Ring-opening metathesis polymerization of 3-substituted cyclooctenes initiated by group 6 alkylidene complexes

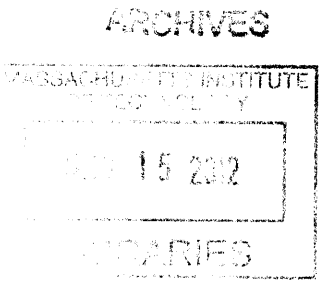
by

Daniel James Kozera

B.Sc. (Hons.) in Chemistry
University of Winnipeg, Winnipeg, MB, Canada

Submitted to the Department of Chemistry
in Partial Fulfillment of the Requirements for the Degree of

Master of Science in Chemistry



at the
Massachusetts Institute of Technology
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Signature of author: .....
Department of Chemistry
August 1, 2012

Certified by: .....
Richard R. Schrock
Frederick G. Keyes Professor of Chemistry
Thesis Supervisor

Accepted by: .....
Robert W. Field
Chairman, Departmental Committee on Graduate Students

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Abstract

The highly *cis*,head-to-tail (*cis*,HT) selective ring-opening metathesis polymerization of 3-substituted cyclooctenes (3-**R**COE; **R** = methyl, hexyl, phenyl) initiated by high oxidation state M and W alkylidene complexes is described herein. W(N*t*Bu)($CHCMe_3$)(pyr)(OHMT) combined high *cis*,HT selectivity (>98% *cis*,HT) with high activity, achieving 76% conversion of 5000 equivalents of 3-**Hex**COE after 24 h at room temperature. The resulting *cis*,HT-poly(3-**R**COE)s (**R** = Me, Hex) were isolated, characterized by ^{1}H and ^{13}C NMR, size-exclusion chromatography, and differential scanning calorimetry, and hydrogenated to generate the corresponding saturated polymer.

Thesis supervisor: Richard R. Schrock

Title: Frederick G. Keyes Professor of Chemistry

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List of abbreviations

Ad	1-adamantyl
AIBN	azobisisobutyronitrile
Anal. Calcd	elemental analysis calculated
Ar'	2,6-dimethylphenyl
ca.	*circa*
coe	cyclooctene
d	day(s)
dme	dimethoxyethane
dppp	1,3-bis(diphenylphosphino)propane
DSC	differential scanning calorimetry
equiv	molar equivalents
Et	ethyl
h	hour(s)
Hex	hexyl
HIPTOH	2,6-bis(2,4,6-triisopropylphenyl)phenol
HMTI	2,6-bis(2,4,6-trimethylphenyl)iodobenzene
HMTOH	2,6-bis(2,4,6-trimethylphenyl)phenol
HRMS	high-resolution mass spectrometry
*i*Pr	isopropyl
${}^{n}J_{AB}$	NMR coupling constant between atoms A and B through n bonds
m	meta
LLDPE	linear low-density polyethylene
M	molar (moles/liter)
MAP	monoalkoxide monopyrrolide complex

Me	methyl
Me_2Pyr	2,5-dimethylpyrrolide
min	minute(s)
mL	milliliter
mM	millimolar
mmol	millimole(s)
M_n	number average molecular weight
mol	mole(s)
M_w	weight average molecular weight
NBS	*N*-bromosuccinimide
NMR	nuclear magnetic resonance
ODFT	2,6-bis(pentafluorophenyl)phenoxide
o/n	overnight (generally 12-16 hours)
OHIPT	2,6-bis(2,4,6-triisopropylphenyl)phenoxide
OHMT	2,6-bis(2,4,6-trimethylphenyl)phenoxide
OTf	trifluoromethanesulfonate
p	para
PDI	polydispersity index
Ph	phenyl
pyr	pyrrolide
ROMP	ring-opening metathesis polymerization
rt	room temperature (approximately 22 °C)
SEC	size-exclusion chromatography
T_g	glass transition temperature
THF	tetrahydrofuran

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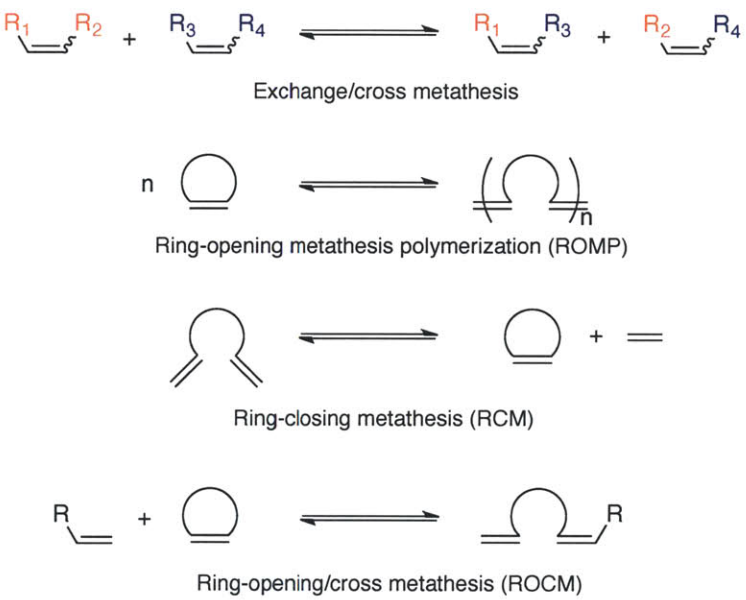
1 Introduction

1.1 Olefin metathesis

Since it was first disclosed in patents[1] and later reported in the literature,[2,3] olefin metathesis – that is, the exchange of substituents between pairs of olefins – has become a reaction of great importance in organic and polymer chemistry and the many disciplines they impact.[4,5] Four basic types of olefin metathesis reactions – exchange/cross metathesis, ring-opening metathesis polymerization (ROMP), ring-closing metathesis (RCM), and ring-opening/cross metathesis (ROCM) – are depicted in Scheme 1.



Scheme 1. Varieties of olefin metathesis. The exchange reaction is known as cross metathesis when $R_1 \neq R_3$ or R_4.

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1 Anderson, A. W.; Merckling, N. G. (Du Pont de Nemours & Co.) Polymeric Bicyclo-(2,2,1)-2-Heptene. U.S. Patent 2,721,189, Oct 18, 1955.

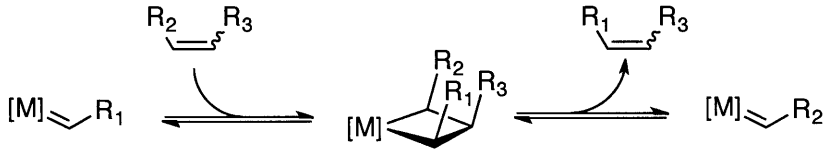
2 Truett, W. L.; Johnson, D. R.; Robinson, I. M.; Montague, B. A. *J. Am. Chem. Soc.* **1960**, *82*, 2337-2340.

[3] Banks, R. L.; Bailey, G. C. *Ind. Eng. Chem. Prod. Res. Dev.* **1964**, *3*, 170-173.

[4] Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, CA, 1997.

[5] For applications in organic and polymer chemistry, see: Grubbs, R. H., Ed. *Handbook of Metathesis*; Wiley-VCH: Weinheim, Germany, 2003; Vol. 2 and 3.

The accepted mechanism for olefin metathesis (Scheme 2) was first proposed by Hérrison and Chauvin.[6] A 2+2 cycloaddition reaction between an olefin and a metal-carbon double bond (i.e. an alkylidene) gives a metallacyclobutane intermediate. Breakup of the metallacycle either regenerates starting materials or generates a new olefin product and a new alkylidene.



Scheme 2. Chauvin's olefin metathesis mechanism.

Early metathesis catalysts were typically ill-defined. For example, in 1967 the ROMP of 8- and 10-membered cyclic olefins was reported using the catalytic system 4:1:1 $WCl_6/EtAlCl_2$/ethanol.[7] Unsurprisingly, early systems were relatively non-selective and hence gave a distribution of olefinic products; this, along with their limited tolerance of functionality, limited their usefulness. Thus, well-defined olefin metathesis catalysts that could be studied and altered on a molecular level were sought. A milestone was reached in 1974, when the first transition metal alkylidene complex, $Ta(CH_2CMe_3)_3(CHCMe_3)$, was reported.[8] This was followed six years later by a report detailing the first isolable, metathetically active alkylidene complexes, which were based on Nb, Ta, and W.[9] In the ensuing decades, further research led to more stable, active,

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[6] Hérisson, P. J.-L.; Chauvin, Y. *Makromol. Chem.* **1971**, *141*, 161-176.

[7] Calderon, N.; Ofstead, E. A.; Judy, W. A. *J. Polym. Sci., Part A-1: Polym. Chem.* **1967**, *5*, 2209-2217.

[8] Schrock, R. R. *J. Am. Chem. Soc.* **1974**, *96*, 6796-6797.

[9] Schrock, R.; Rocklage, S.; Wengrovius, J.; Rupprecht, G.; Fellmann, J. *J. Mol. Catal.* **1980**, *8*, 73-83.

and selective catalysts through alterations of their molecular structure.[4,10] Currently, the majority of olefin metathesis research falls into one of two areas: "Schrock-type" catalysts (d^0 Mo or W imido alkylidene complexes) and "Grubbs-type" catalysts (Ru carbene complexes) (Figure 1).

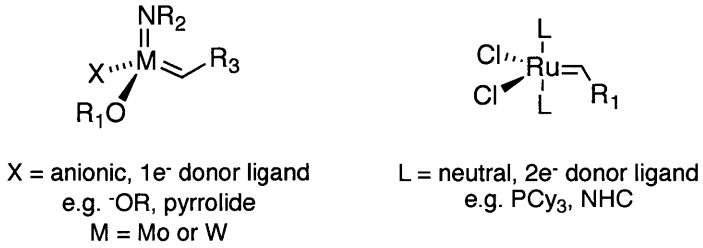

Figure 1. General structure for typical "Schrock-type" (left) and "Grubbs-type" (right) olefin metathesis catalysts.

Historically, the most common Mo and W catalysts have been bisalkoxide complexes (X = $^-$OR in Figure 1). However, in recent years monoalkoxide monopyrrolide (MAP) complexes (X = pyrrolide (pyr) or substituted pyrrolide in Figure 1) have emerged as highly reactive and selective alternatives.[11] The MAP species can be prepared from bispyrrolide precursors by addition of one equivalent of an alcohol.

