Practical Synthesis of Chlorosilyl-Functionalized Triphenylphosphanes

Delphine Quintard, Manfred Keller, Bernhard Breit*
Institut für Organische Chemie und Biochemie, Albert-Ludwigs-Universität Freiburg, Albertstr. 21, 79104 Freiburg, Germany
Fax +49(761)2038715; E-mail: bernhard.breit@organik.chemie.uni-freiburg.de
Received 29 January 2004

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 SN2 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,\textsuperscript{1} Wittig ylide formation,\textsuperscript{2} Mukaiyama redox condensations,\textsuperscript{3} Mitsunobu reactions,\textsuperscript{4} and nucleophilic organocatalysis.\textsuperscript{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,\textsuperscript{6} they may serve as mediators in Staudinger ligation reactions\textsuperscript{7} as well as substrate bound catalyst/reagent-directing groups in organic synthesis and catalysis.\textsuperscript{8}

![Figure 1](image)

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 structure 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).\textsuperscript{9} The intermediate organolithium compound was reacted instantaneously at the same temperature with chlorodiphenylphosphane, which allowed to suppress elimination to benzene. 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](image)

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](image)

Scheme 2 Hydrolysis of chlorosilane 2.
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 diisopropyl dichlorosilane 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).

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 R₃SiCl system of 2.05 Å. 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 S₅₂ nucleophilic displacement at the silicon atom. Thus, X-ray structure of compound 3 may be regarded as a model for the early stages of the S₅₂ nucleophilic displacement reaction at silicon.

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 δ = 142–144. These signals are split to a doublet with a large J_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 J_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. 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 S₅₂ nucleophilic displacement at silicon.

![Figure 3](image_url)
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.

1H, 13C NMR spectra: Varian Mercury 300 HFCP, Bruker AM 400, Bruker DRX 500, with TMS, CHCl₃ or C₆H₆ as internal standards. 31P NMR spectra: Varian Mercury 300 HFCP with 85% H₂PO₄ as external standard. Si NMR: Bruker AM 400 with TMS as internal standard. Melting points: Melting point apparatus by Dr. Tottoli (Büchi). Elemental analyses: Vario EL (Elementaranalysen Geräteh). 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 Et₂O–toluene (60 mL, 1:2) was added, a solution of 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 1.5 h. After phase separation, the aqueous phase was extracted with Et₂O (3 × 75 mL). The combined organic phases were dried (MgSO₄) and all volatile components were removed in vacuo to furnish a solution of 1,2-dibromobenzene (12.4 g, 52.5 mmol).

**Chlorodimethyl(2-diphenylphosphanyl)phenylsilane (2)**

Centered on 1,2-dibromobenzene (1, 170.6 mg, 0.55 mmol) in a mixture Et₂O–toluene (6 mL, 1:2) was added, a solution of BuLi (1.47 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 stirred for further 2 h, followed by successive filtration with a filter paper and a syringe filter (0.45 μm porosity; 30 mm diameter). All volatile components were removed in vacuo to give analytically pure phosphane A yield: 4.0 g (97%); colorless crystals; mp 92 °C.

1H NMR (300.00 MHz, CDCl₃, 25 °C): δ = 0.97 (d, J = 7.7 Hz, CH(C₆H₅)), 1.28 (d, J = 7.7 Hz, CH(CH₃)₂), 2.03 (bp 40–60 °C. The solvents were dried by standard procedures, distilled and stored under argon. All temperatures quoted are not corrected.

1H, 13C NMR (125.7 MHz, CDCl₃, 25 °C): δ = 16.9, 17.80, 18.40, 18.42, 18.44, 18.45, 128.75 (2 C), 128.93 (d, J = 6.5 Hz, 4 C), 129.41 (d, J = 1.2 Hz, 120.31, 133.34 (d, J = 18.1 Hz, 4 C), 134.67, 136.1 (d, J = 16.4 Hz, 4 C), 137.11, 142.08 (d, J = 12.9 Hz, 3 C), 148.21 (d, J = 51 Hz). 31P NMR (121.5 MHz, CDCl₃, 25 °C): δ = –9.7.

Si NMR (79.46 MHz, CDCl₃, 25 °C): δ = 32.6 (d, J = 7.4 Hz). Melting point: Melting point apparatus by Dr. Tottoli (Büchi). Elemental analyses: Vario EL (Elementaranalysen Geräteh). Mass spectrometry: Thermo Finnigan MAT 8200 and TSQ 7000. Flash chromatography: silica gel 40–63 μm (230–400 mesh, Macherey-Nagel).

1H NMR (300.00 MHz, CDCl₃, 25 °C): δ = 7.16, 17.80, 18.40, 18.42, 18.44, 18.45, 128.75 (2 C), 128.93 (d, J = 6.5 Hz, 4 C), 129.41 (d, J = 1.2 Hz, 120.31, 133.34 (d, J = 18.1 Hz, 4 C), 134.67, 136.1 (d, J = 16.4 Hz, 4 C), 137.11, 142.08 (d, J = 12.9 Hz, 3 C), 148.21 (d, J = 51 Hz). 31P NMR (121.5 MHz, CDCl₃, 25 °C): δ = –9.7.

**Degradation Product 4**

X-ray Crystal Structure Analysis of Phosphane 3

Colorless crystals of phosphane 3 were grown from a petroleum ether solution at r.t.: C₂₄H₂₈ClP₂Si, M = 410.97, a = 10.1647(6), b = 12.2576(6), c = 17.7690(10), β = 97.31(9)°. V = 2213.8(2) Å³, Z = 4, dcalcd = 1.233 Mg/m³. Crystal system: monoclinic, space group P2₁/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, Rint = 0.047 (34), 369 (39), 368 (33), 367 (100), 293 (26), 290 (42), 248 (54), 212 (16), 211 (16), 183 (97), 152 (43), 107 (20).

Acknowledgment

We thank the Fonds of the Chemical Industry and the Krupp Foundation (Krupp Award for young university teachers to BB) for financial support.

References


(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)360633; E-Mail: deposit@ccdc.cam.ac.uk].