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Improved preparation of an olefin metathesis catalyst bearing quaternary ammonium tag (FixCat) and its use in ethenolysis and macrocyclization reactions after immobilization on metal-organic framework (MOF)

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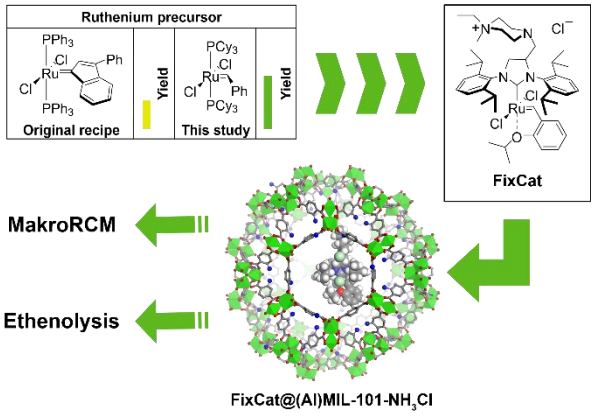
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Dedicated to Professor Zbigniew Czarnocki

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Abstract

An optimized synthesis of a key intermediate **Ru4** in substantially improved yield of 50% and in scale up to 1 gram was described. Such obtained **Ru4** was quantitatively converted into useful quaternary ammonium tagged catalyst **Ru1** (FixCat) and immobilized in a metal-organic framework (MOF). Next, two challenging applications, not studied previously with hybrid **Ru1**@MOF catalyst were attempted. In the case of the RCM reaction yielding a macrocyclic musk lactone, heterogeneous **Ru1**@MOF exhibited under high-dilution conditions high resistance towards unwanted C-C double bond migration, thus offering superior selectivity as compared to analogous homogeneous catalysts. In ethenolysis of ethyl oleate, **Ru1**@MOF exhibited only slightly better selectivity as compared to well-known general-purpose Hoveyda-Grubbs SIMes and SIPr catalysts, while it was not able to challenge the benchmark Bertrand-Hoveyda-Grubbs catalyst in this transformation.



Keywords: olefin metathesis, ruthenium, metal-organic framework (MOF), immobilization, ethenolysis, macrocyclization

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Introduction

Olefin metathesis is a modern catalytic transformation that allows for effective formation of C–C double bonds.[1,2] Therefore, this Nobel-prize winning methodology has emerged as one of the most powerful chemical transformations available to synthetic organic chemists.[3-5] The success of this transformation is mostly due to the discovery of ruthenium, tungsten and molybdenum catalysts. From this successful family, Ru-carbene catalysts are of particular interest, as they combine good catalytic activity with excellent compatibility with a wide number of functional groups, including polar ones. Good air and moisture stability of Ru-catalysts led eventually to development of water soluble catalysts for aqueous metathesis.[6-8] One of the possible ways to make a ruthenium carbene water soluble (or at least *more polar*) is the application of specially designed tags.[9] Among the proposed catalyst architectures, complexes containing "-onium" groups (e.g. quaternary ammonium groups) installed in the backbone of so-called N-heterocyclic carbene (NHC) ligand (Figure 1) gained some popularity and are nowadays commercially available.[10,11]

"Instant" immobilization of a ruthenium complex on various supports to form stable heterogeneous catalysts is another interesting possibility associated with the presence of a polar ammonium tag.[12] In this context polar (but water insoluble) catalyst FixCat (**Ru1**) developed by Skowerski *et al*.[13] was supported on materials such as SBA-15[14] or 13X molecular sieves.[15] Recently, we have developed hybrid metalo-organic systems, where FixCat was immobilized on selected metal-organic frameworks (MOF).[16,17] Such hybrid FixCat@MOF catalysts exhibit several desirable features, such as (*i*) relatively straightforward preparation consisting of simply mixing of a tagged catalyst and a solid MOF, (*ii*) high degree of tunability and modularity, (*iii*) compatibility with environmentally friendly solvents such as ethyl acetate, (*iv*) simple and effective removal of the ruthenium contamination by filtration. One of the most effective metal-organic supports used by us in this context was aluminum MOF—(Al)MIL-101-NH_3Cl.[15]

