FULL PAPER

A Dicationic Ruthenium Alkylidene Complex for Continuous Biphasic **Metathesis Using Monolith-Supported Ionic Liquids**

Benjamin Autenrieth,^[a] Wolfgang Frey,^[b] and Michael R. Buchmeiser^{*[a, c]}

Abstract: A dicationic ruthenium-alkylidene complex $[Ru(dmf)_3(IMesH_2)(=$ $CH-2-(2-PrO)-C_6H_4)][(BF_4)_2]$ (1:IMesH₂=1,3-dimesitylimidazolin-2-ylidene) has been prepared and used in continuous metathesis reactions by exploiting supported ionic-liquid phase (SILP) technology. For these purposes, ring-opening metathesis polymerization (ROMP)-derived monoliths were prepared from norborn-2-ene, tris(norborn-5-ene-2-ylmethyloxy)methylsilane, and $[RuCl_2(PCy_3)_2(CHPh)]$ (Cy = cyclohexyl) in the presence of 2-propanol and toluene and surface grafted with norborn-5-en-2-vlmethyl-N,N,N-trimethylammonium tetrafluoroborate ([NBE-CH₂-NMe₃][BF₄]). Subsequentimmobilization of the ionic liquid (IL), 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([BDMIM][BF₄]), containing ionic catalyst 1 created the SILP catalyst. The use of a second liquid transport phase, which contained the substrate and was immiscible with the IL, allowed continuous metathesis reactions to be realized. High turnover numbers (TONs) of up to 3700 obtained in organic solvents for the ringclosing metathesis (RCM) of, for example, N,N-diallyltrifluoroacetamide, diethyl diallylmalonate, diethyl di(methallyl)malonate, tert-butyl-N,N-diallyl-

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Introduction

Almost 100 years after the discovery of ionic liquids (ILs)^[1-2] by Walden,^[3]interest in this class of compounds has dramatically increased and within a comparably short time ILs have made their way from a physicochemical curiosity into numerous chemical, technical, and industrial applications,^[4] for example, as solvents for catalytic reactions^[5-25] (including asymmetric ones^[26]) and polymerizations,^[27-40] as

- [a] Dipl.-Chem. B. Autenrieth, Prof. M. R. Buchmeiser Lehrstuhl für Makromolekulare Stoffe und Faserchemie Institut für Polymerchemie, Universität Stuttgart Pfaffenwaldring 55, 70569 Stuttgart (Germany) Fax: (+49)711-685-64050 E-mail: michael.buchmeiser@ipoc.uni-stuttgart.de
- [b] Dr. W. Frev Institut für Organische Chemie, Universität Stuttgart Pfaffenwaldring 55, 70569 Stuttgart (Germany)
- [c] Prof. M. R. Buchmeiser Institut für Textilchemie und Chemiefaser (ITCF) Denkendorf Körschtalstr. 26, 73770 Denkendorf (Germany)
- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201201199. It contains details on metathesis reactions: GC chromatograms: NMR spectra of 1, 2 and selected substrates; pore size distribution of the monolith; distribution coefficients of the substrates (IL/organic phase); and structural data of 1.

phenyldiallylsilane, and 1,7-octadiene, as well as in the self-metathesis of methyl oleate, could be further increased by using biphasic conditions with [BDMIM][BF₄]/heptane. Under continuous SILP conditions, TONs up to 900 were observed. Due to the ionic character of the initiator, catalyst leaching into the transport phase was very low (< 0.1 %). Finally, the IL can, together with decomposed catalyst, be removed from the monolithic support by flushing with methanol. Upon reloading with [BDMIM][BF₄]/1, the recycled support material again qualified for utilization in continuous metathesis reactions.

carbamate, N,N-diallylacetamide, di-

coatings and mobile phases in liquid chromatography and electromigration techniques,^[41-45] as low-vapor-pressure solvents for head-space GC analysis,^[46] as coatings for GC columns,^[47] as well as electrolytes in fuel^[48] and solar cells.^[49] In addition, applications in biocatalysis^[50-52] have to be mentioned. The first reports on the use of molten salts as supported ionic-liquid phases (SILPs) for use in heterogeneous catalysis were published in 1988 by Datta and Rao^[53] and by Eyman et al.^[54] Following this concept, the groups of Wasserscheid, Mehnert, Dupont, and others have since published a series of applications of SILPs.^[15,17,19-25,55-59] Using simple adsorption and capillary forces, they immobilized various ILs on silica- and zeolite-type supports and used them as supported solvents for catalytic reactions, for example, for hydroformylations, hydrogenations, methanol carbonylation, and also for enzyme-triggered biocatalysis. Recently, Le Bideau et al. confirmed by ¹H-MAS-NMR spectroscopy experiments that the dynamics of ILs immobilized within the confines of siliceous materials experienced only a minor slow down.^[60] In fact, confinement preserved the IL's properties, while reducing their crystallization temperature relative to genuine ILs. Thus, supported ILs can in fact be compared to unsupported ones in terms of diffusion coefficients, which in turn guarantees fast reaction kinetics for the catalytic reactions within monolith-supported ILs.

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More recently, Wasserscheid et al. reported on metathesis reactions in supported ILs using gaseous reactants as the second (transport) phase.^[61] Such an approach allows the use of "standard" metathesis catalysts within the IL. However, both the metathesis of higher (functional) olefins and metathesis-based polymerizations require the use of a second liquid transport phase that is immiscible with the IL. To prevent catalyst leaching into this second phase, tailored catalysts need to be developed that selectively dissolve in the IL. Equally important, to allow continuous reaction conditions, any substrate and product must have sufficient solubility in both phases to allow substantial turnover numbers (TONs) and prevent product accumulation within the IL. Herein, we report a new dicationic metathesis catalyst dissolved within a polymeric monolith-supported IL phase that allows for the first continuous metathesis reactions using two liquid phases. Scheme 1 illustrates the fundamental concept. In addition to the primary objective to gain catalystfree products, our concept enables continuous product formation simply by cycling liquid reactants or solutions thereof through the support. Most importantly, the entire concept is not limited to gaseous substrates, such as ethene, propene, or butenes. Consequently, no high pressures need to be applied. Finally, the possibility of recycling the monolithic support has been addressed.

