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Synthesis and characterization of bis(trichlorosilylmethyl)benzenes

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Abstract

The compounds *o*-, *m*-, and *p*-$(Cl_3SiCH_2)_2C_6H_4$, 1,4-$(Cl_3SiCH_2)_2$–2,3,5,6-Me_4C_6, and 1,4-$(Cl_3SiCH_2)_2$–2,5-$Me_2C_6H_2$ have been prepared from the appropriate bis(chloromethyl)benzenes and trichlorosilane in tri-*n*-propylamine, and the structure of the compound 1,4-$(Cl_3SiCH_2)_2$–2,5-$Me_2C_6H_2$ has been determined by an X-ray diffraction study.

1. Introduction

Shey and Loy have recently outlined the concept of generating microporous siloxane xerogels from aryl-bridged trifunctionalsilanes, $X_3Si–Ar–SiX_3$ [1]. The aryl spacer groups employed included phenyl, biphenyl and terphenyl. Sol-gel processing of these trifunctional monomers gave monolithic gels. We report the preparation of related bis(trichlorosilylmethyl)benzene compounds, *o*-, *m*- and *p*-$C_6H_4(CH_2SiCl_3)_2$, 1,4-(Cl_3SiCH_2)–C_6Me_4, and 1,4-$(Cl_3SiCH_2)_2$–2,5-$Me_2C_6H_2$, which are precursors for monolithic transparent gels.

2. Results and discussion

There have been a number of studies of the synthesis of bis(organosilylmethyl)benzene compounds. The Grignard reaction has been usefully employed for the synthesis of 1,3- and 1,4-(bis-trimethylsilylmethyl)benzene, *i.e.* *p*- and *m*-$C_6H_4(CH_2SiMe_3)_2$, mixtures of the precursor chloromethylbenzene compounds and trimethylchlorosilane being added to magnesium metal [2]. The problems associated with formation of di-Grignard reagents from bis(chloromethyl)benzenes have been addressed by Lappert and Raston [3]. The compound *p*-$C_6H_4(CH_2SiMe_3)_2$ was also isolated from the reaction between the organopotassium salt *p*-$C_6H_4(CH_2K)_2$ and trimethylchlorosilane [4].

We tried without success to use the *p*-xylenediyl dianion obtained as Grignard and Lochmann (Li^nBu–^tBuOK) reagents for the synthesis of 1,4-bis(trichlorosilylmethyl)benzenes C_6R_4–$(CH_2SiCl_3)_2$. Only diethyl ether-insoluble, polymer-like materials were obtained. Benzyltrichlorosilanes were prepared by Benkeser from the reaction between benzyl halides and trichlorosilane in the presence of amines [5]. We have used this method to synthesise the series of related bis(trichlorosilylmethyl)benzenes; *p*-$C_6H_4(CH_2SiCl_3)_2$ (**1**), 1,4-$(CH_2SiCl_3)_2$–2,5-$Me_2C_6H_2$ (**2**), *p*-$C_6Me_4(CH_2SiCl_3)_2$ (**3**), *m*-$C_6H_4(CH_2SiCl_3)_2$ (**4**), and *o*-$C_6H_4(CH_2SiCl_3)_2$ (**5**). These compounds were formed in high yields when a mixture of Cl_3SiH and the appropriate chloromethylbenzenes was stirred in refluxing tri-n-propylamine. Compounds **1–4** are white solids while **5** is a colourless liquid. As with other trichlorosilyl compounds, **1–5** are readily hydrolysed in moist air. Analytical and spectroscopic data (^1H, ^{13}C and ^{29}Si NMR, IR and m/e) are assembled in Tables 1–4. The spectroscopic data confirm the expected structural features. Chemical shifts (^{28}Si, ^{13}C and ^1H NMR) are very similar for the $-CH_2SiCl_3$ fragments in each of the compounds **1–5**. The ^{13}C NMR chemical shifts of the ring carbons in compounds **1**, **4** and **5** are tentatively assigned in Table 3.

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TABLE 1. Thermal properties and elemental analysis

Compound	Melting points (°C)	Elemental analysis [b] C (%)	H (%)
1	139–141	26.02 (25.76)	2.03 (2.16)
2	109–111.5	30.90 (29.95)	3.10 (3.02)
3	114–115	33.25 (33.59)	3.88 (3.76)
4	45–47	27.07 (25.76)	2.39 (2.16)
5	74 (0.1 mmHg) [a]		

[a] Boiling point. [b] Calculated value in parentheses.

