## Reactions of Silicon–Silicon Bonds, VI[◇]

# Reductive Trichlorosilylation Reactions Leading to Alkyl- and Dialkylaminobis(trichlorosilyl)phosphanes☆

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Reactions of hexachlorodisilane and of trichlorosilane/triethylamine with alkyl- and dialkylaminodichlorophosphanes $RPCl_2$ **1a–f** [R = *i*Pr: **a**; $(Me_3Si)_2CH$: **b**; R = 1-adamantyl: **c**: R = *t*Bu: **d**; R = $Et_2N$: **e**; R = $iPr_2N$: **f**] furnish bis(trichlorosilyl)phosphanes $RP(SiCl_3)_2$ **3a–f**. However, when less bulky substituents are attached to the phosphorus atom, so that there is little steric crowding, the double reductive silylations leading from **1** to **3** are accompanied by side reactions and decomposition of **3**. Therefore, only **3b**, **3c**, **3d** and **3f** were isolated in a pure state. These compounds are more readily prepared by the trichlorosilane/triethylamine method. $^1H$-, $^{31}P$- and $^{29}Si$-NMR spectra confirm their constitution. The structure of solid **3f**, the first aminobis(trichlorosilyl)phosphane, was determined by X-ray crystallography. **3f** contains a phosphorus atom in a pyramidal environment surrounded by two silicon atoms and a planar nitrogen atom of the diisopropylamino group.

The reductive trichlorosilylation of chlorophosphanes with hexachlorodisilane provides a novel, mild access to compounds with silicon–phosphorus bonds[1–4]. Various unstrained dialkylchlorophosphanes are easily converted into dialkyl(trichlorosilyl)phosphanes. However, only one bis(silylation) reaction of an alkyldichlorophosphane with two equivalents of hexachlorodisilane, leading to an alkylbis(trichlorosilyl)phosphane, has hitherto been published. In this example, rather bulky *tert*-butyldichlorophosphane provided the corresponding bis(trichlorosilyl)phosphane in a straightforward reaction, whereas with methyldichlorophosphane and trimethylsilylmethyldichlorophosphane, the unwanted formation of cyclophosphanes took place[3,5]. The course of various reactions of hexachlorodisilane in the presence of nucleophiles appears to be associated with latent trichlorosilyl anions. These trichlorosilyl anion functions are generated from one $SiCl_3$ group of $Si_2Cl_6$ on attack of the other silicon atom by a nucleophile[6–9]. An amino(chloro)phosphane hexachlorodisilane adduct was recently detected by $^{31}P$ and $^{29}Si$ NMR[1].

$$R(R'_2N)PCl + Si_2Cl_6 \longrightarrow [R(R'_2N)(Cl)P\text{-}SiCl_3\text{-}SiCl_3] \longrightarrow$$

$$R(R'_2N)PSiCl_3 + SiCl_4 \qquad \text{[Ref. 1]} \qquad (1)$$

Trichlorosilyl anions are also the key intermediates in numerous reactions involving trichlorosilane/tertiary amine systems[10,11]. The trichlorosilane/triethylamine reagent is known to reduce chlorophosphanes $R_2PCl$ and $RPCl_2$ to phosphanes $R_2PH$ and $RPH_2$[12]. Recently, in the course of such a reaction, the formation of a trichlorosilylphosphane $Ph_3CP(SiCl_3)H$ was recognized by $^{31}P$ NMR[13]. With strict measures to avoid hydrolytic P–Si bond cleavage, the $HSiCl_3/NEt_3$ reagent was successfully used for the selective transformation of several alkyl(diorganylamino)chlorophosphanes into the corresponding alkyl(diorganylamino)trichlorosilylphosphanes[1]. Amino(trichlorosilyl)phosphanes (containing *one* P–Si bond) had previously been generated by (electrophilic) trichlorosilylation of the parent P–H compounds with silicon tetrachloride[14,15].

We expect trichlorosilylphosphanes with *two* P–Si bonds to be potential precursors for the synthesis of multiply-bonded phosphorus species[2], phosphorus heterocycles and metal phosphinidine clusters. This prompted us to explore the scope of the hexachlorodisilane reagent as well as the easily accessible trichlorosilane/triethylamine reagent (avoiding organometallic reagents) as an economic and safe method for accessing alkylbis(trichlorosilyl)phosphanes and the hitherto unknown aminobis(trichlorosilyl)phosphanes as precursors for further synthetic work[16].

### Reactions of Dichlorophopshanes with Hexachlorodisilane

Hexachlorodisilane reduces dichloro(methyl)phosphane to pentamethylcyclopentaphosphane, at which stage the reaction terminates[5]. Similarly, dichloro(isopropyl)phosphane **1a** consumes two equivalents of hexachlorodisilane at −40 °C in toluene, affording tetraisopropylcyclotetraphosphane (**2a**), which was isolated (59%) in a pure state by distillation (eq. 2). **2a** is not further attacked by hexachlorodisilane even at 100 °C. Since the formation of cyclophosphane **2a** might be due to decomposition of the short-lived intermediate chloro(isopropyl)(trichlorosilyl)phosphane, we protected one P–Cl function of **1a** with a diethylamino group. The reaction of chloro(diethylamino)(isopropyl)phosphane with hexachlorodisilane did indeed allow the

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[◇] For part V, see ref.[1].

observation of (isopropyl)bis(trichlorosilyl)phosphane (**3a**) by NMR, but separation of **3a** from the by-products (eq. 3) could not be achieved. Clearly, successful selective bis(trichlorosilylation) of dichlorophosphanes requires substituents which are bulkier than isopropyl (eq. 4).

$$\underset{\mathbf{1a}}{iPrPCl_2} + Si_2Cl_6 \longrightarrow 1/4\,\underset{\mathbf{2a}}{(iPrP)_4} + 2\,SiCl_4 \qquad (2)$$

$$\begin{array}{ll} iPr(Et_2N)PCl & \xrightarrow{Si_2Cl_6} iPr(Et_2N)PCl\text{–}Si_2Cl_6 + \\ iPr(Et_2N)PSiCl_3 & \\ & + iPr(Et_2N)PSi_2Cl_5 + SiCl_4 \\ & + \underset{\mathbf{3a}}{iPrP(SiCl_3)_2} + \underset{\mathbf{2a}}{(iPrP)_4} \qquad (3) \end{array}$$

$$\begin{array}{lll} RPCl_2 & \xrightarrow{+\,Si_2Cl_6} & (RP)_n + 2\,SiCl_4 \\ \mathbf{1b\text{–}d,\ 1f} & & \mathbf{2b,\ 2c} \\ \mathbf{1b}\text{: } R = (Me_3Si)_2CH & & \qquad\qquad (4) \\ \mathbf{1c}\text{: } R = 1\text{-Adamantyl} & & \\ \mathbf{1d}\text{: } R = tBu & \xrightarrow{+\,2\,Si_2Cl_6} & RP(SiCl_3)_2 + 2\,SiCl_4 \\ & & \mathbf{3b}\text{: } R = (Me_3Si)_2CH \\ & & \mathbf{3c}\text{: } R = 1\text{-Adamantyl} \\ & & \mathbf{3d}\text{: } R = tBu \end{array}$$

The rate of the reaction of dichlorobis(trimethylsilyl)methylphosphane (**1b**) with hexachlorodisilane is rather solvent-dependent. After boiling in hexane for 3 d, or stirring at room temperature in dichloromethane for 4 d, **1b** is completely consumed and the new silylphosphane **3b** and a smaller amount of tri[bis(trimethylsilyl)methyl]cyclotriphosphane (**2b**) are formed. Pure **3b** was isolated (76%) by distillation; recrystallization of the distillation residue from dichloromethane provided **2b** as colourless needles. 1-Adamantyldichlorophosphane **1c** reacts with two equivalents of hexachlorodisilane within 4 d at 60 °C in hexane, affording solid 1-adamantylbis(trichlorosilyl)phosphane **3c** in fair yield (60%). Attempted recrystallization led to the formation of decomposition products (1-AdaPH$_2$, [1-AdaP]$_4$).