As mentioned, the main benefit of well-defined olefin metathesis catalysts is the ability to modify them on a molecular level to improve both activity and selectivity. One area of particular interest is *Z* selectivity. In general, *E* olefins are lower in energy than *Z* olefins; thus, the equilibrium ratio of *E* and *Z* olefin products for a given metathesis reaction is typically skewed towards *E*. For example, *trans*-2-butene is ca. 1 kcal/mol

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[10] (i) Schrock, R. R. The Discovery and Development of High Oxidation State Mo and W Imido Alkylidene Complexes for Alkene Metathesis. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Mannheim, Germany, 2003; Vol. 1, pp 8-32. (ii) Nguyen, S. T.; Trnka, T. M. The Discovery and Development of Well-Defined, Ruthenium-Based Olefin Metathesis Catalysts. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Mannheim, Germany, 2003; Vol. 1, pp 61-85.

[11] Schrock, R. R. *Chem. Rev.* **2009**, *109*, 3211-3226 and references therein.

more stable than *cis*-2-butene,[12] an energy difference that corresponds to a ratio of about 5.4:1 *trans*:*cis*-2-butene at equilibrium at 25 °C. Since olefin metathesis is generally thermodynamically controlled, catalysts typically give mixtures of *E* and *Z* products approaching this ratio. However, in 2009, highly *Z*-selective Mo and W MAP catalysts were reported[13,14] along with their applications in ROMP,[13] cross-coupling,[13] and terminal olefin homocoupling[14] reactions. Additional examples of *Z*-selective catalysts were subsequently reported for Mo[15] and W[16,17] as well as Ru[18,19]. It is proposed that *Z* selectivity in the Mo and W cases arises from the size mismatch between a comparatively small imido (or oxo) ligand and a large alkoxide. This forces any substituents in the intermediate metallacyclobutane to point away from the large alkoxide. Breakup of this metallacycle necessarily generates a *Z* olefin (Figure 2).

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[12] Akimoto, H.; Sprug, J. L; Pitts, J. N., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 4850-4855.

[13] Flook, M. M.; Jiang, A. J.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 7962-7963.

[14] Jiang, A. J.; Zhao, Y.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 16630-16631.

[15] Townsend, E. T.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* [Online early access]. DOI: 10.1021/ja303220j. Published online: Jun 26, 2012.

[16] Peryshkov, D. V.; Schrock, R. R.; Takase, M. K.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2011**, *133*, 20754-20757.

[17] Marinescu, S. C.; Schrock, R. R.; Müller, P.; Takase, M. K.; Hoveyda, A. H. *Organometallics* **2011**, *30*, 1780-1782.

[18] Endo, K.; Grubbs, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 8525-8527.

[19] Keitz, B. K.; Endo, K.; Patel, Paresma. R.; Herbert, M. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **2012**, *134*, 693-699.

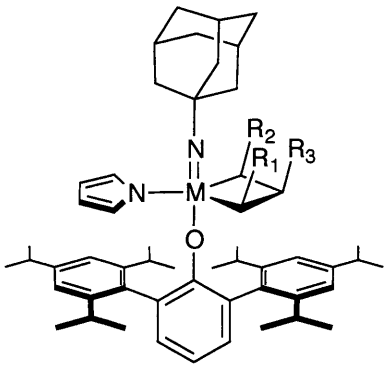


Figure 2. Metallacyclobutane in systems with a large alkoxide and a small imido (or oxo) ligand. The size of the alkoxide precludes the metallacycle substituents from pointing toward the alkoxide. M = Mo or W

1.2 Ring-opening metathesis polymerization (ROMP)

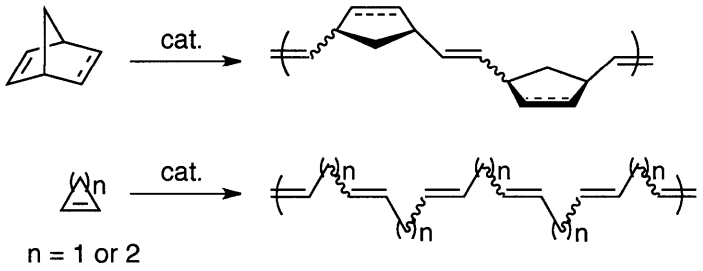
ROMP was the first olefin metathesis reaction to be reported, and research in this area has been fruitful. Indeed, many ROMP polymers have been commercialized.[4] These include Vestenamer 8012 and 6213 (poly(cyclooctene)s used as rubber additives), Zeonex (hydrogenated poly(norbornene) and related monomers useful in optics), and poly(dicyclopentadiene)s such as Telene (used to make very large objects by injection molding, e.g. body panels for trucks, buses, and agricultural equipment).[4]

A chief determinant of a polymer's physical properties is its microstructure, including stereo- and regiochemistry.[20] Thus, controlling polymer microstructure can be used to tailor a polymer's physical properties for a given application. For example, the aftorementioned poly(cyclooctene)s, Vestenamers 8012 and 6213, differ primarily in the *cis/trans* ratio of their backbone double bonds. Vestenamer 8012, which contains ca. 80% *trans* olefins, has a higher melting point and greater crystallinity than Vestenamer

[20] Devaux, J.; Demoustier-Champagne, S. Polymer Chemistry and Microstructure. In *Comprehensive Analytical Chemistry*; Chalmers, J. M., Meier, R. J., Eds.; Elsevier: Amsterdam, 2008; Vol. 53, pp 13-63.

6213, which contains ca. 60% *trans* olefins. This makes Vestenamer 6213 more suitable for low-temperature applications.[21]

In the past two decades, Mo- and W-catalyzed ROMP of high-strain cyclic olefins, including 2,3-disubstituted norbornene and norbornadiene derivatives and 3,3-disubstituted cyclopropene derivatives, has been accomplished with impressive stereoregularity.[22] Since relief from monomer strain is a primary driving force for this reaction (and ring-opening polymerizations in general),[23] these monomers are well-suited to undergo ROMP (Scheme 3).



Scheme 3. Polymers that would result from ROMP of unsubstituted norborn(adi)ene (top), cyclopropene (bottom, n=1), and cyclobutene (bottom, n=2).

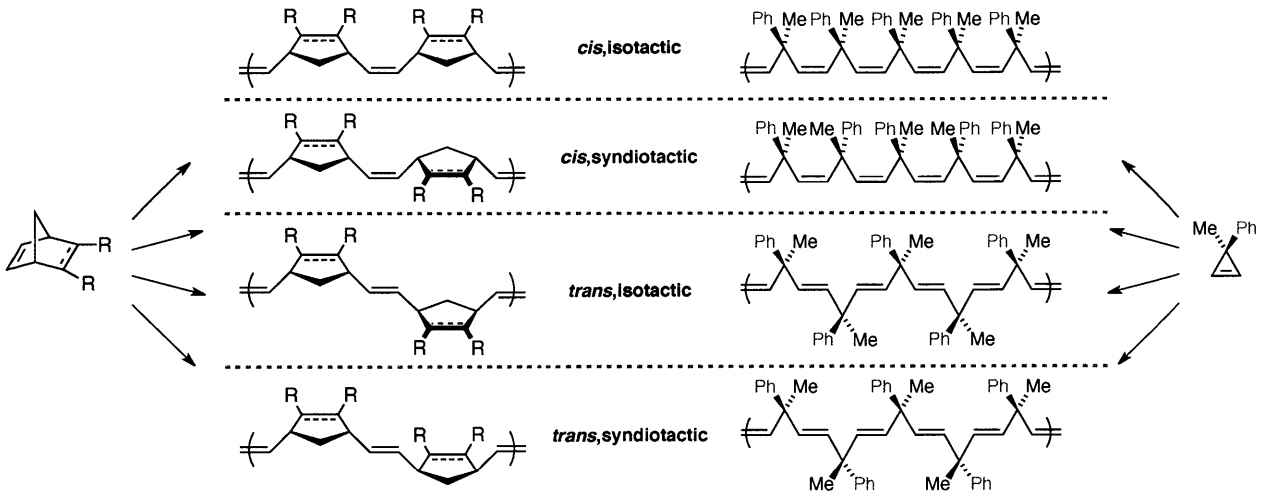
When substituted, the polymer microstructure resulting from ROMP of these types of monomers depends not only on the *cis/trans* nature of the double bonds, but also the polymer's tacticity; that is, the stereochemistry of the chiral centers in the polymer relative to their neighbors. Thus, the four possible regular structures derived from 2,3-disubstituted norborn(adi)enes and 3,3-disubstituted cyclopropenes are *cis*-isotactic, *cis*-syndiotactic, *trans*-isotactic, and *trans*-syndiotactic (Scheme 4). Highly regular polymers have been prepared for each of the four possible microstructures for certain 2,3-disubstituted norbornadienes as well as three of the four for 3,3-

[21] Schneider, W. A.; Müller, M. F. *J. Mol. Catal.* **1988**, *46*, 395-403.

[22] For an overview, see: Schrock, R. R. *Dalton Trans.* **2011**, *40*, 7484-7495.

[23] Bielawski, C. W.; Grubbs, R. H. *Prog. Polym. Sci.* **2007**, *32*, 1-29.

methylphenylcyclopropene (MPCP).[24,25,26,27,28,29] Only *trans*,isotactic-poly(MPCP) remains unknown in regular form.



Scheme 4. Possible microstructures for 2,3-disubstituted norborn(adi)enes and 3,3-methylphenylcyclopropene (MPCP). Highly regular polymers have been prepared for all but *trans*,isotactic-poly(MPCP) (see text for references).

By contrast, less focus has been placed on the less strained cyclic olefins, such as cyclopentene, cycloheptene, and cyclooctene and their derivatives. This is likely because their relative lack of strain (Table 1) results in a number of potential difficulties not encountered with highly strained monomers.

---

[24] *Cis*,isotactic-poly(2,3-R_2norbornadiene) (R = CF_3, CO_2Me): McConville, D. H.; Wolf, J. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 4413-4414.

[25] *Cis*,syndiotactic-poly(2,3-(CO_2Me)norbornadiene): see Ref. 13.

