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Hypervalent neutral O-donor ligand complexes of silicon tetrafluoride, comparisons with other group 14 tetrafluorides and a search for soft donor ligand complexes[†]

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The hypervalent adducts of SiF_4 , *trans*- $[SiF_4(R_3PO)_2]$ (R = Me, Et or Ph),

cis-[SiF₄{R₂P(O)CH₂P(O)R₂}] (R = Me or Ph), cis-[SiF₄(pyNO)₂] and trans-[SiF₄(DMSO)₂] have been prepared from SiF_4 and the ligands in anhydrous CH_2Cl_2 , and characterised by microanalysis, IR and VT multinuclear (¹H, ¹⁹F, ³¹P) NMR spectroscopy. The NMR studies show extensive dissociation at ambient temperatures in non-coordinating solvents, but mixtures of cis and trans isomers of the monodentate ligand complexes were identified at low temperatures. Crystal structures are reported for $trans-[SiF_4(R_3PO)_2]$ (R = Me or Ph), and $cis-[SiF_4(pyNO)_2]$. The GeF₄ analogues $cis-[GeF_4]R_2P(O) (CH_2)_n P(O)R_2$ [R = Me or Ph, n = 1; R = Ph, n = 2) were similarly characterised and the structures of cis-[GeF₄{R₂P(O)CH₂P(O)R₂}] (R = Me or Ph) determined. The reaction of R₃AsO (R = Me or Ph) with SiF₄ does not give simple adducts, but forms $[R_3AsOH]^+$ cations as fluorosilicate salts. SiF₄ adducts of some ether ligands (including THF, 12-crown-4) were also characterised by ¹⁹F NMR spectroscopy in solution at low temperatures (~190 K), but are fully dissociated at room temperature. Attempts to isolate, or even to identify, SiF₄ adducts with phosphine or thioether ligands in solution at 190 K were unsuccessful, contrasting with the recent isolation and detailed characterisation of GeF_4 analogues. The chemistry of SiF_4 with these oxygen donor ligands, and with soft donors (P, As, S or Se), is compared and contrasted with those of GeF₄, SnF₄ and SiCl₄. The key energy factors determining stability of these complexes are discussed.

Introduction

Hypervalent silicon compounds remain an area of great research activity. The majority of examples are organosilicon derivatives or contain anionic bi- or poly-dentate nitrogen or oxygen donor ligands.¹⁻³ Silicon tetrahalides are strong Lewis acids and their complexes with neutral donor ligands constitute a further group of hypervalent compounds,⁴ although their study, particularly those with SiF₄, has been neglected in recent years. The tetrafluorides of the Group 14 elements exhibit the extremes of chemical behaviour.⁴ The lightest member, CF₄, is an extremely inert gas, whilst the heaviest, PbF₄, is a polymeric solid containing six-coordinate lead, only obtained pure by high pressure fluorination.⁵ PbF₄ is a potent fluorinating agent and is incompatible with neutral ligands, and [PbF₆]²⁻ is the only derivative known. The three intermediate members are SiF₄ and GeF₄, which are molecular monomers in gas, liquid and solid phases,^{6,7} and SnF₄ which is an

octahedral polymer.⁵ These three fluorides readily behave as Lewis acids towards F⁻, forming $[MF_6]^{2-}$ (M = Si, Ge, Sn) and $[MF_5]^{-}$ anions.^{8,9} We have recently reported the synthesis, spectroscopic and structural characterisation of a range of neutral ligand adducts of SnF4 and GeF4 with hard N- or O-donor ligands,10-13 and the first examples with soft P- or S-donor ligands.^{11,14,15} Thoroughly characterised complexes of SiF4 with neutral ligands are relatively few and the majority are with N-donor ligands, including $[SiF_4(2,2'-bipy)]$, $[SiF_4(1,10-phen)]$, trans- $[SiF_4(py)_2]$, $[SiF_4(Me_2NCH_2SiF_3)_2],\ [SiF_4\{Me_2N(CH_2)_2NMe_2\}],^{16,17}$ and we have recently reported the first example of displacement of a fluoride ion in $[SiF_3(Me_3-tacn)]^+$ (Me_3-tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane).17 Five- and six-coordinate adducts of SiF₄ with N-heterocyclic carbenes have been described very recently and calculations suggest these should be more stable than amine or phosphine adducts,18 but relatively little is known about O-donor ligand complexes, which appear to be of limited stability.^{19,20} There are also examples of secondary coordination of crown ethers (i.e. the crown is hydrogen bonded to the siliconcoordinated water molecules) in $[SiF_4(H_2O)_2]$ crown (crown = 15crown-5, 18-crown-6).²¹ The only report of soft donor ligand complexes with SiF₄ is SiF₄·*n*PMe₃ (n = 1 or 2) formed at very low

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Scheme 1 Selected reactions of SiF₄.

temperatures in the absence of solvent and identified by tensimetric measurements and Raman spectroscopy.²² The aim of the present study was to investigate the formation of the SiF₄ adducts with O-donor ligands, to establish if soft donor ligands (P, As or S) form adducts, and to draw comparisons with results from our recent work on SnF₄ and GeF₄ adducts; there are notable differences compared with SiCl₄ adducts which will also be discussed.

Results and discussion

In our previous studies of GeF₄ complexes,¹³⁻¹⁵ we found that the complex [GeF₄(MeCN)₂], made by bubbling GeF₄ through anhydrous MeCN, was a convenient solid molecular synthon for other germanium fluoride complexes. However, a suitable analogue does not exist for SiF₄—no solid complex forms between SiF₄ and MeCN at ambient temperatures, and as noted below, ether adducts are only formed at low temperatures. Hence synthesis of SiF₄ adducts was normally achieved by bubbling SiF₄ into a solution of the appropriate ligand in anhydrous CH₂Cl₂ or toluene (see Scheme 1).

O-Donor ligands—phosphine oxides. Passing SiF₄ into solutions of OPMe₃ or OPEt₃ in anhydrous CH₂Cl₂ or OPPh₃ in toluene precipitated [SiF₄(OPR₃)₂] ($\mathbf{R} = \mathbf{Me}$, Et, Ph) in good yield as white solids. Crystals of the same complexes were obtained by refrigerating the filtrates from the preparations. The crystal structures of two examples [SiF₄(OPMe₃)₂] and [SiF₄(OPPh₃)₂] (Tables 1 and 2, Fig. 1 and 2) showed them to contain six-coordinate silicon with very close to octahedral geometry and to

Table 1 Selected bond lengths (Å) and angles (°) for [SiF₄(OPMe₃)₂]

Si1–F1	1.6719(9)	Si1-O1	1.8218(11)
Si1–F2	1.6660(9)	P1-O1	1.5267(11)
P1–C	1.780(2)-1.790(2)	_	_ ``
F1-Si1-F2	90.56(5)	P1-O1-Si1	131.44(7)
F1-Si1-O1	88.92(5)	F2-Si1-O1	90.66(5)

