

The synthesis and characterisation of some Group 14 compounds containing the 2,4,6-(CF₃)₃C₆H₂, 2,6-(CF₃)₂C₆H₃ or 2,4-(CF₃)₂C₆H₃ ligands

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New (aryl)₂ECl₂ and (aryl)ECl₃ compounds [E = Si, Ge or Sn; aryl = 2,4,6-(CF₃)₃C₆H₂ (Ar), 2,6-(CF₃)₂C₆H₃ (Ar') and/or 2,4-(CF₃)₂C₆H₃ (Ar'')] were prepared by reactions of ECl₄ with 2 equivalents of ArLi or of a Ar'Li/Ar''Li mixture. The latter gives predominantly the less sterically hindered product Ar''₂ECl₂ for E = Si or Ge, but Ar'₂SnCl₂ for the larger central atom. The products were characterised by elemental analysis, ¹⁹F and (where appropriate) ¹¹⁹Sn NMR spectroscopy, and single-crystal X-ray diffraction for Ar''₂SiCl₂, ArGeCl₃, Ar₂GeCl₂, Ar''₂GeCl₂, Ar₂SnCl₂ and Ar'₂SnCl₂. For E = Si the synthesis is complicated by Cl/F exchange: besides Ar'₂SiCl₂ and Ar''₂SiCl₂, ¹⁹F NMR spectroscopy identified in solution Ar'₂SiF₂ and Ar''₂SiF₂. The latter was isolated and its X-ray structure determined. In all compounds, the E atom has a strongly distorted tetrahedral coordination, supplemented by short intramolecular E...F contacts (secondary coordination) with *o*-CF₃ group(s).

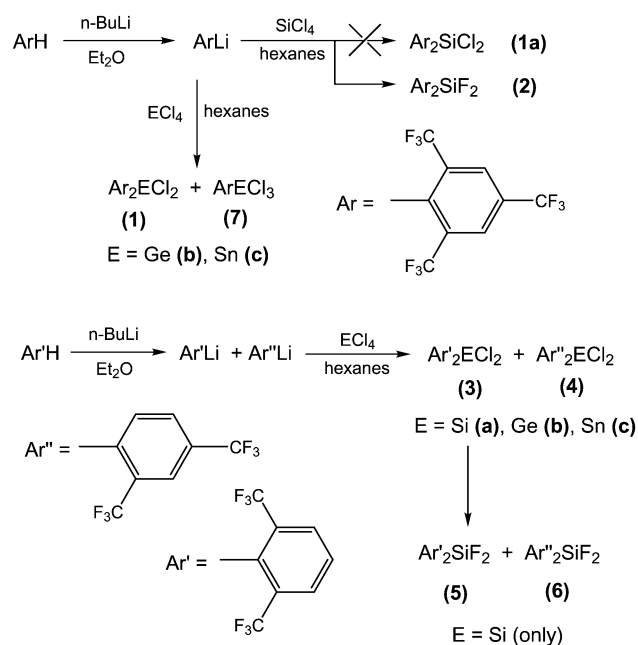
Introduction

The 'fluoromes' ligand 2,4,6-(CF₃)₃C₆H₂ (henceforth, Ar) is known for its stabilising influence in the compounds of transition metals^{1,2} and main group³ elements, including phosphorus⁴ and arsenic.⁵ This is due to the high electronegativity (compared with most aryl ligands) of this group, combined with some ability for M→C π back donation and the steric demands of the two *ortho* trifluoromethyl groups, which can hinder rotation of the ligands as well as favour low coordination numbers by protecting vacant coordination sites. The 'fluoroxyl' 2,6-(CF₃)₂C₆H₃ group (Ar'), possessing similar advantages, is used much less,^{4b,6-8} partly because lithiation of its precursor 1,3-bis(trifluoromethyl)benzene (Ar'H) can proceed in two different positions, leading to a mixture of Ar' and 2,4-(CF₃)₂C₆H₃ (Ar'') derivatives.^{4f,7,8} Recently we undertook a systematic study of a series of Group 15 compounds with Ar, Ar' and/or Ar'' ligands.⁸ The corresponding derivatives of tetravalent Group 14 elements (Si, Ge and Sn), remain comparatively unexplored, particularly simple halides and/or hydrides. Attempts to prepare Ar₂SiCl₂ from reaction of ArLi with SiCl₄, were frustrated by fluorine/chlorine exchange, yielding only Ar₂SiF₂.⁹ Similarly, Ar₂SiHF was obtained from reaction between HSiCl₃ and ArLi.¹⁰ Ar₂GeH₂ was synthesised from the germanium(II) precursor Ar₂Ge,¹¹ while ArSnPh₃ was similarly prepared from ArLi and Ph₃SnCl.¹² Various other derivatives containing Ar groups, often produced by reaction between an E(II) precursor Ar₂E (E = Ge or Sn) and oxidising agents, have been structurally characterised,^{4a,13-16} but none containing Ar' or Ar'' groups, although Ar'SnMe₃,^{7b} Ar''-SnMe₃^{7b} and Ar'₂Sn¹⁷ have been prepared. X-Ray structures of these compounds consistently reveal intramolecular E...F separations shorter than the sums of the van der Waals radii, indicative of additional weak ('secondary') coordination, or attractive electrostatic interactions, which can play an important role in stabilisation of these molecules.

