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Latent ruthenium olefin metathesis catalysts featuring a phosphine or an N-heterocyclic carbene ligand

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ABSTRACT

The synthesis and characterization of latent 18-electron ruthenium benzylidene complexes $(PCy_3)(({}^{\kappa}N,O)$-picolinate$)_2$RuCHPh (**5**) and $(H_2IMes)(({}^{\kappa}N,O)$-picolinate$)_2$RuCHPh (**6**) are described. Both complexes appear as two isomers. The ratio between the isomers is dependent on L-type ligand. The complexes are inactive in ring-closing metathesis and ring-opening metathesis polymerization reactions even at elevated temperatures in the absence of stimuli. Upon addition of HCl, complexes **5** and **6** become highly active in olefin metathesis reactions. The advantage of the latent catalysts is demonstrated in the ring-opening metathesis polymerization of dicyclopentadiene, where the latency of **6** assures adequate mixing of catalyst and monomer before initiation. Trapping experiments suggests that the acid converts the 18-electron complexes into their corresponding highly olefin metathesis active 14-electron benzylidenes.

1. Introduction

Ring-opening metathesis polymerization (ROMP) is a powerful tool for the synthesis of linear as well as branched polymers [1]. Ruthenium catalysts, such as **1**–**4** (Chart 1), have enabled preparation of a variety of functionalized polymers [1]. Important topics such as versatility, high reaction rates, functional group tolerance, and poly dispersity indices (PDI) have been well studied [1,2,3]. For some processes it is desirable that catalyst initiation is controllable. For example, efficient ROMP reactions require adequate mixing of

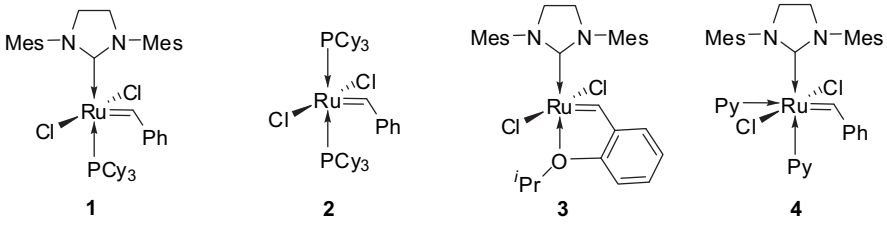

Chart 1.

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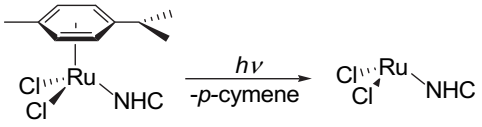
monomer and catalyst before polymerization occur. Therefore, it is of interest to develop latent initiators which only initiate upon a given stimuli.

Methodologies for controlling the initiation with different stimuli have been reported. It has been demonstrated that the initiation can be controlled by, for example, irradiation (eq 1) [4] or addition of acid (eq 2) [5,6,7,8].



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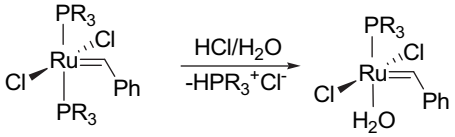
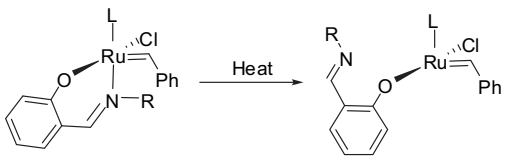


(2)

Currently, the most frequently used method for initiating latent catalysts is thermal initiation. Several different strategies using thermally labile ligands have been shown to be effective. For instance, several groups have shown that a hemi-labile L-type ligand chelated to an alkoxide inhibited metathesis reactions at room temperature. However, at elevated temperatures the olefin metathesis reactions were initiated (eq 3) [9,10,11]. Another successful strategy has been to exchange the ruthenium benzylidene for a Fischer-type carbene ligand [12]. A more recent approach has been to substitute the ether functionality in **3** with a more coordinating group such as an amine [13,14], imine [15], aldehyde or ester [16] (eq 4). A sophisticated control of reaction rates has been achieved by fine-tuning the electronic property and also the steric environment of this ligand. However, none of the catalysts described are completely inactive in the absence of stimuli. Very recently, our group reported a latent catalyst system combining a photoacid generator (PAG) with an acid activated catalyst. The latent system was successfully applied on RCM and ROMP reactions [17].

