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Synthesis of a new class of unsymmetrical PCP′ pincer ligands and their palladium (II) complexes: X-ray structure determination of $PdCl\{C_6H_3\text{-}2\text{-}CH_2PPh_2\text{-}6\text{-}CH_2PBu^t{}_2\}$

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Abstract

The unsymmetrical PCP′ pincer ligands $\{C_6H_4\text{-}1\text{-}CH_2PPh_2\text{-}3\text{-}CH_2PBu^t{}_2\}$ and $\{C_6H_4\text{-}1\text{-}CH_2PPh_2\text{-}3\text{-}CH_2PPr^i{}_2\}$ and the corresponding palladium complexes: $PdCl\{C_6H_3\text{-}2\text{-}CH_2PPh_2\text{-}6\text{-}CH_2PBu^t{}_2\}$ and $PdCl\{C_6H_3\text{-}2\text{-}CH_2PPh_2\text{-}6\text{-}CH_2PPr^i{}_2\}$ have been synthesized in good yields. The molecular structure of $PdCl\{C_6H_3\text{-}2\text{-}CH_2PPh_2\text{-}6\text{-}CH_2PBu^t{}_2\}$ was determined through a single crystal X-ray diffraction study. The palladium center was found to be located into a slightly distorted square planar environment in which the $\{C_6H_4\text{-}1\text{-}CH_2PPh_2\text{-}3\text{-}CH_2PBu^t{}_2\}$ ligand is coordinated as a tridentate, PCP pincer type chelate. The complex, $PdCl\{C_6H_3\text{-}2\text{-}CH_2PPh_2\text{-}6\text{-}CH_2PPr^i{}_2\}$ catalyzes the Heck coupling of iodobenzene with styrene.

Keywords: PCP pincer ligand; Palladium complexes; Heck reaction; Catalysis

1. Introduction

In the recent years, metal complexes containing PCP pincer ligands have been employed in a wide variety of homogeneous and heterogenized (supported) catalytic reactions [1]. Complexes of these tridenate pincer ligands are sufficiently robust to withstand the elevated temperatures at which the activation of aliphatic C–H and C–Cl bonds become thermodynamically favorable. Thus, these complexes have been found to have remarkable catalytic activity in aliphatic dehydrogenation [2–4] and C–C coupling reactions [5–8].

Much of the research on PCP pincer complexes has focused on complexes of diphosphinoxylenes: $\{C_6H_4\text{-}1,3\text{-}(CH_2PR_2)_2\}$ (Scheme 1a). Modifications of the benzylic positions and phosphino *R* groups have been used to "tune", the steric, electronic, and stereochemical properties of these ligands thus their metal complexes [9]. PCP pincer ligands with anthryl backbones, as seen in Scheme 1b, and their metal complexes were recently prepared in an effort to generate pincer complexes of even greater thermal stability [3]. In order to elucidate structure–activity relationships, we have synthesized the first examples PCP pincer ligands of the following types: symmetrical bis-phosphinito (Scheme 2a) [6,7]; unsymmetrical bis-phosphinito (Scheme 2b) [10]; and hybrid phosphinito-phosphino (Scheme 2c and d) [11]. We have explored the reactivity of the palladium and

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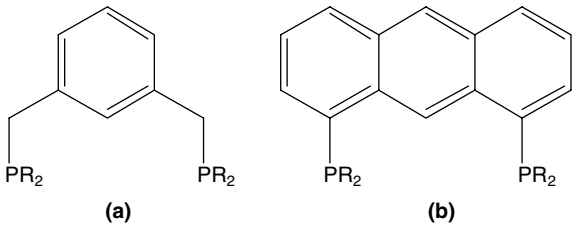


Scheme 1. Structure of the most common types of PCP pincer ligands.

iridium derivatives of these novel ligands, successfully utilizing them as catalysts for Heck couplings [6,7], aliphatic dehydrogenations [4], allylic alkylation [10], and Sonagashira couplings [8]. As part of our effort to create novel PCP pincer systems in which both the electronic and steric properties may be easily modulated, we have designed a novel synthetic route for the high yield synthesis of unsymmetrical phosphino PCP′ pincer type ligands (Scheme 2e). We have also prepared palladium complexes of these novel ligands and investigated their activity as catalysts for the Heck coupling of halo-benzenes and styrene.

2. Experimental

2.1. Materials and methods

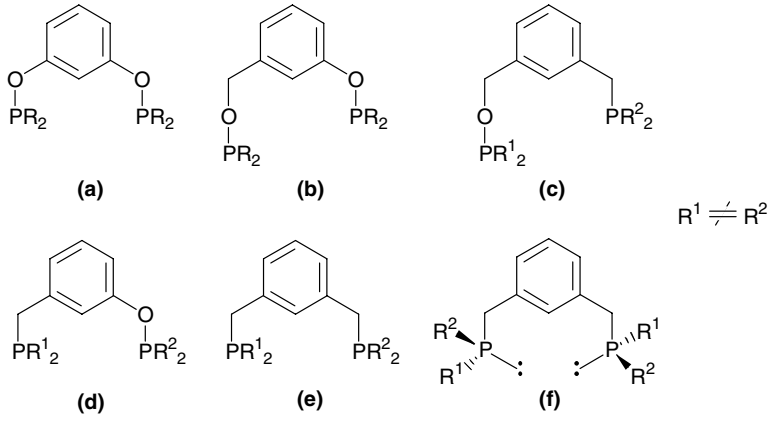
Unless stated otherwise, all reactions were carried out under an atmosphere of purified argon using conventional Schlenk glassware and glovebox techniques, solvents were dried using established procedures and distilled under dinitrogen and freeze–pump–thaw degassed immediately prior to use. The ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ NMR spectra were recorded at 300, 75.4, and 121.4 MHz, respectively, at 295 K, using a Varian Unity Inova 300 NMR spectrometer. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR chemical shifts are reported in ppm downfield from TMS. ^{1}H NMR chemical shifts are referenced to the residual hydrogen signal of the deuterated solvents and in $^{13}C\{^{1}H\}$ NMR the ^{13}C signal of the deuterated solvents was used as a reference. $^{31}P\{^{1}H\}$ NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to high frequency of 85% H_3PO_4. Elemental analyses were determined on a Perkin–Elmer 240. The starting materials 1,3-benzenedimethanol, borane-dimethylsulfide ($BH_3 \cdot Me_2S$), *n*-BuLi, chlorodiisopropyl-phosphine, di-*tert*-butylphosphine, $LiAlH_4$, tetrafluoruboric acid diethylether complex ($BF_4 \cdot Et_2O$), thionylchloride ($SOCl_2$) and triethylamine (NEt_3) were purchased from Aldrich Chemical Co. and used without further purification. The complex [$PdCl_2$(COD)] was synthesized according to the published procedure [13].

