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Synthesis of cyanohydrin trimethylsilyl ethers of acylferrocenes

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Abstract

The addition of trimethylsilyl cyanide to acylferrocenes FcCOR (R = Me, Et, ^{n}Pr, ^{i}Pr, Ph, p-MeOC$_6$H$_4$, o-ClC$_6$H$_4$, m-ClC$_6$H$_4$, p-ClC$_6$H$_4$, Fc; Fc = C$_5$H$_4$FeC$_5$H$_5$) catalyzed by zinc iodide in methylene chloride provided the corresponding cyanohydrin trimethylsilyl ethers in moderate to high yields. Factors affecting the reaction and yields of adducts were investigated. All new compounds were characterized by IR and ^{1}H NMR spectroscopies. In addition, the adducts of p-chlorobenzoylferrocene and diferrocenyl ketone were structurally determined by X-ray crystallography.

Keywords: Acylferrocene; Trimethylsilyl cyanide; Cyanohydrin trimethylsilyl ether

1. Introduction

Cyanohydrin trimethylsilyl ethers are important in organic synthesis since they serve not only for the protection of carbonyl groups [1] but also as versatile intermediates [2] for the synthesis of cyanohydrins, α,β-unsaturated nitriles and β-aminoalcohols. The general method for the preparation of cyanohydrin trimethylsilyl ethers is the addition of trimethylsilyl cyanide (TMSCN) to carbonyl compounds with the aid of a catalyst including Lewis acids, such as ZnI$_2$ [2a,2c,3] and AlCl$_3$ [4], as well as solubilized anionic species, such as K$^+$CN$^-$/18-Crown-6 and ^{n}Bu$_4$N$^+$CN$^-$ [5]. Other catalysts like Lewis bases, inorganic solid acids and bases [6], copper triflate (Cu(OTf)$_2$) [7], tetracyanoethylene [8] and some chiral catalysts [9] have been used in this reaction. In addition, one-pot cyanosilylation of carbonyl compounds has also been carried out by the combined use of Me$_3$SiCl and KCN (or NaCN) [10].

In view of their synthetic potential and ready preparation method, a wide variety of cyanohydrin trimethylsilyl ethers of aldehydes, aliphatic ketones and conjugated aromatic ketones and their derivatives have been synthesized [3–10]. Nevertheless, there are few reports on the preparation of cyanohydrin trimethylsilyl ethers of acylferrocenes except for formylferrocene [11]. In this paper we describe the synthesis of cyanohydrin trimethylsilyl ethers of acylferrocenes via the addition of TMSCN to various acylferrocenes in the presence of ZnI$_2$ in CH$_2$Cl$_2$ (Scheme 1). Factors affecting the reaction and yields of adducts were investigated. The crystal structures of compounds **3i** and **3j** were determined by X-ray diffraction analysis.

2. Experimental

2.1. General

Melting points were obtained by the XT7-4 apparatus and are uncorrected. ^{1}H NMR spectra were recorded in CDCl$_3$ solutions on a Bruker DRX-500 spectrometer with Me$_4$Si as internal standard. IR spectra were recorded on a NEXUS-670FT-IR spectrophotometer using KBr pellets. Elemental analysis were carried out on a Perkin–Elmer-2400 apparatus. X-ray data was collected on a Bruker Smart 1000 diffractometer. Silica gel (60H) plates and alkaline Al$_2$O$_3$ (100–200 mesh) were used for analytical TLC and column chromatography, respectively. TMSCN [12] and acylferrocenes [13] were prepared according to literature methods. ZnI$_2$ was oven-dried at 120 °C overnight. Dry CH$_2$Cl$_2$ was

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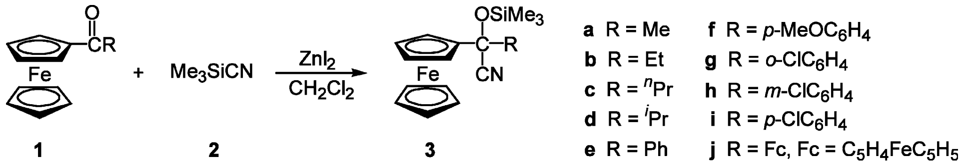

Scheme 1.

distilled from P_2O_5. All other solvents and regents were obtained from commercial sources and used without further purification.