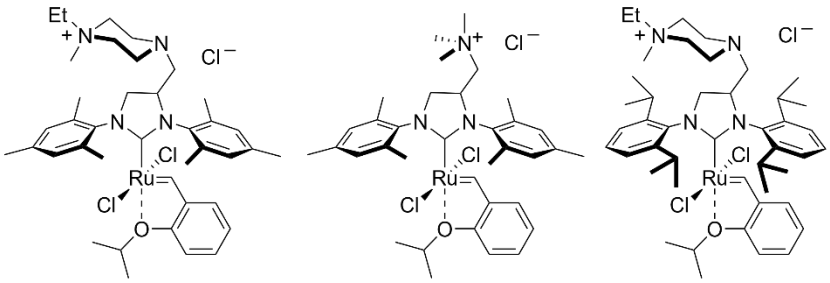


Figure 1. Selected ruthenium-based complexes bearing quaternary ammonium tags.

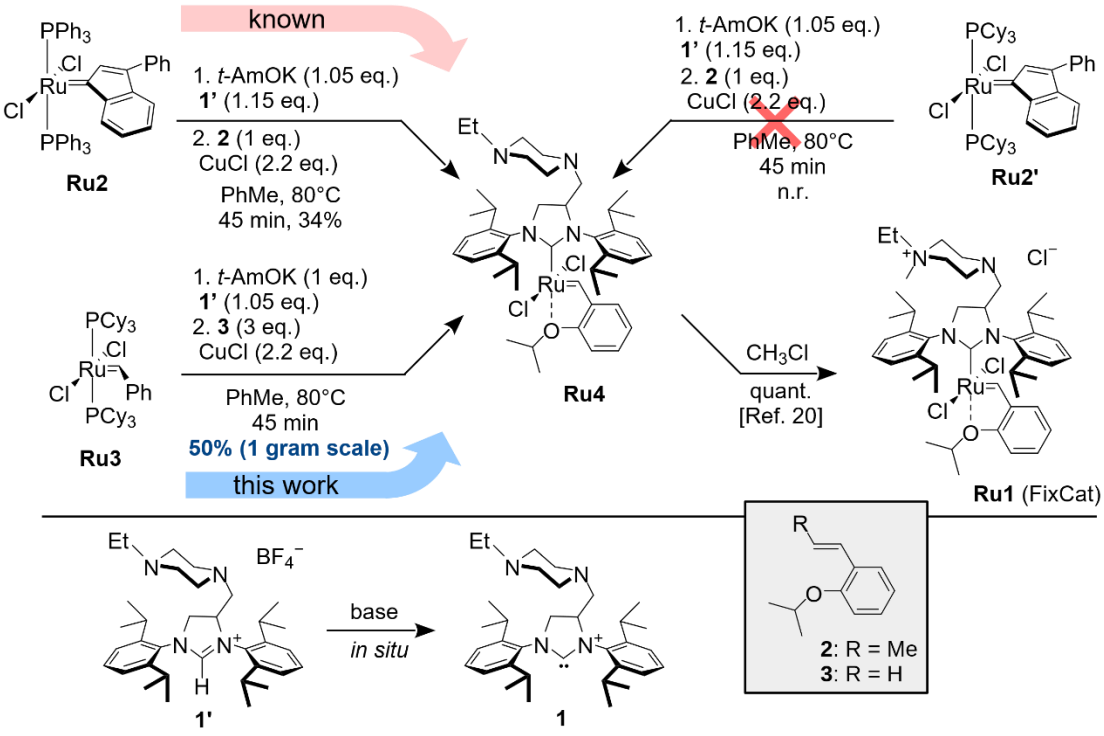
Results and Discussion

Optimized alternative synthesis of Ru1

To continue our research on MOF immobilized Ru catalysts, we needed an independent access to larger quantities of **Ru1**. To do so, we attempted to reproduce its synthesis published by Skowerski *et al*.[13] This procedure consists of a multi-step one-pot reaction between *in situ* generated free carbene **1** with ruthenium precursor **Ru2** in a presence of styrene derivative **2** (Scheme 1). While in our hands the original recipe worked, some inconveniences were noted during its scale up. Firstly, the obtained yields were always below 40%,

