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Synthesis, characterization, and catalytic activity of (1,2-Diaryl)alkenylphosphine palladium complexes

Chanjuan Xi [a,*], Bingran Yu [b], Xiaoyu Yan [a], Ning Tang [b]

[a] Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084, China
[b] State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China

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ABSTRACT

A series of (1,2-diaryl)alkenylphosphine palladium complexes have been designed and synthesized. The structures of palladium complexes depend on the ratio of amount of using $PdCl_2(CH_3CN)_2$ and ligands. Additions of one equivalent of ligands afford dipalladium complexes $[R^1CH{=}CR^2(PR_2)PdCl_2]_2$, $R^1 = R^2 = R = Ph$, (**C1**); $R^1 = R^2 = p$-tolyl, R = Ph, (**C2**); $R^1 = R^2 = Ph$, R = ^{i}Pr, (**C3**). The dipalladium complexes (**C1**–**C3**) adopt a *transoid* conformation and existed as chlorine-bridged dimer with a single alkenylphosphine ligand at each Pd. Complex **C1** is confirmed by X-ray crystallography. Additions of two equivalents of ligands afford monopalladium complexes $\{[R^1CH{=}CR^2(PR_2)]_2PdCl_2\}$, $R^1 = R^2 = R = Ph$, (**C4**); $R^1 = R^2 = p$-tolyl, R = Ph, (**C5**); $R^1 = R^2 = Ph$, R = ^{i}Pr, (**C6**). The monopalladium complexes (**C4**–**C6**) adopt a *transoid* conformation with two alkenylphosphines. Complex **C4** and **C5** were confirmed by X-ray crystallography, respectively. For a crystal structure of complex **C4**, there are two independent palladium complexes in the asymmetric unit. All the complexes as a catalyst show good catalytic activity in Suzuki–Miyaura reaction.

1. Introduction

During the past years, the interest in complexes of transition metals with organophosphorus ligands has been growing considerably in the light of their versatile applications in the coordination chemistry and homogeneous catalysis [1]. Among them, palladium with arylphosphine and alkylphosphine ligands such as $(o\text{-tolyl})_3P$ [2], BINAP [3], biphenylphosphine [4], diadamantylbutylphosphine [5], and tris-*tert*-butylphosphine [6], D^{t}BPF [7], have played important roles. However, alkenylphosphines as ligands remain less studied in the synthesis and application [8]. Recently, we reported a versatile and general method for the formation of various alkenylphosphines [8h,9]. Having an interest in coordination chemistry and homogeneous catalysis for alkenylphosphine as ligands, herein we report on the synthesis, characterization, and catalytic activity of (1,2-diaryl)alkenylphosphine palladium complexes.

2. Experimental section

2.1. Reagents and general considerations

Unless otherwise noted, all chemicals were obtained from commercial sources and used as received. The ligands **L1-L3** were prepared according to the literature method [8h,9a]. NMR data for all ligand **L1**–**L3** were in accordance with literature values. ^{1}H NMR and ^{13}C NMR spectra were recorded on 300 MHz spectrometers at ambient temperature with $CDCl_3$ as the solvent. Chemical shifts (δ) were given in parts per million, referenced to the residual proton resonance of $CDCl_3$ (7.26), and to the carbon resonance of $CDCl_3$ (77.16). Coupling constants (J) were given in hertz (Hz). The terms m, d, and s refer to multiplet, doublet, and singlet. ^{1}H NMR yields, using CH_2Cl_2 or mesitylene as internal standard, were obtained in proportion to the integral area of CH_2Cl_2 or mesitylene signal. ^{31}P NMR spectra were recorded on a Bruker AC 200 NMR spectrometer at 81 MHz under ^{1}H decoupled conditions using 85% H_3PO_4 ($\delta_P = 0$ ppm) as an external standard. Elemental analyses were performed on a Flash EA 1112 instrument. Melting points were determined with a digital electrothermal apparatus without calibration. The IR spectra were obtained on a Perkin–Elmer FT-IR 2000 spectrophotometer by using KBr disks in the range of 4000–400 cm^{-1}. X-ray diffraction data of **C1**, **C4**, and **C5** were carried out on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo KR radiation (λ) 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions.

