Reversible Rearrangements of Chlorophosphane-Dichlorogermylene Ylides to Trichlorogermylphosphanes – Structure Determination of a Tetranuclear Bis(chlorophosphane)bis(trichlorogermylphosphane) Silver Bromide Complex

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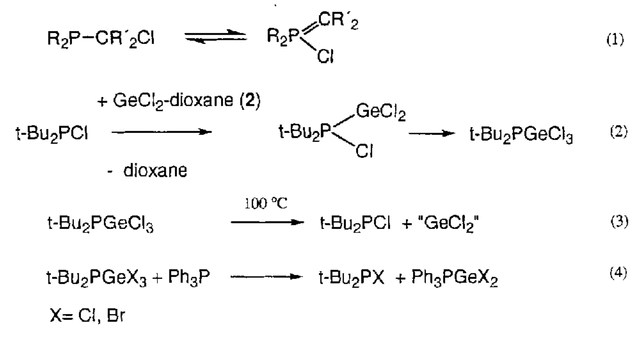
Chlorophosphanes RR'PCl (**1a**: R,R' = *i*Pr; **1b**: R = *t*Bu, R'= *i*Pr, **1c**: R = *i*Pr, R' = Et_2N, **1d**: R = *t*Bu, R' = Et_2N) react with the dichlorogermylene dioxane complex **2** furnishing trichlorogermylphosphanes $RR'PGeCl_3$ **4a–d**. In the cases of **1c**/**4c** and **1d**/**4d** the insertion reactions remain incomplete; similarly, **4a** always contains, shortly after isolation in pure state, small amounts of **1a** that can be detected by NMR. A product with the analytical composition of isomers **3d**/**4d** is provided by the reaction of trichlorosilylphosphane $tBu(Et_2N)PSiCl_3$ (**5d**) with $GeCl_4$. The alkyl(dialkylamino)trichlorogermylphosphane **4d** exists only in an equilibrium with chlorophosphane **1d**, which coordinates $GeCl_2$ leading to the dichlorogermylene complex **3d**. A 1:1 mixture of **4a** with **1a** is formed by the novel cleavage ("chlorogermylation") of the P–P bond of tetraisopropyldiphosphane with germanium tetrachloride. Di-*tert*-butyl(trichlorogermyl)phosphane **4e** (R, R' = *t*Bu) reacts with silver bromide providing a crystalline silver complex **7**. A structure determination by X-ray diffraction reveals that **7** is $[Ag_4Br_4(tBu_2PCl)_2(tBu_2PGeCl_3)_2] \cdot 2\ C_7H_8$. Two of the Ag atoms of the cubane-like $(AgBr)_4$ core of **7** are coordinated by chlorophosphane **1e**, the other two by trichlorogermylphosphane **4e**.

Introduction

Depending on their substitution pattern, P-chloro ylides $R_2(Cl)P{=}CR'_2X$ tend to rearrange by P → C chlorine shifts into the isomeric chloroalkylphosphanes $R_2PCR'_2Cl$.[1][2]



$$R_2P{-}CR'_2Cl \rightleftharpoons R_2P(Cl){=}CR'_2 \quad (1)$$

$$t\text{-}Bu_2PCl \xrightarrow[-\ \text{dioxane}]{+\ GeCl_2\text{-dioxane}\ (2)} t\text{-}Bu_2P(Cl){\rightarrow}GeCl_2 \longrightarrow t\text{-}Bu_2PGeCl_3 \quad (2)$$

$$t\text{-}Bu_2PGeCl_3 \xrightarrow{100\,^{\circ}C} t\text{-}Bu_2PCl + \text{"}GeCl_2\text{"} \quad (3)$$

$$t\text{-}Bu_2PGeX_3 + Ph_3P \longrightarrow t\text{-}Bu_2PX + Ph_3PGeX_2 \quad (4)$$

$$X = Cl,\ Br$$

Such rearrangements have not yet been observed with chloro*silyl*phosphanes $R_2PSiR'_2Cl$, but an isomer of a trichloro*germyl*phosphane, the ylide-type chlorophosphane dichlorogermylene complex $tBu_2(Cl)P \rightarrow GeCl_2$, has been characterised in solution by NMR.[3] This ylide-type dichlorogermylene complex, formed from the dichlorogermylene dioxane complex and di-*tert*-butylchlorophosphane, rearranges by insertion of dichlorogermylene into the P–Cl bond, providing di-*tert*-butyl(trichlorogermyl)phosphane[3][4]. Thermal decomposition of this trichlorogermylphosphane tBu_2PGeCl_3 furnished volatile di-*tert*-butylchlorophosphane tBu_2PCl, i.e., dichlorogermylene was lost by α-elimination at germanium.[4] Di-*tert*-butyl(trichloro- and -tribromogermyl)phosphane are sources of dichlorogermylene and dibromogermylene towards better ligands.[3][4] With triphenylphosphane, α-eliminations lead to ylide-type tertiary phosphane germanium dihalide complexes Ph_3PGeX_2[3][4][5][6][7] by elimination of tBu_2PX (= Cl, Br).

