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Synthesis and characterizations of *N,N*′-bis(diphenylphosphino)-2-(aminomethyl)aniline derivatives: application of a palladium(II) complex as pre-catalyst in Heck and Suzuki cross-coupling reactions

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The reaction of 2-(aminomethyl)aniline with 2 equivalents of PPh_2Cl in the presence of Et_3N, proceeds in CH_2Cl_2 to give *N,N*′-bis(diphenylphosphino)-2-(aminomethyl)aniline 1 in good yield. Oxidation of 1 with aqueous H_2O_2, elemental sulfur or gray selenium gave the corresponding oxide, sulfide and selenide dichalcogenides $[Ph_2P(E)NHC_6H_4CH_2NHP(E)Ph_2]$ (E: O, 2a; S, 2b; Se, 2c), respectively. The reaction of $[Ph_2PNHC_6H_4CH_2NHPPh_2]$ with $PdCl_2(cod)$, $PtCl_2(cod)$ and $[Cu(MeCN)_4]PF_6$ gave the corresponding chelate complexes, $PdCl_2$1, $PtCl_2$1 and $[Cu(1)_2]PF_6$. The new compounds were fully characterized by NMR, IR spectroscopy and elemental analysis. The catalytic activity of the Pd(II) complex was tested in the Suzuki coupling and Heck reactions. The Pd(II) complex catalyzes the Suzuki coupling and Heck reaction, affording biphenyls and stilbenes respectively, in good yields.

Supporting information may be found in the online version of this article.

Keywords: bis(diphenylphosphinoamino) ligands; palladium; platinum; copper; Suzuki reaction; Heck reaction

Introduction

The chemistry of compounds containing phosphorus and nitrogen, with direct bonds between two elements, has been known for many years, but continues to attract considerable attention, with increasing applications in diverse fields.[1,2] Although traditional phosphorus chemistry is dominated by compounds containing P–C and P–O linkages (naturally occurring phosphorus compounds contain P–O bonds), P–N compounds now dominate in main group chemistry. P–N compounds exhibit immense structural diversity and detailed structural information combined with theoretical rationalization of their bonding, and have helped to consolidate the field.[3]

Diphosphine ligands have been widely used throughout organometallic and inorganic chemistry, and are particularly important in homogeneous catalysis.[4,5] Diphosphines, in which the two phosphorus atoms are linked to a carbon chain and have the same substituents on each phosphorus atoms, such as bis(diphenylphosphino)ethane (dppe) and bis-diphenylphosphino)methane (dppm), have been extensively studied.[6,7] Recently, there has been an increasing interest in diphosphines with a heteroatom or bridge linking the two phosphorus atoms. However, in comparison with dppe, dppm and bridged diphosphines, unsymmetrical diphosphines have received relatively little attention.[8,9] Unsymmetrical diphosphines represent an interesting series of compounds because the difference in basicity or steric properties of the two phosphorus atoms could be exploited to obtain different coordination modes, i.e. bidendate versus monodendate.[10]

There has recently been increasing interest in the synthesis of new and highly active transition-metal-based catalysts derived from aminophosphines that can be used in different catalytic reactions including allylic alkylation,[11] amination,[12] Heck,[13] Suzuki,[14] hydroformylation[15] and hydrogenation reactions.[16]

During the final quarter of the twentieth century, the palladium-catalyzed coupling reactions of aryl halides with olefins (the Heck reaction) and with boronic acids (the Suzuki reaction) have emerged as the favored methods for formation of C–C bonds and have found widespread applications in synthetic organic chemistry and materials science[17] (Scheme 1). This popularity stems in part from their tolerance of many functional groups, which allows them to be employed in the synthesis of highly complex molecules.[18]

Herein we describe the synthesis of new diaminophosphine ligand and its corresponding oxides and transition metal complexes {Pd(II) Pt(II) and Cu(I)} (Scheme 2). The compounds were fully characterized by elemental analysis, IR, ^{13}C NMR, ^{1}H NMR and ^{31}P-{^{1}H} NMR spectroscopy. We also report on the catalytic activity of Pd(II) complex of **1** as a pre-catalyst in the Heck and Suzuki cross coupling reactions.

