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# Transformations of Terpenes and Terpenoids *via* Carbon-Carbon Double Bond

## Metathesis

Christian Bruneau,<sup>a,\*</sup> Cédric Fischmeister<sup>a</sup>, Dalmo Mandelli<sup>b</sup>, Wagner A. Carvalho<sup>b</sup>, Eduardo N. dos Santos,<sup>c</sup> Pierre H. Dixneuf<sup>a</sup> and Luciana Sarmento Fernandes<sup>a,b</sup>

### Abstract

Stimulated by the strong interest in replacing fossil raw materials by renewable feedstocks in chemical industry, alkene metathesis of unsaturated bio-sourced olefins has been recently investigated with the objective of producing high-value molecules using green and atom economic strategies. It is due time to review what has been achieved in this field using terpenes and terpenoids as olefin metathesis partners. These substrates, derived from the isoprene structure, present different types of carbon-carbon double bonds that can be involved in self metathesis, ring closing metathesis, cross metathesis including ethenolysis, and ring opening metathesis. The successful achievements and remaining bottlenecks in this field will be discussed.

## Introduction

Terpenes are found in essential oils and constitute a class of natural products that finds direct applications and serves as feedstocks in flavor and fragrance industry and has other potential applications due to their biological properties.<sup>1</sup> They are constructed on the basis of connected isoprene units (2-methyl-1,3-butadiene) and thus contain a number of carbon atoms which is a multiple of five. Terpenoids are chemically modified terpenes, essentially oxygenated derivatives such as alcohols, epoxides, ketones, aldehydes, carboxylic acids and esters. Chemical transformations of terpene derivatives have been investigated with the objective of producing new fine chemicals with high added value for diverse applications. Catalytic isomerization, rearrangements, cyclization, ring opening, hydrogenation, dehydrogenation, epoxidation,

oxidation, hydration, hydroformylation, cyclopropanation are the most studied reactions.<sup>2-5</sup> Recently, computational studies on metathesis transformations of bulky terpenes such as  $\alpha$ - and  $\beta$ -pinene in ring opening and cross metathesis with various types of catalysts (Ru, Mo, W) have appeared.<sup>6,7</sup> The scope of this review is the transformation of unsaturated terpenes and terpenoids involving olefin metathesis processes including ring closing metathesis of dienes, cross metathesis with ethylene and functional olefins to produce fine chemicals, and ring opening metathesis as well as ring opening/cross metathesis for the production of polymers. The present review reports on direct transformations of terpenes *via* double bond metathesis excluding the literature in which terpenes or terpenoids are previously modified to generate a C=C double bond suitable for metathesis processes. These transformations of terpenes *via* alkene metathesis not only add value to renewables but involve green catalytic processes.

## 1 Ring closing metathesis (RCM)

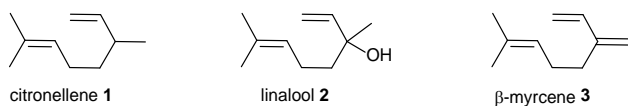
### 1.1 Citronellene

The ring closing metathesis of terpenes has been mainly investigated with citronellene **1**, linalool **2**, and myrcene **3** (Scheme 1).

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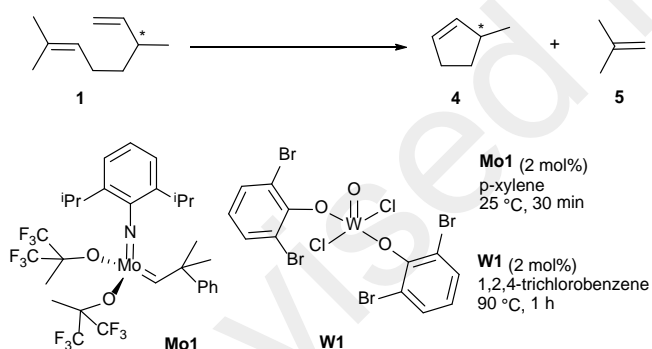
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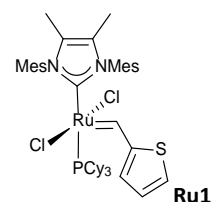
**Scheme 1.** Terpenes used in ring closing metathesis

To the best of our knowledge, the first ring closing metathesis of a terpene containing a 1,6-diene system has been carried out with molybdenum and tungsten catalysts. The Schrock catalyst  $\text{Mo}(\text{=CHC}(\text{Me})_2\text{Ph})((\text{CF}_3)_2\text{MeCO})_2(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N})$  **Mo1** catalyzed the ring closing metathesis of technical grade (-)-citronellene on a preparative scale (50 g) at room temperature in *p*-xylene within 1 h with a catalyst loading of 0.1 mol% leading to 3-methylcyclopentene **4** in 60% isolated yield without isomerization (Scheme 2).<sup>8</sup> Full conversion was obtained in 30 min when 2 mol% of catalyst was used and it was noted that no epimerization took place at low substrate concentration (0.75 M). By contrast, at higher concentration (50 wt%) a mixture of methylcyclopentene isomers was produced. In the presence of 2 mol% of  $\text{WOCl}_2(2,6\text{-Br}_2\text{C}_6\text{H}_3\text{O})_2$  **W1** as catalyst, each optically pure (*R*)- and (*S*)-citronellene enantiomer was converted at 90 °C in 1,2,5-trichlorobenzene for 1 h into the corresponding 3-methylcyclopentene (*R*)-**4** and (*S*)-**4** in 68-70% isolated yield and 97% enantiomeric excess with retention of configuration (Scheme 2).<sup>9</sup>



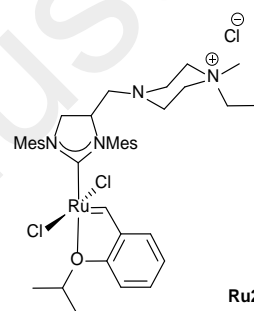
**Scheme 2** Ring closing metathesis of citronellene **1** with molybdenum and tungsten catalysts

Later on, the same RCM reaction was achieved with full conversion of (*R*)-citronellene **1** with 0.5 mol% of the ruthenium catalyst **Ru1** (Scheme 3) in toluene at 80 °C using microwave heating during 20 min.<sup>10</sup>



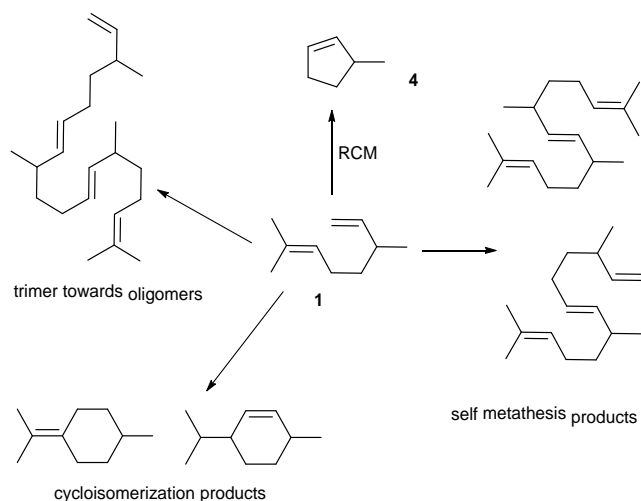
**Scheme 3** Structure of complex **Ru1**

Immobilization of classical Hoveyda type catalysts derived from **Ru6**<sup>11</sup> on silica and mesoporous molecular sieves was detrimental for the RCM of citronellene.<sup>11a</sup> Other Hoveyda type ruthenium catalysts bearing a quaternary ammonium group linked to their *N*-heterocyclic carbene ligand such as **Ru2** (Scheme 4) have been immobilized on silica (SBA-15) and their catalytic activity has been evaluated in different metathesis transformations including RCM of citronellene.<sup>11b</sup>



**Scheme 4** Structure of complex **Ru2**

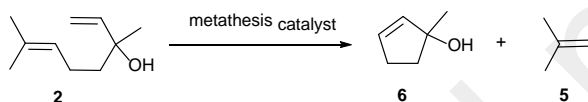
A conversion of 93% was obtained when the reaction was catalyzed by 84 ppm of immobilized catalyst with a substrate/catalyst ratio of 12000 in toluene at 60 °C for 6 h. At 80 °C, a TON of 16000 was reached with very high conversion, and most importantly no formation of byproduct was observed and the catalyst could be recycled. It is noteworthy that the reaction carried out without solvent also gave full conversion of **1** but only 30% of **4** was formed together with considerable amounts of the self metathesis product and oligomers as well as cycloisomerization products (Scheme 5).



**Scheme 5.** Various metathesis and cycloisomerization products formed under neat conditions with SBA15 supported **Ru2**

### 1.2 Linalool

Linalool **2** is the monoterpene derivative that has been most often used in test reaction to evaluate the catalytic properties of new ruthenium catalysts. Its ring closing metathesis reaction leads to 2-methylprop-1-ene **5** and 1-methylcyclopent-2-en-1-ol **6** as primary products.



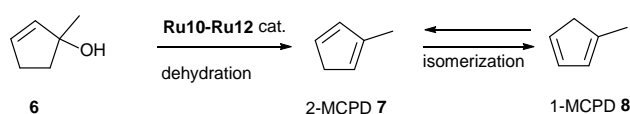
**Scheme 6** Ring closing metathesis of linalool **2**

The ruthenium catalysts that have been used for this RCM reaction are presented in Scheme 8. Initial studies carried out with 4-10 mol% of the first generation Grubbs catalyst **Ru3** at room temperature in  $\text{CDCl}_3$  showed that the presence of the allylic alcohol group in linalool had a beneficial effect on the rate of the metathesis reaction as compared to citronellene **1**.<sup>12</sup> Under similar conditions, the reactivity of linalool **2** was one order of magnitude higher than that of the diene **1**, whereas the *O*-methoxy-protected linalool presented no reactivity even at 65 °C. This enhancement of reactivity was attributed to the acceleration of the rate of carbene exchange between the terminal vinyl group and the ruthenium alkylidene species due to interaction of the alcohol with the catalytic species through chloride or phosphine substitution favouring pre-association of the substrate with the catalytic metal carbene.

