

## Tetrakis[3,5-bis(trifluoromethyl)phenyl]silane

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## Key indicators

Single-crystal X-ray study  
 $T = 120$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.051  
 $wR$  factor = 0.158  
Data-to-parameter ratio = 14.4For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title compound, tetrakis[3,5-bis(trifluoromethyl)phenyl]silane ( $\text{SiAr}''''_4$ ,  $\text{C}_{32}\text{H}_{12}\text{F}_{24}\text{Si}$ ), is a minor product from the reaction of silicon(IV) bromide with lithiated 1,3-bis(trifluoromethyl)benzene ( $\text{Ar}'\text{H}$ ). The structure crystallizes with two half-molecules in the asymmetric unit, with each central Si atom positioned on a twofold axis in a pseudo-tetrahedral environment, with Si—C bond lengths in the range 1.873 (3)–1.879 (3) Å.

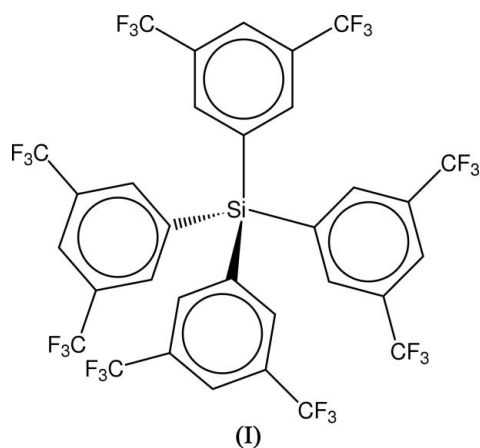
## Comment

The reactions of silicon(IV) chloride in a 1:2 ratio with lithiated trifluoromethyl-substituted aromatic hydrocarbons are complex and interesting (Buijink *et al.*, 1993; Braddock-Wilking *et al.*, 1995; Batsanov *et al.*, 2003). With lithiated 1,3,5-tris(trifluoromethyl)benzene ( $\text{ArH}$ ), the only product identified was  $\text{Ar}_2\text{SiF}_2$ , which was fully characterized crystallographically (Buijink *et al.*, 1993). This result was subsequently confirmed by Batsanov *et al.* (2003). Similarly,  $\text{HSiCl}_3$  reacts with  $\text{ArLi}$  to form  $\text{Ar}_2\text{SiHF}$ , again involving chlorine–fluorine exchange; this has also been characterized by single-crystal X-ray diffraction (Braddock-Wilking *et al.*, 1995). With 1,3-bis(trifluoromethyl)benzene,  $\text{Ar}'\text{H}$ , the system is more complicated because there are various lithiation positions (Bartle *et al.*, 1973; Batsanov *et al.*, 2002, 2003; Cornet *et al.*, 2003). These are *ortho* to both  $\text{CF}_3$  groups, giving 2,6-bis(trifluoromethyl)phenyl ( $\text{Ar}'$ ) derivatives, *ortho* to one  $\text{CF}_3$  group and *para* to the other, yielding 2,4-bis(trifluoromethyl)phenyl ( $\text{Ar}''$ ) species, and, much less likely, *meta* to both  $\text{CF}_3$  groups, giving 3,5-bis(trifluoromethyl)phenyl ( $\text{Ar}'''$ ) derivatives. An analytical gas–liquid chromatography study, following carboxylation of the organolithium compounds and subsequent esterification with diazomethane, showed *ca* 60% of the 2,4-isomer, 40% of the 2,6-isomer and less than 1% of a third component, presumed to be the 3,5-isomer (Bartle *et al.*, 1973). With  $\text{SiCl}_4$ , four of the possible disubstituted products, once F/Cl exchange is taken into account, have been observed spectroscopically, *viz.*  $\text{Ar}'_2\text{SiCl}_2$ ,  $\text{Ar}'_2\text{SiF}_2$ ,  $\text{Ar}''_2\text{SiCl}_2$  and  $\text{Ar}''_2\text{SiF}_2$ ; two of these,  $\text{Ar}'_2\text{SiF}_2$  and  $\text{Ar}''_2\text{SiCl}_2$ , have been characterized by single-crystal X-ray diffraction at 120 K (Batsanov *et al.*, 2003). The results suggested that the F/Cl exchange rate decreased in the order  $\text{Ar} > \text{Ar}' > \text{Ar}''$  (Batsanov *et al.*, 2003). It was therefore of considerable interest to extend this work to reactions of silicon(IV) bromide in a 1:2 molar ratio with the lithium derivatives of  $\text{ArH}$  and  $\text{Ar}'\text{H}$ .

