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Novel Metathesis Catalysts Based on Ruthenium 1,3-Dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidenes: Synthesis, Structure, Immobilization, and Catalytic Activity

Liangru Yang,[a] Monika Mayr,[a] Klaus Wurst,[b] and Michael R. Buchmeiser*[a]

Abstract: The synthesis of novel ruthenium-based metathesis catalysts containing the saturated 1,3-bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene ligand, that is, $[RuCl_2(NHC)\{=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}5\text{-}NO_2\text{-}C_6H_3\}]$ (**1**) and $[Ru(CF_3COO)_2(NHC)\{=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}5\text{-}NO_2\text{-}C_6H_3\}]$ (**2**) (NHC = 1,3-bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene) is described. Both catalysts are highly active in ring-closing metathesis (RCM) and ring-opening cross-metathesis (ROCM). Compound **1** shows moderate activity in enyne metathesis. Compound **2** is not applicable to enyne metathesis since it shows high activity in the cyclopolymerization of diethyl dipropargylmalonate (DEDPM). Poly(DEDPM) prepared by the action of **2** consists of 95% five-membered rings, that is, poly(cyclopent-1-enevinylene)s, and 5% of six-membered rings, that is, poly(cyclohex-1-ene-3-methylidene)s. The polymerization proceeds in a nonliving manner and results in polyenes with broad polydispersities ($1.9 \leqq PDI \leqq 2.3$). Supported analogues of **2** were prepared by immobilization on hydroxymethyl-Merrifield resin and a monolithic support derived from ring-opening-metathesis polymerization (ROMP). Catalyst loadings of 1 and 2.5%, respectively, were obtained. Both supported versions of **2** showed excellent reactivity. With 0.24–2% of the supported catalysts, yields in RCM and ROCM were in the range of 76–100%. Leaching of ruthenium was low and resulted in Ru contaminations of the products of less than 0.000014% (0.14 ppm).

Keywords: heterogeneous catalysis · homogeneous catalysis · metathesis · ruthenium · supported catalysts

Introduction

Carbon–carbon coupling reactions are of enormous importance in organic synthesis. Heck and other palladium-mediated reactions were among the first to fulfill the criteria of high selectivity, tolerance of functional groups, and high catalyst efficiency.[1–8] The development of well-defined initiators for metathesis-based reactions[9] was initially stimulated by reactions related to polymer chemistry.[10–16] However, with these initiators in hand, olefin metathesis has become a powerful tool, maybe *the* tool in organic synthesis.[17,18] With a few exceptions,[19,20] reactions that require high *ee* are still the domain of molybdenum-based Schrock initiators.[21–33] Nevertheless, "simple" metathesis-based reactions such as ring-opening cross-metathesis, enyne metathesis, and others are nowadays preferably accomplished by using air- and moisture-tolerant ruthenium-based catalysts based on N-heterocyclic carbenes (NHCs), usually referred to as Grubbs and Grubbs–Hoveyda catalysts.[1,2,16,34–47] Both NHC ligands and carbene groups in ruthenium-derived catalysts have been optimized over the years. So far, most variations in NHC were accomplished by using different substituents on the NHC and by switching from imidazol-2-ylidene to imidazolin-2-ylidene.[5,38,39,44,48–52] Even small, sometimes incremental, variations resulted in dramatic changes in reactivity. Recently, we reported new systems for olefin metathesis generated by replacing one or two chloro ligands in Grubbs–Hoveyda-type catalysts by strongly electron-withdrawing groups such as trifluoroacetate and trifluoromethanesulfonate, and their special features in organic synthesis and polymer chemistry.[53–59] Our latest goal was to investigate the reactivity of a new class of ruthenium-based metathesis catalysts prepared from tetrahydropyrimidin-2-ylidenes.[60–62] This was accomplished by synthesizing $[RuCl_2(NHC)\{=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}5\text{-}NO_2\text{-}C_6H_3\}]$ (**1**; NHC = 1,3-bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene) and its bis(trifluoroacetate) analogue $[Ru(CF_3COO)_2(NHC)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}5\text{-}NO_2\text{-}C_6H_3)$ (**2**). In view of the strong demand for supported catalysts,[63–68] heterogeni-

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zation of **2** on macroreticular poly(styrene-*co*-divinylbenzene) resins and monolithic disks prepared by ring-opening metathesis polymerization (ROMP) was achieved. To benchmark the new systems, they were all subjected to various metathesis-type reactions such as RCM, ring-opening cross-, cross-, and enyne metathesis. Especially in the first two types of reaction, the new catalysts were found to be equally or more active than existing ruthenium-based metathesis catalysts.

Results and Discussion

Synthesis of $[RuCl_2(NHC)\{=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}5\text{-}NO_2\text{-}C_6H_3\}]$ (1) and $[Ru(CF_3COO)_2(NHC)\{=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}5\text{-}NO_2\text{-}C_6H_3\}]$ (2): Compound **1** was synthesized by a three-step, one-pot process similar to that reported by Grela et al.[69] It comprised reaction of 1,3-dimesityl-3,4,5,6-tetrahydropyrimidinium tetrafluoroborate with potassium *tert*-pentanolate to generate the free carbene, which was subsequently treated with $[RuCl_2(=CHPh)(PCy_3)_2]$ and the ligand inroduced by Grela et al., 2-(2-PrO)-5-NO_2-styrene,[20,69–72] in the presence of CuCl to yield, after flash chromatography, the desired compound as an olive green powder in 50% overall yield (Scheme 1).

Crystals of **1** suitable for X-ray analysis were obtained from CH_2Cl_2/pentane; it crystallizes in the monoclinic space group $P2_1/c$, $a = 1137.30(2)$, $b = 1523.49(3)$, $c = 1797.18(4)$ pm, $\beta = 92.237(1)°$, $Z = 4$ (Figure 1). Selected X-ray data are summarized in Table 1; selected bond lengths and angles are given in Table 2.

The Ru–Cl distances in **1** are virtually identical (234.25(7) and 234.28(7) pm) and only insignificantly longer than those in $[RuCl_2(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}C_6H_4)(IMesH_2)]$ (232.79(12) and 233.93(12) pm; $IMesH_2$ = 1,3-dimesityldihydroimidazol-2-ylidene).[70] The O(1)-Ru(1)-C(1) angle of 175.92(8)° is similar to that in $[RuCl_2(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}C_6H_4)(IMesH_2)]$ (176.22(4)°), but the Ru(1)–C(1) distance is lengthened to 201.3(2) pm compared to 198.1(5) pm in $[RuCl_2(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}C_6H_4)(IMesH_2)]$. Despite this longer distance, a pronounced *trans* effect is observed that leads to a Ru(1)–O(1) distance of 231.03(16) pm as opposed to 226.1(3) pm in $[RuCl_2(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}C_6H_4)(IMesH_2)]$. These findings are indicative of stronger binding of the pyrimidin-2-ylidene ligand compared to its parent imidazolin-2-ylidene analogue.

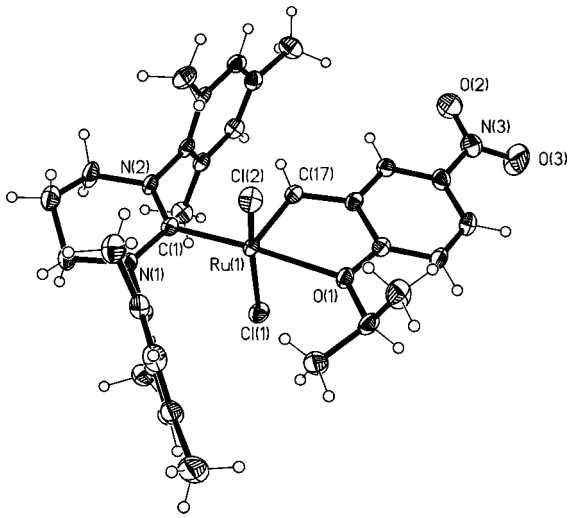
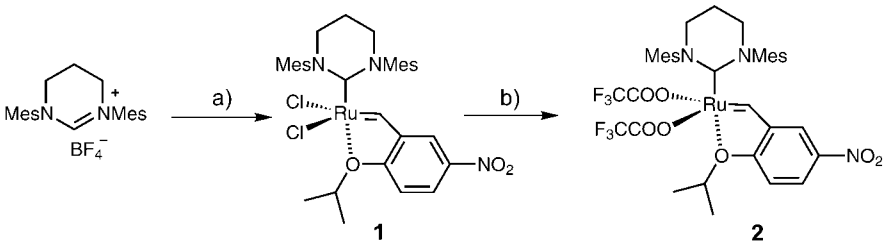


Figure 1. Molecular structure of **1**.

Table 1. Selected crystal data and structure refinement for **1** and **2**.

