

Complexes of germanium(IV) fluoride with phosphane ligands: structural and spectroscopic authentication of germanium(IV) phosphane complexes

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Complexes of germanium(IV) fluoride with phosphane ligands: structural and spectroscopic authentication of germanium(IV) phosphane complexes†

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The first phosphane complexes of germanium(IV) fluoride, *trans*-[GeF₄(PR₃)₂] (R = Me or Ph) and *cis*-[GeF₄(diphosphane)] (diphosphane = R₂P(CH₂)₂PR₂, R = Me, Et, Ph or Cy; *o*-C₆H₄(PR₂)₂, R = Me or Ph) have been prepared from [GeF₄(MeCN)₂] and the ligands in dry CH₂Cl₂ and characterised by microanalysis, IR, Raman, ¹H, ¹⁹F{¹H} and ³¹P{¹H} NMR spectroscopy. The crystal structures of [GeF₄(diphosphane)] (diphosphane = Ph₂P(CH₂)₂PPh₂ and *o*-C₆H₄(PMe₂)₂) have been determined and show the expected *cis* octahedral geometries. In anhydrous CH₂Cl₂ solution the complexes are slowly converted into the corresponding phosphane oxide adducts by dry O₂. The apparently contradictory literature on the reaction of GeCl₄ with phosphanes is clarified. The complexes *trans*-[GeCl₄(AsR₃)₂] (R = Me or Et) are obtained from GeCl₄ and AsR₃ either without solvent or in CH₂Cl₂, and the structures of *trans*-[GeCl₄(AsEt₃)₂] and Et₃AsCl₂ determined. Unexpectedly, the complexes of GeF₄ with arsane ligands are very unstable and have not been isolated in a pure state. The behaviour of the germanium(IV) halides towards phosphane and arsane ligands are compared with the corresponding silicon(IV) and tin(IV) systems.

Introduction

In marked contrast to the very extensive chemistry with d-block metals, complexes of the p-block metals and metalloids with soft neutral ligands such as phosphanes or arsanes have been relatively little investigated. Whilst a variety of phosphane complexes are known for the heavier halides of Ga^{III}, In^{III}, Bi^{III} and Sn^{IV}, little is known about other Lewis acids in this block.^{1–4} Complexes of the p-block fluorides with phosphanes are extremely rare, and apart from some very early work on SiF₄,¹ the only examples are from our recent study of SnF₄ adducts,⁵ which provided detailed spectroscopic and structural data on a range of complexes including [SnF₄(diphosphane)] (diphosphane = *o*-C₆H₄(PR₂)₂, R = Me or Ph; R₂P(CH₂)₂PR₂, R = Me, Et, Cy or Ph) and *trans*-[SnF₄(PR₃)₂] (R = Me or Cy).⁵ There are no reports of tertiary phosphane complexes of GeF₄, and with GeCl₄ the reports are few and apparently contradictory. Beattie⁶ and Ozin⁷ and their coworkers reported the formation of *trans*-[GeCl₄(PMe₃)₂] and [GeX₄(PMe₃)] (X = Cl or Br) respectively, by reaction of GeX₄ and PMe₃ in the absence of a solvent, and used detailed IR and Raman studies to identify the products. In contrast, the reactions of PR₃ (R = ⁱBu or ⁱPr) with GeX₄ in benzene gave the redox products [PR₃X][Ge^{II}X₃].⁸ In a recent study by Godfrey *et al.*,⁹ the reaction of GeCl₄ with a wide range of tertiary phosphanes (PR₃, R = Me, Et, ⁿPr, ⁿBu, Cy *etc.*) in diethyl ether solution was found to give exclusively [PR₃Cl][Ge^{II}Cl₃], identified by microanalysis, ³¹P{¹H} NMR spectroscopy and by the crystal structure of

[PⁿBu₃Cl][GeCl₃]. Similar redox reactions occur with primary and secondary phosphanes, although the initial products often undergo further reaction with elimination of HX to form species such as R₂PGeX₃ or RHPGeX₃.¹⁰ However Godfrey *et al.*⁹ were able to prepare and structurally characterise the first Ge^{IV} arsane, *trans*-[GeCl₄(AsMe₃)₂]. The redox chemistry in the GeX₄–PR₃ reactions (at least under some conditions) contrasts with that of the SnX₄ systems where simple adduct formation occurs with the majority of phosphanes and diphosphanes.^{4–7} It should be noted however that PⁿBu₃ and SnX₄ produce [PⁿBu₃X][SnX₃].⁸ Here we report the synthesis, structural and spectroscopic characterisation of a series of phosphane complexes of GeF₄, further studies into the GeCl₄ and GeBr₄ reactions, and also studies of complexes of GeX₄ with arsane ligands.

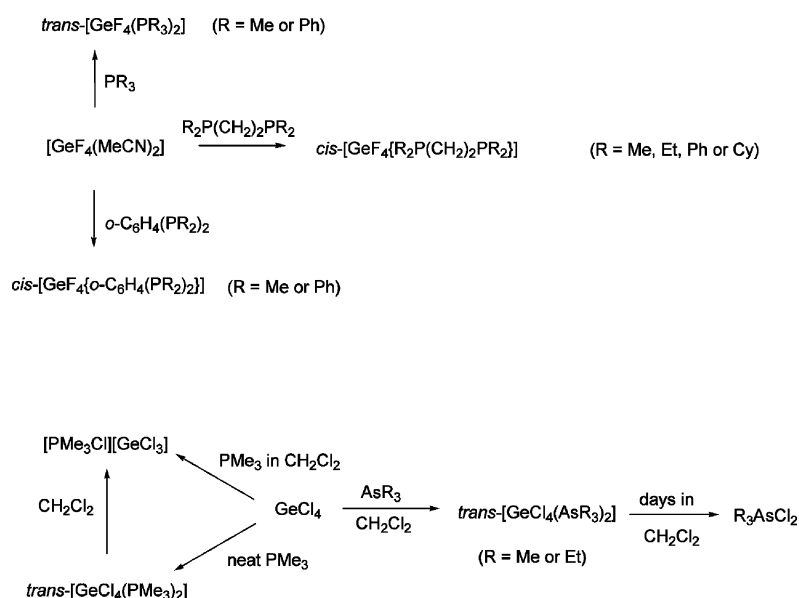
Results and discussion

Germanium(IV) phosphanes

Our previous studies have shown that towards hard N- or O-donor ligands GeF₄ is a much stronger Lewis acid than GeCl₄ or GeBr₄.¹¹ The reaction of [GeF₄(MeCN)₂]¹¹ with two mol. equivalents of PMe₃ in anhydrous CH₂Cl₂ gave [GeF₄(PMe₃)₂] (Scheme 1) as a white, moisture sensitive powder, only slightly soluble in chlorocarbons. The ¹H NMR spectrum in CD₂Cl₂ solution contained a single doublet at δ = 1.46 (²J_{PH} = 12 Hz), the ¹⁹F{¹H} NMR spectrum is a 1 : 2 : 1 triplet at 295 K, and was unchanged on cooling, showing only the *trans* isomer was present in detectable amounts. As expected, the ³¹P{¹H} NMR spectrum is a quintet at δ = –12.4 (²J_{PF} = 196 Hz). The corresponding reaction using PPh₃ gave white *trans*-[GeF₄(PPh₃)₂] (Table 1) which was easily soluble in chlorocarbons, but extensively dissociated at room temperature in solution. The ¹⁹F{¹H} and ³¹P{¹H} NMR data were recorded at 210 K and show the expected multiplets, but

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† Electronic supplementary information (ESI) available: Structures (Fig. S1 and S2), and bond lengths and angles (Table S1 and S2) of [Me₂P(H)(CH₂)₂P(H)Me₂][GeCl₃]₂ and [Me₂P(O)(CH₂)₂P(O)Me₂H][GeCl₃]. CCDC reference numbers 665905–665910. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b716765b



Scheme 1

on warming to >240 K the resonances are lost. In view of the easy chlorination of phosphanes by GeCl_4 (*vide infra*), the reaction of $[\text{GeF}_4(\text{MeCN})_2]$ with excess molten PPh_3 was also carried out, which constitutes more forcing conditions, but examination of the products by $^{31}\text{P}\{^1\text{H}\}$ and $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy revealed only *trans*- $[\text{GeF}_4(\text{PPh}_3)_2]$, traces of $[\text{GeF}_4(\text{OPPh}_3)_2]$ ¹¹ and excess PPh_3 , and there is no evidence for fluorination of the ligand (to Ph_3PF_2). Attempts to isolate *trans*- $[\text{GeF}_4(\text{PCy}_3)_2]$ were unsuccessful, the products obtained were extremely moisture sensitive and NMR studies suggested a mixture of species was present.

