.56 (m, 1H), 7.07 (s, 2H), 6.97–6.89 (m, 3H), 6.87 (m, 1H), 5.08 (hept, *J* = 6.2 Hz, 1H), 4.10–3.82 (m, 4H), 2.46 (s, 3H), 2.26–2.27 (m, 15H), 1.62 (d, *J* = 6.2 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 312.9, 207.5, 152.6, 145.7, 139.4, 138.6, 138.2, 130.9, 129.7, 124.0, 122.8, 113.3, 74.5, 56.3, 51.6, 46.1, 29.8, 22.5, 21.3, 18.4 HRMS (FAB+, (M)): Calculated—564.1249, Found—564.1268.



Preparation of 3.1: In a glovebox, a 20 mL scintillation vial was charged with 3.37 (0.11 g, 0.20 mmol), NaOPiv (0.25 g, 2.0 mmol), THF (4.0 mL), and MeOH (2.0 mL). The vial was capped, removed from the glovebox, and heated at 40 °C for 5 h during which a color change from green to brown to dark purple was observed. The vial was then returned to the box, where the solvent was removed in vacuo and the resulting solid dissolved in CH₂Cl₂ (30 mL), filtered through celite, and concentrated to a deep purple residue. The crude mixture was purified by pipette column (SiO₂, eluent 20% Et₂O in pentane) three times and subsequently recrystallized from pentane to provide 3.1 as a bright purple solid (59 mg, 22%). ¹H NMR (500 MHz, THF-d₈) δ 14.69 (s, 1H), 7.44– 7.36 (m, 1H), 7.32 (m, 1H), 7.07 (m, 1H), 6.88 (m, 1H), 6.72 (s, 2H), 5.04 (hept, J = 6.2Hz, 1H), 3.95-3.72 (m, 4H), 2.82 (d, J = 10 Hz, 1H), 2.38 (s, 3H), 2.38 (overlapped, 1H), 2.14 (s, 3H), 2.13 (s, 3H), 1.45 (d, J = 6.2 Hz, 3H), 1.44 (s, 3H), 1.38 (d, J = 6.2 Hz, 3H), 0.87 (s, 9H), 0.57 (s, 3H). ¹³C NMR (126 MHz, CD₂Cl₂) δ 260.3, 211.4, 188.2, 155.0, 143.7, 137.9, 137.6, 137.0, 136.8, 129.9, 129.2, 126.2, 123.4, 122.7, 114.1, 75.8, 62.6, 51.1, 47.7, 43.9, 39.6, 29.4, 28.1, 23.2, 22.2, 22.0, 21.1, 18.8, 18.7. HRMS (FAB+, [(M+H)-H₂]): Calculated—593.2318, Found—593.2327.



Preparation of 3.39: Compound **3.38** (7.2 g, 27 mmol) and ¹BuNH₂ (4.2 mL, 39 mmol) were dissolved in MeCN (90 mL), K₂CO₃ (5.7 g, 42 mmol) was added, and the solution was refluxed for 24 h. After cooling to r.t., the mixture was filtered over celite and concentrated. The residue was then dissolved in CH₂Cl₂ and filtered over a pad of silica gel (eluent 10% MeOH in CH₂Cl₂). Removal of the solvent *in vacuo* provided **3.39** (6.7 g, 94%) as an off-white solid. ¹H NMR (500 MHz, CDCl₃) δ 9.09 (br s, 1H), 7.18 (m, 1H), 7.16 (m, 1H), 7.09 (m, 1H), 3.41 (s, 2H), 3.03 (m, 1H), 2.22 (s, 3H), 1.71 (br s, 1H), 1.20 (d, *J* = 6.9 Hz, 6H), 1.17 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 171.6, 145.2, 135.6, 132.8, 128.2, 127.5, 123.4, 51.3, 46.1, 29.1, 28.7, 23.4, 18.8. HRMS (FAB+, (M+H)): Calculated—263.2123, Found—263.2111.



Preparation of 3.40: A solution of compound **3.39** (6.7 g, 26 mmol) in THF (10 mL) was added to a 0 °C solution of LiAlH₄ (3.0 g, 79 mmol) in THF (100 mL). The resulting solution was allowed to warm to r.t., then refluxed for 72 h. The mixture was then cooled to 0 °C and carefully quenched via the sequential, dropwise addition of H₂O (3.0 mL), 10% *aq*. NaOH (3.0 mL), and H₂O (3.0 mL). The solution was dried with MgSO₄, filtered, and concentrated. Flash chromatography of the residue (SiO₂, eluent 10% MeOH in CH₂Cl₂) provided **3.40** (3.7 g, 57%) as a pale yellow oil. ¹H NMR (500 MHz, CDCl₃)

δ 7.09 (m, 1H), 6.98 (m, 1H), 6.91 (m, 1H), 3.29 (m, 1H), 3.00 (m, 2H), 2.80 (m, 2H), 2.33 (s, 3H), 1.24 (d, J = 6.9 Hz, 6H), 1.13 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 145.2, 140.7, 130.5, 128.4, 123.6, 122.4, 50.6, 50.3, 42.8, 29.2, 27.5, 24.0, 19.0. HRMS (FAB+, (M+H)): Calculated—249.2331, Found—249.2335.



