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Synthesis, Spectroscopic and Structural Systematics of Complexes of Germanium(IV) Halides (GeX_4, X = F, Cl, Br or I) with Phosphane Oxides and Related Oxygen Donor Ligands

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The first series of phosphane oxide complexes of germanium(IV) halides have been prepared, including *trans*-$[GeF_4(R_3PO)_2]$ (R = Me, Et or Ph), *trans*-$[GeCl_4(Et_3PO)_2]$, *fac*-$[GeCl_3(Me_3PO)_3]_2[GeCl_6]$ and *cis*-$[GeX_2(Me_3PO)_4]X_2$ (X = Cl or Br) and characterised by IR and multinuclear NMR (^1H, $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$) spectroscopy. Crystal structures of all the above (except *trans*-$[GeCl_4(Et_3PO)_2]$) are described. Remarkably, under mild conditions Me_3PO displaces halide ligands from GeX_4 (X = Cl, Br) to form the cationic species above. Ph_3AsO forms *trans*-$[GeF_4(Ph_3AsO)_2]$, but reaction of Ph_3AsO or Me_3AsO with $GeCl_4$ leads to the corresponding R_3AsCl_2. The complexes $[GeF_4(MeCN)_2]$, $[GeF_4(thf)_2]$ and $[GeF_4(MeOCH_2CH_2OMe)]$ are also described and the relative Lewis acidities of GeX_4 established.

Introduction

Germanium is a technologically important element, particularly in the electronics field, and of growing interest in optics and ceramics,[1,2] and new applications often require new Ge-containing precursor compounds. Whilst organogermanium chemistry[3] has been studied in great detail, the coordination chemistry remains little explored.[4] This is in marked contrast to the heavier analogue, tin, whose coordination chemistry is among the most extensive of the p-block metals and metalloids. Studies in the 1960–1970s established that germanium(IV) halides exhibited modest Lewis acidity, although markedly less than that of the Sn^{IV} analogues.[5] A few more examples have been reported in the intervening years, including structurally characterised $[GeCl_3(Me_3[9]aneN_3)]^+$ and $[GeBr_3(1,3,5\text{-trimethyl-}1,3,5\text{-triazacyclohexane})]^+$,[6] $[GeCl_4(2,2'\text{-bipy})]$,[7] $[GeCl_4(Me_2NCH_2CH_2NMe_2)]$,[8] and $[GeCl_4(AsMe_3)_2]$,[9] but data on series of complexes (to reveal trends), solution speciation studies, or even determination of the boundaries of complex formation are lacking. Only two examples with O-donor ligands have been fully characterised, $[GeF_4(Et_2O)_2]$,[10] and $[GeCl_4(dmso)_2]$.[11] We report here studies of the four tetrahalides as Lewis acids towards some neutral oxygen donor ligands.

Results and Discussion

The germanium(IV) halides and their complexes are all moisture sensitive to varying degrees and all syntheses were carried out using rigorously anhydrous conditions. GeF_4 is a gas (sub. 236 K) and although it can be used directly in the syntheses, a solid precursor would be more convenient to handle. One possibility is $[GeF_4(Et_2O)_2]$[10] but this sublimes and dissociates at near ambient temperatures; the adduct $[GeF_4(MeCN)_2]$[12] is a more convenient precursor. The $[GeF_4(MeCN)_2]$ is made by bubbling GeF_4 into excess MeCN at room temperature, whereupon it separates as a white solid, which can be kept indefinitely in a glove box or Schlenk, although it vapourises slowly in a dynamic vacuum. The IR spectrum shows three ν(CN) at 2333, 2295 and 2252 cm^{-1} and broad overlapping features assignable as ν(GeF) at 688, 657 and 639 cm^{-1}, suggesting a mixture of *cis* and *trans* isomers. In CD_2Cl_2 solution at ambient temperatures both the ^1H and $^{19}F\{^1H\}$ NMR spectra are single lines, but at 180 K the $^{19}F\{^1H\}$ NMR spectrum shows a singlet at –108.2 and two rather broad triplets, $\delta = -101.2$ and –134.2 ($^2J_{FF} \approx 55$ Hz), attributable to *trans* and *cis* isomers respectively in approximate ratio 1:10, showing the complex is dynamic in solution down to quite low temperatures.

Phosphane Oxides

The reactions of $[GeF_4(MeCN)_2]$ with R_3PO (R = Me, Et or Ph) in 1:2 molar ratio in dry CH_2Cl_2 afford white powders $[GeF_4(R_3PO)_2]$. Colourless crystals of $[GeF_4(R_3PO)_2]$ (R = Me or Et) were grown from MeCN solution, and crystals of $[GeF_4(Ph_3PO)_2]$ serendipitously from the reaction mixture of $[GeF_4(MeCN)_2]$ and Ph_3P in CH_2Cl_2[13] and crystal structure determinations showed all