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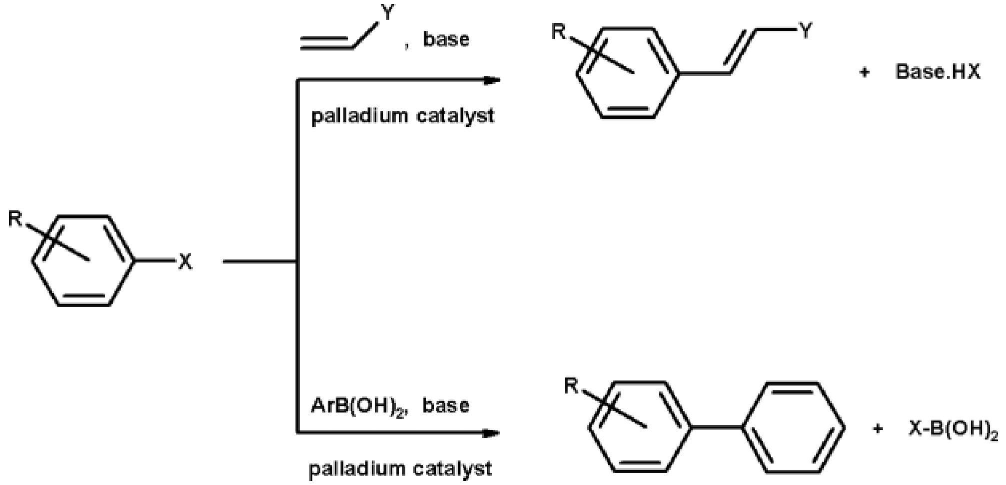
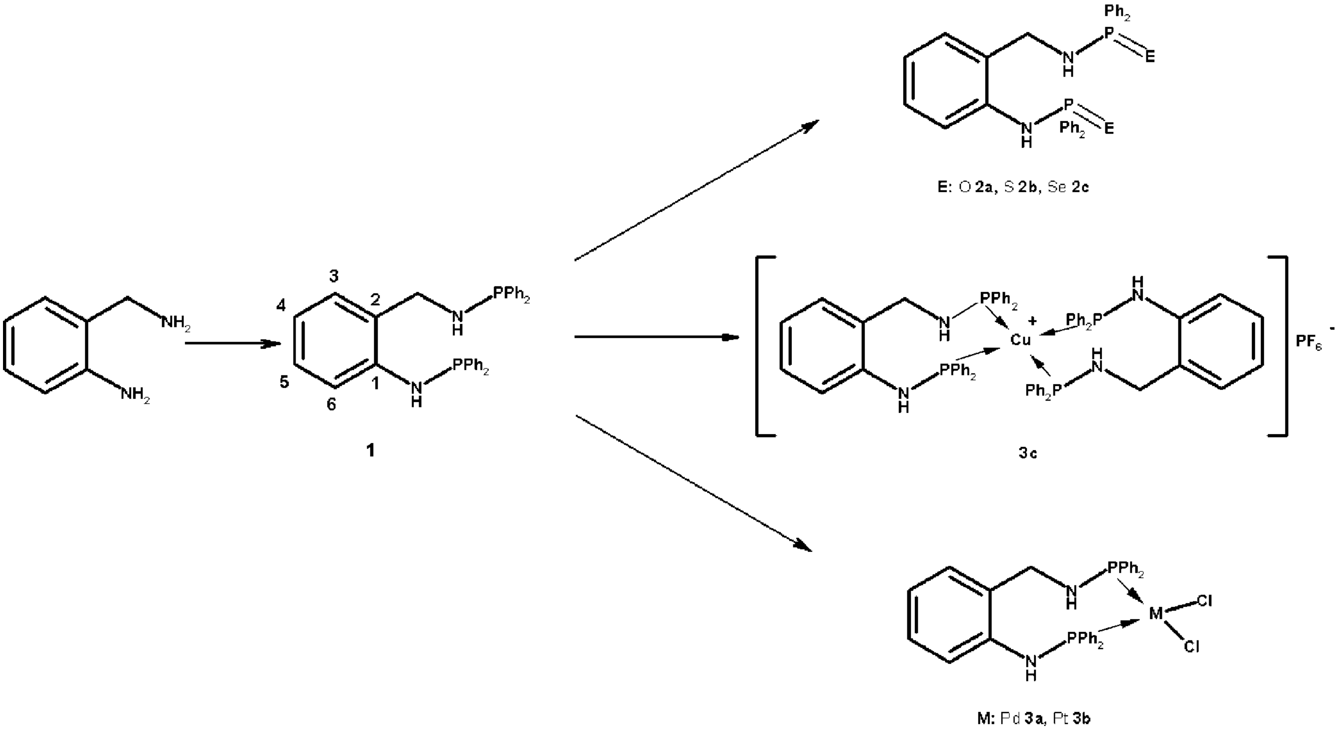


Scheme 1. The Heck and Suzuki cross-coupling of aryl halides.



Scheme 2. Synthesis of *N,N′*-bis(diphenylphosphino)-2-(aminomethyl)aniline and its derivatives. (i) Ph_2PCl, CH_2Cl_2; (ii) H_2O_2 or elemental S or gray Se; (iii) $[Cu(CH_3CN)_4]PF_6^-$; (iv) $[MCl_2(cod)]$ (M = Pd or Pt).

Experimental

All reactions and manipulations were performed under argon unless otherwise stated. Ph_2PCl and 2-aminobenzylamine were purchased from Fluka and used directly. Analytical grade and deuterated solvents were purchased from Merck. The starting materials $[MCl_2(cod)]$ (M = Pd, Pt, cod = 1,5-cyclooctadiene) and $[Cu(MeCN)_4]PF_6$ were prepared according to literature procedures.[19–21] Solvents were dried using the appropriate reagents and distilled prior to use. Infrared spectra were recorded as KBr disks 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 spectra (162.0 MHz) spectra were recorded on a Bruker Avance 400 spectrometer, with δ referenced to external TMS and 85% H_3PO_4, respectively. GC analyses were performed on an HP 6890N gas chromatograph equipped with a capillary column (5% biphenyl, 95% dimethylsiloxane, 30 m × 0.32 mm × 0.25 μm). Elemental analysis was carried out on a Fisons EA 1108 CHNS-O instrument; melting points were determined using a Gallenkamp Model apparatus with open capillaries.

