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Ruthenium Carbenes Supported on Mesoporous Silicas as Highly Active and Selective Hybrid Catalysts for Olefin Metathesis Reactions under Continuous Flow

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Abstract: In the search for a highly active and selective heterogenized metathesis catalyst, we systematically varied the pore geometry and size of various silica-based mesoporous (i.e., MCM-41, MCM-48, and SBA-15) and microporous (ZSM-5 and MWW) versus macroporous materials (D11-10 and Aerosil 200), besides other process parameters (temperature, dilution, and mean residence time). The activity and, especially, selectivity of such “linker-free” supports for ruthenium metathesis catalysts were evaluated in the cyclodimerization of *cis*-cyclooctene to form 1,9-cyclohexadecadiene, a valuable intermediate in the flavor and fragrance industry. The optimized material showed not only exceptionally high selectivity to the valuable product, but also turned out to be a truly heterogeneous catalyst with superior activity relative to the unsupported homogeneous complex.

Keywords: cyclooligomerization • macrocycles • mesoporous materials • metathesis • ruthenium • supported catalysts

Introduction

The catalyst and reactor concepts of the bulk-chemical industry, that is, continuous processing with heterogeneous catalysts, are gaining slowly ground in the fine-chemical and pharmaceutical industry.[1] This development is also true in the field of olefin metathesis,[2] in which classical heterogeneous catalysts have been of limited applicability in pharmaceutical and fine-chemical process development[2–4] due to the either harsh reaction conditions (e.g., WO_3, $>300\,^{\circ}C$)[5] or the coactivators (e.g., tetraalkylstannanes for Re_2O_7)[6] required for the high catalytic activity of those systems. On the other hand, highly active homogeneous early-[7] or late-transition-metal carbenes[8] lack the processability and overall lifetime of classical heterogeneous catalysts,[9] and the separation of the catalyst or catalyst-deactivation products from the valuable product remains a challenge. Consequently, immobilization concepts have been developed to combine the advantages of homogeneous catalysts with those of heterogeneous metathesis catalysts.[10] Those hybrid materials are mostly based on the late-transition-metal ruthenium, albeit there are examples with early-transition-metal complexes.[11] The disadvantageous leaching of precious metal from the support[12] can partially be overcome by a covalent link between the surface and, for example, phosphine ligands,[13] N-heterocyclic carbenes (NHCs),[14] alkylidene groups,[15] or ligands that serve as surrogates for anionic ligands.[16] Thus, besides the ligands, the obligatory solid supports, that is, various polymers,[13b] silicas,[17,18c] aluminas,[18] or polymer/silica hybrids,[19] require appropriate and often laborious functionalization.

In turn, truly heterogeneous hybrid metathesis catalysts based on a weak physical interaction (i.e., in the dimension of a hydrogen-bond bridge)[20] between an unmodified organometallic ruthenium carbene species and an inorganic surface are scarce and were first reported by Sels and co-workers[20] and later others.[21] We have developed tools to identify suitable pairs of organometallic complex and inorganic support based on such a weak physical interaction,[22,23] and indeed a Grubbs/Hoveyda 2 complex supported on the commercially available macroporous silica D11-10 enabled the cross-metathesis of even polar substrates (i.e., methyl oleate) and the ring-opening/ring-closing metathesis (RO-RCM) of cycloalkenes with high catalytic turnover.[24]

RO-RCM allows the one-step assembly of macrocyclic rings, which are attractive intermediates in the flavor and fragrance industry;[3,24–26] for example, 1,9-cyclohexadecadiene would be easily available from *cis*-cyclooctene (COE; Scheme 1, $i=1$), if the intrinsic selectivity issue between polymerization and selective cyclization could be overcome in favor of a maximal selectivity in the cyclic dimer (2 mer). Ways to prevent the formation of polymers by ring-opening

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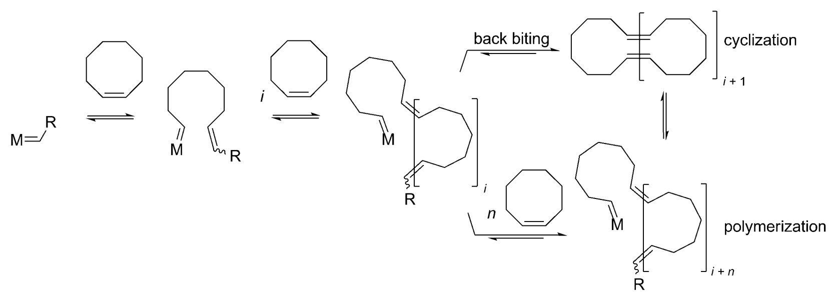


Scheme 1. Ring-chain equilibria and schematic reaction network in the RO-ROMP of *cis*-cyclooctene.

metathesis polymerization (ROMP; Scheme 1)[27] are 1) a kinetic-reaction regime as opposed to a thermodynamically driven reaction, 2) high dilution, 3) low temperature, and 4) minimal conversion, which are all detrimental conditions from a process point of view.

The positive effect of mesoporous molecular sieves on the activity of supported catalysts has already been demonstrated in the metathesis reaction[28,29] and beyond.[30] This effect is why we were interested in a systematic survey on the influence of a "linker-free" hybrid catalytic material on the selectivity in the RO-RCM of *cis*-cyclooctene to 1,9-cyclohexadecadiene. Besides various process parameters (temperature, dilution, and mean residence time (MRT)), we systematically varied the pore size and geometry of various silica-based mesoporous (i.e., MCM-41, MCM-48, and SBA-15), microporous (ZSM-5 and MWW) versus macroporous supports (D11-10 and Aerosil 200).

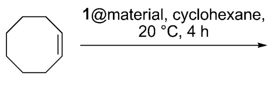
Table 1. Characterization of the materials employed in the current study.

Material	Ø [Å][a]	*V* [mL g^{-1}][a]	*A* [m^{2}g^{-1}][a]	N$_2$ BET [m^{2}g^{-1}]	[Ru] [%]	Loading [%]	Split
MCM-41[b,e]	90	0.77	364	409	0.099	96	+
MCM-41[b,e]	140	0.89	39	668	0.079	90	+
MCM-41[b,e]	160	1.70	232	313	0.083	100	+
MCM-41[b,e]	180	1.30	172	218	0.10	100	+
MCM-41[e,f]	180	3.10	235	325	0.20	95	+
MWW[c,f]	4	4.72	132	293	–	–	–
MWW[c,f]	4	4.72	132	631[g]	0.16	73	+
Alumina[f]	macro	–	–	–	0.17	81	+
ZSM-5[e]	180	0.56	67	750	0.16	76	–[h]
SBA-15[e,f]	60	9.51	408	954	0.22	100	+
Aerosil[f,i]	70	2.22	367	357	0.17	81	+
Aerosil[f,j]	95	2.58	415	343	0.20	95	+[h]
D11-10[f,i]	macro	1.68	262	–	0.22	100	+
D11-10[e,f]	370	0.88	106	–	0.17	81	+[h]
MCM-48[e,f]	60	2.84	314	1252	0.21	100	+[h]

[a] Hg porosimetry; Ø = pore diameter. [b] Strained with Ludox and poly(ethyleneoxide) (PEO; 1–1.6 mm). [c] Deboronated; particle size: 0.6–1 mm; trimodal macroporosity: 12000, 6200, and 1800 Å. [d] Strained with Ludox and PEO (0.6–1 mm). [e] Calcined at 500 °C. [f] Powder. [g] Langmuir [m^{2}g^{-1}]. [h] Isomerization. [i] Uncalcined. [j] Calcined at 550 °C.

Results and Discussion

Preparation of materials and characterization of supports: First, we prepared the Grubbs/Hoveyda 2 complex on various mesoporous and nonmesoporous supports. The activity and selectivity of the thus-obtained materials was first evaluated in suspension in the RO-RCM of *cis*-cyclooctene (Scheme 2, Table 1). The course of the reaction was monitored by GC analysis, and the heterogeneous nature of the catalyst was ensured by a split test.[31] As obvious from previous studies,[3] determination of the selectivity of the catalyst solely based on GC area (%) is misleading, as all higher oligomers and polymers that are untraceable by GC analysis remain undetected, thus leading to high, but biased selectivity in favor of oligomers smaller than the pentamer. Thus, we developed a GC methodology that allowed not only the reliable analysis of the starting material *cis*-cyclooctene, but also of all cyclic oligomers up to the pentamer.[32] *cis*-Cyclooctene and the dimer were calibrated from commercially available samples of *cis*,*cis*-1,9-cyclohexadecadiene[33] and the other cyclic oligomers of cyclooctene (3–5 mers) were assumed to have the same response factor as the dimer. This approximation is good because the ratios of C/H atoms and double bonds/C atoms are identical for all the oligomers, and the response factors of cyclooctene and the dimer are also almost identical.



Scheme 2. RO-RCM of *cis*-cyclooctene to 1,9-cyclohexadecadiene (amongst other oligomers and polymers; see Table 1 and Figure 1a for details).

