

Synthesis and characterization of sterically hindered diarylsilanes containing 2,4,6-trimethylphenyl and 2,4,6-tris(trifluoromethyl) phenyl substituents. X-ray crystal structure of bis[2,4,6-tris(trifluoromethylphenyl)]fluorosilane [☆]

Janet Braddock-Wilking ^{*}, Matt Schieser, Lee Brammer, Jean Huhmann, Raef Shaltout

Department of Chemistry, University of Missouri–St. Louis, St. Louis, MO 63121, USA

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Abstract

Sterically hindered diarylsilanes have been prepared by two synthetic routes. Dimesitylsilane, Mes₂SiH₂ (**1**), (Mes = 2,4,6-trimethylphenyl) was synthesized by reaction of mesityl magnesium bromide with HSiCl₃ followed by reduction with LiAlH₄, or by reaction of mesityl magnesium bromide with (TfO)₂SiH₂. The mixed diaryl system, MesPhSiH₂ (**2**), was prepared by reaction of (TfO)PhSiH₂, with one equivalent of MesMgBr. Diarylsilanes containing the 2,4,6-tris(trifluoromethyl)phenyl substituent, R_F, were prepared by reaction of HSiCl₃ with 2 equivalents of R_FLi to give (R_F)₂SiHF (**3**) through a Cl/F halogen exchange. Reduction of **3** with LiAlH₄ afforded (R_F)₂SiH₂ (**4**) which can also be prepared from R_FLi and (TfO)₂SiH₂. All compounds have been characterized by multinuclear NMR, IR, mass spectrometry and chemical analyses. An X-ray crystallographic study of **3** shows that the immediate geometry about silicon is approximately tetrahedral with a C–Si–C angle of 115.8(1)°. There are unusual intramolecular interactions in **3** with four short Si...F contacts with the ortho-CF₃ substituents on the aromatic ring which results in an overall tetracapped tetrahedral geometry about silicon. Crystal data for **3** are as follows: monoclinic, P2₁/c, with *a* = 9.827(2) Å, *b* = 15.938(3) Å, *c* = 13.239(3) Å, *V* = 2072.6(8) Å³, *Z* = 4, and *R* = 0.0492 (*R*_w = 0.0535). The short intramolecular Si...F contacts are observed in solution for both **3** and **4** by ²⁹Si NMR spectroscopy.

Keywords: Silicon; Group 14; Aryl; Mesityl; Crystal structure; Hindered (bulky) ligands

1. Introduction

Steric encumbrance in substituents bound to main group elements has led to kinetic stability in complexes especially those that contain multiple bonds or sites of unsaturation. A number of bulky organic substituents have been utilized such as mesityl, tert-butyl, bis(trimethylsilyl)methyl, tris(trimethylsilyl)methyl, 2,4,6-tri(*t*-butyl)phenyl, and 2,4,6-tri(*i*-propyl)phenyl [1]. More recently the sterically hindered 2,4,6-tris(trifluoromethyl)phenyl ligand, R_F has been reported to stabilize

a number of reactive main group elements [2]. Compounds have been prepared with the elements Cu [3], Zn [4], Cd [4], Hg [3,4], Sn [3], Si [3,5], Ga [6], and P [7]. Recently, the first homoleptic transition-metal derivatives were prepared containing the σ -bonded R_F ligands with Co and Ni by reaction of the anhydrous MCl₂ compounds with two equivalents of R_FLi [8]. In addition, a large number of organic molecules have been prepared [1]. Surprisingly, there has been little use of this ligand for group 14 compounds except for R_FSiMe₃ [3], R_FSnMe₃ [3], (R_F)₂SiF₂ [5], and two divalent group 14 species, (R_F)₂M where M = Sn and Pb [9]. The reaction chemistry of the stannylene compound has led to the synthesis of some novel Sn (IV) compounds containing the R_F ligand. The present study describes the synthesis and characterization of four sterically en-

[☆] This paper is dedicated to Professor Hideki Sakurai on the occasion of his retirement from Tohoku University.

^{*} Corresponding author.

cumbered secondary and tertiary silanes, two of which contain the 2,4,6-tris(trifluoromethyl)phenyl ligand and two that contain the 2,4,6-trimethylphenyl ligand.

2. Results and discussion

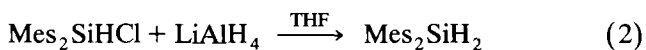
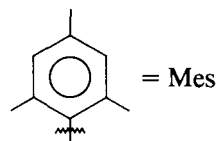
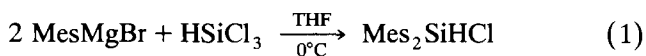
Hydridosilanes are useful synthetic precursors for the preparation of other silicon compounds such as chlorosilanes [10] and as precursors to oligo- and polysilanes through dehydrocoupling [11] in the presence of transition-metal catalysts. Sterically demanding ligands bound to silicon can lend kinetic stability to complexes when silicon is found in a low-valent environment such as in disilenes, silenes, metal–silylene complexes, and other multiply bonded silicon compounds. The steric encumbrance of the mesityl substituent was used to synthesize and characterize the first stable disilene molecule, $\text{Mes}_2\text{Si}=\text{SiMes}_2$ in 1981 [12]. Recently, dimesitylfluorosilane was prepared by fluorination of dimesitylchlorosilane with HF in water. The fluorosilane was used as a precursor for the preparation of the stable silene, dimesitylneopentylsilene, $\text{Mes}_2\text{Si}=\text{CHCH}_2^t\text{Bu}$ [13].

A relatively new ligand to enter the stage of stabilizing groups for low-valent main group elements is the 2,4,6-tris(trifluoromethyl)phenyl ligand. Chambers et al. reported the synthesis of the 1,3,5-tris(trifluoromethyl)benzene in 1987 [3]. The yield was later improved by Edelman et al. in 1989 [4]. All compounds prepared with the R_F ligand start from the R_FLi reagent. The aryl lithium is readily generated by direct reaction of 1,3,5-trifluoromethylbenzene with *n*-butyl lithium. The X-ray crystal structure of the aryl lithium salt as the diethyl ether adduct has been reported [14]. This ligand has a special combination of stabilizing features: steric shielding, electron-donating ability via the lone pairs on fluorine in the ortho- CF_3 positions, and electron withdrawing capability due to the electronegative nature of the trifluoromethyl substituents on the aromatic ring. The R_F ligand has led to the isolation of a stable diphosphene from reaction of R_FPCl_2 with the base DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) whereas only oligomers were isolated when mesityl and 2,4,6-tri(*i*-propyl)phenyl groups were employed [7]. The diphosphene $\text{R}_F\text{P}=\text{PR}_F$ is air stable and was found to be the most stable of the known diphosphenes. Interestingly, the steric requirements of the 2,4,6-tris(trifluoromethyl)phenyl ligand are not much different from the mesityl (the steric bulk of the R_F ligand lies somewhere between a mesityl and a 2,4,6-tri(*i*-propyl)phenyl group) but it has unusual electronic properties that enable it to stabilize otherwise highly reactive compounds such as diphosphenes [7]. Herein we report the synthesis and characterization of diarylsilanes containing the bulky

2,4,6-tris(trifluoromethyl)phenyl and 2,4,6-(trimethyl)phenyl ligands.

