Dichlorogermylene-Alkyldichlorophosphane Reactions Revisited: Characterisation of Bis(trichlorogermyl)phosphanes, Trichlorogermyldiphosphanes, and Ge–P Heterocycles

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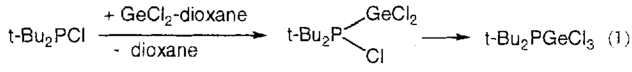
The reactions of alkyldichlorophosphanes **1** ($RPCl_2$; R = *tert*-butyl: **1a**, R = isopropyl: **1b**, R = 1-adamantyl: **1c**) with the germanium dichloride dioxane complex were followed by ^{31}P NMR. Depending on the organic substituents and the reaction conditions, mixtures of trichlorogermylphosphanes $RP(GeCl_3)_2$ **4a–c**, $RPHGeCl_3$ **5a–c**, diphosphanes $R(H)PP(H)GeCl_3$ **6a–c**, $R(Cl)PP(H)GeCl_3$ **7a**, **b**, cyclophosphanes, and Ge-P heterocycles such as triphosphadigermolanes $(RP)_3(GeCl_2)_2$ **8a**, **b** and tetraphosphagermolane $(RP)_4GeCl_2$ **10b** are formed. As a further unexpected byproduct of the reaction of **1a** with $GeCl_2$–dioxane, a small amount of tri-*tert*-butyl(trichlorogermyl)cyclotetraphosphane **9a** was isolated. From the reaction of **1c** with two equivalents of $GeCl_2$–dioxane, separation from byproducts **5c** and **6c** by crystallisation furnished colourless crystals of **4c** (R = 1-adamantyl) as the first pure organylbis(trichlorogermyl)phosphane. Surprisingly, the reaction of *isopropyl*phosphane with germanium tetrachloride, intended to prepare **5b**, led to crystalline isopropylphosphonium trichlorogermanate(II) **11**. The structures of molecular **4c** and **9a** and ionic **11** were determined by X-ray crystallography.

Introduction

Tertiary phosphanes react with dihalogenogermylenes furnishing ylide-type adducts R_3PGeX_2[1][2][3][4]. Related adducts of chloro- and bromodi-*tert*-butylphosphane with dichloro- and dibromogermylene are known to rearrange slowly by insertion of the germylenes into phosphorus–halogen bonds providing di-*tert*-butyltrihalogenogermylphosphanes[3][4]. The metastable ylide-type adduct of chlorodi-*tert*-butylphosphane with dichlorogermylene was detected by NMR in course of the reaction of the dichlorogermylene dioxane complex with di-*tert*-butylchlorophosphane furnishing stable di-*tert*-butyl(trichlorogermyl)phosphane[3][4]. This type of germylene insertion reaction is reversible: even under very mild conditions, "stronger germylene ligands" such as tertiary phosphanes (σ-donor ability: $R_3P > R_2PX$ [X = Cl, Br]) induce α-elimination of halogenphosphanes R_2PX from trihalogenogermylphosphanes R_2PGeX_3 by trapping dichloro- or dibromogermylene as stable adducts R_3PGeCl_2 (X = Cl, Br)[3][4].



$$t\text{-}Bu_2PCl \xrightarrow[\text{- dioxane}]{+\,GeCl_2\text{-dioxane}} t\text{-}Bu_2P\begin{matrix}GeCl_2\\ Cl\end{matrix} \longrightarrow t\text{-}Bu_2PGeCl_3 \quad (1)$$

$$t\text{-}Bu_2PGeX_3 + Ph_3P \longrightarrow t\text{-}Bu_2PX + Ph_3PGeX_2 \quad (2)$$

X= Cl, Br

$$RPCl_2 \xrightarrow[\text{(refluxing dioxane)}]{+\,GeCl_2\text{-dioxane}} RP(H)GeCl_3 \quad (3)$$

$$RPH_2 + GeCl_4 \longrightarrow RP(H)GeCl_3 + HCl \quad (4)$$

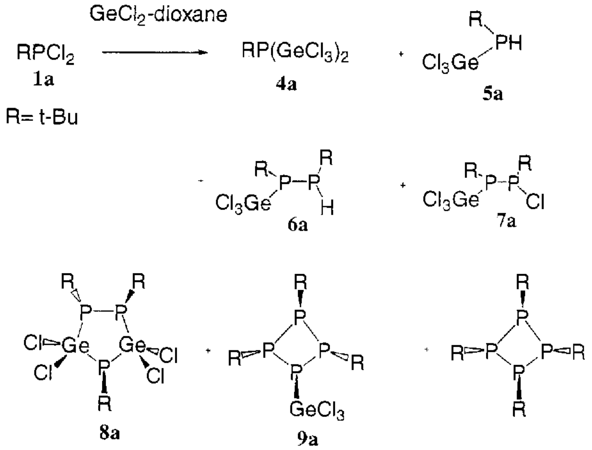
From organyldichlorophosphanes **1**, which are even weaker σ-donors than monochlorophosphanes, neither dichlorogermylene complexes $Cl_2(R)P \rightarrow GeCl_2$ **2** nor products derived from straightforward dichlorogermylene insertion into one or two P–Cl bonds of **1** [compounds $RP(Cl)GeCl_3$ (**3**) or $RP(GeCl_3)_2$ (**4**)] are known. However, heating various organyldichlorophosphanes $RPCl_2$ [R = Ph–, Mes–, 2,4,6-$(tBu)_3C_6H_2$–, *t*Bu–, $(Me_3Si)_2CH$–] with the dichlorogermylene dioxane complex had led to a number of stable trichlorogermylphosphanes $RP(H)GeCl_3$ **5** (Eq. 3). The formation of these products was explained by the formation of phosphinidene intermediates[5]. Phosphinidenes would abstract hydrogen providing primary phosphanes as subsequent intermediates, which can react with germanium tetrachloride leading to compounds **5** by evolution of HCl (Eq. 4)[5]. It has been proposed that thermally labile organyl(chloro)(trichlorogermylphosphanes) $RP(Cl)GeCl_3$ **3** suffering from α-elimination of germanium tetrachloride will be the phosphinidene precursors. However, no direct evidence for the primary products **3** (nor for diinsertion products **4**) from dichlorogermylene insertion into the P–Cl bonds of organyldichlorophosphanes was provided[5]. In the case of Veith's electron-rich bulky cyclic bis(amino)germylene $Me_2Si(N\text{-}tBu)_2Ge$, insertions of one or two of the these germylene moieties into the P–Cl bonds of aryldichlorophosphanes have been observed. *Mono*insertion products $Me_2Si(N\text{-}tBu)_2Ge(Cl)P(Cl)R$ were identified spectroscopically at −70°C in solution, but at room temp. these intermediates decomposed, providing mainly the oxidised germanium species $Me_2Si(N\text{-}tBu)_2GeCl_2$ and cyclophosphanes $(RP)_n$[6].

After the recent preparation of stable alkylbis(trichlorosilyl)phosphanes the question arose whether related alkylbis(trichlorogermyl)phosphanes were intrinsically unstable[7][8]. This led us to reinvestigate reactions of alkyldichlorophosphanes with the dichlorogermylene dioxane complex *under mild conditions.* We chose to compare the behaviour of $t\text{BuPCl}_2$ **1a**, the reaction of which with $GeCl_2$ in boiling dioxane had previously been described[5], with that of less bulky $i\text{PrPCl}_2$ (**1b**). Subsequently, for the reason of favourable crystallisation properties, we introduced 1-adamantyldichlorophosphane (**1c**) (which is closely related to **1a** from the steric point of view) into our investigation.

