Synthesis and Structural Characterization of an Aryl−Hydrido−Silanediol: 2,6-$Mes_2C_6H_3(H)Si(OH)_2$

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*Summary: The synthesis and structural characterization of 2,6-$Mes_2C_6H_3(H)Si(OH)_2$ (**1**), a silanediol with a Si−H functionality, are described.*

Introduction

There are several reports of silanediol compounds with the general formula $RR'Si(OH)_2$ (R = alkyl, aryl, N-substituent, hydride).[1] This interest is due to the utility of silanes containing hydroxide functional groups. These compounds are precursors of metallasiloxanes[2] and are model systems for heterogeneous silica-supported catalysts.[3] Many of the reported silanediol compounds have been studied using X-ray diffraction techniques and have shown complex hydrogen bonding.[1,4] The degree of hydrogen bonding varies, depending on the steric demands of the substituents bound to the silicon atom.

Silanediols with Si−H functionalities have been known for some time. However, these compounds have not yet been structurally characterized by X-ray diffraction. To our knowledge, there are only two reports in the literature pertaining to the structural characterization of silanol compounds that contain both Si−OH and Si−H functional groups.[5] Herein, we describe the synthesis and characterization of the sterically encumbered silanediol 2,6-$Mes_2C_6H_3(H)Si(OH)_2$ (**1**), which is the first structurally characterized example of a silanediol with a Si−H functionality.

Experimental Section

General Considerations. The compound 2,6-$Mes_2C_6H_3SiCl_2H$[6] was prepared according to a literature procedure. ^1H and ^{13}C NMR data were recorded on a Gemini 300 MHz instrument and referenced to the residual protons in C_6D_6. The ^{29}Si NMR spectra were recorded on a Varian 300 MHz instrument and referenced to external Me_4Si. IR data were recorded on a Bomem FTIR instrument.

Table 1. Experimental Details for Data Collection, Reduction, and Refinement

formula	$C_{24}H_{28}O_2Si$
fw	376.55
cryst dimens (mm)	0.6 × 0.3 × 0.3
color	colorless
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	9.267(8)
b (Å)	11.095(12)
c (Å)	11.900(9)
α (deg)	66.39(6)
β (deg)	75.23(6)
γ (deg)	69.25(7)
V (Å^3)	1039.2(16)
Z	2
d_{calcd} (Mg/m^3)	1.203
μ (mm^{-1})	0.129
GOF	1.000
R1 (obsd data)	0.0402
wR2 (all data)	0.1026
largest diff peak (e Å^{-3})	0.297

2,6-$Mes_2C_6H_3(H)Si(OH)_2$ (1). A solution of 2,6-$Mes_2C_6H_3SiCl_2H$ (0.9 g, 2.2 mmol) in Et_2O (20 mL) was added by cannula to a Et_2O (10 mL) solution containing excess H_2O (5 mL) while the mixture was stirred at ambient temperature. This solution was stirred for an additional 16 h. The Et_2O portion was collected and dried with magnesium sulfate. After filtration the volatile materials were removed under reduced pressure to yield an off-white solid. Recrystallization from a Et_2O/CH_2Cl_2 solution gave **1** as colorless crystals. Yield: 0.7 g, 1.9 mmol, 90%. Mp: 210−211 °C. Anal. Calcd for $C_{24}H_{28}O_2Si$: C, 76.55; H, 7.49. Found: C, 74.31; H, 7.54.[7] ^1H NMR (C_6D_6): δ 2.12 (s, 12 H, *o*-Mes), 2.13 (s, 6 H, *p*-Mes), 4.51 (s, 1 H, $J_{H-Si} = 255$ Hz, Si−H), 6.80 (s, 4 H, *m*-Mes), 6.89 (d, 2 H, $J = 7.6$ Hz, *m*-C_6H_3), 7.24 (tr, 1 H, $J = 7.6$ Hz, *p*-C_6H_3). ^{13}C NMR (C_6D_6): δ 20.92 (*o*-Mes), 21.03 (*p*-Mes), 126.64, 128.53, 131.07, 133.39, 136.52, 137.24, 139.26, 148.35 (Ar). ^{29}Si NMR (C_6D_6): δ −31.1 (d, $J_{Si-H} = 255$ Hz). IR (Nujol, cm^{-1}): 3505 (vs), 3281 (vs), 2915 (vs), 2731 (s), 2196 (vs), 1966 (w), 1937 (w), 1610 (m), 1559 (m), 1486 (s), 1443 (s), 1377 (m), 1267 (m), 1125 (m), 954 (s), 744 (s), 638 (m).

