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Controllable ROMP Tacticity by Harnessing the Fluxionality of Stereogenic-at-Ruthenium Complexes

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Abstract: *Readily accessible and easy-to-handle Ru complexes capable of generating all-Z polynorbornene and polynorbornadiene by ring-opening metathesis polymerization (ROMP) with controllable selectivity, ranging from ≈50 to ≥95% syndiotactic, are introduced. It is demonstrated that the rate of non-metathesis based polytopal isomerization and levels of syndiotacticity may be fine-tuned by the adjustment of monomer concentration and catalyst's steric and electronic characteristics.*

Contemporary advances in polymer research have provided ample evidence that desirable macromolecules can be accessed through rational manipulation of microstructures.[1] Predictable implementation of different levels and/or patterns of stereoerror are thus critical, as preparation of polymers that possess a continuum of thermal and physical attributes may then be feasible.[2] Although there has been groundbreaking progress with linear alkenes,[1] tunable stereocontrolled polymer synthesis by ring-opening metathesis polymerization (ROMP) of norbornyl substrates, especially the less functionalized variants, is largely lacking.[3–5] With the advent of *Z*-selective alkene metathesis,[6] efficient and exceptionally syndioselective ROMP processes have been introduced,[7,8] but these transformations are governed by inflexible stereochemical regimes (details below) that are not easily adaptable to strategies capable of delivering variable stereochemical properties. Development of controllable catalytic ROMP that reliably generate different types of polynorbornenes is therefore needed.[3] Easy-to-use catalysts, synthesis and modification of which is not labor-intensive, would be especially attractive. Herein, we report the results of our investigations toward realization of these goals.

A pivotal aspect of olefin metathesis catalyzed by stereogenic-at-metal complexes is that stereochemical inversion occurs each time a metallacyclobutane is generated and cleaved productively.[9] Stereocontrol is directly linked to the relative ease with which these species interconvert.[10–12] In some cases, preserving the fidelity of the chain of events is desirable;[13] in other instances, rapid interconversion between the two catalyst stereoisomers may be manipulated so that high yields and stereoselectivities is attained by channeling the reactions via the more active intermediates (Curtin–Hammett kinetics).[14]

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Ru catechothiolate systems (e.g., **Ru-1a**,**b**; Figure 1) have been shown to promote *Z*-selective ROMP, ring-opening/cross-metathesis (ROCM) and cross-metathesis (CM) reactions,[15] but the issue of tacticity control remains unaddressed.

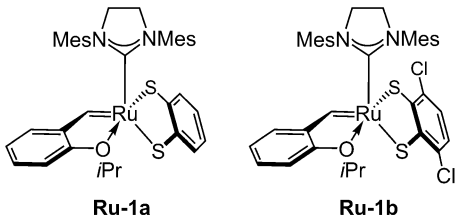
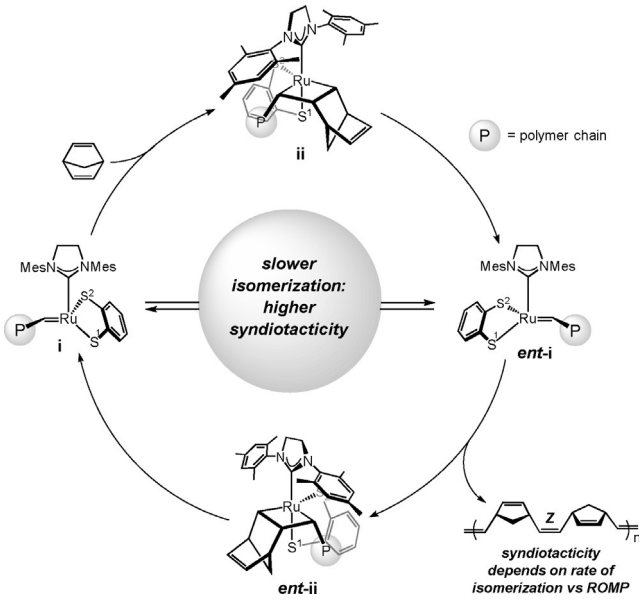


Figure 1. Stereogenic-at-Ru catechothiolate complexes for *Z*-selective olefin metathesis.

