Chapter 1

General Introduction

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The topics covered in this dissertation focus centrally on upgrading simple carbon feedstocks into value-added products via Fischer–Tropsch type chemistry, or olefin polymerization and oligomerization. The research presented here is fundamental in nature, but intended to work toward the goal of discovering or improving homogeneous catalysts for the processes investigated, which are of central importance for our energy supply and economy: Fischer–Tropsch is an attractive alternative route to fuel,[1] while polyolefins are the highest volume commercial class of synthetic polymers with annual worldwide capacity greater than 70 billion kg.[2]

The first chapter focuses on investigating and developing facile methods for C–C bond formation for synthesis gas (syngas; $CO + H_2$) conversion. Syngas is readily available from coal, natural gas, oil shale, and biomass and represents a potential alternative feedstock for fuel and chemicals if methods for its selective transformation into higher carbon products can be discovered; syngas is currently utilized on an industrial scale in the heterogeneously-catalyzed Fischer–Tropsch process, but this process is non-selective and generates a Schultz–Flory distribution of hydrocarbons, which can be difficult and costly to separate. We are interested in developing homogeneous catalysts for syngas conversion, which may offer better opportunities for product selectivity. A fundamental step of any syngas conversion cycle is C–C bond formation; thus, we have sought to study this process by investigating likely intermediates of Fischer–Tropsch. Chapter 2 describes our work with bis(carbene)platinum(II) complexes that may be models for carbene intermediates in Fischer–Tropsch. We report two methods to induce C–C bond formation from these complexes under very mild conditions, as well as mechanistic studies on a Pd-catalyzed carbene dimerization reaction. Ultimately, this work is promising for a multicomponent catalytic system for syngas conversion, in which a late metal catalyst such as Pd or Pt mediates C–C bond formation.

The second part of this dissertation explores polymerization and oligomerization with group 4 post-metallocene complexes. Polymerization and oligomerization both involve conversion of simple and often inexpensive feedstocks (e.g., ethylene or propylene) into more valuable products (e.g., polyethylene, polypropylene, or 1-hexene). The development of post-metallocene olefin polymerization catalysts has led to significant advances in one of the most successful and well-studied organometallic-mediated reactions;[3] olefin polymerization has been extensively investigated in both industrial and academic labs since the discovery of Ziegler-Natta catalysts in the 1950s.[4] Linear α-olefins, which are an important comonomer for many commercial polymers, including linear low density polyethylene (LLDPE), are generated industrially primarily via non-selective oligomerization of ethylene; however, non-metallocene catalysts can mediate selective olefin oligomerization and research in this area remains an important ongoing goal of both academic and industrial labs.[5]

Chapter 3 describes our continued efforts to develop post-metallocene olefin polymerization catalysts based on a triaryl dianionic (XLX) ligand framework developed in our group for supporting early metals.[6] The ligand design takes advantage of the thermal stability of aryl–aryl bonds as well as versatile access to a wide variety of ligand scaffolds using cross-coupling chemistry. Additionally, the ligand scaffold can support various metal geometries, including C_2 and C_{2v}, which suggests the possibility of stereoselective polymerization; however, we have primarily seen stereoirregular polypropylene (PP).[6] Our contribution to this project was to develop and study an asymmetric variant of our triaryl dianionic ligand. A modular anilide(pyridine)phenoxide (NNO) ligand was designed and synthesized that supports group 4 metals, and upon activation with methylaluminoxane (MAO), yields PP with good activity. Interestingly, these asymmetric catalysts produce a new type of stereoirregular and regioirregular PP, and we have synthesized several catalyst variants through ligand modification in an attempt to understand the origin of the unique regioselectivity of these catalysts.

The final chapter in this dissertation (Chapter 4) covers the beginning of our efforts to study selective olefin oligomerization with a Ti phenoxy-imine catalyst reported by Fujita and co-workers, which trimerizes ethylene to 1-hexene with excellent selectivity and activity.[7] Here we report an improved synthesis of the ligand and test reactions to explore the ability of this catalyst to trimerize higher α-olefins. Importantly, initial studies indicate that the Ti catalyst will oligomerize 1-hexene to yield C_{18} products demonstrating the ability of this catalyst to operate with higher α-olefins.

The studies described in this dissertation together represent small steps toward increasing our knowledge of fundamental processes, namely, C–C bond formation and olefin polymerization and oligomerization. Continued research efforts in these areas by both academic and industrial labs will undoubtedly lead to improved homogeneous catalysts for a broad range of applications through rational design.

References

1. West, N. M.; Miller, A. J.; Labinger, J. A.; Bercaw, J. E. *Coord. Chem. Rev.* **2011**, 255, 881-898.
2. (a) Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; Kuhlman, R. L.; Wenzel, T. T. *Science* **2006**, 312, 714-719. (b) Hustad, P. D. *Science* **2009**, 325, 704-707.
3. Natta, G.; Pino, P.; Corradini, P.; Danusso, F.; Mantica, E.; Mazzanti, G.; Moraglio, G. *J. Am. Chem. Soc.* **1955**, 77, 1708-1710.
4. Agapie, T. *Coord. Chem. Rev.* **2011**, 255, 861-880.
5. (a) Agapie, T.; Henling, L. M.; DiPasquale, A. G.; Rheingold, A. L.; Bercaw, J. E. *Organometallics* **2008**, 27, 6245-6256. (b) Golisz, S. R.; Bercaw, J. E. *Macromolecules* **2009**, 42, 8751-8762. (c) Tonks, I. A.; Tofan, D.; Weintrob, E. C.; Agapie, T.; Bercaw, J. E. *Organometallics* **2012**, 31, 1965-1974.
6. Suzuki, Y.; Kinoshita, S.; Shibahara, A.; Ishii, S.; Kawamura, K.; Inoue, Y.; Fujita, T. *Organometallics* **2010**, 29, 2394-2396.