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Synthesis and activity for ROMP of bidentate Schiff base substituted second generation Grubbs catalysts

Bart Allaert [a,*], Nicolai Dieltiens [b], Nele Ledoux [a], Carl Vercaemst [a], Pascal Van Der Voort [a], Christian V. Stevens [b], Anthony Linden [c], Francis Verpoort [a,*]

[a] *Division of Organometallic Chemistry and Catalysis, Department of Inorganic and Physical Chemistry, Faculty of Science, Ghent University, Krijgslaan 281 (S3), B-9000 Ghent, Belgium*
[b] *Research Group SynBioC, Department of Organic Chemistry, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, B-9000 Ghent, Belgium*
[c] *Institute of Organic Chemistry, University of Zurich, Winterhurerstrasse 190, CH-8057 Zurich, Switzerland*

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Abstract

The synthesis and characterisation of Schiff base substituted second generation Grubbs catalysts is described using the pyridine functionalised second generation catalyst and a Schiff base-Tl salt. The complexes are less active for the ROMP of COD (cycloocadiene) than their second generation analogues though their activity for the ROMP of DCPD (dicyclopentadiene) at high temperatures shows great potential due to the thermal stability of the catalysts.

Keywords: Ruthenium; ROMP; DCPD; Schiff base; Metathesis

1. Introduction

Over the last past decades olefin metathesis has emerged as a versatile tool for formation of carbon–carbon double bonds [1] offering a wide range of reactions such as ring opening metathesis polymerization (ROMP), ring closing metathesis (RCM), cross metathesis (CM) and acyclic diene metathesis (ADMET). This success was the result of the continuous development of Schrock molybdenum and Grubbs ruthenium complexes. The extensive research on the synthesis, activity, stability, selectivity and the diversity of applications of ruthenium complexes emerged after the publication of the first well-defined catalyst in 1992 [2]. In particular the commercially available $(PCy_3)_2Cl_2Ru$=CHPh **1** and (SIMES)$(PCy_3)Cl_2Ru$=CHPh **2** (SIMES = 1,3-bis-(2,4,6-trimethylphenyl)imidazolin-2-ylidene), the first and second generation Grubbs systems, have been under great investigation for organic synthesis and polymer chemistry [1,3] and are regarded as the standard for organic chemists. Therein the SIMES substituted complex **2** has shown superior activity and stability upon **1**. This is attributed to the high selectivity of the 14 electron active species to coordinate alkenes compared to the phosphine analogue **1** [4]. The initiation, i.e. the loss of phosphine, of **1** is two orders of magnitude higher than in the case of **2**. However this is more than compensated by the active species' selectivity towards alkenes versus phosphines which is four orders of magnitude higher for **2** compared to **1**.

The introduction of a chelating carbene ligand on **2** by Hoveyda et al. has even increased stability towards air and moisture. This made it possible to recycle catalyst **3** and eliminated excessive catalyst loss by stabilizing the active species in RCM [5].

Many other innovative approaches have been explored [6] including the Schiff base substituted first generation Grubbs catalysts **4** which exhibits high olefin metathesis activity at higher temperatures and proved great stability [7]. These properties could facilitate the mixing and storing of catalysts and monomers for ring opening metathesis polymerization (ROMP) without concomitant polymerization events [8].

Herein we report the combination of a chelating Schiff base and the SIMES ligand onto a single catalyst **5** aiming to exceed

* Corresponding authors. Tel.: +32 92644436; fax: +32 92644983.
E-mail addresses: Bart.Allaert@Ugent.be (B. Allaert), Francis.Verpoort@Ugent.be (F. Verpoort).