* Corresponding author.
E-mail address: cjxi@tsinghua.edu.cn (C. Xi).

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Structure solution and refinement were performed by using the SHELXL-97 package [10].

2.2. General procedure for the synthesis of the dipalladium complexes *C1–C3*

Dipalladium complexes **C1–C3** were synthesized by the following general procedure. $PdCl_2(CH_3CN)_2$ (0.10 mmol) and (*E*)-(1,2-diarylvinyl)diphenylphosphine as ligand (0.10 mmol) were mixed in dichloromethane. The mixture was stirred at room temperature for 12 h, giving an orange suspension. The reaction volume was reduced, diethyl ether was added, and orange solids were obtained, which were washed repeatedly with diethyl ether and dried under vacuum. The red powder was obtained.

2.2.1. Complex *C1*

$PdCl_2(CH_3CN)_2$ (0.10 mmol, 26 mg) and (*E*)-(1,2-diphenylvinyl)diphenylphosphine **L1** (0.10 mmol, 36 mg). Yield: 89% (48 mg). Mp: 159–162 °C. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 6.96–7.74 (m, aromatic, 40H), 8.03 (d, 2H, J_{PH} = 23.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 126.5, 127.2, 128.1, 128.3, 128.4, 128.9, 129.4, 130.1, 130.5, 130.8 (d, J_{PC} = 48.2 Hz), 131.7, 135.0 (d, J_{PC} = 20.8 Hz), 135.6 (d, J_{PC} = 10.8 Hz), 148.7 (d, J_{PC} = 14.3 Hz); ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 44.0. IR (KBr; cm^{-1}): 2953, 2920, 2848, 2678, 2330, 1961, 1607, 1485, 1435, 1266, 1093, 945, 744, 731. *Anal.* Calc. for $C_{52}H_{42}Cl_4P_2Pd_2{\cdot}2CHCl_3$: C, 49.05; H, 3.35. Found: C, 49.14; H, 3.31%.

2.2.2. Complex *C2*

$PdCl_2(CH_3CN)_2$ (0.10 mmol, 26 mg) and (*E*)-(1,2-ditolylvinyl)diphenylphosphine **L2** (0.10 mmol, 39 mg). Yield: 95% (54 mg). Mp: 183–185 °C. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 2.25 (s, 12H); 6.91–7.73 (m, aromatic, 36H), 8.00 (d, 2H, J_{PH} = 23.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 21.4, 125.4, 126.2, 127.7, 128.1, 128.3, 128.4, 128.6, 129.1, 129.2, 129.6, 129.9, 130.0, 130.5, 130.8, 131.0, 131.6, 132.2, 132.4, 132.7, 133.6, 133.8, 135.5, 135.3, 135.6, 137.8138.3, 139.5139.9, 148.8 (d, J_{PC} = 18.6 Hz), 149.0 (d, J_{PC} = 17.9 Hz); ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 43.2. IR (KBr; cm^{-1}): 3072, 3050, 3017, 2918, 2861, 2361, 1604, 1567, 1505, 1479, 1431, 1309, 1183, 1093, 1024, 924, 896, 812, 740. *Anal.* Calc. for $C_{56}H_{50}Cl_4P_2Pd_2$: C, 59.02; H, 4.42. Found: C, 59.22; H, 4.51%.

2.2.3. Complex *C3*

$PdCl_2(CH_3CN)_2$ (0.10 mmol, 26 mg) and (*E*)-(1,2-diphenylvinyl)diisopropylphosphine **L3** (0.10 mmol, 30 mg). Yield: 87% (41 mg). Mp: 134–138 °C. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.33 (m, 24H), 2.46 (m, 4H); 5.28 (s, 1H), 7.00–7.53 (m, aromatic, 20H), 7.62 (d, 2H J_{PH} = 19.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 18.4, 18.5, 18.6,19.6, 19.9, 26.0 (d, J_{PC} = 28.7 Hz), 53.5, 126.6, 127.2, 127.7, 128.3, 128.5, 128.8, 128.9, 129.2, 129.4, 130.4, 136.0 (d, J_{PC} = 19.6 Hz), 137.4, 147.9 (d, J_{PC} = 12.9 Hz); ^{31}P NMR (81 MHz, $CDCl_3$, 85%H_3PO_4) δ 65.2. IR (KBr; cm^{-1}): 2954, 2924, 2855, 2361, 2337, 1461, 1094, 810, 733, 695. *Anal.* Calc. for $C_{40}H_{50}Cl_4P_2Pd_2{\cdot}0.5CH_2Cl_2$: C, 49.14; H, 5.19. Found: C, 48.92; H, 5.03%.

