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(Pentamethylcyclopentadienyl)silanetriol: Synthesis, Derivatization, and X-ray Crystal Structure of Its Hemihydrate

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Summary: Hydrolysis of Cp^*SiCl_3 *affords the silanetriol* $Cp^*Si(OH)_3$ *(**1**) as an amorphous solid. Reaction of **1** with* Me_3SiCl/NEt_3 *and with* $N(SnMe_3)_3$ *leads to* $Cp^*Si(OSiMe_3)_3$ *(**2**) and* $Cp^*Si(OSnMe_3)_3$ *(**3**), respectively. From a concentrated solution of **1** in diethyl ether, the hemihydrate* $Cp^*Si(OH)_3{\cdot}0.5\ H_2O$ *(**4**) is obtained as colorless crystals. An X-ray crystal structure analysis of **4** reveals that* $Cp^*Si(OH)_3$ *and water molecules are hydrogen-bonded to form a multilayer arrangement with the pentamethylcyclopentadienyl groups forming the hydrophobic outer sheets and the silanetriol groups together with the water molecules forming the hydrophilic inner sheets.*

Introduction

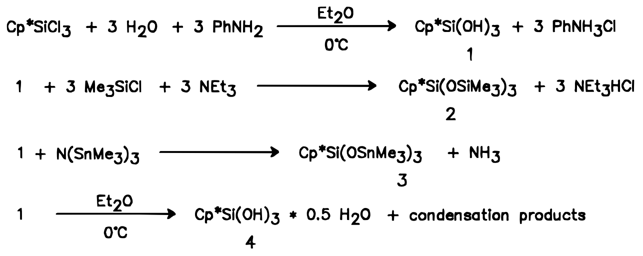
Organosilicon compounds with $Si(OH)_x$ groups ($x = 1-3$) readily undergo self-condensation to give water and species containing the Si−O−Si linkage.[1] This well-known reaction is the basis for the synthesis of silicones of diverse kinds and broad practical applications.[2]

The tendency for the condensation process can be reduced dramatically by introduction of bulky organic groups on silicon. Following this strategy, it was possible to stabilize silanols, silanediols, and even silanetriols in their monomeric form.[3]

In the class of organosilanetriols, $RSi(OH)_3$, the first X-ray crystal structure was published in 1982 for R = cyclohexyl.[4] Later, structures for compounds with R = tris(trimethylsilyl)silyl, tris(trimethylsilyl)methyl,[5] and *tert*-butyl[6] were reported. All show extensively hydrogen-bonded networks.

The organosilanetriols $(Me_3Si)_3SiSi(OH)_3$ and $(Me_3Si)_3CSi(OH)_3$ both crystallize as hexameric, hydrogen-bonded cages with no hydrogen bonding between the cages.[5] The organosilanetriols $C_6H_{11}Si(OH)_3$ and t-$C_4H_9Si(OH)_3$ crystallize as layer structures, in which the organic moieties form the outer sheets and the hydrogen-bonded $Si(OH)_3$ units the respective inner sheets.[4,6]

Scheme 1



Regarding amino- and metallo-substituted species as organosilicon compounds, the recently published silanetriols of Wright et al.,[7] Roesky et al.,[8] and Malisch et al.[9] may also be mentioned.

Our interest is focused on the effect of the pentamethylcyclopentadienyl (Cp*) ligand at silicon on the condensation behavior of corresponding silanols and on their reactivity. The Cp* ligand is regarded to be sterically demanding;[10] this should prevent condensation reactions. Furthermore, the Cp* ligand is a potential leaving group,[10] which should allow further interesting derivatizations. In the context of silanol chemistry, we have already reported the synthesis and X-ray structure of the compound $Cp^*_2Si(OH)_2$.[11] Here, we describe the synthesis of the silanetriol $Cp^*Si(OH)_3$ (**1**), the synthesis of the derivatives $Cp^*Si(OSiMe_3)_3$ (**2**) and $Cp^*Si(OSnMe_3)_3$ (**3**), and the X-ray crystal structure of the hemihydrate $Cp^*Si(OH)_3{\cdot}0.5H_2O$ (**4**).

