SYNTHESIS AND PROPERTIES OF (TRIFLUOROMETHYL)TRICHLOROSILANE, A VERSATILE PRECURSOR FOR CF_3Si COMPOUNDS

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Summary

(Trifluoromethyl)trichlorosilane (I) has been prepared for the first time by the reaction of $CF_3SiH(NMe_2)_2$ (III) with HCl in dibutyl ether and, as a solution in CH_2Cl_2, by nucleophilic trifluoromethylation of $SiCl_4$ with $CF_3Br/P(NEt_2)_3$. From this solution, I may be isolated by HCl cleavage of its insoluble bis(pyridine) adduct (II). The aminosilane III was obtained from the reaction of $HSi(Cl)(NMe_2)_2$ with $CF_3Br/P(NEt_2)_3$. Selective substitution of I without attack on the CF_3Si moiety was achieved in high yields with SbF_3 ($\rightarrow CF_3SiF_3$), Ag(OCN) ($\rightarrow CF_3Si(NCO)_3$ (IV)), MeOH ($\rightarrow CF_3Si(OMe)_3$ (V)), $HNMe_2$ ($\rightarrow CF_3Si(NMe_2)_3$ (VI)), $LiAlH_4$ ($\rightarrow CF_3SiH_3$), MeMgBr ($\rightarrow CF_3SiMe_3$) and LiPh($\rightarrow CF_3SiPh_3$ (VII)). With 2,2'-bipyridyl a 1/1 complex (VIII) was formed. The novel compounds I to VIII have been characterized by their IR, NMR and mass spectra, and for I a vibrational analysis including a normal coordinate treatment has been performed.

Introduction

Trifluoromethylsilicon compounds have only recently become easily available through nucleophilic trifluoromethylation of halosilanes with a reagent prepared from $(Et_2N)_3P$ and CF_3Br in a suitable solvent [1]. Though numerous claims for successful syntheses have been advanced [2], the only satisfactory route previously available to such trifluoromethylsilicon derivatives as CF_3SiF_3 [3] and CF_3SiH_3 [4] required preparation of CF_3SiF_2I [3] by the experimentally demanding insertion of SiF_2 into CF_3I. The observation that dialkylaminochlorosilanes could be converted into dialkylaminotrifluoromethylsilanes by means of $(Et_2N)_3P/CF_3Br$ and the SiN bond then cleaved by HCl to yield (trifluoromethyl)chlorosilanes without concom-

itant cleavage of the Si–C bond [5] seemed to provide an easy route to substantial quantities of these interesting compounds.

Our interest was directed towards the synthesis of the hitherto unknown compound CF_3SiCl_3 (I), which seemed like to act as trifunctional organosilicon halide from which a variety of CF_3Si derivatives could be prepared.

In the present contribution we describe two independent methods that we have found for the synthesis of CF_3SiCl_3. In addition, some of the physical properties of I have been studied, and its ability to undergo substitution reactions with standard reagents evaluated.

Synthesis of CF_3SiCl_3 (I)

The nucleophilic trifluoromethylation with a reagent prepared from $P(NEt_2)_3$ and CF_3Br is assumed to involve a reactive intermediate such as $[P(NEt_2)_3Br]^+$ CF_3^- which can displace a chloro atom from silicon to yield a CF_3Si moiety [1]. eq. 1:

$$[P(NEt_2)_3Br]^- CF_3^+ + \equiv Si-Cl \rightarrow P(NEt_2)_3ClBr + \equiv Si-CF_3 \tag{1}$$
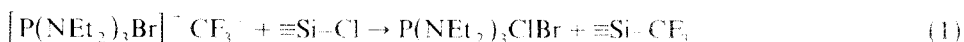
While such a reaction appeared to provide a likely source of CF_3SiCl_3 (I), the actual procedure was not straightforward. It was noticed that the expected ligand scrambling between $P(NEt_2)_3$ and $SiCl_4$ (eq. 2) became important if the reaction was carried out near room temperature:

$$P(NEt_2)_3 + SiCl_4 \rightarrow P(NEt_2)_{3-n}Cl_n + SiCl_{4-n}(NEt_2)_n \tag{2}$$
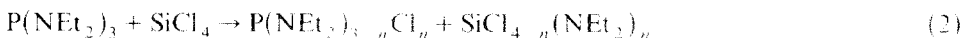
Furthermore, it was found to be essential that I should be isolated from the reaction mixture at low temperature in vacuo because the $P(NEt_2)_3ClBr$ formed in accord with equation 1 tends to decompose I at higher temperatures. Finally, reaction 1 is strongly dependent on the solvent employed, and substantial yields of I were obtained only when CH_2Cl_2 was used. No reaction between $SiCl_4$ and the intermediate $[P(NEt_2)_3Br]CF_3$ occurred either in the absence of a solvent or in solvents such as n-heptane and toluene. Transamination according to eq. 2 was found in diglyme, while HCF_3 was formed in methyl ethyl ketone. Decomposition on work-up was noted when 1,2-dichloroethane or benzonitrile were employed. Thus, of the solvents inert to $SiCl_4$ only CH_2Cl_2 afforded I in reasonable yields (ca. 50%), but the product was not pure. The closeness of the boiling points of CH_2Cl_2 (40°C) and CF_3SiCl_3 (41°C) frustrated all attempts to isolate I from the solvent, and so I and CH_2Cl_2 were separated chemically.

It is well known that silicon tetrahalides form complexes with suitable donor molecules, and a 1/2 complex of $SiCl_4$ with pyridine has been reported [6]. This complex can be sublimed in vacuo, and it has been shown that dissociation occurs in the gas phase [7]. In contrast to $SiCl_4$, CH_3SiCl_3 does not form a complex with pyridine at room temperature. We found that a white solid separated when pyridine was added to a solution of I in CH_2Cl_2. This solid, with the composition $CF_3SiCl_3 \cdot 2$ pyridine (II), was sublimed in vacuo and cleaved quantitatively by liquid HCl according to eq. 3.

$$II + 2HCl \rightarrow I + 2 \text{ pyridine} \cdot HCl \tag{3}$$

The excess of HCl and I were removed from the involatile pyridinium chloride in vacuo, and pure I was obtained after evaporation of the residual HCl.

While synthesizing CF_3SiH_3 via nucleophilic trifluoromethylation, we noticed that $HSiCl(NMe_2)_2$, easily prepared from $HSiCl_3$ and $HNMe_2$, is a particularly reactive species and gives a > 80% yield of $HSi(CF_3)(NMe_2)_2$ (III) upon trifluoromethylation with $CF_3Br/P(NEt_2)_3$ in benzonitrile at 0–20°C. The bis(amino)silane III is readily cleaved by HCl, the products depending on the conditions of the cleavage; reaction at −96°C gives CF_3SiHCl_2 in nearly quantitative yield (eq. 4),

$$III + 4HCl \rightarrow 2Me_2NH_2Cl + CF_3SiHCl_2 \tag{4}$$
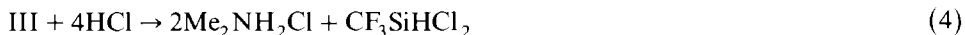
but only traces of I and $HSiCl_3$ were found. The amount of I formed in the course of reaction 4 increases if a solution of HCl in a hydrocarbon solvent is employed, while I is formed nearly quantitatively if III is treated with HCl in di-n-butyl ether (eq. 5). Only traces of CF_3SiHCl_2 were formed.

$$III + 5HCl \rightarrow 2Me_2NH_2Cl + H_2 + I \tag{5}$$

Thus, two syntheses for trifluoromethyltrichlorosilane are now available. If I can be used in solution, direct nucleophilic trifluoromethylation of $SiCl_4$ in CH_2Cl_2 is the method of choice. Pure I may be obtained via cleavage of the pyridine complex or by trifluoromethylation of $HSiCl(NMe_2)_2$ and subsequent reaction with HCl in di-n-butyl ether.

Properties of CF_3SiCl_3

At room temperature CF_3SiCl_3 is a colourless liquid which shows many similarities to $SiCl_4$. It is readily hydrolyzed, and the Si–C bond is quantitatively cleaved by aqueous alkali with formation of HCF_3. Its physical properties are set out in Table 1. In the gas phase thermal decomposition begins at ca. 120°C.

