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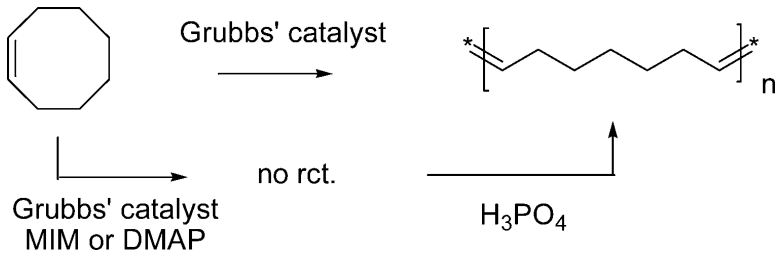

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Reversible Inhibition/Activation of Olefin Metathesis: A Kinetic Investigation of ROMP and RCM Reactions with Grubbs' Catalyst

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Abstract: The metathesis activity of Grubbs' catalyst **1** was investigated in the presence of N-donor ligands (1-methylimidazole [MIM], 4-(*N*,*N*-dimethylamino)pyridine [DMAP], pyridine, and 1-octylimidazole [OIM]). Ring opening metathesis polymerization (ROMP) reactions of cyclooctene (COE), bulk-ROMP reactions of COE and norbornadiene (NBD), and ring closing metathesis (RCM) reactions of diethyl diallylmalonate (DEDAM) were conducted containing various equivalents of N-donor with respect to catalyst. ROMP reactions could be stopped using MIM (1−5 equiv) and DMAP (2−5 equiv), and slowed with pyridine (1−5 equiv) by factors >100, in benzene solution for 24 h. The stopped reactions could be initiated with excess phosphoric acid (H_3PO_4), and the reactions proceeded faster than with uninhibited Grubbs' catalyst in the first 4 min after reactivation. Thereafter, the reaction proceeded at the same rate as the reaction with the uninhibited catalyst. ROMP reactions in neat COE and NBD could be inhibited for 72 h using 2 equiv of MIM, DMAP, or OIM and activated with H_3PO_4 to give polymer gels within minutes or less. RCM reactions could be completely inhibited with MIM (1−5 equiv), but upon treatment with H_3PO_4, the reaction would proceed at a fraction of the initial rate accomplished by uninhibited Grubbs' catalyst **1**. A structural investigation of the inhibited species showed that MIM and DMAP completely or partially transform catalyst **1** into the hexacoordinate species **5a** or **5b** producing free PCy_3, which additionally acts as an inhibitor for the ROMP reaction. Upon reactivation, the PCy_3 is protonated along the N-donor ligand; however, over the period of 5 min, the phosphine has been found to coordinate back to the ruthenium catalyst. Therefore, the reaction slows to the same polymerization rate as the reaction using the uninhibited catalyst at this point. Complexes **5a** and **5b** were isolated, characterized, and employed in ROMP and RCM experiments where they exhibited very low catalytic activity.

Introduction

Olefin metathesis has become a valuable synthetic tool in organic[1−5] and polymer chemistry.[6−9] In particular, homogeneous, ruthenium-alkylidene catalysts have been widely used as they expand the scope of possible transformations due to their high tolerance toward air, moisture, and functional groups.[10] Various structural motifs of these complexes have been developed; yet to date, Grubbs' catalyst **1** (Figure 1) is commercially available and still the most widely used catalyst for many applications. Second generation Grubbs catalyst[11] **2**

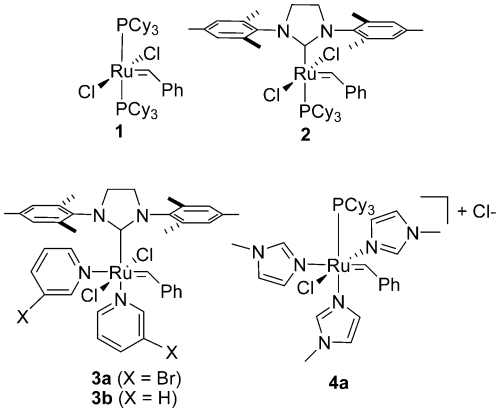

Figure 1. Catalysts **1**−**4**.

(Figure 1) is accessible from complex **1** by exchange of one phosphine ligand with a highly σ-donating NHC ligand. The development of this class has significantly improved the thermal catalyst stability while simultaneously increasing the overall

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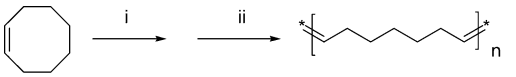
catalytic activity[11a,12] as a result of superior metathesis propagation while the rate of initiation is significantly slower.[13] Hexacoordinate third generation Grubbs-type catalyst **3a** (Figure 1) exhibits fast propagation along with extremely fast initiation, as the 3-bromopyridine ligands dissociate rapidly from the metal center.[14] In fact, in direct comparison to other common ruthenium-benzylidene catalyst motifs, complex **3a** exhibits extraordinary activity during cross metathesis (CM) and ring opening metathesis polymerization (ROMP) reactions.[14] In contrast, analogue complex **3b**, bearing two stronger σ-donating pyridine ligands,[14b] exhibits noncompetitive activity compared to **3a**. Cationic complex **4a** coordinated by three electron-rich 1-methylimidazole ligands exhibits extremely low catalytic activity in RCM reactions of terminal diolefins, and the catalyst was observed to display significant degradation during the reaction.[15]

The influence of ligation, such as nature of donor ligands, carbene moiety, and coordinated halide, on catalyst activity and thermal stability has been investigated extensively, in particular for the first and second generation derivatives.[13,16,17] Apart from these structural parameters, few external controls have been recognized to influence metathesis activity of ruthenium-based catalysts. Activation of the metathesis reaction was observed by the use of phosphine sponge such as CuCl[16] or hydrochloric acid,[12a] and particularly ROMP can be noticeably accelerated upon HCl addition.[18,19] The effect is twofold: (a) the acid addition reduces the hydroxide concentration, which is proven to degrade the catalyst,[18] and (b) the acid traps the dissociating phosphine ligand as protonated species, which causes an increase of the concentration of a mono-phosphine complex, which displays higher metathesis activity. Hence, the rate of initiation and, thus, the overall catalytic activity are elevated. Reduction of the metathesis activity was accomplished when additional equivalents of phosphine were added to the reaction mixture. As a result, phosphine dissociation from the catalyst precursor is reduced, and low concentrations of the metathesis-active mono-phosphine 14-electron intermediate[13] cause slower overall reaction rates.[16] One equivalent of PCy_3 (with respect to catalyst) was shown to decelerate RCM of diethyl diallylmalonate (DEDAM) with Grubbs' catalyst **1** to 5% of the initial activity. With the linear relationship between the rate constant and reciprocal PCy_3 concentration, a theoretical maximum inhibition factor at an infinite excess of PCy_3 can be derived from the *y*-intercept, which corresponds to approximately 1.6% of the initial actvity.[16] Just recently, it was reported that the cross metathesis (CM) reaction of 1-octene in ionic liquids is significantly slowed down in the presence of low amounts of 1-methylimidazole, which may be present as impurity of the ionic liquid.[20] Grubbs and co-workers also have synthesized several slow-initiating ruthenium carbene catalysts bearing one salicyl aldehyde Schiff-base ligand or two acac ligands. Those exhibit low reactivity in ROMP monomer solution, and the catalysts then can be activated by acid addition.[21] The same group also synthesized several species of the general formula $(PCy_3)(RO)_2Ru{=}CHPh$ bearing bulky alkoxide ligands. The catalysts showed very low activity in RCM reactions with DEDAM but could be activated with 2 equiv of HCl.[22] Verpoort and co-workers have recently described the activation of similar Schiff-base complexes using chlorosilanes and Lewis acids.[23] To date, no inhibitor/activator combination for a olefin metathesis catalyst has been reported that reversibly can govern the catalytic activity. We wish to report an unprecedented, straightforward, and reversible inhibition/activation protocol for Grubbs' catalyst **1** that provides a homogeneous, one-pot olefin metathesis system with dramatic activity differences between "on" and "off" states.

Scheme 1. ROMP of COE with Reactivated Catalyst **1**



i) **1** (2 %)+ nL (n = 1, 2, 3, 5; L = MIM, DMAP, pyridine) / 24 h
ii) H_3PO_4 (25 equiv.) for conversions < 2%

Results and Discussion

Due to the obvious relationship between basicity of the N-heterocycle in complexes **3a, 3b** and **4a** and metathesis activity (with reduced basicity resulting in increased activity), we proposed that strongly basic N-heterocycles could function as an inhibitor for Grubbs' catalyst **1**. On the other hand, more basic donors also can be more readily protonated in acidic media and thus, the metathesis reaction can be activated. We have isolated and tested the new catalytic species, but we also investigated the metathesis activity of the catalyst/inhibitor mixture (inhibited state) and the activity of the same mixture after acidification (activated state). Two standard metathesis reactions were investigated, ROMP of cyclooctene (COE) and RCM of diethyl diallylmalonate (DEDAM), using Grubbs' Catalysts **1** with various inhibitor concentrations. The substrate conversion was monitored via ^{1}H NMR spectroscopy, and the relative performances of each mixture to uninhibited Grubbs' Catalysts **1** were determined.

Inhibition/Activation of Ring Opening Metathesis Polymerization (ROMP) of Cyclooctene (COE). We conducted three series of ROMP experiments for using 1-methylimidazole (MIM), *N*,*N*-dimethylaminopyridine (DMAP), and pyridine as N-donor inhibitors (0, 1.0, 2.0, 3.0, and 5.0 equiv with respect to **1**) with COE as a monomer (Scheme 1). The monomer conversion was monitored via ^{1}H NMR (20 °C, [**1**] = 2.0 mM, 2% catalyst loading). We chose d_6-benzene as solvent since several Ru species were formed in CD_2Cl_2 over time whereas the Ru species in benzene remained in a stable equilibrium (*vide*

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Table 1. Observed Conversions and Relative Rate Constants for ROMP of COE with Uninhibited, Inhibited (1−5 equiv of MIM or DMAP), and Reactivated Catalyst **1**

entry[a]	inhibitor	equivalents relative to **1**	% conversion 24 h inhibited[b]	% conversion 6 min active[b,c]	k_{rel}
1[d]	–	–	n.d.	55.0	1 ± 0.004[f]
2[e]	–	–	n.d.	57.8	1.00 ± 0.005[f]
3	MIM	1.0	<2	68.1	1.02 ± 0.008[f]
4	MIM	2.0	<2	68.4	1.01 ± 0.002[f]
5	MIM	3.0	<2	68.4	0.99 ± 0.001[f]
6	MIM	5.0	<2	69.7	0.99 ± 0.001[f]
7	DMAP	1.0	19.7	n.d.	n.d.
8	DMAP	2.0	<2	60.5	0.96 ± 0.005[f]
9	DMAP	3.0	<2	64.1	0.96 ± 0.04[f]
10	DMAP	5.0	<2	65.2	0.96 ± 0.03[f]
11	pyridine	1.0	54.1	n.d.	$(9.79 \pm 0.55) \times 10^{-3}$[g]
12	pyridine	2.0	40.1	n.d.	$(6.20 \pm 0.06) \times 10^{-3}$[g]
13	pyridine	3.0	31.2	n.d.	$(5.30 \pm 0.02) \times 10^{-3}$[g]
14	pyridine	5.0	23.3	n.d.	$(4.01 \pm 0.02) \times 10^{-3}$[g]
15	PCy_3	1.0	9.3	n.d.	n.d.

