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Neutral and cationic germanium(IV) fluoride complexes with phosphine coordination – synthesis, spectroscopy and structures†

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The neutral complexes *trans*-[GeF₄(PⁱPr₃)₂] and [GeF₄(κ²-L)] (L = CH₃C(CH₂PPh₂)₃ or P(CH₂CH₂PPh₂)₃) are obtained from [GeF₄(MeCN)₂] and the ligand in CH₂Cl₂. Treatment of [GeF₄(PMe₃)₂] with *n* equivalents of TMSOTf (Me₃SiO₃SCF₃) leads to formation of the series [GeF_{4-n}(PMe₃)₂(OTf)_{*n*}] (*n* = 1, 2, 3), each of which contains six-coordinate Ge(IV) with *trans* PMe₃ ligands and X-ray structural data confirm that the OTf groups interact with Ge(IV) to varying degrees. Unexpectedly, [GeF₃(PMe₃)₂(OTf)] undergoes reductive defluorination in solution, forming the Ge(II) complex, [Ge(PMe₃)₃][OTf]₂ (and [FPMe₃]⁺). The bulkier PⁱPr₃ leads to formation of the ionic [GeF₃(ⁱPr₃P)₂][OTf], containing a [GeF₃(ⁱPr₃P)]⁺ cation. [GeF₄(*o*-C₆H₄(PMe₂)₂)], containing the *cis*-chelating diphosphine, also reacts with *n* equivalents of TMSOTf to generate [GeF_{4-n}(*o*-C₆H₄(PMe₂)₂)(OTf)_{*n*}] (*n* = 1, 2, 3). As for the PMe₃ system, the trifluoride, [GeF₃(*o*-C₆H₄(PMe₂)₂)(OTf)], is unstable to reductive defluorination in solution, producing the pyramidal Ge(II) complex [Ge(*o*-C₆H₄(PMe₂)₂)(OTf)][OTf], whose crystal structure has been determined. The [GeF₃(Ph₂P(CH₂)₂PPh₂)(OTf)] and [GeF₂(Ph₂P(CH₂)₂PPh₂)(OTf)₂], obtained similarly from the parent tetrafluoride complex, are poorly soluble, however their structures were confirmed crystallographically. The complexes in this work have been characterised *via* variable temperature ¹H, ¹⁹F{¹H} and ³¹P{¹H} NMR studies in solution, IR spectroscopy and microanalysis and through single crystal X-ray analysis of representative examples across each series. Trends in the NMR and structural parameters are also discussed.

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Introduction

p-block coordination and organometallic chemistry has seen a surge in research activity over recent years. There have been a variety of drivers for this, including, for example, our deeper understanding of the intrinsic chemical and structural diversity of the p-block acceptors compared to the d-block ions, the motivation to develop efficient metal-free catalysts, precursors for the growth of semiconductor materials for electronic and optical applications, as well as the range of radionuclides in the p-block that offer exciting prospects in medical imaging and therapy.^{1,2a} Fluoride derivatives of several p-block elements, *e.g.* B, Al, Ga and P, have drawn significant interest as prospective carriers for the positron-emitting fluorine-18

isotope in new positron emitting tomography (PET) imaging agents.³ However, the wider coordination chemistry of the p-block fluorides is still relatively limited in scope, with the majority of examples featuring the Group 13 with hard N- and O-donor ligands.^{3–5} Recently we have reported several series of neutral and cationic Sn(IV) fluoride coordination complexes involving a range of hard and soft donor ligands.⁶

Germanium tetrafluoride is a molecular monomer with boiling point = –36.5 °C, which has been shown to form a range of six-coordinate complexes either by the direct reaction of GeF₄ with the neutral ligands, or by using an appropriate adduct, typically [GeF₄(MeCN)₂]. Other nitriles like NCCH₂X (X = F and Cl) also form [GeF₄(NCCH₂X)₂]; for X = F, the crystal structure shows that the nitrile ligands lie *cis*.⁷ Reacting germanium tetra-ethoxide, aqueous HPF₆ and pyridine under solvothermal conditions forms *trans*-[GeF₄(py)₂].⁸ The reaction of 2,2'-bipyridine, 1,10-phenanthroline, or Me₂NCH₂CH₂NMe₂ with [GeF₄(MeCN)₂] in CH₂Cl₂ leads exclusively to the formation of the *cis*-isomer with the neutral ligand chelating, as expected.^{9,10} The tetra-aza macrocycle Me₄[14]aneN₄ (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) forms [GeF₄(κ²-Me₄[14]aneN₄)], where the ligand binds in an *exocyclic* bidentate fashion and the Ge(IV) retains the four bound fluorides.⁹

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† Electronic supplementary information (ESI) available: X-ray crystallographic parameters for the structures reported (Table S1), the crystal structure of [Ge(*o*-C₆H₄(PMe₂)₂)(OTf)][OTf] (Fig. S1), together with multinuclear NMR and IR spectra associated with each of the new compounds described (Fig. S2–S14). CCDC 2113230, 2113231, 2113232, 2113233, 2113234, 2113235, 2113236, 2113237, 2113415 and 2113416. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1dt03339e



$[\text{GeF}_4(\text{MeCN})_2]$ also reacts with OPR_3 ($\text{R} = \text{Me}, \text{Et}, \text{Ph}$) to form $[\text{GeF}_4(\text{OPR}_3)_2]$, which exist as a *cis/trans* mixture in solution,¹¹ while bidentate phosphine oxides form only the *cis* isomer.¹² While the heavier GeCl_4 and GeBr_4 analogues react with OPMe_3 to form cationic or dicationic complexes of the form $[\text{GeCl}_3(\text{OPMe}_3)_3][\text{GeCl}_6]$ and $[\text{GeX}_2(\text{OPMe}_3)_4][\text{X}]_2$ ($\text{X} = \text{Cl}, \text{Br}$), the latter through self-ionisation, this does not occur for GeF_4 , consistent with the $\text{Ge}-\text{X}$ bonds becoming weaker as the halide becomes heavier.¹¹

There are a few reports of germanium fluoride complexes with neutral, soft donor ligands.³ The reaction of $[\text{GeF}_4(\text{MeCN})_2]$ with two equivalents of PMe_3 forms *trans*- $[\text{GeF}_4(\text{PMe}_3)_2]$, whereas using AsEt_3 does not produce an isolable complex, and while AsEt_3 reacts with GeCl_4 to form *trans*- $[\text{GeCl}_4(\text{AsEt}_3)_2]$, this complex undergoes slow redox chemistry in solution, forming AsEt_3Cl_2 and GeCl_2 .¹³ $[\text{GeCl}_4(\text{PMe}_3)_2]$ can be isolated from the solvent-free reaction of GeCl_4 and PMe_3 ; although, if a solvent is employed, redox chemistry occurs and the product is $[\text{PMe}_3\text{Cl}][\text{GeCl}_3]$ exclusively.¹³ A small number of diphosphine complexes, *cis*- $[\text{GeF}_4(\text{diphosphine})]$ (diphosphine = *o*- $\text{C}_6\text{H}_4(\text{PR}_2)_2$ ($\text{R} = \text{Me}, \text{Ph}$), $\text{R}_2\text{P}(\text{CH}_2)_2\text{PR}_2$; $\text{R} = \text{Me}, \text{Et}, \text{Cy}, \text{Ph}$),¹³ and dithioether complexes, *cis*- $[\text{GeF}_4\{\text{RS}(\text{CH}_2)_2\text{SR}\}]$ ($\text{R} = \text{Me}, \text{Et}, \text{}^i\text{Pr}$) have also been described, with crystal structures reported for representative examples.¹⁴

Examples of cationic $\text{Ge}(\text{IV})$ fluoride complexes are few. The reaction of $[\text{GeF}_4(\text{MeCN})_2]$ with $\text{Me}_3[9]\text{aneN}_3$ (1,4,7-trimethyl-1,4,7-triazacyclononane) in CH_2Cl_2 leads to $[\text{GeF}_3(\text{Me}_3[9]\text{aneN}_3)]_2[\text{GeF}_6]$, with the strong preference for tridentate coordination of the macrocycle causing F^- displacement; this cation has been confirmed crystallographically.⁹ Dicationic germanium fluoride complexes can be obtained by the fluorination of $\text{Ge}(\text{II})$ complexes. The reaction of $[\text{Ge}(\text{BIMeT}_3)]_2[\text{OTf}]_2$ ($\text{BIMeT}_3 = \text{tris}(1\text{-ethyl-benzoimidazol-2-ylmethyl})\text{amine}$) with XeF_2 leads to the clean formation of $[\text{GeF}_2(\text{BIMeT}_3)]_2[\text{OTf}]_2$, driven by the formation of the strong $\text{Ge}-\text{F}$ bonds. The reaction of this difluoride complex with one equivalent of TMSOTf then leads to $[\text{GeF}(\text{OTf})(\text{BIMeT}_3)]_2[\text{OTf}]_2$. This reaction can be

reversed by the addition of one equivalent of NaBF_4 . The structures of both complexes have been reported.¹⁵

We describe here the coordination chemistry of GeF_4 with neutral mono-, bi-, tri- and tetra-phosphine ligands, together with the reactions of $[\text{GeF}_4(\text{PR}_3)_2]$ ($\text{R} = \text{Me}$ or ${}^i\text{Pr}$), $[\text{GeF}_4\{\text{o}-\text{C}_6\text{H}_4(\text{PMe}_2)_2\}]$, and $[\text{GeF}_4\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}]$ with TMSOTf ($\text{Me}_3\text{SiO}_3\text{SCF}_3$), revealing that fluoride ligands can be readily abstracted, in some cases sequentially, generating a range species with OTf^- anions, which interact with the $\text{Ge}(\text{IV})$ centres to varying degrees. The new complexes have been characterised by variable temperature multinuclear NMR (${}^1\text{H}$, ${}^{19}\text{F}\{{}^1\text{H}\}$ and ${}^{31}\text{P}\{{}^1\text{H}\}$) and IR spectroscopy, together with microanalyses, and their identities confirmed by X-ray crystal structures of representative examples.

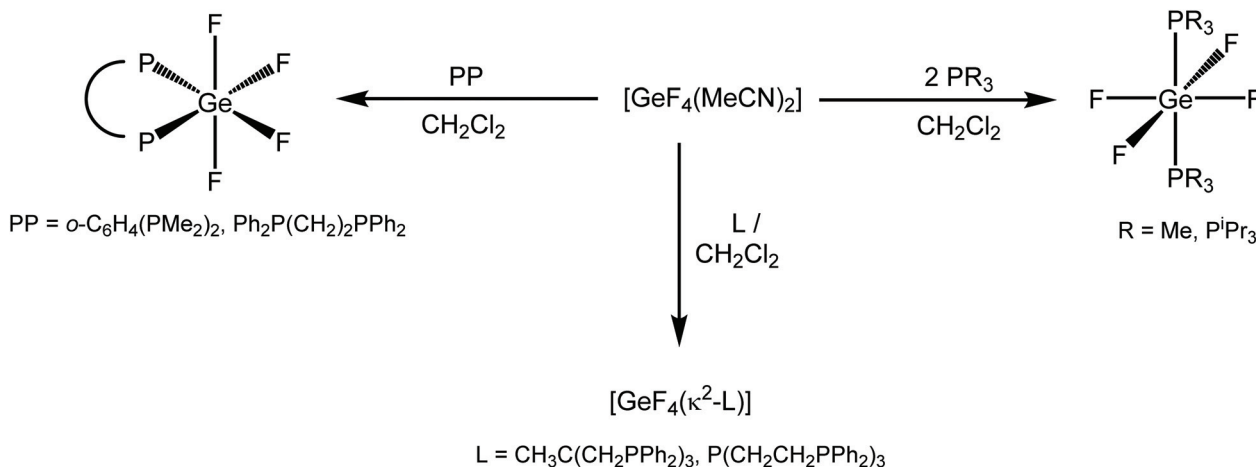
Results and discussion

Germanium tetrafluoride phosphine complexes

Scheme 1 summarises the reactions of $[\text{GeF}_4(\text{MeCN})_2]$ with phosphines in this work.

