Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Mechanism of activation of amidobenzylidene ruthenium chelates – latent catalysts of olefin metathesis

Szymon Rogalski, Patrycja Żak, Natalia Tadeuszyk, Krystian Pyta, Piotr Przybylski and Cezary Pietraszuk*

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

1. Optimization of catalyst / activator ratio

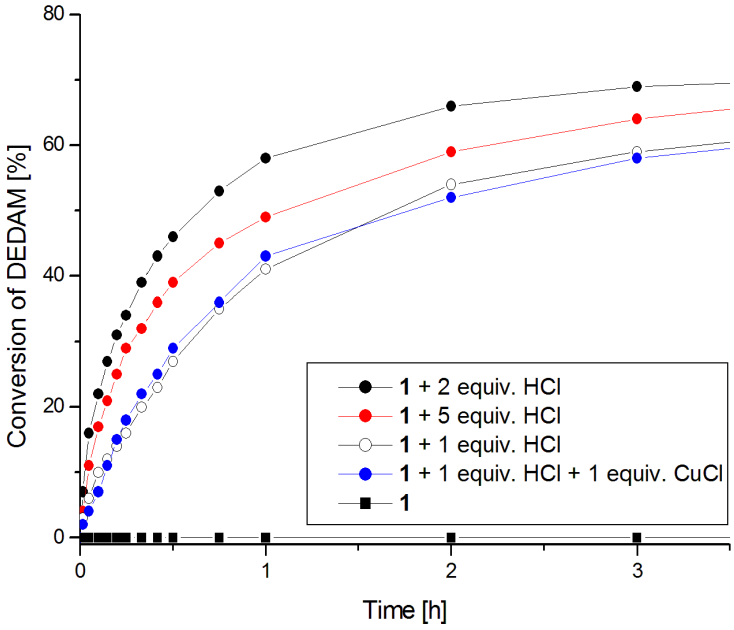


Figure S1. RCM of DEDAM. Activation of **1** with HCl (used in equimolar amounts and in excess). Activation of **1** by combined interaction with CuCl and HCl. Reaction conditions: CH_2Cl_2; 40 °C, 0.1 mol % of [Ru], 0.1 M.

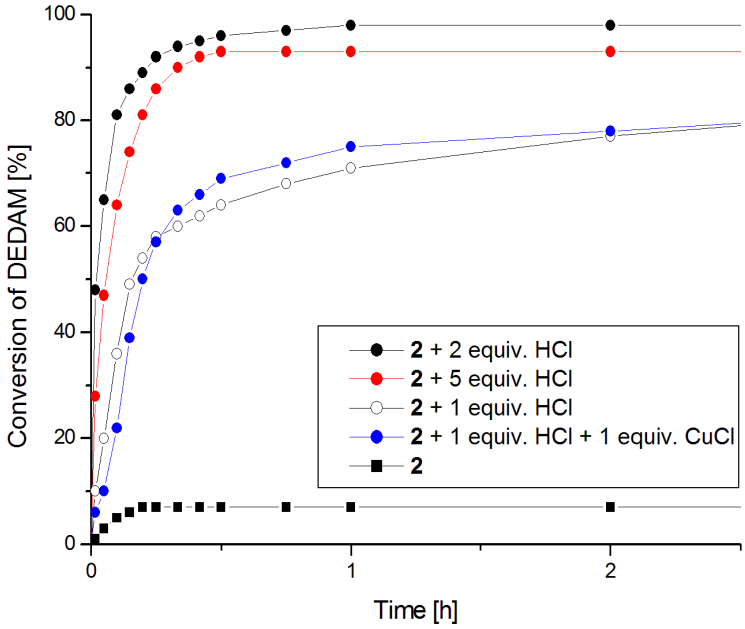
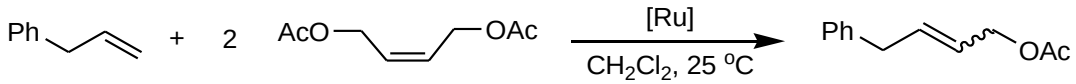


Figure S2. Activation of **2** with HCl (used in equimolar amounts and in excess). Activation of **2** by combined interaction with CuCl and HCl. Reaction conditions: CH_2Cl_2; 40 °C, 0.1 mol % of [Ru], 0.1 M.

