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STUDIES WITH ORGANORUTHENIUM COMPLEXES
OF
SUBSTITUTED ARENES

A Thesis Presented
to the
University of Auckland
for the degree of

Doctor of Philosophy

by

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ABSTRACT

The modified reactivity observed when a substituted arene is complexed to a cyclopentadienylruthenium moiety has been exploited to prepare a range of synthetically interesting target molecules.

Activation of nitrogen- and halogen- substituted arenes has been achieved by complexation to the cyclopentadienylruthenium moiety.

Double nucleophilic substitution reactions between substituted (η^6 -1,2-dichlorobenzene)RuCp⁺ salts and substituted 1,2-benzenediols were carried out under mild conditions to prepare substituted (η^6 -dibenzodioxin)ruthenium complexes. Both mono- and di-substituted dibenzodioxin complexes were prepared. The dibenzodioxin ligands were subsequently liberated by photolysis.

The complexation of a range of substituted benzimidazoles to the cyclopentadienylruthenium moiety has been studied. Several complexes were isolated and structures proposed.

The metal moiety has been used to influence the stereoselection achieved in the reduction of carbonyl substituted arenes. A number of keto-arene complexes were prepared and reduced with sodium borohydride. The resulting alcohol complexes were characterised and the observed diastereoselectivity rationalised.

Yanovsky-like adducts were prepared by nucleophilic addition to the cationic ruthenium salts to produce neutral (η^5 -cyclohexadienyl)ruthenium complexes. A comparison between lithium, silicon and tin enolates was undertaken.