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Note

Olefin metathesis catalyst bearing a chelating phosphine ligand

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ABSTRACT

An improved synthetic procedure for the complex (SPY-5-34)-dichloro-(κ^2(C,P)-diphenyl-(2-benzylidene)-phosphine)-(1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydro-imidazol-2-ylidene)-ruthenium (**2**) was elaborated and the title compound was tested as latent initiator in Ring Opening Metathesis Polymerization (ROMP) and as catalyst for Ring-Closing Metathesis (RCM) at elevated temperatures. While not particularly suited as latent initiator for ROMP, exhibiting a switching temperature of only 42 °C in the polymerization of a typical norbornene derivative, **2** shows an appealing performance in RCM of α,ω-dienes at higher temperatures.

1. Introduction

Over the last decade olefin metathesis has aroused much attention owing to its versatile applicability in organic and polymer chemistry [1]. In particular ruthenium-based homogeneous catalysts have been described in detail due to their remarkable tolerance to moisture and oxygen as well as their high functional group tolerance [2]. Accordingly, a broad variety of ruthenium-based catalysts with various ligands have been developed to receive a subtle balance between stability and activity [3]. The dazzling array of different olefin metathesis catalysts and initiators has been reviewed recently [4]. However, most olefin metathesis reactions are performed with the commercially available catalysts Grubbs 1st, 2nd and 3rd generation (**G1, G2, G3**), Hoveyda 2nd generation (**H2**) or **M2** and **M31** [5] featuring an indenylidene instead of the benzylidene ligand (see Fig. 1).

All these compounds typically exhibit catalytic activity at room temperature. However, for some selected applications and synthetic challenges, high thermal stability and/or a thermal switchability is desired. For that purpose latent catalysts/initiators have been developed [6]. A successful design motif for latent catalysts/initiators is the use of a chelating carbene ligand similar to the one used in Hoveyda type complexes with strongly coordinating co-ligands using O [7], N [8], S [9] and Se [10] donor atoms as the second binding unit.

Herein, a phosphorous based compound, namely (SPY-5-34)-dichloro-(κ^2(C,P)-diphenyl-(2-benzylidene)-phosphine)-(1,3-bis (2,4,6-trimethylphenyl)4,5-dihydro-imidazol-2-ylidene)-ruthenium (**2**) is disclosed. The compound under investigation was briefly described in a recent study on the geometries of chelated ruthenium benzylidenes, however, its metathetical activity was not tested [10]. We describe an improved synthetic procedure for **2** and its performance in ring-closing metathesis (RCM) catalysis as well as in ring opening metathesis polymerization (ROMP) is presented.

2. Results and discussion

The carbene precursor diphenyl-(2-vinylphenyl)-phosphine (**1**) was prepared by a Grignard reaction of chlorodiphenylphosphine with (2-vinylphenyl)magnesium bromide in 55% yield. Characterization by elemental analysis and NMR spectroscopy matches the analytical data recently published [10].

As shown in Scheme 1, complex **2** was prepared by a carbene exchange reaction of (H_2IMes)(pyridine)$_2$(Cl)$_2$Ru=CHPh (**G3**) [11] with **1**. A mixture of 1 equiv. of **G3** and 2 equiv. of **1** was stirred in CH_2Cl_2 at room temperature according to typical protocols [12]. Compound **2** was isolated as micro-crystals by precipitation upon addition of Et_2O and *n*-pentane in good yield (60%). The NMR spectroscopic data of **2** were found in accordance with a *cis*-arrangement of the two halide ligands and were identical to those

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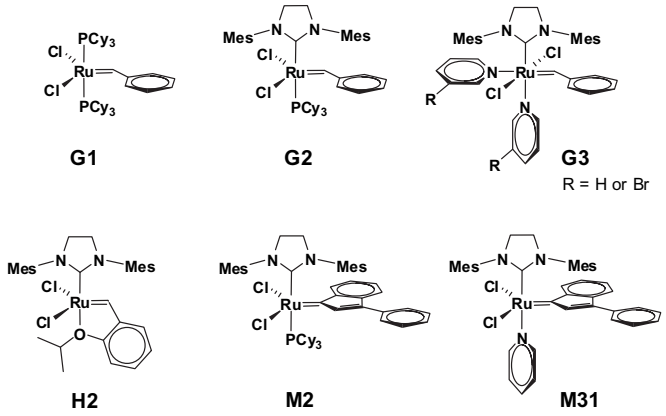


Fig. 1. Commercially available catalysts/initiators for olefin metathesis reactions.

