Synthesis and X-Ray Structure of an sp^2 Silicon stabilized by two Intramolecular Coordinations

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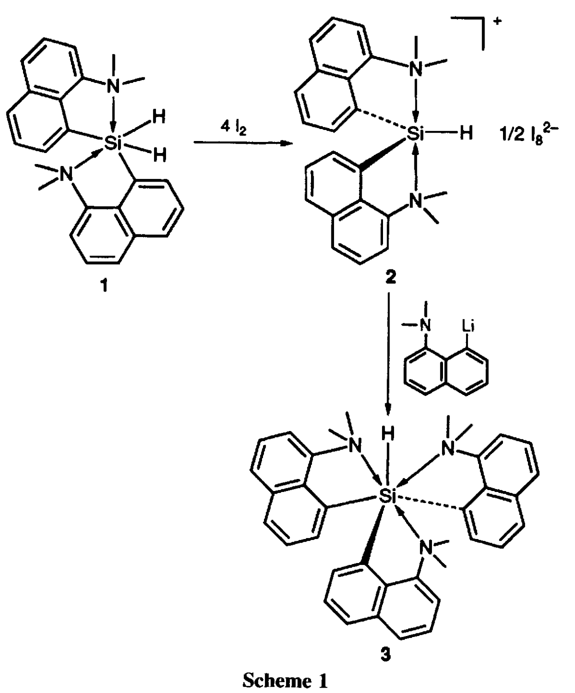
Reaction of bis[8-(dimethylamino)naphthyl]dihydrosilane with iodine gives $2[L_2SiH]^+I_8^{2-}$ {L = [8-(dimethylamino)naphthyl]}; the X-ray crystal structure determination shows a slightly distorted trigonal bipyramid around the silicon atom with apical NMe_2 ligands and short Si–N distances [2.06 and 2.08(1) Å].

There is a considerable debate concerning the existence of the trivalent silycenium ion in the solid state.[1–5] Attempts to isolate such a cation have long been unsuccessful, mainly due to interactions with the counterion or the solvent. Much effort has been expended in order to minimize these interactions; on the one hand by using weakly nucleophilic anions,[6–8] and on the other by performing the reaction in weakly coordinating solvents.[6] Lambert recently reported a silyl cation showing no coordination to the anion and distant coordination to a toluene molecule without any distortion.[9]

Silicon species stabilized by *intermolecular* coordinations have been claimed to be silyl cations.[6,8–10] The 2,2′-bipyridine derivative of Ph_3SiI was formulated as a siliconium ion,[10] although some other interpretations have been proposed.[11] Several silicon adducts, mainly with tertiary organic bases, have also been reported.[12–14] This controversy, and also our interest in the reactivity of hypercoordinated silanes[15] and the stabilization of low valent silicon species by *intramolecular* amino ligands,[16] prompted us to study the possibility of intramolecular stabilization of sp^2 silicon salts. We report here an easy way to obtain such silicon species. Treatment of bis[8-(dimethylamino)naphthyl]dihydrosilane **1** with iodine in toluene led to the corresponding pentacoordinated silicon compound **2** (Scheme 1). The high reactivity of **2** with 8-(dimethylamino)naphthyllithium, leading to the ready formation of a heptacoordinated silane **3**, has already been reported.[17] The ionic structure of **2** is now confirmed by X-ray analysis.†

Fig. 1 clearly shows the separation of the anion and the cation, which are situated in alternate layers in the crystal. The shortest Si–I distance [5.036(4) Å] is far beyond the sum of the van der Waals radii of the two atoms (Σ_r = 4.08 Å). This indicates that there is no covalent interaction or even any close contact between these two elements. It is interesting to note that the anionic part is in the form of the known I_8^{2-} ion[18] lying between two monocations. The main features of the I_8^{2-} species are identical with reported values for such anions: I(1)–I(2)–I(3) and I(3)–I(4)–I(4′) angles, mean 178.0°; I(2)–I(3)–I(4) 90.4°; I–I distances 2.821, 3.022, 3.314(1) and 2.767(2) Å. Furthermore, it appears that the unit cell contains a slight excess of iodine (X–X′, Fig. 1) trapped at the inversion centres between two successive I_8^{2-} anions and also between the hydrogen atoms from the nearest naphthyl rings.



