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Bulky Cyclometalated Ruthenium Nitrates for Challenging Z-Selective Metathesis: Efficient One-Step Access to α -Oxygenated Z-Olefins from Acrylates and Allyl Alcohols

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Abstract: α -Oxygenated Z-olefins are ubiquitous in biologically active molecules and serve as versatile handles for organic synthesis, but their syntheses are often tedious and less selective. Here we report the efficient Z-selective metathesis of various terminal acrylates and allyl alcohols, which enables facile and selective construction of high value-added α -oxygenated Z-olefins from readily available feedstock chemicals. These challenging metathesis transformations are enabled by novel cyclometalated Ru-carbene-nitrate complexes bearing bulky-yet-flexible side arms, whose assembly was unlocked by new organometallic syntheses.

The increasing demand for the timely assembly of biologically active molecules necessitates the development of new carbon-carbon bond-forming methods that construct challenging organic skeletons in a streamlined fashion.¹ Among these, Z-selective olefin metathesis showcases a precise and straightforward approach to important Z-configured C-C double bonds that are often thermodynamically less stable and non-trivial-to-access, and its practicality is further highlighted by the use of only terminal olefins as readily available and functional group-compatible handles.² A wide variety of terminal olefins have been investigated and found to be suitable for Z-selective metathesis catalyzed by Mo,³ W,⁴ or Ru-based catalysts;⁵⁻⁶ however, a long-standing limitation of these transformations is the lack of *any* catalyst that could efficiently process diverse types of terminal acrylates and allyl alcohols. As a result, direct access to high value-added, α -oxygenated Z-olefins from these feedstock chemicals remains a much-desired yet unmet challenge, despite that enriched biological properties are often associated with molecules containing these structural motifs (Scheme 1A).⁷ To date, the only reported Z-selective metathesis of this class is limited to bulky *t*-butyl acrylates, which is promoted by molybdenum monoaryloxide pyrrolide (MAP) complexes,^{3d} and the use of terminal allyl alcohols remains elusive (Scheme 1B).⁸

A. Z-selective olefin metathesis: reaction profile and current limitation

B. Representative known metathesis approaches to corresponding structures

C. The basis of this work:

Scheme 1. Accessing high-value α -oxygenated Z-olefins via metathesis: current approaches and limitations.

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Scheme 2. Preparation and evaluation of cyclometalated Ru-nitrate catalysts. Yields without parenthesis are determined by ^1H NMR analysis of the crude reaction mixtures using anthranthrene as the internal standard. Yields in parenthesis are isolated yields of the Z-products. For the Z/E ratio of each entry, see SI.

Since the discovery of the cyclometalated Ru-based Z-selective metathesis catalysts in 2011,^{5a} our group has observed that the sidearms of the N-heterocyclic carbene (NHC) ligand play an important role in influencing the catalyst activity and the level of stereo-control.⁵ For example, catalysts bearing a 2,6-diisopropylphenyl (Dipp) group (e.g. **Ru-2**^{5c}) in general displayed superior activity and Z-stereoselectivity when compared to their analogs with a smaller mesityl group (e.g. **Ru-1**^{5b}). However, catalysts with even bulkier skeletons are challenging to access using conventional synthetic routes, as the C–H cyclometallation and its following steps are often rather sluggish and result in low-yielding mixtures due to the gradual decomposition of the cyclometalated Ru-carbene complexes.¹³ Very recently, we successfully overcame the challenge in the C–H metalation step through a carefully optimized, “acid-base quenching”-driven approach, and introduced an even bulkier 2,6-diisopentylphenyl (Di pep) sidearm.^{5e} The resulting ruthenium pivalate complex (**Ru-3**) readily promoted the acylamide-olefin cross-metathesis in a highly Z-selective fashion. However, **Ru-3** was found to be ineffective towards acrylate substrates (with a turnover number smaller than 5) and further derivatization of **Ru-3** (e.g. towards complexes bearing other anionic ligands)¹⁴ remains elusive.¹⁵