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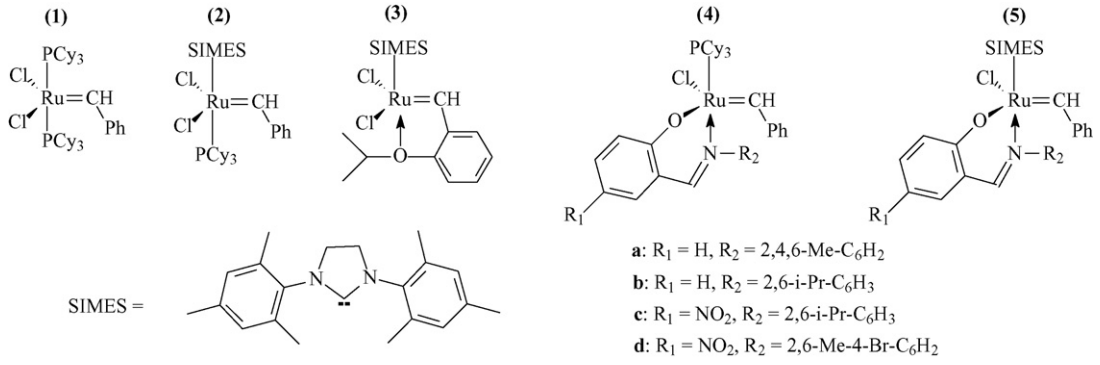


Scheme 1.

the activity and stability of the parent complexes **4**, setting some initial trends for Schiff base variation and exploring harsh reaction conditions for industrial important cycloolefins, e.g. dicyclopentadiene (DCPD) (Scheme 1).

2. Results and discussion

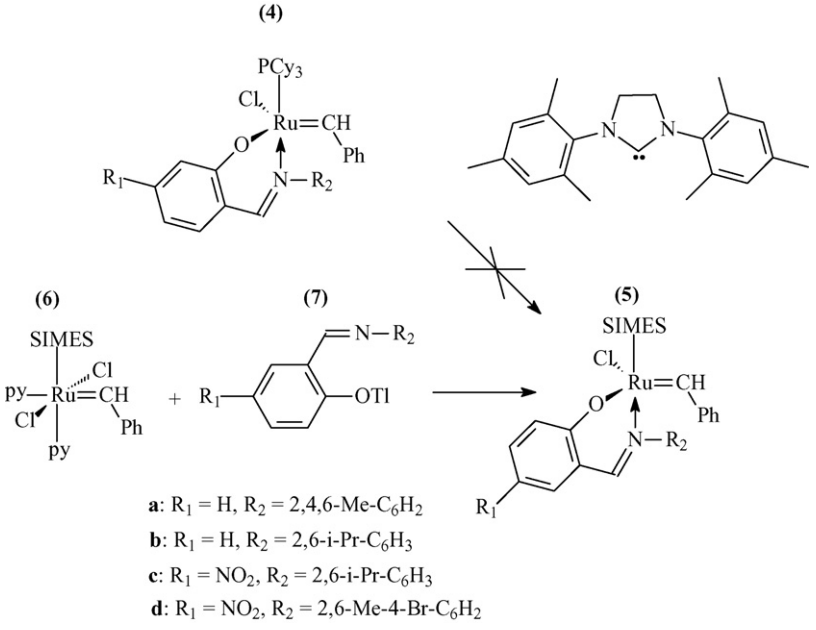
2.1. Preparation of the catalysts

The preparation of complexes of type **5** was previously published by our group [9]. The synthesis involved the reaction of the parent complexes **4** with an in situ generated SIMES-carbene. These catalysts were tested for ROMP and RCM [10]. Surprisingly all our attempts to synthesize **5c** using this previous methodology were unsuccessful. No shift in the carbene proton on ^{1}H NMR spectra from 19.77 to 19.66 ppm was observed [9]. Variation in Schiff base, reaction temperature, solvent, base and SIMES-salt resulted in mixtures with the main product the precursor **4**.

