



Wagner-Meerwein-Type Rearrangements in Oligosilanes

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Linear and cyclic permethylated polysilanes transform in a Lewis acid catalyzed sila-Wagner-Meerwein (SWM) rearrangement into branched isomers and can be used to build complex oligosilane structures.^[1-5] These rearrangements proceed via cationic intermediates and their mechanism was studied previously by us by trapping of reactive intermediates from specially designed precursors and low temperature NMR spectroscopy (Figure 1).^[6,7] Here, we will demonstrate the extension of this methodology to the synthesis of hydrido-bridged oligosilanylsilyl dications, a new class of poly-Lewis acids (Figure 2a).^[8] Furthermore, we will show that the SWM reaction with germaoligosilanes is very selective and can be used to build up complex germaoligosilane clusters (Figure 2b,c).^[9, 10]

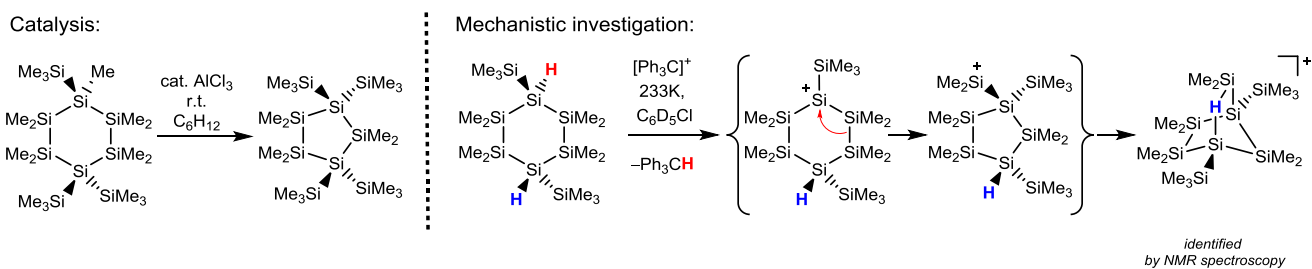


Figure 1. AlCl_3 -catalyzed cyclohexasilane to cyclopentasilane rearrangement and its mechanistic investigation.^[6]

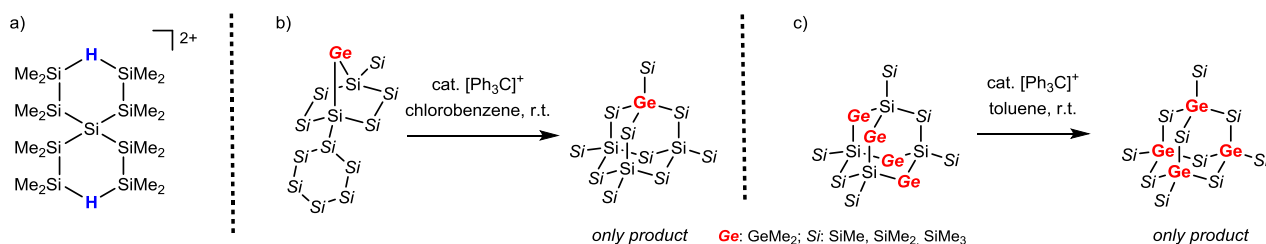


Figure 2. a) A hydrido-bridged oligosilanylsilyl dication.^[8] b) and c) Selective SWM rearrangement of germaoligosilanes.^[10]

References

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