[26] *Trans*,syndiotactic-poly(2,3-R_2norbornadiene) (R = CF3, CO2Me): Bazan, G. C.; 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*, 8378-8387.

[27] *Trans*,isotactic-poly(2,3-(CO_2Me)norbornadiene): (i) Flook, M. M.; Börner, J.; Kilyanek, S. M.; Gerber, L. G.; Schrock, R. R. *Organometallics*. Submitted. (ii) Flook, M. M. *Z*-Selective Olefin Metathesis Processes and *Cis*/Syndioselective ROMP with High Oxidation State Molybdenum Alkylidenes. Ph.D. Thesis, Massachusetts Institute of Technology, February 2012.

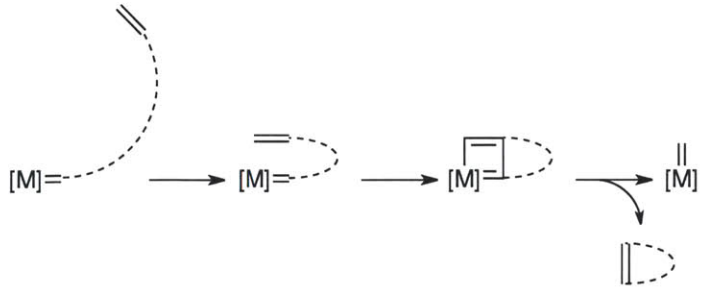
[28] *Cis*,isotactic- and *trans*,syndiotactic-poly(MPCP): Singh, R.; Schrock, R. R. *Macromolecules* **2008**, *41*, 2990-2993.

[29] *Cis*,syndiotactic-poly(MPCP): Flook, M. M.; Gerber, L. C. H.; Debelouchina, G. T.; Schrock, R. R. *Macromolecules* **2010**, *43*, 7515-7522.

Table 1. Ring strain in some cyclic olefins[30] and thermodynamics of their ROMP[31]. All values in kcal/mol.

Monomer	$\Delta H_{f\ exp}^{\circ}$	$\Delta H_{f\ calc}^{\circ}$	Strain	cis/trans content of polymer	ΔH°	ΔS°	ΔG°
cyclopropene	66.6	12.1	54.5				
cyclobutene	37.5	6.9	30.6	*cis*	-28.9	-12.4	-25.1
cyclopentene	8.6	1.8	6.8	*cis*	-3.7	-12.4	-0.1
				trans	-4.3	-12.4	-0.6
cyclohexene	-0.8	-3.3	2.5	*cis*	0.5	-7.4	1.5
				trans	-0.5	-6.7	1.7
cycloheptene	-1.8	-8.5	6.7	70% *trans*	-4.3	-8.8	-1.7
***cis*-cyclooctene**	-6.2	-13.6	7.4	48% *trans*	-3.1	-2.2	-3.1
norbornene	24.7	-2.5	27.2	45% *trans*	-14.9	-12.0	-11.2
norbornadiene	59.7	25.0	34.7				

For one, some low-strain monomers are unpolymerizable due to a positive free energy of reaction; in these cases, the positive -TΔS term is not overcome by the relatively modest ΔH term. One example is cyclohexene, which does not form high polymer at any temperature.[4] Furthermore, as cleavage of the double bond in a low-strain monomer is not very exothermic, olefins in the resulting chain have a tendency to undergo secondary reactions: in particular, they may "backbite" to form cyclic oligomers (Scheme 5). Indeed, though cyclohexene does not polymerize, at -77 °C a 5M solution of cyclohexene containing a metathesis catalyst will form a small amount of 2-6 unit cyclic oligomers.[4]

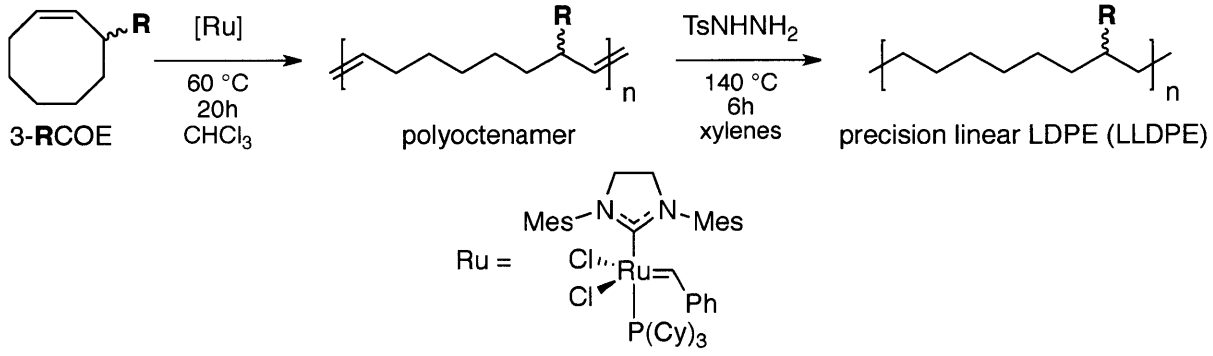


Scheme 5. Backbiting of olefins in a growing chain, forming cyclic oligomers.

[30] Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377-2386.
[31] Ref 4, p 226.

Also, since the equilibrium between monomer, oligomer, and polymer is not far toward polymer (as it is with strained monomers), the polymerization reactions are highly temperature- and concentration-dependent; lower temperatures and higher initial monomer concentrations push the equilibrium more toward polymer formation. For example, the equilibrium concentration cyclooctene and cyclic oligomers thereof is about 0.002 M and 0.25 M, respectively, at 25 °C. Hence, no poly(cyclooctene) is formed when $[coe]_0 = 0.25$ M, while ca. 4.75 M poly(cyclooctene) is formed when $[coe]_0 = 5$ M.[32]

Despite these issues, ROMP of less-strained cyclic olefins remains a topic of interest as ROMP is a convenient way to generate strictly linear (i.e. unbranched) polymers with defined substitution patterns on the backbone. In 2011, a report from Hillmyer *et al.*[33] described the highly *trans*- and head-to-tail-selective (*trans*,HT) ROMP of a series of 3-substituted cyclooctenes (3-**R**COE; **R**=Me, Et, Hex, Ph) using Grubbs' 2nd generation catalyst (**G2**). The resulting poly(3-**R**COE) could be hydrogenated to generate precision linear low-density polyethylene (LLDPE) (Scheme 6).



Scheme 6. ROMP of 3-substituted cyclooctenes catalyzed by **G2** and subsequent hydrogenation to LLDPEs.

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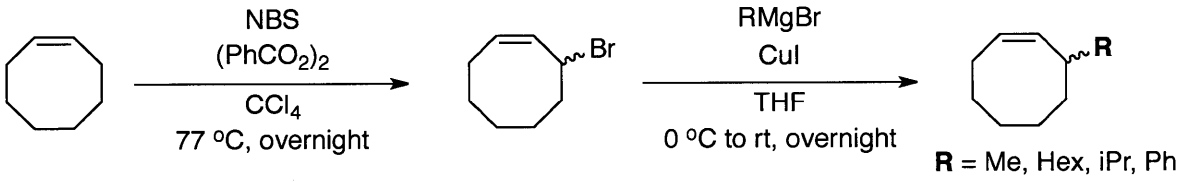
[32] Scott, K. W.; Calderon, N.; Ofstead, E. A.; Judy, W. A.; Ward, J. P. *Adv. Chem. Ser.* **1969**, *91*, 399-418.

[33] Kobayahsi, S.; Pitet, L. M.; Hillmyer, M. A. *J. Am. Chem. Soc.* **2011**, *133*, 5794-5797.

Based on the high stereoregularity exhibited by many Mo and W MAP catalysts in the ROMP of high-strain monomers, we sought to apply them to give highly stereoregular polymers of 3-substituted cyclooctenes with exclusively *cis* double bonds.

2 Results and discussion

Three of the monomers used by Hillmyer *et al.* – 3-**Me**COE, 3-**Hex**COE, and 3-**Ph**COE – as well as the more hindered 3-**iPr**COE, were prepared in two steps from cyclooctene (**Scheme 7**). Allylic bromination of cyclooctene was found to work best under air with

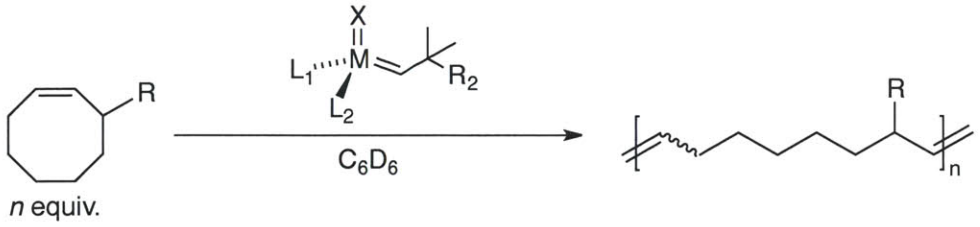


Scheme 7. Synthesis of 3-RCOE monomers from cyclooctene.

benzoyl peroxide as the radical initiator; the literature procedure, using AIBN in an inert (N_2) atmosphere, gave lower yields. 3-bromocyclooctene was then treated with an appropriate Grignard reagent in the presence of CuI to give the 3-alkyl or 3-arylcyclooctene, which was purified by fractional vacuum distillation.

Initially, reactions were performed on an NMR scale to facilitate monitoring. Therefore, ROMP of 3-**Me** and 3-**Hex**, 3-**Ph**, and 3-**iPr**COE were performed in an NMR tube with 15-100 equiv. monomer (1-5 mol% catalyst) and at low concentration ([3-**R**COE]$_0$ = 0.6-1.1 M). The data from these trials are summarized in Table 2.