Further investigations reacting the second generation catalyst **2** with the Schiff base salt **7c** resulted in the product **5c** with a resonance at 18.95 ppm of the alkylidene proton on ^{1}H NMR. This is 0.82 ppm upfield to the parent complex **4c**, exactly the same shift as between the classical Grubbs first and second generation catalysts **1** and **2**. When optimalising the reaction using the pyridine functionalised second generation Grubbs catalyst **6** with the Tl-salts **7** in THF at room temperature, a color change was observed within minutes and a white precipitate (TlCl) is formed (Scheme 2).

^{1}H NMR shows no phenolic proton at 14.35 ppm and the resonances at 8.11 and 8.07 can be ascribed to the Schiff base fragment. Most remarkably three of the ^{i}-Pr protons in **5c** are shifted upfield up to 0.19 ppm. The CH_2CH_2 bridge protons of the SIMES are shifted to 4.12–3.86.

The ^{13}C NMR is even more conclusive showing a resonance of the benzylidene carbene of **5c** at 299.6 ppm, the SIMES carbene resonance at 219.6 ppm and the CH_2CH_2 SIMES-bridge carbons at 51.7 and 50.3. Furthermore, the peak sequence at 174.3, 167.5, 151.4, 148.5, 141.5 ppm for **5c** is corresponding to the peak sequence, respectively, at 174.9, 167.5, 153.1, 148.8, 140.1 for the first generation Schiff base substituted **4c**.



Scheme 2.

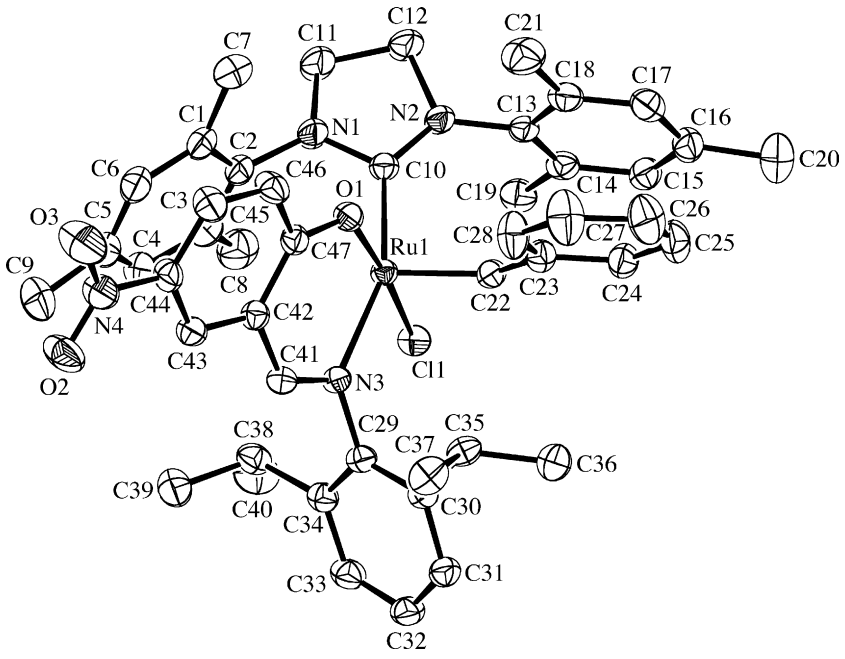


Fig. 1. ORTEP plot of **5c**.

