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In situ modification of the Grubbs first generation catalyst: A highly controllable metathesis catalyst bearing tridentate Schiff base ligands

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ABSTRACT

In this study, a practical and inexpensive procedure for the modification of the Grubbs first generation catalyst is reported. A highly controllable metathesis catalyst system was obtained by in situ modification of the Grubbs catalyst with tridentate Schiff base (O—N—O) ligands. The latent catalyst was activated by the addition of HCl, which allowed control of its initiation rate by varying the HCl/Ru ratio. Due to the superior control over the catalyst initiation step, improved molecular weight control in the ring-opening metathesis polymerization (ROMP) of cyclooctene (COE) was achieved using these complexes. ROMP polymers obtained by these catalyst systems have relatively narrow molecular weight distributions, and the molecular weight of the polymers can be controlled on a wide scale. In addition, the reversible inhibition and activation of the catalysts were studied the in ring-closing metathesis reaction (RCM) of diethyldiallylmalonate. RCM of diethyldiallylmalonate can be halted by the introduction of tridentate Schiff base ligands to the reaction medium. The reaction can be switched on again by the introduction of trace amounts of HCl.

1. Introduction

During the past several decades, olefin metathesis has proven to be a useful synthetic method in both organic and macromolecular chemistry [1]. As a versatile method, olefin metathesis is involved in a wide range of organic transformations, such as ring-opening metathesis polymerization (ROMP) [2], ring-closing metathesis (RCM) [3] and acyclic-diene metathesis polymerization (ADMET) [4], as well as tandem metathesis processes [5]. The scope of olefin metathesis has been extended by the development of well-defined catalytic systems, including the Schrock molybdenum catalyst and the Grubbs ruthenium catalysts (Scheme 1) [6].

Among these catalysts, Grubbs 1st (**G1**) and 2nd (**G2**) generation catalysts are commercially available due to their wide-ranging applications in both industry and academia. Although the **G2** catalyst displays superior activity and high functional group tolerance, the extremely fast propagation step and slow initiation step of the **G2** catalyst render it unsuitable for controlled ring-opening metathesis polymerization reactions [7]. Controlled ROMP examples have been reported in the literature using the Grubbs first and third generation catalysts [8]. Along with the evaluations of more active ruthenium metathesis catalysts, recent studies have focused on controlling their metathesis activity [9]. In this respect, latent ruthenium metathesis catalysts have been reported by several research groups [10a–c]. Among the approaches toward latent ruthenium catalysts, recent studies have focused on the incorporation of chelating ligands to obtain ruthenium-based metathesis catalysts that can be activated on demand by thermal-, chemical- and photoactivation [10a–d]. Thermally stable κ^2-(C—N)-type ruthenium catalysts have been reported by Grubbs, Slugovc and Grela [10a–c]. Grubbs and Keitz also demonstrated the thermal- and photoactivation of ruthenium metathesis catalysts bearing chelating ligands [11]. As a novel concept, Grubbs and co-workers reported a thermally activated ruthenium alkylidene system using bidentate Schiff base ligands [12]. Following these improvements in ruthenium alkylidene chemistry, Verpoort reported Schiff base-substituted analogs of Grubbs 2nd generation catalyst, which turned out to be latent precatalysts for application in the ROMP reactions of dicyclopentadiene (DCPD) and cyclooctadiene (COD) [13]. In addition, Verpoort showed that the catalyst/monomer mixture has a longer shelf life and although an unequivocal increase of viscosities obtained in catalyst/monomer mixture, viscosities does not excess the threshold for the further processing of catalyst/monomer mixture. Another approach to obtain improved molecular weight control in ROMP reactions is the in situ modification of Grubbs 1st and 2nd generation catalysts. Hans et al. showed that commercially available Grubbs first and second generation catalysts could be reversibly inhibited or activated on demand by the introduction of *N*,*N*-dimethylaminopyridine (**1**) or 1-methylimidazole (**2**) ligands and

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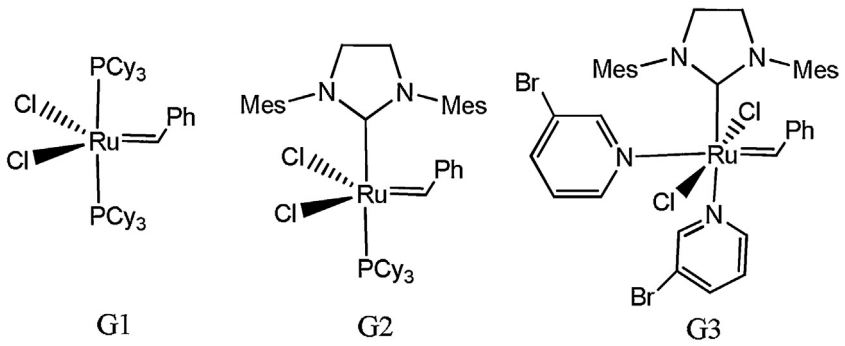


Scheme 1. Grubbs type ruthenium metathesis catalysts.

Bronsted acids (Scheme 2) [14]. This strategy allows for better control in metathesis reactions by the direct manipulation of the catalyst's initiation step. The molecular weight of the polymers can be controlled by varying the amounts of the N-donor and acid. Later, Jensen et al. reported novel ruthenium alkylidene complexes (**3**) bearing a chelating tridentate amine ligand and investigated their metathesis activity in the presence of trace amounts of hydrochloric acid (Scheme 2) [15].

In this paper, we report a novel protocol to obtain a highly controllable metathesis catalyst by the in situ modification of the Grubbs first generation catalyst with tridentate Schiff base ligands to achieve a catalyst that can be activated on demand by the introduction of acids. In comparison to the latent catalytic systems, this study offers a practical and economic methodology for the in situ modification of commercially available Grubbs first generation catalyst.

2. Experimental

All manipulations were performed under an inert atmosphere of nitrogen. All solvents were dried and degassed prior to use. All reagents and monomers were purchased from Sigma–Aldrich and used as received. The Grubbs first generation catalyst was purchased from Sigma–Aldrich and used as received. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded at 25 °C with a Bruker GmbH 400 MHz high performance digital FT-NMR spectrometer using $CDCl_3$ as the solvent.

2.1. Synthesis of tridentate Schiff base ligands

2.1.1. Synthesis of ***1a***

2-Aminophenol (18 mmol, 2.0 g) and salicylaldehyde (18 mmol, 2.10 ml) were refluxed for 2 h in 20 ml ethanol. After the reaction was complete, the reaction mixture was cooled to 0 °C and filtered under vacuum, and the solid products were washed with cold ethanol, resulting in bright orange crystals (Yield: 90%). ^{1}H NMR (400 MHz, DMSO): 13.80 (1H, s), 9.75 (1H, s), 8.97 (1H, s), 7.62 (d, 2H, J = 7 Hz) 7.40 (q, 2H, J = 7 Hz), 7.15 (t, 1 H, J = 8 Hz), 6.96 (t, 3H, J = 8 Hz), 6–87 (t, 1H, J = 7 Hz); ^{13}C NMR (75 MHz, DMSO): 162.05, 161.29, 151.68, 135.40, 133.30, 132.80, 128.57, 120.10, 120.00, 119.98, 119.20, 117.20, 117.04.

