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Chapter 2

A Theoretical Study on Activation of Dihydrogen by N-Heterocyclic Carbenes

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2.1 Introduction:

Density Functional Theory (DFT) is considered as one of the most popular electronic structure methods due to its reasonable accuracy blended with modest cost and has made a remarkable journey in the last few decades in many applications. Carbene is an intriguing class of compounds that contains a divalent carbon atom along with a lone pair of electrons. They are the very reactive and short lived compound that could not be isolated easily.

They exists as either singlet or triplet depending upon their electronic structure. If the electrons are spin paired they are singlet carbenes whereas triplet carbenes have two unpaired electrons. An important derivative of carbene is the N-Heterocyclic carbenes (NHC), where two nitrogen atoms attached to the carbene center and presence of these π-donating heteroatom leads to a stable singlet ground state [1]. In recent years, organometallic chemistry of NHCs have attracted considerable attention due to its potential application as supporting ligand and remains as a major topic in many outstanding research programs. The two adjacent N-atoms fascinate the strong σ-donating capability which leads to their extensive use in the field of catalysis [2-4]. Transition metal complexes those carried the NHC ligand may serve as powerful catalyst in numerous chemical reactions and therefore NHC has been a topic of intense research.

The first stable NHC complex was synthesized by Arduengo and his co-worker in 1991 in form of a bottleable reagent [5] and after that various other derivatives of carbene has been synthesized [6-7]. For instance, Bertrand and his co-worker have synthesized the abnormal carbene where only one heteroatom is attached to the carbene center [8]. Knowing about the importance of carbene complexes, various other types of carbenes are also synthesized and studied [9]. One such type of carbene is the remote carbene, synthesized by Raubenheimeret al. [10], where heteroatom is present at β-position to the carbene centre.

The structural and reactivity studies of N-heterocyclic phosphenium and N-heterocyclic P-halophosphines are also reported [11]. Earlier studies established the stability of nitrenium ions (carbene with nitrogen 'ene' center) also [12].

Very recently, synthetic possibility of a novel class of sandwiched organometallic compounds were also explored where Fe(II) is present between two group 13 analogues of N-heterocyclic carbene ligands [13]. These complexes acquire adequate stability and also attain higher functionality due to presence of two 'ene' centers.

Ligating properties of these carbenes can be enhanced by introducing substituents at different positions of the carbene. Earlier reports suggested that the NHCs exhibit significant σ and π-donation ability and can be tuned by introducing different groups in the heteroatom [14]. Therefore their theoretical studies are very much admirable. The transition metal complexes those carried NHC ligand may serve as powerful catalyst for numerous chemical reactions. Frey et al. reported that NHCsare capable of splitting H_2 and NH_3 by neucleophilic activation of H—H and N—H bonds [15].

Dihydrogen is considered as the future fuel as it can replace the fossil fuel by some eco-friendly way; the only problem arises due to difficulty of its storage.

But if a reversible condition can be made with the reaction of activation of hydrogen molecule the problem regarding its storage will be reduce to some extent.

Keeping these things in mind, I have studied the activation of dihydrogen (H_2) molecule by using various carbene derivatives as shown in **Figure 2.1**. I have considered the first metal-free singlet normal NHC or Arduengo type carbene **(1)** and its saturated derivative **(2)**. The abnormal carbene **(3)**, as well as cyclic alkyl amino carbene **(4)** are also considered. Remote carbene is another type which indicates that no hetero-atom is located in the α-position to the carbene centre and this type of carbine was synthesized by Raubenheimer and his coworkers [10].

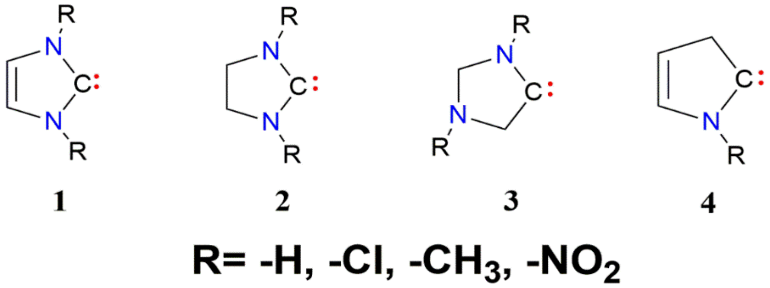


Figure 2.1 Various types of N-Heterocyclic carbene derivatives under investigation

