ABSTRACT

The present thesis deals with the study of a variety of chemical problems using the approaches of modern computational chemistry. The main text of the thesis has been categorized into five chapters of which the first chapter deals with brief introduction to Computational Chemistry. The remaining chapters describe the application of the computational methodologies to chemical problems. A brief overview of all the chapters is given below.

Chapter 1: Brief Introduction to Computational Chemistry.

The works presented in this thesis were being carried out employing Density Functional Theory (DFT) calculations and accordingly, a brief description of DFT as well as all the other computational techniques are provided in this chapter.

Chapter 2: Tuning the Electronic and Ligand Properties of Remote Carbenes.

N-Heterocyclic carbenes (NHCs) have found a great deal of attention after their isolation by Arduengo in 1991 and have grown extensively in the past few years because of the remarkable catalytic activity of the corresponding transition metal complexes. NHCs are found to have excellent σ-donation as well as considerable π-acceptance abilities. In addition to these NHCs, NHC variants known as remote NHCs (rNHCs) have drawn the attention of several researchers as rNHCs are better σ-donors as well as better π-acceptors than their normal NHC counterparts. Interestingly, annulation and/or carbonylation of the NHC ligands were found to significantly increase their π-accepting abilities.

In this chapter, the effect of annulation and carbonylation on the electronic and ligating properties of both five- and six-membered rNHCs (Scheme 1) were studied employing PBE0/6-31+G* level of theory. This study reveals that annulation and carbonylation of rNHCs results in decrease in thermodynamic and kinetic stabilities. Further, both annulation and carbonylation result in decrease in σ-donating ability but significant increase in π-accepting ability. The significant increase in π-acidity has been further corroborated by the calculated electrophilicity index values as well as ^{31}P NMR chemical shift values of the corresponding rNHC-phosphinidene adducts.
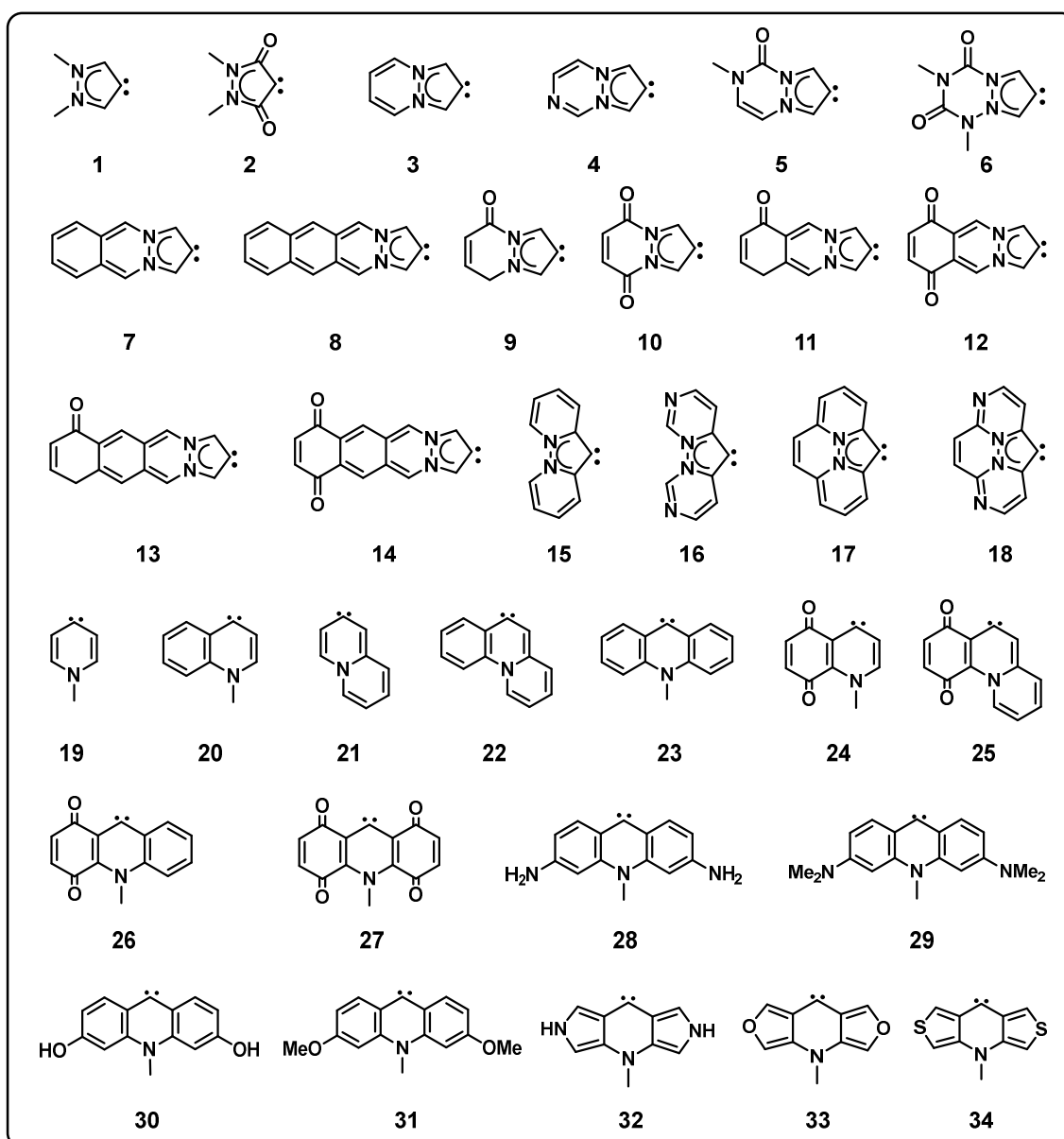
Scheme 1: Schematic representation of the mesoionic (**1−18**) and remote NHCs (**19−34**) considered in this study.