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which we considered to be unsatisfactory. Secondly, the precursor used originally by Skowerski—triphenylphospine complex **Ru2**—is no longer commercially available. While this material can be obtained in the known reaction of $RuCl_2(PPh_3)_3$ and 1,1-diphenyl-2-propyn-1-ol,[18,19] we noted some problems during purification of the product to the sufficient grade. In addition, we observed partial degradation of **Ru2** within several weeks after its synthesis. To overcome this, we decided to replace triphenylphospine (PPh_3) ligands in **Ru2** with tricyclohexylphospine (PCy_3) ones, which are known to give a more stable ruthenium indenylidene complex (**Ru2'**). To our surprise, however, such complex was completely inactive as the precursor in the above multi-component reaction leading to **Ru4**. Interestingly, despite many attempts we were unable to force this reaction to work, as we were not able to isolate or observe any form of ruthenium complex containing tagged NHC ligand **1**. Unfortunately, the reasons of this failure are not clear to us. Facing the risk of a possible dead-end, we decided to switch to a substrate belonging to another class of complexes that can be used as ruthenium precursors—to Grubbs benzylidene I-generation catalyst (**Ru3**). In this case, gratifyingly, even the first exploratory trial gave the expected product **Ru4** with yield similar to the one reported previously by Skowerski.[13] Further optimization experiments showed that replacing 1-isopropoxy-2-(prop-2-en-1-yl)benzene (**2**) with 1-isopropoxy-2-vinylbenzene (**3**) and manipulation the stoichiometry of the reaction gave the desired intermediate **Ru4** in improved yield of 50% (Scheme 1). Worthy of note, the above procedure can be scaled up to 1 gram, producing **Ru4** in fully reproducible yield. Next, the previously described[20] alkylation of **Ru4** with methyl chloride in a pressurized reactor give us the desired catalyst **Ru1** in quantitative yield (Scheme 1).

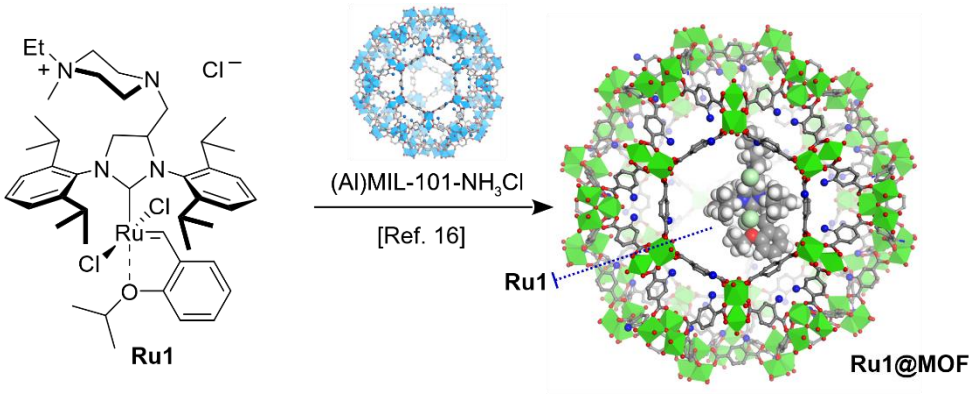


Scheme 1. Comparison of selected synthetic pathways leading to FixCat intermediate **Ru4**.

