

Synthesis of novel ligands: two or more triphenylphosphine units containing polysilicon compounds

Yuki Takuma and Naoshi Imaki *

Mitsubishi Kasei Corporation, Research Center 1000 Kamoshida-cho, Midori-ku, Yokohama 227 (Japan)
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Abstract

Novel phosphine compounds in which two or more triphenylphosphine units are introduced into a polysilicon chain have been synthesized.

Introduction

Organophosphorus species have commonly been used as ligands in soluble transition-metal catalysts which play a major role in homogeneous catalytic reactions. It is well known that steric or electronic effects of ligands drastically affect reaction rates and selectivities. For example, Slaugh and Mullineaux reported the effects of organophosphines on cobalt-catalyzed hydroformylation [1]. Furthermore many chiral ligands are effective in transition metal-catalyzed, asymmetric reactions [2,3]. Of the organophosphorus compounds, triphenylphosphine is the most usually used ligand for transition metal-catalyzed reactions, owing to its moderate properties.

Although many organophosphine compounds have been synthesized, bidentate or multidentate phosphine ligands having triphenylphosphine units have not been reported except for those supported on polymers [4,5]. Bidentate or multidentate phosphine ligands with triphenylphosphine units should afford novel effects, in contrast to other bidentate ligands such as bis(diphenylphosphino)ethane (DPPE) which has a phosphinoalkane type structure.

In this paper we described the first synthesis of some phosphine compounds in which two or more triphenylphosphine units have been introduced into the organosilicon framework.

Results and discussion

At first we tried to make alkane derivatives having two or more triphenylphosphine groups, but the reaction of either *p*-(diphenylphosphino)phenylmagnesium

bromide or *p*-(diphenylphosphino)phenyllithium with a dihaloalkane gave little of the corresponding coupled product. For example, in the presence of a Grignard cross-coupling catalyst such as dichloro[bis(triphenylphosphine)]nickel(II) the reaction of *p*-(diphenylphosphino)phenylmagnesium bromide with 1,4-dibromobutane gave triphenylphosphine (23% yield) and *p*-bromophenyldiphenylphosphine (12% yield). Metal-halogen exchange probably predominates. In view of this we turned our attention to organosilicon skeletons.

