



Supporting Information

© Wiley-VCH 2008

69451 Weinheim, Germany

# Supporting Information

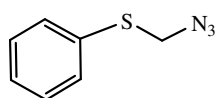
## Pincer Click Ligands

*Elaine M. Schuster, Mark Botoshansky and Mark Gandelman\**

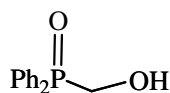
Schulich Faculty of Chemistry  
Technion- Israel Institute of Technology  
Technion City, Haifa 32000, Israel  
Fax: (+972-4) 8295703  
E-mail: [chmark@tx.technion.ac.il](mailto:chmark@tx.technion.ac.il)

**General Methods.** Oxygen- and moisture-sensitive reactions were carried out under an atmosphere of purified nitrogen in a glovebox equipped with an inert gas purifier, or by using standard Schlenk techniques. Dry Et<sub>3</sub>N was obtained by distillation from CaH<sub>2</sub>. Solvents were purified by passing through a column of activated alumina under inert atmosphere. All commercially available reagents were used as received, unless indicated otherwise. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F-254 plates (particle size 0.040-0.055 mm, 230-400 mesh) and visualization was accomplished using UV light or by staining with basic KMnO<sub>4</sub> dye. NMR spectra were recorded at 300 MHz/75 MHz (<sup>1</sup>H/<sup>13</sup>C NMR) in CDCl<sub>3</sub> unless otherwise stated on a Bruker AVANCE 300 MHz spectrometer at 23°C. Chemical shifts (δ) are reported in parts per million and the residual solvent peak was used as an internal standard (CDCl<sub>3</sub>: δ 7.261/77.0, <sup>1</sup>H/<sup>13</sup>C NMR). <sup>31</sup>P NMR signals are in ppm and referenced to external 85% H<sub>3</sub>PO<sub>4</sub>. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, b = broad), integration, and coupling constant(s) (Hz).

Compounds **1**,<sup>1</sup> **3a**,<sup>2</sup> and (TMEDA)PdCl<sub>2</sub><sup>3</sup> were prepared according to literature procedures.

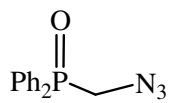


**Azidomethyl phenyl sulfide (6)** To 5.3 mL of freshly distilled acetonitrile was added chloromethyl phenyl sulfide (1.0g, 6.303 mmol), sodium azide (614 mg, 9.45 mmol) and crown ether-5 (0.250 ml, 1.261 mmol). The solution was stirred for 48 hours under a nitrogen atmosphere. After addition of 10 ml water the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 10 ml) and the combined organic layers were washed with water (15 ml) and brine (15 ml). The organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. Product **6** (994 mg, 95%) was obtained after evaporation of the solvent as a pale yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 7.50-7.47 (m, 2H), 7.34-7.30 (m, 3H), 4.52 (s, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 131.5, 129.6, 128.1, 56.3 (CH<sub>2</sub>).

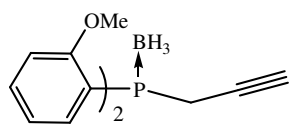


**Hydroxymethyl diphenylphosphine oxide (1a)** This compound was prepared according to literature procedures.<sup>4</sup> To a mixture of HCl (18.9 mL) and aqueous formaldehyde (18.9 mL, 37 wt %) was added diphenyl chlorophosphine (2.80 mL, 10.6 mmol). The reaction mixture was heated to 100°C for 18h under a nitrogen atmosphere. The reaction was neutralized with aqueous NaHCO<sub>3</sub>, and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 30 ml). The organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The product (2.907 g, 89%) was obtained after evaporation of the solvent as a colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 7.71-7.36 (m, 10H, Ar), 6.16 (s, 1H), 4.34 (d, 2H, J=2.1 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 133.9 (d,

$J_{CP} = 2.6$  Hz), 133.2 (d,  $J_{CP} = 9.2$  Hz), 132.3 (d,  $J_{CP} = 97$  Hz), 130.4 (d,  $J_{CP} = 11.6$  Hz), 62.9 (d,  $J_{CP} = 75$  Hz).  $^{31}\text{P}$  NMR (202 MHz)  $\delta$ : 28.6.

