

Alkene Cross-Metathesis with 2,5-Dimethyl-2,4-Hexadiene Enables Isobutylenyl/Prenyl Functionalizations and Rubber Valorization

Paloma Mingueza-Verdejo⁺,^[a] Silvia Rodríguez-Nuévalos⁺,^[a] Judit Oliver-Meseguer,^[a] and Antonio Leyva-Pérez^{*[a]}

2,5-Dimethyl-2,4-hexadiene is a readily available and easily manageable compound, whose symmetric and polymethylated dienic structure should be prone to engage in cross-metathesis reactions with other alkenes, but this has not been apparently exploited so far. Here we show that this reactant enables the easy synthesis of tri- and tetra-substituted alkenes (i.e. isobutylenyl and prenyl groups) from simple alkenes under mild reaction conditions, not only with the conventional 2nd generation Grubbs catalyst but also with other Grela-type

catalysts such as StickyCat,TM AquaMetTM and GreenCatTM. The use of liquid and low volatile 2,5-dimethyl-2,4-hexadiene avoids the use of gaseous alkene reactants and, besides, showcases the reactivity of polyisoprene (rubber), thus allowing to optimize the reaction conditions for rubber upcycling, after metathesis reaction of the pristine or used polymer with simple alkenes. These results bring low volatile isoprene-type compounds as privileged poly-substituted reactants for alkene cross-metathesis reactions.

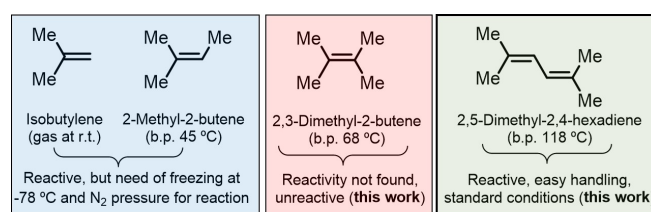
Introduction

The alkene cross-metathesis reaction has become an indispensable tool in modern organic synthesis, with application in complex product and polymer synthesis, to name a few.^[1–3] The resulting alkenes find applications, for instance, as lubricants, plasticizers, cosmetics or insecticides,^[4–9] and industry relies more and more in the cross-metathesis reactions for chemical production.^[10,11] However, the synthesis of well-defined tertiary and quaternary alkenes is still undeveloped respect to secondary ones, which is particularly worrying considering that some of the most abundant functional groups in natural products are isobutylenyl and prenyl alkenes.^[12–17] Therefore, cross-metathesis reactions aimed at synthesizing these alkenes are of interest, in order to constitute an alternative to current synthetic protocols based not only in catalyzed couplings such as Pd-,^[12,18–21] Ir-,^[22] or Rh-catalyzed reactions,^[23] but also in classical acid-catalyzed,^[24–26] base-promoted,^[27] organocatalyzed^[28] and enzyme-catalyzed^[29] reactions, furthermore considering that the very same isobutylenyl and prenyl

groups can be further transformed to highly value functional groups through cross-metathesis reaction methodologies.^[30]

The more obvious synthesis of isobutylenyl and prenyl groups by alkene metathesis makes use of the gaseous or highly volatile isobutylene or 2-methyl-2-butene as reaction partners, which has been achieved in the past satisfactorily but requiring particularly safety conditions, as shown in Figure 1 (top left).^[31–33]

An alternative compound for introducing prenyl groups by alkene cross-metathesis reactions without low temperature or pressure regulation requirements would be the highly symmetric alkene 2,3-dimethyl-2-butene (Figure 1, top middle) which, however, it is difficult to find as a reactant in any reported



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Supporting information for this article is available on the WWW under <https://doi.org/10.1002/chem.202400860>

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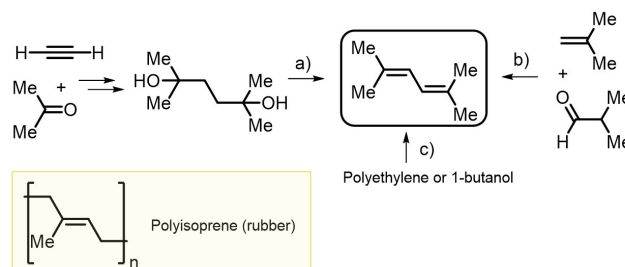


Figure 1. Top: Poly-methylated alkenes for metathesis reactions. Middle: Synthetic methods for 2,5-dimethyl-2,4-hexadiene; a) Dehydration reaction, b) Prins reaction, c) pyrolysis or self-coupling. Bottom: Structure of natural rubber.

metathesis reaction.^[34,35] This can be due to its fully tetrasubstituted alkene structure, which severely hampers the initial formation of the intermediate metal carbene complex.^[36] We will confirm in this work the unreactivity of this alkene under standard alkene metathesis conditions (see ahead).