2.1.2. Synthesis of ***1b***

2-Amino-4-methyl phenol (16.0 mmol, 2.0 g) and salicylaldehyde (16.0 mmol, 1.85 ml) were refluxed for 2 h in 20 ml ethanol. After the reaction was complete, the reaction mixture was cooled to 0 °C and filtered under vacuum, and the products were washed with cold ethanol, resulting in orange crystals. (Yield: 90%). ^{1}H NMR (400 MHz, DMSO): 13.86 (1H, s), 9.52 (1H, s), 8.97 (1H, s), 7.62 (d, 1H, J = 7 Hz), 7.38 (t, 1H, J = 8 Hz), 7.19 (s, 1H), 6.95 (t, 3H, J = 7 Hz), 6.85 (d, 1H, J = 9 Hz), 2.31 (s, 3H); ^{13}C NMR (75 MHz, DMSO): 161.68, 161.47, 149.44, 134.96, 133.18, 132.75, 129.04, 128.88, 120.30, 120.02, 119.12, 117.23, 116.92, 20.63.

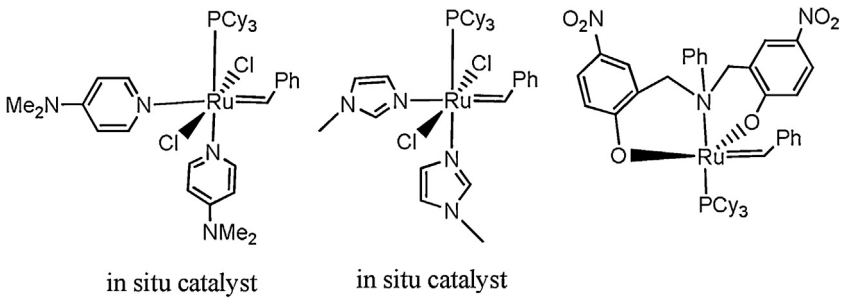
2.1.3. Synthesis of ***1c***

2-Amino-5-nitrophenol (13.0 mmol, 2.0 g) and salicylaldehyde (13.0 mmol, 1.50 ml) were refluxed for 2 h in 20 ml ethanol. After the reaction was complete, the reaction mixture was cooled to 0 °C and filtered under vacuum, and the products were washed with cold ethanol, resulting in red-orange crystals. (Yield: 95%) .^{1}H NMR (400 MHz, DMSO): 13.48 (s, 1H), 10.03 (s, 1H), 8.99 (s, 1H), 7.63 (d, 1H, J = 7 Hz), 7.47 (d, 1H, J = 2 Hz), 7.41 (t, 3H, J = 8 Hz), 6.95 (t, 3H, J = 9 Hz). ^{13}C NMR (75 MHz, DMSO): 165.15, 161.21, 151.63, 146.25, 142.93, 134.29, 133.15, 120.77, 119.85, 119.74, 117.61, 115.41, 111.23.

2.1.4. Synthesis of ***1d***

2-Amino-5-nitrophenol (13.0 mmol, 2.0 g) and salicylaldehyde (13.0 mmol, 1.50 ml) were refluxed for 2 h in 10 ml ethanol. After the reaction was complete, the reaction mixture was cooled to 0 °C and filtered under vacuum, resulting in red-orange crystals (Yield: 93%).

^{1}H NMR (400 MHz, DMSO): 13.22 (s, 1H), 11.39 (s, 1H), 8.28 (s, 1H), 8.18 (d, 1H, J = 8 Hz), 7.70 (d, 1H, J = 8 Hz), 7.43 (t, 1H, J = 8 Hz),



Scheme 2. Controllable ruthenium catalysts.

7.14 (d, 1H, J = 9 Hz), 6.97 (t, 2H, J = 8 Hz). ^{13}C NMR (75 MHz, DMSO): 165.54, 161.10, 158.14, 140.29, 135.90, 133.86, 133.17, 124.04, 119.82, 119.36, 117.58, 117.13, 115.65.

2.2. Synthesis of thallium salts **2a–d**

1a–d (13.0 mmol) were dissolved in 10 ml of dry THF, and thallium ethoxide (26.0 mmol, 1.84 ml) was added under a nitrogen atmosphere, and the reaction mixture was stirred for 2 h at room temperature. The resulting solution was filtered and the thallium salts isolated were used without further purification.

2.3. Synthesis of ruthenium complexes **3a–d**

2.3.1. Synthesis of complex **3a**

The Grubbs first generation catalyst (0.20 g, 0.24 mmol), **2a** (0.163 g, 0.26 mmol) and CuCl (0.26 mmol, 0.026 g) were weighed into a Schlenk flask. The flask was evacuated and filled with nitrogen before the introduction of 10 ml of dry, degassed THF. The mixture was stirred at room temperature for 20 min. The solvent was removed under vacuum and the resulting crude solid product was redissolved in a minimal amount of toluene, followed by filtration under high vacuum. The solvent volume was reduced in half under vacuum, and then 5 ml of cold n-pentane was added to reaction mixture. The resulting brown solids were filtered and washed with cold n-pentane (Yield: 52–60%).

^{1}H NMR ($CDCl_3$, 400 MHz): 18.10 (d, 1H, J = 18 Hz), 8.55 (d, 1H, J = 10 Hz), 7.57 (d, 1H, J = 7 Hz), 7.24 (d, 1H, J = 8 Hz), 7.19–7.05 (m, 5H, J = 9 Hz), 6.82 (t, 2H, J = 7 Hz), 6.65 (m, 3H, J = 8 Hz) 1.85–1.54 (m, 20H,), 1.40–1.11 (m, 10H). ^{13}C NMR ($CDCl_3$, 75 MHz): 171.5, 166.90, 155.5, 148.5, 138, 134.2, 131.6, 129.0, 128.2, 127.85, 127.70, 126.90, 125.20, 124.30, 122.10, 120.90, 119.0, 115.90, 115.81, 114.00, 33.40, 33.20, 29.10, 29.12, 27.90, 27.85, 26.90, 26.80, 26.50, 26.30, 26.10. ^{31}P NMR (161 MHz, $CDCl_3$): 40.15 ppm. Elemental analysis: found (calculated), C, 66.99 (66.84); N, 2.09 (2.05); H, 7.20 (7.09).

2.3.2. Synthesis of complex **3b**

Our attempts to synthesize this compound failed because of the formation of by-products. Although Complex **3b** formed as the major product in the isolated crude solid mixture, we could not purify this complex using chromatographic methods. The ^{31}P NMR spectrum of the mixture consisted of signals coming from Complex **3b** (39.60 ppm), as well as unidentified non-alkylidene by-products. The alkylidene proton peak appeared at 18.11 ppm (d, 1H, J = 18 Hz) together with the imine proton at 8.60 ppm (d, 1H, J = 10 Hz).