[a] All experiments were conducted in d_6-benzene, [**1**] = 2.0 mM, 2% catalyst loading. [b] Determined via ^{1}H NMR. [c] Activation by addition of H_3PO_4 (25 equiv). [d] No H_3PO_4 added. [e] H_3PO_4 (25 equiv) added. [f] Rate constants determined for conversion between 4 and 30 min reaction time. [g] Rate constants determined for conversion between 3 and 48 h.

infra). We also chose COE as monomer as a cyclic olefin with only moderate ring strain.[10a,24] Furthermore, conversion is easily detected via ^{1}H NMR. Thus, the kinetic studies could be conducted at relatively high catalyst loadings which benefited the accuracy by minimizing weighing errors. Each concentration of each inhibitor exhibited a dramatic effect on the conversion rates (Table 1). It was found that the ROMP reaction was entirely suppressed using MIM (1 equiv and higher) or DMAP (2 equiv and higher) as an additive in the reaction mixture. After 24 h reaction time, no ROMP product could be detected via ^{1}H NMR spectroscopy. Low amounts of DMAP (1 equiv) caused a dramatic reduction in reactivity yet did not result in a complete suppression of the polymerization reaction. In comparison to uninhibited Grubbs' Catalyst **1** under identical reaction conditions (20.1% conversion after 1 min), the inhibited catalyst took almost 1500 times longer to reach equal conversion (19.7% after 24 h).

Pyridine also exhibited a strong inhibiting effect on the conversion over time but could not stop the metathesis reaction at any concentration up to 5 equiv with respect to catalyst. A clear trend is visible. As expected, an increased donor concentration results in a slower metathesis reaction. In fact, none of the experiments exhibited noticeable conversion (>2%) after 60 min, which would be consistent with an induction period and slow initiation. However, the ROMP experiments follow first-order kinetics similar to RCM inhibition experiments with PCy_3,[16] in particular when two or more equivalents of pyridine were used. From the logarithmic conversion plot [$\ln(1/(1-x))$ vs time − Figure 2] the polymerization rate constants relative to Grubbs catalyst **1** could be determined, which also follows first-order kinetics. The relative rate constants [$k_{rel} = k_{obs}$(inhibited)/k_{obs}(**1**)] range between 9.8×10^{-3} (1 equiv) and 4.0×10^{-3} (5 equiv). Such dependency of inhibitor concentration and degree of inhibition was previously observed by Grubbs et al. inhibiting RCM of DEDAM with PCy_3.[16] Similar to Grubbs' findings, the plot of relative rate constants vs reciprocal inhibitor equivalents, in this case pyridine, is linear (Figure 3). The

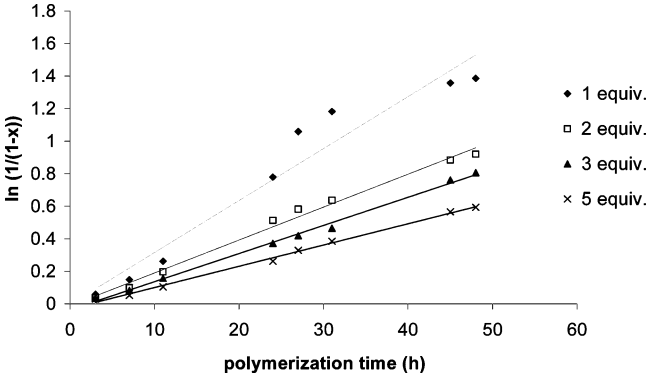

Figure 2. First-order kinetic profiles for the conversion of COE with catalyst **1** and 1−5 equiv of pyridine as inhibitor in benzene; [**1**] = 2.0 mM, 2% catalyst loading.

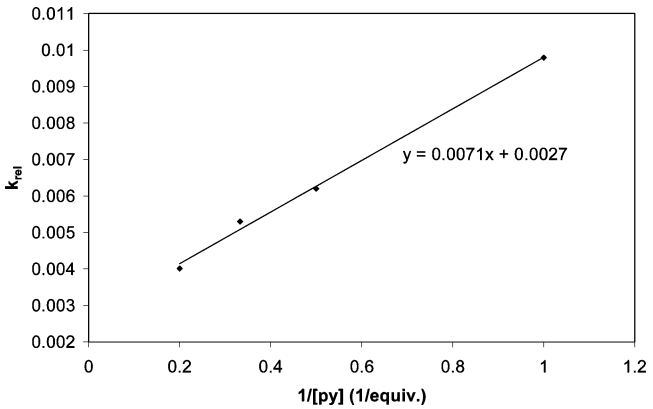

Figure 3. Plot of k_{rel} vs inverse equivalent of pyridine in benzene; [**1**] = 2.0 mM, 2% catalyst loading.

y-intercept of this plot is located at 2.7×10^{-3}, which would mean that, with a large excess of pyridine, the ROMP reaction would theoretically proceed up to 370 times slower at maximum inhibition. It should be noted that large excess of pyridine will result in the formation of a PCy_3 ligated analogue of complex **3b**.[25] Pyridine is a powerful inhibitor for ROMP reactions with Grubbs' catalyst **1**. This observation is in contrast to the initial expectation where third generation catalysts are highly active metathesis initiators. In fact, bis-3-bromopyridine complex **3a** exhibits one of the fastest metathesis initiation rates known to date.[14] However, pyridine complex **3b** is a less-active catalyst than complex **3a**.[14b] The addition of 1 equiv of PCy_3, a known inhibitor, to complex **3b** therefore, should result in a low-activity species. In fact, such experiment would result in the identical catalytic species as the addition of 2 equiv of pyridine to catalyst **1** (entry 12, Table 1), which exhibits low activity indeed. The nature of the inhibited catalytic species using N-donor ligands will be discussed in more detail later in this article (*vide infra*).

A ROMP inhibition experiment was also conducted with 1 equiv of PCy_3 (relative to catalyst **1**) as inhibitor (entry 15, Table 1). The reaction proceeded very slowly at room temperature as there was no conversion detected after 5 h. After 24 h, 9.3% of COE was converted. In contrast to the pyridine inhibited reactions, the conversion did not follow first-order kinetics. The polymerization accelerated over the course of 3 days. After 72 h, the monomer conversion was determined to be 41.2%. The effect can be explained by the different nature of propagating

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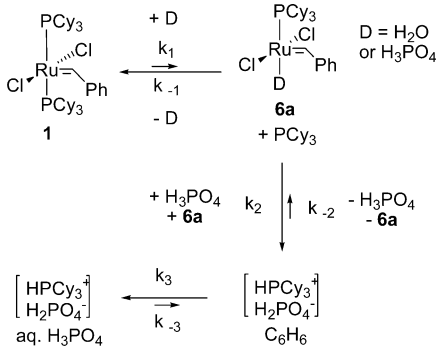
and initiating species. After the first turnover, a new catalytic species is formed. It has been proven that Ru−alkylidene complexes (and one is resulting from ROMP of COE) generally display higher initiation rate constants than Ru−benzylidene complexes.[13,26] Upon very slow initiation rates, the amount of Ru−alkylidene only gradually increases over time, whereas the bulk of the initial catalyst still remains unreacted. Both species were observed via ^{31}P NMR spectroscopy. After 72 h, 70% of the ruthenium species were still present as Grubbs catalyst **1** (δ 37.2 ppm), whereas only 30% of catalyst **1** had been converted into the alkylidene complex (δ 36.6 ppm). As a result, the overall reaction rate was increasing due to the slow formation of the higher active species. An increase in metathesis activity over time (induction period) is very common for catalysts with much faster propagation than initiation rates, such as second generation catalysts.[27] In this particular experiment, however, the induction period stretches over days. In comparison to pyridine, PCy_3 clearly is a superior inhibitor but is not capable of completely stopping the ROMP reaction as accomplished with 1 equiv of MIM. Table 1 summarizes the results of the ROMP inhibition experiments.

ROMP experiments that experienced complete inhibition over 24 h (1−5 equiv of MIM, 2−5 equiv of DMAP) were subjected to reactivation with excess 85% H_3PO_4 (ca. 25 equiv with respect to Ru species), a strong, non-nucleophilic acid. As acid addition has been used to accelerate the rate of initiation due to protonation of the phosphine ligand,[18,19] an elevation of metathesis activity due to excess H_3PO_4 would be not surprising. In fact, H_3PO_4 possesses a higher Brønsted acidity than the $HPCy_3^+$ cation by approximately 7 orders of magnitude,[28] and PCy_3 is even somewhat more basic than the N-donor ligands. This would suggest that alongside the N-donor ligands, all free PCy_3 would be in fact protonated. Yet, adding 25 equiv of H_3PO_4 to uninhibited catalyst **1** does not significantly accelerate the conversion (Table 1); rather, it can be assumed that the slightly elevated conversion observed after 6 min (57.8% vs 55.0% without H_3PO_4) is within the margin of the experimental error. The determined relative reaction rates are identical for both experiments, with or without additional phosphoric acid. A ^{1}H NMR spectroscopic investigation in d_6-benzene of the influence of excess H_3PO_4 on the nature of Grubbs' catalyst **1** indicated no formation of a second mono-PCy_3 species **6a**. Such a species was observed by Grubbs and co-workers using 0.3 equiv of DCl to form complex **6b** (Figure 8) from a water-soluble first generation bis-phosphine catalyst in D_2O.[18a] The addition of 25 equiv of H_3PO_4 to uninhibited catalyst **1** without substrate afforded no changes in the ^{1}H and ^{31}P NMR spectra with the characteristic signals retaining the typical chemical shifts (δ (^{1}H) 20.52 ppm [s], δ (^{31}P) 37.2 ppm) for this compound in d_6-benzene.[29] Due to the Brønsted basicity of PCy_3, this is very surprising. It is likely that upon phosphine dissociation, a mono-phosphine complex intermediate **6a** would be formed (Scheme 2). The ruthenium center becomes very Lewis-acidic and possesses a stronger affinity to the phosphine