Reaction of $[\text{GeF}_4(\text{MeCN})_2]$ with 2 equiv. of PR_3 ($\text{R} = \text{Me}, \text{}^i\text{Pr}$) in CH_2Cl_2 affords the complexes $[\text{GeF}_4(\text{PR}_3)_2]$ in good yield as colourless solids. Spectroscopic data for $[\text{GeF}_4(\text{PMe}_3)_2]$ are in accord with those reported,¹³ and slow evaporation of a CH_2Cl_2 solution deposited crystals suitable for single crystal X-ray analysis. The structure is centrosymmetric (Fig. 1), with a distorted octahedral geometry and confirming the *trans* isomer. This is the first structurally characterised monodentate phosphine complex of germanium fluoride.

The analogous complex $[\text{GeF}_4({}^i\text{Pr}_3\text{P})_2]$ was prepared to allow the effect of the increased steric requirement of the phosphine on the fluoride abstraction chemistry (*vide infra*) to be explored. Its room temperature ${}^{31}\text{P}\{{}^1\text{H}\}$ and ${}^{19}\text{F}\{{}^1\text{H}\}$ NMR spectra contain broad resonances at +24.6 ppm and -65.0 ppm, respectively, indicating fast exchange on the NMR



Scheme 1 Summary of the neutral phosphine complexes of GeF_4 prepared in this work.



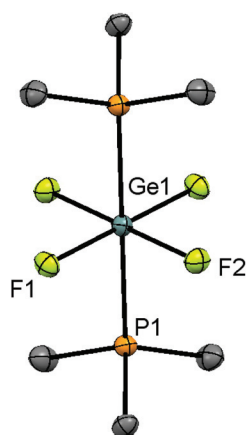


Fig. 1 View of the crystal structure of $[\text{GeF}_4(\text{PMe}_3)_2]$ showing the atom labelling scheme. The ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: $-x, -y, -z$. Selected bond lengths (Å) and angles ($^\circ$) are: Ge1–P1 = 2.3717(6), Ge1–F1 = 1.8240(13), Ge1–F2 = 1.8158(13), F1–Ge1–F2 = 90.99(6).

time scale. Low temperature NMR data support this (see Fig. S2.3 and S2.5[†]).

To expand the range of multidentate phosphine complexes of GeF_4 and test the possibility of increasing the number of coordinated phosphine donors in this work, the tridentate ligand $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$ was reacted with $[\text{GeF}_4(\text{MeCN})_2]$ in a 1:1 ratio to form $[\text{GeF}_4(\kappa^2\text{-CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3)]$, crystals of which were grown by layering a CH_2Cl_2 solution of the compound with hexane. The structure (Fig. 2) shows that the ligand coordinates in a *cis*-bidentate fashion, generating a six-

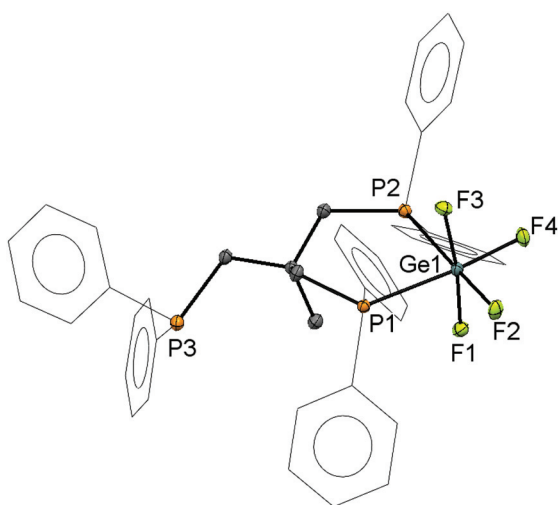


Fig. 2 View of the crystal structure of $[\text{GeF}_4(\kappa^2\text{-CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3)]$ showing the atom labelling scheme. The ellipsoids are drawn at the 50% probability level and H atoms and CH_2Cl_2 solvent molecule are omitted, and phenyl rings are displayed as wireframe for clarity. Selected bond lengths (Å) and angles ($^\circ$) are: Ge1–P1 = 2.4731(4), Ge1–P2 = 2.5030(4), Ge1–F1 = 1.7872(9), Ge1–F2 = 1.7778(9), Ge1–F3 = 1.7976(9), Ge1–F4 = 1.7735(9), P1–Ge1–P2 = 92.886(13), F1–Ge1–F3 = 172.44(4), F2–Ge1–F4 = 92.47(4), P1–Ge1–F4 = 174.90(3), P2–Ge1–F2 = 178.75(3).

membered chelate ring, with the third -PPh_2 group remaining uncoordinated, hence the $\text{Ge}(\text{iv})$ retains all four fluorides.

In CD_2Cl_2 the room temperature ^1H NMR spectrum from a freshly prepared and analytically pure sample of $[\text{GeF}_4(\kappa^2\text{-CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3)]$ shows three sets of methylene resonances, corresponding to the two different environments within the chelated portion, as well as the uncoordinated arms. In the ^{19}F $\{^1\text{H}\}$ spectrum (298 K) two broad resonances of equal intensity are seen at $\delta = -72.2$ and -108.6 , corresponding to the two environments in the *cis* isomer. Another sharper resonance at $\delta = -137.7$ corresponds to GeF_4 . Consistent with this, the ^{31}P $\{^1\text{H}\}$ NMR spectrum shows a broad resonance at $\delta = -4.0$, as well as some uncoordinated triphosphine (-26.4 ppm). These data suggest that the complex is dynamic in solution and the phosphine is weakly bound, with both uncoordinated phosphine and GeF_4 being seen in the NMR spectra. Upon cooling to 183 K the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a tdd at -4.5 ppm and a singlet at -27.9 ppm in the 2:1 ratio expected for κ^2 -coordination.

This triphosphine complex has approximately C_{2v} symmetry at Ge, so group theory predicts four IR active Ge–F stretching vibrations. However, it is common for these to overlap and in the present case only two broad peaks are seen at 517 and 603 cm^{-1} .

The tripodal tetraphosphine, $\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$, was also reacted with $[\text{GeF}_4(\text{MeCN})_2]$ in a 1:1 molar ratio, leading to the formation of $[\text{GeF}_4(\kappa^2\text{-P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3)]$. At 298 K the ^1H NMR spectrum shows two broad singlets in the methylene region at 2.03 and 2.28 ppm, and broad resonances in the aromatic region with a 1:1:5 integration, suggesting a dynamic process interchanging the terminal -PPh_2 groups in solution. This is consistent with the room temperature $^{19}\text{F}\{^1\text{H}\}$ NMR data where a single broad resonance is seen at -94.8 ppm, while the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows broad, ill-defined multiplets to high frequency of the tetraphosphine itself. However, cooling to 183 K causes these broad resonances in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum to sharpen into three resonances in a 1:2:1 ratio, shown in Fig. 3(a). The resonance corresponding to the pendent arms has an integral of two, consistent with bidentate coordination *via* the apical P donor and one -PPh_2 pendant arm. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was also simulated using the SPINACH software package¹⁶ to confirm the coupling scheme (Fig. 3(b)).

The $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum at 213 K supports this (Fig. 4), showing three distinct resonances, a doublet of doublet of triplets at -80.4 ppm and two sets of what appear to be doublets of quartets, but which are in fact doublets of doublets of triplets (Fig. S11.2.5[†]). Overall, the solution data are therefore consistent with the isomer illustrated in Fig. 5, in which the apical P atom and one -PPh_2 arm are coordinated.

Reactions of $[\text{GeF}_4(\text{PMe}_3)_2]$ with TMSOTf

Scheme 2 shows the products from reactions of $[\text{GeF}_4(\text{PMe}_3)_2]$ with different ratios of TMSOTf.

The reaction of $[\text{GeF}_4(\text{PMe}_3)_2]$ with one equivalent of TMSOTf (TMSOTf = $\text{Me}_3\text{SiO}_3\text{SCF}_3$) in CH_2Cl_2 leads to the for-



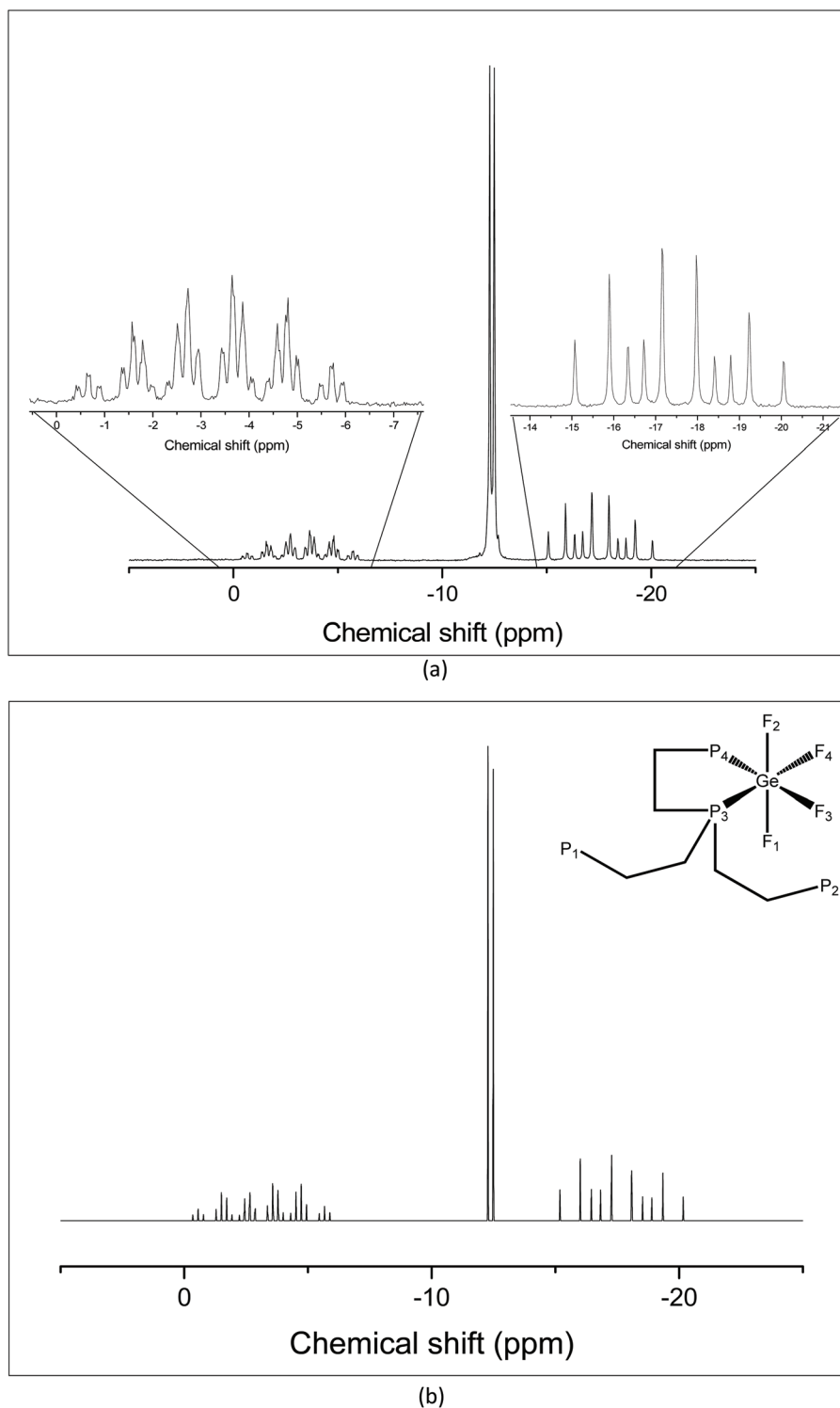


Fig. 3 (a) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{GeF}_4(\kappa^2\text{-P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3)]$ recorded at 183 K (CH_2Cl_2); (b) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{GeF}_4(\kappa^2\text{-P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3)]$ simulated using the SPINACH¹⁶ package; the inset shows the NMR active nuclei giving rise to the coupling scheme. Spin system: $J_{\text{P}_1\text{P}_3} = J_{\text{P}_2\text{P}_3} = 35$ Hz; $J_{\text{P}_3\text{P}_4} = 336$ Hz; $J_{\text{P}_4\text{F}_1} = J_{\text{P}_4\text{F}_2} = 133$ Hz; $J_{\text{P}_3\text{F}_1} = J_{\text{P}_3\text{F}_2} = 153$ Hz; $J_{\text{F}_1\text{F}_3} = J_{\text{F}_1\text{F}_4} = 54$ Hz; $J_{\text{F}_2\text{F}_3} = J_{\text{F}_2\text{F}_4} = 54$ Hz; $J_{\text{F}_3\text{F}_4} = 54$ Hz; $J_{\text{P}_3\text{F}_4} = 188$ Hz; $J_{\text{P}_4\text{F}_3} = 207$ Hz.

