# PROJECT COMPLETION REPORT

## CHEMISTRY OF MONOVALENT GROUP 13 AND DIVALENT GROUP 14 BASES : A THEORETICAL STUDY

**File no. EMR/2016/005294**

**Principal Investigator:**

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Annexure-IX

# PROJECT COMPLETION REPORT

1. Title of the project: Chemistry of Monovalent Group 13 and Divalent Group 14 Bases : A Theoretical Study

2. Principal Investigator:

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3. Implementing Institution(s) and other collaborating Institution(s):

   Tezpur University (A Central University),
   Tezpur, Napaam, 784028 Assam

   Collaborating Institution: Nil

4. Date of commencement: 17 June, 2017

5. Planned date of completion: 16 December, 2020

6. Actual date of completion: 16 December, 2020

7. Objectives as stated in the project proposal:

   (i) Designing of Skeletally Substituted Cyclic Alkyl Amino Carbenes and Study of their Reactivity.
   (ii) Designing of Ambiphilic Silylenes and Germylenes and Study of their Reactivity.
   (iii) Designing of Lewis Basic Boron Bases and Study of Borylene Liberation from Transition Metal Fragments.
   (iv) Stabilization of Singlet Metalla-N-Heterocyclic Carbenes (MNHCs).

8. Deviation made from original objectives if any, while implementing the project and reasons thereof:

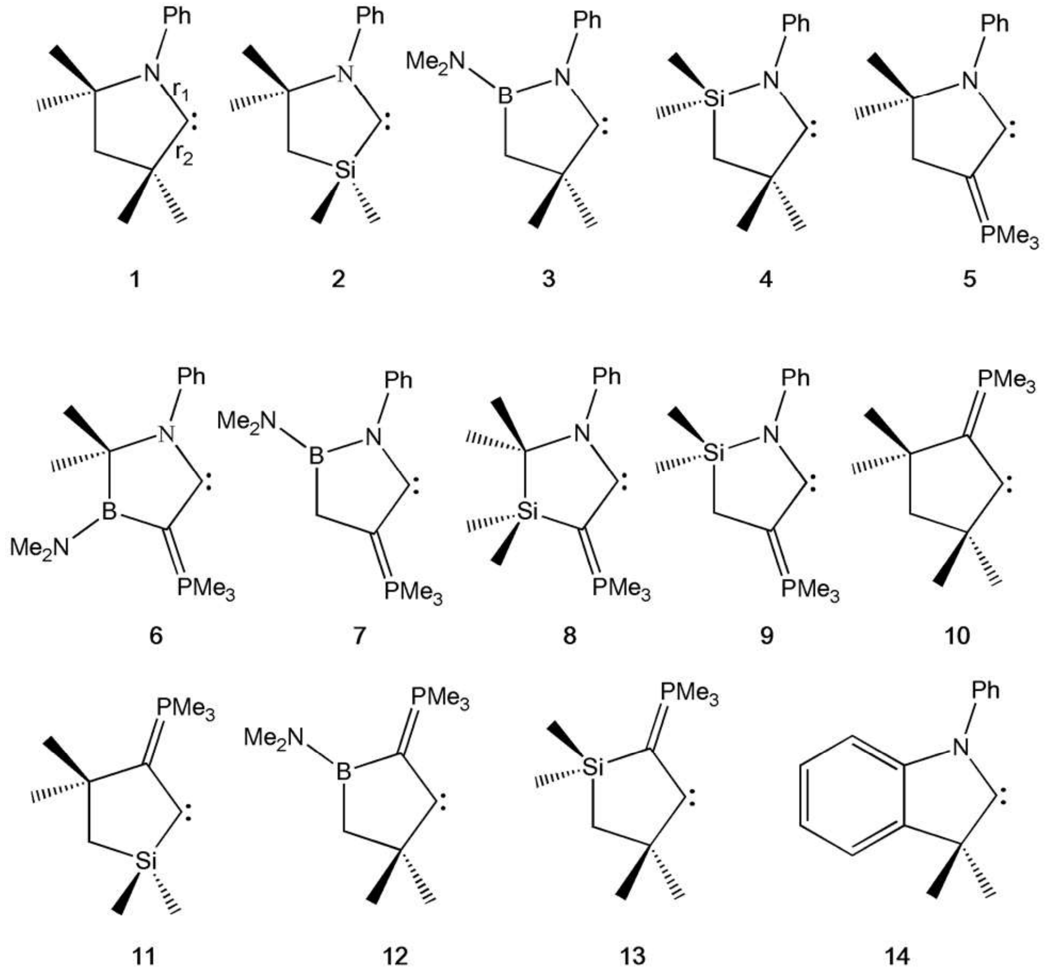
   There was no deviation from the original objectives.

9. Experimental work giving full details of experimental set up, methods adopted, data collected supported by necessary table, charts, diagrams & photographs:

   Being a purely **Computational Chemistry** project, this project did not involve any experimental work.

10. Detailed analysis of results indicating contributions made towards increasing the state of knowledge in the subject:

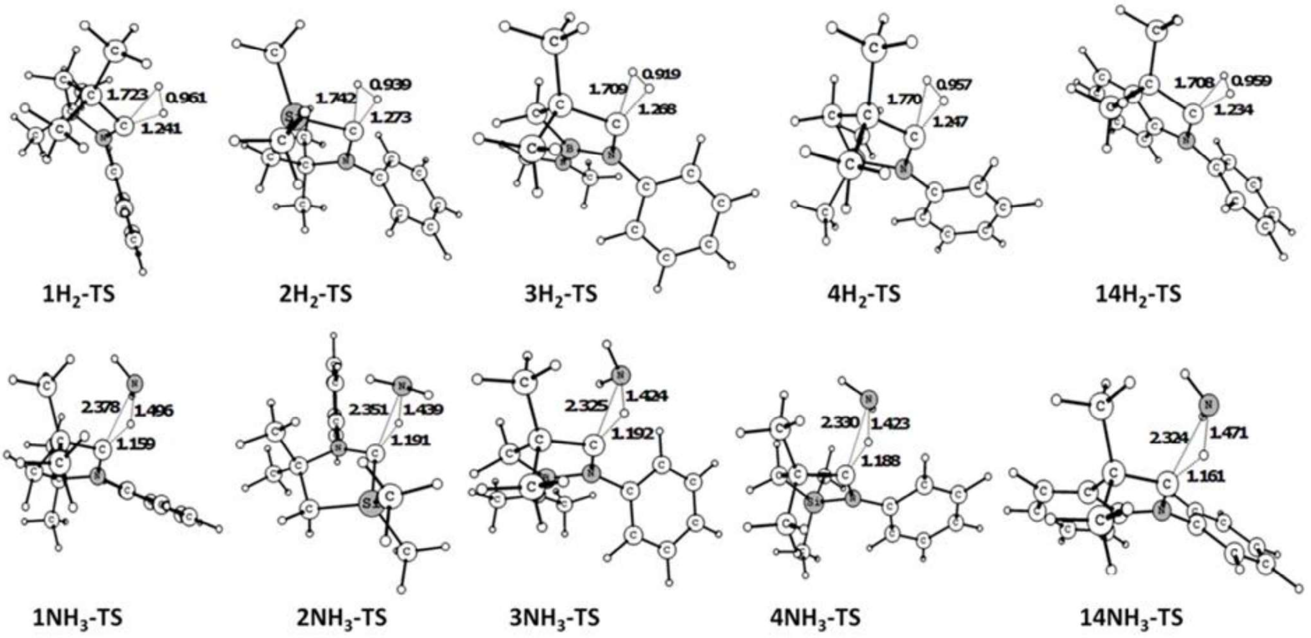
**(i)** The ligand properties of several skeletally modified cyclic alkyl amino carbenes (CAAC, Scheme 1) have been studied quantum chemically. The stability of these carbenes has been assessed from an evaluation of their singlet–triplet and stabilization energy values. Introduction of $\pi$-electron withdrawing boron or silicon atom in the carbene skeleton decreases both thermodynamic and kinetic stability. Ylide substituted carbenes are found to be more stable than non ylidic ones in their optimized singlet state. In addition, ylide substitution results in substantial enhancement and reduction of the of the $\sigma$-donation and $\pi$- acceptance ability respectively. Among all the carbenes, **2**, **3**, **4** and **14** are found to have comparable $\sigma$–donation as well as $\pi$–acceptance ability with that of parent CAAC (**1**). The efficiency of some of these carbenes (**1–4** and **14**) were evaluated towards activation of $H_2$ and $NH_3$ (Table 1 and Figures 1 and 2). By virtue of the absence of a low energy $\pi$-acceptor orbital at the carbenic centre, ylide anchored carbenes are found to be ineffective towards activation of $H_2$ and $NH_3$ ( ***Chem. Eur. J.*** **2017**, *23,* 9926-9936).



Scheme 1

**Table 1**: Calculated reaction free energy (ΔG, kcal/mol) and free energy of activation ($\Delta G^{\ddagger}$, kcal/mol) for the activation of $H_2$ and $NH_3$ by carbenes **1–4** and **14**.

| Molecule | $\Delta G(H_2)$ | $\Delta G(H_2)^{\ddagger}$ | $\Delta G(NH_3)$ | $\Delta G(NH_3)^{\ddagger}$ |
|---|---|---|---|---|
| **1** | -44.2 | 28.8 | -27.8 | 33.2 |
| **2** | -49.4 | 21.1 | -28.2 | 27.4 |
| **3** | -53.9 | 26.2 | -37.9 | 28.5 |
| **4** | -52.1 | 23.5 | -35.5 | 28.3 |
| **14** | -47.5 | 28.2 | -33.1 | 32.5 |



$1H_2$-TS $2H_2$-TS $3H_2$-TS $4H_2$-TS $14H_2$-TS

$1NH_3$-TS $2NH_3$-TS $3NH_3$-TS $4NH_3$-TS $14NH_3$-TS

**Figure 1**. Optimized geometries of the transition states for activation of dihydrogen and ammonia by **1-4** and **14**

(**ii**) High level quantum chemical calculations were carried out to unravel the potential of known but unexplored singlet carbenes in activating enthalpically strong bonds (Scheme 2). Based on the calculated values of activation energy barriers, it was found that for ammonia ($NH_3$), most of the molecules favor an electrophilic mode of activation (Scheme 3). On the other hand, even though the electrophilic pathway is found to be more favorable than the nucleophilic one for activation of phosphine ($PH_2Ph$) by majority of the carbenes, the barrier heights for both pathways are calculated to be comparable for diamidocarbene (DAC, **4**), cyclic amino aryl carbenes (CAArCs, **7-9**) and bicyclic alkyl amino carbene (BICAAC, **11**). In agreement with their better electron donation and acceptance abilities, the hitherto unexplored BICAAC, CAArCs and

