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# In Situ Generation of Ru-Based Metathesis Catalyst. A Systematic Study

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**KEYWORDS:** Olefin metathesis, Ruthenium, Arene complexes, in situ, NHC ligand

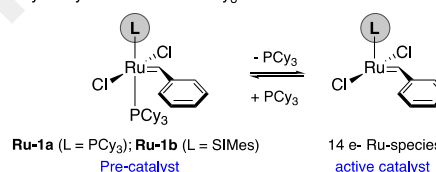
**ABSTRACT:** A practical and cost-effective protocol for the in situ generation of Ru-based metathesis catalysts was developed. Assembly of commercially available and inexpensive reagents [Ru(*p*-cymene)Cl<sub>2</sub>]<sub>2</sub>, SIPr.HCl and *n*-BuLi led to the formation of 18 electron arene-ruthenium complexes that, in the presence of additives such as alkynes, cyclopropenes and diazoesters, generated highly selective and efficient catalytic systems applicable to a variety of olefin metathesis transformations. Notably, we were able to achieve a productive TON of 4500 for the self-metathesis of methyl oleate, a reaction which could be easily upscaled to 2 kg.

Since its discovery in the mid 1950's, the metathesis reaction gained significant importance for organic syntheses and polymer chemistry.<sup>1</sup> In its early days, the metathesis reaction relied on ill-defined in situ generated catalysts. Only upon the emergence of well-defined air stable Ru-complexes, such as the Grubbs 1<sup>st</sup> generation **Ru-1a**, and the more performant Grubbs 2<sup>nd</sup> generation **Ru-1b** containing an *N*-heterocyclic carbene (NHC) ligand, olefin metathesis started to significantly impact organic synthesis.<sup>2</sup> Since then the field has grown steadily, resulting in numerous applications for both academia and industry.<sup>3</sup> An early mechanistic study from Grubbs demonstrated that **Ru-1a,b** are in fact precatalysts which, only after dissociation of the PCy<sub>3</sub> ligand, provide the corresponding catalytically active 14-electron benzylidene-ruthenium species (Figure 1-A).<sup>4</sup> Obviously the dissociated ligand (e.g. PCy<sub>3</sub>) is no longer needed in the catalytic cycle and has been shown to even be involved in catalyst decomposition.<sup>5</sup> In the light of this, several research groups were interested to develop the in situ formation of metathesis active species from alkylidene-free Ru-precatalysts. In that respect, the 18-electron phosphine-based *p*-cymene-ruthenium complex **Ru-2**,<sup>6</sup> and its NHC ligated congeners **Ru-3**,<sup>7</sup> **Ru-4**<sup>8</sup> and **Ru-5**<sup>9,10</sup> showed metathesis activity in the presence of carbene activator (Figure 1-B).<sup>11</sup> This in situ protocol was successfully illustrated in ring-opening metathesis polymerization (ROMP),<sup>6a,12</sup> self-metathesis<sup>13,14d</sup> and ring-closing metathesis (RCM) reactions.<sup>14</sup> Of note, Thieuleux and Basset demonstrated by <sup>1</sup>H-NMR studies that the self-metathesis of ethyl oleate with PCy<sub>3</sub>-based complex **Ru-2** and (trimethylsilyl) diazomethane (TMSD) as carbene activator generated the same observable resting states as the Grubbs-1 catalyst (**Ru-1**).<sup>13</sup> Moreover, independent studies by Fürstner<sup>15</sup> and Noels<sup>12d,16</sup> showed that light could also initiate metathesis reactions with 18-electron arene-ruthenium complexes (e.g. **Ru-2**). More recently, Lewis acid assisted activation of 18-electron arene-ruthenium complexes containing various unsaturated NHCs was reported by Beller and coworkers as well as the influence of trace impurities upon metathesis activity.<sup>17</sup> Despite all these cost-effective methodologies to furnish active metathesis species from simple 18-electron Ru-complexes, few drawbacks merit to be solved to render this protocol more attractive. For instance, the most efficient **Ru-5**

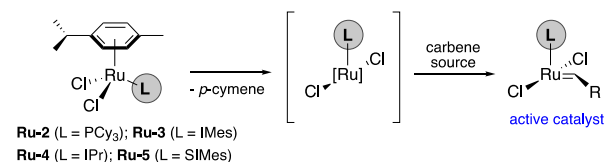
containing the saturated NHC ancillary ligand (SIMes) is quite unstable and remains difficult to isolate.<sup>10,18</sup> Inspired by the pioneering work of Grubbs,<sup>14a</sup> Noels<sup>14c,16</sup> and Dixneuf<sup>14b</sup> we opted for a systematic study to generate 14 electron active species by simply mixing a Ru(II) salt, an ancillary NHC precursors and a carbene activator, thus avoiding any isolation steps of unstable complexes (Figure 1).

