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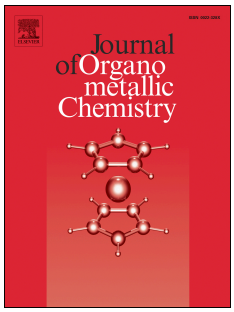

Carbamato-benzylidene ruthenium chelates – Synthesis, structure and catalytic activity in olefin metathesis

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Carbamato-benzylidene ruthenium chelates – synthesis, structure and catalytic activity in olefin metathesis

Szymon Rogalski, Patrycja Żak, Piotr Pawluć, Maciej Kubicki and Cezary Pietraszuk*

Adam Mickiewicz University in Poznań, Faculty of Chemistry, Umultowska 89b, 61-614 Poznań, Poland

*Corresponding author

E-mail: pietrasz@amu.edu.pl

Abstract

New carbamato-κ*N*-benzylidene ruthenium chelates were synthesized from the first [$RuCl_2(PCy_3)_2$(=CHPh)] and second [$RuCl_2$(SIMes)(PCy_3)(=CHPh)] generation Grubbs catalysts by metathetic exchange of benzylidene ligand for *tert*-butyl (2-vinylphenyl)carbamates bearing benzylidene ligand substituted in the position *para* to carbamato functionality with methyl or trifluoromethyl group. In all metathetical transformations tested, i.e. in ROMP of cycloocta-1,5-diene, RCM of diethyl diallylmalonate and diethyl 2-allyl-2-(2-methylallyl)malonate and cross-metathesis of allylbenzene with Z-1,4-diacetoxybut-2-ene, the complexes behave like latent catalysts. Complexes remain completely inactive until they are activated by the addition of ethereal solution of HCl. The presence of the electron-withdrawing group results in a slight increase in the catalytic activity of the activated form of the catalyst relative to a similar form of the unsubstituted complex or the least active complex carrying the electron donating group.

1. Introduction

Olefin metathesis is nowadays a widely used method for the formation of carbon–carbon double bonds [1, 2]. Over the last decades a great number of ruthenium-based catalysts designed for special applications have been developed. The availability of well-defined ruthenium alkylidene catalysts which tolerate moisture, oxygen and a variety of functional groups has significantly expanded the applications of olefin metathesis, thus the reaction has become particularly useful in organic and polymer synthesis [1-3]. One of the challenges in the catalysis of metathesis is to design catalysts permitting the control of the initiation step. Such catalysts are particularly useful in the ring opening metathesis polymerization. Therefore, one of the most intensively studied groups of well-defined metathesis initiators are latent catalysts (Figure 1) [4]. They exhibit no activity under standard conditions and can be easily activated by thermal, chemical or photochemical methods [4].

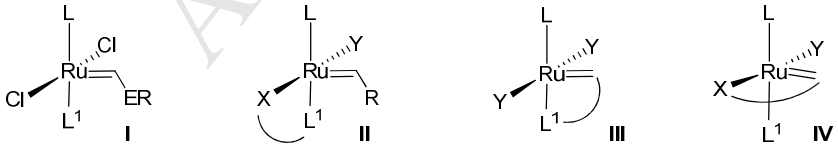


Figure 1. Types of latent catalysts of olefin metathesis [4]

From among numerous examples of latent catalysts, those representing structural motif IV (Figure 1) are relatively rare. The known examples include benzylidenecarboxylates, [5] nitronate complexes [6] and aryloxybenzylidene complexes [7-11].

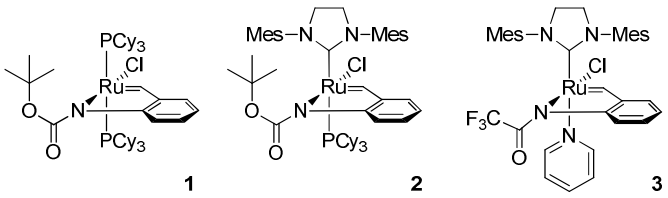
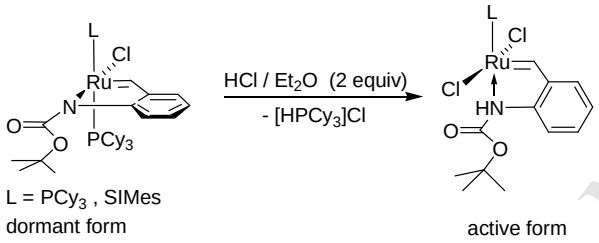


Figure 2. Known carbamato-benzylidene complexes (**1**-**2**) and related amido-benzylidene complex (**3**) [12]

In cooperation with Karol Grela group, we have reported the first examples of carbamato- and amido-benzylidene ruthenium chelates (**1**-**3**, Figure 2), which represent structural motif IV (Figure 1) [12]. Recently, the mechanism of activation of carbamato-benzylidene ruthenium catalysts **1** and **2** in the presence of HCl has been proposed [13].

