JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

# Cis-Selective Ring-Opening Metathesis Polymerization with Ruthenium Catalysts

Benjamin K. Keitz, Alexey Fedorov, and Robert H. Grubbs*

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California, 91125

*Supporting Information*

**ABSTRACT:** Cis-selective ring-opening metathesis polymerization of several monocyclic alkenes as well as norbornene and oxanorbornene-type monomers using a C−H activated, ruthenium-based metathesis catalyst is reported. The cis content of the isolated polymers depended heavily on the monomer structure and temperature. A cis content as high as 96% could be obtained by lowering the temperature of the polymerization.

Ring-opening metathesis polymerization (ROMP) is a powerful methodology for the preparation of a wide range of synthetic polymers, including block,[1] brush,[2] and cyclic architectures.[3] Furthermore, ROMP can also be used to prepare polymers with specific microstructures comprising various tacticities (e.g., atactic, isotactic, syndiotactic), double-bond arrangements (cis/trans), and relative monomer configurations (e.g., head-to-tail, head-to-head, etc.).[4] Control of these microstructures is essential for preparing polymers with well-defined properties. For instance, a higher content of cis double bonds (% cis) is typically associated with lower melting and glass transition temperatures and induces lower rates of crystallization.[5−7] Likewise, the properties of conjugated polymers can be adjusted by varying the percentage of cis double bonds they contain.[8]

Several metathesis catalysts based on Re, Os, Mo, and W have been shown to give high cis content in the ROMP of norbornene and norbornadiene derivatives.[9,10] Many of these catalysts have also demonstrated an ability to generate polymers with well-defined tacticities. Although the % cis varies significantly with the catalyst, monomer, solvent,[11] and temperature,[12] Ru-based initiators such as (PCy$_3$)$_2$Cl$_2$Ru=CHPh give almost exclusively trans polymers.[13,14] Indeed, this has been a serious limitation for previous generations of Ru-based metathesis catalysts, as highlighted by Schrock and co-workers.[10c] The best literature examples of stereoselective ROMP with Ru catalysts include alternating copolymerization of norbornene and cycloalkenes to give polymers with 50−60% cis double bonds and most recently with up to 75%.[15,16] Our group has described similar % cis values for sulfonate and phosphate substituted NHC-based catalysts as well.[17]

We recently reported on a new class of Ru-based metathesis catalysts in which an N-heterocyclic carbene (NHC) ligand is chelated to the metal center through a Ru−C bond formed via C−H activation.[18] These catalysts showed remarkable selectivity for the formation of cis olefins during a wide variety of cross-metathesis reactions. Our initial ROMP experiments with the C−H activated catalysts revealed no significant increase in cis content relative to standard catalysts such as **1** (Figure 1). However, after having discovered the improved activity, stability, and selectivity of nitrato complex **2**,[19] we decided to investigate the ROMP behavior of this catalyst more closely. Herein we show that the cis selectivity of **2** extends to the ROMP of various monomers and consequently establish that Ru-based metathesis catalysts are capable of forming polymers with high cis content. We also demonstrate that classic NHC-based Ru catalysts (e.g., **1**) can give polymers with unexpectedly high cis selectivity in certain situations.

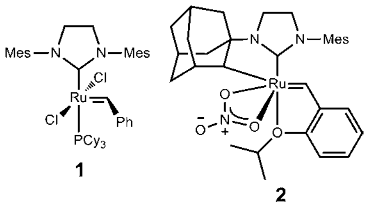


**Figure 1.** Catalysts **1** and **2**. Mes = 2,4,6-trimethylphenyl.

When **2** was added to a solution of norbornene (**3**) in tetrahydrofuran (THF) at room temperature (RT), an immediate increase in the viscosity of the solution occurred. Isolation of the resulting polymer (**poly-3**) and subsequent characterization by $^{1}$H and $^{13}$C NMR spectroscopy revealed that it contained ca. 88% cis double bonds (Figure 2).[20] In contrast, **poly-3** prepared using **1** showed a % cis value of 58% (Table 1).[21] These latter values are typical of NHC-supported Ru-based metathesis catalysts. Importantly, an even higher selectivity of ca. 96% cis could be obtained with **2** by lowering the temperature of the monomer solution prior to the addition of the catalyst. This trend was also observed when norbornadiene (**4**) was reacted with **2** at different temperatures (Figure 3). The almost exclusive formation of *cis*-**poly-4** using **2** is particularly noteworthy since **1** gave no detectable amount of the cis isomer.[22] However, **poly-4** prepared with **2** was atactic, as evidenced by the lack of long-range order in the $^{13}$C NMR spectrum (see the Supporting Information).