Immobilization of Ru1 on MOF and two exemplary applications of the obtained hybrid catalyst

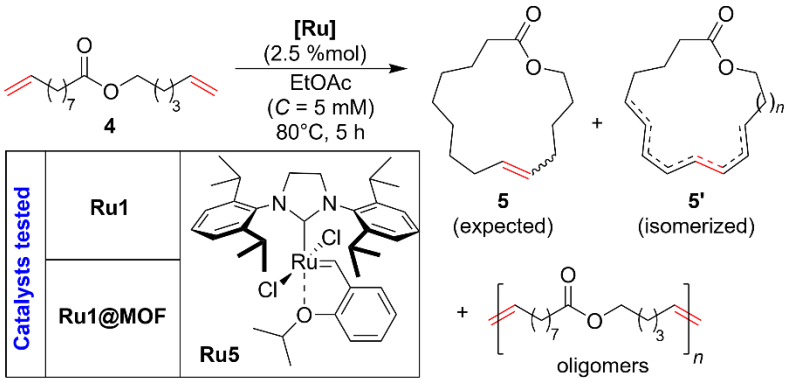
Using a previously described procedure,[16] tagged complex **Ru1** was absorbed in solid (Al)MIL-101-NH_3Cl from a dichloromethane (DCM) solution (Scheme 2). The resulted material contained 2.5 wt.% of **Ru1** inside MOF, which equals 1 catalyst molecule per four cages of MOF.[16]

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Scheme 2. Preparation of Ru1@MOF hybrid material.

Previously, the (Al)MIL-101-NH_3Cl–ruthenium hybrid system has been used only in a few simple model metathesis transformations[16] and in reactive distillation.[21] In the present research, we selected two transformations that are considered very challenging in the context of olefin metathesis. To the best of our knowledge, none of them has been tested with Ru@MOF catalytic systems.



Scheme 3. Formation of 15-membered macrocyclic lactone **5** from hex-5-en-1-yl dec-9-enoate (**4**).

Macrocyclisation by RCM

First, the ring-closing metathesis (RCM) cyclisation of hex-5-en-1-yl dec-9-enoate (**4**) leading to macrocyclic lactone **5**—a valuable musk fragrance[22]—was tried (Scheme 3). Dienes like hex-5-en-1-yl dec-9-enoate (**4**) are known to undergo spontaneous C-C double bond migration ("isomerization") during the metathesis reaction course. This undesirable parasitic process was for the first time noted by Fürstner,[23] and later confirmed by numerous reports.[24,25] We decided to check if **Ru1**@MOF material, where the catalyst molecules are distributed between separate voids present inside a MOF framework,[16] thus mimicking catalysis in confined spaces,[26] can increase the selectivity of the RCM reaction towards cyclic not-isomerized product **5**. To do so, in an exploratory experiments **Ru1** immobilized in (Al)MIL-101-NH_3Cl was reacted with **4** dissolved in EtOAc (Scheme 3). To compare the results obtained with heterogeneous catalyst, we used two non-immobilized catalysts: **Ru1** and the standard non-tagged complex **Ru5**. The reactions were carried in boiling ethyl acetate—a green solvent compatible with ruthenium olefin metathesis catalysts.[27]

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Table 1. RCM reaction of **4** catalyzed under homogeneous and heterogeneous conditions [a]

Entry	Catalyst	Conversion (%)[b]	Yield (%)[c]	Selectivity (%)[d]
1	**Ru5**	99	17	17
2	**Ru1**	99	30	30
3	**Ru1**@MOF	99	51	51

[a] Conditions: Catalyst 2.5 mol%; EtOAc (*C* = 5 mM); 5 h, 80°C. [b] Conversion was determined using internal standard, *Conversion = 100 – [100 × (final moles of **4**/initial moles of **4**)].* [c] GC yield of **5** was determined using calibration curve. [c] Selectivity of the process is described as a ratio between expected RCM product to the sum of RCM product plus isomerization and oligomerization side-products. *Selectivity = (yield of **5**) / (conversion of **4**) × 100*