In the present work we have synthesised a series of the Ar, Ar' and Ar'' derivatives of Group 14 elements (*i.e.* Si, Ge and Sn), which have been characterised by elemental analysis, ¹⁹F and (where appropriate) ¹¹⁹Sn NMR solution-state spectroscopy. X-Ray crystal structures of seven products have been determined at low temperatures.

Results and discussion

All the chloro-derivatives were prepared by reaction of the corresponding Group 14 tetrachloride ECl₄, with 2 equivalents of ArLi (from ArH), or with a mixture of Ar'Li and Ar''Li (to the total of 2 equivalents), obtained by lithiation of Ar'H (Scheme 1). In agreement with earlier reports,^{9,10} the synthesis of Ar₂SiCl₂ (**1a**) was frustrated by chlorine/fluorine exchange and the only product isolated was Ar₂SiF₂ (**2**). For Ar' and Ar'' derivatives, the Cl/F exchange was slower, and the compounds Ar'₂SiCl₂ (**3a**), Ar''₂SiCl₂ (**4a**), Ar'₂SiF₂ (**5**) and Ar''₂SiF₂ (**6**) were all detected in solution by means of ¹⁹F NMR spectroscopy (see Table 1). Of the two isomeric chlorides, the less sterically hindered **4a** was present in larger amount than **3a**, but interestingly, the opposite was observed for the fluorides: **5** was more abundant than **6**. Probably, **3a** undergoes faster Cl/F exchange than **4a**, with the overall order of exchange rates

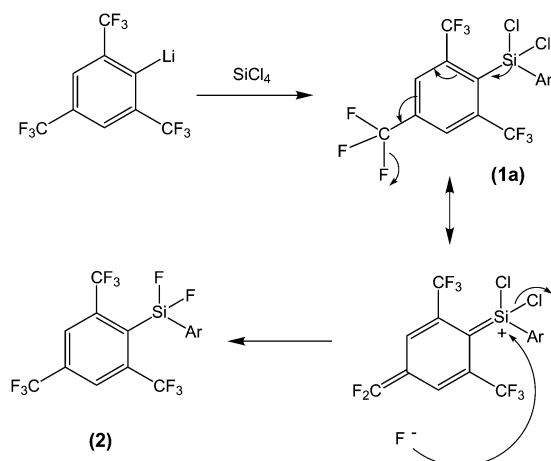


Scheme 1 Synthetic reactions (all performed at -78 °C).

Table 1 ^{19}F NMR spectra for Si(IV) compounds

	<i>o</i> -CF ₃		<i>p</i> -CF ₃ δ/ppm	Si-F	
	δ/ppm	$^5J_{\text{F-F}}/\text{Hz}$		δ/ppm	$^5J_{\text{F-F}}/\text{Hz}$
2	-57.3 t (12F)	12.8	-64.2 s (6F)	-124.5 m (2F)	12.8
3a	-58.9 s (12F)				
4a	-57.9 s (6F)		-64.2 s (6F)		
5	-57.5 t (12F)	12.3		-125.5 m (2F)	12.5
6	-59.2 t (6F)	12.4	-64.1 s (6F)	-133.0 septet (2F)	12.3

decreasing in the sequence $\text{Ar}'_2\text{SiCl}_2 > \text{Ar}''_2\text{SiCl}_2 > \text{Ar}'''_2\text{SiCl}_2$. A possible mechanism for this exchange is presented in Scheme 2. Products **4a** and **5** were isolated as colourless crystalline solids, and their X-ray structures were ascertained.

**Scheme 2** Possible mechanism of Cl/F exchange in Si derivatives.

No F/Cl exchange was observed for the germanium and tin derivatives. This difference possibly arises because the bond energy terms are more favourable for exchange in the case of silicon. The sum of a C-Cl and an Si-F bond energy term (taken from values in tetrahalides¹⁸) is 912 kJ mol⁻¹, whereas the sum of a C-F and an Si-Cl term is 887 kJ mol⁻¹. Thus the exchange should give a net energy gain of 25 kJ mol⁻¹. The corresponding sums for germanium are 792 and 827 kJ mol⁻¹ and for tin, 730 and 803 kJ mol⁻¹, respectively, giving in both cases a negative balance, -35 kJ mol⁻¹ for Ge and -73 kJ mol⁻¹ for Sn. Although the actual bond energies can be somewhat different in the present compounds because of different ligand environment, it is evident from the general trend that the Cl/F exchange is energetically more profitable, the only source of fluorine in each instance being the dissociation of a C-F bond.

The reaction of ArLi with GeCl₄ yielded a mixture of Ar₂GeCl₂ (**1b**) and ArGeCl₃ (**7b**) in a *ca.* 2 : 1 ratio. Both products were isolated and characterised by X-ray crystallography. The Ar'Li/Ar''Li mixture reacted similarly with GeCl₄ to give a solution containing predominantly Ar'₂GeCl₂ (**4b**), according to the ^{19}F NMR spectra. This compound, too, was recrystallised and characterised by X-ray crystallography. A single ^{19}F resonance at -53.8 ppm was tentatively assigned to the symmetrical disubstituted isomer Ar'₂GeCl₂ (**3b**), particularly in view of the similarity of its shift to those of the fluorines in the *o*-CF₃ groups of **1b** (-54.4 ppm) and **7b** (-52.9 ppm). There were other small impurity peaks present, however, and the possibility that the signal at -53.8 ppm could arise from the monosubstituted precursor Ar'GeCl₃, which should also give a single ^{19}F resonance, cannot be entirely discounted.