Results and Discussion

Synthesis and structural determination of 1: As outlined above, the primary objective was to create a supported metathesis catalyst, based on SILP technology, that allowed metathesis reactions to be run under biphasic conditions using two immiscible liquid phases. For this purpose, an





vs. 226.13 pm^[71]). The Ru1A-O2A and Ru1A-O4A distances of the two DMF ligands located trans to each other are virtually identical (203.7(3) vs. 205.6(3) pm). In contrast, the Ru1A-O3A distance of the DMF ligand located trans to the benzylidene ligand is significantly longer (Ru1A-O3A = 222.5(3) pm). Interestingly, the Ru1A-C1A distance is also longer than that in the parent GH catalyst (201.1(4) vs. 198.1(5) pm),^[71] while the Ru-alkylidene bond is somewhat shorter in 1 than that in the parent complex (182.5(5))vs. 185.0(4) pm).^[71] Although some monocationic Ru-alkylidenes have been reported,^[72-74]

Scheme 1. Continuous metathesis under biphasic conditions by using monolith-supported ILs. Y^+X^- [BDMIM][BF₄].



ionic Ru-alkylidene complex for metathesis reactions in ILs had to be created. Since pseudo-halide derivatives of Grubbs and Grubbs-Hoveyda (GH) catalysts are known to possess high activity, resulting from high polarization of the Ru-alkylidene moiety,^[62-70] such electron-deficient cationic catalysts may also be expected to display high activity. Such an ionic metathesis catalyst would selectively dissolve in the IL, but not in the second liquid transport phase, such as heptane. For this reason, the ionic catalyst [Ru(dmf)₃(IMesH₂)- $(=CH-2-(2-PrO)-C_6H_4)][(BF_4)_2]$ (1, IMesH₂=1,3-dimesitylimidazolin-2-ylidene) was prepared in 95% yield by adding three equivalents of DMF and two equivalents of AgBF₄ to the second-generation GH catalyst [RuCl2(IMesH2)(=CH-2- $(2-PrO)-C_6H_4)$] (Scheme 2).



Scheme 2. Synthesis of the dicationic Ru complex 1.

Table 1.

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Figure 1. X-ray structure of 1. Counteranions (BF_4^-) and hydrogen atoms have been omitted for clarity. Ellipsoids are given at the 50% probability level.

it is worth noting that complex **1** is one of the rare examples of a dicationic Ru^{II}–alkylidene^[75] and, to the best of our knowledge, the first example of a metathetically highly active one.

Metathesis reactions in organic solvents: Before we turned our attention to reactions in ILs, we investigated the general reactivity of **1** in various metathesis reactions. Ring-closing metathesis (RCM) reactions in CH₂Cl₂ at T=40 °C with substrates containing coordinating, that is, oxygen- or nitrogencontaining groups, namely, diethyl diallylmalonate (DEDAM), diethyl di(methallyl)malonate, *tert*-butyl-*N*,*N*-diallylcarbamate, diallyldiphenylsilane, or *N*,*N*-diallylacetamide (Table 2) resulted in low TONs (\leq 50) and conversion (\leq 5%). However, with the electron-poor substrate *N*,*N*-diallyl trifluoroacetamide (DAFA), high TONs up to 3500 were

obtained, by far exceeding those obtained with the parent GH catalyst under identical conditions (TON=730). Clearly, even weakly coordinating groups, such as esters and amides, coordinate to the dicationic center, thereby impeding coordination of the alkene. This is further illustrated by comparing the RCM results of DAFA to those of the analogous, non-fluorinated derivative, that is, N,N-diallylacetamide, obtained at T = 40 °C. In these reactions, TONs of 3500 versus 10 were observed (Table 2). To promote the dissociation of any coordinating moieties from the cationic Ru center, all reactions were again run at elevated temperatures. This way the activity of 1 in-

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Ru1A–C22A	185.0(4)
Ru1A–C1A	201.1(4)
Ru1A–O1A	232.5(3)
Ru1A–O2A	203.7(3)
Ru1A–O3A	222.5(3)
Ru1A–O4A	205.6(3)
C22A-Ru1A-C1A	93.30(16)
C22A-Ru1A-O1A	77.50(13)
C22A-Ru1A-O2A	101.39(13)
C22A-Ru1A-O4A	94.12(13)
C22A-Ru1A-O3A	172.22(14)
C1A-Ru1A-O2A	91.70(14)
C1A-Ru1A-O4A	100.64(14)
C1A-Ru1A-O3A	94.27(12)
C1A-Ru1A-O1A	169.26(13)
O2A-Ru1A-O4A	159.59(10)
O2A-Ru1A-O3A	80.22(10)
O2A-Ru1A-O1A	84.81(10)
O3A-Ru1A-O1A	95.15(90)
O4A-Ru1A-O3A	82.69(10)
O4A-Ru1A-O1A	85.70(10)

Table 1. Selected bond lengths [pm] and angles [°] for 1.

creased tremendously for all substrates (Table 2). Thus, when reactions were run in toluene at 100 °C, TONs up to 1300 and 1200, respectively, were obtained in the RCM reactions of DEDAM and 1,7-octadiene. These values are worth highlighting because **1** is poorly soluble in toluene and, consequently, reactions are mostly heterogeneous. Likewise, in the case of *N*,*N*-diallylacetamide, *tert*-butyl-*N*,*N*-diallylcarbamate, and diallyldiphenylsilane, an increase in temperature resulted in increasing TONs reaching values between 130 and 320. The reaction temperature also has a great influence on the selectivity of the RCM of 1,7-octadiene. When conducted at T=40 °C, the formation of purple, conjugated isomerization products was observed,

Table 2.	Selected	substrates f	or metathesis	reactions in	organic solvents	promoted by	catalyst 1
10010 2.	Serected	Substitutes	or metatheoio	reactions in	organic sorrente	promoted by	catalyst 1