Chapter 3: Effect of Ylide Substitution on the Stability and Electron Donation Ability of NHCs.

Following the isolation of the stable singlet NHC in 1991, a number of their structural derivatives have been isolated which possess varying degree of ligand properties. One of the interesting candidate of this family is cyclic(alkyl)(amino)carbene (CAAC), which possesses better σ-basicity and π-acidity than the normal NHCs. Further, the seminal works of Kawashima and Fürstner in 2008 suggest that introduction of

electron-donating phosphorus and sulfur ylide centers into the ring framework also leads to significant increase in σ-donation ability of cyclic carbenes.

This chapter contains two parts – (i) the first part of which deals with the effect of ylide substitution on the electron-donating ability and stability of a number of five- and six-membered cyclic carbenes and (ii) the second part deals with the theoretical studies aimed toward stabilization of five- and six-membered remote carbenes in their singlet ground states.

Section 3.1: Moving Toward Ylide-Stabilized Carbenes.

The electron-donating ability of a carbene ligand has a significant effect on the catalytic activity of the corresponding transition-metal complexes. Hence, the design and synthesis of carbene frameworks with enhanced electron-donating abilities may help to develop novel catalysts for various applications.

In this part, we have investigated the effect of ylide substitution at position α with respect to the carbene carbon on the stability and σ-donating ability of a number of cyclic carbenes (Scheme 2) using PBE0/6-31+G*, SDD level of theory. The introduction of ylide centers into the ring framework dramatically enhances the σ-donating ability. Furthermore, for majority of the carbenes, ylide substitution leads to a significant
