Practical Synthesis of Chlorosilyl-Functionalized Triphenylphosphanes

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Abstract: A practical synthesis of *ortho*-dialkylchlorosilyl-functionalized triarylphosphanes has been developed. An X-ray crystal structure analysis of phosphane **3** unambiguously confirmed the constitution of the new phosphane functionalized chlorosilanes. It also showed an interesting P/Si interaction, which may render this compound a model for the early stages of the mechanism of S_N2 nucleophilic displacement at silicon.

Key words: phosphorus, silicon, ligands

Phosphanes are an important class of organic compounds for a variety of applications ranging from their use as ligands in transition metal catalysis,[1] Wittig ylide formation,[2] Mukaiyama redox condensations,[3] Mitsunobu reactions,[4] and nucleophilic organocatalysis.[5] Particularly useful are triarylphosphanes occupied with a functional group in *ortho*-position, which can be attached easily to organic substrates (Figure 1). Such phosphanes are useful for the preparation of ligand libraries applicable to homogeneous catalysis,[6] they may serve as mediators in Staudinger ligation reactions[7] as well as substrate bound catalyst/reagent-directing groups in organic synthesis and catalysis.[8]

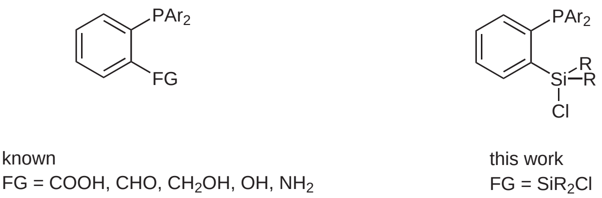
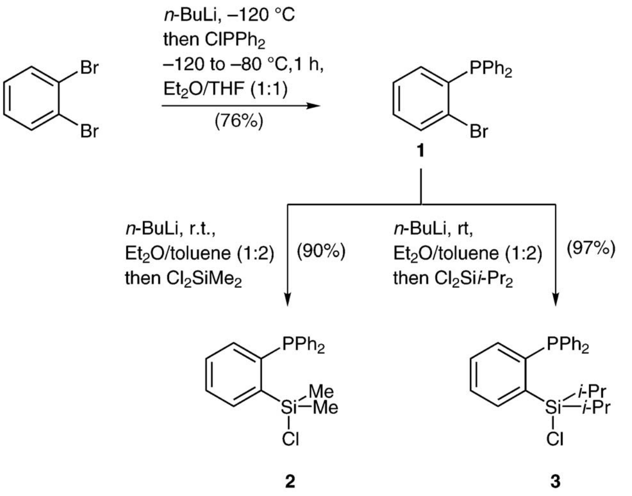


Figure 1 Triarylphosphanes equipped with useful functional groups in the *ortho*-position.

In this respect an interesting, yet unknown, *ortho*-functionalization of a triarylphosphane would be a silyl chloride group, since it can be attached easily to protic functions such as alcohols, phenols, amines, carboxylic acids etc.

We herein report on a first and practical synthesis of *ortho*-dialkylsilyl chloride-functionalized triphenylphosphanes and their characterization via X-ray crystal structrure analysis.

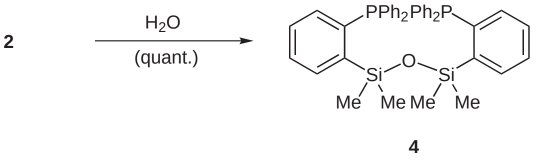
Synthesis of these compounds starts from *ortho*-dibromobenzene, which was treated at –120 °C with one equivalent of *n*-BuLi to undergo smoothly a monohalogen–metal exchange (Scheme 1).[9] The intermediate organolithium compound was reacted instantaneously at the same temperature with chlorodiphenylphosphane, which allowed to suppress elimination to benzyne. After warming of the reaction mixture to –80 °C during one hour and aqueous workup, the *ortho*-bromotriphenylphosphane **1** was obtained in good yield. The reaction has been run on a 12 g scale.



Scheme 1 Preparation of new phosphane functionalized chlorosilanes **2** and **3**.

To install a dialkylchlorosilane function, phosphane **1** was subjected to halogen–metal exchange at room temperature by reacting with *n*-butyllithium. The resulting aryllithium intermediate was quenched at the same temperature with dichlorodimethylsilane to give phosphanyl-substituted chlorosilane **2** (Scheme 1).

