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Novel Ruthenium-Based Metathesis Catalysts Containing Electron-Withdrawing Ligands: Synthesis, Immobilization, and Reactivity

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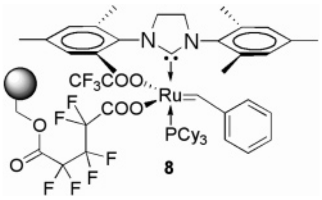

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The syntheses and reactivity of seven different ruthenium-based metathesis catalysts are described. $Ru(CF_3COO)_2(PCy_3)(=CH\text{-}2\text{-}(2\text{-}PrO)C_6H_4)$ (**1**), $Ru(CF_3COO)_2$(1,3-dimesityldihydroimidazolin-2-ylidene)($=CH\text{-}2\text{-}(2\text{-}PrO)C_6H_4$) (**2**), and $Ru(CF_3COO)_2(PCy_3)$(1,3-dimesityldihydroimidazolin-2-ylidene)($=CH\text{-}C_6H_5$) (**3**) were prepared via chlorine exchange by reacting $RuCl_2(PCy_3)_2(=CH\text{-}2\text{-}(2\text{-}PrO)C_6H_4)$, $RuCl_2$(1,3-dimesityldihydroimidazolin-2-ylidene)($=CH\text{-}2\text{-}(2\text{-}PrO)C_6H_4$), and $RuCl_2(PCy_3)$(1,3-dimesityldihydroimidazolin-2-ylidene)($=CHC_6H_5$), respectively, with silver trifluoroacetate (Cy = cyclohexyl). In analogy, $Ru(CF_3CF_2COO)_2$(1,3-dimesityldihydroimidazolin-2-ylidene)($=CH\text{-}2\text{-}(2\text{-}PrO)C_6H_4$) (**4**) and $Ru(CF_3CF_2CF_2COO)_2$(1,3-dimesityldihydroimidazolin-2-ylidene)($=CH\text{-}2\text{-}(2\text{-}PrO)C_6H_4$) (**5**) were prepared from $RuCl_2$(1,3-dimesityldihydroimidazolin-2-ylidene)($=CH\text{-}2\text{-}(2\text{-}PrO)C_6H_4$) via reaction with CF_3CF_2COOAg and $CF_3CF_2CF_2COOAg$, respectively. $Ru(C_6F_5COO)_2$(1,3-dimesityldihydroimidazolin-2-ylidene)($=CH\text{-}2\text{-}(2\text{-}PrO)C_6H_4$) (**6**) and $Ru(C_6F_5O)_2$(1,3-dimesityldihydroimidazolin-2-ylidene)($=CH\text{-}2\text{-}(2\text{-}PrO)C_6H_4$) (**7**) were prepared from $RuCl_2$(1,3-dimesityldihydroimidazolin-2-ylidene)($=CH\text{-}2\text{-}(2\text{-}PrO)C_6H_4$) via reaction with C_6F_5COOTl and C_6F_5OTl, respectively. Supported catalysts Ru(PS-DVB-$CH_2OOCCF_2CF_2CF_2COO)(CF_3COO)(PCy_3)$(1,3-dimesityldihydroimidazolin-2-ylidene)($=CHC_6H_5$) (**8**), Ru(PS-DVB-$CH_2OOCCF_2CF_2CF_2COO)(CF_3COO)(PCy_3)(=CH\text{-}2\text{-}(2\text{-}PrO)C_6H_4)$ (**9**), and Ru(PS-DVB-$CH_2OOCCF_2CF_2CF_2COO)(CF_3COO)$(1,3-dimesityldihydroimidazolin-2-ylidene)($=CH\text{-}2\text{-}(2\text{-}PrO)C_6H_4$) (**10**) were synthesized by reaction of $RuCl_2(PCy_3)$(1,3-dimesityldihydroimidazolin-2-ylidene)($=CHC_6H_5$), $RuCl_2(PCy_3)(=CH\text{-}2\text{-}(2\text{-}PrO)C_6H_4)$, and $RuCl_2$(1,3-dimesityldihydroimidazolin-2-ylidene)($=CH\text{-}2\text{-}(2\text{-}PrO)C_6H_4$), respectively, with a perfluoroglutaric acid-derivatized poly(styrene-*co*-divinylbenzene) (PS-DVB) support (silver form). Halogen exchange in PCy_3-containing systems had to be carried out in dichloromethane in order to suppress precipitation of $AgCl\cdot PCy_3$. The reactivity of all new catalysts in ring-closing metathesis (RCM) of hindered electron-rich and -poor substrates, respectively, at elevated temperature (45 °C) was compared with that of existing systems. Diethyl diallylmalonate (DEDAM, **11**), diethyl allyl(2-methylallyl)malonate (**12**), *N*,*N*-diallyl-*p*-toluenesulfonamide (**13**), *N*-benzyl-*N*-but-1-en-4-ylbut-2-enecarboxylic amide (**14**), and *N*-allyl-*N*-(1-carboxymethyl)but-3-en-1-yl-*p*-toluenesulfonamide (**15**) were used as educts. Supported catalysts were prepared with high loadings (2.4, 22.1, and 160 mg of catalyst/g PS-DVB for **8**, **9**, and **10**, respectively). Catalyst **8** showed higher and catalysts **9** and **10** sowed significantly reduced activities in RCM compared to their homogeneous analogues. Thus, with **8**, turnover numbers (TONs) up to 4200 were realized in stirred-batch (carousel) RCM experiments. To elucidate the nature of the bound species, catalysts **8**−**10** were subjected to ^{13}C- and ^{31}P-MAS NMR spectroscopy. These investigations provided evidence for the proposed structures. Leaching of ruthenium into the reaction mixture was low, resulting in ruthenium contents <85 ppb (ng/g) in the final RCM-derived products.