TABLE 2. ^1H and ^{29}Si NMR data (ppm)

Compound	^{29}Si NMR ($CDCl_3$)	^1H NMR ($CDCl_3$)
1	7.69 (s)	2.92 (s, 4H, CH_2SiCl_3) 7.19 (s, 4H, C_6H_4)
2	7.51 (s)	2.90 (s, 4H, CH_2SiCl_3) 2.31 (s, 6H, CH_3) 7.01 (s, 2H, C_6H_2)
3	8.11 (s)	2.20 (s, 12H, CH_3) 3.10 (s, 4H, CH_2SiCl_3)
4	7.73 (s)	2.91 (s, 4H, CH_2SiCl_3) 7.05–7.14 (m, 4H, C_6H_4)
5	7.14 (s)	3.07 (s, 4H, CH_2SiCl_3) 7.28–7.29 (d, 4H, C_6H_4)

TABLE 4. Infrared and mass spectroscopic data.

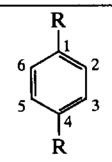
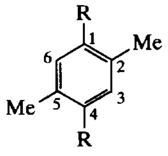
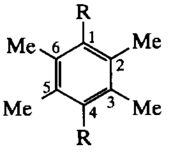
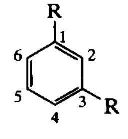
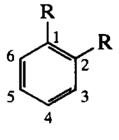
Compound	IR (cm^{-1}) ν(Si–Cl)	(m/e)(%) [fragment]	
1	590 530 441	376 (6) [$C_8H_8Si_2Cl^{25}_3Cl^{37}_3$] 374 (13) [$C_8H_8Si_2Cl^{35}{}_4Cl^{37}{}_2$] 372 (16) [$C_8H_8Si_2Cl^{35}{}_5Cl^{37}$] 370 (8) [$C_8H_8Si_2Cl^{35}{}_6$]	$[M]^+$
		239 (100) $[M–SiCl_3]^+$ 104 (41) $[M–(SiCl_3)_2]^+$	
2	572 469 439	404 (12) [$C_{10}H_{12}Si_2Cl^{35}{}_3Cl^{37}{}_3$] 402 (26) [$C_{10}H_{12}Si_2Cl^{35}{}_4Cl^{37}{}_2$] 398 (15) [$C_{10}H_{12}Si_2Cl^{35}{}_6$]	$[M]^+$
		132 (9) $[M–(SiCl_3)_2]^+$	
3	568 447	430 (44) [$C_{12}H_{16}Si_2Cl^{35}{}_4Cl^{37}{}_2$] 428 (41) [$C_{12}H_{16}Si_2Cl^{35}{}_5Cl^{37}$] 426 (21) [$C_{12}H_{16}Si_2Cl^{35}{}_6$]	$[M]^+$
		295 (100) $[M–SiCl_3]^+$ 160 (5) $[M–(SiCl_3)_2]^+$	
4	597 576 475	Fragmentation same as compound **1**	
5	603 580 485	Fragmentation same as compound **1**	

The assignments are based on those predicted [6] for related *o*-, *m*- and *p*-bis(chloromethyl)benzenes, with one exception, namely that the signal intensities imply that the chemical shift of C1/C2 in compound **5** occur upfield of C4/C5 rather than downfield, as expected and as predicted for the the *o*-chloromethyl compound.

A crystal structure analysis on compound **2** was conducted in order to determine the relative orientation of the trichlorosilyl groups in the solid state. No other compounds bearing trichlorosilylmethyl fragments appear to have been structurally characterized. The structure of **2** is shown in Fig. 1 and the corresponding structural data is given in Tables 5 and 6. The bond lengths and angles are all within expected ranges and there are no short inter- or intra-molecular contacts. The CH_2SiCl_3 groups lie at 23.2° to the plane of the aromatic ring in a *trans* orientation.

Sol-gel processing of compounds **1–3** led to transparent monolithic xerogels with time to gelation under the conditions explored varying from *ca.* 8 h to 5 days. The precise sol-gel formulations and characterization of these materials will be reported elsewhere.

