Dihydroxylation

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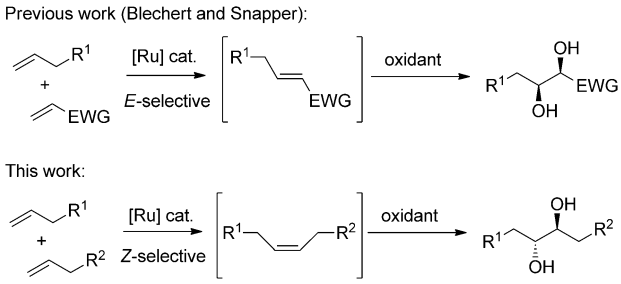
Tandem *Z*-Selective Cross-Metathesis/Dihydroxylation: Synthesis of *anti*-1,2-Diols**

*Peter K. Dornan, Zachary K. Wickens, and Robert H. Grubbs**

Abstract: *A stereoselective synthesis of anti-1,2-diols has been developed using a multitasking Ru catalyst in an assisted tandem catalysis protocol. A cyclometalated Ru complex catalyzes first a Z-selective cross-metathesis of two terminal olefins, followed by a stereospecific dihydroxylation. Both steps are catalyzed by Ru, as the Ru complex is converted to a dihydroxylation catalyst upon addition of $NaIO_4$. A variety of olefins were transformed into valuable, highly functionalized, and stereodefined molecules. Mechanistic experiments were performed to probe the nature of the oxidation step and catalyst inhibition pathways. These experiments point the way to more broadly applicable tandem catalytic transformations.*

Highly functionalized and stereochemically complex motifs are attractive targets in synthesis because of their diverse molecular interactions in therapeutic and other specialty applications. Efficient synthesis of densely functionalized targets from simple starting materials is thus an important challenge. Assisted tandem catalysis, in which coupled catalytic processes are effected by a single catalyst, can significantly increase molecular complexity.[1] Ru metathesis catalysts have frequently been used in tandem reactions, as the C–C bond-forming step in olefin metathesis can be coupled to a structural elaboration step that introduces additional functionality.[2] In 2006, Blechert[2k] and Snapper[2l] demonstrated that cross-metathesis using second-generation catalysts **Ru-1** or **Ru-2** followed by a Ru-catalyzed dihydroxylation in the presence of $NaIO_4$ as an oxidant led to the corresponding diol (Scheme 1). The dihydroxylation step is highly stereospecific, and thus the diastereoselectivity of the diol is determined by the geometry of the olefin. As the metathesis occurs under thermodynamic (i.e. substrate) control, primarily *E* olefins were produced, leading to predominantly *syn*-diols. Thus *anti*-diols,[3] which are important motifs in natural products and intermediates in synthesis, are inaccessible by these methods. If a catalyst-controlled cross-metathesis could be coupled to a dihydroxylation, then *anti*-diols with predictable and high levels of diastereoselectivity could be accessed. Using this multitasking approach, simple allyl alcohol and allyl amine derivatives could be transformed into valuable, densely functionalized products in a catalyst-controlled fashion.



Scheme 1. Tandem metathesis/dihydroxylation. Blechert[2k] and Snapper[2l] demonstrated that substrate-controlled cross-metathesis generally leads to *syn*-diols via the *E* olefins. We demonstrate that *Z*-selective catalysts lead to *anti*-diols in a catalyst-controlled fashion via the *Z*-olefins. In both cases, both reaction steps are catalyzed by a Ru complex. EWG = electron-withdrawing group.

Significant progress has been made in the development of *Z*-selective olefin-metathesis catalysts using Ru,[4–8] Mo,[9–11] and W[12] alkylidene complexes.[13] Highly *Z*-selective cyclometalated Ru complexes (**Ru-3** and **Ru-4**, Figure 1) have been investigated by our group for diverse applications.[14,15] However, these complexes have not been demonstrated to be viable for tandem catalysis, despite the potential to significantly increase the molecular complexity with high stereocontrol in a one-pot sequence.

