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Reaction of $GeCl_4$ with some phosphorus and arsenic donor ligands; crystal structures of the germanium(II) complex $[Bu^n{}_3PCl][GeCl_3]$ and the germanium(IV) complex $GeCl_4(AsMe_3)_2$, the first reported example of a tertiary arsine complex of Ge^{IV}

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Received 7th December 1998, Accepted 2nd March 1999

The tertiary phosphines PR_3 $\{R_3 = Me_3, Et_3, Pr^n{}_3, Bu^n{}_3, Bu^t{}_3, (C_6H_{11})_3, [2,6\text{-}(CH_3O)_2C_6H_3]_3, [2,4,6\text{-}(CH_3O)_3C_6H_2]_3, (C_6H_5CH_2)_3, (Me_2N)_3, (Et_2N)_3, (Pr^n{}_2N)_3, Ph_2Et$ or $Ph_3\}$ and tertiary arsines AsR_3 (R = Ph or Me) have been treated with germanium tetrachloride in both a 1 : 1 and 2 : 1 stoichiometric ratio in diethyl ether solution. In the tertiary phosphine reactions a redox reaction occurs to produce the ionic germanium(II) complexes $[R_3PCl][GeCl_3]$ in near to quantitative yield, the chlorophosphinium cation being identified by $^{31}P\text{-}\{H\}$ NMR spectroscopy. No evidence for the previously reported molecular germanium(IV) adducts $GeCl_4(PR_3)_2$ was observed, apart from the possible assignments of minor peaks in the $^{31}P\text{-}\{H\}$ NMR spectrum for some of the products. The crystal structure of $[Bu^n{}_3PCl][GeCl_3]$ revealed no interaction between the cation and anion, in direct contrast to the only other reported complex of this stoichiometry, $[Pr^i{}_3PBr][GeBr_3]$. No reaction was observed between PPh_3 and $GeCl_4$. The reaction of $AsMe_3$ with $GeCl_4$ in both a 1 : 1 and 2 : 1 stoichiometric ratio produced the molecular *trans*-octahedral germanium(IV) complex, $GeCl_4(AsMe_3)_2$, the first crystallographically characterised germanium(IV) tertiary arsine complex [d(Ge–As) = 2.472(1) Å]. No reaction occurred between $GeCl_4$ and $AsPh_3$.

Introduction

Although the chemistry of transition metal complexes containing tertiary phosphines and arsines has been extensively studied, the corresponding complexes of the p-block metals have received much less attention. This was highlighted by Norman and Pickett[1] in a recent review. More specifically, the co-ordination chemistry of germanium-(II) and -(IV) halides with Group 15 donor ligands has received very little attention which is in contrast to the organometallic chemistry of this element which has received significant study. Consequently, reports regarding the chemistry of germanium are mainly concerned with its 'non-metallic' behaviour, *i.e.* the chemistry of organogermanes and in some cases their co-ordination to a metal centre.

Nevertheless, some studies regarding the co-ordination chemistry of germanium do exist. Amongst the earliest studies were those of King,[2] who treated germanium(II) iodide with a variety of triaryl- and trialkyl-phosphines in hydrocarbon solvents at 130 °C. All products from the reactions had the empirical formula $GeI_2(PR_3)$ ($R_3 = Ph_3, Ph_2Me, Ph_2Et, Ph_2Bu^n, Ph_2H$ or $Bu^n{}_3$) eqn. (1). All of the $GeI_2(PR_3)$ complexes, apart

$$GeI_2 + PR_3 \longrightarrow GeI_2(PR_3) \qquad (1)$$

from $GeI_2(PBu^n{}_3)$, which exists as a viscous yellow oil, were described as air-sensitive yellow solids and could be dissolved in organic solvents. It was also noted that all of the complexes turned red on exposure to the atmosphere, this phenomenon occurring more rapidly with increasing basicity of the tertiary phosphine. King[2] also reported the synthesis of the germanium(II) complex $GeI_2(Ph_2PCH_2CH_2PPh_2)$ from the reaction of germanium(II) iodide and the ligand. The complex was isolated in poor yield and was extremely air and moisture sensitive, turning red on exposure to the atmosphere in a matter of seconds. The sensitivity of all of the complexes described precluded comprehensive characterisation.