2. The study of catalytic performance of catalysts 1 and 2 in cross-metathesis of allylbenzene with Z-1,4-bis(acetoxy)but-2-ene

Procedure for the catalytic tests. The 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, 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 to 40 ºC. Then 0.0035 g (3.9×10^{-6} mol) of **1** or 0.00036 g (3.9×10^{-7} mol) of **2** and 4.0 μL (7.8×10^{-6} mol) of HCl in Et_2O (2 M) (for cat. **1**) or 0.4 μL (7.8×10^{-7} mol) (for cat. **2**) 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 taken, 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.



Scheme S1. Cross-metathesis of allylbenzene with Z-1,4-bis(acetoxy)but-2-ene

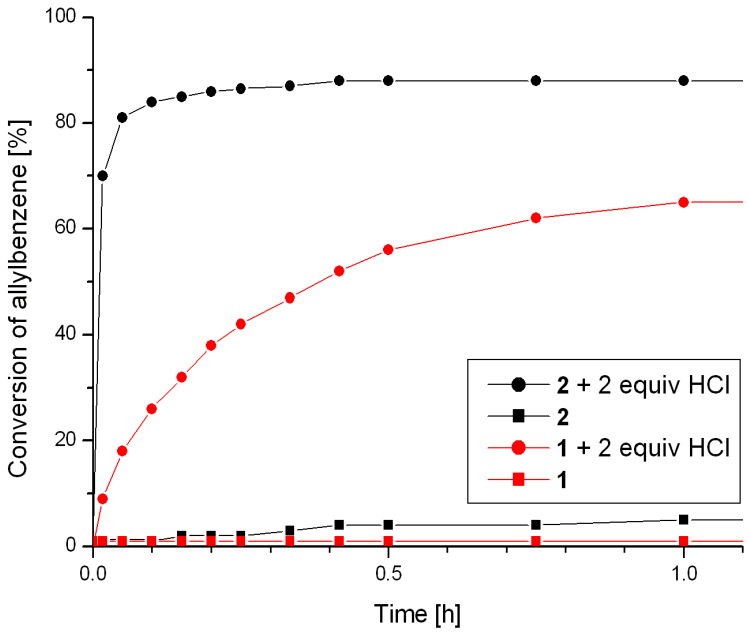


Figure S3. CM of allylbenzene with Z-1,4-bis(acetoxy)but-2-ene. Effect of addition of HCl/Et_2O on the reaction course. Reaction conditions: CH_2Cl_2; 40 °C, [Ru] : [HCl] = 1 : 2; 1 mol % of **1** related to allylbenzene; 0.1 mol % of **2** related to allylbenzene.

3. Complex 1 and 2 stability study

The 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 to 40 ºC. Then 0.0036 g (4.02×10^{-6} mol) of **1** or 0.000075 g (8.04×10^{-8} mol) of **2** was added and the mixture was heated at 40 °C under a gentle flow of argon for 1 h. After this time the reaction was analyzed by Gas Chromatography. Then 40 μL (8.04×10^{-6} mol) of HCl in Et_2O (2 M) (for cat. **1**) or 0.8 μL (1.61×10^{-7} mol) of HCl in Et_2O (for cat. **2**) were added. After a given reaction time 30 μL of the reaction mixture was taken, placed in a 1 mL vial, quenched by the addition of 30 μL vinyl ethyl ether and analyzed by Gas Chromatography.

