Reactions at Silicon–Silicon Bonds, V[1]

Selective Trichlorosilylation of Alkyl(diorganylamino)chlorophosphanes with Hexachlorodisilane or with Trichlorosilane/Triethylamine. – Two Routes to New Functional Trichlorosilylphosphanes

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The reaction of alkyl(diorganylamino)chlorophosphanes $R(R'_2N)PCl$ **1** (**1a**: R = *t*Bu, R' = Et, **1b**: R = *i*Pr, R' = *i*Pr; **1c**: R = *i*Pr, R' = Ph) with hexachlorodisilane, afforded alkyl(diorganylamino)trichlorosilylphosphanes $R(R'_2N)PSiCl_3$ **2** (**2a**: R = *t*Bu, R' = Et; **2b**: R = *i*Pr, R' = *i*Pr; **2c**: R = *i*Pr, R' = Ph) and silicon tetrachloride. An intermediate formed in the reaction of **1b** with hexachlorodisilane, the adduct $i\text{Pr}(i\text{Pr}_2\text{N})(\text{Cl})\text{P}-\text{Si}(\text{Cl})_3-\text{SiCl}_3$ (**3b** = **1b** · Si_2Cl_6), was detected by ^{31}P- and ^{29}Si-NMR spectra that indicate pentacoordinated silicon bound to tetracoordinated phosphorus and tetracoordinated silicon. Trichlorosilylphosphanes **2** are also available from **1** under very mild conditions by reductive trichlorosilylation with trichlorosilane in the presence of triethylamine. Compounds **2** were identified analytically, by mass spectroscopy, multinuclear NMR, and an X-ray structure determination of **2c**.

Recently, the reductive trichlorosilylation of chlorophosphanes with hexachlorodisilane provided a novel, very mild access to molecules with silicon-phosphorus bonds[1–4]. Dialkylchlorophosphanes were easily converted into dialkyl(trichlorosilyl)phosphanes, but the bis(silylation) of alkyldichlorophosphanes with two equivalents of hexachlorodisilane, leading to alkylbis(trichlorosilyl)phosphanes, requires rather bulky alkyl substituents at phosphorus (*tert*-butyl, adamantyl), which prevent the undesired formation of cyclophosphane[3,5]. An alternative approach to bifunctional trichlorosilylphosphanes would be the protection of one reactive P–Cl bond by substitution with an appropriate diorganylamino group. This method would be most useful if the subsequent reductive trichlorosilylation reagent attacked the P–Cl bond selectively. From a rough bond energy estimate, P–N attack with trichlorosilylamine formation also seemed a likely (undesired) reaction pathway. For that reason, we chose three related moderately bulky alkyl(diorganylamino)chlorophosphanes $R(R'_2N)PCl$ **1** (**1a**: R = *t*Bu, R' = Et, **1b**: R = *i*Pr, R' = *i*Pr; **1c**: R = *i*Pr, R' = Ph) as starting materials for the attempted selective trichlorosilylation. The course of various reactions of hexachlorodisilane in the presence of nucleophilic functionalities (such as the long-known phosphane oxide and sulfide reduction[6,7] or the recent Si–Sn bond formation with trimethylstannylphosphanes[8]), appears to be associated with latent trichlorosilyl anions. These trichlorosilyl anion functions are generated from one $SiCl_3$ group of Si_2Cl_6 when the other silicon atom is attacked by a nucleophile[6,7]. Trichlorosilyl anions are also the key intermediates in numerous reactions involving trichlorosilane/tertiary amine systems[9–13]. Among these reactions are the formation of C–Si bonds from halogenoalkanes[9,10]; the related reduction of chlorophosphanes with $HSiCl_3/NEt_3$ furnished the corresponding P–H functions[14], obviously after work-up in the presence of moisture. Molecules with P–Si bonds have been postulated as intermediate species in this reduction[14]. More recently, Schmutzler and Plack detected the trichlorosilylphosphane $Ph_3CP(H)SiCl_3$ by ^{31}P NMR in the mixture of products from the reduction of Ph_3CPCl_2 with $HSiCl_3/NEt_3$[15]. When P–Si cleavage by hydrolysis or by $HNEt_3Cl$ is avoided, the easily available $HSiCl_3/NEt_3$ reagent might be well suited for a novel access to synthetically interesting trichlorosilylphosphanes. In the following we report how the $HSiCl_3/NEt_3$ reagent can be used with **1** as an alternative to hexachlorodisilane for the transformation of P–Cl into P–Si functions, thus providing alkyl(diorganylamino)trichlorosilylphosphanes **2** under very mild conditions.

