

Competing ruthenium catalyzed metathesis condensation and isomerization of allylic olefins

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Accepted 3 September 2002

Abstract

Metathesis condensation and isomerization reactions of allylic compounds were examined using Grubbs' second-generation ruthenium catalyst [Ru*]. Allyl alcohol and allyl cyanide undergo metathesis condensation releasing ethylene, with conversions being the highest reported for these substrates. However, competing olefin isomerization rather than metathesis can occur under certain conditions when heteroatoms are present at the allylic position to the olefin.

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Keywords: ADMET polymerization; Allyl alcohol; Allyl cyanide; Isomerization; Olefin metathesis

1. Introduction

The discovery of functionality tolerant organometallic catalysts has been an important goal for quite some time. In recent years, research with late transition metal-based catalysts has demonstrated their ability to minimize the detrimental effects of air and moisture known to influence the activity of early transition metal complexes [1–3]. One such metathesis catalyst, 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene ruthenium benzylidene chloride [Ru*] (**1**), described by Grubbs and coworkers has been shown to be quite useful even in the presence of a variety of functional groups (Fig. 1) [4].

This complex [Ru*] is the most efficient ruthenium metathesis catalyst to date, displaying substantial enhancements in both activity and versatility when compared to its predecessors [4–15]. It exhibits the ability to metathesize olefins which are essentially unreactive when using either Grubbs' ruthenium first generation [16–18] (**2**) or Schrock's molybdenum [19–23] (**3**) catalysts (Fig. 2). In molecules containing highly Lewis basic functionalities, lack of metathesis reactivity stems from a chelation effect of the ancillary groups after coordination of the olefin site to the metal center [24,25]. This interaction results in the formation of a stable ring, thus preventing any further chemistry at the active site.

Examples of other previously thought to be unreactive olefins include hindered substituted olefins, electron-poor olefins, and allylic ethers [4–10]. These limitations are unfortunate both for economic and scientific reasons, particularly in the case of allylic

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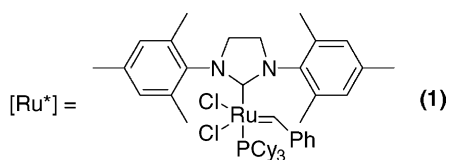


Fig. 1. Grubbs' second generation ruthenium-imidazolium metathesis catalyst.

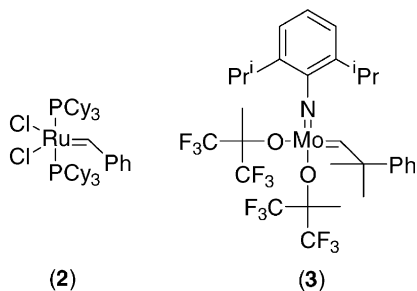


Fig. 2. Earlier generation metathesis catalysts.

substrates, since they are considerably less expensive than other olefins containing functional groups located farther from the double bond. This is a driving force for the development of more functionality tolerant and active metathesis catalyst systems. Until recently, successful use of these “unreactive” olefins has been limited in cross-metathesis (CM), ring closing metathesis (RCM), acyclic diene metathesis (ADMET), and ring opening metathesis polymerization (ROMP) reactions, shown in Fig. 3 [26–28].

The discovery of the second-generation Grubbs' ruthenium catalyst [Ru*] **1** facilitates the synthesis of a broad range of new structures previously not acces-

sible via metathesis chemistry. As a demonstration of this opportunity, we have employed this catalyst to examine the reactivity of two important allylic substrates, allyl alcohol and allyl cyanide. Further, we report that catalyst **1** has the ability to preferentially isomerize olefins containing allylic alcohol and ether groups under certain conditions. While the ruthenium catalyzed isomerization of allylic alcohols has been observed before [29–40], ruthenium carbenes have not been previously seen in the isomerization of allylic ethers. However, a recent report by Nolan and coworkers proposes olefin isomerization may be a competitive process in RCM chemistry [41].