Another alternative compound for the synthesis of poly-methylated alkene compounds by cross-metathesis reactions could be 2,5-dimethyl-2,4-hexadiene (Figure 1, top right). Although this alkene is unsymmetrical, the diene is not, and it might occur that a selective catalyst is able to couple preferentially one of the alkene parts. This compound is relatively cheap and easily synthesized from readily available compounds, i.e. by coupling of acetylene and acetone, after an hydrogenation and dehydration reaction sequence (Figure 1, middle left, a),^[37,38] by Prins reaction of isobutylene and isobutyraldehyde (middle right, b)^[39–41] and, remarkably, by pyrolysis of polyethylene^[42] or self-coupling of 1-butanol (middle, c),^[43] thus manufacturable by sustainable processes. Beyond that, the alkene is liquid up to 118 °C, giving room to explore different reaction conditions without pressure or temperature limitations. Not in vain, this diene motif has been used in different synthetic programs.^[44–51] However, when searching the associated literature, only one study uses 2,5-dimethyl-2,4-hexadiene as a reactant in metathesis reaction, back in 1984 and with a Re-supported catalyst^[52] (a similar catalyst is used in that report for 2,3-dimethyl-2-butene),^[34] which denotes that it is time to test this convenient reactant in alkene metathesis reactions with modern catalysts.^[53–55]

A last but not least positive characteristic of 2,5-dimethyl-2,4-hexadiene as a coupling partner in alkene metathesis is its structural similarity with polyisoprene (rubber, Figure 1 bottom), which converts this alkene in an ideal model to optimize the reactivity in metathesis reactions of rubber, either in pristine (valorization)^[56] or used form (upcycling).^[57,58]

Results and Discussion

Catalyst Screening and Optimization of the Reaction Conditions

The intermolecular cross-metathesis reaction between 1-dodecene **1a** and 2,5-dimethyl-2,4-hexadiene **2** in dichloromethane (DCM) solvent was chosen as a reaction model to study the reactivity of the latter, since the resulting product **3a** is a prenylated compound. The use of a long linear chain terminal alkene such as **1a** also permits to assess the potential occurrence of a chain-walking alkene isomerization reaction.^[59,60] A catalyst screening is shown in Figure 2, which includes the classical Grubbs-type catalysts and also Grela-type catalysts.^[61] The latter have shown enhanced catalytic activity for some alkene metathesis reactions^[54] and are cheaper than the Grubbs-type catalysts in some cases. The reactions were performed in a closed vial at room temperature, with magnetic stirring overnight, using a five-fold excess of **2** under inert atmosphere, and the reaction was measured by gas chromatography (GC) respect to an external standard (ethylbenzene). Mass

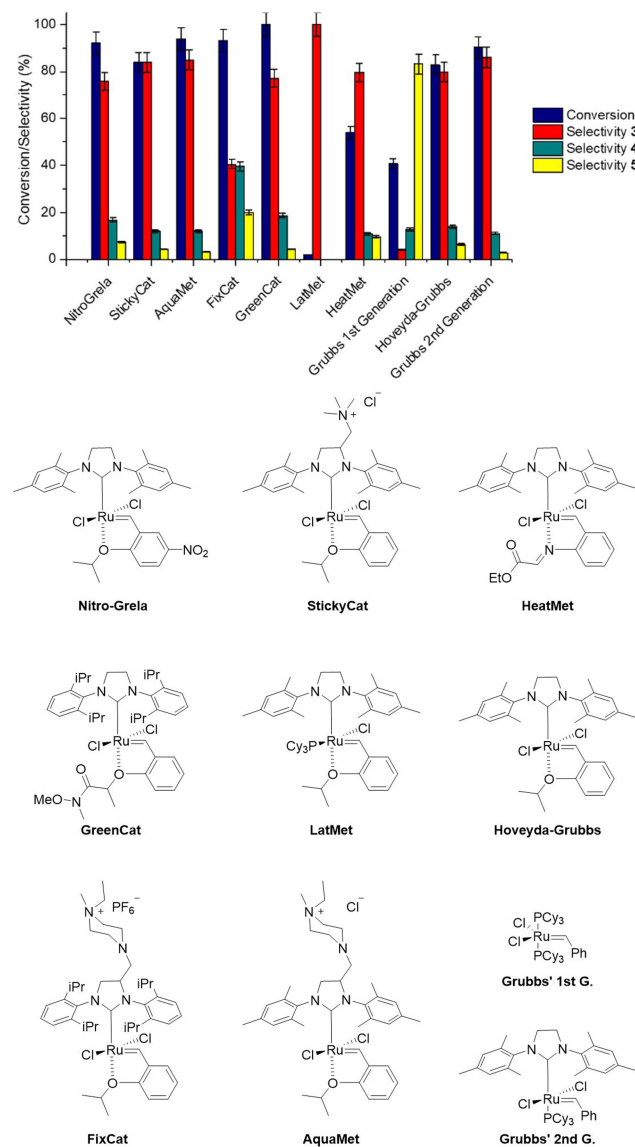
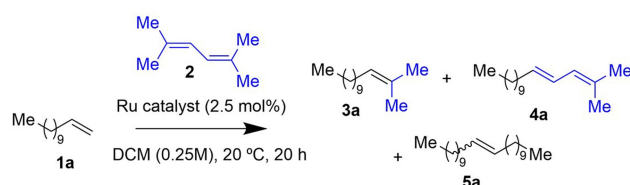


