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Communication

New strategy for production of primary alcohols from aliphatic olefins by tandem cross-metathesis/hydrogenation

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ABSTRACT

Primary alcohols are widely used in industry as solvents and precursors of detergents. The classic methods for hydration of terminal alkenes always produce the Markovnikov products. Herein, we reported a reliable approach to produce primary alcohols from terminal alkenes combining with biomass-derived allyl alcohol by tandem cross-metathesis/hydrogenation. A series of primary alcohol with different chain lengths was successfully produced in high yields (*ca.* 90%). Computational studies revealed that self-metathesis and hydrogenation of substrates are accessible but much slower than cross-metathesis. This new methodology represents a unique alternative to primary alcohols from terminal alkenes.

Primary alcohols have tremendous industrial application as solvent and precursors of chemicals [1,2]. The hydration of terminal olefin to alcohols is an important process in both bulk and fine chemical syntheses [3,4], however, this methodology using acid catalysts always provided the secondary alcohols for the terminal olefin because the reaction follows Markovnikov's rule. Although some progress, to date, has been made on the conversion of terminal olefins to primary alcohols by metal-catalyzed methods and multistep reaction [5–9], directly achieving high selectivity of primary alcohols from terminal olefins is still difficult [10,11]. For example, Grubbs and co-workers [8] reported an effective approach for the direct synthesis of primary alcohols from aryl-substituted terminal olefins *via* triple relay catalysis, however, high regioselectivity for primary alcohols was not successful with respect to aliphatic terminal olefins.

In reality, the two-step process including hydroformylation/reduction (Fig. 1) is currently applied for the industrial production of primary alcohols from terminal olefins [12,13]. Hydroformylation of olefins could occur at the primary, or secondary carbon atoms of the carbon-carbon double bond, and lead to the formation of linear (*n*) and branched (*iso*) aldehydes. Moreover, isomerizaiton of the double bond during the hydroformylation of terminal olefins also afford the increase of *iso*-aldehydes [14–16]. Hydroboration/oxidation sequence could also obtain hydration products with anti-Markovnikov regioselectivity (Fig. 1). However, a stoichiometric borane reagent should be required, and the recycle of boron waste unavoidably generated from this process is difficult. Moreover, the usage of peroxides in the oxidation step of hydroboration could raise safety concerns when the process is applied in large-scale production [17]. Therefore, it is very necessary to develop an alternative environmental friendly approach to produce the primary alcohols from non-activated aliphatic olefins.

Olefin cross-metathesis (CM) has now been an effective route toward the elaboration of olefinic substrates with the advent of well-defined catalysts [18–21]. Glycerol as a byproduct accounting for 10 wt% of the total biodiesel is abundantly generated in the production of biodiesel, and now the serious surplus of glycerol leads to the price decrease [22,23]. The non-catalytic deoxydehydration of glycerol with formic acid to allyl alcohol has been known to be a promising and economically viable route [24], and the high purity of allyl alcohol about 99.9 wt% could be successfully obtained by salting-out method in our lab [25]. Therefore, allyl alcohol could be generated from the biomass-derived chemicals, and is suitable as an intermediate for fabrication of functional organic molecules [26,27].

Herein, a new strategy (Fig. 1) for producing primary alcohols by using allyl alcohols as stating raw material through tandem

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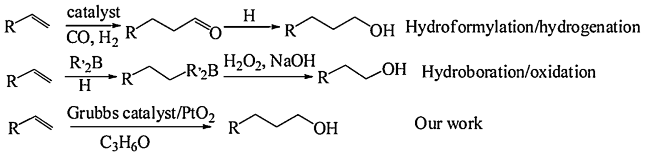


Fig. 1. Current strategies for the production of primary alcohols from terminal alkenes *via* hydroformylation/hydrogenation and hydroboration/oxidation sequence.

cross-metathesis/hydrogenation has been developed, a series of *n*-alcohols could be obtained in good yields, and the tandem procedure is beneficial to enhance the selectivity toward *n*-alcohols.