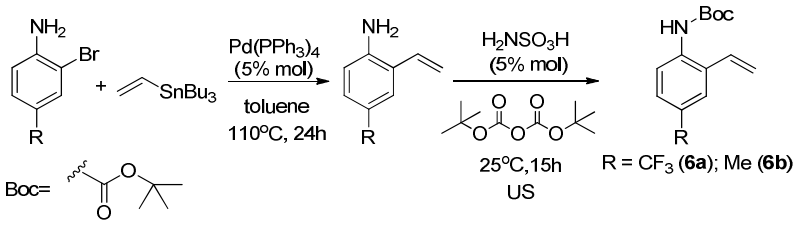


Scheme 1. Activation of carbamato-benzylidene ruthenium chelates [13]

Herein, we report new carbamato-benzylidene ruthenium chelates bearing benzylidene ligand substituted in the position *para* to carbamato group and their catalytic performance in olefin metathesis.

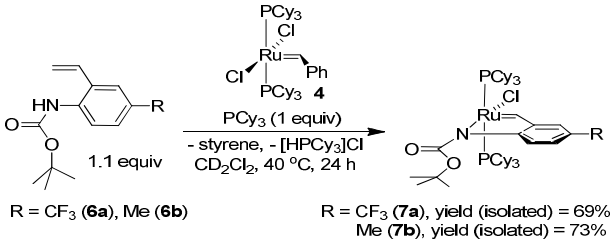
2. Results and discussion

Syntheses of the benzylidene ligand precursors, i.e. (2-vinylphenyl)carbamates were accomplished via a modified two-step literature procedure [14, 15]. Commercially available substituted 2-bromoanilines were reacted with 1 equiv. of tributyl(vinyl)tin in the presence of $[Pd(PPh_3)_4]$ (5 mol%) at 110 °C to form of 4-substituted vinylanilines, which were then subjected to *N*-*tert*-butoxycarbonylation under ultrasound irradiation to give **6a** and **6b** in 60 % and 72 % of overall yield (Scheme 2).

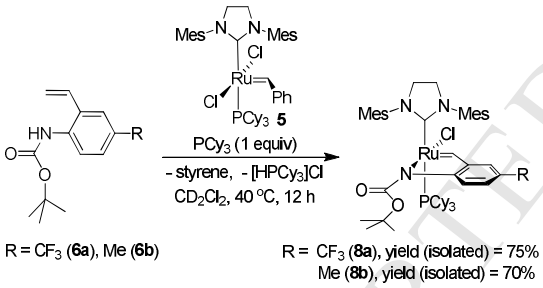


Scheme 2. Synthesis of precursors of benzylidene ligands

New carbamato-benzylidene complexes were synthesized by using the previously described methodology [12], i.e. in the reaction of the first [$RuCl_2(PCy_3)_2$(=CHPh)] (**4**) or second generation Grubbs catalyst [$RuCl_2$(SIMes)(PCy_3)(=CHPh)] (**5**) with substituted *tert*-butyl (2-vinylphenyl)carbamate (Schemes 3 and 4).



Scheme 3. Synthesis of complexes **7a** and **7b**.



Scheme 4. Synthesis of complexes **8a** and **8b**.

Complexes were synthesized in high yields and characterized spectroscopically (see the supplementary information). Moreover, the structures of complexes **8a** and **8b** were confirmed by X-ray structural analysis. Figure 3 shows the perspective views of complexes **8a** and **8b**, respectively. The geometrical features of both molecules are similar (see Figure S1 in supplementary material). This, together with the same level of similarity with the structure of the previously reported compound **2** [12] seems to support a high level of structural rigidity within this class of complexes. The Ru cations are five-coordinated, with the geometry close to that of tetragonal pyramid with double-bonded C7A atom in the apical position (see the supplementary information for the relevant geometrical details). The τ parameter ($\tau = (\beta - \alpha)/60$, where: $\beta > \alpha$ are the two greatest valence angles of the coordination center [16]) which

takes values in the range from 0 for the ideal tetragonal pyramid to 1 for a trigonal bipyramid, equals 0 for complex **8a** and 0.08 for complex **8b**. The Ru-C7A bond lengths determined clearly prove the double character of the ruthenium-carbon bond.