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to be the *trans* isomers. The P–O distances are significantly lengthened from those in the parent phosphane oxide 1.489(6) Å (Me_3PO),[14] 1.483(2) Å (Ph_3PO).[15] The *trans*-[$GeF_4(Me_3PO)_2$] (Figure 1, Table 1) is isostructural with the tin(IV) analogue,[16] and the *d*(P–O) 1.528(5) Å is very similar to that in *trans*-[$SnF_4(Me_3PO)_2$] [1.532(3) Å]. The *d*(Ge–F) 1.772(4) and 1.776(4) Å are longer than in the diethyl ether adduct [$GeF_4(Et_2O)_2$][10] [1.754(2), 1.747(2) Å] and considerably longer than in crystalline GeF_4 [1.661(1) Å].[17] In the ether adduct the *d*(Ge–O) is 1.975(2) Å consistent with the much weaker binding of the ether to the germanium. Similar bond length patterns are seen in the other phosphane oxide structures (Tables 2 and 3, Figures 2 and 3). The trialkylphosphane oxide complexes are easily soluble in chlorocarbons and MeCN, that of Ph_3PO poorly soluble, and in marked contrast to the analogues with the heavier halides, are relatively air-stable in the solid state and do not hydrolyse rapidly even in solution. The $^{19}F\{^1H\}$ NMR spectrum of [$GeF_4(Me_3PO)_2$] in CH_2Cl_2 shows a singlet at $\delta = -109.9$ ppm due to the *trans* isomer and much weaker triplets at $\delta = -107.6$ and -121.6 ppm ($^2J_{FF} = 58$ Hz) of the *cis* isomer, with the latter making up ca. 5% of the sample. The $^{31}P\{^1H\}$ NMR spectrum confirms the assignment with resonances at $\delta = 65.8$ (*trans*) and $\delta = 65.1$ ppm (*cis*). In the presence of added Me_3PO no other complexes were formed, showing that in contrast to the case with the heavier halides (below), the phosphane oxide cannot displace fluoride from the Ge^{IV} centre. The IR spectrum of [$GeF_4(Me_3PO)_2$] shows a very strong, broad band at 1087 cm^{-1}, assigned as ν(PO) (compare 1166 cm^{-1} in Me_3PO) and ν(Ge–F) at 626 and 612 cm^{-1}. The presence of two ν(Ge–F) stretches of similar intensity is a solid state effect (theory for a *trans* isomer is one – e_u), since in CH_2Cl_2 solution a single band at 629 cm^{-1} is present. The [$GeF_4(Et_3PO)_2$] is very similar (Experimental Section) although the *cis* isomer is rather more abundant (≈10% in CH_2Cl_2 solution). The [$GeF_4(Ph_3PO)_2$] shows approximately equal amounts of *cis* and *trans* isomers present in both the $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra at 253 K ($CDCl_3$ solution), but at 295 K only the resonances of the *trans* isomer are evident. The chemical shift in the room temperature $^{19}F\{^1H\}$ spectrum is not a weighted average of the low temperature values, but corresponds to that of the *trans* isomer, indicating that the *cis* isomer is undergoing some dynamic process at ambient temperatures, but that *cis-trans* exchange is slow. The reaction of Et_3PO and $GeCl_4$ in CH_2Cl_2 gave a white solid [$GeCl_4(Et_3PO)_2$]. Although this has not been characterised by an X-ray structure, the spectroscopic properties ν(PO) = 1087 cm^{-1}, ν(Ge–Cl) = 321 cm^{-1} and $\delta(^{31}P\{^1H\}) = 60.1$ (Et_3PO: $\delta = 52.1$ ppm) are consistent with its formulation as the *trans* isomer (cf. the fluoride described above).

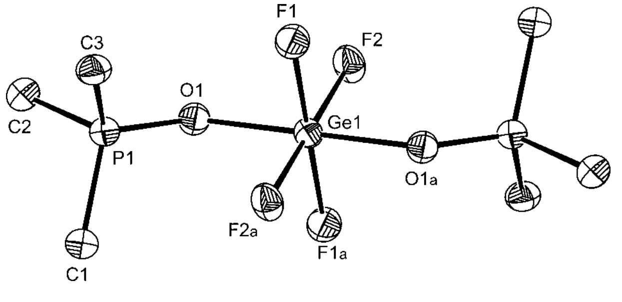

Figure 1. View of the molecule of [$GeF_4(Me_3PO)_2$] with the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation, a: $-x$, $-y$, $1 - z$.

Table 1. Selected bond lengths [Å] and angles [°] for [$GeF_4(Me_3PO)_2$].[a]

Ge1–F1	1.772(4)	Ge1–F2	1.776(4)
Ge1–O1	1.898(5)	P1–O1	1.528(5)
F1–Ge1–F2	90.7(2)	F1–Ge1–O1	90.6(2)
F1–Ge1–F2a	89.3(2)	F2–Ge1–O1	89.1(2)
Ge1–O1–P1	130.4(3)	O1–P1–C	108.2(3)–112.3(3)

[a] Symmetry operation, a: $-x$, $-y$, $1 - z$.

Table 2. Selected bond lengths [Å] and angles [°] for [$GeF_4(Et_3PO)_2$]·1/3CH_2Cl_2.

Ge1–F1	1.770(2)	Ge1–F2	1.769(2)
Ge1–O1	1.904(2)	P1–O1	1.526(2)
P1–C	1.783(2)–1.800(2)		
F1–Ge1–F2	90.24(8)	F1–Ge1–O1	89.72(7)
F2–Ge1–O1	91.17(7)	Ge1–O1–P1	133.8(1)
O1–P1–C	105.4(1)–113.8(1)		

Table 3. Selected bond lengths [Å] and angles [°] for [$GeF_4(Ph_3PO)_2$]·2CH_2Cl_2.

Ge1–F1	1.774(1)	Ge1–F2	1.772(1)
Ge1–O1	1.925(2)	P1–O1	1.522(2)
F1–Ge–F2	89.53(6)	F1–Ge1–O1	91.76(6)
F2–Ge1–O1	90.82(6)	Ge1–O1–P1	142.5(1)
O1–P1–C	107.4(1)–113.5(1)		

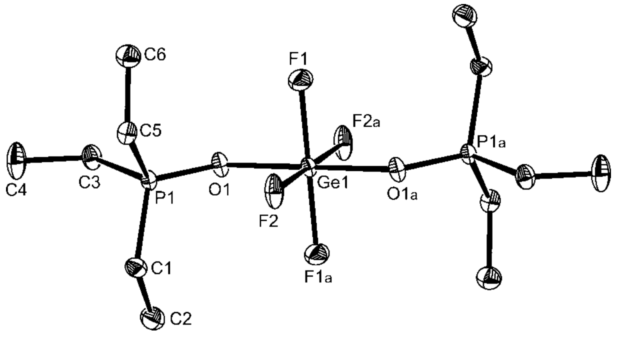

Figure 2. View of the molecule of [$GeF_4(Et_3PO)_2$] with the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation, a: $1 - x$, $1 - y$, $-z$.