Introduction

The development of highly active ruthenium-based catalysts for various applications in metathesis-derived reactions proceeded in an evolutionary way by optimizing the ligand sphere around the corresponding metal center.[1] Thus, replacing phosphines by highly basic N-heterocyclic carbenes (NHCs) increased reactivity by many orders.[2,3] Similarly, the introduction of the "Hoveyda-ligand", i.e., the [$=CH\text{-}2\text{-}(2\text{-}PrOC_6H_4)$] carbene ligand resulted in metathesis catalysts with increased stability and excellent recyclability.[4,5] Further variations and

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improvements of this ligand were reported by the Blechert and Grela groups.[6−15] In a joint research project, Nuyken and Buchmeiser et al. recently reported on the synthesis of various ruthenium-based metathesis catalysts prepared by the replacement of both chlorine atoms in $RuCl_2(NHC)(CHR)$ (NHC = 1,3-dimesitylimidazol-2-ylidene, 1,3-dimesityl-4,5-dihydroimidazolin-2-ylidene, 1,3-dimesityl-3, 4, 5, 6-tetrahydropyrimidin-2-ylidene, R = 2-(2-PrO)-C_6H_4, 2-(2-PrO)-5-$NO_2C_6H_3$) by carboxylates.[16−20] Where fluorinated carboxylates were used, a dramatic increase in reactivity was observed, even allowing the use of these systems in the cyclopolymerization of 1,6-heptadiynes.[18,21] On the basis of the reaction of polymer-bound silver carboxylates, the immobilization of various catalysts was accomplished. However, chemistry was so far restricted to phosphine-free systems, since phosphine-containing catalysts suffered from lack of stability due to the formation of $AgCl{\cdot}PCy_3$ during synthesis. Our aim was to apply the concept of chlorine replacement by ligands containing electron-withdrawing groups to phosphine catalysts. In this paper, we report on the synthesis of metathesis catalysts based on PCy_3 and $IMesH_2$ ligands (PCy_3 = tricyclohexylphosphine, $IMesH_2$ = 1,3-dimesityldihydroimidazolin-2-ylidene) accessible via replacement of both chlorines by trifluoroacetate groups. In addition, heterogenization on poly(styrene-*co*-divinylbenzene) resins is described. The nature of the polymer-bound species was elucidated by ^{1}H-, ^{13}C- and ^{31}P-MAS NMR spectroscopy. To benchmark the new systems in terms of their reactivity, they were all subjected to various RCM reactions using diethyl diallylmalonate (DEDAM, **11**), diethyl allyl(2-methylallyl)malonate (**12**), *N*,*N*-diallyl-*p*-toluenesulfonamide (**13**), *N*-benzyl-*N*-but-1-en-4-ylbut-2-enecarboxylic amide (**14**), and *N*-allyl-*N*-(1-carboxymethyl)but-3-en-1-yl-*p*-toluenesulfonamide (**15**) as substrates. In this paper, the synthesis of the new catalysts, their structure, and catalytic activity shall be outlined in detail. Catalyst loadings were chosen in a way that both the maximum TON as well as the amount of catalyst necessary for a conversion >90% were determined.

Results and Discussion

Synthesis and Structure of Ru Complexes 1−7. The phosphine-containing compounds "Grubbs−Hoveyda 1st generation" and "Grubbs−Herrmann" ("Grubbs 2nd generation") catalyst as well as the phosphine-free Grubbs−Hoveyda 2nd generation catalyst (Figure 1) were used as precursors for the synthesis of the new chlorine-free catalysts.

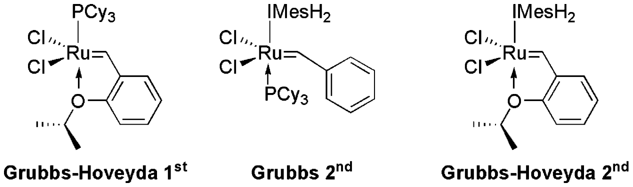

FIGURE 1. Structures of the "Grubbs−Hoveyda 1st generation", "Grubbs−Herrmann" ("Grubbs' 2nd generation"), and "Grubbs−Hoveyda 2nd generation" catalyst ($IMesH_2$ = 1,3-dimesityldihydroimidazolin-2-ylidene).

Though substitution of one chlorine by alkyl carboxylates and substitution of both chlorines by trifluoromethanesulfonate or other electron-withdrawing ligands such as fluoroalkyl carboxylates is meanwhile a well-established proocedure with phosphine-free catalysts,[19,20] substitution of chlorines in *phosphine-based systems* has not been realized yet. This is a direct consequence of the formation of $AgCl{\cdot}PCy_3$ in the course of the reaction, which was carried out in THF so far in order to dissolve the silver carboxylates.[19,20] However, in the case where the (phosphane-containing) catalyst precursor was added to a solution of the corresponding silver carboxylate in *methylene chloride* instead of THF, a clean reaction occurred.

Apparently, the noncoordinating solvent methylene chloride dissolved only small amounts of the silver salt, thus preventing the formation of $AgCl{\cdot}PCy_3$. Keeping this particularity in mind, catalysts **1**−**5** were prepared in yields up to 98% (Scheme 1). To investigate the influence of even more electron-withdrawing and sterically demanding ligands, catalysts **6** and **7** were synthesized. For their synthesis, the corresponding thallium salts had to be used. Apart from toxicity, some advantages have to be mentioned. On one hand, thallium salts are stable toward light; on the other hand, synthesis is simplified,

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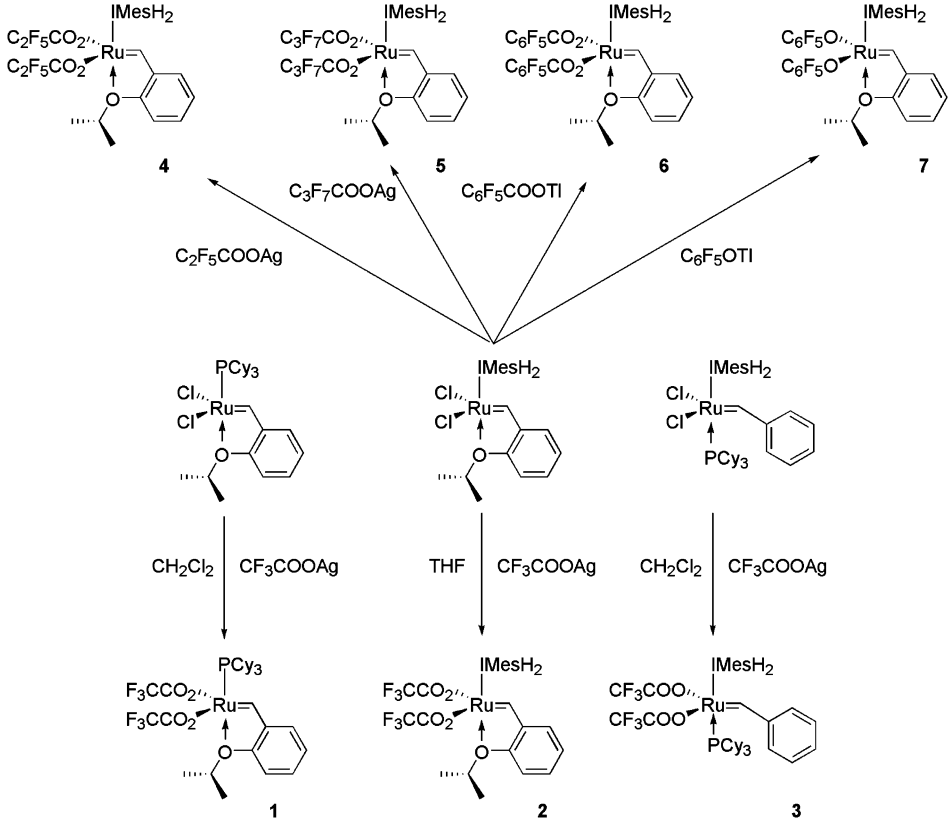
SCHEME 1. Synthesis of Catalysts 1−7



