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Aminophosphine–palladium(II) complexes: Synthsesis, structure and applications in Suzuki and Heck cross-coupling reactions

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ABSTRACT

Reaction of furfurylamine with 1 or 2 equivalents of PPh_2Cl in the presence of Et_3N, proceeds under anaerobic conditions in thf to give furfuryl-2-(*N*-diphenylphosphino)amine, Ph_2PNHCH_2-C_4H_3O, **1** and furfuryl-2-(*N*,*N*-bis(diphenylphosphino)amine), $(Ph_2P)_2NCH_2$-C_4H_3O, **2**, respectively. The reactions of **1** and **2** with MCl_2(cod) (M = Pd, Pt; cod = 1,5-cyclooctadiene) or $Pt(CH_3)_2$(cod) yield complexes $[M(Ph_2PNHCH_2\text{-}C_4H_3O)_2Cl_2]$ (M = Pd **1a**, Pt **1b**), $[Pt(Ph_2PNHCH_2\text{-}C_4H_3O)_2(CH_3)_2]$ (**1c**), and $[M((Ph_2P)_2NCH_2\text{-}C_4H_3O)Cl_2]$ (M = Pd **2a**, Pt **2b**), $[Pt((Ph_2P)_2NCH_2\text{-}C_4H_3O)(CH_3)_2]$ (**2c**), respectively. All the compounds were isolated as analytically pure substances and characterized by NMR, IR spectroscopy and elemental analysis. Representative solid-state structures of **2a** and **2b** were also determined by X-ray single crystal diffraction technique. Furthermore, the palladium complexes **1a** and **2a** were tested and found to be highly active catalysts in the Suzuki coupling and Heck reaction affording biphenyls and *trans*-stilbenes, respectively.

1. Introduction

Phosphorus–nitrogen containing ligands have particular use in catalysis where it is necessary for part of ligand to dissociate to allow an organic fragment to coordinate and undergo transformations [1]. Small variations in these ligands can cause significant changes in their coordination behavior and the structural features of the resulting complexes. Synthesis of new aminophosphines to stabilize transition metals in low valent states is considered to be a most challenging task in view of their potential utility in a variety of metal-mediated organic transformations [2–4]. To date, a number of such systems with a variety of backbone frameworks have been synthesized and their transition metal chemistry has been explored [5–7]. Tertiary phosphines have long been used in the synthesis of transition metal complexes with catalytic properties, especially with electron-rich transition metals like nickel, palladium, platinum and rhodium [8–10].

Transition metal catalysts have been used in a variety of synthetic transformations, including the formation of carbon–carbon and carbon-heteroatom bonds through cross-coupling [11]. The development of highly active catalysts for Heck, Sonogashira, Stille, and Suzuki reactions is noteworthy in this area, where significant advances have culminated to provide an important step-change [12–15]. In addition to the high catalytic activity in these reactions, selectivity of the catalyst, particularly chemo-, regio-, stereo- and enantio-selectivity, is of the utmost importance [16]. Because of their remarkable catalytic potential and their large versatility, palladium complexes have become the most popular organometallics used in organic synthesis [17]. In particular, palladium catalysts have been used in most of the carbon–carbon bond formation reactions such as Heck and Suzuki reactions [18] which are powerful tools for the preparation of unsymmetrical biaryl [19,20] and stilbene compounds [21].

Recently, various bulky and electron-rich phosphines have been developed as ligands to promote the cross-coupling reactions [22]. We have shown that aminophosphine and bis(aminophosphine) palladium(II) complexes offer distinct advantages for Pd/phosphine system in the Suzuki and Heck cross-coupling reactions [23,24]. Extending our study to develop useful catalysts, herein, we report the coordination chemistry of two furfurylamine-functionalised aminophosphine ligands with palladium(II) and platinum(II) ions. The structures of all new compounds have been elucidated by a combination of multinuclear NMR spectroscopy, IR spectroscopy, elemental analysis and by X-ray crystallography. In addition, we tested the catalytic activities of palladium complexes in the Suzuki and Heck coupling reactions.

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2. Experimental

2.1. General

Unless otherwise stated, all reactions were carried out under an atmosphere of argon using conventional Schlenk glass-ware and solvents were dried using established procedures and distilled under argon just prior to use. Analytical grade and deuterated solvents were purchased from Merck. PPh_2Cl and furfurylamine were purchased from Fluka and used as received. The starting materials $[MCl_2(cod)]$ (M = Pd, Pt, cod = 1,5-cyclooctadiene) [25,26] and $[Pt(CH_3)_2(cod)]$ [27] were prepared according to the literature procedures. Infrared spectra were recorded from KBr pellet in the range 4000–400 cm^{-1} on a Mattson 1000 ATI UNICAM FT-IR spectrometer. ^1H (400.1 MHz), ^{13}C NMR (100.6 MHz) and ^{31}P–{1H} NMR (162.0 MHz) spectra were recorded on a Bruker AV 400 spectrometer, with δ referenced to external TMS and 85% H_3PO_4, respectively. Elemental analysis was carried out on a Fisons EA 1108 CHNS-O instrument. Melting points were determined by Gallenkamp Model apparatus with open capillaries.

2.2. GC analysis

GC analyses were performed on a HP 6890N instrument equipped with a capillary column (5% biphenyl, 95% dimethylsiloxane; 30 m × 0.32 mm i.d. × 0.25 μm film thickness). The GC parameters for Suzuki coupling reactions were as follows: initial temperature, 50 °C; initial time, 1 min; solvent delay, 3.70 min; temperature ramp 1, 10 °C/min; final temperature, 150 °C; temperature ramp 2, 15 °C/min; final temperature, 250 °C; final time, 20.67 min; injector port temperature, 250 °C; detector temperature, 250 °C, injection volume, 2.0 μL; for Heck coupling reactions, initial temperature, 50 °C; initial time, 1 min; solvent delay, 3.53 min; temperature ramp, 13 °C/min; final temperature, 300 °C; final time, 40.46 min; injector port temperature, 250 °C; detector temperature, 250 °C, injection volume, 2.0 μL.

2.3. General procedure for the Suzuki coupling reaction

Aminophosphine- or bis(phosphino)amine-palladium(II) complexes (**1a**–**2a**, 0.01 mmol), aryl bromide (1.0 mmol), phenylboronic acid (1.5 mmol), Cs_2CO_3 (2 mmol) and dioxane (3 mL) were added to a Schlenk tube under argon atmosphere and the mixture was heated at 60 °C. After completion of the reaction, the mixture was cooled, extracted with ethyl acetate/hexane (1:5), filtered through a pad of silica gel with copious washing, concentrated and purified by flash chromatography on silica gel. The purity of the compounds was checked immediately by GC and NMR and yields are based on aryl bromide.

2.4. General procedure for the Heck coupling reaction

Aminophosphine- or bis(phosphino)amine-palladium(II) complexes (**1a**–**2a**, 0.01 mmol), aryl bromide (1.0 mmol), styrene (1.5 mmol), K_2CO_3 (2 mmol), DMF (3 mL) for **1a** and dioxane (3 mL) for **2a** were added to a Schlenk tube under argon atmosphere and the mixture was heated to 100 °C. After completion of the reaction, the mixture was cooled, extracted with ethyl acetate/hexane (1:5), filtered through a pad of silica gel with copious washing, concentrated and purified by flash chromatography on silica gel. The purity of the compounds was checked immediately by GC and NMR and yields are based on aryl bromide.

