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Effect of triarylphosphane ligands on the rhodium-catalyzed hydrosilylation of alkene

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A series of triarylphosphanes (1a–11a) have been synthesized. An X-ray crystal structure analysis of (2-bromophenyl) diphenylphosphane (1a) unambiguously confirmed the constitution of the functionalized phosphane. The hydrosilylation reaction of styrene with triethoxysilane catalyzed with $RhCl_3$/triarylphosphane was studied. In comparison with the classic Wilkinson's catalyst, rhodium complexes with functionalized triarylphosphane ligands are characterized by a very high catalytic effectiveness for the hydrosilylation of alkene. Among these catalysts tested, $RhCl_3$/diphenyl(2-(trimethylsilyl)phenyl) phosphane (8a) exhibited excellent catalytic properties. Using this silicon-containing phosphane ligand for the rhodium-catalyzed hydrosilylation of styrene, both higher conversion of alkene and higher β-adduct selectivity were obtained than with Wilkinson's catalyst. Copyright © 2014 John Wiley & Sons, Ltd.

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Keywords: triarylphosphane; hydrosilylation; rhodium complex; alkene

Introduction

Phosphorus ligands are an important class of ligands in transition metal catalysis reactions. In particular, triarylphosphanes possessing functional groups, which can be easily attached to organic compounds, have widely used applications. Numerous catalytic reactions, such as Wittig ylide formation,[1–3] Mukaiyama redox condensations[4] and Mitsunobu reactions,[5–7] have been intensively developed along with thorough research into transition metal complexes coordinated with phosphorus ligands.[8,9] Generally, geometric, steric and electronic properties of the ligand including phosphane are important to the catalytic activity and selectivity of the corresponding metal complex. Recently, Niyomura[10] reported that a bulky bowl-shaped phosphane ligand markedly improved the catalytic activity of rhodium-catalyzed hydrosilylation reactions as compared with that of conventional phosphane ligands such as PPh_3 and P^tBu_3. Another novel bulky phosphane ligand containing an alkyne group also exhibited excellent catalytic properties for the rhodium-catalyzed hydrosilylation of ketones.[11] By using a bulky ligand, resultant rhodium complex bearing only one phosphane ligand was formed. On the other hand, for phosphane-based ligands, the electronic properties, which were highly influenced by modification of the substituents attached to phosphane, are also important for the catalytic properties of corresponding metal complexes.

Hydrosilylation is one of the most significant reactions for Si–C bond formation in organosilicon chemistry.[12,13] Although a wide range of catalysts have been tested for hydrosilylation, industrial syntheses and most research studies have been carried out in the presence of platinum complexes or rhodium complexes.[14–17] It has been reported that Wilkinson's catalyst, $Rh(PPh_3)_3Cl$, effectively catalyzes the hydrosilylation of alkynes or alkenes.[18] In this catalytic process, phosphane ligands play a significant role in hydrosilylation.[19–21] The chief role of the phosphane ligands is to promote the metal in the form of stable species that can subsequently enter the catalytic cycle and prevent the production of inactive metal aggregates.[22–25] However, $Rh(PPh_3)_3Cl$ displayed low catalytic activity and selectivity in the hydrosilylation of substituted alkenes.[18] In this paper, we now report a series of triarylphosphane-based ligands (Scheme 1). Also, the catalytic properties of rhodium complexes coordinated with these triarylphosphane-based ligands with different substituents on phosphane have been compared to classic Wilkinson's catalyst.

Experimental

General Remarks

Styrene was washed with 5% NaOH and dried with Na_2SO_4, and was then distilled under reduced pressure after filtration. All materials were purchased from Aldrich and were used as received.

Gas chromatography: Trace DSQ GC column, DB-5 30 m × 2.5 mm × 0.25 μm; split 50:1, flow 1 ml min^{-1} constant flow; inlet temperature 260 °C; column temperature 50 °C (held for 1 min) then 15 °C min^{-1} up to 260 °C (held for 10 min). GC-MS: Trace DSQ GC-MS column.

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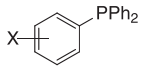


Scheme 1. Structures of triarylphosphane ligands. **1a**: X = *o*-Br; **2a**: X = *m*-Br; **3a**: X = *p*-Br; **4a**: X = *o*-NH_3; **5a**: X = *p*-NH_3; **6a**: X = *p*-COOH; **7a**: X = *o*-Bu; **8a**: X = *o*-$SiMe_3$; **9a**: X = *p*-$SiEt_3$; **10a**: X = *o*-Me; **11a**: X = *o*-OMe.

^{1}H, ^{13}C, ^{29}Si and ^{31}P NMR spectra were measured using a Bruker AV 400 MHz spectrometer operating at 400.13, 100.62, 79.49 and 161.97 MHz, respectively.

IR spectra were recorded on a Nicolet 5700 instrument and elemental analyses were performed on a Vario EL-3 elemental analyzer.