Scheme 2. Equilibrium between Catalysts **1** and **6a** upon Addition of H_3PO_4 in Benzene



than does the H^+ cation under these conditions ($K_1 = k_1/k_{-1} < 1$). An important role in the inability to protonate the PCy_3 ligand of complex **1** by an excess H_3PO_4 may also be attributed to the solvents. Upon acid addition, two phases of low miscibility are present in a ratio of 1:120 v/v between protic acid and organic phase. Free PCy_3 ligand should be protonated $HPCy_3^+H_2PO_4^-$ ($K_2 = k_2/k_{-2} > 1$) which then preferably dissolves in the protic phase ($K_3 = k_3/k_{-3} > 1$), where the concentration of the salt becomes very high. In the present biphasic system, the $HPCy_3^+$ salt still possesses appreciable solubility in the benzene phase, and thus, PCy_3 is not removed effectively from the organic phase. As a result, the equilibrium is located almost complete on the side of catalyst **1** with association of the PCy_3 ligand to the metal center being the dominating factor of the equilibrium. It should be noted that the Lewis acidity of the ruthenium center prevented the complete formation of complex **6b** from a water-soluble first generation bis-phosphine catalyst using 1 equiv of DCl, but instead afforded a 1:2 mixture of the mono and the bis-phosphine complex.[18a]

Not only did no permanent protonation of the PCy_3 ligand result from the acid addition, the near-identical reaction rates of both ROMP experiments using catalyst **1** with and without acid prove that H_3PO_4 also does not affect the rate of polymerization, more precisely, neither the rate of ROMP initiation nor propagation. Therefore, it also can be confidently said that H_3PO_4 does not cause the rate of decomposition of catalyst **1** to increase under these reaction conditions either, neither chemically (as lower propagation rates would be observed over time) nor thermally as a consequence of elevated initiation rates.[13]

Upon acid addition to the MIM and DMAP inhibited reactions, the monomer conversion was followed via ^{1}H NMR spectroscopy. The reactivation was virtually instantaneous as there is no indication of slow initial conversion due to an induction period. Moreover, the conversions over time within the MIM series were virtually identical, independent from initial inhibitor concentration, and they also proceeded at approximately the same rate on average as those inhibited by DMAP after reactivation within the experimental margin of error (all DMAP experiments displayed a slightly lower conversion after 6 min [60.5−65.1%] in comparison to the MIM experiments [68.1−69.7%]). Both series achieved overall faster conversion than uninhibited catalyst **1** and accomplished >95% conversion within 60 min and proceeded according to first-order kinetics for the most part of the polymerization (4−30 min). The logarithmic conversion plots $\ln[1/(1-x)]$ vs time in this period are linear. Interesting is the fact that the activated series exhibited

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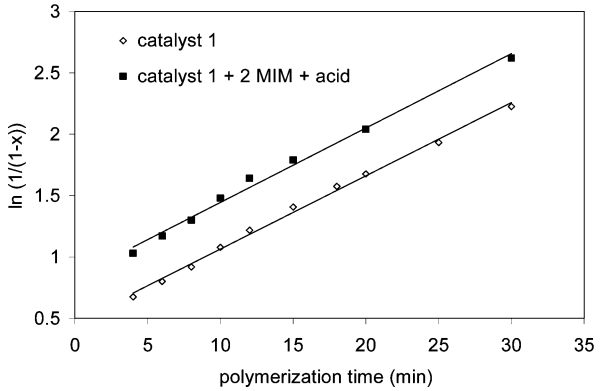
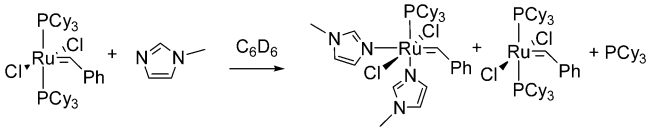


Figure 4. First-order kinetic profiles for conversion of COE with catalyst **1** and reactivated catalyst **1** (inhibited by 2 equiv of MIM for 24 h) between 4 and 30 min in benzene; [**1**] = 2.0 mM, 2% catalyst loading.

Scheme 3. *In-situ* Formation of Complex **5a** upon Addition of Various Amounts MIM to Catalyst **1** in Benzene



1			**5a**			**1**
1	:	1	0.5	:	0.5	: 0.5
1	:	2-5	1	:	0	: 1

higher activities in the early stages (0−4 min) of the reaction. For example, the conversion rate for the activated reaction using MIM (2 equiv) is much higher than for uninhibited catalyst **1** in the initial stages, only to slow down to a near identical rate after ca. 4 min. The linear plot ln [1/(1 − *x*)] vs time in the period between 4 and 30 min actually have near-identical slopes for uninhibited and acid-reactivated reactions (MIM [2 equiv] − Figure 4), which indicates near-equal rates for the polymerization in this time period. In fact, the relative rate constants determined for all experiments with respect to catalyst **1** (Table 1) are all within a range of ± 4%. Considering the margin of error applied when measuring the reactants (±2%) and integration of NMR signals (±1%) on the small scale experimentally used, it seems very likely that the propagation of the reaction occurs with equal rates, and thus, the propagating species are identical for uninhibited and reactivated polymerizations. Hence, the overall faster conversion for the previously inhibited catalysts is accomplished in the first minutes by what could be described as an anti-induction effect. To understand the details of this observation, we investigated the nature of the inhibited species.

Nature of the Inhibited Catalyst Species. Upon addition of N-donor ligand, a dramatic color change was instantly visible. The purple catalyst solution turned brown (1 equiv of MIM, 1−3 equiv of DMAP, 1−5 equiv of pyridine) or bright green (2−5 equiv of MIM, 5 equiv of DMAP) depending on the nature and concentration of the inhibitor. Whereas pyridine at the used concentrations did not cause the obvious formation of a new species that could be detected via NMR spectroscopy, a color change to reddish brown was also observed. ^{1}H and ^{31}P NMR spectroscopy indicated that a new, hexacoordinate Ru species **5a** was formed upon MIM addition, independent of the presence of substrate. One PCy_3 ligand was replaced by two N-donor ligands. It is likely that **5a** is ligated by *trans*-chlorine ligands as it was established for all determined structures of the motif (L)(N-donor)$_2$Cl$_2$Ru=CRR′ (L = PR_3 or NHC, R′ = H, alkyl).[15,25,30] The formation of the new species was almost quantitative with MIM. Upon use of 1 equiv of MIM with respect to catalyst **1**, 50% of catalyst **1** was converted into species **5a**, producing half an equivalent of free PCy_3 (Scheme 3). As a result, the ^{31}P NMR spectrum (d_6-benzene, 20 °C, 121.9 MHz; see Figure 5) exhibited three signals at δ = 37.2 ppm (2 P, **1**), 31.9 ppm (broad, 1 P, **5a**), and 10.6 ppm (1 P, PCy_3). The ^{1}H NMR spectrum at very low field (d_6-benzene, 20 °C, Figure 5) also indicated the presence of two different benzylidene-hydrogen atoms in a 1:1 ratio. The signal at δ 20.86 ppm (**5a**) appears as a doublet due to visible coupling ($^3J(^{31}P^1H)$ = 11.1 Hz). Such splitting of the benzylidene-H NMR signal upon removal of one phosphine ligand from bis-phosphine Ru−carbene complexes has been observed on several occasions previously.[15,18a,22] Addition of two or more equivalents of MIM afforded complete conversion of catalyst **1** into complex **5a**. The chemical shift for the benzylidene-hydrogen atom is shifted toward lower field with increasing MIM concentration (δ 21.43 [5 equiv of MIM]). This is indicative of a dynamic coordination-dissociation process where the observed signal becomes an average between different amounts of the penta and hexacoordinated complexes.[15] It should be noted that Grubbs and coworkers have isolated cationic complex **4a** with excess MIM which precipitated from benzene.[15] Obviously, the higher initial concentrations of the reactants and low solubility of **4a** in the solvent resulted then in the quantitative conversion. Our observation, however, was that the formed species **5a** remained soluble and stable for days under the described conditions with the respective amounts of free PCy_3 in the solution.

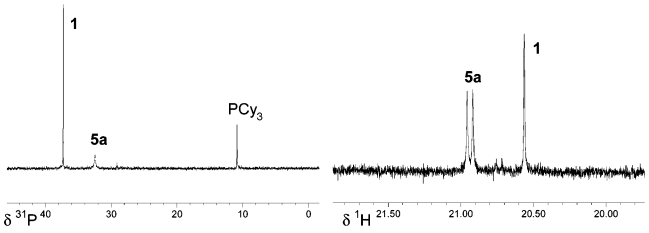
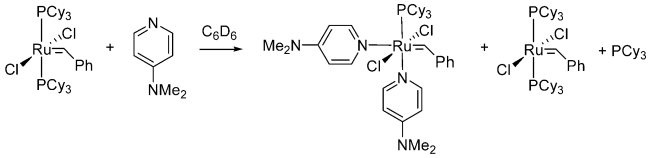


Figure 5. ^{31}P NMR (20 °C, 121.4 MHz) spectrum and ^{1}H NMR (20 °C, 300.1 MHz) spectra (benzylidene-H region) of the reaction solution of complex **1** and 1 equiv of MIM in d_6-benzene; [**1**] = 2.0 mM.

Scheme 4. *In-situ* Formation of Complex **5b** upon Addition of Various Amounts DMAP to Catalyst **1** in Benzene



1			**5b**			**1**
1	:	1	0.32	:	0.68	: 0.32
1	:	2	0.55	:	0.45	: 0.55
1	:	3	0.71	:	0.29	: 0.71
1	:	5	0.84	:	0.16	: 0.84

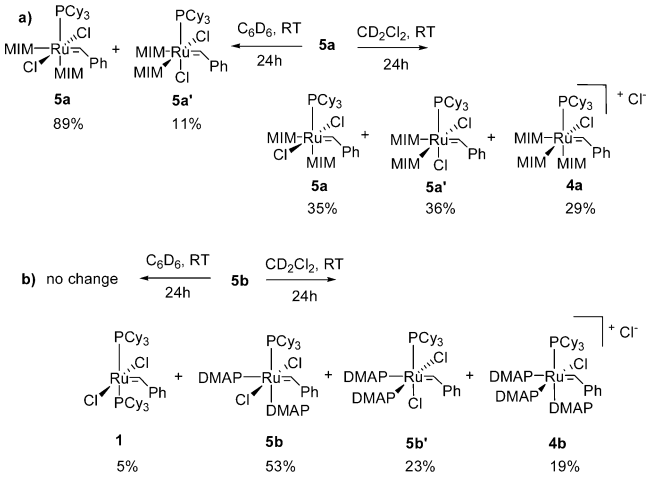
Upon addition of DMAP (Scheme 4), the hexacoordinate species **5b** also can be observed (^{31}P NMR: δ 34.6 ppm, ^{1}H NMR: δ 20.41−21.13 ppm [1−5 equiv of DMAP, d, $^3J(^{31}P^1H)$ = 12.0 Hz, benzylidene-H], but the conversion of catalyst **1** is not quantitative with respect to the added amount of DMAP. Depending on the number of equivalents of DMAP used, a higher degree of formation for complex **5b** could be derived

(30) Clavier, H.; Petersen, J. L.; Nolan, S. P. *J. Organomet. Chem.* **2006**, *691*, 5444−5447.

from ^{1}H NMR spectra (1 equiv, 32%; 2 equiv, 55%; 3 equiv, 71%; and 5 equiv, 84% **5b**). Similar to MIM, with increasing DMAP concentration, the ^{1}H NMR signal of the benzylidene-hydrogen atom noticeably shifted toward lower field. All catalyst plus inhibitor solutions were stable in d_6-benzene at room temperature for 24 h, and no indication was found for the formation of secondary reaction products via NMR spectroscopy.