Preparation of 3.41: A solution of compound **3.40** (3.5 g, 14 mmol) in Et₂O (25 mL) was treated with HCl (14 mL, 2.0 M in Et₂O) and stirred for 15 minutes at r.t. The solid was then filtered, washed with Et₂O, dried, suspended in CH(OEt)₃ (25 mL), and refluxed for 2 h. After cooling the solution to r.t., the solvent was removed *in vacuo* and the resulting solid residue washed rigorously with Et₂O to provide **3.41** (1.5 g, 37%) as an off-white solid. ¹H NMR (500 MHz, CDCl₃) δ 9.02 (br s, 1H), 7.31 (m, 1H), 7.22 (m, 1H), 7.12 (m, 1H), 4.49 (m, 1H), 4.38 (m, 2H), 4.22 (m, 1H), 2.91 (m, 1H), 2.40 (s, 3H), 1.61 (s, 9H), 1.27 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 157.0, 146.4, 135.9, 132.0, 130.5, 129.2, 124.8, 57.8, 52.4, 46.5, 28.6, 28.4, 24.8, 24.2, 18.6. HRMS (FAB+, (M-Cl)): Calculated—259.2174, Found—259.2172.



Preparation of 3.42: In a glovebox, KCOMe₂Et (0.15 g, 1.2 mmol) was added to a suspension of compound **3.41** (0.29 g, 1.0 mmol) in hexanes (12 mL). After stirring at 35 °C for 30 minutes, compound **3.36** (0.60 g, 1.0 mmol) was added, and the reaction mixture was sealed and removed from the glovebox. The solution was stirred for 3 h at 65 °C and subsequently cooled to r.t. The resulting precipitate was filtered, washed with warm hexanes, and further purified by column chromatography (SiO₂, eluent pentane to 20% Et₂O in pentane to DCM) to provide **3.42** (0.55 g, 92%) as a green solid. ¹H NMR (500 MHz, CDCl₃) δ 16.86 (s, 1H), 7.54 (m, 1H), 7.49 (m, 1H), 7.41 (m, 1H), 7.23 (m, 1H), 6.94 (m, 1H), 6.88 (m, 1H), 6.85 (m, 1H), 5.07 (hept, *J* = 6.2 Hz, 1H), 4.02 (m, 2H), 3.91 (m, 2H), 3.17 (hept, *J* = 6.8 Hz, 1H), 2.33 (s, 3H), 2.28 (s, 9H), 1.67 (d, *J* = 6.2 Hz), 1.59 (d, *J* = 6.2 Hz, 3H), 1.19 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 311.0, 207.8, 152.7, 148.8, 145.0, 140.4, 138.0, 130.7, 129.1, 129.0, 124.8, 123.9, 122.6, 113.2, 74.5, 56.3, 53.1, 46.0, 29.8, 27.6, 25.6, 23.8, 22.7, 22.3, 19.0. HRMS (FAB+, (M)): Calculated—578.1405, Found—578.1433.



Preparation of 3.2: In a glovebox, a 20 mL scintillation vial was charged with **3.42** (0.10 g, 0.17 mmol), NaOPiv (0.22 g, 1.7 mmol), THF (6.0 mL) and MeOH (3.0 mL). The vial was capped, removed from the glovebox, and heated at 50 °C for 12 h during which a color change from green to brown to dark purple was observed. The vial was then returned to the glovebox, where the solvent was removed *in vacuo* and the resulting solid was dissolved in CH₂Cl₂ (30 mL), filtered over a pad of celite, and concentrated to a deep purple residue. Purification of the crude mixture by a silica gel plug (eluent pentane to 20% Et₂O in pentane) followed by recrystallized from hexanes provided 3.2 (65 mg, 65%) as a bright purple solid. ¹H NMR (500 MHz, CD₂Cl₂) δ 14.70 (s, 1H), 7.45 (m, 1H), 7.39 (m, 1H), 7.08 (m, 1H), 7.07 (m, 1H), 7.02 (m, 1H), 6.94 (m, 2H), 4.99 (hept, J= 6.4 Hz, 1H), 3.92-3.79 (m, 3H), 3.79-3.69 (m, 2H), 2.79 (d, J = 6.8 Hz, 1H), 2.45 (d, J= 6.8 Hz, 1H), 2.17 (s, 3H), 1.47 (s, 3H), 1.44 (d, J = 6.4 Hz, 3H), 1.40 (d, J = 6.4 Hz, 3H), 1.24 (d, J = 6.9 Hz, 3H), 1.10 (d, J = 6.9 Hz, 3H), 0.91 (s, 9H), 0.56 (s, 3H). ¹³C NMR (126 MHz, CD₂Cl₂) δ 260.2, 210.9, 187.5, 154.5, 147.5, 143.2, 138.4, 137.5, 128.3, 127.5, 125.6, 123.8, 122.9, 122.3, 113.8, 75.5, 62.1, 51.8, 47.3, 43.4, 39.1, 28.8, 27.9, 27.7, 25.5, 23.7, 22.8, 21.8, 21.7, 18.7. HRMS (FAB+, (M)): Calculated-608.2552, Found—608.2536.