2.5. Synthesis and characterization of ligands and their complexes

2.5.1. Synthesis and characterization of ligands

*2.5.1.1. Furfuryl-(N-diphenylphosphino)amine, $[Ph_2PNHCH_2\text{-}C_4H_3O]$, (**1**).* Chlorodiphenylphosphine (0.237 g, 1.02 mmol) was added dropwise over a period of 15 min to a stirred solution of furfurylamine (0.099 g, 1.02 mmol) and triethylamine (0.104 g, 1.02 mmol) in thf (40 mL) at 0 °C. The mixture was then stirred at room temperature for 1 h and the white precipitate (triethylammonium chloride) was filtered under argon and the solvent was removed under reduced pressure. The residue was then washed with cold diethyl ether (2 × 10 mL) and dried *in vacuo* to produce a clear, white viscous oily compound **1** (yield: 0.261 g, 91.1%); ^1H NMR ($CDCl_3$, 400.1 MHz, Me_4Si): δ 7.45–7.48 (m, *o*-protons of phenyls, 4H), 7.36–7.41 (m, *m*- and *p*-protons of phenyls, 6H), 7.35 (d, **H**-5, 1H, ^3J 2.0 Hz), 6.30 (dd, **H**-4, 1H, ^3J 2.0 and 3.2), 6.11 (d, **H**-3, 1H, ^3J 3.2 Hz), 4.01 (dd, –C**H**$_2$–, 2H, ^3J 6.8 and 8.8 Hz), 2.38 (dt, –N**H**–, 1H, J 6.8 and 13.2 Hz); ^{13}C NMR ($CDCl_3$, 100.6 MHz, Me_4Si): δ 154.95 (d, **C**-2, $^3J(^{31}P–13C)$ 6.0 Hz), 141.71 (d, **C**-5), 140.95 ppm (d, *i*-carbons of phenyls, $^1J(^{31}P–13C)$ 12.1 Hz), 131.44 (d, *o*-carbons of phenyls, $^2J(^{31}P–13C)$ 19.0 Hz), 128.58 (s, *p*-carbons of phenyls), 128.30 (d, *m*-carbons of phenyls, $^3J(^{31}P–13C)$ 6.3 Hz), 110.26 (**C**-4), 106.27 (**C**-3), 43.09 (–**C**H$_2$–); assignment was based on the $^1H–13C$ HETCOR and $^1H–1H$ COSY spectra; ^{31}P–{1H} NMR ($CDCl_3$, 162.0 MHz, 85% H_3PO_4): δ 42.71 (s); selected IR (KBr pellet, in cm^{-1}): ν(P–N) 804, ν(P–Ph) 1434, ν(N–H) 3383; *Anal.* Calc. for $C_{17}H_{16}ONP$ (mw: 281.3 g/mol): C, 72.59; H, 5.73; N, 4.98. Found: C, 72.49; H, 5.64; N, 4.95%.

*2.5.1.2. Furfuryl-(N,N-bis(diphenylphosphino))amine, $[(Ph_2P)_2NCH_2\text{-}C_4H_3O]$, (**2**).* Chlorodiphenylphosphine (0.4734 g, 2.04 mmol) was added to a solution of furfurylamine (0.099 g, 1.02 mmol) and triethylamine (0.200 g, 2.04 mmol) in thf (50 mL) at 0 °C with vigorous stirring. The mixture was then stirred at room temperature for 2 h and the white precipitate (triethylammonium chloride) was filtered under argon and the solvent was removed under reduced pressure. The residue was then washed with cold diethyl ether (2 × 15 mL) and dried *in vacuo* to produce a yellow viscous oily compound **2** [28] (yield: 0.215 g, 88.8%). ^1H NMR (δ in ppm rel. to TMS, J Hz, in $CDCl_3$): δ 7.37–7.44 (*o*-protons of phenyls, 8H), 7.28–7.33 (m, *m* and *p*-protons of phenyls, 12H), 7.13 (br, **H**-5, 1H), 6.11 (br, **H**-4, 1H), 5.48 (br, **H**-3, 1H), 4.34 (t, –C**H**$_2$–, 2H, ^3J 8.6 Hz); ^{13}C NMR (δ in ppm rel. to TMS, J Hz, in $CDCl_3$): δ 153.50 (**C**-2), 141.34 (C-**5**), 139.02 ppm (d, *i*-carbons of phenyls, $^1J(^{31}P–13C)$ 5.94 Hz), 132.76 (t, *o*-carbons of phenyls, $^2J(^{31}P–13C)$ 11.1 Hz), 128.75 (s, *p*-carbons of phenyls), 128.10 (d, *m*-carbons of phenyls, $^3J(^{31}P–13C)$ 3.0 Hz), 110.28 (C-**4**), 108.24 (C-**3**), 47.83 (–**C**H$_2$–); assignment was based on the $^1H–13C$ HETCOR and $^1H–1H$ COSY spectra; ^{31}P NMR (δ in ppm rel. to H_3PO_4, in $CDCl_3$): δ 62.54 (s); selected IR (KBr pellet, in cm^{-1}): ν(P–N–P) 921, ν(P–Ph) 1434; *Anal.* Calc. for $C_{29}H_{25}ONP_2$ (mw: 465.5 g/mol): C, 74.83; H, 5.41; N, 3.01. Found: C, 74.72; H, 5.38; N, 3.00%.

2.5.2. Synthesis of metal [Pd(II), Pt(II)] complexes

*2.5.2.1. Synthesis of cis-dichlorobis(furfuryl-(N-diphenylphosphino)methylamine)palladium(II) (**1a**).* A solution of $[PdCl_2(cod)]$ (0.145 g, 0.51 mmol) and furfuryl-(*N*-diphenylphosphino)amine, **1**, (0.287 g, 1.02 mmol) in thf (25 mL) was stirred for 1.5 h at room temperature. The volume was concentrated in vacuum to ca. 1–2 mL and addition of diethyl ether (15 mL) gave **1a** as yellow solid which was collected by filtration and dried in vacuum (yield: 0.324 g, 85.9%, mp 195–197 °C). ^1H NMR ($CDCl_3$, 400.1 MHz, Me_4Si): δ 7.38–7.83 (8H, br, *o*-protons of phenyls), 7.38–7.83 (12H, m, *m*- and *p*-protons of phenyls), 7.23 (s, **H**-5, 2H), 6.21 (br, **H**-4, 2H), 6.11 (br, **H**-3, 2H), 4.36 (s, –N**H**–, 2H), 3.12 (br, –C**H**$_2$–, 4H); ^{13}C NMR ($CDCl_3$, 100.6 MHz, Me_4Si): δ 152.82 (**C**-2), 142.56

(**C**-5), 133.61 (*o*-carbons of phenyls), 130.89 (*p*-carbons of phenyls), 129.24 ppm (*i*-carbons of phenyls), 128.23 (*m*-carbons of phenyls), 112.45 (**C**-4), 105.34 (**C**-3), 43.09 (–**C**H_2–); assignment was based on the ^{1}H–13C HETCOR and ^{1}H–1H COSY spectra; ^{31}P–{1H} NMR ($CDCl_3$, 162.0 MHz, 85% H_3PO_4): δ 46.05 (s, NH–**P**–$(C_6H_5)_2$); selected IR (KBr pellet, in cm^{-1}): ν(P–N) 813, ν(P–Ph) 1437, ν(N–H) 3335; *Anal.* Calc. for $C_{34}H_{32}N_2O_2P_2PdCl_2$ (mw: 730.91 g/mol): C, 55.19; H, 4.36; N, 3.79. Found: C, 55.02; H, 4.29; N, 3.71%.

