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# Thermomorphic Polyethylene-Supported Olefin Metathesis Catalysts

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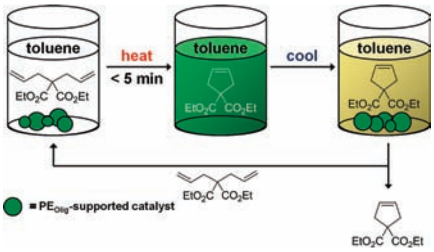
## ABSTRACT



**The preparation of polyethylene-oligomer ($PE_{olig}$)-supported *N*-heterocyclic carbene ligands (NHCs) and their Ru complexes is described. These complexes are structurally analogous to their low molecular weight counterparts and can serve as thermomorphic, recoverable/recyclable ring-closing metathesis (RCM) catalysts. Because of the insolubility of $PE_{olig}$-supported species at 25 °C, such complexes can perform homogeneous RCM reactions at 65 °C and, upon cooling, precipitate as solids. This allows for their quantitative separation from solutions of products.**

Olefin metathesis has become one of the most widely used catalytic reactions for formation of carbon–carbon double bonds in rings (ring-closing metathesis, RCM), in acyclic compounds (cross-metathesis, CM), and in polymerization (ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis polymerization (ADMET)). Because of their reactivity, stability, and functional group tolerance, Ru-based catalysts are widely used in all of these examples of olefin metathesis.[1] Schemes that separate Ru catalyst residues from product or that enable the recovery and recyclability of such catalysts are of continuing interest. Such schemes include the use of catalysts that are immobilized on solid supports and are always biphasic during a reaction as well as soluble polymer-bound complexes.[1a,2] Here we describe a new approach to a recoverable/recyclable, Ru catalyst that uses thermomorphic, polyethylene-bound NHC ligands to form a homogeneous Ru catalyst that can be quantitatively phase separated from soluble products as a solid after an RCM reaction.

Soluble polymer-bound catalysts can be separated from products by a solid/liquid separation after a solvent precipitation of the soluble polymer. However, the large amount of solvent waste generated in this procedure makes this process environmentally problematic. Liquid/liquid separations of soluble polyisobutylene (PIB)-supported Ru complexes[3] are an alternative that minimizes solvent waste. However, while liquid/liquid separations efficiently recover polymer-bound Ru catalysts, isolation of the product is not always quantitative as the products often have slight solubility in the liquid phase that is used to recycle the soluble polymer-bound catalyst. We have previously described terminally functionalized polyethylene oligomers ($PE_{olig}$) as an alternative type of catalyst

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(1) (a) Vougioukalakis, G. C.; Grubbs, R. H. *Chem. Rev.* **2010**, *110*, 1746. (b) *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, Germany, 2003. (c) Samojlowicz, C.; Bieniek, M.; Grela, K. *Chem. Rev.* **2009**, *109*, 3708. (d) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565. (e) Wilson, G. O.; Caruso, M. W.; Reimer, N. T.; White, S. R.; Sottos, N. R.; Moore, J. S. *Chem. Mater.* **2008**, *20*, 3288. (f) South, C. R.; Burd, C.; Weck, M. *Acc. Chem. Res.* **2007**, *40*, 63.

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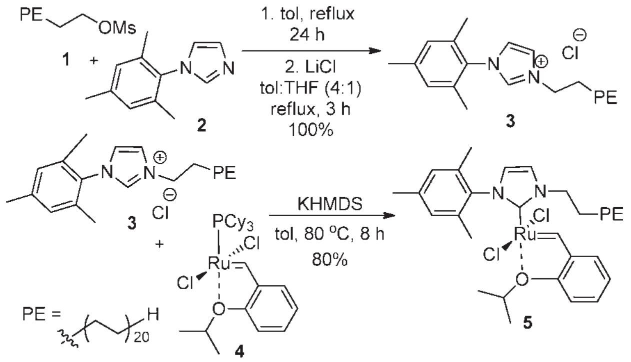
support.[4] Such PE oligomers exhibit thermomorphic solubility and are soluble in hot nonpolar solvents but completely insoluble at room temperature in any solvent. Transition metal complexes bound to such oligomers can catalyze homogeneous reactions at elevated temperatures but can be isolated as solids on cooling. Recently, DuPont reported the preparation of $PE_{olig}$-bound porphyrin and phthalocyanine metal complexes that can be used as catalysts for radical polymerizations,[5] and we recently described similar $PE_{olig}$-supported salen/metal catalysts.[6] Here we describe how $PE_{olig}$-bound NHC ligands can be used in ring-closing metathesis.