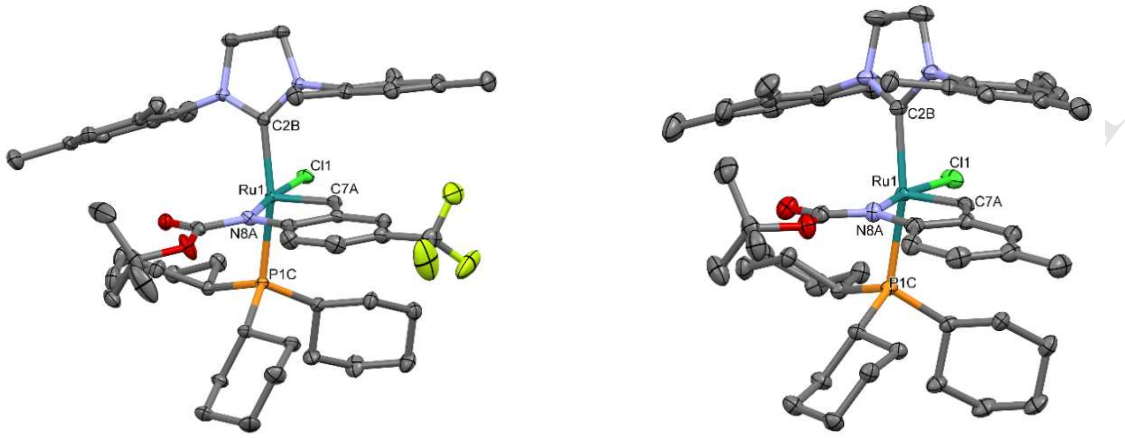


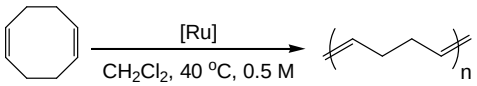
Figure 3. Perspective view of the complexes **8a** (left) and **8b** (right); ellipsoids are drawn at the 33 % probability level, hydrogen atoms are omitted for clarity.

Our preliminary studies have shown the activation effect of addition of ethereal solution of HCl on the catalytic activity of catalysts **1** and **2** [12]. Further experiments revealed that the ruthenium carbamato-benzylidene chelates can be also activated by other Brønsted and Lewis acids such as CF_3COOH or $BClR_2$ (where R = bicyclo[2.2.1]-2-heptyl) [13]. Ethereal solution of HCl was selected for further studies due to its high activating efficiency confirmed in the previously reported experiments [13]. Twofold molar excess of HCl in relation to the catalysts was found to be the most beneficial for both catalysts **1** and **2** (Figures S2 and S3, the supplementary information). Further increase in the [HCl] / [cat.] ratio did not lead to any improvement in the reaction efficiency.

The catalytic activity of complexes **7a**,**b** and **8a**,**b** as well as their unsubstituted analogues **1** and **2** was explored in selected metathetic transformations, i.e. in ring-closing metathesis (RCM) of diethyl diallylmalonate, cross-metathesis (CM) of allylbenzene with Z-1,4-diacetoxybut-2-ene and ROMP of cod with the use of ethereal solution of HCl as an activating agent. The reactions proposed are known as standard tests for evaluation of the catalytic activity of metathesis initiators [17].

Since the latent nature of the catalyst is particularly attractive for ring opening metathesis polymerization we started our catalytic investigation from (ROMP) of 1,5-cyclooctadiene. The results observed (Scheme 5 and Figure 4) confirmed that all tested carbamato-benzylidene complexes behaved like latent catalysts. Complete catalytic inactivity

of all complexes tested in ring-opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene (cod) was observed in dormant forms, while the addition of the activator resulted in a significant increase in the catalytic activity. As expected, the complexes bearing NHC ligand showed a considerably higher catalytic activities. Experiment showed slight effect of the substituent in the para position to the carbamato functionality on the catalytic performance.



Scheme 5. ROMP of cod.

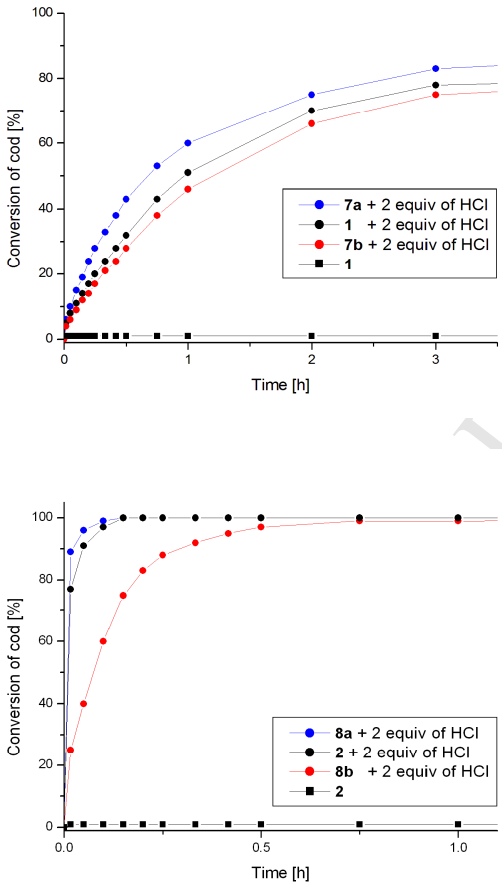
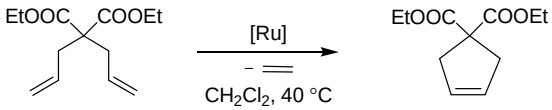


