Chapter 1 gives a brief overview of the concepts key to low-oxidation state main-group chemistry. This covers oxidation state and electronic configuration, bonding in the heavier alkenes and alkynes, kinetic stabilisation, and reductive routes to low-oxidation state element complexes.

Chapter 2 summarises bulky ligands commonly used in the kinetic stabilisation of low-oxidation state element species, and the synthesis of group 14 element(II) halide complexes, which act as precursors to further low-oxidation state chemistry. Following from this, the synthesis of novel bulky monodentate amide ligands is discussed, as is their utilisation in the synthesis of group 14 element(II) halide precursors.

Chapter 3 investigates the use of the aforementioned group 14 element(II) halide precursors in the synthesis of amido-substituted heavier alkyne analogues (i.e. LEEL, E = Ge and Sn), and the reactivity thereof. These reactivity studies cover H₂ activation, CO₂ reduction, and cycloaddition/insertion reactions, involving reversible processes and CH-activation. The activation of H₂ led to the isolation of group 14 element(II) hydride species, which have been shown to be in equilibrium with monomeric hydride species in solution (i.e. hydrido tetrerlenes). Further increasing the ligand’s bulk led to the solid-state characterisation of two examples of monomeric amido Ge(II) hydride species.

Chapter 4 presents the further reactivity of the aforementioned group 14 element (II) hydride species. This culminated in the synthesis of numerous amido alkyl and amido alkoxy germynes and stannylenes through hydroelementation of aldehydes, ketones, and alkenes. The addition to alkenes was found, in some cases, to be reversible, and led to examples of alkene isomerisation at a Ge(II) centre.

Chapter 5 addresses the use of group 14 element(II) species in catalysis, initially through stoichiometric studies involving germynes and stannylenes discussed in Chap. 4. The efficient hydroboration of aldehydes and ketones is described, catalysed by Ge(II) and Sn(II) hydride complexes (i.e. those described in Chap. 3), with the mechanism of reaction studied through in depth kinetic experiments and DFT analyses. The efficient hydroboration of CO₂ was also achieved, with rates comparable to those achieved for transition-metal systems. The mechanism of this
reaction has been elucidated to some degree through stoichiometric reactivity studies.

Chapter 6 describes the synthesis of a novel boryl amide ligand, and its use in the stabilisation of low-oxidation state group 14 compounds. This largely acts as a comparison between the electronics and steric effects of this ligand and those seen in Chaps. 2–5, and as such highlights the importance in understanding how reactivities involved in this thesis can be affected through ligand modification.

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