Preparation of 3.43: 2-Bromo-2-methylpropionyl bromide (4.1 g, 33 mmol) was dissolved in CH₂Cl₂ (60 mL), ^{*I*}BuNH₂ (3.2 mL, 30 mmol) and then Et₃N (12 mL, 60 mmol) were added dropwise, and the mixture was stirred overnight at r.t. The solution was then washed with saturated NH₄Cl (*aq.*) (x2), dried with Na₂SO₄, and concentrated. The resulting residue was dissolved in THF (75 mL), cannulated into a solution of 2-isopropyl-6-methylaniline (5.0 g, 33 mmol) and NaH (1.4 g, 60 mmol) in THF (75 mL), and stirred overnight at r.t. The solution was then diluted with EtOAc, washed with saturated NH₄Cl (*aq.*) and brine, dried using Na₂SO₄, and concentrated. Purification by flash chromatography (SiO₂, eluent 10% MeOH in CH₂Cl₂) provided **3.43** (2.9 g, 33%) as a peach solid. ¹H NMR (500 MHz, CDCl₃) δ 7.83 (br s, 1H), 7.10 (m, 1H), 6.98 (m, 2H), 3.17 (br s, 1H), 3.11 (m, 1H), 2.27 (s, 3H), 1.40 (s, 9H), 1.30 (s, 6H), 1.20 (d, *J* = 6.9 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 176.9, 143.4, 141.3, 132.7, 128.5, 124.1, 123.7, 60.3, 50.2, 28.5, 28.2, 27.1, 23.7, 20.7. HRMS (EI+, (M+H)): Calculated—291.2436, Found—291.2429.



Preparation of 3.44: A solution of BH_3 ·THF (43 mL, 1.0 M in THF) was added dropwise to a 0 °C solution of compound **3.43** (2.5 g, 8.6 mmol) in THF (12 mL). The mixture was stirred overnight at r.t., then quenched via dropwise addition of MeOH at 0

°C and concentrated. The residue was then re-dissolved in MeOH and re-concentrated (x3). Purification by flash chromatography (SiO₂, eluent CH₂Cl₂ then 10% MeOH in CH₂Cl₂) provided **3.44** (1.2 g, 50%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.09 (m, 1H), 7.00 (m, 1H), 6.97 (m, 1H), 3.53 (m, 1H), 2.60 (2, 2H), 2.37 (s, 3H), 1.18 (d, *J* = 6.9 Hz, 6H), 1.15 (s, 9H), 1.06 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 145.5, 142.6, 135.2, 128.1, 123.4, 123.2, 56.0, 54.9, 49.9, 29.3, 27.5, 26.7, 24.1, 20.8. HRMS (EI+, (M+H)): Calculated—277.2644, Found—277.2636.



Preparation of 3.45: A solution of compound **3.44** (1.1 g, 4.0 mmol) in Et₂O (10 mL) was treated with HCl (4.0 mL, 2.0 M in Et₂O) and stirred for 15 minutes at r.t. The solid was then filtered, washed with Et₂O, dried, suspended in CH(OEt)₃ (10 mL), and refluxed for 2 h, at which point the solution was cooled to r.t. and concentrated. The resulting solid residue was washed rigorously with Et₂O to provide **3.45** (0.6 g, 46%) as an off-white solid. ¹H NMR (500 MHz, CDCl₃) δ 9.26 (br s, 1H), 7.30 (m, 1H), 7.21 (m, 1H), 7.13 (m, 1H), 4.07 (d, *J* = 12 Hz, 1H), 4.02 (d, *J* = 12 Hz, 1H), 2.85 (m, 1H), 2.41 (s, 3H), 1.60 (s, 9H), 1.48 (s, 3H), 1.41 (s, 3H), 1.29 (d, *J* = 6.8 Hz, 3H), 1.16 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 156.7, 148.3, 137.8, 130.3, 129.7, 128.9, 124.7, 69.7, 58.7, 57.8, 29.2, 28.3, 26.9, 26.4, 25.9, 22.7, 20.5. HRMS (FAB+, (M-Cl)): Calculated—287.2487, Found—287.2499.



