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Novel trichlorosilylation and trichlorogermylation of a *P*-chlorophosphaalkene leading to functionally substituted diphosphenes *

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Abstract

The reactions of *P*-chlorobis(trimethylsilyl)methylenephosphane with hexachlorodisilane or with dichlorogermylene-dioxane afford the new *Si*-functionalised ditrisyldiphosphene derivative $[(Me_3Si)_2(Cl_3Si)CP]_2$ and the related trichlorogermyl diphosphene $[(Me_3Si)_2(Cl_3Ge)CP]_2$.

Key words: Phosphorus; Silicon; Germanium

P-Silylated phosphaalkenes are synthetically important compounds, and are generally available from the reaction of acyl- or iminoacyl halides with tris(trimethylsilyl)phosphane or with lithium bis(trimethylsilyl) phosphide [1–3]. These reagents provide only those *P*-silylated phosphaalkenes with "stabilising" π-donor-substituents at carbon; phosphaalkenes without such stabilising donor substituents should be accessible by *P*-silylation of *P*-halogeno-phosphaalkenes. As an exceptionally mild method for the intended reductive silylation of *P*-chlorobis(trimethylsilyl)methylenephosphane (**1**) [4], we chose the reaction of the phosphaalkene with hexachlorodisilane [5,6]. Reductive silylations with hexachlorodisilane had previously been employed for the transformation of dialkylchlorophosphanes and alkyldichlorophosphanes into trichlorosilylphosphanes. Thus we expected hexachlorodisilane to behave in a similar way towards the *P*-chloro-phosphaalkene **1**, furnishing the trichlorosilylated phosphaalkene derivative **2**.

$$\underset{\mathbf{1}}{(Me_3Si)_2C{=}PCl} + Si_2Cl_6 \xrightarrow[-SiCl_4]{} \underset{\mathbf{2}}{(Me_3Si)_2C{=}PSiCl_3} \quad (1)$$

1 reacts slowly with hexachlorodisilane at room temperature. ^{31}P-NMR spectra of the reaction mixture reveal that after a few hours the main phosphorus species in the reaction mixture (apart from **1**) is not the *P*-trichlorosilylphosphaalkene (**2**) but apparently its dimer **3** [7*], a new 2,3-diphosphabutene derivative. $(Me_3Si)_2C{=}P{-}P(SiCl_3)C(SiMe_3)_2SiCl_3$ (**3**) is not a normal phosphaalkene dimer from (2 + 2)- or (2 + 1)-cycloaddition [3,8], but it may formally be derived from 1,2-addition of the P–Si bond of **2** to the P=C double bond of a second molecule of **2**. Retrosynthetically, it appears that the phosphorus atom of the P–Si function attacks phosphorus, leading to the P–P bond of **3**, and that the trichlorosilyl group attacks the three-coordinate carbon atom to form the functionally modified trisilylmethyl group of **3**. P–Si additions of *P*-silylated phosphaalkenes to P=C bonds have not yet been reported, whereas P–Si addition reactions to C=N and C=O double bonds are known [3]. A mechanistic alternative would be a 1,2-trichlorosilyl shift within **2** leading to a trichlorosilylbis(trimethylsilyl)phosphinidene species that could insert into the P–Si bond of a second molecule of **2**; another reaction sequence could start by simple 1,2-addition of hexachlorodisilane to the P=C bond of **1**, thus not involving **2** as an interme-

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* Dedicated to Professor Reinhard Schmutzler on the occasion of his 60th birthday.

* Reference number with asterisk indicates a note in the list of references.