Unfortunately, it was found that the dimethylchlorosilane **2** showed extreme sensitivity towards traces of moisture, which led to the immediate formation of the siloxane bridged diphosphane **4** (Scheme 2).



Scheme 2 Hydrolysis of chlorosilane **2**.

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It was envisioned that incorporation of steric hindrance into the chlorosilane function could improve stability of this function towards hydrolysis. Thus, treatment of the *ortho*-lithiotriphenylphosphane obtained from compound **1** with diisopropyldichlorosilane at room temperature furnished in quantitative yield the *ortho*-diphenylphosphanyl-functionalized chlorosilane **3** as colorless crystals. Compound **3** turned out to be rather robust, since it is stable under air and at room temperature for at least one month. From a solution of chlorosilane **3** in petroleum ether suitable single crystals could be obtained which allowed to perform an X-ray-crystal structure analysis (Figure 2, Table 1,2).

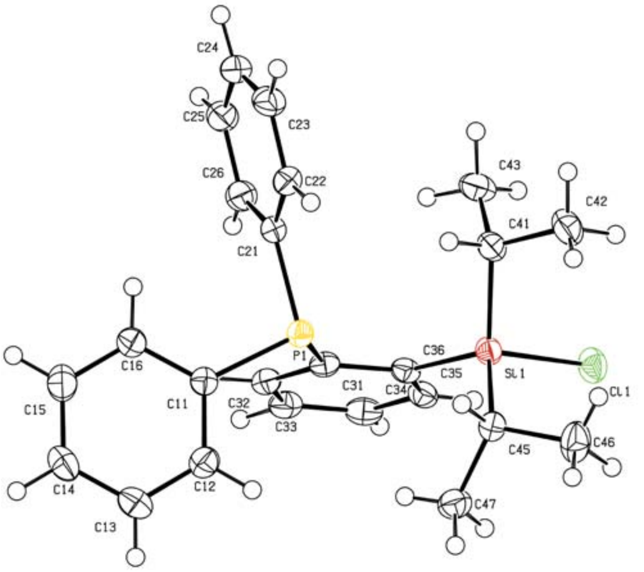

Figure 2 X-ray plot (ORTEP) of the structure of **3** in the solid state.

The X-ray crystal structure of **3** suggests an electronic interaction between the phosphorus and the silicon atom (see Figure 3). Thus, the orientation of the P-lone pair is such that an efficient n(P)–σ*(SiCl) orbital interaction is feasible. Consistently, the P--Si–Cl angle is almost linear with 162.36(0.03)°. As a consequence of this interaction, the distance between the phosphorus and the silicon atom is rather small with 3.31 Å, and the silicon atom adopts a distorted trigonal bipyramidal geometry, which is indicated by significantly increased C–Si–C-angles (112–114°) compared to 109.28° for an ideal tetrahedral system. Finally, the Si–Cl bond distance is elongated with 2.10 Å compared to the standard Si–Cl bond length expected for a tetrahedral R_3SiCl system of 2.05 Å.[10] This interpretation of the geometrical data of **3** is in agreement with a recent series of X-ray crystal structures of *N*-(halogenodimethylsilylmethyl)lactams, which have been discussed as a model of the S_N2 nucleophilic displacement at the silicon atom.[11] Thus, X-ray structure of compound **3** may be regarded as a model for the early stages of the S_N2 nucleophilic displacement reaction at silicon.

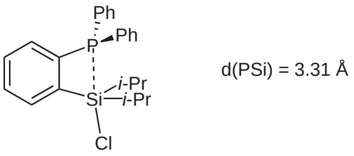

Figure 3 Consideration of chlorosilylphosphane **3** as a model compound for the early stages of the mechanism of S_N2 nucleophilic displacement at silicon.