Substrate	1 [mol %]	Solvent	<i>T</i> [°C]	t	TON
		CH_2Cl_2	40	1 h	50
DEDAM	0.05	$C_2H_4Cl_2$	80	1 h	560
		toluene	100	15 min	1300
	e 0.1	CH_2Cl_2	40	1 h	10
tert-butyl-N,N-diallyl carbamate		$C_2H_4Cl_2$	80	0.5 h	40
		toluene	100	0.5 h	320
		CH_2Cl_2	40	1 h	100
1,7-octadiene	0.05	$C_2H_4Cl_2$	80	15 min	500
		toluene	100	15 min	1200
	0.02	CH_2Cl_2	40	15 min	3500
DAFA		$C_2H_4Cl_2$	80	5 min	3500
		toluene	100	2 min	3700
		CH_2Cl_2	40	4 h	10
N,N-diallylacetamide	0.05	$C_2H_4Cl_2$	80	4 h	30
		toluene	100	1 h	240
dially dia baay lailana	0.2	CH_2Cl_2	40	4 h	5
dianyidiphenyishane		toluene	100	4 h	130
distant di (mathallul) malanata	1.4	CH_2Cl_2	40	12 h	0
diethyl di(methanyl)maionate		toluene	100	0.5 h	6
		CH_2Cl_2	40	12 h	100
methyl oleate	0.05	$C_2H_4Cl_2$	80	4 h	530
		toluene	100	4 h	780

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and consequently, the yield in cyclohexene was low. However, at T = 80 °C, no isomerization products were observed and cyclohexene was the only product detected by means of GC-MS and NMR spectroscopy. This suggests the absence of any active Ru-hydride species at elevated temperatures. Since DAFA does not coordinate to the Ru center through the amide bond, the high TON observed at $T = 40 \,^{\circ}\text{C}$ could not be significantly increased; however, the reaction rate increased. At T=40 °C a TON



Scheme 4. CM reactions between allylbenzene and *cis*-1,4-acetoxy-2-butene (a) and between 5-hexenyl acetate and methyl acrylate (b). Ene–yne metathesis of *N*-allyl-*N*-propargyl trifluoroacetamide (c).

of 3500 was achieved within 15 min, whereas a TON of 3700 was achieved at T=100 °C in less than 2 min. Notably, the reactivity of diethyl di(methallyl)malonate remained low under all conditions.

Reaction temperature also greatly influences the selfmetathesis of methyl oleate (Scheme 3). At T=40 °C, the reaction proceeds slowly with low yields ($\approx 5\%$ of primary



Scheme 3. Self-metathesis of methyl oleate catalyzed by 1.

metathesis products; TON=100). Running the reaction at T=100 °C resulted in TONs of 780. Moreover, again only the desired primary metathesis products were obtained (Scheme 3 and Figure S1 in the Supporting Information), again suggesting the absence of (stable) Ru–hydrides. In contrast, predominantly alkenes with different chain lengths, resulting from secondary cross-metathesis (CM) reactions, were observed with the GH catalyst (Figure S2 in the Supporting Information).

Cross-metathesis (CM) and ene-yne metathesis reactions: In the CM reaction between allylbenzene and *cis*-1,4-ace-toxy-2-butene (Scheme 4a) no conversion was observed at T=40 °C. However, at T=100 °C, product formation was quantitative within 1 h when using a catalyst loading of 0.2 mol% in toluene. The inactivity of 1 at 40 °C was also noted for the CM reaction between 5-hexenyl acetate and methyl acrylate (Scheme 4b). In turn, at 100 °C, 70% conversion was achieved within 1 h when using a catalyst loading of 0.2 mol%. Finally, we applied **1** to the ene-yne metathesis of *N*-allyl-*N*-propargyl trifluoroacetamide (Scheme 4c). When using a catalyst loading of 0.5 mol%, a TON of 60 was obtained in CH_2Cl_2 at 35 °C. Interestingly, at elevated temperatures, only red, polymeric products formed by 1-alkyne polymerization were obtained, as evidenced by the absence of any alkyne groups in the IR spectrum (Figure S16 in the Supporting Information).

Metathesis reactions under biphasic conditions (organic solvent/IL): The RCM of DAFA, DEDAM, and 1,7-octadiene, as well as the self-metathesis of methyl oleate, were carried out under biphasic conditions by using [BDMIM][BF₄] as the IL phase and either neat reactants or heptane as the second liquid phase (Table 3). Generally, the choice of IL

Table 3. Metathesis reactions under biphasic conditions ([BDMIM]-[BF₄])/heptane).

	G . 1 . (5 . 10(1)	m [0.cl]	mostel	
Substrate	Catalyst ([mol%])	$T[^{\circ}C]$	TON	Ru leaching [%]
DAFA ^[c]	1 (0.02)	40	3300	0.09
		80	3600	2.4
DAFA	GH (0.02)	40	600	3.1
		80	1300	8.6
DEDAM ^[d]	1 (0.02)	80	1400	0.02
		100	1650	0.03
DEDAM	GH (0.02)	80	1500	0.03
		100	1900	0.2
1,7-octadiene ^[e]	1 (0.02)	80	810	0.1
		100	1660	0.1
1,7-octadiene	GH (0.02)	80	2300	0.1
		100	2410	0.5
methyl oleate ^[f]	1 (0.05)	40	95	0.07
		80	800	0.11
		110	1000	0.6
methyl oleate	GH (0.05)	40	2000	0.2
		80	2000	0.5
		110	2000	1.4

[a] Determined by GC-MS after 12 h. [b] % of initial Ru (catalyst) loading. [c] Heptane as second liquid phase; IL (0.2 g), heptane (2.0 g), DAFA (0.8 g). [d] Heptane as second liquid phase; IL (0.2 g), heptane (3.0 g), DEDAM (1.25 g). [e] Neat; IL (0.04 g), 1,7-octadiene (0.4 g). [f] Neat; IL (0.05 g), methyl oleate (0.5 g).

