ABSTRACT

The thesis contains five chapters, of which the first chapter deals with brief introduction to computational chemistry. This is followed by application of the computational methodologies to chemical problems in chapter 2, 3, 4, and 5. A brief overview of the chapters 2-5 is given below.

Chapter 1: Brief Introduction to Computational Chemistry

Chapter 2: Theoretical Study of Heterocyclic Carbenes, Silylenes, Germylenes and Donor-Acceptor Complexes of Carbenes

(i) Effect of Substituents at the Heteroatom on the Structure and Ligating Properties of Heterocyclic Carbone, Silylene, Germylene and Abnormal Carbene

The chemistry of N-heterocyclic carbenes (NHC, 1) are thoroughly studied among the heterocyclic carbenes and have been the subject of many reviews. The first NHC was isolated by Arduengo and coworkers in 1991 and it has gained interest among chemist due to its strong σ-donation ability. In 2005, the phosphorus analogue (3) of Ender’s type NHC (2) was synthesized. N-heterocyclic silylene (NHsi 4), the heavier analogue of NHC was synthesized by Denk and coworkers in 1994. Although stable singlet N-heterocyclic germylene (NHGe) was reported much earlier by Meller and Grabe in 1985, the first non-anellated five-membered NHGe 5 was synthesized by Hermann and coworkers later. Another type of NHC in which the carbene centre is no longer located between the two nitrogen atoms is synthesized by the research group of Bertrand in 2009. This type of NHCs are called as abnormal NHC (aNHC 6).
In this part of the chapter, we have studied the steric as well as electronic effect of substituents at the heteroatom on the structure, stability and reactivity of the following ligand system (1-6) at B3LYP/6-31+G*, LANL2DZ level of theory. The extent of cyclic electron delocalization present in these five membered ring systems are quantified by performing Nucleus Independent Chemical Shift (NICS) calculations.

(ii) Donor-Acceptor Complexes of Normal and Abnormal N-Heterocyclic Carbene with Group 13 Elements (E=B, Al, Ga)

The introduction of the concept of “dative” bond by Lewis improved the understanding of the structure, stability and reactivity of donor-acceptor complexes. Although, dative bonds dominate transition-metal coordination chemistry, it is now believed that this concept is also very helpful for many main–group compounds.

In this part of the chapter, donor-acceptor interactions in NHC-EX₃ (NHC=normal and abnormal N-heterocyclic carbene; E=B, Al, Ga; X=H, F, Cl, OH, NH₂, CH₃, CF₃) adducts (1R-EX₃ and 2R-EX₃) have been investigated quantum chemically at B3LYP/6-31+G* level of theory. Topological analysis was performed within the realm of atoms-in-
molecule (AIM) theory. Substituents attached to the E atom have a profound effect on the strength and dissociation energies of the NHC-E bond. AIM analysis suggest that these donor-acceptor bonds have significant covalent character, which follows the order Al<Ga<B.

\[ \text{1R-EX}_3 \quad \text{2R-EX}_3 \]

\begin{align*}
R & = \text{Me;} \ a \\
R & = \text{Ph;} \ b \\
E & = \text{B, Al, Ga} \\
X & = \text{H, F, Cl, OH, NH}_2, \text{ CH}_3, \text{ CF}_3
\end{align*}

**Chapter 3: Electronic Structure Study of Element(0) Compounds**

The element carbon is usually found in tetrahedral form in organic compounds where all of its valence electrons are involved in bonding. However, the divalent carbon can have two different formal oxidation states which are II or zero. N-heterocyclic carbene was the first stable divalent carbon compound having oxidation state II. Recently, it is shown that carbon atom can have zero oxidation state in compounds of the type CL\(_2\) where the carbon atom is stabilized by two neutral electron donating ligands, L (e.g. L=NHC, PPh\(_3\) etc.). The chemistry of divalent element(0) is not limited to carbon only. The heavier analogues of carbon such as silicon and germanium also show element zero property.

The first part of the chapter deals with the effect of substituent at the heteroatom on structure and ligating properties of C(NHC)\(_2\) and Si(NHC)\(_2\). The next part of the chapter deal with the theoretical study on some Si(0) and Ge(0) compounds stabilized by different silylene and germylene ligands.
(i) Effect of Substituents at the Heteroatoms on the Structure and Ligating Properties of Carbodicarbenes and its Silicon Analogs

Theoretical studies on C(NHC)$_2$ and Si(NHC)$_2$ indicate that these compounds show element zero character, and the bond between the central atom (C or Si) and NHC can be described as donor-acceptor type. Recent studies on tetrakis(dimethylamino)allene and tetrakis(diethylamino)allene suggest that the minimum energy structure of the former is linear while that of the later is bent. This shows that substituent at the nitrogen atom play a significant role in dictating the structure of these classes of compounds.