Results

Attempts to perform the monotrichlorosilylation of alkyldichlorophosphanes did not provide the alkyl(chloro)trichlorosilylphosphanes $RP(Cl)(SiCl_3)$; instead, the bis(silylated) products $RP(SiCl_3)_2$ or cyclophosphanes $(RP)_n$ were obtained[3,5,16]. Similarly, the reaction of chloro(diethylamino)(isopropyl)phosphane with hexachlorodisilane led to a mixture of products containing isopropylbis(trichlorosilyl)phosphane and tetraisopropylcyclotetraphosphane (eq. 1)[16]. P–Cl and P–N bonds of the starting phosphane were attacked by hexachlorodisilane.

$$i\mathrm{Pr(Et_2N)PCl} \xrightarrow{\mathrm{Si_2Cl_6}} i\mathrm{PrP(SiCl_3)_2} + (i\mathrm{PrP})_4 + i\mathrm{Pr(Et_2N)PSiCl_3} + \mathrm{SiCl_4} \qquad (1)$$

$$\underset{\mathbf{1a-c}}{\mathrm{R(R'_2N)PCl}} + \mathrm{Si_2Cl_6} \longrightarrow \mathrm{R(R'_2N)PSiCl_3} + \mathrm{SiCl_4} \qquad (2)$$

2a: R = *t*Bu, R' = Et
2b: R = *i*Pr, R' = *i*Pr
2c: R = *i*Pr, R' = Ph

With slightly more bulky alkyl(diorganylamino)chlorophosphanes R(R$'_2$N)PCl **1** (**1a**: R = *t*Bu, R' = Et, **1b**: R = *i*Pr, R' = *i*Pr; **1c**: R = *i*Pr, R' = Ph), the desired selective trichlorosilylation with hexachlorodisilane at room temperature, cleaving only the P−Cl bonds of the starting phosphanes, provides new alkyl(diorganylamino)trichlorosilylphosphanes R(R$'_2$N)PSiCl$_3$ **2** (**2a**: R = *t*Bu, R' = Et; **2b**: R = *i*Pr, R' = *i*Pr; **2c**: R = *i*Pr, R' = Ph) and silicon tetrachloride (eq. 2). The reaction of **1** with hexachlorodisilane without solvent, leading to **2a** and **2c**, are complete within several hours (work-up after one day at room temperature), the preparation of **2b** requires about three days. In the case of **1b** reacting with hexachlorodisilane, an intermediate **3b** of the reaction leading to **2b** could be detected by ^{31}P NMR. Spectra of the reaction mixture recorded after heating hexachlorodisilane and chlorophosphane **1b** at 55 °C for 5 h showed ^{31}P-NMR signals of the starting phosphane **1b** (about 75%, δ^{31}P = 148.4) and of two new species **3b** (about 20%, δ^{31}P = 57.1) and **4b** (about 5%, δ^{31}P = 42.7). Spectra recorded later showed increasing amounts of the final product **2b** (δ^{31}P = 35.8), which was isolated in pure state by distillation at 72 °C. In a higher fraction, trace amounts of **4b** were again detected by ^{31}P NMR. As in the ^{31}P-NMR spectrum of **2b**, the ^{31}P-NMR signals of both **3b** and **4b** show "large" satellite doublets arising from $^1J(^{31}\mathrm{P},^{29}\mathrm{Si})$ [**2b**: 123.8 Hz, **3b**: 160.7 Hz, **4b**: 133.0 Hz]. In the case of intermediate **3b** (on attempted isolation, **3b** decomposed to trichlorosilylphosphane **2b** and silicon tetrachloride), a further pair of satellites (*J* = 24.8 Hz) around the central ^{31}P-NMR signal at δ = 57 arises from $^2J(^{31}\mathrm{P},^{29}\mathrm{Si})$. Further evidence for the P−Si−Si moiety of the transient species **3b** is provided by ^{29}Si-NMR spectra of the reaction mixture at an early stage: the ^{29}Si-NMR signal of the silicon atom adjacent to phosphorus [δ^{29}Si = −69.6, (d) $J(^{31}\mathrm{P},^{29}\mathrm{Si})$ = 160.7 Hz, P*Si*Cl$_3$SiCl$_3$] appears far upfield from the other doublet [^{29}Si NMR: δ = 9.8 (d) $J(^{31}\mathrm{P},^{29}\mathrm{Si})$ = 24.8 Hz, PSiCl$_3$*Si*Cl$_3$]. The magnitude of the ^1J coupling of **3b** is larger than that of any known $\lambda^3\sigma^3$ silylphosphane[2−4]. However, the magnitudes of ^1J and $^2J(^{31}\mathrm{P},^{29}\mathrm{Si})$ of **3b** alone would not allow a *clear* distinction between a hexachlorodisilane-phosphane adduct R(R$'_2$N)(Cl)PSi$_2$Cl$_6$ and a pentachlorodisilanylphosphane R(R$'_2$N)PSi$_2$Cl$_5$. Hexachlorodisilane−phosphane adducts are not yet known, but for tetrachloro*stannane*−phosphane adducts it is known that the couplings $^1J(^{117,119}\mathrm{Sn},^{31}\mathrm{P})$ are significantly larger than those of λ^3,σ^3 stannylphosphanes[17].