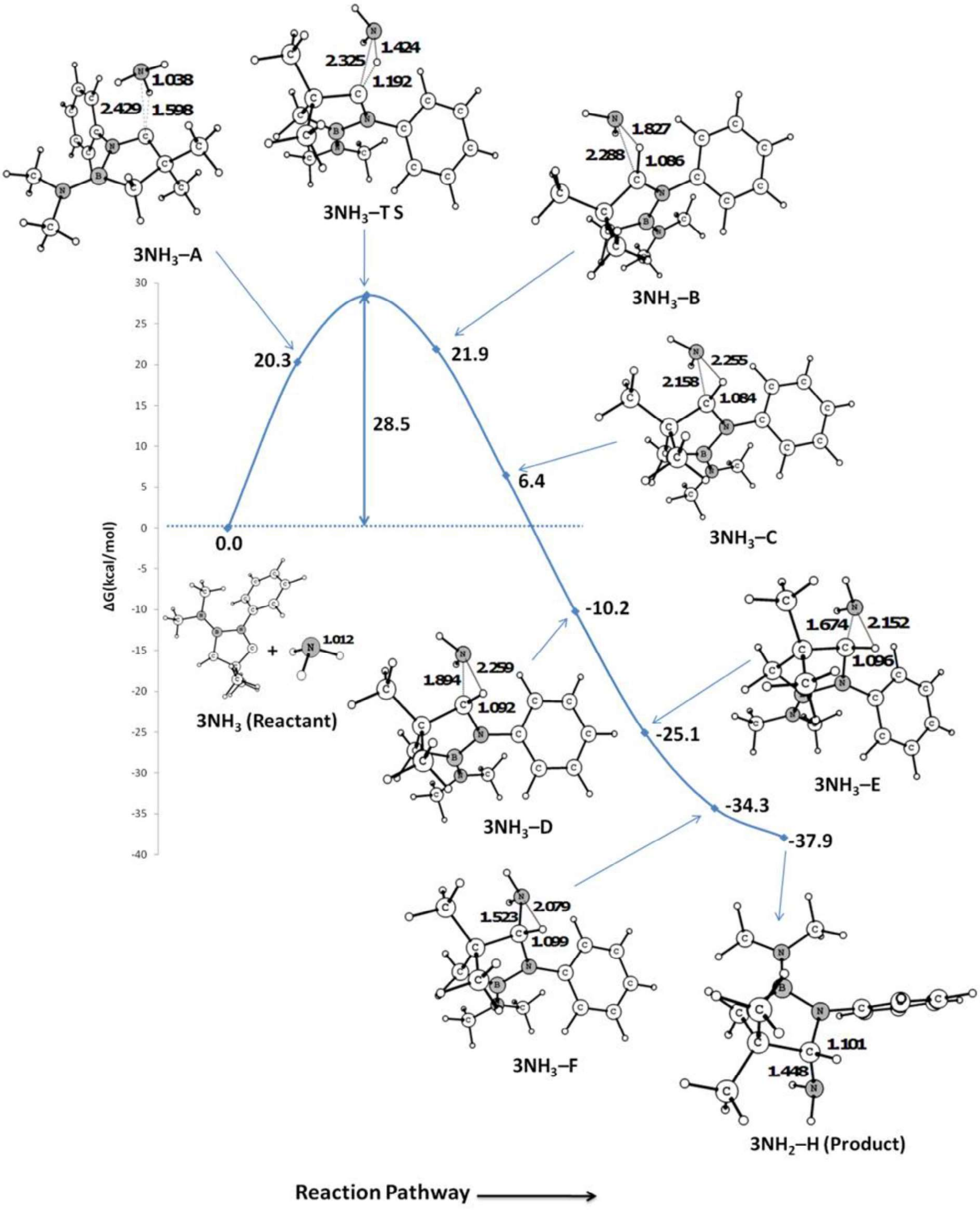
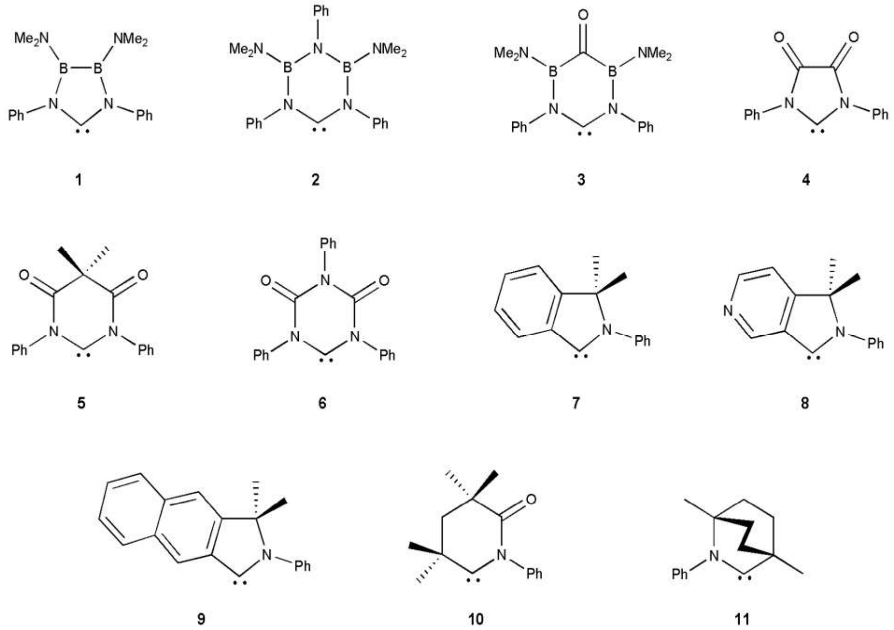
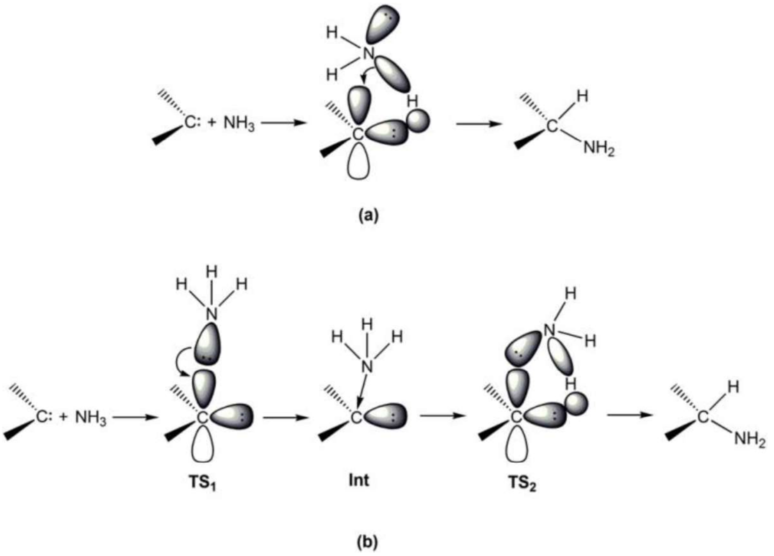


**Figure 2**. Reaction pathway for N–H bond activation of ammonia by the boron substituted CAAC **3**. The Gibbs free energy values and bond lengths are given in kcal/mol and angstrom (Å) respectively

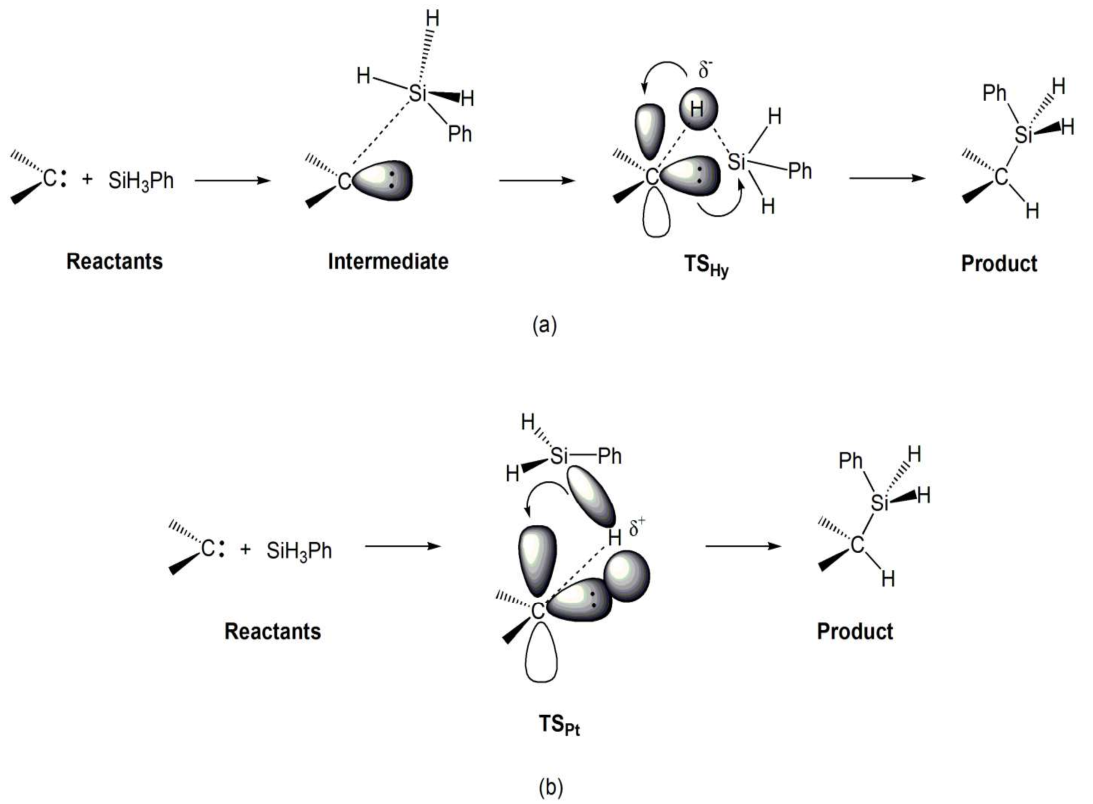
cyclic alkyl amido carbenes (CAAmC, **10**) are predicted to be more effective than cyclic alkyl amino carbenes (CAACs) towards the activation of both ammonia and phosphine. For the activation of silane ($SiH_3Ph$), a hydride transfer pathway is found to be more favorable than the proton transfer pathway (Scheme 4). Further, the calculated values of total Gibbs free energies and activation energy barriers for the splitting of N-H, P-H and Si-H bonds by a majority of the molecules are found to be comparable to those of the experimentally evaluated ones, implying that these known-yet unexplored-carbenes may be considered as suitable candidates for the activation of such enthalpically strong bonds (***Adv. Synth. Catal.*** **2018***, 360,* 4543-4561).



