

Metallacyclobutane Substitution and Its Effect on Alkene Metathesis for Propylene Production over W–H/Al₂O₃: Case of Isobutene/2-Butene Cross-Metathesis

Kai C. Szeto,[†] Etienne Mazoyer,[†] Nicolas Merle,[†] Sebastien Norsic,[†] Jean-Marie Basset,^{*,†,§} Christopher P. Nicholas,^{*,‡} and Mostafa Taoufik^{*,†}

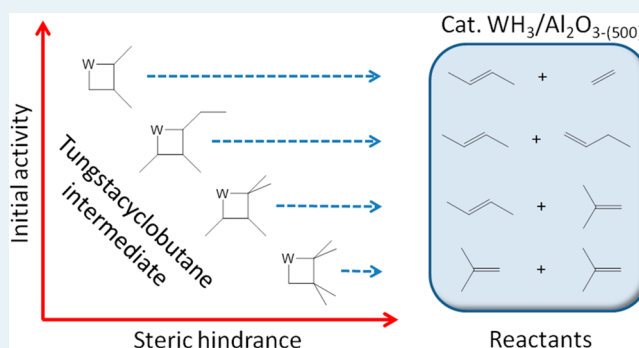
[†]Laboratoire C2P2, team Chimie Organométallique de Surface (CNRS-UMR 5265), Université Lyon 1, ESCPE Lyon, 43 Boulevard du 11 Novembre 1918, 69626 Villeurbanne Cedex, France

[‡]Exploratory Catalysis Research, UOP LLC, a Honeywell Company, 25 East Algonquin Road, Des Plaines, Illinois 60017, United States

Supporting Information

ABSTRACT: Cross metathesis between 2-butenes and isobutene yielding the valuable products propylene and 2-methyl-2-butene has been investigated at low pressure and temperature using WH₃/Al₂O₃, a highly active and selective catalyst. Two parallel catalytic cycles for this reaction have been proposed where the cycle involving the less sterically hindered tungstacyclobutane intermediates is most likely favored. Moreover, it has been found that the arrangement of substituents on the least thermodynamically favored tungstacyclobutane governs the conversion rate of the cross metathesis reaction for propylene production from butenes and/or ethylene.

KEYWORDS: heterogeneous catalysis, alumina, surface organometallic chemistry, tungsten hydride, propylene, tungstacyclobutane



1. INTRODUCTION

The demand for propylene is continuously growing, primarily because of increases in polypropylene, propylene oxide, and acrylonitrile consumption.^{1,2} Consequently, traditional methods such as catalytic or steam cracking used to obtain propylene have difficulties in adjusting their production capacities with the growing demand in the marketplace. In particular, with the growth of shale gas opportunities, steam crackers are becoming fed quite heavily with ethane,³ significantly reducing the propylene byproduct traditionally made when naphtha or other heavy feed sources are used.⁴ Hence, on-purpose propylene production technologies have become more central for the global supply. These methodologies include propane dehydrogenation and oxidative dehydrogenation,^{5–7} olefin metathesis,^{8–11} and methanol to olefins.^{12–14} The production of propylene via olefin metathesis reaction is an established method, having been used in production for tens of years, with a WO₃/SiO₂ catalyst used most frequently. The commercialized and most common reaction is the cross-metathesis of ethylene and 2-butene.^{8,9,11,15,16} However, other metathesis reactions starting from available butene feeds are also important.^{17–25}

Our laboratory has been working extensively to develop alternative methods to produce propylene involving alkene metathesis reactions.^{26–29} In this context, we discovered a new catalytic reaction which transforms ethylene directly to

propylene at low temperature and pressure (150 °C, 1 bar) with a selectivity higher than 95%.³⁰ However, the tungsten hydride on alumina catalyst used here suffers from catalyst deactivation with time on stream, leading to a low yield of propylene. Recent studies reveal that this same WH₃/Al₂O₃₋₍₅₀₀₎ precursor is a stable and highly active catalyst in the formation of propylene from linear butenes under the same conditions (150 °C, 1 bar), with a higher productivity in propylene.^{23,24} Importantly, the first example of propylene production from 2-butene in promising yield has been reported. Note that symmetrical olefins, such as 2-butenes, give degenerate product over a classical olefin metathesis catalyst. However, this catalyst comprises a tungsten-carbene-hydride active site, which after initial activation in the presence of reactant, operates as a “bifunctional catalyst” through the disfavored 2-butene isomerization on W-hydride to 1-butene followed by 2-butenes/1-butene cross-metathesis on W-carbene.²³ Moreover, WH₃/Al₂O₃₋₍₅₀₀₎ is also highly active and selective for cross-metathesis of ethylene and 2-butenes.¹⁶ These former processes require either an ethylene source, something not available in all locations, or isolation of a single butene isomer. For practical reasons, development of new

Received: July 4, 2013

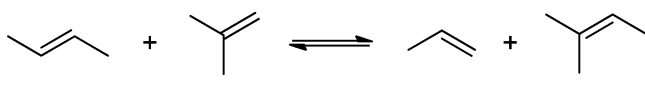
Revised: August 6, 2013

Published: August 7, 2013

metathesis pathways based on the direct utilization of mixed C4 olefin streams to propene is very attractive, both in industrial and academic contexts.³¹ C4 olefin streams are usually obtained as byproducts from steam cracker and FCC units. Among the butene isomers, isobutene is a useful starting material to produce gasoline additives, polymeric materials, and fine chemicals.^{32,33} However, because of its high reactivity, isobutene is also the most troublesome of the butene isomers for inclusion in a mixed butenes feed to a metathesis catalyst.³⁴

Aside from the cross-metathesis and linear butenes to propylene processes discussed above, another more or less forgotten pathway for propylene production is the cross metathesis of 2-butenes and isobutene (Scheme 1).^{35,36} Further