2.3.3. Synthesis of complex **3c**

This complex was synthesized using a similar procedure as used to synthesize Complex **3a**. (Brown solid, Yield: 55–60%). ^{1}H NMR (400 MHz, $CDCl_3$): 18.10 (d, 1H, J = 14 Hz), 8.54 (d, 1H, J = 9 Hz), 7.76 (s, 1H), 7.66 (d, 1H, J = 8 Hz), 7.55 (d, 1H, J = 8 Hz) 7.43 (d, 1H, J = 8 Hz), 6.74 (m, 4H), 6.56 (t, 1H, J = 7 Hz), 2.33–0.90 (m, PCy_3 + n-pentane). ^{13}C NMR (75 MHz, $CDCl_3$): 171.32, 168.75, 153.72, 149.30, 137.91, 136.42, 135.18, 129.05, 128.64, 128.40, 128.25, 125.95, 125.31, 123.81, 122.92, 119.70, 119.02, 115.99, 110.89, 33.96, 33.77, 29.13, 29.04, 27.74, 27.63, 27.34, 27.00, 26.40, 26.35, 26.15, 22.37, 21.49. ^{31}P NMR (161 MHz, $CDCl_3$): 40.26. Elemental analysis: found (calculated), C, 62.83 (62.71); N, 3.88 (3.85); H, 6.62 (6.51).

2.3.4. Synthesis of complex **3d**

This complex was synthesized using a similar procedure as that used to synthesize complex **3a**. (Brown solid, Yield: 58–63%) ^{1}H NMR (400 MHz, $CDCl_3$): 18.36 (d, 1H, J = 13 Hz), 8.86 (d, 1H, J = 9 Hz), 8.12 (d, 1H, J = 9 Hz), 7.46 (d, 1H, J = 8 Hz), 7.17 (d, 2H, J = 8 Hz), 7.10–7.00 (m, 5H), 6.76 (t, 1H, J = 7 Hz), 2.40 (s, 3H), 2.20–1.10 (m, PCy_3 + n-pentane). ^{13}C NMR (75 MHz, $CDCl_3$): 177.52, 168.75, 154.80, 148.70, 136.81, 136.10, 135.00, 133.00, 129.05, 128.60, 128.00, 128.25, 125.45, 125.30, 123.21, 122.0, 119.45, 116.03, 110.99, 33.96, 33.70, 29.10, 29.41, 27.74, 27.63, 27.34, 27.00, 26.40, 26.35, 26.15, 22.37, 21.49. ^{31}P NMR (161 MHz, $CDCl_3$): 40.10. Elemental analysis: found (calculated), C, 62.80 (62.72); N, 3.90 (3.85); H, 6.47 (6.50).

2.4. General procedure for the RCM reactions of diethyldiallylmalonate with isolated complexes **3a**, **3c** and **3d**

A reactor was charged with **3d** (0.025 g, 0.034 mmol) and diethyldiallylmalonate (166.0 μL, 0.69 mmol) in 2 ml dichloromethane under an inert atmosphere of nitrogen. Reactor was heated to 40 °C in an oil bath and HCl (1 M, 68 μL) was introduced into the reaction mixture. The reaction was followed by GC–MS and ^{1}H NMR analysis.

2.5. General procedure for the ROMP reactions of COE with isolated complexes **3a**, **3c** and **3d**

A reactor was charged with **3d** (0.025 g, 0.034 mmol) and COE (2.21 ml, 17 mmol) in 5 ml chlorobenzene under an inert atmosphere of nitrogen. Reactor was heated to 40 °C in an oil bath and HCl (1 M, 68 μL) was introduced into the reaction mixture. Samples were periodically drawn from reaction mixtures and monitored by comparing the integrations of the olefinic monomer peak and polymer peaks in ^{1}H NMR. The reaction was quenched with addition of ethyl vinyl ether (130 μL, 1.36 mmol) and stirred at room temperature for 30 min. The polymer was precipitated by pouring the resulting solution into an excess of methanol and collected by filtration.

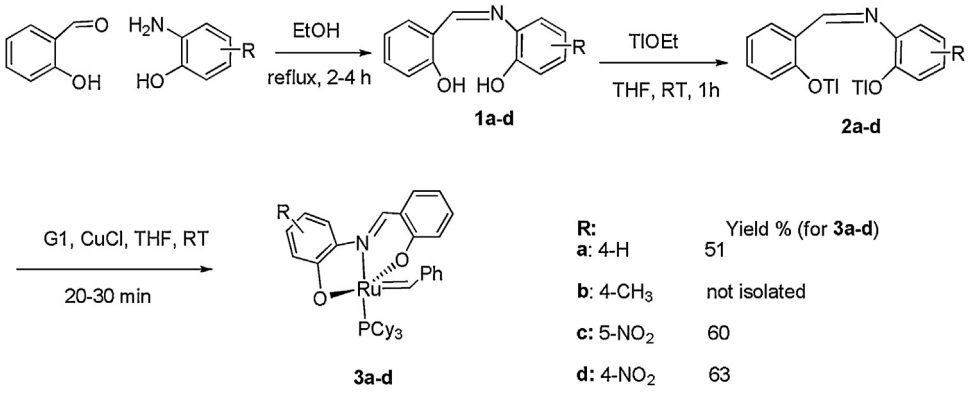
2.6. General procedure for the in situ formation of **3a**, **3c** and **3d**

A reactor was charged with **G1** (0.025 g, 0.030 mmol), **2d** (0.021 g, 0.032 mmol), CuCl (0.0030 g, 0.030 mmol) in 1 ml THF and reacted for 20 min until Grubbs 1st generation catalyst was completely converted to **3a–c**. The formation of **3a–c** was controlled by ^{1}H NMR analysis by taking aliquots from the reaction mixture. After 20 min, the color of the solution turned to dark brown. This solution was filtered to remove thallium(I) chloride before introduction to a dichloromethane solution of diethyldiallylmalonate or chlorobenzene solution of COE.

3. Results and discussion

We hypothesized that the Grubbs first generation catalyst can be modified in situ by using tridentate Schiff base ligands (O—N—O) to obtain a latent and highly controllable catalyst system in a practical manner. We have chosen chelating tridentate Schiff base ligands because they are easy to prepare and they exert electronic and steric effects on the resulting complexes. To avoid metathesis activity at both room temperature and high temperature, the imine group must be in close proximity to the ruthenium center in order to suppress the formation of a 14-electron metathesis-active species by dissociation of the imine group. This approach is believed to reduce the alkene binding to metal center using the current conditions. Consequently, the catalyst/monomer mixture can be stored at room temperature, as well as at relatively high temperatures without any sign of polymerization. Moreover, this latency will allow us to switch the catalytic activity on demand.