Having established that **2** could furnish polymers with high cis content for both **3** and **4**, we turned our attention to more complex monomers. Many of these monomers have been polymerized with very high cis selectivity and tacticity control

**Received:** December 14, 2011
**Published:** January 12, 2012

dx.doi.org/10.1021/ja211676y | J. Am. Chem.Soc. 2012, 134, 2040−2043

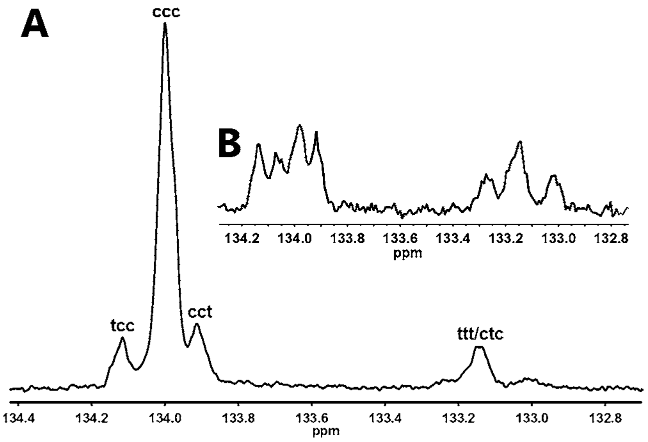


**Figure 2.** (A) $^{13}$C NMR spectrum ($CDCl_3$) of **poly-3** prepared from **3** (0.5 mmol) and **2** (0.005 mmol) in THF (2 mL) at RT. The labels "ccc" and "cct" indicate cis–cis–cis and cis–cis–trans triads, consistent with literature reports.[4] (B) $^{13}$C NMR spectrum of **poly-3** prepared from **1**.

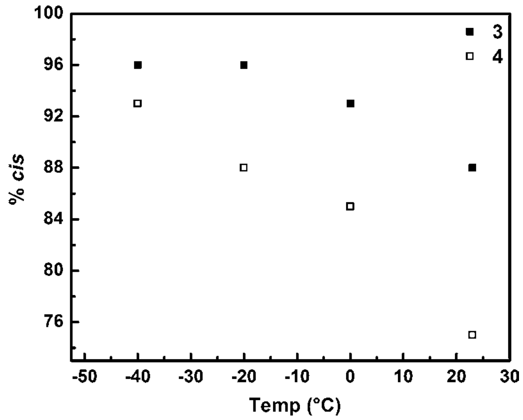
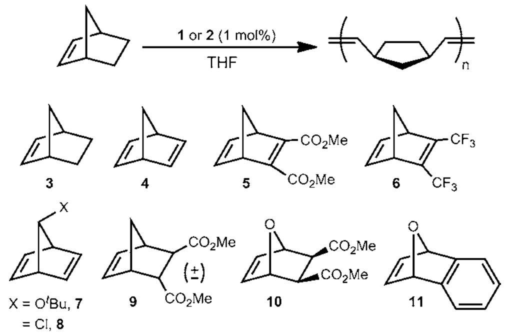


**Figure 3.** Change in % cis with temperature for **poly-3** and **poly-4** polymerized with **2**. Conditions: monomer (0.5 mmol) and **2** (0.005 mmol) in THF (2 mL). The % cis was determined by $^1$H NMR spectroscopy.