In 2005, Hahn and coworkers reported the eighteen electron complex **6b** (Fig. 1) [18]. Two chlorides and pyridines of **4** have been substituted for two picolinate ligands. Complex **6b** was found to be inactive in catalysis during standard reaction conditions. However, upon addition of HCl the complex became activated and performed



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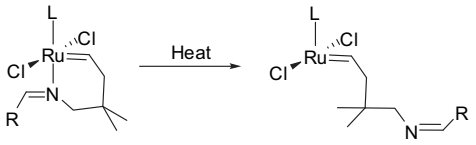

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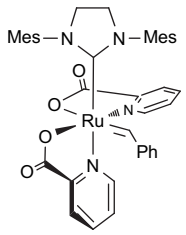


Fig. 1. Reported structure of complex **6b** [18].

ring-closing metathesis. The authors proposed a mechanism of initiation where one of the picolinate ligands was protonated by the acid. We decided to continue the study and also expand it to a picolinate analog of **2**. Herein, a study concerning the structures of these complexes which appear as isomers is presented. The mechanism of the activation step by HCl has been elucidated, and also the advantage of this catalyst has been demonstrated in the ROMP of DCPD.

2. Materials and methods

2.1. General methods

All reactions were run in oven-dried glassware under an argon atmosphere using standard glove-box or Schlenk techniques. Solvents were purified by passage through alumina [19]. Resonances for NMR spectra are reported relative using residual solvent as internal standard, for ^{1}H and ^{13}C, and H_3PO_4 for ^{31}P. Spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Picolinic acid and Ag_2O were purchased from Aldrich and used without prior purification. Catalyst **1** and **2** was obtained from Materia, Inc.

2.1.1. Synthesis of $(PCy_3)(picolinate)_2Ru(CHPh)$ (**5**)

*Synthesis of **5a**.* A Schlenk flask was charged with $(PCy_3)_2Cl_2Ru(CHPh)$ (**1**) (210 mg, 0.26 mmol), picolinic acid (300 mg, 2.4 mmol), and Ag_2O (60 mg, 0.26 mmol) and flushed with argon. Methylene chloride (15 mL) was canula transferred and the reaction was stirred at rt under argon for 1 h during which time a color change from purple to green was observed. The reaction mixture was filtered through a glass-frit and concentrated in vacuo. The resulting solid was purified via column chromatography (TSI silica) using a gradient of ethyl acetate and MeOH to give 150 mg of 5a as a green solid in 72% yield. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 20.23 (d, $J = 12.1$ Hz 1H), 8.82 (d, $J = 4.9$ Hz 1H), 8.19 (m, 1H), 7.97 (m, 1H), 7.84 (m, 1H), 7.77 (d, $J = 7.1$ Hz 2H), 7.60 (m, 3H), 7.48 (m, 1H), 7.23 (m, 2H), 7.03 (m, 1H), 0.8–2.0 overlapping aliphatic signals (33H). ^{13}C NMR (75 MHz, CD_2Cl_2,

10 °C) δ 323.8, 175.0, 171.5, 157.5, 150.1, 148.0, 147.6, 147.1, 146.5, 139.0, 138.5, 130.6, 129.9, 128.8, 127.6 126.7, 125.5, 36.6, 28–30 overlapping signals, 27.1, 26.7. ^{31}P NMR (121 MHz, CD_2Cl_2) δ 33.3. IR (CH_2Cl_2) $\nu = 3457, 2927, 1662\ cm^{-1}$. FAB-HRMS: *m*/*z* calcd for $C_{37}H_{47}N_2O_4PRu$ 716.2317 found 716.2335.