Table 2 Selected bond lengths (Å) and angles (°) for $[SiF_4(OPPh_3)_2]$

Si1-F1 1.667(2) Si1-O1 1.832(3) Si1-F2 1.654(2) Si1-O2 1.842(3) Si1-F3 1.660(3) P1-O1 1.519(3) Si1-F4 1.659(2) P2-O2 1.519(3)	
Si1-F2 1.654(2) Si1-O2 1.842(3) Si1-F3 1.660(3) P1-O1 1.519(3) Si1-F4 1.659(2) P2-O2 1.519(3)	
Si1-F3 1.660(3) P1-O1 1.519(3) Si1-F4 1.659(2) P2-O2 1.519(3)	
Si1–F4 1.659(2) P2–O2 1.519(3)	
$S_{12}-F_5$ 1.657(2) $S_{12}-O_3$ 1.848(3)	
Si2–F6 1.654(2) P3–O3 1.518(3)	
F1–Si1–F2 89.71(13) F3–Si1–F4 90.47(13)	
F2–Si1–F3 89.87(13) F4–Si1–F1 89.94(13)	
O1-Si1-F 89.09(13)-91.10(13) O2-Si1-F 88.96(13)-90.85	(13)
P1-O1-Si1 137.86(18) P2-O2-Si1 138.66(18)	
F5–Si2–F6 89.76(12) F5–Si2–O3 89.02(12)	
F6–Si2–O3 90.16(12) P3–O3–Si2 142.47(19)	



Fig. 1 Structure of the centrosymmetric *trans*-[SiF₄(OPMe₃)₂] showing the atom numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: a = 1 - x, 2 - y, 2 - z.

be *trans* isomers. The former is isomorphous with the germanium analogue,¹² but the [SiF₄(OPPh₃)₂] crystallised in space group $P\bar{1}$ with, unusually, Z = 3, whereas [GeF₄(OPPh₃)₂]·2CH₂Cl₂ crystallised in the space group $P2_1/n$.¹² The Si–F distances fall within a narrow range, 1.654(2)–1.6719(9) Å, with Si–O at 1.8218(11) Å in *trans*-[SiF₄(OPMe₃)₂] and 1.832(3)–1.848(3) Å in *trans*-[SiF₄(OPPh₃)₂]. The P–O distances are essentially identical to those in the germanium analogues¹² and markedly longer than in

88.60(17)

132.6(3)



Fig. 2 Structure of *trans*-[SiF₄(OPPh₃)₂]. There are two molecules in the asymmetric unit. The Sil centred molecule shown here has no symmetry, and the Si2 centred molecule has a crystallographic centre. Displacement ellipsoids are shown at the 50% probability level and H atoms are omitted for clarity. Only the *ipso* C atoms are labelled with the numbering going cyclically round the ring.

the ligands (OPMe₃ 1.489(6), OPPh₃ 1.483(2) Å).²³ The IR spectra show strong P-O stretches, significantly lowered from the values in the ligands,¹² and intense broad $v(SiF) \sim 800 \text{ cm}^{-1}$, consistent with expectation for *trans* isomers (theory, E_{μ}). Solution NMR measurements show the complexes are extensively dissociated in solution at 295 K, and we note that evaporation of CH₂Cl₂ solutions of $[SiF_4(OPPh_3)_2]$ by gentle heating results in a residue identified as OPPh₃, suggesting this complex is largely dissociated into its constituents in solution at room temperature. trans- $[SiF_4(OPPh_3)_2]$ fails to exhibit a ${}^{19}F{}^{1}H{}$ spectrum at 295 K, but on cooling to 243 K, a singlet appears at $\delta = -139$ (s) and at 190 K silicon satellites on the resonance are resolved (${}^{1}J_{\text{SiF}} = 145 \text{ Hz}$). The ${}^{31}P{}^{1}H$ NMR spectrum shows only some free OPPh₃ at 295 K, but at 190 K, a mixture of free and coordinated ($\delta = 36$) phosphine oxide are present. There is no evidence for the presence of a cis isomer, possibly disfavoured on steric grounds on the small silicon centre. The ¹⁹F{¹H} and ³¹P{¹H} NMR spectra of $[SiF_4(OPR_3)_2]$ (R = Me or Et) in CH_2Cl_2 solution show broad singlets consistent with exchanging systems at 295 K, but on cooling the lines split and sharpen. For [SiF₄(OPMe₃)₂] at 200 K, we observed in the ¹⁹F{¹H} spectrum a singlet at $\delta = -116.6$ (s, ¹J_{SiF} = 130 Hz), and two triplets at -115.2 (t, ${}^{2}J_{FF} \sim 7$ Hz, ${}^{1}J_{SiF} = 140$ Hz), -128.5 (br,t, $^{2}J_{\text{FF}} = 7$ Hz, $^{1}J_{\text{SiF}} = 130$ Hz), consistent with *trans* and *cis* isomers in the ratio ~5:1, and two corresponding ${}^{31}P{}^{1}H$ resonances were observed at 60.2 and 61.4 ppm. The spectra of $[SiF_4(OPEt_3)_2]$ (experimental section) were similar except that the trans : cis isomer ratio was ~10:1 and the small ${}^{2}J_{FF}$ couplings in the *cis* isomer were not resolved. Overall the behaviour resembles that observed for $[GeF_4(OPR_3)_2]$ ¹² but the silicon systems are markedly more dissociated in solution. Some R₃PO adducts of SiCl₄ with 2:1 and 4:1 $R_3PO:SiCl_4$ have been reported to be formed from benzene solutions, and identified by microanalysis.^{19c,20} In CH₂Cl₂ solution under similar conditions to those used above with SiF₄, we find that SiCl₄ reacts with R_3PO to form R_3PCl_2 , PR_3 and $[SiCl_4(PR_3)_2]$ identified by *in situ* ³¹P{¹H} NMR studies, with no resonances attributable to phosphine oxide adducts evident (see experimental section); the systems are also extremely sensitive to moisture. SiHCl₃ and Si₂Cl₆ are commonly used to convert R₃PO

 Table 3
 Selected
 bond lengths (Å) and angles (°) for $[GeF_4{Me_2P(O)CH_2P(O)Me_2}]^a$ Ge1-F1 1.787(4)P1-01 1.532(4)Ge1-F2 P1-C1 1.774(7)1.772(5)Ge1-F3 1.780(5)P1-C2 1.774(7)Ge1-O1 1.930(4) P1-C3 1.792(5) F1-Ge1-F2 91.71(18) F1-Ge1-O1 87.98(17) F1-Ge1-F3 91.04(17) F2-Ge1-O1 88.64(18)

F3-Ge1-O1

P1-O1-Ge1

^{*a*} Symmetry operation: a = -x, y, z.