Table 2. Summary of ROMP reaction in C_6D_6 solution. R_2 = Ph for all but Entry 3, where R_2 = Me. [a]trans,HT polymer ≈ 65%, trans oligomer ≈ 20%. TO = turnovers. OF_6 = $OC(CF_3)_2Me$



	R	M	X	L_1	L_2	n	$[3RCOE]_0$	Temp	Time	% conv	% cis,HT	TO
1	Me	Mo	NAd	pyr	OHMT	20	0.5 M	rt	1 h	39	70	8
									1 d	96	40	19
2	Me	Mo	NAd	pyr	OHIPT	50	1.1 M	rt	1 d	22	n/d	11
									4 d	62	75	31
3	Me	W	O	Me_2Pyr	OHMT	20	0.6 M	rt	5 d	40	75	8
									19 d	92	65	18
4	Me	Mo	NAd	OF_6	OF_6	75	0.7 M	rt	1 h	20	n/d	15
									1 d	>99	15[a]	74
5	Hex	Mo	NAd	pyr	OHMT	50	0.6 M	rt	1 d	16	n/d	8
									5 d	75	87	38
6	Hex	Mo	NAd	pyr	OHMT	50	0.6 M	40 °C	1 d	57	92	29
									5 d	87	76	44
7	Hex	Mo	Nar	pyr	OHMT	50	1.0 M	60 °C	1 d	2	n/d	1
									3.5 d	19	n/d	10
8	Hex	Mo	NAd	pyr	OHIPT	15	0.6 M	80 °C	10 d	70	70	10
									30 d	73	73	11
9	Hex	Mo	NAd	OF_6	OF_6	40	0.6 M	rt	4 h	11	n/d	4
									2 d	89	n/d	36
10	Ph	Mo	NAd	pyr	OHMT	50	1.1 M	rt	1 d	7	n/d	4
									5 d	94	n/d	47
11	iPr	Mo	NAd	pyr	OHMT	50	0.9 M	80 °C	1 d	<1	n/d	<1
									3 d	10	n/d	5

Conversion was determined by comparison to an internal standard (anthracene). While peaks in the olefinic region of the spectrum were not always well-resolved, the coupling constants that could be observed, as well as comparison to the spectra reported by Hillmyer *et al.* for the *trans*,HT polymers, were used to provide insight on the *cis/trans* content and regiochemistry of the polymer.

Apart from the bisalkoxide Mo(NAd)(CHCMe$_2$Ph)(OF$_6$)$_2$ (OF$_6$ = OC(CF$_3$)$_2$Me), all catalysts used were *cis*-selective: where determinable, *cis* olefins comprised >95% of the products. Of the *cis*-selective catalysts, Mo(NAd)(CHCMe$_2$Ph)(pyr)(OHMT) (**1**) proved the most active, achieving >95% of 20 equiv. of 3-**Me**COE after 1 d at rt. Unfortunately, while the desired *cis*,HT polymer was formed, it was accompanied by formation of other products; these were assigned as cyclic oligomers containing *cis* linkages. In most cases, the concentration of oligomer increased over time. The series of reaction mixture ^{1}H NMR spectra for the ROMP of 3-**Me**COE catalyzed by **1** is representative and is shown in Figure 3.

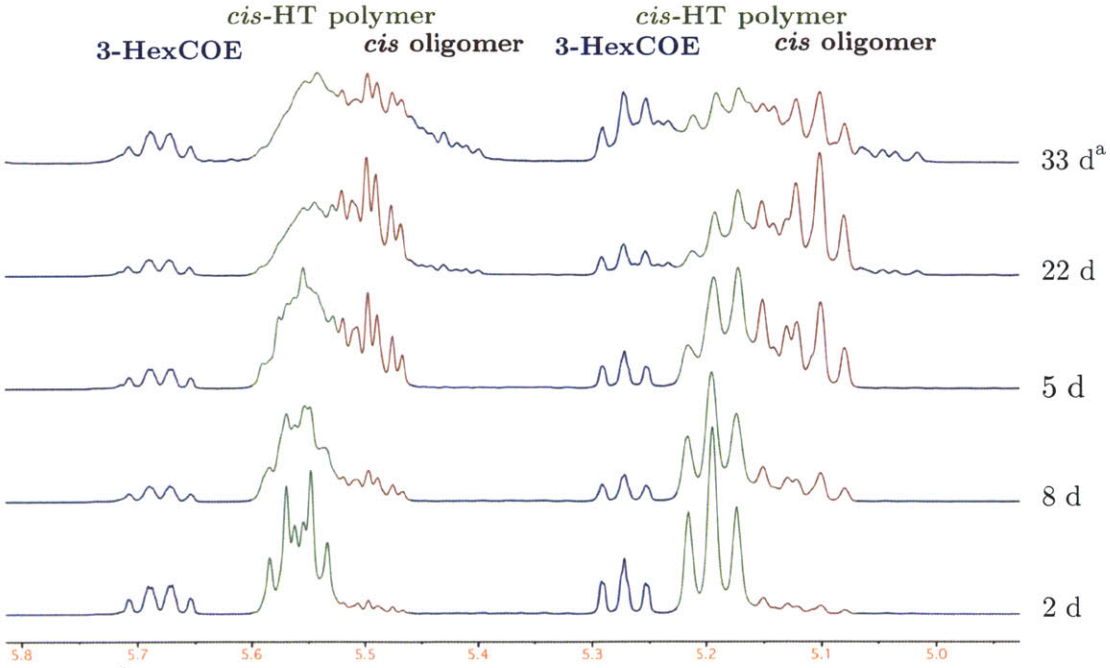


Figure 3. ^{1}H NMR spectra at different times for the ROMP of 3-**Hex**COE at 40° C catalyzed by **1** (**Table 2**, entry 6). [a]Includes 3 d at 60 °C and 2 d at 80 °C

Having established some reactivity trends among both the catalysts and monomers by performing the polymerizations at relatively low concentrations, we next performed the reaction solvent-free, i.e. in neat monomer. This was expected to both increase the reaction rate and decrease the amount of cyclic oligomer present.

Compound **1** was used for initial trials as it had proven to be the most active *cis*-selective catalyst.

Gratifyingly, when 50 equivalents of neat 3-**Me**COE were added to solid **1** at room temperature, the mixture grew extremely viscous in <30 s. Analysis of aliquots by ^{1}H NMR spectroscopy showed that >99% of the monomer was consumed in 1 h, and the only new observable resonances were those of *cis*,HT-poly(3-**Me**COE) (>98% *cis*,HT polymer) (Figure 4).

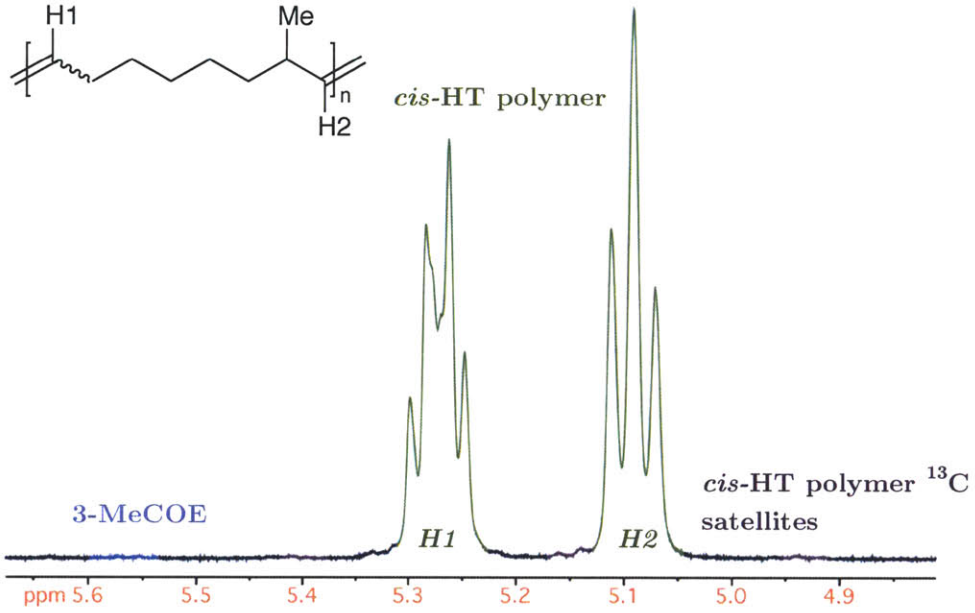


Figure 4. Olefinic region of the ^{1}H NMR spectrum of poly(3-**Me**COE) prepared by ROMP of 50 equiv. of 3-**Me**COE initiated by **1**.

Similarly, ROMP of 100 equiv. of 3-**Hex**COE initiated by **1** was 98% complete after 24 h and gave *cis*,HT polymer as the only observable product (>98%) (**Figure 5**).

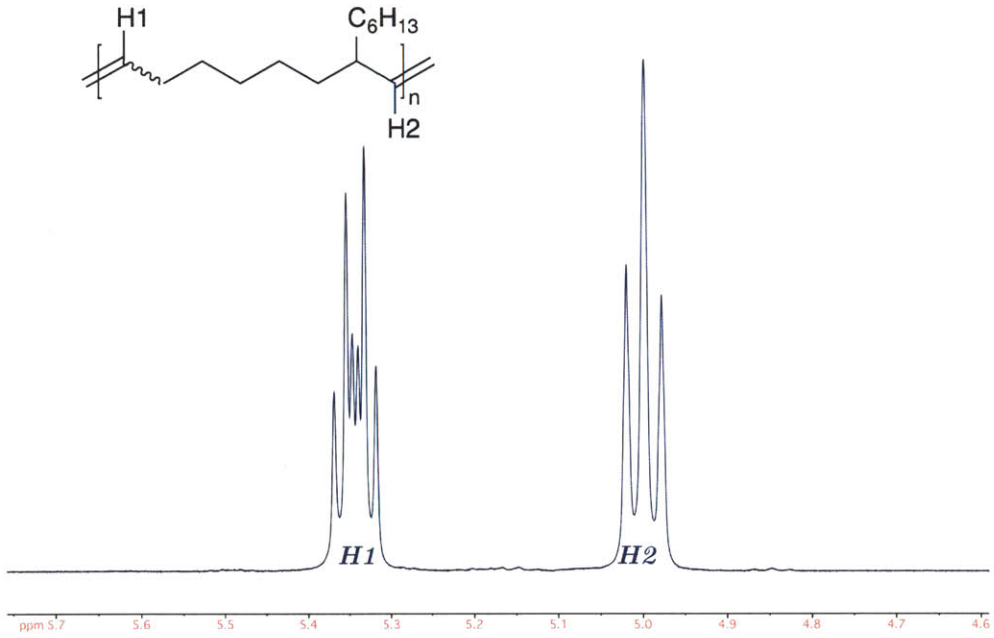


Figure 5. Olefinic region of the ^{1}H NMR spectrum of poly(3-**Hex**COE) prepared by ROMP of 100 equiv. of 3-**Hex**COE initiated by **1**.

