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Ru-Based Olefin Metathesis Catalysts Bearing pH-Responsive N-Heterocyclic Carbene (NHC) Ligands: Activity Control via Degree of Protonation

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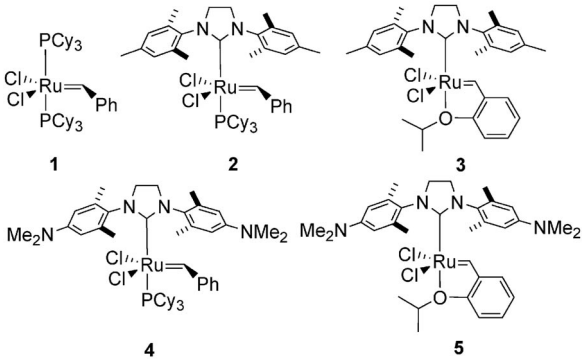
Olefin metathesis catalysts (H_2ITap)(PCy_3)Cl_2Ru=CHPh (**4**) and (H_2ITap)Cl_2Ru=CH-(C_6H_4-O-*i*Pr) (**5**) [H_2ITap = 1,3-bis-(2′,6′-dimethyl-4′-dimethylaminophenyl)-4,5-dihydroimidazol-2-ylidene] were used for the ring-opening metathesis polymerization (ROMP) of *exo*-7-oxanorbornene derivative **7** in the presence of various amounts of acid. Upon gradual protonation of the NMe_2 groups of the H_2Tap ligand, the metathesis activity of both catalysts were gradually reduced due to electronic changes of the N-heterocyclic carbene (NHC) ligand donor capability. The investigation of the ROMP polymer **8**, DFT calculations and measurements of the initiation kinetics prove that the reduced activity is solely due to reduced rates of propagation.

Over the last decade, olefin metathesis has emerged as a powerful technique in organic[1] and polymer synthesis.[2] In particular Ru-based, single-site catalysts such as Grubbs' first- and second-generation catalysts **1** and **2**, and Hoveyda–Grubbs catalyst **3** have gained scientific and commercial importance due to their high tolerance towards moisture and functional groups,[3–5] as these catalysts have significantly expanded the scope of metathesis substrates. In terms of overall activity and thermal stability, catalysts **2** and **3** bearing an N-heterocyclic carbene (NHC) ligand, most commonly the H_2IMes [bis(2,4,6-trimethylphenyl)dihydroimidazol-2-ylidene] ligand, are superior.[4,5] This is due to their slower rates of initiation which is overcompensated by the fact that these catalysts promote extremely fast metathesis propagation.[6,7] On the flip side however, the high propagation rates accomplished with these catalysts makes them unsuitable for controlled ring-opening metathesis polymerization (ROMP) in contrast to catalyst **1**. In fact, only small fractions of catalysts **2** and **3** initiate in a standard ROMP reaction.[7]

Apart from reaction temperature and structural parameters, only a few controls have been recognized to influence the activity of Ru-based olefin metathesis catalysts. The addition of Brønsted[8–15] or Lewis[15–17] acids have been reported to facilitate the donor-ligand dissociation from the Ru carbene complexes which results in an increase of the overall activity. On the other hand, the presence of excess donors such as PCy_3 or N-donor ligands causes lower overall metathesis activities.[17,18] The combination of N-donor inhibition and acid activation has even led to the development of a reversible "off/on" switch for the ROMP reaction with cyclooctene with Grubbs' catalyst **1**.[12] We have recently reported catalysts **4** and **5** coordinated by the H_2ITap [bis-1,3-(4′-aminophenyl-*N*,*N*,3′,5′-tetramethyl)-4,5-dihydroimidazol-2-ylidene] ligand.[19] The catalysts contain two pH-responsive NMe_2 groups at the phenyl rings which can be protonated with strong acid. Whereas the neutral catalysts exhibited similar or even slightly higher activities in ROMP and ring closing metathesis (RCM) reactions as than their very active, commercially available counterparts **2** and **3** in organic solvents, the catalysts failed to perform ROMP of cationic *exo*-7-oxanorbornene **6** derivative in