Scheme 1. Isobutene/*trans*-2-butene Cross-Metathesis



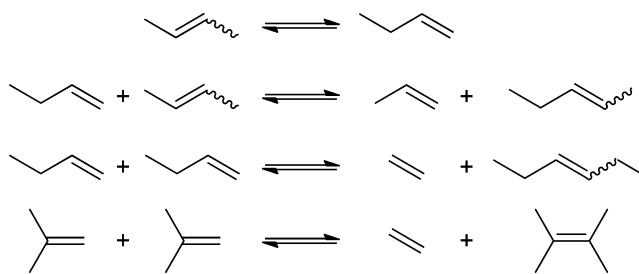
developing this process could thereby benefit the utilization of C4 olefin streams directly without further separation, and provide an alternative route for isobutene utilization. In fact, this cross metathesis reaction also leads to isopentene, an important intermediate for the production of *tert*-amyl methyl ether (TAME).³⁷ This provides an alternative route to produce isopentene and isoprene which are usually obtained in low yield from the C5 fractions of the effluent of steam or catalytic cracking units.³⁸ Thus, it would be of great impact to develop an efficient metathesis process with high selectivities to propylene and isopentene from C4 olefins.

Recently, Zhang et al. reported³⁷ a series of catalysts based on Mo supported on acidic mordenite or alumina in the metathesis reaction using mixed linear and branched butenes as feed at 250 °C and 1 bar. The Mo supported acidic catalysts (mordenite) exhibit low selectivity for metathesis products instead yielding C6+ hydrocarbons as the major products; these arise from oligomerization and alkylation reactions catalyzed by the acidic sites. These secondary reactions decrease when alumina was the sole support, though selectivity to propylene was still moderate.³⁷ Moreover, traditional heterogeneous catalysts suffer from fast deactivation processes or low turnover frequency in the presence of isobutene.^{35–37}

The cross metathesis between isobutene and 2-butenes can hypothetically generate several byproducts because of self-metathesis of C4 olefins in addition to the desired propylene and isoamylene: (a) 2-butenes isomerization to 1-butene; (b) 1-butene and 2-butenes cross-metathesis to form propylene and 2-pentenenes; (c) 1-butene self-metathesis to form ethylene and 3-hexenes; (d) isobutene self-metathesis to ethylene and 2,3-dimethylbutene (Scheme 2). The presence of competitive side reactions can be explained by isomerization on metal hydride and by thermodynamic and mechanistic considerations of the metallacyclobutane intermediates.

In general, supported transition metal oxide catalysts have drawbacks such as unknown activation processes, significant deactivation (metal reduction, coking), broad product distribution, or require severe reaction conditions (temperature and pressure). In an attempt to overcome the disadvantages of the classical olefin metathesis catalysts and to gain better molecular control over the catalyst active site to improve the selectivity and the productivity in propylene, we prepared the $\text{WH}_3/\text{Al}_2\text{O}_{3-(500)}$ catalyst via the Surface Organometallic Chemistry (SOMC) method.³⁹ Herein, we study the cross-

Scheme 2. Side Reactions in Isobutene and 2-Butenes Cross Metathesis



metathesis between isobutene and 2-butenes over $\text{WH}_3/\text{Al}_2\text{O}_{3-(500)}$ to produce propylene and isopentene at low temperature and pressure. Furthermore, the observed activity and selectivity have been compared to other processes to produce propylene from ethylene or linear butene feeds on the same catalyst.

2. MATERIALS AND METHODS

2.1. Catalyst Preparation. The catalyst ($\text{WH}_3/\text{Al}_2\text{O}_{3-(500)}$) was prepared according to a published procedure reported elsewhere.⁴⁰ The preparation consisted of two steps. The first step involved grafting $\text{W}(\equiv\text{CC}(\text{CH}_3)_3)(\text{CH}_2\text{C}(\text{CH}_3)_3)_3$ on γ -alumina at 66 °C under argon to obtain a well-defined $(\equiv\text{Al}-\text{O})\text{W}(\equiv\text{CC}(\text{CH}_3)_3)(\text{CH}_2\text{C}(\text{CH}_3)_3)_2$ fragment on the alumina surface. The γ -alumina (Johnson Matthey, 200 $\text{m}^2\cdot\text{g}^{-1}$) was dehydroxylated at 500 °C prior to the grafting reaction. Excess of the molecular complex was washed off with dry pentane, and the solid was dried under high vacuum. The second step comprised a treatment of the latter solid under H_2 at 150 °C. The catalyst was then stored at -25 °C in the glovebox. Spectroscopic characterizations of the catalyst are consistent with that obtained previously (elemental analysis: 5.5 wt % W).⁴⁰

2.2. Catalyst Evaluation. Evaluation of the catalytic performance of *trans*-2-butene and isobutene cross-metathesis was carried out in a stainless steel continuous flow microactivity reactor purchased from PID Eng&Tech ($P_{\text{C}_4\text{H}_8} = 1$ bar, $T = 150$ °C, total flow rate = 10 $\text{mL}\cdot\text{min}^{-1}$ or $\text{VHSV} = 900$ h^{-1}). *Trans*-2-butene (Scott, 99%) was purified with a column of molecular sieve and activated $\text{Cu}_2\text{O}/\text{Al}_2\text{O}_3$. Isobutene (Scott, 99%) was used as received. The catalyst was charged in a glovebox. A 4-way valve allowed isolation of the charged catalyst in the reactor from the environment and extensive purging of the tubes exposed to air. The products were determined by an online Varian CP 3800 gas chromatograph equipped with $\text{KCl}/\text{Al}_2\text{O}_3$ and HPS columns having their own FID.

3. RESULTS AND DISCUSSION

We previously reported that 1-butene/2-butenes cross metathesis reaction over $\text{WH}_3/\text{Al}_2\text{O}_{3-(500)}$ gives high selectivity to propylene and *n*-pentenes with very low side reaction products.²⁴ As we have reported previously, traditional WO_3/SiO_2 catalysts do not show activity under the same conditions.¹⁶ We have therefore continued these studies on the valorization of C₄ olefins to propylene by studying the cross-metathesis between isobutene and *trans*-2-butene.