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was a crucial feature concerning ruthenium-alkylidene-promoted metathesis reactions.^[34,76,77] The anion in the IL [BDMIM][BF₄] is non-coordinating and identical to the counterion in complex 1. This prevents ligand scrambling, which is often observed for Ru-alkylidenes in ionic solvents with different counterions.^[34] Furthermore, with a melting point of 37 °C, [BDMIM][BF₄] is liquid at a reaction temperature of 40°C. However, the most important property of [BDMIM][BF₄] is its very poor miscibility with common nonpolar organic solvents, such as toluene, diethyl ether, or heptane. However, all substrates investigated displayed sufficient solubility in the IL, as illustrated by their distribution coefficients, $K_{\text{heptane/IL}}$ (Table S2 in the Supporting Information), which were 0.2 (DAFA), 1.2 (DEDAM), and 9 (1,7octadiene). Despite the comparably small amount of IL and large amount of polar substrate, which both favor transfer of the catalyst into the nonpolar phase, a low catalyst leaching of ≤ 0.1 % into the product phase was observed for most reactions. For comparison, leaching of the GH catalyst into the heptane phase under otherwise identical conditions was up to 25 times higher. By running the reaction in the IL, the TONs for the RCM of DAFA could be further increased to 3600 by increasing the temperature, although this was at the expense of a slightly higher metal leaching (2.4%). In the RCM of DEDAM, TONs up to 1600 were obtained, again exceeding those observed in an organic solvent (Table 2). Due to the low polarity of 1,7-octadiene and its immiscibility with the IL, RCM was performed without the use of another liquid transport phase. An increase in reaction temperature from 80 to 100 °C led to an increase in the TON from 800 to 1600 without noticeably affecting catalyst leaching. As observed in organic solvents, only the formation of cyclohexene and no isomerization products were observed. Admittedly, Ru leaching was also low with the parent GH catalyst, giving TONs up to 2400. However, with this catalyst, the IL phase was purple in color, suggesting the formation of conjugated isomerization products. In the self-metathesis of methyl oleate (Scheme 3) catalyzed by 1, an increase in temperature resulted in an increase in TON from 95 to 1000. Reaction monitoring by GC-MS revealed the selective formation of the two desired CM products as well as isomerization of the Z double bond in the substrate molecule (Figure S1 in the Supporting Information). This isomerization

reaction is the predominant reaction at low temperatures, forming a less reactive E double bond, which gives rise to low TONs. At higher temperatures, self-metathesis predominates. Despite high TONs, the use of the GH catalyst yielded a multitude of products (more than 30) by subsequent isomerization and secondary metathesis processes (see the gas chromatogram in Figure S2 in the Supporting Information).

Preparation and characterization of monolithic supports: Polymeric monoliths represent versatile supports for heterogeneous catalysis. They allow high linear flow rates of up to 20 mm s^{-1} at low counter pressure (<3 MPa) and guarantee fast mass transfer between the transport phase and the immobilized catalysts.^[78] Monoliths were prepared by copolymerization of norborn-2-ene (NBE) with the cross-linker (CL) tris(norborn-2-enylmethylenoxy)methylsilane ((NBE- $CH_2O_3SiCH_3$) in the presence of the two porogenic solvents 2-propanol and toluene (Scheme 5). $[RuCl_2(PCy_3)_2]$ - (CHC_6H_5)] (I, Cy=cyclohexyl) was chosen as the initiator, since it possesses a balanced activity for both NBE and the CL.^[79,80] Next, charged groups were introduced onto the inner surface of monoliths, which helped retain ILs that were otherwise only physically adsorbed to the surface of the monoliths. Taking advantage of the "living" character of the ring-opening metathesis polymerization (ROMP)-based protocol,^[81] surface functionalization was accomplished in situ by simply passing a solution of the ionic monomer $[NBE-CH_2-NMe_3][BF_4]$ (2) through the monolith immediately after its synthesis.^[82-84] Finally, the living Ru-alkylidenes were completely removed by treatment with ethyl vinyl ether, as proven by means of inductively-coupled plasma optical emission spectroscopy (ICP-OES) measurements, which indicated a residual Ru content of the monolith of 38 ppm. Elemental analysis confirmed the effective grafting of 2 with an average degree of oligomerization of three. Such low degrees of oligomerization, on one hand, guarantee binding of the IL and, on the other hand, do not give rise to higher back pressures.

In general, a monolith consists of interconnected structure-forming microglobules. Important parameters are the microglobule diameter (d_p) and the microporosity (ε_p) of the microglobules as well as the inter-microglobular porosity



Scheme 5. Preparation of a surface-functionalized monolithic support. p=3.

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 (ε_z) . The total porosity (ε_t) is defined as the sum of ε_p and ε_z . These values, as well as the pore size distribution (Figure S17 in the Supporting Information), were determined by inverse size exclusion chromatography (ISEC).^[85] The corresponding values for the surface-functionalized monolith are summarized in Table 4.

Table 4. Composition and structural data of the monolithic support (V_{column} = 1.66 mL) after ROMP-based grafting of **2**.

$\varepsilon_{\rm p} [{\rm vol}\%]$	$\varepsilon_{\rm z} [{\rm vol} \%]$	$\varepsilon_{t} [vol \%]$	$V_{\rm z}[{\rm mL}]$	${ar \Phi}_{ m m}{}^{[a]}\left[{ m \AA} ight]$
5	75	80	1.25	1160

[a] Average pore diameter.

As observed, the large void volume of 80%, with regard to the total column volume, guarantees low back pressures and is mainly caused by the interstitial porosity ($\varepsilon_z = 75\%$). In other words, the monolith was designed to possess almost exclusively macropores; thus favoring diffusion and allowing high reagent throughput. In contrast to most silica-based materials, which also have a large fraction of micro- and mesopores, this particular feature makes polymeric monoliths ideal support materials for the intended continuous metathesis reactions under biphasic conditions.

Continuous metathesis under biphasic conditions by using **monolith-supported ILs**: Layers of $[BDMIM][BF_4]$ on the surface of monoliths containing 1 were prepared by simply injecting a solution of the IL and $\boldsymbol{1}$ in CH_2Cl_2 . Then, the solvent was completely removed in vacuo. A homogeneous distribution of the IL over the entire support was confirmed by cutting a monolith into pieces of equal weight, which were then extracted with CDCl₃ and subjected to ¹H NMR spectroscopic analysis. Thus, we could also show that the IL could be removed quantitatively by flushing the column with methanol. Finally, NMR spectroscopic analysis helped to confirm that, at flow rates between 0.05 and 2.00 mLmin⁻¹, no [BDMIM][BF₄] was removed from the monolith when heptane was used as a mobile phase and up to 20 vol% of the void volume of the monolith was filled with the IL.