Table 1
Comparison of NMR data for ligand **L1–L3** and complex **C1–C6**.

	L1	L2	L3	C1	C2	C3	C4	C5	C6
$\delta_{C=CH}$	6.57	6.57	6.60	8.03	8.00	7.62	7.93	7.90	7.39
δ_P	9.1	9.0	27.4	44.0	43.2	65.2	35.6	36.5	44.3

2.3. General procedure for the synthesis of the monopalladium complexes *C4–C6*

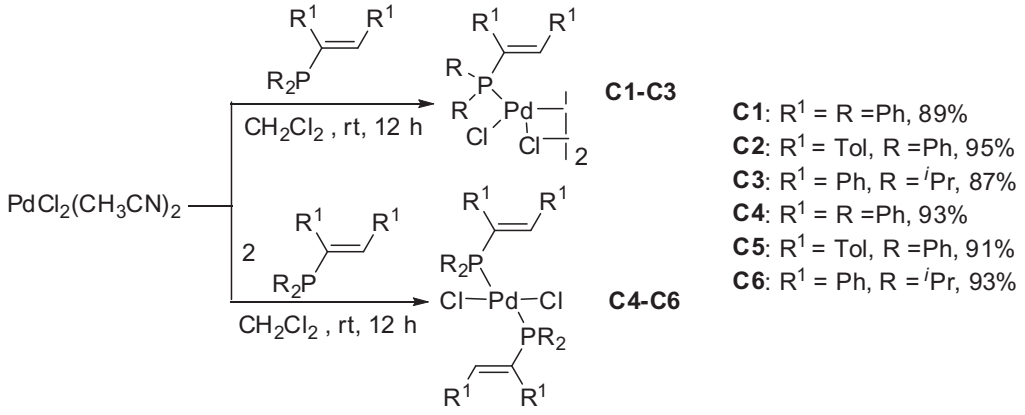
Complexes **C4–C6** were synthesized by the following general procedure. $PdCl_2(CH_3CN)_2$ (0.10 mmol) and (*E*)-(1,2-diarylvinyl)diphenylphosphine as ligand (0.22 mmol) were mixed in dichloromethane. The mixture was stirred at room temperature for 12 h, giving an orange suspension. The reaction volume was reduced, diethyl ether was added, and yellow solids were obtained, which were washed repeatedly with diethyl ether and dried under vacuum. The yellow powder was obtained.

2.3.1. Complex *C4*

$PdCl_2(CH_3CN)_2$ (0.10 mmol, 26 mg) and (*E*)-(1,2-diphenylvinyl)diphenylphosphine **L1** (0.22 mmol, 80 mg). Yield: 93% (84 mg) Mp: 225–230 °C. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 7.03–7.74 (m, aromatic, 40H), 7.93 (t, 2H, J_{PH} = 10.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 127.4, 127.7, 127.8, 128.2, 128.6, 128.9, 129.2, 129.5, 129.9, 130.2, 130.5, 132.5, 132.8, 133.0, 135.6, 135.7, 135.8, 146.5 (d, J_{PC} = 11.5 Hz), 146.7 (d, J_{PC} = 11.5 Hz); ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 35.6. IR (KBr; cm^{-1}): 3049, 3017, 2918, 2858, 2730, 2360, 2336, 1604, 1506, 1432, 1283, 1184, 1094, 812, 741. *Anal.* Calc. for $C_{52}H_{42}Cl_2P_2Pd{\cdot}$·C, 68.92; H, 4.67. Found: C, 68.83; H, 4.64%.