2.2. General procedure for the synthesis of **3a–3j**

Into a 100 ml 3-neck round-bottomed flask equipped with magnetic stirring bar, reflux conditioner and $CaCl_2$ drying tube was placed acylferrocene (10 mmol) in dry CH_2Cl_2 and ZnI_2 (0.5–1 mmol). After stirring for 20-min, TMSCN (20–80 mmol) was added. The resulting solution was stirred under the conditions given in Table 1. The progress of the reaction was monitored by TLC. On completion, the solvent was evaporated under reduced pressure and the residue obtained was extracted with pentane. The solution was washed with saturated cold aqueous $NaHSO_3$ and dried over Na_2SO_4. Removal of the solvent under reduced pressure yielded the crude product that was purified by recrystallization from pentane–ethylether. (The crude product of compound **3j** was purified by alkaline Al_2O_3 column chromatography using 10:1 petroleum ether (60–90 °C)—ethylether as eluent followed by recrystallization.)

3a. Yellow crystal, m.p.: 55–56 °C. IR (KBr) ν 3082 (Fc, CH), 2230 (C≡N), 1254, 835 ($SiCH_3$) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.12 (s, 9H, Si(CH_3)$_3$), 1.97 (s, 3H, CCH_3), 4.28, 4.32, 4.49 (3s, together 9H, ferrocenyl-*H*). Calc. for $C_{16}H_{21}FeNOSi$: C, 58.72; H, 6.47; N, 4.28. *Anal.* Found: C, 58.13; H, 7.03; N, 3.99%.

3b. Yellow crystal, m.p.: 46–48 °C. IR (KBr) ν 3097 (Fc, CH), 2230 (C≡N), 1253, 833 ($SiCH_3$) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.12 (s, 9H, Si(CH_3)$_3$), 1.15 (t, 3H, $J = 7.3$ Hz, CH_2CH_3), 2.09 (m, 1H, C*H*H), 2.21 (m, 1H, CH*H*), 4.27, 4.30, 4.48 (3s, together 9H, ferrocenyl-*H*). Calc. for $C_{17}H_{23}FeNOSi$: C, 59.8; H, 6.79; N, 4.10. *Anal*. Found: C, 59.91; H, 7.02; N, 4.24%.

3c. Orange crystal, m.p.: 60–61 °C. IR (KBr) ν 3092 (Fc, CH), 2233 (C≡N), 1252, 843 ($SiCH_3$) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.12 (s, 9H, Si(CH_3)$_3$), 1.01 (t, $J = 7.4$ Hz, 3H, CH_2CH_3), 1.61 (sext, $J = 7.8$ Hz, 2H, C$H_2$$CH_3$), 2.03 (m, 1H, C*H*H$CH_2CH_3$), 2.14 (m, 1H, CH*H*$CH_2CH_3$), 4.26, 4.29, 4.46 (3s, together 9H, ferrocenyl-*H*). Calc. for $C_{18}H_{25}FeNOSi$: C, 60.84; H, 7.09; N, 3.94. *Anal*. Found: C, 60.74; H, 7.59; N, 3.94%.

3d. Orange crystal, m.p.: 25–27 °C. IR (KBr) ν 3106 (Fc, CH), 2235 (C≡N), 1252, 839 ($SiCH_3$) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.37 (s, 9H, Si(CH_3)$_3$), 0.87 (dd, $J = 6.7$ Hz, 6H, CH(CH_3)$_2$), 2.19 (sept, $J = 6.7$ Hz, 1H, C*H*(CH_3)$_2$), 4.17, 4.20, 4.26, 4.29 (4s, together 9H, ferrocenyl-*H*). Calc. for $C_{18}H_{25}FeNOSi$: C, 60.84; H, 7.09; N, 3.94. *Anal.* Found: C, 61.63; H, 7.64; N, 3.49%.