**Scheme 2**

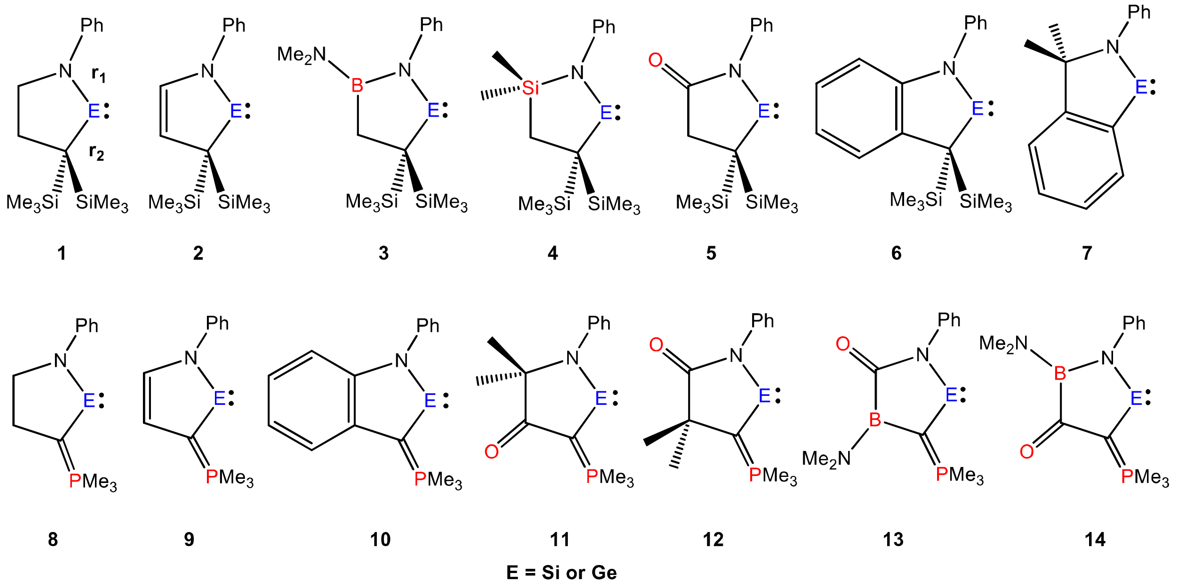


**Scheme 3**: Schematic representation for activation of ammonia *via* (a) nucleophilic and (b) electrophilic pathway.



**Scheme 4**: Schematic representation for activation of Si–H bond of $SiH_3Ph$ *via* (a) Hydride and (b) Proton transfer pathway.

(**iii**) Quantum chemical calculations have been carried out on a series of skeletally modified cyclic alkyl amino silylenes (CAASis) and germylenes (CAAGes) to understand their ligand properties and reactivity towards the activation of a variety of small molecules (Scheme 5). Installation of boron or silicon atom into the ring framework of these silylenes/germylenes led to dramatic increase in their σ–basicity while incorporation of ylidic moieties resulted in sharp reduction of their $\pi$-acidity although it did help in increasing the electron donation ability. The calculated values of energy barriers for activation of H – H, N – H, C – H and Si – H bonds by many of the cyclic silylenes considered here are found to be comparable to those with experimentally evaluated systems indicating the potential of these computationally designed molecules in small molecule activation and calls for synthetic efforts towards their isolation. Further, activations employing CAAGes are found to be more demanding than those with CAASis which may be attributed to the significantly lower Lewis basicity of the former than the latter. Given below is the reaction profile diagram (Figure 3) for the activation of N – H bond of $NH_3$ by **1Si** and **1Ge** as a representative case. That clearly shows the more facile activation by CAASi than CAAGe (***Dalton Trans.*** **2020**, *49*, 13760–13772).



**Scheme 5**: Schematic representation of the range of silylenes and germylenes considered in the present study. [r$_1$ and r$_2$ are the distances between the ene center (E) and $\alpha$-nitrogen atom (E – N) and $\alpha$-carbon atom (E – C) respectively].

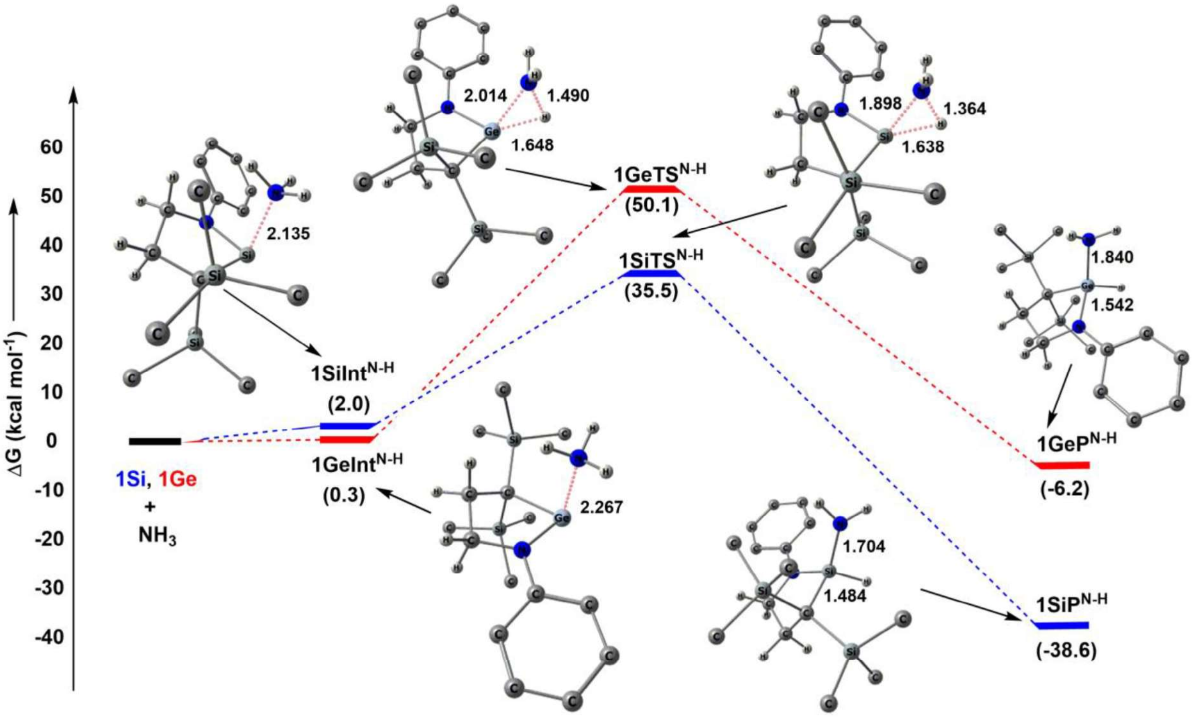
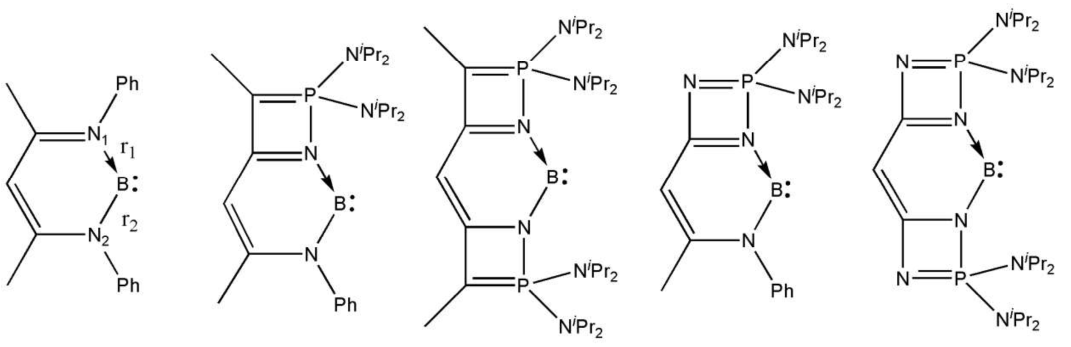


**Figure 3**: Reaction profile diagram for the activation of N – H bond of NH$_3$ by **1Si** and **1Ge**. The hydrogen atoms of the methyl and phenyl groups are omitted for the sake of clarity.

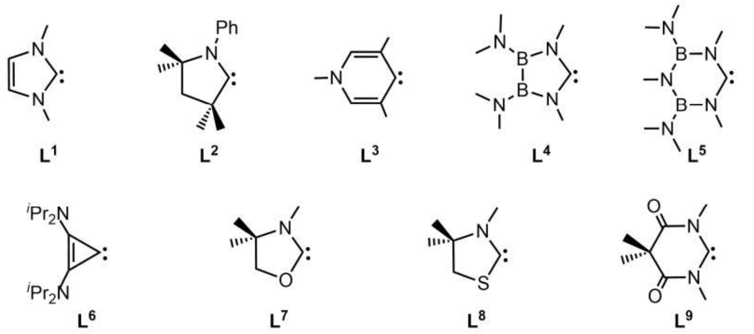
(**iv**) We have computationally designed stable, neutral, monomeric boron (I) carbenoids. Quantum chemical calculations predict that synthetically accessible cyclic four-membered 4π electron ylides could be used as building blocks for the realization of hitherto unknown N-heterocyclic boron(I) carbenoids (Scheme 6). The proposed carbenoids owe their stability not only to substantial transfer of electron density from the nitrogen atoms to boron but also to the presence of thermodynamically robust ylidic bonds. The ylide decorated *N*-heterocyclic borylenes **3** and **5** are found the possess the highest singlet-triplet separation (> 30.0 kcal mol$^{-1}$) known till date and no other cyclic borylene is known with such large singlet-triplet separation. Based on their computed proton affinity and carbonyl stretching frequencies, they may be considered as promising ligands for transition metal complexes (***Inorg. Chem.*** **2019**, *58*, 5428-5432).



