Synthesis and Reactivity of Homogeneous and Heterogeneous Ruthenium-Based Metathesis Catalysts Containing Electron-Withdrawing Ligands

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Abstract: The synthesis and heterogenization of new Grubbs–Hoveyda type metathesis catalysts by chlorine exchange is described. Substitution of one or two chlorine ligands with trifluoroacetate and trifluoromethanesulfonate was accomplished by reaction of $[RuCl_2(=CH\text{-}o\text{-}iPr\text{-}O\text{-}C_6H_4)(IMesH_2)]$ ($IMesH_2$ = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene) with the silver salts CF_3COOAg and CF_3SO_3Ag, respectively. The resulting compounds, $[Ru(CF_3SO_3)_2(=CH\text{-}o\text{-}iPr\text{-}O\text{-}C_6H_4)(IMesH_2)]$ (**1**), $[RuCl(CF_3SO_3)(=CH\text{-}o\text{-}iPr\text{-}O\text{-}C_6H_4)(IMesH_2)]$ (**2**), and $[Ru(CF_3CO_2)_2(=CH\text{-}o\text{-}iPr\text{-}O\text{-}C_6H_4)(IMesH_2)]$ (**3**) were found to be highly active catalysts for ring-closing metathesis (RCM) at elevated temperature (45 °C), exceeding known ruthenium-based catalysts in catalytic activity. Turn-over numbers (TONs) up to 1800 were achieved in RCM. Excellent yields were also achieved in enyne metathesis and ring-opening cross metathesis using norborn-5-ene and 7-oxanorborn-5-ene-derivatives. Even more important, **3** was found to be highly active in RCM at room temperature (20 °C), allowing TONs up to 1400. Heterogeneous catalysts were synthesized by immobilizing $[RuCl_2(=CH\text{-}o\text{-}iPr\text{-}O\text{-}C_6H_4)(IMesH_2)]$ on a perfluoroglutaric acid derivatized polystyrene-divinylbenzene (PS-DVB) support (silver form). The resulting supported catalyst $[RuCl(polymer\text{-}CH_2\text{-}O\text{-}CO\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}COO)(=CH\text{-}o\text{-}iPr\text{-}O\text{-}C_6H_4)(IMesH_2)]$ (**5**) showed significantly reduced activities in RCM (TONs = 380) compared with the heterogeneous analogue of **3**. The immobilized catalyst, $[Ru(polymer\text{-}CH_2\text{-}O\text{-}CO\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}COO)(CF_3CO_2)(=CH\text{-}o\text{-}iPr\text{-}O\text{-}C_6H_4)(IMesH_2)]$ (**4**) was obtained by substitution of both Cl ligands of the parent Grubbs–Hoveyda catalyst by addition of CF_3COOAg to **5**. Compound **4** can be prepared in high loadings (160 mg catalyst g^{-1} PS-DVB) and possesses excellent activity in RCM with TONs up to 1100 in stirred-batch RCM experiments. Leaching of ruthenium into the reaction mixture was unprecedentedly low, resulting in a ruthenium content < 70 ppb (ng g^{-1}) in the final RCM-derived products.

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

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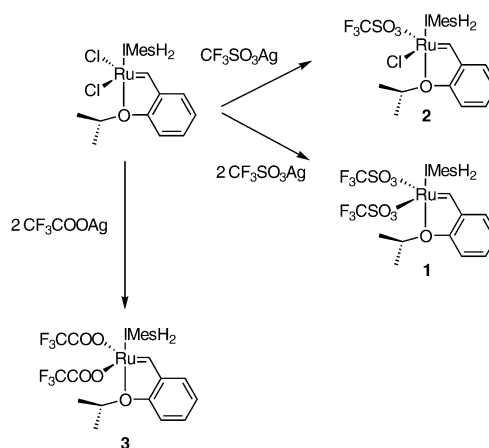
Introduction

With well-defined initiators in hand,[1] olefin metathesis has become a powerful tool in organic synthesis.[2] While high activities have long been the domain of molybdenum-based Schrock initiators, the use of NHCs (NHC: N-heterocyclic carbene) have added another active class of catalysts to the arsenal of synthetic organic chemistry.[3–12] Both NHC ligands and carbene groups in ruthenium-derived catalysts have been optimized through the years. Nevertheless, only little attention has been dedicated to the replacement of the chlorine ligands. This is presumably a consequence of the results reported by Grubbs et al. who varied the halogens in the $[RuCl_2(=CH=CHCPh_2)(PCy_3)_2]$ system.[13] Replacement of both chlorine ligands by bromine, iodine, or trifluoroacetate led to less active or less stable catalysts. In contrast, changing the halide from Cl to Br or I in $[RuCl_2(CHPh)(IMesH_2)]$ results in increased initiation rates in ROMP,

nevertheless, propagation rates were found to be reduced at least in the ROMP of cyclooctene.[14] The results clearly show that replacement of the halide in this type of complex with other groups has a dramatic effect on reactivity, though it is hard to predict whether it will be an increase or decrease. This is further underlined by the finding that an almost dramatic change in enantioselectivity in RCM occurs when the ligand sphere in [RuCl₂(CHPh)(NHC)]-type complexes bearing chiral NHCs is changed from Cl to Br and I.[15] Recently, Buchowicz et al. showed that replacement of both chlorines in [RuCl₂(=CHPh)(PCy₃)₂] with strongly electron-withdrawing fluorocarboxylates results in stable systems and gives access to heterogenization.[16,17] Quite recently, we reported on the synthesis of both homogeneous and heterogeneous catalysts by replacement of one chlorine ligand in an NHC-based Grubbs–Herrmann-catalyst.[18] Though accessible and highly active, any phosphane-containing catalyst suffers from a lack of stability owing to formation of AgCl and AgCl(PCy₃) during synthesis. Our aim was to apply the concept of chlorine replacement by ligands containing electron-withdrawing groups (e.g. fluorinated carboxylates and sulfonates) to a phosphane-free catalyst. In this contribution, we report on the synthesis of a new generation of metathesis catalysts accessible by replacement of one or both chlorines in the phosphane-free Grubbs–Hoveyda catalyst by trifluoroacetate and trifluoromethanesulfonate groups. Furthermore, heterogenization on macroreticular poly(styrene-co-divinylbenzene) resins was achieved. In order to benchmark the new systems, they were all subject to various metathesis-type reactions. The new catalysts were found to be equally or more active in RCM than existing ruthenium-based metathesis catalysts. Excellent reactivity was also observed in enyne metathesis and ring-opening cross metathesis. In the following, the synthesis of the new catalysts, their structure and catalytic activity shall be outlined in detail.