RCM of N,N-diallyl trifluoroacetamide, DEDAM, and 1,7octadiene under biphasic conditions using monolith-supported ILs: Since catalyst 1 showed very high activity in the RCM of DAFA in both CH_2Cl_2 and $[BDMIM][BF_4]$ at T =40°C, we chose this reaction to demonstrate the soundness and viability of the concept of running metathesis reactions biphasic conditions using monolith-supported under $[BDMIM][BF_4]/1$. Due to the high polarity of DAFA, optimization of the reaction conditions, that is, adjusting the thickness of the IL layer and identifying the optimum concentrations was challenging. For comparison, all experiments were additionally carried out with the GH catalyst under identical conditions. Conversions were determined by means of GC-MS; leaching of 1 into the heptane phase was quantified by ICP-OES. Under all conditions, monolith-supported

 $[BDMIM][BF_4]/1$ outperformed the monolith-supported [BDMIM][BF₄]/GH catalyst (Table S1 in the Supporting Information). Metal leaching into the heptane phase was lower by a factor of 4-10 for [BDMIM][BF₄]/1 compared with [BDMIM][BF4]/GH catalyst and resulted in TONs up to 900. Generally, leaching could be reduced by dilution of the mobile phase with heptane, thereby decreasing the polarity of the transport phase. However, this was associated with a decrease in TON. TONs could be increased by reducing the thickness of the immobilized IL layer; however, this occurred at the expense of increased catalyst leaching. The lower TONs obtained in comparison to the biphasic solution experiments may be attributed to reduced contact times and the fact that mixing of the two phases proceeded more effectively under mechanical stirring than on a monolith. Accordingly, halving the flow rate did not increase the TONs (Table S1 in the Supporting Information). Increasing the temperature to T=60 °C led to a higher product fraction in the eluting phase within the first minutes of the reaction; however, deactivation occurred faster than reactions performed at 40°C and the overall TON did not change significantly. Plots of conversion versus time for DAFA under different reaction conditions are shown in Figures S18 and S19 in the Supporting Information. These results show the typical deactivation of a metathesis catalyst over time and clearly demonstrate the advantages of the SILP approach presented herein over traditional immobilization strategies.

As observed for reactions in organic solvents, DEDAM and 1,7-octadiene reacted with catalyst **1** under SILP conditions only at elevated temperatures (T=80 °C), resulting in TONs of 650 and 770 and Ru leaching of 0.2 and 0.05%. While 1,7-octadiene could be passed through the monolith neat, heptane was used as the second liquid transport phase in the RCM of DEDAM to establish a biphasic reaction mixture.

Self-metathesis of methyl oleate under biphasic conditions using monolith-supported ILs: Since the self-metathesis of methyl oleate requires prolonged reaction times, even at 80°C, we decided to cycle the methyl oleate phase, that is, to pass it through the monolith several times at a flow rate of 0.1 mLmin⁻¹. After each run the conversion was checked by GC-MS, then the reaction mixture was again flushed through the monolithic support. This procedure was repeated three times, then catalyst leaching was checked by ICP-OES (Table 5). A total TON of 800 was obtained within 45 min at T=80 °C with the highest conversion occurring within the first cycle. Notably, again only the primary metathesis products formed, suggesting the absence of any active Ru-hydride species. This TON is in view of the low solubility of methyl oleate in the IL ($K_{\text{methyl oleate/IL}} = 34$ at T = 80 °C; Table S2 in the Supporting Information), which is remarkable and underlines the high reactivity of **1**.

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Table 5. Self-metathesis of methyl oleate.

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Cycle	Integral conversion ^[a] [%]
1 (after 15 min)	45
2 (after 28 min)	56
3 (after 45 min)	63
total Ru leaching	0.6%

[a] Primary metathesis products; catalyst **1** (4.5 mg), [BDMIM][BF₄] (90 mg), methyl oleate (1.8 g, 1300 equiv), T=80 °C, flow rate: 0.1 mLmin⁻¹.

Conclusion

The synthesis of new dicationic Ru-alkylidene complex 1 is described. The catalyst can be selectively dissolved in an IL in the presence of a second organic phase and possesses high activity towards dienes lacking coordinating moieties. At elevated temperatures, complex 1 shows also high activity in RCM, CM, and self-metathesis reactions. For RCM and self-metathesis reactions under supported biphasic conditions, surface-functionalized ROMP-derived monoliths were prepared and used for the immobilization of [BDMIM][BF₄] containing catalyst **1**. High TONs and exceptionally low catalyst leaching ($\leq 0.1\%$) were observed. Importantly, our concept also enables continuous product formation, simply by cycling reactants through a monolithic support containing a suitable catalyst dissolved in an IL. The fact that a biphasic liquid/liquid system is used definitely widens the range of potentially accessible substrates. In contrast to any other surface-immobilized catalyst, the facile recycling of the monolithic support by flushing with methanol, for example, represents an additional advantage over existing systems. Current efforts focus on variations in the IL to allow increased substrate concentration in the SILP.

Experimental Section

Materials and characterization: Unless noted otherwise, all preparations were performed in a LabMaster 130 glove box (MBraun; Garching, Germany) or by standard Schlenk techniques under a N₂ atmosphere. CH₂Cl₂, THF, diethyl ether, and pentane were purchased from J. T. Baker (Devender, Netherlands) and were dried by using an MBraun SPS-800 solvent purification system with alumina drying columns. DMF was purchased from Sigma–Aldrich (Munich, Germany) and passed through a pad of alumina prior to use. Starting materials were purchased from Aldrich, TCI Europe (Zwijndrecht, Belgium), and ABCR (Karlsruhe, Germany) and used without further purification. Polystyrene (PS) standards (800 $< M_w < 2000000 \text{ gmol}^{-1}$) used for ISEC were purchased from Polymer Standard Service (Mainz, Germany). The CL (NBE-CH₂O)₃SiCH₃ was prepared as described earlier.^[80]

NMR spectra were recorded on a Bruker Avance III 400 spectrometer or a Bruker DRX 250 spectrometer in the indicated solvent at 25 °C and data are listed in parts per million downfield from tetramethylsilane (TMS) as an internal standard. GC-MS data were obtained by using an Agilent Technologies 5975C inert MSD with triple-axis detector, an 7693 autosampler, and a 7890A GC system equipped with a SPB-5 fused silica column (34.13 m×0.25 mm×0.25 µm film thickness). The injection temperature was set to 150 °C. The column temperature ramped from 45 to 250 °C within 8 min, and was then held for further 5 min. The column

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flow was 1.05 mLmin⁻¹. IR spectra were measured on a Bruker IFS 28 using ATR technology in NaCl cuvettes or as KBr pellets.

