Selective Metathesis of α-Olefins from Bio-Sourced Fischer–Tropsch Feeds

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ABSTRACT: The search for a low-cost process for the valorization of linear α-olefins combining high productivity and high selectivity is a long-standing goal to chemists. Herein, we report a soluble ruthenium olefin metathesis catalyst that performs the conversion of linear α-olefins to longer internal linear olefins with high selectivity (>99%) under neat conditions at low loadings (50 ppm) and without the need of expensive additives. This robust catalytic process allowed to efficiently and selectively re-equilibrate the naphtha fraction (C_5 to C_8) of a Fischer-Tropsch feed derived from non petroleum resources to a higher value product range (C_9 to C_{14}), useful as detergent and plasticizer precursors.

KEYWORDS: *olefin metathesis, ruthenium, unsymmetrical NHC, Fischer-Tropsch feeds, isomerization, selectivity*

The global increase of energy demand, our dependence on the oil price fluctuation and the accelerated transition toward renewable energy is leading to a resurgence of interest in catalytic processes for the production of synthetic fuels and industrial chemicals. In this context, the century-old Fischer-Tropsch (FT) technology (reductive oligomerization of CO and H_2)[1] is considered as one of the most practicable and promising alternatives to upgrade non-petroleum carbon resources such as methane (natural gas, shale gas, biogas…), biomass[2] and CO_2[3] to produce quality sustainable liquid fuels and/or chemicals with reduced CO_2-footprint. Indeed, the FT synthesis is highly versatile and produces a wide range of products in term of carbon number distribution.[1b] While the light fraction (C_2 to C_4) and wax fraction (C_{10+}) are of high demand for various fields of application, the naphtha fraction (C_5 to C_{10}) has instead found limited interest and is, for the most part, engaged in steam cracking to improve the production of ethylene and propylene.[4] Taking into account that the naphtha fraction production represents hundreds million tons per years, a transformation of these low value feedstocks into high added value chemicals intermediates would be beneficial to the global economies of FT processes. The abundant linear α-olefins content (30 to 70%)[5] of the C_5 to C_{10} fraction offers alternative opportunities,[6] among which olefin metathesis appears as an attractive technology.[7,8] Indeed, olefin metathesis provides flexibility to re-equilibrate the carbon number distribution to desired product range and generate the most economic chain length olefins (*i.e.*, detergent and plasticizer precursors).[9] Nevertheless, to date, several key issues remain