Table 1 Selected Bond Lenghts [Å] of **3** in the Solid State

Bond Lenghts (in Å)	
C(41)–Si(1)	1.874(2)
C(45)–Si(1)	1.882(2)
C(36)–Si(1)	1.893(2)
Cl(1)–Si(1)	2.0999(8)
C(31)–C(36)	1.420(3)
C(31)–P(1)	1.845(2)
P(1)–Si(1)	3.3117(8)

Table 2 Selected Bond Angles of **3** in the Solid State

Bond Angles (in degrees)	
C(36)–Si(1)–Cl(1)	104.77(7)
C(41)–Si(1)–C(45)	113.98(11)
C(45)–Si(1)–C(36)	112.25(10)
C(41)–Si(1)–C(36)	113.30(10)
C(31)–C(36)–Si(1)	122.99(16)
C(36)–C(31)–P(1)	117.79(16)
P(1)–Si(1)–Cl(1)	162.36(3)

Furthermore, NMR studies in solution indicate that the P-lone-pair orientation of phosphines **2** and **3** is similar to the one found in the X-ray crystal structure of **3**. Thus, the signal of β-arylcarbon atom (C36, X-ray plot in Figure 2) of phosphanes **2** and **3** was observed at $\delta = 142–144$. These signals are split to a doublet with a large $^2J_{C,P}$ coupling constant of 47–51 Hz. A correlation between the dihedral angle of P-lone-pair P–C–βC and the size of the $^2J_{C,P}$ coupling is well-established and suggests in this case a dihedral angle of approximately 0° which is in agreement with the geometry found in the crystalline state of **3**.[12]

In summary, we have developed a practical high-yielding two-step synthesis of two *ortho*-silyl chloride functionalized triarylphosphanes. X-ray crystal structure analysis of silylphosphane **3** shows an interesting P/Si interaction, which may allow to regard **3** as a model compound for the early stages of the mechanism of S_N2 nucleophilic displacement at silicon.

Reactions were performed in flame-dried glassware under argon (purity >99.998%). Petroleum ether used refers to the fraction with bp 40–60 °C. The solvents were dried by standard procedures, distilled and stored under argon. All temperatures quoted are not corrected. ^{1}H, ^{13}C NMR spectra: Varian Mercury 300 HFCP, Bruker AM 400, Bruker DRX 500, with TMS, $CHCl_3$ or C_6H_6 as internal standards. ^{31}P NMR spectra: Varian Mercury 300 HFCP with 85% H_3PO_4 as external standard. ^{29}Si NMR: Bruker AM 400 with TMS as internal standard. Melting points: Melting point apparatus by Dr. Tottoli (Büchi). Elemental analyses: Vario EL (Elementaranalysen GmbH). Mass spectrometry: Thermo Finnigan MAT 8200 and TSQ 7000. Flash chromatography: silica gel 40–63 μm (230–400 mesh, Macherey-Nagel).

o-Bromodiphenylphosphinobenzene (1)

To a solution of 1,2-dibromobenzene (12.4 g, 52.5 mmol) in Et_2O–THF (100 mL/100 mL) at –120 °C (with a cold bath composed of ca. 85% Et_2O, 10% acetone and 5% pentane and liquid N_2) was added dropwise a solution of *n*-BuLi (1.47 M in hexanes, 35.7 mL, 49 mmol). The resulting mixture was stirred for further 45 min at –120 °C followed by the addition of chlorodiphenylphosphine (11.03 g, 50 mmol). The reaction mixture was allowed to warm to –80 °C during 1 h. At this temperature, a sat. aq solution of NH_4Cl (80 mL) was added. The resulting mixture was then allowed to warm to r.t. during 1.5 h. After phase separation, the aqueous phase was extracted with Et_2O (3 × 75 mL). The combined organic phases were dried ($MgSO_4$) and all volatile components were removed in vacuo to furnish 18 g of the crude product, which directly crystallized. The product was dissolved in CH_2Cl_2 (170 mL) and filtered over a small plug of silica gel to remove the traces of phosphane oxide. Recrystallization from petroleum ether–Et_2O (2:1) gave 12.7 g (76%) of very fine white crystals of **1**; mp 125 °C.

^{1}H NMR (300.00 MHz, $CDCl_3$, 25 °C): δ = 6.75–6.81 (m, 1 H, ArH), 7.16–7.23 (m, 2 H, 2 ArH), 7.30–7.42 (m, 10 H, 2 C_6H_5), 7.58–7.62 (m, 1 H, ArH).

^{13}C NMR (75.45 MHz, $CDCl_3$, 25 °C): δ = 127.6, 128.8 (d, $^3J_{C,P}$ = 7.2 Hz, 4 C), 129.2 (2 C), 130.1 (d, $^2J_{C,P}$ = 30.1 Hz), 130.3, 133.2 (d, $^3J_{C,P}$ = 2.3 Hz), 134.2 (d, $^2J_{C,P}$ = 20.1 Hz, 4 C), 134.6, 136.1 (d, $^1J_{C,P}$ = 11.2 Hz, 2 C), 139.1 (d, $^1J_{C,P}$ = 12.0 Hz).