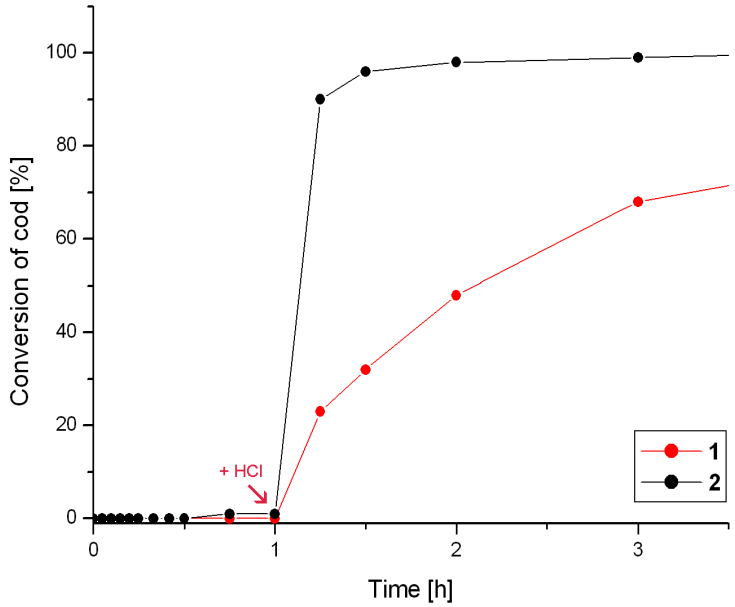


Figure S4. Complex **1** and **2** stability study in ROMP of cod and effect of addition of HCl/Et_2O on the reaction course. Reaction conditions: CH_2Cl_2; 40 °C, [Ru] : [HCl] = 1 : 2; 0.5 mol % of **1**; 0.01 mol % of **2**.

4. Control of ROMP of cod by switching on – switching off the active form of the catalyst

The 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 to 40 ºC. Then 0.0036 g (4.02×10^{-6} mol) of **1** or 0.000075 g (8.04×10^{-8} mol) of **2** was added and the mixture was heated at 40 °C under a gentle flow of argon for 1 h. Then 4 μL (8.04×10^{-6} mol) of HCl in Et_2O (2 M) (for cat. **1**) or 0.08 μL (1.61×10^{-7} mol) of HCl in Et_2O (for cat. **2**) were added under argon and the reaction was continued for another 1 h for cat. **1** and 0.5 h for cat. **2**. After this time 2 equivalents (0.0023 g for **1** and 0.000045 g for **2**) of PCy_3 in relation to Ru was added and the reaction mixture was heated for 1 h. Then another portion of HCl in Et_2O (2 M) 4 μL for cat. **1** or 0.08 μL for cat. **2** were added under argon and

the reaction was continued. After a given reaction time 30 µL of the reaction mixture was taken, placed in a 1 mL vial, quenched by the addition of 30 µL vinyl ethyl ether and analyzed by Gas Chromatography.

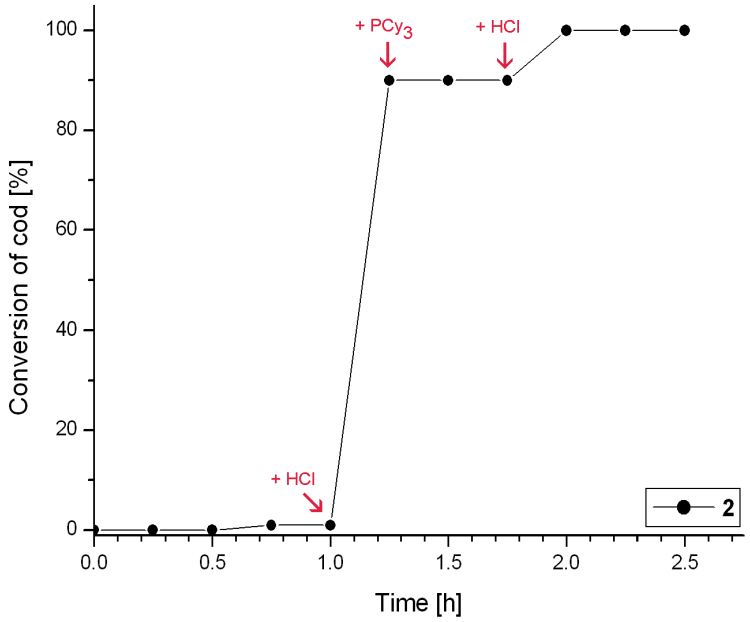


Figure S5. Control of ROMP of cod performed in the presence of catalyst **2.** Reaction conditions: [Ru] : [HCl] = 1 : 2; [Ru] : [PCy_3] = 1 : 2; 0.01 mol % of **2** relative to cod.

