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Reactions of the Disilane Me$_3$SiSiCl$_3$ with *P*-Chlorophosphaalkenes: Transient and Persistent Per-Silylated Phosphaalkenes

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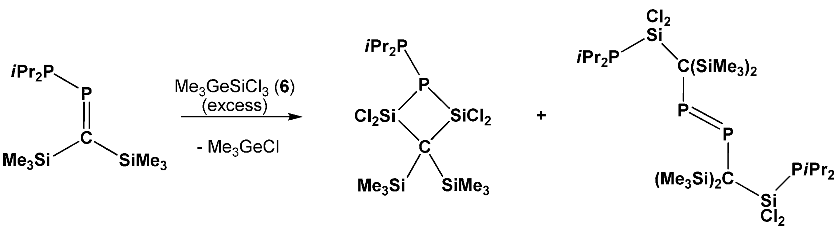
Reactions of *P*-chlorophosphaalkenes (RMe$_2$Si)$_2$C=PCl (**1a**: R = Me; **1b**: R = Ph) with the disilane Me$_3$SiSiCl$_3$ (**5**) furnish diphosphenes (Cl$_3$Si)(RMe$_2$Si)$_2$C–P=P–C(SiCl$_3$)(SiMe$_2$R)$_2$ (**4a**: R = Me; **4b**: R = Ph) by Me$_3$SiCl elimination. The structure of the new compound **4b** was confirmed by X-ray diffraction; it displays crystallographic inversion symmetry. Monitoring the reactions with ^{31}P- and ^{29}Si-NMR spectroscopy detected *P*-(trichlorosilyl)phosphaalkenes (RMe$_2$Si)$_2$C=PSiCl$_3$ (**2a**, R = Me; **2b**, R = Ph) as the primary intermediates from reductive *P*-silylation of **4a**, **4b**, and *P*-[(trichlorosilyl)phosphanyl]phosphaalkenes (RMe$_2$Si)$_2$C=P–P(SiCl$_3$)C(SiCl$_3$)(SiMe$_2$R)$_2$ (**3a**: R = Me; **3b**: R = Ph) as unsymmetric dimerisation products that rearrange to provide **4a**, **4b** in step III of the reaction sequence. This step (the P→C 1,3-trichlorosilyl shift reaction) was mimicked by the synthesis of (Me$_3$Si)$_2$C=P–P(SiCl$_3$)*t*Bu (**7**), which rearranges into an unsymmetric diphosphene *t*BuP=PC(SiMe$_3$)$_2$SiCl$_3$ (**8**). The bulkier *P*-chlorophosphaalkene (*i*PrMe$_2$Si)$_2$C=PCl (**1c**) reacts with **5**, eliminates Me$_3$SiCl and thereby provides the first persistent acyclic per-silylated phosphaalkene (*i*PrMe$_2$Si)$_2$C=PSiCl$_3$ (**2c**) in an incomplete reaction. **2c** exhibits an exceptionally large NMR coupling $^1J(^{31}P,^{29}Si) = \pm 249$ Hz. Within weeks, the mixtures of **1c** and **2c** undergo decomposition with loss of the P=C functions.

Introduction

Most of the significant advances in the chemistry of stable carbenes and group 14 carbene analogues in the last three decades have been based on the use of sterically and electronically stabilising substituents.[1] In contrast, synthetic progress to simple *dihalogenosilylenes* has been very limited since Timms' high-temperature and matrix studies.[2,3] Oligomeric silanes of empirical formula SiCl$_2$ are synthetically available, but they do not behave as sources of monomeric SiCl$_2$,[4] and the alternative use of Si$_2$Cl$_6$[5] or HSiCl$_3$[6] as precursors is very limited. Only very recently, complexes of nucleophilic carbenes with silicon dihalides were isolated,[7] and a carbene adduct of SiCl$_2$ was found to act as source of reactive SiCl$_2$ species.[7b] As a proton-free alternative to HSiCl$_3$, we have reported the use of trichlorosilyltrimethylgermane (Me$_3$GeSiCl$_3$)[8] as a reagent for the transfer of SiCl$_2$ moieties to *P*-phosphanylphosphaalkenes that leads under very mild reaction conditions either to insertion of two equivalents of SiCl$_2$ into the P=C bond, or to a diphosphene with remote C–SiCl$_2$–P*i*Pr$_2$ functions (Scheme 1).[9]



Scheme 1. Dichlorosilylene transfer from Me$_3$GeSiCl$_3$ to a *P*-phosphanylphosphaalkene.[9]

No intermediates of this reaction were observed spectroscopically. A related diphosphene with remote C–SiCl$_3$ functions, and also the corresponding germanium compound, were isolated by Zanin, Karnop, et al. in a previous study on reactions of the *P*-chlorophosphalkene (Me$_3$Si)$_2$-

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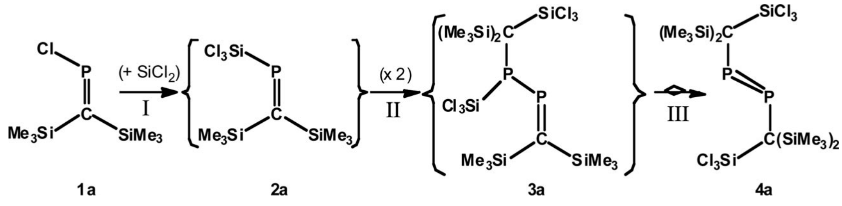


Scheme 2. Expected reaction path of the reaction of **1a** with a dichlorosilylene source.[10]

