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Selective olefin metatheses—new tools for the organic chemist: A review

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Abstract

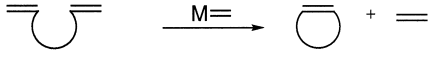
The use of olefin metathesis in synthesis has significantly expanded with the development of tunable, functional group tolerant olefin metathesis catalysts. These structurally defined catalysts have found extensive use in organic synthesis through ring-closing metathesis (RCM) methods. More recently, numerous examples of selective cross-metatheses, including ring-opening metatheses (ROM) and tandem ring-opening/ring-closing metatheses have been reported.

Keywords: Olefin metathesis; Cross; Ring opening; Tandem; Selectivity

1. Introduction

The opportunities for employing olefin metathesis as a tool for the synthetic organic chemist has grown considerably [1–5] with the development of new, structurally defined olefin metathesis catalysts [6–15] of tunable reactivities (Fig. 1). For example, ring-closing metathesis (Eq. (1)), a useful method for the syntheses of carbo- and heterocyclic ring-containing materials [16–20] has recently been utilized as key transformations in a number of impressive natural product syntheses [21–30]. Another area of significant potential is selective cross-metathesis (Eq. (2)), in which two different alkenes undergo an intermolecular transformation to form two new olefinic products. A variation of cross-metathesis is ring-opening metathesis (ROM) (Eq. (3)), where one of the olefin partners is a cyclic alkene. In this reaction, a single product is obtained that incorporates the functionality of both starting olefins.

RCM
(Ring-Closing Metathesis)



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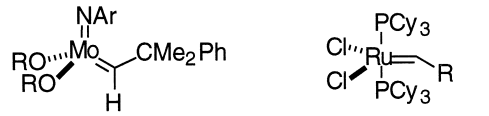
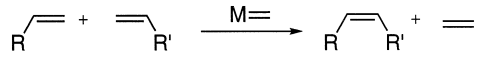


1 Ar = 2,6-diisopropylphenyl, RO = $(CF_3)_2(CH_3)CO$ **2a** R = $CH{=}CPh_2$, **2b** R = Ph

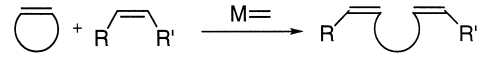
Fig. 1. Structurally-defined olelfin metathesis catalysts.

Cross Metathesis



(2)

ROM
(Ring-Opening Metathesis)

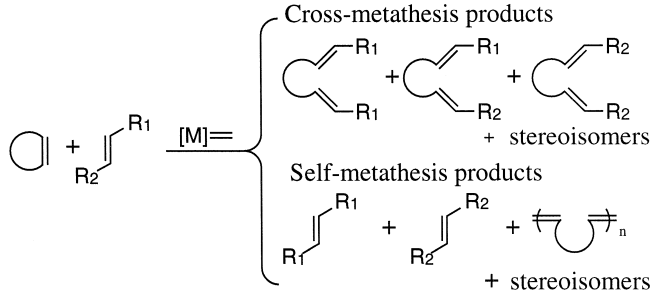


(3)

Because of the potential reversibility of metathesis-based transformations, both thermodynamic and kinetic factors can impact selectivity. For example, whereas RCM benefits from entropy, the factors that govern cross-metathesis selectivity are less obvious. Furthermore, for ROM of even a simple cyclic and acyclic olefin, a large number of possible cross- and self-metathesis products are possible (Scheme 1). Regio- and stereochemical possibilities further increase the pool of potential products. To understand, predict, and possibly control selectivity issues, detailed mechanistic insights into these processes are required.

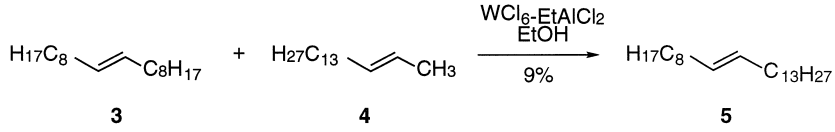
2. Early examples

Notwithstanding selectivity issues, there are several early examples of pheromone syntheses by cross-metathesis [31–41]. For example, cross-metathesis of acyclic olefins **3** and **4** provide a direct



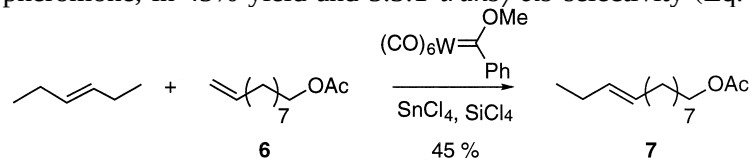
Scheme 1. Potential products from ROM.

route to 9-tricosene (**5**), an insect pheromone, albeit with low overall yield and selectivity (Eq. (4)) [42].