The more hindered 3-**Ph**COE underwent ROMP to give >90% *cis*-HT polymer, with 82% conversion of 100 equivalents of monomer after 21 h using **1** as the initiator (**Figure 6**). An additional product was also generated (red in **Figure 6**) that could not be identified. It is possible that these peaks correspond to cyclic oligomer. However, they may also arise from trace impurities in the monomer, which proved difficult to remove.

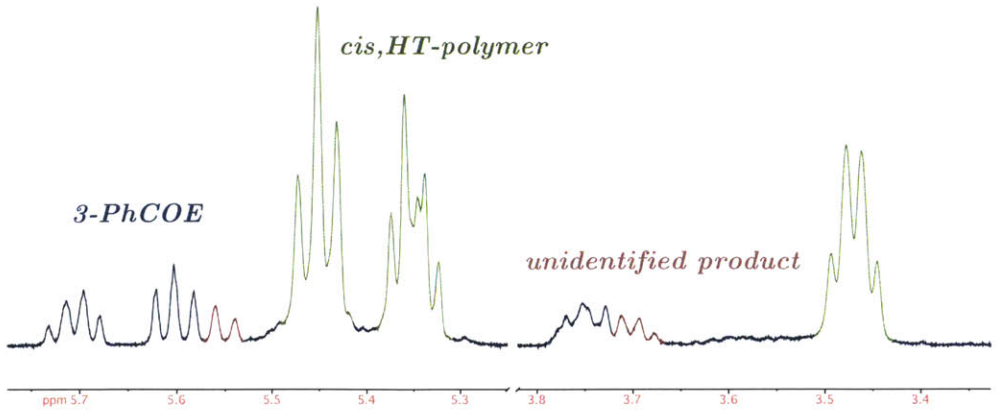
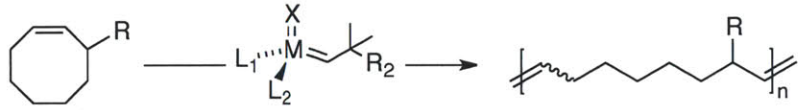


Figure 6. Olefinic and allylic regions of the ^{1}H NMR spectrum of the reaction mixture for ROMP of 100 equiv. of 3-**Ph**COE initiated by **1**.

Having achieved excellent *cis*,HT selectivity and dramatically increased rates with **1** when the reactions were performed neat, we next focused on decreasing the catalyst loading to more industrially relevant (i.e. low ppm) levels.

ROMP of 5000 equiv. 3-**Me**COE (200 ppm catalyst) initiated by **1** proceeded with >95% conversion in 4 h while maintaining the high (>98%) selectivity towards *cis*,HT-poly(3-**Me**COE) observed previously. However, the more hindered 3-**R**COEs reacted more slowly; 3 d were required for 78% conversion of 5000 equiv. 3-**Hex**COE, while 3-**Ph**COE achieved only 63% conversion after 6 d, and negligible conversion of 5000 equiv. 3-**iPr**COE was observed even at elevated temperatures (60 °C) for extended times. The complete absence of conversion in the later case may indicate catalyst decomposition, possibly by trace contaminants in the monomer. Performing the polymerization of 3-**Hex**COE at 60 °C resulted in a faster reaction with no decrease in *cis*,HT selectivity. Data from polymerization trials performed in neat monomer are summarized in Table 3.

Table 3. Summary of ROMP reactions in neat monomer. R_2 = Ph for all but Entries 11-14, where R_2 = Me. OAr^{Ph2Pyr} = 2,6-(2,5-$Ph_2NC_4H_2)_2$-C_6H_3O. OF_6 = $OC(CF_3)_2Me$. [a] Average of 3 trials. [b] Average of 4 trials. [c] Remainder *trans*,HT d Activated with 2.4 equiv. $B(C_6F_5)_3$.



	R	M	NR_3	L_1	L_2	*n*	Temp	Time	% conv	% cis-HT
1	Me	Mo	NAd	pyr	OHMT	50	rt	10 m	86	>98
								1 h	>99	>98
2	Me	Mo	NAd	pyr	OHMT	5000	rt	30 m	40	>98
								4 h	95	>98
3	Hex	Mo	NAd	pyr	OHMT	100	rt	4 h	50	>98
								1 d	98	>98
4	Hex	Mo	NAd	pyr	OHMT	1000	rt	18 h	66[a]	>98[a]
								3 d	97[a]	>98[a]
5	Hex	Mo	NAd	pyr	OHMT	5000	rt	1 d	47[b]	>98[b]
								7 d	93	>98
6	Hex	Mo	NAd	pyr	OHMT	5000	60 °C	1 d	71	>98
								2 d	87	>98
7	Hex	Mo	NAd	pyr	OAr^{Ph2Pyr}	5000	rt	1 d	16	>98
								4 d	42	>98
8	Hex	Mo	NC_6F_5	ODFT	ODFT	5000	rt	4 h	15	83[c]
								24 h	51	82[c]
9	Hex	Mo	NAd	OF_6	OF_6	5000	rt	4 h	7	66[c]
								2 d	48	57[c]
10	Hex	W	NtBu	pyr	OHMT	5000	rt	4 h	29	>98
								1 d	76[a]	>98[a]
11	Hex	W	NtBu	pyr	OHMT	10000	rt	4 h	15	>98
								48 h	78	>98
12	Hex	W	NtBu	pyr	ODFT	5000	rt	4 h	34	96[c]
								48 h	67	93[c]
13	Hex	W	O	Me_2Pyr	OHMT	5000	rt	4 h	<2	n/d
								24 h	<2	n/d
14	Hex	W	O	Me_2Pyr	OHMT	5000	rt	4 h	26	96[c]
								48 h	65	96[c]
15	Hex	W	NAr'	pyr	OHMT	5000	rt	4 h	3	n/d
								48 h	47	>98
16	Ph	Mo	NAd	pyr	OHMT	50	rt	4h	16	ca. 90
								1d	82	ca. 90
17	Ph	Mo	NAd	pyr	OHMT	5000	rt	18h	7	n/d
								6d	63	ca. 90
18	iPr	Mo	NAd	pyr	OHMT	5000	60 °C	1d	<2	n/d
								14d	<2	n/d

The *cis*,HT-poly(3-**R**COE)s obtained from entries 2, 6, and 17 in Table 3 were isolated by pouring a chloroform solution of the reaction mixture into methanol. The ^{1}H and ^{13}C NMR spectra of the isolated polymers confirms that they are highly regular; each polymer displays the number of ^{13}C resonances expected for a perfectly *cis*-HT structure: eight backbone signals (two olefinic and six aliphatic) and one, six, and four side-chain signals for **R** = Me, Hex, and Ph, respectively.

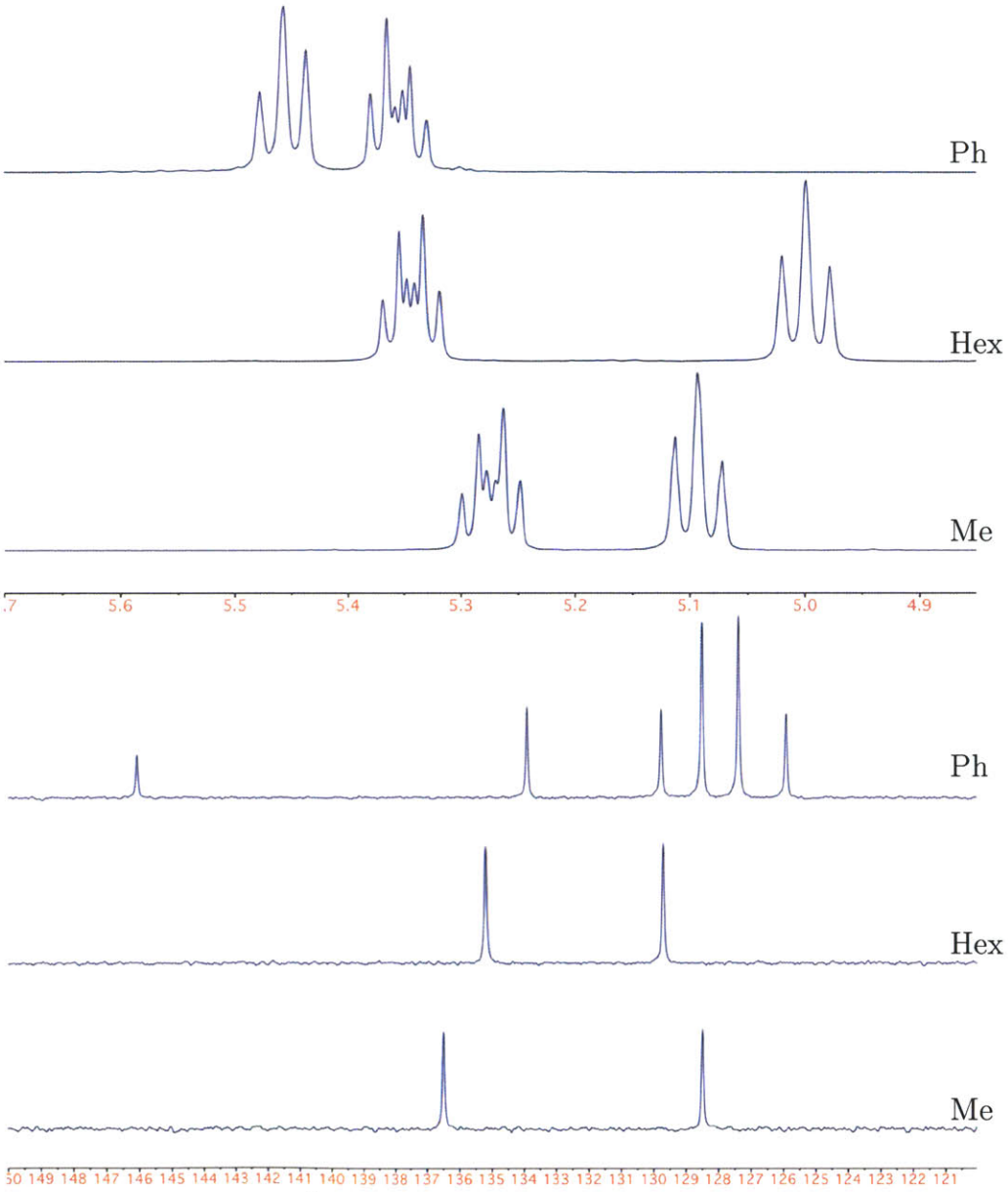


Figure 7. Olefinic region of the ^{1}H NMR spectrum of poly(3-**Me**COE) prepared by ROMP of 50 equiv. of 3-**Me**COE initiated by **1**.

