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Formation and structural characterization of a sterically protected silicic acid diester

Stefan Spirk[1], Martin Nieger[2], Gerald N. Rechberger[3] and Rudolf Pietschnig[1]*

[1]Karl-Franzens-Universität, Institut für Chemie, Schubertstraße 1, A-8010 Graz, Austria
[2]Rheinische Friedrich-Wilhelms-Universität Bonn, Institut für Anorganische Chemie, Gerhard-Domagk-Straße 1, D-53121 Bonn, Germany
[3]Karl-Franzens-Universität, Institut für Molekulare Biowissenschaften, Heinrichstraße 31a, A-8010 Graz, Austria

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The hydrolytic stability of the sterically protected dichlorosilane (Mes*–O)$_2$SiCl$_2$ was investigated. The resulting products have been identified by electrospray mass spectrometry and, in the case of (Mes*–O)$_2$Si(OH)$_2$, the crystal structure was obtained. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: crystal structure; silanol; silicic ester; hydrogen bond; lubricant

INTRODUCTION

The sterically crowded dichlorosilane (Mes*–O)$_2$SiCl$_2$ (Mes* = 2,4,6-tri-*t*-butylphenyl, supermesityl) (**1**) has been employed to improve the frictional properties of lubricants. Thus, lubricating oil containing 2% of (**1**) failed the Falex oil-test at a jaw load of 1450 lb, while oil without this additive failed at a lower final load of 750 lb.[1] Although chlorosilanes in general are prone to undergo hydrolysis in the presence of moisture,[2] the sterically protected (**1**), in particular, has been considered as hydrolytically stable as it reportedly hydrolyzes only partially upon heating in aqueous HCl for several days.[1] Nevertheless, the polarity of the surrounding medium is likely to affect the hydrolytic stability. Therefore, we were interested to assess the hydrolytic stability of compound (**1**) under less drastic conditions in less polar solvents. Herein we report (Mes*–O)$_2$Si(OH)Cl (**2**) and (Mes*–O)$_2$Si(OH)$_2$ (**3**) as products resulting from stepwise hydrolysis of (**1**), which have been identified with ESI-MS and in the case of **3** the molecular structure was determined by single crystal X-ray diffraction.

RESULTS AND DISCUSSION

The starting (Mes*–O)$_2$SiCl$_2$ was prepared from SiCl$_4$ and Mes*–OK according to a published procedure.[3] The moisture present in air is sufficient to induce hydrolysis of **1**. By simply leaving samples of THF solutions of **1** exposed to air over a prolonged period of several weeks, hydrolytic cleavage of the first (**2**) and also the second Si–Cl bond (**3**) can be observed (Scheme 1). Although it is known that steric pressure can induce hydrolytic cleavage even of Si–C bonds,[4] the silicic ester bonds in **1** remain unchanged under these conditions.

The identity of compounds **2** and **3** was corroborated by ESI mass spectrometry. In the ESI-MS/MS spectra of **2** the molecular ion peak at $m/z = 601.3$ could be observed in the negative ionization mode (Fig. 1). M–H$^-$ can be assigned to singly deprotonated **2** and its characteristic fragments are observed at $m/z = 261$ and 339. Similarly, the ESI-MS/MS spectra of **3** in the negative ionization mode show the molecular ion peak at $m/z = 583.3$ corresponding to M–H$^-$ (Fig. 2). In addition, fragmentation peaks of Mes*O$^-$ and Mes*OSiO$_2$$^-$ fragments can be observed.

We have been able to grow single crystals of **3** from its THF solution. The molecular structure is represented in Fig. 3 and selected geometric parameters are collected in Table 1. In the crystal structure of **3** the silicon atom shows an almost tetrahedral coordination environment and the two silanol functions are each connected by hydrogen bridges to one molecule of solvent.

