

Synthesis, Structure, and Reactions of a Novel Triarylsilanol with a Bowl-Type Framework: A Silanol Extremely Resistant to Self-Condensation

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A novel nano-scale triarylsilanol bearing a bowl-shaped framework was synthesized, the structure of which was established by X-ray crystallographic analysis. The silanol was found to be extremely resistant to self-condensation whereas it reacted easily with appropriate molecules to give the corresponding derivatives.

A variety of bulky silyl groups have been developed so far and widely applied to the kinetic stabilization of various highly reactive species as well as to the protection of functional groups in organic synthesis.¹ In the course of our study on the development and application of the bowl-shaped steric protection groups,² we have recently designed a novel triarylmethyl group **1** (denoted as Trm), where the radially extended *m*-terphenyl units forms a large bowl-type cavity.³ The reactive species bearing the Trm group can be prevented from dimerization or self-condensation effectively whereas its reactivity towards appropriate molecules is not so much degenerated because there is a relatively large space around it. By taking advantage of the Trm group, a stable *S*-nitrosothiol (TrmSNO) was successfully synthesized.³ It is expected that the silyl group **2** (tris(2,2",6,6"-tetramethyl-*m*-terphenyl-5'-yl)silyl; denoted as TRMS hereafter), where the central carbon atom of the Trm group is replaced by a silicon atom, will be useful as a nano-scale silyl group possessing the above-mentioned characteristics of the Trm group. We report here the synthesis of a silanol extremely resistant to the self-condensation by taking advantage the TRMS group along with its crystal structure and reactivity.^{4,5}

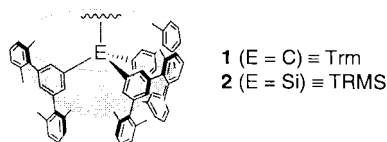
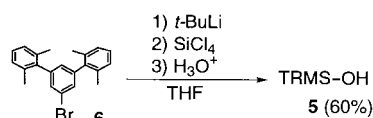


Figure 1 shows the molecular models of (*t*-Bu)₃SiOH (**3**), Ph₃SiOH (**4**), and TRMS-OH (**5**). Inspection of the model of **5** indicates that the central silicon atom is embedded in the shallow bowl-shaped cavity with a diameter of about 16 Å and a depth of about 1.5 Å. Despite the bulkiness of the whole molecule, the steric congestion in the close vicinity of the OH group of **5** is

almost the same as that of **4** and seems less heavier than that of **3**, because there is no *ortho*-substituent on the aromatic rings connected to the silicon atom.

TRMS-OH (**5**) was prepared from bromide **6** and isolated as colorless crystals (Scheme 1).⁶ In the ¹H and ¹³C NMR spectra, all the methyl signals appeared equivalent, indicating that the Si-C bonds rotate rapidly on the NMR time-scale. The IR spectra of **5** in a CH₂Cl₂ solution showed a band at 3648 cm⁻¹, which is assignable to a free SiOH. This band was found to be concentration-independent, indicating that silanol **5** has a monomeric structure in solution.



Scheme 1.

A single crystal of **5** grown from a hexane-benzene solution was studied by X-ray diffraction, and its structure is shown in Figure 2 with selected bond lengths and angles.⁷ The figure shows that the OH group is surrounded from all sides and from a distance as expected by the molecular model. It was found that **5** is solvated by one molecule of hexane, which does not show any particular interaction with the SiOH group. Usually, silanols form strong intermolecular OH...O hydrogen bonding to give oligomeric structures in the crystalline state. For example, Ph₃SiOH (**4**) was reported to have a tetrameric structure with the intermolecular O...O distances of 2.63–2.68 Å.⁸ On the other hand, the shortest intermolecular O...O distance of **5** is 7.80 Å, indicating the absence of OH...O hydrogen bonding. Recently, Eaborn et al. reported that, in the crystal structures of some sterically hindered silanols, the intermolecular OH...π interaction was observed.⁹ Examination of the crystal structure of **5** revealed that the OH hydrogen atom lies above one of the 2,6-dimethylphenyl rings (ring A in Figure 2) of the neighboring molecule at a distance of 2.64 Å from its center, suggesting the possible presence of the intermolecular OH...π interaction in the crystals. The IR spectrum of **5** in the solid state (KBr) showed its ν(OH) band at 3598 cm⁻¹, slightly lower wavenumber than that in solution, also indicating that there is weak