As determined by ^{1}H NMR, the isolated poly(3-**Me**COE) and poly(3-**Hex**COE) were >98% *cis*,HT, while the isolated poly(3-**Ph**COE) was ca. 97% *cis*,HT. By contrast, **G2** displayed slightly lower selectivity; the *trans*,HT content of the polymers was 91%, 97%, and 98% for **R** = Me, Hex, and Ph, respectively.

Size-exclusion chromatography (SEC) and differential scanning calorimetry (DSC) of the isolated *cis*,HT-poly(3-**Me**COE) and *cis*,HT-poly(3-**Hex**COE) samples were performed in the group of Prof. Marc A. Hillmyer (Univ. Minnesota). The data obtained are given in Table 4. These values are similar to the polymers generated by **G2**.[33]

Table 4. Data obtained from SEC (M_n, polydispersity index = M_w/M_n) and DSC (T_g) of poly(3-**R**COE)s obtained using 0.02 mol% **1** (left, this work) and ca. 0.023 mol% **G2** (right, ref. 33). DSC performed up to 250 °C at a rate of 10 °C/min. SEC performed with $CHCl_3$ as eluent at 35 °C.

	0.02% 1			**ca. 0.023% G2**		
R	M_n (kg/mol)	M_w/M_n	T_g (°C)	M_n (kg/mol)	M_w/M_n	T_g (°C)
Me	288	1.77	-64	341	1.64	-67
Hex	331	1.80	-61	162	1.52	-71

Hydrogenation of the isolated *cis*,HT-poly(3-**Me**COE) and *cis*,HT-poly(3-**Hex**COE) generated with **1** using *p*-toluenesulfonhydrazide gave the expected linear low-density polyethylenes (LLDPE) with substitution at every eighth carbon of the main chain, identical to that obtained by Hillmyer *et al.* by hydrogenation of the corresponding *trans*,HT-poly(3-**R**COE).

With excellent *cis*-HT selectivity at low catalyst loadings with **1**, we next sought to find a *cis*-HT-selective initiator with greater activity. Use of ligand 2,6-bis(2,5-diphenyl-1*H*-pyrrol-1-yl)phenol (Figure 8) in place of HMTO gave a less active catalyst, presumably due to the increased size of this ligand relative to HMTO. Interestingly, the

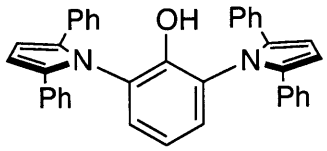


Figure 8. 2,6-bis(2,5-diphenyl-1*H*-pyrrol-1-yl)phenol

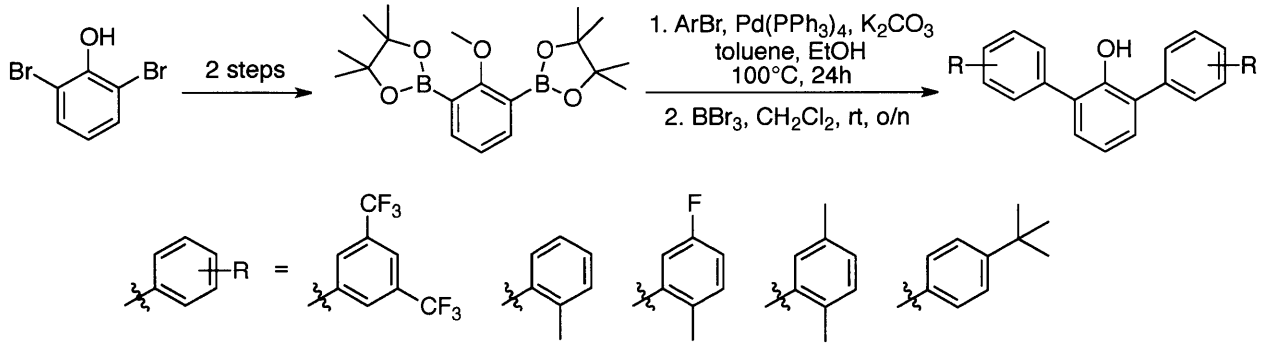
recently developed catalyst W(N*t*Bu)(CHCMe$_3$)(pyr)(OHMT)[34] (**2**) (a gift of Hyangsoo Jeong) proved substantially more active for the ROMP of 3-HexCOE, equaling at rt the conversion at 1 d (71%) that **1** achieved at 60 °C. This is somewhat surprising, as W catalysts are generally considered to be less active than their Mo analogues.[35,14] It is possible, though unexpected, that the steric or electronic properties of the *t*-butylimido group in **2** are sufficiently different from the adamantlyimido group in **1** to make the former the much more active catalyst. Two other W initiators, W(N*t*Bu)(CHCMe$_3$)(pyr)(ODFT) (Table 3, Entry 12) and W(O)(CHCMe$_3$)(Me$_2$Pyr)(OHMT)(PMe$_2$Ph) activated with 2.4 equivalents B(C$_6$F$_5$)$_3$ (Table 3, Entry 14), exhibited activity comparable to **2**, but were less selective (4-7% *trans*,HT linkages). Furthermore, their decreased activity by 48 h relative to **2** suggests that these catalysts may not be as long-lived.

To improve on the activity of **1** and **2** but maintain their *cis* selectivity, complexes with *m*-terphenyl phenols less hindered than HMTO were sought. Unfortunately, addition of one equivalent of either 2,6-diphenylphenol or 2,3,5,6-tetraphenylphenol to the bispyrrolide Mo(NAd)(CHCMe$_2$Ph)(pyr)$_2$ gave a mixture of starting material, the desired MAP complex, and bisalkoxide. Seeking to avoid bisalkoxide formation, but still increase catalyst activity relative to **1**, a series of *m*-terphenyl phenol ligands with substitution on the flanking aryl rings was prepared. The known compound 2,6-di(pinacolboronate)anisole was synthesized in 2 steps from

[34] Jeong, H. *Unpublished results.*

[35] Jiang, A. J.; Simpson, J. H; Müller, P.; Schrock, R. R. *J. Am. Chem. Soc.* **2009**, *131*, 7770-7780

commercially available 2,6-dibromophenol. This compound served as a universal precursor to the *m*-terphenyl phenols, which were prepared by Suzuki coupling with two equivalents of an aryl bromide. Subsequent removal of the methyl protecting group and recrystallization from hexanes gave the pure phenols (Scheme 8). Synthesis and isolation of catalysts containing the corresponding phenoxides as ligands is ongoing.



Scheme 8, Synthesis of substituted m-terphenyl phenols.

3 Conclusion

The highly *cis*,HT-selective ROMP of a series of 3-substituted cyclooctenes (3-**Me**COE, 3-**Hex**COE, and 3-**Ph**COE) with high oxidation state Mo and W alkylidene complexes is reported herein. Formation of cyclic oligomer could be avoided by performing the reactions in neat monomer. The complex Mo(NAd)(CHCMe$_2$Ph)(pyr)(OHMT) (**1**) outperformed Grubbs' 2nd generation catalyst in the case of 3-**Me**COE and 3-**Hex**COE, achieving greater conversion (5000 equiv. monomer, 24 h, rt) than **G2** (ca. 4300 equiv. monomer, 20 h, 60 °C) and exhibiting greater selectivity (>98% *cis*-HT). ROMP of 5000 equiv. of 3-**Ph**COE with **1** was slower (26% conversion, 48 h, rt) and less selective (90% *cis*-HT polymer) than with the 3-**Me** and 3-**Hex** analogues. Surprisingly, W(NtBu)(CHCMe$_3$)(pyr)(OHMT) (**2**) was found to be significantly more active than **1**. A series of *m*-terphenyl phenols was prepared for us in place of OHMT in **1** and **2** to further increase reactivity.

4 Experimental

General considerations. All air- or moisture-sensitive manipulations were performed under an atmosphere of dry nitrogen in a Vacuum Atmospheres glovebox or using a dual-manifold Schlenk line, as indicated. Glassware was oven dried (150 °C) and cooled under vacuum or under a flow of dry nitrogen. Benzene, THF, ether, pentane, toluene, and dichloromethane used for air- or moisture-sensitive reactions were sparged with dry nitrogen, passed through a column of activated alumina, and stored over 4 Å Linde-type molecular sieves. C_6D_6 and CD_2Cl_2 were purchased from Cambridge Isotope Laboratories and stored over 4 Å Linde-type molecular sieves in the glovebox. $CDCl_3$ was purchased from Cambridge Isotope Laboratories and used as received. NMR spectra were obtained on Varian 300, Bruker 400, or Varian 500 MHz spectrometers. ^1H and ^{13}C NMR chemical shifts are reported in δ (parts per million) relative to tetramethylsilane but were referenced to residual ^1H or ^{13}C signals of C_6D_6 (^1H: 7.16 ppm, ^{13}C: 128.1 ppm), CD_2Cl_2 (^1H: 5.32 ppm; ^{13}C: 53.8 ppm), or $CDCl_3$ (^1H: 7.26 ppm, ^{13}C: 77.2 ppm). ^{19}F NMR chemical shifts are reported in δ (ppm) relative to $CFCl_3$ and were referenced to an external standard of fluorobenzene (-113.5 ppm). SEC and DSC measurements of the polymers were performed by the group of Marc A. Hillmyer (Univ. Minnesota). M_n and M_w/M_n were determined by SEC using a Hewlett-Packard 1100 series liquid chromatograph equipped with three Polymer Laboratories PLgel columns (500, 103, and 104 Å pore sizes) and a Hewlett-Packward 1047A refractive index detector; chloroform (1 mL/min) was the eluent and the system was set to 35 °C. The columns were calibrated using Polymer Laboratories polystyrene standards. DSC was performed with a TA Instruments Q1000 using N_2 purge gas at 10 °C/min.

