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Branched tetrasilane substituted phosphines – synthesis and characterisation of PhSi(Si iPr_2)₃P and {PhSi(SiMe_2)₃}₂P₁₄†

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The branched trichlorotetrasilane PhSi(SiMe₂Cl)₃ reacts with P₇(SiMe₃)₃ leading to formation of a new oligophosphane {PhSi(SiMe₂)₃}₂P₁₄ (1), which consists of two PhSi(SiMe₂)₃ substituted P₇ norbornane units. The phosphatetrasila[1.1.1]pentane derivative PhSi(SiiPr₂)₃P (3) was obtained from the reaction of PhSi(SiiPr₂Cl)₃ (2) with Li₃P.

Silicon–phosphorus compounds are still of considerable interest due to their versatile molecular structures and bonding properties. Moreover, they are useful synthons for the formation of several other phosphorus as well as silicon compounds.¹ Silyl groups are also able to stabilise highly reactive phosphorus species such as P_7^{3-} , the silylderivatives of which (*e.g.* $P_7(SiMe_3)_3$ or $P_7(Si(SiMe_3)_3)_3$) are much less reactive during oxidation or hydrolysis.² As shown in recent studies, bridging silyl substituents such as bidentate silyl or siloxane groups have a major impact on the structures and properties of oligophosphanes.³ Thus, we decided to investigate the extent to which tripodal silyl groups are able to stabilise new P_n -compounds.⁴

Herein, we report on the application of the compound $PhSi(SiMe_2Cl)_3$ as a substituent for $P_7{}^{3-}$. Moreover, we present the synthesis of the sterically demanding branched trichlorotetrasilane $PhSi(SiiPr_2Cl)_3$ as well as its reaction with Li_3P .

After work-up of the reaction of $P_7(SiMe_3)_3$ with PhSi(SiMe_2Cl)₃ in DME, {PhSi(SiMe_2)_3}_2P_{14} (1) was obtained as yellow crystals in 53% yield. The latter was formed by dimerisation of the P₇ cage through substitution of the silyl groups and represents a silyl derivative of the so far unknown Zintl anion P_{14}^{6-} . The P_{14} framework of compound 1 consists of two P₇ norbornane cages. In both P₇ norbornane subunits, one P₅ ring is substituted by the branched silyl frame in 1, 2 and 4 positions (Fig. 1). These two P₅Si₄ fragments show the same structure as the P₉ cage in Hittorf's phosphorus, and they are

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Fig. 1 Molecular structure of 1; thermal ellipsoids represent a 50% probability level, hydrogen atoms are not shown, selected bond lengths (pm) and angles (°): Si1–Si2 233.5(4), Si1–Si3 232.9(5), Si1–Si4 234.24(4), Si2–P1 229.3(4), Si3–P2 229.9(4), Si4–P4 228.3(4), P1–P2 225.4(4), P1–P5 221.0(4), P2–P3 221.65(4), P3–P4 217.6(4), P4–P5 219.9(4), P5–P6 218.6(4), P6–P7 229.4(4), P6–P7 224.0(4); Si2–Si1–Si3 98.88(16), Si2–Si1–Si4 107.90(14), Si3–Si1–Si4 106.70(15), P1–Si2–Si1 102.70(15), P2–Si3–Si1 102.57(15), P4–Si4–Si1 110.70(16).

connected through a central P₄ ring. Until now, no comparable P₁₄ substructure has been observed in molecular compounds. The known Zintl ion P₁₄^{4–} consists of two P₇ nortricyclan cages connected by one P–P bond.⁵ P₁₄*i*Pr₄, consists – like compound **1** – of two P₇ norbornane units, which are connected by three P–P bonds *via* P₅ rings in 1, 2, and 4 positions (Scheme 1).⁶ The P₁₄ unit in **1**, however, represents a part within the phosphorus strands in [(CuI)₈P₁₂].⁷

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[†] Electronic supplementary information (ESI) available: DFT calculations, crystallographic data of compound **2**, proposed mechanism for the formation of compound **1** and ³¹PNMR spectrum of compound **1**. CCDC 978105 (1), 978107 (2) and 978106 (3). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc00165f



 $\ensuremath{\text{Scheme 1}}$ Structurally characterised ionic/molecular compounds with $\ensuremath{\text{P}_{14}}$ units.

The ³¹P{¹H} NMR spectrum of **1** shows four signals at 50.9, 9.1, 2.4 and -42.6 ppm corresponding to the four different phosphorus positions within the molecule. Unfortunately, these signals are broad, independent of the temperature and solvent. So, the fine structure can be resolved only for the signal at 50.9 ppm, which shows a triplet structure and represents the symmetrically surrounded phosphorus atoms P4 and P4'.