Figure 4. ROMP of cod in the presence of complexes **1**, **7a**, **7b** (top) and **2**, **8a**, **8b** (bottom). Effect of addition of HCl/Et_2O on the reaction course. Reaction conditions: CH_2Cl_2; 40 °C; Ru : HCl = 1 : 2; 0.5 M; 0.5 mol% [Ru] for cat. **1**, **7a**, **7b**; 0.01 mol% of [Ru] for cat. **2**, **8a**, **8b**. For clarity, only representative profiles for non-activated catalysts are presented.

Figure 5 summarizes the results of the study of catalytic performance of synthesized complexes in ring-closing metathesis (RCM) of diethyl diallylmalonate (Scheme 6).



Scheme 6. RCM of diethyl diallylmalonate

Complexes **1**, **7a** and **7b** remain inactive in the absence of activator and their activity was dramatically increased after addition of HCl/Et_2O. The catalysts **2**, **8a** and **8b**, bearing N-heterocyclic carbene ligand, exhibit limited activity in their dormant forms. When activator was used, complete conversions of the substrate was observed after 30 min of the reaction run.

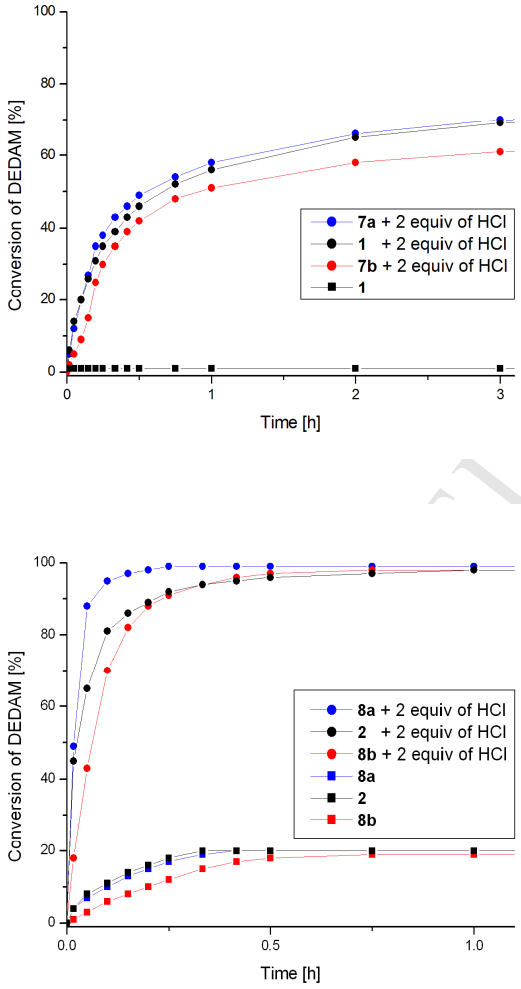
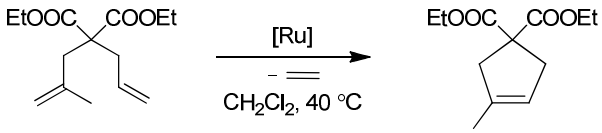


Figure 5. RCM of DEDAM in the presence of complexes **1**, **7a**, **7b** (top) and **2**, **8a**, **8b** (bottom). Effect of HCl/Et_2O addition on the reaction course. Reaction conditions: CH_2Cl_2; 40 °C, [Ru] : [HCl] = 1 : 2; 0.1 mol% of [Ru]; 0.1 M.

RCM of sterically hindered diethyl 2,2-bis(2-methylallyl)malonate proceeded very slowly (see Figure S4, the supplementary information). After 24 h of the reaction course (CH_2Cl_2; 40

°C; 5 mol% of [Ru]; 0.1 M) the conversion did not exceed 20 % in the presence of each of the catalyst tested.