We proposed that cyclometalated complexes would be able to catalyze the dihydroxylation of olefins if conditions could be identified to generate a suitably oxidized Ru

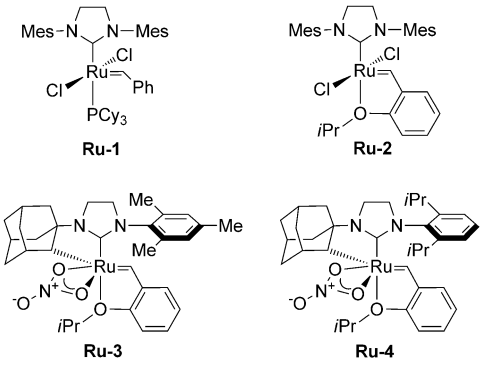


Figure 1. Second-generation (**Ru-1** and **Ru-2**) and cyclometalated (**Ru-3** and **Ru-4**) Ru alkylidene complexes. Cy = cyclohexyl, Mes = mesityl.

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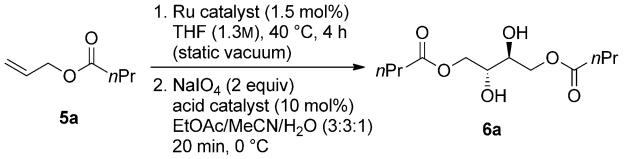
species.[2k–m] We anticipated that under acidic aqueous oxidizing conditions, the adamantyl C–Ru bond would be cleaved, generating a species similar to that generated in the dihydroxylation with **Ru-2**.[2k] Furthermore, we proposed that the catalyst-controlled *Z*-selectivity in the cross-metathesis with **Ru-3** or **Ru-4** would be translated into high *anti* selectivity through a stereospecific pathway. Herein, we report the successful development of a tandem *Z*-selective metathesis/dihydroxylation and preliminary mechanistic studies, which shed light on catalyst inhibition pathways.

The homodimerization/dihydroxylation of allyl butyrate was examined in order to determine the effect of catalyst and reaction conditions on the selectivity (Table 1). The metathesis step was performed under static vacuum conditions in order to keep the concentration of ethylene in solution low. Shing's conditions of $NaIO_4$ in 3:3:1 EtOAc:MeCN:H_2O[16,17] were used for the dihydroxylation step. Brønsted[18] and Lewis acid[19] co-catalysts were investigated, as they have been shown to accelerate dihydroxylation.[20] Second-generation complex **Ru-2**, which is expected to operate under thermodynamic control of olefin geometry, generated the *syn*-diol with 8:1 selectivity (entry 1). The use of cyclometalated mesityl-substituted **Ru-3** and diisopropylphenyl-substituted **Ru-4** generated the desired product **6a** in 56% and 68% yield, respectively, with only trace quantities of the *syn*-diol by-product (entries 2 and 3). This *anti* selectivity can be attributed to the high *Z*-selectivity of these catalysts in cross-metathesis.[6,21]

Achieving high activity and *Z*-selectivity depends on the removal of ethylene from solution. Performing the metathesis under a static vacuum was critical, as the yield was diminished to 49% when the metathesis step was performed at 1 atm (entry 4).[22] The use of additives, such as nBu_4NCl during dihydroxylation, or ethyl vinyl ether after the metathesis reaction, did not improve the yield (entries 5 and 6). Increasing the loading of catalyst **Ru-4** (5 mol%) or $CeCl_3$ (30 mol%) resulted in a small decrease in efficiency (54% and 60% yield, respectively, entries 7 and 8), while performing the dihydroxylation in the absence of a Lewis acid co-catalyst still resulted in productive dihydroxylation, albeit in only 31% yield (entry 9). Other acids, such as H_2SO_4 and $YbCl_3$, were also less effective than $CeCl_3$, producing **6a** in 56% and 61% yield, respectively (entries 10 and 11).

