

Monolith- and Silica-Supported Carboxylate-Based Grubbs–Herrmann-Type Metathesis Catalysts

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Abstract: The synthesis of silica- and monolith-supported Grubbs–Herrmann-type catalysts is described. Two polymerizable, carboxylate-containing ligands, *exo,exo*-7-oxanorborn-2-ene-5,6-dicarboxylic anhydride and 7-oxanorborn-2-ene-5-carboxylic acid were surface-immobilized onto silica- and ring-opening metathesis (ROMP-) derived monolithic supports using “grafting-from” techniques. The “1st generation Grubbs catalyst”, RuCl₂(=CHPh)(PCy₃)₂, was used for these purposes. In addition, a poly(norborn-2-ene-*b-exo,exo*-norborn-2-ene-5,6-dicarboxylic anhydride)-coated silica 60 was prepared. The polymer supported anhydride and carboxylate groups were converted into the corresponding mono- and disilver salts, respectively, and reacted with the Grubbs–Herrmann catalyst RuCl₂(=CHPh)(IMesH₂)(PCy₃) [IMesH₂ = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene]. Heterogenization was accomplished by exchange of one chlorine ligand with the polymeric, immobilized silver carboxylates to yield monolith-supported catalysts **4**, **5**, and **6** as well as silica-supported systems **7**, **8** and **9**. The actual composition of these heterogenized catalysts was proven by the

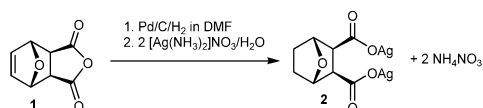
synthesis of a homogeneous analogue, RuCl[7-oxanorbornan-2-(COOAg)-3-COO](=CHPh)(IMesH₂)(PCy₃) (**3**). All homogeneous and heterogeneous catalysts were used in ring-closing metathesis (RCM) of diethyl diallylmalonate, 1,7-octadiene, diallyldiphenylsilane, methyl *trans*-3-pentenoate, diallyl ether, *N,N*-diallyltrifluoroacetamide and *t*-butyl *N,N*-diallylcarbamate allowing turnover numbers (TON's) close to 1000. In a flow-through set-up, an auxiliary effect of pendant silver carboxylates was observed with catalyst **5**, where the silver moiety functions as a (reversible) phosphine scavenger that both accelerates initiation and stabilizes the catalyst by preventing phosphine elution. Detailed catalytic studies were carried out with the monolith-supported systems **4** and **6** in order to investigate the effects of temperature and chain-transfer agents (CTA's) such as *cis*-1,4-diacetoxybut-2-ene. In all RCM experiments Ru-leaching was low, resulting in a Ru-content of the RCM products ≤ 3.5 µg/g (3.5 ppm).

Keywords: carboxylate ligands; heterogeneous catalysis; metathesis; polymers; ruthenium

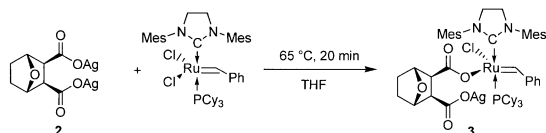
Introduction

Hardly any other field in synthetic organic chemistry has experienced such a rapid development as transition metal-catalyzed C–C coupling reactions.^[1–3] Among these, ring-closing metathesis (RCM), cross and tandem metathesis have gained a strong position. In RCM, *N*-heterocyclic carbene(NHC)-based ruthenium benzyldenes,^[4–6] better known as “2nd generation Grubbs” or “Grubbs–Herrmann” catalysts, are now in the center of interest.^[7,8] Molybdenum-based Schrock carbenes [Mo(=N-2,6-R₂-C₆H₃)(=CHCMe₂Ph)(OCR')₂] are still the compounds of preference in case the reaction needs to be carried out in an asymmetric fashion.^[9–15] Nevertheless, their ruthenium analogues are characterized by an enhanced stability towards oxygen and protic compounds including water, which makes them in due

consequence the catalysts of choice for non-asymmetric RCM. For heterogeneous RCM, we already reported on the synthesis of monolith- and silica-supported Grubbs–Herrmann catalysts.^[16,17] The catalytic systems described there were obtained by heterogenization of a 1st generation Grubbs catalyst *via* the NHC ligand, easily accomplished by an NHC/phosphine exchange. These supported catalysts were characterized by excellent stability, low Ru-bleeding and high turnover numbers (TON's) up to 280. In our search for other heterogenized metathesis catalysts we were encouraged by the reports of Buchowicz et al. and Niecypor et al. on monomeric and supported carboxylate-derived 1st generation Grubbs catalysts.^[18,19] We therefore investigated the general applicability of a halogen exchange between a Grubbs–Herrmann catalyst and a supported functional group, in particular with silver carboxylates.



Scheme 1. Synthesis of compound 2.



Scheme 2. Synthesis of compound 3.

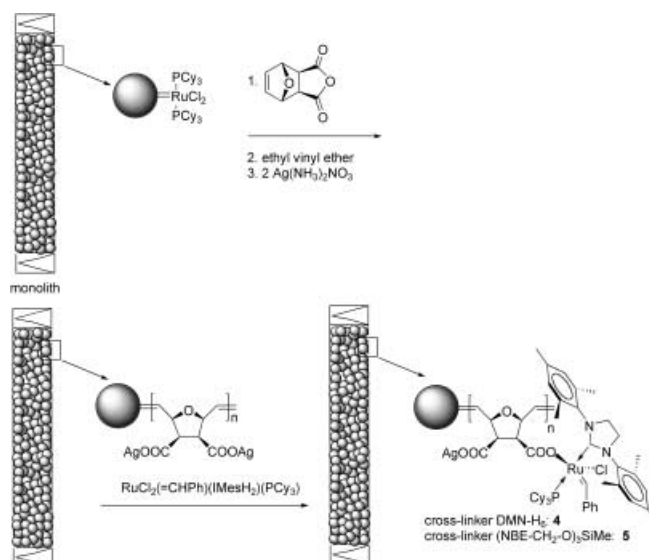
Results and Discussion

Synthesis of Ligands and Homogeneous Catalysts

exo,exo-7-Oxanorbornan-2,3-dicarboxylic anhydride (**1**) was prepared *via* catalytic hydrogenation of 7-oxanorborn-2-ene-5,6-dicarboxylic anhydride and was then converted into the disilver salt by treatment with $\text{Ag}(\text{NH}_3)_2\text{NO}_3$. The product (**2**) was conveniently collected by filtration (Scheme 1).

Halogen exchange of the starting compounds with the Grubbs–Herrmann catalyst was carried out at elevated temperature to form the new catalyst **3**. Interestingly, only one chlorine ligand was exchanged (Scheme 2).