2.1. Synthesis of mesityl-substituted dihydridosilanes

Mesityl-substituted secondary silanes such as Mes_2SiH_2 can be prepared from the conventional route by reaction of two equivalents of mesityl magnesium bromide [15,16] with trichlorosilane in tetrahydrofuran followed by reduction with LiAlH_4 (Eqs. (1) and (2)). The overall yield from this reaction is a modest 46%. Dimesitylsilane has also been prepared by LAH reduction of $\text{Mes}_2\text{SiCl}_2$ but no spectroscopic data were given [17].



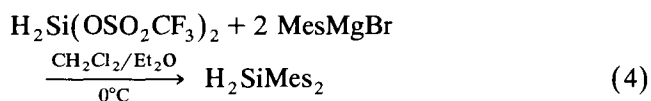
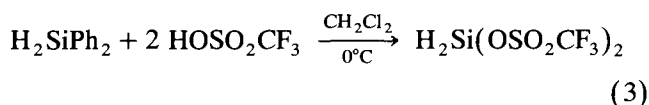
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Although Mes_2SiH_2 has been reported in the literature, incomplete spectroscopic data were given [18,19]. In this report, dimesitylsilane (**1**), was isolated as a white crystalline solid from a concentrated hexane solution at 4 °C. Dimesitylsilane is an air-stable solid that was characterized by ^1H , ^{13}C , ^{29}Si NMR spectroscopy, IR, mass spectrometry, and chemical analysis. Compound **1** is very soluble in both non-polar and polar organic solvents and forms very large colorless prisms upon slow evaporation of solvent.

The presence of the Si–H unit can be seen by two strong Si–H bands in the infrared spectrum at 2153 and 2147 cm^{-1} . The infrared and mass spectral data from this work agree with the literature values of Mes_2SiH_2 obtained by lithium aluminum hydride reduction of tetramesitylcyclodisiloxane [18]. In addition, a ^1H NMR resonance for Si–H is found at $\delta = 5.29$ ppm ($^1J_{\text{SiH}} = 195$ Hz). This is in close agreement with the chemical shift value for Mes_2SiH_2 obtained by hydrolysis of $(\text{THF})_2\text{LiSiHMe}_2$ in air ($\delta = 5.28$ ppm) [19].

In an effort to enhance the yield of Mes_2SiH_2 we investigated the synthesis utilizing a one-pot reaction between MesMgBr and $(\text{TfO})_2\text{SiH}_2$. The bis(triflate) silane can be prepared by reaction of diphenylsilane with 2 equivalents of triflic acid (triflic acid = HOSO_2CF_3) in methylene chloride (Eqs. (3) and (4)) [20]. The silyltriflate was not isolated but generated in

situ and reacted with 2 equivalents of mesityl magnesium bromide.

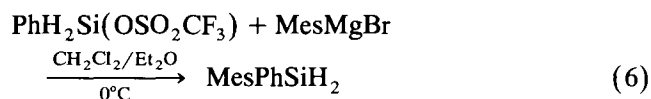
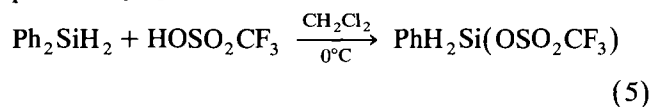


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After an aqueous workup, the organic layer was concentrated and Mes_2SiH_2 was recrystallized from cold hexane (4 °C). The low isolated yield (13%) was unexpected and is probably due to competing side reactions as often seen with silyltriflate reactions where mass balance is low [21].

The spectroscopic data were identical to those obtained from the $\text{MesMgBr}/\text{HSiCl}_3/\text{LiAlH}_4$ reaction described previously. We found that the yield was higher when methylene chloride was used as the solvent. When the reaction was run in toluene the mono-substituted product was the predominant species formed: Mes_2SiH_2 could be detected only in very small quantities by gas chromatography.

Mesitylphenylsilane was synthesized by the silyltriflate route. Reaction of diphenylsilane with one equivalent of triflic acid in methylene chloride followed by quenching with one equivalent of MesMgBr afforded a viscous oil after aqueous workup (Eqs. (5) and (6)). Mesitylphenylsilane has been used in the hydrosilylation of ketones catalyzed by rhodium catalysts but details of the synthesis and characterization were not provided [22].

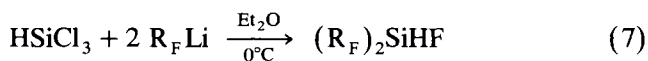


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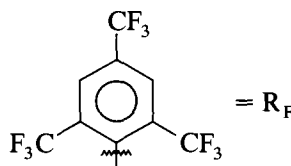
Attempts to purify MesPhSiH_2 by vacuum distillation were unsuccessful due to contamination with mesitylene, (1,3,5-trimethylbenzene), presumably formed by thermal decomposition of MesPhSiH_2 during the distillation procedure. Instead, MesPhSiH_2 (2) was purified by silica gel chromatography using hexane as the eluent and was isolated as a colorless liquid in 27% yield. Mesitylphenylsilane was characterized by ^1H , ^{13}C , ^{29}Si NMR spectroscopy, IR, mass spectrometry, and chemical analysis. The proton NMR spectrum reveals the Si–H resonance at $\delta = 5.20$ ppm ($^1J_{\text{SiH}} = 197$ Hz), slightly upfield from the position of the Mes_2SiH_2 resonance. The infrared spectrum shows a strong Si–H stretch at 2149 cm^{-1} .

2.2. Synthesis of 2,4,6-tris(trifluoromethyl)phenyl-substituted hydrosilanes

We have also investigated the synthesis of aryl-substituted silanes using the 2,4,6-tris(trifluoromethyl)phenyl substituent, R_F . Direct metallation of 1,3,5-trifluoromethylbenzene with *n*-butyl lithium affords the aryl lithium reagent in essentially quantitative yield [3]. Reaction with 1/2 equivalent of trichlorosilane in diethyl ether affords the unexpected product, $(\text{R}_F)_2\text{SiHF}$ (Eq. (7)). The Cl/F halogen exchange presumably occurs through a $(\text{R}_F)_2\text{SiHCl}$ intermediate and reaction with CF_3 substituents on the aromatic ring. The Cl/F halogen exchange reaction was also observed by Edelman et al. in the synthesis of $(\text{R}_F)_2\text{SiF}_2$ from SiCl_4 and two equivalents of R_FLi [5]. Here also, the halogen exchange most likely occurred through a $(\text{R}_F)_2\text{SiCl}_2$ intermediate and CF_3 substituents. The structure of $(\text{R}_F)_2\text{SiF}_2$ was determined by X-ray crystallography [5].