Compounds **5a** and **5b** were synthesized and isolated in reactions of Grubbs' catalyst **1** and slight excess of the N-donor ligand. Complex **5b** was previously synthesized by Grubbs et al. but could not be isolated in pure form as the product contained significant amounts of DMAP. Therefore, no spectroscopic data was reported.[15] By choosing diethyl ether as solvent, complex **5b** precipitated in pure form using 4 equiv of DMAP. Also, in contrast to the same report that afforded the cationic species **4a** bearing three MIM ligands in benzene (*vide supra*), complex **5a** is straightforwardly produced in high yield using *n* heptane as nonpolar solvent instead of benzene. Both complexes precipitated as bright-green solids and were separated by filtration. Both complexes displayed only moderate solubility in d_6-benzene (ca. 3 mg/mL) at ambient temperature. Over the period of 30 min, the formation of a new species was detected via ^{31}P NMR spectroscopy (δ 29.1 ppm) in the d_6-benzene solution from neutral, hexacoordinated bis-MIM complex **5a**. The species is likely to be the isomeric bis-MIM, *cis*-Cl_2 complex **5a′**, rather than a pentacoordinate species (**5a** minus one molecule of MIM), as the new species exhibits a distinct set of NMR signals. Compound **5a** and its pentacoordinate counterpart were present in an equilibrium which on the NMR time scale give an averaged set of NMR signals as observed with mono and bis-pyridine complexes derived from catalyst **1**.[15] The change of N-donor ligand position with a chloride ligand within Ru−carbene complexes has been previously reported.[31] The equilibrium of **5a**/**5a′** = 89:11 remained constant for 24 h. ^{31}P NMR spectra of complex **5b** remained unchanged in benzene solution for 24 h. Only trace amounts (<2%) of catalyst **1** could be detected after 24 h. Solutions of complexes **5a** and **5b** in CD_2Cl_2 at ambient temperature exhibited much faster formation of new species. According to ^{31}P NMR spectra, 46% of complex **5a** were converted into **5a′** (δ 27.9 ppm) after 10 min/ and after 15 min, a new species was detected at δ 20.9/ which is in agreement with the chemical shifts determined for complex **4a**.[15] After 60 min, 64% of the soluble, phosphine containing species is complex **5a′**, which then slowly decreases after that. Over a period of 24 h, the amount of complex **4a** steadily increases and the broad signal for complex **5a** notably shifts toward lower field (δ 33.6 ppm [10 min], δ 37.0 ppm [24 h]), which is in agreement with a reduction of the average coordination number from a maximum of six to a minimum of five. Furthermore, a trace amount of catalyst **1** can be also detected after 24 h. Complex **5b** in CD_2Cl_2 (δ 34.4 ppm [10 min], δ 35.3 ppm [24 h]) showed fast disproportion to a complex **4b** (δ 18.4 ppm), which we assume to be an analogue to **4a** and formation of the *cis*-Cl_2 complex **5b′** (δ 23.7 ppm); however, the complexes reached an equilibrium after 60 min with **5b**/**5b'**/**4b** roughly present in a 2.5:1:1 ratio. After 24 h, significant amounts of catalyst **1** (5% of the overall mixture) were reformed with the distribution of the other three species remaining unchanged. The observed changes of the ruthenium species in d_6-benzene and CD_2Cl_2 solution species are depicted in Scheme 5.

Scheme 5. Formation of Secondary Products from Catalysts (a) **5a** and (b) **5b** in Solutions of Benzene and Methylene Chloride over a Period of 24 h



The metathesis activity of complexes **5a** and **5b** were determined for ROMP of COE in d_6-benzene. Both catalysts performed much slower than catalyst **1** under standard reaction conditions, affording less than 60% conversion after 24 h (**5a**: 55%, **5b**: 45%). Considering the fact that catalyst **1** accomplishes ca. 50% conversion after 4 min, catalysts **5a** and **5b** need roughly 300 times as long to accomplish such conversion. Their activity is in stark contrast to catalyst **3a**, which is an extraordinarily fast initiator.[14] However, catalyst **3b** bearing stronger σ-donating pyridine ligands exhibits significantly lower metathesis activity.[14b] The even stronger σ-donating MIM and DMAP reduce the ROMP activity of complexes **5a** and **5b** to the observed low levels. The dramatic impact of the electronic nature of the N-donor ligand is not surprising considering the dissociative mechanism of the olefin metathesis reaction.[13,16] In contrast to catalyst **1**, two consecutive dissociation steps of the donor ligand from the 18-electron complexes **3** and **5** are required to form the active initiator species. Thus, two equilibrium constants [$k_{\text{dissociation}}$/$k_{\text{association}}$] are affected by the nature of the ligand. For low σ-donating 3-bromopyridine, both rate constants must be very high, and thus, the overall initiation rate is high. With a decrease of both constants, an exponential decrease in the rate of initiation is expected upon increasing σ-donor capabilities. For complexes **5a** and **5b**, both equilibrium constants must be low, and as the overall result, the initiation of the metathesis reaction for both catalysts is slow. Despite the slow initiation, both conversions went beyond 80% within a period of 48 h. The MIM coordinated species **5a** initially is performing at a slightly faster rate than catalyst **5b** but then reaches a conversion plateau at 81%, which indicates catalyst degradation. Interestingly for both catalysts, the plot of conversion vs time (Figure 6) is linear between 10 and 75% conversion after an induction period of several hours to follow pseudo zero-order instead of first-order kinetics for the bulk of the polymerization. We have observed a similar accelerating effect with ROMP of COE with catalyst **1** inhibited by PCy_3 (*vide supra*). Also in this reaction, the formation of the Ru−alkylidene complexes after the first turnover is very

(31) Ung, T.; Hejl, A.; Grubbs, R. H.; Schrodi, Y. *Organometallics* **2004**, *23*, 5399−5401.

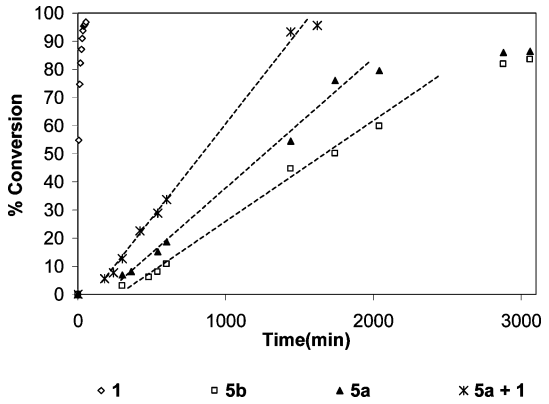


Figure 6. Plot of pseudo zero-order kinetics for the conversion of COE for catalysts **5a**, **5b** and 1:1 **5a** + **1** in comparison to catalyst **1** in benzene; [Ru] = 2.0 mM, 2% catalyst loading.

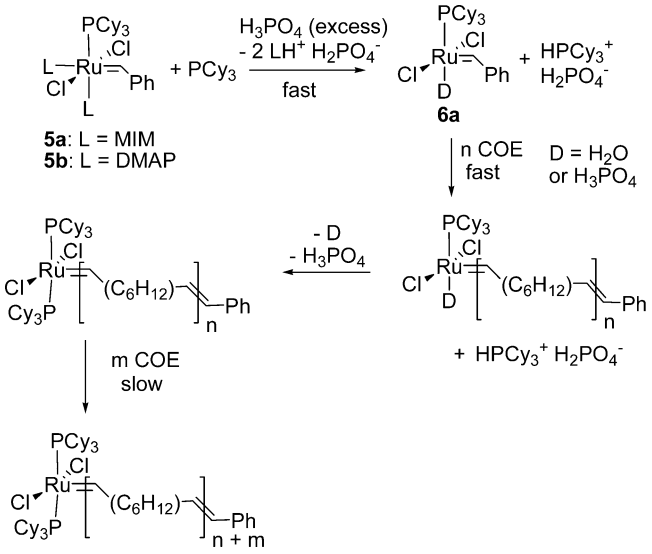
slow due to slow initiation. In fact, the ^{1}H NMR signal for the benzylidene hydrogen atom of catalyst **5a** was still observed after 24 h, which means that after this period of time, not all of catalyst **5a** had initiated the ROMP reaction. For the ROMP reactions with catalysts **5a** and **5b**, the slowing of turnovers based on lower monomer concentration is just compensated by an increasing concentration of the faster initiating alkylidene catalyst to give pseudo zero-order kinetics, assuming the rate of catalyst degradation is very slow.

Although complexes **5a** and **5b** are very slow metathesis initiators, the nature of the complete inhibition of catalyst **1** with MIM or DMAP is not fully explained by their formation as they still promote ROMP of COE to a certain degree. Also, in several experiments (1 equiv of MIM and 2−5 equiv of DMAP), there is still active catalyst **1** present in the inhibited mixture. Thus, complete inhibition had to be caused by a combination of factors. (1) Free PCy_3 is formed upon the adjustment of the equilibrium between the catalysts **1** and **5**. The strong inhibiting capability of PCy_3 has been demonstrated (*vide supra*). (2) The inhibited mixture contains residual free MIM and particularly DMAP, present in the inhibited mixture as part of the equilibrium. Pyridine has been shown to be potent inhibitor without forming significant amounts of a species of the nature of complexes **5** even at 5 equiv added to the catalyst **1**. Both N-donor ligands are even stronger σ-donors should exhibit even enhanced inhibiting capability in the ROMP reactions. (3) In all experiments with MIM and DMAP, the low reactive species **5** is formed to various degrees. All three factors contribute to the inhibition. For example, 2 equiv of MIM resulted in the near-complete formation of low-activity complex **5a** which then additionally was inhibited by free PCy_3, a strong ROMP inhibitor as shown. Only small amounts of free MIM were present in the mixture, reducing the impact of this factor. Addition of two equivalents of DMAP on the other hand resulted in still having approximately 45% of complex **1** alongside a lower formation of only 55% of free PCy_3. On the basis of factors 1 and 3, there may be residual ROMP activity observed. However, the concentration of free DMAP must be >1 equiv with respect to catalyst **1**, which may then contributes toward the zero-activity for 24 h. Either way, the inhibiting factors contributed to the inhibition; all reactions containing significant amounts (2 equiv or more of free N-donor ligands) caused zero-conversion for ROMP of COE over a period of 24 h within the margin of error.