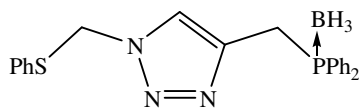


**Azidomethyl diphenylphosphine oxide (1)** This compound was prepared according to a modified literature procedure.<sup>2</sup> To 50 mL of freshly distilled pyridine was added precursor **1a** (2.907 g, 12.5 mmol) and freshly recrystallized toluene sulfonyl chloride (2.862g, 15 mmol). This was stirred at room temperature for 18h under a nitrogen atmosphere. The mixture was then diluted with  $\text{CH}_2\text{Cl}_2$  (50 ml) and washed with  $\text{H}_2\text{O}$  ( $3 \times 50$  ml). The solvent was evaporated, and the material was then redissolved in anhydrous DMF (30 mL). To this mixture was added sodium azide (2.031g, 31.25 mmol). The reaction mixture was heated to  $110^\circ\text{C}$  for 5h under a nitrogen atmosphere. The reaction was quenched with water, and was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 50$  ml). The organic phase was dried with anhydrous  $\text{Na}_2\text{SO}_4$ . The product was purified on silica, eluting with ethyl acetate, to give the azide **1** (1.53g, 51%) as a white powder.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 7.78-7.49 (m, 10H), 3.98 (d, 2H,  $J_{HP}=7.5$  Hz,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 132.6 (d,  $J_{CP} = 2.7$  Hz), 131.2 (d,  $J_{CP} = 9.6$ ), 130.0 (d,  $J_{CP} = 101$  Hz), 128.8 (d,  $J_{CP} = 12.0$  Hz), 49.5 (d,  $J_{CP} = 76.5$  Hz).  $^{31}\text{P}$  NMR  $\delta$ : 28.8.



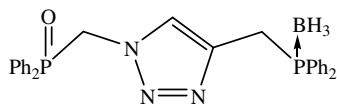
**Bis(2-methoxyphenyl)(prop-2-ynyl)phosphine borane complex (3b)** The starting bis(2-methoxyphenyl)phosphine borane complex was prepared according to literature procedures.<sup>5</sup> To a solution of the bis(2-methoxyphenyl)phosphine borane complex (110 mg, 0.423 mmol) in THF (2 mL), *n*-BuLi (1.6 M in hexane, 265  $\mu\text{L}$ , 0.423 mmol) was added at  $-78^\circ\text{C}$  under argon atmosphere. The solution was stirred for 15 min and propargylbromide (80% in toluene, 110  $\mu\text{L}$ , 0.465 mmol) was added, quenching the phosphine anion at  $-78^\circ\text{C}$ . After 15 minutes water was added and the solution was warmed to room temperature. The water layer was extracted with EtOAc ( $3 \times 10$  mL) and the combined organic layers were washed with water (20 mL) and brine (20 mL). The organic phase was dried with anhydrous  $\text{Na}_2\text{SO}_4$ . Product **5** (87 mg, 69%) was obtained after evaporation of the solvent as a pale yellow oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 7.56-7.44 (m, 4H), 6.98-6.90 (m, 4H), 3.73 (s, 6H, O- $\text{CH}_3$ ) 3.51-3.45 (dd, 2H,  $J_{HH}=2.7$  Hz,  $J_{HP}=13.7$  Hz,  $\text{CH}_2$ ), 1.85 (dt, 1H,  $J_{HH}=2.7$  Hz,  $J_{HP}=5.7$  Hz,  $\text{C}\equiv\text{C-H}$ ), 1.60-0.25 (br m, 3H,  $\text{BH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 161.4, 135.3, 333.6, 121.2, 116.5, 111.6, 77.2 ( $\text{C}\equiv\text{C-H}$ ), 71.4 ( $\text{C}\equiv\text{C-H}$ ), 55.9 ( $\text{OCH}_3$ ), 17.2 ( $\text{CH}_2$ ). The  $^{13}\text{C}$  assignments were confirmed by DEPT.  $^{31}\text{P}$  NMR  $\delta$ : 19.2 (d,  $J_{PB}=61$  Hz) MS-MALDI  $m/z$ : 285 [ $M\text{-BH}_3$ ].