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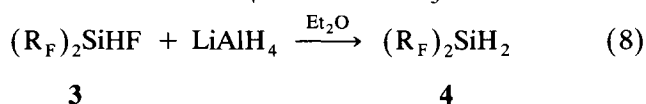


Bis(2,4,6-trifluoromethylphenyl)fluorosilane (3), was isolated as a colorless crystalline solid from a concentrated hexane solution at 4 °C in 37% yield. In most of the literature reports using the 2,4,6-tris(trifluoromethyl)phenyl ligand yields of < 45% are obtained, the reason for which is not clearly understood [2].

Bis(2,4,6-trifluoromethylphenyl)fluorosilane was characterized by ^1H , ^{13}C , ^{19}F , ^{29}Si NMR spectroscopy, IR, mass spectrometry, and chemical analysis. In addition, an X-ray crystal structure was obtained. The Si–H and Si–F stretching frequencies in $(\text{R}_F)_2\text{SiHF}$ are detected as medium intensity peaks in the IR spectrum at 2288 and 834 cm^{-1} , respectively. The proton NMR spectrum reveals two resonances, the aryl protons appear as a singlet at $\delta = 8.18$ ppm and the Si–H resonance appears downfield of TMS at 6.11 ppm. The Si–H resonance appears as a doublet of multiplets (nine lines are observed of the expected 13 line pattern from coupling to 12 equivalent F atoms in the ortho- CF_3 groups) ($^1J_{\text{SiH}} = 288$ Hz). The two-bond coupling to the fluorine bonded to silicon has a coupling constant of 51 Hz. The long-range coupling to the ortho- CF_3 fluorine atoms have a coupling constant of 4.6 Hz. Long-range coupling is seen in the stable compound bis(2,4,6-trifluoromethylphenyl)stannylene, $(\text{R}_F)_2\text{Sn}$, between Sn and the ortho- CF_3 fluorine atoms. Intramolecular Sn–F contacts are observed in the solid state by X-ray crystallog-

raphy [9]. Five-bond coupling is seen in the compound R_FPH_2 between the ortho- CF_3 substituents and the hydrogens bonded to phosphorus ($^5J_{FH} = 5.2$ Hz) [7]. The ^{13}C NMR spectrum assignments are consistent with aromatic compounds containing trifluoromethyl substituents [23]. The ^{29}Si NMR spectrum shows a doublet of multiplets centered at -17.3 ppm. The Si–F coupling was found to be $^1J_{Si-F} = 299.8$ Hz and is within the expected range [24]. The four-bond coupling was determined to be $^4J_{Si-CF_3} = 3.1$ Hz. The ^{19}F NMR exhibits a doublet at -57.5 ppm (*o*- CF_3) from coupling to the F bonded to Si. The *p*- CF_3 groups appear as a singlet at -64.8 and the Si–F resonance appears as a multiplet at -162.3 ppm. The ^{19}F NMR of $(R_F)_2SiF_2$ exhibits a triplet at -57.0 ppm for the *o*- CF_3 groups, a singlet at -63.9 for the *p*- CF_3 groups and a multiplet at -124.2 ppm for the SiF₂ groups [5].

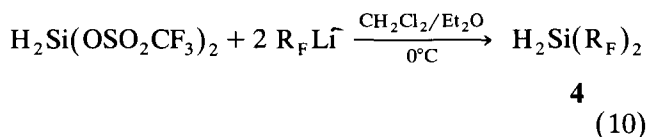
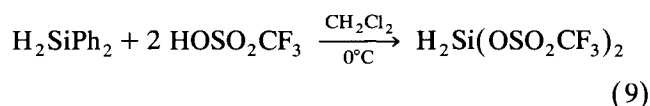
Reduction of compound **3** with $LiAlH_4$ in diethyl ether at room temperature afforded bis(2,4,6-trifluoromethylphenyl)silane in 28% yield (Eq. (8)). Attempts to reduce **3** with $NaBH_4$ or $NaB(OMe)_3H$ failed.



Bis(2,4,6-trifluoromethylphenyl)silane (**4**), was recrystallized from cold hexane (4 °C) and isolated as a white solid. Compound **4** was characterized by 1H , ^{13}C , ^{19}F , ^{29}Si NMR spectroscopy, IR, mass spectrometry, and chemical analysis. The proton NMR spectrum shows the absence of the fluorine substituent at silicon as noted from the lack of a J_{HF} doublet. The Si–H resonance appears as a multiplet (9 lines of an expected 13 line pattern are observed) ($^1J_{SiH} = 241$ Hz). The coupling to the *o*- CF_3 gives rise to a coupling constant of $^5J_{H-CF_3} = 5.0$ Hz. The ^{29}Si NMR spectrum shows a multiplet centered at $\delta = -43.0$ ppm ($^4J_{Si-CF_3} = 4.9$ Hz). The ^{19}F spectrum shows the two expected resonances for the *ortho*- and *para*- CF_3 substituents at

-57.9 and -64.7 ppm, respectively. The infrared spectrum shows an Si–H stretch at 2267 cm^{-1} .

Bis(2,4,6-trifluoromethylphenyl)silane was also prepared by reaction of two equivalents of R_FLi with $(TfO)_2SiH_2$ analogous to the reaction previously described for the preparation of Mes_2SiH_2 (Eqs. (9) and (10)). However, the yield of bis(2,4,6-trifluoromethylphenyl)silane from this route was only 15%. Spectroscopic data for **4** obtained from the triflate reaction were identical to the data obtained from reduction reaction of **3**.



2.3. X-ray crystal structure analysis of $(R_F)_2SiHF$ (**3**)

The structure of bis(2,4,6-trifluoromethylphenyl)fluorosilane was confirmed by single-crystal X-ray diffraction. The molecular structure of compound **3** is shown in Fig. 1 together with the atom-numbering scheme. A summary of the selected bond lengths and angles for compound **3** are shown in Table 1. To our knowledge $(R_F)_2SiHF$ is the first structurally characterized tetracoordinate halosilane containing one or more aryl groups and a SiHF unit. The compound exhibits approximate tetrahedral coordination at silicon with a C–Si–C angle of $115.8(1)^\circ$. The greater than normal angle at silicon presumably arises from the steric bulk present in the aryl substituents. The C–Si–C bond angle in $(R_F)_2SiF_2$ was reported as $119.1(2)^\circ$, an even larger angle than in compound **3** [5]. The F–Si–F angle in $(R_F)_2SiF_2$ was 105.8° . The Si–C distances in **3** (Si–C(1), $1.910(2)$ Å;

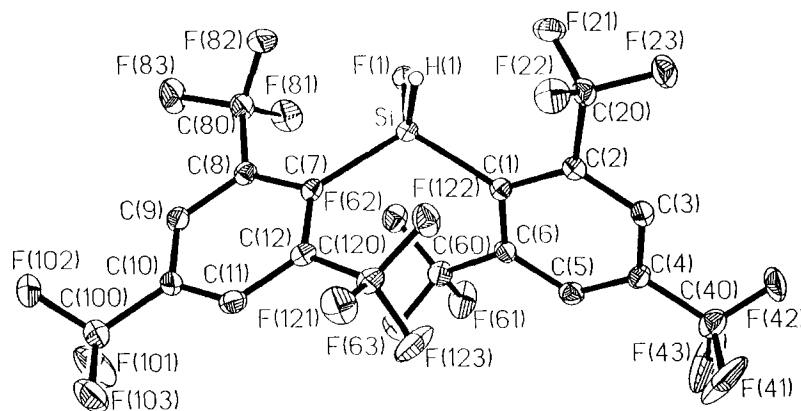


Fig. 1. ORTEP drawing of $(C_6H_2(CF_3)_3)_2SiHF$ (**3**) showing the atom-labeling scheme. Thermal ellipsoids are scaled to 50% probability level.

