ORGANOMETALLICS

Volume 9, Number 10, October 1990

Communications

Unexpected Reactivity of Bifunctional Hexacoordinated Silicon Species

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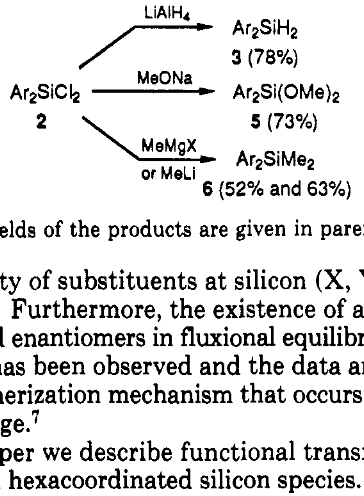
Received March 9, 1990

Summary: **The basic transformations of SiF, SiCl, and SiH in hexacoordinated silicon species are completely different from those observed with the corresponding tetra- and pentacoordinate compounds.**

Until now hexacoordinated silicon species have been investigated mainly from the structural point of view.[1] Some studies have been performed in view of carbon reactivity resulting in Si–C bond cleavage.[2,3] The chemical behavior of the hexacoordinated silicon center was considered only in the case of ionic complexes[4,5] and mainly toward organometallic reagents.[5] Recently the structures of hexacoordinated silicon compounds obtained by intramolecular coordination of two NMe_2 ligands have been determined by X-ray crystallography.[6] On the other hand, NMR study of bis(8-(dimethylamino)naphthyl)silanes has shown that hexacoordination is still present in solution for a wide variety of substituents at silicon (X, Y = F, OMe, H, Me, Ph). Furthermore, the existence of a pair of hexacoordinated enantiomers in fluxional equilibrium for each compound has been observed and the data are consistent with an isomerization mechanism that occurs without any bond cleavage.[7]

Scheme I. Reactivity of Compound 2 (Ar = 8-(Dimethylamino)naphthyl)[a]



[a] Isolated yields of the products are given in parentheses.

In this paper we describe functional transformation of such neutral hexacoordinated silicon species. We studied the reactivity of compounds 1, 2, and 3, containing two silicon–carbon bonds and two functional groups at silicon: 1 and 2 have the same symmetrical structure as 4 (with the two NMe_2 ligands trans to the functional group), whereas 3 gives an unsymmetrical structure (with one H atom trans to one NMe_2 and the other cis to the two NMe_2 groups (Figure 1).

The reactivity of pentacoordinate silicon species has turned out to be very different from that of tetracoordinate ones.[8,9] Thus, it is highly attractive to explore the possible

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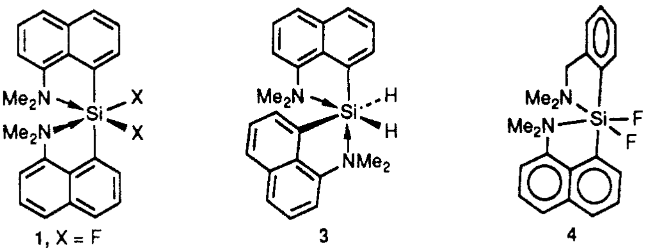


1, X = F
2, X = Cl

3

4

Figure 1. Geometry of compounds 1-4.

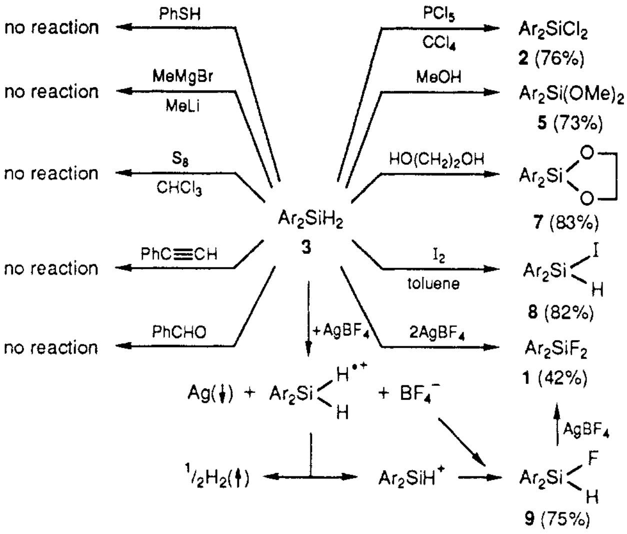
functional transformation in the case of neutral hexacoordinated species, particularly toward nucleophilic reagents.

