

# Synthesis of 16-Electron RuHCl(CO)(PPh<sub>3</sub>)<sub>2</sub> Catalyst Rendering Superior C=C Double Bond Isomerization Activity

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The double bond isomerization of olefins is an atomicefficient, industrially highly relevant chemical reaction. One of its emerging applications is the tandem isomerization metathesis (ethenolysis) reaction (ISOMET or IE) used for transforming plastic waste to propylene. As the double bond isomerization step is the bottleneck of the ISOMET reactions, a series of ruthenium(II) hydride complexes were investigated in the view of their C=C isomerization activity in neat conditions on terminal alkene substrates which are the major components of polyethylene (PE) pyrolysis oil. Our work revealed that the commonly applied RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> (1) complex can be activated with cop-

per(II) chloride, by scavenging one phosphine ligand yielding an isolable, coordinatively unsaturated, highly soluble, and reactive species, RuHCl(CO)(PPh<sub>3</sub>)<sub>2</sub> (2). The structure of the complex is similar to the more bulky and less active RuHCl(CO)(PCy<sub>3</sub>)<sub>2</sub> (3). The bis(triphenylphosphine) complex 2 showed remarkably high olefin isomerization activity even at room temperature with a catalyst loading as low as 0.1 mol%. The functional group tolerances—especially catalyst deactivation caused by dienes—are also discussed briefly; having relevance in tandem catalytic reactions like ISOMET of diene-containing PE pyrolysis oil.

## 1. Introduction

The development of advanced catalyst systems for the chemical recycling of polyolefin waste is one of the most pressing

scientific challenges today. To offer a green catalytic technology having low-energy demand for this purpose, the tandem isomerization metathesis (ethenolysis) reaction (ISOMET or IE) has been developed recently and is used to transform long-chain hydrocarbons to shorter-chain olefins such as propylene.<sup>[1–3]</sup> For this, polyolefin waste is first pretreated by mild cracking (slow pyrolysis) or catalytic dehydrogenation, and the resulting olefin mixtures are subjected to the ISOMET tandem catalytic reaction. Our group focuses on the development of low-energy, high-performance, solely ruthenium(II)-based ISOMET catalyst systems. Since the bottleneck of ISOMET reactions is probably the activity of the alkene isomerization catalyst, a relatively large excess of double bond isomerization catalyst must be used compared to the loading of the state-of-the-art olefin metathesis catalysts. Moreover, as C=C isomerizing co-catalyst, RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> (1) shows the highest activity at elevated reaction temperature, the application of olefin metathesis catalysts in ISOMET reactions is limited to thermally stable, new generation bicyclic (alkyl)(amino)carbene (BICAAC)-Ru(II)-alkylidene complexes.<sup>[1]</sup> Therefore, it can be assumed that the development C=C double bond isomerization catalysts rendering high activity at ambient reaction conditions could open new, environmentally friendly chemical technologies toward high-value, sustainable materials, as well as the development of green chemical processes, including the recycling of persistent plastic wastes under low-energy reaction conditions.<sup>[2,3]</sup>

Beyond ISOMET reactions, the isomerization of olefins is an atomicefficient, industrially highly relevant chemical reaction.<sup>[4,5]</sup> Although the internal position of the C=C bond is thermodynamically favored (reverse reactions are rare),<sup>[6]</sup> many olefins are available in their terminal form: pyrolysis of hydrocarbon

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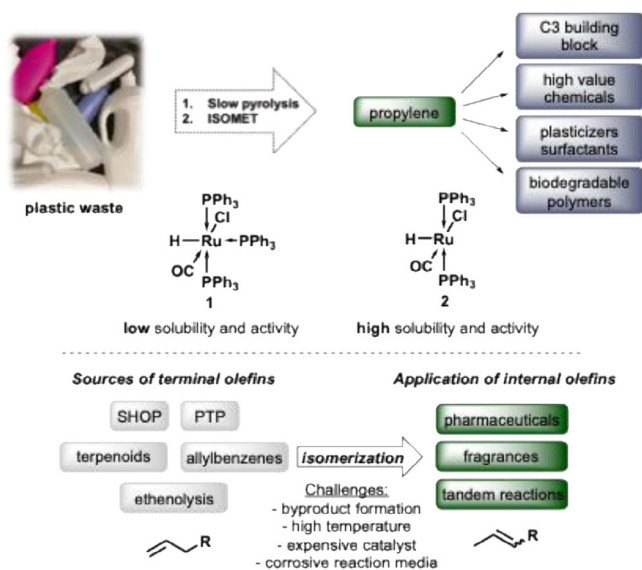
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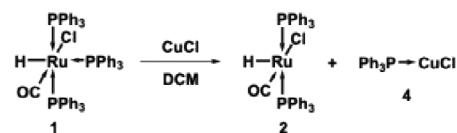
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Scheme 1. Overview of the significance of the topic highlighting complexes 1 and 2 in the view of their solubility in neat hydrocarbons and double bond isomerization activity at room temperature (RT).