Reaction of ArLi with SnCl₄ in a 2 : 1 molar ratio led to the isolation of mainly Ar₂SnCl₂ **1c**, together with a small quantity of ArSnCl₃ **7c**. Similar treatment of the Ar'Li/Ar''Li mixture with SnCl₄ yielded a solution containing mainly the more

Table 2 ^{19}F and ^{119}Sn NMR spectra (δ/ppm) for Ge(IV) and Sn(IV) compounds

	<i>o</i> -CF ₃	$^4J_{\text{Sn-F}}/\text{Hz}$	<i>p</i> -CF ₃	^{119}Sn
1b	-54.4 s (12F)		-64.1 s (6F)	
3b	-53.8 s (12F) ^a			
4b	-58.7 s (6F)		-64.1 s (6F)	
7b	-52.9 s (6F)		-63.5 s (3F)	
1c	-56.9 s (12F) ^b	10.0	-63.9 s (6F)	-146.7
3c	-56.7 s (12F) ^b	10.0		-141.1
4c	-58.9 s (6F) ^c		-63.8 s (6F)	-97.4
7c	-55.9 s (6F) ^b	19.2	-63.0 s (3F)	-140.7

^a See Text. ^b (singlet) with Sn satellites. ^c Weak signal, Sn satellites unobserved.

Table 3 Selected bond distances (Å) and angles (°) in **7b**

Ge-C(1)	1.981(2)	C(1)-Ge-Cl(1)	113.72(4)
Ge-Cl(1)	2.1277(4)	C(1)-Ge-Cl(2)	111.89(6)
Ge-Cl(2)	2.1117(8)	Cl(1)-Ge-Cl(2)	108.46(2)
Ge...F(1)	2.909(2)	Cl(1)-Ge-Cl(1')	99.82(3)
		Cl(1')-Ge...F(1)	168.1(1)

sterically hindered disubstituted product Ar'₂SnCl₂ (**3c**), which has also been characterised crystallographically. The less hindered isomer Ar''₂SnCl₂ (**4c**) was identified in solution from its ^{19}F and ^{119}Sn NMR spectra. The larger size of the Sn atom relative to Si and Ge must reduce the steric hindrance between ligands in these ν -tetrahedral structures, which probably explains the reversal in isomeric ratio between **3** and **4**. ^{19}F and ^{119}Sn NMR data for new Ge and Sn compounds are listed in Table 2.

Molecular structures studied by single-crystal X-ray crystallography are shown in Figs. 1-4, while selected bond distances and angles are compared in Tables 3 and 4. It is noteworthy

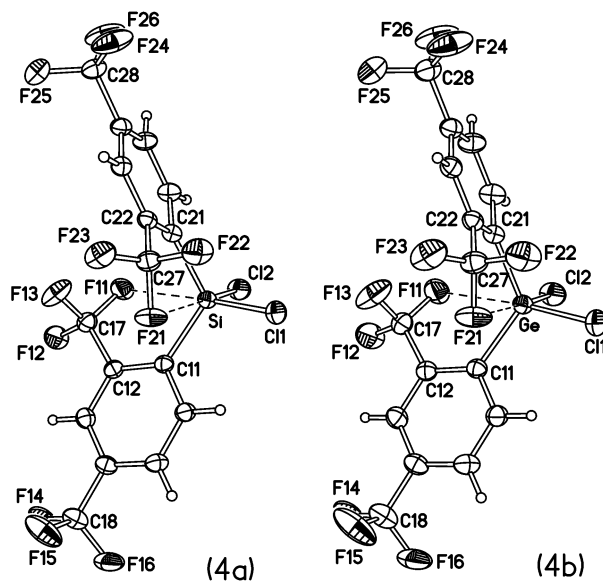
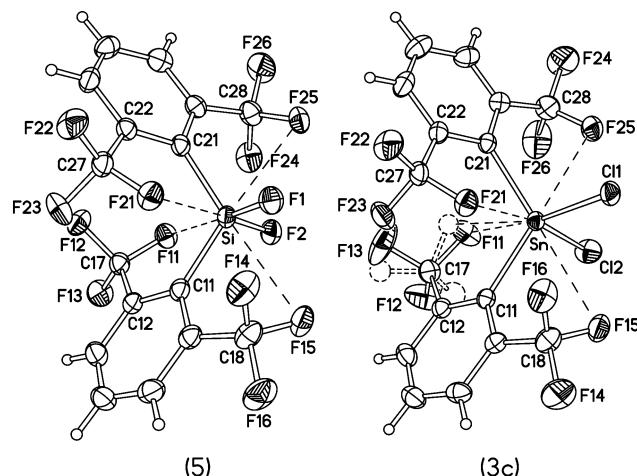
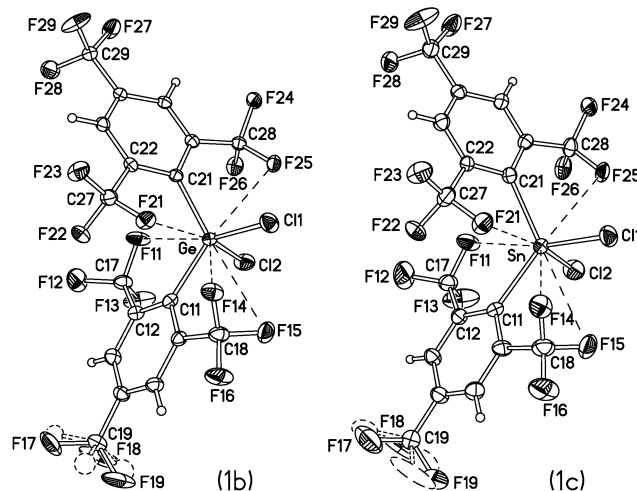
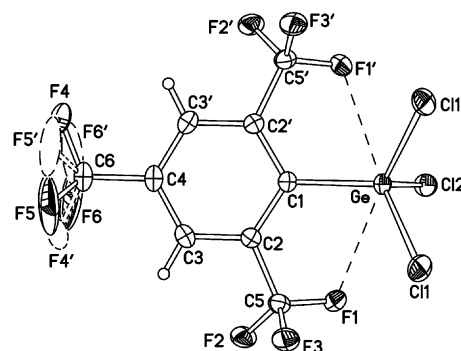
**Fig. 1** Molecular structures of Ar''₂SiCl₂ (**4a**) and Ar''₂GeCl₂ (**4b**). Henceforth atomic displacement ellipsoids are drawn at 50% probability level.