C=PCl (**1a**) with Si_2Cl_6 and with the $GeCl_2$ dioxane complex.[10] In the course of these reactions in a heated solvent, very small ^{31}P-NMR AX patterns were observed, but after complete consumption of **1a**, only the NMR signals of the diphosphene products remained. The intermediacy of a persilylated phosphaalkene $(Me_3Si)_2C{=}PSiCl_3$ (**2a**) in the case **1a**/Si_2Cl_6 was expected by analogy to the *reductive trichlorosilylations* of dialkylchlorophosphanes R_2PCl and bulky alkyldichlorophosphanes $RPCl_2$ with Si_2Cl_6, providing silylphosphanes R_2PSiCl_3 and $RP(SiCl_3)_2$ by elimination of silicon tetrachloride,[11,8b] but the existence of **2a** was not unambiguously demonstrated. The weak ^{31}P-NMR AX pattern was tentatively assigned to a transient dimeric species, the *P*-phosphanylphosphaalkene $(Me_3Si)_2C{=}P{-}P(SiCl_3)C(SiCl_3)(SiMe_3)_2$ (**3a**), which was assumed to rearrange by a trichlorosilyl 1,3-P→C shift reaction (step III, Scheme 2) to $(Cl_3Si)(Me_3Si)_2C{-}P{=}P{-}C(SiCl_3)(SiMe_3)_2$ (**4a**), an inversion-symmetric diphosphene. A similiar pathway presumably leads to the *C*-trichlorogermyl diphosphene $(Cl_3Ge)(Me_3Si)_2C{-}P{=}P{-}C(GeCl_3)(SiMe_3)_2$.

Using bulkier persistent germylenes and stannylenes, primary products from carbene-like insertions into the P–Cl bond of **1a** were identified spectroscopically,[12] but the detailed pathway of the *Zanin*/*Karnop* silylation and germylation reaction is still an unsolved problem.[10]

Open questions concerning the surprising formation of **4a** from **1a** are: is **2a** really an intermediate of the reaction (step I in Scheme 2), *and*, assuming that the role of **2a** were confirmed experimentally: is **2a** formed by $Cl^-/SiCl_3^-$ exchange or by $SiCl_2$ transfer ?[13] Finally, the proposed constitution of **2a** and **3a** has yet to be subjected to experimental evidence by ^{29}Si-NMR including analysis of NMR couplings $J(^{31}P,^{29}Si)$. To obtain access to compounds related to the elusive intermediates **2a** and **3a** from the $(Me_3Si)_2C{=}P{-}Cl/Si_2Cl_6$ reaction, we chose the following experimental variations of the system:

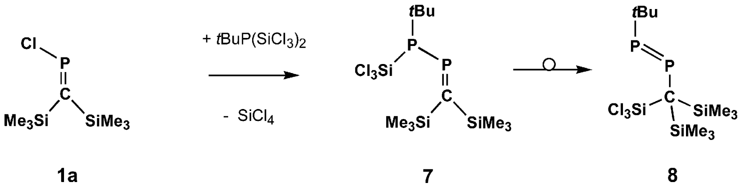
1. Replacement of Si_2Cl_6 by the unsymmetric disilane $Me_3SiSiCl_3$ (**5**) [analogous to the above-mentioned $Me_3GeSiCl_3$ (**6**)] as a more reactive silylating agent,[8] to allow milder reaction conditions for the generation of the short-lived intermediate **2a**.
2. (i) Replacement of Me_3Si groups in $(Me_3Si)_2C{=}P{-}Cl$ (**1a**) by bulkier *i*PrMe_2Si groups,[14] which are expected to affect the rates of steps II (dimerisation) and III (P→C 1,3-silyl shift reaction), leading to enhanced lifetimes of intermediates related to **2a** and **3a**. (ii) Use of $PhMe_2Si$ groups, which are known to be less efficient than Me_3Si in the "hierarchy" of silyl groups as protecting agents, in order to vary the rates of steps I–III and especially to enhance the rate of step I.
3. Independent efficient access to, and unambiguous characterisation of, a *P*-[(trichlorosilyl)phosphanyl]phosphaalkene related to **3a**, which may rearrange to another diphosphene by the postulated 1,3-trichlorosilyl shift reaction (step III).

Results and Discussion

NMR-Study of an Alternative Route to a *P*-[(Trichlorosilyl)-phosphanyl]phosphaalkene Related to 3a

In a variation of McDiarmid's trichlorosilylation of Me_4P_2 with Si_2Cl_6 furnishing two equivalents of Me_2PSiCl_3,[15] Si_2Cl_6 was found to act as a reductive silylating agent towards dialkylchlorophosphanes R_2PCl and bulky alkyldichlorophosphanes $RPCl_2$, providing silylphosphanes R_2PSiCl_3 and $RP(SiCl_3)_2$.[10] This facile conversion of P–Cl to P–$SiCl_3$ functions had prompted the attempt to convert *P*-chlorophosphaalkene $(Me_3Si)_2C{=}PCl$ (**1a**)[16] into the unknown $(Me_3Si)_2C{=}PSiCl_3$ (**2a**); this led, however, experimentally via postulated **3a** to isolated **4a**.[10]

In our search for an alternative access to *P*-[(trichlorosilyl)phosphanyl]phosphaalkenes related to the intermediate **3a**, we considered exploiting the (trichlorosilyl)phosphane method, which is known to convert the chlorophosphaalkene **1a** into *P*-phosphanylphosphaalkenes $(Me_3Si)_2C{=}P{-}PR_2$ by reactions with (trichlorosilyl)phosphanes R_2PSiCl_3;[17] the selective 1:1 reaction of a bis(trichlorosilyl)phosphane $RP(SiCl_3)_2$ with **1a** should provide the corresponding *P*-[(trichlorosilyl)phosphanyl]phosphaalkene $(Me_3Si)_2C{=}P{-}P(R)SiCl_3$. The availability of *t*BuP$(SiCl_3)_2$,[11] either from the Si_2Cl_6 method or the $HSiCl_3/NEt_3$ pathway,[11c] prompted us to choose its the 1:1 reaction with **1a**, which indeed led straightforwardly by elimination of $SiCl_4$ to the desired [*tert*-butyl(trichlorosilyl)phosphanyl] phosphaalkene **7**. This compound exhibits in ^{31}P-NMR a characteristic AX pattern and a large coupling constant $^1J(^{31}P,^{29}Si)$ [$\delta^{31}P$ = 389.3, *P*=C; –24.9, *P*-Si, ^1J(P,Si) = ±112.6, ^1J(P,P) ±232.4 Hz]. Compound **7** is persistent at room temperature, but upon attempted distillation, heating furnishes the unsymmetric diphosphene *t*BuP=PC$(SiMe_3)_2SiCl_3$ (**8**), which is unambiguously characterized by its ^{31}P-NMR pattern [δ = 604.0 and 531.3 ppm, $^1J(^{31}P,^{31}P)$ = ±629.9 Hz]. This result supports the proposed rearrangement **3a** → **4a** (step III, Scheme 2), establishing a pathway to unsymmetric diphosphenes (Scheme 3).[18]



Scheme 3. Formation and rearrangement of a *P*-[(trichlorosilyl)phosphanyl]phosphaalkene.

