CHAPTER – 1

Brief Introduction to Computational Chemistry
[1.0] Introduction

Computational chemistry is an important tool in modern chemistry. Computational chemistry uses models to investigate reaction mechanism, reaction intermediate, transition states which are difficult or impossible to be done by experimental methods. The use of theoretical methodologies in solving chemical problem is recognized by the award of the Nobel prize in chemistry to John A. Pople and Walter Kohn in 1998. In addition, the 2013 Nobel prize in chemistry was awarded to three computational chemists, viz., Martin Karplus, Michael Levitt and Arieh Warshel for the development of multiscale models for complex chemical systems. This signifies the importance of computational chemistry in modern chemistry. A brief background of theoretical methodologies related to the work of following chapters is given below.

[1.1] Density Functional Theory

There are several ways to approximately solve the electronic Schrödinger equation such as Hartree-Fock method, Møller-Plesset perturbation theory, and couple cluster methods. The common feature of these different methods is that they all rely on many body wavefunction as central quantity. The energy of the system and all related properties could be determined only if the wave function is known. But the wavefunction itself is already a complicated quantity as it depends on $3N$ spatial variables together with spin variable, where $N$ is the number of electrons in the system. This severely limits the system sizes that can be treated with wave function based methods. Thus, it is not possible to study systems with hundreds of atoms and large basis sets with wave function based methods.

Density Functional theory (DFT) differs from wave function based methods as it uses the electron density ($\rho(r)$) as the central quantity. The advantage of using the electron density over wave function is the much reduced dimensionality. The density is always three dimensional irrespective of the number of electrons present in the system. This makes DFT applicable to much larger systems, containing hundreds or even thousands of atoms.

As mentioned above, the main variable in DFT is the single particle density $\rho(r)$. For an N particle system, it is defined as

$$\rho(r_1) = N! \int \ldots \int dr_2 dr_3 \ldots \ldots \ldots \ldots dr_N P(r_1, r_2, \ldots, r_N) \quad (1.1)$$

Normalization of $\rho(r)$ gives the total number of electrons, i.e.,

$$\int \rho(r) dr = N \quad (1.2)$$
For a many particle system characterized by an external potential $\nu(r)$ (due to the nuclei), the first Hohenberg-Kohn theorem (HK-I) states that there is a one-to-one mapping between the potential $\nu(r)$, the particle density $\rho(r)$, and the ground state wave function $\psi_0$.

\[(HK-I) \quad \rho(r) \leftrightarrow \nu(r) \leftrightarrow \psi_0\]

The Hamiltonian for a system of $N$ non-relativistic, interacting electrons in an external potential, $\nu(r)$ is given by,

$$H = T + V + G$$

where

$$T = \sum_{i=1}^{N} \frac{1}{2} \nabla_i^2, \quad V = \sum_{i=1}^{N} \nu(r_i) = \sum_{i=1}^{N} \sum_{\alpha=1}^{A} \frac{-Z \alpha}{|R \alpha - r_i|}, \quad G = \sum_{i<j} \frac{1}{r_{ij}}$$

Since $\rho(r)$ determines $N$, $\nu(r)$ and all the properties of the ground state, therefore the total energy of a system should be a functional of $\rho(r)$. Thus, the ground state energy $E_{\nu(0)}[\rho(r)]$ can be expressed as a function of $\rho(r)$ as,

$$E_{\nu(0)}[\rho(r)] = T[\rho(r)] + V_{ne}[\rho(r)] + V_{ee}[\rho(r)]$$

$$= \int \rho(r)\nu(r)dr + F_{HK}[\rho(r)] \quad (1.3)$$

where

$$F_{HK}[\rho(r)] = T[\rho(r)] + V_{ee}[\rho(r)] \quad (1.4)$$

Equation (1.4) can be rewritten as

$$F_{HK}[\rho(r)] = \langle \psi[\rho(r)] | T + V_{ee} | \psi[\rho(r)] \rangle \quad (1.5)$$

where $\psi$ is the ground state wave function associated with $\rho$.

