

ABSTRACT

Historically, the area of chemistry mostly relies on experimental studies. However, over the last few decades, a number of sophisticated computational techniques have been developed which are being extensively used to solve various problems in chemistry. The modern computational technique uses different approximation schemes such as Hartree-Fock, post-Hartree-Fock, semiempirical or forcefield methods to tackle different chemical problems which are otherwise difficult to study experimentally. They are found to be extremely useful in studying reaction mechanisms, determining molecular geometries of ground and excited states, different electronic and spectroscopic properties etc. The works presented in this thesis are divided into six chapters. The first chapter corresponds to the brief introduction to Density Functional Theory (DFT). In the remaining chapters i.e. in chapters 2-6, we have employed computational techniques (DFT calculations) to solve a variety of chemical problems. A brief overview of all the chapters is given below-

Chapter 1: Brief Introduction to Computational Chemistry

All the work that are presented in this thesis were carried out with the help of DFT calculations. Therefore, a brief description of DFT and all other computational techniques is discussed in this chapter.

Chapter 2: In Search of Stable, Singlet Metalla *N*-Heterocyclic Carbene (MNHC) and Probing their Potential in Small Molecule Activation.

The chemistry of carbenes has evolved as an important area of research over the last couple of decades because of their ease of tunability and versatile catalytic applicability [1-3]. Even though the parent carbene (:CH₂) prefers to have a triplet ground state, a thorough search of the literature yields a large number of carbenes which favor the singlet state over the triplet state [4, 5]. A signature example of this class of carbene is *N*-heterocyclic carbene (NHC), which was synthesized and isolated by Arduengo et al. in 1991 [6].

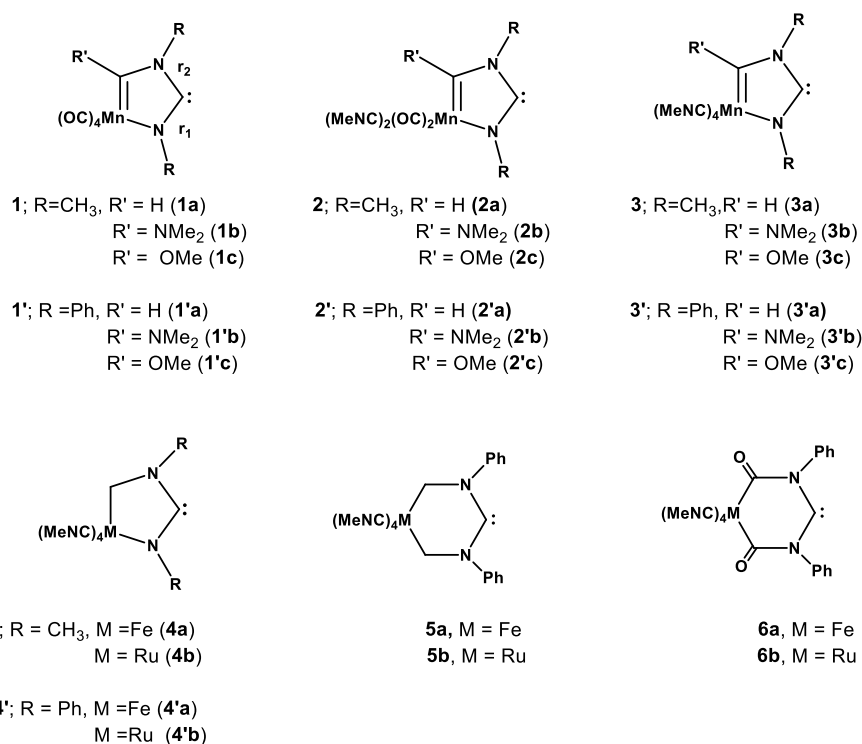
This chapter is divided into parts- the first part deals with the computational study aimed toward designing a series of stable, singlet MNHCs and in the second part, we have probed the potential of the MNHCs toward activation of a variety of enthalpically strong E-H bonds (E = H, N, P, Si and C).

In Search of Stable Singlet Metalla-*N*-Heterocyclic Carbenes (MNHCs): A Contribution from Theory

Many transition metal (TM) complexes have been synthesized bearing NHC as a ligand and some of these complexes are being successfully employed in homogeneous catalysis [7-14]. The electron donation ability of the carbene ligand plays a crucial role in determining the catalytic efficiency of the corresponding TM complexes. Therefore, a lot of emphasis has been put towards the design and synthesis of carbenes with better ligand properties and this was generally accomplished by changing either the heteroatom attached to the carbene center or by changing the substituents at the heteroatom as well as by modifying the ring framework itself. For example, the amino group of the carbene ring framework was substituted by other heteroatoms such as phosphorus (PHC) [15, 16], oxygen (oxazol-2-ylidene) [17] and sulphur (thiazol-2-ylidene) [17-20]. Other strategies include the alteration of the carbene carbon position (a mesoionic or abnormal carbene) [21-24], considering a saturated backbone instead of an olefinic backbone [25], the expansion of the ring size [25-29], etc. Similarly, attempts have been made to incorporate transition metal (TM) fragments into the carbene ring framework by replacing one of the backbone carbon fragments by isolobal metal fragments [30, 31]. These types of NHCs containing TM fragments within the carbene ring framework are commonly known as metalla-*N*-heterocyclic carbenes (MNHCs). Interestingly, the computed proton affinity and the pK_a values for the MNHCs are found to be significantly higher than those of traditional NHCs, indicating their higher degree of σ -donation ability [32]. Even though MNHCs exhibit better electron donation ability than NHCs, their isolation in the free crystalline state remains an experimental challenge. However, they can be trapped by forming adducts with transition metal complexes such as $[AuCl(PPh_3)]$, $[Rh(cod)Cl_2]$ and $CuCl$ [32].

