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Benzylidene-Functionalized Ruthenium-Based Olefin Metathesis Catalysts for Ring-Opening Metathesis Polymerization in Organic and Aqueous Media

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Summary: New catalysts $(PCy_3)_2Cl_2Ru{=}CH(p\text{-}C_6H_4)CH_2\text{-}P(CH_3)_3{}^+Cl^-$ (**5**) *and* $(PCy_3)_2Cl_2Ru{=}CH(p\text{-}C_6H_4)CH_2\text{-}N(CH_3)_2$ (**6**) *as well as the literature compound* $(PCy_3)_2Cl_2Ru{=}CH(p\text{-}C_6H_4)N(CH_3)_2$ (**7**) *have been synthesized via alkylidene exchange from Grubbs' catalyst in a one-step reaction. The catalysts promoted ROMP of the cationic exo-7-oxanorbornene derivative* **11** *under homogeneous conditions in various protic media including aqueous/alcoholic 1:1 mixtures, and in many cases, particularly for catalysts* **5** *and* **6**, *the polymerizations proceeded in a controlled manner.*

There is an increasing demand for (co)polymeric materials in specialty applications with highly advanced architectures and narrow molecular weight distributions. Living ring-opening metathesis polymerization (LROMP) has recently emerged as a powerful tool for the polymer chemist, especially since the discovery of well-defined catalysts/initiators, due to the absence of side reactions such as termination or chain transfer.[1–3] Because of their high tolerance toward air, moisture, and functional groups,[4] Grubbs-type olefin metathesis catalysts have been proven to be particularly useful in organic[5] and polymer synthesis.[6] Their high tolerance also makes them attractive for use in aqueous media,[7] a nonhazardous and commercially highly attractive solvent for organic transformations.[8] There are several examples of ROMP materials prepared with narrow polydispersities using Grubbs' first-generation catalyst **1**,[1,9,10] dinuclear ruthenium alkylidene complexes,[11] and the superfast initiating third-generation catalyst **2**[12] in aprotic, organic solvents. However, there are only very few examples of controlled ROMP in homogeneous solution in protic media.[13] These reactions were conducted with catalysts **3** and **4**, analogues of catalyst **1** bearing water-soluble phosphine ligands, polymerizing water-soluble *exo*-(oxa)norbornene derivatives to access polyionic materials with narrow molecular weight distributions. The downside of catalysts **3** and **4** is their cumbersome synthesis and the costly nature of the water-soluble phosphine ligand of catalyst **3**. More recently, several metathesis-active, cationic catalysts bearing N-heterocyclic carbene (NHC) ligands have been reported. These become soluble in aqueous or protic media based on a hydrophilic NHC ligand[14–16] and/or hydrophilic benzylidene moieties.[16,17] The use of these catalysts for controlled ROMP of water-soluble monomers in protic media, however, very likely did not provide polymers with low polydispersity indices (PDIs), which were not reported,[14–16] due to the unfavorable ratio between the rates of initiation and propagation associated with NHC-ligated catalysts.[18,19] We now wish to report a new strategy to conduct controlled ROMP in protic media via benzylidene-functionalized olefin metathesis catalysts of the first-generation Grubbs-type motif. The catalysts have been used for controlled ROMP in various protic media.

Benzylidene exchange at Grubbs-type olefin metathesis catalysts represents a half-step cross-metathesis reaction and has

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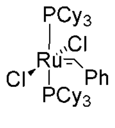

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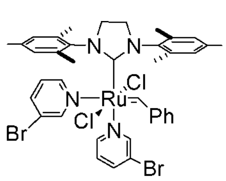

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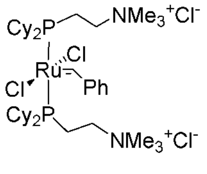

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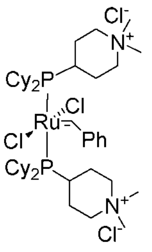

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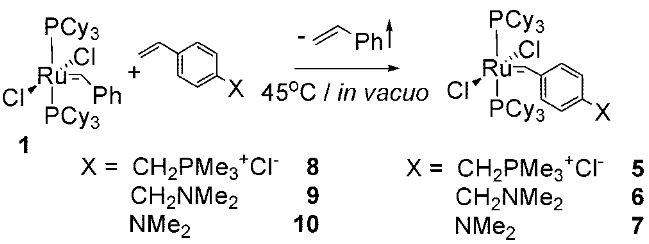
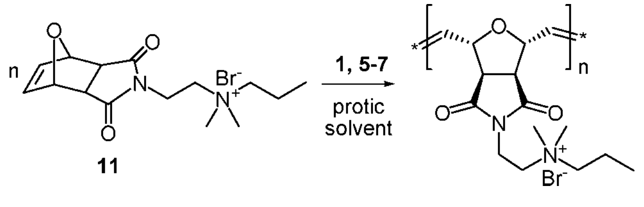
Scheme 1. Synthesis of Catalysts 5–7