Our synthesis of **5c** was confirmed by single-crystal X-ray analysis. The crystals were grown in a solution of a minimum of chloroform in pentane. The ORTEP diagram of the crystal is shown in Fig. 1 and selected bond angles and distances from **2** [11], **4c** [7] and **5c** are shown in Table 1. **5c** has a longer Ru–N bond (2.125 (2) Å) than the first generation analogue **4c** (2.106 (4) Å) and a shorter Ru–C(NN) bond (2.035 (3) Å) than the second generation catalyst **2** (2.085 (2) Å) which can be ascribed to the bigger trans influence from SIMES compared to PCy_3 and the smaller one of the Schiff base compared to PCy_3. The intramolecular π–π stacking does not only seem to be present in the mesityl-benzylidene fragments [12] but also in the mesityl-phenoxy fragments. Indeed the large N–Ru=C angle of 106.3° places the phenoxy fragment more parallel to the mesityl substituent. Furthermore there is an asymmetrical distortion of the SIMES ligand in **5c** compared to **2**. An angle of 9.3° is present between the SIMES and Ru–C(SIMES) direction which is the second biggest torsion angle reported for a saturated imidazole ligand on a Grubbs catalyst [11,12a,13]. The Ru–C(SIMES)–N_1 (117.1°) and C(SIMES)–N_1–C(mesityl) (122.4°) angles are the second smallest and smallest ones reported for saturated imidazole ligands on a Grubbs catalyst [11,12a,13]. We suggest this is also an effect of the enhancement of the π–π stacking of the mesityl-phenoxy fragments; however an angle of 16° is still present between the two planes due to the steric bulk of the ^{i}-Pr group.

Table 1
Selected bond lengths (Å) and angles (°) and structural comparison of **2**, **4c** and **5c**[a]

	4c[b]	**2**[c]	**5c**
Ru=C	1.850 (6)	1.835 (2)	1.846 (3)
Ru–$C_{(NN)}$		2.085 (2)	2.035 (3)
Ru–P	2.345 (2)	2.4245 (5)	
Ru–N	2.106 (4)		2.125 (2)
$RuX_{(1)}$	2.382 (2)	2.3912 (5)	2.3834 (7)
$RuX_{(2)}$	2.055 (4)	2.4245 (5)	2.067 (2)
$N_{(2)}$–$C_{(NN)}$		1.348 (2)	1.341 (4)
$N_{(1)}$–$C_{(NN)}$		1.347 (2)	1.352 (4)
$N_{(2)}$–$C_{(mesityl)}$		1.432 (2)	1.432 (4)
$N_{(1)}$–$C_{(mesityl)}$		1.440 (2)	1.434 (4)
$X_{(1)}$–Ru–$X_{(2)}$	173.0 (1)	167.71 (2)	175.17 (6)
$L_{(1)}$–Ru–$L_{(2)}$	159.8 (1)	163.73 (6)	157.2 (1)
$L_{(1)}$–Ru=C	96.8 (2)	100.24 (8)	96.5 (1)
$L_{(2)}$–Ru=C	103.5 (2)	95.98 (6)	106.3 (1)
$L_{(1)}$–Ru–$Cl_{(1)}$	89.0 (1)	83.26 (5)	90.43 (8)
$L_{(1)}$–Ru–$X_{(2)}$	88.4 (1)	94.55 (5)	90.6 (1)
Ru–$C_{(NN)}$–$N_{(2)}$		128.08 (14)	135.5 (2)
Ru–$C_{(NN)}$–$N_{(1)}$		123.90 (14)	117.1 (2)
$C_{(NN)}$–$N_{(2)}$–$C_{(mesityl)}$		128.39 (16)	127.6 (2)
$C_{(NN)}$–$N_{(1)}$–$C_{(mesityl)}$		127.74 (16)	122.4 (2)

[a] Priority to X is given by Cl > O. Priority to L is given by SIMES > P > N. $N_{(2)}$ is on the benzylidene side of SIMES.
[b] Ref. [7].
[c] Ref. [11].

2.2. Catalytic activity

The four new synthesized complexes (**5a**–**d**) and the 1st generation analogue **4c** were tested for the polymerization of COD (cyclooctadiene). The catalysts are not active at room temperature therefore we have chosen to study the reactivity at 90 °C. The time course of the in situ polymerization using 100 μl of COD in 600 μl of toluene-d8 is depicted in Fig. 2.