Because it was previously shown that complex **2** (activated with HCl) efficiently catalyzed RCM of diethyl 2-allyl-2-(2-methylallyl)malonate (Scheme 7) [12], this reaction was selected to compare the activity of catalyst **2** with that of complexes **8a** and **8b**.



Scheme 7. RCM of diethyl 2-allyl-2-(2-methylallyl)malonate

The results obtained show the lack of activity of the non-activated form of complexes and a rapid increase in activity after treatment with ethereal solution of HCl (Figure 6).

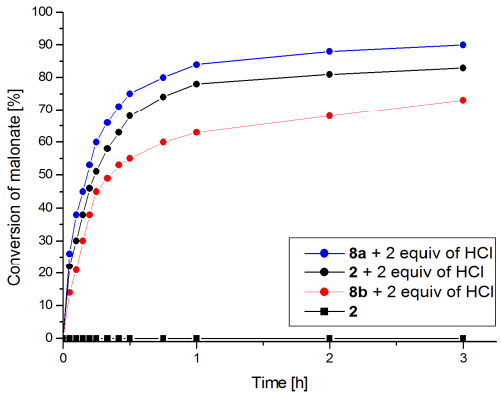
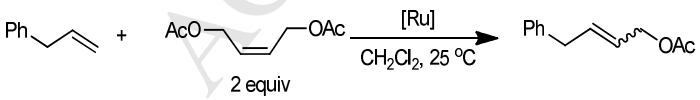


Figure 6. RCM of diethyl 2-allyl-2-(2-methylallyl)malonate in the presence of complexes **2**, **8a** and **8b**. Effect of addition of HCl/Et_2O on the reaction course. Reaction conditions: CH_2Cl_2; 40 °C, [Ru] : [HCl] = 1 : 2; 0.1 mol% of [Ru]; 0.1 M. For clarity, only one representative profile for non-activated catalysts is presented.

Carbamato-benzylidene chelates showed also the latent nature in the cross-metathesis of allylbenzene with Z-1,4-diacetoxybut-2-ene (Scheme 8).



Scheme 8. Cross-metathesis of allylbenzene with Z-1,4-diacetoxybut-2-ene

In the absence of the activating agent the complexes remained inactive, while a drastic increase in the catalytic activity was observed after addition of HCl/Et_2O (Figure 7).

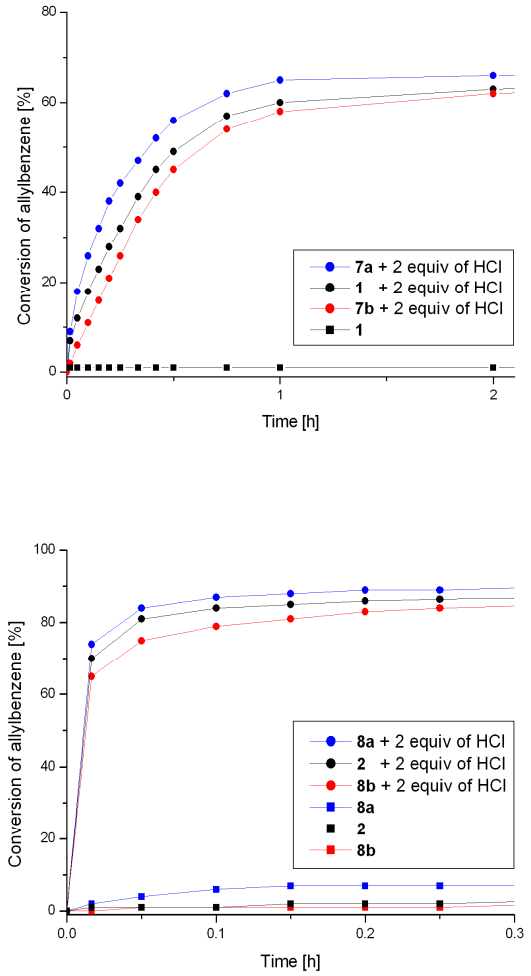


Figure 7. CM of allylbenzene with Z-1,4-diacetoxybut-2-ene in the presence of complexes **1**, **7a**, **7b** (top) and **2**, **8a**, **8b** (bottom). Effect of HCl/Et_2O addition on the reaction course. Reaction conditions: CH_2Cl_2; 40 °C, Ru : HCl = 1 : 2; 1 mol% of [Ru]. For clarity, only one representative profile for non-activated catalysts is presented in Figure 7a.