The first complex of formula $GeX_2(PR_3)$ to be crystallographically characterised was prepared by Bokii *et al.*[3] in 1975 from the reaction of $GeCl_2(O_2C_4H_8)$ with PPh_3 in refluxing THF in an inert atmosphere. The resultant complex, $GeCl_2(PPh_3)$, was recrystallised from chlorobenzene and its crystal structure revealed trigonal pyramidal geometry for the germanium atom, with d(Ge–P) of 2.511(2) Å and d(Ge–Cl) of 2.251(2) and 2.254(1) Å. There is only one other example of a crystallographically characterised germanium(II) phosphine complex of this formula, $GeI_2(PPh_3)$, reported by Inoguchi *et al.*[4] This complex was prepared by refluxing germanium(II) iodide and PPh_3, in ethylcyclohexane and xylene. The crystal structure revealed the same geometry for the germanium atom as that described for $GeCl_2(PPh_3)$, with similar d(Ge–P) bond distances [2.503(4) and 2.510(4) Å; two molecules are present in the asymmetric unit]. Studies regarding the reaction of germanium(II) halides with tertiary arsines are limited to two reports. King[2] investigated the reaction of GeI_2 with $AsPh_3$ in ethylcyclohexane and concluded that no reaction occurs, the starting materials being isolated in quantitative yield. In contrast, Neverov and co-workers[3] reported that $GeCl_2$ reacts with $AsPh_3$ in chlorobenzene to produce an air-stable complex of formula $GeCl_2(AsPh_3)$.

Reports concerning complexes of germanium(IV) halides with tertiary phosphine or arsine donor ligands are even rarer and no single-crystal X-ray data are available. In 1970, Beattie and Ozin[5] reported the formation of some 1 : 1 and 2 : 1 trimethylphosphine adducts of germanium tetrachloride. From vibrational spectroscopic studies of the 2 : 1 adduct, $GeCl_4(PMe_3)_2$, a *trans*-octahedral structure was assigned. Further studies of the same compound by Frieson and Ozin[6] in 1973 again led to the conclusion that $GeCl_4(PMe_3)_2$ is *trans* octahedral in the solid state. The same workers also noted that for the reaction of $GeCl_4$ with PMe_3, if an excess of $GeCl_4$ is used, then the 1 : 1 complex, $GeCl_4(PMe_3)$, and not the 2 : 1 complex, $GeCl_4(PMe_3)_2$, is formed. In addition, it was also observed that the reaction of $GeBr_4$ with PMe_3 always resulted

Table 1 Analytical and spectroscopic data for $[R_3PCl][GeCl_3]$ and $GeCl_4(AsMe_3)_2$