2.2. Synthesis of {C_6H_4-1-(CH_2OH)-3-(CH_2Cl)} (**2**) [14]

To a stirred suspension of 1,3-benzenedimethanol (2.7617 g, 20 mmol) in benzene (100 ml) concentrated hydrochloric acid (10 ml) was added at room temperature, the color of the solution, initially red, was discarded after stirring overnight. After this time, the solution is then washed with aqueous $NaHCO_3$ and water, the organic phase is separated and the aqueous layer extracted twice with CH_2Cl_2 (2×20 ml). The organic phase is dried over $MgSO_4$ and the solvent removed by rotary evaporation to afford **2** as a colorless oil (3.13 g, 20 mmol, 100%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.15 (s, 1H, OH), 4.47 (s, 2H, CH_2Cl), 4.55 (s, 2H, CH_2OH), 7.14–7.22 (m, 4H, ArH). $^{13}C\{^{1}H\}$ NMR: δ 46.08 (CH_2Cl), 64.71 (CH_2OH), 126.84, 126.97, 127.71, 128.87, 137.66, 141.40.

2.3. Synthesis of {C_6H_4-1-(CH_2OH)-3-(CH_2PPh_2)} (**3**)

To a solution of Ph_2PH (1.86 g, 10 mmol) in THF (50 ml) was added dropwise a solution of *n*-BuLi in hexane (12.5 ml of 1.6 M/l hexane solution, 20 mmol) at −78 °C, over a period of 30 min with stirring. After this



Scheme 2. Bis-Phosphinito and unsymmetrical phosphino-phosphinito PCP ligands.

time, the reaction mixture was allowed to reach room temperature. The resulting orange suspension was cooled to −78 °C and a THF solution (50 ml) of *m*-(chloromethyl)benzyl alcohol (**2**) (1.566 g, 10 mmol) was added dropwise with a syringe (30 min). The resulting mixture is allowed to reach room temperature and the stirring continued for an additional 1 h to give a pale yellow mixture. After this time, the resulting reaction mixture is placed in to a salt-ice bath (0 °C) and a solution of NH_4Cl in water (10% wt, 60 ml) carefully added to afford a colorless mixture. The THF layer was separated and the aqueous layer extracted twice with ether (2×20 ml). The combined extracts were dried over $MgSO_4$ and passed through a short column of alumina. Finally, the solvent was removed under vacuum to afford **3** as a colorless oil (2.8 g, 9.3 mmol, 93%): ^{1}H NMR (300 MHz, benzene-d_6): δ 1.16 (s, OH); 2.96 (s, 2H, CH_2P), 3.99 (s, 2H, CH_2O); 6.75 (s, 10H, Ar); 7.07 (m, 4H). $^{31}P\{^1H\}$ NMR (121 MHz, benzene-d_6): δ 9.078 (s), $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6): δ 36.23 (d, J=16.06, CH_2P); 64.89 (CH_2O); 124.61; 128.18, 128.32; 128.52; 128.60; 128.78; 133.29 (d, J=18.33 Hz); 137.88 (d, J=7.99 Hz), 139.02 (d, J=16.06 Hz); 141.92.

2.4. Synthesis of {C_6H_4-1-(CH_2OH)-3-(CH_2PPh_2-(BH_3))} (**4**)

A solution of compound **3** (2.85 g, 9.3 mmol) in THF (30 ml) was placed in a salt-ice bath (0 °C), then, $BH_3\cdot SMe_2$ (0.85 g, 11.25 mmol) was slowly added via syringe under stirring. After the addition is completed, the cooling bath was removed and the solution allowed to reach room temperature. The stirring was continued at room temperature for an extra 2 h. Then, the solvent was evaporated and the crude product dissolved in CH_2Cl_2, passed through a short path of silica gel and the resulting solution evaporated under vacuum to afford **4** as a white solid (2.83 g, 8.84 mmol, 95%): ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (br, q, J_{HP}=94.95 Hz, 3H, BH_3), 1.84 (bs, 1H, OH), 3.51 (d, J_{HP}=12.0 Hz, CH_2P), 4.41 (s, 2H, CH_2O), 6.77–7.06 (m, 4H, ArH), 7.30–7.56 (m, 10H, ArH). $^{13}C\{^1H\}$ NMR (75.40 MHz, $CDCl_3$): δ 33.85 (d, J=32.12 Hz, CH_2P), 64.81 (CH_2OH), 125.51, 128.15, 128.54, 128.68, 128.80 (d, J=4.53 Hz), 129.35 (d, J=4.60 Hz), 131.27, 131.97 (d, J=4.15 Hz), 132.57 (d, J=8.60 Hz), 140.67. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 19.15 (br, m). Anal. Calc. for $C_{20}H_{22}BOP$ (M_r=320.18): C, 75.02; H, 6.93. Found: C, 75.10; H, 6.85%.

2.5. Synthesis of {C_6H_4-1-(CH_2Cl)-3-(CH_2PPh_2-(BH_3))} (**5**)

A solution of compound **4** (2.83 g, 8.84 mmol) in CH_2Cl_2 (70 ml) was placed in to a salt-ice bath (0 °C). Then, $SOCl_2$ (3.9 ml, 53 mmol) was slowly added via syringe under stirring and the resulting solution kept at this temperature for 2 h. The solvent and excess of $SOCl_2$ were removed under vacuum and the residue subjected to column chromatography using silica gel as a solid support (CH_2Cl_2/hexane 1.1:1) to afford **5** as a white solid (2.63 g, 88%): ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (br, q, J_{HP} = 97.95, 3H, BH_3), 3.51 (d, J_{HP} = 12.0 Hz, 2H, CH_2P), 4.32 (s, 2H, CH_2Cl), 6.77–7.20 (m, 4H), 7.30–7.60 (m, 10H). $^{13}C\{^1H\}$ NMR (75.40 MHz, $CDCl_3$): δ 33.93 (d, J_{CP} = 31.52 Hz, CH_2P), 45.90 (CH_2Cl), 127.16, 128.02, 128.41, 128.63, 128.76, 130.29 (d, J = 4.0 Hz), 130.48 (d, J = 4.6 Hz), 131.36, 132.60 (d, J = 8.67 Hz), 137.12. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 19.30 (br, m). Anal. Calc. for $C_{20}H_{21}ClBOP$ (M_r = 338.63): C, 79.94; H, 6.25. Found: C, 80.05; H, 6.17%.

