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Bis(stannyl)phosphanyl-Substituted Dichlorosilanes/Germanes – Potential Precursors for a Novel Strategy Toward P–Si/Ge Multiple Bonds?

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A general synthetic route to bis(stannyl)phosphanyl-substituted dichlorosilanes/germanes of the type $R-SiCl_2-P(SnMe_3)_2$ and $R-GeCl_2-P(SnMe_3)_2$ is reported. For $R = Cp^*$ (= 1,2,3,4,5-pentamethylcyclopentadienyl) crystal structures for the corresponding silane and germane could be obtained. These compounds are the first structurally characterized bis-

Introduction

After the recent success of preparing stable disilynes,^[1–3] the synthesis of triple-bonded systems of silicon and germanium towards other elements remains one of the major challenges in main group chemistry. While examples for transition-metal complexed silylynes and germylynes have been reported,^[4–6] triple bonds of silicon and germanium towards other main group elements have not to date been stabilized, despite theoretical predictions.^[7,8] In this respect, 1,2-chlorosilane elimination has proven to be unsuccessful, while the analogous chlorostannane elimination has not been exploited for this purpose to date. This prompted us to investigate whether chlorostannane elimination might be a better alternative for generating unsaturated PSi and PGe units.

In this contribution we report on the synthesis and structural characterization of $Cp^*-SiCl_2-P(SnMe_3)_2$ and $Cp^*-GeCl_2-P(SnMe_3)_2$ ($Cp^* = 1,2,3,4,5$ -pentamethylcyclopentadienyl). They are the first structurally characterized bis-(stannyl)phosphanyl-substituted dichlorosilanes/germanes. Owing to their functionalities, they should be ideal precursors for the generation of unsaturated PSi and PGe units and possibly phosphasilynes and phosphagermynes.

Results and Discussion

To synthesize $Cp^*-SiCl_2-P(SnMe_3)_2$ (3a) and $Cp^*-GeCl_2-P(SnMe_3)_2$ (4), we started from the corresponding trichlorosilane Cp^*-SiCl_3 (1) and trichlorogermane Cp^*-

GeCl₃ (2), respectively. In order to introduce the bis-(stannyl)phosphanyl group we reacted 1 and 2 with tris-(trimethylstannyl)phosphane $P[Sn(CH_3)_3]_3$ neat in the absence of any solvent. At elevated temperature the reaction proceeds under chlorotrimethylstannane elimination, which is continuously sublimed out of the reaction mixture. This approach is necessary to avoid further exchange reactions of the stannaphosphanes.^[9,10] In both cases the desired products (**3a**) and (**4**) are obtained in high yield. In addition the related bis(stannyl)phosphanyl dichlorosilanes R-SiCl₂– $P(SnMe_3)_2$ [R = Mes (**3b**) (Mes = 2,4,6-trimethylphenyl), Tip (**3c**) (Tip = 2,4,6-triisopropylphenyl)] have been prepared which underlines the generality of this method (Scheme 1).

(stannyl)phosphanyl-substituted dichlorosilanes/germanes

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Scheme 1. Synthesis of bis(stannyl)phosphanyl dichlorosilanes/germanes 3a-c [E = Si; R = Cp* (3a), Mes (3b), Tip (3c)], 4 (E = Ge; R = Cp*) from 1 (E = Si) and 2 (E = Ge).

Compounds **3a–c** and **4** show an NMR signal in the high field region of the ³¹P NMR spectra (Table 1), which is typical for stannylated phosphanes.^[11] Due to the presence of the isotopes ^{117/119}Sn in the molecules, the ¹ $J_{P,Sn}$ coupling constants can be determined directly from the satellite transitions in these spectra. These coupling constants provide valuable information about the P–Sn bond situation which is significantly affected by the electronic behavior of the other substituents at the phosphorous atom. In principle, changing to a more electron-withdrawing substituent (R) should decrease the s-character of the P–Sn σ -bond in compounds of this constitution and therefore the ¹ $J_{P,Sn}$ coupling