In this part, we have performed density functional theory calculations to design a series of stable, singlet MNHCs (Scheme 2.1). We have used hybrid PBE0 exchange–correlation functional [33, 34] in conjunction with the 6-311++G** basis set [35-37] for the main group elements as well as for the first-row transition metals. Furthermore, the relativistic all electron QZP-DKH [38] basis set was considered for heavier transition metal ruthenium with the relativistic second order DKH(DKH2) Hamiltonian [39]. All

the MNHCs considered in this study are found to exhibit a stable singlet ground state. The introduction of π -donor groups such as OMe and NMe₂ at the carbene framework significantly increases the ΔE_{S-T} values for the five-membered MNHCs. Furthermore, the calculated ΔE_{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 the experimentally known carbenes. Therefore, these computationally designed MNHCs – especially those with the ΔE_{S-T} values of more than 40.0 kcal mol⁻¹ may be considered as ideal candidates for experimental realization.

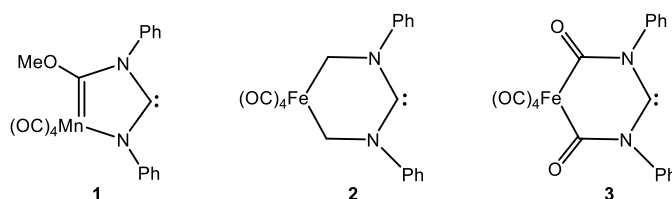


Scheme 2.1: Schematic representation of the range of MNHCs considered in this study.

Probing the Potential of Metalla-*N*-Heterocyclic Carbenes Towards Activation of Enthalpically Strong Bonds

In this part, we have performed in-depth computational studies aimed toward probing the efficacy of the MNHCs in activation of small molecules (Scheme 2.2). We have used meta-GGA M06 exchange–correlation functional [40] in conjunction with the valence polarized def2-TZVP basis set [41, 42] for all the elements. 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. Furthermore, the calculated energy barrier for the activation of a variety of enthalpically

strong bonds for the MNHCs, **1** and **3** are found to be comparable to those obtained for the experimentally evaluated carbenes cyclic(alkyl)(amino)carbene (CAAC) and diamido carbene (DAC), indicating their potential in small molecule activation.

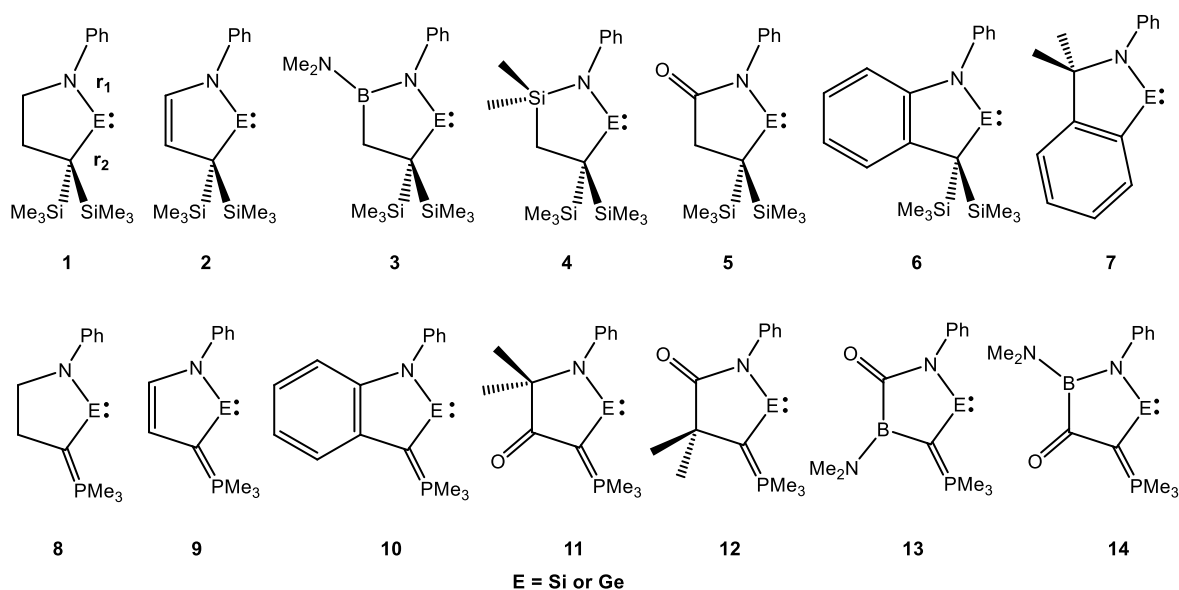


Scheme 2.2: Schematic representation of the MNHCs considered in this study.

Chapter 3: Activation of Small Molecules by Cyclic Alkyl Amino Silylenes (CAASis) and Germylenes (CAAGes): A Theoretical Study

The chemistry of silylenes and germylenes are fairly diverse both in structure and reactivity. *N*-heterocyclic silylene (NHSi) [43] and germylene (NHGe) [44] are neutral divalent species with a vacant p-orbital and a non-bonding pair of electrons. A majority of the silylenes and germylenes possess a singlet ground state which may be attributed to the increased radial extension of ns and np orbitals as we go down the group [45]. The ligating properties of NHEs (E = Si, Ge) are somewhat different from their lighter congeners as NHCs possess a higher Lewis basicity and lower Lewis acidity than NHSis/NHGes [46]. Recently, the research groups of Iwamoto and Kinjo independently reported the isolation of silicon (CAASi) [47] and germanium (CAAGe) [48] analogs of cyclic(alkyl)(amino)carbene (CAAC) where the central silicon or germanium atom is bonded to a nitrogen and a quaternary carbon atom. These cyclic(alkyl)(amino)silylenes (CAASi) and cyclic(alkyl)(amino)germylenes (CAAGe) are found to have better electron donation ability than classical NHSis and NHGes. Very recently, Iwamoto and co-workers found that CAASi could be used as a dehydrogenation reagent [49]. However, compared to the large number of studies being carried out on CAACs, to the best of our knowledge, there exists no systematic and comprehensive study—either experimental or computational, on CAASis and CAAGes.