Two pathways are accepted for transition metal catalyzed isomerization of allylic olefins by pathways other than ruthenium carbene chemistry (Fig. 4) [42]; the phenomenon can occur either via a π -allyl metal or a hydrometalation–dehydrometalation mechanism. The most common route, hydrometalation–dehydrometalation, is co-catalyzed by the addition of a proton or hydrogen, producing a kinetically long-lived metal hydride; coordination of a free olefin followed by its subsequent insertion yields a metal alkyl. As an illustration, Krompiec and coworkers report that $\text{RuClH}(\text{CO})(\text{PPh}_3)_3$ at 60°C isomerizes both allylic alcohols and allylic ethers in quantitative yields [29].

In the less common π -allyl metal mechanism, a free olefin coordinates to the metal followed by oxidative addition of the activated allylic C–H bond, yielding a hydride. In 1994, Trost and Kulawiec discovered a similar ruthenium-based system for the isomerization of allylic alcohols [30]. The catalytic species is activated by the formation of a cation,

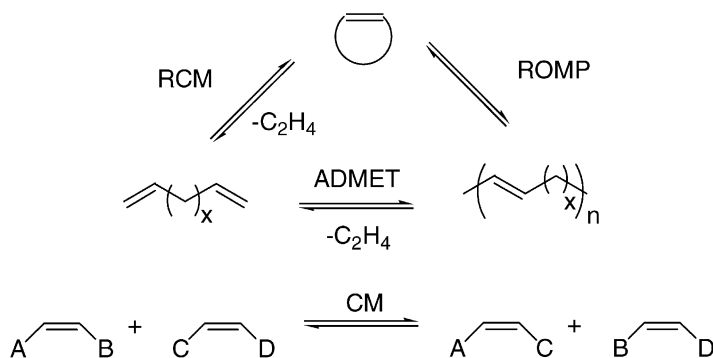


Fig. 3. A variety of metathesis reactions.

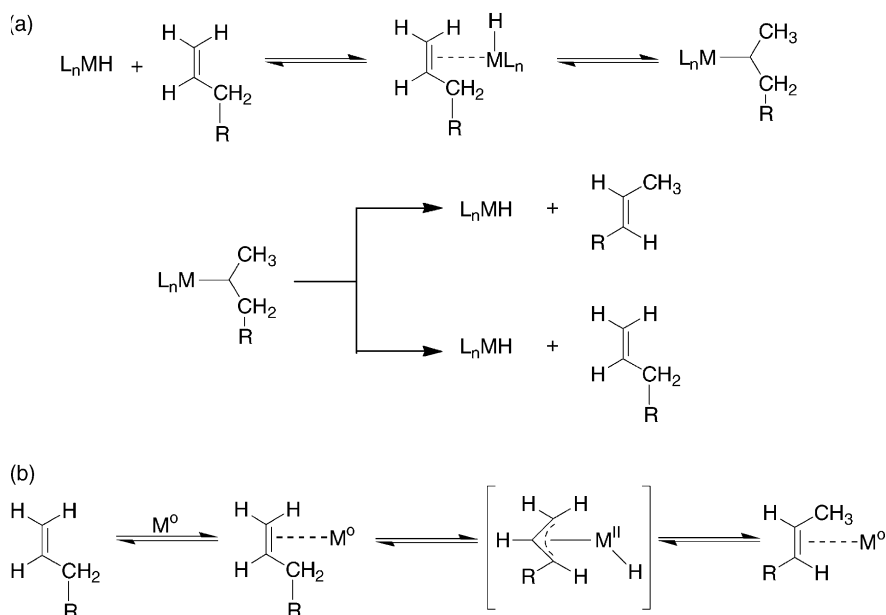


Fig. 4. Common metal-catalyzed olefin isomerization (a) hydrometalation–dehydrometalation mechanism and (b) π -allyl mechanism.

followed by an internal oxidation. This product acts as a bidentate ligand under these conditions and subsequently, β -hydride elimination forms an enone hydride complex. Additionally, McGrath and Grubbs [31] have observed isomerization of allyl alcohol and allyl ethers in the presence of $\text{Ru}(\text{H}_2\text{O})_6(\text{tos})_2$ (tos = *p*-toluenesulfonate), and Kropiec et al. [32] also have seen isomerization when using $\text{Ru}(\text{acac})_3$. Mechanistic studies have shown that ruthenium-assisted isomerizations proceed through an intermolecular 1,3 migration of the allylic C–H, analogous to a π -allyl metal-type mechanism. We now report the first example of preferential allylic ether isomerization using a highly active metathesis (carbene) catalyst; our results are consistent with the modified allyl metal mechanism proposed by Trost and Kulaweic [30] and McGrath and Grubbs [31].