There is still a complete lack of information concerning insertion / elimination equilibria of other dialkyl- and alkyl(dialkylamino)chlorophosphanes toward dichlorogermylene.[8] To study basic effects of substituents on chlorophosphane-dichlorogermylene reactions, we chose chlorodiisopropylphosphane **1a**, *tert*-butyl(isopropyl)chlorophosphane **1b**, isopropyl(diethylamino)chlorophosphane **1c**, and *tert*-butyl(diethylamino)chlorophosphane **1d** as starting materials for dichlorogermylene insertion reactions that were to be compared with the known reaction of di-*tert*-butylchlorophosphane (**1e**)[3] with the dichlorogermylene dioxane complex **2**.

Reactions of Chlorophosphanes 1a–1d with the Dichlorogermylene Dioxane Complex 2

After mixing a toluene solution of chlorodiisopropylphosphane (**1a**) with solid **2**, the course of the reaction was followed by ^{31}P NMR. NMR signals of an ylide-type coordination compound **3a** could not be observed, but ^{1}H and ^{31}P resonances of a new trichlorogermyl phosphane **4a** were soon detected. Within 20 hours the chlorophosphane **1a** was almost completely consumed in favour of **4a**. At-

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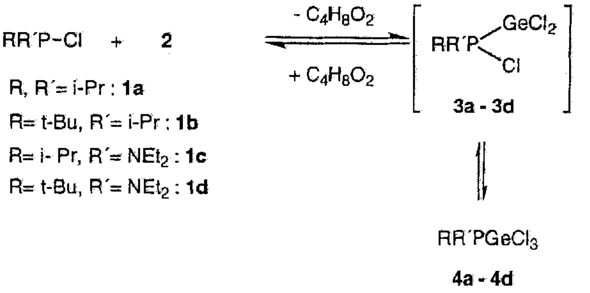
tempted distillation of **4a** provided **1a** and a deep red residue, but work up by removal of all volatiles at room temp. and extraction of the residue with petroleum ether provided a slightly yellowish liquid that contained about 90% **4a** besides **1a** and traces of a hydrolysis product. The liquid gave analytical data that were nearly consistent with **4a**; the molecular ion of **4a** was detected by EI-MS.



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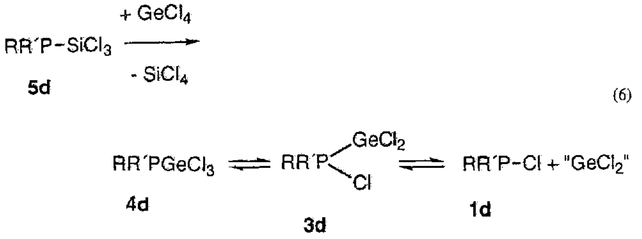

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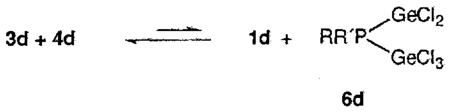

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The reaction of chlorophosphane **1b** with **2** proceeded more slowly than that of **1a**. In course of the reaction, ^{31}P-NMR spectra exhibited the signals of increasing amounts of the new trichlorgermyl phosphane **4b** (d^{31}P = 78.4), and of a transient species (δ^{31}P = 132), assigned to the P-chloro ylide **3b** in a (rapid) equilibrium with unconsumed **1b** (δ^{31}P = 140). Within 5 d, formation of **4b** is almost complete. Work up provided **4b** as a colourless liquid that gave consistent analytical data.

Compared with dialkylchlorophosphanes **1a**, **1b**, the reactions of alkyl(diethylamino)chlorophosphanes **1c**, **1d** with **2** furnished the related insertion products **4c**, **4d** to a much lesser extent. Even after long reaction times, the mixtures still contain large amounts of the chlorophosphanes **1c**, **1d** besides unconsumed **2**. Isolation of pure **4c** and **4d** could not be achieved. The incompleteness of the $GeCl_2$ insertion into **1c**, **1d** is presumably due to the presence of dioxane, whose coordination to $GeCl_2$ competes with the desired insertion reactions. Therefore we sought an access to diethylamino(trichlorogermyl)phosphanes that avoids the presence of dioxane. We chose the cleavage of silylphosphanes with germanium tetrachloride as an alternative route to trichlorogermylphosphanes[9].

