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Preliminary Communication

Unexpected behaviour of a hexacoordinate silicon compound *

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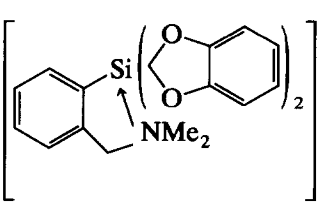
Abstract

The anion $[Si(O_2C_6H_4\text{-}1,2)_2\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]^-$ is hexacoordinate rather than heptacoordinate. Only one NMe_2 group is coordinated. The other NMe_2 group can abstract a proton from methanol to give a compound, the X-ray crystal structure of which reveals a strong hydrogen-bonding interaction between the $NHMe_2$ and a catecholate oxygen atom. This interaction prevents exchange between the two NMe_2 groups.

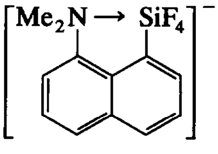
It has been found that anionic pentacoordinate silicon species react readily with nucleophilic reagents [1,2], in some cases faster than the corresponding tetracoordinate ones [2]. Moreover, a structural study of compounds **1** [3] and **2** [4] bearing electron-withdrawing ligands, and in which hexacoordination may be achieved by an intramolecular dative Si–N bond, has shown that both anions adopt quasi-octahedral geometry. These results suggest that reactions between pentacoordinate silicon compounds and nucleophilic reagents proceed via hexacoordinate intermediates or transition states.

(PPN)$^+$



(1)

$PPN^+ = Ph_3P{=}\overset{+}{N}{=}PPh_3$



[K(18-crown-6)]

(2)

The reactivity of some dianionic hexacoordinate silicon species has also been investigated [5]. These species also react readily with nucleophilic reagents, but the mechanism of such reactions has not yet been elucidated. A mechanism involving a heptacoordinate silicon intermediate (or transition state) [6] is possible, since at the moment there is no argument to rule out such a process [7]. In this context, it was of interest to prepare a hexacoordinate silicon species in which heptacoordination might be achieved by intramolecular coordination. Since the hexacoordination of **1** has been demonstrated [3], we decided to prepare the silicate **3** which contains the 2,6-bis[(dimethylamino)methyl]phenyl group, previously used by van Koten *et al.* to stabilize triorganotin cations [8].

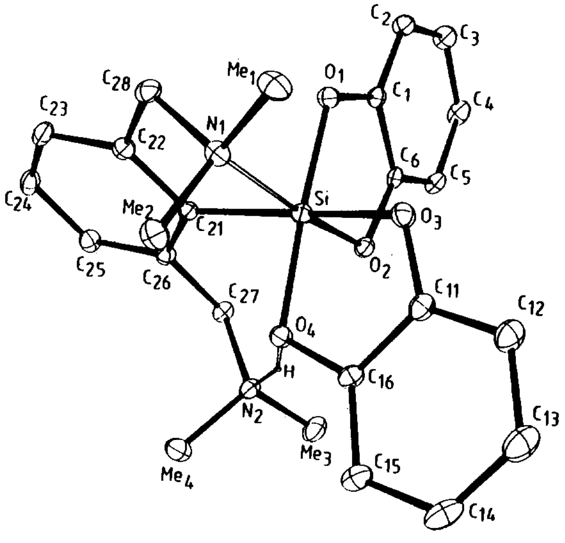


Fig. 1. ORTEP view of **4**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si–O(1) 1.768(3), Si–O(2) 1.778(3), Si–O(3) 1.771(3), Si–O(4) 1.796(3), Si–C(21) 1.943(4), Si–N(1) 2.085(4), Si···N(2) 3.521(4), N(2)–H$^+$ 1.16(10), O(4)–H$^+$ 1.62(10); O(2)–Si–N(1) 174.6(2), O(3)–Si–C(21) 168.8(2), O(2)–Si–O(1) 90.0(1), O(2)–Si–O(4) 90.2(1), Me(3)–N(2)–H$^+$ 109.5.

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* Dedicated to Professor M.G. Voronkov in recognition of his distinguished contributions to organosilicon chemistry.

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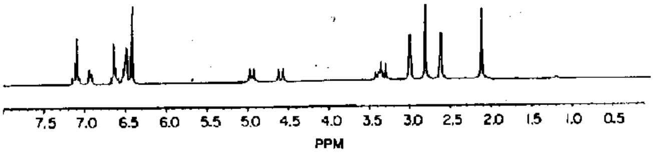


Fig. 2. 250 MHz ^{1}H NMR spectrum of **4** in CD_2Cl_2 at −40°C.

