

Monolithic Disk-Supported Metathesis Catalysts for Use in Combinatorial Chemistry

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Dedicated to Prof. Richard R. Schrock, a brilliant scientist, scholar and friend on the occasion of his 60th birthday.

Abstract: Two metathesis catalysts, $\text{RuCl}_2(\text{PCy}_3)(\text{NHC})(\text{CHPh})$ (**1**) [$\text{NHC} = 1-(2,4,5\text{-trimethylphenyl})-3-(6\text{-hydroxyhexyl})\text{-imidazol-2-ylidene}$] and $\text{Mo}(\text{N-}2,6\text{-}i\text{-Pr}_2\text{-C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(\text{BIPHEN})$ (**2**) [$\text{BIPHEN} = (R)\text{-}3,3'\text{-di-}t\text{-butyl-}5,5',6,6'\text{-tetramethyl-}2,2'\text{-biphenolate}$] have been immobilized on polymeric, monolithic discs using a “grafting from” protocol. Monolithic discs were prepared *via* ring-opening metathesis polymerization (ROMP) from norborn-2-ene (NBE), tris(norborn-5-ene-2-ylmethyleneoxy)methylsilane [$(\text{NBE-CH}_2\text{O})_3\text{-SiCH}_3$], 2-propanol, toluene and $\text{RuCl}_2(\text{PCy}_3)_2(\text{CHPh})$. Catalyst loadings of 0.55 and 0.7 wt %, respectively, were obtained. Monolithic disc-immobilized **1** was used in various metathesis-based reactions including ring-closing metathesis (RCM), ring-opening cross metathesis and enyne metathesis. Using 0.23–0.59 mol % of supported **1**, turnover numbers (TONs) up to 330 were achieved.

Monolithic disc-immobilized **2** was used in various enantioselective RCM and desymmetrization reactions. Using 9–13 mol % of supported catalyst, excellent yields up to 100% and high enantiomeric excess ($ee \leq 88\%$) were observed. In both cases, metal leaching was low (≤ 3 and $\leq 2\%$, respectively). In addition, **1** catalyzed the cyclopolymerization of diethyl dipropargylmalonate (DEDPM) to yield poly(ene)s consisting of 5-membered rings, i.e., cyclopent-1-ene-1-vinylene units. The polymerization proceeded *via* non-stoichiometric initiation yielding polymers with unimodal molecular weight distribution. Using a catalyst to monomer ratio of 1:170, molecular weights of $M_w = 16,400$ and $M_n = 11,700$ g/mol, PDI = 1.40 were obtained.

Keywords: heterogeneous catalysis; high throughput screening; metathesis; molybdenum; polymers; ruthenium

Introduction

The success story of metathesis reactions in both organic and polymer chemistry is strongly related to the development of suitable, highly active and selective catalytic systems. In this context, both molybdenum-based Schrock catalysts^[1–4] and ruthenium-based Grubbs catalysts^[5–8] with all their structural variations define the standard in the field. With the large number of particularly designed catalytic systems in hand, one can now accomplish an almost unlimited range of metathesis-based C–C coupling reactions.^[9–13] Moreover, recent outstanding achievements made in the area of asymmetric metathesis have opened the door to a large variety of enantiomerically pure cyclic and oligocyclic structures, e.g., for pharmaceutical, medical and health-care applications.^[4,14–16]

For obvious reasons, there is an increasing demand for supported versions of these metathesis catalysts.^[17–30] First, contamination of products with metal ions and/or ligands needs to be low, particularly in compounds relevant to pharmaceutical chemistry. Second, modern metathesis catalysts significantly add to the total costs of a product, therefore regeneration and/or reuse are highly desirable. And third, supported catalysts offer access to high-throughput techniques and continuous flow reactors, respectively. Therefore, the key issues relevant for supported metathesis catalysts are (i) preservation of activity, (enantio-) selectivity and reaction rate observed with the parent homogeneous system, (ii) ease of catalyst separation, (iii) (multiple) catalyst recycling, and (iv) formation of metal- and contaminant-free products.