to be addressed to reach a successful catalytic approach in adequacy with large-scale industrial production. First, the catalyst should be robust and exhibit high activity at low loading (ppm level). Secondly, this high catalytic activity must be associated with an extremely high selectivity towards Primary Metathesis Products (**PMP**). Unlike the Shell Higher Olefin Process (SHOP),[9] isomerization of the alkene CC bond must be avoided in order to prevent undesired Secondary Metathesis Products (**SMP**), leading to broad product distribution (Figure 1). Finally, an economically viable process necessitates a low-cost catalyst that must fulfill the requirements without the need of expensive additives. The quest for an efficient metathesis process involving linear α-olefins has been a long-standing goal to chemists. Pioneer investigations with Re-, Mo- or W-based heterogeneous catalysts afforded poor selectivity towards the desired **PMP**.[10-13] More recently, homogeneous ruthenium catalysts, such as phosphine-based complexes (Grubbs catalyst 1st generation), have demonstrated good level of selectivity but with the requirement of high catalyst loading to achieve acceptable yields.[14] In contrast, second generation complexes bearing *N*-heterocyclic carbene (NHC) ligands afforded excellent conversions at lower catalyst loading but to the detriment of the selectivity.[15,16] It has been established that isomerization and subsequent loss of selectivity was due to the presence of hydride-complexes from the premature decomposition of the metal alkylidene species;[17-19] a phenomena that can be partially prevented in presence of expensive benzoquinone additives.[20,21] Here, we report a low-cost, highly
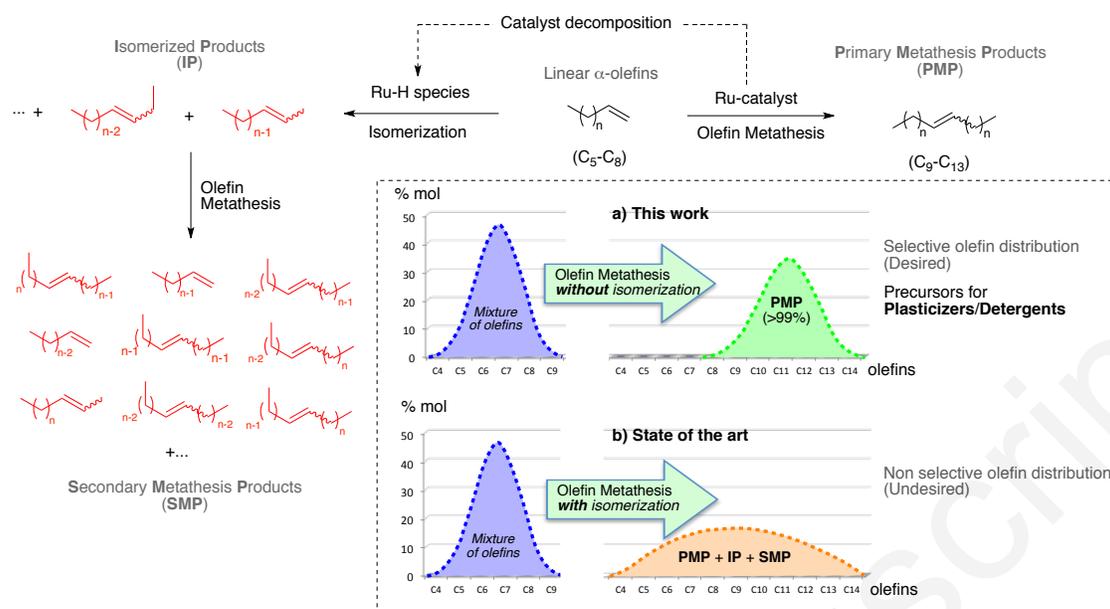
Figure 1. The challenges for the valorization of a Fischer-Tropsch feed *via* olefin metathesis. The desired transformation allows for the selective formation of Primary Metathesis Products (**PMP**) with the absence of olefin Isomerization Products (**IP**) and subsequent Secondary Metathesis Products (**SMP**). Expected (**a**) and non-desired (**b**) olefin distribution.

active and efficient ruthenium-based catalyst able to perform at low loading (50 ppm) the metathesis reaction of linear α-olefin with high selectivity (up to 99%) without the requirement of any additive. We demonstrated that unsymmetrical NHC ligands containing a *N*-substituted cycloalkyl side chain were critical to achieve high selectivity and prevent isomerization (even in the presence of alcohol impurities). Moreover, this remarkable catalytic activity allowed for the efficient and economically sustainable transformation of a representative Fischer-Tropsch feed derived from Biomass.

Because a strong synergic effect exists between the ancillary NHC and the reactive alkylidene ligands to achieve both high activity and high selectivity,[22] we began our investigation by evaluating a selection of second generation ruthenium catalysts[23] at 50 ppm loading in the self-metathesis reaction of 1-octene at 50°C in neat conditions (Figure 2 and Table 1).
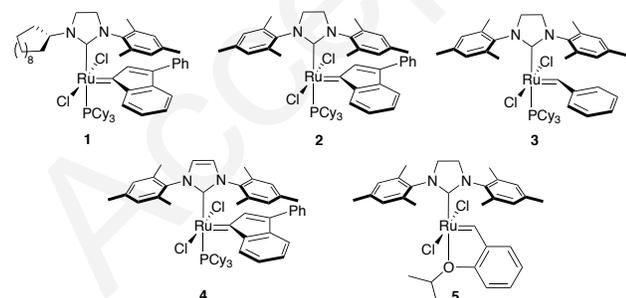

**Figure 2.** Selected Ru-based complexes for Self-Metathesis of terminal and internal olefins.

Gratifyingly, we found that the indenylidene-based complex **1** bearing an unsymmetrical NHC ligand[22b] containing a *N*-substituted cyclododecyl side chain could efficiently convert 70% of 1-octene to the desired PMP (7-tetradecene $C_{14:7}$)

with high 98% selectivity after 1h (see Table 1, entry 1 and Figure S1).