Synthesis of ***5b***. The same procedure as for **5a** was followed, but the reaction time was extended to 1 week or heating to reflux over night was required. **5b** was purified via column chromatography (TSI silica) using a gradient of ethyl acetate and MeOH to give 165 mg of **5b** as a green solid in 90% yield. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 19.58 (d, $J = 11.5$ Hz 1H), 8.36 (d, $J = 4.7$ Hz 1H), 8.22 (m, 1H), 8.13 (m, 1H), 7.81 (m, 2H), 7.53 (m, 2H), 7.47 (m, 1H), 7.38 (m, 1H), 7.19 (m, 2H), 6.89 (m, 1H), 6.09 (m, 1H) 0.9–2.1 overlapping aliphatic signals (33H). ^{13}C NMR (75 MHz, CD_2Cl_2, 10 °C) δ 314.8 (d, $J = 15.1$ Hz), 174.2, 167.3, 157.6, 156.4, 152.0, 146.0, 138.6 (d, 11.7 Hz), 130.2, 129.5, 128.1, 128.0, 127.3, 127.1, 127.1, 126.0, 125.6. 35.3 (d, $J = 19.4$ Hz), 31.9, 29.9, 29.1, 28.1, 27.0, 26.5. ^{31}P NMR (121 MHz, CD_2Cl_2) δ 34.3. IR (CH_2Cl_2) $\nu = 3457, 2925, 2847, 1633, 1599\ cm^{-1}$. FAB-HRMS: *m*/*z* calcd for $C_{37}H_{47}N_2O_4PRu$ 716.2035 found 716.2069. Anal. Calcd. for $C_{37}H_{47}N_2O_4PRu$ C, 62.08; H, 6.62; N, 3.91. found: C, 60.66; H, 6.27; N, 3.41.

2.1.2. Synthesis of (H_2IMes)(picolinate)$_2$Ru(CHPh) (***6***)

A Schlenk flask was charged with (NHC)(PCy_3)Cl_2Ru(CHPh) (**2**) (200 mg, 0.237 mmol), picolinic acid (300 mg, 2.4 mmol), Ag_2O (54 mg, 0.32 mmol) and flushed with argon. Methylene chloride (15 mL) was canula transferred and the reaction was stirred for 2 h at rt under argon during which time a color change from red to yellow was observed. The reaction mixture was filtered through a glass-frit and concentrated in vacuo. The resulting solid was purified via column chromatography (TSI silica) using a gradient of ethyl acetate and MeOH to give **6** in two different fractions (71 mg and 37 mg) as one yellow (**6a**) and one green (**6b**) solid in 72% yield. Major isomer (**6a**): ^{1}H NMR (300 MHz, CD_2Cl_2) δ 18.57 (s,1H), 7.79 (m, 1H), 7.73 (m, 2H), 7.38 (m, 2H), 7.34 (m, 3H), 7.01 (m, 4H), 6.79 (m, 1H), 6.65 (s, 2H), 6.36 (s, 2H), 3.94 (m, 4H), 2.44 (s, 6H), 2.15 (s, 6H), 2.00 (s, 6H). ^{13}C NMR (75 MHz, CD_2Cl_2, −20 °C) δ 315.5, 216.0, 175.3, 172.0, 154.5, 125.1–150.4 (21 signals) 21.2, 21.0 18.5, 18.2. IR (CH_2Cl_2) $\nu = 3442, 2909, 1630, 1596\ cm^{-1}$. FAB-HRMS: *m*/*z* calcd for $C_{40}H_{40}N_4O_4Ru$ 742.1925 found 742.1923. Anal. Calcd. for $C_{40}H_{40}N_4O_4Ru$: C, 64.76; H, 5.43; N, 7.55. Found: C, 63.47; H, 5.24; N, 7.03. Minor isomer (**6b**): in accordance to reference [18].

2.1.3. Study of latency using norbornene

An NMR-tube equipped with a screw-cap was charged with **5b** or **6a** (150 μL, 2.7 mM, 0.4 μmol in C_6D_6), norbornene (38 mg, 0.4 mmol) and 0.6 mL C_6D_6. The NMR-tube was heated at 80 °C for 60 min. ^{1}H NMR revealed only starting material. HCl (10 μL, 1 M, 10 μmol) was added via syringe, the NMR-tube was shaken upon which a color change from green for **5** and bright yellow for **6** to yellowish and brownish respectively was observed. The NMR-tube was heated in an oil-bath at 50 °C for 30 min. ^{1}H NMR showed total conversion to product [20].