**Table 1. Polymerization of 3–11 with Catalysts 1 and 2[a]**



| monomer | catalyst | % cis[b] | yield (%)[c] | $M_n$ (kDa)[d] | PDI[d] |
|---|---|---|---|---|---|
| **3** | **1** | 58 | 88 | 112 | 1.65 |
| | **2** | 88 | 94 | 347 | 1.87 |
| **4** | **1** | <5 | 93 | –[e] | –[e] |
| | **2** | 75 | 88 | – | – |
| **5** | **1** | 93 | 78 | 95.5 | 1.21 |
| | **2** | 86 | 91 | – | – |
| **6** | **1** | 78 | 95 | 179 | 1.24 |
| | **2** | 61 | 40 | 137 | 1.21 |
| **7** | **1** | 58 | 78 | – | – |
| | **2** | 84 | 73 | – | – |
| **8** | **1** | 50 | 64 | 144 | 1.08 |
| | **2** | 69 | 81 | 328 | 1.09 |
| | **2** | 80[f] | 79 | – | – |
| **9** | **1** | 81 | 95 | 484 | 1.49 |
| | **2** | 91 | 78 | 629 | 1.33 |
| **10** | **1** | 66 | >95 | 463 | 1.5 |
| | **2** | 74 | 93 | 183 | 1.2 |
| | **2** | 80[f] | 79 | – | – |
| **11** | **1** | 67 | >95 | – | – |
| | **2** | 76 | 47 | – | – |
| | **2** | 91[f,g] | 80 | – | – |

[a] Conditions were monomer (1 mmol) and catalyst (0.01 mmol) in THF (4 mL, 0.25 M) at RT. [b] Determined by $^1$H NMR and $^{13}$C NMR spectroscopy. [c] Isolated yields. [d] Determined by multiangle light scattering (MALS) gel-permeation chromatography (GPC). [e] Here and below: not determined because of insolubility of the isolated polymer in THF or *N,N*-dimethylformamide (DMF). [f] Reaction performed at −20 °C. [g] 0.3 mol % catalyst was used.

using Mo- and W-derived catalysts but formed predominantly trans polymers when $(PCy_3)_2Cl_2Ru{=}CHPh$ was used.[13] Gratifyingly, we found that in almost every case, **2** yielded a polymer with a high cis content approaching 90%. In the cases where the cis selectivity with **2** at RT was below that value, conducting the ROMP at −20 °C increased the % cis by 6–15% (Table 1). In general, lower fractions of cis double bonds were observed for polymers prepared using **1**. However, for monomers **5**, **6**, and **9**, high cis contents were achieved without the use of a specially designed catalyst! This is particularly surprising since the closely related catalyst $(PCy_3)_2Cl_2Ru{=}CHPh$ is known to give **poly-5** with only 11% cis double bonds.[13] In contrast to **poly-5** and **poly-9** prepared using Mo-based catalysts,[10] no long-range order was observed using either of the Ru-based initiators. With **2**, the formation of atactic polymers can be explained by fast carbene epimerization relative to the rate of propagation. This result is typical of Ru-based catalysts, and only under special circumstances is tacticity control achieved.[14,23]

The experimental number-average molecular weights ($M_n$) for polymers prepared with **2** were generally higher than the predicted values, which is indicative of incomplete catalyst initiation or a high rate of propagation ($k_p$) relative to the rate of initiation ($k_i$). This could be qualitatively observed, as a solution of **2** and **3** remained purple (the color of **2**) even after complete conversion of the monomer. On the basis of the relatively low initiation rate constant of **2**, this result was expected.[24]

In contrast to norbornene and norbornadiene-type monomers, cyclooctadiene (COD, **12**), cyclopentene (**13**), and *cis*-cyclooctene (**14**) are significantly more difficult to polymerize via ROMP because of their lower ring strain.[25] Furthermore, *Z*-selective ROMP of these monomers is particularly challenging because of the prevalence of intra- and intermolecular chain-transfer reactions and secondary metathesis events.[4,26] In fact, the *Z*-selective ROMP of **12** has only recently been reported using a Mo metathesis catalyst.[10a,27] In view of the strong preference of **2** for cis-selective polymerization of bicyclic monomers, the next logical step was to attempt the ROMP of more difficult substrates such as **12–14**.