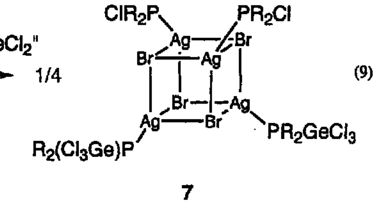
tert-Butyl(diethylamino)(trichlorosilyl)phosphane (**5d**) has recently been prepared from **1d** with $HSiCl_3/NEt_3$[10]. As intended, **5d** is easily cleaved with $GeCl_4$; however, besides $SiCl_4$ two P-containing products are formed by this reaction: the ^{31}P-NMR signal of the one product (δ = 142.7) appears close to the one of **4d** (δ = 141.8 in the mixture from the above mentioned $GeCl_2$ insertion), the other signal was observed between δ = 148 and 152, dependent on the relative amounts of the starting materials. In one sample, the latter signal appeared initially at δ = 140.1; on storing this signal shifted steadily downfield leading to a broad resonance at δ = 149. These resonances are to be assigned to a kinetically labile adduct **3d** of **1d** with $GeCl_2$ in equilibrium with "free" **1d**. Addition of pure **1d** to such a sample does not lead to a separate NMR signal, but now the (averaged) resonance appears very close to the one of "free" **1d** (δ = 158.7).[11] After the removal of all volatiles, the remaining yellowish oil gave reasonably consistent analytical data (for **3d**/**4d**). The mixture decomposes slowly with further loss of $GeCl_2$. It is obvious that trichlorogermylphosphane **4d** intrinsically suffers from loss of $GeCl_2$ by α-elimination. $GeCl_2$ can coordinate to **1d** to give a labile ylide-type adduct **3d**. It is known, that di-*tert*-butyl(trichlorogermylphosphane) (**4e**) coordinates to dichlorogermylene[12]; this coordination leads to upfield shifts of **4e** (i.e. the averaged signal of **4e**/**6e**) in ^{31}P NMR. Similarly, trichlorogermylphosphane **4d** is expected to compete with chlorophosphane **1d** for coordination to dichlorogermylene. Participation in such coordination equlilibria could explain slight variations of the NMR parameters of **4d** (i.e. the averaged signal of **4d**/**6d**) in the reaction mixtures (Eq. 7). **6e** is known to serve as $GeCl_2$ source towards dioxane, whereas **2** acts as $GeCl_2$ source towards **1e**, i.e. towards $GeCl_2$ trichlorogermylphosphane **4e** is a weaker ligand than chlorophosphane **1e**. Similarly, **4d** is a weaker nucleophile than **1d** towards $GeCl_2$.

Compared with alkyl groups, the diethylamino group in **1c** and **1d** apparently does not favour dichlorogermylene insertion. Within the insertion/elimination equilibria (Eq. 5) the diethylamino group favours the relative stability of the P–Cl bond in **1d**/**3d** more than the P–Ge functions in **4d**/**6d**, i.e. chlorophosphane stabilisation might be a source of the (relative) destabilisation of trichlorogermylphosphanes **4c**, **4d**. However, participation of N → Ge coordination[13] from **1c**, **1d** to $GeCl_2$ cannot be excluded at present. Another as yet unexplained observation is the coexistence of chlorophosphanes **1** and trichlorogermylphosphanes **4** in the above mixtures, i.e. the lack of diphosphane formation by elimination of germanium tetrachloride. Trichlorosilylphosphane **5a** or trimethylsilylphosphanes can react with chlorophosphanes providing diphosphanes by elimination of chlorosilanes[14]. To elucidate whether the reaction of **1a** with **4a** is simply kinetically hindered, or if the position of the equilibrium is opposite to the silylphosphane/chlorophosphane case, we reacted tetraisopropyldiphosphane with germanium tetrachloride. The reaction proceeds instantaneously providing a 1:1 mixture of **1a** and **4a**. This novel P–P cleavage reaction is a route to P–Ge bonds meriting further interest.

$$i\text{-}Pr_4P_2 + GeCl_4 \longrightarrow \mathbf{4a} + \mathbf{1a} \quad (8)$$

$$RR'P\text{-}GeCl_3 + AgBr \xrightarrow{-\,^1/_2\,\text{"}GeCl_2\text{"}} 1/4 \quad (9)$$

R, R′ = t-Bu : **4e**



7

Within the elimination/insertion equilibria of P−Cl and P−$GeCl_3$ species, coordination of **1** and **4** with $GeCl_2$ plays an important role for the course of the $GeCl_2$ transfer and possibly also for the position of the equilibria (such as **1d/3d/4d/6d**). Coordination compounds of trichlorogermylphosphanes with Lewis acids have not yet been isolated in pure state[12] nor is the role of coordination for the position of α-elimination/insertion equlibria well understood. For that reason, we intended to prepare a first well-characterised trichlorogermylphosphane metal complex. As a stable ligand we chose **4e**.[9] The related trichlorosilylphosphane **5e** and the related tri*methyl*germylphosphane are known to give inert 1:1 complexes with AgBr that exhibit $^1J(^{107,109}Ag,^{31}P)$ in solution at room temperature[14][15].