No pentachlorodisilanylphosphane R$_2$PSi$_2$Cl$_5$ has been reported in the literature, but the NMR couplings ^1J and $^2J(^{31}\mathrm{P},^{29}\mathrm{Si})$ of the stable disilanylphosphane *t*Bu$_2$PSiMeCl-SiMeCl$_2$ (100.8 and 22.0 Hz)[4,5] are not too different from those of **3b**, compared with the related couplings of *t*Bu$_2$-PSi$_2$Me$_5$ (63.6 and 12.5 Hz)[4,5]. Thus the large ^{29}Si *upfield shift of the one silicon atom* of **3b** (about 80 ppm upfield from the other silicon atom of **3b** or from that of the trichlorosilylphosphane **2b**), indicating five-coordinate silicon[18,19], is very important for the correct description of **3b**. Compound **3b** is obviously a hitherto unknown hexachlorodisilane−phosphane adduct R(R$'_2$N)(Cl)P−Si(Cl)$_3$−SiCl$_3$ with a *coordinative* phosphorus−silicon bond. The ^{29}Si-NMR spectrum of the other product **4b**, obtained from the reaction of **1b** with Si$_2$Cl$_6$, consists also of two doublet signals from ^1J and $^2J(^{31}\mathrm{P},^{29}\mathrm{Si})$. The chemical shifts and coupling constants of **4b** {^{29}Si NMR: δ = 8.9 [d, $J(^{31}\mathrm{P},^{29}\mathrm{Si})$ = 132.0 Hz, P*Si*Cl$_2$SiCl$_3$], δ = 1.1 [d, $J(^{31}\mathrm{P},^{29}\mathrm{Si})$ = 16.6 Hz, PSiCl$_2$*Si*Cl$_3$]} indicate the presence of a P−Si−Si moiety with *two four-coodinated* silicon atoms, i.e. **4b** will be the new pentachlorodisilanylphosphane *i*Pr(*i*Pr$'_2$N)PSiCl$_2$−SiCl$_3$.

A ^{31}P-NMR signal with satellite patterns from transient species closely related to **3b** also appeared in the course of the reaction of **1c** with hexachlorodisilane [after 50 min at 20 °C: about 40% **3c**, ^{31}P-NMR signal at δ = 51.0 surrounded by two pairs of satellites due to $^1J(^{31}\mathrm{P},^{29}\mathrm{Si})$ = 163.6 Hz and $^2J(^{31}\mathrm{P},^{29}\mathrm{Si})$ = 22.6 Hz, besides 15% of another species with δ^{31}P = 55.6 ppm]. After about 24 h at room temperature, the signals of most **1c** and the intermediate **3c** had disappeared in favor of the final product **2c** (eq. 3).

$$\mathbf{1b,c} + \mathrm{Si_2Cl_6} \longrightarrow \underset{\mathbf{3b,\,c}}{[\mathrm{R(R'_2N)(Cl)P{-}Si_2Cl_6}]} \longrightarrow \mathbf{2b,c} + \mathrm{SiCl_4} \qquad (3)$$

$$\mathbf{1a{-}c} + \mathrm{HSiCl_3} + \mathrm{NEt_3} \longrightarrow \mathrm{R(R'_2N)PSiCl_3} + \mathrm{HNEt_3Cl} \qquad (4)$$