The activity of **Ru3** was confirmed in chloroform at room temperature and full conversion of **2** into **6** was observed within 60 min at room temperature. The second generation Grubbs catalyst **Ru4** also gave full conversion whereas the Hoveyda-Grubbs catalysts **Ru5** and **Ru6** exhibited a slightly lower activity (Table 1 - entries 1-4).<sup>13</sup> Other second generation ruthenium complexes (**Ru7**, **Ru8** and **Ru9**), equipped with a very bulky *N*-heterocyclic carbene ligand containing substituted naphthyl groups were found to be very efficient for the ring closing metathesis of linalool. Full conversion with excellent yields of isolated 1-methylcyclopent-2-en-1-ol **6** were obtained in 6-30 min in dichloromethane at room temperature with 1 mol% of catalyst (Table 1 - entries 5-7).<sup>14</sup> **Ru1** (Scheme 3) has been used with a low catalyst loading of 0.1 mol% at 80 °C in toluene and dimethylcarbonate (DMC) but after one hour, the conversion of **2** reached 40-43% only (Table 1- entries 8, 9).<sup>10</sup> A higher conversion of 70% was obtained when the reaction was performed under neat conditions but undesired oligomer formation was observed. It was however possible to reach full conversion within 10 min by increasing the catalyst loading to from 0.1 to 0.5 mol%. The authors confirmed that the presence of the allylic alcohol functionality increased the reaction rate since the full conversion of citronellene under similar conditions required a twice longer time of 20 min. This ring closing metathesis could be scaled-up using microwave heating and continuous flow process.<sup>10</sup> The RCM of linalool has been investigated with Grubbs (**Ru11**, **Ru12**) and Hoveyda (**Ru14**, **Ru15**) second generation catalysts featuring frozen saturated *N*-heterocyclic imidazolynilidene ligands substituted on the backbone of the five-membered ring by two phenyl groups in *syn*-position and by *ortho*-tolyl groups at the nitrogen atoms with a *syn* or *anti*-conformation.<sup>15</sup> Full conversions of linalool were obtained within 7 and 10 min when the reactions were achieved in dichloromethane at 30 °C with 1 mol% of the Grubbs type catalysts **Ru11** and **Ru12**, respectively. The less sterically hindered catalyst **Ru10** was also efficient and led to full conversion in 13 min (Table 1-entries 11-13). With a low catalyst loading of 0.1 mol%, conversions were incomplete and a higher catalytic activity of the *syn*-isomer **Ru11** was observed with a maximum conversion reaching 59% after one hour (Table 1 - entries 14-16).<sup>15</sup> The RCM reactions with the Hoveyda type catalysts **Ru14** and **Ru15** were carried out at 60 °C in deuterated benzene. In the presence of 1 mol% of catalyst, full conversion was rapidly reached within 6 min with **Ru14**, **Ru15** and the analog **Ru13**. With a lower

catalyst loading of 0.1 mol%, full conversion were also obtained with **Ru13** and **Ru14** in one hour at 60 °C, whereas the *anti*-isomer **Ru15** was less efficient giving only 90% conversion after the same reaction time (Table 1 - entries 17-22).

With catalysts **Ru10**, **Ru11** and **Ru12**, it was observed that after formation of 1-methylcyclopent-2-en-1-ol **6**, complete dehydration of the alcohol took place to give first 2-methylcyclopentadiene (2-MCPD) **7** within 2 h, and then a mixture with its isomer 1-methylcyclopentadiene (1-MCPD) **8** (Scheme 7). With the phosphine-free Hoveyda type catalysts **Ru13-Ru15**, these subsequent reactions taking place after formation of **6** were much less efficient.



**Scheme 7** Dehydration of 1-methylcyclopent-2-en-1-ol **6** catalyzed by Grubbs type catalyst

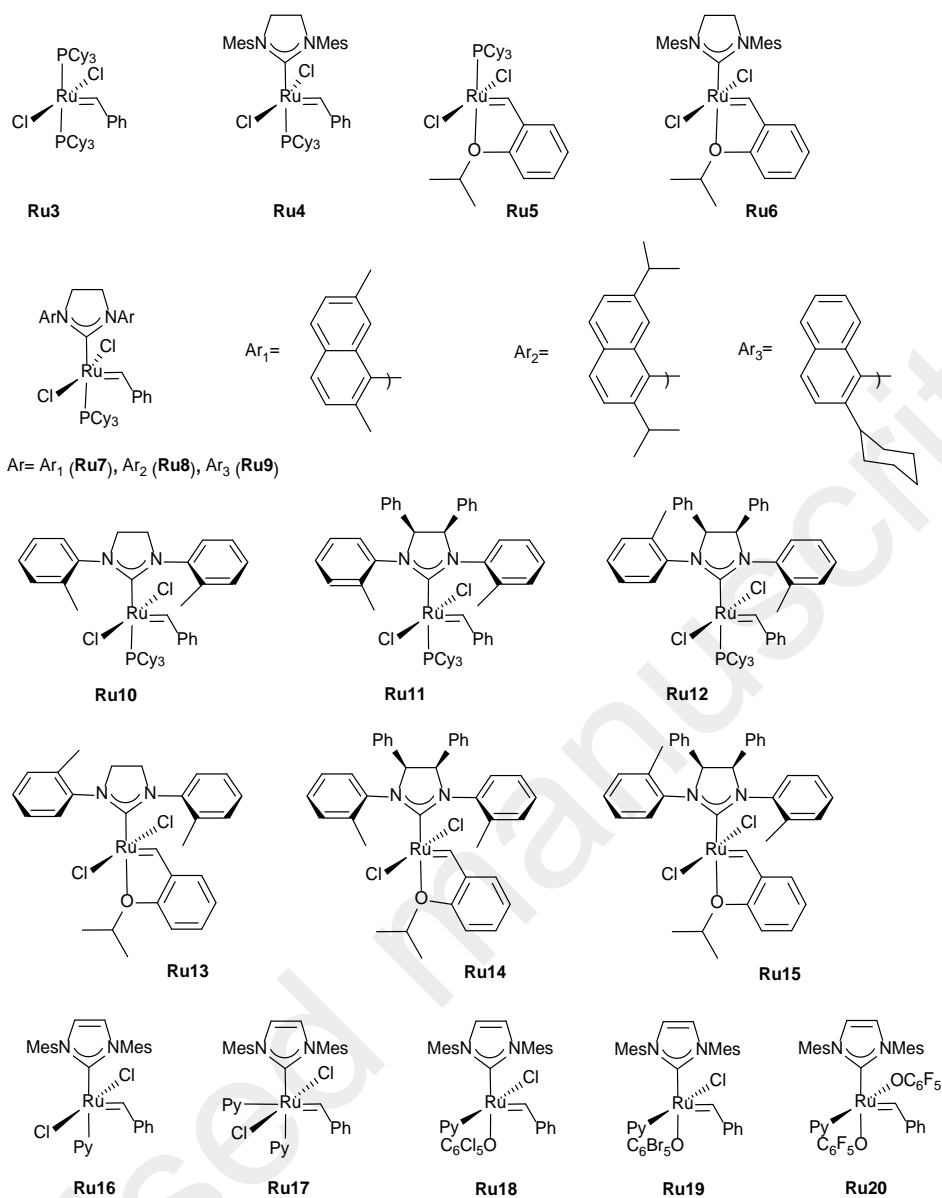
The commercially available catalysts **Ru3**, **Ru6** and **Ru10** were used to evaluate the RCM of linalool without solvent (Table 1, entries 23-26).<sup>16</sup> The second generation Hoveyda type complex **Ru6** appeared to be the best catalyst making the full conversion of **2** possible at room temperature with a catalyst loading of 0.1 mol% (Table 1 - entry 23). The Grubbs type catalysts **Ru3** and **Ru10** were less efficient under neat conditions even at higher temperature. In this case also, dehydration of 1-methylcyclopent-2-en-1-ol **6** to methylcyclopentadienes was observed with **Ru3** and **Ru6** when the temperature was increased to 60 °C. The dehydration process was attributed to the release of a catalytic amount of HCl resulting from decomposition of the ruthenium catalyst, which is able to initiate the acid-catalyzed dehydration of cyclic alcohols.<sup>17</sup>

Ruthenium complexes **Ru18-Ru20** equipped with a benzylidene and a pyridine ligand with at least one chloride atom substituted by an alkoxide have been prepared and evaluated in ring closing metathesis of dienes.<sup>18</sup> In the presence of 0.05 mol% of catalyst in refluxing CDCl<sub>3</sub>, linalool was converted into 1-methylcyclopent-2-en-1-ol **6**. **Ru20** featuring two pentafluorophenoxy ligands exhibited an exceptional activity leading to full conversion in 1 hour, whereas the other catalyst precursors showed conversions located in the range 17-34% (Table 1 - entries 27-31). Nevertheless, all these ruthenium-pseudohalide catalysts led to 100% conversion in 15 min when the catalyst loading was as low as 0.5 mol%.<sup>18</sup>

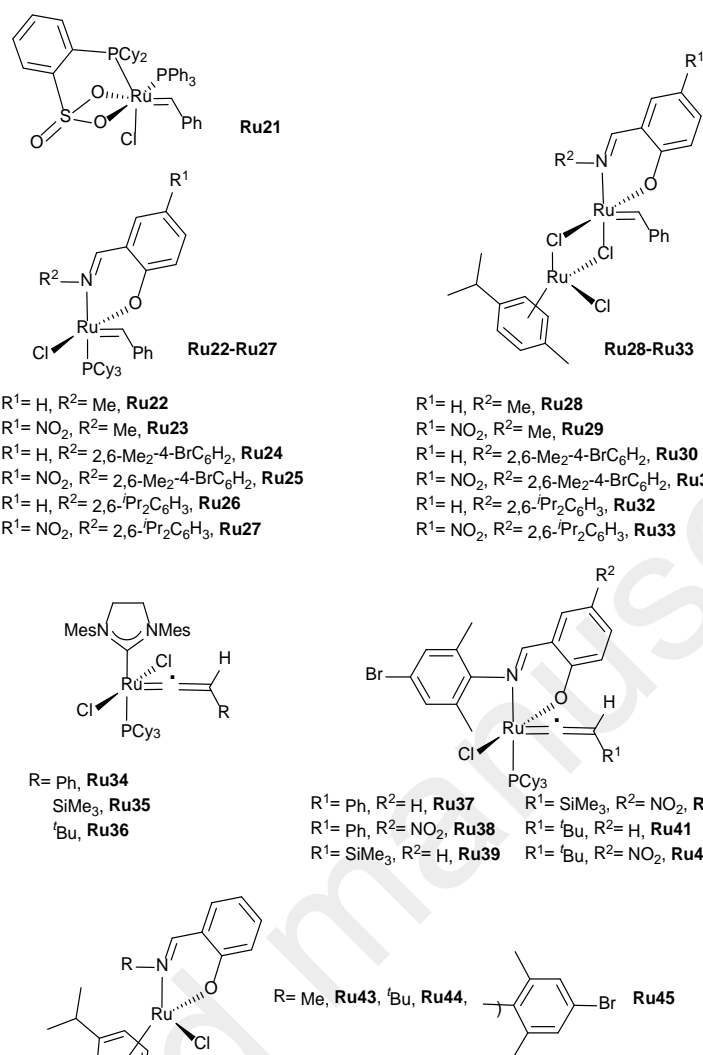
The benzylidene complex **Ru21** containing a tridentate phosphinesulfonate has shown a modest activity for the RCM of linalool **2** with 35% yield of **6** after 20 h in refluxing CDCl<sub>3</sub> with a catalyst loading of 1 mol% (Table 1 - entry 32).<sup>19</sup>