2.6. Synthesis of {C_6H_4-1-($CH_2Bu^t_2$(BH_3))-3-(CH_2-PPh_2(BH_3))} (**6**)

To a mixture of compound **5** (2.63 g, 7.8 mmol) and NaI (2.34 g, 15.6 mmol) in degassed acetone (70 ml), $HPBu^t_2$ (1.47 ml, 7.96 mmol) was added via syringe under stirring. The mixture was set to reflux for 5 h. After the prescribed reaction time the solvent was removed under vacuum. The remaining residue was dissolved in ether (60 ml) and degassed NEt_3 (1.1 ml, 7.8 mmol) and stirred for 1 h. The resulting reaction mixture was filtered off, and the solvent removed from the filtrate at reduced pressure. The remaining solid (that has mixture of protected and unprotected of both *tert*-butylphospine and diphenylphosphine is very difficult to purify so was used without further purification) was dissolved in 50 ml of THF and borane-dimethysulfide (0.68 g, 9 mmol) added at 0 °C under stirring. The reaction mixture was allowed to reach room temperature and stirred for further 2 h. The solvent was then evaporated under vacuum and the residue re-dissolved in CH_2Cl_2 and filtered through a short plug of silica gel. The crude product of **5** was purified by column chromatography using silica gel as support and eluted with a mixture CH_2Cl_2/hexane (1.2:1) to afford pure **6** as a white solid (2.99 g, 6.47 mmol, 81%): ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.00–1.00 (m, 6H, BH_3), 1.19 (d, $^3J_{HP}$ = 12.60 Hz, 18 H, $((CH_3)_3C)_2P$), 2.97 (d, $^2J_{HP}$ = 12.29 Hz, 2H, $CH_2PBu^t_2$), 3.59 (d, $^2J_{HP}$ = 12.0Hz, 2H, CH_2Ph_2), 6.79–7.39 (m, 4H), 7.41–7.66 (m, 10H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 25.60 (d, J = 24.66 Hz, $((CH_3)_3C)_2P$), 28.17 (s, $((CH_3)_3C)_2P$), 32.68 (d, J = 25.26 Hz, $CH_2PBu^t_2$), 33.78 (d, J = 32.12 Hz, CH_2PPh_2), 127.78, 128.48, 128.59, 128.72, 129.08, 129.21, 131.12, 131.72, 132.58 (d, J = 8.60 Hz), 134.62. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 19.11 (br, m, Ph_2PBH_3), 47.49 (br, m, $Bu^t_2PBH_3$). Anal. Calc. for

$C_{28}H_{42}B_2P_2$ (M_r = 462.21): C, 72.76; H, 9.16. Found: C, 72.78; H, 9.06%.

2.7. Synthesis of {C_6H_4-1-($CH_2Bu^t_2$)-3-(CH_2PPh_2)} (7)

$HBF_4 \cdot Et_2O$ complex, 85% (5.54 ml, 32 mmol) was added via syringe to a stirred solution of **6** (1.489g, 3.2 mmol) in 30 ml of CH_2Cl_2 at −5 °C. The mixture was allowed to reach room temperature and stirred overnight. After the prescribed reaction time, 60 ml of ether and 160 ml of a degassed saturated aqueous solution of $NaHCO_3$ were added with vigorous stirring for 10 min. The organic layer was separated and the aqueous layer extracted with ether. The combined organic extracts were washed with water, brine and dried over $MgSO_4$. After filtration, the solution was passed through a short plug of celite and the solvent evaporated under vacuum to afford **7** as colorless oil (1.25 g, 2.87 mmol, 90%). ^{1}H NMR (300 MHz, benzene-d_6): δ 0.769 (d, $^3J_{HP}$ = 10.50 Hz, $(CH_3)_3C$, 2.38 (d, $^2J_{PH}$ = 1.80 Hz, 2H, $CH_2PBu^t_2$), 2.99 (s, 2H, CH_2PPh_2), 6.58–7.44 (m, 14H, Ar). $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6): δ 28.83 (d, J = 25.64 Hz, $(CH_3)_3C$, 29.84 (d, J = 13.20 Hz, $(CH_3)_3C$, 31.61 (d, J = 24.13 Hz, $CH_2PBu^t_2$), 36.16 (d, J = 16.06 Hz, CH_2PPh_2), 126.82 (d, J = 7.24 Hz), 128.49, 128.63 (d, J = 4.00 Hz), 131.25, 131.37, 131.95, 133.30 (d, J = 18.40 Hz), 137.63 (d, J = 8.10 Hz), 139.20 (d, J = 16.60 Hz), 141.93 (d, J = 12.00 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, benzene-d_6): δ −9.39 (PPh_2), 33.87 (PBu^t_2).