2.1.4. Study of latency using diethyl diallylmalonate

An NMR-tube equipped with a screw-cap was charged with **5b** or **6a** (296 μL, 2.7 mM, 0.8 μmol in C_6D_6), diethyl diallylmalonate (19 μL, 80 μmol) and 0.45 mL C_6D_6. The NMR-tube was heated at 80 °C for 60 min. ^{1}H NMR revealed only starting material. HCl (20 μL, 1 M, 20 μmol in ether) was added via syringe; the NMR-tube was shaken upon which a color change from green for **5** and bright yellow for **6** to yellowish and brownish respectively was observed. The NMR-tube was heated in an oil-bath at 50 °C for 30 min. ^{1}H NMR showed total conversion to product [21].

2.2. ROMP of DCPD

6a (18.3 mg, 2.45×10^{-5} mol) dissolved in 1 mL of CH_2Cl_2 and added all at once to a beaker with DCPD (100 g, 0.75 mol) containing 6% trimer. The monomer and complex were mixed to obtain a homogenous solution. This mixture was poured into a mold together with HCl (0.5 mL, 1 M, 0.5 mmol) and shaken. Within 20 seconds the exotherm was reached and total polymerization was observed. The plastic was slowly cooled to room temperature. A heat-distortion temperature of (HDT) 130 °C was observed (expected HDT is between 125–135 °C).

2.3. Influence of acid in RCM of ***8***

An NMR-tube equipped with a screw-cap was charged with **5** or **6** (100 μL, 0.08 mM, 0.8 μmol in CD_2Cl_2), **8** (19 μL, 80 μmol) and 0.60 mL CD_2Cl_2. The NMR-tube was injected into a pre-warmed probe at 35 °C and equilibrated for 5 min. The NMR-tube is ejected and HCl was added via syringe, the NMR-tube was shaken, $t = 0$ was set, and the NMR-tube was re-injected into probe. The conversion was determined by integrating known signals of the starting material and product [21].

2.4. Trapping the 14-electron benzylidene

An NMR-tube equipped with a screw-cap was charged with **5** or **6** (4.2 mg 5 or 4 mg 6, 5.6 μmol), isopropoxy-2-(prop-1-enyl)benzene (10 mg, 56 μmol) and 0.75 mL C_6D_6. HCl (100 μL, 1 M, 100 μmol) was added via syringe, the NMR-tube was shaken upon which a color change from bright yellow for **5** and green for **6** to brownish and yellowish respectively was observed. The NMR-tube was heated in an oil-bath at 50 °C. In the case of **5**, ^{1}H NMR showed total conversion to 3 after 1 h. In the case of **6**, 40% conversion to 9 was observed after 2 h. The samples were compared to authentic samples of catalyst **3** and **9**.

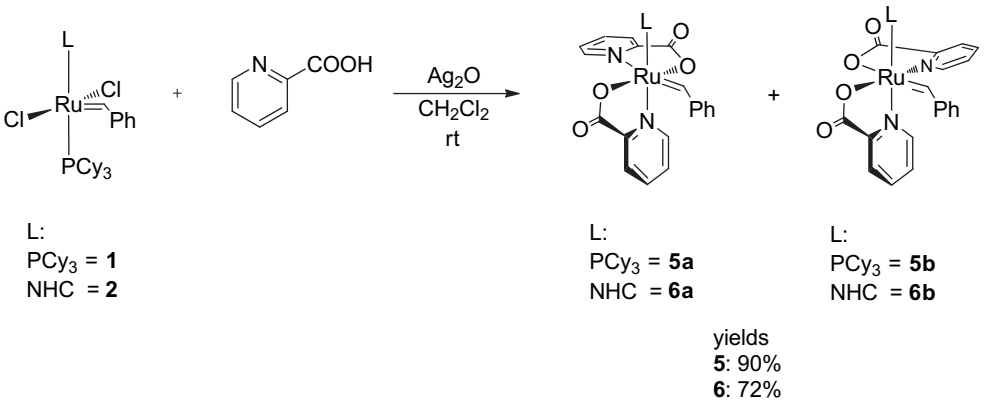
2.5. Selected crystallographic details for ***6a***

