Octacarbonyldicobalt(0)-Catalyzed Ring-Opening Cyanation of Tetrahydrofuran Derivatives with Trimethylsilyl Cyanide

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Tetrahydrofuran, less strained cyclic ether was effectively cyanated by trimethylsilyl cyanide ($(CH_3)_3SiCN$) with its ring-opening to give 5-(trimethylsiloxy)pentanenitrile in 82% yield at 120 °C for 23 h in the presence of a catalytic amount of $Co_2(CO)_8$. Several tetrahydrofuran derivatives having methyl and alkoxyl groups also reacted with trimethylsilyl cyanide to give the corresponding 5-siloxy nitriles in 25—88% yields. On using oxiranes or oxetanes, which are more strained cyclic ethers, however, no reaction proceeded under the same conditions. In the present reaction, $(CH_3)_3SiCN$ would firstly coordinate to the cobalt metal center as its isocyanide form to give a cobalt-isocyanide complex, which would be a precursor of active catalyst species in the reaction.

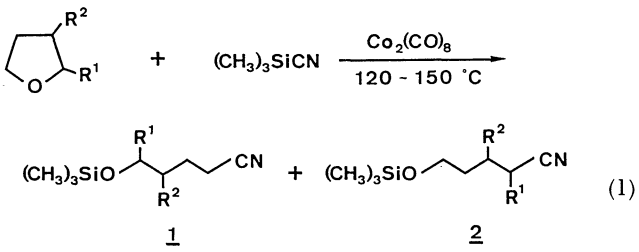
Synthesis of organic nitriles using cyanating reagents is one of important processes in synthetic chemistry. Especially, cyanation of organic halides with inorganic cyanides such as KCN[1] and hydrocyanation of unsaturated compounds with HCN[2] are well-known methods for the preparation of organic nitriles and have been extensively investigated.

On the other hand, it is well-known that trimethylsilyl cyanide, $(CH_3)_3SiCN$ is also an useful cyanating reagent. This reagent has provided an excellent synthetic intermediate in organic chemistry; for examples, the conversion of carbonyl compounds into silylated cyanohydrins.[3] In recent years, it has been reported that $(CH_3)_3SiCN$ could be used as a versatile reagent for cyanation of organic iodides,[4] acetylenes,[5] allenes,[6] cyclopropenones,[7] and oxygen-containing compounds such as cyclic ethers, acetals[8] in the presence of a catalytic amount of transition metal complexes or Lewis acids. With respect to the reaction of cyclic ethers with $(CH_3)_3SiCN$, active investigations have recently been carried out by several groups.[9] Interestingly, oxiranes and oxetanes reacted with $(CH_3)_3SiCN$ to give the corresponding 3- or 4-trimethylsiloxy nitriles in the presence of $AlCl_3$,[9a] Et_2AlCl,[9b] $Al(OPr^i)_3$,[9c] and $Ti(OPr^i)_4$,[9d] whereas the corresponding 2- or 3-trimethylsiloxy isocyanide under the influence of ZnI_2,[9e,f] $ZnCl_2$,[9g] $Pd(CN)_2$, or $SnCl_2$[9c] at room temperature ~70 °C. As for tetrahydrofuran derivatives, less strained cyclic ethers, however, a similar ring-opening reaction has not been reported yet.

We reported recently that ring-opening carbonylation of cyclic ethers including tetrahydrofuran with *N*-trimethylsilyl amines readily proceeded to give the corresponding trimethylsiloxy amides in the presence of a catalytic amount of $Co_2(CO)_8$.[10] In this paper, we describe the first example of $Co_2(CO)_8$-catalyzed ring-opening cyanation of tetrahydrofuran derivatives with $(CH_3)_3SiCN$ to give the corresponding 5-(trimethylsiloxy)pentanenitriles and also discuss the reaction mechanism.

Results and Discussion

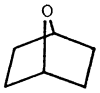
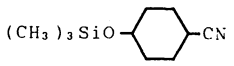
Tetrahydrofurans were smoothly cyanated by $(CH_3)_3SiCN$ with their ring-opening in the presence of a catalytic amount of $Co_2(CO)_8$ to give the corresponding 5-(trimethylsiloxy)pentanenitriles in 25—88% yields (Eq. 1).