All Schiff base substituted catalysts are less active than their phosphine analogues, which activate at room temperature [14]. Comparing the 1st and 2nd generation analogues **4c** and **5c** the

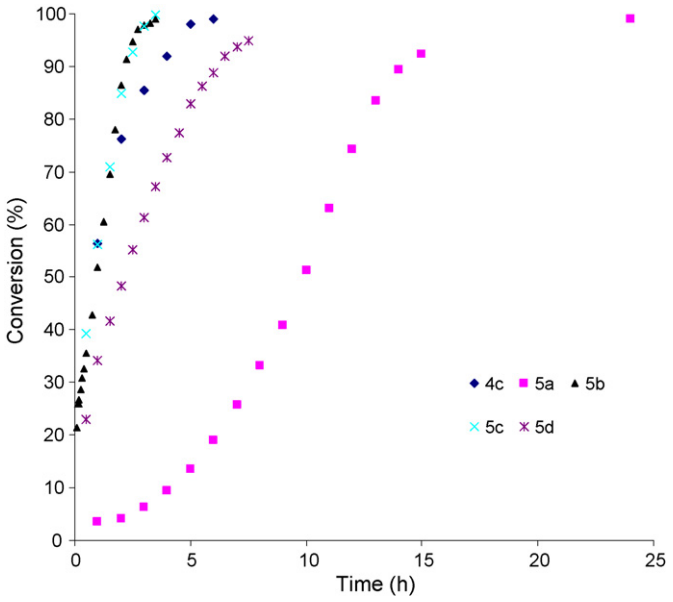


Fig. 2. ROMP of COD at 90 °C in toluene-d8 using catalysts **4c**, **5a**, **5b**, **5c** and **5d**. [Ru]:[COD] = 1:300.

latter is showing higher activity. The 2,6-i-Pr-C_6H_3 Schiff base substituted catalysts **5b–c** have the highest reaction rates which we ascribe to the sterical hindrance of the *iso*-propyl groups. This is increasing the energy of the coordinated Schiff base complex leading to a marginal favoring of the decoordinated form and consequently increasing activity according to a dissociative mechanism.

The activity of the nitro-substituted **5c** is not significantly different compared to its analogue **5b**. This is in sharp contrast to our reasoning that the nitro group should withdraw electron density from the imine-nitrogen, making it a less donating ligand with smoother decoordination and an increasing activity. Furthermore, nitro-substitution on a random place of the phenyl group on the Hoveyda catalyst **3** improves catalyst activity [15]. However the increase in activity of the Hoveyda catalysts may also stem from the withdrawal of electron density from the carbene.

An induction period is clearly visible with **5a** in contrast to the other Schiff base catalysts. Several causes are possible for this such as slow initiation or a competitive associative mechanism which gains in importance with a decrease in steric congestion as in **5a**.

As shown in Table 2, trans percentages of the polymers of **5**(**a–d**) are higher than that of **4c** similar to the trend between **2** and **1** [12a]. The PDIs of the obtained polymers are lower than those of **2** [16]. Relative low Mn values (34300 for **5a**) and low PDIs (1.5 for **5a**) suggest high initiation and relative control in contrast with the suggestion that less of 5% of the catalyst **4c** initiates [1].

The ROMP of 20 000 equivalents of DCPD with **5c** at room temperature is unsuccessful even after a week. In an additional experiment the ROMP of DCPD with catalysts **4c** and **5c** is performed heating up the reaction mixture up to 150 °C. For the polymerization using **5c** an exotherm starts at 130 °C while

Table 2
ROMP of COD[a]

Entry	Catalyst	Conversion (%)	Trans (%)[b]	Mn[c]	PDI[c]
1	**4c**	99	47	45800	1.7
2	**5a**	99	84	34300	1.5
3	**5b**	99	84	38400	1.6
4	**5c**	99	60	119300	1.6
5	**5d**	99	87	58700	1.8

[a] Polymerisations were performed with 0.3 ml of COD in 1.5 ml of toluene at 90 °C for 24 h. Monomer/catalyst ratio 300:1.
[b] Percent trans olefin in the polymer backbone determined by ^{13}C NMR. Procedure in Section 4.3.1.
[c] Determined by $CHCl_3$ GPC and results are reported relative to polystyrene standards.

