

Ligand control in chemo, regio-and enantioselective cycloaddition of alkynes and 1,3-dienes

Dipshi Singh, Mahesh M. Parsutkar and T.V. RajanBabu*

Department of Chemistry and Biochemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210, United States

Asymmetric synthesis of substituted 1,4 cyclohexadienes and cyclobutenes has received great attention in recent years. Strategies such as base metal catalyzed cycloaddition bypass the need of harsh reaction conditions which are often required for synthesis of such motifs. These strategies using base-metals as catalysts are

also valuable in constructing substituted cyclic motifs from readily available and inexpensive materials such as dienes and alkynes. Such reactions can be cost effective and environmentally friendly. In past decade, low valent cobalt has shown promising reactivity in forming new C-C and C-X (e. g., X= Si, B, N) bonds in high stereoselectivity. Through our studies, we found that cationic cobalt(I) complexes can catalyze intermolecular cycloaddition reactions of alkyne and 1,3-dienes in regio-and enantioselective manner. We also discovered that the involvement of 4π electrons or 2π electrons of 1,3-dienes can be controlled by the judicious choice of ligands employed on cobalt leading to [4+2] and [2+2] cycloaddition products respectively in high regio- and stereoselectivity. This excellent selectivity complimented with moderate to good yields provided us with broadly applicable protocol for synthesis of diversely substituted enantiopure cyclic motifs with enantiomeric excesses upto 99%. The scope of this method has been expanded over simple aliphatic and aromatic 1,3-dienes and alkynes bearing various functional groups. The methodical development of this transformation along with the ligand effects and possible mechanisms will be discussed in detail.