When **12** was exposed to **2** (1 mol %) in $C_6D_6$ (0.6 mL), only minimal conversion (<20%) was observed after 24 h at RT. Surprisingly, increasing the temperature did not result in higher conversions, despite the fact that no catalyst decomposition was observed by $^{1}$H NMR spectroscopy. Increasing the substrate concentration and switching the solvent to THF also did not increase the conversion of **12**, nor did repeating the reaction in neat **12**. However, polymerizing **12** with **2** in THF at RT over a period of 3 days provided a modest amount of **poly-12** (19% yield). Isolation and subsequent analysis of **poly-12** via $^{13}$C NMR spectroscopy revealed that it contained 96% cis double bonds, a value comparable to that obtained with the Mo-based system (Table 2). Similar to the ROMP of **3** and **4**, increasing the temperature of the polymerization of **12** resulted in polymers with lower cis content, although it never went below 80%. The extraordinariness of the above result is highlighted by the fact that **1** yielded **poly-12** with 90% trans selectivity.

**Table 2. Polymerization of 12, 13, and 15 with Catalysts 1 and 2[a]**

| monomer | catalyst | time (h) | % cis[b] | yield (%)[c] | $M_n$ (kDa)[d] | PDI[d] |
|---|---|---|---|---|---|---|
| cyclooctadiene (**12**) | **1** | 1 | 10 | 88 | 22.9 | 1.64 |
| | **2** | 36 | 96 | 19 | 99.1 | 1.60 |
| cyclopentene (**13**) | **1** | 5 | 15 | 68 | 11.1 | 1.47 |
| | **2** | 3 | 48 | 24 | 102 | 1.40 |
| *trans*-cyclooctene (**15**) | **1** | 1 | 18 | 49 | –[e] | – |
| | **2** | 1 | 70 | 44 | – | – |

[a]See the Supporting Information for reaction conditions. [b]Determined by $^{1}$H NMR and $^{13}$C NMR spectroscopy. [c]Isolated yields. [d]Determined by MALS GPC. [e]Not determined because of insolubility of the isolated polymer in THF or DMF.

Subsequent to our experiments with **12**, we found that **2** was also effective at polymerizing **13**, although the isolated yield of **poly-13** was still low (Table 2). Characterization of **poly-13** by $^{13}$C NMR spectroscopy revealed 48% cis content, which is significantly lower than that of **poly-12** prepared using **2**. Similar levels of cis selectivity have been reported in copolymerizations with **3**, although these generally resulted from incomplete incorporation of **13**.[15d] Switching to **1** produced **poly-13** with only 15% cis double bonds. Thus, the use of **2** resulted in a significant improvement in the % cis of **poly-13**, albeit to a lesser extent than was anticipated.

Unfortunately, no conversion of **14** was observed when it was exposed to **2** under a variety of conditions.[28] This was surprising since the strain energy of **14** (7.4 kcal/mol) is greater than that of **13** (6.8 kcal/mol).[25] Nevertheless, we reasoned that a more significant increase in strain energy relative to **13**, resulting from the use of *trans*-cyclooctene (**15**), would provide access to the desired polymer.[29] Indeed, reaction of **2** with **15** at RT in THF resulted in the immediate and high-yielding production of **poly-15**. Characterization of this polymer revealed a cis content of 70%, a value that is among the highest reported for Ru-based catalysts.[30] Notably, **poly-15** prepared from **1** contained ~82% trans double bonds.