The 1:1 reaction of **4e** with AgBr shows, however, that **4e**, in contrast to **5e** and the related tri*methyl*germylphosphane, does not give straightforwardly a 1:1 coordination compound with AgBr. ^{31}P-NMR spectra of the reaction mixture from **4e** and AgBr in toluene showed several broad signals. The strongest of these signals at $\delta = +140$ (close to the signal of uncoordinated **1e**) is very broad at room temperature. At −50°C, broadened doublet signals at $\delta = +140$ and $+35$ [^1J(AgP) in the order of 400 Hz] could be resolved. It appears that coordination with AgBr favours the (incomplete) loss of $GeCl_2$ from **4e**. After separation of the solution from the solid residue and removal of a part of the solvent under reduced pressure, the solution was stored at −60°C. This led (after some weeks) to crystallisation of a novel tetrameric silver bromide complex **7**, which contains two molecules of solvating toluene. The colourless crystals were suitable for an X-ray crystal structure determination. Solid **7** contains two molecules of **1e** and two molecules of **4e** coordinated to a cubane-like Ag_4Br_4 core; the complex displays crystallographic twofolds symmetry[16]. Analytical data were resonably consistent with toluene-solvated **7**. Attempts to dissolve **7** led to decomposition; the toluene solution above a precipitate containing AgBr showed a very broad ^{31}P-NMR signal at $\delta = +140$. In a further experiment, the 1:1 complex **8** of chlorophosphane **1e** with AgBr was prepared. **8** was isolated as coulorless solid. The broad (room temp.) ^{31}P-NMR signal of complex **8** in dichloromethane appears in the same region as that of **7**.

The presence of coordinated **1e** and **4e** as ligands in complex **7** allows comparison of ligand properties of the two different phosphanes within the structure of one compound. The two Ag−P distances are very similar [Ag(1)−P(1) (from **1e**) 2.411(3) Å; Ag(2)−P(2) (from **4e**) 2.408(3)]. Average P−C distances and C−P−C angles within coordinated **4e** are slightly larger than those of coordinated **1e**. From the structure of **7** no conclusions can be drawn concerning any "instability" of **4e** with respect to loss of $GeCl_2$ by α-elimination: Ge−P and Ge−Cl bonds are not obviously of reduced strength, and the Ge−P distance of 2.28 Å in **7** is in fact the shortest yet found for a Ge−P single bond (typical Ge−P distances are 2.30−2.35 Å[17][18]); Ge−Cl distances (2.138−2.147 Å) are similar to those of common trichlorogermanium(IV) compounds[18][19].

Figure 1. Compound **7** with symmetry equivalent (crystal solvent and one ligand, **1e**, are ommitted for clearity). Bond lengths and angles: see Table 1

