Hydroboration of Bis(trimethylsilyl)ethynyl)silanes with 9-Borabicyclo[3.3.1]nonane: A New Route to 1-Sila-3-cyclopentenes and to a 1-Sila-2,4-cyclopentadiene

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The hydroboration of bis(trimethylsilyl)ethynyl)silanes Me(R)Si(C≡C–SiMe₃)₂ 1a (R = Me) and 1b (R = H) with 9-borabicyclo[3.3.1]nonane (9-BBN) does not give products related to the usual cis-1,2-hydroboration of one or both C≡C bonds. Instead, the major products obtained from 1a are the two isomers of 2,5-bis(trimethylsilyl)-2,5-bis[9-(9-borabicyclo[3.3.1]-nonyl)]-1-sila-3-cyclopentene 2a and 2a′ (silolenes), and from the reaction of 1b with 9-BBN solely the silolene 2b can be isolated. The silolenes 2a and 2b were studied by X-ray structural analysis. The reaction of 1a with 9-BBN in a 1:1 molar ratio gave a mixture of products, consisting of the silolenes 2a and 2a′, some unidentified material, and 2,5-bis(trimethylsilyl)-3-[9-(9-borabicyclo[3.3.1]nonyl)]-1-sila-2,4-cyclopentadiene 3a. The silole 3a was then prepared in pure state by the reaction of 1a with 9-isobutyl-9-borabicyclo[3.3.1]nonane in boiling toluene, where the borane decomposes slowly into isobuten and 9-BBN which is trapped by 1a. The proposed structures of the heterocycles 2 and 3 in solution follow from a consistent set of NMR data (¹H, ¹¹B, ¹³C, ²⁹Si NMR).

Key words: Alkynes, Silole, Hydroboration, Isomerisation, NMR