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Aminophosphine ligands: synthesis, coordination chemistry, and activity of their palladium(II) complexes in Heck and Suzuki cross-coupling reactions

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Abstract The reaction of 4-aminodiphenylamine or 2-aminofluorene with two equivalents of PPh_2Cl in the presence of Et_3N gives new bis(diphenylphosphino)amines *N,N*-bis(diphenylphosphino)-4-aminodiphenylamine **1** and *N,N*-bis(diphenylphosphino)-2-aminofluorene **2** in good yields. Oxidation of **1** or **2** with hydrogen peroxide, elemental sulfur or gray selenium affords the corresponding chalcogen derivatives. The palladium and platinum complexes of these P–N–P donor ligands were prepared by the reaction of the bis(phosphino)amines with MCl_2(cod) (M = Pd or Pt, cod = cycloocta-1,5-diene). All the new compounds have been characterized by analytical and spectroscopic methods, including ^{1}H-^{31}P NMR, ^{1}H-^{13}C HETCOR, or ^{1}H-^{1}H COSY correlation experiments. The Pd(II) complexes were investigated as catalysts in the Suzuki and Heck reactions; both showed good catalytic activity affording high yields of the desired products.

Introduction

Tertiary phosphines have long been used in the design and synthesis of transition metal catalysts, especially with late transition metals such as nickel, rhodium, ruthenium, platinum, and palladium [1]. Applications of such catalysts include allylic alkylation [2, 3], amination [4, 5], Heck reaction [6, 7], Suzuki coupling [8, 9], hydroformylation [10, 11], and hydrogenation of olefins [12, 13]. In particular, palladium complexes containing phosphine ligands serve as highly active catalysts for the formation of carbon–carbon bonds [14].

In recent years, the Heck and Suzuki reactions have found widespread applications in synthetic organic chemistry and materials science [15]. Their popularity stems in part from their tolerance of many functional groups, which allows them to be employed in the synthesis of highly complex molecules [16]. Recently, various bulky and electron-rich phosphanes have been developed as ligands to promote the cross-coupling reactions [14, 17]. In our previous papers, we have shown that aminophosphine and bis(aminophosphine) palladium(II) complexes can be used in Heck and Suzuki cross-coupling reactions [18, 19]. In the continuation of our interest in new ligand systems with different spacers to control the electronic attributes at phosphorus centers and to explore their coordination chemistry, we report here the synthesis of two new bis(phosphino)amine ligands. We have demonstrated that the palladium(II) complexes of *N,N*-bis(diphenylphosphino)-4-aminodiphenylamine **1** and *N,N*-bis(diphenylphosphino)-2-aminofluorene **2** offer distinct advantages in catalysis of the Suzuki and Heck cross-coupling reactions.

Results and discussion

Synthesis

Aminolysis appears to be the most common method used for the synthesis of phosphinoamines and bis(phosphino)amines [20]. The bis(phosphino)amine ligands **1** and **2** have been prepared by aminolysis of Ph_2PCl with the commercially available aromatic amines 4-aminodiphenylamine and

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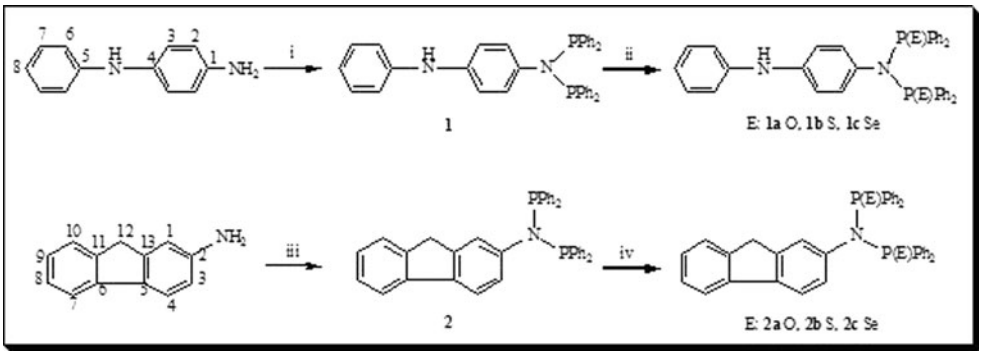
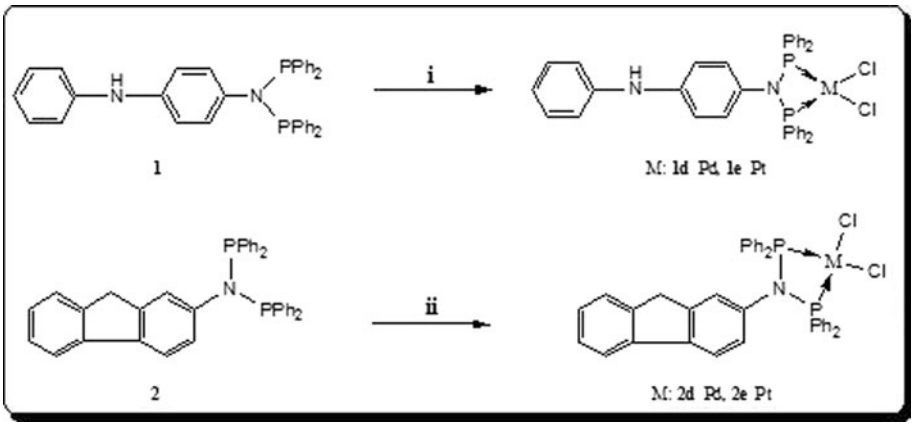