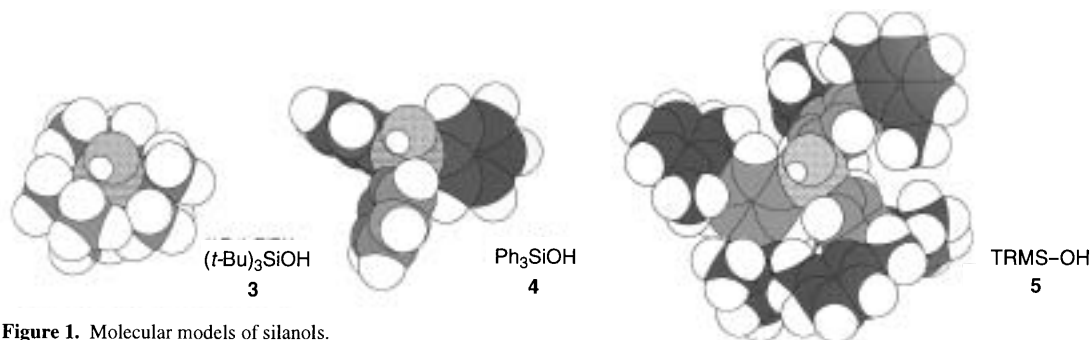


Figure 1. Molecular models of silanols.

interaction in the solid state. These results suggest that the bowl-shaped framework of **5** sterically prevents the formation of the OH...O hydrogen bonding, thus enabling the weak intermolecular OH... π interaction to be observed.

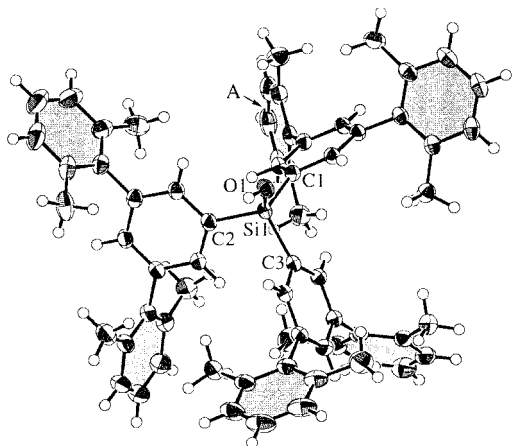
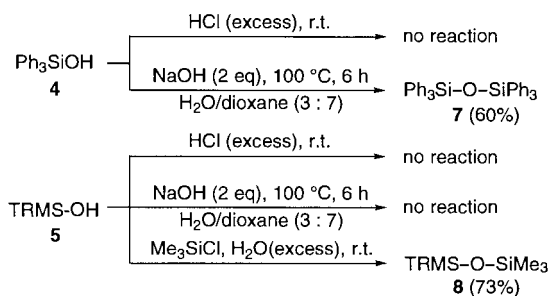


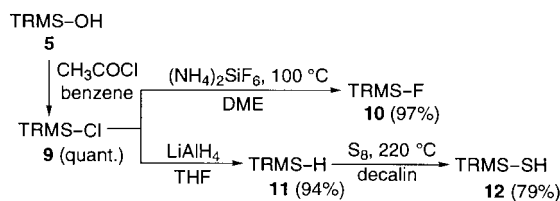
Figure 2. ORTEP drawing of **5** with thermal ellipsoids (50% probability). Selected bond lengths (Å) and angles (deg): Si(1)–O(1), 1.6389(12); Si(1)–C(1), 1.8603(15); Si(1)–C(2), 1.8711(16); Si(1)–C(3), 1.8705(17); C(1)–Si(1)–C(2), 111.07(7); C(2)–Si(1)–C(3), 106.43(7); C(1)–Si(1)–C(3), 108.76(7).

