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Title:	Covalent and Cationic Main-Group (B,Al,Mg) and Zn Complexes Supported by Monoanionic N/P Ligands for Catalytic Hydrosilylation and Hydroboration Reactions Including Detailed Mechanistic Insights
Authors:	Rawat, Sandep
Keywords:	Covalent Monoanionic Hydroboration Hydrosilylation
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Abstract:	Abstract Precious transition metals have undoubtedly played a vital role in the survival and success of chemical/catalytic industry. However, the low abundance, high cost and toxic nature of many of these metals created the need for the development of catalytic methodologies based on earth abundant, inexpensive and environmentally benign elements. In this direction, main group elements particularly B, Al, Mg, Ca etc. and base metals have drawn immense limelight and the interest is growing at an astonishing rate, and shown remarkable potential for important molecular transformations. ¹ Indeed, the rational designs of ligand scaffold around the central atom in the complexes is the first prerequisite to spike up the catalytic performance in homogeneous catalysis. The work presented in the thesis highlights the syntheses and characterization of well-defined low coordinated B, Al, Mg and Zn covalent and cationic complexes featured by monoanionic and chelating bis(phosphinimino)amide (P2N3) and iminophosphonamine (NPN) ligand scaffolds. Further, catalytic activity of these complexes with systematic and detailed mechanistic investigations have been undertaken with the focus on highly atom economic and green hydroelementation reactions. All of the complexes in this research are newly synthesized and well characterized by multinuclear NMR, HRMS and single crystal X-ray techniques. The first section of the thesis deals with hydrido-borenium cation for the hydrosilylation of a broad range of carbonyls under mild conditions. Additionally, the deep insights into mechanism behind the transformation has also been provided. Afterwards, the cationic aluminum methyl/hydride complexes that were exploited for the chemo-selective/regioselective cyanosilylation of carbonyls using trimethyl cyanide (TMS-CN) and controlled semi-reduction of nitriles using triethylsilane (Et ₃ SiH) have been discussed. Second section of the thesis deals with the synthesis of structurally diverse zinc alkyl complexes, these molecules are proven to be the competent catalyst for the dihydroboration of nitriles and hydroboration of imines, carbonyls, esters and pyridine. Subsequently, the role of ligand's steric and electronic parameters to stabilize and fine-tune the reactivity of two coordinated zinc cations has also been discussed. The low-coordinated zinc complex was utilized for the hydrosilylation and hydroboration of imines under ambient conditions. To scrutinize the possible mechanistic pathway several control experiments and DFT calculation have been performed in a conclusive manner. The last part of the thesis is about a homoleptic magnesium complex for selective reduction of more taxing molecules like secondary amide and alkynes via hydroboration approach.
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