Wurtz-type Coupling Reaction of *Pseudo*-pentacoordinate Halodisilanes Using Magnesium: Enhanced Reactivity of the Silicon-Halogen Bond by Intramolecular Amine-coordination to Silicon

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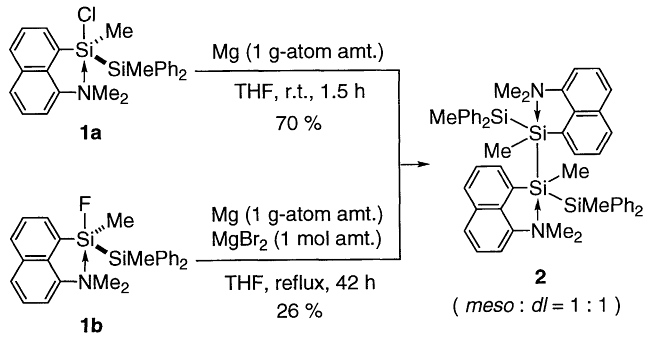
A 2,3-*bis*(*pseudo*-pentacoordinate) tetrasilane was obtained by the reductive dimerization of 1-[8-(dimethylamino)-1-naphthyl]-1-chlorodisilane using magnesium, and also from the analogous 1-fluorodisilane using a mixture of magnesium and magnesium bromide.

The chemistry of polysilanes constitutes one of the most interesting fields of new materials due to their unique properties in photophysics and electrophysics.[1] These properties are attributed to an electron delocalization along the polymer backbone. The introduction of hypercoordinate silicon centers into the polysilane backbone is expected to affect the electron delocalization and provide new properties, but such polysilanes have been unexplored due to the lack of synthetic methodology. Oligosilanes containing both hypercoordinate and tetracoordinate silicon centers ("mixed oligosilanes") have been prepared[2] and their enhanced reactivity toward transition metal-catalyzed and thermal reactions has been pointed out.[2f-h] We have been greatly interested in the "mixed oligosilanes" containing successive hypercoordinate silicon centers. Recently, Belzner and co-workers have reported that the silicon—silicon bond formation between hypercoordinate silicon centers proceeds by the reaction of hypercoordinate dihalosilanes with magnesium to afford cyclic trisilanes, presumably *via* the base-coordinated silylenes.[3,4] Quite recently, Tanaka and co-workers have reported the preparation of "mixed tetrasilane" containing successive pentacoordinate silicon centers by the introduction of coordinating groups in the final step.[5] These papers prompted us to report our findings that the Wurtz-type coupling reaction of a *pseudo*-pentacoordinate chlorodisilane using magnesium affords the corresponding tetrasilane containing successive *pseudo*-pentacoordinate silicon centers, and that the intramolecular amine-coordination to silicon enhances the reactivity of the silicon—halogen bond toward magnesium.

As shown in Scheme 1, by the reaction of 1-chloro-1-[8-(dimethylamino)-1-naphthyl]disilane **1a**[2g] with 1 g-atom amount of magnesium in THF at 15 °C for 1.5 h, 2,3-*bis*(*pseudo*-pentacoordinate) tetrasilane **2** was isolated in 70% yield as a 1:1 mixture of *meso* and *dl* diastereoisomers.[6]