MCM-41,[34] MCM-48,[35] SBA-15,[34,36] ZSM-5,[37] and MWW[38] were prepared according to reported procedures, activated alumina (Wako Presep-C), D11-10, and Aerosil 200 were purchased from commercial sources.[39] As described previously, the hybrid materials were prepared by simple impregnation of a suspension of the inorganic support in a solution of the Grubbs/Hoveyda 2 complex **1** in

CH_2Cl_2 for 3 hours, removal of the solvent, and drying of the material under vacuum at a maximum of 40 °C.[20,22,24] Some materials had been calcined prior to loading with the complex (Table 1). Although the initial loading of **1** on all the materials was high (0.079–0.22 wt % ruthenium corresponds to 73–100 % of the initial complex; Table 1) and resulted in green materials, the alumina-based material **1**@alumina decomposed rapidly as indicated by a color change of green to gray overnight. This intrinsic instability of **1** on alumina might be a consequence of the Lewis acidic properties of the support and opens routes to catalyst deactivation, as already described by Sels and co-workers[20] and us.[22,24] In suspension, all the materials worked as heterogeneous catalysts in the RO-RCM of *cis*-cyclooctene, as indicated by a split test, apart from **1**@ZSM-5, in which **1** leached off the support.

Despite of their good activity in the conversion of *cis*-cyclooctene (53, 99, 92, and 100 % conversion after 1 h; Figure 1 a), **1**@MCM-48, **1**@ZSM-5, and calcined macroporous materials **1**@D11-10 and **1**@Aerosil 200 led to significant isomerization of the olefin double bonds. This side reaction is absolutely detrimental because it leads, through secondary metathesis, to the unsymmetrical cleavage of the so-far symmetrical double bonds in 1,9-cyclohexadecadiene to, for example, cycloheptene and cyclononene instead of two equivalents of *cis*-cyclooctene. Over time, this led to an inseparable mixture of homologous macrocycles (Scheme 3).

The silicate ZSM-5 is Brønsted acidic, which might be the reason for the double-

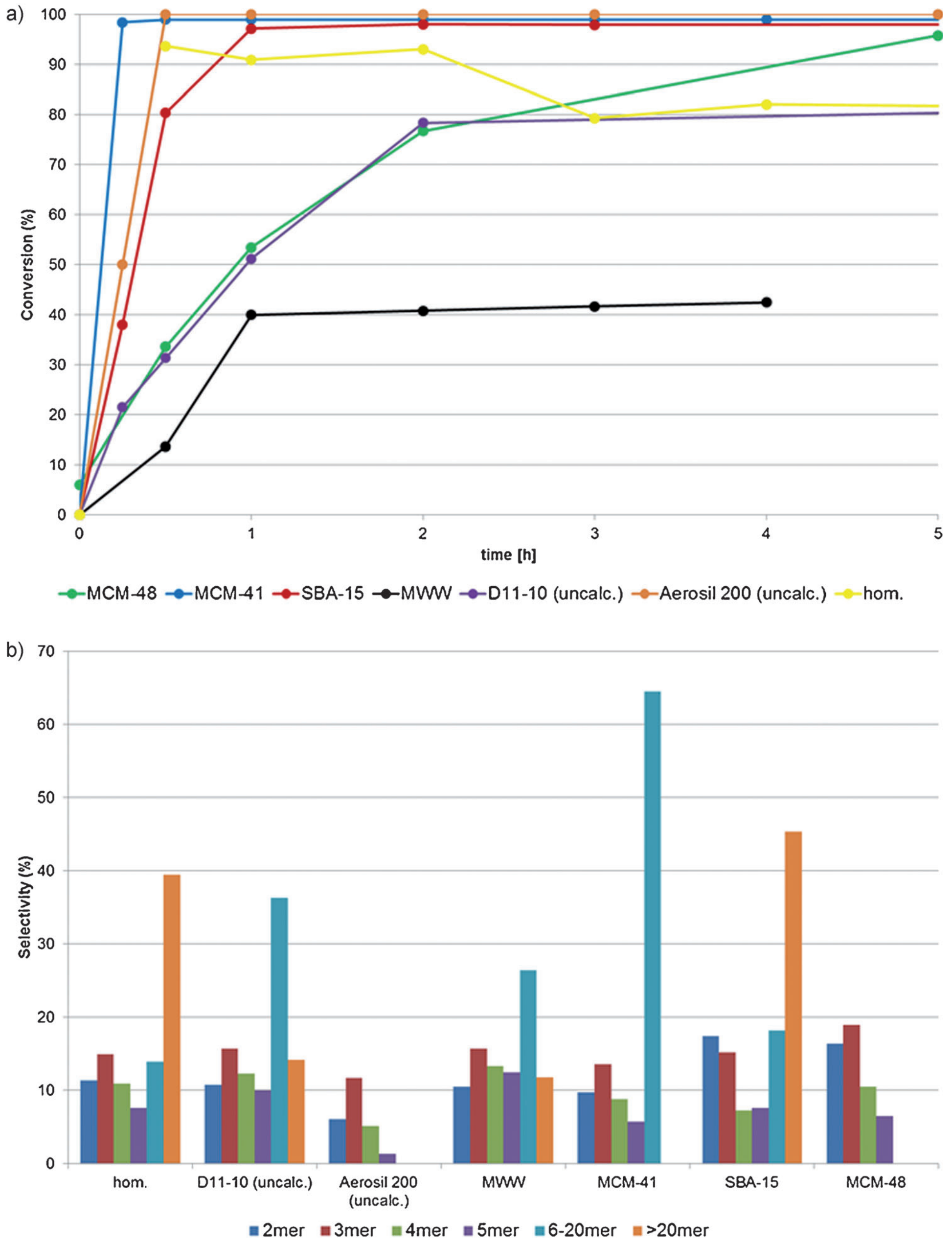
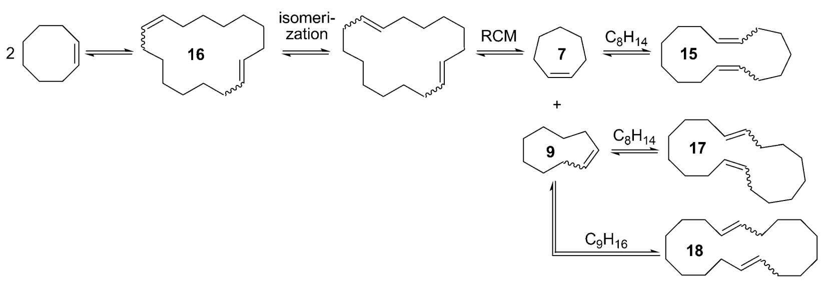


Figure 1. a) Activity test in suspension. b) Selectivity toward small oligomers (2–5 mers), oligomers (6–20 mers), and polymers (> 20 mer) as analyzed by GC and GPC.



Scheme 3. Byproducts formed in the RO-RCM of *cis*-cyclooctene by double-bond isomerization and unsymmetrical metathetical cleavage of $C_{16}H_{28}$.

bond isomerization activity; indeed, Brønsted acidic surface silanol groups might have also been present after calcination[40] on nonmesoporous materials **1**@Aerosil 200 and **1**@D11-10 at approximately 500 °C prior to loading with complex **1**. Although their uncalcined counterparts and **1**@MCM-41 did not show this undesired isomerization activity, we cannot yet exclude that it is a consequence of hydrides formed in the course of the reaction.[41]

In suspension, **1**@MCM-41 turned out to be the most active material, closely followed by **1**@Aerosil 200 (uncalcined) and **1**@SBA-15 (99, 100, and 97 % conversion after 1 h; Figure 1 a). All three materials were at least as active as the homogeneous complex **1** itself under otherwise identical conditions (91 % conversion after 1 h; [COE] = 100 mM in CH_2Cl_2 instead of cyclohexane due to its better solubility, [COE]/[cat.] = ~100:1 at 20 °C). Materials **1**@MCM-48, **1**@D11-10 (uncalcined), and **1**@MWW (uncalcined) turned out to be significantly less active (53, 51, and 44 % conversion after 1 h).

There was a clear effect of pore geometry on selectivity in the RO-RCM of *cis*-cyclooctene (Figure 1 b). Not only did **1**@D11-10 and **1**@Aerosil 200 form a significant amount of higher oligomers (6–20 mers), they yielded > 10 wt % of polymers (> 20 mer), which precipitated during the reaction due to their low solubility. SBA-15 formed up to 45 % of those polymers, despite having a narrow pore size (60 vs. 70 and > 300 Å), which is similar to the reaction catalyzed by the homogeneous complex itself. This outcome might be an indication that the complex did not reside in the pores of the SBA-15, but was deposited on the outside of the particles, thus leading to the low selectivity. Although **1**@MCM-41 gave the lowest selectivity of the valuable dimer, it was most selective for the smaller oligomers amongst all the materials (> 60 % for < 20 mer). As this MCM-41 does not lead to the formation any polymer, indicated by the closed mass balance, we considered MCM-41 to be the preferential support for further studies under continuous-flow conditions to address the influence of pore size of this selected support on selectivity. Four MCM-41-type silicates with pore diameters of 90, 140, 160, and 180 Å were prepared by employing amine templates of various chain lengths,[34] and the thus-derived powders were molded with Ludox[42] and PEO and calcined in air (to remove the PEO binder) to obtain, after splitting and sieving, shaped catalyst bodies with a mean diameter of 1–1.6 mm. This molding had no influence on the pore diameter, but pore