ROMP stereoselectivity is particularly dependent on subtle effects that govern a catalyst's fluxional nature.[16] If the *trans* influence between the NHC and anionic ligand S^1 in complex **i** (Scheme 1) were strong enough to destabilize the ground state 14-electron (14-e) complexes sufficiently, interconversion between catalyst enantiomers (cf. **i**→***ent*-i**, Scheme 1) might be facilitated to the degree that non-metathesis based polytopal isomerization[10,11] competes with chain elongation, engendering low tacticity (i.e., interconversion of **i** and ***ent*-i** versus **i**→**ii**→***ent*-i**→***ent*-ii**). Indeed, we find that norbornene



Scheme 1. The rate of non-metathesis based polytopal isomerization versus chain elongation impacts ROMP stereocontrol.

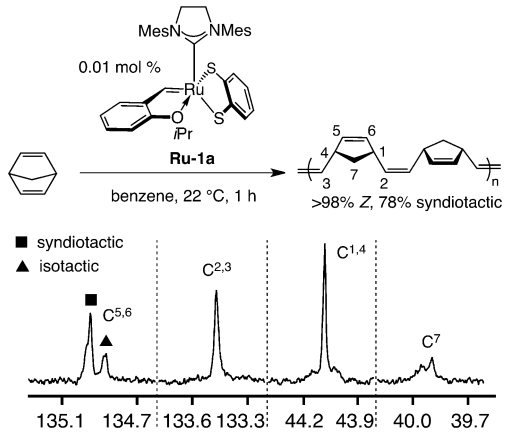
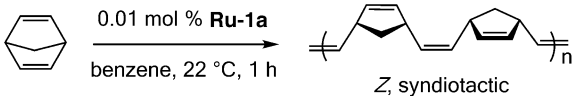


Figure 2. Partial ^{13}C NMR spectra (150 MHz, $CDCl_3$, 55 °C) for ROMP products. (Reactions were performed with 0.01 mol % Ru complex at 22 °C with [monomer] = 0.5 M and 2.5 mol % 1-octene as the chain transfer agent.)

ROMP with **Ru-1a** (> 98 % *Z*) generates a largely atactic polymer (Figure 2). Spectroscopic analysis of polynorbornene and polynorbornadiene and their hydrogenated derivatives[17,18] reveals a similar pattern.[19] Accordingly, we opted to focus on norbornadiene ROMP because of the superior resolution in the ^{13}C NMR spectra and the attendant ease of analysis.

We began by evaluating the effectiveness of a simple strategy, one that is applicable only to readily fluxional catalyst systems: to favor bimolecular propagation versus polytopal rearrangement by enhancing monomer concentration. The data summarized in Table 1 clearly illustrate that as

Table 1: Influence of monomer concentration on tacticity.[a]



Entry	[Momomer] [M]	Syndiotacticity [%][b]
1	0.05	56
2	0.1	63
3	0.5	78
4	1.0	83
5	2.0	85

[a] Reactions were performed under N_2 atmosphere; > 98:2 *Z*:*E* in all cases. [b] Determined by analysis of ^{13}C NMR spectra (150 MHz, $CDCl_3$, 55 °C) by integration of peaks at δ 135.17–135.07 versus δ 135.07–134.98 ppm. See the Supporting Information for details.

monomer concentration is increased, so does the level of syndiotacticity. Whereas isomerization is highly competitive in a 0.05 M solution (56 % syndiotactic, entry 1), at 2.0 M monomer concentration the product is formed with 85 % syndiotacticity (entry 5). As might be expected, the initial stereoselectivity is diminished by 3–5 % towards the end due to a gradual decrease in monomer concentration.[19]

In search of clues as how to implement catalyst-controlled selectivity, DFT studies were performed (Figure 3).[20] We