Compound 1: Under exclusion of light, AgBF₄ (130 mg, 670 µmol) was dissolved in DMF (100 mg, 1.37 mmol) and CH₂Cl₂ (5 mL). Then a solution of the GH catalyst (200 mg, 320 µmol) in CH2Cl2 was slowly added. The immediate formation of AgCl was observed and stirring was continued for 1 h. After filtering off the precipitate and passing the solution through a short pad of Celite, the solvent was removed in vacuo. A light green solid was obtained (290 mg, 305 $\mu mol,\,95\,\%$). Green crystals suitable for X-ray analysis were obtained by layering THF over a concentrated solution of **1** in CH₂Cl₂ at 20°C. ¹H NMR (400.13 MHz, CD₂Cl₂): $\delta =$ 19.28 (s, 1H), 7.94 (s, 1H), 7.88–784 (m, 2H), 7.28 (t, J=7.3 Hz, 1H), 7.06 (d, J=8.5Hz, 1H), 6.96 (s, 4H), 5.64 (s, 2H), 4.99-4.93 (m, 1H), 4.08 (s, 3.95), 3.16-3.10 (m, 6H), 2.60 (d, J=8.0 Hz, 12H), 2.37 (s, 12H), 2.30 (s, 6 H), 1.03 ppm (d, J = 6.4 Hz, 5.70); ¹³C NMR (100.61 MHz, CD₂Cl₂): 114.9, 77.3, 53.0, 39.1, 33.2, 21.7, 21.0, 18.5 ppm; ¹⁹F NMR (376.50 MHz, CD₂Cl₂): $\delta = -152.6$ ppm; IR (KBr): $\tilde{\nu} = 3438$ (b), 3047 (m), 2916 (s), 2856 (m), 2729 (m), 1668 (vs), 1591 (s), 1477 (s), 1383 (s), 1282(m), 1259 (vs), 1215 (m), 1039 (vs), 930 (s), 858 (m), 750 (s), 701 (m), 680 (m), 658 (m), 579 (s), 521 (s), 422 cm^{-1} (s); elemental analysis calcd (%) for $C_{40}H_{59}B_2F_8N_5O_4Ru$ ($M_r = 950.61 \text{ gmol}^{-1}$): C 50.49, H 6.26, N 7.27; found: C 50.58, H 6.21, N 7.13.

(*exo,endo*-Norborn-2-en-5-ylmethyl)dimethylamine: (*exo,endo*-Norborn-2-en-5-ylmethyl)dimethylamine was prepared by Diels–Alder cycloaddition between freshly cracked cyclopentadiene (14.1 g, 214 mmol) and dimethylallylamine (18.20 g, 214 mmol). Hydroquinone (10 mg) was added and the reaction proceeded at 200°C for 48 h in a steel autoclave. Fractional distillation (40°C, 0.1 mbar) yielded (*exo,endo*-norborn-2-en-5-ylmethyl)dimethylamine as a colorless, oily liquid (21.34 g, 141 mmol, 66%). ¹H NMR (250.13 MHz, CDCl₃): δ = 5.90–6.13 (2×m, 21H; -CHE) (2.80–2.72 (m, 2H), 2.19–2.17 (m, 6H; -*N*-(CH₃)₂), 2.05–1.97 (m, 1H), 1.87–1.77 (m, 2H), 1.17–1.43 (m, 3H), 0.54–0.47 ppm (2×m, 1H); ¹³C NMR (62.5 MHz, CDCl₃): δ = 136.5, 132.2, 65.9, 64.3, 49.2, 46.7, 44.5, 42.1, 36.7, 30.9 ppm; IR (film): $\hat{\nu}$ = 3067 (m), 2965 (s), 2860 (m), 2814 (m), 2768 (s), 2360 (m), 1441 (s), 1375 (m), 12223 (m), 1033 (s), 838 (s), 718 cm⁻¹ (s); GC-MS (EI, 70 eV): *m*/*z* calcd for C₁₀H₁₇N: 151.14; found: 151.1, *t*_R = 6.05 min.

Compound 2a: (*exo,endo*-Norborn-2-en-5-ylmethyl)dimethylamine (1.00 g, 6.6 mmol) was dissolved in CH₂Cl₂ (10 mL) and cooled to 0 °C. A solution of methyl iodide (1.22 g, 8.6 mmol) in CH₂Cl₂ (3 mL) was slowly added and the mixture was stirred for 2 h. After solvent removal, compound **2a** was obtained as a white solid (1.71 g, 5.9 mmol, 91%). The product was purified by washing with diethyl ether and dried in vacuo. ¹H NMR (250 MHz, DMSO): $\delta = 6.00-6.27$ (2×m, 2H; -CH=CH-), 3.25-3.14 (m, 2H), 3.07–3.05 (m, 9H; -*N*-(CH₃)₃), 2.83–3.00 (m, 3H), 2.13–2.03 (m, 1H), 1.26–1.52 (m, 3H), 0.77–0.70 ppm (2×m, 1H); ¹³C NMR (62.5 MHz, DMSO): $\delta = 139.4$, 132.3, 71.1, 53.4, 49.9, 46.9, 42.9, 34.3, 33.5 ppm; IR (KBr): $\tilde{\nu} = 3425$ (b), 3053 (s), 2995 (m), 2962 (m), 2866 (s), 2595 (m), 2341 (m), 1477 (vs), 1336 (s), 1252 (m), 1144 (m), 1078 (m), 972 (s), 912 (s), 829 (s), 715 cm⁻¹ (vs).

Compound 2: Under exclusion of light, an aqueous solution of **2a** (0.50 g, 1.76 mmol.) was added dropwise to a solution of silver tetrafluoroborate (0.38 g, 1.90 mmol) in water at 50 °C. The reaction mixture was stirred for 1 h, then the yellow precipitate of silver iodide was filtered off and the solvent was removed in vacuo. Compound **2** was obtained as a colorless solid (0.40 g, 1.58 mmol, 90%). ¹H NMR (400.13 MHz, D₂O): δ = 6.06–6.33 (2×m, 2H; -CH=CH-), 3.56–3.43 (m, 1H), 3.33–3.28 (m, 1H), 3.14–3.12 (m, 9H; -*N*-(CH₃)₃), 2.97–2.85 (m, 3H), 2.13–2.20 (m, 1H), 1.59–1.29 (m, 3H), 0.85–0.80 ppm (m, 1H;); ¹³C NMR (100.61 MHz, D₂O): δ = 139.8, 138.2, 136.5, 131.6, 73.3, 72.0, 53.8, 49.4, 47.7, 46.7, 45.6, 42.8, 42.3, 34.3, 33.5 ppm; ¹⁹F NMR (376.50 MHz, D₂O): δ = -150.2 ppm; IR (KBr): \hat{r} = 3423 (b), 3060 (m), 2972 (s), 2875 (m), 1622 (m), 1487 (s), 1423 (m), 1340 (m), 1268 (m), 1051 (vs), 970 (m), 904 (s), 825 (m), 769 (m), 721 (vs), 521 cm⁻¹ (s); MS (ESI): 166.16 [C₁₁H₂₀N].