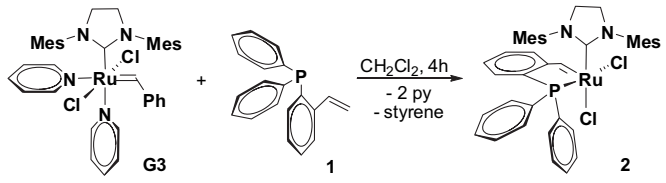
published [10]. Additionally a $^{31}P\{^{1}H\}$ NMR spectrum was acquired which featured a singlet at 57.8 ppm.

Firstly, **2** was evaluated as a latent initiator for ring opening metathesis polymerization (ROMP). A suited latent initiator meets the prerequisite that monomers and initiator may be stored together without reaction and that the polymerization can be triggered by only raising the temperature [6]. To gain information on the latency of **2**, polymers of the monomer (±)-*endo*,*exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester (**3**) were prepared. **3** was polymerized with initiator **2** in a ratio of 300:1 at 110 °C either in solution with toluene as the solvent or neat. Determination of the number average molecular weight (M_n) using gel permeation chromatography in THF calibrated against polystyrene standards, revealed considerably high M_n values (solution: 1,200,000 g/mol; bulk: 2,100,000 g/mol). The polydispersity index (PDI) for both polymers was rather broad (1.6 in solution and 2.0 for the bulk-polymerization). ^{1}H NMR spectroscopy confirmed polymerization via ROMP. The high molecular weights provide evidence for a low initiation efficiency of **2**, which is a characteristic of all latent initiators investigated so far [6–9]. For comparison, under the same conditions as stated above, fast initiating initiators polymerize **3** at room temperature to give polymers with a M_n of about 50,000 g/mol [5]. Furthermore, the polymerization reaction was monitored by ^{1}H NMR spectroscopy in order to check for activity at room temperature. The experiments were either conducted under argon atmosphere or under ambient conditions. Integration of the appropriate signal in the ^{1}H NMR spectrum revealed the transformation of the monomer (6.24, 6.03 ppm, 2H, C*H*=C*H*$_{norbornene}$) to the polymer (5.94–5.14 ppm, 2H, C*H*=C*H*). While the polymerization under inert atmosphere led to the quantitative formation of the according polymer with a polymerization half life of 1.35 h, the polymerization under ambient conditions tends to a half life of 2.15 h. This result points towards a slight air sensitivity of **2** or the propagating species.

Finally, model polymerizations in DSC-pans utilizing (±)-*endo*,*exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid diethyl ester (**4**) as the monomer were conducted in order to evaluate the thermal onset of the reaction. **2** (1 equiv.) and **4** (500 equiv.) were placed in a DSC-pan, which was then transferred into the apparatus. A heating ramp of 10 °C/min was commenced and the reaction exotherm was read out as a function of temperature. A 'switching temperature' for the initiator (i.e. the temperature at which, under certain conditions, the polymerization is detectable), can be determined as the temperature at which the first exothermic heat-flow is detectable. The onset of polymerization under these experimental conditions was 42 °C (see Fig. 2). Triggering at such a low temperature is rather unusual for ruthenium catalysts with a *cis*-dichloro geometry, especially with a strong chelating heteroatom such as phosphorous. Distinctly higher switching temperatures have been reported for related compounds [8]. We surmise that the strong steric interactions between the mesitylene fragments and the phenyl substituent on the P atom lower the initiation temperature.

In organic synthesis, particularly in ring-closing metathesis (RCM), challenging substrates, i.e. highly functionalized ones, sometimes need higher temperatures and high catalyst loadings for complete conversions [13]. Conventional pre-catalysts like **G2** or **H2** show a fast formation of the actual catalyst, the corresponding methylidene species [11]. At higher temperatures, fast decomposition of the methylidene complex occurs, leading to ruthenium hydride species which have been shown to be responsible for side reactions such as double bond isomerization [14–16]. Prevention of this unintended isomerization reaction is particularly important when high reaction temperatures are used. In this context, we aimed at investigating **2** in RCM at elevated temperatures.