The tandem metathesis/hydrogenation proceeded may involve many reactions, such as cross-metathesis, self-metathesis, and hydrogenation among the substrates and intermediate products [28–30]. The first-step cross-metathesis between allyl alcohol and terminal olefin with a high activity and selectivity is of great importance in achieving high yield primary alcohols. We firstly studied the conversion of allyl alcohol by cross-metathesis with 1-ocetene by four olefin metathesis catalysts (Fig. S1 in Supporting information) combining with PtO_2, respectively. Starting from allyl alcohol, as shown in Table 1, the total three main products could be observed with various proportions in the final products. Regarding the four olefin metathesis catalysts, allyl alcohol could be completely converted by metathesis and hydrogenation, however, Grubbs I (GI) combining PtO_2 have a poor yield (42%) toward the goal product of 1-nonanol, probably resulting from that the first-step cross-metathesis of allyl alcohol with 1-octene has a low reaction rate over GI catalyst, and more allyl alcohol were hydrogenated to *n*-propanol over PtO_2 catalyst in the presence of H_2 atmosphere. Hoveyda-Grubbs II (H-GII) catalyst shows the highest yield of 92% for 1-nonaol based on allyl alcohol, with a minor byproduct of *n*-propanol and 1,4-butanediol, indicating that this olefin metathesis catalyst was compatible with PtO_2 hydrogenation catalyst. H-GII catalyst was selected to combine PtO_2 for the synthesis of primary alcohols in our study. The yield of 1-nonanol by tandem method is higher than that by two-step process (entry 5 in Table 1), because metathesis is a reversible reaction, the 2-nonen-1-ol produced from the olefin metathesis could instantaneously be consumed by hydrogenation, leading to the reaction toward the forward reaction.

In fact, the tandem cross-metathesis/hydrogenation process is very complicated, the possible products obtained from allyl alcohol are shown in Fig. 2. To further understand the reaction process, the yields for the possible products based on allyl alcohol were recorded with various reaction times. At the initial reaction stage, the products mainly consist of 2-nonen-1-ol and 1-nonanol, with the yields of 48% and 4%, respectively, and the total of other three products (2-butene-1,4-diol, 1,4-butanediol and *n*-propanol) account for a very minor proportion. The kinetic experimental data shows that the reaction rate for cross-metathesis is much faster than that of hydrogenation. The yield of 2-nonen-1-ol is also much higher than that of the total yields of 2-butene-1,4-diol and 1,4-butanediol, indicating that the reaction rate of cross-metathesis is larger than that for self-metathesis of allyl alcohol. The yield for the goal product of 1-nonanol gradually increases by the continuing hydrogenation of 2-nonen-1-ol with the increase of reaction time. After 50 min, the yield of 1-nonanol could reach a maximum accompanied with the disappearance of 2-nonen-1-ol, indicating that the cross-metathesis of allyl alcohol with 1-octene came to an end.

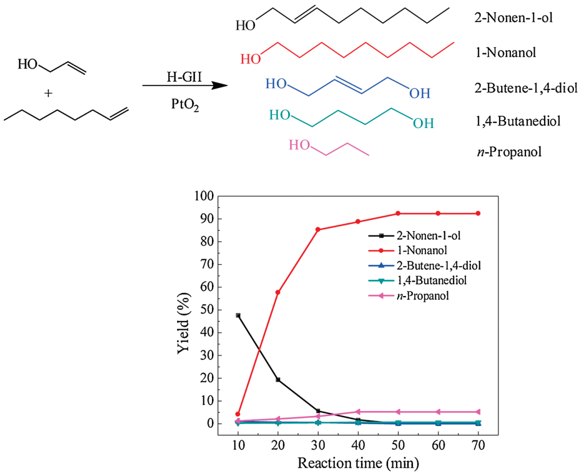
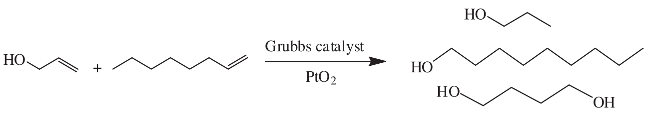


Fig. 2. Yield of products formed from allyl alcohol *vs.* reaction time in the tandem cross-metathesis/hydrogenation.