Scheme 1 Synthesis of the *N*,*N*-bis(diphenylphosphino)-4-aminodiphenylamine, $[(Ph_2P)_2N–C_6H_4–NH–C_6H_5]$, **1** and *N*,*N*-bis(diphenylphosphino)-2-aminofluorene, $[(Ph_2P)_2N–C_6H_3–CH_2–C_6H_4]$, **2** ligands and their chalcogenides; (i) 2 equiv. Ph_2PCl, 2 equiv. Et_3N, thf; (ii) 2 equiv. aqueous hydrogen peroxide, elemental sulfur or gray selenium, thf; (iii) 2 equiv. Ph_2PCl, 2 equiv. Et_3N, thf; (iv) 2 equiv. aqueous hydrogen peroxide, elemental sulfur or gray selenium, thf

2-aminofluorene, respectively, in the presence of Et_3N (Scheme 1). Since the ligands are unstable and rapidly decompose upon exposure to air or moisture, triethylamine hydrogen chloride cannot be separated from them by our previous method [21], which involves washing the solid product with water. Moreover, triethylamine hydrogen chloride is soluble in dichloromethane, rendering this solvent unsuitable for the present case. The reactions proceeded very slowly in diethyl ether or toluene, but were complete within 1 h in thf, so we preferred thf as the solvent. The $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures of **1** and **2** each display singlets, at 69.3 and 68.4 ppm, respectively, which were attributed to the expected bis(phosphino)amines, similar to the structurally related compounds [22]. The ^1H and $^{13}C\{^1H\}$ NMR spectra are also in agreement with the proposed structures. Characteristic $J_{^{31}P-^{13}C}$ coupling constants of the carbons of the phenyls rings were observed in the ^{13}C NMR spectra, consistent with the literature values [23, 24]. The IR spectra of **1** and **2** display absorptions at around 800–900 cm^{-1} characteristic of the P–N–P moiety. The absorptions at around 3,300 cm^{-1} in the IR spectra of **1** and its derivatives are attributed to N–H bonds. Other pertinent spectroscopic and analytical data are given in the "Experimental" section.

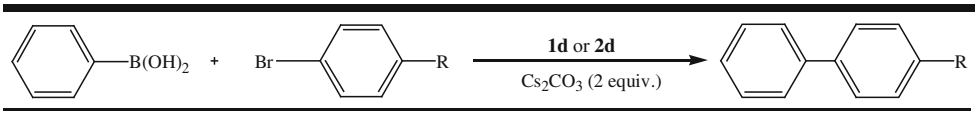
Oxidation of **1** or **2** with aqueous hydrogen peroxide, elemental sulfur, or gray selenium in thf gave the corresponding oxides (**1a**–**2a**), sulfides (**1b**–**2b**), and selenides (**1c**–**2c**), which were characterized by analytical and spectroscopic methods (Scheme 1). Oxidation of the ligands with hydrogen peroxide was rapid at ambient temperature. However, the reaction with elemental sulfur or gray selenium had to be carried out at elevated temperature since sulfur and selenium are weaker oxidizing agents than hydrogen peroxide, especially toward phosphorus atoms with phenyl groups [25, 26]. The $^{31}P\{^1H\}$ NMR spectra of the oxides **1a** and **2a** display singlets at 23.8 and 24.5 ppm, respectively. There were two singlets in the $^{31}P\{^1H\}$ NMR spectra of the reaction media of the sulfides, and the ones at around 50–51 ppm disappeared after reflux for 1–2 h, so they were thought to be an intermediate. The remaining resonances at 68.4 and 68.8 ppm were assigned to the sulfide derivatives of **1b** and **2b**, respectively. The $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures of the selenides also show two singlets; those at 47–48 ppm disappeared after reflux for 1–2 h, so the oxidation is a stepwise process. The signals at 69.3 and 69.7 ppm were attributed to the selenide derivatives **1c** and **2c**, respectively. The $^{31}P\{^1H\}$ NMR resonances of these chalcogenides are within the range for similar compounds [27], and furthermore, in the case of the selenides, there are selenium satellites with a $^1J_{P-Se}$ of ~800 Hz. The P=O bonds in **1a** and **2a** are observed at ca. 1,200 cm^{-1}, while bands at ca. 650–651 cm^{-1} are characteristic of the P=S bonds in **1b** and **2b**, and bands at 566–567 cm^{-1} can be ascribed to the P=Se bond in **1c** and **2c**. The structures of the oxidized derivatives were further confirmed by ^1H and $^{13}C\{^1H\}$ NMR and elemental analysis. The selenium compounds are liable to decompose, upon exposure to air [20]; therefore, they were stored under argon.