Synthesis of *N,N′*-bis(diphenylphosphino)-2-(aminomethyl)aniline (1)

Chlorodiphenylphosphine (0.37 g, 1.60 mmol) was added drop-wise over a period of 30 min to a stirred solution of 2-aminobenzylamine (0.10 g, 0.80 mmol) and triethylamine (0.16 g, 1.60 mmol) in CH_2Cl_2 (30 ml) at 0 °C with vigorous stirring. The mixture was stirred at room temperature for 1 h, and the solvent was removed under reduced pressure. After addition of THF, the white precipitate (triethylammonium chloride) was filtered off under argon, the solvent removed *in vacuo*, and then washed with cold diethyl ether (2 × 10 ml) and dried *in vacuo* to produce a clear, yellow viscous oil compound **1** (yield 0.38 g, 94.7%). ^{1}H NMR (δ, $CDCl_3$): 7.43–7.49 (m, 8H, *o*-protons of phenyls); 7.28–7.42 (m, 13H, *m,p*-protons of phenyls and H-3); 7.22 (dd, 1H, $^3J_{H-H} = 7.6$ Hz and 7.5, H-4); 7.09 (d, 1H, $^3J_{H-H} = 6.8$ Hz, H-6); 6.79 (dd, 1H, $^3J_{H-H} = 7.5$ and 7.3Hz, H-5); 6.10 (d, 1H, $^2J_{NHP} = 8.8$ Hz, Ar$\underline{NH}$-); 4.12 (dd, 2H, $^3J_{CHNH} = 5.6$ Hz, $^3J_{PNCH} = 5.5$ Hz, -C$\underline{H_2}$-); 2.23 (d, 1H, $^2J_{HNP} = 1.1$ Hz, ArCH$_2\underline{NH}$-). ^{13}C-{^{1}H}NMR (δ, $CDCl_3$): 146.5, 140.6, 131.3, 129.7, 129.1, 128.9, 128.8, 128.5, 118.8, 115.8 (carbons of phenyls), 49.6 (-$\underline{C}H_2$-). ^{31}P-{^{1}H} NMR (δ, $CDCl_3$): 39.48 (s, $CH_2NH\underline{P}Ph_2$), 26.20 (s, $ArNH\underline{P}Ph_2$). Selected IR, υ (cm^{-1}): 910 (P–N), 1439 (P–Ph), 3302 (N–H). Anal. found: C, 75.73; H 5.52; N 5.56. Calculated for $C_{31}H_{28}N_2P_2$: C, 75.91; H 5.75; N 5.71%.

Synthesis of *N,N′*-bis(diphenyloxophosphino)-2-(aminomethyl)aniline (2a)

Aqueous hydrogen peroxide (30%, w/w, 0.08 ml, 0.82 mmol) was added dropwise to a suspension of [$Ph_2PNHC_6H_4CH_2NHPPh_2$] (0.20 mg, 0.41 mmol) in CH_2Cl_2 and the mixture was stirred for 30 min at room temperature. The volume was concentrated *in vacuo* to *ca* 1–2 ml and addition of *n*-hexane (20 ml) gave **2a** as a white solid which was collected by filtration (yield 0.19 g, 89.2%; m.p. 100–102 °C). ^{1}H NMR (δ, $CDCl_3$): 7.91 (dd, 4H, $J = 7.6$ and 12.4 Hz, *o*-protons of aromatic-NH-phenyls); 7.70 (dd, 4H, $J = 7.4$ and 12.2 Hz, *o*-protons of aliphatic-NH-phenyls); 7.40–7.54 (m, 12H, *m,p*-protons of phenyls); 7.31 (d, 1H, $^3J_{H-H} = 8.0$ Hz, H-3); 7.16 (d,1H, $^3J_{H-H} = 7.6$ Hz, H-6); 7.03 (dd, 1H, $^3J_{H-H} = 7.7$ and 7.6 Hz, H-4); 6.99 (dd, 1H, $^3J_{H-H} = 7.6$ and 7.5 Hz, H-5); 6.68 (br, 1H, Ar$\underline{NH}$-); 4.18 (dd, 2H, $^3J_{CHNH} = 10.4$ Hz, $^3J_{PNCH} = 10.3$ Hz, -C$\underline{H_2}$-); 3.35 (br, 1H, ArCH$_2\underline{NH}$-). ^{13}C-{^{1}H} NMR (δ, $CDCl_3$): 139.3, 132.6, 132.3, 132.2, 132.1, 132.0, 131.9, 131.7, 131.3, 130.3, 129.1, 128.2, 122.7, 121.5 (carbons of phenyls), 42.4 (-$\underline{C}H_2$-). ^{31}P-{^{1}H} NMR (δ, $CDCl_3$): 26.31 (s, $CH_2NH\underline{P}Ph_2$); 21.08 (s, $ArNH\underline{P}Ph_2$). Selected IR, υ (cm^{-1}): 929 (P–N), 1446 (P–Ph), 3174 (N–H), 1180 (P=O). Anal. found: C, 71.02; H 5.17; N 5.15. Calculated for $C_{31}H_{28}N_2P_2O_2$: C, 71.26; H 5.40; N 5.36%.