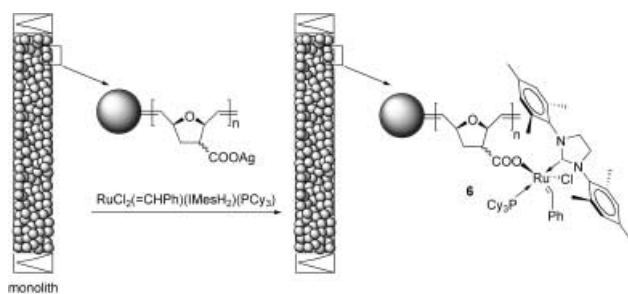
Catalyst **3** was characterized both by ^1H NMR and MALDI-TOF-MS. A single resonance for the alkylidene proton at $\delta = 17.41$ ppm was indicative for the formation of **3**. Although the molecule ion peak was not observed, the m/z of 955.476 was indicative for the presence of a Ru complex containing one chlorine ligand. The presence of a second free Ag carboxylate was proven by reaction of **3** with trimethylchlorosilane. Precipitation of AgCl occurred and the chemical shift for the alkylidene proton shifted to $\delta = 16.82$ ppm. Unfortunately, the resulting compound, presumably $\text{RuCl}[\text{7-oxanorbornan-2-(COOSiMe}_3\text{)-3-COO}](=\text{CHPh})(\text{IMesH}_2)(\text{PCy}_3)$ could not be isolated. All efforts to obtain a catalyst by substitution of both chlorines, e.g., by using the bis-Tl or bis-Cs salts, by adding excess of PCy_3 or by using a phosphine scavenger failed, only decomposition of the catalyst was observed. We tentatively attribute this to the phosphine-scavenging property of the second Ag carboxylate group (*vide infra*), which results in the formation of $\text{AgCl} \cdot \text{PCy}_3$ in course of the (slow) reaction with the second chlorine ligand. This is in strong contrast to the reaction of silver trifluoroacetate or pentafluoropropionate with the 1st generation catalyst, where bridged μ -carboxylato-diruthenium complexes are formed.^[18] As a result of their investigations, Buchowitz et al. proposed that the carboxylates had to possess a pK_a between -7 and 4 in order to allow the synthesis of stable carboxylate-containing 1st generation Grubbs

Scheme 3. Synthesis of monolith-supported Grubbs–Herrmann catalysts [DMN- H_6 -based **4**, (NBE- CH_2O) $_3$ SiMe-based **5**] using a dicarboxylate.

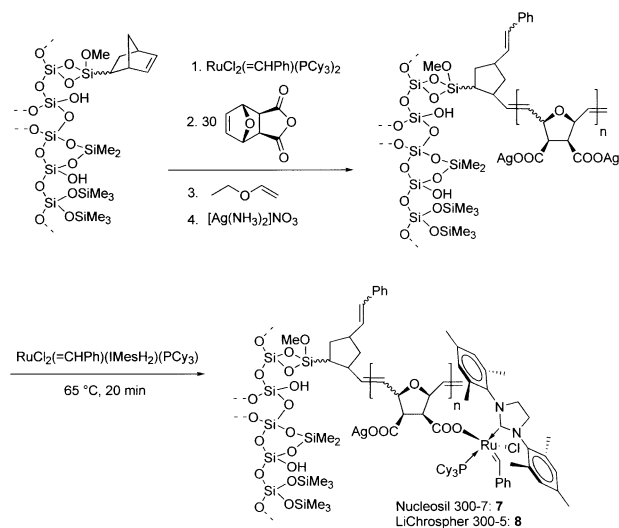
catalyst. This is in contrast to our findings with the dihydroimidazolylidene-based Grubbs–Herrmann catalyst, which appears to be much more tolerant to ligand variation and where the NHC ligand provides enough steric protection to effectively prevent the formation of bridged, dinuclear systems.

Synthesis of Monolith-Supported Catalysts

Metathesis-derived, monolithic supports have already been identified as excellent and easy to make carriers for catalytic systems as well as for separation devices.^[16,20–22] In particular the low back pressure, the accessibility of the solely surface-bound catalytic sites as well as the non-porous character of the support allow the running of such devices in a (continuous) flow-through set-up with high TON's and low catalyst (i.e., ruthenium) bleeding. Monolith-supported systems were prepared according to a protocol similar to the ones described earlier.^[16,23] Briefly, monoliths were synthesized in a one-step procedure within the confines of PEEK (poly ether ether ketone) columns from norborn-2-ene, and 1,4,5,8,8a-hexahydro-1,4,5,8-*exo,endo*-dime-thanonaphthalene (DMN- H_6) or tris(norborn-2-ene-5-ylmethylenoxy)methylsilane [(NBE- CH_2O) $_3$ -SiMe], toluene and 2-propanol. The “living” ruthenium termini located at the surface were used for the graft polymerization of *exo,exo*-7-oxanorborn-2-ene-5,6-dicarboxylic anhydride. The grafted anhydride moieties were finally converted into the bis-silver salt and reacted with $\text{RuCl}_2(=\text{CHPh})(\text{IMesH}_2)(\text{PCy}_3)$ to yield the immobilized catalysts **4** and **5** (Scheme 3). A catalyst loading of 10 and 7 mg/g, respectively, was achieved.



Scheme 4. Synthesis of monolith-supported Grubbs-Herrmann catalyst **6** based on a monocarboxylate.



Scheme 5. Synthesis of a silica-supported Grubbs-Herrmann catalyst based on a dicarboxylate (Nucleosil 300-7-based **7**, LiChrospher 300-5-based **8**).

In order to investigate whether the second (“free”) silver carboxylate had any influence on either the stability or catalytic activity of this system, the same synthetic protocol was applied for the synthesis of a poly(7-oxanorborn-2-ene-5-carboxylic acid) grafted monolith, which was in due consequence used for catalyst immobilization to yield **6** (Scheme 4).

As expected, a similar ruthenium loading of 0.8 mg Ru/g support, corresponding to 9 mg catalyst/g was obtained; nevertheless, a significant difference was observed in catalytic reactivity (*vide infra*).