The preparation of *tert*-butylbis(trichlorosilyl)phosphane **3d** from **1d** and hexachlorodisilane has been reported[3]. Even when **1d** and Si$_2$Cl$_6$ are mixed in a 1:1 ratio, the reaction leads to **3d**; the "1:1 product" *t*BuP(Cl)SiCl$_3$ was not detected. A possible interpretation of this observation is that the expected intermediate *t*BuP(Cl)SiCl$_3$, from the 1:1 reaction of **1d** with hexachlorodisilane, reacts faster than **1d** with a further equivalent of Si$_2$Cl$_6$. If this is the case, it is somewhat surprising that **3d** was *not* formed when *tert*-butylbis(trimethylsilyl)phosphane was treated with hexachlorodisilane; the stable compound *t*BuP(SiMe$_3$)SiCl$_3$ is rather unreactive towards hexachlorodisilane[3].

$$\mathbf{3d} \xrightarrow{C_2Cl_6} \underset{\mathbf{2d}}{(tBuP)_4} + \underset{\mathbf{4d}}{(tBu)(Cl_3Si)PP(tBu)(SiCl_3)}$$

$$tBuPH_2 \xrightarrow[(nBu_2O)]{Si_2Cl_6} \underset{\mathbf{6d}}{tBuP(H)SiCl_3} + \text{other products}$$

Therefore, we performed further experiments aimed at elucidating the reaction of **1d** with hexachlorodisilane and the possible role of "mixed" intermediates *t*BuP(Cl)SiCl$_3$. Only a few compounds of the type *t*BuP(X)SiR$_3$ are as yet known[17,18]. Following the route chosen by Appel et al.[17] to generate chloro(trimethylsilyl)phosphanes, we heated **3d** with hexachloroethane (eq. 5). This cleavage reaction requires several hours at 80 °C, in contrast to the formation of *t*BuP(Cl)SiMe$_3$ from *t*BuP(SiMe$_3$)$_2$ with C$_2$Cl$_6$, which proceeds at room temperature[17]. The products from the cleavage of **3d** with hexachloroethane were isolated by distillation. We obtained a mixture consisting of tetra-*tert*-butylcyclotetraphosphane (**2d**) (about 20%) and 1,2-di-*tert*-butyl-1,2-bis(trichlorosilyl)diphosphane **4d** (about 80%). **4d** gave only *one* set of NMR signals ($^{31}$P main signal singlet and $^{29}$Si satellites as the AA′ part of an AA′X system, $^{29}$Si "pseudotriplet" as the X part of an AA′X system), i.e. only one of the stereoisomers (*meso* or *rac*) was present. **4d** and the cyclotetraphosphane were unreactive towards hexachlorodisilane (100 °C, 3 d, without solvent).

The rate of the reaction of **1d** with two equivalents of hexachlorodisilane, providing **3d**, is significantly influenced by solvents. $^{31}$P-NMR spectra of reaction mixtures showed that *without solvent* **1d** was completely consumed within two weeks at room temperature. In pentane solution, however, no product could be detected after one week at room temperature. In diethyl ether, only minor amounts of **3d** (less than 25%) were present after one week, whereas in dichloromethane the formation of **3d** was complete after one day. Diethyl ether forms a coordination compound with hexachlorodisilane, which is evident from the appearance of additional $^1$H-NMR signals when excess Si$_2$Cl$_6$ is added to a solution of Et$_2$O in C$_6$D$_6$ ($^1$H NMR of the C$_6$D$_6$ solution: "free" Et$_2$O $\delta$ ($^1$H) = 1.08 (t), 3.26 (q), $^3J$(H,H) 6.97 Hz; Et$_2$O/Si$_2$Cl$_6$ adduct $\delta$ ($^1$H) = 1.07 (t), 3.27 (q), $^3J$(H,H) 7.0 Hz). P(III) compounds can also coordinate with Si$_2$Cl$_6$; alkyl(chloro)(amino)phosphane adducts with Si$_2$Cl$_6$ have recently been detected by $^{31}$P and $^{29}$Si NMR[1]. Consumption of these intermediates led not only to stable trichlorosilylphosphanes R(R$'_2$N)PSiCl$_3$, but also to transient pentachlorodisilanylphosphanes R(R$'_2$N)PSi$_2$Cl$_5$[1].

To explore the influence of the leaving group at phosphorus, the hexachlorodisilane reaction was extended to other alkylphosphanes. The phosphane catalysis of Si$_2$Cl$_6$ disproportionation is known[9], but stoichiometric reactions of tertiary, secondary and primary phosphanes with Si$_2$Cl$_6$ have not yet been described. A mixture of triisopropylphosphane with Si$_2$Cl$_6$ in C$_6$D$_6$/CH$_2$Cl$_2$ at room temperature showed severe broadening of the $^{31}$P-NMR signal ($\delta$ = 21.4; $\tau_{1/2}$ ca. 220 Hz). A further NMR experiment confirmed that the $^{31}$P-NMR signal of diisopropylphosphane was also significantly broadened in the presence of Si$_2$Cl$_6$, but a further signal attributable to diisopropyl(trichlorosilyl)phosphane indicated that an incomplete H/Si exchange reaction had occurred. When a mixture of *tert*-butylphosphane **5d** and excess hexachlorodisilane in C$_6$D$_6$ was left in an NMR tube for 10 d, *t*BuPH$_2$ (**5d**) and *t*BuP(H)SiCl$_3$ (**6d**) were detected by $^{31}$P NMR in ratio of approximately 3:1. In a preparative experiment, *tert*-butylphosphane was stirred with an excess of hexachlorodisilane in di-*n*-butyl ether for 1 week at room temp. Thereafter, the $^{31}$P-NMR signal of **5d** was very broad and several new signals had appeared. Addition of further $Si_2Cl_6$ and heating at 60°C led to complete consumption of **5d**. A $^{31}$P-NMR spectrum showed several signals with satellites due to $^{31}$P,$^{29}$Si coupling. These signals split into doublets in a $^{1}$H-coupled $^{31}$P-NMR spectrum. Such signals indicated the presence of five species containing the H–P(III)–Si(IV) moiety (**6d**: $\delta = -67.4$, peak intensity 15%; **7d**: $\delta = -76.4$, 46%; **8d**: $\delta = -82.8$, 7%; **9d**: $\delta = -89.2$, 21%; **10d**: $-110.2$, 11%) (eq. 6). Only $t$BuP(H)SiCl$_3$ (**6d**), formed by H/SiCl$_3$ exchange of the starting materials, could be enriched and unambiguously assigned ($^{1}$H, $^{13}$C, $^{29}$Si and $^{31}$P NMR). The NMR data of the other new species **7d**–**10d** suggest that they are phosphanyl derivatives of hexachlorodisilane disproportionation products.