For this purpose, we have synthesized several tridentate Schiff base ligands by condensation of salicylaldehyde with 2-aminophenol derivatives with various substituents on the phenyl



Scheme 3. Synthesis of **1a–d**, **2a–d** and **3a–d**.

rings (Scheme 3). Thallium salts **2a–d** were obtained by treatment of THF solutions of **1a–d** by thallium(I)ethoxide. Although thallium is a highly toxic compound, this approach was chosen on technical grounds in view of a proof of principle which can be latter adapted to silver or potassium salts of **1a–d** for in situ modification of Grubbs first generation catalyst. These thallium salts, **2a–d**, were reacted with **G1** in the presence of CuCl in THF at room temperature. Resulting complexes **3a**, **3c** and **3d** were isolated and characterized by ^{1}H, ^{13}C, ^{31}P NMR, FT-IR and elemental analysis. In order to determine to optimum reaction conditions for isolated complexes **3a**, **3c** and **3d**, metathesis activity of each isolated complex were tested on ROMP and RCM reactions. Once the optimum metathesis reaction conditions were determined, in situ formed complexes **3a**, **3c** and **3d** were used in RCM and ROMP reactions under predetermined reactions conditions.

3.1. Synthesis of ruthenium alkylidene complexes bearing tridentate Schiff base ligands

Tridentate Schiff bases **1a–d**, were prepared by the condensation of salicylaldehyde derivatives with 2-aminophenol derivatives in high yields (>90%). Their structures were confirmed and characterized by ^{1}H and ^{13}C NMR and FT-IR analysis. Thallium salts, **2a–d**, were obtained by the treatment of THF solutions of **1a–d** with thallium ethoxide, as described by Grubbs et al. [12]. These salts were used in complex synthesis reactions without any further purification. We envisioned that thallium salts **2a–d** would be suitable for simultaneous substitution of one neutral phosphine and two anionic chloride ligands in the Grubbs first generation catalysts in a similar fashion with bidentate Schiff base analogs [12]. For this purpose, **G1** was reacted with 1.1 molar equivalents of **2a** in THF at room temperature under an inert atmosphere of nitrogen.

The reaction was followed by comparing the integrations of the benzylidene proton signals of the **G1** and the resulting complex **3a** by ^{1}H NMR. A peak at 18.10 ppm (d, J = 18 Hz) appeared in addition to the precursor benzylidene signal at 20.00 ppm (s, 1H) in ^{1}H NMR. After 10 min, the intensity of the signal at 18.10 ppm started to decrease indicating the decomposition of the resulting complex **3a** without complete conversion to the desired product. These results indicated that the phosphine ligand does not readily substitute with a neutral imine fragment. Therefore, to increase the efficiency of the synthesis, CuCl, a well-known phosphine scavenger, was employed. **G1** was reacted with 1.1 molar equivalent of **2a** and 1.1 molar equivalent of CuCl in THF at room temperature. The color of the purple solution was immediately darkened, and after 5 min, the color of the solution turned to dark brown. Complete conversion to the desired complex **3a** was obtained only in 20 min, as confirmed by ^{1}H NMR. After the isolation of **3a** as a brown solid, this compound was characterized by ^{1}H, ^{13}C, ^{31}P NMR and FT-IR analysis. Although the presence of the alkylidene group was confirmed by a doublet peak at 18.10 (d, 1H, J = 18 Hz) in ^{1}H NMR, the Ru=C signal, which should be appear in the 290–350 ppm region, was not observed in the ^{13}C NMR. The coordination of the imine and benzyloxide groups of **1a** to the ruthenium center was confirmed by FT-IR analysis. The C=N vibration frequency, which appeared at 1636 cm^{-1} in the **1a**, was shifted to 1597 cm^{-1} indicating the coordination of the imine group to the metal center. In addition, the coordination of the nitrogen atom on the imine group of **1a** was observed by the shift of the HC=N imine proton signal from 8.97 ppm to 8.55 ppm in ^{1}H NMR. Although the isolated complex **3a** can be stored at −24 °C in solid state for nearly two weeks under an inert atmosphere of nitrogen without a sign of decomposition. **3a** is not very stable at room temperature under an inert atmosphere and decomposes after 5–7 days in both solid state and in solution phase (in THF).

To monitor the effect of substituents on the stability and activity of the catalyst, ligand precursor, **2b**, bearing an electron-donating methyl group, was employed. **G1** was reacted with 1.1 molar equivalent of **2b** and 1.1 molar equivalent of CuCl in THF at room temperature Although the ^{1}H NMR analysis of the reaction mixture confirmed the quantitative formation of the desired complex (18.11 ppm, d, 1H, J = 18 Hz), the ^{31}P NMR spectrum of the mixture consisted of signals coming from complex **3b** (39.60 ppm), as well as unidentified non-alkylidene by-products. The alkylidene proton peak appeared at 18.11 ppm (d, 1H, J = 18 Hz) together with the imine proton at 8.60 ppm (d, 1H, J = 10 Hz) in ^{1}H NMR. All our attempts to isolate the pure complex **3b** was failed because complex **3b** is very sensitive to air and moisture in both solid state (as a crude product mixture) and in solution phase (in THF) and decomposes completely during column chromatography studies. As a result, by-products could not be removed from the crude product mixture. For this reason, **3b** did not used in any further catalytic studies. Previous attempts to obtain a stable system failed with electron-donating substituents. These results indicated the need for electron-withdrawing groups at the position para or meta to the imine group to obtain a more stable complex. **G1** was reacted with 1.1 molar equivalent of **2c** or **2d** and 1.1 molar equivalent of CuCl in THF at room temperature. The reaction proceeded very rapidly at room temperature with ligand precursors **2c** or **2d**. Following the addition of **2c** or **2d**, color of the solution turned to dark brown. After 20 min, complete conversions to the desired products were confirmed by ^{1}H NMR. Benzylidene proton peaks appeared at 18.10 ppm (d, 1H, J = 14 Hz) for **3c** and 18.36 ppm (d, 1H, J = 13 Hz) for **3d** in ^{1}H NMR. Ligand precursors; **2c** and **2d**, bearing nitro substituents at the 5- and 4-positions, greatly increased the stability of the corresponding ruthenium alkylidene complexes (**3c** and **3d**) relative to **3a** and **3b** in both solid state and in solution phase (in THF). This observation may be the result of the electron-withdrawing

effect of the nitro groups, which may decrease the electron density at imine fragment making the complex much more stable. Isolated complexes **3c** and **3d** can be stored at room temperature under an inert atmosphere for one month without any sign of decomposition and can be handled for several months at −24 °C under an inert atmosphere of nitrogen in solid state.

Alkylidene proton peaks for **3a–d** appear between 18.10 and 18.36 ppm as doublets with proton–phosphorus coupling values between 13 and 18 Hz. As has been well-documented in literature with Grubbs-type catalysts, the coupling constants J (Hz) between the carbene proton and phosphorus are very sensitive to the relative orientation of the plane, defined by the atoms of the carbene and those of the P–Ru–P plane. When the carbene plane is at a 90° angle to the P–Ru–P plane, J_{PH} = 0 Hz and J_{PH} > 10 Hz when they are co-planar [12]. The coupling constants for **3a–b** (J_{PH} = 18 Hz) and for **3c–d** (J_{PH} = 14 Hz) reflect the effect of substituents on the tridentate Schiff base ligands. While electron-withdrawing substituents gave lower coupling constant values (J_{PH} = 14 Hz), electron-donating substituents resulted in higher coupling constant values (J_{PH} = 18 Hz). Unfortunately, all of our efforts to obtain a single X-ray-quality crystal failed. The best crystals were obtained by slow evaporation of n-pentane into a dichloromethane solution of **3d** at −24 °C, but the crystals obtained by this method were very small and not suitable for single crystal X-ray analysis.