For this purpose, diethyl diallylmalonate (**5**) and N,N-diallyl-4-methyl-benzenesulfonamide (**8**) were chosen as model substrates. All reactions listed below were performed in a Schlenk flask under argon atmosphere with a precatalyst loading of 1 mol%. To find the optimal reaction conditions for full conversion, different reaction temperatures, times and solvents were tested. Results for **5** as the starting material are presented in Table 1. Typically, two different products were formed: the RCM product cyclopent-3-ene-1,1-dicarboxylic acid diethyl ester (**6**) as well as 3-methyl-4-methylene-cyclopentane-1,1-dicarboxylic acid diethyl ester (**7**) as side product (Table 1). A strong dependency of conversion on the reaction temperature was found. At a reaction temperature of 50 °C in toluene (Table 1, entry 1) the desired product was formed in 80% yield after 48 h. An increase to a conversion of >97% towards **6** was



Scheme 1.

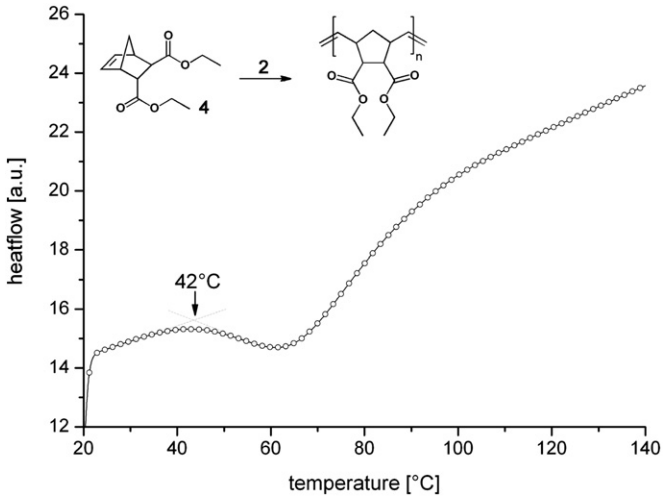
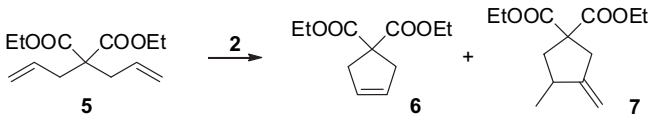


Fig. 2. Course of the polymerization of **4** initiated by **2** (heating rate 10 °C/min, **2**/**4** ratio = 1/500).

Table 1
Ring-closing metathesis of diethyl diallylmalonate (**5**) with catalyst **2**.

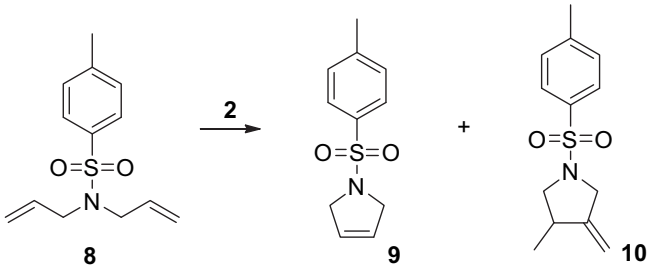


5 **6** **7**

Entry	Additive	Solvent	*T* [°C]	*t* [h]	**5** [%]	**6** [%]	**7** [%]
1	–	Toluene	50	48	20	80	–
2[a]	–	Toluene	110	72	–	>97	Traces
3	–	Toluene	110	72	–	>97	Traces
4	TEMPO	Toluene	110	48	–	75	25
5[b]	TEMPO	Toluene	110	72	>99	–	–
6	–	Acetone	rt	24	>99	–	–
7[c]	–	Acetone	50	48	13	84	Traces
8	–	Acetone	50	72	–	>97	Traces
9	–	$CHCl_3$	50	72	82	18	–
10	–	MeOH	65	72	74	–	16
11	–	C_6F_6	60	72	>99	–	–

[a] Reference reaction with $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CH(Ph)$ [12].
[b] Control reaction without catalyst.
[c] Reaction mixture of entry **6** was heated up to 50 °C after 48 h to give entry **7**.

Table 2
Ring-closing metathesis of N,N-diallyl-4-methyl-benzenesulfonamide (**8**) with catalyst **2**.