Reductive Trichlorosilylation Reactions of Modified *P*-Chlorophosphaalkenes

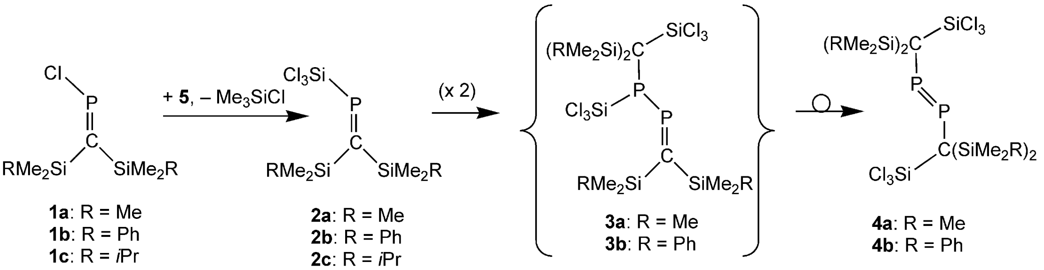
Silylation of 1a with $Me_3GeSiCl_3$ (6)

The reaction of chlorophosphaalkene **1a** with (trichlorosilyl)germane **6** at room temperature can be followed by ^{31}P NMR, exhibiting an AX pattern assigned to intermediate **3a** and the singlet signal of the diphosphene **4a**, which slowly increases in intensity. The use of excess **6** leads to the appearance of further (very weak) AX-patterns in ^{31}P NMR, which are tentatively assigned to products from $SiCl_2$ addition to the P=C bond of **3b**.[9] Compound **2a** can be observed in ^{31}P-NMR at an early stage of the reaction by its very weak singlet signal, which is just strong enough to allow the resolution of ^{29}Si satellites, and exhibits a very large coupling constant $^1J(^{31}P,^{29}Si) = \pm 243.4$ Hz, even larger in magnitude than couplings found in species with P=Si double bonds.[19] This observation correlates well with the exceptionally large coupling constants $^1J(^{31}P,^{117,119}Sn)$ in Niecke's related stannylene insertion product $Ph(Me_3Si)C{=}PSn(Cl)(\mu\text{-}NtBu)_2SiMe_2$, which in ^{31}P-NMR exhibits $^1J(^{31}P,^{117,119}Sn)$ of ±1884.9 Hz and ±1972.5 Hz,[12] i.e., in a similar range to compounds with Sn=P π-bonds and to tin tetrahalide–trialkylphosphane complexes.[20]

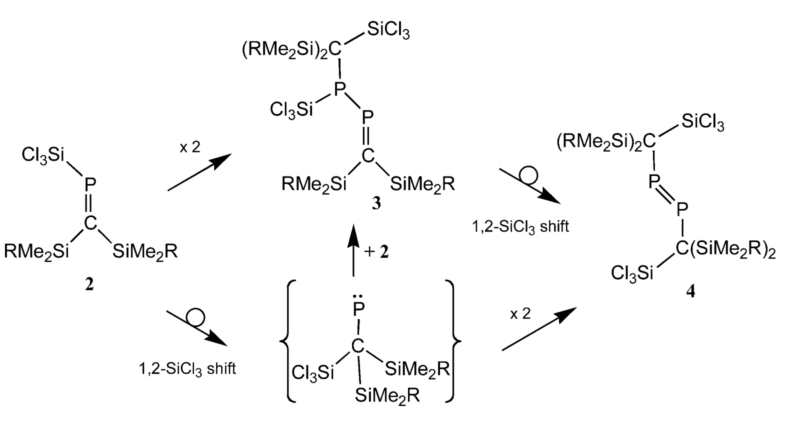
Silylation of 1a with $Me_3SiSiCl_3$ (5)

The reaction of **1a** with **5** at room temperature proceeds significantly faster than with **6**, allowing the observation in ^{31}P-NMR of small amounts of transient **2a** (Scheme 4) and large amounts of **3a** (the main product at room temperature), accompanied by the diphosphene **4a**. After the initial appearance of some **4a** at an early stage of the reaction, its amount does not increase significantly at room temperature. Isolation of pure **3a**, clearly a persistent species at room temperature, from such reaction mixtures was not achieved, but it was spectroscopically analysed by ^{31}P and ^{29}Si NMR spectroscopy. The high concentration of **3a** in the mixture allowed the first determination of its full set of ^{29}Si-NMR parameters (see below).

The complete conversion of the *P*-[(trichlorosilyl)phosphanyl]phosphaalkene **3a** into the known diphosphene **4a** requires heating of the reaction mixture. In this respect intermediate **3a** resembles the model compound **7**. The observation that a considerable amount of **4a** accompanies **3a** at an early stage of the overall reaction, whereas the complete conversion of **3a** into **4a** requires heating (i.e., involving a higher energy of activation for the step III rearrangement) needs an explanation. The source of "early" **4a** may be the



Scheme 4. Products from the reactions of *P*-chlorophosphaalkenes **1a**–**c** with $Me_3SiSiCl_3$ (**5**).



Scheme 5. Possible reaction paths from *P*-(trichlorosilyl)phosphaalkenes to diphosphenes.

direct dimerisation of **2a** to (symmetric) **4a**, competing with the dimerisation delivering (unsymmetric) **3a**. This means that the proposed mechanism **2a** → **3a** → **4a** involves a bifurcated pathway with the additional "shortcut" **2a** → **4a**. When the supply of **2a** is exhausted, **3a** remains the only source of **4a**. The point of bifurcation might be a transient phosphanylidene-like species that can dimerise either by phosphorus insertion into a P–Si bond of **2a** delivering **3a**, or by direct P=P bond formation delivering the diphosphene **4a** (Scheme 5).