Figure 2. Top: Catalytic results for the alkene metathesis reaction between 1-dodecene **1a** and 2,5-dimethyl-2,4-hexadiene **2** with different Ru catalysts. Reaction conditions: **1a** (0.25 mmol), **2** (1.25 mmol), dichloromethane (DCM, 1 ml), room temperature (20 °C), inert atmosphere (closed vial) and overnight (20 h). GC results. Error bars account for a 5% uncertainty. *E* or *Z* configuration of the alkene product **4a** could not be determined, it will be depicted in *E* form throughout the text for the sake of simplification. Bottom: Structures of the different catalysts employed in this study.

spectrometry coupled to GC (GC-MS) was employed to confirm the structure of the products.

The results show that most of the Grela-type catalysts employed in the study possessing isopropoxyl-coordinating group give high conversions (>90%) of **1a** and a high

selectivity towards the prenylated product **3a** (>80% for StickyCat™ and AquaMet™). The other expected cross-metathesis product **4a** was found systematically in minor amounts. For this reason, it was very difficult to assign the *E* or *Z* configuration of the alkene product **4a**, even after purifying some amounts (the alkene signals in ¹H and ¹³C nuclear magnetic resonance, NMR, were too closed). Please notice that it will be depicted in *E* form throughout the text despite the alkene configuration is still unknown. The self-metathesis product of **1a**, i.e. alkene **5a**, was found in very minor amounts, as both *cis* and *trans* isomers, and the self-metathesis products of **2** were not found. Only the LatMet™ catalyst proved inactive for the metathesis reaction, with a conversion of **1a** <5%. In accordance, for Grubbs-type catalyst, the 2nd generation (2nd Gen) and the Hoveyda-Grubbs (1st Gen) catalysts showed good conversion of **1a** and selectivity for **3a** (~80% in both cases), but not the Grubbs 1st Gen without any isopropoxyl, to give just a ~40% conversion. None of the catalysts showed chain-walking alkene isomerized products under the reaction conditions employed. These results confirm the suitability of 2,5-dimethyl-2,4-hexadiene **2** to selectively transfer the prenyl group to alkyl alkene **1a** and generate a new poly-methylated functional group, using isopropoxyl-containing Ru catalysts.

Different solvents were then tested for the reaction, including toluene, tetrahydrofuran (THF) and diethyl ether, and all of them were less effective than DCM (Figure S1 in the Supporting Information). Remarkably, the concentration of **1a** and **2** in the reaction mixture can be increased from 0.25 M to 1 M without any erosion in the final yield of product **3a** (66–69%), indeed, the reaction can be run solventless to give a better yield of **3a** (76%, Table S1). This result is interesting from both a sustainable and practical point of view, since DCM is banned in many countries and a solvent-free reaction is economically more appealing. Notice that recent technologies allow the easy recovery of Ru from the alkene mixture after reaction.^[62]

The amount of Ru catalyst can also be varied while maintaining a good yield for **3a**, ranging from 5 mol% to 0.5 mol% of catalyst (Table S2). It is noteworthy here that the heating of the reaction mixture does not imply pressure issues when the reaction is run under solvent-free conditions, since 2,5-dimethyl-2,4-hexadiene **2** does not generate any additional pressure in the reaction vessel. However, a further decrease in the excess amount of **2** has a linear impact in the final yield of product **3a** (Table S3), thus a five-fold excess is kept to achieve the better yields.

Scope of the Reaction

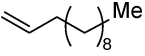
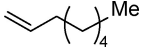
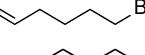
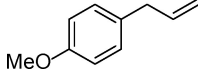

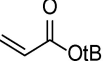
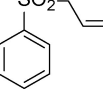
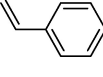
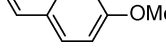
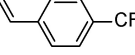
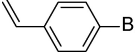
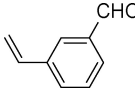
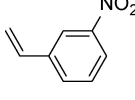
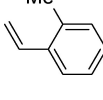
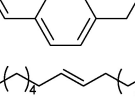
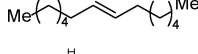
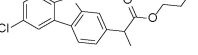
The reactivity of a variety of terminal and secondary alkenes with **2** was tested under the better reaction conditions found, with terminal or secondary alkenes (0.25 mmol), **2** (1.25 mmol), dichloromethane as a solvent (DCM, 1 ml), at room temperature (20 °C), under inert atmosphere (closed vial) and overnight (20 h). As it can be seen in Table 1, the best selectivity towards the prenyl products **3a–c** was observed with aliphatic alkenes

(>80%, entries 1–3). A benzylic alkene also gives a good selectivity towards the prenyl product **3d** (72%). However, allyl and geminal alkenes do not react under the present conditions (Table S4). A competition essay mixing 1-octene **1b** and the geminal alkene 2-methylhept-1-ene **S1b** showed a considerable decrease in the yield of **3b**, from a 94% without **S1b** to 18% with **S1b**, after a 24 h reaction time, thus indicating that geminal alkenes happened to inhibit the reaction.

