

INTRAMOLECULAR HYDROAMINATION BY LOW-COORDINATED CATIONIC ALUMINUM SPECIES Manish Khandelwal and Rudi Wehmschulte

Cationic low coordinated aluminum compounds $\{[\text{Et}_2\text{Al}]^+ ; [\text{ArN}(\text{SiMe}_3)\text{AlR}]^+ ; [\text{TerphAlEt}]^+\}$ $\{\text{Ar} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2 \text{ (Mes)}, 2,4,6\text{-}i\text{Pr}_3\text{C}_6\text{H}_2 \text{ (Dipp)}; \text{Terph} = 2,6\text{-Dipp}_2\text{C}_6\text{H}_3, 2,6\text{-}\{\text{C}_6\text{H}_3\text{Cl}_2\}_2\text{C}_6\text{H}_3 \text{ (DCP)}\}$ were investigated towards intramolecular hydroamination of aminopentenes. The cationic species were generated by employing carborane based weakly coordinating anions (WCAs) such as $[\text{CB}_{11}\text{H}_6\text{X}_6]^-$ ($\text{X} = \text{Cl}, \text{Br}$ or I). The reactivity of the neutral and the cationic species was then tested towards intramolecular hydroamination of substituted aminopentenes. The results show absolute regioselectivity by following Markovnikov's addition across the C-C double bond. In some cases, isomerization of the substrate was also observed which emphasizes on the Markovnikov's type addition based transition state. The neutral compounds were less reactive underlining the enhanced Lewis acidity of the cationic species. A combination of electron withdrawing substituents on the ligand (DCP) and a less sterically crowded substrate, can result into an interesting catalytic system with reactivity similar to the cationic species. The reactions were monitored by ^1H NMR and the yields are based on proton integration with respect to an internal reference.