Standard general-purpose catalyst **Ru5** very quickly consumed the substrate, but among expected products (*E*- and *Z*-isomers of oxacyclopentadecen-2-one, **5**) a large proportion of "isomerized" cyclic products **5'** resulted from C-C double bond migration[28] as well as oligomers exhibiting a broad molecular mass distribution was observed. Because a mixture of **5** and **5'** (isomerized products) was not possible to be separated, GC was used to analyze the reaction mixture and to calculate the yield of **5** using a calibration curve. Comparing with **Ru5**, better selectivity, but still far from satisfying, was observed in the reaction catalyzed by **Ru1** (for these two cases selectivity of the process is described as a ratio of expected RCM product **5** to the sum of RCM product **5** plus *both isomerization and oligomerization byproducts*). Importantly, immobilized **Ru1**@MOF gave no C-C double bond migration, as no isomerized products **5'** were observed in the reaction mixture by GC, and only the oligomers accompanied the expected product **5**. The observed perfect selectivity of the RCM process can be connected with the increased stability of immobilized **Ru1**@MOF, where catalysts molecules are separated in individual voids of the metal-organic framework. We speculate that such encapsulation of **Ru1** shall (at least partially) block the bimolecular decomposition pathway, thus limit formation of isomerization-active species.[29]

The second limitation in macrocyclization of unbiased dienes is related to thermodynamic equilibrium between a cyclic product and the oligomers. It is well known that RCM macrocyclization typically requires high-dilution conditions (*C* ≤ 5 mM) to avoid competitive cross-metathesis oligomerization process.[24,25,30] As the high-dilution conditions are not cost-effective at larger scale, various approaches have been tried to conduct such macrocyclizations in more concentrated solutions. For example, Jee and Hong were able to partially suppress such parasitic oligomerization by placing a ruthenium catalyst inside a carefully designed mesocellular siliceous foam (MCF).[31] In light of this observation, we decided to check if encapsulation of **Ru1** in MOF can offer any advantages in this context as well. Quantitative conversions observed in RCM of **4** (Scheme 3) encouraged us to decrease the catalyst loading to 0.5 mol% only. In addition, we have extended the reaction time to aid the oligomers, which are the kinetic product of the reaction,[32] to possibly be transformed into the desired macrocycle **5** (Table 2). While the RCM reaction with **Ru1**@MOF was selective in terms of C-C bond migration (only **5** was observed after the reaction by GC analysis). Unfortunately, MOF encapsulation did not restrict the oligomerization process. Results (Table 2) show visibly the enhanced formation of oligomers when the concentration of the reaction mixture was increased from the standard 5 to 20 mM. Further

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concentration of the reaction mixture quickly led to even more intensive formation of oligomers, thus limiting the yield of the desired macrocyclic product. In that sense, immobilized **Ru1** resemble homogeneous metathesis catalysts, where the similar disadvantageous influence of concentration was observed.[21]

Table 2. RCM reaction of **4** catalyzed by **Ru1**@MOF at increasing concentration [a]

Entry	Concentration (mM)	Conversion (%)[b]	Yield (%)[c]	Oligomerization (%)[d]
1	5	25	19	24
2	20	65	31	52
3	40	90	26	72
4	80	97	10	89

[a] Conditions: Catalyst 0.5 mol%; EtOAc (C_m = 5–80 mM); 24 h, 80°C. [b] Conversion was determined using internal standard, *Conversion = 100 – [100 × (final moles of **4** / initial moles of **4**)]* [c] GC yield of **5** was determined using calibration curve. [c] *Oligomerization = 100 − [100 × (yield of **5**) / (conversion of **4**)]*

Ethenolysis

The second challenging transformation used by us to test Ru1@MOF was the ethenolysis reaction. Ethenolysis is a sub-type of olefin metathesis process in which an internal olefin is "split" using ethylene as the cross-metathesis partner (Scheme 4). The most promising applications of ethenolysis are directed at using renewable feed stocks.[33,34] For example, ethyl oleate (**6**), derived from natural seed oils, can be converted to 1-decene (**7**) and alkyl 9-decenoate (**8**).[35] The utility of ethenolysis in renewable materials valorization is driven by the low cost of ethylene as a reagent, however high selectivity of this process must be ensured in order to make it cost-effective. In the case of oleic acid esters ethenolysis selectivity is defined as the ratio of the desired terminal alkene products **7** and **8** (α-olefins) versus "homodimers" **9** and **10** that are the unwanted products of parasitic self-cross metathesis process (Scheme 5).