Synthesis of *N,N′*-bis(diphenylthiophosphino)-2-(aminomethyl)aniline (2b)

[$Ph_2PNHC_6H_4CH_2NHPPh_2$] (0.20 mg, 0.41 mmol) and elemental sulfur (0.033 g, 0.82 mmol) were heated to reflux in CH_2Cl_2 (20 ml) for 2 h. After allowing the mixture to cool to room temperature, the yellow solid **2b** was collected by filtration and dried *in vacuo* (yield 0.18 g, 79.7%; m.p. 60–62 °C).^{1}H NMR (δ, $CDCl_3$): 8.06 (dd, 4H, $J = 7.8$ and 13.8 Hz, *o*-protons of aromatic-NH-phenyls); 7.75 (dd, 4H, $J = 8.0$ and 13.2 Hz, *o*-protons of aliphatic-NH-phenyls); 7.41–7.56 (m, 12H, *m,p*-protons of phenyls]; 7.24 [d, 1H, $^3J_{H-H} = 7.2$ Hz, H-3]; 7.19 (d, 1H, $^3J_{H-H} = 7.2$ Hz, H-6); 7.07 (dd, 1H, $^3J_{H-H} = 7.6$ and 7.4 Hz, H-4); 6.87 (dd, 1H, $^3J_{H-H} = 7.5$ and 7.4 Hz, H-5); 6.50 (d, 1H, $^2J_{NHP} = 6.8$ Hz, Ar$\underline{NH}$-); 4.19 (dd, 2H, $^3J_{CHNH} = 7.6$ Hz, $^3J_{PNCH} = 7.5$ Hz, -C$\underline{H_2}$-); 2.73 (br, 1H, ArCH$_2\underline{NH}$-). ^{13}C-{^{1}H} NMR (δ, $CDCl_3$): 139.6, 133.9, 132.5, 132.0, 131.9, 131.6, 131.3, 130.8, 129.2, 128.8, 128.7, 128.5, 121.7, 120.1 (carbons of phenyls), 42.7 (-$\underline{C}H_2$-). ^{31}P-{^{1}H} NMR (δ, $CDCl_3$): 59.94 [s, $CH_2NH\underline{P}Ph_2$]; 53.11 [s, $ArNH\underline{P}Ph_2$]. Selected IR, υ (cm^{-1}): 928 (P–N), 1441 (P–Ph), 3242 (N–H), 642 (P=S). Anal. found: C, 66.94; H 4.86; N 4.87. Calculated for $C_{31}H_{28}N_2P_2S_2$: C, 67.13; H 5.09; N 5.05%.

Synthesis of *N,N′*-bis(diphenylselenophosphino)-2-(aminomethyl)aniline (2c)

[$Ph_2PNHC_6H_4CH_2NHPPh_2$] (0.20 mg, 0.41 mmol) and gray selenium (0.07 g, 0.82 mmol) were heated to reflux in CH_2Cl_2 (20 ml) for 2 h. After allowing the mixture to cool to room temperature the impure white solid **2c** was collected by filtration and dried *in vacuo* (yield 0.22 g, 83.2%; m.p. 149–151 °C). ^{1}H NMR (δ, $CDCl_3$): 7.94 (dd, 4H, $J = 7.8$ and 13.8 Hz, *o*-protons of aromatic-NH-phenyls); 7.86 (dd, 4H, $J = 7.8$ and 13.4 Hz, *o*-protons of aliphatic-NH-phenyls); 7.50–7.52 (m, 12H, *m,p*-protons of phenyls); 7.44 (d, 1H, $^3J_{H-H} = 7.2$ Hz, H-6); 7.31 (dd, 1H, $^3J_{H-H} = 7.7$ and 7.5 Hz, H-4); 7.19 (d, 1H, $^3J_{H-H} = 7.6$ Hz, H-3); 6.97 (dd, 1H, $^3J_{H-H} = 7.5$ and 7.6Hz, H-5); 5.87 (d, 1H, $^2J_{NHP} = 3.6$ Hz, Ar$\underline{NH}$-); 4.24 (dd, 2H, $^3J_{CHNH} = 8.2$ Hz, $^3J_{PNCH} = 8.0$ Hz, -C$\underline{H_2}$-); 3.10 (br, 1H, ArCH$_2\underline{NH}$-). ^{13}C-{^{1}H} NMR (δ, $CDCl_3$): 138.8, 134.4, 133.6, 132.4, 131.9, 131.8, 131.7, 129.7, 129.4, 129.1, 128.8, 127.2, 122.9, 121.8, 42.2 (-$\underline{C}H_2$-). ^{31}P-{^{1}H} NMR (δ, $CDCl_3$): 57.91 (s, J_{PSe}: 747 Hz; $CH_2NH\underline{P}Ph_2$), 48.72 (s, J_{PSe}: 768 Hz, $ArNH\underline{P}Ph_2$). Selected IR, υ (cm^{-1}): 925 (P–N), 1438 (P–Ph), 3220 (N–H), 551 (P=Se). Anal. found: C, 57.19; H 4.17; N 4.15. Calculated for $C_{31}H_{28}N_2P_2Se_2$: C, 57.42; H 4.35; N 4.32%.