In this part of the chapter, we have investigated the effect of substituents, \( R \) (\( R=\text{H, Me, NH}_2, \text{OH, Cl, F} \)) at the heteroatom on the structure and ligating properties of C(NHC)$_2$ (1) and Si(NHC)$_2$ (2) at BP86/TZVP level of theory. The substituents show profound effects not only on the structure but also on the reactivity of these molecules.

![Diagram of C(NHC)$_2$ and Si(NHC)$_2$](image)

\( E=C; 1 \)
\( E=\text{Si}; 2 \)
\( R=\text{H, Me, NH}_2, \text{OH, Cl, F} \)

(ii) Stabilization of Si(0) and Ge(0) Compounds by Different Silylene and Germylene Ligands

The synthesis of different types of silylene and germylene ligands enabled designing of new Si(0) and Ge(0) compounds. We have quantum chemically studied some Si(0) and
Ge(0) compounds stabilized by different silylene and germylene ligands (1-10) as well as by topographical mapping using molecular electrostatic potential (MESP). Molecular orbital analysis shows the presence of two lone pairs for most of the compounds. MESP topography of most of the compounds exhibits two MESP minima corresponding to the π lone pair on the central atom. The nature of the molecular orbitals, negative values of MESP at its critical points, as well as proton affinity values suggest that they are very good nucleophiles.

Chapter 4: Ligand Properties of Boron-Substituted Five-, Six-, and Seven-Membered Heterocyclic Carbenes

Ligand tuning is an important area in rational design of organometallic catalyst. While the σ donor properties of NHCs can be varied to a large extent, the π accepting ability of them was thought to be negligible. However, this early notion about electronic properties of NHCs has changed recently. Recent literature suggests that both π acidity and π basicity of NHCs are not only significant but also tunable. Although the phosphorus analogue of NHC, PHC was synthesized by Bertrand et al. in 2005, the potential of PHC as a ligand is yet to be
explored. Theoretical calculation on PHCs predicted that the PHCs can compete/or complement NHCs as a ligand for transition-metal based catalysis.

In this chapter, we have made a systematic study on how the ligating properties of five-, six-, and seven-membered heterocyclic carbenes vary upon introduction of boron atoms into ring framework (Scheme 1) at PBE1PBE/SDD,6-31+G* level of theory. This study reveal that the stability of NHCs decrease upon substitution of boron atoms into ring framework. However, the $\pi$ acidity of NHCs increases significantly upon such substitution.

**Scheme 1**

\[
\begin{align*}
E=N, \, 5\text{-NHC} & \quad E=P, \, 5\text{-PHC} \\
E=N, \, 5'\text{-NHC} & \quad E=P, \, 5'\text{-PHC} \\
E=N, \, 5\text{-NHC}_{\beta} & \quad E=P, \, 5\text{-PHC}_{\beta} \\
E=N, \, 6\text{-NHC} & \quad E=P, \, 6\text{-PHC} \\
E=N, \, 6\text{-NHC}_{\beta} & \quad E=P, \, 6\text{-PHC}_{\beta} \\
E=N, \, 7\text{-NHC} & \quad E=P, \, 7\text{-PHC} \\
E=N, \, 7'\text{-NHC} & \quad E=P, \, 7'\text{-PHC} \\
E=N, \, 7\text{-NHC}_{\beta} & \quad E=P, \, 7\text{-PHC}_{\beta} \\
E=N, \, 7'\text{-NHC}_{\beta} & \quad E=P, \, 7'\text{-PHC}_{\beta}
\end{align*}
\]

\[R=H, \, \text{Me}, \, \text{tBu}, \, \text{Ph}\]

**Chapter 5: Effect of Annelation and Carbonylation on the Electronic and Ligating Properties of Normal and Abnormal (Mesoionic) N-Heterocyclic Carbenes**

One of the various strategies of tuning the ligand properties of NHCs is annelation. Experimental works suggest that annelation of NHCs lead to modification of their ligand
properties. Similarly, the ligating property of NHCs varies upon introduction of carbonyl group into the NHC scaffold. Thus, we have carried out a systematic theoretical study on the effect of annelation and carbonylation on normal and abnormal NHCs (1-26). This study reveals that both annelation and carbonylation decrease the stability of carbenes. Compared to nonannelated carbenes, annelated and carbonylated carbenes are found to be weaker $\sigma$ donors but better $\pi$ acceptors. However, the effect of carbonylation is more pronounced than annelation towards increasing the $\pi$ acidity of the NHCs. The reactivity of these carbenes has been discussed in terms of nucleophilicity and electrophilicity indices. The calculated values of the relative redox potential and $^{31}$P NMR chemical shifts of corresponding carbene-phosphinidene adducts have been found to correlate well with the $\pi$ acidity of the NHCs.