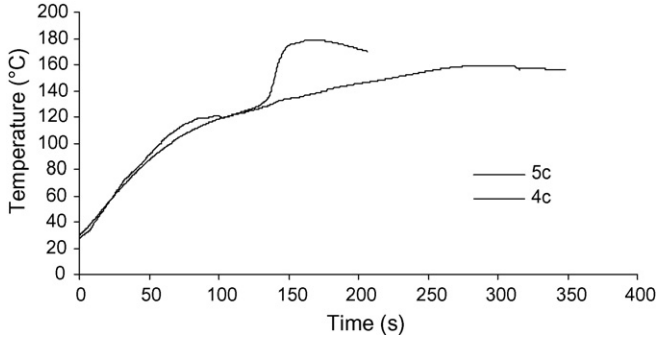


Fig. 3. Thermal analysis of the ROMP of DCPD using catalyst **4c** and **5c**. [Ru]:[COD] = 1: 20 000.

for the phosphine analogue no exotherm is present. From the latter only a gelated polymer was obtained. We suggest that the NHC substitution leads to a higher stability and activity of the catalyst as observed for the NHC substitution of the classical Grubbs systems **1** and **2** [4] (Fig. 3).

The solid catalysts **5** are showing no signs of decomposition when stored under normal atmosphere. Moreover, when the catalysts are left in solution in $CDCl_3$ under normal atmosphere for 1 month no decomposition is observed. This also evidences the robustness of the complexes **5**, a quality that makes it possible for these catalysts to remain stable enough for reactions at higher temperature.

3. Conclusions

In conclusion, we synthesized the first Schiff base functionalised 2nd generation Grubbs catalysts rectifying a previous procedure. We have shown that these catalysts exhibit greater stability and activity for ROMP than their parent 1st generation Schiff base catalysts at high temperatures though much lower activity than their parent 2nd generation Grubbs catalyst. These properties could facilitate the mixing and storing of catalysts without concomitant polymerization [8] where an increase of temperature can induce fast polymerization. Sterical hindrance appears to increase activity therefore we are currently exploring this option to obtain a series of highly stable catalysts that cover a wide range of the activity spectrum. More detailed studies

regarding the steric/electronic effects of the substituents, activation methods and the use of polar solvents will be published in due course.

4. Experimental

4.1. General procedures

All reagents and solvents were obtained from commercial sources. Tetrahydrofuran, toluene and hexane were dried using conventional methods. All reactions were performed under argon. Argon was dried over a column of Drierite®. NMR spectra were recorded on a Varian Unity 300 MHz spectrometer.

4.2. Synthesis and characterization of complexes

(SIMES)(py)$_2$Cl$_2$Ru=CHPh (**6**) [9], Schiff bases, their Tl-salts (**7**) and **4c** [7] were synthesized using well established procedures.

