Article

Preparation of Ruthenium Olefin Metathesis Catalysts Immobilized on MOF, SBA-15, and 13X for Probing Heterogeneous Boomerang Effect

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Abstract: Promoted by homogeneous Ru-benzylidene complexes, the olefin metathesis reaction is a powerful methodology for C-C double bonds formation that can find a number of applications in green chemical production. A set of heterogeneous olefin metathesis pre-catalysts composed of ammonium-tagged Ru-benzylidene complexes **4** (commercial FixCat™ catalyst) and **6** (in-house made) immobilized on solid supports such as 13X zeolite, metal-organic framework (MOF), and SBA-15 silica were obtained and tested in catalysis. These hybrid materials were doped with various amounts of ammonium-tagged styrene derivative **5**—a precursor of a spare benzylidene ligand—in order to enhance pre-catalyst regeneration via the so-called release-return "boomerang effect". Although this effect was for the first time observed inside the solid support, we discovered that non-doped systems gave better results in terms of the resulting turnover number (TON) values, and the most productive were hybrid catalysts composed of **4**@MOF, **4**@SBA-15, and **6**@SBA-15.

Keywords: olefin metathesis; ruthenium; supported catalysts; metal−organic frameworks; SBA-15; microporous materials; boomerang effect

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1. Introduction

It is well established that the initiation step in olefin metathesis reaction catalyzed by the so-called Hoveyda–Grubbs catalyst (**1**) involves the dissociation of the 2-(isopropoxy)benzylidene ligand and the release of 2-(isopropoxy)styrene **2** (Figure 1a) [1,2]. In 1999, Hoveyda showed that after the metathesis reaction, the released styrene **2** can react back with propagating (and unstable) 14 e⁻ ruthenium species to re-create the pre-catalyst (**1**). He called it the release-return (or boomerang) mechanism [3].

Since in many synthetic studies it was found that catalyst **1** can be recovered after the metathesis reaction [3–6] (at least in a good part), many accepted the existence of the boomerang mechanism. In addition, various early labeling studies provided evidence that this mechanism is operative. For example, in 2008 we executed a study showing that during the metathesis reaction conducted in the presence of one equivalent of deuterium labeled styrene **2**, up to 50% of Hoveyda pre-catalyst isolated after the reaction contained the labeled benzylidene ligand, thus the release-return mechanism may be operational [7]. However, since these experiments used relatively high catalyst loading (5 mol %), the relevance of the boomerang mechanism in truly catalytic reaction conditions (≤1 mol % of catalyst loading) was later questioned. Plenio investigated this matter in a scholarly way using a fluorophore-tagged Hoveyda complex [8]. Using a small amount of the catalyst (0.2 mol %), he did not

find evidence of a release-return mechanism in the studied ring-closing metathesis (RCM) reactions. It shall be noted that the complex used in his study formally belonged to a class of fast-activating EWG-substituted Hoveyda–Grubbs complexes [9].
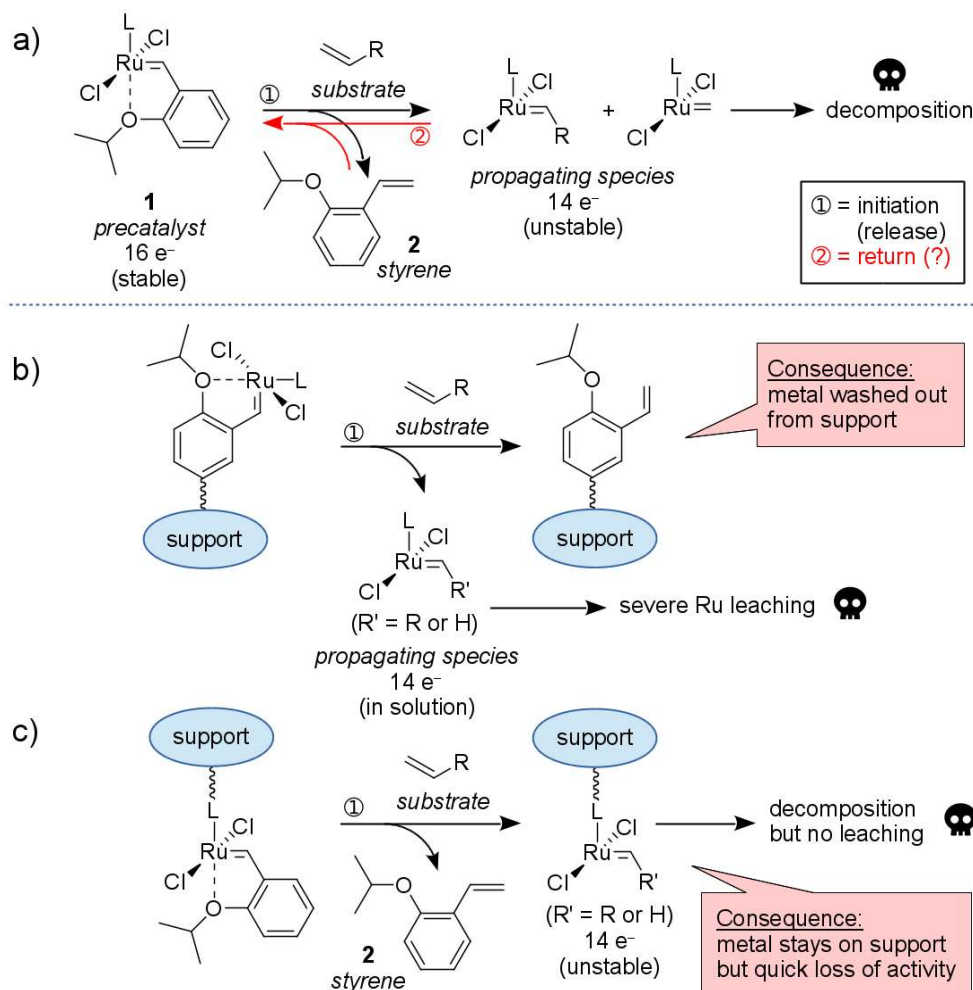

Figure 1. (**a**) Widely accepted dissociative mechanism of initiation of a Ru pre-catalyst (black arrows) and suggested pre-catalyst regeneration via the "boomerang" mechanism (red arrows). (**b**,**c**) Problems in a Ru catalyst immobilization caused by ligand dissociation. For Hoveyda–Grubbs catalysts **1** L = SIMes (1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene).

Fogg undertook another study revisiting our old labeling experiments and addressing their deficiencies [10]. The initial experiments showed that even a small amount of 2-(isopropoxy)styrene **2** can inhibit a model metathesis reaction, indicating that the reaction between propagating 14 e$^-$ ruthenium species and **2** is rapid in both its early and late stages. Next, the cross-over studies with the ^{13}C-labeled styrene **2** showed a very efficient formation of ^{13}C-labeled **1** in a near theoretical equilibrium amount (47%), further supporting the release-return mechanism [10].

Although no consensus has been reached on the existence or lack of the release-return mechanism under "practical" metathesis conditions typically applied in organic synthesis, in the context of catalysts immobilization one can anticipate the apparent problems caused by unavoidable benzylidene ligand dissociation during initiation of a supported Hoveyda–Grubbs catalyst (Figure 1a).