2.3.2. Complex *C5*

$PdCl_2(CH_3CN)_2$ (0.10 mmol, 26 mg) and (*E*)-(1,2-ditolylvinyl)diphenylphosphine **L2** (0.22 mmol, 86 mg). Yield: 91% (88 mg). Mp: 190–192 °C. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ



Scheme 1. General scheme of synthesis of (1,2-diaryl) alkenyl phosphine palladium complex **C1–C6**.

Table 2
Selected X-ray crystallographic data and refinement for **C1**, **C4**, and **C5**.

Complex	**C1**	**C4**	**C5**
Empirical formula	$C_{50}H_{42}Cl_4P_2Pd_2{\cdot}2CHCl_3$	$C_{52}H_{42}Cl_2P_2Pd$	$C_{56}H_{62}Cl_2P_2Pd$
Formula weight	1322.13	906.10	974.32
Crystal color	Red	Yellow	Yellow
T (K)	173.15 K	173.15 K	173.15 K
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
a (Å)	11.152(2)	14.727(3)	10.100(2)
b (Å)	11.957(2)	15.845(3)	11.772(2)
c (Å)	12.576(3)	19.170(4)	11.891(2)
V (Å^3)	1353.6(5)	4263.0(15)	1195.8(4)
Z	1	4	1
D_{calc} (g cm^{-3})	1.622	1.412	1.353
μ (mm^{-1})	1.252	0.672	0.604
F(000)	660	1856	508
Crystal size (mm)	0.23 × 0.18 × 0.10	0.31 × 0.30 × 0.13	0.16 × 0.15 × 0.14
θ (°)	1.80–27.49	1.09–27.48	1.97–30.02
Reflections collected	16671	52610	18784
Unique reflections	6184	19434	6963
Completeness to (%)	99.4 (θ = 27.49°)	99.5 (θ = 27.48°)	99.3 (θ = 30.02°)
No. of params	307	1027	277
Goodness-of-fit (GOF) on F^2	1.221	1.206	1.165
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0391, $wR2$ = 0.1180	$R1$ = 0.0643, $wR2$ = 0.1591	$R1$ = 0.0404, $wR2$ = 0.1469
R indices (all data)	$R1$ = 0.0448, $wR2$ = 0.1331	$R1$ = 0.0749, $wR2$ = 0.1689	$R1$ = 0.0426, $wR2$ = 0.1504
Largest diff peak and hole (e Å^{-3})	1.036 and −1.32	0.593 and −1.166	0.975 and −1.334

2.23 (s, 12H); 6.91–7.73 (m, aromatic, 36H), 7.90 (t, 2H, J_{PH} = 10.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 21.3, 127,5, 127.7, 128.0, 128.9, 129.2, 129.5, 129.7, 129.8, 130.2, 130.3, 131.6, 133.1 (t, J_{PC} = 18.6 Hz), 134.4, 135.6, 135.7135.8, 137.0138.5, 146.4 (d, J_{PC} = 11.4 Hz), 144.6 (d, J_{PC} = 12.2 Hz); ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 36.5. IR (KBr; cm^{-1}): 2953, 2920, 2848, 2678, 1611, 1479, 1433, 1266, 1092, 945, 744, 731. *Anal.* Calc. for $C_{56}H_{50}Cl_2P_2Pd$: C, 69.90; H, 5.24. Found: C, 69.92; H, 5.21%.

2.3.3. Complex ***C6***

$PdCl_2(CH_3CN)_2$ (0.10 mmol, 26 mg) and (*E*)-(1,2-diphenylvinyl)diisopropylphosphine **L3** (0.22 mmol, 65 mg). Yield: 93% (72 mg). Mp: 220–223 °C. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.28 (m, 24H), 2.67 (m, 4H), 5.29 (s, 2H), 7.00–7.56 (m, aromatic, 20H), 7.39 (t, 2H, J_{PH} = 8.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 18.6, 20.1, 23.8, 53.5, 127,6, 127.9, 128.1, 128.3, 128.7, 130.1, 130.4, 133.2 (d, J_{PC} = 16.5 Hz), 136.2 (d, J_{PC} = 7.9 Hz), 138.1, 144.6 (d, J_{PC} = 12.2 Hz); ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 44.3. IR (KBr; cm^{-1}): 2953, 2920, 2848, 2678, 2364, 1604, 1481, 1433, 1183, 1092, 814, 744, 723. *Anal.* Calc. for $C_{40}H_{50}Cl_2P_2Pd{\cdot}CH_2Cl_2$: C, 57.59; H, 6.13. Found: C, 57.72; H, 6.18%.