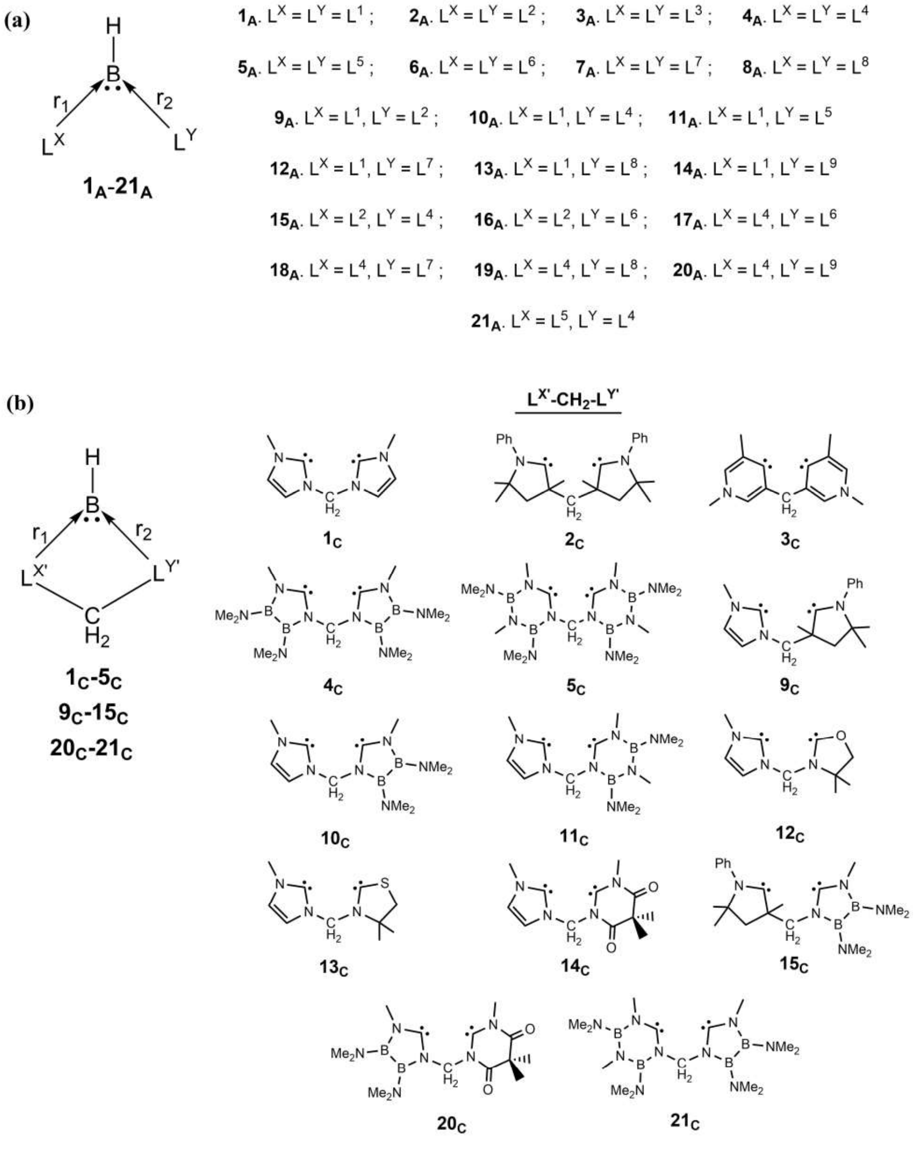
**1** **2** **3** **4** **5**

**Scheme 6**: Schematic representation of the range of borylenes considered in the study

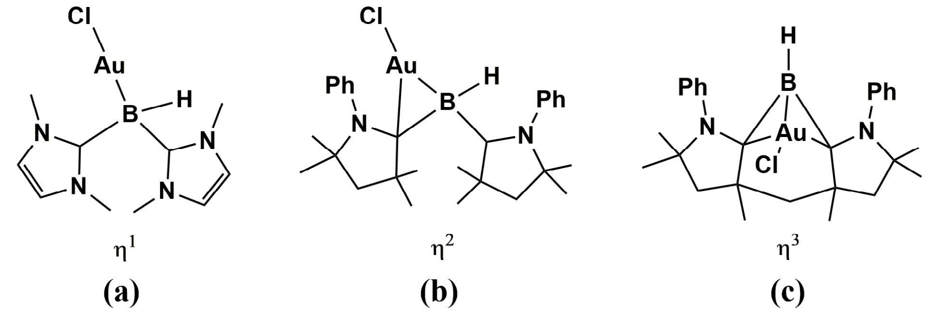
(**v**) In recent years, the isolation of nucleophilic boron bases led to a paradigm shift in boron chemistry which prompted us to perform computational studies on a series of bis(carbene) borylene complexes (Schemes 7 and 8). All the molecules were found to have a trigonal planar geometry around the central boron atom with the cyclic ones having a more acute Cc−B−Cc bond angle. An examination of their ligand properties show that these base stabilized borylenes possess significant π-donation ability as evident from the energies of their lone pair orbitals ($E_{LP}$) values, which is further corroborated by an evaluation of their respective proton affinity and pKa values. Cyclization of the acyclic borylene moieties however stabilizes the HOMO to a considerable extent resulting in reduced proton affinity values. Installation of π-acidic ligands at the boron center increases the B−Cc bond dissociation energy which is in agreement with greater degree of delocalization of the boronic lone pair to the neighbouring carbene center. The free energy of formation of the computationally designed acyclic borylene adducts are found to be comparable to that of the experimentally known ones. Many of the borylenes were found to bind strongly to AuCl in either $\eta^1$ or $\eta^2$ mode as well as in $\eta^3$ mode (Scheme 9). Furthermore, the comparable BDEs of the B−Cc bonds of hitherto unknown acyclic and cyclic borylenes to the synthetically accessible borylenes indicate the likelihood of isolation of these hitherto unknown borylenes and may be considered as potential targets for synthesis (***Organometallics*** **2019**, *38*, 2770-2781).



**Scheme 7**. Schematic representation of the range of carbenes considered towards designing of boron bases



**Scheme 8**. Schematic representation of the (a) acyclic (**$1_A$-$21_A$**) and (b) cyclic (**$1_C$-$5_C$**, **$9_C$-$15_C$** and **$20_C$-$21_C$**) bis(carbene) borylene adducts considered for the present study. The subscript **A** and **C** stands for acyclic and cyclic borylenes respectively



**Scheme 9**: Schematic representations of (a) η$^1$, (b) η$^2$ and (c) η$^3$ binding mode in borylene-AuCl adducts.

(**vi**) As part of a combined experimental and theoretical study, computational investigations were carried out to shed light on the mechanism of isonitrile (*t*BuNC) and CO-mediated borylene liberation from terminal Cr-borylene (Figure 4). A three-step transition state mechanism is envisioned where the addition of the third equivalent of donor ligand to the borylene fragment is found to be rate-limiting. These calculations are in line with the observation that the isonitrile reactions achieve completion in relatively short times (<1 h) at room temperature, whereas the reaction with CO requires much more forcing conditions (***Chem*. *Eur*. *J*.** **2018**, *24,* 6843-6847).

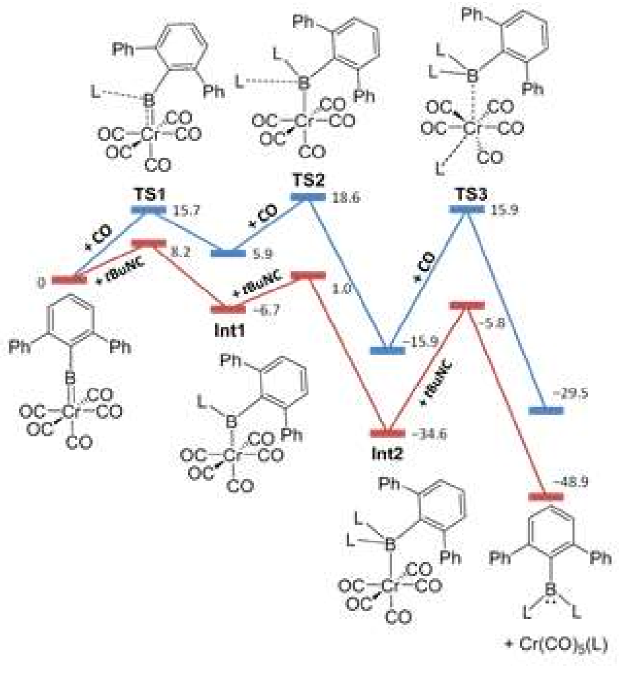
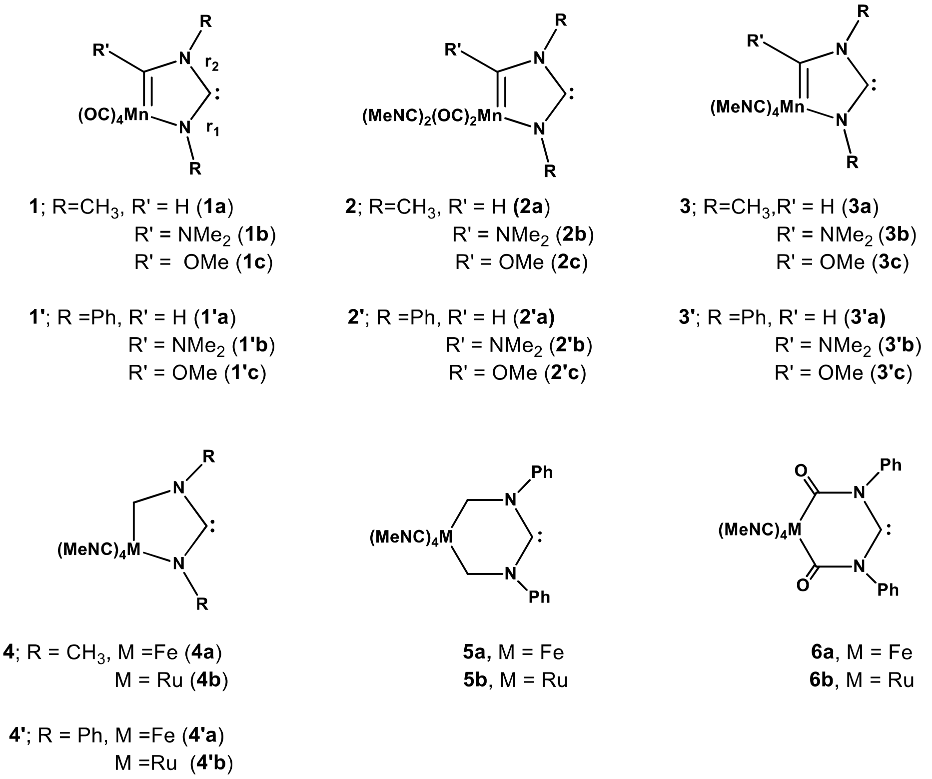


**Figure 4**. Computed reaction pathways for the release of CO and *t*BuNC-stabilized borylenes. Energies in kcal mol$^{-1}$. Blue path (L = CO). Red path (L = *t*BuNC).