3e. Yellow crystal, m.p.: 43–44 °C. IR (KBr) ν 3095 (Fc, CH), 3060, 3026 (Ar, CH), 2243 (C≡N), 1253, 851

Table 1
Influence of substrates and reaction conditions on the addition

Substrate **1a**–**j**	R	Reaction conditions			Yield [a] (%) **3a**–**j**
		Ratio (**2**:**1a**–**j**)	Time (h)	Temperature (°C)	
a	CH_3	2:1	9	r.t.	95.6
b	C_2H_5	2.2:1	5	r.t.	96.8
c	$CH_2CH_2CH_3$	2.2:1	13	r.t.	93.0
d	$CH(CH_3)_2$	2.2:1	16	r.t.	80.5
		3.6:1	16	r.t.	> 99
e	Ph	3:1	21.5	r.t.	65.0
		4:1	21.5	r.t.	> 99
f	*p*-CH_3OPh	3:1	23	r.t.	52.3
		5.5:1	23	r.t.	71.5
g	*o*-ClPh	3:1	48	reflux	32.1
h	*m*-ClPh	3:1	23	reflux	60.6
i	*p*-ClPh	3:1	23	r.t.	70.8
j	Fc	5:1	46	reflux	72.4
		8:1	46	reflux	88.5

[a] Yield of isolated product.

($SiCH_3$) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.15 (s, 9H, Si(CH_3)$_3$), 4.08, 4.20, 4.26, 4.29, 4.53 (5s, together 9H, ferrocenyl-*H*), 7.35–7.64 (m, 5H, Ar). Calc. for $C_{21}H_{23}FeNOSi$: C, 64.78; H, 5.95; N, 3.60. *Anal.* Found: C, 64.77; H, 6.38; N, 3.52%.

3f. Orange crystal, m.p.: 91.5–92.5 °C. IR (KBr) ν 3108 (Fc, CH), 3080, 3050 (Ar, CH), 2231 (C≡N), 1250, 847 ($SiCH_3$) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.14 (s, 9H, Si(CH_3)$_3$), 3.84 (s, 3H, OCH_3), 4.06, 4.18, 4.24, 4.28, 4.50 (5s, together 9H, ferrocenyl-*H*), 6.90 (d, $J = 8.7$ Hz, 2H, Ar), 7.53 (d, $J = 8.7$ Hz, 2H, Ar). Calc. for $C_{22}H_{25}FeNO_2Si$: C, 63.01; H, 6.01; N, 3.34. *Anal.* Found: C, 62.45; H, 6.12; N, 3.04%.

3g. Orange crystal, m.p.: 78–79 °C. IR (KBr) ν 3105 (Fc, CH), 3064 (Ar, CH), 2238 (C≡N), 1256, 848 ($SiCH_3$) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.23 (s, 9H, Si(CH_3)$_3$), 4.24, 4.33, 4.56 (3s, together 9H, ferrocenyl-*H*), 7.32–7.84 (m, 4H, Ar). Calc. for $C_{21}H_{22}ClFeNOSi$: C, 59.52; H, 5.23; N, 3.31. *Anal.* Found: C, 58.95; H, 5.54; N, 3.67%.

3h. Orange crystal, m.p.: 68–69 °C. IR (KBr) ν 3090 (Fc, CH), 3024 (Ar, CH), 2232 (C≡N), 1253, 847 ($SiCH_3$) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.16 (s, 9H, Si(CH_3)$_3$), 4.09, 4.24, 4.31, 4.52 (4d, together 9H, ferrocenyl-*H*), 7.29–7.62 (m, 4H, Ar). Calc. for $C_{21}H_{22}ClFeNOSi$: C, 59.52; H, 5.23; N, 3.31. *Anal.* Found: C, 59.45; H, 5.69; N, 2.99%.

3i. Red Orange crystal, m.p.: 115–116 °C. IR (KBr) ν 3108 (Fc, CH), 3042 (Ar, CH), 2236 (C≡N), 1253, 847 ($SiCH_3$) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.17 (s, 9H, Si(CH_3)$_3$), 4.02, 4.19, 4.25, 4.26, 4.47 (5s, together 9H, ferrocenyl-*H*), 7.37 (d, $J = 8.5$ Hz, 2H, Ar), 7.56 (d, $J = 8.5$ Hz, 2H, Ar). Calc. for $C_{21}H_{22}ClFeNOSi$: C, 59.52; H, 5.23; N, 3.31. *Anal.* Found: C, 59.62; H, 5.41; N, 3.13%.

3j. Red Orange crystal, m.p.: 120–121 °C. IR (KBr) ν 3088 (Fc, CH), 2239 (C≡N), 1251, 843 ($SiCH_3$) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.05 (s, 9H, Si(CH_3)$_3$), 4.24, 4.28, 4.30, 4.47 (4s, together 18H, 2 × ferrocenyl-*H*). Calc. for $C_{25}H_{27}Fe_2NOSi$: C, 60.38; H, 5.47; N, 2.82. *Anal.* Found: C, 59.55; H, 5.62; N, 2.57%.