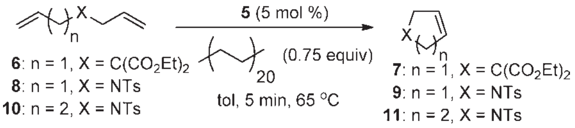
In our initial studies, a thermomorphic $PE_{olig}$-bound NHC-Ru complex **5** was prepared using commercially available $PE_{olig}$-OH[7] and **4** (Scheme 1). In this chemistry, $PE_{olig}$-OH was mesylated to form the $PE_{olig}$-mesylate **1** ($PE_{olig}$-$OMs^{4c}$) which was then allowed to react with *N*-mesityl imidazole **2** to give a $PE_{olig}$-imidazolium mesylate salt whose counterion was exchanged with LiCl to form **3**. Then the $PE_{olig}$-NHC-Ru complex **5** was prepared by reaction of **3** with KHMDS and **4**. After cooling, **5** was isolated by filtration as a brownish/green powder. $^1$H NMR spectroscopy of **5** showed the characteristic benzylidene proton of an Ru benzylidene at 16.6 ppm.

**Scheme 1.** Preparation of $PE_{olig}$-Supported NHC-Ru Complex **5**



The Ru complex **5** was then examined as a catalyst for RCM using three different substrates (Table 1). These experiments were conducted at 65 °C in degassed toluene. Since one of our goals was to test if Ru leaching was a problem, these reactions were carried out with 5 mol % of the Ru catalyst. At this catalyst loading, the reactions were typically complete in $< 5$ min. Recovery of **5** was effected by cooling the reaction mixture to room temperature to precipitate **5**. Centrifugation was used to separate this solid $PE_{olig}$-bound Ru catalyst from the toluene solution of the product. Added toluene facilitated separation of the liquid product containing phase from the catalyst. This separation was followed by a second washing step with more toluene to remove any residual product from the solid. Removal of the toluene from the combined liquid phase under reduced pressure yielded product that was pure by $^1$H and $^{13}$C NMR spectroscopy. Recycling experiments were then carried out. The process of recycling small amounts of a $PE_{olig}$ catalyst and handling of the small amount of precipitated powder was aided by adding additional PE that had not been functionalized with a catalyst or ligand.[4b,d,5] Using this method, complex **5** could be recovered and reused up to four times in good yields.

**Table 1.** Recyclability Data for Catalyst **5**[a]



| | conv (%) | | | | |
|---|---|---|---|---|---|
| substrate[b] | 1 | 2 | 3 | 4 | 5 |
| **6** | 98 | 96 | 95 | 92 | 63 |
| **8** | 94 | 93 | 83 | 50 | – |
| **10** | 99 | 93 | 80 | 71 | – |

[a] RCM reactions were carried out with substrate (0.41 mmol) and **5** (5 mol %) in toluene (3 mL) under $N_2$ at 65 °C for 5 min unless otherwise noted. [b] Yields based on $^1$H NMR conversions. Recycling of **5** consisted of cooling the reaction mixture, adding 10 mL of toluene, followed by centrifugation and decantation of the toluene containing products.This process was repeated to remove any residual product.

Inspection of the isolated product **9** provided visual evidence that using complex **5** gives rise to a product with lower Ru contamination than is the case when **9** is formed using other Ru catalysts for RCM (Figure 1). Comparison of the color of **9** formed using a low-molecular weight Hoveyda–Grubbs second generation catalyst, using a PIB-bound Ru catalyst where Ru recovery is dependent on a "boomerang" process that employed a liquid/liquid separation, and using **5** shows that **5** is visually uncontaminated by Ru. A more quantitative analysis of the efficiency of **5** at removing Ru from the products was evaluated by inductively coupled mass spectrometry (ICP-MS) of the amount of Ru in **9** formed using **5**. Analysis of the product formed from reaction of **8** contained $< 0.65\%$ (77 ppm) of charged Ru, a value similar to the *ca.* 0.5% Ru leaching seen in prior work from our group that used similar Ru catalyst loadings and a liquid/liquid separation of a PIB-bound NHC ligated Hoveyda-Grubbs catalyst.[3] Furthermore, the results here for reactions that used 5 mol %

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(6) Bergbreiter, D. E.; Hobbs, C.; Hongfa, C. *J. Org. Chem.* **2011**, *76*, 523.