Scheme 2. ROMP of Monomer 11 with Catalysts 5–7



been used to prepare a variety of catalysts.[20] Starting from Grubbs' catalyst **1** the addition of excess styrenic derivatives **8–10** afforded catalysts **5–7** in high yields (Scheme 1). The reactions were carried out in high-boiling solvents (**5**: *o*-dichlorobenzene/cyclohexanol (1:1 v/v); **6** and **7**: *o*-dichlorobenzene) under vacuum. Styrene formed as a byproduct of the exchange reaction was removed quantitatively by slow distillation of the solvent at 50 °C. Catalyst **7** has been prepared previously by Grubbs et al. via the aryldiazomethane route.[9] Catalyst **5** is permanently cationic, bearing a terminal $-PMe_3^+$ moiety, and is soluble in polar, aprotic solvents such as CH_2Cl_2 as well as various alcohols and alcohol/water (1:1 v/v) mixtures. In neutral media, catalysts **6** and **7** are neutrally charged and thus soluble in many organic solvents including benzene and CH_2Cl_2. In acidic media, the dimethylamino groups are protonated and thus the catalysts become cationic and are soluble in various alcohols. The protonated complex **6** is also soluble in alcohol/water (1:1 v/v) mixtures. Highly metathesis-active Ru complexes with cationic alkylidene moieties have been reported by Piers et al.,[21] but their potential as catalysts in protic media has not been examined.

In comparison to catalysts **3** and **4** the straightforward synthetic access to complexes **5–7** aided by the commercial availability of **1** makes them a highly attractive class of catalysts for controlled ROMP in protic media. Also, functionalized styrene derivatives are generally more economic and synthetically more readily accessible than the water-soluble phosphine ligands in catalysts **3** and **4**. It also makes the synthesis of a structural variety of catalyst motifs more feasible. With the catalysts in hand, ROMP reactions were conducted with the cationic *exo*-7-oxanorbornene derivative **11** (Scheme 2).[22] Derivative **11** is soluble in water, alcohols, and several nonprotic solvent/alcohol mixtures. Controlled ROMP of monomer **11** was accomplished with catalyst **1** homogeneously in CH_2Cl_2/2,2,2-trifluoroethanol (TFE) (1:1 v/v).[22] The bromide counteranion of the monomer plays a crucial role in the control of the reaction. Due to the vast excess of bromide compared to chloride, there is a rapid exchange with the chloride ligands bound to the metal center. Metathesis-active Br_2Ru(alkylidene) complexes are known to be overall less active catalysts in comparison to their dichloride counterparts, which is due to smaller rates of propagation, while the rates of initiation are higher.[18,20] However, the overall activity is not dramatically lower. Hence, the halide exchange makes this particular rate constant ratio more favorable for the preparation of ROMP (co)polymers with narrow molecular weight distributions, as reported recently for the polymerization of a cationic *exo*-7-oxanorbornene derivative with various Cl^-/Br^- counteranion ratios.[23]

ROMP was conducted under five different solution conditions with catalysts **5–7**, and the kinetics were determined. In all instances we targeted a molecular weight of 20 000 g/mol. In contrast to catalyst **1** catalysts **5–7** did not afford complete conversions in polymerizations in CH_2Cl_2/TFE (1:1 v/v) (entries 1–4, Table 1). After 6–8 min, the reaction slowed dramatically and eventually reached a plateau several minutes later. At this stage, the reason for this behavior is still unclear, in particular since the polymerizations follow near-first-order kinetics in the first 6 min, indicating a constant number of active species in that time period. All catalysts were less active (**5**: 5.9 times, **6**: 2.4 times, and **7**: 3.2 times) than catalyst **1** under these conditions.[21] As the rates of propagation should be virtually equal for all catalysts, the activity differences must be due to different initiation rates based on the different nature of the initial benzylidene. Studies have investigated the influence of the alkylidene moiety on the rates of initiation.[24] It has been demonstrated for benzylidene complexes that *para*-substitution has a slowing influence on the rates of initiation of first-generation Grubbs-type catalysts with the electronic nature of the substituent being of only minor importance.[9] This is consistent with our observation.