• Previous works:

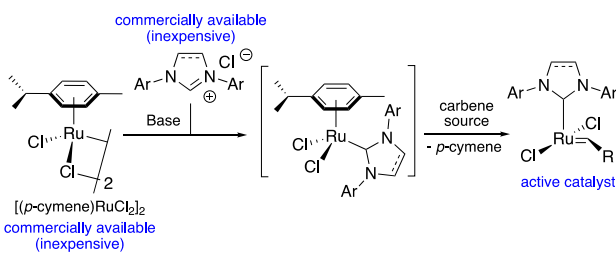
(A) Formation of 14-electron Ru-active species from well-defined Ru-benzylidene precatalysts by dissociation of PCy<sub>3</sub>



(B) Formation of 14-electron Ru-active species from 18-electron Ru-complexes by dissociation of *p*-cymene in presence of carbene source



• This work: In-situ formation of 14-electron Ru-active species from commercially available [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> and azolium NHC precursors

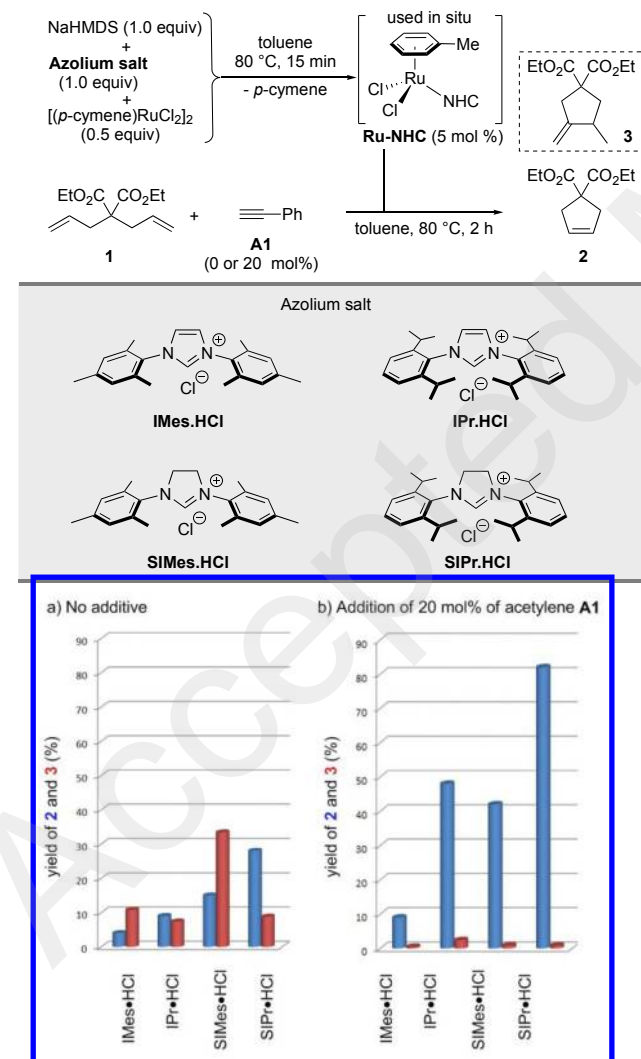


**Figure 1.** Previous strategies used for the formation of 14-electron Ru-active species toward olefin metathesis (A and B). The proposed synthetic route involving inexpensive commercially available reagents (this work). SIMes = *N,N'*-bis-mesityl-imidazolin-2-ylidene

IMes = *N,N'*-bis-mesityl-imidazol-2-ylidene, IPr = *N,N'*-bis-2,6-*i*-Pr-C<sub>6</sub>H<sub>3</sub>-imidazol-2-ylidene.