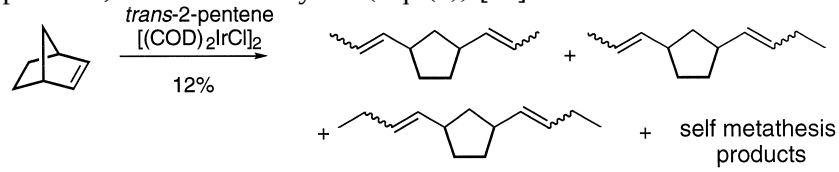
(4)

Similarly, cross-metathesis of acetate **6** with an excess of hex-3-ene provides 9-dodecenylacetate (**7**), another insect pheromone, in 45% yield and 5.3:1 *trans/cis* selectivity (Eq. (5)) [43].



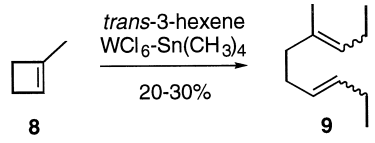
(5)

Early examples of ROM were relatively unselective. For example, ROM of norbornene with 2 equivalents of *trans*-2-pentene results in a statistical distribution of ROM products, as well as self-metathesis products, in low overall yield (Eq. (5)) [44].



(6)

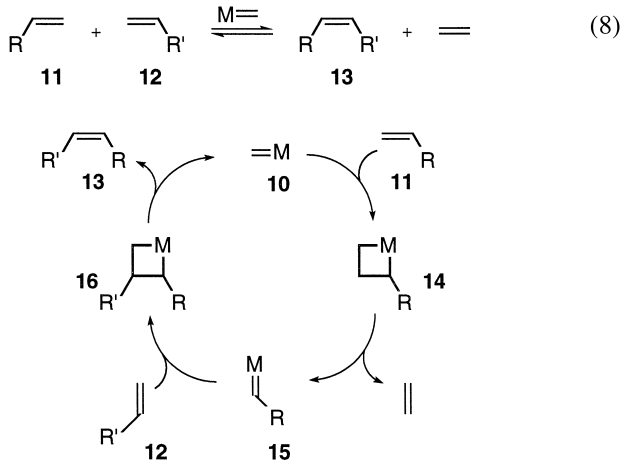
Likewise, ROM of 1-methylcyclobutene (**8**), with an excess of *trans*-3-hexene in the presence of a classical tungsten catalyst, provides diene **9** as a mixture of stereoisomers (Eq. (7)) [45].



(7)

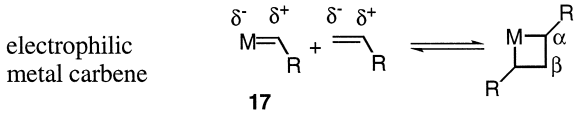
Considering the Chauvin mechanism [46] for the cross-metathesis of two unlike olefins shown in Eq. (8), a number of chemo- and stereoselective transformations are required for a selective metathesis process (Scheme 2). In one possible pathway, initial metathesis of metal alkylidene **10** with terminal olefin **11** provides metallacyclobutane **14**. Fragmentation of **14** can then provide ethylene and metal alkylidene **15**. Regio- and stereoselective reaction of **15** with terminal olefin **12** provides metallacycle **16**, which, upon fragmentation, produces disubstituted product **13** and alkylidene **10**. It is important to understand which factors determine the course of the reaction. Is the reaction kinetically or thermodynamically controlled? Is one metal alkylidene favored over another? Which types of olefins are more reactive?

Studies with a number of metathesis-active metal alkylidenes have suggested that degenerative metathesis with terminal olefins proceeds more rapidly than productive metathesis [47–51]. In other words, one specific metal carbene, metallacyclobutane combination must be favored (Eq. (9) or Eq. (10)). For an electrophilic carbene (**17**), alkyl groups are selectively transferred to the α-position, and degenerative metathesis is favored (Eq. (9)). Alternatively, for nucleophilic, 'Schrock'-type carbene such as **1**, the metal-methylidene **18** is kinetically favored. The metal electronically directs nucleo-



Scheme 2. Chauvin mechanism for cross-metathesis.

philic groups to the β-position (and electrophilic groups to the α-position). As a result, degenerate metathesis prevails (Eq. (10)).