No significant differences in the catalytic activity were observed between the complexes that differed in the nature of substituents at the phenyl ring of chelating ligand. The effect of the nature of functional group in the benzylidene ligand on the catalytic activity is qualitatively similar but much less pronounced than that observed for the Hoveyda-Grubbs catalysts. In any case, the presence of an electron-withdrawing trifluoromethyl group resulted in a slight increase in the catalytic activity of the complex as compared to that of the analogue containing no substituent. The presence of a methyl group resulted in a slight reduction in the catalytic activity. A reasonable explanation seems to be analogous to that proposed for Hoveyda-Grubbs catalyst substituted in position 5 of benzylidene ligand [18]. Electron-withdrawing group reduces the electron density at ruthenium in the activated form of the catalyst (Scheme 1), thereby increasing the initiation rate. Analogously, the presence of the

electron-donating group increases the electron density at ruthenium and decreases the rate of initiation.

3. Conclusions

The synthesis of carbamato-κ*N*-benzylidene ruthenium chelates has been reported. Complexes behave like latent catalysts of olefin metathesis. They exhibit no or nearly no catalytic activity until treated with ethereal solution of HCl. In the activated form complexes efficiently catalyze a set of metathesis transformations. The activating effect of the electron-withdrawing group in benzylidene ligand in *para* position to carbamato functionality on catalytic performance has been demonstrated.

4. Experimental section

4.1. General methods and chemicals

Unless otherwise indicated, all operations were performed by using standard Schlenk techniques. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian 400 operating at 402.6 and 101.2 MHz, respectively. ^{31}P NMR spectra were recorded on a Mercury 300 operating at 121.5 MHz. GC analyses were carried out on a Bruker Scion 436-GC (column: DB-5 30 m I.D. 0.53 mm) equipped with TCD. Mass spectrometry analyses were performed using Synapt G2-S mass spectrometer (Waters) equipped with the Electrospray ion source and quadrupole-Time-of-flight mass analyzer. Acetonitrile was used as a solvent. The measurement was performed in positive ion mode with the desolvation gas flow 200 L/h and capillary voltage set to 5000 V with the flow rate 20 µL/min. The chemicals were obtained from the following sources: first and second generation Grubbs' catalyst, dichloromethane, n-hexane, dichloromethane-d_2, benzene-d_6, anthracene, decane, calcium hydride, diethyl diallyl malonate, 1,5-cyclooctadiene, allylbenzene, Z-1,4-bis(acetoxy)but-2-ene, HCl in Et_2O (2 M) tricyclohexylphosphine and calcium hydride were obtained from Aldrich. Vinyl ethyl ether was obtained from Chempur. All solvents were dried prior to use over CaH_2 and stored under argon. CH_2Cl_2 was additionally passed through a column with alumina and after that it was degassed by repeated freeze-pump-thaw cycles.

4.2. Synthesis of complexes

Synthesis of **7**. Schlenk flask (20 mL) equipped with a magnetic stirring bar was charged under argon with [$RuCl_2(PCy_3)_2$(=CHPh)] (0.1 g, 1.22×10^{-4} mol), 8 mL of dichloromethane, 1.22×10^{-4} mol of tert-butyl 5-trifluoromethyl-2-vinylphenylcarbamate (or 5-methyl derivative) and 0.034 g (1.22×10^{-4} mol) of PCy_3. The mixture was stirred and heated in an oil bath at 40 ºC for 24 h. After this time the solvent was evaporated and the resulting green solid was treated with 4×5 mL of pentane. The green pentane solution was transferred to another Schlenk flask. The solvent was evaporated to dryness and the green solid was washed with cold (-30 ºC) acetone. The precipitate was filtered off and dried under vacuum.

Complex **7a**. Green, microcrystalline crystals, isolated yield = 69 %. Spectroscopic characterization: ^{1}H NMR (C_6D_6; δ (ppm)): 17.23 (s, 1H, Ru=CH); 8.33 (d, 1H, J = 9.1Hz, Ar); 7.87 (d, 1H, Ar); 7.58 (dd, 1H, J = 9.0, 2.0 Hz, Ar), 2.35-0.95 (m, 66H, PCy_3), 1.64 (s, 9H, tBu); ^{13}C NMR (C_6D_6; δ(ppm)): 282.4, 160.6, 159.3, 146.6, 125.3, 118.4, 118.1 (m), 79.3, 33.7 (t, J = 9.1 Hz), 29.9, 29.5, 28.5, 28.0 (t, J = 5.4 Hz), 27.7 (t, J = 4.6 Hz), 26.4; ^{31}P NMR (C_6D_6; δ (ppm)) δ: 38.40 (s, PCy_3); HRMS (ESI): calc: 934.4582; found: 934.4589.