	1	**2**
empirical formula	$C_{32}H_{39}Cl_2N_3O_3Ru$	$C_{36}H_{39}F_6N_3O_7Ru\cdot 2\,CH_2Cl_2$
formula weight	685.63	1010.62
crystal system	monoclinic	monoclinic
space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
a [pm]	1137.30(2)	1116.76(3)
b [pm]	1523.49(3)	2430.80(4)
c [pm]	1797.18(4)	1624.64(5)
α [°]	90	90
β [°]	92.237(1)	90.524(1)
γ [°]	90	90
V [nm^3]	3.11154(11)	4.41010(18)
Z	4	4
T [K]	233(2)	233(2)
ρ_{calcd} [Mg m^{-3}]	1.464	1.522
μ [mm^{-1}]	0.713	0.672
color, habit	yellow prism	colorless prism
no. of rflns with $I > 2\sigma(I)$	4646	6387
GOF on F^2	1.041	1.060
R indices $[I > 2\sigma(I)]$	$R_1 = 0.0296$	$R_1 = 0.0439$
	$wR^2 = 0.0673$	$wR^2 = 0.1145$



Scheme 1. Synthesis of **1** and **2**. a) i) $tC_5H_{11}OK$, *n*-hexane, room temperature, 60 min; ii) $[RuCl_2(PCy_3)_2(CHPh)]$, 80 °C, 30 min; iii) 2-(2-propoxy)-5-nitrostyrene, CuCl, CH_2Cl_2, room temperature, 30 min; b) CF_3COOAg, THF, room temperature, 2 h.

Reaction of **1** with two equivalents of silver trifluoroacetate in CH_2Cl_2/THF yielded **2**. Both chloro ligands could be substituted in a clean reaction to provide pure bis(trifluoroacetate)-substituted catalyst **2**. In principle, this reaction proceeded in quantitative yield, as demonstrated by in situ ^{1}H NMR experiments. Nevertheless, to obtain analytically pure catalyst **2**, AgCl had to be removed by chromatography on silica, which resulted in lower yields (68%). Crystals of **2** suitable for X-ray analysis were ob-

Table 2. Selected bond lengths [pm] and angles [°] for **1**.

Ru(1)–C(17)	182.5(3)	Ru(1)–C(1)	201.3(2)
Ru(1)–O(1)	231.03(16)	Ru(1)–Cl(2)	234.25(7)
Ru(1)–Cl(1)	234.28(7)	C(17)-Ru(1)-C(1)	105.12(11)
Cl(2)-Ru(1)-Cl(1)	163.16(3)	C(1)-Ru(1)-O(1)	175.92(8)

Table 3. Selected bond lengths [pm] and angles [°] for **2**.

Ru(1)–C(17)	182.5(3)	Ru(1)-C(1)	200.7(3)
Ru(1)–O(6)	203.1(2)	Ru(1)–O(4)	204.3(2)
Ru(1)–O(1)	227.8(2)	C(17)-Ru(1)-C(1)	103.81(13)
C(1)-Ru(1)-O(1)	177.58(10)	O(6)-Ru(1)-O(4)	162.51(9)
O(6)-Ru(1)-O(1)	88.52(9)	O(4)-Ru(1)-O(1)	87.10(9)

tained from CH_2Cl_2/pentane (Figure 2); it crystallizes in the monoclinic space group $P2_1/n$, $a=1116.76(3)$, $b=2430.800(4)$, $c=1624.64(5)$ pm, $\beta=90.524(1)°$, $Z=4$. Selected X-ray data are summarized in Table 1; selected bond lengths and angles are given in Table 3.

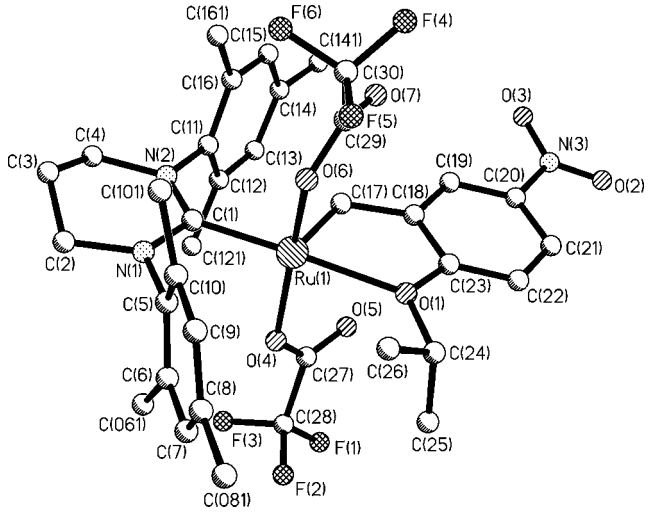


Figure 2. Molecular structure of **2**.

As in **1**, the O(1)-Ru(1)-C(1) (177.58(10)°) angle is similar to that in $[Ru(CF_3COO)_2(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}C_6H_4)(IMesH_2)]$ (178.93(8)°).[53] The Ru(1)–C(1) distance is lengthened to 200.7(3) pm compared to 197.9(25) pm in $[Ru(CF_3COO)_2(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}C_6H_4)(IMesH_2)]$. Again, a pronounced *trans* effect is observed, which leads to a longer Ru(1)–O(1) distance of 227.8(2) pm, as opposed to 224.28(15) pm in $[Ru(CF_3COO)_2(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}C_6H_4)\text{-}(IMesH_2)]$. A striking feature of the NHC-derived ruthenium benzylidenes discussed here is that the ruthenium–benzylidene bond length does not vary. Thus, distances of 182.5 ± 0.5 pm were found in **1**, **2**, $[RuCl_2(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}C_6H_4)(IMesH_2)]$,[70] and $[Ru(CF_3COO)_2(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}C_6H_4)(IMesH_2)]$.[53]

Reactivity in ring-closing metathesis (RCM) and cross-metathesis (CM): To obtain information on the optimum reaction conditions for RCM and differences in reactivity, both **1** and **2** were used in the RCM of diethyl diallylmalonate (DEDAM), one of the most straightforward substrates for such reactions. The results are summarized in Table 4

Turnover numbers (TON) and frequencies (TOF) at 10, 22, and 25% conversion were used instead of yields as measures for reactivity. Reactions in dichloromethane at 40°C gave TONs of up to 1800 for **1** and 3100 for **2** over 1 h (Table 4, entries 9 and 10). Higher and lower reaction temperatures were unfavorable. These data show that both catalysts are among the most reactive reported, and compound **2** is clearly the more reactive. They even exceed the activity of the analogous ruthenium–carbene complexes containing the 1,3-dimesityl-4,5-dihydroimidazolin-2-ylidine ligand, that is, the Grubbs–Hoveyda catalyst $[RuCl_2(IMesH_2)\{=CH\text{-}2\text{-}(2\text{-}PrO\text{-}C_6H_4)\}]$ (**H**)[70] and $[Ru(CF_3COO)_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}C_6H_4)\}]$ (**5**)[53] (Table 4, entries 13 and 14).[53] However, **H** and **5** gave the highest TOFs up to a conversion of 25% (420 and 710 min^{-1}, respectively). These findings are indicative of the high stability of the intermediary Ru methylidenes formed in the catalytic cycles during the action of **1** and **2,** as well as of restricted access due to steric constraints. For further evaluation of the catalysts, reactions with other dienes were carried with **1**, **2**, **H**, and **5** (Table 5, entries 1–12).

Table 4. Activity of compounds **1** and **2** in the RCM of diethyl diallylmalonate (DEDAM) under various conditions.

Entry	Catalyst	T [°C]	Solvent (mol% cat., t)	TON	TOF
1	**1**	RT	CH_2Cl_2 (0.1, 30 min)	100	3[b]
2	**2**	RT	CH_2Cl_2 (0.1, 30 min)	320	10[a]
3	**1**	40	CH_2Cl_2 (1, 30 min)	100	50[a]
4	**2**	40	CH_2Cl_2 (1, 30 min)	100	50[a]
5	**1**	40	CH_2Cl_2 (0.1, 30 min)	330	150[a]
6	**2**	40	CH_2Cl_2 (0.1, 30 min)	630	170[a]
7	**1**	40	CH_2Cl_2 (0.05, 1 h)	980	10[a]
8	**2**	40	CH_2Cl_2 (0.05, 1 h)	2000	94[a]
9	**1**	40	CH_2Cl_2 (0.01, 1 h)	1800	83[a]
10	**2**	40	CH_2Cl_2 (0.01, 1 h)	3100	360[a]
11	**1**	55	$ClCH_2CH_2Cl$ (0.01, 1 h)	1500	37[c]
12	**2**	55	$ClCH_2CH_2Cl$ (0.01, 1 h)	2000	100[a]
13	**H**[d]	40	CH_2Cl_2 (0.1, 1 h)	1500[f]	420[a]
14	**5**[e]	40	CH_2Cl_2 (0.01, 1 h)	1400 [f]	710[a]

[a] TOF [min^{-1}] at 25% conversion. [b] TOF [min^{-1}] at 10% conversion. [c] TOF [min^{-1}] at 22% conversion. [d] $[RuCl_2(IMesH_2)\{=CH\text{-}2\text{-}(2\text{-}PrO\text{-}C_6H_4)\}]$. [e] **5**: $[Ru(CF_3COO)_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}C_6H_4)]$.[53] [f] 0.05 mol% catalyst, values taken from ref. [53].