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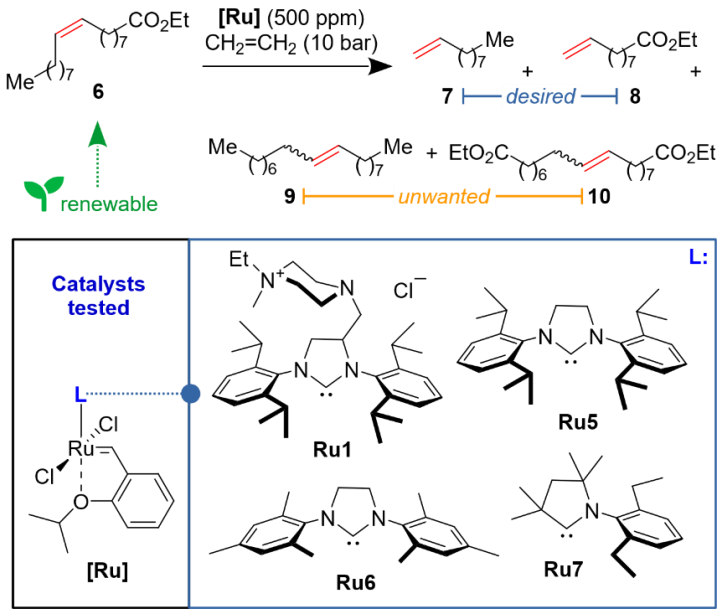


Figure 2. Ethenolysis of ethyl oleate (**6**) leading to mixture of the desired (**7** & **8**) and undesired products (**9** & **10**).

As it can be seen in Table 3, heterogeneous **Ru1**@MOF provided selectivity similar to that obtained with its closest untagged analogue—SIPr Hoveyda-Grubbs catalyst **Ru5**. The other homogeneous catalyst tested, a SIMes bearing **Ru6** provided even lower selectivity (43 vs. 75%). Prolonged reaction time led to practically no erosion of observed selectivity (73 vs. 75%). Interestingly, Bertrand-Hoveyda-Grubbs catalyst **Ru7**—the state-of-the-art catalyst in ethenolysis[36] —gave visibly better selectivity (Table 3, entry 5). These results show that unfortunately, in case of the ethenolysis reaction, the encapsulation in MOF exhibits no, or only little "protecting" effect, and the studied heterogeneous catalyst **Ru1**@MOF cannot rival the best Bertrand-type catalysts.[36,37]

Table 3. Ethenolysis conducted under homo- and heterogeneous conditions[a]

Entry	Catalyst	Conversion (%)[b]	Selectivity (%)[c]	Yield (%)[d]
1	**Ru1**@MOF	73	75	54
2	**Ru1**@MOF (5 h)	72	73	53
3[e]	**Ru5**	80	72	58
4[e]	**Ru6**	71	43	30
5[e]	**Ru7**	84	83	70

[a] Conditions: Catalyst loading 500 ppm; ethylene purity 99.9% (3.0 grade); 3 h, 50°C 10 bar. Reaction conversion and selectivity determined by GC using *n*-tetradecane as the internal standard with calibration curves for ethyl oleate, tetradecane, and all the metathesis products. [b] *Conversion = 100 – 100 × (final moles of **6** / initial moles of **6**)*. [c] *Selectivity = 100 × (moles of **7** + moles of **8**) / [(moles of **7** + moles of **8**) + 2 × (moles of **9** + moles of **10**)]*. [d] *Yield = Conversion × selectivity*. [e] Taken from Ref. 38.

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Conclusions

An optimized synthesis of valuable intermediate **Ru4** in substantially improved yield of 50% was tested up to scale of 1 gram. The newly developed procedure uses easily available substrates: 2-(isopropoxy)styrene and Grubbs' 1-generation catalyst. Such obtained intermediate **Ru4** was then quantitatively converted into useful quaternary ammonium tagged catalyst **Ru1** (FixCat).