Giving that the allyl alcohol as cross-metathesis partner, we extended the substrate scope to prepare various primary alcohols under the optimized conditions. A series of aliphatic olefins were tested as a partner with allyl alcohol, the experiment results were summarized in Table 2. *n*-Alcohols in a high yield around 90% could be successfully obtained from terminal olefins, indicating that the significant variation in chain length for terminal olefins could be tolerated. In the case of PtO_2-free system, primary allyl alcohols could also be prepared in a good yield (*ca.* 85%) only by cross-metathesis of allyl alcohol with terminal olefins. Primary allylic

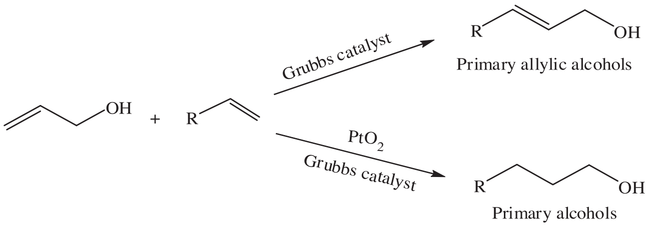
Table 1
Reaction results over various olefin-metathesis for the tandem cross-metathesis/hydrogenation reaction.

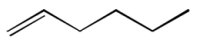
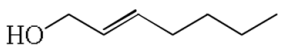
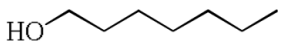
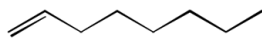
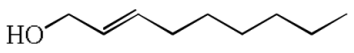
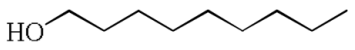
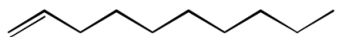
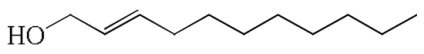
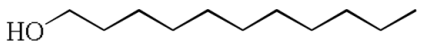
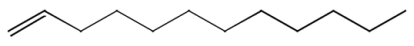
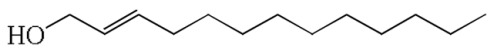
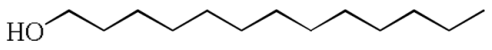
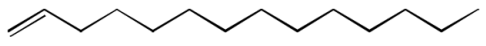
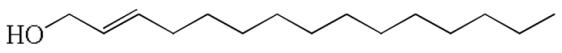
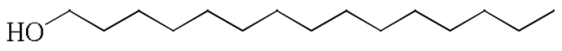
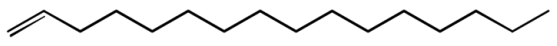
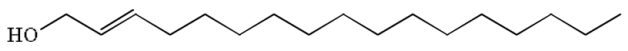
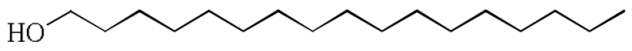


Entry	Catalyst	Conversion (%)[a]	Gas chromatography (GC) yield (%)		
			n-propanol	1,4-butanediol	1-nonanol
1	GI/PtO_2	100	55	<1	42
2	GII/PtO_2	100	11	<1	86
3	$H\text{-}GI/PtO_2$	100	9	<1	88
4	$H\text{-}GII/PtO_2$	100	5	<1	92
5	$H\text{-}GII/PtO_2$[b]	100	9	<1	89

Conditions: allyl alcohol (0.5 mmol), 1-octene (1.0 mmol), Ru catalyst (0.01 mmol), PtO_2 (0.01 mmol), dichloromethane (2.5 mL), H_2 (0.3 MPa), room temperature, 50 min.
[a] Conversion of allyl alcohol.
[b] Two step reaction: First Ru catalyst for 50 min, then PtO_2 for 50 min.

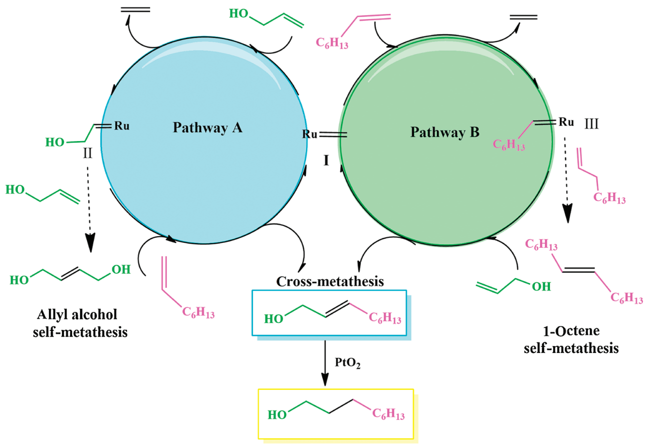
Table 2
Scope of H-GII and PtO_2 catalyzed tandem cross-metathesis/hydrogenation reaction sequence.