The *dl* and *meso* diastereoisomers of **2** were separated by repeated recrystallization and their structures were confirmed by X-ray crystal structure analysis, as shown in Figure 1[7] and Figure 2,[8] respectively. In *dl*-**2**, the two nitrogen atoms weakly interact with the central two silicon atoms, Si1 and Si3*, providing a nearly linear alignment of N1···Si1—Si3*···N2*, with the two N···Si—Si angles of ca. 160° and the Si···N distances of 3.137(3) and 3.196(2) Å,[9] which are shorter than the sum of the van der Waals radii, 3.65 Å,[11] but longer than those of typical hypercoordinate silicon compounds containing electronegative ligands on a silicon atom (≤ 2.8 Å).[12] The bond angles, Si3*—Si1—Si2, Si3*—Si1—C1, and Si3*—Si1—C2, are 108.6°, 102.5°, and 109.9°, respectively.[13] These numbers suggest a very weak coordination of nitrogen atoms, causing a slight deformation of the silicon centers from tetrahedral to a [4+1] geometry.[12] Nevertheless, the central Si1—Si3* bond length (2.431(1) Å) is considerably longer than the terminal Si—Si bonds and the standard values (2.33—2.37 Å),[15] presumably because the central bond connects two *pseudo*-pentacoordinate silicon atoms. In *meso*-**2**, the Si···N distance of 3.341(4) Å is longer than those in *dl*-**2**, the N1···Si2—Si2* angle 126.3(1)° is far from straight, and the bond length of Si2—Si2* (2.405(2) Å) is shorter than that in *dl*-**2**, indicating that the structure around Si2 in *meso*-**2** is much less pentacoordinate in the solid state.[13] From the other viewpoint, it is reasonable to assume that in *dl*-**2** the



Scheme 1.

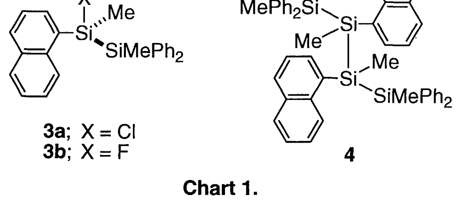


Chart 1.

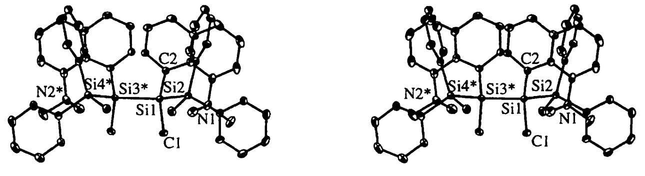


Figure 1. X-ray structure of *dl*-**2** drawn in stereoview at 30% probability level. All hydrogen atoms and crystalline solvent were omitted for clarity. Selected distances (Å) and angles (deg): N1···Si1, 3.196(2); N2*···Si3*, 3.137(3); Si1—Si2, 2.3851(9); Si1—Si3*, 2.431(1); Si3*—Si4*, 2.390(1); N1···Si1—Si3*, 160.19(5); N2*···Si3*—Si1, 162.99(6); Si3*—Si1—Si2, 108.63(3); Si3*—Si1—C1, 102.49(10); Si3*—Si1—C2, 109.89(8).

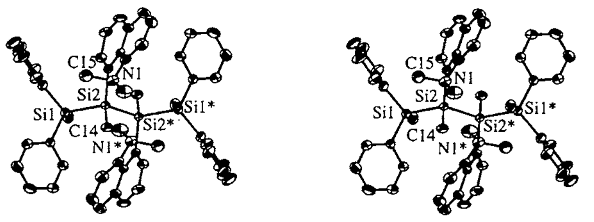


Figure 2. X-ray structure of *meso*-**2** drawn in stereoview at 30% probability level. All hydrogen atoms were omitted for clarity. Selected distances (Å) and angles (deg): N1···Si1, 3.341(4); Si1—Si2, 2.383(2); Si2—Si2*, 2.405(2); N1···Si2—Si2*, 126.3(1); Si2*—Si2—Si1, 109.43(8); Si2*—Si2—C14, 108.1(2); Si2*—Si2—C15, 104.4(1).

central Si—Si bond is elongated due to the steric repulsion between two naphthyl groups to cause the coordination of the amino group more favorable than that in *meso*-**2** where the Si—Si bond is not elongated due to the absence of such steric repulsion.[16]