To begin our investigation, we used reaction conditions of 150 °C at 1 bar and 1:1 ratio isobutene/*trans*-2-butene. At 150 °C, the reaction undergoes a maximal conversion rate of 1.8 $\text{mol}_{\text{C}_4}\cdot\text{mol}_{\text{W}}^{-1}\cdot\text{min}^{-1}$ at the start of reaction (1 h). This

conversion decreases linearly at $0.5\% \cdot \text{h}^{-1}$ to reach $0.8 \text{ mol}_{\text{C}_4} \cdot \text{mol}_{\text{W}}^{-1} \cdot \text{min}^{-1}$ after 57 h with an overall turnover number (TON) of 1000 (Figure 1). At steady state, the products contain mainly branched pentenes, 48.2%, followed by propylene, 44.3%, hexenes, 4.3%, and ethylene, 3.2% (Figure 2).

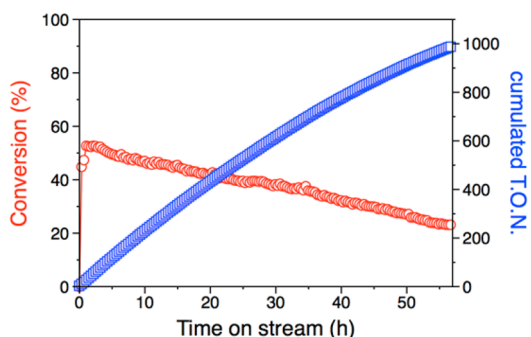


Figure 1. Total carbon conversion (○) and cumulative TON (□) vs time on stream for isobutene/*trans*-2-butene cross metathesis on WH/ $\text{Al}_2\text{O}_3(500)$ at 150°C .

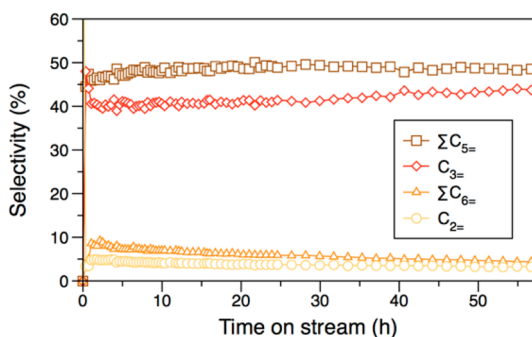
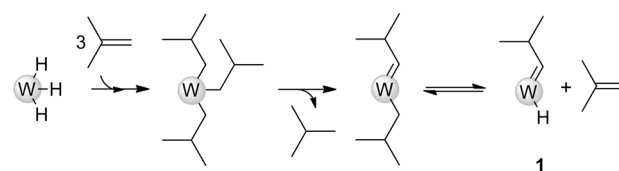


Figure 2. Selectivity vs time on stream for isobutene/*trans*-2-butene cross metathesis on WH/ $\text{Al}_2\text{O}_3(500)$ at 150°C .

To understand how these product selectivities come about, the initiation and propagation steps of this reaction were elucidated by identifying the products formed while heating to the reaction conditions. It is reasonable to postulate that the initiation of the catalytic process occurs with a similar mechanism to that previously described for the direct conversion of ethylene to propylene.³⁰ At the beginning of the reaction, we observe primarily isobutane (0.9 equiv per W) released along with traces of *n*-butane. It can be assumed that three isobutene molecules insert into the tungsten trishydrides precursor, affording a tungsten tris(isobutyl) species, $[\text{W}] \cdot [(\text{CH}_2\text{CH}(\text{CH}_3)_2)_3]$. This selectivity can be explained by rapid isobutene insertion in the W–H bond, which is energetically more favorable rather than insertion of sterically hindered disubstituted olefins (2-butenes),^{42,43} as described by the Cosse–Arlman mechanism.^{44,45} Isobutane formation is due to an α -H abstraction mechanism giving a tungsten isobutyl-isobutylidene species, $[\text{W}](=\text{CHCH}(\text{CH}_3)_2)(\text{CH}_2\text{CH}(\text{CH}_3)_2)$, in equilibrium with a tungsten isobutylidene hydride species, $[\text{W}](=\text{CHCH}(\text{CH}_3)_2\text{H})$, generated after β -H abstraction of the tungsten isobutyl fragment (Scheme 3).

During propagation, the thus formed tungsten carbene hydride **1** may react with different butenes present in the gas phase to start the catalytic cycle. In addition to the *trans*-2-butene and isobutene in the feed, 1-butene and *cis*-2-butene

