

Water-Coordinated Neutral Silane Complex: A Frozen Intermediate of Hydrolysis of Alkoxysilanes

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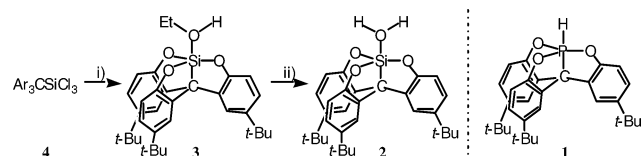
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Alkoxysilanes and halosilanes are important silicon compounds because they are useful precursors of silicon polymers (polysiloxanes).¹ Among polysiloxanes, silsesquioxanes have attracted a wide range of interest from many organic chemists because of their practical applications to heterogeneous catalysts, protective coatings, adhesive-related materials, and so forth.² Extensive studies on the formation mechanism of polysiloxanes have been performed in both experimental and theoretical fields.³ The first step in the reaction is considered to be hydrolysis of the precursors to give polyhydroxysilanes, which undergo polycondensation to yield the corresponding polysiloxanes. The hydrolysis should involve the formation of pentacoordinate silicon species, in which a water molecule coordinates to the silicon center, and subsequent proton migration to the leaving group (alkoxy group or halogen atom for alkoxysilanes or halosilanes, respectively) leading to the elimination of alcohol or hydrogen halide. The latter step, however, is too fast to permit stopping the reaction at the stage of the formation of water-coordinated silicon species. Although many pentacoordinate silicon species have been synthesized as model compounds for the intermediate, there have been few reports of such species containing water as a ligand.⁴ We have recently focused on a novel tetradentate ligand, which can occupy one apical and three equatorial positions of the trigonal bipyramidal (TBP) structure. We succeeded in synthesizing a pentacoordinate phosphorus compound, 1-hydro-5-carbaphosphatane (**1**),⁵ which has a nearly ideal TBP structure with perfectly "anti-apicophilic" arrangement around the phosphorus center, although the arrangement was expected to be thermally unfavorable. Here, we report the synthesis of a silicon analogue of **1**, 1-aquo-5-carbasilatrane **2**, which is to the best of our knowledge, the first example of a neutral silicon compound coordinated by water, and it can be regarded as an intermediate in the hydrolysis of alkoxysilanes.

1-Ethyloxonio-5-carbasilatrane **3** was obtained by treatment of $\text{Ar}_3\text{CSiCl}_3$ (**4**)⁶ with 8.3 molar equiv of BBr_3 in CHCl_3 and subsequent alcoholysis. Although **3** was unstable toward air and decomposed immediately, even in the solid state, coordinated ethanol was easily replaced by water when **3** was treated with water.⁷ ^{29}Si NMR chemical shifts of **2** and **3** are δ_{Si} -69.0 and -66.9 ppm, respectively, indicating that the silicon centers of **2** and **3** take pentacoordinate states as a result of the coordination of water and ethanol, respectively.

Single crystals of **2** were obtained by slow evaporation of the solution (hexane/ Et_2O) of **2**. The crystal structure of **2** was established by X-ray crystallographic analysis, which showed that diethyl ether and hexane are contained in the unit cell (Figure 1).⁸ Compound **2** has a nearly ideal TBP structure with a water molecule at the apical position. The equatorial–equatorial bond angles (O–Si–O) of **2** are $118.09(12)$, $119.92(12)$, and $121.45(12)^\circ$, and the apical–equatorial bond angles (C–Si–O) are $91.52(13)$, $92.74(12)$, and $93.05(13)^\circ$, respectively. In fact, the pentacoordination char-

Scheme 1^a



^a (i) BBr_3 , rt, then EtOH , 98%; (ii) H_2O , 95%.