mation of $[\text{GeF}_3(\text{PMe}_3)_2(\text{OTf})]$, which was isolated as a white powder. The ^1H NMR spectrum shows that the doublet corresponding to the PMe_3 groups at $\delta = 1.68$ ppm, *i.e.* $\Delta\delta =$

$+0.22$ ppm *vs.* $[\text{GeF}_4(\text{PMe}_3)_2]$. The room temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a broad singlet resonance at 3.1 ppm, with $\Delta\delta = +15.5$ ppm *vs.* $[\text{GeF}_4(\text{PMe}_3)_2]$. At 183 K the



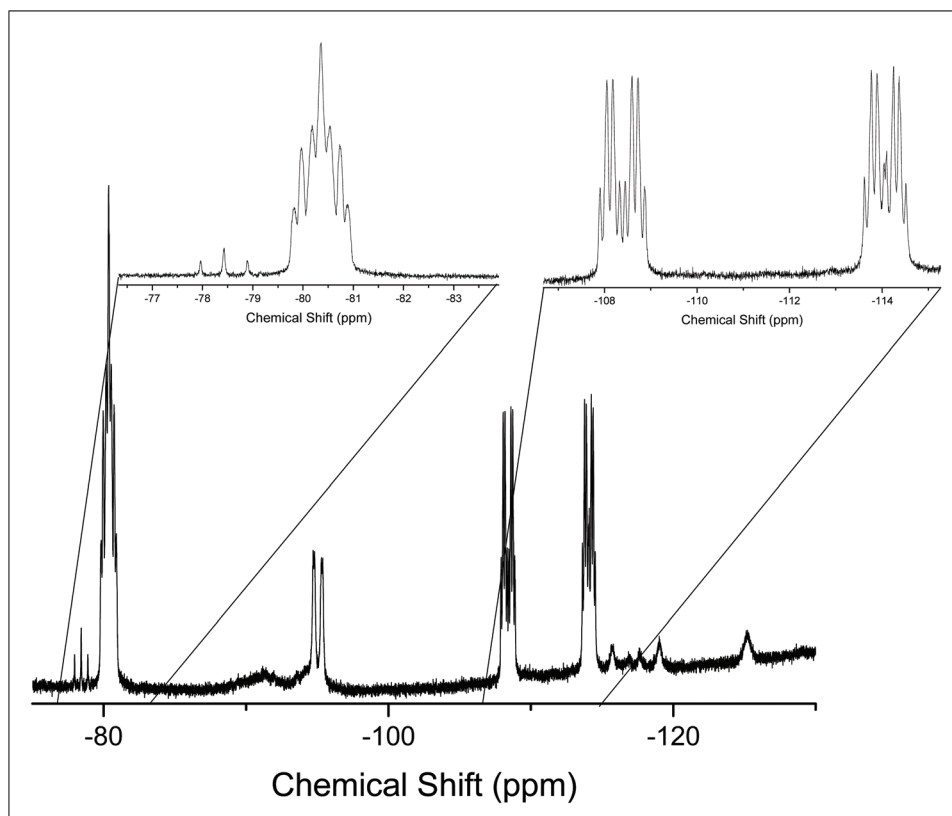


Fig. 4 $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of $[\text{GeF}_4(\kappa^2\text{-P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3)]$ at 213 K (CH_2Cl_2).

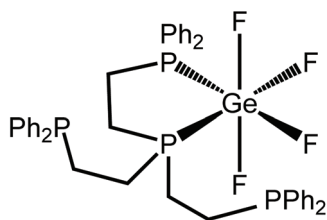


Fig. 5 The isomer of $[\text{GeF}_4(\kappa^2\text{-P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3)]$ present in CH_2Cl_2 at low temperature from the NMR data.

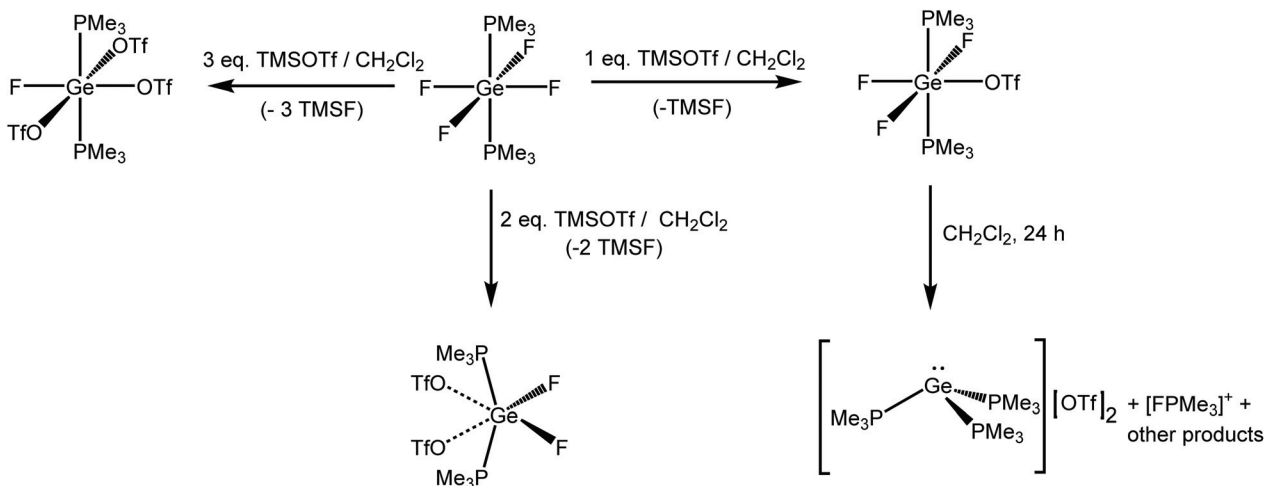
singlet shifts to +5.2 ppm and splits into a triplet of doublets ($^2J_{\text{PF}} = 192, 134$ Hz) as shown in Fig. 6, consistent with the triflate being coordinated to germanium at this temperature; a quartet would be expected if it were not (assuming a trigonal bipyramidal geometry, as seen in $[\text{SnCl}_3(\text{PMe}_3)_2]^+$).¹⁷

The $^{19}\text{F}\{^1\text{H}\}$ NMR data at room temperature show only the triflate resonance, whereas at 183 K three resonances are observed; a triplet of triplets at -123.4 ppm ($^2J_{\text{PF}} = 134, ^2J_{\text{FF}} = 41$ Hz) [F], due to the fluorine *trans* to the triflate, a triplet of doublets at -85.9 ppm [2F] ($^2J_{\text{PF}} = 192, ^2J_{\text{FF}} = 41$ Hz), from the fluorines *cis* to the triflate and a singlet at -78.9 ppm [3F] from the triflate. The couplings are only evident in the $^{19}\text{F}\{^1\text{H}\}$ spectrum at 183 K; around 210 K the couplings are lost and the peaks broaden significantly. Eventually, the peaks merge

together, indicating fast exchange between the different fluorine environments. This is shown by the stacked variable temperature $^{19}\text{F}\{^1\text{H}\}$ NMR spectra in Fig. 7. The exchange of the fluorine environments is probably due to reversible triflate dissociation in solution.

Although the complex can be isolated as a white powder, it is relatively unstable even under inert atmosphere conditions. Over a period of 24 h the colour changes from white to dark brown, and this product is insoluble in CH_2Cl_2 , hence all spectroscopic measurements on this complex were performed on a freshly synthesised sample. The complex is also unstable in solution and a CH_2Cl_2 solution of the compound left to evaporate overnight led to the deposition of crystals of the Ge(II) complex, $[\text{Ge}(\text{PMe}_3)_3][\text{OTf}]_2$, containing a Ge(II) dication, the direct synthesis (from $\text{GeCl}_2(\text{dioxane})$, PMe_3 and TMSOTf) and crystal structure of which we have reported recently.¹⁸ This indicates that the $[\text{GeF}_3(\text{PMe}_3)_2(\text{OTf})]$ is susceptible to redox chemistry and further analysis of its $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum over time shows the appearance of a doublet at -135.7 ppm ($J_{\text{PF}} = 936$ Hz) (Fig. S3.2.5†), consistent with the formation of $[\text{FPMe}_3]^+$,¹⁹ indicating that the Ge(II) dication is a result of reductive defluorination in solution. This can be compared to the reaction of GeCl_4 with PMe_3 in CH_2Cl_2 , which also undergoes a redox process forming $[\text{PMe}_3\text{Cl}][\text{GeCl}_3]$. Notably, the germanium tetrafluoride phosphine complexes do not appear to exhibit any tendency to undergo redox behaviour in solution.





Scheme 2 Summary of the $\text{GeF}_4/\text{PMe}_3/\text{TMSOTf}$ chemistry in this work.

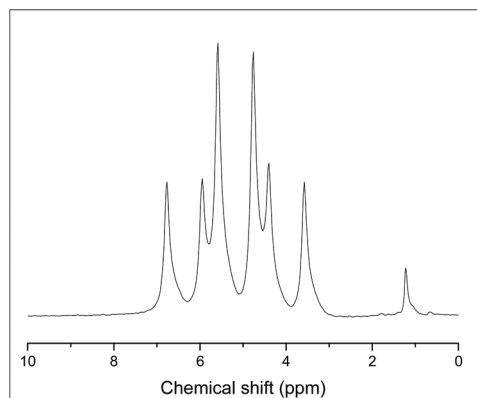


Fig. 6 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{GeF}_3(\text{PMe}_3)_2(\text{OTf})]$ at 183 K (CD_2Cl_2).