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constants. Surprisingly at first sight, we observe just the opposite trend in our series of compounds (Table 1). In the same direction the ³¹P NMR shift values were found to be shifted downfield. Similar observations have been made for other stannylphosphanes.^[9-11] A notable feature is the relatively high ${}^{1}J_{P,Si}$ coupling constant observed in **3a**–c, which can be interpreted as an indication of strong electronic interaction within the silvlphosphane unit. This is also supported by the short Si-P bond length found in the crystal structure of **3a**. Usually typical ${}^{1}J_{P,Si}$ values for silylphosphanes range between 16 and 53 Hz [exception LiP-(SiH₃)₂, 256 Hz].^[12] This strong electronic interaction within the silvlphosphane unit can be understood assuming hyperconjugative interaction of occupied states at the phosphorus atom with vacant σ^* -states derived from the Si–Cl bonds.^[13,14] The decrease of ${}^{1}J_{P,Si}$ on going from **3a** to **3b**,c might be explained by the reduced phosphorus s-character of the P-Si bond due to an increase of the electron demand at the silicon atom. In line with these interpretations, the ³¹P chemical shift of **4** appears at a lower field than that of 3a, since germanium is more electronegative than silicon. Similarly, the formal sp^2 centers attached to silicon in **3b**,c should be more electron withdrawing than the formal sp³ carbon atoms in **3a** resulting in a deshielding of the phosphorus center. Somewhat more subtle is the situation for the ${}^{1}J_{\text{PSn}}$ coupling constants for which an increase is observed with increasing electron demand at the E(IV) center. This trend is most likely a result of two counteracting tendencies. Again a higher electron demand on E(IV) should result in reduced phosphorus s-character of the P-Sn bond and therefore lower ${}^{1}J_{P,Sn}$ coupling constants. This however, is not observed, and therefore this effect is obviously not the dominant mechanism. The dominant effect leading to the observed increase of the ${}^{1}J_{P,Sn}$ coupling constants might, however, be attributed to the above-mentioned hyperconjugative interaction of occupied states at the phosphorus atom with vacant σ^* -states derived from the Si–Cl bonds. Such occupied states could involve the σ -P-Sn bonds or alternatively the phosphorus lone pair. Increasing the electron demand on the E(IV) center should also increase this hyperconjugative interaction. Therefore, the simultaneous interaction of the phosphorus lone pair (predominant s-character) and the σ -P–Sn bonds with the σ^* states at the E(IV) atom might be responsible for an increase of the ${}^{1}J_{P,Sn}$ coupling that even overcompensates the decrease expected for more electron-withdrawing groups.

Table 1. Characteristic NMR spectroscopic data of 3a-c and 4.

	$\delta(^{31}P)$ [ppm]	${}^{1}J(P, {}^{117}Sn) [Hz]$	${}^{1}J(P, {}^{119}Sn) [Hz]$	$^{1}J(\mathbf{P},\mathbf{Si})$ [Hz]
3a	-272.1	669.2	721.0	116.1
3b	-242.5	681.2	713.4	99.0
3c	-235.0	692.9	724.7	101.4
4	-242.4	718.4	751.5	-

We were able to obtain single crystals of 3a and 4 that were suitable for X-ray diffraction. The crystal structure analysis of 3a confirms that one chlorine atom in 1 has been

displaced by a bis(stannyl)phosphanyl group (Figure 1). The phosphorus atom shows a pyramidal coordination environment with an angular sum of 309.83(7)°. The silicon atom shows a slightly distorted tetrahedral environment with a Cl-Si-Cl angle of 100.6(1)° and a Cl(2)-Si-P angle of 114.31(9)°. The central Si-P bond is at 2.209(2) Å short compared to standard bond lengths (2.24-2.28 Å) and the sum of the covalence radii (2.28 Å).[15,16] Again this contraction can be understood assuming hyperconjugative interaction of occupied σ -states assigned to the P-Sn bond with vacant σ^* -states derived from the Si–Cl bonds.^[13,14] This interaction should be concomitant with an elongation of the Si-Cl bonds, which in fact is observed. The Si-Cl distances are at 2.078(2) and 2.080(2) Å longer than the standard bond length of 2.02 Å.^[15] As a consequence of such hyperconjugative interaction also the Sn-P bond length should be affected. However, the values are at 2.505(1) and 2.510(1) Å for **3a** in the typical range for P-Sn single bonds.^[23] The significant elongation of the Si-Cl bonds with no structural change of the P-Sn bonds might be an indication that the hyperconjugative interaction of the phosphorus lone pair with σ^* -states derived from the Si–Cl bonds might in fact be more significant in this case. From a Newman projection along the Si-P bond, the eclipsed conformation becomes obvious (Figure 2). The lone pair of the phosphorus atom points towards the Cp* moiety. The almost perfect synperiplanar arrangement of the stannyl groups relative to the Cl atoms deviates only slightly, with dihedral angles Sn-P-Si-Cl of 0.2° and 7.4°. Within these planes the Sn…Cl distances are at 3.639 and 3.706 Å shorter than the sum of the van der Waals radii (Figure 3).^[17]



Figure 1. ORTEP plot of **3a** (thermal ellipsoids at 30% probability level).