#### General procedure for preparation of pincer-click-ligands in their protected form:

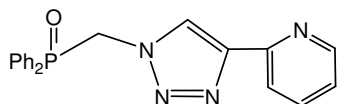


**Protected form of 7:** To the propargyl precursor **3a** (144 mg, 0.605 mmol) in 0.6 ml THF was added azide precursor **2** (100 mg, 0.605 mmol). In a separate vessel,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (75.3 mg, 0.303 mmol) was dissolved in 0.6 ml distilled water. Upon addition of sodium ascorbate (599 mg, 3.025 mmol) to the aqueous mixture, the resulting dark brown mixture was quickly added to the reaction. The reaction mixture was stirred at room temperature for 14 hrs under nitrogen. The aqueous phase was extracted with EtOAc ( $3 \times 10$  ml) and the combined organic layers were washed with water (20 ml) and brine (20 ml). The organic phase was dried with anhydrous  $\text{Na}_2\text{SO}_4$ . The borane complex of ligand **7** (189 mg, 80%) was obtained after evaporation as a white powder.  $^{31}\text{P}$  NMR (202 MHz): 14.5 (d).  $^1\text{H}$  NMR (500 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 7.69-

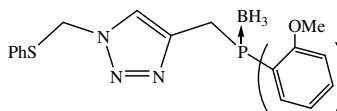
7.65 (m, 4H), 7.36 (s, 1H, triazole-H), 7.08-7.07 (m, 2H), 6.97-6.87 (m, 6H), 6.87 (m, 3H), 4.77 (s, 2H, CH<sub>2</sub>-S), 3.51 (d, 2H,  $J_{HP}$  = 11 Hz, CH<sub>2</sub>-P), 2.2-1.5 (br m, 3H, BH<sub>3</sub>). <sup>13</sup>C NMR (500 MHz, D<sub>2</sub>O)  $\delta$ : 141.1, 134.2 (d,  $J_{CP}$  = 9.23 Hz), 134.1, 133.8, 132.8 (d,  $J_{CP}$  = 2.62 Hz), 131.0, 130.6, 130.4 (d,  $J_{CP}$  = 9.56 Hz), 129.9, 129.8, 129.7, 129.6, 129.5, 129.3, 124.5 (d,  $J_{CP}$  = 3.18 Hz), 54.67 (CH<sub>2</sub>-S), 26.2 (d,  $J_{CP}$  = 36.1 Hz, CH<sub>2</sub>-P). The <sup>13</sup>C assignments were confirmed by DEPT. MS-MALDI  $m/z$  (%): 402 (55) [ $M-1$ ]<sup>+</sup>.



**Protected form of 5:** <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 7.64-7.61 (m, 10H), 7.43-7.36 (m, 11H), 5.11 (d, 2H,  $J_{HP}$  = 6.9 Hz, N-CH<sub>2</sub>-P), 3.66 (d, 2H,  $J_{HP}$  = 11.1 Hz, C-CH<sub>2</sub>-P), 1.5-0.3 (br m, 3H, BH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz)  $\delta$ : 138.8 (d,  $J_{CP}$  = 2.74 Hz), 132.5 (d,  $J_{CP}$  = 2.45 Hz), 132.0 (d,  $J_{CP}$  = 9.23 Hz), 131.0 (d,  $J_{CP}$  = 1.91 Hz), 130.8 (d,  $J_{CP}$  = 9.27 Hz), 128.6, 128.5 (d,  $J_{CP}$  = 68.46 Hz), 128.4, 128.3, 127.6 (d,  $J_{CP}$  = 20.65 Hz), 124.0 (d,  $J_{CP}$  = 2.78 Hz), 49.8 (d,  $J_{CP}$  = 70.36 Hz, CH<sub>2</sub>-P), 24.0 (d,  $J_{CP}$  = 35.83 Hz, CH<sub>2</sub>-P). The <sup>13</sup>C assignments were confirmed by DEPT. <sup>31</sup>P NMR (121 MHz)  $\delta$ : 23.62 (s, 1P, P=O) 14.78 (m, 1P, P-BH<sub>3</sub>).