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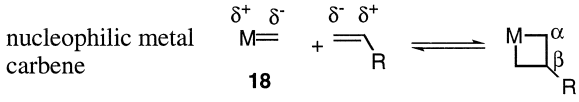
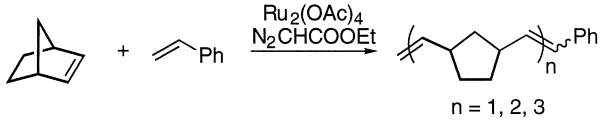


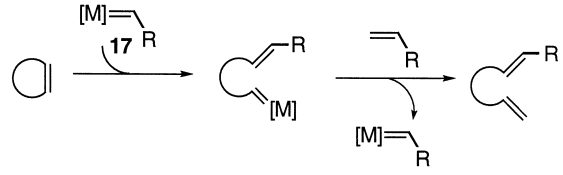
(10)

For asymmetrical, intermolecular metatheses of functionalized olefins, some early evidence for selectivity was noted. ROMP and ROM studies with various metathesis-active catalysts have shown that polymeric and monomeric products are generated with asymmetrical ends [52–58]. For example, ROM of norbornene with styrene using classical olefin metathesis catalysts produce unsymmetrically substituted products, albeit in low yield as a mixture of monomers and oligomers (Eq. (11)) [59].



(11)

This observation provides further support that one metal alkylidene (**17** or **18**) is likely favored. Two possible pathways to achieve unsymmetrical ROM products are shown below. If metal alkylidene **17** is favored, the 'R' group is transferred first, followed by subsequent addition of the methylene substituent and regeneration of the metal alkylidene catalyst (Eq. (12)). Alternatively, addition of metal methylidene (**18**) to the strained-ring compound would transfer the methylene group, followed by addition of the alkyl substituent and regeneration of the methylene catalyst (Eq. (13)).



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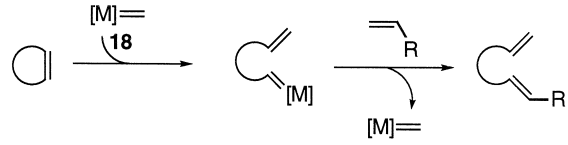
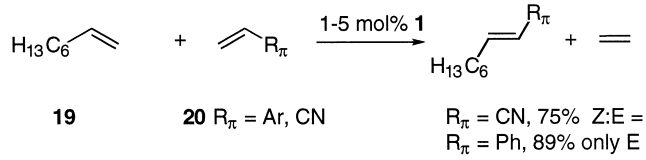


(13)

3. Cross-metatheses

With the development of new, well-defined metal alkylidenes and a better understanding of the nature of these metal alkylidenes, selective cross-metatheses of terminal olefins are now achievable. For example, Crowe et al. have shown that small, alkyl-substituted olefins (**19**) undergo chemo- and stereoselective cross-metathesis with π-substituted terminal olefins (**18**) such as styrene or acrylonitrile in the presence of the Schrock-metal carbene **1** (Eq. (14)) [60–62].



(14)

The Crowe group argues that the extended π-system allows **18** to serve as a good alkylidene donor, favoring formation of metal alkylidene **19**, whereas the alkyl-substituted olefin **17**, being more nucleophilic, prefers to react with metal alkylidene **19** to generate metallacyclobutane **20** (Fig. 2). This can then fragment to form a methylene complex (**16**), and the observed cross metathesis products.

Steric factors also play a role in effecting selective cross-metatheses. For example, Blechert et al. have shown that metathesis of sterically hindered olefin **21**, in the presence of a number of smaller olefins such as **22**, results in selective cross-metatheses (Eq. (15)) [63].