Breaking of H—H bond of H_2 molecule can be taken place by two ways; either by transfer of electron pair of carbene to the antibonding molecular orbital of H_2 or by transfer of bonding electron pair of H_2 to the empty pzorbital of the carbonic carbon. In every case, various factors affect the reaction rates. Since the substituents at N-atoms dictate the ligating property of these carbenes, it will be worthwhile to study their effect on the activation barrier of this reaction.

To investigate the effect of substituents, various substituents such as –H, the electron withdrawing –Cl and $–NO_2$ as well as electron donating $–CH_3$ are substituted at the heteroatom of each class of carbene and their affects are studied.

The reaction scheme for the activation of H_2 molecule by carbene can be represented as-

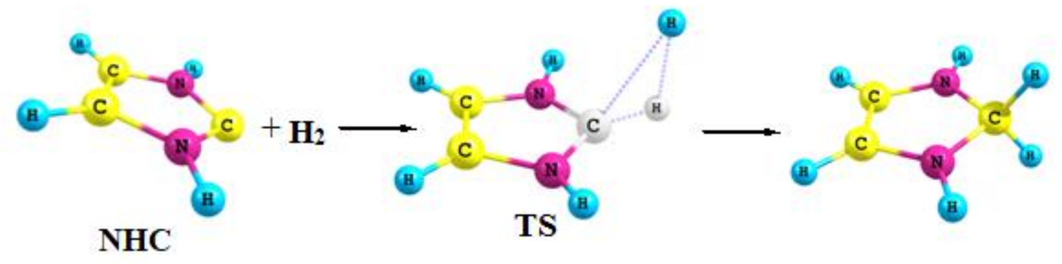


Figure 2.2 The reaction scheme for activation of H_2 molecule by N-Heterocyclic carbine

2.2 Computational Methodology:

The ground state of all the structures are optimized without any symmetry constraints at B3LYP [16] with basis set 6-31+G (d). All the local minimum structures of reactant, product is characterized by real frequencies while the transition states are characterized by one imaginary value of the Hessian matrix.

Further, the imaginary frequencies of the transition states were animated to verify whether they are true intuited transition states or not.

Single point energy calculations were further performed at the MP2/TZVP [17] level on the B3LYP/6-31+G (d) optimized geometries.

All corrections at B3LYP/6-31+G (d) are added to the electronic energies calculated at MP2/TZVP. The nature of the bonds are analyzed using natural bond orbital (NBO) [18] analysis at B3LYP/6-311++G (d, p) level of theory.

All the calculations were performed using Gaussian 03 suite of program and visualization of the molecules are done using Chem Craft trial version.

2.3 Results and Discussions:

2.3.1 Molecular Geometry:

The geometrical parameters of the NHCs are compiled in **Table 2.1** and have in good agreement with X-ray data [15]. For NHC-**1**, C—N bond length and <NCN angle is found to be higher with methyl substituent and lowest for –NO2 substituent. For hydrogen and chlorine substituent they are almost equal. Again, C—N bond order is found to be highest with hydrogen and it decrease with the other substituents. For NHC-2, C—N distance is almost same for all the four substituents. The <NCN bond angle follow the same order with the NHC-**1**. For CAAC **(3)**, C—N bond length is highest for **3-H** and lowest for **3-Cl**. The <NCN angle C—N bond order also follow the same order. For NHC-4, the C—N bond distance is highest for the **4-M**eand lowest for **4-Cl**. Again, <NCN is highest for **4-Me** and is close to **4-Cl**whereas it is lowest for the **4-H**. The C—N bond order follows a different order than the other three type of carbene. Further, it is found to be higher for **4-Cl**while lowest for the **4-Cl**.

Table 2.1 Geometrical parameters of the NHCs calculated at B3LYP/6-31+G (d) level of theory. Experimental values are given in parenthesis. Wiberg Bond Index (WBI) values are also given.

