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Please cite this paper as:

Dalton Transactions, 2008, (17), pp 2261–2269

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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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Received 31st October 2007, Accepted 11th February 2008

First published as an Advance Article on the web 19th March 2008

DOI: 10.1039/b716765b

The first phosphane complexes of germanium(IV) fluoride, *trans*-[GeF<sub>4</sub>(PR<sub>3</sub>)<sub>2</sub>] (R = Me or Ph) and *cis*-[GeF<sub>4</sub>(diphosphane)] (diphosphane = R<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PR<sub>2</sub>, R = Me, Et, Ph or Cy; *o*-C<sub>6</sub>H<sub>4</sub>(PR<sub>2</sub>)<sub>2</sub>, R = Me or Ph) have been prepared from [GeF<sub>4</sub>(MeCN)<sub>2</sub>] and the ligands in dry CH<sub>2</sub>Cl<sub>2</sub> and characterised by microanalysis, IR, Raman, <sup>1</sup>H, <sup>19</sup>F{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. The crystal structures of [GeF<sub>4</sub>(diphosphane)] (diphosphane = Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub> and *o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub>) have been determined and show the expected *cis* octahedral geometries. In anhydrous CH<sub>2</sub>Cl<sub>2</sub> solution the complexes are slowly converted into the corresponding phosphane oxide adducts by dry O<sub>2</sub>. The apparently contradictory literature on the reaction of GeCl<sub>4</sub> with phosphanes is clarified. The complexes *trans*-[GeCl<sub>4</sub>(AsR<sub>3</sub>)<sub>2</sub>] (R = Me or Et) are obtained from GeCl<sub>4</sub> and AsR<sub>3</sub> either without solvent or in CH<sub>2</sub>Cl<sub>2</sub>, and the structures of *trans*-[GeCl<sub>4</sub>(AsEt<sub>3</sub>)<sub>2</sub>] and Et<sub>3</sub>AsCl<sub>2</sub> determined. Unexpectedly, the complexes of GeF<sub>4</sub> 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<sup>III</sup>, In<sup>III</sup>, Bi<sup>III</sup> and Sn<sup>IV</sup>, little is known about other Lewis acids in this block.<sup>1–4</sup> Complexes of the p-block fluorides with phosphanes are extremely rare, and apart from some very early work on SiF<sub>4</sub>,<sup>1</sup> the only examples are from our recent study of SnF<sub>4</sub> adducts,<sup>5</sup> which provided detailed spectroscopic and structural data on a range of complexes including [SnF<sub>4</sub>(diphosphane)] (diphosphane = *o*-C<sub>6</sub>H<sub>4</sub>(PR<sub>2</sub>)<sub>2</sub>, R = Me or Ph; R<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PR<sub>2</sub>, R = Me, Et, Cy or Ph) and *trans*-[SnF<sub>4</sub>(PR<sub>3</sub>)<sub>2</sub>] (R = Me or Cy).<sup>5</sup> There are no reports of tertiary phosphane complexes of GeF<sub>4</sub>, and with GeCl<sub>4</sub> the reports are few and apparently contradictory. Beattie<sup>6</sup> and Ozin<sup>7</sup> and their coworkers reported the formation of *trans*-[GeCl<sub>4</sub>(PMe<sub>3</sub>)<sub>2</sub>] and [GeX<sub>4</sub>(PMe<sub>3</sub>)] (X = Cl or Br) respectively, by reaction of GeX<sub>4</sub> and PMe<sub>3</sub> in the absence of a solvent, and used detailed IR and Raman studies to identify the products. In contrast, the reactions of PR<sub>3</sub> (R = <sup>i</sup>Bu or <sup>i</sup>Pr) with GeX<sub>4</sub> in benzene gave the redox products [PR<sub>3</sub>X][Ge<sup>II</sup>X<sub>3</sub>].<sup>8</sup> In a recent study by Godfrey *et al.*,<sup>9</sup> the reaction of GeCl<sub>4</sub> with a wide range of tertiary phosphanes (PR<sub>3</sub>, R = Me, Et, <sup>n</sup>Pr, <sup>n</sup>Bu, Cy *etc.*) in diethyl ether solution was found to give exclusively [PR<sub>3</sub>Cl][Ge<sup>II</sup>Cl<sub>3</sub>], identified by microanalysis, <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy and by the crystal structure of

[P<sup>n</sup>Bu<sub>3</sub>Cl][GeCl<sub>3</sub>]. 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 R<sub>2</sub>PGeX<sub>3</sub> or RHPGeX<sub>3</sub>.<sup>10</sup> However Godfrey *et al.*<sup>9</sup> were able to prepare and structurally characterise the first Ge<sup>IV</sup> arsane, *trans*-[GeCl<sub>4</sub>(AsMe<sub>3</sub>)<sub>2</sub>]. The redox chemistry in the GeX<sub>4</sub>-PR<sub>3</sub> reactions (at least under some conditions) contrasts with that of the SnX<sub>4</sub> systems where simple adduct formation occurs with the majority of phosphanes and diphosphanes.<sup>4–7</sup> It should be noted however that P<sup>n</sup>Bu<sub>3</sub> and SnX<sub>4</sub> produce [P<sup>n</sup>Bu<sub>3</sub>X][SnX<sub>3</sub>].<sup>8</sup> Here we report the synthesis, structural and spectroscopic characterisation of a series of phosphane complexes of GeF<sub>4</sub>, further studies into the GeCl<sub>4</sub> and GeBr<sub>4</sub> reactions, and also studies of complexes of GeX<sub>4</sub> with arsane ligands.