Table 5. Activity of compounds **1**–**4** in the RCM and CM of simple dienes. Reactions were performed in CH_2Cl_2 at 40 °C. Reaction time: 2 h.

Entry	Compound	Catalyst	mol % catalyst	TON
1	1,7-octadiene	**H**	0.05	1700[53]
2	diallyldiphenylsilane	**H**	0.05	300
3	*tert*-butyl *N*,*N*-diallylcarbamate	**H**	0.05	1900
4	1,7-octadiene	**5**	0.05	1800[53]
5	diallyldiphenylsilane	**5**	0.05	300
6	*tert*-butyl *N*,*N*-diallylcarbamate	**5**	0.05	1000
7	1,7-octadiene	**1**	0.05	2000
8	diallyldiphenylsilane	**1**	0.05	40
9	*tert*-butyl *N*,*N*-diallylcarbamate	**1**	0.05	360
10	1,7-octadiene	**2**	0.05	2000
11	diallyldiphenylsilane	**2**	0.05	480
12	*tert*-butyl *N*,*N*-diallylcarbamate	**2**	0.05	560
13	DEDAM	**3**	0.006	500
14	1,7-octadiene	**3**	0.006	3200
15	diallyldiphenylsilane	**3**	0.012	170
16	*tert*-butyl *N*,*N*-diallylcarbamate	**3**	0.012	80
17	DEDAM	**4**	0.05	280
18	1,7-octadiene	**4**	0.05	960
19	diallyldiphenylsilane	**4**	0.05	80
20	*tert*-butyl *N*,*N*-diallylcarbamate	**4**	0.05	300
21	diethyl bis(2-methallylmalonate)	**1**	0.05	10
22	diethyl bis(2-methallylmalonate)	**2**	0.05	4
23	styrene	**1**	0.1	900
24	styrene	**2**	0.1	970
25	*n*-butyl acrylate	**1**	2	50
26	*n*-butyl acrylate	**2**	2	50
27	ethyl acrylate	**1**	2	50
28	ethyl acrylate	**2**	2	50
29	acrylic acid	**1**	2	0
30	acrylic acid	**2**	2	0
31	acrylonitrile	**1**	2	0
32	acrylonitrile	**2**	2	0

H = $[RuCl_2(IMesH_2)\{=CH\text{-}2\text{-}(2\text{-}PrO\text{-}C_6H_4)\}]$, **5** = $[Ru(CF_3COO)_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}C_6H_4)\}]$.

Excellent activity with TONs of around 2000 was observed for 1,7-octadiene with **1** and **2**, which clearly rival the reactivity of both **H** and **5**. For diallyldiphenylsilane moderate activity (TON = 40) was observed with **1**, but the reactivity of **2** exceeded those of **H** and **5**. For *tert*-butyl *N*,*N*-diallylcarbamate (Table 5, entries 3, 6, 9, and 12) comparable low reactivities (TON = 360 and 560) were found for **1** and **2**, respectively, which compare to TON = 1900 and 2000 for **H** and **5**, respectively.

Supported and unsupported Ru-$IMesH_2$- and Ru-$MesH_2$-derived metathesis catalysts have been reported to exhibit good reactivity in CM of electron-poor substrates and in reactions involving the formation of tetrasubstituted alkenes.[41,47,71,73–75] We therefore investigated the reactivity of our new catalysts for these kinds of substrates. The reactivity of both **1** and **2** for diethyl bis(2-methallylmalonate) was poor (Table 5, entries 21 and 22). In view of the high reactivity of both catalysts for other substrates, we tentatively attribute this to steric effects. However, the high reactivity of **1** and **2** in metathesis reactions involving electron-rich alkenes and their low reactivity for disubstituted and electron-poor alkenes offers in principle access to selective metathesis reactions with molecules containing both types of alkene. Finally, both catalysts showed significant reactivity for electron-poor substrates such as styrene, *n*-butyl acrylate, and ethyl acrylate (Table 5, entries 23–28). Disappointingly, no reaction was observed with acrylic acid and acrylonitrile (Table 5, entries 29–32).

Reactivity in ring-opening cross-metathesis: Ring-opening cross-metathesis (ROCM) reactions were carried out with 7-oxanorborn-5-ene derivatives. As shown in Table 6 (entries 1–8), quantitative yields were obtained throughout with 2 mol % of either **1** or **2** at room temperature, which thus rival and in most cases exceed those reported in the literature, including those for **H** and **5**.[53,76]

Reactivity in enyne metathesis and cyclopolymerization of 1,6-heptadiynes: The catalytic activity of **1** and **2** in enyne metathesis reactions was tested by investigating the reaction of diethyl dipropargylmalonate (DEDPM) with allyltrimethylsilane. With 10 mol % of **1**, only moderate yields (69 %) of the desired compound were obtained (Table 6, entry 9). This is a direct consequence of the high reactivity of **1**, which is capable of oligomerizing DEDPM. When the more reactive catalyst **2** was used, the solution turned deep purple and only 3 % of the desired product was formed (Table 6, entry 10). In fact, **2** in particular is highly active in the polymerization of DEDPM even at room temperature to form poly(DEDPM) consisting of 95 % five-membered rings, that is, poly(cyclopent-1-enevinylene)s, and 5 % of six-membered rings, that is, poly(cyclohex-1-ene-3-methylidene)s, as evidenced by the two different chemical shifts (δ = 171.6 and 170.5 ppm, respectively) of the carbonyl carbon atoms of the two repeat units in the ^{13}C NMR spectrum (Figures 3 and 4).[77]

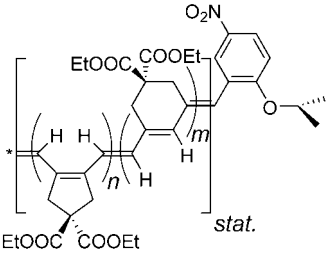
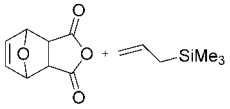
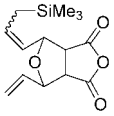
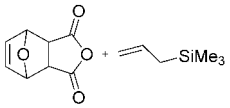
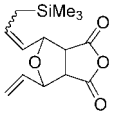
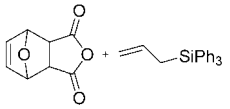
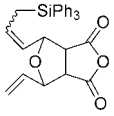
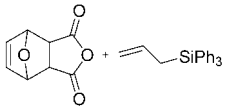
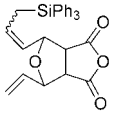
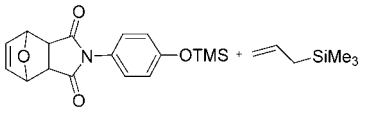
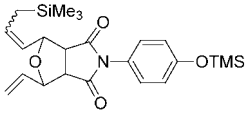
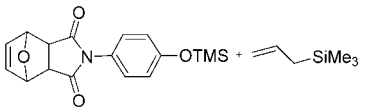
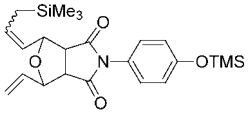
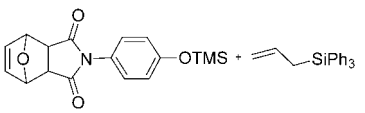
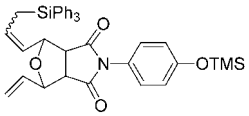
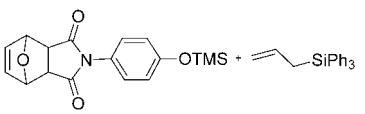
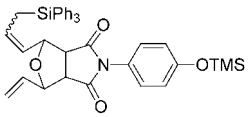
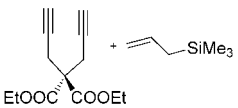
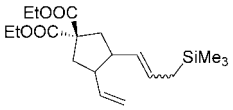
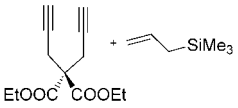
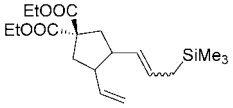


Figure 3. Structure of poly(DEDPM) (*n*:*m* = 95:5).

Table 6. Enyne and ring-opening cross-metathesis reactions with **1** and **2**.

Entry	Reactants	Product	Conditions[a]	Yield [%]
1			**1**, 2 mol %	100
2			**2**, 2 mol %	100
3			**1**, 2 mol %	100
4			**2**, 2 mol %	100
5			**1**, 2 mol %	100
6			**2**, 2 mol %	100
7			**1**, 2 mol %	100
8			**2**, 2 mol %	100
9			**1**, 10 mol %	69 + oligomer
10			**2**, 10 mol %	3 + polymer

[a] Reaction conditions: $CDCl_3$, 12 h, room temperature.