Table 1
Selected bond distances and bond angles associated with the silicon geometry in $[\text{C}_6\text{H}_2(\text{CF}_3)_3]_2\text{SiHF}$ (**3**) and $[\text{C}_6\text{H}_2(\text{CF}_3)_3]_2\text{SiF}_2$ [**5**]

$(\text{C}_6\text{H}_2(\text{CF}_3)_3)_2\text{SiHF}$ (3)		$(\text{C}_6\text{H}_2(\text{CF}_3)_3)_2\text{SiF}_2$	
<i>Bond distances</i> (Å)		<i>Bond distances</i> (Å)	
Si–F1	1.537 (2)	Si–F1	1.557 (3)
Si–H1 ^a	1.48	Si–F2	1.562 (3)
Si–C1	1.910 (2)	Si–C1	1.913 (5)
Si–C7	1.911 (2)	Si–C10	1.888 (4)
Si–F21	2.974	Si–F5	2.715
Si–F62	2.773	Si–F14	3.056
Si–F82	3.075	Si–F25	2.728
Si–F122	2.713	Si–F15	3.006
<i>Bond angles</i> (deg)		<i>Bond angles</i> (deg)	
F1–Si–H1 (plane 1) ^a	107.4	F1–Si–F2 (plane 1)	105.8 (2)
C1–Si–C7 (plane 2)	115.8 (1)	C10–Si–C1 (plane 2)	119.1 (2)
C1–Si–F1	105.9 (1)	C1–Si–F1	112.8 (2)
C1–Si–H1 ^a	107.4	C10–Si–F1	103.3 (2)
C7–Si–F1	112.5 (1)	C1–Si–F2	102.8 (2)
C7–Si–H1 ^a	107.4	C10–Si–F2	112.6 (2)
<i>Interplanar angles</i> (deg)		<i>Interplanar angles</i> (deg) ^b	
F21–Si–F82 (plane 3)	114.9	F25–Si–F14 (plane 3)	110.2
F122–Si–F62 (plane 4)	112.4	F5–Si–F15 (plane 4)	107.4
Plane 1–Plane 2 ^a	92.2	Plane 1–Plane 2	83.3
Plane 1–Plane 3 ^a	67.7	Plane 1–Plane 3	73.7
Plane 1–Plane 4 ^a	4.7	Plane 1–Plane 4	33.1
Plane 2–Plane 3	24.5	Plane 2–Plane 3	7.1
Plane 2–Plane 4	90.5	Plane 2–Plane 4	90.4
Plane 3–Plane 4	66.1	Plane 3–Plane 4	66.6

^a H(1) was not included in the least-squares refinement. These dimensions refer to the calculation of an idealized position for H(1).

^b These angles were calculated from data on $(\text{C}_6\text{H}_2(\text{CF}_3)_3)_2\text{SiF}_2$ obtained from the Cambridge Crystallographic Data Center.

Si–C(7), 1.911(2) Å) are similar to those in $(\text{R}_\text{F})_2\text{SiF}_2$ at 1.913(5) and 1.884(4) Å [5], but lie within the range of values observed for other tetracoordinate diphenyl silicon compounds. A Cambridge Structural Database (CSD) search [25] indicates that the mean Si–C (phenyl) bond lengths for a SiAr_2X_2 compound are 1.872(17) and 1.895(15) Å, for compounds where the ortho substituents of the aryl groups (Ar) are H and Me, respectively. Thus, although a small lengthening of the Si–C bonds might be attributable to the presence of large ortho substituents on the aryl groups, this is only at the level of 1–2 standard deviations based on the distributions of bond lengths surveyed. The fluorine and hydrogen atoms bonded to silicon in **3** are disordered, as is one of the *para*-CF₃ substituents. The hydrogen atom was not experimentally located. The Si–F distances were found to be 1.537(2) and 1.510(3) Å (56% and 44% occupancy of the F positions, respectively) and fall within the expected range for four-coordinate silicon [26]. The Si–F distances in $(\text{R}_\text{F})_2\text{SiF}_2$ were slightly longer, 1.557(3) Å and 1.562(3) Å [5].

The local environment about silicon is shown in Fig. 2 along with the atom-numbering scheme (covalent bonds are shown by a solid line and weaker interactions are designated by a dashed line). There are four short

intramolecular silicon–fluorine contacts in **3** with distances of: Si...F122, 2.71 Å; Si...F62, 2.77 Å; Si...F21, 2.97 Å; and Si...F82, 3.07 Å. Each of these distances are considerably shorter than the sum of the van der Waals radii (3.57 Å) [27]. Examination of the environment about silicon (including the bonded ligands and the four intramolecular Si...F contacts) reveals a (4 + 4) coordination environment which approaches a distorted tetracapped tetrahedron. The four short Si...F contacts occupy approximate faces of the tetrahedron defined by the bonded atoms C1, C7, F1, and H1. This type of geometry at silicon was observed recently in the hypercoordinate complex bis[2,6-(dimethylaminomethyl)]silane where lone pairs on nitrogen coordinate to silicon to give it a (4 + 4) coordination environment [28]. In compound **3**, one of the *ortho*-CF₃ groups on each aryl group provides a short Si...F contact whereas the other *ortho*-CF₃ group, due to steric constraints, has a slightly longer Si...F contact distance. Investigation of the structural parameters of the related compound, $(\text{R}_\text{F})_2\text{SiF}_2$, reveal a similar type of environment about silicon with four short intramolecular Si...F contacts [5]. The geometry about silicon can also be described as a tetracapped tetrahedron with silicon being (4 + 4) coordinated (Fig. 3). A summary of the relevant bond distances and bond angles of compound **3** and $(\text{R}_\text{F})_2\text{SiF}_2$ are shown in Table 1. Short intramolecular M...F contacts are also seen in the bis(2,4,6-trifluoromethylphenyl)stannylenes and plumblyenes complexes [9]. The Sn...F distances were found to be 2.67 Å and 2.82 Å for the averaged distances for two sets of CF₃ groups and are shorter than the sum of the van der Waals radii (3.64 Å) [9]. The Pb...F contacts are weaker but are short enough to contribute to the enhanced stability of the plumblyene species. The four short intramolecular