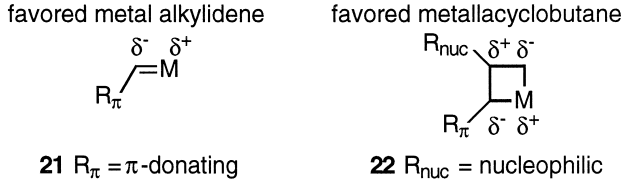
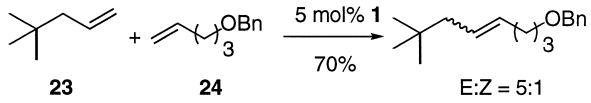
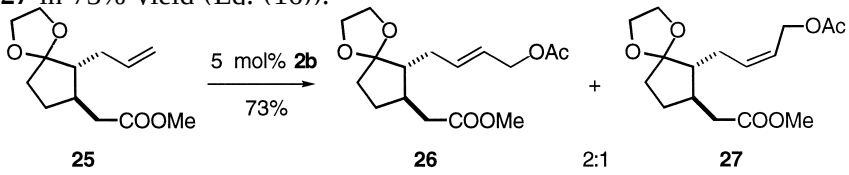


Fig. 2. Electronic contributions towards cross-metathesis.



(15)

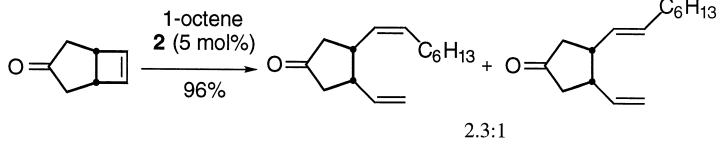
Blechert has prepared various derivatives of jasmonic acid, a plant pheromone, as a demonstration of the synthetic utility of this cross-metathesis [1]. Specifically, a cross-methatesis of functionalized terminal olefin **25** with an excess of 2-propene acetate in the presence of **2b** provides disubstituted olefins **26** and **27** in 73% yield (Eq. (16)).



(16)

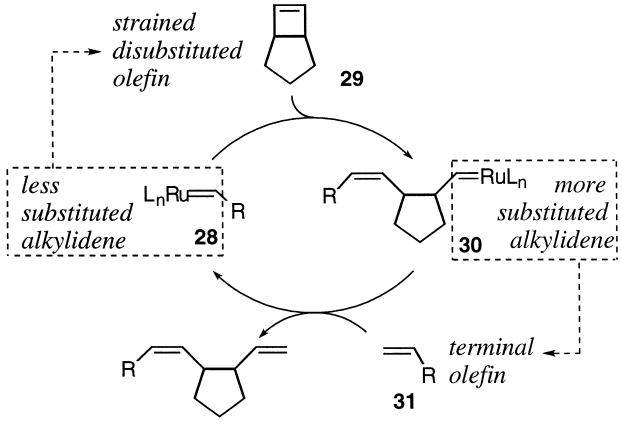
4. Ring-opening metatheses

Historically, poor chemo-, stereo-, and regioselectivity has limited the synthetic utility of ring-opening metathesis. To avoid oligomeric ROM products, the acyclic olefin partner must selectively intercept the competing ROMP process. We have shown that ROM of strained-ring systems, in the presence of as little as 1.5 equivalents terminal olefin and 1–5 mol.% **2**, results in the selective formation of monomeric ring-opened products that contain exclusively one terminal and one disubstituted olefin (Eq. (17)) [64]. Little or no ROMP, self-metathesis of the terminal olefin, or secondary metathesis of the 1,5-diene product are observed while the strained-ring compound is present. Z-olefin geometry is preferred in the newly formed product in a range of 1.5 to 3.5:1.

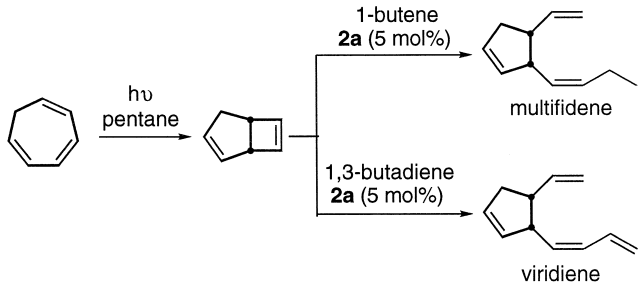


(17)

Cross-metathesis selectivity is likely derived from the alternating reactivity preference of the alkylidenes formed in the catalytic cycle (Scheme 3). Metal alkylidene **28** reacts with the most



Scheme 3. Alternating reactivity preference of metal alkylidenes.