	Analysis (%)[a]				
Product	C	H	Cl	P	^{31}P-{H} NMR, δ[b]
$[Me_3PCl][GeCl_3]$	12.5 (12.4)	3.0 (3.1)	48.4 (48.9)	10.6 (10.7)	76.0
$[Et_3PCl][GeCl_3]$	21.9 (21.6)	5.0 (4.5)	41.9 (42.7)	10.1 (9.5)	Insoluble
$[Pr^n{}_3PCl][GeCl_3]$	37.9 (38.3)	5.9 (5.6)	37.7 (38.0)	8.3 (8.3)	101.1
$[Bu^n{}_3PCl][GeCl_3]$	35.0 (34.6)	6.9 (6.5)	32.9 (33.5)	7.6 (7.4)	103.4,[c] 11.7
$[Bu^t{}_3PCl][GeCl_3]$	34.2 (34.6)	6.5 (6.5)	33.9 (33.5)	7.4 (7.4)	Insoluble
$[(C_6H_{11})_3PCl][GeCl_3]$	44.0 (43.4)	6.9 (6.7)	28.2 (28.7)	13.7 (14.7)	104.9,[c] 76.1
$[\{2,6\text{-}(CH_3O)_2C_6H_3\}_3PCl][GeCl_3]$	43.8 (43.8)	4.1 (4.1)		4.1 (4.7)	−50.1
$[\{2,4,6\text{-}(CH_3O)_3C_6H_2\}_3PCl][GeCl_3]$	43.4 (43.4)	4.4 (4.4)	18.7 (19.0)	4.2 (4.2)	−51,[c] 39.5
$[(C_6H_5CH_2)_3PCl][GeCl_3]$	48.9 (48.6)	3.9 (4.1)	26.7 (28.3)	5.1 (5.9)	60.1
$[(Me_2N)_3PCl][GeCl_3]$	19.1 (19.1)	5.0 (4.8)	36.9 (37.6)	8.3 (8.2)	54.1
$[(Et_2N)_3PCl][GeCl_3]$	31.2 (31.2)	6.5 (6.5)	30.7 (30.7)	6.6 (6.7)	53.0
$[(Pr^n{}_2N)_3PCl][GeCl_3]$	39.7 (39.6)	7.8 (7.7)	25.3 (26.0)	5.8 (5.7)	54.0
$[Ph_2EtPCl][GeCl_3]$	51.9 (52.2)	4.8 (4.7)	22.1 (22.1)	9.4 (9.6)	−79.9
$GeCl_4(AsMe_3)_2$	15.5 (15.8)	4.2 (4.0)	31.9 (31.3)	32.2 (33.0)[d]	—

[a] Calculated values in parentheses. [b] All shifts were recorded in $CDCl_3$ solutions relative to concentrated phosphoric acid as standard. [c] More intense resonance, ratio *ca.* 8 : 1. [d] Arsenic analysis.

in the 1 : 1 complex, $GeBr_4(PMe_3)$, with no evidence for the 2 : 1 complex, regardless of the stoichiometry of the reaction. On the basis of infrared and Raman spectroscopic studies, and X-ray powder diffraction, the 1 : 1 adducts were assigned a trigonal bipyramidal structure where the ligand occupies an axial position.

In contrast to the above studies, du Mont[7,8] reported that the reaction of germanium tetrabromide with bulky tertiary phosphines results in a redox reaction, the products $[R_3PBr][GeBr_3]$ being isolated, which contain a germanium(II) metal centre. Very recently, the crystal structure of one of these compounds, $[Pr^i{}_3PBr][GeBr_3]$, has been reported,[9] the first crystallographic study of a compound of this stoichiometry. It was noted that there was a significant cation–anion interaction between the Br atom on $[Pr^i{}_3PBr]^+$ and one Br atom on $[GeBr_3]^-$, $d(Br\cdots Br) = 3.415(1)$ Å; van der Waals radius[10] for two bromine atoms = 3.9 Å. Studies regarding the reaction of tertiary arsines with germanium(IV) halides are non-existent.

Considering the paucity of data regarding complexes formed from the reaction of tertiary phosphines with germanium(IV) halides, it was decided to undertake a comprehensive study of the reaction of $GeCl_4$ with a wide variety of tertiary phosphines of varying steric bulk and basicity, in order possibly to gain a better understanding of the nature of the products formed. From the small number of reports concerning the reactions of GeX_4 (X = Cl or Br) with tertiary phosphines, it would appear that tertiary phosphines with small cone angles (low steric bulk) form molecular adducts with germanium(IV) centres, whereas for the corresponding reactions with bulky tertiary phosphines a redox reaction occurs to produce the ionic complexes $[R_3PX][GeX_4]$ (X = Cl or Br), which contain germanium(II) metal centres. The aim of the present work, therefore, is to establish crystallographically the germanium-(IV) and -(II) tertiary phosphine complexes described above and possibly to determine from ^{31}P-{H} NMR studies where the changeover in product occurs by gradually changing the steric bulk of PR_3. In addition, considering the fact that there are no reports concerning the reaction of germanium halides with tertiary arsines, we felt that an investigation of this reaction was also worthwhile.