In this part, we present our results of computational studies on the electronic and ligand properties of skeletally substituted CAASis and CAAGes, and based on their ligand properties, some of these molecules are probed towards activation of small molecules (Scheme 3.1). We have employed meta-GGA M06 exchange correlational functional [40] in conjunction with def2-TZVP basis set [41, 42] for all the atoms. All



Scheme 3.1: Schematic representation of the range of silylenes and germylenes considered in the present study.

the skeletally substituted CAASIs and germylenes (CAAGes) considered in this study compute significantly higher or comparable singlet-triplet separation (ΔE_{S-T}) than their synthetically accessible parent analogues implying that all of them may be stable enough for experimental realization. Furthermore, some of the computationally designed CAASIs and CAAGes are probed towards activation of H–H, N–H, C–H and Si–H bonds and the energetics of these reactions are compared with those of the experimentally evaluated systems including Driess’s NacNac stabilized silylene and Kira’s five-membered silylene. Our study successfully explains many of the experimental observations, e.g., requirement of higher temperature for C–H and Si–H bond activations.

Chapter 4: Ylide Decorated Monovalent Group 13 Carbenoids and Probing their potential towards Activation of Enthalpically Strong Bonds.

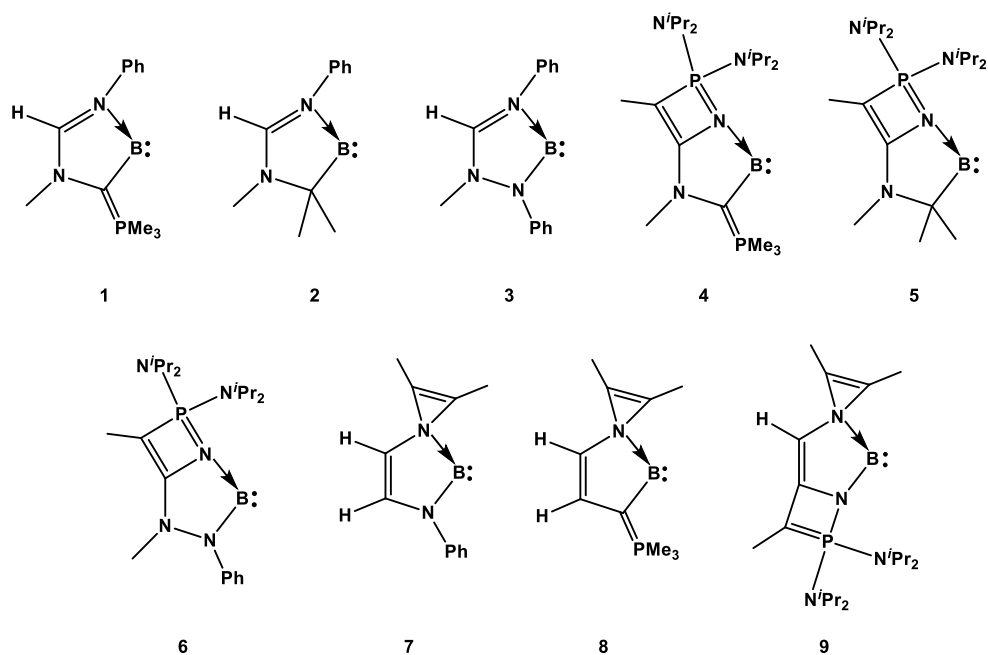
This chapter is divided into two parts-(i) the first part deals with the stabilization of the hitherto unknown five-membered cyclic boron(I) carbenoids and studying their potential in small molecule activation. (ii) In the second part, we have proposed a couple of ylide decorated monovalent five-membered aluminium(I) and gallium(I) carbenoids with enhanced ligand properties and studied their reactivity towards activation of a variety of enthalpically strong bonds.

Stable *N*-Heterocyclic Borylenes with Promising Ligand Properties: A Contribution from Theory

The monovalent group 13 carbenoids which are isoelectronic to the divalent group 14 compounds (e.g. NHC), are known for the heavier Al–Tl(III) derivatives [50–53] and are found to be capable of exhibiting metallomimetic behaviour such as small molecule activation [54]. The first addition to this class of compounds came from Roesky and coworkers with the isolation of a neutral six membered Al(I) carbenoid supported by a bulky β -diketiminato (NacNac) ligand framework [50]. This was followed by the synthesis of its gallium analogue by Power and coworkers [51]. However, the synthesis and isolation of a neutral monomeric cyclic boron(I) carbenoid has remained elusive to date; this may be attributed to smaller energetic separation between the valence *s* and *p* orbitals as well as low singlet–triplet (ΔE_{S-T}) separation. Phosphorous ylides are found to be useful in stabilizing group 14 bases [55–61]. Based on these reports, we envisage that phosphorous ylides could be promising systems for the stabilization and isolation of the hitherto unknown cyclic boron(I) carbenoids.

In this part, we present the results of our computational studies on the stabilization of neutral, monomeric five-membered boron(I) carbenoids by employing two different ylide functionalities, viz., a conventional carbon-based phosphorous ylide and a zwitterionic four-membered cyclic ylide [62] and their potential in small molecule activation. We have used meta-GGA M06 exchange–correlation functional [40] in combination with the valence polarized def2-TZVP basis set [41, 42] for all the elements. Calculations suggest that strongly π -electron donating groups such as amino or ylides may be used for the stabilization of neutral monomeric five-membered boron(I) carbenoids (**1–9**, Scheme 4.1). It is encouraging to note that the molecules **4–7** and **9** compute the highest singlet–triplet separation values ($\Delta E_{S-T} = 25.5–42.3$ kcal mol⁻¹) known to date, and to the best of our knowledge, no other cyclic borylenes are known with such large values thus highlighting the remarkable power of ylides in stabilizing unusual species. In addition, the calculated ΔE_{S-T} values are found to be either comparable or higher than that of the synthetically amenable Roesky’s Al(I) carbenoid (34.1 kcal mol⁻¹) or cAAC (42.7 kcal mol⁻¹) further providing a hint towards their possible isolation. In addition, **4–7** and **9** are remarkably nucleophilic and compute considerably lower barrier heights for the activation of E–H (E = H, C and N) and C–F

bonds compared to that of the experimentally evaluated systems indicating their potential in small molecule activation.