2.4. General procedure for Suzuki–Miyaura reaction

Aryl bromide (1.0 mmol), phenylboronic acid (1.2 mmol), cesium carbonate (2.0 mmol) and toluene (3 mL) were added to the Schlenk tube. Catalyst, 0.01 mol/L in CH_3CN solution, was added to the Schlenk tube. The mixture was stirred at 100 °C. After the reaction had completed, the mixture was quenched with water and extracted with ethyl ether. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using petroleum ether or mixture of petroleum ether and dichloromethane.

3. Results and discussion

3.1. Synthesis of complexes

Palladium (II) complexes **C1**–**C6** were obtained by the reaction of $PdCl_2(CH_3CN)_2$ with the corresponding ligands in dichloromethane at room temperature. When the (1,2-diaryl)alkenylphosphine and $PdCl_2(CH_3CN)_2$ were added in the equivalent amounts, dipalladium complexes **C1**–**C3** were obtained as chlorine-bridged dimers with single alkenylphosphine ligand at each Pd. When the (1,2-diaryl)alkenylphosphine and $PdCl_2(CH_3CN)_2$ were added in two to one ratio of equivalent and monopalladium complexes **C4**–**C6** were obtained (Scheme 1) with two alkenylphosphines as ligands. All complexes tended to precipitate from the reaction solution, and optimized yields were obtained by adding excessive amount of

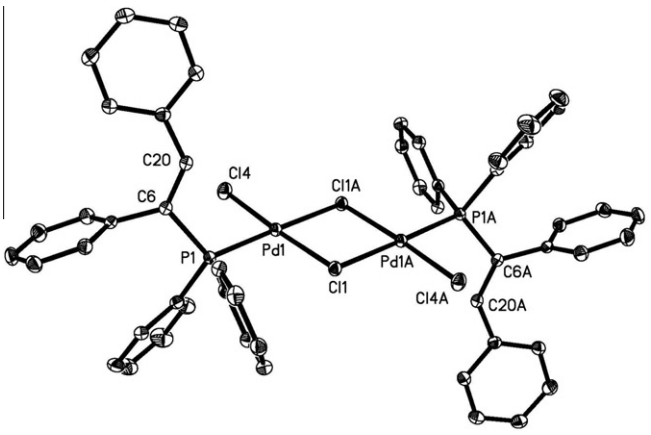


Fig. 1. X-ray diffraction structure of complex **C1**. Thermal ellipsoids are shown at 30% probability; hydrogen atoms and solvent have been omitted for clarity. Selected bond lengths (Å) and angles (°) are Pd(1)–P(1), 2.2291(12), Pd(1)–Cl(4), 2.2717(10), Pd(1)–Cl(1) 2.3260(10), P(1)–C(6), 1.826(3), C(6)–C(20), 1.338(4); P(1)–Pd(1)–Cl(4), 87.46(4), P(1)–Pd(1)–Cl(1), 96.04(4), Cl(4)–Pd(1)–Cl(1), 176.41(3), C(6)–P(1)–Pd(1), 113.13(11), C(20)–C(6)–P(1), 116.2(2).