^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = –4.5.

Chlorodimethyl(2′-diphenylphosphanyl)phenylsilane (2)

To a solution of bromo-2-diphenylphosphinobenzene (**1**; 170.6 mg, 0.5 mmol) in a mixture Et_2O–toluene (6 mL, 1:2) was added, a solution of *n*-BuLi (1.57 M in hexanes, 0.350 mL, 0.55 mmol) at r.t. After 10 min, pure dichlorodimethylsilane (193 mg, 1.5 mmol) was added. The resulting reaction mixture was filtered under argon with a syringe equipped with a syringe filter (0.45 μm porosity, 13 mm diameter). Evaporation of all volatile components in oil pump vacuo furnished **2** quantitatively. Spectroscopical analysis showed the presence of ≤10% impurity by siloxane **4** which could not be separated.

^{1}H NMR (500.00 MHz, $CDCl_3$, 25 °C): δ = 0.74 [s, 6 H, $Si(CH_3)_2$], 7.13–7.18 (m, 6 H, ArH), 7.21–7.25 (m, 5 H, ArH), 7.29 [app td, 1 H, $^3J_{2H}$ = 7.5 Hz, $^4J_{1H}$ = 1.5 Hz, C(5)-H], 7.34 [app tt, 1 H, $^3J_{2H}$ = 7.5 Hz, $^4J_{2H}$ = 1.5 Hz, C(4)-H], 7.93 [dddd, 1 H, $^3J_{1H}$ = 7.5 Hz, $^3J_{H,/P}$ = 2.8 Hz, $^4J_{1H}$ = 1.5 Hz, $^5J_{1H}$ = 0.6 Hz, C(3)-H].

^{13}C NMR (125,7 MHz, $CDCl_3$, 25 °C): δ = 5.78, 5.89, 128.59 (d, $^3J_{C,P}$ = 6.6 Hz, 4 C), 128.62 (2 C), 129.00, 130.54, 133.29 (d, $^2J_{C,P}$ = 18.3 Hz, 4 C), 135.40, 135.53 (d, $^2J_{C,P}$ = 16.4 Hz), 137.22 (d, $^1J_{C,P}$ = 9.4 Hz, 2 C), 142.34 (d, $^1J_{C,P}$ = 10.3 Hz), 144.47 (d, $^2J_{C,P}$ = 47.6 Hz).

^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = –10.4.

MS (EI, 70 eV): *m/z* (%) = 354 (11), 336 (14), 319 (20), 263 (20), 262 (86), 195 (16), 183 (100), 152 (17), 108 (30), 107 (17), 57 (17).

HRMS: *m/z* calcd for $C_{20}H_{20}ClPSi$: 354.07604; found: 354.07601.

Chlorodiisopropyl(2′-diphenylphosphanyl)phenylsilane (3)

To a solution of bromo-2-diphenylphosphinobenzene (**1**; 3.41 g, 10 mmol) in a mixture of Et_2O–toluene (60 mL, 1:2) was added at r.t., a solution of *n*-BuLi (1.6 M in hexanes, 6.87 mL, 11 mmol). After 15 min, pure dichlorodiisopropylsilane (2.77 g, 15 mmol) was added. The resulting mixture was stirred for further 2 h, followed by successive filtration with a filter paper and a syringe filter (0.45μm porosity; 30 mm diameter). All volatile components were removed in vacuo to give analytically pure phosphane **3**; yield: 4.0 g (97%); colorless crystals; mp 92 °C.

^{1}H NMR (300.00 MHz, C_6D_6, 25 °C): δ = 0.97 [d, 6 H, $^3J_{1H}$ = 7.3 Hz, $CH(CH_3)_2$], 1.28 [d, 6 H, $^3J_{1H}$ = 7.3 Hz, $CH(CH_3)_2$], 2.03 [sept, 1 H, $^3J_{6H}$ = 7.3 Hz, $CH(CH_3)_2$], 2.04 [sept, 1 H, $^3J_{6H}$ = 7.3 Hz, $CH(CH_3)_2$], 6.97–7.16 (m, 8 H, ArH), 7.25 (m, 4 H, ArH), 7.36 (m, 1 H, ArH), 8.34 (m, 1 H, ArH).