Red brown crystals of $\cdot 6x \bullet CH_2Cl_2$ were obtained by diffusion of hexanes into a saturated solution of 6*x* in dichloromethane. Selected crystallographic details: size of data crystal $0.32 \times 0.17 \times 0.09\ mm^3$, formula $C_{40}H_{40}N_4O_4Ru \bullet CH_2Cl_2$, $M = 826.76$ a.m.u., monoclinic space group $P2_1/c$, $a = 21.7076(10)$ Å, $b = 9.5645(4)$ Å, $c = 18.0905(9)$ Å, $\beta = 91.289(3)°$, $V = 3755.0(3)$ Å^3, $Z = 4$, $\rho_{calc.} = 1.462\ Mg/m^3$. 9684 data was collected at 100(2) K in the θ-range 2.32–30.25°. Hydrogen atoms reside on calculated positions and were refined as riding atoms. All calculations were carried out with the SHELX program package.[22]

3. Results and discussion

3.1. Synthesis of complexes ***5*** and ***6***

Upon addition of **1** or **2** to a suspension of picolinic acid and Ag_2O in CH_2Cl_2, the corresponding 18-electron (PCy_3)(($^{\kappa}N,O$)-



Scheme 1. Synthesis of **5** and **6**.

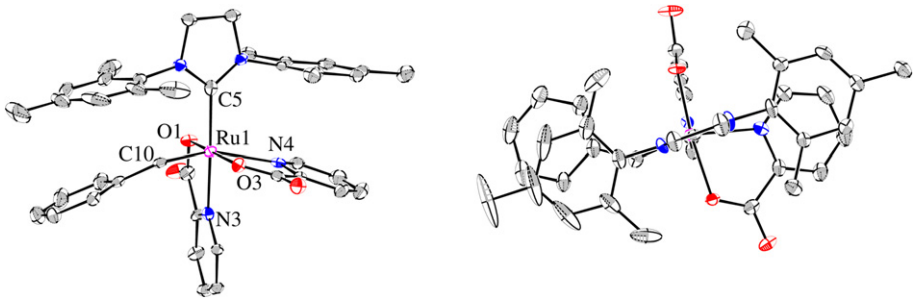


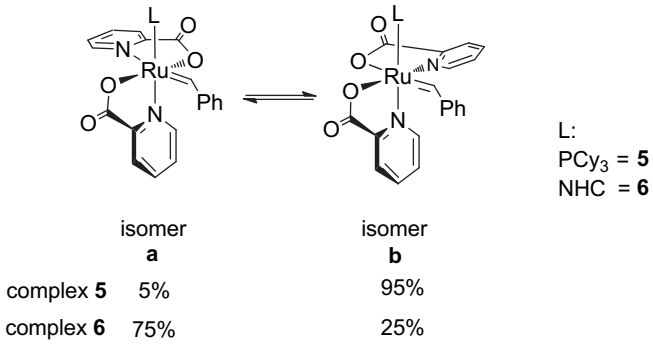
Fig. 2. ORTEP drawing of **6a** with thermal ellipsoids drawn at the 50% probability level (left). Top down view showing π–π slip stacking interaction (right). Hydrogen atoms are omitted for clarity. Representative bond distances (Å) are as follows: Ru1-O1 = 2.071, Ru1-O3 = 2.093, Ru1-N4 = 2.228, Ru1-N3 = 2.115, Ru1-C10 = 1.860, Ru1-C5 = 2.042.

picolinate)$_2$RuCHPh (**5**) and (IH$_2$Mes)(($^{\kappa}$*N,O*)-picolinate)$_2$RuCHPh (**6**) were generated in good to excellent yields (Scheme 1). Noteworthy, both complexes **5** and **6** are formed as mixtures of two isomers where Hahn and coworkers only reported the minor isomer (**6b**). All the isomers of **5** and **6** were isolated and fully characterized. Assignments were based on spectroscopic data, NOE, and crystal structures of **6a** (Fig. 2) and **6b** [18]. In all 4 isomers, the nitrogen atom of one of the picolinates is arranged *trans* to the phosphine ligand in **5** or the NHC ligand in **6**, with the carboxylate group *cis* to the benzylidene. For isomers **5a** and **6a**, the two carboxylate groups of the picolinate ligands are arranged *trans*. Such arrangement of picolinate ligands has been reported for related (PCy$_3$)$_2$(picolinate)$_2$Ru [23].