(**vii**) Density functional theory calculations have been performed on a series of newly designed metalla-*N*-heterocyclic carbenes (MNHCs) to stabilize their singlet states (Scheme 10). All the MNHCs are found to exhibit a stable singlet ground state. The introduction of $\pi$-donor groups such as OMe and NMe$_2$ at the carbene framework significantly increases the singlet-triplet separations ($\Delta E_{S\text{-}T}$) for the five-membered MNHCs. Further, the calculated $\Delta E_{S\text{-}T}$ values for some of the MNHCs are found to be significantly large (30-50 kcal mol$^{-1}$) and lie within the range of experimentally known carbenes. Therefore, these computationally designed MNHCs – especially those with $\Delta E_{S\text{-}T}$ values of more than 40.0 kcal mol$^{-1}$ may be considered as ideal candidates for experimental realization. The substituents at the amino groups of the MNHC ring also play a decisive role in determining the $\Delta E_{S\text{-}T}$ values. MNHCs in which the metal center is attached to strong electron donating ligands such as CNMe results in significant stabilization of the singlet state indicating that in order to achieve or stabilize MNHCs in singlet state, one has to consider an electron rich transition metal fragment. Interestingly, all the MNHCs are found to have better $\sigma$-donation ability than their corresponding parent carbenes. The calculated values of PA, p$K_a$ and gallium pyramidalization for the MNHCs are also found to be in good agreement with the $\sigma$-donation ability of the MNHCs (***Dalton Trans.*** **2019**, *48*, 11772-11780).



**1**; R=CH$_3$, R' = H (**1a**)
R' = NMe$_2$ (**1b**)
R' = OMe (**1c**)

**1'**; R =Ph, R' = H (**1'a**)
R' = NMe$_2$ (**1'b**)
R' = OMe (**1'c**)

**2**; R=CH$_3$, R' = H **(2a**)
R' = NMe$_2$ (**2b**)
R' = OMe (**2c**)

**2'**; R =Ph, R' = H (**2'a)**
R' = NMe$_2$ (**2'b**)
R' = OMe (**2'c**)

**3**; R=CH$_3$,R' = H (**3a**)
R' = NMe$_2$ (**3b**)
R' = OMe (**3c**)

**3'**; R =Ph, R' = H **(3'a)**
R' = NMe$_2$ (**3'b**)
R' = OMe (**3'c**)

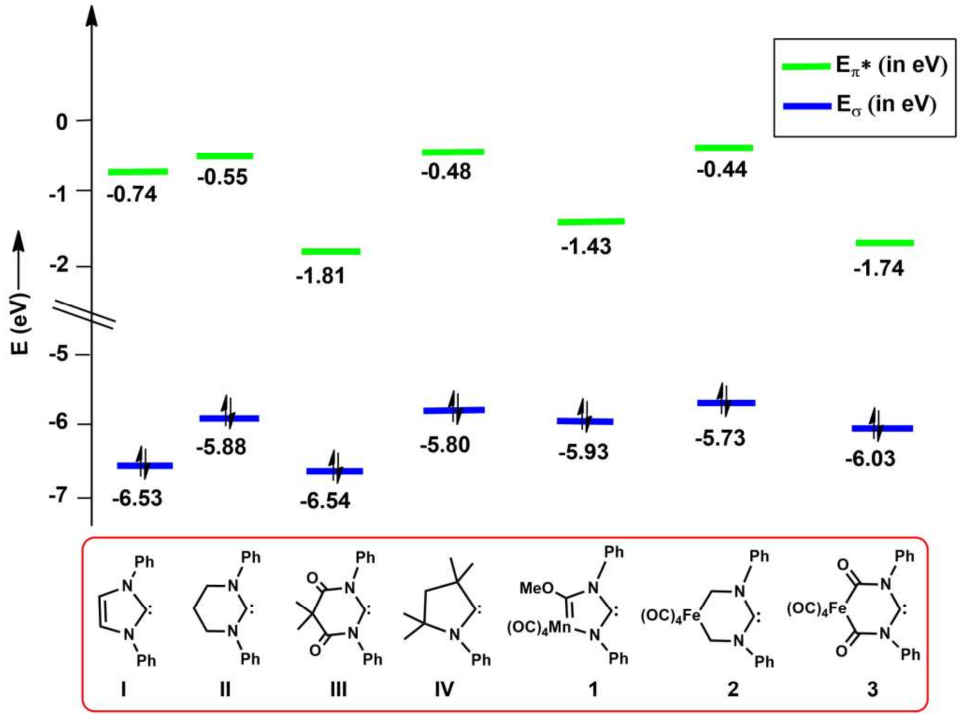
**4**; R = CH$_3$, M =Fe (**4a**)
M = Ru (**4b**)

**4'**; R = Ph, M =Fe (**4'a**)
M =Ru (**4'b**)

**5a,** M = Fe
**5b**, M = Ru

**6a**, M = Fe
**6b**, M = Ru

**Scheme 10**. Schematic representation of the range of metalla-N-heterocyclic carbenes (MNHCs) considered in the study (**viii**) Density functional theory calculations have been carried out to investigate the unprecedented reactivity of the computationally proposed MNHCs towards activation of a range of small molecules ($H_2$, $NH_3$, $PH_3$, $SiH_3Ph$ and $CH_4$). All the MNHCs have been found to have a stable singlet ground state and exhibit superior electron donating and accepting ability compared to their respective parent carbenes (Figure 5). Furthermore, the calculated energy barriers of E-H (E = H, C, N, Si, P) activation for all MNHCs are found to be in agreement with those of the experimentally evaluated cyclic alkyl(amino)carbene (CAAC) and diamidocarbenes (DACs), thereby indicating the activating effect of the incorporation of an ancillary metal center within a cyclic NHC, and highlighting a new, underexplored strategy in achieving difficult bond activations with carbenes. In the case of silane activation (Figure 6), a hydride transfer pathway was found to be more favorable for the activation of Si – H bonds than a proton transfer one (***Dalton Trans.***, **2020**, *49*, 9505–9515).



| | I | II | III | IV | 1 | 2 | 3 |
|---|---|---|---|---|---|---|---|
| $\Delta E_{S-T}$ (kcal mol$^{-1}$) | 69.2 | 53.4 | 43.7 | 42.7 | 43.6 | 46.4 | 36.2 |
| $\Delta E_{H-L}$ (eV) | 5.78 | 5.33 | 4.73 | 5.32 | 4.51 | 4.68 | 4.29 |
| | *4.41* | *3.86* | *3.13* | *3.68* | *3.03* | *3.61* | *2.78* |
| $E_{Hydro}$ (kcal mol$^{-1}$) | -23.3 | -32.1 | -46.9 | -50.6 | -32.0 | -40.0 | -50.8 |

**Figure 5**. Energies (in eV) of the σ-symmetric (donor) and π-symmetric (acceptor) molecular orbitals concentrated at the carbene carbon of MNHCs **1-3** and NHCs **I-IV**. Also given are the values of singlet-triplet ($\Delta E_{S-T}$), HOMO-LUMO gap ($\Delta E_{H-L}$) and hydrogenation energies ($E_{Hydro}$). The values given in italics correspond to HOMO-LUMO gaps in terms of the excitation energies obtained from TDDFT calculations at the same level of theory.

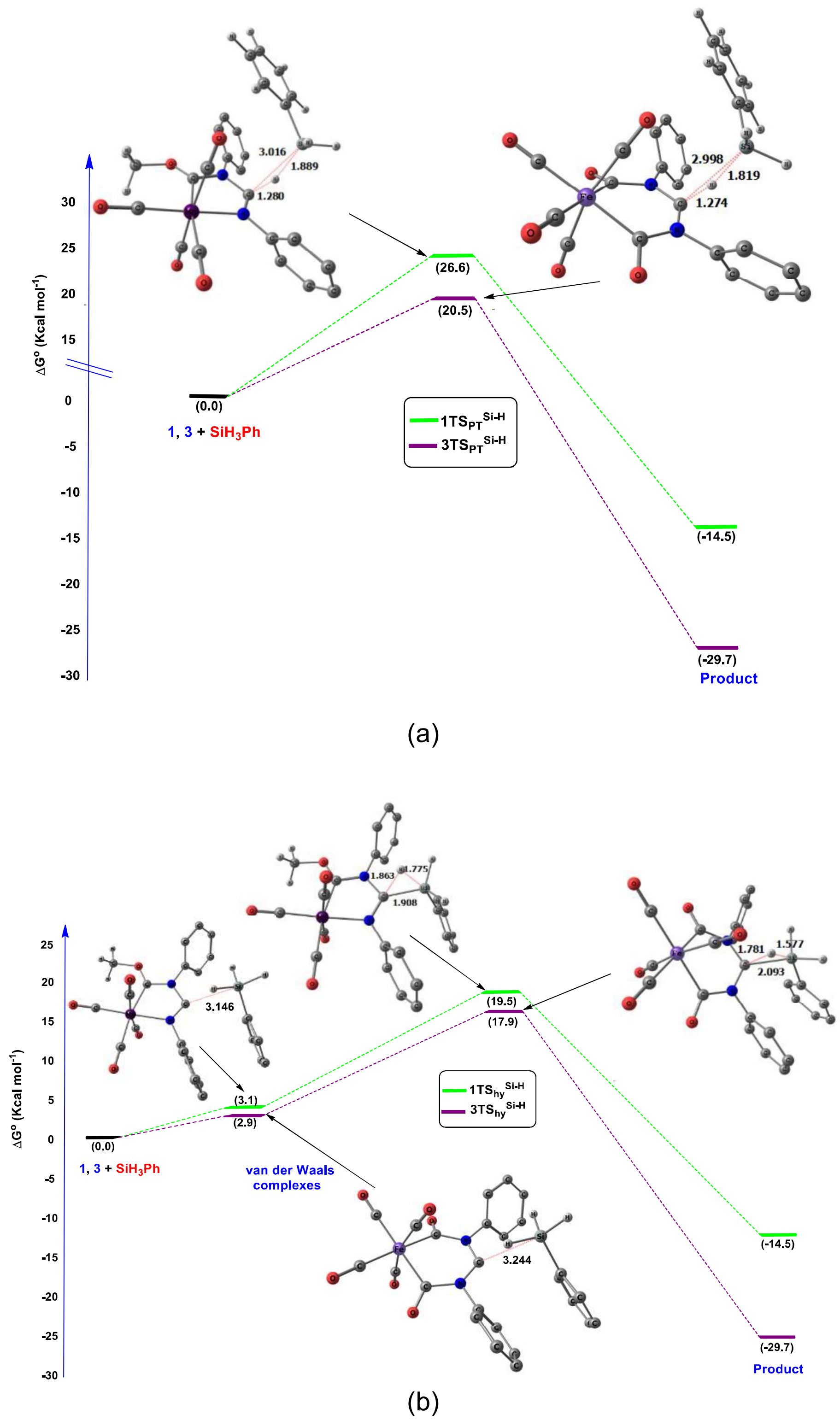


**Figure 6**. Energy profile diagram for the activation of Si – H bond of $SiH_3Ph$ via (a) proton and (b) hydride transfer pathway. The hydrogen atoms of the phenyl rings are omitted for clarity.