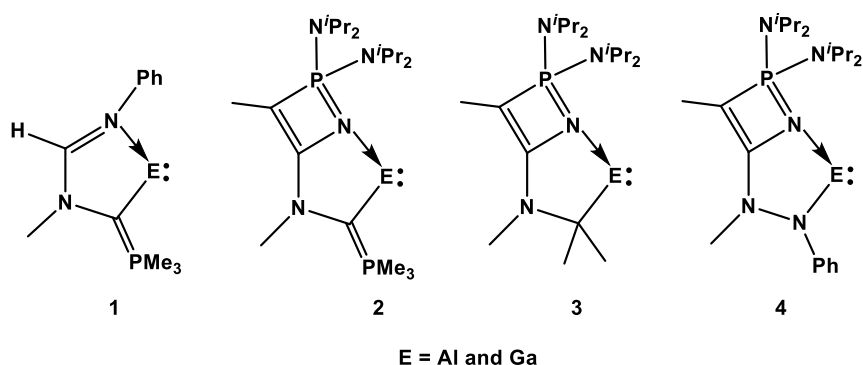


Scheme 4.1: Schematic representation of the cyclic five-membered boron(I) carbenoids considered in this study.

Unravelling the Potential of Ylides in Stabilizing Low-Valent Group 13 Compounds: Theoretical Predictions of Stable, Five-membered Group 13 (Al and Ga) Carbenoids Capable of Small Molecule Activation

Motivated by the lack of isolable neutral monomeric five-membered aluminium carbenoids as well as to contribute to the field of group 13 carbenoids with enhanced ligand properties, density functional theory calculations were carried out on a number of ylide decorated monovalent aluminium and gallium carbenoids (**1–4**, Scheme 4.2). We have employed meta-GGA M06 exchange–correlation functional [40] in combination with the valence polarized def2-TZVP basis set [41, 42] for all the elements. All the computationally proposed molecules (**1–4**) are found to be substantially nucleophilic and exhibit singlet- triplet energy separation values that are either comparable or higher than those obtained for **I**, **II** and **XIa** indicating that all of them could be considered as potential synthetic targets. In addition, the calculated activation energy barriers obtained for **1–4** in different bond activation processes are found to be comparable to those of **I** and **II** which are known to activate a range of small molecules under mild reaction conditions. Therefore, akin to **I** and **II**, all the newly designed ylide anchored group 13

carbenoids may be considered as suitable candidates for small molecule activation and calls for sustained experimental efforts toward their synthesis and isolation.

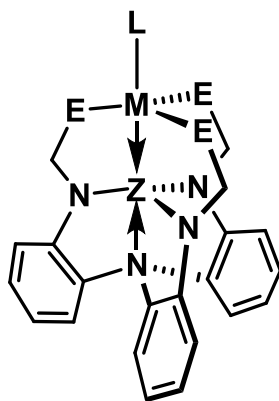


Scheme 4.2: Schematic representation of the group 13 carbenoids considered in this study.

Chapter 5: Understanding, Modulating and Leveraging Transannular M→Z Interactions

Transition metal complexes containing a group 13 element as a σ -acceptor group are commonly known as group 13 metallatranes and feature a transannular M→Z interaction. It is believed that this interaction plays a key role in governing the stability and reactivity of these molecules. Group 13 metallatranes are found to be useful in various catalytic processes, such as dinitrogen activation [63-65], hydrogenation and hydrosilylation of CO₂ [66, 67], heterolytic E–H bond activation (E = O, S, C, N) [68-72] and catalytic olefin hydrogenation [73] among others. The flexibility of the M→Z interaction is believed to play a key role in dictating the catalytic activities of group 13 metallatranes.

In this work, we performed a comprehensive, in-depth analysis of the nature and strength of the intramolecular transannular interaction present in these molecules aiming at providing valuable information for their use in catalysis and small molecule activation reactions. The transannular M→Z interaction is analyzed as a function of different equatorial (E), apical (L), and Lewis acidic (Z) groups (Scheme 5.1). We have used meta hybrid exchange-correlation energy functional M06 [40] in conjunction with the split valence polarized def2-SVP basis set for H, C, N, O, S, and P, and the triple-zeta valence polarized def2-TZVP basis set for Fe, Co, Ni, Al, Ga, and In [41, 42]. The core



E= SⁱPr, P(ⁱPr)₂; M= Fe, Co, Ni; Z= Al, Ga, In

L= NH₃, PMe₃, N₂, CO, NHC, aNHC, CNMe

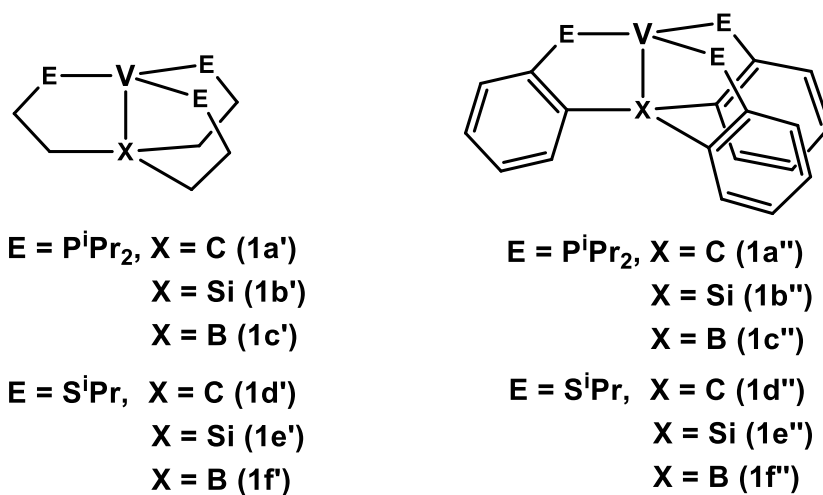
Scheme 5.1: Schematic representation of the metallatranes considered in this study.