Synthesis of Silica-Supported Catalysts

Silica-derived supports were fabricated according to a synthetic procedure elaborated in our group.^[24] Briefly, the corresponding support was surface-derivatized with norborn-2-ene-5-yl-trichlorosilane (*exo/endo*-mixture) or norborn-2-ene-5-yl-triethoxysilane (*exo/endo*-mixture) to obtain surface-immobilized silyl-norborn-2-ene groups. These were consecutively reacted with

$\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2$ and *exo,exo*-7-oxanorborn-2-ene-5,6-dicarboxylic anhydride or, respectively, 7-oxanorborn-2-ene-5-carboxylic acid. By this grafting-from approach, satisfactory amounts of both monomers were grafted onto the support. Thus, anhydride loadings of 0.22 mmol/g (LiChrospher 300-5) and 1.2 mmol/g (Nucleosil 300-7) were achieved. Conversion into the corresponding di- and mono-silver salts and reaction with $\text{RuCl}_2(=\text{CHPh})(\text{IMesH}_2)(\text{PCy}_3)_2$ gave the desired supported catalysts **7** and **8** (Scheme 5).

The catalyst-loading was in the range 42 mg (Nucleosil 300-7) to 63 mg catalyst/g (LiChrospher). Complementary, a poly(norborn-2-ene-*b*-7-oxanorborn-2-ene-5,6-anhydride)-coated silica was prepared from silica-60 and poly(norbornene-*b*-7-oxanorborn-2-ene-5,6-dicarboxylate) and used for catalyst immobilization. The corresponding supported catalyst **9**, containing 7.0 mg Ru/g silica, corresponding to 77 mg catalyst/g, was used as an additional benchmark in the ranking of the catalytic activity.

Catalytic Activity

Non-Supported Catalysts

In order to benchmark all the new systems in terms of reactivity, diethyl diallylmalonate (DEDAM), 1,7-octadiene, diallyldiphenylsilane, 1,1-diallylethanol, diallyl ether, *N,N*-diallyltrifluoroacetamide, and *t*-butyl *N,N*-diallylcarbamate were used in RCM. In addition, methyl *trans*-3-pentenoate was used in cross-metathesis. In a first step, the homogeneous catalyst **3** was investigated. The turnover numbers (TON's) that were achieved (TON = 520, Table 1, entries 7–13) were found to be reduced by a factor of 2 compared to the ones obtained with the Grubbs-Herrmann catalyst (Table 1, entries 1–6) indicating that substitution of one chlorine ligand does in fact change the catalytic activity of the system. The importance of appropriate reaction conditions is illustrated by the low values for TON accomplished in complementary experiments carried out in a different (coordinating) solvent such as THF and at different conditions such as higher concentrations (Table 1, entries 14–20).

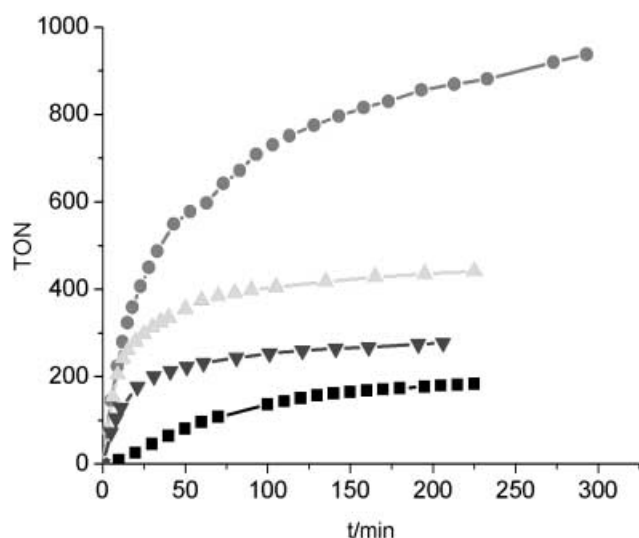
Monolith-Supported Catalysts

The catalytic activity of the carboxylate-based systems was first studied with a DMN- H_6 -derived monolith-supported system (**4**). As can be deduced from Figure 1, the optimum conditions for this catalyst entailed a reaction temperature of 45 °C and the use of a chlorinated solvent.

In fact, we could not find any significant difference between dichloromethane and dichloroethane. The

Table 1. Summary of catalytic activity of homogeneous systems.

#	Compound	Catalyst	T [°C]	Solvent (mol % compound)	TON
1	DEDAM	Grubbs–Herrmann	45	CH ₂ Cl ₂ (0.05)	1300
2	1,7-octadiene	Grubbs–Herrmann	45	CH ₂ Cl ₂ (0.1)	1000
3	diallyldiphenylsilane	Grubbs–Herrmann	45	CH ₂ Cl ₂ (0.1)	400
4	methyl <i>trans</i> -3-pentenoate	Grubbs–Herrmann	45	CH ₂ Cl ₂ (0.01)	600
5	<i>t</i> -butyl <i>N,N</i> -diallylcarbamate	Grubbs–Herrmann	45	CH ₂ Cl ₂ (0.1)	770
6	<i>N,N</i> -diallyltrifluoroacetamide	Grubbs–Herrmann	45	CH ₂ Cl ₂ (0.1)	150
7	DEDAM	3	45	CH ₂ Cl ₂ (0.05)	520
8	1,7-octadiene	3	45	CH ₂ Cl ₂ (0.1)	520
9	diallyldiphenylsilane	3	45	CH ₂ Cl ₂ (0.1)	140
10	1,1-diallylethanol	3	45	CH ₂ Cl ₂ (0.1)	25
11	methyl <i>trans</i> -3-pentenoate	3	45	CH ₂ Cl ₂ (0.01)	280
12	diallyl ether	3	45	CH ₂ Cl ₂ (0.1)	50
13	<i>N,N</i> -diallyltrifluoroacetamide	3	45	CH ₂ Cl ₂ (0.1)	190
14	DEDAM	3	45	THF (9.3)	40
15	1,7-octadiene	3	45	THF (3.8)	20
16	diallyldiphenylsilane	3	45	THF (9.1)	30
17	1,1-diallylethanol	3	45	THF (4.3)	10
18	methyl <i>trans</i> -3-pentenoate	3	45	THF (5.6)	10
19	diallyl ether	3	45	THF (3.4)	90
20	<i>N,N</i> -diallyltrifluoroacetamide	3	45	THF (6.0)	2

**Figure 1.** Catalytic activities of **4** and **5** vs. DEDAM. Flow rate = 0.1 mL/min, *c*(DEDAM) = 10 wt % in ClCH₂CH₂Cl. ● (**5**, T = 45 °C), ▲ (**5**, T = 35 °C), ▼ [**5**, T = 45 °C, *c*(CTA) = 1 wt %], ■ (**4**, T = 45 °C).