4.2.1. Synthesis of complex *5a*

A solution of 0.215 g of the Tl-salt **7a** (0.485 mmol, 1.1 equiv.) in 10 ml of THF was added to a solution of 0.320 g of complex **6** (0.441 mmol) in 10 ml of THF and stirred at room temperature for 2 h. The solution was evaporated and dissolved in 10 ml of toluene, cooled to −20 °C and the TlCl was removed by filtration. The filtrate was evaporated and 10 ml of hexane was added. The dispersion was placed in an ultrasonic bath for 10 min and then cooled to −20 °C for 1 h and a red-orange powder that was obtained and dried under vacuum. Yield: 30%. ^{1}H NMR (CDCl$_3$): (ppm): 18.62 (s, 1H), 7.60 (s, 1H), 7.44–6.50 (br m, 14H), 6.25 (s, 1H), 4.10 (br m, 2H), 3.97 (br m, 2H), 2.61–1.05 (br m, 27H). ^{13}C NMR (CDCl$_3$): (ppm): 297.9, 221.3, 169.6, 167.6, 167.5, 152.0, 149.9, 140.2, 139.2, 138.9, 138.1, 137.7, 137.3, 136.9, 136.6, 134.3, 134.1, 133.8, 131.9, 130.4, 130.1,129.5, 129.3, 129.1, 128.7, 128.0, 127.7, 123.7, 123.4, 119.2, 113.7, 113.5, 51.5, 51.0, 21.3, 21.1, 21.0, 19.0, 18.5, 18.3, 18.0, 17.8; elemental analysis calculated (%) for C$_{44}$H$_{48}$N$_3$ClORu (770.39): C 68.59, H 6.28, N 5.46; found C 68.59, H 6.01, N 5.19.

4.2.2. Synthesis of complex *5b*

A similar procedure was used as for **5a** obtaining a red-pink powder. Yield: 26%. ^{1}H NMR (CDCl$_3$): (ppm): 18.85 (s, 1H), 7.66 (s, 1H), 7.35 (t, 3H), 7.04–6.92 (br m, 9H), 6.80 (d, 1H), 6.67 (s, 1H), 6.55 (s, 1H), 6.48 (t, 1H), 6.10 (s, 1H), 4.19–4.13 (m, 1H), 4.10–4.00 (m, 2H), 3.89–3.83 (t, 1H), 2.71 (s, 3H), 2.51 (sept, 1H), 2.42 (s, 3H), 2.38 (s, 3H), 2.21 (s, 3H), 2.06 (s, 6H), 1.69–1.63 (m, 1H), 1.34–1.31 (d, 3H), 0.83–0.81 (d, 3H), 0.39–0.37 (d, 3H), 0.22–0.20 (d, 3H). ^{13}C NMR (CDCl$_3$): (ppm): 296.4, 221.6, 169.3, 168.0, 154.9, 151.6, 149.8, 142.0, 140.5, 139.3, 138.3, 137.7, 137.0, 136.7–136.6 (m), 133.8, 133.4, 129.4–129.0 (m), 128.0, 127.9, 125.7, 123.4, 123.1, 122.0, 118.0, 113.3, 51.6, 50.4, 29.3, 26.3, 25.0, 24.9, 23.0, 22.2, 21.1, 21.0, 20.0, 18.7, 18.5, 17.8; elemental analysis calculated (%) for C$_{47}$H$_{54}$N$_3$ClRu (813.49): C 69.59, H 6.68, N 5.17; found C 65.59 H 6.02 N 5.11.

4.2.3. Synthesis of complex *5c*

A similar procedure was used as for **5a** except for the precipitation. The filtrate was evaporated to ∼1 and 40 ml of hexane was added. The dispersion was placed in an ultrasonic bath for 30 min and a solid was obtained by filtration. The red precipitate was washed with 10 ml of hexane and dried under vacuum. Yield: 74%. ^{1}H NMR (CDCl$_3$): (ppm): 18.95 (s, 1H), 8.13–8.09 (dd, 1H), 8.01 (d, 1H), 7.70 (s, 1H), 7.41 (t, 2H), 7.38 (s, 1H), 7.06–7.01 (br m, 5H), 6.91–6.88 (d, 1H), 6.82–6.79 (br m, 1H), 6.63 (s, 1H), 6.55 (s, 1H), 6.16 (s, 1H), 4.21–4.16 (t, 1H), 4.12–4.00 (m, 2H), 3.92–3.86 (t, 1H), 2.68 (s, 3H), 2.43–2.32 (br m, 7H), 2.22 (s, 3H), 2.07 (s, 6H), 1.62–1.54 (m, 1H), 1.37–1.35 (d, 3H), 0.87–0.85 (d, 3H), 0.39–0.36 (d, 3H), 0.19–0.18 (d, 3H). ^{13}C NMR (CDCl$_3$): (ppm): 299.6, 219.6, 174.3, 167.5, 151.4, 148.5, 141.5, 139.9, 139.5, 138.9, 138.8, 138.2, 137.7, 136.6, 136.2, 135.2, 134.8, 132.8, 129.3–128.1 (br m), 126.4, 125.3, 123.6, 123.2, 122.3, 117.2, 51.7, 50.3, 29.5, 26.5, 25.1, 25.0, 23.1, 21.9, 21.1, 21.0, 19.9, 18.7, 18.4, 17.8; elemental analysis calculated (%) for C$_{47}$H$_{43}$N$_4$O$_3$ClRu (858.48): C 65.76, H 6.22, N 6.53; found C 65.48, H 6.20, N 6.53.