As mentioned above, secondary metathesis events are common in nonrigid polymers because the active chain end is capable of intra- ("backbiting") and intermolecular chain transfer reactions. In view of this, the cis-selective polymerizations of **12**, **13**, and **15** using **2** are remarkable. Indeed, given the very high % cis of **poly-12** and the lack of erosion of the cis content over the course of the polymerization, one should conclude that **2** is less prone to isomerize or react with internal double bonds in polymers while displaying high kinetic selectivity for the formation of cis double bonds. Our molecular weight data also support this argument, as **poly-12/13** prepared from **2** had much higher molecular weights than **poly-12/13** prepared from **1**. Such a result is consistent with a reduction in the number of chain transfer events, which tend to lower the molecular weight.[31] The importance of controlling secondary metathesis is reinforced by examination of the polymers prepared from **1**. In the case of **poly-5/6/9**, where secondary metathesis is suppressed as a result of steric effects, catalyst **1** yielded polymers with relatively high cis content. In contrast, **poly-12/13** have no protection against secondary metathesis, and thus, the thermodynamically favored trans olefin was eventually formed when these polymers were prepared from **1**. Although we did not specifically investigate the mechanistic origin of the *Z*-selectivity in ROMP, calculations performed on an analogue of **2** indicate that steric pressure exerted by the NHC on side-bound ruthenacycles is responsible for the observed *Z*-selectivity during cross-metathesis.[15c,32] It is likely that a similar mechanism is also responsible for the selectivities observed here.

In conclusion, we have demonstrated the cis-selective ROMP of several monomers using Ru-based catalysts. The resulting polymers were recovered in moderate to high yields, and the cis content ranged from 48 to 96%. While the cis content varied significantly with the monomer structure, our C–H activated catalyst **2** gave polymers with significantly higher % cis values than those prepared using a more traditional Ru metathesis catalyst (**1**) while also showing qualitatively reverse stereoselectivity relative to $(PCy_3)_2Cl_2Ru{=}CHPh$. These results culminated in the highly cis-selective polymerization of **12**, thereby proving that cis-selective ROMP is possible with Ru catalysts, even in the case of monomers that are prone to secondary metathesis. Future work in our laboratory will focus on improving both the activity and cis selectivity of **2**, with an emphasis on the application of this exciting new class of catalysts toward the development of novel polymer architectures.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Full experimental details and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

rhg@caltech.edu

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We thank Dr. Rosemary Conrad Kiser for helpful discussions. This work was financially supported by the NSF (CHE-1048404), the NIH (NIH 5R01GM031332-27), the NDSEG (fellowship to B.K.K.), and the Swiss National Science Foundation (fellowship to A.F.). Portions of this work were conducted on instrumentation facilities supported by NIH RR027690. Materia Inc. is thanked for its donation of **1** and precursors to **2**.

## ■ REFERENCES

(1) (a) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565. (b) Bielawski, C. W.; Grubbs, R. H. *Prog. Polym. Sci.* **2007**, *32*, 1. (c) Sutthasupa, S.; Shiotsuki, M.; Sanda, F. *Polym. J.* **2010**, *42*, 905.

(2) Xia, Y.; Kornfield, J. A.; Grubbs, R. H. *Macromolecules* **2009**, *42*, 3761.

(3) (a) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *Science* **2002**, *297*, 2041. (b) Boydston, A. J.; Xia, Y.; Kornfield, J. A.; Gorodetskaya, I. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2008**, *130*, 12775. (c) Xia, Y.; Boydston, A. J.; Yao, Y.; Kornfield, J. A.; Gorodetskaya, I. A.; Spiess, H. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2009**, *131*, 2670.

(4) Grubbs, R. H. *Handbook of Metathesis*; Wiley-VCH: Weinheim, Germany, 2003.

(5) Dounis, P.; Feast, W. J.; Kenwright, A. M. *Polymer* **1995**, *36*, 2787.

(6) Ofstead, E. A. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1988; Vol. *11*.

(7) Haas, F.; Theisen, D. *Kautsch. Gummi Kunstst.* **1970**, *23*, 502.

(8) (a) Edwards, J. H.; Feast, W. J.; Bott, D. C. *Polymer* **1984**, *25*, 395. (b) Park, L. Y.; Schrock, R. R.; Stieglitz, S. G.; Crowe, W. E. *Macromolecules* **1991**, *24*, 3489. (c) Lee, C.; Wong, K.; Lam, W.; Tang, B. *Chem. Phys. Lett.* **1999**, *307*, 67. (d) Wong, K. S.; Lee, C. W.; Zang, B. Z. *Synth. Met.* **1999**, *101*, 505.