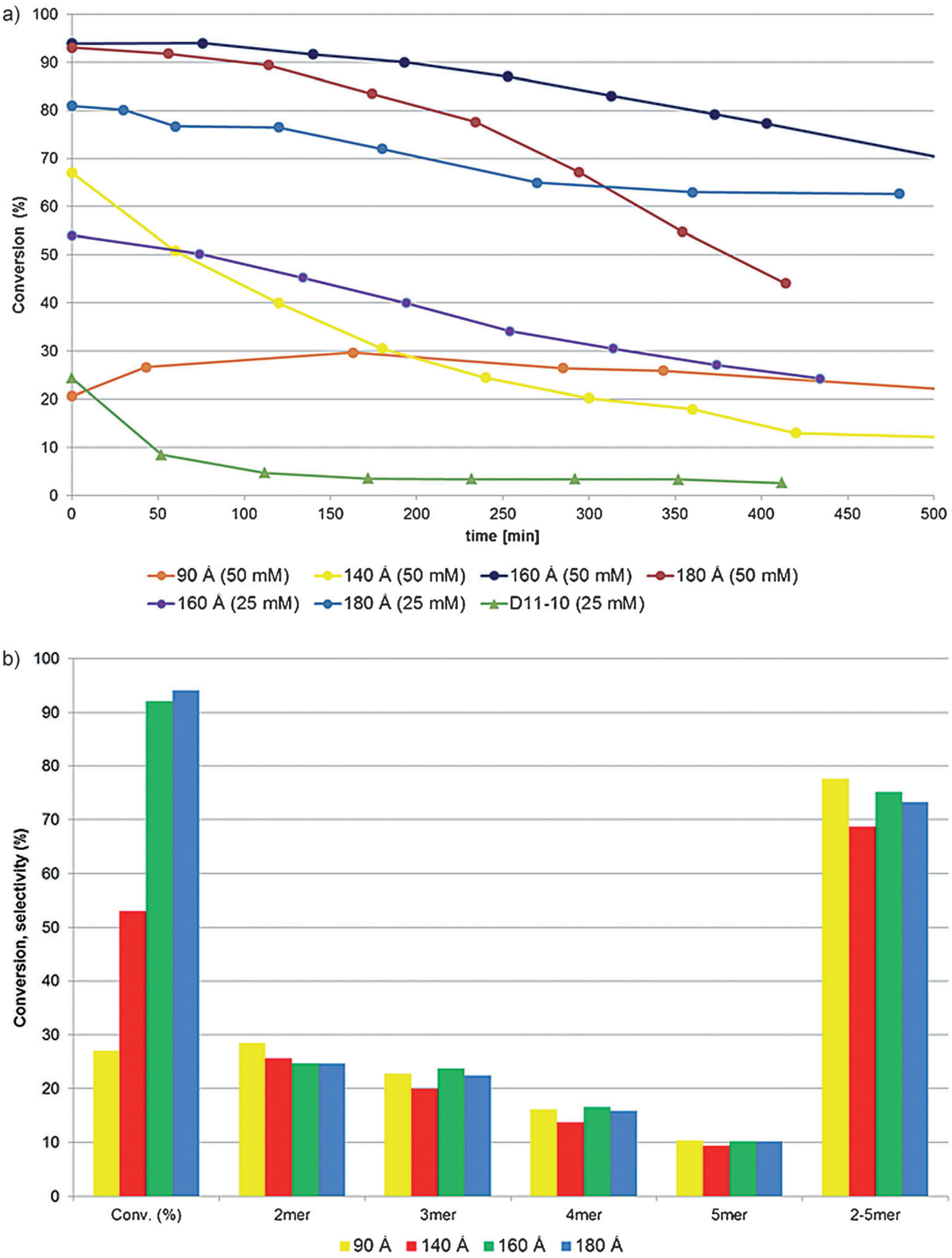


Figure 2. a) Activity over time under continuous-flow conditions. b) Conversion after 1 h at $[COE]_0 = 50$ mM. Selectivity at 30 % (for **1**@MCM-41 with pore sizes of 90 and 140 Å) and 70 % conversion (for **1**@MCM-41 with pore sizes of 160 and 180 Å).

volume and BET surface of the molded catalyst bodies were lower than those of the corresponding powders (Table 1, entries 4 and 5).

We benchmarked the activity and selectivity obtained with mesoporous materials **1**@MCM-41 against strands of the reference material **1**@D11-10 (Figure 2a).[24] The initial activity of all the mesoporous materials was measured at $[COE]_0 = 25$ and 50 mм (i.e., 0.77 and 2.00 wt %) and turned out to be significantly higher throughout the whole experiment (400 min) than that of **1**@D11-10, which started at approximately 25 % conversion and deactivated fast. Nevertheless, the activity of the mesoporous materials correlated well with their pore-size. Although the materials **1**@MCM-41 with pore sizes of 160 and 180 Å started at similar initial activities (i.e., 92 and 94 % conversion after 1 h; [COE] = 50 mм in cyclohexane), the material with the larger pores deactivated faster (77 and 45 % conversion after 400 min). Materials **1**@MCM-41 with pore sizes of 90 and 140 Å were initially the least active (27 and 53 % conversion after 1 h), but the first material kept its activity over 400 minutes at much with a less-pronounced deactivation tendency relative to materials **1**@MCM-41 with pore sizes of 140, 160, or even 180 Å.

The same activity trend was observed for materials **1**@MCM-41 with pore sizes of 160 and 180 Å at [COE] = 25 mм in cyclohexane (52 and 77 % conversion after 1 h). Assuming that most of the catalytically active sites are located at the inner surface of the materials, the reactivity is most likely controlled by the diffusion rate of the substrate into the pore, which is higher at larger pore diameters (Figure 1a). To our surprise, there was only a minor, but nevertheless clear effect on the selectivity toward the dimer and all the other oligomers traceable by GC analysis up to the pentamer: At a smaller pore size, the selectivity towards the dimer and small oligomers (2–5 mers) was higher, for example, 29 and 78 % for **1**@MCM-41 with a pore size of 90 Å

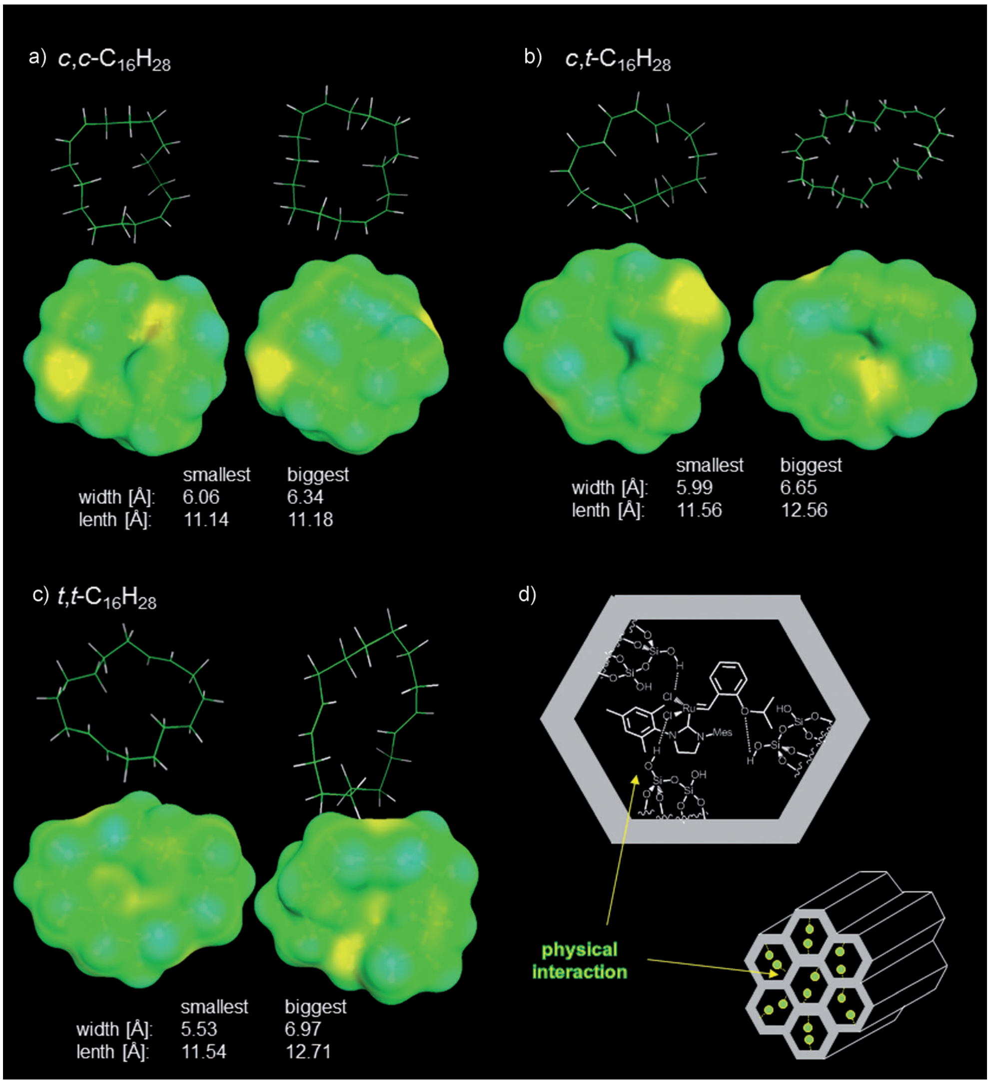


Figure 3. a–c) Geometric dimensions of the three isomers of $C_{16}H_{28}$ as calculated by using DFT calculations. d) Schematic representation of a likely binding mode of the complex on the inorganic support.

versus 26 and 69 % for **1**@MCM-41 with a pore size of 140 Å (both at 30 % conversion), respectively, or 25 and 75 % for **1**@MCM-41 with a pore size of 160 Å versus 25 and 73 % for **1**@MCM-41 with a pore size of 180 Å (both at 70 % conversion; Figure 2 b), respectively.