Synthesis of Triarylphosphane Ligands

Synthesis of (2-bromophenyl)diphenylphosphane ***1a***

A 100 ml three-necked flask equipped with a magnetic stir bar, rubber septum and reflux condenser was charged with NaOAc (1.30 g, 15.8 mmol) and $Pd(OAc)_2$ (17.5 mg, 0.07 mmol), and was evacuated and refilled with argon three times before adding *N*, *N*-dimethylacetamide (35 ml), 1-bromo-2-iodobenzene (2.50 ml, 19.5 mmol) and diphenylphosphine (2.5 ml, 19.5 mmol). The reaction mixture was stirred at 130 °C for 3 days. The reaction mixture was cooled to room temperature and diluted with water (30 ml) and extracted with $CHCl_3$ (20 ml × 3). The combined organic extracts were dried using anhydrous Na_2SO_4. The filtrate was concentrated *in vacuo* and purified by recrystallization in ethanol to give a yellow solid. Further purification was done using flash chromatography (1:2 EtOAc–hexane) to yield a white precipitate **1a**, 92% yield. The data of ^{1}H, ^{13}C, ^{29}Si and ^{31}P NMR spectra, IR spectra and MS were consistent with those reported in the literature (Fig. 1).[26–29]

Synthesis of (3-bromophenyl)diphenylphosphane ***2a***

A 100 ml Schlenk tube equipped with a magnetic stir bar was evacuated and refilled with argon three times before adding a solution of 1-bromo-3-iodobenzene (0.78 ml, 6.1 mmol) in Et_2O (30 ml) under argon atmosphere. The reaction Schlenk tube was cooled to −78 °C and a solution of *n*-BuLi in hexane (1.6 M, 6.5 mmol) was added dropwise slowly. When the addition was complete, the reaction mixture was stirred at the same temperature for 1 h. The reaction mixture was quenched with chlorodiphenylphosphine (1.10 ml, 6.1 mmol) at −78 °C. The resulting mixture was gradually warmed to ambient temperature for 4 h. The mixture was quenched with water and extracted with Et_2O (30 ml × 3). The combined organic layers were dried over magnesium sulfate, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography with hexane to yield **2a** as a colorless viscous oil; 74% yield. ^{1}H NMR ($CDCl_3$) δ: 7.73–7.68 (m, 1H, *p*-H, P–$C_6\mathbf{H}_4$–Br), 7.61–7.58 (m, 1H, *m*-H, P–$C_6\mathbf{H}_4$–Br), 7.54 (m, 4H, *m*-H, $C_6\mathbf{H}_5$–P), 7.51–7.44 (m, 2H, *p*-H, $C_6\mathbf{H}_5$–P; 4H, *o*-H, C_6H_5–P), 7.44–7.38 (m, 1H, *m*-H, P–$C_6\mathbf{H}_4$–Br), 7.27 (m, 1H, *o*-H, P–$C_6\mathbf{H}_4$-Br), due to overlapping of signals, the proton assignment was listed without distinct identification. ^{13}C NMR ($CDCl_3$) δ: 140.98 (J = 20.2 Hz, 1C, P–C, P–$\mathbf{C}_6H_4$–Br), 136.66 (J = 10.8 Hz, 1C, *o*-C, P–$\mathbf{C}_6H_4$-Br), 136.28 (J = 20.2 Hz, 2C, P–C, $\mathbf{C}_6H_5$-P), 134.09 (J = 10.8 Hz, 1C, *o*-C, P–$\mathbf{C}_6H_4$–Br), 132.38 (1C, *p*-C, P–$\mathbf{C}_6H_4$–Br), 131.96 (J = 10.8 Hz, 4C, *o*-C, $\mathbf{C}_6H_5$–P), 130.35 (J = 6.5 Hz, 1C, *m*-C, P–$\mathbf{C}_6H_4$–Br), 129.36 (J = 6.5 Hz, 4C, *m*-C, $\mathbf{C}_6H_5$–P), 128.99 (2C, *p*-C, $\mathbf{C}_6H_5$–P), 123.50 (J = 6.5 Hz, 1C, *m*-C, P–$\mathbf{C}_6H_4$–Br). ^{31}P NMR ($CDCl_3$) δ: −3.97. IR (cm^{-1}): 696 (P–Ph), 742 (P–Ph), 781 (m-Ph), 1476 (Ph), 1552 (Ph), 3070 (Ph). MS: 340.08 (M^+). Anal. Calc. for **2a** ($C_{18}H_{14}BrP$): C, 63.37; H, 4.14. Found: C, 63.38; H, 4.15.

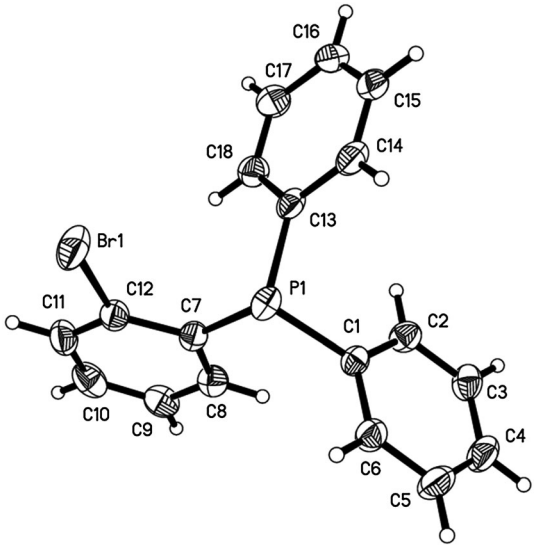


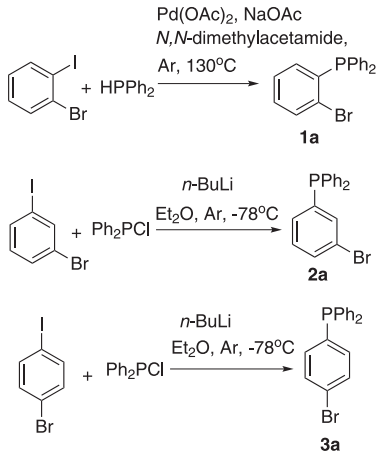
Figure 1. Molecular structure of **1a** drawn with 30% probability displacement ellipsoids.