It remains somewhat surprising that no conversion was observed for ROMP using only 1 equiv of MIM. Assuming a complete or near-complete coordination of MIM by conversion into species **5a** (signals for free MIM could not be detected via ^{1}H NMR spectroscopy), 50% starting catalyst **1** remain in the reaction, which are inhibited by 1 equiv of PCy_3 (with respect to catalyst **1**). The free PCy_3 as inhibitor is capable of strongly reducing the rate of polymerization (*vide supra*), yet the reaction should still display noticeable conversion after 24 h. In an effort to understand the degree of inhibition for low MIM concentrations, we have conducted a standard ROMP experiment of COE using a molar 1:1 mixture of catalysts **1** and **5a** (2% combined catalyst loading, [**1** + **5a**] = 2.0 mM). The catalyst mixture does not contain free PCy_3, and thus, in a mixed system where ligands would not exchange rapidly between the different ruthenium centers, the conversion rate should be additively composed of the individual catalyst performances. As catalyst **5a** performs very much slower than **1**, the conversion constant should have proceeded at approximately half of the conversion rate seen with catalyst **1** (Table 1, entry 1) unless significant amounts of inhibitor would be present due to N-donor dissociation from complex **5a**. In fact, it was observed that this mixture possessed a very low catalytic activity (Figure 6), much lower than the expected 50% of uninhibited catalyst **1** (entry 1, Table 1), and the kinetics followed much rather those of complexes **5**. There was no noticeable conversion within 60 min (complex **1** reaches 97% in the same time period) and after the induction period, the reaction proceeded via near zero-order kinetics up to high conversions of >90% in 24 h. The overall reaction is faster than with catalysts **5a** alone, but only by a factor of 2−3. This means that there must be a noticeable concentration of free MIM functioning as inhibitor in the reaction solution due to a dynamic N-donor ligand dissociation/association process. It was demonstrated that complex **5a** and other hexacoordinate bis-N-donor complexes of the nature of **5a** are present in a dynamic equilibrium with its pentacoordinate counterpart in solution.[15] Therefore, on the basis of the low activity of the mixed catalysts and the inhibiting strength of PCy_3, 0.5 equiv of free PCy_3 (with respect to all Ru species), which will result from addition of 1 equiv of MIM to catalyst **1**, will certainly inhibit the ROMP reaction within 24 h without noticeable monomer conversion.

Proposed Mechanism of the ROMP Reactivation. The protonation of a water-soluble first generation Grubbs-type catalyst with 0.3 equiv of DCl in D_2O afforded a monophosphine complex **6b**, which is suggested to bear a D_2O ligand in place of the phosphine (Figure 8). It was found that ROMP rates of the bis-phosphine precursor could be significantly accelerated upon addition of DCl, very likely due to the significant formation of complex **6b**.[18a] We have demonstrated that H_3PO_4 does not protonate one of the PCy_3 ligands of complex **1** to generate a similar mono-PCy_3 species **6a** in benzene solution. Also, the ROMP reaction of COE proceeded at the same rate with or without the added acid. Yet the significant ROMP acceleration was observed in the first 4 min when the inhibited reactions were reactivated with H_3PO_4. With regard to the inhibited mixtures, the addition of H_3PO_4 should afford protonation of the basic ligands, the free PCy_3, as well as all N-donor ligand in the mixture, which includes the free ligand and ligand bound to complexes **5a** and **5b**, which rapidly dissociates after

Scheme 6. Difference in the Formation of the ROMP Active Species **6** between Catalyst **1**, Reactivated Catalyst **1**, and Catalysts **5a** and **5b**



removing all free N-donor ligand. In fact, during shaking for several seconds after acid addition, the color of the inhibited reaction solution (initially green with large amounts of N-donor present) turns orange brown, which suggests the protonation takes place near-quantitatively within this time period. In particular for the MIM-inhibited (2−5 equiv) catalyst mixtures where the most of the Ru species is converted into complex **5a**, it would mean that the protonation would afford almost exclusively the species **6a** which similar to **6b** should be coordinated with an O-donor molecule (H_2O or H_3PO_4) and is also expected to display a significantly higher ROMP activity than its bis-phosphine precursor (catalyst **1**). The O-donor ligand (if this coordination site is not empty) is bound weakly and dissociates much faster than the PCy_3 ligand of complex **1** producing the initiated 14-electron species and, thus, resulting in faster initiation of the reaction. Upon initiation of complex **6a**, PCy_3, which is produced by deprotonation of the $HPCy_3^+$ cation in the benzene phase (Scheme 2), and substrate are competing for the empty coordination site at the ruthenium center. The initial concentration of PCy_3 is very low, which means the ROMP reaction should proceed very fast in the beginning as the polymerization rate is governed by the high activity of species **6a**. Over the first 4 min, all $HPCy_3^+$ cations become deprotonated and almost completely recoordinated as PCy_3 ligand to the metal center of the propagating species. Therefore, an elevated ROMP activity is observed for the reactivated experiments compared to the uninhibited experiment in the first 4 min due to an initially high concentration of mono-phosphine species. After the first 4 min, the catalyst equilibrium has shifted to the bis-phosphine complex, similar to the equilibrium depicted in Scheme 2 with catalyst **1**, and formed the identical propagating bis-phosphine species as the reaction with the uninhibited catalyst resulting in identical polymerization rates (Scheme 6). Unlike the $HPCy_3^+$salt, the protonated N-donor ligand salt obviously was not playing a significant role in the kinetics of the reactivated reactions. Very likely, the solubility of the salt in benzene is minimal, affording its effective removal from the organic phase where the reaction takes place.

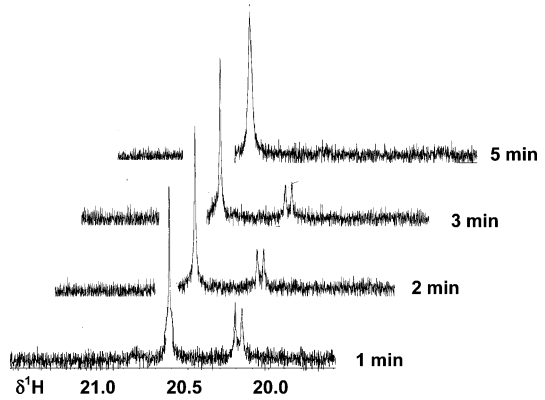


Figure 7. Time-dependent ^1H NMR (20 °C, 300.1 MHz, 1−5 min) spectra (benzylidene-H region) of the reaction solution of complex **1** ([**1**] = 4.0 mM) and 5 equiv of MIM in d_6-benzene after addition of H_3PO_4 (12 equiv) demonstrating the decrease of species **6** due to slow re-coordination of PCy_3.

We investigated the formation of Ru species upon H_3PO_4 addition to a mixture of catalyst **1** and 5 equiv of MIM. Before the addition, only species **5a** could be detected via ^{31}P and ^1H NMR spectroscopy. After the addition and mixing however, the green color instantly turned to orange-brown indicating that complex **5a** was rapidly disappearing from the mixture. The ^1H NMR spectrum after 60 s in the region of δ 18−22 ppm (benzylidene−hydrogen atoms) showed only two signals at δ 20.62 (s, 58%, **1**) and δ 20.18 (d, $^3J(^{31}P^1H)$ = 11.7 Hz, 42%), which is likely to be complex **6a**. The signal at δ 21.43 ppm (**5a**) had completely disappeared. As the waterfall plot of the ^1H NMR signals between δ 19.5−21.6 ppm (Figure 7) demonstrates, the signal for complex **6a** also has completely disappeared after 5 min, leaving catalyst **1** as the sole Ru−benzylidene complex in the mixture. The relatively slow recoordination of PCy_3, which causes species **6a** to have an appreciative lifetime in the reactivated solution (we recall, that >50% conversion were reached in the first 4 min for all reactivated experiments), may also be supported by the fact that upon acid addition, a second, hydrophilic phase was introduced into the reaction mixture with low miscibility in benzene. The formation of an inhomogeneous system was noticed as a slight cloudiness was observed upon shaking the NMR tube. The cationic phosphonium salt may have been mainly dissolved in the acidic phase and only slowly transferred back into the benzene phase where it was deprotonated and recoordinated as PCy_3.

Inhibition/Activation of Bulk Polymerization of COE and Norbornadiene (NBD). One of the major applications of ROMP is the production of poly-DCPD as adhesives[32] and materials of high mechanical strength.[33] Problematic is the addition of catalyst to the monomer, as most catalysts start the exothermic reaction instantly or with a short delay period. We investigated the inhibited catalyst mixtures in neat monomer as alternative with a long shelf life, which can be initiated by an external stimulus. The degree of inhibition was investigated in studies using mixtures of catalyst **1** (0.1% catalyst loading) and 4 equiv of MIM, DMAP, and 1-octylimidazole (OIM) in neat monomer,

(32) (a) Keck, C. G.; Kendall, J. L.; Caster, K. C. *Adv. Syn. Catal.* **2007**, *349*, 165−174. (b) Caster, K. C.; Tokas, E. F.; Keck, C. G.; Hontz, M. E. *J. Mol. Catal. A: Chem.* **2002**, *190*, 65−77. (c) Caster, K. C.; Walls, R. D. *Adv. Syn. Catal.* **2002**, *344*, 764−770.

(33) Trimmer, M. S. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, 2003; Vol. 3, pp 407−418.