With optimized conditions in hand, we next examined the scope of the *Z*-selective homodimerization/dihydroxylation. A wide variety of densely functionalized, stereodefined *anti*-diols could be prepared from comparatively simple starting materials (Table 2). Esters, carbonates, carbamates, and amine derivatives were all well tolerated, generating the corresponding *anti*-diols in up to 72% yield. The molecular structure of **6c** was determined by X-ray crystallography, confirming the *anti* stereochemistry (Figure 2).[23] In addition to probing the overall tandem process, the independent metathesis step was also monitored in each case to ensure high *Z*-selectivity,[24] because only the homodimerization of

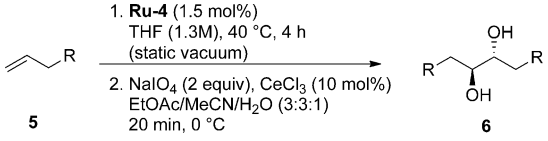
Table 1: Effect of catalyst, additives, and other reaction conditions on the tandem *Z*-selective metathesis/dihydroxylation reaction.

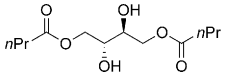
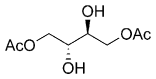
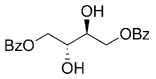
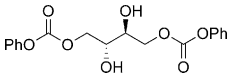
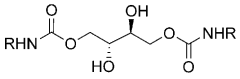
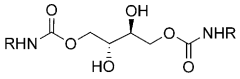
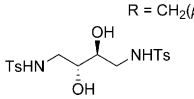
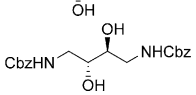


Entry	Ru	Acid	Changes from standard	Yield [%][a] **6a** (*anti*)	Yield [%][a] (*syn*)
1	**Ru-2**	$CeCl_3$	none	5	40
2	**Ru-3**	$CeCl_3$	none	56	12
3	**Ru-4**	**$CeCl_3$**	**none**	**68**	**3**
4	**Ru-4**	$CeCl_3$	no static vacuum	49	4
5	**Ru-4**	$CeCl_3$	nBu_4NCl (10 mol%) during dihydroxylation	62	5
6	**Ru-4**	$CeCl_3$	ethyl vinyl ether (1 equiv) after metathesis step	47	2
7	**Ru-4**	$CeCl_3$	5 mol% **Ru-4**	54	7
8	**Ru-4**	$CeCl_3$	30 mol% $CeCl_3$	60	4
9	**Ru-4**	None	none	31	1
10	**Ru-4**	H_2SO_4	none	56	5
11	**Ru-4**	$YbCl_3$	none	61	3

[a] Determined by integration of the crude ^{1}H NMR spectrum using mesitylene as an internal standard. Entry in bold marks optimized reaction conditions.

Table 2: Tandem *Z*-selective homodimerization/dihydroxylation of allyl-substituted terminal olefins.



Entry	R (**5**)	Product	**6**	Yield [%]
1	OCO*n*Pr (**5a**)		**6a**	72
2	OAc (**5b**)		**6b**	59
3	OBz (**5c**)		**6c**	71
4[a]	OCO_2Ph (**5d**)		**6d**	61
5	OCONHR (**5e**)		**6e**	63
6	OCONHR (**5f**)	R = *p*-$MeOC_6H_4$  R = CH_2(*p*-Tol)	**6f**	39
7	NHTs (**5g**)		**6g**	70
8	NHCBz (**5h**)		**6h**	53

[a] Using 1 mol% catalyst in an open vial in the glove box. Bz = benzoyl, CBz = benzyloxycarbonyl, *p*-Tol = 4-tolyl, Ts = 4-toluenesulfonyl.