Table 1: Self-Metathesis of 1-octene catalyzed by complexes 1-5[a]
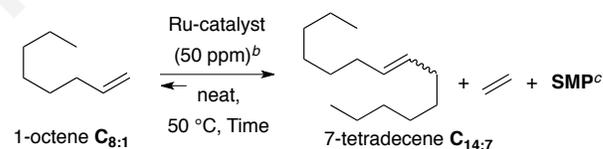
entry	catalyst	Time (h)	conversion (%)[d]	selectivity (%)[d]
1	**1**	1	70	98
2	**1**	4	70	98
3	**2**	1	45	94
4	**2**	2	76	80
5	**3**	2	80	85
6	**4**	4	<1	-
7[e]	**4**	2	75	50
8	**5**	4	30	98

SMP = C_3 (propene) $C_{7:1}$ (1-heptene) $C_{9:2}$ (2-nonene) $C_{12:6}$ (6-dodecene) $C_{13:6}$ (6-tridecene)
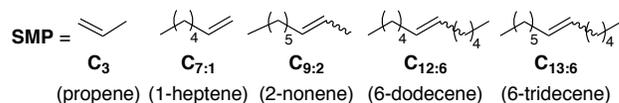
[a]Complexes **1-5** were evaluated in the Self-Metathesis of 1-octene $C_{8:1}$ at 50 °C in neat conditions. The conversion of 1-octene and selectivity toward 7-tetradecene $C_{14:7}$ were monitored over time. [b]Catalyst loading = mole of Ru-catalyst/mole of $C_{8:1}$. For 50 ppm, the ratio is 20 000 (%mol of Ru/mole of $C_{8:1}$). [c]Mixture of C_3-C_{13} olefins. [d]Conversion and selectivity were

monitored by GC (see the Supporting Information for details). [e]Reaction performed at 80 °C.

More importantly, no alteration of the selectivity was observed after an extended period of time (entry 2 and Figure S2). In comparison, the commercially available complex **2** analogue, bearing the symmetrical 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (SIMes) NHC ligand, afforded the self-metathesis product with modest 45% conversion and good 94% selectivity after 1h (entry 3 and Figure S3). While the conversion could be increased to 76% after 2h, the prolonged heating at 50 °C severely impacted the selectivity with the formation of 20% **SMP**, mainly **$C_{9:2}$**, **$C_{12:6}$** and **$C_{13:6}$** internal olefins (2-nonene, 6-dodecene and 6-tridecene, respectively) resulting from the migration of the terminal double bond and subsequent Self- and Cross-Metathesis (entry 4 and Figure S4). The Grubbs complex **3** showed relative good reactivity, affording 7-tetradecene in 75% after 2h (entry 5). However, 15% of **SMP** were also observed. Astonishingly, the indenylidene complex **4** bearing the unsaturated NHC ligand (IMes) appeared totally inactive (<1%, entry 6). An increase of the temperature up to 80°C allowed the reaction to reach a respectable conversion of 75%, but the selectivity was drastically altered (50%, entry 7).[24] Lastly, the Hoveyda-Grubbs complex **5** showed interesting selectivity towards **PMP** (98%, entry 8) but at the detriment of the conversion (30%) despite extended duration of the reaction (4h).

