Supersilylsilane R*SiX₃: Darstellung, Charakterisierung und Strukturen; sterische und van-der-Waals Effekte der Substituenten X [1]

Supersilylsilanes R*SiX₃: Syntheses, Characterization and Structures; Steric and van-der-Waals Effects of Substituents X [1]

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Supersilylsilanes R*SiX₃ (R* = supersilyl = Si₃Bu₃; X = H, Me, tBu, SiMe₃, F, Cl, Br, I, OMe, OSO₂CF₃) are prepared (i) by reactions of supersilylhalosilanes with supersilyl sodium NaR* (Hal/R* exchange), (ii) by reactions of supersilylhalosilanes with hydride H-/;; (Hal/H exchange), (iii) by reactions of supersilylsilanes with halogens Hal₂ (H/Hal exchange, R*/Hal exchange), (iv) by reactions of supersilylhalosilanes with nucleophiles like F-/;;, MeO-/;; (Hal/F or Hal/OMe exchange) and (v) by reactions of supersilylsilanes with strong acids (H/OSO₂CF₃ exchange). NMR chemical shifts δ(²⁹Si) of the SiX₃ groups of R*SiX₃ strongly depends on the nature of X. The supersilylsilanes R*SiX₃ are in part moisture sensitive (especially compounds with SiX₃/SiHHal₂ and SiH₂Hal), in part sensitive against oxygen (compounds with SiX/SiBr or SiI), and some of them react with supersilyl sodium by supersilanidation (for example R*SiF₃, R*SiH₂Cl, R*SiMeHCl) or by reduction (for example R*SiCl₂, R*SiMeBr₂, R*SiPhBrCl). X-ray structure analyses of disilanes tBu₃Si-SiX₃ with SiX₃/SiBu₃, SiPh₃, SiI₃, SiPhCl₂ show a staggered conformation. Due to steric repulsion of the tBu₃Si and SiX₃ groups as well as van-der-Waals attraction of the substituents tBu and X in tBu₃Si-SiX₃ the SiSi bonds are longer than 2.34 Å (the normal SiSi single bond length) and the torsion angles are smaller/larger than 60° (the ideal staggered conformation). From the extent of SiSi bond elongation and CSiSiX angle compression it is concluded that the bulkiness of X increases in direction Cl < I < Ph < SiMe₃ < CMe₃ (tBu₃Si-SiBu₃ has to date the longest SiSi bond of all disilanes) and the van-der-Waals forces between tBu/X increase in direction tBu/I < tBu/tBu < tBu/Ph.