Analysis by gel-permeation chromatography (GPC) of the crude reaction mixture obtained with **1**@D11-10 revealed that greater than 7 % of the starting material was converted into oligomers from >13 mer up to a 48 mer, which represented the upper detection limit of our GPC setup. This reason might explain the fast deactivation of the supported catalyst, whereas the activity and selectivity of **1**@MCM-41 even increased over time and no oligomers greater than a nonamer formed (analyzed by GPC).

This minor influence of even small pores on the selectivity toward small oligomers (2–5 mers) becomes understandable if one considers the actual size of the three isomers of the cyclic dimer, that is, $t,t\text{-C}_{16}\text{H}_{28}$, $c,t\text{-C}_{16}\text{H}_{28}$, and $c,c\text{-C}_{16}\text{H}_{28}$ ($t,t\text{-C}_{16}\text{H}_{28}/c,t\text{-C}_{16}\text{H}_{28}/c,c\text{-C}_{16}\text{H}_{28}$ = 29:58:13 at 25 °C).[43] We have determined the geometry of these conformers in the gas phase with single-point DFT calculations (cp2k MD, 1200 °C, small basis set, COSMO). A hull was created and the minimal/maximal diameter of each individual conformer was determined (Figure 3 a–c). Even the biggest isomer $t,t\text{-C}_{16}\text{H}_{28}$ has only a width and length of approximately 7×13 Å, which is much too small to be influenced by a pore size of 90–180 Å in diameter.

The nature of the catalytically active species on the support remains elusive. Most likely, we expect it to be the unmodified or isomerized Grubbs/Hoveyda 2 complex[19b] hydrogen bonded through one or two anionic chloride ligands to the surface silanol groups of the support (Figure 3 d). This supposition is in line with observations that complexes containing P ligands are not stable on silica materials such as SBA-15[20,23,44] because the P ligand would be most likely protonated off.

Optimization of the reaction parameters for MCM-41: There was a clear positive correlation between reaction temperature and the activity and selectivity obtained in the RO-RCM reaction under continuous-flow conditions (Figure 4 a). Whereas the activity of the catalyst increased with temperature (e.g., 48 % conversion at 40 °C versus 76 % conversion at 60 °C after 100 min), the selectivity for all thre small oligomers up to the pentamer reached nearly 100 % at

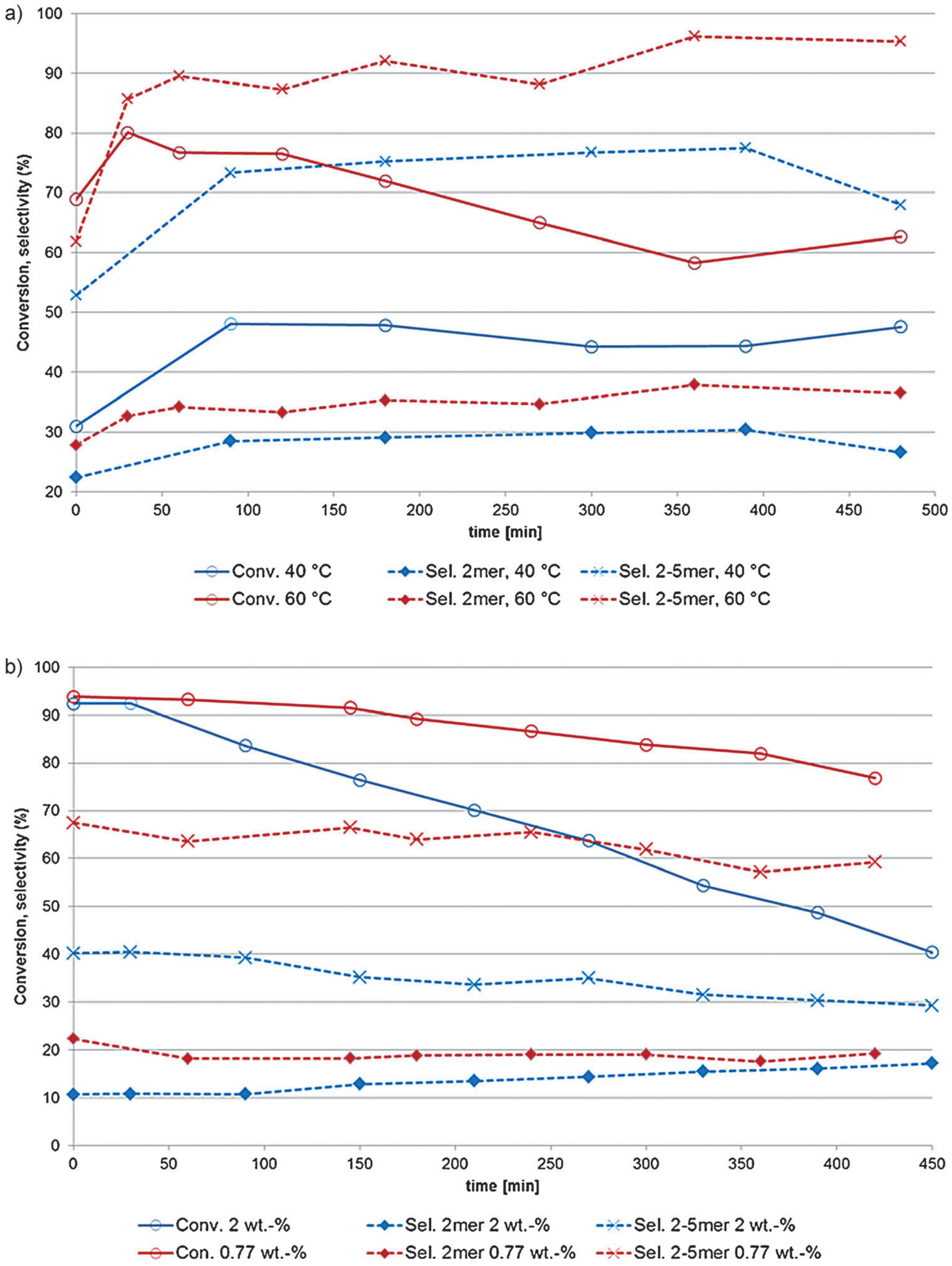


Figure 4. a) Influence of temperature and b) $[\text{COE}]_0$ on the activity and selectivity of **1**@MCM-41 with a pore diameter of 180 Å under continuous-flow conditions.

60 °C, which means that virtually all *cis*-cyclooctene is converted into small oligomers, which stay in solution. In turn, the deactivation rate of **1**@MCM-41 was higher at 60 than at 40 °C (i.e., 45 % conversion at 40 °C versus 60 % conversion at 60 °C after 400 min), and this material deactivated within minutes at 80 °C. To clarify whether catalyst deactivation was a consequence of a slow but steady coating of the catalyst surface with oligomers and/or polymers, the reaction was stopped after 480 minutes, and the catalyst was washed with pure cyclohexane under the reaction conditions for approximately 17 hours. After this time, the initial solution of *cis*-cyclooctene in cyclohexane was fed again (Figure 5).

Although we expected desorption of oligomers from the coated catalyst surface during the washing in case of polymer poisoning, less than 6 % of small oligomers up to the pentamer were eluted. By GPC analysis, there were less than 15 % of other medium-size polymers present in the collected crude-product fractions before washing, and approximately 8 % afterward washing. Elemental analysis of the spent support after the reaction revealed that besides virtually no loss of ruthenium (0.100 of fresh material vs. 0.097 wt % Ru after the run), there was only a minimal amount of 0.5 wt % of carbon on the support. Upon restarting of the reaction after the purge, there was a significant drop in catalyst activity (30 vs. 60 % conversion), thus pointing to other intrinsic deactivation pathways rather than deactivation through polymer deposition.

The outcome of the reaction was strongly dependent on the initial concentration of *cis*-cyclooctene in the feed (Figure 4b). The catalyst deactivated faster at constant MRT at 2.00 wt % *cis*-cyclooctene in cyclohexane relative to a feed of lower concentration (0.77 wt %). Again, the lower concentration had a major influence on the selectivity to the dimer, which was approximately two times higher for the diluted feeds (e.g., 20 % selectivity in dimer at 90 % conversion for $[\mathrm{COE}]_0 = 0.77$ wt % vs. 10 % selectivity at 90 % conversion for $[\mathrm{COE}]_0 = 2.00$ wt %). This effect was even more pronounced for the small oligomers (2–5 mers; e.g., 65 % selectivity to dimer at 90 % conversion for $[\mathrm{COE}]_0 = 0.77$ wt % vs. 40 % selectivity at 90 % conversion for $[\mathrm{COE}]_0 = 2.00$ wt %) because high dilution favors backbiting of the growing oligomer chain to the ruthenium carbene (Scheme 1).

Finally, to maximize the selectivity toward the dimer and small oligomers, the MRT in the reactor was varied (Figure 6a). Its effect on catalyst activity was obvious because the catalyst had longer contact with the feed at the slowest flow rate (4 mL min^{-1}, MRT = 20 min) relative to higher flow rates (8 and 16 mL min^{-1}, MRT = 10 and 5 min, respectively), in which the catalyst had less time to react to result in decreasing conversion at shorter MRTs (45, 67, and 93 % conversion after 4 h at MRT = 5, 10, and 20 min, respectively). The selectivity toward the dimer at approximately 45 % conversion (the only point at which all three experiments were comparable at the same conversion) decreased with increasing MRT (10, 18, and 29 % selectivity at MRT = 20, 10, and 5 min, respectively). This observation implies that the small oligomers are kinetic products and are not formed through backbiting from a larger oligomer or polymer chain (Scheme 1).[25] The same trend applied for the shorter oligomers (2–5 mers: 30, 30, and 76 % selectivity at MRT = 20, 10 and 5 min, respectively).