We have investigated the behaviour of I in a range of standard reactions of (organo)silicon halides. In these reactions chlorine was selectively replaced without rupture of the silicon–carbon bond.

(i) Halogen exchange

Compound I does not react with BF_3 during 3 h at 100°C, but it is converted into CF_3SiF_3 [3] by treatment with SbF_3. In accord with the position of Cl in the conversion series [8], I reacts with AgOCN to yield the novel compound $CF_3Si(NCO)_3$ (IV).

(ii) Alkoxides and amides

The Cl atoms in I may be replaced by OR and NR_2 groups in the same way as those in $MeSiCl_3$ and $SiCl_4$. Reaction with MeOH and Me_2NH gave the first trifluoromethylsilicon trialkoxide $CF_3Si(OMe)_3$ (V) and trifluoromethylsilicon tris(dialkylamide) $CF_3Si(NMe_2)_3$ (VI) in high yields.

(iii) Hydride and organometallic derivatives

Reduction of I with $LiAlH_4$ proceeded in the same way as that of CF_3SiF_2I [4], and CF_3SiH_3 was obtained in high yield. Similarly, MeMgBr and PhLi afforded the known species CF_3SiMe_3 [1] and the novel triphenyl derivative CF_3SiPh_3 (VII).

(iv) Complex formation

The formation of the bis(pyridine) adduct II has been mentioned previously.

TABLE 1

PHYSICAL PROPERTIES AND NMR SPECTRA OF COMPOUNDS I AND III TO VII

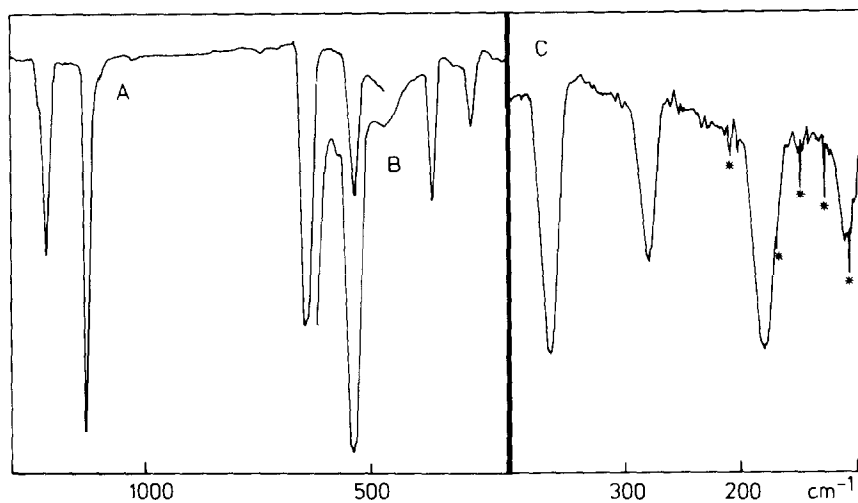| Compound	B.p. (M.p.) (°C/Torr(°C))	$\delta(^1H)$ (ppm)	$^3J(HF)$ (Hz)	$\delta(^{19}F)$ (ppm)	$^1J(F^{13}C)$ (Hz)	$^2J(F^{29}Si)$ (Hz)	$^3J(FH)$ (Hz)	$\delta(^{13}C)$ (ppm)	$^1J(^{13}CF)$ (Hz)
CF_3SiCl_3 (I)	40.6/753			-70.5	314.7	76.2		123.6.q	314.3
$CF_3SiH(NMe_2)_2$ (III)	69/137	4.4 q (SiH) 2.5 (CH$_3$)	3.85	-63.8 d	322.3	44.6	3.95	129.5.q	322.2
$CF_3Si(NCO)_3$ (IV)	60.4/30			-69.5	312.3	69.4			
$CF_3Si(OMe)_3$ (V)	62.8/150	3.4		-65.7	315.5	53.6			
$CF_3Si(NMe_2)_3$ (VI)	60.6/17	2.3		59.1	324.4	41.0			
CF_3SiPh_3 (VII)[a]	(168-170)	7.0		57.4	322.9	38.1			

[a] In C_6D_6.