N,*N*-Diallylacetamide: Over a period of 1 h, diallylamine (15.0 g, 154 mmol) was added to ice cold acetic anhydride (26.8 g, 263 mmol) under vigorous stirring. Then the temperature was raised to 100 °C and

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stirring was continued for a further 2 h. Fractional distillation yielded *N*,*N*-diallylacetamide (70 °C, 0.1 mbar) as a colorless liquid (18.3 g, 131 mmol, 85 %). ¹H NMR (400.13 MHz, CDCl₃): δ = 5.76–5.65 (m, 2 H), 5.16–5.04 (m, 4 H), 3.87 (dd, *J* = 5.8 Hz, 4 H), 2.04 ppm (s, 3 H); ¹³C NMR (100.61 MHz, CDCl₃): δ = 170.5, 132.8, 116.7, 48.7, 21.2 ppm; IR (film): $\tilde{\nu}$ = 3473 (b), 3078 (s), 2991 (m), 2979 (s), 2912 (m), 2354 (m), 1718 (m), 1633 (vs), 1448 (m), 1407 (vs), 1261 (s), 1241 (vs), 1192 (s), 1008 (m), 982 (s), 918 (s), 773 (m), 687 (s), 600 (s), 557 cm⁻¹ (m); GC-MS (EI, 70 eV): *m/z* calcd for C₈H₁₃NO: 139.10; found: 139.1, *t*_R = 6.268 min.

N-Allyl-N-propargyltrifluoroacetamide

N-Allyl-N-propargylamine: This compound was prepared according to a procedure reported in the literature.^[86] A solution of allylamine (7.660 g, 134 mmol) in 2 M aqueous NaOH (50 mL) was warmed to 40 °C. Propargyl chloride (5 g, 67 mmol) was then added dropwise over a period of 3 h. Stirring was continued for a further 3 h, then the reaction mixture was allowed to cool to ambient temperature. The mixture was extracted with diethyl ether (3 × 30 mL) and the combined organic phases were washed with brine (2 × 50 mL). After drying over MgSO₄, the solvent was removed. *N*-Allyl-*N*-proparglamine was isolated by column chromatography (silica, pentane/diethyl ether gradient) as a colorless liquid (2.3 g, 24 mmol, 36 %). ¹H NMR (400.13 MHz, CDCl₃): δ = 5.76–5.66 (m, 1 H), 5.29–5.21 (m, 2 H), 4.17–4.10 (m, 4 H), 2.32–2.26 ppm (m, 1 H); ¹³C NMR (100.61 MHz, CDCl₃): δ = 134.6, 118.5, 78.5, 73.0, 56.0, 41.5 ppm; GC-MS (EI, 70 eV): *m/z* calcd for C₆H₃N: 95.14; found: 95.1, *t*_R=3.258 min.

Alongside the desired product, the dialkylated species *N*-allyl-*N*,*N*-dipropargylamine was isolated (1.83 g, 14 mmol, 21 %). ¹H NMR (400.13 MHz, CDCl₃): δ =5.86–5.76 (m, 1H), 5.22 (d, *J*=11.1 Hz, 2H), 3.41 (s, 4H), 3.14 (d, *J*=6.7 Hz, 2H), 2.21 ppm (s, 2H); ¹³C NMR (100.61 MHz, CDCl₃): δ =134.6, 118.5, 78.5, 73.0, 56.0, 41.5 ppm; GC-MS (EI, 70 eV): *m*/*z* calcd for C₉H₁₁N: 133.09; found: 133.1, *t*_R=5.141 min.

N-Allyl-N-propargyl trifluoroacetamide: A mixture of N-allyl-N-propargylamine (1.00 g, 11 mmol) and triethylamine (1.34 g, 13 mmol) in CH2Cl2 (18 mL) was cooled to 0°C. Trifluoroacetic anhydride (2.66 g, 13 mmol) in CH₂Cl₂ (5 mL) was added dropwise over a period of 30 min. The reaction mixture then was warmed to 30 °C and stirring was continued for 15 h. A saturated aqueous solution of NaHCO_3 (30 mL) was added and the mixture was then extracted with CH_2Cl_2 (2×30 mL). The organic phase was washed with water (30 mL) and then dried over MgSO₄. After solvent removal, the residue was subjected to column chromatography (silica, diethyl ether) to yield the target compound as a colorless liquid (1.71 g, 8.9 mmol, 81%). ¹H NMR (400.13 MHz, CDCl₃): $\delta = 5.91-5.80$ (m, 1H), 5.22–5.09 (m, 2H), 3.40 (d, J = 4.5 Hz, 2H), 3.31 (d, J = 5.3 Hz, 2H), 2.21–2.19 ppm (m, 1H); ¹³C NMR (100.61 MHz, CDCl₃): $\delta = 135.9$, 116.6, 81.9, 71.3, 50.8, 37.2 ppm; ¹⁹F NMR (376.50 MHz, CDCl₃): $\delta = -75.7$ ppm; IR (film): $\tilde{\nu} = 3292$ (vs), 3083 (m), 2985 (m), 2923 (m), 2343 (m), 2123 (m), 1691 (vs), 1419 (vs), 1353 (s), 1277 (s), 1205 (vs), 1141 (vs), 1003 (s), 937 (s), 756 s), 698 $\rm cm^{-1}$ (s); GC-MS (EI, 70 eV): m/z calcd for C₈H₈F₃NO: 191.06; found: 190.1, $t_{\rm R} =$ 4.964.

Preparation of surface-functionalized monoliths: Monoliths were prepared in 125×4.4 mm I.D. stainless-steel tubings, according to a well-established procedure.^[80] The polymerization mixture composed of NBE (15 wt.-%), the CL (NBE-CH₂O)₃SiCH₃ (15 wt%), the porogenic solvents toluene (20 wt%) and 2-propanol (50 wt%), as well as the initiator [RuCl₂(PCy₃)₂(=CHC₆H₅)] (0.4 wt%). The steel column was placed vertically, one end closed, in an ice bath. Polymerization proceeded at 0°C for 30 min, then the temperature was raised to 20°C for another 30 min.