The reactions of $[\text{GeF}_4(\text{MeCN})_2]$ with the diphosphanes $\text{R}_2\text{P}(\text{CH}_2)_2\text{PR}_2$ ($\text{R} = \text{Me, Et, Ph or Cy}$) and $o\text{-C}_6\text{H}_4(\text{PR}_2)_2$ ($\text{R} = \text{Me or Ph}$) in anhydrous CH_2Cl_2 were undertaken with the aim of obtaining *cis* isomers and in the expectation that chelation would produce more stable complexes. These readily gave *cis*- $[\text{GeF}_4(\text{diphosphane})]$ as white powders, which can be handled briefly in air with no detectable decomposition. Like the tin analogues, the solids tenaciously retain chlorinated solvents (evident in the ^1H NMR spectra). The complexes exhibit several strong, overlapping $\nu(\text{GeF})$ vibrations in their IR spectra in the range $620\text{--}560\text{ cm}^{-1}$ (theory for a *cis*- MF_4P_2 is four IR active

stretches: $2a_1 + b_1 + b_2$) which may be compared with the t_{1u} mode in $[\text{GeF}_6]^{2-}$ at 600 cm^{-1} .¹² $[\text{GeF}_4\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}]$ is only slightly soluble in CH_2Cl_2 but the other complexes dissolve easily in chlorocarbons. The ^1H NMR spectra in CD_2Cl_2 or CDCl_3 solution at 295 K are simple, showing only coordinated diphosphane ligands present. At ambient temperatures both the $^{19}\text{F}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra are broad lines with ill-defined or unresolved couplings, indicative of reversible dissociation or chelate ring-opening on the appropriate NMR time-scales. On moderate cooling of the solutions (273–243 K depending on the ligand present), the resonances sharpen and show the coupling patterns expected for *cis*-octahedral complexes (Table 1).⁵ The $^{31}\text{P}\{^1\text{H}\}$ spectra are 12 line patterns (d,d,t) and the $^{19}\text{F}\{^1\text{H}\}$ spectra show two resonances; a t,t for the two axial fluorines and a d,d,t for the fluorines *trans* to phosphorus. The chemical shifts and coupling constants are shown in Table 1. Notably the spectra show no other species present in significant amounts and are unchanged after the solutions have been allowed to stand for several hours. The $^{31}\text{P}\{^1\text{H}\}$ chemical shifts are very similar to those observed in the analogous $[\text{SnF}_4(\text{diphosphane})]$ complexes,⁵ and as in those cases the coordination shifts Δ ($\Delta = \delta_{\text{complex}} - \delta_{\text{ligand}}$) are irregular, although generally the stronger σ -donor ligands produce high frequency

Table 1 Selected NMR data for GeF_4 complexes^a

Compound	$\delta\ ^{31}\text{P}\{^1\text{H}\}^b$	Δ^c	$\delta\ ^{19}\text{F}\{^1\text{H}\}$	$^2J(^{31}\text{P}\text{--}^{19}\text{F})/\text{Hz}$	$^2J(^{19}\text{F}\text{--}^{19}\text{F})/\text{Hz}$
$[\text{GeF}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}]$	-31.8(t, d, d)	23	-97.2(t,t), -126.0(d,d,t)	77, 135, 155	54
$[\text{GeF}_4\{o\text{-C}_6\text{H}_4(\text{PPh}_2)_2\}]$	-17.1(t, d, d)	-4	-81.9(t,t), -121.9(d,d,t)	64, 110, 129	65
$[\text{GeF}_4\{\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2\}]$	-9.2(t, d, d)	9	-91.9(t,t), -113.6(d,d,t)	66, 131, 136	55
$[\text{GeF}_4\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}]$	-24.6(t, d, d)	23	-96.2(t,t), -121.2(d,d,t)	80, 135, 149	55
$[\text{GeF}_4\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}]$	-17.1(t, d, d)	-4	-73.7(t,t), -110.3(d,d,t)	64, 119, 151	61
$[\text{GeF}_4\{\text{Cy}_2\text{P}(\text{CH}_2)_2\text{PCy}_2\}]$	-8.7(t, d, d)	-11	-81.2(t,t), -103.1(d,d,t)	60, 121, 122	57
<i>trans</i> - $[\text{GeF}_4(\text{PMe}_3)_2]$	-12.4(q)	50	-96.9(t)	196	
<i>trans</i> - $[\text{GeF}_4(\text{PPh}_3)_2]^d$	2.8(q)	8	-70.6(t)	180	

^a In $\text{CH}_2\text{Cl}_2\text{--}10\%$ CDCl_3 . Spectra were typically recorded at 240 K to resolve couplings (see text). ^b Ligand chemical shifts are: $o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$ -55; $o\text{-C}_6\text{H}_4(\text{PPh}_2)_2$ -13; $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ -13; $\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2$ -18; $\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2$ -48; $\text{Cy}_2\text{P}(\text{CH}_2)_2\text{PCy}_2$ +2; PMe_3 -62; PPh_3 -6 ppm. ^c Coordination shift ($\Delta = \delta_{\text{complex}} - \delta_{\text{ligand}}$). ^d At 190 K. Resonances disappear >240 K.

coordination shifts and the weaker donor aryl-diphosphanes low frequency shifts. Only $[\text{GeF}_4\{\text{C}_6\text{H}_4(\text{PMe}_2)_2\}]$ does not conform to this pattern, exhibiting a coordination shift of -11 , despite being a strong σ -donor. It is likely that steric factors from this bulky ligand on the small germanium centre are a major contributor here. These erratic coordination shifts are seen in phosphane complexes of Sn^{IV} and Ga^{III} ,¹³ but the cause is presently unclear. The $^{19}\text{F}\{^1\text{H}\}$ chemical shifts are higher frequency than those observed in the $[\text{SnF}_4(\text{diphosphane})]$ analogues⁵ and the $^2J_{\text{FF}}$ and $^2J_{\text{PF}}$ couplings are larger in the germanium systems. Similar $^2J_{\text{FF}}$ values (50–60 Hz) are found in *cis*- $[\text{GeF}_4(\text{OPR}_3)_2]$ ¹¹ and in $[\text{GeF}_4(\text{L-L})]$ (L-L = 2,2'-bipyridyl, 1,10-phenanthroline, $\text{Me}_2\text{N}(\text{CH}_2)_2\text{NMe}_2$),¹⁴ although rather larger values (70–80 Hz) are seen in $[\text{GeF}_4\{\text{RS}(\text{CH}_2)_2\text{SR}\}]$.¹⁵

Confirmation of the $[\text{GeF}_4(\text{diphosphane})]$ constitution was provided by X-ray crystal structures of two examples, with the diphosphanes *o*- $\text{C}_6\text{H}_4(\text{PMe}_2)_2$ and $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$. The structure of the former is shown in Fig. 1, and Table 2 contains selected bond lengths and angles. The germanium environment is approximately octahedral with the angles F–Ge–F slightly greater than 90° , F–Ge–P slightly less than 90° , and P–Ge–P $85.61(4)^\circ$. As observed in GeF_4 complexes with N- or O-donor ligands,^{11,14} Ge–F_{trans} (1.809(2), 1.815(2) Å) are longer than Ge–F_{trans} (1.765(2), 1.772(2) Å). Similar patterns of bond lengths and angles are found in the structure of $[\text{GeF}_4\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}]$ (Fig. 2, Table 3) although the Ge–P bonds are slightly longer in the complex of the aryl-diphosphane, possibly due to its weaker σ -donation.