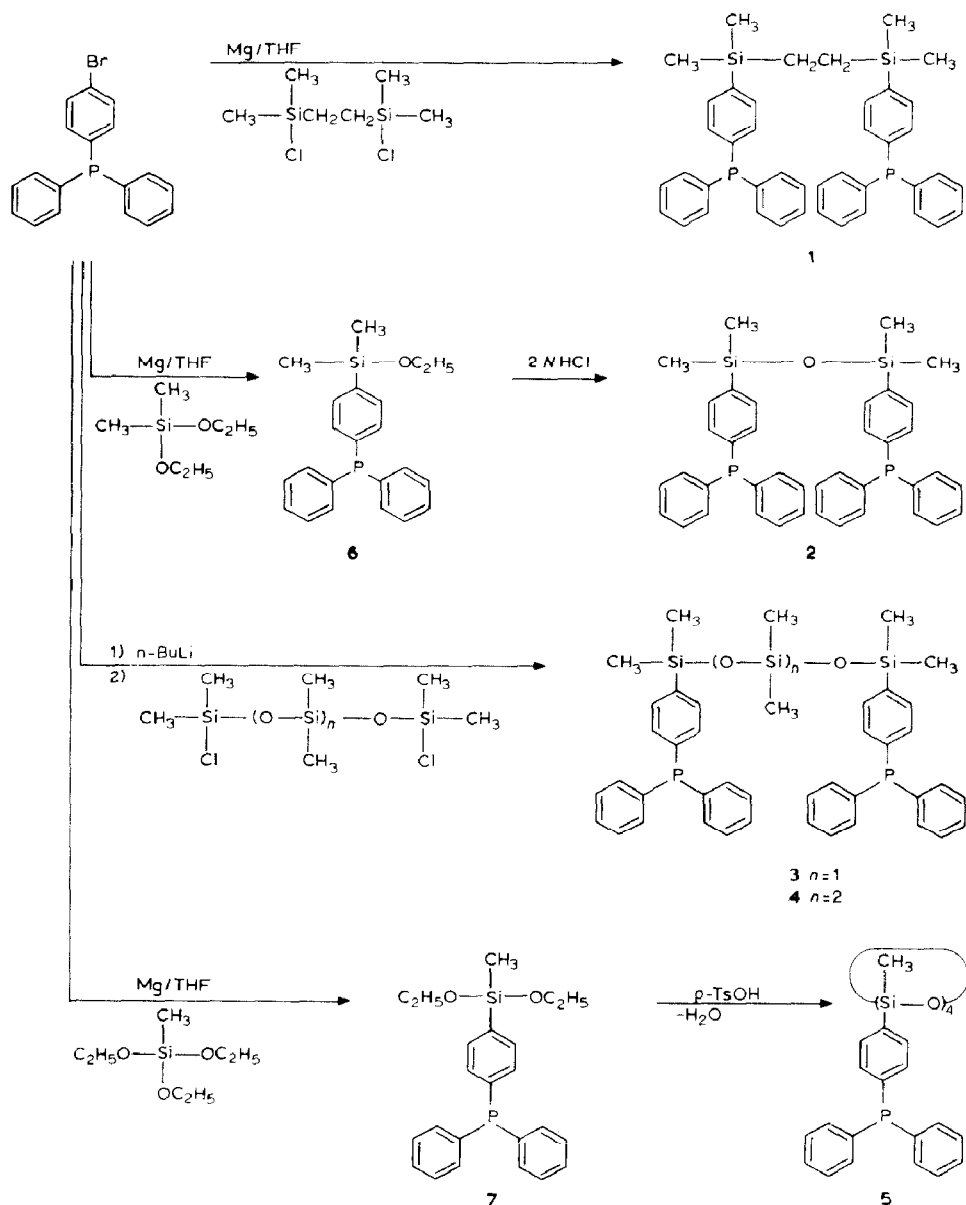


Fig. 1. Synthetic routes to new phosphine compounds.

Synthesis of silicon compounds having triphenylphosphine units

Grignard or organolithium reagents react readily with silicon halides and alkoxides [6]. The nucleophilic substitution of alkoxy or halosilanes by *p*-(diphenylphosphino)phenylmagnesium bromide and *p*-(diphenylphosphino)phenyllithium successfully gives the corresponding phosphorus compounds. The various new phosphine compounds are depicted in Fig. 1.

Thus, 1,2-bis[dimethyl(*p*-diphenylphosphino)phenylsilyl]ethane (**1**), hexamethyl-1,5-bis[*p*-(diphenylphosphino)phenyl]trisiloxane (**3**) and octamethyl-1,7-bis[*p*-(di-