chains and polyolefins like PE,<sup>[7]</sup> several natural products like terpenoids,<sup>[8,9]</sup> or ethenolysis of internal olefins<sup>[10,11]</sup> all provide terminal olefins. In addition, the Phillips triolefin process (PTP),<sup>[12]</sup> shell higher olefin process (SHOP)<sup>[13]</sup> can also result in terminal alkenes. Dehydrogenation of alkanes sometimes yields mixtures of terminal and internal olefins, whose separation may be difficult.<sup>[14,15]</sup> Noteworthy, internal alkenes tend to have higher cost compared to their terminal analogs.<sup>[16]</sup> On industrial scale, the isomerization of terminal alkenes is conducted at elevated temperature (over 200 °C) using heterogeneous catalyst systems (microporous minerals). The selectivity of these reactions is often limited, as dimerization, oligomerization, skeletal isomerization, or reduction side reactions require costly separation procedures and reduce the overall yield of the desired products.<sup>[17]</sup> The de novo synthesis of internal olefinic C=C double bonds from Wittig reaction is cumbersome and has low atomic efficiency,<sup>[18]</sup> while olefin metathesis sometimes requires specific substitution of the substrate.<sup>[19]</sup> In the literature, several isomerization strategies can be found. Acidic reagents (inorganic acids, Brønsted-acidic minerals like zeolites) can convert the terminal olefins to internal ones, but these can cause corrosion of the reaction vessel or may lead to the formation of undesired byproducts.<sup>[20,21]</sup> These circumstances rationalize the transition metal-catalyzed chemical processes as viable alternatives. According to the mechanism, the isomerization can proceed via either metal hydride—metal alkyl intermediates or allylic transition metal complex intermediates.<sup>[22]</sup>

In addition to the ISOMET process, catalytic alkene double bond isomerization can serve a wide variety of chemical needs (Scheme 1). Compatibility with other catalytic reactions is also of great importance.<sup>[23]</sup> Such tandem reactions offer a valuable opportunity to perform one-pot consecutive reactions or may provide tools for cooperative tandem catalysis. Ruthenium(II) hydride species have already proven to be effective cocatalysts for relevant tandem reactions, involving alkenes and



Scheme 2. Activation of the RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> (1) complex.

carbonyl compounds, transfer hydrogenation of carbonyl compounds containing C=C unsaturation,<sup>[24]</sup> their coupling with themselves<sup>[25]</sup> or alcohols, or the conversion of allylic alcohols to carbonyl compounds.<sup>[26]</sup> These reactions can be used for cyclization purposes.<sup>[27]</sup>

In this work, ruthenium(II)-hydride complex-catalyzed alkene isomerization reactions have been investigated.<sup>[5]</sup> In addition, we set our focus on the activation of the widely used RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> complex (1), enabling the solvent-free isomerization reaction at ambient reaction conditions. This suggests a potential to those tandem catalytic reactions, which usually run at elevated temperatures, including the ISOMET reaction and other tandem reactions involving alkene isomerization steps.

