

# Ru-Based Complexes with Quaternary Ammonium Tags Immobilized on Mesoporous Silica as Olefin Metathesis Catalysts

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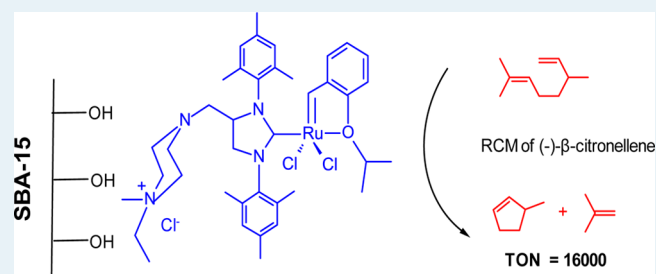
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## S Supporting Information

**ABSTRACT:** Ruthenium olefin metathesis catalysts bearing a polar quaternary ammonium group in N-heterocyclic ligand were immobilized on silica and siliceous mesoporous molecular sieves with different pore sizes (SBA-15 and MCM-41). The activity of the heterogeneous catalysts was found to increase with an increase in pore size of the support used, with the best results observed for SBA-15-supported catalyst. The influence of reaction conditions (temperature, solvent, catalyst, and substrate concentration) on the efficiency of new heterogeneous catalysts was established. A significant influence of the counterion present in the ruthenium complex on the activity of immobilized catalysts was also found: those derived from chloride containing ion exhibited the highest activity. High activity in ring-closing metathesis of substrates as citronellene, 1,7-octadiene, and diallyl compounds as well as in cross-metathesis of unsaturated aliphatic compounds with methyl acrylate was observed under optimized conditions. In some cases, heterogenization led to catalysts with efficiency higher than those observed for corresponding homogeneous complexes.

**KEYWORDS:** olefin metathesis, heterogeneous catalysts, mesoporous molecular sieves, catalyst immobilization, ruthenium



## 1. INTRODUCTION

Formation of new C=C bonds via olefin metathesis is an extremely important and useful step in many areas of modern chemistry, including industrial transformations.<sup>1</sup> Inexpensive, poorly defined heterogeneous catalysts (supported W, Mo, and Re oxides) proved to be useful tools in the processing of simple alkenes in continuous flow mode.<sup>2</sup> Those materials, however, suffer from low functional group tolerance.<sup>3</sup> Development of stable and well-defined Ru-based homogeneous catalysts with high activity and excellent functional group tolerance produced the real breakthrough in the synthesis of complex molecules.<sup>4</sup> Today, a vast array of ruthenium complexes such as Grubbs and Hoveyda–Grubbs alkylidenes **GII**, **HGII**, and **HGIIN**<sup>+</sup>**Cl**<sup>−</sup> (Chart 1) are commercially available, facilitating the dissemination of metathesis technology. In the synthesis of several simple as well as highly functionalized molecules containing a C=C bond, metathesis has already been established as a methodology of choice.

Despite the undeniable advantages, homogeneous catalysts have some drawbacks such as (i) difficult catalyst separation, (ii) possible contamination of products with heavy metal residue, and (iii) difficult control of the contact time between catalyst and alkenes. In some cases, the last issue can cause a certain decrease in reaction selectivity, which is highly undesirable, especially when an industrial process is consid-

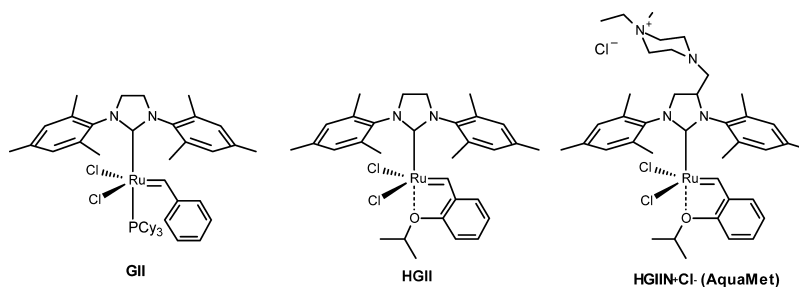
ered.<sup>5</sup> All these handicaps can be circumvented by the application of well-defined heterogeneous catalysts preferably in continuous flow (CF) mode.<sup>6,7</sup> Several methodologies for heterogenization of originally homogeneous catalysts have been developed. These methods include catalyst immobilization mainly through (i) a phosphine or benzylidene ligand, (ii) an anionic ligand, and (iii) an N-heterocyclic ligand (NHC).<sup>8</sup> In most cases, obtained heterogeneous catalysts provided products with a low ruthenium level.<sup>9</sup> However, usually the lower activity [slow initiation rate, low turnover frequency (TOF)] and efficiency [low turnover number (TON)] of these heterogeneous catalysts in comparison with those of their homogeneous analogues,<sup>10</sup> and more importantly their rather complicated synthesis, limit practical applications of such materials. An alternative method of heterogenization was described by Jacobs et al., who immobilized commercially available Hoveyda–Grubbs catalyst **HGII** on silica gel via physisorption.<sup>11</sup> Subsequently, a similar concept was reported and used by others who deposited commercially available catalysts on silica and different porous supports.<sup>5a,b,12</sup> In particular, mesoporous molecular sieves—siliceous materials with regular architectures,

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Chart 1. Examples of Commercially Available Second-Generation Ru Complexes (Cy = cyclohexyl)



large surface areas, and pore sizes in the mesopore region,<sup>13</sup> are known as superior supports for transition metal-based complexes, including metathesis catalysts.<sup>14</sup> Similarly, two-dimensional zeolites offer interesting properties for immobilization.<sup>15</sup> Catalyst **HGII** deposited on mesoporous MCM-41 (**HGII/MCM41**) exhibited good efficiency in ring-opening/ring-closing (RO-RCM) metathesis of cyclooctene.<sup>5a</sup> This transformation represents one of the shortest routes to macrocyclic skeletons, and therefore, it is highly attractive for industry. Importantly, RO-RCM of cyclooctene was significantly more selective with **HGII/MCM41** in continuous flow mode than in a batch reactor with **HGII** catalyst. Unfortunately, weak interactions of ruthenium complexes with a support in this kind of heterogeneous catalyst prevent their application in a polar medium, because of the possible high rate of leaching of metal-containing species. Thus, only nonpolar solvents, such as cyclohexane, can be used, and polar substrates should be avoided (even methyl oleate can cause an increased level of ruthenium leaching).<sup>5b</sup>

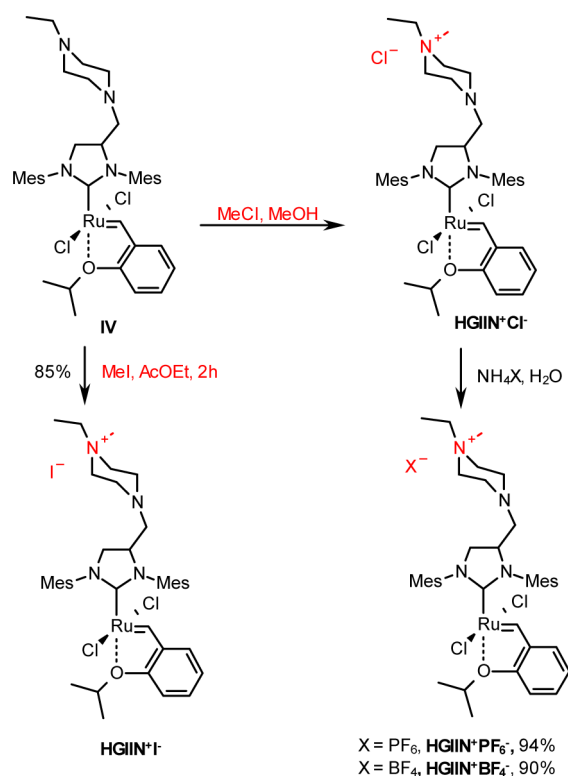
Undoubtedly, heterogeneous catalysts that would be easily available in large quantities and could be used with a broad spectrum of solvents and substrates, including polar ones, are in great demand. Therefore, in this work, we report new heterogeneous catalysts prepared by simple deposition of a commercially available **HGIIN<sup>+</sup>Cl<sup>-</sup>** catalyst and its analogues with different counterions on solid supports (ordinary silica and mesoporous molecular sieves MCM-41 and SBA-15). Systematic study of the effect of the support, counterions, and reaction conditions on the catalyst activity and efficiency as well as the scope of catalyst applications is reported. We assumed that noncovalent but very strong interaction of the ammonium group present in **HGIIN<sup>+</sup>X<sup>-</sup>** type catalysts with surface silanol groups of the siliceous materials will prevent catalyst leaching even during metathesis conducted in polar systems. Applications of mesoporous molecular sieves as supports were expected to increase the activity of prepared catalysts by enhancing the rate of diffusion of reactants as well as products formed.