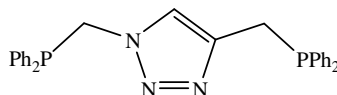


**Protected form of 6:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.58 (s, 1H), 8.44 (s, 1H), 8.02 (d, 1H), 7.81-7.47 (m, 11H, Ar), 7.21 (m, 2H), 5.32 (d, 2H,  $J_{HP}$  = 7.2 Hz, CH<sub>2</sub>-P). <sup>13</sup>C NMR (125 MHz)  $\delta$ : 149.7, 149.4, 136.8, 133.0 (d,  $J_{CP}$  = 2.7 Hz), 131.2 (d,  $J_{CP}$  = 10.0 Hz), 129.3, 129.1 (d,  $J_{CP}$  = 12.1 Hz), 123.4, 122.9, 120.2, 50.3 (d,  $J_{CP}$  = 70.1 Hz, CH<sub>2</sub>-P). <sup>31</sup>P NMR (120 MHz)  $\delta$ : 24.4. MS-ESI<sup>+</sup>  $m/z$ : 361 [ $M+I$ ].



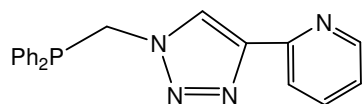
**Protected form of 8:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.80-7.75 (m, 2H, Ar) 7.56 (d, 1H), 7.05-7.03 (m, 4H Ar), 6.88-6.87 (m, 2H, Ar), 6.67-6.64 (m, 2H, Ar), 6.34-6.31 (m, 2H, Ar), 4.62 (s, 2H, CH<sub>2</sub>-S), 4.26 (d, 2H,  $J_{HP}$  = 12.5 Hz, CH<sub>2</sub>-P), 3.18 (s, 6H, O-Me), 2.2-1.8 (br m, 3H, BH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz)  $\delta$ : 163.1, 142.5, 134.4 (d,  $J_{CP}$  = 10.9 Hz), 134.4 (d,  $J_{CP}$  = 1.76 Hz), 133.8, 130.9, 129.7, 129.5, 129.3, 129.1, 124.0 (d,  $J_{CP}$  = 2.98 Hz), 122.4 (d,  $J_{CP}$  = 11.0 Hz), 119.0 (d,  $J_{CP}$  = 54.6 Hz), 113.0 (d,  $J_{CP}$  = 4.6 Hz), 56.8 (O-Me), 54.5 (CH<sub>2</sub>-S), 25.1 (d,  $J_{CP}$  = 50.0 Hz, CH<sub>2</sub>-P). The <sup>13</sup>C assignments were confirmed by DEPT. <sup>31</sup>P NMR (202 MHz)  $\delta$ : 15.2 (m). MS-ESI<sup>+</sup>  $m/z$  (%): 462 (100) [ $M-1$ ]<sup>+</sup>.

#### General Procedure for Removal of Protecting Groups BH<sub>3</sub> and Reduction of Phosphine Oxide:

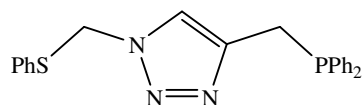


**Ligand 5:** To the protected form of **5** (458.2 mg, 0.93 mmol) in toluene (30 mL) and dichloromethane (5 mL) was added trichlorosilane (934  $\mu$ L, 9.25 mmol) and triethyl amine (2.60 mL, 18.5 mmol). This was stirred in a closed, argon-filled flask and heated to 100°C for 18h. The reaction material was then cooled, and filtered through a pad of celite under inert conditions resulting in the reduced phosphine. The material was concentrated, and then re-dissolved in anhydrous THF (10 mL). To this solution was added DABCO (124 mg, 1.11 mmol). The reaction mixture was then heated to 70°C for 4h resulting in full deprotection of the borane from the phosphine group. Remaining DABCO was removed by filtration through a short plug of silica, washing with diethyl ether to give **13** as a colorless solid (400 mg, 93% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.41- 7.30 (m, 15H, Ar), 6.94 (s, 1H, triazole-H), 4.96 (d, 2H,  $J_{HP}$ =4.8 Hz, N-CH<sub>2</sub>-P), 3.47 (s, 2H,