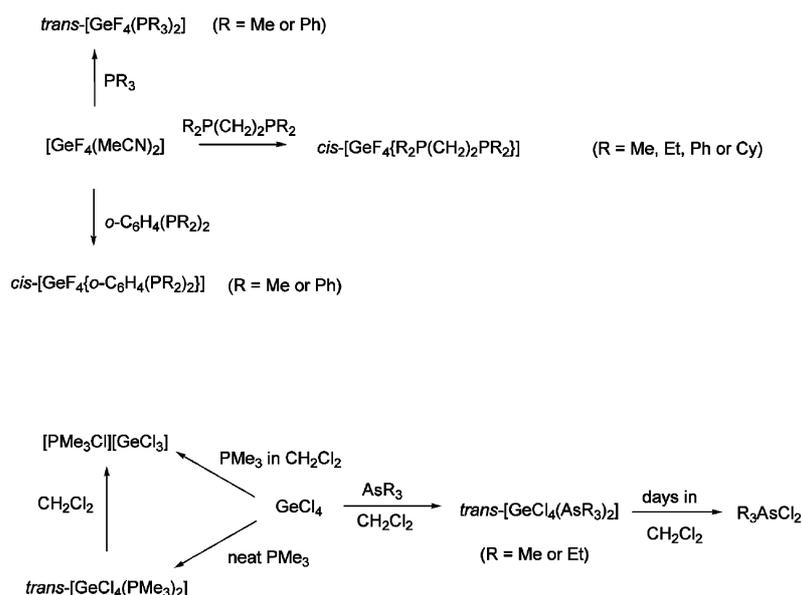
## Results and discussion

### Germanium(IV) phosphanes

Our previous studies have shown that towards hard N- or O-donor ligands GeF<sub>4</sub> is a much stronger Lewis acid than GeCl<sub>4</sub> or GeBr<sub>4</sub>.<sup>11</sup> The reaction of [GeF<sub>4</sub>(MeCN)<sub>2</sub>]<sup>11</sup> with two mol. equivalents of PMe<sub>3</sub> in anhydrous CH<sub>2</sub>Cl<sub>2</sub> gave [GeF<sub>4</sub>(PMe<sub>3</sub>)<sub>2</sub>] (Scheme 1) as a white, moisture sensitive powder, only slightly soluble in chlorocarbons. The <sup>1</sup>H NMR spectrum in CD<sub>2</sub>Cl<sub>2</sub> solution contained a single doublet at  $\delta = 1.46$  (<sup>2</sup>J<sub>PH</sub> = 12 Hz), the <sup>19</sup>F{<sup>1</sup>H} 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 <sup>31</sup>P{<sup>1</sup>H} NMR spectrum is a quintet at  $\delta = -12.4$  (<sup>2</sup>J<sub>PF</sub> = 196 Hz). The corresponding reaction using PPh<sub>3</sub> gave white *trans*-[GeF<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (Table 1) which was easily soluble in chlorocarbons, but extensively dissociated at room temperature in solution. The <sup>19</sup>F{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} 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 [Me<sub>2</sub>P(H)(CH<sub>2</sub>)<sub>2</sub>P(H)Me<sub>2</sub>][GeCl<sub>3</sub>]<sub>2</sub> and [Me<sub>2</sub>P(O)(CH<sub>2</sub>)<sub>2</sub>P(O)Me<sub>2</sub>][GeCl<sub>3</sub>]. 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  $\text{GeCl}_4$  (*vide infra*), the reaction of  $[\text{GeF}_4(\text{MeCN})_2]$  with excess molten  $\text{PPh}_3$  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  $[\text{GeF}_4(\text{OPPh}_3)_2]$ <sup>11</sup> and excess  $\text{PPh}_3$ , and there is no evidence for fluorination of the ligand (to  $\text{Ph}_3\text{PF}_2$ ). 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  $\text{CH}_2\text{Cl}_2$  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  $^1\text{H}$  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*- $\text{MF}_4\text{P}_2$  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  $600\text{ cm}^{-1}$ .<sup>12</sup>  $[\text{GeF}_4\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}]$  is only slightly soluble in  $\text{CH}_2\text{Cl}_2$  but the other complexes dissolve easily in chlorocarbons. The  $^1\text{H}$  NMR spectra in  $\text{CD}_2\text{Cl}_2$  or  $\text{CDCl}_3$  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).<sup>5</sup> 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,<sup>5</sup> and as in those cases the coordination shifts  $\Delta$  ( $\Delta = \delta_{\text{complex}} - \delta_{\text{ligand}}$ ) are irregular, although generally the stronger  $\sigma$ -donor ligands produce high frequency

