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Communications

Hexacoordination at Silicon: The Case of Silatranes

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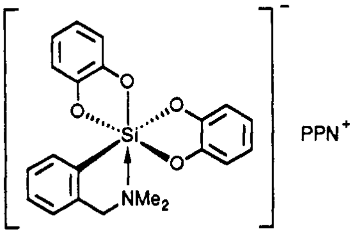
Summary: (2-(1-(Dimethylamino)ethyl)phenyl)silatrane and (8-(dimethylamino)-1-naphthyl)silatrane have been prepared in order to study the possibility of intramolecular coordination at silicon by a nucleophilic atom in the silatrane structure. The structure of the former exhibits no chelation of the NMe_2 group; the geometry around the silicon atom remains trigonal bipyramidal. In contrast, the structure of the latter suggests a weak interaction between the silicon atom and the NMe_2 group.

Species containing a hexacoordinated silicon atom have often been proposed as intermediates or transition states in the course of nucleophilic substitution reactions at silicon.[1,2] In all cases, the mechanism proposed involves nucleophilic attack on an anionic or neutral pentacoordinated species.

A few years ago, we showed that anionic pentacoordinated silicates[3] could undergo nucleophilic displacement at silicon by strong nucleophiles. Interest in nucleophilic attack on anionic pentacoordinated silicon compounds has been further stimulated recently by the determination by X-ray crystallography of the structure of the silicate 1,[4] which is a possible model[5] for nucleophilic attack on an anionic pentacoordinated species. This compound adopts a quasi-octahedral geometry with a very short dative Si←N bond (2.15 Å), shorter than those observed in some neutral compounds with pentacoordinated and hexacoordinated silicon (2.4–2.6 Å)[2b,6,7] but longer than covalent Si–N bonds[8] (1.72 Å). This result illustrates the ability of a pentacoordinated silicon center to undergo a nucleophilic attack.



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It is important to know if this ability to become hexacoordinated is a general trend for pentacoordinated silicon species. Therefore, we have studied other pentacoordinated silicon compounds.