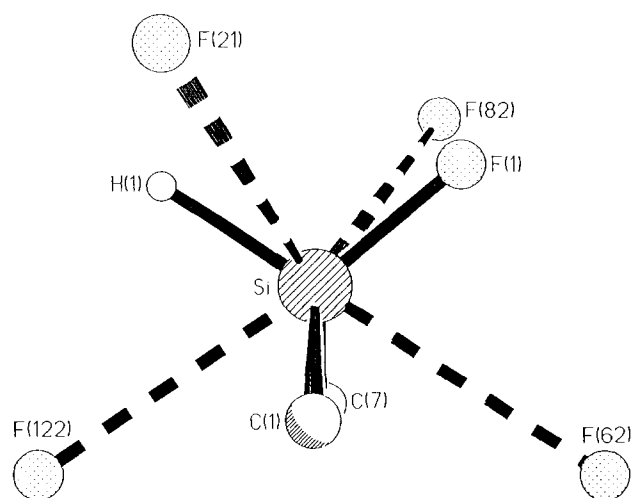


Fig. 2. Partial molecular structure of $(\text{C}_6\text{H}_2(\text{CF}_3)_3)_2\text{SiHF}$ (**3**) showing the coordination environment around silicon with the atom-labeling scheme.

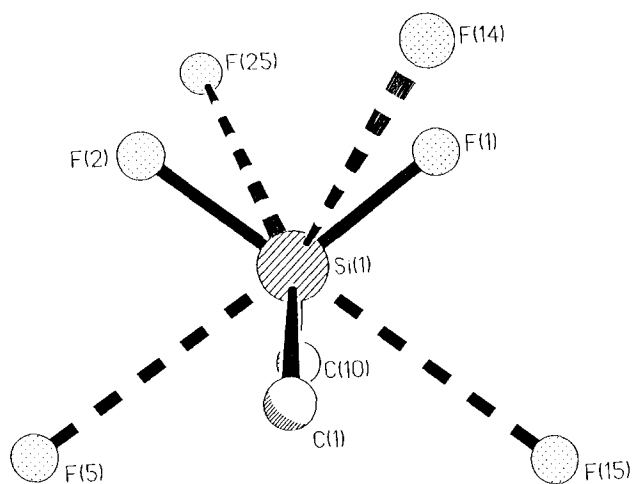


Fig. 3. Partial molecular structure of $(C_6H_2(CF_3)_3)_2SiF_2$ showing the coordination environment around silicon with the atom-labeling scheme [5].

Pb...F distances were 2.785, 2.793, 2.839, and 2.966 Å (the Pb–F distance in PbF_2 is 2.033 Å) [29]. Six intramolecular Ga...F contacts were found in $(R_F)_3Ga$ and were in the range of 2.665(19)–2.844(16) Å, considerably shorter than the sum of the van der Waals radii (3.45 Å) [6]. The R_F ligands are arranged in a propeller-like fashion around the gallium center with one CF_3 group above and below the Ga atom to give an overall trigonal-prismatic environment. The F...Ga interactions place the Ga center in an environment with pseudo-nine-coordinate geometry [6]. Weak metal...fluorine interactions are also observed in the group 12 complexes, $(R_F)_2M$ ($M = Zn, Hg$), and $(R_F)_2Cd(MeCN)$ [4].

2.4. Conclusion

The synthesis of some bulky diarylsilanes, Ar_2SiHX ($Ar = 2,4,6$ -(trifluoromethylphenyl), $X = H$ or F ; $Ar = 2,4,6$ -(trimethylphenyl), $X = H$) have been performed by coupling reactions using aryl Grignard reagents and chlorosilane precursors. In addition, the diarylsilanes, $ArAr'SiH_2$, ($Ar = Ar' = 2,4,6$ -(trimethylphenyl); $Ar = 2,4,6$ -(trimethylphenyl), $Ar' =$ phenyl) have been prepared by coupling reactions involving silyltriflate precursors and the appropriate aryl Grignard reagent. The focus of this report has been on the characterization of the diarylsilanes which include 1H , ^{13}C , ^{29}Si NMR and ^{19}F (for $(R_F)_2SiHF$ and $(R_F)_2SiH_2$) spectroscopy, IR, mass spectrometry, and chemical analysis. The fluorosilane, $(R_F)_2SiHF$ ($R_F = 2,4,6$ -(trifluoromethylphenyl), was structurally characterized by X-ray crystallography and was found to contain short intramolecular Si...F contacts involving the *ortho*- CF_3 substituents on the aromatic ring. The immediate geometry at silicon is approximately tetrahedral. The intramolecular Si...F

contacts place the silicon in a (4 + 4) coordination environment with a tetrapped tetrahedral geometry where the F atoms occupy four faces of the tetrahedron. These short Si...F contacts were also revealed in the ^{29}Si NMR spectrum for $(R_F)_2SiHF$ ($^4J_{Si-CF_3} = 3.1$ Hz) and $(R_F)_2SiH_2$ ($^4J_{Si-CF_3} = 4.9$ Hz). Future work will continue with the synthesis of sterically hindered secondary silanes and their utility as precursors for the synthesis of multiply bonded silicon species.

3. Experimental

All reactions were performed under nitrogen atmosphere using standard Schlenk techniques. Diethyl ether and tetrahydrofuran were distilled over sodium-benzophenone ketyl under nitrogen. Methylene chloride was distilled over CaH_2 . Trichlorosilane, *n*-butyl lithium (2.5 M in hexanes), 2-bromomesitylene, magnesium powder, triflic acid, mesityl magnesium bromide (1 M in diethyl ether), and $LiAlH_4$ are commercially available and were used without further purification. Tris(1,3,5-trifluoromethyl)benzene was obtained from PCR Chemicals, Inc. Diphenylsilane was prepared by reduction of dichlorodiphenylsilane with lithium aluminum hydride [30]. NMR solvents were obtained from Cambridge Isotopes Laboratories.

1H , ^{13}C , ^{19}F , and ^{29}Si NMR spectra were obtained on a Bruker ARX-500 NMR spectrometer at frequencies of 500 MHz, 125 MHz, 470 MHz, and 99 MHz, respectively (using a 5 mm inverse broad band or a 5 mm broad band tuneable probe). All NMR spectra were referenced to solvent or internal or external standard, and the chemical shifts are reported in δ units (positive shifts to higher energies). Infrared spectra were recorded on a Perkin–Elmer 1600 Series FT-IR. Mass spectral data were collected on a Hewlett–Packard Model 5988A GC/MS instrument equipped with an RTE-A data system. Gas chromatography was performed on a Hewlett–Packard 5890 Series II gas chromatograph with a 30 m by 0.32 mm (ID) DB-5 capillary column of 0.25 μm film thickness.