2. Experimental

2.1. General comments

All manipulations were performed using standard Schlenk, high vacuum line, or dry box techniques.

All chlorinated solvents were dried from CaH_2 and all non-halogenated solvents were distilled from sodium or potassium benzophenone ketyl. Allyl alcohol, allyl cyanide, and 2-ethoxyethanol were purchased from Aldrich and distilled from CaH_2 . Phenylmethylethanolamine, 25 wt.% NaOCH_3 methanol solution, allyl bromide, diethyl malonate, allyl glycidyl ether, acetic anhydride were purchased from Aldrich and used as received. The olefin metathesis catalyst $\text{IMesH}_2\text{RuCl}_2(\text{CHPh})(\text{PCy}_3)_3$ was synthesized following the literature procedure [4]. All reactions were performed in duplicate to ensure reproducibility of the results. The reactions were terminated by exposure to air and immediate analysis of the crude reaction mixture was performed. In all cases the metathesis or isomerization reaction had no effect on the mass balance of the reaction. All ^1H (300 MHz) and ^{13}C NMR (75 MHz) spectroscopic experiments were performed on a Varian Mercury-300 superconducting system using CDCl_3 as the solvent and referenced to internal TMS. Fourier transform infrared (FT-IR) spectrometry was performed using a Bio-Rad FTS-40A spectrometer. Sample preparation involved dissolving the compound in CHCl_3 and making a thin film on KBr discs. Elemental

analyses were performed by Atlantic Microlab Inc. (Norcross, Ga.) GC–MS data were acquired using HP 6890 Series GC System and the HP 5973 Mass Selective Detector. Gel permeation chromatography (GPC) molecular weight data were obtained using two 300 mm polymer laboratories gel 5 μm mixed-C columns (polystyrene/divinylbenzene matrix). The instrument was composed of a Hewlett-Packard 1047-A RI detector, Kratos Analytical Spectroflow 757 UV detector, Rainin SD-300 pump, TC-45 Eppendorf column heater, and U6K Waters injector. The solvent used was CHCl_3 at 1.0 ml/min and all peaks were referenced to narrow polydispersity polystyrene standards from polymer laboratories (Amherst, MA).

2.2. Representative procedure for condensation self-metathesis: allyl alcohol

Allyl alcohol, (63.0 mg, 1.10 mmol) and catalyst **1** (9.20 mg, 0.0110 mmol) were weighed in an argon-purged dry box and placed into a 5 ml round bottom flask equipped with a reflux condenser and Teflon stir bar. Solvent (approximately 1 ml) was added and the reaction was stirred for 12 h under argon. Exposure of the flask contents to the atmosphere terminated the reaction. The crude product mixture was dissolved in CDCl_3 and analyzed spectroscopically (^1H and ^{13}C NMR).

2.3. Representative procedure for condensation self-metathesis: allyl cyanide

Allyl cyanide, (70.0 mg, 1.03 mmol) and catalyst **1** (8.70 mg, 0.0103 mmol) were weighed in an argon-purged dry box and placed into a 5 ml round bottom flask equipped with a reflux condenser and Teflon stir bar. Solvent (approximately 1 ml) was added and the reaction was stirred for 12 h under argon. Exposure of the flask contents to the atmosphere terminated the reaction. The crude product mixture was dissolved in CDCl_3 and analyzed spectroscopically (^1H and ^{13}C NMR).