Schiff bases derived from salicylaldehyde were coordinated to mononuclear (**Ru22-Ru27**) and homobimetallic (**Ru28-Ru33**) ruthenium benzylidene complexes.<sup>20</sup> Ring closing metathesis of linalool **2** was attempted with these two series of complexes with a catalyst loading of 5 mol% in C<sub>6</sub>D<sub>5</sub>Cl at 70 °C for the mononuclear and at 55 °C for the binuclear catalysts. In a general manner, the binuclear were more active than the mononuclear complexes equipped with the same Schiff base ligand as after 4 h the reactions carried out at 55 °C with **Ru28-Ru33** (Table 1 - entries 39-44) gave better yields of **6** than **Ru23-Ru27** (Table 1 - entries 33-38) at 70 °C. Even though some differences were also observed related to the nature of the Schiff base ligand, these complexes showed moderate catalytic activities.

It has been shown that ruthenium vinylidene complexes were efficient catalyst precursors for olefin metathesis.<sup>21</sup> Ruthenium vinylidene complexes (**Ru34-Ru36**) analogs of second generation Grubbs catalysts **Ru4**, and ruthenium vinylidene complexes with a Schiff base as ligand (**Ru37-Ru42**) were prepared and used for ring closing metathesis of linalool.<sup>22</sup> Catalyst **Ru34-Ru36** led to satisfactory yields of 1-methylcyclopent-2-en-1-ol **6** in 2 h at 60 °C in C<sub>6</sub>D<sub>6</sub> with a catalyst loading of 5 mol% (Table 1 - entries 45-47). On the other hand, complexes **Ru37-Ru42** were much less active and required 24 h at 80 °C to reach the same level of conversion (Table 1 - entries 48-53). The ring closing metathesis of linalool has also been attempted with catalysts generated *in situ* from a ruthenium complex in the presence of trimethylsilyldiazomethane as carbene precursor according to an established methodology.<sup>23</sup> The Schiff base complexes **Ru43-Ru45** activated by 2.2 equivalents of TMSD at 70 °C in toluene for 1 h led to modest yields of **6** (Table 1 - entries 54-56).<sup>24</sup> Even though it is difficult to compare all the results of Table 1, which have been obtained under different experimental conditions, it appears that the best ruthenium catalysts for the ring closing metathesis of linalool are second generation Grubbs and Hoveyda catalysts equipped with a bulky *N*-heterocyclic carbene ligand. It is noteworthy that the complex **Ru20** containing two aryloxy ligands instead of chlorides and an unsaturated NHC ligand was very active at 60 °C with a low catalyst loading of 0.05 mol%.



**Scheme 8.** Selected ruthenium catalysts used for terpene metathesis transformations



**Scheme 8 (continued).** Selected ruthenium catalysts used for terpene metathesis transformations

**Table 1.** Ring closing metathesis of linalool

Entry	Catalyst	Cat. loading (mol%)	Solvent	Temperature (°C)	Time (min)	Conversion or yield* (%)	Ref
1	<b>Ru3</b>	5	$\text{CDCl}_3$	rt	60	100	13
2	<b>Ru4</b>	5	$\text{CDCl}_3$	rt	60	100	13

3	<b>Ru5</b>	5	CDCl <sub>3</sub>	rt	60	65	13
4	<b>Ru6</b>	5	CDCl <sub>3</sub>	rt	60	95	13
5	<b>Ru7</b>	1	CH <sub>2</sub> Cl <sub>2</sub>	rt	30	92*	14
6	<b>Ru8</b>	1	CH <sub>2</sub> Cl <sub>2</sub>	rt	6	88*	14
7	<b>Ru9</b>	1	CH <sub>2</sub> Cl <sub>2</sub>	rt	6	94*	14
8	<b>Ru1</b>	0.1	toluene	80	60	43	10
9	<b>Ru1</b>	0.1	DMC	80	60	40	10
10	<b>Ru1</b>	0.5	toluene	80	10	100	10
11	<b>Ru10</b>	1	CD <sub>2</sub> Cl <sub>2</sub>	30	13	100	15
12	<b>Ru11</b>	1	CD <sub>2</sub> Cl <sub>2</sub>	30	7	100	15
13	<b>Ru12</b>	1	CD <sub>2</sub> Cl <sub>2</sub>	30	10	100	15
14	<b>Ru10</b>	0.1	CD <sub>2</sub> Cl <sub>2</sub>	30	60	30	15
15	<b>Ru11</b>	0.1	CD <sub>2</sub> Cl <sub>2</sub>	30	60	59	15
16	<b>Ru12</b>	0.1	CD <sub>2</sub> Cl <sub>2</sub>	30	60	33	15
17	<b>Ru13</b>	1	C <sub>6</sub> D <sub>6</sub>	60	6	100	15
18	<b>Ru14</b>	1	C <sub>6</sub> D <sub>6</sub>	60	6	100	15
19	<b>Ru15</b>	1	C <sub>6</sub> D <sub>6</sub>	60	6	100	15
20	<b>Ru13</b>	0.1	C <sub>6</sub> D <sub>6</sub>	60	6	>98	15
21	<b>Ru14</b>	0.1	C <sub>6</sub> D <sub>6</sub>	60	6	>98	15
22	<b>Ru15</b>	0.1	C <sub>6</sub> D <sub>6</sub>	60	6	90	15
23	<b>Ru6</b>	0.1	neat	rt	45	100	16
24	<b>Ru6</b>	0.01	neat	rt	60	44	16
25	<b>Ru10</b>	0.1	neat	60	30	36	16
26	<b>Ru3</b>	0.1	neat	45	60	55	16
27	<b>Ru16</b>	0.05	CDCl <sub>3</sub>	reflux	60	24	18
28	<b>Ru17</b>	0.05	CDCl <sub>3</sub>	reflux	60	29	18
29	<b>Ru18</b>	0.05	CDCl <sub>3</sub>	reflux	60	17	18
30	<b>Ru19</b>	0.05	CDCl <sub>3</sub>	reflux	60	34	18
31	<b>Ru20</b>	0.05	CDCl <sub>3</sub>	reflux	60	100	18
32	<b>Ru21</b>	1	CDCl <sub>3</sub>	reflux	1200	35	19
33	<b>Ru22</b>	5	C <sub>6</sub> D <sub>5</sub> Cl	70	240	12	20
34	<b>Ru23</b>	5	C <sub>6</sub> D <sub>5</sub> Cl	70	240	13	20
35	<b>Ru24</b>	5	C <sub>6</sub> D <sub>5</sub> Cl	70	240	18	20
36	<b>Ru25</b>	5	C <sub>6</sub> D <sub>5</sub> Cl	70	240	25	20
37	<b>Ru26</b>	5	C <sub>6</sub> D <sub>5</sub> Cl	70	240	41	20
38	<b>Ru27</b>	5	C <sub>6</sub> D <sub>5</sub> Cl	70	240	56	20
39	<b>Ru28</b>	5	C <sub>6</sub> D <sub>5</sub> Cl	55	240	32	20
40	<b>Ru29</b>	5	C <sub>6</sub> D <sub>5</sub> Cl	55	240	25	20
41	<b>Ru30</b>	5	C <sub>6</sub> D <sub>5</sub> Cl	55	240	69	20
42	<b>Ru31</b>	5	C <sub>6</sub> D <sub>5</sub> Cl	55	240	66	20
43	<b>Ru32</b>	5	C <sub>6</sub> D <sub>5</sub> Cl	55	240	87	20
44	<b>Ru33</b>	5	C <sub>6</sub> D <sub>5</sub> Cl	55	240	74	20
45	<b>Ru34</b>	5	C <sub>6</sub> D <sub>6</sub>	60	120	69	22
46	<b>Ru35</b>	5	C <sub>6</sub> D <sub>6</sub>	60	120	89	22
47	<b>Ru36</b>	5	C <sub>6</sub> D <sub>6</sub>	60	120	80	22
48	<b>Ru37</b>	5	C <sub>6</sub> D <sub>6</sub>	80	1440	27	22
49	<b>Ru38</b>	5	C <sub>6</sub> D <sub>6</sub>	80	1440	54	22
50	<b>Ru39</b>	5	C <sub>6</sub> D <sub>6</sub>	80	1440	70	22
51	<b>Ru40</b>	5	C <sub>6</sub> D <sub>6</sub>	80	1440	81	22
52	<b>Ru41</b>	5	C <sub>6</sub> D <sub>6</sub>	80	1440	68	22
53	<b>Ru42</b>	5	C <sub>6</sub> D <sub>6</sub>	80	1440	75	22
54	<b>Ru43</b>	5 + TMSD	toluene	70	60	16	24
55	<b>Ru44</b>	5 + TMSD	toluene	70	60	21	24
56	<b>Ru45</b>	5 + TMSD	toluene	70	60	28	24

### 1.3 $\beta$ -Myrcene and its *cis*- and *trans*- $\beta$ -ocimene isomers

The ring closing metathesis of  $\beta$ -myrcene **3** was first achieved with the second generation Grubbs catalyst **Ru4** at 40 °C in decaline as solvent (Scheme 9).<sup>25</sup>

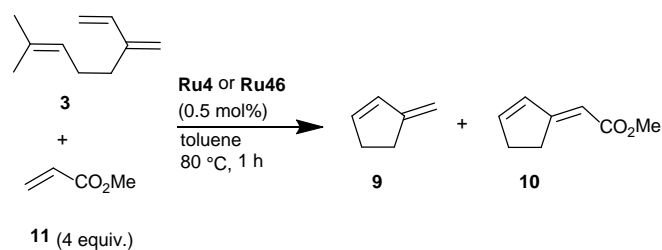




**Scheme 9** Ring closing metathesis of  $\beta$ -myrcene **3** into 3-methylenecyclopentene **9**

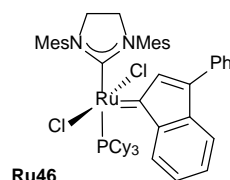
From this triene, a conversion of 68% and an isolated yield of 45% of 3-methylenecyclopentene **9** were obtained after 5 h with a catalyst loading of 0.2 mol%, but full conversion was achieved in the presence of 1 mol% of catalyst. The diene **9** was then used for controlled cationic polymerization with a catalytic system based on  $t$ BuOCH(Cl)Me/ZnCl<sub>2</sub>/Et<sub>2</sub>O in toluene.

