

## Exploring para-substituted phenylisonitriles for the dimerization of LAOs

Meredith Stetter, 2025

The purpose of this project was to explore the dimerization of linear alpha olefins (LAOs) in the presence of a cobalt catalyst with a para-substituted phenylisonitrile as the ligand. Linear alpha olefins are hydrocarbon chains of various lengths, all of which containing a terminal alkene. They are of great industrial use, especially in the production of detergents, lubricants, and soaps. However, the current synthetic pathway is expensive and environmentally harmful, producing significant amounts of waste each year. Thus, finding a cheaper and more environmentally conscious synthetic route is of the utmost importance. A route developed by Brookhart and Broene includes the selective dimerization of linear alpha olefins in the presence of a cobalt catalyst. This catalyst is known as bis-( $\eta^2$ -ethene) ( $\eta^5$ -pentamethylcyclopentadienyl) cobalt(I) (aka bis-ethene) and can be activated with  $\text{HBAr}^F$ , or Brookhart's acid.

Previously, the trimethylphosphine ligand was used to coordinate to the metal center in the previously mentioned process. However, past work demonstrated that the branched to linear ratio when using this ligand was unfavorable for formation of linear alpha olefins. Branched LAOs have little commercial value and are therefore not the desired product. This work demonstrated that this ratio was due to a measure of steric interaction known as cone angle. This disproved the theory that this unfavorable ratio was due to electronics. Therefore, my project aims to continue her work in investigating a ligand with a smaller cone angle while maintaining the electronic properties of the trimethylphosphine ligand.

Phenylisonitriles have a smaller cone angle than the trimethylphosphine ligand. Reference this The cone angle is a measure of the three dimensional space that the ligand occupies. Furthermore, para-substituted phenylisonitriles lend the question of how electron donating ability could effect the branched to linear ratio. Therefore, my project aimed to first determine the branched to linear ratio of linear alpha olefins when using the isonitrile as the ligand. Additionally, I hope to compare this ratio for isonitriles with different para-substituents, each with different electron donating capabilities. The parasubstituents that I explored are bromine, fluorine, a methoxy group, methyl group, and trifluoromethyl group. Each of these has various electron donating abilities that will effect the electronics of the ligand as a whole and allow us to explore the effects that this has on the ratio following dimerization.

To do this, we first started by synthesizing the formamide precursor to the isonitrile. After we successfully synthesized the formamide, we synthesized the isonitrile, which depending on the para-substituent, required different reagents and purification methods. After the isonitrile was synthesized, both mono and bis coordinations were attempted. Future directions intend to focus on confirming these synthetic attempts and moving forward with activation in the presence of LAOs.

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