In course of ongoing projects on supported Grubbs and Schrock catalysts,^[18,31–36] we investigated the immo-

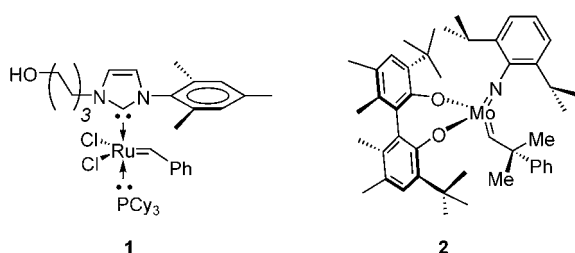


Figure 1. Structures of **1** and **2**.

bilization of a new version of Grubbs' catalyst (**1**), recently reported by Fürstner et al.,^[22,37] as well as of a chiral version of Schrock's catalyst (**2**)^[29,30] on a monolithic support (Figure 1).

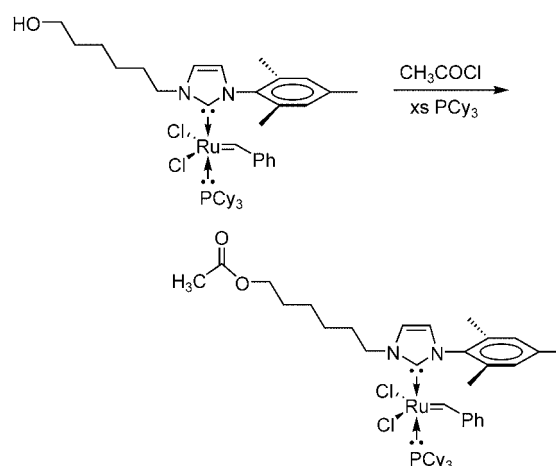
Additionally, and in contrast to previously reported monolith-immobilized catalytic systems,^[18,31–35,38] we focused on the development of disc-shaped monolithic systems applicable to high-throughput screening^[28] rather than on previously published monolithic supports designed for continuous flow applications.

Results and Discussion

Synthesis of Monolith-Immobilized **1**

Monolithic supports were prepared from norborn-2-ene (NBE), tris(norborn-5-ene-2-ylmethylenoxy)methylsilane [(NBE-CH₂O)₃-SiCH₃], 2-propanol, toluene and RuCl₂(PCy₃)₂(CHPh) using the ring-opening metathesis polymerization (ROMP) based protocol developed by our group.^[39–46] A 1:1 ratio (by weight) of NBE and the cross-linker (NBE-CH₂O)₃-SiCH₃ and a weight fraction of 40 wt % of these two monomers with respect to the entire polymerization mixture were chosen throughout. This ratio and weight fraction led to the formation of a monolithic structure with roughly 67% interparticle porosity. Such a high porosity was necessary for two reasons. First, it provided enough free volume for the grafting of the monomer of interest. Second, no clogging of the monolithic support was observed, either during synthesis or during use. For monolith manufacture, NBE and the cross-linker were dissolved in 2-propanol and a solution of RuCl₂(PCy₃)₂(CHPh) in toluene was added. The mixture was placed inside a suitable column and polymerization was allowed to proceed for 25 minutes at 0 °C and a further 25 minutes at room temperature. After careful washing of the monolith with toluene and CH₂Cl₂, the active, surface-immobilized catalyst moieties were used for surface derivatization.

Prior to that, suitable heterogenization conditions had to be elaborated. In a ¹H NMR experiment, **1** was treated with excess acetyl chloride in the presence of pyridine and tricyclohexylphosphine (PCy₃), respectively. Fürstner et al.^[22] reported that addition of pyridine to **1** leads



Scheme 1. Acetylation of **1**.

to the rearrangement of the catalyst. Therefore, PCy₃ was used as base in the reaction of **1** with acetyl chloride for both the removal of HCl and the structural preservation of **1** (Scheme 1).

Applying reaction conditions identical to those used for heterogenization (1.5 hours, 25 °C, CDCl₃, *vide infra*), the disappearance of the signal at δ = 3.62 ppm (CH₂OH) and the appearance of a new signal at δ = 4.06 ppm (m, CHCOOCH₃) was observed. The alkylidene signal at δ = 19.23 ppm remained unchanged. Due to the overlap with resonances of the PCy₃

group, the resonance for the acetyl group could not unambiguously be assigned. For the immobilization of **1**, a solution of norborn-5-ene-2-carboxylic chloride in CH₂Cl₂ was passed over the support and graft-polymerization was allowed to proceed overnight (Scheme 2).