2.4. Preparation of *N,N*-bis[3-(allyloxy)-2-hydroxypropyl]aniline (**5a**)

Monomer **5a** was synthesized via a similar method by Mleziva [43]. Aniline (20.0 g, 0.220 mol) was

added to a 250 ml round bottom flask. An addition funnel filled with allyl glycidyl ether (50.0 g, 0.440 mol) was attached to the flask and the entire system was purged with N_2 . An oil bath was placed underneath the flask and heated to 130–140 $^\circ\text{C}$. At this point, allyl glycidyl ether was added dropwise to the flask while the temperature was maintained at 130–140 $^\circ\text{C}$. Once addition of the ether was complete, the mixture was stirred for an additional 2 h at 130 $^\circ\text{C}$ and the product was purified by vacuum distillation (bp 182–184 $^\circ\text{C}$ at 0.01 mmHg). Yield: 62.9 g, 92%. ^1H NMR (CDCl_3) δ = 6.8 (m, 5H), 5.9 (m, 2H), 5.3 (d, 2H), 5.2 (d, 2H), 4.0 (m, 4H), 3.5 (m, 8H), and 3.1 (m, 2H) ppm. IR (film) 3349, 2890, 1598, 1504, and 1200 cm^{-1} . Anal. calc. for $\text{C}_{19}\text{H}_{29}\text{NO}_4$: H, 8.71; C, 68.03; N, 4.18. Found: H, 8.75; C, 68.13; N, 4.16.

2.5. Preparation of *N,N*-bis[3-(allyloxy)-2-acetoxypropyl]aniline (**5b**)

Monomer **5a** (5.00 g, 0.015 mol) and CHCl_3 (10 ml) were mixed in a 250 ml round bottom flask equipped with an addition funnel and a Teflon stir bar. Acetic anhydride (79.4 g, 0.780 mol) was added over 30 min, after which the mixture was heated to 50 $^\circ\text{C}$ for 4 h. The reaction was monitored using TLC (3:1 hexane:ethyl acetate). The product was dissolved in ether (100 ml) and washed with 10% aqueous NaHCO_3 (3 \times 20 ml) and water (3 \times 20 ml). The ether was dried over Na_2SO_4 . The product was purified using column chromatography (silica gel, 3:1 hexane:ethyl acetate), producing a pale yellow liquid. Yield: 5.75 g, 91.5%. ^1H NMR (CDCl_3) δ = 7.2 (m, 2H, C_6H_5), 6.9 (m, 2H, C_6H_5), 6.7 (t, 1H, C_6H_5), 5.9 (m, 2H, vinyl CH), 5.3 (m, 2H, $\text{CH}-\text{COOCH}_3$), 5.2 (m, 4H, vinyl CH_2), 4.0 (m, 4H, allylic CH_2), 3.7 (m, 4H, RCH_2-O), 3.5 (m, 4H, RCH_2-N), and 2.0 (s, 6H, $-\text{COOCH}_3$) ppm. ^{13}C NMR (CDCl_3) δ = 171.2, 148.9, 148.0, 134.5, 129.0, 117.1, 116.8, 113.5, 112.6, 72.5, 72.2, 72.0, 68.7, 68.4, 57.3, 55.4, and 17.2 ppm. IR (film) 3349, 2890, 1680, 1598, 1504, 1250, and 1200 cm^{-1} . Anal. calc. for $\text{C}_{22}\text{H}_{31}\text{NO}_6$: H, 7.71; C, 65.17; N, 3.45. Found: H, 7.73; C, 65.13; N, 3.44.