Reactions and Spectra

Reactions of $GeCl_2$–Dioxane with $tBuPCl_2$ (**1a**): Heating **1a** with $GeCl_2$–dioxane in boiling dioxane had provided trichlorogermylphosposphane $t\text{BuP(H)GeCl}_3$ (**5a**)[5]. Our experiments concerning the reaction of **1a** with $GeCl_2$–dioxane at room temperature in toluene were carried out by adding one equivalent of **1a** to suspensions of one and of two equivalents of the dichlorogermylene dioxane complex in toluene (1:1 and 1:2). Both experiments were followed by ^{31}P NMR. In the 1:1 experiment, products of the type $t\text{Bu(Cl)}_2\text{PGeCl}_2$ **2a** and $RP(Cl)GeCl_3$ **3a** from coordination or insertion of a single dichlorgermylene molecule with **1a** were not detected. After 1 d stirring at room temperature, apart from the starting material **1a** (45%) and minor amounts (10%) of known **5a**, the ^{31}P-NMR signal (45% of the overall intensity) of the novel bis(trichlorogermyl)phosphane **4a** appeared at $\delta = +27$ (Eq. 5). The products could not be separated. In experiments with two equivalents of dichlorogermylene, after stirring 4 d the consumption of **1a** is still incomplete, but now the ^{31}P signal of product **4a** is up to 80% by the total intensity. However, the products could still not be separated. Heating the mixture from the 1:2 experiment (attempted completion of the consumption of **1a**, or attempted distillation) or storing the mixture for a longer time leads to the evolution of further new decomposition products. Four sets of ^{31}P-NMR AM patterns of these products have to be assigned to a mixture of pairs of enantiomers of new trichlorogermyldiphosphanes $t\text{Bu(H)PP}(t\text{Bu})\text{GeCl}_3$ **6a** and $t\text{Bu(Cl)PP}(t\text{Bu})\text{GeCl}_3$ **7a**. Assignment of the diastereomeric mixture of compounds **6a** was supported by P-H coupling in the ^1H-coupled ^{31}P-NMR spectra; a solution enriched with **6a** was obtained by reacting $t\text{Bu(H)PP}(t\text{Bu})\text{K}$ with germanium tetrachloride. This solution contained up to 70% **6a** (the ratio of the diastereomers of **6a** was about 9:1) besides **4a** and $(t\text{BuP})_4$. Assignment of **7a** was supported by ^{31}P-NMR shifts and couplings $^1J(PP)$ of the pair of diastereomers and by independent formation of **7a** (up to 60% enriched, ratio of the diastereomers about 7:1) from 1,2-di-*tert*-butyl-1,2-dichlorodiphosphane with dichlorogermylene. The latter reaction was accompanied by the formation of **1a**, **4a**, **5a**, **6a**, $(t\text{BuP})_4$, and traces of the four-membered Ge-P heterocyle 1,1-dichloro-2,3,4-tri-*tert*-butyl-2,3,4-triphosphagermetane[7]. In each case, diphosphanes **6a** and **7a** could not be isolated in pure state.

Scheme 1. Products of the reaction of **1a** with the $GeCl_2$–dioxane complex



Attempted distillation of the reaction mixture from a 1:1 experiment of **1a** with dichlorogermylene provided mainly volatile **1a**; extraction of the red distillation residue with pentane and subsequent crystallisation allowed the isolation of a mixture of cyclic and heterocyclic phosphanes: $(t\text{BuP})_4$ ($\delta^{31}P = -57$), $(t\text{BuP})_3(\text{GeCl}_2)_2$ [**8a**: $\delta^{31}P = +11.2$, $+3.4$, and -42.5; ABX pattern, $J(AB) = \pm 296$, $J(AX) = \pm 16.9$, $J(BX) = \pm 23.9$ Hz] and $(t\text{BuP})_3\text{PGeCl}_3$ [**9**: $\delta^{31}P = -15.5$, -58.0, -93.3; AM_2X pattern, $J(AM) = \pm 142.2$, $J(AX) = \pm 21.5$, $J(BX) = \pm 114.2$ Hz]. A few crystals of **9a** suitable for an X-ray crystal structure determination and a mass spectrum (M^+: $m/z = 474$) could be separated.

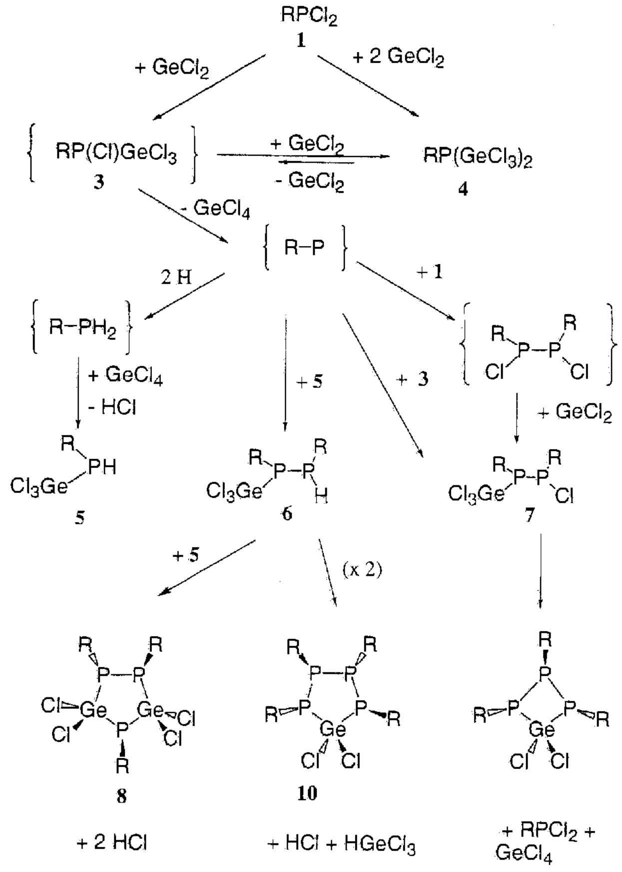
Reactions of $GeCl_2$–Dioxane with $iPrPCl_2$ (**1b**): ^{31}P-, ^1H-, and ^{13}C-NMR spectra reveal that two hours after adding one equivalent of **1b** to the dichlorogermylene dioxane complex suspended in cold toluene (≤ −20°C, followed by warming to room temperature), a clear solution containing uncoordinated dioxane and the 1:1 mixture of **1b** and the new isopropylbis(trichlorogermyl)phosphane **4b** is formed. "1:1 products" **2b** and **3b** were not detected. Attempts to isolate **4b** by removing volatile **1b** led to crude products containing up to 80% **4b**, but the procedure is accompanied by decomposition of **4b**. Extraction of the oily residue with pentane followed by evaporation of the solvent provided a yellowish liquid, the ^{31}P-NMR spectrum of which revealed the presence of isopropyl(trichlorogermyl)phosphane **5b** (10%), $(i\text{PrP})_4$ (10%), and the new heterocycle $(i\text{PrP})_4\text{GeCl}_2$ (**10b**, 80%).