Later, it was shown that even in the presence of methyl acrylate as cross metathesis partner, the ring closing metathesis of  $\beta$ -myrcene was favoured over the direct cross metathesis reaction.<sup>26</sup> The first generation Grubbs catalyst **Ru3** was almost inactive for this transformation. Only second generation benzylidene and indenylidene ruthenium catalysts such as **Ru4** and **Ru46** were efficient, leading to almost full conversion of  $\beta$ -myrcene at 80 °C in the presence of 0.5 mol% of catalyst within 1 h with production of **9** in 62-67% GC yields and the cross metathesis product **10** in 13-14% (Scheme 10). A low amount of catalyst (0.25 mol%) favoured the formation of **9** (54%) but the conversion of **3** was lower (64%). Increasing the catalyst loading somehow increased the production of **10** but at the same time led to polymers upon consumption of **2** *via* ring opening. When the ratio  $\beta$ -myrcene **3** /acrylate **11** was varied from 1:2 to 1:16, the ratio of **9** to **10** decreased from 5:74 to 20:47 with an overall full conversion of **3**, but when the proportion of acrylate **11** became too important, products resulting from its self metathesis appeared. Up to 0.5 mol.L<sup>-1</sup> concentration of  $\beta$ -myrcene, no significant effects on reactivity and selectivity were observed, but above this value a drop of the conversion attributed to catalyst inhibition was noted.



**Ru4** : conv. 98%, **9** (62%), **10** (13%)

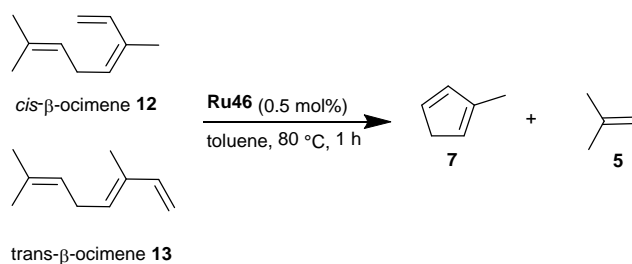
**Ru46** : conv. 95%, **9** (67%), **10** (14%)



**Scheme 10** Ring closing metathesis of  $\beta$ -myrcene **3** in the presence of methyl acrylate **11**

The RCM of the isomers of  $\beta$ -myrcene, *cis*- and *trans*-  $\beta$ -ocimene **12** and **13** in a respective 33:67 ratio (Scheme 11) was then studied in the presence of catalyst **Ru46**. The *cis*-derivative **12** was very reactive and led to 94% conversion after 1 h at 80 °C, whereas only 33% of the *trans*-isomer **13** was converted under the same conditions. However, the yield of the expected 2-methylcyclopentadiene **7** was only 24% indicating that side or subsequent reactions took place.

As compared to  $\beta$ -myrcene, which contains two terminal double bonds, the  $\beta$ -ocimene isomers present only one terminal and an internal double bond in position 3 hindering the necessary conformation for RCM, which seems to have a strong effect on the reactivity and favours the polymerization *via* acyclic diene metathesis with respect to the ring closing metathesis process.



**Scheme 11.** RCM of *cis*- and *trans*-  $\beta$ -ocimene in the presence of **Ru46** as catalyst

## 2 Cross Metathesis (CM)

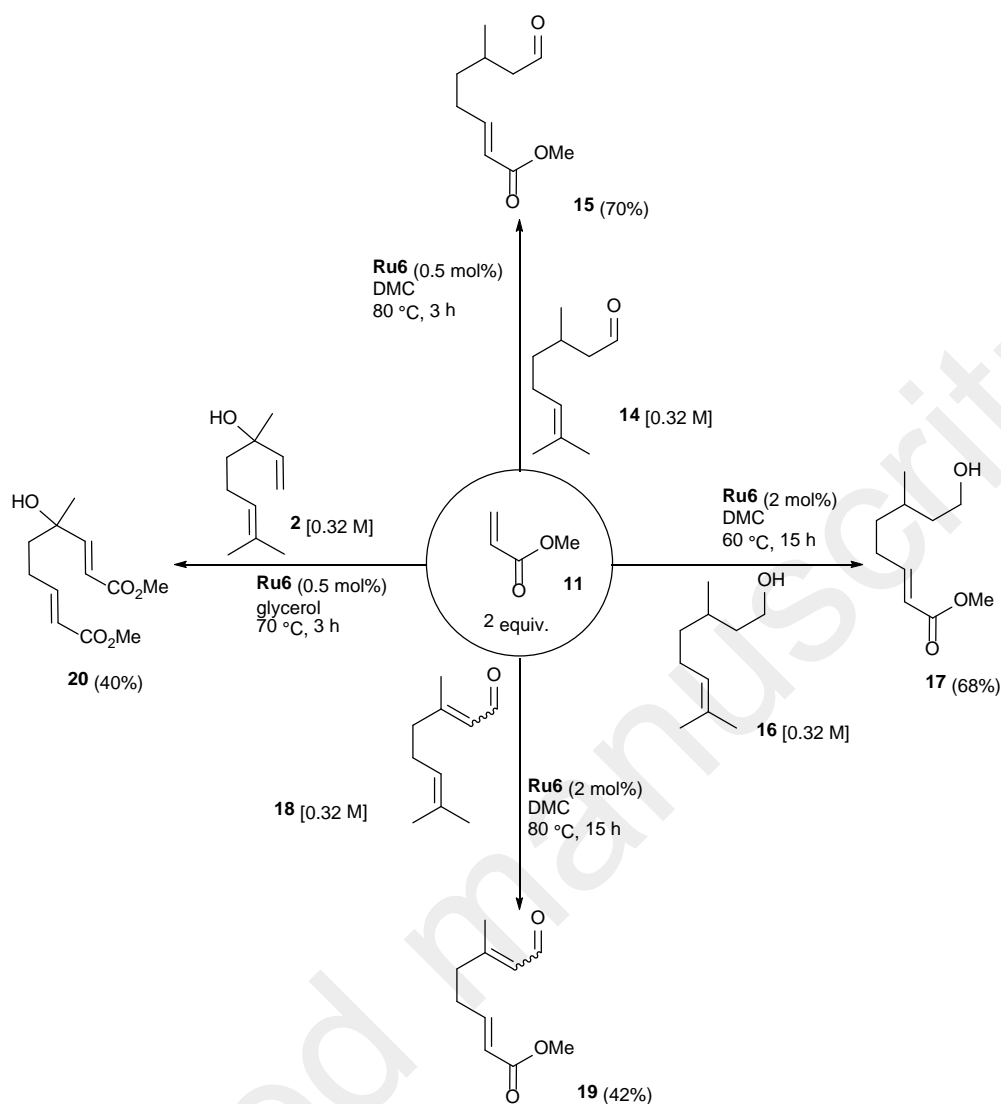
Olefin cross metathesis is a very practical method to introduce functional groups on a hydrocarbon skeleton and to generate higher internal olefins from simple alkenes. The interest of olefin

metathesis for the transformations of terpenoid derivatives into industrially valuable products has been emphasized in a patent.<sup>27</sup> However, although general trends for selective cross metathesis reactions have been proposed,<sup>28</sup> there are not many examples based on terpene derivatives. Three major types of carbon-carbon double bonds are encountered in terpenes: i) monosubstituted terminal double bonds, ii) trisubstituted double bonds featuring two methyl groups in a 2-methylprop-1-en-1-yl (prenyl) arrangement, and iii) internal endocyclic double bonds. According to the classification described in reference 28, the first ones belong to type I olefins and are subject to fast self metathesis but also to cross metathesis with olefins of other types. The second ones are olefins of type III with no possibility of self metathesis but prone to react with olefins of type II such as electron deficient olefins. As far as internal endocyclic double bonds are concerned, they are potential substrates for ring opening metathesis polymerization and copolymerization, and eventually ring opening/cross metathesis sequences.

### 2.1 Cross metathesis of terpenes with electron deficient olefins

The second generation Hoveyda catalysts have been found to be the most efficient catalysts for cross metathesis of terpenes and

