## Abstract

The objectives of this thesis include: a) identification of aromaticity in non-carbocyclic  $\pi$ - and  $\sigma$ -aromatic molecules (all-metal and all-nonmetal) with the aid of computational techniques, b) studying the mechanism of transition metal catalyzed reactions involving selected aromatic molecules, c) study of an exotic phenomenon, *viz.*, bond-stretch isomerism associated with an aromatic molecule, Be<sub>3</sub><sup>2-</sup>, and d) looking for aromaticity in extended networks containing periodic array of metals.

In **Chapter 1** we have discussed a brief introduction to the history and recent developments in aromaticity and theoretical background of the computational methods used in this thesis. Our efforts to characterize aromaticity in novel molecular environments are discussed in **Chapters 2** and **3**. In **Chapter 2**, we have discussed  $\pi$ -aromaticity in all-pnictogen cyclic anions. In addition, we have studied the mechanism of a plausible synthetic pathway for the smallest analogue, and a potential use of these anions as  $\eta^{5}$ ligands in metallocenes. Similarly in **Chapter 3**, we have analyzed the  $\sigma$ -aromaticity of  $M_3^+$  (M = Cu, Ag, Au) and compared with that in Li<sub>3</sub><sup>+</sup> and H<sub>3</sub><sup>+</sup>. We have also explored the stabilization of  $M_3^+$  by coordination with various ligands, noble gases, and CO.

Reactivity in transition-metal catalyzed reactions involving some selected aromatic molecules, *viz.*, Ru(II)-catalyzed aromatic substitution and Au(III)-catalyzed benzannulation reactions, is rationalized in **Chapters 4** and **5**, respectively. We have described the mechanism of regio- and stereoselective addition of alkynes to pyrazole catalyzed by Ru(II)-catalysts in **Chapter 4**. By exploring the catalytic cycle, we have established a unique structure–selectivity relationship of two catalysts. Similarly, in **Chapter 5** we have analyzed the electronic effects of substituents on chemo- and regioselectivity in Au(III)-catalyzed benzannulation of nicotinaldehydes with alkynes.

Bond-stretch isomerism, a much-debated phenomenon, is explored in the  $\pi$ -aromatic Be<sub>3</sub><sup>2-</sup> molecule, in **Chapter 6**. Two isomers are distinguished on different potential energy surfaces even at the sophisticated level of calculations. In **Chapter 7**, we have described the search for aromaticity in extended three-dimensional (3-D) networks containing infinite chains of Sr<sub>n</sub> and Ba<sub>n</sub> rectangles. Although the existence of aromaticity was proposed, the analysis of the structures has proven that the metals are not covalently bonded with each other and hence are not aromatic. Meanwhile, our studies have shown that these porous 3-D metal–organic frameworks could have a potential use for noble gas storage or as a filter to separate Ne from a gas mixture.

**Keywords**: Aromaticity, Electronic structure calculations, Bonding, Electron density analysis, Energy decomposition analysis, Reaction mechanism.