Results and Discussion

Following known procedures,[1] hydrolysis of Cp^*SiCl_3 in diethyl ether solution with aniline as HCl acceptor led in good yield to the silanetriol $Cp^*Si(OH)_3$ (**1**) (Scheme 1), which is an amorphous solid, readily soluble in diethyl ether, THF, acetone, and dimethyl sulfoxide and nearly insoluble in toluene, chloroform, and hexane. The stability of **1** depends on the respective conditions. In the solid state, **1** decomposes slowly at room temperature;[12] it can be stored without decompositon at

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[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1996.

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[12] Cp*H was detected as a decomposition product.

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Table 1. Crystallographic Data for Diffraction Studies of 4

empirical formula	$C_{10}H_{15}Si(OH)_3 \cdot 0.5\ H_2O$
cryst size, mm^3	$0.80 \times 0.80 \times 0.60$
fw	223.34
cryst syst	monoclinic
space group	*C*2/*c*
unit cell dimensions	
a, Å	25.090(3)
b, Å	8.5180(10)
c, Å	11.5050(10)
β, deg	93.610(10)
V, Å^3	2453.9(5)
Z	8
d_{calc}, g/cm^3	1.209
diffractometer	Siemens P2$_1$
F(000)	968
temp, K	173(2)
no. of data collcd	5453
residuals:[a] R_F, wR_{F_2}	0.0440, 0.1282
largest diff peak	0.3
abs correction	semiempirical

[a] Based on 4111 reflections with $I > 2\sigma(I)$.

Table 2. Selected Bond Lengths (A) and Angles (deg) for 4

Si(1)–O(3)	1.6270(7)	C(2)–C(3)	1.346(2)
Si(1)–O(1)	1.6291(8)	C(2)–C(7)	1.507(2)
Si(1)–O(2)	1.6209(8)	C(3)–C(4)	1.459(2)
Si(1)–C(1)	1.8759(10)	C(3)–C(8)	1.506(2)
C(1)–C(5)	1.5056(14)	C(4)–C(5)	1.356(2)
C(1)–C(2)	1.5074(14)	C(4)–C(9)	1.498(2)
C(1)–C(6)	1.5402(14)	C(5)–C(10)	1.497(2)
O(2)–Si(1)–O(1)	106.13(4)	C(3)–C(2)–C(7)	127.97(12)
O(3)–Si(1)–O(2)	108.61(5)	C(3)–C(2)–C(1)	108.84(11)
O(1)–Si(1)–O(2)	108.20(5)	C(7)–C(2)–C(1)	123.15(11)
O(3)–Si(1)–C(1)	113.51(4)	C(2)–C(3)–C(4)	109.48(11)
O(1)–Si(1)–C(1)	111.27(4)	C(2)–C(3)–C(8)	126.8(2)
O(2)–Si(2)–C(1)	108.96(4)	C(4)–C(3)–C(8)	123.7(2)
C(5)–C(1)–C(2)	103.53(9)	C(5)–C(4)–C(3)	109.78(11)
C(5)–C(1)–C(6)	113.37(9)	C(5)–C(4)–C(9)	127.3(2)
C(2)–C(1)–C(6)	113.01(9)	C(3)–C(4)–C(9)	122.9(2)
C(5)–C(1)–Si(1)	108.50(7)	C(4)–C(5)–C(10)	128.11(12)
C(2)–C(1)–Si(1)	107.71(7)	C(4)–C(5)–C(1)	108.27(11)
C(6)–C(1)–Si(1)	110.35(7)	C(10)–C(5)–C(1)	123.62(11)

temperatures lower than 0 °C. In dilute solutions, no decomposition is observed. Compound **1** was characterized by ^1H, ^{13}C, and ^{29}Si NMR data. In the ^1H NMR spectrum of **1**, the methyl groups of the Cp* fragment give rise to three signals in the region expected for a σ-bonded species; the OH protons give rise to a single resonance. Similarly, the ^{13}C NMR data are typical for a σ-bonded Cp* ligand. The high-field signal in the ^{29}Si NMR spectrum is characteristic for compounds with Si(OR)$_3$ units.[4-6]