The advantage provided by the unsymmetrical cyclododecyl-based NHC Ru-indenylidene catalyst **1** over its symmetrical SIMes-based analogue **2** was further confirmed in a cross-metathesis experiment involving a mixture of linear-α and linear internal olefins (83% of 1-octene and 17% of 2-octene); a composition representative of a FT feed. In regards to the activity, both catalysts **1** and **2** at 50 ppm loading afforded high conversion after 4h (Table 2). Catalyst **1** converted 77% of 1-octene and 91% of 2-octene, while conversions of 79% and 98% were observed with complex **2** (Figures S5-S6). Interestingly, the excellent conversion observed for 2-octene is attributed to the formation of highly reactive Ru-methylidene species through the reaction with 1-octene. Regarding selectivity, significant differences between catalysts were observed. Indeed, catalyst **1** provided an excellent selectivity toward PMP products as evidenced by the formation of equimolar amounts (4.9%) of 2-nonene (**$C_{9:2}$**) and 1-heptene (**$C_{7:1}$**) resulting from the cross-metathesis between 1-octene and 2-octene. On the other hand, the product distribution obtained with catalyst **2** attested that isomerisation occurred during the process. In fact, 1-heptene and 2-nonene are being formed in different amounts, along with a higher production of 6-dodecene (**$C_{12:6}$**) at the detriment of 2-nonene (**$C_{9:2}$**). It should also be noted that in both cases, 6-tridecene (**$C_{13:6}$**) was the predominant CM product relative to 2-nonene (**$C_{9:2}$**) and 1-heptene (**$C_{7:1}$**), favoured by the concomitant production of propylene gas.

Table 2. Olefin-Metathesis of a synthetic FT feed.[a]

entry	catalyst	conv. of $C_{8:1}$ (%)[c]	conv. of $C_{8:2}$ (%)[c]	Product distribution (mol%)[d]							
				$C_{7:1}$	$C_{7:2}$	$C_{9:2}$	$C_{10:5}$	$C_{11:5}$	$C_{12:6}$	$C_{13:6}$	$C_{14:7}$
1	**1**	77	91	4.9	<0.1[e]	4.9	<0.1[e]	<0.1[e]	2.5	24	63.8
2	**2**	79	98	5.1	<0.1[e]	2.2	<0.1[e]	0.2	4.1	27.7	60.8

[a]The product distribution was determined after the olefin metathesis reaction of a mixture of linear-α and linear internal olefins (83% of 1-octene $C_{8:1}$ and 17% of 2-octene $C_{8:2}$) at 50 °C for 4h in neat with both catalyst **1** and **2**. [b]Catalyst loading = mole of Ru-catalyst/mole of $C_{8:1}$ + $C_{8:2}$. [c]Conversions were monitored by GC (see the Supporting Information for details). [d]These distributions (based on 100%) do not include light olefins C_2 to C_4 for more clarity. [e]Under the limit of detection of GC.

As depicted in table 3, a number of variables can affect catalyst activity. In the present case, the conversion was slightly impacted by the olefin dilution (60% in octane), while the selectivity remained excellent with catalyst **1** (entries 1-2 and Figures S7-S8). On the other hand, since linear alcohols are usually detected in noticeable amount in FT feeds,[25a-b] it appeared important to us to evaluate the potential impact of this oxygenated impurities on the activity and the selectivity of our selected catalysts. Indeed, alcohols are known to act as a poison, speeding up the catalyst death and/or promoting the formation of ruthenium hydrides.[25c] Therefore, the percentage of 1-pentanol was deliberately set high enough that very notable differences could be appreciated in the CM of 1-octene. As expected, for both catalysts **1** and **2** the conversion was largely affected by the severe alcohol contamination, which rapidly degraded the catalytic active species. Astonishingly, and unlike catalyst **2**, our catalyst **1** remained highly selective under these challenging conditions (95% vs. 58%, entries 3 and 4, Figures S9-S10).[25d]

Table 3. Self-Metathesis of 1-octene in the presence of *n*-octane and 1-pentanol[a]
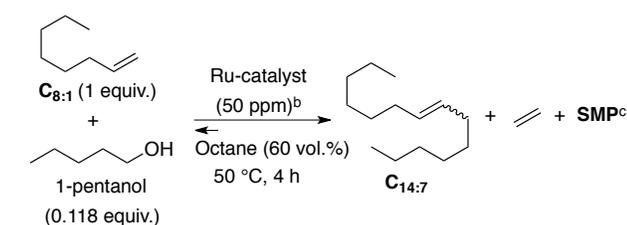
entry	catalyst	1-pentanol	conversion (%)[d]	selectivity (%)[d]
1	**1**	without	57	98
2	**2**	without	42	96
3	**1**	with	18	95
4	**2**	with	22	58

[a]Determination of the impact of alcohol contamination on the conversion and selectivity for the Self-Metathesis of 1-octene catalyzed by complexes **1** and **2** under the standard conditions. [b]Catalyst loading = mole of Ru-catalyst/mole of $C_{8:1}$. [c]Mixture of C_3-C_{13} olefins. [d]Conversion and selectivity were monitored by GC (see the Supporting Information for details).