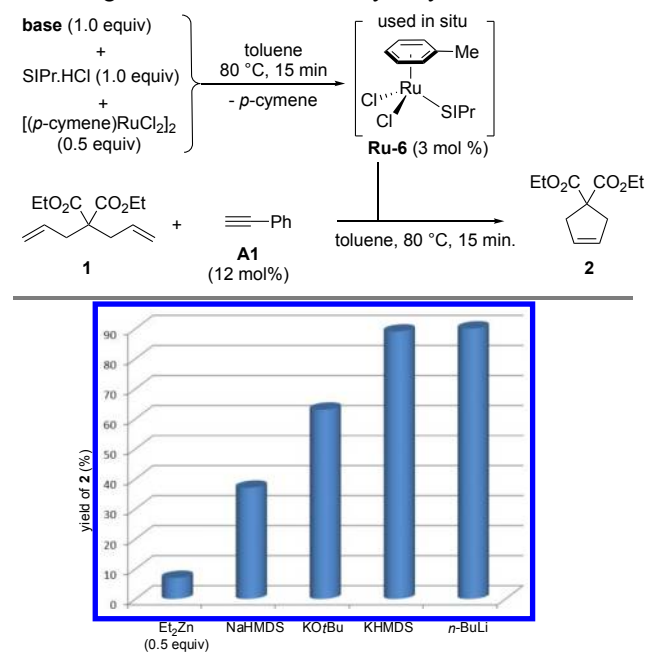
We report herein that transient alkylidene Ru-species may be readily formed by mixing inexpensive commercially available [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub>,<sup>19</sup> an azolium salt, a base and a carbene activator (Figure 1-this work). The choice of the base and the activator appeared to be pivotal factors in the quest for highly active catalytic species towards the targeted metathesis transformation. Furthermore, the results of this systematic approach led to the development of in situ made ruthenium-catalysts exhibiting catalytic performances that can compete with some well-defined 1<sup>st</sup> generation catalysts (e.g. **Ru-1a**).

We began our study by in situ generation of ruthenium arene complex **Ru-NHC** from four commercially available azolium salts which were deprotonated with NaHMDS and then exposed to [(*p*-cymene)RuCl<sub>2</sub>] (Figure 2).<sup>20</sup> There is literature precedent on the exchange of *p*-cymene to deuterated benzene and based on this observation,<sup>9</sup> it is reasonable to assume that *p*-cymene is rapidly replaced by toluene at 80 °C.<sup>21</sup> The solution of the in situ generated 18-electron complex **Ru-NHC** was then immediately tested for the ring-closing metathesis (RCM) of diethyl diallylmalonate **1**.



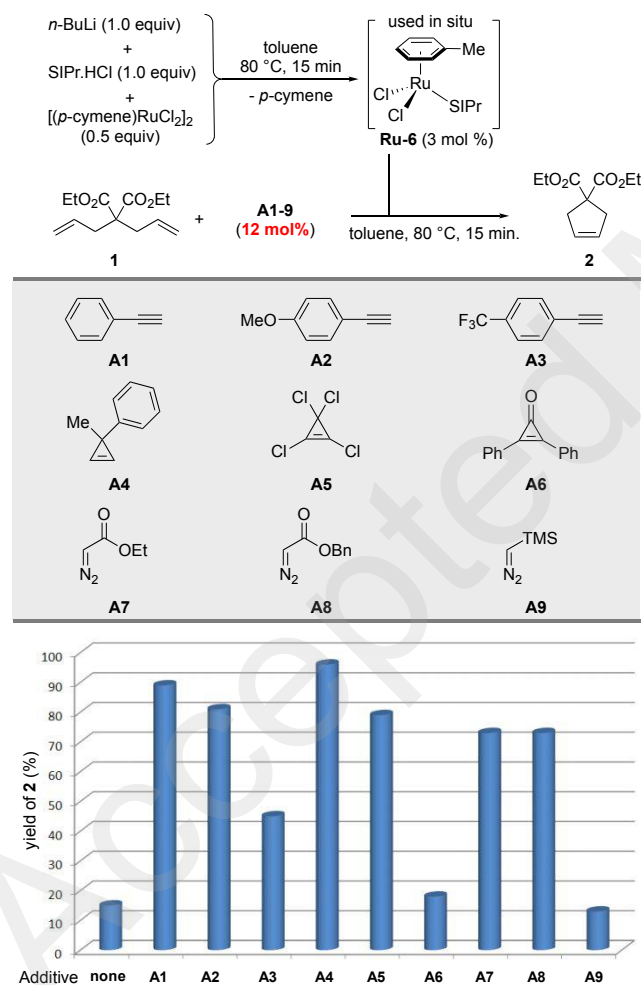
**Figure 2.** Ratio of RCM-product **2** (blue) and cycloisomerization product **3** (red) in the absence (a) and in the presence (b) of phenyl acetylene **A1**. SIPr = *N,N'*-bis-2,6-*i*-Pr-C<sub>6</sub>H<sub>3</sub>-imidazol-2-ylidene.