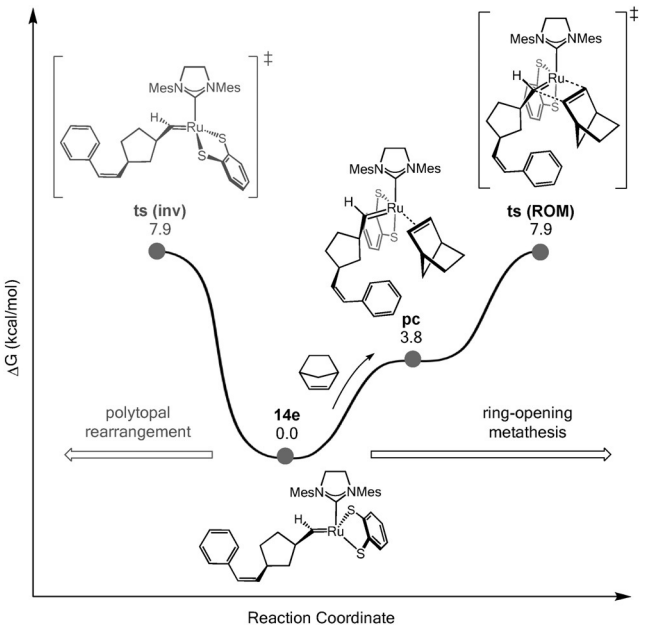
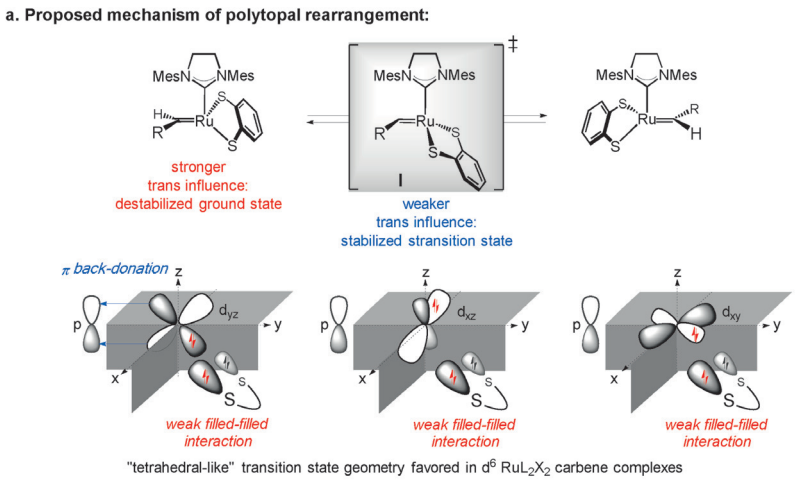


Figure 3. Competition between catalyst isomerization [transition state for complex inversion; **ts(inv)**] and ring-opening metathesis [transition state for ring-opening metathesis; **ts(ROM)**] computed at the ωB97XD/Def2TZVPP$_{benzene(SMD)}$//ωB97XD/Def2SVP$_{thf(PCM)}$ level of theory (ΔG in kcal mol^{-1}); norbornene instead of norbornadiene has been used in the simulations. Abbreviations: ts, transition state; pc, π-complex.

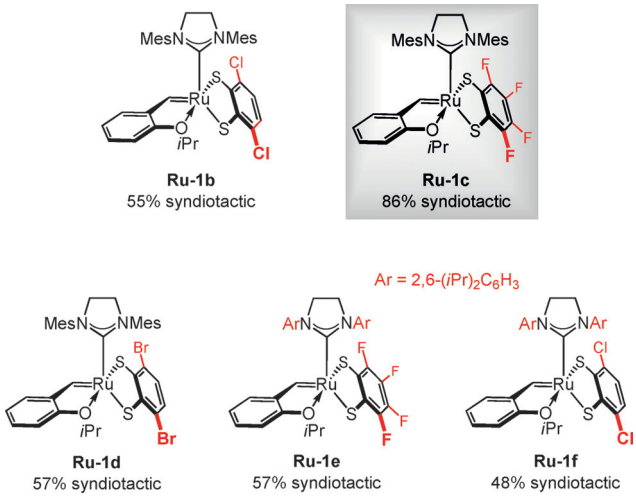
found that the transition states for non-metathesis based polytopal rearrangement [**ts(inv)**] and ring-opening metathesis [**ts(ROM)**] are of similar energy (7.9 kcal mol^{-1} relative to **14e**).[21] This suggested that alterations within the catalyst structure could engender significant selectivity changes, but the question was: Exactly what catalyst features would help reduce the rate of polytopal isomerization without diminishing efficiency?

