CHAPTER 2

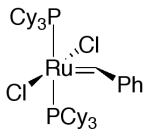
A PEG-Displaying Water-Soluble Olefin Metathesis Catalyst Containing an *N*-Heterocyclic Carbene Ligand

Abstract

The synthesis of an olefin metathesis catalyst displaying a poly(ethylene glycol) (PEG) chain from its *N*-heterocyclic carbene ligand is described. The PEG chain facilitates the dissolution of this catalyst in both aprotic and protic solvents, including water. While it appears to form aggregates resembling micelles in water, this catalyst is active in water and readily catalyzes the aqueous ring-opening metathesis polymerization of norbornene derivatives. The catalyst can mediate ring-closing metathesis reactions in both aprotic and protic organic solvents but is unable to perform metathesis on acyclic substrates in water. Also, the catalyst demonstrates the potential to use PEG's solubility properties to remove ruthenium from metathesis product mixtures.

Introduction

As outlined in Chapter 1, ruthenium complexes **1**–**4** are stable and active olefin metathesis catalysts that enable a variety of reactions useful in small-molecule,[1-3] macromolecular,[1,4,5] and supramolecular synthesis.[6-8] Also, since their first discovery, ruthenium-based metathesis catalysts have shown a tremendous resilience to polar protic solvents including water.[9-11] This stability toward moisture allowed for the development of water-soluble bis(phosphine) catalysts **5** and **6**.[12-15] These catalysts were capable of performing ROMP in water in a living manner and were the first catalysts to mediate ring-closing metathesis in polar protic solvents.[16] However, the inadequate stability of their alkylidene and methylidene derivatives limited the ability of catalysts **5** and **6** to perform metathesis on acyclic substrates in water.[15]



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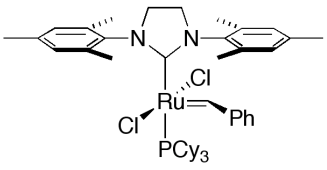

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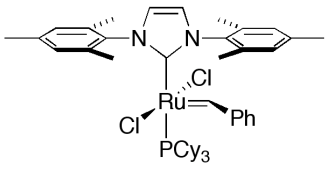

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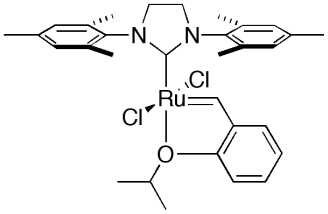

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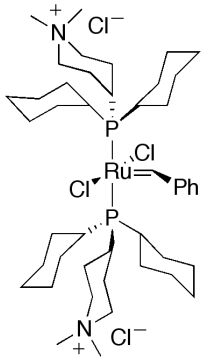

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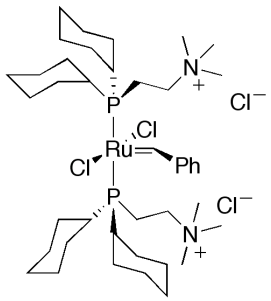

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Ruthenium complexes **2** and **3**, which contain an *N*-heterocyclic carbene (NHC) ligand, are both more stable and more active than their bis(phosphine) counterparts.[17-19] Moreover, tethering the isopropoxybenzylidene ligand of catalyst **4** to a polyethylene glycol (PEG)-displaying resin produces a catalytic system capable of performing ring-closing metathesis in both methanol and water.[20] However, this catalytic resin is incapable of performing metathesis on hydrophilic substrates in water and is, therefore, believed to perform metathesis within the pores of the resin instead of the surrounding water.[20] This chapter describes the synthesis of a homogenous, water-soluble catalyst that harnesses the increased activity provided by an NHC ligand.