8 **9** **10**

Entry	Additive	Solvent	*T* [°C]	*t* [h]	**8** [%]	**9** [%]	**10** [%]
1	–	Toluene	110	72	–	>97	Traces
2	–	Toluene	50	48	47	52	–
3	–	Toluene	50	72	52	48	–
4	–	Acetone	50	72	42	51	7
5	–	$CHCl_3$	50	72	–	89	11
6	Benzoquinone	$CHCl_3$	50	72	18	82	–

only possible when heating up to 110 °C (Table 1, entry 3). Minor amounts (<3%) of **7** were formed under these conditions. The same results were obtained in a reference reaction using **G2** (Table 1, entry 2) [12]. Upon addition of TEMPO (2,2,6,6-tetramethylpiperidinyloxyl) to the reaction mixture (Table 1, entry 4), the ratio of **6**:**7** was shifted in favor of **7**.

It is to note, that only the combination of TEMPO and **2** increased the amount of **7** in the reaction mixture. The formation of *exo*-methylene-cyclopentane derivatives like **7** from 1,6 dienes is, according to literature, most probably catalyzed by Cl–Ru–H species [17]. In case of addition of radical scavengers, such as TEMPO (2,2,6,6-tetramethylpiperidinyloxyl) or phenol derivatives an increase of the side product has been observed in literature. These results were rationalized by an increased tendency of formation of Cl–Ru–H species in the presence of the above mentioned additives [16]. Changing the solvent from toluene to acetone, chloroform or methanol did not lead to significant improvements. In case of acetone, first the reaction was carried out at room temperature (rt) for 24 h (Table 1, entry 6) and subsequently the reaction mixture was heated up to 50 °C (Table 1, entry 7). At room temperature no conversion was detectable, but when heating up to 50 °C formation of the desired product was noted. After a reaction time of 48 h, 84% of **5** had been converted to **6**. Minor amounts of **7** were detected. Only after 72 h full conversion was noted (Table 1, entry 8). In contrast, only 18% of **6** was formed after 72 h at 50 °C in $CHCl_3$ and **7** was not detected under these reaction conditions (Table 1, entry 9). Notably, when using methanol as the solvent, **5** was converted exclusively to **7** and **6** was not observed. However, even after heating for 72 h at 65 °C, only 16% of **5** was converted to **7** (Table 1, entry 10). Finally, hexafluorobenzene [18] was used as the solvent. Surprisingly, neither **6** nor **7** was formed after heating the reaction mixture for 72 h at 60 °C (Table 1, entry 11).

Further examples comprise the transformation of N,N-diallyl-4-methyl-benzenesulfonamide (**8**) with catalyst **2** (1 mol%) under various conditions (Table 2, entries 1–6). In toluene, **8** was completely consumed after 72 h at 110 °C giving rise to more than 97% of the RCM product 2,5-dihydro-1-tosyl-1H-pyrrole (**9**) and traces of 3-methylene-1-tosylpyrrolidine (**10**) (Table 2, entry 1). Conversion of **8** is lower, when compared to **5**, which is also indicated by only 52% formation of **9** after 48 h in toluene at 50 °C. The same holds true for acetone as the solvent. Moreover, the corresponding *exo*-methylene-cyclopentane derivative **10** formed to a larger extent (Table 2, entry 4).

In sharp contrast to the aforementioned experiments, the use of $CHCl_3$ as the solvent afforded a more effective transformation of **8**, when compared to **5** (Table 1, entry 9 and Table 2, entry 5). Thus, 89% **9** and 11% **10** were obtained by reacting **8** with catalyst **2** in $CHCl_3$. An attempt to prevent the formation of **10** upon addition of 1,4-benzoquinone [16] (10 equiv. in relation to **2**) led to lower conversions, nevertheless, the formation of **10** was effectively impeded (Table 2, entry 6).