*2.5.2.2. Synthesis of cis-dichloro(furfuryl-2-(N,N -bis(diphenylphosphino))amine)palladium(II) (**2a**).* A solution of [$PdCl_2$(cod)] (0.291 g, 1.02 mmol) and furfuryl-(*N*,*N*-bis(diphenylphosphino))amine, **2**, (0.475 g, 1.02 mmol) in thf (25 mL) was stirred for 2 h at room temperature. The volume was concentrated in vacuum to ca. 1–2 mL and addition of diethyl ether (15 mL) gave **2a** as bright yellow solid which was collected by filtration and dried in vacuum (yield: 0.621 g, 94.8%, mp 229–231 °C). ^{1}H NMR (DMSO, 400.1 MHz, Me_4Si): δ 7.87 (dd, *o*-hydrogen of phenyls, 8H, ^3J 6.78 and 12.42 Hz), 7.66 (t, *p*-hydrogen of phenyls, 4H, ^3J 6.76), 7.55 (t, *m*-hydrogen of phenyls, 8H, ^3J 6.46), 7.02 (br, **H**-5, 1H), 6.12 (br, **H**-4, 1H), 5.81 (d, **H**-3, 1H, ^3J 3.52 Hz), 4.06 (t, –C**H**$_2$–, 2H, ^3J 11.80 Hz); ^{13}C NMR (δ in ppm rel. to TMS, *J* Hz, in $CDCl_3$): δ 147.06 (**C**-2), 143.17 (C-**5**), 133.62 (t, *o*-carbons of phenyls, $^2J(^{31}P–13C)$ 6.54 Hz), 133.27 (s, *p*-carbons of phenyls), 129.44 (d, *m*-carbons of phenyls, $^3J(^{31}P–13C)$ 6.04 Hz), 126.53 ppm (d, *i*-carbons of phenyls, $^1J(^{31}P–13C)$ 58.35 Hz), 111.32 (C-**4**), 110.90 (C-**3**), 44.01 (–**C**H_2–); assignment was based on the ^{1}H–13C HETCOR and ^{1}H–1H COSY spectra; ^{31}P–{1H} NMR (DMSO, 162.0 MHz, 85% H_3PO_4): δ 33.17 (s, N–(**P**–$(C_6H_5)_2)_2$); selected IR (KBr pellet, in cm^{-1}): ν(P–N–P) 824, ν(P–Ph) 1436; *Anal.* Calc. for $C_{29}H_{25}ONP_2PdCl_2$ (mw: 642.79 g/mol): C, 54.19; H, 3.92; N, 2.18. Found: C, 54.07; H, 3.88; N, 2.15%.

*2.5.2.3. Synthesis of cis-dichlorobis(furfuryl-(N-diphenylphosphino)amine)platinum(II) (**1b**).* A solution of [$PtCl_2$(cod)] (0.191 g, 0.51 mmol) and furfuryl-(*N*-diphenylphosphino)amine, **1**, (0.287 g, 1.02 mmol) in thf (25 mL) was stirred for 1.5 h. The volume was concentrated in vacuum to ca. 1–2 mL and addition of diethyl ether (15 mL) gave **1b** as white solid which was collected by filtration and dried in vacuum (yield: 0.391 g, 92.7%, mp 96–98 °C). ^{1}H NMR ($CDCl_3$, 400.1 MHz, Me_4Si): δ 7.55 (dd, *o*-hydrogen of phenyls, 8H, ^3J 8.00 and 12.00 Hz), 7.45 (t, *p*-hydrogen of phenyls, 4H, ^3J 7.00), 7.31 (t, *m*-hydrogen of phenyls, 8H, ^3J 8.16), 7.24 (d, **H**-5, 2H, ^3J 3.40 Hz), 6.21 (dd, **H**-4, 2H, ^3J 2.52 and 3.40), 5.89 (d, **H**-3, 2H, ^3J 2.52 Hz), 4.30 (m, –N**H**–, 2H); 3.52 (br, –C**H**$_2$–, 4H); ^{13}C NMR (δ in ppm rel. to TMS, *J* Hz, in $CDCl_3$): δ 151.77 (d, **C**-2, $^3J(^{31}P–13C)$ 4.00 Hz), 141.98 (**C**-5), 133.37 (t, *o*-carbons of phenyls, $^2J(^{31}P–13C)$ 6.04 Hz), 131.47 (s, *p*-carbons of phenyls), 129.65 ppm (d, *i*-carbons of phenyls, $^1J(^{31}P–13C)$ 75.45 Hz), 128.34 (d, *m*-carbons of phenyls, $^3J(^{31}P–13C)$ 5.53 Hz), 110.28 (**C**-4), 107.04 (**C**-3), 40.09 (–**C**H_2–); assignment was based on the ^{1}H–13C HETCOR and ^{1}H–1H COSY spectra; ^{31}P–{1H} NMR ($CDCl_3$, 162.0 MHz, 85% H_3PO_4): δ 34.45, (s, NH–**P**–$(C_6H_5)_2$, $^1J_{(PtP)}$: 3946.26 Hz); selected IR (KBr pellet, in cm^{-1}): ν(P–N) 811, ν(P–Ph) 1436, ν(N–H) 3292; *Anal.* Calc. for $C_{34}H_{32}N_2O_2P_2PtCl_2$ (mw: 828.5726 g/mol): C, 49.29; H, 3.89; N, 3.38. Found: C, 49.12; H, 3.85; N, 3.35%.

*2.5.2.4. Synthesis of cis-dichloro(furfuryl-(N,N-bis(diphenylphosphino))amine)platinum (**2b**).* A solution of [$PtCl_2$(cod)] (0.382 g, 1.02 mmol) and furfuryl-(*N*,*N*-bis(diphenylphosphino))amine, **2**, (0.475 g, 1.02 mmol) in thf (25 mL) was stirred for 2 h. The volume was concentrated in vacuum to ca. 1–2 mL and addition of diethyl ether (15 mL) gave **2b** as pale green which was collected by filtration and dried in vacuum (yield: 0.680 g, 91.2%, mp 201–203 °C). ^{1}H NMR (DMSO, 400.1 MHz, Me_4Si): δ 7.84 (dd, *o*-hydrogen of phenyls, 8H, ^3J 7.50 and 13.50 Hz), 7.64 (t, *p*-hydrogen of phenyls, 4H, ^3J 3.67), 7.53 (t, *m*-hydrogen of phenyls, 8H, ^3J 7.26), 7.01 (br, **H**-5, 1H), 6.11 (br, **H**-4, 1H), 5.79 (d, **H**-3, 1H, ^3J 2.89 Hz), 3.95 (t, –C**H**$_2$–, 2H, ^3J 11.90 Hz); ^{13}C NMR (δ in ppm rel. to TMS, *J* Hz, in $CDCl_3$): δ 147.49 (**C**-2), 143.14 (C-**5**), 133.47 (t, *o*-carbons of phenyls, $^2J(^{31}P–13C)$ 7.65 Hz), 133.07 (s, *p*-carbons of phenyls), 129.22 (d, *m*-carbons of phenyls, $^3J(^{31}P–13C)$ 6.25 Hz), 134.45 ppm (d, *i*-carbons of phenyls, $^1J(^{31}P–13C)$ 66.80 Hz), 110.80 (C-**4**), 110.78 (C-**3**), 44.82 (–**C**H_2–); assignment was based on the ^{1}H–13C HETCOR and ^{1}H–1H COSY spectra; ^{31}P–{1H} NMR (DMSO, 162.0 MHz, 85% H_3PO_4): δ 19.32, (s, N–(**P**–$(C_6H_5)_2)_2$, $^1J_{(PtP)}$: 3300.84 Hz); selected IR (KBr pellet, in cm^{-1}): ν(P–N–P) 809, ν(P–Ph) 1436; *Anal.* Calc. for $C_{29}H_{25}ONP_2PtCl_2$ (mw: 731.46 g/mol): C, 47.62; H, 3.45; N, 1.92. Found: C, 47.54; H, 3.38; N, 1.90%.