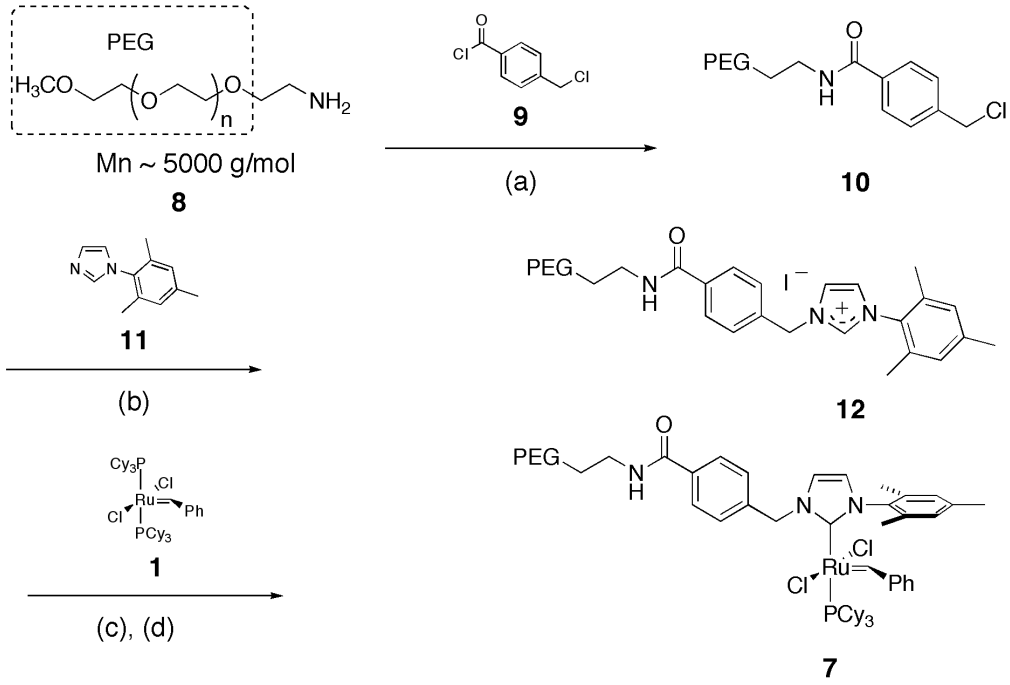
Results and Discussion

Catalyst synthesis and characterization. PEG was chosen to facilitate the targeted catalyst's solubility in water. PEG was anticipated to render this catalyst soluble in both water and also some common organic solvents but insoluble in diethyl ether. This solubility profile may allow for the facile removal of the PEG catalyst from organic products. For example, the catalyst could be removed from organics simply by the precipitation of the product mixture into diethyl ether. With these goals in mind, catalyst **7**, which incorporates PEG onto one of the nitrogen substituents of its NHC ligand, was synthesized (Scheme 2.1).

The synthesis of catalyst **7** is straightforward and is accomplished in three steps. Mixing PEG amine **8** (MW ≈ 5000 g/mol) with acid chloride **9** in the presence of proton-scavenging pyridine and dimethylamino pyridine (DMAP) catalyst yields benzyl chloride **10**. The sodium-iodide-catalyzed reaction of **10** with mesityl imidazole (**11**) then produces imidazolium salt **12**. Finally, the deprotonation of **12** with potassium *tert*-

butoxide followed by ligand exchange with ruthenium bis(phosphine) complex **1** gives catalyst **7** in moderate yield.

Scheme 2.1.

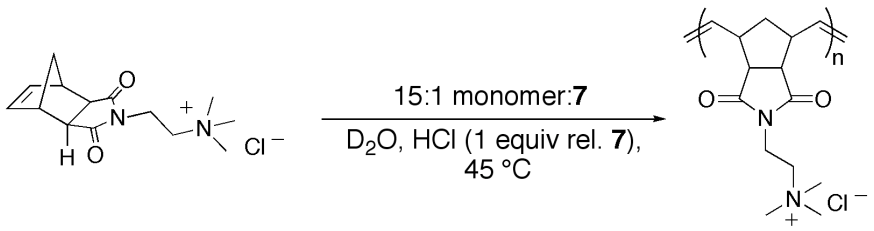


Reagents and conditions: (a) DMAP, pyridine, CH_2Cl_2, 25 °C, 4 h (87%), (b) NaI, acetone, 60 °C, 14 h (98%), (c) KO^tBu, toluene, 25 °C, 15 min, (d) **1**, toluene, 25 °C, 20 min (58 %).