## 2. EXPERIMENTAL SECTION

**2.1. Materials and Techniques.** Siliceous SBA-15 and MCM-41 were prepared according to the literature methods.<sup>16</sup> The conventional silica (silica gel 40) was purchased from Merck. Toluene (Lach-Ner) was dried for 12 h over anhydrous Na<sub>2</sub>SO<sub>4</sub>, then distilled with Na, and stored over molecular sieves type 4A. Dichloromethane (Lach-Ner) was dried for 12 h over anhydrous CaCl<sub>2</sub> and then distilled with P<sub>2</sub>O<sub>5</sub>. Tetrahydrofuran was dried for 12 h with molecular sieves type 4A and then distilled with Na and benzophenone. Distillation started when the color of THF in the distillation

flask changed to dark blue. All dry solvents were distilled and stored under Ar. Ethyl acetate (Aldrich, 99.9%), (–)-β-citronellene (Aldrich, purity of ≥90%), 1,7-octadiene (Fluka, purity of ≥97%), *N,N*-diallyl-2,2,2-trifluoroacetamide (Aldrich, 98%), and methyl oleate (Research Institute of Inorganic Chemistry, a.s., Czech Rep., purity of 94%, with methyl palmitate, methyl stearate, and methyl linolate being the main impurities) were used after being passed through a column filled with activated alumina. Substrates **10–12**, **14**, and **15** were prepared according to the literature methods and purified by silica gel column chromatography. Freshly distilled methyl acrylate **13** was used for CM reactions. **HGIIN<sup>+</sup>Cl<sup>-</sup>** is commercially available from Apeiron Catalysts (as AquaMet). **HGIIN<sup>+</sup>I<sup>-</sup>** was prepared by alkylation of tertiary amine-containing complex **IV** with methyl iodide (*vide infra*, Scheme 1). **HGIIN<sup>+</sup>PF<sub>6</sub><sup>-</sup>** and **HGIIN<sup>+</sup>BF<sub>4</sub><sup>-</sup>** were prepared by dissolving **HGIIN<sup>+</sup>Cl<sup>-</sup>** in water followed by precipitation of the desired catalysts with an aqueous solution of either ammonium hexafluorophosphate or ammonium tetrafluoroborate and filtration. Details of catalyst preparation are given in the Supporting Information.

Scheme 1. Synthesis of Catalysts with Different Counterions



Textural parameters of supports and catalysts were determined using nitrogen adsorption isotherms at  $-196\text{ }^{\circ}\text{C}$  with a Micromeritics ASAP 2020 instrument. All the materials were degassed before adsorption was measured using a temperature program from ambient temperature to  $110\text{ }^{\circ}\text{C}$  (heating ramp of  $0.5\text{ }^{\circ}\text{C}/\text{min}$ ) until a residual pressure of  $1\text{ Pa}$  was reached. The sample was degassed at this temperature under turbomolecular pump vacuum for 8 h. X-ray powder diffraction (XRD) data were obtained on a Bruker AXS D8 Advance diffractometer with a graphite monochromator and a Vântec-1 position sensitive detector using  $\text{Cu K}\alpha$  radiation (at  $40\text{ kV}$  and  $30\text{ mA}$ ) in Bragg–Brentano geometry.

The X-ray photoelectron spectra of the catalyst were measured using a modified ESCA 3 MkII multitechnique spectrometer equipped with a hemispherical electron analyzer operated in a fixed transmission mode. Al  $\text{K}\alpha$  radiation was used for electron excitation. The binding energy scale was calibrated using the Au  $4f_{7/2}$  ( $84.0\text{ eV}$ ) and Cu  $2p_{3/2}$  ( $932.6\text{ eV}$ ) photoemission lines. The pressure in the X-ray photoelectron spectroscopy (XPS) analysis chamber during spectra acquisition was  $6 \times 10^{-9}\text{ mbar}$ . The samples were spread on an aluminum surface. The spectra were collected at a takeoff angle of  $45^{\circ}$  with respect to the macroscopic surface normal. Survey scan spectra and high-resolution spectra of overlapping Ru  $3d + \text{C } 1s$  photoelectrons, and N  $1s$ , Cl  $2p$ , I  $3d$ , and F  $1s$  photoelectrons were measured. The spectra were curve fit after subtraction of the Shirley background<sup>17</sup> using the Gaussian–Lorentzian line shape and nonlinear least-squares algorithms. Quantification of the elemental concentrations was accomplished by correcting the photoelectron peak intensities for their cross sections<sup>18</sup> and for the analyzer transmission function. The typical error of quantitative analysis by XPS is  $\sim 10\%$ .<sup>19</sup>

The determination of ruthenium content was performed by inductively coupled plasma mass spectrometry (ICP-MS) by the Institute of Analytical Chemistry (ICT, Prague, Czech Republic). The estimation error was 5%.

**2.2. Immobilization of Ruthenium Complexes.** Preparation of catalyst  $\text{HGIIN}^+\text{Cl}^-/\text{SBA-15}$  was performed in  $\text{CH}_2\text{Cl}_2$  at room temperature under an argon atmosphere. In a typical procedure,  $1000\text{ mg}$  of SBA-15 (calcined at  $300\text{ }^{\circ}\text{C}$  for 3 h) was suspended in  $15\text{ mL}$  of  $\text{CH}_2\text{Cl}_2$  in a Schlenk tube prior to addition of  $103\text{ mg}$  of  $\text{HGIIN}^+\text{Cl}^-$ , and the mixture was stirred for 3 h at  $25\text{ }^{\circ}\text{C}$ . The liquid phase was decanted, and the product was washed under argon with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 10\text{ mL}$ ). Traces of  $\text{CH}_2\text{Cl}_2$  were removed on a rotavapor and by drying of  $\text{HGIIN}^+\text{Cl}^-/\text{SBA-15}$  on high vacuum at room temperature for 1 h (see Table S1 of the Supporting Information for details). The preparation of  $\text{HGIIN}^+\text{Cl}^-/\text{MCM-41}$ ,  $\text{HGIIN}^+\text{Cl}^-/\text{silica}$ , and  $\text{HGIIN}^+\text{X}/\text{SBA-15}$  ( $\text{X} = \text{I}^-$ ,  $\text{BF}_4^-$ , or  $\text{PF}_6^-$ ) was conducted according to the same procedure (see Table S2 of the Supporting Information for details). The catalysts were stored in dried glass tubes sealed under an argon atmosphere. All manipulations with catalysts and catalytic experiments were conducted under an argon atmosphere using the standard Schlenk tube technique.