The reactivities of compounds 1 and 2 with nucleophiles were surprisingly very different: difluorosilane 1 appears to be completely inert to any nucleophilic reagent ($LiAlH_4$, RM, ROH, RONa), in contrast with the high reactivity of pentacoordinated fluorosilicates.[10] In all cases, 1 is recovered quantitatively.

In contrast, dichlorosilane 2 is substituted very easily by nucleophiles, giving functional transformations with good yields (Scheme I).[11]

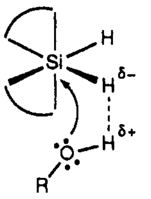
This pronounced difference of reactivity was completely unexpected, since the structures of compounds 1 and 2 are basically similar: both have hexacoordinated structures with the NMe_2 ligands opposite to the halogen atom, and they display similar NMR behavior. A possible explanation for the high reactivity of the chlorosilane 2 could be a longer Si-Cl bond in a "semi-ionic" state due to the higher polarizability of the chlorine atom, as observed recently in some pentacoordinated structures.[12] In addition, it has been shown that the Si-Cl bond can be stretched by approximately 17%.[13] Furthermore, in agreement with our previous results and with use of another model Bassindale has recently pointed out the higher ability of Si-Cl to favor intramolecular coordination in comparison with the Si-F bond.[14] The lack of reactivity of fluorosilane 1 could be attributed to both the minimal elongation of the Si-F bonds (as shown for difluorosilane 4[6]) and a maximal hindrance around the silicon atom (back and front preferential positions for a nucleophilic reagent are both occupied by nitrogens and prevent substitution of the Si-F bond). This lack of reactivity of fluorosilane 1 toward nucleophilic reagents contrasts completely with the behavior of tetra- and pentacoordinated fluorosilanes, which exhibit high reactivity, and confirms the complete coordination of compound 1 in solution: pentacoordinated fluorosilanes have been shown to be more reactive toward nucleophilic reagents than the corresponding tetracoordinate ones.[15] If cleavage of one of the Si-N coordinative bonds were significant, we should observe substitution at silicon.

Scheme II. Reactivity of Compound 3 (Ar = 8-(Dimethylamino)naphthyl)[a]



[a] Isolated yields of the products are given in parentheses.

Scheme III. Possible Intermediate for Reaction of 3 with Alcohols



The reactivity of the hydrosilane 3 toward nucleophiles is again very different from that observed for 1 and 2 (Scheme II). It reacts very quickly with all hydroxyl-containing compounds, leading to alkoxysilanes. A bidentate reagent such as ethylene glycol leads to a cyclic hexacoordinated complex. Interestingly, silane 3 reacts readily with iodine and chlorination is possible by an exchange reaction with PCl_5.[16]

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(11) The new compounds were characterized by elemental analyses and spectroscopic data. Compound 1 was prepared by reaction of 1 equiv of (8-(dimethylamino)naphthyl)lithium with (8-(dimethylamino)naphthyl)trifluorosilane; mp 174 °C; Anal. Calcd for $C_{24}H_{24}F_2N_2Si$: C, 70.90; H, 5.95; N, 6.89. Found: C, 70.44; H, 6.06; N, 7.19. ^1H NMR δ 1.17 (s, 6 H, NMe_2), 2.43 (s, 6 H, NMe_2), 7.03-8.38 (m, 12 H, arom) ^{29}Si NMR: δ -61.37 (J_{SiF} = 276.9 Hz). MS (EI): *m/z* 406 (15%). Compound 2 was prepared by reaction of 3 with PCl_5 in CCl_4; mp 186 °C. Anal. Calcd for $C_{24}H_{24}Cl_2N_2Si$: C, 65.59; H, 5.50; N, 6.37; Cl, 16.13. Found: C, 64.77; H, 5.61; N, 6.01; Cl, 15.90. ^1H NMR δ 1.29 (s, 6 H, NMe_2), 2.51 (s, 6 H, NMe_2), 7.15-8.12 (m, 12 H, arom). ^{29}Si NMR δ -33.66. MS (EI): *m/z* 439 (30.8%). Compound 5: mp 135 °C. Anal. Calcd for $C_{26}H_{30}N_2O_2Si$: C, 72.52; H, 7.02; N, 6.51. Found: C, 72.45; H. 6.84; N, 6.23. ^1H NMR: δ 1.0 and 2.28 (2 s, 12 H, NMe_2), 3.3 (s, 6 H, OMe), 6.97-8.62 (m, 12 H, arom). ^{29}Si NMR δ -46. MS (EI): *m/z* 430 (10%). Compound 6: mp 99.5-101 °C. ^1H NMR: δ 0.94 (s, 6 H, $SiMe_2$), 1.61 and 2.46 (2 s, 12 H, NMe_2), 7.17-8.35 (m, 12 H, arom). ^{29}Si NMR: δ -11.91. MS (EI): *m/z* 398 (7.5%). Compound 7: mp 210 °C. Anal. Calcd for $C_{26}H_{28}N_2O_2Si$: C, 72.86; H, 6.58; N, 6.54. Found: C, 72.84; H, 6.78; N, 6.25. ^1H NMR: δ 1.18 and 2.57 (2 s, 12 H, NMe_2), 3.91-4.12 (m, 20 peaks, AA'BB'' spectrum, 4 H, OCH_2), 6.95-8.41 (m, 12 H, arom). ^{29}Si NMR: δ -35.1 MS (EI): *m/z* 488 (100%). Compound 8: mp 115-117 °C. ^1H NMR: δ 3.24 and 3.29 (2 s, 12 H, NMe_2), 5.38 (s, 1 H, SiH), 7.50-8.05 (m, 12 H, arom). ^{29}Si NMR: δ -45.26 (J_{SiH} = 290.16 Hz). MS (EI): *m/z* $(M - 1)^+$ 369 (1%). At room temperature, the ^1H NMR spectrum of 8 exhibits two different NMe groups, and a variable-temperature study (down to -100 °C) shows no modification of the spectrum. This suggests that 8 is pentacoordinated at silicon with an ionic Si-I bond, since a covalent compound should exhibit two different naphthyl groups and four different NMe signals.