Basically, the immobilization can be made via a dissociating benzylidene ligand (Figure 1b) or via a non-dissociating ligand L (Figure 1c). Both these approaches are not free from potential problems that can lead to two extremes:

(i) For systems where the support is connected via a dissociating ligand (Figure 1b), initiation of the catalysts must lead to leaching metal out of the support. Despite some spectacular failures of such systems in continuous flow experiments [11], this mode of immobilization was surprisingly popular in the early years of the metathesis research [12,13];

(ii) For systems where the support is connected to a non-dissociating ligand (Figure 1b) the situation is seemingly better because usually there is no heavy leaching observed with such systems. However, as the initiation step leaves the catalysts stripped off the stabilizing alkylidene ligand, the remaining fragile 14 e$^-$ Ru complexes are totally exposed to harmful factors such as oxygen or impurities from solvents and reagents. As a result, such immobilized complexes quickly die, and as their cadavers stay attached to the support, usually there is no strong leaching of metal to the organic products [14].

Interestingly, many of these immobilized systems were reported to work well in batch and even enabled the catalysts recycling from 3 to 10 times (however, usually applied at relatively large loading, such as ≥5 mol %). In this context, it was often suggested that the presence of the release-return boomerang mechanism may help to regenerate the pre-catalysts on the support [12,13].

Despite the lack of a general consensus regarding the existence of the release-return process, the boomerang mechanism has already been applied to improve the outcome of heterogeneous metathesis reactions involving immobilized Hoveyda–Grubbs type catalysts. While Hoveyda has unambiguously shown [3] that the participation of the release-return mechanism in the case of **1** bounded to glass-sol pellets in a batch is not high (measured as the propagating 14 e$^-$ species cross-over between two separate pellets, Figure 2a), other trials were continued. Skowerski [15] very elegantly utilized the boomerang effect to prolong the length of life of commercial FixCat™ catalyst **4** immobilized on SBA-15 under batch and continuous flow conditions (Figure 2b). In the initial experiment in batch, it was shown that the addition of the benzylidene ligand precursor **3** (100 ppm, 1 equiv. relative to the Ru catalyst used) to the solution of a metathesis substrate resulted in the reduction of immobilized catalyst **4** activity, which is in full accordance with the results obtained earlier by Fogg [10]. At the same time, a visible stabilization of **4**@SBA-15 system was observed in continuous flow when styrene derivative **3** was added to the substrate feed (Figure 2b). Although the catalyst initiated more slowly, it maintained reasonable activity longer, which allowed it to more than double the resulting total turnover number (TON) (from 9149 to 21,660) [15].

We hypothesized that the release-return mechanism can be one of the contributors to higher productivity of immobilized Hoveyda–Grubbs catalysts. Owing to the ease of initiation and possibility of regeneration in the presence of styrene **2**, the immobilized Hoveyda pre-catalyst can be viewed as the resting state which protects the active propagating species from decomposition and readily re-enters the catalytic cycle. For obvious reasons, both interacting elements (i.e., the pre-catalyst and the benzylidene ligand precursor) have to be immobilized on the support close to each other and with flexibility allowing for their subsequent mating. In the present report we disclose our results on testing the validity of such "boomerang inside support's pores" idea (Figure 2c). For grafting of Ru pre-catalysts and their benzylidene ligand precursor on solid supports we decided to use a non-covalent immobilization strategy utilizing quaternary ammonium groups as anchors [16]. Next, the reaction between **5** and activated **6** should re-create the stable pre-catalyst form. At the same time, the tagged styrene derivative **5** will not be washed out from the support and contaminate the product (contrary to Skowerski's approach).
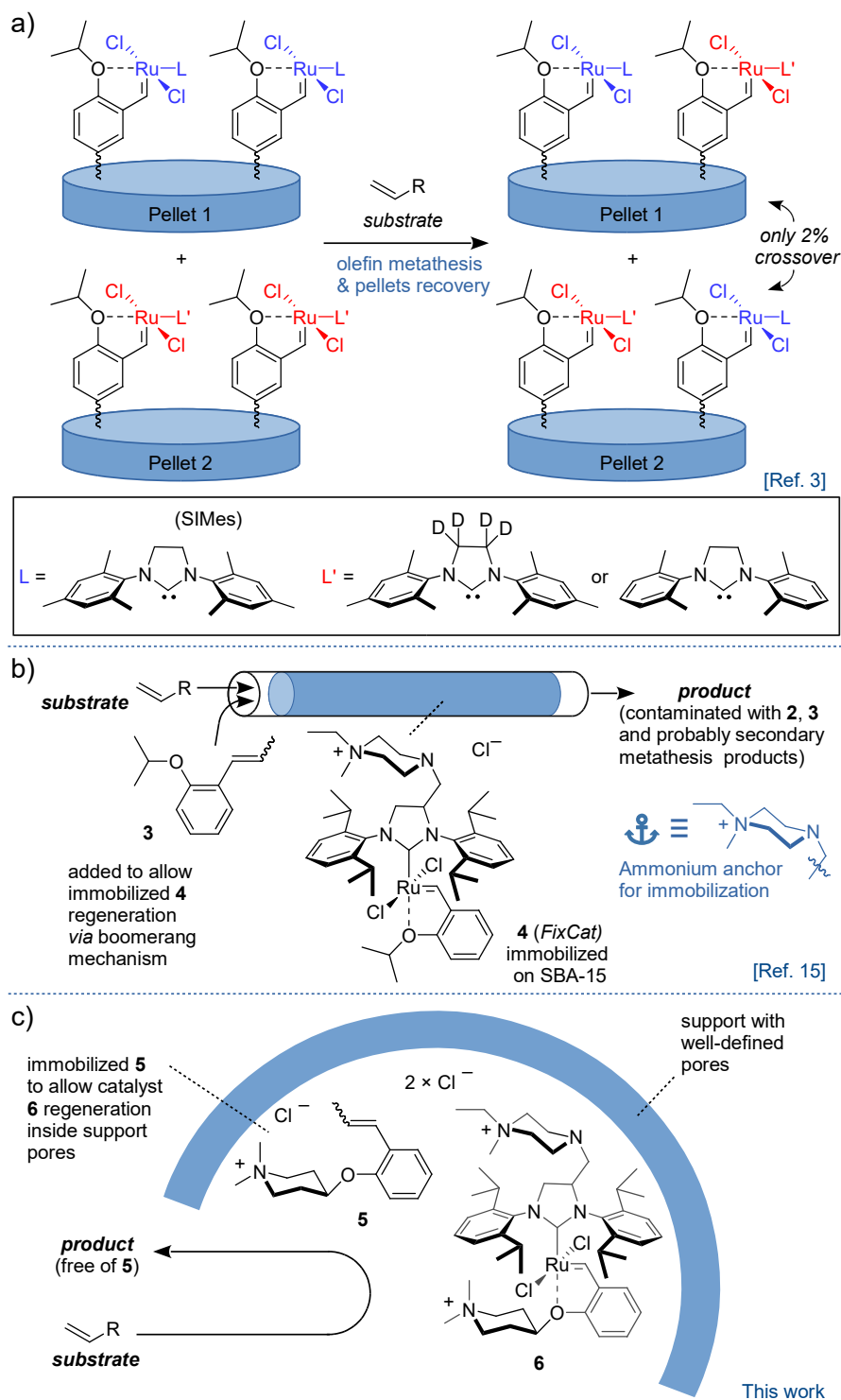
Figure 2. (**a**) Cross-over experiment by Hoveyda showing some (2%) existence of the boomerang effect in the case of pellet-immobilized catalysts under batch conditions [3]. (**b**) Skowerski's approach to extending the lifetime of non-covalently immobilized catalyst **4** in continuous flow [15]. (**c**) Idea of "boomerang inside support's pores" explored in this work.