**2.3. Metathesis Reactions.** Metathesis reactions were performed under an Ar atmosphere in a Schlenk tube equipped with a magnetic stirring bar. In a typical RCM experiment,  $10.5\text{ mg}$  of  $\text{HGIIN}^+\text{Cl}^-/\text{SBA-15}$  was placed into the reactor,  $16.6\text{ mL}$  of toluene was added, and the suspension was heated to  $60\text{ }^{\circ}\text{C}$ . Then  $452\text{ }\mu\text{L}$  of citronellene ( $500\text{ ppm Ru}$ ,  $c^0\text{I} = 0.15\text{ mol/L}$ ) was added while the mixture was being stirred. At

appropriate time intervals, samples ( $0.1\text{ mL}$ ) were taken and quenched with ethyl vinyl ether, and after centrifugation, the supernatants were analyzed by gas chromatography (GC). A high-resolution gas chromatograph (Agilent model 6890) with a DB-5 column (length of  $50\text{ m}$ , inner diameter of  $320\text{ }\mu\text{m}$ , stationary phase thickness of  $1\text{ }\mu\text{m}$ ) was used for reaction product analysis. *n*-Nonane was used as an internal standard, whenever required. Individual products (all are known compounds) were identified by gas chromatography and mass spectrometry (GC–MS) (ThermoFinnigan, FOCUS DSQ II Single Quadrupole) or by comparison with samples previously authenticated by nuclear magnetic resonance (NMR). The absolute error in the determination of citronellene conversion was  $\pm 2\%$ .

### 3. RESULTS AND DISCUSSION

**3.1. Catalyst Preparation and Characterization.** We decided to start our research with the use of the commercially available  $\text{HGIIN}^+\text{Cl}^-$  catalyst, bearing a quaternary ammonium group with a chloride counterion placed in the NHC ligand. Mesoporous supports were highly ordered and showed a narrow pore size distribution, as proven by X-ray diffraction patterns and nitrogen adsorption isotherms (Figures S1 and S2a of the Supporting Information, respectively). Addition of  $\text{HGIIN}^+\text{Cl}^-$  to the well-stirred suspension of support (calcined at  $300\text{ }^{\circ}\text{C}$  prior to use) in dichloromethane resulted in the deposition of 75–99% of the initial amount of homogeneous catalyst. The exact amount of ruthenium loaded onto supports was determined by ICP-MS and was as follows:  $\text{HGIIN}^+\text{Cl}^-/\text{SBA-15}$ ,  $1.17\text{ wt } \%$  of Ru;  $\text{HGIIN}^+\text{Cl}^-/\text{MCM-41}$ ,  $1.17\text{ wt } \%$  of Ru; and  $\text{HGIIN}^+\text{Cl}^-/\text{SiO}_2$ ,  $0.92\text{ wt } \%$  of Ru. Textural characteristics of heterogeneous materials were determined by nitrogen adsorption isotherms and are listed in Table 1.

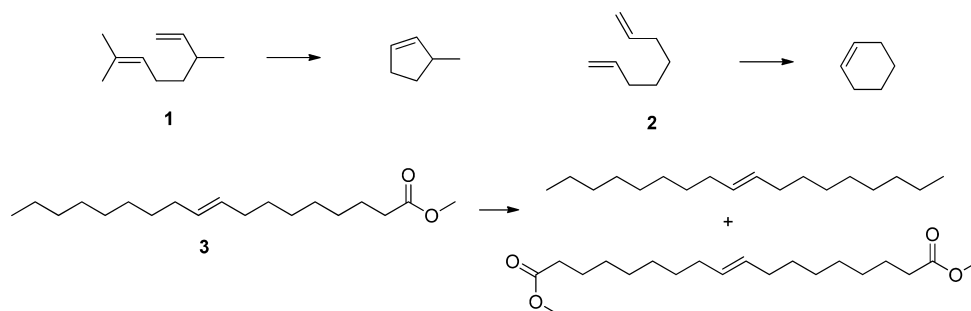
**Table 1. Textural Parameters of Supports and Catalysts**

material	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{ME}}$ ( $\text{cm}^3/\text{g}$ )	$D_{\text{ME}}$ (nm)
SBA-15	739	1.15	6.7
$\text{HGIIN}^+\text{Cl}^-/\text{SBA-15}$	492	0.92	6.6
MCM-41	972	1.14	4.0
$\text{HGIIN}^+\text{Cl}^-/\text{MCM-41}$	640	0.68	3.9
silica gel 40	559	0.47	4.6
$\text{HGIIN}^+\text{Cl}^-/\text{silica}$	387	0.45	4.5

A significant decrease in the surface area ( $S_{\text{BET}}$ ) has been observed for all materials after deposition of the ruthenium complex as in the cases described previously.<sup>20</sup> The pore volumes of SBA-15 and MCM-41 were also noticeably reduced after the immobilization of  $\text{HGIIN}^+\text{Cl}^-$  (by 20 and 40%, respectively), while the pore volume of silica gel 40 was reduced by only 4%. However, pore size diameters did not change as a result of complex immobilization, and the support architecture and narrow pore size distribution were preserved, as well (see Figure S2b of the Supporting Information).

To elucidate the effect of anion type in our systems, we decided to synthesize analogues of  $\text{HGIIN}^+\text{Cl}^-$  with different counterions. First, we prepared ruthenium complex IV (Scheme 2), bearing tertiary amine, according to the method reported previously.<sup>21</sup> Alkylation of IV with methyl iodide gave  $\text{HGIIN}^+\text{I}^-$  in 85% yield. Then, we used the good solubility of commercially available  $\text{HGIIN}^+\text{Cl}^-$  in neat water to prepare catalysts having hexafluorophosphate and tetrafluoroborate counterions. Mixing of aqueous  $\text{HGIIN}^+\text{Cl}^-$  with aqueous

## Scheme 2. Ring-Closing Metathesis and Homometathesis Studied



ammonium hexafluorophosphate or ammonium tetrafluoroborate resulted in the precipitation of  $\text{HGIIN}^+\text{PF}_6^-$  and  $\text{HGIIN}^+\text{BF}_4^-$ , respectively. New complexes were isolated by simple filtration and after drying were deposited on SBA-15 using the procedure described for  $\text{HGIIN}^+\text{Cl}^-$ . The Ru contents of these catalysts were 1.09 wt % for  $\text{HGIIN}^+\text{PF}_6^-/\text{SBA-15}$ , 1.15 wt % for  $\text{HGIIN}^+\text{BF}_4^-/\text{SBA-15}$ , and 1.12 wt % for  $\text{HGIIN}^+\text{I}^-/\text{SBA-15}$ .

To determine the surface stoichiometry of the catalysts prepared, XPS analysis was conducted. The results obtained are summarized in Table 2, where atomic concentrations of N, F,

**Table 2. Atomic Concentrations of N, F, Cl, and I Related to the Atomic Concentration of Ru for  $\text{HGIIN}^+\text{X}^-$  and  $\text{HGIIN}^+\text{X}^-/\text{SBA-15}$  ( $\text{X} = \text{Cl}, \text{PF}_6^-, \text{BF}_4^-, \text{or I}$ )**

sample	N	Cl	F	I
$\text{HGIIN}^+\text{Cl}^-$	4.2	3.0	0	0
$\text{HGIIN}^+\text{Cl}^-/\text{SBA}$	4.0	3.0	0	0
$\text{HGIIN}^+\text{BF}_4^-$	4.2	2.2	3.9	0
$\text{HGIIN}^+\text{BF}_4^-/\text{SBA}$	3.7	nm <sup>a</sup>	4.3	0
$\text{HGIIN}^+\text{PF}_6^-$	3.8	nm <sup>a</sup>	6.1	0
$\text{HGIIN}^+\text{PF}_6^-/\text{SBA}$	3.8	nm <sup>a</sup>	5.6	0
$\text{HGIIN}^+\text{I}^-$	4.0	nm <sup>a</sup>	0	0.8
$\text{HGIIN}^+\text{I}^-/\text{SBA}$	3.6	nm <sup>a</sup>	0	0.3

<sup>a</sup>Not measured.