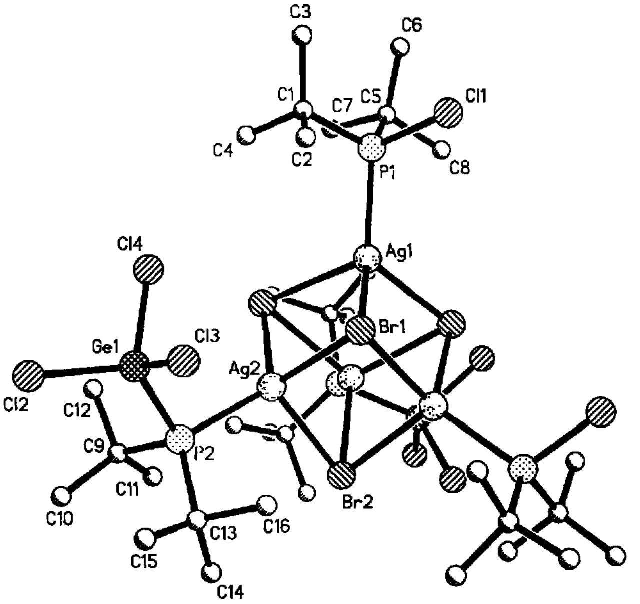


Table 1

Coordinated 1e		Coordinated 4e	
Ag(1)-P(1)	2.411(3)	Ag(2)-P(2)	2.408(3)
P(1)-Cl(1)	2.070(4)	P(2)-Ge(1)	2.282(3)
P(1)-C(1)	1.880(11)	P(2)-C(9)	1.866(12)
P(1)-C(5)	1.844(12)	P(2)-C(13)	1.960(9)
C(5)-P(1)-C(1)	114.1(5)	C(9)-P(2)-C(13)	111.6(5)
C(5)-P(1)-Cl(1)	101.1(4)	C(9)-P(2)-Ge(1)	105.3(4)
C(1)-P(1)-Cl(1)	101.9(4)	C(13)-P(2)-Ge(1)	104.3(3)
C(1)-P(1)-Ag(1)	113.4(4)	C(9)-P(2)-Ag(2)	113.6(3)
Cl(1)-P(1)-Ag(1)	112.5(2)	Ge(1)-P(2)-Ag(2)	105.41(12)
Br(1)-Ag(1)-Br(2)#2	97.86(4)	Br(1)-Ag(2)-Br(2)#2	101.51(4)
Br(1)-Ag(1)-Br(1)#1	98.87(4)	Br(1)-Ag(2)-Br(2)	101.61(4)
Br(1)#1-Ag(1)-Br(2)#1	100.34(4)	Br(2)#1-Ag(2)-Br(2)	101.37

NMR Spectra of Trichlorogermylphosphanes 4 and of Chlorophosphane−Dichlorogermylene Complexes 3

In Table 1, ^{31}P-NMR data of the new trichlorogermylphosphanes **4** and their ylide-type isomers **3** are compared with those of chlorophosphanes **1** and trichlorosilylphosphanes **5**. The ^{31}P-NMR signals of trimethylgermylphosphanes generally appear downfield from the related trimethylsilylphosphanes[20]. This finding has been correlated with the electronegativity of germanium, which is larger than that of silicon. Similarly, ^{31}P-NMR resonances of tri*chloro*germylphosphane **4a**–**e** appear about 70(±5) ppm downfield from those of trichlorosilylphosphanes **5a**–**e**[9][14][21]. In the case of di*alkyl*phosphorus derivatives, resonances of germanium derivatives **4a**, **b**, **e** appear instead *between* those of chlorophosphanes and trichlorosilylphosphanes (for instance **4a:** 68 ppm upfield from **5a**, 83 ppm downfield from **1a**). The resonances of alkyl(diethylamino)-(trichlorogermyl)phosphanes **4c**, **d**, however, appear close to those of chlorophosphanes **1a**, **b** [**4d** (in presence of **1d**) 68 ppm upfield from **5d**, only 20 ppm from (pure) **1d**]. In the presence **4c**, **d**, the resonances of chlorophosphanes **1c**, **d** appear always upfield from those of pure **1c**, **d**: these shifts indicate coordination of chlorophosphanes **1** with dichlorogermylene leading to ylides **3** in equilibrium mixtures (Eq. 7). As shown from steadiliy varying ^{1}H-, ^{13}C-, and ^{31}P-NMR parameters of **1/3** and **4/6**, $GeCl_2$ transfer reactions between "ligands" **1** and **4** are rapid on the NMR time scale (Table 2). Because chlorophosphanes are the better nucleophiles towards $GeCl_2$, we expect the observed NMR data of **4c**, **d** in mixtures to be close to those of "pure species" **1c**, **d**. α-Elimination/insertion reactions at germanium, however, are apparently slow processes. Diastereotopic splitting of ^{1}H- and ^{13}C resonances of CH_3 groups of the isopropyl substituent of **4a** and **4b** indicates that inversion at phosphorus as well as intermolecular exchange processes of these trichlorogermylphosphanes are also slow processes at room temperature.

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Experimental Section

General: ^{1}H, ^{13}C, and ^{31}P NMR: Bruker AC-200 spectrometer (^{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: Finigan Mat 8430. – IR: FT-IR Biorad 165. – Elemental analyses: Mikroanalytisches Laboratorium Beller, Göttingen, and Analytisches Laboratorium des Instituts für Anorganische und Analytische Chemie der Technischen Universität Braunschweig. – All experiments were carried out under deoxygenated dry nitrogen as inert gas, solvents were dried according to standard procedures.