Results and Discussion

Synthesis and structure of Ru complexes 1 and 2: Catalysts **1** and **2** were obtained by adding two or one equivalent of CF₃SO₃Ag, respectively, to [RuCl₂(=CH-*i*Pr-O-C₆H₄)(IMesH₂)] (Scheme 1).

Whereas the substitution of the first ligand proceeds smoothly, replacement of the second requires prolonged reaction times. Both compounds were obtained in virtually quantitative yields, as demonstrated by in situ ¹H NMR experiments, and can be used without any purification. In case AgCl needs to be removed, the protocol described in the Experimental Section offers access to a silver-free catalyst, however, reduced yields (52–56%) have to be accepted. In order to retrieve structural information, **2** was subjected to X-ray crystallographic analysis (Figure 1). Compound **2** crystallizes in the monoclinic space group $P2_1/c$, $a = 1234.41(3)$ pm, $b = 1604.50(3)$ pm, $c = 1704.55(3)$ pm, $\beta = 91.077(2)°$, $Z = 4$. Selected X-ray data are summarized in Table 1, bond lengths and angles are given in Table 2. The Ru–Cl distances of 232.79(12) and 233.93(12) pm,[19] in the parent

Scheme 1. Synthesis of catalysts **1**, **2**, and **3**.

complex [RuCl₂(=CH-*i*Pr-O-C₆H₄)(IMesH₂)] are reduced to 231.82(7) pm for Ru(1)–Cl(1) in **2**. As a consequence of this stronger binding, substitution of the second chlorine is less favored. In addition, replacement of the second Cl ligand is hampered because of the higher pK_a of the conjugated acid (CF₃SO₃H) of the ligand to be introduced. These effects together result in the longer reaction times observed. Similar to **3** (see below), the angle O(1)-Ru(1)-C(2) is close to 180° (178.17(8)°). Compared with the parent complex [RuCl₂-(=CH-*i*Pr-O-C₆H₄)(IMesH₂)][19] and **3**, the angle between the chlorine ligand and the trifluoromethanesulfonate group is widened to 160.87(6)°.

Synthesis and structure of Ru complex 3: For the synthesis of catalyst **3** (Figure 2), a similar procedure was used. Presumably because of the softer character of the CF₃COO ligand (according to the HSAB principle) and the larger pK_a of the corresponding conjugated acid (CF₃COOH), both chlorines can be substituted in a clean reaction. All attempts to isolate the monotrifluroacetate-substituted catalyst failed; under all chosen conditions between −196°C and
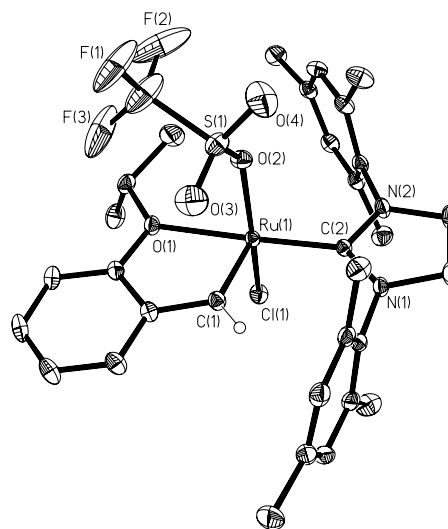

Figure 1. X-ray structure of **2**.

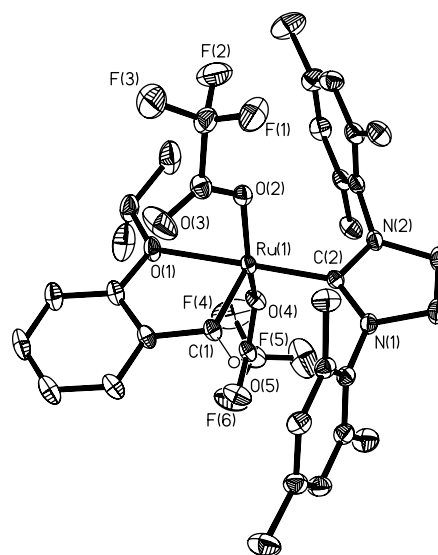Table 1. Selected X-ray data for compounds **2** and **3**.

	2	**3**
formula	$C_{32}H_{38}ClF_3N_2O_4RuS$	$C_{35}H_{38}F_6N_2O_5Ru$
F_W	740.22	781.74
cryst. system	monoclinic	monoclinic
space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
a [pm]	1234.41(3)	1189.39(3)
b [pm]	1604.50(3)	1664.62(3)
c [pm]	1704.55(3)	1862.86(3)
α [°]	90	90
β [°]	91.077(2)	90.086(2)
γ [°]	90	90
V [nm³]	3.37545(12)	3.68824(13)
Z	4	4
T [K]	233(2)	233(2)
ρ_{calcd} [Mg m⁻³]	1.457	1.408
μ [mm⁻¹]	0.660	0.496
color, habit	yellow plate	reddish prism
refls with $I > 2\sigma(I)$	5211	6169
GOF on F^2	1.052	1.054
R indices $I > 2\sigma(I)$		
R_1	0.0315	0.0300
wR2	0.0789	0.0749