In marked contrast to the stable fluoride adduct, the phosphane oxide complexes of $GeCl_4$ and $GeBr_4$ with Me_3PO are moisture sensitive and very labile in solution. The reaction of Me_3PO and $GeCl_4$ in a 2:1 molar ratio in rigorously anhydrous CH_2Cl_2 resulted in a white powder with an analytical composition corresponding to $GeCl_4(Me_3PO)_2$. Crystals grown from an CH_2Cl_2 solution of this material were found to be *fac*-[$GeCl_3(Me_3PO)_3$]$_2$-

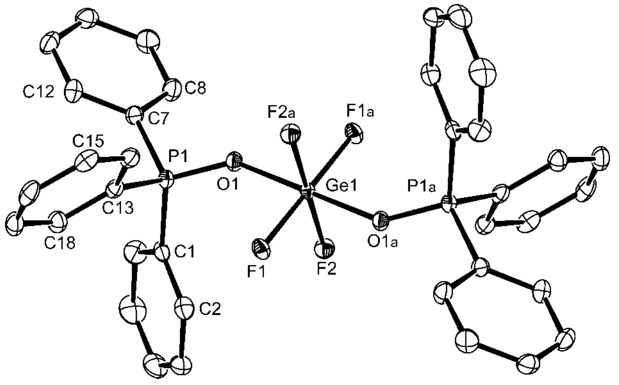

Figure 3. View of the molecule of $[GeF_4(Ph_3PO)_2]$ with the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation, a: 1 – *x*, 1 – *y*, 1 – *z*.

$[GeCl_6]$, (which has the same 1:2 Ge:Me_3PO stoichiometry). The structure (Figure 4, Table 4) shows an octahedral cation with a *facial* arrangement of ligands *d*(Ge–O) = 1.891(3) Å, not significantly different from that in the fluoride complex above, and with *d*(Ge–Cl) = 2.260(1) Å. The $[GeCl_6]^{2-}$ anion is very close to a regular octahedron with *d*(Ge–Cl) = 2.289(1) Å, which compares with the values in $[Ph_4P]_2[GeCl_6]$ of 2.283–2.298 Å.[19] The Nujol mull IR spectrum of the bulk powder and of the crystals were the same and showed two ν(PO) absorptions at 1122(m) and 1065 (s, br) cm^{-1}, and ν(Ge–Cl) at 344 (m), 308 (m), 293 (s) cm^{-1}. The 293 cm^{-1} band is assigned as the t_{1u} mode of $[GeCl_6]^{2-}$,[20] and the higher frequency Ge–Cl modes are the a_1 and e expected for the *fac* (C_{3v}) cation. The material has an essentially identical IR spectrum to the compound formulated as $[GeCl_4(Me_3PO)_2]$ in an early report[21] and it is clear from the results above that this complex should be reformulated. In anhydrous CH_2Cl_2 solution at ambient temperatures the complex exhibits a broad singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ ca. 41. On cooling the solution the resonance broadens, then sharpens on further cooling, and at 180 K the major resonance is now at δ = 63.7 ppm with much weaker features at δ = 67.4, 66.5 and 65.7 ppm. The behaviour suggests a rapidly exchanging system, extensively dissociated at room temperature and which has several species present at low temperatures (no "free" Me_3PO, δ = 38 ppm, was observed at low temperature). In the presence of added Me_3PO the solution shows a broad resonance consistent with fast exchange at $T > 220$ K, but at 180 K several resonances are resolved in addition to that of uncoordinated Me_3PO, notably the species with δ = 63.7 ppm is absent and the three higher frequency resonances are now dominant. Under different experimental conditions a second complex, identified as *cis*-$[GeCl_2(Me_3PO)_4]Cl_2$ was produced, also as colourless crystals. The structure (Figure 5, Table 5) shows a distorted octahedral cation with rather shorter *d*(Ge–Cl) [2.228(2) Å] than in the $[GeCl_3(Me_3PO)_3]^+$ [2.260(1) Å] and the $d(\text{Ge–O})_{trans\text{-O}}$ [1.886(4) Å] is significantly longer than $d(\text{Ge–O})_{trans\text{-Cl}}$ [1.857(4) Å]. In solution the variable temperature $^{31}P\{^1H\}$ NMR spectra are qualitatively similar to those described above for $[GeCl_3(Me_3PO)_3]^+$, except that at 180 K some "free" Me_3PO is present. Whilst a definitive assignment of the low temperature spectra of the two $GeCl_4$/Me_3PO systems is not possible, a plausible interpretation consistent with the ratios of $GeCl_4$:Me_3PO present, and the effect of added Me_3PO, is that the resonances at δ = 67.4 and 66.5 ppm (which are always of equal intensity) correspond to the di-cation *cis*-$[GeCl_2(Me_3PO)_4]^{2+}$, the resonance at δ = 65.7 ppm is of the *fac*-$[GeCl_3(Me_3PO)_3]^+$ and the major feature at δ = 63.7 ppm is a $[GeCl_4(Me_3PO)_2]$ complex (since this resonance largely disappears when a large excess of Me_3PO is present). Repeated attempts to isolate adducts of $GeCl_4$ with Ph_3PO were unsuccessful, no solids separated from solutions of the constituents in anhydrous CH_2Cl_2, and removal of all volatiles from the reaction mixtures in vacuo resulted in loss of the $GeCl_4$. Attempts to isolate complexes with the diphosphane dioxides $Ph_2P(O)CH_2P(O)Ph_2$ or *o*-$C_6H_4[P(O)Ph_2]_2$ also failed. All of these form complexes with $SnCl_4$,[16,18] and although $GeCl_4$ is clearly a weaker Lewis acid, it is possible that steric factors disfavour complexes with these bulky ligands on the small Ge^{IV} centre.