*2.5.2.5. Synthesis of cis-dimethylbis(furfuryl-(N-diphenylphosphino) amine)platinum (**1c**).* A solution of [$Pt(CH_3)_2$(cod)] (0.100 g, 0.25 mmol) and furfuryl-(*N*-diphenylphosphino)amine, **1**, (0.150 g, 0.51 mmol) in thf (25 mL) was stirred for 1 h. The volume was concentrated in vacuum to ca. 1–2 mL and addition of diethyl ether (15 mL) gave **1c** as white solid which was collected by filtration and dried in vacuum (yield: 0.190 g, 87.5%, mp 64–65 °C). ^{1}H NMR ($CDCl_3$, 400.1 MHz, Me_4Si): δ 7.52 (dd, *o*-hydrogen of phenyls, 8H, ^3J 8.00 and 12.40 Hz), 7.44 (t, *p*-hydrogen of phenyls, 4H, ^3J 7.20), 7.32 (t, *m*-hydrogen of phenyls, 8H, ^3J 8.16), 7.20 (d, **H**-5, 2H, ^3J 3.20 Hz), 6.22 (dd, **H**-4, 2H, ^3J 2.46 and 3.20), 5.86 (d, **H**-3, 2H, ^3J 2.46 Hz), 4.31 (m, –N**H**–, 2H); 3.52 (br, –C**H**$_2$–, 4H), 1.32 (m, –C**H**$_3$, 6H, $^2J_{(PtH)}$ 63.50 Hz); ^{13}C NMR (δ in ppm rel. to TMS, *J* Hz, in $CDCl_3$): δ 151.79 (d, **C**-2, $^3J(^{31}P–13C)$ 4.00 Hz), 141.99 (**C**-5), 133.37 (t, *o*-carbons of phenyls, $^2J(^{31}P–13C)$ 6.04 Hz), 131.47 (s, *p*-carbons of phenyls), 129.65 ppm (d, *i*-carbons of phenyls, $^1J(^{31}P–13C)$ 74.07 Hz), 128.34 (d, *m*-carbons of phenyls, $^3J(^{31}P–13C)$ 5.53 Hz), 111.02 (**C**-4), 107.78 (**C**-3), 40.09 (–**C**H_2–), 28.78 (–**C**H_3); assignment was based on the ^{1}H–13C HETCOR and ^{1}H–1H COSY spectra; ^{31}P–{1H} NMR ($CDCl_3$, 162.0 MHz, 85% H_3PO_4): δ 60.07 (s, NH–**P**–$(C_6H_5)_2$, $^1J_{(PtP)}$: 2042.49 Hz); selected IR (KBr pellet, in cm^{-1}): ν(P–N) 854, ν(P–Ph) 1435, ν(N–H) 3227; *Anal.* Calc. for $C_{34}H_{32}N_2O_2P_2Pt(CH_3)_2$ (mw: 787.736 g/mol): C, 54.89; H, 4.86; N, 3.56. Found: C, 54.76; H, 4.80; N, 3.53%.

*2.5.2.6. Synthesis of cis-dimethyl(furfuryl-(N,N-bis(diphenylphosphino))amine)platinum (**2c**).* A solution of [$Pt(CH_3)_2$(cod)] (0.340 g, 1.02 mmol) and furfuryl-(*N*,*N*-bis(diphenylphosphino))amine, **2**, (0.475 g, 1.02 mmol) in thf (25 mL) was stirred for 2 h. The volume was concentrated in vacuum to ca. 1–2 mL and addition of diethyl ether (15 mL) gave **2c** as white solid which was collected by filtration and dried in vacuum (yield: 0.622 g, 88.4%, mp 132–134 °C). ^{1}H NMR (DMSO, 400.1 MHz, Me_4Si): ^{1}H NMR (δ in ppm rel. to TMS, *J* Hz, in $CDCl_3$): δ 7.86 (dd, *o*-hydrogen of phenyls, 8H, ^3J 6.40 and 12.26 Hz), 7.66 (t, *p*-hydrogen of phenyls, 4H, ^3J 3.54), 7.57 (t, *m*-hydrogen of phenyls, 8H, ^3J 7.00), 7.01 (br, **H**-5, 1H), 6.11 (br, **H**-4, 1H), 5.81 (d, **H**-3, 1H, ^3J 2.89 Hz), 3.95 (t, –C**H**$_2$–, 2H, ^3J 11.90 Hz), 0.95 (m, –C**H**$_3$, 6H, $^2J_{(PtH)}$ 67.90 Hz); ^{13}C NMR (δ in ppm rel. to TMS, *J* Hz, in $CDCl_3$): δ 148.67 (**C**-2), 143.14 (C-**5**), 133.58 (t, *o*-carbons of phenyls, $^2J(^{31}P–13C)$ 6.54 Hz), 133.27 (s, *p*-carbons of phenyls), 129.42 (d, *m*-carbons of phenyls, $^3J(^{31}P–13C)$ 10.56 Hz), 126.47 ppm (d, *i*-carbons of phenyls, $^1J(^{31}P–13C)$ 58.35 Hz), 111.26 (C-**4**), 110.87 (C-**3**), 43.87 (–**C**H_2–), 29.28 (–**C**H_3); assignment was based on the ^{1}H–13C HETCOR and ^{1}H–1H COSY spectra; ^{31}P–{1H} NMR (DMSO, 162.0 MHz, 85% H_3PO_4): δ 50.59, (s, N–(**P**–$(C_6H_5)_2)_2$, $J_{(PtP)}$: 1546.26 Hz); selected IR (KBr pellet, in cm^{-1}): ν(P–N–P) 816, ν(P–Ph) 1434; *Anal.* Calc. for $C_{29}H_{25}ONP_2Pt(CH_3)_2$ (mw: 731.46 g/mol): C, 53.91; H, 4.52; N, 2.03. Found: C, 53.77; H, 4.48; N, 2.00%.

2.5.3. X-ray diffraction analysis

For the crystal structure determination, the single-crystals of the complexes **2a** and **2b** were used for data collection on a four-circle Rigaku R-AXIS RAPID-S diffractometer (equipped with a two-dimensional area IP detector). The graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and oscillation scans technique with $\Delta\omega = 5°$ for one image were used for data collection. The lattice parameters were determined by the least-squares methods on the basis of all reflections with $F^2 > 2\sigma(F^2)$. H atoms were positioned geometrically and refined using a riding model. Integration of the intensities, correction for Lorentz and polarization effects and cell refinement was performed using CrystalClear software [29]. The structures were solved by direct methods using SHELXS-97 and refined by a full-matrix least-squares procedure using the program SHELXL-97 [30]. The final difference Fourier maps showed no peaks of chemical significance. Details of the crystal parameters, data collection and refinement are summarized in Table 1.

3. Results and discussion

3.1. Synthesis and characterization

Although aminolysis of chlorophosphines is an efficient method for preparing $R_2PN(H)R'$ or $(R_2P)_2NR'$ it has not widely been exploited yet, in part possibly because of the associated instability of the P–N bonds in these ligands [31–33]. Furfuryl-2-(*N*-diphenylphosphino)amine, **1** and furfuryl-2-(*N*,*N*-bis(diphenylphosphino) amine), **2** were prepared from the commercially available starting materials furfurylamine and 1 or 2 equivalents of Ph_2PCl in the presence of triethylamine by aminolysis [34–37] in thf at 0 °C, respectively (Scheme 1). Compounds **1** and **2** were fully characterized by multinuclear NMR, infrared spectroscopy and microanalysis. All the compounds gave reasonable microanalyses results. The $^{31}P–\{^1H\}$ NMR spectra of **1** and **2** showed single resonances at δ(P) 42.71 and 62.54 ppm, respectively, similar to those found for closely related compounds [38–40]. Compounds **1** and **2** are not stable and decompose rapidly on exposure to air or moisture. When the reactions were monitored by ^{31}P NMR spectroscopy, the formation of $P(O)Ph_2PPh_2$ was observed, as indicated by signals at δ 35.20 (d) ppm and δ −25.10 (d) ppm, {^1J(PP) 224 Hz}[41–43]. In the ^1H NMR spectrum, the NH resonance of **1** is observed as slightly broad doublet of triplets at 2.38 ppm due to the multiple coupling of $^3J_{(CH_2NH)}$ and $^2J_{(NHP)}$ and was confirmed by H/D exchange experiments. In addition, the methylene groups give doublet of doublet at 4.01 ppm (^3J 6.80 and 8.80 Hz) and triplet at 4.34 ppm (^3J 8.60 Hz) for **1** and **2**, respectively. Furthermore, characteristic $J(^{31}P–^{13}C)$ coupling constants of the carbons of the phenyl rings are observed in the ^{13}C NMR spectra (including *i*-, *o*-, *m*-, *p*-carbons of phenyl rings, for details see Section 2), which are consistent with the literature values [44,45].