Warming a mixture of **1b** and *two* equivalents of $GeCl_2$–dioxane in toluene from −78° to room temperature leads to complete consumption of **1b**, but again the primary main product **4b** is accompanied by increasing amounts of a number of decomposition products in the reaction mixture:

trichlorogermylphosphane **5b**, traces of 1,2-diisopropyl-1-trichlorogermyldiphosphane (^{31}P-NMR AM patterns of a pair of enantiomers) **6b**, 1,1,3,3-tetrachloro-2,4,5-tri-isopropyl-2,4,5-triphospha-1,3-digermolane [**8b**, (iPrP)$_3$(GeCl$_2$)$_2$, ^{31}P-NMR ABX pattern], and 1,1-dichloro-2,3,4,5-tetra-isopropyl-2,3,4,5-tetraphosphagermolane [**10b**, (iPrP)$_4$(GeCl$_2$), ^{31}P-NMR AA'BB' pattern]. (iPrP)$_4$ was not detected in the reaction mixture of the 1:2 experiment, whereas the new triphosphadigermolane heterocycle **8b** was not formed in the 1:1 experiment.

Removal of solvent and other volatile products followed by extraction of the residue provided a yellow liquid containing **10b** (50%) and **8b** (40%) as major species accompanied by 5% of each **4b** and **5b**. **8b**, and **10b** could also be detected by mass spectroscopy (**8b**: M$^+$ m/z = 440; **10b**: M$^+$ m/z = 510).

Scheme 2. Course of reactions of alkyldichlorophosphanes with the GeCl$_2$–dioxane complex



As in the reactions of the *tert*-butyl compound **1a**, dichlorophosphane **1b** appears to provide straightforwardly the bis-insertion product **4b** at an early stage of the reaction with GeCl$_2$–dioxane, products from the decomposition of **4b** (or **3b**) appear subsequently. Decomposition of **4b** is always accompanied by the formation of products with P–H bonds (**5b**, **6b**). Subsequently, these compounds appear to be consumed in favour of Ge-P heterocycles, which were found highly enriched in the "final" mixtures of products.

The complete absence of *mono*-insertion products **3a**, **3b** indicates that reactions of these compounds with GeCl$_2$ proceed significantly faster than those of **1a**, **b**. To disfavour *di*-insertion of GeCl$_2$, we followed the reaction of GeCl$_2$–dioxane with an excess (two equivalents) of dichlorophosphane **1b** in toluene by ^{31}P NMR. Signals assignable to species **2b** or **3b** did not appear. Removal of **1b** and toluene under vacuum led to a crude product containing (iPrP)$_4$ (50%), **5b** (30%), **6b** (< 10%), and **10b** (< 10%) (see Scheme 2).

Our conclusion is that **3b** formed at the surface of suspended GeCl$_2$–dioxane will be reactive towards the insertion of a second GeCl$_2$ molecule (providing **4b**), compared with its intrinsic instability (favouring elimination of GeCl$_4$).

Studies concerning reactions of tetraalkyldiphosphanes with germanium tetrachloride have shown that P–P bond cleavage leads straightforwardly to mixtures of chlorophosphanes and trichlorogermylphosphanes[7]. This implies that the reverse reaction, i.e. P-P coupling by GeCl$_4$ elimination, is not a generally favourable process[7]. Mixtures of starting materials **1** and products **4** will – if ever – only slowly couple with elimination of GeCl$_4$ and formation of asymmetric diphosphanes **7**. Fair amounts of **7a** but only traces of **7b** had been detected in reaction mixtures from 1:1 experiments. Compounds **7** could condense or disproportionate further, providing cyclophosphanes. Cyclophosphanes themselves are susceptible to cleavage by GeCl$_4$ and to insertion of GeCl$_2$ providing Ge-P heterocycles[7].

Intramolecular elimination of GeCl$_4$ from **3**[5] would be a side reaction competing with the formation of **4**. However, side products **5** and **6** from intermediate phosphinidene formation are scarce at the early stages of **1**/GeCl$_2$ reactions under mild conditions. Another source of phosphinidene precursors **3** could be dismutation of starting materials **1** with products **4** (Cl/GeCl$_3$ exchange).

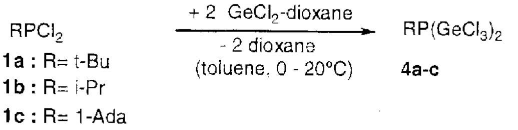
H-abstraction by alkylphosphinidenes leads to primary phosphanes, which can react further with GeCl$_4$ providing trichlorogermylphosphanes **5** and HCl[5]. However, the exact source of H atoms has not yet been determined: a separate 1:1 experiment of **1b** with GeCl$_2$–dioxane in C$_6$D$_6$ did not allow the identification of any P-D species by ^{31}P NMR. Dioxane (from GeCl$_2$–dioxane) and the alkyl group attached to phosphorus remain possible H sources. In boiling dioxane, H abstraction was indeed the predominant reaction pathway[5] leading from **1a** to high yields of **5a**; only traces of other compounds were observed under those conditions[5].

Formation of asymmetric diphosphanes **6** is easily explained by the insertion of phosphinidenes into P–H (or P–Ge) bonds of **5**. Similarly, phosphinidene insertion into a P–Cl bond of **1** could lead to 1,2-dialkyl-1,2-dichlorodiphosphanes, which are susceptible to GeCl$_2$ insertion providing **7** (as shown by the formation of **7a**). **7** could also be derived from phosphinidene insertion into P–Cl or P–Ge bonds of intermediate **3**.

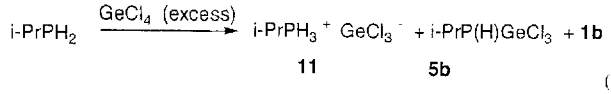
The remarkable amount of heterocycle **8b** from **1b**/GeCl$_2$ 1:2 [whereas from **1b**/GeCl$_2$ 1:1 no **8b**, but instead (iPrP)$_4$ was formed] would be consistent with competition between different cyclisation reactions involving diphosphane **6b**:

coupling with **7b** (favoured by excess **1b**) or self-condensation will produce P_4-moieties such as those of **10b** and (iPrP)$_4$, whereas coupling of **6b** with **4b** (larger concentration of **4b** in the 1:2 experiment) will produce the triphosphadigermolane **8b**. Separate studies on Ge-P heterocycles have shown that **8b** and (iPrP)$_4$ equilibrate very slowly (3 months at 20°C) providing nearly pure **10b**[7].

