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Full Paper

Olefin Metathesis

# Ruthenium Amide Complexes – Synthesis and Catalytic Activity in Olefin Metathesis and in Ring-Opening Polymerisation

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**Abstract:** A set of olefin metathesis catalysts bearing a ruthenium amide moiety was synthesised. In the ruthenium amide form these complexes exhibit very low activity in standard metathesis reactions. However, a dramatic increase of activity was observed upon in situ activation with trimethylsilyl chloride or HCl, allowing successful application of such catalysts in a number of model ring-closing metathesis, cross-metathesis and enyne transformations. Moreover, such activated complexes proved to be very effective catalysts for bulk polymerisation of dicyclopentadiene (DCPD). The influence of factors such as temperature and the nature of additives on the properties of poly-DCPD was examined.

## Introduction

In the past decade, the development of well-defined catalysts has established olefin metathesis as a useful synthetic tool in both organic and materials chemistry.[1] The transformation itself has been known for many years, as early examples of these metal-mediated reactions in ring-opening metathesis polymerisation (ROMP) of cyclic olefins date back to the 1960s.[2] Ring-closing metathesis (RCM), acyclic diene metathesis, cross-metathesis (CM), ring-opening metathesis (ROM) and combinations of these more recently explored transformations have now developed into powerful methods leading to previously difficult-to-reach synthetic targets.[3]

As the number of applications utilising olefin metathesis catalysts is growing constantly, research into more efficient complexes with high stability and, at the same time, high activity and selectivity remains a key concern for the organic and pharmaceutical communities. On the other hand, intensive research is also carried out on the synthesis of latent catalysts, the initiation of which can be easily controlled, thermally, chemically or photochemically.[4] Such a possibility is beneficial mainly in ROMP.[5] The availability of well-defined ruthenium-based catalysts (Figure 1) resistant to moisture, oxygen and the presence of various functional groups, as well as optimisation of the reaction conditions, have significantly extended the scope and application of this process and made it widely used in synthesis.[6]

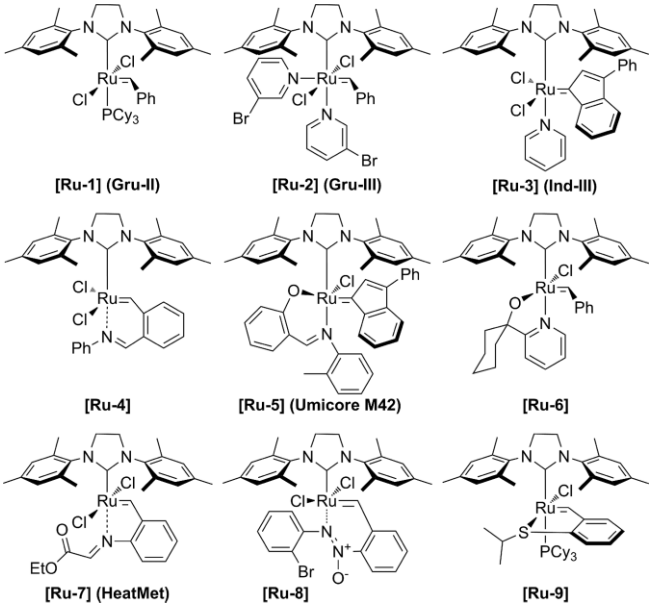


Figure 1. Examples of well-defined ruthenium catalysts of general use (**[Ru-1]** to **[Ru-3]**) and latent catalysts for ROMP (the rest).[5a–c,7]

Recently, we reported the synthesis of new ruthenium phenolate chelate complexes bearing altered anionic ligands (Figure 2, **[Ru-10]**).[8] These complexes exhibit almost no activity in metathesis reactions, but they can easily be switched on by adding Brønsted acids. Detailed research on their catalytic activity has shown that after activation with, for example, HCl, $Me_3SiCl$ or $C_2Cl_6$, they promote RCM, enyne and CM reactions, including butenolysis, with good results. Catalyst **[Ru-10]** demonstrated high usefulness in the ROMP of dicyclopentadiene (DCPD), which is related to its good solubility in neat DCPD as well as with an easy-to-control initiation process and therefore was commercialised under the trade name LatMet™.[9]

The same switchability in the presence of Lewis acids was observed during a collaboration with Pietraszuk et al. on Ru

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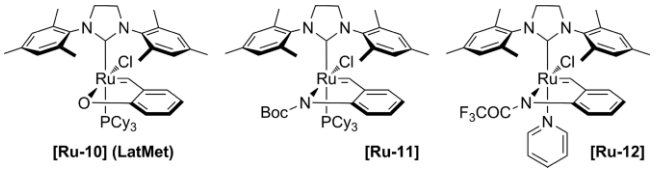



Figure 2. Our previously synthesised latent Ru catalysts bearing anionic benzylidene ligands.

complexes bearing amidobenzylidene chelating ligands (Figure 2, **[Ru-11]** and **[Ru-12]**).[10] In this preliminary study the addition of $Me_3SiCl$ or HCl caused a significant increase in catalytic activity in two RCM reactions. The mechanism of activation of these complexes in the presence of HCl was also thoroughly investigated by FTIR spectroscopy and DFT calculations.[11] Herein, we extend this preliminary study by synthesis of more structurally diverse analogues of **[Ru-11]** and **[Ru-12]** (Figure 3) and checking their activity in model RCM, CM and enyne reactions of functionalised substrates. In addition to transformations of small molecules, we also explored their utilisation in the production of macromolecules, by exploiting the potential switchability of such catalysts, which can be of key importance in ROMP of some monomers.

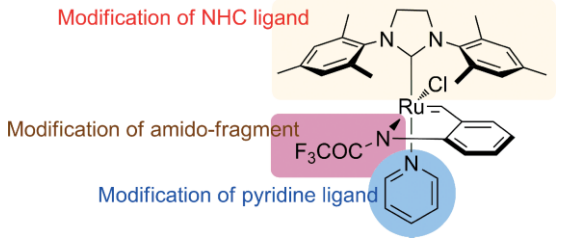
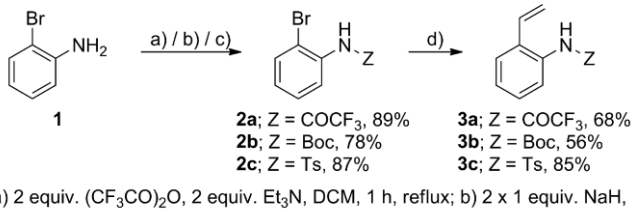



Figure 3. Structural modifications of **[Ru-12]** examined in this study.