The catalyst and unreacted monomer were removed by washing the support with a solution of ethyl vinyl ether in CH₂Cl₂. Finally, a mixture of **1** and PCy₃ in CH₂Cl₂ was added. Following this protocol, a loading of 0.55 wt % of **1** on the monolithic support was achieved. The monolith was dried, removed from the cartridge, cut in pieces of 0.5 cm thickness and encased. Such encased monolithic discs simultaneously served as support, reaction vessel and filtration unit. Once a proper encasement is performed, one can in principle use such systems in commercially available machines for combinatorial chemistry and high-throughput screening, respectively. For the present investigations, poly(ethylene) and glass syringes, respectively, were used. Nevertheless, these could still be assembled in a way that the reactions of interest can be run simultaneously under identical and defined conditions.

Catalytic Performance of Monolith-Bound **1**

In order to get additional information on the reactivity of **1**,^[22] it was used in various standard metathesis-based

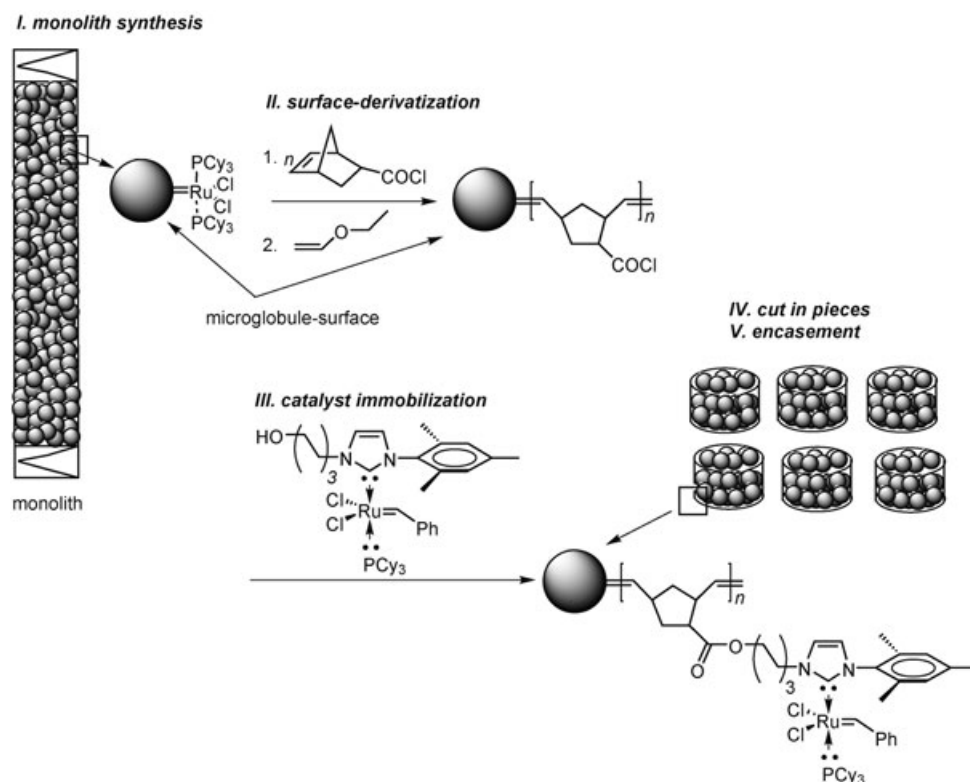


Table 1. Summary of RCM, ring-opening cross metathesis and enyne metathesis reactions performed with free **1** and monolith-bound **1**, respectively.

Substrate	Product	Mol % 1 /time [h]	Yield [%]	TON	Mol % immobilized 1 /time [h]	Yield [%]	TON
DEDAM		0.1 ^[c] /3.5 0.5/24 ^[22]	16 95 ^[22]	160 190 ^[22]	0.47 ^[c] /2.8 0.5/24 ^[c]	29 98	60 200
1,7-octadiene	cyclohexene	0.1 ^[d] /3.5	55	550	0.23 ^[d] /3.5	75 ^[f]	330
<i>tert</i> -butyl- <i>N,N</i> -diallylcarbamide		0.1 ^[c] /3.5	18	180	0.41 ^[c] /2.8	54	130
<i>N,N</i> -diallyltrifluoro-acetamide		0.25 ^[c] /3.5 0.49 ^[c] /3.5	14 40	60 70	0.48 ^[c] /2.8	73	150
		1.0 ^[d] /5.5	> 95	100	1.4 ^[d] /4	50	40
		polymer	–	–	polymer	–	–

All reactions were run at 45 °C.

[a] Catalyst **1**.