92.1(2)

91.9(2)

114.3(4)

F1-Ge1-F1a

O1-Ge1-O1a

P1-C3-P1a

Table 4	Selected	bond	lengths	(Å)	and	angles	(°)	for
$[GeF_4{P$	$h_2 P(O) CH_2$	$P(O)Ph_2$	$]\cdot CH_2Cl_2$					

Ge1-F1	1.770(4)	Ge1–O1	1.928(5)
Ge1-F2	1.772(4)	Ge1–O2	1.926(5)
Ge1-F3	1.757(4)	P1O1	1.525(5)
Ge1-F4	1.771(5)	P2–O2	1.519(5)
F1-Ge1-F2	91.1(2)	F2-Ge1-F4	92.0(2)
F1-Ge1-F3	92.1(2)	F3-Ge1-F4	92.6(2)
F1-Ge1-F4	94.2(2)	F2-Ge1-O2	87.9(2)
F1-Ge1-O1	88.9(2)	F3-Ge1-O2	88.5(2)
F2-Ge1-O1	88.8(2)	F4–Ge1–O2	89.9(2)
F3-Ge1-O1	86.4(2)	P1-O1-Ge1	131.3(3)
O1-Ge1-O2	87.0(2)	P2-O2-Ge1	129.8(3)

to PR_3 —oxidochlorosilanes are the other products²⁴—and similar behaviour for SiCl₄ is not unexpected, but contrasts starkly with that of SiF₄.

Two diphosphine dioxide complexes $[SiF_4]R_2P(O)CH_2$ - $P(O)R_2$ (R = Ph or Me) were isolated by reaction of the ligands with SiF₄ in CH₂Cl₂ solution. The [SiF₄{Ph₂P(O)CH₂P(O)Ph₂}] showed several overlapping v(SiF) and two v(PO) vibrations in the IR spectrum, consistent with the expected cis isomer. In solution at ambient temperature, the complex is extensively dissociated, showing no ${}^{19}F{}^{1}H$ NMR resonance, but on cooling the solution to 273 K, a broad line appears at $\delta = -125.0$ and by 180 K two resonances of equal intensity are seen at $\delta = -112.2, -133.6$, but even at this temperature no ${}^{2}J_{\rm FF}$ couplings were resolved. The ³¹P{¹H} NMR spectrum at 295 K showed only free diphosphine dioxide ($\delta = 25$), but at 180 K the resonance had shifted to $\delta = 39$, consistent with coordination. The $[SiF_4{Me_2P(O)CH_2P(O)Me_2}]$ complex was very poorly soluble in chlorocarbons, acetone or MeCN, and decomposed by DMSO or DMF with displacement of the diphosphine dioxide. Hence no useful solution data were obtained. The reaction of $SiCl_4$ with $Me_2P(O)CH_2P(O)Me_2$ produced mixtures containing chlorophosphonium(V) species and was not pursued.

In view of the limited data obtainable on the silicon complexes, we also prepared three GeF₄ adducts with diphosphine dioxides, $[GeF_4{Me_2P(O)CH_2P(O)Me_2}]$, $[GeF_4{Ph_2P(O)CH_2P(O)Me_2}]$ and $[GeF_4{Ph_2P(O)(CH_2)_2P(O)Ph_2}]$, which formed in high yields from reaction of $[GeF_4(MeCN)_2]$ in CH₂Cl₂ solution with the appropriate ligand. Crystal structures were obtained for the first two examples and show (Tables 3 and 4, Fig. 3 and 4) the expected *cis*-chelate geometries. The bond lengths and angles are unexceptional, showing a near to octahedral arrangement of the donor atoms. The structure of $Me_2P(O)CH_2P(O)Me_2$ was also determined (Fig. 5); it proves to be a strongly coordinating O-donor ligand, although it has been very little



Fig. 3 Structure of $[GeF_4\{Me_2P(O)CH_2P(O)Me_2\}]$ showing the atom numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are omitted for clarity. The molecule has mirror symmetry. Symmetry operation: a = -x, y, z.



Fig. 4 Structure of $[GeF_4{Ph_2P(O)CH_2P(O)Ph_2}]\cdot CH_2Cl_2$ showing the atom numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms and the solvate molecule are omitted for clarity.

used since it was first reported.25 The P-O distances show the expected increase on coordination. The multinuclear spectra obtained for $[GeF_4{Ph_2P(O)CH_2P(O)Ph_2}]$ NMR and $[GeF_4{Ph_2P(O)(CH_2)_2P(O)Ph_2}]$ (experimental section) show reversible dissociation/exchange in solution at ambient temperatures, which slows on cooling and, by 273 K, the expected features of cis isomers are resolved. The solution behaviour of [GeF₄{Me₂P(O)CH₂P(O)Me₂}] was unexpectedly more complicated. At 295 K in CD₃CN solution (the complex is insoluble in chlorocarbons) the ${}^{19}F{}^{1}H$ NMR spectrum shows two broad resonances of equal intensity and the corresponding ${}^{31}P{}^{1}H$ NMR spectrum is a singlet. On cooling the solution to ~260 K the fluorine resonances are resolved into the expected triplets, but on further cooling, two new resonances, also triplets of 1:1 intensity, appear, as does a second phosphorus resonance; the behaviour is reversible with temperature. The



Fig. 5 Structure of $[Me_2P(O)CH_2P(O)Me_2]$ showing the atom numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P1–O1 = 1.489(3), P2–O2 = 1.492(3), P1–C3 = 1.819(4), P2–C3 = 1.805(4), P–C(Me) = 1.781(4)–1.805(4), P1–C3–P2 = 116.0(2).

involvement of the solvent in the speciation is ruled out by the observation of similar spectra in DMF solution with the chemical shifts differing only slightly. The probable explanation is that the first set of resonances belong to the octahedral [GeF₄{Me₂P(O)CH₂P(O)Me₂}] monomer, and the second to the dimer [GeF₄{ μ -Me₂P(O)CH₂P(O)Me₂}] cGeF₄]. Even near ambient temperatures the ¹H NMR spectrum in CD₃CN shows two CH₃ and two CH₂ resonances, consistent with this explanation.