A similar situation is found in the crystal structure of dichlorogermane **4** (Figure 4). The P–Ge distance is at 2.274(2) Å in the short range of single bond lengths observed for this element combination (2.30-2.36 Å).^[18,19] Again, the substituents flanking this central bond show an eclipsed conformation concomitant with attractive Sn···Cl

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Figure 2. Newman projection and selected bond lengths of **3a** and **4** (in brackets).



Figure 3. Relevant intramolecular distances of **3a** and **4** (in brackets).

interaction. The Sn····Cl distances are at 3.701 and 3.784 Å close to those found in **3a**. The Ge–Cl distances show values of 2.189(2) and 2.192(2) Å. As in **3a**, the P–Sn distances in **4** show with values of 2.511(2) and 2.519(2) Å no peculiarities. The dihedral angles, by which the Sn–P–Ge–Cl planes differ from a perfect synperiplanar arrangement, are 1.1° and 6.2°.

In both structures the short Si–P or Ge–P bond lengths in addition to the attractive Sn···Cl interaction seem to underline the tendency of both molecules to eliminate chlorostannane. Interestingly in the mass spectra of 3a and 4, the molecular ions both lose one equivalent of chlorotrimethylstannane. The elimination of a second equivalent of chlorotrimethylstannane from the resulting phosphasilene and phosphagermene cations is not observed, however.

While solutions of these compounds in aprotic solvents are stable at room temperature, heating of 3a or 4 as neat substances up to 200 °C leads to elimination of trimethylchlorostannane. During this process polymeric materials are formed which we have not been able to characterize yet. Preliminary results suggest that intermolecular condensa-



Figure 4. ORTEP plot of **4** (thermal ellipsoids at 30% probability level).

tion processes via chlorostannane elimination are favored over intramolecular elimination under these conditions.^[20]

As outlined earlier, the structural and spectroscopic parameters of 3a-c and 4 suggest significant hyperconjugative interaction in this type of molecules. To get further insight into the bonding situation we performed quantum chemical calculations on the germanium compound 4 which shows the largest hyperconjugative effect. As a result we find good agreement of the theoretical with the experimental structural data. Moreover, a population analysis provides evidence that bonding states at the phosphorus atom as well as the lone pair interact with σ^* -states derived from the Ge-Cl bonds. The HOMO-1 of 4 is mainly located at the phosphorus atom but shows some mixing with the Ge-Cl bonds (Figure 5). Quite similar is the situation for the Cp*centered HOMO-2 that also partially involves the phosphorus atom. In the HOMO-3 the antibonding Ge–Cl σ^* -states mix with bonding Sn–P σ -states (Figure 6).



Figure 5. Surface plot of the HOMO-1 (left) and the HOMO-2 (right) in **4**.

In summary, we presented a general synthetic route to bis(stannyl)phosphanyl-substituted dichlorosilanes and germanes that should allow a novel approach towards the first



Figure 6. Surface plot of the HOMO-3 in 4.

generation of hypothetical phosphasilylynes and phosphagermylynes. The molecular structures of two representative examples show substantial hyperconjugative interaction between the stannylphosphanyl and the chlorosilyl/germyl units, which are ideally preorganized for chlorostannane elimination.

Experimental Section

All chemical experiments were performed under argon using standard Schlenk techniques or a glovebox. Solvents were dried with sodium/potassium alloy and stored under argon. ¹H, ¹³C, ³¹P, ²⁹Si, and ¹¹⁹Sn NMR spectra were recorded with a Bruker AMX 300 at room temperature. Chemical shift values are given in ppm and were referenced to external standards. Mass spectra were measured on Kratos MS-50 and Masslab VG 12–250 spectrometers using the EI ionization technique. Compounds **1**, **2**, and P(SnMe₃)₃ were prepared according to published procedures.^[21,22]

Synthesis of 3a–c and 4: Tris(trimethylstannyl)phosphane (1.05 g, 2 mmol) was placed in a sublimation apparatus together with an equimolar amount of the corresponding trichlorosilanes 1a-c or trichlorogermane 2. The mixture was heated to 150 °C until all the chlorotrimethylstannane sublimed off (approximately 1 h). The remaining residue was dissolved in pentane (10 mL) and stored at –20 °C. After 12 h, 3a–c precipitated as colorless (3a) to slightly yellow (3b,c; 4) crystalline solids in 95% (3a), 92% (3b), 94% (3c) and 95% (4) yield.