ROMP of monomer **11** in TFE afforded conversions >95% for catalysts **5–7** within 16–18 min. The addition of 2 equiv of 1 M HCl_{aq} was necessary to produce homogeneous solutions with pH-responsive catalysts **6** and **7**. TFE has a high dielectric constant, and this should improve the rates of initiation.[20] Indeed, reactions with catalysts **5** and **6** followed first-order kinetics and also more than double the conversion rate for catalyst **5**. For cationic catalyst **5** both conditions were applied, pure TFE and TFE + 2 equiv of 1.0 M HCl_{aq} (entries 5 and 6, Table 1), with no visible effect on activity. This is somewhat surprising,

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Table 1. Conversion of Monomer 11 with Catalysts 1 and 5–7 (10.0 mM catalyst solution, M_n(theory) = 20.000 g/mol)

entry	catalyst	solvent	% conversion (8 min)	k_{rel}
1[a]	**1**	CH_2Cl_2/TFE (50:50 v/v)	97.6	1 (±0.010)
2	**5**		42.5	0.170 (±0.011)[b]
3	**6**		72.9	0.418 (± < 0.001)[b]
4	**7**		63.2	0.317 (±0.003)[b]
5	**5**	TFE	78.3	0.357 (±0.004)
6	**5**	TFE + 2 equiv HCl	75.5	0.369 (±0.002)
7	**6**		81.6	0.416 (±0.003)
8	**7**		50.9	
9	**5**	TFE/1 M HCl_{aq} (50: 50 v/v)	76.4	0.323 (±0.006)
10	**6**		42.0	0.164 (±0.002)
11	**5**	TFE/0.1 M HCl_{aq} (50: 50 v/v)	24.4	0.070 (±0.001)
12	**6**		25.2	0.092 (±0.001)

[a] Data attained from ref 21. [b] Relative rate determined for 0–6 min (first-order kinetics).

as strong acids are able to protonate the basic phosphine ligand once dissociated from the metal center and thus increase the metathesis activity.[13,14,19,25] In contrast to complex **5** the ROMP activity of catalyst **6** (entry 7, Table 1) remains almost unchanged in TFE + 2 equiv of 1.0 M HCl_{aq} in the early minutes compared to TFE/CH_2Cl_2 (1:1 v/v). Apparently, the electronic change in the initial benzylidene moiety from amino to ammonium group upon protonation counterbalances the solvent effect, with the result being near-identical rates of initiation. However, there is no plateau reached in TFE + 2 equiv of 1.0 M HCl_{aq}, and the conversion goes beyond 95% within 16 min. ROMP with catalyst **7** (entry 8, Table 1) accelerated during the reaction as a result of a long induction period, which made the assessment of the catalyst activity only qualitative. In the first 10 min, the polymerization was significantly slower than with **5** and **6**, however proceeded at a faster rate after that time and also yielded >95% of polymer within 18 min. Such induction periods for ROMP reactions with slow-initiating second-generation catalysts have been observed before,[25] but it is rather likely that this is due to a low initial solubility of catalyst **7**. With progression of the polymerization, however, the polycationic polymer tethered to the ruthenium center improved the overall solubility of the propagating species. As a consequence, more initial catalyst gradually dissolved, initiated ROMP, and produced more propagating species. Such solubility effect by a hydrophilic propagating polymer chain was observed by Grubbs et al. when water-insoluble catalyst **1** was used in aqueous media in the presence of surfactant and a small amount of CH_2Cl_2 where the catalyst was initially dissolved.[26] The low solubility became apparent when catalyst **7** is used in mixed aqueous/alcoholic media under acidic conditions. In TFE/HCl_{aq} (0.1 M) (1:1 v/v), no ROMP product could be detected after 20 min, and only when the acid concentration was increased (TFE/$HCl_{aq.}$ (1 M), 1:1 v/v) was 5.5% of monomer converted after 20 min.