This reaction was carried out in the presence (Figure 2-a) and absence (Figure 2-b) of phenyl acetylene **A1**,<sup>20</sup> which has been previously described as a convenient and efficient activator.<sup>14c,d</sup> In the absence of phenylacetylene, the use of SIPr.HCl salt as NHC precursor afforded the highest selectivity towards the metathesis product **2** (Figure 2-a). In fact, the noticeable activity observed using SIMes ligand precursor led mostly to the cycloisomerization product **3**. Interestingly, in all examined cases a strong enhancement of the metathesis reactivity and selectivity could be observed upon the addition of 20 mol% of phenyl acetylene,<sup>14c,d</sup> with the SIPr-based complex demonstrating the highest catalytic activity (Figure 2-b). It should be noted that a reduction of the 4:1 phenyl acetylene:ruthenium ratio significantly lowered yields and selectivities towards the metathesis product **2** (see Supporting Information; SI). Encouraged by these initial results, we decided to further investigate the influence of the base on the outcome of the metathesis reaction. Therefore, the catalytic activity obtained with 3 mol% of SIPr-based complex generated using NaHMDS was compared in terms of efficiency to catalytic systems generated from the use of other bases such as ZnEt<sub>2</sub>, KHMDS, *n*-BuLi and KOtBu (Figure 3). The catalytic systems generated from the various bases evidenced tremendous metathesis activity differences after 15 min of reaction. Whereas Et<sub>2</sub>Zn gave a very modest 7% yield of the desired RCM-product **2**, NaHMDS and KOtBu gave significantly improved results (37% and 63% yield). The best performances were obtained with KHMDS and *n*-BuLi (~90 % GC-yield), which compare favorably to the previous procedure described by Grubbs requiring prolonged reaction times and higher catalyst loading for similar results (5 mol%, 10 h).<sup>14a</sup> With the objective to provide catalytic systems of broad application, we therefore decided to continue our study with *n*-BuLi, which has the advantage of only producing butane and LiCl side products with low potential for interfering with the metathesis catalytic cycle.



**Figure 3.** Influence of the base on the catalytic efficiency after 15 min in the RCM of diethyl diallylmalonate **1** using 3 mol% of in situ generated **Ru-6**. In all cases, the **2:3** ratio was >98:2.

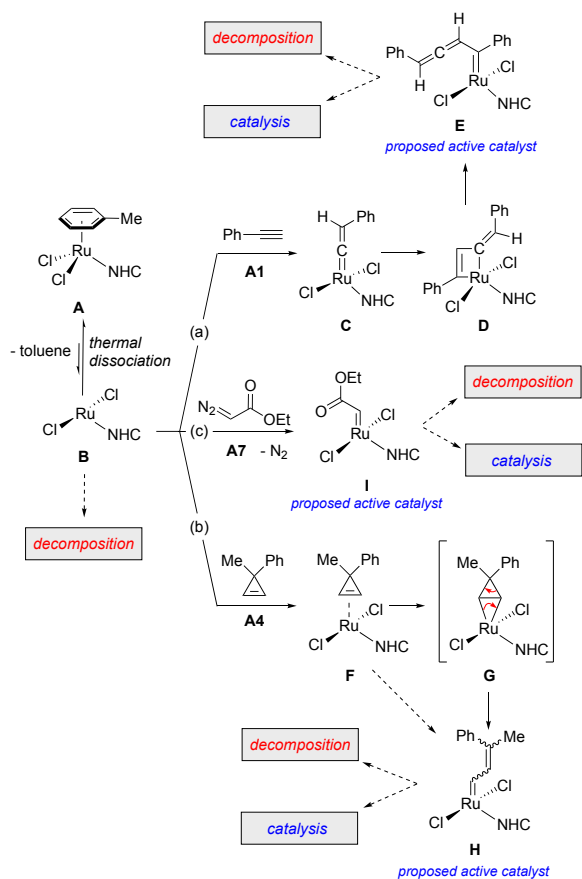
Next, we evaluated and compared the catalytic activity resulting from the use of nine different activators; 3 representatives of each activator type shown in Figure 4. First, the electronic properties of alkyne activators demonstrated an influence on the catalyst activity. While electron neutral or rich alkynes (**A1** and **A2**) afforded the desired RCM product **2** in good 87 and 79% yield, modest 42% yield was obtained with the electron poor alkyne **A3**. Then, cyclopropenes additives, which have never been previously considered as activator for 18 electron arene-ruthenium complexes, proved beneficial to the performance of the metathesis reaction. Again, the electronic property of the carbene source is reflected in the catalytic activity: electron rich cyclopropene **A4**<sup>22</sup> generated a metathesis catalytic system, affording product **2** in high 96% yield, whereas the more electron deficient cyclopropenes **A5** and **A6** gave inferior results. Finally, the addition of diazocompounds such as **A7** or **A8** showed similar activity to produce the RCM product in 70% yield, whereas TMSD (**A9**) gave only sluggish reactivity.