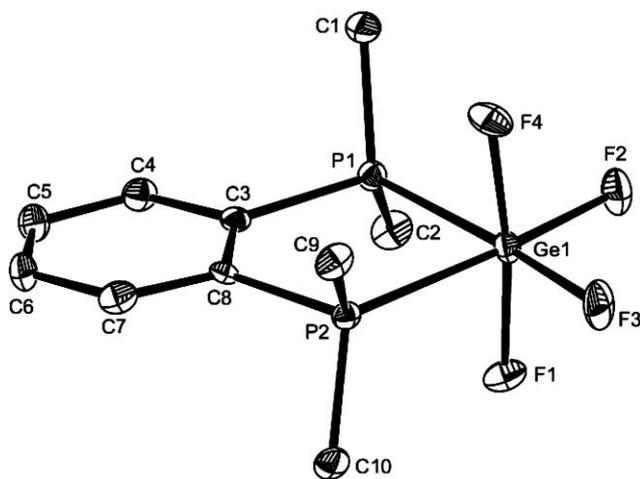
Table 1 Selected NMR data for  $\text{GeF}_4$  complexes<sup>a</sup>

Compound	$\delta\ ^{31}\text{P}\{^1\text{H}\}^b$	$\Delta^c$	$\delta\ ^{19}\text{F}\{^1\text{H}\}$	$^2J(^{31}\text{P}\text{--}^{19}\text{F})/\text{Hz}$	$^2J(^{19}\text{F}\text{--}^{19}\text{F})/\text{Hz}$
$[\text{GeF}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}]$	-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	

<sup>a</sup> In  $\text{CH}_2\text{Cl}_2\text{--}10\%$   $\text{CDCl}_3$ . Spectra were typically recorded at 240 K to resolve couplings (see text). <sup>b</sup> 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;  $\text{PMe}_3$  -62;  $\text{PPh}_3$  -6 ppm. <sup>c</sup> Coordination shift ( $\Delta = \delta_{\text{complex}} - \delta_{\text{ligand}}$ ). <sup>d</sup> 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  $\sigma$ -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  $\text{Sn}^{\text{IV}}$  and  $\text{Ga}^{\text{III}}$ ,<sup>13</sup> but the cause is presently unclear. The  $^{19}\text{F}\{^1\text{H}\}$  chemical shifts are higher frequency than those observed in the  $[\text{SnF}_4(\text{diphosphane})]$  analogues<sup>5</sup> 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*- $[\text{GeF}_4(\text{OPR}_3)_2]$ <sup>11</sup> and in  $[\text{GeF}_4(\text{L-L})]$  (L-L = 2,2'-bipyridyl, 1,10-phenanthroline,  $\text{Me}_2\text{N}(\text{CH}_2)_2\text{NMe}_2$ ),<sup>14</sup> although rather larger values (70–80 Hz) are seen in  $[\text{GeF}_4\{\text{RS}(\text{CH}_2)_2\text{SR}\}]$ .<sup>15</sup>

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  $90^\circ$ , F–Ge–P slightly less than  $90^\circ$ , and P–Ge–P  $85.61(4)^\circ$ . As observed in  $\text{GeF}_4$  complexes with N- or O-donor ligands,<sup>11,14</sup> Ge–F<sub>trans</sub> (1.809(2), 1.815(2) Å) are longer than Ge–F<sub>trans</sub> (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  $\sigma$ -donation.



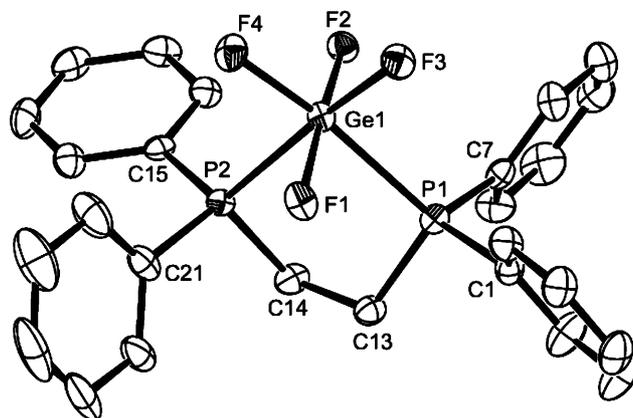
**Fig. 1** Structure of  $[\text{GeF}_4\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}]$  with the atom numbering scheme adopted. H atoms are omitted for clarity and displacement ellipsoids are shown at the 50% probability level.

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

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)