Molecule	**$r_{N\text{-}C}$(Å)**	**<NCN (degree)**	**WBI (C—N)**
1-H	1.360	100.64	1.282
1- Me	1.369 (*1.362*)	102.1 (*102.2*)	1.244
1-Cl	1.360	99.07	1.243
1-NO_2	1.358	98.67	1.231
2-H	1.348	104.56	1.324
2-Me	1.347	106.07	1.290

Molecule	**$r_{N\text{-}C}$(Å)**	**<NCN (degree)**	**WBI (C—N)**
2-Cl	1.341	102.61	1.243
2-NO_2	1.345	101.76	1.257
3-H	1.315	105.08	1.552
3-Me	1.310	118.65	1.529
3-Cl	1.280	102.93	1.243
3-NO_2	1.300	102.94	1.257
4-H	1.362	112.90	1.248
4-Me	1.366	116.72	1.153
4-Cl	1.334	116.38	1.287
4-NO_2	1.335	114.21	1.285

2.3.2 Ligating Properties:

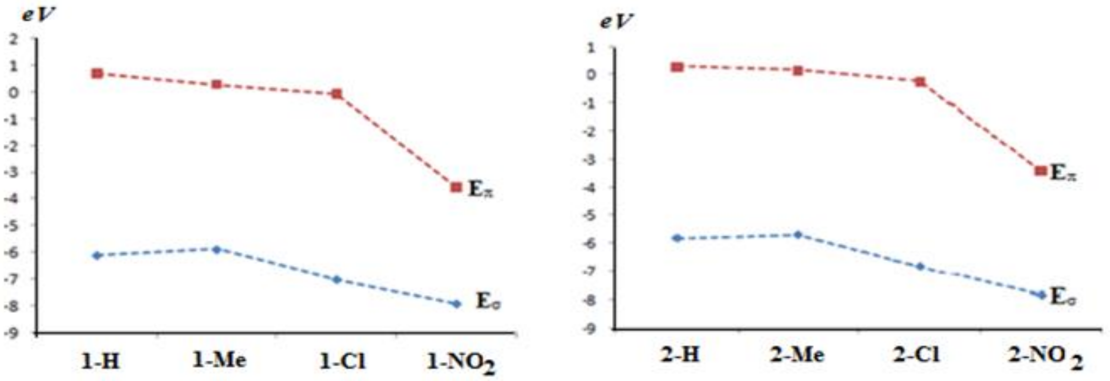
The ligating property of a particular NHC is dependent on the energy of the σ-symmetric HOMO and π-symmetry LUMO of a compound. We computed these energies with B3LYP/6-311++G (d, p) level of theory and their variations are ploted in **Figure 2.3**.

Higher the energy of the σ-symmetry MO (Eσ), NHC will be the better σ-donor and lower the energy of the π-symmetry orbital (Eπ), NHC will be better π-acceptor.

The variation of the σ-donating capacity depends on the electron density at the heteroatom. Here the increasing order of σ-donating capacity and π-accepting ability with different substituent follows the following order-

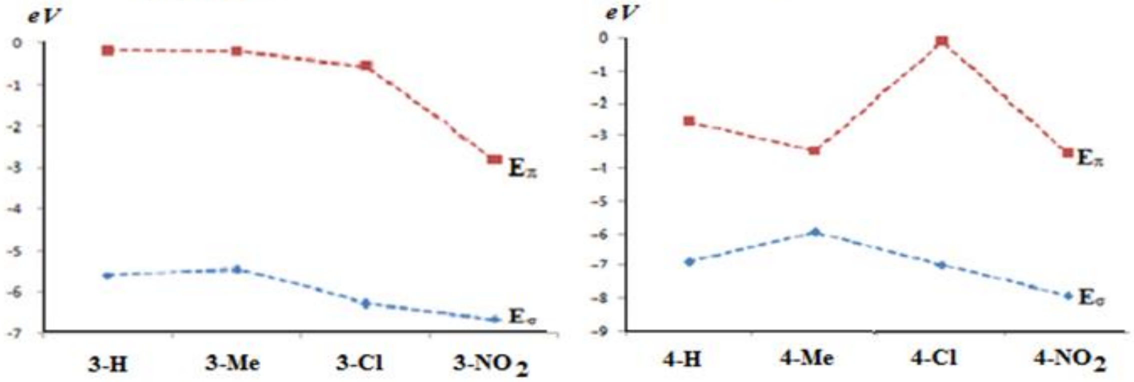
σ- Donation ability: $-NO_2 < -Cl < -H < -Me$