A CH_2Cl_2 solution of the Ge(IV) complex layered with hexane and stored at -78°C (dry ice), however, produced crystals of $[\text{GeF}_3(\text{PMe}_3)_2(\text{OTf})]$. The structure shows (Fig. 8) that the triflate is coordinated in the solid state, with a distorted octahedral geometry at Ge, similar to the case for $[\text{SnX}_3(\text{PMe}_3)_2(\text{OTf})]$ ($\text{X} = \text{F}$ or Cl).^{6,17}

A similar reaction with TMSOTf was undertaken using $[\text{GeF}_4(\text{P}^i\text{Pr}_3)_2]$. P^iPr_3 has a larger Tolman cone angle than PMe_3 (160° vs. 118°),²⁰ hence the increased steric requirement may reduce the likelihood of triflate coordination. The room temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the resulting $[\text{GeF}_3(\text{P}^i\text{Pr}_3)_2][\text{OTf}]$ shows a quartet at 46.8 ppm (Fig. 9(a), contrasting with the behaviour of the PMe_3 analogue, and the quartet remains at 183 K. The quartet coupling indicates that the three fluorides are in the same environment, therefore, the triflate is not bound in solution. In the $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum a triplet is seen at -56.7 ppm, together with a sharp singlet at -79.0 ppm (OTf), with a 1 : 1 integration ratio. The large positive shift of the fluorine resonance is also consistent with a large increase in positive charge on the GeF_3 unit, and hence

supports the conclusion that the complex is ionic in solution, *i.e.* $[\text{GeF}_3(\text{P}^i\text{Pr}_3)_2][\text{OTf}]$ (Fig. 9(b)).

The addition of two equivalents of TMSOTf to $[\text{GeF}_4(\text{PMe}_3)_2]$ in CH_2Cl_2 results in the formation of $[\text{GeF}_2(\text{PMe}_3)_2(\text{OTf})_2]$ as a white powder, which is stable for several weeks under inert atmosphere conditions. The room temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a broad resonance at $+25.8$ ppm, which corresponds to $\Delta\delta = +22.6$ ppm vs. the trifluoride, $[\text{GeF}_3(\text{PMe}_3)_2(\text{OTf})]$. At 233 K, this resonance shifts to $+27.8$ ppm and splits into a triplet ($^2J_{\text{PF}} = 83$ Hz). In the room temperature $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum two resonances are observed, one at -78.3 ppm corresponding to triflate and a broad peak at -119.5 ppm due to the germanium bound fluorines. At 233 K this broad resonance sharpens into a triplet at -122.3 ppm ($^2J_{\text{PF}} = 83$ Hz). These data are consistent with the formation of the bis-triflate complex.

The evaporation of a concentrated CH_2Cl_2 solution of $[\text{GeF}_2(\text{PMe}_3)_2(\text{OTf})_2]$ deposited crystals, and the X-ray structure of this complex is shown in Fig. 10(a). It has pseudo-octahedral coordination with two relatively long contacts to the oxygen atoms of the κ^1 -triflates, $\text{Ge}-\text{Otf} = 2.375(3)$ and $2.396(3)$ Å, which are ~ 0.3 Å longer than the $\text{Ge}-\text{Otf}$ bond in $[\text{GeF}_3(\text{PMe}_3)_2(\text{OTf})]$. The $\text{P}-\text{Ge}-\text{P}$ bond angle is $150.29(5)^\circ$, a significant deviation from an ideal octahedral complex. This, together with the large *cis* $\text{F}-\text{Ge}-\text{F}$ bond angle of $97.4(14)^\circ$, suggests that the core of the 'GeF₂(PMe₃)₂' unit could alternatively be described as a pseudo-tetrahedral dication, with the triflates interacting only weakly.

A concentrated solution containing $\text{GeCl}_4:2\text{TMSOTf}:2\text{AsEt}_3$ in CH_2Cl_2 left to evaporate slowly also afforded crystals, in this case of $[\text{GeCl}_2(\text{AsEt}_3)_2(\text{OTf})_2]$ (Fig. 10(b)). This complex is analogous to $[\text{GeF}_2(\text{PMe}_3)_2(\text{OTf})_2]$, although in the dichloro species $\text{Ge}\cdots\text{Otf}$ contacts are even longer, at $2.6848(19)$ and $2.7436(2)$ Å, indicating that the $\text{Ge}-\text{Otf}$ interactions are even weaker. The $\text{As}-\text{Ge}-\text{As}$ angle is $125.186(16)^\circ$ and the $\text{Cl}-\text{Ge}-\text{Cl}$ bond angle is $101.36(3)^\circ$, *i.e.* significantly closer to ideal angles for a tetrahedral species than an octahedron.



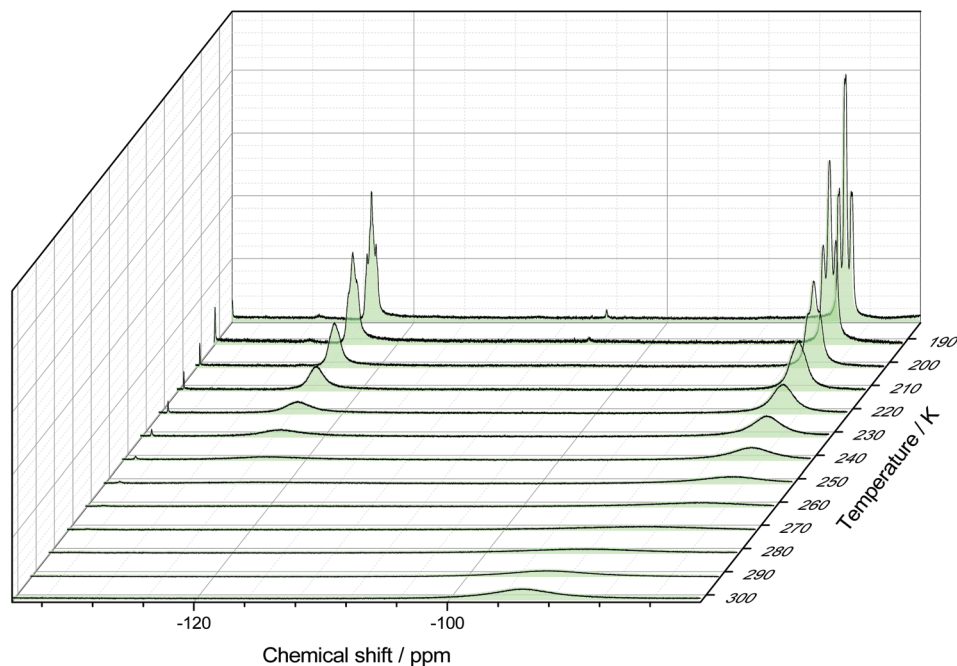


Fig. 7 Stacked $^{19}\text{F}\{^1\text{H}\}$ NMR spectra of $[\text{GeF}_3(\text{PMe}_3)_2(\text{OTf})]$ in CD_2Cl_2 showing the temperature dependant behaviour.

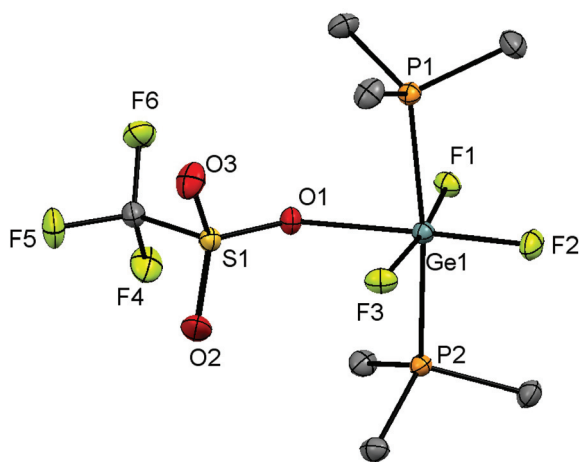


Fig. 8 The structure of $[\text{GeF}_3(\text{PMe}_3)_2(\text{OTf})]$ showing the atom labelling scheme. The ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$) are: Ge1–P1 = 2.3546(3), Ge1–P2 = 2.3655(3), Ge1–F1 = 1.8149(7), Ge1–F2 = 1.7753(7), Ge1–F3 = 1.8015(7), Ge1–O1 = 2.1878(9), P1–Ge1–P1 = 171.122(11), F1–Ge1–F3 = 170.48(3), O1–Ge1–F2 = 177.54(3).

The addition of three equivalents of TMSOTf to $[\text{GeF}_4(\text{PMe}_3)_2]$ in CH_2Cl_2 forms $[\text{GeF}(\text{PMe}_3)_2(\text{OTf})_3]$ as a stable white solid. In the ^1H NMR spectrum a doublet of doublets can be seen at 2.02 ppm, which continues the trend of increasing chemical shift going from the tetrafluoride to the mono-fluoride species, and consistent with an increasing positive charge along the series.

The room temperature $^{31}\text{P}\{^1\text{H}\}$ spectrum shows a sharp doublet at 32.3 ppm ($^2J_{\text{PF}} = 75$ Hz) as expected for the mono-

fluoride complex, while the room temperature $^{19}\text{F}\{^1\text{H}\}$ spectrum shows a sharp triplet at -107.2 ppm ($^2J_{\text{PF}} = 75$ Hz) as well as two broad triflate resonances at -77.6 and -78.1 ppm. The broad triflate peaks suggest that there is a triflate exchange process occurring in solution at this temperature (Table 1).

For the phosphine complexes in Table 2, a decrease in both the Ge–P and Ge–F bond distances is observed as the fluorides are replaced by triflates, consistent with an increase in positive charge and Lewis acidity at the germanium centre. This picture is also supported by the increase in the average C–P–C bond angle of the phosphine ligand going down the series, with the bond angle in the bis-triflate complex being almost 10° larger than in the phosphine itself and almost 3° larger than in $[\text{GeF}_4(\text{PMe}_3)_2]$. The same trends are seen with the germanium chloride arsine complexes. Scheme 1 summarises the chemistry of the monophosphine complexes with TMSOTf.

Reactivity of GeF_4 complexes bearing bi- and multi-dentate phosphines with TMSOTf

Scheme 3 summarises the reaction chemistry involving $[\text{GeF}_4(\text{diphosphine})]$ with TMSOTf.

The reaction of $[\text{GeF}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}]$ with one equivalent of TMSOTf in CH_2Cl_2 leads to the formation of $[\text{GeF}_3\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{OTf})]$, with a small high frequency shift for the Me resonance in the ^1H NMR spectrum. With one triflate bound, two isomers are possible, with *mer* or *fac* fluorines (Fig. 11).

The $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of this complex at 183 K (Fig. 12) has a resonance at -109.5 ppm, which appears as a doublet of doublet of doublets with two different $^2J_{\text{PF}}$ couplings and one $^2J_{\text{FF}}$ coupling, as well as a triplet of triplets at



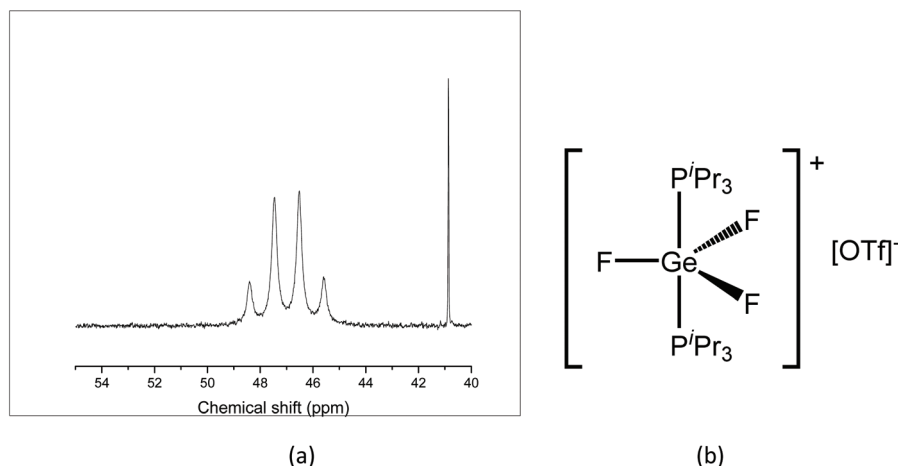


Fig. 9 (a) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{GeF}_3(\text{iPr}_3\text{P})_2][\text{OTf}]$ (298 K, CH_2Cl_2) showing the quartet resonance due to the $[\text{GeF}_3(\text{iPr}_3\text{P})_2]^+$ cation; (b) proposed solution structure of $[\text{GeF}_3(\text{iPr}_3\text{P})_2][\text{OTf}]$ (the singlet at ca. 41 is due to a small amount of $[\text{HP}^i\text{Pr}_3]^+$).