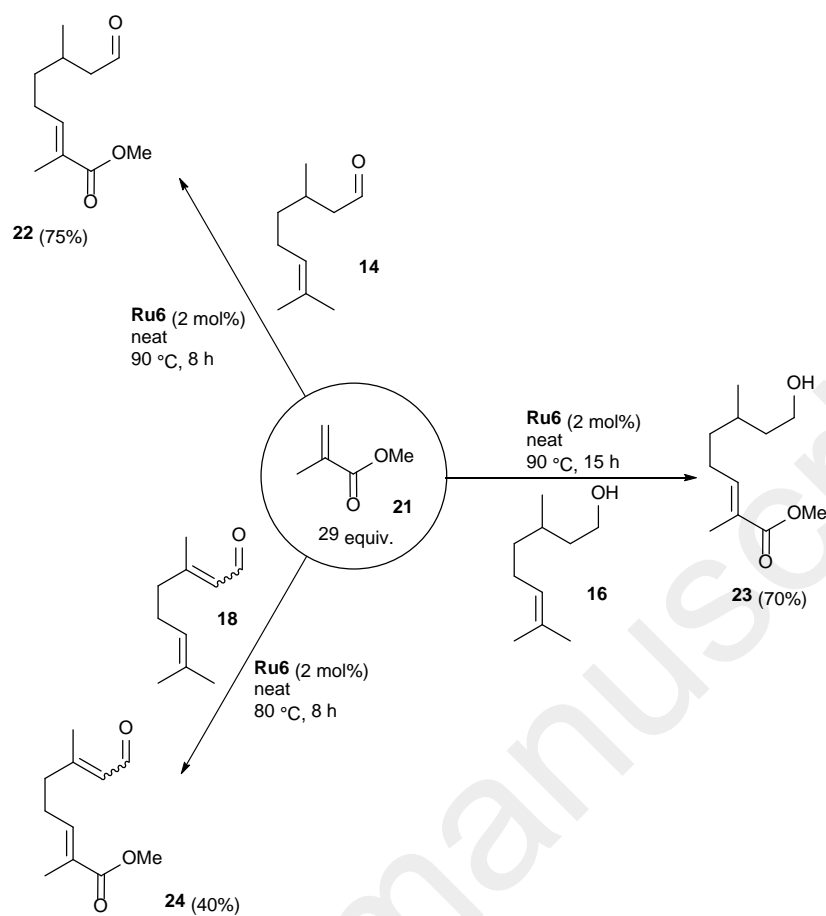
terpenoids with acrylic substrates. We have successfully achieved the cross metathesis of methyl acrylate **11** with the monoterpenes citronellal **14**, citronellol **16** and citral **18** in the presence of catalytic amounts of **Ru6** (0.5 - 2 mol%) in the green solvent dimethyl carbonate (DMC) at 60-80 °C leading to the cross metathesis products isolated in 42-70% yield (Scheme 12).<sup>29</sup> As expected with methyl acrylate as cross metathesis partner, the resulting double bond presented an *E*-configuration, exclusively. Methyl (*E*)-6-methyl-8-oxo-2-octenoate **15** has also been obtained in 40% yield upon cross metathesis of **11** (10 equiv.) and **14** using 2 mol% of **Ru4** as catalyst in refluxing dichloromethane for 1 h.<sup>30</sup> Glycerol has also been used as a green solvent for the cross metathesis of citral, linalool and geraniol. In the presence of 2 equiv. of methyl acrylate and 2 mol% of catalyst **Ru6**, full conversions of these terpenoids were obtained at 60-80 °C within 15 h, but the isolated yields of the expected products from geraniol and citral were modest (below 45%).<sup>31</sup> In the case of linalool the terminal and prenyl double bonds were involved in the cross metathesis process leading to the formation of the 1,9-diester **20** with two (*E*)-double bonds in 40% yield obtained with only 0.5 mol% of catalyst **Ru6** (Scheme 12).



**Scheme 12** Cross metathesis of terpenoids with methyl acrylate

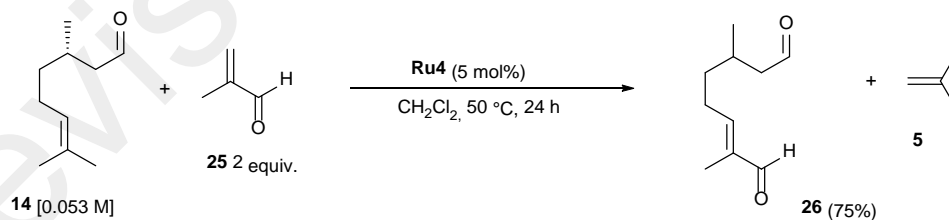
Cross metathesis of the more sterically hindered methyl methacrylate **21** required more demanding conditions in terms of solvents and temperature. We found that the best conditions for the transformation of **14**, **16** and **18** were obtained under neat conditions at 80-90 °C with 2 mol% of catalyst Ru6 (Scheme 13).<sup>29</sup> In these conditions polymerization of methyl methacrylate occurred, which made the isolation of the metathesis products more difficult. Again, the reaction was stereoselective and only the (*E*)-isomers **22**,

**23**, **24** were isolated in 75, 70 and 40% yield, respectively. These products formally correspond to new terpenoids with an oxidized prenyl group obtained without oxidation steps. These reactions constitute a clear example of green catalysis as the new terpenoids **22**, **23**, **24** were obtained in one step without solvent and avoided the usual 2-3 step synthesis with oxidation steps accompanied by production of large amount of wastes.

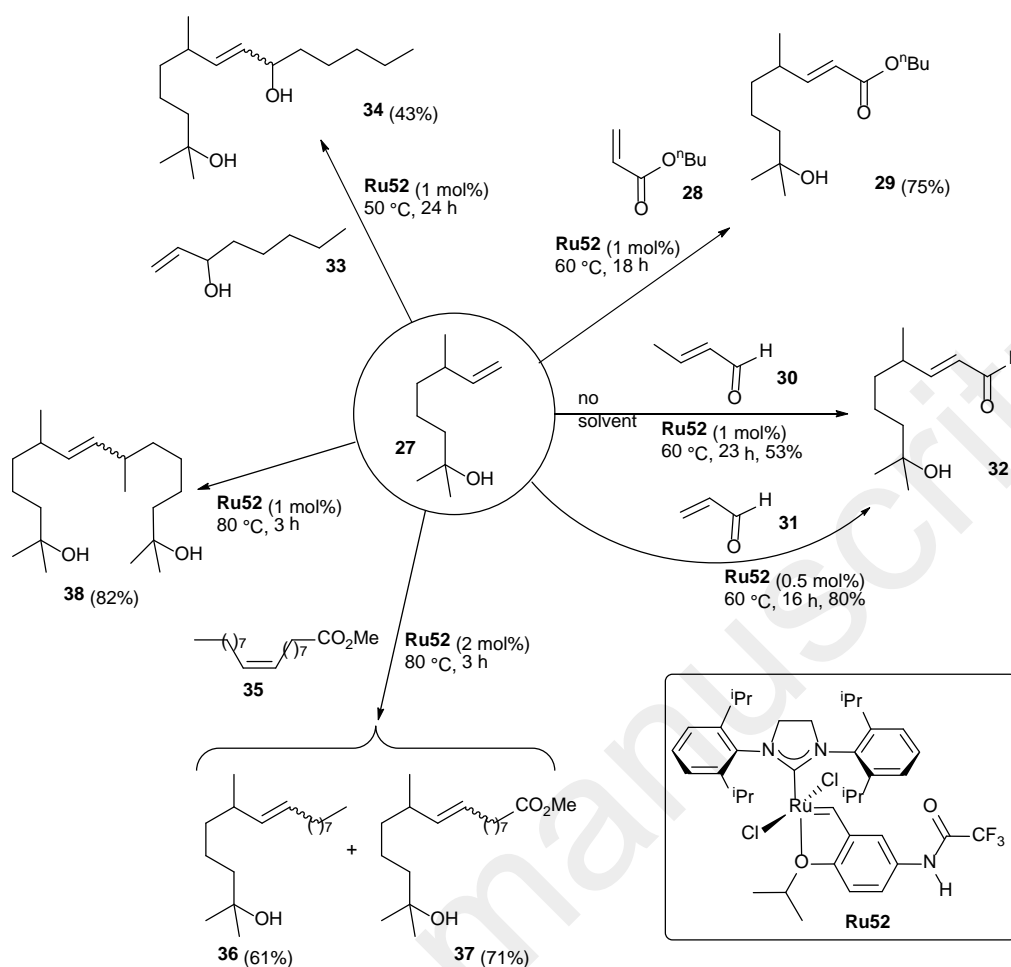


**Scheme 13** Cross metathesis of terpenoids with methyl methacrylate

Cross metathesis of (*S*)-citronellal (**14**) with methacrolein (**25**) was used to produce the optically pure dialdehyde **26** as the first step of the synthesis of the biologically active (-)-fusarisetin A.<sup>32</sup> The reaction was achieved in 75% yield with 5 mol% of the second



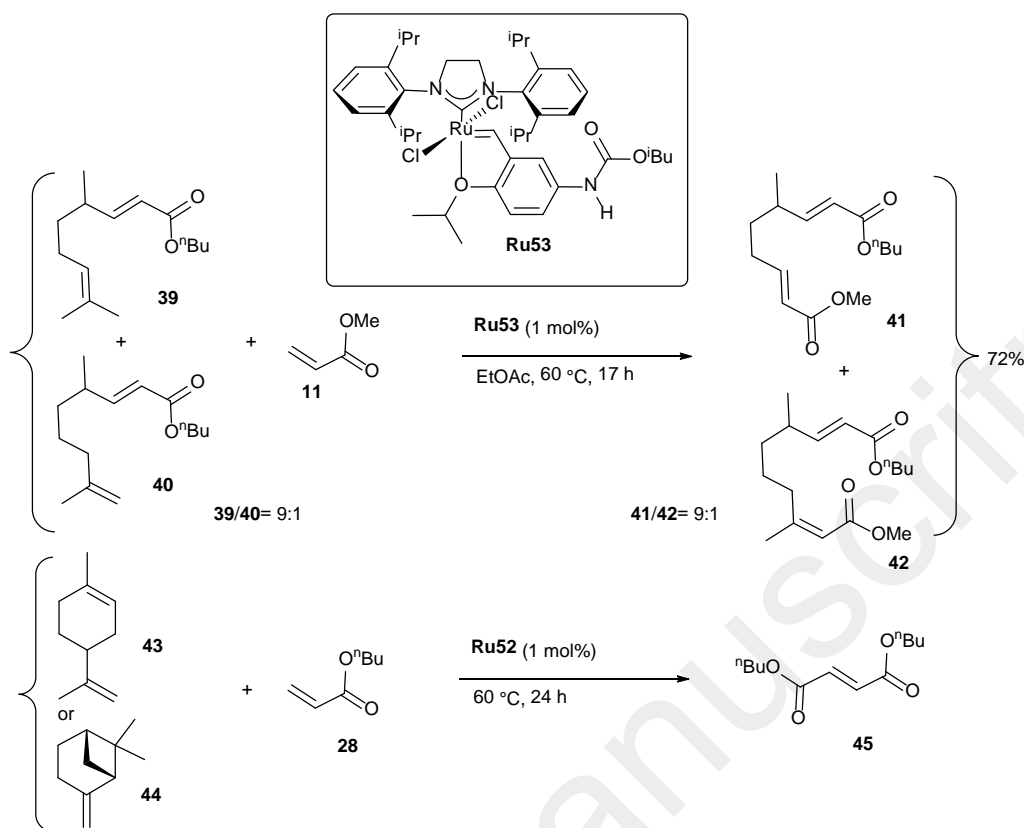
**Scheme 14** Cross metathesis of (*S*)-citronellal with methacrolein



**Scheme 15** Cross metathesis of dihydromyrcenol with various olefins

Dihydromyrcenol **27** is a monoterpene derivative featuring only one terminal double bond that has been used in cross metathesis with various partners.<sup>33</sup> In the presence of 1 mol% of the ruthenium catalyst **Ru52** (Scheme 15), *n*-butyl acrylate **28** provided the (*E*)-isomer **29** after 18 h at 60 °C without solvent. Lower catalyst loading (0.2, 0.5 mol%) were detrimental to the productivity of the reaction. With the same catalyst **Ru52**, cross metathesis performed at 60 °C with crotonaldehyde **30** and acrolein **31** gave the same product, namely (*E*)-8-hydroxy-4,8-dimethylnon-2-enal **32**, with high stereoselectivity (*E/Z*= 95:5 and 94:6, respectively). Acrolein **31** was more reactive than crotonaldehyde **30** as a lower catalyst loading of 0.5 mol% gave **32** in 80% yield after 16 h whereas crotonaldehyde led to 53% yield of **32** after 23 h with 1 mol% of catalyst (Scheme 15).