Heating 1,2-di-*tert*-butyl-1,2-dichlorodiphosphane with hexachlorodisilane did not lead to any P–Si-bonded species (neither **4d** nor **3d**). In a further NMR experiment, a mixture of *tert*-butyldiiodophosphane and hexachlorodisilane in toluene/$C_6D_6$ was kept in a sealed ampoule for 2 h. The resulting $^{31}$P-NMR singlet at $\delta = -57.2$ was indicative of quantitative formation of tetra-*tert*-butylcyclotetraphosphane (**2d**).

Aminobis(silyl)phosphanes $R_2NP(SiX_3)_2$ are of synthetic interest, because in these compounds the phosphorus atom bears one more electronegative and two less electronegative substituents. In other words, aminobis(silyl)phosphanes might be used as $P^-$ equivalents.

The reaction of chloro(diethylamino)(isopropyl)phosphane with hexachlorodisilane led to a mixture of products containing **3a** and **2a** (eq. 3)[1]. With slightly more bulky alkyl(diorganylamino)chlorophosphanes $R(R'_2N)PCl$ ($R = t$Bu, $R' =$ Et; $R = i$Pr, $R' = i$Pr; $R = i$Pr, $R' =$ Ph), the selective trichlorosilylation with hexachlorodisilane furnished alkyl(diorganylamino)trichlorosilylphosphanes $R(R'_2N)PSiCl_3$ and silicon tetrachloride[1]. Generally speaking, bulky substituents at phosphorus inhibit P–N cleavage with hexachlorodisilane; the sterically congested aminophosphane $t$Bu$_2$PNEt$_2$ is unreactive toward hexachlorodisilane, whereas the P–N bonds of $i$Pr$_2$PN$i$Pr$_2$ and $i$Pr$_2$PNEt$_2$ are slowly cleaved by $Si_2Cl_6$ to give $i$Pr$_2$PSiCl$_3$[2] (eq. 7).

$$i\mathrm{Pr_2PNR_2 + Si_2Cl_6 \longrightarrow}\ i\mathrm{Pr_2PSiCl_3 + R_2NSiCl_3} \qquad (7)$$

$$\underset{\mathbf{1f}}{i\mathrm{Pr_2NPCl_2}} + 2\,\mathrm{Si_2Cl_6} \longrightarrow \begin{cases} \underset{\mathbf{3f}}{i\mathrm{Pr_2NP(SiCl_3)_2}} \\ \underset{\mathbf{11f}}{(i\mathrm{Pr_2NP})_3\mathrm{PSiCl_3}} \end{cases} \qquad (8)$$

$$\underset{\mathbf{2f}}{(i\mathrm{Pr_2NP})_4} \xrightarrow{\mathrm{Si_2Cl_6}} \underset{\mathbf{11f}}{(i\mathrm{Pr_2NP})_3\mathrm{PSiCl_3}} + \text{other products} \qquad (9)$$

The reaction of dichloro(diethylamino)phosphane **1e** with hexachlorodisilane is apparently quite unselective. Within 12 h, **1e** was completely consumed and a yellow precipitate was formed that was insoluble in common ethers and hydrocarbons. The reaction of dichloro(diisopropylamino)phosphane (**1f**) with hexachlorodisilane was slower and somewhat more selective (eq. 8). After heating for 5 d at 100°C, pure **3f** could be isolated in low yield by distillation. Single crystals of solid **3f** were obtained by recrystallization from pentane. In the distillation residue, a significant amount of a further new compound **11f** [$^{31}$P NMR: AM$_2$X pattern, $\delta(P_A) = +91.2$, $\delta(P_M) = +10.9$, $\delta(P_X) = -139.1$] was detected. From this NMR pattern, **11f** can be assigned as a cyclotetraphosphane structure with an exocyclic silyl group, e.g. ($i$Pr$_2$N)$_3$(Cl$_3$Si)P$_4$. In a further experiment to prepare the hitherto unknown compound ($i$Pr$_2$N)$_3$(Cl$_3$Si)P$_4$, a sample of ($i$Pr$_2$NP)$_4$ (**2f**) was heated with excess hexachlorodisilane (eq. 9). After several days at 80°C, ($i$Pr$_2$NP)$_4$ was completely consumed and three new compounds, among them compound **11f**, were detected by their multiplets in the $^{31}$P-NMR spectrum. One of the further unknown compounds, **12**, exhibited a set of $^{31}$P-NMR signals [AM$_2$X: $\delta(P_A) = +98.6$, $\delta(P_M) = +3.7$, $\delta(P_X) = -139.8$] only slightly different from those of **11f**. The other unknown compound **13** was detected by its multiplet pattern [$\delta(P) = +72$ and $\delta(P) = -160$]. After heating the mixture of **11f** and the unknown species **12** and **13** for 2 h at 140°C, only **11f** and **13** remained. However, attempts to isolate **11f** by crystallization were not successful. Further NMR experiments showed that P–P bonds of the cyclotetraphosphane ($t$BuP)$_4$ are resistant to attempted "dismutation reactions" with hexachlorodisilane[5,19]. Thus, it seems probable that **11f** was formed by P–N cleavage, not by P–P cleavage of ($i$Pr$_2$NP)$_4$ with $Si_2Cl_6$. **1f** reacts with $Si_2Cl_6$ in at least two ways: by simple double trichlorosilylation leading to stable **3f**, and by reduction (dehalogenation) leading to ($i$Pr$_2$NP)$_4$. Cleavage of one P–N bond of this cyclophosphane with the excess hexachlorodisilane will then furnish **11f**. Stable **11f** should be the *all-trans*-cyclotetraphosphane isomer of ($i$Pr$_2$N)$_3$(Cl$_3$Si)P$_4$; the unassigned molecule **12** with very similar NMR shifts and couplings could be an isomer of **11f** or another closely related species that rearranges slowly into the more stable **11f** or **13**.