Acrylonitrile (**1e**) and an acrylate derivative (**1f**) were also evaluated (entries 5 and 6), exhibiting the opposite selectivity, to give the isobutylenyl products **4e–f** (although in very low conversion for **1e**). Varying the function at the allylic position by including a sulfone group, also induced a change in the selectivity towards the formation of the isobutylenyl product **4g**, instead of **3g** (entry 7). The effect of a heteroatom directly joined to the vinylic moiety was checked, but reaction did not take place (Table S4, entry 4). Next, a variety of styrenes **1h–o** were evaluated. Contrary to neutral aliphatic compounds and in line with what has been observed for electron deficient alkenes, the selectivity for styrenes is slightly better for products **4h–o**, although the amount of undesired homocoupling products is augmented. Despite it was not possible to establish a tendency in terms of selectivity, it could be established in terms of reactivity. The higher is the electronic delocalization and the further from the vinylic system is located the substituent of the aromatic ring, the higher is the reactivity. For that reason, the higher conversions were obtained for styrenes **1h–k** (entries 8 to 11). Following this steric reactivity pattern, the *meta* substituted rings were less reactive than the *para* substituted rings but more reactive than the *ortho* substituted rings (compare entries 12 and 13, on one hand, and also entry 14). However, the lower reactivity among the active alkenes tested was found for 1-(chloromethyl)-4-vinylbenzene **1o** (entry 15), probably due its incapability to delocalize electronic density. When the alkene presented a bulky functional group in the vinyl moiety (Table S4, entries S5 and S6), the metathesis reaction did not proceed. In the case of 3-vinylaniline **S1g** (Table S4, entry S7), the reaction was fully quenched due to the potential coordination of the amine with the catalyst. In an attempt to improve the selectivity with the aromatic derivatives, the change of concentration, catalyst and temperature was analyzed for 4-vinylanisole **1i** and 3-vinylbenzaldehyde **11** (Tables S5), achieving better conversions but not better selectivities. Additionally, internal alkenes were also evaluated, and 7-tetradecene **1p** (entry 16) reacted well to provide the target molecule, but with a lower selectivity due to some isomerization of the double bond. Remarkably, the cross-metathesis reaction was also tested with a much more complex alkene, the ester of Carprofen **1q** (entry 17, see SI for preparation details), providing the prenyl product **3q** in >98% yield, in accordance with the aliphatic nature of the alkene tested. This last result suggests that the present cross-metathesis methodology could be of interest for late-stage synthetic modifications.

A last alkene was tested, **1r**, as it is shown in Figure 3. The prenylated product of this alkene (**3r**) is a benchmark substrate for intramolecular carbonyl-olefin metathesis reactions.^[61–64] Indeed, alkene **3r** was obtained in 63% isolated yield after thin-

Table 1. Scope for the cross-metathesis reaction of different alkenes **1 a–q** with 2,5-dimethyl-2,4-hexadiene **2**. GC yields. *E* or *Z* configuration of the alkene products **4** could not be determined, it will be depicted in *E* form throughout the text for the sake of simplification.

Entry	1	Conv. (%)	Selectivity (%)		
			3	4	5
1		90	86	11	3
2		94	100	0	0
3		84	81	17	0
4		89	72	19	8
5		5	0	100	0
6		33	0	100	0
7		73	41	59	0
8		100	0	51	49
9		63	18	26	19 ^[a]
10		70	34	43	23
11		72	27	47	26
12		59	46	54	0
13		64	48	52	0
14		47	49	0	51
15		43	49	51	0
16		51	40	28	32 ^[a]
17		> 98	100	0	0

[a] Other by-products found.

layer chromatography purification (Figure 3, top), highlighting the suitability of the present methodology based on alkene **2** to prepare substrates ready to be engaged in the related carbonyl-olefin metathesis reaction. Comparison of the corresponding ¹H NMR spectra of **1 r** and **3 r** clearly shows the change in the H atoms of the terminal alkene group (Figure 3, bottom), since

the vinylic H atoms of **1 r** at 5.78 ppm disappear to give rise to a new signal at 5.00 ppm, which exhibited the typical coupling pattern for the prenyl group of **3 r**.