The characterization of catalyst **7** is complicated by the presence of the large, polydisperse PEG chain. Even so, the catalyst can be characterized by NMR spectroscopy in deuterated benzene. The benzylidene proton resonance at 19.7 ppm in the ^{1}H NMR spectrum is consistent with a catalyst containing an NHC ligand.[21,22]

The PEG chain does facilitate the solubility of catalyst **7** in organic solvents such as dichloromethane and toluene, though it is insoluble in diethyl ether. Furthermore, catalyst **7** readily forms homogenous solutions in both methanol and water. However, in water, catalyst **7**'s ^{1}H NMR spectrum is very different from the spectrum obtained in

benzene and cannot be readily assigned. Initially, this result was interpreted to arise from rapid catalyst decomposition in water. However, later research on a different PEG-containing ruthenium metathesis catalyst revealed that, in water, it formed micelle-like aggregates.[23] The ^{1}H NMR spectrum of this catalyst in water closely resembled the spectrum of catalyst **7** in water. Therefore, it is now believed that catalyst **7** also forms micelle-like aggregates in water.



13 **14**

Catalyst activity. The ring-opening metathesis polymerization (ROMP) of *exo*-norbonene monomer **13** was used to investigate the reactivity of catalyst **7** in water. In deuterium oxide at 45 °C, catalyst **7** initiated the ROMP of **13** to give polynorbornene **14** in 73% conversion after 24 hours, as measured by ^{1}H NMR spectroscopy. Further conversion was not observed even after an additional 12 hours at 45 °C. However, the addition of one equivalent of hydrochloric acid allowed catalyst **7** to polymerize monomer **13** to 95% conversion within 15 minutes. This observation is consistent with mechanistic studies by Grubbs and co-workers, which showed that phosphine dissociation from catalysts **1**–**3** is required for entry into the catalytic cycle.[24] It is believed that dissociation of phosphine from catalyst **7** might be disfavored in water due to the energetic cost of solvating two neutral molecules. Thus, protonation of phosphine by hydrochloric acid scavenges free phosphine, which in turn promotes phosphine

dissociation, thereby increasing catalyst activity. Additionally, studies of water-soluble bis(phosphine) catalysts **5** and **6** showed that the addition of 0.3 to 1.0 equivalents of hydrochloric acid increased catalyst activity with the concomitant observation of protonated phosphine.[13-15]

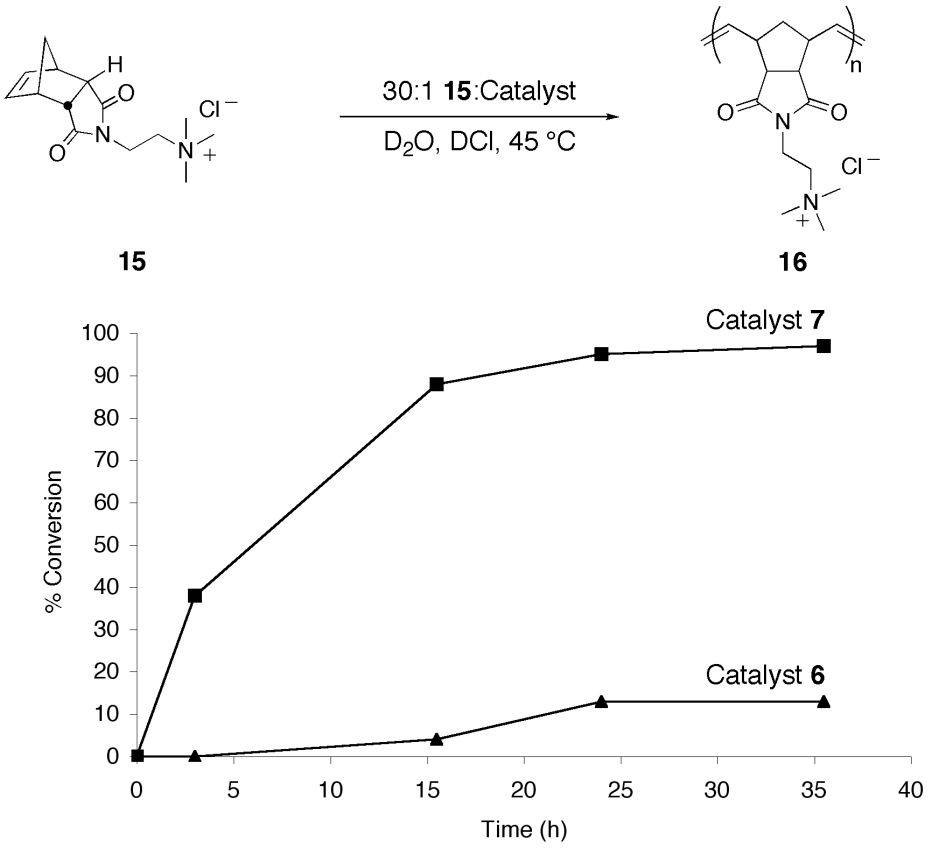
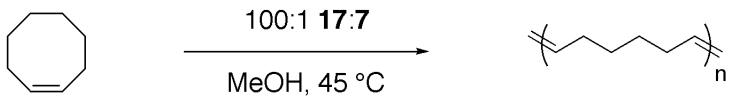


