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# Supported organometallic complexes[☆] Part XXIII. A general synthetic route for the synthesis of mono-T-silyl functionalized aromatic phosphines as ligands for chemistry in interphases

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Dedicated to Professor Marianne Baudler on the occasion of her 80th birthday

**Abstract**

The triphenylphosphine ligand $(C_6H_5)_2PC_6H_4(CH_2)_4Si(OCH_3)_3$ **5(T$^0$)** being provided with a T-silyl functionalized $(CH_2)_4$ spacer in *para*-position of only one aryl ring is obtained by a simple four-step reaction starting with *p*-bromobutenylbenzene **1**. **1** is hydrosilylated with $HSiCl_3$ to the silyl species **2** in which the chlorine atoms are exchanged by O*i*-Pr groups to give **3(T$^0$)**. P–C coupling of **3(T$^0$)** with $Ph_2PCl$ is achieved with a Grignard reaction. Finally the O*i*-Pr functions in the resulting phosphine **4(T$^0$)** are replaced by OMe substituents with methanol in the presence of $CH_3C_6H_4SO_3H$. Treatment of the modified phosphine **5(T$^0$)** with $[\mu\text{-ClRh(CO)}_2]_2$ gave the T-silyl functionalized rhodium(I) complex **6(T$^0$)** which is a suitable precursor for sol–gel processing. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* T-Silyl functionalized phosphines; Supported complexes; Rhodium(I)

## 1. Introduction

In a recent review article we introduced the concept of interphases [2]. These are systems in which a stationary phase and a mobile component penetrate each other on a molecular scale without forming a homogeneous phase. Whereas the stationary phase consists of a swellable polymer (e.g. inorganic–organic hybrid polymer [3]), a spacer unit, and a reactive center, the mobile component is a gaseous, liquid, or dissolved reactant or even a solvent. This principle can be employed successfully for combining the advantages of homogenous and heterogeneous catalysis [4–6]. The catalytic activity strongly depends on the mobility of the stationary phase. To achieve high mobility of the reactive center, it is important that the spacer is located at the periphery of the ligand system [7,8]. In this note we present a simple method for the preparation of a modified triphenylphosphine which is provided with a T-silyl functionalized spacer in the *para*-position of only one aryl ring. Such a phosphine can be used for different purposes. One possibility is the surface modification of silica [9,10]. On the other hand, it can be subjected to a sol–gel process [8,11,12]. As an example this phosphine ligand was introduced in a rhodium(I) complex.

## 2. Results and discussion

The synthesis of the T-silyl functionalized phosphine **5(T$^0$)** starts with the aromatically substituted olefin **1**, which is hydrosilylated by $HSiCl_3$ in the presence of the catalyst $H_2PtCl_6$ to give the trichlorosilylated derivate **2** (Scheme 1). It is not necessary to isolate **2**. In a subsequent reaction, the crude liquid **2** is treated with triisopropyl orthoformate at ambient temperature. Un-

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[☆] Part XXII, see Ref. [1].

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der these very mild conditions, the chlorine atoms are exchanged quantitatively by O*i*-Pr groups. The presence of O*i*-Pr residues in **3(T$^0$)** is a necessary precondition for a successful Grignard reaction with the aryl bromide **3(T$^0$)**. After the addition of magnesium, the reaction mixture has to be cooled to $-20$°C to avoid the formation of tetraphenyldiphosphine. Because hydrolysis of crude **4(T$^0$)** is not possible, it has to be extracted with *n*-pentane to give the coupling product **4(T$^0$)** in good yield. To accelerate the sol–gel process, finally the O*i*-Pr groups were replaced by OMe. The T-silyl functionalized triphenylphosphine **5(T$^0$)** is obtained as bright yellow oil, which is sensitive to moisture and air and dissolves readily in all common organic solvents.

