Carbon-carbon Bond Forming Reactions from Bis(carbene)-platinum(II) Complexes

-and-

Olefin Polymerization and Oligomerization Using Group 4 Post-metallocene Complexes

Thesis by

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With gratitude to all the teachers, mentors, family, and friends who helped me get to where I am today.

I found Sherlock Holmes alone, however, half asleep, with his long, thin form curled up in the recesses of his armchair. A formidable array of bottles and test-tubes, with the pungent cleanly smell of hydrochloric acid, told me that he had spent his day in the chemical work which was so dear to him.

"Well, have you solved it?" I asked as I entered.

"Yes. It was the bisulphate of baryta."

"No, no, the mystery!" I cried.

- *The Adventures of Sherlock Holmes: A Case of Identity*
by Sir Arthur Conan Doyle

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Looking back at my time at Caltech, I can sincerely say I’ve had a wonderful experience here and I’m humbled and extremely thankful to the people who helped me on this path; it’s not an easy one!

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Jay is a great teacher and much like John, Jay has played a very large role in shaping me into the scientist I am today. Thank you Jay.

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Abstract

A long-standing challenge in transition metal catalysis is selective C–C bond coupling of simple feedstocks, such as carbon monoxide, ethylene or propylene, to yield value-added products. This work describes efforts toward selective C–C bond formation using early- and late-transition metals, which may have important implications for the production of fuels and plastics, as well as many other commodity chemicals.

The industrial Fischer-Tropsch (F-T) process converts synthesis gas (syngas, a mixture of CO + H_2) into a complex mixture of hydrocarbons and oxygenates. Well-defined homogeneous catalysts for F-T may provide greater product selectivity for fuel-range liquid hydrocarbons compared to traditional heterogeneous catalysts. The first part of this work involved the preparation of late-transition metal complexes for use in syngas conversion. We investigated C–C bond forming reactions via carbene coupling using bis(carbene)platinum(II) compounds, which are models for putative metal–carbene intermediates in F-T chemistry. It was found that C–C bond formation could be induced by either (1) chemical reduction of or (2) exogenous phosphine coordination to the platinum(II) starting complexes. These two mild methods afforded different products, constitutional isomers, suggesting that at least two different mechanisms are possible for C–C bond formation from carbene intermediates. These results are encouraging for the development of a multicomponent homogeneous catalysis system for the generation of higher hydrocarbons.

A second avenue of research focused on the design and synthesis of post-metallocene catalysts for olefin polymerization. The polymerization chemistry of a new class of group 4 complexes supported by asymmetric anilide(pyridine)phenolate (NNO) pincer ligands was explored. Unlike typical early transition metal polymerization catalysts, NNO-ligated catalysts produce nearly regiorandom polypropylene, with as many as 30–40 mol % of insertions being 2,1-inserted (versus 1,2-inserted), compared to <1 mol % in most metallocene systems. A survey of model Ti polymerization catalysts suggests that catalyst modification pathways that could affect regioselectivity, such as C–H activation of the anilide ring, cleavage of the amine R-group, or monomer insertion into metal–ligand bonds are unlikely. A parallel investigation of a Ti–amido(pyridine)phenolate polymerization catalyst, which features a five- rather than a six-membered Ti–N chelate ring, but maintained a dianionic NNO motif, revealed that simply maintaining this motif was not enough to produce regioirregular polypropylene; in fact, these experiments seem to indicate that only an intact anilide(pyridine)phenolate ligated-complex will lead to regioirregular polypropylene. As yet, the underlying causes for the unique regioselectivity of anilide(pyridine)phenolate polymerization catalysts remains unknown. Further exploration of NNO-ligated polymerization catalysts could lead to the controlled synthesis of new types of polymer architectures.

Finally, we investigated the reactivity of a known Ti–phenoxy(imine) (Ti-FI) catalyst that has been shown to be very active for ethylene homotrimerization in an effort to upgrade simple feedstocks to liquid hydrocarbon fuels through co-oligomerization of heavy and light olefins. We demonstrated that the Ti-FI catalyst can homo-oligomerize 1-hexene to C_{12} and C_{18} alkenes through olefin dimerization and trimerization, respectively. Future work will include kinetic studies to determine monomer selectivity by investigating the relative rates of insertion of light olefins (e.g., ethylene) vs. higher α-olefins, as well as a more detailed mechanistic study of olefin trimerization. Our ultimate goal is to exploit this catalyst in a multi-catalyst system for conversion of simple alkenes into hydrocarbon fuels.

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