Results and discussion

The compound $GeCl_4$ was treated with each tertiary phosphine in both a 1 : 1 and 1 : 2 stoichiometric ratio. In both cases 1 : 1 adducts were formed, with no evidence for the possible 1 : 2 adduct, eqn. (2) {$n = 1$ or 2; $R_3 = Me_3$, Et_3, $Pr^n{}_3$, $Bu^n{}_3$, $Bu^t{}_3$, $(C_6H_{11})_3$, $(C_6H_5CH_2)_3$, $(Me_2N)_3$, $(Et_2N)_3$, $(Pr^n{}_2N)_3$, Ph_2Et $[2,6\text{-}(CH_3O)_2C_6H_3]_3$ or $[2,4,6\text{-}(CH_3O)_3C_6H_2]_3$}. The products formed precipitated almost immediately upon addition of PR_3 to a diethyl ether solution of $GeCl_4$. The reaction was left stirring for *ca.* 1 d however to ensure complete reaction. The resultant complexes had the formula $GeCl_4(PR_3)$, and proved to be extremely moisture sensitive, decomposing to produce an oil in a matter of a few seconds if exposed to the atmosphere. In an inert (N_2) atmosphere however they could be easily isolated by standard Schlenk techniques. Elemental analyses and ^{31}P-{H} NMR spectroscopic data for the complexes are presented in Table 1. In addition to the tertiary phosphines listed in eqn. (2), the reaction of Ph_3P with $GeCl_4$ was also investigated. No precipitation of product was noted when this tertiary phosphine was added to a solution of $GeCl_4$, in diethyl ether and indeed, upon removal of approximately half of the solvent *in vacuo*, after *ca.* 2 d white crystals formed in the reaction vessel. Elemental analysis of this solid revealed it to be unchanged PPh_3 suggesting no reaction between PPh_3 and $GeCl_4$ in diethyl ether solution. The reason for this is presumed to be the low basicity of PPh_3 compared to that of the other tertiary phosphines listed in Table 1, and not steric effects since several of the tertiary phosphines listed have larger cone angles than that of PPh_3.

$$GeCl_4 + nPR_3 \xrightarrow[ca.\ 1\ d,\ N_2]{Et_2O,\ R.T.} GeCl_4(PR_3) \qquad (2)$$

^{31}P-{H} NMR Spectroscopic studies

The ^{31}P-{H} NMR spectra of all the $GeCl_4(PR_3)$ complexes, where possible, were recorded in $CDCl_3$ solution, Table 1. In most cases a single resonance was observed which exhibited a high positive value. Significantly, the resonances observed are very similar to those we have previously recorded for R_3PCl_2 compounds in the same solvent, which are known to ionise to produce $[R_3PCl]Cl$.[11] The great similarity in ^{31}P-{H} NMR values for $GeCl_4(PR_3)$ and $[R_3PCl]Cl$ for a given tertiary phosphine in $CDCl_3$ solution strongly suggests that these germanium complexes contain $[R_3PCl]^+$ cations. This observation appears to be at odds with previous reports by King and Beattie and Ozin, who reported that GeX_4 (X = Cl or Br) forms molecular 1 : 1 and 1 : 2 adducts with tertiary phosphines, the former having trigonal bipyramidal geometry and the latter having *trans*-octahedral geometry. No evidence for the formation of an ionic species containing a $[R_3PX]^+$ cation (X = Cl or Br) has been reported. It is also important to note, however, that in some cases a second peak (albeit a minor one) was also observed in the ^{31}P-{H} NMR spectrum of certain $GeCl_4(PR_3)$ complexes described here, which could be assignable to a molecular trigonal bipyramidal species, Table 1. Unfortunately, no ^{31}P-{H} NMR data are available for

Table 2 Selected bond lengths (Å) and angles (°) for $[Bu^n_3PCl][GeCl_3]$ with estimated standard deviations (e.s.d.s) in parentheses