Despite the quantitative conversion of **G1** to **3a–d** by ^{1}H NMR, the isolated yields were lower due to the high solubility of the complexes. All our attempts to purify **3b** complex with column chromatography was failed. In all cases, **3b** complex was decomposed during chromatography process. Combining the relatively fast conversion of **G1** into **3a–d** in the presence of **2a–d** and CuCl, we envisioned that these catalytic transformations could be applied as an in situ modification of the Grubbs catalyst to obtain a latent catalytic system that can be activated on demand. Therefore, further catalytic studies were focused on **3a**, **3c** and **3d** that were either isolated or formed in situ in THF.

3.2. Metathesis activity of the complexes *3a*, *3c* and *3d*

To optimize the metathesis reaction conditions, first tests were performed on isolated complexes **3a**, **3c** and **3d**. The metathesis activity of **3a**, **3c** and **3d** was first tested in the ring-closing metathesis reaction of diethyldiallylmalonate under a variety of reaction conditions, and the results are listed in Table 1.

3a, **3c** and **3d** displayed no catalytic activity when the reaction was performed in the absence of HCl. Followed by the addition of 1 M HCl, the catalysts were activated, and conversion values ranging from low to high were obtained for the RCM of diethyldiallylmalonate. The first reaction was performed with a catalytic loading of 5%, in $CDCl_3$ which may contain trace amounts of HCl, as reported by Jensen et al. [15] However, only a 5% conversion of diethyldiallylmalonate was obtained, and increasing the amount of solvent had no beneficial effect on the conversion rate. These preliminary results indicate the need for an acid to obtain a reasonable reaction rate and conversion to the final product. The highest conversion value (65%) was obtained by using a 2/1 HCl/Ru ratio in dichloromethane at 40 °C with a catalytic loading of 5%. No further conversion of diethyldiallylmalonate was obtained after 30 min because of complete catalyst decomposition.

ROMP activity of the isolated complexes **3a**, **3c** and **3d** was tested on COE, a more challenging monomer with moderate ring strain (results are listed in Table 2). Although **3a**, **3c** and **3d** display low RCM activity, these complexes exhibit high ROMP activity in the presence of HCl (1 M). In several cases, complete conversion to the product was obtained in 4 h. Increasing the HCl/Ru ratio above 10/1 increased the catalyst decomposition rate; thus, conversion of COE was decreased when the ROMP reaction was performed with HCl/Ru loadings of 20/1 and 40/1. To determine the functional group tolerance of these complexes, ROMP reactions were performed on several norbornene derivatives (Table 3). **3d** were found to catalyze the ROMP of oxygen-containing norbornene derivatives. 5-Norbornene-2-methanol (endo-exo mixture), 5-norbornene-2-carboxaldehyde (endo-exo mixture), and 5-norbornene-2-yl-acetate (endo-exo mixture) were polymerized at catalyst loadings of 1%. The corresponding ROMP polymers were obtained in moderate yields (54–85%). Complexes **3a** displayed relatively low functional group tolerance, whereas their analogs complexes **3c–d** exhibited remarkable functional group tolerance during the ROMP of oxygen-containing norbornene derivatives.

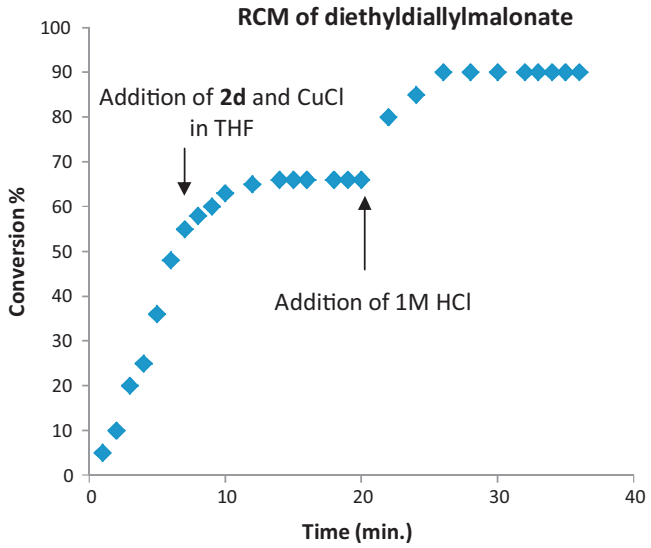
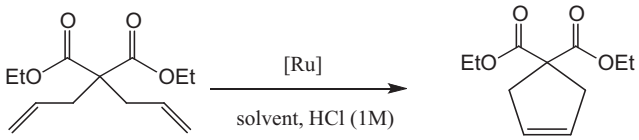


Fig. 1. Inhibition studies of RCM reactions catalyzed by in situ obtained complex **3d**.

3.3. In situ modification studies of the Grubbs first generation catalysis

After the preliminary metathesis activities of the isolated complexes **3a**, **3c** and **3d** were tested and crucial reaction parameters were determined, in situ modification of the **G1** was performed. For this purpose, a reactor was charged with **G1**, **2d** and CuCl in THF and reacted for 20 min. The complete formation to **3d** was confirmed by ^{1}H NMR analysis. Then this solution was filtered before being introduced into a 0.1 M diethyldiallylmalonate solution in CH_2Cl_2. RCM of diethyldiallylmalonate was performed at optimum reaction conditions (Table 1, entry 13) and a conversion of 63% was obtained, which corresponds with the results obtained with the isolated catalyst **3d**. Additionally, frequently encountered side-reactions, such as olefin isomerization, were not observed during the RCM of diethyldiallylmalonate. After this catalyst was tested on the RCM of diethyldiallylmalonate, the reversible inhibition of the **G1**-catalyzed RCM of diethyldiallylmalonate was studied. For this purpose, an NMR tube was charged with 5% **G1** and diethyldiallylmalonate in $CDCl_3$ and reacted at 25 °C. The reaction was monitored by ^{1}H NMR, and, after an induction period (at 60% conversion of diethyldiallylmalonate), the reaction was inhibited by the addition of thallium salt **2d** (1.2 molar equivalents) and CuCl (1.0 molar equivalent) in THF. Following the addition of **2d**, the reaction instantly stopped (64% conversion). After 5 min, the catalytic precursor was activated by the introduction of HCl (1.0 M) to the reaction medium. At this level, diethyldiallylmalonate underwent the RCM reaction to provide an overall 90% conversion (Fig. 1). The same strategy was applied to the ROMP of COE. An NMR tube

Table 1
RCM of diethyldiallylmalonate under various reaction conditions.