The O–Si–O angles of the central [SiO$_4$]–tetrahedron vary between 104.7(1) and 114.4(1)° and interestingly the smallest value is observed between the oxygen atoms adjacent to the supermesityl units. Owing to steric congestion, the supermesityl groups are pointing away from each other and the corresponding Si–O–C angles differ by almost 10°. The Si–O bond distances are in the narrow range between 1.625(3) and 1.667(2) Å, indicating no systematic trends as the longest and the shortest value are observed for the silanol

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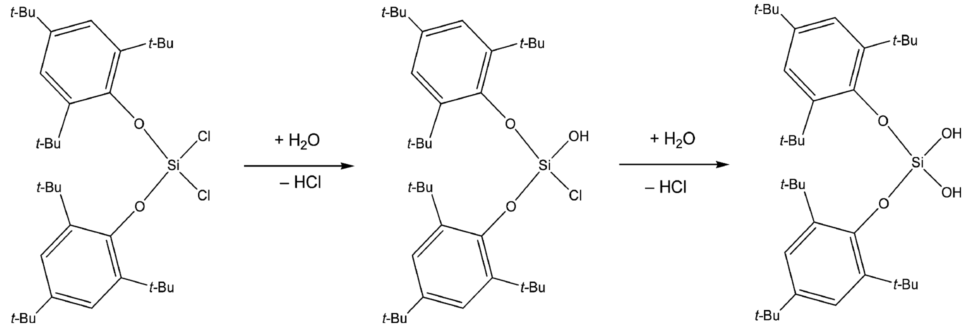
*Correspondence to: Rudolf Pietschnig, Karl-Franzens-Universität, Institut für Chemie, Scubertstraße 1, A-8010 Graz, Austria.
E-mail: rudolf.pietschnig@uni-graz.at



1 **2** **3**

Scheme 1. Formation of **2** and **3**.

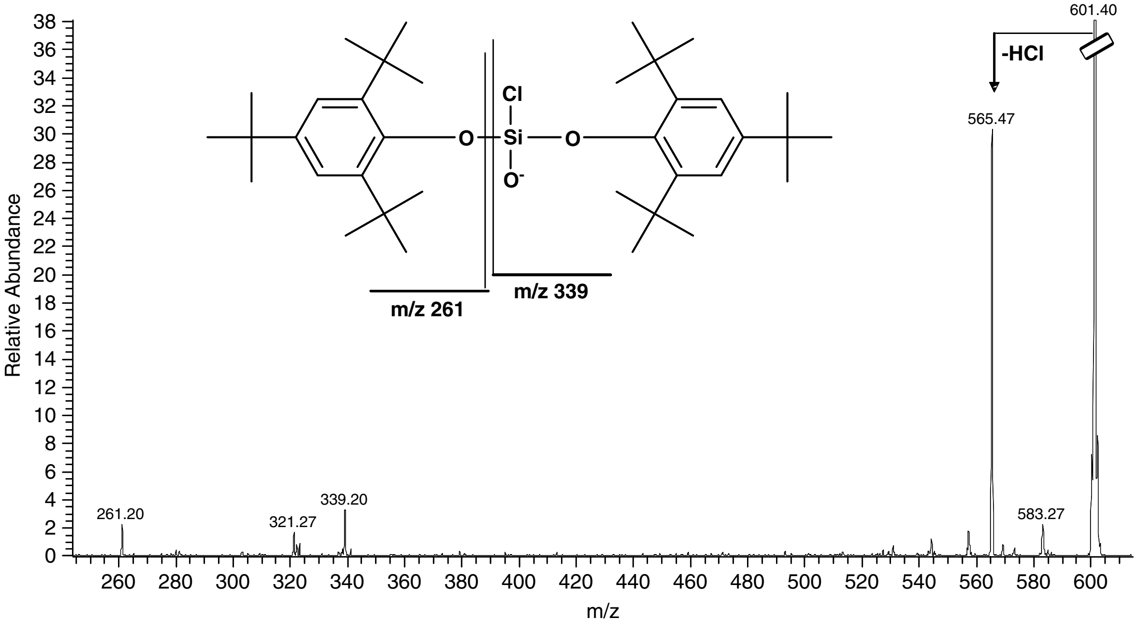


Figure 1. ESI-MS/MS spectrum of **2** (molecular ion peak cut off).

Table 1. Selected bond distances (Å) and angles (deg) for $(Mes^*O)_2Si(OH)_2$ (**3**)

Si1–O1	1.642(2)	O1–Si1–O2	104.72(11)
Si1–O2	1.633(2)	O1–Si1–O3	107.50(11)
Si1–O3	1.667(2)	O1–Si1–O4	114.38(13)
Si1–O4	1.625(3)	O2–Si1–O3	111.66(12)
O1–C1	1.396(3)	O2–Si1–O4	110.93(12)
O2–C19	1.393(3)	O3–Si1–O4	107.67(15)
		C1–O1–Si1	123.03(18)
		C19–O2–Si1	132.78(19)

functionalities. Each of these silanol groups serves as proton donor towards the oxygen atom of molecule of THF so that H3o···O1T is 1.824(19) Å and H4o···O2T is 1.88(3) Å with the respective angles at H being 154(4) and 139(4)°.