1 **2** **3** **4** **5**

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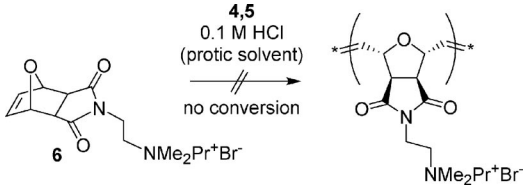
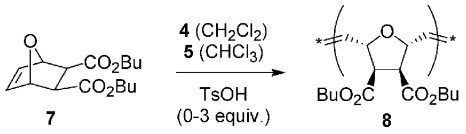


Scheme 1. Failed ROMP of monomer **6** with catalysts **4** and **5** ([Ru] = 2 mM, 4% loading) in acidic protic media.

acidic protic media (Scheme 1). This is somewhat surprising since the same substrate has been polymerized with > 95% conversion in our laboratories with other catalysts at lower loadings in alcoholic/organic[20] and acidic alcoholic/aqueous media,[21] frequently in time periods < 30 min. We now wish to report our experimental and computational investigation of the influence of the degree of protonation on the ROMP activity of catalysts **4** and **5**.

The protonation of the NMe_2 groups in catalysts **4** and **5** clearly reduces the catalyst activity. This is counterintuitive to all previous reports, where addition of acid to a Ru-based olefin metathesis catalyst accelerated the overall rate.[8–15] Therefore, the transformation of the π-donating NMe_2 group into an σ-withdrawing NMe_2H^+ moiety must have caused significant electronic changes in the H_2ITap ligand. These changes also impact the catalyst electronic environment and thus cause a reduced metathesis activity. The effect of different substitution in the 4-position of the phenyl rings on the NHC ligand properties has been studied by Plenio et al. by generating a library of symmetric and unsymmetric ligands.[22–24] It was found that the change from electron-withdrawing to donating groups in the phenyl-*para* position had a significant impact on the redox potentials of Ir and Ru complexes. NHC-Ir complexes bearing π-donating NEt_2 groups had the lowest cathodic redox potential in the series indicating significantly enhanced donating properties of this ligand.[23] This effect also translated into elevated RCM and CM activities of the corresponding NHC-Ru carbene complexes.[24] In the light of these results, we were expecting that gradual protonation of the NMe_2 groups in the H_2ITap ligand in catalysts **4** and **5** should gradually convert the donating amino groups into withdrawing ammonium groups and thus, should gradually lower their metathesis activity. This would provide us with a novel and unique external activity control for the ROMP reaction via degree of protonation.

We conducted a series of ROMP reactions with *exo*-7-oxanorbornene monomer **7** with catalysts **4** and **5** in the presence of variable amounts of toluenesulfonic acid (TsOH) (Scheme 2). We selected TsOH for this study as a non-nucleophilic acid which does not cause precipitation of the catalysts from the organic reaction medium (CH_2Cl_2 and $CHCl_3$). The amounts of TsOH were increased in increments of 0.4 equiv. with respect to Ru complex. The experiments were conducted in the NMR tube and the monomer conversion was monitored. The catalyst concentration and loadings were kept identical ([Ru] = 1 mM, 1% loading). Our initial hypothesis of the external activity control by acid addition was confirmed as the conversion plots (see Figures 1 and 2) for both series exhibit a significant impact of each increase in the acid equivalents on the reaction rate. The deceleration of the reaction is more dramatic for catalyst **4** in CD_2Cl_2 at room temperature. For each 0.4 equiv. of acid, the time intervals to reach the 95% conversion mark is are nearly double for additions up to 0.8 equiv. and then increase even more for higher acid amounts (Table 1). The reactions containing 2.0 and 3.0 equiv. of acid plateau at 70% and 27% conversion respectively after approx. 10 h indicating substantial catalyst decomposition after this time period. Such decomposition with strong acid was observed earlier with catalyst **4** due to partial protonation of the basic PCy_3 ligand. The ROMP reactions with catalyst **5** in $CDCl_3$ at room temperature also were converting slower with higher acid amounts. In comparison to catalyst **4** the increase of the acid amount in 0.4 equiv. increments, resulted in significantly faster conversions for catalyst **5** than for the reactions with catalyst **4** at all acid amounts. Furthermore, the time differences to reach the 95% conversion mark were much smaller (Table 1), and even at 2 equiv. TsOH, the reactions still goes to > 95% conversion in approx. 2 h. This activity difference must be related to the PCy_3 ligand. The phosphane ligand is a known inhibitor to the Ru-based metathesis reaction.[12,17] Upon dissociation, the PCy_3 ligand may be partially protonated by the acid. Such partial protonation of the basic phosphane ligand was observed before with by the addition of aqueous hydrochloric acid to complex **4**.[19] The PCy_3 ligand is more Brønsted basic than the aniline nitrogen atoms by approx. four orders of magnitude.[25] However, even a very strong acid such as HCl does not afford a quantitative protonation of the phosphane ligand when added in equimolar amounts without the presence of other basic groups due to the Lewis acidity of the Ru center.[9a] Therefore, the higher the degree of partial protonation of the PCy_3 ligand is in the reaction solution, the more significant should be the impact of the H_2ITap ligand protonation on the overall ROMP kinetics. A low degree of PCy_3 protonation would result in a lower impact of the NHC ligand protonation as the inhibiting effect of the donor ligand will contribute strongly to the overall kinetics of the ROMP reaction.