Ge(1)–Cl(1)	2.230(9)	Cl(1)–Ge(1)–Cl(1)	96.1(4)
Cl(2)–P(1)	1.82(2)	C(1)–P(1)–Cl(1)	106(1)
P(1)–C(1)	1.83(4)	C(1)–P(1)–Cl(2)	113(1)

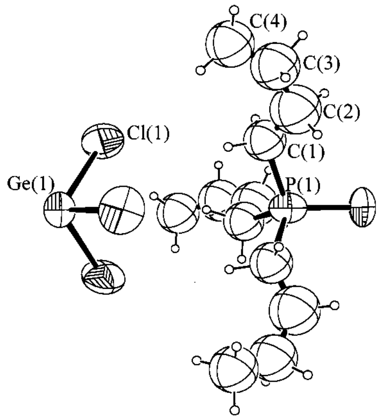

Fig. 1 The crystal structure of the ionic germanium(II) complex $[Bu^n_3PCl][GeCl_3]$.

comparative purposes for these compounds and so this assertion remains speculative.

In order to confirm our hypothesis that the compounds $GeCl_4(PR_3)$ contain the $[R_3PCl]^+$ cation we recrystallised a sample of $GeCl_4(PBu^n_3)$ from diethyl ether solution at room temperature. After *ca.* 7 d colourless crystals appeared in the reaction vessel. They were plunged into an inert oil under anaerobic conditions and subsequently one was chosen for analysis by single crystal X-ray diffraction. The crystal structure of the complex $[Bu^n_3PCl][GeCl_3]$, Fig. 1, does indeed confirm our hypothesis that the chlorophosphonium cation is present and it therefore seems very likely that all of the $GeCl_4(PR_3)$ complexes, described herein, are of the type $[R_3PCl][GeCl_3]$ by comparison of their $^{31}P-\{H\}$ NMR data with those of the corresponding $[R_3PCl]Cl$ species, previously reported.[11] Existing reports concerning compounds of formula $GeX_4(PR_3)$, which are very limited, concluded that tertiary phosphines of low steric requirements at the germanium atom resulted in the formation of a trigonal bipyramidal or *trans* octahedral molecular species, *i.e.* a neutral germanium(IV) adduct.[5,6] However, du Mont[7,9] reported that for tertiary phosphines of large steric requirements a redox reaction occurs to produce the ionic germanium(II) complexes, $[R_3PX][GeX_3]$. The work described here clearly shows that in our hands all of the complexes of formula $GeCl_4(PR_3)$ are in fact ionic species, $[R_3PCl][GeCl_3]$, and contain germanium(II) and not germanium(IV) metal centres, irrespective of the steric bulk of PR_3. Although no complex of formula $[R_3PCl][GeCl_3]$ has previously been reported, the existence of the $[GeCl_3]^-$ anion is well recognised and has been detected crystallographically in a variety of ionic complexes.[12–17] The anion in the complex $[Bu^n_3PCl][GeCl_3]$, described here, is unremarkable, exhibiting bond lengths and angles consistent with other previously crystallographically characterised complexes containing the $[GeCl_3]^-$ anion. The cation, however, exhibits a very short *d*(P–Cl) of 1.82(2) Å (Table 2), which is in fact shorter than for the cation in PCl_5, 1.903(2) Å.[18] No compound containing this cation has previously been the subject of a crystallographic study. We have previously[11] described the crystal structure of $[Pr^n_3PCl]Cl$ which displays *d*(P–Cl) 2.008(9) and 1.980(3) Å (two molecules are present in the asymmetric unit), and du Mont and co-workers[9] described the crystal structure of $[Pr^i_3PCl]Cl$, *d*(P–Cl) = 2.002(1) Å. The reason for the significantly longer *d*(P–Cl) in $[Pr^n_3PCl]Cl$ and $[Pr^i_3PCl]Cl$ compared to that in $[Bu^n_3PCl][GeCl_3]$ is due to the fact that in both the former compounds significant cation–anion interactions occur [$d(Cl\cdots Cl) = 3.207(3)$ and 3.234(1) Å for $Pr^n_3PCl_2$ and $Pr^i_3PCl_2$, respectively], which serve to weaken the P–Cl bond. No such interactions are present in $[Bu^n_3PCl][GeCl_3]$ which is in contrast to the only other crystallographically characterised compound of formula $[R_3PX][GeX_3]$, $[Pr^i_3PBr][GeBr_3]$, which also exhibits cation–anion interaction [$d(Br\cdots Br) = 3.415(1)$ Å, van der Waals radius for two bromine atoms = 3.9 Å].