X-ray Crystallography. A colorless crystal of **1** with dimensions 0.6 × 0.3 × 0.3 mm was coated in paraffin oil, mounted on a glass fiber, and placed under a cold stream of nitrogen.[8] All manipulations were carried out at 159 K using Mo Kα (0.710 73 Å) radiation on a Syntex $P2_1$ diffractometer. Unit cell parameters were obtained by a least-squares analysis of 20 well-centered reflections with $20° \geq 2\theta \geq 30°$. Additional experimental details are given in Table 1. The structure of **1** was solved by direct methods.[9] All hydrogen atoms were located from a difference map and refined using a riding model with isotropic thermal parameters of 1.2 times the value of

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the atoms to which they are attached, except for the methyl and hydroxyl hydrogens, which used a factor of 1.5 times the isotropic thermal parameter of the atoms to which these hydrogens were attached. Compound **1** was refined to convergence using anisotropic thermal parameters for all nonhydrogen atoms.

Results and Discussion

2,6-$Mes_2C_6H_3(H)Si(OH)_2$ (**1**) is prepared by the reaction of 2,6-$Mes_2C_6H_3SiCl_2H$ and water and is isolated as colorless crystals (mp 210−211 °C) (eq 1). The

$$\text{2,6-}Mes_2C_6H_3SiCl_2H + 2H_2O \xrightarrow[-2HCl]{Et_2O} \underset{\mathbf{1}}{\text{2,6-}Mes_2C_6H_3Si(OH)_2H} \quad (1)$$

structure of **1** is consistent with the ^{1}H, ^{13}C, and ^{29}Si NMR and IR spectroscopic data. The IR spectra for **1** in the solid state (Nujol mull) and in solution (CCl_4) are essentially identical and show an absorbance in the Si−H region at 2196 cm^{-1}.[10] Broad stretching frequencies centered at 3505 and 3281 cm^{-1} are assigned to free Si−O−H and Si−O−H−O−Si, respectively.[11] The most notable feature in the ^{1}H NMR spectrum is the Si−H (4.51 ppm) resonance with satellite peaks due to coupling to the silicon atom ($J_{H-Si} = 255$ Hz). The Si−OH resonance is not observed in the ^{1}H NMR spectrum. A similar observation was reported for the silanol $((Me_3Si)_3C)SiMe_2(OH)$.[12] The proton-coupled ^{29}Si NMR shows a doublet centered at −31 ppm ($J_{H-Si} = 255$ Hz). This value can be compared to those for the sterically hindered silanediols $Ar(SiMe_3)Si(Me)(OH)_2$ (Ar = sterically hindered N-bonded aryl ligands), which have ^{29}Si NMR chemical shifts of ca. −29 ppm.[1b,13]

A crystal of **1** was studied by X-ray diffraction, and its structure is shown in Figure 1. Selected bond distances and angles are given in Table 2. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ ($Z = 2$). The structure of **1** deviates only slightly from tetrahedral geometry at the silicon atom with O2−Si−O1 (111.4(1)°), O1−Si−C1 (105.7(1)°), and O2−Si−C1 (113.7(1)°) bond angles. The Si−C1 (1.874(3) Å) and Si−O1 (1.649(2) Å) bond distances are normal and fall within the range of Si−C (1.86−1.92 Å) and Si−O (1.63−1.65 Å) bond distances reported for silanediols.[4] In contrast, the Si−O2 (1.622(2) Å) bond distance is short when compared to the same parameters. The hydrogen atom bonded to the silicon atom was located from the difference map at a Si−H distance of 1.44 Å. The hydrogen atoms bonded to the oxygen atoms were located from a difference map at O1−H1 and O2−H2 distances of 0.83(2) and 0.85(3) Å, respectively.