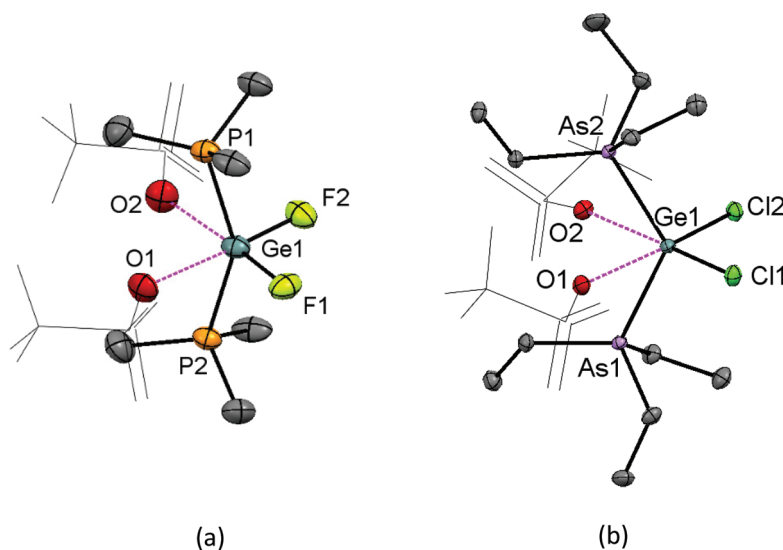


Fig. 10 The structures of (a) $[\text{GeF}_2(\text{PMe}_3)_2(\text{OTf})_2]$ showing the atom labelling scheme (there are three independent molecules in the asymmetric unit). The ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity and only the closest oxygen of the triflate is drawn as an ellipsoid for clarity. Selected bond lengths (Å) and angles ($^\circ$) for the Ge1-centred moiety are: Ge1–P1 = 2.3100(12), Ge1–P2 = 2.3074(12), Ge1–F1 = 1.747(3), Ge1–F2 = 1.748(3), Ge1...O1 = 2.374(3), Ge1...O2 = 2.396(3) P1–Ge1–P2 = 150.29(5), F1–Ge1–F2 = 97.40(14); (b) $[\text{GeCl}_2(\text{AsEt}_3)_2(\text{OTf})_2]$ showing the atom labelling scheme. The ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity and only the closest oxygen of the triflate is drawn as an ellipsoid for clarity. Selected bond lengths (Å) and angles ($^\circ$) are: Ge1–As1 = 2.4048(4), Ge1–As2 = 2.4169(4), Ge1–Cl1 = 2.1453(7), Ge1–Cl2 = 2.1602(7), Ge1...O1 = 2.6848(19), Ge1...O2 = 2.7436(19), As1–Ge1–As2 = 125.186(16), Cl1–Ge1–Cl2 = 101.36(3).

Table 1 Selected multinuclear data for the complexes $[\text{GeF}_{4-n}(\text{PMe}_3)_2(\text{OTf})_n]$ for $n = 0, 1, 2, 3$

Complex	$\delta^{31}\text{P}\{^1\text{H}\}/\text{ppm}$	$\delta^{19}\text{F}\{^1\text{H}\}/\text{ppm}$	$^2J(^{31}\text{P}-^{19}\text{F})/\text{Hz}$	$^2J(^{19}\text{F}-^{19}\text{F})/\text{Hz}$
<i>trans</i> - $[\text{GeF}_4(\text{PMe}_3)_2]^{13}$ (240 K)	−12.4 (quin)	−96.9 (t)	196	—
$[\text{GeF}_3(\text{PMe}_3)_2(\text{OTf})]$ (183 K)	5.2 (dt)	−85.9 (td), −123.4 (tt)	192, 134	41
$[\text{GeF}_2(\text{PMe}_3)_2(\text{OTf})_2]$ (233 K)	27.4 (t)	−122.3 (t)	83	—
$[\text{GeF}(\text{PMe}_3)_2(\text{OTf})_3]$ (298 K)	32.3 (d)	−107 (t)	75	—

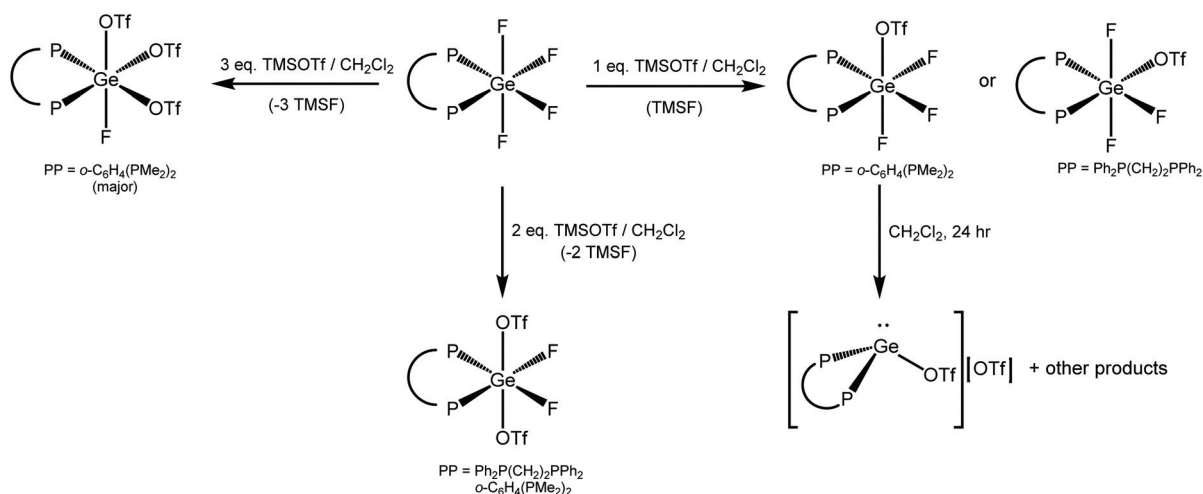
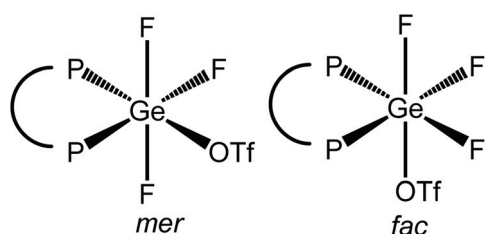
^a Excluding the triflate resonances.



Table 2 Selected geometric parameters for complexes of the form $[\text{GeF}_{4-n}(\text{PMe}_3)_2(\text{OTf})_n]$ for $n = 0, 1, 2$ and $[\text{GeCl}_4(\text{AsEt}_3)_2]$ and $[\text{GeCl}_2(\text{AsEt}_3)_2][\text{OTf}]_2$

Complex	$d(\text{Ge}-\text{E})$ (E = P or As)/Å	$d(\text{Ge}-\text{X})$ (X = F or Cl)/Å	E-Ge-E angle/°	Range of C-E-C angles ^a /°
$[\text{GeF}_4(\text{PMe}_3)_2]$	2.3717(6)	1.8158(13), 1.8240(13)	180.0	105.83(13)–106.93(11)
$[\text{GeF}_3(\text{PMe}_3)_2(\text{OTf})]$	2.3655(3), 2.3546(3)	1.8015(7)(<i>cis</i>), 1.8149(7) (<i>cis</i>), 1.7753(7) (<i>trans</i>)	171.122(11)	106.27(6)–109.00(6)
$[\text{GeF}_2(\text{PMe}_3)_2(\text{OTf})_2]$	2.3074(12), 2.3100(12)	1.747(3), 1.748(3)	150.29(5)	107.0(2)–110.9(3)
$[\text{GeCl}_4(\text{AsEt}_3)_2]^{13}$	2.4904(9)	2.3233(19), 2.3296(19)	180.0	105.1(4)–106.4(4)
$[\text{GeCl}_2(\text{AsEt}_3)_2][\text{OTf}]_2$	2.4048(4), 2.4169(4)	2.1453(7), 2.1602(7)	125.186(16)	105.79(12)–113.81(12)

^a C–P–C angle of free $\text{PMe}_3 = 99.46^\circ$, C–As–C angle of free $\text{AsEt}_3 = 98.50^\circ$.

**Scheme 3** Reactions involving $[\text{GeF}_4(\text{diphosphine})]$ with TMSOTf in this work.**Fig. 11** The two isomers possible for $[\text{GeF}_3\{\text{o}-\text{C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{OTf})]$ with the triflate coordinated.

–123.7 ppm with one $^2J_{\text{PF}}$ coupling and one $^2J_{\text{FF}}$. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (183 K) there is a resonance at –23.1 ppm, which is a doublet of doublet of doublets with three distinct $^2J_{\text{PF}}$ couplings, indicating that there is only one phosphorus chemical environment. These data are consistent with the *fac* isomer being present at this temperature.

A CH_2Cl_2 solution of this complex layered with hexane deposited some crystals identified as $[\text{Ge}\{\text{o}-\text{C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{OTf})][\text{OTf}]$, which is clearly not representative of the bulk product. The reduction from Ge(IV) to Ge(II) with concomitant complete defluorination was also seen in the PMe_3 system (above). While in that case the doublet due to $[\text{FPMe}_3]^+$ was observed, the corresponding fluorophosphorane derived from $\text{o}-\text{C}_6\text{H}_4(\text{PMe}_3)_2$ is not known, and no obvious by-product of

this type was evident. However, the reductive defluorination is also assumed to proceed *via* fluorination of the diphosphine, which may then undergo further reaction. The structure of $[\text{Ge}\{\text{o}-\text{C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{OTf})][\text{OTf}]$ shows (Fig. S1, ESI[†]) one of the triflates coordinated to the Ge(II) centre, $d(\text{Ge}-\text{OTf}) = 2.0968(15)$ Å. There are two longer contacts to the weakly interacting triflates at 2.6438(17) Å and 2.971 Å, completing an approximately five-coordinate geometry around the germanium, the complex exists as weakly associated dimers in the solid state. The complex has a similar geometry to the previously reported complex $[\text{GeCl}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)][\text{OTf}]$, however the structural data in this case are not available so more detailed comparisons cannot be made.²¹

Using two equiv. of TMSOTf to $[\text{GeF}_4\{\text{o}-\text{C}_6\text{H}_4(\text{PMe}_2)_2\}]$ in CH_2Cl_2 led to the formation of $[\text{GeF}_2\{\text{o}-\text{C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{OTf})_2]$. Here the methyl ^1H NMR resonance at 2.03 ppm, is to high frequency of both the tetrafluoride and trifluoride derivatives. In this difluoride complex three possible isomers exist if the triflates are bound (Fig. 13).

The room temperature $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum shows a resonance at –100.5 ppm as doublet of doublets, correspondingly in the room temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum there is a doublet of doublets at –23.2 ppm, which both have the same coupling constants ($^2J_{\text{PF}} = 121, 74$ Hz). This is consistent with the 3rd isomer (rhs) being present in solution at room temperature.



