



Synthesis and Exploration of the Reactivity of a Chiral ansa-Bis(indenyl) Zirconocene Bearing a Chiral Backbone Derived from L-tartaric Acid

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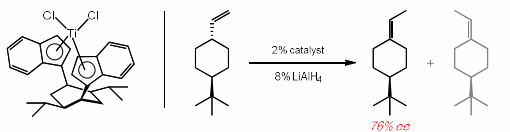
Introduction

Chiral compounds hold significant industrial importance in the pharmaceutical, agrochemical and fine chemical industries as well as significant biological importance in nature.¹ The world market for chiral chemicals is over \$39 billion as of 2015, and the demand continues to increase.² However, producing chiral molecules often involves laborious synthetic strategies, such as chiral resolution.³ **The high demand for chiral compounds necessitates the development of cost effective and reliable technology to produce these compounds on an industrial scale.**

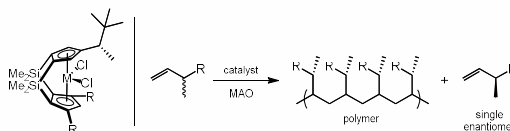
Background

Chiral ansa-metalocene complexes have previously been explored for their ability to catalyze asymmetric transformations.³ **Titanium and zirconium ansa-metalocene complexes are widely explored precatalysts for the stereoregular polymerization of olefins, such as in the selective formation of isotactic polypropylene like Ziegler-Natta catalysts.**³⁻⁵ **The reactivity can be further explored in areas such as olefin isomerization and kinetic resolution by stereoselective polymerization.**

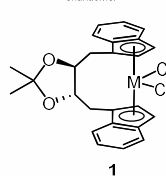
Olefin isomerization is a useful synthetic technique for the synthesis of industrially and pharmaceutically relevant products.³ **Halterman and coworkers achieved selective olefin isomerization through the following scheme**³ Other olefin isomerization catalysts, like the Grubbs catalysts, rely on later transition metals which are disadvantageous due to cost. A facile synthetic route is needed towards these cheaper chiral early transition metal catalysts, as Halterman's catalyst requires a long multistep synthesis.³



Kinetic resolution allows for facile separation of highly versatile substrates for asymmetric synthesis.⁶ **Bercaw and coworkers explored the use of an enantio-rich C₂-symmetric catalyst with the cocatalyst methylaluminoxane (MAO) for kinetic resolution of racemic olefins.**^{7,8} However, the C₂-symmetric catalyst reported by Bercaw and coworkers was difficult to prepare.⁷ Easily obtainable and inexpensive C₂-symmetric metallocenes represent a promising alternative.⁷

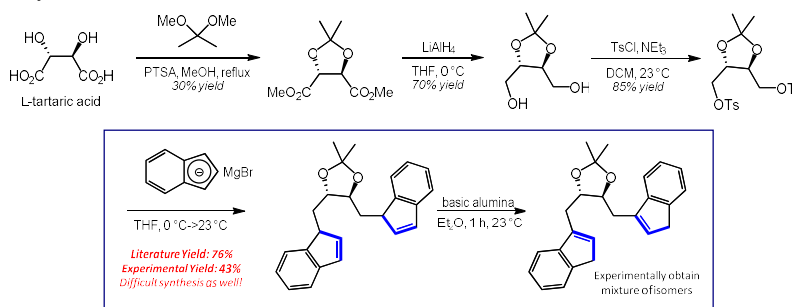


We sought to explore the reactivity of the metallocene complex **1** reported by Bandy et al.,¹⁰ accessible in five steps from L-tartaric acid. **This complex is desirable due to its low preparation cost, its C₂ symmetry, which imparts planar chirality, its preference to form a single stereoisomer of the desired complex, and its simple synthetic route.**¹⁰

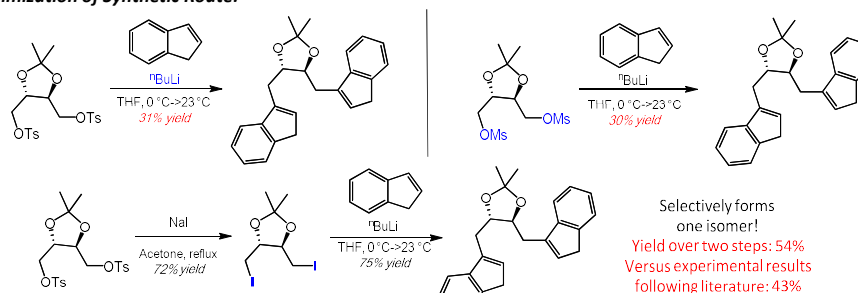


Synthesis

Literature Synthetic Route:¹⁰

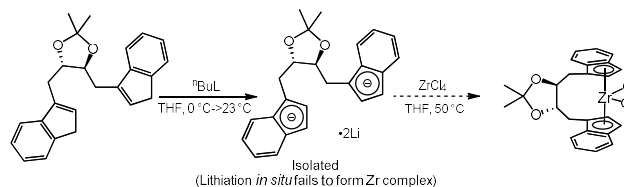


Optimization of Synthetic Route:¹¹⁻¹³

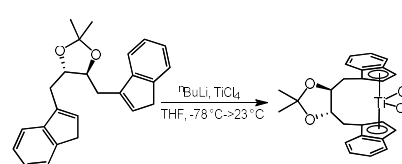


Results

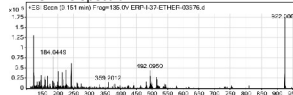
Towards the zirconium complex:



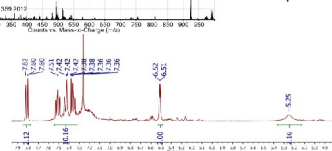
Towards the titanium complex:



TOF MS Spectrum:



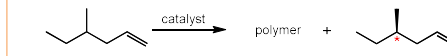
¹H-NMR Spectrum:



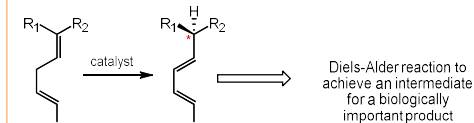
Future Directions

Future work involves the completion of synthesis of the precatalyst by successfully performing and optimizing the metalation reaction. The metalation reaction can be further performed on larger scale to attempt to isolate a small amount of the metallocene complex for characterization. Other reaction conditions such as heating or longer reaction times can be explored.

Thereafter, we plan to attempt asymmetric polymerization of a racemic compound to achieve chiral resolution of the monomer. We will specifically be using 4-methyl-1-hexene to observe kinetic resolution through polymerization, as previously studied by Chien et al. using heterogeneous catalysts.¹⁴



In addition, we will explore the transformation in the scheme below, which relies on olefin isomerization using a chiral catalyst.⁶⁻⁹ The product of isomerization can be used in a Diels-Alder reaction to produce chemically and biologically relevant molecules.



Acknowledgements

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