Preparation of 3.46: In a glovebox, KCOMe₂Et (57 mg, 0.45 mmol) was added to a suspension of compound **3.45** (0.14 g, 0.43 mmol) in hexanes (13 mL). The solution was then stirred at r.t. for 2 h, at which point 3.36 (0.31 g, 0.52 mmol) was added and the reaction mixture subsequently sealed and removed from the glovebox. The solution was stirred for 3 h at 65 °C and then cooled to r.t. The resulting precipitate was filtered, washed thoroughly with warm hexanes, and further purified by flash chromatography (SiO₂, eluent pentane to 20% Et₂O in pentane to CH₂Cl₂) to provide **3.46** (0.21 g, 86%) as a green solid. ¹H NMR (500 MHz, CDCl₃) δ 16.66 (s, 1H), 7.57–7.42 (m, 3H), 7.24–7.20 (m, 1H), 6.93 (d, J = 8.4 Hz, 1H), 6.90–6.83 (m, 2H), 5.06 (hept, J = 6.3 Hz, 1H), 3.84 (d, J = 9.9 Hz, 1H), 3.65 (d, J = 9.8 Hz, 1H), 3.25 (hept, J = 6.7 Hz, 1H), 2.29 (overlapped, 12H), 1.68 (d, J = 6.2 Hz, 3H), 1.58 (d, J = 6.2 Hz, 3H), 1.40 (s, 3H), 1.24 (d, J = 6.8 Hz, 3H), 1.12 (s, 3H), 0.75 (d, J = 6.6 Hz, 3H).¹³C NMR (126 MHz, CDCl₃) δ 310.79, 207.99, 152.78, 150.31, 144.75, 140.38, 138.56, 130.61, 129.54, 128.67, 125.33, 124.12, 122.65, 113.34, 74.45, 65.40, 61.19, 56.32, 29.79, 28.33, 27.99, 25.63, 25.26, 23.92, 22.86, 22.29, 21.32. HRMS (FAB+, (M+H)-H₂): Calculated—605.1640, Found— 605.1618.



Preparation of 3.3: In a glovebox, a 20 mL scintillation vial was charged with 3.46 (60 mg, 0.10 mmol), NaOPiv (0.12 g, 1.0 mmol), THF (2.0 mL), and MeOH (2.0 mL). The vial was capped, removed from the glovebox, and heated at 40 °C for 21 h during which a color change from green to brown to dark purple was observed. The vial was returned to the box, where the solvent was removed *in vacuo* and the resulting solid dissolved in CH₂Cl₂ (15 mL), filtered through celite, and concentrated to a deep purple residue. The residue was purified by pipet column (SiO₂, eluent 20% Et₂O in pentane) and subsequently recrystallized from hexanes to provide 3.3 (25 mg, 40%) as a bright purple solid. ¹H NMR (500 MHz, C₆D₆) δ 14.98 (s, 1H), 7.47 (dd, J = 7.4, 1.7 Hz, 1H), 7.23 (td, J = 8.0, 1.7 Hz, 1H), 7.07 (overlapped, 2H), 6.97–6.99 (m, 1H), 6.88 (t, J = 7.4 Hz, 1H), 6.60 (d, J = 8.3 Hz, 1H), 4.63 (hept, J = 6.3 Hz, 1H), 3.98 (hept, J = 6.8 Hz, 1H), 3.35– 3.21 (m, 2H), 2.80-2.69 (m, 2H), 2.32 (s, 3H), 1.46 (d, J = 6.4 Hz, 3H), 1.40 (s, 3H), 1.35(s, 3H), 1.31 (d, J = 6.9 Hz, 3H), 1.24 (d, J = 6.1 Hz, 3H), 1.18 (s, 9H), 1.12 (d, J = 6.9Hz, 3H), 0.76 (s, 3H), 0.61 (d, J = 9.0 Hz, 3H). ¹³C NMR (126 MHz, C₆D₆) δ 260.95, 211.46, 187.86, 155.35, 149.68, 144.03, 139.68, 136.90, 128.69, 127.87, 127.57, 125.73, 124.69, 123.15, 122.70, 113.79, 75.07, 64.80, 62.12, 57.77, 47.76, 39.61, 30.87, 28.77, 28.69, 28.39, 25.63, 24.67, 24.12, 22.87, 22.01, 21.82, 20.68. HRMS (FAB+, (M+H)-H₂): Calculated—635.2787, Found—635.2788.