π- Acceptance ability: -Cl <-H < -Me < -NO_2



(a) 1- NHC

(b) 2-NHC



(c) 3-NHC

(d) 4-NHC

Figure 2.3. Plot of energies (eV) of the σ-symmetric lone pair (Eσ) and π-symmetry unoccupied MO (Eπ*) of the NHCs as a function of substituents in case of NHC-1, energy of the σ symmetry orbital is highest for **-H** and **-Me** substituted NHC and lowest for **-NO2** substituted NHC **[Figure 2.3(a)]**. NHC with **Me**act as better σ-donor and it is due to +I effect of methyl group. Presence of Methyl group at N-atom provides more electron density at N-atom as well as in the carbene centre causes high energy at the σ-symmetry orbital and therefore it acts as better σ-donor.

On the other hand, when electronegative chlorine is present at the heteroatom, electron density at N decreases and energy becomes lower which in turn decreases the ligating property. For **–NO_2** substituent, energy of σ-donating orbital is very low.

This dramatic change is due to the delocalization of electron at the **$–NO_2$** group. The resonance effect dominates in case of the **$–NO_2$**group, hence system becomes more stable and become least σ-donor. Accordingly, the π-acceptance ability of –NO2 substituted **1-NHC** is highest. Almost identical results has been observed for the **2-NHC**, **3-NHC** and **4-NHC**. Only in case of the **4-NHC** the change in π-acceptance ability is somewhat different from the others.

2.3.3 Singlet-Triplet Energy Separation (ΔEST):

Due to presence of lone pair at the heteroatom, singlet state is more stable for NHCs. The singlet-triplet energy separations for the NHCs under investigation are given in **Table 2.3**. The energy gap varies with substituent at the heteroatom. In case of 1-NHC, the energy gap is highest when**-H** is present at nitrogen whereas it is found to be lowest with**$–NO_2$**.

In case of **2-** and **3-NHC** the same is highest for **$–CH_3$** substituent while lowest in case of **–Cl**. However, in case of **4-NHC**, effect of substituent is quite negligible.

Table 2.2 MP2/TZVP calculated singlet-triplet energy separations (in kcal mol-1) of the NHCs.

Molecule	**ΔE_{ST}**	**Molecule**	**ΔE_{ST}**
1-H	83.16	**3-H**	48.44
1-Me	81.31	**3-Me**	47.36
1-Cl	79.12	**3-Cl**	17.90
$1\text{-}NO_2$	55.02	**$3\text{-}NO_2$**	33.99
2-H	69.19	**4-H**	50.73
2-Me	69.96	**4-Me**	47.55
2-Cl	26.80	**4-Cl**	43.17

Molecule	**ΔE_{ST}**	**Molecule**	**ΔE_{ST}**
2-NO$_2$	53.07	**4-NO$_2$**	44.96

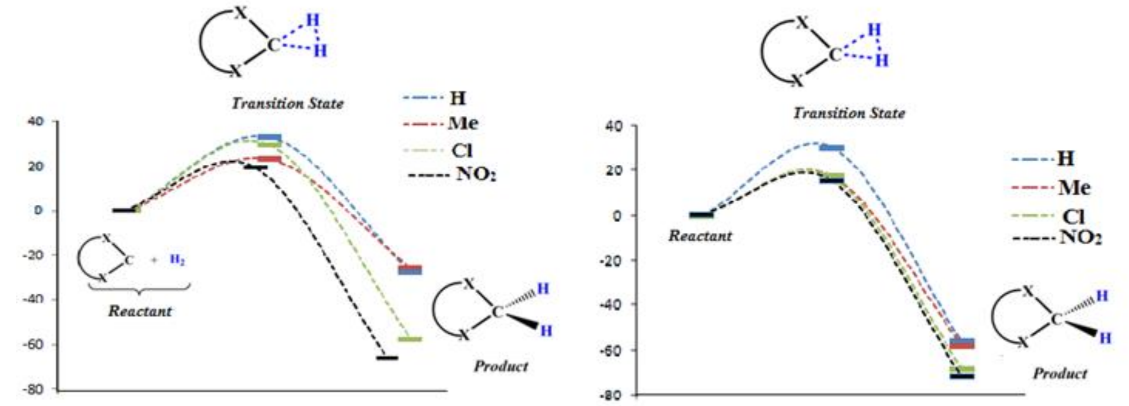
2.3.4 The Reaction Kinetics:

The activation energy (E_a) and free energy (ΔG) play significant role in studying the mechanism of a reaction. Variation of these two parameters with substituent at the heteroatom of NHCs are studied and the results are compiled in **Table 3**. These parameters calculated at MP2/TZVP//B3LYP/6-31+G (d) level of theory.

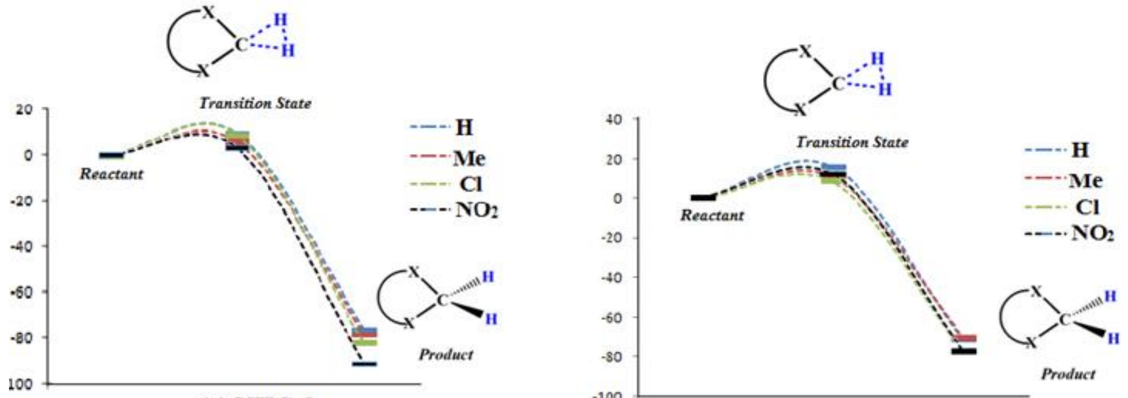
Table 2.3. Activation barriers (Ea) and ΔG at 298 K for the activation of dihydrogen by the NHCs. All values are in kcal mol-^{1}.

Molecule	**E_a**	**ΔG**	**Molecule**	**E_a**	**ΔG**
1-H	32.91	-27.93	**3-H**	9.60	-76.24
1-Me	22.99	-25.90	**3-Me**	6.16	-78.26
1-Cl	29.59	-57.83	**3-Cl**	9.35	-82.31
1-NO$_2$	19.41	-65.98	**3-NO$_2$**	2.97	-91.90
2-H	30.45	-56.11	**4-H**	15.80	-71.31
2-Me	17.45	-57.96	**4-Me**	10.84	-69.99
2-Cl	17.46	-68.37	**4-Cl**	8.32	-77.53
2-NO$_2$	15.20	-72.15	**4-NO$_2$**	11.99	-77.25

The activation energy is found to be highest FOR**1-NHC** and lowest for **3-NHC**. Among each class of carbenes, substituents have significant effect and are clearly observed from **Figure 2.4**. The highest activation energy is recorded for **1-NHC** lowest for **1-NHC–NO$_2$**. The results are identical for all the **NHC**s under consideration. Only in case of **4-NHC**–**C**litis slightly lower than corresponding –**NO$_2$** substituent. The ΔG value is found to be negative that suggest the feasibility of the reaction (**Table 2.3**).