## 2. Results and Discussion

### 2.1. Preparation of the Activated Catalyst 2

In 2009, the Marciniak group reported that complex 1 and RuHCl(CO)(PCy<sub>3</sub>)<sub>2</sub> (3) both show higher activity in the silylative coupling of oligosiloxanes, when copper(I) chloride additive was used.<sup>[28]</sup> In 2017, the Yin group reported that magnesium(II) salts could propagate the initialization step, the dissociation of one phosphine ligand from RuH<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>3</sub> (8), and stabilize the ruthenium(II)-hydride intermediates during the alkene isomerization catalytic cycle.<sup>[29]</sup> The phosphine scavenging ability of copper(I) chloride was also used in the metathesis chemistry: the activation of Ru(II)-alkylidene phosphine complexes was published in 1997 by Grubbs,<sup>[30]</sup> and, in 2020, the Hong group showed that copper(I) species enhance the ruthenium(II) alkylidene olefin metathesis catalysts activity.<sup>[31]</sup>

Based on these reports and preliminary experiments, we found that complex 1 exhibits remarkable activity in isomerization of 1-octene (10) in neat when copper(I) chloride is added to the reaction mixture. To investigate this phenomenon in detail, we aimed to isolate the activated ruthenium species (2). Upon the addition of 0.5 equivalents of CuCl to a deuterated chloroform suspension of complex 1, the formation of an orange reaction mixture was observed. A new hydride shift appeared at −14.8 ppm in the <sup>1</sup>H NMR spectrum (triplet, *J* = 19.6 Hz), while besides the initial <sup>31</sup>P NMR resonances (39.0 and 12.8 ppm), a new signal appeared (42.7 ppm). Increasing the CuCl equivalent to 1.0 resulted in the full conversion of the initial complex. A broad signal was detected at −1 ppm in the <sup>31</sup>P spectrum, indicating the formation of CuClPPh<sub>3</sub> species (4, Scheme 2 and Figure 1).

The activated bisphosphine complex 2 was synthesized in dichloromethane, and after removal of the solvent, the evaporation residue was extracted with diethyl ether giving the product

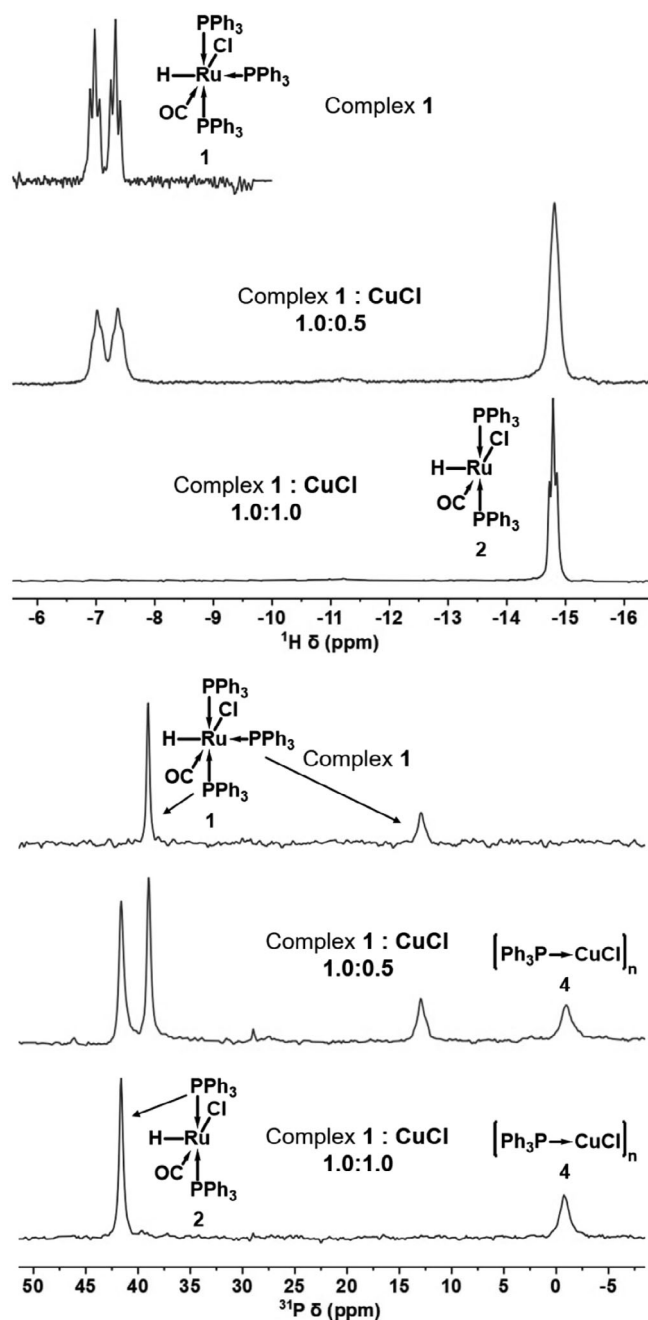


Figure 1. NMR observation of the formation of the activated complex 2 at different CuCl molar ratios. Top triad:  $^1\text{H}$  hydride region, bottom triad:  $^{31}\text{P}$ .