3.1. Bis(2,4,6-trimethylphenyl)silane, Mes_2SiH_2 (1)

In a three-neck 250 ml round bottom flask equipped with a magnetic stir bar, gas inlet adapter, condenser, and a 25 ml pressure-addition funnel was placed enough THF to cover Mg metal (4.83 g, 0.21 mol). 2-Bromomesitylene (10.04 g, 50.4 mmol) was placed in the pressure addition funnel and added dropwise with rapid stirring over 35 min [15]. After approximately 4–5 min no visible reaction had occurred. Ethyl dibromide (75 μl) was added and the flask warmed with a water bath. Vigorous bubbling was observed and the solution

turned a green–grey color. An additional 50 ml of THF were added to the flask from a syringe and the solution stirred for 1 h and 45 min. The solution was used for subsequent reactions.

In a separate three-neck 250 ml round bottom flask equipped with a magnetic stir bar, condenser, 50 ml pressure-addition funnel, and a gas inlet adapter was placed HSiCl_3 (3.30 g, 24.4 mmol) in 50 ml of THF. The reaction flask was cooled to 0 °C. The solution of MesMgBr prepared from the above procedure was transferred to the pressure addition funnel and added dropwise to the $\text{HSiCl}_3/\text{THF}$ solution over 30 min. After 1 h and 45 min the reaction mixture was warmed to room temperature then gently heated for 38 h. The reaction mixture was transferred to a glass fritted filter containing a pad of celite, attached to a 100 ml round bottom flask and filtered to give a clear yellow solution. The volume was reduced to approximately 25 ml then 50 ml of diethyl ether were added and the solution filtered again through a glass fritted filter. The clear filtrate was transferred to a 25 ml pressure addition funnel and added dropwise to a slurry of LiAlH_4 (1.04 g, 27.4 mmol) in 25 ml of diethyl ether (250 ml round bottom flask) over 2 h, and stirred at room temperature for 17 h. The solution was filtered to remove the lithium salts and the volume was reduced to approximately 20 ml then cooled to 4 °C overnight to give a white crystalline solid. Mes_2SiH_2 was obtained in 48% yield (3.11 g), m.p. 111–112 °C [18,19]. ^1H NMR (C_6D_6): δ 2.08 (6 H, s, *p*- CH_3); 2.36 (12 H, s, *o*- CH_3); 5.29 (2 H, s, Si–H); 6.71 (4 H, s, Ar–H). ^{13}C NMR (C_6D_6): δ = 21.1 (*p*- CH_3); 23.5 (*o*- CH_3); 127.8 (m-ring carbon); 129.2 (p-ring carbon); 139.6 (o-ring carbon); 145.1 (ipso-ring carbon). ^{29}Si NMR (C_6D_6): δ –62.0 ppm. IR (KBr pellet): ν (Si–H) 2153, 2147 cm^{-1} . MS (EI, 70 eV): m/z 268 (37, M^+), 253 (13, $\text{M}-\text{CH}_3$), 148 (100), 133 (68), 120 (39), 105 (27), 91 (12), 67 (8), 53 (6). Anal. Found: C, 80.48%; H, 9.10%. $\text{C}_{18}\text{H}_{24}\text{Si}$ calcd.: C, 80.53%; H, 9.01%.

3.2. Alternative preparation of Mes_2SiH_2 (1)

In a three-neck 50 ml round bottom flask equipped with a magnetic stir bar, gas inlet adapter, and a 25 ml pressure-addition funnel were placed 0.50 g (2.7 mmol) of diphenylsilane in 20 ml of methylene chloride [20]. The flask was cooled to 0 °C and 0.85 g (5.6 mmol) of triflic acid was added dropwise from a syringe. Over a period of 20 min the mixture turned from a light pink to a pale yellow. The solution was stirred for 1 h at 0 °C then warmed to room temperature and recooled to 0 °C before addition of the Grignard reagent. Mesityl magnesium bromide (5.7 ml of 1.0 M in diethyl ether, 5.7 mmol) was transferred to the pressure addition funnel and added dropwise to the Ph_2SiH_2 solution over approximately 10 min. The resulting mixture was stirred

at room temperature for 20 h. The reaction mixture was transferred to a 250 ml separatory funnel and 50 ml of water was added. An additional 15 ml of diethyl ether and saturated ammonium chloride, NH_4Cl , were added until the aqueous layer became clear. The organic layer was extracted and dried over anhydrous magnesium sulfate for 1 h. The solution was filtered by gravity and concentrated on a rotary evaporator. Mes_2SiH_2 was recrystallized from cold hexane (4 °C) and obtained in 13% yield (0.095 g). Spectroscopic data were identical to Mes_2SiH_2 obtained from the $\text{HSiCl}_3/\text{MesMgBr}$ reaction above.

3.3. Mesitylphenylsilane, MesPhSiH_2 (2)

In a three-neck round bottom flask equipped with a magnetic stir bar, 25 ml pressure-addition funnel, and gas inlet adapter was placed 0.99 g (5.4 mmol) of diphenylsilane in 30 ml of methylene chloride. The reaction flask was cooled to 0 °C then triflic acid (0.5 ml, 0.85 g, 5.6 mmol) was added dropwise from a syringe [20]. The solution was stirred for 15 min at 0 °C then the ice bath was removed and the mixture stirred at room temperature for 15 min. The reaction flask was recooled to 0 °C before the Grignard reagent was added. Mesityl magnesium bromide (1 M in diethyl ether, 5.4 ml, 5.4 mmol) was transferred to the pressure-addition funnel and added dropwise over 30 min. After the addition was completed the reaction mixture was stirred at room temperature overnight. The reaction mixture was transferred to a 250 ml separatory funnel and 100 ml of water and an additional 40 ml of diethyl ether were added. The organic layer was extracted then dried over anhydrous magnesium sulfate. The solution was filtered by gravity and concentrated on a rotary evaporator to give a viscous yellow liquid. The product was purified by silica gel column chromatography with hexane as the eluent. MesPhSiH_2 was isolated as a colorless liquid in 27% yield (0.33 g). ^1H NMR (C_6D_6): δ 2.11 (3 H, s, *p*- CH_3); 2.37 (6 H, s, *o*- CH_3); 5.20 (2 H, s, Si–H); 6.74 (2 H, s, Mes–H); 7.07–7.12 (3 H, m, Ph–H); 7.50 (2H, dd, Ph–H). ^{13}C NMR (C_6D_6): δ 21.2 (*p*- CH_3); 23.9 (*o*- CH_3); 126.1 (m-ring carbon); 128.4 (Ph); 128.75 (Ph); 129.8 (p-ring carbon); 132.2 (Ph); 135.5 (Ph); 140.1 (o-ring carbon); 145.2 (ipso-ring carbon). ^{29}Si NMR (C_6D_6): δ –49.4 ppm. IR (neat): ν (Si–H) 2150 cm^{-1} . Mass spectral data: MS (EI, 70 eV): m/z 226 (83, M^+), 148 (100, $\text{M}-\text{Ph}$), 133 (58), 119 (38), 105 (63), 91 (10), 79 (10), 53 (11). Anal. Found: C, 79.47%; H, 8.59%. $\text{C}_{15}\text{H}_{18}\text{Si}$ calcd.: C, 79.58%; H, 8.01%.