2.3. Single crystal X-ray diffraction analysis of 3i and 3j

Data of **3i** and **3j** were collected on a Bruker Smart 1000 4-circle diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K in the θ–2θ scan mode, and corrected for absorption semiempirically. The two structures were solved by direct methods (SHELXL-97) and refined by full-matrix least-squares. The non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were placed in calculated positions and refined isotropically. All calculations were performed using the SHELXTL program system. Crystal data and structure refinement parameters are listed in Table 2.

Table 2
Crystal data and structure refinement for compounds **3i** and **3j**

Compound	**3i**	**3j**
Empirical formula	$C_{21}H_{22}ClFeNOSi$	$C_{25}H_{27}Fe_2NOSi$
Formula weight	423.79	497.27
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	18.420(2)	13.820(1)
b (Å)	7.3401(7)	20.094(2)
c (Å)	16.401(2)	17.127(2)
α (°)	90	90
β (°)	109.878(2)	105.114(2)
γ (°)	90	90
V (Å^3)	2085.4(4)	4591.4(7)
Z	4	8
Calculated density (Mg m^{-3})	1.350	1.439
Absorption coefficient (mm^{-1})	0.918	1.332
F(0 0 0)	880	2064
θ range for data collection (°)	2.35–28.27	1.53–28.32
Limiting indices	$-24 \leq h \leq 16$, $-9 \leq k \leq 9$, $-20 \leq l \leq 21$	$-13 \leq h \leq 18$, $-25 \leq k \leq 26$, $-22 \leq l \leq 17$
Reflection collection/unique	11 854/4773	27 943/10 698
Max. and min. transmission	1.0000 and 0.6334	1.0000 and 0.7690
Data/restraints/parameters	4773/0/255	10 698/0/743
Goodness-of-fit on F^2	0.882	0.871
Final R indices [$I > 2\sigma(I)$] R_1, wR_2	0.0418, 0.0926	0.0408, 0.0700
R indices (all data) R_1, wR_2	0.0667, 0.0985	0.0750, 0.0783
Largest difference peak and hole (e Å^{-3})	0.667, −0.276	0.483, −0.249

3. Results and discussion

3.1. Factors affecting the reaction

Although the addition reaction of carbonyl compounds with TMSCN in the presence of ZnI_2 usually can be carried out under mild conditions to give the cyanohydrin trimethylsilyl ethers in good yields, we have found that the reaction is still influenced by some factors such as steric effect, electronic effect and TMSCN/substrate ratio when the substrates are acylferrocenes.

3.1.1. Influence of steric effect

We investigated the influence of steric effect of a substrate and found that the reaction was very sensitive to the steric hindrance near the carbonyl group. As is shown in Table 1, the reaction activity and yield were high when the substrate bears a less bulky group as in **1a** (R = Me) and **1b** (R = Et), while in the case of hindered **1d** (R = ^{i}Pr) the reaction rate was relatively slow (16 h at r.t.) and the yield of **3d** decreased to 80.5%. Similarly, the steric hindrance increases in the sequence: **1g** > **1h** > **1i**, but there is inversion of the order of reaction activity. For example, treatment of **1i** at room temperature for 23 h gave **3i** in 70.8% yield, but when **1g** was treated at high