Reaction of **1** with excess chlorotrimethylsilane and with triethylamine as HCl acceptor led to the silyl derivative $Cp^*Si(OSiMe_3)_3$ (**2**); with tris(trimethylstannyl)amine the stannyl derivative $Cp^*Si(OSnMe_3)_3$ (**3**) was formed (Scheme 1). Both compounds were characterized by ^1H, ^{13}C, and ^{29}Si NMR as well as by IR and MS data. Additionally, **3** was characterized by ^{119}Sn NMR spectroscopy.

Concentration of a solution of **1** in diethyl ether at room temperature led to the formation of an orange-yellow precipitate of a so far unknown composition.[12] After cooling to 0 °C, colorless crystals of the hemihydrate $Cp^*Si(OH)_3 \cdot 0.5\ H_2O$ (**4**) were obtained from the resulting solution (Scheme 1). Obviously, the decomposition process includes a partial condensation connected with the formation of water, which is needed to build up the hemihydrate **4**. Compound **4** was characterized by analytical and spectroscopic data as well as by an X-ray crystal structure determination.

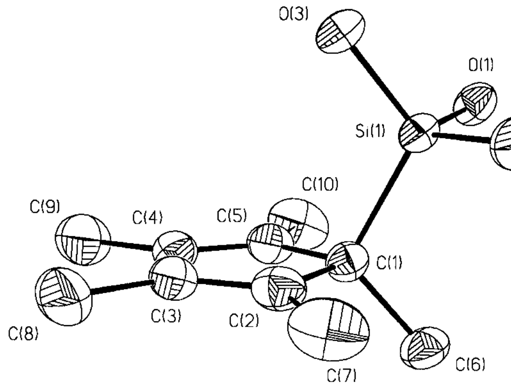

Figure 1. Plot of the $Cp^*Si(OH)_3$ unit in **4**.

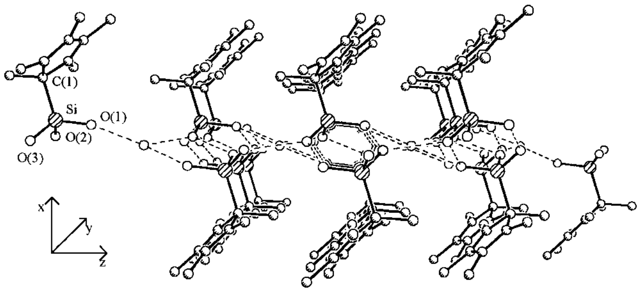

Figure 2. Orientation of **4** with view in direction of the *y*-axis.

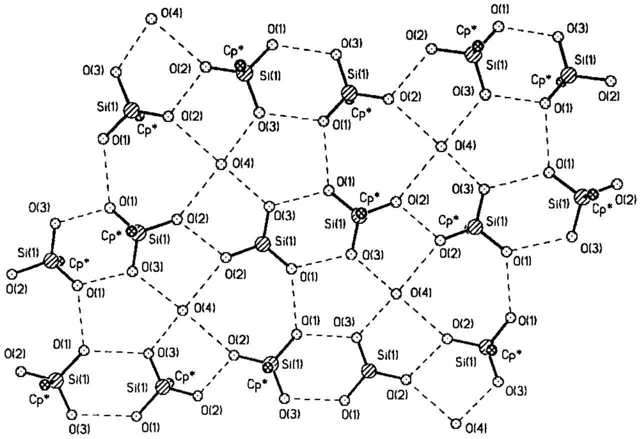

Figure 3. Hydrogen-bonded network in **4**.

Crystallographic data for **2** are collected in Table 1, and important bond lengths and angles are presented in Table 2. The hydrogen atoms of the $Cp^*Si(OH)_3$ unit were placed at calculated positions with idealized geometry and bond lengths, whereas the hydrogen atoms of the water molecules could be located referring to electron density. All hydrogen atoms bonded to oxygen atoms are disordered with ratio 1:1. They are omitted in the figures. Figure 1 displays the molecular structure of **4**, and Figure 2 shows the solid-state structure with view along the *y*-axis. Figure 3 gives a representation of the hydrogen-bonded network.