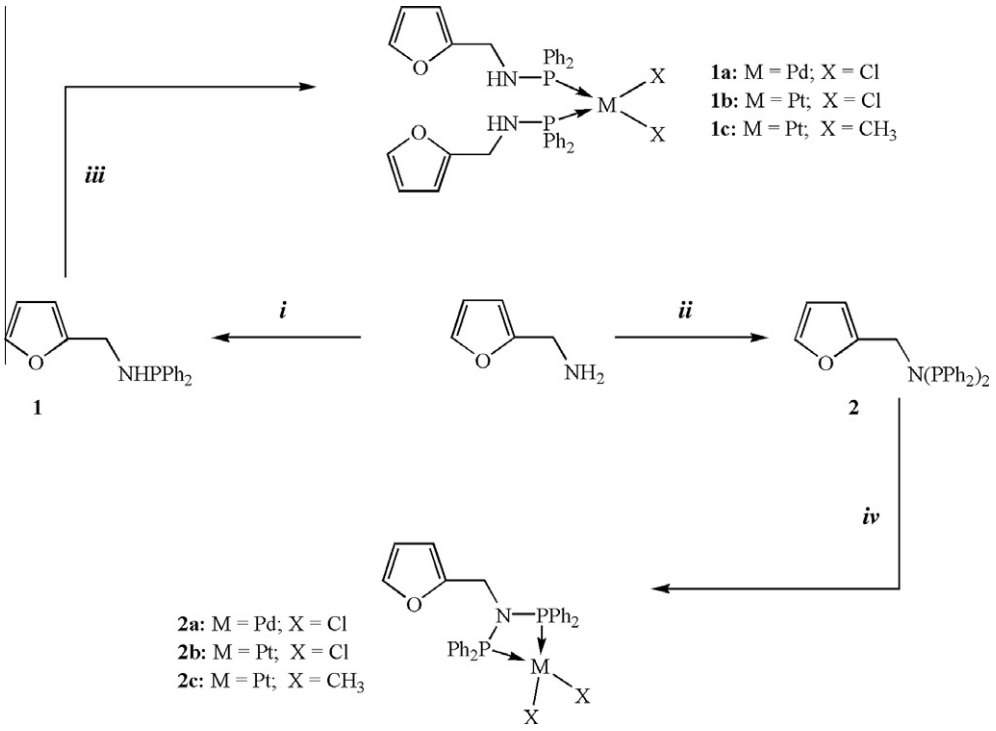
The coordination chemistry of the ligands Ph_2PNHCH_2-C_4H_3O, **1** and $(Ph_2P)_2NCH_2$-C_4H_3O, **2** was studied by forming their palladium and platinum complexes. Reaction of **1** or **2** with $[Pd(cod)Cl_2]$ (cod = 1,5-cyclooctadiene) give the corresponding Pd(II) complexes **1a** and **2a** in high yields (ca. 90%). Both of the isolated dichloropalladium(II) complexes **1a** and **2a** were found to have the *cis*-configration, characteristic of phosphines having mutually *cis*-arrangement [46–49] (Scheme 1). In the $^{31}P–\{^1H\}$ NMR spectrum, each of **1a** and **2a** gives one signal at 46.05 and 33.17 ppm, respectively, which are within the expected range of other reported structurally similar complexes [50–52]. The $^{13}C–\{^1H\}$ NMR spectrum displays well-resolved signals for the phenyls carbons [53]. Furthermore, ^1H NMR spectral data of the complexes **1a** and **2a** are consistent with the structures proposed and the compositions of the two complexes have been confirmed by elemental analysis. In the IR spectra, one observes very strong absorption bands at ca. 813 for **1a** and 824 cm^{-1} for **2a** due to the ν(P–N) stretching. In addition, single crystal of $[Pd((Ph_2P)_2NCH_2$-$C_4H_3O)Cl_2]$, **2a** suitable for X-ray diffraction study was obtained by slow diffusion of diethyl ether into solution of the compound in dichloromethane.

The reaction of $[Pt(cod)X_2]$ (cod = 1,5-cyclooctadiene; X = Cl, CH_3) with 2 equivalents of **1** affords the formation of complexes $[Pt(Ph_2PNHCH_2$-$C_4H_3O)_2X_2]$, (X = Cl **1b**, X = CH_3 **1c**), in high yields as the main products. In both complexes, **1** binds the metal center as monodentate ligand. The formation of compounds **1b** and **1c** was followed by recording the $^{31}P–\{^1H\}$ NMR spectra giving single resonances at δ 34.45 and 60.07 ppm, respectively, consistent with the structures of the complexes [54]. The complexes **1b** and **1c** show large $^1J_{PtP}$ coupling 3946 and 2042 Hz, respectively, which are characteristic of phosphines having mutually *cis*-arrangement [55] (Fig. 1). ^1H NMR spectral data of **1b** and **1c** are consistent with the structures proposed. Furthermore, in the $^{13}C–\{^1H\}$ NMR spectra of **1b** and **1c**, $J(^{31}P–^{13}C)$ coupling constants are measured for the carbons of the phenyl rings and they are consistent with the literature values [56,57]. The IR spectra of **1b** and **1c** show very strong absorption bands at ca. 811 and 854 cm^{-1}, respectively, due to ν(PN) stretching. PN stretching frequencies are shifted to lower values compared to that of the free molecule (804 cm^{-1} for **1**). The compositions of two complexes were also confirmed by elemental analysis.

In the reaction of $[Pt(cod)X_2]$ (cod = 1,5-cyclooctadiene; X = Cl, CH_3) with 1 equivalent of **2** in thf solution, cod is replaced by the

Table 1
Details of the crystal parameters, data collection and refinement for complexes **2a** and **2b**.

Crystal data	**2a**	**2b**
Empirical formula	$[C_{29}H_{25}NP_2Cl_2Pd]\cdot CH_2Cl_2$	$[C_{29}H_{25}NP_2Cl_2Pt]\cdot CH_2Cl_2$
Formula weight	727.7	816.4
T (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions		
a (Å)	13.2262(2)	13.2659(4)
b (Å)	12.4866(3)	12.5326(2)
c (Å)	19.1989(4)	19.2205(6)
α (°)	90	90
β (°)	101.06(3)	101.31(3)
γ (°)	90	90
V (Å^3)	3111.8(1)	3133.5(2)
Z	4	4
Density (calculated) (Mg/m^3)	1.55	1.73
Absorption coefficient (mm^{-1})	1.068	4.946
F(0 0 0)	1464	1592
Crystal	block; pale green	block; pale green
Crystal size (mm^3)	0.13 × 0.14 × 0.21	0.10 × 0.13 × 0.21
θ-Range for data collection (°)	2.1–26.5	2.3–26.4
Index ranges	$-16 \leqslant h \leqslant 16$, $-15 \leqslant k \leqslant 15$, $-23 \leqslant l \leqslant 23$	$-16 \leqslant h \leqslant 16$, $-15 \leqslant k \leqslant 15$, $-24 \leqslant l \leqslant 22$
Reflections collected	67 151	53 382
Independent reflections (R_{int})	6401 (0.086)	6420 (0.075)
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/parameters	4280/352	5197/353
Goodness-of-fit (GOF) on F^2	1.034	1.103
Final R indices [$F^2 > 2\sigma(F^2)$]	R_1 = 0.065, wR_2 = 0.122	R_1 = 0.041, wR_2 = 0.093
R indices (all data)	R_1 = 0.109, wR_2 = 0.137	R_1 = 0.055, wR_2 = 0.107
Extinction coefficient	0.00	0.0009
Largest difference in peak and hole (e Å^{-3})	0.604 and −0.792	1.938 and −0.946



Scheme 1. Synthesis of furfuryl-2-(*N*-diphenylphosphino)amine, **1** and furfuryl-2-(*N*,*N*-bis(diphenylphosphino)amine), **2** and their metal complexes (i) 1 equivalent Ph_2PCl, 1 equivalent Et_3N, thf; (ii) 2 equivalents Ph_2PCl, 2 equivalents Et_3N, thf; (iii) 1/2 equivalents $[MCl_2(cod)]$: (M = Pd, **1a** or Pt, **1b**) or $[Pt(CH_3)_2(cod)]$: **1c**, thf; (iv) 1 equivalent $[MCl_2(cod)]$: (M = Pd, **2a** or Pt, **2b**) or $[Pt(CH_3)_2(cod)]$: **2c**, thf.