A small selection of precomplexes **1**–**5** with chelating ligands (Figures 6b and 7), that is, the Hoveyda paragon **1**,[45] the Grela nitro catalyst **2**,[15d] *O*-chelated lactate **3**,[46] *S*-chelate **4**,[47] and *N*-chelate **5**[48] were chosen to determine the effect of the organometallic species on the outcome of the reaction. As anticipated, the initial activity of **2** was highest due to its fast initiation (71 % conversion after 1 h). Due to its fast deactivation after approximately 300 minutes, catalyst **2** reached the break-even point to **1** at approximately 30 % conversion. Lactate **3** had an initial activity similar to **2** (45 vs. 52 % conversion after 1 h, respectively) but also deactivated more quickly. In our heterogeneous reaction setup, the Umicore catalys **5** and the Evonik catalyst **4** showed virtually no activity (< 5 %) at 40, 60, or 80 °C. Amongst complexes **1**–**3**, there was no effect of the chelate structure on selectivity because all the complexes gave virtual-

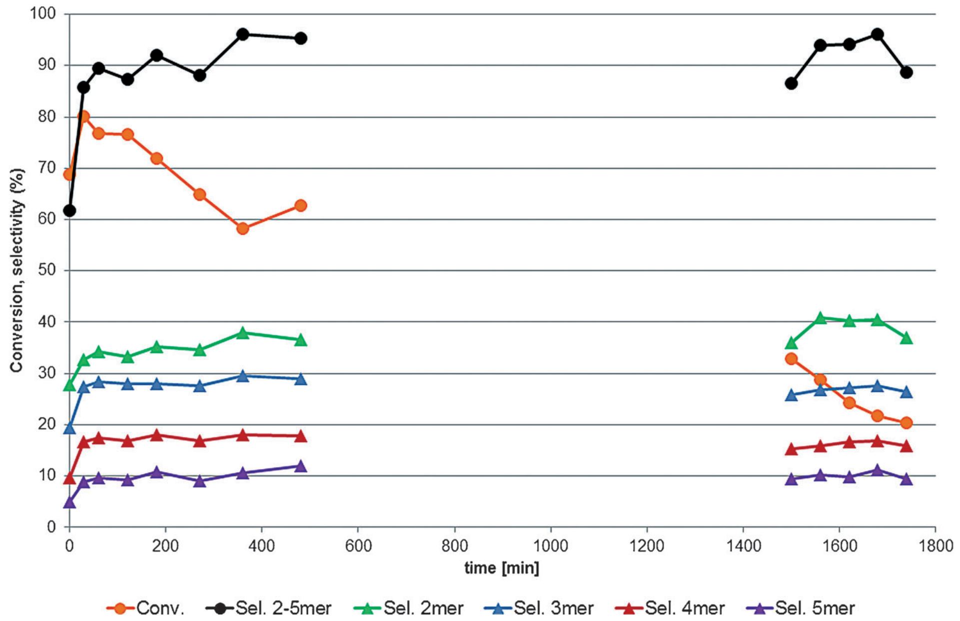


Figure 5. Conversion and selectivity over time with a solvent flush run overnight. Conditions: 60 °C, 16 mL min^{-1}, 0.35 wt % *cis*-cyclooctene, **1**@MCM-41(pore size: 180 Å).

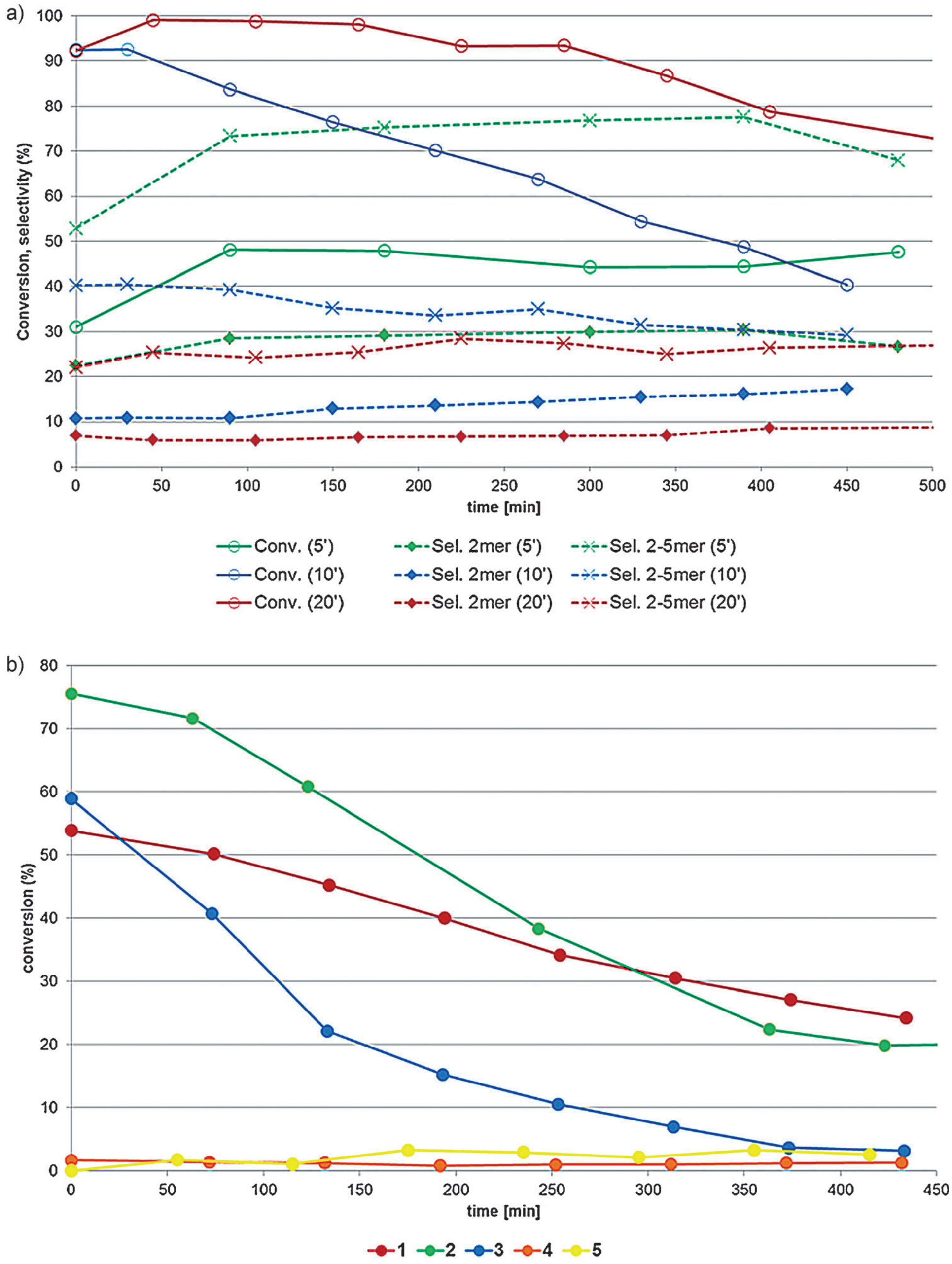


Figure 6. a) Influence of MRT on the activity and selectivity of **1**@MCM-41 with a pore diameter of 180 Å under continuous-flow conditions. b) Evaluation of precomplexes **1–5** adsorbed on MCM-41 in the RO-RCM of *cis*-cyclooctene under continuous-flow conditions.

ly the same selectivity of approximately 35 % toward the dimer at 50 % conversion.[49]

Conclusion

We have found that the longevity and the selectivity of a heterogenized Grubbs/Hoveyda complex in a RO-RCM reaction was significantly increased by running the reaction under continuous-flow conditions on a mesoporous support. By tuning the pore diameter of the mesoporous support, substrate concentration, temperature, and finally mean residence time, we obtained a maximal selectivity of 35 % toward a cyclic dimer, which is a remarkable value in view of the wealth of potentially possible products. Although the pore diameter had little effect on the selectivity, the competing ROMP reaction was virtually suppressed. The nature of the initial ruthenium carbene species had no effect on the selectivity, but had a strong impact on the activity of the catalytic material. This difference in reactivity might be a consequence of the individual sensitivity of the complexes to acid surface silanols, which were responsible for double-bond isomerization as a major side reaction and is a future field of development of this valuable technology.