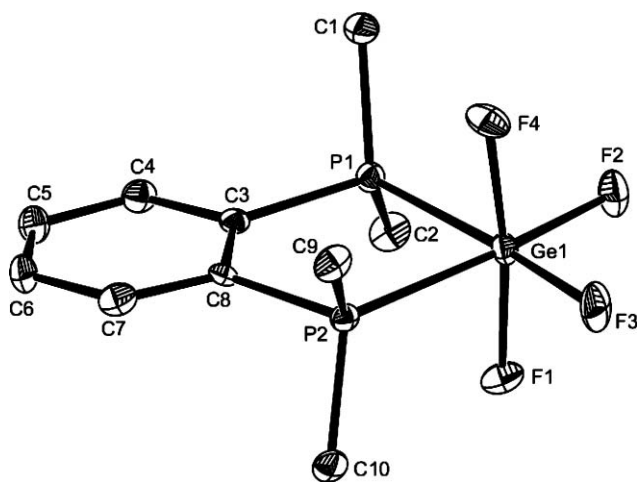


Fig. 1 Structure of $[\text{GeF}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}]$ with the atom numbering scheme adopted. H atoms are omitted for clarity and displacement ellipsoids are shown at the 50% probability level.

Table 2 Selected bond lengths (Å) and angles ($^\circ$) for $[\text{GeF}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}]$

Ge1–F1	1.815(2)	Ge1–F3	1.772(2)
Ge1–F2	1.765(2)	Ge1–F4	1.809(2)
Ge1–P1	2.4273(12)	Ge1–P2	2.4273(11)
F2–Ge1–F3	93.91(10)	F2–Ge1–F4	92.49(12)
F3–Ge1–F4	93.18(12)	F2–Ge1–F1	92.76(12)
F3–Ge1–F1	91.56(12)	F2–Ge1–P1	89.80(8)
F4–Ge1–P1	87.65(9)	F1–Ge1–P1	87.26(8)
F3–Ge1–P2	90.70(9)	F4–Ge1–P2	86.77(9)
F1–Ge1–P2	87.59(8)	P1–Ge1–P2	85.61(4)

Table 3 Selected bond lengths (Å) and angles ($^\circ$) for $[\text{GeF}_4\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}]$

Ge1–F1	1.7987(14)	Ge1–F3	1.7731(14)
Ge1–F2	1.7829(13)	Ge1–F4	1.7692(14)
Ge1–P1	2.4636(7)	Ge1–P2	2.4822(7)
F4–Ge1–F3	93.21(7)	F4–Ge1–F2	93.44(6)
F3–Ge1–F2	93.44(7)	F3–Ge1–F1	93.02(7)
F4–Ge1–F1	92.71(7)	F2–Ge1–P1	89.28(4)
F4–Ge1–P2	90.18(5)	F1–Ge1–P1	83.94(5)
F2–Ge1–P2	88.08(5)	F1–Ge1–P2	85.08(5)
F3–Ge1–P1	92.44(5)	P1–Ge1–P2	84.08(2)

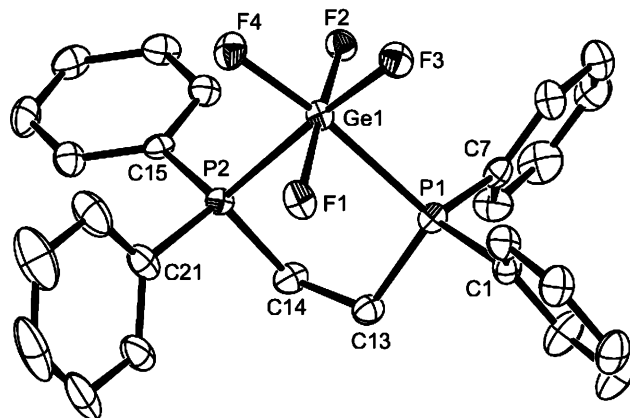


Fig. 2 Structure of $[\text{GeF}_4\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}]$ with the atom numbering scheme adopted. H atoms are omitted for clarity and displacement ellipsoids are shown at the 50% probability level. Only the *ipso* C atom labels are shown and C atoms are numbered sequentially round the ring starting at the label shown.

Studies of the $\text{SnX}_4\text{-PR}_3$ systems⁵ showed that in the presence of air, the corresponding phosphane oxide complexes, $[\text{SnX}_4(\text{OPR}_3)_2]$,¹⁶ form, and we have shown¹⁷ using $^{18}\text{O}_2$, that the source of the oxygen is dioxygen rather than water. Using SnI_4 the reaction provides a convenient catalytic route to phosphane oxides.¹⁷ A solution of $[\text{GeF}_4(\text{PPh}_3)_2]$ in CH_2Cl_2 exposed to dry air, deposited crystals identified by an X-ray structure to be *trans*- $[\text{GeF}_4(\text{OPPh}_3)_2]$,¹¹ and since PPh_3 is air stable in solution, this demonstrates that the reaction was promoted by the germanium complex. In view of the generation of $[\text{PR}_3\text{X}][\text{GeX}_3]$ in the cases of X = Cl or Br, which could hydrolyse to OPR_3 , it was important to establish the source of the oxygen atoms incorporated. Exposure of a solution of $[\text{GeF}_4\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}]$ in CH_2Cl_2 to dry $^{18}\text{O}_2$ resulted in the slow formation of the diphosphane dioxide complex (monitored *in situ* by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy). After the reaction appeared complete the complex was decomposed by treatment with aqueous NaOH, and separation of the organic layer, drying and evaporation produced a white solid. The EI mass spectrum of this solid showed a base peak at $m/z = 433$ corresponding to $[\text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_2\text{P}(\text{O})\text{PPh}_2 - \text{H}]^+$, and the IR spectrum showed $\nu(\text{PO})$ at 1153 cm^{-1} . The $\text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_2\text{P}(\text{O})\text{PPh}_2$ exhibits $\nu(\text{PO})$ at 1177 cm^{-1} , and the simple diatomic oscillator model predicts the effect of ^{18}O substitution will lower this vibration to 1133 cm^{-1} . Coupling with the $\nu(\text{PC})$ mode at $\sim 1120\text{ cm}^{-1}$ probably causes the higher frequency observed experimentally.¹⁷ Thus, like SnX_4 ,^{5,17} GeF_4

promotes air/dioxygen oxidation of phosphanes, although the reaction is considerably slower with germanium.