Synthesis of {*N,N′*-bis(diphenylphosphino)-2-(aminomethyl)aniline} dichloropalladium(II) (3a)

[$Pd(cod)Cl_2$] (0.18 g, 0.61 mmol) and [$Ph_2PNHC_6H_4CH_2NHPPh_2$] (0.30 mg, 0.61 mmol) were dissolved in dry CH_2Cl_2 (20 ml) and stirred for 2 h. The volume was concentrated to *ca* 1–2 ml under reduced pressure and addition of diethyl ether (20 ml) gave a clear yellow solid **3a**. The product was collected by filtration and dried *in vacuo* (yield 0.36 g, 88.1%; m.p. 196–198 °C). ^{1}H NMR (δ, DMSO): 7.68 (dd, 4H, $J = 7.6$ and 11.8 Hz, *o*-protons of aromatic-NH-phenyls); 7.61 (dd, 4H, $J = 8.0$ and 11.6 Hz, *o*-protons of aliphatic-NH-phenyls); 7.37–7.56 (m, 12H, *m,p*-protons of phenyls); 7.02 (m, 2H, H-3 and H-4); 6.82 (d, 1H, $^3J_{H-H} = 6.8$ Hz, H-6); 6.76 (s, 1H, H-5); 6.54 (br, 1H, Ar$\underline{NH}$-); 4.39 (d, 2H, $J = 7.6$ Hz, –C$\underline{H_2}$–); 2.31 (br, 1H, ArCH$_2\underline{NH}$-). ^{13}C–{^{1}H} NMR (δ, DMSO): 135.8, 135.7, 135.1, 133.9, 133.5, 130.3, 128.8, 128.7, 128.6, 128.4, 128.3, 128.1, 125.9, 123.3, 51.2 (–$\underline{C}H_2$–). ^{31}P-{^{1}H} NMR (δ, DMSO): 77.64 (d, $CH_2NH\underline{P}Ph_2$, $^2J_{PP}$ 44.6 Hz), 65.54 (d, $ArNH\underline{P}Ph_2$, $^2J_{PP}$ 44.6 Hz). Selected IR, υ (cm^{-1}): 928 (P–N), 1441 (P–Ph), 3216 (N–H). Anal. found: C, 55.56; H 4.01; N 3.97. Calculated for $C_{31}H_{28}N_2P_2PdCl_2$: C, 55.75; H 4.23; N 4.19%.

Synthesis of {*N,N′*-bis(diphenylphosphino)-2-(aminomethyl)aniline} dichloroplatinum(II) (3b)

[$Pt(cod)Cl_2$] (0.23 g, 0.61 mmol) and [$Ph_2PNHC_6H_4CH_2NHPPh_2$] (0.30 mg, 0.61 mmol) were dissolved in dry CH_2Cl_2 (20 ml) and stirred for 2 h. The volume was concentrated to *ca* 1–2 ml by evaporation under reduced pressure and addition of diethyl ether (20 ml) gave a white solid **3b**. The product was collected by filtration and dried *in vacuo* (yield 0.43 g, 92.9%; m.p. >300 °C). ^{1}H NMR (δ, DMSO): 7.68–7.64 (m, 8H, *o*-protons of phenyls); 7.37–7.49 (m, 12H, *m,p*-protons of phenyls); 7.02 (m, 2H, H-3 and H-4); 6.76 (d, 1H, $^3J_{H-H} = 6.8$ Hz, H-6); 6.42 (s, 1H, H-5); 6.03 (br, 1H, Ar$\underline{NH}$-); 4.51 (d, 2H, $J = 8.0$ Hz, –C$\underline{H_2}$–); 2.52 (br, 1H, ArCH$_2\underline{NH}$-). ^{13}C-{^{1}H} NMR (δ, DMSO): 141.5, 135.6, 134.8, 133.9, 132.4, 131.6, 131.5, 130.9, 130.2, 128.4, 128.3, 128.1, 126.2, 123.2, 51.1 (–$\underline{C}H_2$–). ^{31}P-{^{1}H}NMR (δ, DMSO): 52.75 (d, J_{PtP}: 3348 Hz, $CH_2NH\underline{P}Ph_2$, $^2J_{PP}$ 9.5 Hz); 39.01

(d, J_{PtP}: 3454 Hz, ArNH<u>P</u>Ph$_2$, $^2J_{PP}$) 9.5 Hz). Selected IR, υ (cm^{-1}): 925 (P–N), 1438 (P–Ph), 3202 (N–H). Anal. found: C, 48.97; H 3.91; N 3.54. Calculated for $C_{31}H_{28}N_2P_2PtCl_2$: C, 49.22; H 3.73; N 3.70%.

