

Phenylisocyanide Ligand Synthesis and Coordination to Cobalt as a Catalyst for Dimerization of Linear Alpha Olefins

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Linear alpha olefins (LAOs) are used as precursors to various shampoos, lubricants, and detergents, and are essential within the petrochemical industry.¹ This project aims to develop a cationic cobalt catalyst for the linear dimerization of LAOs. The current catalyst yields an unfavorable branched to linear product ratio, which is due to the steric bulk of the supporting ligand.² To optimize the formation of the linear product, I synthesized a less bulky supporting ligand using 4-substituted phenylisocyanides. These ligands were successfully coordinated to the neutral pre-catalyst, and various purification techniques were used to isolate the mono-coordinated product required for the dimerization of LAOs.

The current catalyst for the selective dimerization of LAOs uses a phosphite ligand that yields an unfavorable branched to linear product ratio. The sigma bonding of the alkene to cobalt allows for free bond rotation and, due to the size of the supporting ligand, the equilibrium favors C-C bond formation at the less sterically hindered position of the olefin, which gives the branched product via 1,2-insertion. To improve the branched to linear product ratio, we hypothesized that a smaller supporting ligand, with similar electronic properties, could be used, which would favor the desired 2,1-insertion by limiting the steric interaction between the ligand and the alkyl portion of the olefin.

Phenylisocyanides were chosen as the new ligand because they mimic the steric properties of the phosphite ligand but have less steric bulk. The steric bulk is measured in cone angle. By using the phenylisocyanide, the cone is elongated which decreases its angle. This decreases the steric hinderance of the ligand and allows for 2,1-insertion.³ The goal of this project is to synthesize various 4-substituted phenylisocyanides and coordinate them to $Cp^*Co(C_2H_4)_2$ (*aka* bis-ethene), and then activate these compounds with $HBAr^F$ in the presence of linear alpha olefins. This process requires four steps: the synthesis and purification of 4-substituted phenylisocyanides starting with 4-substituted anilines, the synthesis and purification of $Cp^*Co(C_2H_4)_2$, the mono-coordination of $Cp^*Co(C_2H_4)_2$ with the isocyanide ligands, and the activation of the mono-coordinated product with $HBAr^F$ in the presence of LAOs.

I have successfully coordinated 4-bromo-, 4-methoxy-, and 4-methyl-phenylisocyanides to the cobalt pre-catalyst. The 4-

References:

¹ Lappin, G. R., *Alpha Olefins Applications Handbook*. Marcel Dekker: New York, 1989.

² Broene, R. D.; Brookhart, M.; Lamanna, W. M.; Volpe, A. F., Cobalt-Catalyzed Dimerization of α -Olefins to Give Linear α -Olefin Products.