A promising direction would be to prepare and investigate the less electron-rich nitrate analogs of **Ru-3** that are equipped with equally or even more sterically demanding sidearms.^{5b} However, the seemingly easy-to-run anion exchange reaction quickly proved to be a

formidable challenge in such a sterically encumbered environment. For example, under conventional conditions using a large excess of NH_4NO_3 in THF,^{5b} the reaction not only failed to reach full conversion, but also led to two unidentified Ru-carbene side-products. Significant catalyst decomposition also occurred concomitantly (see *Supporting Information* for details), making purification of the desired nitrate catalyst extremely difficult (Scheme 2A). To overcome this, we envisioned that a suitable nitrate source with a more acidic cation could potentially provide an additional driving force for this challenging anion exchange *via* another formal “acid-base quenching” process. Specifically, if the pivalate anion of the delicate cyclometalated ruthenium-carbene complexes could be exchanged and readily removed from the system *through* irreversible protonation, a much-simplified reaction system, e.g. with low equivalent of the nitrate reagent and short reaction period, might diminish or even eliminate the undesired side-pathways. Guided by this designing principle, we identified 3-fluoropyridinium nitrate (**A1**) as a suitable reagent, which is easily prepared and has a pK_a value approximately two units lower than that of pivalic acid. With only one equivalent added, **A1** fully “protonates” ruthenium-pivalates containing a Di pep or even a diisopentylphenyl (Di pep) sidearm within 15 minutes at room temperature, with the release of *neutral* (instead of *ionic*) by-products, pivalic acid and 3-fluoropyridine. Upon workup, the corresponding bulky nitrate catalysts (**Ru-4** and **Ru-6**) were prepared in high yields and, more importantly, in high purity for the first time.

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Scheme 3. Substrate scope with various acrylates and common olefins.

^a General reaction conditions: **1** (0.15 mmol), **2** (0.24 mmol), and **Ru-4** (0.0045 mmol) in THF, N₂, room temperature. All yields are isolated yields of the Z-products. The stereoselectivity was determined by ¹H NMR analysis of the crude reaction mixture. ^b **2** was used in 2 equiv. ^c **Ru-4** was used in 2 mol%. ^d **Ru-4** was used in 4 mol% and **2** was used in 2 equiv. ^e **Ru-4** was used in 5 mol% and **2** was used in 2 equiv. ^f **Ru-4** was used in 3.3 mol% and **2** was used in 2 equiv. ^g **Ru-4** was used in 5 mol%. For details, see SI.

With this result, we then evaluated a series of cyclometalated Ru-nitrate catalysts (Scheme 2B) using 1-dodecene (**2a**) as a model olefin and either cyclohexyl acrylate (**1a**) or allyl alcohol (**4a**) as its coupling partner. **Ru-4** bearing a Dipec ligand was found to be the best catalyst to process acrylate substrates, reaching TON > 50 even at high conversion (entry 5). Interestingly, increasing or decreasing the size of the NHC sidearm leads to much lower yields (entries 1-3 and 7), and **Ru-8** bearing an unsymmetric 2,7-diisopropynaphthalen-

1-yl (DipN) group was also found to be inefficient (entry 4). Under a slightly modified condition using 2.5 mol% **Ru-4**, pure **3a** could be isolated in 77% yield; also, > 20:1 Z-selectivity was maintained throughout the course of the reaction (entry 6). When allyl alcohol **4a** was used as the substrate, **Ru-4** was again much more efficient than the Dipp-containing benchmark **Ru-2** (entry 9 vs entry 8), and further increasing the size of the sidearm led to an even higher yield (**Ru-6**, entry 10). Note that allyl alcohol **4a** was used in excess to promote a high degree of cross-metathesis, as both **4a** and **2a** readily dimerize under the given conditions. Finally, by lowering the equivalence of **4a** and increasing the loading of **Ru-6** to 2.5%, desired **5a** was obtained in 60% yield with >20:1 Z-selectivity. Though the detailed influence of the N-aryl substituents on the catalytic activity of cyclometalated ruthenium catalysts remains unclear when acrylates or allyl alcohols were used as substrates, it has been previously observed that altering the side-arms of NHC ligands could have a significant effect in suppressing the undesired pathways and achieving superior TONs in many transition metal-catalyzed transformations;¹⁶ on the other hand, the incorporation of bulkier N-aryl substituents improves the Z-selectivity (for details, see *Supporting Information*), likely due to a stronger sterically shielding effect during the side-bound metathesis pathway.¹⁷