An important intermediate step providing P−H phosphanes **5** is the (known) trichlorogermylation of primary phosphanes with $GeCl_4$[5]. Since our **1b**/$GeCl_2$ reactions did not provide pure **5b**, we attempted to isolate **5b** from isopropylphosphanc and $GeCl_4$.



$$\underset{\substack{\mathbf{1a}:\ R=t\text{-Bu}\\ \mathbf{1b}:\ R=i\text{-Pr}\\ \mathbf{1c}:\ R=1\text{-Ada}}}{RPCl_2} \xrightarrow[\substack{-\,2\ \text{dioxane}\\ (\text{toluene, } 0-20°\text{C})}]{+\,2\ GeCl_2\text{-dioxane}} \underset{\mathbf{4a\text{-}c}}{RP(GeCl_3)_2} \qquad (5)$$



$$i\text{-PrPH}_2 \xrightarrow{GeCl_4\ (\text{excess})} \underset{\mathbf{11}}{i\text{-PrPH}_3{}^{+}\ GeCl_3{}^{-}} + \underset{\mathbf{5b}}{i\text{-PrP(H)GeCl}_3} + \mathbf{1b} \qquad (6)$$

The condensation of isopropylphosphane into a toluene solution of germanium tetrachloride (excess) at −78°C provided instantaneously a white precipitate which was separated by filtration. In the supernatant solution were present **1b**, **5b**, and iPrPH$_2$. Surprisingly, recrystallisation of the precipitate from hot toluene allowed the isolation of crystalline $[i\text{PrPH}_3]^+[GeCl_3]^-$ (**11**) in 21% yield. The structure of **11** was determined by X-ray diffraction. **11** is obviously the product of an unusual redox reaction that led partly to oxidation of iPrPH$_2$ to iPrPCl$_2$ (**1b**) and to reduction of Ge^{IV} to Ge^{II}. Solid **11** − the first known primary phosphonium trihalogenogermanate(II) − is thermally stable at room temperature. **11** is moderately soluble in acetonitrile. In this solvent ^1J(PH) is observable from a broadened quartet in ^{31}P NMR [$\delta = -38$, $^1J(\text{PH}) = \pm450$ Hz]; in THF, however, a broad signal appears at $\delta = -94$. Addition of methanol to the THF solution leads to iPrPH$_2$ ($\delta^{31}P = -104$).

Solutions that contain the desired **5b** enriched up to 70% were obtained by addition of a solution of iPrP(H)K in THF to $GeCl_4$ at −40°C. The main impurity was (iPrP)$_4$. Carrying out the reaction at −20°C led to a large amount of further byproducts (**6b**, **10b**) and unidentified species).

Reactions of $GeCl_2$−Dioxane with 1-Adamantyldichlorophosphane (**1c**)[9]: Formation and decomposition of *tert*-butylbis(trichlorogermyl)phosphane (**4a**) proceeded significantly more slowly than the corresponding reactions from **1b** to **4b** and other products. To improve the chance of separating a solid compound **4** from its byproducts, we decided to prepare the 1-adamantyl derivative **4c**, which would sterically be closely related to **4a**. 1:1 and 1:2 experiments of **1c** with $GeCl_2$−dioxanc were carried out at room temperature in toluene. Within two hours, in both experiments about half of the starting material **1c** was consumed in favour of new 1-adamantylbis(trichlorogermyl)phosphane (**4c**, $\delta^{31}P = +23.5$). In the 1:2 experiment, a further signal at $\delta^{31}P = -25.5$ appears with about 15% of the overall intensity (Table 1, 2). The assignment of the signal at $\delta^{31}P = -25.5$ to adamantyl(trichlorogermyl)phosphane (**5c**) was established by a proton-coupled ^{31}P-NMR spectrum showing a doublet with $^1J(^{31}P, {}^1H) = \pm196$ Hz. Continued stirring of the reaction mixture of the 1:1 experiment leads to further consumption of **1c**, but the amount of **4c** in the mixture decreases and that of **5c** increases; after 20 h, about the same percentage of **4c** and **5c** is present in solution. A set of signals with an AM-type ^{31}P-NMR pattern of the new asymmetric diphosphane **6c** appears in the reaction mixtures of both (1:1 and 1:2) experiments (Table 1). Couplings $^1J(^{31}P,^{31}P) = \pm208$ Hz and coupling $^1J(^{31}P,^1H) = \pm190$ Hz of only the more upfield phosphorus nucleus (in a proton-coupled spectrum) indicate that the other phosphorus atom of the diphosphane bears a trichlorgermyl substituent. There is no indication of the loss of 1-adamantyl groups; thus the NMR data of **6c** have to assigned to 1,2-bis(1-adamantyl)-1-trichlorogermyldiphosphane. One of the two possible diastereoisomers of **6c** is obviously predominant in solution (one pair of enantiomers, see Table 1). Keeping the 1:1 mixture for 10 days at room temperature led to complete decomposition of **4c**; **5c**, and **6c** were then the main products. Hydrolysis of the sample (open NMR tube) led to a product with $\delta P = +43$[7].

After keeping a separate sample of the mixture from the 1:1 reaction for several months at −60°C, **5c** was again the predominant species, but approximately equal amounts of **1c** and **4c** were still present, and besides the predominant pair of enantiomers of **6c**, the other diastereoisomer **6c′** could be detected by ^{31}P NMR (weak signal, $\delta P = +14$, -77 [$^1J(^{31}P,^{31}P) = \pm209$ Hz]. Chemical shifts and couplings of **6c** are similar to those of the corresponding *tert*-butyl compound **6a** (of which both diastereoisomers were detected), and quite different from **7a**.

Table 1. ^{31}P-NMR shifts and intensities of products from reactions of **1c** with $GeCl_2$−dioxane

		^{31}P NMR δ [ppm]	Signal intensity after 2 h		Signal intensity after 20 h	
Ratio of starting materials:			1 : 1	1 : 2	1 : 1	1 : 2
compound:						
1-Ada-PCl_2	**1c**	+192	45 %	40 %	25 %	5 %
1-Ada-$P(GeCl_3)_2$	**4c**	+23.5	45 %	40 %	30 %	65 %
1-Ada-$PH(GeCl_3)$	**5c**	–25.5	5–10 %	15 %	30 %	10 %
1-AdaP(H)P($GeCl_3$)1-Ada	**6c**	–5.8; –64.9	–	< 5 %	10 %	20 %
1-AdaP(H)P($GeCl_3$)1-Ada	**6c′**	+14; –77	–	–	–	–
unidentified species		+ 115 and ±0	< 5%	–	< 5%	–

In the reaction mixture of the 1:2 experiment after 20 h, **1c** is nearly completely consumed, **4c** is the predominant reaction product and **5c** and **6c** are also present (Table 2). Work-up by removal of all volatile material and subsequent recrystallisation from hexane allowed the isolation of pure **4c** in about 30% yield as colourless crystals.

4c is the first bis(trichlorogermyl)phosphane that was isolated in a pure state. EI-mass spectra of **4c** did not allow the detection of its molecular ion. The cation of the adamantyl group is a very strong peak, and the $GeCl3^+$ cation was also detected. Among the further signals were the cation of tetraadamantylcyclotetraphosphane and its fragments, other signals such as m/z = 782 indicated the existence of volatile decomposition products containing several adamantyl groups and germanium and chlorine atoms. These might be related to Ge-P heterocycles related to **10b**.

In solution, decomposition of **4c** is favoured by the presence of the dichlorophosphane **1c** (the 1:1 experiment). When no more dichlorogermylene is present to react with the short-lived chloro(trichlorogermyl)phosphane **3c**, or when **3c** is formed from **4c** with **1c**, 1-adamantylphosphinidene formation by elimination of $GeCl_4$ from **3c**, subsequent hydrogen abstraction and trichlorogermylation could lead to **5c**. As in the cases of **5a** and **5b**, further phosphinidene insertion into a P–Ge or a P–H bond of **5c** will provide the diphosphane **6c** (Scheme 2).