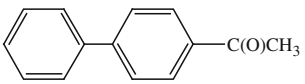
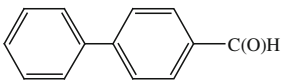
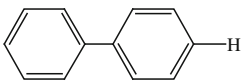
The coordination chemistry of **1** and **2** with Pd and Pt was explored. Reaction of **1** and **2** with $MCl_2(cod)$ (M = Pd or Pt, cod = cycloocta-1,5-diene) gave the respective palladium(II) and platinum(II) complexes in high yields (Scheme 2). The $^{31}P\{^1H\}$ NMR spectra of the palladium complexes **1d** and **2d** display singlets at 35.9 and 35.4 ppm, respectively, which are shifted to lower frequencies by ca. 33 ppm compared with the free ligand. The $^{31}P\{^1H\}$ NMR spectra of the platinum complexes **1e** and **2e** exhibit singlets at 21.2 and 21.3 ppm, respectively, accompanied by the platinum satellites (3335.8 and 3337.1 Hz for **1e** and **2e**, respectively), indicative of *cis* geometry [28, 29]. The $^{31}P\{^1H\}$ NMR chemical shifts of the complexes are within the range observed for structurally similar complexes [30]. The IR spectra and microanalyses of the complexes were also in good agreement with the proposed formulae.



Scheme 2 Synthesis of metal complexes of *N*,*N*-bis(diphenylphosphino)-4-aminodiphenylamine, $[(Ph_2P)_2N–C_6H_4–NH–C_6H_5]$, **1** and *N*,*N*-bis(diphenylphosphino)-2-aminofluorene, $[(Ph_2P)_2N–C_6H_3–CH_2–C_6H_4]$, **2**; (i) 1 equiv. $[MCl_2[cod)]$ (M = Pd or Pt), thf; (ii) 1 equiv. $[MCl_2[cod)]$ (M = Pd or Pt), thf

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



Entry	R	Cat	Product	Conv.(%)	Yield(%)	TOF(h^{-1})
1	4-$CH_3C(O)$-	1d		98.5	91.5	46
		2d		96.2	88.7	44
2	4-CH(O)-	1d		99.8	92.5	46
		2d		98.1	90.1	45
3	4-H	1d		75.9	73.6	37
		2d		81.9	75.7	38

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, 0.01 mmol (1%) Pd, dioxane (3.0 mL). Purity of compounds was checked by ^1H NMR, and yields are based on aryl bromide. All reactions were monitored by GC: 80 °C, 2.0 h. TOF = (mol product/mol Cat) × h^{-1}. GC-yield using diethyleneglycol-di-*n*-butylether as internal standard

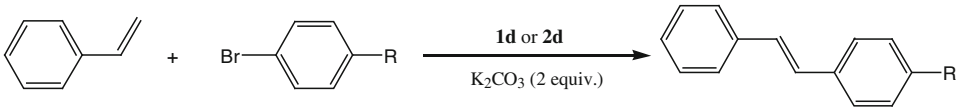
The Suzuki coupling

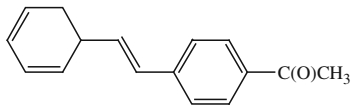
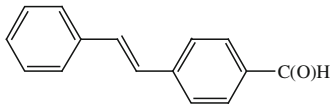
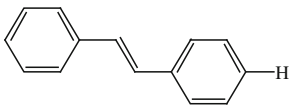
The palladium complexes **1d** and **2d** were investigated as catalysts in the Suzuki reactions between aryl and vinyl halides with boronic acid. In order to survey the reaction parameters for the Suzuki reaction, we examined Cs_2CO_3, K_2CO_3, and K^{t}OBu as bases and DMF and dioxane as solvents. Following optimization experiments, 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 complexes for the coupling of *p*-bromoacetophenone with phenylboronic acid. Control experiments showed that the coupling reaction did not occur in the absence of the palladium complexes. However, when the catalyst was added, *p*-bromoacetophenone, *p*-bromobenzaldehyde, and *p*-bromobenzene reacted with phenylboronic acid to give good yields of the expected products (Table 1).

The Heck coupling

The palladium complexes **1d** and **2d** were also studied as catalysts in the palladium-catalyzed coupling of aryl/vinyl halides with olefins. Generally, when the Heck reaction is conducted with tertiary phosphine or aminophosphine complexes, high temperatures (>120 °C) and polar solvents are required. For the choice of base, we surveyed Cs_2CO_3, K_2CO_3, and K^{t}OBu. After screening experiments, we found that the use of 0.01 mmol (1%) of **1d** or **2d** and 2 equivalents of K_2CO_3 in DMF at 120 °C led to the best conversion within 1.5 h. We initially tested the catalytic activity of both complexes for the coupling of

Table 2 The Heck coupling reactions of aryl bromides with styrene



Entry	R	Cat	Product	Conv.(%)	Yield(%)	TOF(h^{-1})
1	4-$CH_3C(O)$-	1d		95.1	93.7	62
		2d		92.9	91.6	61
2	4-CH(O)-	1d		96.6	94.2	63
		2d		97.1	94.7	63
3	4-H	1d		81.7	79.3	53
		2d		78.5	72.9	49

Reaction conditions: 1.0 mmol of *p*-R-C_6H_4Br aryl bromide, 1.5 mmol of styrene, 2.0 mmol K_2CO_3, 0.01 mmol (1%) Pd, DMF (3.0 mL). Purity of compounds was checked by ^1H NMR, and yields are based on arylbromide. All reactions were monitored by GC: 120 °C, 1.5 h. TOF = (mol product/mol Cat) × h^{-1}. GC-yield using diethyleneglycol-di-*n*-butylether as internal standard

p-bromoacetophenone with styrene. Control experiments indicated that the coupling reaction did not occur in the absence of catalyst. Under the determined reaction conditions, several aryl bromides were reacted with styrene, affording the coupled products in excellent yields. As expected, electron-deficient bromides were beneficial for the conversions (Table 2).