Scheme 2. ROMP of monomer **7** with catalysts **4** and **5** ([Ru] = 1.0 mM, 1% loading) in the presence of TsOH.

We have investigated the influence of TsOH addition to catalyst **4** in CD_2Cl_2 under reaction conditions by ^{31}P NMR spectroscopy. The addition of 1 equiv. TsOH with respect to catalyst **4** resulted in the formation of the mostly mono-protonated derivative of catalyst **4** (δ = 30.2 ppm) and a second phosphane species (δ = 27.8 ppm) in a ratio of 97:3. This new species is the $HPCy_3^+$ salt and it is ob-

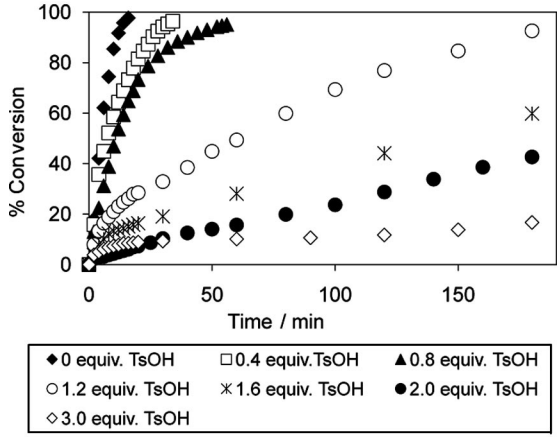


Figure 1. Acid-dependent ROMP of monomer **7** with catalysts **4** ([Ru] = 1.0 mM, 1.0% catalyst loading).

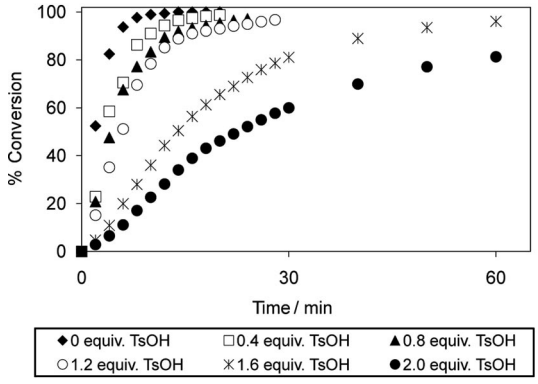


Figure 2. Acid-dependent ROMP of monomer **7** with catalysts **5** ([Ru] = 1.0 mM, 1.0% catalyst loading).

Table 1. Conversion of monomer **7** with catalysts **4** (in CH_2Cl_2) and **5** (in $CHCl_3$) and corresponding properties of polymer **8**.

Catalyst	TsOH [equiv.]	Time [min] (>95% conv.)	M_P (theory)	M_P (GPC)	PDI
4	0	14	27,600	> 150,000	*1.23*
	0.4	32		138,700	*1.34*
	0.8	56		141,000	*1.31*
	1.2	210		119,200	*1.33*
	1.6	600		95,900	*1.60*
	2.0	–		55,500	*1.73*
5	0	8		80,000	*1.64*
	0.4	14		75,300	*1.57*
	0.8	20		68,200	*1.52*
	1.2	24		66,800	*1.46*
	1.6	60		34,700	*1.63*
	2.0	*100*		*9,000*	*1.80*