The ligand field in the 14-e complexes is likely determined by the two strongly σ-donating carbene ligands, favoring a C-Ru-C angle of ≈ 90°; such an arrangement lessens the repulsive *trans* influence between the C-based ligands, causing electron donation into the vacant Ru $d_{x^2-y^2}$ and d_{z^2} orbitals. To curtail unfavorable filled-filled interactions with the d_{xz} and in particular the d_{xy} orbital during isomerization, the catechothiolate ligand may slide at an angle of ≈ 45° with respect to the *xy* or *xz* plane (Scheme 2 a).[22,23] In this way, the steric strain between the larger N-aryl moiety of the NHC ligand[24] and the dithiolate substituent would be minimized (**II**→**III**→***ent*-II**; Scheme 2 b). The above arguments suggest that more sizeable NHC and/or catechothiolate substituents should promote faster isomerization and lower tacticity. The impact of electronic factors, on the other hand, was more difficult to predict.

To shed light on the above issues, we probed the stereoselectivity patterns generated by **Ru-1a**–**f**, easily accessible variants wherein the NHC and/or the catechothiolate ligands is sterically and/or electronically modified. Reactions were carried out with norbornadiene at 0.5 M monomer concentration and ambient temperature (Scheme 3).



Scheme 2. Rationale for polytopal rearrangement with 14-e Ru catechothiolate complexes, and possible influence of steric factors. Abbreviations: R, functional group; Mes, 2,4,6-$Me_3C_6H_2$.



Scheme 3. Influence of catalyst structure on norbornadiene ROMP tacticity based on ^{13}C NMR analysis (150 MHz, $CDCl_3$, 55 °C). (With 0.01 mol % Ru complex, [monomer] = 0.5 M at 22 °C for 1 h; >98:2 *Z*:*E* in all cases; syndiotactic:isotactic ratios determined by integration of peaks at δ 135.17–135.07 versus 135.07–134.98 ppm. See the Supporting Information for details.)

Whereas ROMP with tetrafluoro species **Ru-1c** was found to be more syndioselective than unsubstituted **Ru-1a** (86:14 versus 78:22 syndiotactic:isotactic), polymerizations with 3,6-dichloro and 3,6-dibromo complexes **Ru-1b** and **Ru-1d** gave mostly atactic materials (≈50:50 syndiotactic:isotactic). The syndiotacticity profile H > Cl ≈ Br thus emerged, implying that steric repulsion between the NHC and a nearby *ortho*-halogen substituent in **Ru-1b** and **Ru-1d** probably facilitates polytopal rearrangement. In the case of **Ru-1e** and **Ru-1f** the larger N-aryl groups accelerate isomerization, discouraging bimolecular propagation likely due to a more limited access to the active site. With **Ru-1b** and **Ru-1f**, when monomer concentration is between 1.0 and 0.05 M and syndiotactic/isotactic ratios are near unity ROMP is almost entirely subject to chain-end control because polytopal rearrangement is just too facile (cf. Scheme 2b).[19]

It may be argued that tetrafluorocatechothiolate complex **Ru-1c** affords superior syndiotacticity compared to **Ru-1a**, despite the longer C–F bond (versus C–H) due to the strongly electron withdrawing impact of the halogen atoms; that is, the less donating sulfide ligands may induce less *trans* influence, raising the barrier to rearrangement. The more active (Lewis acidic) complex (**Ru-1c**) might also promote ROMP faster than polytopal isomerization. Still, the selectivity profile derived from the data in Figure 1 and Scheme 3 (**Ru-1c** > **Ru-1a** ≫ **Ru-1b** ≈ **Ru-1d**) suggests that electronic effects are less important than steric factors. This contention is supported by the Ru^{II}/Ru^{III} one-electron oxidation potentials determined by cyclic voltammetry relative to the ferrocene/ferrocenium (Fc/Fc^+) couple (Figure 4), which reveal the following order: **Ru-1c** > **Ru-1b** ≈ **Ru-1d** > **Ru-1a**. The weaker impact of electronic factors is underscored by the fact that the most stereo-regular polymer can be obtained by the use of complexes with the lowest (**Ru-1a**) or the highest oxidation potential (**Ru-1c**).