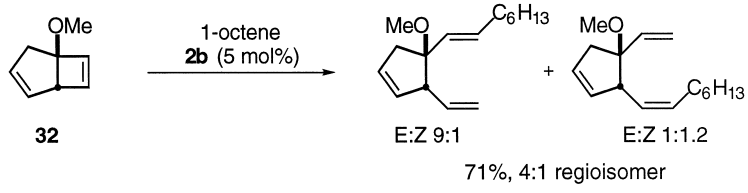


Scheme 4. ROM route to multifidene and viridiene.

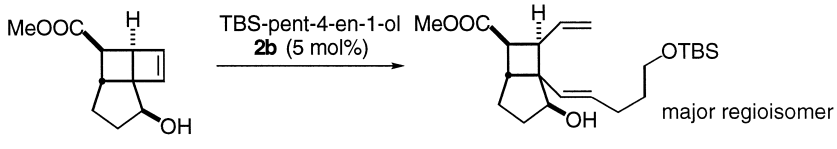
reactive olefin partner, that of strained-ring system **29**, to produce a new, more substituted metal alkylidene (**30**). This sterically encumbered alkylidene now chooses to react with the less hindered, terminal olefin **31** instead of the disubstituted strained olefin to release the desired monomeric 1,5-diene, as well as to regenerate the starting metal alkylidene complex (**28**).

This metathesis methodology was featured in the concise syntheses of two brown algae pheromones, multifidene and viridiene [65,66]. Both are prepared in two steps from cycloheptatriene (Scheme 4).

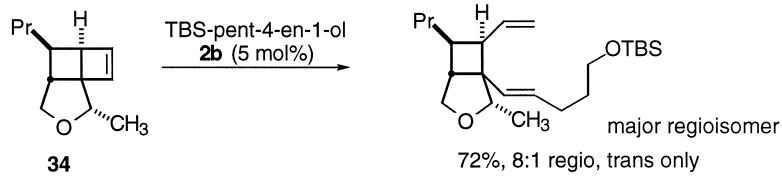
Of relevance to synthetic applications, unsymmetrical cyclobutenes such as **32**–**34** undergo a regio- as well as stereoselective cross-metathesis to form 1,5-dienes [67]. In these cases, the more sterically demanding portion of the terminal olefin is transferred to the more hindered side of the cyclobutene. Interestingly, the major regioisomers strongly favor the (E)-stereochemistry.



32 (18)

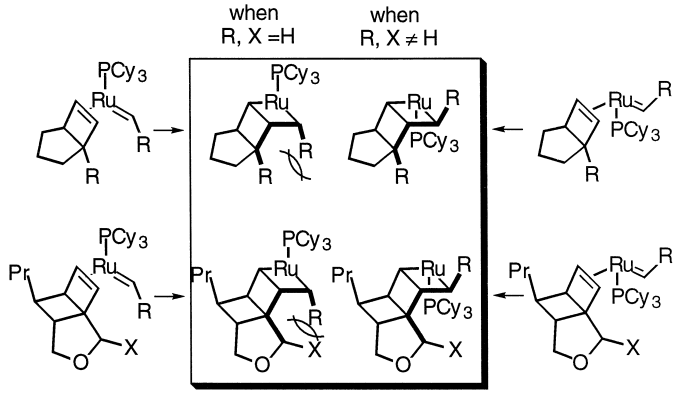


33 (19)



34 (20)

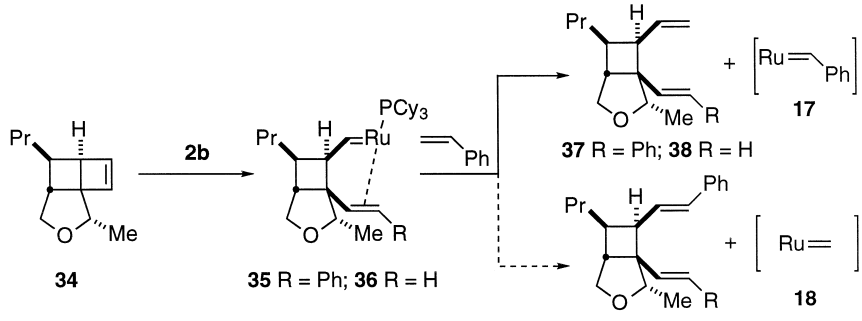
A model to explain this selectivity is illustrated is Scheme 5. Studies by Grubbs [13,30,68], as well as by our lab [69,70], suggest that only one trialkylphosphine remains bound to the metal center during the catalytic cycle. In this case, the alkylidene substituent is likely directed away from the single bulky phosphine ligand. Likewise, the incoming cyclobutene also prefers to approach the