Run	Catalyst[a]	Catalyst %	Solvent	Temperature (°C)	Acid/catalyst	Time (h)	Conversion[b] %
1	**3a**	5	$CDCl_3$	40	–	24	5
2	**3a**	5	CH_2Cl_2	40	2	0.5	32
3	**3c**	5	CH_2Cl_2	40	–	24	0
4	**3c**	5	CH_2Cl_2	40	2	0.5	63
5	**3c**	5	$CDCl_3$	40	–	24	4
6	**3c**	5	$CDCl_3$	40	2	0.5	50
7	**3c**	5	Toluene	70	2	1	42
8	**3c**	5	No solvent	40	3	1	51
9	**3c**	5	CH_2Cl_2	40	4	0.5	33
10	**3c**	10	CH_2Cl_2	40	3	0.5	48
11	**3c**	4	Toluene	70	10	1	42
12	**3d**	5	CH_2Cl_2	40	–	24	0
13	**3d**	5	CH_2Cl_2	40	2	0.5	65
14	**3d**	5	$CDCl_3$	40	–	24	5
15	**3d**	5	$CDCl_3$	40	2	0.5	55
16	**3d**	5	Toluene	70	2	1	40
17	**3d**	5	No solvent	40	3	1	50
18	**3d**	5	CH_2Cl_2	40	4	0.5	28
19	**3d**	10	CH_2Cl_2	40	3	0.5	51
20	**3d**	4	Toluene	70	10	1	40

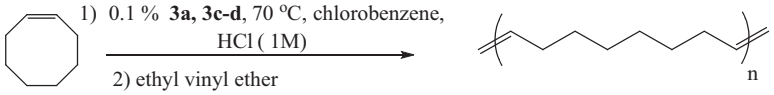
[a] A reactor was charged with **3d** (0.025 g, 0.034 mmol) and diethyldiallylmalonate (166.0 μL, 0.69 mmol) in 2 ml solvent under an inert atmosphere of nitrogen. Reactor was heated to 40 °C in an oil bath and HCl (1 M, 68 μL) was introduced into the reaction mixture.
[b] Conversion values were determined by ^{1}H NMR analysis.

was charged with 0.1% **G1** and COE in $CDCl_3$ and the conversion to the desired product was monitored by ^{1}H NMR. After 20 min (at 30% conversion of COE), the reaction was inhibited by the addition of thallium salt **2d** (1.2 molar equivalents) and CuCl (1.0 molar equivalent) in $CDCl_3$. The reaction was stopped at 34% conversion of COE. After 5 min, the catalytic precursor was activated by introduction of HCl (1.0 M) to the reaction medium. After the addition of HCl, 70% conversion of COE was obtained in 60 min (Fig. 2). The results indicated that the **G1** catalyst could be reversibly inhibited by tridentate Schiff base ligands and CuCl.

To monitor the possible effect of the mixture of CuCl and **2d** on metathesis reactions, a control reaction was performed under the same conditions but without the **G1** catalyst for both the RCM of diethyldiallylmalonate and ROMP of COE. In all cases, no conversion to the expected metathesis or isomerization products were observed.

This in situ modification strategy was extended to the ROMP of COE, and the effect of the acid/Ru ratio on the molecular weight distribution of the polymers was investigated (Table 4). We had already seen that initiation of the catalyst could be controlled by the addition of HCl (1.0 M) in varying amounts, which results in controlled molecular weight distribution and molecular weight of the ROMP polymers. For this purpose, ROMP reactions were performed with in situ formed **3d** complex by varying the HCl/Ru

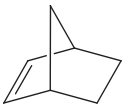
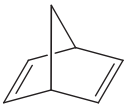
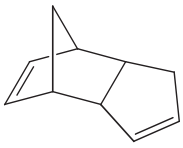
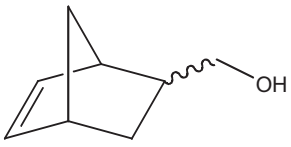
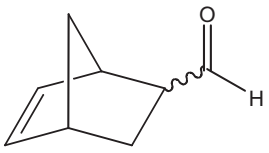
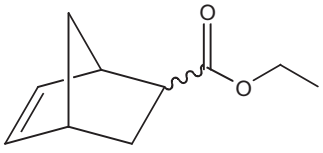
Table 2
ROMP of cyclooctene under various reaction conditions.



Run[a]	Catalyst[b]	Acid/Ru	Conversion %[c]	TON
1	**3a**	2	91	910
2	**3c**	1	97	670
3	**3c**	2	100	1000
4	**3c**	5	100	1000
5	**3c**	10	100	1000
6	**3c**	20	90	900
7	**3c**	40	40	400
8	**3d**	1	90	900
9	**3d**	2	100	1000
10	**3d**	5	100	1000
11	**3d**	10	100	1000
12	**3d**	20	90	900
13	**3d**	40	35	350

[a] A reactor was charged with **3d** (0.025 g, 0.034 mmol) and COE (4.42 ml, 34 mmol) in 5 ml chlorobenzene under an inert atmosphere of nitrogen. Reactor was heated to 40 °C in an oil bath and HCl (1 M, 68 μL) was introduced into the reaction mixture. The reaction was quenched with addition of ethyl vinyl ether (130 μL, 1.36 mmol) and stirred at room temperature for 30 min. The polymer was precipitated by pouring the resulting solution into an excess of methanol and collected by filtration.
[b] Isolated catalyst.
[c] Determined by ^{1}H NMR.

Table 3
ROMP of various norbornene derivatives.

Monomer[a]	Temperatures (°C)	Time (h)	Monomer/catalyst	Ru/HCl	Yield[b]% (with isolated catalyst)	Yield[c] % (with in situ catalyst)
	25	1	1000	2/1	>99	>99
			5000	2/1	90	83
	25	1	1000	2/1	>99	>99
			5000	2/1	91	90
	70	24	100	2/1	>99	90
	70	5	100	2/1	80	78
	70	24	100	2/1	54	50
	70	24	100	2/1	85	82

[a] All reactions were carried out in chlorobenzene with isolated or in situ obtained complex **3d.**
[b] A reactor was charged with 0.02–0.1% isolated complex **3d** (0.025 g, 0.034 mmol), HCl (1 M, 68 μL) and norbonene derivative in 3 m chlorobenzene and reacted at 25–70 °C for 1–24 h.
[c] A reactor was charged with **G1** (0.025 g, 0.030 mmol), **2d** (0.021 g, 0.032 mmol), CuCl (0.0030 g, 0.030 mmol) in 1 ml THF and reacted until Grubbs 1st generation catalyst is completely converted to complex **3d**, confirmed by ^{1}H NMR analysis. This reaction mixture was filtered before introduction to a solution of norbornene derivate and HCl (1 M, 68 μL) in 3 ml chlorobenzene. The resulting solution was reacted at 25–70 °C for 1–24 h.

ratios, and the effect of HCl on the initiation rate, as well as on the average polymer molecular weight was investigated in detail. The ROMP reactions were performed at 0.2–0.02% catalyst loadings of in situ obtained **3d** complex in chlorobenzene at 70 °C and at HCl/Ru ratios of 2/1, 4/1, 5/1 and 10/1. Although high yields were obtained at a catalytic loading of 0.2%, lower yields were obtained for 0.02% loading. M_n values agreed with our expected values (Table 4). The initiation rate of the catalyst is strongly influenced by the HCl/Ru ratio. These results are not surprising because the effect of HCl on catalyst activation and on controlled ROMP has been well-documented in the literature. Due to the fast initiation/propagation step, polymers obtained by this method have narrow PDI (1.30–1.60) values. In addition, molecular weight control can be achieved in a wide range between M_n: 56000 and 407000 Da.