2.6. Preparation of *N,N*-bis[2-(allyloxy)ethyl]aniline (**6a**)

A mixture of phenyldiethanolamine (25.0 g, 0.140 mol) and toluene (100 ml) was dried

azotropically by heating under reflux at 115 °C. The water–toluene azeotrope was collected in a Dean-Stark trap and the resulting mixture was cooled to 40 °C. A solution of NaOCH₃ (25 wt.% in CH₃OH; 75 ml, 0.33 mol) was added. When the addition was complete, a condenser was attached and the solution was heated to 70 °C; portions of allyl bromide (15 ml) and NaOCH₃ solution (35 ml) were added every 12 h for 2 days. Excess CH₃OH was collected in a Dean-Stark trap and discarded. The product was extracted with 3 × 100 ml portions of DI H₂O and the solvent was removed in vacuo. The resulting crude product was then vacuum distilled, producing a light yellow liquid (bp 130–140 °C at 0.1 mmHg). Yield: 20.0 g, 56%. ¹H NMR (CDCl₃)δ = 7.35 (m, 2H, C₆H₅), 6.9 (m, 3H, C₆H₆), 6.0 (m, 2H, vinyl CH), 5.3 (m, 4H, vinyl CH₂), 4.0 (d, 4H, allyl CH₂), 3.7 (m, 4H, CH₂–O), and 3.6 (m, 4H, CH₂–N) ppm. ¹³C NMR (CDCl₃)δ = 144.0, 135.6 (CH=CH₂), 129.4, 118.0, 114.5 (CH=CH₂), 113.1, 73.1 (allyl CH₂), 65.1 (CH₂–O), and 56.0 ppm (CH₂–N). IR (film) 3349, 2890, and 1220 cm⁻¹. Anal. calc. for C₁₆H₂₃NO₂: H, 8.87; C, 73.53; N, 5.36. Found: H, 8.84; C, 73.33; N, 5.34.

2.7. Reaction of diene **5a** under ADMET-type metathesis reaction conditions: synthesis of **5c**

Monomer **5a**, (1.00 g, 3.11 mmol) and catalyst **1** (26.4 mg, 0.0311 mmol) were weighed in an argon-filled dry box and placed into a 5 ml round bottom flask equipped with Teflon high vacuum valve and stir bar. The flask was connected to a vacuum line, and its contents were stirred under high vacuum (10⁻³ mmHg) for 24 h at 50 °C or until solution color change. Exposing the flask contents to the atmosphere terminated the reaction. The crude product mixture was dissolved in CDCl₃ and analyzed spectroscopically (¹H and ¹³C NMR). Yield: 0.980 g, 98%. ¹H NMR (CDCl₃)δ = 7.2 (m, 2H, C₆H₅), 6.8 (d, 1H, C₆H₅), 6.7 (m, 2H, C₆H₅), 6.2 (dd, 1H, vinyl CH), 5.9 (m, 1H, vinyl CH), 4.8 (m, 1H, vinyl CH), 4.4 (m, 1H, vinyl CH), 4.1 (dd, 2H), 3.6 (m, 4H), 3.5 (m, 3H), 3.1 (m, 1H), and 1.6 (m, 6H, RCH=CH–CH₃) ppm. ¹³C NMR (CDCl₃)δ = 148.8, 145.7 (vinyl CH), 129.4, 117.5, 112.3, 99.3 (vinyl CH), 73.5 (allylic CH₂), 68.1 (R₂CH–OH), 57.7 (RCH₂–N), and 12.6 (RCH=CH–CH₃) ppm. IR (film) 3349, 2890, 1598, 1504, and 1250 cm⁻¹. Anal. calc. for C₁₉H₂₉NO₄: H,

8.71; C, 68.03; N, 4.18. Found: H, 8.62; C, 68.33; N, 4.56.

2.8. Reaction of diene **5b** under ADMET reaction conditions: synthesis of **5d**

The metathesis condensation of **5b** was performed in the same manner as described above for **5a**. Yield: 0.700 g, 70%. ¹H NMR (CDCl₃)δ = 7.2 (m, 2H, C₆H₅), 6.9 (m, 2H, C₆H₅), 6.7 (t, 1H, C₆H₅), 6.3 (1H, d, vinyl CH), 5.9 (m, 1H, vinyl CH), 5.3 (2H, m), 4.8 (m, 1H, vinyl CH), 4.4 (m, 1H, vinyl CH), 3.8 (d, 4H, RCH₂–O), 3.75 (d, 4H, RCH₂–N), 2.00 (s, 6H, –OCOCH₃), and 1.6 (m, 6H, RCH=CH–CH₃) ppm. ¹³C NMR (CDCl₃)δ = 171.2, 145.9, 145.0 (vinyl CH), 129.0, 117.1, 113.5, 92.3 (vinyl CH), 75.5, 72.2, 57.3, 55.4, 17.2, and 13.3 ppm. IR (film) 3349, 2890, 1680, 1598, 1504, 1250, and 1200 cm⁻¹. Anal. calc. for C₂₂H₃₁NO₆: H, 7.71; C, 65.17; N, 3.45. Found: H, 7.53; C, 62.13; N, 3.14.