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

Ru(1)–C(1)	182.0(3)
Ru(1)–C(2)	198.4(2)
Ru(1)–O(2)	209.86(19)
Ru(1)–O(1)	224.99(17)
Ru(1)–Cl(1)	231.82(7)
C(1)-Ru(1)-C(2)	102.34(11)
C(1)-Ru(1)-O(2)	98.87(10)
C(2)-Ru(1)-O(2)	93.50(9)
C(1)-Ru(1)-O(1)	79.31(10)
C(2)-Ru(1)-O(1)	178.17(8)
O(2)-Ru(1)-O(1)	85.43(7)
C(1)-Ru(1)-Cl(1)	97.21(9)
C(2)-Ru(1)-Cl(1)	93.12(7)
O(2)-Ru(1)-Cl(1)	160.87(6)
O(1)-Ru(1)-Cl(1)	87.44(5)

Figure 2. X-ray structure of **3**.

ty and stability of **3** can be explained by the *trans*-effect of the NHC ligand on the *i*Pr-O group (O(1)-Ru(1)-C(2) 178.93(8)°, parent complex 176.22(14)°).

The fact that only monomeric compounds are obtained is in strong contrast to the findings of Buchowitz et al. for the [RuCl₂(=CHPh)(PCy₃)₂]-derived catalysts.[16, 17] The clear advantage of such monomeric catalysts is that no dissociation of any dimeric catalyst precursor is necessary, which enhances both the reaction rates and stability of the entire catalytic setup. In contrast to the work by Hoveyda,[19] in which the weaker electron-donating character of the oxygen in the isopropoxide group should result in an upfield shift of the benzylidene proton, we could not observe such correlation in catalysts **1**–**3**.

Synthesis of heterogeneous catalysts 4 and 5: For purposes of heterogenization, hydroxymethyl-polystyrene (PS-DVB-CH₂-OH, 1.7 mmol CH₂-OH g⁻¹, crosslinked with 1% DVB) was treated with perfluoroglutaric anhydride following a procedure published by Nieczypor et al.[20] Deprotonation and formation of the silver salt were accomplished by reaction with aqueous sodium hydroxide followed by treatment

room temperature and with varying stoichiometry, only a 1:1:8 mixture of reactants, bis-, and monoadduct (identified by means of ¹H NMR spectroscopy) could be isolated. We therefore were only able to isolate the bis(trifluoroacetate)-substituted catalyst **3** in a pure form. As for **1** and **2**, **3** is obtained in virtually quantitative yield as again demonstrated by in situ ¹H NMR experiments, and can be used without any purification. Removal of AgCl to obtain analytically pure catalyst results in reduced yields (71%).

Compound **3** (Figure 2) crystallizes in the space group $P2_1/n$, $a = 1189.39(3)$, $b = 1664.62(3)$, $c = 1862.86(3)$ pm, $\beta = 90.086(2)°$, $Z = 4$. Selected X-ray data are summarized in Table 1, bond lengths and angles are given in Table 3. The angle formed by O(2)-Ru(1)-O(4) is 157.23(6)°, which is similar to the angle of 156.47(5)° found for Cl(1)-Ru-Cl(2) in the parent complex [RuCl₂(=CH-*o*-*i*Pr-O-C₆H₄)(IMesH₂)].[19] The Ru(1)–O(1) distance is basically unchanged (2.261(3) Å in the parent complex versus 2.2458(15) Å in **3**), which is in accordance with the high stability of **3**. As for the parent complex, both the high reactivi-

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

Ru(1)–C(1)	182.6(2)
Ru(1)–C(2)	197.9(2)
Ru(1)–O(4)	202.58(15)
Ru(1)–O(2)	203.65(16)
Ru(1)–O(1)	224.58(15)
C(1)-Ru(1)-C(2)	100.83(9)
C(1)-Ru(1)-O(4)	97.91(8)
C(2)-Ru(1)-O(4)	92.26(7)
C(1)-Ru(1)-O(2)	103.11(8)
C(2)-Ru(1)-O(2)	92.31(7)
O(4)-Ru(1)-O(2)	157.23(6)
C(1)-Ru(1)-O(1)	79.20(8)
C(2)-Ru(1)-O(1)	178.93(8)
O(4)-Ru(1)-O(1)	86.67(7)
O(2)-Ru(1)-O(1)	88.73(7)

with AgNO$_3$. [RuCl$_2$(=CH-o-iPr-O-C$_6$H$_4$)(IMesH$_2$)] was dissolved in THF and added to the silver salt. By this approach, [RuCl(polymer-CH$_2$-O-CO-CF$_2$-CF$_2$-CF$_2$-COO)(=CH-o-iPr-O-C$_6$H$_4$)(IMesH$_2$)] (**5**) was obtained. In order to synthesize an almost identical analogue to **3**, the second Cl ligand was reacted with CF$_3$COOAg yielding [Ru(polymer-CH$_2$-O-CO-CF$_2$-CF$_2$-CF$_2$-COO)(CF$_3$CO$_2$)(=CH-o-iPr-O-C$_6$H$_4$)(IMesH$_2$)] (**4**) as a lilac powder (Scheme 2).

A catalyst-loading of 160 mg g^{-1} (16%) was determined for **4**, indicating that more than 80% of the polymer-bound silver perfluoroglutarate groups were accessible for reaction with [RuCl$_2$(=CH-o-iPr-O-C$_6$H$_4$)(IMesH$_2$)]. This corresponds to a catalyst amount five times higher than reported for other heterogeneous systems.[20]