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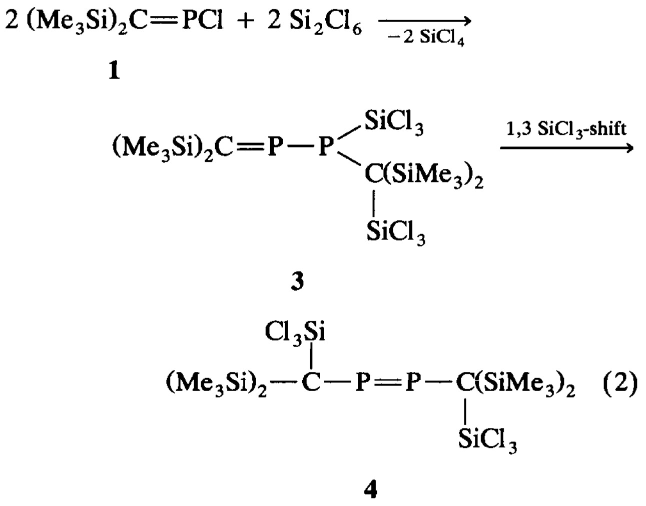
diate in the course of the formation of **3**. ^{31}P-NMR spectra of the reaction mixture show that, before the educt **1** is completely consumed by the hexachlorodisilane reaction in favour of **3**, a novel Si-functionalised ditrisyldiphosphene **4** can be detected. The formation of **4** as the final reaction product from **3** is due to a 1,3-trichlorosilyl shift from phosphorus to carbon, forming another modified trisylmethyl group.



$$2\,(\mathrm{Me_3Si})_2\mathrm{C{=}PCl} + 2\,\mathrm{Si_2Cl_6} \xrightarrow[-2\,\mathrm{SiCl_4}]{}$$

1

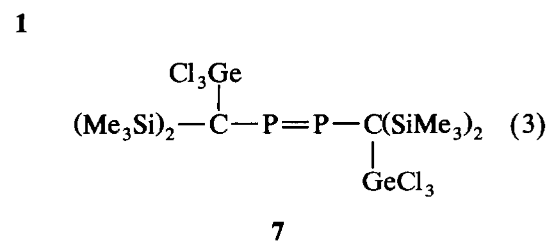
$$(\mathrm{Me_3Si})_2\mathrm{C{=}P{-}P}{<}\begin{matrix}\mathrm{SiCl_3}\\ \underset{\mathrm{SiCl_3}}{\underset{|}{\mathrm{C}}}(\mathrm{SiMe_3})_2\end{matrix} \xrightarrow{\text{1,3 SiCl}_3\text{-shift}}$$

3

$$(\mathrm{Me_3Si})_2{-}\overset{\mathrm{Cl_3Si}}{\overset{|}{\mathrm{C}}}{-}\mathrm{P{=}P}{-}\underset{\mathrm{SiCl_3}}{\underset{|}{\mathrm{C}}}(\mathrm{SiMe_3})_2 \qquad (2)$$

4

Because the desired *P*-trichlorosilylphosphaalkene **2** was not available from the hexachlorodisilane reaction of **1**, we attempted to prepare the related *P*-trichlorogermylphosphaalkene $(\mathrm{Me_3Si})_2\mathrm{C{=}PGeCl_3}$ (**5**) by dichlorogermylene insertion into the P–Cl bond of **1**. Surprisingly, as in the case of the attempted *P*-trichlorosilylation of **1**, the simple *P*-trichlorogermylphosphaalkene **5** could not be detected by NMR spectroscopic investigation of the reaction mixture, but another new intermediate **6** containing a P–P bond was observed and the final reaction product is a novel trichlorogermyl-functionalised diphosphene **7**.



$$2\,(\mathrm{Me_3Si})_2\mathrm{C{=}PCl} + 2\,\mathrm{GeCl_2\cdot C_4H_8O_2} \xrightarrow[-\mathrm{C_4H_8O_2}]{}$$

1

$$(\mathrm{Me_3Si})_2{-}\overset{\mathrm{Cl_3Ge}}{\overset{|}{\mathrm{C}}}{-}\mathrm{P{=}P}{-}\underset{\mathrm{GeCl_3}}{\underset{|}{\mathrm{C}}}(\mathrm{SiMe_3})_2 \qquad (3)$$

7

The ^{31}P-NMR shifts of the assumed diphosphene precursors **3** and **6** are surprisingly different. The chemical shifts of the λ^2P and λ^3P nuclei, and ^1J(PP) of **3**, are in accord with a diphosphabutene structure, but in the germanium compound **6** the resonance of the more shielded ^{31}P nucleus appears far downfield from that of **3** and the less shielded ^{31}P-NMR signal of the germanium compound **6** appears about 250 ppm upfield from the corresponding signal of the trichlorosilyl compound **3**.