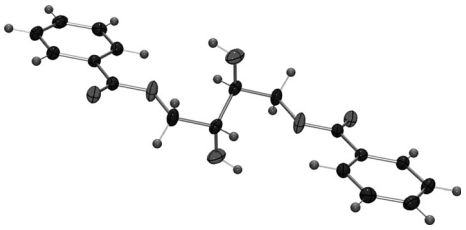
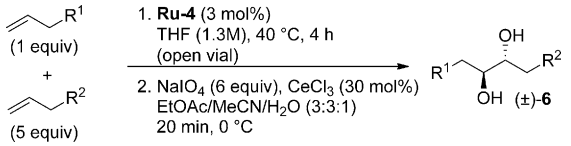


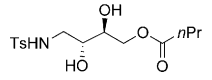
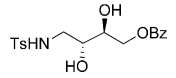
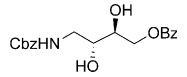
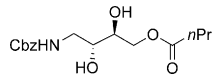
Figure 2. POV-ray depiction of the structure of *anti*-diol **6c** determined by X-ray crystallography. Atoms are represented by ellipsoids at the 50% probability level. The crystal was disordered, as it contained two conformers; only one has been shown for clarity.

allyl acetate has been explored previously with these chelated catalysts.[5]

Achieving unsymmetrical substitution patterns through hetero-cross-metathesis/dihydroxylation is an appealing target, particularly if differentially protected products can be obtained. *Z*-selective hetero-cross-metathesis can be achieved by using an excess of one of the olefin partners.[21,25] Tosyl- and Cbz-protected allyl amines were used as coupling partners with allyl butyrate or allyl benzoate (Table 3),

Table 3: *Z*-selective hetero-cross-metathesis/dihydroxylation of allyl-substituted terminal olefins.



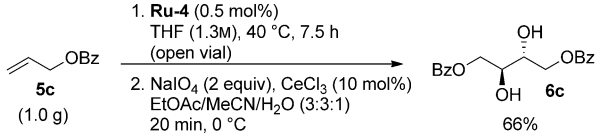
Entry	R^1	R^2	Product	6	Yield [%]
1	NHTs	OCO*n*Pr		**6i**	63[a]
2	NHTs	OBz		**6j**	39
3	NHCbz	OBz		**6k**	55
4	NHCbz	OCO*n*Pr		**6l**	47

[a] 1.5 mol% **Ru-4**, 35 °C.

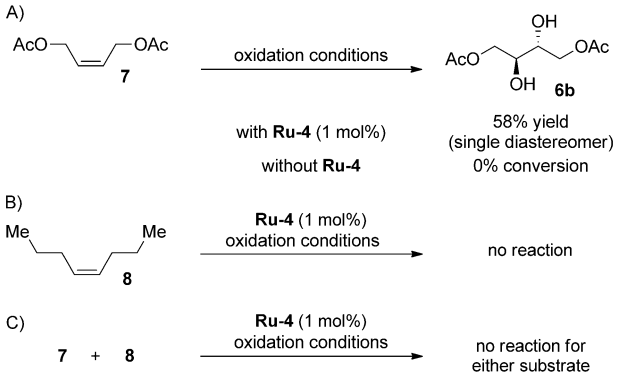
generating the corresponding substituted amino triols in up to 63% yield. Such orthogonally protected products are valuable building blocks for target-oriented synthesis.

We next examined the tandem methodology on a gram scale in order to probe the scalability of the process. Allyl benzoate was subjected to cross-metathesis with 0.5 mol% of **Ru-4** in an open vial in an inert atmosphere glove box, followed by dihydroxylation using the standard conditions outside the glove box (Scheme 2). Isolation of the target diol was conveniently achieved without the need for column chromatography: trituration of the crude reaction mixture with ether provided **6c** in 66% yield.

In order to probe the role of Ru in the dihydroxylation step, a series of control experiments were performed. First, *Z*-



Scheme 2. Tandem *Z*-selective metathesis/dihydroxylation on a gram scale.

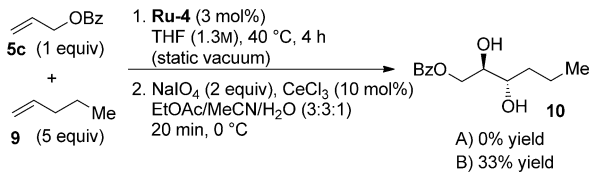


Scheme 3. A) Ru catalyst **Ru-4** is required for dihydroxylation. B) *Z*-4-octene (**8**) is unreactive in dihydroxylation. C) **8** inhibits the dihydroxylation of **7**. Oxidation conditions: $NaIO_4$ (2 equiv), $CeCl_3$ (10 mol%), EtOAc/MeCN/H_2O (3:3:1), 20 min, 0 °C.