The catalyst price accounts for a significant percentage of the total cost of an industrial manufacturing process. Moreover, the ligands surrounding the metal are the most expensive components of the Ru-based homogeneous catalyst. This is reinforced by the fact that, unlike the metal, the ligands cannot be recycled. Therefore, despite the efficiency contributed by the designed NHC-based catalyst **1**, the development of a lower-cost catalyst appeared necessary to extend the validity of the technology to a large-scale process. Fortunately, during the course of this project, we developed a one-step multicomponent synthesis of unsaturated unsymmetrical NHC ligands bearing a cycloalkyl side chain[26] that could provide a cost-effective alternative to the multi-step synthe-

sis of their saturated ligand analogues. Thanks to the potency of this ligand synthesis, catalysts **6** and **7** (bearing a cyclododecyl and a cyclopentyl moiety respectively) could be prepared[27] and evaluated in the self-metathesis reaction of 1-octene under the standard conditions (Table 4). Pleasantly, the structural modification of the ligand had no effect on the catalyst selectivity and only a modest impact on the reactivity[27]; the catalyst **7** affording the best compromise with similar high selectivity (99%) and with no evolution over the time and good 59% conversion at 50 ppm loading (entry 2, Figure S11). This result also confirms that regardless the size of the cycloalkyl substituent of the ancillary diaminocarbene ligand, this fragment is critical to limit isomerization and subsequent formation of undesired SMP (*vide infra* Figure 3).

Table 4. Self-Metathesis of 1-octene catalyzed by unsymmetrical NHC-based complexes 6-7[a]
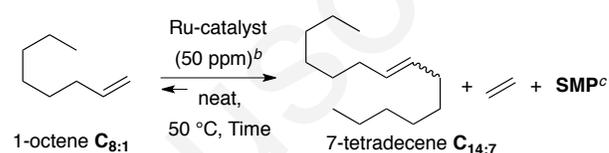
entry	catalyst	Time (h)	conversion (%)[d]	selectivity (%)[d]
1	**6**	4	55	98
2	**7**	2	59	99
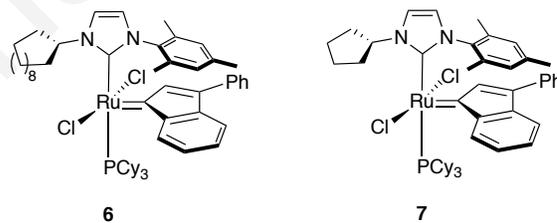
[a]Complexes **6-7** were evaluated in the Self-Metathesis of 1-octene $C_{8:1}$ at 50 °C in neat conditions. The conversion of 1-octene and selectivity toward 7-tetradecene $C_{14:7}$ were monitored over time. [b]Catalyst loading = mole of Ru-catalyst/mole of $C_{8:1}$. [c]Mixture of C_3-C_{13} olefins. [d]Conversion and selectivity were monitored by GC (see the Supporting Information for details).