In summary, the lubricant additive dichloro-bis(2,4,6-tris-*tert*-butyl-phenoxy)silane does not seem to be as stable against hydrolytic cleavage as previously reported. In organic solvents displacement of chloride vs hydroxyl groups occurs even in the absence of base under mild conditions. The presence of the H-bonded THF molecules demonstrates that even two Mes*O ligands do not prevent the approach of small molecules to the silicon core; this observation suggests that the reason previously outlined for the apparent hydrolytic stability of **1** is questionable.

EXPERIMENTAL

Materials

Dichloro-bis(2,4,6-tris-*tert*-butyl-phenoxy)silane (**1**) was prepared according to a literature procedure.[3] In addition to the

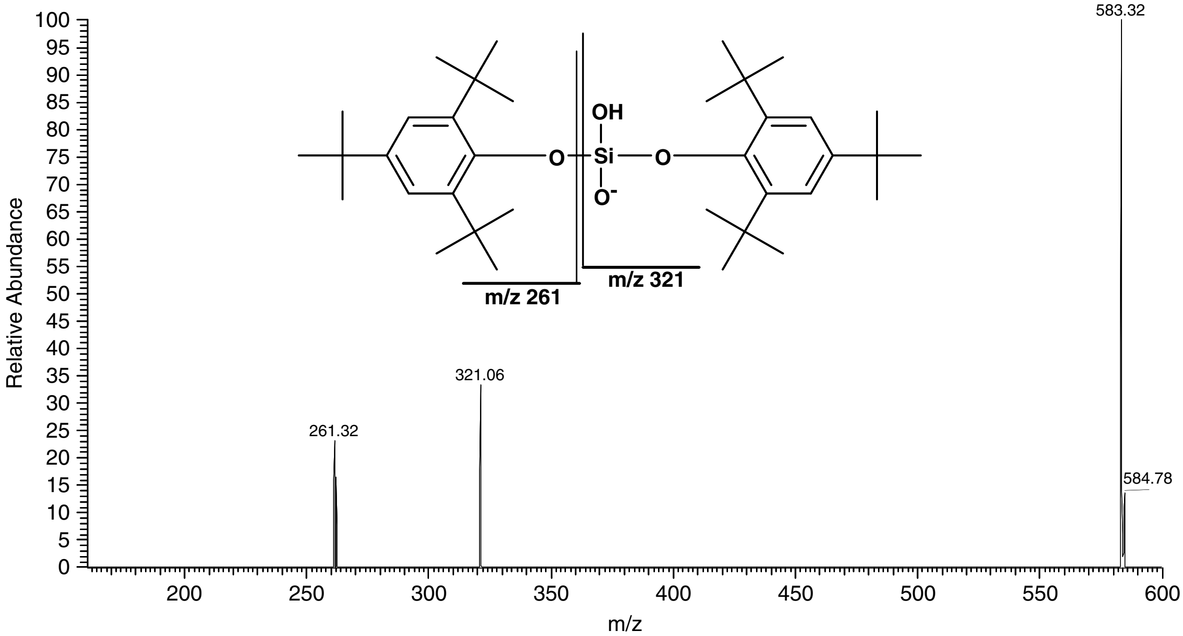


Figure 2. ESI-MS/MS spectrum of **3**.