TON found for DEDAM was 180 (Table 2, entry 21). From previous investigations concerning the microstructure of DMN-H₆-derived monoliths we found that a significant percentage of this rigid cross-linker did not take part in the cross-linking reaction, resulting in the presence of a substantial number of norborn-2-ene-subunits.^[23] Since these are highly reactive, we could not rule out an interference with the RCM reactions of interest. We therefore changed the polymeric matrix by using the more flexible (NBE-CH₂O)₃-SiMe as a cross-linker instead of DMN-H₆. Due to a reduced meso-

porosity,^[23] smaller amounts of the anhydride or, respectively, the catalyst (i.e., 7 mg/g) could be immobilized. Nevertheless, with the corresponding monolith-supported catalyst **5** we could achieve the *highest TON's ever reported for a supported system*, partially reaching the TON's that were observed with the Grubbs–Herrmann catalyst in solution (e.g., for 1,7-octadiene, Table 2, entries 22–28). The finding that TON's were even higher than those obtained with **3** is attributed to the immobilization itself, which eliminates bimolecular reactions between two catalyst moieties.^[25] CTA's (chain-transfer agents) are often used to enhance the stability of a system.^[16,17] More detailed investigations carried out with DEDAM revealed that neither higher nor lower temperatures (Table 2, entries 30 and 31) nor the use of a CTA (Table 2, entry 29) had a positive influence on the persistence, i.e., stability of this system as reflected by the corresponding TON's.

In order to shed some light on the (potentially synergistic) role of the second silver-carboxylate ligand present in the system we prepared a monolith-supported catalyst starting with a mono-silver carboxylate (**6**). As can be seen (Table 2, entry 32, Figure 2), the TON for DEDAM (110) was comparably low under conditions identical to the ones previously used. In addition, we could monitor increased amounts of free PCy₃ in the effluent.

This is in strong contrast to what was observed with catalyst **5**, where no PCy₃ was observed at all. In view of this and the differences in catalytic activity of **5** and **6** we conclude that the second, pendant silver carboxylate functions as an internal reversible phosphine scavenger during the RCM process, which reduces the loss of

Table 2. Summary of catalytic activity of heterogeneous systems.

#	Compound	Catalyst	T [°C]	Solvent (Conc. [wt. %])	TON
21	DEDAM	4	45 ^[a]	ClCH ₂ CH ₂ Cl (10)	180
22	DEDAM	5	45 ^[a]	ClCH ₂ CH ₂ Cl (10)	940
23	1,7-octadiene	5	45 ^[a]	CH ₂ Cl ₂ (10)	900
24	diallyldiphenylsilane	5	45 ^[a]	CH ₂ Cl ₂ (10)	90
25	methyl <i>trans</i> -3-pentenoate	5	45 ^[a]	ClCH ₂ CH ₂ Cl (47.5)	340
26	methyl <i>trans</i> -3-pentenoate	5	45 ^[a]	ClCH ₂ CH ₂ Cl (10)	30
27	<i>N,N</i> -diallyltrifluoroacetamide	5	45 ^[a]	ClCH ₂ CH ₂ Cl (10)	70
28	<i>t</i> -butyl <i>N,N</i> -diallylcarbamate	5	45 ^[a]	ClCH ₂ CH ₂ Cl (10)	140
29	DEDAM	5	45 ^[a, c]	ClCH ₂ CH ₂ Cl (10)	280
30	DEDAM	5	35 ^[a]	ClCH ₂ CH ₂ Cl (10)	442
31	DEDAM	5	55 ^[a]	ClCH ₂ CH ₂ Cl (10)	220
32	DEDAM	6	45 ^[a]	ClCH ₂ CH ₂ Cl (10)	110
33	DEDAM	7	50 ^[b]	ClCH ₂ CH ₂ Cl (1.5)	10
34	DEDAM	7	65 ^[b]	ClCH ₂ CH ₂ Cl (1.5)	10
35	DEDAM	7	50 ^[b, c]	ClCH ₂ CH ₂ Cl (1.5)	1
36	DEDAM	8	45 ^[b]	CH ₂ Cl ₂ (2)	90
37	1,7-octadiene	8	45 ^[b]	CH ₂ Cl ₂ (2)	50
38	diallyldiphenylsilane	8	45 ^[b]	CH ₂ Cl ₂ (2)	40
39	<i>N,N</i> -diallyltrifluoroacetamide	8	45 ^[b]	CH ₂ Cl ₂ (2)	70
40	<i>t</i> -butyl <i>N,N</i> -diallylcarbamate	8	45 ^[b]	CH ₂ Cl ₂ (2)	60
41	DEDAM	9	45 ^[a]	CH ₂ Cl ₂ (10)	20
42	DEDAM	9	50 ^[a, d]	CH ₂ Cl ₂ (10)	3
43	DEDAM	9	50 ^[b, c]	CH ₂ Cl ₂ (5)	0.1

^[a] Flow-through.^[b] Stirred batch.^[c] 1% *cis*-1,4-diacetoxy-2-butene.^[d] 0.1% *cis*-1,4-diacetoxy-2-butene.

phosphine and thus stabilizes the ruthenium core in the absence of a diene.

Silica-Supported Catalysts

Synthetic routes based on combinatorial chemistry usually entail the use of combi-chem machines. If used in catalytic processes, stirred reactions are usually the preferred set-up. For this purpose, the silica-based systems **7**, **8** and **9** were prepared. After verifying the optimum conditions (Table 2, entries 33–35), a surface-grafted system based on Nucleosil 300–5 was used in stirred batch RCM reactions. TON's in the range of 60–90 were achieved (Table 2, entries 36–40). This definitely allows its use in combinatorial chemistry. Furthermore, the surface-grafting of silica provided supports that were really comparable to their monolithic analogues because of the identical set-up. In view of the quite different catalytic data achieved with these two supports, one obtains a nice illustration of the superiority of monolith-based systems used in a flow-through set-up over classic supports.