5. ^{1}H NMR spectra of activated catalyst generated *in situ*

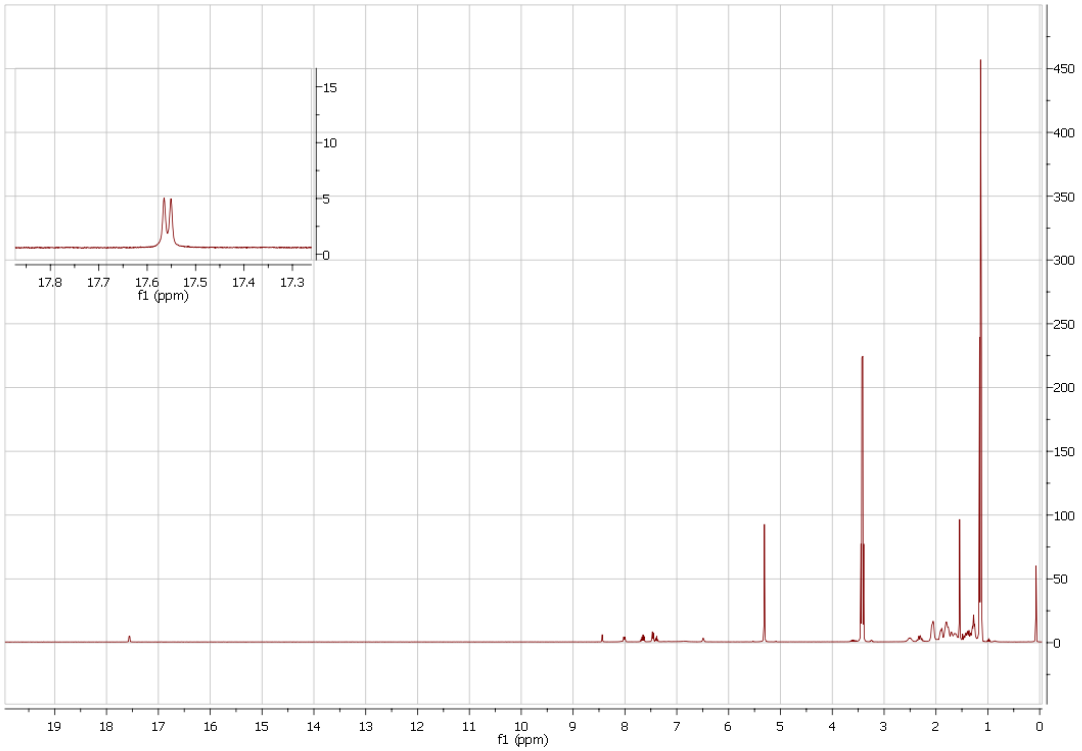


Figure S6. Treatment of **1** with 2 equiv of HCl (Et_2O solution). ^{1}H NMR spectrum of the reaction mixture. Reaction conditions: CH_2Cl_2; 22 °C, 5 min.

