Synthesis of [ethene-η^5-[1-(8-quinolyl)-2,3,4,5-tetramethylcyclopentadiene]-cobalt(I) for Linear α-Olefin Dimerization

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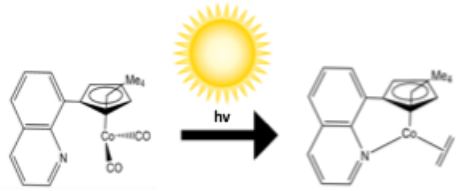
The primary objective of this project is the synthesis of a cobalt pre-catalyst that demonstrates potential for linear α-olefin dimerization. Current industrial processes produce linear α-olefins through ethylene oligomerization to yield olefins that are predominantly 4-30 carbon atoms long. The most useful linear α-olefins are 4-16 carbon atoms long and are utilized in the production of plasticizers, household detergents, and synthetic oils. Linear α-olefins with chain lengths longer than 16 carbon atoms are commonly discarded, finding some usage in the production of tar and wax.

L	Cone Angle	Tolman Electronic Parameter (cm^{-1})	Branched:Linear Ratio
$P(OMe)_3$	107°	2079.5	4.5:1
PMe_3	118°	2064.1	20:1
PPh_3	145°	2068.9	>100:1

When designing our catalyst, the core concept taken into consideration is cone angle. Cone angle is defined as the angle that is formed from placing the metal atom at the vertex with the outermost atoms placed at the perimeter of the cone. We have researched a variety of ligands, and our data indicates a strong correlation between cone angle and linear α-olefin dimerization efficiency. As the cone angle of the supporting ligand decreases the branched to linear product ratio decreases, meaning that we obtain more of the desired linear α-olefin. Whereas there is no clear trend with the Tolman electronic parameter.

Rather than coordinate another ligand to the former cobalt pre-catalyst $CoCp^*(CO)_2$, we decided to replace pentamethylcyclopentadienyl (Cp^*) with the closely related ligand 8-quinolylcyclopentadienyl. This ligand possesses an aromatic nitrogen atom with a free lone pair that is capable of bonding to the cobalt center. This bidentate ligand is incapable of rotating due to the aromatic moiety, eliminating the concept of cone angle. The reactions to coordinate 8-quinolylcyclopentadienyl to the carbonyl cobalt species have been optimized in the past. However, going from the carbonyl species to the cobalt pre-catalyst requires removal of strongly coordinating carbonyl ligands. Previous attempts to synthesize the pre-catalyst involved oxidizing the carbonyl species with diidoine followed by reduction, but were unsuccessful.



This summer we were interested in implementing photochemistry to synthesize the pre-catalyst. When irradiated with UV light we theorized that the carbonyl ligands would dissociate, allowing free ethene to coordinate. We tested our hypothesis using the closely related species $CoCp^*(CO)_2$. When irradiated with UV light in the presence of ethene, NMR indicates removal of the carbonyl ligands and coordination of ethene. Unfortunately, I was unable to synthesize enough of the carbonyl species to run photochemistry experiments. Future work will be directed at synthesizing greater amounts of the carbonyl species and testing the efficiency of UV light for promoting synthesis of the cobalt pre-catalyst.

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