A kinetic experiment to check how the selectivity varies between the 1-dodecene **1 a** (alkyl alkene) and styrene **1 h** (aromatic alkene) was performed by placing both terminal

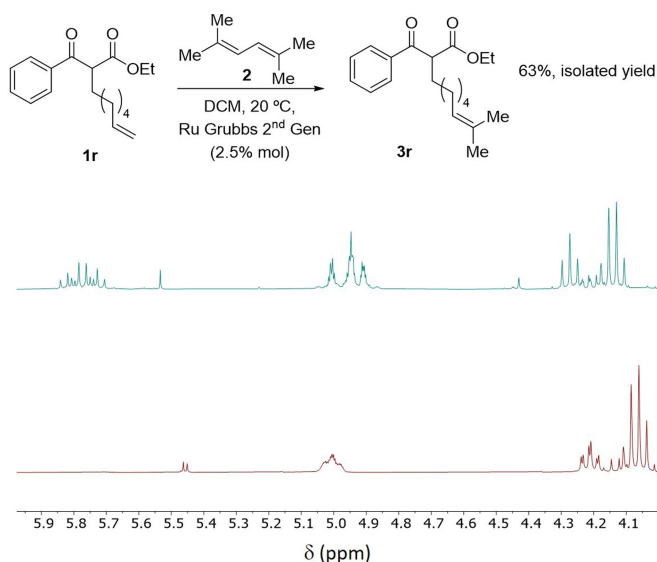


Figure 3. Top: Cross-metathesis reaction of alkene **1r** with 2,5-dimethyl-2,4-hexadiene **2**. Bottom: Compared alkene area in the ^1H NMR spectra of **1r** (blue line) and **3r** (red line).

alkenes in the same reaction. To do so, 1 equiv. of 1-dodecene (**1a**) and 1 equiv. of styrene (**1h**) were mixed with 5 equiv. of 2,5-dimethyl-2,4-hexadiene, and the reaction run under optimized conditions. The type and distribution of products are summarized in Figure 4.

As it can be seen in the plot above, conversion was 70% for **1a** and 60% for **1h**, a high conversion in line with the results in Table 1 (notice that here a half amount of **2** is employed, relative to both terminal alkenes). The selectivity was also

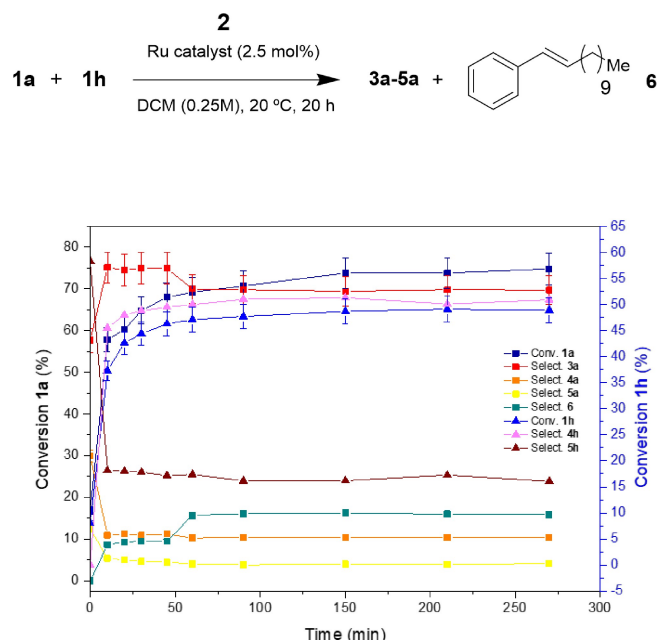


Figure 4. Competitive reaction between 1-dodecene **1a** and styrene **1h** with 2,5-dimethyl-2,4-hexadiene **2** under optimized conditions, to analyze the difference in selectivity. GC results. Error bars account for a 5% uncertainty.

maintained for both alkenes **1a** and **1h** as that in Table 1, i.e. when they are reacted separately, the prenyl compound **3a** and the isobutylenyl compound **4h** are the major products. Even the homocoupling reaction occurred in a similar extent than in the individual reactions, while the cross-metathesis reaction between **1a** and **1h** gave product **6** in <20% yield. Thus, we can conclude that the cross-metathesis reactions occur separately on the Ru catalyst and that the metathesis with **2** is preferred under the present reaction conditions, since the different terminal alkenes barely interact during reaction.

In order to evaluate the reactivity of the simpler alkene 2,3-dimethyl-2-butene (see Figure 1 above) as a potential prenylating agent, the metathesis reaction with **1a** was carried out (Figure S2). The major product found was the homocoupling product **5a**, with a 66% yield, and <5% of the targeted prenylated product **3a**. This result is in line with previous literature,^[34,36] and remarks the suitability of 2,5-dimethyl-2,4-hexadiene **2** as a prenylating agent in cross-metathesis reactions with neutral aliphatic alkenes.