[b] Monolith-immobilized **1**.

[c] CH₂Cl₂.

[d] CHCl₃.

[e] Silica-immobilized version described by Fürstner et al.^[22]

[f] Polymer formed.

Synthesis of Monolith-Immobilized **2**

With a few exceptions,^[11,53] asymmetric metathesis reactions that require high enantiomeric excess (ee) are still a domain of molybdenum-based Schrock initiators.^[54–66] So far, there exist only few reports on the immobilization of chiral Schrock catalysts. The supported systems reported so far were either prepared *via* free radical polymerization^[29] or ring-opening metathesis precipitation polymerization.^[36] In order to immobilize **2** on a monolithic support, a similar protocol as was used for the immobilization of **1** was applied. After rod formation was complete and unreacted monomer had been removed from the support, a polymerizable analogue of BI-PHEN, (*R*)-5,5'-bis-(norborn-5-ene-2-ylmethyleneoxymethyl)-3,3'-di-*t*-butyl-6,6'-dimethylbiphen-2,2'-diol,^[29] was grafted to the surface (Scheme 3).

In contrast to molybdenum-initiated polymerizations,^[36] no protection of the free phenolic groups was necessary.^[36] The grafted phenolic moieties were deprotonated by adding KN[Si(CH₃)₃]₂ and subsequently reacted with the catalyst precursor Mo(N-2,6-*i*-Pr₂-C₆H₃)-

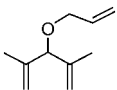
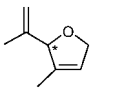
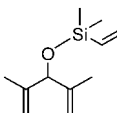
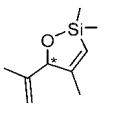
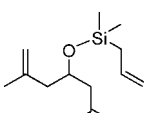
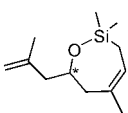
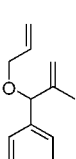
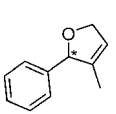
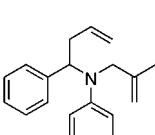
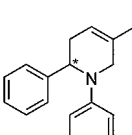
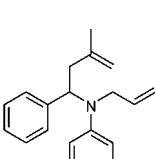
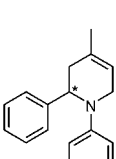
(CHCMe₂Ph)(OTf)₂·DME. Following this protocol, a loading of 0.7 wt % of **2** on the monolithic support was achieved. Similar to the protocol described for monolith-immobilized **1**, the monolith loaded with **2** was cut in pieces 1 cm in height and encased using SPE syringes. Alternatively, encasement may be performed in a way that polymer-encased membranes, which may directly be used as reaction vessels/filtration units in commercially available machines for parallel synthesis and high-throughput screening (HTS), respectively, are obtained (Figure 2).

Catalytic Performance of Monolith-Bound **2**

Enantioselective RCM was carried out with monolith-bound **2** using the substrates summarized in Table 2. Using 9–13 mol % of catalyst, yields were virtually quantitative throughout.

For 3-allyloxy-2,4-dimethylpenta-1,4-diene and 2,4-dimethyl-3-(dimethylvinylsilyloxy)-penta-1,4-diene (Table 2, entries 1 and 2), the enantiomeric excess (ee)

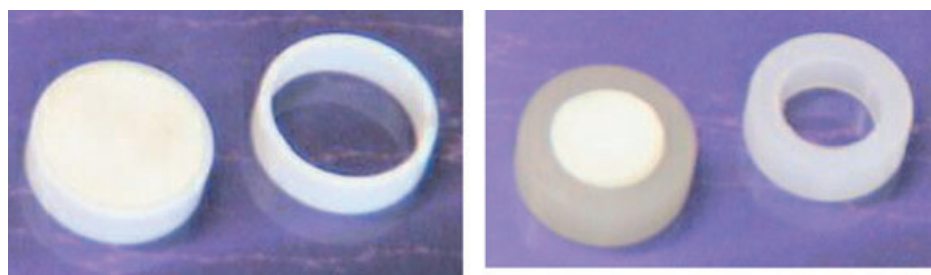
Table 2. Summary of asymmetric RCM and desymmetrization reactions performed with monolith-bound **2**.