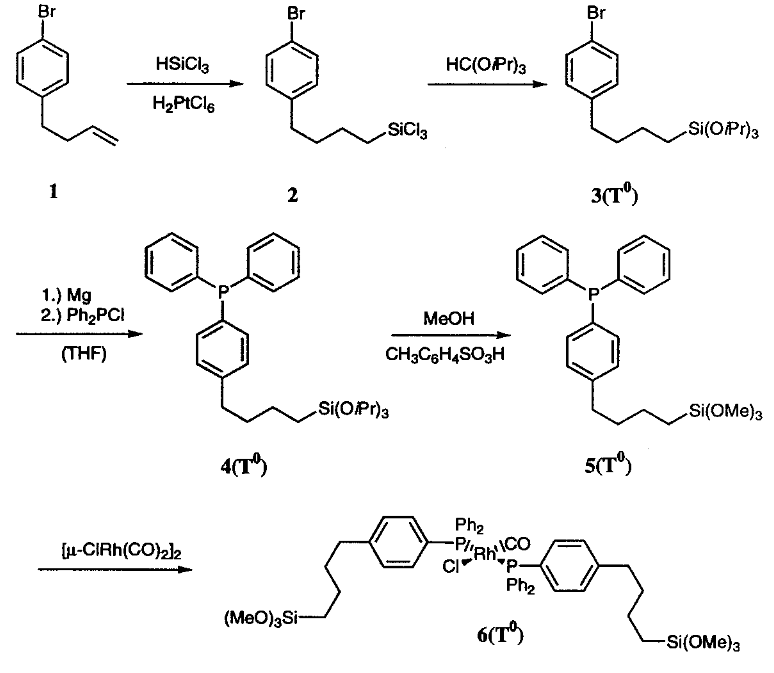
A similar phosphine ligand with a triethoxysilyl function has been published 25 years ago [13]. However, the authors did not report on any spectral data and it was not possible to reproduce the synthetic procedure.

Both intermediates **3,4(T$^0$)** were characterized by EIMS, $^1$H, $^{13}$C{$^1$H}, $^{29}$Si{$^1$H}, and $^{31}$P{$^1$H} spectroscopy, and elemental analyses (see Section 3). The composition of the trimethoxysilyl functionalized phosphine **5(T$^0$)** was corroborated by its EI mass spectrum showing the molecular peak at $m/z = 438$. In the $^{31}$P{$^1$H}-, and $^{29}$Si{$^1$H}-NMR spectra of **5(T$^0$)** each signal is observed at $\delta = -5.02$ and $-41.3$, respectively. Compared to triphenylphosphine the *para*-positioned spacer function exerts nearly no influence on the chemical shift of the $^{31}$P nucleus in **5(T$^0$)**. The completeness of the exchange of the O*i*-Pr groups by OMe residues can be monitored by $^1$H- and $^{13}$C{$^1$H}-NMR spectroscopy.

Since phosphinerhodium(I) complexes play an important role as catalysts in the hydroformylation of olefins the modified triphenylphosphine **5(T$^0$)** was reacted with [$\mu$-ClRh(CO)$_2$]$_2$. After evaporation of the solvent, a yellow waxy product is obtained which proved to be the T-silyl functionalized rhodium(I) complex **6(T$^0$)**.

Only one doublet with a $^1J_{\mathrm{RhP}}$ coupling constant of 126.2 Hz occurs in the $^{31}$P{$^1$H}-NMR spectrum of complex **6(T$^0$)**, which is indicative of a *trans*-position of the phosphine ligands. A characteristic absorption at 1974 cm$^{-1}$ in the IR spectrum of **6(T$^0$)** is assigned to the carbonyl stretching vibration. Other analytic data are summarized in Section 3.

It is a great advantage that it is possible to generalize the synthetic route for the T-silyl functionalized phosphine **5(T$^0$)** presented in Scheme 1. Not only can the spacer length be varied by the employment of different alkenylbenzenes of the type **1**, it is also conceivable to incorporate other phosphorus attached substituents, if in the case of the Grignard reaction step other chlorodiorganylphosphines are used. In addition, the availability of the modified triphenylphosphine **5(T$^0$)** and the rhodium(I) complex **6(T$^0$)** allows to compare reactions in interphases with those of the corresponding triphenylphosphinerhodium(I) complex in homogeneous phase.



Scheme 1.