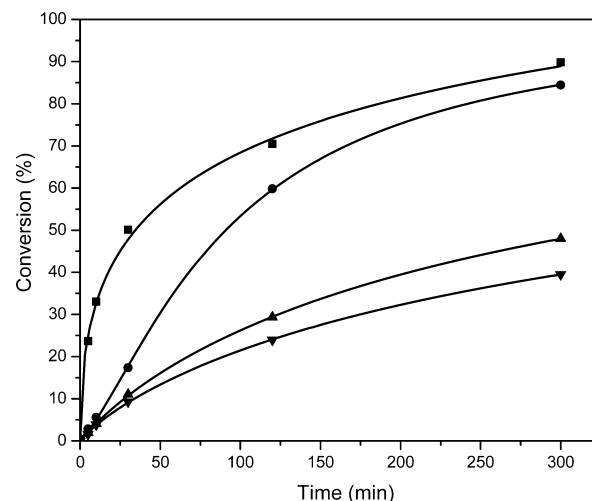
Cl, and I related to the atomic concentration of Ru are displayed for parent complexes  $\text{HGIIN}^+\text{X}^-$  and catalysts  $\text{HGIIN}^+\text{X}^-/\text{SBA-15}$  ( $\text{X} = \text{Cl}, \text{PF}_6^-, \text{BF}_4^-, \text{or I}$ ). The survey scans for measured samples are shown in Figure S3 of the Supporting Information. In agreement with the molecular structure, the spectra of N 1s photoelectrons of the measured samples revealed the presence of two different chemical states of nitrogen in a concentration ratio of 3:1 (Figure S4 of the Supporting Information) with the less intense component belonging to the positively charged nitrogen atoms. The amounts of Cl and F found in catalysts indicate anions  $\text{Cl}^-$ ,  $\text{BF}_4^-$ , and  $\text{PF}_6^-$  are present in the catalyst in an approximately 1:1 stoichiometry with respect to Ru. However, in the case of  $\text{HGIIN}^+\text{I}^-/\text{SBA}$ , the I:Ru atomic ratio of 0.3 suggests incomplete trapping of  $\text{I}^-$  on the support surface or later catalyst decomposition. This behavior may be connected with the lower electronegativity of I, but details are not clear.

Taking into account the surface stoichiometry, we assume that both the cationic and anionic parts of our catalysts are bound to the silica surface by adsorption probably with a participation of surface silanol bonds, similarly as it was proposed for tetrabutylammonium fluoride on silica.<sup>22</sup> This assumption is in accord with the dependence of catalytic

activity of our heterogeneous catalysts on the type of counteranion (*vide infra*). The details will be a subject of further study.

**3.2. Influence of Support on Catalytic Activity.** We choose  $(-)\text{-}\beta\text{-citronellene}$  (**1**), 1,7-octadiene (**2**), and methyl oleate (**3**) (Scheme 2) to determine the influence of support on the activity and efficiency of heterogeneous materials in RCM and homometathesis (HM) reactions.

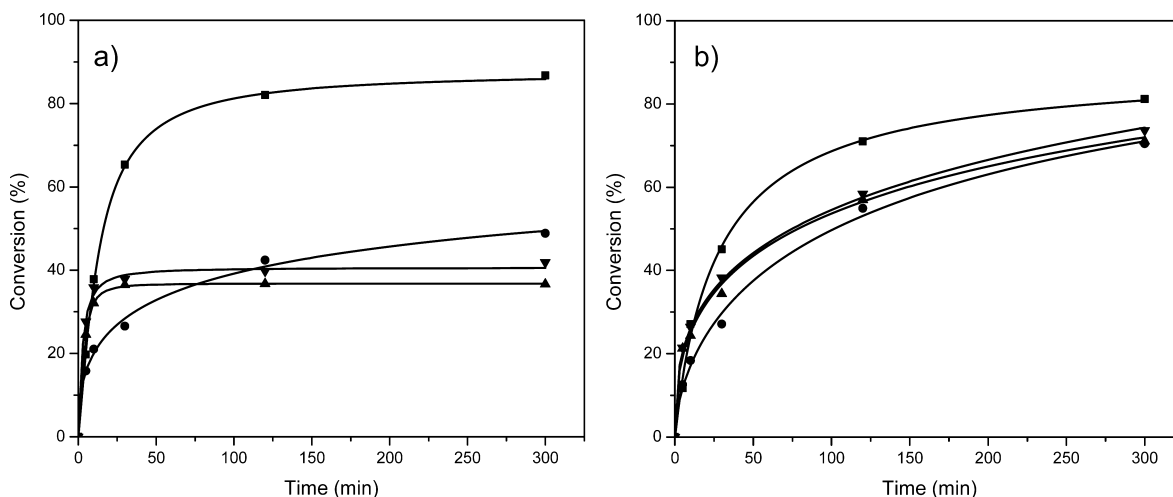
Catalytic tests were conducted in toluene at a substrate concentration of 0.15 mol/L using 500 ppm of catalyst (Ru/substrate molar ratio of 0.0005) for RCM of **1** and 4000 ppm of catalyst (Ru/substrate molar ratio of 0.004) for RCM of **2** and HM of **3**. For homogeneous reactions,  $\text{HGIIN}^+\text{Cl}^-$  was dissolved in a small amount (0.5 mL) of dichloromethane and then diluted with toluene to ensure sufficient solubility of the catalyst. In RCM of highly reactive 1,7-octadiene at 0 °C (Figure 1), the system with  $\text{HGIIN}^+\text{Cl}^-/\text{SBA-15}$  showed a



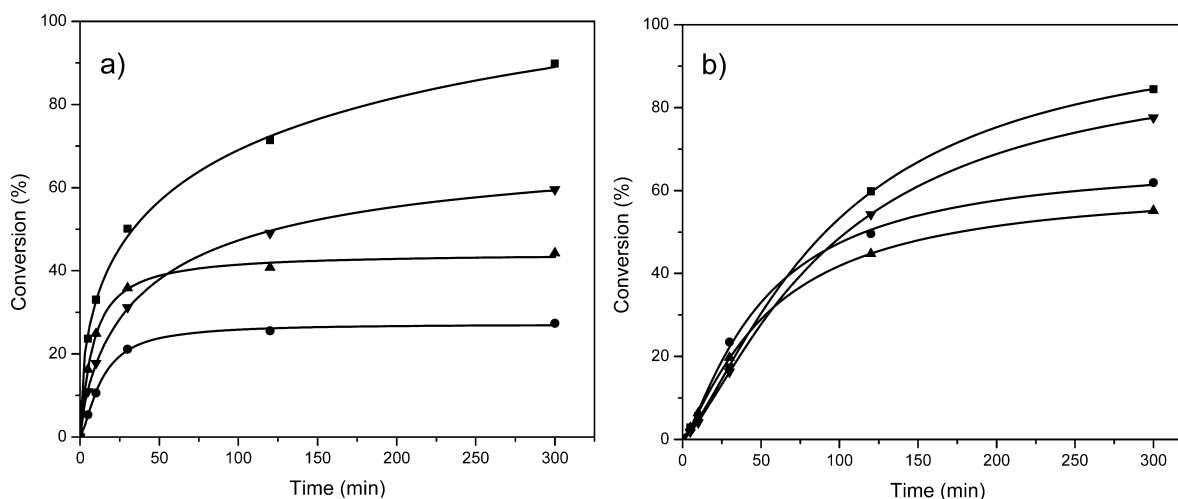
**Figure 1.** RCM of **2** with catalysts  $\text{HGIIN}^+\text{Cl}^-$  (■),  $\text{HGIIN}^+\text{Cl}^-/\text{SBA-15}$  (●),  $\text{HGIIN}^+\text{Cl}^-/\text{MCM-41}$  (▲), and  $\text{HGIIN}^+\text{Cl}^-/\text{silica}$  (▼), at 0 °C, 4000 ppm of catalyst, toluene, and  $c^0_2 = 0.15$  mol/L.

higher initial reaction rate (calculated from conversions at 30 min) than systems with  $\text{HGIIN}^+\text{Cl}^-/\text{MCM-41}$  and  $\text{HGIIN}^+\text{Cl}^-/\text{silica}$  and a final TON similar to that observed in a homogeneous reaction. Cyclohexene was found as the only product in all cases.