Complex **7b**. Green, microcrystalline crystals, isolated yield = 73 %. Spectroscopic characterization: ^{1}H NMR (C_6D_6; δ(ppm)): 17.30 (s, 1H, Ru=CH); 8.42 (d, 1H, J = 8.7 Hz, Ar); 7.38 (s, 1H, Ar); 7.31 (dd, 1H, J = 9.0, 2.0 Hz, Ar), 2.48-1.18 (m, 66H, PCy_3), 2.35 (s, 3H, Ar-Me), 1.79 (s, 9H, tBu); ^{13}C NMR (C_6D_6; δ(ppm)): 283.6, 159.7, 157.4, 148.4, 130.6, 126.7, 121.6, 119.2, 34.19 (t, J = 8.4 Hz), 30.3, 30.0, 29.2, 28.5, 28.2, 26.9; ^{31}P NMR (C_6D_6; δ(ppm)): 38.25 (s, PCy_3); HRMS (ESI): calc: 880.4864; found: 880.4855;

Synthesis of **8**. Schlenk flask (20 mL) equipped with a magnetic stirring bar was charged under argon with [$RuCl_2(PCy_3)$(SIMes)(=CHPh)] (0.1 g, 1.18×10^{-4} mol), 6 mL of CH_2Cl_2, (2.28×10^{-4} mol) of tert-butyl 5-trifluoromethyl-2-vinylphenylcarbamate (or 5-methyl derivative) and 0.032 g (1.18×10^{-4} mol) of PCy_3. The mixture was stirred at 40 ºC for 12 h. After this time the solvent was evaporated and the residue was extracted with 3×5 mL of pentane. The green solution was transferred via cannula to another Schlenk flask and evaporated to dryness. The complex was purified by column chromatography over silica gel (60 mesh) using n-hexane/ethyl acetate (25/1) as an eluent. Single crystal was obtained by slow evaporation from cold (0 ºC) pentane solution.

Complex **8a**. Green, microcrystalline crystals, isolated yield = 75 %. Spectroscopic characterization: ^{1}H NMR (C_6D_6; ppm) δ: 16.49 (s, 1H, Ru=CH); 8.32 (d, 1H, J = 9.0Hz, Ar-NBoc); 7.57(dd, 1H, J = 9.0 Hz, J = 2.2 Hz, Ar); 7.25 (s, 1H, Ar); 7.21(s, 1H, Ar); 7.10 (m, 1H, Ar); 6.15 (s, 1H, Ar); 6.72 (s, 1H, ArNBoc); 6.15 (s, 1H, Ar-NBoc); 3.41-3.05 (m, 4H NCH_2CH_2N); 2.95 (s, 3H, Mes CH_3); 2.73(s, 3H, Mes CH_3); 2.65 (s, 3H, Mes CH_3); 2.35(s, 3H, Mes CH_3); 2.25(s, 3H, Mes CH_3); 1.73 (s, 9H, OtBu); 1.42 (s, 3H, Mes CH_3); 2.0-0.9 (m, 33H, PCy_3); ^{13}C NMR (C_6D_6; δ(ppm)):220.6; 159.6; 158.9; 145.7; 139.3; 138.9; 137.6; 136.1; 130.3; 129.7; 128.0; 124.7; 118.3; 78.9; 52.0; 51.2; 33.4; 31.7; 29.7; 29.6; 29.2; 28.4; 27.7; 26.6; 25.6; 21.3; 20.8; 20.1; 19.2; 17.1; 31P NMR (C_6D_6; ppm) δ: 34.22 (s, PCy_3); HRMS (ESI): calc: 995.4046; found: 995.4039.

Complex **8b**. Green, microcrystalline crystals, isolated yield = 70 %. Spectroscopic characterization: ^{1}H NMR (C_6D_6; ppm) δ: 16.38 (s, 1H, Ru=CH); 8.19 (d, J = 8.6 Hz, 1H, Ar-NBoc); 7.25-7.09 (m, 2H, Ar); 7.00 (s, 1H, Ar); 6.71 (s, 1H, Ar); 6.54 (s, 1H, Ar-NBoc); 6.06 (s, 1H, Ar-NBoc); 3.43-3.03 (m, 4H, NCH_2CH_2N); 2.93 (s, 3H, Mes CH_3); 2.72 (s, 3H, Mes CH_3); 2.66 (s, 3H, Mes CH_3); 2.34 (s, 3H, Mes CH_3); 2.29 (s, 3H, Mes CH_3); 2.08 (s, 3H, Mes CH_3); 1.72 (s,9H,OtBu); 2.23-1.0 (m, 33H, PCy_3); ^{13}C NMR: (C_6D_6; ppm) δ: 284,8; 222,4; 221,7; 159.9; 155,5; 147.3; 139.6; 138.9; 137.6; 137.4; 136.9; 130.2; 129.9; 128.0; 124.9; 121.4; 118.5; 77.9; 51.6; 33.5; 29.8; 29.7; 29.5; 28.5; 26.7; 25.5; 21.3; 20.3; 19.3; 17.3; ^{31}P NMR (C_6D_6; ppm) δ: 33.67 (s, PCy_3); HRMS (ESI): calc: 941.4329; found: 941.4335.