## 3. Experimental

### 3.1. General remarks

If not stated otherwise, all experiments were carried out under dry argon. THF was distilled from sodium benzophenone ketyl. MeOH was dried and distilled from magnesium and $CH_2Cl_2$ from $CaH_2$. $RhCl_3 \cdot xH_2O$ was a gift from Degussa AG. $[\mu\text{-ClRh(CO)}_2]_2$ [14] and the starting compound **1** [15] were prepared according to the literature methods. $HSiCl_3$ and $Ph_2PCl$ were purchased from Acros and distilled prior to use. Triisopropyl orthoformate and all other chemicals were purchased from Fluka and Merck/Germany, respectively, and used without further purfication. Elemental analyses were carried out on an Elementar Vario EL analyzer. High-resolution $^1H$-, $^{13}C\{^1H\}$-, $^{29}Si\{^1H\}$-, and $^{31}P\{^1H\}$-NMR spectra were recorded on a Bruker DRX 250 spectrometer at 296 K. Frequencies are as follows: $^1H$-NMR — 250.12 MHz; $^{13}C\ \{^1H\}$-NMR — 62.90 MHz; $^{29}Si\ \{^1H\}$-NMR — 49.69 MHz; $^{31}P\{^1H\}$-NMR — 101.25 MHz. The chemical shifts in the $^1H$-, $^{13}C\{^1H\}$-, $^{29}Si\{^1H\}$-, and $^{31}P\{^1H\}$-NMR spectra were measured relative to partially deuterated solvent peaks which are reported relative to TMS. Mass spectra: EIMS; Finnigan TSQ 70 (200°C). FABMS; Finnigan 711A (8 kV), modified by AMD and reported as mass/charge ($m/z$).

### 3.2. p-Bromo[4-(trichlorosilyl)butyl]benzene (**2**)

A mixture of *p*-bromobutenylbenzene (**1**) (27.6 g, 130.7 mmol), trichlorosilane (26.6 g, 196.1 mmol) and hexachloroplatinic(IV) acid (15 mg, 0.029 mmol) in 25 ml of THF was stirred for 1 day at room temperature (r.t.). Distillation under vacuum affords **2** as a colorless, airstable oil which is sensitive to moisture. Yield 33.1 g (73.1%), b.p. 145°C (0.3 mbar). $^1H$-NMR ($CDCl_3$): $\delta = 7.31$ (d, $^3J_{HH} = 8.16$ Hz, 2H, 2,6-benzene), 6.96 (d, $^3J_{HH} = 8.16$ Hz, 2H, 3,5-benzene), 2.51 (t, $^3J_{HH} = 6.91$ Hz, 2H, Br–$C_6H_4$–$CH_2$), 1.56 (m, 4H, $CH_2$–$CH_2$–$CH_2$–$CH_2$), 1.34 (m, 2H, $CH_2$–$SiCl_3$) — $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta = 141.1$ (s, *C*–$CH_2$), 131.8 (s, *C*H–CBr), 130.5 (s, *C*H–C–$CH_2$), 120.0 (s, CBr), 35.1 (s, $C_6H_4$–$CH_2$), 33.8 (s, $C_6H_4$–$CH_2$–$CH_2$), 24.5 (s, $CH_2$–$CH_2$–$SiCl_3$), 22.3 (s, $CH_2$–$SiCl_3$).

### 3.3. p-Bromo[4-(triisopropoxysilyl)butenyl]benzene [**3($T^0$)**]

Under ambient temperature, triisopropyl orthoformate (67.4 g, 354.0 mmol) was added dropwise to *p*-bromo[4-(trichlorosilyl)butyl]benzene (**2**) (33.1 g, 95.5 mmol). After the addition, the solution was stirred for 3 days. Distillation under vacuum affords **3($T^0$)** as a colorless, airstable oil that is sensitive to moisture. Yield 36.4 g (91.3%), b.p. 135°C (0.1 mbar). $^1H$-NMR ($CDCl_3$): $\delta = 7.28$ (d, $^3J_{HH} = 8.17$ Hz, 2H, 2,6-benzene), 6.95 (d, $^3J_{HH} = 8.16$ Hz, 2H, 3,5-benzene), 4.10 (hept, $^3J_{HH} = 6.28$ Hz, 3H, O–CH), 2.46 (t, $^3J_{HH} = 7.85$ Hz, 2H, Br–$C_6H_4$–$CH_2$), 1.54 (m, 2H, $C_6H_4$–$CH_2$–$CH_2$), 1.38 (m, 2H, $CH_2$–$CH_2$–Si(O*i*-Pr)$_3$), 1.09 (d, $^3J_{HH} = 6.28$ Hz, 18H $CH_3$), 0.52 (m, 2H, $CH_2$–Si(O*i*-Pr)$_3$) — $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta = 142.1$ (s, *C*–$CH_2$), 131.6 (s, *C*H–CBr), 130.6 (s, *C*H–C–$CH_2$), 119.6 (s, CBr), 65.2 (s, CH–O), 35.3 (s, $C_6H_4$–$CH_2$), 35.1 (s, $C_6H_4$–$CH_2$–$CH_2$), 25.7 (d, $^3J_{HH} = 6.29$ Hz, 18H, $CH_3$), 23.0 (s, $CH_2$–$CH_2$–Si(O*i*-Pr)$_3$), 12.2 (s, $CH_2$–Si(O*i*-Pr)$_3$) — $^{29}Si\{^1H\}$-NMR ($CDCl_3$): $\delta = -48.8$ (s). EIMS; $m/z$: 418 $[M]^+$. Anal. Found: C, 54.61; H, 7.90. Calc. for $C_{19}H_{33}BrO_3Si$: C, 54.67; H, 7.97%.