The fact that no evidence for the presence of a compound **3** in solution could be provided by NMR, even in the 1:1 experiments, allows three hypotheses (Scheme 2):

a) Concerning the $GeCl_2$ insertion, **3** is much more reactive than **1** [**3** is the better nucleophile for the first step of the reaction, see eq. (2)]; formation of intermediate **3** will be the rate-determining step when **1** and $GeCl_2$ furnish **4**. In this respect, **1**/$GeCl_2$ reactions are very much related to **1**/$HSiCl_3$/NEt_3 reactions[8].

b) When no germylene source is available for the transformation of **3** into **4**, phosphinidene formation by α-elimination of $GeCl_4$ could subsequently lead to the detected products **5**[5] and **6**. **6** is apparently the product from phosphinidene insertion into a P–H or a P–Ge bond of **5**. Loss of $GeCl_2$ from **4** by α-elimination might be a further pathway leading to phosphinidene precursor **3**.

Trichlorogermylphosphanes related to **5** are known to require bases such as DBU (1,5-diazabicyclo[5.4.0]undec-5-ene) to act as phosphinidene sources[10]. The related trichlorosilylphosphane $(Me_3Si)_2NP(H)SiCl_3$ is known to decompose in the presence of triethylamine to provide the diphosphane $(Me_3Si)_2NP(H)P(SiCl_3)N(SiMe_3)_2$, which will be a product from phosphinidene insertion into $[(Me_3Si)_2N]P(H)SiCl_3$[11]. The decomposition of $Me_2Si(N\text{-}t\text{Bu})_2Ge(Cl)P(Cl)R$ into $Me_2Si(N\text{-}t\text{Bu})_2GeCl_2$ and $(RP)_n$ is a related reaction[6].

c) The existence of **4** in the presence of **1** (in many of the reaction mixtures from **1**/$GeCl_2$) indicates that – if **3** is in an equilibrium with **1** and **4** – the equilibration will be a slow process. The disproportionation of **3** into **1** and **4** would compete with the α-elimination of $GeCl_4$ from **3**.

The mode of decomposition of Veith's monoinsertion product related to **3** does not give any hint of disproportionation into dichlorophosphane and di-insertion product[6].

^{31}P-NMR Spectra of **4–11**: As expected from the comparison of the ^{31}P-NMR shifts of tBuP(GeMe$_3$)$_2$ (δ = -82.3) and tBuP(SiMe$_3$)$_2$ (δ = -108)[12], the ^{31}P-NMR signals of alkylbis(trichlorogermyl)phosphanes **4a–c** appear about 20–35 ppm downfield from the related alkylbis(trichlorosilyl)phosphanes[8]. In trichlorogermyldiphosphanes **6** and **7**, assignment of the ^{31}P nuclei bonded to trichlorogermyl groups is straightforward: in the diastereomers of **6a–c** they appear about 50–70 ppm downfield from the ^{31}P nuclei adjacent to ^{1}H (assigned with help of ^1J(PH) between 192 and 208 Hz); in the diastereomers of **7a** and **7b** they appear about 70–110 ppm upfield from the ^{31}P(–Cl) nuclei. **6** and **7** exist as mixtures of pairs of enantiomers (at the asymmetric phosphorus centres) (1*R*,2*R*/1*S*,2*S*) and (1*R*,2*S*/1*S*,2*R*). In asymmetric diphosphanes $R^1R^2P–PR^1R^2$ a correlation of increasing steric requirements of substituents R^1,R^2 with downfield ^{31}P-NMR shift and increasing *magnitude* of $^1J(^{31}P,^{31}P)$ has been observed[13]. In the case of **7a**, **b** the ^{31}P nuclei of the pair of enantiomers with the larger P-P coupling appear at lower field in ^{31}P NMR (average of the two ^{31}P resonances), but in the case of **6a–c** such a correlation is not valid. On basis of these data, a consistent assignment of "isomers 1 and 2" (Table 1, 2) to the (1*R*,2*R*/1*S*,2*S*) and (1*R*,2*S*/1*S*,2*R*) diastereomers of **6** and **7** cannot be made.

The cyclic germylphosphanes **8**, **9**, and **10** are assigned with help of their characteristic spin systems. The presence

Table 2. Comparison of ^{31}P-NMR data of compounds **1–11**[a]

Compound			**a**: R = tBu		**b**: R = iPr		**c**: R = 1-Ada	
$RPCl_2$	**1**	δ	+198		+199		+192	
$RP(GeCl_3)_2$	**4**	δ	+27.0		–2.8		+23.5	
$RP(H)GeCl_3$	**5**	δ	–21.5		–56		–25.5	
^1J(PH)			±192		±191		±196	
$R(GeCl_3)P_AP_M(H)R$	**6**		P_A	P_M	P_A	P_M	P_A	P_M
Isomer 1		δ	+11.1;	–64.4	–3.8;	–74.5	–5.8;	–64.9
$^1J(P_AP_M)$			±210		±208		±208	
$^1J(P_MH)$			±192		±193		±190	
Isomer 2		δ	–2.2;	–52.1	–19.5;	–76.5	+ 14;	–77
$^1J(P_AP_M)$			±214		±231.8		±209	
$^1J(P_MH)$			±200		±210			
$R(Cl)P_AP_M(GeCl_3)R$	**7**		P_A	P_M	P_A	P_M		
Isomer 1		δ	+118.8;	+42	+111;	+20.4		
$^1J(P_AP_M)$			±310		±296.4			
Isomer 2		δ	+116,	+25.3	+ 116;	+6.1		
$^1J(P_AP_M)$			±298		±247.3			
$(RP)_3(GeCl_2)_2$	**8**	δ	+11.2, +3.4, –42.5		–15.5, –18.8, –104.6			
ABX , $^1J(P_AP_B)$			±296		±299.6			
$^2J(P_AP_X)$			±16.9		±24.1			
$^1J(P_BP_X)$			±23.9		±23.0			
$(RP)_3PGeCl_3$	**9**	δ	–15.5, –58.8, –93.3					
AM_2X , $^1J(P_AP_M)$			±142.2					
$^2J(P_AP_X)$			±21.5					
$^1J(P_MP_X)$			±114.2					
$(RP)_4GeCl_2$	**10**	δ			–7.6, –25.1			
AA'MM', $^1J(P_AP_M)$					±316.9			
$^1J(P_{A'}P_M)$					±0.5			
$^1J(P_AP_{A'})$					±53.1			
$^1J(P_MP_{M'})$					±306.1			
$(RPH_3)^+(GeCl_3)^-$	**11**[b]	δ			–38			
^1J(PH)					±450			

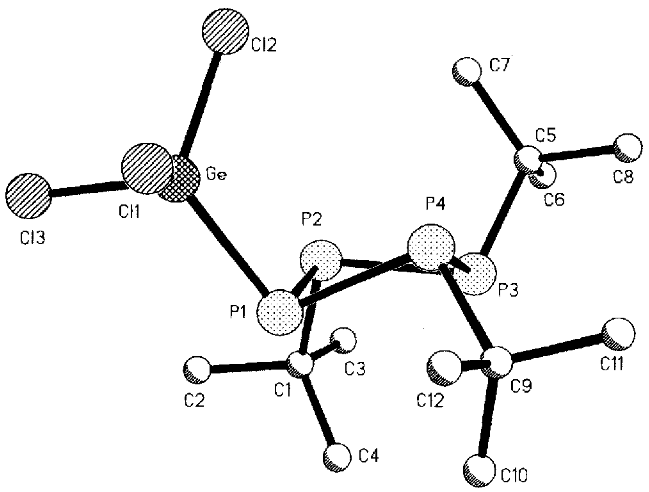
[a] δ[ppm], J [Hz]; solvents (if not otherwise stated): [D$_6$]benzene/toluene. – [b] In CH_3CN solution.

of an ABX pattern (*not* A_2X) for **8** excludes rapid inversion at P_X.