3. Conclusion

Concluding the evaluation of **2**, it was established that **2** exhibits a surprisingly low switching temperature of about 42 °C in ROMP and promotes the polymerization of a typical norbornene derivative even at room temperature. Accordingly, **2** is not particularly suited as latent initiator for ROMP. **2** shows an appealing performance in RCM at higher temperatures, especially in case toluene is used as the solvent. Depending on the used solvent, temperature and reaction times, minor amounts of a catalytic by-products were observed, which evidences limited temperature stability of either **2** or one of the intermediate products formed in the catalytic cycle. Although formation of this side product can be suppressed upon addition of a hydride scavenger, namely 1,4-benzoquinone, it constitutes a major complication in RCM at higher temperatures. Future work should emphasise this limitation and take this issue into consideration [19]. Until now relatively few publications have been focused on solvent effects regarding ring-closing metathesis [18], particularly at higher temperatures. This study gives a first impression of the importance of solvent effects in RCM with latent catalysts at elevated temperatures.

4. Experimental

4.1. General remarks

Manipulations were performed under an inert atmosphere of purified nitrogen or argon using Schlenk techniques. Unless otherwise noted, materials were obtained from commercial sources (Aldrich, Fluka or Lancaster) and were used without further

purification. Monomers **3** and **4** were prepared according to the literature procedures [20]. CH_2Cl_2 was distilled over CaH_2 and degassed with argon. All experiments were carried out under inert atmosphere. Gel permeation chromatography (GPC) was used to determine molecular weights and the polydispersity index (PDI) of polymer samples with THF as the solvent with the following arrangement: a Merck Hitachi L6000 pump, separation columns from Polymer Standards Service [8 × 300-mm STV 5-μm-grade size (10^6, 10^4, and 10^3 Å)], a refractive-index detector from Wyatt Technology, a model Optilab DSP interferometric refractometer, and polystyrene standards purchased from Polymer Standard Service was used for calibration. ^{1}H NMR spectra were recorded on a Varian INOVA 500-MHz spectrometer 2 versus $SiMe_4$ as a standard at 500 MHz; $^{13}C\{^1H\}$ NMR spectra were recorded at 125 MHz. The solvent residual peak of $CDCl_3$ was used for referencing the NMR spectra to 7.26 and 77.16 ppm, respectively. The relaxation delay for ^{1}H NMR spectra was set to 5 s. DSC measurements were made with a Perkin Elmer Pyris Diamond Differential Scanning Calorimeter equipped with a Perkin Elmer CCA7 cooling system using liquid nitrogen. A nitrogen flow of 20 mL/min and a heating rate of 10 °C/min were used.

4.2. Synthesis of diphenyl-(2-vinylphenyl)-phosphine (*1*)

Magnesia (0.66 g, 0.027 mol) and 1-bromo-2-vinylbenzene (5.00 g, 0.027 mol) were mixed in THF (10 mL) under argon atmosphere. The reaction mixture was heated using a heatgun until the reaction started. Subsequently the mixture was cooled with an ice bath and stirred until all Mg was dissolved. Chlorodiphenylphosphine (4.82 g, 0.021 mol), dissolved in 6 mL of THF was slowly added to keep the solution gently boiling. The reaction was stirred for 1 h at reflux and then poured into 500 mL of water and ice. The product was extracted with Et_2O and precipitated in *n*-pentanes. Purification was done by flash chromatography (SiO_2, CH_2Cl_2:*n*-pentane = 1:1). The product was evaporated to dryness under reduced pressure. Yield: 3.46 g (55%)

Anal. calcd. for: $C_{20}H_{17}P$ (MW: 288.32): C, 83.31; H, 5.94. Found: C, 83.72; H, 5.99. ^{1}H NMR (δ, 20 °C, $CDCl_3$, 500 MHz): 7.62 (m, 1H, Ph^3), 7.35, 7.29 (m, 12H, Ph, −C*H*−CH_2), 7.18 (t, 1H, Ph^4), 6.83 (m, 1H, Ph^5), 5.65 (dd, 1H, $^3J_{HHtrans}$ = 17.5 Hz, $^2J_{HH}$ = 1.0 Hz, CH_2=CH), 5.24 (dd, 1H, $^3J_{HHcis}$ = 10.5 Hz, CH_2=CH). $^{31}P\{^1H\}$ NMR (δ, 22 °C, $CDCl_3$, 200 MHz): −15.4. $^{13}C\{^1H\}$ NMR (δ, 20 °C, $CDCl_3$, 125 MHz): 142.6 (1C, $^1J_{CP}$ = 21.9 Hz, C1), 136.6 (1C, J_{CP} = 10.0 Hz, C6), 135.6 (2C, $^1J_{CP}$ = 23.9 Hz, C1′,1″), 135.3 (1C, $^2J_{CP}$ = 13.8 Hz, C2), 134.2 (4C, $^2J_{CP}$ = 19.5 Hz, C2′,2″,6′,6″), 133.4, 129.2, 128.1, (3C,C3,4,5), 129.0 (2C, C4′,4″), 128.7 (4C, $^3J_{CP}$ = 7.1 Hz, C3′,3″,5′,5″), 125.8 (1C, $^3J_{CP}$ = 4.75 Hz, *C*H=CH_2), 116.3 (1C, $^4J_{CP}$ = 2.4 Hz, *C*H_2=CH).