A more straightforward synthetic route to silica-based supports is the synthesis of coated analogues. These are easy and straightforward to prepare, yet suffer from a reduced accessibility of the catalytic sites, since these are

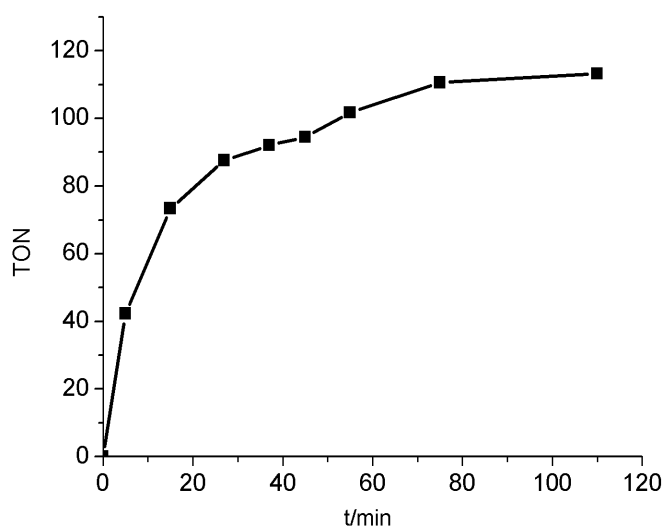


Figure 2. Catalytic activity of **6** for DEDAM. T = 45 °C, flow rate = 0.1 mL/min, c(DEDAM) = 10 wt % in ClCH₂CH₂Cl.

located within the polymer film deposited on the silica surface. Not unexpected, if used in a flow-through or stirred batch set-up (Table 2, entries 41–43), comparably low TON's were achieved with the coated support **9**, which justifies the synthesis of defined surfaces *via* grafting techniques in heterogeneous catalysis. In order

to determine the Ru content of the final RCM products, ICP analyses were carried out. These revealed a Ru-content as low as $= 3.5 \mu\text{g Ru/g}$, which gives another nice illustration of the applicability of these systems.

Conclusion

For the first time, Grubbs–Herrmann-type catalysts have been immobilized on monolithic and silica-based supports *via* exchange of one chlorine ligand. The disilver salts of *vic*-dicarboxylates turned out to be superior to silver carboxylates since the second, pendant silver carboxylate functions as a reversible phosphine scavenger. Both the monolith- and silica-based catalytic systems turned out to be stable, allowing high TON's in RCM for a large number of compounds. Ruthenium leaching was low, resulting in virtually Ru-free products. The catalytic systems described here can be used as monolith-based flow-through reactors as well as surface-grafted silica-based supports in slurry-type reactions. Together with their stability and high activity, this is believed to make them attractive for both combinatorial chemistry and large-scale industrial applications.

Experimental Section

General Remarks

NMR data were obtained at 300.13 MHz for proton and at 75.74 MHz for carbon in the indicated solvent at 25 °C on a Bruker Spectrospin 300 and are listed in parts per million downfield from tetramethylsilane for proton and carbon. IR spectra were recorded on a Bruker Vector 22 using ATR technology. GC-MS investigations were carried out on a Shimadzu GCMS-QP5050, using a SPB-5 fused silica column (30 m $\times$ 0.25 mm $\times$ 25 μm film thickness). Elemental analyses were carried out at the Institute of Physical Chemistry, University of Vienna and at the Mikroanalytische Laboratorium, Anorganisch-Chemisches Institut, TU München, Germany. A Jobin Yvon JY 38 plus was used for ICP-OES measurements, an MLS 1200 mega for microwave experiments. PEEK columns (100 $\times$ 4 mm i.d., 125 $\times$ 4 mm i.d. and 150 $\times$ 4 mm i.d.) were purchased from Berger (Linz, Austria). Further instrumentation is described elsewhere^[26]. MALDI-TOF experiments were carried out on a Bruker Biflex III using an N₂ laser ($\lambda = 337 \text{ nm}$). Dithranol (1,8-dihydroxyanthron) was used as the matrix.

Syntheses of the ligands and polymerizations were performed under an argon atmosphere by standard Schlenk techniques or in an N₂-mediated dry-box (MBraun, Germany) unless stated otherwise. Reagent grade diethyl ether, pentane, THF and toluene were distilled from sodium benzophenone ketyl under argon. Reagent grade triethylamine, dichloromethane, 1,2-dichloroethane were distilled from calcium hydride under argon. Other solvents and reagents were used as purchased. Deionized water was used throughout. Diethyl diallylmalonate (DEDAM), 1,7-octadiene, diallyl ether, *N,N*-

diallyltrifluoroacetamide, diallyldiphenylsilane, methyl *trans*-3-pentenoate, *t*-butyl *N,N*-diallylcarbamate, *cis*-1,4-diacetoxy-2-butene, ethyl vinyl ether (EVE), RuCl₂(=CHPh)(PCy₃)₂, and RuCl₂(=CHPh)(IMesH₂)(PCy₃) [IMesH₂ = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene] were purchased from Fluka (Buchs, Switzerland). A ruthenium standard containing 1000 ppm of ruthenium was purchased from Alfa Aesar/Johnson Matthey (Karlsruhe, Germany). Bicyclo[2.2.1]hept-2-ene-5-yl(trichloro)silane and bicyclo[2.2.1]hept-2-ene-5-yl(triethoxy)silane were purchased from ABCR (Darmstadt, Germany). *exo,exo*-7-Oxanorborn-2-ene-5,6-dicarboxylic anhydride,^[27] methyl 7-oxanorborn-2-ene-5-carboxylate,^[28] 7-oxanorborn-2-ene-5-carboxylic acid,^[29] tri-(norborn-2-ene-5-yl-methoxy)methylsilane (NBE-CH₂O)₃-SiMe₃,^[23] and 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo,endo*-dime-thanonaphthalene (DMN-H₆),^[30] were prepared according to literature procedures and checked for purity by means of NMR. Nucleosil 300-7 (300 Å, 7 μm , pore volume 1.0 mL/g), LiChrospher wp300 (300 Å, 5 μm , 80 m²/g) and silica 60 (230–400 mesh, 40–63 μm , 480–540 m²/g, pore volume = 0.74–0.84 mL/g) were purchased from Merck, Germany. C-18 derivatization of silica-60^[31] as well as the synthesis of poly-(norborn-2-ene-*b*-7-oxanorborn-2-ene-5,6-anhydride)-coated silica^[32] were carried out according to the literature.

exo,exo-4,10-Dioxatricyclo[5.2.1.0^{2,6}]decane-3,5-dione (7-Oxanorbornan-2,3-dicarboxylic Anhydride)

exo,exo-7-Oxanorborn-2-ene-5,6-dicarboxylic anhydride (1, 25 g, 150 mmol) was dissolved in 100 mL of dry DMF and Pd/C (10%, 1.3 g) was added. Hydrogenation was carried out at 1 bar for 6 h. After addition of 50 mL Et₂O the mixture was filtered over celite, reduced to 5 mL and filtered again. After evaporating to dryness the residue was recrystallized from CHCl₃. The crystals were dried giving the anhydride as a white solid; yield: 21.85 g (130 mmol, 86%); ¹H NMR (DMSO-*d*₆, 25 °C): $\delta = 4.86$ (s, 2H, CH₂CH), 3.40 (s, 2H, COCH), 1.65 (s, 4H, CH₂); ¹³C NMR (DMSO-*d*₆, 25 °C): $\delta = 171.4$ (CO), 80.2 (CHO), 50.6 (CHCO), 28.1 (CH₂); FT-IR (ATR-mode): $\tilde{\nu} = 3478.11$ (w), 3379.01 (w), 2883.83 (w), 2627.02 (w), 1841.36 (w), 1769.84 (s), 1681.46 (s) cm⁻¹; GC-MS (EI, 70 eV): calcd. for C₈H₈O₄: $m/z = 168.04$ (M⁺); found: 168.0.