The reaction of $GeCl_4$ with AsR_3 (R = Ph or Me)

As previously stated, the reaction of $GeCl_4$ with tertiary arsines has never been reported and literature studies regarding the interaction of tertiary arsines with any germanium halide are limited to the two conflicting studies regarding the reaction of triphenylarsine with GeX_2 (X = Cl or I) previously described; $GeCl_2(AsPh_3)$ was said to be air stable whereas $GeI_2(AsPh_3)$ was reported to be moisture sensitive. These results appear curious since binding of the soft ligand to a germanium(II) centre ought to be facilitated by soft I^- rather than hard Cl^- ligands. Additionally, the formation of an air-stable complex of formula $GeCl_2(AsPh_3)$ is rather surprising considering the acute moisture sensitivity of the corresponding tertiary phosphine complexes of this stoichiometry described by previous workers, and the fact that we were unable to prepare a complex from the reaction of $GeCl_4$ with triphenylphosphine, the starting materials being recovered.

We therefore treated $GeCl_4$ with AsR_3 (R = Ph or Me) in diethyl ether solution in a 1 : 1 and 2 : 1 stoichiometry, eqn. (3)

$$GeCl_4 + AsR_3 \xrightarrow[ca.\ 1\ d,\ N_2]{Et_2O,\ R.T.} GeCl_4(AsR_3)_2 \qquad (3)$$

(n = 1 or 2; R = Me). For the reaction of $GeCl_4$ with $AsPh_3$ no product formation was observed and the starting materials were recovered by removal of the solvent *in vacuo*, *i.e.* analogous to our results concerning the reaction of $GeCl_4$ with PPh_3. To our surprise, however, reaction of $GeCl_4$ with $AsMe_3$ produced a complex of stoichiometry $GeCl_4(AsMe_3)_2$, from elemental analysis results. This complex was produced regardless of the stoichiometry of the reactants (*i.e.* in both the 1 : 1 and 2 : 1 $AsMe_3 : GeX_4$ stoichiometric ratios).

Considering there are no crystallographic reports concerning any germanium(IV) halide complexes containing either a tertiary phosphine or arsine ligand, we decided to prepare crystals of the proposed $GeCl_4(AsMe_3)_2$ from dichloromethane solution at *ca.* 50 °C. After standing at room temperature for *ca.* 5 d large colourless crystals appeared in the reaction vessel. The crystals proved to be very moisture sensitive and were quickly removed from the reaction vessel in an inert atmosphere and plunged into an inert oil. A suitable crystal was chosen for examination by single crystal X-ray diffraction after viewing under the microscope. The structure of $GeCl_4(AsM_3)_2$, Fig. 2, indeed reveals a molecular germanium(IV) chloride–trimethylarsine adduct. Selected bond lengths and angles are displayed in Table 3. The molecule adopts *trans*-octahedral geometry with *d*(Ge–As) of 2.472(1) Å, the first reported germanium(IV)–arsenic bond; *d*(Ge–Cl) = 2.307(4) and 2.341(4) Å. Perhaps surprisingly, only one other complex of $GeCl_4$ containing a donor ligand has been crystallographically characterised,[19] the five-co-ordinate complex $GeCl_4(NMe_3)$. This compound exhibits *d*(Ge–Cl) of 2.130(2)–2.241(2) Å, rather shorter than those of $GeCl_4(AsMe_3)_2$ [2.307(4)–2.341(4) Å], as expected with the lower co-ordination number at the germanium centre. The *trans*-octahedral structure of $GeCl_4(AsMe_3)_2$ is the same as that predicted for the analogous tertiary phosphine complex, $GeCl_4(PMe_3)_2$, which was prepared by Ozin and co-workers[5,6] and studied spectroscopically. In our hands, however, reaction of trimethylphosphine with germanium tetrachloride did not