**Figure 4.** Screening of activators for the RCM of diethyl diallylmalonate **1**.

Concerning the activation of 18 electron arene-ruthenium-complex **Ru-6** with alkyne, cyclopropene and diazo activators we propose the mechanistic scenarios described in Scheme 1. Based on the work of Werner<sup>23</sup> and Ozawa<sup>24</sup> on vinylideneruthenium complexes it was speculated in the past that the addition of alkynes to 18 electron Ru-complexes would lead to vinylidene species as the active catalyst.<sup>14</sup> However, recent reports by Delaude on homobimetallic ruthenium complexes suggest that the initially generated vinylidene species **C** undergoes ene-yne metathesis with excess alkyne to produce after cycloaddition/cycloreversion benzylidene complex **E** which is very likely responsible for the catalytic activity (Scheme 1-a).<sup>25</sup> This hypothesis is further supported by our experimental findings that an alkyne:Ru ratio inferior to 4:1 resulted in a strong drop of activity and selectivity.<sup>20</sup> For the reaction with cyclopropenes, we propose the following mechanism (Scheme 1-b). First, thermal de-coordination<sup>6b</sup> of toluene gives the coordinately unsaturated, highly reactive 12 electron ruthenium complex **B** which rapidly reacts with cyclopropene **A4** to give the more stable  $\pi$ -complex **F**. In fact a recent report by Occhipinti and Jensen described species **B** to be responsible for common catalyst degradation by intramolecular C–H activation and hydride-mechanism isomerization.<sup>9</sup> Hydride ruthenium species were evoked by Beller as the responsible species for producing cycloisomerization products (e.g. **3**; Figure 2).<sup>17a</sup> An alternative isomerization pathway was proposed by Dixneuf who reported that **B** can promote cycloisomerization of dienes via formation of a bis- $\pi$ -complex followed by oxidative addition,  $\beta$ -elimination and reductive elimination.<sup>14b</sup> This is very likely the reason why in the absence of activator the cycloisomerized product **3** was formed as the major species (Figure 2). In analogy to the corresponding tungsten complexes we then propose the subsequent formation of metallacyclopropane **G** which then rearranges to give the active vinyl alkylidene complex **H**.<sup>26</sup>





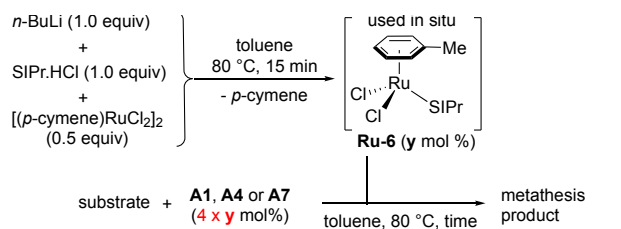
**Scheme 1. Postulated mechanisms for the activation with alkynes, cyclopropenes and diazocompounds**

Alternatively, the  $\pi$ -complex F could also react to H without formation of the metallacyclopropane intermediate.<sup>27</sup> Due to the known lack of stability of complex H we can expect that there will be a partial loss of material due to decomposition.<sup>44</sup> Therefore the *in situ* generated 18-electron complex A needs to be added to the activator and the substrate at the same time. In this case the transiently generated active species H will immediately enter the catalytic cycle thus diminishing inadvertent decomposition.<sup>28</sup> According to reactions between Ru-complexes and diazocompounds described in the literature,<sup>10,29</sup> we propose the formation of I from B and A7 under concomitant nitrogen evolution (Scheme 1-c). Indeed, gas evolution is observed even at room temperature upon addition of A7 to Ru-6.

With the optimized conditions in hand for the *in situ* generation of the complex Ru-6 that use *n*-BuLi as the base to deprotonate the SIPr ligand precursor, we investigated the substrate scope (Table 1). In order to minimize the risk of potential mismatch between substrates and activators, we decided to evaluate several activators (or no activator) for each of the metathesis reactions. RCM reactions with diallyl-*N*-tosylamine 4 was carried out at 80 °C and 22 °C (entries 1-8). At 80 °C complete conversion was observed with only 2 mol % of Ru-6 in combination with activator A1 (entry 2). In contrast, carrying out the same reactions at 22 °C (entries 5-8) gave similar results only with cyclopropene A4 (entry 7). This indicates that the rate determining step in the *in situ* formation of active 14-electron ruthenium complexes is very likely not the thermal dissociation of the toluene substituent (A  $\rightarrow$  B; Scheme 1) but rather the formation of E (Scheme 1-a) in the