2a: R = *t*Bu, R' = Et
2b: R = *i*Pr, R' = *i*Pr
2c: R = *i*Pr, R' = Ph

Compounds **2a**−**c**, formed in good crude yields (confirmed by ^{31}P NMR; solid by-products had only to be separated from **2a** by filtration or decantation), were isolated in satisfactory yields as pure colorless compounds after distillation. Compounds **2** are thermally stable, but very sensitive to air and moisture. They are volatile as monomeric molecules (M$^+$ observed in the mass spectra).

As an alternative preparation of compounds **2**, the reductive trichlorosilylation of **1a**−**c** in pentane with trichlorosilane in the presence of approximately equimolar amounts of triethylamine was carried out (eq. 4). In all three cases, the reductive trichlorosilylations proceeded much faster with HSiCl$_3$/NEt$_3$ in pentane than with hexachlorodisilane. One or two hours after mixing of the starting compounds in pentane, triethylammonium chloride could be removed by filtration, leading to crude products that were subjected to distillation, leading to pure **2a**−**c** in satisfactory yields. Intermediates **3** and **4b** were *not* observed in the reaction mixtures from **1b** and **c** with HSiCl$_3$/NEt$_3$ in pentane.

Recrystallization of **2c** from pentane provided crystals suitable for an X-ray structure determination.

NMR Spectra of **2a–c**

Like **1a–c**, **2a–c** are chiral. Diastereotopic splitting of the ^{13}C- and ^{1}H-NMR signals of the two types of methyl groups within the isopropyl groups attached to phosphorus is well resolved for **2b** and **2c**. Therefore, rapid inversion at the phosphorus atom of **2b** and **2c** is excluded. In the case of **2b**, for the ^{13}C resonances of the $i\mathrm{Pr_2N}$ groups one broad signal at $\delta = 24.5$ has to be assigned to the two CH_3 groups and two broad signals at $\delta = 45$ and 55 appear where the CH resonance is expected. The corresponding CH_2 signal of **2a** is a doublet at $\delta = 49.6$ [$^{2}J(^{31}P,^{13}C) = 13.1$ Hz]. The P–Si bonds of **2a–c** are confirmed by ^{29}Si- and ^{31}P-NMR spectra (Table 1).

Table 1. ^{31}P- and ^{29}Si-NMR data of compounds **1–4**

Compound	$\delta^{31}P$	$\delta^{29}Si$	$^{1}J(^{31}P,^{29}Si)$[a] [Hz]	$^{2}J(^{31}P,^{29}Si)$[a] [Hz]
1a	156.7			
2a	74.0	6.6 (d)	125.7	
1b	148.4			
2b	35.8	10.1 (d)	123.8	
3b	57.1	9.8 (d)		24.8
		−69.6 (d)	160.7	
4b	42.7[b]	8.9 (d)	132.0	
		1.1 (d)		16.6
1c	144.1			
2c	42.6	9.1 (d)	125.3	
3c	51.0		163.6	22.6
Byproduct of **2c**/**3c**	55.6[c]			

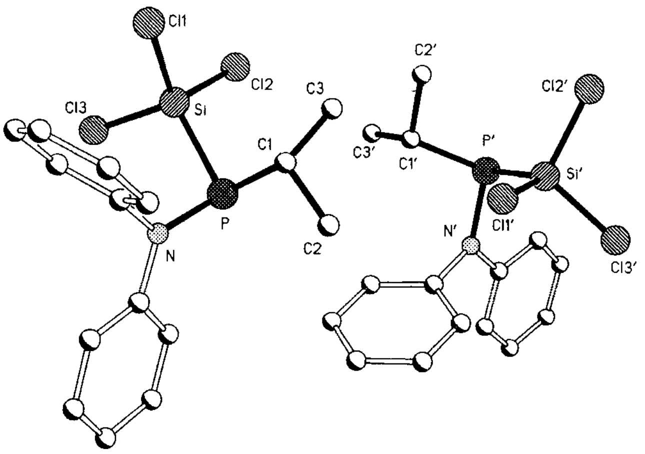
[a] Magnitudes, signs of J were not determined. – [b] In the ^{31}P NMR spectrum of **4b**, $^{2}J(^{31}P,^{29}Si)$ was not resolved. – [c] No ^{29}Si satellites detected.