served when TsOH is added to PCy_3 in CD_2Cl_2 solution. This strongly suggests that 3% of the catalyst has dissociated the PCy_3 ligand under these conditions. The addition of 2 equiv. TsOH to catalyst **4** resulted in the formation of the mostly di-protonated derivative of catalyst **4** (δ = 29.5 ppm) and the second phosphane species (δ = 27.8 ppm) in a ratio of 95:5. The Ru species are stable for 3 h at room temperature (the time frame of most ROMP reactions) as determined via ^{1}H NMR spectroscopy by integration of the signals at (δ = 19.01 ppm, benzylidene H) vs. a internal standard (δ = 7.82 ppm – 2H of TsOH) as no change in the integration values are observed. Over the course of 3 d, significant degradation occurred (1 equiv. TsOH: 27% dec.; 2 equiv. TsOH: 73% dec.). Therefore, only a small percentage of the donor ligand is protonated during the ROMP reactions and, as a result, the PCy_3 ligand is still capable of slowing the overall reaction with catalyst **4**. Such a donor-ligand-based inhibiting effect is unlikely with phosphane-free catalyst **5** and this would explain the overall faster reactions and the more significant impact of the degree of the H_2ITap ligand protonation.

We were investigating the impact of the moderated catalyst activity of complexes **4** and **5** on the polymer molecular weight. Due to the unfavorable ratio of the rates of initiation and propagation, the H_2IMes ligated catalysts **2** and **3** do not promote controlled ROMP, meaning that the polymer molecular weights obtained with these catalysts are substantially higher than the theory. Catalysts **4** and **5** exhibit a similar reactivity profile and the measured average molecular weights (M_P) of polymer **8** (Scheme 2) are significantly larger (> 150,000 [**4**], 80,000 [**5**]) than the theory (27,600) also indicating incomplete initiation under these reaction conditions (Table 1). The question was if the activity moderation mostly affects the initiation or the propagation rates. If propagation would be predominantly slowed down, then acid addition could permit an improved molecular weight control of the ROMP reaction and increase the initiation efficiency. This then could be observed by a lowering of the average molecular weights of the polymers. All polymerization reactions were carried out under identical reaction conditions as the kinetic NMR experiments and polymer **8** was isolated and investigated via GPC. The average molecular weights of the polymer indeed were determined to grow progressively smaller with increased TsOH amounts present during the ROMP reaction. For catalyst **4**, the M_P was reduced to 55,500 (approx. one third of the M_P obtained for the acid-free ROMP with catalyst **4**). This is only close to double of the target M_P and indicates that the initiation efficiency has been increased significantly. For catalyst **5**, the addition of 1.6 equiv. of TsOH was already producing polymer **8** with an M_P of 34,600 which is very close to the theoretical value. Further reduction also reduced the molecular weights far below the theoretical value which are partially due to incomplete polymerizations and also possible catalyst decomposition. However, the trend is indicative of the acid addition mostly affecting the rates of propagation. As a result, the initiation efficiency for both catalysts was enhanced and the molecular weights became better controlled. To the best of our knowledge, this is the first example of the external control of the ROMP propagation rates. Slow propagation in olefin metathesis usually is not desired because for most applications, the optimal catalyst is highly active and thermally very stable. Slowing the propagation accomplishes the opposite by

worsening the propagation/initiation and thus the turnover/decomposition ratio. The one exception is controlled ROMP where a low propagation/initiation ratio is desired to have a close to simultaneous start of all growing polymer chains.