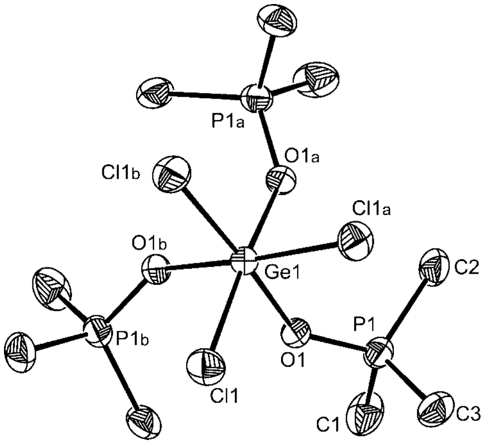

Figure 4. View of the cation in $[GeCl_3(Me_3PO)_3]_2$ $[GeCl_6]$ with the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation, a: 1 – *y*, 1 + *x* – *y*, *z*; b = – *x* + *y*, 1 – *x*, *z*.

Table 4. Selected bond lengths [Å] and angles [°] for $[GeCl_3(Me_3PO)_3]_2[GeCl_6]$.[a]

Ge1–Cl1	2.260(1)	Ge1–O1	1.891(3)
Ge2–Cl2	2.289(1)	P1–O1	1.530(3)
O1–Ge1–O1a	85.6(1)	O1–Ge1–Cl1a	93.3(1)
O1–Ge1–Cl1	88.1(1)	Cl1–Ge1–Cl1a	92.89(5)
O1–P1–C	107.4(2)–113.6(2)	Ge1–O1–P1	140.8(2)
Cl2–Ge2–Cl2c	89.97(4)		

[a] Symmetry operations, a: 1 – *y*, 1 + *x* – *y*, *z*; c: –*y*, *x* – *y*, *z*.

The $GeBr_4$/R_3PO systems in CH_2Cl_2 or MeCN are more extensively dissociated and it is harder to obtain a pure complex. However, as described in the Experimental Section, colourless crystals were obtained which proved to be *cis*-$[GeBr_2(Me_3PO)_4]Br_2$ (Table 6, Figure 6). The structure

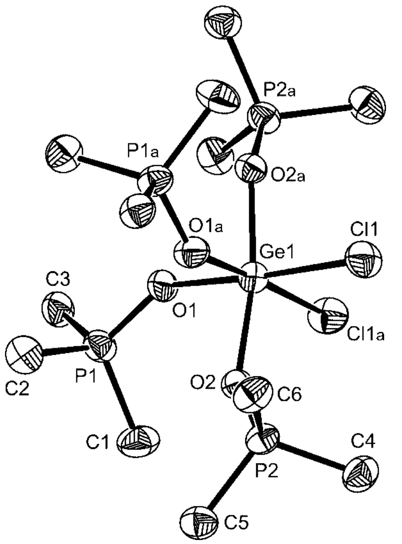

Figure 5. View of the cation in $[GeCl_2(Me_3PO)_4]Cl_2$ with the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation, a: 1 – *x*, *y*, 1/2 – *z*.

Table 5. Selected bond lengths [Å] and angles [°] for $[GeCl_2(Me_3PO)_4]Cl_2$.[a]

Ge1–Cl1	2.228(2)	P1–O1	1.530(4)
Ge1–O1	1.857(4)	P2–O2	1.538(4)
Ge1–O2	1.886(4)		
O1–Ge1–O1a	91.0(3)	O1–Ge1–O2	88.0(2)
O1–Ge1–O2a	85.2(2)	O2–Ge1–O2a	170.3(2)
O1–Ge1–Cl1	176.3(1)	O1a–Ge1–Cl1	89.8(2)
O2–Ge1–Cl1	95.7(1)	O2–Ge1–Cl1a	91.2(1)
Cl1–Ge1–Cl1a	89.6(1)	Ge1–O1–P1	141.6(2)
O1–P1–C	107.1(3)–114.1(3)	Ge1–O2–P2	137.1(3)
O2–P2–C	108.1(3)–113.7(3)		

[a] Symmetry operation, a: 1 – *x*, *y*, 1/2 – *z*.

is analogous to that of the chloride, with a corresponding pattern of bond lengths. In CH_2Cl_2 solution the complex exhibits a very broad $^{31}P\{^1H\}$ NMR resonance at δ ca. 42 ppm, which on cooling to < 220 K resolves into a major peak at 65.5 ppm, and very minor features at 67.6 and 68.7 ppm in addition to some "free" Me_3PO. Addition of excess Me_3PO to the solution results in a broad signal, typical of an exchanging system, down to very low temperatures, and even at 180 K the features δ ca. 65–69 ppm are broad, showing that the low temperature limiting spectrum cannot be reached before the solvent freezes. Based upon the spectroscopic data it can be concluded that solution lability increases in these systems with halide F << Cl < Br. Comparison of the four crystal structures containing Me_3PO (Table 1, 4, 5 and 6) shows only small differences in *d*(Ge–O), although only for the two $[GeX_2(Me_3PO)_4]^{2+}$ ions are the Ge environments the same. It is possible that the effects of increasing formal charge on the Ge along the series $[GeF_4(Me_3PO)_2]$, $[GeCl_3(Me_3PO)_3]^+$, $[GeCl_2(Me_3PO)_4]^{2+}$ obscures any differences due to stronger Lewis acidity in the fluoride. Certainly charge seems to have a marked effect on *d*(Ge–Cl) along the series $[GeCl_6]^{2-}$ [2.289(1) Å], $[GeCl_3(Me_3PO)_3]^+$ [2.260(1) Å], $[GeCl_2(Me_3PO)_4]^{2+}$ [2.228(2) Å].