As in known trichlorosilylphosphanes R_2PSiCl_3[2], large magnitudes of $^{1}J(^{29}Si,^{31}P)$ of **2a–c** (above 100 Hz) reflect the electron-withdrawing effect of three chlorine atoms attached to silicon and the steric requirements of the other two substituents at phosphorus. There is some evidence that the large couplings $^{1}J(^{29}Si,^{31}P)$ of trichlorosilylphosphanes R_2PSiCl_3 coincide with strong P–Si bonds: trichlorosilylphosphanes R_2PSiCl_3 are not cleaved by Me_3GeCl and Me_3SnCl; tri*methyl*silylphosphanes, however, give straightforward exchange reactions with these reagents, providing trimethylgermyl- and -stannylphosphanes[20]. Molecular structures of trichlorosilylphosphanes have not yet been determined. It is known, however, that the P–Si bond of H_2PSiF_3 (220.7 pm)[21] is significantly shorter than the P–Si bond of H_2PSiH_3 (224.9 pm)[22]. *P–Ge*-bonds of trichloro*germyl*phosphanes are also significantly shorter than standard P–Ge single bond lengths[23]. In chlorosilyl derivatives of dicyclopentadienyltungsten, the coincidence of large couplings $^{1}J(^{183}W,^{29}Si)$ with strong W–Si- and weak Si–Cl bonds was attributed to M–Si π-backbonding from the metal into Si–Cl σ* orbitals, leading to some degree of silylene character of the chlorosilyl substituents[24]. It therefore seemed important, to carry out an X-ray crystal structure determination on **2c**, which is a solid at room temperature.

Structure Determination of **2c**

Figure 1 shows the molecular structure of the two independent molecules of crystalline **2c**.

Figure 1. The two independent molecules of crystalline **2c**[a]



[a] H atoms are omitted; selected geometrical parameters [pm, °]: P–C(1) 185.5(5), P–Si 224.9(2), P–N 171.3(4), Cl(1)–Si 202.6(2), Cl(2)–Si 204.3(2), Cl(3)–Si 203.5(2); N–P–C(1) 104.1(2), C(1)–P–Si 103.6(2), N–P–Si 103.57(13), Cl(1)–Si–Cl(3) 108.27(8), Cl(1)–Si–Cl(2) 106.99(8), Cl(3)–Si–Cl(2) 105.78(8), Cl(1)–Si–P 119.40(8), Cl(2)–Si–P 107.89(7), Cl(3)–Si–P 107.74(7); values for the other molecule are similar

The coordination geometry of the phosphorus atoms of both molecules of **2c** is essentially pseudo-tetrahedral (all angles at phosphorus are between 103 and 104°); the nitrogen atom of the diphenylamino group is planar. The P–Si bond length is "normal" (224.9 pm), closely similar to that in H_2PSiH_3; silicon–chlorine distances (203.5 pm) are also as expected for $RSiCl_3$ species, and there is no indication of significant π-backbonding from the phosphorus lone pair into Si–Cl σ* orbitals. Structures of comparable diorganylamino(tri*methyl*silyl)phosphanes $R(R'_2N)PSiMe_3$ are not yet known. The recent structure determination of a triphosphane containing P–N bonds and a P–SiMe₃ group within the molecule (but not involving the same phosphorus atom)[25] revealed P–N and P–Si bond lengths similar to those of **2c**. In summary, the rather large magnitude of the NMR coupling $^{1}J(^{31}P,^{29}Si)$ of **2c** does *not* coincide with an unusually short P–Si bond length.

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Experimental

^{1}H-, ^{13}C-, ^{31}P-, and ^{29}Si-NMR spectra: Bruker AC-200 spectrometer, solvent [D$_6$]benzene. – MS: Finigan Mat 8430. – Elemental analyses: Carlo Erba analytical gaschromatograph. – All experiments were carried out under deoxygenated dry nitrogen as inert gas, solvents were dried according to standard procedures.

