

Table of Contents

- 1. General Introduction - 1 -
- Part I: Electrochemical and Optical Properties of Redox-Active Heteroatom-Functionalized Polyacetylenes- 3 -
- 2. Introduction - 5 -
 - 2.1. Metal-Like Conductivity in Polyacetylenes - 5 -
 - 2.2. Soluble Heteroatom-Functionalized Polyacetylenes. - 6 -
 - 2.3. Motivation - 8 -
- 3. Results and Discussion..... - 9 -
 - 3.1. Electrochemical Characterization - 9 -
 - 3.1.1. Cyclic Voltammetry of the Monomers- 9 -
 - 3.1.2. Cyclic Voltammetry of the Polymers- 11 -
 - 3.2. Optical Properties of the Polymers..... - 14 -
 - 3.3. Summary..... - 19 -
- Part II: (Electro)chemical Activation of N₂ with Transition Metal Complexes- 21 -
- 4. Introduction - 23 -
 - 4.1. Thermodynamic and Kinetic Challenges of N₂ Activation - 24 -
 - 4.2. Metal Based N₂ Reduction - 26 -
 - 4.2.1. Associative N₂ Activation- 27 -
 - 4.2.1.1. Transition Metal Catalysts for N₂-to-NH₃ Reduction..... - 28 -
 - 4.2.1.2. Electrocatalysts for N₂-to-NH₃ Reduction.... - 33 -

4.2.2.	Dissociative N ₂ Activation.....	- 37 -
4.2.2.1.	Molecular Bimetallic Systems and Splitting into Terminal Nitrido Compounds	- 37 -
4.2.2.2.	Molecular Electrochemical N ₂ Splitting.....	- 45 -
	Dinuclear Nickel Dinitrogen Complexes Supported by β-Diketiminato Ligands.....	- 52 -
5.	Introduction.....	- 52 -
5.1.	Motivation	- 56 -
6.	Results and Discussion	- 57 -
6.1.	Electrochemical Conversion	- 57 -
6.1.1.	Dinickel Bromido, Hydroxido and Dihydrido Complexes	- 57 -
6.1.2.	Dinickel Dinitrogen Complexes.....	- 63 -
6.1.3.	PCET of the Dinickel Dinitrogen Complexes	- 67 -
6.2.	Attempts for Electrocatalytic N ₂ RR	- 73 -
6.3.	Summary and Outlook.....	- 74 -
	(Electro)chemical N ₂ Splitting in the Coordination Sphere of Molybdenum	- 78 -
7.	Motivation.....	- 78 -
8.	Results and Discussion	- 80 -
8.1.	Syntheses.....	- 80 -
8.1.1.	Synthesis of LH	- 80 -
8.1.2.	Synthesis of [Mo(LH)Cl ₃] (20H).....	- 81 -
8.1.3.	Synthesis of [Mo(LH)NCl ₂] (21H)	- 84 -
8.2.	Thermochemistry of 20H	- 88 -
8.2.1.	(De)protonation Study and pK _a Determination	- 88 -

8.2.2.	Electrochemical Characterization and BDFE Calculation	- 91 -
8.3.	Reactivity Towards N ₂	- 97 -
8.3.1.	Chemical N ₂ -to-NH ₃ Reduction	- 97 -
8.3.2.	Electrochemical N ₂ Splitting	- 101 -
8.3.3.	Insights into the Mechanism of Electrochemical N ₂ Splitting	- 108 -
8.4.	Summary and Outlook.....	- 113 -
9.	Experimental.....	- 117 -
9.1.	Analytical Methods.....	- 117 -
9.1.1.	NMR Spectroscopy	- 117 -
9.1.2.	Mass Spectrometry.....	- 117 -
9.1.3.	IR Spectroscopy	- 117 -
9.1.4.	EPR Spectroscopy	- 118 -
9.1.5.	Elemental Analysis.....	- 118 -
9.1.6.	UV/Vis/nIR Spectroscopy.....	- 118 -
9.1.7.	X-Ray Crystallography.....	- 119 -
9.1.8.	Gas Chromatography.....	- 119 -
9.1.9.	Electrochemical Measurements	- 119 -
9.1.9.1.	Cyclic Voltammetry.....	- 120 -
9.1.9.2.	Controlled Potential Coulometry.....	- 120 -
9.1.9.3.	UV/Vis/nIR-Spectroelectrochemistry	- 121 -
9.1.9.4.	IR-Spectroelectrochemistry	- 122 -
9.2.	Syntheses.....	- 122 -
9.2.1.	General Considerations	- 122 -
9.2.2.	2,6-Dimethyl-4-ethoxymethoxy pyridine (17).....	- 123 -

9.2.3.	2,6-Bis(di- <i>tert</i> -butylphosphinomethyl)-4-ethoxymethoxy pyridine (18)	- 124 -
9.2.4.	2,6-Bis(di- <i>tert</i> -butylphosphinomethyl)-4-pyridone (LH)	- 125 -
9.2.5.	[Mo(LH)Cl ₃] (20H)	- 127 -
9.2.6.	[Mo(LH)NCl ₂] (21H).....	- 128 -
9.2.7.	General Procedure for N ₂ -to-NH ₃ Reduction .	- 128 -
9.3.	UV/Vis Titration of 20H	- 129 -
9.3.1.	pK _a Calculation.....	- 130 -
9.4.	Ammonia Quantification	- 131 -
9.4.1.	General Procedure	- 131 -
9.4.2.	[Ni(NH ₃) ₆]Cl ₂	- 132 -
9.4.3.	CPEs of 9	- 132 -
9.4.4.	Catalytic N ₂ -to-NH ₃ Reduction Catalyzed by 20H	- 136 -
9.4.5.	Catalytic N ₂ -to-NH ₃ Reduction Catalyzed by 21H	- 138 -
9.5.	CV Titration of SmI ₃ (thf) _{3.5}	- 140 -
9.6.	Electrochemical N ₂ Splitting of 20H into 22 ⁻	- 142 -
9.6.1.	Quantification <i>via</i> ³¹ P-NMR Spectroscopy.....	- 142 -
9.6.2.	Quantification <i>via</i> ¹ H-NMR Spectroscopy	- 144 -
9.6.3.	CPE under ¹⁵ N ₂ and Quantification <i>via</i> ¹ H-NMR Spectroscopy	- 145 -
9.7.	Spectroelectrochemistry	- 147 -
9.7.1.	UV/Vis/nIR-SEC of 3 , 4 and 5	- 147 -
9.7.2.	UV/Vis-SEC of 20H	- 147 -
9.7.3.	IR-SEC of 20H	- 148 -

10.	Literature	- 149 -
11.	Appendix.....	- 159 -
11.1.	Additional CVs.....	- 159 -
11.2.	Additional Spectra	- 165 -
11.2.1.	nIR-SEC Spectra.....	- 165 -
11.2.2.	NMR Spectra	- 170 -
11.2.3.	IR Spectra	- 176 -
11.2.4.	Mass Spectra.....	- 177 -
11.3.	Crystallographic Data.....	- 180 -
11.4.	List of Compounds	- 181 -
11.5.	List of Abbreviations	- 186 -
	Scientific Contributions	- 189 -