GeX₄-PMe₃ (X = Cl or Br) systems

Following the successful characterisation of the phosphane adducts of GeF₄, we re-examined the GeCl₄-PMe₃ reaction in an attempt to elucidate the apparently contradictory literature,⁶⁻⁹ and found that the reports from Beattie⁶ and Godfrey⁹ and coworkers are both valid, and that the species formed are extremely dependent upon the conditions. We distilled GeCl₄ onto neat PMe₃ at 77 K and allowed the mixture to thaw slowly. On melting, a vigorous reaction occurred which was moderated by judicious cooling, resulting in formation of a white powder. The Raman spectrum of this product (Fig. 3, top) was in excellent agreement with that reported by Beattie with a *very strong* feature at 267 cm⁻¹ assigned as the a_{1g} vibration of *trans*-[GeCl₄(PMe₃)₂] (lit.,⁶ 268 cm⁻¹)—compare also the values of the corresponding vibration in the crystallographically characterised *trans*-[GeCl₄(AsR₃)₂] (*vide infra*). The sample was then dissolved in rigorously dried CH₂Cl₂ and the mixture immediately pumped to dryness. The Raman spectrum of this sample showed the features of the initial spectrum and some new bands in the region >350 cm⁻¹. The sample was redissolved in CH₂Cl₂, allowed to stand for 3 h and then taken to dryness. The Raman spectrum of this sample (Fig. 3, bottom) showed loss of the 267 cm⁻¹

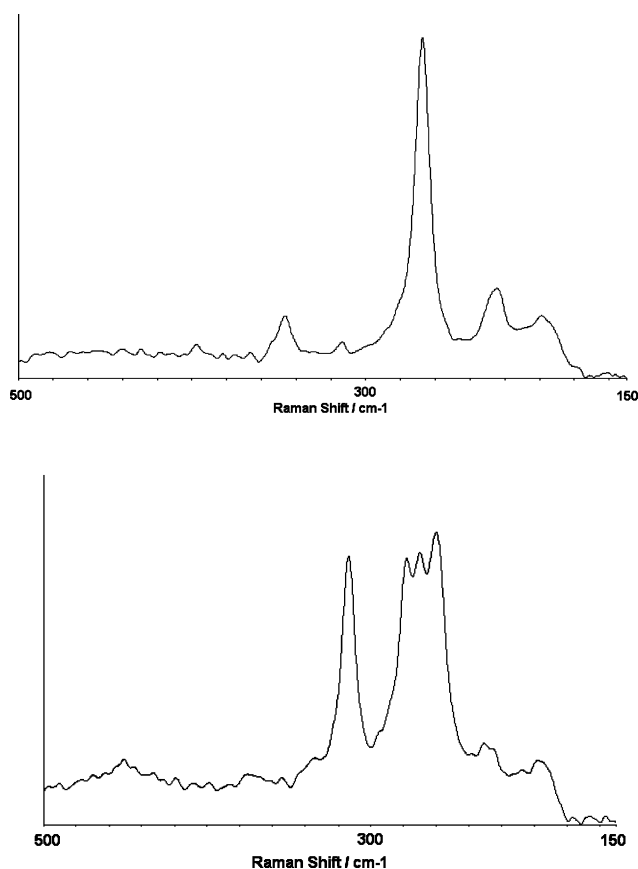


Fig. 3 Raman spectrum of [GeCl₄(PMe₃)₂] (above) and of [PMe₃Cl][GeCl₃] (below). From comparison of the intensities in the ligand modes (not shown) the features in the upper spectrum are ~10 times more intense than those in the lower.

feature, but new medium intensity bands at 314 and 260 cm⁻¹ which correspond to [GeCl₃]⁻ ([NBu₄][GeCl₃]⁺ has features at 320, 255 cm⁻¹). The reactions can also be monitored by NMR spectroscopy. The initial solid, dissolved in CH₂Cl₂ at 273 K and immediately cooled to 200 K, does not show a ³¹P{¹H} NMR resonance from the initial complex, but on standing a new feature at δ = +92 attributable[‡] to [PMe₃Cl]⁺ appeared. The absence of a phosphorus resonance for the Ge^{IV} complex is consistent with extensive dissociation/fast exchange even at low temperatures. This explanation is supported by the ¹H NMR spectrum of *trans*-[GeCl₄(PMe₃)₂] obtained immediately after dissolution in CDCl₃, which shows a doublet at δ = 2.75, ²J_{PH} = 13.5 Hz (assigned to [PMe₃Cl]⁺) and a doublet at δ = 1.8, ²J_{PH} = 13 Hz for the Ge^{IV} complex. Trace hydrolysis of the solution also produces [PMe₃H][GeCl₃], δ(³¹P) = -4.9, and from such a hydrolysed sample we obtained crystals identified by their unit cell as [PMe₃H][GeCl₃].¹⁹ Hence, as described by Beattie and Ozin,⁶ the reaction of GeCl₄ with PMe₃ in the absence of a solvent does indeed give *trans*-[GeCl₄(PMe₃)₂], but this rapidly rearranges in solution in chlorocarbons or ethers to [PMe₃Cl][GeCl₃], and the latter is obtained when the reaction is performed in solution (Scheme 1).^{8,9} The recrystallisation of [GeCl₄(PMe₃)₂] from hot GeCl₄ was reported to give [GeCl₄(PMe₃)₂], believed to be an axially-substituted trigonal bipyramid molecule,⁷ however the reported Raman spectrum is very similar to that of [PMe₃Cl][GeCl₃] and we suggest the latter is the correct formulation. We also reacted GeBr₄ and PMe₃ in the absence of solvent and obtained a cream powder with a Raman spectrum identical to that reported⁷ for [GeBr₄(PMe₃)₂]. In this case also, the strongest features in the low energy region correspond to [GeBr₃]⁻, and on dissolution in dry CH₂Cl₂ the ³¹P{¹H} NMR resonance is found at δ = +68, probably corresponding to [PMe₃Br]⁺.

We have not examined other tertiary phosphanes, but it seems likely that similar reactions would occur with initial formation of a tetrachlorogermanium(IV) adduct which then (especially in solution) undergoes a redox reaction to form [PR₃Cl][GeCl₃]⁺—in some cases the rearrangement may be so rapid that the Ge(IV) species is only a transient intermediate. The GeBr₄-PMe₃ reaction appears to give [PMe₃Br][GeBr₃]⁺ without any evidence that a Ge(IV) complex is isolable. In contrast, the silicon(IV) and tin(IV) complexes are stable (although very moisture sensitive) and *trans*-[SiCl₄(PMe₃)₂]²⁰ and several SnX₄-phosphane complexes^{4,5} have been authenticated by X-ray crystal structures.

In the hope of obtaining more stable Ge(IV) complexes, we examined the reaction of the bidentate Me₂P(CH₂)₂PMe₂ with GeCl₄ under a variety of reaction conditions (mixed in the absence of solvent, in solution in CH₂Cl₂ or Et₂O, at room or low temperatures) and monitored reactions by *in situ* ³¹P{¹H} NMR spectroscopy. The reactions are very sensitive to the conditions, and resonances due to mono- and di-chlorinated and -protonated phosphane groups could be identified, the relative amounts varying with conditions and reaction times, and with trace hydrolysis in some samples. We were unable to unequivocally identify resonances in the ¹H or ³¹P{¹H} NMR spectra due

[‡] The observed ³¹P chemical shift of “[PMe₃Cl]⁺” seems to vary with solvent, concentration and anion, probably due to subtle speciation involving [PMe₃Cl]⁺, Me₃PCl₂ and Me₃PCl...Cl forms (see reference 18 and references therein).

to $[\text{GeCl}_4\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}]$, although this may be due to fast dissociative ligand exchange even at low temperature. The only species identified crystallographically were $[\text{GeCl}_3]^-$ salts with $[\text{Me}_2\text{PH}(\text{CH}_2)_2\text{PHMe}_2]^+$ or $[\text{Me}_2\text{P}(\text{O})(\text{CH}_2)_2\text{P}(\text{O})\text{Me}_2\text{H}]^+$ deposited over several days or weeks (see ESI†). We conclude that the reactions of the diphosphane with GeCl_4 are similar to those with PMe_3 , with the trichlorogermanate(II) as the final product.