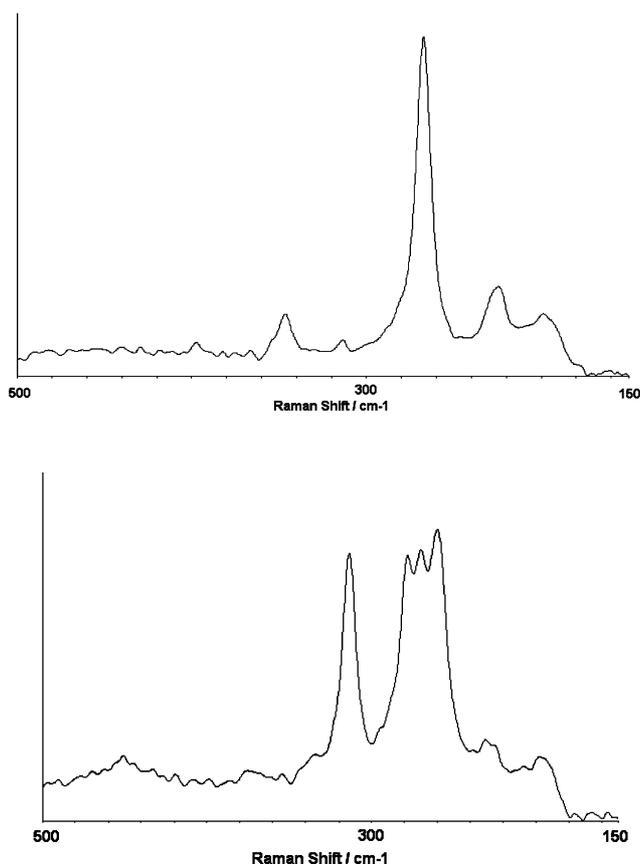
**Fig. 2** Structure of  $[\text{GeF}_4\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}]$  with the atom numbering scheme adopted. H atoms are omitted for clarity and displacement ellipsoids are shown at the 50% probability level. Only the *ipso* C atom labels are shown and C atoms are numbered sequentially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

Studies of the  $\text{SnX}_4\text{-PR}_3$  systems<sup>5</sup> showed that in the presence of air, the corresponding phosphane oxide complexes,  $[\text{SnX}_4(\text{OPR}_3)_2]$ ,<sup>16</sup> form, and we have shown<sup>17</sup> using  $^{18}\text{O}_2$ , that the source of the oxygen is dioxygen rather than water. Using  $\text{SnI}_4$  the reaction provides a convenient catalytic route to phosphane oxides.<sup>17</sup> A solution of  $[\text{GeF}_4(\text{PPh}_3)_2]$  in  $\text{CH}_2\text{Cl}_2$  exposed to dry air, deposited crystals identified by an X-ray structure to be *trans*- $[\text{GeF}_4(\text{OPPh}_3)_2]$ ,<sup>11</sup> and since  $\text{PPh}_3$  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  $\text{OPR}_3$ , 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  $\text{CH}_2\text{Cl}_2$  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  $1153\text{ cm}^{-1}$ . The  $\text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_2\text{P}(\text{O})\text{PPh}_2$  exhibits  $\nu(\text{PO})$  at  $1177\text{ cm}^{-1}$ , and the simple diatomic oscillator model predicts the effect of  $^{18}\text{O}$  substitution will lower this vibration to  $1133\text{ cm}^{-1}$ . Coupling with the  $\nu(\text{PC})$  mode at  $\sim 1120\text{ cm}^{-1}$  probably causes the higher frequency observed experimentally.<sup>17</sup> Thus, like  $\text{SnX}_4$ ,<sup>5,17</sup>  $\text{GeF}_4$

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

### GeX<sub>4</sub>-PMe<sub>3</sub> (X = Cl or Br) systems

Following the successful characterisation of the phosphane adducts of GeF<sub>4</sub>, we re-examined the GeCl<sub>4</sub>-PMe<sub>3</sub> reaction in an attempt to elucidate the apparently contradictory literature,<sup>6-9</sup> and found that the reports from Beattie<sup>6</sup> and Godfrey<sup>9</sup> and coworkers are both valid, and that the species formed are extremely dependent upon the conditions. We distilled GeCl<sub>4</sub> onto neat PMe<sub>3</sub> 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<sup>-1</sup> assigned as the a<sub>1g</sub> vibration of *trans*-[GeCl<sub>4</sub>(PMe<sub>3</sub>)<sub>2</sub>] (lit.,<sup>6</sup> 268 cm<sup>-1</sup>)—compare also the values of the corresponding vibration in the crystallographically characterised *trans*-[GeCl<sub>4</sub>(AsR<sub>3</sub>)<sub>2</sub>] (*vide infra*). The sample was then dissolved in rigorously dried CH<sub>2</sub>Cl<sub>2</sub> 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<sup>-1</sup>. The sample was redissolved in CH<sub>2</sub>Cl<sub>2</sub>, 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<sup>-1</sup>