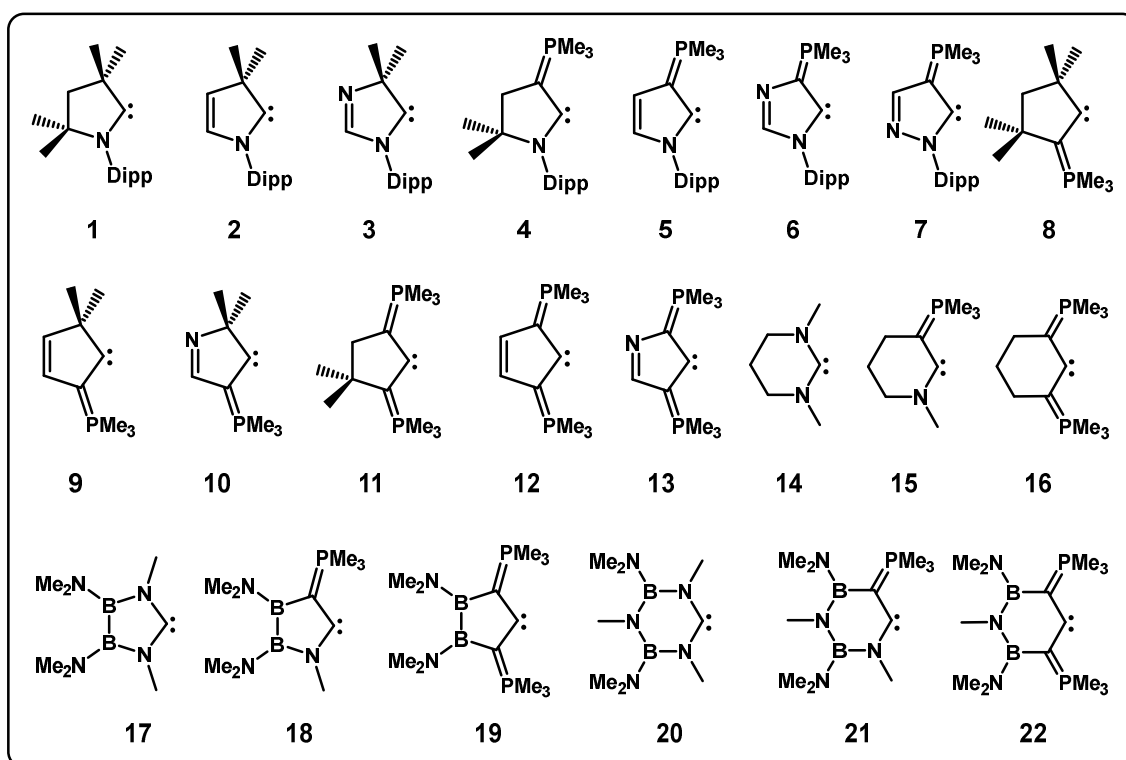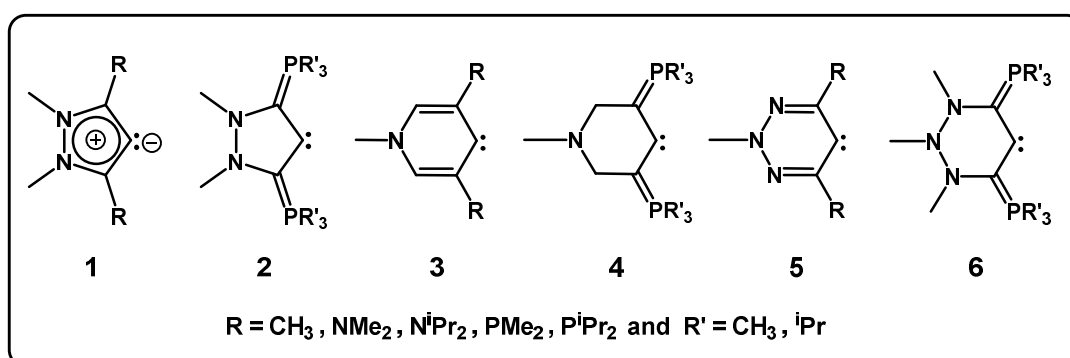

Scheme 2: Schematic representation of the range of carbenes considered in this study (Dipp: 2,6-diisopropylphenyl).

increase in stability. The increase in σ-basicity in the ylide substituted ones has been further assessed by the calculation of carbonyl-stretching frequencies of the corresponding metal complexes, proton affinity values and the extent of gallium pyramidalization in the corresponding $GaCl_3$ adducts.

Section 3.2: Theoretical Strategies Toward Stabilization of Singlet Remote *N*-Heterocyclic Carbenes.

Even though the remote NHCs (rNHCs) possess superior ligand properties in terms of both σ-donation and π-acceptance ability compared to the classical NHCs, so far no rNHCs have been isolated in their free state. In case of normal NHCs, the singlet state stability can be attributed to effective π delocalization from the nitrogen lone pairs to the formally vacant p orbital at the carbene carbon. However, unlike in normal NHCs, π stabilization is not so effective in rNHCs resulting in lower singlet state stability.

In this part, we present the results of theoretical studies aimed toward stabilization of five- and six-membered remote carbenes (Scheme 3) in their singlet ground states. The quantum-mechanical calculations carried out at PBE0/6-31+G*, SDD level of theory predict that the singlet states of ylide-substituted remote carbenes are significantly stable and comparable to those of experimentally known NHCs. Further, NICS and QTAIM based bond magnetizability calculations indicate the presence of cyclic electron delocalization in majority of the molecules.

Scheme 3: Schematic representation of the range of cyclic carbenes considered in this study.

Chapter 4: Carbene Driven Stabilization of the H_{red} State of Biomimetic Model [FeFe]-Hydrogenase Complexes.