(**ix**) As part of a combined experimental and theoretical study, we performed computational studies to ascertain the nature of bis(σ)-borane complexes of Group 6 transition metals. Quantum theory of atoms in molecules (QTAIM) calculations demonstrated (Figure 7) that the borane complexes may be described as pure bis(σ)-borane complexes rather than elongated or stretched examples since the calculations do not show the presence of a ring critical point (RCP) at the ring formed by the interactions of the B-H moiety with metal centre (***Chem. Eur. J.*** **2019**, *25*, 8585-8589).

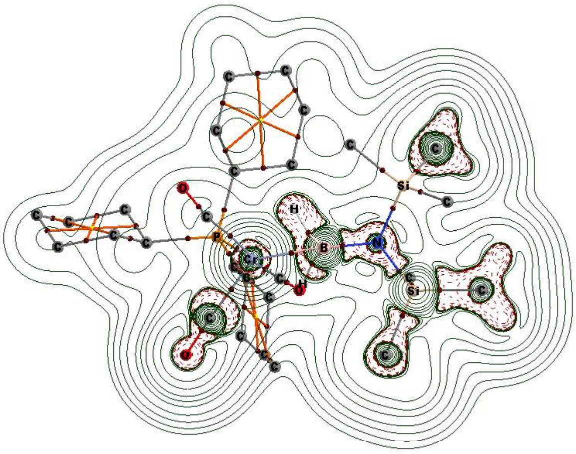
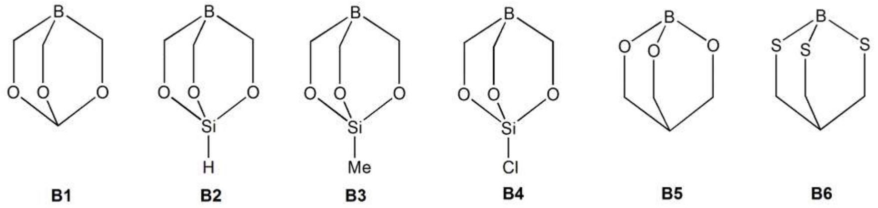


**Figure 7**. Contour line diagram $\nabla^2\rho\,(r)$ in the Cr-B-H plane

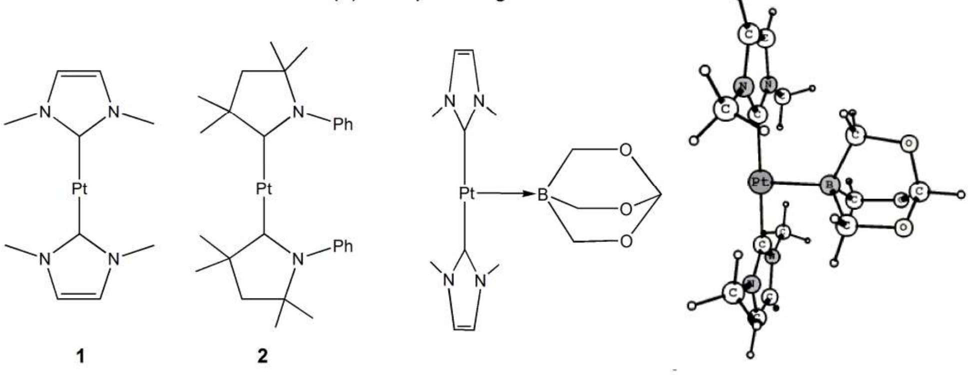
(**x**) Theoretical investigations were carried out toward realization of unsupported transition metal (TM) – boron (B) donor-acceptor complexes. The instability of unsupported Lewis pairs featuring TM→B dative bond may be attributed to larger preparation energy required by planar boron acceptors to achieve pyramidal conformation upon complexation with a Lewis basic metal fragment. Pre-pyramidalization of the boron centre in the Lewis acidic groups facilitates the formation of unsupported donor-acceptor complexes with zero valent group 10 metal complexes (Scheme 11). The stability of these donor-acceptor complexes can be judged from their respective bond dissociation energies (BDE, Table 2). (***Chem. Comm.*** **2018**, *54*, 4975-4978)

**Table 2**: Calculated values of bond lengths ($r_{Pt\text{-}B}$, in Å) and BDE (kcal $mol^{-1}$)

| Molecule | $r_{Pt\text{-}B}$ | BDE | Molecule | $r_{Pt\text{-}B}$ | BDE |
|---|---|---|---|---|---|
| 1-B1 | 2.126 | 56.3 | 2-B1 | 2.149 | 48.9 |
| 1-B2 | 2.140 | 55.7 | 2-B2 | 2.160 | 47.2 |
| 1-B3 | 2.143 | 54.0 | 2-B3 | 2.165 | 46.3 |
| 1-B4 | 2.132 | 61.0 | 2-B4 | 2.152 | 52.9 |
| 1-B5 | 2.099 | 41.4 | 2-B5 | 2.113 | 38.7 |
| 1-B6 | 2.068 | 62.4 | 2-B6 | 2.079 | 54.3 |



(a) Acceptor Fragments



(b) Donor Fragments

(c)

**Scheme 11**: Schematic representation of the (a) acceptor fragments, (b) donor fragments and (c) representative donor-acceptor complex 1-B1 (left) and its optimized geometry (right).

11. Conclusions summarizing the achievements and indication of scope for future work:

**Achievements**:

(i) We could successfully design and show that skeletally substituted (with boron and silicon) and benzannulated derivatives of cyclic alkyl amino carbenes (CAAC) are more effective than the parent CAAC in activating $H_2$ and $NH_3$. On the other hand, ylide decorated CAACs – even though significantly more stable than other CAACs, are found to be ineffective towards activation of $H_2$ and $NH_3$ which may be attributed to the absence of a low energy $\pi$-acceptor orbital at the carbenic centre.

(ii) We, for the first time, could successfully unravel the potential of known yet unexplored singlet carbenes in activating enthalpically strong bonds. A range of carbenes with varying degrees of electron donation and acceptance abilities such as strongly electrophilic five- and six-membered diamido carbenes, ambiphilic cyclic amino aryl carbenes (CAArCs) and bicyclic alkyl amino carbene (BICAAC) etc. were considered for activation of N-H, P-H and Si-H bonds. An in-depth study was conducted on the mechanistic detail of these activation processes. This comprehensive study is one of the salient outcomes of this DST-SERB project.

(iii) A comprehensive study was carried out to understand the reactivity profile of recently synthesised cyclic alkyl amino silylenes (CAASis) and germylenes (CAAGes) as well as their skeletally modified variants towards small molecule activation. Owing to their low Lewis basicity, CAAGes were found to be significantly less efficient than the more Lewis basic CAASis for such activation process indicating the requirement of elevated reaction conditions for activation by CAAGes.

(iv) We could computationally design a neutral, stable, monomeric N-heterocyclic borylene – a system isoelectronic to the more famous N-heterocyclic carbene (NHC) by fusing a cyclic four-membered $4\pi$ electron ylidic ring with a six-membered β-diketiminate scaffold. This ylide decorated N-heterocyclic borylene is found to possess the highest computed singlet-triplet separation (> 30.0 kcal mol$^{-1}$) known till date *and no other cyclic borylene is known with such large singlet-triplet separation*. We consider this as one of the major finding and achievement of this research project.

(v) We have designed a series of acyclic and cyclic borylene molecules in which the central BH fragment is stabilized by two carbene ligands with varying degrees of ambiphilicity. To the best of our knowledge, *this is the first study dealing with cyclic base stabilized borylenes*. The basicity of these borylenes were assessed from an evaluation of the energies of the lone pair orbital at the boron atom which in turn is substantiated by calculating their proton affinity and pKa values. Furthermore, we have studied their complexation with AuCl and found that many of the borylenes bind strongly to AuCl in either $\eta^1$ or $\eta^2$ mode and in one case binds via the highly unusual $\eta^3$ mode.

(vi) By means of DFT based mechanistic studies, we could shed light on the mechanism of isonitrile (*t*BuNC) and CO-mediated borylene liberation from terminal Cr-borylene. A three-step transition state mechanism is envisioned where the addition of the third equivalent of donor ligand to the borylene fragment is found to be rate-limiting. These calculations are in line with the observation that the isonitrile reactions achieve completion in relatively short times (<1 h) at room temperature, whereas the reaction with CO requires much more forcing conditions.

(vii) Till date, no metalla-*N*-heterocyclic carbenes (MNHCs), i.e., carbenes in which one of the backbone CH groups is replaced by an isolobal transition metal fragment, are isolated till date in free state which may be attributed to their low singlet-triplet separations. We found that introduction of $\pi$-donor groups such as OMe and $NMe_2$ at the carbene framework significantly increases the singlet-triplet separations ($\Delta E_{S-T}$) for the five-membered MNHCs. The calculated $\Delta E_{S-T}$ values for some of the MNHCs are found to be significantly large (30-50 kcal mol$^{-1}$) and lie within the range of experimentally known carbenes. Further, MNHCs in which the metal center is attached to strong electron donating ligands such as CNMe results in significant stabilization of the singlet state indicating that in order to achieve or stabilize MNHCs in singlet state, one has to consider an electron rich transition metal fragment.

(viii) Computational investigations were carried out towards understanding the feasibility of metalla-*N*-heterocyclic carbenes (MNHCs) in the activation of several small molecules such as $H_2$, $CH_4$ etc. The calculated energy barriers of E-H (E = H, C, N, Si, P) activation for all MNHCs are found to be in agreement with those of the experimentally evaluated cyclic alkyl(amino)carbene (CAAC) and diamidocarbenes (DACs), thereby indicating the activating effect of the incorporation of an ancillary metal center within a cyclic NHC.

(ix) To the best of our knowledge, no unsupported transition metal (TM) – boron (B) donor-acceptor complexes are known till date. The instability of unsupported Lewis pairs featuring TM→B dative bond may be attributed to larger preparation energy required by planar boron acceptors to achieve pyramidal conformation upon complexation with a Lewis basic metal fragment. We envisage that it may be possible to stabilize complexes featuring unsupported TM→boron dative bond using pre-pyramidalized boron centers. Theoretical investigations showed that pre-pyramidalization of the boron centre in the Lewis acidic groups facilitate the formation of unsupported donor-acceptor complexes with zero valent group 10 metal complexes. *In view of the paucity of unsupported TM→B complexes*, this study could be of significant help to the synthetic chemist towards realization of unsupported transition metal (TM) – boron (B) donor-acceptor complexes.