It is interesting to note that attempts to perform cross metathesis of acrylates with hindered terminal double bonds involved in cyclic terpenes such as limonene **43** or  $\beta$ -pinene **44** have failed and only the self metathesis product of the acrylate **45** was obtained (Scheme 16).<sup>33</sup> On the other hand, it is quite surprising since the cross metathesis of acrylates with acyclic terpenes containing a terminal monosubstituted (**2**, **27** - Schemes 12, 15) or 2,2-disubstituted (**40** - Scheme 16) double bond or a prenyl non terminal double bond (**14**, **16**, **18**, **39** - Schemes 12, 13, 14, 16) have been carried out successfully with second generation Hoveyda catalysts.



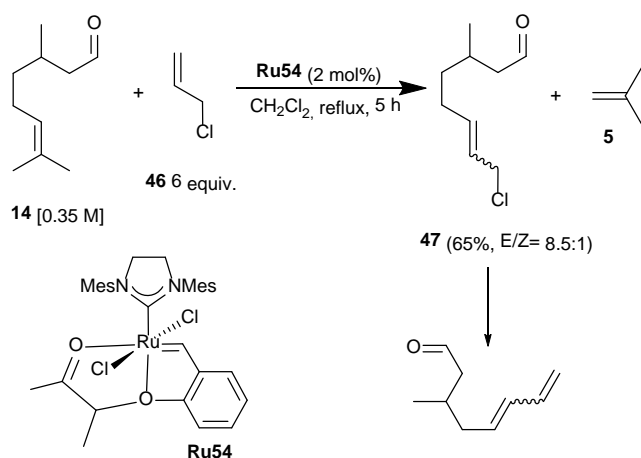
**Scheme 16** Cross metathesis of acrylate with various types of acyclic double bonds

## 2.2 Cross metathesis of acyclic terpenes with terminal and internal olefins

Terminal olefins of type I<sup>28</sup> such as dihydromyrcenol **27** are known to be prone to self metathesis. Indeed, this is verified by the formation of a mixture of stereoisomers of **38** in 82% yield when dihydromyrcenol **27** was treated at 80 °C for 3 h with 1 mol% of catalyst **Ru52** under neat conditions (Scheme 15).<sup>33</sup> When the terminal allylic alcohol **33** (Matsutake alcohol) was used as cross metathesis partner, 43% of **34** was obtained after 24 h at 50 °C. Much better results were obtained with the internal *cis* double bond of methyl oleate **35**. The two products corresponding to the reaction of **27** with each side of the double bond of **35** were

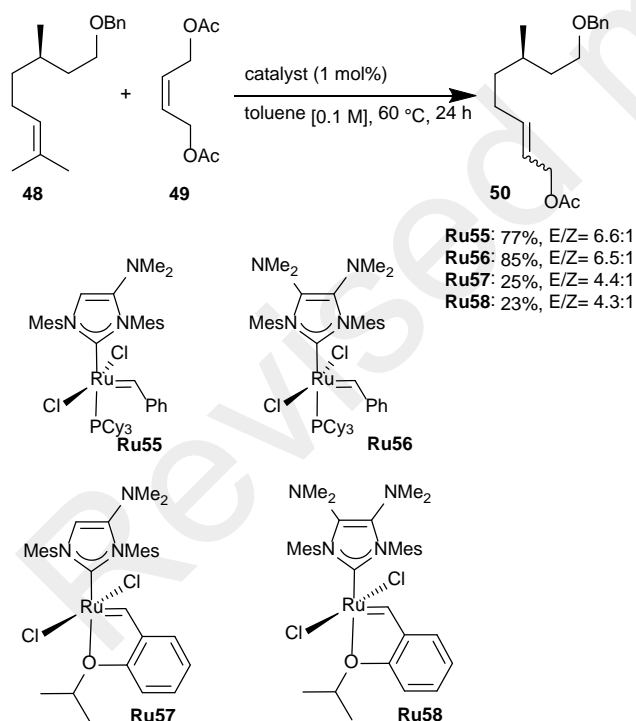
isolated in 61% (**36**) and 71% (**37**) yields (Scheme 15). In this case, the (*E*)-stereoisomers are the major ones (*E/Z*= 86:14 and 87:13) but as expected in a much less pronounced selectivity than with the acrylic electron deficient olefins **11**, **21**, **25**, **28**, **30**, **31**.

In order to prepare dienes from bio-resources using a ruthenium-catalyzed dehydrohalogenation reaction, we prepared the allylic chloride **47** by cross metathesis of citronellal **14** with allyl chloride **47** (Scheme 17).<sup>34</sup> The reaction was performed in refluxing dichloromethane for 5 h in the presence of 2 mol% of catalyst **Ru54** with a 6-fold excess of **46**, and **47** was isolated in 65% yield with a *E/Z* ratio of 8.5:1. The latter can be easily converted into a terminal diene by elimination HCl catalyzed by [Cp\*Ru(MeCN)<sub>3</sub>][PF<sub>6</sub>].



**Scheme 17** Cross metathesis of citronellal **14** with allylchloride

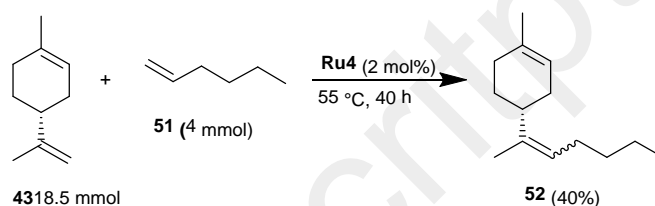
The ruthenium complexes **Ru55-Ru58** featuring 4-NMe<sub>2</sub>-substituted and 4,5-(NMe<sub>2</sub>)<sub>2</sub>-disubstituted imidazolylidene carbene ligands were evaluated in the cross metathesis of citronellol benzyl ether **48** with *cis*-1,4-diacetoxybut-2-ene **49** containing an internal double bond. Under the conditions reported in Scheme 18, the catalysts bearing the non-chelated ruthenium benzylidene moiety showed much better reactivity leading to 77 and 85% yield of **50** with **Ru55** and **Ru56**, respectively.<sup>35</sup>



**Scheme 18** Cross metathesis of citronellol benzyl ether **48** with *cis*-1,4-diacetoxybut-2-ene **49**

### 2.3 Cross metathesis of cyclic terpenes

Cyclic terpenes are more sterically hindered than the acyclic ones, and the access to the reactive catalytic center might be difficult in some cases. For instance, the lack of reactivity of limonene and  $\beta$ -pinene with *n*-butyl acrylate has been shown (Scheme 16).<sup>33</sup> However, with the non-functional terminal olefin 1-hexene **53**, limonene reacted in the presence of 2 mol% of **Ru4** at 55 °C without solvent to give the cross metathesis product **54** in 40% yield (Scheme 19).<sup>36</sup>

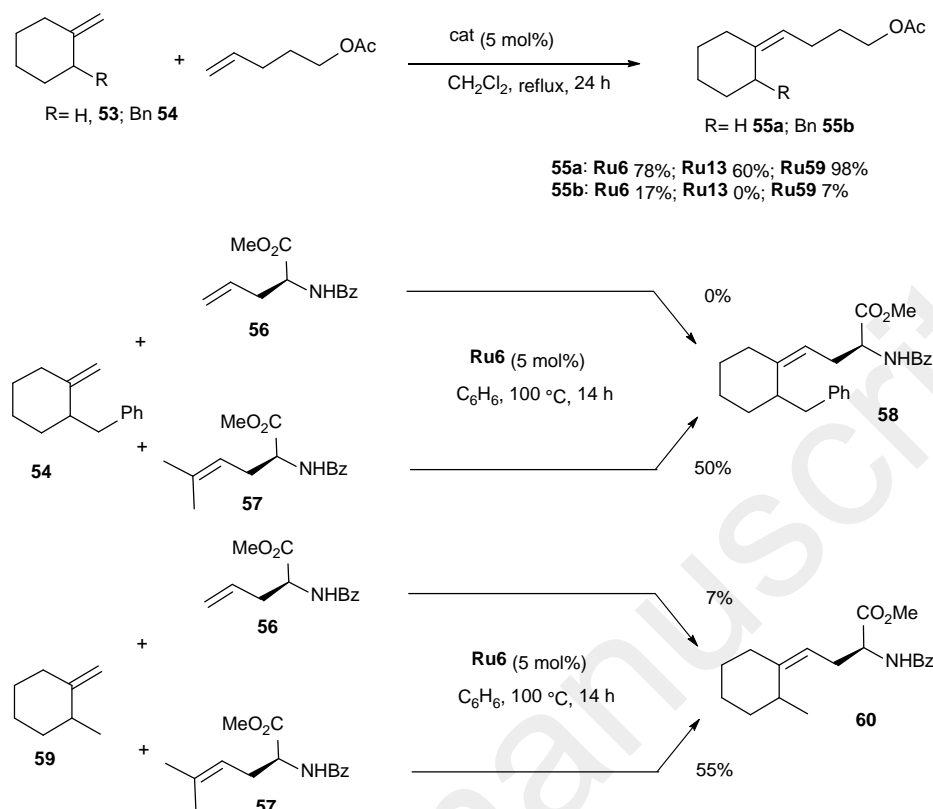


**Scheme 19** Cross metathesis of (*D*)-limonene with 1-hexene

This reactivity of limonene with a terminal olefin has been extended to the production of co-oligomers with 1,5-hexadiene in the presence of **Ru4** (1 mol% with respect to the diene) in an excess of limonene as solvent (30 equiv.) at 45 °C. Polyhexadiene was formed together with hexadiene oligomers featuring one or two limonene ends, the proportions of which depended on the 1,5-hexadiene concentration.<sup>36</sup>

It has been shown that cross metathesis of the exocyclic double bond of methylenecyclohexane **53** with the terminal double bond of 5-acetoxy-1-pentene could be achieved efficiently in refluxing dichloromethane for 24 h with various second generation catalysts such as **Ru6**, **Ru13** and their analog equipped with a 1,6-diisopropylphenylimidazolylidene carbene **Ru59** with a catalyst loading of 5 mol%.<sup>37</sup> However, the strong influence of the steric hindrance introduced by a benzyl substituent close to the double bond of methylenecyclohexane in **54** was obvious with a drastic decrease of the yields in **55b** as compared to **55a** from 78 to 17% with **Ru6**, 60 to 0% for **Ru13** and 98 to 7% for **Ru59** (Scheme 20).<sup>37</sup> The same absence of reactivity of 2-benzyl-1-methylenecyclohexane **54** was observed with **Ru6** (5 mol%, 100 °C in benzene) when protected allylglycine **56** was used as cross metathesis partner.<sup>38</sup> However, it was possible to produce **58** from the bulky cyclohexane derivative by replacing the terminal double bond of the allyl group of **56** by the geminal dimethyl analogue in prenylglycine **57**. Using a large excess of **54** (30 equiv.), the cross

metathesis was achieved in 50% yield. The less hindered methylene-substituted methylenecyclohexane **59** exhibited a similar behavior with the cross metathesis partners **56** and **57** to lead to **60** (Scheme 20).