## Results and Discussion

### Complexes with Modified Amido Benzylidene Ligands

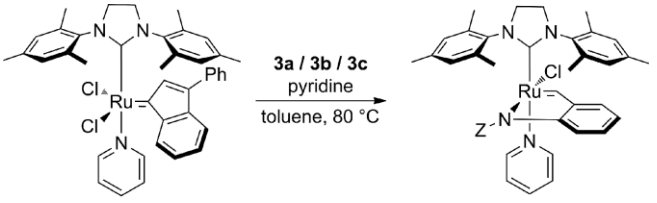
In the first stage of the study, the main focus was on preparing analogues of the previously obtained third-generation complex **[Ru-12]** containing different substituents Z that can modify the acidity of the amido group. To do so, the corresponding ligand precursors **3a**–**3c** were obtained in two-step synthesis starting from commercially available 2-bromoaniline (**1**, Scheme 1). Compound **1** was transformed into amido-bearing ligand precursors by reaction with the appropriate acid anhydride or chloride (Scheme 1 a–c) followed by Stille cross-coupling with tri-*n*-butylvinyltin to produce styrenes **3a**–**3c** in good yields.




a) 2 equiv. $(CF_3CO)_2O$, 2 equiv. $Et_3N$, DCM, 1 h, reflux; b) 2 x 1 equiv. NaH, 1 equiv. $(Boc)_2O$, THF, RT→reflux; c) 1.5 equiv. *p*-TsCl, pyridine, 24 h, 65 °C; d) 1.2 equiv. $Bu_4SnCH{=}CH_2$, $Pd(PPh_3)_4$, toluene, reflux

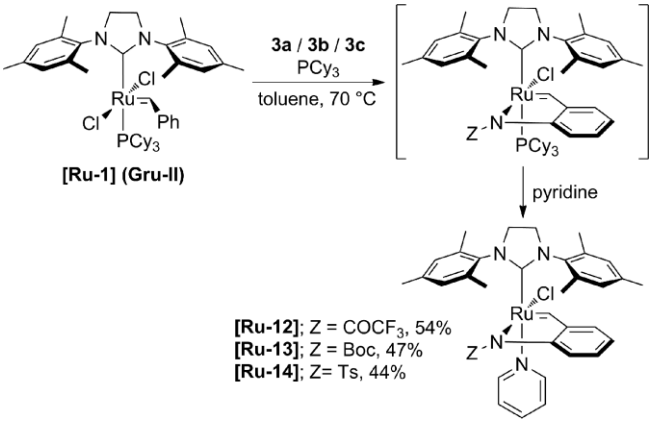
Scheme 1. Synthesis of ligands **3a**–**3c**.

With styrenes **3a**–**3c** in hand the reaction with **[Ru-3]** (commercially available Umicore M31 ruthenium indenylidene complex) was performed in toluene at 80 °C (Scheme 2). Since previous studies showed that the addition of an excess of pyridine to the reaction mixture leads to higher yields,[10] the same strategy was applied here. New complexes were isolated by column chromatography and characterised by standard analytical techniques.




Scheme 2. Synthesis of complexes **[Ru-12]**–**[Ru-14]**.

Next, an alternative method of synthesis of complexes **[Ru-12]**–**[Ru-14]** was tested (Scheme 3). In the first step, the reaction between the previously obtained benzylidene ligand precursors **3a**–**3c** and the Grubbs second-generation complex (**Gru-II**) in the presence of 3 equiv. of free tricyclohexylphosphane ($PCy_3$) was performed. The reaction was carried out in toluene at 70 °C and monitored by TLC. When full conversion of **[Ru-1]** was observed, 3 equiv. of pyridine were added. This pathway enabled the synthesis of complexes **[Ru-12]**–**[Ru-14]** from more stable **Gru-II**, although the amide complexes were obtained in lower yields as compared with the procedure described in Scheme 2.

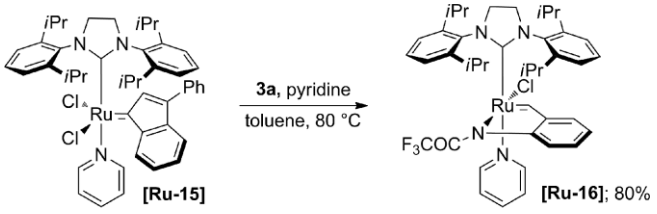



Scheme 3. Alternative synthesis of complexes **[Ru-12]**–**[Ru-14]**.

### Amido Complexes with Modified NHC Ligands

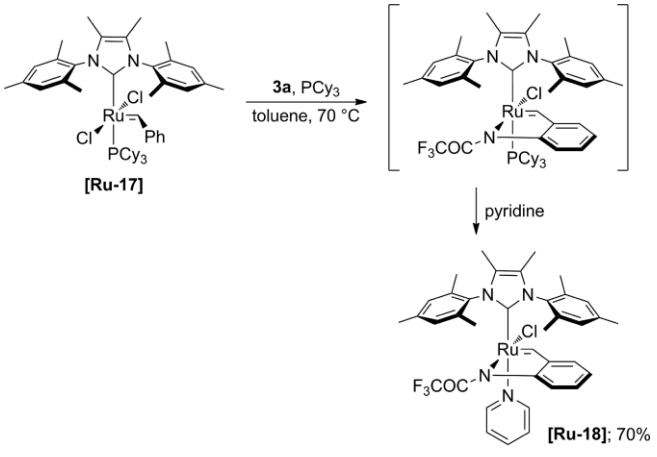
Next we investigated the influence of the N-heterocyclic carbene (NHC) ligand on the behaviour of this class of complexes. The first attempt to form complexes containing a modified NHC was the reaction of **3a** with **[Ru-15],** which is an SIPr analogue

of **[Ru-3]**. The ligand-exchange reaction was performed in toluene at 80 °C in presence of an excess of pyridine (Scheme 4). Addition of the amidobenzylidene ligand precursor (**3a**) in portions significantly increased the yield. Complex **[Ru-16]** was isolated as a green solid in 80 % yield.




Scheme 4. Synthesis of complex **[Ru-16]**.

To obtain another complex with modified NHC ligand we used **[Ru-17]**, the so-called Turbo-IMes Grubbs-type complex,[12] as starting material. Complex **[Ru-18]** was obtained by a pathway similar to that presented in Scheme 3. Ligand precursor **3a** and 2 equiv. of $PCy_3$ were added to **[Ru-17]** followed by an excess of pyridine. Complex **[Ru-18]** was isolated as a green solid in 70 % yield (Scheme 5).




Scheme 5. Synthesis of complex **[Ru-18]**.

### Amido Complexes Bearing Various Pyridine Derivatives

To complete the picture, we obtained complexes with a modified pyridine ligand. For that purpose we treated Grubbs second-generation catalyst **[Ru-1]** with **3a** in the presence of 3-bromopyridine or 4-dimethylaminopyridine (DMAP). The reactions were performed in toluene at 80 °C and provided complexes **[Ru-19]** and **[Ru-20]** in 62 and 80 % yield, respectively. Due to low solubility of **[Ru-19]** and **[Ru-20]** in toluene, these complexes precipitated from the reaction mixture as pure products, and further purification was not required in these cases (Scheme 6).

### Activity Studies

Prior to ROMP tests, the general activity of amido complexes in standard metathesis reactions was briefly examined. The structures of complexes used in tests are shown in Figure 4.

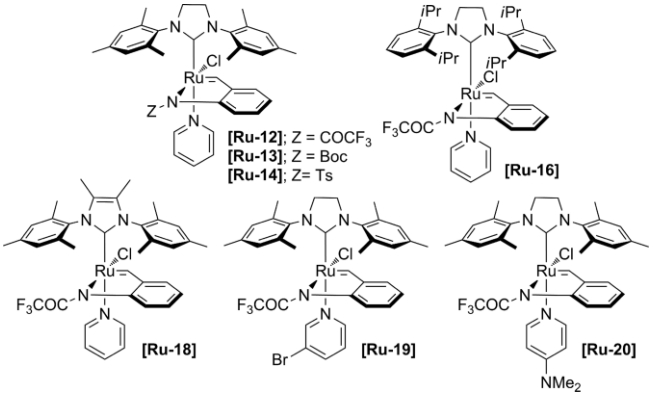
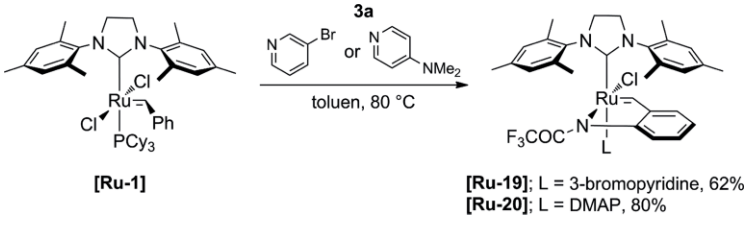



Figure 4. Structure of complexes utilised in this study.