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However, **3** is completely chemically inert toward strong nucleophiles (RLi, RMgX), whereas organolithium reagents are able to substitute the Si–H bond in tetra- and pentacoordinate silicon compounds.[15]

Furthermore, those reagents that have been reported to react efficiently with the pentacoordinate dihydrosilanes, such as S_8, CS_2[17] or carbonyl groups,[8] and acid derivatives,[9] exhibit no reactivity toward compound **3** even with reaction times much longer than usual.

Similarly to fluorosilane **1**, this lack of reactivity is also a demonstration of hexacoordination in solution, since an equilibrium between penta- and hexacoordinated species[18] by opening of one of the Si–NMe_2 bonds should lead to the same reactivity as in the case of pentacoordinate species.

The lack of reactivity toward nucleophiles can be explained, as in the case of the fluorosilane **1**, by both the intramolecular coordination and the nonstretching of the Si–H bond, as shown in the structure of **3** (Si–H bond lengths 1.44 (5) and 1.54 (6) Å,[6] very close to the 1.46 Å observed for tetracoordinated compounds[19]). Concerning the reactivity toward hydroxylated reagents, we suggest that the driving force of this reaction could be the hydridic character of the Si–H bond. The interaction with the positively charged hydrogen of the OH group could lead to the elimination of hydrogen, allowing the reaction of the oxygen atom at silicon through a more or less concerted mechanism (Scheme III).

Another unexpected reaction was observed with oxidizing reagents: the reaction of **3** with $AgBF_4$ (1 equiv) gives the hydrofluorosilane **9** with evolution of H_2 and precipitation of silver at room temperature; the difluorosilane **1** can be isolated with 2 equiv of $AgBF_4$. This reaction suggests the transitory formation of pentacoordinated siliconium ions. This oxidation reaction of the hexacoordinated hydrosilanes does not take place in the case of the tetracoordinate silanes under the same conditions. Ph_3SiH and Ph_2SiH_2 do not exhibit any evolution of H_2 when they are treated with $AgBF_4$ at room temperature.

Unfortunately, the stereochemical behavior of these reactions cannot, of course, be discussed because of the fluxional isomerization in solution,[7] which leads always to the most stable conformer. For instance, we observed the same dimethoxysilane **5** from **2** and **3**, which have two different structures.

In conclusion, the results presented here illustrate the specific reactivity of hexacoordinated silicon species, which is quite different from that of either pentacoordinated or tetracoordinated species. Interestingly the hexacoordinate silicon compounds can undergo a nucleophilic substitution when the Si–X bond (X = leaving group) could be susceptible to stretching. This is the case with the Si–Cl bond due to its polarizability. Reaction at the Si–H bond is observed only with hydroxylic compounds, where evolution of hydrogen is a necessary part of the mechanism (Scheme III). In both cases the reactions are taking place with hexacoordinated silicon compounds, showing, under certain conditions, the possibility of nucleophilic substitution through heptacoordinated intermediates (or transition states).

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