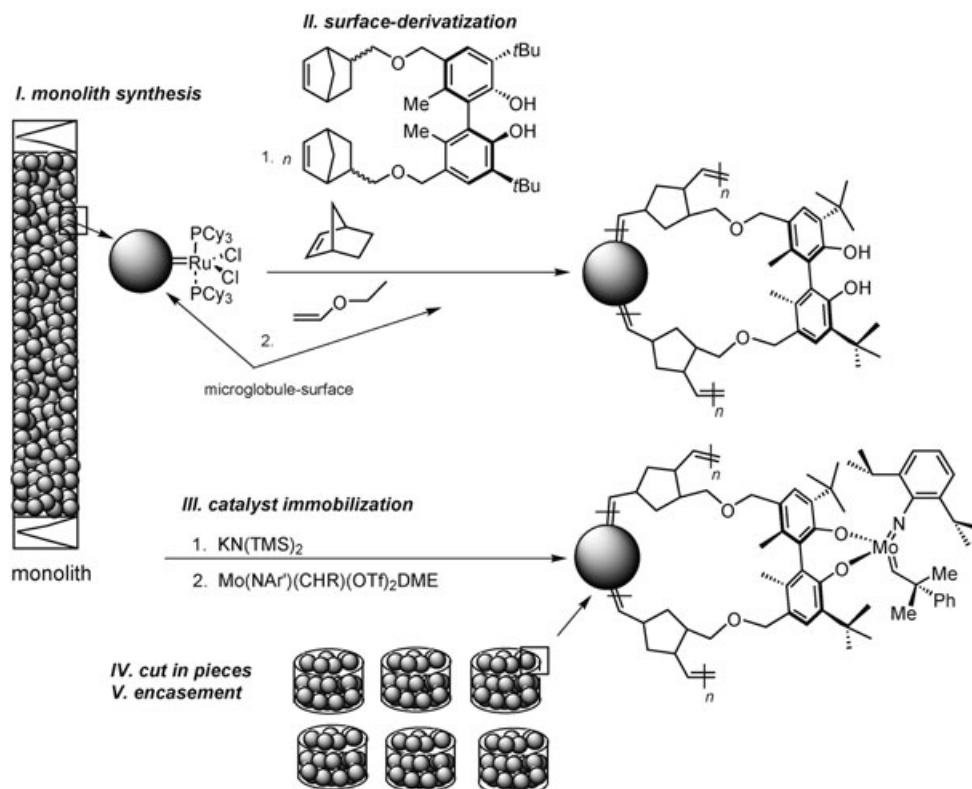
Entry	Educt	Product	Mol % catalyst	Yield [%]	ee [%]
1			11	99	79 (90, ^[36] 89 ^[29]) ^[a]
2			9	95	88 (95 ^[36]) ^[a]
3			13	99	43 (90, ^[36] 89 ^[58]) ^[a]
4			9	> 99	4 (25 ^[36]) ^[a]
5			13	75	43 ± 5 (53, ^[36] 47 ^[55]) ^[b]
6			13	99	45 ± 5 (50, ^[36] 45 ^[55]) ^[c]

^[a] Separated by GC.^[b] Mobile phase: 70% buffer (0.1 M triethylamine, acetic acid, pH=4), 30% mix (80% acetonitrile, 20% water).^[c] Mobile phase: heptane:2-propanol (99:1). Unless stated otherwise, all r.s.d.'s were =2%.

was comparable to that achieved with other immobilized versions of **2**. 2,4-Dimethyl-3-(dimethylvinylsilyloxy)-penta-1,4-diene and particularly 3-allyloxy-3-phenylisobut-1-ene (Table 2, entries 3 and 4) showed significantly reduced ees of 43 and 4% (compared to 90 and 25%, respectively). So far, we cannot explain this drop in ee, yet tentatively attribute it to geometric constraints

within the monolithic support. However, *N*-allyl-*N*-(2-methyl-4-phenylbut-1-en-4-yl)aniline and *N*-(isobut-1-en-3-yl)-*N*-(4-phenylbut-1-en-4-yl)aniline were converted in 75 and 99% yield, respectively (Table 2, entries 5 and 6). The ees found were slightly lowered, yet similar to those reported with other systems. In all cases, contamination of products with molybdenum was < 2 wt %.

**Figure 2.** Encasements suitable for monolith-supported **1** (left) and **2** (right).



Scheme 3. Synthesis of monolithic discs and an immobilized version of **2**.

