

8-Quinoyl-Tetramethylcyclopentadiene: A Supporting Ligand for the Cobalt Catalyzed Dimerization of Linear α -Olefins

Ryan Keefe, Class of 2018

Linear α -olefins are a class of unbranched hydrocarbon chains defined by a terminal double bond. These molecules are highly valued in the petrochemical industry as PVC plasticizers, comonomers for polyethylene, as well as precursors to detergents, soaps, shampoos, and lubricants.¹ Commercial quantities of linear α -olefins are currently produced through the oligomerization of ethene.² The major issue with the oligomerization of ethene is that it lacks specificity and produces a mix of olefin products typically ranging from 4 to over 40 carbons long.¹ The applications of linear α -olefins vary with their chain length, with olefins longer than 18 carbons typically of little value.

Linear α -olefin production through a dimerization process would allow for chain length specificity, thereby reducing the waste produced by the oligomerization of ethene. Previous research by Brookhart and Broene showed that a cationic cobalt catalyst, $[\text{Cp}^*\text{P}(\text{OMe})_3\text{CoCH}_2\text{CH}_3]^+$, can dimerize linear α -olefins.³ However, the majority product was the undesired branched olefin instead of the linear olefin product.⁴

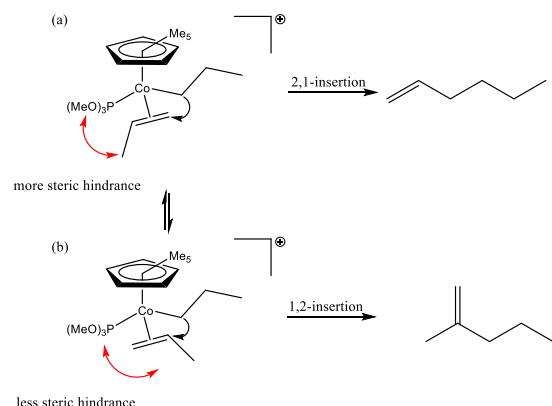


Figure 1: Carbon-carbon bond formation through (a) 2,1-insertion and (b) 1,2-insertion which yield the linear and branched olefin products, respectively.

The branched olefin product was most likely favored because of less steric hindrance between the supporting ligand and the alkene group (figure 1).

Based on these two insertion mechanisms, it was hypothesized that the bulkiness of the trimethylphosphite supporting ligand is responsible for the branched olefin majority product. This hypothesis was confirmed by synthesizing cationic cobalt catalysts with different supporting ligands with varying steric properties and relatively similar electronic properties. The bulkiness of the supporting ligand was calculated as the cone angle which is measured as the angle made between the central cobalt atom and the atoms in the supporting ligand that form the largest angle⁵.

This summer I worked on synthesizing another cobalt precatalyst with a different supporting ligand that actually coordinated in two places which would prevent it from rotating and would essentially not have a cone angle. I was able to successfully synthesize one of the precursor molecules for this synthesis. In the future I am going to try and use photochemical techniques to carry out the final reaction which involves breaking two strongly coordinated carbonyl groups off and replacing them with an ethene group coordinated through a pi bond.

Faculty Mentor: Rick Broene, PhD.

Funded by the Coles Research Fellowship

References

1. Lappin, G., *Alpha Olefins Applications Handbook*. Taylor & Francis: 1989.
2. Lutz, E. F., Shell Higher Olefins Process. *Journal of Chemical Education* **1986**, 63 (3), 202.
3. Brookhart, M.; Lincoln, D. M.; Volpe, A. F.; Schmidt, G. F., Ligand and Substituent Effects on the Dynamics and Structure of Agostic Ethylenecobalt Complexes of the Type $C_5R_5(L)Co(CH_2CHR'-\mu-H)^+ BF_4^-$ [L = P(OMe)₃, PMe₃; R = H, Me; R' = H, Me]. *Organometallics* **1989**, 8 (5), 1212-1218.
4. Broene, R. D.; Brookhart, M.; Lamanna, W. M.; Volpe, A. F., Cobalt-Catalyzed Dimerization of α -Olefins to Give Linear α -Olefin Products. *Journal of the American Chemical Society* **2005**, 127 (49), 17194-17195.
5. Tolman, C. A., Steric Effects of Phosphorus Ligands in Organometallic Chemistry and Homogeneous Catalysis. *Chemical Reviews* **1977**, 77 (3), 313-348.