**Fig. 3** Raman spectrum of [GeCl<sub>4</sub>(PMe<sub>3</sub>)<sub>2</sub>] (above) and of [PMe<sub>3</sub>Cl][GeCl<sub>3</sub>] (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<sup>-1</sup> which correspond to [GeCl<sub>3</sub>]<sup>-</sup> ([NBu<sub>4</sub>][GeCl<sub>3</sub>] has features at 320, 255 cm<sup>-1</sup>). The reactions can also be monitored by NMR spectroscopy. The initial solid, dissolved in CH<sub>2</sub>Cl<sub>2</sub> at 273 K and immediately cooled to 200 K, does not show a <sup>31</sup>P{<sup>1</sup>H} NMR resonance from the initial complex, but on standing a new feature at δ = +92 attributable<sup>‡</sup> to [PMe<sub>3</sub>Cl]<sup>+</sup> appeared. The absence of a phosphorus resonance for the Ge<sup>IV</sup> complex is consistent with extensive dissociation/fast exchange even at low temperatures. This explanation is supported by the <sup>1</sup>H NMR spectrum of *trans*-[GeCl<sub>4</sub>(PMe<sub>3</sub>)<sub>2</sub>] obtained immediately after dissolution in CDCl<sub>3</sub>, which shows a doublet at δ = 2.75, <sup>2</sup>J<sub>PH</sub> = 13.5 Hz (assigned to [PMe<sub>3</sub>Cl]<sup>+</sup>) and a doublet at δ = 1.8, <sup>2</sup>J<sub>PH</sub> = 13 Hz for the Ge<sup>IV</sup> complex. Trace hydrolysis of the solution also produces [PMe<sub>3</sub>H][GeCl<sub>3</sub>], δ(<sup>31</sup>P) = -4.9, and from such a hydrolysed sample we obtained crystals identified by their unit cell as [PMe<sub>3</sub>H][GeCl<sub>3</sub>].<sup>19</sup> Hence, as described by Beattie and Ozin,<sup>6</sup> the reaction of GeCl<sub>4</sub> with PMe<sub>3</sub> in the absence of a solvent does indeed give *trans*-[GeCl<sub>4</sub>(PMe<sub>3</sub>)<sub>2</sub>], but this rapidly rearranges in solution in chlorocarbons or ethers to [PMe<sub>3</sub>Cl][GeCl<sub>3</sub>], and the latter is obtained when the reaction is performed in solution (Scheme 1).<sup>8,9</sup> The recrystallisation of [GeCl<sub>4</sub>(PMe<sub>3</sub>)<sub>2</sub>] from hot GeCl<sub>4</sub> was reported to give [GeCl<sub>4</sub>(PMe<sub>3</sub>)<sub>2</sub>], believed to be an axially-substituted trigonal bipyramid molecule,<sup>7</sup> however the reported Raman spectrum is very similar to that of [PMe<sub>3</sub>Cl][GeCl<sub>3</sub>] and we suggest the latter is the correct formulation. We also reacted GeBr<sub>4</sub> and PMe<sub>3</sub> in the absence of solvent and obtained a cream powder with a Raman spectrum identical to that reported<sup>7</sup> for [GeBr<sub>4</sub>(PMe<sub>3</sub>)<sub>2</sub>]. In this case also, the strongest features in the low energy region correspond to [GeBr<sub>3</sub>]<sup>-</sup>, and on dissolution in dry CH<sub>2</sub>Cl<sub>2</sub> the <sup>31</sup>P{<sup>1</sup>H} NMR resonance is found at δ = +68, probably corresponding to [PMe<sub>3</sub>Br]<sup>+</sup>.

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 [PR<sub>3</sub>Cl][GeCl<sub>3</sub>]<sup>-</sup>—in some cases the rearrangement may be so rapid that the Ge(IV) species is only a transient intermediate. The GeBr<sub>4</sub>-PMe<sub>3</sub> reaction appears to give [PMe<sub>3</sub>Br][GeBr<sub>3</sub>] 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*-[SiCl<sub>4</sub>(PMe<sub>3</sub>)<sub>2</sub>]<sup>20</sup> and several SnX<sub>4</sub>-phosphane complexes<sup>4,5</sup> 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 Me<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PMe<sub>2</sub> with GeCl<sub>4</sub> under a variety of reaction conditions (mixed in the absence of solvent, in solution in CH<sub>2</sub>Cl<sub>2</sub> or Et<sub>2</sub>O, at room or low temperatures) and monitored reactions by *in situ* <sup>31</sup>P{<sup>1</sup>H} 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 <sup>1</sup>H or <sup>31</sup>P{<sup>1</sup>H} NMR spectra due

<sup>‡</sup> The observed <sup>31</sup>P chemical shift of “[PMe<sub>3</sub>Cl]<sup>+</sup>” seems to vary with solvent, concentration and anion, probably due to subtle speciation involving [PMe<sub>3</sub>Cl]<sup>+</sup>, Me<sub>3</sub>PCl<sub>2</sub> and Me<sub>3</sub>PCl⋯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  $\text{GeCl}_4$  are similar to those with  $\text{PMe}_3$ , with the trichlorogermanate(II) as the final product.

The reason for the easier reduction of  $\text{GeX}_4$  ( $X = \text{Cl}$  or  $\text{Br}$ ) by phosphanes compared with  $\text{SnX}_4$  or  $\text{SiX}_4$  (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  $\text{As}^{\text{V}}$ ,  $\text{Se}^{\text{VI}}$  and  $\text{Br}^{\text{VII}}$  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.<sup>21</sup>