Conclusion

We have developed a synthetic approach that allows the immobilization of both ruthenium-based Grubbs and molybdenum-based, chiral Schrock catalysts on monolithic discs. The supported versions of these catalysts are readily accessible and can, due to their disc-like nature, be used in combinatorial chemistry, parallel synthesis and high throughput screening (HTS). Thus, the placement of these discs in compartments that fit commercially available HTS machines is expected to allow running the desired reactions in one single batch under defined conditions. The fact that the discs themselves simultaneously serve as support, reaction vessel and filtration unit underlines the simplicity of this set-up. Further investigations on this issue including the development of technically relevant devices are under way.

Experimental Section

General Remarks

NMR data were obtained at 300 MHz in the indicated solvent at 25 °C on a Bruker Spectrospin 300 and are listed in parts per million downfield from tetramethylsilane. Spectra are reported in reference to CDCl_3 (7.24 and 77.0 ppm for proton and carbon, respectively). Coupling constants are listed in Hertz. IR

spectra were recorded on a Bruker FT-IR. GC-MS measurements were carried out on a Shimadzu GCMS QP5050, using a SPB-5 fused silica column (30 m $\times$ 0.25 mm, 25 μm film thickness) and He as carrier gas. Enantiomeric excess (ee) was determined *via* GC on a Shimadzu GCMS-QP 5050 equipped with a Supelco Beta DexTM 120 fused silica capillary column (30 m $\times$ 0.25 mm $\times$ 0.25 μm film thickness) or *via* chiral HPLC. The HPLC system was equipped with a Cyclobond I 2000 (Astec, USA, 150 mm $\times$ 2.0 mm), separations were carried out using the mobile phases indicated in Table 2. Separations were carried out at $T=0^\circ\text{C}$; flow = 0.2 mL/min. The injection volume was 1 μL , a UV detector (Linear Uvis 200, 254 nm) was used. Compounds were identified by their mass spectra. Elemental analyses were carried out at the Institute of Physical Chemistry, University of Vienna. A Jobin Yvon JY 38 plus was used for ICP-OES measurements, an MLS 1200 mega for microwave experiments. Further instrumentation is described elsewhere.^[51] Gel permeation chromatography (GPC) using UV/RI/LS detection was carried out on a Waters Styragel column (HR4E 7.8 $\times$ 300 mm) equipped with a Styragel guard column (4.6 $\times$ 30 mm). A 717 plus autosampler, a 2414 differential refractometer, a 484 UV detector (all Waters) and a Minidawn light scattering detector (Wyatt Technologies, USA, $\lambda=690\text{ nm}$) was used for measurements in CHCl_3 . A dn/dc of 0.465 mL/g was used for poly(DEDPM). Samples were filtered through 0.2 μm Teflon filters (Millipore) in order to remove particles. GPC columns were calibrated *vs.* polystyrene standards [Polymer Standards Service (PSS), molecular weights 580 to $1.57 \times 10^6\text{ g/mol}$]. Syntheses and polymerizations were performed under an argon atmosphere by standard

Schlenk techniques or in an N₂-mediated dry-box (Braun, Germany) unless stated otherwise. Reagent grade diethyl ether, pentane, tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone ketyl under argon. Reagent grade CH₂Cl₂ and 1,2-dichloroethane were distilled from calcium hydride under argon. Other solvents and reagents were used as purchased. Deionized water was used throughout. RuCl₂(PCy₃)₂(CHPh) was purchased from Fluka. *endo*-Norborn-2-ene-5-carboxylic chloride,^[67] (NBE-CH₂O)₃SiCH₃,^[42] (*R*)-5,5'-bis-(norborn-5-ene-2-ylmethylenoxymethyl)-3,3'-di-*tert*-butyl-6,6'-dimethylbiphen-2,2'-diol,^[29] 2,6-dimethyl-4-(allyldimethylsilyloxy)-hepta-1,6-diene,^[58] 2,4-dimethyl-3-(dimethylvinylsilyloxy)-penta-1,4-diene,^[68–70] *N*-(isobut-1-en-3-yl)-*N*-(4-phenylbut-1-en-4-yl)aniline,^[55] *N*-(allyl)-*N*-(2-methyl-4-phenylbut-1-en-4-yl)aniline,^[55] 3-allyloxy-3-phenylisobut-1-ene,^[65] 3-allyloxy-2,4-dimethylpenta-1,4-diene,^[29,68–70] RuCl₂(PCy₃)(NHC)(CHPh) [NHC = 1-mesityl-3-(6-hydroxyhexyl)imidazol-2-ynylidene],^[22] and Mo[*N*-2,6-(*i*-Pr)₂-C₆H₃](CHCMe₂Ph)(OSO₂CF₃)₂DME^[71] were prepared according to literature procedures and checked for purity by means of NMR.