4.3. Preparation of (SPY-5-34)-dichloro-(κ²(C,P)-diphenyl-(2-vinylbenzylidene)-phosphine)-(1,3-bis(2,4,6-trimethylphenyl) 4,5-dihydro-imidazol-2-ylidene)-ruthenium (*2*)

To a solution of **1** (50 mg, 0.42 mmol) in CH_2Cl_2 (6 mL) **G3** (148 mg, 0.20 mmol) was added and the reaction mixture was stirred at 25 °C for 4 h. Afterwards, the mixture was evaporated to dryness and the residue was redissolved in CH_2Cl_2/Et_2O. Upon addition of heptanes a brown precipitate formed which was separated by filtration washed with heptanes and dried in vacuum. Yield: 92 mg (60%)

Anal. calcd. for: $C_{40}H_{41}Cl_2N_2PRu$ (MW: 752.72): C, 63.83; H, 5.49. Found: C, 63.72; H, 5.43. ^{1}H NMR (δ, 22 °C, $CDCl_3$, 500 MHz): 17.06 (s, 1H, Ru=C*H*), 7.78, 7.56, 7.47, 7.40, 7.35, 7.19, 7.16, 7.11, 6.70 (vt, 14H, aromatic signals), 7.00, 6.93, 6.84, 5.91 (bs, 4H, $Mes^{3,3',5,5'}$), 4.26, 4.04, 3.96 (bm, 4H, N-CH_2), 2.77, 2.71, 2.38, 2.31, 2.27, 2.20 (bs, 18H, MesCH_3). $^{31}P\{^1H\}$ NMR (δ, 22 °C, $CDCl_3$, 200 MHz): 57.8. $^{13}C\{^1H\}$ NMR (δ, 22 °C, $CDCl_3$, 125 MHz): 283.8 (1C, Ru=*C*H), 216.7 (1C, NH*C*), 142.3, 140.2, 139.8, 138.5, 138.0, 136.8 (6C, Cq), 136.0 (1C, Ct), 135.6, 134.8,132.2 (3C, Cq), 131.1, 131.0, 129.8, 129.7, 128.5, 128.2, 127.8 (7C, Ct), 120.0 (1C, Cq), 51.2, 51.1 (2C, N-CH_2), 21.4, 21.0, 20.1, 18.4, 18.3, 16.3 (b, MesCH_3).

4.4. General procedure for the RCM of DEDAM

In a Schlenk-tube, a mixture of **2** (0.5 mg, 1 mol%) and **5** (20 mg, 0.08 mmol) was stirred in dry solvent (10 mL). For solvent and reaction conditions, see Table 1. Purification was done by flash chromatography (SiO_2, Cy:EA = 2:1). The obtained product was evaporated to dryness and dried under vacuum.

RCM product (**6**): ^{1}H NMR (δ, 20 °C, $CDCl_3$, 500 MHz): 5.60 (s, 2H, $cp^{3,4}$), 4.19 (q, 4H, OC$H_2$$CH_3$), 3.00 (s, 4H, $cp^{2,5}$), 1.24 (t, 6H, OCH_2CH_3). ^{13}C NMR (δ, 20 °C, $CDCl_3$, 500 MHz): 172.5 (2C, C$OOCH_2CH_3$), 128.0 (2C, $cp^{3,4}$), 61.8 (2C, OCH_2CH_3), 59.0 (1C, cp^1), 41.1 (2C, $cp^{2,5}$), 14.3 (2C, OCH_2CH_3).