as an orange solid in 77% yield (Scheme 2). It was presumed that the driving force of the reaction was the formation of the copper-phosphine complex. Therefore, other soft, first-row  $d$ -filed metal salts were also investigated as additives: nickel(II) ( $\text{NiCl}_2$ ), cobalt(II) ( $\text{CoCl}_2$ ), and zinc(II) ( $\text{ZnCl}_2$ ) chlorides. Only  $\text{ZnCl}_2$  showed some phosphine-scavenging activity (see section 2.5 in Supporting Information).<sup>[32]</sup> In another experiment, reacting complex (2) with one equivalent of triphenylphosphine resulted in the formation of complex 1 (see section 2.7 in Supporting Information).

Interestingly, the only successful XRD-quality single-crystal growing experiment succeeded with a crude material contain-

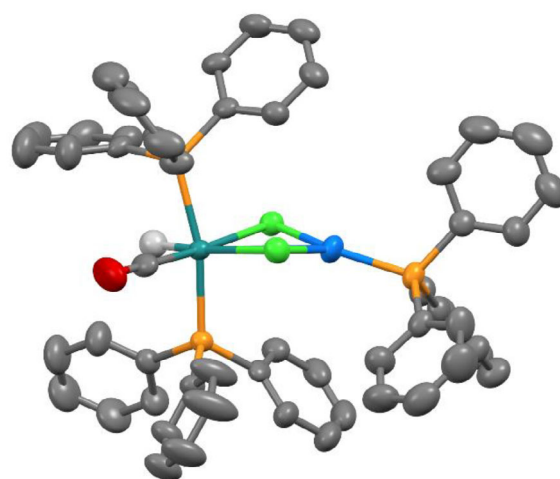


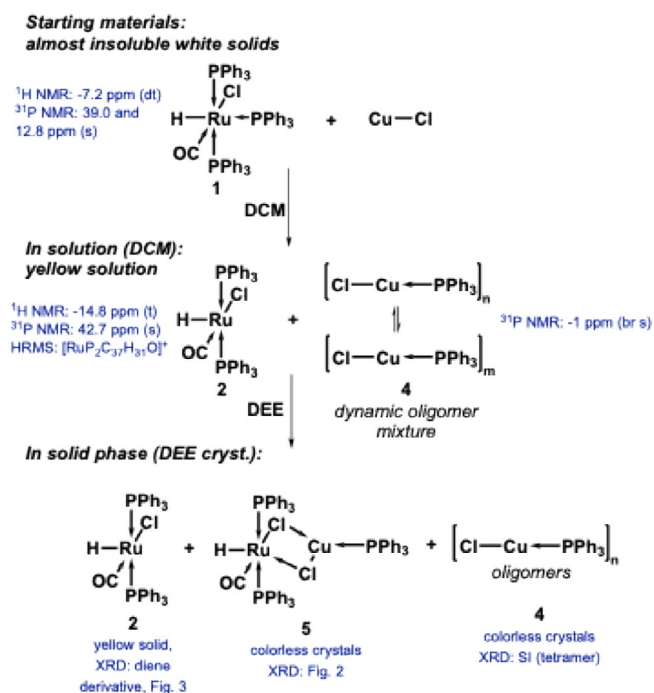
Figure 2. ORTEP view of the Ru–Cu adduct 5 at 40% probability level. Solvent benzene molecule and hydrogen atoms are omitted for clarity, except the hydride hydrogen.