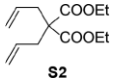
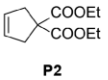
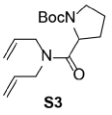
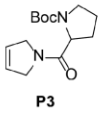
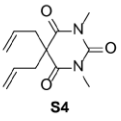
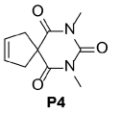
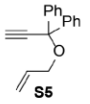
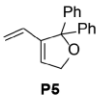
Previously, we showed that this type of Ru complexes are inactive in metathesis in the Ru amide form, and they had to be activated, for example, by addition of $Me_3SiCl$ as the activating agent.[10] So, catalysts **[Ru-12]**–**[Ru-14]**, **[Ru-16]** and **[Ru-18]**–**[Ru-20]** (1 mol-%) were screened in a selected set of RCM, enyne and CM reactions in the presence of $Me_3SiCl$ as activator (Table 1). The reactions were conducted for 2 h at 40 °C and then the reaction mixtures were analysed by GC with durene as internal standard. When diallyl tosylamide (**S1**), a straightforward substrate in RCM, was tested, all amido complexes (1 mol-%, see Figure 4, entry 1) gave complete reaction. Similarly high conversions (> 94 %) were reached when a second standard model substrate,[13] namely, diethyl diallylmalonate (**S2**; Table 1, entry 2) was used.

Proline-derived **S3** and allyl-decorated barbiturate **S4** were chosen as examples of more functionalised substrates, the complexity of which resembles that of simple active pharmaceutical ingredients synthesised by the pharmaceutical industry.[14] Again, RCM of *tert*-butyl-2-(diallylcarbamoyl)pyrrolidine-1-carb-




Scheme 6. Synthesis of complexes **[Ru-19]** and **[Ru-20]**.

Table 1. Comparative study of catalysts **[Ru-12]**–**[Ru-14]**, **[Ru-16]** and **[Ru-18]**–**[Ru-20]**.[a]

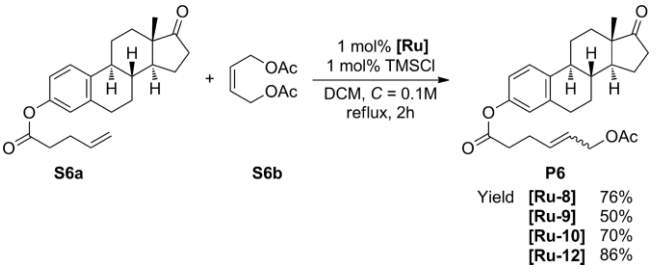
| Entry | Substrate | Product | [Ru] | Isolated Yield (Conv.) [%][b] |
|---|---|---|---|---|
| 1 |  S1 |  P1 | **[Ru-12]**<br>**[Ru-16]**<br>**[Ru-13]**<br>**[Ru-14]**<br>**[Ru-20]** | (97)<br>(99)<br>(95)<br>(99)<br>(99) |
| 2 |  S2 |  P2 | **[Ru-12]**<br>**[Ru-13]**<br>**[Ru-19]**<br>**[Ru-20]** | (>99)<br>(94)<br>(>99)<br>(>99) |
| 3 |  S3 |  P3 | **[Ru-12]**<br>**[Ru-18]**<br>**[Ru-13]**<br>**[Ru-14]**<br>**[Ru-20]** | (>99)<br>(>99)<br>97 (>99)<br>(>99)<br>(>99) |
| 4 |  S4 |  P4 | **[Ru-12]**<br>**[Ru-13]**<br>**[Ru-14]** | (91)<br>(>99)<br>(>99) |
| 5 |  S5 |  P5 | **[Ru-12]**<br>**[Ru-16]**<br>**[Ru-18]**<br>**[Ru-13]**<br>**[Ru-14]**<br>**[Ru-19]**<br>**[Ru-20]** | (>99)<br>(>99)<br>(>99)<br>(>99)<br>(>99)<br>93 (>99)<br>(>99) |

[a] Conditions: $CH_2Cl_2$ (0.1 M), 40 °C, 2 h, catalyst 1 mol-%, $Me_3SiCl$ 10 mol-%. [b] Conversion was determined by GC with durene as internal standard; yields after purification by column chromatography. [c] *t* = 5 min. [d] *t* = 15 min.

oxylate (**S3**) proceeded well, full conversion was reached in the presence of all tested complexes and product **P3** could be isolated in high yield. Good reactivity of selected Ru amide complexes was observed also when 5,5-diallyl-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (**S4**) was used as starting material (Table 1, entry 4). Next, the amido complexes were found to be effective catalysts of enyne cycloisomerisation (Table 1, entry 5). When [1-(allyloxy)prop-2-yne-1,1-diyl]dibenzene (**S5**) was utilised, quantitative conversion was reached in all cases.

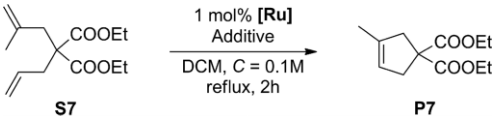
Finally the moderately challenging CM reaction between estrone derivative **S6a** and *cis*-1,4-diacetoxy-2-butene (**S6b**, 2 equiv.) was examined with selected Ru amido complexes.[15] Also in this case the reaction proceeded smoothly and the desired product **P6** was obtained in moderate to high yield (Scheme 7). Importantly, this reaction finally showed the differences in catalytic activity of the studied complexes.

To underline the differences in catalyst activity, we selected three representative complexes **[Ru-12]**, **[Ru-13]** and **[Ru-16]** as well as commercially available **Ind-III** (**[Ru-3]**) for the RCM reaction of diethyl allylmethallylmalonate (a standard substrate of medium difficulty; Scheme 8).[13a,13b] From the tested Ru




Scheme 7. Model CM reaction of substrates **S6a** and **S6b**. Conditions: $CH_2Cl_2$ (0.1 M), 40 °C, 3 h, catalyst 1 mol-%, $Me_3SiCl$ 10 mol-%; *E*/*Z* ratio of **P6** was not determined.

amide complexes activated by HCl (10 mol-%) the SIPr-bearing complex **[Ru-16]** exhibited the highest activity, followed by **[Ru-12]** and **[Ru-13]** (Table 2). The latter SIMes amide complex exhibited slightly lower activity than **[Ru-3]**.



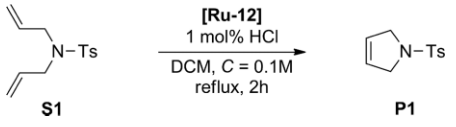

Scheme 8. Model RCM reaction of substrate **S7**.