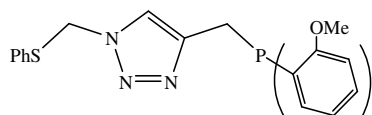
C-CH<sub>2</sub>-P). <sup>13</sup>C NMR (125 MHz) δ: 145.8 (d, *J*<sub>CP</sub>=11.0 Hz), 139.5 (d, *J*<sub>CP</sub>=14.0 Hz), 136.3 (d, *J*<sub>CP</sub>=12.7 Hz), 134.7 (d, *J*<sub>CP</sub>=13.9 Hz), 134.5 (d, *J*<sub>CP</sub>=13.2 Hz), 131.5, 130.7, 130.6 (d, *J*<sub>CP</sub>=3.8 Hz), 130.3, 130.2, 123.5, 55.8 (d, *J*<sub>CP</sub>=19.6 Hz, N-CH<sub>2</sub>-P), 27.1 (d, *J*<sub>CP</sub>=14.9 Hz, C-CH<sub>2</sub>-P). <sup>31</sup>P NMR (202 MHz) δ: -16.7. The <sup>13</sup>C assignments were confirmed by DEPT. MS-MALDI *m/z*: 488 [*M*+*Na*]. Anal. Calcd. (air-sensitive): mono-phosphine oxide form: C, 69.85; H, 5.23; di-oxide form: C, 67.60; H, 5.07. Found: C, 68.57; H, 5.98.



**Ligand 6:** <sup>31</sup>P NMR (120 MHz) δ: -13.4. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.56 (d, 1H), 8.25 (d, 1H), 8.12 (s, 1H), 7.74 (t, 1H), 7.45-7.34 (m, 10H, Ar), 7.20 (m, 1H), 5.14 (d, 2H, *J*<sub>HP</sub>=4.5 Hz, CH<sub>2</sub>-P).



**Ligand 7:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.42-7.19 (m, 15H, Ar), 7.10 (s, 1H, triazole-H), 5.48 (s, 2H, CH<sub>2</sub>-S), 3.50 (s, 2H, CH<sub>2</sub>-P). <sup>13</sup>C NMR (125 MHz) δ: 14.2 (d, *J*<sub>CP</sub>=10.8 Hz), 139.4 (d, *J*<sub>CP</sub> = 14.1 Hz), 134.6, 134.5, 134.1, 133.6, 131.2, 130.1, 130.4 (d, *J*<sub>CP</sub> = 7.5 Hz), 130.3, 122.8 (d, *J*<sub>CP</sub> = 6.9 Hz), 55.6 (CH<sub>2</sub>-S), 27.1 (d, CH<sub>2</sub>-P, *J*<sub>CP</sub> = 15.4 Hz). The <sup>13</sup>C assignments were confirmed by DEPT. <sup>31</sup>P NMR (202 MHz) δ: -16.68. MS-MALDI *m/z*: 390 [*M*+*I*]. Anal. Calcd.: C, 67.85; H, 5.18. Found: C, 67.05; H, 5.69.