4.3. Procedures for the catalytic tests

ROMP of 1,5-cyclooctadiene. An oven dried 5 mL glass reactor equipped with a condenser and magnetic stirring bar was charged under argon with 2 mL of CH_2Cl_2, 100 μL of cyclooctadiene (8.04×10^{-4} mol) and 80 μL of dodecane (internal standard). The reaction mixture was placed in an oil bath and preheated at 40 ºC. Then (4.02×10^{-6} mol) of **7** or (8.04×10^{-8} mol) of **8** and 4 μL (8.04×10^{-6} mol) of HCl in Et_2O (2 M) (for cat. **7**) or 0.08 μL (1.68×10^{-7} mol) (for cat **8**) were added under argon. The mixture was heated at 40 ºC under a gentle flow of argon. After a given reaction time, 30 μL of the reaction mixture was removed , placed in a 1 mL vial and quenched by the addition of 30 μL vinyl ethyl ether and analyzed by Gas Chromatography.

RCM of DEDAM. Glass reactor (5 mL) equipped with a condenser and magnetic stirring bar was charged under argon with 2.5 mL of CH_2Cl_2, 60 μL of diethyl diallyl malonate (2.55×10^{-4}

mol) and 20 μL of decane (internal standard). The reaction mixture was preheated in an oil bath at 40 °C. Then (2.55×10^{-7} mol) of catalyst was added under argon followed by 0.26 μL (5.07×10^{-7} mol) of HCl in Et_2O (2 M). The mixture was heated at 40 ºC under a gentle flow of argon. After a given reaction time 30 μL of the reaction mixture was taken, placed in a 1 mL vial and quenched by the addition of 30 μL vinyl ethyl ether and then analyzed by Gas Chromatography.

RCM of diethyl 2-allyl-2-(2-methylallyl)malonate. Glass reactor (5 mL) equipped with a condenser and magnetic stirring bar was charged under argon with 2.5 mL of CH_2Cl_2, 62 μL of diethyl 2-allyl-2-(2-methylallyl)malonate (2.55×10^{-4} mol) and 20 μL of decane (internal standard). The reaction mixture was preheated in an oil bath at 40 ºC. Then (2.55×10^{-7} mol) of **2**, **8a** or **8b** was added under argon followed by 0.26 μL (5.07×10^{-7} mol) of HCl in Et_2O (2 M) for diethyl 2-allyl-2-(2-methylallyl)malonate. The mixture was heated at 40ºC under a gentle flow of argon. After a given reaction time 30 μL of the reaction mixture was taken, placed in a 1 mL vial and quenched by the addition of 30 μL vinyl ethyl ether and then analyzed by Gas Chromatography.

CM of allylbenzene with Z-1,4-bis(acetoxy)but-2-ene. Glass reactor (5 mL) equipped with a condenser and magnetic stirring bar was charged under argon with 2 mL of CH_2Cl_2, 52 μL of allylbenzene (3.92×10^{-4} mol), 125 μL of Z-1,4-bis(acetoxy)but-2-ene (7.83×10^{-4} mol) and 40 μL of decane (internal standard). The reaction mixture was placed in an oil bath and preheated at 40ºC. Then (3.90×10^{-6} mol) of **7** or (3.9×10^{-7} mol) of **8** and 4.0 μL (7.8×10^{-6} mol) of HCl in Et_2O (2 M) (for cat **7**) or 0.4 μL (7.8×10^{-7} mol) (for cat **8**) were added under argon. The mixture was heated at 40 ºC under a gentle flow of argon. After a given reaction time 30 μL of the reaction mixture was removed, placed in a 1 mL vial and quenched by the addition of 15 μL vinyl ethyl ether and analyzed by Gas Chromatography. The conversion of the substrates was calculated using the internal standard method.

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Supplementary material

Supplementary data associated with this article: synthesis of benzylidene ligand precursors **6a** and **6b**, X-ray examinations details, crystal data, optimization of catalyst / activator ratio, comparison of activity of **2**, **8a** and **8b** in RCM of diethyl bis(methylallyl)malonate, NMR spectra of new complexes.

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- Ruthenium carbamate-benzylidene chelates are latent olefin metathesis catalysts
- Complexes exhibit high catalytic activity after activation with acids
- Substituents in benzylidene ring slightly affect the catalytic activity