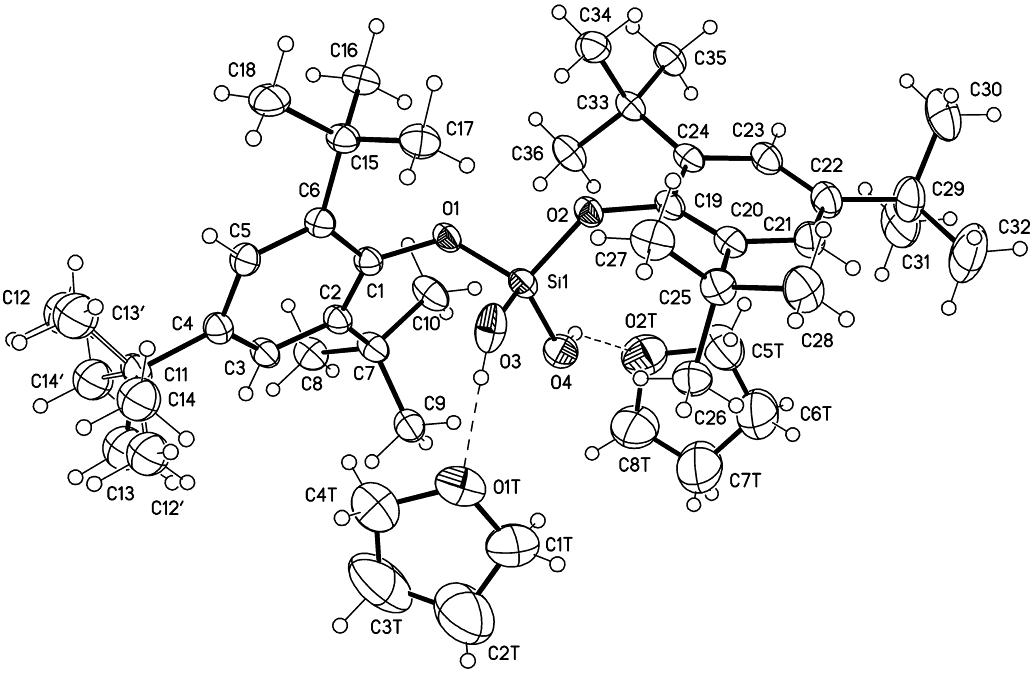


Figure 3. ORTEP plot of the molecular structure of **3** with labels on non-hydrogen atoms.

characterization given in the original procedure we have been able to measure ^{13}C and ^{29}Si NMR data for this compound. ^{29}Si NMR (CDCl$_3$, δ ppm): −64.7. ^{13}C NMR (CDCl$_3$, δ ppm): 32.21 (*t*-Bu-CH$_3$), 35.77 [*t*-Bu-C(CH$_3$)], 123.38 (*m*-C$_6$H$_2$), 140.41 (C$_q$-aryl), 144.54 (*p*-C$_6$H$_2$), 148.21 (C$_q$-aryl).

The conversion of **1** to **2** and **3** was effected by slowly evaporating a THF solution of **1** to dryness over 4 weeks while exposed to ambient air. During this process, compound **2** was identified from the evaporating solution by mass spectrometry. After complete evaporation of the solvent, the resulting colorless crystals of **3** were analyzed by mass spectrometry and X-ray diffraction; m.p. >200 °C. ^{1}H NMR (CDCl$_3$): 1.31 (18 H, *para-t*-butyl), 1.50 (36 H, *ortho-t*-butyl), 5.09 [2 H, Si(OH)$_2$], 7.27 (4 H, aryl).

Mass spectrometry

Electrospray mass spectra have been recorded on a Thermo LCQ-DUO ion trap mass spectrometer (Thermo, San Jose, CA, USA) equipped with a nano-ESI-source using metal-coated nano-ESI-needles (Proxxeon, Odense, Denmark; outer diameter 360 μm, inner diameter 75 μm, tip diameter 6 μm) employing a spray voltage of 1.5 kV and a collision energy of 30%.

Crystal structure determination

Intensity data were collected at 123 K on a Nonius Kappa CCD for a colorless plate $0.15 \times 0.35 \times 0.45 \text{mm}^3$. $C_{36}H_{60}O_4Si.2$ THF, $M = 729.14$, triclinic, P-1, $a = 10.1957(2)$, $b = 11.4035(2)$, $c = 19.3841(4)$ Å, $\alpha = 82.795(1)$, $\beta = 84.937(1)$, $\gamma = 88.106(1)^\circ$, $V = 2226.65(7)$ Å^3, $Z = 2$, 7788 unique data ($\theta_{\max} = 25.0^\circ$), 6088 data with $I > 2\sigma(I)$, $R = 0.084$ (observed data), $wR^2 = 0.254$ (all data). CCDC deposition no. = 604903. Programs used: SHELXS-97, SHELXL-97 and ORTEP. The methyl groups of the *tert*-butyl substituent in the *para* position of one supermesityl group are disordered over two sites (C12, C13, C14) with relative occupancies of 0.68 : 0.32 and have been refined isotropically. As a consequence of this, and due to the presence of solvent molecules (thf) in the unit as well as the poor quality of the available crystals, the R-value remains rather high.

Acknowledgement

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