Table 6. Selected bond lengths [Å] and angles [°] for $[GeBr_2(Me_3PO)_4]Br_2$.[a]

Ge1–Br1	2.399(1)	P1–O1	1.547(6)
Ge1–O1	1.901(5)	P2–O2	1.528(6)
Ge1–O2	1.859(6)		
O2–Ge1–O2a	90.5(4)	O2a–Ge1–O1	87.5(3)
O2–Ge1–O1	85.6(3)	O1–Ge1–O1a	170.2(4)
O1–Ge1–Br1	97.1(2)	O2–Ge1–Br1	90.4(2)
O1a–Ge1–Br1	89.9(2)	Br1–Ge1–Br1a	89.12(7)
Ge1–O1–P1	137.8(4)	Ge1–O2–P2	143.7(4)
O1–P1–C	107.8(4)–113.7(4)	O2–P2–C	107.8(4)–114.2(4)

[a] Symmetry operation, a: 1 – *x*, *y*, 1/2 – *z*.

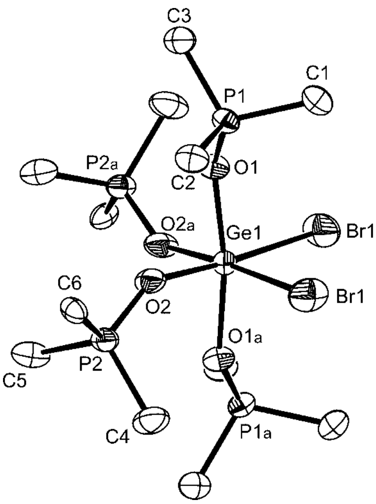

Figure 6. View of the cation in $[GeBr_2(Me_3PO)_4]Br_2$ with the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation, a: 1 – *x*, *y*, 1/2 – *z*.

The reactions of GeI_4 with Me_3PO in CH_2Cl_2 gave red solutions, but crystals obtained from these were found by crystal structure determinations to be GeI_4 and $[Me_3POH][I_3]$, and we have been unable to isolate any phosphane oxide adducts.

The ability of Me_3PO to displace chloride or bromide from the germanium centre was entirely unexpected; in the extensively studied systems SnX_4–R_3PO (X = Cl, Br or I; R = Me, Ph etc)[21,22] all the complexes are of type $[SnX_4(R_3PO)_2]$ (usually a mixture of *cis*/*trans* isomers) and complexes with higher R_3PO/SnX_4 ratios do not form.

Arsane Oxides

The reaction of $[GeF_4(MeCN)_2]$ with Ph_3AsO in CH_2Cl_2 gave white $[GeF_4(Ph_3AsO)_2]$ which exhibited a strong broad ν(AsO) at 868 cm^{-1} and ν(Ge–F) at 608 cm^{-1}. In solution the $^{19}F\{^1H\}$ NMR spectrum in CH_2Cl_2 contains a singlet at δ = –98.2, and two triplets at –94.4 and –112.9 ($^2J_{FF}$ = 60 Hz), consistent with a mixture of *cis* and *trans* isomers.

However, the products isolated from stirring R_3AsO (R = Me or Ph) with $GeCl_4$ in MeCN or CH_2Cl_2 solution were colourless crystalline solids which showed no evidence for ν(AsO) vibrations in their IR spectra. The crystals were identified by comparison of their unit cells with literature data,[23,24] as the dichlorotriorganoarsenic(V), R_3AsCl_2, and this was confirmed by comparison of their IR spectra with literature data.[25,26] In a similar way, $GeBr_4$ and Me_3AsO gave Me_3AsBr_2. The conversion of R_3AsO to R_3AsCl_2 has been reported to be achieved by a number of reagents including MeCOCl,[27] $COCl_2$,[28] PCl_3 and $AsCl_3$,[29] and with aqueous HCl,[30] but for $GeCl_4$ to behave in this way under such mild conditions was unexpected, and again contrasts with $SnCl_4$ which readily forms $[SnCl_4(R_3AsO)_2]$ adducts.[31]

The ether adducts $[GeF_4(thf)_2]$ and $[GeF_4(MeOCH_2CH_2OMe)]$, both reported some years ago[12,32] but with few details, were reexamined. Both are moisture sensitive white solids, with unexceptional spectroscopic properties (see Experimental section). The $[GeF_4(thf)_2]$ is a mixture of *cis* and *trans* isomers in solution in CH_2Cl_2 at low temperatures, but on warming the solution to > ca. 243 K the triplets in the $^{19}F\{^1H\}$ NMR spectrum due to the *cis* isomer collapse and then disappear, whilst the singlet due to the *trans* form is unchanged. This behaviour is similar to that of $[GeF_4(Ph_3PO)_2]$ (q.v.) and similarly rationalised.

Conclusions

A series of neutral O-donor complexes of GeX_4 have been prepared and characterised structurally and spectroscopically. The data support the expected trend that Lewis acidity decreases $GeF_4 > GeCl_4 > GeBr_4 >> GeI_4$, and are consistent with lower acceptor power for Ge compared with Sn. We note that the overall trends will reflect both the strength of the donor-acceptor interaction and also the reorganisation energy ("floppiness") consumed in deforming the tetrahedral GeX_4 into a four-coordinate fragment of the octahedron produced on bonding the Lewis base.[33] Completely unexpected was the displacement of halide by Me_3PO in GeX_4 (X = Cl or Br) to form mono- or di-cations; whilst the cationic species are probably stabilised in the solid state by the lattice, the displacement of X^- by the weakly bound phosphane oxide in solution is surprising. The stronger Ge–F bond presumably prevents this happening in the fluorides under similar conditions. Also surprising was the conversion of R_3AsO into R_3AsX_2 by GeX_4 (X = Cl or Br) under mild conditions, again the strength of the Ge–F bond would account for the different reaction (simple adduct formation) observed with GeF_4.