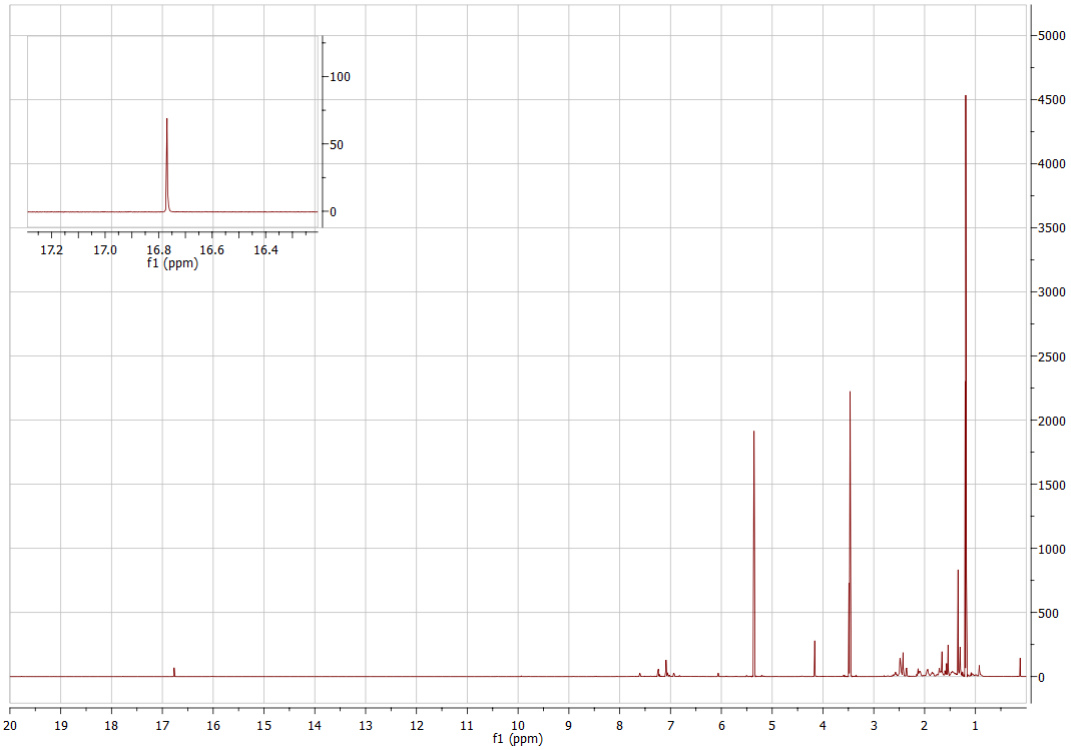


Figure S7. Treatment of **2** with 2 equiv of HCl (Et_2O solution). ^{1}H NMR spectrum of the reaction mixture. Reaction conditions: CH_2Cl_2; 22 °C, 5 min.

6. The preliminary studies of activation of catalyst 1 with $ClBR_2$.

According to Table 1 (entries 7 and 17) bis(bicyclo[2.2.1]-2-heptyl)chloroborane shows a similar activating effect on complexes **1** and **2** as hydrogen chloride. To get more insight into the activating effect of chloroborane[1] addition on the catalytic activity of amidobenzylidene complexes, complex **1** was reacted with two equivalents of $BClR_2$ (where R = bicyclo[2.2.1]-2-heptyl). The reaction was performed in a measuring cell in CH_2Cl_2 and monitored by FTIR. It was found that the addition of $BClR_2$ caused spectral changes similar to those noted in the spectrum of catalyst **4**, i.e. the appearance of ν(C=O) band at 1766 cm^{-1} and increase in its intensity, as well as a decrease in the intensity of ν(C=O) band at 1640 cm^{-1}. These bands indicate the formation of complex **4.** The results obtained are consistent with NMR experiments, in which addition of two equivalents of $BClR_2$ to the solution of **1** in CD_2Cl_2 revealed rapid formation of complex **4** (doublet at δ = 17.56 ppm, $J_{P,H}$ = 5.7 Hz) with the 62 % NMR yield.

7. Procedure for IR measurements

The FT-IR spectra of **1**, **2**, **1**+HCl, **2**+HCl and *tert*-butyl *N*-(2-ethenylphenyl)carbamate were recorded in the mid infrared region 4000-400 cm^{-1} in CH_2Cl_2 and CD_2Cl_2 solutions (0.1 mol L-1). A cell with Si windows and wedge-shaped layers was used to avoid interferences (mean layer thickness 170 μm) for measurements in solution. All spectra were taken with an Nicolet iS50 FT-IR spectrophotometer (Thermo Fisher Scientific, Madison, WI, USA) equipped with a DTGS detector; resolution 1 cm^{-1}, 128 scans. The Happ-Genzel apodization function was used. All manipulations with the samples analyzed were performed in argon atmosphere.

8. Procedure for DFT calculations

Structures of the activated complexes were calculated by DFT method - DGauss using the B88-LYP GGA energy functional with the DZVP basis sets (Scigress package version FJ. 2.4. EU 3.1.8. The initial model of **1**+HCl and **2**+HCl complexes were built on the basis of determined X-ray structures of non-activated complexes and then optimized via molecular mechanics with MO-MM3/Conflex method. The energetically the most favorable and initially optimized structures of **1**+HCl and **2**+HCl were at the next step optimized with DFT method - B88-LYP GGA energy functional with the DZVP basis sets with the energy gradient not exceeding 0.05 kcal mol^{-1} at one step. For the most favored **1**+HCl and **2**+HCl structures shown in Figures 5 and 6, characterized by the most negative change values of enthalpy of formation (ΔHf^{o}), the frequencies of ν(C=O) IR transitions were calculated by one of DFT methods - B88-LYP GGA energy functional with the DZVP basis sets Compute Engine FJ. 2.4 (EU 3.1.8), Fujitsu 2008-2015.

1 E. Vedrenne, H. Dupont, S. Oualef, L. Elkaïm, L. Grimaud, *Synlett*, 2005, 670–672.