However, the coordination of the amino group to silicon in solution is supported by the NMR measurement as follows. In the ^{1}H and ^{13}C NMR spectra, two signals were observed for the two methyl groups on the two magnetically equivalent dimethylamino groups in each case of *meso-* and *dl*-**2**, indicating that the rotation around the naphthyl carbon—nitrogen bond is hindered due to the coordination of the amino group to the silicon atom. In the ^{29}Si NMR spectra, the aminonaphthyl-containing silicon atoms of **2** (–22.9 ppm for *meso-* and –22.6 ppm for *dl*-isomer) resonate ca. 20 ppm downfield in comparison with the naphthyl containing silicon atoms in the tetracoordinate counterpart **4** (–42.2 ppm for *meso-* and –41.9 ppm for *dl*-isomer) (Chart 1).[17] This downfield shift is opposite to the usual upfield shifts by the coordination,[18] but in accord with shifts by weak coordination in the absence of the electronegative ligands.[2f,19]

In the case of the 1-fluorodisilane analogue **1b**,[20] a similar reductive coupling reaction did proceed but it was necessary to add magnesium bromide[21] (1 mol. amt.) under forcing conditions (reflux, 42 h) to obtain **2** in 26% yield.

It was confirmed that the reductive coupling reaction of the tetracoordinate halodisilanes **3** did not proceed under essentially the same conditions as those for the corresponding *pseudo*-pentacoordinate halodisilanes. Thus, no coupling products were obtained by the reaction of the tetracoordinate 1-chlorodisilane **3a** with magnesium. Here again, the addition of a 1 molar amount of magnesium bromide facilitated the coupling reaction of **3a** to afford the corresponding tetrasilane **4** in 70% yield (*meso*:*dl* = 1:2). In the case of the tetracoordinate fluorodisilane **3b**, no coupling product was obtained even in the presence of magnesium bromide under forcing conditions. These results clearly indicate that the intramolecular coordination of the 8-dimethylamino-1-naphthyl group enhances the reactivity of the silicon—halogen bonds toward magnesium.

The preparation of "mixed polysilanes" by the methodology described herein is in progress in our laboratory and will be reported in due course.

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6 In the reaction of **1a** with sodium instead of magnesium in THF, the starting material was recovered at 15 °C and a complex mixture containing no coupling product **2** was formed under reflux, thus indicating the importance of the choice of reducing reagent.

7 Crystal data for *dl*-**2**: $C_{59}H_{64}N_2Si_4$, M = 913.52, monoclinic, space group $P2_1/n$, a = 16.2324(9) Å, b = 17.9541(9) Å, c = 18.5083(9) Å, β = 110.149(4)°, V = 5063.8(9) Å^3, Z = 4, D_c = 1.188 g/cm^3, T = 173 K, μ(MoKα) = 1.57 cm^{-1}, R = 0.068, R_w= 0.106, 9983 unique reflections with $2\theta_{max}$ = 110.6°.

8 Crystal data for *meso*-**2**: $C_{52}H_{56}N_2Si_4$, M = 821.37, monoclinic, space group $P2_1/n$, a = 13.075(2) Å, b = 13.785(3) Å, c = 14.166(2) Å, β = 116.767(7)°, V = 2279.6(6) Å^3, Z = 2, D_c = 1.197 g/cm^3, T = 295 K, μ(MoKα) = 14.86 cm^{-1}, R = 0.055, R_w = 0.074, 3739 unique reflections with $2\theta_{max}$ = 120.2°.

9 These numbers may be compared with 155.94° and 3.159 Å observed in a trisilane containing the same aminonaphthyl group at the central silicon atom.[2f] Quite recently, long-range N···Si interactions in organosilicon molecules containing seven- or eight–coordinate Si centers have been approximated by density functional theory calculations.[10]

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17 Terminal silicon atoms resonate in the same region as follows: –19.1 ppm for *meso*-**2**, –18.4 ppm for *dl*-**2**, –17.1 ppm for *meso*-**4**, and –16.7 ppm for *dl*-**4**.

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