Experimental Section

All reactions were conducted using Schlenk, vacuum line and glove-box techniques and under a dry dinitrogen atmosphere. The germanium(IV) halides GeF_4, $GeBr_4$ and GeI_4 were obtained from Aldrich and used as received. $GeCl_4$ (Aldrich) was distilled from a mixture of $CaCl_2/Na_2CO_3$, which removes traces of water and HCl. MeCN and CH_2Cl_2 were dried by distillation from CaH_2, THF and $MeOCH_2CH_2OMe$ distilled from Na-benzophenone ketyl. Me_3PO and Et_3PO were freshly sublimed in vacuo. Ph_3PO and Ph_3AsO were heated in vacuo. IR spectra were recorded as Nujol mulls with a Perkin–Elmer PE 983G spectrometer, ^1H NMR spectra in $CDCl_3$, CD_2Cl_2 or CD_3CN solutions with a Bruker AV300, $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectra with a Bruker DPX400 and referenced to 85% H_3PO_4 and $CFCl_3$, respectively. Microanalytical measurements on new complexes were performed by the microanalytical service at Strathclyde University.

$[GeF_4(MeCN)_2]$: Prepared as described.[12] ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ = 1.99 (s) ppm. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 180 K): δ = –101.2 (t, $^2J_{FF}$ ≈ 55 Hz), –108.2 (s), –134.2 (t) ppm. IR (Nujol): $\tilde{\nu}$ = 2333, 2295, 2252 [ν(CN)], 688 (s), 657 (vs), 639 (s) [ν(Ge–F)] cm^{-1}.

$[GeF_4(Me_3PO)_2]$: Freshly sublimed Me_3PO (0.046 g, 0.50 mmol) was added to a solution of $[GeF_4(MeCN)_2]$ (0.058 g, 0.25 mmol) in CH_2Cl_2 (20 mL) at room temperature with stirring. A white precipitate formed gradually in the reaction mixture. After stirring for 10 min, the $^{19}F\{^1H\}$ NMR spectrum showed one major singlet at δ = –109.9 ppm and two minor triplets at –107.6 and –121.6 ppm. The solvent was removed in vacuo, and the white residue was dissolved in CH_3CN. Colourless air-stable crystals were obtained by vapour diffusion of diethyl ether into the solution. Yield 0.07 g, 85%. $C_6H_{18}F_4GeO_2P_2$ (332.7): calcd. C 21.7, H 5.5; found C 22.0, H 5.5. ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ = 1.76 (*d*, $^2J_{HP}$ = 13.5 Hz) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ = 65.8 (s, major), 65.1 (s, minor) ppm. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 293 K): δ = –107.6 (t, $^2J_{FF}$ = 58 Hz), –109.9 (s), –121.6 (t) ppm. IR (Nujol): $\tilde{\nu}$ = 1087 (vs, br) [ν(P=O)], 626 (s), 612 (s) [ν(Ge–F)] cm^{-1}.

$[GeF_4(Et_3PO)_2]$: Et_3PO (0.067 g, 0.50 mmol) was added to a solution of $[GeF_4(MeCN)_2]$ (0.058 g, 0.25 mmol) in CH_2Cl_2 (20 mL) at room temperature to give a clear solution. The $^{19}F\{^1H\}$ NMR spectrum showed one major singlet at –110.2 and two minor triplets at –107.8 and –121.8 ppm. The solvent and volatiles were evaporated, and the white residue was washed with diethyl ether (10 mL) and dried. Yield 0.93 g, 90%. Colourless crystals were obtained from CH_2Cl_2 solution by slow evaporation of solvent under N_2. $C_{12}H_{30}F_4GeO_2P_2$ (416.9): calcd. C 34.4, H 7.2; found C 34.8, H 7.1. ^1H NMR (300 MHz, $CDCl_3$, 295 K): δ = 1.1 (m, 3 H), 2.05 (m, 2 H) ppm. $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ = –107.8 (t, $^2J_{FF}$ = 59 Hz), –110.1 (s), –122.1 (t) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 76.4 (s, major), 76.1 (s, minor) ppm. IR (Nujol): $\tilde{\nu}$ = 1092 (vs, br) [ν(P=O)], 614 (s) [ν(Ge–F)] cm^{-1}.

$[GeF_4(Ph_3PO)_2]$: Ph_3PO (0.146 g, 0.50 mmol) was added to a solution of $[GeF_4(MeCN)_2]$ (0.058 g, 0.25 mmol) in MeCN (20 mL) at room temperature, which led to the gradual formation of a white precipitate. After stirring for 10 min, the solvent was removed in vacuo, and the white residue was washed with small amount of CH_2Cl_2 and dried in vacuo. Yield 0.090 g, 90%. $C_{36}H_{30}F_4GeO_2P_2$ (705.2): calcd. C 61.3, H 4.3; found C 60.7, H 4.2. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 253 K): δ = –100.9 (t, $^2J_{FF}$ = 64 Hz), –105.3 (s), –120.6 (t) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 253 K): δ = 40.8, 40.2 ppm. IR (Nujol): $\tilde{\nu}$ = 1133, 1078 [ν(P=O)], 636 (s) [ν(Ge–F)] cm^{-1}.