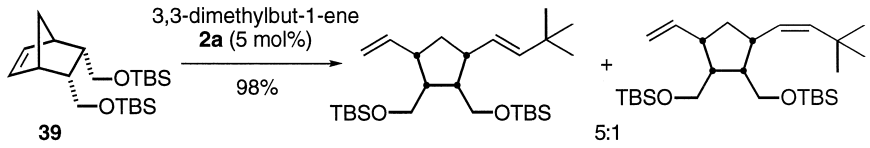
Scheme 5. Regio- and stereoselective ROM.

alkylidene away from the bulky phosphine to provide products of Z-olefin geometry (Eq. (17)). If, however, the cyclobutene (**32**–**34**) is substituted at the allylic position, such approach becomes disfavored, and the cyclobutene now approaches towards the bulky phosphine ligand to give products of E-olefin geometry. From a regiochemical perspective, the major products are derived from a pathway wherein the sterically encumbered side of the cyclobutene approaches away from the metal and its ligands.

Our chemo-, regio- and stereoselectivity models assume that the metathesis-active ruthenium carbene is a metal alkylidene (**17**) instead of a methylidene (**18**). Support for this conclusion was demonstrated in the stoichiometric reaction shown below [70]. When metal alkylidenes **35** or **36** are treated with styrene, exclusive formation of **37** or **38**, respectively, is observed (Eqs. (21) and (22)). This supports the involvement of metal alkylidene **17** in the ROM catalytic cycle. Furthermore, the regioselective formation of **35** when **34** is treated with 1 equivalent of **2b** supports the proposal that the metal and its bulky ligands add away from the sterically demanding side of **34**.



Recently, Blechert et al. extended selective ROM to bicyclo [2.2.1]-ring systems [71,72]. For example, ROM of **39** with either terminal or disubstituted olefins, catalyzed by **2**, proceeds with good selectivity and yield (Eq. (23)).



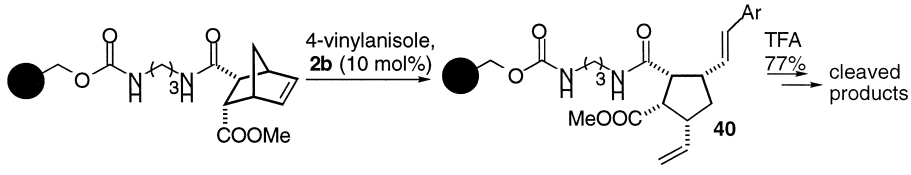
(23)

High dilution conditions (i.e., slow addition of strained olefin to catalyst) are often employed in ROM to minimize competing ROMP pathways. One interesting solution to this limitation, reported by Cuny et al., is the immobilization of the strained ring system on a solid support [73,74]. For the resin-bound bicyclo [2.2.1] system illustrated in Scheme 6, selective ROM with **2b** (10 mol.%) and 10 equivalents of 4-vinylanisole provides the desired 1,5-diene **40**, which cyclizes upon cleavage to give a fused bicyclic lactam in 77% overall yield. Interestingly, this reaction is completely regio- and stereospecific. This selectivity was found to be, in part, dependent upon the tether to the solid support. When a longer tether, such as poly(ethyleneglycol) is used, the regioselectivity falls to 3.3:1, and when the reaction is performed solution phase, regioselectivity drops further to 1.5:1. This is an example where the solid support functions to limit ROMP pathways, as well as to promote a regioselective transformation.