Reaction of 1b with $Me_3SiSiCl_3$ (5)

This reaction basically follows the reaction sequence corresponding to the Zanin–Karnop mechanism[10,13] (Schemes 2 and 4) when we consider the formation of **2b** and **3b** as intermediate products, but it is faster than the reaction of **1a** with **5**. High concentrations of intermediate **2b** at an early stage of the reaction indicate that step I particularly is accelerated when **1b** is used as starting material. However, in this case there is also evidence for a competing second reaction pathway leading initially to an asymmetric diphosphene that finally delivers the symmetric diphosphene **4b**, the final product and the only isolated and completely characterized compound from the reaction of **1b** with **5**.

In the case of **1b** + **5** we observed in the reaction mixture by ^{31}P NMR, apart from **2b**, **3b**, and **4b**, also the AX-pattern of a further transient species [δ^{31}P = 401.9 ppm (d), 332.3 ppm (d), ^1J(P,P) = ±597 Hz]. Both ^{31}P-NMR shifts are in the "phosphaalkene range", but the magnitude of ^1J(P,P) would fit to a P=P double bond. This species of unknown structure is apparently a precursor to an asymmetric diphosphene [δ^{31}P = 561.9 (d), 502.5 (d), ^1J(P,P) = 620.5 Hz]. The appearance of these transient species with ^{31}P-NMR AX patterns suggests the existence of a further reaction path (independent of the Zanin–Karnop mechanism)[10,13] to final **4b**. The aspect of an intermediate asymmetric diphosphene has been neglected so far; traces of an asymmetric diphosphene were also noticed after the silylation of **1a** [δ^{31}P = 569.1 ppm (d), 504.7 ppm (d), ^1J(P,P) = ±616 Hz (P=P)].

The chemical composition of compound **4b** has been confirmed by a correct elemental analysis and by mass spectrometry. The mass spectrum shows a characteristic isotopic distribution for the molecular ion {[M]$^+$, *m/z* = 895.9 }, {[M – CH$_3$]$^+$, *m/z* = 880.9}, {[(M – SiCl$_3$)$^+$], *m/z* = 761}. The base peak at *m/z* = 135 corresponds to the (SiMe$_2$Ph)$^+$ ion according to the isotopic distribution. **4b** shows in ^{31}P-NMR a singlet at δ = 573.6 ppm. The ^{29}Si-NMR chemical shifts have been assigned according to an INEPT measurement that allowed a correct calculation of the integrals for the two distinct ^{29}Si nuclei δ = –4.3 ppm (*Si*Me$_2$Ph, integral 2Si) and –7.1 ppm (*Si*Cl$_3$, integral 1Si). Both resonances (expected to be X-parts of AA′X pattern) appear as broad signals, ruling out the determination of coupling constants with ^{31}P. The ^{13}C-NMR signals appear as broadened multiplets, also providing little information about the coupling constants with ^{31}P. The two types of chemically equivalent, but magnetically inequivalent CH$_3$ groups (diastereomers) appear as X parts of AA′X systems, δ = 0.88 ppm ("t", *C*H$_3$), 2.86 ppm ("t", *C*H$_3$). Their protons also exhibit diastereomeric behavior, i.e. ^{1}H-NMR presents two singlets in the SiCH$_3$ region, δ = 0.7 ppm (s, C*H*$_3$, 6 H) and 0.35 ppm (s, C*H*$_3$, 6 H). The quaternary carbon atom at δ = 40.9 ppm was assigned according to the data offered by H,C-HMBC correlation [^2J(H,C) with methyl protons]. An H,C-HSQC correlated spectrum also allowed the assignment of the NMR resonances corresponding to phenyl protons, as follows: 7.45 (d, t, *ortho*, 2 H), 7.23–7.29 (m, *para*, 1 H), 7.15–7.22 (m, *meta*, 2 H).

Solid **4b** is a inversion-symmetric diphosphene with a central P=P bond length of 2.0347(4) Å and C–P=P angles of 106.83(3)°. (Figure 1). Searches of the Cambridge Database (Version 1.12)[21] revealed the following results: (i) The fragment C–P=P–C with two-coordinate phosphorus, no coordination to metals and no annelation appears 23 times with P=P 1.985–2.050, av. 2.024 Å. (ii) There are only three other structures with Si$_3$C substituents at phosphorus, namely Zanin's compound **4a**,[10] our derivative with remote C–SiCl$_2$–P*i*Pr$_2$ functions[9] (Scheme 1), and the bis[tris(trimethylsilyl)methyl]diphosphene investigated independently by two groups;[22] all these molecules display inversion symmetry and the C–P=P angles are 106.0–108.3, av. 107.4°.

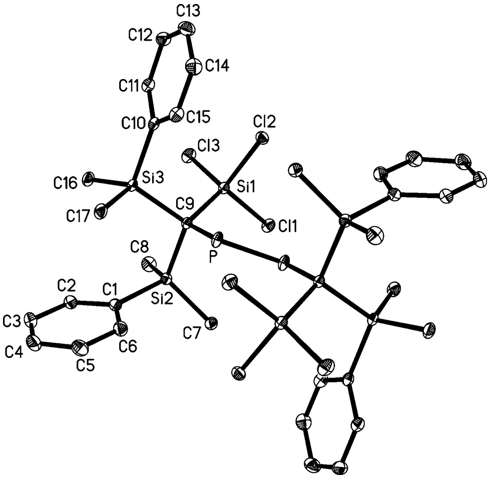


Figure 1. Molecular structure of **4b** (H atoms omitted). Thermal ellipsoids are set at 50% probability. Selected bond lengths [Å]: P–P#1 2.0347(4), P–C(9) 1.8863(8), C(9)–Si(3) 1.9663(8), C(9)–Si(1) 1.8522(9), C(10)–Si(3) 1.8762(9), C(16)–Si(3) 1.8656(9), Cl(1)–Si(1) 2.0553(3). Selected bond angles [°]:C(9)–P–P#1 106.83(3), P–C(9)–Si(2) 109.26(4), P–C(9)–Si(3) 101.91(4), Si(1)–C(9)–P 112.13(4), C(9)–Si(1)–Cl(2) 114.73(3), Cl(2)–Si(1)–Cl(3) 105.178(14).