Other O-donor ligands. The reaction of $OAsPh_3$ with SiF_4 in either toluene or CH₂Cl₂ produced a white precipitate identified as $[Ph_3AsOH][SiF_5]$ by microanalysis, IR spectroscopy (v = 743(vs,br) (AsOH), 894, 800 ([SiF_5]-) cm^{-1} 8b,26,27 and $^{19}F\{^1H\}$ NMR spectroscopy (CD₂Cl₂, 295 K) $\delta = -138.1 [SiF_5]^{-8b}$). Some samples also contained varying amounts of $[SiF_6]^{2-}$ ($\delta = -126$). Colourless crystals obtained separately from the filtrate were identified by their unit cell²⁸ and ¹⁹F{¹H} NMR spectrum which is a singlet at $\delta = -91$, as Ph₃AsF₂.²⁹ The corresponding reaction using OAsMe₃ gave a mixture, the major components of which were similarly identified as $[SiF_6]^{2-}$, $[SiF_5]^{-}$ and $[Me_3AsOH]^+$ and there is an unidentified species with $\delta(^{19}\text{F}) = -79.9$. In this case, Me₃AsF₂ $(\delta(^{19}\text{F}) = -53.7)^{30}$ was not detected among the products. The structure of colourless crystals grown from CH2Cl2 solution showed them to be [Me₃AsOH]₂[SiF₆] (Fig. 6). The cation has been structurally characterised once before as an iodide salt.³¹ The reactions were repeated several times and produced the same products, although the relative amounts of the fluorosilicate anions varied from preparation to preparation. The same products formed when the reaction was conducted in plastic equipment, eliminating the involvement of the glass vessels in the reaction. The reaction of SiCl₄ with Me₃AsO gives Me₃AsCl₂ cleanly. Whilst the reaction of metal and non-metal halides with phosphine oxides usually results in simple adducts, the products with arsine oxides are more variable. Thus, SnX_4 (X = F, Cl, Br, I),¹⁰ GeF₄,¹² $TiF_{4^{32}}$ and $VOF_{3^{33}}$ give simple adducts, but GeX_{4} (X = Cl or Br) give R₃AsX₂,¹² and Ph₃AsF₂ was a decomposition product of [VOF₃(Ph₃AsO)] in solution.³³ Aqueous HF also converts Ph₃AsO to Ph₃AsF₂.³⁴

The complexes $[SiF_4(pyNO)_2]$ and $[SiF_4(dmso)_2]$ have been described several times,^{19b,19c,35} but with limited data. Both are readily isolated as hygroscopic white crystalline solids by reaction



Fig. 6 Structure of one of the cations in $[Me_3AsOH]_2[SiF_6]$ showing the atom numbering scheme, and the H-bond to F5 of the $[SiF_6]^{2-}$ anion. There are two cations in the asymmetric unit and the figure shows the As1 centred cation. The other cation is very similar and forms an H-bond to F3. Displacement ellipsoids are shown at the 50% probability level and H bonds to C atoms are omitted for clarity. Symmetry operation: a = x, y + 1, z. Selected bond lengths (Å) and angles (°): As1–C = 1.890(6)–1.910(6), As1–O1 = 1.731(5), O1–H1 = 0.84(2), O1 ··· F5a = 2.616(6), Si1–F5 = 1.701(5), Si1–F3 = 1.720(5), Si1–F(rest) = 1.666(4)–1.694(5), C–As1–C = 111.3(3)–116.9(3), O1–As1–C = 102.2(3)–107.9(3).

of SiF_4 with the ligands in CH_2Cl_2 or toluene solution. In solution in CD₂Cl₂ at 295 K neither complex shows a ¹⁹F NMR resonance, but at 180 K resonances of both cis and trans isomers are present, with the *cis* the more abundant form in each (cis: trans ~10:1). The crystal structure of [SiF₄(pyNO)₂] has been determined (Table 5 and Fig. 7) and this shows it to be the cis isomer with approximate two-fold symmetry (O1-Si1-O2 87.9(1)° and cis F-Si-F greater than 90°). The isolation of the cis isomer in the solid state was unexpected compared with the structures of the phosphine oxide examples above. The reaction of the stable radical TEMPO, (2,2,6,6-tetramethylpiperidine-N-oxyl) with SiCl₄ affords [Si(TEMPO)Cl₃], in which the Si-O bond is much shorter (1.619(1) Å) and is viewed as a hydroxylammonium derivative.³⁶ In contrast the white $[SiF_4(DMSO)_2]$ has single strong and broad features at v = 1018 and 801 cm⁻¹, which we assign to the SO and SiF stretches of a trans isomer (theory $D_{4h} = E_u(SiF_4)$ and A_{2u} (SO), respectively). Attempts to obtain a crystal structure of the complex were unsuccessful, all crystals examined appeared to be twinned. The reaction of SiCl₄ with DMSO results in deoxygenation, with formation of Me₂S and $MeSCH_2Cl.^{37}$ In contrast, the reaction with $GeCl_4$ gives the structurally authenticated trans-[GeCl₄(DMSO)₂].³⁸

Ether complexes of SiF₄ are unstable. Tensimetric studies of SiF₄/R₂O (R₂ = Me₂, (CH₂)₄, (CH₂)₅ *etc.*) showed the formation of adducts at low temperatures (~200 K),^{19a} which dissociated on warming, and in some cases polymerisation of the ether occurred. We recorded ¹⁹F{¹H} NMR spectra on mixtures of SiF₄ and

 Table 5
 Selected bond lengths (Å) and angles (°) for [SiF₄(pyNO)₂]

Si1-F1	1.658(2)	Si1-O1	1.863(2)
Si1-F2	1.660(2)	Si1–O2	1.878(2)
Si1-F3	1.658(2)	O1-N1	1.354(3)
Si1–F4	1.651(2)	O2–N2	1.359(3)
F1-Si1-F2	91.87(11)	F2-Si1-F3	93.14(11)
F1-Si1-F3	93.75(11)	F2-Si1-F4	93.89(11)
F1-Si1-F4	171.33(11)	F3-Si1-F4	92.39(11)
F1-Si1-O1	90.90(10)	Sil-Ol-N1	120.57(19)
F1-Si1-O2	83.34(10)	Si1-O2-N2	116.46(18)
O1-Si1-O2	87.91(11)	—	_



Fig. 7 Structure of *cis*-[SiF₄(PyNO)₂] showing the atom numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are omitted for clarity.

various ethers in CD₂Cl₂ solution over the temperature range 295– 180 K. No adduct formation was evident above ~200 K, but from the SiF₄/THF mixture a singlet at $\delta = -128.0$ appeared at 200 K and at 185 K two additional broader resonances (1:1 intensity) appeared at $\delta = -130.2$, -139.2. The behaviour is reversible with temperature, leading to an assignment of these resonances to *trans*and *cis*-[SiF₄(THF)₂]. Similarly, from mixtures of SiF₄ and 12crown-4 in CD₂Cl₂ solution, new resonances appeared on cooling to 180 K at $\delta = -125.0$, -127.6 and -135.7, the last two with some evidence of poorly resolved couplings. However, even at 180 K in CD₂Cl₂ there was no evidence for the formation of adducts with MeO(CH₂)₂OMe or 15-crown-5. We note that GeF₄-ether adducts are more stable but still dissociate at ambient temperatures.¹²