Experimental Section

General: All the reactions and manipulations were performed in an argon atmosphere by using standard Schlenk techniques. Cyclohexane, diethyl ether, THF, and dichloromethane were dried by means of a MBraun solvent-purification system. All the solvents were degassed with argon prior to use. GC analyses were carried out on a Agilent 6890N modular GC base equipped with a split-mode capillary-injection system and flame-ionization detector by using a standard HP-5 capillary column (30 m × 0.32 mm × 0.25 μm; He flow: 2.0 mL min^{-1}; program: 50 °C (1 min), 50–250 °C (20 °C min^{-1}), 250 °C (10 min). GC-MS analyses were carried out on a Agilent 19091S-433 modular GC base equipped with a split-mode capillary-injection system and flame-ionization detector by using a standard HP-5 capillary column (30 m × 0.25 mm × 0.25 μm; He flow: 0.6 mL min^{-1}; program: 50 °C (1 min), 50–250 °C (20 °C min^{-1}), 250 °C (10 min)). GPC was measured on a 55er system with refraction index (RI) detection equipped with four columns of 7.5 × 300 mm; PLgel: 5 μm, pore width: 5 nm, eluent: THF, flow: 1 mL min^{-1}, temperature: 35 °C. Polystyrene (266–5000 Da) was used as a reference material for the assignment of molecular weight. All the other starting materials were purchased in reagent-grade purity from Acros, Aldrich, Fluka, or Strem and were used without further purification.

Procedure for the heterogenization of complexes on solid support: The solid support (1.5 g) was suspended under argon in CH_2Cl_2 (10 mL). A

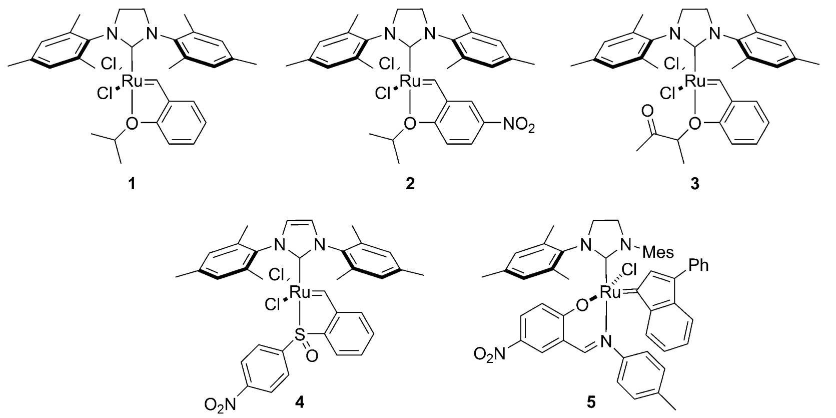


Figure 7. Ruthenium carbenes **1–5** with various chelating ligands employed in the flow study (see Figure 6b for details).

solution of Grubbs/Hoveyda 2 complex (20.5 mg, 32.7 μg) in CH_2Cl_2 (10 mL) was added to this suspension. The green suspension was shaken for 4 h (200 min) at room temperature under argon. The solvent was removed under vacuum at a maximum of 40 °C to give the loaded materials as green solids. The content of ruthenium was measured by means of inductively coupled plasma/mass spectrometry (ICP-MS).

MWW: Ru calcd (%): 0.22; found: 0.16 (73 % of theory); alumina-activated (Wako 45 μm; 300 mesh): Ru calcd (%): 0.22; found: 0.17 (81 % of theory); D11-10 (calcined): Ru calcd (%): 0.22; found: 0.17 (81 % of theory); D11-10 (uncalcined): Ru calcd (%): 0.22; found: 0.22 (100 % of theory); SBA-15: CH_2Cl_2 (30 mL); Ru calcd (%): 0.22; found: 0.22 (100 % of theory); MCM-41: Ru calcd (%): 0.21; found: 0.20 (95 % of theory); ZSM-5: Ru calcd (%): 0.21; found: 0.16 (76 % of theory); MCM-48: Ru calcd (%): 0.21; found: 0.21 (100 % of theory); Aerosil 200 (uncalcined): Ru calcd (%): 0.21; found: 0.17 (81 % of theory); Aerosil 200 (calcined): Ru calcd (%): 0.21; found: 0.20 (95 % of theory).

Procedure for the catalytic testing of the loaded materials and the split test to determine the heterogeneity of the catalyst: In the glove box, dodecane (1.008 g, internal standard) and *cis*-cyclooctene (131.9 mg, 1.15 mmol, 96.5 %) were added to a suspension of the supported material (720 mg) in a vial (50 mL) in hexane (16 mL), and the suspension was shaken at room temperature at 200 rpm. Samples were taken in the given time intervals and the samples were quenched with a drop of ethyl vinyl ether. GC analyses were performed on a DB-5 column (30 m, ID: 0.32 mm, film: 0.25 μm; temperature program: 60 °C (5 min), 60–300 °C (10 °C min^{-1}), 300 °C (15 min), 300–320 °C (10 °C min^{-1}), 320 °C (18 min).

After a conversion of approximately 50 %, two samples were taken from the reaction mixture, one was quenched with a drop of ethyl vinyl ether and the other one remained unquenched. The conversion in the unquenched sample was compared after 4 h to the conversion of the quenched sample. If the conversion of the samples remained equal, the reaction was heterogeneous. Consecutive conversion indicated that there was a species catalytically active in the liquid phase.

MWW: 720 mg material (0.16 wt % Ru).

MWW (strands, 0.6–1 mm): *cis*-Cyclooctene (156.1 mg, 1.367 mmol), material **1**@MWW (735.1 mg, [Ru] = 0.18 %).

Alox: *cis*-Cyclooctene (153.8 mg, 1.35 mmol), material **1**@Alox (739.2 mg, [Ru] = 0.18 %).

ZSM-5: *cis*-Cyclooctene (143.6 mg, 1.258 mmol), material **1**@ZSM-5 (698.8 mg, [Ru] = 0.16 %).

D11-10 (uncalcined): *cis*-Cyclooctene (176.8 mg, 1.550 mmol), material **1**@D11–10 (743.0 mg, [Ru] = 0.21 %).

D11-10 (calcined): *cis*-Cyclooctene (185.2 mg, 1.620 mmol), material **1**@D11–10 (721.3 mg, [Ru] = 0.18 %).

MCM-48: *cis*-Cyclooctene (153.8 mg, 1.347 mmol), material **1**@MCM-48 (704.6 mg, [Ru] = 0.21 %).

Aerosil 200 (uncalcined): *cis*-Cyclooctene (162.6 mg, 1.424 mmol), material **1**@Aerosil 200 (742.9 mg, [Ru] = 0.17 %).

Aerosil 200 (calcined at 200 °C): *cis*-Cyclooctene (149.7 mg, 1.311 mmol), material **1**@Aerosil 200 (725.8 mg, [Ru] = 0.16 %).

Aerosil 200 (calcined at 600 °C; SJ 3-41): *cis*-Cyclooctene (158.8 mg, 1.391 mmol), material SJ3–39 (738.6 mg, [Ru] = 0.20 %).

MCM-41 (180 Å): *cis*-Cyclooctene (145.6 mg, 1.275 mmol), material **1**@MCM-41 (764.9 mg, [Ru] = 0.20 %).

MCM-41 (180 Å, strands, 0.6–1 mm): *cis*-Cyclooctene (135.4 mg, 1.186 mmol), material **1**@MCM-41 (678.0 mg, [Ru] = 0.25 %).

MCM-41 (180 Å, strands, 1–1.6 mm): *cis*-Cyclooctene (135.3 mg, 1.154 mmol), material **1**@MCM-41 (668.4 mg, [Ru] = 0.22 %).

SBA-15: *cis*-Cyclooctene (149.3 mg, 1.620 mmol), material **1**@SBA-15 (743.3 mg, [Ru] = 0.22 %).

Procedure for the preparation and testing of various precomplexes on MCM-41 under continuous-flow conditions: Shaped and split MCM-41 (1–1.6 mm, 15.12–15.59 g) was suspended under argon in CH_2Cl_2 (75 mL). A solution of the precomplex (80–144 mg, 127–128 μg) in CH_2Cl_2 (10 mL) was added to this suspension. The green suspension was shaken for 2 h (200 min) at room temperature under argon. The solvent was removed under vacuum at a maximum of 40 °C to give the loaded materials as green solids. The content of ruthenium was measured by means of ICP-MS.

A steel reactor (diameter: 14 mm, length: 45 cm) was charged with the catalyst. COE in cyclohexane solution (0.35 % by weight, 25 mmol L^{-1}) was pumped through the reactor at 60 °C with a flow rate of 16 mL min^{-1} and a pressure of 2 bar. The reactions were monitored by sampling the resulting solution with a GC-MS probe.

1: 80 mg (128 μmol), 15.12 g MCM-41; [Ru] = 0.082 %. **2**: 85 mg (127 μmol), 15.58 g MCM-41; [Ru] = 0.075 %. **3**: 82 mg (127 μmol), 15.52 g MCM-41; [Ru] = 0.077 %. **4**: 94 mg (128 μmol), 15.58 g MCM-41; [Ru] = 0.060 %. **5**: 144 mg (128 μmol), 15.59 g MCM-41; [Ru] = 0.075 %.

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[1] L. Malet-Sanz, F. Susanne, *J. Med. Chem.* **2012**, *55*, 4062–4098; J. Pesti, *Org. Process Res. Dev.* **2012**, *16*, 843–843.

[2] a) S. Monfette, M. Eyholzer, D. M. Roberge, D. E. Fogg, *Chem. Eur. J.* **2010**, *16*, 11720–11725; b) J. Lim, S. S. Lee, J. Y. Ying, *Chem. Commun.* **2010**, *46*, 806–808.

[3] S. M. Rountree, M. C. Lagunas, C. Hardacre, P. N. Davies, *Appl. Catal. A* **2011**, *408*, 54–62.