[FeFe]–hydrogenase is an enzyme which catalyzes the reversible activation of dihydrogen involving two key intermediates (H_{ox} and H_{red}, Scheme 4). One of the
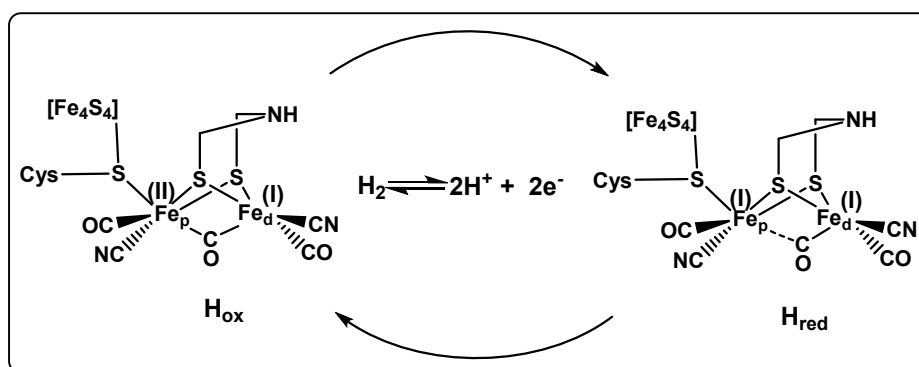
Scheme 4: Schematic representation of the active site structure of [FeFe]-hydrogenase.

important structural features of both H_{ox} and H_{red} state of the native enzyme is the presence of an inverted square pyramidal geometry (or rotated geometry) at one of the iron center (distal) with a carbonyl group in bridging position between the two iron centers. The vacant site at the distal iron center is the probable site for coordination of H^+/H_2 during reversible dihydrogen production. Even though a number of model complexes for the H_{ox} state have been isolated with a rotated conformation, only a few model complexes for the H_{red} state were known with an inverted square pyramidal geometry at one of the iron center.