Synthesis of (4-bromophenyl)diphenylphosphane ***3a***

An oven-dried, 100 ml Schlenk tube equipped with a magnetic stir bar was evacuated and refilled with argon three times before adding a solution of 1-bromo-4-iodobenzene (0.78 ml, 6.1 mmol) in Et_2O (30 ml) under argon atmosphere. The reaction Schlenk tube was cooled to −78 °C and a solution of *n*-BuLi in hexane (1.6 M, 6.5 mmol) was added dropwise slowly. When the addition was complete, the reaction mixture was stirred at same temperature for 1 h. The reaction mixture was quenched with chlorodiphenylphosphine (1.10 mL, 6.1 mmol) at −78 °C. The resulting mixture was gradually warmed to ambient temperature for 4 h. The mixture was quenched with water and extracted with Et_2O (30 ml × 3). The combined organic layers were dried over magnesium sulfate, filtered and evaporated under reduced pressure. The solution was concentrated *in vacuo*, and the residue was purified by flash chromatography with hexane to yield **3a** as a white solid; 76% yield. These data of ^{1}H, ^{13}C, ^{29}Si and ^{31}P NMR spectra, IR spectra and MS were consistent with those reported in the literature.[30–32] See Scheme 2.

Synthesis of (2-aminophenyl)diphenylphosphane ***4a***

An oven-dried, 25 ml three-necked flask equipped with a magnetic stir bar, rubber septum and reflux condenser was charged with CuI (78 mg, 0.41 mmol), followed by anhydrous toluene (0.887 ml), diphenylphosphine (1.42 ml, 8.2 mmol) and *N*,*N*-dimethylethylenediamine (0.3 ml, 2.87 mmol) under Ar. After 10–15 min of stirring, the 2-iodoaniline (1.80 g, 8.2 mmol) and Cs_2CO_3 (513 mg, 1.64 mmol) were added at once, followed by anhydrous toluene (1.15 ml) under Ar. The reaction mixture was heated at 110 °C for 35 h, The resulting mixture from the completed reaction was cooled to room temperature, diluted with water (20 ml) and extracted with ethyl acetate (40 ml × 4). The combined organic extracts were concentrated *in vacuo* and purified by flash chromatography with EtOAc–hexane (5% EtOAc–hexane) to yield **4a** as a yellow solid;



Scheme 2. Synthesis of **1a**[26–29] to **3a**.[30–32]

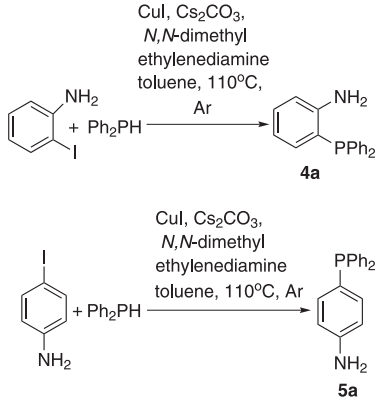
86%yield. The data of ^{1}H, ^{13}C, ^{29}Si and ^{31}P NMR spectra, IR spectra and MS were consistent with those reported in the literature.[33–35]

Synthesis of (4-aminophenyl)diphenylphosphane ***5a***

An oven-dried, 25 ml three-necked flask equipped with a magnetic stir bar, rubber septum and reflux condenser was charged with CuI (78 mg, 0.41 mmol), followed by anhydrous toluene (0.887 ml), diphenylphosphine (1.42 ml, 8.2 mmol) and *N,N*-dimethylethylenediamine (0.3 ml, 2.87 mmol) under Ar. After stirring for 10–15 min, 4-iodoaniline (1.80 g, 8.2 mmol) and Cs_2CO_3 (513 mg, 1.64 mmol) were added at once, followed by anhydrous toluene (1.15 ml) under Ar. The reaction mixture was heated at 110 °C for 35 h. The resulting mixture from the complete reaction was cooled to room temperature, diluted with water (20 ml) and extracted with ethyl acetate (40 ml × 4). The combined organic extracts were concentrated *in vacuo*, and purified by flash chromatography with EtOAc–hexane (5% EtOAc–hexane) to yield **5a** as a colorless viscous oil; 88% yield. The data of ^{1}H, ^{13}C, ^{29}Si and ^{31}P NMR spectra, IR spectra and MS were consistent with those reported in the literature.[36–38] See Scheme 3.

Synthesis of 4-diphenylphosphanylbenzoic acid ***6a***

A 50 ml Schlenk tube equipped with a magnetic stir bar, rubber septum and reflux condenser was charged with 4-iodobenzoic acid (10 mmol, 2.48 g) and $Pd(OAc)_2$ (0.05 mmol, 12.5 mg), followed by distilled triethylamine (10 mmol, 1.4 ml), diphenylphosphine



Scheme 3. Synthesis of **4a**[33–35] and **5a**.[36–38]

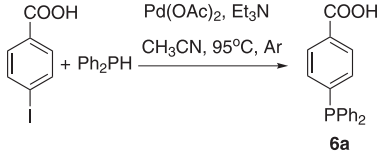
(10 mmol, 1.75 ml) and acetonitrile (30 ml). After the mixture was refluxed at 95 °C for 40 h, the reaction mixture was concentrated *in vacuo* to give a light-yellow solid. The solid was dissolved in 0.1 N NaOH solution (60 ml) and the solution was extracted with diethyl ether (10 ml × 3). On acidifying the aqueous phase with 3 N HCl, phosphane **6a** was precipitated as a cream-colored solid, then filtered and dried *in vacuo*; 50% yield. The data of ^{1}H, ^{13}C, ^{29}Si and ^{31}P NMR spectra, IR spectra and MS were consistent with those reported in the literature.[39–41] See Scheme 4.

