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Title: Complexes of Group 13 and 14 Elements with Monoanionic [N,N'] Chelating Ligands: Synthetic, Reactivity and Structural Investigations Including Co(II), Ni(II) and Cu(II) Complexes with Neutral N-Arylimidoamidines

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Abstract: In recent years, a renaissance in the field of main group chemistry has been witnessed, covering a diverse array of developments and potential applications in fields spanning from catalysis to molecular electronics. These have often evolved from studies in fundamental chemistry such as studies of the chemistry of low oxidation state and/or low coordination number compounds of the main group elements, fundamental studies in Lewis-acid/Lewis-base reactivity, main group heterocycles, free radicals and studies of the structure and bonding in main group compounds. From the p-block of the periodic table, the chemistry of group 13 and 14 elements has gained particular attention not just with the focus to study fundamental aspects including structure and bonding but also to explore their applications that range from Lewis acids to catalysts and catalyst promoters. The synthetic approach to realize these tailor made highly reactive molecules require kinetic stabilization offered by the supporting ligand. Among many features, steric and electronic parameters are the most crucial ones to design/select a ligand to serve these purposes. The thesis will describe: (i) Rational for the selection of monoanionic [N,N'] chelating ligands with N2P and N3P2 backbone over the conventional C/N based ligands by direct comparison of their steric and electronic features. (ii) Use of these ligands in the synthesis of stable complexes of group 13 elements, their reaction chemistry with a focus on the preparation of cationic borenium and organolauminum complexes with weakly coordinating anions. (iii) Preparation of heteroleptic germylenes and stannylenes in the form of stable four membered metallacycles of the type N2PGe and N2PSn respectively, to investigate their robustness towards Lewis-acid/Lewis-base reactivity, metathesis and oxidation reactions. Synthesis of Co(II), Ni(II) and Cu(II) complexes with neutral bidentate [N,N'] ligands based on the C2N3 backbone will be presented in the last part of the thesis. Two types of ligand, N-benzyl-pyridylbenzaamidines and N-arylimidoamidines, with slightly different backbone will be focused. The symmetrical and unsymmetrical isomer of the later ligand and exclusive synthesis of the unsymmetrical ligand will also be discussed. Unambiguous composition of all the newly synthesized compounds have been established by heteronuclear NMR (¹H, ⁷Li, ¹¹B, ¹³C, ¹⁹F, ²⁷Al, ³¹P{¹H}), FT-IR, UV-Vis spectroscopy, elemental analyses, mass spectrometry and single crystal X-ray diffraction techniques


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