furfuryl-2-(*N*,*N*-bis(diphenylphosphino)amine), **2**, as bidentate ligand yielding the respective $[Pt((Ph_2P)_2NCH_2\text{-}C_4H_3O)X_2]$, (X = Cl **2b**, X = CH_3 **2c**), complexes **2b** and **2c**, respectively. $^{31}P\text{–}\{^1H\}$ NMR spectra of complexes **2b** and **2c** show singlets at δ 19.32 and 50.59 ppm, respectively [58–60]. The large $^1J(^{195}Pt\text{–}^{31}P)$ coupling constants of 3300.84 Hz for **2b** and 1546.26 Hz for **2c** are indicative of a *cis*-arrangement of phosphines around a platinum(II) centers [61–63] (Fig. 2). As expected, the $^1J(^{195}Pt\text{–}^{31}P)$ coupling constant value of **2c** is much lower than that of **2b** [62]. The IR spectra show adsorption bands at 809 for ν(PNP) and 1436 cm^{-1} for ν(PPh) in **2b** and at 816 for ν(PNP) and 1434 cm^{-1} for ν(PPh) in **2c**. Characteristic J_{PC} coupling constants were observed in the ^{13}C NMR spectra, which are consistent with the literature values [63]. ^1H NMR spectra of the compounds, **2b** and **2c**, are consistent with the structural compositions. These complexes could be isolated as analytically pure solid materials and characterized by elemental analysis. Furthermore, the crystal structure of complex $[Pd((Ph_2P)_2NCH_2\text{-}C_4H_3O)Cl_2]$, **2b** was further confirmed by single crystal X-ray diffraction.

Single crystal X-ray diffraction studies of compounds $[M((Ph_2P)_2NCH_2\text{-}C_4H_3O)Cl_2]$, M = Pd (**2a**), Pt (**2b**) were undertaken to elucidate the coordination sphere of palladium(II) and platinium(II) atoms. The molecular structures of palladium(II) and platinum(II) complexes with the atomic numbering scheme are shown in Fig. 3 and selected bond lengths and angles are given in Table 2. Both complexes crystallize in the monoclinic space group $P2_1/n$ containing four formula units and the disordered solvent CH_2Cl_2 in the unit cell. Structures of complexes **2a** and **2b** in the solid state are given Fig. 3. The key bond lengths and angles of complexes **2a** and **2b** in the solid state are very similar (see Table 2).

The coordination environments of palladium(II) and platinum(II) ions are distorted square-planar, formed by two P atoms and two Cl atoms. The Pd and Pt atoms are at distance of 0.0375(5) and 0.0239(4) Å, respectively, from the basal plane defined by the atoms Cl(1), Cl(2), P(1), P(2). The MP_2Cl_2 squares adopt a *cis*-configuration, which is consistent with preparation method. The angles around Pd and Pt atoms (Table 2) deviate significantly from the values for a regular square-planar coordination mode. The formation of four-membered chelate ring imposes a considerable distortion around the palladium and platinum atoms. The P(1)–Pt–P(2) angle [72.8(2)°] is acute, whereas the Cl(1)–Pt–Cl(2) angle is obtuse by more than 3° [93.8(2)°] (see Table 2 for **2a**). The corresponding M–P and M–Cl bond distances (Table 2) are almost equal to our previously reported isomorphous $[M\{(Ph_2P)_2N\text{-}C_6H_4\text{-}2\text{-}CH(CH_3)_2\}Cl_2]$, where M = Pd and Pt)] [58] structures, but *d*(Pd–P) bond distances are shorter than the values of complex $[PdLCl_2)]$ [64] (the molecule has crystallographic *m* symmetry, with *d*(Pd–P) = 2.2572(11) and *d*(Pd–Cl) = 2.3536 Å).

Analysis of the geometric parameters indicates that the coordination around P atoms are distorted tetrahedral in each of two structures, with the angles varying from 93.3(2)° to 119.8(2)°. The spatial requirements of the substituted moieties and the presence of the chelate ring have an influence on the angular deformations of these tetrahedrons. Especially, the different orientations of phenyl rings do not permit the intermolecular $\pi\cdots\pi$ stacking interactions, but the C–H$\cdots\pi$ (*furan*) and C–H$\cdots$Cl interactions help to consolidate the packing (details in Table. 3), which are similar to reported $[Pt(CH_3)Cl(C_{25}H_{23}N_2P)_2]$ structure [65].

3.2. The Suzuki coupling reactions

The palladium-catalyzed cross-coupling of aryl halides with aryl boronic acids (Suzuki reaction) is one of the most powerful and popular methods for the construction of unsymmetrical biaryls, which are widely used for the synthesis of valuable organic compounds such as pharmaceuticals and agrochemicals [66]. Although several other cross-coupling reactions are available to produce biaryls, the Suzuki reaction has widely been used over the course of the last few years, since it has several advantages

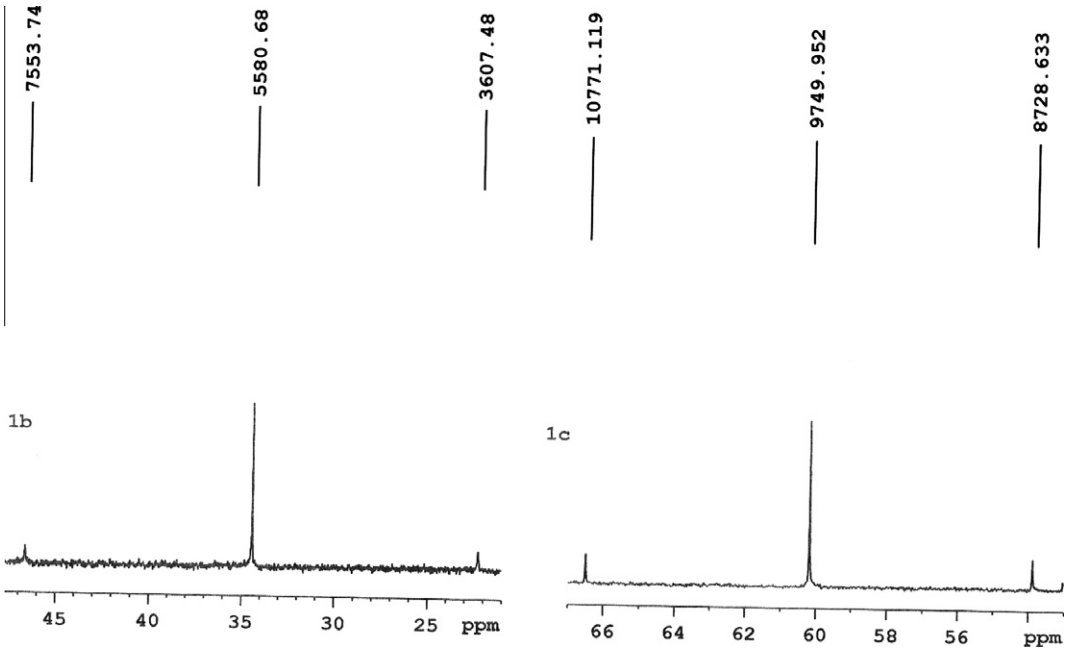


Fig. 1. The $^{31}P-\{^{1}H\}$ NMR spectra of complexes; **1b**: *cis*-dichlorobis(furfuryl-(*N*-diphenylphosphino)amine)platinum(II), **1c**: *cis*-dimethylbis(furfuryl-(*N*-diphenylphosphino)-amine)platinum(II).