Soft donor ligand complexes. Based upon previous successful characterisations of GeF₄ complexes,^{14,15} the reaction of SiF₄ with alkylphosphines, including Et₂P(CH₂)₂PEt₂, PMe₃, o- $C_6H_4(PMe_2)_2$, and alkyldithioethers, $RS(CH_2)_2SR$ (R = Me, Et), were explored. The reactions were carried out in anhydrous CH_2Cl_2 or toluene solutions with rigorous exclusion of oxygen and moisture. The work-up involved removing volatile materials in vacuo, by slow evaporation of the solvent at room temperature in a glove box, or refrigeration at -18 °C. No phosphine or thioether adducts were isolated from any of these systems; occasionally very small amounts of white solids formed, which on examination proved to be phosphine oxides or phosphonium fluorosilicates.[‡] The possible formation of adducts was also explored by VT NMR spectroscopy over the range 295–190 K. Mixtures of SiF₄ and the phosphines showed ${}^{31}P{}^{1}H$ and ${}^{1}H$ NMR resonances of 'free' ligands (with small temperature drifts), whilst in the ${}^{19}F{}^{1}H{}$ spectra the only new resonances seen were attributed to trace amounts of $[SiF_5]^-$. The ${}^{31}P{}^{1}H$ NMR results are potentially slightly ambiguous since in other systems, including the tetrafluoride complexes of Ge, Sn or Ti, the coordination shifts were small and erratic,11,14,15,32 but the absence of new resonances attributable to the target complexes in the ${}^{19}F{}^{1}H$ NMR spectra suggest any interaction is very weak even at the lowest temperatures.

We also attempted to extend the range of ligand types coordinated to GeF_4 , but were unable to isolate any adducts

[‡] Alkylphosphines slowly react with chlorocarbons by quaternisation at P, although this is very slow for CH₂Cl₂ at ambient temperatures or below.

with MeSe(CH₂)₂SeMe, phosphine sulfides or phosphine selenides. Low temperature ¹⁹F{¹H} NMR studies of the system GeF₄/MeSe(CH₂)₂SeMe in anhydrous CD₂Cl₂, showed no new resonances above ~220 K, but on further cooling two singlets appeared, which at 185 K had resolved into two 1 : 2 : 1 triplets with 1 : 1 intensities, the effects being reversible with temperature. Comparison of the chemical shifts $\delta = -72.5$ (t), -115.7 (t) J = ~82 Hz, with those in [GeF₄{MeS(CH₂)₂SMe}] ($\delta = -87.0$ (t), -123.0 (t) ² $J_{FF} = 77$ Hz)¹¹, strongly suggest some [GeF₄{MeSe(CH₂)₂SeMe}] forms at very low temperatures, although uncomplexed GeF₄ is still the major feature in the ¹⁹F{¹H} spectrum. We were unable to observe a ⁷⁷Se NMR spectrum from the solution at 185 K, which could be due either to the presence of some dynamic process or to the rather low sensitivity of the isotope.

Comparisons of the acceptor properties within the Group 14 tetrafluorides. Comparison of the abilities of SnF₄, GeF₄ and SiF₄ to form complexes with neutral donor ligands shows the ability to decrease $SnF_4 > GeF_4 \gg SiF_4$.¹⁰⁻¹⁹ Coordination ability falls very rapidly down both Groups 15 and 16. Hard N- and Odonor ligands form complexes readily with all three fluorides, with N-donors giving the more robust examples, while O-donor adducts are often hygroscopic and are usually partially dissociated in solution at ambient temperature. Softer phosphines and thioethers give isolable complexes only with SnF_4 and GeF_4 , whereas with alkylarsines no pure complexes have been isolated, although some reaction was evident for SnF4 and GeF4.^{10,11} A major factor behind these experimental observations is the increasing mismatch of orbital size and energy between the hard contracted Lewis acid acceptor orbitals and the more diffuse ligand donor orbitals as Groups 15 and 16 are descended. Theoretical investigations have shown that the reorganisation energy to convert a tetrahedral MF₄ unit to the four-coordinate fragment of the octahedron is substantial, particularly for SiF₄ where the reorganisation severely disrupts the very strong Si-F bonding.³⁹⁻⁴¹ Fleischer³⁹ has shown by DFT calculations that the generally stronger Lewis acidity of GeF₄ vs. SiF₄ is not due to inherently stronger donor-acceptor bonds (which actually fall in bond energy from Si to Ge), but is due to the lower energy required to rearrange/deform the tetrahedral GeF₄. These calculations are for the gas-phase molecules and so do not take into account solvent or lattice energy factors. Both of these are important in the real system since the calculations suggest the rearrangement energies and donor-acceptor bond energies almost cancel out in some cases.

The very strong Si–F bond (~582 kJmol⁻¹), which is the strongest single bond in Group 14 compounds, plays a key role and is retained in the complexes formed with R₃PO or DMSO, whereas with the weaker Si–Cl bond in SiCl₄, Cl/O exchange occurs with the same ligands. This chemistry remains unpredictable in detail, since both GeF₄ and GeCl₄ give simple adducts with R₃PO or DMSO, whereas arsine oxides form adducts with all four SnX₄'s and with GeF₄, but undergo Cl/O exchange to form R₃AsCl₂ with SiCl₄ and GeCl₄. The SiF₄/R₃AsO systems differ again in that protonation of R₃AsO occurs to form [R₃AsOH]⁺.

The mismatch in orbital size and energy between SiF_4 and soft phosphines or thioethers mean that donor-acceptor bond energies will be smaller (although still likely to be inherently favourable). Presumably these are not sufficient to pay back the high reorganisation energy of SiF₄, hence the complexes do not form, at least under the conditions used in this study. As reorganisation energies fall, complex formation becomes more favourable and this is confirmed experimentally.^{14,15} Finally, we note that our inability to isolate phosphine complexes of SiF₄, or to detect such species at low temperature in solution by multinuclear NMR spectroscopy, does not necessarily conflict with the report of SiF₄/PMe₃ adducts²² formed at very low temperature in the absence of a solvent. Matrix-isolation IR/Raman studies of the PMe₃/SiF₄ system would seem worthwhile.

Conclusions

The first detailed characterisation of neutral O-donor ligand adducts of SiF₄ has been achieved with phosphine oxides, pyNO and DMSO ligands and evidence for complex formation in solution at very low temperatures for some ethers presented. Arsine oxides do not form isolable complexes, but react to produce mixtures of R_3AsF_2 , $[R_3AsOH]^+$ and fluorosilicate anions. This work completes the series of Group 14 tetrafluorides with neutral amine, N-heterocycles, phosphines, arsines, thioethers and their oxides. The combination of these experimental data and the theoretical work available from other research groups has provided a basis for understanding this chemistry in some detail.