Preparation of 3.48: In a glovebox, a suspension of KCOMe₂Et (75 mg, 0.57 mmol) in hexanes (6 mL) was added to **3.47** (0.19 g, 0.52 mmol), and the resulting solution was stirred in the glovebox at 30 °C for 30 minutes. Compound **3.36** (0.31 g, 0.52 mmol) was then added, and the vessel was sealed, taken out of the glovebox, and stirred for 2 h at 65 °C. After cooling the mixture to r.t., the precipitated solids were collected via filtration and washed thoroughly with warm hexanes, providing **3.48** (0.22 g, 65%) as a green powder. ¹H NMR (CDCl₃) d 16.89 (1H, s), 7.54 (1H, m), 7.50 (1H, m), 7.41 (1H, m), 7.23 (1H, m), 6.93 (1H, m), 6.85 (1H, m), 5.07 (1H, m), 4.05 (2H, m), 3.88 (2H, m), 3.15 (1H, m), 2.97 (4H, m), 2.42 (3H, m), 2.33 (3H, s), 1.95 (3H, m), 1.84 (3H, m), 1.69 (3H, d, *J* = 6.1 Hz), 1.60 (3H, d, *J* = 6.1 Hz), 1.19 (3H, d, *J* = 6.7 Hz), 0.89 (3H, d, *J* = 6.7 Hz); ¹³C NMR (CDCl₃) d 208.6, 152.9, 149.0, 145.6, 141.0, 138.3, 131.0, 129.5, 129.3, 125.2, 124.2, 122.9, 113.6, 74.6, 57.6, 53.1, 44.9, 42.6 (2C), 36.5 (3C), 30.4 (3C), 28.0, 25.9, 24.2, 23.1, 22.6, 19.3; HRMS (FAB+, (M)): Calculated—656.1875, Found—656.1894.



Preparation of 3.49: In a glovebox, a 20 mL scintillation vial was charged with 3.48 (0.10 g, 0.15 mmol), NaOPiv (0.19 g, 1.5 mmol), THF (1.5 mL), and MeOH (1.5 mL). The solution was heated at 40 °C for 10 hours in the glovebox during which a color change from green to brown to dark purple was observed. The solvent was then removed in vacuo, and the resulting residue was dissolved in CH₂Cl₂, filtered over celite, and concentrated. Purification via a short plug of silica gel (eluent 20% Et₂O in pentane) provided **3.49** (52 mg, 52%) as a bright purple solid. ¹H NMR (CD₂Cl₂) d 14.66 (1H, s), 7.38 (2H, m), 7.11 (2H, m), 6.98 (1H, m), 6.94 (1H, m), 6.92 (1H, m), 5.00 (1H, m), 3.88 (3H, m), 3.76 (3H, m), 2.20 (2H, m), 2.16 (3H, s), 2.15 (1H, m), 1.97 (2H, m), 1.71 (1H, m), 1.54 (3H, d, J = 6.1 Hz), 1.52 (3H, m), 1.40 (3H, d, J = 6.1 Hz), 1.25 (3H, d, J = 6.7 Hz), 1.21 (3H, d, J = 6.7 Hz), 1.00 (9H, s), 0.98 (1H, m), 0.23 (1H, m); ¹³C NMR (CD₂Cl₂) d 215.8, 154.2, 147.7, 143.4, 138.7, 138.1, 128.8, 128.1, 125.8, 124.3, 123.2, 123.0, 114.1, 74.9, 69.3, 63.0, 53.1, 43.5, 41.9, 40.6, 39.4, 38.2, 37.9, 37.1, 33.7, 31.2, 30.1, 28.5, 28.3 (3C), 26.3, 24.0, 21.9, 21.8, 19.5; HRMS (FAB+, (M+H)-H₂): Calculated—686.3022, Found—686.3039.



Preparation of 3.8: In a glovebox, complex **3.49** (0.11 g, 0.15 mmol) and NH₄NO₃ (0.12 g, 1.5 mmol) were dissolved in THF (8 mL), stirred for 3 h at r.t., and concentrated. The resulting solids were washed with Et₂O followed by THF to provide **3.8** (70 mg, 72%) as a bright purple solid. ¹H NMR (CD₂Cl₂) d 14.98 (1H, s), 7.48 (1H, m), 7.43 (1H, m), 7.13 (1H, m), 7.09 (1H, m), 6.98 (3H, m), 5.10 (1H, m), 3.90 (4H, m), 3.70 (2H, m), 2.23 (1H, m), 2.18 (3H, s), 2.07 (1H, m), 1.99 (1H, m), 1.93 (1H, m), 1.72 (1H, m), 1.65 (1H, m), 1.59 (1H, m), 1.55 (2H, m), 1.49 (3H, d, J = 6.1 Hz), 1.24 (3H, d, J = 6.1 Hz), 1.18 (3H, d, J = 6.7 Hz), 1.13 (3H, d, J = 6.7 Hz), 0.99 (2H, m), 0.25 (1H, m); ¹³C NMR (CD₂Cl₂) d 213.2, 154.9, 147.8, 143.2, 138.1, 137.5, 128.8, 128.4, 127.3, 124.2, 123.6 (2C), 113.1, 74.6, 67.8, 63.6, 52.8, 43.4, 42.4, 40.5, 38.0, 37.9, 37.8, 33.4, 31.1, 29.9, 28.5, 26.4, 23.7, 21.5, 20.8, 17.7; HRMS (FAB+, (M+H)-H₂): Calculated—645.7706, Found—646.2040.