NBS (Alfa Aesar) was recrystallized from hot (ca. 95 °C) water and dried *in vacuo* prior to use. $Pd(PPh_3)_4$ (Strem), *cis*-cyclooctene (Alfa Aesar), 2,6-dibromophenol (Accela ChemBio), CuI (Aldrich), mesityl bromide (Aldrich), Mg turnings (Alfa Aesar),

2,6-dichloroiodobenzene (Matrix Scientific), I_2 (Aldrich), ethylmagnesium bromide (3.0 M in diethyl ether, Alfa Aesar), isopropylmagnesium bromide (2.0 M in diethyl ether, Aldrich), and $B(C_6F_5)_3$ (Alfa Aesar) were used as received. Pinacolborane and aryl bromides used for Pd-catalyzed coupling reactions were purchased from Oakwood and used as received. W(N*t*Bu)($CHCMe_3$)(pyr)(OHMT) and W(N*t*Bu)($CHCMe_3$)(pyr)(ODFT) were gifts of Hyangsoo Jeong. W(O)($CHCMe_3$)(2,5-Me_2Pyr)(OHMT)(PMe_2Ph) was a gift of Janna Börner. Mo(NC_6F_5)($CHCMe_2Ph$)$(ODFT)_2$ was a gift of Jian Yuan. 2,6-bis(2,5-diphenyl-1*H*-pyrrol-1-yl)phenol was a gift of Michael Reithofer. Mo$(NAd)_2Cl_2$DME,[36] Mo$(NAd)_2(CH_2CMe_2Ph)_2$,[36] Mo(NAd)($CHCMe_2Ph$)$(OTf)_2$DME,[36] Mo(NAd)($CHCMe_2Ph$)$(pyr)_2$,[37] Mo(NAd)($CHCMe_2Ph$)(OHMT)(pyr) (**1**),[38] Mo(NAd)($CHCMe_2Ph$)(OHIPT)(pyr),[13] Mo(NAd)($CHCMe_2Ph$)$(OC(CF_3)_2Me)_2$,[36] Mo(NAr')$_2Cl_2$DME,[39] Mo(NAr')$_2$($CHCMe_2Ph$)$_2$,[36] Mo(NAr')($CHCMe_2Ph$)$(OTf)_2$DME,[36] HIPTI,[40] HIPTOH,[41] HMTOH[42], 2,6-dibromoanisole,[43] and 2,6-di(pinacolboronate)anisole (2,2'-(2-methoxy-1,3-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane))[43] were prepared as previously reported. HMTI was prepared using the procedure modified from the literature[42] described below. 3-**Br**COE was synthesized

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[36] Oskam, J. H.; Fox, H. H.; Yap, K. B.; McConville, D. H.; O'Dell, R.; Lichtenstein, B. J.; Schrock, R. R. *J. Organomet. Chem.* **1993**, *459*, 185-198.

[37] Hock, A. S.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2006**, *128*, 16373-16375.

[38] Flook, M. M.; Ng, V. W. L.; Schrock, R. R. *J. Am. Chem. Soc.* **2011**, *133*, 1784-1786.

[39] Fox, H. H.; Yap, K. B.; Robbins, J.; Cai, S.; Schrock, R. R. *Inorg. Chem.* **1992**, *31*, 2287-2289.

[40] Schiemenz, B.; Power, P. P. *Organometallics* **1996**, *15*, 958-964.

[41] Stanciu, C.; Olmstead, M. M.; Phillips, A. D.; Stender, M.; Power, P. P. *Eur. J. Inorg. Chem.* **2003**, 3495-3500.

[42] Dickie, D. A.; MacIntosh, I. S.; Ino, D. D.; He, Q.; Labeodan, O. A.; Jennings, M. C.; Schatte, G.; Walsby, C. J.; Clyburne, J. A. *Can. J. Chem.* **2008**, *86*, 20-31.

[43] (i) Chan, J. M. W.; Swager, T. M. *Tetrahedron Lett.* **2008**, *49*, 4912-4914. (ii) Chan, J. M. W. Design and Synthesis of Conjugated Macrocycles and Polymers. Ph.D. Thesis, Massachusetts Institute of Technology, June 2010.

using the modified literature procedure[44] detailed below. 3-**Me**COE, 3-**Hex**COE, and 3-**Ph**COE were synthesized as reported[33] and were degassed by a minimum of three freeze-pump-thaw cycles and dried over 4Å Linde-type molecular sieves prior to use. Hydrogenation of the polymers was performed as described by Hillmyer *et al.*[33] Grignard reagents were titrated against *n*-butanol with 1,10-phenanthroline as an indicator immediately prior to use.

HMTI

Under N_2 (Schlenk line), a solution of mesityl bromide (15.4 mL, 0.10 mol, 2.6 equiv.) in THF (ca. 15 mL) was added to a suspension of Mg turnings (2.48 g, 0.10 mol, 2.6 equiv., activated by stirring with one crystal of I_2) in THF (60 mL) over 30 min. *via* an addition funnel. The suspension became yellow-brown and some refluxing was observed. The mixture was then heated to reflux for 3 h, after which the mixture was cooled to rt. Ethylmagnesium bromide (12.9 mL as a 3.0 M solution in diethy ether, 0.039 mol, 1.0 equiv.) was added to a dark yellow solution of 2,6-dichloroiodobenzene (10.59 g, 0.039 mol, 1.0 equiv. at 0 °C. The resulting solution was stirred and allowed to slowly warm to rt over 5 h. The two solutions were combined and heated to reflux o/n (ca. 14 h). To the resulting green-brown solution there was added a solution of I_2 (31 g, 0.12 mol, 3.2 equiv.) in THF (50 mL) *via* cannula, and the mixture was stirred for 2.5 h. The mixture was then treated with a solution of $Na_2S_2O_3 \bullet H_2O$ in water until the dark colour dissipated. 100 mL diethyl ether was added and the aqueous layer was extracted with diethyl ether (4 x 50 mL). The organic layers were combined, washed with water (2 x 50 mL) and brine (2 x 50 mL), dried ($MgSO_4$), and filtered, and the volatiles were removed *in vacuo*. The resulting light brown solid was washed with methanol to give 9.93 g (58%) of HTMI as a white solid. Spectroscopic data matched that previously reported.[42]

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[44] Cope, A. C.; Estes Jr., L. L. *J. Am. Chem. Soc.* **1950**, *72*, 1128-1132.

3-bromocyclooctene (3-**Br**COE)

The reaction and all manipulations were performed under air. Into a 2-necked 2L flask equipped with a stir bar and a condenser there was added NBS (210.4 g, 1.0 equiv.), CCl_4 (600 mL), benzoyl peroxide (0.84 g, 0.3 mol%), and cyclooctene (154 mL, 1.0 equiv.). The white suspension was heated to reflux with stirring. NMR analysis of an aliquot revealed the reaction to be complete after 1 h 40 m, at which point the mixture was cooled to room temperature. The succinimide was removed by filtration and the solvent was removed *in vacuo*. The resulting brown residue was rapidly vacuum distilled. To the colourless distillate, which contained cyclooctene, 3-bromocyclooctene, and some minor impurities, there was added dichloromethane (100 mL). The resulting solution was washed with 5% aqueous $NaHCO_3$ (2 x 100 mL) then water (2 x 100 mL), dried with $MgSO_4$, and filtered. The solvent was removed *in vacuo*. 3-bromo-*Z*-cyclooctene was isolated from this liquid by fractional vacuum distillation (30 cm vacuum-jacketed Vigreux column, 200-250 mTorr, b.p. 30 °C). The ^1H spectrum matched that previously reported.[10]

3-*iso*-propylcyclooctene (3-**iPr**COE)

In the glovebox, 3-**Br**COE (10 mL, 71.2 mmol), CuI (162 mg, 0.85 mmol), and THF (150 mL) were added to a 250 mL Schlenk flask containing a stir bar. The flask was sealed with a septum, removed from the glovebox, and connected to the Schlenk line. The light brown suspension was cooled to 0 °C (ice/water bath) and *iso*-propylmagnesium bromide (2.0 M in ether, 45 mL, 90.0 mmol) was added *via* syringe over 10 min. The mixture was allowed to warm to rt o/n with stirring. To the resulting suspension, water (50 mL) was slowly added. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The organic layers were combined, dried ($MgSO_4$), and the solvent removed *in vacuo*. The residue was taken up in diethyl ether and passed through a short silica plug. The solvent was removed, and

the resulting viscous liquid was subjected to fractional vacuum distillation to give 3-iPrCOE (5.7 g, 52%) as a colourless liquid. Boiling point = 42 °C at ca. 3.1 Torr. ^{1}H NMR (500.43 MHz, $CDCl_3$, δ): 5.66 (dd, J = 17.9, 8.7 Hz, 1H), 5.30 (t, J = 9.9 Hz, 1H), 2.25-2.18 (m, 2H), 2.05-1.99 (m, 1H), 1.70-1.60 (m, 3H), 1.56-1.43 (m, 3H), 1.37-1.24 (m, 2H), 1.15-1.08 (m, 1H), 0.91-0.87 (m, 6H).

