Synthesis and coordination of various phenylisocyanide ligands for dimerization of linear alpha olefins

Julia Morris, Class of 2018

The study and practice of organic chemistry focuses heavily on molecules called Hydrocarbons which take various forms, depending on the type of bond between carbon atoms (single, double, triple, etc.) One particular type of hydrocarbon molecule is called an Alkene which has a double carbon bond and example is a linear alpha olefin. This is used as a precursor of various products such as lubricants, detergents, shampoos, etc. Because this alkene is “linear” rather than “branched”, however, it breaks down in nature after use much more quickly. Hydrocarbons (combinations of hydrogen and carbon atoms) occur naturally in crude oil produced by the decomposition of vegetable matter. There are a number for chemical methods for producing these linear alpha olefins from the hydrocarbon product ethylene, including one invented by scientist at Shell Oil in the 1960s called the Shell Higher Olefins process (or “SHOP”).[1] While this process is more efficient than previous methods, it still produces considerable waste and is not coast effective because of the large number of unwanted by-products. The aim of this research project would be to focus on ways of reducing these by-products by investing methods to create a more effective precatalyst in the dimerization process of linear alpha olefin.

Dimerization can be considered an improvement on alternative methods such as ethane oligomerization because it allows for carbon chain length specificity. The ability to control the chain-lengthy of linear α-olefin means that the environmentally damaging and costly chemical waste of the petrochemical industry can be reduced. Brookhart and Broene successfully developed a cationic cobalt catalyst which they were able to use in creating dimerized linear α-olefin. Unfortunately, use of this catalyst did not yield favourable product distribution with a majority of branch olefin produce being produced as opposed to the desired linear product. In chemical synthesis a major barrier to the production of desired product is the result of steric hindrance. Steric hindrance is essentially when the size of substituents in a molecule physically prevent reactions at certain chemical sites.[2] In the case of Brookhart and Broene’s cationic cobalt catalyst the steric hindrance that caused the creation of the major branched project was between the trimetylphosphite supporting ligand and the alkyl substituent.

In theory the electron-donating abilities of the phosphine and the phenylisocyanide are very similar and any differences should be small. Placing a Cp* ligand in the place of a Cp ligand will increase electron density at the metal for the Cp*. This electron density will decrease the σ donation from the isocyanides and consequently weakening the isocyanides-metal bond. In my project, multiple isocyanides-ligated catalyst will synthesised in a manner to determine if electron-withdrawing or electron donating groups para to the isocyano group influence the catalytic process. Their efficacy as catalysts will be assessed by activation with HBArF in the presence of linear α-olefins, which will allow testing of the hypothesis that olefin insertion preference is not altered significantly by electronics.[1] I began my work in the summer of 2017 doing a ten-week research fellowship in Professor Broene’s lab.

I have continued on throughout the school year doing research and I have acquired specialized organometallic synthesis techniques and gained experience doing independent research. I spent much of my time this year not only conducting experiments in a lab but also reading related scientific literature, discussing ideas with my research advisor and peers. I was able to present my research at the National ACS conference this March in New Orleans. This semester I was able to refine various synthetic procedures and take a new approach to certain experiments avoiding previous difficulties. In the past year I was able to not only synthesize the desired cobalt pre-catalyst but also run a preliminary test on the interaction it would have once activated with Brookhart’s acid. Though these first results were inconclusive, they were promising and with my one year remaining at Bowdoin College, I aim to continue my work on this project. I hope that this research will also be a starting point for any independent study or honors project that I wish to carry out my senior year. Potential future directions for my project include activating the neutral cobalt precatalyst with Brookhart's acid in the presence of LAOs in order to assess its ability to catalyze dimerization of a linear product.

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[1] Broene, R. D.; Brookhart, M.; Lamanna, W. M.; Volpe, A. F., Cobalt-Catalysed Dimerization of α-Olefins to Give Linear α-Olefin Products. *Journal of the American Chemical Society* **2005,** *127* (49), 17194-17195.

[2] Clark, Graham: Synthesis of a Phenylisocyanide Ligand and Its Coordination to a Cobalt-based Catalyst for the Dimerization of Linear α-olefins, 2016.