as TlOEt deprotonates and forms the thallium salt in situ. Using this approach, compounds **6** and **7** were prepared in 87 and 85% yield, respectively. Generally, catalysts **1**−**7** are stable in the solid state even upon exposure to air; however, solutions (particularly diluted ones) cannot be stored for an unlimited amount of time.

Reactivity of Catalysts 1−7 in Ring-Closing Metathesis (RCM). Turnover numbers (TONs) rather than yields are given as a measure for reactivity. Though organic chemists are more interested in yields when running a particular reaction, TONs allow for estimating the reactivity of a catalyst, particularly in the case where yields are <85%. In this case, TONs represent the *maximum reactivity* attainable in the chosen solvent at a certain concentration, catalyst-to-substrate ratio, and temperature and are therefore the preferred indicator for catalyst evaluation. In a first set of reactions, catalysts **1**−**7** were used for the RCM of diethyl diallylmalonate (DEDAM, **11**). As can be deduced from Table 1, the phosphane-based catalyst **1** showed basically no reactivity at all. Reactivity was also comparably low for **3** (Table 1); therefore, its use was limited to the reaction with DEDAM. Good reactivity in terms of turnover numbers (TONs) was observed for the NHC-based catalysts **2** and **4**−**7**. In particular, catalyst **5** showed high reactivity; however, none of the systems could rival the reactivity of the parent systems (Grubbs−Hoveyda 1st generation", "Grubbs 2nd generation", Grubbs−Hoveyda 2nd generation catalyst). Similar results were obtained in the RCM reaction of diethyl allyl-(2-methylallyl)malonate (**12**) and *N*,*N*-diallyl-*p*-toluenesulfonamide (**13**), Scheme 2, Tables 2 and 3) Surprisingly, the reactivity of catalysts **1**, **2**, and **4**−**6** for *N*-benzyl-*N*-but-1-en-4-ylbut-2-enecarboxylic amide (**14**) was quite low. In contrast, **1**, **2**, and **6** showed good reactivity in terms of TONs for *N*-allyl-*N*-(1-carboxymethyl)but-3-en-1-yl-*p*-toluenesulfonamide (**15**), with catalyst **2** almost rivaling the parent catalysts. Again in terms of TONs, the use of benzoate ligands, yielding **6**, results in a catalyst with good reactivity for DEDAM, **12**, and **13** yet modest reactivity for **14** and **15**. However, substitution of the chlorines with a perfluorated phenoxide dramatically decreased reactivity. In fact, reactivity

TABLE 1. Results for the RCM of Diethyl Diallylmalonate (DEDAM, 11) with Catalysts 1, 2, 4−7, and 8−10[a]

catalyst	mol % of compd	yield (%)	TON
Grubbs 1st	0.02	53	2650
Grubbs−Hoveyda 1st	0.02	81	4050
Grubbs−Hoveyda 1st	0.1	>99	1000
Grubbs 2nd	0.01	61	6100
Grubbs 2nd	0.02	85	4250
Grubbs−Hoveyda 2nd	0.02	91	4550
1	0.02	<1	
1	0.1	4	40
2	0.02	43	2150
3	0.02	9	450
4	0.02	50	2500
5	0.02	67	3350
6	0.02	51	2550
7	0.02	8	400
8	0.01	37	3660
8	0.02	54	2680
9	0.02	<1	
9	0.1	4	40
10	0.02	6	300
10	0.1	18	180

[a] Conditions: solvent, CH_2Cl_2; $T = 45$ °C; $t = 18$ h.

SCHEME 2. Summary of RCM Experiments with Monomers 11−15 Carried out with Catalysts 1−9

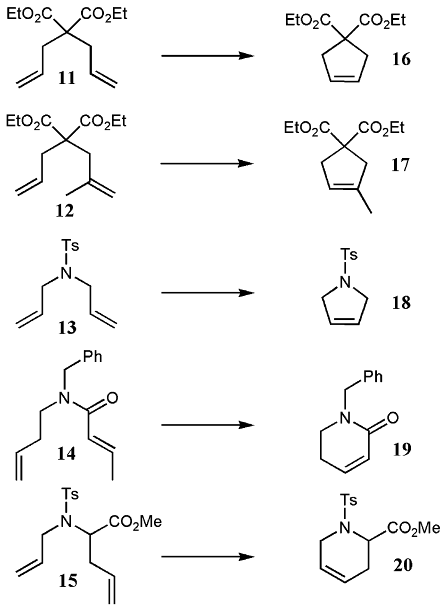


TABLE 2. Results for the RCM of Diethyl Allyl(2-methylallyl)malonate (12) with Catalysts 1, 2, 6, and 8−10[a]

catalyst	mol % of compd	yield (%)	TON
Grubbs 1st	0.2	83	410
Grubbs−Hoveyda 1st	0.2	81	410
Grubbs 2nd	0.05	36	720
Grubbs 2nd	0.2	99	500
Grubbs−Hoveyda 2nd	0.2	98	500
1	0.2	2	2
2	0.2	3	15
6	0.2	84	420
8	0.05	29	570
8	0.2	90	450
9	0.2	0	
9	0.5	0	
10	0.1	19	190
10	0.2	32	160

[a] Conditions: solvent, CH_2Cl_2; $T = 45$ °C; $t = 18$ h.