Table 4 Selected bond distances (Å) and angles (°)

Compound	4a	5	1b	4b	1c	3c
E	Si	Si	Ge	Ge	Sn	Sn
E–C(11)	1.884(2)	1.899(2)	1.997(3)	1.958(2)	2.183(6)	2.177(2)
E–C(21)	1.884(2)	1.895(2)	2.017(3)	1.957(2)	2.195(6)	2.183(2)
E–Cl(1)	2.050(1)	1.579(1) ^a	2.1513(9)	2.1484(7)	2.326(2)	2.3266(7)
E–Cl(2)	2.048(1)	1.569(1) ^a	2.1174(9)	2.1496(7)	2.298(2)	2.3372(7)
C(11)–E–C(21)	117.47(8)	115.53(8)	120.07(12)	119.95(10)	120.3(2)	115.73(7)
C(11)–E–Cl(1)	108.88(6)	113.17(8) ^a	113.46(9)	107.77(7)	119.0(2)	120.66(6)
C(11)–E–Cl(2)	108.22(7)	105.27(7) ^a	103.34(9)	108.65(7)	96.1(2)	98.18(6)
C(21)–E–Cl(1)	108.00(7)	104.65(7) ^a	96.65(9)	108.26(7)	103.8(2)	100.96(6)
C(21)–E–Cl(2)	109.29(6)	113.76(7) ^a	118.17(9)	108.21(7)	113.9(2)	121.53(6)
Cl(1)–E–Cl(2)	104.17(5)	104.06(6) ^a	104.33(4)	102.64(3)	102.58(7)	100.11(3)
E...F(11)	2.901(2)	2.793(1)	2.757(2)	2.860(2)	2.720(4)	2.686(2)
E...F(21)	2.882(2)	2.745(1)	2.809(2)	2.848(2)	2.799(4)	2.768(1)
E...F(14)	–	–	3.379(2)	–	3.344(4)	–
E...F(15)	–	3.054(1)	3.399(2)	–	3.382(4)	3.203(2)
E...F(25)	–	3.073(1)	3.010(2)	–	2.979(3)	3.002(2)
Cl(1)–E...F(11)	174.30(4)	172.60(6)	167.77(5)	172.45(5)	170.6(1)	168.26(5)
Cl(2)–E...F(21)	176.92(4)	173.14(5)	169.32(5)	177.20(4)	170.3(1)	169.33(3)
C(11)–E...F(25)	–	160.3(1)	164.5(1)	–	164.6(2)	160.69(6)
C(21)–E...F(15)	–	160.5(1)	152.6(1)	–	154.1(2)	153.91(6)

^a F ligands instead of Cl.**Fig. 2** Molecular structures of Ar'₂SiF₂ (**5**) and Ar'₂SnCl₂ (**3c**), showing the disorder of one *o*-CF₃ group in **3c**.**Fig. 3** Molecular structures of Ar₂GeCl₂ (**1b**) and Ar₂SnCl₂ (**1c**), showing the disorder of one *p*-CF₃ group.

that compound **4a** is crystallographically isostructural (isomorphous) with **4b**, and **1b** with **1c**. In molecules **1b** and **1c**, the *para*-CF₃ group of *one* Ar ligand is rotationally disordered;

**Fig. 4** Molecular structure of ArGeCl₃ (**7b**), showing the disorder of the *p*-CF₃ group. Atoms generated by the mirror plane are primed.

such disorder has been frequently observed for both Group 14^{10,14c} and Group 15^{3c,d,8} derivatives of Ar. In **3c**, one *ortho*-CF₃ group is rotationally disordered.