The reason for the easier reduction of GeX_4 ($X = \text{Cl}$ or Br) by phosphanes compared with SnX_4 or SiX_4 (or the relative instability of the $[\text{GeX}_4(\text{PR}_3)_2]$), may be an example in germanium chemistry of the lower stability of the element of period 4 in the group oxidation state compared with analogues in periods 3 or 5. This effect is well known for As^{V} , Se^{VI} and Br^{VII} and is usually rationalised as the result of increased nuclear charge from the 3d transition metals not completely balanced by screening from the 3d electrons.²¹

Germanium(IV) arsanes

The reactions of $[\text{GeF}_4(\text{MeCN})_2]$ with $o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$ or AsMe_3 in CH_2Cl_2 afford unstable, very moisture sensitive white solids, with IR and Raman spectra which show the presence of the appropriate ligand and Ge–F bonds and no MeCN. The ^1H NMR spectra in CD_2Cl_2 show the arsane resonances shifted to high frequency from those of the “free” ligands. None of the samples showed $^{19}\text{F}\{^1\text{H}\}$ NMR resonances at room temperature, but on cooling to $< 220\text{ K}$ two triplets of equal intensity appear in regions typical of “*cis*”- GeF_4 units. However, microanalytical data obtained from different samples were always significantly low in C and H compared with expectation for $[\text{GeF}_4\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}]$, and the microanalytical data on the $\text{GeF}_4\text{-AsR}_3$ systems reproducibly approximate to 1:1 compounds. In the latter case, the spectroscopic data (see Experimental section) would be consistent with either a *cis* disubstituted octahedron or an equatorially substituted trigonal bipyramid. We have been unable to obtain crystals of these complexes for X-ray studies and their precise nature remains unclear. There appeared to be no complex formation between GeF_4 and the weaker σ -donor $\text{Ph}_2\text{As}(\text{CH}_2)_2\text{AsPh}_2$. Thus, although GeF_4 appears to form adducts with some arsane ligands, these appear to be extensively dissociated in solution and far less stable than the phosphane analogues—a pattern also observed in the SnF_4 systems.⁵ Isolation of pure complexes in the tin systems is complicated by the “ SnF_4 ” formed on dissociation, precipitating as polymeric $[\text{SnF}_4]_n$, but in the germanium systems dissociation simply forms GeF_4 monomer, and the instability is therefore a direct result of the low affinity of the hard germanium Lewis acid for the soft arsenic centre.

The reaction of GeCl_4 with AsMe_3 in CH_2Cl_2 or Et_2O at ambient temperatures, produced colourless crystals of *trans*- $[\text{GeCl}_4(\text{AsMe}_3)_2]$ which were identified by comparison of their unit cell with the literature data.⁹ A similar reaction using AsEt_3 in CH_2Cl_2 followed by rapid isolation of the product gave white *trans*- $[\text{GeCl}_4(\text{AsEt}_3)_2]$ and crystals obtained from CH_2Cl_2 showed a similar structure (Fig. 4, Table 4). The centrosymmetric molecule has Ge–As = 2.490(1) Å, slightly longer than that in *trans*- $[\text{GeCl}_4(\text{AsMe}_3)_2]$ (2.472(1) Å). If the solution was allowed to stand for a few days very pale yellow crystals were deposited which were identified by their IR and Raman spectra as Et_3AsCl_2 .²² The identity was confirmed by the crystal structure (Fig. 5,

Table 4 Selected bond lengths (Å) and angles (°) for *trans*- $[\text{GeCl}_4(\text{AsEt}_3)_2]$

Ge1–Cl1	2.3296(19)	Ge1–Cl2	2.3233(19)
Ge1–As1	2.4904(9)	As1–C	1.930(8)–1.944(8)
Cl2–Ge1–Cl1	90.67(7)	Ge1–As1–C	110.9(2)–116.0(2)
Cl2–Ge1–As1	87.03(5)	C–As1–C	105.1(4)–106.4(4)
Cl1–Ge1–As1	88.29(5)		

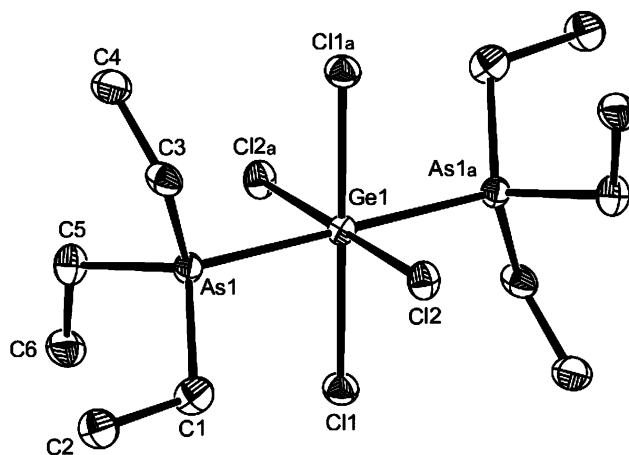


Fig. 4 Structure of the centrosymmetric *trans*- $[\text{GeCl}_4(\text{AsEt}_3)_2]$ with the atom numbering scheme adopted. H atoms are omitted for clarity and displacement ellipsoids are shown at the 50% probability level. Symmetry operation: $a = -x, -y, -z$.

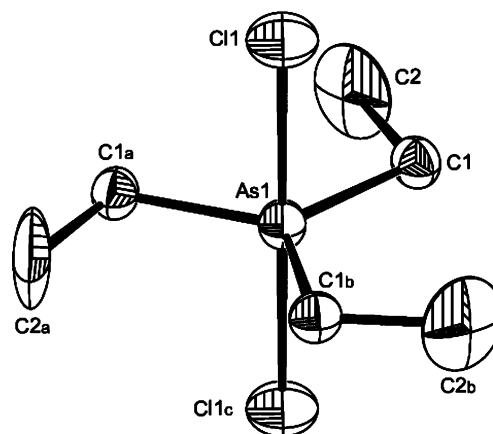


Fig. 5 Structure of Et_3AsCl_2 with the atom numbering scheme adopted. H atoms are omitted for clarity and displacement ellipsoids are shown at the 50% probability level. There are two molecules in the asymmetric unit. The second has the same symmetry and similar bond lengths and angles (see Table 5). Symmetry operations: $a = 1 - y, x - y, z$; $b = 1 - x + y, 1 - x, z$; $c = x, y, -z$.

Table 5) which showed the expected trigonal bipyramid geometry with similar As–Cl and As–C bond lengths to those in related compounds such as Me_3AsCl_2 and Cy_3AsCl_2 .^{23,24} The *trans*- $[\text{GeCl}_4(\text{AsR}_3)_2]$ were also made by reaction of GeCl_4 with the ligands in the absence of a solvent (*cf.* the $\text{GeCl}_4\text{-PMe}_3$ reactions *vide supra*) and had identical Raman spectra to samples obtained using CH_2Cl_2 as solvent.