The reaction scope was then investigated, first with various acrylates (Scheme 3A). Excellent Z-selectivity (>20:1) was obtained in nearly all cases under the standard or slightly modified conditions. The amino acid-derived substrate **3q** was the only exception where a slightly decreased, 17:1 Z/E ratio was observed. The desired products were generally isolated in pure Z-form with ease. Primary, secondary and tertiary acrylates were all suitable substrates, including acrylates bearing multiple heteroatoms (e.g. O and N) that may potentially coordinate with the catalyst (**3p**, **3q**, and **3r**). Despite severe steric repulsion, (Z)-α,β-unsaturated esters bearing γ-substituents could be formed with high stereoselectivity, highlighting the robustness of the presented method (**3f**).¹⁸ Both nucleophilic and electrophilic functional groups are well-tolerated, including bromides (**3b**), boronic esters (**3j**), epoxides (**3g**), sulfonates (**3h**), and aldehydes (**3i**). Efficient Z-selective metathesis was also observed in the presence of unprotected alcohols (**3c**) and phenols (**3e**), which are less likely to be tolerated in many conventional transformations that construct (Z)-α,β-unsaturated esters, such as Wittig-type reactions or esterification with Z-alkenyl acyl chlorides. Moreover, inexpensive trimethylsilyl acrylate (**1s**) could serve as a convenient surrogate for acrylic acid.¹⁹ Using the standard metathesis condition followed by flash column chromatography over silica gel, Z-alkenyl acids (e.g. **3t**) could be readily isolated in good yield and high stereoselectivity (Scheme 3B).

Z-selective metathesis with various allyl alcohols was next investigated (Scheme 4). When feedstock allyl alcohols were used, olefin **2** was typically selected as the limiting reagent (e.g. **5b** and **5e**). Alternatively, **2** could also be added in excess, especially when heavy and valuable α-hydroxylated olefins were employed as the substrates (e.g. **5d**). Note that in a stereoretentive metathesis reaction, Z-configured olefins are often needed as the starting materials. While (Z)-but-2-ene-1,4-diol is still commercially available as a surrogate for the simplest allyl alcohol,^{9a} the corresponding “Z-dimer” of substituted allyl alcohols (e.g. **4c'**, “Z-dimer” of **4c**) are usually quite challenging to access. Therefore, the facile and direct incorporation of substituted allyl alcohols, such as in the cases of in **5e**, **5f**, and **5g**, showcases the unique benefit of this Z-selective approach. Moreover, enantio-

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enriched **4c** are also easily accessible, which are meaningful for the straightforward construction of chiral natural products bearing such Z-allyl alcohol motifs (c.f. Scheme 1A).^{7a} Various functional groups are tolerated, and a 1,1-disubstituted olefin remains untouched (**5b**).²⁰ Again, > 20:1 Z-selectivity was observed in all the examined cases. Since substituted allyl alcohols are commonly used as a versatile synthetic handle, such a method may allow the rapid assemble of other challenging chemical structures through further derivatization.

Scheme 4. Substrate scope with various allyl alcohols and common olefins.

^a General reaction conditions: **4** (0.6 mmol), **2** (0.15 mmol), and **Ru-6** (0.00375 mmol) in THF, N₂, room temperature. All yields are isolated yields of the Z-products. The stereoselectivity was determined by ¹H NMR analysis of the crude reaction mixture. ^b **4** was used in 1 equiv. and **2** was used in 8 equiv. ^c **4** was used in 8 equiv. and **Ru-6** was used in 4 mol%. ^d **4** was used in 8 equiv. and **Ru-6** was used in 5 mol%. For details, see SI.

In summary, we have described a type of novel approaches to α -oxygenated Z-olefins by efficient Z-selective metathesis using feedstock chemicals. These transformations are enabled by sterically congested cyclometalated ruthenium-nitrate complexes, whose synthesis are made possible by a new anion exchange method via “acid-base quenching”. High stereoselectivity and good functional group compatibility were observed with various types of acrylates and allyl alcohols. Given the ubiquity of α -oxygenated Z-olefins in natural products and synthetic intermediates, such a method may find further application in streamlining the access to diverse organic molecules in a stereoselective fashion.

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Keywords: Z-selective olefin-metathesis • ruthenium • acrylates • allyl alcohols • α -oxygenated Z-olefins

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A persistent challenge in olefin metathesis is the lack of widely applicable method that converts feedstock allyl alcohols and acrylates to valuable α -oxygenated Z-olefins. Here, enabled by bulky cyclometalated Ru-nitrate catalysts whose syntheses were newly unlocked, Z-selective metathesis between terminal olefins could now be used to access Z-allyl alcohols, Z-alkenyl esters, and Z-alkenyl acids in high yields and $>20:1$ Z:E selectivity.