### Reactions with the Trichlorosilane/Triethylamine Reagent

Moderately bulky alkyldichlorophosphanes **1b**–**d** and dialkylaminodichlorophopshane **1f** react under very mild conditions with the trichlorosilane/triethylamine reagent, furnishing alkyl- and dialkylaminobis(trichlorosilyl)phosphanes (eq. 10). The reaction is sometimes accompanied by cyclophosphane formation, but bis(trichlorosilyl)phosphanes **3b**–**d** and **3f** could be isolated in fair yields from the reaction mixtures. Cyclophosphane formation in the course of the silylation reactions can be explained by decomposition of unstable chloro(silyl)phosphane intermediates[17,18].

$$\underset{\mathbf{1b\text{–}d,\ 1f}}{\mathrm{RPCl_2}} + 2\,\mathrm{HSiCl_3} + 2\,\mathrm{NEt_3} \longrightarrow \underset{\mathbf{3b\text{–}d,\ 3f}}{\mathrm{RP(SiCl_3)_2}} + 2\,\mathrm{HNEt_3Cl} \qquad (10)$$

$$\mathbf{1a} + 2\,\mathrm{HSiCl_3} + 2\,\mathrm{NEt_3} \longrightarrow \mathbf{2a} + \mathbf{3a} + \mathbf{14} + \mathbf{15} + \mathbf{16} + 2\,\mathrm{HNEt_3Cl} \qquad (11)$$

With less bulky isopropyldichlorophosphane (**1a**) as starting material, formation of tetraisopropylcyclotetraphosphane (**2a**) and of cyclic silylphosphanes such as $(i\mathrm{PrP})_3\mathrm{SiCl}_2$ (probably a silatriphosphetane **15**) and $(i\mathrm{PrP})_4(\mathrm{SiCl}_2)$ (**16**) in the course of the distillation prevented the isolation of **3a** in a pure state (eq. 11). Similarly, **3e** decomposed upon attempted distillation with formation of an insoluble residue.

In general, trichlorosilylation reactions of dichlorophosphanes with the trichlorosilane/triethylamine reagent proceed under milder conditions and are much faster than the related hexachlorodisilane reactions. Thus short-lived intermediates $\mathrm{RP(Cl)SiCl_3}$, which may lead to irreversible cyclophosphane formation, are consumed much more rapidly by reaction with the second $\mathrm{SiCl_3^-}$ equivalent. Competition by P–N cleavage reactions was not observed in the course of trichlorosilylation of **1e** and **1f** with the trichlorosilane/triethylamine reagent.

## NMR Spectroscopic Characterization of Trichlorosilylphosphanes

Compared with the corresponding trimethylsilylphosphanes, the $^{31}$P-NMR signals of the trichlorosilylphosphanes **3**, **4** and **6** appear significantly downfield, and the magnitudes of coupling constants $^1J(^{31}\mathrm{P},^{29}\mathrm{Si})$ are significantly larger[1–3]. In contrast to the related chlorophosphanes **1f** and **1e**, the $^{31}$P signal of the diisopropylaminobis(trichlorosilyl)phosphane (**3f**) appears at higher frequency than that of the diethylamino derivative **3e**[1]. $^{29}$Si-NMR resonances of compounds **3**, **4** and **6** appear in the narrow range from $\delta = +1.8$ to $+13$. Among these compounds, the $^{29}$Si-NMR shifts of aminobis(trichlorosilyl)phosphanes **3e** and **3f** are in the upfield range. The $^{29}$Si-NMR signal of 2-trichlorosilyl-1,3-di-*tert*-butyl-1,3,2-diazaphosphorinane [a cyclic bis(amino)trichlorosilylphosphane] was reported to appear even further upfield [$\delta(^{29}\mathrm{Si}) = -57$, $^1J(\mathrm{P, Si}) = 41.7$ Hz][15]. The $^1$H-NMR multiplet of the single proton of the $i\mathrm{Pr_2N}$ group and the $^{13}$C-NMR resonances of **3f** appear as broad signals.

Table 1. $^{31}$P- and $^{29}$Si-NMR data of new chlorosilylphosphanes

| | $\delta\,^{31}$P [ppm] | $\delta\,^{29}$Si [ppm] | $\lvert ^1J(^{31}\mathrm{P},^{29}\mathrm{Si})\rvert$ [Hz] |
|---|---|---|---|
| $i\mathrm{Pr(Et_2N)(Cl)P{-}Si_2Cl_6}$ | +77.7 | | |
| $i\mathrm{Pr(Et_2N)P(SiCl_3)}$ | +55.2 | +10.9 | 131.8 |
| $i\mathrm{Pr(Et_2N)P(Si_2Cl_5)}$ | +58.2 | | |
| $i\mathrm{PrP(SiCl_3)_2}$ (**3a**) | –78.0 | + 8.0 | 72.7 |
| $(i\mathrm{PrP})_3(\mathrm{SiCl_2})$ [a] (**15**) | –34.6, –50.7 [$\mathrm{A_2M}$] | | |
| $(i\mathrm{PrP})_4(\mathrm{SiCl_2})$ [a] (**16**) | –18.2, –61.1 [AA'XX'] | | |
| $\mathrm{(Me_3Si)_2CHP(SiCl_3)_2}$ (**3b**) | –82.8 | + 6.2 | 85.1 |
| 1-$\mathrm{AdaP(SiCl_3)_2}$ (**3c**) | –56.1 | + 7.2 | 79.8 |
| $t\mathrm{BuP(SiCl_3)_2}$ (**3d**) [2] | –55.3 | +7 | 77.3 |
| $\mathrm{Et_2NP(SiCl_3)_2}$ (**3e**) | +11.7 | +1.8 | 75 |
| $i\mathrm{Pr_2NP(SiCl_3)_2}$ (**3f**) | –9.3 | +1.8 | 70.9 |
| 1,2-$(t\mathrm{Bu})_2$-1,2-$\mathrm{(SiCl_3)_2P_2}$ (**4d**) | –34.1 | +7.2 | 98 |
| $i\mathrm{PrP(H)(SiCl_3)}$ (**6a**) | –78 | | |
| $t\mathrm{BuP(H)(SiCl_3)}$ (**6d**) | –66.9 | +12.9 | 82.5<br>$J$(PH) 201.5 |

[a] Proposed structure.

## Structure Determination of 3f

Regarding the molecular structures of aminobis(silyl)phosphanes, there is still a complete lack of information in the literature. It therefore seemed important to carry out an X-ray crystal structure determination on **3f**, which is a solid at room temperature. Figure 1 shows the molecular structure of two independent molecules of crystalline **3f**; the conformations of the two molecules are similar (Figure 2).

Figure 1. ORTEP drawing of **3f** (two molecules per unit); selected bond lengths [Å] and angles [°]: P1–N1 1.679(3), P1–Si1 2.235(2), P1–Si2 2.238(2), Si–Cl between 2.019(2) and 2.033(2), N1–P1–Si1 107.22(13), N1–P1–Si2 106.86(13), Si1–P1–Si2 102.54(7); bond lengths and angles of the second molecule are similar

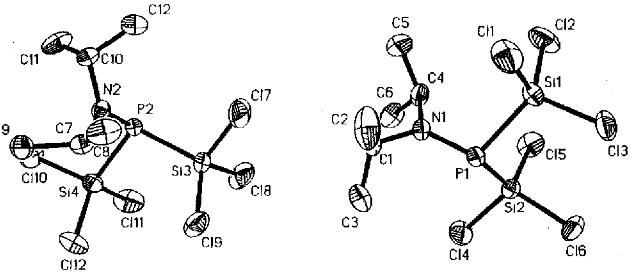
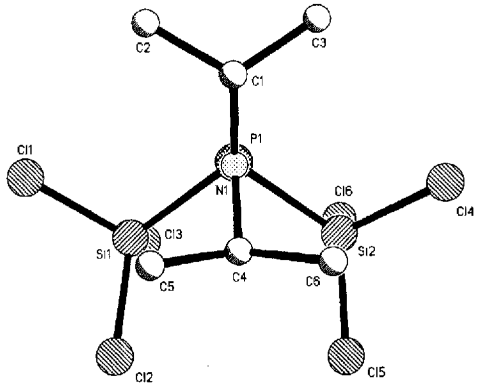