ing some copper species, since  $\text{RuHCl}(\text{CO})(\text{PPh}_3)_2$  (2) has low crystallinity. The found structure for 5 shows that the activated ruthenium bisphosphine is being coordinated by the remaining copper chloride phosphine complex—stabilized via halide bridges (Figure 2). It is worth noting that in structure 5 the Ru–H distance is 1.52(7) Å giving direct evidence for the presence of the coordinated hydrogen atom. Search of the Cambridge Structural Database (Ver. 5.46 update November, 2024)<sup>[33]</sup> revealed, that the average Ru–H distance for similar ruthenium-bisphosphine-carbonyl-chloro complexes being 1.6(2) Å for 84 hits. Further geometric data are given in the Supporting Information (section 8). Similar heterobimetallic structures are rare.<sup>[34,35]</sup> FTIR measurement showed a characteristic carbonyl resonance at  $1921\text{ cm}^{-1}$ , while in  $^{13}\text{C}$  NMR, this carbonyl ligand had the chemical shift at 203 ppm ( $\text{CDCl}_3$ ). As shown in the  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra, the structure of 2 is similar to the bis- $\text{PCy}_3$  analog (3), with the phosphines in *trans* position to each other. In the solution phase, only complexes 2 and 4 can be identified, while complex 5 was probably formed during solvent evaporation. In HRMS, the bisphosphine ruthenium species was clearly present: the ESI-MS spectrum reveals the presence of ion  $\text{RuH}(\text{CO})(\text{PPh}_3)_2^+$  at  $m/z$  655.0895 (the most intensive isotope peak) formed from the complex  $\text{RuHCl}(\text{CO})(\text{PPh}_3)_2$  by the elimination of the chloride ion. These analytical results support the dissociative activation mechanism of complex 1, with the role of CuCl being the scavenger of the phosphine ligand (Scheme 3).

These observations rationalize the preparation of the activated complex 2: when washing with diethyl ether, the Ru-species is extracted, allowing the remaining copper complexes (oligomers, 4) to crystallize. The tetramer of complex 4 with the known cubic  $[(\text{PPh}_3)_3\text{Cu-Cl}]_4$  structure was also confirmed by XRD measurements.

## 2.2. Catalytic Investigations

Having complex 2 in hand, its activity has been compared with commercially available Ru(II)-hydride double bond isomerization



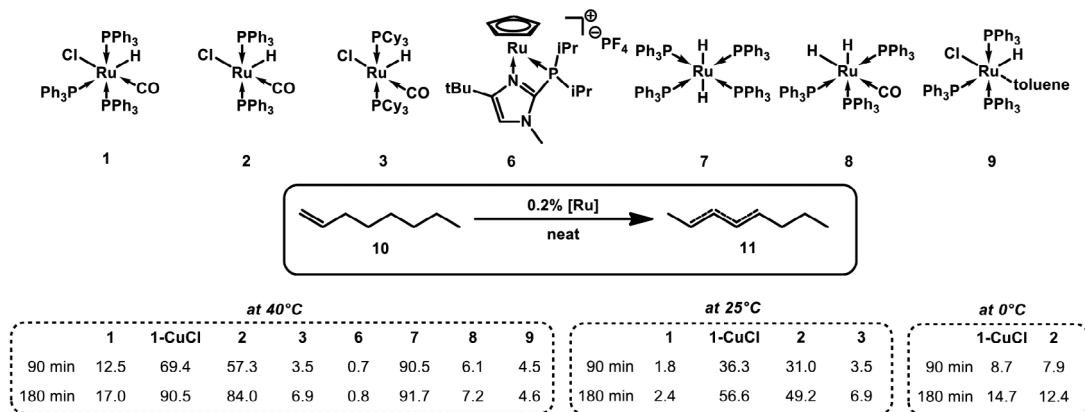
Scheme 3. Complex mixtures during the activation. Analytical data are marked in blue.

catalysts. The isomerization of 1-octene (10) model substrate was investigated in neat conditions, at 40 °C, using 0.2 mol% catalyst loading (Scheme 4). Although several olefin isomerization catalysts are known, many of them are only soluble in polar solvents making them unsuitable for isomerization of non-polar aliphatic olefins efficiently in neat or apolar media (a typical example is the cationic Grotjahn<sup>[36]</sup> complex, 6). Although the  $\text{RuH}_2(\text{PPh}_3)_4$  complex (7) is widely recognized for its high activity, it exhibits poor compatibility with other catalysts compared to catalyst 2, thereby diminishing the overall catalytic efficiency in tandem catalyst systems. For example, the ISOMET reaction of 1-octadecene with a  $\text{NMe}_2$ -functionalized BICAAC olefin metathesis Scheme 5 catalyst and the isomerization catalyst  $\text{RuH}_2(\text{PPh}_3)_4$  (7) results in one magnitude lower propylene for-