Synthesis of (2-butylphenyl)diphenylphosphane ***7a***

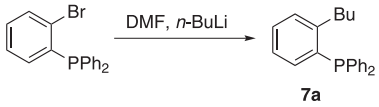
A 100 ml Schlenk tube equipped with a magnetic stir bar was evacuated and refilled with argon three times before adding a solution of **1** (1.51 g, 4.44 mmol) in THF (30 ml) under argon atmosphere. The Schlenk tube was cooled to −78 °C and a solution of *n*-BuLi in hexane (1.6 M, 5.33 mmol) was added dropwise slowly. When the addition was complete, the reaction mixture was stirred at the same temperature for 1 h. The reaction mixture was quenched with DMF (0.68 ml, 8.84 mmol) at −78 °C. The resulting mixture was gradually warmed to ambient temperature for 2 h, then quenched with water and extracted with ethyl acetate (30 ml × 3). The combined organic layers were dried over magnesium sulfate, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography with hexane to yield **7a** as a white solid; 70% yield; m.p. 44 °C. ^{1}H NMR ($CDCl_3$) δ: 7.40–7.23 (m, 2H, *p*-H, $C_6\mathbf{H}_5$–P; 4H, *m*-H, $C_6\mathbf{H}_5$–P; 4H, *o*-H, $C_6\mathbf{H}_5$–P; 2H, *m*-H, P–$C_6\mathbf{H}_4$–CH_2), 7.14–7.07 (m, 1H, *p*-H, P–$C_6\mathbf{H}_4$–CH_2), 6.93–6.84 (m, 1H, *o*-H, P–$C_6\mathbf{H}_4$–CH_2), 2.91–2.82 (t, J = 7.3 Hz, 2H, C_6H_4–$C\mathbf{H}_2CH_2CH_2CH_3$), 1.52–1.62 (m, 2H, C_6H_4–$CH_2C\mathbf{H}_2CH_2CH_3$), 1.37–1.27 (m, 2H, C_6H_4–$CH_2CH_2C\mathbf{H}_2CH_3$), 0.84 (t, J = 7.3 Hz, 3H, C_6H_4–$CH_2CH_2CH_2C\mathbf{H}_3$); due to overlapping of signals, the proton assignments were listed without distinct identification. ^{13}C NMR ($CDCl_3$) δ: 147.59 (J = 10.5 Hz, 1C, *o*-C, P-$\mathbf{C}_6H_4$-C), 136.89 (J = 20.5 Hz, 1C, P–C, P–$\mathbf{C}_6H_4$–C), 135.09 (J = 10.5 Hz, 1C, *o*-C, P–$\mathbf{C}_6H_4$–C), 133.93 (J = 20.5 Hz, 2C, P–C, $\mathbf{C}_6H_5$–P), 133.65 (J = 10.5 Hz, 4C, *o*-C, $\mathbf{C}_6H_5$–P), 129.13 (J = 6.8 Hz, 4C, *m*-C, $\mathbf{C}_6H_5$–P), 129.00 (2C, *p*-C, $\mathbf{C}_6H_5$–P), 128.68 (1C, *p*-C, P–$\mathbf{C}_6H_4$–C), 128.52 (J = 6.8 Hz, 1C, *m*-C, P–$\mathbf{C}_6H_4$–C), 126.03 (J = 6.8 Hz, 1C, *m*-C, P–$\mathbf{C}_6H_4$–C), 34.29 (1C, C_6H_4–$\mathbf{C}H_2CH_2CH_2CH_3$), 33.53 (1C, C_6H_4–$CH_2\mathbf{C}H_2CH_2CH_3$), 22.67 (1C, C_6H_4–$CH_2CH_2\mathbf{C}H_2CH_3$), 13.97 (1C, C_6H_4–$CH_2CH_2CH_2\mathbf{C}H_3$). ^{31}P NMR ($CDCl_3$) δ: −14.70. IR (cm^{-1}): 699 (P–Ph), 742 (P–Ph), 1432 (Ph), 1591 (Ph), 2858 (CH_2), 2954 (CH_3), 3052 (Ph). MS: 318.08 (M^+). Anal. Calc. for **7a** ($C_{22}H_{23}P$): C, 82.99; H, 7.28. Found: C, 83.00; H, 7.27. See Scheme 5.

Synthesis of diphenyl(2-trimethylsilylphenyl)phosphane ***8a***

1a (3.41 g, 9.99 mmol) was dissolved in degassed Et_2O (30 ml) under argon atmosphere. The reaction flask was cooled to 0 °C and a solution of *n*-BuLi in hexane (1.6 M, 10.1 mmol) was added dropwise slowly. When the addition was complete, the reaction mixture was stirred at room temperature for 2 h, then chlorotrimethylsilane (1.40 ml, 11.1 mmol) was added at 0 °C. The resulting mixture was gradually warmed to ambient



Scheme 4. Synthesis of **6a**.[39–41]

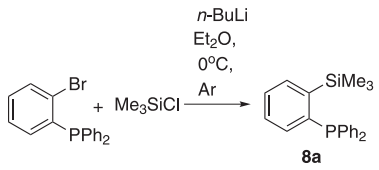


Scheme 5. Synthesis of **7a**.