Structure Determinations: **9a** is the first trichlorogermylphosphane and **4c** is the first bis(trichlorogermyl)phosphane whose structure has been solved crystallographically. The solid compound **4c** (space group $P2_1/c$, $Z = 8$) contains two conformationally very similar molecules in the asymmetric unit. Phosphorus is pyramidally surrounded by one carbon and two germanium atoms. Compared with the 1-adamantyl group, the trichlorogermyl groups of **4c** behave as less bulky substituents at phosphorus (molecule 1: both $\angle$CPGe 104.6°, $\angle$GePGe = 97.2°). Two of the angles $\angle$PGeCl of each $PGeCl_3$ moiety are close to tetrahedral whereas the third angle is in the range of 117–122°, but all Ge–Cl distances lie in a narrow range [2.117(2) to 2.135(2) Å]. Compared with average Ge–P single bond lengths (Ge–P 2.322 Å[14]), all Ge–P distances in **4c** [2.298(2) to 2.3100(14) Å] are slightly shorter.

The molecular structure of **9a** (space group $P2_1/c$, $Z = 4$) is closely related to that of $(t\text{BuP})_4$[15]. The deviation of the $PGeCl_3$ group from tetrahedral symmetry [$\angle$PGeC 109.37(4), 111.46(4) and 118.40°] is comparable to the distortion of the *tert*-butyl groups (two angles PCC close to 105–106°, the third one around 115°). On average, Ge–Cl distances in **9a** are slightly longer [2.1359(10) to 2.1408(11) Å] and the Ge–P distance is about 0.03 Å shorter than in **4c**. The Ge–P distance in **9a** is about 0.05 Å shorter than standard Ge–P single bonds[14] but still 0.14 Å longer than Ge=P double bond lengths[16].

Figure 1. Structure of tri-*tert*-butyl(trichlorogermyl)cyclotetraphosphane **9a**[a]



[a]Ge–P1 2.2825(10), P–P 2.221–2.225, Ge–Cl 2.136–2.141 Å; P2–P1–Ge 98.84(4), P4–P1–Ge 96.69(4), P–P–P 86.1–87.2°.

Compound **11** (space group $P2_1/c$, $Z = 4$) consists of $i\text{PrPH}_3^+$ cations and chains of $GeCl_3^-$ anions. The tendency of trichlorogermanate(II) anions in solids to exhibit secondary interionic Ge$\cdots$Cl contacts is well documented [17–19]. The shortest such Ge$\cdots$Cl contacts in **11** [3.721(3), 3.872(2), 4.096(2) Å] are still 1.4 Å longer than the average of the Ge–Cl distances within the anion of **11** [2.290(2), 2.306(2), and 2.322(2) Å].

Conclusion

Alkylbis(trichlorogermyl)phosphanes **4** are formed by insertion of dichlorogermylene into the two P–Cl bonds of alkyldichlorophosphanes under mild conditions; the adamantyl derivative **4c** was isolated and its structure determined. Depending on organic substituents and the reaction conditions, compounds **4** are accompanied by mixtures of products that contain trichlorogermylphosphanes $RPHGeCl_3$ **5**, reported previously by Satgé et al.[5], diphosphanes $R(H)PP(H)GeCl_3$ **6** and $R(Cl)PP(H)GeCl_3$ **7**, cyclophosphanes, and Ge-P heterocycles such as triphosphadigermolanes $(RP)_3(GeCl_2)_2$ **8a, b** and tetraphosphagermolane $(RP)_4GeCl_2$ **10b**. Extension of the reaction sequence proposed by Satgé et al. to describe the formation of compounds **5**[5], i.e. insertion of transient phosphinidenes into P–Cl, P–H, and P–Ge bonds and subsequent dismutation reactions allow an understanding of the formation of the new germyl diphosphanes and cyclophosphanes. The reactive behaviour of germanium tetrachloride and germanium dichloride towards phosphinidenes, diphosphenes, diphosphanes and cyclophosphanes merits further interest and is at present under investigation[7].

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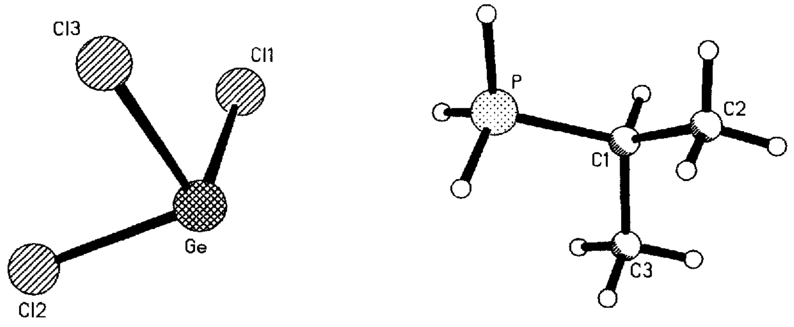
Experimental Section

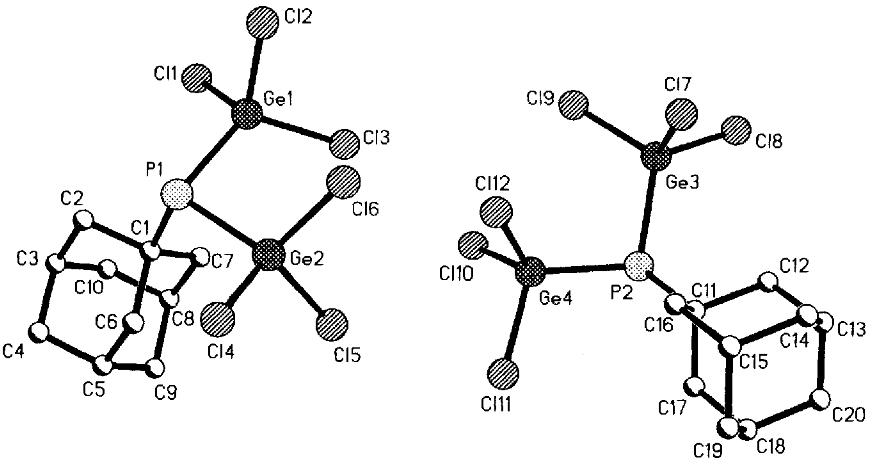
General: All experiments were carried out under deoxygenated dry nitrogen as inert gas; solvents were dried according to standard

Figure 2. Structure of isopropylphosphonium trichlorogermanate(II) **11**[a]