Homogeneous RCM experiments: In order to benchmark the new systems, we tested their catalytic activity in RCM using a set of six different compounds. Diethyl diallylmalonate (DEDAM), 1,7-octadiene, diallyldiphenylsilane, *trans*-3-methylpentenoate, *N,N*-diallyltrifluoroacetamide, and *N,N*-diallyl-*tert*-butylcarbamide were used. Catalysts **1** and **2** displayed lower activities than the parent catalyst (Table 4, entries 21–32). However, RCM experiments with **3** could be carried out with high turn-over numbers (TONs) even at room temperature. As can be deduced from Table 4, TONs obtained with **3** at 45°C (Table 4, entries 11–18) exceed those obtained with the Grubbs–Herrmann (Table 4, entries 1–5) or the parent Grubbs–Hoveyda catalysts in most cases (Table 4, entries 6–10). Even more interesting, high TONs (600 for DEDAM and 1380 for 1,7-octadiene, see Table 4, entries 17–18) were obtained at 20°C, underlining the high activity of this catalytic system. Since the activity of a new metathesis catalyst is best demonstrated by the RCM of tri- and tetrasubstituted dienes, we carried out RCM of diethyl allylmethallyl malonate and diethyl dimethallylmalonate (Table 4, entries 19–20). TONs of 80 and 70, respectively were achieved. Though slightly higher numbers (TON = 99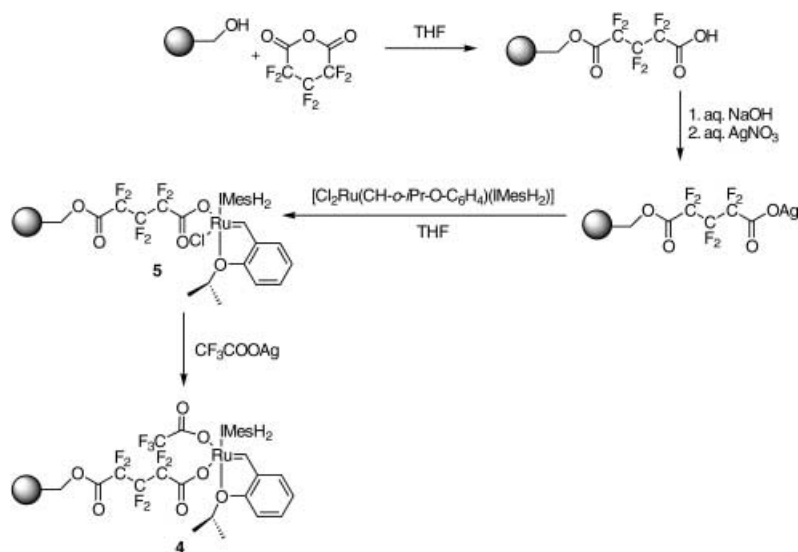) were obtained by other groups using [RuCl$_2$(CH-2-iPrO-5-NO$_2$-C$_6$H$_3$)(IMesH$_2$)],[21] these data still exceed or at least rival the activity of [RuCl$_2$(CH-Ph)(IMesH$_2$)(PCy$_3$)], [RuCl$_2$(=CH-(1-(2-iPrO-naphth-1-yl)-2-iPrO-naphth-3-yl)-(IMesH$_2$)(PCy$_3$)], and [Mo(*N*-2,6-iPr$_2$-C$_6$H$_3$)(CHCMe$_2$-Ph)(OCMe(CF$_3$)$_2$)$_2$].[22–24]

Homogeneous enyne and ring-opening cross metathesis experiments: In addition to RCM experiments, enyne metathesis reactions were carried out. Diethyl dipropargylmalonate (DEDPM) was treated with trimethylallylsilane and triphenylallylsilane. The corresponding products were obtained in high yields (95%). Conditions identical to those reported in the literature[25] were chosen in order to allow for comparison of the reported yields. As can be deduced from Table 5 (entries 43 and 44), **3** again showed enhanced activity. Finally, ring-opening cross metathesis reactions carried out with both norborn-5-ene and 7-oxanorborn-5-ene derivatives were investigated (Table 5, entries 45–45). Excellent yields (95%) were obtained, again exceeding those reported in the literature.[26]

Heterogeneous RCM experiments: For purposes of comparison, DEDAM, 1,7-octadiene, diallyldiphenylsilane, *trans*-3-methylpentenoate, and *N,N*-diallyl-*tert*-butylcarbamide were used in heterogeneous RCM to benchmark the heterogeneous catalysts **4** and **5**. For most of these monomers, both catalyst **5** and **4** displayed high activities in RCM, the latter being the superior system with TONs approaching 1100 (Table 4, entries 31–35). With **5**, TONs of 380 were achieved (Table 1, entries 36–40). With this catalytic activity, both heterogeneous systems presented here far exceed any other supported metathesis catalyst. The fact that **4** exceeds **5** in catalytic activity clearly accentuates the necessity of careful catalyst design; in our case the substitution of both chlorine ligands results in an almost perfect mimic of the homogeneous analogue **3**. For both heterogeneous systems **4** and **5**, leaching of ruthenium into the various reaction mixtures was unprecedentedly low, resulting in a ruthenium content <70 ppb (ng g^{-1}) in the final RCM-derived products.

Conclusion

With the synthesis of catalysts **1**-**3** we have shown that the concept of the fixation of strongly electron-withdrawing ligands accelerates the catalytic activity of Grubbs–Hoveyda type catalysts, a finding that is in contrary to previous experiments with Grubbs-type catalysts. The resulting catalysts are monomeric rather than dimeric and exhibit surprising stability. Thus, **3** can be stored under ambient conditions (i.e., room temperature, air, and moisture)
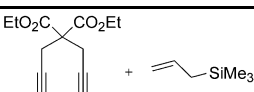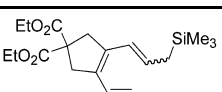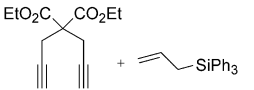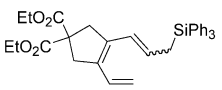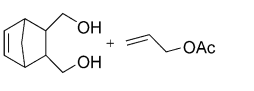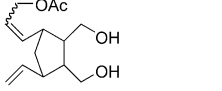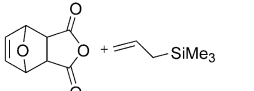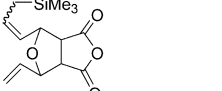

Scheme 2. Synthesis of heterogeneous catalysts **4** and **5**.