(9) (a) Hamilton, J. G.; Ivin, K. J.; Rooney, J. J. *J. Mol. Catal.* **1985**, *28*, 255. (b) Cobo, N.; Esteruelas, M. A.; Gonzalez, F.; Herrero, J.; Lopez, A. M.; Lucio, P.; Olivan, M. *J. Catal.* **2004**, *223*, 319−327.

(10) (a) Flook, M. M.; Jiang, A. J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 7962. (b) Flook, M. M.; Ng, V. W. L.; Schrock, R. R. *J. Am. Chem. Soc.* **2011**, *133*, 1784. (c) Schrock, R. R. *Dalton Trans.* **2011**, *40*, 7484.

(11) Al Samak, B.; Amir-Ebrahimi, V.; Corry, D. G.; Hamilton, J. G.; Rigby, S.; Rooney, J. J.; Thompson, J. M. *J. Mol. Catal. A: Chem.* **2000**, *160*, 13.

(12) Alimuniar, A. B.; Blackmore, P. M.; Edwards, J. H.; Feast, W. J.; Wilson, B. *Polymer* **1986**, *27*, 1281.

(13) (a) Delaude, L.; Demonceau, A.; Noels, A. F. *Macromolecules* **1999**, *32*, 2091. (b) Amir-Ebrahimi, V.; Corry, D. A.; Hamilton, J. G.; Thompson, J. M.; Rooney, J. J. *Macromolecules* **2000**, *33*, 717. (c) Delaude, L.; Demonceau, A.; Noels, A. F. *Macromolecules* **2003**, *36*, 1446. (d) Peeck, L. H.; Leuthäusser, S.; Plenio, H. *Organometallics* **2010**, *29*, 4339.

(14) (a) Lin, W.-Y.; Murugesh, M. G.; Sudhakar, S.; Yang, H.-C.; Tai, H.-C.; Chang, C.-S.; Liu, Y.-H.; Wang, Y.; Chen, I.-W. P.; Chen, C.-H.; Luh, T.-Y. *Chem.—Eur. J.* **2006**, *12*, 324. (b) Lee, J. C.; Parker, K. A.; Sampson, N. S. *J. Am. Chem. Soc.* **2006**, *128*, 4578. (c) Chou, C.-M.; Lee, S.-L.; Chen, C.-H.; Biju, A. T.; Wang, H.-W.; Wu, Y.-L.; Zhang, G.-F.; Yang, K.-W.; Lim, T.-S.; Huang, M.-J.; Tsai, P.-Y.; Lin, K.-C.; Huang, S.-L.; Chen, C.-H.; Luh, T.-Y. *J. Am. Chem. Soc.* **2009**, *131*, 12579. (d) Leitgeb, A.; Wappel, J.; Slugovc, C. *Polymer* **2010**, *51*, 2927.

(15) (a) Vehlow, K.; Wang, D.; Buchmeiser, M. R.; Blechert, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 2615. (b) Lichtenheldt, M.; Wang, D.; Vehlow, K.; Reinhardt, I.; Kühnel, C.; Decker, U.; Blechert, S.; Buchmeiser, M. R. *Chem.—Eur. J.* **2009**, *15*, 9451. (c) Torker, S.; Müller, A.; Chen, P. *Angew. Chem., Int. Ed.* **2010**, *49*, 3762. (d) Buchmeiser, M. R.; Ahmad, I.; Gurram, V.; Kumar, P. S. *Macromolecules* **2011**, *44*, 4098.

(16) **Poly-3** with cis content as high as 81% has been previously reported, albeit in very low conversion. See: Ledoux, N.; Allaert, B.; Verpoort, F. *Eur. J. Inorg. Chem.* **2007**, 5578.

(17) Teo, P.; Grubbs, R. H. *Organometallics* **2010**, *29*, 6045.

(18) (a) Endo, K.; Grubbs, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 8525. (b) Keitz, B. K.; Endo, K.; Herbert, M. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 9686.

(19) Keitz, B. K.; Endo, K.; Patel, P. R.; Herbert, M. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **2012**, *134*, 693.

