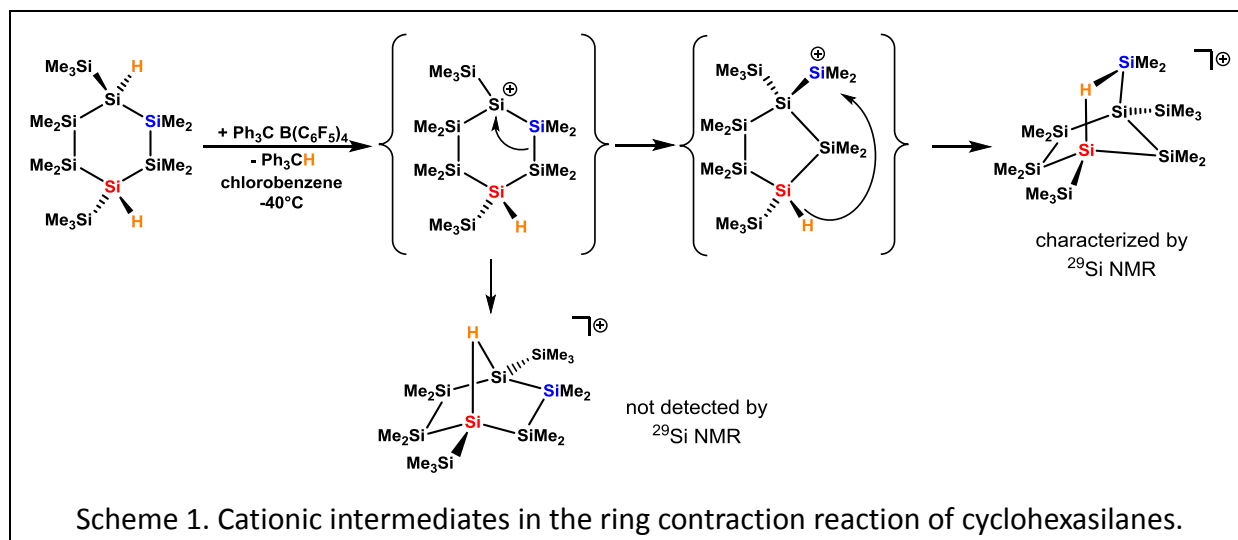


Wagner-Meerwein-Type Rearrangements of Polysilanes - Subtle Trapping of Intermediates

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Linear and cyclic, permethylated polysilanes^[1,2] transform in a Lewis acid catalyzed Wagner-Meerwein analogue rearrangement into branched isomers. Our experimental investigations on Lewis acid catalyzed rearrangements of polysilanes give astonishing insights into silyl cation chemistry. We use hydrogen-substituted polysilanes to define the position of the initial positively charged atom via a Bartlett-Condon-Schneider hydride transfer reaction. The rearrangement reaction of the formed cation is followed by ²⁹Si NMR spectroscopy. Cationic intermediates of these skeletal rearrangements are stabilized and trapped by the formation of Si-H-Si bridges (see Scheme 1 for an example). This structural motif^[3] is easily detected by its characteristic NMR parameter. Based on the results of our stable silicon cation study we are able to provide important insights into the skeletal rearrangement reactions of polysilanes



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