Figure 2. View of one molecule along the N1–P1 bond: torsion angle C1–N1–P1–Si1 –125.5° (the other molecule: C10–N2–P2–Si4 –125.4°)



The coordination geometries of the phosphorus atoms in the two molecules of **3f** are essentially pseudotetrahedral (angles at phosphorus are between 103.8 and 107.2°). The nitrogen atom of the diisopropylamino group is planar and the two isopropyl groups are nonequivalent. As in $i\mathrm{Pr(Ph_2N)PSiCl_3}$[1], the P–Si bond length is "normal" (2.235 and 2.238 Å), and is very similar to the single bond length in $\mathrm{H_2PSiH_3}$ (2.249 Å)[20] Molecular structures of comparable (amino)(tri*methyl*silyl)phosphanes are not known. Silicon–chlorine distances (2.014–2.033 Å) in **3f** are also in the expected range for $\mathrm{RSiCl_3}$ species. As in the related compound $t\mathrm{Bu(Ph_2N)PSiCl_3}$[1], the structural features of **3f** (e.g. P–N and P–Si distances) do not indicate significant π-backbonding from the phosphorus lone pair into vacant Si–Cl σ* orbitals. In summary, the rather large magnitudes of the NMR couplings $^1J(^{31}\mathrm{P},\ ^{29}\mathrm{Si})$ of (diorganylamino)(trichlorosilyl)phosphanes[1] do *not* coincide with unusually short P–Si bond lengths.

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## Experimental Section

*General:* $^1H$, $^{13}C$, $^{31}P$ and $^{29}Si$ NMR spectra: Bruker AC-200 spectrometer; solvent $[D_6]$benzene. – MS: Finnigan Mat 8430. – Elemental analyses: Carlo Erba analytical gas chromatograph. – All experiments were carried out under deoxygenated dry nitrogen as inert gas; solvents were dried according to standard procedures.

*Chloro(diethylamino)(isopropyl)phosphane,* $^{31}P$ NMR: $\delta = 158.9$. – $^{13}C$ NMR: $\delta = 14.2$ [d, $^3J(^{13}C,^{31}P) = 5.8$ Hz, 2 C, $N(CH_2CH_3)_2$], 17.8 [d, $^2J(^{13}C,^{31}P) = 28.3$ Hz, 1 C, $CH(CH_3)_2$], 17.8 [d, $^2J(^{13}C,^{31}P) = 19.8$ Hz, 1 C, $CH(CH_3)_2$], 33.1 [d, $^1J(^{13}C,^{31}P) = 24.9$ Hz, 1 C, $CH(CH_3)_2$], 43.7 [d, $^2J(^{13}C,^{31}P) = 12.0$ Hz, 2 C, $N(CH_2CH_3)_2$], was prepared by reaction of $i$PrPCl$_2$ (**1a**) with $Et_2NSiMe_3$ (60%, b.p. 72 °C/5 mbar).

*Reaction of Dichloro(isopropyl)phosphane* (**1a**) *with $Si_2Cl_6$:* 5.9 g (0.0219 mol) $Si_2Cl_6$ in 10 ml of toluene was slowly added to 3.15 g (0.0217 mol) **1a** at −40 °C. After warming to room temperature, a $^1H$-NMR spectrum indicated complete consumption of **1a**. Distillation provided 0.95 g (59%) of cyclotetraphosphane **2a** [b.p. 98 °C at 0.1 mbar; $\delta(^{31}P) = -61.5$]. After heating **2a** (3 d, 100 °C) with an excess of $Si_2Cl_6$, only **2a** was observed by $^{31}P$ NMR.

*Reaction of Chloro(diethylamino)(isopropyl)phosphane with $Si_2Cl_6$:* 2.5 g (0.0093 mol) of $Si_2Cl_6$ was added to $i$Pr(Et$_2$N)PCl (1.7 g, 0.0094 mol) and the yellow solution was stirred for 20 h at room temp. $^{31}P$-NMR spectra recorded 1 h and 20 h after the addition of $Si_2Cl_6$ showed that, in both cases, about 40% of the chlorophosphane remained unconsumed. After 1 h (20 h), about 35% (24%) of "[$i$Pr(Et$_2$N)PCl−Si$_2$Cl$_6$]" [$\delta(P) = +77$], 7% (3%) of $i$Pr(Et$_2$N)PSi$_2$Cl$_5$ [$\delta(P) = +58.2$] and 4% (24%) of $i$Pr(Et$_2$N)PSiCl$_3$ [$\delta(P) = +55.3$] were present. After 20 h, about 7% of $i$PrP(SiCl$_3$)$_2$ [$\delta(P) = -78.1$] and about 2% of ($i$PrP)$_4$ [$\delta(P) = -61.7$] were also detected in the mixture.

*Reaction of Dichloro(isopropyl)phosphane* (**1a**) *with Trichlorosilane/Triethylamine:* To a stirred solution of $i$PrPCl$_2$ (2.56 g, 0.018 mol) and $Et_3N$ (4.40 g, 0.044 mol) in toluene (10 ml), $HSiCl_3$ (6.0 g, 0.044 mol) in toluene (5 ml) was added dropwise. Stirring was continued for 2 h to ensure complete reaction. After removal of the precipitate by filtration, a $^{31}P$-NMR spectrum showed two products: **3a** ($\delta = -78.2$) and a broad signal at $\delta = -63.4$ (**14**). The toluene was then removed under reduced pressure and distillation was attempted. However, at 71 °C (0.01 mbar) a liquid mixture of **3a** and cyclophosphanes ($i$PrP)$_x$(SiCl$_2$)$_y$ [$x = 3, y = 0$: triisopropylcyclotriphosphane; $x = 4, y = 0$: **2a**; $x, y$ unknown: **14**; $x = 3, y = 1$: (probably) **15**] was obtained. The distillation residue showed the same set of $^{31}P$-NMR signals with different relative intensities and one new AA′XX′ multiplet [**16**, presumably ($i$PrP)$_4$SiCl$_2$]. – $i$PrP(SiCl$_3$)$_2$ **3a**: $^{31}P$ NMR: $\delta = -78.2$ (s). – $^{29}Si$ NMR: $\delta = 8.0$ [d, $J(^{31}P,^{29}Si) = 72.7$ Hz]. – **14**: $\delta = -63.4$. – ($i$PrP)$_4$ **2a**: $^{31}P$ NMR: $\delta = -61.5$ (s). – ($i$PrP)$_3$SiCl$_2$ **15**: $^{31}P$ NMR: $A_2M$ pattern, $\delta = -34.6$ (A), −50.7 (M); simulation of the $A_2M$ pattern gave a satisfactory fit with $^{1,3}J(^{31}P,^{31}P) = 140.1$ Hz. – ($i$PrP)$_4$(SiCl$_2$) **16**: $^{31}P$ NMR: $\delta = -18.2$ (m), 61.1 (m).

