

Poly(fluoroalkyl acrylate)-Bound Ruthenium Carbene Complex: A Fluorous and Recyclable Catalyst for Ring-Closing Olefin Metathesis

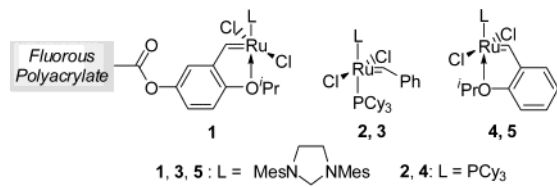
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Since reported in 1994 by Horváth,¹ fluoruous biphasic chemistry has evolved into a rich and fruitful research area due to its potential as a new paradigm of green chemical processes.² The development of various fluoruous reagents and catalysts enables fluoruous technology to be increasingly applied to the isolation of reaction products and the recovery of recyclable catalysts. We now wish to report examples of olefin metathesis using a fluoruous ruthenium catalyst. The fluoruous catalyst **1** effects the ring-closing metathesis (RCM) of a broad spectrum of diene and enyne substrates in *minimally fluoruous solvent systems* (PhCF₃/CH₂Cl₂, 1:9–1:49 v/v) with high reactivity. The catalyst can be readily recycled by fluoruous extraction and repeatedly reused.

The advent of several well-defined ruthenium catalysts, most notably the Grubbs-type Ru alkylidenes **2**^{3a} and **3**,^{3b} has fueled the widespread application of olefin metathesis.⁴ A major recent advance in this area is the discovery by Hoveyda et al. of the robust and recyclable Ru catalysts **4** and **5**.⁵ We⁶ and others⁷ have established that various polymeric and solid supports can be used to immobilize these catalysts. The development of fluoruous olefin metathesis catalysts⁸ is a highly desirable goal since this would lead to a further expansion of the scope of this important reaction.



Incorporation of perfluoroalkyl groups² into the ligands would conceivably render a Ru catalyst fluoruous. Given the capricious nature of the Ru catalysts, however, even a cautious alteration of the ligand structure may result in an unpredictable change in activity. We therefore elected to use a suitably fluoruous polymer⁹ as a fluoruous tag^{2g} to the catalyst. To this end, fluoruous polymer **8** bearing a bidentate isopropoxystyrene ligand⁵ was designed and synthesized as shown in Scheme 1. The commercially available fluoroacrylate **6** was copolymerized with acryloyl chloride in the presence of AIBN under heating in PhCF₃. The resulting acyl chloride copolymer was then coupled to the known ligand **7**⁶ under standard conditions to give **8** as a white powder. Polymer **8** is fully soluble in fluoruous solvents such as PhCF₃ and FC-72 but insoluble in common organic solvents such as CH₂Cl₂ and EtOAc. ¹H NMR spectroscopy (500 MHz) revealed a clean incorporation of the styrene ligand in about 1:10 ratio relative to the fluoroalkyl groups, corresponding to a loading of 0.19 mmol/g of the ligand. Treatment of **8** with catalyst **3** in the presence of CuCl^{5b} resulted in the exchange of the styrene groups in >90% conversion to deliver the air stable greenish powder **1**.

The activity of catalyst **1** was evaluated using three test dienes, as shown in Table 1. The disubstituted dienes **9** and **10** underwent

Scheme 1. Synthesis of Fluorous Ru-Catalyst **1**

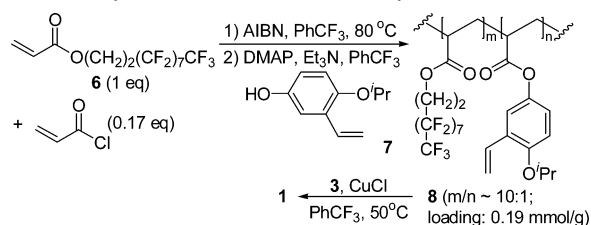


Table 1. Recycling and Reuse of Fluorous Ru-Catalyst **1** in the Ring-Closing Metathesis of Test Dienes **9**–**11**

9 → 12		10 → 13	
cycle ^b	1 to 15	1 to 9	10 to 12
% conv ^d	>98	>98	98, 96, 95

11 → 14	
cycle ^e	1 to 6 ¹³
% conv ^d	>98, >98, >98, >98, >98, 96

^a Bath temperature. ^b Cycles 1–15: with 0.5 mmol **9** and 1 mol % **1** for 1 h; cycles 16–20: with 1 mmol **9** and 0.5 mol % **1** for 2 h. ^c With 0.5 mmol **10** and 1 mol % **1** for 1 h. ^d Determined by ¹H NMR spectroscopy. ^e With 0.5 mmol **11** and 2 mol % **1** for 1.5 h.