Scheme 3. Formation of Tungsten Carbene Hydride by Isobutene Insertion

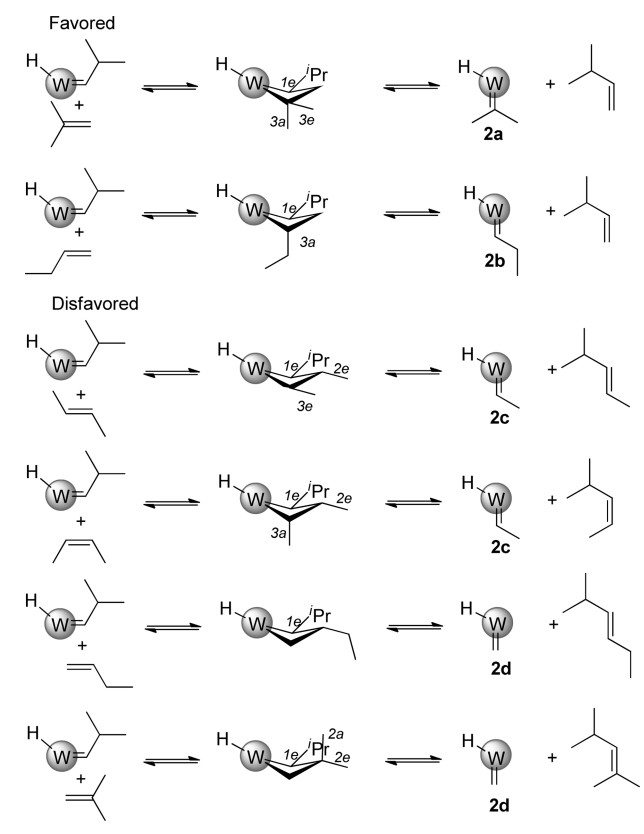


isomers begin to appear in the gas phase at early times on stream. At low conversion (extrapolated to 0%), the initial 1-butene/*trans*-2-butene/*cis*-2-butene/isobutene isomeric distribution is 0:50:0:50 and changed over time, trending to the ratio 3.7:23:12.1:61.2 after 100 min at 53% conversion (Supporting Information, Figure S1). A blank experiment with $\text{Al}_2\text{O}_3(500)$ over equimolar isobutene/*trans*-2-butene under the same condition shows only the *trans*/*cis* isomerization reaction is taking place (Supporting Information, Figure S2) in thermodynamic ratio (*trans*/*cis* = 2.0). Thus, formation of 1-butene, as observed previously from *trans*-2-butene,²³ can be explained by an isomerization process on the W–H moiety after insertion of *trans*-2-butene, giving a tungsten *sec*-butyl species, which affords 1-butene after β -H elimination from the primary carbon (Supporting Information, Scheme S1). Meanwhile, *cis*-2-butene can be formed by either insertion on W–H or protonation by acidic alumina followed by β -H elimination from the secondary carbon. It should be noted that the ratio of linear butenes observed here is different than that observed from *trans*-2-butene only feed at the same conditions, with higher ratios here of 1-butene and *cis*-2-butene to *trans*-2-butene, so the presence of the partial pressure of the isobutene may affect the isomerization reaction rate. In the systems we have previously studied, 1-butene to propylene,²⁴ *trans*-2-butene to propylene,²³ cross-metathesis of butene and ethylene,¹⁶ and isobutene self-metathesis,³³ we have never observed isomerization of linear butenes to isobutene or vice versa, so it is reasonable to assume iso- and normal butenes do not interconvert here. Therefore, we conclude that the greater than 50% isobutene content in the product is due to the reactivity difference between it and the linear butenes, an unsurprising thought given our discussion of metallacyclobutanes below.

Among the different initial products (Figure 2 and Supporting Information, Figure S3), only pentenes and minor amounts of hexenes are clearly observed. According to the Chauvin mechanism, the expected isoamylene (3-methyl-1-butene) can be generated when **1** reacts with isobutene or 1-butene, giving **2a** (tungsten isopropylidene) or **2b** (tungsten propylidene), respectively. The formation of **2b** is anticipated to be limited because of the low 1-butene concentration. Rather than solely 3-methyl-1-butene, an equilibrium distribution of branched pentene isomers is observed,⁴⁶ indicating a fast double bond isomerization reaction occurring either on W–H or on the acidic alumina sites.²⁴ During this first metathesis step, (*cis*/*trans*)-4-methyl-2-pentenenes are also expected from coordination of (*cis*/*trans*)-2-butenes to **1**, leading to the tungsten ethylidene **2c**. As in the case of the isoamylenes, the released branched hexenes undergo fast isomerization to the thermodynamically favored 2-methyl-2-pentene with low amounts of 2-methyl-1-pentene and 4-methyl-2-pentenenes. The ratio of branched C5 (2-methyl-butenes)/C6 (2-methyl-pentenenes) obtained during the initial metathesis step is 12 and reflects the relative stability of the possible tungstacyclo-

butane intermediates, with more stable tungstacyclobutanes made by avoiding 1,2-substituents and minimizing 1,3 interactions (Scheme 4). The hypothesis regarding the

Scheme 4. Interaction of Carbene 1 with Butene Reactants

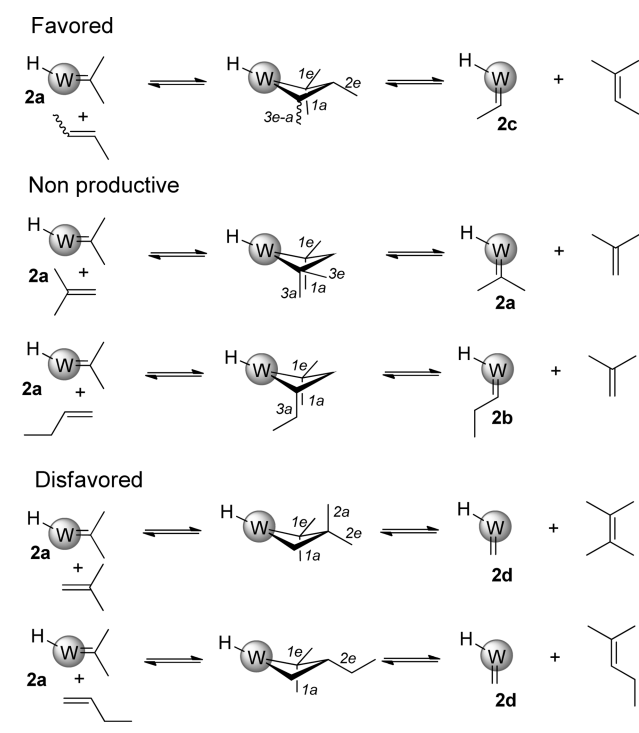


presence of two substituents in (1e,2e) positions in the metallacyclobutane was first formulated in the early studies on the stereoselectivity of olefin metathesis with W based catalyst.⁴⁷ At that time, it was concluded that a (1e,2e) disubstituted metallacyclobutane was unfavored over a 1e,3e disubstituted metallacyclobutane. Leconte and Basset showed that monosubstituted metallacyclobutanes were the most favored, and that (1e,2e) and (1e,3e) substitution was always favored over the disubstituted (1e,1a) or (2e,2a) or (3e,3a). The tetra substituted metallacyclobutane was the least favored. These products arise from the initial steps, which is clearly a cross-metathesis reaction. We note that branched heptenes, which could be obtained hypothetically by coordination of 1-butene or isobutene to 1 through sterically disfavored 1,2-substituted tungstacyclobutanes thereby generating the tungsten methylidene species 2d, are not observed.