Some years ago, several groups reported on their attempts to synthesise a 1-phospha-2,3,4,5-tetrasila[1.1.1]pentane.⁸ These experiments, however, always led to the formation of other bicyclic silylphosphines as shown in Scheme 2.

In order to avoid decomposition of the Si₄ substructure, we synthesised the sterically more demanding substituted branched trichlorotetrasilane PhSi(Si*i*Pr₂Cl)₃ (2) as starting compound. 2 was obtained in a two-step synthesis by a reductive coupling of PhSiCl₃ and *i*Pr₂SiHCl with elementary lithium and subsequent chlorination with trichloroisocyanuric acid (TCCA) (Scheme 3).⁹

After work-up, the reaction of **2** with Li_3P in THF provides the target molecule as a white crystalline solid in small but reproducible yields (Fig. 2). Other products could not be characterised to date. The crystal structure analysis shows the strained molecular structure with endocyclic bond angles all below 90°: Si-Si-Si: 81.6–82.5°, Si-Si-P: 80.2–80.6° and Si–P–Si: 83.3–83.6°. The bond lengths in compound **3**, however, are only slightly longer than the usual single bond between these elements (Fig. 2). Worth mentioning are the short distances between the atoms Si2, Si3 and Si4 (307.7(9)–309.0(12) pm) and between Si1 and P (301.2(10) pm), which are significantly shorter than the sum of the van der Waals radii.



Scheme 2 Reported attempts to synthesise a 1-phospha-2,3,4,5-tetrasila-[1.1.1]pentane and the obtained products.⁸



Scheme 3 Synthesis pathway of compound 2.



Fig. 2 Molecular structure of **3**; thermal ellipsoids represent a 50% probability level, hydrogen atoms are not shown, selected bond lengths (pm) and angles (°): Si1–Si2 235.46(8), Si1–Si3 235.01(14), Si1–Si4 233.61(12), Si2–P 230.05(14), Si3–P 232.56(9), Si4–P 231.60(11); Si–Si1–Si 81.61(4)–82.52(4), Si1–Si–P 80.19(4)–80.68(4), Si–P–Si 83.30(4)–83.60(4).

The ³¹P NMR spectrum of compound 3 shows a typical upfield shift for silylphosphines at -241.7 ppm. In the ²⁹Si{¹H} NMR, two doublet signals can be observed at 15.4 and -58.2 ppm. The signal at 15.4 ppm corresponds to the Si/Pr₂ groups and shows a remarkably large ¹J_{Si,P} coupling constant of 53.2 Hz. This large coupling constant suggests a high s-orbital contribution to the Si–P σ -bonds and matches the results of DFT calculations (see ESI†), which show a high p-orbital character of the phosphorus lone pair and a symmetric bonding orbital with significant contributions of Si1–Si4 and P atomic s-orbitals. For comparison, the similar substituted but planar compound P(Si/Pr₃)₃ shows a ¹J_{Si,P} coupling of only 9 Hz.¹⁰

All working procedures were conducted under rigorous exclusion of oxygen and moisture using a Schlenk line and an argon atmosphere. Solvents were dried and freshly distilled before use. NMR spectra were recorded using a BRUKER AVANCE 300 or a BRUKER DRX 400. The structural analysis was carried out using appropriate single crystals on an automatic diffractometer (STOE-IPDS-2T, STOE-IPDS-2 or BRUKER D8-Quest). The structures were solved and refined using SHELXS-97¹¹ and SHELXL-2013.¹² The presentation of crystal structures was effected by DIAMOND3.2. IR vibrational spectra were recorded using the BRUKER ALPHA ATR-FT-IR. The starting materials PhSi(SiMe₂Cl)₃,⁴ $P_7(SiMe_3)_3$,² and Li₃P¹³ were prepared by reported methods.

Crystal data for 1: $C_{24}H_{46}Si_8P_{14}\cdot 1.5 C_7H_8$, 100 K, triclinic, $P\overline{1}$, a = 931.0(2), b = 1656.6(4), c = 1880.4(4) pm, $\alpha = 88.880(19)^\circ$, $\beta = 87.593(19)^\circ$, $\gamma = 77.702(18)^\circ$, V = 2830.9(11) Å³, Z = 2, density = 1.327 g cm³, $\mu = 0.619$ mm⁻¹, F(000) = 1174, GOF = 0.742, theta range: 1.26–24.00°, 12 809 reflections collected, 8177 unique ($R_{int} = 0.1002$). R_1 (wR_2) = 0.0716 (0.1586) for 530 parameters and 3183 reflections with $I > 2\sigma(I)$.

