

Table of Contents

A. Introduction	1
A.1 Molecular Calcium Hydrides	1
A.2 Divalent Lanthanide Hydrides.....	3
A.3 Hydroelementation of Olefins	4
A.4 Hypervalent Silicates.....	7
A.6 Alkali Metal Silanides	8
A.6 Aims and Scope of this Thesis	9
A.7 References	10
B. Results and discussion	14
B.1 Synthesis and Characterization of Molecular Calcium Hydrides Stabilized by Macrocyclic Ligands.....	14
B.1.1 Introduction	14
B.1.2 Synthesis and Characterization of Calcium Hydrides Stabilized by Me ₄ TACD	15
B.1.3 Synthesis and Characterization of Calcium Hydrides Stabilized by Me ₃ TACN	25
B.1.4 Synthesis and Characterization of Calcium Hydrides Stabilized by Me ₃ PACP	30
B.1.5 Conclusion.....	32
B.1.6 Experimental Section	33
B.1.7 References	42
B.2 Reactivity of Molecular Calcium Hydrides Stabilized by a Macrocyclic Ligand.....	44
B.2.1 Introduction	44
B.2.2 Results and Discussion.....	44
B.2.2.1 Isotopic Exchange of H ₂ and D ₂	44
B.2.2.2 Hydrogenation of Unactivated Olefins	45
B.2.2.3 Regioselective Hydrosilylation of Olefins Catalyzed by a Molecular Calcium Hydride Cation.....	49
B.2.2.4 Reactivity toward Functionalized Silanes	56
B.2.2.5 Reactivity toward Terminal and Internal Acetylenes.....	59
B.2.2.6 Silylation of Aromatic C–H bonds.....	61
B.2.2.7 Hydrodefluorination of Fluorobenzene	62
B.2.2.8 Reduction of Cyclooctatetraene (COT).....	64
B.2.2.9 Reduction of CO ₂ and CO.....	66
B.2.2.9 Reactivity toward BH ₃ ·thf.....	69

B.2.3 Conclusion.....	71
B.2.4 Experimental Section	71
B.2.5 References	80
B.3 Molecular Hydrides of Divalent Ytterbium: Selective Catalyst for Hydrofunctionalization of Olefins.....	83
B.3.1 Introduction	83
B.3.2 Results and Discussion.....	83
B.3.3 Conclusion.....	97
B.3.4 Experimental Section	97
B.3.5 Supporting Information	102
B.3.6 References	103
B.4 Hypervalent Hydrosilicates Connected to Light Alkali Metal Amides: Synthesis, Structure, and Hydrosilylation Catalysis.....	105
B.4.1 Introduction	105
B.4.2 Results and Discussion.....	105
B.4.3 Conclusion.....	111
B.4.4 Experimental Section	111
B.4.5 Supporting Information	115
B.4.6 References	115
B.5 Alkali Metal Triphenyl- and Trihydridosilanides Stabilized by a Macrocyclic Ligand..	117
B.5.1 Introduction	117
B.5.2 Results and Discussion.....	117
B.5.3 Conclusion.....	125
B.5.4 Experimental Section	125
B.5.5 Supporting Information	129
B.5.6 References	130
C. Summary.....	132
D. Appendix	135
D.1 General Experimental Details	135
D.2 References	136
D.3 List of Abbreviations.....	136
D.4 List of Compounds.....	138
D.5 Curriculum Vitae.....	140
D.6 Publications in Peer-Reviewed Journals	141