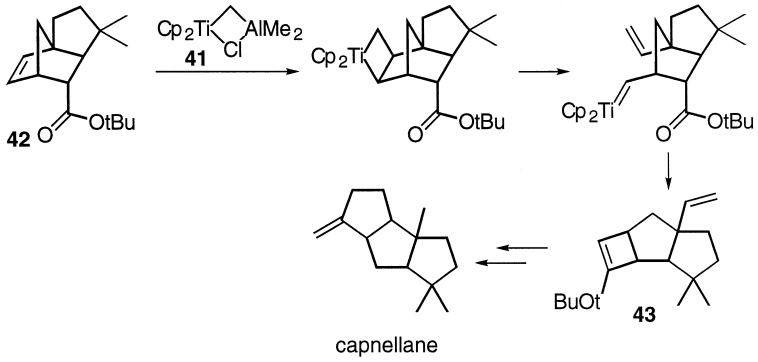
5. Tandem metatheses

The development of a tandem ROM/RCM strategy further expands the synthetic utility of cross-metathesis. An early example, which utilizes the stoichiometric 'metal alkylidene' precursor **41** to synthesize $\Delta^{9,12}$ capnellane, is shown below (Scheme 7) [75,76]. Regio- and chemoselective addition of Tebbe reagent to strained ring compound **42** provides a new metal alkylidene which, upon subsequent carbonyl olefination, gives cyclobutene **43**.

The Grubbs' group has also reported an interesting, catalytic variant of the tandem ring-opening/ring closing methodology (Eq. (24)) [77]. In this case, cyclic olefins flanked by two terminal olefins (**44**) undergo sequential olefin metatheses to produce polycyclic ethers (**45**). This reaction is driven by the release of ring strain and removal of volatile by-products. Reactivity was found to be related to ring size. For systems with little or no strain, the tandem ROM/RCM is achieved by

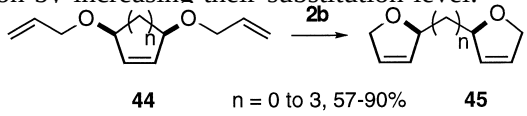


Scheme 6. Selective ROM on a solid support.



Scheme 7. ROM/RCM route to capnellane.

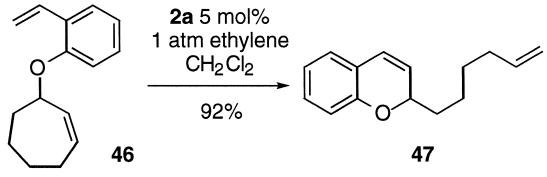
running the transformations at high dilution, as well as by attenuating the reactivity of the acyclic olefins toward oligomerization by increasing their substitution level.



(24)

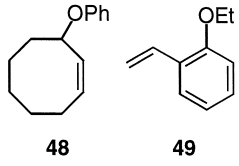
These observed affects of olefinic substitution and high dilution conditions suggest that in the cases involving terminal olefins, the reaction proceeds by initial metathesis at the terminal olefin, followed by metathesis at the cyclic olefin to form the first ring and produce a new metal alkylidene, that then closes, forming the second ring. Pathways by which reaction first occurs at the cyclic olefin, however, cannot be excluded, and may be favored for the more strained cyclic olefins.

More recently, a tandem metathesis was utilized by Hoveyda and coworkers in the synthesis of chromenes (Eq. (25)) [78,79]. In a reaction driven by release of ring strain, styrenyl allyl ether **46** undergoes ring opening/ring closing rearrangement to form the less strained chromene **47**. When the transformation is performed in the presence of ethylene, a 92% yield of the desired monomer is obtained.



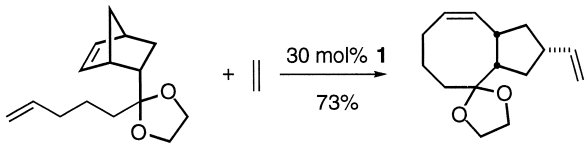
(25)

The observation that olefin metathesis of **48** alone forms oligomeric products, yet no productive reaction ($< 2\%$) occurs for the attempted ROM of **48** with styrenyl ether **49**, suggests that the observed metathesis rearrangement is occurring through initial metathesis at the terminal olefin. The resulting benzylidene then undergoes an intramolecular metathesis with the new neighboring disubstituted olefin to provide **47**.



Blechert also recently reported a novel variant of the tandem olefin metathesis. For example, metathesis of norbornene derivative **50** with 30 mol% **1** and an excess of ethylene provides compound

51 in 73% yield [1,2,80] (Eq. (26)). By varying the tether length, a variety of bicyclic ring systems may be obtained.



50 **51** (26)

6. Future prospects

The development of tunable, well-defined olefin metathesis catalysts have resulted in the recent introduction of selective new olefin cross metatheses. By developing a deeper understanding of the reactive nature of metal alkylidenes and issues that determine selectivity, the rational design of the next generation of catalysts should provide even greater potential for the application of olefin metathesis towards challenges in organic synthesis.

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