Crystal data for 3: $C_{24}H_{47}Si_4P_1$, 100 K, triclinic, $P\overline{1}$, a = 916.4(3), b = 1020.7(3), c = 1644.1(9) pm, $\alpha = 92.88(4)^\circ$, $\beta = 94.84(4)^\circ$, $\gamma = 110.34(2)^\circ$, V = 1431.7(10) Å³, Z = 2, density = 1.111 g cm³, $\mu = 0.273$ mm⁻¹,

F(000) = 524, GOF = 1.036, theta range: $1.25-25.00^{\circ}$, 9353 reflections collected, 4731 unique ($R_{int} = 0.0205$). R_1 (w R_2) = 0.0247 (0.0657) for 262 parameters and 4266 reflections with $I > 2\sigma(I)$.

1: PhSi(SiMe₂Cl)₃ (0.42 g, 1.1 mmol) in dme (20 mL) was added dropwise to a solution of P_7 (SiMe₃)₃ (0.48 g, 1.1 mmol) in dme (20 mL) at -45 °C. The reaction mixture was allowed to warm up within 4 h to ambient temperature, the solvent was removed under reduced pressure and the residue was dissolved in 5 mL toluene. Subsequently, after 2 days yellow crystals of [{PhSi(SiMe₂)₃}₂P₁₄]·1.5 tol were obtained at 20 °C in a yield of 53% (0.29 g). Elemental analysis (%): calc. for C₂₄H₄₆Si₈P₁₄: C 29.03, H 4.67, found: C 29.09, H 5.07.

¹H-NMR (thf-d₈): δ /ppm = 0.35 (m, *CH*₃, 12H), 0.78 (m, *CH*₃, 12H), 0.92 (m, *CH*₃, 12H), 7.28 (m, *C*₆*H*₅, 6H), 7.39 (m, *C*₆*H*₅, 4H). ¹³C{¹H}-NMR (thf-d₈): δ /ppm = 2.96 (m, *CH*₃), 3.68 (m, *CH*₃), 128.24 (s, *C*₆*H*₅), 128.66 (s, *C*₆*H*₅), 129.11 (s, *C*₆*H*₅), 136.56 (s, *C*₆*H*₅). ²⁹Si{¹H}-NMR (thf-d₈): δ /ppm = -4.3 (m, *Si*(*CH*₃)₂), -5.8 (m, *Si*(*CH*₃)₂), -77.5 (s, *Si*C₆*H*₅). ³¹P-NMR (thf-d₈): δ /ppm = 51.0 (t, ¹*J*_{PP} = 328.1 Hz), 9.1 (m), 2.4 (m), -42.6 (m). MS(ESI⁺) *m/z* (%) calc.: 992.8153 [M⁺ + H], found: 992.8265 (45).

PhSi(Si*i*Pr₂H)₃: A solution of PhSiCl₃ (12.63 g, 0.06 mol) and *i*Pr₂HSiCl (44.96 g, 0.29 mol) in thf (250 mL) was slowly dropped at ambient temperature to a vigorously stirred suspension of Li cuts (3.32 g, 0.48 mol) in thf (250 mL) over 3 h, and stirring was continued for 24 h. The suspension was poured into a mixture of ice and HCl (200 mL, 1 M) and *n*-pentane (100 mL) was added. The organic phase was separated, the aqueous layer was extracted twice with *n*-pentane (100 mL) and the combined organic phases were dried with MgSO₄ and filtered. After evaporation of the solvents, the raw product was distilled fractionally under vacuum to afford PhSi(Si*i*Pr₂H)₃ (10⁻² mbar, 120 °C) in a yield of 62.8% (16.9 g).

¹H-NMR (C₆D₆): δ /ppm = 1.18 (d, ³J_{HH} = 7.4 Hz, CH(CH₃)₂, 18H), 1.20 (d, ³J_{HH} = 7.4 Hz, CH(CH₃)₂, 18H), 1.42 (d, sep, ³J_{HH} = 7.4 Hz, and 2.7 Hz, CH(CH₃)₂, 6H), 4.18 (t, ³J_{HH} = 2.7 Hz, SiH, 3H), 7.11 (m, C₆H₅, 3H), 7.80 (m, C₆H₅, 2H). ¹³C{¹H}-NMR (C₆D₆): δ /ppm = 13.96 (s, CH(CH₃)₂), 21.40 (s, CH(CH₃)₂), 22.98, (s, CH(CH₃)₂), 128.51 (s, C₆H₅), 129.29 (s, C₆H₅), 135.52 (s, C₆H₅), 138.42 (s, C₆H₅). ²⁹Si-NMR (C₆D₆): δ /ppm = -6.4 (d, m, ¹J_{SiH} = 172.3 Hz, *Si*CH(CH₃)₂), -81,2 (s, *Si*C₆H₅). MS(APCI⁺) *m*/*z* (%) calc.: 449.2906 [M⁺ - H], found: 449.2903 (15); IR [cm⁻¹]: 463(w), 584(w), 650(m), 698(s), 744(vs), 877(m), 917(m), 1003(m), 1067(m), 1233(vw), 1363(w), 1383(w), 1427(w), 1460(m), 2073(m, Si-H), 2861(m), 2940(m).