(20) In early-metal metathesis systems, solvents such as dioxane have been shown to increase the cis content (see ref 13b). In the case of **2**, no change in cis content (for **poly-3**) was observed when the solvent was changed from THF to benzene, dioxane, or DME.

(21) The cis content of **poly-3** did not change when the structurally related catalysts $(H_2IMes)Cl_2Ru{=}CH(o\text{-}^iPr\text{-}Ph)$ and $(H_2IMes)Cl_2Ru(C_5H_5N)_2$ were used as catalysts in place of **1**. This should not be surprising, since all three catalysts initiate to give the same propagating species.

(22) Lowering the temperature of polymerizations using **1** resulted in only a slight increase in % cis that was never more than 5%. See the Supporting Information for details.

(23) (a) Weskamp, T.; Kohl, F. J.; Herrmann, W. A. *J. Organomet. Chem.* **1999**, *582*, 362. (b) Hamilton, J. G.; Frenzel, U.; Kohl, F. J.; Weskamp, T.; Rooney, J. J.; Herrmann, W. A.; Nuyken, O. *J. Organomet. Chem.* **2000**, *606*, 8. (c) Lin, W.-Y.; Wang, H.-W.; Liu, Z.-C.; Xu, J.; Chen, C.-W.; Yang, Y.-C.; Huang, S.-L.; Yang, H.-C.; Luh, T.-Y. *Chem.—Asian J.* **2007**, *2*, 764.

(24) The initiation rate constants of **1** and **2** are $4.6 \times 10^{-4}$ $s^{-1}$ and $8.4 \times 10^{-4}$ $s^{-1}$, respectively. Both of these values are significantly smaller than the initiation rate constant of $(H_2IMes)Cl_2Ru(C_5H_5N)_2$ ($>0.2$ $s^{-1}$), which is the preferred catalyst for ROMP. It should be noted that the initiation rate constant of **2** was dependent on the olefin concentration. For a discussion of initiation in ruthenium metathesis catalysts, see: (a) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543. (b) Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4035.

(25) Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377.

(26) Bielawski, C. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2903.

(27) For examples of cis-selective ROMP of **13** using tungsten catalysts, see: (a) Oreshkin, I.; Redkina, L.; Kershenbaum, I.; Chernenko, G.; Makovetsky, K.; Tinyakova, E.; Dolgoplosk, B. *Eur. Polym. J.* **1977**, *13*, 447. (b) Ceausescu, E.; Cornilescu, A.; Nicolescu, E.; Popescu, M.; Coca, S.; Cuzmici, M.; Oprescu, C.; Dimonie, M.; Hubca, G.; Teodorescu, M.; Grosescu, R.; Vasilescu, A.; Dragutan, V. *J. Mol. Catal.* **1986**, *36*, 163. (c) Wei, J.; Leonard, J. *Eur. Polym. J.* **1994**, *30*, 999.

(28) Subsequent addition of norbornene to the reaction mixture containing **14** and **2** gave **poly-3** with the same selectivity as obtained in the individual polymerization of **3** with **2**, thus demonstrating that *cis*-cyclooctene did not decompose or inhibit **2**.

(29) Walker, R.; Conrad, R. M.; Grubbs, R. H. *Macromolecules* **2009**, *42*, 599.

(30) (a) Bielawski, C. W.; Scherman, O. A.; Grubbs, R. H. *Polymer* **2001**, *42*, 4939. (b) Abdallaoui, I. A.; Semeril, D.; Dixneuf, P. H. *J. Mol. Catal. A: Chem.* **2002**, *182*, 577.

(31) Odian, G. *Principles of Polymerization*, 4th ed.; Wiley: Hoboken, NJ, 2004; pp 238−239.

(32) (a) Bornand, M.; Chen, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 7909. (b) Liu, P.; Xu, X.; Dong, X.; Keitz, B. K.; Herbert, M. B.; Grubbs, R. H.; Houk, K. N. *J. Am. Chem. Soc* **2012**, DOI: 10.1021/ja2108728.