Fig. 1. IR spectrum of I: A: 10 cm cell, KBr windows, 3 mbar, resolution 1–2 cm^{-1}. B: 18 cm cell, polythene windows, 12 mbar, resolution 2–4 cm^{-1}. C: 18 cm cell, polythene windows, 30 mbar, resolution 1 cm^{-1}. Rotational lines of HCl are marked by an asterisk.

Formation of a dipyridyl complex $CF_3SiCl_3 \cdot$ bipy (VIII), presumably with *cis* configuration has been demonstrated.

To sum up, I undergoes a variety of reactions typical of $SiCl_4$ and $RSiCl_3$ without attack on the CF_3Si moiety. Cleavage of the Si–C bond is however observed in the presence of aqueous alkali and at elevated temperature. Thus, I, and its
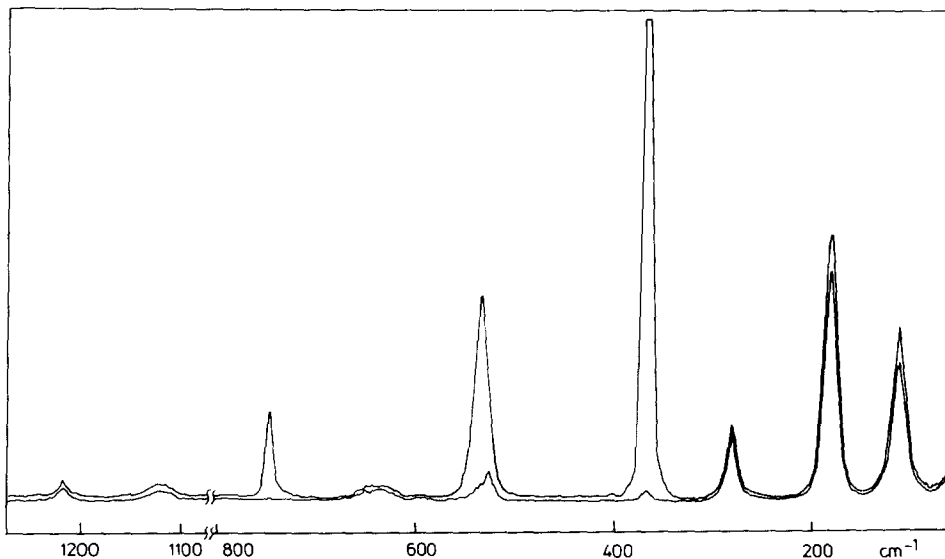

Fig. 2. Raman spectrum of I: 1 mm o.d. capillary, slit width 4 cm^{-1}, parallel and perpendicular polarization.

derivatives are versatile starting materials for the synthesis of a variety of trifluoro-methylsilicon derivatives.

Spectra

The new compounds I and III to VII were characterized by their ^{19}F NMR spectra (Table 1). The complexes dissociate in solution, and so give the NMR spectra of the constituents. The H, CH$_3$ and F derivatives were identified by means of their known ^{19}F NMR spectra. In addition the ^{1}H NMR data for III and V to VII and the ^{13}C data of I and III are given in Table 1. The $^2J(F-^{29}Si)$ coupling constant varies from 76.2 to 38.1 Hz, and the variation seems to be correlated with the fluorine chemical shift. For some of the compounds the mass spectra have also been recorded, and selected m/e peaks are noted in the experimental section.

Because of the expected analogy with SiCl$_4$ and SiCl$_3$Br, the vibrational spectrum of I was evaluated in greater detail, and a normal coordinate analysis performed. The IR and Raman spectra are displayed in Fig. 1 and 2, and numerical data are set out in Table 2.