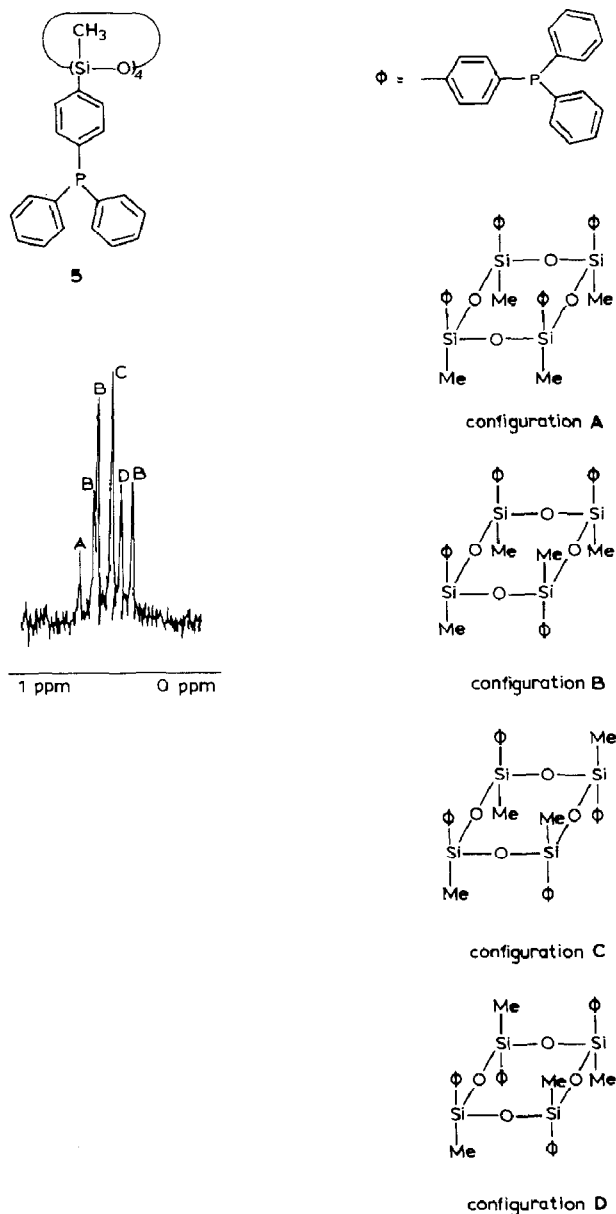


Fig. 2. The ^1H NMR spectrum (in the methyl region) of cyclotetrasiloxane (**5**) and the assignment of resonances to its configurational isomers.

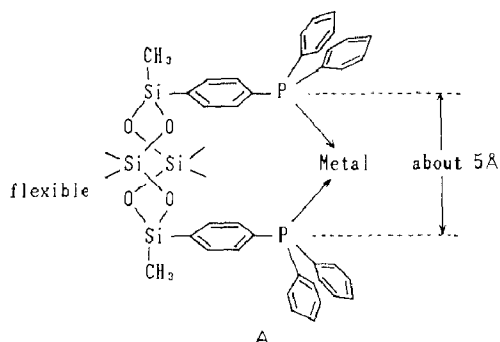


Fig. 3. A possible structure of metal complexes with cyclotetrasiloxane (**5**) as ligand.

phenylphosphino)phenyl]tetrasiloxane (**4**) were synthesized in good yields from the corresponding halosilanes. Tetramethyl-1,3-bis[*p*-(diphenylphosphino)phenyl]siloxane (**2**) was prepared by hydrolysis–condensation with 2 *N* HCl in acetone of dimethylethoxy[*p*-(diphenylphosphino)phenyl]silane (**6**), which had been synthesized previously by heating a mixture of magnesium, *p*-(diphenylphosphino)bromobenzene and diethoxydimethylsilane.

Furthermore it is known that cyclic polysiloxanes are formed by the polycondensation of dialkoxysilanes. The cyclotetrasiloxane having triphenylphosphine units (**5**) was prepared by the hydrolysis of methyl-diethoxy[*p*-(diphenylphosphino)phenyl]silane (**7**) followed by azeotropic distillation. The silane (**7**) was synthesized by heating a mixture of magnesium, *p*-(diphenylphosphino)bromobenzene and methyltriethoxysilane.

The new cyclic tetrasiloxane (**5**) was found to be a mixture of four configurational isomers by ^1H NMR spectroscopy (Fig. 2). The methyl protons of (**5**) show six singlet signals attributable to four configurational isomers. This pattern is similar to that of 2,4,6,8-tetraphenyl-2,4,6,8-tetramethylcyclotetrasiloxane which was shown to consist of four isomers by Hickton's NMR study [7].

In view of the flexibility of cyclotetrasiloxane and the bulkiness of the triphenylphosphine substituent, structure *A* seems to be the best isomer to coordinate to a metal center (Fig. 3). These complexes thus resemble the 1,1'-bis(diphenylphosphino)ferrocene-metal complexes [8].

Procedures to synthesize metal complexes with ligand **5** are currently under investigation.

Experimental

The ^1H NMR (100 MHz) spectra were recorded on a JEOL FX-100 instrument. IR spectra were obtained with a JASCO IRA-1 spectrometer. All organosilicon derivatives were purchased from Shin-Etsu Chemical Co., Ltd.