2: A solution of PhSi(Si*i*Pr₂H)₃ (16.9 g, 0.038 mol) in thf (250 mL) was cooled down to -20 °C. Afterwards, TCCA (10 g, 0.043 mol) was slowly added and the solution was warmed up to ambient temperature. The solvent was removed under reduced pressure and the residue was dissolved in *n*-pentane (60 mL). The insoluble white precipitate was filtrated and washed two times with *n*-pentane (25 mL). The volume of the combined filtrates was reduced to 50 mL. After 4 days at -8 °C, colourless crystals of PhSi(Si*i*Pr₂Cl)₃ were obtained, the yield being 71.0% (14.9 g). Elemental analysis (%): calc. for C₂₄H₄₇Si₄Cl₃: C 52.00, H 8.55, found C 52.01, H 8.97.

¹H-NMR (C₆D₆): δ /ppm = 1.13 (d, ³J_{HH} = 7.4 Hz, CH(CH₃)₂, 18H), 1.24 (d, ³J_{HH} = 7.4 Hz, CH(CH₃)₂, 18H), 1.70 (sep, ³J_{HH} = 7.4 Hz, CH(CH₃)₂, 6H), 7.10 (m, C₆H₅, 3H), 8.14 (m, C₆H₅, 2H). ¹³C{¹H}-NMR (C₆D₆): δ /ppm = 19.08 (s, CH(CH₃)₂), 19.36 (s, CH(CH₃)₂), 20.14 (s, CH(CH₃)₂), 129.06 (s, C₆H₅), 129.32 (s, C_6H_5), 132.31 (s, C_6H_5), 138.85 (s, C_6H_5). ²⁹Si{¹H}-NMR (C_6D_6): δ /ppm = 33.4 (s, SiCH(CH₃)₂), -70.6 (s, SiC₆H₅). MS(APCI⁺) *m*/*z* (%) calc.: 517.2126 [M⁺ - Cl], found: 517.2126 [M⁺ - Cl] (100); IR [cm⁻¹]: 424(w), 463(s), 553(vs), 599(s), 621(m), 655(m), 700(m), 735(m), 760(w), 875(s), 991(m), 1233(vw), 1365(w), 1427(w), 1461(m), 2867(m), 2948(m).

3: PhSi(Si*i*Pr₂Cl)₃ (1.34 g, 2.42 mmol) in thf (10 mL) was added to a suspension of Li₃P (0.13 g, 2.50 mmol) in thf (100 mL) at -30 °C. Subsequently, the reaction mixture was first warmed-up to room temperature and stirred for 16 hours and then heated to reflux for 4 days. Thereafter, the solvent was removed under reduced pressure, and the residue was dissolved in *n*-pentane (25 mL). After filtration, the volume of the solution was reduced to 2 mL and cooled down to -30 °C. Compound 3 was obtained as colourless crystals within 4 days in a yield of 8.8% (0.10 g). Elemental analysis (%): calc. for C₂₄H₄₈Si₄P: C 60.19, H 9.89, found: C 60.24, H 10.03.

¹H-NMR (C₆D₆): δ /ppm = 1.36 (d, ³J_{HH} = 7.5 Hz, CH(CH₃)₂, 18H), 1.38 (d, ³J_{HH} = 7.5 Hz, CH(CH₃)₂, 18H), 1.71 (sep, ³J_{HH} = 7.5 Hz, CH(CH₃)₂, 6H), 7.09 (m, C₆H₅, 3H), 7.70 (m, C₆H₅, 2H). ¹³C{¹H}-NMR (C₆D₆): δ /ppm = 18.91 (d, ²J_{CP} = 5.2 Hz, CH(CH₃)₂), 20.92 (d, ²J_{CP} = 1.1 Hz, CH(CH₃)₂), 21.36 (d, ³J_{CP} = 1.5 Hz, CH(CH₃)₂), 128.67 (s, C₆H₅), 129.22 (s, C₆H₅), 133.40 (s, C₆H₅), 138.25 (s, C₆H₅). ²⁹Si{¹H}-NMR (C₆D₆): δ /ppm = 15.4 (d, ¹J_{SiP} = 53.2 Hz, Si₃P), -58.2 (d, ²J_{SiP} = 8.5 Hz, SiC₆H₅). ³¹P-NMR(C₆D₆): δ /ppm = -241.7 (s). MS(APCI⁻) m/z (%) calc.: 479.2565 [M + H], found: 479.2560 [M + H] (30).

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