Figure 2.1. The relative activities of catalysts **6** and **7** were examined using the ROMP of challenging *endo*-norbornene monomer **15**.

Earlier work demonstrated that *endo*-norbornene monomers are challenging ROMP substrates.[25,26] For this reason, the ROMP of *endo*-norbornene **15** was used to compare the activities of catalyst **7** and the bis(phosphine) catalyst **6** (Figure 2.1). Gratifyingly, catalyst **7** was able to effect the ROMP of hindered norbornene **15**, and the polymerization proceeded to 95% conversion within 24 hours as judged by ^{1}H NMR

spectroscopy. The ROMP of **15** with catalyst **6** was slower and proceeded to only 13% conversion after 24 hours (Figure 2.1). These results suggest that, in aqueous media, the NHC-containing catalyst, **7**, is significantly more active for the polymerization of hindered norbornenes than the previous generation of bis(phosphine) catalysts.

Although an active catalyst species was not detected spectroscopically, the relatively long reaction times required to completely polymerize **15** suggested that some potentially active species must be present in solution beyond 24 hours. To further investigate the lifetime of **7** in solution, upon completion of the reaction detailed in Figure 2.1, the catalyst **7** reaction mixture was incubated at room temperature for 56 hours prior to the addition of ~8 equivalents of *exo*-monomer **13**. After 24 hours at 45 °C, ^{1}H NMR spectroscopy showed that 87% of the newly added monomer had been converted to polymer. In contrast, the addition of monomer **13** to a solution of **7** in acidic deuterium oxide that had undergone the same schedule of heating and standing gave only 4% polymer after 24 hours at 45 °C. This implies that some metathesis-active species is generated during ROMP with **7** that is more stable in acidic water than the parent benzylidene.

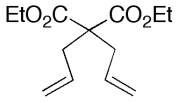
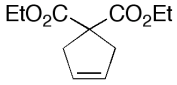
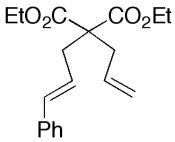
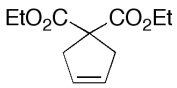
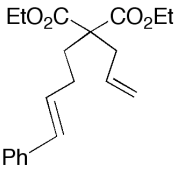
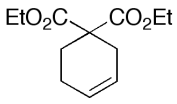


17 **18**

In methanol, polymerization of cyclooctene by catalyst **7** goes to 86% conversion within 14 hours at 45 °C, which demonstrates this catalyst's activity in protic organic solvents. To further examine the activity of **7**, several ring-closing metathesis reactions were attempted in methanol (Table 2.1). As an initial test, the ring closing of diethyl