Diargento-*exo,exo*-[2.2.1]bicycloheptane-2,3-dicarboxylate (2)

A solution of NH₃ in water (1:5) was added dropwise to a stirred solution of AgNO₃ (1.009 g, 5.94 mmol) in 10 mL water until the precipitate of silver hydroxide had disappeared. *exo,exo*-4,10-Dioxatricyclo[5.2.1.0^{2,6}]decane-3,5-dione (0.5 g, 2.97 mmol, 0.5 equiv.), dissolved in 2 mL of THF, was added to the clear solution resulting in the formation of a white precipitate. After stirring for 30 minutes, the precipitate was separated from the solution and washed consecutively with water, THF and Et₂O. Finally, the white solid was dried under vacuum; yield: 0.57 g (1.43 mmol, 48%); FT-IR (ATR-mode): $\tilde{\nu} = 3381.07$ (s), 3190.38 (w), 3000.85 (w), 2946.94 (w), 2873.07 (w), 1629.33 (vs), 1540.95 (vs), 1445.40 (s), 1395.29 (vs) cm⁻¹; anal. calcd. for C₈H₈Ag₂O₅ (M_r = 399.88 g/mol): C 24.03, H 2.02, Ag 53.95; found: C 24.33, H 2.12, Ag 53.60.

RuCl₂(COO[C₆H₅O]COOAg)(=CHPh)(IMesH₂)(PCy₃) (3)

Compound **2** (23.6 mg, 0.059 mmol) was added to a stirred solution of RuCl₂(=CHPh)(IMesH₂)(PCy₃) (50 mg, 0.059 mmol) in 10 mL of dry THF. The solution was stirred for 20 min at 65 °C. The color of the solution changed from red to green, the precipitate was filtered off and the filtrate evaporated to dryness. It was re-dissolved in a small amount of benzene and the solid was separated and washed with benzene, giving the product as a green powder; yield: 10 mg (0.009 mmol, 15%); FT-IR (ATR): $\tilde{\nu}$ = 2960 (w), 2921 (s), 2847 (w), 1781 (w), 1651 (s), 1585 (w), 1478 (w), 1444 (w), 1411 (s), 1259 (vs), 1173 (w), 1090 (vs), 1016 (vs), 851 (s), 798 (vs) cm⁻¹; ¹H NMR (CDCl₃, 25 °C): δ = 17.41 (s, 1H, PhCH), 7.87 (d, 2H, CHCCCH), 7.06 – 7.22 (m, 7H, aromatics), 4.57 (d, 2H, CHO), 3.91 (b, 4H, NCH₂), 3.80 (m, 2H, CHCO), 2.30 (s, 12H, NCCCCH₃), 2.14 (s, 6H, CHCCCH₃), 1.94 (s, 3H, PCH), 1.80 (s, 12H, PCHCH₂), 1.60 (s, 12H, CHCH₂CH₂), 1.21 (m, 6H, CHCH₂CH₂CH₂); MALDI-TOF calcd. for C₅₄H₇₃AgClN₂O₅: *m/z* = 1104.304; found: 955.476 (MH⁺ – COOAg); anal. calcd. for C₅₄H₇₃AgClN₂O₅PRu (M_r = 1105.549 g/mol): C 58.67, H 6.66, N 2.53; found: C 58.53, H 6.28, N 3.78.

Synthesis of Monolith-Supported Catalysts Based on Dicarboxylates

A. Using DMN-H₆ as Cross-linker (4): Column dimensions: V = 1.57 mL (125 × 4 mm i. d.). The following amounts were used: norborn-2-ene (NBE, 1.00 g, 10.6 mmol), DMN-H₆ (0.96 mL, ρ = 1.038 g/mL, 6.3 mmol), 2-propanol 2.94 mL, toluene 0.63 mL, RuCl₂(=CHPh)(PCy₃)₂ (20 mg, 0.024 mmol), PPh₃ (0.07 mL of a solution containing 30 mg PPh₃/10 mL of toluene). This corresponds to a ratio of NBE:DMN-H₆:2-propanol:toluene:initiator:PPh₃ of 20:20:46.2:13.4:0.4 (all wt %). A solution of 2-propanol, NBE and DMN-H₆ was stirred for 30 minutes and added to a stirred solution of toluene, the initiator and the PPh₃ solution, chilled to –30 °C. Stirring was continued for 2 min after which the column (chilled to 0 °C) was filled with the reaction mixture. After polymerization for 30 minutes at 0 °C and another 30 minutes at room temperature the column was washed with dry THF. A solution of *exo*, *exo*-7-oxanorborn-2-ene-5,6-dicarboxylic anhydride (0.2 g, 1.2 mmol) in dry DMF (20 wt %) was added and graft-polymerization was carried out at 45 °C over 12 h. The column was washed with a 40 vol. % solution of EVE in THF, followed by pure THF. A solution of AgNO₃ (340 mg, 2.0 mmol) in 2 mL of a 1:5 mixture of NH₃ and water was prepared and passed through the column maintaining a temperature of 45 °C. The support was consecutively washed with water until a base- and silver-free effluent was assured, then with dry THF. RuCl₂(=CHPh)(IMesH₂)(PCy₃) (50 mg, 0.059 mmol) dissolved in 2 mL of dry THF was added and reaction was allowed to proceed at 65 °C over 20 min. Finally, the monolith was washed with dry THF until the washings were colorless. Ru-loading 0.9 mg/g, corresponding to 10 mg catalyst/g.

B. Using (NBE-CH₂O)₃SiMe as a Cross-linker (5): Column dimensions: V = 1.57 mL (125 × 4 mm i. d.). The following amounts were used: NBE (0.5 g), (NBE-CH₂O)₃SiMe (0.5 mL), 2-propanol (1.46 mL), toluene (0.39 mL), RuCl₂(=CHPh)(PCy₃)₂ (10 mg, 0.012 mmol). This corresponds

to a ratio of (NBE-CH₂O)₃SiMe:2-propanol:toluene:initiator of 20:20:45.7:13.9:0.4 (all wt %). Monolith synthesis was carried out as described above. Surface-grafting and initiator-immobilization was accomplished according to the procedure described above using a solution of *exo*, *exo*-7-oxanorborn-2-ene-5,6-dicarboxylic anhydride (0.32 g, 1.93 mmol) in DMF (20 wt %), AgNO₃ (340 mg, 2.0 mmol) in 2 mL of a 1:5 mixture of NH₃/water and RuCl₂(=CHPh)(IMesH₂)(PCy₃) (50 mg, 0.059 mmol) in 2 mL of THF. Ru-loading 0.6 mg/g, corresponding to 7 mg catalyst/g.

