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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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Readily Accessible and Easily Modifiable Ru-Based Catalysts for Efficient and *Z*-Selective Ring-Opening Metathesis Polymerization and Ring-Opening/Cross-Metathesis

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Supporting Information

ABSTRACT: Rationally designed Ru-based catalysts for efficient *Z*-selective olefin metathesis are featured. The new complexes contain a dithiolate ligand and can be accessed in a single step from commercially available precursors in 68–82% yield. High efficiency and exceptional *Z* selectivity (93:7 to >98:2 *Z*:*E*) were achieved in ring-opening metathesis polymerization (ROMP) and ring-opening/cross-metathesis (ROCM) processes; the transformations typically proceed at 22 °C and are operationally simple to perform. Complete conversion was observed with catalyst loadings as low as 0.002 mol %, and turnover numbers of up to 43 000 were achieved without rigorous substrate purification or deoxygenation protocols. X-ray data and density functional theory computations provide support for key design features and shed light on mechanistic attributes.

Reliable access to *Z* alkenes has far-reaching implications in chemistry and related disciplines,[1] rendering it critical that entities containing such functional groups are made available through catalytic, efficient, and stereoselective processes. Accordingly, the discovery of highly active olefin metathesis catalysts that deliver effective control of stereoselectivity is a compelling objective of research in modern chemistry.[2] Because olefin metathesis is a reversible process, isomerization of kinetically generated *Z* olefin products to the thermodynamically favored *E* alkenes, particularly at late stages of a process, is frequently a significant complication, rendering the development of high-yielding *Z*-selective catalytic transformations a difficult task. The first general advance in this area arrived in the form of reactions catalyzed by Mo- and W-based monoaryloxide pyrrolide complexes,[3] and this was followed by applications to stereoselective synthesis of biologically active natural products.[3c,d,g,h] Subsequent investigations led to Ru catalysts bearing a bidentate P-based ligand for chemo- and stereoselective ring-opening metathesis polymerization (ROMP)[4] or a bidentate N-heterocyclic carbene (NHC) moiety for various olefin metathesis processes;[5] in many instances, the latter set furnish moderate to high *Z* selectivity for reactions of unhindered terminal alkenes (e.g., without a secondary allylic substituent). Additionally, a monothiolate Ru chloride was recently shown to promote homodimerization of similar types of terminal olefins with moderate *Z*:*E* ratios.[6] In most cases, substantial amounts of the *E* isomer were generated at higher conversions and/or improved stereoselectivity was achieved at the expense of diminished catalytic activity.

Herein we report stereogenic-at-Ru complexes that are easily accessed from commercially available sources in a single step and can be used to catalyze *Z*-selective ROMP and ring-opening/cross-metathesis (ROCM) efficiently with turnover numbers (TONs) of up to 43 000. The transformations are exceptionally *Z*-selective, typically delivering *Z*:*E* ratios of >98:2 at >90% conversion; hydroxyl groups do not adversely affect the catalyst activity. We provide the first examples of *Z*-selective Ru-catalyzed ROCM reactions involving styrenes or other sterically hindered olefin cross-partners such as vinylcyclohexane.

The present studies were inspired by the principles that have emerged from our efforts to develop high-oxidation-state Mo and W complexes for *Z*-selective olefin metathesis.[3,7] We surmised that high *Z* selectivity might be attained if the complex contains axial moieties that are significantly different in size and an alkene approaches preferentially through the equatorial plane (**I** in Figure 1; association syn to L or s); in such a manner, transformations via metallacyclobutanes bearing syn substituents (oriented away from the sizable axial group) would deliver *Z* alkenes predominantly. In the context of dichlororuthenium systems,[8] $\mathbf{II}_{syn}$ (Figure 1) contains ligands properly arranged for

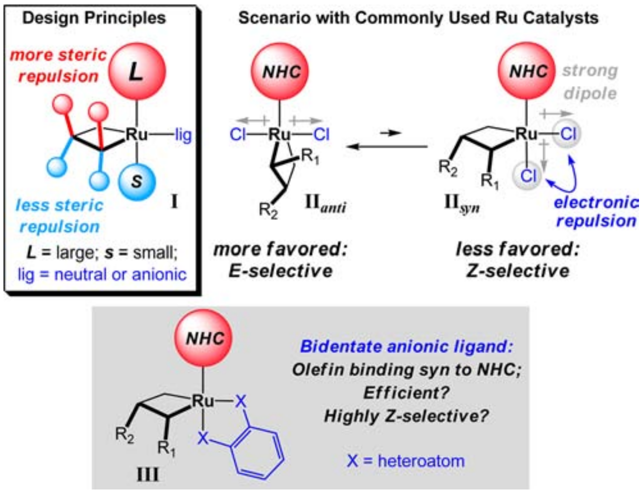


Figure 1. Key structural features and rationale for the design of *Z*-selective Ru catalysts.

