**N-Heterocyclic Carbenes in Main Group Chemistry**

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By

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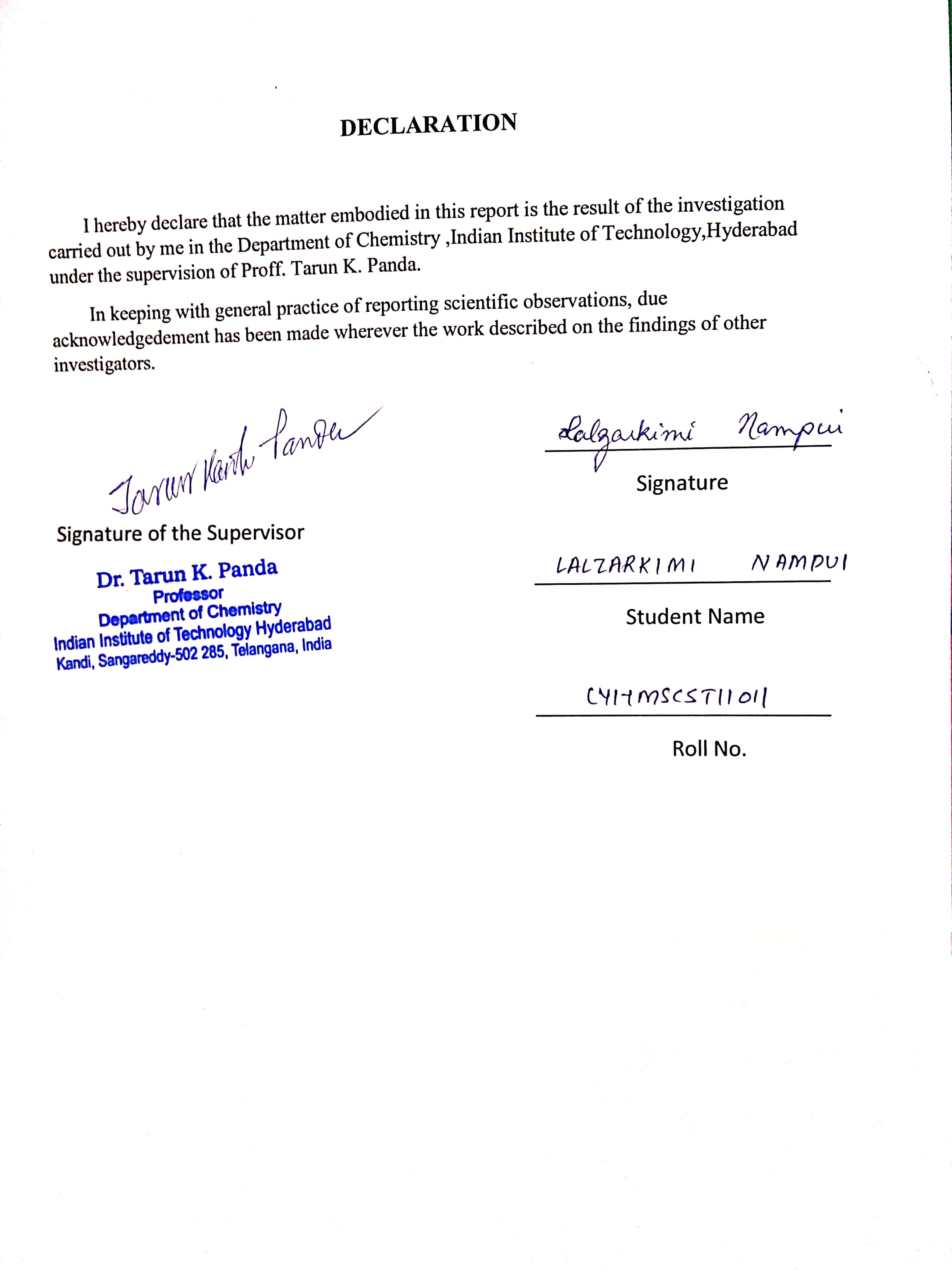
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Approval Sheet

This thesis entitled “**NHCs in main group element**” by **Lalzarkimi Nampui** is approved for the degree of Master from IIT Hyderabad.

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**(LALZARKIMI NAMPUI)**

**Abstract**

The discovery of N-heterocyclic carbene (NHC) in the early 1990 lead to the profound application of these compounds in the academic as well as industrial research. The NHC compounds are divalent compounds which play an important role in two electron donor ligandsand also in catalyzing a reaction. The study of low-coordinate main group compounds has gained attentionin the area ofresearch in the past decades. Remarkable results were observed when the main group elements complexes along with N-heterocyclic compounds were used inorder to be stabilized and isolated as Lewis acid/base adducts. This feature has enabled researchers to investigate a number of syntheseswith specific electronic properties, which in turn opened ways for new discoveries in theformation of new organic catalysts.