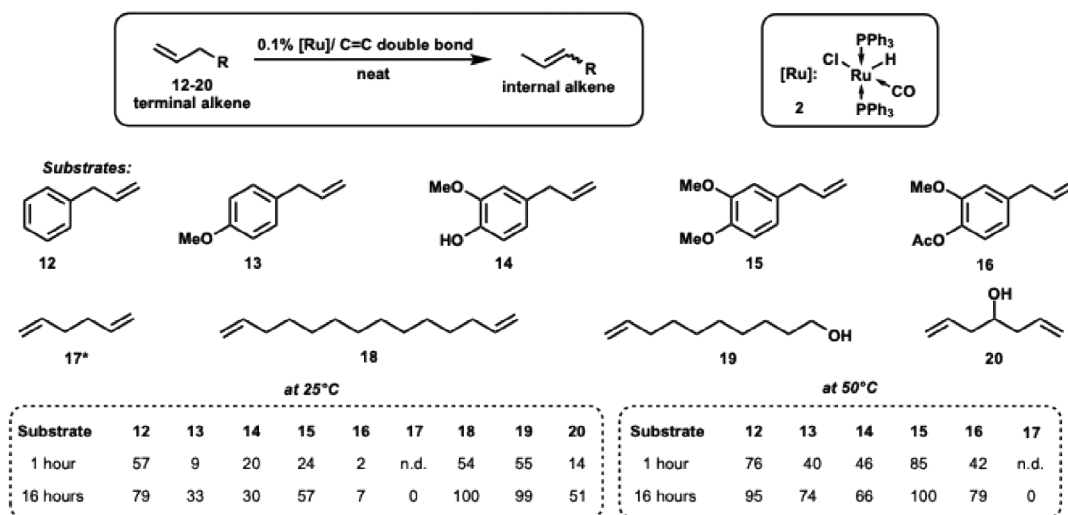
mation, than the same reaction using complex 1 and  $\text{CuCl}$  (see section 3.3 in Supporting Information). Presumably, the combined presence of the carbonyl ligand and the chloride anion ensures the robustness and reasonable activity of the catalysts. Among the examined complexes,  $\text{RuHCl}(\text{CO})$ -phosphine, that is, *tris*-triphenylphosphine (1) and *bis*-tricyclohexylphosphine (3) complexes showed the highest activity. However, in the presence of copper(I) chloride, the isomerization catalytic activity of 1 increased significantly (at room temperature, complex 1 gave 2.4% conversion in the absence and 56.6% conversion in the presence of  $\text{CuCl}$  within 3 h). The activated complex (2) showed superior catalytic activity; either generated in situ (1 +  $\text{CuCl}$ ), or applied as isolated complex (2). Using magnesium salts as additives did not increase the conversions, probably due to their poor solubility in the apolar media (note that the Hong group used ethanol solvent).<sup>[31]</sup> Zinc(II) chloride was also found to be an ineffective additive (for further details, see section 5.1 in Supporting Information).

### 2.3. Substrate Scope of the Activated Catalyst System

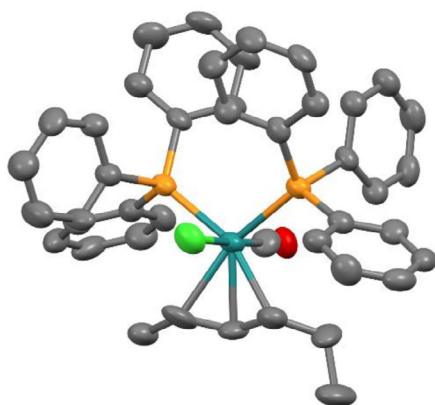
In the following experiments (Figure 3), the activated catalyst system (2) was tested on terminal olefin substrates (12–20). For example, allylbenzene (12) and its derivatives (13–16) are of industrial importance in the production of pharmaceuticals and fragrances.<sup>[4]</sup> In most cases, the isomerization of the investigated terminal linear alkenes, especially allylbenzene derivatives, was achieved in good conversion. The lower limit of catalyst loading was 0.1 mol%, as an order of magnitude lower loading (0.01 mol%) resulted in 0% conversion of 15 at 50 °C (16 h). Hydroxyl functional groups have little effect on the activity of isomerization of the activated complex (substrates 14, 19, and 20). Sterics, however, play an important role. Neither internal, nor sterically congested alkenes could be isomerized. This is consistent with the observations reported in the literature for the unactivated triphenylphosphine complex 1.<sup>[37]</sup> Moreover, additional bulkiness on the chain could prevent the isomerization (diethyl diallylmalonate, allyl benzoate, detailed in section 5.2 in Supporting Information). Interestingly, short terminal dienes can only