1 **2** **3**

Scheme 1

Fig. 2 reveals a pentacoordinated silicon atom σ-bonded to two carbon atoms (*ipso*-carbon of the naphthyl groups) and one hydrogen atom, which undergoes two intramolecular coordinations with the two nitrogen atoms. A slightly distorted trigonal bipyramidal geometry around the silicon atom is observed with the three σ-bonded atoms (C and H) lying in the equatorial positions [C(11)–Si–C(21) 118.4(6), C(1)–Si–H 125.7(3.6) and C(21)–Si–H 114.1(3.5)°]. The two nitrogen atoms are *trans* to each other [N(1)–Si–N(2) 167.8(4)°] in the apical positions. Interestingly, the previously claimed triphenyl(bipyridyl)siliconium ion[10] exhibits the two nitrogen atoms in the *cis* position due to the structure of the ligand used. On the other hand, the structure of **2** confirms our previous hypothesis for the geometry of pentacoordinated silicon salts. The Si–N distances [Si–N(1) 2.08(1), Si–N(2) 2.06(1) Å] are *ca.* 0.34 Å longer than the typical Si–N bond (1.70–1.76 Å)[22] but they are shorter than those of silane **1** [Si–N 2.610(7), 2.800(8) Å][23] and also than the sum of van der Waals radii (3.6 Å) of the two elements. In addition, there is an approximate (non-crystallographic) C_2 axis coincident with the Si–H bond.

Compound **2** is very air-sensitive and, besides being completely insoluble in common hydrocarbon solvents, it is quite soluble in chlorinated solvents ($CHCl_3$ or CH_2Cl_2). Both the ^1H and ^{13}C NMR spectra exhibit two singlets for the methyl groups at nitrogen (δ 3.24 and 3.29, 48.1 and 52.9, respectively) indicating two non-equivalent methyl groups due

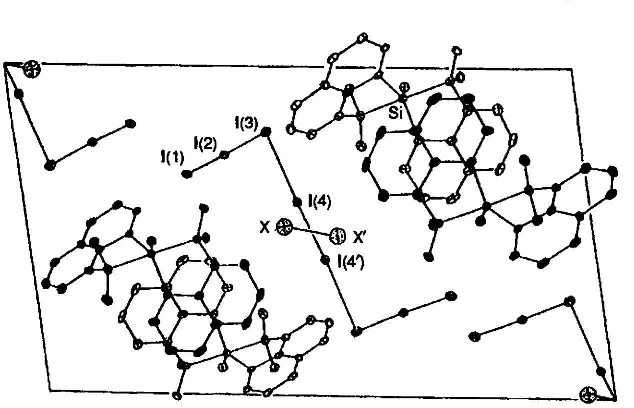


Fig. 1 ORTEP drawing showing the crystal packing of compound **2**. The iodine atoms are located approximately near the diagonal plane (101) of the unit cell. Iodine layers alternate with organosilicon moieties. The structure is viewed down the *b* axis. The vibrational ellipsoids are drawn at the 20% probability level. The atoms X are represented by spheres of arbitrary radius.

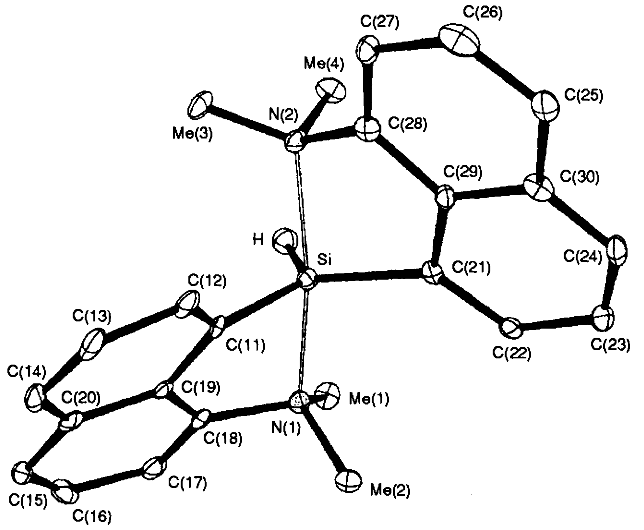


Fig. 2 ORTEP drawing of the cation in **2** showing the molecular conformation and atom numbering. Atoms are represented as 20% probability ellipsoïds. Selected bond lengths (Å) and angles (°): Si–H 1.73(12), Si–C(11) 1.90(1), Si–C(21) 1.85(1), Si–N(1) 2.08(1), Si–N(2) 2.06(1), N(1)–Si–N(2) 167.8(4), C(11)–Si–C(21) 118.4(6), C(11)–Si–H 126(4), C(21)–Si–H 114(4), Si–C(11)–C(19) 106.5(9), Si–C(21)–C(29) 110.2(9), N(1)–C(18)–C(19) 110.6(1.0), N(2)–C(28)–C(29) 113.4(1.1).