**Introduction**

Before the investigation on Carbenes started, they were thought to be difficult to isolate as they were highly unstable. This was proved otherwise by the beginning of 1980s by Wazick. Wazick and co-workers did a series of reactions to study the properties of NHCs regarding their stability.They were successful in isolating an N-heterocyclic compound which could be used as ligands in different metal complexes

NHCs were then concluded to be species with one or more nitrogen atoms/atoms and a carbine carbon.Under this broad category, NHCs were further classified into many factors like ring size, heteroatom etc.They are electronically and sterically stabilized and generally have bulky substituents near the carbon atom attached to nitrogen atoms. The substituents provide kinetic stability due to their bulky size, as they do not allow the olefin to be dimerized.The task of stabilizing the compound electronically is determined by the nitrogen that is present.

First, stable NHC was discovered by scientist Arduengo. Upon the successful synthesis and characterization of an N-heterocyclic carbene in 1991, a new class of ligand was introduced. There was a swift surge in studies of NHC’s for their synthesis and their application.Also, over the past few years, NHC’s have become well-known accessory ligands for the preparation of transition metal-based catalyst. This is due to the strong binding tendency of NHC’s to the metal center and thereby eliminating the need for an excess of a ligand in catalytic reactions.

NHC ligands due to their ability to be strong sigma donor and the metal, which is also a back donor, are known to form strong metal bonds. Therefore, some of these complexes exhibit remarkable photophysical properties, giving highly luminescent organometallic compounds.



It has also been observed that low valent main group elements and their compounds and the transition metals have similar properties with respect to the bonding and also chemical nature. In main group element chemistry, NHCs are have been successfully used for stabilizing low-coordinate elements in several oxidation states,which. This in turn, made way not only to study the various properties of these species like reactivity, but also their usefulness in synthesis and catalysis.

**Electronic Effects and Bonding in Main Group Element –NHC Complexes**

Different NHCs differ in their structure by the number of nitrogen atoms adjacent to the carbene carbon atom, in the ring size, ring constitution and functionalization. It has been observed that the effect of the σ-electron-withdrawing and the π-electron-donating capacity of nitrogen is immense . It hereby decreses the HOMO and the LUMO energies which leads to the energy separation between the orbitals and the ground states.This character gives NHCs an advantage i.e their nucleophilicity, and theirσ-donating characters.



Figure 1

To date, the most studied carbenes have been the classical NHCs and the CAACs [cyclic (alkyl)-(amino) carbenes , where their electronic properties have been compared taking the example of imidazol(id)in-2-ylidenes (classical NHCs) with those in pyrrolydin-2-ylidenes(CAACs).



The main advantage of CAACs over NHCs is because of the presence of quaternary carbons which are strong σ-donor, next to the carbeneswhich decreases the HOMO-LUMO energy gap. Other advantages of CAACs include the stronger nucleophilicity and electrophilicity which enables them to activate H2 , CO and NH3 .

Majority of the paramagnetic main group species are not stable due to the presence of the unpaired electron. So, the NHCs play an important role here by helping them stabilize as they have strong σ-donating properties. There are many ways to determine the donating capacity of NHCs, but the most commonly used one is the Tolman electronic parameter (TEPs) which is determined by measuring the frequency of the A1 C-O vibrational mode by infrared spectroscopy.



Figure 3

The TEP values are usually in the range from ca.2030-2068 cm-1 and they decrease when the donation takes places from the metal to the π\*(CO) –orbital . This method is not exempted from limitations as it is unable to describe properly the M-L bonding in the transition metal complexes and also the characterization of of σ-donation and and π-accepting properties .

This limitation creates problem for when the strength of M-L bond has been determined by the TEP method and is compared with the ligands which have different π-accepting properties.



Increasing π-acidity(increasing chemical shift values)

Figure 4

Another important method to find out about the M-L bond is my analyzing the NMR data, i.e by keeping into view the NMR signalsinvovled in the CNHC –E bond and hereby assessing the σ-donor properties of the NHCs.

**Synthetic Methodology**

The application of NHCs in the main group chemistry is immense after their discovery.But turning point in this field was when the first carbodicarbenes L2C was experimentally discovered by G. Bertrand et al. in 2008 which was followed by the NHC allotropes L2X2 (E=B,Si ,P) with the oxidation state zero experimentally discovered by G. Robinson et at. in 2008.The concept of dative bonding were further successfully studied after a many reaction were carried out. These discoveries were of importance in this field as it helped in stabilizing the main group element species.

**Scheme 1: Typical Reactivity of Imidazol(id)in-2-ylidenes toward Main Group Element Compounds**

A series of reactions have been carried out here. The first type includes the addition reaction which gives rise to the products **1**and **2**. For the formation of product 3, redox reaction was carried out along with the removal of protons. Products **5**and 6 were obtained by elimination reaction.

The result of the **Scheme 1** can be altered to many other different products26,27.



**Experimental Method**

**NHC Complexes in Group 1 Metals**

Majority of the alkali metal NHC complexes are simplistic Lewis adducts which have been formed by adding alkali metal base to free NHC or to their respective imidazolium salt antecedents. Out of the elements of Group 1, Rband Cs have not been able to form their NHC adducts till date.

