N-Heterocyclic Carbenes as Ligand Precursors to An Olefin Dimerization Catalyst

Charlie McLarnon, Class of 2024

Purpose:

This project seeks to identify the materials and conditions necessary to synthesize a catalyst with potential applications to the plastics industry. Theoretically, coordinating cobalt to an N-heterocyclic carbene, a particular type of organic compound, might yield a catalyst with unique structural properties. Such a catalyst could reduce the waste produced during the dimerization, or doubling in length, of linear α-olefins, another class of organic compound. This reaction is pertinent to plastics manufacturers because when linear α-olefins are within a certain range of lengths, they feature in shampoos, detergents, and many other common products.

Beyond synthesizing the proposed compound, the goal of this project is to analyze its effectiveness as a catalyst for dimerizing shorter-chain linear α-olefins into longer-chain, commercially viable linear α-olefins. Moreover, the umbrella of N-heterocyclic carbene is expansive, containing compounds with nuanced structural differences that might alter a catalyst's efficacy. While starting with the investigation of a catalyst that has previously been synthesized and partially analyzed[1], this project also hopes to examine related catalysts containing different N-heterocyclic carbenes.

Methods:

The formation of our catalyst required several synthetic steps. First, N,N'-dimethylimidazolium-2-carboxylate was produced from 1-methylimidazole and dimethylcarbonate. Also, $Cp^*Co(ethene)_2$ was formed from the starting materials dicobalt octacarbonyl and pentamethylcyclopentadiene in a four-step process. These two products were reacted to synthesize the complex Cp*Co(ethene)(N,N'-dimethylimidazolium-2-ylidene), our precatalyst.

To determine whether this final material was of practical value, its effectiveness in catalyzing the dimerization of 1-hexene was examined. The desired product in this reaction was 1-dodecene, a linear α-olefin, while 5-methylundecane, which has a branched rather than linear structure and lacks commercial value, could be a byproduct. The precatalyst was activated using Brookhart's acid in the presence of 1-hexene. To quantify the efficacy of the catalyst, the composition of the reaction mixture was monitored over the course of eleven days with gas chromatography-mass spectrometry (GC-MS) analysis.

Results:

Cp*Co(ethene)(N,N'-dimethylimidazolium-2-ylidene), the initial precatalyst under investigation, was successfully synthesized with 95% purity. GC-MS analysis of the activated precatalyst with 1-hexene resulted in the detection of 1-dodecene after 48 hours; furthermore, it did not indicate the presence of the unwanted byproduct 5-methylundecene at any point in the eleven day period. However, quantification of 1-dodecene by comparison to an internal standard suggested that dimerization was extremely slow under the given conditions, so catalytic dimerization did not occur using this original precatalyst.

Similar experimentation with a new, related precatalyst, Cp*Co(ethene)(N,N'-dimethylbenzimidazolium-2-ylidene), was also attempted. While the synthesis of the reactants needed to form this product were successful, the final material was never conclusively characterized due to time limitations and technical issues with the NMR instrument.

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[1] Harris, M., N,N'-Dimethyimidazolium-2-Carboxylate as a Ligand Precursor for the Accession of a Constrained Olefin Dimerization Catalyst. **2020**.