TABLE 2

INFRARED AND RAMAN SPECTRA OF CF$_3$SiCl$_3$

IR, gas	Raman, liquid	Assignment
103.5w	110s	ν_{12}, $\rho(SiCl_3)$
107.5w		
176m	178s	ν_5, $\delta_s(SiCl_3)$; ν_{11}, $\delta_{as}(SiCl_3)$
277.7m	280m	ν_6, $\rho(CF_3)$
365s	364vs p	ν_3, $\nu(SiC)$
469w		$107.5 + 365 = 472.5$
	525w	ν_8, $\nu_{as}(CF_3)$
538s	532s p	ν_4, $\nu_s(SiCl_3)$
640vs		
646vs	637w	ν_{10}, $\nu_{as}(SiCl_3)$
710w		$176 + 538 = 714$
747m, PQR	745sp	ν_2, $\delta_s(CF_3)$
809w		$277.7 + 538 = 815.7$ (HSiCl$_3$?)
818wsh		$176 + 646 = 822$
852w		$107.5 + 747 = 854.5$
902w		$365 + 538 = 903$
1027w		$277.7 + 747 = 1024.7$
1098m }		
1130vs }	1118w	ν_7, $\nu_{as}(CF_3)$ ^{13}C, ^{12}C
1167w		$525 + 646 = 1171$
1183w }		
1218s }	1215w p	ν_1, $\nu_s(CF_3)$ ^{13}C, ^{12}C
1272m		$525 + 747 = 1272$
1321vw		$107.5 + 1218 = 1325.5$
1402w		$277.7 + 1130 = 1407.7$
1495w		$277.7 + 1218 = 1495.7$
1655w		$525 + 1130 = 1655$
1740w		$525 + 1218 = 1743$
1870m		$747 + 1130 = 1877$
1962w		$747 + 1218 = 1965$

On the assumption of C_{3v} symmetry, CF_3SiCl_3 exhibits 5 a_1 and 6 e vibrations, and in addition an inactive a_2 torsion which was not observed. The inner vibrations of the CF_3 group, $\nu_1(a_1)$ 1218 cm^{-1}, $\nu_2(a_1)$ 747 cm^{-1}, $\nu_7(e)$ 1130 cm^{-1} and $\nu_8(e)$ 525 cm^{-1} appear in the expected regions. The CF_3 rocking mode $\nu_9(e)$, 278 cm^{-1}, is closer to that in CF_3Br, 303 cm^{-1} [9] than that in CF_3SiH_3, 217 cm^{-1} [5], because of repulsion by ν_{11} and ν_{12}. The vibrations $\nu_3-\nu_5$ and $\nu_{10}-\nu_{12}$ correspond closely to those of $SiCl_3Br$, and are related to those of $SiCl_4$ [10]:

		CF_3SiCl_3	$SiCl_3Br$		$SiCl_4$
a_1	ν_3	365	368	a_1	424
	ν_4	538	545	e	150
	ν_5	176	190	f_2	608
e	ν_{10}	646	610		221
	ν_{11}	176	205		
	ν_{12}	106	135		

The assignment of the observed vibrational transitions is therefore straightforward. PQR structure was only observed for $\nu_2(a_1)$ and $\nu_{12}(e)$. Owing to the

TABLE 3

MAIN INNER FORCE CONSTANTS OF I, CF_3SiH_3 AND $SiCl_4$ SCALED TO 1 Å (N cm^{-1})

	CF_3SiCl_3	CF_3SiH_3 [5]	$SiCl_4$ [11]
SiC	2.899	2.537	
SiCl	3.383		3.37(4)
CF	5.818	5.602	
CF/CF′	0.967	0.936	
SiCl/SiCl′	0.125		0.12(2)
CF/SiC	0.158	0.150	
SiCl/SiC	0.122		
α-$\alpha\alpha$	1.515	1.512	
β-$\beta\beta$	0.671	0.545	
γ-$\gamma\gamma$	0.720		0.77(2)
δ-$\delta\delta$	0.596		

TABLE 4

POTENTIAL ENERGY DISTRIBUTION (ONLY CONTRIBUTIONS $\geq$ 15%) OF NORMAL MODES OF CF_3SiCl_3

ν(cm^{-1})	
a_1 1218	44(CF), 26(SiC), 24(α), 15(CF/CF′)
747	33(CF), 18(SiC), 17(α)
365	32(SiC), 32(SiCl)
538	63(SiCl), 21(SiC)
176	41(γ), 30(δ)
e 1130	122(CF), 24(α), $-$20(CF/CF′)
525	87(α)
278	66(β)
646	103(SiCl)
176	87(γ), 21(β)
105	91(δ), 21(γ), 17(β)

presence of two Cl isotopes, some absorption bands show complex envelopes, e.g. ν_{10} near 640 cm^{-1}. Furthermore, the presence of hot bands perturbs the band contours.