Mechanism of the Reaction

A kinetic study was performed to determine the order of appearance of the products during the cross-metathesis reaction between **1a** and **2**, under optimized conditions. Figure 5 shows that the first product to appear, after just a couple of minutes reaction time, is not only the co-metathesis product **3a** but also the self-metathesis product **5a**, both in nearly a 1:1 ratio. While product **3a** keeps increasing with time, product **5a** rapidly decreases, concomitantly with the formation of product **4a**. In other words, the kinetic results clearly show that the self-metathesis product **5a** acts as an intermediate reactant to give, in a significant amount, products **3a** and **4a**. An independent reactive experiment with the secondary alkene **5b** as the starting material, under identical reaction conditions

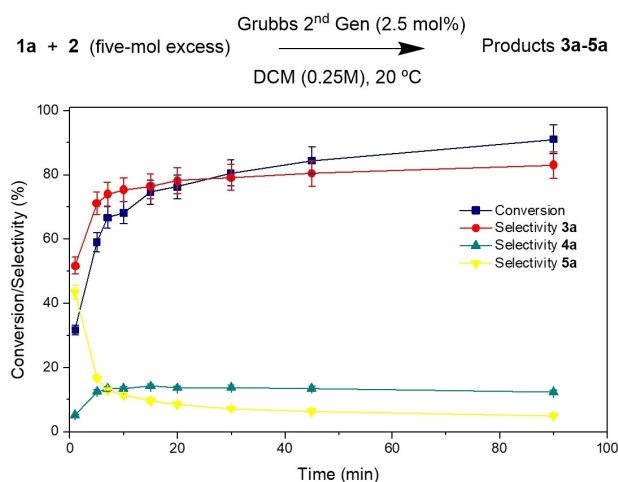


Figure 5. Kinetics for the alkene cross-metathesis reaction of **1a** and **2** catalyzed by the Grubbs 2nd Gen catalyst, under the indicated reaction conditions. GC results. Error bars account for a 5% uncertainty.

(Figure S3), shows that both **3b** and **4b** are formed, which confirms the kinetic observations.

The kinetic curve shown in Figure 5 levels off after 20 min reaction time, for both the reactants and the products, despite conversion is not complete yet. The resulting products are stable for at least 1.5 h reaction time. In-situ analysis of the reaction by absorption ultraviolet-visible spectrophotometry (UV-vis) and ^{31}P NMR (Figures S4 and S5) shows that the Ru catalyst rapidly degrades, thus explaining the abrupt decrease of the catalytic activity, and perhaps the lack of reactivity of the resulting alkene products. An additional experiment to determine if the target molecule modified the activity of the catalyst was performed. To do so, the fresh catalyst was placed with **3c** and, after 24 h reaction time, any new product from **3c** was not observed. This pointed out that the target molecule was not poisoning the catalyst (see Figure S6). The equation rate of the reaction was then determined on the basis of individual kinetic measurements. The representation of the initial reaction rate vs the amount of each reactant under pseudo-stationary reaction conditions (keeping constant the rest of reactants) shows that the reaction order is +1 for the Ru catalyst, alkene **1a** and alkene **2** (Figure S7). Thus, the equation rate can be expressed as $v_0 = k_{\text{exp}}[\text{Ru}][\mathbf{1a}][\mathbf{2}]$ (where k_{exp} is an experimental constant), which denotes that the Ru catalyst and both alkenes participate in the rate determining step (r.d.s.) of the reaction. In other words, the activation of the more sluggish alkene **2** by the Ru catalyst is also behind the control of the reaction rate. The lack of cross-metathesis reaction of **1a** with 2,3-dimethyl-2-butene (see above) but the occurrence of self-metathesis in that experiment, to form **5a**, strongly supports the r.d.s. proposed for the reaction. A reaction order of +1 for Ru discards the possibility that some kind of Ru aggregates,^[58] formed in-situ after the complex degradation, are behind the catalytic activity. With the above data in hand, a reaction mechanism for the metathesis reaction of terminal alkyl alkene **1a** with 2,5-dimethyl-2,4-hexadiene **2** is proposed in Figure 6.

The reaction starts with the self-coupling of the terminal alkyl alkene **1a** catalyzed by the Ru complex catalyst, to give the corresponding secondary alkene **5a** in a fast process [the methylidene complex ($\text{Ru}=\text{CH}_2$) stays in equilibrium during reaction, as usual in these alkene metathesis reactions]. Concomitantly, the more crowded alkene **2** is also activated by the Ru catalyst in a process which also controls the reaction rate, to give the corresponding prenyl carbene as the major

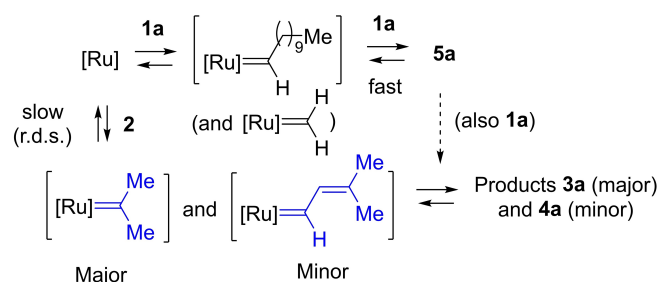


Figure 6. Proposed reaction mechanism for the alkene metathesis reaction of alkenes **1a** and **2**; (r.d.s.) is rate determining step.

intermediate. After that, the Ru carbene intermediates reacts with either **1a** or **5a** (both are in equilibrium), to give the final products **3a** and **4a**. These products do not react further, probably by a combination of the intrinsic lack of reactivity of the just-added prenyl or isobutenyl group, and a degradation of the Ru metathesis catalyst.