[a] Ge–Cl 2.290–2.322 Å; Cl1–Ge–Cl2 93.55(8), Cl1–Ge–Cl3 95.46(7), Cl2–Ge–Cl3 94.88(8)°

Figure 3. Structure of 1-adamantylbis(trichlorgermyl)phosphane **4c** (two independent molecules)[a]



[a] Ge1–P1 2.3100(14), Ge2–P1 2.302(2), Ge3–P2 2.306(2), Ge4–P2 2.298(2), Ge–Cl 2.122(2)–2.135(2) Å; Ge1–P1–Ge2 97.23(5), Ge3–P2–Ge4 97.19(6)°.

procedures. – NMR: Bruker AC 200 (^{1}H: 200.1 MHz; ^{13}C: 50.3 MHz; ^{31}P: 81.0 MHz); solvent [D$_6$]benzene; room temp.; reference substances were $SiMe_4$ (TMS) ext. (^{1}H, ^{13}C) and 85% H_3PO_4 ext. (^{31}P). – MS: Finnigan MAT 8430. – Elemental analyses: Mikroanalytisches Laboratorium Beller, Göttingen, and Analytisches Laboratorium des Institutes für Anorganische und Analytische Chemie der Technischen Universität, Braunschweig.

1:1 Reaction of **1a** *with $GeCl_2$–Dioxane:* A mixture of 3.2 g ($13.8 \cdot 10^{-3}$ mol) of **1a** and 2.2 g ($13.8 \cdot 10^{-3}$ mol) of $GeCl_2$–dioxane in 40 ml of toluene is stirred 1 d at room temp.; subsequent evaporation of the solvent provides a mixture of about 45% **1a**, 45% **4a**, and 10% **5a** (by ^{31}P NMR, for all shifts and coupling constants see Table 2). Keeping the reaction mixture for several days at room temp. or heating the mixture to 80°C leads to increasing amounts of diphosphanes **6a** and **7a**. After attempted distillation (140°C, 0.5 mbar), recrystallisation of the residue provides mixutures of **8a** (ABX-type ^{31}P-NMR pattern) and $(t\mathrm{BuP})_4$ ($\delta^{31}\mathrm{P} = -57$), and a few crystals of 4-trichlorogermyl-1, 2,3-tri-*tert*-butyltetraphosphetane **9a** (AM_2X-type ^{31}P-NMR pattern). **9a**: $C_{12}H_{27}Cl_3GeP_4$ (474.19); MS (70 eV): *m/z* (%) 474 (6) [M$^+$, correct isotopic pattern], 417 (2) [$M^+ - C_4H_9$], 361 (2) [$M^+ - C_4H_9$, $- C_4H_8$], 352 (16) [$(t\mathrm{BuP})_4^+$], 325 (4) [$M^+ - 2\ C_4H_9$, $-$Cl], 295 (16) [$(t\mathrm{BuP})_3\mathrm{P}^+$], 239 (50) [$(t\mathrm{BuP})_2\mathrm{P_2H}^+$], 183 (38) [$(t\mathrm{BuP})\mathrm{P_3H_2}]^+$, 57 (100) [$C_4H_9^+$].

1:2 Reaction of **1a** *with $GeCl_2$–Dioxane:* A mixture of 0.64 g ($4.0 \cdot 10^{-3}$ mol) of **1a** and 1.87 g ($8.1 \cdot 10^{-3}$ mol) of $GeCl_2$–dioxane in 30 ml of toluene is stirred 4 d at room temp., subsequent evaporation of the solvent provides a yellow oil. Extraction of the oil with hexane furnishes a mixture of products that contains about 80% **4a** accompanied by **1a** and **5a**.

1:1 Reaction of 1,2-Dichloro-1,2-di-tert-butyldiphosphane with $GeCl_2$–Dioxane: At about −80°C to a solution of 1.9 g ($7.7 \cdot 10^{-3}$ mol) of 1,2-dichloro-1,2-di-*tert*-butyldiphosphane in 40 ml of toluene are added 2.67 g ($7.7 \cdot 10^{-3}$ mol) of $GeCl_2$–dioxane. The mixture is allowed to warm up and is stirred until nearly complete consumption of the diphosphane. Subsequent evaporation of the solvent and extraction of the residue with petroleum ether ether (b.p. 40–60°C) provides a liquid that contains about 60% **7a**; the ratio of the pairs of enantiomers is 10:1 [by ^{31}P NMR, predominant species with P_A $\delta = +118.8$, P_B $\delta = +41.2$, *J*(PP) 310 Hz]. The liquid also contains **1a**, **4a**, 1,1-dichloro-2,3,4-tri-*tert*-butyl-2,3,4-triphosphadigermetane [$\delta^{31}\mathrm{P} = +89.1$ (d), −32.5 (t); $^{1,3}J$(PP) = ±181 Hz][7] and $(t\mathrm{BuP})_4$.

1:1 Reaction of **1b** *with $GeCl_2$–Dioxane:* A stirred mixture of 0.5 g ($3.5 \cdot 10^{-3}$ mol) of **1b** and 0.8 g ($3.5 \cdot 10^{-3}$ mol) of $GeCl_2$–dioxane in 10 ml of toluene is prepared at low temp. (about −80°C), allowed to warm up and kept 2 h at room temp., when it contains **1b** and **4b** in a 1:1 ratio (^{31}P NMR). After further stirring for 15 h (or longer), increasing ^{31}P-NMR signals of **5b**, **6b**, and **7b** can also be detected (Table 2). Subsequent evaporation of the solvent and extraction of the oily residue with pentane provides a mixture of about 80% **10b**, 10% **5b**, and 10% $(i\mathrm{PrP})_4$ (by ^{31}P NMR). MS (70 eV): *m/z* (%) 440 (20) [M$^+$ of **10b** = $(i\mathrm{PrP})_4\mathrm{GeCl}_2^+$, $C_{12}H_{28}Cl_2GeP_4$, correct isotopic pattern], 405 (<5) [$M^+ - Cl$], 397 (15) [$M^+ - C_3H_7$], 355 (<5) [$M^+ - C_3H_7$, $- C_3H_6$], 296 (30) [$(i\mathrm{PrP})_4^+$], 253 (100) [$(i\mathrm{PrP})_3\mathrm{P}^+$], 211 (55) [$(i\mathrm{PrP})_2\mathrm{P_2H}^+$], 169 (exceeding 100) [$(i\mathrm{PrP})\mathrm{P_3H_2^+}$].

1:2 Reaction of **1b** *with $GeCl_2$–Dioxane:* A stirred mixture of 1.3 g ($9 \cdot 10^{-3}$ mol) of **1b** and 4.15 g ($18 \cdot 10^{-3}$ mol) of $GeCl_2$–dioxane in 40 ml of toluene is prepared at −78°C, allowed to warm up, kept 24 h at room temp. and concentrated to dryness under vacuum. Extraction of the residue with pentane furnishes a mixture of about 50% **10b**, 40% **8b**, 5% **4b**, and 5% **5b** (^{31}P NMR). – MS (70eV): *m/z* (%) 510(2) [M$^+$ of **8b**, $C_9H_{21}Cl_4Ge_2P_3$, correct isotopic pattern], 468(1) [**8b**$^+$ $- C_3H_6$], 440 (20) [M$^+$ of **10b** = $(i\mathrm{PrP})_4\mathrm{GeCl}_2^+$, correct isotopic pattern].