Molecules of all the diaryl-dihalo compounds have no crystallographic symmetry and show a distorted tetrahedral coordination of the central atom (E), with the C–E–C bond angle the widest and the Cl–E–Cl angle (or F–E–F in **5**) the smallest. This distortion can be explained by the steric repulsion between bulky aryl groups. However, the difference between these two angles is higher in **4b** than in **4a**, and in **1c** than in **1b**, *i.e.* the distortion *increases* with the increase of the E atom size, which should apparently relieve the steric overcrowding. It is also noteworthy that in Ar' derivatives **4a** and **4b** all four Cl–E–C angles are similar, while in Ar and Ar' derivatives **1b,c** and **3c** two Cl–E–C angles are much wider than the other two. The F–E–C angles in **5** show a similar, but more regular, distortion. These distortions are obviously due to the fact that both Ar and Ar' ligands have two CF₃ groups in *ortho* positions to E and thus cause more steric overcrowding than Ar'', which has only one *ortho*-CF₃. Similar asymmetry has been observed earlier for Ar₂EX(Y) compounds, where E = Si or Sn, X = F or Cl, and Y is a unidentate ligand.^{9,10,14} Thus, in Ar₂SiF₂ the F–Si–C angles vary from 102.8(2) to 112.8(2)°,⁹ and in Ar₂SiHF from 105.9(1) to 112.5(1)°.¹⁰ Even larger variations occur in Ar₂Sn(Cl)(μ₂O)Sn(Cl)Ar₂ (Cl–Sn–C angles 99.1(1)–119.7(1)°)^{14a} and in Ar₂Sn(F)L, where L = *N*-(1-adamantyl)-[[pentafluoro-2-propenyl]thio]amine, C₁₃H₁₅F₅NS (C–Sn–F angles 90.1(2)–107.7(2)°).^{14c}

Molecule **7b** lies on a crystallographic mirror plane normal to the benzene ring and passing through the Ge, Cl(2), C(1) and C(4) atoms. Here the Ge atom also has distorted tetrahedral coordination and the CF₃ group in the *para*-position to the Ge is disordered between two orientations (related in this case by the mirror plane).

The E–F and E–Cl bonds in diaryldihalogenides are 0.03–0.05 Å longer than in the corresponding Group 14 tetrahalogenides, *viz.* SiF₄ (1.540(1) Å),^{19a} SiCl₄ (2.008(1) Å),^{19b} GeCl₄ (2.096(2) Å in the crystal,²⁰ 2.113(3) Å in the gas phase²¹) and SnCl₄ (2.279(3) Å).²² The lengthening is obviously due to the replacement of the halogen by a less electronegative aryl ligand, and correspondingly the effect is smaller in the monoaryltrichloride **7b** (*ca.* 0.02 Å) than in the diaryl analogue **1b**, and it increases with decreasing number of electron-withdrawing CF₃ groups (compare **1b** with **4b**, and **1c** with **3c**).

Structural studies of Group 14 compounds containing *only* aryl and halogen ligands, are scarce, especially for Si and Ge. The Si–C bonds in Ph₃SiCl (1.862 Å)²³ are slightly shorter than in **4a** (1.884(2) Å), while still shorter Si–C bonds (*ca.* 1.84 Å) were found in two compounds where Si atoms are incorporated into fused-ring systems, *viz.* 9,9,10,10-tetrachloro-9,10-disila-9,10-dihydroanthracene²⁴ and 9,9-dichloro-9-sila-9-hydrofluorene.²⁵ The mean Si–C bond distance in **5** (1.897(2) Å) can be compared with those in **2** (1.901(5) Å),⁹ Ar₂SiHF (1.906(5) Å),¹⁰ and *o*-Tol₃SiF (1.861 Å).²⁶ Finally, comparison can be made with tetraaryl derivatives, *e.g.* SiPh₄²⁷ and Si(*p*-Tol)₄²⁸ with Si–C distances 1.877 and 1.873(3) Å, respectively. Thus halogeno ligands have no definite effect on the Si–C(aryl) bonds, while CF₃ substituents in the aryl ligands tend to weaken them, probably by diminishing the electron density on the benzene ring and hence the π back-donation.

No compound with Ge–C(aryl) and Ge–Cl bonds has been structurally characterised before, except 10,10-dichloro-10-germa-9-oxa-9,10-dihydroanthracene,²⁹ where the Ge–C bonds of 1.890 Å are incorporated into a fused-ring system. The Ge–C bonds in Ar derivative **1b** are 0.05 Å longer than in its Ar' analogue **4b**, and in the latter nearly the same as in tetra-aryl compounds GePh₄³⁰ (1.957(4) Å) and Ge(*p*-Tol)₄²⁸ (1.948(5) Å). On the other hand, the Sn–C(Ar) bonds in **1c** are less than 0.01 Å longer than Sn–C(Ar') in **3c**, and in both cases are substantially weaker than in Ph₂SnCl₂ (2.113(5) Å),³¹ or (mes)₂SnCl₂, a non-fluorinated analogue of **1c** (2.117 Å).³² Thus a CF₃ group in an *ortho* position affects an E–C bond much more than one in a *para* position, which can be attributed to higher steric overcrowding and direct CF₃ ··· E interactions (see below), rather than to mere electron withdrawing by this group. Indeed, bulkier *ortho*-substituents cause similar Sn–C(aryl) bond lengths even in the absence of fluorination, *e.g.* in (2,4,6-Pr^t₃C₆H₂)₂SnCl₂ (2.147(4) Å)³³ and (2,4,6-Bu^t₃C₆H₂)₂SnCl₂ (2.198(4) Å).³⁴