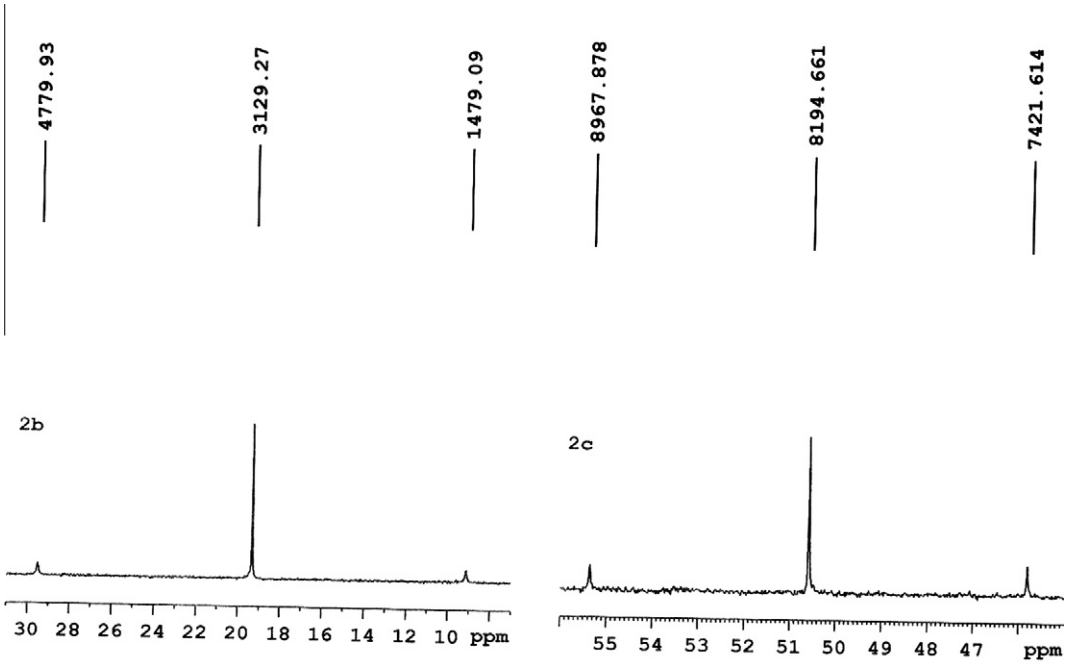


Fig. 2. The $^{31}P-\{^{1}H\}$ NMR spectra of complexes; **2b**: *cis*-dichloro(furfuryl-(*N*,*N*-bis(diphenylphosphino))amine)platinum(II). **2c**: *cis*-dimethyl(furfuryl-(*N*,*N*-bis(diphenyl-phos-phino))amine)platinum(II).

compared with other available methods. One particular advantage of this reaction is that it can be performed under mild conditions in aqueous solutions that tolerates a broad range of functional groups [67]. Boronic acids are generally nontoxic, stable, and environmentally benign, and the boron containing by-products can easily be removed from the reaction medium after the reaction [68,69].

The palladium complexes **1a** and **2a** were tested as catalysts in the Suzuki reaction of aryl bromides with boronic acid [70]. Following optimization experiments we found that the use of 0.01 mmol the palladium complexes (**1a**, **2a**) with Cs_2CO_3 as the base at 60 °C in dioxane appeared to be best. We initially tested the catalytic activity of the complexes (**1a**, **2a**) for the coupling of *p*-bromoacetophenone with phenylboronic acid and the control experiments showed that the coupling reaction does not occur in the absence of the catalyst. Under these conditions, *p*-bromoacetophenone, *p*-bromobenzaldehyde, *p*-bromobenzene, *p*-bromoanisole and *p*-bromotoluene react cleanly with phenylboronic acid in high yields (Table 4).

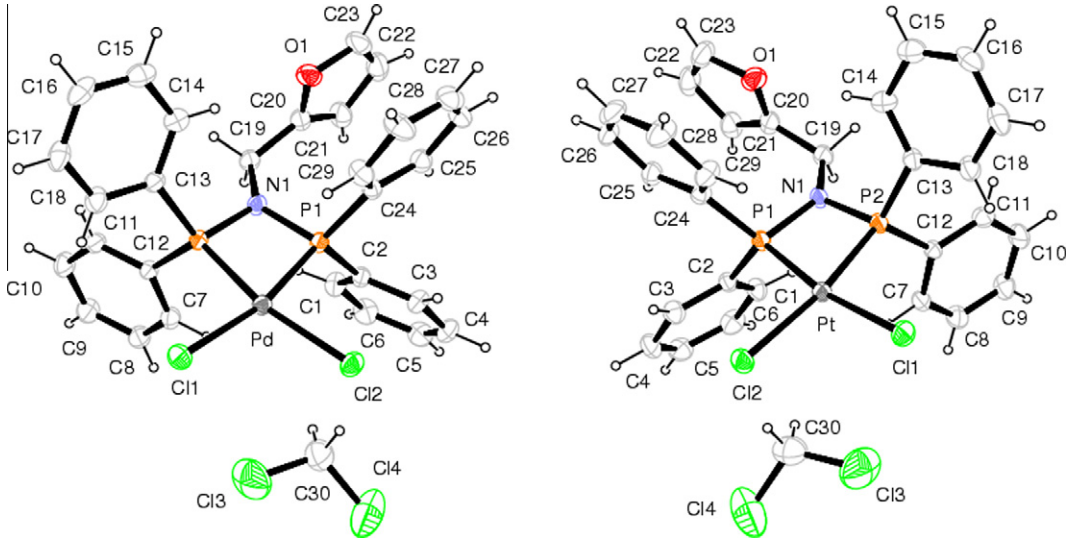


Fig. 3. Structures of palladium(II) (**2a**) and platinum(II) (**2b**) complexes. Note that both molecules in structures **2a** and **2b** are asymmetric.

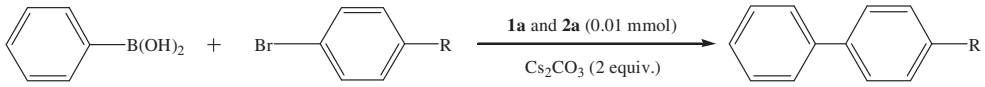
Table 2
Selected bond lengths (Å), bond and torsion angles (°) for the structures of asymmetric **2a** and **2b** complexes (M = Pd and Pt, respectively).

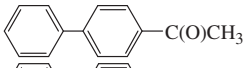
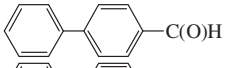
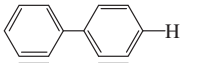
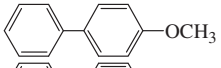
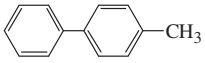
	2a	**2b**		**2a**	**2b**
M–CL(2)	2.357(2)	2.357(2)	M–P(1)	2.214(2)	2.203(2)
M–P(2)	2.208(3)	2.203(2)	M–CL(1)	2.354(2)	2.349(2)
P(1)–N(1)	1.702(4)	1.708(6)	P(1)–C(2)	1.789(6)	1.805(6)
P(1)–C(24)	1.798(6)	1.804(5)	P(2)–N(1)	1.689(5)	1.699(6)
P(2)–C(13)	1.791(6)	1.789(6)	P(2)–C(12)	1.800(6)	1.792(7)
P(1)···P(2)	2.608(4)	2.616(4)			
P(1)–M–CL(2)	93.8(1)	95.9(1)	P(1)–M–P(2)	72.3(1)	72.8(1)
P(1)–M–CL(1)	167.3(1)	169.7(1)	CL(2)–M–P(2)	166.1(1)	168.7(1)
CL(2)–M–CL(1)	98.2(1)	93.8(1)	P(2)–M–CL(1)	95.7(1)	97.5(1)
M–P(1)–N(1)	93.3(2)	93.3(2)	M–P(1)–C(24)	115.5(2)	116.1(3)
M–P(1)–C(2)	117.9(2)	118.2(3)	N(1)–P(1)–C(24)	111.0(3)	111.4(3)
N(1)–P(1)–C(2)	111.1(3)	110.1(3)	C(24)–P(1)–C(2)	107.4(3)	107.0(4)
M–P(2)–N(1)	93.8(2)	93.6(2)	M–P(2)–C(12)	119.8(2)	119.2(3)
Torsion angles (°)					
CL(2)–Pd–P(1)–N(1)		178.4	CL(2)–Pd–P(1)–C(24)		−66.5
CL(2)–Pd–P(1)–C(2)		62.4	P(2)–Pd–P(1)–N(1)		−0.7
P(1)–Pd–P(2)–N(1)		0.7	P(2)–Pd–P(1)–C(24)		114.5
P(1)–PD–P(2)–C(12)		112.8			
CL(2)–Pt–P(1)–N(1)		−178.1	CL(2)–Pt–P(1)–C(24)		66.1
CL(2)–Pt–P(1)–C(2)		−63.2	P(2)–Pt–P(1)–N(1)		0.9
P(1)–Pt–P(2)–N(1)		−0.9	P(2)–Pt–P(1)–C(24)		−115.0
P(1)–Pt–P(2)–C(12)		−112.5			

Table 3
Hydrogen-bond geometry (Å, °). *Cg*(1) is the centroid of the furan ring.