TABLE 3. Results for the RCM of *N,N*-Diallyl-*p*-toluenesulfonamide (13) with Catalysts 1, 2, 6, and 8−10

catalyst	mol % of compd	yield (%)	TON
Grubbs 1st	0.02	52	2600
Grubbs−Hoveyda 1st	0.02	92	4600
Grubbs 2nd	0.01	34	3400
Grubbs 2nd	0.02	54	2700
Grubbs−Hoveyda 2nd	0.02	66	3300
1	0.1	76	760
2	0.02	59	3000
6	0.02	58	2900
8	0.01	42	4200
8	0.05	91	1820
9	0.1	21	210
9	0.5	92	180
10	0.02	< 1	-
10	0.1	< 1	-

[a] Conditions: solvent, CH_2Cl_2; $T = 45$ °C; $t = 18$ h.

versus DEDAM was low (TON = 400), and its reactivity for **14** was actually zero. This is in strong contrast to a paper by Fogg et al.[22] Here, the synthesis of Ru(Py)-(C_6F_5O)(IMes)(CHPh) and TONs up to 40 000 in the RCM of DEDAM were reported. Since no further RCM data were reported for this catalyst, it is hard to judge whether these differences are substrate specific or a result of the combination of the pyridine with IMes ligand. So far, effects of replacement of the chlorines by other ligands on reactivity are still based on serendipity. Thus, Grubbs et al. performed halogen variations with the $RuCl_2(=CH-CHCPh_2)(PCy_3)_2$ system.[23] Replacement of both chlorine ligands by bromine, iodine, or trifluoroacetate lead 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.[24] In asymmetric RCM, an almost dramatic change in enantioselectivity was found when the ligand sphere in $RuCl_2$(CHPh)-(NHC)-type complexes bearing chiral NHCs is changed from Cl to Br and I, respectively.[25] Thus, substitution of the halides in this type of complexes by other groups has in fact a dramatic effect on reactivity; however, it is hard to predict whether it will be an increase or decrease since electronic and steric factors play an important role.

From this set of data, three conclusions can be drawn. First, the reactivity of soluble, monomeric, both phosphine- and NHC-based catalysts bearing electron-withdrawing ligands in RCM is generally equal or lower than that of the parent, chlorine-containing systems. Second, it is evident that with catalysts **1**−**7** electron-poor double bonds give lower TONs, whereas electron-rich double bonds tend to give higher TONs. This finding is in accordance with the fact that only catalysts containing electron-withdrawing substituents can in contrast to their precursor catalysts cyclopolymerize the rather electron-rich 1,6-heptadiynes.[18,21]

Finally, reactivity, in particular the differences in reactivity of the catalysts presented here, clearly underlines an early statement given by Fürstner that no catalyst is an equally good one for every substrate one can offer, i.e., that reactivity in RCM (and other metathesis based reactions) depends on distinct catalyst−substrate issues.[26]

Synthesis and Structure of Supported Catalysts 8−10. Numerous immobilized versions of ruthenium-based metathesis catalysts have been reported so far.[27,28] For the purpose of preparing immobilized versions of catalysts **1**−**3**, hydroxymethylpolystyrene (PS-DVB-CH_2-OH, 1.7 mmol of CH_2OH/g, cross-linked with 1% DVB) was reacted with perfluoroglutaric anhydride following a procedure published by Nieczypor et al.[29,30] and later optimized by our group (Scheme 3).[16−21]

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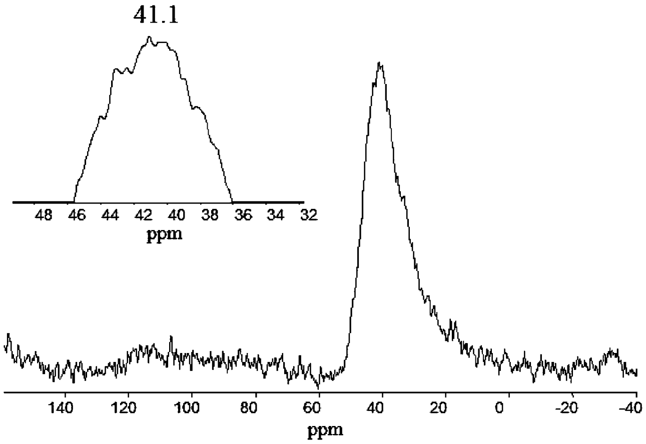

FIGURE 2. ^{31}P-MAS NMR of Ru(PS-DVB-$CH_2OCOCF_2CF_2CF_2COO$)(CF_3CO_2)(PCy_3)($IMesH_2$)(=CHC_6H_5) (**8**).

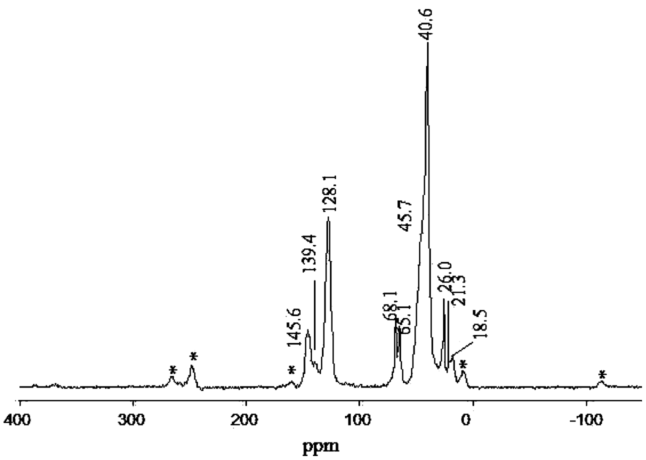

FIGURE 3. ^{13}C-CP-MAS NMR of Ru(PS-DVB-$CH_2OCOCF_2CF_2CF_2COO$)(CF_3CO_2)(PCy_3)($IMesH_2$)(=CHC_6H_5) (**8**) (* = rotating sidebands).