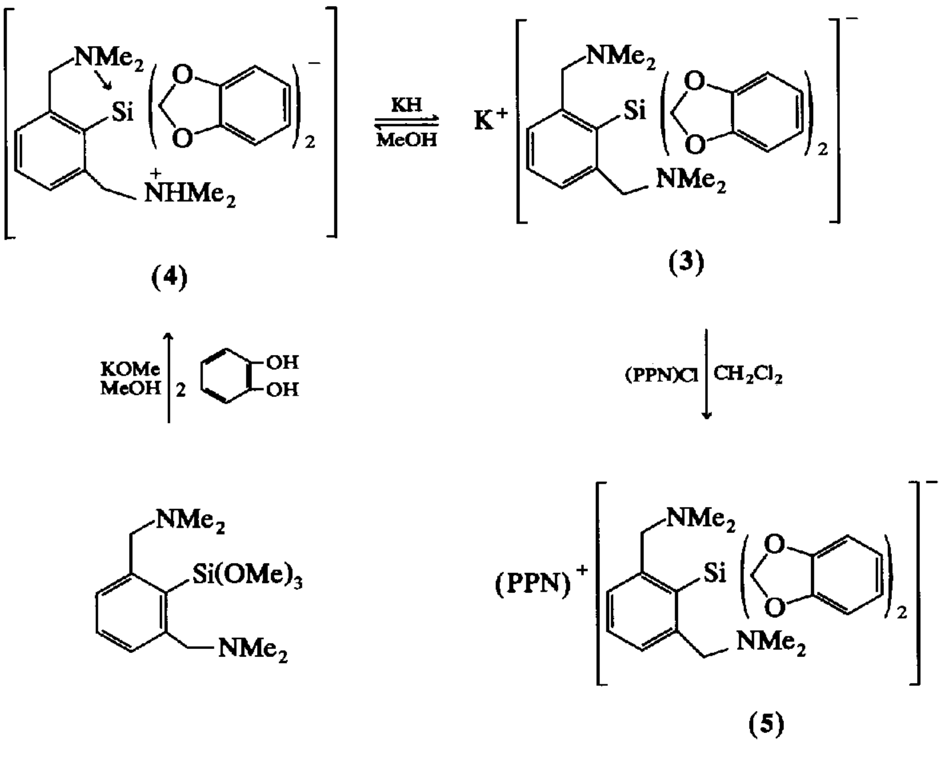
The purpose of the present communication is to report the unexpected reactivity of **3** towards protic compounds.

Surprisingly, it was not possible to synthesize **3** by the route previously used for the preparation of **1** [3]. Under these conditions, the zwitterion **4** was obtained [9*] instead of the potassium salt **3** (Scheme 1).

The molecular structure of **4** was determined by X-ray crystal structure analysis, which revealed an overall octahedral geometry (Fig. 1) [10*] with an Si–N bond (2.085 Å) shorter than that observed in the compound **1** [3] (2.15 Å). The proton which imposes electrical neutrality is bonded to the other nitrogen atom and is also involved in a hydrogen-bonding interaction with O(4).

The ^{1}H NMR spectrum of **4** at −40°C, shown in Fig. 2, exhibits interesting features. The resonances of the two NMe_2 groups are totally distinct. That arising from the NMe_2 group coordinated to the silicon atom is resolved into two singlets. The second NMe_2 group is a protonated group and gives rise to two distinct doublets. These two doublets indicate not only that the hydrogen-bonding interaction with O(4) is maintained in solution, but that there is no hydrogen-exchange between the two NMe_2 groups. The diastereotopy observed for the two NMe_2 groups also results from the hydrogen-bonding with O(4). This interaction hinders an intramolecular non-dissociative isomerization process. In contrast, it was shown for compound **1** that this process requires a very low activation energy [3].