RCM of more challenging  $(-)\text{-}\beta\text{-citronellene}$  and HM of methyl oleate were conducted at 60 °C (see Figures S5 and S6 of the Supporting Information, respectively). Also, in these reactions, the initial reaction rates decreased with the type of catalysts in the following order:  $\text{HGIIN}^+\text{Cl}^- > \text{HGIIN}^+\text{Cl}^-/$



**Figure 2.** Influence of counterion X on conversion of **1** in RCM with HGIIN<sup>+</sup>X (a) and HGIIN<sup>+</sup>X/SBA-15 (b), at 60 °C, toluene,  $c^0_1 = 0.15$  mol/L, and 500 ppm of catalyst. X = Cl<sup>-</sup> (■), I<sup>-</sup> (●), BF<sub>4</sub><sup>-</sup> (▲), and PF<sub>6</sub><sup>-</sup> (▼).

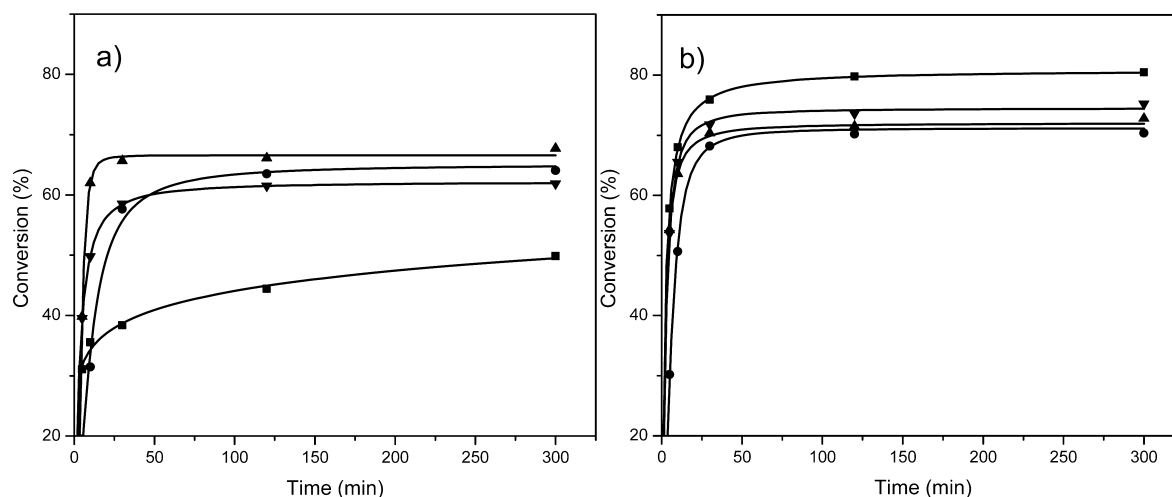


**Figure 3.** Influence of counterion X on conversion in RCM of **2** with HGIIN<sup>+</sup>X (a) and HGIIN<sup>+</sup>X/SBA-15 (b), at 0 °C, toluene,  $c^0_2 = 0.15$  mol/L, and 4000 ppm of catalyst. X = Cl<sup>-</sup> (■), I<sup>-</sup> (●), BF<sub>4</sub><sup>-</sup> (▲), and PF<sub>6</sub><sup>-</sup> (▼).

**SBA-15 > HGIIN<sup>+</sup>Cl<sup>-</sup>/MCM-41 > HGIIN<sup>+</sup>Cl<sup>-</sup>/silica.** HGIIN<sup>+</sup>Cl<sup>-</sup>/SBA-15 proved to be the most active heterogeneous catalyst, producing an initial reaction rate almost as high as that observed for homogeneous HGIIN<sup>+</sup>Cl<sup>-</sup> (33 and 10% reduction in RCM of **1** and HM of **3**, respectively). With all catalysts, reactions proceeded selectively to methylcyclopentene and dimethyl octadecenyldioate, respectively, as the only reaction products. The high activity of HGIIN<sup>+</sup>Cl<sup>-</sup>/SBA-15 can be ascribed to the relatively large pore diameter of the support not restricting mass transport. The positive effect of catalyst pore size on catalyst activity has already been observed.<sup>20,23</sup>

In the next step, we proved the heterogeneous nature of the reaction promoted by HGIIN<sup>+</sup>Cl<sup>-</sup>/SBA-15 by performing a split test during the RCM of **2** conducted at 40 °C (Figure S7 of the Supporting Information). After 5 min, the reaction mixture was split by filtration and no reaction progress was observed in the filtrate. Only 2.6% of the initial amount of Ru was washed out from the support placed in the original reactor after 5 h (which corresponds to the maximal level of 17 ppm of Ru in the product). According to the foregoing results, we choose HGIIN<sup>+</sup>Cl<sup>-</sup>/SBA-15 for further study.

Then, we checked the influence of calcination temperature of SBA-15 on Ru loading and the catalytic activity of HGIIN<sup>+</sup>Cl<sup>-</sup> immobilized on these materials. The catalyst was deposited on SBA-15 previously heated to 300, 500, and 700 °C under vacuum for 3 h, giving HGIIN<sup>+</sup>Cl<sup>-</sup>/SBA-15(300), HGIIN<sup>+</sup>Cl<sup>-</sup>/SBA-15(500), and HGIIN<sup>+</sup>Cl<sup>-</sup>/SBA-15(700), respectively. The ruthenium loading on SBA-15(300) and SBA-15(500) was 1.86 wt % of Ru (i.e., 14.8 wt % of HGIIN<sup>+</sup>Cl<sup>-</sup>). The capacity of SBA-15(700) was lower; the maximal achievable ruthenium loading was 1.32 wt % (10.49 wt % of HGIIN<sup>+</sup>Cl<sup>-</sup>), which probably originated from the decrease in the number of surface OH groups.<sup>24</sup> Catalysts were compared in RCM of **1** conducted in toluene at 60 °C (Figure S8 of the Supporting Information). Almost no differences in activity and efficiency were noted between HGIIN<sup>+</sup>Cl<sup>-</sup>/SBA-15(300) and HGIIN<sup>+</sup>Cl<sup>-</sup>/SBA-15(500) (no significant differences in initial reaction rates were observed; conversions after 5 h were 80 and 82%, respectively, with a TON of ~1600), while HGIIN<sup>+</sup>Cl<sup>-</sup>/SBA-15(700) showed a slightly lower efficiency (conversion of 72% and TON of 1440 after 5 h). Thus, we decided to continue our study using parent SBA-15 calcined at 300 °C as a support.



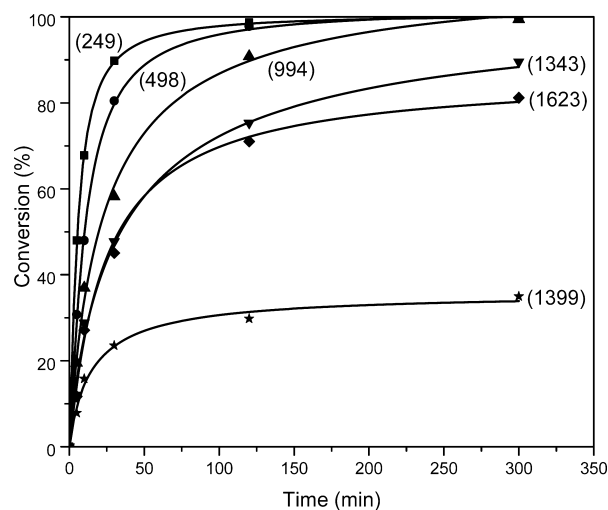
**Figure 4.** Influence of counterion X on conversion in RCM of **4** with  $\text{HGIIN}^+\text{X}$  (a) and  $\text{HGIIN}^+\text{X}/\text{SBA-15}$  (b), at 30 °C, toluene,  $c^0_4 = 0.15$  mol/L, and 4000 ppm of catalyst. X =  $\text{Cl}^-$  (■),  $\text{I}^-$  (●),  $\text{BF}_4^-$  (▲), and  $\text{PF}_6^-$  (▼).