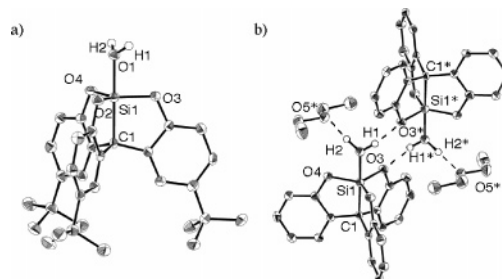
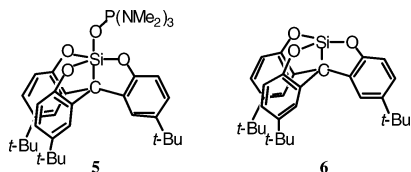


Figure 1. ORTEP drawings of **2** (50% probability). (a) Sideview and (b) intermolecular hydrogen bonding (*t*-Bu groups are omitted for clarity). Selected bond lengths (Å) and angles (deg): Si1–O1, 1.794(3); Si1–O2, 1.683(3); Si1–O3, 1.732(2); Si1–O4, 1.691(2); Si1–C1, 1.940(3); O3*···H1, 1.78(5); O5*···H2, 1.59(6); O2–Si1–O3, 118.09(12); O2–Si1–O4, 121.45(12); O3–Si1–O4, 119.92(12); C1–Si1–O2, 93.05(13); C1–Si1–O3, 91.52(13); C1–Si1–O4, 92.74(13); O1–Si1–C1, 178.30(15).

acters, % TBP_a and % TBP_e, were calculated to be 88 and 98%, respectively.⁹ The apical interatomic distance of O1–Si1 (1.794(3) Å) is slightly longer than those of the three equatorial bonds, which is a typical feature of TBP structures. However, this is significantly shorter than the reported values of 1.916(9), 1.843(9), and 1.9114(14) Å for the water-coordinated ionic silicon compounds.^{4b,c} The hydrogen atoms, H1 and H2, of the water ligand in **2** are hydrogen bonded to the oxygen atoms of the neighboring molecule (O3*) and diethyl ether (O5*) with bond lengths of 1.78(5) and 1.59(6) Å for H1–O3* and H2–O5*, respectively, forming a dimeric structure in which the bond length of Si1–O3 is significantly longer than those of Si1–O2 and Si1–O4, probably because of the hydrogen bonding. Therefore, this dimeric structure can be recognized as a transition state for the theoretically proposed proton transfer catalyzed by another hydroxy species, such as water,^{3c,h} which should assist elimination of the leaving group, producing the hydroxysilane.

In the ^1H and ^{13}C NMR spectra of **2** obtained after removal of diethyl ether in vacuo, three equivalent benzene rings were observed, indicating that **2** exists as a monomer in solution, in contrast to the crystal structure, and that rapid rotation around the Si1–O1 bond or rapid elimination and recombination of water at the silicon center must occur relative to the NMR time scale in solution. Because the signal due to the water ligand of **2** was observed separately from that of free water in the ^1H NMR, the latter possibility can be ruled out. However, the slow exchange of

water was suggested by a labeling experiment using H_2^{18}O .¹⁰ It is also interesting that the bond cleavage of Si–OAr does not occur, even in the presence of water; in other words, the reaction is frozen at the stage of the formation of **2**, reflecting the high stability of the TBP structure of **2** due to a rigid tetradentate ligand.



Although the water ligand in **2** could be replaced with other Lewis bases, such as HMPA, to give **5**,¹⁰ the attempted removal of water in vacuo with heating was unsuccessful because of thermal decomposition. Furthermore, the corresponding tetracoordinate silane **6** was never observed, neither in the formation reaction of **2** nor in the ligand exchange reactions. These results indicate that **6** is very liable to take the pentacoordinate state by complexation with water or other nucleophiles and prompted us to perform the theoretical calculations to estimate the stabilizing energy associated with complexation. The theoretical calculations were performed with the model compounds **7** and **8**, in which the *t*-Bu groups were omitted, at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level.¹¹ We calculated **8** to be 20 kcal mol⁻¹ more stable than a system of **7** and water, suggesting that **7** has a potentially strong Lewis acidity. The sum (348.4°) of the three calculated bond angles (O–Si–O) around the silicon of **7** indicated that **7** has a structure that deviates from tetrahedral (328.5°) to the trigonal pyramidal structure (360°), and preorganization of the TBP structure of **7** seems to be the origin of the strong Lewis acidity of **7**. Moreover, the Mulliken charge of the proton was enhanced by complexation, from 0.39 (free water) to 0.46 (**8**). Judging from the fact that complete deprotonation of **2** was achieved by use of pyridine ($\text{p}K_{\text{a}} = 5.24$ for the conjugate acid) as a base, but not by use of *m*-nitroaniline ($\text{p}K_{\text{a}} = 2.60$ for the conjugate acid), it follows that the $\text{p}K_{\text{a}}$ value of **2** is estimated to be 10–13 $\text{p}K_{\text{a}}$ units lower than that of free water.¹²