The shelf lives of the monomer/isolated catalyst and the monomer/in situ-modified catalyst mixtures were tested at three different temperatures, 0, 25 and 60 °C. COE was charged with 0.2% isolated complex **3d** and stored under an inert atmosphere of nitrogen at 0, 25 and 60 °C for 24 h. Samples were periodically drawn

Table 4
Controlled ROMP studies of COE.

Run[a]	HCl/Ru	COE/Ru	Conversion	Theorical M_n ($\times 10^3$)	Observed M_n ($\times 10^3$)	PDI[b]	TON[c]
1	0.5	5000/1	19	550	407	1.65	950
2	1	5000/1	24		404	1.62	1200
3	2	5000/1	32		265	1.30	1600
4	4	500/1	>99	55	72	1.40	495
5	5	500/1	>99		61	1.38	495
6	10	500/1	>99		56	1.36	495

[a] A reactor was charged with **G1** (0.025 g, 0.030 mmol), **2d** (0.021 g, 0.032 mmol), CuCl (0.0030 g, 0.030 mmol) in 1 ml THF and reacted for 20 min. After 20 min, the color of the solution turned to dark brown. This solution was filtered to remove thallium(I) chloride before introduction to a chlorobenzene solution of COE.
[b] According to GPC analysis in THF with polystyrene calibration standards.
[c] Turnover number.

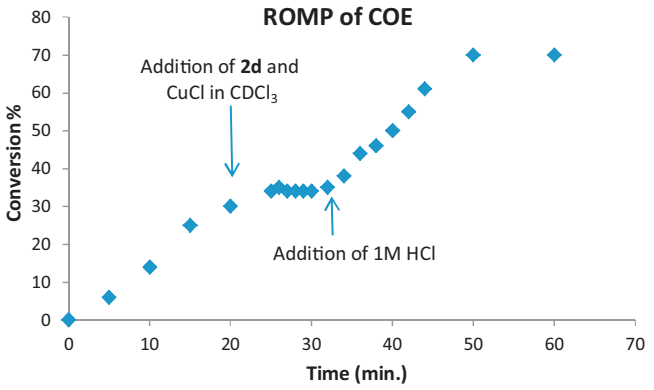


Fig. 2. Inhibition studies of ROMP reactions catalyzed by in situ obtained complex **3d**.

from reaction mixtures and monitored by comparing the integrations of the olefinic monomer peak and polymer peaks. At 0 °C and 25 °C, no polymerization of COE was observed after 24 h. Then the resulting monomer/catalyst mixtures were polymerized at a 100% conversion by the introduction of 2 molar equivalents of HCl (1 M) relative to the ruthenium content. At 60 °C, 4% polymerization product was observed after 24 h. Similar results were observed in the cases of the in situ-modified catalysts-monomer mixtures. No sign of polymerization were observed for either of the solutions at the specified temperatures.

3.4. Mechanistic studies

To gain insight into the reaction mechanism, several experiments were performed by ^{1}H and ^{31}P NMR. There are two possibilities to explain the mechanism of catalyst activation. The first is the dissociation of a phosphine ligand and subsequent protonation by HCl, forming a 14-electron active Ru alkylidene species. The second is the more plausible explanation, which is the protonation of phenoxide moieties by HCl and decomposition of the tridentate Schiff base ligand to form a coordination hole at the position para to the coordinated phosphine ligand. We first investigated the dissociation of the phosphine ligand before the metathesis reaction started. For this purpose, a well-known phosphine scavenger, CuCl, was added to a solution of the catalyst precursor **3d** and COE, rather than HCl. COE did not polymerize for nearly 30 min, and after 24 h, only 10% conversion of COE was observed. This observation clearly indicated that the tridentate Schiff base ligand, not the phosphine, acts as a dissociated ligand. To extend the scope of the mechanistic study, an NMR tube was charged with **3d** in $CDCl_3$ and analyzed by ^{1}H and ^{31}P NMR. At this stage, the NMR spectrum only consisted of a benzylidene proton peak at 18.36 (d, 1H, J = 13 Hz), and a single phosphine signal (40.10 ppm) was observed. After the addition of 2 molar equivalents of HCl (1 M), relative to the ruthenium content, a signal at 19.97 ppm appeared in addition to the catalyst precursor signal at 18.36 ppm (Fig. 3). The signal at 19.97 ppm indicated the formation of the **G1** catalyst by subsequent exchange of chloride ions with phenoxy moieties [16]. This observation was the first indication of the dissociation of tridentate Schiff base ligands during catalyst activation. It is possible that a small amount of phosphine, which is coordinated to ruthenium center, may be protonated. The dissociated phosphine ligand then re-coordinates to the ruthenium center, which is formed by the dissociation of the tridentate Schiff base ligand, giving the characteristic alkylidene proton peak of **G1** at 19.97 ppm. In addition, the ^{31}P NMR spectrum supported this observation. A signal at 36.36 ppm indicated the formation of the Grubbs catalyst. To support this idea with additional experimental observations, an excess of tricyclohexylphosphine was added to the NMR tube. Following the addition of PCy_3, the signal at 19.97 ppm greatly increased (Fig 3 and Fig. 4). Although the ^{31}P NMR spectrum supports our observations, a series of phosphine peaks appeared in addition to a peak at 36.36 ppm, which is correlated to the **G1** catalyst, and a small peak at 39.75 ppm, belonging to the catalyst precursor of **3d**. Two unidentified peaks appeared at 30 ppm and 60 ppm, together with some smaller peaks. The tridentate Schiff base ligand dissociation can also be monitored by ^{1}H NMR. In the presence of trace amounts of water, the imine bond decomposes to starting materi-