To confirm these findings of the external propagation control with acid, DFT calculations were used to determine the Mulliken atomic charges for model complexes **11**, **11′** and **11′′** which bear a PMe_3 ligand instead of the PCy_3 ligand and differ in the degree of protonation at the H_2ITap ligand (Table 2). The charges were calculated using a B3LYP method with a large basis [6-311++G(2d.2p)] for first-coordination-shell atoms on geometries optimized by using the mPW1PW91/sdd method (details in Supporting Information), which were found to give good predictions of geometric and electronic properties for late transition metal complexes.[26,27] A recent report described a correlation between the Mulliken atomic charges at the metal center in Ru carbene complexes and the rate of metathesis initiation.[28] It was demonstrated that the Ru center in slow-initiating catalyst **2** in fact is more positively charged than in fast-initiating catalyst **1**. This was used as a rational to explain the influence of the remaining donor ligand (NHC vs. PCy_3) on the dissociation rates of the other PCy_3 ligand which determines the initiation rate. For this reason, the calculations also included catalysts **9** and **10**, the PMe_3-ligated counterparts of complexes **1** and **2**, for comparison. Similar to the reported calculations,[28] we also found the Ru center to be more positively charged in the NHC ligated complex **10** than in complex **9**. The Mulliken atomic charges for the Ru center in complex **11** were nearly identical to complex **10** which is not surprising with respect to the similar activities for catalysts **2** and **4** in ROMP and RCM reactions.[19] More interestingly, the charges became less positive with increasing protonation to complexes **11′** and **11′′**, however, these charges are still much more positive than for complex **9**. This is somewhat surprising since the H_2ITap ligand becomes positively charged and thus an increase in the charge at the metal center could have been expected. Following the rational of the previous calculations, it can only mean that the π-acceptor capability of the H_2ITap ligand is reduced upon protonation.[28] But this result also means, that the initiation rates of model complexes **11′** and **11′′** most certainly should not be lowered in comparison to complex **11**. Therefore, these calculations suggest that the reduced overall activity exhibited by gradual protonation of catalysts **4** and **5** is a result of slower ROMP propagation.

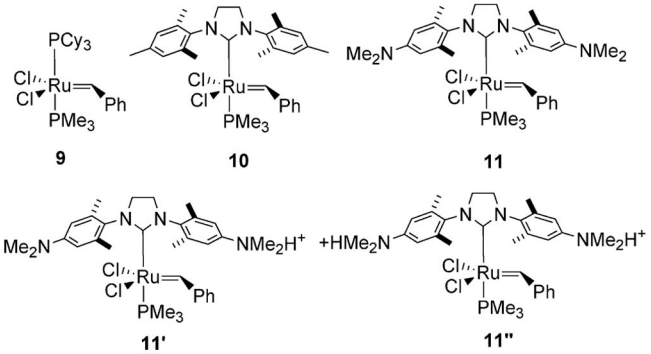
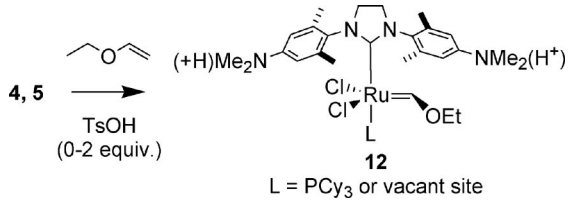


Table 2. DFT-calculated Mulliken atomic charges at the Ru center for model complexes **9**–**11**, **11′** and **11′′**.

Complex	q^{Mlk}	Δq^{Mlk} (**9**)	Δq^{Mlk} (**10**)
9	0.313	–	–0.621
10	0.834	+0.621	–
11	0.851	+0.638	+0.017
11′	0.831	+0.618	–0.003
11′′	0.712	+0.499	–0.122

We also have experimentally determined the relative initiation rates for complexes **4** and **5** without and in the presence of TsOH. For that purpose, we have measured the conversion of the Ru species with ethyl vinyl ether (EVE).[6] The reaction affords one turnover to form the metathesis-inactive Fischer-carbene complexes **12** (Scheme 3). We monitored the changes for the ^{1}H NMR signal for the benzylidene-H atom (δ = 19.01 ppm [**4**]; δ = 16.78 ppm [**5**]). PCy_3-containing complex **4** is converted into the respective ethoxymethylidene species **12** which was observed via the methylidene-H signal at δ = 13.73 ppm. The acid-containing reaction with catalyst **4** and the reactions with catalyst **5** did not afford a stable ethoxymethylidene complex containing a ^{1}H NMR signal which could be reliably integrated. A species at δ = 13.73 ppm was observed with complex **4** solution in the presence of TsOH, however, over time the signal disappeared, very likely due to degradation. Solutions of complex **5** generated multiple broad signals in the range between 9 and 16 ppm in the presence of EVE. Hence, the conversion was monitored by the reduction of the benzylidene-H signal vs. an internal standard. In agreement with our computational results, the conversion rates now slightly increase with increased acid amounts. Only 24% of catalyst **4** initiate in 60 min, whereas 52.7% conversion was observed in the presence of 1 equiv. of TsOH in the same time period. With 2 equiv. of TsOH, the conversion reached a plateau at 67% conversion after 30 min but reached > 50% conversion already after 5 min (Figure 3, a). Catalyst **5** generally exhibits faster initiation than catalyst **4** and the differences in the conversion of EVE in the presence of TsOH were much less pronounced (Figure 3, b). However, the trend also is that the EVE conversion proceeded faster at higher acid concentrations. For example, after 6 min complex **5** is converted by 52.0% (acid-free), 58.2% (1 equiv. TsOH) and 63.3% (2 equiv. TsOH). All conversions with complex **5** went > 95% within 30 min.

