SiF-NH-Funktionelle Cyclodisilazane – Synthese und Reaktivität

SiF-NH-Functional Cyclodisilazane – Synthesis und Reactivity

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Dichlorosilanes with bulky substituents R(Me₃C)SiCl₂ react with liquid ammonia to give geminal silvldiamines $[R(Me_3C)Si(NH_2)_2, 1: R = CH_2Me_2, 2: R = CHMe_2]$. In the reaction of the monolithium derivatives of these compounds with halosilanes 1-amino-1.3-disilazanes are obtained $[(NH_2)(Me_3C)RSi-NH-SiR_1R_2R_3; 3: R = CMe_3, R_1 = R_2 = R_3 = Me_3; 4: R = R_1 = CMe_3, R_2 = R_3$ = Me; 5: $R = R_1 = R_2 = CMe_3$, $R_3 = H$; 6: $R = R_1 = CMe_3$, $R_2 = Me$, $R_3 = F$; 7: $R = CHMe_2$, $R_1 = R_2 = R_3 = Me$]. If monolithiated diamines are treated with trifluorosilanes cyclisation occurs to give $(NH-Si(CMe_3)2-NH-SiFR)$ cyclodisilazanes $[R = N(SiMe_3)(CMe_3)(8); R = N(SiMe_2CMe_3)_2$ (9)]. 50% of the educts are recovered. The spirocyclic compound 10 is isolated from the reaction of the dilithiated 1-amino-1.3-disilazane **3** with F₃SiN(SiMe₂CMe₃)₂. NH-SiF-Functional cyclodisilazanes can be obtained in the reaction of the dilithium derivative of compound 4 with trifluorosilanes $[(N(SiMe_2CMe_3)-Si(CMe_3)_2-NH-SiFR), R = Ph (11); R = CMe_3 (12)]$. The lithium derivative of 12 crystallises with TMEDA as adduct 13. In the reaction of the lithiated compound 12 with Me₃SiCl. LiCl elimination and substitution of the N-atom is observed (14). The treatment of 13 with PhCHO leads to a 1.3-diaza-5-oxa-2.4-disila-cyclohexane (15 a, b). Starting from lithiated 12 the methoxysubstituted cyclodisiloxane 16 is accessible in the reaction with MeOH. As result of its reactivity towards Me₂SiF₂ the fluorosilyl-substituted cyclodisilazane 17 is obtained. Crystal structures of 9-11 and 13 have been determined.

Key words: Cyclodisilazanes, Spirocycle, Aldehyde-Insertion