$[GeCl_3(Me_3PO)_3]_2[GeCl_6]$: Trimethylphosphane oxide (0.09 g, 1.0 mmol) was added to a solution of $GeCl_4$ (0.11 g, 0.5 mmol) in CH_2Cl_2 (20 mL) at room temperature, and stirred overnight. The solution, now containing some precipitate, was taken to dryness in vacuo to leave the white solid. Yield 0.15 g, 90%. Colourless crystals separated from the solution in CH_2Cl_2 kept at –20 °C for a few days. $C_{18}H_{54}Cl_{12}Ge_3O_6P_6$ (1195.7): calcd. C 18.1, H 4.6; found C

18.6, H 4.7. ^{1}H NMR (300 MHz, $CDCl_3$, 295 K): δ = 1.45 (d, $^2J_{HP}$ = 13.5 Hz) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): δ = 45.0 (br) ppm. IR (Nujol): $\tilde{\nu}$ = 1065 [ν(P=O)], 344, 308, 295 [ν(Ge–Cl)] cm^{-1}.

[GeCl$_2$(Me$_3$PO)$_4$]Cl$_2$: Trimethylphosphane oxide (0.18 g, 2.0 mmol) was added to a solution of $GeCl_4$ (0.11 g, 0.5 mmol) in MeCN (20 mL) at room temperature, and stirred overnight. The solution was filtered and concentrated to ca. 5 mL. Colourless crystals separated from the solution kept at –20 °C for a few days. Yield 0.23 g, 80%. $C_{12}H_{36}Cl_4GeO_4P_4$ (582.7): calcd. C 24.7, H 6.2; found C 24.6, H 6.6. ^{1}H NMR (300 MHz, $CDCl_3$, 295 K): δ = 1.40 (d, $^2J_{HP}$ = 13.5 Hz) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 295 K): δ = 40.1 (br) ppm. IR (Nujol): $\tilde{\nu}$ = 1138 (sh), 1053 (s, br) [ν(P=O)], 352 (m), 300 (w) [ν(Ge–Cl)] cm^{-1}.

[GeBr$_2$(Me$_3$PO)$_4$]Br$_2$: Trimethylphosphane oxide (0.09 g, 1.0 mmol) was added to a solution of $GeBr_4$ (0.19 g, 0.5 mmol) in CH_2Cl_2 (20 mL) at room temperature that lead to the immediate formation of a white solid. After stirring for several minutes, the solvent was removed in vacuo. The solid residue was dissolved in MeCN (20 mL), filtered, and concentrated. Colourless crystals separated from the solution kept at –20 °C for a few days. Yield 0.16 g, 55%. $C_{12}H_{36}Br_4GeO_4P_4$ (760.5): calcd. C 19.0, H 4.8; found C 19.2, H 4.7. ^{1}H NMR (300 MHz, $CDCl_3$, 295 K): δ = 1.40 (d, $^2J_{HP}$ = 13.5 Hz) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 295 K): δ = 41.8 (v.br) ppm. See text for low temperature data. IR (Nujol): $\tilde{\nu}$ = 1131 (sh), 1101 (sh), 1051 (s, br) [ν(P=O)], 245 (m) [ν(Ge–Br)] cm^{-1}.

[GeCl$_4$(Et$_3$PO)$_2$]: Freshly sublimed Et_3PO (0.13 g, 1.0 mmol) was added to a solution of $GeCl_4$ (0.11 g, 0.5 mmol) in CH_2Cl_2 (20 mL) at room temperature. The reaction mixture was stirred overnight giving a clear solution. The solvent and all volatiles were removed in vacuo, leaving the product as solid. Yield 0.22 g, 90%. $C_{12}H_{30}Cl_4GeO_2P_2$ (481.96): calcd. C 30.0, H 6.3; found C 29.8, H 6.1. $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 295 K): δ = 60.1 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 1087 (br) [ν(P=O)], 321 (m, br) [ν(Ge–Cl)] cm^{-1}.

[GeF$_4$(Ph$_3$AsO)$_2$]: Ph_3AsO (0.16 g, 0.5 mmol) was added to a solution of $[GeF_4(MeCN)_2]$ (0.058 g, 0.25 mmol) in CH_2Cl_2 (20 mL) at room temperature with stirring. A white precipitate formed gradually in the reaction mixture. After continued stirring overnight, the solution was filtered. The white solid residue was washed with CH_2Cl_2 (10 mL) and dried in vacuo. Yield 0.22 g, 90%. $C_{36}H_{30}As_2F_4GeO_2\cdot CH_2Cl_2$ (878.0): calcd. C 50.6, H 3.7; found C 50.1, H 3.3. $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ = –94.4 (t, $^2J_{FF}$ = 60 Hz), –98.2 (s), –112.9 (t) ppm. IR (Nujol): $\tilde{\nu}$ = 868 (s) [ν(As=O)], 608 (s) [ν(Ge–F)] cm^{-1}.

[GeF$_4$(MeOCH$_2$CH$_2$OMe)]:[12,32] $[GeF_4(MeCN)_2]$ (0.550 g, 2.38 mmol) was dissolved in CH_2Cl_2 (10 mL) and stirred while $MeOCH_2CH_2OMe$ (0.215 g, 2.39 mmol) was added dropwise. The solution was stirred for 3 h before half the solvent was removed in vacuo. Hexane (15 mL) was added and stirring continued for a further 30 min. The solid was filtered and dried briefly in vacuo. Yield 0.25 g, 44%. ^{1}H NMR (300 MHz, $CDCl_3$, 243 K): δ = 4.22 (s, CH_2), 4.00 (s, Me) ppm. $^{19}F\{^1H\}$ NMR (CH_2Cl_2, 223 K): δ = –131.0 (t, $^2J_{FF}$ = 81 Hz), –151.1 (t) ppm. IR (Nujol): $\tilde{\nu}$ = 671 (s), 639 (s) [ν(Ge–F)] cm^{-1}.