General Procedure for the Determination of Initiation Rates: In a glovebox, a 4 mL vial was charged with catalyst (12 μ mol) and diluted with 1 mL C₆D₆ to create a stock solution (12 mM). A portion of the stock solution (0.25 mL, 3.0 μ mol catalyst) was added to an NMR tube and diluted with C₆D₆ (0.35 mL). The NMR tube was sealed with a septum cap and placed in an NMR spectrometer heated to 30 °C. Butyl vinyl ether (12 μ L, 0.090 mmol) was added and the disappearance of the benzylidene proton resonance was monitored by arraying the 'pad' function in VNMRj.

All reactions displayed clean first-order kinetics over a period of at least three half-lives. Spectra were baseline corrected and integrated with MestReNova Ver. 7.1.

General Polymerization Procedure: In a glovebox, an 8 mL vial with a septum cap was charged with catalyst (9.8 µmol) and THF (.84 mL) to make a stock solution (0.012 M). On a vacuum manifold, a Schlenk flask was flame-dried and charged with monomer (7.8 mmol) and THF (24 mL) to make a second stock solution (0.32 M). The monomer solution was degassed via freeze-pump-thaw (3x). An aliquot (2.0 mL, 0.64 mmol) of monomer stock solution was added via gas-tight syringe to an airtight vial with a septum cap under an argon balloon. An aliquot (0.55 mL, ca. 6.4 µmol, 1 mol %) of catalyst solution was then injected via gas-tight syringe. After stirring for 1 h at r.t., the polymerization was quenched with ethyl vinyl ether (0.1 mL) and precipitated into vigorously stirred MeOH. The precipitate was collected by vacuum filtration using either a medium or fine porosity frit and dried under vacuum.

General Method for Determining Bond Formation Probabilities: Bond formation probabilities in Scheme 2 were calculated as outlined in Reference 18.

Scheme 3.6. Probability formulas for the formation of *cis* or *trans* double bonds in the metal-catalyzed ROMP of norbornene (3.5). P_c refers to a propagating species that has just formed a *cis* double bond, while P_{tc} and P_{tt} describe species that have just formed a *trans* double bond but have different penultimate double bonds (*cis* and *trans*, respectively).

The probability of forming a *cis* double bond in a species in which the last-formed double bond is *cis* (P_c) is equivalent to the number of *cc* dyads present in the polymer divided by the total number of *cx* dyads (x = c or *t*), or (*cc*)/(*cc* + *ct*). Because $r_c = (cc)/(ct)$, this can also be written as $r_c/(1 + r_c)$. The probability of forming a *trans* double bond in P_c is equal to $1 - [r_c/(1 + r_c)]$, or $1/(1 + r_c)$. Dyad values can be determined by ¹³C NMR.^{13b}

Calculations that also take into account the identity of the penultimate double bond require triad-level NMR analysis (see reference 18 for peak assignments). For example, the probability of forming a *trans* double bond in a species in which the lastformed double bond is *trans* and the penultimate double bond is *cis* (P_{tc}) is equivalent to the proportion of *ctt* triads divided by all possible *ctx* triads, or (*ctt*)/(*ctt* + *ctc*). If we define $r_{tc} = (ctt)/(ctc)$, this can also be written as $r_{tc}/(1 + r_{tc})$. Similarly, the probability of forming a *cis* double bond in P_{tt} is equal to $1/(1+r_{tt})$, where $r_{tt} = (ttt)/(ttc)$. **Preparation of Poly(3.5) Using Catalysts 3.1–3.4 and 3.8–3.13: Poly(3.5)** was prepared according to the general procedure using catalysts **3.1–3.4** and **3.8–3.13**. NMR samples were prepared by stirring **poly(3.5)** in CDCl₃. ¹³C NMR spectral assignments were consistent with the literature.¹³



Figure 3.14. ¹³C NMR (126 MHz, CDCl₃) spectrum of poly(3.5)/3.1.



Figure 3.15. ¹³C NMR (126 MHz, CDCl₃) spectrum of poly(3.5)/3.2.



Figure 3.16. ¹³C NMR (126 MHz, CDCl₃) spectrum of **poly(3.5)/3.3** (peaks at 25.76 and 68.11 ppm are residual THF).



Figure 3.17. ¹³C NMR (126 MHz, CDCl₃) spectrum of poly(3.5)/3.4.



Figure 3.18. ¹³C (126 MHz, CDCl₃) spectrum of **poly(3.5)/3.8** (peaks at 25.76 and 68.11 ppm are residual THF).



Figure 3.19. ¹³C (126 MHz, CDCl₃) spectrum of poly(3.5)/3.9.



Figure 3.20. ¹³C (126 MHz, CDCl₃) spectrum of poly(3.5)/3.10 (peaks at 25.76 and 68.11 ppm are residual THF).



Figure 3.21. 13 C (126 MHz, CDCl₃) spectrum of poly(3.5)/3.11 (peaks at 25.76 and 68.11 ppm are residual THF).



Figure 3.22. ¹³C (126 MHz, CDCl₃) spectrum of poly(3.5)/3.12.