The Raman spectra obtained from solid *trans*- $[\text{GeCl}_4(\text{AsR}_3)_2]$ ($\text{R} = \text{Me}$ or Et) show very strong bands at 266 cm^{-1} (Me) or

Table 5 Selected bond lengths (Å) and angles (°) for Et₃AsCl₂

As1–Cl1	2.382(4)	As2–Cl2	2.362(4)
As1–Cl	1.927(6)	As2–C3	1.918(7)
Cl1–C2	1.604(13)	C3–C4	1.637(12)
C–As1–C	120.0	C–As2–C	120.0
C–As1–Cl	90.0	C–As2–Cl	90.0
As1–Cl1–C2	105.4(5)	As2–C3–C4	105.9(6)

259 cm⁻¹ (Et) which are assigned as the a_{1g} modes, but in Nujol mulls (the solids dissolve in the Nujol), the strongest band in each far-IR spectrum is at 456 cm⁻¹ which corresponds to the t₂ mode of tetrahedral GeCl₄,²⁵ showing that they are substantially dissociated even in this medium. The ¹H NMR spectra of both complexes are little different to those of the ligands and do not change even on cooling to 190 K, again consistent with extensive dissociation. Upon standing, the solution of *trans*-[GeCl₄(AsEt₃)₂] in CD₂Cl₂ develops new features at δ = 1.60 (t, ³J_{HH} = 7.5 Hz) and 3.06 (q), which correspond to Et₃AsCl₂,²² confirming the slow decomposition. We confirm the previous report⁹ that no reaction occurs between GeCl₄ and AsPh₃ in either CH₂Cl₂ or Et₂O at ambient temperatures. No reaction occurred with GeCl₄ and the diarsane Ph₂As(CH₂)₂AsPh₂, or (very surprisingly) with *o*-C₆H₄(AsMe₂)₂, which suggests that the stereochemistry at germanium also plays a role (*i.e.* *cis* isomers are even less favoured than the *trans* and the normally expected greater stability of chelate complexes is not found here). The reaction of GeBr₄ and AsEt₃ in the absence of solvent gave a clear viscous yellow liquid with strong bands in the Raman spectrum at 311, 267, 240 and 205 cm⁻¹ which do not correspond with tetrahedral GeBr₄ (328, 234 cm⁻¹) or to Et₃AsBr₂,²² and when dissolved in CD₂Cl₂ the ¹H NMR spectrum is little different to that of AsEt₃. This suggests that the oil may be *trans*-[GeBr₄(AsEt₃)₂], again extensively dissociated in solution; extrapolation from the chloride suggests the Raman active a_{1g} Ge–Br vibration will be ~180 cm⁻¹, below the limit of the instrument.

These results show that weak adducts form between GeCl₄ and AsR₃ (R = alkyl), but these are highly dissociated in solution, and slowly convert into R₃AsCl₂. The slower reduction by AsR₃ than by PR₃ reflects the relatively weaker reducing power of the arsanes.

Conclusions

The work has resulted in characterisation of the first phosphane adducts of GeF₄ and has shown that while GeCl₄ forms (unstable) complexes with some arsanes (but not others), these slowly convert into R₃AsCl₂. With phosphanes the reduction to Ge^{II} is usually rapid and [GeCl₄(PR₃)₂] complexes can only be obtained in the absence of solvents. The stability of Lewis acid–base complexes depends upon two major factors—the strength of the donor–acceptor bond and the energy needed to reorganise the tetrahedral GeX₄ unit into the four-coordinate fragment of the octahedron. The latter is constant for fixed X, and thus the relative affinity for PR₃ vs. AsR₃ which is GeF₄ > GeCl₄ for the phosphanes, but appears to be reversed for the arsane compounds, must mainly reflect the difference in orbital energies and donor atom ‘softness’ between P and As. The reduction of Ge^{IV} to Ge^{II} is not evident in the fluoride systems, but is favoured for the GeCl₄ (and GeBr₄) reactions. This contrasts with the chemistry of SnX₄ (X = F, Cl,

Br or I) all of which form phosphane adducts, although again the affinity of SnF₄ for arsanes is much less than for phosphanes. The chemistry observed with GeX₄ also seems to differ from the limited data reported for the SiX₄ systems, but we reserve detailed comparisons here until much more complete data are available. Studies are underway on the silicon tetrahalide complexes.

Experimental

GeF₄ was obtained from Aldrich and used as received. GeCl₄ (Aldrich) was distilled from a mixture of CaCl₂–Na₂CO₃, which removes traces of water and HCl. MeCN and CH₂Cl₂ were dried by distillation from CaH₂, and diethyl ether from sodium benzophenone ketyl. Ligands were obtained from Aldrich or Strem: PMe₃, PPh₃, PCy₃, AsMe₃, AsEt₃, Me₂P(CH₂)₂PMe₂, Et₂P(CH₂)₂PEt₂, Cy₂P(CH₂)₂PCy₂, or were made by literature methods: *o*-C₆H₄(PPh₂)₂, Ph₂P(CH₂)₂PPh₂, *o*-C₆H₄(PMe₂)₂, *o*-C₆H₄(AsMe₂)₂.^{26–29} All reactions were conducted using Schlenk, vacuum line and glove-box techniques and under a dry dinitrogen atmosphere. IR spectra were recorded from Nujol mulls on a Perkin Elmer PE 983G spectrometer, Raman spectra using a Perkin Elmer FT Raman 2000R with a Nd:YAG laser. ¹H NMR spectra were from CDCl₃ or CD₂Cl₂ solutions on a Bruker AV300, ¹⁹F{¹H} and ³¹P{¹H} NMR spectra on a Bruker DPX400 and referenced to CFCl₃ and 85% H₃PO₄ respectively. Microanalytical measurements on new complexes were performed by the micro-analytical service at Strathclyde University. [GeF₄(MeCN)₂] was made as described.¹¹

[GeF₄{*o*-C₆H₄(PMe₂)₂}]

[GeF₄(MeCN)₂] (0.23 g, 1.0 mmol) was dissolved in CH₂Cl₂ (10 mL) and *o*-C₆H₄(PMe₂)₂ (0.198 g, 1.0 mmol) added dropwise; the mixture was stirred for 4 h at ambient temperatures. Most of the solvent was removed *in vacuo* and the white powder produced was filtered off and dried *in vacuo*. Yield 0.32 g, 92%. Required for C₁₀H₁₆F₄GeP₂ (346.8): C, 34.6; H, 4.7. Found: C, 34.9; H, 4.9%. ¹H NMR (300 MHz, CDCl₃, 295 K): δ = 1.81 (t, ²J + ⁵J_{PH} = 4.5 Hz, 12H, Me), 7.73–7.83 (m, 4H, C₆H₄). IR (Nujol): 607(br), 580(sh), 567(br) ν(GeF) cm⁻¹.

[GeF₄{Ph₂P(CH₂)₂PPh₂}]

[GeF₄(MeCN)₂] (0.23 g, 1.0 mmol) was dissolved in CH₂Cl₂ (10 mL), Ph₂P(CH₂)₂PPh₂ (0.40 g, 1.0 mmol) in CH₂Cl₂ (5 mL) was added and the mixture stirred for 3 h. Most of the solvent was removed *in vacuo* and the white precipitate was washed with hexane (10 mL), filtered off and dried *in vacuo*. Yield 0.37 g, 68%. Required for C₂₆H₂₄F₄GeP₂ (547.0): C, 57.1; H, 4.4. Found: C, 56.2; H, 4.5%. ¹H NMR (300 MHz, CDCl₃, 298 K): δ = 2.71 (s, br, H, CH₂), 7.79–7.38 (m, 5H, Ph). IR (Nujol): 603(s), 586(br) ν(GeF) cm⁻¹.

[GeF₄{*o*-C₆H₄(PPh₂)₂}]

[GeF₄(MeCN)₂] (0.23 g, 1.0 mmol) and *o*-C₆H₄(PPh₂)₂ (0.45 g, 1.0 mmol) were weighed out and CH₂Cl₂ (10 mL) added, the solution was stirred for 4 h, during which the solution began to turn cloudy and a white precipitate formed. The precipitate was filtered off and dried *in vacuo*. Yield 0.25 g, 42%. Required for

$C_{30}H_{24}F_4GeP_2 \cdot \frac{1}{3}CH_2Cl_2$ (623.4): C, 58.5; H, 4.0. Found: C, 58.7; H, 3.8%. 1H NMR (300 MHz, $CDCl_3$, 298 K): $\delta = 7.2$ – 7.65 (m, Ph). IR (Nujol): 619(s), 607(vs, br) $\nu(GeF)$ cm^{-1} .