[4] J. Kong, C.-y. Chen, J. Balsells-Padros, Y. Cao, R. F. Dunn, S. J. Dolman, J. Janey, H. Li, M. J. Zacuto, *J. Org. Chem.* **2012**, *77*, 3820–3828.

[5] R. L. Banks, S. G. Kukes, *J. Mol. Catal.* **1985**, *28*, 117–131.

[6] E. F. G. Woerlee, R. H. A. Bosma, J. M. M. Van Eijl, J. C. Mol, *Appl. Catal.* **1984**, *10*, 219–229.

[7] a) J. H. Wengrovius, R. R. Schrock, M. R. Churchill, J. R. Missert, W. J. Youngs, *J. Am. Chem. Soc.* **1980**, *102*, 4515 – 4516; b) M. Yu, I. Ibrahem, M. Hasegawa, R. R. Schrock, A. H. Hoveyda, *J. Am. Chem. Soc.* **2012**, *134*, 2788 – 2799.

[8] a) G. C. Fu, S. T. Nguyen, R. H. Grubbs, *J. Am. Chem. Soc.* **1993**, *115*, 9856 – 9857; b) B. J. Keitz, K. Endo, P. R. Patel, M. B. Herbert, R. H. Grubbs, *J. Am. Chem. Soc.* **2012**, *134*, 693 – 699.

[9] Recent reviews: a) M. R. Maurya, J. C. Pessoa, *J. Organomet. Chem.* **2010**, *695*, 244 – 254; b) A. C. Marr, P. C. Marr, *Dalton Trans.* **2011**, *40*, 20 – 26; c) A. Corma, H. Garcia, *Top. Catal.* **2008**, *48*, 8 – 31; d) R. Duque, E. Ochsner, H. Clavier, F. Caijo, S. P. Nolan, M. Mauduit, D. J. Cole-Hamilton, *Green Chem.* **2011**, *13*, 1187 – 1195.

[10] Reviews: C. Copéret, J.-M. Basset, *Adv. Synth. Catal.* **2007**, *349*, 78 – 92; H. Hagiwara, *Synlett* **2012**, *23*, 837 – 850; M. R. Buchmeiser, *Chem. Rev.* **2009**, *109*, 303 – 321.

[11] a) V. Riollet, E. A. Quadrelli, C. Copéret, J.-M. Basset, R. A. Andersen, K. Köhler, R.-M. Böttcher, E. Herdtweck, *Chem. Eur. J.* **2005**, *11*, 7358 – 7365; b) F. Blanc, C. Copéret, J. Thivolle-Cazat, J.-M. Basset, A. Lesage, L. Emsley, A. Sinha, R. R. Schrock, *Angew. Chem.* **2006**, *118*, 1238 – 1242; *Angew. Chem. Int. Ed.* **2006**, *45*, 1216 – 1220; c) B. Rhers, A. Salameh, A. Baudouin, E. A. Quadrelli, M. Taoufik, C. Copéret, F. Lefebvre, J.-M. Basset, X. Solans-Monfort, O. Eisenstein, W. W. Lukens, L. P. H. Lopez, A. Sinha, R. R. Schrock, *Organometallics* **2006**, *25*, 3554 – 3557; d) K. R. Jain, F. E. Kühn, *J. Organomet. Chem.* **2007**, *692*, 5532 – 5540.

[12] a) M. Ahmed, A. G. M. Barrett, D. C. Braddock, S. M. Cramp, P. A. Procopiou, *Tetrahedron Lett.* **1999**, *40*, 8657 – 8662; b) H. D. Maynard, R. H. Grubbs, *Tetrahedron Lett.* **1999**, *40*, 4137 – 4140; c) K. Grela, M. Tryznowski, M. Bienik, *Tetrahedron Lett.* **2002**, *43*, 9055 – 9059; d) F. Koc, F. Michalek, L. Rumi, W. Bannwarth, R. Haag, *Synthesis* **2005**, *19*, 3362 – 3372; e) F. Michalek, D. Mädge, J. Rühe, W. Bannwarth, *J. Organomet. Chem.* **2006**, *691*, 5172 – 5180.

[13] a) S. T. Nguyen, R. H. Grubbs, *J. Organomet. Chem.* **1995**, *497*, 195 – 200; b) K. Melis, D. De Vos, P. Jacobs, F. Verpoort, *J. Mol. Catal. A* **2001**, *169*, 47 – 56; c) S. Gatard, S. Nlate, E. Cloutet, G. Bravic, J.-C. Blais, D. Astruc, *Angew. Chem.* **2003**, *115*, 468 – 472; *Angew. Chem. Int. Ed.* **2003**, *42*, 452 – 456.

[14] a) M. Ahmed, A. G. M. Barrett, D. C. Braddock, S. M. Cramp, P. A. Procopiou, *Synlett* **2000**, *7*, 1007 – 1010; b) S. C. Schürer, S. Gessler, N. Buschmann, S. Blechert, *Angew. Chem.* **2000**, *112*, 4062 – 4065; *Angew. Chem. Int. Ed.* **2000**, *39*, 3898 – 3901; c) M. Mayr, B. Mayr, M. R. Buchmeiser, *Angew. Chem.* **2001**, *113*, 3957 – 3960; *Angew. Chem. Int. Ed.* **2001**, *40*, 3839 – 3842; d) S. Randl, N. Buschmann, S. J. Connon, S. Blechert, *Synlett* **2001**, 1547 – 1551; e) J. P. Gallivan, J. P. Jordan, R. H. Grubbs, *Tetrahedron Lett.* **2005**, *46*, 2577 – 2580; f) I. Karamé, M. Boualleg, J.-M. Camus, T. K. Maishal, J. Alauzun, J.-M. Basset, C. Coperet, R. J. P. Corriu, E. Jeanneau, A. Mehdi, C. Reye, L. Veyre, C. Thieuleux, *Chem. Eur. J.* **2009**, *15*, 11820 – 11823; g) A. Monge-Marcet, R. Pleixats, X. Cattoën, M. W. Chi Man, *J. Mol. Catal. A* **2012**, *357*, 59 – 66.

[15] a) A. G. M. Barrett, S. M. Cramp, R. S. Roberts, *Org. Lett.* **1999**, *1*, 1083 – 1086; b) Q. Yao, *Angew. Chem.* **2000**, *112*, 4060 – 4062; *Angew. Chem. Int. Ed.* **2000**, *39*, 3896 – 3898; c) J. S. Kingsbury, S. B. Garber, J. M. Giftos, B. L. Gray, M. M. Okamoto, R. A. Farrer, J. T. Fourkas, A. H. Hoveyda, *Angew. Chem.* **2001**, *113*, 4381 – 4386; *Angew. Chem. Int. Ed.* **2001**, *40*, 4251 – 4256; d) S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. Hoveyda, *J. Am. Chem. Soc.* **2000**, *122*, 8168 – 8179; e) S. Varray, R. Lazaro, J. Martinez, F. Lamaty, *Organometallics* **2003**, *22*, 2426 – 2435; f) A. Keraani, c. Fischmeister, T. Renouard, M. Le Floch, A. Baudry, C. Bruneau, M. Rabiller-Baudry, *J. Mol. Catal. A* **2012**, *357*, 73 – 80.

[16] a) P. Nieczypor, W. Buchowicz, W. J. N. Meester, F. P. J. T. Rutjes, J. C. Mol, *Tetrahedron Lett.* **2001**, *42*, 7103 – 7105; b) J. O. Krause, S. H. Lubbad, O. Nuyken, M. R. Buchmeiser, *Macromol. Rapid Commun.* **2003**, *24*, 875 – 878; c) J. O. Krause, S. H. Lubbad, O. Nuyken, M. R. Buchmeiser, *Adv. Synth. Catal.* **2003**, *345*, 996 – 1004; d) T. S. Halbach, S. Mix, D. Fischer, S. Maechling, J. O. Krause, C. Sievers, S. Blechert, O. Nuyken, M. R. Buchmeiser, *J. Org. Chem.* **2005**, *70*, 4687 – 4694.

[17] Representative examples: a) B. Çetinkaya, N. Gürbüz, T. Seçkin, I. Özdemir, *J. Mol. Catal. A* **2002**, *184*, 31 – 38; b) M. Mayr, M. R. Buchmeiser, K. Wurst, *Adv. Synth. Catal.* **2002**, *344*, 712 – 719; c) D. Fischer, S. Blechert, *Adv. Synth. Catal.* **2005**, *347*, 1329 – 1332; d) H. Staub, R. Guillet-Nicolas, N. Even, L. Kayser, F. Kleitz, F.-G. Fontaine, *Chem. Eur. J.* **2011**, *17*, 4254 – 4265.

[18] Representative examples: a) F. Blanc, M. Chabanas, C. Copéret, B. Fenet, E. Herdweck, *J. Organomet. Chem.* **2005**, *690*, 5014 – 5026; b) K. Weiss, G. Loessel, *Angew. Chem.* **1989**, *101*, 75; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 62; c) J. Joubert, F. Delbecq, P. Sautet, E. Le Roux, M. Taoufik, C. Thieuleux, F. Blanc, C. Copéret, J. Thivolle-Cazat, J.-M. Basset, *J. Am. Chem. Soc.* **2006**, *128*, 9157 – 9169; d) N. Rendón, R. Berthoud, F. Blanc, D. Gajan, T. Masihal, J.-M. Basset, C. Copéret, A. Lesage, L. Emsley, S. C. Marinescu, R. Singh, R. R. Schrock, *Chem. Eur. J.* **2009**, *15*, 5083 – 5089.