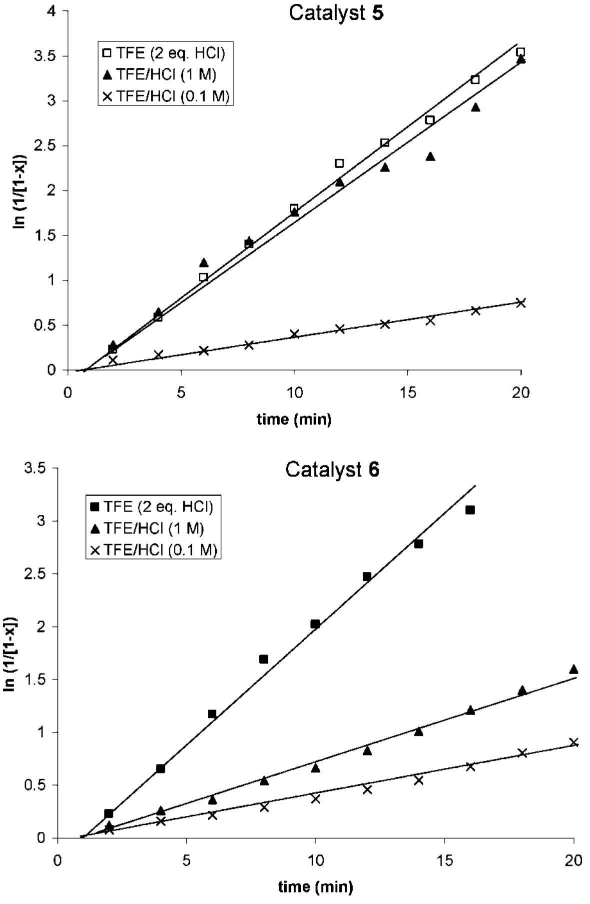

Figure 1. Conversion plots ln(1/[1 − *x*]) vs time for ROMP of monomer **11** with catalysts **5** and **6** under various protic solvent conditions.

ROMP was conducted with catalysts **5** and **6** in TFE/HCl_{aq} (1:1 v/v) mixtures. The acid was necessary not only to protonate the amino group in catalyst **6** but also to reduce the rate of recoordination of the hydrophobic PCy_3 ligand by converting it into the cationic, water-soluble $HPCy_3^+$ salt.[14] The necessity of this process becomes apparent when ROMP of monomer **11** was conducted with catalyst **5** in TFE/H_2O (1:1 v/v) without acid, and no detectable amounts of polymer were afforded after 20 min. In contrast, the polymerization proceeded with first-order kinetics (entries 9–12, Table 1) in the presence of HCl_{aq}. Figure 1 depicts the pseudo-first-order kinetic plots ln(1/[1 − *x*]) versus time for the ROMP of monomer **11** with catalysts **5** and **6**. Also, a significant difference in the rate of polymerization was observed with a higher acid concentration, resulting in faster conversions. This effect may be caused by two factors. (1) A higher acid concentration produces more $HPCy_3^+Cl^-$ salt. Despite the relatively high basicity of PCy_3,[27] protonation does not occur quantitatively due to the Lewis acidity of the ruthenium center. This has been observed previously by Grubbs et al. when adding various levels of DCl/D_2O to an aqueous solution of catalyst **3**, which resulted in an equilibrium between mono- and diphosphine complexes.[13a] It is suggested that the monophosphine complex has a water molecule coordinated to the open site, and the resulting species is a much faster

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Table 2. End-Group Analysis Data for Polymers Obtained from Conversion of Monomer 11 with Catalysts 5–7 (5.0 mM catalyst solution)

entry	catalyst	solvent	% conversion (30 min)[a]	M_n (theory)	M_n (determined)[a]	initiation efficiency[b]
1	**5**	CH_2Cl_2/TFE 1:1 v/v	64.9	10 000	9.340	0.69
2	**6**		81.1		9.700	0.84
3	**7**		65.7		16.530	0.40
4	**5**	TFE + 2 equiv of HCl	84.1		11.140	0.75
5	**6**		81.4		10.060	0.81
6	**7**		98.0		20.120	0.49
7	**5**	TFE/1 M HCl_{aq} (1:1 v/v)	92.4		17.600	0.53
8	**6**		95.4		16.170	0.59
9	**5**	TFE/0.1 M HCl_{aq} (1:1 v/v)	73.1		11.140	0.66
10	**6**		84.7		9.340	0.91

[a] Determined via ^1H NMR spectroscopy of aliquots taken and quenched after 30 min. [b] Initiation efficiency = [% conversion × M_n(theory)]/[M_n(determined) × 100].

metathesis initiator than the diphsophine complex **3**.[13a] Therefore, with higher acid concentration a higher degree of protonation can be averaged and, thus, a greater amount of fast initiating catalyst is present. (2) With higher HCl concentration, the chloride/bromide ratio becomes larger, thus averaging a faster propagating species.[23] Yet, with both acid concentrations, all reactions proceeded with first-order kinetics, meaning that under aqueous/alcoholic conditions, the ratio between the rates of initiation and propagation was still high and thus produced a constant number of metathesis-active species.

