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Title:	Well-defined Zn-CAAC and Hg-CAAC Complexes and BICAAC Complexes of Si, Ni and Zn: Catalytic activity and Mechanistic Insights of Ni(II)-BICAAC and Ni(O)-BICAAC Complexes in Negishi Cross-Coupling Reaction
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Abstract:	<p>Abstract: Carbenes are well known divalent carbon species with six valence electrons. The singlet and triplet electronic states of carbenes have been clearly identified and are governed by the steric and electronic properties of the substituents on the divalent carbon. Owing to two unpaired electrons in two degenerate orbitals, the triplet carbenes exhibit biradical behavior whereas, the singlet carbenes show ambiphilic reactivity due to the presence of a filled HOMO and a low-lying LUMO orbitals. The ambiphilic characteristics of singlet carbenes has been a great advantage to exploit their binding as ligands with metal/non-metal species. Several stable singlet carbenes have been developed in the last few decades of which the N-heterocyclic carbenes (NHCs) and their complexes have shown immense importance owing to their countless applications in the domain of catalysis, organometallics and metallodrugs. The ease of synthesis of a library of diverse carbene complexes with metals and non-metals opened up the doors to explore new dimensions in the field of low valent chemistry, supramolecular chemistry, and important organic transformations. In the present work, we have utilized the potential of an advanced version of NHCs, particularly cyclic (alkyl)(amino)carbenes (CAACs) and bicyclic (alkyl)(amino)carbenes (BICAACs) having better ambiphilic behavior (-donor and -acceptor properties) for a diverse range of applications. The CAAC carbenes have been applied to synthesize new complexes of Zn(II) and Hg(II). These complexes are further utilized in the synthesis of derivatives via salt metathesis reactions which afforded either covalent or cationic metal complexes depending upon the nature of salts used for metathesis reaction (AgNO₃, AgClO₄ and AgOTf) and the reaction conditions. In the second section, low valent chemistry of silicon supported by BICAAC has been explored. A number of low-valent paramagnetic and diamagnetic silicon compounds have been synthesized using BICAAC as a strong - acceptor ligand scaffold. These complexes are characterized by multinuclear NMR, HRMS, EPR, and SQUID techniques along with the thorough DFT studies on molecular geometries and nature of bonding. The last section involves the synthesis of a series of BICAAC supported Ni(II) complexes and a Ni(0) complex and exploitation of these complexes towards the Negishi cross-coupling reaction. Several control experiments and stoichiometric reactions were performed to ascertain various key intermediates that revealed the catalytic cycle for BICAAC-Ni(0) catalyst involve Ni(0)/Ni(II) intermediates whereas BICAAC-Ni(II) catalyst proceed via Ni(I)/Ni(III) intermediates. The outcome of my research will provide a systematic understanding of the role of carbene complexes in catalysis and identify the key intermediates.</p>
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