We have performed a normal coordinate analysis assuming the following geometry: SiC 1.900 Å, SiCl 2.019 Å, CF 1.348 Å, angle FCF 107.9°(α), FCSi 111.0°(β), ClSiCl(γ) and ClSiC(δ) 109.47°. Force constants of the SiCl$_3$ part were taken to be the same as for SiCl$_4$ [11] and those for the CF$_3$Si fragment the same as for CF$_3$SiH$_3$ [5], and values were then refined to fit the observed wavenumbers exactly by use of a computer program [12]. The main inner force constants for I are listed in Table 3, and compared with those of CF$_3$SiH$_3$ [5] and SiCl$_4$ [11]. Table 4 gives the potential energy distribution in terms of inner force constants.

The SiC stretching force constant of I, which reflects the strength of the SiCF$_3$ bond, lies between that of CF$_3$SiH$_3$ and CH$_3$SiCl$_3$, 3.35 N cm^{-1} [13]. This is what one would expect from taking account of atomic charges [14] and inductive effects.

Experimental

(Trifluoromethyl)bis(dimethylamino)silane (III). A pressure of 35 mbar CF$_3$Br was maintained as 213 g (861 mmol) P(NEt$_2$)$_3$ was added to a solution of 107.6 g (705 mmol) HSi(Cl)(NMe$_2$)$_2$ in 500 ml C$_6$H$_5$CN at 0°C during 1 h. The mixture was then brought to room temperature with vigorous stirring and the vessel charged with gaseous CF$_3$Br for 2.5 h. Then volatile material was distilled off at 50°C and 4 mbar and collected in a −78°C trap. Impurities (< 5%) were removed by fractional distillation through a a slit tube column, to give I in 86% yield. Elemental analyses are given in Table 5. Selected IR absorptions: 2168s (ν(SiH)), 1308s (δ(CH$_3$)), 1224s (ν_s(CF$_3$)), 1082vs (ν_{as}(CF$_3$)), 1004vs (ν(NC$_2$)), 858s cm^{-1} (δ(SiH)). MS:

TABLE 5

ELEMENTAL ANALYSES

Compound	Formula	Analyses (Found (calcd.)(%))				
		C	H	Cl	F	N
I	CCl$_3$F$_3$Si	6.0 (5.90)	< 0.2 (0.0)	52.0 (52.28)	27.5 (28.01)	
II	C$_{11}$H$_{10}$Cl$_3$F$_3$N$_2$Si	36.4 (36.53)	3.2 (2.79)			7.8 (7.75)
III	C$_5$H$_{13}$F$_3$N$_2$Si	32.5 (32.24)	7.1 (7.04)		31.0 (30.60)	15.1 (15.04)
IV	C$_4$F$_3$N$_3$O$_3$Si	21.6 (21.53)	< 0.2 (0.0)		25.6 (25.54)	
V	C$_4$H$_9$F$_3$O$_3$Si	25.6 (25.26)	4.8 (4.77)		29.8 (29.97)	
VI	C$_7$H$_{18}$F$_3$N$_3$Si	36.7 (36.66)	7.7 (7.91)		25.1 (24.85)	18.2 (18.32)
VII	C$_{10}$H$_{14}$F$_3$Si	71.1 (69.49)	4.9 (4.60)		17.0 (17.35)	
VIII	C$_{11}$H$_8$F$_3$Cl$_3$N$_2$Si	36.4 (36.73)	2.4 (2.24)			7.6 (7.79)

$m/e = 186$ $(M)^+$, 55%; 117 $(SiH(NMe_2)_2)^+$, 100%; 92$(F(H)SiNMe_2)^+$, 47%; 74 $(H_2SiNMe_2)^+$, 45%; 44 $(NMe_2)^+$, 64%.