The results demonstrate unambiguously that the reduced ROMP rate in the conversion of monomer **7** is based on slowing the propagation rate with increased acid amounts. The reasons for this deceleration effect at this stage are speculative. It appears likely that the slow propagation is due to an elevation of the energy level of the metallacyclobutane intermediate and the corresponding transition state. The experiments with EVE do not suggest a slow or com-



Scheme 3. Conversion of catalysts **4** and **5** with EVE into ethoxymethylidene complexes **12**.

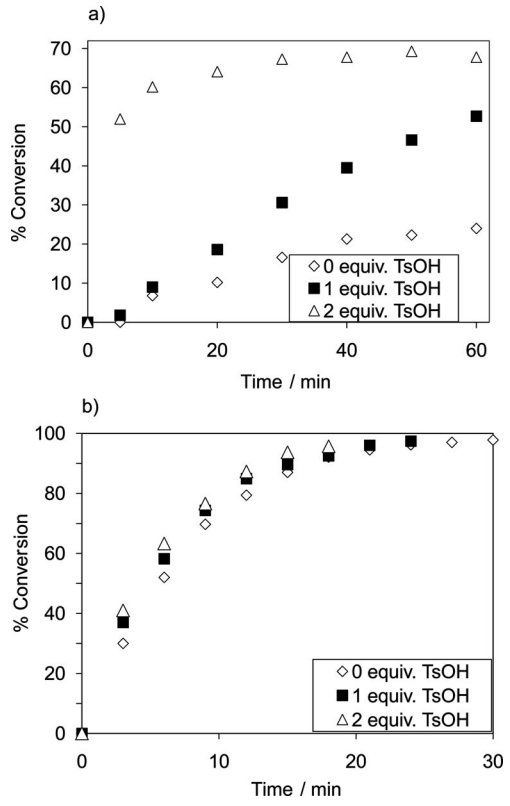


Figure 3. Catalyst conversion with 100 equiv. of EVE: a) catalyst **4** ([Ru] = 4 mM, CD_2Cl_2, 20 °C); b) catalyst **5** ([Ru] = 2 mM, $CDCl_3$, 20 °C).

petitive coordination of the olefin. Although the reaction with EVE also must proceed once through the metallacyclobutane, it seems that the effect becomes noticeable at high turnover numbers. Certainly, the protonation of the NMe_2 groups in the H_2ITap ligand has an impact on the ligand electronics. How these are affecting the electronics at the metal center has not been clearly demonstrated. Further experimental and theoretical investigations of this phenomenon are currently under way.

The polydispersity indices (PDIs) of polymer **8** were also determined (Table 1). Catalyst **5** exhibits the expected development of the PDIs for the better controlled ROMP reactions with increasing acid amounts present during the polymerization. The values were reduced from 1.64 to 1.46 when 1.2 equiv. of TsOH were present. Further increase of the acid amount then led to a higher PDI's again (1.93 for 3.0 equiv. of acid). For catalyst **4**, the increased ROMP propagation control was not reflected in lower PDIs. However, the "uncontrolled" ROMP with the acid-free catalyst produces a polymer with an amazingly low PDI of 1.23 which is in stark contrast to the high experimental M_n. The PDIs then gradually increase to 1.73 with increased TsOH amounts present during the reaction. In general, the determined PDIs do not give a consistent picture of the improved propagation control with catalysts **4** and **5** upon the addition of TsOH. Very likely, despite the lowered propagation rates, the ROMP reaction can still not be considered as controlled enough to give very well-defined polymeric materials.