Table 2. Conversions reached in the presence of ruthenium amide complexes in the RCM reaction of **S7**.[a]

| Entry | [Ru] | Additive | Conversion [%][b] |
|---|---|---|---|
| 1 | **[Ru-3]** | – | 48 |
| 2 | **[Ru-12]** | – | 5 |
| 3 | **[Ru-12]** | HCl (10 mol-%) | 55 |
| 4 | **[Ru-13]** | HCl (10 mol-%) | 44 |
| 5 | **[Ru-16]** | HCl (10 mol-%) | 82 |

[a] Conditions: $CH_2Cl_2$ (0.1 M), 40 °C, 2 min, [Ru] 1 mol-%, HCl 10 mol-%. [b] Conversion was determined by GC with durene as internal standard.

Attempts to decrease catalyst loading have been an important area of research in recent years.[16] It is essential because it can lead to lower costs and minimisation of ruthenium residues in products.[17] We studied it for the RCM reaction of **S1** (Scheme 9), which was performed in refluxing $CH_2Cl_2$. Using 500 ppm of the representative **[Ru-12]** gave greater than 80 % conversion [turnover number (TON) = 1760], and 50 ppm gave 20 % (TON = 4400; Figure 5 and Table 3). General-purpose catalysts, such as **[Ru-1]** or recently developed CAAC complexes can lead to much higher TONs in easy RCM reactions,[16b] the present results are, to the best of our knowledge, quite high for the latent catalysts.




Scheme 9. Model RCM reaction of **S1** at low loading.

To evaluate the potential of the amide catalysts in ROMP, the performances of selected complexes **[Ru-12]**, **[Ru-18]** and

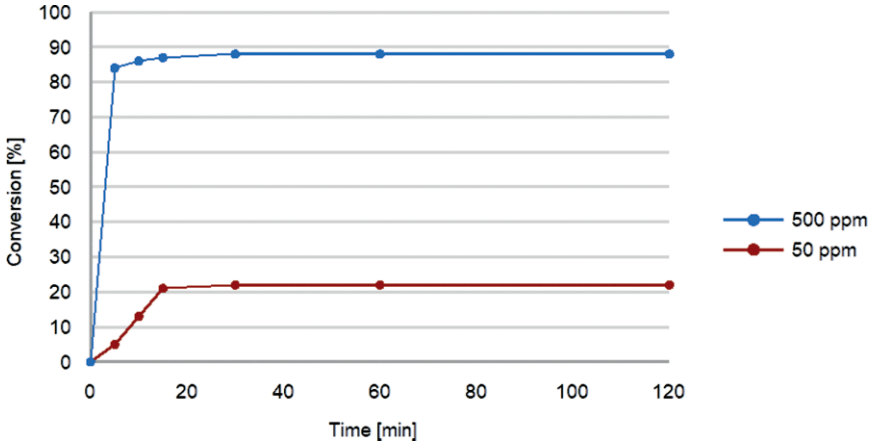


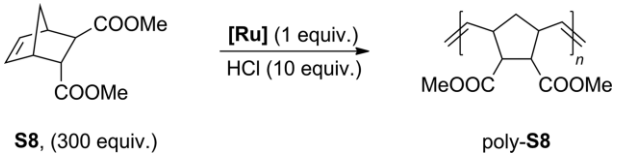

Figure 5. Activity of **[Ru-12]** in the model RCM reaction of **S1**.

Table 3. Conversions and TONs reached in the presence of **[Ru-12]** in RCM reaction of **S1**.[a]

| Entry | Ru [ppm] | Conversion [%][b] | TON |
|---|---|---|---|
| 1 | 500 | 88 | 1760 |
| 2 | 50 | 22 | 4400 |

[a] Conditions: $CH_2Cl_2$ (0.1 M), 40 °C, 30 min, **[Ru-12]**, HCl 1 mol-%. [b] Conversion was determined by GC with durene as internal standard.

**[Ru-20]** were tested in polymerisation with *endo,exo*-bicyclo-[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester (**S8**) as monomer (Scheme 10).




**S8**, (300 equiv.) poly-**S8**

Scheme 10. Benchmark ROMP reaction of **S8**.

This reaction is well-established for benchmarking initiator systems,[8,18] because the resulting polymers are hardly prone to degradation by secondary metathesis reactions (e.g., backbiting).[19] Accordingly, the number-average molecular weight $M_n$ of the produced polymers readily permits assessment of the initiation efficiency of the catalysts, as it is indirectly proportional to the ratio of initiation rate to propagation rate constants $k_i/k_p$. We investigated the activity of the catalysts at room temperature in different solvents (toluene, $CH_2Cl_2$ and $CCl_4$) and the role of HCl activation at room temp. and elevated temperature (40, 80 °C) in $CH_2Cl_2$ and toluene. The standardised protocol was followed under inert conditions by using Schlenk techniques: the (pre)catalyst was dissolved in the respective solvent, and then the monomer was added in an excess of 300 equiv. with respect to the initiator. After completion of the polymerisation (monitored by TLC), the reaction was quenched by the addition of an excess of ethyl vinyl ether. Subsequently the polymers were precipitated in cold methanol, dried and analysed by gel permeation chromatography in THF against a polystyrene standard.

First, initiators **[Ru-12]**, **[Ru-18]** and **[Ru-20]** were employed for benchmark reaction with **S8** at room temperature in different solvents ($CH_2Cl_2$, $CCl_4$ and toluene) without the addition of acid. After 20 h the conversions of polymerisations were determined by $^1$H NMR spectroscopy by evaluating the ratio of the double-bond signals (at $\delta$ = 6.27 and 6.27 ppm for the monomer **S8** and the area between 5.62 and 5.09 ppm for the polymer). We would expect an increase in activity from toluene to dichloromethane to tetrachloromethane, as activation in presence of chloride seems obvious for this type of catalysts. However, this trend was not obtained in our studies, as shown in Table 4. While catalysts **[Ru-12]** and **[Ru-20]** showed hardly any activity in toluene (14 and 1 %, respectively), catalyst **[Ru-18]** gave an impressive conversion of 40 %. However, the values are not representative, as all three catalysts showed limited solubility in toluene: catalyst **[Ru-18]** dissolved the best followed by **[Ru-12]** and finally **[Ru-20]**, which is in accordance with the activities. In dichloromethane, (pre-)catalyst **[Ru-18]** showed the worst performance (18 %) closely followed by **[Ru-12]** (23 %). On the contrary, **[Ru-20]** nearly reached full conversion (up to 96 %). On changing the solvent to tetrachloromethane, again deviating behaviour was found for the three catalysts: **[Ru-12]** showed the highest conversion (83 %), while for **[Ru-20]** polymerisation terminated at 71 % (instead of 96 % in dichloromethane), which might be traced back to decomposition of the catalyst, as suggested by a colour change. The lowest activity (52 % conversion) was found for **[Ru-18]**, which seems to be the most suitable catalyst in this context, as it has the best solubility in toluene and the highest robustness in all three solvents.

Table 4. Conversion of the ROMP benchmark reaction of **S8** in toluene, $CH_2Cl_2$ and $CCl_4$.[a]

| Entry | Solvent | Conversion [%][b] | | |
|---|---|---|---|---|
| | | **[Ru-12]** | **[Ru-18]** | **[Ru-20]** |
| 1 | toluene | 14 | 40 | 1 |
| 2 | $CH_2Cl_2$ | 23 | 18 | 96 |
| 3 | $CCl_4$ | 83 | 52 | 71 |

[a] Reaction conditions: [mon] = 0.1 M, [mon]/[Ru] = 300, room temp. [b] Conversion of polymerisation was determined by $^1$H NMR spectroscopy after 20 h.