2.8. Synthesis of [PdCl{C_6H_3-2-(CH_2PPh_2)-6-($CH_2PBu^t_2$)} (11)

To a stirred suspension of [$PdCl_2$(COD)] (0.819 g, 2.87 mmol) in toluene (30 ml) a solution of ligand **7** (1.250 g, 2.87 mmol) in toluene (30 ml) was slowly added. The resulting solution was set to reflux for 5 h. After this time, the solution was filtered over a cotton pad and pumped off under vacuum to dryness. The crude solid was purified by recrystallization from $CHCl_3$/MeOH to afford complex **11** as white crystals (1.24 g, 2.15 mmol, 75%): ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.37 (d, $^3J_{PH}$ = 13.49 Hz, CH_3, 18H), 3.23 (d, $^2J_{PH}$ = 9.3 Hz, 2H, $CH_2PBu^t_2$), 3.84 (d, $^2J_{PH}$ = 10.80 Hz, 2H, CH_2PPh_2), 6.88–7.18 (m, 3H, Ar), 7.29–7.83 (m, 10H, Ar). $^{13}C\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ 29.34 (d, J = 3.5 Hz, CH_3), 34.33 (dd, J = 23.53 Hz, J = 2.3 Hz), 35.23 (dd, J = 12.1 Hz, J = 3 Hz), 42.27 (d, J = 3.1 Hz), 122.40, 122.58, 122.67, 122.89, 125.34, 128.60 (d, J = 9.73 Hz), 130.31, 133.00 (d, J = 11.46 Hz), 147.90 (d, J = 23.00 Hz), 151.30 (d, J = 18.93 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 31.62 (d, $^2J_{PP}$ = 394 Hz, PPh_2), 78.14 (d, $^2J_{PP}$ = 394 Hz, PBu^t_2). Anal. Calc. for $C_{28}H_{35}ClP_2Pd$ (M_r = 575.388): C, 58.45; H, 6.13. Found: C, 58.40; H, 6.13%.

2.9. Synthesis of $Pr^i_2P(H)BH_3$ (8)

$LiAlH_4$ (10 mmol, 10 ml of 1 M/l ether solution) and $BH_3 \cdot SMe_2$ (1.14 ml, 12 mmol) were added consecutively by syringe to a stirred solution of $ClPPr^i_2$ (1.526 g, 1.59 ml, 10 mmol) in THF (40 ml) at 0 °C. After warming to room temperature and stirring for 2 h, the reaction mixture was treated with HCl (5 ml), ice ca. 12 g and CH_2Cl_2 (20 ml). The organic layer was separated, and the aqueous layer extracted twice with CH_2Cl_2 (2×10 ml). The combined extracts were dried over $MgSO_4$ and then the solvent evaporated under vacuum to afford pure diisopropylphosphine-borane adduct as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.46 (br, q, J_{HP} = 93.45 Hz, 3H, BH_3), 1.30 (m, 12H, $(CH_3)_2CH$), 2.17 (m, 2H, $(CH_3)_2CH$), 4.22 (m, J_{HP} = 350.82 Hz, 1H, PH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 18.16 (d, J = 138.82 Hz), 19.43 (d, J = 34.46 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 28.01 (br, q, m). Anal. Calc. for $C_6H_{18}BP$ (M_r = 131.995): C, 54.60; H, 13.75. Found: C, 54.75; H, 13.72%.

2.10. Synthesis of {C_6H_4-1-($CH_2PPh_2(BH_3)$)-3-($CH_2PPr^i_2(BH_3)$)} (9)

To a stirred solution of phosphine **8** (0.412 g, 3.12 mmol) in THF (30 ml) was added slowly a 1.6 M solution of *n*-BuLi in hexane (1.95 ml, 3.12 mmol) at −78 °C (dry ice–acetone bath). The reaction mixture was allowed to reach room temperature to afford a colorless mixture. The dry ice–acetone bath is replaced and a solution of **5** (1.097 g, 3.12 mmol) in THF (20 ml) added drop wise by syringe over a period of 30 min. The temperature was allowed to reach room temperature over a period of 3 h and kept at this temperature for further 2 h. The reaction mixture was quenched by adding an aqueous solution of NH_4Cl (wt 10%, 30 ml). The product was extracted with CH_2Cl_2 and the combined extracts dried over $MgSO_4$. The solvent was removed under reduced pressure and the solid residue subjected to column chromatography using silica gel as a solid support and eluted with CH_2Cl_2/hexane (1.15:1) to afford **9** as a white solid (1.259 g, 2.90 mmol, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.30 (br, m, 6H, BH_3), 1.01 (m, 12H, $(CH_3)_2CH$), 1.85 (m, 2H, $(CH_3)_2CH$), 2.84 (d, J_{HP} = 11.10 Hz, $CH_2PPr^i_2$), 3.53 (d, J_{HP} = 12.29 Hz, CH_2PPh_2), 6.73–7.07 (m, 4H, Ar), 7.34–7.60 (m, 10H, Ar). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 16.97 (d, J = 10.33 Hz, $(CH_3)_2CH$, 21.41 (d, J = 32.12 Hz, $(CH_3)_2CH$), 27.92 (d, J = 27.52, $CH_2PPr^i_2$), 33.76 (d, J = 32.12 Hz, CH_2PPh_2), 128.18, 128.27, 128.63, 128.76, 128.99, 131.30, 131.39, 132.21, 132.51 (d, J = 8.60 Hz), 133.52. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 18.88 (Ph_2PBH_3), 35.10 ($Pr^i_2PBH_3$). Anal. Calc. for $C_{26}H_{38}B_2P_2$ (M_r = 434.16): C, 71.93; H, 8.82. Found: C, 72.10; H, 8.75%.

2.11. Synthesis of {C_6H_4-1-(CH_2PPh_2)-3-($CH_2PPr^i_2$)} (**10**)

To a stirred solution of **9** (1.259 g, 2.90 mmol) in CH_2Cl_2 (25 ml), HBF_4–Et_2O complex 85% (5.0 ml, 29 mmol) was added at −5 °C and the resulting mixture allowed to react overnight. After this time, 25 ml of ether and 75 ml of a saturated aqueous solution of $NaHCO_3$ were added. The organic layer was separated and the aqueous layer extracted with ether. The combined extracts were dried over $MgSO_4$ and filtered over a short plug of celite. The solvent was then removed under vacuum to afford **10** as a colorless oil (1.119 g, 2.75 mmol, 95%). ^{1}H NMR (300 MHz, benzene-d_6): δ 0.91 (dd, J_{HP} = 12.30 Hz, J_{CH_3CH} = 7.20 Hz, 12H, $(CH_3)_2CH$), 1.51 (m, 2H, $(CH_3)_2CH$), 2.54 (s, 2H, $CH_2PPr^i_2$), 3.21 (s, 2H, CH_2PPh_2), 6.81–7.00 (m, 4H, Ar), 7.01–7.34 (m, 10H, Ar). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6): δ 19.33 (d, J = 11.54 Hz, $CH(CH_3)_2$), 19.75 (d, J = 14.40 Hz, $CH(CH_3)_2$), 23.66 (d, J = 16.06 Hz, $CH(CH_3)_2$), 30.04 (d, J = 21.79 Hz, $CH_2PPr^i_2$), 36.23 (d, J = 16.06 Hz, CH_2PPh_2), 126.97 (d, J = 6.33 Hz), 127.31 (d, J = 5.20 Hz), 128.49, 128.57, 128.69, 130.85 (d, J = 6.94 Hz), 133.28 (d, J = 18.93), 137.72 (d, J = 8.00 Hz), 139.18 (d, J = 16.06 Hz), 140.38 (d, J = 8.00Hz). ^{31}P{^{1}H} NMR (121 MHz, benzene-d_6): δ −9.46 (PPh_2), 10.68 (PPr^i_2).