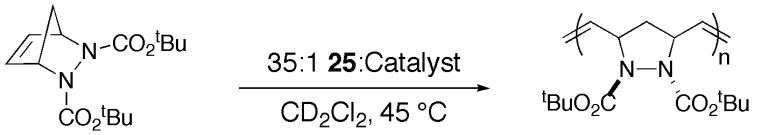
diallylmalonate (**19**) was attempted. Although the conversion for this transformation was low (40%), it represented a significant improvement over previous results with methanol-soluble bis(phosphine) catalysts (less than 5% product).[16] The low yields for the bis(phosphine) catalysts were attributed to the instability of the ruthenium methylidene intermediate produced after a single turnover.[16] Consistent with this hypothesis, ring-closing reactions using the phenyl-substituted substrates **21** and **23**, which avoid the methylidene intermediate, gave higher yields of cyclized product with bis(phosphine) catalysts **5** and **6**.[16] Similarly, catalyst **7** also generated higher cyclized yields with substrate **21** and **23** than with **19**, which suggests that the methylidene derivative of **7** is also unstable or less active in methanol**.** Accordingly, the cross metathesis of terminal olefins, which must proceed through a methylidene intermediate,[27] has currently been unsuccessful in protic media.

Table 2.1. Ring-closing metathesis reactions in methanol with catalysts **5**, **6**, and **7**

Substrate	Product	% Conversion with Catalyst		
		7[a]	**5**[b]	**6**[b]
 **19**	 **20**	40	<5	0
 **21**	 **22**	62	80	95
 **23**	 **24**	82	45	55

[a]Reactions were performed at 45 °C with 5 mol% catalyst and an initial substrate concentration of 0.2 M in methanol-d_4. Conversions were measured by ^{1}H NMR spectroscopy. [b]Data from reference 16.

Catalyst **7** also showed activity in aprotic organic solvents. For example, **7** mediates the ring-closing metathesis of substrate **19** in dichloromethane in 96% conversion, as measured by ^{1}H NMR spectroscopy. To further examine the activity of **7** in aprotic solvents, challenging monomer **25** was used to compare the activity of **7** to parent catalyst **3** in dichloromethane. This monomer has previously been polymerized by a molybdenum catalyst.[28] However, the polymerization of 35 equivalents of monomer **25** with catalyst **1** at 45 °C in dichloromethane proceeds in only 8% conversion after 24 hours.[29] Consistent with the increased activity of catalysts containing an NHC ligand, under the same conditions, catalyst **3** mediates the ROMP of monomer **25** to polymer **26** in 88% conversion after 24 hours.[29] In contrast, PEG catalyst **7** is unable to polymerize monomer **25** even after extended reaction times. This loss of activity is not fully understood but is likely the result of poor catalyst stability and/or the long PEG chain limiting access to catalyst **7**'s ruthenium center.



25 **26**

Catalyst **7** is insoluble in diethyl ether. Therefore, precipitation of a reaction mixture followed by filtration is expected to provide a simple way to remove **7** from organic products. This is an attractive feature as ruthenium by-products are often difficult to remove from metathesis reactions.[30,31] Gratifyingly, precipitation of the reaction mixture from the ring-closing of **23** with catalyst **7** (Table 2.1) from diethyl ether followed by filtration reduces the mixture's PEG content by nearly 97%.[29] While the diminution of the mixture's PEG content does not guarantee a reduction of its ruthenium

content, this is a promising result for the proposed strategy of ruthenium extraction. Indeed, later research demonstrates that PEG's solubility properties can be used to remove ruthenium form olefin metathesis product mixtures.[18,32]

Summary

This chapter described the synthesis and activity of PEG-displaying catalyst **7**, which was the first homogenous olefin metathesis catalyst containing an NHC ligand that was soluble and active in water. While **7** appeared to form aggregates resembling micelles in water, it was active in water and readily mediated the aqueous ROMP of monomer **13**. Catalyst **7** showed increased activity over catalyst **6** for the ROMP of challenging *endo*-norbornene monomer **15** in water, and, though **7** was unable to perform ring-closing metathesis or cross metathesis in water, it was able to cyclize dienes **19**, **21**, and **23** in methanol. In addition, **7** performed metathesis in aprotic organic solvents, although it showed a lower activity than parent catalyst **3**. Finally, catalyst **7** was used to demonstrate the potential for utilizing the solubility properties of PEG to remove ruthenium from olefin metathesis product mixtures.