The ^{31}P-NMR signals of trichlorogermylphosphanes appear, indeed, significantly downfield from those of

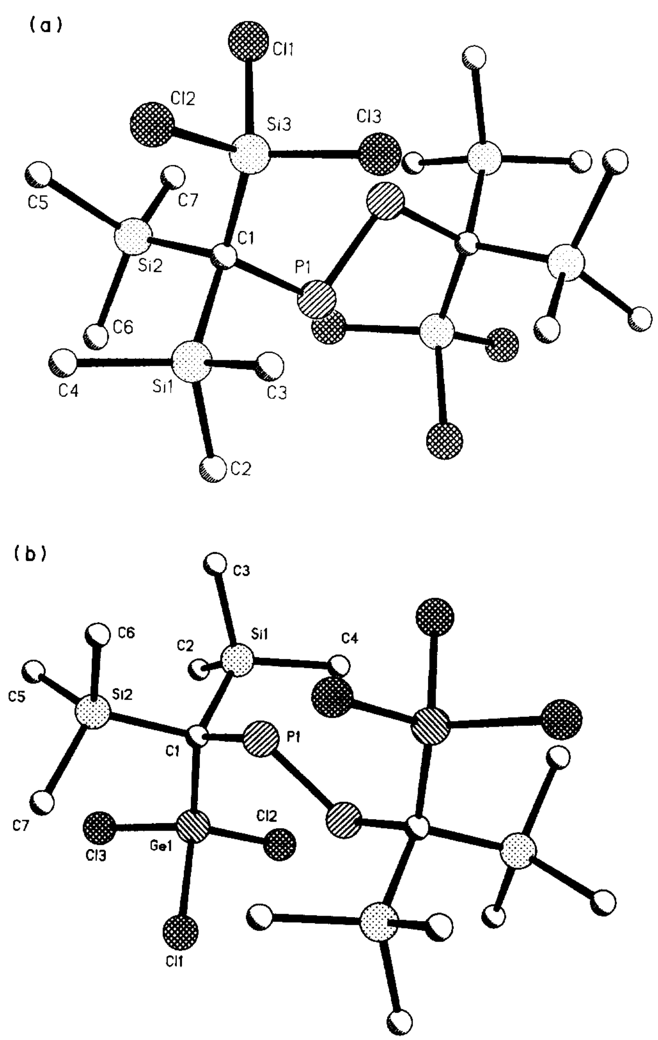


Fig. 1. (a) Molecular structure of one of two independent molecules of **4**. H-atoms are omitted. Only the asymmetric unit is numbered. Selected geometrical parameters (pm, °): P(1)-P(1)' 201.9(2), P(1)-C(1) 188.2(3), Si(1)-C(1) 195.8(3), Si(2)-C(1) 194.8(3), Si(3)-C(1) 184.4(3), Si(3)-Cl(1) 204.5(8), C(1)-P(1)-P(1)' 106.9(4), P(1)-C(1)-Si(1) 102.4(1), P(1)-C(1)-Si(2) 106.1(3), P(1)-C(1)-Si(3) 114.5(2). Values for the second molecule are similar. (b) Molecular structure of one of two independent molecules of **7**. H-atoms are omitted. Only the asymmetric unit is numbered. Selected geometrical parameters (pm, °): P(1)-P(1)' 201.9(3), P(1)-C(1) 186.9(5), Si(1)-C(1) 194.1(5), Si(2)-C(1) 195.7(5), Ge(1)-C(1) 193.6(5), Ge(1)-Cl(1) 214.2(2), C(1)-P(1)-P(1)' 106.6(2), P(1)-C(1)-Si(1) 106.3(2), P(1)-C(1)-Si(2) 103.1(2), P(1)-C(1)-Ge(1) 115.4(2). Values for the second molecule are similar.