2.12. Synthesis of [PdCl{C_6H_3-2-(CH_2PPh_2)-6-($CH_2PPr^i_2$)}] (**12**)

A solution of the ligand **10** (1.119 g, 2.75 mmol) in toluene (20 ml) was added dropwise to a suspension of [$PdCl_2$(COD)] (0.786 g, 2.75 mmol) in toluene (30 ml). The resulting reaction mixture was set to reflux for 5 h. The solution was filtered over a short pad of silica gel and the solvent evaporated under vacuum. Recrystallization of the crude product from CH_2Cl_2/hexane resulted in the quantitative formation of a colorless microcrystalline solid (1.11 g, 1.93 mmol, 70%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10 (dd, $^3J_{HP}$ = 14.40 Hz, $^2J_{CHCH_3}$ = 6.70 Hz, 6H, $CH(CH_3)_2$), 1.37 (dd, $^3J_{HP}$ = 17.40 HZ, $^2J_{CHCH_3}$ = 6.70 Hz, 6H, $CH(CH_3)_2$), 2.38 (m, 2H, $CH(CH_3)_2$), 3.18 (d, $^2J_{HP}$ = 10.19 Hz, $CH_2PPr^i_2$), 3.85 (d, $^2J_{HP}$ = 10.79 Hz, CH_2PPh_2), 6.87–7.01 (m, 3H, Ar), 7.27–7.83 (m, 10H, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 17.91 (s, $CH(CH_3)_2$), 18.92 (d, J = 4.60 Hz, $CH(CH_3)_2$), 24.06 (d, J = 20.66 Hz, $CH(CH_3)_2$), 33.29 (d, J = 26.40 Hz, $CH_2PPr^i_2$), 41.97 (d, J = 30.39 Hz, CH_2PPh_2), 122.72, 122.89, 123.01, 123.18, 125.46, 128.68 (d, J = 9.80 Hz), 130.32, 132.89 (d, J = 12.07 Hz), 148.03 (d, J = 22.40 Hz), 150.21 (d, J = 19.53 Hz). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 29.92 (d, J_{PP} = 400 Hz, PPh_2), 68.94 (d, J_{PP} = 400.00 Hz, PPr^i_2). Anal. Calc. for $C_{26}H_{31}ClP_2Pd$ (M_r = 547.355): C, 55.06; H, 5.71. Found: C, 54.95; H, 5.67%.

2.13. Data collection and refinement for PdCl{C_6H_3-2-CH_2PPh_2-6-$CH_2PBu^t_2$} (**11**)

Crystalline yellow prisms of **11** grown by slow diffusion from a CH_3Cl/MeOH solvent system; were glued to a glass fiber. The X-ray intensity data was measured at 293 K on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (λ = 0.71073 Å). The detector was placed at a distance of 4.837 cm from the crystal. A total of 1800 frames were collected with a scan width of 0.3° in ω and an exposure time of 10 s/frame. The frames were integrated with the Bruker SAINT software package [15] using a narrow-frame integration algorithm. The integration of the data was done using a monoclinic unit cell to yield a total of 21,167 reflections to a maximum 2θ angle of 50.00° (0.93 Å resolution), of which 4657 were independent. Analysis of the data showed negligible decays during data collection. The structure was solved by Patterson method using SHELXS-97 [16] program. The remaining atoms were located via few cycles of least squares refinements and difference Fourier maps, using the space

Table 1
Crystal data and structure refinement for compound PdCl{C_6H_3-2-CH_2PPh_2-6-$CH_2PBu^t_2$} (**11**)

Empirical formula	$C_{28}H_{35}Cl_1P_2Pd_1$
Formula weight	575.35
Temperature	291(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*C2/c*
Unit cell dimensions	a = 25.896(2) Å, α = 90° b = 11.1359(7) Å, β = 91.608(1)° c = 18.305(1) Å, γ = 90°
Volume	5276.6(6) Å^3
Z	8
Density (calculated)	1.448 Mg/m^3
Absorption coefficient	0.940 mm^{-1}
F(000)	2368
Crystal size	0.24×0.20×0.18 mm
θ range for data collection	1.99–25.0°
Index ranges	$-30 \leqslant h \leqslant 30$, $-13 \leqslant k \leqslant 13$, $-21 \leqslant l \leqslant 21$
Reflections collected	21,167
Independent reflections	4657 [R(int) = 0.0379]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4657/0/295
Goodness-of-fit on F^2	0.955[a]
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0229, wR_2 = 0.0532[a]
R indices (all data)	R_1 = 0.0279, wR_2 = 0.0541[b]
Largest diff. peak and hole	0.316 and −0.220 eÅ^{-3}

[a] $S = [w((F_o)^2 - (F_c)^2)^2/(n-P)]^{1/2}$, where n is number of reflections and p is total number of parameters.

[b] $R_1 = |F_o - F_c|/|F_o|, wR_2 = [w((F_o)^2 - (F_c)^2)^2/w(F_o)^2]^{1/2}$.