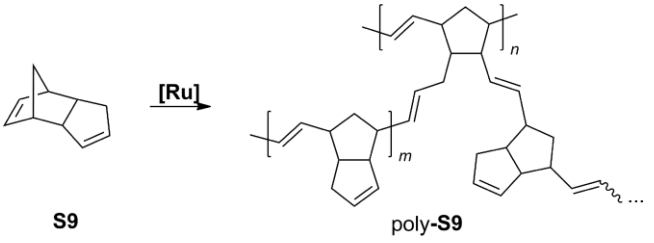
Table 5. ROMP benchmark reaction of **S8**.[a]

| Entry | Solvent | $T$ [°C] | [Ru-3] | | [Ru-12] | | [Ru-18] | | [Ru-20] | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $M_n$ [kg/mol] | PDI | $M_n$ [kg/mol] | PDI | $M_n$ [kg/mol] | PDI | $M_n$ [kg/mol] | PDI |
| 1 | $CH_2Cl_2$ | 25 | 62[8] | 1.05 | 60.4 | 1.2 | 82.6 | 1.7 | 106.4 | 1.7 |
| 2 | $CH_2Cl_2$ | 40 | 55 | 1.07 | 52.4 | 1.3 | 63.4 | 1.5 | 89.7 | 1.8 |
| 3 | toluene | 80 | – | – | 65.0 | 1.3 | 59.7 | 1.4 | 63.0 | 2.1 |

[a] Conditions: [mon] = 0.1 M, [mon]/[Ru] = 300, [HCl]/[Ru] = 10, reaction time: 20 h. Determined by GPC in THF on the basis of polystyrene calibration.

The addition of 10 equiv. of HCl (with respect to initiator) to the reactions in $CH_2Cl_2$ (Table 4, entry 2) after 20 h led to completion of the polymerisations initiated with catalysts **[Ru-18]** and **[Ru-20]** after 30 min. The progress of polymerisation initiated by **[Ru-12]** remained unchanged at 23 %, which was not surprising, as a preceding colour change from green to brown indicated decomposition of the catalyst within the first 20 h. To investigate the influence of acid on the performance of **[Ru-12]**, **[Ru-18]** and **[Ru-20]**, 10 equiv. HCl was added from the beginning to the previously described protocol at 25 °C, at 40 °C (both in $CH_2Cl_2$) and at 80 °C (toluene). For comparison, **[Ru-3]** was purchased as a commercial initiator that is suitable for performing living polymerisation. Its fast initiation at room temperature leads to a short chain length of 62 kg/mol and a polydispersity index (PDI) of < 1.1.[20] Results of all polymerisations are summarised in Table 5. In all cases, completion of polymerisation was found after less than 20 h. Although these results clearly indicate that the activity of chemo-activated complexes can be further improved by raising the reaction temperature, none of the catalysts is characterised by living polymerisation character. Considering $M_n$ values, catalyst **[Ru-12]** approaches most closely the defined requirements, but the PDI of 1.3 is still too high. Initiators **[Ru-18]** and **[Ru-20]** showed more latent behaviour, similar to an analogous Hoveyda–Grubbs-type catalyst with naphthalene ligand ($M_n$ = 89 kg/mol and PDI = 1.3).[18d] In toluene at 80 °C this trend completely stagnates, most probably for two reasons: worse solubility of the catalyst in toluene and decomposition of the catalyst at elevated temperature. The effect is small but apparent when comparing results at 40 and 80 °C: in the case of **[Ru-12]**, an increased $M_n$ (52.4–65.0 kg/mol with unchanged PDI) was found, whereas for **[Ru-20]** the PDI rose from 1.8 to 2.1 although $M_n$ decreased. Only (pre-)catalyst **[Ru-18]** showed a steady improvement of both $M_n$ and PDI with increasing reaction temperature.

Next, complexes **[Ru-12]**, **[Ru-18]** and **[Ru-20]** were tested in bulk polymerisation in neat DCPD (**S9**, cf. Scheme 11). Commercially available indenylidene second-generation catalyst **Ind-II** was utilised as reference material, since it is known to give sufficient mechanical properties of industrially produced poly-DCPD.[21] To get a first impression of the switchability, initiator **[Ru-20]** was used (with and without acid) for simultaneous thermal analysis with DCPD as monomer. For this purpose, initiator (100 ppm dissolved in toluene) was added to DCPD (1 mL). Subsequently, the formulation was homogenised, cooled with liquid $N_2$ and placed in differential scanning calorimetry (DSC) pans. The measurements were commenced at 20 °C with a heating rate of 3 °C/min. The polymerisation exotherm was read out as a function of temperature; switching temperatures for the initiators were taken as equal to the onset temperature of the exothermic heat flow.




Scheme 11. ROMP benchmark reaction of DCPD.

A mass loss is expressed in an endotherm originating from a retro-Diels–Alder reaction of the monomer occurring at 69 °C to give volatile cyclopentadiene.[2] Without the addition of HCl, no polymerisation exotherm was found (mass loss: 62 %). Indeed, the addition of acid could improve results, but still no complete conversion was observed (mass loss: 47.7 %), due to poor solubility of the (pre-)catalyst and its subsequent decomposition. The atypical DSC curves (see the Supporting Information) suggest that no polymerisation exotherm was found because of the poor solubility of the catalyst.

To obtain mechanical properties of the obtained poly-DCPD materials, tensile strength tests were performed with the above-mentioned concentrations (100 ppm of initiator). For this experiment, a pre-prepared mixture containing 30 µL of toluene per 1 mL of monomer was used to keep the monomer liquidised to allow better handling at room temperature. Initiators **[Ru-12]**, **[Ru-18]** and **[Ru-20]** were dissolved in the appropriate amount of $CH_2Cl_2$ (as the solubility in toluene was unsatisfactory) and mixed with the liquidised monomer to reach a total concentration of 60 µL solvent/mL DCPD. Additionally, 9 equiv. of HCl were added to the DCPD/[Ru] formulation and the moulds were put in an oven to cure the polymer for 24 h at 75 °C. Although all test bars entrapped some air (originating from $CH_2Cl_2$) tensile strength measurement revealed that poly-DCPDs initiated with **[Ru-12]** and **[Ru-20]** exhibit Young's moduli $E$ of 1.6–1.9 GPa and maximum stresses $R_m$ of 45 and 53 MPa, respectively (see the Supporting Information). Mechanical properties are in accordance with experimentally observed values of poly-DCPD prepared with commercially available **Ind-II** (1.6–1.9 GPa, 40–50 MPa, elongation at yield or break: 4–5 %), which are representative for industrially produced and applied poly-DCPD.[22]

## Conclusions

We have synthesised new olefin metathesis catalysts **[Ru-12]**–**[Ru-14]**, **[Ru-16]** and **[Ru-18]**–**[Ru-20]**. After activation with tri-

methylsilyl chloride or HCl they can be used as very active catalysts for numerous metathesis reactions, such as RCM, enyne cycloisomerisation and CM, also with more functionalised substrates such as **S3**, **S4** and **S6a**. Moreover, due to their latency and possibility of on-demand activation, the Ru amide complexes can be used in ROMP of DCPD (**S8**) and *endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid (**S9**). Although the best catalysts (**[Ru-12]**, **[Ru-18]** and **[Ru-20]**) produced poly-DCPD that showed reasonable results in mechanical tests, the low solubility of the new complexes in non-polar solvents could restrict their commercial applications, as compared to the fully soluble LatMet catalyst family.[8]

## Experimental Section

**General Procedure for Synthesis of Complexes (Method I):** A Schlenk flask equipped with a magnetic stirring bar was charged under argon with complex **[Ru-3]** (0.13 mmol), the first portion of ligand (**3a**–**3c**) (0.13 mmol), anhydrous toluene (7 mL) and anhydrous pyridine/DMAP/3-bromopyridine (0.27 mmol). The reaction mixture was stirred for 15 min at 70 °C. Than the second portion of **3a**–**3c** (0.13 mmol) was added and the reaction was allowed to proceed for 15 min. After this time the resulting mixture was purified by column chromatography with 10–30 % hexane/ethyl acetate. After evaporation of solvents, the resulting solid was collected, dissolved in $CH_2Cl_2$ and washed a few times with *n*-pentane to give the pure product.

