## ABSTRACT

This thesis demonstrates that appropriate ligands can create stable complexes with main group elements, including uncommon bonding patterns and certain clusters displaying extraordinary hypercoordination of carbon and boron in planar forms in the global minimum energy structures. To optimize geometries and explore bonding in these molecules and clusters, sophisticated computational approaches have been used. The fullerene cage ( $C_{60}$ ) can accommodate two Mg atoms inside it, and computational investigations support the host-guest complex,  $Mg_2@C_{60}$ , as a molecular electride. The Gibbs free energy change ( $\Delta G$ ) for this encapsulation process is negative, which indicates that the formation of this endohedral system is spontaneous. Four isoelectronic monoanionic ligands ( $L = C_5H_5^-$ ,  $N_5^-$ ,  $P_5^-$ , and  $A_{55^-}$ ) stabilize the low valent M(I)-M(I) bond (M = Be and Mg), and the resulting complexes behave as molecular electrides. These ligands can bind with the metals through  $\eta^n$  (n = 1-5) modes. The  $\eta^5$  mode of binding is the most stable among all of the binding modes under consideration. The complexes of Be show higher thermodynamic stability as compared to their Mg analogues. DFT has been used to study the structure, stability, and bonding in the  $Li_2L_2$  complexes containing Li(0)-Li(0) bonds using both normal ( $L = NHC^{Me}$ ,  $SNHC^{Me}$ , and  $cAAC^{Me}$ ) and mesoionic carbenes (L = MIC1, and MIC2) as binding ligands (L) with the Li<sub>2</sub> molecule, and the complexes behave as molecular electrides. DFT-based calculations have been carried out to explore the potential energy surfaces (PES) of  $CSi_nGe_{4-n}^{2+/+/0}$  (*n* = 1–3) systems. The global minima in the di-cationic states contain a planar tetracoordinate carbon (ptC) but the neutral and mono-cationic states are not planar. The PES was explored for  $BSi_nGe_{4-n}$  (n = 0-2) clusters using DFT, and the global minimum energy structures contain a planar tetracoordinate boron (ptB) atom. The global minima of CB<sub>6</sub>Al<sup>0/+</sup> clusters contain a planar hexacoordinate boron (phB) atom. The electronic interaction between the central B atom and the six peripheral atoms (five boron atoms and one carbon atom) makes the phB structures stable in planar forms.

**Keywords:** Density Functional Theory; Molecular Electrides; Metal-Metal Bond; Global Optimization; Planar Hypercoordination