Synthesis and Coordination of Isocyanide Ligands to a Cobalt Catalyst to Optimize Dimerization of Linear α-olefins

Malik McKnight, 2015

Linear α-olefins are carbon chains ending with a terminal double bond. These compounds have many commercial uses and are relevant to many industries. For example, linear α-olefins are produced and used as surfactants, shampoo, synthetic oils, and as co-monomers in a variety of plastics. Linear α-olefins that have chain lengths within the range of six to eighteen carbons are most important in today’s industry; therefore a selective method for the production of linear α-olefins is warranted.

The dimerization process enables increased selectivity of the length of linear α-olefin chains, but branched α-olefins are also a byproduct. The branched α-olefins, unlike the desired linear α-olefins, lack versatility and aren’t industrially useful. Previous work with the cobalt catalyst attached to different phosphorus ligands shows that the branched product is favored over the desired linear product (Tolman, 1977). Furthermore, the branched to linear ratio has been correlated with the cone angle of the ligand and it’s been found that a smaller cone angle resulted in a more favorable ratio. Thus, by replacing the phosphorus-based ligand of the cobalt catalyst with ligand that has a smaller cone angle it suspected that the branched to linear ratio of dimerized olefins will be more favorable. The proposed catalyst is a cobalt catalyst containing an isocyanide ligand, which has a cone angle of only 57°, therefore dimerization will favor the desired linear product. Additionally, much like the previous phosphorus ligand, the isocyanide ligand is a good sigma donors and capable of π back bonding. Finally, the electronic properties of the isocyanides were manipulated by the addition of different functional groups, in this case a methoxy group, to see how coordination to the cobalt complex was impacted.

My goal this past summer was to synthesize 4-methoxyphenyisocyanide and singly coordinate it to the Cp*Co(C₂H₄)₂. The pre-catalyst, Bis(η-ethene)(η⁵-pentamethylcyclopentadienyl)cobalt (I), is developed in a five step synthetic process from a previous study (Frith et al, 1992). The synthesis of the 4-methoxyphenyisocyanide ligand is a two-step process. First, the amine group on p-anisidine displaces the hydroxyl group on formic acid via an acid-catalyzed addition-elimination reaction to yield the 4-methoxyphenyforamide. Next, the 4-methoxyphenyforamide was dehydrated by a strong dehydrating agent, phosphorus oxychloride, in the presence of the weak base triethylamine to yield the desired 4-methoxyphenyisocyanide ligand. Purity of the cobalt pre-catalyst and the 4-methoxyphenyisocyanide ligand were ascertained using HNMR and GC-MS.

In the future, I will attempt to singly 4-methoxyphenylisocyanide to the cobalt bisethene complex. If my coordination attempt is successful, then this catalyst will be in the dimerization of linear α-olefins.

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