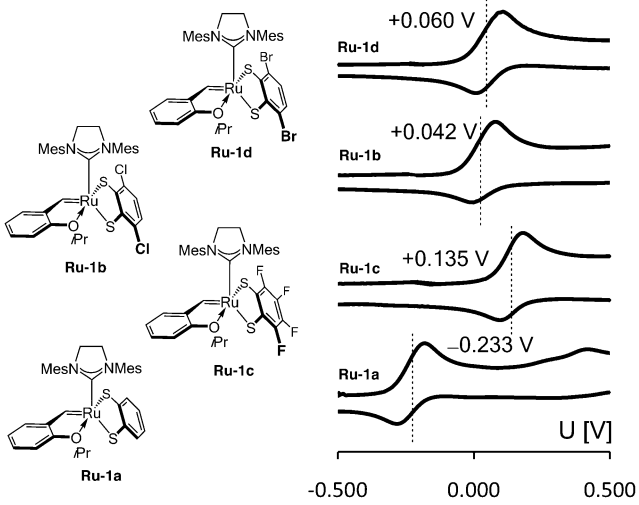


Figure 4. Ru^{II}/Ru^{III} oxidation potentials determined by cyclic voltammetry relative to Fc/Fc^+ couple (Fc, ferrocene).

Guided by the above observations and analyses, we were able to identify a monomer concentration/Ru complex combination that generates decidedly improved stereoselectivity. When norbornadiene ROMP was performed with 0.01 mol % **Ru-1c** at 2.0 M monomer concentration the polymeric product was obtained with 93% syndiotacticity (versus 85% with **Ru-1a**; entry 5, Table 1); at 5.0 M concentration (Figure 5), selectivity was further increased to ≥95% (i.e., isotactic sequences were below detection limit; >98:2 *Z*:*E*; 74% yield).[25]

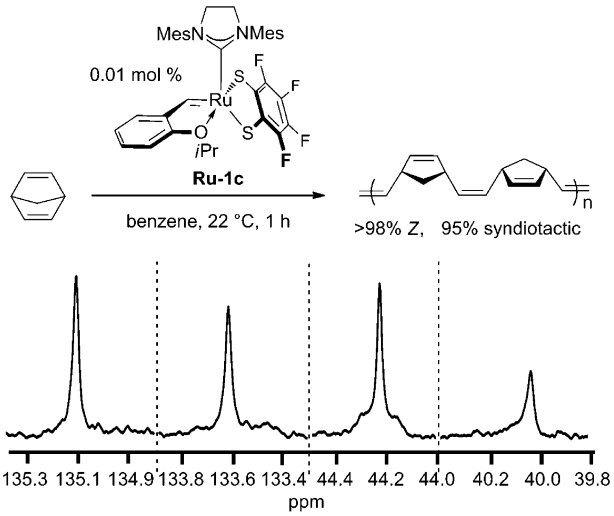
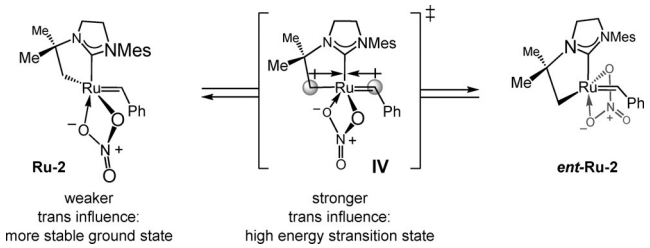


Figure 5. ^{13}C NMR spectrum (150 MHz, $CDCl_3$, 55 °C) of highly *Z*- and syndiotactic polynorbornadiene (>98% *Z* and ≥95% syndiotacticity: isotacticity) generated by the use of 0.01 mol % tetrafluoro-catechothiolate complex **Ru-1c** at [monomer] = 5.0 M. (Ratios determined by integration of peaks at δ 135.17–135.07 and 135.07–134.98 ppm.)

Reactions with **Ru-1a** or **Ru-1c** can be performed without rigorous exclusion of air and moisture. Samples of catechothiolate complexes were weighed out in air and unpurified monomer was used (e.g., norbornadiene with 0.01 mol % **Ru-1c** after 1 h: 76% yield, and ≥95% syndiotacticity). This is in contrast to ROMP with Mo monoaryloxide pyrrolide (MAP)[7] or bidentate Ru complexes (e.g., **Ru-2**[8]), for which inert atmosphere conditions (glovebox) is critical.[26]

