Note

Synthesis and structure of silyl acetonitriles

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Abstract

An efficient route for the preparation of Mes_2HSiCH_2CN (**1**) and $(Mes_2HSi)_2CHCN$ (**2**) is reported (Mes = 2,4,6-trimethylphenyl). Although the X-ray analyses for **1** and **2** reveal the CH_nCN functionality ($n = 1, 2$) to be shielded by the Mes_2HSi group, hydrolysis under basic conditions gave exclusively Mes_2HSiOH (**3**), as a result of hydroxide-induced Si–C bond cleavage. In the solid state **3** is a tetramer forming an eight membered ring by H-bond interactions.
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1. Introduction

α-Silyl carbonitrile [1] compounds containing the general bond sequence Si–C–CN have attracted great interest due to their multi functionality that can be used in Peterson [2] and related reaction for the synthesis of biologically active compounds [3]. Particularly, the high acidity of silyl acetonitriles (R_3SiCH_2CN) facilitates the generation of lithiated and dilithiated species [4] that are useful as highly reactive synthons in organic synthesis [3f,3g,5]. As a part of our ongoing studies on polyfunctional silanols [6], we report herein on the selective synthesis of the sterically demanding silyl acetonitriles Mes_2HSiCH_2CN (**1**) and $(Mes_2HSi)_2CHCN$ (**2**), and their conversion into Mes_2HSiOH (**3**) (Mes = 2,4,6-trimethylphenyl). In addition, the solid-state structures of **1**–**3** derived from X-ray data will be reported.

2. Results and discussion

Silyl acetonitriles are accessible by direct Si–C bond formation via salt metathesis between silicon halides and deprotonated acetonitrile [2a,2d,2e,7]. In fact, a pentane

solution of Mes_2HSiCl was slowly dropped to a large excess of a $Li–CH_2CN$ suspension in THF, derived from the reaction of CH_3CN with *n*-BuLi at −78 °C. After aqueous workup under acidic conditions Mes_2HSiCH_2CN (**1**) was obtained as a thermally stable, colourless solid in a yield of 69% (Scheme 1). Surprisingly, by reducing the molar ratio of $Li–CH_2CN$ to Mes_2HSiCl to a ratio of 2:1 at low temperatures, among small amounts of **1**, the doubly silylated compound $(Mes_2HSi)_2CHCN$ (**2**) was obtained as the main product after hydrolysis under acidic conditions in 53% yield (Scheme 1).

The formation of **2** may be rationalised by assuming that a facile deprotonation of **1**, formed during the course of the reaction, by the stronger base $Li–CH_2CN$ occurs. The resulting $Mes_2HSiCHLiCN$ (**4**) rapidly reacts with a second equiv of Mes_2HSiCl with elimination of LiCl to give **2**. Interestingly, we have found that the presence of a slight excess of $Li–CH_2CN$ seems to be crucial to obtain **2** in higher yields after hydrolytic workup (Scheme 2). This observation is consistent with a deprotonation of **2** which finally produces $(Mes_2HSi)_2CLiCN$ (**5**) with consumption of $Li–CH_2CN$. However, due to the steric demand of the Mes_2SiH group products resulting from a silylation of **5** could not be observed.

When the reaction mixture was hydrolyzed under basic conditions, independently from the molar ratio used, a solid compound was formed that could be clearly identified
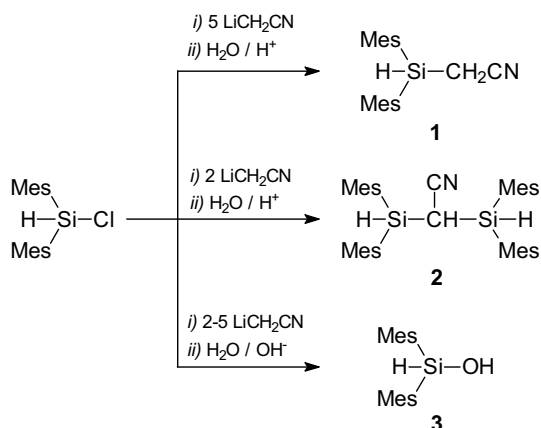

Scheme 1. Synthesis of **1**–**3** (Mes = 2,4,6-trimethylphenyl).

as the silanol **3**. The electron withdrawing cyano group activates significantly the Si–C bond sequence towards nucleophilic attack, which implies the CH_2CN substituent to be a good leaving group, being exchanged quite easily by small nucleophiles such as hydroxide. Obviously, the silanol **3** can also be produced by hydrolysis of Mes_2HSiCl in the presence of a base.

The proposed structures of the compounds **1**–**3** were in full agreement with the NMR, IR and MS data and the results of an elemental analysis. Particularly, the IR spectra of **1** and **2** are useful for the assignment of functional groups in the molecules. Thus, compounds **1** and **2** exhibit narrow bands at around 2235 cm^{-1} (**1**) and 2215 cm^{-1} (**2**), consistent with CN groups in the molecules. The stretching frequencies found are in good agreement with those observed in the recent literature for closely related trimethylsilyl substituted derivatives, e.g. 2233 cm^{-1} for Me_3SiCH_2CN [8], 2227 cm^{-1} for $(Me_3Si)_2CHCN$ [8] and 2210 cm^{-1} for $(Me_3Si)_3CCN$ [9]. In addition, a second band for **1** was found at 2172 cm^{-1} and in case of **2** two relatively sharp bands appear at 2190 and 2177 cm^{-1}, undoubtedly arising from the Si–H stretching modes. Further evidence for the existence of the Si–H groups is given
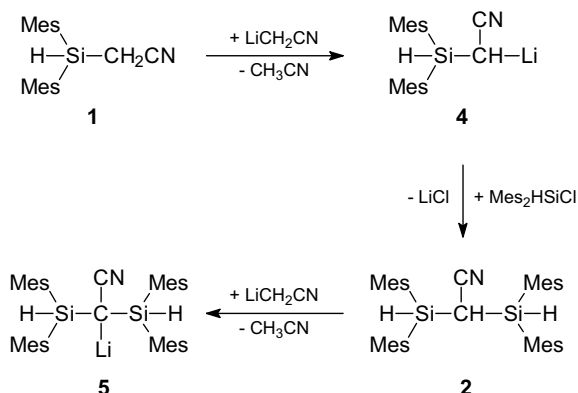
by the ^{29}Si NMR spectra, which exhibit doublets for the Si atoms of the Si–H groups, with coupling constants of 211.6 Hz (**1**) and 203.1 Hz (**2**), respectively.

To our surprise, a structural search in the Cambridge crystallographic database gave only three compounds [10] with a Si–C–CN bond sequence, for which X-ray data are available and among these there were none of general formulae R_3Si–CH_2CN and $(R_3Si)_2CHCN$. Therefore, we have determined the solid-state structures of **1** and **2** by X-ray crystallography; suitable single crystals were grown from n-heptane solutions. The analysis reveals the geometry around the central silicon atoms in **1** and **2** to be distorted tetrahedral, with large C(Mes)–Si–C(Mes) angles [**1**, C3–Si1–C12, 114.1(2)°; **2**, C12–Si1–C3, 112.98(9)°, C30–Si2–C21, 115.86(9)°], which is ascribed to the steric repulsion of both mesityl groups. However, most of the Si–C, Si–O and C–C bond lengths in **1** and **2** are in the normal range. Due to the disorder within the CH_2CN moiety in **1**, the given distances between Si1 and the disordered carbon atom differ markedly from the distances usually found for those Si–C bonds [10]. The result for **2** confirm the expected shielding of the CHCN group by the bulky Mes_2HSi substituents enforcing an elongation of the central Si1–C1 and Si2–C1 bonds with values of 1.917(2) Å and 1.929(2) Å, respectively. However, the bond parameters for the CH_2CN group are unaffected by the steric requirements in the molecule, thus the C2–N1 and C1–C2 distances with 1.144(3) Å and 1.460(3) Å, respectively and the C1–C2–N1 angle with 179.2(3)° are comparable to those found in organic nitriles according to a search in the Cambridge database (see Figs. 1,2).

In addition, the solid-state structure of the silanol **3** was determined by X-ray crystallography. The Si–C(mesityl) distances, with 1.866(3) Å and 1.881(3) Å are similar to those of the silyl acetonitriles **1** and **2**. As a result of the steric demand of both mesityl groups, the silicon atom shows
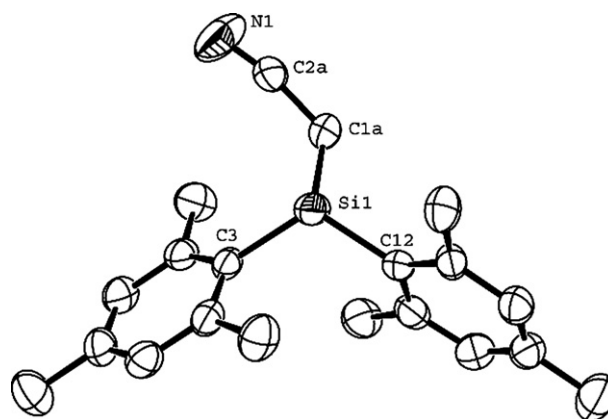

Scheme 2. Proposed mechanism for the formation of **2** (Mes = 2,4,6-trimethylphenyl).

Fig. 1. Molecular structure of **1** in the crystal (ORTEP, 50% probability level, for clarity only one position of the disordered CH_2CN group is shown and except for Si–H all H-atoms are omitted). Selected bond lengths (Å) and angles (°): Si1–C1A, 1.734(8), Si1–C3, 1.877(5), Si1–C12, 1.881(5), Si1–H1A, 1.48(2), N1–C2A, 1.155(10), C1A–C2A, 1.472(11), C1A–Si1–C3, 119.0(3), C1A–Si1–C12, 111.5(3), C3–Si1–C12, 114.1(2), C2A–C1A–Si1, 118.3(6), N1–C2A–C1A, 167.9(10).
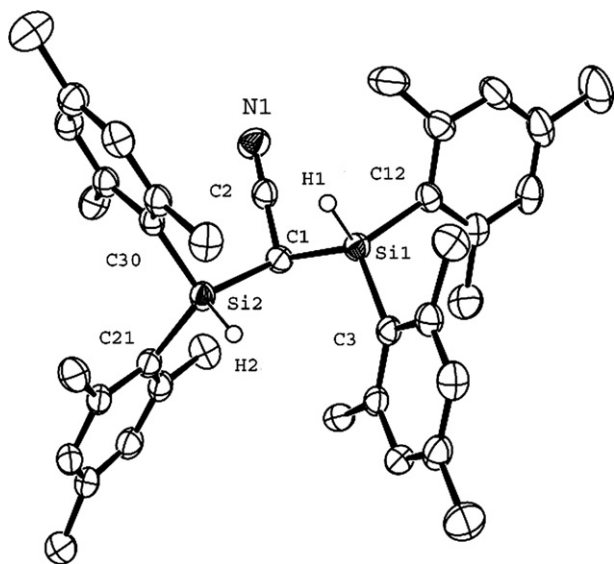
Fig. 2. Molecular structure of **2** in the crystal (ORTEP, 50% probability level, except for Si–H all H-atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Si1–C12, 1.887(2); Si1–C3, 1.889(2); Si1–C1, 1.917(2); Si1–H1Si, 1.415(19); Si2–C30, 1.881(2); Si2–C21, 1.890(2); Si2–C1, 1.929(2); Si2–H2Si, 1.36(2); N1–C2, 1.144(3); C1–C2, 1.460(3); C12–Si1–C3, 112.98(9); C12–Si1–C1, 113.77(9); C3–Si1–C1, 114.88(9); C30–Si2–C21, 115.86(9); C30–Si2–C1, 108.83(9); C21–Si2–C1, 117.46(9); C2–C1–Si1, 106.93(14); C2–C1–Si2, 112.70(14); Si1–C1–Si2, 108.06(10); N1–C2–C1, 179.2(3).
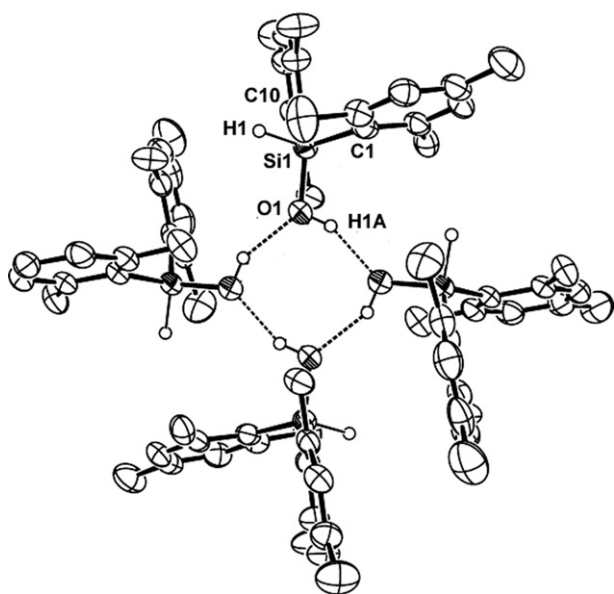

Fig. 3. Molecular structure of **3** in the crystal (ORTEP, 50% probability level, except for SiH and OH all H-atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Si1–O1, 1.644(2); Si1–C10, 1.866(3); Si1–C1, 1.881(3); Si1–H1, 1.36(3); O1–H1A, 0.84; O1–Si1–C10, 109.84(12); O1–Si1–C1, 113.54(12); C10–Si1–C1, 114.99(12); O1–Si1–H1, 104.3(10); C10–Si1–H1, 109.6(11); C1–Si1–H1, 103.8(11); O1–H1A 0.840; O1–H2A, 1.921; O2–H2A, 0.840; O2–H1A, 1.883; O2–H2A–O1, 150.1; H2A–O1–H1A, 117.2; O1–H1A–O2, 155.1; H1A–O2–H2A, 115.7.

a distorted tetrahedral configuration with a slightly widened C10–Si1–C1 bond angle of 114.99(12)°. In the closely related derivatives t-Bu₂HSiOH [11a] and t-Bu₂FSiOH

[11b] the angles are 117.9(2)° and 120.5(6)°, respectively. The two symmetry independent molecules of the asymmetric unit are linked to each other by a hydrogen bridge with a short O···O distances of 2.667 Å. Due to the centre of inversion this motif forms in its turn an eight membered ring structure consisting of four molecules with O–O distances being 2.68 Å (Fig. 3). Interestingly, the same structural motif is present in t-Bu₂HSiOH, t-Bu₂FSiOH, Ph₃SiOH, Ph₃GeOH and Ph₃COH with O···O distances within the range 2.61–2.90 Å [12].

As mentioned above, the sterically protected silyl acetonitriles **1** and **2** readily undergo hydrolytic Si–C bond scission with formation of **3**. However, the Si–H group seems to be unaffected under the conditions applied. In order to transform the Si–H group into the Si–OH functionality we have investigated oxidative reactions involving the use of m-chloroperbenzoic acid (m-CPBA), AIBN and acetone triperoxide [13]. But in view of the extreme bulkiness of the two mesityl groups protecting the central Si atom, even simple oxidations are difficult and we observed no significant conversions of **1** and **2** into the desired silanols.

3. Conclusion

An efficient route for the synthesis of the new sterically demanded silyl acetonitriles **1** and **2** has been reported. Despite the extensive shielding of the CH_nCN functionality by the Mes₂HSi group, both compounds undergo hydroxide-induced Si–C bond cleavage to give the silanol **3**, which in the solid state forms a tetramer through hydrogen bonding. However, the Si–H group is effectively protected by the mesityl groups and remains unchanged towards oxidative reactions.

4. Experimental

All reactions involving organometallic reagents were carried out under an atmosphere of argon using standard Schlenk techniques. Mes₂HSiCl was prepared as previously described [14]. ¹H, ¹³C and ²⁹Si NMR spectroscopic measurements were done on a Bruker AC 250 and a Bruker ARX 300. IR: Nicolet 205 FT-IR.

4.1. Cyano-[bis(2,4,6-trimethylphenyl)silyl]methane (**1**)

Forty milliliters of n-BuLi (2.5 M, 100 mmol) were added at −78 °C to a vigorously stirred solution of CH₃CN (5.7 mL, 148.6 mmol) in THF (200 mL). Stirring was continued for 1 h and Mes₂HSiCl (6 g, 19.8 mmol) dissolved in THF (100 mL) was slowly dropped to the resulting suspension. After stirring was continued for an additional hour, the mixture was allowed to warm up to room temperature and then poured into a mixture of ice and 1.5 M HCl (130 mL). The organic phase was separated, dried with MgSO₄, filtered and evaporated. The solid raw product was distilled under vacuum using a Kugelrohr apparatus (10⁻² mbar, 175 °C) to afford pure **1** as a white solid. Yield

4.22 g (69%). M.p. 94 °C. IR (nujol) $\tilde{v}$ = 2235 (CN), 2172 (SiH) cm^{-1}. ^{1}H NMR (C_6D_6, 250 MHz): δ 6.62 (s, CH-arom., 4 H), 5.44 (t, $^3J_{H-H}$ = 4.25 Hz, SiH, 1 H), 2.21 (s, o-CH$_3$, 12 H), 2.04 (s, p-CH$_3$, 6 H), 1.62 (d, $^3J_{H-H}$ = 4.25 Hz, CH$_2$, 2H). ^{13}C NMR (C_6D_6, 62.9 MHz): δ 144.3, 140.2, 127.5 (CCH$_3$, arom.), 129.6 (CH, arom.), 118.6 (CN), 23.4 (o-CH$_3$), 21.0 (p-CH$_3$), 4.4 (CH$_2$). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ −33.6 (d, $^1J_{Si-H}$ = 211.6 Hz, SiH). Anal. Calc. for $C_{20}H_{25}NSi$ (307.51): C, 78.12; H, 8.19; N, 4.55. Found: C, 78.28; H, 8.36; N, 4.44%.

4.2. Cyano-bis[bis(2,4,6-trimethylphenyl)silyl]methane (2)

Sixteen milliliters of n-BuLi (2.5 M, 40 mmol) were added at −78 °C to a vigorously stirred solution of CH$_3$CN (2.0 mL, 52 mmol) in THF (100 mL). Stirring was continued for 1 h and Mes$_2$HSiCl (6 g, 19.8 mmol) dissolved in THF (100 mL) was slowly dropped to the resulting suspension. After stirring was continued for an additional hour the mixture was allowed to warm up to room temperature and then poured into a mixture of ice and 1.5 M HCl (130 mL). The organic phase was separated, dried with MgSO$_4$, filtered and evaporated. Compound 1 (1.28 g, 21%) obtained as a side product was separated by Kugelrohr distillation (10^{-2} mbar, 190 °C). The residue was recrystallized from n-heptane to give colourless crystals of 2. Yield 3.4 g (53%). M.p. 176 °C. IR (nujol) $\tilde{v}$ = 2215 (CN), 2190, 2177 (SiH) cm^{-1}. ^{1}H NMR (C_6D_6, 250 MHz): δ 6.70, 6.59 (2s, CH-arom., 2 × 4H), 5.75 (d, $^3J_{H-H}$ = 4.25 Hz, SiH, 2H), 3.15 (t, $^3J_{H-H}$ = 4.25 Hz, CH, 1H), 2.52, 2.35 (2s, o-CH$_3$, 2 × 12H), 2.04, 2.01 (2s, p-CH$_3$, 2 × 6H). ^{13}C NMR (C_6D_6, MHz): δ 145.3, 144.6, 140.2, 139.9, 128.5, 127.1 (CCH$_3$, arom.), 2 × 129.8 (CH, arom.), 120.6 (CN), 24.1, 23.7 (o-CH$_3$), 21.1, 21.0 (p-CH$_3$), 5.8 (CH$_2$). ^{29}Si NMR (C_6D_6, 59.6 MHz): δ −32.8 (d, $^1J_{Si-H}$ = 203.1 Hz, SiH). Anal. Calc. for $C_{38}H_{47}NSi_2$ (573.96): C, 79.52; H, 8.25; N, 2.44. Found: C, 79.56; H, 8.35; N, 2.40%.

4.3. Bis(2,4,6-trimethylphenyl)silanol (3)

Method A: In analogy to the synthesis of 1, an excess of LiCH$_2$CN, derived from the reaction of acetonitrile with BuLi at −78 °C, was reacted with Mes$_2$SiHCl. The resulting reaction mixture was hydrolyzed in water at room temperature to give the silanol 3 almost quantitatively.

Method B: A two phase mixture of Mes$_2$HSiCl (2 g, 6.6 mmol) dissolved in ether (50 mL) and 1 M aqueous NH$_4$(COONH$_2$) (6.6 mL) dissolved in water (50 mL) was stirred for one day at room temperature. The organic phase was separated, dried with MgSO$_4$, and evaporated to leave 3 as a colourless solid that can be recrystallized from n-heptane at −40 °C to give an analytically pure sample of 3. Yield 1.72 g (91%).

Data of 3: M.p. 97 °C. IR (nujol) $\tilde{v}$ = 2157 cm^{-1} (SiH), 3201 cm^{-1} (SiOH). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ −22.5 (d, $^1J_{Si-H}$ = 172.5 Hz, SiH). The other obtained analytical data are identical to those in the literature [15].

Table 1
Crystallographic parameters for compounds 1–3

	1	2	3
Formula	$C_{20}H_{25}NSi$	$C_{38}H_{47}NSi_2$	$C_{18}H_{24}OSi$
Weight	307.50	573.95	284.46
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	$Pca2_1$	$P2_1/n$	$P\bar{1}$
a (Å)	20.1888(10)	15.9784(10)	11.6991(7)
b (Å)	8.7345(5)	9.1324(5)	12.8437(14)
c (Å)	10.2447(6)	23.4929(12)	12.8797(8)
α (°)	90	90	103.689(4)
β (°)	90	101.661(2)	110.701(3)
γ (°)	90	90	100.307(4)
V (Å^3)	1806.54(17)	3357.4(3)	1683.9(2)
Z	4	4	4
μ (mm^{-1})	0.127	0.132	0.134
Unique observed reflections	2977	5889	5753
Observed reflections with $I > 2\sigma(I)$	2567	4323	3792
R (observed)	0.0598	0.0424	0.065
$R\omega$ (all)	0.1346	0.1153	0.1791

4.4. Crystal structure determination of 1–3

The X-ray diffraction data for the compounds 1–3 were collected on a Bruker X8Apex CCD diffractometer system at temperatures between 173 and 193 K. The structures were solved by direct methods and refined anisotropically by the full-matrix least-squares method of the Bruker SHEL-XTL software package. The principal crystallographic data are given in Table 1. The hydrogen atoms were put into theoretical positions and refined using the riding model. The position disorder of the CH$_2$CN moiety of compound 1 was refined freely, and best results were obtained with a ratio of 0.65 to 0.35.

5. Supplementary material

CCDC 277053, 277054 and 277052 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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