The trend in the metal-NHC for the elements of Group 1 have been found to be as such- their strength decreases as the atomic number of the element increases. This can be explained by studying the NMR shift. The increase in the atomic number of the element, the more downfield shifted is the carbene carbon atom28,29

**Table 1.** Comparison of the 13C NMR Data [ppm] of NHC Alkali Metal Complexes



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **NHC** | **Free NHC** | **Li-NHC** | **Na-NHC** | **K-NHC** |
| 776 | 236.1 | 216.8 | 221.3 | 226.7 |
| 876 | 206.8 | 195.7 | 196.4 | 201.1 |
| 977 | 242.7 | 219.4 | 224.9 | 241.0 |

**Scheme 2 : Ring opening of complex 10**



Hevia et al. were the first ones to carry out the ring opening reaction on NHCs with the help of the elements of Group 1 or the alkali metals.When LiCH2SiMe3 was added onto SIMes the formation **10** could be seen.(**Scheme 2**). The products **11** and **12** were further attained by carryng out reactions which required the reactants to be trapped.30

**Scheme 3 : Synthesis of aNHC Li Complex**

Bertrand et al. synthesized **13** by obstructing the C2 position of the NHC , which was then followed by removal of the proton with the help of a base Lithium diisopropylamide.

Roesky and Stalke et al. produced a complex where Li is coordinated abnormally to the NHC (**14a**). The compound formed was made into being by adding BH3 to IDipp. Now if we heat the THF solution of complex **15**, a C2 lithiated compound is formed .

Upon reacting an NHC diphosphorous adduct and lithium metal, Robinson et al. were successful in isolating the product **16**.31-33.



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**Scheme 4 :Synthesis of Mg-Hydride cluster**



This synthesis was carried out byconverting Mg-bis(N(TMS)2) IDipp complex **19**taking the help of PhSiH3 .The compound hereby formed had an adamantine like structure with Mg4H 6 as the core surrounded by two coordinating NHCs34

**Group 13 and their NHC complexes**

**Scheme 5:Synthesis of first Carbene-Borane Complex 23**



The isolation of the first ever carbine-borane i.e Oxazolidin-2-ylidene triphenylborane was carried out in 1968 by Bittner et al. The reaction of isonitrile-triohenylborane, **21** along with a Li base and acetone with an in situ condition produced complex **22**.

Upon treating **21** in an aqueous environment, complex **22**, it forms the desired final product i.e triphenyl borane complex35.

**Scheme 6: Synthesis of NHC-Stabilized Al=S and Al=Te double bonded complexes**



Synthesis of aluminium sulfide compounds were done by reacting the aluminium complex **24** with cyclic thioureas . Cyclic thioureas further go through cleavage of C=S bond at the Al center to produce **25** and **26**.

The complex**29**,aluminium telluride, which contains an Al=Te bond was synthesized by Franz *et al.* This was a three-step reaction. 1,3-diethyl-4,5-dimethyl-imidazolin-2-ylidene was used along with electron-rich *N-*heterocyclic imine which is sterically hindered to produce isolate the final product.36-37

**Scheme 7: NHC Adduct with Electron poor allenes**



When electron deficient difluorenylidene allene (**31**) reacts with N-Alkylimidazolin-2-ylidenes , they form adducts (**32a,b**) which are stable in nature.This reaction was also carried on electron-poor allenes, which yielded their corresponding adducts, found to stable at room temperature. But it has also been observed that the formation of these adducts is not possible at low temperatures ,i.e at around -7838

**Scheme 8 : Synthesis of aNHC-Dichlorosilane Adduct**



In this reaction, a strong electron donor/electrophilic abnormal NHC in the presence of HSiCl3 yields the NHC-dichlorosilane adduct **36** . Here SiCl4 is eliminated owing to which SiHCl3 was dismutated, instead of an aNHC-silicochloroform formation.39

**Scheme 9 : Reaction of NHCs with Nitrous Oxide**



When imidazolin-2-ylidenes generated insitu reacts with nitrous oxide ,it forms NHC-N2O which is stable in air and moisture. N2 is released which yields respective ureas upon heating the adducts with a temperature of around 65-100.40-41

**Scheme 10 : Synthesis of NHC-Phosphinidene Complexes**



Arduengo and Cowley were the first ones to in 1997 to successfully yield NHC stabilized Phosphinidenes. This reaction was carried out reacting NHC with cyclic phosphinidenes orby reaction with P(III) dichlorides.42-44

**Conclusions**

In conclusion, we have described about the importance of NHC in main group element chemistry. Notably, this protocol exclusively described about its application as catalysis in synthesis of many building blocks. However, as being chemically less reactive due to its stabilization,it can be comparable with other catalysts like transition metal. Overall, this area of research contributed greatly to the development of donor-acceptor concepts in main group chemistry.

Using this strategy,various other complexes have been synthesized by substitution due to the tunable nature of the NHC ligand. with various substitution pattern is possible. This area of research wil further be explored for novel synthetic methodology, for energy storage devices etc.

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