To prove the merits of the tagged catalyst, complex **Ru1** was immobilized in a metal-organic framework (MOF) according to previously described procedure. Next, two challenging applications, not studied previously with hybrid **Ru1**@MOF catalyst, were attempted. In the case of the RCM reaction yielding a macrocyclic musk lactone, heterogeneous **Ru1**@MOF exhibited much better resistance towards unwanted C-C double bond migration, thus offering perfect selectivity as compared to analogous homogeneous catalysts. Unfortunately, this macrocyclization still required high-dilution conditions (5 mM) to avoid extensive formation of oligomers. Ethenolysis of ethyl oleate was selected as the second target-ground to test the performance of **Ru1**@MOF. In this transformation the hybrid catalyst exhibited only slightly better selectivity levels as compared to well-known general-purpose Hoveyda-Grubbs SIMes and SIPr catalysts, and was not able to challenge the current ethenolysis benchmark—the Bertrand-Hoveyda-Grubbs catalyst.

Experimental Section

General. Reactions were carried using standard Schlenk technique using argon 6.0 grade as an inert gas unless otherwise stated. All glassware was dried overnight in oven (130 °C) prior to use. GC analyses were performed by means of PerkinElmer Clarus 580 chromatograph with FID detector and GL Sciences InertCap 5MS/Sil Capillary Column (Inner Diameter 0.25 mm, Length 30 m, df 0.50 μm). Calibration curves were made for ethyl oleate, tetradecane and all the metathesis products described in paper. Reaction mixtures were analyzed using the following method: initial temperature 145°C — 0.1 min. — 9°C /min to 180°C — 0.1 min — 20°C /min to 305°C — 2 min.). The flash column chromatography was performed using Merck silica gel 60 (230–400 mesh) typically using an *n*-hexane/ethyl acetate eluent system.

Unless otherwise noted, all common laboratory reagents were purchased from Avantor Performance Materials Poland S.A. and used as received. Ethyl acetate and *n*-hexane were distilled before used as eluent in column chromatography. Technical oleic acid (purity 90%), 9-decenoic acid and hex-5-en-1-ol were purchased from Sigma-Aldrich. Ethylene gas 3.0 grade (99.9%) was purchased from Linde (3.0 grade; O_2 < 30 ppm, N_2 <150 ppm, C_nH_m <1800 ppm). Tetradecane (purity 99%) and SnatchCat scavenger were purchased from Sigma-Aldrich, ethanol (purity 96%) was purchased from Linegal Chemicals. Dry DCM was obtained from MB SPS-800 solvent purification system. Ethyl oleate was prepared according to a published procedure.[38] Hex-5-en-1-yl dec-9-enoate was prepared according to a published procedure.[39] The structure of synthesized substrates was confirmed using ^{1}H and ^{13}C NMR spectroscopy.

Synthesis of NHC precursor 1'

Tetraamine (synthesized according to the procedure described in the literature[13]) (28.8 g, 56.8 mmol) was dissolved in triethyl orthoformate (96.6 mL, 568 mmol) and HCl (4 M in 1,4-dioxane, 28.4 mL, 114 mmol) and methanol (35 mL) were added. The resulted mixture was stirred at 95°C for 2 h. Solvents were removed and water (650 mL) was added followed by addition of NH_3 (28% in water, 11.4 mL, 170 mmol). Insoluble material was filtered off and rejected; saturated solution of NH_4BF_4 in water (12.3 g, 114 mmol) was added to the

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filtrate and product was extracted with dichloromethane (3 × 70 mL). The solvents were evaporated and the formed yellow solid was crystallized from the MeOH/Et_2O at -6°C, which allowed to obtain a colorless crystalline powder (23 g, 67%).