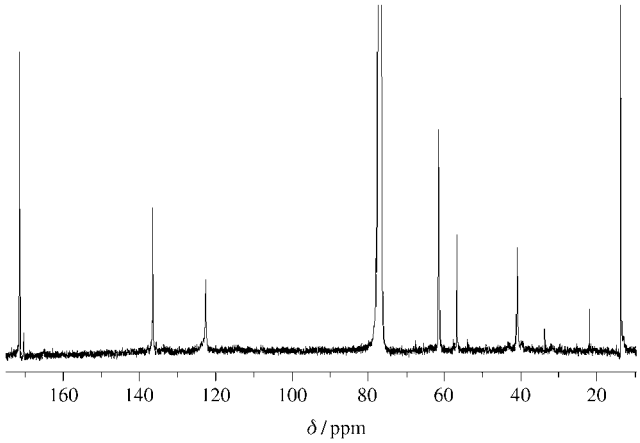


Figure 4. ^{13}C NMR spectrum of poly(DEDPM) in $CDCl_3$ prepared by the action of **2**.

Unlike with other Ru-based metathesis catalysts,[54,57] the polymerization does not proceed in a living[78] manner: it yields poly(DEDPM) with $M_n = 20000$ and a PDI of 1.9–2.3.

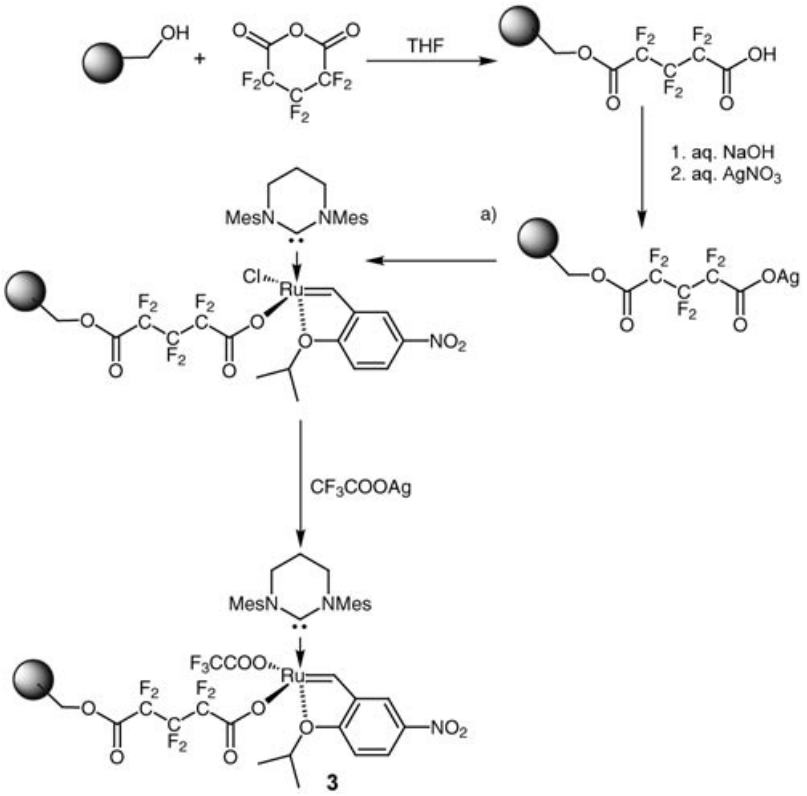
In terms of stability, both **1** and **2** behave similar to **H** and **5**. Thus, they may be purified by chromatography on silica after synthesis or after metathesis reactions. When reactions are performed with low catalyst loadings (< 0.05 mol %), no catalyst can be recycled.

Synthesis of immobilized versions of 2: For several reasons, demand for supported metathesis catalysts is increasing.[63–68,79,80] First, contamination of products with metal ions and/or ligands must be low, particularly in compounds relevant to pharmaceutical chemistry. Second, since modern metathesis catalysts significantly add to the total costs of a product, regeneration and/or reuse are highly desirable.

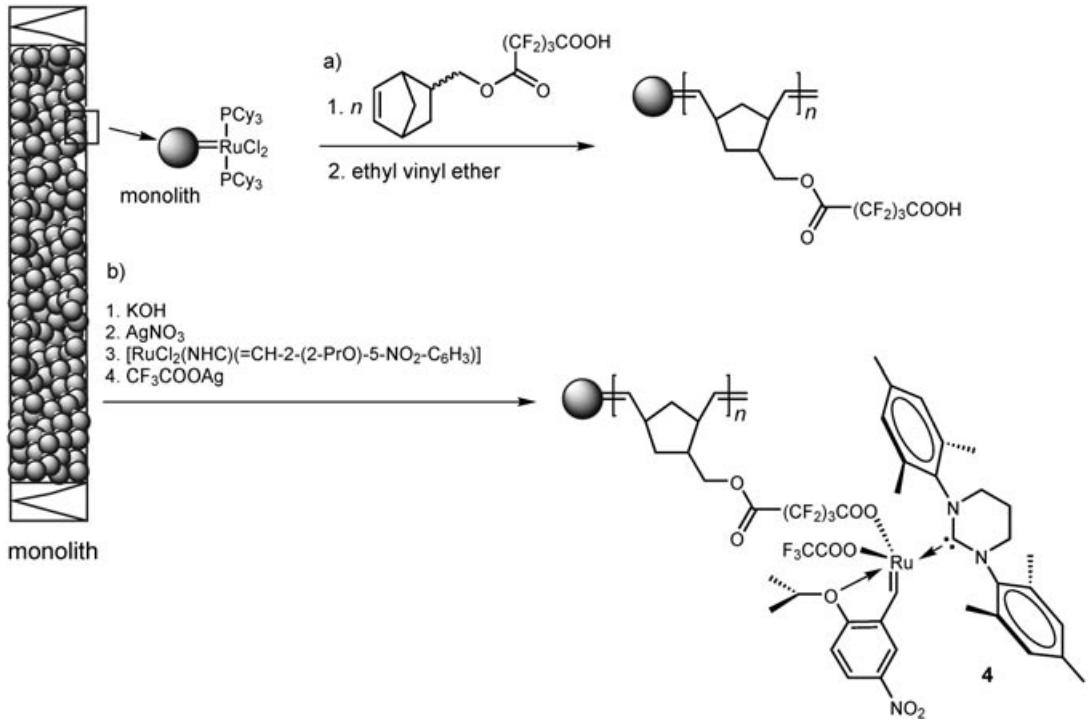
Third, supported catalysts are suitable for high-throughput techniques and continuous flow reactors. Therefore, the key issues for supported metathesis catalysts are 1) preservation of the activity and reaction rates of the parent homogeneous system, 2) ease of catalyst separation, 3) (multiple) catalyst recycling, and 4) metal- and contaminant-free products.

In a first step, a hydroxymethyl-Merrifield resin (PS-DVB-CH_2OH, 1.1 mmol-$CH_2OH\,g^{-1}$) was treated with perfluoroglutaric anhydride by following a procedure published by Nieczypor et al.[53,81] Deprotonation and formation of the silver salt were accomplished by reaction with aqueous sodium hydroxide followed by treatment with $AgNO_3$. Complex **1** was dissolved in THF and added to the polymer-bound silver salt. By this approach, intermediary (polymer–$CH_2OCOCF_2CF_2CF_2COO$)RuCl(NHC)(=CH-2-(2-PrO)-5-NO_2–C_6H_3) was obtained. The second chloro ligand was allowed to react with CF_3COOAg to yield (polymer–$CH_2OCOCF_2CF_2CF_2COO$)Ru(CF_3COO)(NHC)(=CH-2-(2-PrO)-5-NO_2-C_6H_3) (**3**) as a brown powder (Scheme 2). A catalyst loading of $10\,mg\,g^{-1}$ (1%) was determined for **3** by means of ICP-OES.

As an alternative to the Merrifield support, a monolithic support was synthesized by ring-opening-metathesis poly-



Scheme 2. Synthesis of hydroxymethyl-Merrifield resin supported catalyst **3**. a) [$RuCl_2$(NHC)(CH-2-(2-PrO)-5-NO_2-C_6H_3)], THF.