the corresponding trichlorosilylphosphanes [9], but the relative upfield shift of what might be the λ^2-P atom of **6** is still unexplained; thus structures isomeric to the proposed diphosphabutene still have to be considered for the intermediate **6**. A crossing experiment was conducted, as a one-pot reaction of **1** with half an equivalent of each reagent (hexachlorodisilane and the dichlorogermylene dioxane complex). Within 3 h at 68°C only the resonances of **6** and **7** had appeared, but after 12 h **1** was completely consumed, and **4** and **7** were present in nearly 1:1 ratio. No asymmetrical diphosphene was observed. The presence of **4** and **7** as the only products indicates that the rearrangements **3** → **4** and **6** → **7** must be *intra*molecular. The diphosphenes **4** and **7** were isolated in a pure state and were characterised by spectroscopic methods and X-ray crystal structure determinations.

Diphosphenes **4** and **7** (Fig. 1) are isostructural; both display two independent molecules, each with crystallographic inversion symmetry. The $SiCl_3$- and $GeCl_3$-groups adopt *trans*-positions at the central C–P=P–C moieties. The severe steric strains within **4** and **7** are reflected by characteristic elongation of the internal Si–C bonds of the C–$SiMe_3$ fragments. It is surprising that the Si–C and Ge–C bond lengths of the C–$SiCl_3$ and C–$GeCl_3$ (184.4 and 193.6 pm) moieties of **4** and **7** are not greatly influenced by steric effects, whereas the angles ClSiCl and ClGeCl (about 105.3° and 103.7°) are — as expected — smaller than in CH_3SiCl_3 or CH_3GeCl_3 [10–12]. The known distortion by steric strain reflected by uneven bond lengths of the internal C–Si bonds [13] within ditrisyldiphosphene is transformed into a distortion of the C–Si bonds of **4** and **7** due to the presence of tightly bound $SiCl_3$ or $GeCl_3$ groups. It is remarkable that **4** and **7**, with such distorted bulky substituents, are formed from **1** with hexachlorodisilane or with the dichlorogermylene dioxane complex by $SiCl_3$ or $GeCl_3$ migration under very mild conditions. A 1,3-trimethylsilyl shift leading to a diphosphene with a "normal" trisyl group had previously been proposed when the synthesis of a bulky *P*-trimethylsilyldiphosphapropene derivative related to **3** was attempted; spectroscopic evidence for the intermediacy of the species related to **3** could not then be provided [14]. Sterically less crowded diphosphabutenes of the type $(Me_3Si)_2C{=}P{-}P(R)SiMe_3$ do not give rearrangements into the corresponding diphosphenes [14,15]. The formation of the sterically protected but functionally substituted diphosphenes **4** and **7** from **1** indicates that reductive metallation steps at electron-poor phosphaalkenes, similar to our novel trichlorosilylation and trichlorogermylation reactions, will provide a versatile and novel entry into diphosphene chemistry.

1. Experimental details

4: A suspension of 4.0 g (17.8 mmol) **1** and 5.62 g (20.9 mmol) hexachlorodisilane was heated for 8 days at 60°C in 50 ml hexane. Concentration of the solution and crystallisation at −25°C gave 4.1 g (71%) of **4** as an orange solid.

7: A suspension of 1.16 g (5.16 mmol) **1** and 1.20 g (5.16 mmol) dichlorogermylene dioxane was heated for 8 h in 20 ml toluene. Concentration of a pentane extract and crystallisation at −20°C furnished 400 mg (26%) of **7** as a yellow solid.