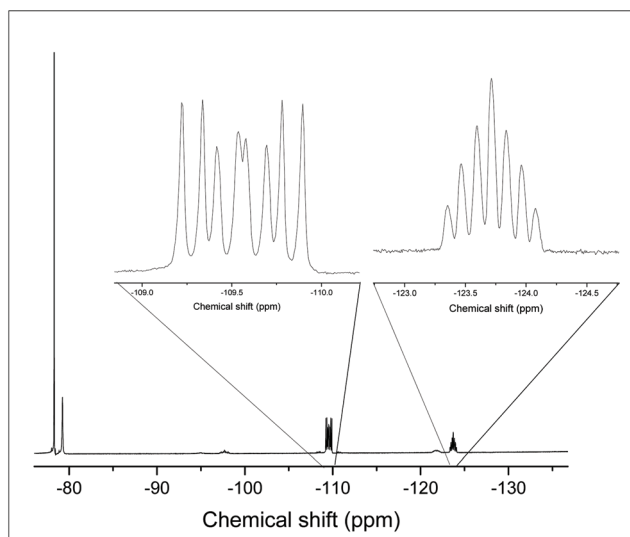


Fig. 12 $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of $[\text{GeF}_2\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{OTf})]$ at 183 K (CH_2Cl_2).

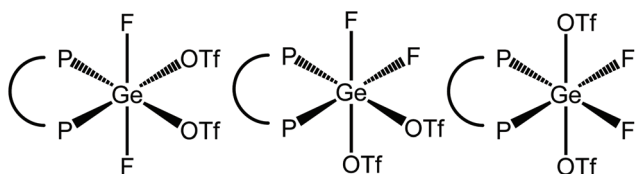


Fig. 13 The three possible isomers of (six-coordinate) $[\text{GeF}_2\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{OTf})_2]$.

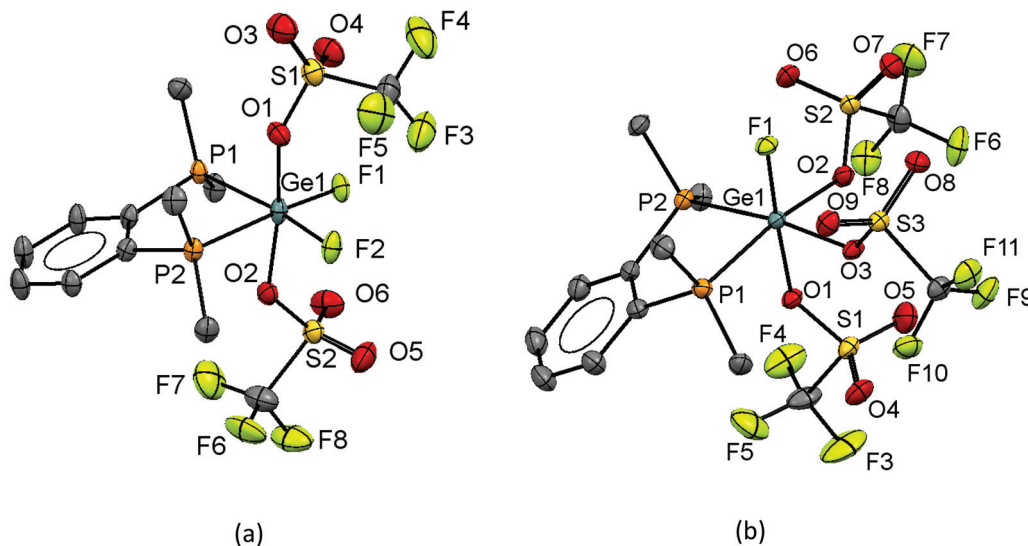


Fig. 14 (a) The structure of $[\text{GeF}_2\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{OTf})_2]$ showing the atom labelling scheme. The ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are: $\text{Ge1-P1} = 2.4033(16)$, $\text{Ge1-P2} = 2.3814(17)$, $\text{Ge1-F1} = 1.751(4)$, $\text{Ge1-F2} = 1.776(4)$, $\text{Ge1-O1} = 1.949(5)$, $\text{Ge1-O2} = 2.018(5)$, $\text{P1-Ge1-P2} = 86.33(6)$, $\text{O1-Ge1-O2} = 172.4(2)$, $\text{F1-Ge1-F2} = 92.7(2)$; (b) the structure of $[\text{GeF}\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{OTf})_3]$ showing the atom labelling scheme. There are two $[\text{GeF}\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{OTf})_3]$ in the asymmetric unit; only one is shown. The ellipsoids are drawn at the 50% probability level and H atoms and a CH_2Cl_2 solvent molecule are omitted for clarity. Selected bond lengths (Å) and angles (°) are: $\text{Ge1-P1} = 2.3900(9)$, $\text{Ge1-P2} = 2.3840(9)$, $\text{Ge1-F1} = 1.7681(18)$, $\text{Ge1-O1} = 1.948(2)$, $\text{Ge1-O2} = 1.939(2)$, $\text{Ge1-O3} = 1.917(2)$, $\text{P1-Ge1-P2} = 86.54(3)$, $\text{O2-Ge1-O3} = 83.67(10)$, $\text{O1-Ge1-F1} = 176.27(9)$.

Crystals from this product grown from a CH_2Cl_2 solution of the complex layered with hexane were indeed shown to be $[\text{GeF}_2\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{OTf})_2]$ and the structure is shown in Fig. 14(a). In the structure the triflates are *trans* to each other and the fluorines are *cis*, consistent with the NMR data.

Addition of three equiv. of TMSOTf to $[\text{GeF}_4\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}]$ in CH_2Cl_2 leads to the formation of $[\text{GeF}\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{OTf})_3]$. There are two possible isomers in the case where the triflates are bound (Fig. 15).

The room temperature $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum shows a triplet at -94.1 ppm, while in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum a doublet at -13.5 ppm with a coupling constant of $^2J_{\text{PF}} = 73$ Hz is evident, consistent with the *fac* isomer in solution. A CH_2Cl_2 solution of the complex layered with hexane deposited crystals and X-ray structure analysis (Fig. 14(b)) confirmed the *fac* geometry is maintained in the solid state.

The reaction of $[\text{GeF}_4\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}]$ with TMSOTf in CH_2Cl_2 leads to $[\text{GeF}_3\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}(\text{OTf})]$. Crystals of this compound were grown by layering a CH_2Cl_2 solution of the complex with hexane, and the structure is shown in Fig. 16(a).

In the structure of $[\text{GeF}_3\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}(\text{OTf})]$ the diphosphine ligand is chelating and the fluorines are *mer*, this is in contrast to $[\text{GeF}_2\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{OTf})]$ where the NMR data suggests a *fac* arrangement. It is likely that the different electronic and steric properties of the ligands dictate the preferred isomer.

From the same batch of crystals, a crystal of $[\text{GeF}_2\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}(\text{OTf})_2]$ was also identified. The structure of this complex is shown in Fig. 16 (b). The geometry is analogous to



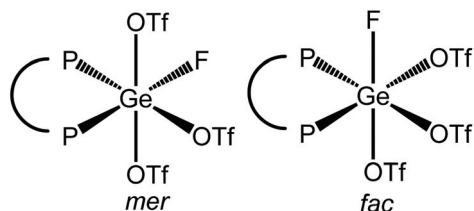


Fig. 15 The two possible isomers of (six-coordinate) $[\text{GeF}(\text{o-C}_6\text{H}_4(\text{PMe}_2)_2)(\text{OTf})_3]$.

the $\text{o-C}_6\text{H}_4(\text{PMe}_2)_2$ complex with both fluorides *trans* to the phosphine ligand and the triflates mutually *trans*.

As with monodentate phosphines, there is a decrease in $d(\text{Ge-P})$ and an increase in the P-Ge-P bond angles as fluoride is replaced by triflate, while the Ge-F distances remain largely unaffected (Table 3). The $d(\text{Ge-O})$ distances are much shorter for the diphosphine complexes compared to the monophosphine complexes.

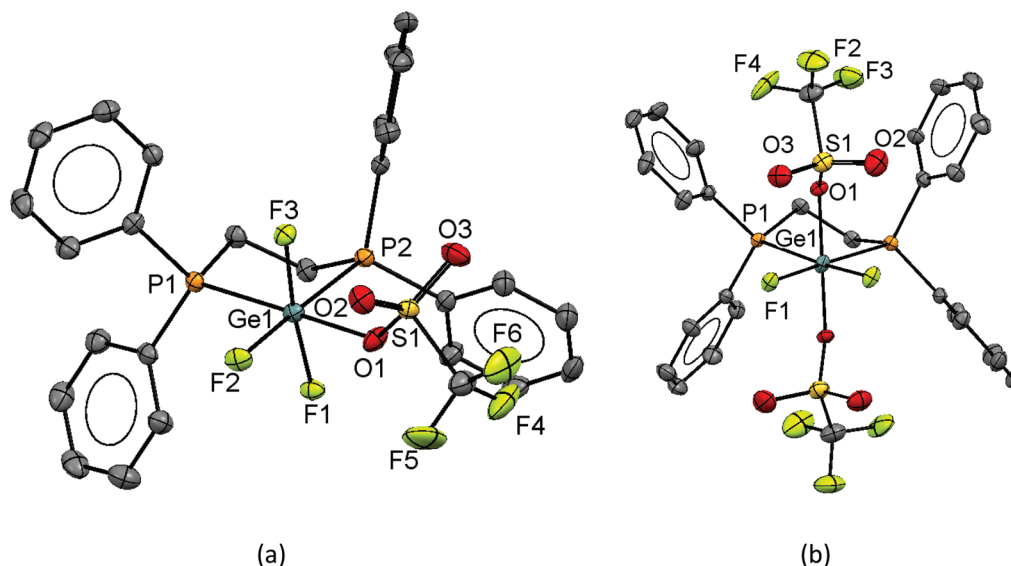


Fig. 16 (a) The structure of $[\text{GeF}_3\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}(\text{OTf})]$ showing the atom labelling scheme. The ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$) are: Ge1-P1 = 2.4294(10), Ge1-P2 = 2.4321(11), Ge1-F1 = 1.791(2), Ge1-F2 = 1.762(2), Ge1-F3 = 1.775(2), Ge1-O1 = 1.965(3), P1-Ge1-P2 = 85.49(3), F1-Ge1-F3 = 173.69(10), P1-Ge1-O1 = 177.73(8), P2-Ge1-F2 = 173.04(8); (b) the structure of $[\text{GeF}_2\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}(\text{OTf})_2]$ showing the atom labelling scheme. The ellipsoids are drawn at the 50% probability level and H atoms and a CH_2Cl_2 solvent molecule are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$) are: Ge1-P1 = 2.4217(6), Ge1-F1 = 1.7641(11), Ge1-O1 = 1.934(7), P1-Ge1-P1 = 86.25(2), F1-Ge1-F1 = 91.43(8), O1-Ge1-O1 = 172.3(5).

