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Alkyl group-tagged ruthenium indenylidene complexes: Synthesis, characterization and metathesis activity

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ABSTRACT

We report on the synthesis of ruthenium indenylidene catalysts [$RuCl_2$(3-R-1-indenylidene)(PCy_3)$_2$ in which R is *iso*-propyl (**7a**), *tert*-butyl (**7b**) or cyclohexyl (**7c**)]. The obtained alkyl tagged indenylidene catalysts were analyzed by means of IR, elemental analysis, NMR and single crystal X-Ray diffraction analysis. Furthermore, the catalytic performance of these new complexes was examined in different metathesis reactions: ring-closing metathesis (RCM), ring-closing ene-yne metathesis (RCEYM), ring-opening metathesis polymerization (ROMP) and cross metathesis (CM), exhibiting a comparable activity in comparison with the commercially available catalyst **3a**.

1. Introduction

Olefin metathesis as a powerful synthesis tool plays an important role in synthetic chemistry [1]. The suitability of ruthenium based olefin metathesis catalysts over other transition metals is based on their ability to combine both high activity and excellent stability [2]. Since the discovery of the 1st generation ruthenium benzylidene catalyst **1a** (Fig. 1) by Grubbs and coworkers [3], the great focus of metathesis pioneers has been on the development of new catalysts with enhanced catalytic performance. A notable development was the substitution of one of the labile phosphines by *N*-heterocyclic carbenes (NHC), which resulted in the more stable 2nd generation catalyst **1b** [4]. Another important contribution in this area was the development of the chelating benzylidene Grubbs-Hoveyda type catalyst **2**, which showed an increased stability in comparison to complex **1a** [5]. Besides ruthenium benzylidene catalysts **1** and **2**, the ruthenium indenylidene catalysts have also been well-studied, for example complex **3a** [6]. The peculiar attribution of ruthenium indenylidene catalysts is their ease of synthesis [7], and increased stability under harsh conditions. Additionally, they exhibit a comparable (or sometimes higher) catalytic performance than their benzylidene counterparts [7a,8]. Furthermore, the ruthenium indenylidene catalysts were often employed as starting materials for the synthesis of other families of ruthenium catalysts, *e.g.* benzylidene [9] or ether chelating benzylidene catalysts [10].

The ease of synthesis and high catalytic performance of ruthenium indenylidene catalysts have encouraged some researchers to modify these basic indenylidene structures. In 2010, the catalyst **4a**, bearing the bidentate *iso*-propoxyindenylidene ligand, was reported by Bruneau's group which was an analogue of complex **2**. Although a lower catalytic initiation speed was observed, the reported complex showed improved thermal stability in comparison with its benzylidene analogue **2** [11]. Later on, substituted variants with the general structure of **4b** of the chelating indenylidene complexes were reported by the same group [12]. Moreover, Schrodi et al. reported on the *in-situ* generated methoxy coordinated bidentate indenylidene catalyst **4c**, which showed a comparable activity to complex **2** [13]. Recently, we have reported the

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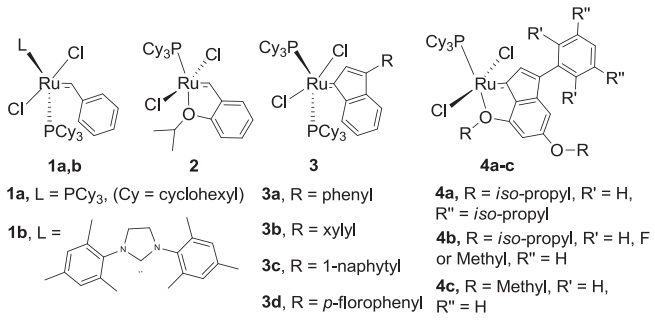


Fig. 1. Ruthenium based olefin metathesis catalysts.

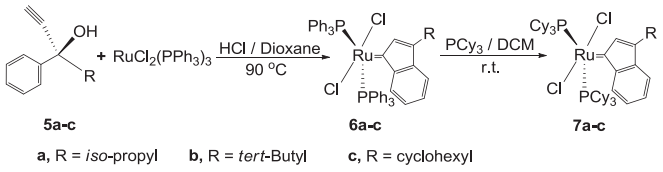
synthesis of first generation ruthenium indenylidene complexes **3b-d** featuring a functionalized 3-phenyl group based on the general scaffold of complex **3a**, the resulting complexes showed comparable catalytic activity relative to the reference catalyst **3a** [14].

So far, all the reported ruthenium indenylidene catalysts were derived from 1,1-diaryl-propargylic alcohols [11–13,15]. Nevertheless, only one of the two aryl groups is necessary to be involved in the indenylidene formation process. Some attempts for obtaining ruthenium indenylidene complexes from a mono aryl propargylic alcohol were not successful [13b,16]. Herein, we report on the successful synthesis of ruthenium indenylidene catalysts employing a library of 1-alkyl-1-phenyl-2-propyn-1-ol ligands. The characterization and catalytic activity of the obtained first generation single species with the general structure of $RuCl_2$(3-alkyl-1-indenylidene)$(PCy_3)_2$ are described.