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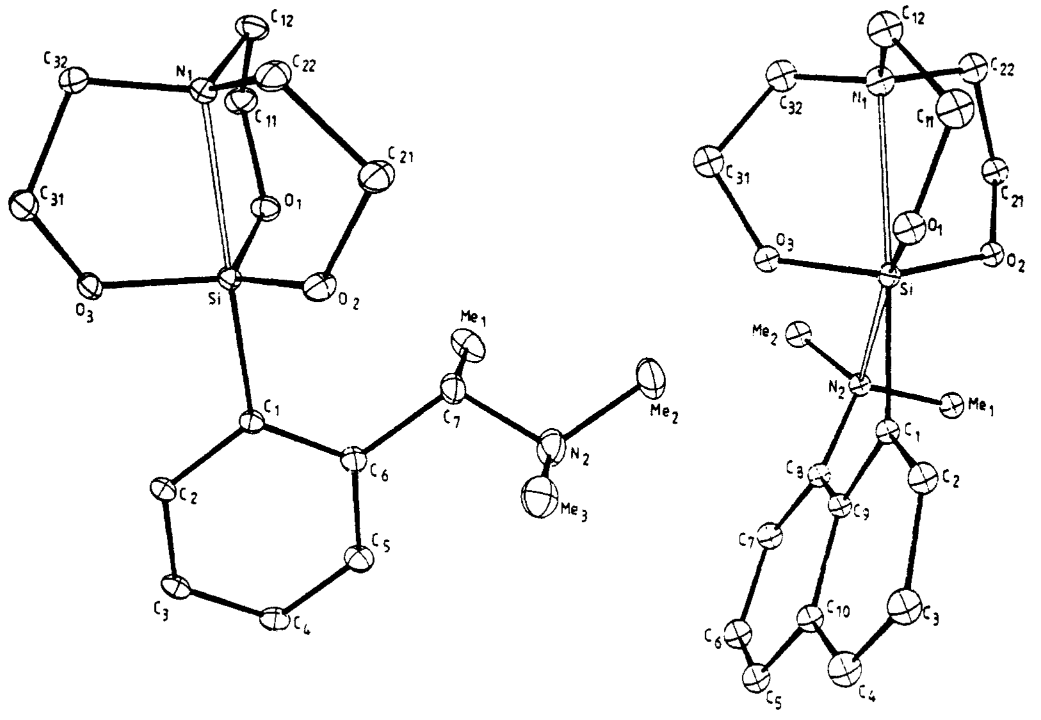
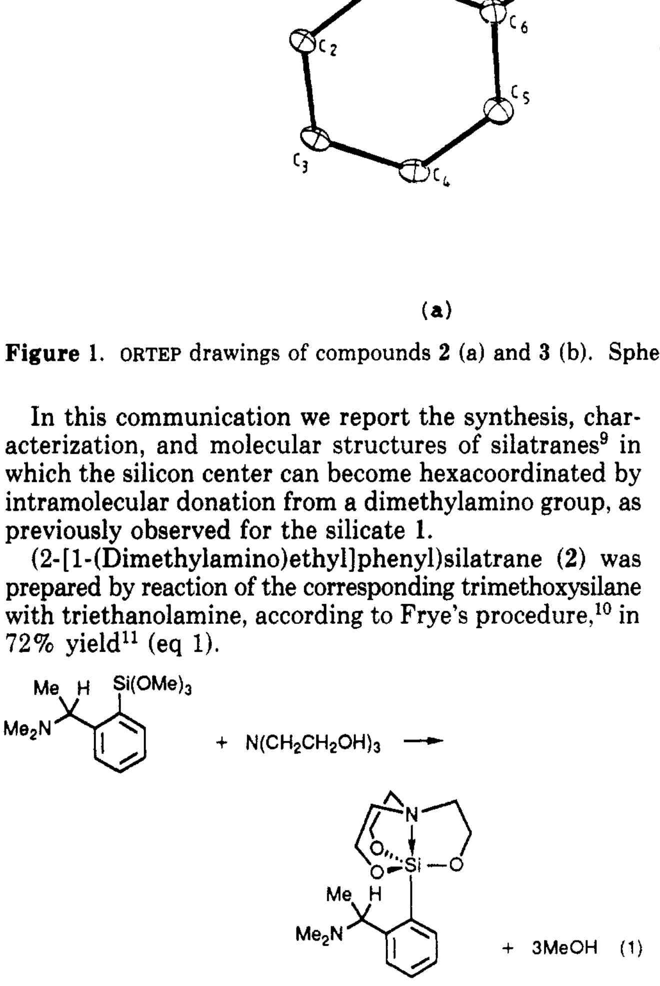


(a) (b)

Figure 1. ORTEP drawings of compounds 2 (a) and 3 (b). Spheres and ellipsoids are at the 10% probability level.

In this communication we report the synthesis, characterization, and molecular structures of silatranes[9] in which the silicon center can become hexacoordinated by intramolecular donation from a dimethylamino group, as previously observed for the silicate 1.

(2-[1-(Dimethylamino)ethyl]phenyl)silatrane (2) was prepared by reaction of the corresponding trimethoxysilane with triethanolamine, according to Frye's procedure,[10] in 72% yield[11] (eq 1).



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Compound 2 was identified on the basis of its mass and NMR spectra. In solution the ^1H NMR spectrum shows the resonance of the NMe_2 group as a sharp singlet at room temperature; the ^{29}Si chemical shift (δ = −78.6 ppm) is similar to that observed for phenylsilatrane[9] (δ = −80.5 ppm). A single-crystal X-ray diffraction analysis of 2 was performed.[12] The striking feature of this structure (Figure 1a) is that the NMe_2 group is not coordinated to the silicon, in contrast to the situation for the anionic pentacoordinated silicate 1.[4] The structure of compound 2 displays the same geometry (trigonal bipyramid) about the silicon atom that is usually observed with silatranes.[9] Selected bond lengths and bond angles are given in Table I. It is worthy of note that the Si–N(1) bond length (2.28 Å) is slightly longer than in phenylsilatrane[9] (2.19 Å).