electrons of In were replaced by an effective core potential (ECP). The extent of these transannular M···Z interactions depends to a large extent on the size and polarizability of the group 13 element (Z group). Furthermore, it should be noted that the strength of the transannular interaction plays a decisive role in governing the reactivity of the TM center in metallatranes. For example, the calculated reaction free energies (ΔG°) for binding of different Lewis bases are found to be more exergonic for the larger, more polarizable Lewis acidic In(III) ion than those for Al(III) or Ga(III) ions. Therefore, such transannular interactions could be leveraged towards the binding of σ -donor or π acidic ligands to a given transition metal center. The quantum theory of atoms in molecules study also suggests the presence of considerable electron density (ρ) at the BCP of the M···Z bonds, which gradually increases as Z is varied down group 13 from Al to Ga to In. In addition, the calculated local electronic energy density ($H(r)$) values are found to be negative, indicating the covalent nature of the M···Z bonds. Furthermore, EDA-NOCV analysis indicates the strong binding ability of these metallatranes not only to different σ -donor and π acceptor ligands but also to relatively inert species, such as N₂.

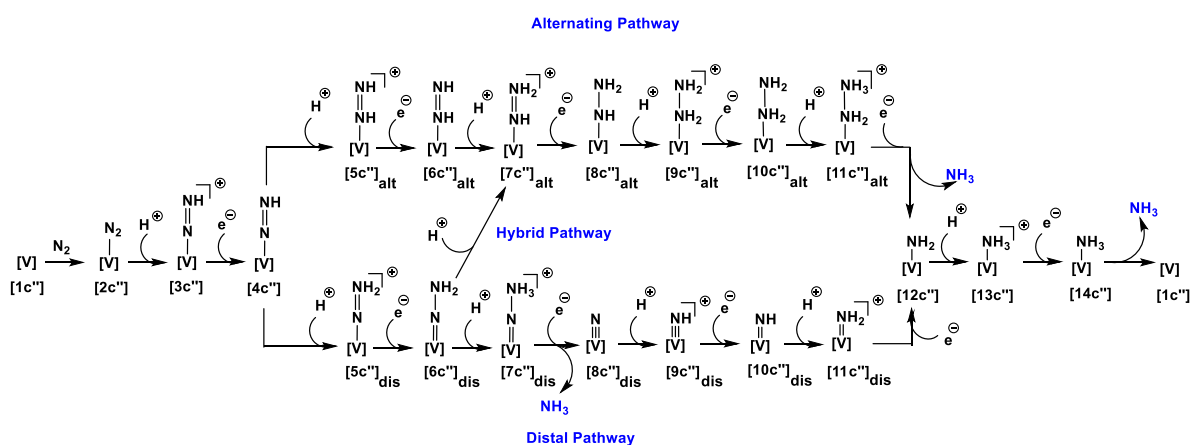
Chapter 6: Unravelling the Potential of Tripodal Vanadium Catalysts for Dinitrogen Reduction

In this work, we have performed in depth comprehensive study aimed towards designing of a series of tetradenate tripodal vanadium complexes (Scheme 6.1) and studied their efficacy in some of the key steps involved in the dinitrogen reduction process. We have

used M06-L functional [74] in conjunction with 6-311+G* [35-37] basis set for all the elements. The proposed complexes were probed towards understanding their efficiency in some of the key steps involved in the dinitrogen fixation process. All the complexes were found to be successful in preventing the release of hydrazine during the nitrogen reduction reaction. We have performed a comprehensive mechanistic study by considering all the possible pathways (distal, alternate and hybrid) (Scheme 6.2) to understand the efficiency of some of the proposed catalysts towards dinitrogen reduction



Scheme 6.1: Schematic representation of the model vanadium complexes considered in this study.



Scheme 6.2: Alternating and distal pathways for dinitrogen reduction to NH_3

process. In addition, interconversion of the isomeric nitrogenous species involved in the alternating ([5]_{alt}, [6]_{alt} and [7]_{alt}) and distal ([5]_{dis}, [6]_{dis} and [7]_{dis}) pathways is unlikely to occur. The exergonic reaction free energies obtained for some of the key steps as well

as the presence of thermally surmountable barrier heights involved in the catalytic cycle indicate that the proposed vanadium complexes may be considered as suitable platforms for the functionalization of dinitrogen.

Bibliography

- [1] Hopkinson, M. N., Richter, C., Schedler, M., and Glorius, F. An overview of N-heterocyclic carbenes. *Nature*, 510(7506):485-496, 2014.
- [2] Nolan, S. P. The Development and Catalytic Uses of N-Heterocyclic Carbene Gold Complexes. *Accounts of Chemical Research*, 44(2):91-100, 2011.
- [3] Vougioukalakis, G. C., and Grubbs, R. H. Ruthenium-Based Heterocyclic Carbene-Coordinated Olefin Metathesis Catalysts. *Chemical Reviews*, 110(3):1746-1787, 2010.
- [4] Allen, W. D., and Schaefer III, H. F. Geometrical structures, force constants, and vibrational spectra of SiH, SiH₂, SiH₃, and SiH₄. *Chemical Physics*, 108(2):243-274, 1986.
- [5] Balasubramanian, K., and McLean, A. D. The singlet–triplet energy separation in silylene. *The Journal of Chemical Physics*, 85(9):5117-5119, 1986.
- [6] Arduengo III, A. J., Harlow, R. L., and Kline, M. A Stable Crystalline Carbene. *Journal of the American Chemical Society*, 113(1):361-363, 1991.
- [7] Dröge, T., and Glorius, F. The Measure of All Rings—N-Heterocyclic Carbenes. *Angewandte Chemie International Edition*, 49(39):6940-6952, 2010.
- [8] Frémont, de P., Marion N., and Nolan, S. P. Carbenes: Synthesis, properties, and organometallic chemistry, *Coordination Chemistry Reviews*, 253(7-8):862–892, 2009.
- [9] Hahn, F. E., and Jahnke, M. C. Heterocyclic Carbenes: Synthesis and Coordination Chemistry. *Angewandte Chemie International Edition*, 47(17):3122-3172, 2008.
- [10] Wanzlick, H. W., and Schönherr, H. J. Direct Synthesis of a Mercury Salt-Carbene Complex. *Angewandte Chemie International Edition in English*, 7(2):141-142, 1968.
- [11] Hitchcock, P. B., Lappert M. F., and Pye, P. L. Carbene Complexes. Part 14. The Synthesis and Steric and Electronic Effects in Electron-rich Olefin-derived Bis-, Tris-, and Tetrakis-(Carbene)-ruthenium(II) and a Tetrakis (carbene)osmium(II) Complex; the Crystal and Molecular Structure of *trans*-Dichlorotetrakis(1, 3-diethylimidazo-lidin-2-