Mo(NAd)(CHCMe$_2$Ph)(pyr)(2,6-(2,5-Ph$_2$NC$_4$H$_2$)$_2$-C$_6$H$_3$O)[45]

In the glovebox, 152 mg Mo(NAd)(CHCMe$_2$Ph)(pyr)$_2$ (0.30 mmol, 1.0 equiv.) and 156 mg 2,6-(2,5-Ph$_2$NC$_4$H$_2$)$_2$-C$_6$H$_3$OH (0.30 mmol, 1.0 equiv.) were dissolved in 5 mL benzene in a 25 mL Schlenk flask. The flask was sealed, removed from the box, and heated to 70 °C with stirring. In the glovebox, the resulting mixture was filtered through Celite and dried *in vacuo* to give a yellow/brown solid. This solid was washed with 2 mL cold (-30 °C) ether followed by 5 mL cold (-30 °C) pentane to give 139 mg (49%) of the title compound as a yellow powder. ^{1}H NMR (500.43 MHz, C_6D_6, δ): 12.29 (s, 1H, Mo=C*H*, J_{CH} = 121.4 Hz), 7.34 (m, 2H), 7.24-6.96 (m, 25H), 6.74 (m, 2H), 6.65 (m, 2H), 6.56 (m, 4H), 6.11 (m, 1H), 1.78 (s, 3H), 1.73 (m, 8H), 1.50 (s, 3H), 1.33 (m, 7H). ^{13}C NMR (125 MHz, C_6D_6, δ): 283.6 (Mo=C), 158.5, 148.9, 138.4, 138.0, 133.6, 133.5, 133.0, 131.8, 131.6, 128.8, 128.7, 128.5, 128.2, 128.1, 126.9, 126.6, 126.4, 120.4, 112.2, 111.1, 110.4, 77.6, 52.3, 43.7, 35.7, 32.5, 31.1, 29.8. Anal. Calc. (%) for $C_{62}H_{58}MoN_4O$: C, 76.68; H, 6.02; N, 5.77. Found: C, 76.47; H, 6.31; N, 5.58.

General procedure A: NMR-scale polymerizations in C$_6$D$_6$ solution

To a solution of the Mo or W catalyst in 0.5 mL C_6D_6 in a small vial there was added the monomer *via* syringe. The mixture was stirred for 15 s, then transferred to a J. Young tube with a 0.2 mL C_6D_6 rinse. The mixture sat at rt or was heated in an oil bath and the reaction was monitored by ^{1}H NMR.

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[45] ^{13}C NMR and elemental analysis data obtained by M. Reithofer.

General procedure B: ambient temperature polymerizations, neat monomer

In the glovebox, the Mo or W initiator was added as a stock solution in benzene to an 8 mL vial containing a stir bar. The benzene was frozen and removed by sublimation, and the monomer (250 μL, 5000 equiv.) was added *via* syringe. The vial was capped and the mixture stirred at ambient temperature. Aliquots were removed from the box and quenched with wet $CDCl_3$ (stored under air without desiccant). The polymerization reactions were quenched by addition of 5 mL wet $CHCl_3$ (stored under air without desiccant) followed by sonication for 30 min. The polymers were precipitated by addition of this solution to 50 mL methanol. The precipitated polymers were freeze-dried overnight from frozen benzene solutions.

General procedure C: elevated temperature polymerizations, neat monomer

Polymerizations at elevated temperatures were performed identically to those at ambient-temperature with the following exceptions: a small Schlenk tube with PTFE plug was used instead of a vial and, once the monomer was added, the tube was sealed, removed from the box, and heated with stirring in an oil bath. Aliquots were taken for monitoring in the glovebox.

***cis*,HT-poly(3-hexylcyclooctene)**

Prepared following general procedure B with **1** as initiator. ^{1}H NMR (500.43 MHz, $CDCl_3$, δ): 5.34 (dt, J = 10.9, 7.2 Hz, 1H), 5.00 (apparent t, J = 10.5 Hz, 1H), 2.25 (m, 1H), 1.98 (m, 2H), 1.40-1.05 (overlapping peaks, 18H), 0.88 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125.79 MHz, $CDCl_3$, δ): 135.2, 129.7, 37.4, 36.2, 36.2, 32.1, 30.2, 29.9, 29.8, 28.0, 27.5, 27.5, 22.9, 14.3.

***cis*,HT-poly(3-methylcyclooctene)**

Prepared following general procedure C (60 °C) with **1** as initiator. ^{1}H NMR (500.43 MHz, $CDCl_3$, δ): 5.27 (dt, J = 10.8, 7.3 Hz, 1H), 5.09 (apparent t, J = 10.3 Hz, 1H), 2.40 (m, 1H), 2.00 (m, 2H, J = 7.2 Hz), 1.38-1.10 (overlapping peaks, 8H), 0.91 (d, J =

6.7 Hz, 3H). ^{13}C NMR (125.79 MHz, $CDCl_3$, δ): 136.5, 128.5, 37.7, 31.8, 30.1, 29.7, 27.7, 27.6, 21.6.

***cis*,HT-poly(3-phenylcyclooctene)**

Prepared following general procedure C (60 °C) with **1** as initiator. ^{1}H NMR (500.43 MHz, $CDCl_3$, δ): 7.27-7.24 (overlapping peaks, 2H), 7.16-7.13 (overlapping peaks, 3H), 5.46 (apparent t, J = 10.3 Hz, 1H), 5.36 (dt, J = 10.7, 7.1 Hz, 1H), 3.48 (apparent q, J = 7.8 Hz, 1H), 2.03 (m, 2H), 1.66-1.60 (m, 1H), 1.57-1.51 (m, 1H), 1.32-1.21 (overlapping peaks, 5H), 1.18-1.12 (m, 1H). ^{13}C NMR (125.79 MHz, $CDCl_3$, δ): 146.1, 129.8, 128.5, 127.4, 127.4, 125.9, 43.6, 37.1, 29.7, 29.5, 27.7, 27.6.

Hydrogenated *cis*,HT-poly(3-methylcyclooctene)

Following the procedure of Kobayashi *et al.*[33] using 33 mg of *cis*,HT-poly(3-**Me**COE) (Table 3, Entry 2) gave 96:4 hydrogenated:unhydrogenated polymer, as determined by ^{1}H NMR. ^{1}H and ^{13}C NMR spectral data of the hydrogenated portion matched those reported for the hydrogenated *trans*,HT-poly(3-**Me**COE).

Hydrogenated *cis*,HT-poly(3-hexylcyclooctene)

Following the procedure of Kobayashi *et al.*[33] suing 27 mg of *cis*,HT-poly(3-**Hex**COE) (Table 3, Entry 6) gave 72:28 hydrogenated:unhydrogenated polymer, as determined by ^{1}H NMR. ^{1}H and ^{13}C NMR spectral data of the hydrogenated portion matched those reported for the hydrogenated *trans*,HT-poly(3-**Hex**COE).

General procedure for $Pd(PPh_3)_4$-catalyzed Suzuki coupling

In the glovebox, 2,6-di(pinacolboronate)anisole (ca. 300 mg, 1.0 equiv.), K_2CO_3 (5.0 equiv.), $Pd(PPh_3)_4$ (0.06 equiv.), the aryl bromide (3.0 equiv.), toluene (7 mL), and degassed absolute ethanol (1.5 mL) were added to a 15 or 75 mL pressure tube (ChemGlass) containing a stir bar. The tube was sealed, removed from the glovebox, and heated to 100 °C for 24 h. After cooling to r.t., water (50 mL) and ether (50 mL) were added to the yellow/brown suspension. The organic layer was separated and the

aqueous layer was further extracted with ether (3 x 50 mL). The organic layers were combined, dried ($MgSO_4$), filtered, and the volatiles were removed *in vacuo*. Passage of this residue through a silica gel plug (ca. 40 mL silica gel) eluted with 250 mL of a 98:2 mixture of hexanes:ethyl acetate gave a colourless to off-white oil or solid. In the glovebox, the residue was dissolved in 10 mL CH_2Cl_2 in a 20 mL vial and BBr_3 (2.0 equiv.) was added in one portion at r.t. The mixture was stirred o/n. The vial was removed from the glovebox, the mixture cooled to 0 °C, and, under N_2, the remaining BBr_3 was quenched slowly with water (3 mL). Additional water (27 mL) and CH_2Cl_2 (20 mL) were added. The organic layer was separated and the aqueous layer was further extracted with CH_2Cl_2 (3 x 30 mL). The organic layers were combined, dried ($MgSO_4$), filtered, and the volatiles were removed *in vacuo*. The resulting solid or oil was recrystallized from a minimal amount of hexanes.

2,6-bis(3,5-trifluoromethylphenyl)phenol

Prepared using the general procedure beginning with 102 mg 2,6-di(pinacolboronate)anisole gave 60 mg white solid (40%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.03 (s, 4H), 7.92 (s, 2H), 7.37 (d, J = 7.6 Hz, 2H), 7.19 (t, J = 7.6 Hz, 1H), 5.21 (s, 1H).

2,6-di(2-methylphenyl)phenol[46]

Prepared using the general procedure beginning with 308 mg 2,6-di(pinacolboronate)anisole gave 95 mg off-white solid (38%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.34-7.29 (overlapping signals, 8H), 7.17 (d, J = 7.4 Hz, 2H), 7.04 (t, J = 7.1 Hz, 1H), 4.80 (s, 1H), 2.24 (s, 6H).

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[46] Ueji, S.; Ueda, N.; Kinugasa, T. *J. Chem. Soc., Perkin Trans. 2.* **1976**, 178-180.

2,6-di(2-methyl-5-fluorophenyl)phenol

Prepared using the general procedure beginning with 299 mg 2,6-di(pinacolboronate)anisole gave 86 mg solid (33%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.28-7.25 (m, 2H), 7.15 (d, J = 7.4, 2H), 7.06-7.00 (overlapping signals, 5H), 4.74 (s, 1H), 2.17 (s, 6H).

2,6-bis(2,5-dimethylphenyl)phenol

Prepared using the general procedure beginning with 304 mg 2,6-di(pinacolboronate)anisole gave 112 mg off-white solid (44%). Spectra matched that previously reported.[47] ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.21 (d, J = 8.0 Hz, 2H), 7.16-7.12 (overlapping signals, 6H), 7.03 (t, J = 7.1 Hz, 1H), 4.84 (s, 1H), 2.37 (s, 6H), 2.19 (s, 6H).

2,6-bis(4-*t*-butylphenyl)phenol[48]

Prepared using the general procedure beginning with 309 mg 2,6-di(pinacolboronate)anisole gave 82 mg white solid (19%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.49 (s, 8H), 7.26 (d, J = 7.6 Hz, 2H), 7.03 (t, J = 7.6 Hz, 1H), 5.48 (s, 1H), 1.36 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 150.6, 149.6, 134.7, 129.9, 129.1, 128.7, 125.9, 120.7, 34.8, 31.5.

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[47] Bedford, R. B.; Limmert, M. E. *J. Org. Chem.* **2003**, *68*, 8669-8682.

[48] Yang, H.; Hay, A. S. *Synthesis* **1992**, *467-472.*