Synthesis of Ru4

Complex **Ru4** was synthesized based on the procedure available in the literature[13] with the following changes: Potassium *t*-amylate (25% in toluene, 1.35 mL, 2.41 mmol) was added to the suspension of NHC precursor **1'** (1.53 g, 2.53 mmol) in degassed toluene (50 mL). Reaction mixture was stirred for 10 minutes at room temperature. Next, Grubbs I generation catalyst **Ru3** (2.00 g, 2.41 mmol) was added and resulted mixture immersed into oil bath preheated to 80°C and stirred for 30 minutes. Then 1-isopropoxy-2-vinylbenzene (1.17 g, 7.23 mmol) and CuCl (0.50 g, 5.3 mmol) were added and stirring was continued for 15 minutes at 80°C. After cooling down to room temperature the solvent was evaporated and the residue was dissolved in EtOAc and filtered through cotton wool. After evaporation of EtOAc the crude product was purified using column chromatography (eluent: from 5 to 20% of EtOAc in *n*-hexane). Product (1.01 g, 50%) was isolated as a green powder. ^{1}H and ^{13}C NMR spectra of the obtained material correspond to those reported in literature.[13] The brown band before main product was also collected and crystallized from cold *n*-pentane leading to obtain Hoveyda first generation catalyst (210 mg, 14% based on starting material).

Macrocyclization

Synthesis of hex-5-en-1-yl dec-9-enoate (**4**) was performed using literature procedure.[40] In a 100 mL Schlenk vessel equipped with magnetic stirrer hex-5-en-1-yl dec-9-enoate (101 mg, 0.4 mmol) and tetradecane (80 mg, 0.4 mmol, 10 µL) were dissolved in anhydrous and degassed EtOAc (80 mL). The resulting 5 mM solution was stirred for 10 minutes and used as mother solution for following reactions. More concentrated solutions were prepared in the same way.

Using the protective atmosphere of an inert gas in a 20 mL Schlenk vessel equipped with a magnetic stirrer, 8 mL of previously prepared 5 mM solution of ester hex-5-en-1-yl dec-9-enoate was added. The solution was then placed in an oil bath preheated to the 80°C, conditioning the mixture for about 1 minute. Then the MOF supported catalyst (35.5 mg of support containing 2.5% weight of FixCat catalyst (0.887 mg, 1 µmol) was weighed and immediately added to the solution. The vessel was equipped with a reflux condenser and heated at a set temperature by stirring (400 rpm) for next 5 h. The progress of reaction was monitored by thin layer chromatography (5% EtOAc in *n*-hexane, visualization was made using anisadehyde solution). After that time the reaction mixture was cooled to room temperature. The supported catalyst was filtered using a syringe filter and the filtrate was concentrated on a rotary evaporator. The resulting oil was transferred entirely to a GC vial and then diluted with dichloromethane up to 1.5 mL. The post-reaction mixture prepared in this way was subjected to GC and TLC analysis. Reactions at a higher concentration or lower concentration of the catalyst were carried out in a similar manner.

For reference reactions with catalysts without support the appropriate solutions in DCM were prepared (5 mg of ruthenium complex in 1 mL of dry DCM). To stop catalyst, the SnatchCat metal scavenger was used after mixture was cooled down do rt. After stirring for 30 minutes mixture was filtered through syringe filter and then concentrated under reduced pressure. The resulting oil was subjected to GC and TLC analysis as was mentioned earlier.

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Ethenolysis

Reactions were performed as was described in literature, with minor changes as indicated.[38] Each reaction was repeated twice, and the average result of both reactions was calculated. Reactions were performed using Armar and Roth autoclaves. Catalysts' stock solution was made in air using DCM. A solution of a catalyst (500 ppm) in DCM (100 µL) was added to a mixture of ethyl oleate (4.66g, 15.0 mmol) and tetradecane (0.61 g, 3.05 mmol) placed in a glass vessel containing a magnetic stir bar. The vessel was immediately installed into an autoclave which was then flushed three times with ethylene (10 bar). The mixture was stirred for 3 or 5 h at 50°C. After that time a sample of the reaction mixture was collected (1 mL) and immediately quenched with ethyl vinyl ether (4 mL, used as 2 M solution in DCM). Next an aliquot (0.2 mL) was taken from this mixture and diluted with DCM (0.8 mL). Such obtained solution was analyzed by GC. Conversion was calculated using the internal standard and calibration curves.

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