Compound **4b** also displays two short contacts: intramolecular P···Cl1#1 3.469 Å and intramolecular H14···Cl1 2.94 Å, connecting the molecules by translation parallel to the *a* axis.

Reactions of Phosphaalkene 1c with 5 and with 6

This variation of the system – a starting material with bulkier *C*-silyl substituents – was intended to inhibit the dimerisation process **2** → **3**, allowing the enrichment and isolation of compound **2c**.

However, addition of germylsilane **6** to **1c** leads to the formation of only traces of the new species **2c**. Enrichment of **2c** from such mixtures was not achieved. The ^{31}P-NMR signals of starting material **1c** and product **2c** (traces) are accompanied by those of another *P*-trichlorosilyl species [δ = –93 ppm, ^{1}J(P,Si) = ±128.8, ^{1}J(P,H) = ±220 Hz] that can be assigned the structure (iPrMe$_2$Si)$_2$C(SiCl$_3$)–PH(SiCl$_3$). The amount of this species (^{31}P-NMR intensity < 5% relative to that **1c**) does not increase further, even after three weeks.

Addition of disilane **5** to **1c** leads to the formation of considerable amounts of the new species **2c**, and with excess of **5** the approximate content of **2c** in the mixture (from ^{31}P-NMR intensities) can reach 35–45%. Further enrichment of **2c** from such mixtures was not achieved. The above-mentioned species (iPrMe$_2$Si)$_2$C(SiCl$_3$)–PH(SiCl$_3$) also appears in the reaction mixture from **1c** and **5**, but in even smaller amounts than in the previous case.

A careful analysis of the ^{29}Si-satellite pattern in the ^{31}P-NMR of **2c** spectrum allowed us to identify only two of the Si,P coupling constants, ^{1}J(P,Si) = ±249.2 Hz and ^{2}J(P,Si) = ±32.3 Hz. The exceptional magnitudes of ^{1}J(P,Si) in **2a**–**2c** gave rise to a quantum chemical consideration of compounds related to **2a**. For reasons of simplicity, *P*-(trichlorosilyl)phosphaalkenes with less bulky *C*-silyl substituents were studied. The calculations were performed with Gaussian on B3LYP/6-31G* geometry with GIAO/BHandHLYP/B2. The calculated coupling constants of compound (H$_3$Si)$_2$C=PSiCl$_3$ are ^{1}J(^{31}P, ^{29}Si) = –368, ^{2}J(^{31}P, ^{29}Si) [*cis*-silyl groups] = –28, ^{2}J(^{31}P, ^{29}Si) [*trans*-silyl groups] = +32 Hz.[24]

The ^{31}P-NMR signal of **2c** (δ^{31}P = 377.2 ppm) appears about 33 ppm downfield shifted from the starting material **1c**. The high concentration of **2c** in the mixture allowed for the first time the determination of the full set of ^{29}Si-NMR parameters of a "per-silylated" *P*-(trichlorosilyl)phosphaalkene. The three ^{29}Si nuclei appear as doublets as a consequence of the coupling with ^{31}P. The two *C*-silyl groups *cis*- and *trans*-oriented relative to the *P*-bonded SiCl$_3$ group at the C=P double bond in *P*-trichlorosilyl[bis(isopropyldimethylsilyl)methylene]phosphane (**2c**) give separate doublet signals in the ^{29}Si-NMR spectrum. In *C*-bis(trimethylsilyl)-phosphaalkenes the silyl group with the larger (by magnitude) coupling constant ^{2}J(^{31}P, ^{29}Si) is generally assigned to be oriented *cis* to the phosphorus lone pair, i.e. *trans* to the substituent at phosphorus.[23] In **2c** the most deshielded ^{29}Si-NMR doublet signal at δ = 7.9 ppm exhibiting ^{2}J(P,Si) = ±32.3 Hz is assigned to the iPrMe$_2$Si group *trans* to the SiCl$_3$ group (*cis* to the phosphorus lone pair), the resonance at 1.9 ppm [^{2}J(P, Si) = ±11.4 Hz] corresponds to the other iPrMe$_2$Si group. Compared with the starting material **1c** [δ = ^{29}Si 2.6 ppm, ^{2}J(P, Si) = ±39.9 Hz, *trans* to Cl and 1.9 ppm, ^{2}J(P, Si) = ±4.3 Hz, *cis* to Cl], the *trans*-iPrMe$_2$Si group in **2c** appears less deshielded and with a smaller coupling constant. In contrast, the ^{29}Si chemical shifts of the *cis*-iPrMe$_2$Si groups of **1c** and **2c** are very similar, but in **2c** the coupling constant is larger than that of **1c** (in magnitude). This virtual "confusion" correlates with the opposite signs of the two coupling constants ^{2}J(P,Si) suggested by DFT calculations (see above). The ^{29}Si nucleus of the trichlorosilyl group in **2c** appears at δ = –0.1 ppm as the center of a doublet [^{1}J(P,Si) = ±248.4 Hz] (see below).

In mixtures containing **1c**, **2c**, and **5** almost 60% of the starting material **1c** remains unconsumed for more than two weeks, before detectable amounts of a further product start to appear in solution, indicated by an AX pattern in the ^{31}P-NMR upfield region [^{31}P NMR at 81 MHz, C$_6$D$_6$: δ = –117.0 ppm (d), –129 ppm (d), ^{1}J(P,P) = ±189 Hz]. This pattern is consistent with a diphosphabicyclobutane structure, which can be explained by a reaction between **1c** and **2c** from the reaction mixture with elimination of SiCl$_4$. Related bicyclobutanes were detected by Niecke et al., when *P*-chlorophosphaalkenes were reduced by insertion of 1,3-di-*tert*-butyl-2,2-dimethyl-1,3,2,4λ^2-diazasilastannetidine, a cyclic aminostannylene, into the P–Cl bonds.[12] Keeping the bicyclic product from **1c**/**2c** in solution leads within two months to the appearance of another species with *three* inequivalent phosphorus atoms (see Exp. Section).