3a: M.p. 181 °C. ³¹P NMR (C₆D₆): $\delta = -272.1$ (¹*J*_{P(119),Sn} = 721.0, ¹*J*_{P(117),Sn} = 669.2 Hz) ppm. ²⁹Si NMR (C₆D₆): $\delta = 33.1$ (d, ¹*J*_{Si,P} = 116.1 Hz) ppm. ¹¹⁹Sn NMR (C₆D₆): $\delta = 36.6$ (d, ¹*J*_{Sn,P} = 721.0, ¹*J*_{Sn,C} = 320.4, ²*J*_{Sn,Si} = 36.7, ²*J*_{(119)Sn,(117)Sn} = 219.3 Hz) ppm. ¹H NMR (C₆D₆): $\delta = 1.90$ (12 H), 1.85 (3 H), 0.44 (d, 18 H, ³*J*_{H,P} = 2.39, ²*J*_{H(119),Sn} = 54.9, ²*J*_{H(117),Sn} = 52.7 Hz) ppm. ¹³C NMR (C₆D₆): $\delta = 140.0$, 134.5, 33.0 (d, ²*J*_{C,P} = 12.0 Hz), 12.7, 12.2, -3.1 (d, ²*J*_{C,P} = 7.6 Hz; ¹*J*_{C(119),Sn} = 320, ¹*J*_{C(117),Sn} = 305 Hz) ppm. MS (EI): *m*/*z* = 589.9510 ($\delta = 0.67$ ppm dev.) [M]⁺, 12%, 394 [M - ClSn(CH₃)₃]⁺, 40%, 379 [M - ClSn(CH₃)₃ - CH₃]⁺, 60%, 165 [Sn(CH₃)₃]⁺, 100%, 135 [Cp*]⁺, 50%. C₁₆H₃₃Cl₂PSiSn₂ (592.82): calcd. C 32.42, H 5.61; found C 32.60, H 5.72.

3b: ³¹P NMR (C₆D₆): $\delta = -242.5$ (¹J_{P(119),Sn} = 713.4, ¹J_{P(117),Sn} = 681.2 Hz) ppm. ²⁹Si NMR (C₆D₆): $\delta = 25.3$ (d, ¹J_{Si,P} = 99.0 Hz) ppm. ¹³C NMR (C₆D₆): $\delta = 156.0$, 152.1, 147.6, 122.8, 25.6, 24.0, 7.9 (d, ²J_{C,P} = 7.2 Hz) ppm. C₁₅H₂₉Cl₂PSiSn₂ (576.78): calcd. C 31.24, H 5.07; found C 31.38, H 5.18.

3c: ³¹P NMR (C₆D₆): $\delta = -235.0$ (¹ $J_{P(119),Sn} = 724.7$, ¹ $J_{P(117),Sn} = 692.9$ Hz) ppm. ²⁹Si NMR (C₆D₆): $\delta = 24.4$ (d, ¹ $J_{Si,P} = 101.4$ Hz) ppm. ¹H NMR (C₆D₆): $\delta = 6.93$ (s, 2 H), 4.13 (2 H, sept,

 ${}^{3}J_{H,H} = 6.9 \text{ Hz}$), 2.73 (1 H, sept, ${}^{3}J_{H,H} = 10.3 \text{ Hz}$), 1.23 (d, 12 H, ${}^{3}J_{HH} = 6.9 \text{ Hz}$), 1.17 (d, 6 H, ${}^{3}J_{H,H} = 10.3 \text{ Hz}$), 0.29 (d, 18 H, ${}^{3}J_{H,P} = 2.3 \text{ Hz}$) ppm. ${}^{13}\text{C}$ NMR (C₆D₆): $\delta = 155.9$, 152.2, 129.7, 122.7, 34.6, 33.3, 25.6, 24.0, -4.1 (d, ${}^{2}J_{C,P} = 7.0 \text{ Hz}$) ppm. MS (EI): m/z = 662.0136 ($\delta = 2.6 \text{ ppm dev.}$) [M]⁺, 50%, 447 [M - ClSn(CH₃)₃ - CH₃]⁺, 70%, 278 [TipSiPCH₄]⁺, 100%, 262 [TipSiP]⁺, 5%. C₂₁H₄₁Cl₂PSiSn₂ (660.93): calcd. C 38.16, H 6.25; found C 38.34, H 6.36.