Diisopropyl(trichlorogermyl)phosphane (**4a**): A mixture of 0.83 g ($5.44 \cdot 10^{-3}$ mol) of **1a** and 1.3 g ($5.7 \cdot 10^{-3}$ mol) of $GeCl_2$–dioxane (**2**) in 30 ml of toluene is stirred 1 d at room temp., subsequent evaporation of the solvent, extraction of the residue with petroleum ether, filtration, and removal of the extractant provides 1.6 g of nearly colourless oil. This product consists of about 90% of **4a** (89% yield), small amouts of **1a** and traces of a hydrolysis product (by ^{31}P NMR). Attempted distillation of the oil led to volatile **1a** and a non-volatile red residue. – ^{1}H NMR(200 MHz, C_6D_6): δ = 0.93 [d,d, ^{3}J(H,H) = 7.14 Hz, ^{3}J(P,H) = 15.1 Hz, 6 H, CH_3], 1.07 [d,d, ^{3}J(H,H) = 7.03 Hz, ^{3}J(P,H) = 13.3 Hz, 6 H, CH_3], 2.09 (sept., line distances 7.1 Hz, 2 H, C*H*). – ^{13}C NMR (75.47 MHz, C_6D_6): δ = 20.8 [d, ^{2}J(P,C) = 15.4 Hz, *C*H_3], 21.8 [d, ^{2}J(P,C) = 10.8 Hz, *C*H_3], 24.3 [d, ^{1}J(P,C) = 24.6 Hz, *C*H-P]. – ^{31}P NMR (81.02 MHz, C_6D_6) δ = 49. – MS(EI, 70 eV) *m/z*(%) = 296 (0.4) [M^+], 254(0.4) [$M^+ - C_3H_6$], 214(1.3) [$GeCl_4^+$], 179 (8) [$GeCl_3^+$], 152(16) [*i*Pr_2PCl^+, 118(20) [*i*Pr_2PH^+], 110 (20) [*i*$PrPHCl^+$], 43 (100) [$C_3H_7^+$]. – $C_6H_{14}Cl_3GeP$ (296.1): C 25.52 (calc. 24.34), H 5.47 (calc. 4.7).

tert-Butyl(isopropyl)(trichlorogermyl)phosphane **4b**: Similar to the preparation and work up of **4a**, a mixture of 0.92 g ($5.5 \cdot 10^{-3}$ mol) of **1b** and 1.35 g ($5.8 \cdot 10^{-3}$ mol) of **2** in 20 ml of toluene led within 5 d at room temp. to 1.3 g (76%) of **4b**, as colourless liquid. – ^{1}H NMR(200 MHz, C_6D_6): δ = 1.08 [d,d, ^{3}J(H,H) = 7.2 Hz, ^{3}J(P,H) = 18.8 Hz, 3 H, (CH_3)$_2$CH], 1.09 [d, ^{3}J(P,H) = 13.2 Hz, 9 H, (CH_3)$_3$C], 1.29 [d,d, ^{3}J(H,H) = 7.0 Hz, ^{3}J(P,H) = 9.3 Hz, (CH_3)$_2$CH), 1.98 (sept., line distances 7.1 Hz, 1 H, C*H*). – ^{13}C NMR (50 MHz, C_6D_6): δ = 23.5–23.8 [4 signals, two diastereotopic CH_3 groups of (*C*H_3)$_2$CHP], 25.2 [d, ^{1}J(P,C) 30.0 Hz, (CH_3)$_2$*C*HP], 30.6 [d, ^{2}J(P,C) 13.4 Hz, (*C*H_3)$_3$CP], 34.6 [d, ^{1}J(P,C) = 28.9 Hz, (CH_3)$_3$*C*P]. – ^{31}P NMR (81.02 MHz, C_6D_6) δ = 78.4. – $C_7H_{16}Cl_3GeP$ (310.13): C 27.93 (calc. 27.11), H 5.21 (calc. 5.20).

Reaction of **1c** *with* **2**: A mixture of 0.45 g ($2.5 \cdot 10^{-3}$ mol) of **1c** and 0.59 g ($2.6 \cdot 10^{-3}$ mol) of **2** in 10 ml of toluene is stirred for 3 d at room temp.; at this stage the incomplete insertion reaction does not proceed further. Subsequent removal of unconsumed **2** and evaporation of the solvent provides a nearly colourless liquid containing **1c** and **4c**.

1c (ref.[22], signals overlapped by those of **4c**): ^{1}H NMR: δ = 0.64–0.92 [several lines, (CH_3)$_2$CHP], 0.8 [t, ^{3}J(H,H) 7.1 Hz, CH_3CH$_2$N], 1.01–1.14 [several lines, (CH_3)$_2$C*H*P], 2.74 [m, (CH_3CH_2)$_2$N]. – ^{13}C NMR: δ = 14.0 [d, ^{3}J(P,C) 5.7 Hz, *C*H$_3$CH$_2$NP], 17.4, 17.5, 17.9, 18.0 [2 d of (*C*H_3)$_2$CHP]; 33.1 [d, ^{1}J(P,C) = 23.9 Hz,CH_3*C*HP]; 43.6 [d, ^{2}J(P,C) 11.5 Hz, CH_3*C*H$_2$NP]. – ^{31}P NMR: δ = 156.7 (ref.[22]: δ = 158.9).