1.1. Spectroscopic data

4: Orange crystals; m.p. 246°C (dec.). MS [EI, 25°C, m/z (%)] 646 (4.6, M^+) correct isotopic distribution; ^1H NMR (200 MHz, C_6D_6) δ 0.40 (s, 36H, $Si(CH_3)_3$); ^{13}C NMR (50.3 MHz, C_6D_6, X-components of AA′X-spectra) δ 39.9 (2C, C–P=P–C); 3.74 (12C, $(CH_3)_3Si$–); ^{31}P NMR (81 MHz, C_6D_6) δ 578.2 (s, 2P, –P=P–); ^{29}Si NMR (39.67 MHz, C_6D_6, X-components of AA′X-spectra) δ 3.0 (2 Si, 3 signals, distance 4.4 Hz), −4.3 (2 Si, 3 signals, distance 6.0 Hz, intensity 30% of the signal at δ 3.0); Anal. $C_{14}H_{36}Cl_6P_2Si_6$ (647.5) calc. C 25.96, H 5.55; found C 24.60, H 5.54%.

7: Yellow crystals; m.p. 205°C (dec., at 160°C colour turns to brown). MS [EI, 25°C, m/z (%)] 736 (8.0, M^+) correct isotopic distribution; ^1H NMR (200 MHz, C_6D_6) δ 0.58 (s, 36H, $Si(CH_3)_3$); ^{13}C NMR (50.3 MHz, C_6D_6, X-components of AA′X-spectra) δ 71.02 (2C, C–P=P–C); 3.06 (12C, $(CH_3)_3Si$–); ^{31}P NMR (81 MHz, C_6D_6) δ 553.7 (s, 2P, –P=P–); Anal. $C_{14}H_{36}Cl_6Ge_2P_2Si_4$ (736.6) calc. C 22.83, H 4.93; found C 22.85, H 4.90%.

1.2. Crystal data

4: $C_{14}H_{36}Cl_6P_2Si_6$, $M = 647.61$, $P\bar{1}$, $a = 8.942(3)$, $b = 9.070(2)$, $c = 2214.8(5)$ Å, $\alpha = 88.95(2)°$, $\beta = 83.04(2)°$, $\gamma = 62.08(2)°$, $U = 1.5740(7)$ A^3, $Z = 2$, $\mu = 0.9$ mm^{-1}, $T = -100$°C. A yellow plate $0.48 \times 0.40 \times 0.20$ mm was mounted in inert oil (type RS3000, donated by Messrs. Riedel de Haën). Using Mo Kα radiation on a Siemens R3 diffractometer, 8061 intensities were measured to $2\theta_{max}$ 50°, of which 5571 were unique (R_{int} 0.020) and 5565 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 0.107, with conventional $R(F)$ 0.037 for 265 parameters.

7: $C_{14}H_{36}Cl_6Ge_2P_2Si_4$, $M = 736.61$, $P\bar{1}$, $a = 9.003(3)$, $b = 9.108(3)$, $c = 2210.2(7)$ Å, $\alpha = 88.63(2)°$, $\beta = 82.73(2)°$, $\gamma = 61.84(2)°$, $U = 1583.7(9)$ A^3, $Z = 2$, $\mu = 2.6$ mm^{-1}, $T = -130$°C. A yellow plate $0.35 \times 0.35 \times 0.10$ mm was mounted as above. Using Mo Kα radiation on a Stoe STADI4 diffractometer, 8611 intensities were measured to $2\theta_{max}$ 50°, of which after absorption corrections 5576 were unique (R_{int} 0.039) and 5566 used for all calculations. The structure was solved and refined as above. The final $wR(F^2)$ was 0.102, with conventional $R(F)$ 0.042 for 265 parameters.

Further details of the structure determinations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the reference number CSD-400831 for **4**, CSD-400832 for **7**, the names of the authors and the journal citation.

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7 Selected spectroscopic data for **3**: ^{31}P NMR (81 MHz, C_6D_6) δ 395.3 (d, 1P, ^1J 253.1 Hz, =*P*–P), –25.3 (d, 1P, ^1J 254.6 Hz, =P–*P*); for **6**: ^{31}P NMR (81 MHz, C_6D_6) δ 152.9 (d, 1P, ^1J 241.4 Hz, =*P*–P), 78.8 (d, 1P, ^1J 238.6 Hz, =P–*P*).

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