Scheme 7. Bulk Polymerization of COE and NBD with Reactivated Catalyst **1** and Catalysts **5a** and **5b**

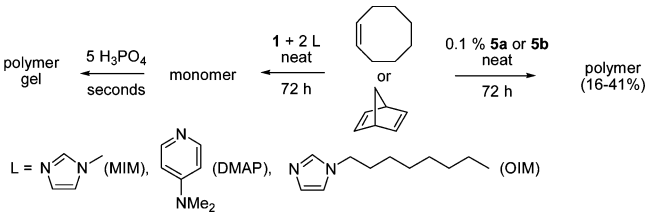


Table 2. Observed Conversions or Gel Times for Bulk-ROMP of COE and NBD with Inhibited (2 equiv of MIM, DMAP, or OIM) and Reactivated Catalyst **1** and Catalysts **5a** and **5b**

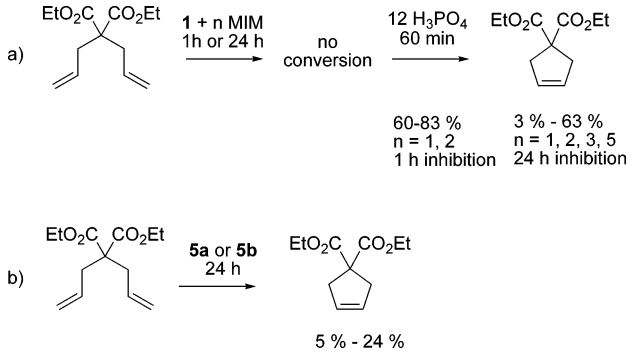
entry	catalyst[a]	substrate	inhibitor (2 equiv)	% conversion[b] 72 h	gel time active[c] (sec)
1	**5a**	COE	−	23.3	−
2	**5a**	NBD	−	41.0	−
3	**5b**	COE	−	19.3	−
4	**5b**	NBD	−	16.4	−
5	**1**	COE	MIM	<2	120
6	**1**	COE	DMAP	<2	330
7	**1**	COE	OIM	<2	105
8	**1**	NBD	MIM	<2	56
9	**1**	NBD	DMAP	<2	20
10	**1**	NBD	OIM	<2	15

[a] Catalyst loading (0.1%) in neat monomer. [b] Determined via ^{1}H NMR. [c] Activation by addition of H_3PO_4 (5 equiv).

COE, and NBD (Scheme 7). The solutions were stirred under nitrogen atmosphere in equal-sized test tubes and with equal-sized stirring bars in a parallel set up. Over the course of 72 h, the solutions were still liquid with no indication of significant polymerization. However, within several hours, a bright-green precipitate was formed with MIM and DMAP (complexes **5a** and **5b**) and the solution colors turned much lighter. The solutions remained liquid with low viscosity in this time period. Much less precipitate formation was observed with OIM, and a discoloration was much less noticeable than for the other inhibitors. It can be assumed that, due to the long alkyl substituent, the inhibited catalyst **5c** is formed and retained better solubility in the highly nonpolar monomer solutions. NMR samples were taken from the six polymerization reactions, and no indication of polymer formation was detected in either reaction via ^{1}H NMR spectroscopy. Experiments were also conducted with catalysts **5a** and **5b** (0.1% catalyst loading) in COE and NBD. The solid catalysts did only dissolve partially as there remained solid catalyst in the light-green solutions. Over time, however, a significant increase in viscosity was noticed, indicating significant polymerization. NMR samples were taken after 72 h, and all mixtures contained polymer (16.4% to 41.0%) at that time (entries 1−4, Table 2). Also, the stirring bar was frozen within the formed gel for the reaction of NBD with **5a**.

After 72 h, 85% H_3PO_4 (5 μL, 10 equiv relative to **1**) was added to the inhibited ROMP mixtures to initiate the polymerization, and the time intervals between acid addition and gelling of the mixtures (stirring bar stopped spinning) were determined (Table 2). Assuming that the point of gelling, among other factors, is a function of conversion, the gel time qualitatively correlates inversely to the ROMP activity. Polymerizations of NBD reached the gel point in less than 1 min for all inhibitors, COE in less than 7 min. With the previous inhibited/activated ROMP experiments in solution (*vide supra*), it has been shown that conversion rates of acid activated

Scheme 8. RCM of DEDAM with (a) Reactivated Catalyst **1**, and (b) Catalysts **5a** and **5b**



polymerizations are dependent on the electronic nature of inhibitor only to a minor degree. Thus, it can be assumed that ROMP activity within the series of bulk polymerizations for one monomer is mainly governed by the initial concentration of the inhibited catalyst. This will obviously cause a higher initial concentration of active catalyst upon acid addition and, thus, will provide an overall faster polymerization. As expected, OIM inhibited reactions (entries 7 and 10, Table 2) proceeded fastest with both monomers as the inhibited catalyst was present in the highest initial concentration. Acid induced ROMP with MIM and DMAP as inhibitors do not show a clear trend of preferred initial solubility. For COE, it took approximately three times as long to reach the gel point with DMAP as inhibitor than with MIM whereas the scenario is reversed for NBD, where gel point was reached twice as fast with the DMAP inhibited reaction after acid activation as with the MIM inhibited.

Ring Closing Metathesis (RCM) of Diethyl Diallylmalonate (DEDAM). Similar to the ROMP experiments, we conducted two series of inhibition experiments using MIM as N-donor inhibitor (0, 1.0, 2.0, 3.0, and 5.0 equiv with respect to **1**) in combination with DEDAM, a standard RCM substrate for kinetic NMR experiments,[12,16,17] as substrate (Scheme 8a). The substrate conversion was monitored via ^{1}H NMR (d_6-benzene, 20 °C, [**1**] = 4.0 mM, 5% catalyst loading). Similar to ROMP of COE, for all N-donor concentrations, no product formation could be detected over a period of 24 h. In the same fashion as the inhibited ROMP reactions, we initiated the RCM reactions, which were completely inhibited for 24 h using H_3PO_4 (ca. 25 equiv with respect to Ru species). A significant discrepancy in reactivity is observed after 24 h of inhibition. All conversion rates are dramatically decreased. No reaction reached 70% conversion after 60 min where uninhibited catalyst **1** reaches 88% conversion. It seems likely that significant catalyst degradation has occurred over the time period of inhibition without noticeable product formation (Table 3). The observed trend is that with higher inhibitor concentration, the remaining catalyst activity also is higher. The catalyst inhibited by 5 equiv of MIM over 24 h displayed the most residual activity achieving 63% conversion after 60 min and a maximum of 83% conversion after 24 h. The lowest conversion after 24 h was obtained when 1 equiv of MIM was used before activation (3% after 60 min). The observed degradation during RCM, which is not present during ROMP, suggests the slow formation of an unstable intermediate. Although strongly inhibited, it seems likely that over the time period, carbene exchange is possible. In contrast to ROMP, where the propagating species is a substituted Ru−alkylidene intermediate, RCM affords a Ru−

Table 3. Observed Conversions for RCM of DEDAM with Uninhibited, MIM-Inhibited (1−5 equiv, 1 or 24 h Inhibition Time), and Reactivated Catalysts

entry	catalyst[a]	equiv MIM	% conversion[b] 24 h	inhibition time (h)	% conversion[b] 60 min active[c]
1	**5a**	−	4.5	−	−
2	**5b**	−	24.4	−	−
3	**1**	−	n.d.	−	88.2
4	**1**	1	<2[d]	24	2.8
5	**1**	2	<2[d]	24	23.3
6	**1**	3	<2[d]	24	34.4
7	**1**	5	<2[d]	24	62.9
8	**1**	1	−	1	59.8
9	**1**	2	−	1	82.8

[a] All experiments conducted in d_6-benzene, [Ru] = 4.0 mM, 5% catalyst loading. [b] Determined via ^{1}H NMR. [c] Activation by addition of H_3PO_4 (12 equiv). [d] Conversion for inhibited catalyst.

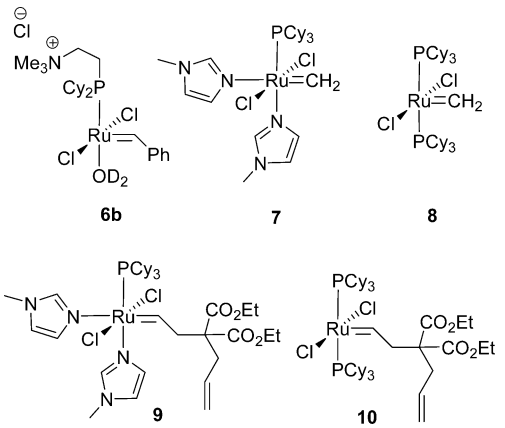


Figure 8. Complex **6b** and RCM intermediates **7**−**10**.

alkylidene and a Ru−methylidene species as intermediates. Also, it has been established that terminal olefins (as used in RCM of DEDAM) generally are more reactive substrates for metathesis than 1,2-disubstituted olefins (as used in ROMP).[4] Therefore, initiation of RCM is faster than ROMP. It has been observed previously that slow initiating (PCy_3)(N-donor)Ru carbene complexes degrade during RCM of DEDAM affording generally incomplete conversions before quantitative catalyst degradation.[15] With the almost quantitative ligand replacement of PCy_3 with two MIM in catalyst **1** to yield the low-activity species **5a** in the reaction solution, Ru−methylidene species **7** is formed after the first catalytic turnover. Species **7** (Figure 8) is also expected to cause catalyst degradation during RCM of DEDAM with pure catalyst **5a**. It has been established that intermediate Ru=CH_2 complexes follow a unique, monomolecular degradation pathway,[34−36] which is independent from the catalyst concentration. If complex **7** exhibits a rate of degradation higher than or at least comparable to the rate of the metathesis reaction, a steady loss of catalyst would be the consequence without noticeable RCM conversion.

We investigated the reaction of DEDAM with catalyst **1** (20.0 mM in d_6-benzene, 15% catalyst loading) inhibited by 1 equiv of MIM containing Ph_3PO in 5 mM concentration as internal standard by following the change of the catalytic species via ^{1}H and ^{31}P NMR spectroscopy. Upon addition of MIM to the catalyst solution, the color turned from pinkish purple to brown, and after the addition of DEDAM, the color remained for several hours. After 3 h, the ^{31}P NMR spectrum of the reaction solution still contained all phosphorus containing species in solution according to the internal standard. The spectrum exhibited three new signals at δ 38.4 ppm (6.0% signal intensity), δ 34.7 ppm (4.2% signal intensity), and δ 27.0 ppm (<1% signal intensity) alongside the initial the signals for complexes **1** (δ 37.2 ppm − 43.5% P-intensity), **5a** (δ 31.0 ppm − 21.3% signal intensity), and free PCy_3 ligand (δ 10.8 ppm − 23.4% signal intensity). The species at δ 34.7 ppm had been observed by Grubbs et al. as decomposition product of methylidene complex **8** (Figure 8) and identified as methyltricyclohexylphosphonium chloride.[34−36] The signal at δ 38.4 ppm likely is caused by either alkylidene complex **9** or **10** (Figure 8). Although the first suspicion was that this signal may correspond to complex **7**, as a shift of + 6−8 ppm in the ^{31}P NMR spectrum has been observed for replacing the benzylidene with a methylidene group in other ruthenium complexes,[11,29,35] the ^{1}H NMR spectrum after 3 h does indicate a significant presence of this methylidene species which under these circumstances should produce a signal (d) about half the integral of either complexes **1** or **5a**. The ^{31}P NMR signal at δ 27.0 ppm is caused by an unknown species and may be a (partially) soluble ruthenium phosphine complex formed upon degradation of complex **7**. It should be noted that the ^{31}P NMR spectrum does not indicate the presence of complex **8**.[16] The ^{1}H NMR spectrum after 3 h does indicate the formation of a minor amount of ring closed product (approximately 1%). In the area between δ 15 and 23 ppm, two signals with significant intensities were present at δ 20.51 ppm (s, **1**) and δ 20.86 ppm (d, **5a**). Additionally, a broad signal with low intensity at δ 19.23 ppm (m) was observed that would be consistent with the expected chemical shift[16] and signal pattern for complexes **9** or **10**. The signal could not be accurately integrated, and therefore, no conclusive assignment could be made as the signal intensity for complex **9** should be twice as strong as for complex **10** based on the ^{31}P NMR intensity of the signal at δ 38.4 ppm. After 20 h, the reaction solution had turned from brown to deep green. Moreover a dark-colored precipitate was formed. In the ^{1}H NMR spectrum at this time, only the broad signal at δ 19.23 ppm (m) had an appreciable intensity in the range between δ 15 ppm and δ 23 ppm. Obviously, most of the ruthenium carbene species had degraded at this point. Some formation of ring closed product was observed (11.2% conversion of DEDAM). The ^{31}P NMR spectrum exhibited four major signals and several signals of small intensity, and none of those corresponded to the chemical shifts of complexes **1** or **5a**. Obviously, both starting catalysts have been completely converted. The signals at δ 38.4 ppm (23.8% signal intensity), δ 34.7 ppm (45.1% signal intensity), and δ 27.0 ppm (20.0% signal intensity) were still present in solution alongside small amounts of PCy_3 (11.1% signal intensity). According to the internal standard, overall only 60% of the initial phosphorus-containing species are still in solution.