case of alkynes. Another explanation for the sluggish reactivity with A1 and A7 at 22 °C might be that these catalytic systems require thermal activation.<sup>30</sup> Trisubstituted olefin 6 reacted cleanly in the presence of cyclopropene A4 (entry 11). Surprisingly, in the absence of activator very high RCM selectivity was observed (entry 9). This illustrates the unpredictable behavior of Ru-6 in the absence of activator, which often results in mixtures of metathesis, cycloisomerization and isomerization products (e.g. entries 13, 17 and 21) but in some cases, can also afford relatively clean reactions (entries 9 and 33). Interestingly, 6-membered RCM product 9 was obtained in high yields independent on the source of activator (entries 14-16). RCM reactions with substrate 10 were carried out either under standard conditions with non-degassed toluene (entries 17-20) or using degassed toluene (entries 21-24). In general yields and conversions were similar in the two cases. However, we found the reaction with activator A7 to be more selective towards the metathesis product 11 with degassed toluene (entries 20 and 24). For the synthesis of macrocycle 13 we noticed that the use of degassed toluene gave better reproducibility compared to standard conditions. The yields were somewhat lower compared to 7-membered cycle 11 (entries 25-28), very likely due to the formation of oligomeric side products.<sup>31</sup> Surprisingly, activators A1 and A7 performed significantly better than A4 (entries 26-28). Cross-metathesis reactions between 14 and 15 were very sluggish and low yielding (entries 29-32). We noticed that upon addition of Ru-6 to a mixture of 14 and 15 a black slimy residue appeared within seconds. The observed degradation might be similar to the corresponding PCy<sub>3</sub> ligated complex which was reported to decompose in the presence of allylic alcohols.<sup>32</sup>

**Table 1. Reaction scope.<sup>a</sup>**



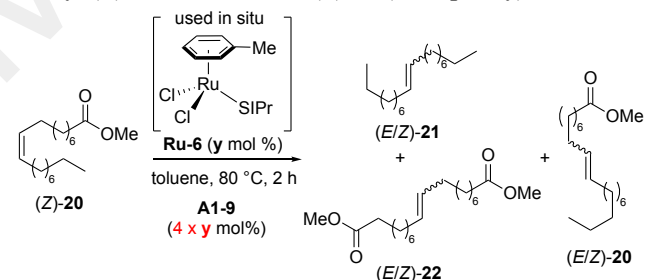
Entry	Substrate	Product	Ru-6 (y mol %)	AX	Time (min)	conv. (%) / yield (%)
1			2	none	15	45 / 36 <sup>b</sup>
2			2	<b>A1</b>	15	>98 / 91
3			2	<b>A4</b>	15	97 / 89
4			2	<b>A7</b>	15	55 / 64 <sup>b</sup>
5 <sup>c</sup>			2	none	15	18 / 12
6 <sup>c</sup>			2	<b>A1</b>	15	23 / 18
7 <sup>c</sup>			2	<b>A4</b>	15	90 / 81
8 <sup>c</sup>			2	<b>A7</b>	15	29 / 22
9			3	none	120	19 / 18
10			3	<b>A1</b>	120	76 / 73
11			3	<b>A4</b>	120	>98 / 95
12			3	<b>A7</b>	120	92 / 86
13			3	none	120	>98 / 24 <sup>b</sup>
14			3	<b>A1</b>	120	>98 / 98
15			3	<b>A4</b>	120	>98 / 99
16			3	<b>A7</b>	120	96 / 88 <sup>b</sup>
17			3	none	240	84 / 27 <sup>b</sup>
18			3	<b>A1</b>	240	88 / 78
19			3	<b>A4</b>	240	88 / 74
20			3	<b>A7</b>	240	84 / 62 <sup>b</sup>
21 <sup>d</sup>			3	none	240	91 / 6 <sup>b</sup>
22 <sup>d</sup>			3	<b>A1</b>	240	88 / 81
23 <sup>d</sup>			3	<b>A4</b>	240	90 / 72
24 <sup>d</sup>			3	<b>A7</b>	240	93 / 81
25 <sup>d</sup>			10	none	120	>98 / 18 <sup>b,e</sup>
26 <sup>d</sup>			10	<b>A1</b>	120	>98 / 55 <sup>b,e</sup>
27 <sup>d</sup>			10	<b>A4</b>	120	>98 / 40 <sup>e</sup>
28 <sup>d</sup>			10	<b>A7</b>	120	>98 / 54 <sup>e</sup>
29 <sup>f</sup>			5	none	240	14 / <2 <sup>g</sup>
30 <sup>f</sup>			5	<b>A1</b>	240	18 / 5 <sup>g</sup>
31 <sup>f</sup>			5	<b>A4</b>	240	47 / 33 <sup>g</sup>
32 <sup>f</sup>			5	<b>A7</b>	240	23 / 10 <sup>g</sup>
33			3	none	240	90 / 84 <sup>g</sup>
34			3	<b>A1</b>	240	85 / 75 <sup>g</sup>
35			3	<b>A4</b>	240	91 / 81 <sup>g</sup>
36			3	<b>A7</b>	240	90 / 84 <sup>g</sup>