After completion of the initial evaluation and optimization phase, during which complex **7** was identified as the catalyst of choice for the selective metathesis of linear α-olefin, we then applied the technology to the naphtha fraction of a Fischer-Tropsch feed derived from biomass (Figure 3 and Table S5). Among the 37% of C_4-C_8 olefins contained in the feed; the remaining components being alkanes; 82% were linear α-olefins.
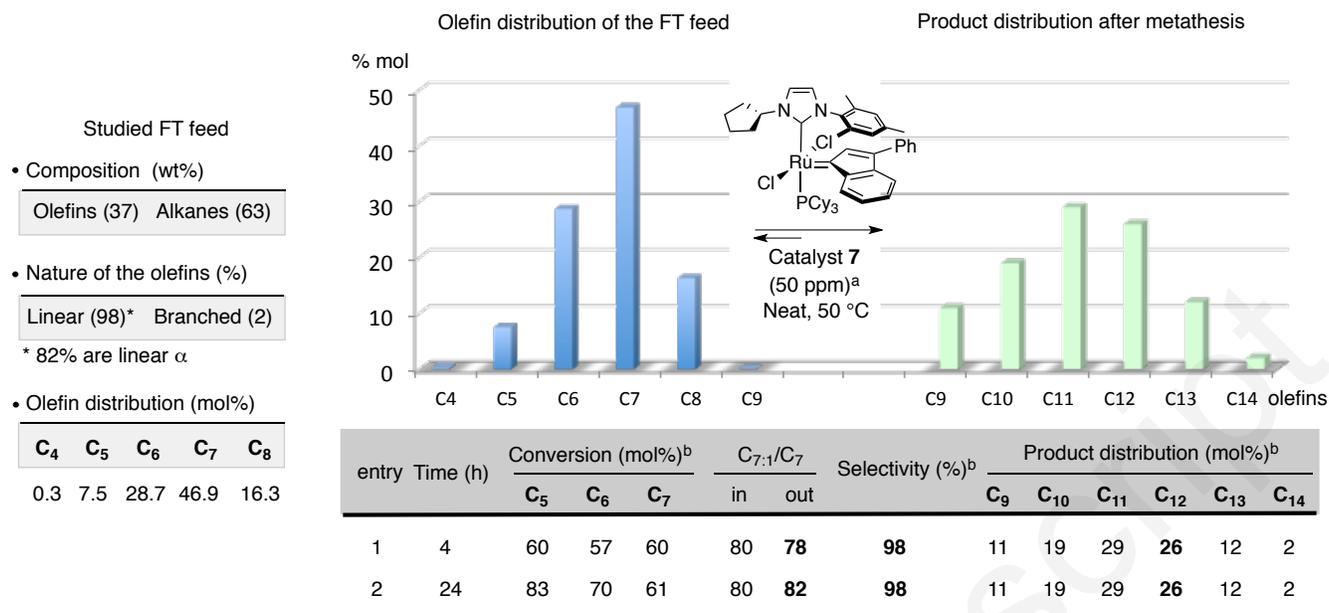
Figure 3. Olefin metathesis of the Fischer-Tropsch feed from Biomass catalyzed by Ru-based complexes **7**. [a]Catalyst loading = wt% of Ru-catalyst/wt% of olefins in the feed. [b]Conversion, selectivity and distribution were monitored by GC (see the Supporting Information for details).

As depicted in Figure 3, the reaction process was monitored by determination of C_5, C_6 and C_7 conversion and the isomerization was expressed as the 1-heptene ($C_{7:1}$) content in the C_7 fraction ($C_{7:1}+C_{7:2}+C_{7:3}$) before (in) and after (out) metathesis. Gratifyingly, catalyst **7** exhibited good conversion at low catalyst loading at 50°C. Importantly, the catalytic process showed complete selectivity with respect to the product distribution after olefin metathesis, as shown by the stable 1-heptene/C_7 fraction ratio even after 24 hours (Figure 3, entries 1 and 2, Figures S12-S13). It is important to note that under the same conditions, by comparison, the 1-heptene/C_7 ratio dropped down to 64% after 24h with the commercially available complex **2** (Table S5, entry 4). Therefore, we successfully demonstrated that catalyst **7** could selectively re-equilibrate a low-value naphtha fraction to a higher value product range (C_9 to C_{14}) that can serve as detergent and plasticizer precursors.