Acknowledgements

First and foremost, the author wishes to acknowledge the extensive contributions of Professor Justin P. Gallivan to this work. The PEG catalyst was his idea, and he performed many of the experiments described in this chapter. Drs. J. P. Morgan, Jen Love, Tina Trnka, Steve Goldberg, and Brian Connell are also acknowledged for helpful discussions.

Experimental

General considerations. All glove-box manipulations were performed in a N_2-filled Vacuum Atmospheres glove box (O_2 < 2.5 ppm). Otherwise reactions run under inert conditions were performed using standard Schlenk techniques under an atmosphere of dry argon employing flame or oven-dried glassware. All NMR spectra were recorded on a Varian Mercury 300 (299.817 MHz for ^{1}H, 75.4 MHz for ^{13}C, and 121 MHz for ^{31}P) and reported in parts per millon (ppm) downfield from trimethylsilane as referenced to residual protio solvent peaks. Multiplicity abbreviations used when reporting ^{1}H NMR spectra are: s = singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, br = broad. All thin-layer chromatography (TLC) of organic compounds was accomplished on silica-gel 60 F254 percoated plates with a fluorescent indicator and visualized by UV light and/or by standard potassium permanganate stains. All flash chromatography of organic compounds was performed with silica-gel 60 (230–400 mesh).

Materials. All deuterated solvents and deuterium chloride were purchased from Cambridge Isotope Laboratories. Deuterated dichloromethane was dried over 4 Å molecular sieves, and deuterated methanol was dried over calcium sulfate. Both deuterated methanol and deuterated dichloromethane were degassed by three freeze, pump, and thaw cycles while deuterium oxide was degassed by a generous argon sparge. All other solvents were purchased from Fischer Scientific. Solvents were dried by passage through purification columns packed with alumina and degassed by a generous argon sparge. All commericial materials were used as obtained, and ruthenium complex **1**

was a gift from Materia. 4-(chloromethyl)Benzoyl chloride (**9**), *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride, *N,N*-dimethyl-ethylenediamine, anhydrous pyridine, potassium *tert*-butoxide, 4-dimethylaminopyridine, and Amberlite IRA-400(Cl) ion-exchange resin were purchased from Aldrich. Molecular weight 5000 methoxy poly(ethylene glycol) amine (**8**) was purchased from Shearwater, and sodium iodide was purchased from Mallinckrodt. Sodium sulfate was purchased from EMS, and iodomethane was purchased from Alfa Aesar. 1-Mesitylimidazole (**11**),[33] monomer **13**,[14] substrate **21**,[34] substrate **23**,[16] monomer **25**,[28] and catalysts **3**[21] and **6**[12] were prepared following literature procedures.

Synthesis of 4-chloromethyl-*N*-{methoxy-poly(ethylene glycol)}-benzamide (10). A flame-dried round-bottom flask, equipped with a stir bar, was charged with compound **8** (3.5 g, 0.67 mmol) and compound **9** (298 mg, 1.6 mmol, 2.4 equiv). The solids were dissolved in dry, degassed dichloromethane (15 mL) followed by the addition of 4-dimethylaminopyridine (56 mg, 0.46 mmol, 0.70 equiv) and anhydrous pyridine (200 μL, 0.025 mmol, 0.037 equiv). The reaction was allowed to continue for 2.5 hours at ambient temperature under a positive argon pressure. The product was isolated by precipitation of the reaction mixture into diethyl ether (200 mL) followed by vacuum filtration. The filtered solid was rinsed generously with diethyl ether and purified by column chromatography (6% methanol in chloroform) to obtain 2.8 g (77%) of a white, crystalline product. ^{1}H NMR ($CDCl_3$, ppm): δ 7.79 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 6.96 (s, 1H), 4.58 (s, 2H), 3.81–3.40 (broad m), 3.35 (s, 3H). ^{13}C NMR ($CDCl_3$,

ppm): δ 166.62, 140.40, 134.372, 128.40, 127.47, 73.57, 71.76, 70.40 (br, polymeric), 58.89, 45.35, 39.69.