Table 2
Selected bond distances (Å) and angles (°) for PdCl{C_6H_3-2-CH_2PPh_2-6-$CH_2PBu^t_2$} (**11**)

Bond lengths (Å)		Angles (°)	
Pd(1)–C(2)	2.023(2)	C(2)–Pd(1)–P(1)	82.82(6)
Pd(1)–P(1)	2.2867(6)	C(2)–Pd(1)–P(2)	82.84(6)
Pd(1)–P(2)	2.3120(6)	P(1)–Pd(1)–Cl(1)	94.12(2)
Pd(1)–Cl(1)	2.4069(6)	P(2)–Pd(1)–Cl(1)	100.24(2)
		P(1)–Pd(1)–P(2)	165.65(2)
		C(2)–Pd(1)–Cl(1)	175.96(7)

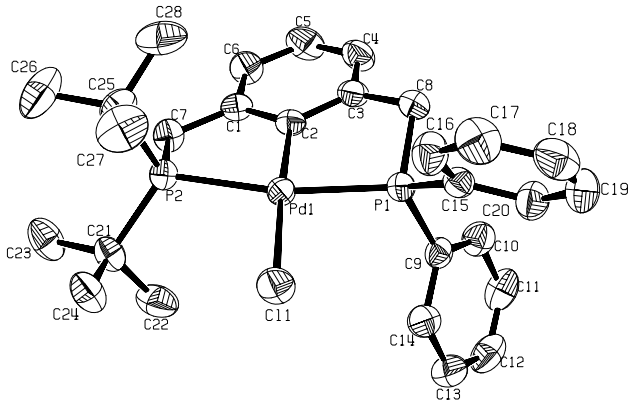


Fig. 1. An ORTEP representation of the structure of PdCl{C_6H_3-2-CH_2PPh_2-6-$CH_2PBu^t_2$} (**11**) at 50% of probability showing the atom labeling scheme.

group *C2/c* with $Z=8$. Hydrogen atoms were input at calculated positions, and allowed to ride on the atoms to which they are attached. Thermal parameters were refined for hydrogen atoms on the phenyl groups using a $U_{eq}=1.2$ Å to precedent atom. The final cycle of refinement was carried out on all non-zero data using SHELXL-97 [17] and anisotropic thermal parameters for all non-hydrogen atoms. The details of the structure determination are given in Table 1 and selected bond lengths (Å) and angles (°) in Table 2. The numbering of the atoms is shown in Fig. 1 (ORTEP) [18].

2.14. General procedure for the palladium catalyzed Heck reaction

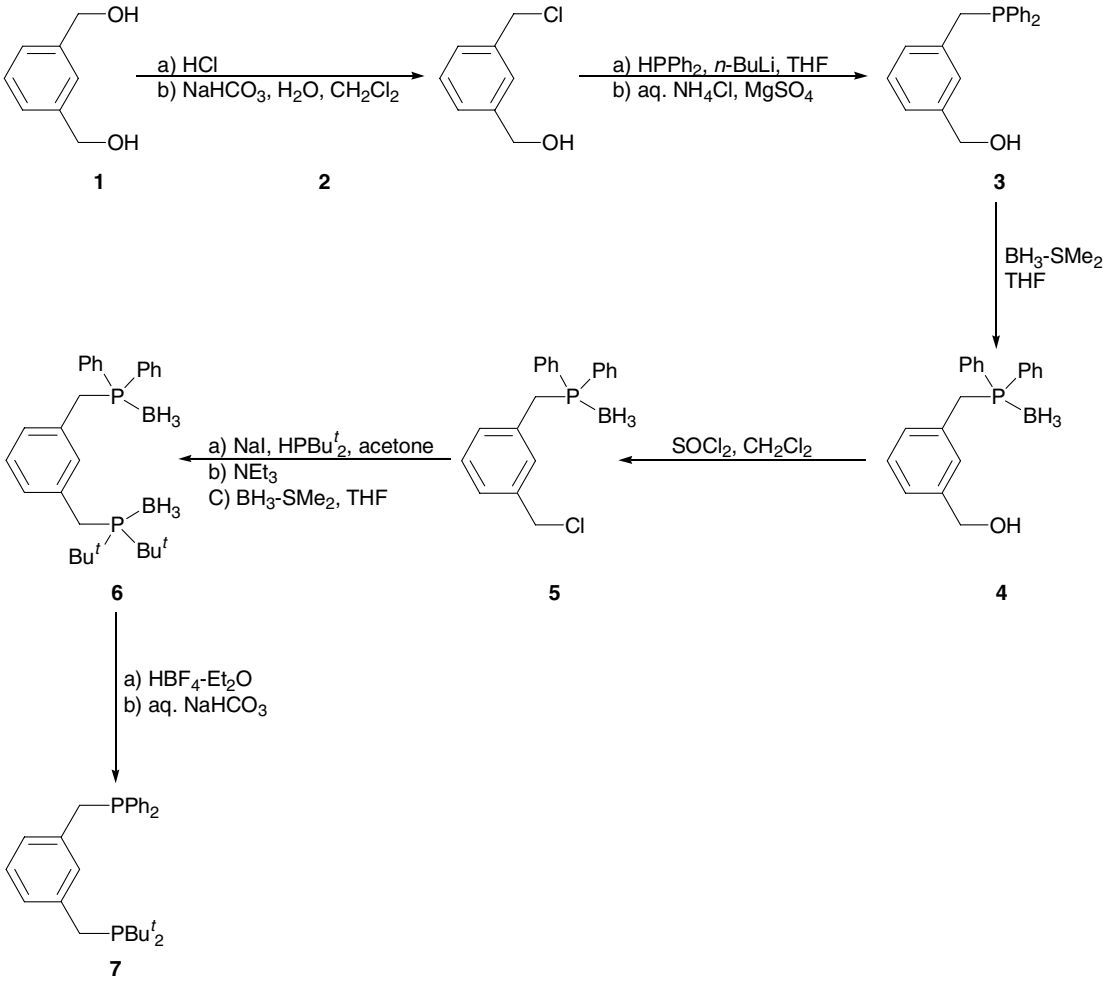
A DMF solution (3 ml) of 5.0 mmol of halogen benzene, 6.0 mmol of alkene, and the prescribed amount of catalyst (5 or 8 mol%) was introduced into a Schlenk tube in the open air. The tube was charged with a magnetic stir bar and 1.1 equivalent of base, sealed, and fully immersed in a 180 °C silicon oil bath. After the prescribed reaction time, the mixture was cooled to room temperature and the organic phase was analyzed by gas chromatography (GC/FID, GC–MS). A Hewlett Packard 5980A gas chromatograph with flame ionization detector (FID), and an HP-1 capillary column (25.0 m) was used for quantitative GC analysis.