**Ligand 8:** <sup>31</sup>P NMR (202 MHz) δ: -33.7. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.25-7.08 (m, 9H), 7.07-6.78 (m, 5H), 5.39 (s, 2H, CH<sub>2</sub>-S), 3.70 (s, 6H, O-Me), 3.52 (s, 2H, CH<sub>2</sub>-P). <sup>13</sup>C NMR (202 MHz) δ: 161.2 (d, *J*<sub>CP</sub>=13 Hz), 145.7 (d, *J*<sub>CP</sub>=11.9 Hz), 133.0, 132.9, 132.3, 130.2, 129.3, 128.4, 142.3 (d, *J*<sub>CP</sub>=15.8 Hz), 120.9, 120.8, 110.1, 55.5 (O-Me), 51.1 (d, CH<sub>2</sub>-S), 21.4 (d, CH<sub>2</sub>-P, *J*<sub>CP</sub>=14.7 Hz). The <sup>13</sup>C assignments were confirmed by DEPT. MS-ESI<sup>+</sup> *m/z*: 488 [*M*+*K*]. Anal. Calcd. (air-sensitive): phosphine oxide form: C, 61.92; H, 5.20. Found: C, 61.75; H, 5.90.

### General Procedure for Preparation of Pincer-Click Palladium Complexes.

**Complex 9:** Ligand **5** (20mg; 0.043 mmol), (TMEDA)PdCl<sub>2</sub> (12 mg; 0.043 mmol) and triethylamine (10 equiv) were combined in 2 ml of DMF. The resulting solution was heated at 70°C for 12 hours. <sup>31</sup>P{<sup>1</sup>H} NMR showed quantitative formation of **9** as a single product. Solvent was evaporated and the residue was washed with ether (3X3ml) and extracted with toluene/THF (3X3ml). The combined extractions were evaporated resulting in pure complex **9** in yield of 78%. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) 33.1 (d, *J*<sub>PP</sub> = 462.0 Hz); 23.4 (d, *J*<sub>PP</sub> = 462.0 Hz). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.30-6.79 (m, 20H, Ar), 4.86 (d, *J*<sub>HP</sub> = 4.7 Hz, 2H, N-CH<sub>2</sub>-P), 3.68 (d, *J*<sub>HP</sub> = 5.2 Hz, 2H, C-CH<sub>2</sub>-P). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 163.02 (bs, C<sub>ipso</sub>), 132.61 (s, Ar), 132.55 (s, Ar), 132.48 (s, Ar), 132.40 (s, Ar), 132.31 (s, Ar), 131.33 (s, Ar), 130.72 (s, Ar), 130.31 (s, Ar), 128.88 (s, Ar), 128.70 (s, Ar), 128.56 (s, Ar), 128.40 (s, Ar), 128.12 (s, Ar), 67.25 (d, *J*<sub>CP</sub> = 30.0 Hz, N-CH<sub>2</sub>-P), 52.34 (d, *J*<sub>CP</sub> = 39.5 Hz, C-CH<sub>2</sub>-P) (assignment of <sup>13</sup>C{<sup>1</sup>H} NMR signals was confirmed by <sup>13</sup>C DEPT). Anal. Calcd.: C, 55.46; H, 3.99. Found: C, 53.93; H, 3.78.

**Complex 10:** <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): 21.4 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.43-7.01 (m, 14H, Ar), 5.30 (d, *J*<sub>HP</sub> = 6.9 Hz, 2H, N-CH<sub>2</sub>-P). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 153.92 (bs, C<sub>ipso</sub>), 149.52 (s, Ar), 136.45 (s, Ar), 133.08 (s, Ar), 133.00 (s, Ar), 132.14 (s, Ar), 131.25 (d, *J*<sub>CP</sub> = 3.1 Hz), 129.04 (d, 2.4 Hz), 123.31 (s, Ar), 122.92 (s, Ar), 120.25 (s, Ar), 68.01 (d, *J*<sub>CP</sub> = 24.7 Hz, N-CH<sub>2</sub>-P). (Assignment of <sup>13</sup>C{<sup>1</sup>H} NMR signals was confirmed by <sup>13</sup>C DEPT). Anal. Calcd.: C, 49.51; H, 3.32. Found: C, 49.36; H, 3.54.