1 2 (1)

The results are summarized in Table 1. Unsubstituted tetrahydrofuran gave 5-(trimethylsiloxy)pentanenitrile at 120 °C in 82% yield (run 1). Monosubstituted tetrahydrofurans including methyl and alkoxyl substituents also smoothly reacted with $(CH_3)_3SiCN$ to give the corresponding nitriles whose substituents remained intact, and the best yield was obtained in the reaction of 3-methyltetrahydrofuran with $(CH_3)_3SiCN$ (runs 2—5). In the cyanation of tetrahydrofurans having the methyl substituent, the mixture of two regioisomers (**1**,**2**) was obtained, whereas only single products were obtained in the reaction of tetrahydrofurans containing alkoxyl substituents. The products where 5-position carbons of original tetrahydrofurans were cyanated were mainly obtained except 2-ethoxytetrahydrofuran. The opposite selectivity was observed in a case of 2-ethoxytetrahydrofuran which could be regarded as an acetal rather than a cyclic ether. Since it has been reported that the conversion of acetals with $(CH_3)_3SiCN$ to 2-alkoxy nitriles was catalyzed by $CoCl_2$,[8c] $ZnCl_2$ or $BF_3 \cdot OEt_2$,[8b] the similar reaction may take place under the present reaction conditions using $Co_2(CO)_8$ as catalyst. Bicyclic ether such as 7-oxabicyclo[2.2.1]-

Table 1. $Co_2(CO)_8$-Catalyzed Ring-Opening Cyanation of Tetrahydrofurans[a]

Run	Tetrahydrofurans		Temp/°C	Time/h	Yield/%[b]	Siloxy nitrile
	R^1	R^2				1/2[c]
1	H	H	120	23	82 (59)	—
2	H	CH_3	150	24	(88)	77/ 23
3	CH_3	H	120	23	(34)	53/ 47
4	H	OCH_3	150	40	(34)	100/ 0
5	OC_2H_5	H	150	24	(47)	0/100
6			150	24	 (25)	—

a) $(CH_3)_3SiCN$ (4.5 mmol), tetrahydrofurans (3.0 mmol), $Co_2(CO)_8$ (0.15 mmol), and benzene (3.0 ml). b) Determined by GLC based on the amount of tetrahydrofurans charged and figures in parentheses are isolated yields. c) Shown in Eq. 1.

Table 2. Effect of Various Reaction Conditions[a]

Run	THF/mmol	$(CH_3)_3SiCN$/mmol	Temp/°C	Yield/%[b]
1	34	3.0	180	65
2	34	3.0	150	71
3	34	3.0	120	68
4	34	3.0	100	Trace
5	34	3.0	60	0
6[c]	34	3.0	120	Trace
7[d]	3.0	3.0	120	78
8[d]	3.0	4.5	120	82(59)
9[d]	3.0	6.0	120	65
10[e]	3.0	4.5	120	0

a) $Co_2(CO)_8$ (0.15 mmol), THF (3.0 ml=34 mmol), for 23 h. b) 5-(Trimethylsiloxy)pentanenitrile. Determined by GLC and figure in parentheses is isolated yield. c) Triphenylphosphine (0.30 mmol) was added. d) Benzene (3.0 ml) was used as a solvent. e) Acetonitrile (3.0 ml) was used as a solvent.

Table 3. Catalytic Activities of Several Transition Metal Complexes[a]

Run	Catalyst	Yield/%[b]
1	$Co_2(CO)_8$	68
2	$CoCl_2$	7
3	$CoCl_2(PPh_3)_2$	5
4[c]	$K_3[Co(CN)_6]$	0
5	$Rh_6(CO)_{16}$	24
6	$Pt(CO)_2(PPh_3)_2$	(5)[d]
7	$Ru_3(CO)_{12}$	0
8	$Mn_2(CO)_{10}$	0
9	$Cr(CO)_6$	0
10	$Fe(CO)_5$	Trace
11[c]	$AlCl_3$	5

a) $(CH_3)_3SiCN$ (3.0 mmol), THF (3.0 ml), catalyst (10 mol% as metal atom), at 120 °C, for 23 h. b) 5-(Trimethylsiloxy)pentanenitrile. Determined by GLC and figure in parentheses is isolated yield. c) $(CH_3)_3SiCN$ (4.5 mmol), $(CH_3)_3SiCN$/THF=1.5, benzene (3.0 ml). d) 4-(Trimethylsiloxy)butyl isocyanide ($(CH_3)_3SiO(CH_2)_4NC$) was isolated.