Table 4. Summary of catalytic activities.

	Compound	Catalyst	mol% compound	TON
1	DEDAM	Grubbs–Herrmann[a]	0.05	1300
2	1,7-octadiene	Grubbs–Herrmann[a]	0.08	1000
3	diallyldiphenylsilane	Grubbs–Herrmann[a]	0.10	400
4	methyl *trans*-3-pentenoate	Grubbs–Herrmann[a]	0.01	600
5	*tert*-butyl *N,N*-diallylcarbamide	Grubbs–Herrmann[a]	0.10	770
6	DEDAM	Grubbs–Hoveyda[a]	0.05	1500
7	1,7-octadiene	Grubbs–Hoveyda[a]	0.05	1700
8	diallyldiphenylsilane	Grubbs–Hoveyda[a]	0.10	180
9	methyl *trans*-3-pentenoate	Grubbs–Hoveyda[a]	0.10	60
10	*tert*-butyl *N,N*-diallylcarbamide	Grubbs–Hoveyda[a]	0.10	100
11	DEDAM	**3**[a]	0.05	1400
12	1,7-octadiene	**3**[a]	0.05	1800
13	diallyldiphenylsilane	**3**[a]	0.10	750
14	methyl *trans*-3-pentenoate	**3**[a]	0.01	300
15	*tert*-butyl *N,N*-diallylcarbamide	**3**[a]	0.10	780
16	*N,N*-diallyltrifluoroacetamide	**3**[a]	0.10	1000
17	DEDAM	**3**[b]	0.10	590
18	1,7-octadiene	**3**[b]	0.05	1400
19	diethyl allylmethallylmalonate	**3**[c]	0.10	80
20	diethyl dimethallylmalonate	**3**[c]	0.10	70
21	DEDAM	**2**[a]	0.05	600
22	1,7-octadiene	**2**[a]	0.05	300
23	diallyldiphenylsilane	**2**[a]	0.10	10
24	methyl *trans*-3-pentenoate	**2**[a]	0.01	300
25	*tert*-butyl-*N,N*-diallylcarbamide	**2**[a]	0.10	710
26	*N,N*-diallyltrifluoroacetamide	**2**[a]	0.10	630
27	DEDAM	**1**[a]	0.05	500
28	1,7-octadiene	**1**[a]	0.05	500
29	diallyldiphenylsilane	**1**[a]	0.10	20
30	methyl *trans*-3-pentenoate	**1**[a]	0.01	500
31	*tert*-butyl-*N,N*-diallylcarbamide	**1**[a]	0.10	110
32	*N,N*-diallyltrifluoroacetamide	**1**[a]	0.10	190
33	DEDAM	**4**[a]	0.05	200
34	1,7-octadiene	**4**[a]	0.05	1100
35	diallyldiphenylsilane	**4**[a]	0.10	100
36	*tert*-butyl *N,N*-diallylcarbamide	**4**[a]	0.10	350
37	*N,N*-diallyltrifluoroacetamide	**4**[a]	0.10	70
38	DEDAM	**5**[a]	0.05	200
39	1,7-octadiene	**5**[a]	0.05	400
40	diallyldiphenylsilane	**5**[a]	0.10	130
41	*tert*-butyl *N,N*-diallylcarbamide	**5**[a]	0.10	190
42	*N,N*-diallyltrifluoroacetamide	**5**[a]	0.10	130

[a] 2 h, 2 mL CH_2Cl_2, 45 °C. [b] 2 h, 2 mL CH_2Cl_2, 20 °C. Grubbs–Hoveyda catalyst = $[RuCl_2(=CH\text{-}o\text{-}i\text{Pr-O-}C_6H_4)(IMesH_2)]$. [c] 2 h, 3 mL $CDCl_3$, 45 °C.

Table 5. Enyne and ring-opening cross-metathesis reactions using **3**.

	Reactants	Product	Conditions	*E*/*Z*	Yield[a]
43			[b]	1:3.5	95% (65%)[25]
44			[b]	1:6	95%
45			[c]	1:2	95% (58)[26]
46			[c]	1.1	95%

[a] Yields in parentheses are those reported by other groups using standard Ru-based metathesis catalysts. [b] CH_2Cl_2, 12 h, room temperature, 10 mol% catalyst. [c] 2 mol%, 2 h, $CDCl_3$, room temperature. Reactants for entries 45 and 46 consisted of a 1:1 mixture of the corresponding *exo* and *endo* compounds.

without loss of activity. In various RCM, enyne metathesis, and ring-opening cross metathesis experiments, **3** revealed the highest activity ever reported both at elevated and room temperature. Moreover, substitution of the chlorine ligands with trifluoroacetate groups or polymer-bound analogous ligands offers simple access to heterogeneous analogues, as has been demonstrated with the syntheses of **4** and **5**. The high catalytic activity can be retained during the heterogenization process, and ruthenium leaching was unprecedentedly low, giving access to virtually Ru-free products. Investigations on the applicability of **3** and **4** in various metathesis-based reactions including polymerizations and heterogenization on monolithic supports[27,28] are under way.

