

N-Heterocyclic Carbenes as Constrained Ligands for Selective Olefin Dimerization

Michael Harris, 2020

A significant market share of modern plastics is held by long-chain polymers, most commonly seen by consumers as polyethylene and polypropylene.¹ While these polymers are ubiquitous, their properties can be modified by the addition of linear alpha olefins, single-chain hydrocarbons with a double bond at the terminal position.² In addition to plasticizers, linear alpha olefins are also industrially valuable as lubricants, and detergents; this industrial versatility is precious, and more than 4.5 million tons were produced in 2018 alone.³

The current industrial process for the production of linear alpha olefins is the Shell Higher Olefin Process (SHOP) which outputs olefins from 4 to 50 carbons in length by polymerizing ethene with a nickel catalyst.⁴ One major drawback however, is the full range nature of the catalytic process, as only olefins under length 20 carbons are useful.¹ This presents a problem, as a significant portion of the olefins produced by SHOP is waste.

One potential solution is the use of a cobalt catalyst to selectively dimerize linear alpha olefins to create an olefin of exactly double the length, for example, the creation of 1-dodecene from 1-hexene (Fig. 1).⁵ Further problems arise from this, as past attempts have struggled with creating linear dimers; branched products are more sterically favorable to form and therefore a ligand that makes the formation of the linear product kinetically likely is required.⁵ Significant work has been done previously in crafting a catalyst that can do this, and it is believed that a constrained ligand will contain less steric volume and will likely make the linear product.⁶ Prior work has focused on tethered, chelating ligands to avoid rotation of the ligand, with limited success, however.⁶ This work will focus on another route to a constrained ligand, namely N-Heterocyclic Carbenes (NHCs).

NHCs are a class of carbene that is stable enough to exist in the free form and have the unusual characteristic of carbenes, a lone pair of electrons on an uncharged carbon. More specifically, a carbene is any divalent carbon atom with a lone pair and no charge.⁷ This gives the ligand properties that are very favorable, including strong sigma donation by the lone pair, and strong pi acceptance by the empty p-orbitals on the carbon.⁷ Hence, the carbene can form strong carbon-metal bond with partial pi character, and the ligand is constrained. One difficulty is that NHCs are only stable as the free carbene when protected by bulky side chains, however the use of bulky side chains would favor the branched products.⁸ An investigation into using NHC salts with small side chains was begun to see if the linear product could be obtained. Synthesis of a variety of N,N'-dimethylimidazolium salts was performed to eventually coordinate to cobalt, in order to form the proposed catalyst (Fig. 2). It was determined that forming the dimethylimidazolium ring from basic building blocks was unfavorable, so various methylation pathways of 1-methylimidazole were explored. We discovered that N,N'-dimethylimidazolium methyl sulfate was not a favorable salt, but literature and preliminary experiments suggest that N,N'-dimethylimidazolium iodide is easily coordinated to metals in the presence of a strong base.⁸ Additionally, N,N'-dimethylimidazolium-2-carboxylate has shown promise as an easily accessed reagent that does not require strong base or halogens, both of which can lead to byproducts or complications.⁹ However, further work is needed to completely characterize the reaction products between the cobalt center and the carboxylate salt.

Overall, my summer work has shown that the desired catalyst is a synthetically viable target, with easily obtained reagents at each step. Coordination of these ligands to the catalytic cobalt species is the next challenge, and will be the focus of more research. Future work will certainly involve catalytic testing of the catalysts, and investigations into other, possibly more favorable ligands for catalysis.

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Figures

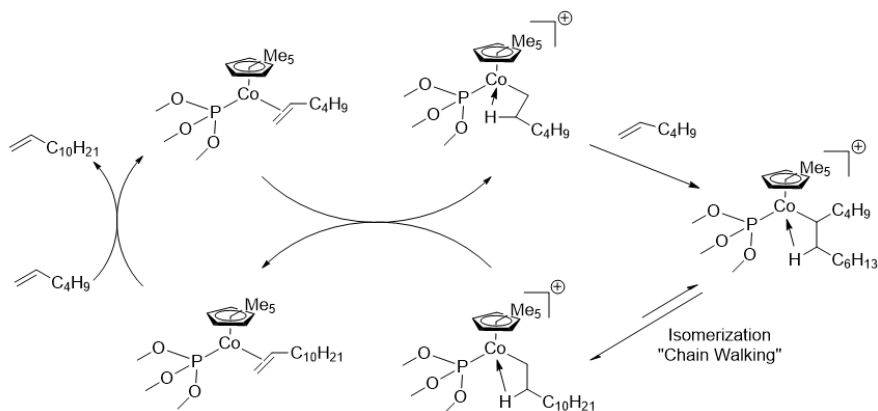


Fig. 1: The proposed catalytic cycle for the selective dimerization of Linear Alpha Olefins showing a cobalt precatalyst, activation of the catalyst, insertion of the olefin, elimination, and release of the olefin product.

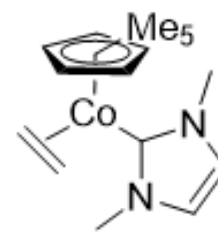


Fig. 2: The desired precatalyst and synthetic goal of this project.

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