*[Bis(trimethylsilyl)methyl]bis(trichlorosilyl)phosphane* (**3b**). – *From Hexachlorodisilane:* A mixture of 2.9 g (0.0112 mol) **1b** and 6.3 g (0.0234 mol) hexachlorodisilane in 15 ml dichloromethane was stirred for 4 d at room temp. Distillation furnished 3.9 g (76%) of **3b**, b.p. 97 °C/0.01 mbar. Recrystallization of the residue gave a small amount of **2b** as colourless needles. – *From Trichlorosilane/Triethylamine:* To a mixture of 1.2 g (0.0057 mol) **1b** and 1.5 g (0.0115 mol) trichlorosilane in 30 ml hexane at 0 °C, 1.16 g (0.0115 mol) triethylamine was added. After stirring the mixture for 1 h at room temp., the precipitate was filtered off. Distillation of the filtrate furnished 1.85 g (71%) of **3b** as an oily, yellowish liquid.

**3b**: $^{31}P$ NMR: $\delta = -82.8$ (s). – $^{29}Si$ NMR: $\delta = 6.2$ (d), $^2J(P,Si) = 7.7$ Hz [SiMe$_3$]; 7.3 (d), $^1J(P,Si) = 85.0$ Hz. – $^{13}C$ NMR: $\delta = 2.1$ (d), $^3J(P,C) = 5.0$ Hz [SiMe$_3$]; 4.2 (d) $^1J(P,C)$. – $^1H$ NMR: $\delta = 0.18$ (s) [SiMe$_3$]; 0.51 (d), $^2J(P,H) = 10.2$ Hz [CH]. – MS (EI, 70 eV), *m/z* (%): 458 (0.8) [M$^+$], 443 (1.3) [M$^+$ − CH$_3$], 192 (17) [M$^+$ − 2 SiCl$_3$], 73 (100) [SiMe$_3^+$]. – $C_7H_{19}Cl_6PSi_4$ (458.7): calcd. C 18.3, H 4.1; found C 18.27, H 4.1. – **2b**: $^{31}P$ NMR: $\delta = -128.1$ (d) $^2J(P,P) = 204.2$ Hz; −154.5 (t) $^2J(P,P) = 206.1$ Hz[21].

*1-Adamantylbis(trichlorosilyl)phosphane* (**3c**). – *From Hexachlorodisilane:* A mixture of 1.2 g (0.00506 mol) **1c** and 2.95 g (0.011 mol) hexachlorodisilane in 10 ml hexane was stirred for 4 d at 60 °C. Removal of all volatile material at room temp. provided 1.4 g (64%) of **3c** as a colourless gel-like solid. – *From Trichlorosilane/Triethylamine:* To a mixture of 1.0 g (0.0042 mol) **1c** and 1.14 g (0.0084 mol) trichlorosilane in 30 ml hexane at 0 °C, 0.85 g (0.0084 mol) triethylamine was added. After precipitation of triethylammonium chloride, the solid was filtered off and washed with hexane. Removal of the solvent from the combined filtrate and washings at room temp. provided 1.13 g (62%) of **3c** as a colourless gel.

**3c**: $^{31}P$ NMR: $\delta = -56.1$ (s). – $^{29}Si$ NMR: $\delta = 7.2$ (d), $^1J(P,Si) = 79.7$ Hz. – $^{13}C$ NMR: $\delta = 29.6$ (d), $^3J(P,C) = 8.3$ Hz; 35.7 (s) [$^4J(P,C) < 1$ Hz]; 44.0 (d), $^2J(P,C) = 8.3$ Hz; 44.9 (d), $^1J(P,C) = 8.5$ Hz. – MS (EI, 70 eV), *m/z* (%): 434 (0.2) [M$^+$], 299 (0.5) [M$^+$ − SiCl$_3$], 264 (0.4) [M$^+$ − SiCl$_4$], 229 (0.2) [M$^+$ − SiCl$_3$ − 2 Cl], 135 (100) [$C_{10}H_{15}^+$]. – $C_{10}H_{15}Cl_6PSi_2$ (434.7): calcd. C 27.60, H 3.45; found C 27.46, H 3.40.

*NMR Experiments Comparing Solvent Effects on the Reaction of tBuPCl$_2$* (**1d**) *with Hexachlorodisilane Furnishing* **3d**[3]. – *Without Solvent:* 12.10 g (0.045 mol) $Si_2Cl_6$ was added to **1d** (3.60 g, 0.023 mol). After 14 d at room temperature **1d** was completely consumed. – *In Dichloromethane:* 4.13 g (0.0154 mol) of $Si_2Cl_6$ was added to **1d** (1.22 g, 0.0077 mol) in $CH_2Cl_2$ (5.4 ml). After 20 h at room temperature **1d** was completely consumed. – *In Pentane:* 3.08 g (0.0115 mol) of $Si_2Cl_6$ was added to **1d** (0.91 g, 0.0057 mol) in pentane (4.0 ml). After 7 d at room temperature no reaction was detected. – *In Diethyl Ether:* 4.06 g (0.0151 mol) of $Si_2Cl_6$ was added to **1d** (1.20 g, 0.076 mol) in $Et_2O$ (5.2 ml). After 7 d at room temperature **1d** was almost completely consumed (13% **1d**, 87% **3d**). – *Coordination of Hexachlorodisilane with $Et_2O$:* An excess of $Si_2Cl_6$ was added to a solution of $Et_2O$ in $C_6D_6$. The $^1H$-NMR spectrum of the mixture showed two sets of signals for $Et_2O$. "Free" $Et_2O$: $^1H$ NMR: $\delta = 1.08$ [t, $J(^1H,^1H) = 6.97$ Hz, 6 H, $CH_3CH_2O$], 3.26 [q, $J(^1H,^1H) = 6.97$ Hz, 4 H, $CH_3CH_2O$]. – $Si_2Cl_6$–$Et_2O$ adduct: $^1H$ NMR: $\delta = 1.07$ [t, $J(^1H,^1H) = 7.00$ Hz, 6 H, $CH_3CH_2O$–], 3.27 [q, $J(^1H,^1H) = 7.00$ Hz, 4 H, $CH_3CH_2O$–].

*tert-Butylbis(trichlorosilyl)phosphane* (**3d**): To a stirred solution of $t$BuPCl$_2$ (**1d**) (10.98 g, 0.069 mol) and $HSiCl_3$ (18.71 g, 0.136 mol) in toluene (50 ml), $NEt_3$ (13.80 g, 0.138 mol) in toluene (20 ml) was added dropwise. Stirring was continued for 14 h to ensure complete reaction. After separation from the precipitate and removal of toluene under reduced pressure, distillation at 85 °C (0.01 mbar) furnished 17.2 g (70%) of **3d** ($\delta^{31}P = -54.2$[3]).