Experimental

All reactions were conducted using Schlenk, vacuum line and glove-box techniques and under a dry dinitrogen atmosphere. Solvents were dried by distillation from sodium benzophenoneketyl (toluene, THF) or CaH₂ (DMSO, CH₂Cl₂). Electronic grade SiF4 and GeF4 were obtained from Aldrich and used as received. OPMe₃ and OPEt₃ (Strem) were freshly sublimed in vacuo. OPPh₃, pyNO and OAsPh₃ (Aldrich) were heated in vacuo. OAsMe3 was made as described⁴² and freshly sublimed in vacuo. Me₂P(O)CH₂P(O)Me₂ was made by H₂O₂ oxidation of Me2PCH2PMe2.25 o-C6H4(PMe2)2, o-C6H4(AsMe2)2, EtS(CH₂)₂SEt and MeS(CH₂)₂SMe were made by literature methods,⁴³⁻⁴⁵ and $R_2P(CH_2)_2PR_2$ (R = Me or Et) and PMe₃ were obtained from Strem and used as received. IR spectra were recorded as Nujol mulls on Perkin Elmer PE 983G or Spectrum 100 spectrometers, ¹H NMR spectra in CDCl₃, CD₂Cl₂ or CD₃CN solutions on a Bruker AV300, ³¹P{¹H} and ¹⁹F{¹H} NMR spectra on a Bruker DPX400 and referenced to 85% H₃PO₄ and CFCl₃, respectively. Microanalytical measurements on new complexes were performed by Medac Ltd.

[SiF₄(OPMe₃)₂]. OPMe₃ (0.046 g, 0.5 mmol) was dissolved in anhydrous CH₂Cl₂ (10 mL) under dinitrogen, and then the solution frozen in liquid N₂. The apparatus was evacuated, then allowed to warm to room temperature and a slow stream of SiF₄ passed into the solution for 20 min. The mixture was stirred overnight, and the white solid collected by filtration and dried *in vacuo*. Yield: 0.073 g, 51%. Required for C₆H₁₈F₄O₂P₂Si·CH₂Cl₂: C, 22.5; H, 5.6. Found: C, 22.1; H, 5.9%. ¹H NMR (400 MHz, CD₂Cl₂, 293 K): $\delta = 1.60$ (d, ²*J*_{HP} = 13.5 Hz); (200 K): $\delta = 1.69$ (d, ²*J*_{HP} = 13 Hz), ratio ~5:1. ³¹P{¹H} NMR (CD₂Cl₂/CH₂Cl₂, 293 K): $\delta = 51.2$ (br, s); (200 K): $\delta = -116.5$ (s); (243 K): -115.0, -116.6, -128.8; (200 K): -116.6 (s, ¹*J*_{SiF} = 130 Hz), -115.2 (t, ²*J*_{FF}

[SiF₄(OPEt₃)₂]. [SiF₄(OPEt₃)₂] was prepared as described for the OPMe₃ analogue. Yield: 82%. Required for C₁₂H₃₀F₄O₂P₂Si: C, 38.7; H, 8.1. Found: C, 38.3; H, 8.2%. ¹H NMR (400 MHz, CD₂Cl₂, 293 K): δ = 1.16 (t, [3H], Me), 1.94 (br, [2H], CH₂); no change at 190 K. ³¹P{¹H} NMR (CD₂Cl₂/CH₂Cl₂, 293 K): δ = 66.3 (br s); (200 K): 72.3 (s), 71.8 (s), ratio ~10:1. ¹⁹F{¹H} NMR (CD₂Cl₂/CH₂Cl₂, 293 K): δ = -137 (vbr, s); (223 K): -114.5, -116.3, -128.0; (200 K): -116.6 (s, ¹J_{SiF} = 128 Hz), -114.5 (br s, ¹J_{SiF} = 136 Hz), -127.8 (br s, ¹J_{SiF} = 128 Hz). IR (Nujol): v = 1114 (vs, br), v(P=O), 798, v(SiF) cm⁻¹.

[SiF₄(OPPh₃)₂]. Into a solution of OPPh₃ (0.13 g, 0.48 mmol) in toluene (10 mL) SiF₄ was bubbled for 20 min. The white precipitate was filtered off and dried *in vacuo*. Yield: 0.09 g, 57%. Crystals were deposited on refrigerating the filtrate. Required for $C_{36}H_{30}F_4O_2P_2Si$: C, 65.5; H, 4.6. Found: C, 65.2; H, 4.7%. ¹H NMR (400 MHz, CD₂Cl₂, 293 K): $\delta = 7.2-7.7$ (m). ³¹P{¹H} NMR (CD₂Cl₂/CH₂Cl₂, 293 K): $\delta = 29.4$ (br s); (180 K): 29.6 (s), 36.0 (s), ratio ~3: 1.¹⁹F{¹H} NMR (CD₂Cl₂/CH₂Cl₂, 293 K): $\delta = not$ observed; (243 K): –139 (s); (190 K): –139.0 (s, ¹J_{SiF} = 145 Hz). IR (Nujol): $\upsilon = 1089$ (vs, br), $\upsilon(P=O)$, 801, $\upsilon(SiF)$ cm⁻¹.

[SiF₄{Ph₂P(O)CH₂P(O)Ph₂}]. SiF₄ gas was bubbled slowly through a solution of Ph₂P(O)CH₂P(O)Ph₂ (0.21 g, 0.5 mmol) in 15 mL of anhydrous CH₂Cl₂ for 1 h. The mixture was left to stir for 1 h which resulted in a white precipitate. The solid was isolated through filtration and dried *in vacuo*. Yield: 0.19 g, 75%. Required for C₂₅H₂₂F₄O₂P₂Si: C, 57.7; H, 4.3. Found: C, 58.7; H, 4.0%. ¹H NMR (CD₂Cl₂, 295 K): δ = 3.6 (t, [2H], CH₂), 7.97–7.27 (m, [20H], Ph); (185 K): 3.88 (br), 7.93–7.21 (m). ¹⁹F{¹H} NMR (CD₂Cl₂ 293 K): no resonance; (273 K): -125.0 (vbr); (180 K): -112.2 (br s), -133.6 (br s) (couplings unclear). ³¹P{¹H} NMR (CD₂Cl₂/CH₂Cl₂, 293 K): δ = 25.6 (s); (180 K): 39.6 (s). IR (Nujol): v = 1154 (s), 1096(m) v(P=O), 810(sh), 802(s) 790(sh) v(SiF) cm⁻¹.

[SiF₄{Me₂P(O)CH₂P(O)Me₂}]. SiF₄ gas was bubbled slowly through a solution of Me₂P(O)CH₂P(O)Me₂ (0.085 g, 0.5 mmol) in anhydrous CH₂Cl₂ (15 mL) for 1 h. The mixture was left to stir for a further 2 h, and then the solvent was removed *in vacuo* to yield a white solid. Yield: 0.125 g, 92%. Required for C₅H₁₄F₄O₂P₂Si: C, 22.1; H, 5.2. Found: C, 22.2; H, 4.7%. IR (Nujol): $\upsilon = 1124$, 1098 (s, br), υ (P=O), 820(m), 792(s) υ (SiF) cm⁻¹.