(Trifluoromethyl)trichlorosilane (I). (a) 35 g HCl was condensed into a solution of 31.3 g (168 mmol) III in 1 l dibutyl ether at $-78°C$. The mixture was slowly warmed to room temperature, volatile products were boiled off at 55°C and 40 mbar, and the crude product collected in a $-140°C$ trap. After distillation under reduced pressure (< 500 mbar) through a slit-tube column a yield of 79% was obtained. MS: $m/e = 137/135/133$ $(SiCl_3)^+$, 33/100/100%; 119/117 $(FSiCl_2)^+$, 26/27%; 63 $(SiCl)^+$, 35%.

(b) Under argon 29.8 g (200 mmol) CF_3Br was condensed into a solution of 34 g (200 mmol) $SiCl_4$ in 50 ml CH_2Cl_2 at $-78°C$ and a solution of 49.5 g (200 mmol) $P(NEt_2)_3$ in 35 ml CH_2Cl_2 was added. The mixture was slowly warmed to room temperature and volatile products were then distilled off as the temperature was raised to 75°C. 5.0 g (63.2 mmol) pyridine was added to 14.3 g of the volatile products, the precipitate II filtered off, washed with ether, and dried in vacuo. An excess of HCl was condensed on to II at $-90°C$ and the volatile products were collected; I was obtained by fractional condensation in vacuo in ca. 50% yield.

(Trifluoromethyl)trichlorosilane-2-pyridine (II). II was also obtained from pure I and pyridine in 91% yield. (II may be sublimed in vacuo at ca. 50°C, but then the product shows a slight deficiency of pyridine (composition ca. I · 1.8 pyridine)). MS: $m/e = 135/133$ $(SiCl_3)^+$, 15/15%; 79 $(C_5H_5N)^+$, 100%; 52 $(C_4H_4)^+$, 78%; 51 $(C_4H_3)^+$, 27%; 50 $(C_4H_2)^+$, 16%.

(Trifluoromethyl)trichlorosilane-2,2'-bipyridyl (VIII). I (0.85 g, 4.2 mmol) was added to a solution of 2,2'-bipyridyl (0.74 g, 4.7 mmol) in 10 ml ether, and the resulting solution was filtered, washed, and dried, to give VIII in 93% yield. (VIII may be sublimed in vacuo at 80°C, but the product then contains an excess of 2,2'-dipyridyl.) MS: $m/e = 158$ $(C_{10}H_8N_2)^+$, 100%; 157 $(C_{10}H_7N_2)^+$, 40%; 135/133 $(SiCl_3)^+$, 33%; 128 $(C_8H_4N_2)^+$, 20%.

(Trifluoromethyl)triisocyanatosilane (IV). I (0.37 g, 1.82 mmol) was condensed onto AgOCN (1.5 g, 10 mmol) and the mixture was warmed to room temperature with vigorous shaking. Then volatile products were collected in vacuo and purified by fractional condensation, yield 88%. IR: 2320s, 2290vs ($\nu_{as}(NCO)$), 1473s ($\nu_s(NCO)$), 1234s ($\nu_s(CF_3)$), 1117vs ($\nu_{as}(CF_3)$), 748vs ($\nu_{as}(SiN_3)$), 625s cm^{-1} ($\delta(NCO)$). MS: $m/e = 154$ $(Si(NCO)_3)^+$, 100%; 131 $(SiF(NCO)_2)^+$, 35%; 112 $(Si(NCO)_2)^+$, 22%; 70 $(SiNCO)^+$, 15%.

(Trifluoromethyl)trifluorosilane. I (0.26 g, 1.28 mmol) was condensed onto SbF$_3$ (1.17 g, 6.54 mmol) and the mixture was shaken for 2 h. Volatile products were distilled off in vacuo and purified by fractional condensation in vacuo. CF_3SiF_3, yield 67%, was identified from its IR spectrum [3].