1,2-Bis[dimethyl{*p*-(diphenylphosphino)phenyl}silyl]ethane (**1**)

To *p*-bromophenyldiphenylphosphine (2.0 g) in dry THF (15 ml) and magnesium (1.43 g) was added 1,2-bis(dimethylchlorosilyl)ethane (0.632 g). The mixture was stirred and heated to reflux for 10 h. Removal of solvent after separation from salts under nitrogen gave the crude product. Recrystallization from benzene/ethanol

gave 1.35 g (70% yield) of pure **1**. $^1\text{H NMR}$ (acetone- d_6) δ 0.3 (s,12H), 0.6 (s,4H), 7.2 ~ 8.0 (m,28H); IR (KBr) (cm^{-1}) 3040, 2920, 1580, 1470, 1430, 1250, 1120, 820, 810, 775, 745, 700.; mass spectra $M^+ = 666$. Anal. Found: C, 75.39; H, 6.65; P, 8.90; Si, 7.80. $\text{C}_{42}\text{H}_{44}\text{P}_2\text{Si}_2$ calcd.: C, 75.64; H, 6.65; P, 9.29; Si, 8.42%

*Dimethylethoxy[*p*-(diphenylphosphino)phenyl]silane (6)*

To *p*-bromophenyldiphenylphosphine (5 g, 14.7 mmol) in dry THF (30 ml) and magnesium (0.36 g) was added dimethyldiethoxysilane (3.26 g). The mixture was stirred and heated to reflux for 3 h under nitrogen. The mixture became a homogeneous dark-red solution. Direct distillation of the mixture gave 3.91 g (73% yield) of **6**; b.p. 158 ~ 165 °C/1.0 Torr; $^1\text{H NMR}$ (acetone- d_6) δ 0.5 (s,6H), 1.2 (t,3H), 4.0 (q,2H) 7.4 ~ 8.0 (m,14H); IR (neat) (cm^{-1}) 3030, 2960, 1585, 1480, 1435, 1395, 1260, 1160, 1130, 1110, 1080, 950, 830, 790, 750, 700. Anal. Found: C, 71.79; H, 6.81; P, 8.50; Si, 7.00. $\text{C}_{22}\text{H}_{25}\text{OPSi}$ calcd.: C, 72.49; H, 6.91; P, 8.49; Si, 7.70%.

*Tetramethyl-1,3-bis[*p*-(diphenylphosphino)phenyl]disiloxane (2)*

To 0.47 g of dimethylethoxy[*p*-(diphenylphosphino)phenyl]silane in acetone (0.5 ml) and H_2O (0.5 ml) was added 2 *N* HCl (0.03 ml) by syringe. The mixture was stirred for 20 h at room temperature under nitrogen. Removal of the solvent gave the crude product. Recrystallization from benzene/ethanol gave quantitatively pure **2**, 0.45 g; m.p. 82 ~ 84 °C; $^1\text{H NMR}$ (acetone- d_6) δ 0.4 (s,12H), 7.2 ~ 8.0 (m,28H); IR (neat) (cm^{-1}) 3040, 2940, 1590, 1480, 1440, 1260, 1135, 1050, 1110, 835, 800, 750, 700.; mass spectra $M^+ = 654$. Anal. Found: C, 73.40; H, 6.05; P, 9.40; Si, 8.30. $\text{C}_{40}\text{H}_{40}\text{O}_1\text{P}_2\text{Si}_2$ calcd.: C, 73.36; H, 6.16; P, 9.46; Si, 8.58%.