RuCl₂(PCy₃)₂(1-mesityl-3-(6-acetoxyhexyl)imidazol-2-ynylidene) (CHPh)

Compound **1** (20 mg, 24 μmol) was dissolved in absolute CH₂Cl₂. Tricyclohexylphosphine (6.5 mg, 24 μmol) and acetyl chloride (75 mg, 950 μmol) were added and the reaction mixture was stirred at 20 °C for 1.5 h. The solvent was removed under vacuum and the residue was extracted with pentane. Crystallization at –37 °C yielded 5 mg of the product. ¹H NMR (CDCl₃): δ = 19.23 (Ru=CH), 7.51 (m, 1H), 7.33 (m, 2H), 7.18 (m, 1H), 7.09 (t, 2H, *J* = 7.3 Hz), 6.95 (b, 2H), 6.79 (m, 1H), 4.69 (t, 2H, *J* = 6.5 Hz), 4.06 (m, 2H, CH₃COOCH₂), 2.6–1.0 (m, 55H); MS (FAB): *m/z* calcd. for C₄₅H₆₈Cl₂N₂O₂PRu: 871.34; found: 870.89 [M + H⁺], 835.26 [M + H – HCl⁺].

Synthesis of Monolith-Supported Catalyst 1

Synthesis of monoliths was carried out according to published procedures.^[39–46] The following amounts were used: norborn-2-ene (NBE, 1.6 g, 17 mmol), (NBE-CH₂O)₃SiCH₃ (1.54 mL, 1.6 g, 3.74 mmol), 2-propanol (4.8 mL), toluene (1.1 mL), RuCl₂(PCy₃)₂(CHPh) (32 mg). Column dimensions: 60 × 12 mm i.d., *V* = 7 mL. After monolith synthesis, the monolith was washed with dry CH₂Cl₂. Norborn-5-ene-2-carboxylic chloride (0.225 mL) was dissolved in 6 mL of dry CH₂Cl₂ and the solution was passed over the column. Graft-polymerization was carried out at 45 °C for 15 h. The column was washed with a 40 vol % solution of ethyl vinyl ether in dry CH₂Cl₂ followed by dry CH₂Cl₂. A solution of **1** (20 mg, 24 μmol) and tricyclohexylphosphine (14 mg, 48 μmol) in 5 mL of dry CH₂Cl₂ was prepared and 4 mL of this solution were introduced to the column. The reaction was allowed to proceed for 1.5 h at 25 °C. Afterwards, the column was washed with dry CH₂Cl₂ until the washings were colorless. Then the monolith was dried under vacuum and brought into a glove box. The monolith was removed from the SPE column and chopped into pieces of 200–250 mg (approximately 0.5 cm in height). Syringes for solid-phase extrac-

tions (SPE, ICT, Isolute, Austria) were used as encasements for these pieces. Ru loading: 6.6 μmol Ru/g monolith corresponding to 5.5 mg catalyst/g monolith (0.55 wt %).

RCM/Ring-Opening Cross-Metathesis

A representative RCM procedure was as follows: The monolithic membrane (0.23 g, 1.5 μmol catalyst) was treated with 0.76 g of a 10 wt % solution of diethyl diallylmalonate (DE-DAM) in CH₂Cl₂. This volume was readily absorbed by the monolith. Other monolithic discs were treated in a similar way using the monomers indicated in Table 1. The reaction vessels were sealed, removed from the glove box and heated to 45 °C for 2.8 h. Finally, reaction mixtures were eluted with CH₂Cl₂. Yields were determined by GC-MS and ¹H NMR (using CDCl₃ as solvent), respectively. In order to determine the total loss of ruthenium, the washings of all RCM investigations were combined, digested in aqua regia by a microwave unit and the ruthenium content was acquired by ICP-OES. A ruthenium loss < 3% was determined.