[GeF$_4$(thf)$_2$]:[32] $[GeF_4(MeCN)_2]$ (0.62 g, 2.67 mmol) was stirred in thf (20 mL) for 3 h. The solvent was then removed in vacuo to leave a white solid. Yield 0.75 g, 96%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 2.13 (s), 4.45 (s) ppm. $^{19}F\{^1H\}$ NMR (CH_2Cl_2, 243 K): δ = –166.7 (s), –166.2 (t, $^2J_{FF}$ = 72 Hz), –178.8 (t) ppm. IR (Nujol): $\tilde{\nu}$ = 1017 (s, br), 852 (s, br) [ν(COC)], 650 (vbr) [ν(Ge–F)] cm^{-1}.

X-ray Crystallography: Details of the crystallographic data collection and refinement parameters are given in Table 7 and Table 8. Colourless, air-stable crystals of $[GeF_4(Me_3PO)_2]$ were obtained by diffusion of diethyl ether vapour into a MeCN solution; $[GeF_4(Et_3PO)_2]\cdot 1/3CH_2Cl_2$ crystals were obtained from a CH_2Cl_2 solution by slow evaporation of the solvent under N_2; $[GeF_4(Ph_3PO)_2]\cdot 2CH_2Cl_2$ crystals were obtained from CH_2Cl_2; crystals of $[GeCl_3(Me_3PO)_3]_2[GeCl_6]$ separated from the CH_2Cl_2 reactant solution kept at –20 °C for a few days; $[GeCl_2(Me_3PO)_4]Cl_2$ and $[GeBr_2(Me_3PO)_4]Br_2$ crystals separated from a MeCN solution kept at –20 °C for a few days. Data collections used a Bruker-Nonius Kappa CCD diffractometer fitted with Mo-K_α radiation (λ = 0.71073 Å) and either a graphite monochromator or confocal mirrors, with the crystals held at 120 K in a nitrogen gas stream. Struc-

Table 7. Crystallographic parameters.[a]

Compound	$[GeF_4(Me_3PO)_2]$	$[GeF_4(Et_3PO)_2]\cdot 1/3CH_2Cl_2$	$[GeF_4(Ph_3PO)_2]\cdot 2CH_2Cl_2$
Formula	$C_6H_{18}F_4GeO_2P_2$	$C_{12.33}H_{30.67}Cl_{0.67}F_4GeO_2P_2$	$C_{38}H_{34}Cl_4F_4GeO_2P_2$
M	332.73	445.20	874.98
Crystal system	monoclinic	trigonal	monoclinic
Space group	$P2_1/n$ (no. 14)	$R\bar{3}$ (no. 148)	$P2_1/n$ (no. 14)
a [Å]	6.300(4)	25.711(4)	8.840(2)
b [Å]	9.536(5)	25.711(4)	14.769(3)
c [Å]	10.368(4)	7.3385(10)	14.174(3)
α [°]	90	90	90
β [°]	96.33(3)	90	94.824(10)
γ [°]	90	120	90
V [Å^3]	619.0(5)	4201.1(11)	1844.0(6)
Z	2	9	2
μ(Mo-K_α) [mm^{-1}]	2.763	1.946	1.263
Total no. reflections	6778	9949	16281
R_{int}	0.062	0.046	0.048
Unique reflections	1206	2134	4227
No. of parameters	74	103	232
R_1 [$I_o > 2\sigma(I_o)$]	0.059	0.035	0.036
R_1 [all data]	0.072	0.046	0.051
wR_2 [$I_o > 2\sigma(I_o)$]	0.161	0.087	0.074
wR_2 [all data]	0.169	0.092	0.080

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

Table 8. Crystallographic parameters.

Compound	$[GeCl_3(Me_3PO)_3]_2[GeCl_6]$	$[GeCl_2(Me_3PO)_4]Cl_2$	$[GeBr_2(Me_3PO)_4]Br_2$
Formula	$C_{18}H_{54}Cl_{12}Ge_3O_6P_6$	$C_{12}H_{36}Cl_4GeO_4P_4$	$C_{12}H_{36}Br_4GeO_4P_4$
M	1195.60	582.68	760.52
Crystal system	trigonal	monoclinic	monoclinic
Space group	$P\bar{3}$ (no. 147)	$C2/c$ (no. 15)	$C2/c$ (no. 15)
a [Å]	13.448(2)	17.0680(18)	17.296(3)
b [Å]	13.448(2)	11.634(2)	11.6929(16)
c [Å]	7.4233(10)	13.226(2)	13.907(3)
α [°]	90	90	90
β [°]	90	92.227(9)	92.612(10)
γ [°]	120	90	90
V [Å^3]	1162.5(3)	2624.2(7)	2809.7(8)
Z	1	4	4
μ(Mo-K_α) [mm^{-1}]	2.853	1.833	7.020
Total no. reflections	34223	16460	14426
R_{int}	0.069	0.214[a]	0.086
Unique reflections	1775	3027	3238
No. of parameters	72	120	120
R_1 [$I_o > 2\sigma(I_o)$]	0.043	0.068	0.073
R_1[all data]	0.062	0.173	0.125
wR_2 [$I_o > 2\sigma(I_o)$]	0.103	0.128	0.126
wR_2 [all data]	0.112	0.164	0.148

[a] Very weak data [50% of reflections with $I > 2\sigma(I)$].

ture solution and refinement were straightforward,[34–36] with H atoms introduced into the models in calculated positions. Selected bond lengths and angles are given in Tables 1, 2, 3, 4, 5, and 6.

CCDC-637438 (for F/Me), -637439 (for F/Et), -637440 (for F/Ph), -637441 (for Cl/Me), -637442 (for Cl/Me), -637443 (for Br/Me) contain the supplementary crystallographic data for this paper (the groups in parentheses indicate the species in the compounds). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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