Preparation of Alkylchlorodiorganylaminophosphanes $R(R'_2N)$-PCl: $t\mathrm{Bu(Et_2N)PCl}$ (**1a** ($\delta^{31}P = 156.7$) was prepared by reaction of $t\mathrm{BuPCl_2}$ with $\mathrm{Et_2NH}$[26], $i\mathrm{Pr}(i\mathrm{Pr_2N})\mathrm{PCl}$ (**1b**) ($\delta^{31}P = 148.4$) and $i\mathrm{Pr(Ph_2N)PCl}$ (**1c**) ($\delta^{31}P = 144.1$) were prepared by reaction of the corresponding chlorophosphanes $RPCl_2$ with the appropriate lithium amides R'_2NLi.

tert-Butyl(diethylamino)(trichlorosilyl)phosphane (tBu(Et_2N)-$PSiCl_3$, **2a**). – a) *By Reaction with Si_2Cl_6*: 1.30 g (0.007 mol) of Si_2Cl_6 was added to tBu(Et_2N)PCl (1.77 g; 0.007 mol) and the mixture was stirred for 20 h at room temp. After this time a yellow-white precipitate had formed. To this suspension was added pentane (10 ml) and the precipitate was filtered off. The volatile substances were removed under reduced pressure and the residue was distilled at 58°C (0.01 mbar) to yield 0.60 g (31%) of tBu(Et_2N)$PSiCl_3$.

b) *By Reaction with $HSiCl_3$*: To a stirred solution of tBu(Et_2N)PCl (13.00 g; 0.067 mol) and $HSiCl_3$ (16.53 g; 0.122 mol) in pentane (100 ml) was added dropwise NEt_3 (12.37 g; 0.122 mol) in pentane (50 ml). Stirring was continued for 2 h to ensure complete reaction and the $HNEt_3Cl$ precipitate was filtered off. From the filtrate pentane was removed under reduced pressure. Distillation of the residue at 58°C (0.01 mbar) yielded 7.10 g (36%) of tBu(Et_2N)$PSiCl_3$. – ^{31}P NMR: $\delta = 74.0$ (s). – ^{29}Si NMR: $\delta = 6.6$ [d, $J(^{31}P,^{29}Si) = 125.7$ Hz]. – ^1H NMR: $\delta = 1.12$ [t, $J(^1H,^1H) = 7.04$ Hz, 6H, $N(CH_2C\mathit{H}_3)_2$], 1.63 [d, $J(^1H,^{31}P) = 15.1$ Hz, 9H, $C(C\mathit{H}_3)_3$], 3.15 [m, 4H, br)]. – ^{13}C NMR: $\delta = 15.3$ [s, 2C, $N(CH_2\mathit{C}H_3)_2$], 29.1 [d, $J(^{13}C,^{31}P) = 16.2$ Hz, 3C, $C(\mathit{C}H_3)_3$], 39.9 [d, $J(^{13}C,^{31}P) = 29.0$ Hz, 1C, $\mathit{C}(CH_3)_3$], 49.6 [d, $J(^{13}C,^{31}P) = 13.1$ Hz, 2C, $N(\mathit{C}H_2CH_3)_2$]. – MS (EI, 70 eV), *m/z* (%): 293 (8) [M^+]. – $C_8H_{19}Cl_3NPSi$ (294.71): calcd. C 32.61, H 6.50, N 4.75; found C 32.65, H 6.72, N 4.96.

Isopropyl(diisopropylamino)(trichlorosilyl)phosphane (iPr($i$$Pr_2N$)-$PSiCl_3$, **2b**). – a) *By Reaction with Si_2Cl_6*: 1.16 g (0.004 mol) of Si_2Cl_6 was added to iPr($i$$Pr_2N$)PCl (0.90 g, 0.004 mol) and the mixture was stirred for 3 d at room temp. $SiCl_4$ was removed under reduced pressure. Distillation of the residue at 72°C (0.01 mbar) yielded 0.40 g (30%) of iPr($i$$Pr_2N$)$PSiCl_3$.