Conclusion

The activity of olefin metathesis catalysts can be externally controlled with acid addition by changing the electronic nature of pH-responsive H_2ITap ligand due to the gradual protonation of the ligand NMe_2 groups. Kinetic experiments clearly demonstrated that gradually increased levels of toluenesulfonic acid (TsOH) were gradually reducing the rate of the ROMP reaction with *exo*-7-oxanorbornene derivative **7**. The average molecular weights of the produced polymers were also gradually reduced with the addition of acid which indicates a higher initiation efficiency of both catalysts mostly due to slower propagation. This was confirmed by DFT calculations of the Mulliken atomic charges at the metal center for the model Ru carbene complexes **11**, **11′** and **11′′** bearing the H_2ITap ligand with different degrees of protonation. The charges became slightly less positive with higher degrees of protonation which in turn should result in equal or even slightly faster initiation rates for these complexes. Experimentally, it was found that the rate of initiation is in fact slightly accelerated in the presence of acid by measuring the complex conversion with EVE. This confirms that the reduced activity is solely based on reduced rates of propagation. Although the slowing the propagation improved the molecular weight control of the ROMP reaction, polymers **8** were still somewhat polydisperse indicating that the initiation rates are still significantly slower than the propagation rates. To the best of our knowledge, this is the first example where the propagation rates can be controlled by an external stimulus. The development of improved pH-responsive catalysts and reaction conditions which can be used for controlled living ROMP is under current investigation.

Supporting Information (see also the footnote on the first page of this article): Experimental and computational procedures as well as detailed kinetic measurements are available.

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[1] a) R. H. Grubbs (Ed.), *Applications in Organic Synthesis* in: *Handbook of Metathesis*, Wiley-VCH, Weinheim, **2003**, vol. 2; b) M. Bieniek, A. Michrowska, D. L. Usanov, K. Grela, *Chem. Eur. J.* **2008**, *14*, 806–818; c) A. H. Hoveyda, A. R. Zhugralin, *Nature* **2007**, *450*, 243–251; d) H. Clavier, K. Grela, A. Kirschning, M. Mauduit, S. P. Nolan, *Angew. Chem. Int. Ed.* **2007**, *46*, 6786–6801; e) Su. Ghosh, Sa. Ghosh, N. Sarkar, *J. Chem. Sci.* **2006**, *118*, 223–235; f) J. C. Conrad, D. E. Fogg, *Curr. Org. Chem.* **2006**, *10*, 185–202; g) A. K. Chatterjee, T.-L. Choi, D. P. Sanders, R. H. Grubbs, *J. Am. Chem. Soc.* **2003**, *125*, 11360–11370; h) D. L. Wright, *Curr. Org. Chem.* **1999**, *3*, 211–240.

[2] a) R. H. Grubbs (Ed.), *Applications in Polymer Synthesis* in: *Handbook of Metathesis*, Wiley-VCH, Weinheim, **2003**, vol. 3; b) C. W. Bielawski, R. H. Grubbs, *Prog. Polym. Sci.* **2007**, *32*, 1–29; c) U. Frenzel, O. J. Nuyken, *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2895–2916; d) C. Slugovc, *Macromol. Rapid Commun.* **2004**, *25*, 1283–1297; e) O. A. Scherman, I. M. Rutenberg, R. H. Grubbs, *J. Am. Chem. Soc.* **2003**, *125*, 8515–8522; f) C. W. Bielawski, D. Benitez, T. Morita, R. H. Grubbs, *Macromolecules* **2001**, *34*, 8610–8618; g) T. W. Baughman, K. B. Wagener, *Adv. Polym. Sci.* **2005**, *176*, 1–42; h) G. Trimmel, S. Riegler, G. Fuchs, G. Slugovc, F. Stelzer, *Adv. Polym. Sci.* **2005**, *176*, 43–87; i) R. H. Grubbs, *Tetrahedron* **2004**, *60*, 7117–7140.

[3] a) S. T. Nguyen, L. K. Johnson, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1992**, *114*, 3974–3975; b) P. Schwab, R. H. Grubbs, J. W. Ziller, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2039–2041; c) C. Fraser, R. H. Grubbs, *Macromolecules* **1995**, *28*, 7248–7255; d) P. Schwab, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1996**, *118*, 100–110.

[4] a) C. W. Bielawski, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2000**, *39*, 2903–2906; b) E. Colacino, J. Martinez, F. Lamaty, *Coord. Chem. Rev.* **2007**, *251*, 726–764.