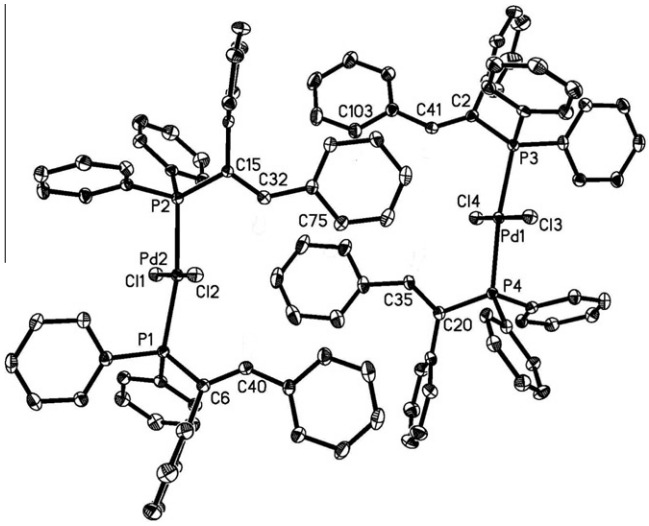


Fig. 2. X-ray diffraction structure of complex **C4**. Thermal ellipsoids are shown at 30% probability; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) are Pd(1)–Cl(3), 2.2895(11), Pd(1)–Cl(4), 2.3172(11), Pd(1)–P(3), 2.3245(14), Pd(1)–P(4), 2.3416(14), P(4)–C(20), 1.831(4), C(20)–C(35), 1.349(5), P(3)–C(2), 1.827(4), C(2)–C(41), 1.340(5), Pd(2)–Cl(2), 2.3116(11), Pd(2)–Cl(1), 2.2895(11), Pd(2)–P(2), 2.3280(14), Pd(2)–P(1), 2.3386(14), P(1)–C(6), 1.830(4), C(6)–C(40), 1.349(5), P(2)–C(15), 1.824(4), C(15)–C(32), 1.342(5), C(32)–H(32A), 0.9500; Cl(3)–Pd(1)–Cl(4), 174.25(4), Cl(3)–Pd(1)–P(3), 91.01(4), Cl(4)–Pd(1)–P(3), 87.17(4), Cl(3)–Pd(1)–P(4), 92.08(4), Cl(4)–Pd(1)–P(4), 88.92(4), P(3)–Pd(1)–P(4), 170.90(4), Pd(1)–P(4)–C(20), 115.04(13), P(4)–C(20)–C(35), 113.50(3), Pd(1)–P(3)–C(2), 115.98(13), P(3)–C(2)–C(41), 116.10(3), Pd(2)–P(2)–C(15), 116.08(12), P(3)–C(2)–C(41), 116.10(3), Pd(2)–P(1)–C(6), 115.89(13), P(1)–C(6)–C(40), 114.4(3).

Et_2O in the reaction solution. The dipalladium complexes **C1**–**C3** are red solids. The complexes **C4–C6** are yellow solids. All preparations proceeded in satisfactory yields. All the complexes are remarkably stable under ambient atmosphere.

3.2. Spectroscopic characterization of complexes

All of the complexes were authenticated by elemental analyses, solution NMR studies. In their ^{1}H NMR spectra, the proton signal of C=CH appeared at 8.03, 8.0, 7.62, 7.93, 7.90, 7.39 ppm for **C1**, **C2**, **C3**, **C4**, **C5**, **C6**, respectively (Table 1). All complexes showed a remarkable downfield shift for proton of alkenylphosphine upon coordination. Upon coordination, the typical coordination shift of 30–40 ppm towards lower filed is observed in the ^{31}P NMR spectra.

3.3. Structural features

Single crystals of the complex **C1**, **C4**, and **C5** were obtained at ambient temperature by slow evaporation of chloroform/hexane for **C1**, dichloromethane/hexane for **C4** and **C5**. The single crystals of the complex **C1** contained two molecular chloroforms. Crystallographic data and refinement residuals for complex **C1**, **C4**, and **C5** are summarized in Table 2. The ORTEP diagrams of the complexes are presented in Fig. 1–3 with their corresponding bond lengths and angles in the coordination palladium frame, respectively. As shown in Fig. 1, the complex **C1** adopts a *transoid* conformation and exists as chlorine-bridged dimer with an inversion center in the structure. The data of bond lengths and angles are common for this type of complex and we do not give any further comments. As shown in Figs. 2 and 3, the palladium atom is coordinated by two alkenylphosphines *via* their phosphorus atoms and two chlorine atoms in a square-planar fashion. The two alkenylphosphines are arranged in *trans*-fashion. For **C4**, there are two independent palladium complexes in the asymmetric unit. *ortho*-H from each