ylidene)ruthenium(II). *Journal of the Chemical Society, Dalton Transactions*, (7):826–836, 1978.

[12] Doyle M. J. and Lappert M. F., Activation Parameters for Rotation about an M–C_{carb} Bond from Temperature Dependent ¹H N.m.r. Spectra of Rh^I Carbene Complexes. *Journal of the Chemical Society, Chemical Communications*, (17):679–680, 1974.

[13] Lappert, M. F., and Maskell, R. K. Homogeneous catalysis: VIII. Carbene-transition-metal complexes as hydrosilylation catalysts. *Journal of Organometallic Chemistry*, 264(1-2):217-228, 1984.

[14] Öfele, K. 1, 3-Dimethyl-4-imidazolinyliiden-(2)-pentacarbonylchrom ein neuer Übergangsmetall-carben-komplex. *Journal of Organometallic Chemistry*, 12(3):P42-P43, 1968.

[15] Martin, D., Baceiredo, A., Gornitzka, H., Schoeller, W. W., and Bertrand, G. A Stable P-Heterocyclic Carbene. *Angewandte Chemie International Edition*, 44(11):1700-1703, 2005.

[16] Masuda, J. D., Martin, D., Lyon-Saunier, C., Baceiredo, A., Gornitzka, H., Donnadieu, B., and Bertrand, G. Stable P-Heterocyclic Carbenes: Scope and Limitations, *Chemistry—An Asian Journal*, 2(1):178-187, 2007.

[17] Ruiz, J., and Perandones, B. F. Metal-induced tautomerization of oxazole and thiazole molecules to heterocyclic carbenes. *Chemical Communications*, (19):2741-2743, 2009.

[18] Vougioukalakis, G. C., and Grubbs, R. H. Synthesis and Activity of Ruthenium Olefin Metathesis Catalysts Coordinated with Thiazol-2-ylidene Ligands. *Journal of the American Chemical Society*, 130(7):2234-2245, 2008.

[19] Raubenheimer, H. G., and Cronje, S. Carbene complexes derived from lithiated heterocycles, mainly azoles, by transmetallation. *Journal of Organometallic Chemistry*, 617-618:170-181, 2001.

[20] Raubenheimer, H. G., Stander, Y., Marais, E. K., Thompson, C., Kruger, G. J., Cronje, S., and Deetlefs, M. Group 6 carbene complexes derived from lithiated azoles and the crystal structure of a molybdenum thiazolinyliidene complex. *Journal of Organometallic Chemistry*, 590(2):158-168, 1999.

[21] Gründemann, S., Kovacevic, A., Albrecht, M., Robert, J. W. F., and Crabtree, H. Abnormal binding in a carbene complex formed from an imidazolium salt and a metal hydride complex. *Chemical Communications*, (21):2274-2275, 2001.

- [22] Gruendemann, S., Kovacevic, A., Albrecht, M., Faller, J. W., and Crabtree, R. H. Abnormal Ligand Binding and Reversible Ring Hydrogenation in the Reaction of Imidazolium Salts with IrH₅(PPh₃)₂. *Journal of the American Chemical Society*, 124(35):10473-10481, 2002.
- [23] Mathew, P., Neels, A., and Albrecht, M. 1, 2, 3-Triazolylidenes as Versatile Abnormal Carbene Ligands for Late Transition Metals. *Journal of the American Chemical Society*, 130(41):13534-13535, 2008.
- [24] Guisado-Barrios, G., Bouffard, J., Donnadiou, B., and Bertrand, G. Crystalline 1*H*-1, 2, 3-Triazol-5-ylidenes: New Stable Mesoionic Carbenes (MICs). *Angewandte Chemie International Edition*, 49(28):4759-4762, 2010.
- [25] Arduengo III, A. J., Goerlich, J. R., and Marshall, W. J. A Stable Diaminocarbene. *Journal of the American Chemical Society*, 117(44):11027-11028, 1995.
- [26] Gusev, D. G. Electronic and Steric Parameters of 76 N-Heterocyclic Carbenes in Ni(CO)₃(NHC). *Organometallics*, 28(22):6458-6461, 2009.
- [27] Iglesias, M., Beetstra, D. J., Stasch, A., Horton, P. N., Hursthouse, M. B., Coles, S. J., Cavell, K.J., Dervisi, A., and Fallis, I. A. First Examples of Diazepanylidene Carbenes and Their Late-Transition-Metal Complexes. *Organometallics*, 26(19):4800-4809, 2007.
- [28] Scarborough, C. C., Guzei, I. A., and Stahl, S. S. Synthesis and isolation of a stable, axially-chiral seven-membered *N*-heterocyclic carbene. *Dalton Transactions*, (13):2284-2286, 2009.
- [29] Iglesias, M., Beetstra, D. J., Knight, J. C., Ooi, L. L., Stasch, A., Coles, S., Male, L., Hursthouse, M. B., Cavell, K. J., Dervisi, A. and Fallis, I. A. Novel Expanded Ring N-Heterocyclic Carbenes: Free Carbenes, Silver Complexes, and Structures. *Organometallics*, 27(13):3279-3289, 2008.
- [30] Ruiz, J., García, L., Perandones, B. F., and Vivanco, M. A Fischer carbene within an Arduengo carbene. *Angewandte Chemie International Edition*, 50(13):3010-3012, 2011.
- [31] Ruiz, J., García, L., Mejuto, C., Vivanco, M., Díaz, M. R., and García-Granda, S. Strong electron-donating metalla-N-heterocyclic carbenes. *Chemical Communications*, 50(17):2129-2132, 2014.