2.9. Reaction of diene **6a** under ADMET reaction conditions: synthesis of **6b**

The metathesis condensation of **6a** was performed in the same manner as described above for **5a**. Yield: 0.680 g, 68%. ¹H NMR (CDCl₃)δ = 7.35 (m, 2H, C₆H₅), 6.9 (m, 3H, C₆H₆), 6.25 (m, 1H, vinyl CH), 5.95 (m, 1H, vinyl CH), 4.81 (m, 1H, vinyl CH), 4.42 (m, 1H, vinyl CH), 3.8–4.0 (m, 4H, RCH₂–O–), 3.6 (m, 4H, RCH₂–O–), and 1.6 (m, 6H, RCH=CH–CH₃) ppm. ¹³C NMR (CDCl₃)δ = 144.5, 144 (–O–CH=CH), 129.4, 118, 113.1, 96 (–O–CH=CH) 69.1 (CH₂–O), 57 (CH₂–N), and 13.5 ppm (RCH=CH–CH₃). IR (film) 3349, 2890, and 1220 cm⁻¹. Anal. calc. for C₁₆H₂₃NO₂: H, 8.87; C, 73.53; N, 5.36. Found: H, 8.50; C, 73.79; N, 5.74.

3. Results and discussion

We have explored the metathesis reactivity of two common allylic compounds, allyl alcohol and allyl cyanide (Fig. 5). They are interesting molecules for investigation, since their self-metathesis condensation products can lead to precursors for commercial polymers. Condensation metathesis of allyl alcohol produces 2-butene-1,4-diol which, when hydrogenated, is

compared to the results obtained for CH_2Cl_2 . However, the selectivity ratio of condensation metathesis product to isomerization product is highest in THF. Another observation is that at elevated temperatures (60°C), isomerization selectivity becomes favored over metathesis and total allyl alcohol conversion increases. The result shown in Table 1 also demonstrates the need to fully dry all solvents and monomers while performing metathesis chemistry. The metathesis condensation not performed under anhydrous conditions shows a 100% increase in the formation of propionaldehyde under the same reaction conditions. Regardless of the reaction temperature or conditions employed by us, complete suppression of isomerization was unable to be achieved.

Using allyl cyanide as the substrate, condensation metathesis is less efficient than allyl alcohol [11–15,50]. While no metathesis product was observed spectroscopically (^1H and ^{13}C NMR) at catalyst loadings of less than 0.5 mol%, employment of higher catalyst concentrations does promote metathesis, and we observed a maximum 28% conversion of allyl cyanide to 1,4-dicyano-2-butene product with 10 mol% catalyst loading, the highest ever reported in the literature (see Table 2) [11–15]. Regardless of the quantity of catalyst utilized, the reaction mixture becomes dark brown within 90 min after the substrate is added, strongly indicative of catalyst decomposition. No competing isomerization products were observed. We believe that the moderately strongly coordinating $-\text{CN}$: group interacts with the ruthenium center, thus deactivating the catalyst for olefin metathesis. Addition of coordinating solvents such as THF or acetone proved to be ineffective at increasing the yield of metathesis product. In comparison, catalysts **2** and **3** are unable to promote condensation metathesis of allyl cyanide.