In this chapter, we present our results of theoretical investigation toward stabilization of rotated structure in carbene substituted [FeFe]–hydrogenase model complexes (Scheme 5) carried out at BP86/Def2-SVP, Def2-TZVP(Fe) level of theory. Stabilization of fully rotated conformation at one of the iron center has been achieved for the reduced Fe(I)Fe(I) state in chelated CAAC substituted biomimetic hydrogenase model complex. This study indicates that the spatial orientation of the chelated NHCs at one of the iron center (Fe_p) plays a major role in determining the geometry at the other (Fe_d). We also made an attempt at explaining the electronic origin behind the favorability of rotated vs unrotated structure in asymmetrically substituted chelated vs monodentate NHC complexes.
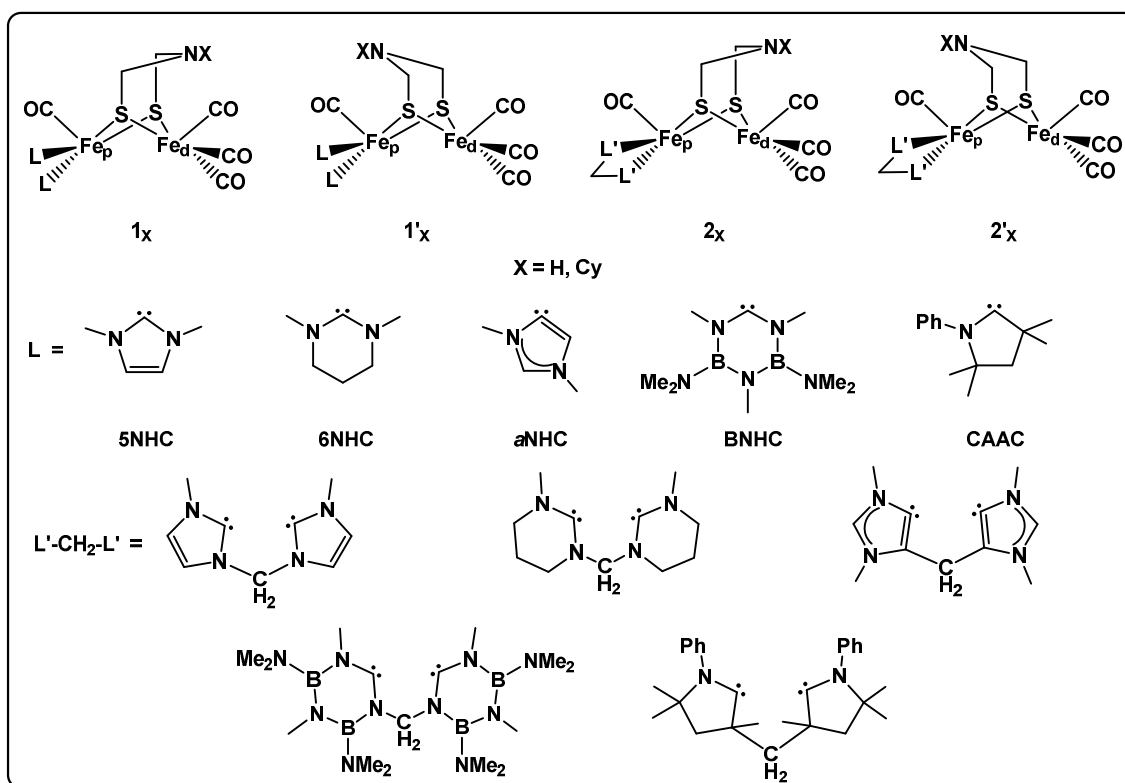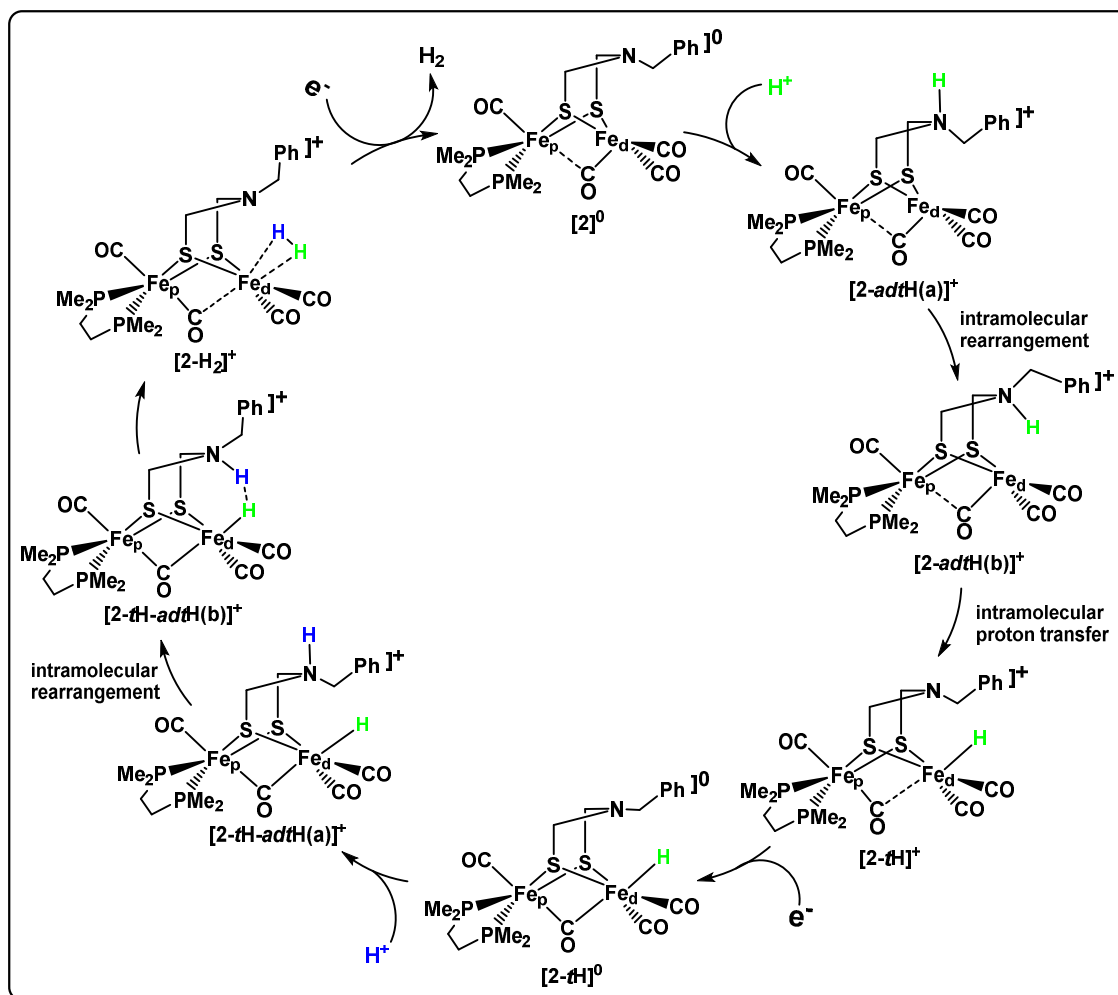
Scheme 5: Schematic representation of the molecules considered in the present study (X= H/Cyclohexyl).