*Reaction of* **3d** *with Hexachloroethane:* A mixture of 3.67 g (0.01028 mol) **3d** and 2.42 g (0.01022 mol) hexachloroethane in 15 ml toluene was stirred for 1 d at room temp. (no consumption of **3d**). After heating for 10 h at 80 °C, **3d** was completely consumed. Distillation furnished a fraction at 130–140 °C (0.1 mbar) which consisted of about 80% **4d** and 20% **2d** (estimation on the basis of $^{31}P$ NMR and analytical data).

**4d**: $^{31}$P NMR: $\delta$ = 34.1 (s) (with "two pairs of satellites", AA' part of an AA'X pattern). – $^{29}$Si NMR: $\delta$ = 7.2 (3 lines, line distances 55.2 Hz, X part of an AA'X pattern). Simulation of the AA'X pattern gave a satisfactory fit with $J$(P,P) = 202 (± 3) Hz, $^{1}J$(P,Si) 98 (± 3) Hz, $^{2}J$(P,Si) 12 (± 3) Hz. – Elemental analysis of the mixture: for **4d/2d** (4:1) calcd. C 27.03, H 5.11, Cl 39.89; found C 27.26, H 5.25, Cl 40.67.

*NMR Experiments on the Cleavage of P–H Bonds with Hexachlorodisilane. – Reaction of Diisopropylphosphane with $Si_2Cl_6$:* A mixture of 0.17 g (0.0029 mol) $Si_2Cl_6$ and $i$Pr$_2$PH (0.61 g, 0.0052 mol) was stirred for 20 h at room temp. and then heated for 1 h at 60 °C. – $^{31}$P NMR: $\delta$ = –1 (very broad, $\tau_{1/2}$ = ca. 1480 Hz) [$i$Pr$_2$PH]; $\delta$ = –19.1 (slightly broadened, $\tau_{1/2}$ = 4.2 Hz) [$i$Pr$_2$PSiCl$_3$]. – *Reaction of tert-Butylphosphane* (**5d**) *with $Si_2Cl_6$ at Room Temp. in $C_6D_6$:* In an NMR tube, an excess of $Si_2Cl_6$ was added to a solution of $t$BuPH$_2$ in $C_6D_6$. After 10 d, the $^{31}$P-NMR spectrum showed two signals [**5d**/$t$BuP(H)SiCl$_3$ (**6d**) = 1:3]: **5d** $^{31}$P NMR: $\delta$ = –78.0 (s); **6d** $^{31}$P NMR: $\delta$ = –66.0 (s). – *Reaction of tert-Butylphosphane* (**5d**) *with $Si_2Cl_6$ in Di-n-butyl Ether:* To a stirred solution of $t$BuPH$_2$ (3.56 g, 0.040 mol) in di-$n$-butyl ether (3 ml) was added $Si_2Cl_6$ (13.45 g, 0.050 mol). After stirring at room temp. for 10 d and heating for 10 h to 65 °C, an NMR spectrum showed that the mixture still contained **5d**. Hence, a further 7.85 g (0.029 mol) of $Si_2Cl_6$ was added and stirring was continued for an additional 5 d at room temp. to ensure complete consumption of **5d**.

$t$BuP(H)SiCl$_3$ (**6d**): $^{31}$P NMR: $\delta$ = –66.9 (s). – $^{29}$Si NMR: $\delta$ = 12.9 [d, $J$($^{31}$P,$^{29}$Si) = 82.5 Hz]. – $^{13}$C NMR: $\delta$ = 33.0 [d, $J$($^{31}$P,$^{13}$C) = 12.7 Hz, 3 C, $(CH_3)_3$C], 30.6 [d, $J$($^{31}$P,$^{13}$C) = 14.0 Hz, 1 C, $(CH_3)_3C$]. – $^{1}$H NMR: $\delta$ = 1.2 [dd, $J$($^{31}$P,$^{1}$H) = 13.5 Hz, $J$($^{1}$H,$^{1}$H) = 0.4 Hz, 9H, $(CH_3)_3$C], 3.0 [dd, $J$($^{31}$P,$^{1}$H) = 201.4 Hz, $J$($^{1}$H,$^{1}$H) = 0.4 Hz, 1H, P$H$]. – Further products $t$BuP(H)SiCl$_n$X$_m$ (**7d**–**10d**, $n + m$ = 3; X is probably SiCl$_3$ or Si$_2$Cl$_5$): **7d**: $^{31}$P NMR: $\delta$ = –76.3 $J$($^{31}$P,$^{1}$H) = 203.2 Hz, Si-sat. $J$($^{31}$P,$^{29}$Si) = 90.9 Hz. – $^{13}$C NMR: $\delta$ = 33.7 [d, $J$($^{31}$P,$^{13}$C) = 12.5 Hz, 3 C, $(CH_3)_3$C], 31.5 [d, $J$($^{31}$P,$^{13}$C) = 17.1 Hz, 1 C, $(CH_3)_3C$]. – **8d**: $^{31}$P NMR: $\delta$ = –82.8 $J$($^{31}$P,$^{1}$H) = 205.0 Hz (signal too weak to resolve $^{29}$Si satellites). – **9d**: $^{31}$P NMR: $\delta$ = –89.9 $J$($^{31}$P,$^{1}$H) = 199.3 Hz, Si-sat. $J$($^{31}$P,$^{29}$S) = 92.7 Hz. – **10d**: $^{31}$P NMR $\delta$ = –110.2 $J$($^{31}$P,$^{1}$H) = 195.2 Hz, Si-sat. $J$($^{31}$P,$^{29}$Si) = 81.1 Hz.

*Reactions of (Dialkylamino)diisopropylphosphanes with Hexachlorodisilane Monitored by NMR. – Reaction of (Diethylamino)diisopropylphosphane with $Si_2Cl_6$:* 7.40 g (0.028 mol) $Si_2Cl_6$ was added to $i$Pr$_2$PNEt$_2$ (2.70 g, 0.014 mol) and the mixture was stirred for 6 d at room temp. After this time, nearly ll the $i$Pr$_2$PNEt$_2$ had been consumed in facour of $i$Pr$_2$PSiCl$_3$. – *Reaction of Diisopropyl(diisopropylamino)phosphane with $Si_2Cl_6$:* 2.48 g (0.0092 mol) $Si_2Cl_6$ was added to $i$Pr$_2$PN$i$Pr$_2$ (1.00 g, 0.0046 mol). The mixture was stirred for 16 h at room temp. and then heated for 1 h to 120 °C. In the $^{31}$P-NMR spectrum of the mixture of products, signals attributable to three compounds were detected: $i$Pr$_2$PN$i$Pr$_2$ $^{31}$P NMR: $\delta$ = 52.9 (s); $i$Pr$_2$PCl: $^{31}$P NMR: $\delta$ = 134.4 (s); $i$Pr$_2$PSiCl$_3$ $^{31}$P NMR: $\delta$ = –18.9 (s).

*Reaction of Dichloro(diethylamino)phosphane with Hexachlorodisilane:* Hexachlorodisilane (1.00 g, 0.0056 mol) was added slowly to 1.70 g (0.0063 mol) diethylamino(dichloro)phosphane at 0 °C. After stirring for 12 h at room temp., a yellow solid separated from the solution. No $^{31}$P NMR signal could be observed from the supernatant solution. The solid was found to be insoluble in common organic solvents.

