

Dehydrocoupling of amine boranes via transition metal and main group metal catalysts

Amine boranes have elicited heightened interest in recent years due to their potential use in hydrogen storage systems, as hydrogenation reagents, and as polymer precursors. Methods to access dehydrocoupled amine-borane products are desirable and have been increasingly studied. The dehydrocoupling of primary and secondary amine boranes will be presented using a non-metallocene, early transition-metal catalyst, κ^5 -[(Me₃SiNCH₂CH₂)₂NCH₂CH₂NSiMe₂CH₂]Zr (**1**). Complex **1** has demonstrated high catalytic reactivity towards primary and secondary amine boranes at ambient temperature cleanly yielding borazines and cyclic dimers, respectively. Of interest is the observation of a highly reactive amino-borane as an intermediate in the formation of [^tBuNBH]₃ that is not observed during dehydrocoupling of Me₂NHBH₃. A variety of amine borane dehydrocoupled products such as borazines, borazanes, and μ -aminodiboranes (NRR'B₂H₅ [R = R' = Me; R = ^tBu, R' = H]) can be accessed using a Cp*₂SnCl₂ (Cp* = pentamethylcyclopentadienyl) (**2**) catalyst. Though these reactions are less clean, they serve as an uncommon example of p-block metal dehydrocoupling. The optimized substrate scope and reactivity of **2** and other related tin-based complexes (Ph₂SnCl₂ and SnCl₂) will be presented as well as mechanistic insights.