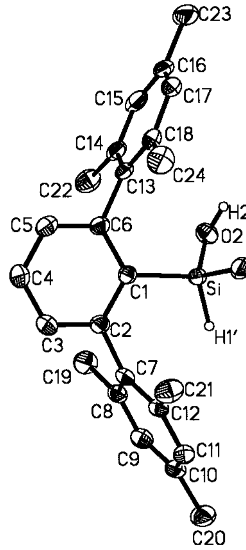

Figure 1. Molecular structure of 2,6-$Mes_2C_6H_3(H)Si(OH)_2$ (**1**) with thermal ellipsoids drawn at 30% probability. Phenyl and mesityl hydrogen atoms have been omitted for clarity.

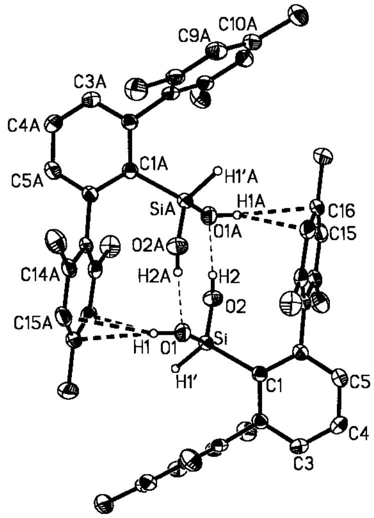

Figure 2. Crystal structure of 2,6-$Mes_2C_6H_3(H)Si(OH)_2$ (**1**) showing hydrogen bonding. Thermal ellipsoids are drawn at 30% probability. Phenyl and mesityl hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2,6-$Mes_2C_6H_3(H)Si(OH)_2$ (1)

Si−C1	1.874(3)	O1−H	0.83(2)
Si−O1	1.649(2)	O1A−O2B	2.848(3)
Si−O2	1.622(2)	O1A- - -H2B	2.02(3)
O1−Si−O2	111.4(1)	C1−Si−O2	113.7(1)
C1−Si−O1	105.7(1)	O1−H- - -O2A	175(2)

Compound **1** crystallizes as a cyclic hydrogen-bonded dimer, and this is illustrated in Figure 2. Each dimer is discrete, with no further interactions to neighboring dimers. Two hydrogen-bonding interactions form the eight-membered ring $(O-Si-O-H)_2$, which is nearly planar. The average deviation from the plane is 0.06 Å, with the largest deviation at O2A (0.17 Å). The hydrogen-bonding interactions lead to O1−O2A (2.848(3) Å) and O1−H2A (2.02(3) Å) distances which are quite normal

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(7) The low percent carbon analysis is due to water present in the bulk sample. The ^{1}H NMR showed residual water present even after the sample was dried for 16 h at 70 °C under reduced pressure.

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(13) The ^{29}Si chemical shift for 2,6-$Mes_2C_6H_3(H)Si(OH)_2$ (**1**) (−31 ppm) is shifted upfield when compared to the same value reported for the silane precursor 2,6-$Mes_2C_6H_3SiHCl_2$ (−8 ppm) in ref 6.

when compared to the same values reported for the only other example of a silanediol with solely dimeric interactions.[4b]

It is notable that H1 is directed toward C16 and is nearly perpendicular to the mesityl ring. The H1−C16 interaction is only 2.39 Å, and the distances from H1 and the adjacent carbon atoms (C15 and C17) are 2.68 and 2.59 Å, respectively. Similar interactions have been described for the silanols $(Me_2PhSi)_3CSi(Me)(H)(OH)$[5a] and octaphenyl-1,3,5,7-tetrasiloxane-1,7-diol.[14]

Conclusions

Silanediol **1** is the first example of a silanediol with a Si−H functionality that has been structurally characterized. The sterically hindered terphenyl ligand 2,6-$Mes_2C_6H_3$ effectively limits the degree of intermolecular hydrogen bonding and permits only discrete cyclic dimeric association of silanediol monomers. Compound **1** displays further intramolecular hydrogen-bonding interactions between the hydrogen atom attached to an oxygen atom and the π-cloud of a mesityl ring. The hydrogen atom is nearly perpendicular to the $(O-Si-O-H)_2$ plane and is directed toward a mesityl ring, affording a hydrogen−π-electron interaction.

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Supporting Information Available: Tables giving crystal data and structure refinement details, positional and thermal parameters, bond distances and angles, and torsion angles for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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