Contents

1 Introduction **1**
- 1.1 Hydrogen – Fuel of the Future? . . . 2
- 1.2 Basic Principles of Dihydrogen Activation . . . 3
- 1.3 Frustrated Lewis Pairs (FLPs) . . . 5
  - 1.3.1 General Concept . . . 6
  - 1.3.2 Mechanism of H_2 Activation in FLPs . . . 8
  - 1.3.3 Transition Metal-Based FLPs . . . 9
- 1.4 Hydrogenases – The Natural Hydrogen Economy . . . 11
  - 1.4.1 [FeFe] and [NiFe] Hydrogenases . . . 12
  - 1.4.2 The [Fe] Hydrogenase – A Novel Kind of Hydrogenase . . . 15
- 1.5 Model Complexes: Learning from Nature . . . 21
- 1.6 Objective . . . 24

2 Mimicking the Natural Hydride Acceptor Methenyl-H_4MPT$^+$ **27**
- 2.1 Hydride Acceptors in Biology and Chemistry . . . 28
  - 2.1.1 Imidazolium Ions as Hydride Acceptor Molecules . . . 28
  - 2.1.2 Models for N^5,N^{10}-Methenyltetrahydrofolate . . . 29
- 2.2 Synthesis of Imidazolinium Ions . . . 31
  - 2.2.1 General Strategy . . . 32
  - 2.2.2 Synthesis of Amidines . . . 34
  - 2.2.3 Formation of the Imidazolinium Heterocycle . . . 35
  - 2.2.4 Further Attempts to Synthesize Imidazolinium Salts . . . 37
- 2.3 Properties of Imidazolinium Ions . . . 40
  - 2.3.1 Structural Parameters of Imidazolinium Ions . . . 41
  - 2.3.2 Electrochemical Properties of Imidazolinium Ions . . . 44
  - 2.3.3 Reactivity of Imidazolinium Ions . . . 47
- 2.4 Conclusion . . . 51

3 The Chemistry of Amidines: Isomers and Silver Complexes **53**
- 3.1 General Aspects of Amidines . . . 54
  - 3.1.1 Classification of Amidines . . . 54
  - 3.1.2 Isomerism in Amidines . . . 55
  - 3.1.3 Molecular Association . . . 57
- 3.2 Structural Parameters of Amidines . . . 58

3.3 The Chemistry of Amidines in Solution . . . 61
3.3.1 Temperature and Concentration Dependencies . . . 62
3.3.2 Identification of Isomers . . . 68
3.4 The Coordination Chemistry of Amidines . . . 78
3.4.1 General Aspects . . . 78
3.4.2 Amidinatosilver(I) Complexes . . . 79
3.5 Summary . . . 83

4 The Transition Metal Lewis Base 85
4.1 The Choice and Synthesis of a Suitable Lewis Base . . . 86
4.1.1 General Aspects . . . 86
4.1.2 Synthesis of Carbonyl Metalates . . . 87
4.1.3 Alternative Metal Complexes . . . 88
4.2 Revisiting the Synthesis of K[CpRu(CO)$_2$] (**KRp**) . . . 90
4.2.1 A Revised Synthetic Protocol . . . 90
4.2.2 Isotope Labeling . . . 91
4.2.3 Elucidating the Structure and Further Properties of **KRp** . . . 92
4.3 **Rs** – A Metalate with Interesting Properties . . . 94
4.3.1 IR Spectroscopy . . . 95
4.3.2 Mass Spectrometry and UV/Vis Spectroscopy . . . 96
4.3.3 Solid-State ^{13}C MAS NMR Spectroscopy . . . 97
4.3.4 Elemental Analysis and Bulk Morphology . . . 101
4.3.5 Conclusion . . . 103
4.4 Summary and Outlook . . . 103

5 Transition Metal Frustrated Lewis Pairs 105
5.1 Synthesis of Transition Metal Frustrated Lewis Pairs . . . 106
5.1.1 Proof of Principle: Synthesis of **[Im^{-2H}]$^+$Fp$^-$** . . . 107
5.1.2 Imidazolinium-Based Lewis Pairs Lacking Frustration . . . 108
5.2 Nucleophilic Substitution Reactions . . . 110
5.2.1 The adduct **[Fp–C$_6$F$_4$MesIm]$^+$** . . . 110
5.2.2 Mechanistic Details . . . 113
5.2.3 A Second Example: Ruthenium Adduct **[Rp–TolFIm]$^+$** . . . 114
5.2.4 Consequences for Reactions with H_2 and Other Substrates . . . 117
5.3 Electron Transfer Reactions . . . 118
5.3.1 General Considerations . . . 118
5.3.2 Electron Transfer between **TolFIm$^+$Br$^-$** and **KFp** . . . 119
5.3.3 Structure of the Radical **TolFIm** . . . 121
5.3.4 Competing ET and Nucleophilic Substitution Reactions . . . 122
5.3.5 Dihydrogen Splitting Despite Other Reactivities? . . . 124
5.4 Further Examples and Unclear Reactions . . . 126
5.5 **TolFIm$^+$Br$^-$** and **Rs**: A Novel H_2 Splitting System . . . 128
5.5.1 DFT Calculations . . . 128
5.5.2 Advantages of **Rs** and H/D Exchange Reactions . . . 130
5.5.3 Heterolytic Splitting of Diydrogen . . . 131
5.6 Summary and Conclusion . . . 137

6 Experimental Section **139**
6.1 General Considerations . . . 139
6.2 Synthesis of Amidines . . . 141
6.3 Synthesis of Bisamidinatodisilver(I) Complexes . . . 149
6.4 Synthesis of Imidazolium Salt **[Im^{-2H}]$^{+}$Br^{-}** . . . 151
6.5 Synthesis of Imidazolinium Salts . . . 152
6.6 Synthesis of Imidazolidines . . . 160
6.7 Synthesis of Carbonyl Metalates . . . 163
6.8 Attempted Syntheses of Transition Metal FLPs . . . 166
6.9 Reactions with H_2 or D_2 . . . 170
6.10 Reactions with Other Substrates . . . 172
6.11 DFT Calculations . . . 172

Bibliography **175**

List of Abbreviations **197**

Appendix **201**
Structures of Important Compounds . . . 203
Crystallographic Data . . . 206
Electron Microprobe Analysis . . . 214
Additional NMR Data . . . 215
List of Scientific Contributions . . . 219
Acknowledgments . . . 221
Curriculum Vitae . . . 223