4: ³¹P NMR (C₆D₆): $\delta = -242.4$ (¹ $J_{P(119),Sn} = 751.5$, ¹ $J_{P(117),Sn} = 718.4$ Hz) ppm. ¹H NMR (C₆D₆): $\delta = 1.94$ (15 H), 0.50 (d, 18 H, ³ $J_{H,P} = 2.5$ Hz) ppm. ¹³C NMR (C₆D₆): $\delta = 12.1$ (m), -3.01 (d, ² $J_{C,P} = 7.5$ Hz; ¹ $J_{C(119),Sn} = 160.9$, ¹ $J_{C(117),Sn} = 153.6$ Hz) ppm. MS (EI): m/z = 635.8953 ($\delta = 0.57$ ppm dev.) [M]⁺, 12%, 438 [M - ClSn(CH₃)₃]⁺, 35%, 423 [M - ClSn(CH₃)₃ - CH₃]⁺, 58%, 165 [Sn(CH₃)₃]⁺, 100%. C₁₆H₃₃Cl₂GePSn₂ (637.34): calcd. C 30.15, H 5.22; found C 30.26, H 5.28.

Crystallographic Details for 3a: A colorless crystal of **3a** with dimensions $0.40 \times 0.35 \times 0.35$ mm was sealed in a glass capillary. The measurements were performed with a Nicolet R3M diffractometer using graphite-monochromatized Mo- K_a radiation at 273 K. A total of 4578 reflections were collected ($\Theta_{max} = 25.00^\circ$), from which 4383 were unique ($R_{int} = 0.0361$), with 4380 having $I > 2\sigma(I)$. The structure was solved by direct methods and refined by full-matrix least-squares techniques against F^2 with SHELXTL-Plus^[28]. The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. For 210 parameters final R indices of R = 0.0573 and $wR_2 = 0.1048$ (GOF = 0.989) were obtained.

Crystallographic Details for 4: A yellow crystal of **4** with dimensions 0.55×0.25 mm was sealed in a glass capillary. The measurements were performed with a Nicolet R3M diffractometer using graphite-monochromatized Mo- K_a radiation at 293 K. A total of 4549 reflections were collected ($\Theta_{\text{max}} = 25.00^\circ$), from which 4399 were unique ($R_{\text{int}} = 0.0780$), with 4396 having $I > 2\sigma(I)$. The structure was solved by direct methods and refined by full-matrix least-squares techniques against F^2 with SHELX-97.^[28] The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. For 210 parameters final R indices of R = 0.0744 and $wR_2 = 0.1174$ (*GOF* = 0.946) were obtained (Table 2).

Table 2. Crystal data and structure refinement for 3a and 4.

Reference	3a	4		
Formula	C ₁₆ H ₃₃ Cl ₂ PSiSn ₂	C ₁₆ H ₃₃ Cl ₂ GePSn ₂		
Formula weight	592.8	637.3		
Temp. [K]	293	293		
Wavelength	0.71073	0.71073		
Crystal system	monoclinic	monoclinic		
Space group	$P2_1/c$	$P2_1/c$		
Unit cell dimensions				
a [Å]	10.004(3)	10.027(2)		
b [Å]	14.326(2)	14.325(2)		
c [Å]	17.908(3)	17.916(3)		
a [°]	90	90		
β [°]	103.56(2)	102.95(1)		
γ [°]	90	90		
Volume [Å ³]	2495.0(9)	2508.0(1)		
Ζ	4	4		
Density (calcd.) [Mg/m ³]	1.578	1.688		
$\mu [{\rm mm}^{-1}]$	0.710	3.440		
Goodness-of-fit on F^2	0.989	0.946		
R_1 (obsd. data)	0.0573	0.0744		
wR_2 (all data)	0.1048	0.1174		

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Computational Details: Ab initio quantum chemical calculations were performed for compound **4** using the program Gaussian 03^[23] on Hartree–Fock and DFT(B3LYP) level, employing a Dunning/ Huzinaga full double zeta basis set on first row elements,^[24] and Los Alamos ECP plus DZ on Na-Bi.^[25–27] The harmonic vibrational frequencies and their infrared intensities for all of the optimized structures were evaluated by the B3LYP method to determine if a structure is a genuine minimum. Representations of the molecular orbitals are shown at a contour value of 0.04.

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