The introduction of the energy variational principle as suggested by the second Hohenberg-Kohn theorem (HK-II) gives,

$$E_{\nu(0)}[\rho(r)] = F_{HK}[\rho(r)] + \int \rho(r)\nu(r)dr \geq E_{\nu(0)}[\rho_0(r)]$$

where $E_{\nu(0)}[\rho_0(r)]$ and $\rho_0(r)$ are the ground state energy and density respectively. The variationally stable energy functional for a system of non-interacting electrons and a given external potential $\nu_s$ is,

$$E_s[\rho] = \langle \psi_s[\rho] | T + V_s | \psi_s[\rho] \rangle = T_s[\rho] + \int \nu_s(r)\rho(r)dr \geq E_{s,0}$$

(1.7)
The Hohenberg-Kohn functional, $F_{HK}$ can be written as

$$F_{HK}[\rho(r)] = T_s[\rho(r)] + J[\rho(r)] + E_{xc}[\rho(r)]$$  \hspace{1cm} (1.8)

where $T_s[\rho(r)]$ is the kinetic energy functional of a non-interacting system given by,

$$T_s[\rho(r)] = \sum_i^N \langle \psi_i \left| -\frac{1}{2} \nabla^2 \right| \psi_i \rangle$$  \hspace{1cm} (1.9)

$J[\rho(r)]$ is the classical Coulombic interaction energy,

$$J[\rho(r)] = \frac{1}{2} \iint \frac{\rho(r)\rho(r')}{|r-r'|} \, dr \, dr'$$  \hspace{1cm} (1.10)

and $E_{xc}[\rho(r)]$ is the exchange-correlation energy.

The only difference between Hartree-Fock approximation and the above theory is the presence of the exchange-correlation term, $E_{xc}$ in the later. Combining equations (1.3), (1.6), (1.8) and (1.9), one gets

$$E_{\nu(r)}[\rho(r)] = \int \rho(r)\nu(r) \, dr + \sum_i^N \langle \psi_i \left| -\frac{1}{2} \nabla^2 \right| \psi_i \rangle + \frac{1}{2} \iint \frac{\rho(r)\rho(r')}{|r-r'|} \, dr \, dr' + E_{xc}[\rho(r)]$$  \hspace{1cm} (1.11)

Minimization of the energy functional $E_{\nu(r)}[\rho(r)]$ results in the following one particle Kohn-Sham (KS) equation,

$$\left[-\frac{1}{2} \nabla^2 + \nu_{eff}(r; [\rho])\right] \psi_i = \epsilon_i \psi_i$$  \hspace{1cm} (1.12)

where the density $\rho(r)$ is obtained as the sum

$$\rho(r) = \sum_i^N |\psi_i(r)|^2$$  \hspace{1cm} (1.13)

And the KS effective potential $\nu_{eff}$ is given by

$$\nu_{eff}(r) = \nu(r) + \frac{\delta[\rho(r)]}{\delta \rho(r)} + \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)}$$

$$= \nu(r) + \int \frac{\rho(r')}{|r-r'|} \, dr' + \nu_{xc}(r)$$  \hspace{1cm} (1.14)

The energy correlation function of the above equation is defined as
The ground state energy is given by,
\[
E = \sum_{i} \epsilon_i - \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} \, dr \, dr' + E_{XC}[\rho(r)] - \int \nu_{XC}(r) \rho(r) \, dr
\]  
(1.16)

where \( \epsilon_i \) and \( \rho \) are the self-consistent quantities.

It is important to have a good approximation for the exchange-correlation energy, \( E_{XC}[\rho] \) and the local density approximation (LDA) is found to be one of the simplest and efficient approximation for \( E_{XC}[\rho] \). It is given by,
\[
E_{XC}^{LDA}[\rho(r)] = \int \rho(r) \epsilon_{XC}[\rho(r)] \, dr
\]  
(1.17)

where \( \epsilon_{XC}(\rho) \) is the exchange-correlation energy per particle of a uniform electron gas of density \( \rho \). The corresponding exchange-correlation potential represented by eqn.(1.14) becomes,
\[
\nu_{XC}^{LDA}(r) = \frac{\delta E_{XC}^{LDA}[\rho]}{\delta \rho(r)} = \epsilon_{XC}[\rho(r)] + \rho(r) \frac{\delta E_{XC}(\rho)}{\delta \rho(r)}
\]  
(1.18)

Also, the Kohn-Sham orbitals are now given by,
\[
\left[-\frac{1}{2} \nabla^2 + \nu(r) + \int \frac{\rho(r')}{|r-r'|} \, dr' + \nu_{XC}^{LDA}(r) \right] \psi_i = \epsilon_i \psi_i
\]  
(1.19)

The self-consistent solution of the above equation is called as the LDA method.