After the initial metathesis steps, the products contain mainly branched pentenes, 48.2%, followed by propylene, 44.3%, hexenes, 4.3%, and ethylene 3.2% (Figure 2). Surprisingly, 2,3-dimethylbutene arising from isobutene self-metathesis is not observed. This could be explained by required formation of a thermodynamically disfavored metallacyclobutane intermediate with gem-dimethyl substituents in both the 1 and 2 positions (Scheme 5), an explanation which is consistent with the low initial rate observed in the isobutene self-metathesis over tungsten hydride on alumina ($0.6 \text{ mol}_{\text{C}_4\text{H}_8} \cdot \text{mol}_{\text{W}}^{-1} \cdot \text{min}^{-1}$).^{33,48}

The stability of the various metallacyclobutane intermediates thus can help to determine the product selectivity in this

Scheme 5. Interaction of Carbene 2a with Butene Reactants



system. As shown in Figure 2, the major products of *trans*-2-butene/isobutene cross-metathesis are propylene and pentenes. Among the pentene isomers, the branched pentenes (2-methylbutenes) constitute 90% in relative selectivity (Figure 3).

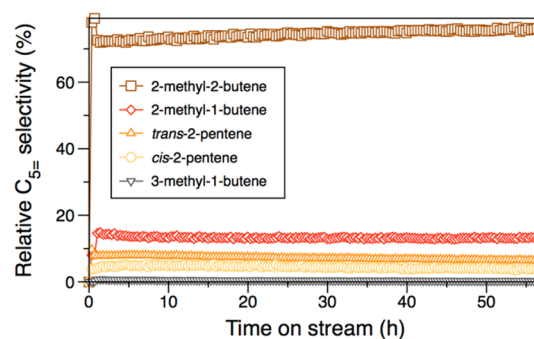


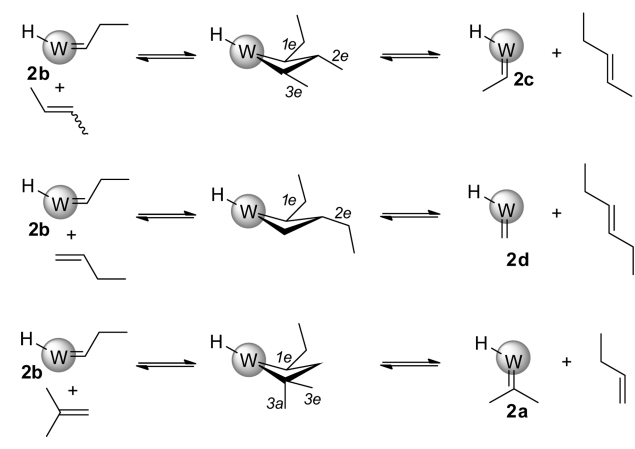
Figure 3. Relative selectivity of C5 alkenes.

Scheme 5 summarizes the possible reaction pathways between the likely entry point into the catalytic cycle, isopropylidene 2a, and the reactants. Considering productive metathesis, the most favorable pathway is with 2-butenes as reactant, thereby producing the dominant product, 2-methyl-2-butene and ethylidene 2c. By way of double bond isomerization, methyl-2-butene can give the other isopentene isomers observed in thermodynamic equilibrium. For the interaction of isobutene with isopropylidene 2a, a productive path leading to 2,3-dimethylbutene (not observed as discussed above) or a degenerate path giving isobutene and the starting isopropylidene 2a could occur. The interaction of isopropylidene 2a with 1-butene can yield a metallacyclobutane with ethyl substituent at the 2 position (disfavored axial position not shown) and thereby yield 2-methyl-2-pentene and methylidene 2d or a nonproductive pathway leading back to isobutene and the propylidene 2b. The detected branched hexene isomers

comprise 33% of the total hexenes and are 2-methyl-2-pentene (28.2%) and 2-methyl-1-pentene (5.5%) which likely comes from isomerization of the 2-methyl-2-pentene (Supporting Information, Figure S4). The observed ratio between the branched hexenes is close to the thermodynamic equilibrium. Given the product selectivities observed, the described path with 2-butene to yield 2-methyl-2-butene or the degenerate path with isobutene is likely the dominant pathway from the isopropylidene **2a**.

We now turn to propylidene **2b**, which can be formed in low concentration from **2a** and 1-butene. Notably, linear C5 olefins are detected at all times in low quantities, indicating the presence of secondary reactions. The major byproducts are 2-pentenes (11.5% in relative selectivity, Figure 3) in a *trans/cis* ratio close to the thermodynamic equilibrium (1.5). Similar observation has also been reported.²⁴ 2-Pentenes can be formed from carbene hydride **2b** following coordination of 2-butenes thereby leaving ethylidene **2c** behind (Scheme 6 and Supporting Information, Scheme S2). The low selectivity to linear pentenes is also reflected by the low concentration of **2b** and 1-butene (Supporting Information, Figure S1a).

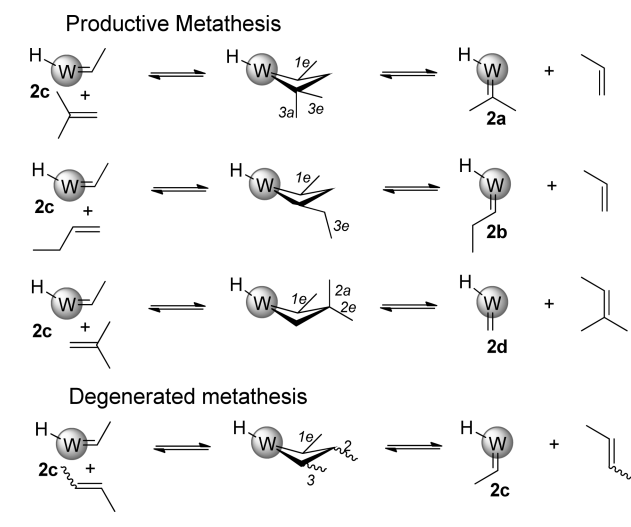
Scheme 6. Interaction of Propylidene **2b** with Butene Reactants



Other observed products in low quantities are equimolar amounts of ethylene and hexenes (linear and branched), of which 3-hexenes (*trans/cis* ratio is 5) constitute 66.3% in relative selectivity at all times (Supporting Information, Figure S4). Like the linear pentenes, 3-hexenes can be formed from propylidene **2b**, in this case by reaction with 1-butene also yielding methylidene **2d** (Scheme 6). The *trans* selectivity observed is likely due to the steric repulsions in the metallacyclobutane intermediate when one of the ethyl groups is in the axial position as required to make *cis*-3-hexene (Supporting Information, Scheme S3). Alternatively, propylidene **2b** can react with isobutene nonproductively via a trisubstituted metallacyclobutane to yield 1-butene and ethylidene **2c** (Scheme 6). While the concentration of propylidene **2b** is likely to be low, it is clear that many of the byproducts in the reaction come from this intermediate.