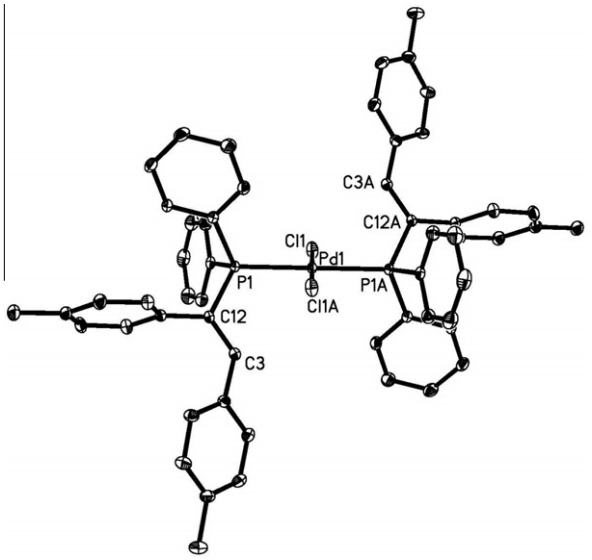


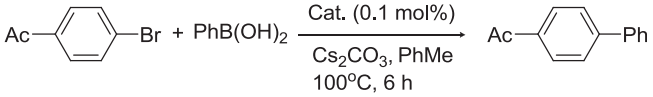
Fig. 3. X-ray diffraction structure of complex **C5**. Thermal ellipsoids are shown at 30% probability; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) are Pd(1)–Cl(1), 2.2908(8), Pd(1)–P(1), 2.3287(11), P(1)–C(12), 1.821(2), C(3)–C(12), 1.345(3), C(3)–H(3A), 0.9500; Cl(1)–Pd(1)–P(1), 91.59(3), C(12)–P(1)–Pd(1), 113.21(7), C(3)–C(12)–P(1), 115.51(15).

phenyl ring points towards the center of other phenyl ring at the 2-position of alkenylphosphines. The distances are in the range of 3.00–3.10 Å. These data indicate that intermolecular C_{Ph}-H···Ph π interactions [11] occur between *ortho*-CH bonds of phenyl ring at terminal alkene and phenyl rings at other terminal alkene, and result in two independent palladium complexes in the asymmetric unit. In contrast to complex **C4**, the complex **C5** does not have any intermolecular interactions between tolyl. The difference may be attributed to the effect of substituent on the phenyl ring. The palladium atom in **C5** sits on the inversion center.

3.4. Catalysis

The palladium-catalyzed coupling reaction of aryl halides and organometallic reagents (Sn, Mg, B, Li, Zn) has become one of most

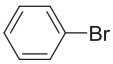
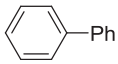
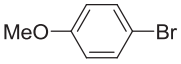
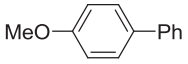
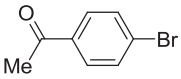
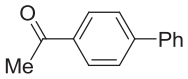
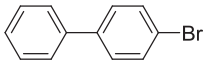
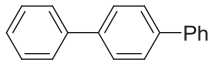
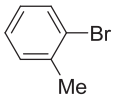
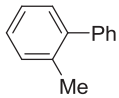
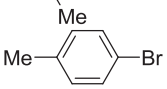
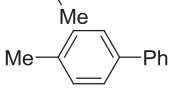
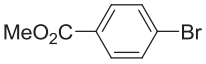
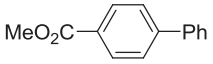
Table 3
Pd/alkenyl phosphine complexes as catalysts in Suzuki–Miyaura reaction.[a]



Entry	Cat.	Yield (%)[b]
1	C1	69
2	C2	78
3	C3	64
4	C4	98
5	C5	99
6	C6	93
7	C1 + L1	95[c]
8	$Pd(CH_3CN)_2Cl_2$	34[d]
9	$Pd(CH_3CN)_2Cl_2$ + L1	58[e]
10	$Pd(CH_3CN)_2Cl_2$ + 2L1	65[f]

