

Olefin Metathesis with a Polymer Supported Ruthenium Catalyst Complex

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Abstract

Ruthenium catalysts for olefin metathesis are known to be tolerant of various functionalities and conditions, but over longer periods of time and especially at elevated temperatures, these catalysts will degrade. Our initial research objective has been the integration a ruthenium catalyst into the framework of a linear polymer with the intent of increasing stability and recyclability. In order to incorporate the catalyst in a such a framework, we have synthesized a hydroxyl substituted N-heterocyclic carbene (NHC) ligand precursor. A nucleophilic substitution with mesylated poly(ethylene glycol) monomethyl ether couples the NHC ligand precursor to the linear polymer. A ruthenium precursor (Grubbs or Grubbs-Hoveyda 1st generation catalyst) added to this poly(ethylene glycol) ligand produces the polymer-supported catalyst complex, which can catalyze cross metathesis (and other olefin metathesis reactions). Commercially available Grubbs and Grubbs-Hoveyda 2nd generation catalysts have been utilized as benchmarks. We will expand on these results by incorporating the ruthenium catalyst into a structured polymer and determining if reaction selectivity could be affected by the steric environment of the material.

Catalytic runs: Cross metathesis

Type	1	2	3
1	97%		
2			
3			0%

General cross metathesis reaction: $R_1-CH=CH_2 + R_2-CH=CH_2 \xrightarrow[45^\circ C, 15hrs]{1\text{ mol\% catalyst}} R_1-CH=CH-R_2$

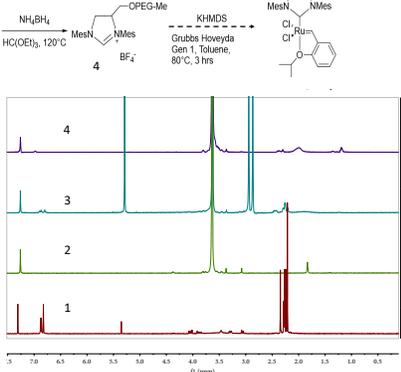
Type 1: Hexene
Type 2: Ethyl acrylate
Type 3: Tert-butylethylene

Olefins have been classified into 4 types of olefins based on their likelihood to homodimerize with the ruthenium catalyst.² In general, Type 1 olefins readily homodimerize (green), Type 2 will slowly homodimerize (yellow), Type 3 will not homodimerize (red), but will react with Type 1, and Type 4 will not react (thus these were left off of the table). The olefins listed on the right are classified based on expected reactivity using Grubbs 2nd Generation catalyst. The percentages in the boxes of the table indicate %conversion in the homodimerization benchmarking reaction we ran with Grubbs 2nd Generation catalyst.

Current work: Linear polymer support

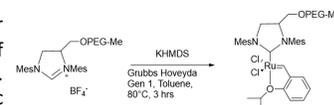


Starting from 2,4,6-trimethylaniline, we can synthesize a ruthenium catalyst supported by linear poly(ethylene glycol) (PEG).³ We will compare its reactivity with that of the commercial catalyst. Currently, we are two steps from the ruthenium complex.

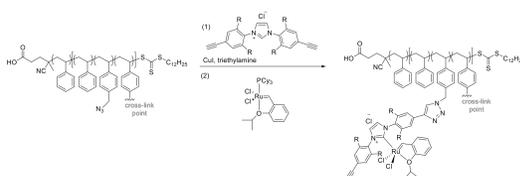


Next steps: More catalysis and polymer architecture studies

The last step to make the linear polymer appended catalyst will be the attachment of the ruthenium to our polymeric precursor. Once this is done, we can run the catalytic trials with our polymeric supported catalyst and compare the results to our benchmarking reactions.



We are also looking into star polymer architectures. A star polymer would introduce a more sterically hindered environment for the catalyst to work in. The structure it provides may also lead to a more stable catalyst at higher temperatures.



Research questions

- How do we synthesize a catalyst with a polymer support?
- Will the sterically crowded environment produced by the polymer around the catalytic metal species lead to an effectively site-isolated reaction?
- Will the presence of the polymer support lead to a more stable catalyst at higher temperatures?
- Will all types of metathesis reactions be affected by changing from a small molecule catalyst to a supported catalyst?
- Is a linear polymer architecture sufficient to change reactivity and stability or will a more structured polymer support be necessary to observe the desired effects?

Citations

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2. Chatterjee, A. K.; Choi, T.; Sanders, D. P.; Grubbs, R. H. A General Model for Selectivity in Olefin Cross Metathesis. *J. Am. Chem. Soc.* **2003**, *125*, 11360–11370.
3. Hong, S. H.; Grubbs, R. H. Highly active water-soluble olefin metathesis catalyst. *J. Am. Chem. Soc.* **2006**, *128*, 3508–3509.

Acknowledgements

Radlauer Research Group

Ruthenium Catalysis Team

- Juan Moreno
- Zehra Hamidi

Funding Sources

College of Science
Department of Chemistry
Office of Research
Center for Faculty Development