Entry	Substrate	CM (GC yield%)[a]	CM/Hydrogenation (GC yield%)[b]
1		 (90)	 (93)
2		 (89)	 (92)
3		 (87)	 (90)
4		 (85)	 (90)
5		 (84)	 (89)
6		 (82)	 (86)

[a] Reaction conditions for CM: allyl alcohol (0.5 mmol, 1.0 equiv.), aliphatic olefins (1.0 mmol, 2 equiv.), H-GII (2 mol%, 0.02 equiv.), dichloromethane (2.5 mL), H_2 (0.3 MPa), room temperature, 50 min.

[b] CM/Hydrogenation condition is identical to the CM besides the introduction of PtO_2 (2 mol%, 0.02 equiv.).



Scheme 1. Possible pathways for cross-metathesis of allyl alcohol with 1-octene.

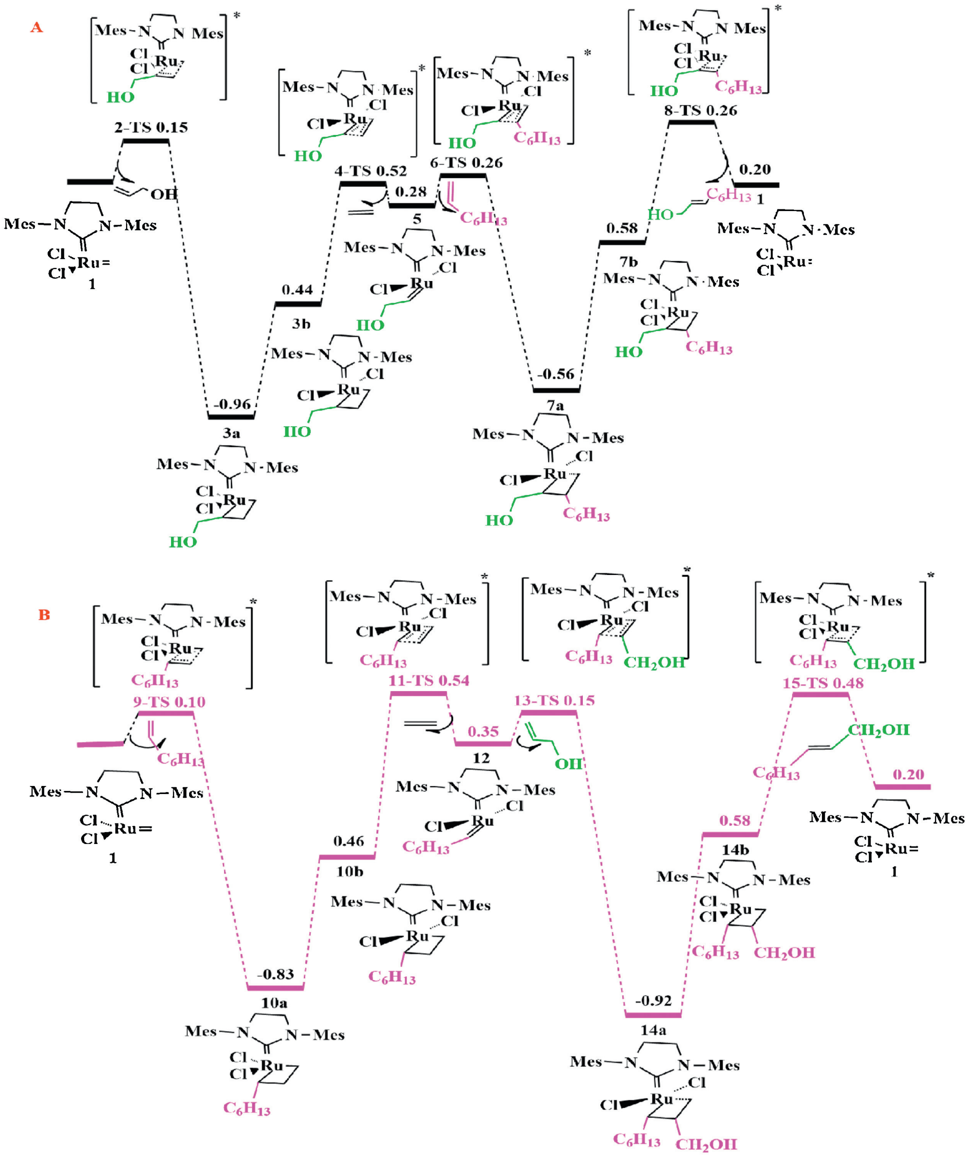
alcohols are an important class of versatile building blocks, because they allow for a wide range of subsequent conversions, including many possibilities for carbon-carbon bond formation reactions, and introduction of functional groups [31,32]. This tandem cross-metathesis/hydrogenation displays excellent generality for production of primary alcohols in a good yield. Compared to the two indirect routes for primary alcohols from terminal olefins, including hydroformylation/reduction and hydroboration/oxidation, this tandem strategy shows much more superiority owing to the mild reaction condition and high yield for goal products, moreover, the used allyl alcohol as a partner could be obtained from bio-mass raw materials [24].