Table 3 Selected bond lengths (Å) and angles (°) for $GeCl_4(AsMe)_2$ with e.s.d.s in parentheses

Ge(1)–Cl(1)	2.307(4)	Ge(1)–As(1)	2.472(1)
Ge(1)–Cl(2)	2.341(4)		
Cl(1)–Ge(1)–Cl(1)	180.0	As(1)–Ge(1)–As(1)	180.0
Cl(1)–Ge(1)–Cl(2)	89.9(1)	C(1)–As(1)–Ge(1)	113.3(6)
Cl(2)–Ge(1)–Cl(2)	180.0	C(2)–As(1)–Ge(1)	115.2(5)
Cl(1)–Ge(1)–As(1)	88.8(1)	C(3)–As(1)–Ge(1)	109.0(6)
Cl(2)–Ge(1)–As(1)	92.6(1)		

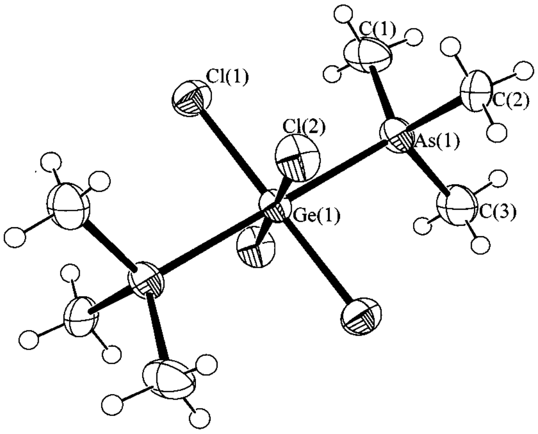

Fig. 2 The crystal structure of the molecular germanium(IV) complex $GeCl_4(AsMe_3)_2$.

produce a molecular germanium(IV) complex, but rather an ionic germanium(II) complex, $[Me_3PCl][GeCl_3]$. In fact, in the present study it would appear that the reaction of any tertiary phosphine with $GeCl_4$ predominantly produces an ionic germanium(II) complex. Nevertheless, from the spectroscopic studies of Ozin, and the fact that we quantitatively prepared the analogous complex $GeCl_4(AsMe_3)_2$, one would expect that $GeCl_4(PMe_3)_2$ should exist, however repeat reactions of $GeCl_4$ with PMe_3 in a variety of different stoichiometric ratios always resulted in isolation of $[Me_3PCl][GeCl_3]$, from ^{31}P-{H} NMR studies. The reasons why we are unable to prepare $GeCl_4(PMe_3)_2$ and the fact that reaction of $GeCl_4$ with $AsMe_3$ produces $GeCl_4(AsMe_3)_2$ appear curious and defy easy explanation since neither steric nor electronic factors would appear to be responsible.

Conclusion

The reaction of PR_3 with $GeCl_4$ produces the ionic complexes $[R_3PCl][GeCl_3]$ in near to quantitative yields irrespective of R. No evidence for the previously described neutral germanium(IV) complexes $GeCl_4(PR_3)_n$ ($n = 1$ or 2) was noted, apart from the possible assignment of unknown minor resonances in the ^{31}P-{H} NMR spectrum for some of the products which could be ascribed to this species, Table 1. Crystallographic characterisation of $[Bu^n{}_3PCl][GeCl_3]$, only the second compound of general formula $[R_3PX][GeX_3]$ to be crystallographically characterised, shows no cation–anion interaction (in contrast to $[Pr^i{}_3PBr][GeBr_3]$) and a very short *d*(P–Cl), 1.82(2) Å. In contrast, the reaction of Me_3As with $GeCl_4$ produces the *trans*-octahedral complex $GeCl_4(AsMe_3)_2$ which contains a germanium(IV) metal centre, and this has been established crystallographically, the first report of a germanium(IV) tertiary arsine complex. No reaction occurred between $GeCl_4$ and $AsPh_3$.