[19] a) M. Mayr, D. Wang, R. Kröll, N. Schuler, S. Prühs, A. Fürstner, M. R. Buchmeiser, *Adv. Synth. Catal.* **2005**, *347*, 484 – 492; b) S. Prühs, C. W. Lehmann, A. Fürstner, *Organometallics* **2004**, *23*, 280 – 287; c) F. Michalek, D. Maedge, J. Ruehe, W. Bannwarth, *Eur. J. Org. Chem.* **2006**, 577 – 581.

[20] B. van Berlo, K. Houthoofd, P. A. Jacobs, *Adv. Synth. Catal.* **2008**, *350*, 1949 – 1953.

[21] H. Balcar, T. Shinde, N. Žilková, Z. Bastl, *Beilstein J. Org. Chem.* **2011**, *7*, 22 – 28.

[22] J. A. Schachner, J. Cabrera, R. Padilla, C. Fischer, P. A. van der Schaaf, R. Pretot, F. Rominger, M. Limbach, *ACS Catal.* **2011**, *1*, 872 – 876.

[23] J. Cabrera, R. Padilla, R. Dehn, S. Deuerlein, Ł. Gułajski, E. Chomiszczak, J. H. Teles, M. Limbach, K. Grela, *Adv. Synth. Catal.* **2012**, *354*, 1043 – 1051.

[24] J. Cabrera, R. Padilla, M. Bru, R. Lindner, T. Kageyama, K. Wilckens, S. L. Balof, H.-J. Schanz, R. Dehn, J. H. Teles, S. Deuerlein, K. Müller, F. Rominger, M. Limbach, *Chem. Eur. J.* **2012**, *18*, 14717 – 14724.

[25] S. Kavitake, M. K. Samantaray, R. Dehn, S. Deuerlein, M. Limbach, J. A. Schachner, C. Copéret, C. Thieuleux, *Dalton Trans.* **2011**, *40*, 12443 – 12446.

[26] A. M. J. Rost, H. Schneider, J. P. Zoller, W. A. Herrmann, F. E. Kühn, *J. Organomet. Chem.* **2005**, *690*, 4712 – 4718; S. Warwel, H. Kätker, C. Rauenbusch, *Angew. Chem.* **1987**, *99*, 714 – 715; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 702 – 703; S. Warwel, H. Kätker, *Synthesis* **1987**, 935 – 937.

[27] K. Höcker, W. Reimann, L. Reif, K. Riebel, *J. Mol. Catal.* **1980**, *8*, 191 – 202; L. Reif, H. Höcker, *Macromolecules* **1984**, *17*, 952 – 956.

[28] D. Bek, H. Balcar, N. Žilková, A. Zukal, M. Horáček, J. Čejka, *ACS Catal.* **2011**, *1*, 709 – 718.

[29] a) R. M. Martín-Aranda, J. Čejka, *Top. Catal.* **2010**, *53*, 141 – 153; b) D. Bek, N. Žilková, J. Dédeček, J. Sedláček, H. Balcar, *Top. Catal.* **2010**, *53*, 200 – 209; c) H. Balcar, D. Bek, J. Sedláček, J. Dédeček, Z. Bastl, M. Lamač, *J. Mol. Catal. A* **2010**, *332*, 19 – 24; d) D. Bek, R. Gawin, K. Grela, H. Balcar, *Catal. Commun.* **2012**, *21*, 42 – 45; e) B. Marciniec, S. Rogalski, M. J. Potrzebowski, C. Pietraszuk, *ChemCatChem* **2011**, *3*, 904 – 910; f) S. Rogalski, C. Pietraszuk, B. Marciniec, *J. Organomet. Chem.* **2009**, *694*, 3918 – 3922; g) X. Elias, R. Pleixats, M. W. C. Man, J. J. E. Moreau, *Adv. Synth. Catal.* **2007**, *349*, 1701 – 1713; h) H. Balcar, N. Žilková, J. Sedláček, J. Zedník, *J. Mol. Catal. A* **2005**, *232*, 56 – 58; see also reference [17d].

[30] M. Onaka, T. Oikawa, *Chem. Lett.* **2002**, *8*, 850 – 851; C. Zhang, Q. Wang, H. Long, W. Zhang, *J. Am. Chem. Soc.* **2011**, *133*, 20995 – 21001; M. Iwamoto, K. Kasai, T. Haishi, *ChemSusChem* **2011**, *4*, 1055 – 1058; V. Nair, R. Szostak, P. K. Agrawal, T. L. Thomas, *Stud. Surf. Sci. Catal.* **1988**, *38*, 209 – 219; E. G. Derouane, *Stud. Surf. Sci. Catal.* **1980**, *5*, 5 – 18.

[31] J. E. Hamlin, K. Hirai, A. Millan, P. M. Maitlis, *J. Mol. Catal.* **1980**, *7*, 543 – 544.

[32] Column DB-5: 15 m; ID: 0.32 mm; film thickness: 0.25 μm; temperature program: 60 °C (5 min), 60–300 °C (10 °C min^{-1}), 300 °C (15 min), 300–320 °C (10 °C min^{-1}), 320 °C (18 min): t_R (*cis*-cyclooc-

tene): 5.5 min, t_R ($C_{16}H_{28}$, 2 mer): 20.1 min, t_R ($C_{24}H_{42}$, 3 mer): 28.2 min, t_R ($C_{32}H_{56}$, 4 mer): 37.1 min, t_R ($C_{40}H_{70}$, 5 mer): 55.1 min.

[33] *cis,cis*-1,9-Cyclohexadecadiene is a commercial product of Sigma-Aldrich.

[34] P. Topka, H. Balcar, J. Rathouský, N. Žilková, F. Verpoort, J. Čejka, *Microporous Mesoporous Mater.* **2006**, *96*, 44–54; J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowice, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, J. L. Schlenker, *J. Am. Chem. Soc.* **1992**, *114*, 10834–10843.

[35] A. Zukal, H. Šiklová, J. Čejka, *Langmuir* **2008**, *24*, 9837–9842.

[36] a) T.-W. Kim, F. Kleitz, B. Paul, R. Ryoo, *J. Am. Chem. Soc.* **2005**, *127*, 7601–7610; b) H. Zhang, J. Sun, D. Ma, G. Weinberg, D. S. Su, X. Bao, *J. Phys. Chem. B* **2006**, *110*, 25908–25915; c) V. Meynen, P. Cool, E. F. Vansant, *Microporous Mesoporous Mater.* **2009**, *125*, 170.

[37] J. H. Koegler, H. van Bekkum, J. C. Jansen, *Zeolites* **1997**, *19*, 262.

[38] L. Liu, M. Cheng, D. Ma, G. Hu, X. Pan, X. Bao, *Microporous Mesoporous Mater.* **2006**, *94*, 304.

[39] D11-10 is a precipitated silica, which is available from BASF SE on request; Aerosil 200 is a hydrophilic fumed silica with a specific surface area of 200 m^2g^{-1}, which is available from Evonik Industries.

[40] A. J. van Roosmalen, M. C. G. Hartmann, J. C. Mol, *J. Catal.* **1980**, *66*, 112–120; J. Sauer, J.-R. Hill, *Chem. Phys. Lett.* **1994**, *218*, 333–337.

[41] M. B. Dinger, J. C. Mol, *Organometallics* **2003**, *22*, 1089–1095.

[42] Ludox (CAS 7631-86-9) is a colloidal silica that is used as binder, is a commercial product of Helm AG, and can be purchased from Sigma-Aldrich.

[43] J. Dale, C. Moussebois, *J. Chem. Soc. C* **1966**, 264–267; H. Höcker, R. Musch, *Die Makromolekulare Chemie* **1974**, *175*, 1395–1409.

[44] F. M. de Rege, D. K. Morita, K. C. Ott, W. Tumas, R. D. Broene, *Chem. Commun.* **2000**, 1797–1798; see also reference [17d].

[45] K. Grela, S. Harutyunyan, A. Michrowska, *Angew. Chem.* **2002**, *114*, 4210–4212; *Angew. Chem. Int. Ed.* **2002**, *41*, 4038–4040.

[46] M. Bieniek, C. Samojłowicz, V. Sashuk, R. Bujok, P. Śledź, N. Lugan, G. Lavigne, D. Arlt, K. Grela, *Organometallics* **2011**, *30*, 4144–4158.

[47] A. Szadkowska, A. Makal, K. Wozniak, R. Kadyrov, K. Grela, *Organometallics* **2009**, *28*, 2693–2700.

[48] D. Schaubroeck, S. Monsaert, N. Ledoux, F. Verpoort, R. Drozdzak, US20070043188 A1; 2007.02.22.

[49] The broader applicability of the methodology has successfully been demonstrated in the RCM of 5-hexenyl undec-10-enoate (reference [2a]) to give a mixture of (*E*/*Z*)-exaltolide in 80% yield ($E/Z=2.46{:}1$); experimental conditions: 5-hexenyl undec-10-enoate (3.39 g, 12.7 mmol), **1**@MCM-41 (9.75 g), 0.17 wt% olefin in cyclohexane, 60 °C, 25 h; GC-conditions: HP-5 capillary column (30 m × 0.32 mm × 0.25 μm; He flow: 2.0 mL min^{-1}; program: 60 °C (5 min), 60–300 °C (10 °C min^{-1}), 300 °C (11 min), 300–320 °C (10 °C min^{-1}), 320 °C (18 min).

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