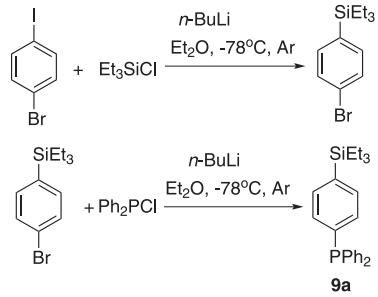
temperature for 3 h and quenched by a saturated aqueous solution of NH_4Cl (30 ml). The mixture was extracted with Et_2O (30 ml × 3). The combined organic layers were dried over magnesium sulfate, filtered and evaporated under reduced pressure. The solution was concentrated *in vacuo*, and the residue was subjected to column chromatography on silica gel with hexane ($R_f = 0.40$) to give **8a** as a white solid; 82% yield. The data of ^{1}H, ^{13}C, ^{29}Si and ^{31}P NMR spectra, IR spectra and MS were consistent with those reported in the literature.[42] See Scheme 6.

Synthesis of diphenyl(4-triethylsilylphenyl)phosphane ***9a***

A 100 ml Schlenk tube equipped with a magnetic stir bar was evacuated and refilled with argon three times before a solution of 1-bromo-4-iodobenzene (0.78 ml, 6.1 mmol) in THF (30 ml) was added under argon atmosphere. The Schlenk tube was cooled to −78 °C and a solution of *n*-BuLi in hexane (1.6 M, 6.1 mmol) was added dropwise slowly. After the addition was complete, the reaction mixture was stirred at the same temperature for 1 h, and then chlorotriethylsilane (3.10 ml, 6.7 mmol) was added at −78 °C. The resulting mixture was gradually warmed to ambient temperature for 4 h. The mixture was quenched with water and extracted with Et_2O (30 ml × 3). The combined organic layers were dried over magnesium sulfate, filtered and evaporated under reduced pressure to give 1-bromo-4-(triethylsilyl) benzene as a colorless liquid. A solution of 1-bromo-4-triethylsilylbenzene (1.36 g, 5 mmol) in Et_2O (30 ml) was added slowly to a solution of *n*-BuLi (2.5 M in hexane, 5 mmol) in 15 ml hexane at −78 °C. The resulting mixture was stirred for 2 h at −78 °C, followed by the addition of a solution of chlorodiphenylphosphine (0.89 ml, 5.0 mmol) and then allowed to warm to room temperature. After stirring overnight, the reaction mixture was quenched with water and extracted by CH_2Cl_2. The organic phases were dried with Na_2SO_4 and evaporated *in vacuo*. The crude product was purified by flash chromatography (5% EtOAc–hexane) to give **9a** as a colorless viscous oil; 45% yield. ^{1}H NMR ($CDCl_3$) δ: 7.57–7.26 (m, 2H, *m*-H, P–C$_6$**H**$_4$–Si; 2H, *o*-H, P–C$_6$**H**$_4$–Si; 2H, *p*-H, C$_6$**H**$_5$–P; 4H, *m*-H, C$_6$**H**$_5$–P; 4H, *o*-H, C$_6$**H**$_5$–P), 0.98 (t, $J = 7.4$ Hz, 9H, C**H**$_3$), 0.86 (q, $J = 7.4$ Hz, 6H, C**H**$_2$). Due to overlapping of signals, the proton assignments were listed without distinct identification. ^{13}C NMR ($CDCl_3$) δ: 138.21 (1C, *p*-C, P–**C**$_6$H$_4$–Si), 137.48 ($J = 19.4$ Hz, 1C, P–C, P–**C**$_6$H$_4$–Si), 137.10 ($J = 6.4$ Hz, 2C, *m*-C, P–**C**$_6$H$_4$–Si), 134.28 ($J = 10.2$ Hz, 2C, *o*-C, P–**C**$_6$H$_4$-Si), 133.89 ($J = 19.4$ Hz, 2C, P–C, **C**$_6$H$_5$–P), 132.73 ($J = 10.2$ Hz, 4C, *o*-C, **C**$_6$H$_5$–P), 128.80 ($J = 6.4$ Hz, 4C, *m*-C, **C**$_6$H$_5$–P), 128.54 (2C, *p*-C, **C**$_6$H$_5$–P), 7.49 (3C, **C**H$_3$), 3.35 (3C, **C**H$_2$). ^{29}Si NMR ($CDCl_3$) δ: 2.02. ^{31}P NMR ($CDCl_3$) δ: −5.02. IR (cm^{-1}): 696 (P–Ph), 744 (P–Ph), 809 (Si–C), 1434 (Ar–Si), 2873 (CH_3), 2933 (CH_2), 2952 (CH_3), 3052 (Ph). MS: 376.15 (M^+). Anal. Calc. for **9a** ($C_{24}H_{29}PSi$): C, 76.55; H, 7.76. Found: C, 76.57; H, 7.76. See Scheme 7.



Scheme 6. Synthesis of **8a**.[42]



Scheme 7. Synthesis of **9a**.