[$GeF_4\{Me_2P(CH_2)_2PMe_2\}$]

$Me_2P(CH_2)_2PMe_2$ (0.15 g, 1.0 mmol) was added dropwise to a solution of [$GeF_4(MeCN)_2$] (0.23 g, 1.0 mmol) in CH_2Cl_2 (10 mL); the mixture was stirred overnight at room temperature. A white precipitate was filtered off and dried *in vacuo*. Yield 0.29 g, 97%. Required for $C_6H_{16}F_4GeP_2 \cdot \frac{1}{2}CH_2Cl_2$ (341.2): C, 22.9; H, 5.0. Found: C, 22.6; H, 5.2%. 1H NMR (300 MHz, $CDCl_3$, 295 K): $\delta = 1.39$ (m, 3H, Me), 2.05 (m, 2H, CH_2). IR (Nujol): 565(vbr) $\nu(GeF)$ cm^{-1} .

[$GeF_4\{Et_2P(CH_2)_2PEt_2\}$]

$Et_2P(CH_2)_2PEt_2$ (0.206 g, 1.0 mmol) was added dropwise to a solution of [$GeF_4(MeCN)_2$] (0.23 g, 1.0 mmol) in CH_2Cl_2 (10 mL); the mixture was stirred for 4 h. Most of the solvent was removed *in vacuo*, the solid filtered off and dried *in vacuo*. Yield 0.29 g, 82%. Required for $C_{10}H_{24}F_4GeP_2 \cdot \frac{1}{2}CH_2Cl_2$ (397.3): C, 31.7; H, 6.3. Found: C, 31.2; H, 7.0%. 1H NMR (300 MHz, $CDCl_3$, 295 K): $\delta = 1.25$ (m, 3H, Me), 1.97 (m, 2H, CH_2), 2.06 (m, 2H, CH_2). IR (Nujol): 605(sh), 577(vbr), 560(sh) $\nu(GeF)$ cm^{-1} .

[$GeF_4\{Cy_2P(CH_2)_2PCy_2\}$]

1,2-Bis(dicyclohexylphosphino)ethane (0.47 g, 1.1 mmol) in CH_2Cl_2 (5 mL) was added to a stirred solution of [$GeF_4(MeCN)_2$] (0.28 g, 1.2 mmol) in CH_2Cl_2 (10 mL) and the mixture was stirred for 2 h. The solvent was removed *in vacuo* to give a white solid which was washed with hexane (10 mL), filtered off and dried *in vacuo*. Yield 0.43 g, 68%. Required for $C_{26}H_{48}F_4GeP_2 \cdot \frac{1}{2}CH_2Cl_2$ (613.5): C, 51.8; H, 8.3. Found: C, 52.0; H, 8.5%. 1H NMR (300 MHz, $CDCl_3$, 295 K): $\delta = 1.28$ – 2.22 (m, CH_2). IR (Nujol): 592(s,vbr) $\nu(GeF)$ cm^{-1} .

trans-[$GeF_4(PMe_3)_2$]

Trimethylphosphine (0.152 g, 2.0 mmol) was added dropwise to a solution of [$GeF_4(MeCN)_2$] (0.23 g, 1.0 mmol) in CH_2Cl_2 (10 mL); the mixture was stirred for 2 h. Most of the solvent was removed *in vacuo* and then filtered to give a white powder which was dried *in vacuo*. Yield 0.15 g, 48%. Required for $C_6H_{18}F_4GeP_2 \cdot \frac{1}{2}CH_2Cl_2$ (343.5): C, 22.7; H, 5.5. Found: C, 22.7; H, 5.6%. 1H NMR (300 MHz, $CDCl_3$, 295 K): $\delta = 1.46$ (d); $^2J_{PH} = 12$ Hz. IR (Nujol): 575(s,vbr). Raman: 508(ms) $\nu(GeF)$ cm^{-1} .

trans-[$GeF_4(PPh_3)_2$]

A solution of triphenylphosphine (0.52 g, 2.0 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of [$GeF_4(MeCN)_2$] (0.23 g, 1.0 mmol) in CH_2Cl_2 (10 mL); the mixture was stirred for 3 h. A white precipitate was filtered off and dried *in vacuo*. Yield 0.60 g, 89%. Required for $C_{36}H_{30}F_4GeP_2 \cdot \frac{1}{4}CH_2Cl_2$ (694.4): C, 62.7; H, 4.4. Found: C, 63.0; H, 4.4%. 1H NMR (300 MHz, $CDCl_3$, 295 K): $\delta = 7.2$ – 7.6 (m). IR (Nujol): 607(s,vbr) $\nu(GeF)$ cm^{-1} .

Reaction of GeF_4 with *o*- $C_6H_4(AsMe_2)_2$

o- $C_6H_4(AsMe_2)_2$ (0.29 g, 1.0 mmol) was added dropwise to a solution of [$GeF_4(MeCN)_2$] (0.23 g, 1.0 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 2 h. The white precipitate was filtered off and dried *in vacuo*. Yield 0.15 g. 1H NMR (300 MHz, CD_2Cl_2 , 295 K): $\delta = 1.45$ (s, 12H, Me), 7.43–7.56 (m, 4H, C_6H_4). $^{19}F\{^1H\}$ NMR (CD_2Cl_2 , 220 K): $\delta = -77.7$ (t), -118.1 (t); $^2J_{FF} = 66$ Hz. IR (Nujol): 657(s), 629(m), 613(m), 595(m) $\nu(GeF)$ cm^{-1} . Raman: 664(w), 630(s, br), 602(s, br), $\nu(GeF)$ cm^{-1} .

Reaction of GeF_4 with $AsMe_3$

GeF_4 was bubbled through a stirred solution of trimethylarsine (0.30 g, 2.5 mmol) in hexane (10 mL). A white solid precipitated which was filtered off and dried *in vacuo*. 1H NMR (300 MHz, $CDCl_3$, 295 K): $\delta = 1.16$ (s, Me). $^{19}F\{^1H\}$ NMR (CD_2Cl_2 , 220 K): $\delta = -127.3$ (t), -149.8 (t); $^2J_{FF} = 80$ Hz. IR (Nujol): 646(s), 635(s), 600(sh) $\nu(GeF)$ cm^{-1} . Raman: 642(s), 596(s, br), $\nu(GeF)$ cm^{-1} . The same product was isolated from reaction of $AsMe_3$ with [$GeF_4(MeCN)_2$] in CH_2Cl_2 solution.

trans-[$GeCl_4(AsMe_3)_2$]

Trimethylarsine (0.341 mL, 3.19 mmol) was added to a stirred solution of germanium(IV) chloride (0.343 g, 1.59 mmol) in diethyl ether (10 mL). This was stirred for 2 d before 5 mL of solvent was removed *in vacuo* and a white solid precipitated out. The solid was filtered off and the filtrate was put in a freezer for 5 d. Colourless crystals formed which were identified by a unit cell determination as *trans*-[$GeCl_4(AsMe_3)_2$].⁹ The crystals and powder were the same spectroscopically. IR (Nujol): 456(s) $\nu_3(GeCl_4)$ cm^{-1} . Raman: 266(vs) $a_{1g}(GeCl)$ cm^{-1} .

trans-[$GeCl_4(AsEt_3)_2$]

Triethylarsine (0.388 mL, 2.76 mmol) was added to a stirred solution of germanium(IV) chloride (0.296 g, 1.38 mmol) in diethyl ether (10 mL). This was stirred overnight before 5 mL of solvent was removed *in vacuo* and was refrigerated when a white solid precipitated, which was filtered off and dried *in vacuo*. Yield 45%. Required for $C_{12}H_{30}As_2Cl_4Ge$ (538.6): C, 26.8; H, 5.6. Found: C, 24.3, H 5.5%. 1H NMR (300 MHz, $CDCl_3$, 295 K): $\delta = 1.15$ (t, 3H CH_3), 1.42 (q, 2H, CH_2). IR (Nujol): 456(s) $\nu_3(GeCl_4)$ cm^{-1} . Raman: 259(vs) $a_{1g}(GeCl)$ cm^{-1} .