Received: April 30, 2013
Published: July 3, 2013

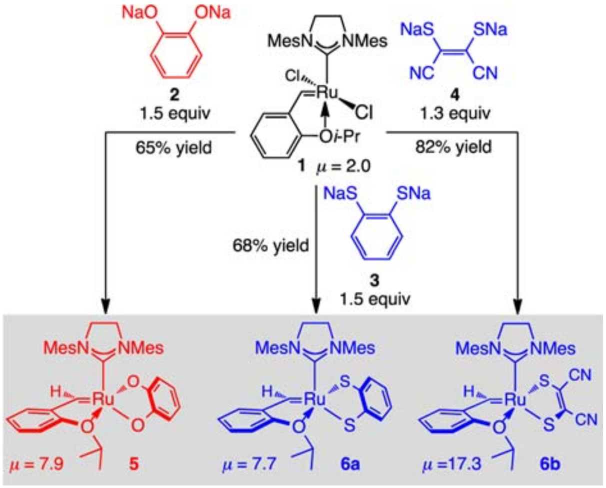
dx.doi.org/10.1021/ja404208a | *J. Am. Chem. Soc.* 2013, 135, 10258–10261

attaining *Z* selectivity. Nonetheless, reaction via such an intermediate would be energetically disfavored for several reasons (cf. Figure 1): electron−electron repulsion between the axially and equatorially situated syn Cl ligands,[9] high dipole moment,[10,11] and steric repulsion between the NHC and ruthenacycle substituents. Accordingly, the preferred pathways generally involve the intermediacy of entities represented by $\mathbf{II}_{anti}$,[12] as depicted in Figure 1. The symmetric nature of $\mathbf{II}_{anti}$, however, translates into the predominant formation of the thermodynamically favored *E* isomer in most instances.[13,14]

To conceive a *Z*-selective Ru catalyst, we opted to pursue a scaffold that possesses the structural attributes of complex $\mathbf{II}_{syn}$ and has the ability to avoid the intermediacy of a species represented by $\mathbf{II}_{anti}$. We envisioned that replacement of the halogen groups with a bidentate dianion such as a catecholate or a related S-based analogue would allow us to achieve the aforementioned objective, as the two anionic ligands would be forced to adopt a syn orientation[9] (**III** in Figure 1).

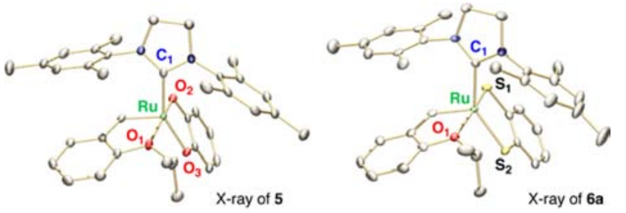
Replacement of chlorides of a Ru complex with a catecholate has previously been accomplished, but by procedures that require toxic thallium salts and sensitive pyridyl complex precursors.[15] To devise a more practical and easily generalizable route, we envisaged a transformation between the robust and commercially available phosphine-free Ru carbene **1**[16] and disodium catecholate (**2**) (Scheme 1). The above considerations led us to establish that double displacement of the chlorides proceeds to completion in 3 h [22 °C in tetrahydrofuran (thf)], affording complex **5** in 65% yield after purification. Similarly, the dithio-based carbenes **6a** and **6b** were synthesized and isolated in 68−82% yield. The polarity of Ru carbenes **5**, **6a** and **6b** (calculated dipole moments: 7.9, 7.7, and 17.3 D, respectively)[17] allowed for ease of purification and removal of trace impurities, including any unreacted **1** (2.0 D), which is highly active and typically gives rise to *E*-selective reactions. The latter characteristics minimized the possibility of competitive nonselective side reactions by any catalytically active contaminants.

Scheme 1. Preparation of Ru-Based Complexes 5, 6a, and 6b[a]



[a]See the Supporting Information for details. Mes = 2,4,6-$Me_3C_6H_2$.