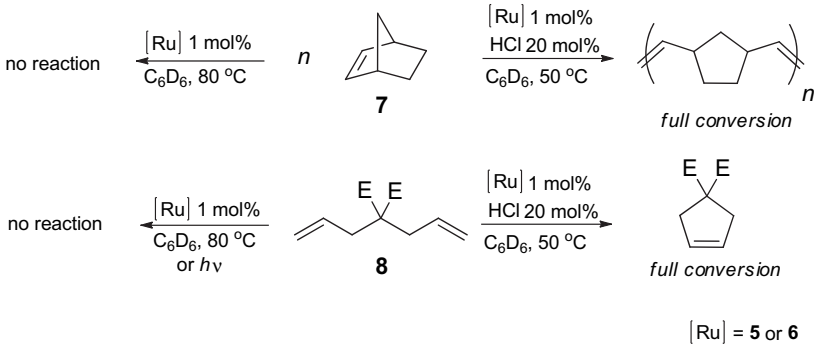
3.2. Isomerization of complexes *5* and *6*

For complex **5**, isomer **5a** is kinetically favored, while **5b** is more thermodynamically stable. When either isomer of **5** was heated in CD_2Cl_2 overnight, a 95:5 ratio of **5b**:**5a** was obtained (Scheme 2) [24]. Apparently, the benzylidene ligand has stronger *trans* influence than the carboxylate group.

In contrast, the isomers of **6** gave a 3:1 ratio of **6a**:**6b**. In the X-ray structure of **6b** [18], a π–π stacking interaction between one of the picolinate ligands and one of the mesityl groups in the NHC was observed (2.3 Å). The thermodynamic preference for **6a** is the result of an additional π–π stacking interaction between the remaining mesityl group of the NHC and the phenyl group of the benzylidene (Fig. 2).



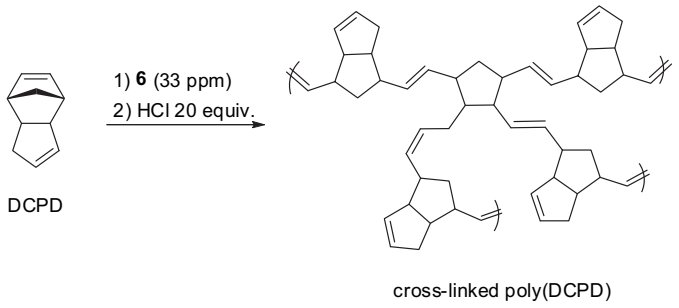
Scheme 2. Isomerization of **5** and **6**.



Scheme 3. Latency of **5** and **6**.

3.3. Latency of complexes *5* and *6*

The latency of complexes **5** and **6** was tested in the ROMP of norbornene (**7**) and the ring-closing metathesis (RCM) of diethyl diallylmalonate (**8**) (Scheme 3). No catalyst activity was observed in any of these reactions when heated in C_6D_6 to 80 °C for 1 h. Also attempts to initiate **6** by UV-irradiation for 12 h failed in the RCM of **8**. However, upon addition of HCl (20 equivalents relative to Ru), complexes **5** and **6** became highly active and initiated ROMP of **7** and RCM of **8**. The reactions were run at 50 °C and all four reactions reached full conversion in less than 30 min.



Scheme 4. Polymerization of DCPD by **6**.

3.4. Activity of *6* in ROMP of Dicyclopentadiene

ROMP of dicyclopentadiene (DCPD) was performed with complex **6** to evaluate catalyst activity in polymerization reactions. The challenge with this type of substrate is to insure adequate mixing of the catalyst and the monomer before initiation takes place. Upon initiation, ring-strain is released followed by an increase of temperature (exotherm). The polymer formed is a cross-linked plastic. When fast initiating catalysts such as **1**–**4** are used, the polymerization can occur faster than monomer and catalyst mixing. This can lead to microencapsulation of the catalyst and the resulting plastic from the incomplete polymerization is therefore not homogenous. Using a latent form of catalyst would enable adequate mixing of monomer and catalyst before initiation.