Synthesis of diphenyl(2-tolyl)phosphane ***10a***

Magnesium turnings (313 mg, 12.8 mmol) and a piece of I_2 were stirred under argon for 2 h and then overlaid with THF (30 ml). Three drops of 1,2-dibromoethane were added, followed by a few drops of a solution containing 2-bromotoluene (1.30 ml, 10.8 mmol) in THF (5 ml). Upon starting the reaction the remaining solution of 2-bromotoluene in THF was added dropwise. The reaction mixture was heated to reflux until all magnesium was dissolved. A solution of diphenylphosphine chloride (2.70 ml, 15.0 mmol) in THF (2 ml) was cooled to −78 °C and the reaction mixture was added dropwise. The reaction mixture was stirred overnight at room temperature and extracted twice with saturated aqueous of NaCl and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product oil treated with EtOH. The formed solid was filtered and washed with cold ethanol and the supernatant was concentrated and purified by column chromatography (hexane–EtOAc, 1:0– > 5:1) to give the title compound **10a** as a white solid; 86% yield; m.p. 65 °C. ^{1}H NMR ($CDCl_3$) δ: 7.41–6.81 (m, 1H, *p*-H, P–C$_6$**H**$_4$–C; 2H, *m*-H, P–C$_6$**H**$_4$–C; 2H, *p*-H, C$_6$**H**$_5$–P; 4H, *m*-H, C$_6$**H**$_5$–P; 4H, *o*-H, C$_6$**H**$_5$–P; 1H, *o*-H, P–C$_6$**H**$_4$–C), 2.43 (s, 3H, C**H**$_3$). Due to overlapping of signals, the proton assignment was listed without distinct identification. ^{13}C NMR ($CDCl_3$) δ: 142.25 ($J = 10.5$ Hz, 1C, *o*-C, P–**C**$_6$H$_4$–C), 136.30 (J =19.8 Hz, 1C, P–C, P–**C**$_6$H$_4$–C), 136.01 ($J = 10.5$ Hz, 1C, *o*-C, P–**C**$_6$H$_4$–C), 134.16 (J =19.8 Hz, 2C, P–C, **C**$_6$H$_5$–P), 133.97 ($J = 10.5$ Hz, 4C, *o*-C, **C**$_6$H$_5$–P), 132.79 ($J = 6.4$ Hz, 4C, *m*-C, **C**$_6$H$_5$–P), 130.11 (2C, *p*-C, **C**$_6$H$_5$–P), 128.78 ($J = 6.4$ Hz, 1C, *m*-C, P–**C**$_6$H$_4$–C), 128.61 (1C, *p*-C, P–**C**$_6$H$_4$–C), 126.06 ($J = 6.4$ Hz, 1C, *m*-C, P–**C**$_6$H$_4$–C), 21.18 (1C, **C**H$_3$). ^{31}P NMR ($CDCl_3$) δ: −12.68. IR (cm^{-1}): 694 (P–Ph), 742 (P–Ph), 1434 (CH_3), 2846 (CH_3), 3049 (Ph). MS: 275.1 (M^+). Anal. Calc. for **10a** ($C_{19}H_{17}P$): C, 82.59; H, 6.20. Found: C, 82.60; H, 6.21.

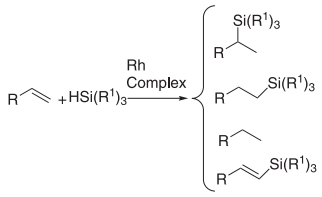
Synthesis of 2-methoxyphenyldiphenylphosphane ***11a***

Magnesium turnings (313 mg, 12.8 mmol) and a piece of I_2 were stirred under argon for 2 h and then overlaid with THF (30 ml). Three drops of 1,2-dibromoethane were added, followed by a few drops of a solution containing 2-bromotoluene (1.34 ml, 10.8 mmol) in THF (5 ml). Upon starting the reaction, the remaining solution of 2-bromotoluene in THF was added dropwise. The reaction mixture was heated to reflux until all magnesium was dissolved. A solution of diphenylphosphine chloride (2.70 ml, 15.0 mmol) in THF (2 ml) was cooled to −78 °C and the reaction mixture was added dropwise. The reaction mixture was stirred overnight at room temperature and extracted twice with a saturated aqueous solution of NaCl and dried over

$MgSO_4$. The solvent was removed under reduced pressure and the crude product oil treated with EtOH. The formed solid was filtered and washed with cold ethanol and the supernatant was concentrated and purified by column chromatography (hexane–EtOAc, 1:0– > 5:1) to give the title compound **11a** as white solid; 90% yield; m.p. 118 °C. ^{1}H NMR ($CDCl_3$) δ: 7.42–7.22 (m, 1H, *p*-H, P–C_6**H**$_4$–O) (m, 2H, *p*-H, C_6**H**$_5$–P; 4H, *m*-H, C_6**H**$_5$–P; 4H, *o*-H, C_6**H**$_5$–P), 6.96–6.83 (m, 2H, *m*-H, P–C_6**H**$_4$–O), 6.74–6.65 (m, 1H, *o*-H, P–C_6**H**$_4$–O), 3.76 (s, 3H, O**CH**$_3$). Due to overlapping of signals, the proton assignment was listed without distinct identification. ^{13}C NMR ($CDCl_3$) δ: 161.19 (J = 10.2 Hz, 1C, *o*-C, P–**C**$_6$H$_4$–O), 136.61 (J = 10.2 Hz, 1C, *o*-C, P–**C**$_6$H$_4$–O), 134.03 (J =19.8 Hz, 2C, P–C, **C**$_6$H$_5$–P), 133.76 (J = 10.2 Hz, 4C, *o*-C, **C**$_6$H$_5$–P), 130.42 (1C, *p*-C, P–**C**$_6$H$_4$–O), 128.64 (J = 6.4 Hz, 4C, *m*-C, **C**$_6$H$_5$–P), 128.40 (2C, *p*-C, **C**$_6$H$_5$–P), 125.50 (J =19.8 Hz, 1C, P–C, P–**C**$_6$H$_4$–O), 121.08 (J = 6.4 Hz, 1C, *m*-C, P–**C**$_6$H$_4$–O), 110.25 (J = 6.4 Hz, 1C, *m*-C, P–**C**$_6$H$_4$–O), 55.72 (1C, O**C**H$_3$). ^{31}P NMR ($CDCl_3$) δ: −16.06. IR (cm^{-1}): 696 (P–Ph), 748 (P–Ph), 1020 (C–O–C), 1431 (CH_3), 1473 (Ph), 2841 (CH_3), 3068 (Ph). MS: 292.1 (M^+). Anal. Calc. for **11a** ($C_{19}H_{17}OP$): C, 78.07; H, 5.86; O, 5.47. Found: C, 78.08; H, 5.85; O, 5.48. See Scheme 8.