The decomposition study proved that catalyst degradation in the RCM reaction of complex **1** inhibited by MIM is a significant factor over a period of 24 h. Although complex **7** could not be detected in solution, the positive RCM conversion of DEDAM proves that complex **7** had been formed. In fact, the conversion did not reach 15% (catalyst loading), which

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proves that complex **7** does not facilitate another turnover but degrades rather quickly without accumulation of significant amounts in solution, meaning that the rate of decomposition is much faster than the RCM rate of complex **7**.

To exclude the possibility that the decomposition occurs during the activated state as a consequence of thermal degradation of fast-initiating complex **6a**, we repeated the experiments inhibited with 1 and 2 equiv of MIM under identical conditions reactivating the inhibited mixtures after 60 min instead of 24 h inhibition (Table 3). After 60 min reactivation with H_3PO_4, both reactions (60 and 83%, entries 8 and 9 − Table 3) clearly performed better than after 24 h inhibition and almost to the level seen for uninhibited catalyst **1** (88%). However, the experiment with 1 equiv of MIM also shows a reduced performance, showing that catalyst degradation has become a factor even after 1 h.

The catalysts **5a** and **5b** performed very slowly, affording 4.5% (**5a**) and 24.4% (**5b**) conversion under equal conditions after 24 h (Scheme 8b). The relative RCM activity is reversed now for catalysts **5** in comparison to the ROMP reaction, where catalyst **5a** was performing slightly faster. The conversions, however, do not reach completion. After 48 h, the RCM reaction leveled off at conversions of 8.1 (**5a**) and 33.9% (**5b**) due to catalyst degradation. Such catalyst degradation in RCM reactions of DEDAM had been observed for catalyst **4a** in CD_2Cl_2.[15] It appears likely that the MIM coordinated species **7** has a less favorable ratio between the rates of metathesis and decomposition than its DMAP analogue. Therefore, catalyst **5a** is providing lower conversions than catalyst **5b**.

Conclusions

Investigating the influence of N-donor ligands on the metathesis activity of Grubbs' catalyst **1**, we have shown that the olefin metathesis reaction can be completely or strongly inhibited. For the first time, complete inhibition of the usually fast proceeding ROMP reaction with cyclooctene was observed with 1-methylimidazole or 4-dimethylaminopyridine. Investigations of the inhibited species showed that complexes **5a** and **5b** are completely formed or formed to a significant degree during the inhibition process. They were detected via NMR spectroscopy, isolated, and identified as hexacoordinate complexes that replace one PCy_3 with two N-donor ligands. The species in the inhibited mixtures containing free PCy_3 remain unchanged for 24 h. The pure complex **5a** exhibits minor formation of secondary products (approximately 10%) in benzene solution for 24 h, whereas complex **5b** remained unchanged under these conditions. Both complexes display significant secondary product formation in methylene chloride. They exhibited low ROMP activity when used in benzene or neat monomer. They also slowly promoted RCM of DEDAM. We concluded that the complete metathesis inhibition is a combination of three factors: free PCy_3-inhibition, free N-donor-inhibition, and the formation of catalysts **5a** and **5b** with low metathesis activity.

The ROMP reaction containing N-donor which exhibited no monomer conversion after 24 h could be activated using H_3PO_4 as non-nucleophilic acid. The reactions proceeded faster than using uninhibited Grubbs' catalyst in the first 4 min of the reaction, after which the polymerization rates became identical to ROMP with the uninhibited catalyst **1**. We concluded that the effect is based on a high initial concentration of highly metathesis-active mono-phosphine initiator species **6a** formed by fast dissociation and irreversible protonation of the N-donor ligand and the free PCy_3 ligand under these conditions. As the reaction rates become nearly identical between ROMP of COE with reactivated and uninhibited Grubbs' catalyst after the initial 4 min, we concluded that the mono-phosphine propagating species of type **6a** converts back to the bis-phosphine complex which is identical to the propagating species of the uninhibited reaction. This is accomplished by recoordination of the PCy_3 ligand over the first 4 min. In a ^1H NMR experiment, we have demonstrated that significant amounts of complex **6a** is formed alongside catalyst **1** upon acid addition to a mixture of catalyst **1** and 5 equiv of MIM. Within 5 min, complex **6a** was completely converted back into complex **1**.

Addition of weaker donating pyridine reduces the ROMP rate dramatically but did not inhibit the reaction completely. In contrast to MIM and DMAP, a formation of a hexacoordinate species could not be detected via NMR spectroscopy. Similar to reports of RCM inhibition experiments with PCy_3, pyridine also displayed a linear relationship between factors of inhibition and reciprocal inhibitor concentration.

We have also demonstrated that bulk polymerizations of norbornadiene and cyclooctene with Grubbs' catalyst were completely inhibited for 72 h with 1-methylimidazole, 1-octylimidazole, or 4-dimethylaminopyridine. The reactions could be activated with H_3PO_4 to give polymer gels within 15−330 s. Polymerizations using 1-octylimidazole as inhibitor performed fastest compared to the other inhibitors due to highest initial solubility of the ruthenium species in the nonpolar monomer.

RCM reactions of diethyl diallylmalonate (DEDAM) could be completely inhibited with MIM (1−5 equiv) for 24 h, but upon treatment with H_3PO_4, the reaction would proceed at a fraction of the initial rate accomplished by uninhibited Grubbs' catalyst **1**. Higher amounts of MIM as inhibitor afforded higher RCM activities upon acid treatment. Thermal decomposition studies proved that the initial catalyst can produce one turnover; however, the resulting species **7** decomposes much more quickly than the rate of RCM. As a consequence, higher amounts of inhibitor reduce the rate for the first turnover and therefore experience lower degree of catalyst degradation.

To the best of our knowledge, we have described the first protocol to allow complete reversible inhibition/activation of the ROMP reaction with a Grubbs-type catalyst. A more detailed study involving different first and second generation olefin metathesis catalysts, different ROMP substrates and reaction solvents of different polarity, and an investigation of the corresponding polymer molecular weight distributions is currently under way.

Experimental Section

General Procedures. All experiments with organometallic compounds were performed under dry nitrogen atmosphere using standard Schlenck techniques or in an MBraun drybox (O_2 < 2 ppm). NMR spectra were recorded at a Varian Inova instrument (300.1 MHz for ^1H, 75.9 MHz for ^{13}C, and 121.4 MHz for ^{31}P). ^1H NMR spectra were referenced to the residual solvent, and ^{31}P NMR spectra were referenced using H_3PO_4 ($\delta = 0$ ppm) as external standard. Elemental microanalyses were performed at the University College Dublin Microanalysis Laboratories, Dublin, Ireland.

Materials and Methods. Heptane and diethyl ether were dried by passage through solvent purification (MBraun-Auto-SPS), and d_6-

benzene was degassed prior to use. Reagents and monomers were purchased from commercial sources, degassed and stored in the drybox when directly used in combination with organometallic complexes, and otherwise used without further purification. 1-Octylimidazole[37] (OIM) and diethyl diallylmalonate (DEDAM)[38] were prepared according to literature procedures. Grubbs' catalyst **1** was purchased from Aldrich, degassed, and stored in the drybox.

$(PCy_3)(H_3C-C_3H_3N_2)_2Cl_2Ru=CHPh$ (5a). 1-Methylimidazole (40 μL, 39 mg, 0.5 mmol) was added to a slurry of Grubbs' catalyst **1** (167 mg, 0.20 mmol) in 10 mL of heptane and stirred for 24 h. A bright-green precipitate was formed in this time period, which was filtered and washed once with 5 mL of heptane. The residue was dried under vacuum to afford complex **5a** (116 mg, 82%). ^{1}H NMR (d_6-benzene): δ 20.86 (d, $^3J(^{31}P^1H) = 11.1$ Hz, 1H, Ru=C*H*−Ph), 8.62 (d, $^3J(^1H^1H) = 7.4$ Hz, 2H, ortho C*H*), 7.33 (t, $^3J(^1H^1H) = 7.7$ Hz, 1H, para C*H*), 7.15 (m, 2H, meta C*H*), 7.95−8.05 (3 signals poorly resolved, 3H), 7.44 (s, 1H), 6.22 (s, 1H), 5.73 (s, 1H, 2×$H_3C-C_3H_3N_2$), 2.45 (s, 3H), 1.91 (s, 3H, 2×$H_3C-C_3H_3N_2$), 2.45−2.65 (br m, 3 H), 2.13−2.27 (br m, 6 H), 1.91−2.08 (br m, 6 H), 1.74−1.84 (br m, 6 H), 1.56−1.64 (br m, 3 H), 1.17−1.40 (br m, 9 H, PCy_3). ^{31}P {^{1}H} NMR (d_6-benzene, 20 °C): δ 31.9 (br). Anal. Calcd for $C_{33}H_{51}Cl_2N_4PRu$: C, 56.08; H, 7.27; N, 7.93. Found: C, 56.30; H, 7.31; N, 7.71.