[1.2] Basis Set

A basis set is a mathematical description of orbitals of a system, which is used for approximate theoretical calculation or modelling. There are two types of basis functions commonly used in electronic structure calculations: Slater type Orbitals (STO) and Gaussian type Orbitals (GTO). Slater type orbitals have the functional form shown in eq. (1.20)
\[
\chi_{\zeta,n,l,m}(r, \theta, \varphi) = N Y_{l,m}(\theta, \varphi) r^{n-\frac{1}{2}} e^{-\zeta r}
\]  
(1.20)

where \( N \) is a normalization constant and \( Y_{l,m} \) are spherical harmonics, \( r, \theta, \) and \( \varphi \) are the polar coordinate with respect to the nucleus, \( n \) the principal quantum number and \( \zeta \), the orbital exponent.
Gaussian type orbitals can be written in terms of polar or cartesian coordinates as shown in eq. (1.21).

\[
\chi_{\zeta n, l, m}(r, \theta, \phi) = N Y_{l, m}(\theta, \phi) r^{2n-2-l} e^{-\frac{\rho^2}{2}}
\]

\[
\chi_{\zeta n, l, m}(x, y, z) = N x^l y^l z^l e^{-\frac{\rho^2}{2}}
\]  

The \( r^2 \) dependence in the exponential makes the GTOs inferior to the STOs in two aspects. At the nucleus, a GTO has a zero slope in contrast to a STO which has a “cusp”, and GTOs consequently have problems representing the proper behaviour near the nucleus. The other problem is that the GTO falls off too rapidly far from nucleus compared with an STO, and consequently the “tail” of the wave function is represented poorly.

Standard basis sets for electronic structure calculations use linear combination of gaussian functions to form orbitals. In general, linear combinations of Gaussian primitives are used as basis functions, given by the following relationship:

\[
\psi_i = \sum g_i \mu_i
\]  

where \( \psi_i \) is called a contracted Gaussian type function and the \( g_i \)'s are called Gaussian primitives. In general, the Gaussian type orbitals are obtained by least square fit of STOs. These are called STO-nG basis sets where n is the number of Gaussian primitives used to fit a STO.

A minimal basis set contain only one basis function for each atomic orbital of a particular atom with one coefficient assigned to it. The STO-nG is a minimal basis set.

A better MO wave function can be obtained by replacing an AO with an extended basis set, which consist of more than one function characterized by its own coefficient. If every MO of a minimal basis set is replaced by two functions having different orbital exponents (\( \zeta \)), then the basis set is a double-zeta basis set (DZ). Dunning-Huzinaga (D95) and cc-pCVDZ are examples of such a basis set. Similarly, a triple zeta basis set is obtained by using three basis functions per AO. An example of such a basis set is cc-pCVTZ.

The split-valence basis set is another type of basis set which can be formed by using two basis functions for the valence AOs and a single function for each inner shell orbital. The basis sets 6-31G and 6-311G are examples of split-valence double and triple zeta basis sets respectively. Even though split-valence basis sets change the size of orbitals, it lacks the ability to distort the shape of orbitals. This can be overcome by the addition of orbitals with
higher angular momentum than what is necessary to describe the ground state of an atom. The basis set thus obtained is called a polarized basis set. A polarized basis set is indicated by putting a ‘star’ after the basis set or by putting the higher angular momentum orbitals within parenthesis. For example, 6-31G** or 6-31G(d,p) indicates that d-functions and p-functions are added as polarization on heavy atoms and H-atom respectively of the standard 6-31G basis sets. In general, one adds d-functions to heavy atoms, f-functions to transition metal elements and p-functions to H atom to account for polarization. It may be noted that the d-type functions that are added to a particular basis set to get a polarized basis set are a single set of uncontracted Gaussian primitives. There are two types of d-functions, viz., pure and Cartesian as given below.