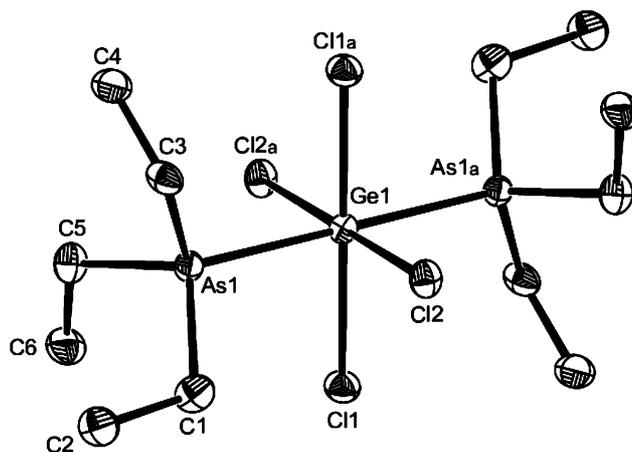
### Germanium(IV) arsanes

The reactions of  $[\text{GeF}_4(\text{MeCN})_2]$  with  $o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$  or  $\text{AsMe}_3$  in  $\text{CH}_2\text{Cl}_2$  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  $^1\text{H}$  NMR spectra in  $\text{CD}_2\text{Cl}_2$  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  $< 220$  K two triplets of equal intensity appear in regions typical of “*cis*”- $\text{GeF}_4$  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  $\text{GeF}_4$  and the weaker  $\sigma$ -donor  $\text{Ph}_2\text{As}(\text{CH}_2)_2\text{AsPh}_2$ . Thus, although  $\text{GeF}_4$  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  $\text{SnF}_4$  systems.<sup>5</sup> Isolation of pure complexes in the tin systems is complicated by the “ $\text{SnF}_4$ ” formed on dissociation, precipitating as polymeric  $[\text{SnF}_4]_n$ , but in the germanium systems dissociation simply forms  $\text{GeF}_4$  monomer, and the instability is therefore a direct result of the low affinity of the hard germanium Lewis acid for the soft arsenic centre.

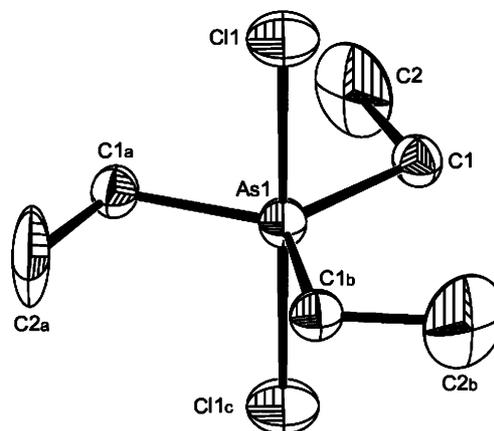
The reaction of  $\text{GeCl}_4$  with  $\text{AsMe}_3$  in  $\text{CH}_2\text{Cl}_2$  or  $\text{Et}_2\text{O}$  at ambient temperatures, produced colourless crystals of *trans*- $[\text{GeCl}_4(\text{AsMe}_3)_2]$  which were identified by comparison of their unit cell with the literature data.<sup>9</sup> A similar reaction using  $\text{AsEt}_3$  in  $\text{CH}_2\text{Cl}_2$  followed by rapid isolation of the product gave white *trans*- $[\text{GeCl}_4(\text{AsEt}_3)_2]$  and crystals obtained from  $\text{CH}_2\text{Cl}_2$  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  $\text{Et}_3\text{AsCl}_2$ .<sup>22</sup> 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  $\text{Et}_3\text{AsCl}_2$  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  $\text{Me}_3\text{AsCl}_2$  and  $\text{Cy}_3\text{AsCl}_2$ .<sup>23,24</sup> The *trans*- $[\text{GeCl}_4(\text{AsR}_3)_2]$  were also made by reaction of  $\text{GeCl}_4$  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  $\text{CH}_2\text{Cl}_2$  as solvent.

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

**Table 5** Selected bond lengths (Å) and angles (°) for Et<sub>3</sub>AsCl<sub>2</sub>

As1–Cl1	2.382(4)	As2–Cl2	2.362(4)
As1–Cl1	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–Cl1	90.0	C–As2–Cl1	90.0
As1–Cl1–C2	105.4(5)	As2–C3–C4	105.9(6)

259 cm<sup>-1</sup> (Et) which are assigned as the a<sub>1g</sub> modes, but in Nujol mulls (the solids dissolve in the Nujol), the strongest band in each far-IR spectrum is at 456 cm<sup>-1</sup> which corresponds to the t<sub>2</sub> mode of tetrahedral GeCl<sub>4</sub>,<sup>25</sup> showing that they are substantially dissociated even in this medium. The <sup>1</sup>H 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*-[GeCl<sub>4</sub>(AsEt<sub>3</sub>)<sub>2</sub>] in CD<sub>2</sub>Cl<sub>2</sub> develops new features at δ = 1.60 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz) and 3.06 (q), which correspond to Et<sub>3</sub>AsCl<sub>2</sub>,<sup>22</sup> confirming the slow decomposition. We confirm the previous report<sup>9</sup> that no reaction occurs between GeCl<sub>4</sub> and AsPh<sub>3</sub> in either CH<sub>2</sub>Cl<sub>2</sub> or Et<sub>2</sub>O at ambient temperatures. No reaction occurred with GeCl<sub>4</sub> and the diarsane Ph<sub>2</sub>As(CH<sub>2</sub>)<sub>2</sub>AsPh<sub>2</sub>, or (very surprisingly) with *o*-C<sub>6</sub>H<sub>4</sub>(AsMe<sub>2</sub>)<sub>2</sub>, 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 GeBr<sub>4</sub> and AsEt<sub>3</sub> 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<sup>-1</sup> which do not correspond with tetrahedral GeBr<sub>4</sub> (328, 234 cm<sup>-1</sup>) or to Et<sub>3</sub>AsBr<sub>2</sub>,<sup>22</sup> and when dissolved in CD<sub>2</sub>Cl<sub>2</sub> the <sup>1</sup>H NMR spectrum is little different to that of AsEt<sub>3</sub>. This suggests that the oil may be *trans*-[GeBr<sub>4</sub>(AsEt<sub>3</sub>)<sub>2</sub>], again extensively dissociated in solution; extrapolation from the chloride suggests the Raman active a<sub>1g</sub> Ge–Br vibration will be ~180 cm<sup>-1</sup>, below the limit of the instrument.