3.4. Bis[2,4,6-tris(trifluoromethylphenyl)]fluorosilane, $(\text{R}_F)_2\text{SiHF}$ (3)

In a 100 ml Schlenk flask equipped with a magnetic stir bar was placed 4.69 g (16.6 mmol) of 1,3,5-trifluo-

romethylbenzene in 30 ml of diethylether [3]. The flask was cooled with an ice bath. In a separate 100 ml Schlenk flask were placed n-BuLi (7.0 ml 2.5 M in hexanes, 17.5 mmol) and 30 ml of diethyl ether. The BuLi solution was added dropwise by a cannula to the cooled R_FH solution over 25 min. After the addition was complete the reaction mixture was allowed to warm to room temperature and stirred overnight.

Trichlorosilane (1.21 g, 8.9 mmol) and 30 ml of diethyl ether were placed in a 100 ml Schlenk flask and cooled with an ice bath. The R_FLi solution from above was added dropwise to the trichlorosilane solution from a cannula over 1 h. The ice bath was removed after the addition was completed. The reaction mixture was stirred overnight at room temperature. The solution was filtered through a glass fritted filter and the volatiles were removed under vacuum. An off white crystalline material precipitated. Hexanes (25 ml) were added and the flask cooled to 4 °C overnight. The solid was washed with two 15 ml aliquots of cold pentane to afford bis[2,4,6-tris(trifluoromethylphenyl)]fluorosilane as a white crystalline solid in 37% yield (1.99 g), m.p. 108–109 °C. 1H NMR ($CDCl_3$): δ 6.11 (1 H, dm, $^2J_{H-F} = 51.1$ Hz; $^5J_{H-CF_3} = 4.6$ Hz, Si–H); 8.18 (4 H, s, Ar–H). ^{13}C NMR ($CDCl_3$): δ 122.2 (q, $^1J_{C-F} = 273.2$ Hz, *p*- CF_3); 122.9 (q, $^1J_{C-F} = 275.4$ Hz, *o*- CF_3); 126.7 (s, m-ring carbon); 134.2 (q, $^2J_{C-F} = 34.9$ Hz, p-ring carbon); 134.5 (s, ipso-ring carbon); 138.5 (q, $^2J_{C-F} = 34.0$ Hz, o-ring carbon). ^{29}Si NMR ($CDCl_3$): δ –17.3 ppm (dm, $^1J_{Si-F} = 299.8$ Hz, $^4J_{Si-CF_3} = 3.1$ Hz). ^{19}F NMR ($CDCl_3$): δ –57.48 ppm (d, $^5J_{F-CF_3} = 13.6$ Hz, *o*- CF_3); –64.82 (s, *p*- CF_3); –162.23 (m, Si–F). IR (KBr pellet): ν (Si–H) 2288 cm^{-1} ; ν (Si–F) 834 cm^{-1} . MS (EI, 70 eV): m/z 591 (0.1, M–F), 436 (11), 418 (35), 328 (100, M– $C_9H_2F_9$), 262 (22, M– $C_9H_2F_8$), 243 (20, ($C_6H_2(CF_2)_2CF_3^+$)), 224 (48), 205 (85), 193 (15), 174 (36), 156 (47), 143 (19), 75 (15), 69 (27, CF_3). Anal. Found: C, 35.06%; H, 0.94%. $C_{18}H_5F_{19}Si$ calcd.: C, 35.42%; H, 0.82%.

3.5. Bis[2,4,6-tris(trifluoromethylphenyl)]silane, $(R_F)_2SiH_2$ (4)

In a 100 ml Schlenk flask equipped with a magnetic stir bar were placed 1.41 g (2.3 mmol) of bis[2,4,6-tris(trifluoromethylphenyl)]fluorosilane and 45 ml of diethyl ether. In a separate 100 ml Schlenk flask equipped with a magnetic stir bar and a 25 ml pressure-addition funnel was placed 95 mg (2.5 mmol) of $LiAlH_4$ in a few ml of diethyl ether. The $(R_F)_2SiHF$ solution was transferred to the addition funnel and approximately 25 ml of the solution was added to the LAH slurry. The remaining silane solution was added dropwise over 15 min. The reaction mixture was stirred overnight at room temperature. The reaction mixture was filtered by gravity and condensed on a rotary evaporator to give a solid

residue. The crude product was recrystallized from pentane at 4 °C. Bis[2,4,6-tris(trifluoromethylphenyl)]silane was isolated as a white solid in 28% yield (0.38 g) m.p. 113–114 °C. 1H NMR ($CDCl_3$): δ 5.38 (2 H, m, $^5J_{H-CF_3} = 5.0$ Hz, Si–H); 8.14 (4 H, s, Ar–H). ^{13}C NMR ($CDCl_3$): δ 122.4 (q, $^1J_{C-F} = 271$ Hz, *p*- CF_3); 123.1 (q, $^1J_{C-F} = 274$ Hz, *o*- CF_3); 126.4 (s, m-ring carbon); 133.4 (q, $^2J_{C-F} = 35$ Hz, p-ring carbon); 135.0 (s, ipso-ring carbon); 138.9 (q, $^2J_{C-F} = 33$ Hz, o-ring carbon). ^{29}Si NMR ($CDCl_3$): δ –43.0 ppm (m, $^4J_{Si-CF_3} = 4.9$ Hz). ^{19}F NMR ($CDCl_3$): δ –57.99 ppm (s, *o*- CF_3); 64.73 (s, *p*- CF_3). IR (KBr pellet): ν (Si–H) 2267 cm^{-1} . MS (EI, 70 eV): m/z 486 (1), 418 (38), 400 (28), 368 (10), 263 (32), 241 (17), 225 (28), 206 (68), 193 (10), 187 (97), 174 (18), 156 (100), 143 (15), 138 (19), 125 (12), 105 (13), 99 (13), 87 (12), 75 (25), 69 (40). Anal. Found: C, 36.21%; H, 1.12%. $C_{18}H_6F_{18}Si$ calcd.: C, 36.50%; H, 1.02% H.

3.6. Alternative preparation of $(R_F)_2SiH_2$ (4)

In a three-neck, 50 ml round bottom flask equipped with a magnetic stir bar, gas inlet adapter, 25 ml pressure-addition funnel, and condenser was placed 1.78 g (6.3 mmol) of tris-(1,3,5-trifluoromethyl)benzene in 10 ml of diethyl ether. Butyl lithium (2.6 ml, 2.5 M in hexanes, 6.5 mmol) was added to the R_FH solution dropwise over 15 min followed by stirring at room temperature for 1 h.