Application to Polyisoprene (Rubber) Metathesis Reactions

The structure of the alkene **2** somewhat resembles that of natural rubber and related polymers (see Figure 1 above), although it is true that the double bonds are conjugated and they have a 1,4-*trans* configuration, in contrast to natural rubber. Nevertheless, the results obtained here could be of application for the degradation of rubber, used or not. Beyond the classical use in tires, micro-structured rubber is massively employed in public floors (playgrounds, paddle and tennis courts, football fields,...), and it will be banned from 2028 due to its suspected toxicity, which urges to find recycling solutions for these materials.^[56–58] The reactivity of polyisoprene in cross-metathesis reactions has been studied before but only with Grubbs-type catalysts,^[63–66] thus we thought that the information obtained in the present study could be of utility. Figure 7 shows the results obtained for the metathesis reaction of commercial polyisoprene (*trans*-1,4) with 1-dodecene **1a** employing the Grubbs 2nd Gen catalyst. The identified reaction products, after combining GC-MS and ^1H and ^{13}C NMR analysis, are also depicted in Figure 7. It was possible to identify four types of products from the reaction. The first group consisted in 1-dodecene **1a** isomers, due to the ability of Ru to catalyze the

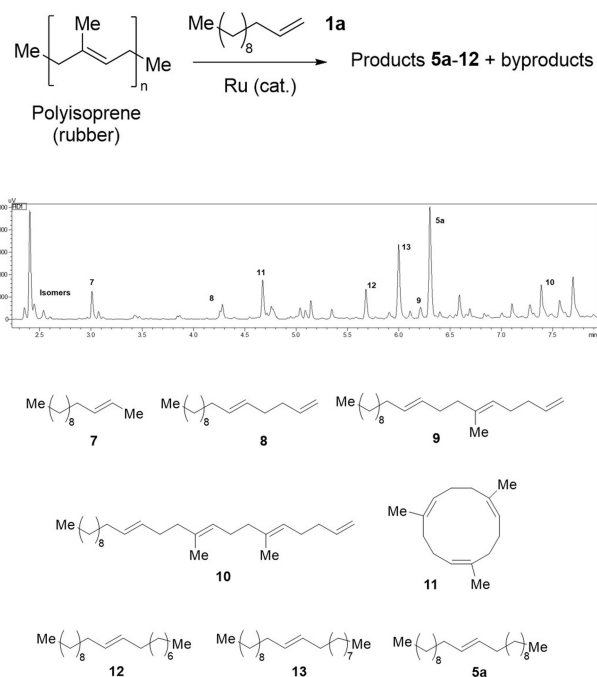


Figure 7. Results for the cross-metathesis reaction of polyisoprene with 1-dodecene **1a** catalyzed by the Grubbs 2nd Gen. catalyst, under optimized reaction conditions.

alkene-isomerization reaction.^[57,58] Next, we found products from the cross-metathesis reaction of **1a** with fragments of polyisoprene (products **7–10**). In the third group, we found compound **11** as a mixture of isomers, formed spontaneously from the component monomers of the polyisoprene. Finally, the last identified group contained products derived from the self-coupling metathesis reaction of **1a** with its isomers (products **5a** and **12–13**). Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) analysis revealed that the initial polyisoprene sample is composed by around ten monomers (peak at 638 Da. in Figure 8) and that, after the addition of the catalyst, the polymer was fragmented until arriving to short chains. At that moment, but not before, the small fragments were able to interact with *n*-dodecene **1a** and underwent the metathesis reaction, as the MALDI-TOF outcomes show, since any recombination with *n*-dodecene **1a** was not identified for the larger fragmentation peaks (dark and light blue lines virtually equals in Figure 8).

For the sake of comparison, the Hoveyda-Grubbs catalyst and other Grela catalysts, such as GreenCatTM and Nitro-GrelaTM, were also tested. The results in Figure 9 show that the outcome from these catalysts is very similar to that obtained with the Grubbs 2nd Gen catalyst, after comparing the gas chromatograms and mass fragmentations for both reactions. The Ru catalyst alone already induces the breaking of the polymer (Figure S8). A similar catalytic study was performed with polybutadiene-styrene (PBS) and polybutadiene (PB), and the results show a similar reactivity in the cross-metathesis reaction

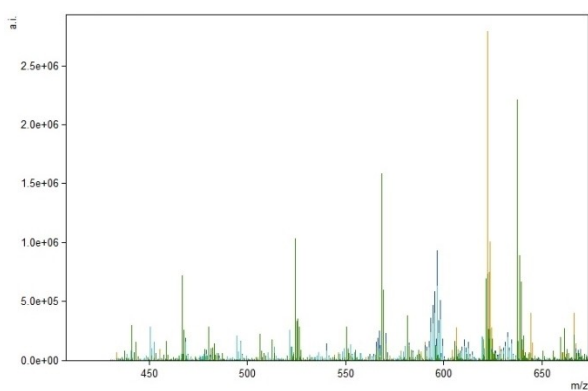


Figure 8. MALDI-TOF results for: matrix (orange line), polyisoprene (green line), polyisoprene with catalyst (2.5 mol%, dark blue line) and polyisoprene with catalyst (2.5 mol%) and **1a** (0.25 mmol, light blue line).