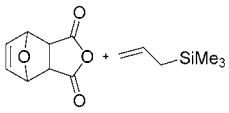
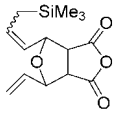
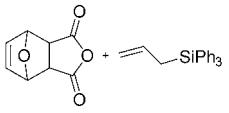
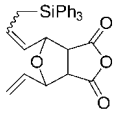
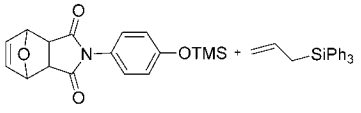
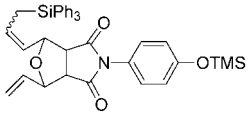
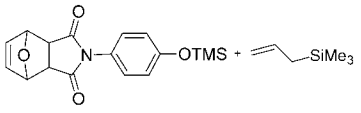
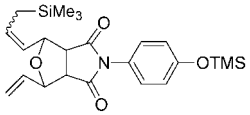
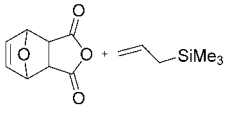
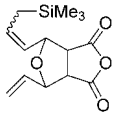
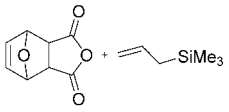
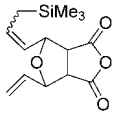
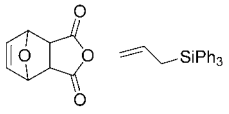
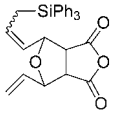
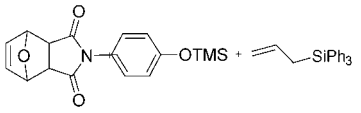
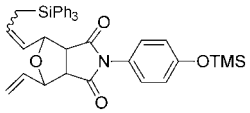
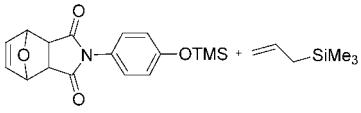
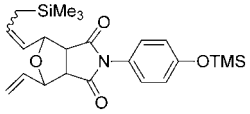
Scheme 3. Synthesis of the monolith-supported catalyst **4**.

merization (ROMP) of norborn-2-ene (NBE) and (NBE-$CH_2O)_3SiCH_3$ in a suitable mixture of porogens with first-generation Grubbs catalyst $[RuCl_2(PCy_3)_2(=CHPh)]$ according to published procedures.[56,58,59,82] Since the catalyst remains active on the inner surface of the monolith after rod formation is complete, it was used for grafting of the perfluoroglutaric ligand norborn-5-ene-2-ylmethyl hexafluoroglutarate (Scheme 3). The initiator was removed by extensive flushing with ethyl vinyl ether, which resulted in a Ru-free support. After deprotonation of the carboxylic acid groups of the graft polymer with aqueous KOH, the potassium salt was transformed into the corresponding silver salt with aqueous $AgNO_3$. After reaction with catalyst **1**, CF_3COOAg was added to substitute the second chloro ligand. By following this procedure, 25 mg g^{-1} (i.e., 66 % of the original amount of catalyst **1** used) was bound to the support. Unconsumed catalyst was recovered quantitatively as **2**.

Disk-shaped monolithic systems applicable to high-throughput screening, similar to the silica-based systems described by Hoveyda et al.,[83] were obtained by drying and subsequent cutting of the parent monolith into pieces of 1 cm in height.

RCM and ROCM experiments with supported catalysts 3 and 4: For the purpose of comparison, DEDAM, 1,7-octadiene, diallyldiphenylsilane, and *tert*-butyl *N*,*N*-diallylcarbamate were used in heterogeneous RCM reactions to benchmark heterogeneous catalysts **3** and **4** (Table 5, entries 13–16 and 17–20, respectively). Excellent reactivity was observed for the Merrifield-supported version of **2** with TONs in the range of 80–3200. The monolithic disk immobilized catalyst showed somewhat reduced TONs in the range of 80–960. This clearly stems from the fact that reactions within these disks were not stirred and therefore depended on diffusion of the substrates to the catalytic site. Nevertheless, the reactivity observed with these systems definitely justifies the use of such monolith-supported catalysts in high-throughput screening, where the disk serves simultaneously as support, reaction vessel, and filtration unit and can in principle be di-

Table 7. Ring-opening cross-metathesis reactions with **3** and **4**.

Entry	Reactants	Product	Conditions[a]	Yield [%]
1			**3**, 2 mol %	100
2			**3**, 2 mol %	99
3			**3**, 2 mol %	71
4			**3**, 0.24 mol %	94
5			**3**, 0.24 mol %	76
6			**4**, 2 mol %	81
7			**4**, 2 mol %	89
8			**4**, 2 mol %	83
9			**4**, 2 mol %	89

[a] Reaction conditions: entries 1–9: $CDCl_3$, 12 h, room temperature.

rectly used in combination with commercially available machines. In ROCM, excellent yields were achieved at room temperature with 2 mol% of **3** (Table 7, entries 1–3). Even when only 0.24 mol% of **3** was used, yields were in the range of 76–94% (Table 7, entries 4 and 5). Again, yields obtained with **2** immobilized on monolithic disks were somewhat lower (81–89%, entries 6–9, Table 7) compared to the homogenous analogue, yet can still be regarded as good.

Finally, in terms of product purity, it is noteworthy that metal leaching from the supported systems **3** and **4** was low. Thus, the typical Ru contamination of the products was in the range of 0.14 ppm (0.000014%), as evidenced by ICP-OES.

Conclusion

A new family of metathesis catalysts based on tetrahydropyrimidin-2-ylidenes has been synthesized and immobilized on different polymeric supports. With the supported systems, access to both slurry-type reactions and high-throughput screening methodologies was gained. Both the homogeneous and supported systems are highly active in various metathesis reactions including ring-closing, cross-, ring-opening cross-, and enyne metathesis. In addition, they showed activity in the cyclopolymerization of 1,6-heptadiynes such as diethyl dipropargylmalonate. The restrictions in the search for even more active metathesis catalysts clearly become obvious. Similar to other highly active catalytic systems, the new systems presented here are no longer allrounders. While they became active enough to promote classical RCM with high TON and reactions such as cyclopolymerizations dominated so far by molybdenum catalysts, they can no longer be used for related chemistry such as enyne metathesis. Ruthenium-based metathesis chemistry has thus reached the point where particular catalysts will be designed for distinct synthetic problems.

Experimental Section

General: All experiments involving transition metals were performed under a nitrogen atmosphere in an MBraun glove box or by standard Schlenk techniques. Reagent-grade THF, toluene, hexane, and pentane were distilled from sodium benzophenone ketyl under argon. Dichloromethane and [D_1]chloroform were distilled from calcium hydride under argon. 1,3-Dimesityl-3,4,5,6-tetrahydropyrimidin-1-ium tetrafluoroborate was synthesized according to published procedures.[60] All other reagents were commercially available and used as received. Column chromatography was performed with silica gel 60 (220–440 mesh, Fluka, Buchs, Switzerland). NMR spectra were recorded at 25°C on a Bruker Spektrospin 300 at 300.13 MHz for proton and at 75.47 MHz for carbon in the indicated solvent and referenced to the solvent peaks ($CDCl_3$: $\delta = 7.24$ ppm, 77.0 ppm). FTIR spectra were recorded on a Bruker Vector 22 using ATR technology. GC-MS measurements were carried out on a Shimadzu GCMS QP 5050 using a SPB-5 fused silica column (30 m × 0.25 mm × 25 μm film thickness) and helium as carrier gas. Elemental analyses were performed at the Institute of Physical Chemistry, University of Vienna, Austria, and at the Mikroanalytisches Labor, Technische Universität München, Garching, Germany. Further Instrumentation is described elsewhere.[53,60] Yields for RCM and enyne experiments were determined by GC with the corresponding diene compound as internal standard, with the exception of 1,7-octadiene, for which yields were determined by ^{1}H NMR in $CDCl_3$. Yields in ring-opening cross-metathesis experiments were determined by ^{1}H NMR in $CDCl_3$.

[$RuCl_2$(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene){=CH-2-(2-PrO)-5-NO_2-C_6H_3}]: Potassium *tert*-amylate (22 mg, 0.17 mmol) was added to a suspension of of 1,3-dimesityl-3,4,5,6-tetrahydropyrimidinium tetrafluoroborate (75 mg, 0.19 mmol) in *n*-hexane (5 mL) and the resulting slightly turbid, yellow solution was stirred at room temperature for 1 h. [$RuCl_2(PCy_3)_2$(=CHC_6H_5)] (123 mg, 0.15 mmol) was added as a solid and the reaction mixture was heated to reflux for 30 min. A solution of 2-(2-propoxy)-5-nitrostyrene (34 mg, 0.16 mmol) in CH_2Cl_2 (5 mL) and CuCl (16 mg, 0.16 mmol) were added to the brown-pink suspension at room temperature. The resulting mixture was stirred at room temperature for 30 min and then concentrated in vacuo. The resultant material was purified by column chromatography using silica 60 and diethyl ether:pentane (50:50). Evaporation of the solvent and crystallization from CH_2Cl_2/pentane afforded green crystals (51 mg, 0.074 mmol, 50%). IR (ATR mode): $\tilde{\nu} = 2923$ (m), 2851 (w), 1603 (w), 1518 (w), 1484 (m), 1440 (m), 1336 (s), 1303 (m), 1295 (m), 1258 (s), 1090 (s), 1026 (s), 798 (s), 744 cm^{-1} (m); ^{1}H NMR (CD_3Cl) $\delta = 16.38$ (s, 1H; H-17), 8.43 (dd, $J =$ 12.08, 3.8 Hz, 1H; H-21), 7.88 (d, $J = 3.8$ Hz, 1H; H-19), 7.14 (s, 2H; H-13, H-15), 7.04 (s, 2H; H-7, H-9), 6.78 (d, $J = 12.68$, 1H; H-22), 4.79 (m, 1H; H-24), 3.67 (m, 4H; H-2, H-4), 2.56, 2.33, 2.32 (3×s, 20H; H-3, H-061, H-081, H-101, H-121, H-141, H-161), 1.07 ppm (d, $J = 8.28$, 6H; H-25, H-26); ^{13}C NMR (CD_3Cl): $\delta = 298.0$ (C17), 200.1 (C1), 155.5 (C23), 145.9 (C18), 144.3 (C20), 143.0 (C19), 141.6 (C21), 139.8 (C22), 138.8 (C11), 137.2 (C5), 136.7 (C12), 130.1 (C6), 129.6 (C13), 124.2 (C7), 117.7 (C14), 112.8 (C8), 65.8 (C24), 49.9 (C2, C4), 21.7 (C3), 21.4, 21.1, 21.0 (C121, C141, C161), 18.3 ppm (C25, C26). Elemental analysis (%) calcd for $C_{32}H_{39}Cl_2N_3O_3Ru$ (685.63): C 56.06, H 5.73, N 6.13; found: C 56.27, H 5.66, N 5.73.

