ABSTRACT

This work presents the quantum mechanics calculation based on density functional theory (DFT) for the design of new asymmetric diphosphine ligands. Complexes of this ligand can be expected to combine high catalytic activity with thermal stability under the mind conditions of methanol carbonylation process.

Chapter 1 introduces quantum mechanics, asymmetric/unsymmetric diphosphine ligand, methanol carbonylation cycle and homogeneous catalysis.

Chapter 2 provides the literature review.

Chapter 3 presents scope, aim, methodology and apparatus.

Chapter 4 presents the design and study of new asymmetric diphosphine ligands, which contain this asymmetric diphosphine ligand **1.1** which can be a promoter for methanol carbonylation. Because **1.1** has a chiral center with electron withdrawing group and electron donating group. This would be the reason that the different trans-influence and trans effect of complex type "Rh(L)L'(**1.1**)" would favor the formation of different isomers. Complex **1.5** is the most stable isomer among its four isomers. It cans notices that the stereochemistry at rhodium in which the $P(Me)_2$ *trans* to the CO and the PF_2 lies *trans* to the Me group are preferred. The presence of strong electronegativity fluorine atoms in PF_2 makes them weak σ-donors but much stronger π- acceptors and the presence of Me groups in $P(Me)_2$ makes them stronger σ-donors but much weaker π-acceptors, with confirming by the Rh-P bond distances. The electronic property is in a good agreement. All considered complexes adopt a square-planar geometry. The molecular orbital confirmed that the d_z^2 orbital is lower energy than $d_{x^2-y^2}$ orbital as expected for a low-spin d^8 orbital Rh (I) configuration. In a homogeneous methanol carbonylation process as developed by Forster, the outer processes involve organometallic compounds. The process made up of some four separation stoichiometric reactions, namely the oxidative addition, migratory insertion, CO ligand insertion and reductive elimination. The full catalytic cycle of asymmetric diphosphine rhodium complex **1.5** methanol carbonylation process are investigated. The investigation involves consideration of many possible structures of reaction intermediate. Isomer **1.5** is formed to be the initial catalytically active species. The interaction with the substrate CH_3I results in the formation of the six coordinated complexes **N1** and **N2**. Later, they transform into the isomeric five coordinated acetyl complexes **O3** and **O4**, as the result of migratory insertion process. Isomers **O3** and **O4** react rapidly with CO to form the six coordinated dicarbonyl complexes **P5** and **P6**. Finally, the acetyl iodide hydrolysis leads to the formation of the target product, acetic acid. By consideration of the difference of energy (ΔE) values, the calculated equilibrium constant confirmed the possibility to make this model **1.5**.

Chapter 5 presents the investigation of asymmetric rhodium catalysis **1.3** as the starting material for the methanol carbonylation cycle. Again, the outer four process are investigated. From the optimization data, the methyl iodide oxidative addition to the four coordinated reactant **1.3** is six coordinated isomers **B5**. The CO migratory insertion of octahedral isomers **B5** yield the square pyramidal structures **C2** and **C3**. The product of CO ligand addition to the five coordinated isomers **C2** and **C3** are six coordinated acetyl structures **D5** and **D6** which also are the precursor of the last reaction step, acetlyiodide elimination. In this last reaction, the six coordinated isomers **D5** and **D6** transform into square planar isomer **1.3**. As regard the optimization energy, the methanol carbonylation process can separate into 2 routes. The first one is **1.3**+Me → **B5** → **C3** +CO → **D6**. The second route is **1.3**+MeI → **B5**→ **C2** +CO → **D5**. The reaction energy of these two steps is about the same. This is confirmed that the oxidative addition of methyl iodide to **1.3** may have only isomer **B5**. Form the enthalpy energy, the product from oxidative addition to migratory insertion change rapidly, indicating from the similar energy. Once again, the difference of energy (ΔE) values are used to calculated equilibrium constant and confirmed the possibility to make this model **1.3**.