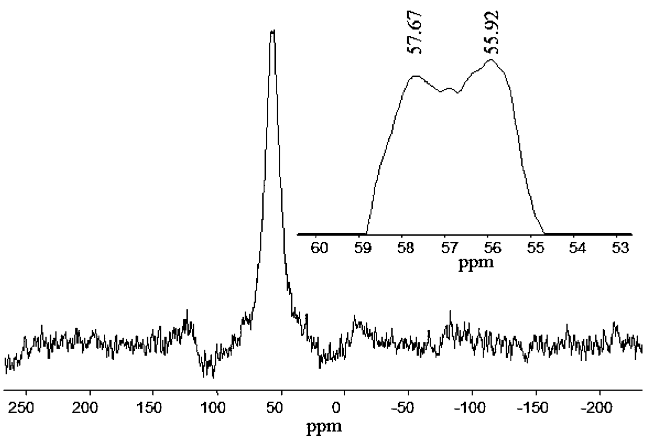

FIGURE 4. ^{31}P-MAS NMR of Ru(PS-DVB-$CH_2OCOCF_2CF_2CF_2COO$)(CF_3CO_2)(PCy_3)(=CH-2-(2-PrO)C_6H_5) (**9**).

Catalyst loadings of 2.4 and 22.1 mg/g were determined for catalysts **8** and **9**, respectively. As reported previously, the catalyst loading for **10** was 160 mg/g.[20] It is worth mentioning that catalysts **8** and **9** represent the first permanently bound versions of both Grubbs' 2nd and the Grubbs–Hoveyda 1st generation catalyst. In contrast to compound **3**, the supported version **8** was accessible in pure analytical form after excessive washing with THF as evidenced through MAS NMR spectroscopy. Thus, all supported catalysts were subjected to ^{1}H-, ^{13}C-, and ^{31}P-MAS NMR spectroscopy. To confirm the structures of the bound species, both the benzylidene and phosphine signals were considered. The ^{31}P-MAS NMR spectrum of **8** shows one (broad) phosphine species at $\delta = 41.1$ ppm (Figure 2). For comparison, **3** shows two signals at $\delta = 41.2$ and 45.1, the latter resulting from contaminant AgCl·PCy_3 ($\delta = 43.3$ ppm in $CDCl_3$). The ^{13}C NMR-CP-MAS spectrum of **8** shows a signal at $\delta = 18.5$ ppm (*o*-CH_3 of the $IMesH_2$-ligand) and shoulder at 21.3 ppm (*p*-CH_3 of the $IMesH_2$-ligand, Figure 3). The ^{31}P-MAS NMR of **9** (Figure 4) showed a resonance at $\delta = 56.8$ ppm, which is basically the identical shift found in the homogeneous mimic (**1**, $\delta = 57.5$ ppm). The doublet results from the coupling of the phosphine with the benzylidene proton.

SCHEME 3. Synthesis of Catalysts 8–10

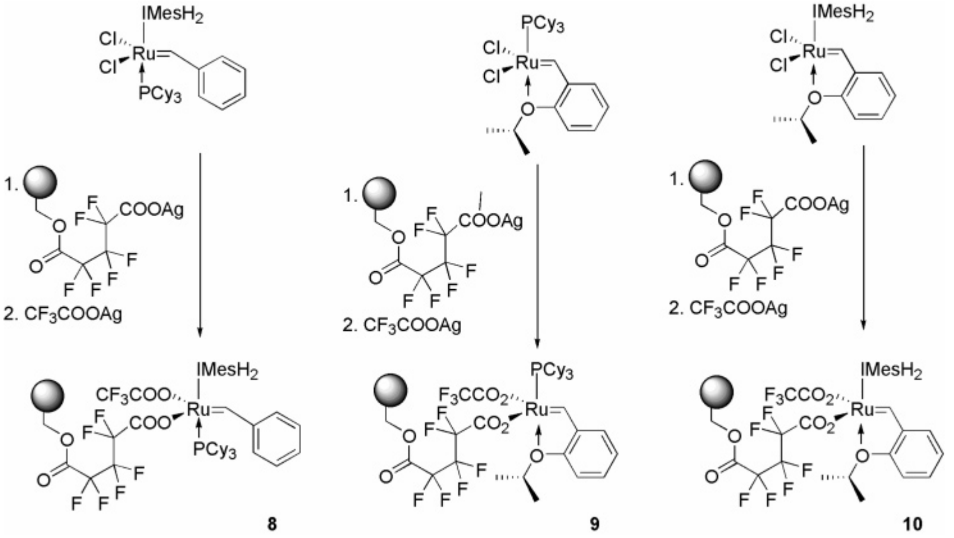

TABLE 4. Results for the RCM of *N*-Benzyl-*N*-but-1-ene-4-ylbut-2-enecarboxylic Amide (14) with Catalysts 1, 2, and 4−10

catalyst	mol % of compd	yield (%)	TON
Grubbs 1st	0.01	4	40
Grubbs−Hoveyda 1st	0.1	11	100
Grubbs−Hoveyda 1st	0.5	92	180
Grubbs 2nd	0.02	58	2900
Grubbs 2nd	0.1	93	930
Grubbs−Hoveyda 2nd	0.1	80	800
1	0.1	<1	
1	0.5	8	16
2	0.1	3	30
4	0.1	3	30
5	0.1	2	20
6	0.1	13	130
7	0.1	<1	
8	0.02	29	1450
8	0.1	99	1000
9	0.1	4	40
9	0.5	49	100
10	0.1	<1	

[a] Conditions: solvent, CH_2Cl_2; $T = 45$ °C; $t = 18$ h.

TABLE 5. Results for the RCM of *N*-Allyl-*N*-(1-carboxymethyl)but-3-en-1-yl-*p*-toluenesulfonamide (15) with Catalysts 1, 2, 6, and 8−10[a]

catalyst	mol % of compd	yield (%)	TON
Grubbs 1st	0.02	20	1000
Grubbs−Hoveyda 1st	0.1	65	650
Grubbs 2nd	0.01	31	1560
Grubbs−Hoveyda 2nd	0.02	35	1760
1	0.1	72	720
2	0.02	28	1400
6	0.02	19	950
8	0.02	55	2750
8	0.1	98	980
9	0.02	3	150
9	0.1	36	360
9	0.5	100	200
10	0.02	1	70
10	0.1	8	80

[a] Conditions: solvent, CH_2Cl_2; $T = 45$ °C; $t = 18$ h.