[$Ru(CF_3COO)_2$(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene){= CH-2-(2-PrO)-5-NO_2-C_6H_3}]: Compound **1** (150 mg, 0.22 mmol) was dissolved in CH_2Cl_2 (5 mL), and a solution of CF_3COOAg (2 equiv, 97 mg, 0.44 mmol) in THF (5 mL) was slowly added to the stirred solution. Stirring was continued for 2 h and formation of a precipitate was observed. The precipitate was filtered off and the solution was evaporated to dryness. It was redissolved in CH_2Cl_2, flashed over a pad of silica gel (5 cm), and evaporated to dryness, yielding **2** as a light green powder (123 mg, 0.15 mmol, 68%). Crystals suitable for X-ray analysis were obtained by layering pentane over a solution of **2** in CH_2Cl_2. IR (ATR mode): $\tilde{\nu} =$ 2922 (w), 1687 (s), 1606 (w), 1519 (w), 1495 (m), 1476 (w), 1443 (w), 1397 (m), 1344 (m), 1312 (m), 1299 (m), 1276 (s), 1180 (s), 1128 (s), 1091 (s), 781 (s), 722 cm^{-1} (s); ^{1}H NMR (CD_3Cl): $\delta = 16.77$ (s, 1H; H-17), 8.27 (dd, $J = 6.21$, 2.85 Hz, 1H; H-21), 7.90 (d, $J = 2.4$ Hz, 1H; H-19), 7.19 (s, 4H; H-7, H-9, H-13, H-15), 6.65 (d, $J = 9.06$ Hz, 1H; H-22), 4.57 (m, 1H; H-24), 3.61 (t, $J = 5.25$, 4H; H-2, H-4), 2.58, 2.45, 2.42, 2.00 (4×s, 18H; H-061, H-081, H-101, H-121, H-141, H-161), 2.30 (m, 2H; H-3), 0.76 ppm (d, $J = 6.18$, 6H; H-25, H-26); ^{13}C NMR (CD_3Cl): $\delta = 315.0$ (C17), 198.7 (C1), 156.6 (C23), 144.2 (C18), 143.3 (C20), 143.2 (C19), 142.3 (C21), 140.9 (C22), 139.2 (C11), 136.4 (C5), 134.2 (C12), 130.3 (C6), 130.2 (C13), 125.1 (C7), 118.8 (C14), 115.8 (C28), 112.0 (C8), 110.3 (C27), 65.9(C24), 49.8, 49.5 (C2, C4), 21.3 (C3), 21.1, 21.0, 20.2 (C121, C141, C161), 19.2 ppm (C25, C26). For atom numbering, see Figure 2. Elemental analysis (%) calcd for $C_{36}H_{39}F_6N_3O_7Ru$ (840.77): C 51.43, H 4.68, N 5.00; found: C 51.42, H 4.83, N 4.82.

Heterogenization on hydroxymethylpolystyrene, generation of (polymer-$CH_2OCOCF_2CF_2CF_2COO$)(CF_3CO_2)Ru(NHC){=CH-2-(2-PrO)-5-$NO_2C_6H_3$} (3): PS-CH_2−OH (2.00 g, 1% cross-linked with divinylbenzene, mesh, 1.1 mmol OH g^{-1}) was suspended in dry THF (40 mL), and perfluoroglutaric anhydride (1 equiv, 488 mg, 2.2 mmol) was added. Stirring was continued for 3 h, then the product was collected by filtration and washed three times with THF. It was dried in vacuo to give a slightly yellow solid (2.35 g). FTIR (ATR mode): $\tilde{\nu} = 3025$ (br), 2920 (br), 1773 (vs), 1601 (br), 1492 (s), 1451 (s), 1241 (w), 1175 (vs), 1141 (vs), 1046 (vs), 910 (s), 871 (w), 822 (w), 751 (s), 697 cm^{-1} (vs). The solid was resuspended in THF (20 mL), and an excess of NaOH (181 mg dissolved in 40 mL of water) was added. The mixture was stirred for 3 h. The precipitate was filtered off, washed three times with water, and finally suspended in water (25 mL). $AgNO_3$ (1.2 equiv, 448 mg, 2.64 mmol) in water

(15 mL) was added. Stirring was continued for 2 h, and the product was filtered off and washed three times each with water, Et_2O, and pentane. Drying in vacuo gave a white solid (1.94 g). FTIR (ATR mode): $\tilde{\nu}$ = 3058 (br), 3024 (br), 2918 (br), 2849 (br), 2324 (br), 1868 (w), 1773 (w), 1511 (w), 1492 (s), 1451 (s), 1373 (w), 1311 (w), 1178 (w), 1154 (w), 1069 (w), 1028 (w), 945 (w), 906 (w), 836 (w), 817 (w), 754 (s), 696 cm^{-1} (vs). The use of excess NaOH leads to partial hydrolysis of the ester. If high catalyst loadings are required, equimolar amounts of NaOH or NH_3 should be used.

This solid (0.8 g) was resuspended in THF (25 mL), and **1** (70 mg, 0.102 mmol) was added. Stirring was continued for 2 h. Intermediary polymer-$CH_2OCOCF_2CF_2CF_2COO$)RuCl(NHC){=CH-2-(2-PrO)-5-NO_2–C_6H_3} was filtered off, washed with THF, and dried in vacuo to yield an off-white powder. FTIR (ATR mode): $\tilde{\nu}$ = 3058 (w), 3024 (w), 2919 (br), 2849 (w), 1601 (w), 1492 (s), 1451 (s), 1421 (w), 1179 (br), 1153 (w), 1053 (w), 1028 (w), 906 (w), 822 (w), 750 (s), 697 cm^{-1} (vs).

CF_3COOAg (1 equiv, 23 mg, 0.10 mmol) was dissolved in THF (2 mL) and the solution was added to intermediary polymer-CH_2OC-$OCF_2CF_2CF_2COO$)RuCl(NHC){=CH-2-(2-PrO)-5-NO_2–C_6H_3} suspended in THF (10 mL), and the mixture was stirred for 90 min. Extensive washing with THF and drying in vacuo gave **3** as a brown powder (0.77 g). Ru content 0.012 mmol g^{-1}, corresponding to 10.1 mg of **2** per gram (1.01 % catalyst loading). FTIR (ATR mode): $\tilde{\nu}$ = 3058 (w), 3024 (w), 2919 (br), 2849 (w), 2360 (w), 1870 (w), 1774 (w), 1655 (w), 1600 (w), 1582 (w), 1492 (s), 1451 (s), 1421 (w), 1364 (w), 1285 (w), 1065 (w), 1028 (w), 906 (w), 837 (w), 750 (s), 697 cm^{-1} (vs).

Synthesis of monolith-supported catalyst 4: The monolithic support was synthesized according to published procedures[58,59,82] from norborn-2-ene (NBE, 1.0 g, 10.6 mmol), (NBE-CH_2O)$_3SiCH_3$ (1.0 g, 2.42 mmol), 2-propanol (2.9 mL), toluene (0.8 mL), and [$RuCl_2(PCy_3)_2$(CHPh)] (20 mg). Column dimensions: 60 × 8 mm i.d., V = 5 mL. The monolith was washed with dry toluene (5 mL). Argon was passed through the monolith for 30 min to elute the solvent. Hexafluoroglutaric anhydride (0.40 mL, 2.98 mmol) was added dropwise to a solution of norborn-5-ene-2-methanol (0.30 mL, 2.48 mmol) in 6 mL of freshly distilled dichloromethane. The mixture was stirred for 1 h in a Schlenk tube under argon at room temperature. A 3 mL portion of this solution was introduced into the monolith, which was sealed and kept at 40 °C overnight. Then the monolith was flushed with ethyl vinyl ether (40 vol % in THF) to remove the initiator, and then with water, each for 30 min. An aqueous solution of KOH (10 mL, 0.05 M) was passed through the monolith at a flow rate of 0.1 mL min^{-1}, followed by water until the washings were neutral. An aqueous solution of $AgNO_3$ (3.0 mL, 0.5 M) was introduced into the monolith, then the supports were washed with water until the effluent was free of silver, as checked with aqueous sodium iodide solution. The monolith was then flushed with dry THF. **1** (60 mg, 0.087 mmol) was dissolved in freshly distilled CH_2Cl_2 (3 mL), and the solution was introduced into the monolith, which was then kept sealed at room temperature for 1 h. Then silver trifluoroacetate (21.2 mg, 0.096 mmol) was dissolved in freshly distilled THF (3 mL), and the solution was introduced into the monolith, which was again kept sealed at room temperature for 1 h. Finally, the monolith was flushed with freshly distilled THF until the effluent was colorless and dried in vacuo. Ru loading: 0.03 mmol Ru per gram corresponding to 25 mg of **2** per gram monolith. The monolith was chopped into pieces of approximately 1 cm in height and put into syringes for solid-phase-extraction (SPE) (ICT, Isolute, Austria).