heptane also gave the corresponding nitrile (run 6). In the present reaction, the corresponding isocyanides which were produced from a reaction of oxiranes or oxetanes using ZnI_2,[9e,f] $ZnCl_2$[9g] and $Pd(CN)_2$[9c] as catalysts were not obtained at all. Tetrahydrofurans having 2-CH_2OCH_3, 2-CH_2Cl, and 2-CH_2NH_2 groups did not react with $(CH_3)_3SiCN$ under the same reaction conditions. Furthermore, cyclohexene oxide or oxetane did not afford the corresponding nitriles, and intractable mixtures were obtained after the reaction.

The effects of reaction conditions were examined with tetrahydrofuran (THF) and $(CH_3)_3SiCN$ as the substrates (Table 2). In the case of large excess tetrahydrofuran as solvent, this reaction required the temperature over 120 °C, and no reaction occurred at the lower temperatures (runs 1—5). Reducing the amount of tetrahydrofuran by use of benzene as a solvent led to an increase in the yield of the nitrile. Although a large excess amount of $(CH_3)_3SiCN$ to tetrahydrofuran also suppressed the yield reversely (run 9), the use of a small excess amount of $(CH_3)_3SiCN$ to tetrahydrofuran gave the best result (run 8, 82% yield). In the case of an addition of triphenylphosphine and an use of acetonitrile which has strong coordinating ability as a solvent, the present reaction did not occur (runs 6, 10).

Catalytic activities of several transition metal complexes were examined in the reaction of tetrahydrofuran with $(CH_3)_3SiCN$. The results are listed in Table 3. Among the transition metal complexes employed, octacarbonyldicobalt(0), $Co_2(CO)_8$ had the highest catalytic activity in this reaction (run 1). Nevertheless, on using the other cobalt complexes including $CoCl_2$, $CoCl_2(PPh_3)_2$ and $K_3[Co(CN)_6]$, the present reaction hardly proceeded (runs 2, 3, 4). Hexadecacarbonylhexarhodium(0), $Rh_6(CO)_{16}$ showed a little catalytic activity under the present reaction conditions (run 5). In the reaction using $Pt(CO)_2(PPh_3)_2$, however, 4-(trimethylsiloxy)butyl isocyanide was isolated in low yield instead of the nitrile (run 6). Other metal carbonyls were totally inactive for the present reaction (runs 7—10). This reaction was not essen-

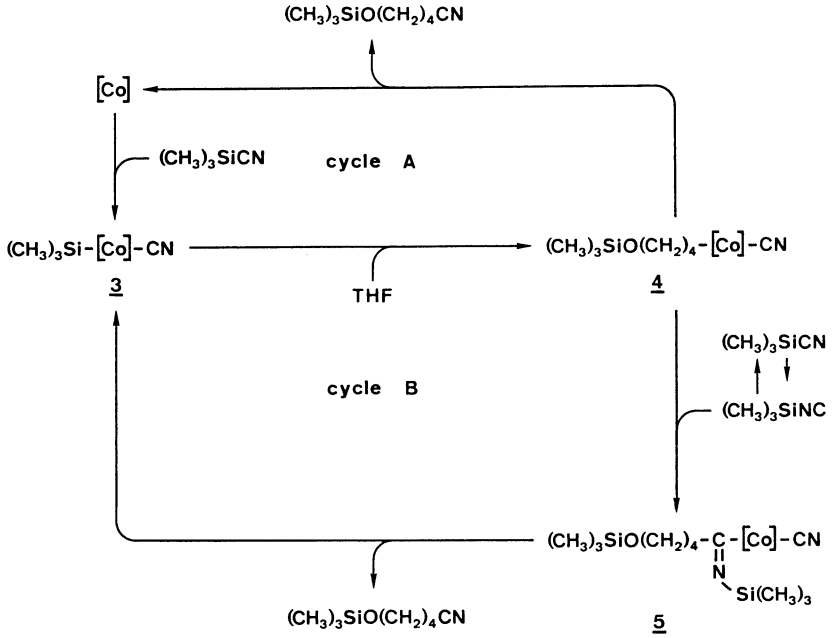
tially catalyzed by $AlCl_3$ which is effective for the reaction of oxiranes (run 11).