4c (signals overlapped by those of **1c**): ^{1}H NMR: δ = 0.64–0.92 [several lines, (CH_3)$_2$CHP], 0.71 [t, ^{3}J(H,H) 7.1 Hz, CH_3CH$_2$N], 1.01–1.14 [several lines, (CH_3)$_2$C*H*P], 2.74 [m, (CH_3CH_2)$_2$N]. ^{13}C NMR: δ = 14.4 (*C*H$_3$CH$_2$NP), 15.2, 15.3, 15.7, 16.1, 16.6 [5 lines resolved from two diastereotopic CH_3 groups of (*C*H_3)$_2$CHP]; 26.3 [d, ^{1}J(P,C) = 14.5 Hz,CH_3*C*HP]; 40.7 [d, ^{2}J(P,C) 12.9 Hz, CH_3*C*H$_2$NP]. – ^{31}P NMR: δ = 121.7 . – MS (EI, 70 eV), *m/z* (%) = 181 (30) [M^+ of **1c**]; 179 (6) [$GeCl_3^+$], 146 (50) [*i*Pr(Et_2N)P^+], 138 (100) [Et_2NPCl^+], 104 (74) [Et_2NPH^+], 74 (29) [$Et_2NH_2^+$].

Reaction of **1d** *with* **2**: As in the reaction of **1d** with **2**, 0.6 g ($3.1 \cdot 10^{-3}$ mol) of **1d** and 0.72 g ($3.1 \cdot 10^{-3}$ mol) of **2** in 40 ml of lead within 5d to a mixture of **1d** and **4d** as slightly yellowish oil.

1d (ref.[11], signals overlapped by those of **4d**): ^{1}H NMR: δ = 0.87 (t, ^{3}J(H,H) 7.1 Hz, CH_3CH$_2$N), 1.10 [d, ^{3}J(P,H) = 14.9 Hz, (CH_3)$_3$CP], 2.88 [m, line distances 7.1 Hz, (CH_3CH_2)$_2$N]. – ^{13}C NMR: δ = 14.2 [d, ^{3}J(P,C) 4.9 Hz, *C*H$_3$CH$_2$NP], 26.1 [d, ^{2}J(P,C) 19.4 Hz, (*C*H_3)CP]; 38.1 [d, ^{1}J(P,C) = 30.2 Hz, (CH_3)*C*P]; 44.8 [d, ^{2}J(P,C) 14.5 Hz, CH_3*C*H$_2$NP]. – ^{31}P NMR: δ = 157.2 (ref.[11] δ = 156.7).

4d (signals overlapped by those of **1d**): ^{1}H NMR: δ = 0.81 [t, ^{3}J(H,H) 7.1 Hz, CH_3CH$_2$N], 1.10 [d, ^{3}J(P,H) = 14.9 Hz, (CH_3)$_3$CP, overlapped with the signal of **1d**], 2.88 [m, (CH_3CH_2)$_2$N]. – ^{13}C NMR: δ = 14.9 (*C*H$_3$CH$_2$NP), 28.3 [d, ^{2}J(P,C) 17.8 Hz, (*C*H_3)CP]; 49.5 [d, ^{2}J(P,C) 12.3 Hz, CH_3*C*H$_2$NP]. – ^{31}P NMR: δ = 141.8.

A further weak ^{31}P NMR signal from the mixture appears at δ = 52.5 (^{1}J(P, H) ca. 530 Hz; ^{1}H NMR: δ = 0.68 [d, ^{3}J(P,H) 18.8 Hz, (C*H*)$_3$)$_3$CP], 6.5 [d, ^{1}J(PH) 534 Hz]; this indicates a *t*BuP(=O)H function.

Reaction of **5d** *with* $GeCl_4$: Addition of 2.18 g ($10.2 \cdot 10^{-3}$ mol) of $GeCl_4$ to 3.0g ($10.2 \cdot 10^{-3}$ mol) of **5d** in 10 ml of toluene at −20°C and subsequent warming up to room temp. leads within 1 h to complete consumption of **5d**. Removal of the solvent under vacuum provides a yellow liquid that contains **1d/3d** and **4d/6d**. –

1d/3d (different shifts and couplings from different samples); ^{1}H NMR (signals overlapped by those of **4d**): δ = 0.78 [t, ^3J(H,H) 7.1 Hz, CH_3CH$_2$N], 1.00 [d, ^3J(P,H) = 15.1−15.3 Hz, (CH_3)$_3$CP], 2.85−2.88 [m, (CH$_3$CH_2)$_2$N]. − ^{13}C NMR: δ = 14.2 [d, ^3J(P,C) 4.8−4.9 Hz, CH$_3$CH$_2$NP], 26.2 [d, ^2J(P,C) 16.6−17.6 Hz, (CH$_3$)CP]; 39.0 [d, ^1J(P,C) = 28.8−30.0 Hz, (CH$_3$)CP]; 44.6 [d, ^2J(P,C) 11.5−12.8 Hz, CH$_3$$CH_2$NP]. − ^{31}P NMR: δ = 148.1−151.8.