Table I. Bond Lengths (Å) and Bond Angles (deg) at Silicon for Compound 2 (Standard Deviations in Parentheses)

Si-O(1)	1.651 (4)	Si-C(1)	1.895 (5)
Si-O(2)	1.656 (3)	Si···N(1)	2.283 (4)
Si-O(3)	1.649 (3)		
C(1)-Si···N(1)	179.1 (2)	N(1)···Si-O(2)	80.9 (2)
C(1)-Si-O(1)	98.3 (2)	N(1)···Si-O(3)	81.4 (2)
C(1)-Si-O(2)	99.1 (2)	O(1)-Si-O(2)	120.6 (2)
C(1)-Si-O(3)	99.4 (2)	O(2)-Si-O(3)	115.3 (2)
N(1)···Si-O(1)	81.0 (2)	O(3)-Si-O(1)	117.1 (2)

As a further test of possible hexacoordination, we also synthesized (8-(dimethylamino)-1-naphthyl)silatrane (3), intramolecular donor–acceptor interactions in 1,8-disubstituted naphthalenes having been extensively studied by

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[10] Frye, C. L.; Vincent, G. A.; Finzel, W. A. *J. Am. Chem. Soc.* **1971**, *93*, 6805.

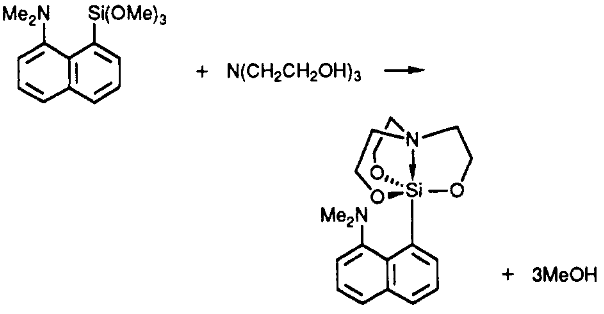
[11] A mixture of (2-(1-(dimethylamino)ethyl)phenyl)trimethoxysilane (20 mmol) and triethanolamine (20 mmol) was heated at 50 °C in the presence of a catalytic amount of KOH (1 mmol). The methanol formed during the reaction was progressively removed by distillation; when no more methanol distilled (ca. 45 min), the silatrane was precipitated by addition of pentane. After filtration, the resulting solid was purified by crystallization from hexane–CH_2Cl_2 to give white crystals of 2: 72% yield; mp 193–194.5 °C; ^1H NMR (CD_2Cl_2) δ 1.25 (3 H, d, J = 6.3 Hz, CH_3), 2.18 (6 H, s, NMe_2), 2.86 (6 H, t, J = 5.8 Hz, NCH_2), 3.55 (1 H, q, J = 6.3 Hz, $CHCH_3$), 3.85 (6 H, t, J = 5.7 Hz, OCH_2), 7.05 (1 H, dd, J = 7.25 and 7.40 Hz, Ar), 7.20 (1 H, dd, J = 7.75 and 7.25 Hz, Ar), 7.48 (1 H, d, J = 7.25 Hz, Ar), 7.78 (1 H, d, J = 7.40 Hz, Ar); ^{29}Si NMR δ −78.57; MS *m/e* 322 (M^+), 174 (100%).

[12] X-ray crystal structure of 2: orthorhombic, space group $P2_12_12_1$; a = 12.783 (2), b = 12.752 (2), c = 10.544 (2) Å; V = 1719 Å^3; Z = 4; d_{calcd} = 1.246, d_{measd} = 1.24 (2) g cm^{-3}; μ(Mo Kα) = 1.44 cm^{-3}. A colorless block was abraded to a sphere of diameter 0.6 mm and sealed in a capillary. A total of 2636 unique reflections were collected and 1565 kept for the refinement of the structure ($F_o > 3\sigma(F_o)$]. The silicon atom and nitrogen, oxygen, and carbon atoms were refined anisotropically. The hydrogen atoms were taken into account in the refinement. Final residuals: R = 0.048, R_w = 0.053. Full details of the structure determination for 2 are available as supplementary material.

