ABSTRACT

Synthesis of novel [2.2]paracyclophane derivatives
as potential chiral substrates and chiral ligands

Alicia Reid

This dissertation presents the work of two areas of research. The first area of study describes efficient syntheses of a unique amino acid, 4-amino-13-carboxy [2.2]paracyclophane 39 and its amino ester derivative 82. Novel oxazolinyd [2.2]paracyclophane derivatives are used as intermediates and the oxazolinyd group is shown to be an excellent pseudo-geminal directing group for the electrophilic aromatic bromination reaction.

The unique transannular interaction in the [2.2]paracyclophane system was evidenced in the formation of the first [6.2.2]cyclophane 103, described in this work.

The second body of work describes the synthesis of unique PHANEPHOS derivatives, which can be used as either chiral ligands or chiral catalysts. A new ortho-lithiation reaction of 4-N,N-diethylcarboxamido[2.2]paracyclophane 154 leading to the preparation of 4,5-disubstituted[2.2]paracyclophane derivatives is outlined. Pseudo-geminal bromination of 4-N,N-diethylcarboxamido [2.2]paracyclophane giving access to a variety of 4,13-disubstituted compounds is
also discussed. The ortho-lithiation and pseudo-geminal substitution reactions are used sequentially to give 4,5,13-trisubstituted compounds in which two ligand groups have the same geometrical relationship as in PHANEPHOS.

It is shown that $N,N$-diethylcarboxamido derivatives can be reduced to $N,N$-diethylaminomethyl and hydroxymethyl compounds thus increasing the variety of potential ligands available.

Finally, a preliminary study to explore the potential of a number of chiral oxazoliny1 and $N,N$-diethylcarboxamido derivatives to catalyze the addition of diethylzinc to benzaldehyde is described.

**Keywords:** Alicia Reid, amino acid, chiral, catalyst, ligands, oxazoliny1, $N,N$-diethylcarboxamido, [2.2]paracyclophane, PHANEPHOS, pseudo-geminal, ortho-lithiation, transannular.