[GeF₄**{Ph**₂**P(O)CH**₂**P(O)Ph**₂**}].** [GeF₄(MeCN)₂]¹¹ (0.15 g, 0.5 mmol) and Ph₂P(O)CH₂P(O)Ph₂ (0.21 g, 0.5 mmol) were dissolved in anhydrous CH₂Cl₂ (15 mL), and the mixture was stirred for 30 min. The solution was concentrated to ~5 mL and the white precipitate isolated by filtration and dried *in vacuo*. Yield: 0.22 g, 78%. Required for C₂₅H₂₂F₄GeO₂P₂: C, 53.2; H, 3.9. Found: C, 52.7; H, 4.0%. ¹H NMR (400 MHz, CDCl₃, 293 K): δ = 3.81 (t, [2H], CH₂, ²J_{HP} = 13.5 Hz), 7.45–7.76 (m, [20H], Ph). ³¹P{¹H} NMR (CD₂Cl₂/CH₂Cl₂, 293 K): δ = -102.7 (br), -132.4 (br); (273 K): -102.6 (t, ²J_{FF} = 61 Hz), -131.9 (t). IR (Nujol): υ = 1157, 1074 (s, br), υ (P=O), 648, 634, 625(s) υ (GeF) cm⁻¹.

[GeF₄{Ph₂P(O)(CH₂)₂P(O)Ph₂}]. [GeF₄(MeCN)₂] (0.075 g, 0.25 mmol) and Ph₂P(O)(CH₂)₂P(O)Ph₂ (0.14 g, 0.25 mmol) was dissolved in anhydrous CH₂Cl₂ (15 mL) and the mixture stirred for

30 min. The solution was concentrated to ~5 mL, and the white solid formed was filtered off and dried *in vacuo*. Yield: 0.12 g, 83%. Required for C₂₆H₂₄F₄GeO₂P₂·1/3CH₂Cl₂: C, 52.1; H, 4.1. Found: C, 52.1; H, 4.2%. ¹H NMR (400 MHz, CDCl₃, 293 K): $\delta = 2.93$ (m, [4H], CH₂), 7.61–7.91 (m, [20H], Ph). ³¹P{¹H} NMR (CD₂Cl₂/CH₂Cl₂, 293 K): no resonance; (253 K): $\delta = 46.4$ (s). ¹⁹F{¹H} NMR (CD₂Cl₂, 293 K): $\delta = -106.4$ (br), -129.5 (br); (273 K): -101.3 (t, ²*J*_{FF} = 58 Hz), -129.7 (t). IR (Nujol): $\upsilon = 1150$, 1096 (s, br), υ (P=O), 648, 634, 624(s) υ (GeF) cm⁻¹.

[GeF₄{**Me**₂**P**(**O**)**CH**₂**P**(**O**)**Me**₂}]. [GeF₄{**Me**₂**P**(**O**)**CH**₂**P**(**O**)-**Me**₂}] was made similarly to the above. Yield: 90%. Required for C₅H₁₄F₄GeO₂P₂: C, 19.0; H, 4.4. Found: C, 18.9; H, 3.6%. ¹H NMR (CD₃CN, 295 K): 1.80 (br), 2.11 (br), 2.96 (br), 3.05 (m); (245 K): 1.89 (m), 2.11 (m, both CH₃), 3.00, 3.02 (2 × t, ²J_{PH} = 13 Hz, CH₂). ³¹P{¹H} NMR (CD₃CN, 295 K): $\delta = 62.8(s)$; (227 K): 64.5 (s), 64.6 (s) ~2:1 ratio. ¹⁹F{¹H} NMR (CD₃CN, 295 K): $\delta = -102.6$ (br), -129.1 (s); (253 K): -103.8 (t, ²J_{FF} = 55 Hz), -128.6 (t ²J_{FF} = 55 Hz), -117.4 (br), -134.6 (br); (225 K): -103.1 (t, ²J_{FF} = 58 Hz), ratio of species ~2:1. IR (Nujol): $\upsilon = 1126$ (vbr) υ (P=O), 644, 610, 579(s) υ (GeF) cm⁻¹.

In situ NMR experiments. Reactions were conducted in 5 mm OD NMR tubes loaded in a glove box. To dry CD₂Cl₂ (2 mL) was added R₃PO and SiCl₄ in 1 : 1 or 2 : 1 molar ratios, the tubes were sealed and the ³¹P{¹H} and ³¹P-¹H NMR spectra recorded immediately, and again after 3 h. The relative amounts of the products varied with the ratio of reactants and with time, but no other products were Me₃PCl₂ δ_P = 96.0, [SiCl₄(Me₃P)₂] δ_P = -6.0, Me₃P δ_P = -62.0. Ph₃PO gave Ph₃PCl₂ δ_P = 66.5, Ph₃P δ_P = -6.0, [SiCl₄(Ph₃P)₂] δ_P = 5.5. Traces of water lead to the generation of [R₃PH]⁺, easily identified by the chemical shifts and large ¹J_{PH} couplings. The chemical shift of [SiCl₄(Me₃P)₂] δ_P = -6.0 was established from an *in situ* mixture of Me₃P and SiCl₄; the complex has been authenticated by a crystal structure.⁴⁶

[Ph₃AsOH][SiF₅]. Ph₃AsO (0.16 g, 0.5 mmol) was dissolved in anhydrous toluene (15 mL) and SiF₄ gas was slowly bubbled through the solution for 1 h. After a further 30 min a large amount of white precipitate had formed, which was isolated by filtration and dried *in vacuo*. Yield: 0.07 g, 31%. Required for C₁₈H₁₆AsF₅OSi: C, 48.4; H, 3.6. Found: C, 47.9; H, 3.5%. ¹⁹F{¹H} NMR (CD₂Cl₂, 295 K): $\delta = -138.1$ (s). IR (Nujol): v = 743 (vs,br) (v As-OH), 894, 800 v(SiF) cm⁻¹.

Reaction of OAsMe₃ with SiF₄. The ligand OAsMe₃ (0.068 g, 0.50 mmol) was dissolved in anhydrous toluene (15 mL) and SiF₄ gas was bubbled through the solution for 1 h. A further 30 min of stirring yielded a large amount of white precipitate. The white solid was isolated through filtration. ¹H NMR (CD₂Cl₂, 223 K): $\delta = 2.12$ (s). ¹⁹F{¹H} NMR (CD₂Cl₂, 295 K): $\delta = -79.7$ (s), -128.1 (s), -137 (w). IR (Nujol): v = 747 (v As–OH), 879, 795 (SiF) cm⁻¹. Crystals were grown from CH₂Cl₂.