Table 3 Selected structural parameters for the Ge(IV) diphosphine complexes

Complex	$d(\text{Ge-P})/\text{Å}$	$d(\text{Ge-F})/\text{Å}$	P-Ge-P angle/ $^\circ$	$d(\text{Ge-O})/\text{Å}$
$[\text{GeF}_4\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}]^{13}$	2.4273(12) 2.4273(11)	1.815(2) 1.809(2) (<i>cis</i>) 1.765(2)	85.61(4)	—
$[\text{GeF}_2\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{OTf})_2]$	2.4033(16) 2.3814(17)	1.751(4) 1.776(4)	86.33(6)	1.949(5) 2.018(5)
$[\text{GeF}\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{OTf})_3]$	2.3900(9) 2.3840(9)	1.7681(18)	86.54(3)	1.948(2) 1.939(2) 1.917(2)
$[\text{GeF}_4\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}]^{13}$	2.4636(7) 2.4822(7)	1.7692(14) (<i>trans</i>) 1.7731(14) 1.7829(13) (<i>cis</i>) 1.7987(14)	84.08(2)	—
$[\text{GeF}_3\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}(\text{OTf})]$	2.4294(10) 2.4321(11)	1.791(2) 1.775(2) (<i>cis</i>) 1.762(2) (<i>trans</i>)	85.49(3)	1.965(3)
$[\text{GeF}_2\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}(\text{OTf})_2]$	2.4217(6)	1.7641(11)	86.25(2)	1.934(7)



The complexes involving the $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ ligand were very poorly soluble, hindering acquisition of solution NMR data. Finally, attempts to increase the number of phosphine donor groups at Ge(IV) through fluoride abstraction led to mixtures of species (from the NMR data) for both the triphosphine and tetraphosphine complexes, along with evidence of reduction to Ge(II). Hence this was not pursued further.

Experimental

The syntheses were carried out using standard Schlenk and vacuum line techniques, with samples handled and stored in a glove box under a dry dinitrogen atmosphere to exclude moisture. TMSOTf was obtained from Sigma-Aldrich and distilled before use. Germanium tetrafluoride was obtained from Fluorochem and GeCl_4 from Acros Organics and were used as received. Phosphine ligands and AsEt_3 were obtained from Sigma-Aldrich or Strem and used as received, except for $o\text{-C}_6\text{H}_4(\text{PMe}_3)_2$ which was made by the literature route.²² CH_2Cl_2 and MeCN were dried by distillation from CaH_2 and n-hexane from sodium wire. $[\text{GeF}_4(\text{PMe}_3)_2]$, $[\text{GeF}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_3)_2\}]$ and $[\text{GeF}_4\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}]$ were made as described.¹³

Infrared spectra were recorded as Nujol mulls between CsI plates using a PerkinElmer Spectrum 100 spectrometer over the range 4000–200 cm^{-1} . ^1H , $^{19}\text{F}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded from $\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2$ solutions unless otherwise stated, using a Bruker AV400 spectrometer and are referenced to TMS *via* the residual solvent resonance, CFCl_3 , and 85% H_3PO_4 respectively. Microanalyses were undertaken by London Metropolitan University or Medac.

$[\text{GeF}_4(\text{P}^i\text{Pr}_3)_2]$

To a suspension of $[\text{GeF}_4(\text{MeCN})_2]$ in CH_2Cl_2 (5 mL) two equiv. of P^iPr_3 was added as a solution in CH_2Cl_2 (2 mL) and the reaction mixture stirred for 2 h to yield a clear colourless solution. The volatiles were removed *in vacuo* to leave a white solid which was washed with hexane (3×10 mL) and dried *in vacuo*. Yield: 0.941 g (76%). Satisfactory analytical data could not be obtained despite repeated attempts on different samples, with the elemental compositions varying from sample to sample. ^1H NMR (CD_2Cl_2 , 298 K): $\delta = 1.33$ (dd, $^3J_{\text{HH}} = 15$ Hz, $^3J_{\text{PH}} = 7$ Hz, [6H]), 2.38 (m, [1H]), $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 298 K): $\delta = -65.0$ (s); (183 K): $\delta = -62.9$ ($^2J_{\text{PF}} = 162$ Hz) $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 298 K): $\delta = 24.6$ (s); (183 K): $\delta = 24.9$ (quint, $^2J_{\text{PF}} = 162$ Hz). IR (Nujol/ cm^{-1}): $\nu = 590$ s (Ge-F).

$[\text{GeF}_3(\text{PMe}_3)_2(\text{OTf})]$

To a solution of $[\text{GeF}_4(\text{PMe}_3)_2]$ (0.100 g, 0.33 mmol) in CH_2Cl_2 (2 mL), a solution of TMSOTf (0.074 g, 0.33 mmol) in CH_2Cl_2 (2 mL) was added dropwise to form a clear solution. The reaction was stirred for 2 h, when the volatiles were removed *in vacuo* leaving a solid that was washed with hexane (3×10 mL) and dried *in vacuo* to form a white powder. Yield: 0.080 g (56%). Required for $\text{C}_7\text{H}_{18}\text{F}_6\text{GeO}_3\text{P}_2\text{S}$ (430.86): C, 19.5; H, 4.2.

Found: C, 19.6; H, 4.3%. ^1H NMR (CD_2Cl_2 , 298 K): $\delta = 1.68$ (d, $^2J_{\text{HP}} = 13.2$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 298 K): $\delta = -78.76$ (s, [3F], OTf), -94.74 (br, [3F]); (183 K): $\delta = -78.9$ (s, [3F], OTf), -85.9 (td, [2F], $^2J_{\text{PF}(\text{cis-OTf})} = 192$ Hz, $^2J_{\text{FF}} = 41$ Hz, GeF), -123.4 (tt, [F], $^2J_{\text{PF}(\text{trans-OTf})} = 134$ Hz, $^2J_{\text{FF}} = 41$ Hz, GeF). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 298 K): $\delta = 5.2$ (br s); (183 K): $\delta = 5.2$ (td, $^2J_{\text{PF}(\text{cis-OTf})} = 192$ Hz, $^2J_{\text{PF}(\text{trans-OTf})} = 134$ Hz). IR (Nujol/ cm^{-1}): 572 (br, m), 515 (m) Ge-F.

$[\text{GeF}_2(\text{PMe}_3)_2(\text{OTf})_2]$

Method as above using $[\text{GeF}_4(\text{PMe}_3)_2]$ (0.100 g, 0.33 mmol) and TMSOTf (0.148 g, 0.66 mmol). White solid. Yield: 0.140 g (75%). Required for $\text{C}_8\text{H}_{18}\text{F}_8\text{GeO}_6\text{P}_2\text{S}_2$ (560.63): C, 17.1; H, 3.2. Found: C, 17.0; H, 3.3%. ^1H NMR (CD_2Cl_2 , 298 K): 1.96 (m); (233 K): $\delta = 1.98$ (d, $^2J_{\text{HP}} = 12$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 298 K): $\delta = -78.3$ (s, [6F], OTf), -119.5 (br s, [2F], GeF); (233 K): $\delta = -78.3$ (br, [6F], OTf), -122.3 (t, [2F], $^2J_{\text{PF}} = 83$ Hz, GeF). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 298 K): $\delta = 25.8$ (br); (233 K): $\delta = 27.8$ (t, $^2J_{\text{PF}} = 83$ Hz). IR (Nujol/ cm^{-1}): $\nu = 573$ (br m) (Ge-F).

$[\text{GeF}(\text{PMe}_3)_2(\text{OTf})_3]$

Method as above using $[\text{GeF}_4(\text{PMe}_3)_2]$ (0.100 g, 0.33 mmol) and TMSOTf (0.222 g, 1.00 mmol). White solid. Yield: 0.175 g (76%). Required for $\text{C}_9\text{H}_{18}\text{F}_{10}\text{GeO}_9\text{P}_2\text{S}_3$ (691.00): C, 15.6; H, 2.6. Found: C, 15.8; H, 2.6%. ^1H NMR (CD_2Cl_2 , 298 K): $\delta = 2.03$ (dd, $^2J_{\text{HP}} = 13.8$ Hz, $^4J_{\text{FH}} = 1$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 298 K): $\delta = -77.6$ (br s, OTf), -78.1 (br s, OTf, total OTf integral [9F]), -107.2 (t, $^2J_{\text{PF}} = 75$ Hz, [F], Ge-F). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 298 K): $\delta = 32.3$ (d, $^2J_{\text{PF}} = 75$ Hz). IR (Nujol/ cm^{-1}): 583 (br, m) Ge-F.

$[\text{GeF}_3(\text{P}^i\text{Pr}_3)_2][\text{OTf}]$

Method as above using $[\text{GeF}_4(\text{P}^i\text{Pr}_3)_2]$ (0.100 g, 0.33 mmol) and TMSOTf (0.074 g, 0.33 mmol). White powder. Yield: 0.188 g (48%). Required for $\text{C}_{18}\text{H}_{42}\text{F}_6\text{GeO}_3\text{P}_2\text{S}\cdot 1/2\text{CH}_2\text{Cl}_2$ (629.63): C, 35.3; H, 6.9. Found: C, 35.3; H, 6.9%. ^1H NMR (CD_2Cl_2 , 298 K): $\delta = 1.43$ (dd, $^3J_{\text{HH}} = 16$ Hz, $^3J_{\text{PH}} = 7$ Hz, [6H]), 2.69 (m, [1H]). $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 298 K): $\delta = -79.0$ (s, [3F], OTf), -56.7 (t, $^2J_{\text{PF}} = 153$ Hz, [3F], Ge-F). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 298 K): $\delta = 46.8$ (q, $^2J_{\text{PF}} = 153$ Hz). IR (Nujol/ cm^{-1}): 572 m (br m) Ge-F.

$[\text{GeF}_3\{o\text{-C}_6\text{H}_4(\text{PMe}_3)_2\}(\text{OTf})]$

Method as above using $[\text{GeF}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_3)_2\}]$ (0.100 g, 0.288 mmol) and TMSOTf (0.064 g, 0.288 mmol) and stirring for 30 min. White solid. Yield: 0.084 g (61%). Required for $\text{C}_{11}\text{H}_{16}\text{F}_6\text{GeO}_3\text{P}_2\text{S}$ (476.86): C, 27.7; H, 3.4. Found: C, 27.5; H, 3.6%. ^1H NMR (CD_2Cl_2 , 298 K): $\delta = 1.90$ (m, [12H], Me), 7.84 (m, [4H], Ar-H). $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 298 K): $\delta = -78.3$ (s, OTf), -113.3 (br s, GeF); (183 K): $\delta = -78.3$ (s, [3F], [OTf]), -109.5 (ddd, [2F], $^2J_{\text{PF}} = 135$, 76 Hz; $^2J_{\text{FF}} = 43$ Hz), -123.7 (tt, [1F], $^2J_{\text{PF}} = 94$ Hz; $^2J_{\text{FF}} = 43$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 298 K): $\delta = -24.1$ (br s); (183 K): $\delta = -23.1$ (ddd, $^2J_{\text{PF}} = 135$, 94, 76 Hz). IR (Nujol/ cm^{-1}): 518 (m), 579 (m), 602 (m) Ge-F.



[GeF₂{*o*-C₆H₄(PMe₃)₂}(OTf)₂]

Method as above using [GeF₄{*o*-C₆H₄(PMe₃)₂}] (0.100 g, 0.288 mmol) and TMSOTf (0.128 g, 0.576 mmol) and stirring for 30 min. White solid. Yield: 0.102 g (58%). Required for C₁₂H₁₆F₈GeO₆P₂S₂·CH₂Cl₂ (691.84): C, 22.6; H, 2.6. Found: C, 22.7; H, 3.1%. ¹H NMR (CD₂Cl₂, 298 K): δ = 2.03 (m, [12H], Me), 7.91 (m, [4H], Ar-H). ¹⁹F{¹H} NMR (CD₂Cl₂, 298 K): δ = -77.5 (s, OTf), -78.2 (s, OTf), -100.5 (dd, ²J_{PF} = 121 Hz, 74 Hz); (183 K): δ = -77.7 (s, OTf), -78.0 (s, OTf), -78.3 (s, OTf), -79.1 (s, OTf), -101.1 (dd, ²J_{PF} = 126, 72 Hz), ³¹P{¹H} NMR (CD₂Cl₂, 298 K): δ = -23.2 (dd, ²J_{PF} = 121 Hz, 74 Hz); (183 K): δ = -19.9 (dd, ²J_{PF} = 126, 72 Hz) IR (Nujol/cm⁻¹): 637 (m) Ge-F.