In order to investigate the reaction mechanism, the reaction of $Co_2(CO)_8$ with $(CH_3)_3SiCN$ was carried out. Thus, when $Co_2(CO)_8$ (1.3 mmol) was treated with 15 equiv $(CH_3)_3SiCN$ in benzene (10 ml) at room temperature, vigorous evolution of carbon monoxide was observed. After 1.0 h, the light brown mixture showed an IR absorption at 2060, 1886, and 1257 cm^{-1}, which suggested that cobalt-isocyanide complex may be produced by coordination of $(CH_3)_3SiCN$ as its isocyanide form to the cobalt metal. Trimethylsilyl cyanide has been known to exist in an equilibrium $(CH_3)_3SiCN \leftrightarrows (CH_3)_3SiNC$, which lies so far to the left.[11] It has been reported that pentacarbonyliron(0), $Fe(CO)_5$ reacted with $(CH_3)_3SiCN$ as its isocyanide form to give an isocyanide complex, $Fe(CO)_4[CNSi(CH_3)_3]$.[12] This is, to our knowledge, the only complex which is generated from the reaction of group VIII transition metal carbonyl complexes and $(CH_3)_3SiCN$ and identified fully.[13] Since $Co_2(CO)_8$ was treated with usual organic isocyanides (RNC) at room temperature to afford $[Co(RNC)_5][Co(CO)_4]$,[14] the similar reaction seems to occur in this reaction judging from IR spectrum of 1886 cm^{-1} assignable to $Co(CO)_4$ anion. Furthermore, this reaction mixture was heated at 80 °C for 9 h to give orange-yellow solution, showing new IR absorption bands at 2172, 2146, and 1253 cm^{-1} with disappearance of a very strong absorption at 1886 cm^{-1}. This observation suggests the formation of Co-CN species,[15] though the complex formed is not identified fully because it is extremely air-sensitive. Yamamoto et al. reported that $\{Co[2,6\text{-}(CH_3)_2C_6H_3NC]_5\}[Co(CO)_4]$ gave $Co[2,6\text{-}(CH_3)_2C_6H_3NC]_8$ in the presence of 2,6-xylyl isocyanide with further evolution of carbon monoxide on heating at 80 °C.[16] In our case, however, such homoleptic isocyanide complex was not found, judging from that bridging isocyanide ligands at about 1650 cm^{-1} was not detected by IR spectroscopy.[17]

The solution after the present reaction contained blue crystal precipitate, and show no infrared absorption of carbon monoxide and isocyanide ligands. By infrared analysis, the resulting blue crystal was identified as $Co(CN)_2$, which had little activity in the present reactions. This shows that the cobalt catalyst is already deactivated at time that the reaction is stopped (23 h). The similar deactivation of the catalyst also occurred in hydrocyanation of olefins. For example, during the hydrocyanation catalyzed by $Co_2(CO)_8$[18] or $Ni[P(OPh)_3]_4$,[19] less inactive carbonylcyanocobalt complex or $Ni(CN)_2$ was formed respectively.

Tetrahydrofurans have been already known to be carbonylated with the ring-opening using $HSiEt_2Me$ in the presence of a catalytic amount of $Co_2(CO)_8$.[20] In the reaction, silicon-cobalt bonded complex such as $Et_2MeSiCo(CO)_4$ was considered an active species for ring-opening of tetrahydrofurans, where high oxophilicity of silicon atom was regarded as driving force for the reaction. Therefore, in the present reaction, there exists a possibility that such silicon-cobalt species also causes the ring-opening of tetrahydrofurans.

On the basis of the results of IR study and the fact mentioned above, the most plausible route to 5-siloxy nitriles is illustrated in Scheme 1. Firstly, a complex such as **3** possessing trimethylsilyl and cyano group is formed. A existence of the intermediate such as **3** has been insinuated in addition of $(CH_3)_3SiCN$ to allenes



Scheme 1.

