

Contents	Page No
Abstract	i
Declaration by the Candidate	ix
Certificate of the Supervisor	x
Certificate of the External Examiner and ODEC	xi
Acknowledgements	xii
Table of Contents	xiii
List of Tables	xvii
List of Figures	xxi
List of Schemes	xxv
List of Abbreviations	xxvii
Chapter 1: Brief Introduction to Computational Chemistry	1-26
[1.1] Introduction	1
[1.2] Density Functional Theory	1
[1.2.1] The Hohenberg-Kohn Theorems	2
[1.2.2] The Kohn-Sham Energy	2
[1.2.3] The Local Density Approximation (LDA)	4
[1.2.4] The Generalized-Gradient Approximation (GGA)	5
[1.2.5] Hybrid Functional	6
[1.3] Basis Set	6
[1.4] Effective Core Potential (ECP)	8
[1.5] Gauge-Independent Atomic Orbital (GIAO) Method	9
[1.6] Quantum Theory of Atoms in Molecules (QTAIM)	9
[1.6.1] Bond Magnetizability	11
[1.7] Brief Overview of the Remaining Chapters	11
[1.7.1] Chapter 2: Tuning the Electronic and Ligand Properties of Remote Carbenes	11
[1.7.2] Chapter 3: Effect of Ylide Substitution on the Stability and Electron Donation Ability of NHCs	13
[1.7.2.1] Moving Toward Ylide-Stabilized Carbenes	13
[1.7.2.2] Theoretical Strategies Toward Stabilization of Singlet Remote <i>N</i> -Heterocyclic Carbenes	14

Contents	Page No
[1.7.3] Chapter 4: Carbene Driven Stabilization of the H _{red} State of Biomimetic Model [FeFe]-Hydrogenase Complexes	15
[1.7.4] Chapter 5: Can Carbene Decorated [FeFe]-Hydrogenase Model Complexes Catalytically Produce Dihydrogen? An Insight from Theory	16
[1.8] Bibliography	19
Chapter 2: Tuning the Electronic and Ligand Properties of Remote Carbenes	27-56
[2.1] Introduction	27
[2.2] Computational Details	29
[2.3] Results and Discussion	29
[2.3.1] Molecular Geometries	29
[2.3.2] Singlet–Triplet and HOMO–LUMO Gaps	33
[2.3.3] Hydrogenation and Stabilization Energies	35
[2.3.4] Ligand Properties	38
[2.3.5] Nucleophilicity and Electrophilicity	42
[2.3.6] ³¹ P NMR Spectroscopy	45
[2.4] Conclusions	49
[2.5] Bibliography	51
Chapter 3: Effect of Ylide Substitution on the Stability and Electron Donation Ability of NHCs	57-103
[3.1] Moving Toward Ylide-Stabilized Carbenes	57
[3.1.1] Introduction	57
[3.1.2] Computational Details	59
[3.1.3] Results and Discussion	60
[3.1.3.1] Molecular Geometries	60
[3.1.3.2] Singlet–Triplet Separation and Thermodynamic Stabilities	64
[3.1.3.3] Ligand Properties	66
[3.1.3.4] Nucleophilicity Index	71
[3.1.4] Conclusions	74

Contents	Page No
[3.2] Theoretical Strategies Toward Stabilization of Singlet Remote <i>N</i> -Heterocyclic Carbenes	75
[3.2.1] Introduction	75
[3.2.2] Computational Details	77
[3.2.3] Results and Discussion	77
[3.2.3.1] Molecular Geometries	77
[3.2.3.2] Singlet–Triplet Separation	80
[3.2.3.3] Aromaticity–NICS and QTAIM Analysis	84
[3.2.3.4] Hydrogenation and Dimerization Energies	87
[3.2.3.5] Ligand Properties	89
[3.2.4] Conclusions	93
[3.3] Bibliography	94
Chapter 4: Carbene Driven Stabilization of the H_{red} State of Biomimetic Model [FeFe]-Hydrogenase Complexes	104-127
[4.1] Introduction	104
[4.2] Computational Details	107
[4.3] Results and Discussion	110
[4.3.1] Model Complexes with Normal Five-Membered NHCs (5NHC)	110
[4.3.2] Model Complexes with Normal Six-Membered NHCs (6NHC), Abnormal NHCs (<i>a</i> NHC) and Boron Substituted NHCs (BNHC)	114
[4.3.3] Model Complexes with Cyclic Alkyl Amino Carbene (CAAC)	115
[4.3.4] To Rotate or not to Rotate? The Role of Chelation	116
[4.4] Conclusions	118
[4.5] Bibliography	120
Chapter 5: Can Carbene Decorated [FeFe]-Hydrogenase Model Complexes Catalytically Produce Dihydrogen? An Insight from Theory	128-149
[5.1] Introduction	128

Contents	Page No
[5.2] Computational Details	129
[5.3] Results and Discussion	131
[5.3.1] Hydrogen Evolution Catalyzed by [1] ⁰	131
[5.3.2] Hydrogen Evolution Catalyzed by [2] ⁰	134
[5.3.3] Mechanistic Details for H ₂ Evolution Using [1] ⁰ and [2] ⁰	135
[5.3.4] Mössbauer Spectroscopy and Mulliken Spin Densities	139
[5.3.5] Redox and Acid-Base Properties	141
[5.4] Conclusions	143
[5.5] Bibliography	144
[6.1] List of Publications/Book Chapter	150
[6.2] List of Conference/Workshop attended	152