Abstract

This thesis describes the synthesis and characterisation of a number of novel main group metallacarboranes and the adducts that they form when treated with Lewis bases. The structures of these species are discussed in detail, focusing in particular on the orientation and inclination of the Lewis base and the slippage of the metal atom.

Chapter 1 outlines the most significant literature in the fields of boranes, carboranes and metallacarboranes, providing the reader with an overview of these topics. The area of main group metallacarboranes is covered in significant detail, as the running theme of this thesis is the investigation of the role of main group metals in supraicosahedral heteroboranes.

Chapter 2 details the syntheses and characterisations of icosahedral main group metallacarboranes, as well as the adducts these species form with bipy. The significant structural features of these adducts and the different factors that contribute to them are discussed.

Chapter 3 features the preparation of a series of adducts formed with the 13-vertex stannacarborane 1,6-Me2-4,1,6-closo-SnC2B10H10, accompanied by a systematic structural study of these compounds.

Chapter 4 reports the synthesis and crystallographic characterisation of 1,2-µ-(CH2)3-4,1,2-closo-SnC2B10H10 and its adducts with a series of Lewis bases. An examination into the structural differences found in this carbons-adjacent system compared to the 4,1,6-SnC2B10 carbons-apart system is presented.

Chapter 5 presents two new isomer types within the supraicosahedral main group metallacarborane system. The synthesis and characterisation of the first 4,1,10-closo-SnC2B10 species is described, together with its thermal isomerisation to the 4,1,12-analogue. The importance and relevance of these results is fully discussed. This chapter also includes evidence for the formation of a novel supraicosahedral mixed
metal species, with both a transition metal and a $p$-block metal incorporated into the cage framework.

Chapter 6 gives full details of the experimental procedures undertaken and also provides spectroscopic and analytical data for all the new compounds reported herein.

Appendix 1 provides details of the crystal structure determinations of compounds synthesised. Appendix 2 (provided on compact disk) gives the appropriate files in RTF and CIF format.