**3.3. Influence of Counterion on Catalytic Activity.** The influence of the type of counterion on catalytic activity of ammonium-tagged ruthenium catalysts was reported by Gulajski and Grela for homogeneous olefin metathesis in neat water.<sup>25</sup> They found that a higher anion hydrophilicity led to a higher catalyst activity. However, contrary to our systems, in their catalysts ammonium tags were attached to the alkylidene ligand, which is replaced during the initiation step.

The performance of catalysts differing in the counteranion used was determined in RCM of substrates **1** and **2** and diallyltrifluoroacetamide **4** (Figures 2–4). The kind of counterion proved to have a much stronger influence on the results of homogeneous metathesis than on heterogeneous metathesis. As observed previously,  $\text{HGIIN}^+\text{Cl}^-/\text{SBA-15}$  exhibited an activity and an efficiency somewhat lower than those of homogeneous  $\text{HGIIN}^+\text{Cl}^-$  in RCM of **1** and **2**. However, all other heterogeneous catalysts were in these reactions significantly more stable and gave final conversions higher than those of their homogeneous counterparts. The reason for the observed low stability of  $\text{HGIIN}^+\text{X}$  catalysts with X = I,  $\text{BF}_4$ , or  $\text{PF}_6$  is not completely clear. The order of activity and efficiency of homogeneous catalysts with different counterions varied with different substrates tested. In particular, in RCM of **4**, the low efficiency of  $\text{HGIIN}^+\text{Cl}^-$  was repeatedly observed, which may indicate that substrate polarity may affect the stability and/or solubility of the homogeneous catalyst significantly. Results with heterogeneous catalysts seem to be more predictable because  $\text{HGIIN}^+\text{Cl}^-/\text{SBA-15}$  proved to be the best catalyst in all tested reactions, closely followed by  $\text{HGIIN}^+\text{PF}_6^-/\text{SBA-15}$ . The intriguing positive effect of heterogenization on ammonium-tagged catalyst efficiency is the subject of further research in our laboratories. The kind of counterion had no effect on catalyst selectivity: in all homogeneous and heterogeneous RCM of **1**, **2**, and **4**, methylcyclopentene, cyclohexene, and *N*-(trifluoroacetyl)-3-pyrroline, respectively, were found as the only products.

**3.4. Influence of Reaction Conditions on Catalytic Activity.** Once we proved that  $\text{HGIIN}^+\text{Cl}^-$  and  $\text{SBA-15}(300)$  make up the best ruthenium complex–support pair, we decided to check if we can increase the maximal TON in the metathesis reaction by changing reaction conditions. For this purpose, we choose RCM of **1** as a model reaction. To check what is the highest possible TON in RCM of **1** conducted under our

standard conditions (toluene,  $c^0_1 = 0.15$  mol/L, 60 °C, 5 h), we ran this reaction with the use of a varied amount of  $\text{HGIIN}^+\text{Cl}^-/\text{SBA-15}$  (Figure 5). With a decreasing amount



**Figure 5.** Influence of  $\text{HGIIN}^+\text{Cl}^-/\text{SBA-15}$  loading on conversion in RCM of **1**, in toluene,  $c^0_1 = 0.15$  mol/L, 60 °C, and 4000 (■), 2000 (●), 1000 (▲), 750 (▼), 500 (◆), and 250 ppm of catalyst (★). Maximal TONs achieved are given in parentheses.

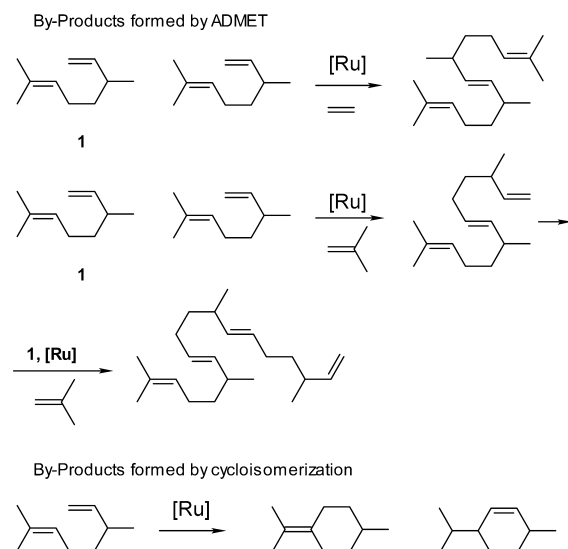
of catalyst, the initial reaction rate decreased. Full conversion of substrate was observed with catalyst loading as low as 1000 ppm (the highest achievable TON was 1000). Further reduction of the catalyst amount resulted in incomplete conversions; however, the TON increased to the maximal level (1623) when 500 ppm of catalyst was used. A 2-fold lower catalyst loading (250 ppm) gave a lower TON (1390) at only 35% of final conversion. Importantly, 100% selectivity for methylcyclopentene was achieved in all experiments.

A high TON was observed in RCM of **1**, and catalyst could be recycled when used at a low loading (Table S3 of the Supporting Information). With 4000 ppm loading of  $\text{HGIIN}^+\text{Cl}^-/\text{SBA-15}$ , four cycles of RCM of **1** were accomplished with consumption of >90% of substrate and conversion dropped to 47% in the fifth run. The cumulative TON in this experiment reached 1069. A catalyst loading of

1000 ppm allowed us to obtain a TON of 2110 in three consecutive cycles before conversion dropped below 10% in the fourth run.

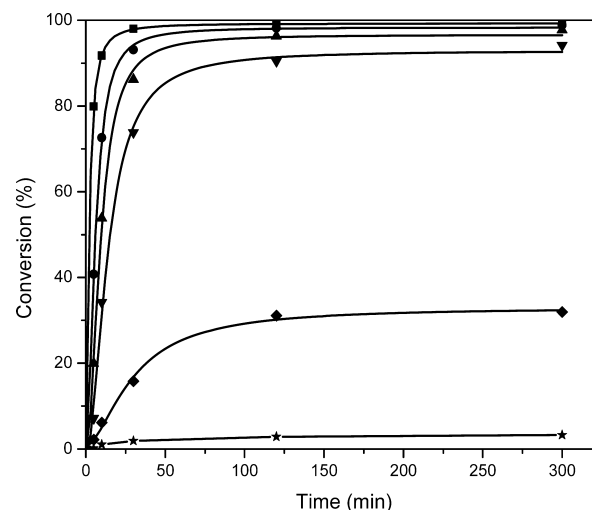
Next, we performed RCM of **1** at different substrate concentrations using a catalyst loading of 500 ppm (see Figure S9 of the Supporting Information). A significant positive effect of increasing substrate concentration on TON and especially on TOF was observed. Maximal TON and TOF in a reaction conducted at 0.15 mol/L reached 1623 (5 h reaction time) and  $0.93 \text{ s}^{-1}$  (TOF calculated after 10 min), respectively. In turn, at a concentration of 1 mol/L, a TON of 2000 (5 h) and a  $\text{TOF}_{10 \text{ min}}$  of  $3.1 \text{ s}^{-1}$  were noted. When the reaction was conducted in neat substrate, we obtained full conversion even at shorter times. Encouraged by these results, we further reduced the catalyst loading to 21 ppm in RCM of **1** conducted in neat substrate. A TON as high as 33451 was achieved with still very good conversion of 70% (see Figure S10 of the Supporting Information). Unfortunately, quantitative analysis revealed that for all reactions with neat substrate only 30% of **1** was converted into the methylcyclopentene (productive TON of  $\sim 11000$ ). Isolation of byproducts followed by GC–MS analysis allowed the identification of a dimer and two trimers formed in acyclic diene metathesis (ADMET) and two cyclic olefins, products of cycloisomerization reaction (Scheme 3).