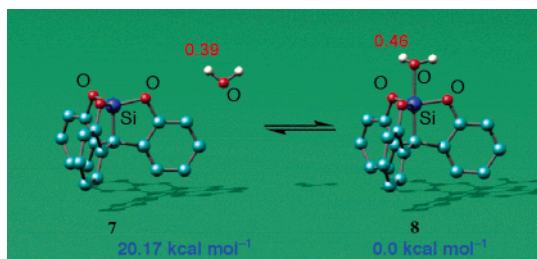


Figure 2. Calculated structures of **7** and **8**. Each of the structures was obtained at the B3LYP/6-31G(d) level. B3LYP/6-31G(d)//B3LYP/6-31G(d) enthalpy values are given in kcal mol⁻¹, including zero-point energies. Mulliken charge of hydrogen atoms are in red.

In summary, we have synthesized the water- and ethanol-coordinated neutral silane complexes **2** and **3**, which can be regarded as intermediates in the hydrolysis or alcoholysis of alkoxyasilanes, respectively. The rigid tetradentate ligand based on the triarylmethyl unit enabled stabilization of the water- or ethanol-coordinated neutral silane complexes. Theoretical calculations showed that the tetracoordinate silane **6** has unusually high Lewis acidity. Isolation of **6** and further investigations on its Lewis acidity and application to organic synthetic reactions are in progress.

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Supporting Information Available: Experimental procedures for the synthesis and reactions of **2**, and X-ray structural information on **2** (PDF), as well as an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- Data for **2**: colorless crystals, mp 260–267 °C dec; ¹H NMR (500 MHz, C₆D₆, 24 °C) δ 1.31 (s, 27H), 6.62 (d, 3H, *J* = 8.4 Hz), 6.93 (dd, 3H, *J* = 8.4, 2.2 Hz), 7.87 (d, 3H, *J* = 2.2 Hz), 11.4 (brd, 2H); ¹³C NMR (125 MHz, CDCl₃, 24 °C) δ 25.16, 32.04, 34.63, 113.18, 123.45, 125.83, 137.94, 143.33, 156.74; ²⁹Si NMR (99.3 MHz, CDCl₃, 24 °C) δ -69.0. Anal. Calcd for C₃₁H₃₈O₄Si·(C₂H₅)₂O: C, 72.88; H, 8.39. Found: C, 72.88; H, 8.39. Data for **3**: colorless crystals, mp 452–458 °C dec (in a sealed capillary); ¹H NMR (500 MHz, THF-*d*₈, 24 °C) δ 1.30 (s, 27H), 1.53 (t, 3H, *J* = 7.2 Hz), 3.41 (br s, 1H), 4.41 (q, 2H, *J* = 7.2 Hz), 6.64 (d, 3H, *J* = 8.4 Hz), 6.94 (dd, 3H, *J* = 8.4, 2.2 Hz), 7.86 (d, 3H, *J* = 2.2 Hz); ¹³C NMR (125 MHz, THF-*d*₈, 24 °C) δ 16.11, 24.06, 29.26, 31.92, 61.55, 110.60, 120.91, 123.12, 134.82, 140.95, 154.02; ²⁹Si NMR (99.3 MHz, CDCl₃, 24 °C) δ -66.9.
- Crystal data for **2**·Et₂O·hexane: C₃₈H₅₅O₅Si, monoclinic, *P*2₁/*n*, colorless, *a* = 10.451(3) Å, *b* = 20.497(6) Å, *c* = 16.753(5) Å, β = 90.3493(11)°, *V* = 2588.7(18) Å³, *T* = 130(2) K, *Z* = 4, *M*_w = 619.91, *D*_c = 1.147 Mg m⁻³, *R* [*I* > 2σ(*I*)] = 0.0566, w*R*₂ [all data] = 0.1384, GOF = 1.105.
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