3. Results and discussion

3.1. Synthesis of the ligands {C_6H_4-1-(CH_2PPh_2)-3-($CH_2PBu^t_2$)} (**7**) and {C_6H_4-1-(CH_2PPh_2)-3-($CH_2PPr^i_2$)} (**10**)

1,3-Benzenedimethanol (C_6H_4-1,3-$(CH_2OH)_2$) is readily transformed to 2-(chloromethyl)benzyl alcohol (**2**) {C_6H_4-1-(CH_2OH)-3-(CH_2Cl)} [14]. The chloride can be further functionalized to unsymmetrical PCP′ pincer type ligands. For example, the reaction of **2** with lithium diphenylphosphide gives compound **3** in high yield. Protection of the phosphine, by forming the borane adduct, affords compound **4** in good yield. This compound, is halogenated with $SOCl_2$ to afford compound **5**, which in turn is reacted with the lithium salt of the borane adduct of the di-*tert*-butylphosphine to obtain compound **6**. Further deprotection of **6**, with $HBF_4\cdot Et_2O$ affords the unsymmetrical ligand {C_6H_4-1-(CH_2PPh_2)-3-($CH_2PBu^t_2$)} (**7**) as a colorless oil in good yield (Scheme 3). Analysis by multinuclear NMR spectroscopy of this ligand exhibits signals in the ^1H NMR spectra corresponding to the methyls of the Bu^t groups in the *P* moiety (d, 0.77 ppm) and those corresponding to the two different CH_2 groups attached to the two different phosphino moieties, one at 2.38 ppm corresponding to the $CH_2PBu^t_2$ and the other at 2.99 ppm due to the CH_2PPh_2. Other signals between 7.4 and 6.6 ppm are due to the aromatic rings in the ligand. The $^{31}P\{^1H\}$ NMR experiment is very illustrating, showing two signals (singlets) in the spectra which are in accordance with the presence of two different phosphorus nuclei, one located at −9.39 ppm corresponding to the *P* center in PPh_2 and the other at lower field (33.87 ppm) corresponding to the presence of the *P* nuclei of the PBu^t_2 moiety.

The isopropyl derivative, {C_6H_4-1-(CH_2PPh_2)-3-($CH_2PPr^i_2$)} (**10**) was synthesized and isolated in an analogous manner to that of ligand **7**, in good yield as a colorless oil (Scheme 4). Similar spectroscopic analysis exhibits signals due to the presence of the isopropyl substitutents in the *P* moiety at 0.9 ($(CH_3)_2CH$) and 1.5 ppm ($(CH_3)_2CH$), respectively. Analogously to ligand **7**, ligand **10** also exhibits two different signals for the two different CH_2 groups in the phosphino moieties, one at 2.54 ppm corresponding to the $CH_2PPr^i_2$ and the other at 3.21 ppm due to the CH_2 in CH_2PPh_2. As expected, compound **10** exhibits the same behavior in the $^{31}P\{^1H\}$ NMR spectra as that observed for ligand **7**, presenting two different singlets, one at −9.46 ppm due to the PPh_2 substituent and the other displaced to lower field due to the presence of the PPr^i_2 moiety at 10.68 ppm.



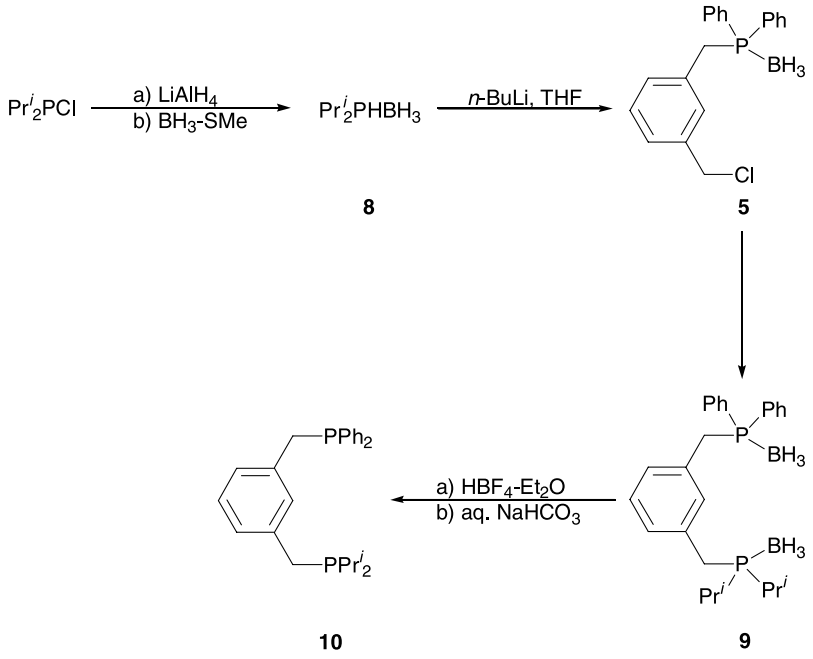
Scheme 3. Synthesis of the ligand $\{C_6H_4\text{-}1\text{-}(CH_2Bu^t{}_2)\text{-}3\text{-}(CH_2PPh_2)\}$ (**7**).