**General Procedure for Synthesis of Complexes (Method II):** A Schlenk flask equipped with a magnetic stirring bar was charged under argon with complex **[Ru-1]** (0.053 mmol), ligand (**3a**–**3c**) (0.116 mmol), tricyclohexylphosphane (0.159 mmol) and anhydrous toluene (4 mL). The reaction mixture was stirred for 15 min at 70 °C. Then anhydrous pyridine/DMAP/3-bromopyridine (0.27 mmol) was added and the reaction mixture was heated for a further 15 min. The resulting mixture was purified by column chromatography with 10–30 % hexane/ethyl acetate. After evaporation of solvents, the resulting solid was collected, dissolved in $CH_2Cl_2$ and washed a few times with *n*-pentane to give the pure product.

**[Ru-12]:** (85 % method I, 54 % method II). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 17.46 (s, 1 H), 8.67 (d, $J$ = 4 Hz, 1 H), 7.51 (m, 2 H), 7.40–7.14 (m, 2 H), 7.01–6.97 (m, 4 H), 6.9 (t, $J$ = 7.4 Hz, 1 H), 6.63 (dd, $J$ = 7.4, 1.4 Hz, 1 H), 4.14–3.35 (m, 4 H), 2.82, 2.56, 2.43, 2.32, 2.16 (br. s, 18 H) ppm. $^{13}$C NMR (101 MHz, $CD_2Cl_2$): $\delta$ = 301.4, 218.6, 150.4, 150.1, 137.5, 137.3, 131.5, 130.9, 130.1, 129.2, 128.2, 128.0, 127.9, 127.4, 126.6, 126.3, 125.7, 124.9, 123.7, 122.5, 122.5, 121.3, 51.6, 35.2, 29.6, 22.3, 20.7, 18.4, 13.8 ppm. IR (film $CH_2Cl_2$): $\tilde{\nu}$ = 3284, 3024, 2918, 2858, 1942, 1727, 1621, 1578, 1537, 1485, 1458, 1448, 1417, 1282, 1266, 1240, 1231, 1204, 1160, 1034, 930, 852, 761, 724, 695, 578, 423 cm$^{-1}$. MS (ESI, *m/z*) [M – Cl]$^+$: 687.2. Complex **[Ru-12]** was described previously.[10]

**[Ru-13]:** (72 % method I, 47 % method II). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 16.80 (s, 1 H), 8.17 (d, $J$ = 8.5 Hz, 1 H), 7.42 (d, $J$ = 4.9 Hz, 3 H), 7.38–7.28 (m, 1 H), 7.03 (s, 3 H), 6.95–6.89 (m, 2 H), 6.59 (t, $J$ = 7.2 Hz, 2 H), 6.49 (dd, $J$ = 7.6, 1.4 Hz, 1 H), 3.73 (s, 4 H), 2.38–1.52 (m, 18 H), 0.97 (s, 9 H) ppm. $^{13}$C NMR (101 MHz, $CD_2Cl_2$): $\delta$ = 221.1, 195.1, 160.9, 158.2, 150.2, 149.2, 136.1, 135.8, 129.9, 129.5, 129.0, 128.8, 123.3, 121.4, 119.6, 117.9, 117.0, 77.5, 51.3, 28.6, 27.9, 27.7, 20.8 ppm. IR (film $CH_2Cl_2$): $\tilde{\nu}$ = 3356, 2916, 1699, 1604, 1584, 1518, 1482, 1445, 1263, 1153, 1043, 757, 694, 577 cm$^{-1}$. HRMS (ESI, *m/z*) [M – Cl]$^+$ calcd. 691.2586, found 691.2599.

**[Ru-14]:** (62 % method I, 44 % method II). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 16.81 (s, 1 H), 8.68 (d, $J$ = 5.2 Hz, 1 H), 8.35 (t, $J$ = 7.8 Hz, 1 H), 7.92–7.81 (m, 1 H), 7.77 (d, $J$ = 8.0 Hz, 1 H), 7.55 (d, $J$ = 5.2 Hz, 1 H), 7.41 (t, $J$ = 7.6 Hz, 1 H), 7.25 (s, 2 H), 7.09–6.99 (m, 3 H), 6.80 (d, $J$ = 6.6 Hz, 4 H), 6.66 (d, $J$ = 8.3 Hz, 1 H), 6.46 (t, $J$ = 7.2 Hz, 1 H), 4.22–3.89 (m, 4 H), 2.74 (s, 6 H), 2.42 (s, 6 H), 2.27 (s, 3 H), 1.94 (s, 6 H) ppm. $^{13}$C NMR (101 MHz, $CD_2Cl_2$): $\delta$ = 309.6, 214.7, 153.1, 150.8, 141.1, 140.3, 138.8, 138.3, 137.7, 136.4, 135.7, 131.0, 129.9, 129.7, 128.6, 128.3, 127.8, 126.7, 124.1, 121.8, 117.0, 116.2, 52.0, 20.9, 19.1, 18.0 ppm. IR (film $CH_2Cl_2$): $\tilde{\nu}$ = 2955, 2912, 1600, 1583, 1458, 1447, 1314, 1259, 1152, 1020, 957, 853, 826, 751, 655, 565 cm$^{-1}$. HRMS (ESI, *m/z*) [M – Cl]$^+$ calcd. 745.2150, found 745.2159.

**[Ru-16]:** (88 % method I, 53 % method II). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 17.23 (s, 1 H), 8.48 (d, $J$ = 20.8, Hz, 1 H), 7.66–7.63 (m, 1 H), 7.62–7.53 (m, 2 H), 7.46–7.37 (m, 2 H), 7.44–7.38 (m, 1 H), 7.28 (d, $J$ = 7.5 Hz, 2 H), 6.87–6.80 (m, 1 H), 6.78–6.67 (m, 5 H), 4.42–4.19 (m, 2 H), 4.19–4.02 (m, 2 H), 3.95–3.75 (m, 2 H), 3.40–3.03 (m, 2 H), 1.44 (d, $J$ = 14.6 Hz, 6 H), 1.36–1.26 (m, 6 H), 1.22–1.11 (m, 6 H), 0.65–0.25 (m, 6 H) ppm. $^{13}$C NMR (101 MHz, $CD_2Cl_2$): $\delta$ = 312.1, 311.7, 215.6, 151.9, 151.1, 148.9, 137.1, 136.7, 131.0, 129.7, 124.9, 124.6, 123.5, 122.4, 121.2, 119.6, 31.9, 28.7, 28.2, 26.9, 26.2, 22.7, 22.4, 13.9 ppm. IR (film $CH_2Cl_2$): $\tilde{\nu}$ = 3284, 3063, 2965, 2928, 2869, 1932, 1726, 1618, 1578, 1539, 1461, 14057, 1326, 1267, 1237, 1160, 1048, 932, 760, 724, 694, 550, 458 cm$^{-1}$. MS (FD, *m/z*): 806.2 [M]$^+$.