As the ethylidene **2c** is the most likely to be generated from **2a**, we now describe the possible products starting from **2c** and the reactants in Scheme 7. Two feasible pathways for productive metathesis via interaction with isobutene are either the production of propylene and isopropylidene **2a** via a head to tail coordination, or the formation of 2-methyl-2-butene and

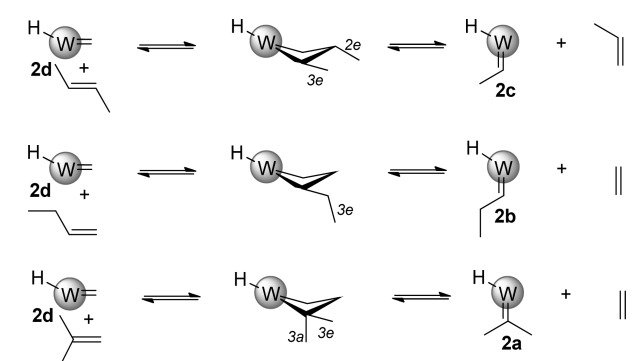
Scheme 7. Interaction of Ethylidene **2c** with Butene Reactants



methylidene **2d** via a head to head arrangement. Alternatively, propylene can also be formed, as reported previously,²⁴ from the interaction of **2c** with 1-butene, thereby again yielding propylidene **2b**.

Also shown in Scheme 7 is the nonproductive, often degenerate, metathesis pathway resulting from 2-butenes coordination. In addition to the metal hydride catalyzed isomerization described earlier, this pathway is an alternative method of *cis/trans* isomerization of the *trans*-2-butene feed. The *trans/cis* 2-butene ratio increases with time (Supporting Information, Figure S1). At the beginning where the conversion is high, this ratio (1.94) is close to the thermodynamic value (2.0) at 150 °C.⁴⁶ The *trans/cis*-2-butene ratio (Supporting Information, Figure S1b) can provide information about the deactivation process. With the catalytic evolution, this ratio increases to 4.9 after 3000 min. The decrease of *cis*-2-butene production may come from deactivation of acidic alumina sites (as observed in the blank test described in Supporting Information, Figure S2) or from gradual decrease in tungsten hydride concentration by favored insertion of isobutene in the W–H bond. Moreover, it is known in the literature that olefin metathesis catalysts undergo a decrease of rate in *trans/cis* isomerization with time by degenerate olefin metathesis (Scheme 7). This latter process generates a disfavored 1,2,3-trisubstituted metallacyclobutane, but *cis*–*trans* selectivity effects can be subtle.⁴⁹

Once methylidene **2d** has been formed, whether from the disfavored pathways coming from isopropylidene **2a**, the interaction of 1-butene with propylidene **2b** as described above or the interaction of isobutene and the ethylidene **2c** as just described, the most likely result is interaction with *trans*-2-butene to yield the second most prevalent product, propylene, and ethylidene **2c** as shown in Scheme 8. This reaction proceeds with high productivity and selectivity as is well-known for the cross-metathesis of ethylene and 2-butenes.¹⁶ Reaction of methylidene **2d** with 1-butene or isobutene can yield, via productive pathways, ethylene and propylidene **2b** or isopropylidene **2a**, respectively. The metallacyclobutanes for these two intermediates are disfavored versus that for 2-butenes interaction because of the ethyl substituent from 1-butene reaction or the gem-dimethyl substituent from isobutene, so

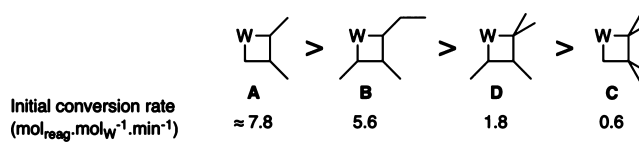
Scheme 8. Interaction of Methylidene **2d** with Butene Reactants

while ethylene is produced from methylidene **2d**, it is a minor product with selectivity less than 5%.

On the basis of these results, two parallel catalytic cycles for isobutene/2-butenes cross metathesis to produce propylene and isopentenes (Scheme 9) can be proposed. The right cycle is most likely favored since the tungstacyclobutane intermediates are less sterically hindered and have minimized interactions between the substituents. However, current data are unable to discriminate the thermodynamic and kinetics between these cycles. Interestingly, 1-butene, whose presence in the linear butenes to propylene systems, previously studied, is necessary to achieve the high propylene yields observed, is somewhat detrimental to the propylene/isopentene yield in this system. Reaction of 1-butene, as discussed, with **2a**, **2c**, or **2d** leads to propylidene **2b** from where linear pentene and hexene byproducts are the most likely outcomes. Ongoing theoretical calculations of the relative energies of the different tungstacyclobutane intermediates may help suggest the most favored pathway.

Based on current and previous reported studies for the production of propylene using alternative feeds including ethylene/2-butenes, 1-butene/2-butenes, isobutene/2-butenes cross-metathesis and isobutene self-metathesis over the multifunctional alumina supported tungsten hydride catalyst, a clear tendency is observed between the initial rates and the crowdedness of the tungstacyclobutane intermediates. It is apparent that the number of substituents on the intermediate metallacyclobutane governs the conversion rate of metathesis reaction (Scheme 10). The different reactions can thus be classified from higher to lower activity: (i) ethylene/*trans*-2-

Scheme 10. Influence of the Substituent of the Metallacyclobutane on the Conversion Rate of Metathesis Reactions



butene cross-metathesis where **A** is the more thermodynamically favored intermediate, (ii) 1-butene/*trans*-2-butene cross-metathesis (**B**), (iii) isobutene/*trans*-2-butene cross-metathesis (**D**), and (iv) isobutene self-metathesis (**C**).