*Reaction of Dichloro(diethylamino)phosphane with Trichlorosilane and Triethylamine:* To a stirred solution of Et$_2$NPCl$_2$ (8.59 g, 0.049 mol) and HSiCl$_3$ (21.33 g, 0.158 mol) in pentane (30 ml), Et$_3$N (15.80 g, 0.158 mol) was added dropwise at –40 °C. The reaction mixture was kept at –40 °C for 1 h and then allowed to warm to room temp. The HNEt$_3$Cl precipitate was filtered off and pentane was removed from the filtrate under reduced pressure. NMR spectra of the residue showed the presence of diethylaminobis(trichlorosilyl)phosphane Et$_2$NP(SiCl$_3$)$_2$ (**3e**). Upon attempted distillation, **3e** decomposed to form an insoluble residue. – Et$_2$NP(SiCl$_3$)$_2$ (**3e**): $^{31}$P NMR: $\delta$ = 11.7 (s). – $^{29}$Si NMR: $\delta$ = 1.8 [d, $J$($^{31}$P,$^{29}$Si) = 75.0 Hz].

*(Diisopropylamino)bis(trichlorosilyl)phosphane* (**3f**). – *From Hexachlorodisilane:* 6.20 g (0.023 mol) of $Si_2Cl_6$ was added to $i$Pr$_2$NPCl$_2$ (2.00 g, 0.010 mol) and the mixture was heated at 100 °C for 5 d. SiCl$_4$ was then removed under reduced pressure. Distillation of the residue at 92 °C (0.01 mbar) yielded 0.70 g (0.002 mol, 18%) of $i$Pr$_2$NP(SiCl$_3$)$_2$ (**3f**); m.p. 62.4 °C. The solid product was recrystallized twice from pentane at –20 °C to give single crystals for the X-ray structure determination. – Investigation of the distillation residue by $^{31}$P NMR: **11f**: AM$_2$X system, $\delta$ = 91.2 [(pseudo d, t) d: 228.3 Hz, t: 157.2 Hz]; 10.9 [(pseudo t), 157.2 Hz]; –139.8 [(pseudo d, t) d: 228.3 Hz, t: 157.2 Hz]. – *From Trichlorosilane/Triethylamine:* To a stirred solution of $i$Pr$_2$NPCl$_2$ (6.44 g, 0.033 mol) and HSiCl$_3$ (15.78 g, 0.117 mol) in pentane (100 ml), Et$_3$N (11.70 g, 0.117 mol) was added dropwise. Stirring was continued for 14 h to ensure complete reaction, and then the HNEt$_3$Cl precipitate was filtered off. Pentane was removed from the filtrate under reduced pressure. Distillation of the residue at 92 °C (0.01 mbar) yielded 6.27 g (0.016 mol, 50%) of $i$Pr$_2$NP(SiCl$_3$)$_2$ (**3f**) as colourless crystals, m.p. 62.4 °C.

$^{31}$P NMR: $\delta$ = –9.3 (s). – $^{29}$Si NMR: $\delta$ = 1.8 [d, $J$($^{31}$P,$^{29}$Si) = 70.9 Hz]. – $^{1}$H NMR: $\delta$ = 0.4 [d, $J$($^{1}$H,$^{1}$H) = 6.6 Hz, 12H, NCH$(CH_3)_2$], 3.1–3.4 [m, br., NC$H$(CH$_3$)$_2$]. – $^{13}$C NMR: $\delta$ = 23.3 (s) NCH$(CH_3)_2$, N$C$H(CH$_3$)$_2$, broad (separate signals not resolved). – MS (EI, 70 eV), $m/z$ (%): 399 (46) [M$^+$]. – $C_6H_{14}Cl_6NPSi_2$ (400.03): calcd. C 18.01, H 3.53, N 3.50; found C 18.15, H 3.63, N 3.35.

*Structure Determination of* **3f**[22]: Crystal data: $C_6H_{14}Cl_6NPSi_2$, $M$ = 400.03, $P\bar{1}$, $a$ = 12.361(5), $b$ = 12.483(5), $c$ = 13.271(5) Å, $\alpha$ = 72.42(3), $\beta$ = 66.22(3), $\gamma$ = 68.84(3)°, $V$ = 1719.7(12) Å$^3$, $Z$ = 4, $d_{calcd}$ = 1.547 mg/m$^3$, $\mu$ = 1.210 mm$^{-1}$, $T$ = 143 K. A colourless plate (0.50× 0.35 × 0.30 mm) was mounted in inert oil. 8953 intensities were measured (2Θ 6–50°) by using Mo-$K_\alpha$ radiation on a STOE Stadi-4 diffractometer. Of these, 6025 were unique ($R_{int}$ = 0.0296) and 6018 were 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 0.1395 with conventional $R(F)$ 0.0468 for 297 parameters.

*Reaction of Tetrakis(diisopropylamino)cyclotetraphosphane with $Si_2Cl_6$:* 11.7 g (0.043 mol) of $Si_2Cl_6$ was added to a stirred solution of ($i$Pr$_2$NP)$_4$ (**2f**) (7.58 g, 0.081 mol) in toluene (30 ml). The mixture was heated at 80 °C for 4 d, after which **2f** was not completely consumed. Subsequently, a further 10.4 g (0.038 mol) of $Si_2Cl_6$ was added and the red mixture was heated for a further 2 d. $^{31}$P NMR data of the reaction mixture: **11f**: ($i$Pr$_2$N)$_3$(SiCl$_3$)P$_4$ $^{31}$P NMR: $\delta$ = 91.2 [dt, $J$($^{31}$P,$^{31}$P) = 228.7 Hz, $J$($^{31}$P,$^{31}$P) = 157.5 Hz, 1P, P$_A$]; 10.9 [t, $J$($^{31}$P,$^{31}$P) = 157.5 Hz, 2 P, P$_M$]; –139.1 [dt, $J$($^{31}$P,$^{31}$P) = 228.7 Hz, $J$($^{31}$P,$^{31}$P) = 157.5 Hz, 1 P, P$_A$]. – **12**: (unknown structure) $^{31}$P NMR: $\delta$ = 98.6 [dt, $J$($^{31}$P,$^{31}$P) = 240.5 Hz, $J$($^{31}$P,$^{31}$P) = 162.5 Hz, 1 P, P$_A$]; 3.7 [t, $J$($^{31}$P,$^{31}$P) = 162.5 Hz, 2 P, P$_M$]; –139.8 [dt, $J$($^{31}$P,$^{31}$P) = 240.5 Hz, $J$($^{31}$P,$^{31}$P) = 162.5 Hz, 1 P, P$_A$]. – **13**: $\delta^{31}$P = 72 (m); –160 (m). – After further heating of the sample (2 h, 140 °C), only **11f** and **13** could be detected by $^{31}$P NMR:

☆ Dedicated to Professor *Walter Siebert* on the occasion of his 60th birthday.

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[22] Further details of the structure determination may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the reference number CSD-405766, the names of the authors, and the journal citation.

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