Synthesis of bis{*N,N′*-bis(diphenylphosphino)-2-(aminomethyl)aniline} copper(I)hexafluorophosphate (3c)

A solution of [Cu(MeCN)$_4$]PF$_6$ (0.11 g, 0.31 mmol) and [Ph$_2$PC$_6$H$_4$CH$_2$NPPh$_2$] (0.30 mg, 0.61 mmol) were dissolved in CH$_2$Cl$_2$ (20 ml) and stirred at room temperature for 2 h. The volume was concentrated to *ca* 1–2 ml under reduced pressure and addition of diethyl eter (20 ml) gave a white solid **3c** which was collected by filtration and dried *in vacuo* (yield 0.29 g, 79.7%; m.p. 132–134 °C). ^{1}H NMR (δ, DMSO): 7.38–7.72 [m, 20H, protons of phenyls]; 6.83–7.04 [m, 4H, protons of benzyl]; 5.95 [br, 1H, Ar<u>NH</u>–]; 4.24 [d, 2H, $J = 7.8$ Hz, –C<u>H$_2$</u>–]; 3.08 [br, 1H, ArCH$_2$<u>NH</u>-]. ^{13}C-{^{1}H} NMR (δ, DMSO): 142.2–121.3 [14 ArC], 53.5 (-<u>C</u>H$_2$-). ^{31}P-{^{1}H} NMR (δ, DMSO): 38.71 [d, CH$_2$NH<u>P</u>Ph$_2$, $^2J_{PP}$ 142.6 Hz]; 33.62 [d, ArNH<u>P</u>Ph$_2$, $^2J_{PP}$ 142.6 Hz]. Selected IR, υ (cm^{-1}): 847 (P–N), 1441 (P–Ph), 3342 (N–H). Anal. found: C, 62.38; H 4.54; N 4.48. Calculated for $C_{62}H_{56}N_4P_5F_6Cu$: C, 62.60; H 4.74; N 4.71%.

General Procedure for the Suzuki Coupling Reaction

Aminophosphine–palladium complex (**3a**, 0.01 mmol), aryl bromide (1.0 mmol), phenylboronic acid (1.5 mmol), Cs$_2$CO$_3$ (2 mmol) and dioxane (3 ml) were added to a small Schlenk tube in argon atmosphere and the mixture was heated at 80 °C for 1.5 h. After the completion of the reaction, the mixture was cooled, extracted with ethyl acetate–hexane (1 : 5), filtered through a pad of silicagel with copious washings, concentrated and purified by flash chromatography on silica gel. The purity of the compounds was checked by GC and NMR and yields are based on the aryl bromide.

General Procedure for the Heck Coupling Reaction

Aminophosphine–palladium complex (**3a**, 0.01 mmol), aryl bromide (1.0 mmol), styrene (1.5 mmol), K$_2$CO$_3$ (2 mmol) and DMF (3 ml) were added to a small Schlenk tube in argon atmosphere and the mixture was heated to 120 °C for 1 h. After the completion of the reaction, the mixture was cooled, extracted with ethyl acetate–hexane (1 : 5), filtered through a pad of silicagel with copious washings, concentrated and purified by flash chromatography on silica gel. The purity of the compounds was checked by GC and NMR and yields are based on the aryl bromide.

Results and Discussion

The aminolysis of chlorophosphines is an efficient method for preparing R$_2$PN(H)R′ or (R$_2$P)$_2$NR′, yet this procedure has not widely been exploited, in part possibly because of the associated instability of the P–N bonds in these ligands.[22] The new aminophosphine **1** was prepared from the commercially available 2-(aminomethyl)aniline via the classical aminolysis[23–25] reaction with diphenylphosphine chloride in dichloromethane at 0 °C in a very good yield (94.7%) (Scheme 2).

The reaction of Ph$_2$PCl with 2-(aminomethyl)aniline yielded the product with single resonances at δ 39.48 ppm (ArCH$_2$NH<u>P</u>Ph$_2$) and 26.10 ppm (ArNH<u>P</u>Ph$_2$) comparable to those of other aminophosphines.[26] Solutions of **1** in CDCl$_3$, prepared under anaerobic conditions, are unstable and decompose gradually to give [Ph$_2$P(O)NHC$_6$H$_4$CH$_2$NHP(O)Ph$_2$] **2a,** PPh$_2$P(O)Ph$_2$ and [Ph$_2$PH=NC$_6$H$_4$CH$_2$N=PHPh$_2$]. Compound **1** is unstable in air, presumably due to the fact that aminophosphine can exist in two isomeric forms, R$_2$P–NHR′ ↔ R$_2$P(H)=NR′.[27] However, under argon atmosphere and in solution it undergoes decomposition in time. In its ^{1}H NMR spectra, the CH$_2$ group lies at 4.12 ppm. Oxidation of **1** with aqueous hydrogen peroxide, elemental sulfur and gray selenium gave the corresponding oxide **2a**, sulfide **2b** and selenide **2c** derivatives, respectively (Scheme 2).