It is notable that the sum of the C–Si–C bond angles of **5** is 326.3°, somewhat smaller than that of Ph₃SiOH (**4**) (331°, the mean of those of eight fragments).⁸ This is in contrast with other bulky silyl derivatives such as trimesitylsilyl azide¹⁰ and tri(9-anthryl)silyl fluoride,¹¹ for which the sums of the C–Si–C angles increase to 342.1° and 345.7°, respectively. These results indicate that, in the dendrimer-type silanol **5**, the molecular size is enlarged in comparison with **4** without increasing steric repulsion among three aryl groups.

It is known that Ph₃SiOH (**4**) is fairly resistant to self-condensation and stable under acidic conditions. It was reported, however, that **4** undergoes condensation to disiloxane **7** upon heating under basic conditions.¹² Actually, when **4** was heated at 100 °C in the presence of NaOH in water/dioxane (3:7), **4** was converted to **7** in 60% yield (Scheme 2). By contrast, no condensation was observed when TRMS–OH (**5**) was heated under the same conditions (Scheme 2). Silanol **5** was also stable in the presence of hydrochloric acid similarly to **4**. In spite of such high stability towards self-condensation, **5** readily reacted with Me₃SiOH generated in situ by hydrolysis of Me₃SiCl to give the unsymmetrical disiloxane **8**, indicating that there is a space around the SiOH functionality of **5** large enough for its reaction with an appropriate molecule. Silanol **5** can be readily converted to various derivatives by the usual methods (Scheme 3). Treatment of **5** with acetyl chloride afforded the corresponding chlorosilane **9** quantitatively, which



Scheme 2.



Scheme 3.

was further converted to fluorosilane **10** and hydrosilane **11** in good yields. The reaction of **11** with elemental sulfur in decalin¹³ afforded the corresponding silanethiol **12**. Silanethiol **12** can be stored for more than several months in an open atmosphere.

In summary, a novel nano-scale silyl group with a bowl-shaped cavity, the TRMS group, was designed, and a silanol and its derivatives bearing this framework were synthesized. Further investigations on the application of the TRMS group to the stabilization of highly reactive species as well as to the synthetic use are currently in progress.

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- 5**: colorless crystals; mp 262.5–263.0 °C; ¹H NMR(CDCl₃, 500 MHz) δ 1.92 (s, 36H), 2.51 (s, 1H), 7.00 (t, *J* = 1.5 Hz, 3H), 7.03–7.12 (m, 18H), 7.42 (d, *J* = 1.5 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 20.8 (q), 127.0 (d), 127.2 (d), 131.4 (d), 133.8 (d), 135.4 (s), 135.8 (s), 140.8 (s), 141.5 (s). IR (CH₂Cl₂) 3648 cm⁻¹ (ν_{OH}). Found: C, 87.74; H, 7.16%. Calcd for C₆₆H₆₄O₃Si: C, 87.95; H, 7.16%.
- Crystallographic data for **5**: C₆₆H₆₄O₃Si·C₆H₁₄, *M_r* = 987.43, monoclinic, space group C2/c, *a* = 31.121(1), *b* = 15.460(1), *c* = 26.376(1) Å, β = 110.283(1)°, *U* = 11903.4(10) Å³, *Z* = 8, *D_c* = 1.102 g cm⁻³, *T* = 148 K, μ(Mo Kα) = 0.082 mm⁻¹, *R*₁ = 0.0554 (*I* > 2σ(*I*)), *wR*₂ = 0.1577 (all data).
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