- [32] Ruiz, J., García, L., Vivanco, M., Berros, Á., and Van der Maelen, J. F. Generating and Trapping Metalla-N-Heterocyclic Carbenes. *Angewandte Chemie International Edition*, 54(14):4212-4216, 2015.
- [33] Ernzerhof, M., and Scuseria, G. E. Assessment of the Perdew–Burke–Ernzerhof exchange–correlation functional. *The Journal of Chemical Physics*, 110(11):5029-5036, 1999.
- [34] Adamo, C., and Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *The Journal of Chemical Physics*, 110(13):6158-6170, 1999.
- [35] Francl, M. M., Pietro, W. J., Hehre, W. J., Binkley, J. S., Gordon, M. S., DeFrees, D. J., and Pople, J. A. Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements. *The Journal of Chemical Physics*, 77(7):3654-3665, 1982.
- [36] Rassolov, V. A., Pople, J. A., Ratner, M. A., and Windus, T. L. 6-31G* basis set for atoms K through Zn. *The Journal of Chemical Physics*, 109(4):1223-1229, 1998.
- [37] Rassolov, V. A., Ratner, M. A., Pople, J. A., Redfern, P. C., and Curtiss, L. A. 6-31G* basis set for third-row atoms. *Journal of Computational Chemistry*, 22(9):976-984, 2001.
- [38] Ceolin, G. A., de Berrêdo, R. C., and Jorge, F. E. Gaussian basis sets of quadruple zeta quality for potassium through xenon: application in CCSD (T) atomic and molecular property calculations. *Theoretical Chemistry Accounts*, 132:1339, 2013.
- [39] Jansen, G., and Hess, B. A. Revision of the Douglas-Kroll transformation. *Physical Review A*, 39(11):6016, 1989.
- [40] Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn. *Physical Chemistry Chemical Physics*, 8(9):1057-1065, 2006.
- [41] Grimme, S., Antony, J., Ehrlich, S., and Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *The Journal of Chemical Physics*, 132(15):154104, 2010.
- [42] Cossi, M., Scalmani, G., Rega, N., and Barone, V. New developments in the polarizable continuum model for quantum mechanical and classical calculations on molecules in solution. *The Journal of Chemical Physics*, 117(1):43-54, 2002.

- [43] Denk, M., Lennon, R., Hayashi, R., West, R., Belyakov, A. V., Verne, H. P., Haaland, A., Wagner, M., and Metzler, N. Synthesis and Structure of a Stable Silylene. *Journal of the American Chemical Society*, 116(6):2691-2692, 1994.
- [44] Meller, A., and Gräbe, C. P. Synthese und Isolierung neuer Germanium(II)-Verbindungen und freier Germylene. *Chemische Berichte*, 118(5):2020-2029, 1985.
- [45] (a) Gaspar, P. P., Xiao, M., Pae, D. H., Berger, D. J., Haile, T., Chen, T., Lei, D., Winchester, W. R., and Jiang, P. The quest for triplet ground state silylenes. *Journal of Organometallic Chemistry*, 646(1-2):68-79, 2002; (b) Lee, V. Y., and Sekiguchi, A. (2010). *Organometallic Compounds of Low-Coordinate Si, Ge, Sn and Pb: From Phantom Species to Stable Compounds*, John Wiley & Sons, pages.139-197.
- [46] (a) Gehrhus, B., and Lappert, M. F. Chemistry of thermally stable bis(amino)silylenes. *Journal of Organometallic Chemistry*, 617-618:209-223, 2001; (b) Gehrhus, B., Lappert, M. F., Heinicke, J., Boese, R., and Bläser, D. Synthesis, structures and reactions of new thermally stable silylenes. *Journal of the Chemical Society, Chemical Communications*, (19):1931-1932, 1995.
- [47] Kosai, T., Ishida, S., and Iwamoto, T. A Two-Coordinate Cyclic (Alkyl)(amino)silylene: Balancing Thermal Stability and Reactivity. *Angewandte Chemie International Edition*, 55(50):15554-15558, 2016.
- [48] Wang, L., Lim, Y. S., Li, Y., Ganguly, R., and Kinjo, R. Isolation of a Cyclic (Alkyl)(amino)germylene. *Molecules*, 21(8):990, 2016.
- [49] Koike, T., Kosai, T., and Iwamoto, T. 1, 4-Dehydrogenation with a Two-Coordinate Cyclic (Alkyl)(amino)silylene. *Chemistry—A European Journal*, 25(39):9295-9302, 2019.
- [50] Cui, C., Roesky, H. W., Schmidt, H. G., Noltemeyer, M., Hao, H., and Cimpoesu, F. Synthesis and Structure of a Monomeric Aluminum(I) Compound $[\{\text{HC}(\text{CMeNAr})_2\}\text{Al}](\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$: A Stable Aluminum Analogue of a Carbene. *Angewandte Chemie International Edition*, 39(23):4274-4276, 2000.
- [51] Hardman, N. J., Eichler, B. E., and Power, P. P. Synthesis and characterization of the monomer $\text{Ga}\{(\text{NDippCMe})_2\text{CH}\}(\text{Dipp} = \text{C}_6\text{H}_3\text{Pr}^i_{2-2,6})$: a low valent gallium(I) carbene analogue. *Chemical Communications*, (20):1991-1992, 2000.
- [52] Hill, M. S., and Hitchcock, P. B. A mononuclear indium(I) carbene analogue. *Chemical Communications*, (16):1818-1819, 2004.