In a separate three-neck round bottom flask equipped with a magnetic stir bar, gas inlet adapter, and 25 ml pressure-addition funnel was placed 0.58 g (3.1 mmol) of diphenylsilane in 20 ml of methylene chloride [20]. The flask was cooled to 0 °C and 0.95 g (6.3 mmol) of triflic acid was added dropwise from a syringe. The solution was stirred for 1 h at 0 °C then warmed to

Table 2
Data collection, structure solution, and refinement parameters for 3

Crystal system	Monoclinic
Space group, Z	$P2_1/c$, Z = 4
a (Å)	9.827(2)
b (Å)	15.938(3)
c (Å)	13.239(3)
β (°)	91.74(2)
V (Å ³)	2072.6(8)
Density (g cm ⁻³)	1.956
Temperature (K)	125(5)
X-ray wavelength (Å)	0.71073
μ (Mo K α) (mm ⁻¹)	0.289
2 θ range (°)	3.0–62.0
Reflections collected	7150
Independent Reflections (R_{int})	6572 (0.014)
Observed ($F > 3.0 \sigma(F)$)	4707
L.S. parameters	397
$R(F)$, $R_w(F)$	0.049, 0.054
S(F)	1.38

room temperature. The $\text{Ph}_2\text{SiH}_2/\text{HOTf}$ solution was cooled to 0 °C before dropwise addition of the R_FLi solution, over approximately 15 min. The resulting mixture was stirred for 18 h and then was transferred to a 250 ml separatory funnel and 60 ml of water and 15 ml of diethyl ether were added. An additional 45 ml of ether was added and the resulting organic layer was extracted with 60 ml of water then dried over anhydrous magnesium sulfate. The solution was filtered by gravity

and concentrated on a rotary evaporator. Cooling of the solution to 4 °C gave $(\text{R}_F)_2\text{SiH}_2$ (**4**), in 15% yield (0.28 g). Spectroscopic data were identical to the $(\text{R}_F)_2\text{SiH}_2$ obtained from the $(\text{R}_F)_2\text{SiHF}/\text{LiAlH}_4$ reaction.

3.7. X-ray crystallography

Experimental data pertaining to the crystal structure determination of **3** are summarized in Tables 2 and 3. The crystal structure of **3** was solved by direct methods and refined to convergence by full-matrix least-squares using the SHELXTL suite of programs [31]. All non-hydrogen atoms were refined anisotropically and the phenyl hydrogen atoms were refined freely with isotropic displacement parameters. The structure exhibits disorder of one of the CF_3 groups (C(40), F(41)–F(43)) resulting in two orientations of the set of fluorine atoms, with occupancies of 55.3(2)% and 44.7(1)%, respectively. The fluoride and hydride substituents at silicon are also disordered. The structure was refined using two positions for the fluorines (F(1) and F(1')) with occupancies of 56.2(1)% and 43.8(1)%, respectively. The hydride substituent was not included in the refinement model, but is depicted in the figures in a calculated position (Si–H(1) 1.48 Å) in order that the chemical significance of the coordination geometry at silicon is more clearly illustrated. A complete list of bond distances and bond angles, positional and isotropic displacement coefficients for the hydrogen atoms, a list of the anisotropic coefficients for the non-hydrogen atoms, an ORTEP drawing of **3** including disordered atoms and the atom-labeling scheme, and calculated and observed structure factors are available from the authors (JB-W) and will be deposited in the Cambridge Crystallographic Data Center.

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Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **3**

Atom	x	y	z	U(eq)
Si	7551(1)	9914(1)	342(1)	18(1)
F(1) ^a	6449(2)	10519(1)	–72(2)	21(1)
F(1') ^b	8616(3)	9927(2)	–457(2)	24(1)
C(1)	6684(2)	8847(1)	449(1)	15(1)
C(2)	6804(2)	8226(1)	–308(2)	15(1)
C(3)	6239(2)	7432(1)	–221(2)	18(1)
C(4)	5494(2)	7232(1)	618(2)	19(1)
C(5)	5285(2)	7832(1)	1352(2)	19(1)
C(6)	5869(2)	8622(1)	1264(2)	17(1)
C(7)	8439(2)	10323(1)	1548(2)	15(1)
C(8)	8268(2)	11153(1)	1905(2)	16(1)
C(9)	8874(2)	11431(1)	2806(2)	19(1)
C(10)	9702(2)	10899(1)	3378(2)	19(1)
C(11)	9968(2)	10100(1)	3035(2)	20(1)
C(12)	9352(2)	9824(1)	2133(2)	17(1)
C(20)	7509(2)	8402(1)	–1291(2)	19(1)
F(21)	7137(1)	9143(1)	–1690(1)	27(1)
F(22)	8862(1)	8402(1)	–1178(1)	28(1)
F(23)	7198(2)	7823(1)	–1995(1)	30(1)
C(40)	4899(3)	6365(2)	704(2)	29(1)
F(41) ^c	5822(5)	5833(2)	1105(4)	73(1)
F(42) ^c	4520(6)	6039(3)	–139(2)	76(1)
F(43) ^c	3908(4)	6315(3)	1323(4)	74(1)
F(41') ^d	3851(7)	6293(4)	46(6)	115(1)
F(42') ^d	5703(6)	5787(3)	500(6)	97(1)
F(43') ^d	4352(8)	6238(4)	1529(4)	92(1)
C(60)	5552(2)	9229(1)	2099(2)	22(1)
F(61)	4329(2)	9093(1)	2475(1)	37(1)
F(62)	5570(1)	10028(1)	1783(1)	24(1)
F(63)	6462(2)	9178(1)	2882(1)	31(1)
C(80)	7468(2)	11807(1)	1307(2)	22(1)
F(81)	6123(1)	11669(1)	1304(1)	31(1)
F(82)	7842(2)	11835(1)	341(1)	28(1)
F(83)	7657(2)	12579(1)	1681(1)	38(1)
C(100)	10315(3)	11214(2)	4363(2)	29(1)
F(101)	10975(2)	11931(1)	4237(1)	66(1)
F(102)	10975(2)	10676(1)	4797(1)	39(1)
C(120)	9744(2)	8944(1)	1841(2)	21(1)
F(121)	11065(1)	8797(1)	2025(1)	33(1)
F(122)	9517(1)	8784(1)	853(1)	25(1)
F(123)	9060(2)	8365(1)	2347(1)	42(1)
H(1) ^e	8896	9838	–435	–
H(3)	6379(14)	7043(12)	–709(13)	22(2)
H(5)	4703(14)	7704(11)	1899(12)	18(2)
H(9)	8758(14)	11996(12)	3014(13)	24(2)
H(11)	10556(14)	9755(11)	3384(12)	13(2)

^a 56.2(1)% occupancy. ^b 43.8(1)% occupancy. ^c 55.3(2)% occupancy.

^d 44.7(1)% occupancy. ^e Calculated position for Si–H. This atom is not included in the least-squares refinement.

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