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Title: Syntheses, Reactivity and Catalytic Applications of Electronically Unsaturated Cationic Aluminum Complexes Including Redox Active Bis(imino) acenaphthene (BIAN) Aluminum Complexes

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Abstract: Abstract The current quest to develop sustainable chemistry, with efficient surrogates to the precious transition metals, by utilizing highly earth abundant sources have gained tremendous significance. In this regard, complexes of main group elements have drawn an incredible attention over the past few decades, in particular from group 13 elements the mononuclear cationic aluminum complexes are at the limelight attributed by its high earth abundance and Lewis acidic nature. The earlier investigations on these Al complexes were purely driven from synthetic and structural curiosity however, the recent implications in catalytic realm particularly in small molecule activation has gained an entirely new perspective. Though, the synthesis of such low coordinated and reactive Al species is not an easy task and entails the careful tailoring and scrutiny of steric and electronic parameters of the ligand framework to render access for the development of sustainable catalytic system and proper understanding of structural-reactivity relationship and mechanistic insights. The thesis will delineate the systematic and rational approaches to gain an in-depth understanding of the activation of unsaturated molecules mediated by cationic aluminum complexes as efficient catalysts for organic transformations. The first chapter of the thesis gives a brief description of the introductory remarks and perspective of the work. Second chapter deals with the synthesis of bis(phosphinimino)amide featured highly Lewis acidic three coordinated cationic aluminum hydride and aluminum methyl complexes. The electronic unsaturation of these Al cations benefitted to activate the substrates with functional groups such as carbonyls, imines and alkynes via Lewis adduct formation, subsequent activation and the selective addition of hydride. Therefore, these cations work as competent catalysts to facilitate the reduction of unsaturated species using HBpin/PhSiH₃ as reducing agents. Special emphasis has been given to comprehend the mechanistic insights via several control experiments, isolation and characterization of intermediates and DFT calculations. The third chapter of the thesis presnets a systematic fine-tuning of Lewis acidity via placement of electronegative substituents in the primary coordination sphere of aluminum center resulted in the generation of intriguing cationic aluminum alkoxide complexes. The qualitative as well as quantitative estimation of Lewis acidity has been done via experimental and theoretical approaches. In the subsequent section, β -diketiminate stabilized cationic aluminum methyl complex has been successfully exploited towards the selective deoxygenation of amides to afford the primary, secondary and tertiary amines. The fourth chapter of the thesis describes the application of the cations in deoxygenative reduction of tertiary, secondary and primary amides. The last section of the presentation aims to present our efforts towards successful synthesis and characterization of redox active mono- and di-anionic BIAN ligand stabilized paramagnetic and diamagnetic aluminum sulfur metallacycles including the Al₂S₂ metallacycles. All of the new molecules have been characterized by single crystal X-Ray and as applicable by multinuclear NMR and EPR.

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