^{31}P- and ^{29}Si-NMR Spectroscopic Data of Compounds 2–7

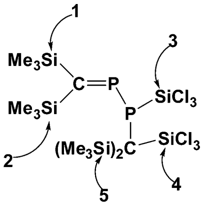
In the three known *P*-(trichlorosilyl)phosphaalkenes **2a**–**c**, coupling constants ^{1}J(P,Si) are generally significantly larger that those of (trichlorosilyl)phosphane functions[8] (as in **3a**–**b**); they are influenced by the substitution pattern of neighbouring *C*-silyl groups in the range iPrMe$_2$Si > Me$_3$Si > PhMe$_2$Si; i.e. bulkier alkyl substituents correlate with larger ^{1}J(P,Si) couplings. An overview of the NMR spectroscopic data is given in Table 1.

Table 1. Selected ^{31}P- and ^{29}Si-NMR spectroscopic data of phosphaalkenes with P–SiCl$_3$ moieties.

	δ = ^{31}P (σ^2,λ^3) [ppm]	δ = ^{31}P (σ^3,λ^3) [ppm]	^{1}J(P,P) [Hz]	δ = ^{29}Si(*S*-*i*Cl$_3$) [ppm]	^{1}J(P,Si) [Hz]
2a	371.6	–	–	*[a]	243.4
2b	389.2	–	–	*	236.0
2c	377.4	–	–	–0.1	249.2**
3a	394.1	–26.1	254.6	2.9	172.0
3b	417.5	–21.3	260.0	*	169.8
7	389.3	–24.9	232.4	*	112.6

[a] (* = not observed; ** value from the ^{31}P-NMR spectrum).

For the transient compound **3a**, the proposed assignment for the ^{29}Si-NMR signals (for the numbering see Scheme 6) is as follows: δ_1 = 5.1 ppm (d,d), ^{2}J(P,Si) = ±47.9, ^{3}J(P,Si) = ±9.5 Hz; δ_2 = 2.4 ppm (d,d), ^{2}J(P,Si) = ±12, ^{3}J(P,Si) =



3a

Scheme 6. Numbering of ^{29}Si nuclei in the intermediate **3a**.

$\pm$8.7 Hz; δ_3 = 2.9 ppm (d,d), ^1J(P,Si) = $\pm$172, ^2J(P,Si) = $\pm$10.1 Hz; δ_4 = –0.6 ppm (d,d), ^2J(P,Si) = $\pm$40.9, ^3J(P,Si) = $\pm$24.1 Hz; δ_5 = 0.9 ppm (d), ^2J(P,Si) = $\pm$4.7 Hz [^3J(P,Si) <1 Hz].

Conclusions

Reactions of *P*-chlorophosphaalkenes $(\text{RMe}_2\text{Si})_2\text{C=PCl}$ (**1a–c**; R = Me, Ph, *i*Pr) with the disilane $\text{Me}_3\text{SiSiCl}_3$ (**5**) furnish by Me_3SiCl elimination the new per-silylated phosphaalkenes $(\text{RMe}_2\text{Si})_2\text{C=PSiCl}_3$ (**2a–c**) as the first spectroscopically detectable products (step I). The subsequent step (II) of the reaction is the dimerisation of **2a**, **2b** providing isomeric *P*-[(trichlorosilyl)phosphanyl]phosphaalkenes $(\text{RMe}_2\text{Si})_2\text{C=P–P(SiCl}_3)\text{C(SiCl}_3)(\text{SiMe}_2\text{R})_2$ (**3a**: R = Me; **3b**: R = Ph) and diphosphenes $(\text{Cl}_3\text{Si})(\text{RMe}_2\text{Si})_2\text{C–P=P–C(SiCl}_3)(\text{SiMe}_2\text{R})_2$ (**4a**: R = Me; **4b**: R = Ph). Heating of these mixtures or the reference compound $(\text{Me}_3\text{Si})_2\text{C=P–P(SiCl}_3)t\text{Bu}$ (**7**) leads by 1,3(P→C) SiCl_3 group shift reactions (step III) to the corresponding diphosphenes **4a**, **4b** and **8**. The structure of the new diphosphene **4b** was determined crystallographically. The rates of reaction steps I–III can be influenced by variation of the *C*-silyl groups in the parent chlorophosphaalkenes **1a–c**. With the bulkier $i\text{PrMe}_2\text{Si}$ group, the dimerisation of **2c** (step III) is precluded and solutions containing approximately equivalent amounts of **2c** and **1c** can be generated. The remarkable resistance of **2c** to dimerisation allowed for the first time the ^{31}P- and ^{29}Si-NMR spectroscopic characterisation of a per-silylated *P*-(trichlorosilyl)phosphaalkene. On the agenda of open questions in this context are still the mechanisms of (i) the formation of compounds **2a–c** [SiCl_2 insertion into the P–Cl bonds vs. S_N-like Cl/SiCl_3 group exchange at $\text{P}(\sigma^2\lambda^3)$] and (ii) the dimerisation step II (possible role of phosphanylidene species).

Experimental Section

General Methods: All experiments were carried out under oxygen-free nitrogen by using standard Schlenk techniques. NMR spectra were recorded using Bruker spectrometers AC 200, Avance 200, Avance 400 and AMX 300, with 85% H_3PO_4, and SiMe_4 as external or internal standards.