Table 3
Selected bond distances (Å) and angles (°) of **3i** and **3j**

3i				**3j**			
Bond distances							
O–C(11)	1.413(3)	Si–O	1.655(2)	O(1)–C(11)	1.420(3)	Si(1)–O(1)	1.642(2)
C(10)–C(11)	1.507(3)	Si–C(18)	1.858(3)	C(10)–C(11)	1.514(3)	Si(1)–C(23)	1.842(4)
C(11)–C(12)	1.528(3)	Si–C(19)	1.844(3)	C(11)–C(12)	1.490(3)	Si(1)–C(24)	1.855(5)
C(11)–C(21)	1.500(3)	Si–C(20)	1.857(4)	C(11)–C(13)	1.518(3)	Si(1)–C(25)	1.832(5)
N–C(21)	1.131(3)	C(15)–Cl	1.740(2)	N(1)–C(12)	1.137(3)		
Bond angles							
O–C(11)–C(10)	106.8(2)	O–Si–C(18)	108.7(1)	O(1)–C(11)–C(10)	108.0(2)	O(1)–Si(1)–C(23)	102.9(2)
O–C(11)–C(12)	110.1(2)	O–Si–C(19)	102.8(1)	O(1)–C(11)–C(12)	106.6(2)	O(1)–Si(1)–C(24)	112.8(2)
O–C(11)–C(21)	110.2(2)	O–Si–C(20)	109.9(1)	O(1)–C(11)–C(13)	112.0(2)	O(1)–Si(1)–C(25)	110.9(2)
C(10)–C(11)–C(12)	112.1(2)	C(19)–Si–C(18)	110.8(2)	C(12)–C(11)–C(10)	109.1(2)	C(23)–Si(1)–C(24)	109.4(2)
C(21)–C(11)–C(10)	108.5(2)	C(19)–Si–C(20)	112.5(2)	C(10)–C(11)–C(13)	112.2(2)	C(25)–Si(1)–C(23)	111.8(3)
C(21)–C(11)–C(12)	109.0(2)	C(20)–Si–C(18)	111.8(2)	C(12)–C(11)–C(13)	108.7(2)	C(25)–Si(1)–C(24)	109.0(4)
C(11)–O–Si	132.7(1)	N–C(21)–C(11)	179.6(3)	C(11)–O(1)–Si(1)	138.2(2)	N(1)–C(12)–C(11)	179.4(3)

temperature (reflux) for 48 h compound **3g** was obtained only in 32.1% yield. With two bulky ferrocenyls near the carbonyl group, compound **1j** was treated with a large amount of TMSCN (8 equiv.) to give **3j** in 88.5% yields. Obviously, the higher steric hindrance of an acyl residue, the more difficult is the addition reaction.

3.1.2. Influence of electronic effect

We investigated also the dependence of yields on benzene ring substituents by reacting three typical acylferrocenes **1f**, **1e** and **1i** with TMSCN under the same reaction condition (the ratio of **2** to **1** was 3:1, r.t., 23 h) (Table 1). It was found that the yield of adduct was generally better in the case of **1i** which contains an electron withdrawing group (*p*-Cl, yield 70.8%) than that of unsubstituted substrate **1e** (yield 65.0%), while in the case of substrate **1f** bearing an electron donating group (*p*-MeO) the yield of adduct decreased (52.3%). This can be explained by the fact that an electron donating group decreases the electrophilicity of the C=O carbon atom and deactivates the addition reaction, while on the contrary, an electron withdrawing group increases the electrophilicity of the C=O carbon atom and facilitates the reaction.

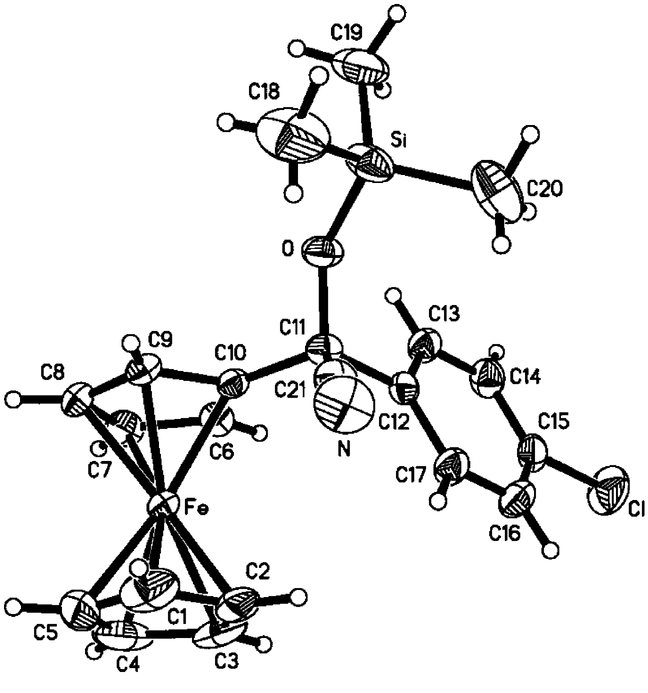

Fig. 1. X-ray structure of **3i**.

3.1.3. TMSCN/substrate ratio

In order to conduct the reaction smoothly TMSCN must be in excess (Table 1). We found that an increased amount of TMSCN led to a higher yield of the target product for the same substrate. For instance, changing the ratio of TMSCN to **1e** from 3:1 to 4:1 resulted in increasing the yield of **3e** from 65 to 99%. In addition, substrates of large steric hindrance need more TMSCN than those of less steric hindrance.