For the grafting of monomer **2** to the surface of the monoliths, the column was provided with adapters and flushed with CH_2Cl_2 for 2 h at a flow rate of 0.1 mLmin⁻¹. The monomer (10 equiv with respect to the initiator) was dissolved in CH_2Cl_2 (1.2 mL) and introduced into the monolith. The loaded monolith was sealed and kept at 45 °C for 12 h. To remove the initiator, the column was flushed with a 1:1 mixture of ethyl vinyl ether and CH_2Cl_2 for 2 h at a flow rate of 0.1 mLmin⁻¹. After this, flushing was continued with pure CH_2Cl_2 for a further 2 h at a flow rate of 0.1 mLmin⁻¹.

Immobilization of [BDMIM][BF₄] and the catalyst on the surface of the monoliths: Complex 1 (2.5 mg, 2.6 \mumol) and [BDMIM][BF₄] (100 mg)

were mixed and dissolved in CH₂Cl₂ (1.2 mL). The solution was then introduced into the monolith. Vacuum was applied for 3 h at 40 °C to remove the solvent. Prior to use, the support was flushed with heptane for 1 h at 40 °C by applying a flow rate of 0.1 mL min⁻¹.

Metathesis under biphasic conditions: Complex 1 (2.5 mg, 2.6 μ mol) was dissolved in [BDMIM][BF₄] (200 mg) and the solution was heated to 40 °C. Then a solution of the substrate (0.6–13 mmol) in heptane (2 mL) was added and the biphasic system was stirred vigorously (600 rpm) for 12 h. Reactions were quenched by adding ethyl vinyl ether (1 mL). After removing the nonpolar phase, the IL phase was extracted extensively with diethyl ether. The organic phases were combined and subjected to GC-MS analysis to determine conversion.

Metathesis under biphasic conditions using monolith-supported ILs: Metathesis reactions under SILP conditions were performed in air. The loaded monolithic support was placed inside a Merck L-5025 column thermostat and warmed to the indicated temperature (Table S1 in the Supporting Information). By using a syringe pump (WPT, Aladdin-1000), the substrate (diallyl trifluoroacetamide and DEDAM dissolved in heptane; 1,7-octadiene and methyl oleate as neat reactants) was flushed through the monolith at a flow rate of 0.1 mLmin⁻¹. The eluent was collected and subjected to GC-MS analysis to determine conversion. Used SILP phases were removed by subsequent flushing with methanol (5 mL) and CH₂Cl₂ (5 mL). The cleaned monolithic supports were again charged and used for catalysis.

Ru measurements: The Ru content was measured by ICP-OES (λ = 240.272 nm, ion line, background lines at λ_1 =240.254 nm and λ_2 = 240.295 nm) using a Spectro Arcos device (Ametek GmbH; Meerbusch, Germany). Standardization was carried out with Ru standards containing 0.1, 0.5, 1.0, 2.5, and 5 ppm of Ru. The Ru content of both the support and in the product fraction was determined by dissolving samples (100 mg) in aqua regia.

Determination of the distribution coefficients (Ksolvent/IL): For 1,7-octadiene, DEDAM, and DAFA, the distribution coefficients, $K_{\text{heptane/IL}} =$ (heptane), were determined for the solvent system heptane/[BDMIM][BF₄] at 40 and 80 °C, respectively. In addition, for $K_{\text{dodecane/IL}} = \frac{c(\text{substrate in dodecane})}{c(\text{substrate in IL})}$ DAFA, was determined for dodecane/[BDMIM][BF4] at 40 and 80°C as well. Four measurements were performed for each substrate/solvent/temperature system to yield an average distribution coefficient with sufficient validity. Substrate (50 mg) and an internal standard (15 mg) were dissolved in solvent (200 mg) and added to [BDMIM][BF₄] (200 mg). Dodecane was used as an internal standard when heptane was the organic solvent and dicyclopentadiene served as the nonpolar reference for the determination in dodecane. The biphasic system was stirred with 600 rpm at the indicated temperature for 1 h. Then a sample was removed from the organic phase and examined by means of GC measurements. The immiscibility of the internal standards with the IL was checked by ¹H NMR spectroscopy. Comparing the integral areas for the substrate signal and the signal caused by the internal standard, before and after mixing, allowed the distribution coefficient to be calculated.

 $K_{substrate/IL}$ for neat 1,7-octadiene and methyl oleate in [BDMIM][BF₄]: Substrate (200 mg) and dodecane (50 mg) as the internal standard were added to [BDMIM][BF₄] (200 mg). The biphasic system was stirred at 600 rpm at the indicated temperature for 1 h. Then a sample was removed from the organic phase and analyzed by GC-MS. The ratio of the integral areas for the substrate signal and the signal caused by the internal standard, before and after mixing, corresponded directly to the distribution coefficient.

X-ray measurements and structural determination of 1: Data were collected on a Bruker Kappa Apex 2 duo diffractometer at 100 K. The structure was solved by using direct methods with refinement by full-matrix least-squares on F^2 , with the program system SHELXL 97 in connection with a multiscan absorption correction.^[87] All non-hydrogen atoms were refined anisotropically.

CCDC-900128 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Inverse size exclusion chromatography (ISEC): Functionalized monoliths were characterized by ISEC measurements in terms of inter-microglobular porosity (ε_z), microporosity (ε_p), and total porosity (ε_t). A volume of 10 µL per sample of individual PS standard (0.25 mg mL⁻¹) dissolved in the mobile phase (CHCl₃) was injected into the column at a flow rate of 0.6 mL min⁻¹. The total accessible porosity was determined by injecting a 10 µL sample of toluene. A wavelength of 254 nm was applied to record the chromatograms. Retention times and volumes corresponding to each injection were determined from the peak maximum. Each retention volume was corrected for the extra-column volume of the equipment. For calculations it was assumed that the hydrodynamic radii of the PS standards in CHCl₃ did not differ significantly from those reported in CH₂Cl₂^[85]

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Vital support: A dicationic Ru–alkylidene (see figure) was prepared and used in continuous heterogeneous liquid–liquid metathesis reactions by using supported ionic-liquid-phase technology. This approach allows reuse of the support and synthesis of the target compounds with low Ru contamination.



Heterogeneous Catalysis -

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