2. Results and Discussion

2.1. Tagged Ligand Precursor and Catalyst Synthesis

Tagged catalyst **4** is commercially available (Apeiron Synthesis FixCat™) [17]. However, in order to study the boomerang effect in solid supports, a tagged benzylidene ligand precursor (styrene derivative **5**) and a double-tagged catalyst **6** were prepared. Using a method previously developed in our laboratory [18], known 2-propenyl-phenol **7** [19] was converted into ether **8**, a common starting material for the synthesis of tagged ligand precursor **5** and tagged catalyst **6**. To obtain the latter, salt **9** [18] was deprotonated using potassium tert-amylate to form in situ the free *N*-heterocyclic carbene (NHC), which later in the sequence of one-pot transmetalation reactions was transformed into Ru complex **11** in 34% overall yield starting from **9**. The final quaternization with MeCl in a glass ampule led to the formation of new double-tagged complex **6** in 65% yield (Scheme 1). Interestingly, contrary to the commercially available FixCat™ catalyst **4** [17], which is not soluble in water (0.45 mg/mL), the double-tagged complex **6** exhibited high water solubility, exceeding 100 mg/mL.
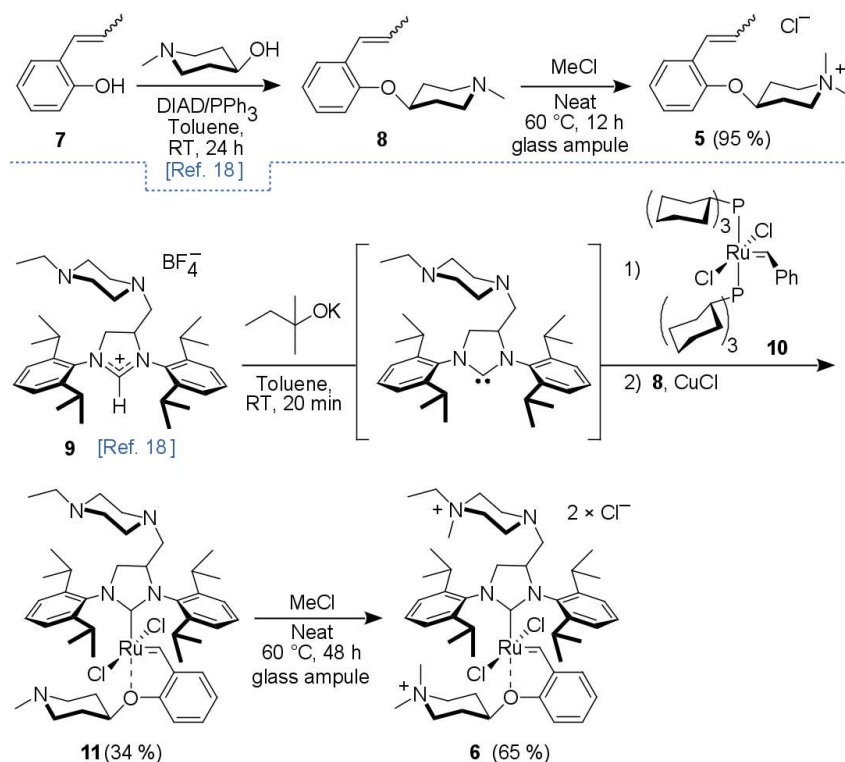
Scheme 1. Synthesis of double-tagged pre-catalyst **6** and tagged benzylidene ligand precursor **5** designed for testing the "boomerang inside support's pores" idea.

Single crystals of **6** suitable for XRD were obtained by layering a MeOH/MeCN solution of the complex with an Et$_2$O/MTBE (methyl *tert*-butyl ether) solvent mixture and allowing the precipitated oil to recrystallize over two weeks (Figure 3). Remarkably, the formed needle-like crystals were stable for several months in the mother liquor in a closed flask without deoxygenation. To our knowledge, this is the first measured crystal structure of a double ammonium-tagged olefin metathesis catalyst [15].
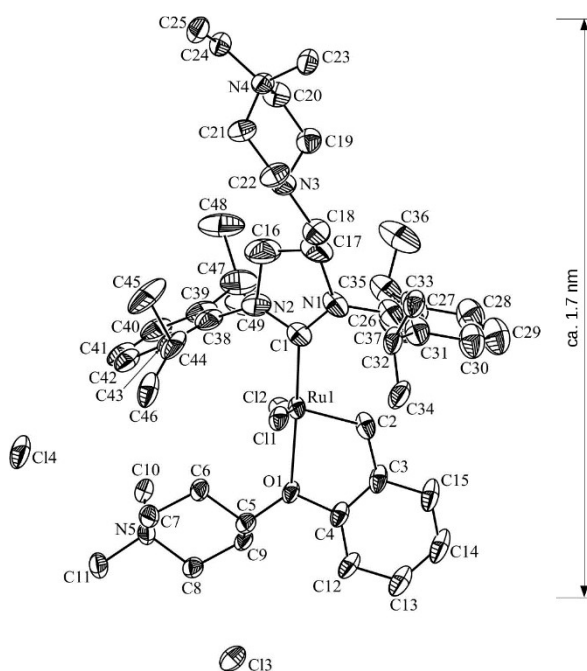
Figure 3. Solid-state structure of **6**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Approximate molecular dimensions of **6** molecule: $1.7 \times 1.2 \times 0.9$ nm (height $\times$ width $\times$ depth).

2.2. Supports and Catalysts Immobilization

Three different types of porous materials for immobilization purposes: 13X, (Al)MIL-101-NH$_3$Cl, and SBA-15 were used in this study (Figure 4). Support 13X is a representative of molecular sieves (aluminosilicates); it is crystalline and has micropores 0.8 to 1.0 nm in diameter [20]. A metal-organic framework (MOF) coded (Al)MIL-101-NH$_3$Cl is a crystalline hybrid organic-inorganic material bearing two types of differently-sized mesopores, 2.6 nm and 3.2 nm in diameter [21]. SBA-15 is a crystalline, mesoporous siliceous material with 8 nm mesopores [22]. The (Al)MIL-101-NH$_3$Cl and SBA-15 have already proved to be effective supports for olefin metathesis catalyst [15,23,24].
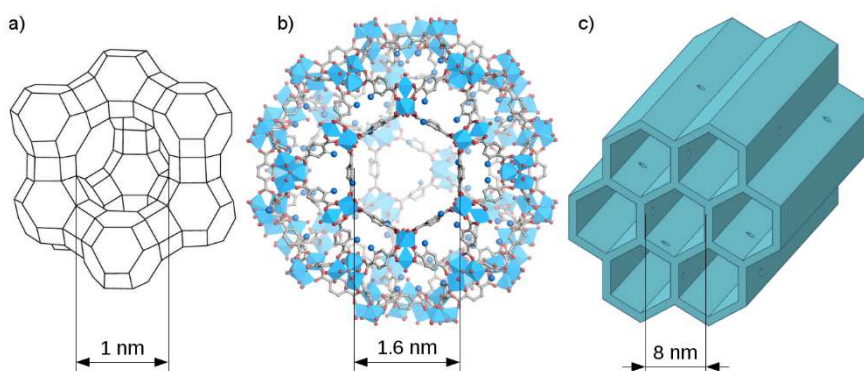

Figure 4. Solid supports selected for this study: (**a**) zeolite 13X, (**b**) metal-organic framework (Al)MIL-101-NH3Cl, and (**c**) mesoporous silica SBA-15).

The immobilization of Ru complexes **4** or **6** was accomplished by sorption from dichloromethane (DCM) solution under an argon atmosphere. Stirring of a catalyst solution with any of the three sorbents for 1 hour resulted in quantitative adsorption of the catalyst, as confirmed by UV–Vis spectroscopy of the supernatant (see Supplementary Materials). Subsequent removal of the solvent by decantation and drying under vacuum produced heterogeneous catalysts as greenish powders.

It shall be noted that the immobilization procedure is easily scalable, and large amounts of adsorbed ruthenium complexes can be stored in a freezer under an argon atmosphere for at least a month without losing catalytic activity. Materials containing 1.0–0.05 wt % of ruthenium complexes were characterized by nitrogen sorption analysis which showed that the specific surface areas of these materials were not significantly decreased.