- [53] Hill, M. S., Hitchcock, P. B., and Pongtavornpinyo, R. Neutral carbene analogues of the heaviest Group 13 elements: Consideration of electronic and steric effects on structure and stability. *Dalton Transactions*, (2):273-277, 2005.
- [54] Chu, T., and Nikonov, G. I. Oxidative Addition and Reductive Elimination at Main-Group Element Centers. *Chemical Reviews*, 118(7):3608-3680, 2018.
- [55] Nakafuji, S. Y., Kobayashi, J., and Kawashima, T. Generation and Coordinating Properties of a Carbene Bearing a Phosphorus Ylide: An Intensely Electron-Donating Ligand. *Angewandte Chemie International Edition*, 47(6):1141-1144, 2008.
- [56] Fürstner, A., Alcarazo, M., Radkowski, K., and Lehmann, C. W. Carbenes Stabilized by Ylides: Pushing the Limits. *Angewandte Chemie International Edition*, 47(43):8302-8306, 2008.
- [57] Borthakur, B., and Phukan, A. K. Moving toward Ylide-Stabilized Carbenes. *Chemistry—A European Journal*, 21(32):11603-11609, 2015.
- [58] Bharadwaz, P., Chetia, P., and Phukan, A. K. Electronic and Ligand Properties of Skeletally Substituted Cyclic(Alkyl)(Amino)Carbenes (CAACs) and Their Reactivity towards Small Molecule Activation: A Theoretical Study. *Chemistry—A European Journal*, 23(41):9926-9936, 2017.
- [59] Asay, M., Inoue, S., and Driess, M. Aromatic Ylide-Stabilized Carbocyclic Silylene. *Angewandte Chemie International Edition*, 50(41):9589-9592, 2011.
- [60] Alvarado-Beltran, I., Baceiredo, A., Saffon-Merceron, N., Branchadell, V., and Kato, T. Cyclic Amino(Ylide)Silylene: A Stable Heterocyclic Silylene with Strongly Electron-Donating Character. *Angewandte Chemie International Edition*, 55(52):16141-16144, 2016.
- [61] Berthe, J., Garcia, J. M., Ocando, E., Kato, T., Saffon-Merceron, N., De Cózar, A., Cossío, F. P., and Baceiredo, A. Synthesis and Reactivity of a Phosphine-Stabilized Monogermanium Analogue of Alkynes. *Journal of the American Chemical Society*, 133(40):15930-15933, 2011.
- [62] Tejada, J., Reau, R., Dahan, F., and Bertrand, G. Synthesis and Molecular Structure of a $1,2\lambda^5$ -azaphosphete: A Cyclic 4- π -Electron Ylide. *Journal of the American Chemical Society*, 115(17):7880-7881, 1993.
- [63] Anderson, J. S., Rittle, J., and Peters, J. C. Catalytic conversion of nitrogen to ammonia by an iron model complex. *Nature*, 501(7465):84-87, 2013.

- [64] Rudd, P. A., Planas, N., Bill, E., Gagliardi, L., and Lu, C. C. Dinitrogen Activation at Iron and Cobalt Metallaluminatranes. *European Journal of Inorganic Chemistry*, 2013(22-23):3898-3906, 2013.
- [65] Clouston, L. J., Bernales, V., Carlson, R. K., Gagliardi, L., and Lu, C. C. Bimetallic Cobalt–Dinitrogen Complexes: Impact of the Supporting Metal on N₂ Activation. *Inorganic Chemistry*, 54(19):9263-9270, 2015.
- [66] Takaya, J., and Iwasawa, N. Synthesis, Structure, and Catalysis of Palladium Complexes Bearing a Group 13 Metalloligand: Remarkable Effect of an Aluminum–Metalloligand in Hydrosilylation of CO₂. *Journal of the American Chemical Society*, 139(17):6074-6077, 2017.
- [67] Cammarota, R. C., Vollmer, M. V., Xie, J., Ye, J., Linehan, J. C., Burgess, S. A., Appel, A. M., Gagliardi, L., Lu, C. C. A Bimetallic Nickel–Gallium Complex Catalyzes CO₂ Hydrogenation via the Intermediacy of an Anionic d¹⁰ Nickel Hydride. *Journal of the American Chemical Society*, 139(40):14244-14250, 2017.
- [68] Nesbit, M. A., Suess, D. L., and Peters, J. C. E–H Bond Activations and Hydrosilylation Catalysis with Iron and Cobalt Metalloboranes. *Organometallics*, 34(19):4741-4752, 2015.
- [69] Harman, W. H., Lin, T. P., and Peters, J. C. A d¹⁰ Ni–(H₂) Adduct as an Intermediate in H–H Oxidative Addition across a Ni–B Bond. *Angewandte Chemie International Edition*, 53(4):1081-1086, 2014.
- [70] Harman, W. H., and Peters, J. C. Reversible H₂ Addition across a Nickel–Borane Unit as a Promising Strategy for Catalysis. *Journal of the American Chemical Society*, 134(11):5080-5082, 2012.
- [71] Suess, D. L., and Peters, J. C. H–H and Si–H Bond Addition to Fe≡NNR₂ Intermediates Derived from N₂. *Journal of the American Chemical Society*, 35(13):4938-4941, 2013.
- [72] Zeng, G., and Sakaki, S. Unexpected Electronic Process of H₂ Activation by a New Nickel Borane Complex: Comparison with the Usual Homolytic and Heterolytic Activations. *Inorganic Chemistry*, 52(6):2844-2853, 2013.
- [73] Cammarota, R. C., and Lu, C. C. Tuning Nickel with Lewis Acidic Group 13 Metalloligands for Catalytic Olefin Hydrogenation. *Journal of the American Chemical Society*, 137(39):12486-12489, 2015.

[74] Zhao, Y., and Truhlar, D. G. A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions. *The Journal of Chemical Physics*, 125(19):194101, 2006.

Keywords

Carbene, Silylene, Germylene, Singlet-Triplet Gap, Proton Affinity, Small Molecule, Activation, Stability, Metallatranes, Dinitrogen Activation, Distal Pathway, Alternate Pathway.