Side product (**7**): ^{1}H NMR (δ, 20 °C, $CDCl_3$, 500 MHz): 4.89, 4.77 (2 × s, 2H, CH_2), 4.17 (q, 4H, OC$H_2$$CH_3$), 3.05, 3.02 (1H, cp^2), 2.95, 2.91 (1H, cp^2), 2.60–2.50 (m, 1H, cp^4), 2.16, 1.74 (2H, cp^5), 1.23 (t, 6H, OCH_2CH_3), 1.10 (d, 3H, CHCH_3). ^{13}C NMR (δ, 20 °C, $CDCl_3$, 500 MHz): 171.2, 171.1 (2C, C$OOCH_2CH_3$), 152.6 (1C, *C*=CH_2), 104.6 (1C, C=*C*H_2), 60.7 (2C, $COOCH_2CH_3$), 57.3 (1C, cp^1), 41.3, 39.7, 36.5 (3C, $cp^{2,4,5}$), 17.2 (1C, CHCH_3), 13.3 (2C, $COOCH_2CH_3$).

4.5. General procedure for the RCM of Tos-DAA

In a Schlenk-tube, a mixture of catalysts **2** (0.5 mg, 1 mol%) and **8** (20 mg, 0.08 mmol) was stirred in dry solvent (10 mL). For solvent and reaction conditions, see Table 1. Purification was done by flash chromatography (SiO_2, Cy:EE = 2:1). The obtained product was evaporated to dryness and dried under vacuum.

RCM product (**9**): ^{1}H NMR (δ, 20 °C, $CDCl_3$, 500 MHz): 7.65 (d, 2H, $ph^{3,5}$), 7.28 (d, 2H, $ph^{2,6}$), 5.60 (s, 2H, $cp^{3,4}$), 4.09 (s, 4H, $cp^{2,5}$), 2.38 (s, 1H, −CH_3). ^{13}C NMR (δ, 20 °C, $CDCl_3$, 125 MHz): 140.9 (1C, ph^4), 136.3 (1C, ph^1), 129.5 (2C, $ph^{3,5}$), 125.9, 125.4 (4C, $ph^{2,6}$, CH_2CH=*C*HCH_2), 46.9 (2C, N-CH_2), 20.9 (1C, ph-CH_3).

Side product (**10**): ^{1}H NMR (δ, 20 °C, $CDCl_3$, 500 MHz): 7.70, 7.32 (2 × d, 2 × 2H, $ph^{2,3,5,6}$), 4.90, 4.85 (2 × s, 2H, CH_2), 4.11, 3.95, 3.80, 3.73, 3.57 (5H, $cp^{1,2,5}$), 2.43 (s, 4H, ph-CH_3, cp^4), 1.04 (d, 3H, CHCH_3). ^{13}C NMR (δ, 20 °C, $CDCl_3$, 125 MHz): 149.4 (1C, cp^1), 143.7 (1C, ph^4), 133.0 (1C, ph^1), 129.8 (2C, $ph^{3,5}$), 127.9 (2C, $ph^{2,6}$), 106.1 (1C, *C*CH_2), 55.2, 52.3 (2C, $cp^{2,5}$), 37.6 (1C, cp^4), 21.7 (1C, ph-CH_3), 16.2 (1C, CHCH_3).

4.6. General polymerization procedure in NMR-tube

Monomer **3** (100 mg, 0.5 mmol) was dissolved in $CDCl_3$ and subsequently **2** (1 mg, 0.002 mmol), dissolved in $CDCl_3$, was added. ^{1}H NMR (δ, 20 °C, 500 MHz, $CDCl_3$): 5.94–5.14 (bm, 2H, C*H*=C*H*), 4.32–3.98 (bm, 4H, C$H_2$$CH_3$), 3.40–2.57 (bm, 4H, $cp^{1,2,3,4}$), 2.14–1.77 (bm, 1H, cp^5), 1.66–1.37 (bm, 1H, cp^5), 1.32–1.14 (bm, 6H, CH_2CH_3). ^{13}C NMR (δ, 20 °C, 125 MHz, $CDCl_3$): 174.1–173.1 (*C*=O), 133.5–130.0 (*C*H=*C*H), 60.8–60.6 (CH_2CH_3), 53.1–51.9 (*C*H−COO), 47.2–39.0 (CH_2, *C*H−CH=), 15.0–14.0 (CH_2CH_3).

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