Experimental Section

General: NMR data were obtained at 300.13 MHz for proton and at 75.74 MHz for carbon in the indicated solvent at 25 °C on a Bruker Spectrospin 300 and are listed in parts per million downfield from tetramethylsilane for proton and carbon. IR spectra were recorded on a Bruker Vector 22 using ATR technology. GC-MS investigations were carried out on a Shimadzu GCMS-QP5050, using a SPB-5 fused silica gel column (30 m × 0.25 mm × 25 μm film thickness). Elemental analyses were carried out at the Mikroanalytical Laboratory, Anorganisch-Chemisches Institut, TU München, Germany, and at the Institute of Physical Chemistry, University of Vienna, Austria. A Jobin Yvon JY 38 plus was used for ICP-OES measurements, a MLS 1200 mega for microwave experiments. Syntheses of the ligands and catalysts were performed under an argon atmosphere by standard Schlenk techniques or in an N_2-mediated dry-box (Labmaster 130, MBraun, Germany) unless stated otherwise. Reagent grade diethyl ether, pentane, THF, and toluene were distilled from sodium/benzophenone under argon. Reagent grade dichloromethane was distilled from calcium hydride under argon. Other solvents and reagents were used as purchased. Deionized water was used throughout. Diethyl diallylmalonate (DEDAM), 1,7-octadiene, diallyl ether, N,N-diallyltrifluoroacetamide, diallyldiphenylsilane, methyl *trans*-3-pentenoate, *tert*-butyl N,N-diallycarbamate, ethyl vinyl ether (EVE), [RuCl$_2$(=CHPh)-(IMesH$_2$)(PCy$_3$)] (IMesH$_2$ = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene), CF$_3$SO$_3$Ag, CF$_3$COOAg, PS-DVB-CH$_2$-OH (100–300 mesh, 1.7 mmol Ar-CH$_2$-OH g^{-1}, 1% crosslinked), perfluoroglutaric anhydride, salicylaldehyde, 2-propyliodide, norborn-5-ene-2,3-dimethanol, and 7-oxanorborn-5-ene-2,3-dicarboxylic anhydride were purchased from Fluka (Buchs, Switzerland). [RuCl$_2$(=CH-*o*-*i*Pr-O-C$_6$H$_4$)(IMesH$_2$)],[19] diethyl diallylmalonate[29] and diethyl dimethallylmalonate[23] were prepared according to the literature. A ruthenium standard containing 1000 ppm of ruthenium was purchased from Alfa Aesar/Johnson Matthey (Karlsruhe, Germany).

[Ru(CF$_3$SO$_3$)$_2$(=CH-*o*-*i*Pr-O-C$_6$H$_4$)(IMesH$_2$)] (1): Under glovebox conditions [RuCl$_2$(=CH-*o*-*i*Pr-O-C$_6$H$_4$)(IMesH$_2$)] (200 mg, 0.32 mmol) was dissolved in THF (10 mL) and a solution of CF$_3$SO$_3$Ag (2 equiv, 164 mg, 0.64 mmol) in THF (2 mL) was slowly added to the stirred solution. Stirring was continued for 3 h. A color change from green to red and the formation of a precipitate were observed. The precipitate was filtered off and the solution evaporated to dryness. The solid was redissolved in CH$_2$Cl$_2$ and flashed over a short pad of silica gel. Drying in vacuo provided a green powder (152 mg, 56%, 0.18 mmol). ^{1}H NMR (300.13 MHz, CDCl$_3$, 25 °C): δ = 18.49 (s, 1H; Ru=CHAr), 7.51 (dd, 1H; aromatic CH), 7.10–7.19 (5H; aromatic CH), 6.97 (dd, 1H; aromatic CH), 6.78 (d, 1H; aromatic CH), 4.72 (septet, 1H; (CH$_3$)$_2$CHOAr), 4.16 (s, 4H; N(CH$_2$)$_2$N), 2.38 (m, 12H; mesityl *o*-CH$_3$), 2.17 (s, 6H; mesityl *p*-CH$_3$), 1.11 (d, 6H; (CH$_3$)$_2$CHOAr); ^{13}C NMR (75.47 MHz, CDCl$_3$, 25 °C): δ = 332.4, 203.9, 154.0, 145.5, 139.9, 138.6, 136.8, 135.1, 132.5, 130.8, 129.1, 122.1, 118.6, 114.4, 112.2, 52.1, 49.6, 24.8, 20.4, 19.4, 17.8, 17.1; FT-IR (ATR-mode): $\tilde{\nu}$ = 2962 (br), 2910 (br), 1587 (s), 1481 (s), 1447 (s), 1331 (s), 1259 (vs), 1233 (w), 1190 (vs), 1088 (vs), 1015 (vs), 983 (s), 932 (w), 864 (w), 796 (vs), 754 (w), 696 cm^{-1} (w); elemental analysis calcd for

$C_{33}H_{38}F_6N_2O_7RuS_2\cdot AgCl$ (997.176): C 39.75, H 3.84, N 2.81; found C 40.07, H 4.45, N 2.64.

[RuCl(CF$_3$SO$_3$)(=CH-*o*-*i*Pr-O-C$_6$H$_4$)(IMesH$_2$)] (2): Under glovebox conditions [RuCl$_2$(=CH-*o*-*i*Pr-O-C$_6$H$_4$)(IMesH$_2$)] (200 mg, 0.32 mmol) was dissolved in THF (10 mL) and a solution of CF$_3$SO$_3$Ag (1 equiv, 82 mg, 0.32 mmol) in THF (2 mL) was slowly added to the stirred solution. Stirring was continued for 90 minutes. A color change from green to green-yellow and the formation of a precipitate were observed. The precipitate was filtered off and the solution evaporated to dryness. The solid was redissolved in CH$_2$Cl$_2$ and flashed over a short pad of silica gel. Drying in vacuo provided a green powder (123 mg, 0.17 mmol, 52%). Green crystals suitable for X-ray analysis were obtained by layering pentane over a concentrated solution of **2** in CH$_2$Cl$_2$ at −36 °C. ^{1}H NMR (300.13 MHz, CDCl$_3$, 25 °C): δ = 17.49 (s, 1H; Ru=CHAr), 7.46 (dd, 1H; aromatic CH), 7.18–6.95 (5H; aromatic CH), 6.86 (dd, 1H; aromatic CH), 6.73 (d, 1H; aromatic CH), 4.74 (septet, 1H; (CH$_3$)$_2$CHOAr), 4.12 (s, 4H; N(CH$_2$)$_2$N), 2.55–2.15 (m, 18H; mesityl CH$_3$), 1.25 (d, 3H; (CH$_3$)$_2$CHOAr), 1.04 (d, 3H; (CH$_3$)$_2$CHOAr); ^{13}C NMR (75.47 MHz, CDCl$_3$, 25 °C): δ = 313.8, 207.1, 152.1, 144.9, 139.4, 139.1, 138.8, 138.0, 136.8, 135.8, 131.6, 130.3, 128.8, 128.4, 121.7, 119.1, 114.9, 111.9, 74.7, 51.4, 49.4, 24.6, 20.2, 19.2, 19.0, 17.8, 17.2, 16.8; FT-IR (ATR-mode): $\tilde{\nu}$ = 2963 (br), 2915 (br), 1584 (s), 1479 (s), 1444 (s), 1389 (w), 1325 (w), 1261 (s), 1229 (w), 1190 (vs), 1100 (s), 1003 (vs), 934 (w), 848 (w), 801 (s), 749 (s), 697 cm^{-1} (w); elemental analysis calcd for $C_{32}H_{38}ClF_3N_2O_4RuS$ (740.24): C 51.92, H 5.17, N 3.78; found C 47.20, H 5.83, N 2.86.