2.3. Optimization of Metathesis Reaction Conditions

Using a popular model ring-closing metathesis (RCM) reaction of diethyl 2,2-diallylmalonate (**12**) (DEDAM) [25] we established the optimal application regimes for the studied hybrid catalysts (Scheme 2).
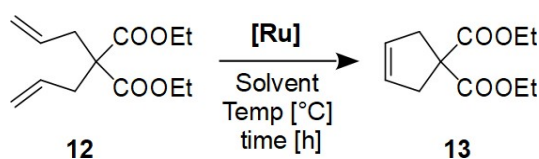
Scheme 2. Model ring-closing metathesis reaction of **12** (DEDAM) used in this study.

First, to set up a benchmark for further comparisons, we outlined the activity of the commercial FixCat™ catalyst (**4**) in the above RCM reaction under homogeneous conditions (in dichloroethane (DCE) solution at 50 °C, 24 h) and obtained a turnover number (TON) of 12,400. The same reaction conducted in toluene (**4** is insoluble in this solvent, so the catalyst was dissolved in a minimal volume of DCM (25 µL) and added to the solution of **12** in toluene (1 mL)) gave a TON of 9000. The double-tagged highly polar **6** under homogeneous conditions (in DCE solution) gave a TON of 8800, while in toluene the obtained TON was only 600. It should be noted that the use of an ammonium-tagged Ru catalyst as a fine suspension in toluene was previously proposed by the authors of this study as a simple and efficient quasi-heterogeneous method to obtain organic products with a low ruthenium contamination level [14].

Next, in a set of experiments, we checked the optimal temperature in the application of heterogeneous catalysts based on **4**. To do so, the RCM reaction of **12** was run at temperatures varying from 30 to 110 °C. Interestingly, while non-immobilized **4** showed maximum reactivity at 80 °C, the immobilized systems were the most active in 40–60 °C window (Figure 5).
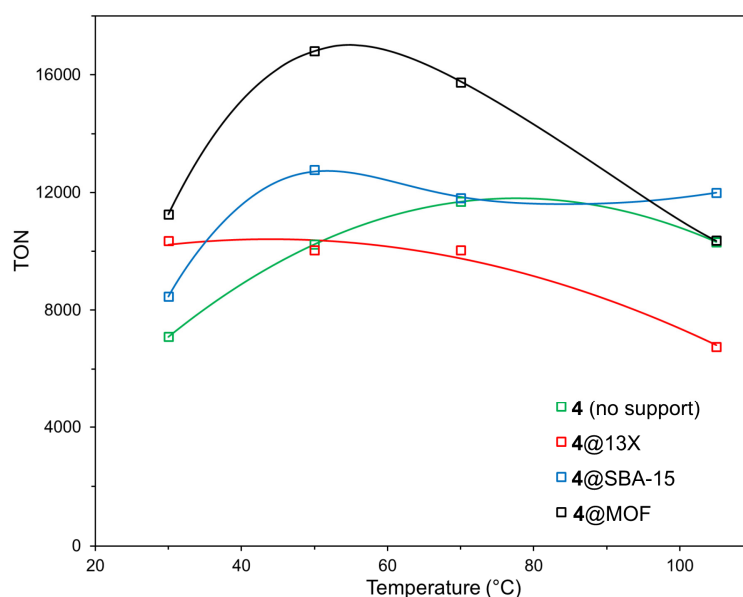

Figure 5. Effect of temperature on catalyst productivity. Conditions: 0.5 M **12** in toluene, 50 ppm or 35 ppm for MOF, 24 h, 0.5 wt % on support. Lines are a visual aid only.

Finally, we repeated the model RCM reaction using various amounts of **4** immobilized on a support (given in wt %, see Table 1 and Figure 6). As before, the temperature for the RCM test reactions was set at 50 °C. In general, we found that 0.5 wt % of catalyst loading on the support gives the best results in the context of RCM productivity. Despite the fact that MOF seemed to work even better at lower loading values (see Table 1 and Figure 6), we decided to use 0.5 wt % of Ru on the support because this loading was optimal for the majority of tested systems. Lower loading values were excluded from further tests because using such materials would lead to significantly larger volumes of the support (and then the solvent), which may be problematic from a practical point of view.

Table 1. Effect of catalyst **4** loading (wt % with respect to the support) on productivity of the heterogeneous system in ring-closing metathesis (RCM) of **12**. [1]

Catalyst/Support	Catalyst Loading on Support (wt %)			
	1.0	**0.5**	**0.1**	**0.05**
4@13X	9 400	10 000	7 500	4 400
4@SBA-15	8 000	12 800	12 800	12 800
4@MOF	17 800	19 700	21 600	24 100

[1] Test RCM reaction conditions: substrate **12** in toluene (0.5 M), 50 °C, 50 ppm of catalyst for 13X and SBA-15 or 35 ppm for MOF (relative to substrate **12**).
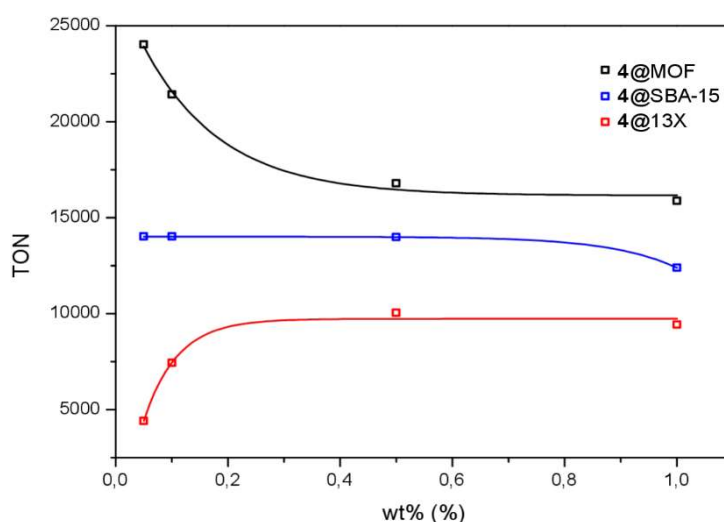

Figure 6. Effect of catalyst **4** loading on the support (wt %) on productivity of the heterogeneous system in RCM of **12**. Lines are a visual aid only. For the RCM reaction conditions, see Table 1.

Having established the basic set of conditions for an application of FixCat™ catalyst (**4**) immobilized on various supports, we decided to study the effect of extra added benzylidene ligand precursor **5** on the productivity of the resulting hybrid system. We believed that the propagating 14 e⁻ species resulted upon initiation of Ru pre-catalyst (**4** or **6**) could perhaps rebound to molecules of **5** present in the support cavities, thus increasing the lifetime of the hybrid catalyst (this concept is explained in Figure 2c). At the same time, one can expect that this process will compete with RCM of **12**, thus slowing down the productive metathesis process. To test these speculations, a number of RCM experiments were performed utilizing 0.5 wt % catalyst immobilized on supports impregnated with various amounts of **5** (0–100 equiv. relative to Ru). Using the prepared catalysts for RCM of DEDAM **12** (50 ppm of Ru relative to **12**, 0.5 M of **12** in toluene, 50 °C, 24 h), we expected to quantify the effect of the additional ligand precursor present in the support.

The impregnation of the support with **5** and **4** or **6** was done as before: a stock solution of Ru catalyst in dry dichloromethane was added to a solid support placed in a dry vial (in an amount required to obtain 0.5 wt % of catalyst relative to the mass of a support). After 30 min of stirring, 1, 10,

or 20 equiv. of **5** were added as a stock solution and the suspension was stirred for an additional 30 min. Then the solvent was evaporated and the resulting solid dried under high vacuum at 30 °C for 2 h. The obtained heterogeneous systems were thus used in the model RCM reaction of **12** (Scheme 2) and the results are compiled in Table 2.