Reactivity of Supported Catalysts 8−10 in RCM. All three supported catalysts were investigated for their RCM reactivity. While the use of the supported catalysts **9** and **10** in the RCM of diethyl diallylmalonate (DEDAM, **12**), diethyl allyl(2-methylallyl)malonate (**11**), *N*,*N*-diallyl-*p*-toluenesulfonamide (**14**), *N*-benzyl-*N*-but-1-en-4-ylbut-2-enecarboxylic amide (**13**), and *N*-allyl-*N*-(1-carboxymethyl)but-3-en-1-yl-*p*-toluenesulfonamide (**15**) resulted in TONs up to 360 (Tables 1−5), the reactivity of **3** was dramatically increased by immobilization (resulting in **8**). In fact, reactivity in some cases rivaled and exceeded reactivity of the precursor catalysts (Tables 3−5). We attribute this to two different effects. On one hand, catalyst reformation via phosphine exchange is certainly faster than it is the case with **9** and **10**, which require metathesis with the intermediary formed 2-(2-PrO)styrene. On the other hand, bimolecular decomposition is certainly more effectively suppressed via immobilization, leading to improved stability and durability compared to parent **3**.

Recyclability and Leaching. Reactions described in this paper were run to an extent where no unreacted catalyst could be recovered. This implies that all catalyst was consumed, took part in the RCM reactions, and finally decomposed. Therefore, no recycling studies have been performed. In the case of supported catalysts, leaching was low, resulting in an average ruthenium contamination of the products of 83, 15, and 70 ppb, respectively, for catalysts **8**, **9**, and **10**.

Conclusion

In summary, a series of novel supported and unsupported metathesis catalysts have been prepared. No general trend in terms of reactivity was observed upon heterogenization. With Hoveyda 1st generation type catalysts, a significant loss of reactivity was observed. Both monomeric and polymer-bound catalysts showed similar behavior. Hoveyda 2nd generation-type catalysts based on fluorinated carboxylates and phenolates distinguished between electron-poor substrates and electron-rich substrates. Lower reactivity was observed with the former ones, while reactivity appears to be preserved with the latter. Finally and important enough, immobilization of Grubbs' 2nd generation catalyst using fluorinated carboxylates resulted in the preservation, sometimes even in an increase in RCM reactivity, making this supported version a highly attractive one for various application that require catalyst immobilization, e.g., for high-throughput screening.

Experimental Section

General Remarks. NMR data were obtained at 300 K at 300.13 (500) MHz for proton, 121.49 (202.48) MHz for phosphorus, and at 75.74 (126.23) MHz for carbon, respectively, in the indicated solvent and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Coupling constants are listed in Hz. IR spectra were recorded using ATR technology. Mass spectra were recorded using EI (70 eV). Syntheses of the ligands and catalysts were performed under an argon atmosphere by standard Schlenk techniques or in an Ar-mediated drybox unless stated otherwise. Reagent-grade diethyl ether, pentane, THF, and toluene were distilled from sodium benzophenone ketyl under argon. Reagent-grade dichloromethane was distilled under argon from calcium hydride or sicapent (P_4O_{10}), respectively. Other solvents and reagents were used as purchased. Deionized water was used throughout. $RuCl_2(=CHPh)(IMesH_2)(PCy_3)$ ($IMesH_2$ = 1,3-bis-(2,4,6-trimethylphenyl)-4,5-dihydroimidazolin-2-ylidene), $RuCl_2(=CH\text{-}2(2\text{-}PrO)C_6H_4)(PCy_3)$, CF_3SO_3Ag, CF_3COOAg, PS-DVB-CH_2OH (100−300 mesh, 1.7 mmol Ar-CH_2OH/g, 1% cross-linked), and perfluoroglutaric anhydride were purchased. A ruthenium standard containing 1000 ppm of ruthenium (in 1 M HNO_3) was used. Catalysts **2**, **4**, **5**, and **10** were prepared as described in previous disclosures.[20,21]

MAS Experiments. Samples were packed into 4 mm ZrO_2 rotors. Measurements were performed at $B_0 = 11.7$ T. The samples were spun at 15 kHz unless stated otherwise. ^{1}H NMR spectra were recorded as the sum of 100 scans with a recycle time of 2 s. A 2.8 μs pulse was applied. The RF field was 89 kHz. Spectra were calibrated against an external standard of adamantane (2.00 ppm). ^{13}C-CP-MAS NMR was measured using cross-polarization with gradient pulses. The contact time was 2 ms. Continuous wave decoupling was applied during data acquisition. The spectra consisted of at least 10 000 scans with a recycle rate of 5 s. For calibration, the peak of the CH groups in adamantane was set to 29.472 ppm. To recognize spinning sidebands, a second spectrum was recorded at a spinning rate of 12 kHz, so that spinning sidebands appeared with different shifts. For ^{31}P NMR spectra, 12000 scans were recorded with a recycle time of 5 s. A 4 μs pulse was used. The RF field was 63 kHz. Chemical shifts for phosphorus are reported relative to $(NH_4)H_2PO_4$ at 1.11 ppm.

RCM Experiments. Reactions were run for 18 h in order to achieve complete conversion. For the homogeneous catalysts, a carousel working station under N_2 was used. The reaction volume was 1−4 mL. Heterogeneous catalysts were run in a N_2-mediated drybox using microreactors in a thermo shaker. Analyses were done by NMR after filtration for catalysts **2**, **4**, and **6** and by HPLC for catalysts **8** and **10**. No other products were found.

Ru(CF$_3$COO)$_2$(PCy$_3$)(=CH-2-(2-PrO)C$_6$H$_4$) (1). Silver trifluroacetate (23.2 mg, 0.105 mmol) was suspended in 10 mL of CH_2Cl_2. RuCl$_2$(PCy$_3$)(=CH-2-(2-PrO)C$_6$H$_4$) (30 mg, 0.05 mmol), dissolved in 0.5 mL of CH_2Cl_2, was added, and the solution was stirred for 30 min in the absence of light. The mixture was filtered through Celite/cellulose, and the solvent was reduced in vacuo. The product (37 mg, 0.049 mmol, 98%) was obtained as a red, foamy solid. Recrystallization from hexane/CH_2Cl_2 yielded red needles. IR (cm^{-1}): 724 (m), 735 (m), 863 (m), 929 (w), 1144 (s), 1190 (ss), 1391 (w), 1453 (m), 1642 (m), 1712 (s), 2854 (m), 2931 (s). ^{1}H NMR (500 MHz; CDCl$_3$): δ 1.22−1.33 (m, 9H), 1.45 (d, $J = 6.7$, 6H), 1.48−1.58 (m, 6H), 1.67−1.76 (m, 3H), 1.78−1.95 (m, 12H), 2.02−2.12 (m, 3H), 4.96−5.05 (m, 1H), 7.03 (d, $J = 8$, 1H), 7.19 (dd, $J_1 = J_2 = 7.5$, 1H), 7.62 (dd, $J_1 = J_2 = 8$, 1H), 7.80 (d, $J = 7.5$, 1H), 18.39 (d, $J = 6$, 1H). ^{13}C NMR (125.8 MHz; CDCl$_3$): δ 21.1, 26.3, 27.7, 29.0, 34.2, 34.4, 76.7, 112.7, 113.8 (q, $J = 288.5$), 123.4, 124.4, 131.2, 144.2 (q), 155.22 (q), 163.48 (q, $J = 33.7$), 308.5 (d, $J = 15.1$). ^{31}P NMR (202.5 MHz; CDCl$_3$): δ 56.6. ^{19}F NMR (470.6 MHz; CDCl$_3$): δ −74.6. EI-MS (200 °C): *m/z* = 756 (M$^+$), 642 (46), 600 (6), 404 (10), 375 (10), 281 (24), 243 (100%), 198 (54), 120 (62), 91 (36), 83 (54), 78 (60), 55 (75). HR-MS calcd for $C_{32}H_{45}F_6O_5PRu$): 756.1946, found 756.1933.