Experimental

All manipulations were performed under an inert atmosphere of dry argon. Solvents were dried using the appropriate reagents and distilled prior to use. The starting materials $[MCl_2(cod)]$ (M = Pt, Pd) were prepared according to literature procedures [1, 2]. Other starting materials were obtained commercially and used as received.

NMR spectra were obtained on a Bruker Avance 400 spectrometer operating at the appropriate frequencies using $SiMe_4$ as internal standard for ^1H and ^{13}C and 85% H_3PO_4 as external standard for ^{31}P spectra. IR spectra were recorded on a Mattson 1000 ATI UNICAM FTIR spectrometer in the range 4,000–400 cm^{-1} in KBr matrix. Elemental analyses were carried out using a Fisons EA 1108 CHNS-O instrument. GC analyses were performed on a Hewlett-Packard 6890N gas chromatograph equipped with capillary column (5% biphenyl, 95% dimethylsiloxane) (30 m × 0.32 mm × 0.25 μm). Melting points were determined in capillary tubes using a Gallenkamp MID 350 BM 2.5 apparatus.

GC analyses were performed on a Hewlett-Packard 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 were as follows for the Suzuki reactions: initial temperature, 50 °C; initial time, hold time (1), 1 min; solvent delay, 3.70 min; temperature ramp 1, 10 °C/min; final temperature, 150 °C; hold time (2), 0; temperature ramp 2, 15 °C/min; final temperature, 250 °C; hold time (3), 3; final time, 20.67 min; injector port temperature, 250 °C; detector temperature, 250 °C; and injection volume, 2.0 μL. The GC parameters were as follows for the Heck reactions: initial temperature, 50 °C; initial time, hold time (1), 1 min; solvent delay, 5.93 min; temperature ramp 1, 13 °C/min; final temperature, 300 °C; hold time (2), 20.23 min; final time, 40.46 min; injector port temperature, 250 °C; detector temperature, 250 °C; and injection volume, 2.0 μL.

*Synthesis of N,N-bis(diphenylphosphino)-4-aminodiphenylamine, (**1**)*

Ph_2PCl (1.26 g, 5.42 mmol) was added dropwise to a solution of 4-aminodiphenylamine (0.50 g, 2.71 mmol) and Et_3N (0.55 g, 5.42 mmol) in thf (25 mL) at room temperature with vigorous stirring. The reaction mixture was stirred at room temperature for 1 h, and then, the white precipitate of $Et_3N.HCl$ was filtered off under argon, and the solvent was removed in vacuum. The light blue solid residue was washed with cold diethyl ether (5 mL) and dried in vacuum. Yield: 0.81 g (54. %), mp: 117–119 °C. ^1H NMR (ppm, $CDCl_3$): δ 6.58 (d, 2H, ^3J = 8.6 Hz, **H**-2), 6.70 (d, 2H, ^3J = 8.7 Hz, **H**-6), 6.91–7.88 (m, 25H, **H**-3, **H**-7, **H**-8 and *o*-, *m*-, *p*-hydrogens of phenyls), 5.70 (br, 1H, N**H**). $^{13}C\{^1H\}$ NMR (ppm, $CDCl_3$): δ 145.6 (**C**-1), 143.5

(C-4), 142.0 (d, *i*-carbons of phenyls, $^{1}J_{^{31}P-^{13}C} = 17.5$ Hz), 133.4 (t, *o*-carbons of phenyls, $^{2}J_{^{31}P-^{13}C} = 11.4$ Hz), 131.4 (s, *p*-carbons of phenyls), 130.2 (C-5), 129.2 (C-7), 129.7 (C-3), 128.0 (t, *m*-carbons of phenyls, $^{3}J_{^{31}P-^{13}C} = 3.1$ Hz), 120.5 (C-8), 117.9 (C-6), 115.4 (C-2), assignment was based on the ^{1}H-^{13}C HETCOR and ^{1}H-^{1}H COSY spectra. ^{31}P{^{1}H} NMR (ppm, $CDCl_3$): δ 69.3 (s). Selected IR (υ, cm^{-1}): 893 (P–N–P), 1,439 (P–Ph), 3,391 (N–H). $C_{36}H_{30}N_2P_2$ (mw: 552.6 g/mol): calcd. C, 78.3; H, 5.5; N, 5.1; found C, 77.9; H, 5.3; N, 4.9%.