**[Ru-18]:** (70 % method II). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 17.12 (s, 1 H), 8.45 (d, $J$ = 8.3 Hz, 1 H), 7.48–7.37 (m, 2 H), 7.31 (s, 2 H), 7.26 (dd, $J$ = 6.6, 1.4 Hz, 2 H), 6.95 (s, 2 H), 6.93–6.89 (m, 1 H), 6.88–6.75 (m, 3 H), 2.51 (s, 6 H), 2.33 (s, 6 H), 1.85 (s, 6 H), 1.58 (s, 6 H) ppm. $^{13}$C NMR (101 MHz, $CD_2Cl_2$): $\delta$ = ppm: 314.0, 177.6, 161.9, 161.6, 153.5, 151.8, 148.9, 139.7, 138.0, 137.5, 136.2, 134.4, 130.4, 129.5, 127.2, 124.6, 123.5, 122.7, 120.9, 20.9, 18.6, 17.6, 8.8 ppm. IR (film $CH_2Cl_2$): $\tilde{\nu}$ = 3654, 3441, 2922, 1609, 1564, 1484, 1462, 1359, 1291, 1235, 1144, 1133, 1034, 942, 857, 757, 701, 589 cm$^{-1}$. HRMS (ESI, *m/z*) [M + Na]$^+$ calcd. 771.1627; found 771.1611.

**[Ru-19]:** (62 % method I, 38 % method II). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 16.92 (s, 1 H), 8.55 (d, $J$ = 8.4 Hz, 1 H), 7.63–7.48 (m, 1 H), 7.39 (s, 1 H), 7.29–7.21 (m, 3 H), 7.10 (d, $J$ = 5.6 Hz, 1 H), 6.92 (s, 2 H), 6.77 (d, $J$ = 4.0 Hz, 2 H), 6.65–6.48 (m, 1 H), 4.30–3.68 (m, 4 H), 2.60 (s, 6 H), 2.45 (s, 6 H), 1.90 (s, 6 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 213.6, 153.4, 152.4, 150.7, 149.2, 139.2, 138.9, 138.3, 132.0, 129.9, 124.8, 124.1, 122.6, 121.4, 120.5, 51.9, 21.2, 18.9, 18.0 ppm. IR (film $CH_2Cl_2$): $\tilde{\nu}$ = 2912, 1721, 1628, 1577, 1480, 1447, 1266, 1228, 1160, 1123, 1041, 760, 732, 696, 576 cm$^{-1}$. HRMS (ESI, *m/z*) [M – Cl]$^+$ calcd. 765.0990; found 765.0988.

**[Ru-20]:** (80 % method I). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 17.06 (s, 1 H), 8.42 (d, $J$ = 8.3 Hz, 1 H), 7.37 (m, 1 H), 7.21 (s, 2 H), 6.91 (s, 2 H), 6.81 (s, 2 H), 6.74–6.47 (m, 2 H), 6.03 (d, $J$ = 7.4 Hz, 2 H), 4.06 (s, 4 H), 2.89–2.44 (m, 18 H), 1.94 (s, 6 H) ppm. $^{13}$C NMR (101 MHz, $CD_2Cl_2$): $\delta$ = 214.9, 157.8, 153.5, 151.2, 148.5, 138.7, 138.4, 130.1, 129.7, 123.4, 122.4, 120.8, 107.1, 51.8, 38.8, 20.8, 18.8, 17.8 ppm. IR (film $CH_2Cl_2$): $\tilde{\nu}$ = 3325, 2911, 1621, 1562, 1541, 1394, 1229, 1146, 1032, 806, 578, 515 cm$^{-1}$. HRMS (ESI, *m/z*) [M – Cl]$^+$ calcd. 730.2307; found 730.2309.

**Representative Procedure for Catalytic Test RCM of Substrate S1:** Comparative RCM experiments with substrate **S1** ($CH_2Cl_2$, $c$ = 0.1 M, 40 °C) were performed as follows. The catalyst (1 mol-%, 500 ppm or 50 ppm) and an ethereal solution of HCl (0.0399 mmol, 10 mol-%) were added in a single portion to a stirred solution of **S1** (100 mg, 0.399 mmol) and durene (internal standard, 54 mg, 0.399 mmol) in $CH_2Cl_2$ (4 mL) under argon in a Schlenk tube at

40 °C, and the reaction mixture was stirred for 2 h at the same temperature. Aliquots (0.05 mL), taken in regular intervals, were quenched immediately with an ice-cold solution of ethyl vinyl ether (0.1 mL) in $CH_2Cl_2$ (0.5 mL) and analysed by GC by using an EP Clarus 580 chromatograph with InertCap MS5/Sil column.

**Representative Procedure for Catalytic Test RCM of Substrate S2:** Comparative RCM experiments with substrate **S2** ($CH_2Cl_2$, $c$ = 0.1 M, 40 °C) were performed as follows. The catalyst (0.00204 mmol, 1 mol-%) and $Me_3SiCl$ (0.0204 mmol, 10 mol-%) were added in a single portion to a stirred solution of substrate **S2** (50 mg, 0.204 mmol) and durene (internal standard, 27 mg, 0.204 mmol) in $CH_2Cl_2$ (2 mL) under argon in a Schlenk tube at 40 °C, and the reaction mixture was stirred for 2 h at the same temperature. Aliquots (0.05 mL), taken in regular intervals, were quenched immediately with an ice-cold solution of ethyl vinyl ether (0.1 mL) in $CH_2Cl_2$ (0.5 mL) and analysed by GC by using an EP Clarus 580 chromatograph with InertCap MS5/Sil column.

**Representative Procedure for Catalytic Test RCM of Substrate S3:** Comparative RCM experiments with substrate **S3** ($CH_2Cl_2$, $c$ = 0.1 M, 40 °C) were performed as follows. The catalyst (0.0034 mmol, 1 mol-%) and $Me_3SiCl$ (0.034 mmol, 10 mol-%) were added in a single portion to a stirred solution of substrate **S3** (100 mg, 0.34 mmol) and durene (internal standard, 32 mg, 0.34 mmol) in $CH_2Cl_2$ (2 mL) under argon in a Schlenk tube at 40 °C, and the reaction mixture was stirred for 2 h at the same temperature. Aliquots (0.05 mL), taken in regular intervals, were quenched immediately with an ice-cold solution of ethyl vinyl ether (0.1 mL) in $CH_2Cl_2$ (0.5 mL) and analysed by GC by using an EP Clarus 580 chromatograph with InertCap MS5/Sil column. After complete conversion the solvent was evaporated, and the crude mixture was purified by column chromatography. The column was eluted with cyclohexane/ethyl acetate (10 % v/v). The product was obtained as a brown oil. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.84–5.64 (m, 2 H), 4.57–4.05 (m, 5 H), 3.53–3.29 (m, 2 H), 2.13–1.93 (m, 2 H), 1.87–1.68 (m, 2 H), 1.34–1.27 (m, 9 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 171.2, 170.8, 154.4, 153.7, 126.1, 126.0, 124.9, 124.7, 79.4, 74.3, 57.6, 57.5, 53.1, 52.9, 46.8, 46.7, 30.2, 29.3, 28.4, 28.2, 24.2, 23.7 ppm. Analytical data were in good agreement with previously reported values.[23]