Synthesis of Monolith-Supported Catalysts Based on Mono-Carboxylates (6)

Column dimensions: V = 1.26 mL (100 mm × 4 mm). The following amounts were used: NBE (0.5 g mmol), (NBE-CH₂O)₃SiMe (0.5 mL, 0.54 mg, 1.28 mmol), 2-propanol (1.455 mL), toluene (0.391 mL), RuCl₂(=CHPh)(PCy₃)₂ (10 mg, 0.012 mmol). This corresponds to a ratio of 20:20:45.7:13.9:0.4 (all wt %). Monolith synthesis was carried out as described above. Surface-grafting and initiator-immobilization was accomplished according to the procedure described above using a solution of 7-oxanorborn-2-ene-5-carboxylic acid (0.32 g, 2.28 mmol) in DMF (20 wt %), AgNO₃ (300 mg, 1.76 mmol) in 2 mL of a 1:5 mixture of NH₃/water and RuCl₂(=CHPh)(IMesH₂)(PCy₃) (50 mg, 0.059 mmol) in 2 mL of THF. Ru-loading 0.8 mg/g, corresponding to 9 mg catalyst/g.

Synthesis of Silica-Supported Catalysts 7 and 8 Based on Dicarboxylates

Preparation of Norborn-2-ene Derivatized Nucleosil 300–7 (NBE-Nucleosil 300–7): Nucleosil 300–7 was suspended in 200 mL of toluene and refluxed in a Dean-Stark apparatus for 24 h until all water was removed. The silica was filtered off, dried under vacuum and re-suspended in 150 mL of dry CH₂Cl₂. Dry triethylamine (3.36 mL 2.44 g, 24.63 mmol) and (norborn-2-ene-5-yl)trichlorosilane (0.79 mL, 1.02 g, 4.5 mmol) were added to the stirred suspension. After refluxing for 6 h, trimethylchlorosilane (0.68 mL, 0.58 g, 5.38 mmol) and dimethyldichlorosilane (0.34 mL, 0.36 g, 2.78 mmol) were added and the suspension was refluxed for another 2 h. 25 mL of dry MeOH were added and the mixture was stirred for 15 min, then the suspension was filtered off, washed with dry MeOH, dry CH₂Cl₂, dry Et₂O and dried under vacuum. Elemental anal. found: C 2.98, H 0.47, N 0.00.

Determination of Norborn-2-ene Loading: Br₂ (65 μ L, 1.26 μ mol) was added to 500 mL of MeOH and the solution was saturated with NaBr. Titration of the solution with a solution of 2.5 mmol/L Na₂S₂O₃ revealed a concentration of 2.97 × 10⁻⁶ mol Br₂/mL. Three samples (180 mg each) of the derivatized Nucleosil were suspended in MeOH and 10 mL of the Br₂ solution and 1 mL of a saturated NaI solution in water were added. A few drops of a freshly prepared aqueous starch solution were added and stirring was continued for 20 min. Then the suspension was titrated with a 2.5 mmol/L Na₂S₂O₃ solution revealing a loading of 7.7 × 10⁻⁵ mol norborn-2-ene/g Nucleosil.

Grafting of NBE-Nucleosil 300–7: NBE-Nucleosil 300–7 (3.37 g) was suspended in 50 mL dry DMF, RuCl₂(=CHPh)-

(PCy₃)₂ (221 mg, 0.268 mmol) was added to the stirred solution and stirring was continued for 30 minutes. *exo,exo*-7-Oxanorborn-2-ene-5,6-dicarboxylic anhydride (1.29 g, 7.75 mmol) was added and polymerization was allowed to proceed for 18 h at 45 °C. In course of the reaction, the color of the suspension changed from yellow to green. Finally, ethyl vinyl ether (74 mg, 1.03 mmol) was added and stirring was continued for another 15 min at 45 °C. The product was filtered off, washed three times with DMF, THF, Et₂O and dried under vacuum. FT-IR (ATR): $\tilde{\nu}$ = 2324 (w), 1985 (w), 1125 (s), 1050 (vs), 964 (s), 721 (s) cm⁻¹; anal. found: C 13.66, H 1.36.

Titration of Grafted NBE-Nucleosil 300–7: The grafted NBE-Nucleosil 300–7 (0.100 g) was suspended in 15 mL of water and 20 mL of a 0.05 mol/L solution of NaOH were added. The mixture was stirred for 5 h, filtered and titrated with 0.05 mol/L HCl versus phenolphthalein. This procedure revealed 1.2 mmol anhydride/g silica, corresponding to an average degree of polymerization (DP) of 20.

Conversion of Grafted NBE-Nucleosil 300–7 into the Disilver Salt: The grafted NBE-Nucleosil 300–7 (3.40 g) was suspended in 20 mL of THF and a solution of AgNO₃ (2.06 mg, 12.14 mmol) in 10 mL of a 1:5 mixture of NH₃/H₂O was added. After stirring for 30 minutes, the product was filtered off and washed three times with H₂O, THF and Et₂O. The product was dried over night under vacuum resulting in a white product; yield: 3.6 g; FT-IR (ATR): $\tilde{\nu}$ = 2541 (w), 2286 (w), 1057 (vs) cm⁻¹.

Fixation of RuCl₂(=CHPh)(IMesH₂)(PCy₃) on Grafted Nucleosil 300–7 (Disilver-Form) (7): The disilver salt of the grafted Nucleosil 300–7 (1.50 g) was suspended in dry toluene, RuCl₂(=CHPh)(IMesH₂)(PCy₃) (100 mg, 0.12 mmol) was added and the mixture was stirred at 65 °C for 20 min. The product was filtered off and washed with dry Et₂O until the washings were colorless to give a brownish solid; yield: 1.33 g; FT-IR (ATR): $\tilde{\nu}$ = 2981 (b), 2285 (w), 2118 (w), 1731 (s), 1665 (s), 1562 (s), 1392 (s), 1056 (vs) cm⁻¹. Ru-loading: 3.9 mg/g corresponding to 42 mg catalyst/g.