Scheme 4. Benchmark reaction for the comparison for different Ru(II) alkene isomerization catalysts: isomerization of 1-octene (10). Conversions are given in % based on  $^1\text{H}$  NMR.



**Scheme 5.** Substrate scope of the activated alkene isomerization catalyst (**2**). Conversions are given in % based on <sup>1</sup>H NMR. \*Substrate **17** could only be isomerized at an elevated temperature of 100 °C (see [Supporting Information](#)).



**Figure 3.** ORTEP view of the Ru-hexadiene complex (**21**) at 40% probability level. Hydrogen atoms are omitted for clarity.

be isomerized at elevated temperature: while 1,13-tetracosadiene (**18**) could be easily isomerized at room temperature, while 1,5-hexadiene (**17**) requires heating (100 °C). This phenomenon was also observed at the ISOMET reaction.<sup>[2,38]</sup> PE-derived pyrolysis oils having low-molecular weight diene content shows limited ISOMET-propylene yield compared to batches, where the light fractions were removed by distillation. It is noteworthy that the initially yellow solution of **2** turns red upon addition of **17**, while no color change was observed in the case **10**. In NMR studies with 1,5-hexadiene (**17**), titration experiments indicated the formation of hexadiene isomers and their catalytically inactive ruthenium-allyl complexes (section 2.6 in [Supporting Information](#)). The formation of such an  $\eta^3$ -allyl ruthenium complex (**21**) has also been confirmed by XRD. This complex (**21**) consists of an isomerized hexadiene-derived allyl ligand instead of the hydride, while the phosphines have changed their original *trans*-position to *cis*. For the allyl ligand, the C4–C3–C2 angle for the central carbons is 128(1)° (Figure 3, see [Supporting Information](#)). A similar structure can be found for Ir complexes.<sup>[39]</sup> Longer terminal diolefins are unlikely to be able to form a sim-

ilar structure due to the large distance between the double bonds. In summary, it was concluded that short-chain dienes can inactivate the isomerization catalyst via the formation of catalytically inactive  $\eta^3$ -allyl ruthenium species and thus inhibit the ISOMET reaction of PE pyrolysis oil. It was also found that the isomerization is mostly selective for the  $\alpha/\beta$  position change, the terminal unsaturation seems to be moving only one, marginally two positions ahead, as unsaturated aliphatic alcohol substrates showed. For instance, 1,6-heptadien-4-ol (**20**) gave at room temperature 51% conversion, and 35%  $\alpha/\beta$ , 14%  $\beta/\beta$  unsaturated dienols, while only traces of the corresponding ketones could be detected (1%–1% for both the  $\alpha$  and  $\beta$  hepten-4-ons, respectively, see product distribution in section 6 of [Supporting Information](#)).

### 3. Conclusion

In this communication, the activation of  $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$  (**1**) was reported by scavenging one of the phosphine ligands with copper(I) chloride. The resulted, coordinatively unsaturated, 16-electron complex,  $\text{RuHCl}(\text{CO})(\text{PPh}_3)_2$  (**2**) could be isolated with good yield, being similar structure to its sterically more crowded  $\text{PCy}_3$  analog (**3**). Comparing the activated catalyst system with known catalysts and testing it on several substrates showed its superb activity at the isomerization of linear, terminal alkenes. The inhibitory effect of diene substrates was also discussed. In addition to their own relevance to the isomerization of terminal alkenes, the results may contribute to a better understanding of tandem isomerization reactions such as ISOMET, which provide powerful tools for persistent plastic recycling.

### Supporting Information

The authors have cited additional references within the Supporting Information.<sup>[1,40–44]</sup>

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## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the [Supporting Information](#) of this article.

**Keywords:** Alkene isomerization · CuCl · Diene · ISOMET · Ruthenium hydride

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