RCM quantitatively in the presence of only 0.5–1 mol % of **1**¹⁰ in the solvent system PhCF₃/CH₂Cl₂ (1:19 v/v).¹¹ Importantly, **1** can be cleanly recovered by FC-72 extraction and repeatedly reused.¹² The catalyst remained highly active even after 20 cycles in the case of **9**. Diene **11** also cyclized cleanly to give the trisubstituted cyclic olefin **14** with 2 mol % of **1**. The catalyst was recycled and reused for six runs with only a very slight drop in its activity.¹³

Having established the recyclability and reusability of **1**, we next examined its performance in the RCM of a variety of di-, tri-, and tetrasubstituted diene and enyne substrates leading to the formation of various carbocyclic and heterocyclic olefins (Table 2). The benchmark diene **15** cyclized with excellent conversion in the presence of 1 mol % of **1** for up to seven cycles, further corroborating the high level of recyclability of **1**. With one single batch of **1** (2 mol %), the trisubstituted dienes **17**–**21** underwent RCM to form the respective products, all in excellent conversion. Similarly, another batch of **1** was used to catalyze the reactions of substrates **27**–**29** in a consecutive manner with good to excellent yields. Finally, **1** proved to be reactive toward the RCM of tetrasubstituted diene **30**, albeit a higher loading of **1** and a longer reaction time were required to achieve a high conversion. With the more challenging diene **31**,¹⁵ the reaction went only to half completion even after an extended reaction time. Remarkably,

Table 2. Activity and Recyclability of Fluorous Ru-Catalyst **1**^a

catalyst batch	cycle	substrate	product	time [h]	% conv ^b (yield) ^c		
A	1 ^d and 2			1	>98		
	3 and 4			1	98		
	5			1	95		
	6			1	93		
	7			1	92		
B	1			3	>98 (94)		
	2			1.5	>98 (90)		
	3			1.5	>98 (94)		
	4			1.5	>98 (96)		
	5 ^e			3	>98 (91)		
	C	1			2	>98 (95)	
		2			5	89 (85)	
		3			5	80 (74)	
		D	1 ^f			6	43 (39)
			2 ^{g,14}			16	94 (93)
E	1 ^{h,14}			36	51 (50)		
	2 ⁱ			2.5	96 (96)		

^a Unless otherwise noted, all reactions were performed with 0.50 mmol substrate and 2 mol % **1** in PhCF₃/CH₂Cl₂ (1:19 v/v, 10 mL) at 50 °C.^b Determined by 500 MHz ¹H NMR. ^c Yield of isolated pure product. ^d 1 mol % **1** for all cycles (1–7). ^e In PhCF₃/CH₂Cl₂ (1:49 v/v, 25 mL). ^f **30** (0.25 mmol) and 5 mol % **1** in PhCF₃/CH₂Cl₂ (1:9 v/v, 5 mL). ^g **30** (0.25 mmol) and 5 mol % **1** in PhCF₃ (5 mL). ^h **31** (0.10 mmol) and 5 mol % **1** in PhCF₃ (2 mL). ⁱ **23** (0.25 mmol) and 2 mol % **1** in PhCF₃/CH₂Cl₂ (1:9 v/v, 5 mL).

however, the recovered catalyst still remained highly active, further attesting to the stability and recyclability of **1**.

In conclusion, we have shown that catalyst **1** can be readily assembled from an easily accessible fluorous polymer. Compared with catalyst **3** and other immobilized Ru catalysts, **1** has the combined advantage of high reactivity and a high level of recyclability and reusability. Given the growing interest in fluorous chemistry and the widespread application of olefin metathesis, **1** should prove to be of unique utility in both areas.

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Supporting Information Available: Experimental details and full characterization of all new compounds (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) The loading of **1** was estimated based on full conversion of the styrene ligand of **8**. The estimated value represents an upper limit of the actual amount of the catalyst, which should be slightly lower due to the presence of a small amount of free ligand that remained unreacted (less than 10% as revealed by 500 MHz ¹H NMR spectroscopy).
- (11) In the PhCF₃/CH₂Cl₂ (1:9 to 1:49 v/v) mixed solvent system the reaction was monophasic, whereas the biphasic system FC-72/CH₂Cl₂ (1:1 v/v) gave less satisfactory results (see the Supporting Information for details).
- (12) The recycling of **1** can simply be carried out in the air by fluorous extraction of the crude reaction mixture dissolved in EtOAc with FC-72. The FC-72 solvent can be conveniently recycled and reused provided an efficient cooling trap is attached to the evaporator.
- (13) For further recycling and reuse of **1**, see the Supporting Information.
- (14) Only the less volatile PhCF₃ was used as the solvent when an extended reaction time was required.
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