Not surprisingly, the only product observed from  $\text{SiBr}_4$  and  $\text{ArLi}$  was  $\text{Ar}_2\text{SiF}_2$ ; Si—Br bonds are weaker than Si—Cl bonds, so facile exchange could reasonably be expected. The  $^{19}\text{F}$  NMR data are given in Table 2, with literature data for

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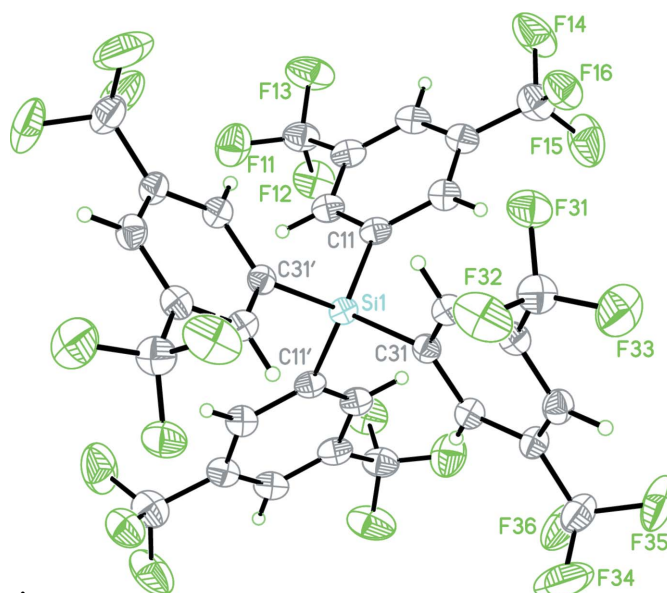
comparison (Batsanov *et al.*, 2003). With lithiated Ar'H and SiBr<sub>4</sub>, the products Ar'<sub>2</sub>SiF<sub>2</sub> (Batsanov *et al.*, 2003), Ar''<sub>2</sub>SiBr<sub>2</sub> and Ar''<sub>2</sub>SiBrF were identified by <sup>19</sup>F NMR solution state spectroscopy (Table 2). The results thus lend support to the idea that halogen exchange is slowest in the Ar'' species. After the mixture had been left to stand for some time, a few crystals were isolated, and proved to be of the fully substituted silane with no *ortho* CF<sub>3</sub> groups, *i.e.* tetrakis[3,5-bis(trifluoromethyl)phenyl]silane. Since there is little or no steric hindrance around silicon, further substitution beyond the disubstituted product is clearly more favourable for 3,5-derivatives than for 2,4- or 2,6-compounds. Nevertheless this product is a surprising one, in view of the work of Bartle *et al.* (1973).



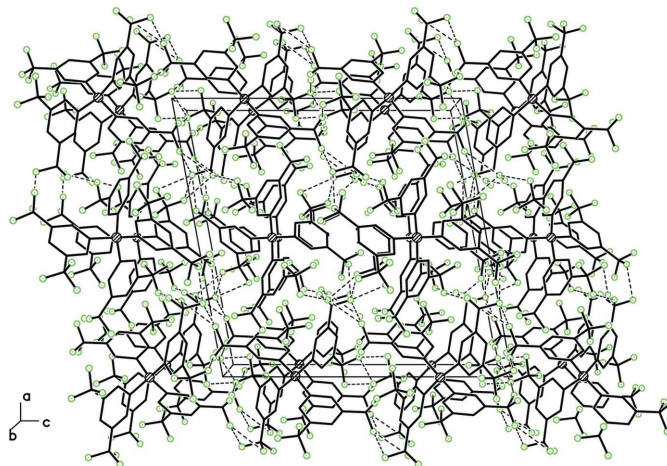
The compound tetrakis[3,5-bis(trifluoromethyl)phenyl]silane, (I), crystallizes in the monoclinic space group *P2<sub>1</sub>/c*, with two half molecules in the asymmetric unit and the molecular structure is shown in Fig. 1. Selected bond distances and angles are listed in Table 1. The central Si atom is in a tetrahedral environment, with bond angles around Si between 106.27 (16) and 110.97 (11)°. The Si—C bond lengths are all very similar, between 1.873 (3) and 1.877 (3) Å. The CF<sub>3</sub> groups are all ordered, presumably due to the weak F···F interactions (Fig. 2 and Table 1). While this species has not been reported previously, the structurally similar tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ion has been widely used in recent years, since the first report by Nishida *et al.* (1984), as a large lipophilic stable counter-ion for a variety of cationic complexes; it features in 291 structures in the Cambridge Structural Database (November 2004 edition; Allen, 2002). The structures of neutral tris[3,5-bis(trifluoromethyl)phenyl]phosphane (Jessop *et al.*, 2002) and -arsane (Dietzel & Jansen, 2004) have also been described. However, these species were all made directly from 3,5-bis(trifluoromethyl)phenyl-substituted aromatic starting materials.