*Synthesis of N,N-bis(diphenylphosphino)-2-aminofluorene, (**2**)*

Ph_2PCl (1.28 g, 5.52 mmol) was added dropwise to a solution of 2-aminofluorene (0.50 g, 2.76 mmol) and Et_3N (0.56 g, 5.52 mmol) in thf (15 mL) at room temperature with vigorous stirring. The mixture was stirred at room temperature for 1 h, and then, the white precipitate of $Et_3N{\cdot}HCl$ was filtered off under argon, and the solvent removed in vacuum. The white solid was washed with cold diethyl ether (5 mL) and dried in vacuum. Yield: 1.03 g (68%), mp: 123–125 °C. ^{1}H NMR (ppm, $CDCl_3$): δ 6.70–7.68 (m, 27H, aromatic hydrogens and *o*-, *m*-, *p*-hydrogens of phenyls), 3.59 (s, 2H, CH_2). ^{13}C{^{1}H} NMR (ppm, $CDCl_3$): δ 144.9 (d, C-2, $^{2}J_{(^{31}P-^{13}C)} = 16.9$ Hz), {144.0, 141.4, 140.9, 131.5, 125.5, 124.1, 123.7, 119.4, 118.6 ((C-4)-(C-11), C-13)}, 114.0 (d, C-3, $^{3}J_{(^{31}P-^{13}C)} = 11.8$ Hz), 111.4 (d, C-1, $^{3}J_{(^{31}P-^{13}C)} = 14.0$ Hz), 35.8 (CH_2), 139.0 (d, $^{1}J_{(^{31}P-^{13}C)} = 12.7$ Hz, *i*-carbons of phenyls), 130.2 (t, $^{2}J_{(^{31}P-^{13}C)} = 7.4$ Hz, *o*-carbons of phenyls), 130.0 (s, *p*-carbons of phenyls), 127.5 (t, $^{3}J_{(^{31}P-^{13}C)} = 8.1$ Hz, *m*-carbons of phenyls), assignment was based on the ^{1}H–^{13}C HETCOR and ^{1}H–^{1}H COSY spectra. ^{31}P{^{1}H} NMR (ppm, $CDCl_3$): δ 68.4 (s). Selected IR (υ, cm^{-1}): 901 (P–N–P), 1,433 (P–Ph). $C_{37}H_{29}NP_2$ (mw: 549.6 g/mol): calcd. C, 80.9; H, 5.3; N, 2.6; found C, 80.5; H, 5.1; N, 2.4%.

*Synthesis of N,N-bis(diphenyloxophosphino)-4-aminodiphenylamine, (**1a**)*

Aqueous H_2O_2 (30%, w/w, 0.04 g, 0.36 mmol) was added dropwise to a suspension of (**1**) (0.10 g, 0.18 mmol) in thf, and the mixture was stirred for 2 h at room temperature. The solution was concentrated in vacuum to ca. 1–2 mL, and addition of *n*-hexane (15 mL) gave **2a** as a gray solid, which was collected by filtration and dried in vacuum. Yield: 0.08 g (73%), mp: 195–197 °C. ^{1}H NMR (ppm, $CDCl_3$): δ 6.63 (d, 2H, $^{3}J = 8.6$ Hz, H-2), 6.80 (d, 2H, $^{3}J = 8.2$ Hz, H-6), 6.90 (t, 1H, $^{3}J = 7.2$ Hz, H-8), 7.18–7.32 (m, 16H, H-3, H-7 and *m*-, *p*-hydrogens of phenyls), 7.85–7.90 (dd, 8H, *o*-hydrogens of phenyls, $^{3}J = 7.6$ and 11.4 Hz), 4.07 (br, 1H, NH). ^{13}C{^{1}H} NMR (ppm, $CDCl_3$): δ 142.7 (C-1), 141.5 (C-4), 140.4 (d, *i*-carbons of phenyls, $^{1}J_{(^{31}P-^{13}C)} = 127.3$ Hz), 132.7 (t, *o*-carbons of phenyls, $^{2}J_{(^{31}P-^{13}C)} = 4.8$ Hz), 132.0 (C-5), 131.4 (s, *p*-carbons of phenyls), 130.8 (C-7), 129.2 (C-3), 127.8 (t, *m*-carbons of phenyls, $^{3}J_{(^{31}P-^{13}C)} = 6.6$ Hz), 121.0 (C-8), 117.6 (C-6), 117.5 (C-2), assignment was based on the ^{1}H–^{13}C HETCOR and ^{1}H-^{1}H COSY spectra. ^{31}P{^{1}H} NMR (ppm, $CDCl_3$): δ 23.8 (s). Selected IR (υ, cm^{-1}): 895 (P–N–P), 1209 (P=O), 1446 (P–Ph), 3295 (N–H). $C_{36}H_{30}N_2P_2O_2$(mw: 584.6 g/mol): calcd. C, 74;0 H, 5.2; N, 4.8; found C, 73.7; H, 5; N 4.6%.

*Synthesis of N,N-bis(diphenyloxophosphino)-2-aminofluorene, (**2a**)*

Aqueous H_2O_2 (30%, w/w, 0.04 g, 0.36 mmol) was added dropwise to a suspension of (**2**) (0.10 g, 0.18 mmol) in thf (10 ml), and the mixture was stirred for 2 h at room temperature. The solution was concentrated in vacuum to ca. 1–2 mL, and addition of *n*-hexane (15 mL) gave 2a as a light yellow solid which was filtered off and dried in vacuum. Yield: 0.07 g (64%), mp: 235–237 °C. ^{1}H NMR (ppm, $CDCl_3$): δ 7.14–7.62 (m, 19H, aromatic hydrogens and *m*-,*p*-hydrogens of phenyls), 7.86 (br, 8H, *o*-hydrogens of phenyls), 3.60 (s, 2H, CH_2). ^{13}C{^{1}H} NMR (ppm, $CDCl_3$): δ {143.4, 140.8, 139.9, 137.2, 131.4, 126.7, 127.3, 126.7, 125.3, 124.9, 119.9, 119.6 ((C1)-(C11), C13)}, 36.6 (CH_2), 138.3 (d, $^{1}J_{(^{31}P-^{13}C)} = 129.4$ Hz, *i*-carbons of phenyls), 132.6 (br, *o*-carbons of phenyls), 131.6 (s, *p*-carbons of phenyls), 127.9 (d, $^{3}J_{(^{31}P-^{13}C)} = 6.6$ Hz, *m*-carbons of phenyls), assignment was based on the ^{1}H-^{13}C HETCOR and ^{1}H–^{1}H COSY spectra. ^{31}P{^{1}H} NMR (ppm, $CDCl_3$): δ 24.5 (s). Selected IR (υ, cm^{-1}): 939 (P–N–P), 1,215 (P=O), 1,440 (P–Ph). $C_{37}H_{29}NP_2O_2$ (mw: 581.6 g/mol): calcd. C, 76.4; H 5.0; N, 2.4; found C, 76.0; H, 4.8; N, 2.2%.