4d/6d (signals overlapped by those of **1d/3d**): ^{1}H NMR: δ = 0.76 [t, ^3J(H,H) 7.1 Hz, CH_3CH$_2$N], 1.03 [d, ^3J(P,H) = 15.8 Hz, (CH_3)$_3$CP], 2.85 [m, (CH$_3$CH_2)$_2$N]. − ^{13}C NMR: δ = 15.2 [d, ^3J(P,C) 3.7 Hz, CH$_3$CH$_2$NP], 28.7 [d, ^2J(P,C) 17.6 Hz, (CH$_3$)CP]; 39.0 [d, ^1J(P,C) 26.6 Hz]; 49.6 [d, ^2J(P,C) 12.0 Hz, CH$_3$$CH_2$NP]. − ^{31}P NMR: δ = 142.7. − **3d/4d**: $C_8H_{19}Cl_3GeNP$ (339.17): calcd. C 28.33, H 5.65, N 4.13; found C 29.50, H 6.32, N 4.52.

Reaction of Tetraisopropyldiphosphane with GeCl$_4$: Addition of 1.1 g (5.1·10^{-3} mol) of GeCl$_4$ to 1.2 g (5.1·10^{-3} mol) of tetraisopropyldiphosphane in 30 ml of toluene at −76°C and subsequent warming up to room temp. leads within 4 h to complete consumption of the diphosphane. Removal of the solvent under vacuum provides a liquid that contains **1a** and **4a**. Complete removal of more volatile **1a** under vacuum (up to 0.1 mbar) could not be achieved. − **1a**: δ ^{31}P = 133; **4a**: δ ^{31}P = 49.5.

1:1 Reaction of **4e** *with AgBr:* Addition of 2.0 g (6.2·10^{-3} mol) of **4e** to 1.16 g (6.2·10^{-3} mol) of AgBr in 40 ml of toluene at −20°C and subsequent warming up to room temp. leads to a suspension that is stirred 14 d in the dark. **4e** is completely consumed (^{31}P NMR). Subsequently the solution is decanted and concentrated under vacuum. Storing the liquid at −60°C provided about 0.5 g (≤ 20%) toluene-solvated **7** as colourless crystals (m.p. 130°C, dec.). − NMR of **7** dissolved (decomposed) in toluene: d^{1}H = 1.35 [d, ^3J(P,H) 16 Hz], δ^{31}P = 140 [very broad, J(Ag,P) not resolved]. − $C_{32}H_{72}Ag_4Br_4Cl_8Ge_2P_4 \cdot 2\ C_7H_8$ (1994.94): calcd. C 28.41, H 4.56; found C 30.22, H 4.85.

1:1 Reaction of **1e** *with AgBr:* Addition of 0.72 g (4·10^{-3} mol) of **1e** to 0.75 g (4·10^{-3} mol) of AgBr in 10 ml of CH_2Cl_2 at room temp. leads to a suspension that is stirred 20 h in the dark. Subsequently the solution is filtered and the solvent is removed under vacuum. The white residue is washed twice with 10 ml of pentane. After drying under vacuum 0.76 g (52.%) of **8** were isolated as a white solid (m.p. 180°C, dec.). − ^{1}H NMR: δ = 1.27 [d, ^3J(P,H) 15.3 Hz]. − ^{31}P NMR (CH_2Cl_2): δ = 138 [very broad, J(Ag,P) not resolved]. − IR (KBr): $\tilde{\nu}$ = 528 cm^{-1} (vs) (PCl). − $C_8H_{18}AgBrCl$: calcd. C 26.08, H 4.92; found C 25.93, H 4.99.

Structure Determination of **7**: Crystal data: $C_{46}H_{88}Ag_4Br_4Cl_8Ge_2P_4$, M = 1944.94, $Fdd2$, a = 26.460(6), b = 51.575(12), c = 10.231(4) Å, V = 13962(7) Å^3, Z = 8, d_{calc} = 1.851 Mg/m^3, μ = 4.667 mm^{-1}, T = 173 K. A cut colourless prism (0.55 × 0.38 × 0.20 mm) was mounted in inert oil. 10613 intensities were measured (2Θ 6−55°) using Mo-K_α radiation on a Siemens R3 diffractometer. After absorption correction (ψ-scans) 6601 were unique (R_{int} = 0.0671) and 6566 used for all calculations (program SHELXL-93). The absolute structure was solved by direct methods and refined anisotropically on F^2 to x = −0.008(13). The methyl hydrogens of the toluene were not included in the refinement. The final $wR(F^2)$ was 0.1470 with conventional $R(F)$ 0.0501 for 302 parameters and 160 restraints. Highest peak 820, hole −945 e/nm^3.

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-100273. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033; E-mail: deposit@chemcrys.cam.ac.uk].

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