2-butenyl 1,4-diacetate (**7**) was subjected to the standard dihydroxylation conditions in the presence or absence of **Ru-4** (Scheme 3A). Without **Ru-4**, no conversion was observed, indicating that Ru is a catalyst for both the metathesis and dihydroxylation steps. In the presence of **Ru-4** (1 mol%), *anti*-diol **6b** was generated as a single diastereomer, thus confirming the stereospecificity of the dihydroxylation.

Next, the relative reactivity of electron-neutral and electron-deficient internal olefins toward dihydroxylation with **Ru-4** was investigated. *Z*-4-butene (**8**) was subjected to the standard dihydroxylation conditions with **Ru-4** (1 mol%), and no diol was observed (Scheme 3B). Furthermore, when a 1:1 mixture of **8** and **7** was subjected to the same conditions, no diol from either alkene was observed (Scheme 3C). As **7** is successfully dihydroxylated when it is the only substrate present, this result indicates that **8** is not only unreactive, but also inhibits the dihydroxylation of **7**. We propose that the formation of a stable ruthenate ester from a [3+2] cycloaddition between **8** and a Ru species with at least two oxo ligands sequesters the Ru catalyst, thus making it unavailable for catalysis of the dihydroxylation of **7**. Hydrolysis of osmate esters is known to be a slow step in the osmium-catalyzed dihydroxylation of certain olefins.[26,27] The allylic functional groups could either be acting as electron-withdrawing groups to render the Ru center more electrophilic, or as coordinating groups.[28]

In order to probe the inherent reactivity of cross-metathesis intermediates containing functionality on only one side of the olefin, we performed the tandem sequence using allyl benzoate and 1-pentene. Under standard conditions, no product was obtained (Scheme 4A). However, when the volatiles were removed in vacuo prior to the addition of the



Scheme 4. Cross-metathesis/dihydroxylation of allyl benzoate and 1-pentene under A) standard conditions and B) with removal of volatile intermediates prior to the oxidation step.

reagents for dihydroxylation, diol **10** was produced in 33% yield under unoptimized conditions (Scheme 4B). Therefore, the removal of the inhibitory olefins 4-octene and residual 1-pentene led to the restoration of the dihydroxylation activity, albeit with slightly lower efficiency.[29] This result points the way to the expansion of the substrate scope for this tandem transformation.

In summary, we have disclosed an assisted tandem catalysis procedure for the *Z*-selective cross-metathesis/dihydroxylation of terminal olefins to obtain *anti*-diols. Ru catalyzes both transformations, and the *Z*-selectivity observed in the cross-metathesis is translated to *anti* selectivity through the stereospecific dihydroxylation. Densely functionalized *anti*-diols with four contiguous heteroatom-substituted carbon atoms can be synthesized from simple allyl alcohol and allyl amine derivatives. The behavior of the in situ generated Ru-based oxidation catalyst was probed with unfunctionalized electron-rich alkenes, and these were found to inhibit dihydroxylation. Further studies are ongoing to elucidate details of the reaction mechanism. It is envisioned that this methodology will have applications in target-oriented synthesis involving *anti*-diols, and the mechanistic insights will help to uncover further applications of cyclometalated Ru alkylidene catalysts.

Keywords: *anti*-diols · dihydroxylation · metathesis · tandem reactions · *Z*-selectivity

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Angew. Chem. **2015**, *127*, 7240–7244

[1] a) D. E. Fogg, E. N. dos Santos, *Coord. Chem. Rev.* **2004**, *248*, 2365–2379; b) A. Ajamian, J. L. Gleason, *Angew. Chem. Int. Ed.* **2004**, *43*, 3754–3760; *Angew. Chem.* **2004**, *116*, 3842–3848.

