Isolation of a Protonated Silanol: $Bu^t_3Si(OH_2)^+$

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The *basicity* of a silanol is demonstrated in the isolation and structural characterization of a stable salt of $Bu^t_3Si(OH_2)^+$; the inert counterion is the brominated carborane $Br_6CB_{11}H_6^-$.

The Brønsted acidity of silanols, typically greater than in the corresponding alcohols, is widely recognized.[1] On the other hand, little is known about the Brønsted *basicity* of silanols, particularly in condensed media. Solution IR measurements of $v(O-H)$ have been used to infer that silanols have comparable basicity to alcohols.[2] Protonated silanols have been identified in the gas phase by MS and ICR (ion cyclotron resonance) techniques, and under these conditions, silanols appear to be more basic than alcohols.[3,4] Sulfuric acid converts silanols to silyl hydrosulfates,[5] presumably *via* displacement of water in $[R_3Si(OH_2)]^+$ by hydrosulfate ion. To our knowledge, the protonation of silanols in superacid media has not been reported. However, protonation of the corresponding ethers, R_3SiOR, has been investigated in FSO_3H-SbF_5.[6] There is ¹H NMR evidence for the protonated species $[Me_3Si(OMeH)]^+$ at −70 °C but, upon warming, methanol is displaced by coordinating anions such as F^- or SbF_6^-. These two examples point towards the need for less coordinating anions if protonated species with Si–O bonds are to be isolated.

We have recently shown that certain *closo*-carboranes are among the least coordinating anions presently known for silicon.[7,8] The best of these is the large, exceptionally inert, brominated carborane, $Br_6CB_{11}H_6^-$. It has led to the closest structural approach to date to the long sought silylium ion (R_3Si^+) in $Pr^i_3Si(Br_6CB_{11}H_6)$.[8] A variety of evidence suggests that this type of species has a high degree of ionic character: $(Pr^i_3Si^{\delta+})(Br_6CB_{11}H_6^{\delta-})$.[9] We now report that careful treatment of such species with wet solvents (*i.e.* undried after aerobic exposure) leads to displacement of the weakly coordinated anion and formation of $[R_3Si(OH_2)]^+$ cations. This is equivalent to protonating a silanol with a strong acid. For the case of R = *tert*-butyl we have been able to isolate the protonated silanol as a crystalline salt that is stable at room temperature.
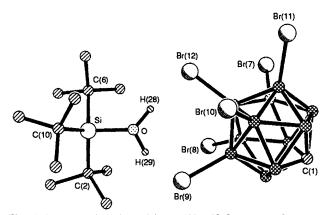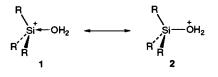
The ¹H NMR spectrum of a $[^2H_2]$dichloromethane solution of this salt provides strong evidence for the formulation of the cation as a protonated silanol. The water protons (δ 8.04) appear as a somewhat broad singlet several ppm downfield of the hydroxy resonance of tri-*tert*-butylsilanol (δ 3.12).[10] The *tert*-butyl protons appear as a sharp singlet with the correct relative integrated intensity (*i.e.* 27:2) at δ 1.25. The CP-MAS ²⁹Si NMR resonance appears downfield at δ 46.7, not unlike structurally related cations such as $[Pr^i_3Si(MeCN)]^+$ (δ 37.2).[7] As expected, the ¹¹B NMR spectrum of the anion is that of the free ion. The infrared spectrum (KBr) shows $v(O-H)$ from coordinated water at 3568 cm⁻¹. This can be compared to $v(O-H)$ at 3450 cm⁻¹ in the corresponding silanol.[10]

X-Ray quality crystals of $[Bu^t_3Si(OH_2)]^+[Br_6CB_{11}H_6]^-$ were grown from fluorobenzene.† The crystal structure consists of weakly associated cations and anions. The closest approaches are the 3.14 and 3.17 Å distances between the water oxygen atom and Br(12) and Br(9) respectively. This suggests some hydrogen-bonding of the acidic O–H bonds of the cation to the bromine atoms of the anion. A perspective view is shown in Fig. 1. The most notable features are the trigonal flattening of the four-coordinate silicon centre and the long Si–O bond. The average C–Si–C angle is 116.0(6)°, well removed from tetrahedrality (109.5°). This is very similar to trialkylsilicon cations with coordinated acetonitrile $[115.6(1.7)°]$.[7] The $Si–OH_2$ distance is 1.779(9) Å which is at least 0.1–0.2 Å longer than typical Si–OH or Si–OR bonds.[11] It is useful to view this as the distinction between a Lewis acid–base dative bond and a covalent bond.[12] Together, the geometry and bond length data suggest a predominance of silyl cation character **1** over onium ion character **2**.

The present structure has mechanistic implications for the hydrolysis of silyl compounds. Dissolution of the $[Bu^t_3-Si(OH_2)]^+$ salt in basic solvents (*e.g.* ethers, nitriles), or simply treating toluene solutions with excess water, leads to the formation of tri-*tert*-butylsilanol and a strongly acidic solution of $[H(solvent)_n]^+[Br_6CB_{11}H_6]^-$. Thus, water is very strongly implicated as the attacking nucleophile in the hydrolysis of R_3SiY species to silanols (and siloxanes) when Y^- is a weakly coordinating anion. Even for the very common reaction of the hydrolysis of chlorosilanes (*i.e.* $Y^- = Cl^-$), the present work supports the notion of an intermediate having water coordinated to silicon.

The isolation of the first acid of $Br_6CB_{11}H_6^-$ is important from the point of view of reagent development since stable, crystalline strong acids with 'innocent' anions are rare. The protonated silanol salt can be viewed as a derivative of the hypothetical superacid $H[Br_6CB_{11}H_6]$ whose acidity has been levelled by the basicity of the silanol. It should be possible to increase the acidity of such reagents by treatment of $R_3Si(Br_6-CB_{11}H_6)$ with acids (HX) other than water. The only requirements are that X^- be more strongly coordinating than $Br_6CH_{11}H_6^-$ and that R_3SiX be less basic than R_3Si-OH. HF is an attractive example. Work along these lines is in progress.

Fig. 1 A perspective view of $[Bu^t_3Si(OH_2)]^+[Br_6CB_{11}H_6]^-$. Bond angles (°): C(2)–Si–C(6) 116.0(6), C(2)–Si–C(10) 116.1(6), C(6)–Si–C(10) 115.9(7), O–Si–C(2) 100.7(5). Bond distances (Å): Si–O 1.779(9), Si–C(2) 1.897(17), Si–C(6) 1.897(15), Si–C(10) 1.884(12). H(28) was found, H(29) is calculated.

1 **2**

Footnote

† *Crystal data* for $[Bu^t_3Si(OH_2)]^+[Br_6CB_{11}H_6]^-$: The structure was solved by direct methods; monoclinic, $P2_1/n$ (no. 14), $a = 15.874(3)$, $b = 12.307(2)$, $c = 16.799(3)$ Å, $\beta = 114.83(3)°$, $V = 2979.2(7)$ Å^3 for $Z = 4$, $R = 0.0608$ for 2525 reflections with $F > 3.0\sigma(F)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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