## Experimental

All manipulations of air- and/or moisture-sensitive compounds were performed either under an inert atmosphere of dry nitrogen or *in*



**Figure 1**  
View of one of the independent molecules of (I) with selected atoms labelled. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code for primed and unlabelled atoms:  $1 - x, y, \frac{1}{2} - z$ .] The other molecule is very similar.



**Figure 2**  
Crystal packing in the title compound, viewed down the *b* axis, showing short intermolecular F···F contacts as dashed lines. H atoms have been omitted for clarity.

*vacuo*, using standard Schlenk and cannula techniques, or in a nitrogen-filled glovebox. <sup>19</sup>F NMR spectra were recorded on a Varian Unity 300 Fourier transform spectrometer at 282.2 MHz; chemical shifts were measured relative to external CFCl<sub>3</sub>. A solution of SiBr<sub>4</sub> (1.7 ml, 13.5 mmol) in diethyl ether was added dropwise, *via* a cannula, to a solution of ArLi (8 ml, 27 mmol) in diethyl ether at 195 K [the lithiated solutions of both ArH and Ar'H were prepared as described previously by Batsanov *et al.* (2002)]. White fumes were evolved. The mixture was allowed to warm to room temperature and stirred for 5 h, giving a pale-yellow oil. The presence of Ar<sub>2</sub>SiF<sub>2</sub> as the only major silicon-containing component was confirmed by <sup>19</sup>F NMR solution state spectroscopy (Table 2). Similarly, a solution of SiBr<sub>4</sub> (0.7 ml, 5.6 mmol) in diethyl ether was added slowly, *via* a cannula, to

a solution of lithiated Ar'H (4 ml, 11.3 mmol) in diethyl ether at 195 K. The mixture was allowed to reach room temperature and stirred overnight, giving a pale-brown solution. Analysis by <sup>19</sup>F NMR spectroscopy indicated three main components (Table 2). When the mixture was allowed to stand for some weeks, a few crystals appeared; these were isolated, and analysed by single-crystal X-ray diffraction. As indicated above, they proved to be of tetrakis[3,5-bis(trifluoromethyl)phenyl]silane.

Crystal data

C <sub>32</sub> H <sub>12</sub> F <sub>24</sub> Si	Z = 4
M <sub>r</sub> = 880.51	D <sub>x</sub> = 1.808 Mg m <sup>-3</sup>
Monoclinic, P2/c	Mo Kα radiation
a = 18.3760 (4) Å	μ = 0.24 mm <sup>-1</sup>
b = 9.5325 (2) Å	T = 120 (2) K
c = 18.7776 (4) Å	Block, colourless
β = 100.388 (1)°	0.20 × 0.12 × 0.10 mm
V = 3235.34 (12) Å <sup>3</sup>	

Data collection

Bruker SMART-6000 CCD diffractometer	28959 measured reflections
ω scans	7404 independent reflections
Absorption correction: integration (XPREP in SHELXTL; Sheldrick, 1997b)	5078 reflections with I > 2σ(I)
T <sub>min</sub> = 0.957, T <sub>max</sub> = 0.977	R <sub>int</sub> = 0.040
	θ <sub>max</sub> = 27.5°