Indeed, a salient feature of all the compounds studied herein is short intramolecular E ··· F contacts with *o*-CF₃ groups of the aryl ligands. Such contacts have been observed earlier in numerous Group 14 derivatives,^{3a,9–16} as well as in some Group 15 compounds.⁸ Although the van der Waals radii of Group 14 elements are difficult to determine directly (because these atoms are seldom exposed sufficiently to participate in intramolecular contacts), a variety of indirect techniques gives consistent values of 2.1 Å for Si and Ge and 2.25 Å for Sn.³⁵ Thus (assuming a radius of 1.5 Å for F), each molecule contains 2 to 5 E ··· F contacts well below the sum of the van der Waals radii, which are listed in Tables 3 and 4. These contacts can be compared also with the sums of “equilibrium” radii, the sums of which correspond to the minimum of the atom–atom potential curve and hence the point of zero van der Waals force,³⁶ *viz.* 2.26 Å (Si), 2.32 Å (Ge), 2.46 Å (Sn) and 1.65 Å (F).³⁵ Thus, insofar as van der Waals forces are concerned, the E ··· F interactions should be substantially repulsive. They, however, can be counterbalanced by electrostatic attraction (E and F

carrying opposite charges) and/or weak (“secondary”) coordination, *i.e.* donation of lone electron pairs of F into the outer-shell orbitals of E. The latter interpretation agrees with relatively high chemical stability of the compounds. It is also noteworthy that the Ge ··· F distances in **4b** are *shorter* by 0.04 Å than Si ··· F in the isostructural **4a**, which contradicts the simple repulsive model (the Ge atom is larger than Si), but can be explained by a weakly-bonding model (the outer orbitals of Ge are more diffuse and hence more suitable for interaction with F).

In the Ar' derivatives **4a** and **4b**, the coordination of Si and Ge is complemented to (4 + 2) by the F(11) and F(21) atoms (belonging to different Ar' ligands), approximately in *trans* positions to the chloro ligands; there is no other E ··· F contact within 3.7 Å. A similar pair of short E ··· F contacts exists in each of the bis-Ar and bis-Ar' derivatives also (which can be regarded as evidence of specific character of these interactions), but the presence of two more *o*-CF₃ groups gives rise to additional, somewhat longer, E ··· F contacts. In the Ar' derivatives **5** and **3c**, these “additional” *o*-CF₃ groups contribute one contact each, *viz.* E ··· F(15) and E ··· F(25), both approximately in *trans* positions to E–C bonds. The resulting (4 + 4) coordination of E can be described as a tetrahedron capped on each face. The same description was applied previously to the structures of Ar₂SiF₂⁹ and Ar₂SiHF.¹⁰ In **5**, the E ··· F(15) and E ··· F(25) distances are almost equal, while in **3c** they differ by 0.2 Å. This non-equivalence is obviously connected with strongly asymmetric distortions of bond angles (between covalent bonds) at the Sn atom, the causes of which are unclear. In **1b** and **1c**, one of the *o*-CF₃ groups adopts a different orientation: instead of one F atom pointing roughly towards the E atom, there are two longer contacts, E ··· F(14) and E ··· F(15), the E atom lying close to the bisectral plane of the F(14)C(18)F(15) angle.

Molecule **7b** contains two (symmetrically related) Ge ··· F(1) contacts in *trans* positions to Cl(1) and its equivalent. It is noteworthy that the Ge–Cl(1) bond is 0.016 Å longer than Ge–Cl(2), which suggests a certain (if small) covalent character of the Ge ··· F(1) interaction.

Experimental

All manipulations, including NMR sample preparation, were carried out either under an inert atmosphere of dry nitrogen or *in vacuo*, using standard Schlenk procedures or a glovebox. Chemicals of the best available commercial grades were used, in general without further purification. ¹⁹F NMR spectra were recorded on a Varian Mercury 200, Varian VXR 400, or Varian Inova 500 Fourier-transform spectrometer at 188.18, 376.35, and 470.26 MHz, respectively. ¹¹⁹Sn NMR spectra were recorded on the Varian Inova 500 spectrometer at 186.37 MHz. Chemical shifts were measured relative to external CFCl₃ (¹⁹F) or Me₄Sn (¹¹⁹Sn), with the higher frequency direction taken as positive. Microanalyses were performed by the microanalytical services of the Department of Chemistry, University of Durham.

Syntheses

Lithiation reactions were carried out as described previously.^{4,8,37} **WARNING:** It is important in these reactions to keep a slight excess of the hydrocarbon (ArH or Ar'H) to *n*-butyllithium at all times, to avoid any attack on a CF₃ group and the possible **explosive** formation of LiF.