End-group analyses were performed for polymers of monomer **11** targeting a molecular weight of 10 000 g/mol using catalysts **5**–**7** via ^1H NMR spectroscopy. Experiments were conducted for 30 min and then quenched with ethyl vinyl ether under the following solvent conditions: CH_2Cl_2/TFE, 1:1 v/v, TFE (2 equiv of HCl_{aq}) and TFE/HCl_{aq} (0.1 or 1 M), 1:1 v/v. The determined M_n values are given in Table 2. Furthermore, aliquots were taken from the quenched mixtures and the conversion was determined. From the M_n values and the conversion, the initiation efficiency was calculated, meaning the fraction of catalyst that had initiated (for controlled ROMP the ideal value is 1). Catalyst **7** [CH_2Cl_2/TFE, 1:1 v/v, TFE (2 equiv of HCl_{aq})] displays the lowest initiation efficiencies with 40% and 49%. Therefore, less than half of the catalyst had initiated the metathesis reaction. The most efficient initiation was determined for catalyst **6** under all conditions, with the highest value found for TFE/HCl_{aq} (0.1 M), 1:1 v/v (91%). Therefore, the ratio between the rates of initiation and propagation are the most favorable for this catalyst under these conditions. This is somewhat surprising, as these conditions provide the slowest overall polymerizations. Obviously, the slow reaction is mainly due to decreased propagation rates rather than initiation rates. In CH_2Cl_2/TFE (1:1 v/v) [84%] and TFE (2 equiv of $HCl_{aq.}$) [81%] the efficiency is slightly lower. Catalyst **5** performs in between the other two catalysts, with values between 66% and 75%. Only polymerizations carried out in TFE/HCl_{aq} (1 M), 1:1 v/v, appear unfavorable for controlled ROMP (**5**: 53%; **6**: 59%). Although, the highest conversions are accomplished in these experiments, it appears likely that the increased ROMP reactivity is based on increased rates of propagation. This effect is expected due to the high Cl^-/Br^- anion ratio in solution.

In conclusion, for the first time, a one-step synthetic method to access first-generation Grubbs-type olefin metathesis catalysts with cationic or neutral, pH-sensitive benzylidene moieties has been established by alkylidene exchange from commercially available Grubbs catalyst. The catalysts $(PCy_3)_2Cl_2Ru{=}CH(p\text{-}C_6H_4)CH_2\text{-}P(CH_3)_3{}^+Cl^-$ (**5**), $(PCy_3)_2Cl_2Ru{=}CH\text{-}(p\text{-}C_6H_4)CH_2\text{-}N(CH_3)_2$ (**6**), and $(PCy_3)_2Cl_2Ru{=}CH(p\text{-}C_6H_4)N(CH_3)_2$ (**7**) perform ROMP in protic media. Their attraction lies in their straightforward preparation compared to the two other cationic catalysts performing controlled aqueous ROMP bearing water-soluble phosphine ligands. Catalysts **5** and **6** are the first representatives of $(PCy_3)_2Ru$ compounds that are capable of performing controlled ROMP of strained cyclic olefins in protic, acidic media. HCl_{aq} has been used to protonate the pH-sensitive $-NMe_2$ groups of catalysts **6** and **7** and to enhance the dissociation of the PCy_3 ligand of catalysts **5** and **6** for effective initiation in mixed alcoholic/aqueous solution. Catalysts **5** and **6** perform ROMP of the cationic *exo*-7-oxanorbornene derivative TFE (2 equiv of HCl_{aq}) and TFE/HCl_{aq} (0.1 or 1 M), 1:1 v/v, according to first-order kinetics, indicating a constant amount of active species. The slowest polymerizations were observed in alcoholic/aqueous mixtures, very likely due to the hydrophobicity of the dissociating phosphine ligand. End-group analyses established high initiation efficiency for catalyst **6** in particular. With catalysts **6** the most effective initiation is observed in TFE/HCl_{aq} (0.1 M), 1:1 v/v, whereas providing the least effective initiation is TFE/HCl_{aq} (1 M), 1:1 v/v, as solvent. It appears likely that aqueous alcoholic conditions generally are not unfavorable for controlled ROMP, but the increase of the Cl^- anion concentration in the stronger acidic solution causes slower initiation alongside faster propagation. This results in overall faster, but also less controlled, polymerizations.

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Supporting Information Available: Experimental details, ^1H, ^{13}C, and ^{31}P NMR spectra of the synthesized Ru complexes **5** and **6**, and kinetic experimental data are available free of charge via the Internet at http://pubs.acs.org.

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