The crystal structure determination revealed a layer structure (see Figure 2) with the Cp* groups forming the hydrophobic outer sheets and with an extensively hydrogen-bonded network of Si(OH)$_3$ moieties and water molecules forming the hydrophilic inner sheets within the repeating unit of the layer structure. The Cp* ligands are arranged in an eclipsed orientation in the direction of the *y*-axis, as shown in Figure 2. In the same direction, the hydrogen-bonded Si(OH)$_3$ units are oriented in a zigzag chainlike fashion. These chains are interconnected to a double sheet by additional hydrogen bonds between Si−OH units and by hydrogen bonds between incorporated water molecules and Si−OH units. The hydrogen-bonded network is schematically depicted in Figure 3.

The incorporation of 0.5 equiv of water is necessary to allow hydrogen bonding to each of the OH groups on silicon. The water molecules result from the condensation process as described above.

Condensation studies with **4** are currently subject of our investigations.

Experimental Section

General Procedure. All preparations were carried out under an atmosphere of dry, oxygen-free argon using standard Schlenk techniques. Solvents and reagents were dried and purified prior to use. The melting point was determined with a Büchi 510 capillary melting point apparatus and is uncorrected. The mass spectra were determined using a VG AutoSpec. Only characteristic fragments are listed. ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz, ^{1}H decoupled), ^{29}Si NMR (59.6 MHz, ^{1}H decoupled), and ^{119}Sn NMR (111.9 MHz, ^{1}H decoupled) spectra were recorded on a Bruker AM 300 spectrometer. IR spectra were recorded on a Mattson Polaris FTIR spectrometer. Elemental analyses were carried out by Mikroanalytisches Laboratorium der Fakultät für Chemie, Universität Bielefeld, Bielefeld, Germany.

(Pentamethylcyclopentadienyl)trichlorosilane (Cp*SiCl$_3$)[13] was prepared as described in the literature.

(Pentamethylcyclopentadienyl)silanetriol (1). A solution of 12.6 g (47.0 mmol) of **1** in 50 mL of diethyl ether was added at 0 °C to a stirred solution of 2.50 g (140 mmol) of water and 13.1 g (140 mmol) of aniline in 650 mL of diethyl ether. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The mixture was filtered to remove anilinium hydrochloride. The solvent was removed under reduced pressure to yield 7.33 g of **1** as an amorphous solid (41.0 mmol, 87%). ^{1}H NMR (DMSO-d_6): $\delta = 1.07$ (s, 3H, CH$_3$), 1.70 (s, 6H, CH$_3$), 1.82 (s, 6H, CH$_3$), 5.67 (s, 3H, OH). ^{13}C NMR (DMSO-d_6): $\delta = 11.2$, 11.8, 15.1 (Cp* ring C), 53.1, 132.7, 137.9 (Cp*Me). ^{29}Si NMR (DMSO-d_6): $\delta = -48.7$. Mp: 175 °C (dec).

(Pentamethylcyclopentadienyl)tris(trimethylsiloxy)silane (2). A 1.53 g (15.1 mmol) amount of NEt$_3$ and 15.3 g (141 mmol) of Me$_3$SiCl were added to a solution of 1.00 g (4.70 mmol) of **1** in 100 mL of diethyl ether at 0 °C. The reaction mixture was allowed to warm to room temperature and was stirred overnight. After filtration the solvent was removed under reduced pressure. The remaining yellow liquid was distilled in vacuo to give 1.07 g (2.49 mmol, 53%) of **2** as a light yellow liquid, which crystallized on cooling. Bp: 85 °C/0.01 Torr. ^{1}H NMR (CDCl$_3$): $\delta = 0.04$ (s, 27H, SiMe$_3$), 1.10 (s, 3H, CH$_3$), 1.79 (s, 6H, CH$_3$), 1.82 (s, 6H, CH$_3$). ^{13}C NMR (CDCl$_3$): $\delta = 1.77$ (SiMe$_3$), 11.4, 12.0, 14.8 (Cp*Me), 52.8, 134.4, 137.9 (Cp* ring C). ^{29}Si NMR (CDCl$_3$): $\delta = -73.9$. IR (CsI): 1070 (vs), 1102 cm^{-1} (sh, ν(SiOSi)). MS (EI; *m*/*z* (fragment, relative intensity, %): 430 (M$^+$ − H, 20), 415 (M$^+$ − H − CH$_3$, 8), 295 (M$^+$ − Cp*, 4). Anal. Calcd for C$_{19}$H$_{42}$O$_3$Si$_4$ (431.01): C, 52.94; H, 9.84. Found: C, 53.47; H, 9.98.