As expected, the oxidation reaction using aqueous hydrogen peroxide was very rapid for**1** and takes place under ambient conditions spontaneously. The ^{31}P-{^{1}H} NMR spectra of **2a** displayed singlets at 26.31 and 21.08 ppm, suggesting that both phosphorus atoms are not chemically equivalent in the solution. In addition, a small amount of iminophosphine R$_2$P(H)=NR′ and the hydrolysis product PPh$_2$P(O)H were formed as evidenced by the signals at about 14.0 and 20.0 ppm in the ^{31}P-{^{1}H} NMR spectra, respectively.[28] In contrast, oxidation with sulfur and selenium had to be carried out at elevated temperatures and a stepwise oxidation process was further observed. For example, in the sulfurization of **1**, resonance due to the starting compound **1** (39.48; 26.10 ppm) and the desired product **2b** (59.94; 53.11 ppm) were observed at the beginning of the reaction.[29] This is not surprising since elemental sulfur and selenium are weaker oxidizing agents than hydrogen peroxide. After the completion of the reaction, the signal of the starting compound **1** disappeared because of the desired product **2b**. Similarly, ^{31}P-{^{1}H} NMR showed single resonances (CDCl$_3$) at 59.94, 53.11 ppm for **2b** and 59.91, 48.72 ppm with selenium satellites (J_{PSe} 747 Hz, J_{PSe} 768 Hz) for **2c**, which is typical for a compound containing P=Se moiety. Attempts to control the reaction conditions to yield the mono-oxide intermediates were unsuccessful. Furthermore, the IR spectrum have bands at 1180, 642 and 551 cm^{-1} that were assigned to υ(P=O), υ(P=S) and υ(P=Se), respectively. The structures of the oxidized derivative **2a**, sulfide **2b** and selenide **2c** were further confirmed by microanalysis and IR spectroscopy, and were found to be in good agreement with the theoretical values.

The co-ordination chemistry of **1** with various transition-metals was explored. Reaction of **1** with MCl$_2$(cod) (where M = Pd, Pt; cod = 1,5-cyclooctadiene) in dichloromethane gave the corresponding metal(II) complexes **3a** and **3b** in high yields (80–90%; see Scheme 2). In both complexes **3a** and **3b,** the nitrogen atom in the amine group was not involved in any coordination to the metal centers because the phosphorus atoms in the aminophosphine ligand are much stronger donor centers and, thus, coordination to the metal center takes place preferentially at the phosphorus atoms. In the ^{31}P-{^{1}H} NMR spectra, the chemical shifts of **3a** and **3b** 77.64, 65.54 ppm and 52.75, 39.01 ppm, respectively, are similar and within the expected range of other reported structurally similar complexes.[30–32] The geometry of complex **3b** was confirmed by examination of Pt–P coupling constants (J_{PtP} 3348 Hz, J_{PtP} 3454 Hz), which are characteristic of compounds having mutually *cis*-dispositions.[33] In addition, the ^{31}P-{^{1}H} NMR spectrum of Pd(II) complex displayed a large $^2J_{PP}$ spin–spin coupling (44.6 Hz), derived from *cis*-coordination of the ligand to Pd(II). However, much smaller $^2J_{PP}$ coupling (9.5 Hz) was also observed for Pt(II) complex. In the ^{1}H-NMR spectra, the chemical shifts of CH$_2$ group attached to the aliphatic carbon lie at δ 4.39 and 4.51 ppm, slightly downfield with respect to the aminophosphine (4.12 ppm) **1**.

The reactions of [Cu(MeCN)$_4$]PF$_6$ with 2 equivalents of **1** in dichloromethane at room temperature afforded the corresponding d^{10} copper(I) diaminophosphine complex **3c** in high yield

(Scheme 2). The ^{31}P-{^{1}H} NMR spectrum of **3c** in DMSO exhibited a pair of doublets, which could be assigned to non-equivalent phosphorus environments (δ 38.71, 33.62, $^{2}J_{PP}$ 142.6 Hz). In the ^{1}H NMR spectrum, the CH_2 group displayed a singlet at 4.24 ppm and the IR spectrum had υ(NH) at 3282 cm^{-1}, and υ(PPh) and υ(PN) at 1441 and 847 cm^{-1}. All the three complexes **3a–c** could be isolated as analytically pure solid materials and fully characterized by elemental analysis and IR spectroscopy as well.

The Suzuki Coupling

Palladium-catalyzed coupling via Suzuki reaction has become, over the last 10 years, the method of choice for biaryl and heterobiaryl synthesis.[34] This moieties are widely present in numerous classes of organic compounds, such as natural product, pharmaceuticals, agrochemicals and ligands for asymmetric synthesis and in new materials, such as liquid crystals.[35] The reaction generally results in excellent yields when performed at temperatures of 80–100 °C with aryl iodides and bromides. Recently, the Suzuki reaction of aryl chlorides catalyzed by palladium-tertiary phosphine[36] systems has been studied extensively due to the the economically attractive nature of the starting materials.