[GeF{*o*-C₆H₄(PMe₃)₂}(OTf)₃]

Method as above using [GeF₄{*o*-C₆H₄(PMe₃)₂}] (0.100 g, 0.288 mmol) and TMSOTf (0.192 g, 0.864 mmol) and stirring for 30 min., then the solution was layered with hexane (10 mL). After 3 days the product crystallised. Crystals were collected by filtration, washed with hexane (3 × 10 mL), and dried *in vacuo*. Yield: 0.086 g (40%). Required for C₁₃H₁₆F₁₀GeO₉P₂S₃ (736.98): C, 21.2; H, 2.2. Found: C, 22.1; H, 3.8%. ¹H NMR (CD₂Cl₂, 298 K): δ = 2.03 (m, Me), 2.16 (m, Me), 2.25 (m, Me) (sum of methyl resonances [12H]), 7.97 (m, [4H], Ar-H). ¹⁹F{¹H} NMR (CD₂Cl₂, 298 K): δ = -77.1 (s, OTf), -77.3 (s, OTf), -77.6 (s, OTf), -78.2 (br, OTf), -81.8 (t, ²J_{PF} = 82 Hz)⁺, -91.9 (t, ²J_{PF} = 69 Hz)⁺, -94.0 (t, ²J_{PF} = 73 Hz, GeF)*. ³¹P{¹H} NMR (CD₂Cl₂, 298 K): δ = -13.5 (d, ²J_{PF} = 73 Hz)*, -8.53 (d, ²J_{PF} = 69 Hz); (* = major species; + = minor species). IR (Nujol/cm⁻¹): 633 (m) Ge-F.

[GeF₃{Ph₂P(CH₂)₂PPh₂}(OTf)]

Method as above using [GeF₄{Ph₂P(CH₂)₂PPh₂}] (0.100 g, 0.183 mmol) and TMSOTf (0.041 g, 0.184 mmol). White solid. Yield: 0.045 g (36%). Required for C₂₇H₂₄F₆GeO₃P₂S (677.12): C, 47.9; H, 3.6. Found: C, 47.7; H, 3.7%. The product was not sufficiently soluble in CH₂Cl₂ or CD₃NO₂ to obtain reliable solution NMR data. IR (Nujol/cm⁻¹): 519 (m), 526 (m), 573 (m) Ge-F.

[GeF₂{Ph₂P(CH₂)₂PPh₂}(OTf)₂]

Method as above using [GeF₄{Ph₂P(CH₂)₂PPh₂}] (0.100 g, 0.183 mmol) and TMSOTf (0.081 g, 0.364 mmol). White solid. Yield: 0.119 g (81%). Required for C₂₈H₂₄F₈GeO₆P₂S₂·1/2CH₂Cl₂ (849.60): C, 40.3; H, 3.0. Found: C, 39.9; H, 3.0%. The product was not sufficiently soluble in CH₂Cl₂ or CD₃NO₂ to obtain reliable solution NMR data. IR (Nujol/cm⁻¹): 502 (m), 527 (m) Ge-F.

[GeF₄{κ²-CH₃C(CH₂PPh₂)₃}]

To a suspension of [GeF₄(MeCN)₂] (0.200 g, 0.867 mmol) in CH₂Cl₂ (2 mL), CH₃C(CH₂PPh₂)₃ (0.541 g, 0.867 mmol) was added as a solid and the resulting solution is stirred for 2 h forming a clear colourless solution. Volatiles were removed *in vacuo* to yield a white solid, which was washed with hexane (3 × 10 mL) and dried *in vacuo*. Yield: 0.413 g (62%) Required for

C₄₁H₃₉F₄GeP₃·1/2 CH₂Cl₂ (815.70): C, 61.1; H, 4.9. Found: C, 61.2; H, 5.1%. ¹H NMR (CD₂Cl₂, 298 K): δ = 0.87 (s, [3H] CH₃), 2.69 (br s, [6H], CH₂), 7.28–7.58 (m, ArH); (183 K): δ = 0.73 (s, [3H]), 2.01 (br m, [2H]), 2.79 (br s, [2H]), 2.90 (br s, [2H]), 7.28–7.58 (m, ArH). ¹⁹F{¹H} NMR (CD₂Cl₂, 298 K): δ = -108.6 (br s, GeF), -72.2 (br s, GeF); (243 K): δ = -74.4 (overlapping multiplets, [2F]), -109.3 (ddt, ²J_{PF} = 125, 67 Hz, ²J_{FF} = 62 Hz); (183 K): δ = -77.7 (br m, [2F]), -110.3 (br m, [2F]). ³¹P{¹H} NMR (CD₂Cl₂, 298 K): δ = -4.0 (br s), -23.5(s); (183 K): δ = -4.5 (tdd, [2P], ²J = 142, 125, 67 Hz), -27.9 (s, [1P]). IR (Nujol/cm⁻¹): 517 (br), 603 (br) Ge-F.

[GeF₄{κ²-P(CH₂CH₂PPh₂)₃}]

To a suspension of [GeF₄(MeCN)₂] (0.200 g, 0.867 mmol) in CH₂Cl₂ (2 mL), P(CH₂CH₂PPh₂)₃ (0.581 g, 0.867 mmol) was added as a solid and the resulting solution was stirred for 2 h to give a clear colourless solution, from which volatiles were removed *in vacuo* to yield a white solid. The resulting solid was washed with hexane (3 × 10 mL) and dried *in vacuo*. Yield 0.408 (57%). Required for C₄₂H₄₂F₄GeP₄ (819.25): C, 61.6; H, 5.2. Found: C, 62.1; H, 5.5%. ¹H NMR (CD₂Cl₂, 298 K): δ = 2.03 (br s, [6H], CH₂), 2.28 (br s, [6H], CH), 7.38–7.48 (br m, [30H], ArH). ¹⁹F{¹H} NMR (CD₂Cl₂, 298 K): δ = -94.8 (br s), -114.2 (br s); (213 K): δ = -80.4 (ddt, ²J_{PF} = 153, 133 Hz, ²J_{FF} = 54 Hz, [2F]), -108.4 (ddt, ²J_{PF} = 205, ²J_{FF} = 54, 54 Hz, [F]), -114.1 (ddt, ²J_{PF} = 188 Hz, ²J_{FF} = 54, 54 Hz, [F]), ³¹P{¹H} NMR (CD₂Cl₂, 183 K): δ = -3.2 (ddtt, [P], ²J_{PP} = 336, ²J_{PF} = 188, 153, ³J_{PP} = 35 Hz), -12.4 (d, [2P], ³J_{PP} = 35 Hz), -17.6 (ddt, [P], ²J_{PF} = 336, 207, 133 Hz). IR (Nujol/cm⁻¹): 508 (m), 517 (m), 589 (m), 608 (m) Ge-F.

Reaction of GeCl₄ two eq. of AsEt₃ and two eq. of TMSOTf

To a solution of GeCl₄ (0.134 g, 0.625 mmol) in CH₂Cl₂ (2 mL), AsEt₃ (0.200 g, 1.23 mmol) was added as a solution in CH₂Cl₂ (2 mL). To this mixture TMSOTf (0.274 g, 1.23 mmol) in CH₂Cl₂ (2 mL) was added and the reaction mixture was stirred for 1 h, during which the solution remained colourless. The solution was concentrated to 1 mL, layered with hexane (3 mL) and stored at -18 °C. After a few days a colourless crystalline material formed, which was collected by filtration and dried *in vacuo* to yield a white powder. Yield: 0.261 g. ¹H NMR (CD₂Cl₂, 298 K): indicates a complex mixture of species, which could not be identified with certainty.

X-Ray experimental

Crystals were grown as described above. Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum (λ = 0.71073 Å) rotating anode generator with VHF Varimax optics (70 μm focus) with the crystal held at 100 K. Structure solution and refinement were performed using SHELX(S/L)97, SHELX-2013, or SHELX-2014/7.41 and OLEX.²³ H atoms bonded to C were placed in calculated positions using the default C-H distance and refined using a riding model. [GeF₂{Ph₂P(CH₂)₂PPh₂}(OTf)₂] contains



some substitutional disorder between OTf and F on the axial positions (ratio 85 : 15), which was modelled satisfactorily. The structures of $[\text{GeF}_2(\text{PMe}_3)_2(\text{OTf})_2]$ and $[\text{Ge}\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{OTf})][\text{OTf}]$ contained disordered triflate which was modelled using split occupancies. Details of the crystallographic parameters are given in Table S1 (ESI[†]). CCDC reference numbers for the crystallographic information files in cif format are 2113230 $[\text{GeF}_4(\text{PMe}_3)_2]$, 2113231 $[\text{GeF}_3(\text{PMe}_3)_2(\text{OTf})]$, 2113232 $[\text{GeF}_2(\text{PMe}_3)_2(\text{OTf})_2]$, 2113233 $[\text{GeF}_2\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{OTf})_2]$, 2113234 $[\text{GeF}\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{OTf})_3]$, 2113235 $[\text{GeCl}_2(\text{AsEt}_3)_2(\text{OTf})_2]$, 2113236 $[\text{Ge}\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{OTf})][\text{OTf}]$, 2113237 $[\text{GeF}_3\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}(\text{OTf})]$, 2113415 $[\text{GeF}_4(\kappa^2\text{-CH}_3\text{C}(\text{CH}_2)_2\text{PPh}_2)_3]$, 2113416 $[\text{GeF}_2\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}(\text{OTf})_2]$.[†]

Conclusions

This work shows that neutral complexes of GeF_4 can be extended to the tri- and tetraphosphine ligands $\text{CH}_3\text{C}(\text{CH}_2)_2\text{PPh}_2$ and $\text{P}(\text{CH}_2)_2\text{PPh}_2$, both of which bond in a bidentate κ^2 -mode only. The treatment of $[\text{GeF}_4(\text{PMe}_3)_2]$ with n equivalents of TMSOTf leads to formation of the series of complexes, $[\text{GeF}_{4-n}(\text{PMe}_3)_2][\text{OTf}]_n$ ($n = 1, 2, 3$), each based on six-coordinate Ge(IV). $[\text{GeF}_3(\text{PMe}_3)_2(\text{OTf})]$ is unstable in solution, with the Ge(II) complex, $[\text{Ge}(\text{PMe}_3)_3][\text{OTf}]_2$, crystallising from the solution. The observation of $[\text{FPM}_3]^+$ in the NMR spectrum strongly suggests the occurrence of reductive defluorination in solution. Using the bulkier P^iPr_3 allows formation of $[\text{GeF}_3(\text{P}^i\text{Pr}_3)_2][\text{OTf}]$, whose variable temperature NMR spectra strongly indicate is a triflate salt of the $[\text{GeF}_3(\text{P}^i\text{Pr}_3)_2]^+$ monocation.

$[\text{GeF}_4\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}]$ reacts with n equivalents of TMSOTf to generate the $[\text{GeF}_{4-n}\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}][\text{OTf}]_n$ ($n = 1, 2, 3$) series, and again the trifluoride, $[\text{GeF}_3\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{OTf})]$, was shown to be unstable to reductive defluorination in solution, producing $[\text{Ge}\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{OTf})][\text{OTf}]$, which features a Ge(II) monocation.

The ^{19}F and ^{31}P NMR chemical shifts and couplings and the X-ray structural trends observed with sequential fluoride removal across the series are consistent with an increase in positive charge at germanium as fluoride is replaced with triflate.

Conflicts of interest

The authors have no conflicts to declare.

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