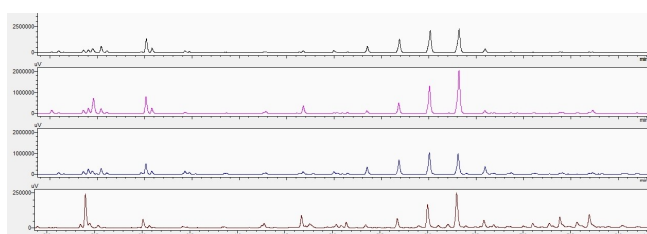


Figure 9. Gas chromatograms for the cross-metathesis reaction of polyisoprene with 1-dodecene **1a** catalyzed by: Grubbs 2nd Gen catalyst (red line), GreenCatTM (blue line), Hoveyda-Grubbs catalyst (pink line) and Nitro-GrelaTM catalyst (black line). For product assignments, see Figure 7.

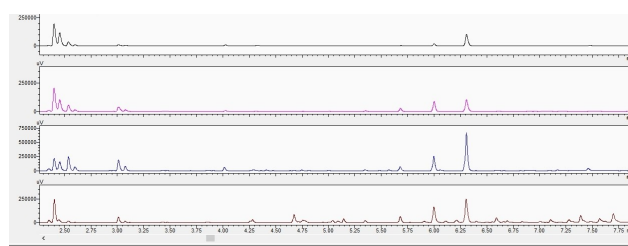


Figure 10. Gas chromatograms of the cross-metathesis reactions between a sample of recycled rubber with 1-dodecene **1a** catalyzed by: Grubbs 2nd Gen catalyst (red line), GreenCatTM (blue line), Hoveyda-Grubbs catalyst (black line) and Nitro-GrelaTM catalyst (pink line). For product assignments, see Figure 7.

for both polymers, under the optimized reaction conditions (Figures S9 and S10).

A sample of used rubber from a park playground was then tested in the reaction. Previously, Fourier-transformed infrared spectroscopy (FT-IR) measurements allowed us to check that the structure of the recycled rubber is similar to that of the commercial polyisoprene (Figure S11). The results of the cross-metathesis reaction between the recycled rubber and **1a**, shown in Figure 10, confirm that the alkene metathesis reaction also occurs in the recycled polymer. Other alkenes have been used before for the metathesis of polymers.^[67–69] Therefore, we can conclude that the catalytic results here obtained can be of application for the valorization of used rubber, which constitutes a new example of metathesis technologies for sustainable solutions.^[55,56,70]

Conclusions

The alkene cross-metathesis reaction of a variety of terminal and secondary alkenes with 2,5-dimethyl-2,4-hexadiene **2** proceeds selectively to the isobutenyl/prenyl products, employing a variety of Ru catalysts. Terminal alkyl alkenes are more reactive than styrenes and selective to the prenylated product. Mechanistic studies suggest that the terminal alkene is in equilibrium with the corresponding self-metathesis products, and both react with **2** to give the cross-metathesis products, which do not evolve further. The reaction can be run under ambient conditions without any special pressure or temperature control, even under solventless reaction conditions, and rubber-type polymers (also recycled) engage well in the reaction. These results constitute an example of alkene metathesis reaction based on modern catalysts with synthetic and sustainable interest.

Supporting Information Summary

An experimental section, including the reaction procedures, can be found in the Supporting Information, together with the additional Figures S1–S20 and Tables S1–S5.

Acknowledgements

This work is part of the project PID2020-115100GB-I00 funded by MCIN/AEI/10.13039/501100011033MICIIN (Spain). Financial support by Severo Ochoa centre of excellence program (CEX2021-001230-S) is gratefully acknowledged. The work has also been funded by Generalitat Valenciana (INNEST/2022/20 from Agència Valenciana de la Innovació). P.M.-V. thanks ITQ, UPV-CSIC for concession of a contract (PAID 01–20). S.R.-N. thanks Agència Valenciana de la Innovació for a contract (INNEST/2022/20). J.O.-M. thanks the MICIIN for the concession of the Ramón y Cajal contract RYC2022-036154-I (funded by MCIN/AEI/10.13039/501100011033). We thank Miguel Sanz-Abad for carrying out some experimental work.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Alkene cross-metathesis · 2,5-Dimethyl-2,4-hexadiene · Rubber valorization · Prenylation · and Isobutenyl

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Manuscript received: February 29, 2024
Accepted manuscript online: May 3, 2024
Version of record online: May 17, 2024