Synthesis of 1-(4-{methoxy poly(ethylene glycol) carbamoyl}-benzyl)-3-(2,4,6-trimethyl-phenyl)-3*H*-imidazol-1-ium; idodide (12). A flask, equipped with stir bar, was charged with compound **10** (2.5 g, 0.46 mmol), compound **11** (107 mg, 0.58 mmol, 1.3 equiv), sodium iodide (150 mg, 1.0 mmol, 2.2 equiv), and acetone (25-30 mL). The reaction flask was attached to a condenser and brought to reflux (~60 ˚C). After refluxing overnight (14 h), the product was isolated by precipitation of the reaction mixture into diethyl ether (200 mL) followed by vacuum filtration. The product was rinsed with diethyl ether, dissolved in dichloromethane, and dried over sodium sulfate. The volatiles were removed by rotary evaporation before lyophilization from benzene yielded 2.2 g (83%) of a pale yellow powder. ^{1}H NMR ($CDCl_3$, ppm): δ 9.96 (s, 1H), 7.82 (s, 1H), 7.75 (d, J = 8.1 Hz, 2H), 7.54 (d, J = 8.1 Hz, 2H), 7.18 (s, 2H), 6.86 (s, 2H), 5.87 (s, 2H), 3.64–3.41 (broad m), 3.23 (s, 3H), 2.20 (s, 3H), 1.93 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 166.37, 140.98, 136.87, 136.45, 135.21, 133.89, 130.34, 129.56, 128.65, 128.00, 123.40, 123.34, 73.57, 71.67, 70.31 (br, polymeric), 58.81, 52.39, 39.56, 20.97, 17.66.

Synthesis of PEG-conjugated catalyst (7). In a N_2-filled glove box, compound **12** (527.7 mg, 0.092 mmol), ruthenium complex **1** (117 mg, 0.14 mmol, 1.5 equiv), and potassium *tert*-butoxide (10.6 mg, 0.094 mmol, 1.0 equiv) were weighed into separate vials. The potassium *tert*-butoxide was transferred into the vial containing compound **12** using dry, degassed toluene (10–11 mL). The reaction mixture, consisting of undissolved

PEG-ligand and potassium *tert*-butoxide in a clear, yellow solution, was mixed vigorously and allowed to react for 20 minutes prior to the addition of ruthenium complex **1.** The dark maroon solution was mixed vigorously and removed from the glove box. The product mixture was filtered through celite, and the product was isolated by precipitation into diethyl ether (150 mL) followed by vacuum filtration while minimizing exposure to air. The product was lyophilized from benzene to obtain 258.6 mg (46%) of a light brown powder. ^{1}H NMR (C_6D_6, ppm): δ 19.7 (benzylidene proton resonance), ^{31}P NMR (C_6D_6, ppm): δ 37.5. (Note: This reaction gave inconsistent yields and did not always provide product. Optimization of the reaction conditions would likely solve this problem, but its poor activity precipitated the abandonment of this catalyst prior to such an optimization.)

Synthesis of *endo*-*N*-(*N*',*N*'-dimethylammonio)ethyl-bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide. A flame-dried round-bottom flask, equipped with a stir bar, was charged with c*is*-5-norbornene-*endo*-2,3-dicarboxylic anhydride (1.03 g, 6.3 mmol), *N,N*-dimethyl-ethylenediamaine (0.67 mL, 6.1 mmol, 0.97 equiv), and dry, degassed benzene (50 mL). This flask was equipped with a Dean-Stark trap and a reflux condenser, and the reaction mixture was heated to 110 ˚C and stirred for 18 hours at this temperature. Upon cooling to room temperature, the volatiles were removed by rotary evaporation to yield a dark maroon, highly viscous liquid. Distilled water (30 mL) was added and the solution was made acidic with concentrated hydrochloric acid. The water layer was rinsed with diethyl ether (5×), neutralized with sodium bicarbonate, and extracted with diethyl ether (5×). The combined diethyl ether extracts were dried over sodium sulfate, and the

volatiles were removed by rotary evaporation to obtain a flaky, white solid, which was dried under high vacuum to give 630 mg (44%) of product. ^{1}H NMR ($CDCl_3$, ppm): δ 6.03 (dd, J = 1.8Hz, 2H), 3.39 (t, J = 7.0 Hz, 2H), 3.34–3.31 (m, 2H), 3.22 (d, J = 1.5 Hz, 1H), 3.21 (d, J = 1.5 Hz, 1H), 2.27 (t, J = 7.0 Hz, 2H), 2.17 (broad s, 6H), 1.67 (dt, J_D = 8.6Hz, J_T = 1.8Hz , 1H), 1.49 (doublet of broad singlets, J = 8.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, ppm): δ 177.62, 134.36, 56.36, 52.20, 45.88, 45.51, 44.97, 36.33.