[2] For metathesis/hydrogenation, see: a) J. Louie, C. W. Bielawski, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 11312–11313; b) K. D. Camm, N. Martinez Castro, Y. Liu, P. Czechura, J. L. Snelgrove, D. E. Fogg, *J. Am. Chem. Soc.* **2007**, *129*, 4168–4169; for metathesis/olefin isomerization, see: c) A. E. Sutton, B. A. Seigal, D. F. Finnegan, M. L. Snapper, *J. Am. Chem. Soc.* **2002**, *124*, 13390–13391; d) B. Schmidt, *Eur. J. Org. Chem.* **2003**, 816–819; for metathesis/atom-transfer radical cyclization, see: e) B. Schmidt, M. Pohler, *J. Organomet. Chem.* **2005**, *690*, 5552–5555; f) B. A. Seigal, C. Fajardo, M. L. Snapper, *J. Am. Chem. Soc.* **2005**, *127*, 16329–16332; for metathesis/cyclopropanation, see: g) B. G. Kim, M. L. Snapper, *J. Am. Chem. Soc.* **2006**, *128*, 52–53; for metathesis/oxidation, see: h) H. Kato, T. Ishigame, N. Oshima, N. Hoshiya, K. Shimawaki, M. Arisawa, S. Shuto, *Adv. Synth. Catal.* **2011**, *353*, 2676–2680; i) B. Schmidt, S. Krehl, *Chem. Commun.* **2011**, *47*, 5879–5881; j) B. Schmidt, S. Krehl, S. Hauke, *J. Org. Chem.* **2013**, *78*, 5427–5435; for metathesis/dihydroxylation, see: k) S. Beligny, S. Eibauer, S. Maechling, S. Blechert, *Angew. Chem. Int. Ed.* **2006**, *45*, 1900–1903; *Angew. Chem.* **2006**, *118*, 1933–1937; l) A. A. Scholte, M. H. An, M. L. Snapper, *Org. Lett.* **2006**, *8*, 4759–4762; m) N. M. Neisius, B. Plietker, *J. Org. Chem.* **2008**, *73*, 3218–3227.

[3] For representative examples of *anti*-1,2-diol syntheses, see: a) H. C. Kolb, M. S. VanNieuwenhze, K. B. Sharpless, *Chem. Rev.* **1994**, *94*, 2483–2547; b) H. C. Brown, G. Narla, *J. Org. Chem.* **1995**, *60*, 4686–4687; c) A. B. Northrup, D. W. C. MacMillan, *Science* **2004**, *305*, 1752–1755; d) S. M. Lim, N. Hill, A. G. Myers, *J. Am. Chem. Soc.* **2009**, *131*, 5763–5765; e) S. B. Han, H. Han, M. J. Krische, *J. Am. Chem. Soc.* **2010**, *132*, 1760–1761; f) D. Kim, J. S. Lee, S. B. Kong, H. Han, *Angew. Chem. Int. Ed.* **2013**, *52*, 4203–4206; *Angew. Chem.* **2013**, *125*, 4297–4300; g) J. Hartung, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2014**, *53*, 3885–3888; *Angew. Chem.* **2014**, *126*, 3966–3969.

[4] K. Endo, R. H. Grubbs, *J. Am. Chem. Soc.* **2011**, *133*, 8525–8527.

[5] B. K. Keitz, K. Endo, P. R. Patel, M. B. Herbert, R. H. Grubbs, *J. Am. Chem. Soc.* **2012**, *134*, 693–699.

[6] L. E. Rosebrugh, M. B. Herbert, V. M. Marx, B. K. Keitz, R. H. Grubbs, *J. Am. Chem. Soc.* **2013**, *135*, 1276–1279.

[7] S. M. Bronner, M. B. Herbert, P. R. Patel, V. M. Marx, R. H. Grubbs, *Chem. Sci.* **2014**, *5*, 4091–4098.

[8] M. J. Koh, R. K. M. Khan, S. Torker, M. Yu, M. S. Mikus, A. H. Hoveyda, *Nature* **2015**, *517*, 181–186.