Upon addition of complex **6** to neat DCPD, no reaction occurred. The monomer and pre-catalyst could be mixed efficiently at room temperature to form a homogenous solution without any reaction [25]. Upon addition of HCl (20 equivalents), the exotherm was reached within 15 seconds, demonstrating the controllability of this methodology (Scheme 4). The resulting poly-DCPD was analyzed and a heat-distortion temperature of 130 °C was measured which is expected for well cured poly-DCPD [26].

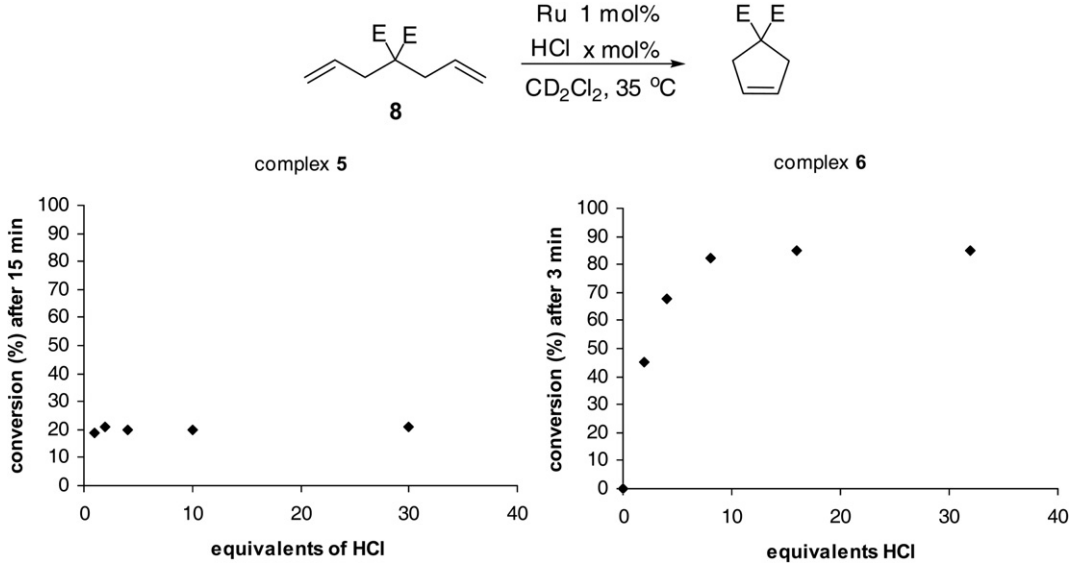
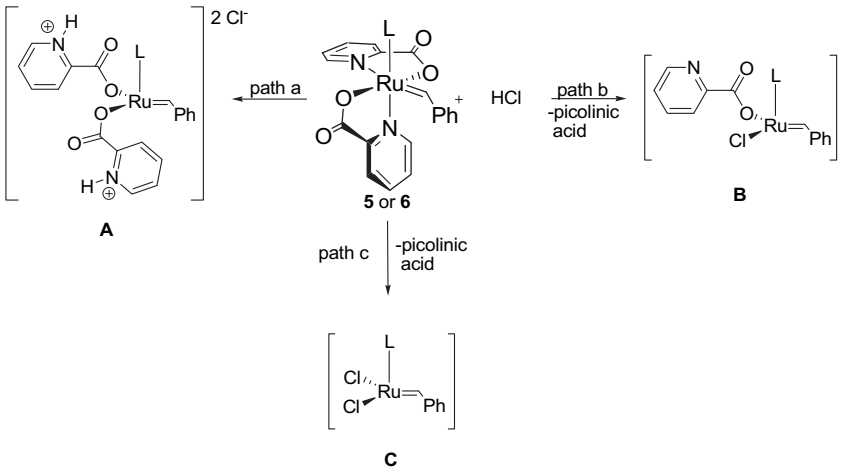


Fig. 3. The reactions were performed on a 0.08 mmol scale in CD_2Cl_2 (0.75 mL) at 35 °C using 1 mol% of catalyst, and monitored by ^1H NMR.