[Ru(CF$_3$CO$_2$)$_2$(=CH-*o*-*i*Pr-O-C$_6$H$_4$)(IMesH$_2$)] (3): Under dry glovebox conditions, [RuCl$_2$(=CH-*o*-*i*Pr-O-C$_6$H$_4$)(IMesH$_2$)] (200 mg, 0.319 mmol) was dissolved in THF (10 mL) and a solution of CF$_3$CO$_2$Ag (2 equiv, 141 mg, 0.64 mmol) in THF (2 mL) was slowly added to the stirred solution. Stirring was continued for 20 minutes. A color change from green to lilac and the formation of a precipitate were observed. The precipitate was filtered off and the solution evaporated to dryness. It was redissolved in CH$_2$Cl$_2$ (1 mL), flashed over 5 cm silica gel and evaporated to dryness, giving a lilac powder (177 mg, 0.23 mmol, 71%). Lilac crystals suitable for X-Ray analysis were obtained by layering pentane over a dilute solution of **3** in Et$_2$O at −36 °C. ^{1}H NMR (300.13 MHz, CDCl$_3$, 25 °C): δ = 17.38 (s, 1H; Ru=CHAr), 7.28 (dd, 1H; aromatic CH), 7.08 (s, 4H; mesityl aromatic CH), 7.00 (dd, 1H; aromatic CH), 6.86 (dd, 1H; aromatic CH), 6.56 (d, 1H; aromatic CH), 4.55 (septet, 1H; (CH$_3$)$_2$CHOAr), 4.05 (s, 4H; N(CH$_2$)$_2$N), 2.37 (s, 6H; mesityl *p*-CH$_3$), 2.20 (s, 12H; mesityl *o*-CH$_3$), 0.88 (d, 6H; (CH$_3$)$_2$CHOAr); ^{13}C NMR (75.47 MHz, CDCl$_3$, 25 °C): δ = 314.7, 209.1, 159.0, 152.1, 142.4, 138.4, 137.9, 133.4, 129.2, 128.7, 122.6, 121.8, 111.2, 109.9, 73.2, 50.3, 24.6, 19.1, 16.8; FT-IR (ATR-mode): $\tilde{\nu}$ = 2982 (br), 2925 (br), 1698 (s), 1609 (w), 1593 (w), 1577 (w), 1478 (w), 1451 (w), 1393 (s), 1260 (s), 1180 (vs), 1141 (vs), 1033 (w), 937 (w), 877 (s), 844 (s), 812 (w), 780 (w), 748 (s), 722 cm^{-1} (s); elemental analysis calcd for $C_{35}H_{38}F_6N_2O_5Ru$ (781.75): C 53.77, H 4.90, N 3.58; found: C 53.63, H 4.90, N 3.63.

Heterogenization on a polystyrene-divinylbenzene support, generation of [Ru(polymer-CH$_2$-O-CO-CF$_2$-CF$_2$-CF$_2$-COO)(CF$_3$CO$_2$)(=CH-*o*-*i*Pr-O-C$_6$H$_4$)(IMesH$_2$)] (4) and [RuCl(polymer-CH$_2$-O-CO-CF$_2$-CF$_2$-CF$_2$-COO)(=CH-*o*-*i*Pr-O-C$_6$H$_4$)(IMesH$_2$)] (5): PS-DVB-CH$_2$-OH (1.00 g) was suspended in dry THF (20 mL) and of perfluoroglutaric anhydride (1 equiv, 377 mg, 1.70 mmol) was added. Stirring was continued for 2 h, then the product was filtered and washed three times with THF. It was dried under high vacuum giving a white solid (1.33 g). FT-IR (ATR-mode): $\tilde{\nu}$ = 3025 (br), 2920 (br), 2442 (br), 1772 (vs), 1600 (br), 1489 (w), 1448 (w), 1375 (w), 1312 (s), 1245 (s), 1175 (vs), 1145 (vs), 1044 (s), 915 (w), 867 (w), 823 (w), 755 (s), 697 cm^{-1} (vs). The solid was resuspended in THF (10 mL) and excess NaOH (140 mg in 30 mL water) was added. The mixture was stirred for 2 h, the product was filtered and washed three times with water. The precipitate was suspended in water (20 mL) and AgNO$_3$ (1.2 equiv, 350 mg, 2.1 mmol) in water (10 mL) was added. Stirring was continued for 2 h, the product was filtered and washed three times each with water, Et$_2$O, and pentane. Drying in vacuo gave a white solid (0.85 g). FT-IR (ATR-mode): $\tilde{\nu}$ = 3056 (br), 3023 (br), 2918 (br), 2854 (br), 2336 (br), 1808 (w), 1596 (w), 1490 (w), 1446 (w), 1364 (w), 1285 (w), 1216 (s), 1067 (w), 1027 (w), 896 (w), 840 (w), 812 (w), 754 (s), 694 cm^{-1} (vs). The solid was resuspended in THF (25 mL) and [RuCl$_2$(=CH-*o*-*i*Pr-O-C$_6$H$_4$)(IMesH$_2$)] (99.8 mg, 0.159 mmol) was added. Stirring was continued for 90 min. [RuCl(polymer-CH$_2$-O-CO-