Experimental

All of the compounds described herein are extremely moisture sensitive, decomposing in a few seconds if exposed to the atmosphere. Consequently, strictly anaerobic and anhydrous conditions were employed for their synthesis. Any subsequent manipulations were carried out inside a Vacuum Atmospheres HE-493 glove-box. Diethyl ether (BDH) was dried by standing over sodium wire for *ca.* 1 d and subsequently refluxed over CaH_2 in an inert atmosphere and distilled directly into the reaction vessel. Tertiary phosphines were obtained commercially and used as received, as was the germanium(IV) halide, $GeCl_4$.

Table 4 Crystal data and details of refinement for $[Bu^n{}_3PCl][GeCl_3]$ and $GeCl_4(AsMe_3)_2$

	$[Bu^n{}_3PCl][GeCl_3]$	$GeCl_4(AsMe_3)_2$
Chemical formula	$C_{12}H_{27}Cl_4GeP$	$C_6H_{18}As_2Cl_4Ge$
M	416.70	454.43
Crystal system	Cubic	Monoclinic
Space group	*I*23	$P2_1/c$ (no. 14)
a/Å	15.986(2)	6.712(2)
b/Å	—	8.341(2)
c/Å	—	13.554(2)
β/°	—	100.96(2)
$U/Å^3$	4085.0(9)	744.9(3)
T/K	293(2)	293(2)
Z	8	2
μ/cm^{-1}	6.42	51.64
Crystal size/mm	0.25 × 0.25 × 0.25	0.30 × 0.20 × 0.15
F(000)	1712	440
No. unique reflections	392	1430
No. observed reflections $[I > 2.00\sigma(I)]$	82	1309
No. parameters	35	61
Final *R*1, *wR*2 $[I > 2\sigma(I)]$	0.055, 0.137	0.0655, 0.1603
(all data)	0.282, 0.235	0.1819, 0.1987
Minimum and maximum transmission	0.8560, 0.5823	0.3065, 0.5114

All of the germanium complexes were prepared in the same way, from the stoichiometric reaction of $GeCl_4$ and either one or two equivalents of ER_3 (E = P or As). The same products were obtained from both the 1 : 1 and 1 : 2 reactions in every case. The synthesis of $[Bu^t{}_3PCl][GeCl_3]$ is typical. Tri-*tert*-butylphosphine (0.50 g, 2.47 mmol) was suspended in Et_2O (*ca.* 50 cm^3) and subsequently germanium tetrachloride (0.53 g, 0.28 cm^3, 2.47 mmol) was added. After *ca.* 1 d the resultant white solid was isolated using standard Schlenk techniques. The solids were then transferred to pre-dried argon-filled ampoules which were flame sealed.

Elemental analyses were performed by the analytical laboratory of this department and the results are presented in Table 1. The ^{31}P-{H} NMR spectra were recorded as $CDCl_3$ solutions in a Bruker AC200 high-resolution multiprobe spectrometer relative to concentrated phosphoric acid as standard.

Crystallography

Crystal data and details of refinement for both structures are presented in Table 4. Colourless crystals of both species were removed from the reaction vessels in an inert atmosphere, plunged into an inert oil and then subsequently mounted in Lindeman tubes. All measurements were performed on a MAC3 CAD4 ($[Bu^n{}_3PCl][GeCl_3]$) or a Rigaku AFC6S [$GeCl_4(AsMe_3)_2$] diffractomer. Both diffractometers employing graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) and *ω*–*θ* scans. Both structures were solved by direct methods. Unit cell dimensions were derived from the setting angles of 25 accurately centred reflections. Lorentz-polarisation corrections were applied. Hydrogen atoms were confined to chemically reasonable positions. Neutral atom scattering factors were taken from ref. 20. Analogous dispersion effects were taken from ref. 21. All calculations were performed using SHELXS 86 and SHELXL 93 crystallographic software packages.[22,23]

CCDC reference number 186/1371.

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