^{13}C NMR (125.7 MHz, C_6D_6, 25 °C): δ = 17.69, 17.80, 18.40, 18.42, 18.44, 18.45, 128.75 (2 C), 128.83 (d, $^3J_{C,P}$ = 6.5 Hz, 4 C), 129.41 (d, $^4J_{C,P}$ = 1.2 Hz), 130.21, 133.48 (d, $^2J_{C,P}$ = 18.1 Hz, 4 C), 135.90 (d, $^4J_{C,P}$ = 1 Hz), 137.71 (d, $^2J_{C,P}$ = 17.6 Hz), 142.08 (d, $^1J_{C,P}$ = 8.8 Hz, 3 C), 142.81 (d, $^2J_{C,P}$ = 51 Hz).

^{31}P NMR (121.5 MHz, C_6D_6, 25 °C): δ = –9.7.

^{29}Si NMR (79.46 MHz, $CDCl_3$, 25 °C): δ = 32.6 (d, $J_{Si,P}$ = 7.4 Hz).

MS (EI, 70 eV): *m/z* (%) = 410 (34), 369 (39), 368 (33), 367 (100), 325 (26), 290 (42), 248 (54), 212 (16), 211 (16), 183 (97), 152 (43), 107 (20).

HRMS: *m/z* calcd for $C_{24}H_{28}ClPSi$: 410.1386; found: 410.1387.

Anal. Calcd for $C_{24}H_{28}ClPSi$ (410.97): C, 70.14; H, 6.86. Found: C, 70.05; H, 6.87.

X-ray Crystal Structure Analysis of Phosphane 3[13]

Colorless crystals of phosphane **3** were grown from a petroleum ether solution at r.t.: C24 H28 Cl P Si, M = 410.97, a = 10.1647(6), b = 12.3576(6), c = 17.7690(10) Å, β = 97.319(3)°, V = 2213.8(2) Å^3, Z = 4, d_{calcd} = 1.233 Mg/m^3. Crystal system: monoclinic, space group $P2_1/c$. Data collection and processing: crystal size: 0.3 × 0.1 × 0.08 mm, Enraf-Nonius KappaCCD diffractometer, λ = 0.71073 Å, collected reflections: 8505, independent: 5024 (R_{int} = 0.048), observed: 3036 [I > 2σ(I)], μ = 0.306 mm^{-1}, no absorption correction. Solution by direct phase determination (SIR-97), full-matrix least-squares refinement on F^2 (SHELXL-97), and hydrogen positions were refined isotropically. Parameters 356, final indices [I > 2 σ(I)]: R = 0.0432, R_w^2 = 0.0822, Goodness-of-fit on F^2: 0.915, largest diff. peak: 0.292 eÅ^{-3}.

Degradation Product 4

Exposure of the arylchlorodimethylsilane **2** to air led to the quantitative formation of siloxane **4**; colorless crystals; mp 141 °C.

^{1}H NMR (500.00 MHz, $CDCl_3$, 25 °C): δ = 0.49 (s, 12 H, 4 CH_3), 7.15–7.23 (m, 10 H, ArH), 7.25–7.30 (m, 12 H, ArH), 7.30–7.36 (m, 4 H, ArH), 7.88 [m, 2 H, 2 C(3)-H].

^{13}C NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 9.6 (2 C), 10.1 (2 C), 128.25 (4 C), 128.41 (d, $^3J_{C,P}$ = 6.4 Hz, 8 C), 128.48 (2 C), 129.49 (2 C), 133.36 (d, $^2J_{C,P}$ = 18.5 Hz, 8 C), 135.06 (d, $^2J_{C,P}$ = 16.4 Hz, 2 C), 135.18 (2 C), 138.21 (d, $^1J_{C,P}$ = 11.5 Hz, 4 C), 141.9 (d, $^1J_{C,P}$ = 12.0 Hz, 2 C), 148.1 (d, $^2J_{C,P}$ = 47.1 Hz, 2 C).

^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = –9.94.

MS (EI, 70 eV): *m/z* = 654 (38), 577 (48), 468 (90), 377 (28), 327 (25), 319 (62), 262 (68), 195 (32), 183 (100), 108 (26).

HRMS: *m/z* calcd for $C_{40}H_{40}OPSi$: 654.2092; found: 654.2090.

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(13) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-229247. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [Fax: +44(1223)336033; E-Mail: deposit@ccdc.cam.ac.uk].