*Synthesis of N,N-bis(diphenylthiophosphino)-4-aminodiphenylamine, (**1b**)*

A mixture of (**1**) (0.10 g, 0.18 mmol) and S_8 (0.01 g, 0.36 mmol) in thf (15 mL) was refluxed for 5 h. After cooling, the gray solid was filtered off and dried in vacuum. Yield: 0.06 g (55. %), mp: 177–179 °C. ^{1}H NMR (ppm, $CDCl_3$): δ 6.46 (d, 2H, $^{3}J = 8.4$ Hz, H-2), 6.70 (d, 2H, $J = 7.8$ Hz, H-6), 6.80 (t, 1H, $^{3}J = 6.1$ Hz, H-8), 6.94–7.43 (m, 16H, H-3, H-7 and *m*-, *p*-hydrogens of phenyls), 8.0 (dd, 8H, *o*-hydrogens of phenyls, $^{2}J = 7.6$ Hz and 12.9 Hz), 5.27 (br, 1H, NH). ^{13}C{^{1}H} NMR (ppm, $CDCl_3$): δ 141.4 (C-1), 140.7 (C-4), 132.6 (t, *o*-carbons of phenyls,

$^{2}J_{(^{31}P-^{13}C)}$ = 5.5 Hz), 130.9 (d, $^{1}J_{(^{31}P-^{13}C)}$ = 101.6 Hz, *i*-carbons of phenyls), 130.3 (s, *p*-carbons of phenyls), 128.5 (C-5), 128.2 (C-7), 127.8 (C-3), 126.5 (t, *m*-carbons of phenyls, $^{3}J_{(^{31}P-^{13}C)}$ = 6.7 Hz), 120.3 (C-8), 116.8 (C-6), 115.8 (C-2), assignment was based on the ^{1}H–^{13}C HETCOR and ^{1}H-^{1}H COSY spectra. $^{31}P\{^{1}H\}$ NMR (ppm, $CDCl_3$): δ 68.4 (s). Selected IR (υ, cm^{-1}): 650 (P=S), 875 (P–N-P), 1,440 (P–Ph), 3313 (N–H). $C_{36}H_{30}N_2P_2S_2$ (mw: 616.7 g/mol): calcd. C, 70.1; H, 4.9; N, 4.5; found C, 69.8; H, 4.7; N, 4.4%.

*Synthesis of N,N-bis(diphenylthiophosphino)-2-aminofluorene, (**2b**)*

A mixture of (**2**) (0.10 g, 0.18 mmol) and S_8 (0.01 g, 0.36 mmol) in thf (15 mL) was refluxed for 5 h. After cooling, the light yellow solid was filtered off and dried in vacuum. Yield: 0.07 g (64.%), mp: 184–187 °C. ^{1}H NMR (ppm, $CDCl_3$): δ 7.15–7.79 (m, 19H, aromatic hydrogens and *m-, p*-hydrogens of phenyls), 8.15 (dd, 8H, *o*-hydrogens of phenyls, ^{3}J = 6.8 Hz and 13.4 Hz), 3.60 (s, 2H, C**H**$_2$). $^{13}C\{^{1}H\}$ NMR (ppm, $CDCl_3$): δ {144.5, 143.5, 142.7, 137.6, 131.3, 126.7, 125.9, 124.9, 120.0, 119.2 (C-2, (C-4)-(C-11), C-13)}, 118.0 (d, C-3, ^{3}J = 7.1 Hz), 115.9 (d, C-1, ^{3}J = 6.8 Hz), 36.6 (CH_2), 136.5 (d, $^{1}J_{(^{31}P-^{13}C)}$ = 100.5 Hz, *i*-carbons of phenyls), 133.6 (d, $^{3}J_{(^{31}P-^{13}C)}$ = 12.2 Hz, *o*-carbons of phenyls), 128.9 (s, *p*-carbons of phenyls), 127.5 (d, $^{3}J_{(^{31}P-^{13}C)}$ = 13.8 Hz, *m*-carbons of phenyls), assignment was based on the ^{1}H-^{13}C HETCOR and ^{1}H-^{1}H COSY spectra. $^{31}P\{^{1}H\}$ NMR (ppm, $CDCl_3$): δ 68.8 (s). Selected IR (υ, cm^{-1}): 651 (P=S), 920 (P–N–P), 1,440 (P–Ph). $C_{37}H_{29}NP_2S_2$ (mw: 613.7 g/mol): calcd. C, 72.4; H, 4.8; N, 2.3; found C, 72.0; H, 4.5; N, 2.1%.