Abstraction of the proton from **4** is difficult: **4** does not react with potassium methoxide or sodium hydride, but it is quantitatively converted into **3** when treated with potassium hydride [11*] (Scheme 1). The protonation of **3** to give **4** occurs very rapidly in methanol. The ^{1}H NMR spectrum of the PPN salt **5** [12*] shows the two NMe_2 groups to be equivalent at room temperature (the methyl resonance appears as a sharp singlet). Furthermore, since the ^{29}Si chemical shift of **5** ($\delta = -127.2$ ppm, in the solid state) is very close to that of **4** ($\delta = -134.9$ ppm, in the solid state), it is concluded that **5** is also hexacoordinate. The equivalence of the two NMe_2 groups apparently results from rapid exchange (on the NMR time scale) of one NMe_2 group for the other in the hexacoordinate silicon complex.



Scheme 1.

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* Reference number with asterisk indicates a note in the list of references.

This can be interpreted as a nucleophilic attack on a hexacoordinate silicon species.

Further studies on **5** are in progress.

References and notes

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9 To a solution of MeOK (580 mg, 8.3 mmol) in methanol (20 ml) were added successively a solution of catechol (1.85 g, 16.8 mmol) in methanol (15 ml) and a solution of 2,6-bis(dimethylaminomethyl)phenyltrimethoxysilane (2.7 g, 8.65 mmol) in methanol (10 ml). The reaction mixture was stirred for 3 h and then the solvent was removed under vacuum. The resulting white powder was washed twice with ether and dried under vacuum (0.1 mmHg) by heating (140°C) for 1 h. The crude product was purified by two recrystallizations from acetone/CH_2Cl_2 (50/50), to give 1.5 g of compound **4**; m.p. 219–221°C. ^1H NMR (CD_2Cl_2, −40°C): δ 2.13 (s, 3H); 2.63 (d, 3H, $J = 4.7$ Hz); 2.82 (s, 3H); 3.02 (d, 3H, $J = 4.8$ Hz); 3.33 (d, 1H, $J = 13.8$ Hz); 3.4 (dd, 1H, $J = 10.2$ Hz, $J = 2.8$ Hz); 4.6 (d, 1H, $J = 14$ Hz); 4.95 (d, 1H, $J = 12$ Hz); 6.38–6.7 (m, 8H); 6.9–7.15 (m, 3H). ^{29}Si NMR (CD_2Cl_2): δ −134.9 ppm (in the solid state). Negative-ion FAB MS m/z 435 $(M-H)^-$; positive-ion FAB MS m/z 437 $(M+H)^+$. IR ν(NH) = 3422 cm^{-1}. Anal. Found: C, 65.93; H, 6.52; N, 6.42. $C_{24}H_{28}N_2O_4Si$: C, 66.05; H, 6.42; N, 6.42%.

10 Crystal structure analysis of **4**: $P2_1/c$, a 12.738(12), b 18.150(3), c 11.962(2) Å, β 106.66(4)°, V 2649.3 $Å^3$, $Z = 4$, $R = 0.059$ for 2173 independent reflections with $F > 2.8\sigma(F)$ (Enraf-Nonius CAD-4 diffractometer, Mo $K\alpha$). A list of atomic coordinates and all crystal data may be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

11 To a solution of compound **4** (1.5 g, 3.44 mmol) in CH_2Cl_2 (45 ml) was added a suspension of KH (3.44 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred at room temperature for 5 h and then a grey solid was filtered (1.5 g, 98%) and identified as compound **3** from ^{29}Si NMR: δ −129.8 ppm (solid state) and mass spectrum. Negative-ion FAB MS m/z 435 $(M-K)^-$, 909 $(2M-K)^-$.

12 A solution of [PPN]Cl (0.87 g, 1.52 mmol) in 20 ml of CH_2Cl_2 was added dropwise to a suspension of **4** (0.8 g, 1.68 mmol) in CH_2Cl_2 (50 ml) at 0°C under nitrogen. The mixture was stirred for 15 min, then filtered under nitrogen to remove KCl. The solution was concentrated under vacuum; the residue was washed twice with ether to give 1.3 g (84%) of white powder which was crystallized from CH_2Cl_2/Et_2O (95/5) to afford 0.81 g (55%) of **5**; m.p. 171–72°C. ^1H NMR (CD_2Cl_2): δ 2.4 (s, 12H, NMe_2); 3.76 (s, 4H, CH_2N); 6.32–6.48 (m, 8H); 7–7.08 (m, 3H); 7.4–7.68 (m, 30H). ^{29}Si NMR: δ −127.2 ppm (in the solid state). Negative-ion FAB MS m/z 435 $(M-PPN)^-$; positive-ion FAB MS m/z 538 $(PPN)^+$.