Synthesis of *endo*-*N*-(*N*',*N*',*N*'-trimethylammonio)ethyl-bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide; chloride (15). A round-bottom flask, equipped with a stir bar, was charged with *endo*-*N*-(*N*',*N*'-dimethylammonio)ethyl-bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (433 mg, 1.9 mmol), iodomethane (0.57 mL, 9.2 mmol, 4.8 equiv), and THF (9 mL). The reaction mixture was stirred at room temperature for 10 minutes. The product precipitated during the course of the reaction and was isolated by vacuum filtration and rinsed liberally with diethyl ether. The product was dissolved in a minimal amount of distilled water and passed through a column packed with Amberlite IRA-400(Cl) ion-exchange resin to generate the chloride salt. Water was removed by lyophilization to obtain 447 mg (85%) of a white, solid product. ^{1}H NMR (D_2O, ppm): δ 6.13 (dd, J = 1.8 Hz, 2H), 3.84 (t, J = 7.5 Hz, 2H), 3.51 (d, J = 1.7 Hz, 1H), 3.50 (d, J = 1.7 Hz, 1H), 3.39–3.34 (m, 4H), 3.16 (s, 9H), 1.72 (dt, J_D = 9.0 Hz, J_T = 1.7 Hz, 1H), 1.61 (doublet of broad singlets, J = 9.0 Hz, 1H). ^{13}C NMR (D_2O, ppm): δ 180.71, 134.69, 61.66, 53.34, 52.25, 46.12, 44.99, 32.10.

General procedures for experiments comparing the ring opening metathesis polymerization of monomer 15 with catalysts 6 and 7. In a N_2-filled glove box, compound **15** (25 mg, 0.095 mmol, 30 equiv) and catalyst (0.0032 mmol) were weighed directly into a screw-cap NMR tube. Outside of the glove box, a solution of 0.0032 M deuterium chloride and 0.031 M 3-(trimethylsilyl)-1-propane sulfonic acid, sodium salt in degassed deuterium oxide (1 mL) was added to each sample using an air-tight syringe. The samples were heated to 45 ˚C, and the reaction conversions were followed using ^{1}H NMR spectroscopy (reported times reflect the time spent on heat). For subsequent monomer additions, in a N_2-filled glove box, monomer (7.6 mg, 0.027 mmol, 8.3 equiv) was weighed into a round-bottom flask. This flask was equipped with a stir bar, sealed with a septum and removed from the glove box. Employing standard Schlenk techniques, the monomer was dissolved in degassed deuterium oxide and transferred to the NMR tube containing catalyst **7**.

General procedures for ring-closing metathesis experiments. In a N_2-filled glove box, catalyst **7** (15 mg, 0.0024 mmol) and substrate (0.048 mmol, 20 equiv) were weighed into a screw-cap NMR tube. Methanol-d_4 (0.6 mL) was added, and the tube was sealed with a septa-cap. Outside of the box, the reaction mixture was heated to 45 °C, and the conversion was followed by ^{1}H NMR spectroscopy. For substrate **19**, 0.01 mmol of catalyst and 0.2 mmol of substrate were mixed in 1 mL of deuterated methanol.

General procedures for comparing the ring opening metathesis polymerization of monomer 25 with catalysts 1, 2, and 7. In a N_2-filled glove box, catalyst (0.0033 mmol)

was weighed into a screw-cap NMR tube. The tube was sealed with a septa-cap and removed from the glove box. A 0.11 M solution of monomer **25** in dry, degassed deuterated dichloromethane (1.0 mL, 33 equiv) was added to this NMR tube using an air-tight syringe. The sample was heated to 45 °C, and its conversion was followed using ^{1}H NMR spectroscopy.

References and Notes

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