To further understand the tandem cross-metathesis/hydrogenation reaction of allyl alcohol with aliphatic olefins, the reaction process has been studied by using DFT calculaitons with VASP [33–35]. There are two possible pathways to prepare primary allylic alcohols by cross-metathesis (Scheme 1). In pathway A, a vinylcarbene II is first formed from the reaction of methylidene I with allyl alcohol, then the vinylcarbene II reacts with the 1-octene to form 2-nonen-1-ol. For the pathway B, alkylidene III is formed from the reaction of methylidene I with 1-octene, then alkylidene III reacts with the allyl alcohol to form 2-nonen-1-ol.

As show in Scheme 2, the corresponding energy barriers of the most favorable pathways for the cross-metathesis of allyl alcohol-first and 1-octene-first have similar energy barriers based on the methylidene complex. The ring-opening of metallacycle forming vinylcarbene and ethylene has the highest energy barriers of allyl alcohol-first and 1-octene-first, wherever the corresponding energy barriers are 0.52 eV and 0.54 eV, respectively. In the case of H-GII, the highest energy barrier of allyl alcohol-first and 1-octene-first are 0.59 eV and 0.55 eV, respectively (Figs. S5 and S6 in Supporting information). The results show that both allyl alcohol-first and 1-octene-first are possible for allyl alcohol and 1-octene cross-metathesis whatever the model of catalyst is methylidene complex or H-GII. The reaction pathways of allyl alcohol and 1-octene cross-metathesis are different from that for diene and alkene cross-metathesis, which Grubbs and co-workers find that the pathway of diene-first is more easily than that of alkene-first [36].

Considering that self-metathesis of substrates have a significant effect on the final products, the allyl alcohol self-metathesis and 1-octene self-metathesis have been investigated by means of DFT calculations. The energy barrier for the reaction of vinylcarbene 5 with allyl alcohol is 0.72 eV (Fig. S7 in Supporting information), which is much higher than that of vinylcarbene 5 with 1-octene (0.26 eV). Similarity, the energy barrier for the reaction of vinylcarbene 12 with 1- octene is 0.66 eV (Fig. S8 in Supporting information), which is also well above that of vinylcarbene 12 with allyl alcohol (0.15 eV). The result demonstrates that the cross-metathesis of 1-octene with allyl alcohol occurs more easily than the self-metathesis of the substrates, which is similar with the calculated results of diene and alkene cross-metathesis [36].

Finally, hydrogenation of allyl alcohol and 1-octene (Figs. S9 and S10 in Supporting information) over the Pt(100) surface are studied. The highest energy barriers for the formation of *n*-propanol and *n*-octane corresponding to allyl alcohol and 1-octene hydrogenation are 0.90 eV and 0.88 eV, respectively, which is much higher than that of allyl alcohol and 1-octene cross-metathesis (0.52 eV). The calculation result also indicates that the hydrogenation rate of allyl alcohol and 1-octene are much slower



Scheme 2. Most favorable pathways for the cross-metathesis of allyl alcohol-first (A) and 1-octene-first (B) (unit: eV). Olefin π-complexe have been omitted in the scheme. Letters a and b refer to conformational changes of the chlorine ligand.

than that for allyl alcohol and 1-octene cross-metathesis, which is in good agreement with our experimental results.

In conclusion, we have developed a new synthetic methodology to produce primary alcohols by tandem cross-metathesis/hydrogenation of allyl alcohol with terminal aliphatic olefins. The experimental and DFT theoretical results suggest that hydrogenation rate of olefin substrates are much slower than olefin metathesis, and the cross-metathesis of substrates has an overwhelming advantage over self-metathesis. Compared to the classic hydroformylation/reduction and hydroboration/oxidation routes, our strategy allows for the reaction can proceed in a more mild condition to obtain primary alcohols in high yields and excellent selectivity from aliphatic olefins, thus rendering this methodology attractive for industrial applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cclet.2019.10.001.

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