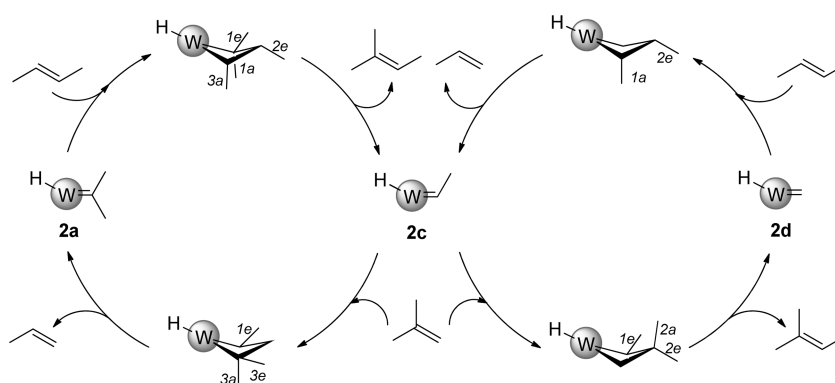
4. CONCLUSION

Valuable products, propylene and isopentene, can be obtained selectively by cross metathesis between isobutene and 2-*trans*-butene catalyzed by $\text{WH}_3/\text{Al}_2\text{O}_3$ prepared by the SOMC method. In contrast to the classical system, the present catalyst yields exceptional productivity of propylene and isopentene at low temperature and pressure. The mechanism of this reaction has been proposed. From the two parallel catalytic cycles for this reaction, the cycle involving the less sterically hindered tungstacyclobutane intermediates is most likely favored. Moreover, it has been found that the arrangement of the substituent of the less thermodynamically favored metallacyclobutane governs the conversion rate of the cross metathesis reaction for propylene production from butenes and/or ethylene. It explains the high activity of ethylene/2-butenes cross metathesis which still remains a dominant process for on-purpose propylene production. However, isobutene/2-butenes cross-metathesis remains an economically important process which produces the valuable isopentene and utilizes a more abundant feedstock (branched and linear butenes).

■ ASSOCIATED CONTENT

Supporting Information

Additional curves displaying selectivities and the blank experiment, as well as supplementary schemes describing formation of the minor products (linear pentenes and hexenes). This material is available free of charge via the Internet at <http://pubs.acs.org>.

Scheme 9. Mechanisms Proposed for the Production of 2-Methyl-2-butene and Propylene from Isobutene/*Trans*-2-butene Cross-Metathesis

AUTHOR INFORMATION

Corresponding Author

*E-mail: jeanmarie.basset@kaust.edu.sa (J.-M.B.), Christopher.Nicholas@uop.com (C.P.N.), Mostafa.Taoufik@univ-lyon1.fr (M.T.). Fax: (+1) 8473911287 (C.P.N.), (+33) 472431795 (M.T.).

Present Address

§(J.-M.B.) KCC, 4700 King Abdullah University of Science and Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

UOP is acknowledged for generous financial support.