Table 2

Metathesis results of allyl cyanide using variable catalyst ratios of **1**

Entry number ^a	Solvent	Substrate:catalyst molar ratio	1,4-Dicyano-2-butene molar (mmol)/yield (%) ^b
13	CH_2Cl_2	250:1	0
14	CH_2Cl_2	60:1	0.08/16
15	CH_2Cl_2	10:1	0.14/28
16	THF	10:1	0.14/28
17	Acetone	10:1	0.14/28

^a Typical reaction conditions: 70 mg (1.03 mmol) allyl cyanide, 1 ml solvent, 40°C , 12 h under Ar.

^b Determined by ^1H NMR.

The ability of catalyst **1** to condense both allyl alcohol and allyl cyanide encouraged us to use this complex to attempt the metathesis of other functionalized dienes containing functionality in the allylic positions, which can form polymers under ADMET conditions (neat substrate and high vacuum) [51,52]. Initially, we examined two molecules containing allylic ether units, *N,N*-bis[3-(allyloxy)-2-hydroxypropyl]aniline (**5a**) and its acetylated derivative **5b** as potential polymerization monomers. Curiously, monomer **5a** does not undergo ADMET polymerization when reacted neat under vacuum at 50°C using catalyst **1** [5–10,51]. Although the reaction mixture changed from tan to bright orange-yellow in color, the viscosity of the reaction mixture did not increase nor was ethylene evolution observed, direct evidence for ADMET chemistry. No oligomers were detected by GC–MS or GPC, and NMR analyses indicated the dominant reaction product (98%) was the isomerization product, **5c** (Fig. 6). Interestingly, isomerization of *both* olefin sites from allyl to vinyl ether groups occurs. The acetylated derivative **5b** reacts in a similar manner as does its unsubstituted analog *N,N*-bis[2-(allyloxy)ethyl]aniline (**6a**) (Fig. 7).

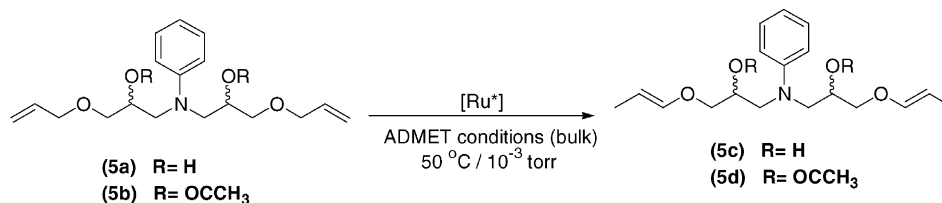


Fig. 6. Selective isomerization of allylic ethers.

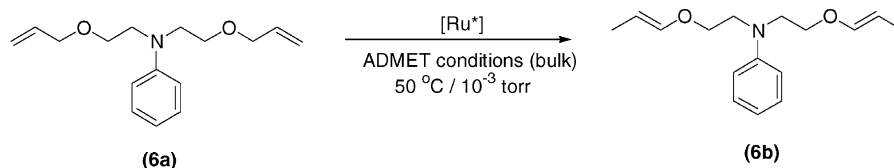


Fig. 7. Isomerization of substituted aniline containing no additional groups.

Apparently the ability of catalyst **1** and earlier Grubbs-type ruthenium catalysts to isomerize *N,N*-disubstituted anilines is not dependent on the identity of the substituents in close proximity. This unreactivity in RCM and cross-metathesis has been reported previously concerning effects of chelation [9,25,56]. However, in the case of these *N,N*-disubstituted monomers it is clear that the isomerization using catalyst **1** has some other root cause, observations which are similar to metathesis results obtained by others using earlier generation ruthenium catalysts [29–40].