4.2.4. Synthesis of complex *5d*

A similar procedure was used as for **5c** obtaining a red-brown powder. Yield: 76%. ^{1}H NMR (CDCl$_3$): (ppm): 18.50 (s, 1H), 8.07 (s, 1H), 7.58–6.75 (br m, 11H), 6.43 (s, 1H), 6.36 (s, 1H), 4.12 (m, 2H), 4.01 (m, 2H), 2.57 (s, 3H), 2.40 (s, 3H), 2.28 (s, 3H), 2.25 (s, 3H), 2.14 (s, 3H), 1.48 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (CDCl$_3$): (ppm): 301.4, 219.1, 174.6, 167.2, 151.7, 150.0, 140.2, 139.3, 138.4, 137.7, 136.7, 136.3, 135.5, 135.1, 133.8, 133.4, 131.4, 130.6, 130.5, 129.9, 129.5, 129.2, 129.1, 129.0, 128.3, 128.2, 128.1, 123.9, 118.7, 117.9, 51.6, 50.9, 20.0, 18.8, 18.3, 18.2, 17.8, 17.7, 17.6; elemental analysis calculated (%) for C$_{43}$H$_{34}$N$_4$O$_3$ClRu (881.27): C 58.60, H 5.03, N 6.36: found C 58.81, H 5.87, N 6.38.

4.2.5. ^{13}C NMR of complex *4c*

The product was obtained using well established methods and confirmed by ^{1}H NMR [5]. ^{13}C NMR (CDCl$_3$): (ppm): 297.6, 174.9, 167.5, 153.1, 148.8, 140.1, 135.0, 129.7–128.6 (8C), 126.7, 123.5, 123.3, 122.5, 117.2, 32.8–22.6 (24C). ^{1}H NMR is in accordance to literature [7].

4.3. Activity tests

4.3.1. ROMP kinetics of COD

A 2.717 μmol of catalyst is transferred in a NMR tube and the tube is degassed while heating it. The tube is brought under Argon applying three Argon-vacuum cycles and 600 μl of toluene-d8 and 8.15 mol (100 μl) of COD is added. The tube is transferred in the preheated NMR at 90 °C and the spectra are obtained choosing reasonable time intervals. To determine the yield the allylic protons are integrated.

4.3.2. Thermal analysis of the ROMP of DCPD

A 10 mg catalyst is weighed of in a 15 ml vial. The vial is degassed and flame dried. The vial is brought under Argon atmosphere applying three Argon-vacuum cycles after which 500 μl of toluene is added. In a 15 ml vial put under Argon 2 g of DCPD is added and the appropriate amount of catalyst from the stock solution is added under Argon to obtain a 20 000:1 monomer:catalyst ratio. The vial is closed, a thermocouple is pierced through the septum in the reaction mixture and it is placed in a thermostat at 150 °C.

5. Supplemantary material available

Crystallographic data for the structural analysis of compound **5c** have been deposited to the Cambridge Crystallographic Data Centre as No. CCDC 603686. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or by emailing http://www.data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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