(a) NHC-1 (b) NHC-2



(c) NHC-3 (d)NHC-4

Figure 2.4 Reaction barriers for the activation of dihydrogen by NHCs

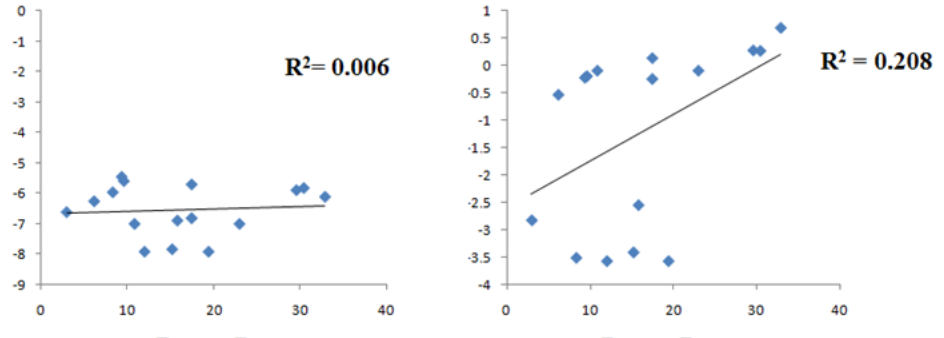
2.3.5 Correlation of Activation Energy with Various Factors:

Among various factors we try to find out the most important factor which dictates the activation energy of the reaction under study.

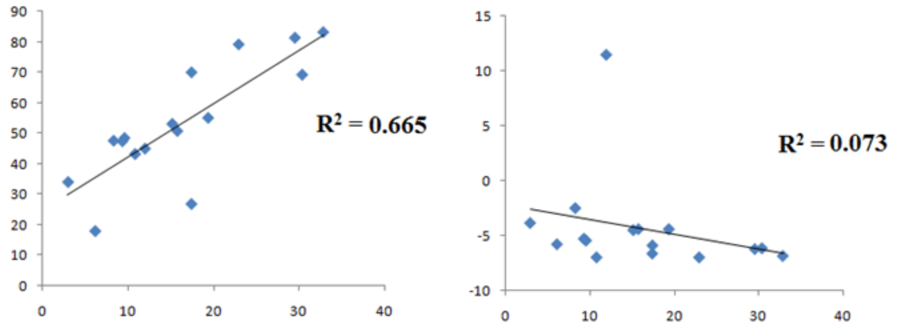
To investigate this, we plot energy of the σ-symmetry orbital (a), π-symmetry orbital (b), singlet-triplet energy gap (c), and energy difference between σ-symmetry orbital and π-symmetry orbital (d) respectively with the activation energy and calculate the correlation as shown in

Figure 2.5. Among these parameters, correlation of activation energy is found to be highest with the singlet-triplet energy gap.

Therefore, activation energy of the reaction is mainly dictated by singlet-triplet energy gap. Energy of the π-symmetry orbital has also significant effect.



(a) E_a vs. E_σ (b) E_a vs. E_π



(c) E_a vs. $\Delta E_{S\text{-}T}$ (d) E_a vs. $\Delta E_{\sigma\text{-}\pi}$

Figure 2.5 Correlation graph of different parameters with activation energy.

2.4 Conclusions:

In this chapter, activation of Hydrogen molecule is studied theoretically by four different N-Heterocyclic carbine. To investigate the probable factors that responsible for activation barrier, four different substituents are introduced in N-atom. It has been observed that the substituent has a negligible effect on the geometrical parameters but have significant effect on HOMO and LUMO energy.

Presence of electron donating group increases the ligating property of the NHCs. Electron donation capability as well as electron delocalization of substituent also have substantial effect on the singlet-triplet energy gap. Activation barrier of the reaction is affected by the substituent at the heteroatom and from correlation study of all these factor it may be concluded that the singlet-triplet energy gap of carbine compound plays the most important role in activation barrier during dihydrogen activation.

Since there are two possibilities of the breaking of the H—H bond in H_2 molecule, firstly transfer of electron pair of carbene centre to the anti-bonding orbital of H_2 molecule and secondly through transfer of bonding electron pair from H_2molecule to the unhybridized p- orbital of carbene centre. From the correlation of energy of σ-symmetry and π-symmetry with activation energy it has been observed that Eπ has highest correlation with Ea, there is maximum probability of transfer the lone pair of the electron of the carbine centre to the anti-bonding orbital of the Hydrogen molecule.

2.5 References:

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