*Synthesis of N,N-bis(diphenylselenophosphino)-4-aminodiphenylamine, (**1c**)*

A mixture of (**1**) (0.10 g, 0.18 mmol) and Se (0.03 g, 0.36 mmol) in thf (15 mL) was refluxed for 5 h. After cooling, the gray solid was filtered off and dried in vacuum. Yield: 0.07 g (54. %), mp: 191–194 °C. ^{1}H NMR (ppm, $CDCl_3$): δ 6.56 (d, 2H, ^{3}J = 8.7 Hz, **H**-2), 6.8 (d, 2H, ^{3}J = 8.5 Hz, **H**-6), 6.91 (t, 1H, ^{3}J = 7.9 Hz, **H**-8), 7.06–7.53 (m, 16H, **H**-3, **H**-7 and *m-, p*-hydrogens of phenyls), 8.16–8.21 (dd, 8H, *o*-hydrogens of phenyls, ^{3}J = 7.9 and 13.8 Hz), 5.45 (br, 1**H**, NH). $^{13}C\{^{1}H\}$ NMR (ppm, $CDCl_3$): δ 142.3 (C-1), 141.9 (C-4), 136.3 (d, $^{1}J_{(^{31}P-^{13}C)}$ = 92.0 Hz, *i*-carbons of phenyls), 134.3 (t, *o*-carbons of phenyls, $^{2}J_{(^{31}P-^{13}C)}$ = 11.6 Hz), 131.5 (s, *p*-carbons of phenyls), 130.7 (C-5), 129.2 (C-7), 128.6 (C-3), 127.5 (t, *m*-carbons of phenyls, $^{3}J_{(^{31}P-^{13}C)}$ = 13.7 Hz), 121.4 (C-8), 118.1 (C-6), 116.4 (C-2), assignment was based on the ^{1}H-^{13}C HETCOR and ^{1}H-^{1}H COSY spectra. $^{31}P\{^{1}H\}$ NMR (ppm, $CDCl_3$): δ 69.3 (s, $^{1}J_{P-Se}$: 794.9 Hz). Selected IR (υ, cm^{-1}): 566 (P=Se), 875 (P–N–P), 1,440 (P–Ph), 3314 (N–H). $C_{36}H_{30}N_2P_2Se_2$ (mw: 710.5 g/mol): calcd. C, 60.9; H, 4.3; N, 3.9; found C, 60.5; H, 4.1; N, 3.7%.

*Synthesis of N,N-bis(diphenylselenophosphino)-2-aminofluorene, (**2c**)*

A mixture of (**2**) (0.10 g, 0.18 mmol) and Se (0.03 g, 0.36 mmol) in thf (15 mL) was refluxed for 5 h. After cooling, the gray solid was filtered off and dried in vacuum. Yield: 0.10 g (77%), mp: 187–190 °C. ^{1}H NMR (ppm, $CDCl_3$): δ 7.17–7.78 (m, 19H, aromatic hydrogens and *m-, p*-hydrogens of phenyls), 8.14–8.22 (dd, 8H, *o*-hydrogens of phenyls, ^{3}J = 12.4 Hz and 19.8 Hz), 3.54 (s, 2H, CH_2). $^{13}C\{^{1}H\}$ NMR (ppm, $CDCl_3$): δ {143.6, 142.5, 140.7, 140.4, 137.0, 129.9, 126.8, 126.7, 124.9, 120.1, 118.9, 116.1 ((C-1)-(C-11), C-13)}, 36.60 (CH_2), 136.5 (d, $^{1}J_{(^{31}P-^{13}C)}$ = 92.2 Hz, *i*-carbons of phenyls), 134.3 (d, $^{3}J_{(^{31}P-^{13}C)}$ = 11.7 Hz, *o*-carbons of phenyls), 131.6 (s, *p*-carbons of phenyls), 127.5 (d, $^{3}J_{(^{31}P-^{13}C)}$ = 13.9 Hz, *m*-carbons of phenyls), assignment was based on the ^{1}H-^{13}C HETCOR and ^{1}H–^{1}H COSY spectra. $^{31}P\{^{1}H\}$ NMR (ppm, $CDCl_3$): δ 69.7 (s, $^{1}J_{P-Se}$: 796.0 Hz). Selected IR (υ, cm^{-1}): 567 (P=Se), 912 (P–N–P), 1,439 (P–Ph). $C_{37}H_{29}NP_2Se_2$ (mw: 707.5 g/mol): calcd. C, 62.8; H, 4.1; N, 1.9; found C, 62.5; H, 3.9; N, 1.8%.