Table 2. Effect of ligand precursor **5** co-immobilized on a support on productivity of the model heterogeneous systems. [1]

Entry	Catalyst@support	5 (equiv.)	Conversion (%)	Turnover Number (TON)
1	**4@13X**	0	50	10,000
		1	15	3000
		10	27	5400
		20	21	4200
2	**6@13X**	0	41	8200
		1	42	8400
		10	30	6000
		20	25	5000
3	**4@SBA-15**	0	64	12,800
		1	40	8000
		10	30	6000
		20	15	3000
4	**6@SBA-15**	0	70	14,000
		1	68	13,600
		10	49	9800
		20	31	6200
5	**4@MOF**	0	91	18,200
		1	90	18,000
		10	83	16,600
		20	81	16,200
		60	57	11,400
6	**6@MOF**	0	33	6600
		20	13	2600
		100	4	800

[1] Test RCM reaction conditions: 0.5 wt % catalyst and 0–100 equiv. **5** (relative to catalyst) immobilized on different supports, 50 ppm Ru used relatively to substrate **12** in toluene (0.5 M), 50 °C, 24 h.

Results compiled in Table 2 show that in all cases the presence of ligand precursor **5** on a support resulted in a decrease of the hybrid catalyst's productivity. Interestingly, this inhibiting effect was the strongest in the case of 13X support. For MOF and SBA-15, the increase in the amount of **5** decreases the activity proportionally, and the presence of just one equivalent of **5** seems to have only a small effect on catalyst activity. We speculate that this result can be explained by different support morphologies. In the case of 13X, the bonding of the Ru catalyst, as well as catalysis itself, takes place preferentially at the surface of the support, so the increase in the amount of **5** does not lead to a proportional decrease of activity because it can be adsorbed inside of the pores support. For MOF and SBA-15, the catalytic activity of the resulting system decreases proportionally with the amount of the tagged styrene derivative added, because the internal channels and voids in these porous materials are clogged by numerous molecules of **5**, thus blocking the access of substrate **12** to the catalyst molecules immobilized inside. Since the MOF used in this study had a better developed internal surface in comparison with SBA-15, the latter material needed relatively smaller amounts of **5** to be "saturated" (e.g., Table 2 entry 3 versus entry 5). In addition, the relative mobility of tagged polar molecules of **4**, **6**, and **5** inside the support pores may be different in the case of SBA-15 and MOF. Specifically, for the MOF support which has rather cramped narrowing (1.6 nm) between the voids, the mobility of molecules can be limited in contrast to SBA-15 containing huge and straight 8 nm channels. While

the sum of all these subtle effects translates into the observed differences in reactivity of the tested Ru catalysts, the involvement of Ru catalyst molecules into non-productive metathesis with **5** is obviously responsible for visible hampering of catalytic activity of all the systems.

2.4. Reuse of Heterogeneous Catalysts

To test the longevity of the SBA-15 and MOF-based heterogeneous systems, a number of recycling experiments were performed in batch (13X was not included in these tests due to its inferiority noted in previous experiments). Supports bearing Ru pre-catalysts (500 ppm relative to the substrate) impregnated with various amounts of **5** were used in a series of RCM reactions of **12** (0.5 M solution in toluene, 50 °C, 1 h). The solid catalysts were recovered after each cycle using a centrifuge (the clear supernatant solution was decanted, and the conversion of **12** was determined by gas chromatography (GC) analysis) and washed with anhydrous toluene (4×) by repeating the centrifugation-decantation procedure. Then a new portion of substrate **12** solution was added, and the RCM reaction was repeated until the final cycle. The results varied depending on the catalyst and support used. It turned out that adding the benzylidene ligand precursor **5** to the system with FixCat **4** on MOF had no visible effect on the catalyst productivity. Interestingly in the case of **6** on MOF, the presence of **5** seems to reduce the hybrid catalyst productivity (Figure 7a). In the case of SBA-15, the productivity of the system also decreases with increasing the amount of **5** (Figure 7b). We also see that the double-tagged catalyst **6** on SBA-15 is slightly more stable than **4**, reaching a TON of 8900 for **6** versus 8800 for **4**. The recycling experiment clearly shows that the double-tagged **6** in MOF is definitely less active (we have no clear explanation of this effect). The addition of the benzylidene ligand precursor to **6** on MOF leads to even stronger hampering of catalyst activity, thus suggesting that the catalyst is mostly engaged in the non-productive boomerang cycles with **5** instead of converting substrate **12** into product **13**.
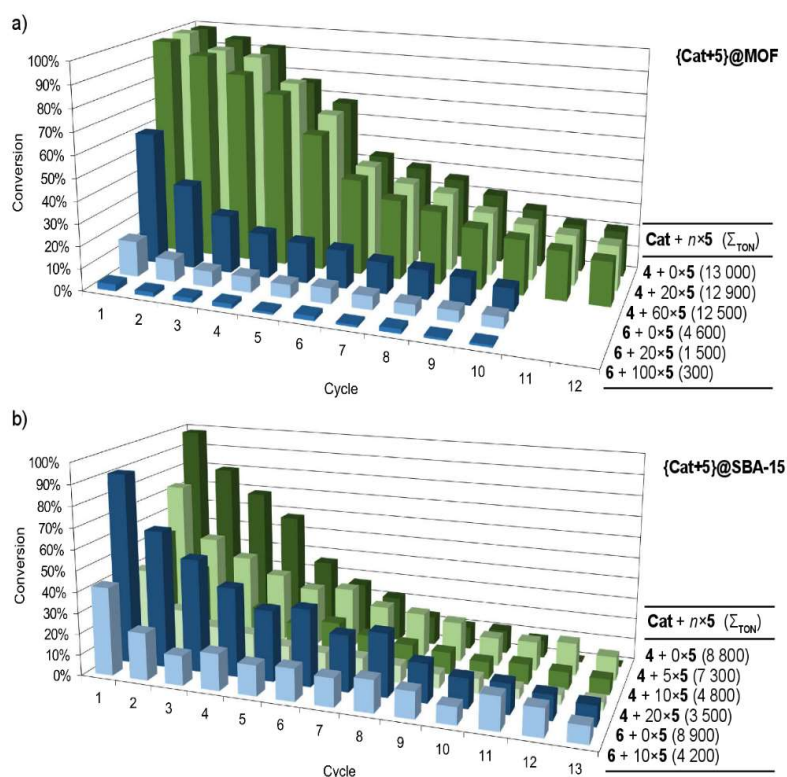

Figure 7. Effect of catalysts **4** and **6** and benzylidene ligand precursor **5** (n equivalents) on recycling and reuse of immobilized catalyst in RCM of **12**. (**a**) Catalyst **4** or **6** and styrene derivative **5** immobilized on MOF. (**b**) Catalysts **4** or **6** and styrene derivative **5** immobilized on SBA-15. Conditions for each run: 500 ppm of Ru relative to **12** in toluene (0.5 M), 50 °C, 1 h.