[5] a) S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. Hoveyda, *J. Am. Chem. Soc.* **2000**, *122*, 8168–8179; b) J. J. Van Veldhuizen, S. B. Garber, J. S. Kingsbury, A. H. Hoveyda, *J. Am. Chem. Soc.* **2002**, *124*, 4954–4955; c) A. Michrowska, L. Gulajski, K. Grela, *Chem. Commun.* **2006**, 841–843.

[6] M. S. Sanford, J. A. Love, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 6543–6554.

[7] J. A. Love, M. S. Sanford, M. W. Day, R. H. Grubbs, *J. Am. Chem. Soc.* **2003**, *125*, 10103–10109.

[8] J. Huang, H.-J. Schanz, E. D. Stevens, S. P. Nolan, *Organometallics* **1999**, *18*, 5375–5380.

[9] a) D. M. Lynn, B. Mohr, R. H. Grubbs, L. M. Henling, M. W. Day, *J. Am. Chem. Soc.* **2000**, *122*, 6601–6609; b) D. M. Lynn, B. Mohr, R. H. Grubbs, *J. Am. Chem. Soc.* **1998**, *120*, 1627–1628.

[10] J. P. Gallivan, J. P. Jordan, R. H. Grubbs, *Tetrahedron Lett.* **2005**, *46*, 2577–2580.

[11] M. S. Sanford, L. M. Henling, M. W. Day, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2001**, *39*, 3451–3452.

[12] S. J. P'Pool, H.-J. Schanz, *J. Am. Chem. Soc.* **2007**, *129*, 14200–14212.

[13] L. Gulajski, A. Michrowskaa, R. Bujok, K. Grela, *J. Mol. Catal. A* **2006**, *254*, 118–123.

[14] R. Gawin, A. Makal, K. Wozniak, M. Mauduit, K. Grela, *Angew. Chem. Int. Ed.* **2007**, *46*, 7206–7209.

[15] N. Ledoux, R. Drozdzak, B. Allaert, A. Linden, P. Van Der Voort, F. Verpoort, *Dalton Trans.* **2007**, 5201–5210.

[16] N. Ledoux, B. Allaert, D. Schaubroeck, S. Monsaert, R. Drozdzak, P. Van Der Vort, F. Verpoort, *J. Organomet. Chem.* **2006**, *691*, 5482–5486.

[17] E. L. Dias, S. T. Nguyen, R. H. Grubbs, *J. Am. Chem. Soc.* **1997**, *119*, 3887–3897.

[18] A. Stark, M. Ajam, M. Green, H. G. Raubenheimer, A. Ranwell, B. Ondruschka, *Adv. Synth. Catal.* **2006**, *348*, 1934–1941.

[19] S. L. Balof, S. J. P'Pool, N. J. Berger, E. J. Valente, A. M. Schiller, H.-J. Schanz, *Dalton Trans.* **2008**, 5791–5799.

[20] D. Rankin, K. McLemore, S. J. P'Pool, H.-J. Schanz, A. B. Lowe, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 2113–2128.

[21] A. N. Roberts, A. C. Cochran, D. A. Rankin, A. B. Lowe, H.-J. Schanz, *Organometallics* **2007**, *26*, 6515–6518.

[22] M. Süßner, H. Plenio, *Chem. Commun.* **2005**, 5417–5419.

[23] S. Leuthäußer, D. Schwarz, H. Plenio, *Chem. Eur. J.* **2007**, *13*, 7195–7203.

[24] S. Leuthäußer, V. Schmidts, C. M. Thiele, H. Plenio, *Chem. Eur. J.* **2008**, *14*, 5465–5481.

[25] C. A. Streuli, *Anal. Chem.* **1960**, *32*, 985–987.

[26] Y. Zhang, Z. J. Guo, X. Z. You, *J. Am. Chem. Soc.* **2001**, *123*, 9378–9387.

[27] Y. Zhang, J. C. Lewis, R. G. Bergman, J. A. Ellman, E. Oldfield, *Organometallics* **2006**, *25*, 3515–3519.

[28] K. Getty, M. U. Delgado-Jaime, P. Kennepohl, *J. Am. Chem. Soc.* **2007**, *129*, 15774–15776.

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