Ru(CF$_3$COO)$_2$(=CHC$_6$H$_5$)(IMesH$_2$)(PCy$_3$) (3). CF$_3$COOAg (10 mg, 0,043 mmol) was suspended in 10 mL of CH_2Cl_2 and stirred for 5 min. A solution of RuCl$_2$(=CH−C$_6$H$_5$)(IMesH$_2$)(PCy$_3$) (17.8 mg, 0.021 mmol) in 2 mL of CH_2Cl_2 was added. Stirring was continued for 5 min. A color change from red to green-brown and the formation of a precipitate was observed. The precipitate was filtered off, and the solution was filtered through Celite. Drying in vacuo provided a red powder. No satisfying elemental analysis was obtained due to coprecipitation of AgCl·PCy$_3$. Yield: 18.5 mg (0.018 mmol, 85%). IR-ATR (cm^{-1}): 2925 (s), 2851 (s), 1686 (s), 1631 (s), 1482 (s), 1448 (s), 1265 (s), 1192 (vs), 1136 (vs), 1030 (w), 1003 (w), 962 (vw), 851 (s), 785 (w), 737 (vs), 695 (s), 618 (vw). ^{1}H NMR (CDCl$_3$): δ 18.34 (s, 1 H, Ru=C*H*), 7.45 (d, 1 H, $J = 5.5$), 7.27 (m, 4 H), 6.93 (d, 1H, $J = 6.3$), 6.77 (m, 2 H), 4.09 (s, 4 H), 2.17 (m, 17 H), 1.80 (s, 20 H), 1.19 (m, 20 H). ^{13}C NMR (CDCl$_3$): δ 289.2, 184.4, 159.6, 140.7, 137.3, 135.4, 134.7, 129.7, 128.7, 127.8, 52.0, 31.9, 29.0, 27.8, 26.2, 20.8, 17.7, 14.1. Additional signals for AgCl·PCy$_3$: 31.2, 27.1, 25.8. ^{31}P{^{1}H}-NMR (CDCl$_3$): δ = 41.2, 45.1 (AgCl·PCy$_3$).

Ru(C$_6$F$_5$CO$_2$)$_2$(IMesH$_2$)(=CH-2-(2-PrO)C$_6$H$_4$) (6). RuCl$_2$(IMesH$_2$)(=CH-2-(2-PrO)C$_6$H$_4$) (200 mg, 0.32 mmol) was dissolved in 10 mL of THF, and a solution of TlCO$_2$C$_6$F$_5$ (2 equiv, 266 mg, 0.64 mmol), generated in situ from TlOC$_2$H$_5$ and C$_6$F$_5$CO$_2$H in a mixture of 1 mL of THF, 1 mL of methanol, and 1 mL of toluene, was slowly added. Stirring was continued for 3 h. A color change from red to brown and the formation of a precipitate was observed. The precipitate was filtered off and the solution evaporated to dryness. The solid was redissolved in CH_2Cl_2, centrifuged, and flashed over Celite. Drying in vacuo provided a lilac powder (272 mg, 0.28 mmol, 87%). IR (cm^{-1}): 2924 (br), 1663 (vs), 1594 (w), 1517 (s), 1479 (vs), 1333 (vs), 1267 (vs), 1210 (w), 1098 (s), 1034 (w), 987 (vs), 920 (s), 878 (w), 842 (w), 745 (vs), 699 (s), 574 (s). ^{1}H NMR (CDCl$_3$): δ 17.33 (s, 1 H, Ru=CHAr), 7.43 (d, 1 H, aromatic CH, $J = 9.0$), 7.01 (s, 4 H, mesityl CH), 7.23 (dd, 1 H, aromatic CH, $J_1 = 7.5$, $J_2 = 9.0$), 6.83 (dd, 1 H, aromatic CH, $J_1 = 7.5$, J_2 7.3), 6.59 (d, 1 H, aromatic CH, $J = 8.3$), 4.57 (sep, 1 H, (CH$_3$)$_2$CHOAr, $J = 6.0$), 3.98 (s, 4 H, N(CH$_2$)$_2$N), 2.36 (s, 6 H, mesityl *p*-CH$_3$), 2.03 (s, 12 H, mesityl *o*-CH$_3$), 0.98 (d, 6 H, (CH$_3$)$_2$CHOAr, $J = 6.0$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 313.5, 211.6, 160.7, 153.7, 144.8, 143.8, 139.2, 134.8, 129.6, 129.5, 128.6, 126.5, 123.5, 122.6, 111.0, 74.4, 51.3, 21.1, 20.0, 17.9. ESI-MS (acetonitrile/water) calcd for $C_{45}H_{38}N_2F_{10}O_5Ru$: 978.17, found 782.9 ($M^{+\bullet} + H^+ - C_6F_5CO$, 33), 307.4 (IMesH$_2$ + H$^+$, 29). Anal. Calcd for $C_{45}H_{38}N_2F_{10}O_5Ru$: C, 55.21; H, 3.92; N, 2.86. Found: C, 54.93; H, 4.30; N, 2.53.