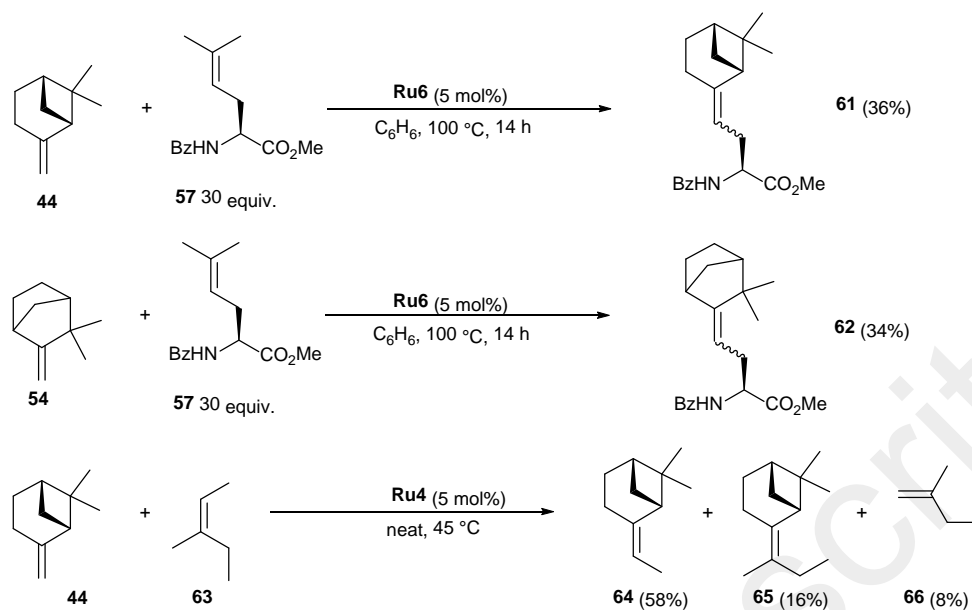


**Scheme 20** Influence of steric hindrance on cross metathesis efficiency

Gratifyingly, this strategy was applied with success for the cross metathesis of bulky terpenes featuring a methylene substituent of a bicyclic structure. Indeed,  $\beta$ -pinene **44** and camphene **54** reacted with prenylglycine **57** in the presence of catalyst **Ru6** to give the cross metathesis products **61** and **62** as mixtures of *E*- and *Z*-isomers in 36 and 34% yield, respectively (Scheme 21).<sup>38</sup> Again, with these terpenes, the reaction with the allylglycine partner **56** failed. The cross metathesis with the aliphatic internal olefin (*Z*)-3-methylpent-2-ene with  $\beta$ -pinene has been carried out with 5 mol% of catalyst **Ru4** at 45 °C without solvent and the two possible cross metathesis products **64** and **65** have been observed (Scheme 21).<sup>39</sup> The general idea to make these cross metathesis reactions with

bulky double bonds successful was to favour the productive pathway with respect to the non-productive one by playing on the steric parameters of the cross metathesis partner e. g. on increasing the substitution pattern of the double bond. In this respect, the cross metathesis of  $\beta$ -pinene appeared to be more efficient with a trisubstituted internal olefin as cross metathesis partner (Scheme 21). This is in line with the computational studies, which indicated that non-productive metathesis of  $\beta$ -pinene in the presence of another olefin takes place in the presence of second generation ruthenium catalysts *via* formation of a carbene involving the pinene substrate, and that its self metathesis does not occur because it is inhibited both by kinetic and thermodynamic factors.<sup>7</sup>





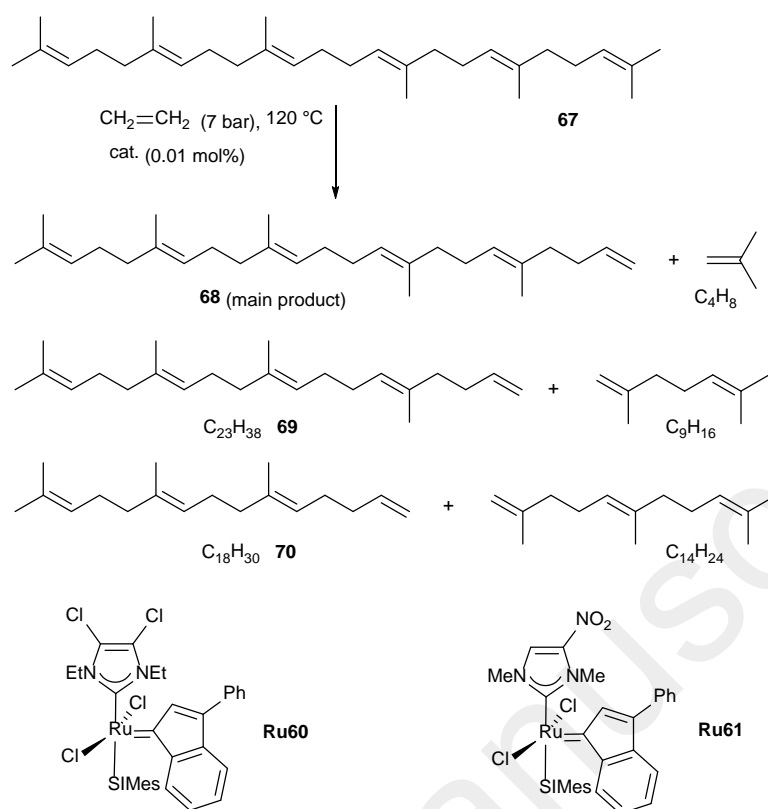
**Scheme 21** Cross metathesis involving  $\beta$ -pinene **44** and camphene **54**

#### 2.4 Cross metathesis with ethylene: ethenolysis for terpene scission

Productive ethenolysis takes place between an internal olefin and ethylene and leads to the cleavage of the internal double bond to give two terminal olefins. This simple cross metathesis reaction has found applications for the scission of long chain unsaturated molecules and polymers, and has made possible the preparation of

dienes from cyclic alkenes. In particular, it has recently found useful applications in the field of natural products transformations.<sup>40,41</sup>

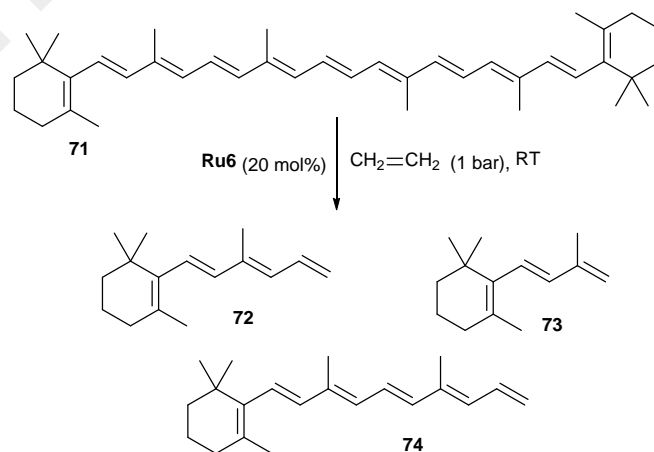
Ethenolysis of the squalene **67**, the  $\text{C}_{30}\text{H}_{50}$  triterpene containing six isoprene units has been carried out with ruthenium indenylidene complexes equipped with two different NHC carbenes (Scheme 22).<sup>42</sup>



**Scheme 22.** Primary ethenolysis products from squalene

The ruthenium complexes **Ru60** and **Ru61** used at 0.01 mol% loading were the most efficient catalysts for the cleavage of the trisubstituted double bonds of these substrates under 7 bar of ethylene in toluene at  $120\text{ }^\circ\text{C}$ . The high amount of  $\text{C}_{28}\text{H}_{46}$  **68** as compared to  $\text{C}_{23}\text{H}_{38}$  **69** and  $\text{C}_{18}\text{H}_{30}$  **70** indicated that ethenolysis preferably occurred at the external double bonds rather than in the core of the molecule (Scheme 22).<sup>42</sup>

$\beta$ -Carotene **71** is a tetraterpene based on two cyclohexenyl rings connected by a C18 chain composed of 9 conjugated *trans* carbon-carbon double bonds that contains alternating 1,1,2-trisubstituted and 1,2-disubstituted double bonds. Some double bond cleavage were observed when **Ru6** was used as catalyst in toluene under bubbling ethylene at room temperature.<sup>43</sup> The first cleavage provided the tetraene **72**, whereas the triene **73** and the hexaene **74** were formed only after one hour of reaction (Scheme 23). It is noteworthy that the first scission did not involve the most accessible central *trans* 1,2-disubstituted double bond.