Preparation of Norborn-2-ene-Derivatized LiChrospher 300–5 (NBE-LiChrospher 300–5): The same protocol as described for Nucleosil 300–7 was applied using LiChrospher, 200 mL of toluene for drying, NBESi(OEt)₃ (2.56 g, 10.0 mmol), trimethylchlorosilane (1.4 mL, 1.19 g, 11.08 mmol), dimethyldichlorosilane (1.4 mL, 1.48 g, 11.45 mmol), triethylamine (7 mL, 5.08 g, 51.31 mmol) and dry MeOH (25 mL); elemental anal. found: C 1.30, H 0.67, N 0.00.

Determination of Norborn-2-ene Loading: The same protocol as described for Nucleosil 300–7 was applied using Br₂ (65 μ L), 500 mL of MeOH saturated with NaBr, 0.0025 mol/L Na₂S₂O₃. The NBE loading was 3.0×10^{-4} mol NBE/g Nucleosil.

Grafting of NBE-LiChrospher 300–5: The same protocol as described for Nucleosil 300–7 was applied using NBE-Nucleosil-300-5 (3.00 g), 50 mL of dry DMF, 1 equiv. of RuCl₂(=CHPh)(PCy₃)₂ (0.9 mmol, 0.74 g), 30 equiv. of 7-oxanorborn-2-ene-5-carboxylic acid (27 mmol, 4.48 g), and 74 mg of EVE. FT-IR (ATR): $\tilde{\nu}$ = 2324.15 (w), 1984.74 (w), 1125.19 (s) and 1049.57 (vs) cm⁻¹; elemental anal. found: C 1.32, H 0.60, N 0.00.

Titration of Grafted NBE-LiChrospher 300–5: The same protocol as described for NBE-Nucleosil-300-7 was applied. A loading of 0.22 mmol anhydride/g Nucleosil was found.

Conversion of Grafted NBE-LiChrospher 300–5 into the Silver Salt: The same protocol as described for Nucleosil 300–7 was applied using 2.00 g of the grafted Nucleosil-300-7 and AgNO₃ (200 mg, 1.18 mmol) in 1:5 NH₃/H₂O. FT-IR (ATR): $\tilde{\nu}$ = 2541.41 (w), 2285.82 (w) and 1057.33 (vs) cm⁻¹; elemental anal. found: C 0.94, H 0.13, N 0.00.

Fixation of RuCl₂(=CHPh)(IMesH₂)(PCy₃) on Grafted LiChrospher 300–5 (Silver-Form) (8): The same protocol as described for Nucleosil 300–7 was applied using 1.4 g of the silver salt in 20 mL of THF, 115 mg (0.135 mmol) of RuCl₂(=CHPh)(IMesH₂)(PCy₃) in 2 mL of THF. FT-IR (ATR): $\tilde{\nu}$ = 2360.80 (w), 2340.39 (w), 1057.33 (vs) cm⁻¹; elemental anal. found: C 1.88, H 0.44, N 0.16. This corresponds to 63 mg catalyst/g.

Determination of Anhydride Capacity of Coated Silica 60

Poly(norborn-2-ene-*b*-7-oxanorborn-2-ene-5,6-anhydride)-coated silica (200 mg) was stirred in 10 mL of 0.05 M NaOH for 24 h. The resin was filtered off and washed with water. The combined washings were titrated with 0.05 M HCl vs. phenolphthalein. Capacity: 0.96 mmol acid/g silica.

Disilver Salt of Poly(norborn-2-ene-*b*-7-oxanorborn-2-ene-5,6-anhydride)-Coated Silica 60

Poly(norborn-2-ene-*b*-7-oxanorborn-2-ene-5,6-anhydride)-coated silica (0.500 g) was dissolved in 5 mL of THF and 2 equiv. of NaOH (191 mg, 14.8 mmol) dissolved in 22 mL of water were added. After 2 h of stirring, the polymer was filtered off and washed three times with water. The polymer was re-dissolved in 5 mL of THF and 2 mL of water. AgNO₃ (2 equiv., 815 mg, 4.8 mmol) was added and stirring was continued for another 4 h. The polymer was filtered off, washed twice with water, THF, Et₂O and dried under vacuum to give a white solid; yield: 4.9 g (98%); FT-IR (ATR): $\tilde{\nu}$ = 2363.5 (w), 1747.3 (w), 1056.0 (vs) cm⁻¹.

Fixation of RuCl₂(=CHPh)(IMesH₂)(PCy₃) on Poly(norbornene-*b*-7-oxanorborn-2-ene-5,6-dicarboxylate)-Coated Silica 60 (Disilver Form) (9)

The disilver salt of poly(norborn-2-ene-*b*-7-oxanorborn-2-ene-5,6-anhydride)-coated silica 60 (1 equiv., 123 mg) was suspended in 5 mL of THF and added to a stirred solution of RuCl₂(=CHPh)(IMesH₂)(PCy₃) (50 mg, 0.059 mmol) in 5 mL of THF. After stirring for 30 minutes at 55 °C, the support was filtered off, washed with diethyl ether and evaporated to dryness under vacuum. FT-IR (ATR): $\tilde{\nu}$ = 3337 (b), 2282 (w), 2115 (w), 1733 (s), 1372 (w), 1049 (vs), 798 (s) cm⁻¹.

RCM-Experiments (Slurry Reactions)

The following procedure is representative for all experiments. DEDAM (20 mg, 0.08 mmol) was dissolved in the corresponding solvent (e.g., 1,2-dichloroethane, 2 mL) and the supported catalyst (40 mg) was added. The reaction mixture was heated to

45 °C for 2 hours. After removal of the catalyst by filtration, the yield was determined by GC-MS and ¹H NMR in CDCl₃, respectively.

RCM-Experiments (Flow-Through Reactions)

The following procedure is representative for all experiments. DEDAM (20 mg, 0.08 mmol) was dissolved in the corresponding solvent (e.g., 1,2-dichloroethane, 2 mL) and this solution was pumped through a cartridge filled with the supported catalyst (either monolith- or silica-based) heated to 45 °C at a flow rate of 0.1 mL/min unless stated otherwise. The effluent was collected in 0.5 mL portions and the yield was determined by GC-MS and ¹H NMR in CDCl₃, respectively.

Leaching of the Support

All volatiles were removed from the combined effluents and aqua regia (3.0 mL) was added. The mixture was placed inside high-pressure Teflon tubes and leaching was carried out under Microwave conditions (50, 600, and 450 W pulses, respectively, *t* = 32 minutes). After cooling to room temperature, the mixture was filtered and water was added up to a volume of 10.00 mL.

Ru Measurements

Ru was measured by ICP-OES (λ = 240.272 nm, ion line). The background was measured at λ = 240.287 and 240.257 nm, respectively. Standardization was carried out with Ru standards containing 0, 5 and 10 ppm of Ru.

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