**Complex 11:**  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) 24.17 (s).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.96-7.24 (m, 15H, Ar), 5.82 (s, 2H,  $\text{CH}_2\text{-S}$ ), 3.84 (d,  $J_{\text{HP}} = 11.3$  Hz, 2H,  $\text{CH}_2\text{-P}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 151.35 (d,  $J_{\text{CP}} = 6.1$  Hz  $\text{C}_{\text{ipso}}$ ), 136.72 (s, Ar), 136.50 (s, Ar), 135.40 (d,  $J_{\text{CP}} = 3.2$  Hz, Ar), 135.01 (s, Ar), 132.76 (s, Ar), 132.34 (s, Ar), 132.10 (s, Ar), 131.61 (s, Ar), 131.40 (s, Ar), 130.33 (s, Ar), 130.11 (s, Ar), 127.04 (d,  $J_{\text{CP}} = 13.2$  Hz), 58.11 ( $\text{CH}_2\text{-S}$ ), 30.12 (d,  $J_{\text{CP}} = 33.1$  Hz,  $\text{CH}_2\text{-P}$ ) (assignment of  $^{13}\text{C}\{^1\text{H}\}$  NMR signals was confirmed by  $^{13}\text{C}$  DEPT). Anal. Calcd.: C, 49.83; H, 3.61. Found: C, 50.31; H, 4.09.

**Complex 12:**  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) 25.35 (s).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 8.03-6.55 (m, 13H, Ar) 4.86 (s, 2H,  $\text{CH}_2\text{-S}$ ), 4.51 (d,  $J_{\text{HP}} = 7.4$  Hz, 2H,  $\text{CH}_2\text{-P}$ ), 3.42 (s, 6H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 166.25 (s, Ar), 156.51 (bs,  $\text{C}_{\text{ipso}}$ ), 139.89 (s, Ar), 139.70 (s, Ar), 137.40 (s, Ar), 136.9 (s, Ar), 134.06 (s, Ar), 132.84 (s, Ar), 132.61 (s, Ar), 132.43 (s, Ar), 127.11 (s, Ar), 125.45 (d,  $J_{\text{CP}} = 9.2$  Hz, Ar), 116.05 (d,  $J_{\text{CP}} = 3.9$  Hz, Ar), 59.82 ( $\text{O-CH}_3$ ), 57.61 ( $\text{CH}_2\text{-S}$ ), 28.13 (d,  $J_{\text{CP}} = 38.3$  Hz,  $\text{CH}_2\text{-P}$ ) (assignment of  $^{13}\text{C}\{^1\text{H}\}$  NMR signals was confirmed by  $^{13}\text{C}$  DEPT). Anal. Calcd.: C, 48.83; H, 3.93. Found: C, 49.51; H, 4.78.

$^{31}\text{P}$  NMR data for the free ligands and their corresponding palladium complexes are summarized in Table.

**Table:**  $^{31}\text{P}$  NMR data for **5-8** vs **9-12** in  $\text{CDCl}_3$

Compound	Shift (ppm)	Compound	Shift
<b>5</b>	-16.7	<b>9</b>	33.1(d), 23.4(d)
<b>6</b>	-13.4	<b>10</b>	21.4(s)
<b>7</b>	-16.7	<b>11</b>	24.2(s)
<b>8</b>	-33.7	<b>12</b>	25.4(s)

s = singlet, d = doublet

<sup>1</sup> F. Palacios, J. Pagalday, *Eur. J. Org. Chem.* **2003**, 913.

<sup>2</sup> R. D. Detz, S. Heras, R. de Gelder, P. W. N. M. van Leeuwen, H. Hiemstra, J. N. H. Reek, J. H. van Maarseveen *Org. Lett.* **2006**, 8, 3227.

<sup>3</sup> W. De Graaf, J. Boersma, W. J. J. Smeets, A. L. Spek, G. Van Koten, *Organometallics* **1989**, 8, 2907.

<sup>4</sup> N. J. Lawrence, D. Jackson, *J. Chem. Soc., Perkin Trans.* **2002**, 1, 2260.

<sup>5</sup> C. A. Busacca, C. H. Senanayake, *Org. Lett.* **2005**, 7, 4277.