*Hexamethyl-1,5-bis[*p*-(diphenylphosphino)phenyl]trisiloxane (3)*

To *p*-bromophenyldiphenylphosphine (5.0 g, 14.7 mmol) in dry diethyl ether (30 ml) was added dropwise *n*-BuLi (11 ml, 1.37 mmol/ml of hexane) at -70°C . The mixture was gradually heated to room temperature over 2.5 h. To this solution was added hexamethyl-1,5-dichlorotrisiloxane (2.03 g) at -20°C , stirred at room temperature overnight, and hydrolyzed with water. The organic layer and benzene extracts from the aqueous layer were combined, washed with water, and dried over anhydrous sodium sulfate. Removal of the solvent gave quantitatively 5.62 g of **3**; $^1\text{H NMR}$ (acetone- d_6) δ 0.1 (s, 12H), 0.3 (s,6H), 7.2 ~ 8.0 (m,28H); IR (neat) (cm^{-1}) 3060, 2960, 1590, 1480, 1440, 1260, 1140, 1100, 1050, 840, 800, 760, 700.; mass spectra $M^+ = 728$. Anal. Found: C, 69.55; H, 6.49; P, 7.80; Si, 10.58. $\text{C}_{42}\text{H}_{46}\text{O}_2\text{P}_2\text{Si}_3$ calcd.: C, 69.19; H, 6.36; P, 8.50; Si, 11.56%.

*Octamethyl-1,7-bis[*p*-(diphenylphosphino)phenyl]tetrasiloxane (4)*

To *p*-(diphenylphosphino)phenyllithium (14.7 mmol) in dry diethyl ether (30 ml) was added octamethyl-1,7-dichlorotetrasiloxane (14.7 mmol) to give **4** quantitatively; $^1\text{H NMR}$ (acetone- d_6) δ 0.1 (s, 12H), 0.3 (s,12H), 7.2 ~ 8.0 (m,28H); IR (neat) (cm^{-1}) 3060, 2960, 1590, 1480, 1440, 1260, 1140, 1100, 1050, 840, 800, 760, 700. Anal. Found: C, 66.78; H, 6.66; P, 7.80; Si, 12.30. $\text{C}_{44}\text{H}_{52}\text{O}_3\text{P}_2\text{Si}_4$ calcd.: C, 65.80; H, 6.53; P, 7.71; Si, 13.99%.

Diethoxymethyl[p-(diphenylphosphino)phenyl]silane (7)

To a mixture of *p*-bromophenyldiphenylphosphine (10 g, 29.3 mmol) and magnesium (0.78 g, 32 mmol) in dry THF (145 ml) was added methyltriethoxysilane (5.74 g, 32 mmol). The mixture was stirred and heated under reflux for 9 h under nitrogen. The reaction mixture became a homogeneous dark-red solution. Direct distillation of the mixture gave 6.55 g (57% yield) of **7**; b.p. 140 ~ 165 °C (mainly 162/1.0 Torr; ¹H NMR (CCl₄) δ 0.6 (s,3H), 1.5 (t,6H), 4.1 (q,4H), 7.4 ~ 8.0 °C (m,14H); IR (KBr) (m⁻¹) 3040, 2960, 1950, 1480, 1435, 1400, 1270, 1170, 1135, 1110, 1080, 960, 800, 775, 750, 700.; mass spectra *M*⁺ = 394. Anal. Found: C, 69.04; H, 7.12; P, 7.80; Si, 7.00. C₂₃H₂₇O₂PSi calcd.: C, 70.02; H, 6.90; P, 7.85; Si, 7.12%.

2,4,6,8-Tetrakis[p-(diphenylphosphino)phenyl]2,4,6,8-tetramethylcyclotetrasiloxane (5)

To 13.85 g of methyldiethoxy[*p*-(diphenylphosphino)phenyl]silane in THF (80 ml) and H₂O (1.3 ml) was added *p*-toluenesulfonic acid (0.9 g). The mixture was stirred and heated to reflux for 1 h and azeotropically distilled under nitrogen during 12 h to remove H₂O. Removal of the solvent gave crude product. Recrystallization (4 times) from benzene/ethanol gave 9.1 g (81% yield) of almost pure **5**; ¹H NMR (acetone-*d*₆) δ 0.3 ~ 0.8 (six s, 12H), 7.2 ~ 7.9 (m,56H); IR (KBr) (cm⁻¹) 3040, 1585, 1480, 1435, 1270, 1135, 1070, 1010, 800, 750, 700; mass spectra *M* + 1 = 1345 (four phosphines were oxidized). Anal. Found: C, 70.49; H, 5.38; P, 9.50; Si, 8.60. C₇₆H₆₈O₄P₄Si₄ calcd.: C, 71.22; H, 5.35; P, 9.67; Si, 8.77%.

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