[a] Reaction conditions: phenylboronic acid (1.2 mmol), *p*-bromoacetophenone (1.0 mmol), Cs_2C0_3 (2.0 mmol), toluene (3 ml);
[b] NMR yield;
[c] using 0.1 mol% C1 and 0.1 mol% **L1**;
[d] using 0.1 mol% $Pd(CH_3CN)_2Cl_2$;
[e] using 0.1 mol% $Pd(CH_3CN)_2Cl_2$ and 0.1 mol% **L1**;
[f] using 0.1 mol% $Pd(CH_3CN)_2Cl_2$ and 0.2 mol% **L1**.

Table 4
Coupling of aryl bromide with phenyl boronic acid using complex **C5** as catalyst.[a]

Entry	Aryl bromide	Product	Yield (%)[b]	TON[c]
1			92 (90)	920
2			93 (89)	930
3			99 (95)	990
4			99 (96)	990
5			96 (94)	960
6			98 (93)	980
7			99 (96)	990

[a] Reaction conditions: aryl bromide(1.0 mmol), $PhB(OH)_2$ (1.2 mmol), C5 (0.1 mol%), Cs_2C0_3 (2.0 mmol), toluene (3 ml), 100 °C for 6 h;
[b] NMR yields, isolated yields are in parentheses;
[c] TON = mol of product/mol of the catalyst.

powerful methods for a variety of synthetic transformations [12–13]. Many efforts towards the coupling reaction have been achieved using available phosphine ligands such as Ph_3P, (*o*-tolyl)$_3$P, biphenylphosphine, and tris-*tert*-butylphosphine. These ligands are commonly electron rich and bulky. In our ligand, (1,2-diaryl)alkenylphosphine, one aryl group at the α-position and one aryl group at β-position on alkenylphosphine made the ligand more bulky and electron rich around the phosphorus atom. Accordingly, we investigated the (1,2-diaryl)alkenylphosphine palladium complexes as catalysts in Suzuki–Miyaura reaction. At first, we examined the reaction of phenylboronic acid with *p*-bromoacetophenone in toluene with 2 equiv. of Cs_2CO_3 as base in the presence of the complex **C1**–**C6** (Table 3). The dipalladium complex **C1**–**C3** as catalyst made Suzuki–Miyaura reaction in moderate yields (entries 1–3). When complex **C4**–**C6** as catalyst was applied and excellent yields were obtained at 100 °C for 6 h (entries 4–6). In addition, when additional ligand **L1** added to the **C1** reaction system and the yield of the coupling reaction raised to 95% (entry 7). When $Pd(CH_3CN)_2Cl_2$ or a mixture of the $Pd(CH_3CN)_2Cl_2$ ligand **L1** was examined in the reaction under the reaction conditions, a moderate yield was observed (entries 8–10).

The complexes **C4**–**C6** were all effective for the Suzuki–Miyaura reaction, the use of **C5** as an illustrated catalyst was studied further in the coupling of a number of aryl bromides and phenylboronic acid. The results are summarized in Table 4. Both electron-rich and electron-poor aryl bromides could be successfully converted into the desirable product in excellent yields.

4. Conclusions

We have described the synthesis and structural features of new (1,2-diaryl)alkenylphosphine palladium complexes. The coordination modes of the (1,2-diaryl)-alkenylphosphine fragment onto the palladium center depend on the ratio of amount of using $PdCl_2(CH_3CN)_2$ and the ligand. The complex **C1–C3** adopted a *transoid* conformation and existed as a chlorine-bridged dimer. In complexes **C4**–**C6**, the palladium atom is coordinated by two alkenylphosphines *via* their phosphorus atoms and two chlorine atoms in a square-planar fashion. The two alkenylphosphines are arranged in *trans*-fashion. A preliminary study also revealed that all complexes as catalysts showed a good catalytic activity in Suzuki–Miyaura reaction.

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Appendix A. Supplementary data

CCDC 755248, 755249, and 755250 contains the supplementary crystallographic data for **C1**, **C4**, and **C5**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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