<sup>a</sup>Reactions carried out in argon-flushed vials with dry solvents (MBraun® solvent system). Conversions and yields were determined by GC-analysis with internal standards (see SI). <sup>b</sup>Significant amounts of side products from cycloisomerization and isomerization processes were observed (see SI). <sup>c</sup>Reactions carried out at room temperature. <sup>d</sup>Reactions carried out in the glove-box with degassed solvents. <sup>e</sup>Low yield due to oligomeric side products. <sup>f</sup>**Ru-6** was synthesized in toluene and then added to a solution of **14** and **15** in THF. Reactions in toluene afforded even lower yields. <sup>g</sup>Apart from the desired products (**16** or **19**) we observed products from isomerization and self-metathesis of the terminal alkene substrates (**14** or **17**).

This assumption gains further credence when compared to the reactions with diacetate **18** which afforded CM product **19** in good yields with all activators (entries 33-36). Having tested several RCM and cross-metathesis reactions with substrates containing terminal olefins, we then decided to focus our attention on the self-metathesis of methyl oleate (*i.e.* methyl (*Z*)-9-octadecenoate) (**Z**)-**20** (99% purity) which is an

important chemical feedstock from biomass, leading to valuable hydrocarbon **21** and mono-unsaturated diester **22** (Table 2).<sup>33</sup> Surprisingly, activators like phenyl acetylene **A1** and cyclopropene **A4**, which were among the best activators for RCM or CM reactions with terminal alkenes, gave poor or no conversion in the self-metathesis of (*Z*)-**20** (entries 3 and 6). In contrast, when the reaction was carried out in the absence of activator the self-metathesis still proceeded, however producing many isomerization side-products (entry 1). The best productivity was found at low catalyst loading in the presence of diazocompounds **A7** and **A8** (entries 9-14). The reasons for the dramatic decrease of activity with alkyne and cyclopropene activators are still unclear. We postulate that the intermediate **E** generated from phenyl acetylene (Scheme 1a) is too sterically encumbered to efficiently react with the internal olefin of (*Z*)-**20**. In contrast, steric arguments cannot be evoked to explain the lack of efficiency with cyclopropene **A4**. In this case, the sterically more demanding cyclopropene **A5** shows in fact better efficiency (entries 6-7). However, an electronic argument might be considered: Internal alkenes are more electron rich compared to terminal alkenes. Therefore, we postulate that electron poor cyclopropenes **A5** and **A6** lead to a better electronic match for in situ generated ruthenium catalyst with (*Z*)-**20**. On the other hand, we observed that, at high catalyst loading, the in situ generated ruthenium catalyst produces significant amounts of isomerization side-product (entries 9 and 13; see SI). Fortunately, lowering the catalyst loading to less than 500 ppm favors the metathesis reaction over undesired isomerization (entries 10-12 and 14).

**Table 2: Screening of activators for the self-metathesis of methyl (*Z*)-9-octadecenoate (**Z**)-**20** (99% purity)<sup>a</sup>**