Chapter 5: Can Carbene Decorated [FeFe]-Hydrogenase Model Complexes Catalytically Produce Dihydrogen? An Insight from Theory.

In this chapter, we have studied the mechanistic details of catalytic production of dihydrogen using bio-inspired [FeFe]–hydrogenase model complexes which possess rotated conformation at one of the iron centers ($[1]^0$ and $[2]^0$, Schemes 6 and 7). The catalytic evolution of H_2 is found to be highly favorable using both the complexes as evident from high exergonicity of the overall reaction as well as very shallow activation energy barrier for the transition states involved. The computed reduction potential values are found to be less negative compared to those reported earlier for experimentally known systems.
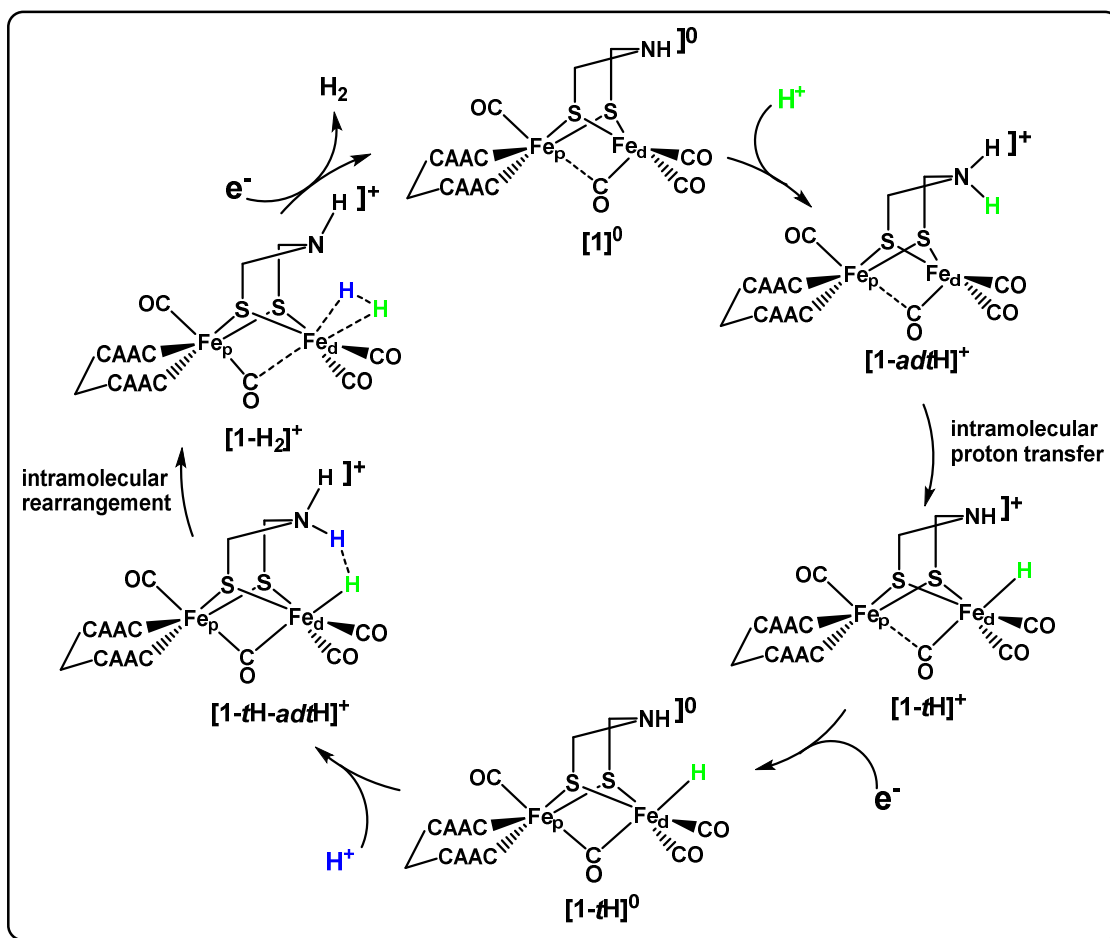
Scheme 6: Schematic representation of the catalytic cycle of H_2 production catalyzed by $[1]^0$.

Scheme 7: Schematic representation of the catalytic cycle of H$_2$ production catalyzed by [2]^0.