CF$_2$-CF$_2$-CF$_2$-COO)(=CH-*o*-*i*Pr-O-C$_6$H$_4$)(IMesH$_2$)] (**5**) was filtered off, washed with THF, and dried in vacuo to yield an off-white powder. FT-IR (ATR-mode): $\tilde{\nu}$ = 3057 (w), 3024 (w), 2917 (br), 2848 (w), 1600 (w), 1492 (w), 1451 (w), 1420 (w), 1180 (br), 1154 (w), 1027 (w), 1014 (w), 906 (w), 841 (w), 751 (s), 697 cm^{-1} (vs). CF$_3$COOAg (1 equiv, 35.2 mg, 0.159 mmol) was dissolved in THF (2 mL) and the solution was added to **5**, dissolved in THF (10 mL), and the mixture was stirred for 90 min. Extensive washing with THF and drying in vacuo gave [Ru(polymer-CH$_2$-O-CO-CF$_2$-CF$_2$-CF$_2$-COO)(CF$_3$CO$_2$)(=CH-*o*-*i*Pr-O-C$_6$H$_4$)(IMesH$_2$)] (**4**) as a lilac powder (0.7 g). Ru content 0.18 mmol g^{-1}, corresponding to 160 mg catalyst g^{-1} (16% catalyst loading). FT-IR (ATR-mode): $\tilde{\nu}$ = 3060 (w), 3023 (w), 2919 (br), 2852 (w), 2378 (w), 1942 (w), 1874 (w), 1805 (w), 1595 (w), 1488 (w), 1447 (w), 1365 (br), 1185 (br), 1019 (w), 817 (w), 754 (s), 695 cm^{-1} (vs).

2-Isopropoxystyrene (6): Salicylaldeyde (10.3 g, 84 mmol), NBu$_4$Br (25.1 g, 78 mmol), and *i*PrI (20 mL, 0.2 mol) were dissolved in CH$_2$Cl$_2$ (300 mL). NaOH (3.5 g, 88 mmol) dissolved in water (150 mL) was slowly added to the stirred solution. After stirring for 2 d, the organic phase was separated and the aqueous phase was washed with CH$_2$Cl$_2$ (3×50 mL). The combined organic phase was dried in vacuo, redissolved in ethyl acetate, and filtered. The filtrate was dried over Na$_2$SO$_4$ and evaporated to dryness, giving a yellow oil (5.7 g). MePPh$_3$Br (13 g, 34.7 mmol) was dried in a Schlenk tube and put under argon. Dry THF (50 mL) was added, followed by *n*BuLi (2 N in pentane, 17.4 mL, 34.7 mmol) at 0°C. It was stirred for 30 minutes at 0°C and another 30 minutes at room temperature. The aldehyde (5.7 g, 34.7 mmol) was slowly added at 0°C and stirring was continued for 12 h. Water (5 mL) was added to the yellow solution, which was then dried in vacuo. The product was extracted with Et$_2$O (3×25 mL), dried over Na$_2$SO$_4$, and evaporated to dryness. Column chromatography over silica gel using ethyl acetate/pentane (2:98) as eluent provided the product in the first fraction (R_f = 0.5). It was dried over Na$_2$SO$_4$ and evaporated to dryness to give the product as a clear liquid (3.2 g, 20 mmol, 23%). ^{1}H NMR (300.13 MHz, CDCl$_3$, 25°C): δ = 7.37 (d, 1H; Ar), 7.07 (m, 1H; Ar), 6.97 (dd, 1H; CH), 6.76 (m, 2H; Ar), 5.63 (dd, 1H; *trans*-CHCH$_2$), 5.12 (dd, 1H; *cis*-CHCH$_2$), 4.40 (sept, 1H; CH(CH$_3$)$_2$), 1.21 (d, 6H; CH(CH$_3$)$_2$); ^{13}C NMR (75.47 MHz, CDCl$_3$, 25°C): δ = 155.0, 131.9, 128.6, 127.7, 126.4, 120.5, 114.0, 70.6, 22.1; FT-IR (ATR-mode): $\tilde{\nu}$ = 2978 (s), 2933 (br), 1625 (w), 1597 (w), 1484 (s), 1453 (s), 1383 (w), 1290 (w), 1240 (vs), 1118 (s), 997 (w), 955 (w), 906 (w), 751 cm^{-1} (w); GC-MS: calcd for C$_{11}$H$_{14}$O: 162.1, found 162.1 $[M]^+$.

RCM-, ring-opening cross metathesis and enyne-metathesis experiments (slurry reactions): The following procedure is representative of all experiments. DEDAM (520 mg, 2.16 mmol) was dissolved in CH$_2$Cl$_2$ (2 mL) and the homogeneous catalyst (0.01–0.10 mol% as indicated in Table 4) or supported catalyst (12.0 mg) was added. The reaction mixture was heated to 45°C for 2 h. After removal of the catalyst by filtration, the yield was determined by GC-MS and ^{1}H NMR spectroscopy in CDCl$_3$.

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

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

X-ray measurement and structure determination of 2 and 3: The data collection was performed 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. Intensities were integrated using DENZO and scaled with SCALEPACK.[30] Several scans in ϕ and ω direction were made to increase the number of redundant reflections, which were averaged in the refinement cycles. This procedure replaces in a good approximation an empirical absorption correction. The structures were solved with direct methods SHELXS86 and refined against F^2 SHELX97.[31] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined at calculated positions with isotropic displacement parameters, except the hydrogen atoms at C(1), which were found and refined normally. For compound **2** the flu-

orine atoms of the CF$_3$ groups and the methyl parts of the isopropyl group are 2:1 disordered. Relevant crystallographic data are summarized in Tables 1–3.

CCDC-215892 (**2**) and -215891 (**3**) contains 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)1223–336033; or email: deposit@ccdc.cam.ac.uk.

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