TABLE 3. ^{13}C NMR data

	 **(1)**	 **(2)**	 **(3)**	 **(4)**	 **(5)** [a]
C1	130.48	133.48	132.79	132.82	130.47
C2	129.73	129.13	128.80	129.24	130.47
C3	129.73	132.28	128.80	132.82	127.31
C4	130.48	133.89	132.79	127.56	131.15
C5	129.73	129.13	128.80	130.20	131.15
C6	129.73	132.28	128.80	127.56	127.31
$-CH_2$	32.58	29.74	28.89	32.91	30.59
$-CH_3$		19.88	18.57		

[a] $R = CH_2SiCl_3$.

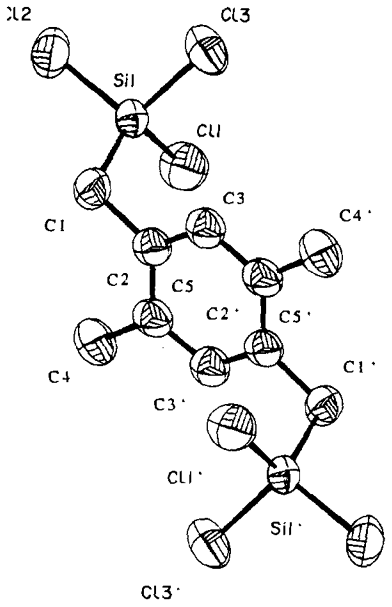


Fig. 1. Structure of p-$(CH_2SiCl_3)_2$-2,5-$Me_2C_6H_2$ (2).

TABLE 5. Bond lengths (Å) and bond angles (°) for $C_{10}H_{12}Cl_6Si_2$

Cl(1)–Si(1)	2.013(4)	Cl(2)–Si(1)	2.017(4)
Cl(3)–Si(1)	2.016(4)	C(1)–Si(1)	1.844(8)
C(2)–C(1)	1.511(9)	C(5)–C(2)	1.389(8)
C(5)–C(3)′	1.382(8)	C(5)–C(4)	1.486(10)
Cl(2)–Si(1)–Cl(1)	107.7(2)	Cl(3)–Si(1)–Cl(1)	108.0(2)
Cl(3)–Si(1)–Cl(2)	106.8(2)	C(1)–Si(1)–Cl(1)	111.5(3)
C(1)–Si(1)–Cl(2)	111.7(3)	C(1)–Si(1)–Cl(3)	110.9(4)
C(2)–C(1)–Si(1)	111.8(5)	C(5)–C(2)–C(1)	122.0(7)
C(3)′–C(5)–C(2)	117.2(6)	C(4)–C(5)–C(2)	123.4(7)
C(4)–C(5)–C(3)′	119.4(7)	C(2)–C(3)–C(5)′	123.8(7)

3. Experimental details

All reactions were carried out under purified nitrogen. Melting points were measured with samples sealed in capillaries under nitrogen on an electrothermal melting point apparatus. Elemental analyses were from University College London Analytical Service. Spectrometers: IR, Perkin-Elmer FT IR 1720 X (spectra in

TABLE 6. Fractional atomic coordinates ($\times 10^4$) for $C_{10}H_{12}Cl_6Si_2$

	x	y	z
Si(1)	2545(3)	1573(1)	1992(2)
Cl(1)	4215(3)	942(1)	521(2)
Cl(2)	−82(3)	2153(1)	684(2)
Cl(3)	4953(3)	2321(1)	3002(2)
C(1)	1325(12)	1003(4)	3492(8)
C(2)	3185(10)	462(3)	4268(6)
C(3)	5078(11)	−716(3)	4553(6)
C(4)	1429(17)	−611(5)	2583(10)
C(5)	3238(10)	−277(3)	3809(6)

Anisotropic temperature factors ($Å^2 \times 10^3$) for $C_{10}H_{12}Cl_6Si_2$ [a]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si(1)	35(1)	52(1)	58(1)	4(1)	7(1)	1(1)
Cl(1)	77(1)	71(1)	81(1)	−10(1)	34(1)	−1(1)
Cl(2)	45(1)	95(1)	101(1)	38(1)	4(1)	8(1)
Cl(3)	62(1)	77(1)	85(1)	−12(1)	9(1)	−23(1)
C(1)	58(4)	53(4)	58(4)	−2(4)	8(4)	0(4)
C(2)	45(3)	48(3)	47(3)	0(3)	11(3)	−3(3)
C(3)	67(4)	36(3)	51(3)	−1(3)	16(3)	0(3)
C(4)	67(6)	72(5)	65(5)	−7(4)	2(4)	−9(4)
C(5)	51(4)	51(3)	45(3)	0(3)	8(3)	−10(3)