[9] S. J. Malcolmson, S. J. Meek, E. S. Sattely, R. R. Schrock, A. H. Hoveyda, *Nature* **2008**, *456*, 933–937.

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

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

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

[13] S. Shahane, C. Bruneau, C. Fischmeister, *ChemCatChem* **2013**, *5*, 3436–3459.

[14] For examples of *Z*-selective cross-metathesis, see: a) B. K. Keitz, K. Endo, M. B. Herbert, R. H. Grubbs, *J. Am. Chem. Soc.* **2011**, *133*, 9686–9688; for examples of ROMP, see: b) B. K. Keitz, A. Fedorov, R. H. Grubbs, *J. Am. Chem. Soc.* **2012**, *134*, 2040–2043; c) L. E. Rosebrugh, V. M. Marx, B. K. Keitz, R. H. Grubbs, *J. Am. Chem. Soc.* **2013**, *135*, 10032–10035; for examples of enantioselective catalysis, see: d) J. Hartung, R. H. Grubbs, *J. Am. Chem. Soc.* **2013**, *135*, 10183–10185; e) J. Hartung, P. K. Dornan, R. H. Grubbs, *J. Am. Chem. Soc.* **2014**, *136*, 13029–13037; for examples of macrocyclizations, see: f) V. M. Marx, M. B. Herbert, B. K. Keitz, R. H. Grubbs, *J. Am. Chem. Soc.* **2013**, *135*, 94–97.

[15] For mechanistic studies on the origin of *Z*-selectivity, see: a) P. Liu, X. Xu, X. Dong, B. K. Keitz, M. B. Herbert, R. H. Grubbs, K. N. Houk, *J. Am. Chem. Soc.* **2012**, *134*, 1464–1467; b) H. Miyazaki, M. B. Herbert, P. Liu, X. Dong, X. Xu, B. K. Keitz, T. Ung, G. Mkrtumyan, K. N. Houk, R. H. Grubbs, *J. Am. Chem. Soc.* **2013**, *135*, 5848–5858.

[16] T. K. M. Shing, V. W.-F. Tai, E. K. W. Tam, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2312–2313; *Angew. Chem.* **1994**, *106*, 2408–2409.

[17] T. K. M. Shing, E. K. W. Tam, V. W.-F. Tai, I. H. F. Chung, Q. Jiang, *Chem. Eur. J.* **1996**, *2*, 50–57.

[18] B. Plietker, M. Niggemann, *Org. Lett.* **2003**, *5*, 3353–3356.

[19] B. Plietker, M. Niggemann, *J. Org. Chem.* **2005**, *70*, 2402–2405.

[20] It has been proposed that acids facilitate the hydrolysis of a ruthenate ester intermediate.

[21] B. L. Quigley, R. H. Grubbs, *Chem. Sci.* **2014**, *5*, 501–506.

[22] Presumably a larger concentration of ethylene in solution results in slower productive metathesis and more secondary-metathesis processes.

[23] CCDC 1048930 contains the supplementary crystallographic data for compound **6c**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[24] In all cases, over 90% *Z*-selectivity was obtained.
[25] J. S. Cannon, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2013**, *52*, 9001 – 9004; *Angew. Chem.* **2013**, *125*, 9171 – 9174.
[26] K. B. Sharpless, W. Amberg, Y. L. Bennani, G. A. Crispino, J. Hartung, K. S. Jeong, H. L. Kwong, K. Morikawa, Z. M. Wang, *J. Org. Chem.* **1992**, *57*, 2768 – 2771.
[27] M. H. Junttila, O. E. O. Hormi, *J. Org. Chem.* **2007**, *72*, 2956 – 2961.
[28] Further studies are ongoing to distinguish these possibilities. For directed dihydroxylation, see: T. J. Donohoe, *Synlett* **2002**, 1223 – 1232.
[29] Some olefin intermediate remained after the 20 min oxidation, resulting in low yield. Therefore dihydroxylation to give diol **10** is likely slower than the formation of **6c**.

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