*3.2. Synthesis of the complexes $PdCl\{C_6H_3\text{-}2\text{-}CH_2PPh_2\text{-}6\text{-}PBu^t{}_2\}$ (**11**) and $PdCl\{C_6H_3)\text{-}2\text{-}(CH_2PPh_2)\text{-}6\text{-}(CH_2PPr^i{}_2)\}$ (**12**)*

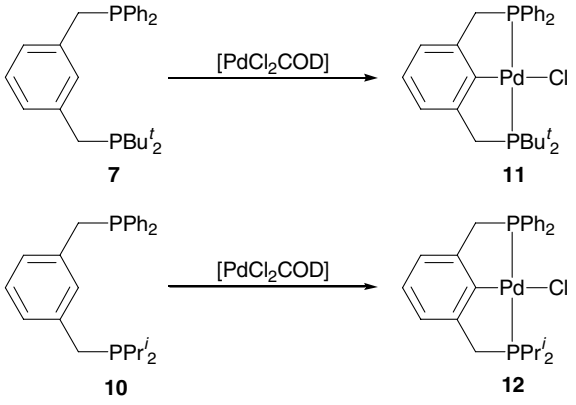
The reaction of stoichiometric amounts of ligands **7** or **10** with the starting material $[PdCl_2(COD)]$ under reflux of toluene (5 h), affords complexes $PdCl\{C_6H_3\text{-}2\text{-}CH_2PPh_2\text{-}6\text{-}PBu^t{}_2\}$ (**11**) and $PdCl\{C_6H_3)\text{-}2\text{-}(CH_2\text{-}PPh_2)\text{-}6\text{-}(CH_2PPr^i{}_2)\}$ (**12**) in good yields (Scheme 5). Both complexes were isolated from the corresponding reaction mixtures as colorless microcrystalline powders. The NMR spectra of both complexes exhibits the signals corresponding to the presence of the substituents in the *P* moieties and those due to the aromatic rings present in the backbones of the ligands. However, more informative analysis by $^{31}P\{^1H\}$ NMR spectroscopy reveals similar patterns as those observed for the free ligands **7** and **10**, however the signals in these cases are shown as doublets, due to the coupling established by the two different *P* nuclei by having the Pd metal center coordinated to both phosphorus centers. The $^{31}P\{^1H\}$ NMR spectrum of complex **11** exhibits signals at 31.62 and 78.14 ppm for PPh_2 and $PBu^t{}_2$ respectively with a coupling constant of $^2J_{PP} = 394$ Hz, which is in agreement with a *trans* conformation of the two *P* nuclei. Complex **12** exhibits a similar pattern, with signals located at 29.92 and 68.94 ppm for PPh_2 and $PPr^i{}_2$ respectively with a coupling constant of $^2J_{PP} = 400$ Hz, this value being consistent with a *trans* arrangements of both *P* nuclei (Scheme 5).

*3.3. X-ray crystal structure of $PdCl\{C_6H_3\text{-}2\text{-}CH_2PPh_2\text{-}6\text{-}PBu^t{}_2\}$ (**11**)*

Single, colorless prismatic crystals of $PdCl\{C_6H_3\text{-}2\text{-}CH_2PPh_2\text{-}6\text{-}PBu^t{}_2\}$ (**11**), that were suitable X-ray diffraction analysis were obtained from a $CHCl_3$/MeOH solvent system. The details of the structure determination are given in Table 1 and selected bond lengths and angles are listed in Table 2. A thermal ellipsoid drawing of **11** with atomic number scheme of the obtained structure is presented in Fig. 1. Analysis of the colorless crystals reveals the palladium center to be located into a lightly distorted square planar environment,



Scheme 4. Synthesis of the ligand $\{C_6H_4\text{-}1\text{-}(CH_2PPh_2)\text{-}3\text{-}(CH_2PPr^i_2)\}$ (**10**).



Scheme 5. Synthesis of the complexes $PdCl\{C_6H_3\text{-}2\text{-}CH_2PPh_2\text{-}6\text{-}CH_2PBu^t_2\}$ (**11**) and $[PdCl\{C_6H_3\text{-}2\text{-}(CH_2PPh_2)\text{-}6\text{-}(CH_2PPr^i_2)\}]$ (**12**).

with angles of 165.65(2)° and 175.96(7)° for P(1)–Pd(1)–P(2) and C(1)–Pd(1)–Cl(1), respectively. Two chelated five membered rings formed by Pd(1)–P(2)–C(7)–C(1)–C(2) and Pd(1)–P(1)–C(8)–C(3)–C(2) are present in the complex. These rings are quite strained due to the constrains imposed by the atoms forming the two adjacent, five membered chelated rings. Part of this strain is released by formation of unequal P(1)–Pd(1)–Cl(1) (94.12(2)°) and P(2)–Pd(1)–Cl(1) (100.24(2)°) angles being the larger angle value the reflex of the presence of the bulkier substituents Bu^t on the *P* moiety, as a result of this the Pd(1)–P(2) distance (2.3120(6) Å) is slightly longer than Pd(1)–P(1) (2.2867(6) Å). In addition, the methylene carbons, C(7) and C(8), are located slightly above and below the plane defined Pd(1), C(2), Cl(1), P(1) and P(2). Furthermore, while the pseudoaxial substituent on one side of the molecule is above the coordination plane, the corresponding substituent on the other side is below the coordination plane. This imposed asymmetric environment is expected to lead to reactivities that are different than complexes of pincer ligands with equivalent substituents in both sides of the tridentated ligand. The Pd–P(2) bond length of 2.3120(6) Å is significantly longer than the 2.2867(6) Å length found for Pd–P(1). This is counter to the situation that would be expected upon consideration of the relative σ donor strengths of dialkylaryl- vs. trialkyl-phosphines. Thus the shorter Pd–P(1) distance apparently reflects that the pendent aryl group confers P(2) with a significant π bonding component in its interaction with the palladium center. Except for the above mentioned features, the bond angles and lengths determined for **11** are similar to those observed in other PCP-complexes [6,9,10,12,19].

The novel PCP pincer complexes **11** and **12** were tested as catalysts for the olefination of aryl halides with styrene. Complex **12** was found to catalyze the coupling of iodobenzene and styrene. Yields of 80% (based on iodobenzene) were achieved in reaction mixtures containing 5 mol% of **12**. However, **12** was ineffective as a catalyst for the coupling of styrene with bromo or chlorobenzene. Complex **11** did not exhibit any detectable activity as a catalyst for the Heck coupling of styrene with any of the halo-benzenes, even upon increasing the loadings of the complex to 8 mol%. The greater bulk of the Bu^t substituents apparently creates steric congestion such that there is insufficient access of substrates to the palladium center of **11**.

In order to extend our studies of structure–activity relationships in C–C coupling reactions catalyzed by PCP pincer complexes, efforts to synthesize other classes of PCP ligands are currently underway in our laboratories.

4. Supplementary material

Supplementary data for complex **11** have been deposited at the Cambridge Crystallographic Data Centre. Copies of this information are available free of charge on request from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) quoting the deposition number CCDC 225523.

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