Figure 3.23. ¹³C (126 MHz, CDCl₃) spectrum of poly(3.5)/3.13.

Preparation of Poly(3.6) Using Catalysts 3.1–3.4 and 3.8–3.13: Poly(3.6) was prepared according to the general procedure using catalysts **3.1–3.4** and **3.8–3.13**. NMR samples were prepared by stirring **poly(3.6)** in CDCl₃. ¹³C NMR spectral assignments were consistent with the literature.¹⁵ Samples of **poly(3.6)** prepared using catalysts **3.1–3.3** were virtually identical by ¹³C NMR; thus, only the ¹³C NMR spectrum of **poly(3.6)/3.1** is presented below.



Figure 3.24. ¹³C (126 MHz, CDCl₃) spectrum of poly(3.6)/3.1.



Figure 3.25. ¹³C (126 MHz, CDCl₃) spectrum of poly(3.6)/3.4.



Figure 3.26. ¹³C (126 MHz, CDCl₃) spectrum of poly(3.6)/3.8.



Figure 3.27. ¹³C (126 MHz, CDCl₃) spectrum of poly(3.6)/3.9.



Figure 3.28. ¹³C (126 MHz, CDCl₃) spectrum of poly(3.6)/3.10.



Figure 3.29. ¹³C (126 MHz, CDCl₃) spectrum of poly(3.6)/3.11.



Figure 3.30. ¹³C (126 MHz, CDCl₃) spectrum of poly(3.6)/3.12.



Figure 3.31. ¹³C (126 MHz, CDCl₃) spectrum of poly(3.6)/3.13.



Figure 3.32. ¹³C (126 MHz, CDCl₃) spectrum of **poly(3.6)/3.4** at 0 °C.



Figure 3.33. ¹³C (126 MHz, CDCl₃) spectrum of poly(3.6)/3.4 at 40 °C.

Preparation of Poly(3.7) Using Catalysts 3.1–3.3: Poly(3.7) was prepared according to the general procedure using catalysts **3.1–3.3**. NMR samples were prepared by stirring **poly(3.7)** in CDCl₃. Major ¹³C NMR spectral assignments were consistent with the literature on *cis,syndiotactic* **poly(3.7)**,^{6a} while the ¹³C chemical shifts of the minor compound were consistent with those reported for the *trans,syndiotactic* **poly(3.7)**.^{5b} Samples of **poly(3.7)** prepared using catalysts **3.1–3.3** were virtually identical by ¹³C NMR; thus, only the ¹³C NMR spectrum of **poly(3.7)**/**3.1** is presented below.



Figure 3.34. ¹³C NMR (126 MHz, CDCl₃) spectrum of poly(3.7)/3.1.



Figure 3.35. ¹H-¹³C HSQC (CDCl₃) spectrum of **poly(3.7)/3.1**.

Preparation of Poly(3.14) Using Catalysts 3.1, 3.4, and 3.9: Poly(3.14) was prepared according to the general procedure using catalysts **3.1, 3.4, 3.9**. NMR samples were prepared by stirring **poly(3.14)** in $(CD_3)_2CO$. ¹³C NMR spectral assignments were consistent with the literature.¹⁹



Figure 3.36. ¹³C NMR (126 MHz, (CD₃)₂CO) spectrum of poly(3.14)/3.1.


Figure 3.37. ¹³C NMR (126 MHz, (CD₃)₂CO) spectrum of poly(3.14)/3.4.



Figure 3.38. ¹³C NMR (126 MHz, (CD₃)₂CO) spectrum of **poly(3.14)/3.9**.

Preparation of Poly(3.15) Using Catalysts 3.1, 3.4, and 3.9: Poly(3.15) was prepared according to the general procedure using catalysts **3.1, 3.4**, and **3.9**. NMR samples were prepared by stirring **poly(3.15)** in CD_2Cl_2 . ¹³C NMR spectral assignments were consistent with the literature.¹⁵



Figure 3.39. ¹³C NMR (100 MHz, CD₂Cl₂) spectrum of poly(3.15)/3.1.



Figure 3.40. ¹³C NMR (100 MHz, CD₂Cl₂) spectrum of **poly(3.15)/3.4**.



Figure 3.41. ¹³C NMR (100 MHz, CD₂Cl₂) spectrum of poly(3.15)/3.9.

Preparation of Poly(3.16) Using Catalysts 3.1 and 3.4: Poly(3.16) was prepared according to the general procedure using catalysts **3.1** and **3.4**. NMR samples were prepared by stirring **poly(3.16)** in CDCl₃. ¹³C NMR spectral assignments were consistent with the literature.²⁰



Figure 3.42. ¹³C NMR (100 MHz, CDCl₃) spectrum of poly(3.16)/3.1.



Figure 3.43. ¹³C NMR (100 MHz, CDCl₃) spectrum of poly(3.16)/3.4.