Table II. Bond Lengths (Å) and Bond Angles (deg) at Silicon for Compound 3 (Standard Deviations in Parentheses)

Si⋯N(1)	2.421 (8)	Si-O(2)	1.644 (6)
Si⋯N(2)	2.952 (7)	Si-O(3)	1.635 (6)
Si-O(1)	1.658 (6)	Si-C(1)	1.892 (8)
C(1)-Si-O(1)	99.0 (3)	N(1)⋯Si-O(1)	78.7 (3)
C(1)-Si-O(2)	105.8 (3)	N(1)⋯Si-O(2)	78.2 (3)
C(1)-Si-O(3)	99.7 (3)	N(1)⋯Si-O(3)	78.3 (3)
O(1)-Si-O(2)	110.5 (3)	N(2)⋯Si-C(1)	69.4 (3)
O(2)-Si-O(3)	123.9 (3)	N(2)⋯Si-O(2)	74.0 (2)
O(3)-Si-O(1)	113.7 (3)	N(2)⋯Si-O(3)	69.7 (2)
N(1)⋯Si-C(1)	175.9 (3)	N(1)⋯Si⋯N(2)	112.9 (2)
N(2)⋯Si-O(1)	168.4 (3)		

Dunitz.[13] The silatrane 3 was prepared from the corresponding trimethoxysilane in 54% yield[14] (eq 2).



(2)

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In solution, the ^1H NMR spectrum of 3 again exhibits the resonance of the NMe_2 group as a sharp singlet at room temperature; the ^{29}Si chemical shift of 3 appears at $\delta = -70.56$ ppm downfield from that of the (1-naphthyl)silatrane[15] ($\delta = -80.49$ ppm).

The X-ray analysis of 3[16] (Figure 1b) reveals that the silicon atom is hexacoordinated in a nonclassical geometry. Selected bond lengths and angles are given in Table II. The main features of this structure are as follows.

(1) The average of the N(1)-Si-O angles is 78.4°, compared with 81° for 2 and about 83° for classical silatranes.[9]

(2) The Si-N(1) bond distance is 2.42 Å, which is about 10% longer than the Si-N bond in phenylsilatrane[9] (2.19 Å). (The structure of (1-naphthyl)silatrane without the NMe_2 group in the 8-position has not been determined.)

(3) The low value of the N(2)-Si-C(1) angle (69.4°), as well as the length of the Si-N(2) bond (2.95 Å), indicates a weak interaction between the silicon and nitrogen atoms. (The sum of the van der Waals radii of the silicon and nitrogen atoms[9] is 3.5 Å.) The existence of this Si-N(2) interaction is due to the rigid geometry of the 8-(dimethylamino)-1-naphthyl group, which imposes the coordination at silicon. The reluctance of silicon to become hexacoordinated in the silatrane structure is illustrated by the Si-N(1) bond lengthening (2.42 Å) and by the distortion of the naphthyl group due to the abnormally long Si-N(2) bond (2.95 Å). As shown in Figure 1b, the naphthyl group is no longer planar: for instance, the C(2)-C(3) and C(7)-C(6) bonds make a dihedral angle of 9.6°; the displacements of the silicon and the nitrogen atoms to either side of the naphthyl mean plane are respectively 0.67 and 0.36 Å. A measure of this out-of-plane deformation is given by the dihedral angle N(2)-C(8)⋯C(1)-Si, the value of which is as large as 27°. The naphthyl group is much more twisted than in other hexacoordinated structures[7] in which the interaction between the NMe_2 group and the silicon atom is stronger.