$(PCy_3)[(H_3C)_2N-C_5H_4N]_2Cl_2Ru=CHPh$ (5b). 4-Dimethylaminopyridine (97 mg, 0.80 mmol) was added to a slurry of Grubbs' catalyst **1** (159 mg, 0.19 mmol) in 15 mL of diethyl ether and stirred for 24 h. A bright-green precipitate was formed in this time period, which was filtered and washed once with 5 mL of heptane. The residue was dried under vacuum to afford complex **5b** (119 mg, 78%). ^{1}H NMR (d_6-benzene, 20 °C): δ 20.89 (d, $^3J(^{31}P^1H) = 12.0$ Hz, 1H, Ru=C*H*−Ph), 8.65 (d, $^3J(^1H^1H) = 7.5$ Hz, 2H, ortho C*H*), 7.30 (t, $^3J(^1H^1H) = 7.5$ Hz, 1H, para C*H*), 7.13 (m, 2H, meta C*H*), 9.34 (d, $^3J(^1H^1H) = 6.6$ Hz, 2H), 8.49 (d, $^3J(^1H^1H) = 6.6$ Hz, 2H), 6.15 (d, $^3J(^1H^1H) = 6.6$ Hz, 2H), 5.61 (d, $^3J(^1H^1H) = 6.6$ Hz, 2H, 2×$(H_3C)_2N-C_5H_4N$), 2.16 (s, 6H), 1.83 (s, 6H, 2×$(H_3C)_2N-C_5H_4N$), 2.59−2.77 (br m, 3 H), 2.27−2.41 (br m, 6 H), 1.88−2.10 (br m, 6 H), 1.73−1.85 (br m, 6 H), 1.57−1.68 (br m, 3 H), 1.19−1.40 (br m, 9 H, PCy_3). ^{13}C {^{1}H} NMR (d_6-benzene, 20 °C) δ 315.8 (m br, Ru=*C*H), 154.8. 130.8, 129.9, 129.5 (s, Ph-*C*), 154.5, 153.7 (s, quart. *C*), 153.2, 151.9, 107.0, 106.5 (s, *C*H), 36.1, 35.9 (s, *C*H$_3$, DMAP), 38.4 (d, $^1J(^{13}C^{31}P) = 25.8$ Hz), 30.4 (s), 28.7 (d, $^3J(^{13}C^{31}P) = 9.7$ Hz), 27.4 (s, PCy_3). ^{31}P {^{1}H} NMR (d_6-benzene, 20 °C): δ 32.4 (br). Anal. Calcd for $C_{39}H_{59}Cl_2N_4PRu$: C, 59.53; H, 7.56; N, 7.12. Found: C, 59.60; H, 7.67; N, 6.98.

ROMP of Cyclooctene (COE) with Grubbs' Catalyst 1. An NMR tube was charged with a stock solution of Grubbs' first generation catalyst **1** in C_6D_6 (2.0 mM, 0.60 mL, 1.2 μmol), and the tube was closed with a septum. Then COE (7.8 μL, 60 μmol) was added via microliter syringe, and the monomer conversion was monitored at 20 °C via ^{1}H NMR spectroscopy by integration of the sufficiently separated multiplett signals at δ = 5.51 ppm (m, monomer =C*H*−) and 5.46 ppm (m, polymer =C*H*−) recording multiple spectra for 60 min.

ROMP of COE with Grubbs' Catalyst 1 and H_3PO_4. In a NMR tube, H_3PO_4 (85 wt. %, 5.0 μL, 30 μmol, 25 equiv with respect to **1**) was added to a stock solution of Grubbs' first generation catalyst **1** in C_6D_6 (2.0 mM, 0.60 mL, 1.2 μmol), and the tube was closed with a septum. Then COE (7.8 μL, 60 μmol) was added via microliter syringe, and the monomer conversion was monitored at 20 °C via ^{1}H NMR spectroscopy as described above.

General Procedure for Inhibition/Activation of ROMP of COE with Grubbs' Catalyst 1. In a NMR tube, a 0.40 M solution of 1-methylimidazole (MIM), 4-*N*,*N*-dimethylaminopyridine (DMAP), pyridine, or PCy_3 in C_6D_6 (3.0 μL, 1.2 μmol for 1 equiv) was added via microliter syringe to a stock solution of Grubbs' first generation catalyst **1** in C_6D_6 (2.0 mM, 0.60 mL, 1.2 μmol), and the tube was closed with a septum. The solution changed colors from purple to brown or green depending on the nature and amount of inhibitor. Then COE (7.8 μL, 60 μmol) was added via microliter syringe, and the monomer conversion was monitored at 20 °C via ^{1}H NMR spectroscopy for 24 h (DMAP, MIM) or 48 h (pyridine, PCy_3) as above. H_3PO_4 (85 wt. %, 5.0 μL, 30 μmol, 25 equiv with respect to **1**) was added via microliter syringe to those experiments that did not show conversion (<2%) and the conversion again was monitored via ^{1}H NMR spectroscopy as described above.

Addition of H_3PO_4 to Grubbs' Catalyst 1 and 5 equiv of MIM. In a NMR tube, a 0.40 M solution of 1-methylimidazole (MIM) in C_6D_6 (30 μL, 12 μmol) was added via microliter syringe to a stock solution of Grubbs' first generation catalyst **1** in C_6D_6 (4.0 mM, 0.60 mL, 2.4 μmol), and the tube was closed with a septum. The solution changed color to bright green. A ^{1}H NMR spectrum was recorded indicating a sole signal at δ 21.37 ppm for the presence of **5a**. Then H_3PO_4 (85 wt. %, 5.0 μL, 30 μmol, 12 equiv with respect to **1**) was added via microliter syringe. The conversion of the mixture was monitored via ^{1}H NMR spectroscopy recording spectra in minute time intervals observing the benzylidene-H region (15−23 ppm).

ROMP of COE with Catalysts 5a and 5b. In an NMR tube, cyclooctene (7.8 μL, 60 μmol) was added to a stock solution of catalyst **5** in C_6D_6 (2.0 mM, 0.60 mL, 1.2 μmol) via microliter syringe through a septum. The monomer conversion was monitored at 20 °C via ^{1}H NMR spectroscopy for 72 h as described above.

ROMP of COE with Catalysts 5a/1 (1:1). In an NMR tube, cyclooctene (7.8 μL, 60 μmol) was added to a stock solution of a molar 1:1 mixture of catalyst **5a** and **1** in C_6D_6 (2.0 mM ruthenium, 0.60 mL, 1.2 μmol) via microliter syringe through a septum. The monomer conversion was monitored at 20 °C via ^{1}H NMR spectroscopy for 48 h as described above.

General Procedure for Inhibition/Activation of Bulk-ROMP of COE and Norbornadiene (NBD) with Grubbs' Catalyst 1. Grubbs' catalyst **1** (5.0 mg, 6 μmol) was added to standard 20 mL test tubes charged with inhibitor (24 μmol [MIM: 1.8 mg; OIM: 4.3 mg; DMAP: 2.9 mg]) and monomer (6.0 mmol [COE: 0.78 mL, 0.66 g; NBD: 0.60 mL, 0.54 g]) and a standard-size small stir bar. The tubes were capped with a septum, and the reactions were stirred in parallel fashion at the same rate for 72 h. Then a sample (5 μL) was taken from all reactions, and ^{1}H NMR spectra were recorded to monitor the monomer conversion by integration of the sufficiently separated multiplett signals at [COE: δ = 5.51 ppm (m, monomer =C*H*−) and 5.46 ppm (m, polymer, =C*H*−); NDB: δ 6.68 ppm (m, monomer =C*H*−) and 4 multiplett signals δ 5.30−5.80 ppm (m, polymer =C*H*−). No conversion could be detected for either experiment. H_3PO_4 (85 wt. %, 10.0 μL, 60 μmol, 2.5 equiv with respect to inhibitor) was added via microliter syringe under continued stirring, and the time was recorded between acid addition and the point when the stirring bar stopped spinning in the test tube.

General Procedure for Bulk-ROMP of COE and NBD with Catalysts 5a and 5b. The catalyst (**5a**: 4.2 mg, 6 μmol; **5b**: 4.7 mg, 6 μmol) was added to a standard 20 mL test tube charged with monomer (6.0 mmol [COE: 0.78 mL, 0.66 g; NBD: 0.60 mL, 0.54 g]) and a standard-size small stir bar. The tubes were capped with a septum and the reactions were stirred in parallel fashion at the same rate for 72 h. Over that time period, a significant increase in viscosity was noted and samples were taken for ^{1}H NMR analysis to monitor the monomer conversion as described above.

RCM of Diethyl Diallylmalonate (DEDAM) with Grubbs' Catalyst 1. An NMR tube was charged with a stock solution of catalyst **1** (0.60 mL, 4.0 mM, 2.4 μmol), and the tube was closed with a septum. Then DEDAM (11.6 μL, 11.5 mg, 48 μmol) was added via microliter syringe, and the monomer conversion was monitored at 20 °C via ^{1}H NMR spectroscopy by integration of the sufficiently separated multiplett

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signals at $\delta = 2.78$ ppm (m, allyl-CH_2, DEDAM) and 3.13 ppm (m, ring-CH_2, cyclopentene derivative) for 120 min.

General Procedure for Inhibition/Activation of RCM of DEDAM with Grubbs' Catalyst 1. In a NMR tube, a 0.40 M solution of 1-methylimidazole (MIM) in C_6D_6 (6.0 μL, 2.4 μmol for 1 equiv) was added via microliter syringe to a stock solution of Grubbs' first generation catalyst **1** in C_6D_6 (0.60 mL, 4.0 mM, 2.4 μmol), and the tube was closed with a septum. The solution changed colors from purple to brown or green depending on the nature and amount of inhibitor. Then DEDAM (11.6 μL, 11.5 mg, 48 μmol) was added via microliter syringe, and the monomer conversion was monitored at 20 °C via ^{1}H NMR spectroscopy for 60 min or 24 h as described above. No conversion could be detected for either experiment. H_3PO_4 (85 wt. %, 5.0 μL, 30 μmol, 12 equiv with respect to **1**) was added via microliter syringe, and the conversion again was monitored via ^{1}H NMR spectroscopy recording multiple spectra for 120 min.

Decomposition of Grubbs' Catalyst 1 with MIM and DEDAM. In an NMR tube, Grubbs' catalyst **1** (9.8 mg, 12 μmol) and Ph_3PO (0.8 mg, 3 μmol) were dissolved in C_6D_6 (0.60 mL). 1-Methylimidazole (1.0 μL, 1.0 mg, 12 μmol) and DEDAM (19.3 μL, 19.2 mg, 80 μmol) were added via microliter syringe. The solution was monitored via ^{1}H and ^{31}P NMR spectroscopy over a period of 24 h.

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Supporting Information Available: ^{1}H, ^{13}C, and ^{31}P NMR spectra of the synthesized Ru complexes as well as tables of kinetic experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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