Ring-opening cross metathesis and enyne metathesis reactions catalyzed by 1–3: The following procedure is representative for all homogeneous and slurry-type reactions: DEDAM (500 mg, 2.08 mmol) was dissolved in CH_2Cl_2 (2 mL) and the catalyst (homogeneous or supported, 0.006–10 mol %, as indicated in Tables 5–7) was added. The mixture was heated to the temperature indicated in Tables 5–7 and stirred for the indicated time. After removal of the catalyst by filtration, yields were determined by GC-MS and ^1H NMR spectroscopy (in $CDCl_3$).

Ring-opening cross metathesis catalyzed by monolith-supported catalyst 4: The monolith was removed from the SPE column and chopped into pieces of 140–200 mg (approximately 1 cm in length). Syringes for SPE were used as encasements for these pieces. The following procedure is representative: the monolithic disk (0.147 g, 4.41 μmol catalyst) was treated with 4.24 g of a 50 wt % solution of diethyl diallylmalonate (DEDAM) in CH_2Cl_2. Other monolithic disks were treated in a similar way with the monomers indicated in Tables 5–7. The reaction vessels were removed from the glove box and reactions were allowed to proceed for the time given there. Finally, the reaction mixtures were eluted with CH_2Cl_2 or $CDCl_3$. Yields were determined by GC-MS and ^1H NMR (in $CDCl_3$).

Leaching of the support: Aqua regia (3.0 mL) was added to the combined effluents from which the solvent had been removed. The mixture was placed in high-pressure Teflon tubes and leaching was carried out under Microwave conditions (50, 600, and 450 W pulses, t = 32 min). After cooling to room temperature, the mixture was filtered and water was added up to a volume of 10.00 mL.

Ruthenium analysis: Ru was anlyzed by ICP-OES (λ = 240.272 nm, ion line). The background was measured at λ = 240.287 and λ = 240.257 nm. Standardization was carried out with aqueous Ru standards containing 0 and 4 ppm of Ru.

X-ray structure determination of 1 and 2: Data were collected on a Nonius Kappa CCD equipped with graphite-monochromatized $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) and a nominal crystal to area detector distance of 36 mm. The structures were solved with direct methods (SHELXS86) and refined against F^2 using SHELX97.[84] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined on calculated positions, except at C(17), which was located and refined with isotropic displacement parameters for **1** and **2**.

CCDC-233916 and CCDC-233917 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[1] W. A. Herrmann, C. Köcher, *Angew. Chem.* **1997**, *109*, 2256–2282; *Angew. Chem. Int. Ed.* **1997**, *36*, 2162–2187.
[2] T. Weskamp, V. P. W. Böhm, W. A. Herrmann, *J. Organomet. Chem.* **2000**, *600*, 12–22.
[3] M. Regitz, *Angew. Chem.* **1996**, *108*, 791–794; *Angew. Chem. Int. Ed.* **1996**, *35*, 725–728.
[4] W. A. Herrmann, M. Elison, J. Fischer, C. Köcher, G. R. J. Artus, *Chem. Eur. J.* **1996**, *2*, 772–780.
[5] J. Huang, E. D. Stevens, S. P. Nolan, J. L. Petersen, *J. Am. Chem. Soc.* **1999**, *121*, 2674–2678.
[6] J. Huang, H.-J. Schanz, E. D. Stevens, S. P. Nolan, *Organometallics* **1999**, *18*, 5375–5380.
[7] D. S. McGuinness, K. J. Cavell, B. W. Skelton, A. H. White, *Organometallics* **1999**, *18*, 1596–1605.
[8] D. S. McGuinness, K. J. Cavell, *Organometallics* **2000**, *19*, 741–748.
[9] M. R. Buchmeiser, *Chem. Rev.* **2000**, *100*, 1565–1604.
[10] R. R. Schrock in *Ring-Opening Polymerization* (Ed.: D. J. Brunelle), Hanser, Munich, **1993**, p. 129.
[11] R. R. Schrock, *Polyhedron* **1995**, *14*, 3177–3195.
[12] R. R. Schrock, *J. Chem. Soc. Dalton Trans.* **2001**, 2541–2550.
[13] R. R. Schrock, *Chem. Rev.* **2002**, *102*, 14–179.
[14] R. H. Grubbs, W. Tumas, *Science* **1989**, *243*, 907.
[15] R. H. Grubbs, *J. Macromol. Sci. Pure Appl. Chem.* **1994**, *A31*, 1829–1833.
[16] *Handbook of Metathesis*, *Vols. 1–3* (Ed.: R. H. Grubbs), Wiley-VCH, Weinheim, **2003**.
[17] A. Fürstner, *Angew. Chem.* **2000**, *112*, 3140–3172; *Angew. Chem. Int. Ed.* **2000**, *39*, 3012–3043.
[18] M. Schuster, S. Blechert, *Angew. Chem.* **1997**, *109*, 2124–2144; *Angew. Chem. Int. Ed.* **1997**, *36*, 2036–2056.
[19] T. J. Seiders, D. W. Ward, R. H. Grubbs, *Org. Lett.* **2001**, *3*, 3225–3228.