with palladium or nickel catalyst.[6] Then, the ring-opening of tetrahydrofuran by **3** affords **4**, followed by formation of siloxy nitriles via a reductive elimination (cycle A). Also, the other route includes the coordination of trimethylsilyl *iso*cyanide to **4** and subsequent insertion reaction into alkyl-cobalt bond to give **5**. Then, the desired nitriles are eliminated from **5** to regenerate **3** (cycle B). Eisch et al. found that the mixture of nickel complex and diphenylacetylene was treated with $(CH_3)_3SiCN$, followed by work-up with HCl to give nitriles and aldehydes or cyclic ketones. From the facts, they concluded an existence of intermediates which result from insertion of trimethylsilyl *iso*cyanide to metal-carbon bond.[21] In our system, the addition of triphenylphosphine as a ligand and the employment of acetonitrile as a solvent retarded the reaction completely. Therefore, the cycle B involving coordination of *iso*cyanide could not be eliminated fully. In hydrocyanation of olefins, a mechanism including coordination and insertion of hydrogen *iso* cyanide (HNC) analogous to cycle B has been postulated.[22] This mechanism is based on experimental results by Kwiatek[23] or Johnson et al.[24] that hydrogen *iso*cyanide ligand formed by protonation of alkylpentacyanocobaltate ($[Co(CN)_5R]^{3-}$) inserts into the alkyl-cobalt bond, and subsequent treatment with base eliminates alkanenitrile (RCN).

Experimental

Materials. 3-Methoxytetrahydrofuran was prepared from 3-hydroxytetrahydrofuran and methyl iodide with sodium metal. The other chemicals employed in this study were commercially available and purified by distillation under an argon atmosphere. $Co_2(CO)_8$ was recrystallized from pentane at low temperature (about −10 °C). $CoCl_2(PPh_3)_2$,[25] $Rh_6(CO)_{16}$,[26] and $Pt(CO)_2(PPh_3)_2$[27] were prepared according to procedures in the literature. $Ru_3(CO)_{12}$, $Fe(CO)_5$, $Mn_2(CO)_{10}$, and $Cr(CO)_6$ were purchased from Strem Chemicals or Kanto Reagents and used without further purification.

General Procedure. A 50 ml stainless steel reactor (Taiatsu scientific glass Co., Ltd., TVS-1 type) equipped with a glass liner was used in the reaction. A mixture of $(CH_3)_3SiCN$ (4.5 mmol), tetrahydrofuran (3.0 mmol), $Co_2(CO)_8$ (0.15 mmol), and benzene (3.0 ml) was placed in the glass liner. After sealing the reactor, argon was introduced with three 10 kg cm^{-2} pressurization-depressurization cycles. The reactor was heated to 120 °C in 1.0 h with magnetic stirring and kept this temperature for 23 h. The reaction was terminated by rapid cooling. The resulting dark blue solution was analyzed by GLC.

Analytical Procedure. The products were isolated by kugelrohr distillation and identified by ^{1}H NMR, ^{13}C NMR, IR spectra, GC-MS, and elemental analysis. ^{1}H NMR spectra were obtained at 270 MHz on a JEOL GSX-270 and ^{13}C NMR spectra at 22.05 MHz on a JEOL JNM FX-100 spectrophotometer using $CDCl_3$ as a solvent. IR spectra were recorded on a NICOLET 5-MX Fourier transform infrared spectrophotometer. GLC analyses were carried out with Shimadzu GC-8APF chromatograph equipped with a glass column (2.6 mmϕ×3 m) packed with Poly I 110 (5% on supported Chromosorb W AW DMCS, 60/80 mesh). Yields of the products were determined by GLC internal standard method. Elemental analyses were performed at the Microanalytical Center of Kyoto University. Mass spectra were obtained on a Shimadzu QP-1000 spectrometer.

The spectral and analytical data of products are shown below.

5-(Trimethylsiloxy)pentanenitrile: colorless oil; kugelrohr distillation (121 °C/12 mm Hg; 1 mm Hg=133.322 Pa); IR (neat) 2245 cm^{-1} (CN), 1252 cm^{-1} ($SiCH_3$); ^{1}H NMR ($CDCl_3$) δ=−0.048 (s, 9H, -Si(CH_3)$_3$), 1.5—1.65 (m, 4H, -CH_2CH_2-), 2.27 (t, 2H, -CH_2CN), 3.51 (t, 2H, -CH_2OSi-); ^{13}C NMR ($CDCl_3$) δ=−0.70 (q, -Si(CH_3)$_3$), 16.8 (t, -CH_2CN), 22.1 (t, -CH_2CH_2CN), 31.2 (t, -SiOCH$_2$$CH_2$-), 61.2 (t, -SiO$CH_2$-), 119.4 (s, -CN); MS, *m/z* 156 (M−15). Calcd for $C_8H_{17}NOSi$: C, 56.09; H, 10.00; N, 8.18%. Found: C, 56.04; H, 10.17; N, 8.25%.