Synthesis of Monolith-Supported Catalyst 2

Synthesis of monoliths was carried out according to published procedures.^[39–46] The following amounts were used: 2-propanol (2.9 mL), (NBE-CH₂O)₃SiMe (1.000 g, 2.426 mmol), NBE (1.000 g, 10.621 mmol), toluene (0.8 mL) and RuCl₂(PCy₃)₂(CHPh) (0.020 g, 0.024 mmol). PEEK column dimensions (70 × 4.6 mm i.d., *V* = 1.2 mL). After synthesis, the monolith was flushed with CH₂Cl₂ and filled with a solution of 5,5'-bis(bicyclo[2.2.1]hept-5-ene-2-ylmethoxymethyl)-3,3'-di-*tert*-butyl-6,6'-dimethylbiphenyl-2,2'-diol (0.060 g, 0.100 mmol) and NBE (0.020 g, 0.212 mmol) in 0.5 mL of CH₂Cl₂. The column was sealed and stored at 50 °C overnight. The next day, the monolith was flushed for 30 min with diethyl ether and further 30 min with ethyl vinyl ether in diethyl ether (10 vol % EVE, 0.2 mL/min). The monolith was dried under vacuum. Potassium bis(trimethylsilyl)amide [KN(SiMe₃)₂] (0.200 g, 1.003 mmol) dissolved in a 1:1 mixture of diethyl ether and THF was introduced into the monolith and kept at room temperature overnight. Then, the monolith was flushed thoroughly with diethyl ether. Mo[*N*-2,6-(*i*-Pr)₂-C₆H₃](CHCMe₂Ph)(OTf)₂(DME) (0.238 g, 0.301 mmol) dissolved in 4 mL of diethyl ether was injected over a period of 2 h. Finally, the monolith was flushed with diethyl ether until the washings run through colorless and dried under vacuum. The monolith was removed from the PEEK column. The dry monolith was cut into pieces of about 1 cm in height. Each piece was placed inside a syringe. The average molybdenum content was 0.094 mmol/g, corresponding to a catalyst loading of 7 wt %.

General Procedure for RCM of (Pro-) Chiral Monomers

A solution of the corresponding monomer in CH₂Cl₂ was added. The soaked monolith was kept at room temperature for 2 h. Then, the monolith was flushed with pure CH₂Cl₂ and the combined washings were measured by GC-MS. In order to determine the total loss of molybdenum, the washings of all RCM

investigations were combined, digested in aqua regia by a microwave unit and the molybdenum content was acquired by ICP-OES. A molybdenum loss < 2% was determined.

Determination of the Metal Content

For the determination of catalyst loading, the monolithic supports (60.5 mg) were dried, mortared, placed inside high-pressure teflon tubes and dissolved in aqua regia (3 mL). For the determination of metal leaching, the combined effluents were dried, the residue was placed inside high-pressure teflon tubes and then aqua regia (3 mL) was added. Leaching was carried out under microwave conditions (250, 600 and 450 W pulses; $t = 32$ min). After cooling to room temperature, the mixture was filtered and water was added up to a weight of 10.00 g. Quantification of the corresponding metal ion was accomplished by ICP-OES (ion line for Mo $\lambda = 202.030$ nm; background $\lambda_1 = 202.015$ and $\lambda_2 = 202.045$ nm, respectively; ion line for Ru $\lambda = 240.272$ nm, background $\lambda_1 = 240.287$ and $\lambda_2 = 240.257$ nm, respectively). Standardization was carried out using 0.0, 5.0, and 10.0 ppm standards of the corresponding metal ion.

Polymerization of Diethyl Dipropargylmalonate (DEDPM) with **1**

Inside a glove-box, DEDPM (50 mg, 2112 μ mol) was dissolved in CH_2Cl_2 (0.5 mL) and treated with a solution of **1** (1.0 mg, 1.2 μ mol) in CH_2Cl_2 (0.5 mL). Reactions were run at room temperature and 40 °C, respectively, for 3 h. During this time, the solution changed its color to dark violet. The reaction mixture was concentrated to 0.5 mL and added to 50 mL of pentane under stirring. A violet precipitate formed. It was collected by means of centrifugation, the supernatant solution was decanted off, and the residue was washed with pentane (2 $\times$ 4 mL) and dried under vacuum. The UV spectrum in CHCl_3 showed a maximum at $\lambda = 535$ nm, respectively, with an additional shoulder at 575 nm. GPC (room temperature polymerization): $M_w = 15,500$; $M_n = 11,100$, PDI = 1.4; GPC (polymerization at 40 °C): $M_w = 16,400$; $M_n = 11,700$, PDI = 1.4 (values from RI). The ^{13}C NMR spectrum was in accordance with one of poly(DEDPM) consisting at least 95% of 5-membered rings.^[47,72–76]

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