Hydrogen fractional atomic coordiantes ($\times 10^4$) and isotropic temperature factors ($Å^2 \times 10^3$) for $C_{10}H_{12}Cl_6Si_2$

	x	y	z	U
H(11)	1276(84)	1340(25)	4238(49)	39(15)
H(12)	470(97)	748(28)	2971(57)	53(20)
H(31)	4899(78)	1196(23)	5690(46)	38(14)
H(41)	1707(95)	−1152(30)	2232(55)	70(18)
H(42)	1481(101)	−384(31)	1486(68)	89(21)
H(43)	238(104)	−530(41)	2760(80)	99(35)

[a] The temperature factor exponent takes the form $-2\pi^2(U_{11} \times h^2 \times a^{*2} + \cdots + 2U_{12} \times h \times k \times a^* \times b^*)$.

TABLE 7. Crystal data, intensity measurements and structure refinement

Formula	$C_{10}H_{12}Cl_6Si_2$
M	401.092
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	5.573(4)
b (Å)	17.982(5)
c (Å)	8.583(2)
α (°)	90
β (°)	97.42(4)
γ (°)	90
U (Å^3)	852.93(0.69)
Z	2
D_c (g cm^{-1})	1.562
$F(000)$	404
Radiation	Mo Kα
λ (Å)	0.71069
μ (cm^{-1}	11.34
$\theta_{min/max}$ (°)	1.5,25
Total no. of reflections	2005
No. of unique reflections	1507
No. of observed reflections ($F_o > 3\sigma(F_o)$)	955
No. of refined parameters	106
Weighting scheme parameter g in $w = 1/[\sigma^2(F) + gF^2]$	0.000021
Final R	0.0521
Final R_w	0.0416

Nujol mulls or thin films); NMR, Bruker WP-80 (^{1}H, 80 MHz), AW-250 (^{13}C, 62.89 MHz, ^{28}Si, 49.66 MHz) (data recorded on samples in $CDCl_3$). Mass, Kratos MS 50RF.

3.1. *1,4-Bis(trichlorosilylmethyl)benzene (1)*

A mixture of *p*-dichloromethylbenzene (3.5 g, 20 mmol), and trichlorosilane (6.1 cm^3, 60 mmol) in tri-n-propylamine (7.6 cm^3) was kept at 90–110°C (24 h). Addition of diethyl-ether (40 cm^3) to the cooled mixture resulted in precipitation of the amine hydrochloride. Filtration followed by removal of volatiles under vacuum afforded the crude product as a white powder. Recrystallization from CH_2Cl_2 gave pure **1** (4.74 g, 60%) as colourless crystals.

3.2. *2,5-Bis(trichlorosilylmethyl)-p-xylene (2)*

Prepared as described for **1** from 2,5-bis(chloromethyl)-*p*-xylene (4.0 g, 20 mmol), trichlorosilane (6.1 cm^3, 60 mmol), and tri-n-propylamine (7.6 cm^3). Yield, 7.4 g (92%).

3.3. *3,6-Bis(trichlorosilylmethyl)durene (3)*

Prepared in the manner described for **1** from 3,6-bis(chlormethyl)durene (2.3 g, 10 mmol), trichlorosilane (3.0 cm^3, 30 mmol) and tri-n-propylamine (3.8 cm^3, 20 mmol). Yield, 4.0 g (93.2%).

3.4. *1,3-Bis(trichlorosilylmethyl)benzene (4)*

Prepared as described for **1** from α,α'dichloro-*m*-xylene (1.75 g, 10 mmol), trichlorosilane (3.0 cm^3, 30 mmol), and tri-n-propylamine (3.8 cm^3, 20 mmol). Sublimation of the crude product afforded 3.13 g (83.9%) of polycrystalline **4**.

3.5. *1,2-Bis(trichorosilylmethyl)benzene (5)*

Prepared as described for **1** from α,α'dichloro-*o*-xylene (1.75 g, 10 mmol), trichlorosilane (3.0 cm^3, 30 mmol) and tri-n-propylamine (3.8 cm^3, 20 mmol). Distillation of the crude product afforded compound **5** (2.96 g, 79.4%) as a colourless liquid.

3.6. *Crystallography*

Data were recorded with a CAD4 diffractometer in ω–2θ scan mode. The crystal data and other details are given in Table 7. The structure was solved by direct methods and refined by least squares. Lists of thermal parameters have been deposited at the Cambridge Data base, and structure factors are available from the authors.

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