2.5. Substrate Scope and Limitations Study

The most promising catalysts based on MOF and SBA-15 supports were then tested in a number of metathesis reactions presented in Scheme 3, including more challenging self-cross metathesis of α-olefins [26–28] and RCM. The progress of each reaction was monitored by gas chromatography (GC).
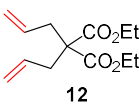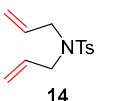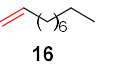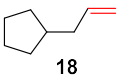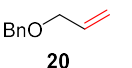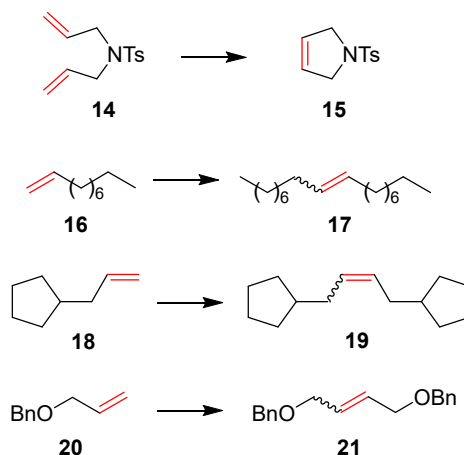

Scheme 3. More advanced metathesis reactions studied. Conditions: substrate (1 M) in toluene, 50 °C, 24 h.

To start, the model RCM of **12** leading to product **13** was repeated once again, using only 50 ppm of Ru at optimized conditions (Table 3, entry 1), and reaching TON values up to 19,000. In addition, another diene **14** (entry 2) underwent RCM reactions using as low as 20 ppm of Ru with good results (TON up to 27,000).

Next, the industrially relevant self-cross metathesis (self-CM) reaction of α-olefins—substrates particularly susceptible to migration of double bond—was attempted (Table 3) [26–29]. It is known that many homogeneous Ru catalysts lead to severe isomerization (shifting of double bond position) of C-C double bonds in this reaction [29,30]. We were therefore curious whether the new hybrid catalysts would show good selectivity in this challenging reaction. Firstly, the self-CM reaction of 1-decene (**16**), a good representative of the Fischer–Tropsch class of α-olefins, was conducted at 50 °C with 50 to 100 ppm of Ru (entry 3). Pleasingly, both **4** and **6** at MOF and SBA-15 provided the expected product—an internal olefin **17**—in conversion not exceeding 50%, but with very good selectivity of ≥98%. However, it should be noted that the obtained numbers do not outperform the results obtained with homogeneous catalysts especially designed for this transformation [26–29]. The next challenging substrate, **18**, also underwent self-CM with perfect selectivity, and 100 ppm of Ru on SBA-15 led to a complete conversion (entry 4). Interestingly, when a fragile *O*-allyl [31] that substituted substrate **20** was used in the self-CM reaction with 50–100 ppm of Ru carried out at 50 °C no significant isomerization (selectivity 96%) was noted only for the MOF-based catalysts, while almost complete isomerization was observed for SBA-15 systems (entry 5). As self-CM of *O*-allyl decorated substrates is used in preparation of "dimers" of biologically active substrates and active pharmaceutical ingredients (APIs), and a number of problems caused by the C-C double bond migration during metathesis has been reported in these studies [31], the exceptionally high selectivity exhibited by Ru@MOF in self-CM of **20** is interesting and will be studied further in due course.

Table 3. Substrate scope [1].

Entry	Substrate	Catalyst (Loading)	Conv. (Selec.) [2] (%)	*E/Z* Ratio	TON	TOF (min $^{-1}$) [3]
1	**12** (CO₂Et, CO₂Et)	4@MOF (50 ppm)	95 (>99)	-	19 000	370
		6@MOF (50 ppm)	47 (>99)	-	9 400	93
		4@SBA-15 (50 ppm)	83 (>99)	-	16 600	209
		6@SBA-15 (50 ppm)	79 (>99)	-	15 800	99
2	**14** (NTs)	4@MOF (50 ppm)	86 (>99)	-	17 200	320
		6@MOF (50 ppm)	58 (>99)	-	11 600	160
		4@SBA-15 (20 ppm)	54 (>99)	-	27 000	1498
		6@SBA-15 (20 ppm)	51 (>99)	-	25 500	1528
3	**16**	4@SBA (50 ppm)	29 (99)	3.3	5 800	116
		6@SBA (50 ppm)	27 (99)	3.2	5 600	77
		4@MOF (100 ppm)	65 (99)	4.6	6 500	203
		6@MOF (100 ppm)	60 (99)	4.1	6 000	93
		4@SBA (100 ppm)	48 (98)	4.5	4 800	nd
		6@SBA (100 ppm)	44 (98)	4.3	4 400	nd
4	**18**	4@MOF (50 ppm)	57 (>99)	3.8	11 400	207
		6@MOF (50 ppm)	46 (>99)	3.2	9 200	33
		4@SBA (50 ppm)	50 (>99)	3.2	10 000	242
		6@SBA (50 ppm)	51 (>99)	3.2	10 500	211
		4@SBA (100 ppm)	100 (>99)	3.9	10 000	nd
		6@SBA (100 ppm)	100 (>99)	4.0	10 000	nd
5	**20** (BnO)	4@MOF (250 ppm)	70 (96)	11.8	2 800	87
		6@MOF (250 ppm)	68 (95)	10.1	2 700	40
		4@SBA (250 ppm)	38 (4)	6.1	750	5
		6@SBA (250 ppm)	34 (3)	5.3	670	6

[1] Conditions: substrate (1 M) in toluene, 50 °C, 24 h. [2] Conversions and yields were calculated based on internal standard (1,2,4,5-tetramethylbenzene, durene) using theoretical response gas chromatography (GC) factors method [32]. Selectivity = yield/conversion × 100%. [3] Turnover frequency (TOF) was measured after 30 min. nd = not determined.

2.6. Probing the Boomerang Existence

To understand the processes ongoing inside the solid support during the course of metathesis, we performed the following experiment (Figure 8). Using a hybrid catalyst composed of **4** (5 wt %) and 10 equiv. of **5** immobilized in MOF, the RCM reaction of **12** (1 mol % of Ru, toluene, 50 °C, 1 h) was conducted. This RCM reaction was repeated twice (with 3 mL toluene wash between cycles), then the MOF-adsorbed organometallic complexes were washed out from the support using methanol, and the collected solution was concentrated and analyzed directly by HPLC. The same experiment was repeated using an SBA-15 supported **4** containing 10 equiv. of **5**. The composition of organometallics washed out from SBA-15 was also analyzed by HPLC and the results are presented in Figure 9. It seems that in the RCM reaction in MOF some ligand scrambling took place, as the material washed out from the support consisted of ca. 1:1 mixture of **4** and **6** (so: **4** + **5** → **6**, Figure 9b), while initially only complex **4** and styrene **5** were loaded on the support. HPLC analysis of the organometallic material washed out from the SBA-15 hybrid catalyst divulged **4** and **6** in proportion 5:95. This result shows that almost all **4** initially present in the support was converted during the course of metathesis reaction into **6** (Figure 9c), thus strongly suggesting the existence of the boomerang process.