   Cartesian : \( d_x^2, d_y^2, d_z^2, d_{xy}, d_{yz}, d_{zx} \)

   Pure: \( d_x^2-d_y^2, d_z^2, d_{xy}, d_{yz}, d_{zx} \)

   Similarly, f-polarization function can be of 7-pure types, which are formed by linear combination of a set of ten cartesian f functions.

   However, the above mentioned basis sets failed to satisfactorily describe the molecules containing lone pairs, anions or systems with low ionization potential or system in excited states. This was overcome by the addition of diffuse functions, which are larger in size than the standard valence size functions. These Gaussian have very small exponents and decay slowly with increasing distance from the nucleus. Diffuse functions allow orbitals to occupy a larger region of space. They are indicated by a ‘+’ sign. For example, a 6-31+G(d) basis set indicates that diffuse functions are added to the heavy atoms.

   In electron correlation methods much larger basis sets are needed to describe the interaction between electrons. Such a basis set, known as high angular momentum basis sets can be generated by the addition of multiple polarization functions both on heavy atoms (d and f functions) and hydrogen atoms (d and p functions). For example, if the basis set is 6-311G(3df, 2df,p), it contains 3d functions and 1f function on heavy atoms of the second and higher rows, 2d functions and 1f function on first row heavy atoms and 1p function on H atoms.

   Computation involving heavier atoms (third and higher rows of the periodic table) are relatively troublesome than those involving first and second row atoms. The chief source of this problem is an increase in the number of two-electron integrals and the relativistic effects. These dilemmas are encompassed by the use of pseudopotentials. Since the core (inner shell) orbitals are not affected by the changes in chemical bonding, one can treat them as average potential. The valence electrons are described by basis functions.
There are two types of pseudopotentials: ab initio model potential (AIMP) and effective core potential (ECP). The ECP has the general form,

$$ECP(r) = \sum_{i=1}^{k} c_i r^{n_i} e^{-\alpha_i r^2}$$ (1.23)

where \( k \) is the number of terms in the expansion, \( c_i \) is a coefficient characteristic of each term, \( r \) is the distance from the nucleus with a power of \( n_i \) for the \( i^{th} \) term, and \( \alpha_i \) is an exponent for \( i^{th} \) term. The use of ECP is found to be computationally very efficient, particularly for transition metals, because it reduces the number of basis functions. One needs to consider the basis functions for only the valence electrons. ECP also makes room for the incorporation of relativistic effects.

[1.3] Quantum Theory of Atoms in Molecules (QTAIM)

Bader’s Quantum theory of Atoms in Molecules (QTAIM) is an important tool in analyzing the electron density in a molecule. The molecule is partitioned into atomic basins, whose boundary surfaces are the ones of zero flux in the gradient vector field of the electron density. The Laplacian, \( \nabla^2 \rho(r) \) is an important parameter and is defined as the sum of the three curvatures (or eigenvalues of the Hessian) of the electron density (\( \lambda_1, \lambda_2, \) and \( \lambda_3 \)). The line of maximum electron density which links two bonded atoms is termed as a bond path. The point where electron density is minimum along a bond path is termed as bond critical point (bcp) and this point lies on the boundary surfaces of the atomic basins. There is one positive curvature, \( \lambda_3 \), along the bond path and two negative curvatures, \( \lambda_1 \) and \( \lambda_2 \), perpendicular to it.

Bader pointed out that the sign of the Laplacian of the electron density is the result of two competing processes: the compression of electron density perpendicular to the bond path (giving negative eigenvalues \( \lambda_1 \) and \( \lambda_2 \)) and its expansion along the bond path (giving the positive eigenvalue \( \lambda_3 \)). For a homopolar covalent bond, the Laplacian is negative at bond critical point as sum of the negative eigenvalues is greater in magnitude than the positive one. On the other hand, in case of closed shell bonding interactions (ionic, hydrogen bonding, etc.), the Pauli exclusion principle operates to remove electron density from interatomic surface resulting in a positive Laplacian and low electron density at the bond critical point.