b) *By Reaction with $HSiCl_3/NEt_3$*: To a stirred solution of iPr($i$$Pr_2N$)PCl (10.25 g, 0.049 mol) and 10.36 g (0.076 mol) of $HSiCl_3$ in pentane (100 ml) was added dropwise NEt_3 (7.68 g, 0.076 mol) in pentane (50 ml). Stirring was continued for 2 h to ensure complete reaction and the $HNEt_3Cl$ precipitate was filtered off. From the filtrate pentane was removed under reduced pressure. Distillation of the residue at 72°C (0.01 mbar) yielded 9.80 g (64.8%) of iPr($i$$Pr_2N$)$PSiCl_3$). – ^{31}P NMR: $\delta = 35.8$ (s). – ^{29}Si NMR: $\delta = 10.1$ [d, $J(^{31}P,^{29}Si) = 123.8$ Hz]. – ^1H NMR: $\delta = 0.99$ [t, $J(^1H,^{31}P) = 7.2$ Hz, 6H, $CH(C\mathit{H}_3)_2$], 1.097 {d, $J(^1H,^1H) = 7.2$ Hz, 6H, $N[CH(CH_3)_2]_2$}; 1.108 {d, $J(^1H,^1H) = 6.6$ Hz, 6H, $N[CH(C\mathit{H}_3)_2]_2$}, 2.32 [m, $J(^1H,^{31}P) = 7.0$ Hz, 1H, $C\mathit{H}(CH_3)_2$], 3.3 [m, (br)]. – ^{13}C NMR: $\delta = 18.5$ [d, $J(^{13}C,^{31}P) = 21.8$, 1C, $CH(\mathit{C}H_3)_2$], 21.54 [d, $J(^{13}C,^{31}P) = 20.9$ Hz, 1C, $CH(\mathit{C}H_3)_2$], 24.5 {m (br), $N[CH(\mathit{C}H_3)_2]_2$}, 25.0 [d, $J(^{13}C,^{31}P) = 11.5$ Hz, 1C, $\mathit{C}H(CH_3)_2$], 45.0 {m, (br), $N[\mathit{C}H(CH_3)_2]_2$}; 55.0 {m, (br), $N[\mathit{C}H(CH_3)_2]_2$}. – MS (EI, 70 eV), *m/z* (%): 307 (2) [M^+]. – $C_9H_{21}Cl_3NPSi$ (308.69): calcd. C 35.02, H 6.8, N 4.54; found C 36.54, H 7.20, N 5.76.

iPr($i$$Pr_2N$)$PClSi_2Cl_6$ (**3b**): To a stirred solution of iPr($i$$Pr_2N$)PCl (2.83 g; 0.014 mol) in CH_2Cl_2 (10 ml) was added Si_2Cl_6 (4.00 g; 0.015 mol). The solution was heated to 55°C for 6 h. ^{31}P-NMR spectra of the solution were recorded aftet 1 h, 4 h, and 5 h. After 6 h the volatile substances were removed under reduced pressure and the ^{29}Si-NMR spectrum was recorded. **3b**: ^{31}P NMR: $\delta = 57.1$ (s). – ^{29}Si NMR: $\delta = 9.8$ [d, $J(^{31}P,^{29}Si) = 24.8$ Hz, $PSiCl_3\mathit{Si}Cl_3$], -69.6 [d, $J(^{31}P,^{29}Si) = 160.7$ Hz, $P\mathit{Si}Cl_3SiCl_3$].

4b: ^{31}P NMR: $\delta = 42.7$ (s). – ^{29}Si NMR: $\delta = 8.9$ [d, $J(^{31}P,^{29}Si) = 132.0$ Hz, $P\mathit{Si}Cl_2SiCl_3$], 1.1 [d, $J(^{31}P,^{29}Si) = 16.6$ Hz, $PSiCl_2\mathit{Si}Cl_3$].

Table 2. Integrals of the compounds **1b**–**4b** in the mixture

	δ(^{31}P-NMR)	*I* (1 h)[a]	*I* (4 h)	*I* (5 h)	*I* (6 h)	*I* (20 h)
1b	148.4	100.0	100.0	100.0	100.0	100.0
2b	35.8	–	–	–	–	3.5
3b	57.1	–	8.0	24.5	29.5	29.5
4b	42.7	–	2.5	8.0	9.0	13.5

[a] *I* = integrals (highest value: 100)

Isopropyl(diphenylamino)(trichlorosilyl)phosphane (iPr(Ph_2N)-$PSiCl_3$, **2c**). – a) *By Reaction with Si_2Cl_6*: Si_2Cl_6 (7.65 g; 0.028 mol) was added to iPr(Ph_2N)PCl (7.89 g; 0.028) and the mixture was stirred at room temperature. The intermediate **3c** was detected in the ^{31}P-NMR spectrum [$\delta = 51.0$, $^1J(^{31}P,^{29}Si) = 163.6$ Hz, $^2J(^{31}P,^{29}Si) = 22.6$ Hz] of the reaction mixture 50 min after the addition of Si_2Cl_6. After 24 h $SiCl_4$ was removed under reduced pressure. Distillation of the residue at 145°C (0.01 mbar) yielded 8.39 g (79.6%) of iPr(Ph_2N)$PSiCl_3$.

