Cyclization of Di(tert-butyl-methyl)ketazine to 1,2-Diaza-3-bora- and 1,2-Diaza-3-sila-cyclopent-5-enes

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The results of quantum chemical calculations on lithium ketazides suggest mainly four isomeric structures with different modes of lithium coordination (A – D). A monolithium ketazide thf-adduct (1) was isolated supporting the results of the quantum chemical calculations. In reactions of the lithiated di(tert-butyl-methyl)ketazine with BCl\textsubscript{3} and Cl\textsubscript{2}BPh\textsubscript{3}, 1,2-aza-azonia-3-borata-cyclopent-5-enes (2, 3) were isolated. Substitution of a chlorine atom of 2 and 3 with \textit{t}-BuLi leads to the formation of derivatives 4 and 5. HCl elimination from 2 with Et\textsubscript{3}N gives – via a diazaboracyclopentene (6) – a bicyclus 7. In the reaction of the dilithiated ketazine with F\textsubscript{2}BN(SiMe\textsubscript{3})\textsubscript{2}, the diaza-boracyclopentene 8 is obtained while with Cl\textsubscript{4}Si, F\textsubscript{3}SiN(SiMe\textsubscript{3})\textsubscript{2}, and Cl\textsubscript{2}SiMe\textsubscript{2} the diazasilacyclopentenes 9 – 11 are generated. SiF\textsubscript{4} reacts with the dilithium ketazine to give a spirocycly (12). The monolithium ketazide and Cl\textsubscript{2}SiMe\textsubscript{2} react at 30 °C to give a four-membered ring isomer of the substitution product which is formed via a 1,3-chlorine shift from silicon to carbon (13). A tetrameric silanolate was isolated as a by-product in this reaction. It gives evidence for the structure of lithium ketazide A. Crystal structures of 5, 7, 10, and 14 are reported.

Key words: Lithium Ketazides, Quantum Chemical Calculations, Diaza-bora-cyclopentenes, Diaza-sila-cyclopentenes, Aza-silacyclobutane