(x) Computational studies were carried out to ascertain the nature of experimentally characterized bis(σ)-borane complexes of Group 6 transition metals and QTAIM analysis reveal that the borane complexes may be described as pure bis(σ)-borane complexes rather than elongated or stretched examples since the calculations do not show the presence of a ring critical point (RCP) at the ring formed by the interactions of the B-H moiety with metal centre.

**Scope for future work**:

We not only hope but also highly confident that many of our studies could provide a strong basis for future experimental studies. For example, our study indicate that the hitherto unexplored stable cyclic singlet carbenes such as cyclic amino aryl carbenes (CAArCs), bicyclic alkyl amino carbene (BICAAC) and cyclic alkyl amido carbenes (CAAmC) are more effective than cyclic alkyl amino carbenes (CAACs) towards the activation of both ammonia and phosphine which should inspire synthetic chemists for the experimental evaluation of these systems in small molecule activation. Further, our study towards achieving a neutral, stable, monomeric N-heterocyclic borylene by fusing cyclic ylides with a six-membered β-diketiminate scaffold could be helpful in the experimental realization of a hitherto unknown ambiphilic cyclic borylene. Our study on the potential of metalla-N-heterocyclic carbenes (MNHCs), cyclic alkyl amino silylenes (CAASis) and germylenes (CAAGes) could provide guidance for the synthesis of efficient systems for use in small molecule activation. Last but not the least, our work on possible realization of unsupported transition metal (TM)–boron (B) donor-acceptor complexes that identifies pre-pyramidalization of the boron centre in the Lewis acidic groups as a *prerequisite* for their formation of unsupported donor-acceptor complexes with Lewis basic metal fragments is a key finding of this project that could inspire experimental chemists in making efforts towards their isolation.

12. S&T benefits accrued:

i. List of Research publications

| S No | Authors | Title of paper | Name of the Journal | Volume | Pages | Year |
|---|---|---|---|---|---|---|
| 1 | P. Bharadwaz, P. Chetia and A. K. Phukan | Electronic and Ligand Properties of Skeletally Substituted Cyclic(Alkyl)(Amino)Carbenes (CAACs) and Their Reactivity Towards Small Molecule Activation: A Theoretical Study | ***Chem. Eur. J.*** | 23 | 9926-9936 | **2017** |
| 2 | M. Nutz, B. Borthakur, C. Pranckevicius, R. D. Dewhurst, M. Schäfer, T. Dellermann, F. Glaab, M. Thaler, A. K. Phukan and H. Braunschweig | Release of Isonitrile- and NHC-stabilized Borylenes from Group VI Terminal Borylene Complexes | ***Chem. Eur. J.*** | 24 | 6843-6847 | **2018** |
| 3 |  | Metal-Free Activation of Enthalpically Strong Bonds: Unraveling the Potential of Hitherto Unexplored Singlet Carbenes | ***Adv. Synth. Catal.*** | 360 | 4543-4561 | **2018** |
| 4 | . P. Bharadwaz and A. K. Phukan | Introducing N-Heterocyclic Borylenes: Theoretical Prediction of Stable, Neutral, Monomeric Boron(I) Carbenoids | ***Inorg. Chem.*** | 58 | 5428-5432 | **2019** |
| 5 | S. S. Rohman, B. Sarmah, B. Borthakur, G. S. Remya, C. H. Suresh and A. K. Phukan | Extending the Library of Boron Bases: A Contribution from Theory | ***Organometallics*** | 38 | 2770-2781 | **2019** |
| 6 | S. S. Rohman, B. Ghosh and A. K. Phukan | In Search of Stable Singlet Metalla-N-Heterocyclic Carbenes | ***Dalton Trans.*** | 48 | 11772-11780 | **2019** |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | (MNHCs): A Contribution from Theory | | | | |
| 7 | B. Ghosh and A. K. Phukan | Probing the Potential of Metalla-N-Heterocyclic Carbenes Towards Activation of Enthalpically Strong Bonds | ***Dalton Trans.*** | 49 | 9505-9515 | **2020** |
| 8 | B. Ghosh,<br>P. Bharadwaz,<br>N. Sarkar and<br>A. K. Phukan | Activation of small Molecules by cyclic alkyl amino silylenes (CAASis) and germylenes (CAAGes): a theoretical study | ***Dalton Trans.*** | 49 | 13760–13772 | **2020** |
| 9 | B. Borthakur, B. Ghosh and A. K. Phukan | The flourishing chemistry of carbene stabilized compounds of group 13and 14 elements | ***Polyhedron*** | 197 | https://doi.org/10.1016/j.poly.2021.115049 | **2021** |
| 10 | B. Borthakur, S. Das and A. K. Phukan | Strategies toward Realization of Unsupported Transition Metal–Boron Donor–Acceptor Complexes: An Insight from Theory | ***Chem. Comm.*** | 54 | 4975-4978 | **2018** |
| 11 | C. Lenczyk, D. K. Roy, B. Ghosh, J. Schwarzmann,<br>A. K. Phukan and<br>H. Braunschweig | First Bis(σ)-borane Complexes of Group 6 Transition Metals: Experimental and Theoretical Studies | ***Chem. Eur. J.*** | 25 | 8585-8589 | **2019** |

- ➢ *Publications given in serial number **1 – 9** are direct outcome of this project.*
- ➢ *Publications given in serial number **10 – 11** are not directly related to this project. However, both involved Boron – a key Group 13 element that has played an important role in this project and the computational facilities provided by SERB under this project were used for the same.*

ii. Manpower trained on the project

a) Research Scientists or Research Associates : Nil
b) No. of Ph.D. produced : One (01)
c) Other Technical Personnel trained: Nil

iii. Patents taken, if any : Nil

13. Financial Position:

| No | Financial Position/ Budget Head | Funds Sanctioned | Expenditure | % of Total cost |
|---|---|---|---|---|
| I | Salaries/ Manpower costs | | | |
| II | Equipment | | | |
| III | Supplies & Materials | | | |
| IV | Contingencies | | | |
| V | Travel | | | |
| VI | Overhead Expenses | | | |
| VII | Others, if any | | | |
| | Total | | | 100% |

14. Procurement/ Usage of Equipment

a)

| S No | Name of Equipment | Make/Model | Cost (FE/ Rs) | Date of Installation | Utilization Rate (%) | Remarks regarding maintenance/ |
|---|---|---|---|---|---|---|
| 1 | HPC Cluster | **Make**: HP<br>**Model**: Proliant DL360 Gen 10 | 21,35,175/- | | 100 | So far, we did not notice any major issue that warrants frequent Maintenance. |
| 2 | UPS | **Make**: ORION<br>**Model**: CHROMA Series | 2,83,695/- | | 100 | |
| 3 | Laptop | **Make**: HP<br>**Model**: Probook 450 G5 | 81,900/- | | 100 | |

b) Plans for utilizing the equipment facilities in future

The equipments are going to remain in my laboratory at the Dept. of Chemical Sciences, Tezpur University for future use.

Ashwini k Phukan

Name and Signature with Date

Ashwini K. Phukan
(Principal Investigator)

# RECURRING

GFR 12 – A
[(See Rule 238 (1))]
**UTILIZATION CERTIFICATE (UC) FOR THE YEAR 2020-21**
**in respect of *RECURRING***
**as on 16th December, 2020 to be submitted to SERB**
Is the UC ……………………..*(Provisional/Audited)*
*(To be given separately for each financial year ending on 31st March)*

1. Name of the grant receiving Organization : **TEZPUR UNIVERSITY**.
2. Name of Principal Investigator(PI) :**Prof. Ashwini K. Phukan**
3. SERB Sanction order no. & date : **EMR/2016/005294** dated **09-06-2017**
4. Title of the Project : **Chemistry of Monovalent Group 13 and Divalent Group 14 Bases : A Theoretical Study**
5. Name of the SERB Scheme : **CRG**
6. Whether recurring or non-recurring grants : **Recurring**.
7. Grants position at the beginning of the Financial year (Grants released by SERB)

    (i) Carry forward from previous financial year : **Rs. 8,23,482/-**

    (ii) Others, If any : Nil

    (iii) Total : **Rs. 8,23,482/-**

8. Details of grants received, expenditure incurred and closing balances: (Actuals)

| Unspent Balance of Grants received previous years [figure as at Sl. No. 7(iii)] | Interest Earned thereon | Interest deposited back to the SERB | Grants received during the year | | | Total Available funds (1+2-3+4) | Expenditure incurred | Closing Balances (5-6) |
|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | | | 5 | 6 | 7 |
| | | | Sanction No. (i) | Date (ii) | Amount (iii) | | | |
| Rs. 8,23,482/- | Rs. 17,730.70 | Nil | Nil | | | Rs. 8,41,212.70 | Rs. 67,881/- | Rs. 7,73,331.70 |

Component wise utilization of grants:

| Grants-in-aid- General | Total |
|---|---|
| 1. Manpower : Nil<br>2. Consumables : Nil<br>3. Travel : Nil<br>4. Contingencies : Rs. 2,950/-<br>5. Overhead : Rs. 64,931/- | Rs. 67,881/- |

Details of grants position at the end of the year

(i) Cash in Hand/Bank : Rs. 7,73,331.70

(ii) Refunds to SERB, If any : Nil

(iii) Balance (Carry forward to next financial year) : Rs. 7,73,331.70

| | | |
|---|---|---|
| Ashwini K. Phukan<br>08/04/21<br>**Signature of PI** | **Signature with Seal :**<br>**Name:**<br>**Chief Finance Officer**<br>**(Head of Finance)**<br>Finance Officer<br>Tezpur University | 3/5/21<br>**Signature with Seal**<br>**Name:**<br>**Head of Organisation**<br>Registrar<br>Tezpur University |

GFR 12 – A
[(See Rule 238 (1))]
**UTILIZATION CERTIFICATE (UC) FOR THE YEAR 2020-21**
**in respect of *RECURRING***
**as on 16th December, 2020. to be submitted to SERB**
Is the UC ……………………..*(Provisional/Audited)*
*(To be given separately for each financial year ending on 31st March)*

Certified that I have satisfied that the conditions on which grants were sanctioned have been duly fulfilled/are being fulfilled and that I have exercised following checks to see that the money has been actually utilized for the purpose for which it was sanctioned:

(i) The main accounts and other subsidiary accounts and registers (including assets registers) are maintained as prescribed in the relevant Act/Rules/Standing instructions (mention the Act/Rules) and have been duly audited by designated auditors. The figures depicted above tally with the audited figures mentioned in financial statements/accounts.