We obtained X-ray structures for complexes **5** and **6a**, which elucidate some of their key structural characteristics (Figure 2). The isopropoxy ligands are chelated syn to the NHC moiety,[9] reflecting the manner in which a substrate alkene might associate with a catalytically active Ru carbene.[18] Another prominent feature relates to the tendency to avoid unfavorable donor−donor interactions between the strongly donating NHC and an anionic ligand, as evidenced by the deviation from linearity of the C_1−Ru−O_3 (149.2°) and C_1−Ru−S_2 (143.4°) angles (Figure 2). Finally, the C_1−Ru and O_1−Ru bonds are longer in **6a** than in **5**, probably as a consequence of stronger electron donation (trans influence) by S versus O.

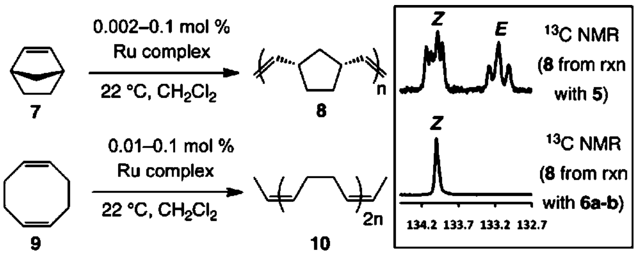


	5		6a
C_1–Ru	2.015 Å	C_1–Ru	2.061 Å
O_1–Ru	2.192 Å	O_1–Ru	2.277 Å
C_1–Ru–O_3	149.2°	C_1–Ru–S_2	143.4°
O_1–Ru–O_2	169.3°	O_1–Ru–S_1	169.8°

Figure 2. ORTEP representations of the X-ray structures of (left) **5** and (right) **6a** with selected bond lengths and angles.

Next, we evaluated the ability of Ru carbenes **5**, **6a**, and **6b** to promote ROMP processes (Table 1). Polymerization of norbornene (**7**) took place readily in the presence of 0.1 mol % **5** at 22 °C in dichloromethane (96% yield of **8** after 1 h), albeit with a minimal preference for *Z* isomers (58:42 *Z*:*E*; Table 1, entry 1). In contrast, with S-containing complexes **6a** and **6b**, the same reaction proceeded with similarly high efficiency but was exceptionally *Z*-selective (>98% *Z*; entries 2 and 3).[19] To evaluate the robustness of the catalytic system, we carried out these latter transformations without purification of the norbornene monomer. The high stereoregularity of the poly(norbornene) (**8**) generated through the use of **6a** or **6b** (vs **5**) is clearly illustrated by comparison of the olefin regions of the corresponding ^{13}C NMR spectra (Table 1).[20] A similar trend in the *Z* content was observed for **10** obtained from ROMP of less

Table 1. *Z*-Selective Ru-Catalyzed ROMP Reactions[a]



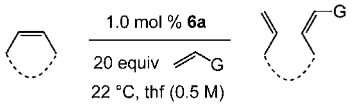
entry	monomer	complex; mol %	time (h); yield[b]	*Z*:*E*[b]	TON
1	7	**5**; 0.1	1.0; 96	58:42	960
2	7	**6a**; 0.1	1.0; 93	>98:2	930
3	7	**6b**; 0.1	1.0; 90	>98:2	900
4	9[c]	**5**; 0.1	24; 88	72:28	880
5	9[c]	**6a**; 0.1	24; 75	>98:2	750
6	9[c]	**6b**; 0.1	24; 75	>98:2	750
7	7[c]	**6b**; 0.01	1.0; 92	>98:2	9200
8	7[c]	**6b**; 0.002	1.0; 86	>98:2	43000
9	9[c]	**6b**; 0.01	24; 35	>98:2	3500
10	9[c]	**6b**; 0.01	48; 54	>98:2	5400

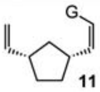
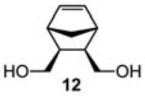
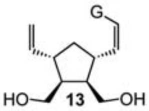
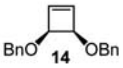
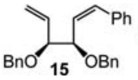
[a]See the Supporting Information for experimental details. [b]Determined by ^1H NMR analysis of the purified products. [c]The substrate was passed through a short column of basic alumina before use.

strained 1,5-cyclooctadiene (**9**): whereas 72% *Z* selectivity[21] was obtained with Ru carbene **5**, there was a complete preference for the higher-energy isomer when **6a** or **6b** was used (>98% *Z*; entries 5 and 6).[20] To gain further insight into the activity levels that can be provided by complex **6b**, we performed the aforementioned polymerizations with reduced catalyst loadings (entries 7−10). With as little as 0.002 mol % **6b**, **8** was generated with a TON of 43 000 in 1 h (entry 8). Equally notable is the TON of 3500 achieved for polymerization of **9** after 24 h at a **6b** loading of 0.01 mol % (entry 9), a value that increased to 5400 after 48 h (entry 10), underlining the considerable longevity of the catalytically active Ru carbene. These findings compare favorably with the *Z* selectivities (e.g., 88:12 *Z*:*E* for **8** and 96% *Z*[21] for **10**) and TONs (e.g., 38 in 72 h for **10**) reported recently for the same ROMP process catalyzed by a Ru-based catalyst.[22]