Ar₂SiF₂ (2). A solution of ArLi (100 ml, 30 mmol) in diethyl ether was added dropwise to a solution of SiCl₄ (2.5 g, 1.72 ml, 15 mmol) in hexanes at –78 °C. The solution was allowed to warm to room temperature and stirred for 5 h. A precipitate formed. The solution was filtered and solvents were removed

under vacuum, leaving a yellow oil. This oil was distilled under reduced pressure (0.01 Torr), giving a yellow oil, bp 85 °C. Yield 1.8 g (19% based on ArH). Anal. Calc. for C₁₈H₄F₂₀Si: C 34.41, H 0.64. Found: C 32.9, H 0.75%.

Ar'₂SiCl₂ (4a). An Ar'/Li/Ar''Li (50 ml, 20 mmol) solution in diethyl ether was added dropwise to a solution of SiCl₄ (1.7 g, 10 mmol) in pentane at -78 °C. The solution was allowed to warm to room temperature and stirred for 3 h. The precipitated LiCl was filtered off and the solvents and excess SiCl₄ were removed under vacuum, leaving a yellow sticky oil which was distilled under reduced pressure (0.01 Torr). The fraction collected at 120 °C was recrystallised from pentane, yielding 1.8 g (32.4%) of **4a**. Anal. Calc. for C₁₆H₆Cl₂F₁₂Si: C 36.6, H 1.15. Found: C 36.8, H 1.24%.

Ar'₂SiF₂ (5). An Ar'/Li/Ar''Li (50 ml, 40 mmol) solution in diethyl ether was added dropwise to a solution of SiCl₄ (3.39 g, 2.3 ml, 20 mmol) in hexanes at -78 °C. The solution was allowed to warm to room temperature and stirred for 3 h. The precipitated LiCl was filtered off, and the solvents and excess SiCl₄ were removed under vacuum, leaving a yellow oil (**4a**) and a white solid. The solid was washed three times with hexanes and purified by sublimation under vacuum, giving white crystals of **5**. Yield: 2.5 g (12.7%). Anal. Calc. for C₁₆H₆F₁₄Si: C 39.04, H 1.23. Found: C 38.3, H 1.24%.

Ar₂GeCl₂ (1b) and ArGeCl₃ (7b). An ArLi (50 ml, 30 mmol) solution in diethyl ether was added dropwise to a GeCl₄ solution (3.2 g, 1.71 ml, 15 mmol) in hexanes at -78 °C. The solution was allowed to warm to room temperature and stirred for 4 h. A white precipitate of LiCl appeared and was filtered off. The solvents and excess GeCl₄ were removed under vacuum, leaving a yellow oil and a white solid. The oil was filtered and then distilled under reduced pressure (0.01 Torr), giving a colourless oil, bp 85 °C. Analysis showed that this was impure but contained mainly **7b**. Yield: 2.6 g (19%). After one month, fine crystals of **7b** formed. There was insufficient material for further analysis but a single-crystal X-ray structure determination was carried out. The filtered-off solid was washed three times with hexanes, yielding 3.17 g (30%) of **1b**. Crystals were grown from dichloromethane. Anal. Calc. for C₁₈H₄Cl₂F₁₈Ge: C 30.64, H 0.57. Found C: 30.59, H 0.58%.

Ar'₂GeCl₂ (4b). A solution of Ar'/Li/Ar''Li (60 ml, 40 mmol) in diethyl ether was added dropwise to a solution of GeCl₄ (4.29 g, 2.6 ml, 20 mmol) in diethyl ether at -78 °C. The solution was allowed to warm to room temperature and stirred for 2 h. A white precipitate of LiCl formed. The solution was filtered and the solvents were removed under vacuum, leaving a black oil. The oil was distilled under reduced pressure (0.01 Torr), and a fraction was collected at 80–90 °C. Yield: 5.8 g (51%). After one week, small crystals formed. Anal. Calc. for C₁₆H₆Cl₂F₁₂Ge: C 33.7, H 1.06, Cl 12.45. Found: C 32.4, H 1.53, Cl 12.8%.

Ar₂SnCl₂ (1c) and ArSnCl₃ (7c). An ArLi (50 ml, 30 mmol) solution in diethyl ether was added slowly to a solution of SnCl₄ (3.90 g, 2.75 ml, 15 mmol) in hexanes. The solution was then allowed to warm to room temperature and stirred for 5 h. A white precipitate of LiCl appeared. The solution was filtered and the solvents were removed under vacuum, leaving a brown oil and a solid. The oil was filtered and distilled under reduced pressure, giving a yellow oil of **7c** (bp 85 °C) in a small quantity. The solid (**1c**) was washed three times with hexanes, dried under vacuum and recrystallised from diethyl ether. Yield 3.8 g (51%). Anal. Calc. for C₁₈H₄Cl₂F₁₈Sn: C 28.76, H 0.54. Found: C 28.60, H 0.78%.