Table 3. Integrals of the compounds **1c**–**3c** in the mixture

	δ(^{31}P-NMR)	*I*[a] (50 min)	*I* (24 h)
1c	144.1	30.8	35.0
2c	42.6	89.1	100.0
3c	51.0	100.0	2.0
Byproduct[b]	55.6	38.4	24

[a] *I* = integrals (highest value: 100). – [b] Byproduct: not identified, no satellite signals due to $J(^{31}P,^{29}Si)$.

b) *By Reaction with $HSiCl_3$*: To a stirred solution of iPr(Ph_2N)PCl (5.43 g; 0.020 mol) and $HSiCl_3$ (3.32 g; 0.024 mol) in pentane (50 ml) was added dropwise 2.40 g (0.024 mol) of NEt_3 in pentane (20 ml). Stirring was continued for 1 h to ensure complete reaction and the $HNEt_3Cl$ precipitate was filtered off. From the filtrate pentane was removed under reduced pressure. The solid product was recrystallized twice from pentane at −20°C to give 4.74 g (63%) of iPr(Ph_2N)$PSiCl_3$; m. p. 48°C. – ^{31}P NMR: $\delta = 42.6$ (s). – ^{29}Si NMR: $\delta = 9.1$ [d, $J(^{31}P,^{29}Si) = 125.3$ Hz]. – ^1H NMR: $\delta = 0.97$ [dd, $J(^1H,^{31}P) = 9.55$ Hz, $J(^1H,^1H) = 6.50$ Hz, 3H, $CH(C\mathit{H}_3)_2$], 1.06 [pseudo t, $J(^1H,^{31}P) = 6.50$ Hz, $J(H,^1H) = 6.50$ Hz, 3H, $CH(C\mathit{H}_3)_2$], 2.63 [pseudo oct, $J(^1H,^{31}P) = 6.98$ Hz, $J(^1H,^1H) = 6.98$ Hz, 1H, $C\mathit{H}(CH_3)_2$], 6.98–7.25 (m, 10H, aromatic H). – ^{13}C NMR: $\delta = 17.53$ [d, $J(^{13}C,^{31}P) = 26.8$ Hz, $\mathit{C}H(CH_3)_2$], 20.30 [d, $J(^{13}C,^{31}P) = 19.1$ Hz, $CH(\mathit{C}H_3)_2$], 26.25 [d, $J(^{13}C,^{31}P) = 15.2$ Hz, $CH(\mathit{C}H_3)_2$], 124.2 [s, *C*-4, Ph_2N], 125.0 [d, $J(^{13}C,^{31}P) = 6.1$ Hz, *C*-2/6, Ph_2N], 129.5 [s, C-3/5, Ph_2N], 148.8 [d, $J(^{13}C,^{31}P) = 7.2$ Hz, *C*-1, Ph_2N]. – $C_{15}H_{17}Cl_3NPSi$ (376.76): calcd. C 47.82, H 4.55, N 3.72; found C 48.33, H 4.80, N 3.63.

Structure Determination of **2c**[27]: Crystal data: $C_{15}H_{17}Cl_3NPSi$, $M = 376.71$, $P2_1/c$, $a = 1999.2(2)$, $b = 983.27(10)$, $c = 1961.8(2)$ pm, $\beta = 112.712(6)°$, $V = 3.5574(5)$ nm^3, $Z = 8$, $\mu = 0.67$ mm^{-1}, $T = -100$°C. A colorless plate (0.60 × 0.40 × 0.35 mm) was mounted in inert oil. 8177 intensities were measured to 2 Θ_{max} 55° by using Mo-K_α radiation on a Siemens R4 diffractometer. Of these 8104 were unique ($R_{int} = 0.0113$) and 8049 used for all calculations (program SHELXL-92). The structure was solved by direct methods and refined anisotropically on F^2. The final $wR(F^2)$ was 0.124, with conventional R(F) = 0.059 for 381 parameters.

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[27] 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-401536, the names of the authors and the journal citation.

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