Scheme 5. Different routes of activation.

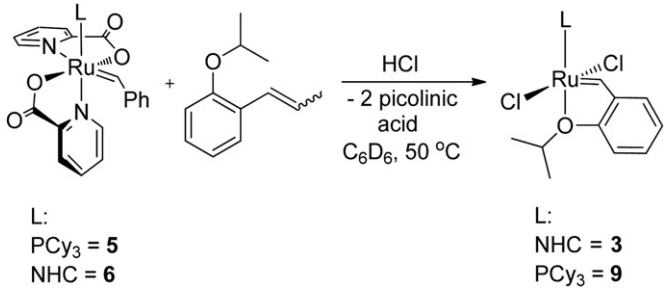
3.5. Influence of acid

To gain information about the activation step by the acid, the dependency of HCl for the reaction rate in the RCM of **8** was studied for complexes **5** and **6** at 35 °C. Interestingly, complex **5** showed no rate-dependence of HCl in RCM of **8**, while complex **6** did. The observed kinetics was similar whether RCM of **8** was run in equimolar or large excess of HCl for complex **5**. Thus, approximately 20% conversion was reached after 15 min running the RCM of **8** with either 2 equivalents or 32 equivalents of HCl (Fig. 3). Even when the reaction was run using less than 2 equivalents of HCl, no decrease in initial reaction rate was observed [27]. On the other hand, complex **6** showed rate-dependence of HCl. Thus, when the RCM of **8** was run with 2 equivalents of HCl, the reaction had reached less than 50% conversion after 3 min (Fig. 3). When doubling the concentration of HCl (4 equivalents), the reaction proceeded to 70% conversion in 3 min. At above eight equivalents of HCl, negligible rate increase was observed. Clearly, complex **5** shows no rate-dependence on HCl while complex **6** does. Overall **6** showed faster initiation and increased reaction rates compared to **5**.

3.6. Trapping the active species

There are several potential pathways by which HCl could activate complexes **5** and **6** (Scheme 5). One possibility is that the acid protonates both nitrogens of the picolinate ligands which would subsequently decoordinate from ruthenium and generate **A** (Scheme 5, path a). The acid could also protonate one of the picolinates and perform a salt-exchange of the picolinate ligand for a chloride to generate **B** (Scheme 5, path b). This pathway was proposed by Hahn and coworkers [18]. The pyridine of the remaining coordinated ligand could be hemi-labile, similar to the ones described in eq 3. Alternatively, this remaining pyridine moiety could be protonated, giving a decoordinated pyridine discussed in path a [28]. Finally, the acid could protonate both ligands, exchanging both picolinates for two chlorides, leading to the 14-electron benzylidene **C** (Scheme 5, path c).

To elucidate the mechanism of HCl activation, complexes **5** and **6** were tested in the cross metathesis (CM) of β-methyl-2-isopropoxy styrene (Scheme 6). This reaction produced solely complexes **3** and **9** that are in agreement to path c (Scheme 5), where the strong acid protonates both picolinates and exchanges both picolinate ligands for chlorides leading to corresponding active 14-electron benzylidene complexes **C**.



Scheme 6. Trapping the active catalyst.

4. Conclusions

The synthesis and characterization of fully latent Ru benzylidenes containing either phosphine or NHC ligand has been described. Both complexes appear as mixtures of two isomers. The ratio of the two isomers depends on the L-type ligand. Upon addition of HCl these latent forms become highly active olefin metathesis catalysts. The utility of these catalysts has been demonstrated in ROMP of DCPD. In the case of **6**, a rate-dependence in the RCM of **8** was correlated to the HCl concentration and in the case of **5** no such correlation was observed. Trapping experiments support, that the role of the acid is to transform the inactive 18-electron complexes into their corresponding highly olefin metathesis active 14-electron benzylidenes.

Acknowledgment

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Appendix Supplementary material available.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 669032.

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