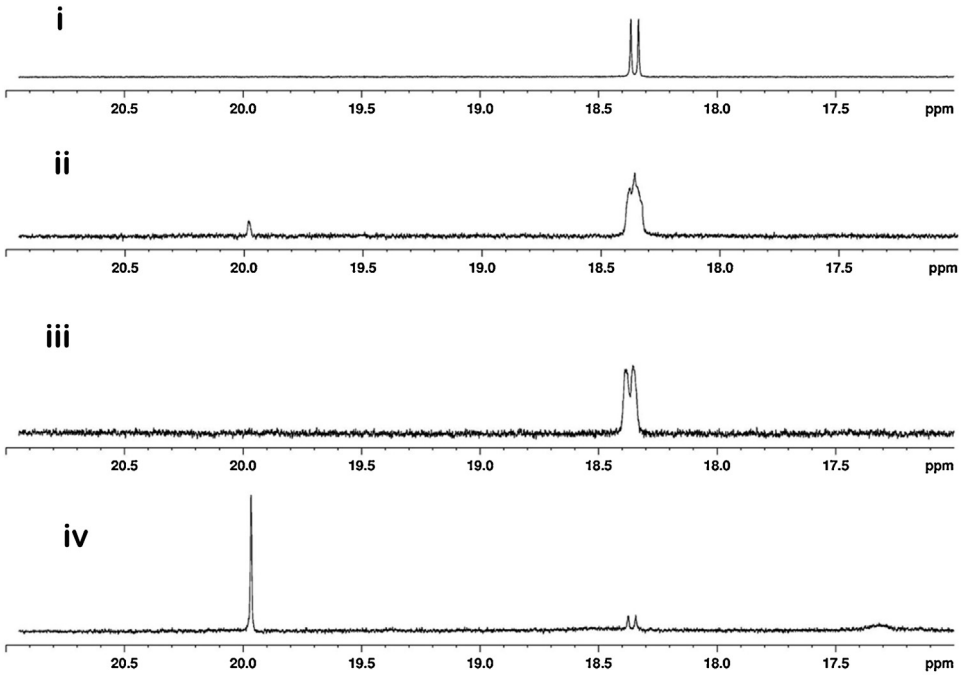


Fig. 3. Mechanistic studies of complex **3d**. An NMR tube was charged with **3d** and $CDCl_3$ and periodically analyzed by ^{1}H and ^{31}P NMR analysis. (i) ^{1}H NMR spectrum of complex **3d** before addition of 1 M HCl, (ii) after addition of 1 M HCl, (iii) 1H NMR spectrum after 5 min and (iv) After addition of excess PCy_3.

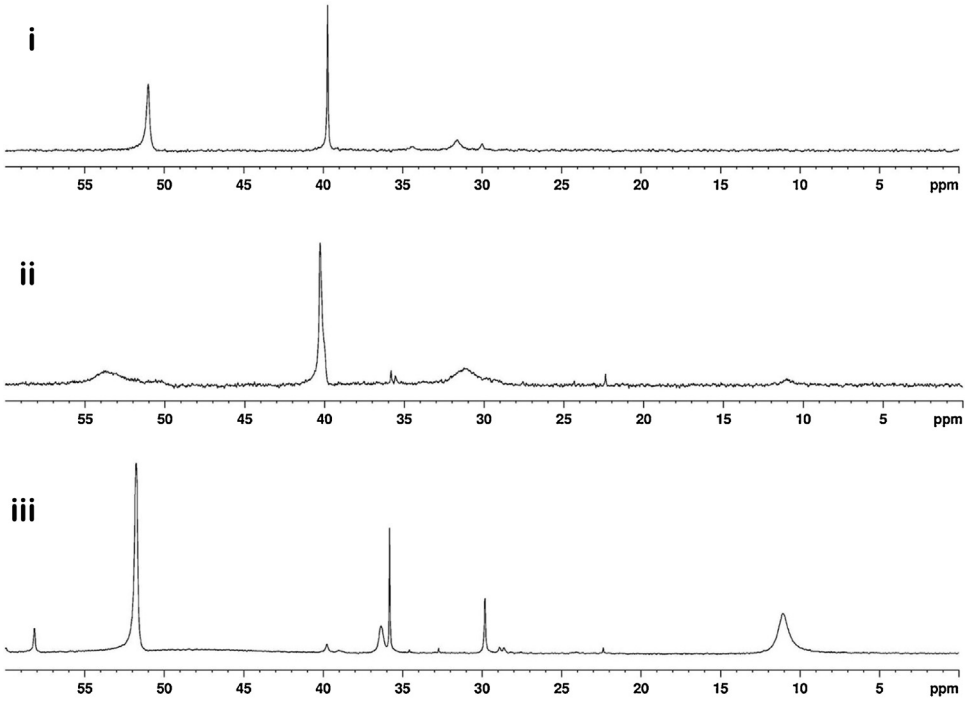


Fig. 4. Mechanistic studies of complex **3d**. (i) ^{31}P NMR spectrum of complex **3d** after addition of 1 M HCl, (ii) After 5 min and (iii) After addition of excess PCy_3.

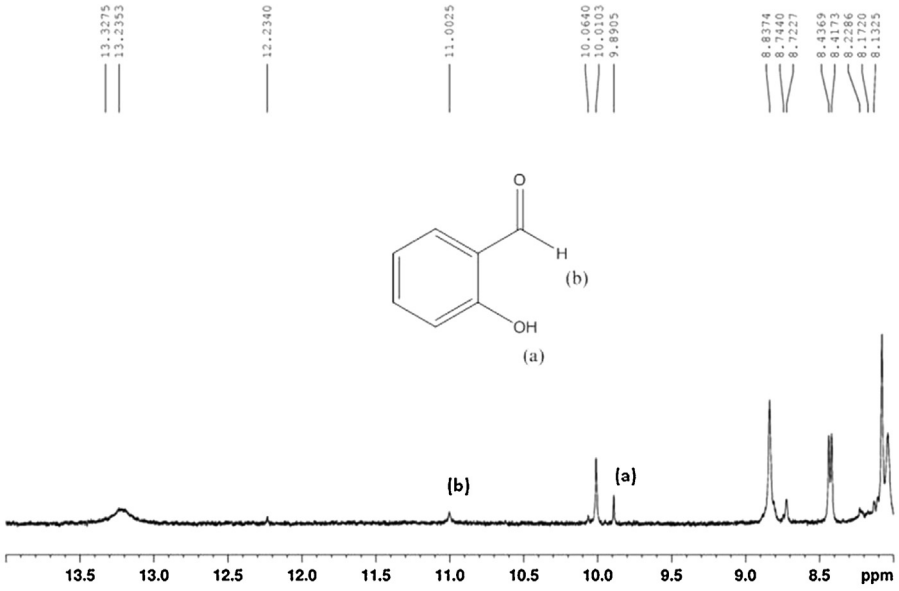


Fig. 5. Partial ^{1}H NMR spectrum of complex **3d** after addition of 1 M HCl.

als salicyclaldehyde and 2-amino-4-nitrophenol. As seen in Fig. 5, single peaks appearing at 10.07 ppm and 11.10 ppm are associated with phenol and aldehyde protons. In addition, a single peak at 13.10 ppm may be proof of imine protonation. From these observations, we can clearly conclude that the tridentate Schiff base ligand acts as a dissociating ligand by protonation of benzyloxide groups, followed by decomposition of the tridentate Schiff base ligand to starting materials.

4. Conclusion

In this study, we have demonstrated that the commercially available Grubbs 1st Generation catalyst can be modified in situ by tridentate Schiff base ligands to obtain latent and highly controllable metathesis catalysts. This in situ modification strategy is a practical and inexpensive method for ruthenium-catalyzed metathesis reactions. These catalytic precursors can be activated on demand by the introduction of hydrochloric acid. All catalytic tests were performed using both isolated catalysts and in situ-modified catalysts, and comparable metathesis activities were obtained by both types of catalysts. Preliminary tests of the catalysts showed that the initiation rate of the catalyst is strongly influenced by the HCl/Ru ratio. Due to a fast initiation/propagation step, polyoctenamers obtained by this method have narrow PDI (1.30–1.60) values. In addition, molecular weight control can be achieved over a wide range, between M_n: 56000 and 407000 Da, for the ROMP of cyclooctene.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2013.04.010.

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