These results show that weak adducts form between GeCl<sub>4</sub> and AsR<sub>3</sub> (R = alkyl), but these are highly dissociated in solution, and slowly convert into R<sub>3</sub>AsCl<sub>2</sub>. The slower reduction by AsR<sub>3</sub> than by PR<sub>3</sub> reflects the relatively weaker reducing power of the arsanes.

## Conclusions

The work has resulted in characterisation of the first phosphane adducts of GeF<sub>4</sub> and has shown that while GeCl<sub>4</sub> forms (unstable) complexes with some arsanes (but not others), these slowly convert into R<sub>3</sub>AsCl<sub>2</sub>. With phosphanes the reduction to Ge<sup>II</sup> is usually rapid and [GeCl<sub>4</sub>(PR<sub>3</sub>)<sub>2</sub>] 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 GeX<sub>4</sub> unit into the four-coordinate fragment of the octahedron. The latter is constant for fixed X, and thus the relative affinity for PR<sub>3</sub> vs. AsR<sub>3</sub> which is GeF<sub>4</sub> > GeCl<sub>4</sub> 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<sup>IV</sup> to Ge<sup>II</sup> is not evident in the fluoride systems, but is favoured for the GeCl<sub>4</sub> (and GeBr<sub>4</sub>) reactions. This contrasts with the chemistry of SnX<sub>4</sub> (X = F, Cl,

Br or I) all of which form phosphane adducts, although again the affinity of SnF<sub>4</sub> for arsanes is much less than for phosphanes. The chemistry observed with GeX<sub>4</sub> also seems to differ from the limited data reported for the SiX<sub>4</sub> systems, but we reserve detailed comparisons here until much more complete data are available. Studies are underway on the silicon tetrahalide complexes.

## Experimental

GeF<sub>4</sub> was obtained from Aldrich and used as received. GeCl<sub>4</sub> (Aldrich) was distilled from a mixture of CaCl<sub>2</sub>–Na<sub>2</sub>CO<sub>3</sub>, which removes traces of water and HCl. MeCN and CH<sub>2</sub>Cl<sub>2</sub> were dried by distillation from CaH<sub>2</sub>, and diethyl ether from sodium benzophenone ketyl. Ligands were obtained from Aldrich or Strem: PMe<sub>3</sub>, PPh<sub>3</sub>, PCy<sub>3</sub>, AsMe<sub>3</sub>, AsEt<sub>3</sub>, Me<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PMe<sub>2</sub>, Et<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PEt<sub>2</sub>, Cy<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PCy<sub>2</sub>, or were made by literature methods: *o*-C<sub>6</sub>H<sub>4</sub>(PPh<sub>2</sub>)<sub>2</sub>, Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>, *o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub>, *o*-C<sub>6</sub>H<sub>4</sub>(AsMe<sub>2</sub>)<sub>2</sub>.<sup>26–29</sup> 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. <sup>1</sup>H NMR spectra were from CDCl<sub>3</sub> or CD<sub>2</sub>Cl<sub>2</sub> solutions on a Bruker AV300, <sup>19</sup>F{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR spectra on a Bruker DPX400 and referenced to CFCl<sub>3</sub> and 85% H<sub>3</sub>PO<sub>4</sub> respectively. Microanalytical measurements on new complexes were performed by the micro-analytical service at Strathclyde University. [GeF<sub>4</sub>(MeCN)<sub>2</sub>] was made as described.<sup>11</sup>

### [GeF<sub>4</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub>}]

[GeF<sub>4</sub>(MeCN)<sub>2</sub>] (0.23 g, 1.0 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and *o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub> (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 C<sub>10</sub>H<sub>16</sub>F<sub>4</sub>GeP<sub>2</sub> (346.8): C, 34.6; H, 4.7. Found: C, 34.9; H, 4.9%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 295 K): δ = 1.81 (t, <sup>2</sup>J + <sup>5</sup>J<sub>PH</sub> = 4.5 Hz, 12H, Me), 7.73–7.83 (m, 4H, C<sub>6</sub>H<sub>4</sub>). IR (Nujol): 607(br), 580(sh), 567(br) ν(GeF) cm<sup>-1</sup>.