(ii) There exist internal controls for safeguarding public funds/assets, watching outcomes and achievements of physical targets against the financial inputs, ensuring quality in asset creation etc. & the periodic evaluation of internal controls is exercised to ensure their effectiveness.

(iii) To the best of our knowledge and belief, no transactions have been entered that are in violation of relevant Act/Rules/standing instructions and scheme guidelines.

(iv) The responsibilities among the key functionaries for execution of the scheme have been assigned in clear terms and are not general in nature.

(v) The benefits were extended to the intended beneficiaries and only such areas/districts were covered where the scheme was intended to operate.

(vi) The expenditure on various components of the scheme was in the proportions authorized as per the scheme guidelines and terms and conditions of the grants-in-aid.

(vii) It has been ensured that the physical and financial performance under **CRG** has been according to the requirements, as prescribed in the guidelines issued by Govt. of India and the performance/targets achieved statement for the year to which the utilization of the fund resulted in outcomes given at Annexure – I duly enclosed.

Date: 08/04/21
Place: Tezpur

| | | |
|---|---|---|
| 08/04/21<br>Signature of PI | Signature with Seal :<br>Name: Finance Officer Tezpur University<br>Chief Finance Officer<br>(Head of Finance) | 3/5/21<br>Signature with Seal Registrar Tezpur University<br>Name:<br>Head of Organization |

# NON-RECURRING

**GFR 12 – A**
**[(See Rule 238 (1))]**
**UTILIZATION CERTIFICATE (UC) FOR THE YEAR 2020-21**
**in respect of *NON-RECURRING***
**as on 16th December, 2020 to be submitted to SERB**
Is the UC ……………………..*(Provisional/Audited)*
*(To be given separately for each financial year ending on 31st March)*

1. Name of the grant receiving Organization : **TEZPUR UNIVERSITY**
2. Name of Principal Investigator(PI) : **Prof. Ashwini K. Phukan**
3. SERB Sanction order no. & date : **EMR/2016/005294** dated **09-06-2017**
4. Title of the Project : **Chemistry of Monovalent Group 13 and Divalent Group 14 Bases : A Theoretical Study**
5. Name of the SERB Scheme : **CRG**
6. Whether recurring or non-recurring grants : **Non-recurring**
7. Grants position at the beginning of the Financial year (Grants released by SERB)
   (i) Carry forward from previous financial year : **Rs. 55,329/-**
   (ii) Others, If any : Nil
   (iii) Total : **Rs. 55,329/-**
8. Details of grants received, expenditure incurred and closing balances: (Actuals)

| Unspent Balance of Grants received previous years [figure as at Sl. No. 7(iii)] | Interest Earned thereon | Interest deposited back to the SERB | Grants received during the year | | | Total Available funds (1+2-3+4) | Expenditure incurred | Closing Balances (5-6) |
|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | | | 5 | 6 | 7 |
| | | | Sanction No. (i) | Date (ii) | Amount (iii) | | | |
| Rs. 55,329/- | Rs. 1,191.30 | Nil | Nil | | | Rs. 56,520.30 | Nil | Rs. 56,520.30 |

Component wise utilization of grants:

| Grant-in-aid-creation for capital assets | Total |
|---|---|
| | |

Details of grants position at the end of the year

(i) Cash in Hand/Bank : Rs. 56,520.30
(ii) Refunds to SERB, If any : Nil
(iii) Balance (Carry forward to next financial year) : Rs. 56,520.30

| | | |
|---|---|---|
| Ashwini K. Phukan<br>28/04/21<br>Signature of PI | Signature with Seal :<br>Name:<br>Chief Finance Officer<br>(Head of Finance)<br>Finance Officer<br>Tezpur University | 3/5/21<br>Signature with Seal<br>Name:<br>Head of Organisation<br>Registrar<br>Tezpur University |

**GFR 12 – A**
**[(See Rule 238 (1))]**
**UTILIZATION CERTIFICATE (UC) FOR THE YEAR 2020-21**
**in respect of *NON-RECURRING***
**as on 16th December, 2020 to be submitted to SERB**
Is the UC ……………………..*(Provisional/Audited)*
*(To be given separately for each financial year ending on 31st March)*

Certified that I have satisfied that the conditions on which grants were sanctioned have been duly fulfilled/are being fulfilled and that I have exercised following checks to see that the money has been actually utilized for the purpose for which it was sanctioned:

(i) The main accounts and other subsidiary accounts and registers (including assets registers) are maintained as prescribed in the relevant Act/Rules/Standing instructions (mention the Act/Rules) and have been duly audited by designated auditors. The figures depicted above tally with the audited figures mentioned in financial statements/accounts.

(ii) There exist internal controls for safeguarding public funds/assets, watching outcomes and achievements of physical targets against the financial inputs, ensuring quality in asset creation etc. & the periodic evaluation of internal controls is exercised to ensure their effectiveness.

(iii) To the best of our knowledge and belief, no transactions have been entered that are in violation of relevant Act/Rules/standing instructions and scheme guidelines.

(iv) The responsibilities among the key functionaries for execution of the scheme have been assigned in clear terms and are not general in nature.

(v) The benefits were extended to the intended beneficiaries and only such areas/districts were covered where the scheme was intended to operate.

(vi) The expenditure on various components of the scheme was in the proportions authorized as per the scheme guidelines and terms and conditions of the grants-in-aid.

(vii) It has been ensured that the physical and financial performance under **CRG** scheme has been according to the requirements, as prescribed in the guidelines issued by Govt. of India and the performance/targets achieved statement for the year to which the utilization of the fund resulted in outcomes given at Annexure – I duly enclosed.

Date: 08/04/21
Place: Tezpur

| | | |
|---|---|---|
| 08/04/21<br>**Signature of PI** | **Signature with Seal :**<br>**Name:** Finance Officer<br>**Chief Finance Officer**<br>**(Head of Finance)** Tezpur University | 3/5/21<br>**Signature with Seal**<br>**Name:** Registrar<br>**Head of Organisation** Tezpur University |

# UP-TO-DATE STATEMENT OF EXPENDITURE

1. SERB Sanction Order No and date : EMR/2016/005294 dated 09-06-2017
2. Name of the PI : PROF. ASHWINI K. PHUKAN
3. Total Project Cost : Rs. 43,77,560.00
4. Revised Project Cost : NA
5. Date of Commencement : 17th June, 2017
6. Statement of Expenditure

(Month wise expenditure incurred during current financial year)

| **Month & year** | **Expenditure incurred/committed** |
|---|---|
| April 2020 | Nil |
| May 2020 | Nil |
| June 2020 | Nil |
| July 2020 | Nil |
| August 2020 | Nil |
| September 2020 | Nil |
| October 2020 | 2,950.00 |
| November 2020 | Nil |
| December 2020 | 64,931.00 |
| **Total Expenditure during F. Y. 2020-2021** | **67,881.00** |

7. Grant received in each year
   - a. 1st Year : Rs. 31,25,800.00
   - b. 2nd Year : Rs. 4,00,000.00
   - c. 3rd Year : Rs. 5,00,000.00
   - c. Interest, if any: : Rs. 1,26,524.00
   - d. Total (a+b+c+d) : Rs. 41,52,324.00

Annexure-II

# Statement of Expenditure

**For the period 1st April, 2020 to 16th December 2020**

**Title: Chemistry of Monovalent Group 13 and Divalent Group 14 Bases: A Theoretical Study.**

**Sanction No. EMR/2016/005294**

| Sr No (I) | Sanctioned Heads (II) | Total Fund Allocated (Sanctioned) (III) (Rs.) | | | | Expenditure Incurred | | | | Total Expenditure till 16th December, 2020 (VIII = IV + V+ VI+VII) (Rs.) | Balance as on 16th December, 2020 (IX = III – VIII) (Rs.) | Require-ment of Funds upto 31st March 2021 (Rs.) | Remark (If any) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1st Year | 2nd Year | 3rd Year | 4th Year (01 April -16 December, 2020) | 1st Year (IV) (Rs.) | 2nd Year (V) (Rs.) | 3rd Year (VI) (Rs.) | 4th Year (VII) (Rs.) | | | | |
| 1. | Manpower | 3,30,000/- | 1,00,000/- | 2,50,000/- | Nil | 1,06,065/- | 1,44,000/- | 30,000/- | Nil | 2,80,065/- | 3,99,935/- | Nil | NIL |
| 2. | Consumables | 63,147/- | 50,000/- | 50,000/- | Nil | 36,635/- | 9,060/- | 4,985/- | Nil | 50,680/- | 1,12,467/- | Nil | NIL |
| 3. | Travel | 50,000/- | 50,000/- | 50,000/- | Nil | 43,141/- | 12,560/- | Nil | Nil | 55,701/- | 94,299/- | Nil | NIL |
| 4. | Contingencies | 50,000/- | 50,000/- | 50,000/- | Nil | 14,300/- | 5,344/- | 43,006/- | 2,950/- | 65,600/- | 84,400/- | Nil | NIL |
| 5. | Others, if any | Nil | Nil | Nil | Nil | Nil | Nil | Nil | Nil | Nil | NIL | Nil | NIL |
| 6. | Equipment | 25,00,000/- | Nil | Nil | Nil | Nil | 25,00,000/- | Nil | Nil | 25,00,000/- | NIL | Nil | NIL |
| 7. | Overhead | 1,32,653/- | 1,50,000/- | 1,00,000/- | Nil | 82,906/- | 770/- | 2,21,819/- | 64,931/- | 3,70,426/- | 12,227/- | Nil | *Nil* |
| 8. | Interest | 69,161/- | 19,205/- | 19,236/- | 18,922/- | - | - | - | - | - | 1,26,524/- | - | |
| 9. | Total | 41,52,324/- | | | | 2,83,047/- | 26,71,734/- | 2,99,810/- | 67,881/- | 33,22,472/- | 8,29,852/- | -8,29,852/- | Refunde |

Amount to be refunded/ reimbursed (whichever is appropriate): An amount of **Rs. 8,29,852.00** (Rupees eight lakh twenty nine thousand eight hundred and fifty two only) is already refunded vide **Demand Draft No. 535048 dated 10-03-2021**.

Name of the Principal Investigator: **Prof. Ashwini K. Phukan**

Date: 08/04/21 Ashwini Ku. Phukan

Signature of competent financial authority:

(with seal) Finance Officer Tezpur University Date: