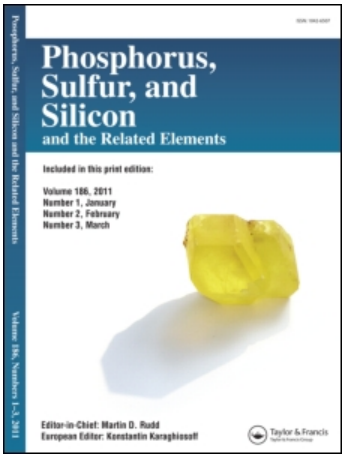


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Characterization of Benzonitrile-Substituted Silyl Ethers

Christopher Hubrich[a]; Axel Schulz[ab]; Harald Brand[c]; Alexander Villinger[a]
[a] Universität Rostock, Institut für Chemie, Abteilung Anorganische Chemie, Rostock, Germany [b] Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Rostock, Germany [c] Department Chemie und Biochemie, Ludwig-Maximilians-Universität München, München, Germany

To cite this Article Hubrich, Christopher , Schulz, Axel , Brand, Harald and Villinger, Alexander(2009) 'Synthesis and Characterization of Benzonitrile-Substituted Silyl Ethers', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 9, 2179 — 2196
To link to this Article: DOI: 10.1080/10426500903074874
URL: http://dx.doi.org/10.1080/10426500903074874

Phosphorus, Sulfur, and Silicon, 184:2179–2196, 2009

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500903074874

Taylor & Francis
Taylor & Francis Group

Synthesis and Characterization of Benzonitrile-Substituted Silyl Ethers

Christopher Hubrich,[1] Axel Schulz,[1,2] Harald Brand,[3] and Alexander Villinger[1]

[1]Universität Rostock, Institut für Chemie, Abteilung Anorganische Chemie, Rostock, Germany
[2]Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Rostock, Germany
[3]Department Chemie und Biochemie, Ludwig-Maximilians-Universität München, München, Germany

*The silyl ethers (siloxanes) $Me_{4-x}Si(OC_6H_5CN)_x$ (x = 1–4) (**1–4**), $O(Si(OC_6H_4CN)(Me)_2)_2$ (**5**), and $Me_3Si–O–C_6F_4CN$ (**6**) have been synthesized by the reaction of the respective p-hydroxybenzonitriles and chlorosilanes in the presence of N,N,N′,N′-tetramethylethylenediamine (TMEDA) as hydrogen chloride acceptor. All compounds have been fully characterized by CHN-analysis, melting point, IR, Raman, mass spectroscopy, and ^1H, ^{13}C, ^{29}Si NMR spectroscopy. Furthermore, the crystal structures of these compounds—with the exception of $Me_2Si(OC_6H_5CN)_2$, which is a liquid—were determined by X-ray diffractometry.*

Keywords Benzonitrile substituted silyl ethers; crystal structure; (*p*-cyanophenoxy)-silanes; perfluorinated compounds; siloxanes; synthesis

INTRODUCTION

Silyl ethers (siloxanes) have many applications in polymer chemistry and also in organic chemistry as protecting groups. Aromatic silyl ethers of the composition $Me_{4-x}Si(OC_6H_5)_x$ (x = **1–4**)[1–4] and $O(Si(OC_6H_5)(Me)_2)_2$[5] have been known for a long time. In contrast, there are only two examples of the analogous compounds with a

Received 7 May 2009; accepted 28 May 2009.
We are indebted to Prof. T. M. Klapötke (LMU München) for the allocation of X-ray measurement time and to Dr. Kurt Polborn (formerly LMU München) for the X-ray analysis of compound **1**.
Address correspondence to Axel Schulz, Universität Rostock, Institut für Chemie, Abteilung Anorganische Chemie, Albert-Einstein-Straße 3a, 18059 Rostock, Germany. E-mail: axel.schulz@uni-rostock.de

benzonitrile instead of a phenyl group: (*p*-cyanophenoxy)trimethylsilane, $Me_3Si{-}O{-}C_6H_4CN$[6] (**1**) and bis(*p*-cyanophen-oxy)dimethylsilane $Me_2Si(-O-C_6H_4CN)_2$ (**2**).[7] Both compounds have been only partially characterized.

Furthermore, the utilization of fluorinated silyl ethers like $Me_3SiOC_6F_4X$ (X = H, F)[8–11] as transfer agents has provided a powerful preparative pathway for the synthesis of new and difficultly accessible per- and polyfluorinated compounds.[8,12] $Me_3SiOC_6F_5$ has been also used for the syntheses of metal complexes,[13–15] alky- or aryloxysilyl-substituted lactams,[16] aryloxy-substituted sulfur(IV)fluorides,[17] and polyfluorinated phenyl-phosphonium ions.[18] Other studies have involved the reactivity[19] and detailed analytical characterizations[20] of this compound. To the best of our knowledge, the analogous compound of $Me_3SiOC_6F_5$ with a fluorinated benzonitrile group, however, is not known so far.

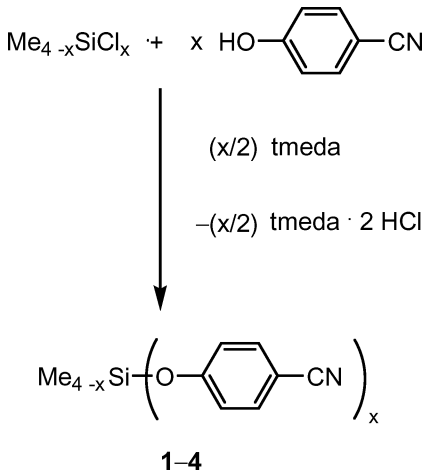
In this article, we report on the synthesis and full characterization of the silyl ethers $Me_{4-x}Si(OC_6H_5CN)_x$ (x = **1**–**4**) (**1**–**4**). In addition, the silyl ethers $O(Si(OC_6H_4CN)(Me)_2)_2$ (**5**) and $Me_3Si{-}O{-}C_6F_4CN$ (**6**), the perfluorinated analogous of **1**, were prepared and fully characterized. The crystal structures of the compounds **1** and **3**–**6** were determined by X-ray studies and are discussed herein.

RESULTS AND DISCUSSION

Synthesis

The silyl ethers $Me_{4-x}Si(OC_6H_5CN)_x$ (x = 1–4) (**1**–**4**) were synthesized by the reaction of *p*-cyanophenol with the respective (methyl)chlorosilanes in tetrahydrofuran, whereas *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) was added as hydrogen chloride acceptor (Scheme 1).

The silyl ethers $Me_{4-x}Si(OC_6H_4CN)_x$ (x = 1–3) (**1**)–(**3**) were obtained after removal of the solvent under vacuum as (colorless) oils, while $Si(OC_6H_4CN)_4$ (**4**) was obtained as a brown solid. $(Me_3Si)OC_6H_4CN$ (**1**) was purified by vacuum distillation, and the obtained oil slowly crystallized to give a colorless crystalline solid. In the case of $Me_2Si(OC_6H_4CN)_2$ (**2**), we were not able to obtain crystals suitable for an X-ray study, either by cooling with liquid nitrogen or by recrystallization or further distillation (boiling point[7b]: 197–201°C/10^{-3} mbar). The oil obtained from the synthesis of $MeSi(OC_6H_4CN)_3$ (**3**) was cooled with liquid nitrogen under vacuum, yielding a colorless crystalline solid. Recrystallization of the solid from toluene afforded crystals of **3** suitable



1–4

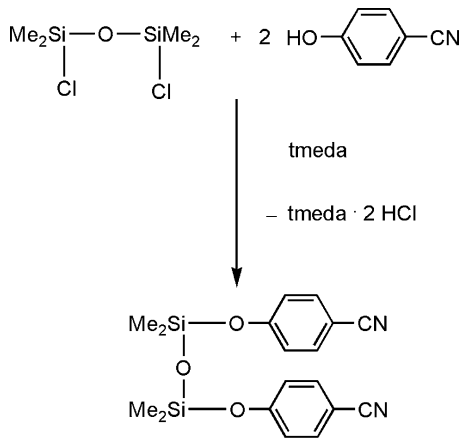
SCHEME 1 x = 1 (**1**), 2 (**2**), 3 (**3**), 4 (**4**). tmeda = *N,N,N′,N′*-tetramethylethylenediamine.

for X-ray analysis. X-ray quality crystals of $Si(OC_6H_4CN)_4$ (**4**) were also obtained by recrystallization from toluene.

The silylethers **1–4** can be isolated in good yields (96–66%). These yields are comparable with those reported in literature, e.g., 60–70% can be achieved for **1**, while Renga and Wang reported 88%[6b] for the reaction of the phenol with trimethylsilyl trichloroacetate $(Cl_3C)CO_2(SiMe_3)$ in the presence of a catalytic amount of K_2CO_3/18-crown-6 at 150°C. The yield of **2** (96%) is somewhat higher than that reported by Ismail, who used cyclic silazanes as silylating reagent (88%).[7b]

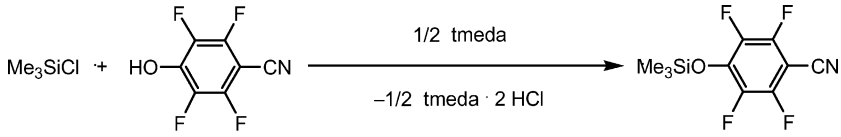
In a next series of reactions, we tried to prepare the analogous disiloxanes utilizing the same procedure as described above. For instance, 1,3-bis(*p*-cyanophenoxy)-1,1,3,3-tetramethyl-disiloxane (**5**) was synthesized from $O(ClSi(Me_2))_2$, HOC_6H_4CN, and TMEDA in a 1:2:1 ratio (Scheme 2). Pure $O(Si(Me_2)OC_6H_4CN)_2$ (**5**) was obtained after removal of the solvent as a brown solid (isolated yield 23%). Crystals of **5** suitable for X-ray analysis were obtained by recrystallization from diethylether and toluene.

Analogous to the formation of **1**, perfluorinated phenols such as HOC_6F_4CN can also be transformed into (*p*-cyano-(tetrafluoro)-phenoxy)-trimethylsilane $(Me_3Si)OC_6F_4CN$ (**6**) when Me_3SiCl and TMEDA are added (Scheme 3). Similar to **1**, $(Me_3Si)OC_6F_4CN$ was obtained as colorless oil after removal of the solvent under vacuum (isolated yield 44%). Further purification including distillation and



5

SCHEME 2 tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.



6

SCHEME 3 tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

recrystallization steps finally yielded crystalline **6**, suitable for an X-ray analysis.

Characterization

All silyl ethers **1**–**6** were characterized by CHN analysis, melting point, IR, Raman, mass spectroscopy, and ^{1}H, ^{13}C, ^{29}Si NMR spectroscopy. (With the exception of **2**, the crystal structures of all compounds could be determined by X-ray analysis).

As expected, the resonances in the $^{29}Si\{^{1}H\}$ NMR spectra of $Me_3SiO(C_6H_4)CN$ ($\delta = 22.31$), $Me_2Si(O(C_6H_4)CN)_2$ ($\delta = -2.39$), and $MeSi(O(C_6H_4)CN)_3$ ($\delta = -52.56$) are shifted to a higher field with progressive substitution of methyl- by $NC(C_6H_4)O$-groups, due to an increasing shielding of the ^{29}Si nucleus. Thus, the ^{29}Si nuclei in $O(SiMe_2(O(C_6H_4)CN))_2$ ($\delta = -10.52$) are stronger shielded than those in $Me_2Si(O(C_6H_4)CN)_2$ ($\delta = -10.52$ vs. -2.39). By comparing the ^{29}Si

NMR signals of $Me_3SiO(C_6H_4)CN$ ($\delta = 22.31$) and $Me_3SiO(C_6F_4)CN$ ($\delta = 30.29$), the electron-withdrawing effect of fluorine clearly exhibits in the low-field shift of the perfluorinated compound.

Following the tendency in the ^{29}Si NMR spectra, the ^{13}C NMR signals of the methyl group are also increasingly shifted to a higher field [$Me_3SiO(C_6H_4)CN$ $\delta = -0.18$, $Me_2Si(O(C_6H_4)CN)_2$ $\delta = -2.64$, and $MeSi(O(C_6H_4)CN)_3$ $\delta = -6.19$].

In the mass spectra of $Me_2Si(O(C_6H_4)CN)_2$, $MeSi(O(C_6H_4)CN)_3$, $Si(O(C_6H_4)CN)_4$, and $O(SiMe_2(O(C_6H_4)CN))_2$, a cleavage of both oxygen bonds in the phenolate substituent is observed. Hence, fragments of benzonitrile (C_6H_4CN) and the corresponding silane fragments are found.

As expected, the stretching vibration of the nitrile moiety in the IR and Raman spectra of the compounds with an tetrahydro(*p*-cyanophenoxy)-substituent are found between 2222 and 2229 cm^{-1} as a strong (IR) or most intensive vibration (Raman), respectively. The stretching vibrations of the nitrile moiety in $(Me_3Si)OC_6F_4CN$ (Raman: $\nu = 2248$ cm^{-1}; IR: $\nu = 2238$ cm^{-1}) are shifted to higher wave numbers in comparison with those in $(Me_3Si)OC_6H_4CN$ (Raman: $\nu = 2225$ cm^{-1}; IR: $\nu = 2225$ cm^{-1}).

X-Ray Analyses

Selected bond lengths and angles are listed in Table I, crystallographic data in Table II.

$(Me_3Si)OC_6H_4CN$ (**1**) crystallizes in the orthorhombic space group *Pnma* with four molecules in the unit cell (Figure 1). Except for two of the methyl groups attached to the silicon atom, all nonhydrogen atoms lie in a mirror plane [$\angle$ (C4–C3–O–Si) = 180°]. As was found for the other silyl ethers **2**–**6**, the silicon atom sits in a distorted tetrahedral

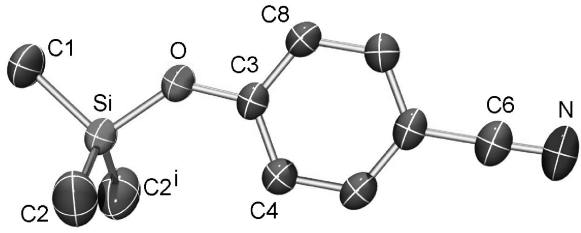


FIGURE 1 ORTEP drawing of $(Me_3Si)OC_6H_4CN$ (**1**). Thermal ellipsoids with 50% probability at 295 K (hydrogen atoms omitted). Symmetry operator: i = x, −y + 0.5, z.

TABLE I Selected Bond Lengths (Å) and Angles (°) in 1 and 3–6

Compound	Si–O [Å]	O–C [Å]	Si–O–C [°]	C–Si–O [°]	O–Si–O [°]
1	1.6663 (16)	1.3574 (17)	133.09 (12)	103.83 (10)	—
				109.80 (5)	—
				111.12 (7)	
3	1.619 (2)[a]	1.379 (3)[a]	129.40 (19)[a]	114.19 (13)[a]	106.38 (11)[a]
	1.621 (2)[a]	1.374 (3)[a]	125.37 (17)[a]	112.83 (14)[a]	105.11 (10)[a]
	1.629 (3)[a]	1.374 (3)[a]	127.44 (17)[a]	112.11 (12)[a]	105.50 (11)[a]
	1.617 (2)[b]	1.376 (3)[b]	129.47 (18)[b]	114.53 (13)[b]	106.36 (10)[b]
	1.618 (2)[b]	1.382 (3)[b]	124.62 (17)[b]	112.60 (14)[b]	105.48 (11)[b]
	1.630 (2)[b]	1.368 (3)[b]	129.73 (18)[b]	112.19 (13)[b]	104.92 (11)[b]
4					108.60 (10)
	1.5997 (18)	1.390 (3)	127.36 (16)		107.85 (10)
	1.6080 (18)	1.393 (3)	129.28 (15)	—	112.51 (10)
	1.6175 (18)	1.383 (3)	135.60 (16)		113.75 (10)
	1.6209 (17)	1.391 (3)	126.13 (15)		106.49 (9)
					107.73 (9)
5		1.360 (3)	130.60 (19)	103.88 (12)[e]	108.60 (8)
	1.6278 (11)[c]			109.79 (12)[e]	
	1.6582 (19)[d]			112.31 (14)[f]	
				108.12 (13)[f]	
6	1.684 (3)	1.337 (4)	134.4 (2)	108.29 (16)	—
				107.23 (18)	
				102.55 (19)	

[a]Molecule 1 in the asymmetric unit (Figure 5).
[b]Molecule 2 in the asymmetric unit.
[c]Si–O–Si bond.
[d]Si–O–C bond (Figure 8).
[e]C–Si–O2 angle (Figure 8).
[f] C–Si–O1 angle.

environment [∠ (O–Si–C) or ∠ (C–Si–C) = 104–111°]. The Si–O bond length of 1.666(2) Å is slightly shorter than expected for a typical Si–O bond [cf. *d*(Si–O) 1.77 Å].[21] The C–N bond length of 1.131(3) Å is in the expected range and in accordance with those found for compounds **3–6**. In the unit cell, an interesting π stacking between the aromatic rings is observed (Figure 2). The molecules attached mutually by π stacking to adopt a "head-to-tail" configuration.

In contrast to **1**, the perfluorinated analogous $(Me_3Si)OC_6F_4CN$ (**6**) crystallizes in the triclinic space group $P-1$ with two molecules in the unit cell (Figure 3). The Me_3Si group is rotated out of the plane formed by the $O(C_6F_4)CN$-unit [∠ (C2–C1–O–Si) = 115.2 (4)°]. Due to the electron-withdrawing effect of fluorine, the C–O bond length of 1.337 (4) Å is slightly shortened compared to that in $(Me_3Si)OC_6H_4CN$ (**1**)

TABLE II Crystallographic Details of 1 and 3–6

	1	**3**	**4**	**5**	**6**
Chem. formula	$C_{10}H_{13}NOSi$	$C_{22}H_{15}N_3O_3Si$	$C_{28}H_{16}N_4O_4Si$	$C_{18}H_{20}N_2O_3Si_2$	$C_{10}H_9F_4NOSi$
Form. wt. [g mol^{-1}]	191.30	397.46	500.54	368.54	263.27
Color	Colorless	Colorless	Colorless	Colorless	Colorless
Cryst. system	Orthorhombic	Orthorhombic	Triclinic	Monoclinic	Triclinic
Space group	Pnma	$P2_12_12_1$	P-1	C2/c	P-1
a [Å]	8.7307 (17)	12.995 (3)	10.6822 (15)	15.392 (3)	7.2588 (12)
b [Å]	7.1399 (14)	16.392 (3)	11.1981 (18)	6.7615 (13)	7.5381 (13)
c [Å]	17.624 (4)	18.924 (4)	12.396 (2)	19.695 (3)	11.856 (2)
α [°]	90.00	90.00	108.270 (15)	90.00	84.672 (14)
β [°]	90.00	90.00	109.848 (14)	108.152 (15)	70.569 (15)
γ [°]	90.00	90.00	104.123 (13)	90.00	87.518 (14)
V [Å^3]	1098.6 (4)	4031.1 (14)	1218.2 (4)	1947.7 (6)	609.11 (18)
Z	4	8	2	4	2
$\rho_{calc.}$ [g cm^{-3}]	1.157	1.310	1.365	1.257	1.435
μ [mm^{-1}]	0.177	0.145	0.140	0.200	0.226
Measured reflections	2410	17707	7166	5430	3582
Independent reflections	1205	6358	5517	2220	2748
Reflections with $I \geq 2\sigma(I)$	1052	4707	2944	1186	1207
$R_{int.}$	0.0184	0.0406	0.0476	0.0694	0.0693
F (000)	408	1648	516	776	268
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0426	0.0390	0.0555	0.0549	0.0635
wR_2 (F^2)	0.1174	0.0796	0.1349	0.1191	0.1570
GooF	1.107	0.999	0.924	0.981	0.920
Parameters	75	525	334	114	154
CCDC #	733380	733381	733382	733383	733384

[1.357 (2) Å]. In contrast, the Si—O bond length of 1.684 (3) Å is slightly expanded [**1**: 1.666 (2) Å]. The C—CN [**1**: 1.444 (3) Å, **6**: 1.436 (5) Å] and CN bond lengths [**1**: 1.131 (3) Å, **6**: 1.142 (5) Å], respectively, are almost identical in both compounds. Moreover, only small differences in the C—O—Si angles have been observed for both compounds [**1**: ∠ = 133.09 (12)°, **6**: ∠ = 134.4 (2)°].

Similar to **1**, π stacking between the aromatic rings is observed in the unit cell of **6**, and the molecules attached mutually adopt a "head-to-tail" configuration (Figure 4).

$MeSi(OC_6H_4CN)_3$ (**3**) crystallizes in the orthorhombic space group $P2_12_12_1$ with eight molecules in the unit cell (Figure 5). The asymmetric unit consists of two molecules of $MeSi(OC_6H_4CN)_3$. Both independent molecules display only small differences in bond lengths and

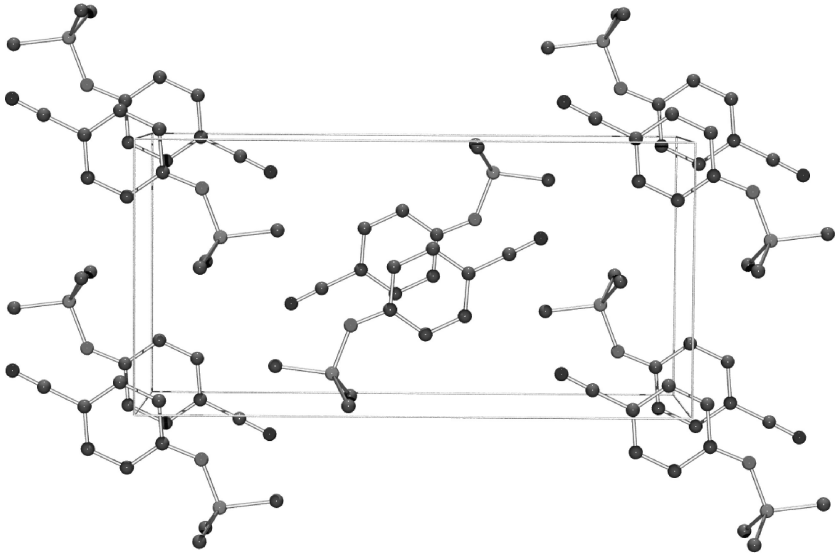


FIGURE 2 Unit cell of $(Me_3Si)OC_6H_4CN$ (**1**). Projection along [010].

angles. The Si—O—C angles at the Si1-atom are 125.37 (17), 129.40 (19), and 127.44 (17)° and at the Si2-atom 129.47 (18), 124.62 (17), and 129.73 (18)°. Thus, these angles are slightly smaller compared to those in $(Me_3Si)OC_6H_4CN$ (**1**) or $(Me_3Si)OC_6F_4CN$ (**6**). This observation can be explained by an increased steric repulsion between the

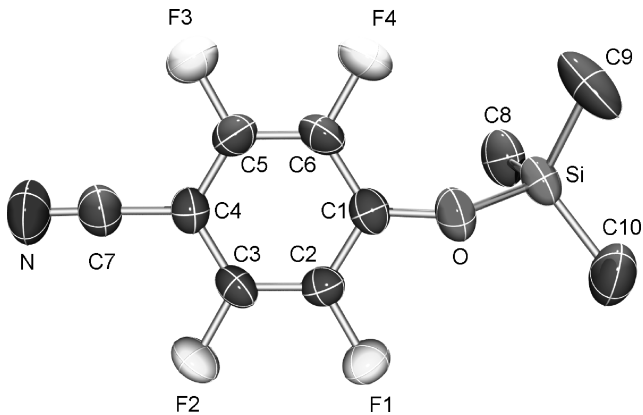


FIGURE 3 ORTEP drawing of $(Me_3Si)OC_6F_4CN$ (**6**). Thermal ellipsoids with 50% probability at 200 K (hydrogen atoms omitted).

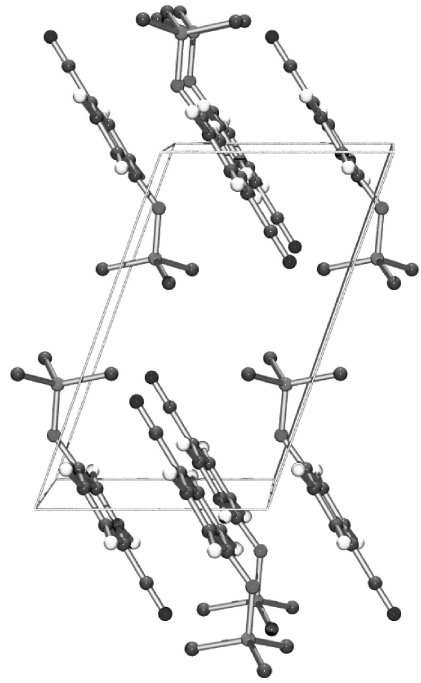


FIGURE 4 Unit cell of $(Me_3Si)OC_6F_4CN$ (**6**). Projection along [010].

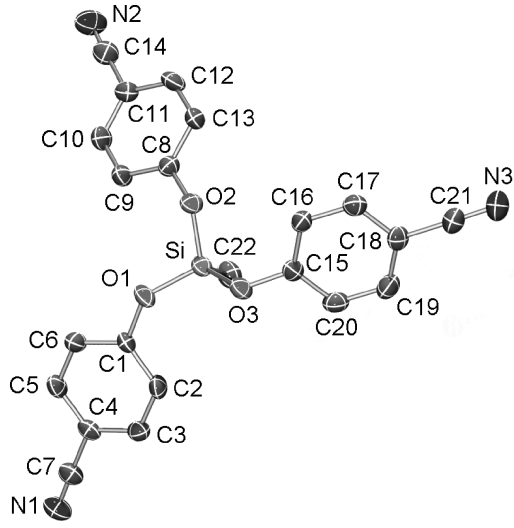


FIGURE 5 ORTEP drawing of $MeSi(OC_6H_4CN)_3$ (**3**). Thermal ellipsoids with 50% probability at 173 K (hydrogen atoms omitted).

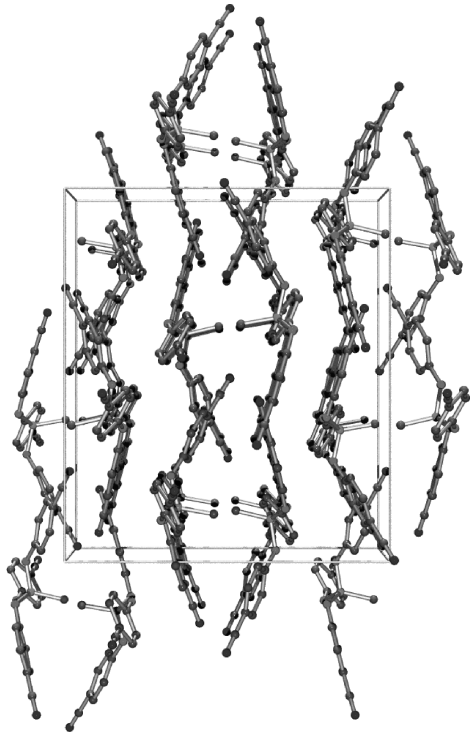


FIGURE 6 Unit cell of $MeSi(OC_6H_4CN)_3$ (**3**). Projection along [100].

three OC_6H_4CN-units at the silicon atom. The Si–O bond lengths of 1.62−1.63 Å are slightly shortened (0.03 Å) compared with those in $(Me_3Si)OC_6H_4CN$. Both molecules in the asymmetric unit adopt a "propeller" configuration, but none of them has exact local C_3 symmetry.

In the unit cell, the molecules are arranged in such a way that "zigzagging" channels are formed (Figure 6).

$Si(OC_6H_4CN)_4$ (**4**) crystallizes in the triclinic space group $P-1$ with two molecules in the unit cell (Figure 7). As discussed before, the silicon atom sits in a distorted tetrahedral environment and possesses approximate local C_2 symmetry. The Si–O bond lengths of 1.60−1.62 Å are slightly shortened compared with those in $Me_3SiOC_6H_4CN$ [1.666 (2) Å] and $MeSi(OC_6H_4CN)_3$ (1.62–1.63 Å). The Si—O−C bond angles vary much more than those in $MeSi(OC_6H_4CN)_3$ (125−129°). Two of the four (*p*-cyanophenoxy)-units in **4** are always arranged parallel to each other, while both pairs are almost perpendicular to one another (Figure 7).

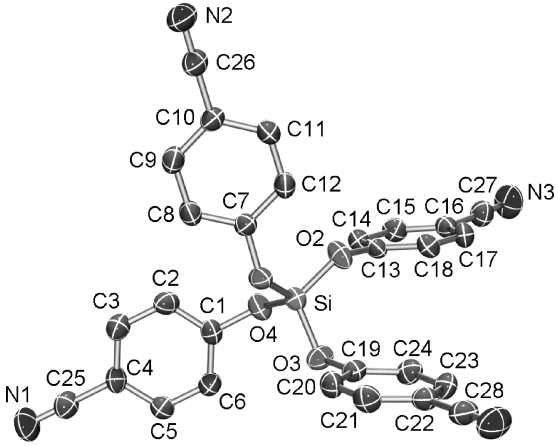


FIGURE 7 ORTEP drawing of $Si(OC_6H_4CN)_4$ (**4**). Thermal ellipsoids with 50% probability at 200 K (hydrogen atoms omitted).

$O(Si(Me_2)OC_6H_4CN)_2$ (**5**) crystallizes in the monoclinic space group $C2/c$ with four molecules in the unit cell (Figure 8). The molecule has C_2 symmetry, with a *trans* arrangement of both oxygen atoms along the Si–Si axis [$\angle$ O2–Si–Si^i–$O2^i$ = 174.45 (17)°]. The Si—O bonds of the Si—O—Si bridge [Si—O1 = 1.6278 (11) Å] are slightly shorter than the Si–O(*p*-cyanophenoxy) bonds [Si—O2 = 1.6582 (19) Å]. In

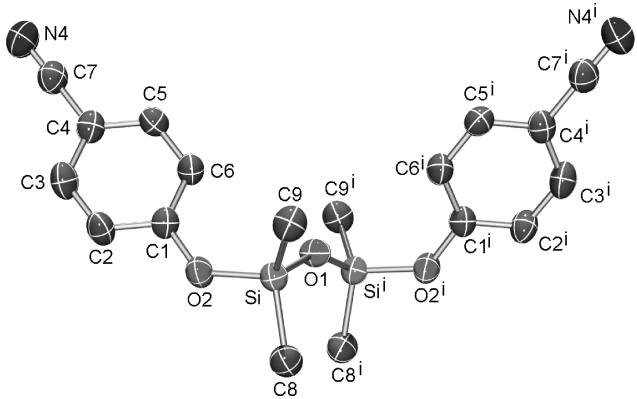


FIGURE 8 ORTEP drawing of $O(Si(Me_2)OC_6H_4CN)_2$ (**5**). Thermal ellipsoids with 50% probability at 200 K (hydrogen atoms omitted). Symmetry operator: i = −x +1, y, −z + 1.5.

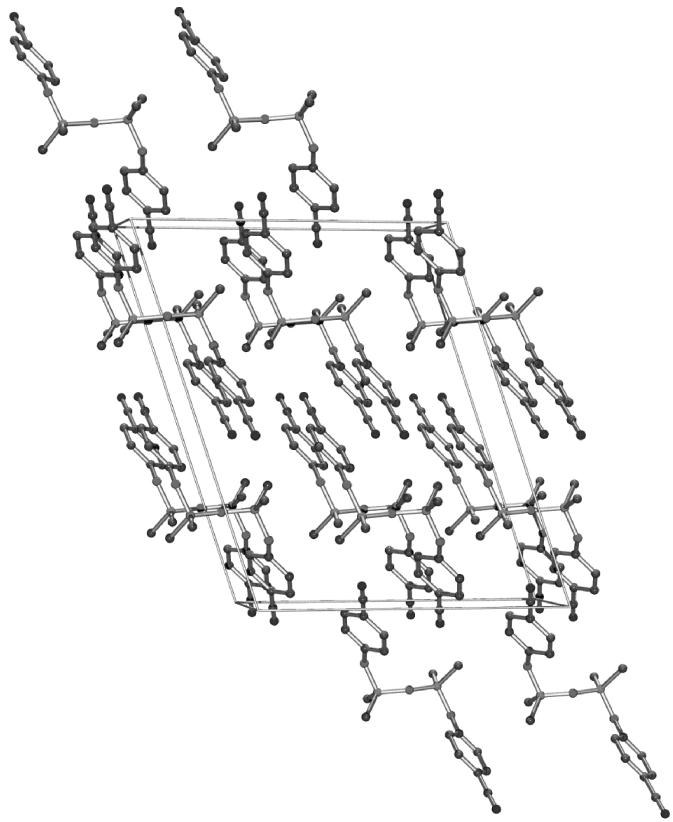


FIGURE 9 Unit cell of $O(Si(Me_2)OC_6H_4CN)_2$ (**5**). Projection along [010].

the unit cell, alternating layers of benzonitrile units and layers of $O-(Me_2)Si-O-Si(Me_2)-O$ units (Figure 9) are found.

EXPERIMENTAL

General Information

All manipulations were carried out under oxygen- and moisture-free conditions under nitrogen using standard Schlenk or drybox techniques. Tetrahydrofuran, diethylether, toluene, and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA; Aldrich) were dried over sodium and freshly distilled prior to use. Tetrafluoro-4-hydroxybenzonitrile (HOC_6F_4CN) was prepared according to a procedure in the literature.[22] Me_3SiCl (Merck), Me_2SiCl_2 (Acros), $MeSiCl_3$

(Acros), $SiCl_4$ (Acros), and $(Me_2(Cl)Si)_2O$ (Acros) were always freshly distilled prior to use. *p*-Cyanophenol (Fluka) was used as received.

NMR: ^1H, $^{13}C\{^1H\}$, ^{29}Si, and ^{19}F-NMR spectra were obtained on a Jeol EX400 Delta, a Jeol EX 400 Eclipse or a Bruker ARX 300 spectrometer and were referenced internally to the deuterated solvent (^{13}C, $\delta_{reference} = 54$ ppm) or to protic impurities in the deuterated solvent (^1H, $\delta_{reference} = 5.31$ ppm). **IR:** Perkin-Elmer One FT-IR spectrometer with a DuraSampl*IR*II Diamond ATR Sensor by SensIR Technologies. **Raman:** Perkin Elmer Spectrum 2000R NIR FT-Raman, equipped with a Nd:YAG-Laser (1064 nm). **MS:** JEOL MStation JMS 700. **CHN analyses:** Analysator Elementar Vario EL. **Melting points:** Uncorrected (Büchi B540 or EZ-Melt, Stanford Research Systems).

X-Ray Structure Determination

X-ray quality crystals of **1**, **3**, **4**, **5**, and **6** were selected in Kel-F-oil (Riedel deHaen) at ambient temperatures. All samples were cooled to 173(2) K (**3**) or 200 (2) K (**4**, **5**, **6**) during measurement. Compound **1** was measured at ambient temperatures (295 (2) K). The data were collected on a Nonius MACH3 diffractometer (**1**), on a Bruker-Nonius Apex X8 CCD diffractometer (**3**), or on a Oxford Xcalibur3 CCD diffractometer (**4**, **5**, **6**), using graphite-monochromated Mo Kα radiation ($\lambda =$ 0.71073). The structures were solved by direct methods (*SHELXS-97*)[23] and refined by full-matrix least squares procedures (*SHELXL-97*).[24] Semi-empirical absorption corrections were applied for **1** (MolEN)[25] and **3** (*SADABS*).[26] All nonhydrogen atoms were refined anisotropically, and hydrogen atoms were included in the refinement at calculated positions using a riding model. The methyl group at C2 in **1** was found to be disordered and was split in two parts. The occupancy of each part was refined freely [0.62(2)/0.38 (2)].

Full crystallographic data are deposited at the Cambridge Crystallographic Data Centre (CCDC), U.K.

$Me_3SiOC_6H_4CN$ (1)

To a solution of *p*-cyanophenol (13.79 g, 115.77 mmol, 1 eq) in 250 mL tetrahydrofuran, Me_3SiCl (12.58 g, 14.80 mL, 115.80 mmol, 1 eq) was added at ambient temperature with stirring. To this reaction mixture, $Me_2N(CH_2)_2NMe_2$ (6.73 g, 8.74 mL, 57.91 mmol, 0.5 eq) was added over a period of 5 min. Subsequently, the resulting suspension was heated under reflux for 6 h. After cooling, the mixture was filtered through a G4 frit, and the insoluble solid was washed with tetrahydrofuran

(2 × 10 mL). The filtrate and the washing solutions were combined, and the solvent was distilled off under vacuum. The resulting oily red residue was distilled under vacuum (10^{-2} mbar, 81°C) yielding an oil, which crystallized upon standing to give a colorless solid of **1**. Yield: 14.59 g (76.26 mmol, 65.87%), mp 41°C. IR (cm^{-1}): ν = 3048 (w), 2961 (w), 2902 (w), 2559 (w), 2225 (m), 1602 (s), 1506 (vs), 1415 (w), 1288 (m), 1271 (s), 1253 (vs), 1168 (m), 1105 (w), 901 (s), 835 (vs), 755 (m), 695 (w), 641 (w). Raman (100 mW, 25°C, cm^{-1}): ν = 3078 (21), 2967 (9), 2903 (19), 2225 (100), 1603 (46), 1417 (3), 1293 (11), 1191 (9), 1173 (24), 906 (6), 850 (3), 775 (11), 645 (20), 591 (9), 548 (6), 481 (8), 342 (8), 248 (8), 199 (9), 160 (8). ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C): δ = 0.23 (s, 9H, $(H_3C)_3Si$), 6.88 (d, J = 9.9 Hz, 2H, O-C-CH), 7.53 (d, J = 8.2 Hz, 2H, NC—C—CH). ^{13}C NMR ($CDCl_3$, 101 MHz, 25°C): δ = −0.18 ($(H_3C)_3Si$), 104.58 (**C**—CN), 119.36 (**C**N), 121.00 (OC-**C**H), 133.81 (NC—C—**C**H), 159.43 (**C**—O). ^{29}Si{^{1}H} NMR ($CDCl_3$, 79 MHz, 25°C): δ = 22.31 (s, $SiMe_3$). MS (EI+, 70 eV); *m/z* (%): 191 (27) $[M]^+$, 177 (15), 176 (100) $[M - Me]^+$, 102 (6), 75 (16), 73 (12) $[Me_3Si]^+$, 43 (8), 28 (12), 18 (50), 17 (11). $C_{10}H_{13}NOSi$ (191.30): calc: N 7.32%, C 62.79%, H 6.85%; found: N 7.31%, C 62.39%, H 7.33%.

$Me_2Si(OC_6H_4CN)_2$ (2)

2 was synthesized using the same method as for **1**, but with the following quantities: *p*-cyanophenol (5.00 g, 41.97 mmol, 2 eq), 125 mL tetrahydrofuran, Me_2SiCl_2 (2.70 g, 2.55 mL, 20.92 mmol, 1 eq), and $Me_2N(CH_2)_2NMe_2$ (2.43 g, 3.16 mL, 20.91 mmol, 1 eq). **2** was afforded as a colorless oil. Yield: 5.90 g (20.04 mmol, 95.66%). IR (cm^{-1}): ν = 2967 (w), 2562 (w), 2226 (s), 1600 (s), 1498 (vs), 1415 (w), 1277 (m), 1249 (vs), 1168 (s), 1106 (w), 1015 (w), 911 (vs), 832 (s), 807 (s), 683 (w), 655 (w), 620 (w). Raman (100 mW, 25°C, cm^{-1}): ν = 3075 (21), 2968 (5), 2902 (11), 2228 (100), 1605 (77), 1285 (11), 1261 (9), 1190 (27), 1169 (37), 919 (5), 841 (17), 776 (25), 719 (5), 684 (10), 654 (10), 588 (4), 547 (6), 481 (7), 416 (6), 279 (7), 261 (7), 192 (11), 163 (11). ^{1}H NMR (C_6D_6, 400 MHz, 25°C): δ = 0.13 (s, 6H, $(H_3C)_2Si$), 6.61 (d, J = 8.8 Hz, 2H, O-C-CH), 7.08 (d, J = 8.76 Hz, 2H, NC—C—CH). ^{13}C NMR (C_6D_6, 101 MHz, 25°C): δ = −2.66 ($(H_3C)_2Si$), 106.52 (**C**—CN), 118.76 (CN), 120.59 (OC-**C**H), 134.28 (NC—C—**C**H), 157.37 (**C**—O). ^{29}Si{^{1}H} NMR (C_6D_6, 79 MHz, 25°C): δ = −2.39 ($Si(CH_3)_2$). MS (DEI+, 70 eV); *m/z* (%): 369 (11), 368 (37) $[O(Me_2SiOC_6H_4CN)_2]^+$, 354 (6), 353 (19), 325 (8), 324 (29), 308 (5), 295 (9), 294 (39) $[M]^+$, 279 (22) $[M - Me]^+$, 261 (12), 252 (9), 251 (23), 250 (100), 236 (7), 235 (11), 234 (52), 177 (8), 176 (43) $[Me_2Si(OC_6H_4CN)]^+$, 160 (6), 133 (11), 119 (6), 116 (15), 102

(13) $[C_6H_4CN]^+$, 90 (6), 75 (11), 73 (13). $C_{16}H_{14}N_2O_2Si$ (294.38): Calc: N 9.52%, C 65.28%, H 4.79%; found: N 9.63%, C 65.55%, H 4.89%.

$MeSi(OC_6H_4CN)_3$ (3)

3 was synthesized using the same method as for **1**, but with the following quantities: *p*-cyanophenol (7.50 g, 62.96 mmol, 3 eq), 250 mL tetrahydrofuran, $MeSiCl_3$ (3.14 g, 2.47 mL, 20.99 mmol, 1 eq), and $Me_2N(CH_2)_2NMe_2$ (3.66 g, 4.75 mL 31.50 mmol, 1.5 eq). Cooling down the afforded colorless oil with liquid nitrogen under vacuum twice gave **3** as a colorless, crystalline solid. Yield: 6.44 g (16.20 mmol, 77.18%). Crystals suitable for X-ray analysis were grown in the following manner: A small amount of **3** was dissolved in a little toluene, and the solution was filtered through a G4 frit. The solvent was distilled off, and the residual oil crystallized at ambient temperature for 2 days to give colorless crystals. mp 82–83°C. IR (cm^{-1}): $\nu = 3100$ (w), 3065 (w), 3002 (w), 2912 (w), 2567 (w), 2224 (vs), 1913 (w), 1600 (vs), 1497 (vs), 1416 (w), 1291 (w), 1283 (w), 1246 (vs), 1168 (s), 1108 (m), 1016 (w), 927 (vs), 841 (s), 826 (s), 801 (s), 771 (m), 739 (m), 662 (w), 638 (w), 601 (w). Raman (100 mW, 25°C, cm^{-1}): $\nu = 3077$ (26), 2984 (4), 2913 (9), 2229 (100), 1603 (48), 1299 (9), 1271 (6), 1191 (20), 1172 (21), 931 (8), 840 (6), 801 (18), 742 (11), 718 (6), 653 (7), 547 (6), 480 (7), 158 (9). ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C): $\delta = 0.62$ (s, 3H, $(H_3C)Si$), 7.04 (d, $J = 8.9$ Hz, 2H, O-C-CH), 7.59 (d, $J = 8.8$ Hz, 2H, NC–C–CH). ^{13}C NMR ($CDCl_3$, 76 MHz, 25°C): $\delta = -6.19$ ($(H_3\mathbf{C})Si$), 107.07 (**C**–CN), 118.30 (**C**N), 120.36 (OC-**C**H), 134.36 (NC–C–**C**H), 155.72 (**C**–O). ^{29}Si{^{1}H} NMR ($CDCl_3$, 60 MHz, 25°C): $\delta = -52.56$ ($(H_3C)_3Si$). MS (DEI+, 70 eV); *m/z* (%): 399 (8), 398 (30), 397 (100) $[M]^+$, 280 (6), 279 (27) $[MeSi(OC_6H_4CN)_2]^+$, 263 (6), 262 (8), 261 (36), 160 (7), 119 (9), 102 (7) $[C_6H_4CN]^+$. $C_{22}H_{15}N_3O_3Si$ (397.46): calc.: N 10.57%, C 66.48%, H 3.80%; found: N 10.22%, C 66.52%, H 4.40%.

$Si(OC_6H_4CN)_4$ (4)

4 was synthesized using the same method as for **1**, but with the following quantities: *p*-cyanophenol (30.00 g, 251.85 mmol, 4 eq), 250 mL tetrahydrofuran, $SiCl_4$ (10.70 g, 7.23 mL, 62.98 mmol, 1 eq), and $Me_2N(CH_2)_2NMe_2$ (14.63 g, 19.00 mL, 125.89 mmol, 2 eq). In this reaction, the insoluable solid was washed with 100 mL of tetrahydrofuran. The procedure afforded a brownish amorphous solid. Recrystallization from toluene gave a reddish brown oil, from which crystals of **4** grew at 0°C. Yield: 26.26 g (52.46 mmol, 83.40%). Crystals suitable for X-ray

analysis were obtained by twice recrystallizing from diethylether followed by twice recrystallizing from toluene. mp 131°C. IR (cm^{-1}): ν = 3273 (m), 3099 (m), 2569 (w), 2229 (s), 1908 (w), 1783 (w), 1599 (vs), 1494 (vs), 1450 (w), 1410 (w), 1374 (w), 1284 (m), 1230 (vs), 1163 (s), 1101 (m), 1015 (w), 998 (m), 961 (vs), 920 (m), 840 (s), 820 (m), 799 (m), 717 (w), 702 (w), 666 (m), 648 (w). Raman (200 mW, 25°C, cm^{-1}): ν = 3076 (24), 2229 (100), 1600 (57), 1324 (6), 1299 (9), 1242 (9), 1190 (17), 1182 (13), 1167 (13), 918 (13), 772 (22), 649 (9), 243 (8), 192 (10), 145 (9). ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C): δ = 7.09 (d, J = 8.8 Hz, 2H, O-C-CH), 7.63 (d, J = 8.9 Hz, 2H, NC—C—CH). ^{13}C NMR ($CDCl_3$, 76 MHz, 25°C): δ = 108.07 (**C**—CN), 117.97 (**C**N), 120.17 (OC-**C**H), 134.49 (NC—C—**C**H), 154.71 (**C**—O). MS (DEI+, 70 eV); m/z (%): 502 (11), 501 (37), 500 (100) $[M]^+$, 364 (10), 264 (6), 263 (29) $[Si(OC_6H_4CN)_2 - H]^+$, 119 (25) $[HOC_6H_4CN]^+$, 102 (12) $[C_6H_4CN]^+$, 92 (10), 91 (16), 90 (5), 64 (6), 63 (6). $C_{28}H_{16}N_4O_4Si$ (500.54): calc.: N 11.19%, C 67.19%, H 3.22%; found: N 11.34%, C 65.93%, H 3.64%.

$(Me_2Si(OC_6H_4CN))_2O$ (5)

5 was synthesized using the same method as for **1**, but with the following quantities: *p*-cyanophenol (11.92 g, 100.07 mmol, 2 eq), 250 mL tetrahydrofuran, $(Me_2(Cl)Si)_2O$ (9.80 g, 9.52 mL, 48.23 mmol, 1 eq), and $Me_2N(CH_2)_2NMe_2$ (5.81 g, 7.55 mL, 50.00 mmol, 1 eq). The procedure gave a brown solid. Recrystallization from toluene followed by recrystallization from diethylether three times afforded crystals of **5** suitable for X-ray analysis. Yield: 5.54 g (11.07 mmol, 22.95%), mp 62–64°C. IR (cm^{-1}): ν = 3076 (w), 3048 (w), 2968 (w), 2912 (w), 2561 (w), 2350 (w), 2286 (w), 2224 (s), 2172 (w), 1902 (w), 1603 (vs), 1560 (w), 1508 (vs), 1418 (w), 1285 (s), 1273 (vs), 1258 (vs), 1191 (w), 1173 (m), 1106 (w), 1052 (m, br), 960 (w), 944 (w), 913 (s), 836 (vs), 806 (vs), 800 (vs), 704 (w), 676 (m), 656 (m), 625 (w), 606 (m). Raman (100 mW, 25°C, cm^{-1}): ν = 3076 (40), 2980 (20), 2910 (27), 2222 (100), 1606 (87), 1394 (7), 1286 (13), 1261 (9), 1191 (23), 1178 (35), 830 (10), 776 (23), 703 (9), 658 (10), 481 (13), 424 (9), 363 (17), 313 (10), 278 (11), 240 (13), 202 (19), 151 (8). ^{1}H NMR (C_6D_6, 400 MHz, 25°C): δ = 0.17 (s, 12H, $(H_3C)_2Si$), 6.68 (d, 4H, J = 8.8 Hz), 7.14 (d, 4H, J = 7.7 Hz). ^{13}C NMR (C_6D_6, 101 MHz, 25°C): δ = −0.87 ($(H_3C)_2Si$), 106.23 (**C**—CN), 118.70 (**C**N), 120.00 (OC—**C**H), 133.76 (NC—C—**C**H), 157.93 (**C**—O). ^{29}Si{^{1}H} NMR (C_6D_6, 79 MHz, 25°C): δ = −10.52 ($(H_3C)_2Si$). MS (DEI+, 70 eV); m/z (%): 398 (9), 370 (5), 369 (14), 368 (45) $[M]^+$, 354 (7), 353 (24) $[M - Me]^+$, 252 (10), 251 (22), 250 (100) $[(Me_2Si)_2O(OC_6H_4CN)]^+$, 236 (6), 235 (10) $[(MeSiOSiMe_2(OC_6H_4CN)]^+$, 234 (46), 176 (8), 133 (10), 119

(13), 116 (10), 102 (8) $[C_6H_4CN]^+$, 91 (5), 75 (11), 73 (17). $C_{18}H_{20}N_2O_3Si_2$ (368.53): calc.: N 7.60%, C 58.66%, H 5.47%; found: N 7.17%, C 56.93%, H 5.36%.

$Me_3SiOC_6F_4CN$ (6)

6 was synthesized using the same method as for **1**, but with the following quantities: (tetrafluoro)-*p*-cyanophenol (5.27 g, 27.58 mmol, 1 eq), 125 mL tetrahydrofuran, Me_3SiCl (3.02 g, 3.55 mL, 27.80 mmol, 1 eq), and $Me_2N(CH_2)_2NMe_2$ (1.60 g, 2.08 mL, 13.77 mmol, 0.5 eq). The procedure gave a yellow oily residue, which was distilled under vacuum (10^{-2} mbar, 60°C) yielding an oil, from which crystals of **6** suitable for X-ray analysis precipitated. Further stirring under vacuum afforded **6** as a pale brown solid. Yield: 3.19 g (12.12 mmol, 43.93%), mp 102–104°C. IR (cm^{-1}): ν = 3515 (w), 3427 (m), 3299 (w), 2961 (w), 2904 (w), 2350 (w), 2238 (w), 2050 (w), 1650 (vs), 1616 (m), 1517 (s), 1490 (vs), 1418 (s), 1396 (s), 1317 (m), 1290 (w), 1256 (vs), 1145 (s), 983 (vs), 925 (m), 841 (vs), 819 (s), 786 (m), 764 (m), 750 (s), 707 (w), 681 (w), 663 (m), 628 (m). Raman (100 mW, 25°C, cm^{-1}): ν = 2967 (23), 2908 (50), 2246 (88), 1651 (100), 1511 (9), 1443 (53), 1323 (11), 1168 (5), 630 (39), 524 (58), 478 (19), 431 (15), 407 (8), 390 (17), 340 (15), 314 (8), 238 (15), 185 (19), 132 (7). ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C): δ = −0.32 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$, 25°C, 75.47): δ = −0.05 ($(CH_3)_3Si$), 106.75 (t, **C**–CN, $^2J_{CF}$ = 16.3 Hz), 136.85 (m, **C**N), 140.73 (dm, OC–**C**F), 144.92 (dm, NC-C-**C**F), 160.79 (s, **C**–O). ^{19}F NMR ($CDCl_3$, 282.40 MHz, 25°C): δ = − 142.43 (dm, 2F), − 156.87 (dm, 2F). ^{29}Si{^{1}H} NMR ($CDCl_3$, 59.67 MHz, 25°C): δ = 30.29 ($Si(CH_3)_3$). MS (DEI+, 70 eV); *m/z* (%): 264 (9), 263 (55) $[M]^+$, 249 (12), 248 (79) $[M - Me]^+$, 191 (11), 170 (14), 148 (6), 147 (25), 124 (13), 120 (11), 81 (17), 78 (8), 77 (100) $[Me_2SiF]^+$, 76 (6), 75 (42), 74 (8), 73 (92) $[Me_3Si]^+$, 63 (9), 49 (11), 47 (17), 45 (8), 43 (8), 18 (29). $C_{10}H_9F_4NOSi$ (263.26): calc.: N 5.32%, C 45.62%, H 3.45%; found: N 5.34%, C 45.48%, H 3.48%.

REFERENCES AND NOTES

[1] J. L. Speier Jr., *J. Am. Chem. Soc.,* **74,** 1003 (1952).
[2] E. Larsson, *Chem.Ber.,* **86,** 1382 (1953).
[3] P. D. George and A. E. Newkirk, US-Patent 2837552 (1958).
[4] R. A. Thompson and F. A. Kipping, *J. Chem. Soc.,* 1176 (1929).
[5] A. M.Youssef, *Phosphorus, Sulfur, and Silicon,* **73**(1–4), 257 (1992).
[6] (a) J. C. Ellington Jr. and E. M. Arnett, *J. Am. Chem. Soc.,* **110**(23), 7778 (1988); (b) J. M. Renga and P. C. Wang, *Tetrahedron Lett.*, **26**(9), 1175 (1985); (c) P. C. Wang and J. M. Renga, U.S. Patent 4360686 (1982).

[7] (a) M. R. Ismail, Ger. Patent 1244183 (1967);(b) M. R. Ismail, *Helv. Chim. Acta,* **8,** 2405 (1964).
[8] B. Krumm, A. Vij, R. L. Kirchmeier, and J. M. Shreeve, *Inorg. Chem.,* **36**(3), 366 (1997).
[9] E. Steiner, H. Beyeler, M. Riediker, V. Desobry, K. Dietliker, and R. Huesler, Eur. Pat. Appl. EP 401165 (1990).
[10] A. J. Oliver and W. A. G. Graham, *J. Organomet. Chem.,* **19**(1), 17 (1969).
[11] M. G. Hogben and W. A. G. Graham, *J. Am. Chem. Soc.,* **91**(2), 283 (1969).
[12] A. J. Oliver and W. A. G. Graham, *J. Organomet. Chem.,* **19**(1), 17 (1969).
[13] (a) M. G. Hogben and W. A. G. Graham, *J. Am. Chem. Soc.,* **91**(2), 283 (1969); (b) Y. F. Zhang, X. Zheng, A. Vij, D. Wingate, D. Meng, K. White, R. L. Kirchmeier, and J. M. Shreeve, *Inorg. Chem.,* **35,** 1590 (1996); (c) M. Nishida, A. Vij, R. L. Kirchmeier, and J. M.Shreeve, *Inorg. Chem.,* **34**(24), 6085 (1995).
[14] T. T.Wenzel and Z. D. Dixon, U.S. Pat. 2005182212 (2005).
[15] J. I. Amor, N. C. Burton, T. Cuenca, P. Gomez-Sal, and P. Royo, *J. Organomet. Chem.,* **485**(1–2), 153 (1995).
[16] A. Majid, D. W. A. Sharp, J. M. Winfield, and I. Hanley, *J. Chem. Soc., Dalton Trans.,* **18,** 1876 (1973).
[17] (a) O. B. Artamkina, E. P. Kramarova, A. G. Shipov, Y. I. Baukov, A. A. Macharasvili, Y. E. Ovchinnikov, and T. Struchkov, *Zh. Obshch. Khim.,* **63**(10), 2289 (1993); (b) O. B. Artamkina, A. G. Shipov, and Y. I. Baukov, *Zh. Obshch. Khim.,* **65**(12), 2005 (1995).
[18] J. I. Darragh, S. F. Hossain, and D. W. A. Sharp, *J. Chem. Soc., Dalton Trans.,* **3,** 218 (1975).
[19] G. G. Furin, T. V. Terent'eva, A. I. Rezvukhin, and G. G. Yakobson, *Zh. Obshch. Khim.,* **45**(7), 1473 (1975).
[20] M. G. Voronkov, E. I. Dubinskaya, S. F. Pavlov, and V. G. Gorokhova, *Izv. Akad. Nauk SSSR, Ser. Khim.,* **10,** 2355 (1976).
[21] (a) G. G. Furin, A. I. Rezvukhin, M. A. Fedotov, and G. G. Yakobson, *J. Fluorine Chem.,* **22**(3), 231 (1983); (b) N. V. Kozlova, I. F. Kovalev, and M. G. Voronkov, *Dokl. Akad. Nauk*., **236**(2), 383 (1977); (c) V. A. Pestunovich, M. F. Larin, E. I. Dubinskaya, and M. G. Voronkov, *Dokl. Akad. Nauk*, **233**(3), 378 (1977); (d) N. V. Kozlova, I. F. Kovalev, Y. I. Khudobin, and M. G. Voronkov, *Dokl. Akad. Nauk,* **223**(6), 1401 (1975); (e) G. F. Lanthier, J. M. Miller, and A. J. Oliver, *Can. J. Chem.,* **51**(12), 1945 (1973).
[22] A. F. Holleman and E. Wiberg, *Lehrbuch der Anorganischen Chemie* (W. de Gruyter, Berlin, New York, 1995), 101st ed., Anhang V, p. 1842.
[23] J. M. Birchall, R. N. Haszeldine, and M. E. Jones, *J. Chem. Soc. (C),* 1343 (1971).
[24] G. M. Sheldrick, SHELXS-97: Program for the Solution of Crystal Structures, University of Göttingen, Germany (1997).
[25] Enraf–Nonius. OpenMolEN. Enraf–Nonius, Delft, The Netherlands (1997).
[26] G. M. Sheldrick, SADABS. Version 2. University of Göttingen, Germany (2004).