Refinement

Refinement on F <sup>2</sup>	w = 1/[σ <sup>2</sup> (F <sub>o</sub> <sup>2</sup> ) + (0.0779P) <sup>2</sup> + 2.8011P]
R[F <sup>2</sup> > 2σ(F <sup>2</sup> )] = 0.051	where P = (F <sub>o</sub> <sup>2</sup> + 2F <sub>c</sub> <sup>2</sup> )/3
wR(F <sup>2</sup> ) = 0.158	(Δ/σ) <sub>max</sub> < 0.001
S = 1.02	Δρ <sub>max</sub> = 0.62 e Å <sup>-3</sup>
7404 reflections	Δρ <sub>min</sub> = -0.37 e Å <sup>-3</sup>
515 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Si1—C11	1.873 (3)	Si2—C41	1.876 (3)
Si1—C31	1.877 (3)	Si2—C21	1.879 (3)
F12···F14 <sup>i</sup>	2.847 (3)	F21···F44 <sup>iii</sup>	2.861 (3)
F13···F31 <sup>ii</sup>	2.919 (3)	F31···F41	2.901 (3)
F16···F42	2.997 (3)	F33···F26	2.969 (3)
F16···F43	2.848 (3)	F33···F41	2.852 (3)
C11 <sup>iv</sup> —Si1—C11	106.27 (16)	C41 <sup>v</sup> —Si2—C41	105.22 (16)
C11 <sup>iv</sup> —Si1—C31 <sup>iv</sup>	110.63 (11)	C41 <sup>v</sup> —Si2—C21	111.80 (11)
C11—Si1—C31 <sup>iv</sup>	110.97 (11)	C41—Si2—C21	110.87 (11)
C11 <sup>iv</sup> —Si1—C31	110.97 (11)	C41 <sup>v</sup> —Si2—C21 <sup>v</sup>	110.87 (11)
C11—Si1—C31	110.63 (11)	C41—Si2—C21 <sup>v</sup>	111.80 (11)
C31 <sup>iv</sup> —Si1—C31	107.40 (16)	C21—Si2—C21 <sup>v</sup>	106.39 (16)

Symmetry codes: (i) -x + 1, y, -z + 1/2; (ii) -x, y, -z + 1/2; (iii) -x + 1, -y, -z + 1; (iv) -x + 1, -y + 1, -z + 1; (v) x, -y + 1, z - 1/2.

Table 2

<sup>19</sup>F NMR (p.p.m., Hz) data for reaction products.

Group	No. of Fs	δ <sup>19</sup> F	<sup>5</sup> J <sub>FF</sub>	δ <sup>19</sup> F <sup>a</sup>	<sup>5</sup> J <sub>FF</sub> <sup>a</sup>
Ar <sub>2</sub> SiF <sub>2</sub>					
o-CF <sub>3</sub>	12	-57.7	t, 12.4	-57.3	t, 12.8
p-CF <sub>3</sub>	6	-63.8	s	-64.2	s
Si—F	2	-125.7	m, NR <sup>b</sup>	-124.5	m, 12.8
Ar' <sub>2</sub> SiF <sub>2</sub>					
o-CF <sub>3</sub>	12	-57.5	t, 12.8	-57.5	t, 12.3
Si—F	2	-125.4	m, 12.8	-125.5	m, 12.5
Ar'' <sub>2</sub> SiBrF					
o-CF <sub>3</sub>	6	-57.6	s		
p-CF <sub>3</sub>	6	-64.5	s		
Ar'' <sub>2</sub> SiBrF					
o-CF <sub>3</sub>	6	-59.6	d, 12.8		
p-CF <sub>3</sub>	6	-64.6	s		
Si—F	1	-158.4	m, 12.8		

Notes: (a) literature data from Batsanov *et al.* (2003); (b) not resolved.

All H atoms were positioned geometrically (C—H = 0.95 Å) and refined using a riding model with U<sub>iso</sub>(H) = 1.2U<sub>eq</sub>(C).

Data collection: SMART-NT (Bruker, 2000); cell refinement: SMART-NT; data reduction: SAINT-NT (Bruker, 2000); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: SHELXTL.

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