The Selective Oligomerization of Ethylene Using Chromium Diphosphine Catalysts

and

The Synthesis and Reactivity of Group 7 Carbonyl Derivatives Relevant to Synthesis Gas Conversion

Thesis by
Paul Richard Elowe

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Dédiée à ma famille,

and to An

Acknowledgments

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Abstract

The work presented in this thesis explores two distinct fields of organometallic chemistry with a common goal of selectively transforming cheap and abundant feedstocks to value-added chemicals using homogeneous catalysts.

Chapter 1 presents the synthesis and characterization of a series of *bis*(diphenylphosphino)amine ligands and their corresponding chromium(III) trichloride complexes. The isolated chromium complexes are precursors to highly active catalysts for the selective oligomerization of ethylene to 1-hexene and 1-octene. The unique feature of the ligands presented herein is the presence of coordinating functionalities tethered to the nitrogen backbone. These act as hemilabile donors, which stabilize the active species and/or transition states during catalysis. This increased stability leads to more productive catalysts. Furthermore, important solvent and additive effects have been investigated. While reactions in non-polar solvents exhibit poor activity at lower ethylene pressures, those in more polar solvents are highly active and generate very little undesired polymer. Varying the solvent has a significant impact on 1-hexene/1-octene selectivity as well. Experiments with potentially coordinating additives result in a higher tendency for 1-octene formation. An investigation of catalyst decomposition is also discussed.

Chapter 2 presents synthetic, structural and reactivity studies on a series of Group 7 carbonyl derivatives relevant to synthesis gas conversion. Reduction of the carbonyl precursors with a hydride source generates the corresponding formyl species. This reaction is facilitated when more electrophilic carbonyl complexes are employed. Neutral and cationic Fischer carbene complexes were prepared by the reaction of the formyl

species with boranes and alkyltriflates, respectively. Further reduction of Group 7 methoxycarbenes with a hydride leads to the formation of a reactive methoxymethyl species. Dimethyl ether release is obtained from treatment of a manganese methoxymethyl species with a hydride. Moreover, subjecting manganese methoxymethyl complexes to an atmosphere of CO generates acyl complexes *via* migratory insertion. Preliminary mechanistic details are presented.