### 3.4. [p-Butyl(4-triiosopropoxysilyl)phenyl]diphenylphosphine [**4($T^0$)**]

Magnesium (1.20 g, 50.0 mmol) and 50 ml of THF were placed in a three-necked flask equipped with a magnetic stirrer, a condenser, and a dropping funnel. After activation of the magnesium by some pieces of iodine, a solution of **3($T^0$)** (20.87 g, 50.0 mmol) in 50 ml of THF was added dropwise. The reaction mixture was refluxed for 3 h, decanted from excess magnesium and cooled to −20°C. Subsequently dichlorophenylphosphine (10.14 g, 45.0 mmol) was added to the Grignard solution. The mixture was stirred for 12 h at r.t. THF was removed and *n*-pentane (300 ml) was added. After filtration and removal of the solvent under vacuum, an oily product was obtained which is sensitive to moisture and air. Yield 17.5 g (63.0%). $^1H$-NMR ($CDCl_3$): $\delta =$ 7.24–7.08 (m, 14H, phenyl + phenylene), 4.10 (hept, $^3J_{HH} = 6.27$ Hz, 3H, O–CH), 2.53 (t, $^3J_{HH} = 7.85$ Hz, 2H, $C_6H_4$–$CH_2$), 1.58 (m, 2H, $C_6H_4$–$CH_2$–$CH_2$), 1.37 (m, 2H, $CH_2$–$CH_2$–Si(O*i*-Pr)$_3$), 1.09 (d, $^3J_{HH} = 6.28$ Hz, 18H, $CH_3$), 0.54 (m, 2H, $CH_2$–Si(O*i*-Pr)$_3$) — $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta = 143.7$ (s, *para*-C-phenylene), 137.5 (d, $^1J_{PC} = 10.6$ Hz, *ipso*-C-phenyl), 133.8 (d, $^2J_{PC} = 20.2$ Hz, *ortho*-C-phenylene), 133.7 (m, *ipso*-phenylene), 133.5 (d, $^2J_{PC} = 19.1$ Hz, *ortho*-C-phenyl), 128.7 (d, $^3J_{PC} = 7.4$ Hz, *meta*-C-phenylene), 128.5 (d, $^1J_{PC} = 9.4$ Hz, *ipso*-C-phenylene), 128.3 (d, $^3J_{PC} = 6.7$ Hz, *ortho*-C-phenyl), 64.8 (s, CH–O), 35.3 (s, $C_6H_4$–$CH_2$), 34.7 (s, $C_6H_4$–$CH_2$–$CH_2$), 25.5 ($CH_3$), 22.6 (s, $CH_2$–$CH_2$–Si(O*i*-Pr)$_3$), 11.8 (s, $CH_2$–Si(O*i*-Pr)$_3$) — $^{29}Si\{^1H\}$-NMR ($CDCl_3$): $\delta = -48.6$ (s) — $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta = -4.98$ (s). EIMS; $m/z$: 522 $[M]^+$. Anal. Found: C, 70.61; H, 8.23. Calc. for $C_{31}H_{43}O_3PSi$: C, 71.23; H, 8.29%.