We then examined *Z*-selective ROCM,[3a,e,5e] which to date has been limited to enol ether cross-partners when a Ru catalyst is involved.[5e] Catalytic ROCM of **7** with styrene in the presence of 1.0 mol % **6a** generated **11a** in 75% yield with 98:2 *Z*:*E* (Table 2, entry 1). Such exceptional stereoselectivity underscores the efficient stereocontrol induced by the Ru catalyst to disfavor the corresponding *E* alkene, which is 2.9 kcal/mol lower in energy than the *Z* isomer.[17] Catalytic ROCM of **7** with more hindered and less reactive vinylcyclohexane delivered **11b** in 59% yield with complete *Z* selectivity (<2% *E*; entry 2). The disulfide complexes are fully tolerant of alcohols, as evidenced by the efficient ROCM of **12** with styrene (entry 3), which readily afforded substituted styrene **13a** in 92% yield with high *Z* selectivity (97%). The Ru-catalyzed ROCM reactions of **12** were found to be exceptionally *Z*-selective with different cross-partners, regardless of their electronic or steric attributes (entries 3−6). Finally, the ROCM of 2,3-dibenzyloxycyclobutene (**14**) with styrene proceeded to completion in 12 h at 40 °C in the presence of 3.0 mol % **6a**, affording the desired 1,5-diene **15** in 63% yield with 93:7 *Z*:*E* (entry 7).[23] The present class of Ru-catalyzed olefin metathesis reactions are operationally simple to perform. For example, when a sample of **6a** (1.0 mol %) was weighed in air and the ROCM in entry 3 of Table 2 was performed under a N_2 atmosphere in a typical fume hood, the transformation proceeded with the same level of efficiency and *Z* selectivity (1.0 h, 22 °C, thf).

Table 2. *Z*-Selective ROCM with Styrenes and Vinylcylohexane[a]



entry	substrate	G	time (h)	product	conv (%);[b] yield (%)[c]	*Z*:*E*[b]
1	 **7**	**a** C_6H_5	1.0	 **11**	>98; 75	98:2
2		**b** Cy	2.0		>98; 59	>98:2
3	 **12**	**a** C_6H_5	1.0	 **13**	>98; 92	97:3
4		**b** *m*-FC_6H_4	1.0		>98; 93	96:4
5		**c** *p*-$MeOC_6H_4$	1.0		>98; 82	98:2
6		**d** Cy	8.0		88; 61	>98:2
7	 **14**	C_6H_5	12	 **15**	94; 63	93:7

[a] See the Supporting Information for details. In entry 7, 3.0 mol % **6a** was used at 40 °C. [b] Determined by ^{1}H NMR analysis of the unpurified mixtures. [c] Yields of isolated and purified products.

Analysis of the calculated free energy surfaces of the four possible modes of reaction involving carbenes **A** and **B** associated with ROCM of **7** and styrene catalyzed by **6a** (cf. Table 2, entry 1), as outlined in Figure 3, lends credence to the proposed stereochemical model (cf. Figure 1).[24] The transition states **ts1**$_{Z\text{-B}}$ and **ts1**$_{E\text{-B}}$ associated with the formation of metallacycles **mcb**$_{Z\text{-B}}$ and **mcb**$_{E\text{-B}}$, respectively, appear to be strongly disfavored because of unfavorable steric repulsion between the carbene's phenyl group and the NHC ligand, which forces the heterocyclic moiety and the Mes plane to undergo a tilt (cf. **ts1**$_{E\text{-B}}$). The latter effect is evident in the distortion of the Ru carbene to give a S−Ru−C angle of 139° in **ts1**$_{E\text{-B}}$ (vs 109° and 110° in **ts1**$_{Z\text{-A}}$ and **ts1**$_{E\text{-A}}$, respectively).[24] Furthermore, comparison of the energetically favored modes of reaction involving isomer **A** suggests that **ts1**$_{Z\text{-A}}$ (3.2 kcal/mol), which leads to the *Z* alkene, is energetically more favored than **ts1**$_{E\text{-A}}$ (6.4 kcal/mol); unlike the bridgehead of the bicyclic moiety in **ts1**$_{Z\text{-A}}$, which is oriented away from the NHC, this substrate moiety suffers from unfavorable propinquity with the bulky heterocyclic ligand in **ts1**$_{E\text{-A}}$.