Cremer and Kraka suggested the use of energy density at bond critical point \( H(r) \) [sum of kinetic \( G(r) \) and potential \( V(r) \) energy densities] to ascertain the nature of a chemical
bond. Covalent bonds are generally characterized by a negative $H(r)$ value, whereas ionic bonds and van der Waals complexes have $H(r) \geq 0$. The magnitude of $H(r)$ reflects the degree of covalency. Consequently, it is necessary to consider several parameters at bond critical point ($\rho_b$, $\nabla^2 \rho_b$, $H$, or $G$) to characterize the type of bonding.$^{10,13}$

[1.4] Molecular Electrostatic Potential (MESP)

Molecular scalar fields such as molecular electron density (MED) and molecular electrostatic potential (MESP) play a basic role in the interpretation of a variety of physicochemical phenomena. Topographical features of MESP reveal several chemically salient features such as bonding, lone pairs, molecular structure and bond strength which have been well explored by Gadre and coworkers.$^{14-17}$ The MESP, $V(r)$ generated by a molecule having $N$ nuclei with charges $\{Z_A\}$ located at $\{R_A\}$, and the corresponding continuous electron density, $\rho(r)$ is given by

$$V(r) = \sum_A \frac{Z_A}{|r - R_A|} - \int \frac{\rho(r') \, d^3 r'}{|r - r'|}$$

(1.28)

The topographical features of MESP can be summarized in terms of its critical points (CP), i.e. points where all the first order partial derivatives of a function vanish. A CP is characterized as $(R, \sigma)$ where $R$ denotes the rank of the corresponding Hessian matrix, viz. the number of non zero eigenvalues, and signature, $\sigma$ denotes the sum of the sign of the eigenvalues. For a three-dimensional scalar field, the nondegenerate CPs can be classified in four different types, viz. $(3, +3)$ minimum, $(3, +1)$ saddle, $(3, -1)$ saddle and $(3, -3)$ maximum. In brief, the chemical significance of the CPs of MESP is as follows:

1. Bond between two atoms is reflected by the presence of a positive valued $(3, -1)$ CP.
2. A lone pair is generally shows up as a $(3, +3)$ CP.
3. A $(3, +1)$ CP generally connects neighboring $(3, +3)$ CPs. It is also a signature of a ring structure.
4. A $(3, +3)$ CP only represents presence of nuclei in MESP topography, as MESP cannot exhibits non-nuclear maximum.$^{18}$
[1.5] Brief Overview of the Remaining Chapters

[1.5.1] Chapter 2: Theoretical Study of Heterocyclic Carbenes, Silylenes, Germynes and Donor-Acceptor Complexes of Carbenes

[1.5.1.1] Effect of Substituents at the Heteroatom on the Structure and Ligating Properties of Heterocyclic Carbene, 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.
[1.5.1.2] 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\(^\text{27}\) 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.\(^\text{28}\)

In this part of the chapter, donor-acceptor interactions in NHC-EX\(_3\) (NHC=normal and abnormal N-heterocyclic carbene; E=B, Al, Ga; X=H, F, Cl, OH, NH\(_2\), CH\(_3\), CF\(_3\)) adducts (1R-EX\(_3\) and 2R-EX\(_3\)) 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.
[1.5.2] 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 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 CL₂ where the carbon atom is stabilized by two neutral electron donating ligands, L (e.g. L=NHC, PPh₃ 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.

[1.5.2.1] Effect of Substituents at the Heteroatom 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=H, Me, NH₂, 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.

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[1.5.2.2] 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.
[1.5.3] 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 $\sigma$ donor properties of NHCs can be varied to a large extent, the $\pi$ 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 $\pi$ acidity and $\pi$ 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. Schematic representation five-, six, and seven-membered heterocyclic carbenes along with boron substituted ones.

{Scheme image with structures and labels}

E=N, 5-NHC
E=P, 5-PHC
E=N, 5'-NHC
E=P, 5'-PHC
E=N, 5-NHCB
E=P, 5-PHCB
E=N, 6-NHC
E=P, 6-PHC
E=N, 6-NHCB
E=P, 6-PHCB
E=N, 7-NHC
E=P, 7-PHC
E=N, 7'-NHC
E=P, 7'-PHC
E=N, 7-NHCB
E=P, 7-PHCB
E=N, 7'-NHC
E=P, 7'-PHCB

R=H, Me, tBu, Ph
[1.5.4] 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) at PBE1PBE/SDD,6-31+G* level of theory. This study reveals that both annelation and carbonylation decrease the stability of carbenes. It is found that compared to nonannelated carbenes, annelated and carbonylated carbenes are found to be weaker σ donors but better π acceptors.