(Trifluoromethyl)trimethoxysilane (V). I (3.18 g, 15.6 mmol) was added to 2 ml CH_3OH at 0°C and the mixture was stirred for 30 min and the HCl then boiled off at 55°C. V and the excess of CH_3OH were separated by fractional condensation in vacuo, yield 90%. IR: 2990s, 2960s, 2865s ($\nu(CH_3)$), 1252s ($\nu_s(CF_3)$), 1200vs ($\rho(CH_3)$), 1150vs, 1123vs ($\nu(CO)$), 1085vs ($\nu_{as}(CF_3)$), 845s ($\nu_{as}(SiO_3)$), 747s ($\nu_s(SiO_3)$), 685s, 485s cm^{-1}. MS: $m/e = 121$ $(Si(OMe)_3)^+$, 100%; 109 $(FSi(OMe)_2)^+$, 26%; 91 $(HSi(OMe)_2)^+$, 34%; 79 $(F(H)SiOMe)^+$, 12%.

(Trifluoromethyl)tris(dimethylamino)silane (VI). I (3.78 g, 18.6 mmol) in 10 ml n-pentane was added to a solution of HNMe$_2$ (6 g, 133 mmol) in 50 ml n-pentane at

$-78°C$ and the mixture kept at room temperature for several hours. The ammonium salt was filtered off and the solution distilled in vacuo, to give VI in 65% yield. IR: 1306s (δ_s(CH$_3$)), 1216m (ν_s(CF$_3$)), 1182s (ρ(CH$_3$)), 1071vs (ν_{as}(CF$_3$)), 1001vs (ν_s(NC$_2$)), 737s (ν_{as}(SiN$_3$)), 622m cm^{-1} (ν_s(SiN$_3$)). MS: $m/e = 229$ (M)$^+$, 14%; 160 (Si(NMe$_2$)$_3$)$^+$, 100%; 135 (FSi(NMe$_2$)$_2$)$^+$, 18%; 117 (HSi(NMe$_2$)$_2$)$^+$, 23%; 92 (F(H)SiNMe$_2$)$^+$, 16%.

(Trifluoromethyl)silane. I (3.0 g, 14.8 mmol) was condensed into a solution of LiAlH$_4$ (0.5 g, 13.2 mmol) in 150 ml dibutyl ether and the mixture was brought to room temperature then stirred for 15 min. Volatile products were then distilled off in vacuo and purified by fractional condensation in vacuo. CF$_3$SiH$_3$, yield 90%, was identified from its IR spectrum [5].

(Trifluoromethyl)trimethylsilane. To a solution of I (0.47 g, 2.3 mmol) in 10 ml dibutyl ether, 4 ml of a 2 M solution of CH$_3$MgBr in dibutyl ether was added at $0°C$. After 2 h stirring at room temperature, 10 ml of cold 3% aqueous HCl was added and the ether fraction worked up. CF$_3$Si(CH$_3$)$_3$, yield 85%, was identified from its NMR [1] and IR spectrum [15].

(Trifluoromethyl)triphenylsilane (VII). To a solution of I (1.37 g, 6.7 mmol) in 30 ml ether, 11 ml of a 2 M solution of phenyllithium in 3/1 C$_6$H$_6$/ether was added at $-78°C$ and the mixture was stirred for 30 min at room temperature, and 20 ml of cold, aqueous HCl (10%) then added. Work-up gave colourless crystals of VII (from C$_6$H$_6$), yield 75%. IR (KBr): 1201 s (ν_s(CF$_3$)), 1060vs (ν_{as}(CF$_3$)). Phenyl vibrations (on Whiffen's notation [16]): 1430s (n), 1116s (q), 1029m (b), 997m (p), 741m (f), 717s (r), 697s (r'), 678m cm^{-1} (v). MS: $m/e = 328$ (M)$^+$, 0.3; 259 (SiPh$_3$)$^+$, 100%; 181 (SiPhC$_6$H$_4$)$^+$, 27%.

Spectra

IR: Perkin–Elmer 580 B, gaseous samples unless otherwise stated. FIR: Nicolet Series 8000 vacuum interferometer, resolution 1 cm^{-1}. Raman: Cary 82, excitation Kr$^+$ 6471 Å. NMR: ^{1}H/^{19}F Varian EM 390, external standard TMS/CFCl$_3$, ^{13}C Varian FT 80, internal standard C$_6$D$_6$ 128.0 ppm. MS: MAT 311, E. I., 70 eV.

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