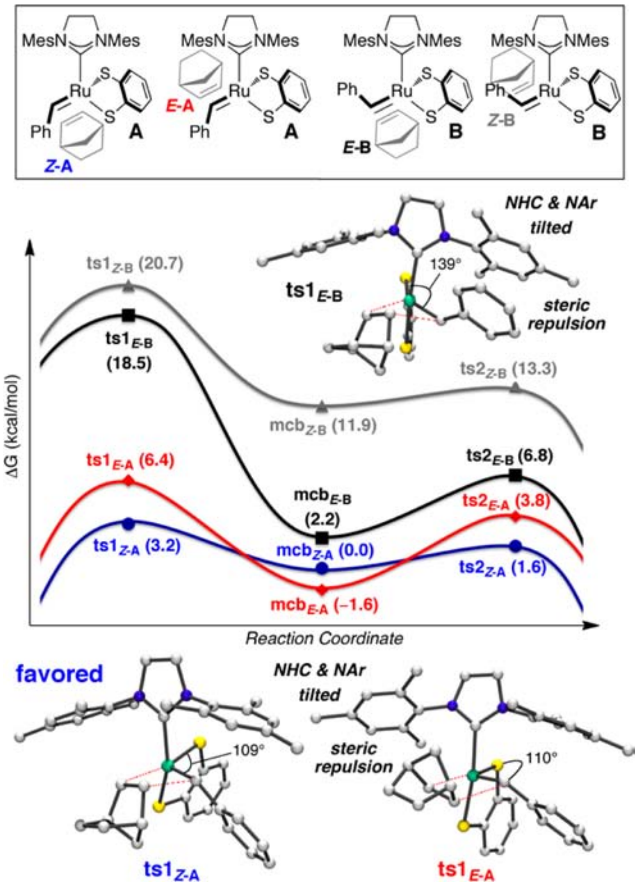


Figure 3. Stereochemical model and rationale for the *Z* selectivity (mcb = metallacyclobutane, ts = transition state).

In brief, we have designed Ru complexes that catalyze ROMP and ROCM reactions with high efficiency and *Z* selectivity; their tolerance of hydroxyl units, high turnover numbers, and ease of use foreshadow substantial utility. The preparation of derivatives, made feasible by the readily modular nature of the complexes, should result in the identification of analogues that possess special features; related investigations are in progress.

ASSOCIATED CONTENT

Supporting Information

Procedures and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support was provided by the NSF (CHE-1111074). R.K.M.K. and S.T. acknowledge LaMattina Graduate and Swiss NSF Postdoctoral Fellowships, respectively. We thank Dr. Bo Li for assistance with obtaining X-ray data.

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(16) (a) Garber, S. B.; Kingsbury, J. S.; Gray, B. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 8168. (b) Reference 2d.

(17) The dipole moments (μ) of complexes **1**, **5**, **6a**, and **6b** and the energies of (*E*)- and (*Z*)-**11a** were calculated at the BP86/basis1 level. See the Supporting Information for details.

(18) For the isolation of a Ru complex with an alkene coordinated syn to the NHC, see: Anderson, D. R.; Hickstein, D. D.; O'Leary, D. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 8386.

(19) Initial studies suggested that catecholate complex **5** decomposes more readily and that the observed lack of selectivity might therefore be spurious; efforts to elucidate these and related issues are underway.

(20) For *Z*-selective ROMPs of **7** and **9** with Mo-based alkylidenes, see: (a) Reference 3b. (b) Yuan, J.; Schrock, R. R.; Gerber, L. C. H.; Müller, P.; Smith, S. *Organometallics* **2013**, *32*, 2983.

(21) The actual *Z* selectivity in ROMP of **9** is less than the reported value, since only one of the two alkenes undergoes reaction.

(22) Keitz, B. K.; Fedorov, A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2012**, *134*, 2040.

(23) The elevated temperature (vs 22 °C) and catalyst loading (vs 1.0 mol %) required in this case might be a consequence of intramolecular chelation of the Ru center with the benzyloxy group, which would decrease the catalyst activity.

(24) Free energy (ΔG) surfaces were computed at the ωB97XD/basis2$_{\mathrm{THF}}$//ωB97XD/basis1$_{\text{gas-phase}}$ level. For more extensive investigations with other density functionals (BP86, M06, M06-2X) and computational details, see the Supporting Information.