4a: A mixture of (224 mg, 1.0 mmol) **1a** and (414 mg, 2.0 mmol) **5** in 2 mL of toluene was stirred at room temperature. The new species **2a** [δ = +371.6 ppm C=*P*, ^1J(P,Si) = $\pm$43.4 Hz] was observed about 20 min after the reaction began. This is consumed to give **3a** [δ = +394.1 ppm (d) C=*P*-P, ^1J(P,P) = $\pm$254.6 Hz, –26.1 ppm (d) C=P–*P*, ^1J(P,P) = $\pm$254.6 Hz]. The reaction is very slow. After 5 d the reaction shows three products in ^{31}P NMR: **3a** as major product, **4a** beginning to be formed, and traces of an asymmetric diphosphene [δ = 569.1 ppm, ^1J(P,P) = $\pm$616 Hz, 504.7 ppm, ^1J(P,P) = $\pm$616 Hz (P=P)]. The concentration of **3a** in this case is sufficient for ^{29}Si NMR spectroscopy (C_6D_6): δ = 5.1 pm [dd, ^2J(Si,P) = $\pm$47.9, ^3J(Si,P) = $\pm$9.5 Hz, P=C*Si*Me$_3$], 2.4 ppm [dd, ^2J(Si,P) = $\pm$12, ^3J(Si,P) = $\pm$8.7 Hz, P=C*Si*Me$_3$], 2.9 ppm [dd, ^1J(Si,P) = $\pm$172, ^2J(Si,P) = $\pm$10.1 Hz, C–P–*Si*Cl$_3$], –0.6 ppm [dd, ^2J(Si,P) = $\pm$40.9, ^3J(Si,P) = $\pm$24.1 Hz, P–C–*Si*Cl$_3$], 0.9 ppm, [d, ^2J(Si,P) = $\pm$4.7, ^3J(Si,P) < 1 Hz, C(*Si*Me$_3$)$_2$]. The mixture was converted to **4a** after 10 d reflux in toluene. The asymmetric diphosphene is also consumed to give **4a**.

4b: A mixture of **1b** (1.6 g, 4.58 mmol) in 3 mL of C_6D_6 and **5** (1.04 mg, 5.0 mmol) was stirred at room temperature and ^{31}P-NMR spectroscopically analyzed. The reaction was spontaneous: first the compound **2b** [δ^{31}P = 389.2 ppm (s), C=*P*, ^1J(P,Si) = $\pm$236 Hz] was formed, which after 1 d was consumed in favor of **3b** [δ^{31}P = 417.5 ppm (d), C=*P*-P, ^1J(P,P) = $\pm$260 Hz], –21.3 ppm [d, C=P-*P*, ^1J(P,P) = $\pm$260, ^1J(P,Si) = $\pm$169.8 Hz] and finally of **4b**. A competing reaction takes place, leading to small amounts of an asymmetric diphosphene δ^{31}P = 561.9 ppm [d, ^1J (P,P) = $\pm$620.5 Hz], 502.5 ppm [d, ^1J (P,P) = $\pm$620.5 Hz]. A transient precursor of this compound was observed 30 min after the reaction started: δ = ^{31}P = 401.9 [d, ^1J(P,P) = $\pm$597 Hz], 332.3 [d, ^1J(P,P) = $\pm$597 Hz]. The asymmetric diphosphene was consumed after about 10–14 d. After 30 d NMR spectra of the reaction mixture showed compounds **4b** and **3b** in the ratio 95:5 (high crude yield). All volatiles were removed in vacuo and 0.5 mL of CDCl_3 was added to the residual brown oil. At 0 °C a few colorless crystals of **4b**, appropriate for X-ray analysis, were obtained.

4b: ^{1}H-NMR: δ = 0.7 (s, C*H*$_3$, 6 H), 0.35 (s, C*H*$_3$, 6 H) diastereotopes (Me$_2$Si), 7.45 (d,“t”, *ortho*, 2 H), 7.23–7.29 (m, *para*, 1 H), 7.15–7.22 (m, *meta*, 2 H). ^{13}C-NMR: δ = 0.88 (“t”, *C*H$_3$), 2.86 (“t”, *C*H$_3$), 40.9 [m, *C*(SiCl$_3$)(SiMe$_2$Ph)$_2$], 127.7 (s, *m*-C), 129.9 (s, *p*-C), 135.6 (s, *o*-C), 136.7 (s, *ipso*-C); ^{29}Si-NMR: δ = –4.3 (br. s, *Si*Me$_2$Ph, Integr. 2Si), –7.1 (br. s, *Si*Cl$_3$, integr. 1 Si); ^{31}P-NMR: δ = 573.6 (s, *P*=*P*). MS(EI): *m*/*z* (%) = 895.9 [M$^+$, 4], 880.9 [(M – CH$_3$)$^+$, 1], 761 [(M – SiCl$_3$)$^+$, 1], 743.8 [(M – SiCl$_3$–CH$_3$)$^+$, 1], 723.9 [(M – SiCl$_4$)$^+$, 4], 478.9 [M – (C(SiCl$_3$)(SiMe$_2$Ph)$_2$)$^+$, 3], 135 [(SiMe$_2$Ph)$^+$, 100], 62.9 [(P=P)$^+$, 22]. Elemental analysis (%): $\text{C}_{34}\text{H}_{44}\text{Cl}_6\text{P}_2\text{Si}_6$ (895.89) calcd.: C 45.58, H 4.95; found C 43.55, H 5.02.

Reaction of 1c with 6: 153 mg (0.6 mmol) **6** were added in one portion to a solution of 170 mg (0.6 mmol) **1c** and 0.5 mL of C_6D_6. After 10 min, a small peak corresponding to the short-lived species **2c** was observed with ^{31}P NMR spectroscopy; δ = 377.4 ppm, ^1J(P,Si) = 248.4 Hz. After 5 d, another compound is identified as $[(\text{Me}_2i\text{Pr})\text{Si}]_2\text{C(SiCl}_3)\text{–P(H)SiCl}_3$ [δ = –93.4 ppm, s, ^1J(P,H) = 220, ^1J(P,Si) = 127.1 Hz]. Even 27 d later the reaction does not proceed further, and the two reaction products mentioned so far are still clearly distinguished in ^{31}P NMR spectrum together with **1c**.

Reaction of 1c with 5: To (0.5 g, 1.78 mmol) of **1c** in 0.3 mL of C_6D_6, 2 equiv. of **5** (0.70 g, 3.5 mmol) was added at room temperature. From the mixture, an NMR sample was prepared and sealed by melting. The signals assigned to **2c** are stable for several weeks, but their intensity shows a conversion of only 35–40%, while **1c** remains unconsumed.

2c: ^{29}Si NMR (C_6D_6): δ = 7.9 ppm ^2J(P,Si) = 32.3 Hz [d, *Si*-(CH$_3$)$_2$*i*Pr]; 1.9 ppm ^2J(P,Si) = 11.4 Hz [d, *Si*(CH$_3$)$_2$*i*Pr]; –0.1 ppm, ^1J(P,Si) = 248.4 Hz (d, *Si*Cl$_3$). ^{31}P NMR (81 MHz, C_6D_6): δ = +377.2 ppm, ^1J(P,Si) = 249.2, ^2J(P,Si) = 32.3 Hz.