We propose that the distinction between the catechothiolate systems and entities such as **Ru-2**[8] or a MAP species[7] is rooted in the ease with which polytopal rearrangement occurs. As noted before, a catechothiolate 14-e species (cf. **i**, Scheme 1) is destabilized by the *trans* influence between NHC and anionic sulfide ligands; this is alleviated in the transition state for isomerization (cf. **i**→***ent*-i**, Scheme 1), which as a result becomes energetically less costly. There is no significant repulsive force in the 14-e ground states of a Mo MAP alkylidene,[27] nor is there any major destabilizing interaction in the ground state complexes represented by **Ru-2** (Scheme 4). With three strong C-based donor groups in the latter Ru system inversion would have to proceed through a high-energy transition state geometry (**IV**).[28]

In brief, we disclose catalytic ROMP processes that can be used to obtain all-*Z* polymers with controllable selectivity ranging from ≈50% (chain-end control) to ≥95% syndiotactic (stereogenic-at-metal control). By mechanism-based tuning of steric and electronic attributes of Ru catechothiolate complexes and adjustment of monomer concentration, ROMP of unfunctionalized norbornenes can be carried out to access products of varying tacticity in a predictable fashion.



Scheme 4. Strong *trans* influence raises the barrier to polytopal rearrangement.

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Keywords: catalysis · olefin metathesis · polytopal rearrangement · ring-opening metathesis polymerization (ROMP) · stereochemistry

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[19] See the Supporting Information for details.

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[21] Modeling of dispersion interactions (e.g., ωB97XD) is key for obtaining a reliable comparison of unimolecular as opposed to bimolecular events. A similar result was obtained at the PBE0-D3BJ/Def2TZVPP$_{benzene(SMD)}$//ωB97XD/Def2SVP$_{thf(PCM)}$ level (9.1 and 8.2 kcal mol^{-1}), whereas the bimolecular ROM step is significantly disfavored with PBE0 [3.7 versus 16.8 kcal mol^{-1} for **ts(inv)** versus **ts(ROM)**]. See the Supporting Information for further details including investigation with density functionals M06, MN12SX, MN12L, M06L, BP86-D3BJ and BP86.

[22] For an illustrative animation extracted from intrinsic reaction coordinate (IRC) calculations, see the Supporting Information.

[23] Inversion through polytopal rearrangement of five-coordinate species (e.g., **Ru-1a**) are energetically more demanding (> 30 kcal mol^{-1}); see: Ref. [10b].

[24] The rotational barrier around the Ru–C^{NHC} bond in the 14-e complex **II**→**III** (cf. Scheme 2b, X = H and R = Ph) has been calculated to be only 4.3 kcal mol^{-1} (M06/Def2QZVP$_{benzene(PCM)}$//BP86/basis1$_{gas-phase}$). Furthermore, steric interaction between the rotating NHC ligand and the *ortho* substituent on the dithiolate might be transmitted via solvent molecules. See the Supporting Information for details.

[25] The melting point of the hydrogenated polymer (from reaction with **Ru-1c**), determined by differential scanning calorimetry (DSC), is 124.6 °C; this is consistent with the trend reported previously (cf. Ref. [3]) illustrating that the melting point decreases in case of hydrogenated polynorbornenes as syndiotacticity is enhanced.

[26] For example, in our hands, ROMP of norbornene with 0.05 mol % of a commercially available analogue of **Ru-2** (Ref. [8]) proceeded to > 98 % conversion in one hour when performed in a glovebox but there was only 25 % conversion when carried out in a fume hood under otherwise identical conditions; see the Supporting Information for details.

[27] We are not aware of any experimental evidence regarding polytopal isomerization in a four-coordinate Mo MAP species. Only stereochemical inversion of a five-coordinate complex, generated by the addition of a donor ligand (PMe_3), has been

reported; see: S. C. Marinescu, R. R. Schrock, B. Li, A. H. Hoveyda, *J. Am. Chem. Soc.* **2009**, *131*, 58 – 59.

[28] A related study has recently appeared; see: L. E. Rosebrugh, T. S. Ahmed, V. M. Marx, J. Hartung, P. Liu, J. G. Lopez, K. N. Houk, R. H. Grubbs, *J. Am. Chem. Soc.* **2016**, *138*, 1394 – 1405. It was shown that in ROMP processes performed with **Ru-2** there are no concentration effects on stereoselectivity, and it is unlikely that polytopal rearrangements occur. This serves as additional support regarding the distinction between the mechanistic attributes of Ru catechothiolate complexes and those that contain a bidentate NHC ligand in promoting ROMP processes, which behave similarly to Mo MAP systems.

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