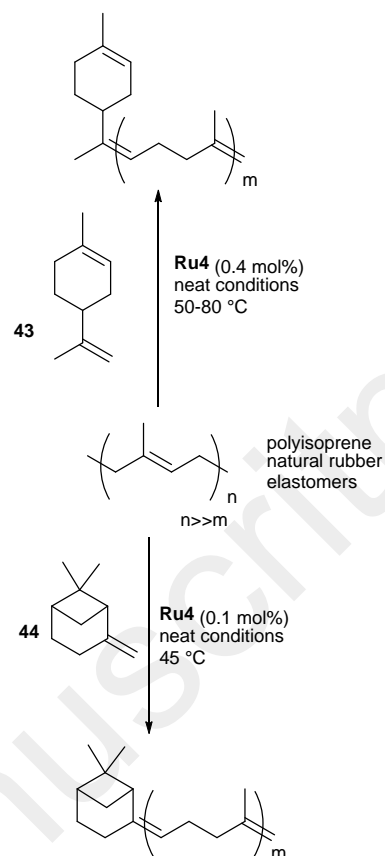
**Scheme 23.** Ethenolysis of  $\beta$ -carotene **71**

The selective scission of carbon-carbon double bonds by cross-metathesis with short alkenes has been advantageously used to degrade elastomers such as polyisoprene natural rubber, and synthetic polyolefins including polyisoprene and copolymers into shorter polymers and small molecules with various catalysts based on molybdenum, tungsten and ruthenium.<sup>44,45</sup> Initially tungsten salts associated with  $\text{AlCl}_2\text{Et}$  were used for the degradation of

polyisoprene and natural rubber by self metathesis in the absence of an external olefin,<sup>46</sup> and the second generation **Ru4** catalyst was used for the degradation of polyisoprene-polystyrene-polyisoprene block polymers.<sup>47</sup> Then, treatment of poly-*trans*-isoprene and a polystyrene/polybutadiene diblock copolymer, under 1-6 bar ethylene pressure in the presence of the well-defined  $(\text{Me}(\text{F}_3\text{C})_2\text{CO})_2\text{W}(\text{=N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3))(\text{=CHCMe}_2\text{Ph})$  catalyst **W2** yielded low molecular weight oligomers and small amounts of  $\alpha,\omega$ -alkadienes.<sup>48</sup> Degradation of *trans*-1,4-polyisoprene under ethenolysis conditions has also been performed with ruthenium catalyst.<sup>39,49</sup> For instance, ethenolysis of *trans*-1,4-polyisoprene was very fast with the ruthenium catalyst **Ru4**, which depolymerized a polymer with high molar mass of 400 000 g/mol into oligomers of low molar mass of 500 g/mol after 2 h at 60 °C in toluene with a (isoprene units)/catalyst ratio of 200.<sup>50</sup> Catalysts **Ru60** and **Ru61** (Scheme 22) were also efficient for depolymerization of natural rubber in the presence of ethylene with a catalyst loading of 0.1 mol% per double bond.<sup>42</sup> Catalyst **Ru60** as well as **Ru6** have been successfully employed for ethenolysis of end-of-life tire granulates leading to about 50 weight% of the substrates converted into organic soluble products.<sup>51</sup>

Depolymerization of cross-linked styrene-isoprene copolymers by ethenolysis was investigated in the presence of  $(\text{Me}(\text{F}_3\text{C})_2\text{CO})_2\text{Mo}(\text{=N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3))(\text{=CHCMe}_2\text{Ph})$  **Mo1**, **Ru3** and **Ru4**. Under low pressure of ethylene at 20 °C, catalyst **Ru4** made possible the scission of the trisubstituted double bonds of cross-linked polyisoprene to form soluble oligomers in short reaction times at room temperature.<sup>52</sup>

It must be noted that not only ethylene has been used for polyolefin including polyisoprene degradation but also other internal olefins in the presence of ruthenium catalysts **Ru3** and **Ru4**.<sup>53</sup> Even D-limonene<sup>54</sup> and  $\beta$ -pinene<sup>39</sup> have been used in cross metathesis with polyisoprene for the synthesis of terpene-terminated oligomers (Scheme 24). A protocol involving cross metathesis with *cis*-1,4-diacetoxybut-2-ene / hydrogenation of natural rubber in the presence of **Ru4** provided hydrogenated oligomers.<sup>55</sup>



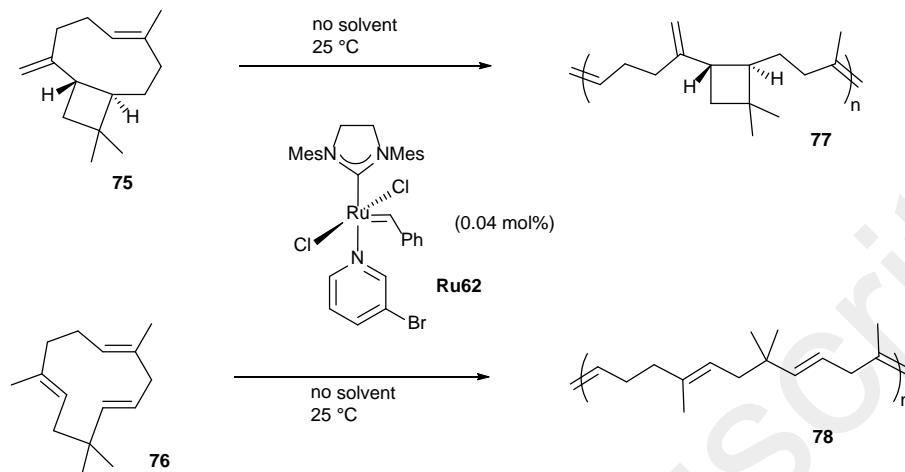
**Scheme 24** Cross metathesis of polyisoprene with D-limonene **43** and  $\beta$ -pinene **44**

Opening of the cyclohexene ring, which is a common substructure of cyclic monoterpenes, by ethylene under metathesis conditions to form 1,7-octadiene has just been reported with a heterogeneous ruthenium catalyst operating under flow conditions,<sup>56</sup> but no application to terpene is reported so far. It must be noted here that ruthenium complexes equipped with a CAAC ligand (CAAC: CycloAlkylAminoCarbene), which generate the most efficient catalysts in ethenolysis of long chain fatty acid derivatives<sup>57</sup> have not been evaluated with terpene substrates.

### 3. Ring opening metathesis polymerization

Polymerization of strained cyclic structures under metathesis conditions is very common with norbornene derivatives,<sup>58</sup> but has been much less studied with less strained monomers in particular with terpenes. Recently, the ring opening metathesis of the sesquiterpenes caryophyllene **75** and humulene **76** has been reported.<sup>59</sup> The first generation ruthenium complexes **Ru3** and **Ru5** were inactive for this metathesis transformation and the second

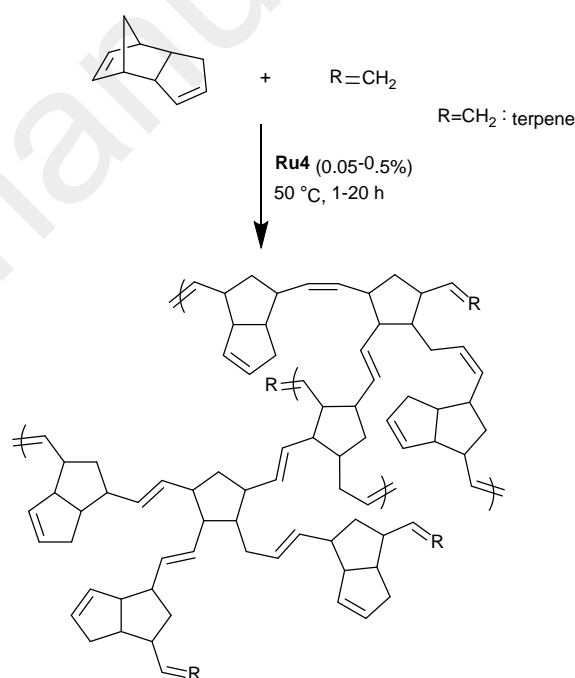
generation catalysts **Ru4** and **Ru62** appeared to be the most active ones (Scheme 25). Complete conversion of **75** was achieved even with 0.04 mol% of **Ru62** at 25 °C and its exocyclic methylene group was not involved in the polymerization process. Only trisubstituted double bonds were involved in the polymerization.



**Scheme 25** Ring opening metathesis of two sesquiterpenes

It can be noted that the ring opening metathesis polymerization of apopinene, exhibiting a polycyclic structure derived from  $\alpha$ -pinene, was successfully achieved with second and third generation benzylidene ruthenium Grubbs catalysts (**Ru4**, **Ru6**,  $(\text{RuCl}_2(=\text{CHPh})(\text{H}_2\text{IMes})(3\text{-Br-Py})_2)$ ) leading to a polyolefin incorporating a cyclobutane ring.<sup>60</sup>

Finally, functional hyperbranched polymers have been produced *via* ring opening metathesis polymerization of dicyclopentadiene in the presence of terpenes (Scheme 26). D-Limonene, limonene oxide,  $\beta$ -pinene, carvone have been used as chain transfer agent to modify the physical properties and thermal stability of thermosets based on polydicyclopentadiene.<sup>61,62</sup>



**Scheme 26** Example of branched polymers obtained by ROMP of dicyclopentadiene in the presence of terpenes.

## Conclusion

Transformations of terpenes by olefin metathesis processes can take place at any type of carbon-carbon double bond of these substrates. From 1,6-dienes, the ring closing metathesis easily

affords cyclopentene derivatives as observed with citronellene, linalool, myrcene, and ocimene. This RCM reaction often competes with other metathesis reaction such as cross metathesis with functional olefins.

Terminal double bonds of acyclic terpenes are prone to cross metathesis with other olefins as well as to self metathesis.

Cross metathesis with acrylic olefins have been achieved with the monosubstituted terminal double bonds and trisubstituted prenyl double bonds of terpenes, mainly with second generation ruthenium catalysts.

Cross metathesis of bulky cyclic terpenes is more difficult and requires olefin partners favouring the productive cross metathesis versus the non-productive one.

The special case of cross metathesis with ethylene has been used for degradation of long chain polyunsaturated terpenes such as  $\beta$ -carotene and squalene, as well as polyisoprene and polymers containing polyisoprene blocks. It has notably been applied to the degradation of end-of-life tire granulates.

As far as ring opening metathesis polymerization is concerned, it seems that only the case of caryophyllene and humulene is reported.

It appears that terpenes have not been extensively studied in olefin metathesis transformations and that future applications have to be discovered, including couplings with other unsaturated natural resources such as fatty acid derivatives and phenylpropenoids arising from lignin.

Finally, the efficiency of olefin metathesis for the selective transformation of terpenes offers straightforward and green processes for the access to value-added products from bio-sourced substrates extracted from renewables.

## Conflicts of interest

There are no conflicts to declare.

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