A brief investigation of the catalyst decomposition afforded elements for an understanding of the superior selectivity observed with our low-cost catalyst **7** (Figure 4). Unlike alcoholysis of catalyst **2** that led predominantly to the NHC based hydrido-Ru complex **8**,[28] the catalyst **7** decomposed exclusively to the less isomerization-active [RuCl(H)(CO)(PCy$_3$)$_2$] complex **9** (Figures S14 and S15)[29]; a phenomena that could be explained by the favorable protonolysis of N-substituted cycloalkyl NHC ligands (Figure S16).[30] In the assumption that hydrido-Ru complex **9** is formed from the initial decomposition products **8** and **10**,[28,31] density functional theory calculations gratifyingly indicated that NHC dissociation from **10**, promoted by attack of an ethanol molecule to the Ru center, is favored by 3.9 kcal/mol over NHC dissociation from **8** (Figure 5 and Scheme S1). The easier displacement of the unsymmetrical NHC ligand is essentially due to the reduced hindrance of the cyclopentyl N-substituent.
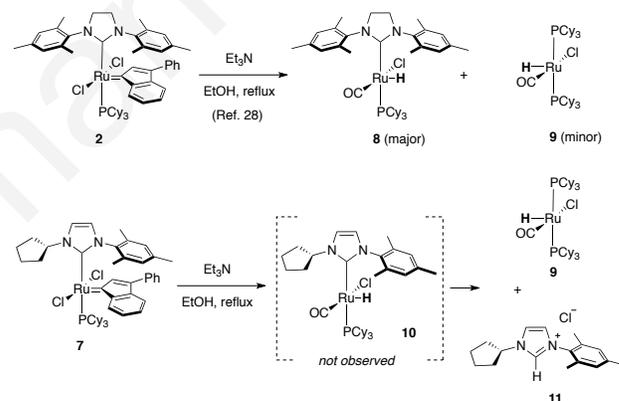

Figure 4. Alcoholysis of complexes **2** and **7**. The degradation of complex **7** in the presence of ethanol and triethylamine under reflux condition led exclusively to the less isomerization active hydrido-complex **9**.

This results in a large rotation of the NHC ligand, as indicated by the dihedral angle θ = O–Ru–C–N, which assumes a value of 155° with **10** (Figure 5). This rotation of the NHC allows an easier approach of ethanol to the metal center (Figure 5, S17, S19, and S20). Differently, two of the ortho methyl groups of the bulky mesityl N-substituents in **8**, indicated by a shadow in Figure 5, close the reaction channel to the attacking ethanol, preventing SIMes displacement (Figures S23 and S24). Furthermore, the latter explanations are in totally agreement with the *in-silico* calculation for the IMes system (Scheme S1), which NHC displacement is placed 1.2 kcal/mol below in energy with respect to SIMes, but still 2.7 kcal/mol above in energy with respect to the NHC owned by **7**.