Reaction of iPrPH$_2$ with GeCl$_4$: To 1.0 g ($13.1 \cdot 10^{-3}$ mol) of $i\mathrm{PrPH_2}$ in 20 ml of toluene an approximately threefold excess of $GeCl_4$ is condensed at −78°C. Immediately a white precipitate forms, which is separated by filtration and washed with *n*-hexane. Recrystallisation of the solid from about 80 ml of toluene (heating to 80°C and slow cooling) provides 0.7 g (21%) of crystalline **11** melting at 90°C. – ^{31}P NMR (CH_3CN) $\delta = -38$ [q, ^{1}J(PH) = 450 Hz]; (THF) $\delta = -94$ [very broad]. – $C_3H_{10}PGeCl_3$ (256.04): calcd. C 14.07, H 3.94; found C 14.91, H 3.98. – Compound **5b** (in the reaction solution): ^{1}H NMR: $\delta = 3.3$ [d,d, ^{1}J(P,H) = ±190 Hz, ^3J(H,H) = ±4.4 Hz, $H\mathrm{PCH(CH_3)_2}$], 1.8 [m, only sept from ^3J(H,H) = 6.9 Hz was fairly resolved, $\mathrm{(H_3C)_2C}H\mathrm{PH}$], 1.08 [d,d, ^3J(H,H) = 6.9 Hz, ^3J(H,P) = 15.5 Hz $(H_3\mathrm{C})_2\mathrm{CHPH}$]. – ^{31}P NMR $\delta = -56.5$, ^{1}J(PH) 190 Hz. MS (70 eV); *m/z* (%) 254 (0.7) [M$^+$ = $i\mathrm{PrP(H)GeCl_3^+}$, $C_3H_8PGeCl_3$], 219 (0.5) [$M^+ - Cl$], 214 (2) [$GeCl_4$], 179 (20) $[GeCl_3^+]$, 144 (34) $[GeCl_2^+]$, 109 (35) $[GeCl^+]$, 76 (75) $[iPrPH_2^+]$, 44 (100) $[C_3H_8^+]$.

1-Adamantylbis(trichlorogermyl)phosphane (**4c**): A stirred mixture of 0.76 g ($3.2 \cdot 10^{-3}$ mol) of **1c** and 1.5 g ($6.4 \cdot 10^{-3}$ mol) of $GeCl_2$–dioxane in 20 ml of toluene is prepared at −78 °C, allowed to warm up and kept 22 h at room temp. When nearly complete consumption of the starting material **1c** is confirmed by ^{31}P NMR, the remaining solid is filtered off, and the solution is concentrated to dryness under vacuum. Extraction of the residue with hexane and crystallisation at −20°C furnishes about 300−400 mg of **4c** (about 30%), colourless crystals m.p. 75°C (dec.). A few further cystals of **4c** were isolated from the concentrated mother liquor. − ^{31}P NMR: $\delta = +23$ (s). − EI-MS (70 eV, 25−400°C) *m/z* (%) 782 (1) $[C_{30}H_{41}P_3Ge_2Cl_4^+]$, 664 (1) $[(C_{10}H_{15}P)_4^+]$, 638 (1) $[(C_{10}H_{15})_3P_4GeCl^+]$, 636 (1) $[C_{30}H_{43}P_4GeCl^+]$, 578 (2) $[C_{20}H_{27}P_3Ge_2Cl_2^+]$, 498 (4) $[(C_{10}H_{15}P)_3^+]$, 363 (6) $[(C_{10}H_{15})_2P_3^+]$, 233 (6), 179 (6) $[GeCl_3^+]$, 135 (100) $[C_{10}H_{15}{}^+]$. − $C_{10}H_{15}Cl_6Ge_2P$ (524.10): calcd. C. 22.92, H 2.88, found. C 23.93%; H 3.00%.

In solution: 1-Adamantyl(trichlorogermyl)phosphane **5c** ($C_{10}H_{16}Cl_3GeP$, 346.16): ^{31}P NMR: $\delta = -25.5$ (d, $^1J(PH) = \pm 196$ Hz). − 1,2-Di(1-adamantyl)-1-trichlorgermyldiphosphane **6c** ($C_{20}H_{31}Cl_3GeP_2$, 512.36): ^{31}P NMR: $\delta = -5.8$ (d), −64.9 (d), $^1J(PP) = \pm$ 208 Hz.

Structure Determinations

4c: Crystal data: $C_{10}H_{15}Cl_6PGe_2$, $M = 524.07$, $P2_1/c$, $a = 21.581(3)$, $b = 9.382(2)$, $c = 17.834(3)$ Å, $\beta = 95.46(2)°$, $V = 3594.6(11)$ Å^3, $Z = 8$, $d_{calc} = 1.937$ Mg/m^3, $\mu = 4.309$ mm^{-1}, $T = 143$ K. A colourless plate (0.6 × 0.6 × 0.2 mm) was mounted in inert oil. 7432 intensities were measured (2Θ 6−50°) using Mo-K_α radiation on a STOE Stadi-4 diffractometer. After absorption correction (ψ-scans) 6323 were unique ($R_{int} = 0.0361$) and 6302 used for all calculations (program SHELXL-93). The structure was solved by direct methods and refined anisotropically on F^2. The final $wR(F^2)$ was 0.1008 with conventional $R(F)$ 0.0411 for 343 parameters.

9a: Crystal data: $C_{12}H_{27}Cl_3P_4Ge$, $M = 474.16$, $P2_1/c$, $a = 9.847(3)$, $b = 22.958(9)$, $c = 10.198(3)$ Å, $\beta = 110.74(3)°$, $V = 2156.0(12)$ Å^3, $Z = 4$, $d_{calc} = 1.461$ Mg/m^3, $\mu = 2.080$ mm^{-1}, $T = 143$ K. A colourless prism (0.4 × 0.4 × 0.3 mm) was mounted in inert oil. 7143 intensities were measured ($2\Theta = 6-55°$) of which after absorption correction 4946 were unique ($R_{int} = 0.0305$) and 4936 used for all calculations (see above). The final $wR(F^2)$ was 0.0879 with conventional $R(F)$ 0.0353 for 190 parameters.

11: Crystal data: $C_3H_{10}Cl_3PGe$, $M = 256.02$, $P2_1/c$, $a = 11.506(5)$, $b = 7.068(5)$, $c = 12.338(4)$ Å, $\beta = 106.74(4)°$, $V = 960.9(3)$ Å^3, $Z = 4$, $d_{calc} = 1.77$ Mg/m^3, $\mu = 4.107$ mm^{-1}, $T = 143$ K. A colourless plate (0.7 × 0.6 × 0.1 mm) was mounted in inert oil. 1962 intensities were measured ($2\Theta = 6-50°$) of which after absorption correction 1660 were unique ($R_{int} = 0.0466$) and used for all calculations (see above). The final $wR(F^2)$ was 0.1591 with conventional $R(F)$ 0.0625 for 87 parameters and 15 restraints.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100246. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB 2 1EZ, UK [fax: int. code +44(1223)336-033; E-mail: deposit@chemcrys.cam.ac.uk].

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