We performed a series of experiments in an attempt to minimize or prevent the isomerization of these *N,N*-disubstituted anilines used in this study. Initially, our focus was on varying the catalyst ratio and temperature. However, neither catalyst concentration nor reaction temperature variation affects the amount of isomerization observed in these compounds. We also examined the likelihood of the existence of a trace amount of Ru–H containing species being formed in situ or formed during the synthesis of catalyst **1**. It is well known that ruthenium-hydride complexes are efficient isomerization catalysts [29] and, recently, ruthenium hydrides have been isolated as a major decomposition pathway for Grubbs' type complexes [53,54]. However, no Ru–H species were observed spectroscopically throughout the entire reac-

tion time period. In order to minimize the possibility of any presence of hydride, catalyst **1** was purified by refluxing with several different halocarbons (CH₂Cl₂, CHCl₃, and α,α -dichlorotoluene), which are known to undergo Ru–H/Ru–Cl exchange reactions [18]. The reaction results observed are not affected by these treatments. Trace Ru–H in the catalyst can not be ruled out due its undetectability and robust nature in even small amounts. However, the use of halocarbons such as CHCl₃ as reaction solvents significantly decreases isomerization from 98 to 41% (Table 3) using monomer **5a**, and promotes the formation of the condensation dimer (Fig. 6). These results correspond with the similar observations by Grubbs and coworkers for allyl alcohol terminated ROMP of 1,5-cyclooctadiene [48].

However, isomerization of monomers **5b** and **6a** still occurs regardless of the lack of a protic alcohol group present, and the addition of coordinating solvents such as THF does little to inhibit it. Since, the metathesis reactions of these *N,N*-disubstituted anilines were performed with or without solvent present and isomerization still occurs in the absence of a credible proton source, it is likely that a π -allyl type or similar mechanism proposed by Grubbs and Trost is in effect [30,31].

The findings that substrates **5a** and **6a** under ADMET conditions (bulk, 50 °C) undergo no

Table 3
Metathesis of allylic monomers using catalyst **1**

Entry number ^a	Substrate	Solvent	Metathesis product ^b (%)	Isomerization product molar (mmol)/yield (%)
18	5a ^a	Neat	0	2.95/98 of 5c
19	5a ^c	CHCl ₃	0.09/10 ^d	0.38/41 of 5c
20	5b ^a	Neat	0	1.73/70 of 5d
21	6a ^a	Neat	0	2.12/68 of 6b
22	6a ^c	THF	0	2.17/70 of 6b

^a ADMET conditions: 26.4 mg [Ru*], monomer (3.11 mmol), 50 °C, 100:1 monomer:catalyst, 24 h at 10⁻³ mmHg.

^b Determined by ¹H NMR.

^c 26.4 mg [Ru*], 1 ml refluxing solvent, 100:1 monomer:catalyst, 24 h under 1 atm argon.

^d Condensation dimer.

metathesis and only isomerization under the conditions employed is surprising since several groups have reported the successful metathesis of allylic ethers. Additional metathesis attempts using butyl allyl ether and propyl allyl ether were performed to determine if isomerization is typical under ADMET-type conditions for other allylic ethers. Both molecules were exposed to catalyst **1** under identical conditions to the substituted aniline experiments. Minimal isomerization or metathesis activity was observed with both molecules. These results compared to others [55–57] may stem from the different reaction conditions employed in these studies (RCM performed in solution versus neat ADMET) and perhaps an inherent isomerization mechanism found in catalyst **2**. It is plausible that both catalyst concentration and the presence of solvent play a significant role in the selectivity observed in metathesis chemistry. Therefore, it is cautionary to consider the nature of the chemistry being performed (RCM, CM, ADMET, or ROMP) and the choice of metathesis catalysts when attempting to compare results obtained from olefin metathesis experiments and predict the results of a new untested substrate.

4. Conclusions

The metathesis condensation of allyl alcohol and allyl cyanide can be accomplished in reasonably high yields, important observations that can lead to viable alternate synthetic routes to 1,4-butanediol and 1,6-hexanediamine. In the case of allyl alcohol, the yield of the condensation product increases concurrently with decreasing isomerization by the addition of coordinating solvents such as THF or by addition of halocarbon hydride exchangers. When allylic ethers contain other functional groups, isomerization is the favored reaction pathway. Further studies are currently underway to elucidate this phenomenon.

Acknowledgements

The authors would like to thank the National Science Foundation (NSF), Army Research Office (ARO) and the Milliken Chemical Company for the generous support of this research. We also thank Professor

Bob Grubbs and his students for helpful discussions regarding the ruthenium catalyst used in this research.

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