D–H···A	*D*–H	H···A	*D*···A	<*D*–H···A
2a				
C(19)–H(19A)···*Cg*(1)^{i}	0.97	2.76	3.665(7)	155
Symmetry codes: (i) 1 − *x*, −*y*, 1 − *z*				
2a				
C8–H8···Cl(1)^{i}	0.93	2.79	3.558(6)	140
C10–H10···Cl(2)^{ii}	0.93	2.79	3.634(6)	151
C30–H30B···Cl(1)^{i}	0.97	2.78	3.647(10)	149
Symmetry codes: (i) 3/2 − *x*, −1/2 + *y*, 1/2 − *z*; (ii) 1/2 + *x*, 1/2 − *y*, 1/2 + *z*				
2b				
C(19)–H(19A)···*Cg*(1)^{i}	0.97	2.76	3.658(9)	153
Symmetry codes: (i) 1 − *x*, 1 − *y*, −*z*				
2b				
C(8)–H(8)···Cl(1)^{i}	0.93	2.82	3.579(8)	140
C(10)–H(10)···Cl(2)^{ii}	0.93	2.80	3.656(8)	153
C(30)–H(30B)···Cl(1)^{i}	0.97	2.81	3.654(13)	146
Symmetry codes: (i) 1/2 − *x*, 1/2 + *y*, 1/2 − *z*; (ii) −1/2 + *x*, 1/2 − *y*, −1/2 + *z*				

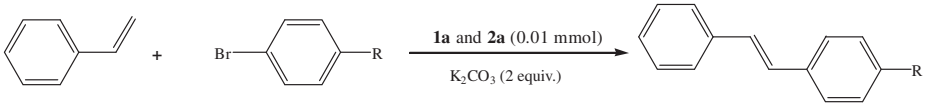
Table 4
The Suzuki coupling reactions of aryl bromides with phenylboronic acid.

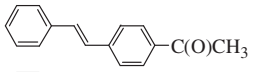
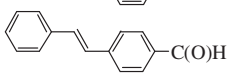
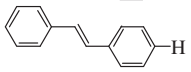
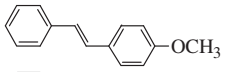
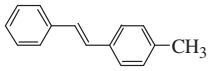


Entry	R	Catalyst	Product	Time	Conversion (%)	Yield (%)	TOF (h^{-1})
1	4-$CH_3C(O)$–	**1a**		10 min	97.2	96.1	577
2		**2a**		10 min	99.9	98.7	592
3	4-CH(O)–	**1a**		10 min	97.7	96.0	576
4		**2a**		10 min	99.6	98.2	598
5	4-H	**1a**		30 min	86.4	84.3	169
6		**2a**		30 min	89.9	88.0	176
7	4-CH_3O–	**1a**		1 h	66.3	60.7	61
8		**2a**		1 h	73.1	65.4	65
9	4-CH_3–	**1a**		1 h	60.7	53.9	54
10		**2a**		1 h	65.1	58.5	59

Reaction conditions: 1.0 mmol of *p*-R-C_6H_4Br aryl bromide, 1.5 mmol of phenylboronic acid, 2.0 mmol Cs_2CO_3, 1.0 mmol cat., dioxane 3.0 (mL). Purity of compounds was checked by NMR and yields are based on arylbromide. All reactions were monitored by GC; 60 °C. for **1a** and **2a**. TOF = (mol product/mol cat.) × h^{-1}.

Table 5
The Heck coupling reactions of aryl bromides with styrene.



Entry	R	Catalyst	Product	Time	Conversion (%)	Yield (%)	TOF (h^{-1})
1	4-$CH_3C(O)$–	**1a**		15 min	95.2	93.9	376
2		**2a**		15 min	97.2	96.4	386
3	4-CH(O)–	**1a**		15 min	94.9	92.3	369
4		**2a**		15 min	98.6	96.0	384
5	4-H	**1a**		30 min	77.5	75.2	150
6		**2a**		30 min	82.4	80.8	162
7	4-CH_3O–	**1a**		1 h	60.4	54.5	54
8		**2a**		1 h	64.0	58.7	59
9	4-CH_3–	**1a**		1 h	55.5	50.2	50
10		**2a**		1 h	59.2	53.4	53

Reaction conditions: 1.0 mmol of *p*-R-C_6H_4Br aryl bromide, 1.5 mmol of styrene, 2.0 mmol K_2CO_3, 1.0 mmol% cat., DMF 3.0 (mL) for **1**–**2a**. Purity of compounds was checked by NMR and yields are based on arylbromide. All reactions were monitored by GC; 100 °C for **1a** and **2a**. TOF = (mol product/mol cat.) × h^{-1}.

3.3. The Heck coupling reactions

The reactions involved in forming carbon–carbon bonds are unquestionably the most important processes in organic chemistry, as they present key steps in the building of more complex molecules from simple precursors. Among the different methods used to form carbon–carbon bonds, Pd(0)-mediated reactions have been widely used because of their selective and versatile applications [71]. The Pd(0)-catalyzed Heck reaction has been called 'one of the true power tools of contemporary organic synthesis' because of its versatility and broad tolerance of functional groups [72]. The Pd-catalyzed arylation or vinylation of olefins, universally referred to as the "Heck reaction", has received increasing attention in the last decade, as it is a selective method to form new C–C bonds in a single operational step [73,74]. It constitutes a powerful and versatile method for the synthesis of polyfunctional compounds, e.g., dienes, cinnamic esters, and other variously substituted olefinic compounds, which are primarily applied as dyes, UV absorbers, and intermediates for pharmaceuticals, agrochemicals, and fragrances [75,76]. The rate of coupling is dependent on a variety of parameters such as temperature, solvent, base and catalyst loading. Generally, the Heck reaction conducted with tertiary phosphine complexes require high temperatures (higher than 120 °C) and polar solvents. For the choice of base, we surveyed Cs_2CO_3, K_2CO_3 and K^tOBu. Finally, we found that use of 0.01 mmol cat, 2 equivalents K_2CO_3 in DMF at 100 °C for **1a** and **2a** led to the best conversions. We initially tested the catalytic activities of **1a** and **2a** for the coupling of *p*-bromoacetophenone with styrene.

A control experiment indicated that the coupling reaction did not occur in the absence of **1a** and **2a**. Under the determined reaction conditions, a wide range of aryl bromides bearing

electron-donating and electron-withdrawing groups reacted with styrene, affording the coupled products in good yields. As expected, electron-deficient bromides were beneficial for the conversions (Table 5). Using aryl chlorides instead of aryl bromides yielded only small amount of stilbene derivatives under the conditions employed to bromides.

4. Conclusion

In summary, the coordination behavior of ligands **1** and **2** towards palladium(II) and platinum(II) were described. We also demonstrated the application of palladium complexes of these aminophosphine ligands as pre-catalyst in the Suzuki coupling and Heck reactions of aryl halides. Because of the strength of the Pt–C bonds, Pt(II)-bis(phosphino)amine **1b–c** and **2b–c** system exhibited no catalytic activity [77]. Only the palladium complexes were found to show catalytic activity in both the Suzuki and Heck coupling reactions of aryl bromides. In both cases, the catalytic activities of complexes **1a** and **2a** were found to be higher in reactions of aryl bromides with electron-withdrawing substituent than those with electron-releasing substituent. The procedure is quite simple and efficient towards various aryl bromides and does not require an induction period.

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Appendix A. Supplementary material

CCDC 815246 contains the supplementary crystallographic data for **2a** and **2b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.07.056.

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