entry	Time (h)	Conversion (mol%)[b]			C$_{7:1}$/C$_7$[b]		Selectivity (%)[b]	Product distribution (mol%)[b]					
		C$_5$	**C$_6$**	**C$_7$**	in	out		**C$_9$**	**C$_{10}$**	**C$_{11}$**	**C$_{12}$**	**C$_{13}$**	**C$_{14}$**
1	4	60	57	60	80	**78**	**98**	11	19	29	**26**	12	2
2	24	83	70	61	80	**82**	**98**	11	19	29	**26**	12	2
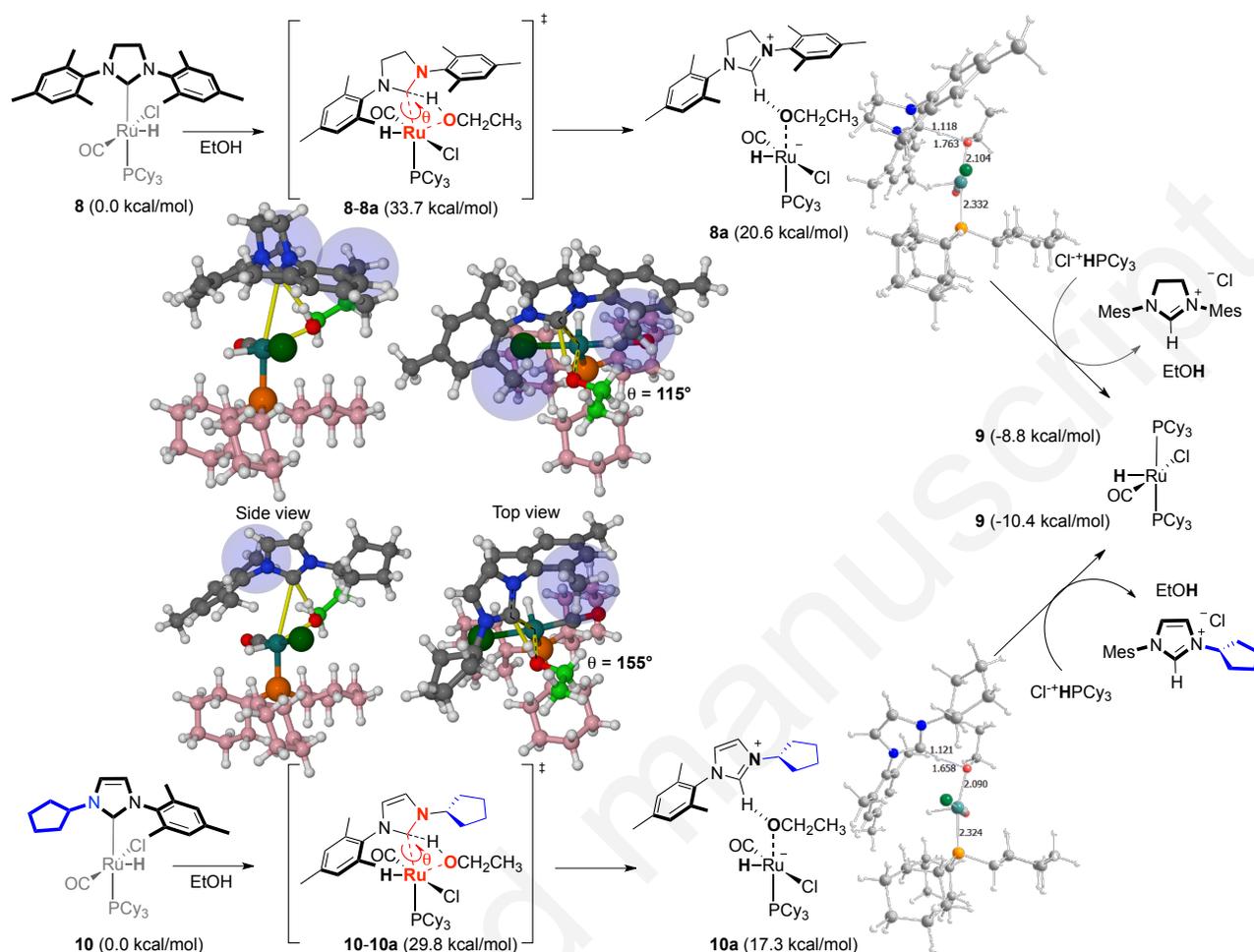
Figure 5. Decomposition pathway of NHC-based hydrido-Ru complexes **8** and **10** and related Density functional theory calculations. The transition state for NHC displacement by ethanol is easier with the less bulky *N*-substituted cycloalkyl NHC ligand. The torsional angle θ is defined by the dashed bonds. The Van der Waals radius of the ortho C-atoms of the protruding mesityl rings interfering with the attack of ethanol is shown as shadow (selected distances in Å).

To conclude, a set of Ru-based complexes were screened in self-metathesis of linear terminal olefins. Interestingly, indenylidene pre-catalysts bearing unsymmetrical NHC ligands with a *N*-cycloalkyl moiety have demonstrated efficiency at low loading (50 ppm) and remarkable 99% selectivity. This methodology was successfully applied to the transformation of Fischer-Tropsch feed derived from Biomass with the cyclopentyl-IMes Ru-catalyst **7**. Excellent olefin distribution with no isomerization was observed even in the absence of benzoquinone additives and after 24h of reaction. Although in-depth mechanistic studies are required, the results from this work have demonstrated that the selective conversion of terminal α-olefins to internal olefins can be conducted selectively and cost-effectively with a low-loading of a homogeneous catalyst. Because selectivity issues remain a major obstacle to numerous industrial applications of olefin metathesis in the fields of petrochemicals, oleochemistry, pharmaceuticals, flavors and fragrances, we anticipate that

this technology will be of great interest to a wide range of end-users.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ASSOCIATED CONTENT
Supporting Information

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PMP = **P**rimary **M**etathesis **P**roducts