### Scheme 3. Byproducts Detected after RCM of **1** Conducted in Neat Substrate



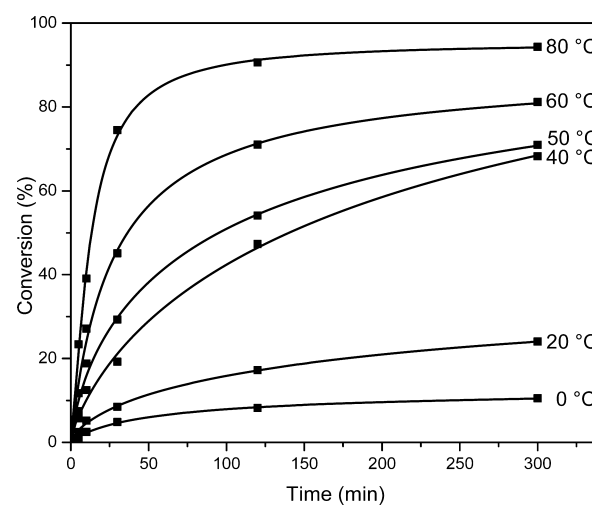
Therefore, we ran RCM of **1** at a concentration of 1 mol/L using different amounts of catalyst (Figure 6). Almost full conversion was observed after 2 h in the presence of 500–125 ppm of catalyst. Conversion in reaction promoted by only 84 ppm of  $\text{HGIIN}^+\text{Cl}^-/\text{SBA-15}$  (substrate/catalyst ratio of 12000) reached 93%, which corresponds to an excellent TON of 11300 and a very high  $\text{TOF}_{10 \text{ min}}$  of  $7 \text{ s}^{-1}$ . At  $80 \text{ }^\circ\text{C}$ , a TON as high as 16000 was achieved in this reaction. Thus, the productive TON at  $c^0_1 = 1 \text{ mol/L}$  was almost identical to that observed in a reaction run in neat substrate. Importantly, selectivity was dramatically improved as no byproducts were detected in the reaction conducted in the presence of solvent.

Interestingly, a sharp decrease in catalyst efficiency was observed when catalyst loading was further reduced from 84 to 63 ppm, and almost no activity was observed when 42 ppm of catalyst was applied.



**Figure 6.** Influence of  $\text{HGIIN}^+\text{Cl}^-/\text{SBA-15}$  loading on conversion in RCM of **1**, in toluene,  $c^0_1 = 1 \text{ mol/L}$ ,  $60 \text{ }^\circ\text{C}$ , and 500 (■), 250 (●), 125 (▲), 84 (▼), 63 (◆), and 42 ppm of  $\text{HGIIN}^+\text{Cl}^-/\text{SBA-15}$  (★).

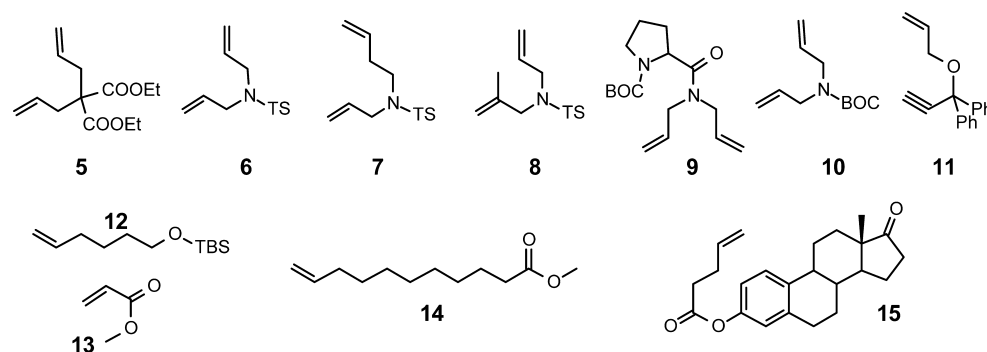
Finally, we determined the influence of temperature on TON and TOF in RCM of **1** (Figure 7). In these experiments, we



**Figure 7.** Influence of temperature on conversion in RCM of **1**, 500 ppm of  $\text{HGIIN}^+\text{Cl}^-/\text{SBA-15}$ , toluene,  $c^0_1 = 0.15 \text{ mol/L}$ , and 0, 20, 40, 50, 60, and  $80 \text{ }^\circ\text{C}$ .

kept other reaction parameters constant ( $c^0_1 = 0.15 \text{ mol/L}$ , 500 ppm of catalyst). As could be expected, the increased temperature increased the reaction rates as well as final TONs and the best result was obtained at  $80 \text{ }^\circ\text{C}$  (TON of 1880 and TOF of  $1.3 \text{ s}^{-1}$ ). Nevertheless, reasonable activity was observed at  $40 \text{ }^\circ\text{C}$ . The Arrhenius plot was linear in the studied region of temperatures, and the apparent activation energy determined from it was  $31.1 \text{ kJ/mol}$  (Figure S11 of the Supporting Information). Similar values of apparent activation energy were found for supported Hoveyda–Grubbs catalysts recently ( $42 \text{ kJ/mol}$  for methyl oleate metathesis<sup>26</sup>). A high concentration (1 mol/L) and a suitable temperature for individual substrates seem to be necessary to observe the high activity and efficiency of  $\text{HGIIN}^+\text{Cl}^-/\text{SBA-15}$ .

**3.5. Scope of the Application to Catalytic Activity.** To check the scope of the application of our heterogeneous material, we ran several RCM and cross-metathesis (CM)

Chart 2. Substrates Investigated in Olefin Metathesis over HGIIN<sup>+</sup>Cl<sup>-</sup>/SBA-15Table 3. Olefin Metathesis Reactions Catalyzed by HGIIN<sup>+</sup>Cl<sup>-</sup>/SBA-15, in Toluene at 80 °C for 1 h

entry	substrate	C (mol/L)	HGIIN <sup>+</sup> Cl <sup>-</sup> /SBA-15 (ppm)	GC conversion (%) (E/Z) <sup>a</sup>	TON	Ru (ppm)
1	5	1	500	60	1200	1.3
2	6	1	500	80	1600	7.3
3	7	1	500	60	1200	2.0
4	8	1	500	78	1560	4.5
5	9	1	500	50	1000	14
6	10	1	500	80	1600	7.5
7	10	1	250	63	2520	ND <sup>b</sup>
8	10	1	125	42	3360	ND <sup>b</sup>
9	10	neat	125	40	3200	ND <sup>b</sup>
10	11	0.15	500	8	160	30
11	11	1	500	6	120	ND <sup>b</sup>
12	11	0.15	2500	20	80	ND <sup>b</sup>
13	12 + 13 <sup>c</sup>	1	2500	91 (19/1)	364	2.8
14	14 + 13 <sup>c</sup>	1	2500	98 (19/1)	392	5.3
15	15	1	1000	51 (9/1)	510	ND <sup>b</sup>
16	15 + 13 <sup>c</sup>	1	2500	95 <sup>d</sup> (19/1)	380	6.2

<sup>a</sup>Determined by GC. <sup>b</sup>Not determined. <sup>c</sup>Four equivalents of **13** was used. <sup>d</sup>Determined by <sup>1</sup>H NMR.