We were, of course, aware of the possibility that **6** may be prepared during the impregnation of the support with a solution of **4** and 10 equiv. of **5** in DCM, before the RCM reaction shown in Figure 8 was made, thus forming a false positive. A clarification experiment was therefore conducted consisting of washing out the organometallic complexes from the support with methanol 30 min after the impregnation. Analysis of the extracts showed no formation of **6** in both cases (for MOF and for SBA-15). In the second blind test, the material consisting of **4** and 10 equiv. of **5** immobilized on the support was heated in toluene at 50 °C for 3 h (so, under the same conditions as the RCM reaction, but in the absence of diene **12**). After washing out organometallic complexes from the support, again, **6** was not observed in the extract (so: **4** + **5** ↛ **6**; see Supplementary Materials for details). Finally,

we considered the possibility that the exchange between **4** and **5** might occur during the prolonged handling of the methanol solutions of washed-out organometallic complexes after the RCM reaction (Figure 8). To check this possibility, we mixed **4** and 10 equiv. of **5** in methanol and stirred the resulting solution for 3 h at room temperature followed by evaporation of the solvent. Once again, this process did not yield any amount of complex **6**.
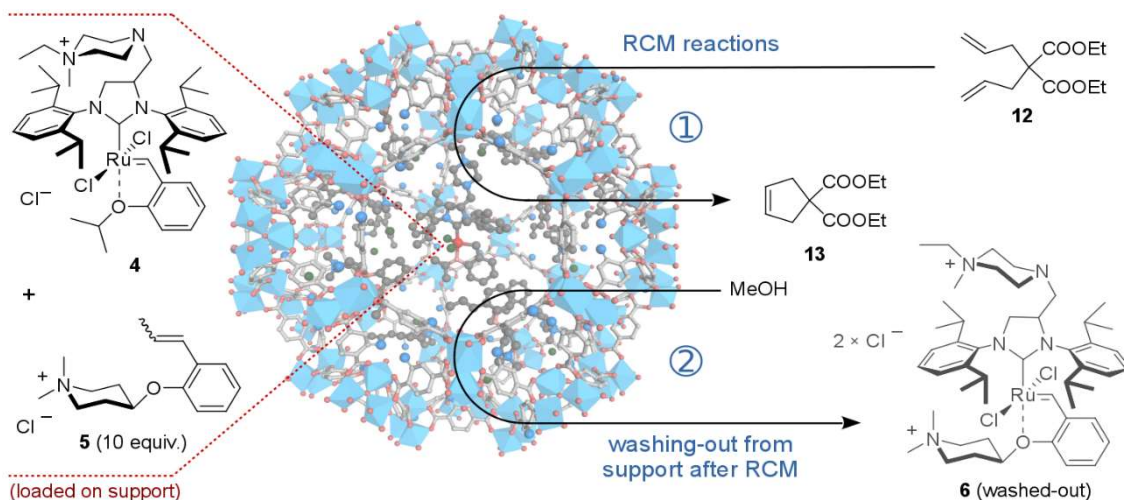

Figure 8. Ligand scrambling during the course of olefin metathesis: (1) RCM reactions carried out with hybrid catalyst composed of **4** and 10 equiv. of **5** on MOF. (2) Ru complexes are washed out from MOF after RCM reactions are done. The same experiment was also done with (**4** + **5**)@SBA-15 system, see discussion in the text.
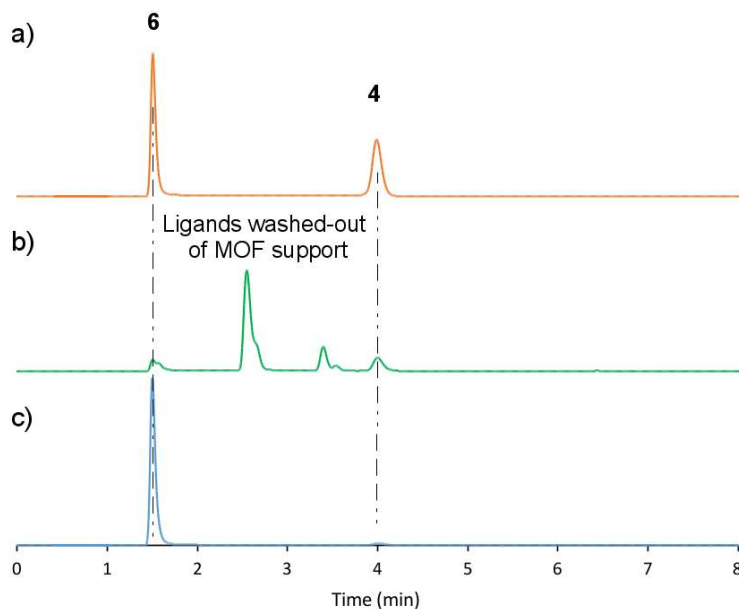

Figure 9. HPLC analysis of mixtures washed-out from supports after RCM reactions. (**a**) Reference mixture of **6** and **4** showing its separation on HPLC column; (**b**) Chromatogram of mixture washed out from MOF-based catalyst used in RCM reactions; (**c**) Chromatogram of mixture washed out from SBA-15-based catalyst used in RCM reactions.

Although we have no direct definite proof for the boomerang inside pores of the support, we think that the above experiments suggest the existence of the ligand exchange ongoing exclusively during the catalysis.

3. Materials and Methods

3.1. General

Reactions requiring the use of a protective atmosphere were conducted using Schlenk technique in either Schlenk flasks or 4 mL vials, which were dried at 130 °C for at least 12 h prior to use. All metathesis reactions and sorption of the catalysts were carried out in vials equipped with magnetic stirrers. Purging vials with argon was performed after closing them with a screw cap with a septum and piercing it with a needle connected to a Schlenk line.

Commercially available (HPLC grade) dichloromethane (DCM), tetrahydrofuran (THF), diethyl ether, toluene, and *n*-hexane were purified using solvent purification system MBRAUN SPS-800 and stored in ampules under argon over activated 4 Å molecular sieves for at least 12 h prior to use. Water content was measured with Karl Fisher apparatus (Titroline® 7500 KF trace) and did not exceeded 2 ppm in each case. DMF (anhydrous), pyridine (anhydrous), *n*-heptane, and MeOH were purchased from Sigma Aldrich and used as received. *n*-Hexane, EtOAc, and DCM for column chromatography were purchased from Avantor Performance Materials Poland S.A. and distilled prior to use.

Substrates **12** [33], **14** [34], **18** [35], and **20** [36] were prepared according to literature procedures. Substrate **16** was supplied by Sigma Aldrich. All substrates were freeze-pump-thaw degassed and stored under argon over activated 4 Å molecular sieves for at least 12 h prior to use. MOF (Al)MIL-101-NH_2 was synthesized according to literature procedure [23], activated in 130 °C under the reduced pressure of an oil pump and stored in a Schlenk flask in an argon atmosphere. Ruthenium catalysts were prepared using a known literature procedure [15] or stated in Section 3.2, stored in argon atmosphere, and refrigerated at 4 °C. Unless otherwise noted, all common laboratory reagents (NaOH, KOH, Na_2SO_4, $MgSO_4$, KI, NaCl, NH_4Cl, HCl, H_2SO_4, Na_2CO_3, $NaHCO_3$) were purchased from Avantor Performance Materials Poland S.A. and used as received. Aluminum oxide (Neutral, Brockmann grade I) was purchased from Sigma Aldrich and activated by heating for at least 3 days at 200 °C prior to use. SnatchCat^{TM} metal scavenger was synthesized according to known literature procedure [37] and used as 4.5 mM solution in DCM. Silica gel 60 (230–400 mesh) was purchased from Merck and used as received. Sodium hydride (60% in mineral oil) was purchased from TCI Chemicals and used as received. Molecular sieve 13X and mesoporous SBA-15, <150 μm particle size, pore size 8 nm, hexagonal pore morphology were purchased from Sigma Aldrich and activated by heating for 24 h at 200 °C under the reduced pressure of an oil pump and stored in an argon atmosphere.

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). GC-MS analyses were performed by means of PerkinElmer Clarus 680 chromatograph with Mass Spectrometer Clarus SQ 8C detector and GL Sciences InertCap 5MS/Sil Capillary Column (inner diameter 0.25 mm, length 30 m, df 0.50 μm).

NMR spectra were recorded on an Agilent 400-MR DD2 400 MHz spectrometer. NMR chemical shifts are reported in ppm with solvent residual peak as a reference (7.26 and 77.16 ppm for ^{1}H and ^{13}C in $CDCl_3$, respectively; 4.87 and 49.00 ppm for ^{1}H and ^{13}C in CD_3OD, respectively). Deuterated solvents (chloroform, methanol) were purchased from Euroisotop, stored over molecular sieves and used without further purification. The following abbreviations were used in reporting NMR data: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sex (sextet), sep (septet), m (multiplet), br (broad). ^{1}H NMR signals were given followed by multiplicity, coupling constants J in Hertz, and integration in parentheses.