**Representative Procedure for Catalytic Test RCM of Substrate S4:** Comparative RCM experiments with substrate **S4** ($CH_2Cl_2$, $c$ = 0.1 M, 40 °C) were performed as follows. The catalyst (0.00423 mmol, 1 mol-%) and $Me_3SiCl$ (0.0197 mmol, 10 mol-%) were added in a single portion to a stirred solution of substrate **S4** (100 mg, 0.423 mmol) and durene (internal standard, 57 mg, 0.423 mmol) in $CH_2Cl_2$ (4.3 mL) under argon in a Schlenk tube at 40 °C, and the reaction mixture was stirred for 2 h at the same temperature. Aliquots (0.05 mL), taken in regular intervals, were quenched immediately with an ice-cold solution of ethyl vinyl ether (0.1 mL) in $CH_2Cl_2$ (0.5 mL) and analysed by GC by using an EP Clarus 580 chromatograph with InertCap MS5/Sil column.

**Representative Procedure for Catalytic Test Cycloisomerisation of Substrate S5:** Comparative enyne experiments with substrate **S5** ($CH_2Cl_2$, $c$ = 0.1 M, 40 °C) were performed as follows. The catalyst (0.00201 mmol, 1 mol-%) and $Me_3SiCl$ (0.0201 mmol, 10 %mol) were added in a single portion to a stirred solution of substrate **S6** (100 mg, 0.201 mmol) and durene (internal standard, 27 mg, 0.201 mmol) in $CH_2Cl_2$ (2 mL) under argon in a Schlenk tube at 40 °C, and the reaction mixture was stirred for 2 h at the same temperature. Aliquots (0.05 mL), taken in regular intervals, were quenched immediately with an ice-cold solution of ethyl vinyl ether (0.1 mL) in $CH_2Cl_2$ (0.5 mL) and analysed by GC by using an EP Clarus 580 chromatograph with InertCap MS5/Sil column. After complete conversion the solvent was evaporated, and the crude mixture was purified by column chromatography. The column was eluted with cyclohexane/ethyl acetate (10 % v/v). The product was obtained as a colourless oil. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.10–7.40 (m, 10 H), 6.20–6.27 (m, 1 H), 6.16–6.18 (m, 1 H), 5.31 (dd, $J$ = 17.7, 0.8 Hz, 1 H), 5.10 (dd, $J$ = 11.2, 0.8 Hz, 1 H), 4.11 (q, $J$ = 7.1 Hz, 1 H) ppm. $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 171.1, 143.6, 143.3, 129.7, 127.9, 127.8, 124.8, 117.5, 94.5, 60.3 ppm. Analytical data were in good agreement with previously reported values.[24]

**Representative Procedure for Catalytic Test CM Reaction of Substrates S6a and S6b:** Comparative CM experiments with substrates **S6a** and **S6b** ($CH_2Cl_2$, $c$ = 0.1 M, 40 °C) were performed as follows. The catalyst (0.0034 mmol, 1 mol-%) and $Me_3SiCl$ (0.034 mmol, 10 mol-%) were added in a single portion to a stirred solution of **S6a** (120 mg, 0.34 mmol), **S6b** (117 mg, 0.68 mmol, 2 equiv.) and durene (internal standard, 45 mg, 0.34 mmol) in $CH_2Cl_2$ (7 mL) under argon in a Schlenk tube at 40 °C, and the reaction mixture was stirred for 2 h at the same temperature. After 2 h the solvent was evaporated, and the crude mixture was purified by column chromatography. The column was eluted with cyclohexane/ethyl acetate (10 % v/v). The product was obtained as a white solid. $^1$H NMR (400 MHz, $CDCl_3$, *E* isomer): $\delta$ = 7.73 (d, $J$ = 8.0 Hz, 1 H), 7.30 (dd, $J$ = 8.0, 2.0 Hz, 1 H), 6.34–6.27 (m, 1 H), 6.19–6.11 (m, 1 H), 5.00 (d, $J$ = 6.0 Hz, 2 H), 3.37–3.35 (m, 2 H), 3.13–3.09 (m, 2 H), 3.00–2.93 (m, 3 H), 2.88–2.84 (m, 1 H), 2.76–2.71 (m, 1 H), 2.63–2.61 (m, 1 H), 2.52–2.41 (m, 7 H), 2.14–1.85 (m, 7 H), 1.37 (s, 3 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$, *E* isomer): $\delta$ = 220.8, 171.7, 170.9, 148.6, 138.1, 137.5, 133.5, 126.5, 125.6, 121.6, 118.8, 64.9, 50.5, 48.0, 44.3, 38.1, 36.0, 33.7, 31.7, 29.5, 27.6, 26.4, 25.9, 21.7, 20.9, 13.9 ppm. IR (KBr): $\tilde{\nu}$ = 3453, 2930, 2871, 1737, 1495, 1376, 1223, 1155, 1020, 958, 888, 824, 777 cm$^{-1}$. HRMS (ESI): $m/z$ [M + Na]$^+$. HRMS calcd. 261.1830, found. 261.1835.

**Representative Procedure for Catalytic Test RCM of Substrate S7:** Comparative RCM experiments with substrate **S7** ($CH_2Cl_2$, $c$ = 0.1 M, 40 °C) were performed as follows. The catalyst (0.00197 mmol, 1 mol-%) and an ethereal solution of HCl (0.0197 mmol, 10 mol-%) were added in a single portion to a stirred solution of substrates (50 mg, 0.197 mmol) and durene (internal standard, 68 mg, 0.197 mmol) in $CH_2Cl_2$ (2 mL) under argon in a Schlenk tube at 40 °C, and the reaction mixture was stirred for 2 h at the same temperature. Aliquots (0.05 mL), taken in regular intervals, were quenched immediately with an ice-cold solution of ethyl vinyl ether (0.1 mL) in $CH_2Cl_2$ (0.5 mL) and analysed by GC by using an EP Clarus 580 chromatograph with InertCap MS5/Sil column.

**Representative Procedure for ROMP of S8 in Solution:** The appropriate complex (0.00159 mmol, 1 equiv.) was weighed in a Schlenk flask and dissolved in toluene/$CH_2Cl_2$/$CCl_4$ (3.8 mL, $c$[**S8**] = 0.1 M). The reaction mixture was either maintained at room temperature or heated to 40 or 80 °C with or without the addition of 2 M ethereal HCl (7.9 µL, 0.0159 mmol, 10 equiv.). A solution of the monomer (100 mg, 0.48 mmol, 300 equiv.) in toluene (1 mL) was added. The conversion of the reaction was monitored by TLC [cyclohexane/ethyl acetate (25 % v/v)] by staining with $KMnO_4$ solution. After full conversion, the reaction mixture was quenched by addition of ethyl vinyl ether (200 µL). Subsequently, the solvent was evaporated and the polymer was dissolved in $CH_2Cl_2$, precipitated in cold methanol and finally dried in vacuo. $^1$H NMR spectra were recorded in $CDCl_3$ for unfinished polymerisation after 24 h. For this a 200 µL sample of the reaction mixture was taken, quenched with ethyl vinyl ether (50 µL) and dried in vacuo.

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