Ru(C$_6$F$_5$O)$_2$(IMesH$_2$)(=CH-2-(2-PrO)C$_6$H$_4$) (7). RuCl$_2$(IMesH$_2$)(=CH-2-(2-PrO)C$_6$H$_4$) (200 mg, 0.32 mmol) was dissolved in 10 mL of THF, and a solution of TlOC$_6$F$_5$ (2 equiv, 260 mg, 0.64 mol), generated in situ from TlOC$_2$H$_5$ and C$_6$F$_5$OH in a mixture of 1 mL of THF, 1 mL of methanol, and 1 mL of toluene, was slowly added. Stirring was continued for 3 h. A color change from red to brown and the formation of a precipitate was observed. The precipitate was filtered off and the solution evaporated to dryness. The solid was redissolved in CH_2Cl_2, centrifuged, and filtered through Celite. Drying in vacuo provided a brown powder (249 mg, 0.27 mmol, 85%). IR-ATR (cm^{-1}): 2966 (br, s), 2921 (br, s), 1644 (w), 1617 (w), 1591 (w), 1575 (w), 1495 (vs), 1455 (vs), 1379 (w), 1294 (w), 1260 (vs), 1203 (w), 1158 (s), 1112 (s), 1106 (vs), 980 (vs), 851 (s), 794 (vs), 741 (vs), 629 (w). ^{1}H NMR (CDCl$_3$): δ 17.10 (s, 1 H, Ru=CHAr), 7.44 (dd, 1 H, aromatic CH, $J_1 = 1.5$, $J_2 = 2.0$), 7.11 (*s*, 4 H, mesityl CH), 7.26 (dd, 1 H, aromatic CH, $J_1 = 7.3$, $J_2 = 7.8$), 6.97 (dd, 1 H, aromatic CH, $J_1 = 1.5$, $J_2 = 1.5$), 6.80 (d, 1 H, aromatic CH, $J = 8.3$), 3.82 (sep, 1 H, (CH$_3$)$_2$CHOAr, $J = 6.0$), 4.10 (*s*, 4 H, N(CH$_2$)$_2$N), 2.41 (*s*, 6 H, mesityl *p*-CH$_3$), 2.28 (*s*, 12 H, mesityl *o*-CH$_3$), 0.67 (d, 6 H, (CH$_3$)$_2$CHOAr, $J = 6.0$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 296.3, 210.4, 150.2, 143.3, 142.3, 139.3, 136.1, 129.5, 128.7, 127.8, 126.5, 123.3, 122.0, 111.4, 74.7, 51.2, 21.2, 19.3, 18.1. HRMS calcd for $C_{43}H_{38}N_2F_{10}O_3Ru$: 922.18, found 922.30.

Ru(PS-DVB-CH$_2$OCOCF$_2$CF$_2$CF$_2$COO)(CF$_3$CO$_2$)(=CHC$_6$H$_5$)(IMesH$_2$)(PCy$_3$) (8). PS-DVB-CH$_2$OCOCF$_2$CF$_2$CF$_2$COOAg was prepared according to the literature.[31] PS-DVB-CH$_2$OCOCF$_2$CF$_2$CF$_2$COOAg (500 mg) was suspended in CH_2Cl_2 (15 mL), and RuCl$_2$(=CHC$_6$H$_5$)(IMesH$_2$)(PCy$_3$) (80 mg, 0.094 mmol), dissolved in CH_2Cl_2 (2 mL), was added slowly. The mixture was stirred for 90 min in the absence of light, and CF$_3$COOAg (21 mg, 0.094 mmol), dissolved in 2 mL of THF, was added. The reaction mixture was stirred for a further 90 min. The product was filtered and washed three times with THF (10 mL) until the filtrate was colorless. Drying in vacuo provided a red-lilac powder (450 mg). IR-ATR (cm^{-1}): 3082 (w), 3058 (w), 3024 (s), 2918 (br), 2849 (w), 1869 (w), 1773 (br), 1660 (br), 1601 (s), 1510 (s), 1492 (s), 1308 (w), 1265 (s), 1154 (br), 1029 (br), 908 (w), 819 (w), 751 (s), 697 (s). ^{1}H-MAS NMR: δ 6.99 (br), 3.79 (sh), 1.95 (sh). ^{13}C-CP-MAS NMR: δ 18.5, 21.3 (sh), 26.0, 40.6, 45.7 (sh), 65.1, 68.1, 128.1, 139.4, 145.6. ^{31}P-MAS NMR: δ 41.1. ICP-OES: 0.22 mg Ru/g. Anal. Found: C, 75.24; H, 6.45; N, 0.47.

Ru(PS-DVB-CH$_2$OCOCF$_2$CF$_2$CF$_2$COO)(CF$_3$CO$_2$)(=CH-2-(2-PrO)C$_6$H$_4$)(PCy$_3$) (9). PS-DVB-CH$_2$OCOCF$_2$CF$_2$CF$_2$COOAg (850 mg) was suspended in CH_2Cl_2 (25 mL), and RuCl$_2$(=CH-2-(2-PrO)C$_6$H$_4$)(PCy$_3$) (95.5 mg, 0.152 mmol) in CH_2Cl_2 (2 mL) was added. The mixture was stirred for 90 min in the absence of light. CF$_3$COOAg (35.2 mg, 0.152 mmol) was dissolved in THF (2 mL) and added to the catalyst. Stirring was continued for another 90 min. The product was filtered and washed three times with THF (10 mL) until the filtrate was colorless. Drying in vacuo provided a red-lilac powder (650 mg). IR (cm^{-1}): 3082 (w), 3058 (w), 3024 (s), 2919 (br), 2849 (w), 1939 (w), 1773 (br), 1656 (br), 1510 (s), 1451 (s), 1308 (w), 1154 (br), 1029 (br), 907 (w), 819 (w), 749 (s), 697 (s). ^{1}H-MAS NMR δ 7.34 (br), 4.05 (sh), 2.00 (sh). ^{13}C-CP-MAS NMR δ 40.7, 45.2 (sh), 65.1, 68.1, 128.0, 146.0. ^{31}P-MAS NMR δ 56.81 (d). ICP-OES: 2.62 mg Ru/g. Anal. Found: C, 73.55; H, 6.36.

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(31) Yang, L.; Mayr, M.; Wurst, K.; Buchmeiser, M. R. *Chem. Eur. J.* **2004**, *10*, 5761−5770.

Determination of Ruthenium Content. 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, $t = 32$ min). 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 ($\lambda = 240.272$ nm, ion line). The background was measured at $\lambda = 240.287$ and 240.257 nm, respectively. Standardization was carried out with Ru standards containing 0, 5, and 10 ppm of Ru.

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