Elemental analyses (EA) were provided by the EA analytical laboratory at the Institute of Organic Chemistry, Polish Academy of Sciences (PAS).

High-resolution mass spectra (HRMS) were provided by the Faculty of Chemistry at the University of Warsaw or the analytical laboratory at the Institute of Organic Chemistry, PAS.

UV–Vis spectra were collected with Thermo Fisher Scientific Evolution 300 UV–Vis spectrometer in 10.00 mm QS cuvettes with scan speed 600 nm/min, range 300–500 nm, bandwidth 1 nm, and data interval 1 nm.

All powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Discover X-ray diffractometer (CuK$_\alpha$ radiation, parallel beam formed by Goebel mirror) equipped with a VANTEC 1 position sensitive detector. All measurements were performed on standard aluminum holders.

For measurement of N$_2$ sorption isotherms, samples were thermally activated and degassed immediately prior to the N$_2$ physisorption measurements for at least 12 h at 80 °C. The nitrogen sorption isotherms were determined at liquid nitrogen temperature (77 K) using Micrometrics ASAP 2020 or Quantachrome Autosorb-IQ-MP sorption analyzer. The specific surface areas were calculated according to the Brunauer–Emmett–Teller (BET) method using P/P$_0$ values in the range 0.05–0.2.

3.2. Synthesis of Complexes *11* and *6*

Synthesis of complex **11**: NHC precursor **9** (466 mg, 0.771 mmol, 1.15 equiv.) was dried under vacuum at 60 °C for 1 h, suspended in toluene (2 mL), and treated with potassium tert-amylate in toluene (1.7 M, 200 μL, 0.704 mmol, 1.05 equiv). A turbid carbene adduct solution was formed over 10 min at ambient temperature. Then Grubbs 1st Generation Catalyst (551 mg, 0.67 mmol, 1 equiv.) was added and the mixture was stirred at 80 °C. The solution turned dark red over 20 min and then **8** (341 mg, 1.47 mmol, 2.2 equiv.) was added in toluene (2 mL) followed by the addition of CuCl (168 mg, 1.68 mmol, 2.5 equiv.). The solution turned dark green over 15 min with the formation of brown precipitate. The mixture was then cooled down to RT, filtered through a celite pad, evaporated, and the product was isolated using column chromatography (silica, 0–5% gradient of NEt$_3$/EtOAc). The green fractions were evaporated yielding dark green oil, which was again purified by column chromatography (neutral alumina, 5–20% EtOAc/hexane). The pure fractions were combined and evaporated, yielding crude green crystalline product (205 mg, 0.23 mmol, 34%) which was immediately used in the next step without further purification.

Synthesis of complex **6:** At −78 °C an excess of liquid MeCl was transferred into a glass pressure-resistant ampule previously cooled down to −78 °C. Then complex **11** (205 mg, 0.23 mmol, 1 equiv.) was added and dissolved. The vessel was closed and put in a heated bath at 60 °C for 48 h. During the process, a precipitation was observed. After 48 h the ampule was cooled down to ambient temperature and excess MeCl was evaporated. The crude product was purified by column chromatography (acidic activated alumina, gradient 0–5% MeOH/DCM). The pure fractions were combined, evaporated, and dried under vacuum, yielding green hygroscopic product (149 mg, 0.15 mmol, 65%).

3.3. Catalysts and Ligand Immobilization

In an oven-dried and purged with argon vial, closed with a screw cap containing a magnetic stirrer, MOF (Al)MIL-101-NH$_2$ was weighted (100 mg). Then 1 M solution of HCl in anhydrous diethyl ether was added (2 mL). The suspension was sonicated and then stirred at RT for 0.5 h. After that, the vial was centrifuged, the solvent was removed, and the MOF was left to dry for several minutes under vacuum. Mass of the MOF increased to 120 mg because of HCl accumulation. After that, the stock solution of catalyst in DCM was added (0.59 mg of the catalyst, concentration 1 mg/mL). In the case of experiments with the addition of **5**, the previous was followed by the addition of a stock solution of **5** (concentration 10 mg/mL, quantity dependent on the catalyst/**5** ratio). The vial was sonicated and stirred for 1 h. Then it was centrifuged, the solvent was removed, and the catalytic material was left to dry under vacuum overnight. Catalyst@MOF was obtained as yellow powder (ca. 120 mg, 0.5 wt % of the catalyst). The same procedure was used for SBA-15 and 13X and supports omitting the HCl treatment. Prepared materials with catalyst can be stored refrigerated under argon atmosphere for at least a month without a significant decrease in catalytic activity.

3.4. Catalysis

Homogeneous reactions: In a 4 mL vial covered with a septum cap and purged with argon (3×), 0.5 M solution of substrate with internal standard (0.05 M durene) in toluene or DCE (1 mL) was placed followed by the addition of a stock solution of the catalyst (concentration 1 mg/mL, ca. 50 μL, the amount corresponding to 50 ppm loading of the catalyst). The reaction was stirred at 50 °C for 24 h. After that, 1 mL of 4.5 mM solution of SnatchCat^{TM} in DCM was added, and the conversion was measured by GC.

Heterogeneous reactions: to a 4 mL vial, equipped with a magnetic stirrer, catalytic material (the mass of the material was determined by catalyst to substrate ratio; catalyst loading on the support was 0.5 wt %)was weighted (on air). The vial was purged with Ar (3×) which was realized by closing it with a screw cap with a septum and piercing it with a needle connected to a Schlenk line. Then 1 mL of 1 M substrate solution in toluene (1 mmol) with internal standard (0.1 M durene) was added and mixed at 50 °C for 24 h. The catalytic material was filtered off and the conversion determined by GC analysis. TOF was calculated after 30 min by taking a sample from the reaction and SnachCat^{TM} was added to stop the reaction.

4. Conclusions

Two ammonium-tagged homogeneous Ru-benzylidene catalysts: the commercially available FixCat™ (**4**) and new double-tagged **6** were immobilized on solid supports such as 13X, metal organic framework (MOF), and SBA-15. Such obtained heterogeneous systems were tested in a model ring-closing metathesis (RCM) reaction of diene **12** (DEDAM). The initial results showed that the 13X-based catalyst is the least productive in olefin metathesis. Two remaining hybrid materials, based on MOF and SBA-15, were doped with various amounts of an ammonium-tagged styrene derivative **5**—a precursor of a benzylidene ligand—in order to enhance pre-catalyst regeneration via the so-called release-return "boomerang" mechanism. The ligand scrambling experiments suggested, indeed, that during the RCM reaction the boomerang effect can exist inside a solid support. At the same time, it was observed that non-doped catalysts give better results in terms of resulting turnover number (TON) values than systems loaded with additional amounts of ligand precursor **5**. The most productive were the hybrid catalysts composed of 4@MOF, **4**@SBA-15, and **6**@SBA-15. Using these heterogeneous catalysts, a small set of model metathesis substrates were transformed reaching TON values up to 27,000.

Author Contributions: Investigation, MOF preparation, visualization, supervision, A.C.; investigation, synthesis of compounds **5** and **6**, model experiments with MOF, W.N.; investigation, model reactions with SBA-15 and 13X, M.P.; investigation, optimization, boomerang studies, visualization, P.K.; discussion and review, M.J.C.; supervision, writing—original draft preparation, review and editing, A.K. and K.G. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest. K.G. is an advisory board member of the Apeiron Synthesis company, the producer of catalyst **4**.

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