4-Methyl-5-(trimethylsiloxy)pentanenitrile: colorless oil; kugelrohr distillation (140—150 °C/16 mmHg); IR (neat) 2247 cm^{-1} (CN), 1252 cm^{-1} ($SiCH_3$); ^{1}H NMR ($CDCl_3$) δ=0.003 (s, 9H, -Si(CH_3)$_3$), 0.80 (d, 3H, -CH_3), 1.08—2.12 (m, 3H, CH_3CH-, -CH_2CH_2CN), 2.21—2.38 (m, 2H, -CH_2CN), 3.27—3.37 (m, 2H, -CH_2OSi-); ^{13}C NMR ($CDCl_3$): δ=−1.02 (q, -Si(CH_3)$_3$), 14.5 (t, -CH_2CN), 15.6 (q, -CH_3), 28.8 (t, -CH_2CH_2CN), 34.2 (d, -$CHCH_3$), 66.5 (t, -CH_2OSi-), 119.5 (s, -CN).

2-Ethoxy-5-(trimethylsiloxy)pentanenitrile: colorless oil; kugelrohr distillation (150—160 °C/19 mmHg); IR (neat) 2239 cm^{-1} (CN), 1252 cm^{-1} ($SiCH_3$); ^{1}H NMR ($CDCl_3$) δ=0.06 (s, 9H, -Si(CH_3)$_3$), 1.19 (t, 3H, -OCH_2CH_3), 1.61—1.75 (m, 2H, -CH_2-), 1.82—1.97 (m, 2H, -CH_2-), 3.46 (dq, 1H, -OC*H*H'CH_3, *J*=8.8 Hz), 3.57 (t, 2H, -CH_2OSi-), 3.76 (dq, 1H, -OCH*H'*CH_3, *J*=8.8 Hz), 4.14 (t, 1H, -CHCN); ^{13}C NMR ($CDCl_3$) δ=−0.70 (t, -Si(CH_3)$_3$), 14.6 (q, -OCH_2CH_3), 27.6 (t, -CH_2CHCN), 30.3 (t, -CH_2CH_2OSi-), 61.4 (t, -OCH_2CH_3), 65.9 (t, -CH_2OSi-), 68.4 (d, -CHCN), 118.4 (s, -CN).

4-Methoxy-5-(trimethylsiloxy)pentanenitrile: colorless oil; kugelrohr distillation (172—175 °C/3 mmHg); IR (neat) 2247 cm^{-1} (CN), 1248 cm^{-1} ($SiCH_3$); ^{1}H NMR ($CDCl_3$) δ=0.08 (s, 9H,-Si(CH_3)$_3$), 1.70—1.93 (m, 2H, -CH_2CH_2CN), 2.41—2.47 (m, 2H, -CH_2CN), 3.24—3.33 (m, 1H, -C*H*OCH_3), 3.39 (s, 3H, -OCH_3), 3.51—3.66 (m, 2H, -CH_2OSi-); ^{13}C NMR ($CDCl_3$) δ=−0.70 (q, -Si(CH_3)$_3$), 13.1 (t, -CH_2CN), 27.3 (t, -CH_2CH_2CN), 57.7 (q, -OCH_3), 62.8 (t, -CH_2OSi-), 79.1 (d, -CHOCH_3), 119.6 (s, -CN).

4-(Trimethylsiloxy)cyclohexanecarbonitrile: colorless oil; IR (neat) 2239 cm^{-1} (CN), 1252 cm^{-1} ($SiCH_3$); ^{1}H NMR ($CDCl_3$) δ=0.09 (s, 9H, -Si(CH_3)$_3$), 1.31—2.55 (m, 8H, -CH_2-), 2.46—2.55 (m, 1H, -CHCN), 3.65—3.74 (m, 1H, -CHOSi-); ^{13}C NMR ($CDCl_3$) δ=0.058 (q, -Si(CH_3)$_3$), 26.4 (t, -CH_2CHCN), 27.2 (d, -CHCN), 32.9 (t, -CH_2CHOSi-), 67.9 (d, -CHOSi-), 122.1 (s, -CN).

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