(Pentamethylcyclopentadienyl)tris(trimethylstannoxy)silane (3). A solution of 1.88 g (3.70 mmol) of N(SnMe$_3$)$_3$[14] in 3 mL of hexane was added to a suspension of 0.79 g (370 mmol) of **1** in 10 mL of hexane. The formation of NH$_3$ was observed. After the solution was stirred for 12 h at room temperature and for 1 h under reflux, the solvent was removed under reduced pressure. Distillation in vacuo gave 1.40 g (2.10 mmol) (57%) of a colorless liquid, which crystallized on cooling. Bp: 130 °C/0.04 Torr. ^{1}H NMR (CDCl$_3$): $\delta = 0.28$ (s, $J_{\mathrm{SnH}} = 56$ and 58 Hz, 27H, SnMe$_3$), 1.49 (s, 3H, CH$_3$), 1.98 (s, 6H, CH$_3$), 2.19 (s, 6H, CH$_3$). ^{13}C NMR (CDCl$_3$): $\delta = -2.53$ (SnMe$_3$), 11.5, 12.4, 16.6 (Cp*Me), 56.0, 132.0, 140.0 (Cp* ring C). ^{29}Si NMR (CDCl$_3$): $\delta = -56.8$. ^{119}Sn NMR (CDCl$_3$): $\delta = 94.8$. IR (CsBr): 929, 978 cm^{-1} (ν(SiOSn)). MS (EI; *m*/*z* (fragment, relative intensity), %): 687 (M$^+$ − H − CH$_3$, 4), 567 (M$^+$ − Cp* − H, 100), 537 (M$^+$ − SnMe$_3$, 10). Anal. Calcd for C$_{19}$H$_{42}$O$_3$SiSn$_3$ (702.76): C, 32.47; H, 6.02. Found: C, 32.53; H, 5.93.

(Pentamethylcyclopentadienyl)silanetriol Hemihydrate (4). Concentration of a solution of **1** (2.60 g) in 40 mL of diethyl ether at room temperature led to the formation of an orange-yellow precipitate of so far unknown composition. From the resulting solution, which was kept for several hours at 0 °C, 460 mg (18%) of **4** crystallized in the form of a colorless compound. NMR spectra: see **1** plus additional water resonance in the ^{1}H NMR spectrum at 3.49 ppm. Ms (EI; *m*/*z* (relative intensity, %)): 214 ([M$^+$ − 0.5 H$_2$O] = M**1**$^+$, 100), 199 ([M**1**$^+$ − CH$_3$], 7.25), 135 ([Cp*]$^+$, 85), 79 ([M**1**$^+$ − Cp*], 88). Anal. Calcd for C$_{10}$H$_{19}$SiO$_{3.5}$ (224.10): C, 53.77; H, 8.57. Found: C, 53.49; H, 8.28.

X-ray Structure Determination. A single crystal was coated with a layer of hydrocarbon oil, attached to a glass fiber, and cooled to 173 K for data collection. Crystallographic programs used for structure solution and refinement were from SHELXTL PLUS and SHELXL 93. The structure was solved by using direct methods and refined by using full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms.

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Supporting Information Available: Tables of X-ray parameters, complete atomic coordinates, isotropic and anisotropic displacement parameters, and bond distances and angles (6 pages). Ordering information is given on any current masthead page.

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