In order to survey the reaction parameters for the catalytic Suzuki reaction, we examined Cs_2CO_3, K_2CO_3 and K^{t}OBu as base and DMF and dioxane as solvent. We found that the reaction performed in dioxane, with Cs_2CO_3 as the base at 80 °C appeared to be best. We initially tested the catalytic activity of the complex **3a** for the coupling of *p*-bromoacetophenone with phenylboronic acid and the control experiments showed that the coupling reaction did not occur in the absence of the catalyst. Under these conditions, *p*-bromoacetophenone, *p*-bromobenzaldehyde, *p*-bromobenzene, *p*-bromoanisole and *p*-bromotoluene react with phenylboronic acid in good yields (Table 1). We also tested the catalytic activity of **3a** for the coupling of aryl chlorides. Unfortunately, chlorides were found to be generally unreactive under the conditions employed for bromides.

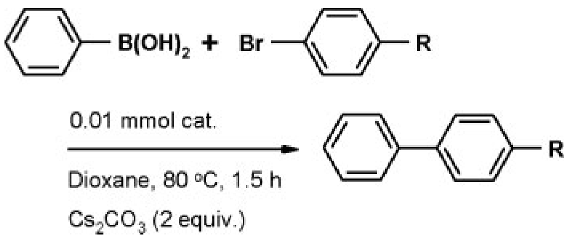
The Heck Coupling

In the last 30 years, the selective palladium-catalyzed transformation, known as the Heck reaction, has been extensively explored and used in several diverse areas such as the preparation of hydrocarbons, novel polymers, pharmaceuticals, agrochemicals, dyes and new enantioselective syntheses of natural products, because of the mild conditions required for the reaction.[37–41] The Heck reaction has been shown to be very useful for the preparation of disubstituted olefins.[42] 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^{t}OBu. Finally, we found that use of 1.0% mmol **3a** and 2 equivalents of K_2CO_3 in DMF at 120 °C led to the best conversion within 1 h. We initially tested the catalytic activity of **3a** for the coupling of *p*-bromoacetophenone with styrene.

A control experiment indicated that the coupling reaction did not occur in the absence of **3a**. 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 excellent yields. As expected, electron-deficient bromides were beneficial for the conversions (Table 2). Using aryl chlorides instead of aryl bromides yielded only a small amount of stilbene derivatives under the conditions employed for bromides.

Experiments using Pd(COD)Cl_2 and Pd(COD)Cl_2/diaminophosphine as pre-catalyst were also performed. We observed that isolated diaminophosphine palladium(II) complex, **3a**, gave better yields in the both coupling reactions compared with the Pd(COD)Cl_2 or the *in situ*-formed Pd-diaminophosphine catalyst, which consists of mixtures of palladium and ligand (Tables 1 and 2).

Table 1. The Suzuki coupling reactions of aryl bromides with phenylboronic acid

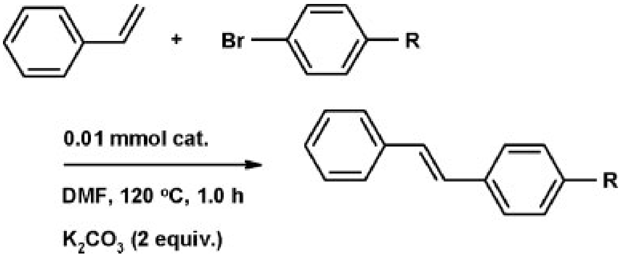


		Yield^{a} (%)		
Entry	**R**	Pd(COD)Cl_2	Pd(COD)Cl_2/L	**3a**
1	$COCH_3$	64.2	75.1	97.6
2	CHO	55.6	63.1	98.8
3	H	48.6	62.8	90.8
4	OCH_3	22.7	47.6	53.8
5	CH_3	25.8	44.4	57.2

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. The purity of compounds was checked by NMR and yields are based on arylbromide. All reactions were monitored by GC; 80 °C. 1.5 h.

[a] GC yield.

Table 2. The Heck coupling reactions of aryl bromides with styrene



		Yield^{a} (%)		
Entry	**R**	Pd(COD)Cl_2	Pd(COD)Cl_2/L	**3a**
1	$COCH_3$	80.8	75.3	92.1
2	CHO	82.3	74.4	93.4
3	H	56.8	55.3	62.7
4	OCH_3	42.7	38.5	51.7
5	CH_3	49.3	42.9	52.9

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. The purity of compounds was checked by NMR and yields are based on arylbromide. All reactions were monitored by GC; 120 °C, 1.0 h.

[a] GC yield.

Conclusion

In conclusion, we have prepared a new bis(diphenyl)phosphino ligand and its derivatives including oxide, sulfide and selenide, as well as transition metal complexes containing Pd(II), Pt(II) and Cu(I) centers. All these new compounds were characterized using NMR, IR and elemental analysis. The catalytic behavior of the Pd(II) complex **3a** was investigated in the Suzuki coupling and Heck reactions. In general, **3a** appears to be more efficient for the Suzuki and Heck reactions of aryl bromides, but its activity is much lower for the coupling of aryl chlorides. The complex **3a** exhibited relatively higher activity with electron-withdrawing substituents than electron-donating substituents on the aryl bromides in both reactions. The activity was improved for the latter by enhancing the reaction time. The procedure is simple and efficient towards various aryl bromides and does not require induction period.

Supporting information

Supporting information may be found in the online version of this article.

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