### [GeF<sub>4</sub>{Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>}]

[GeF<sub>4</sub>(MeCN)<sub>2</sub>] (0.23 g, 1.0 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub> (0.40 g, 1.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (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 C<sub>26</sub>H<sub>24</sub>F<sub>4</sub>GeP<sub>2</sub> (547.0): C, 57.1; H, 4.4. Found: C, 56.2; H, 4.5%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K): δ = 2.71 (s, br, H, CH<sub>2</sub>), 7.79–7.38 (m, 5H, Ph). IR (Nujol): 603(s), 586(br) ν(GeF) cm<sup>-1</sup>.

### [GeF<sub>4</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(PPh<sub>2</sub>)<sub>2</sub>}]

[GeF<sub>4</sub>(MeCN)<sub>2</sub>] (0.23 g, 1.0 mmol) and *o*-C<sub>6</sub>H<sub>4</sub>(PPh<sub>2</sub>)<sub>2</sub> (0.45 g, 1.0 mmol) were weighed out and CH<sub>2</sub>Cl<sub>2</sub> (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*-[ $GeCl_4(AsMe_3)_2$ ].<sup>9</sup> 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<sup>a</sup>

Compound	[GeF <sub>4</sub> { <i>o</i> -C <sub>6</sub> H <sub>4</sub> (PMe <sub>2</sub> ) <sub>2</sub> }]	[GeF <sub>4</sub> {Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> }]	[GeCl <sub>4</sub> (AsEt <sub>3</sub> ) <sub>2</sub> ]	Et <sub>3</sub> AsCl <sub>2</sub>
Formula	C <sub>10</sub> H <sub>16</sub> F <sub>4</sub> GeP <sub>2</sub>	C <sub>20</sub> H <sub>24</sub> F <sub>4</sub> GeP <sub>2</sub>	C <sub>12</sub> H <sub>30</sub> As <sub>2</sub> Cl <sub>4</sub> Ge	C <sub>6</sub> H <sub>15</sub> AsCl <sub>2</sub>
<i>M</i>	346.76	546.98	538.59	233.00
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Hexagonal
Space group (no.)	<i>Pna</i> 2 <sub>1</sub> (33)	<i>Cc</i> (9)	<i>P</i> 2 <sub>1</sub> / <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)
$\alpha$ /°	90	90	90	90
$\beta$ /°	90	105.003(8)	93.721(15)	90
$\gamma$ /°	90	90	90	120
<i>U</i> /Å <sup>3</sup>	1339.9(4)	2423.3(5)	1019.1(5)	521.5(2)
<i>Z</i>	4	4	2	2
$\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>	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> <sub>int</sub>	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> <sup>2</sup>	1.04	1.05	1.21	1.02
Resid. electron density/ $\epsilon$ Å <sup>-3</sup>	-0.53 to +0.46	-0.26 to +0.29	-0.81 to +1.00	-0.47 to +0.60
<i>R</i> <sub>1</sub> <sup>b</sup> [ <i>I</i> <sub>o</sub> > 2 $\sigma$ ( <i>I</i> <sub>o</sub> )]	0.039	0.022	0.067	0.034
<i>R</i> <sub>1</sub> (all data)	0.051	0.023	0.114	0.044
<i>wR</i> <sub>2</sub> <sup>b</sup> [ <i>I</i> <sub>o</sub> > 2 $\sigma$ ( <i>I</i> <sub>o</sub> )]	0.070	0.054	0.109	0.088
<i>wR</i> <sub>2</sub> (all data)	0.074	0.054	0.126	0.093

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

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 GeCl<sub>4</sub>-PMe<sub>3</sub> reaction

In a small Schlenk tube, GeCl<sub>4</sub> (~0.15 g) was distilled *in vacuo* onto PMe<sub>3</sub> (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 CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and the solution allowed to stand for 3 h and then pumped dry. The solid was identified as [PMe<sub>3</sub>Cl][GeCl<sub>3</sub>] (see text for spectroscopic data).

### X-Ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 6. Crystals of [GeF<sub>4</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub>}] were obtained from a solution in CH<sub>2</sub>Cl<sub>2</sub>-*n*-hexane by slow evaporation; [GeF<sub>4</sub>{Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>}] from CH<sub>2</sub>Cl<sub>2</sub>-*n*-hexane cooled in a freezer; and Et<sub>3</sub>AsCl<sub>2</sub> and *trans*-[GeCl<sub>4</sub>(AsEt<sub>3</sub>)<sub>2</sub>] from Et<sub>2</sub>O solution by slow evaporation under dinitrogen. Data collection used a Nonius Kappa CCD diffractometer using graphite or confocal mirror monochromated Mo-K $\alpha$  X-radiation ( $\lambda$  = 0.71073 Å). Crystals were held at 120 K in a nitrogen gas stream. Structure solution and refinement were generally routine,<sup>30–33</sup> except as described below with hydrogen atoms on C introduced in calculated positions using the default C–H distance.

The data for Et<sub>3</sub>AsCl<sub>2</sub> was collected as a monoclinic *C* lattice using the automated software with  $\beta$  close to 90°, however inspection of the data with Layer<sup>34</sup> 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 (*R1* = 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 *R1* = 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

### Acknowledgements

We thank the EPSRC (GR/T09613/01) for support and Dr F. Cheng for help in running the Raman spectra.

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