[SiF₄(pyNO)₂]. [SiF₄(pyNO)₂] was made similarly to the phosphine oxide examples by bubbling SiF₄ though a solution of pyNO in CH₂Cl₂. Yield 80%. Colourless small crystals were formed by slow evaporation of a CH₂Cl₂ solution of the complex. Required for C₁₀H₁₀F₄N₂O₂Si: C, 40.8; H, 3.4; N, 9.5. Found: C, 40.6; H,

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Table 6Crystal data and structure refinement details^a

Compound	[SiF4(OPMe3),]	[SiF4(OPPh ₃),]	[GeF4{Me,P(O)-	[GeF4 {Ph,P(O)-	[Me,P(O)-	[Me ₃ AsOH] ₂ [SiF ₆]	[SiF4(PVNO),]
4			CH ₂ P(O)Me ₂ }]	CH ₂ P(O)Ph ₂ }].CH ₂ Cl ₂	CH ₂ P(0)Me ₂]	1	
Formula	$C_6H_{18}F_4O_2P_2Si$	$C_{36}H_{30}F_4O_2P_2Si$	$C_5H_{14}F_4GeO_2P_2$	$C_{26}H_{24}Cl_2F_4GeO_2P_2$	$C_5H_{14}O_2P_2$	$\mathrm{C_6H_{20}As_2F_6O_2Si}$	$C_{10}H_{10}F_4N_2O_2Si$
M	288.23	660.63	316.69	649.88	168.10	416.15	294.29
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Monoclinic	Tetragonal	Monoclinic
Space group (no.)	$P2_{1}/n$ (14)	$P\overline{1}$ (2)	Cmca (64)	$P2_1/n$ (14)	C2/c (15)	$P4_{3}$ (78)	$P2_1/c$ (14)
a/Å	6.285(2)	12.6885(15)	13.533(4)	12.870(3)	31.360(6)	7.9450(5)	7.7086(15)
$b/ m \AA$	9.560(3)	13.7509(15)	11.142(4)	13.779(3)	5.7109(15)	7.9450(5)	12.844(3)
$c/ m \AA$	10.287(3)	14.869(2)	14.620(4)	15.830(3)	9.488(4)	22.347(3)	12.532(2)
α (°)	90.0	62.564(6)	90.06	90.06	90.0	90.0	90.0
β (°)	96.845(15)	82.697(6)	0.06	92.748(12)	95.231(15)	90.0	105.119(10)
γ (°)	90.0	80.305(6)	0.06	90.06	90.0	90.0	90.0
U/A^3	613.7(3)	2266.0(5)	2204.4(12)	2804.0(10)	1692.1(9)	1410.6(2)	1197.8(4)
Z	2	3	8	4	8	4	4
$\mu(Mo K\alpha)/mm^{-1}$	0.483	0.243	3.098	1.447	0.450	4.879	0.248
F(000)	300	1026	1264	1312	720	824	009
Total no. reflections	4787	45143	12581	26962	11012	8762	13512
Unique reflections	1389	10387	1324	5479	1645	2712	2737
$R_{ m int}$	0.031	0.087	0.114	0.121	0.140	0.037	0.066
Min., max. transmission	0.817, 1.000	0.859, 1.000	0.307, 1.000	0.372, 1.000	0.868, 1.000	0.814, 1.000	0.861, 1.000
No. of parameters, restraints	73, 0	610, 0	72, 0	344, 3	86, 0	167, 3	172, 0
Goodness-of-fit on F^2	1.02	1.11	1.12	1.12	1.03	1.11	1.08
Resid. electron density/e Å ⁻³	-0.32 to $+0.33$	-0.47 to +0.46	-0.73 to $+1.51$	-1.08 to +1.12	-0.47 to +0.39	-0.54 to $+0.77$	-0.38 to $+0.38$
$R_1^{\ b} \left[I_{\circ} > 2\sigma(I_{\circ}) \right]$	0.029	0.082	0.068	0.096	0.056	0.037	0.066
R_1 (all data)	0.034	0.149	0.084	0.154	0.106	0.041	0.106
$wR_2^{\ b} \left[I_o > 2\sigma(I_o) \right]$	0.073	0.132	0.136	0.161	0.123	0.079	0.110
wR_2 (all data)	0.077	0.159	0.146	0.186	0.149	0.081	0.126
^{<i>a</i>} Common items: $T = 120$ K; $\lambda($	Mo K α) = 0.71073 Å; θ	$(\max) = 27.5^\circ$. ^b $R_1 = \Sigma$	$ F_\circ - F_\circ /\Sigma F_\circ $. w R_2	$= [\Sigma w(F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w F_{o}^{4}]^{1/2}.$			

3.3; N, 9.3%. ¹H NMR (CD₂Cl₂, 295 K): δ = 7.53 (s, [2H]), 7.64 (s, [H]), 8.36 (s, [2H]); (180 K): 7.34 (br, [3H]), 8.17 (br, [2H]). ¹⁹F{¹H} NMR (CD₂Cl₂, 295 K): no resonance; (180 K): δ = -133.6 (s), -136.7 (t, ²*J*_{FF} = 13 Hz), -140.9 (t, ²*J*_{FF} = 13 Hz). IR (Nujol): *v* = 862 (sh), 840 (s), 814 (s) (SiF) cm⁻¹.

[SiF₄(DMSO)₂]. [SiF₄(DMSO)₂] was prepared similarly to the phosphine oxide adducts. White powder. Yield 93%. Required for C₄H₁₂F₄O₂S₂Si·CH₂Cl₂: C, 17.4; H, 4.1. Found: C, 17.4; H, 4.5%. ¹H NMR (CD₂Cl₂, 295 K): $\delta = 2.66$ (s); (180 K): 2.66 (s). ¹⁹F{¹H} NMR (CD₂Cl₂, 295 K): no resonance; (200 K): $\delta = -123.0$ (s); (180 K): -122.8 (s), -123.0 (s), -135.9 (s). IR (Nujol): v = 1018 (s, br), (SO), 801 (vs) (SiF) cm⁻¹.

X-Ray crystallography. Details of the crystallographic data collection and refinement parameters are given in Table 6. Crystals suitable for single crystal X-ray analysis were obtained as described above. Data collections used a Bruker-Nonius Kappa CCD diffractometer fitted with Mo K_a radiation ($\lambda = 0.71073$ Å) and either a graphite monochromator or confocal mirrors, with the crystals held at 120 K in a nitrogen gas stream. Structure solution and refinement were straightforward,⁴⁷⁻⁴⁹ with a few points of interest described below; H atoms bonded to C were introduced into the models in idealised positions using the default C-H distance. The Z = 3 arose for $[SiF_4(OPPh_3)_2]$ from one centrosymmetric molecule and one general molecule in space group P1. The two distinct molecules had very similar bond lengths. The H atoms bonded to O in [Me₃AsOH]₂[SiF₆] were clearly identified in a late difference electron-density map as the two highest peaks. They showed sensible O-H and As-O-H parameters, together with plausible O-H ··· F H-bonds and were introduced into the model with refined coordinates and a DFIX restraint on the O–H distance. The structure of $[SiF_4(pyNO)_2]$ proved curiously intractable. The systematic absences pointed to the space group $P2_1/c$, but attempts with several packages to find a solution failed. However, a solution in Pc readily emerged (with two molecules in the asymmetric unit) with $R_1 = 0.06$, suggesting possible pseudo-symmetry. However, the vector set of the four Si atoms in the Pc solution was consistent with the vectors of $P2_1/c$, and introducing the calculated Si atom position into a structurefactor/electron-density calculation readily yielded the solution in this space group.

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