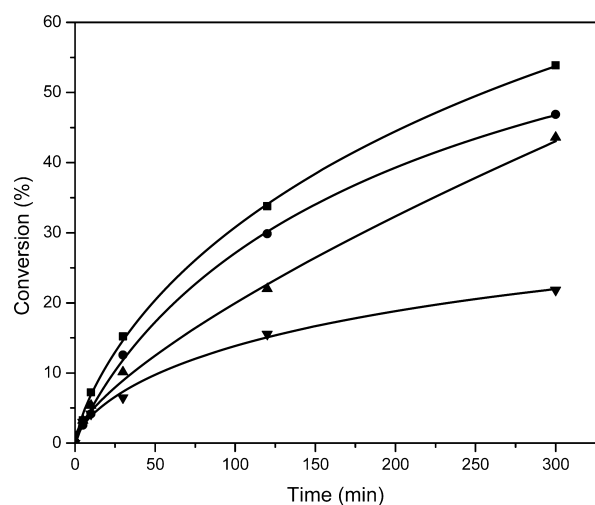
reactions as well as enyne metathesis under optimized conditions using substrates presented in Chart 2.

The results of metathesis reactions catalyzed by HGIIN<sup>+</sup>Cl<sup>-</sup>/SBA-15 are summarized in Table 3. TONs of ≤1600 were observed in RCM reactions between 50 and 80% conversion. The maximal TON achieved at 42% conversion of diene **10** was 3360 (Table 3, entry 8), and no improvement could be achieved by running the reaction in neat substrate, which might originate from less effective removal of ethylene (formed at high speed) from the reaction mixture. As one can see, TONs noted in RCM of substrates **5**–**10** were significantly lower than those observed in RCM of **1**. This may be the consequence of the formation of relatively unstable ruthenium methylidene species during the reaction between two terminal double bonds. The monomolecular decay of these ruthenium methylidenes can lead to the loss of catalytic activity.<sup>27</sup> RCM of **1** leads to the formation of more stable ruthenium isobutylene instead of ruthenium methylidene, resulting in a longer catalyst lifetime and higher TONs. Similar observations have already been reported in the literature.<sup>28</sup> The very low activity of HGIIN<sup>+</sup>Cl<sup>-</sup>/SBA-15 in enyne metathesis even at increased catalyst loading was found, and the reason for this is not clear. The results of metathesis with substrate **11** could not be improved by changing the reaction concentration or catalyst loading. On the other hand, challenging CM reactions with electron deficient methyl acrylate were accomplished with excellent conversions (91–98%) in the presence of only 2500 ppm of catalyst. It is worth noting that products of CM were

formed exclusively. Importantly, products of RCM and CM contained a very small amount of residual ruthenium, as proven by ICP-MS analysis, after separation of catalyst by simple filtration on a Schott funnel.

**3.6. Influence of Solvent on Catalytic Activity.** Being aware of a growing interest in environmentally and user-friendly solvents, we checked if HGIIN<sup>+</sup>Cl<sup>-</sup>/SBA-15 can be applied in ethyl acetate (AcOEt), which was recently reported to be an exceptionally good solvent for homogeneous metathesis.<sup>29</sup> In RCM of **1** and **2** as well as in HM of **3**, the final conversion obtained in AcOEt was very close to that observed in toluene (Figure 8 and Figures S12 and S13 of the Supporting Information). We ran these reactions also in another solvent, tetrahydrofuran (THF), and for comparison in dichloromethane (DCM), which is still typically used for metathesis. In RCM of **2**, AcOEt turned out to be a better solvent (with regard to both initial reaction rate and final conversion reached) than DCM, while in HM of **3**, the initial reaction rate and final conversion were almost the same for all solvents used except THF. The catalyst activity in THF was very low, which can be explained by coordination of ethereal oxygen to the catalytically active species.<sup>30</sup> This suggestion was supported by a separate experiment in which we stirred the catalyst in THF for 24 h prior to using it in RCM of **1** in toluene (after filtration and drying). The activity and efficiency of such HGIIN<sup>+</sup>Cl<sup>-</sup>/SBA-15 were almost the same as the activity of a fresh portion of catalyst (Figure S14 of the Supporting Information). Thus, the decreased activity in metathesis





**Figure 8.** Influence of solvent on conversion in RCM of **1**, in 500 ppm of  $\text{HGIIN}^+\text{Cl}^-/\text{SBA-15}$ ,  $c^0\text{1} = 0.15 \text{ mol/L}$ , and  $0^\circ\text{C}$ : toluene (■),  $\text{CH}_2\text{Cl}_2$  (●), ethyl acetate (▲), and THF (▼).

conducted in THF was probably not the effect of  $\text{HGIIN}^+\text{Cl}^-/\text{SBA-15}$  decomposition. The level of Ru leaching in RCM of **1** in all tested solvents was very low: 0.96, 1.04, and 0.87 wt % from the original amount of Ru used in reaction for ethyl acetate, DCM, and THF, respectively. Catalyst recycling in RCM of **1** was tested in AcOEt. As for  $\text{HGIIN}^+\text{Cl}^-/\text{SBA-15}$  in toluene (4000 ppm), four cycles were accomplished with conversions of >90% and a cumulative TON after five cycles of 1167 (see Table S3 of the Supporting Information). This result further confirms the suitability of AcOEt to serve as an alternative solvent for olefin metathesis.

#### 4. CONCLUSIONS

New heterogeneous metathesis catalysts were prepared by linker free immobilization of Hoveyda–Grubbs type alkylidenes with quaternary ammonium-tagged N-heterocyclic ligands ( $\text{HGIIN}^+\text{X}$ , where  $\text{X} = \text{Cl}^-$ ,  $\text{I}^-$ ,  $\text{PF}_6^-$ , or  $\text{BF}_4^-$ ) on silica and siliceous mesoporous molecular sieves SBA-15 and MCM-41. Depending on the support used, the catalyst activity was found to increase in the following order: silica < MCM-41 < SBA-15. The filtration test indicated the heterogeneous catalyst is fully responsible for the catalytic activity. The counteranion had a significant effect on catalyst activity in tested RCM reactions. Especially in homogeneous systems rapid deactivation leading to incomplete conversion was observed for  $\text{X} = \text{I}^-$ ,  $\text{PF}_6^-$ , and  $\text{BF}_4^-$ . Heterogenization by support on SBA-15 led to the certain stabilization, and in RCM over  $\text{HGIIN}^+\text{X}/\text{SBA-15}$ , final conversions were higher than in corresponding homogeneous systems (for  $\text{X} = \text{I}^-$ ,  $\text{PF}_6^-$ , and  $\text{BF}_4^-$ ).

$\text{HGIIN}^+\text{Cl}^-/\text{SBA-15}$ , which can be easily obtained by immobilization of  $\text{HGIIN}^+\text{Cl}^-$  on SBA-15 (both being commercially available materials), exhibited the highest activity from all heterogeneous catalysts prepared. TONs of  $\leq 3360$  in RCM of Boc protected diallylamine and  $\leq 16000$  in RCM of (–)- $\beta$ -citronellene were obtained in toluene at a substrate concentration of 1 mol/L and elevated temperatures.  $\text{HGIIN}^+\text{Cl}^-/\text{SBA-15}$  also exhibited high activity and selectivity in a series of RCM of different substrates, in homometathesis of methyl oleate, and in enyne metathesis of allyl diphenylpropargyl ether, giving rise to products with a very low content of residual Ru (<10 ppm in most cases). Worth highlighting is the

very good efficiency of  $\text{HGIIN}^+\text{Cl}^-/\text{SBA-15}$  in CM with electron deficient methyl acrylate, where TONs of 500 were achieved at conversion of >90%. Moreover, TON and TOF do not change significantly with a change in solvent from toluene to more environmentally and user-friendly ethyl acetate, in which leaching of ruthenium from support was still marginal.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

Preparation and characterization of Ru complexes, preparation of heterogeneous catalysts, XRD data and  $\text{N}_2$  adsorption isotherms, RCM conversion curves, split test, and catalyst reuse. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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##### Notes

The authors declare no competing financial interest.

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