(7) Baker Hughes: http://www.bakerhughes.com/assets/media/technicaldatasheets (accessed April 2011).

of catalyst also compare favorably with other experiments that rely on extra purification steps for the removal of Ru contaminants. In many of those examples, the products contained as much as 100 ppm of Ru even after (i) chromatographic purification, (ii) washing with excess solvents, or (iii) the addition of excess scavenger ligands.[1a,2a,9]

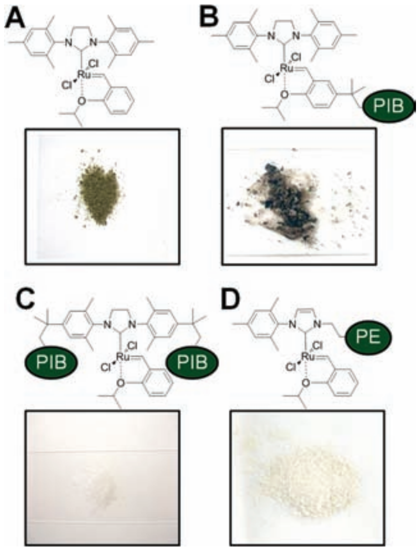
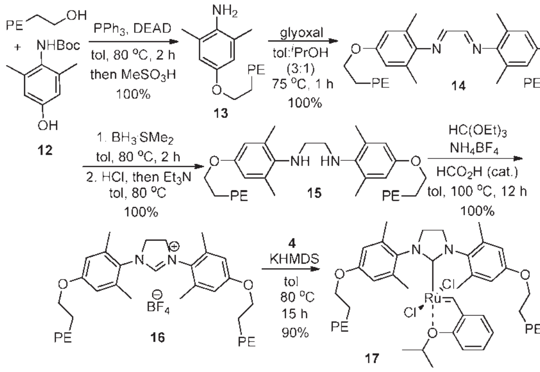


**Figure 1.** Comparison of the color of the product **9** with Hoveyda–Grubbs 2nd generation catalyst (A), PIB-supported catalysts (B)[3a] and (C),[3b] and PE$_{\mathrm{Olig}}$-supported complex **5** (D).

Although these results show that the thermomorphic PE$_{\mathrm{olig}}$ NHC ligand used to form complex **5** facilitated Ru separation from products and produced a recyclable RCM catalyst, the results in Table 1 show that **5**'s recyclability was limited to three or four cycles. We postulate that this is because the NHC ligand in **5** contains an *N*-alkyl group. Others have noted that catalysts with less-hindered NHC ligands can decompose faster than complexes that contain bulkier NHC ligands.[1a,b,8] Therefore, we prepared a more hindered PE$_{\mathrm{olig}}$-supported SIMes-like NHC ligand and examined the separation, recoverability, and recyclability of Ru RCM catalysts of its complexes.

Preparation of the desired Ru complex **17** (Scheme 2) began with a Mitsunobu[6] reaction of PE$_{\mathrm{olig}}$-OH with *N*-Boc-4-amino-3,5-xylenol (**12**). Deprotection with methanesulfonic acid afforded the PE$_{\mathrm{olig}}$-supported aniline **13** as a light brown powder in quantitative yield. Coupling of this PE$_{\mathrm{olig}}$-bound aniline **13** with aqueous glyoxal in a mixture of toluene and 2-propanol (3:1) at 75 °C quantitatively formed the bisimine **14** as a bright yellow solid. Reduction of **14** followed by standard cyclization procedures of **15** then produced the PE$_{\mathrm{olig}}$-bound imidazolium salt **16** as a white powder. As is generally true in syntheses of soluble polymer-bound ligands and catalysts, all these interemediates could be characterized by $^{1}$H and $^{13}$C NMR spectroscopy (in these cases NMR analyses have to be carried out at 70 °C or higher in benzene-$d_6$ or toluene-$d_8$). The desired Ru complex **17** was then formed by reaction of **16** with KHMDS and **4** in anhydrous toluene at 80 °C. The pale green powder **17** was characterized by $^{1}$H NMR spectroscopy which showed that the methine proton of **16** at 5.95 ppm had disappeared coincident with the appearance of a new singlet at 16.9 ppm corresponding to the benzylidene proton of **17**.

**Scheme 2.** Preparation of PE$_{\mathrm{olig}}$-Supported Ru Complex **17**



We next examined **17** as a recoverable catalyst for various RCM reactions again using a relatively high loading of catalyst to test the extent of Ru leaching. The results in Table 2 show that **17** is as expected a competent RCM catalyst, yielding complete conversion of substrates to products in <5 min with the catalyst loadings used. Recovery of **17** was carried out in the same manner as discussed for **5**. In this case, complex **17** was recycled up to 10 times with little change in product yields though the ninth and tenth cycles required slightly increased reaction times. Leaching of Ru was again examined both visually and by ICP-MS. As was true for reactions forming **9** with **5**, the product was visually uncontaminated with grayish Ru residue. ICP-MS analysis confirmed this observation and showed that <0.3% of the charged Ru was present in the product **9**.