### *3.5. [p-Butyl(4-trimethoxysilyl)phenyl]diphenylphosphine* ***[5(T$^0$)]***

A solution of **4(T$^0$)** (5.0 g, 9.6 mmol) in methanol (20 ml) was stirred at ambient temperature for 24 h in the presence of *p*-toluenesulfonic acid (10 mg, 0.05 mmol). Then the solvent was removed under vacuum. The residue was dissolved in methanol (20 ml) and the mixture was stirred for one more day. To achieve a complete exchange reaction, this operation was repeated three times. A bright yellow oily product was obtained which is sensitive to moisture and air. Yield 3.5 g (83%). $^1$H-NMR ($CDCl_3$): $\delta = 7.26–7.07$ (m, 14H, phenyl + phenylene), 3.49 (s, 9H, O–$CH_3$), 2.55 (t, $^3J_{HH} = 7.85$ Hz, 2H, $C_6H_4$–$CH_2$), 1.60 (m, 2H, $C_6H_4$–$CH_2$–$CH_2$), 1.43 (m, 2H, $CH_2$–$CH_2$–Si(OMe)$_3$), 0.62 (m, 2H, $CH_2$–Si(OMe)$_3$) — $^{13}$C{$^1$H}-NMR ($CDCl_3$): $\delta = 143.5$ (s, *para*-C-phenylene), 137.5 (d, $^1J_{PC} = 10.3$ Hz, *ipso*-C-phenyl), 133.9 (d, $^2J_{PC} = 20.2$ Hz, *ortho*-C-phenylene), 133.6 (d, $^1J_{PC} = 9.2$ Hz, *ipso*-C-phenylene), 133.5 (d, $^2J_{PC} = 19.3$ Hz, *ortho*-C-phenyl), 128.7 (d, $^3J_{PC} = 7.4$ Hz, *meta*-C-phenylene), 128.6 (s, *para*-C-phenyl), 128.5 (d, $^3J_{PC} = 6.7$ Hz, *ortho*-C-phenyl), 50.5 (s, O–$CH_3$), 35.4 (s, $C_6H_4$–$CH_2$), 34.6 (s, $C_6H_4$–$CH_2$–$CH_2$), 22.3 (s, $CH_2$–$CH_2$–Si(OMe)$_3$), 9.0 (s, $CH_2$–Si(OMe)$_3$) — $^{29}$Si{$^1$H}-NMR ($CDCl_3$): $\delta = -41.3$ (s) — $^{31}$P{$^1$H}-NMR ($CDCl_3$): $\delta = -5.02$ (s). EIMS; *m/z*: 438 [M]$^+$. Anal. Found: C, 68.67; H, 7.14. Calc. for $C_{25}H_{31}O_3PSi$: C, 68.47; H, 7.12%.

### *3.6. Bis{[p-butyl(4-trimethoxysilyl)phenyl]diphenylphosphine}carbonylchlororhodium(I)* ***[6(T$^0$)]***

To a solution of [μ-ClRh(CO)$_2$]$_2$ (0.25 g, 0.64 mmol) in 10 ml of benzene was added dropwise a solution of **5(T$^0$)** (1.12 g, 2.57 mmol) in 10 ml of benzene. The reaction mixture was stirred for 1 h at ambient temperature. After drying the product for 3 h in vacuum a yellow waxy solid was obtained which is sensitive to moisture and air. Yield: 1.26 g, (94.5%). $^1$H-NMR ($CD_2Cl_2$): $\delta = 7.61–7.18$ (m, 14H, phenyl + phenylene), 3.47 (s, 9H, O–$CH_3$), 2.60 (t, $^3J_{HH} = 7.85$ Hz, 2H, $C_6H_4$–$CH_2$), 1.59 (m, 2H, $C_6H_4$–$CH_2$–$CH_2$), 1.40 (m, 2H, $CH_2$–$CH_2$–Si(OMe)$_3$), 0.61 (m, 2H, $CH_2$–Si(OMe)$_3$) — $^{13}$C{$^1$H}-NMR ($CD_2Cl_2$): $\delta = 144.7$ (s, *para*-C-phenylene), 137.5, 133.8, 132.6, 129.3, 127.4 (m, phenyl + phenylene), 49.5 (s, O–$CH_3$), 34.6 (s, $C_6H_4$–$CH_2$), 33.7 (s, $C_6H_4$–$CH_2$–$CH_2$), 21.6 (s, $CH_2$–$CH_2$–Si(OMe)$_3$), 8.2 (s, $CH_2$–Si(OMe)$_3$) — $^{31}$P{$^1$H}-NMR ($CDCl_3$): $\delta = 29.7$ (d, $^1J_{RhP} = 126.2$ Hz). FABMS; *m/z*: 1042 [M]$^+$, 1014 [M$^+$ − CO]. Anal. Found: C, 57.68 [16]; H, 5.94. Calc. for $C_{51}H_{62}ClO_7P_2RhSi_2$: C, 58.70; H, 5.99%.

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