Catalytic Hydrosilylation of Alkene with Triethoxysilane

A 10 ml three-necked flask equipped with a magnetic stirrer was charged with $RhCl_3.3H_2O$ (8.0×10^{-3} mmol) and prepared triarylphosphane (4.0×10^{-2} mmol) under argon atmosphere. The alkene (4 mmol) and silane (4.87 mmol) were then added via syringe. The hydrosilylation reaction proceeded with constant stirring under an appropriate temperature for 5 h. At the end of the reaction, the conversion of alkene and selectivity were determined by GC. See Scheme 9.



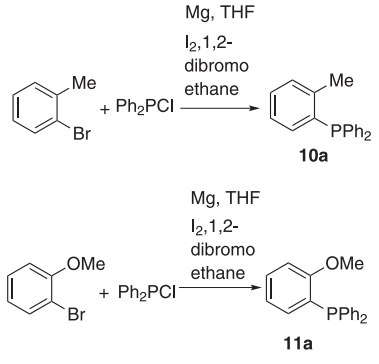
Scheme 9. Hydrosilylation reaction of alkenes catalyzed by rhodium complex. R: Ph, CH_3Ph, CH_3OPh, C_4H_9, C_6H_{13}, $C_{10}H_{21}$; R^1: OEt, Et.

Table 1. Crystal data, data collection and structure refinement details for **1a**

Empirical formula	$C_{18}H_{14}BrP$
Formula weight	341.17
Crystal system	Monoclinic
space group	*P*, $2_1/c$
Unit cell dimensions	
a (Å)	9.2195(11)
b (Å)	17.155(2)
c (Å)	9.8057(12)
β (°)	96.450(2)
Volume (Å^3)	1541.0(3)
Z, calculated density	4, 1.471 Mg m^{-3}
Abs. coeff. (mm^{-1})	2.758
F(000)	688
Reflections collected/unique	10607/2757 [*R*(int) = 0.0329]
Goodness-of-fit on $F^2_{\theta\max\ 25.2}$	1.03
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.032, wR_2 = 0.080
R indices (all data)	R_1 = 0.053, wR_2 = 0.089

X-Ray Structure Determinations of 1a

Colorless single crystals of the compounds (dimensions: **1a**: 0.26 × 0.20 × 0.17 mm) were produced by slow evaporation of the solvents (hexane–dichloromethane) at 25 °C. Diffraction data were collected at room temperature by the ϕ-scan and ω-scan technique on a Smart Apex Duo diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXTL-PLUS)[43] and subsequent Fourier difference syntheses, and were then refined by full-matrix least squares on F^2 (SHELXL-97).[44] All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically idealized positions. Crystal data and details of the structures are given in Table 1.



Scheme 8. Synthesis of **10a** and **11a**.

Results and Discussion

Synthesis of Various Types of Triarylphosphane[45,46]

A series of highly efficient protocols for the synthesis of triarylphosphane are shown in Schemes 2–8. (2-Bromophenyl) diphenylphosphane (**1a**) was synthesized by the reaction of 1-bromo-2-iodobenzene and diphenylphosphine. The formation of (2-aminophenyl)diphenylphosphane (**4a**), (4-aminophenyl) diphenylphosphane (**5a**) and 4-diphenylphosphanylbenzoic acid (**6a**), respectively, is similar to the formation of **1a**. (2-Butylphenyl)diphenylphosphane (**7a**) was synthesized by the reaction of (2-bromophenyl)diphenylphosphane and *n*-BuLi. (3-Bromophenyl)diphenylphosphane (**2a**) was synthesized by the reaction of 1-bromo-3-iodobenzene and chlorodiphenylphosphine. (4-Bromophenyl)diphenylphosphane (**3a**) is similar to the formation of **2a**. Diphenyl(2-trimethylsilylphenyl) phosphane (**8a**) was synthesized by the reaction of **1a** and chlorotrimethylsilane. Interestingly, diphenyl(4-triethylsilylphenyl)-phosphane (**9a**) was not obtained by the reaction of **1a** and chlorotriethylsilane. 4-Bromophenyltriethylsilane was obtained by the reaction of 1-bromo-4-iodobenzene and chlorotriethylsilane; **9a** was synthesized by the reaction of (4-bromophenyl)triethylsilane and chlorodiphenylphosphine. Diphenyl(2-tolyl)phosphane

(**10a**) was synthesized by the reaction of 2-bromotoluene and chlorodiphenylphosphine. Formation of (2-methoxyphenyl) diphenylphosphane (**11a**) is similar to that of **10a**. These 11 products are characterized by NMR, IR spectroscopy and MS. Furthermore, the NMR, IR spectroscopy and MS data of the prepared compounds are in agreement with the assigned structures.