In conclusion, this work points out the difficulty for silatranes to become hexacoordinated, in contrast to the case for the anionic pentacoordinated silicate 1.[4] This is consistent with the low reactivity of silicon functional silatranes toward nucleophiles, illustrated by the following experimental observations: the lack of reactivity of chlorosilatrane,[10] the low reactivity of hydrosilatrane[17] toward carbonyl compounds in comparison with that observed for other pentacoordinated hydrosilanes,[18,19] and the inability of (1-allyl)silatrane to transfer the allylic group[20] with or without nucleophilic activation, whereas allylsilicates do so.[20-22]

The rigidity of the silatrane cage appears not to be favorable for hexacoordination, because of the narrowing of the O-Si-O bond angles required for the conversion into a near-octahedral structure. Moreover, the electrophilic character of a pentacoordinated silicon atom must depend on the nature of the surrounding atoms. Studies to investigate this point are in progress.

Supplementary Material Available: Tables of crystal data, intensity collection, and refinement, atomic coordinates for the non-H atoms, bond distances, bond angles, anisotropic thermal parameters, and calculated atomic coordinates for the H atoms for 2 and of crystal data, intensity collection, and refinement, atomic coordinates and thermal parameters for the non-H atoms, bond distances, bond angles, and calculated atomic coordinates for H atoms for 3 (11 pages); listings of structure factor amplitudes for 2 and 3 (12 pages). Ordering information is given on any current masthead page.

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(14) (8-(Dimethylamino)-1-naphthyl)silatrane (3) was prepared in the same way as 2 from (8-(dimethylamino)-1-naphthyl)trimethoxysilane. The reaction mixture was heated at 80 °C for 45 min. After precipitation of the silatrane with pentane, the resulting solid was crystallized from $MeOH-CHCl_3$ to give white crystals of 3: 54% yield; mp 163.8–165 °C; ^1H NMR (CD_2Cl_2) δ 2.64 (6 H, s, NMe_2), 2.88 (6 H, t, $J = 5.5$ Hz, NCH_2), 3.82 (6 H, t, $J = 5.5$ Hz, OCH_2), 7.4 (3 H, m, Ar), 7.6 (1 H, m, Ar), 7.75 (1 H, d, $J = 8.2$ Hz, Ar), 8.25 (1 H, d, $J = 6.9$ Hz, Ar); ^{29}Si NMR δ −70.56; MS *m/e* 344 (M^+), 174 (100%).

(15) (1-Naphthyl)trimethoxysilane (20 mmol) in 80 mL of xylene was added to 20 mmol of triethanolamine in 25 mL of xylene. The mixture was heated for 3 h; the methanol formed was removed continuously by distillation. The silatrane was precipitated by addition of methanol; after filtration the resulting solid was purified by crystallization from chloroform to give (1-naphthyl)silatrane: 76% yield; mp 248.5–250 °C; ^1H NMR ($CDCl_3$) δ 2.82 (6 H, dist t, NCH_2), 3.8 (6 H, dist t, OCH_2), 7.1–8.3 (7 H, m, Ar); ^{29}Si NMR ($CDCl_3$) δ −80.49; MS *m/e* 301 (M^+), 174 (100%).

(16) X-ray crystal analysis of 3: monoclinic, space group $P2_1/n$; $a = 9.021$ (2), $b = 12.849$ (2), $c = 15.766$ (3) Å; $\beta = 101.07$ (2)°; $V = 1793$ Å^3; $Z = 4$; $d_{calcd} = 1.276$, $d_{measd} = 1.29$ (3) g cm^{-3}; μ(Mo Kα) = 1.43 cm^{-1}. A colorless parallelepiped (0.20 × 0.35 × 0.35 mm^3) was crystallized from a mixture of chloroform and methanol (1:1) and sealed in a Lindemann glass capillary. A total of 2412 unique reflections were collected, but only 1129 were observed ($F_o > 3\sigma(F_o)$) (CAD4 diffractometer, Enraf-Nonius, graphite monochromator, Mo Kα radiation). Solution was by direct methods. Due to the low number of observed reflections, only the silicon atom was refined anisotropically. The hydrogen atomic positions were determined by calculation (SHELX-76 program), and the hydrogen atoms were taken into account in the refinement. Final residuals: $R = 0.069$, $R_w = 0.074$. Full details of the structure determination for 3 are available as supplementary material.

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