2. Results and discussion

A convenient way to obtain a ruthenium based alkylidene catalyst (vinylidene [17], allenylidene [6c,18] and indenylidene [7a,12,19]) is the direct treatment of non-hazardous propargylic alcohols with $RuCl_2(PPh_3)_3$ [20]. However, the ruthenium indenylidene catalysts were generally preferred among these three families since they showed a relatively more active performance in olefin metathesis reactions in comparison to their vinylidene or allenylidene analogues [15b]. Especially, the latter two catalysts types could be decomposed by H_2O [21] or O_2, [22] consequently, the cleavage of the $C_\alpha = C_\beta$ bond resulted in a formation of a CO ligand. Thus, in terms of catalyst efficiency and hence the cost effectiveness of the expensive ruthenium used, ruthenium indenylidene catalysts are more preferred [15b,20c,f]. The indenylidene precursor complex **3a** could be obtained from a well-established general strategy, which involves the reaction of $RuCl_2(PPh_3)_3$ and 1,1-diphenyl-2-propyn-1-ol in THF/dioxane in presence of acid and followed by an exchange of PPh_3 with PCy_3 [7b].

The propargylic alcohols **5a** [23], **5b** [24] and **5c** [25] (Scheme 1) were prepared by direct addition of ethynylmagnesium bromide to the relative keton in THF and were purified by column chromatography. Subsequently, **5a-c** were allowed to react with $RuCl_2(PPh_3)_3$ in dioxane in the presence of HCl at 90 °C [26]. The



Scheme 1. Synthesis of complexes **7a-c** from **5a-c**.

reactions yielding complexes **6a-c** were monitored by ^{31}P NMR spectroscopy. The reaction solutions all showed a dark red color after 10 min and according to the ^{31}P NMR spectra the reactions were finished. Single phosphine peaks for each compound were observed at 29.6 ppm for **6a**, 29.1 ppm for **6b** and 29.5 ppm for **6c** from the ^{31}P NMR spectra (see Fig. S.4,6,8), after purification by simply washing with *n*-hexane and methanol. The structural configurations of **6a-c** were confirmed by single crystal X-ray analysis (see the section "Single crystal X-ray diffraction analysis"). Later on, complexes **7a-c** were obtained by the exchange of the PPh_3 on **6a-c** by PCy_3 in dichloromethane (Scheme 1) as reddish brown solids in high yield (91–95%) after washing with *n*-pentane. The purities of the obtained complexes **7a-c** were analyzed by elemental analysis. The characterization of **7a-c** was done by means of IR, NMR and single crystal X-ray diffraction (see the section "Single crystal X-ray diffraction analysis"). For the NMR data, assignment of each proton and carbon resonance of the ^1H- (see Fig. S.9,12,15) and $^{13}C\{^1H\}$ (see Fig. S.10,13,16) NMR spectra was achieved by a combination of the 1D and 2D ($^1H\{^1H\}$COSY, $^1H\{^{13}C\}$HSQC and HMBC) NMR data (see the section of "Structure elucidation of NMR spectral data" in the ESI).

2.1. Single crystal X-ray diffraction analysis

Crystallization of **6a-c** was carried out by incubation of reaction solutions at room temperature for two days affording crystals, suitable for X-ray structure determination. Their structures are shown in Fig. 2.

Compounds **6a** and **6c** crystallized both in the centro-symmetric triclinic space group *P*-1, while compound **6b** crystallized in the centro-symmetric monoclinic space group *I*2/a. The asymmetric unit of the structures consists of one ruthenium complex molecule and additional dioxane solvent molecules (one dioxane molecule for **6a**, two-and-a-half for **6b** and three for **6c**). For **6a**, the 3-*iso*-propyl-1-indenylidene moiety is completely disordered over two

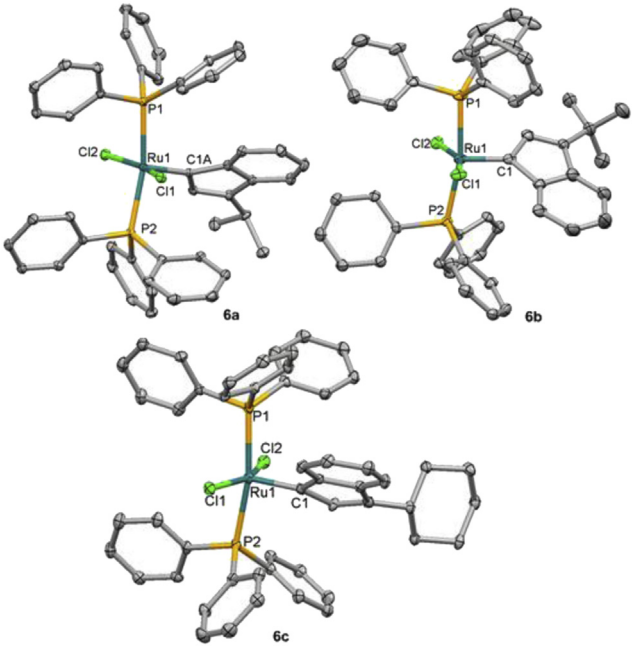


Fig. 2. ORTEP representations of the structures of complexes **6a-c** (thermal ellipsoids are shown at the 30% probability level), showing the atom labeling scheme of the heteroatoms and carbon atom C1 and C1A. Hydrogen atoms and dioxane solvent molecules are omitted for clarity. For **6a,** the disorder of the 3-*iso*-propyl-1-indenylidene moiety is omitted for clarity.