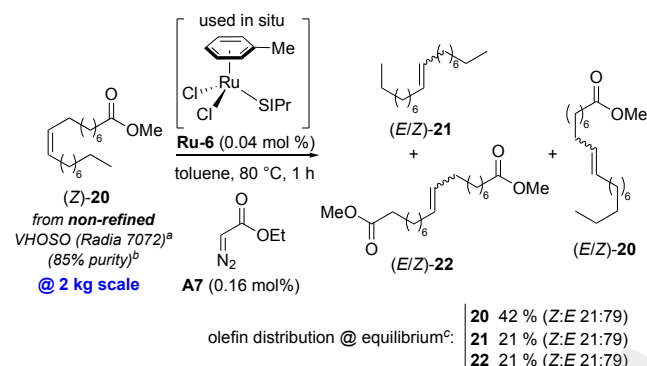


Entry	Ru-6 (y mol %)	AX	<b>20</b> (%) <sup>b</sup> (Z:E ratio)	<b>21</b> (%) <sup>b</sup>	<b>22</b> (%) <sup>b</sup> (Z:E ratio)
1	2	none	36 (21:79)	15	15 (25:75)
2 <sup>c</sup>	0.1	none	93 (59:41)	3	3 (32:68)
3	2	<b>A1</b>	100 (>99:1)	0	0
4	2	<b>A2</b>	100 (>99:1)	0	0
5	2	<b>A3</b>	100 (>99:1)	0	0
6	2	<b>A4</b>	92 (82:18)	4	4 (30:70)
7	2	<b>A5</b>	51 (24:76)	20	21 (22:78)
8	2	<b>A6</b>	68 (35:65)	16	16 (24:76)
9	2	<b>A7</b>	38 (21:79)	18	18 (25:75)
10 <sup>c</sup>	0.05	<b>A7</b>	51 (21:79)	24	24 (23:77)
11 <sup>d</sup>	0.02	<b>A7</b>	51 (21:79)	24	25 (22:78)
12 <sup>d</sup>	0.01	<b>A7</b>	55 (30:70)	22	23 (24:76)
13	2	<b>A8</b>	15 (13:87)	19	16 (19:81)
14 <sup>c</sup>	0.05	<b>A8</b>	50 (21:79)	24	24 (24:76)
15	2	<b>A9</b>	72 (32:68)	14	14 (27:73)

<sup>a</sup>Reactions performed in argon flushed vials on a 0.3 mmol scale (MO of 99% purity, Sigma Aldrich; used as received). The other products observed are unidentified isomerization products; see SI. <sup>b</sup>Determined by GC. <sup>c</sup>Carried out on a 8.0 mmol scale. <sup>d</sup>Reactions were carried out in the glove box (See SI for details).

When working with degassed solvents in a glove box, we even achieved 45% productive conversion (50% being the

maximum) with only 100 ppm of in situ generated **Ru-6** and 400 ppm of activator **A7** (entry 12). It is noteworthy that this is currently the best effective turn over number (TON = 4500) achieved with in situ generated ruthenium catalysts.<sup>13</sup> This TON is even higher compared to effective TON previously achieved with the Grubbs-1 catalyst **Ru-1** (TON = 2500).<sup>34</sup> To demonstrate the robustness of in situ generated catalyst **Ru-6**, we tested the optimized catalytic system towards a non-refined methyl oleate **Z-20** (technical grade, 85% purity) derived from very high oleic sunflower oils (VHOSO) on a 2-kg scale (Scheme 2). We were delighted that with only 400 ppm of catalyst full equilibrium of **20**, **21** and **22** was achieved within only 1 hour at 80 °C (See SI for a detailed description of the experiments including pictures). Of note, due to the low cost of [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub>, *n*-BuLi, SIPr.HCl and ethyl diazoacetate **A7**, this catalytic system showing a TON of 1250 appeared quite competitive to the most efficient well-defined Ru-catalysts.<sup>33</sup>



**Scheme 2. Kg-scale self-metathesis of non-refined methyl oleate (Z)-20 (technical grade, 85% purity) catalyzed by optimized in situ catalytic system Ru-6/A7**

<sup>a</sup>Radia 7072 is commercialized by Oleon. <sup>b</sup>The other compounds were identified as saturated and mono- or poly-unsaturated fatty methyl esters: C16:0 (3.4 wt.%); C16:1 (0.1 wt.%); C18:0 (1.8 wt.%); C18:2 (3.1 wt.%); C18:3 (1.8 wt.%); C20:0 (0.2 wt.%) C22:0 (0.3 wt.%) and C22:1 (0.7 wt.%). <sup>c</sup>Determined by GC.

In conclusion, we have reported a systematic study concerning the in situ formation of Ru-alkylidene catalytic species for olefin metathesis. By combining commercially available and inexpensive reagents [Ru(*p*-cymene)Cl<sub>2</sub>]<sub>2</sub>, SIPr.HCl and *n*-BuLi in toluene, the resulting 18 electron arene-ruthenium complex promoted, in the presence of activators such as alkynes, cyclopropenes and diazoesters, highly selective and efficient catalytic systems toward a variety of olefin metathesis transformations. Furthermore, we introduced for the first time cyclopropenes as efficient activators for the in situ generation of Ru-metathesis catalysts. Our investigations concerning the self-metathesis of methyl oleate (MO) showed an unprecedented substrate dependence on the activators. The diazoester **A7** was identified to be most efficient to convert the MO (**Z-20**) (@99% purity) into highly valuable mono-unsaturated diester and hydrocarbon with a catalyst loading as low as 100 ppm (TON of 4500). Moreover, the robustness of the newly developed catalytic system was demonstrated with the 2 kg-scale transformation of a non-refined technical grade MO (**Z-20**) (85% purity) using only 400 ppm of catalyst loading (TON = 1250). This highly

competitive and cost-effective catalytic process is underway in other valuable metathesis transformations.

## ASSOCIATED CONTENT

**Supporting Information.** Optimization reactions, experimental procedures and characterization data (<sup>1</sup>H NMR, <sup>13</sup>C NMR, GC-traces). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interests

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