3.2. Spectral properties

The cyanohydrin trimethylsilyl ethers of acylferrocenes were characterized by means of spectroscopic methods. The IR spectra of compounds **3a–j** showed the presence of ferrocenyl, nitrile and silyl groups in region of 3090, 2235 and 1253 cm^{-1}, respectively. In the ^{1}H NMR spectra, nine $(CH_3)_3Si$ protons appeared at δ 0.37–0.05 as a singlet, and the ferrocenyl protons resonated in the region of 4.56–4.06 ppm. In addition, the two methyl protons ($CH(CH_3)_2$) of **3d** were characterized by a typical double doublet at δ 0.87 ($J = 6.7$ Hz) due to the influence of the chiral carbon atom attached to the isopropyl group. Analogously, the ^{1}H NMR spectrum of **3b** showed two groups of multiplets for methylene protons at δ 2.21 and 2.09. Because of the deshielding effect of the phenyl ring, the chemical

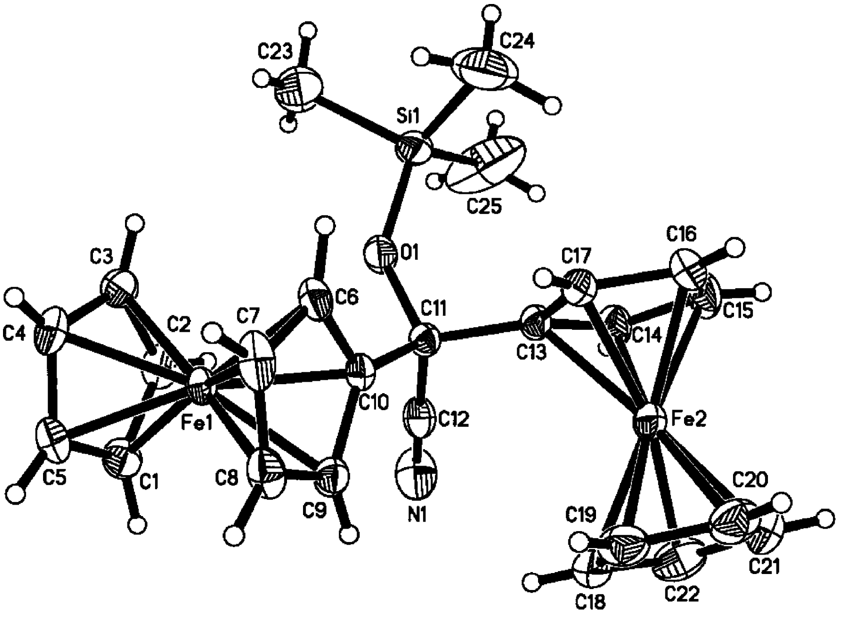

Fig. 2. X-ray structure of **3j**.

shift of OCH_3 protons in **3f** occurred at a lower field (δ 3.84) than those of alkylmethylether (δ 3.20).

*3.3. X-ray structure analysis of **3i** and **3j***

To firmly establish the structures of the new compounds **3a**–**j**, X-ray crystallographic analysis of compounds **3i** and **3j** was carried out. Selected bond distances and angles are given in Table 3. The molecular structures are shown in Figs. 1 and 2. The asymmetric unit of **3j** contains two independent molecules, only one of which is presented. The structure of **3i** is very similar to that of **3j**. The central tetrahedral C11 atom is bonded to $C\equiv N$ and $(CH_3)_3SiO$ groups in both compounds. The bond angles of C11–C21–N in **3i** and C11–C12–N1 in **3j**, both close to 180°, shows sp hybridisation for the $C\equiv N$ carbon atoms. The bond angles of Si–O–C in **3i** (132.7°) and **3j** (138.2°) are all large compared to that of a regular tetrahedron (109.5°). Moreover, because of the influence of neighbouring Csp^2 and Csp atoms, the bond distances of C–C adjacent to the C11 atom in either molecule (see Table 3) are shorter than those of a normal bond distance of C–C (1.54 Å).

4. Supplementary data

Full details of data collection and structure refinements have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 196916 for compound **3i**, 196915 for compound **3j**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk/conts/retrieving.html).

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