Effect of different ligands on the hydrosilylation reaction

The catalytic properties of $RhCl_3$–triarylphosphane in the hydrosilylation reaction of styrene with triethoxysilane were investigated and the results are listed in Table 2. It is seen that $RhCl_3$–**1a** had low catalytic activity. $RhCl_3$–**3a** had higher conversion and low selectivity of β-product. The structure of **2a** was similar to those of **1a** and **3a**. Interestingly, when $RhCl_3$ was mixed with **2a**, it exhibited greater catalytic activity and higher selectivity of β-product. This result indicates that the substituent attached to the benzene ring of triarylphosphane has a strong impact on the catalytic process. When **7a** was used as ligand, highest catalytic activity, selectivity of β-product and a small quantity of dehydrogenative silyation product were detected. The $RhCl_3$–**9a** catalytic system showed higher catalytic activity, selectivity of β-product and lower dehydrogenative silyation product. In particular, when **8a** was used as ligand, higher catalytic activity and highest selectivity of β-product with no dehydrogenative silyation product were obtained. This suggests that the silicon group had a significant impact on the catalytic process. It was reported that organic fatty acids and amino acid could be used as promoters in the hydrosilylation processes.[47] Unfortunately, low conversion and low selectivities of the product were usually observed by the use of $RhCl_3$–**4a**, $RhCl_3$–**5a** and $RhCl_3$–**6a**, respectively, as a catalytic system. $RhCl_3$–**10a** and $RhCl_3$–**11a** catalytic systems showed higher conversion and lower selectivity of β-product. To compare all these ligands with PPh_3, it was found that triarylphosphane containing aliphatic and silicon groups promoted the hydrosilylation processes; furthermore, triarylphosphane ligands containing silicon and/or halogen group improved the selectivity of β-product (Table 2).

Scope of the Hydrosilylation Reaction

With preferred conditions in hand, we next carried out the hydrosilylation reaction of other alkenes with triethoxysilane. When another alkene such as 2-methylstyrene, 3-methylstyrene, 4-methylstyrene, 3-methoxystyrene, 1-hexene or 1-octene replaced styrene as one of the substrates, excellent conversions and selectivities were obtained with the $RhCl_3$–**2a** catalytic system. However, when triethylsilane replaced triethoxysilane as

Table 2. Effect of triarylphosphane ligands on the rhodium-catalyzed hydrosilylation reaction

Entry	Ligands	Conv. (%)	Selectivity (%)				β/α
			β	α	Unsaturated	1-Ethylbenzene	
0	PPh_3	94.3	65.9	5.5	13.6	5.45	12.1
1	**1a**	69.0	73.4	3.5	8.7	14.4	21.1
2	**2a**	100	79.1	2.6	4.6	13.6	30.2
3	**3a**	80.7	61.4	8.2	15.7	14.7	7.5
4	**4a**	6.8	55.2	6.4	13.5	24.9	8.6
5	**5a**	61.8	53.3	5.5	18.0	23.2	9.7
6	**6a**	68.3	49.4	9.0	11.0	30.7	5.5
7	**7a**	>99.9	83.0	6.7	4.4	5.7	12.4
8	**8a**	95.4	84.8	6.2	—	9.0	13.8
9	**9a**	95.8	83.2	2.8	5.8	8.2	29.7
10	**10a**	99.0	54.5	28.0	9.1	8.4	1.9
11	**11a**	96.9	65.3	14.2	11.4	9.1	4.6

Reaction conditions: styrene 4 mmol, triethoxysilane 4.4 mmol; catalyst: $RhCl_3$ 0.2 mol%, ligand 1.0 mol% based on styrene; 90 °C; 5 h.

Table 3. Scope of the hydrosilylation reaction

Entry	Alkene	Silane	Conv. (%)	Selectivity (%)		
				β	α	Unsaturated product
1	2-Methylstyrene	Triethoxysilane	95.8	87.4	2.8	3.4
2	3-Methylstyrene		87.3	86.6	1.6	4.7
3	4-Methylstyrene		83.2	82.5	2.6	3.4
4	4-Methoxystyrene		88.6	86.5	1.4	5.6
5[a]	1-Hexene		91.0	>99.9	—	—
6[a]	1-Octene		89.7	99.9	—	—
7	Styrene	Triethylsilane	100	48.5	2.1	32.6

Reaction conditions: alkene, 4 mmol; silane, 4.4 mmol; catalyst: $RhCl_3$ 0.2 mol%, **2a** 1.0 mol% based on alkene; 90 °C, 5 h.
[a]**2a** 1.0 %mol based on alkene.

one of the substrates, a high-selectivity dehydrogenative silylation product was obtained (Table 3).

In summary, a series of triarylphosphane (**1a–11a**) have been synthesized. An X-ray crystal structure analysis of (2-bromophenyl)diphenylphosphane **1a** unambiguously confirmed the constitution of the functionalized phosphane. Hydrosilylation reactions of styrene with triethoxysilane catalyzed by $RhCl_3$–triarylphosphane were investigated. In comparison with all catalysts, $RhCl_3$–diphenyl(2-trimethylsilylphenyl)phosphane (**8a**) exhibited higher activity as well as higher levels of β-adduct selectivity. The results showed that substituents attached to triarylphosphane ligands had a significant impact on the rhodium-catalyzed hydrosilylation process. Further studies on the structures of rhodium–triarylphosphane complexes and the reaction mechanism are ongoing.

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