After 2–3 weeks, in ^{31}P-NMR an AX pattern and subsequently (2 months) also an AMX-pattern appear in at the expense of both **1c** and **2c**. AX pattern: ^{31}P NMR (81 MHz, C_6D_6): δ = –117.0 ppm (d), –129 ppm (d), ^1J(P,P) = 189 Hz. AMX pattern: δ_A = 184.7 ppm (dd), $^1J(\text{P}_\text{A},\text{P}_\text{M})$ = $\pm$149, $^2J(\text{P}_\text{A},\text{P}_\text{X})$ = $\pm$111.9, $^1J(\text{P}_\text{A},\text{H})$ = $\pm$14.7 Hz, δ_M = 28.3 ppm (dd), $^1J(\text{P}_\text{A},\text{P}_\text{M})$ = $\pm$149, $J(\text{P}_\text{M},\text{P}_\text{X})$ = $\pm$141.5 Hz, δ_X = –55.9 ppm (dd), $^2J(\text{P}_\text{A},\text{P}_\text{X})$ = $\pm$111.9, $J(\text{P}_\text{M},\text{P}_\text{X})$ = $\pm$141.5 Hz.

Reaction of 1a with tBuP($SiCl_3$)$_2$: A mixture of 2.33 g (10.4 mmol) of **1a** and 3.7 g (10.4 mmol) *tert*-butylbis(trichlorsilyl)phosphane was refluxed for 5 h in 20 mL of dichloromethane. The consumption of **1a** and tBuP($SiCl_3$)$_2$ in favour of compound **7** was confirmed by ^{31}P-NMR spectroscopy. The solvent and silicon tetrachloride were removed in vacuo; attempts to distil the orange reside led to thermal decomposition. In the residue from the attempted distillation, compounds **7** and **8** could be identified by ^{31}P NMR spectroscopy. Separation of **8** from this mixture was not achieved.

7: ^{1}H NMR (C_6D_6): δ = 0.2 ppm [d, 9 H, ^{4}J(H,P) = 2.4 Hz Si(CH_3)$_3$], 0.4 ppm [s, 9 H, Si(CH_3)$_3$], 1.3 ppm [d, 9 H, ^{3}J(H,P) = 13.1 Hz C(CH_3)$_3$]. ^{13}C NMR (C_6D_6): δ = 2.0 ppm [d, ^{3}J(C,P) = 14.7 Hz, Si(CH_3)$_3$], 4.3 ppm [dd, ^{3}J(C,P) = 7.8, ^{4}J(C,P) = 2.9 Hz, Si(CH_3)$_3$], 32.2 ppm [dd, ^{2}J(C,P) = 12.4, ^{3}J(C,P) = 3.6 Hz, C(CH_3)$_3$], 35.5 ppm [dd, ^{1}J(C,P) = 23.7, ^{2}J(C,P) = 3.8 Hz, *C*(CH_3)$_3$], 236.5 ppm [dd, ^{1}J(C,P) = 99.7, ^{2}J(C,P) = 11.2 Hz, *C*=P], ^{29}Si NMR (C_6D_6): δ = –4.1 ppm [dd, ^{2}J(Si,P) = 11.7, ^{3}J(Si,P) = 12.8 Hz, *Si*(CH_3)$_3$], 0.1 ppm [dd, ^{2}J(Si,P) = 39.2, ^{3}J(Si,P) = 22.1 Hz, *Si*(CH_3)$_3$], ^{31}P NMR (C_6D_6): δ = –24.9 ppm [d, ^{1}J(P,P) = 232.4 Hz, ^{29}Si satellites: ^{1}J(Si,P) = 112.6, ^{3}J(Si,P) = 22.1, ^{3}J(Si,P) = 12.8 Hz, *P*($SiCl_3$)tBu], 389.3 ppm [d, ^{1}J(P,P) = 232.4 Hz, ^{29}Si satellites: ^{2}J(Si,P) = 39.2, ^{2}J(Si,P) = 11.7 Hz, C=*P*]. MS(EI) *m*/*z* (%) = 444 (1) [not assigned], 412 (2) [M]$^+$, 387 (2) [?]$^+$, 355 (3) [M – tBu]$^+$, 325 (4) [M – $SiMe_3$–CH_2]$^+$, 209 (14) [P($SiCl_3$) Bu]$^+$, 147 (40) [Me_3SiCPP]$^+$, 93(100) [tBuH+Cl]$^+$, 73 (82) [Me_3Si]$^+$, 57(56) [tBu]$^+$.

8: ^{31}P NMR (C_6D_6): δ = 531.3 ppm [d, ^{1}J(P,P) = 628.9 Hz, P=*P*tBu], 604.0 [d, ^{1}J(P,P) = 628.9 Hz, *P*=PtBu].

X-ray Structure Determination of Compound 4b: *Crystal data*: $C_{34}H_{44}Cl_6P_2Si_6$, M_r = 895.87, triclinic, space group $P\bar{1}$, a = 9.4125(4), b = 10.9299(4), c = 11.8668(4) Å, α = 66.618(3), β = 71.536(3), γ = 88.715(3)°, V = 1055.4 Å^3, Z = 1, ρ_{calc} = 1.410 Mg/m^3, μ(Mo-K_α) = 0.68 mm^{-1}, F(000) = 464, T = 100 K; yellow block $0.45 \times 0.3 \times 0.2$ mm^3. Of 37527 reflections collected to 2θ 63°, 6912 were independent (R_{int} = 0.021). Final $R1$ = 0.0209 [$I > 2\sigma(I)$], $wR2$ = 0.0601 (all data) for 221 parameters; S = 1.05, max. $\Delta\rho$ 0.5 eÅ^{-3}.

Data were recorded using Mo-K_α radiation (λ = 0.71073 Å) on an Oxford Diffraction Xcalibur S diffractometer. An absorption correction was based on multi-scans. The structure was refined using the program SHELXL-97 [25]. Hydrogen atoms were included using rigid methyl groups or a riding model.

CCDC-777799 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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