We also examined the recovered catalyst after two reaction cycles using $^{1}$H NMR spectroscopy. This analysis showed that the only detectable Ru-NHC complex was the relatively stable species **17** which presumably formed from the $H_2C{=}Ru(Cl_2)(NHC)$ catalyst and the alkoxystyrene formed from **8** and **17**.

As noted above, liquid/liquid separations of soluble, polymer-bound catalysts can be efficient in separating catalysts from products. Small amounts of product

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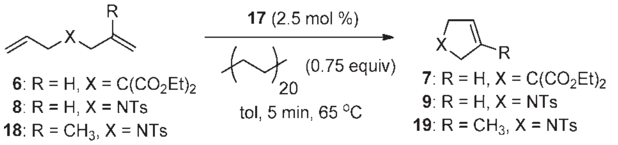
**Table 2.** Recyclability Data for Catalyst **17**[a]



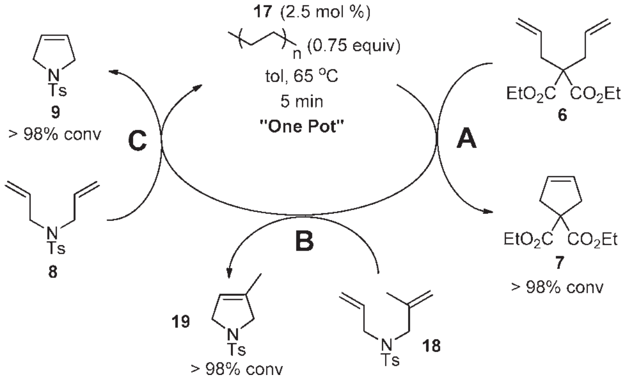
| | conv (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| substrate[b] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| **6**[c] | 99 | 98 | 99 | 98 | 98 | 98 | 94 | 93 |
| **8** | 99 | 99 | 99 | 99 | 99 | 99 | 95 | 81 |
| **18** | 99 | 99 | 99 | 99 | 97 | 97 | 95 | 83 |

[a] Ring closing metathesis reactions of the diene substrate (0.41 mmol) using **17** as a catalyst (2.5 mol %) were carried out in degassed toluene (3 mL) under $N_2$ at 65 °C for 5 min unless otherwise noted. [b] Yields based on $^1$H NMR conversions. Recycling of **17** was accomplished by cooling the reaction mixture to room temperature. Addition of toluene (10 mL) followed by centrifugation and decantation of the toluene solution containing the product separated the solid **17**. The solid **17** that was isolated was washed a second time to remove any residual product. [c] Ten cycles (average conversion was 96%) were carried out. Cycles 9 and 10 were carried out with reaction times of 15 min.

partitioning into the catalyst phase are inconsequential in multiple cycles once the catalyst-containing phase is saturated with product. However, this product contamination precludes performing sequential reactions of different substrates with the same catalyst.[4e] This is not the case with the thermomorphic complex **17** because **17** precipitates from the solution of the soluble products. Indeed prior work that used $PE_{olig}$-bound Ru catalysts in the synthesis of a series of different vinyl esters suggests this should be an additional advantage for **17**.[10]

The reactions in Scheme 3 were used to demonstrate the practicality of using **17** in a series of "one-pot" catalytic reactions to form different RCM products uncontaminated by prior reaction products. In this scheme, the initial substrate **6** was added to a suspension of **17** in toluene. Heating generated the RCM product, and cooling precipitated **17**. After separation of the solution of the product, fresh solvent and substrate **18** were added to the reaction flask. This process was repeated with substrate **8**. The products **7**, **19**, and **9** of reaction **A**, **B**, and **C**, respectively, were isolated by removal of the solvent of each separate sample and were characterized by $^1$H and $^{13}$C NMR spectroscopy. These analyses showed quantitative formation of each RCM product and showed that there was no contamination (i.e., $<$ 5% contamination based on $^1$H NMR spectroscopy) of any of the RCM products with product residues of an earlier reaction.

**Scheme 3.** "One-Pot" Catalytic Procedure Using **17** To Catalyze the RCM of Three Different Substrates



In conclusion, we have shown that the $PE_{olig}$-supports can be used to prepare RCM catalysts and that these thermomorphic supports are a simple efficient way to recover and recycle RCM catalysts. Using a $PE_{olig}$-bound SIMes NHC ligand, Ru catalysts could be recycled up to 10 times. In addition, we were able to use catalyst **17** in a "one-pot" system in which the same **17** was used in three successive RCM reactions of three different substrates affording the respective products in high yields and with no contamination from the previous reaction(s).

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**Supporting Information Available.** Synthetic procedures for $PE_{olig}$-bound species and procedures for RCM reactions are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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