The filtrate was put in a freezer for 5 days before the solvent was removed *in vacuo* which gave pale yellow crystals identified as Et_3AsCl_2 from an X-ray structure determination. 1H NMR (300 MHz, $CDCl_3$, 295 K): $\delta = 1.60$ (t, $^3J_{HH} = 7.5$ Hz, 9H, Me), 3.06 (q, 6H, CH_2). Raman: 611(m), 527(vs), 413(m), 338(m), 254(vs) cm^{-1} .

Oxidation reactions of germanium coordinated phosphanes

A sample of [$GeF_4\{Ph_2P(CH_2)_2PPh_2\}$] (0.1 g) was dissolved in degassed anhydrous CH_2Cl_2 under dinitrogen in a small Schlenk tube and the solution frozen solid at 77 K. The system was evacuated and then filled with $^{18}O_2$ to 1 atm and allowed to warm to room temperature. After 2 weeks a sample was removed for ^{31}P NMR study, and the remaining solution shaken up with 1 M aqueous NaOH. The organic layer was separated, dried

Table 6 Crystal data and structure refinement details^a

Compound	[GeF ₄ { <i>o</i> -C ₆ H ₄ (PMe ₂) ₂ }]	[GeF ₄ {Ph ₂ P(CH ₂) ₂ PPh ₂ }]	[GeCl ₄ (AsEt ₃) ₂]	Et ₃ AsCl ₂
Formula	C ₁₀ H ₁₆ F ₄ GeP ₂	C ₂₀ H ₂₄ F ₄ GeP ₂	C ₁₂ H ₃₀ As ₂ Cl ₄ Ge	C ₆ H ₁₅ AsCl ₂
<i>M</i>	346.76	546.98	538.59	233.00
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Hexagonal
Space group (no.)	<i>Pna</i> 2 ₁ (33)	<i>Cc</i> (9)	<i>P</i> 2 ₁ / <i>n</i> (14)	<i>P</i> $\bar{6}$ (174)
<i>a</i> /Å	12.307(3)	10.6765(12)	7.849(2)	8.354(2)
<i>b</i> /Å	10.1285(10)	16.466(2)	13.643(4)	8.354(2)
<i>c</i> /Å	10.749(3)	14.2710(16)	9.537(3)	8.629(2)
<i>α</i> /°	90	90	90	90
<i>β</i> /°	90	105.003(8)	93.721(15)	90
<i>γ</i> /°	90	90	90	120
<i>U</i> /Å ³	1339.9(4)	2423.3(5)	1019.1(5)	521.5(2)
<i>Z</i>	4	4	2	2
<i>μ</i> (Mo-Kα)/mm ⁻¹	2.547	1.439	5.238	3.702
<i>F</i> (000)	696	1112	536	236
Total no. reflections	8863	12784	9942	7342
Unique reflections	2871	4506	2340	861
<i>R</i> _{int}	0.057	0.024	0.079	0.050
Min., max. transmission	0.742, 1.000	0.886, 1.000	0.713, 1.000	0.721, 1.000
No. of parameters, restraints	158, 1	298, 2	91, 0	36, 2
Goodness-of-fit on <i>F</i> ²	1.04	1.05	1.21	1.02
Resid. electron density/e Å ⁻³	-0.53 to +0.46	-0.26 to +0.29	-0.81 to +1.00	-0.47 to +0.60
<i>R</i> ₁ ^b [<i>I</i> _o > 2σ(<i>I</i> _o)]	0.039	0.022	0.067	0.034
<i>R</i> ₁ (all data)	0.051	0.023	0.114	0.044
<i>wR</i> ₂ ^b [<i>I</i> _o > 2σ(<i>I</i> _o)]	0.070	0.054	0.109	0.088
<i>wR</i> ₂ (all data)	0.074	0.054	0.126	0.093

^a Common items: temperature = 120 K; wavelength (Mo-Kα) = 0.71073 Å; *θ*(max) = 27.5°. ^b $R_1 = \sum \|F_o\| - |F_c| / \sum |F_o|$. $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$.

with molecular sieve, and then the solution decanted off and pumped dry. The white solid obtained was used directly for EI mass spectrometry and IR spectroscopy studies (see Results and discussion for spectroscopic data).

The GeCl₄-PMe₃ reaction

In a small Schlenk tube, GeCl₄ (~0.15 g) was distilled *in vacuo* onto PMe₃ (0.105 g, 1.38 mmol) at 77 K. The mixture was cautiously allowed to warm and on melting immediately transformed into a white solid. The Schlenk was briefly evacuated to remove any excess reagent and then filled with dry dinitrogen; the Raman spectrum of the solid was recorded without removing it from the Schlenk. The solid was then dissolved in CH₂Cl₂ (20 mL) and the solution allowed to stand for 3 h and then pumped dry. The solid was identified as [PMe₃Cl][GeCl₃] (see text for spectroscopic data).

X-Ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 6. Crystals of [GeF₄{*o*-C₆H₄(PMe₂)₂}] were obtained from a solution in CH₂Cl₂-*n*-hexane by slow evaporation; [GeF₄{Ph₂P(CH₂)₂PPh₂}] from CH₂Cl₂-*n*-hexane cooled in a freezer; and Et₃AsCl₂ and *trans*-[GeCl₄(AsEt₃)₂] from Et₂O solution by slow evaporation under dinitrogen. Data collection used a Nonius Kappa CCD diffractometer using graphite or confocal mirror monochromated Mo-Kα X-radiation (*λ* = 0.71073 Å). Crystals were held at 120 K in a nitrogen gas stream. Structure solution and refinement were generally routine,^{30–33} except as described below with hydrogen atoms on C introduced in calculated positions using the default C–H distance.

The data for Et₃AsCl₂ was collected as a monoclinic *C* lattice using the automated software with *β* close to 90°, however inspection of the data with Layer³⁴ gave an orthorhombic system as being probable. No satisfactory solution emerged in any of the possible orthorhombic space groups with the initial promising molecules failing to refine. The strategy of trying to solve the structure in *P1* was explored and the transformation matrix by good fortune produced a cell that looked remarkably hexagonal. A solution with *Z* = 2 in *P1* readily followed (*R*₁ = 0.042), but with severe correlation problems during refinement. The triclinic coordinates were finally transformed to the correct hexagonal system. The systematic absences for the transformed data gave 0001 = 2*n*, but it was likely from the As positions that this was not arising from relationships between symmetry related molecules, but rather from the difference in the *z* coordinates of these two atoms (and the other atoms). The only hexagonal space group that would accommodate the molecular symmetry found in the triclinic model was *P* $\bar{6}$ (no. 174). This model converged to *R*₁ = 0.034 with 36 refined parameters compared with 164 parameters in the triclinic model. Chemically the two models are the same, but in crystallographic terms the higher symmetry is preferred. Selected bond lengths and angles are given in Tables 2–5.

CCDC reference numbers 665905–665910.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b716765b

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