REFERENCES

- (1) Plotkin, J. S. *Catal. Today* **2005**, *106*, 10–14.
- (2) Tullo, A. H. *Chem. Eng. News* **2003**, *81*, 15–16.
- (3) Tullo, A. H.; Johnson, J. *Chem. Eng. News* **2013**, *91*, 9–13.
- (4) Chauvel, A.; Lefevre, G. Sources of Olefinic and Aromatic Hydrocarbons. In *Petrochemical Processes, Synthesis Gas Derivatives and Major Hydrocarbons*; Institut Francais du Petrole: Paris, France, 1985; Vol. 1.
- (5) Cavani, F.; Ballarini, N.; Cericola, A. *Catal. Today* **2007**, *127*, 113–131.
- (6) Fukudome, K.; Ikenaga, N.-o.; Miyake, T.; Suzuki, T. *Catal. Sci. Technol.* **2011**, *1*, 987–998.
- (7) Vora, B. V. *Top. Catal.* **2012**, *55*, 1297–1308.
- (8) Liu, H.; Huang, S.; Zhang, L.; Liu, S.; Xin, W.; Xu, L. *Catal. Commun.* **2009**, *10*, 544–548.
- (9) Liu, S.; Li, X.; Xin, W.; Xie, S.; Zeng, P.; Zhang, L.; Xu, L. *J. Nat. Gas Chem.* **2010**, *19*, 482–486.
- (10) Mol, J. C. *J. Mol. Catal. A* **2004**, *213*, 39–45.
- (11) Zhao, Q.; Chen, S.-L.; Gao, J.; Xu, C. *Trans. Met. Chem.* **2009**, *34*, 621–627.
- (12) McCann, D. M.; Lesthaeghe, D.; Kletnieks, P. W.; Guenther, D. R.; Hayman, M. J.; Van Speybroeck, V.; Waroquier, M.; Haw, J. F. *Angew. Chem., Int. Ed.* **2008**, *47*, 5179–5182.
- (13) Svelle, S.; Olsbye, U.; Joensen, F.; Bjørgen, M. *J. Phys. Chem. C* **2007**, *111*, 17981–17984.
- (14) Ilias, S.; Bhan, A. *ACS Catal.* **2013**, *3*, 18–31.
- (15) Huang, S.; Chen, F.; Liu, S.; Zhu, Q.; Zhu, X.; Xin, W.; Feng, Z.; Li, C.; Wang, Q.; Xu, L. *J. Mol. Catal. A* **2007**, *267*, 224–233.
- (16) Mazoyer, E.; Szeto, K. C.; Merle, N.; Norsic, S.; Boyron, O.; Basset, J.-M.; Taoufik, M.; Nicholas, C. P. *J. Catal.* **2013**, *301*, 1–7.
- (17) Debecker, D. P.; Stoyanova, M.; Colbeau-Justin, F.; Rodemerck, U.; Boissiere, C.; Gaigneaux, E. M.; Sanchez, C. *Angew. Chem., Int. Ed.* **2012**, *51*, 2129–2131.
- (18) Harmse, L.; van Schalkwyk, C.; van Steen, E. *Catal. Lett.* **2010**, *137*, 123–131.
- (19) Hu, J.-C.; Wang, Y.-D.; Chen, L.-F.; Richards, R.; Yang, W.-M.; Liu, Z.-C.; Xu, W. *Microporous Mesoporous Mater.* **2006**, *93*, 158–163.
- (20) Hua, D.; Chen, S.-L.; Yuan, G.; Wang, Y.; Zhao, Q.; Wang, X.; Fu, B. *Microporous Mesoporous Mater.* **2011**, *143*, 320–325.
- (21) Huang, S.; Liu, H.; Zhang, L.; Liu, S.; Xin, W.; Li, X.; Xie, S.; Xu, L. *Appl. Catal., A* **2011**, *404*, 113–119.
- (22) Li, X.; Zhang, W.; Liu, S.; Xu, L.; Han, X.; Bao, X. *J. Catal.* **2007**, *250*, 55–66.
- (23) Mazoyer, E.; Szeto, K. C.; Basset, J.-M.; Nicholas, C. P.; Taoufik, M. *Chem. Commun.* **2012**, *48*, 3611–3613.
- (24) Mazoyer, E.; Szeto, K. C.; Norsic, S.; Garron, A.; Basset, J.-M.; Nicholas, C. P.; Taoufik, M. *ACS Catal.* **2011**, *1*, 1643–1646.
- (25) Liu, H.; Zhang, L.; Li, X.; Huang, S.; Liu, S.; Xin, W.; Xie, S.; Xu, L. *J. Nat. Gas Chem.* **2009**, *18*, 331–336.
- (26) Basset, J. M.; Thivolle-Cazat, J.; Taoufik, M.; Le Roux, E.; Coperet, C. Patent FR 2872509, 2006.
- (27) Coperet, C.; Basset, J. M.; Thivolle-Cazat, J.; Le Roux, E.; Taoufik, M. Patent WO 2006013251, 2006.
- (28) Nicholas, C. P.; Mazoyer, E.; Taoufik, M.; Basset, J. M.; Barger, P. T. Patent US 20110245569, 2011.
- (29) Nicholas, C. P.; Mazoyer, E.; Taoufik, M.; Basset, J. M.; Barger, P. T.; Rekoske, J. E. Patent US 20110245570, 2011.
- (30) Taoufik, M.; Le Roux, E.; Thivolle-Cazat, J.; Basset, J.-M. *Angew. Chem., Int. Ed.* **2007**, *46*, 7202–7205.
- (31) Sigl, M.; Schubert, M.; Stephan, J.; Poplow, F. Patent WO/2006/089956, 2006.
- (32) Yoon, J. W.; Jhung, S. H.; Kim, T.-J.; Lee, H.-D.; Jang, N. H.; Chang, J.-S. *Bull. Korean Chem. Soc.* **2007**, *28*, 2075–2078.
- (33) Garron, A.; Stoffelbach, F.; Merle, N.; Szeto, K. C.; Thivolle-Cazat, J.; Basset, J.-M.; Norsic, S.; Taoufik, M. *Catal. Sci. Technol.* **2012**, *2*, 2453–2455.
- (34) Nakamura, R.; Iida, H.; Echigoya, E. *Chem. Lett.* **1972**, 273–275.
- (35) Banks, R. L. Olefin metathesis: technology and application. In *Applied Industrial Catalysis*; Leach, B. E., Ed.; Academic Press: New York, 1984; p 215.
- (36) Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 5074–5075.
- (37) Zhang, D.; Li, X.; Liu, S.; Huang, S.; Zhu, X.; Chen, F.; Xie, S.; Xu, L. *Appl. Catal., A* **2012**, *439*, 171–178.
- (38) Frey, S. J.; Liu, D. W.; Luebke, C. P.; Marker, T. L. Patent US5491267, 1996.
- (39) Merle, N.; Trebosc, J.; Baudouin, A.; Del Rosal, I.; Maron, L.; Szeto, K.; Genelot, M.; Mortreux, A.; Taoufik, M.; Delevoye, L.; Gauvin, R. M. *J. Am. Chem. Soc.* **2012**, *134*, 9263–9275.
- (40) Le Roux, E.; Taoufik, M.; Coperet, C.; de Mallmann, A.; Thivolle-Cazat, J.; Basset, J. M.; Maunders, B. M.; Sunley, G. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6755–6758.
- (41) Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774–6776.
- (42) Li, X.; Guan, J.; Zheng, A.; Zhou, D.; Han, X.; Zhang, W.; Bao, X. *J. Mol. Catal. A* **2010**, *330*, 99–106.
- (43) Malani, H.; Hayashi, S.; Zhong, H.; Sahnoun, R.; Tsuboi, H.; Koyama, M.; Hatakeyama, N.; Endou, A.; Takaba, H.; Kubo, M.; Del Carpio, C. A.; Miyamoto, A. *Appl. Surf. Sci.* **2008**, *254*, 7608–7611.
- (44) Cossee, P. *J. Catal.* **1964**, *3*, 80–88.
- (45) Herisson, J. L.; Chauvin, Y. *Makromol. Chem.* **1971**, *141*, 161–176.
- (46) Alberty, R. A.; Gehrig, C. A. *J. Phys. Chem. Ref. Data* **1985**, *14*, 803–820.
- (47) Leconte, M.; Basset, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7296–7302.
- (48) Merle, N.; Stoffelbach, F.; Taoufik, M.; Le Roux, E.; Thivolle-Cazat, J.; Basset, J.-M. *Chem. Commun.* **2009**, 2523–2525.
- (49) Bahri-Laleh, N.; Credendino, R.; Cavallo, L. *Beilstein J. Org. Chem.* **2011**, *7*, 40–45.