Preparation of Poly(3.17) Using Catalysts 3.1, 3.4, and 3.9: Poly(3.17) was prepared according to the general procedure using catalysts **3.1**, **3.4**, and **3.9**. NMR samples were prepared by stirring **poly(3.17)** in CDCl₃. ¹³C NMR spectral assignments were consistent with the literature.²²



Figure 3.44. ¹³C NMR (126 MHz, CDCl₃) spectrum of poly(3.17)/3.1 (peak at 29.86 is residual "grease").



Figure 3.45. ¹³C NMR (126 MHz, CDCl₃) spectrum of poly(3.17)/3.4.



Figure 3.46. ¹³C NMR (126 MHz, CDCl₃) spectrum of poly(3.17)/3.9.

Preparation of Poly(3.18) Using Catalysts 3.1 and 3.4: Poly(3.18) was prepared according to the general procedure using catalysts **3.1** and **3.4**. NMR samples were prepared by stirring **poly(3.18)** in CDCl₃. ¹³C NMR spectral assignments were consistent with the literature.²³



Figure 3.47. ¹³C NMR (100 MHz, CDCl₃) spectrum of poly(3.18)/3.1.



Figure 3.48. ¹³C NMR (100 MHz, CDCl₃) spectrum of poly(3.18)/3.4.



Figure 3.49. ¹H NMR (500 MHz, THF-d₈) spectrum of **3.1**.



Figure 3.50. ¹³C NMR (126 MHz, CD₂Cl₂) spectrum of 3.1.



Figure 3.51. ¹H NMR (500 MHz, CD₂Cl₂) spectrum of **3.2**.



Figure 3.52. ¹³C NMR (126 MHz, CD₂Cl₂) spectrum of **3.2**.



Figure 3.53. ¹H NMR (500 MHz, C₆D₆) spectrum of **3.3**.



Figure 3.54. ¹³C NMR (126 MHz, C₆D₆) spectrum of **3.3**.



Figure 3.55. ¹H NMR (500 MHz, CD₂Cl₂) spectrum of **3.8**.



Figure 3.56. ¹³C NMR (126 MHz, CD₂Cl₂) spectrum of 3.8.



Figure 3.57. Free energies and enthalpies (in parentheses) for interconversion between ruthenium alkylidenes *anti*- and *syn*-(R,R)-3.32 via alkylidene rotation. All energies are with respect to the ruthenium alkylidene complex *anti*-(R,R)-3.4 and are given in kcal/mol.



Figure 3.58. Free energies and enthalpies (in parentheses) for interconversion between ruthenium alkylidenes *anti*- and *syn*-(R,S)-**3.32** via alkylidene rotation. All energies are with respect to the ruthenium alkylidene complex *anti*-(R,R)-**3.4** and are given in kcal/mol.



Figure 3.59. *Endo* transition states in the [2 + 2] cycloaddition for the polymerization of monomer 3.6 with catalyst 3.30. Energies are with respect to the separated ruthenium alkylidene and monomer 3.6.



Figure 3.60. Bottom-bound transition states in the [2 + 2] cycloaddition for the polymerization of monomer 3.6 with catalyst 3.30. Energies are with respect to the separated ruthenium alkylidene and monomer 3.6.



M06(SMD,THF)/SDD-6-311+G(d,p)//B3LYP/SDD-6-31G(d)

M06-2X(SMD,THF)/SDD-6-311+G(d,p)//B3LYP/SDD-6-31G(d)

Figure 3.61. *Endo* transition states in the [2 + 2] cycloaddition for the polymerization of monomer **3.6** with catalyst (*R*,*R*)-**3.32**. Energies are with respect to the separated ruthenium alkylidene and monomer **3.6**.



Figure 3.62. Bottom-bound transition states in the [2 + 2] cycloaddition for the polymerization of monomer 3.6 with catalyst (R,R)-3.32. Energies are with respect to the separated ruthenium alkylidene and monomer 3.6.



Figure 3.63. *Endo* transition states in the [2 + 2] cycloaddition for the polymerization of monomer **3.6** with catalyst (*R*,*S*)-**3.32**. Energies are with respect to the separated ruthenium alkylidene and monomer **3.6**.



M06(SMD,THF)/SDD-6-311+G(d,p)//B3LYP/SDD-6-31G(d)

M06-2X(SMD,THF)/SDD-6-311+G(d,p)//B3LYP/SDD-6-31G(d)

Figure 3.64. Bottom-bound transition states in the [2 + 2] cycloaddition for the polymerization of monomer 3.6 with catalyst (*R*,*S*)-3.32. Energies are with respect to the separated ruthenium alkylidene and monomer 3.6.



Figure 3.65. DSC curve for *cis,syndiotactic* poly(3.5) prepared with catalyst 3.1.



Figure 3.66. TGA curve for *cis,syndiotactic* poly(3.5) prepared with catalyst 3.1.



Figure 3.67. TGA curve for *trans,atactic* **poly(3.5)** prepared with (1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(*o*-isopropoxyphenylmethylene)-ruthenium.