Ar'₂SnCl₂ (3c) and Ar''₂SnCl₂ (4c). An Ar'/Li/Ar''Li (250 ml, 94 mmol) solution in diethyl ether was added dropwise to

4a		5		1b		4b		7b		1c		3c	
205552		205553		205554		205556		205555		205557		205558	
Formula	C ₁₆ H ₆ Cl ₂ F ₁₂ Si	C ₁₆ H ₆ F ₁₄ Si	C ₁₈ H ₄ Cl ₂ F ₁₈ Ge	C ₁₆ H ₆ Cl ₂ F ₁₂ Ge	C ₉ H ₂ Cl ₃ F ₉ Ge	C ₁₈ H ₄ Cl ₂ F ₁₈ Sn	C ₁₆ H ₆ Cl ₂ F ₁₂ Sn						
Formula weight	525.20	492.30	705.70	569.70	460.05	751.80	615.80						
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic						
Space group	P2 ₁ /n (no. 14)	P1̄ (no. 2)	P2 ₁ /c (no. 14)	P2 ₁ /n (no. 14)	Pnma (no. 62)	P2 ₁ /c (no. 14)	P1̄ (no. 2)						
Crystal size /mm	0.40 × 0.40 × 0.26	0.32 × 0.25 × 0.12	0.34 × 0.20 × 0.08	0.4 × 0.12 × 0.12	0.40 × 0.28 × 0.28	0.46 × 0.22 × 0.06	0.5 × 0.4 × 0.38						
T/K	120	120	120	150	120	150	150						
d/Å	10.429(7)	8.221(2)	8.3893(6)	10.547(2)	11.284(1)	8.465(1)	8.783(2)						
b/Å	11.534(7)	9.644(2)	30.043(2)	11.661(2)	12.541(1)	30.409(4)	9.095(2)						
c/Å	16.608(10)	12.267(3)	8.6373(6)	16.636(3)	9.710(3)	8.724(1)	12.162(3)						
α/°	90.00	98.48(1)	90.00	90.00	90.00	90.00	81.697(4)						
β/°	107.84(2)	100.30(1)	96.433(1)	108.21(1)	90.00	96.635(2)	83.970(4)						
γ/°	90.00	112.50(1)	90.00	90.00	90.00	90.00	82.135(4)						
V/Å ³	1902(2)	858.8(4)	2163.2(3)	1943.7(6)	1374.1(5)	2230.6(5)	948.7(4)						
Z	4	2	4	4	4	4	2						
D _c /g cm ⁻³	1.834	1.904	2.167	1.947	2.224	2.239	2.156						
μ/mm ⁻¹	0.520	0.284	1.826	1.964	2.906	1.543	1.744						
Reflections, total	17420	6314	16108	14919	11660	11861	7949						
Reflections, unique	5059	3601	4795	5376	1921	4298	5003						
R _{int}	0.032	0.022	0.042	0.033	0.022	0.052	0.015						
Refls. with I > 2σ(I)	4018	2970	3860	3900	1743	3130	4708						
R [I > 2σ(I)]	0.036	0.034	0.041	0.036	0.022	0.052	0.025						
wR ₂ (F ²), all data	0.094	0.085	0.087	0.087	0.056	0.117	0.069						
No. of variables	304	280	365	304	125	345	299						

Table 5 Crystallographic data

a solution of SnCl₄ (12.24 g, 8.63 ml, 47 mmol) at room temperature. The solution was stirred for 4 h. A white precipitate of LiCl appeared. The brown solution was filtered and solvents and excess SnCl₄ were removed under vacuum, leaving a brown sticky oil and a brown solid. The oil (**4c**) was filtered, the solid washed with pentane and dichloromethane and dried *in vacuo*, giving a beige solid (**3c**), which was recrystallised from pentane and diethyl ether. Yield (**3c**) 3.48 g (57%). Anal. Calc. for C₁₆H₆Cl₂F₁₂Sn: C 31.21, H 0.98. Found C 29.7, H 1.26%.

X-Ray crystallography

Single crystal X-ray diffraction experiments were carried out at low temperature, 120 or 150 K, using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) on a Bruker SMART (CCD 1 K area detector) diffractometer equipped with a Cryostream N₂ open-flow cooling device.³⁸ Series of narrow ω -scans (0.3°) were performed at several ϕ -settings in such a way as to cover a sphere of reciprocal space to a maximum resolution between 0.70 and 0.77 \AA . Cell parameters were determined and refined using the SMART software,³⁹ and raw frame data were integrated using the SAINT program.⁴⁰ The structures were solved by direct methods and refined by full-matrix least squares on F^2 using SHELXTL software.⁴¹ Crystal data and experimental details are listed in Table 5. For structure **4b**, the reflection intensities were corrected by numerical integration based on measurements and indexing of the crystal faces (using SHELXTL software).⁴¹ For the remaining structures, the absorption corrections were carried out by the multi-scan method, based on multiple scans of identical and Laue equivalent reflections (using the SADABS software).⁴² Non-hydrogen atoms were refined anisotropically, except for the disordered component of structure **1b**. For structures **4a, b** and **7b** the hydrogen atoms were found in difference Fourier maps. For structures, **1b, c**, **3c** and **5** the hydrogen atoms were positioned geometrically and refined using a riding model.

CCDC reference numbers 205552–205558.

See <http://www.rsc.org/suppdata/dt/b3/b302544f/> for crystallographic data in CIF or other electronic format.

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