to the coordination of nitrogen atom to silicon. The ^{29}Si NMR spectrum shows a doublet with a large Si–H coupling constant (290 Hz) consistent with a high amount of s-character in the Si–H bond as expected for sp^2 hybridized silicon.[24,25] In this case, the sp^2 silicon is assumed to be intramolecularly stabilized by the amino nitrogens, and these coordinations may account for the large upfield shift in the ^{29}Si spectrum ($\delta = -43.5$).

The facile nucleophilic attack of 8-(dimethylamino)-naphthyllithium at the sterically hindered silicon atom of compound **2**, giving rise to **3** (Scheme 1),[17] indicates that the silicon atom remains an electrophilic centre, although the overall positive charge may be delocalized to some extent on the nitrogens. We are focusing our current work on studying the reactivity of compound **2**.

Received, 21st April 1994; Com. 4/02372B

Footnote

† *Crystal data* for **2**: $C_{24}H_{25}N_2SiI_{4.1}$, $M = 889.9$, monoclinic, space group $P2_1/n$, $a = 13.571(4)$, $b = 9.417(2)$, $c = 23.141(4)$ Å, $\beta = 99.07(2)°$, $U = 2920(1)$ Å^3, $Z = 4$, $D_c = 2.024$ g cm^{-3}. Mo-Kα radiation (graphite monochromator), $\lambda = 0.71069$ Å, $\mu = 43.8$ cm^{-1}. 2478 unique reflections were collected at 207 K in a ω/θ scan. The structure was solved by direct methods (MULTAN-80) and refined using the SHELX-76 program. A semi-empirical absorption correction was applied. In the primary stages of the refinement a peak **X** of density 5.54 e Å^{-3} was observed near the inversion centres of the lattice. The conventional R factor was 0.056 and from this point three hypotheses were examined: (i) CH_2Cl_2 having been used as crystallizing solvent, **X** was assumed to be a chlorine atom with an occupancy of 0.33. However the reported Cl···Cl separation in CH_2Cl_2 [2.88(2) Å] is, within 3 sigma, well beyond the **X**–**X**′ distance found [2.66(4) Å]; (*ii*) as suggested by one of the referees of this paper, peak **X** could correspond to the oxygen atom of a water molecule. The O···O distance in ice (O–H···O) is *ca* 2.73 Å: having in view the low accuracy for the **X**···**X**′ interatomic distance, the possibility of two water molecules opposite to each other through an inversion centre cannot be ruled out on the sole examination of the crystallographic results. However we must emphasize that **2** was prepared in anhydrous solvents, being extremely moisture-sensitive and stable in nitrogen atmosphere at room temperature. This excludes the possibility of having one equivalent of water confined nearby a reactive organosilicon moiety; (*iii*) peak **X** can also be accounted for as iodine with a low occupancy factor ($m = 0.104$). The refined **X**–**X**′ distance [2.66(4) Å] agrees with the bond lengths for both gaseous [2.661(5) Å], and solid [2.68(5) Å] iodine molecules. It is noteworthy that *none* of the separations between **X** and its iodine neighbours are shorter than *twice* the iodine van der Waals radius (3.96–4.08 Å), the shortest value being 4.20(1) Å for the **X**···**I**(4) distance. Moreover the **X**···**H**(12) and **X**···**H**(13) distances are 3.3 and 3.1 Å, respectively, corresponding to the sum of the van der Waals radii of hydrogen and iodine atoms (1.2 + 2.0 Å). The value of m was fixed at 0.1, and refinement converged with R (R_w) = 0.040(0.048) for 2473 observed independant reflections with $F > 3.0\sigma(F)$. The final minimum and maximum residual electron densities were −0.73 and 2.18 e Å^{-3}. All hydrogen atoms were placed at calculated positions except the H atom on silicon which was revealed in a difference Fourier synthesis map and refined isotropically. All non-hydrogen atoms were refined anisotropically. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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