[20] J. J. Van Veldhuizen, S. B. Garber, J. S. Kingsbury, A. H. Hoveyda, *J. Am. Chem. Soc.* **2002**, *124*, 4954–4955.
[21] S. J. Dolman, R. R. Schrock, A. H. Hoveyda, *Org. Lett.* **2003**, *5*, 4899–4902.
[22] S. J. Dolman, E. S. Sattely, A. H. Hoveyda, R. R. Schrock, *J. Am. Chem. Soc.* **2002**, *124*, 6991–6997.
[23] W. C. P. Tsang, J. A. Jernelius, G. A. Cortez, G. S. Weatherhead, R. R. Schrock, A. H. Hoveyda, *J. Am. Chem. Soc.* **2003**, *125*, 2591–2596.
[24] X. Teng, D. R. Cefalo, R. R. Schrock, A. H. Hoveyda, *J. Am. Chem. Soc.* **2002**, *124*, 10779–10784.
[25] A. F. Kiely, J. A. Jernelius, R. R. Schrock, A. H. Hoveyda, *J. Am. Chem. Soc.* **2002**, *124*, 2868–2869.
[26] J. B. Alexander, R. R. Schrock, W. M. Davies, K. C. Hultzsch, A. H. Hoveyda, J. H. Houser, *Organometallics* **2000**, *19*, 3700–3715.
[27] D. S. La, E. S. Sattely, J. G. Ford, R. R. Schrock, A. H. Hoveyda, *J. Am. Chem. Soc.* **2001**, *123*, 7767–7778.
[28] G. S. Weatherhead, J. H. Houser, J. G. Ford, J. Y. Jamieson, R. R. Schrock, A. H. Hoveyda, *Tetrahedron Lett.* **2000**, *41*, 9553–9559.
[29] S. L. Aeilts, D. R. Cefalo, P. J. Bonitatebus, J. H. Houser, A. H. Hoveyda, R. R. Schrock, *Angew. Chem.* **2001**, *113*, 1500–1504; *Angew. Chem. Int. Ed.* **2001**, *40*, 1452–1456.
[30] D. R. Cefalo, A. F. Kiely, M. Wuchrer, J. Y. Jamieson, R. R. Schrock, A. H. Hoveyda, *J. Am. Chem. Soc.* **2001**, *123*, 3139–3140.
[31] S. S. Zhu, D. R. Cefalo, D. S. La, J. Y. Jamieson, W. M. Davies, A. H. Hoveyda, R. R. Schrock, *J. Am. Chem. Soc.* **1999**, *121*, 8251–8259.
[32] D. S. La, J. B. Alexander, D. R. Cefalo, D. D. Graf, A. H. Hoveyda, R. R. Schrock, *J. Am. Chem. Soc.* **1998**, *120*, 9720–9721.
[33] J. B. Alexander, D. S. La, D. R. Cefalo, A. H. Hoveyda, R. R. Schrock, *J. Am. Chem. Soc.* **1998**, *120*, 4041–4042.
[34] K. Öfele, *J. Organomet. Chem.* **1968**, *12*, P42-P43.
[35] H.-W. Wanzlick, *Angew. Chem.* **1962**, *74*, 129–134; *Angew. Chem. Int. Ed.* **1962**, *1*, 75–80.
[36] H. W. Wanzlick, H. J. Schönherr, *Angew. Chem.* **1968**, *80*, 154–155; *Angew. Chem. Int. Ed.* **1968**, *7*, 141–142.
[37] W. A. Herrmann, M. Elison, J. Fischer, C. Köcher, G. R. J. Artus, *Angew. Chem.* **1995**, *107*, 2602–2605; *Angew. Chem. Int. Ed.* **1995**, *34*, 2371–2374.
[38] T. Weskamp, F. J. Kohl, W. A. Herrmann, *J. Organomet. Chem.* **1999**, *582*, 362–365.
[39] T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich, W. A. Herrmann, *Angew. Chem.* **1999**, *111*, 2573–2576; *Angew. Chem. Int. Ed.* **1999**, *38*, 2416–2419.
[40] U. Frenzel, T. Weskamp, F. J. Kohl, W. C. Schattenmann, O. Nuyken, W. A. Herrmann, *J. Organomet. Chem.* **1999**, *586*, 263–265.
[41] L. Ackermann, A. Fürstner, T. Weskamp, F. J. Kohl, W. A. Herrmann, *Tetrahedron Lett.* **1999**, *40*, 4787–4790.
[42] J. G. Hamilton, U. Frenzel, F. J. Kohl, T. Weskamp, J. J. Rooney, W. A. Herrmann, O. Nuyken, *J. Organomet. Chem.* **2000**, *606*, 8–12.
[43] W. Baratta, E. Herdtweck, W. A. Herrmann, P. Rigo, J. Schwarz, *Organometallics* **2002**, *21*, 2101–2106.
[44] C. W. Bielawski, R. H. Grubbs, *Angew. Chem.* **2000**, *112*, 3025–3028; *Angew. Chem. Int. Ed.* **2000**, *39*, 2903–2906.
[45] A. J. Arduengo III, H. V. Rasika Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530–5534.
[46] A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363.
[47] T. M. Trnka, R. H. Grubbs, *Acc. Chem. Res.* **2001**, *34*, 18–29.
[48] M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953–956.
[49] M. Scholl, T. M. Trnka, J. P. Morgan, R. H. Grubbs, *Tetrahedron Lett.* **1999**, *40*, 2247–2250.
[50] T. Weskamp, W. C. Schattenmann, M. Spiegler, W. A. Herrmann, *Angew. Chem.* **1998**, *110*, 2631–2633; *Angew. Chem. Int. Ed.* **1998**, *37*, 2490–2492.
[51] V. P. W. Böhm, C. W. K. Gstöttmayr, T. Weskamp, W. A. Herrmann, *J. Organomet. Chem.* **2000**, *595*, 186–190.
[52] M. Tafipolsky, W. Scherer, K. Öfele, G. Artus, B. Pedersen, W. A. Herrmann, G. S. McGrady, *J. Am. Chem. Soc.* **2002**, *124*, 5865–5880.
[53] J. O. Krause, K. Wurst, O. Nuyken, M. R. Buchmeiser, *Chem. Eur. J.* **2004**, *10*, 778–785.
[54] J. O. Krause, O. Nuyken, M. R. Buchmeiser, *Chem. Eur. J.* **2004**, *10*, 2029–2035.
[55] J. O. Krause, M. Mayr, S. Lubbad, O. Nuyken, M. R. Buchmeiser, *e-Polymers-conference papers section* **2003**, P_007.
[56] J. O. Krause, S. H. Lubbad, O. Nuyken, M. R. Buchmeiser, *Macromol. Rapid Commun.* **2003**, *24*, 875–878.
[57] J. O. Krause, M. T. Zarka, U. Anders, R. Weberskirch, O. Nuyken, M. R. Buchmeiser, *Angew. Chem.* **2003**, *115*, 6147–6151; *Angew. Chem. Int. Ed.* **2003**, *42*, 5965–5969.
[58] J. O. Krause, S. Lubbad, O. Nuyken, M. R. Buchmeiser, *Adv. Synth. Catal.* **2003**, *345*, 996–1004.
[59] J. O. Krause, S. Lubbad, M. Mayr, O. Nuyken, M. R. Buchmeiser, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2003**, *44*, 790–791.
[60] M. Mayr, K. Wurst, K.-H. Ongania, M. R. Buchmeiser, *Chem. Eur. J.* **2004**, *10*, 1256–1266.
[61] M. Mayr, K. Wurst, K.-H. Ongania, M. R. Buchmeiser, *Chem. Eur. J.* **2004**, *10*, 2622.
[62] M. Sakamoto, S. Okada, Y. Tsunogae, S. Ikeda, W. A. Herrmann, K. Öfele, *PCT Int. Appl.* WO 2003027079 **2003**.
[63] J. S. Kingsbury, A. H. Hoveyda in *Polymeric Materials in Organic Synthesis and Catalysis* (Ed.: M. R. Buchmeiser), Wiley-VCH, Weinheim, **2003**, pp. 467–502.
[64] A. H. Hoveyda, D. G. Gillingham, J. J. Van Veldhuizen, O. Kataoka, S. B. Garber, J. S. Kingsbury, J. P. A. Harrity, *Org. Biomol. Chem.* **2004**, *2*, 8–23.
[65] M. R. Buchmeiser, *New J. Chem.* **2004**, *28*, 549–557.
[66] S. Randl, N. Buschmann, S. J. Connon, S. Blechert, *Synlett* **2001**, 1547–1550.
[67] S. C. Schürer, S. Gessler, N. Buschmann, S. Blechert, *Angew. Chem.* **2000**, *112*, 4062–4065; *Angew. Chem. Int. Ed.* **2000**, *39*, 3898–3901.
[68] S. J. Connon, A. M. Dunne, S. Blechert, *Angew. Chem.* **2002**, *114*, 3989–3993; *Angew. Chem. Int. Ed.* **2002**, *41*, 3835–3838.
[69] K. Grela, M. Kim, *Eur. J. Org. Chem.* **2003**, 963–966.
[70] S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. Hoveyda, *J. Am. Chem. Soc.* **2000**, *122*, 8168–8179.
[71] J. S. Kingsbury, J. P. A. Harrity, P. J. Bonitatebus, Jr., A. H. Hoveyda, *J. Am. Chem. Soc.* **1999**, *121*, 791–799.
[72] K. Grela, S. Harutyuyan, A. Michrowska, *Angew. Chem.* **2002**, *114*, 4210–4212; *Angew. Chem. Int. Ed.* **2002**, *41*, 4038–4040.
[73] T. M. Trnka, M. W. Day, R. H. Grubbs, *Angew. Chem.* **2001**, *113*, 3549–3552; *Angew. Chem. Int. Ed.* **2001**, *40*, 3441–3444.
[74] Q. Yao, Y. Zhang, *J. Am. Chem. Soc.* **2004**, *126*, 74–75.
[75] Q. Yao, A. R. Motta, *Tetrahedron Lett.* **2004**, *45*, 2447–2451.
[76] M. F. Schneider, N. Lucas, J. Velder, S. Blechert, *Angew. Chem.* **1997**, *109*, 257–259; *Angew. Chem. Int. Ed.* **1997**, *36*, 257–259.
[77] H. H. Fox, M. O. Wolf, R. O'Dell, B. L. Lin, R. R. Schrock, M. S. Wrighton, *J. Am. Chem. Soc.* **1994**, *116*, 2827–2843.
[78] K. Matyjaszewski, *Macromolecules* **1993**, *26*, 1787–1788.
[79] M. Mayr, B. Mayr, M. R. Buchmeiser, *Des. Monomers Polym.* **2002**, *5*, 325–338.
[80] M. Mayr, B. Mayr, M. R. Buchmeiser in *Studies in Surface Science and Catalysis: Scientific Bases for the Preparation of Heterogeneous Catalysts, Vol. 143* (Eds.: E. Gaigneaux, D. E. DeVos, P. Grange, P. A. Jacobs, J. A. Martens, P. Ruiz, G. Poncelet), Elsvier, Amsterdam, **2002**, pp. 305–312.
[81] P. Nieczypor, W. Buchowicz, W. J. N. Meester, F. P. J. T. Rutjes, J. C. Mol, *Tetrahedron Lett.* **2001**, *42*, 7103–7105.
[82] M. Mayr, B. Mayr, M. R. Buchmeiser, *Angew. Chem.* **2001**, *113*, 3957–3960; *Angew. Chem. Int. Ed.* **2001**, *40*, 3839–3842.
[83] J. S. Kingsbury, S. B. Garber, J. M. Giftos, B. L. Gray, M. M. Okamoto, R. A. Farrer, J. T. Fourkas, A. H. Hoveyda, *Angew. Chem.* **2001**, *113*, 4381–4383; *Angew. Chem. Int. Ed.* **2001**, *40*, 4251–4256.
[84] G. M. Sheldrick, Program package SHELXTL V.5.1, Bruker Analytical X-ray Instruments Inc, Madison, USA **1997**.

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