*Synthesis of dichloro{N,N-bis(diphenylphosphino)-4-aminodiphenylamine}palladium(II), (**1d**)*

A solution of $[Pd(cod)Cl_2]$ (0.05 g, 0.18 mmol) and (**1**) (0.10 g, 0.18 mmol) in thf (15 mL) was stirred for 1 h at room temperature. The volume was reduced to ca. 1–2 mL under reduced pressure, and addition of diethyl ether (15 mL) gave **1d** as a light brown solid, which was filtered off and dried in vacuum. Yield: 0.10 g (77%), mp: 279–281 °C (dec.). ^{1}H NMR (ppm, $CDCl_3$): δ 6.31 (d, 2H, ^{3}J = 8.6 Hz, **H**-3), 6.70 (d, 2H, ^{3}J = 8.8 Hz, **H**-2), 6.87 (t, 1H, ^{3}J = 7.3 Hz, **H**-8), 7.00 (d, 2H, ^{3}J = 7.89 Hz, **H**-6), 7.21 (t, 2H, ^{3}J = 7.8 Hz, **H**-7), 7.67 (t, 8H, ^{3}J = 6.9 Hz, *m*-hydrogens of phenyls), 7.78 (t, 4H, ^{3}J = 7.3 Hz, *p*-hydrogens of phenyls), 7.84 (dd, 8H, *o*-hydrogens of phenyls, ^{3}J = 7.6 Hz and 12.6 Hz), 8.36 (br, 1H, NH). $^{13}C\{^{1}H\}$ NMR (ppm, $CDCl_3$): δ 144.3 (C-1), 142.2 (C-4), 136.8 (d, $^{1}J_{(^{31}P-^{13}C)}$ = 17.0 Hz, *i*-carbons of phenyls), 134.3 (s, *p*-carbons of phenyls), 134.0 (t, *o*-carbons of phenyls, $^{2}J_{(^{31}P-^{13}C)}$ = 6.3 Hz), 130.1 (t, *m*-carbons of phenyls, $^{3}J_{(^{31}P-^{13}C)}$ = 5.8 Hz), 129.7 (C-7), 128.8 (C-3), 126.9 (C-5), 121.6 (C-8), 118.8 (C-6), 115.7 (**C**-2), assignment was based

on the ^{1}H-^{13}C HETCOR and ^{1}H-^{1}H COSY spectra. $^{31}P\{^{1}H\}$ NMR (ppm, $CDCl_3$): δ 35.9 (s). Selected IR (υ, cm^{-1}): 906 (P–N–P), 1,439 (P–Ph), 3,300 (N–H). $C_{36}H_{30}N_2P_2PdCl_2$ (mw: 729.9 g/mol): calcd. C, 59.2; H, 4.1; N, 3.8; found C, 58.9; H, 4; N, 3.7%.

*Synthesis of dichloro{N,N-bis(diphenylphosphino)-2-aminofluorene}palladium(II), (**2d**)*

A solution of $[Pd(cod)Cl_2]$ (0.05 g, 0.18 mmol) and (**2**) (0.10 g, 0.18 mmol) in thf (15 mL) was stirred for 1 h at room temperature. The volume was reduced to ca. 1–2 mL under reduced pressure, and addition of diethyl ether (15 mL) gave **2d** as a yellow solid which was collected by filtration and dried in vacuum. Yield: 0.09 g (69%), mp: 255–258 °C (dec.). ^{1}H NMR (ppm, $CDCl_3$): δ {6.30 (s, 1H), 6.55 (s, 2H), 7.28–7.67 (m, 16H, aromatic hydrogens and *m-*, *p*-hydrogens of phenyls}, 7.94 (br, 8H, *o*-hydrogens of phenyls), 3.62 (s, 2H, $\underline{C}H_2$). $^{13}C\{^{1}H\}$ NMR (ppm, $CDCl_3$): δ {144.5, 143.2, 141.6, 139.9, 138.3, 127.2, 125.1, 124.3, 123.6, 120.6, 120.2, 116.8 (($\underline{C}$-1)-($\underline{C}$-11), $\underline{C}$-13)}, 36.9 ($\underline{C}H_2$), 137.2 (d, $^{1}J_{(^{31}P-^{13}C)} = 14.2$ Hz, *i*-carbons of phenyls), 134.0 (t, $^{3}J_{(^{31}P-^{13}C)} = 6.6$ Hz, *o*-carbons of phenyls), 133.5 (s, *p*-carbons of phenyls), 129.4 (t, $^{3}J_{(^{31}P-^{13}C)} = 6.3$ Hz, *m*-carbons of phenyls), assignment was based on the ^{1}H-^{13}C HETCOR and ^{1}H-^{1}H COSY spectra. $^{31}P\{^{1}H\}$ NMR (ppm, $CDCl_3$): δ 35.4 (s). Selected IR (υ, cm^{-1}): 910 (P–N–P), 1,434 (P–Ph). $C_{37}H_{29}NP_2PdCl_2$ (mw: 726.9 g/mol): calcd. C, 61.1; H,4.0; N, 1.9; found C, 60.6; H, 3.8; N, 1.7%.

*Synthesis of dichloro{N,N-bis(diphenylphosphino)-4-aminodiphenylamine} platinum(II), (**1e**)*

A solution of $[Pt(cod)Cl_2]$ (0.07 g, 0.18 mmol) and (**1**) (0.10 g, 0.18 mmol) in thf (15 mL) was stirred for 1 h at room temperature. The volume was reduced to ca. 1–2 mL under reduced pressure, and addition of diethyl ether (15 mL) gave **1e** as a light blue solid which was filtered off and dried in vacuum. Yield: 0.10 g (67%), mp: >300 °C (dec.). ^{1}H NMR (ppm, $CDCl_3$): δ 6.25 (d, 2H, $^{3}J = 8.0$ Hz, $\underline{H}$-6), 6.72 (d, 2H, $^{3}J = 8.2$ Hz, $\underline{H}$-2), 6.91 (t, 1H, $^{3}J = 7.2$ Hz, $\underline{H}$-8), 7.00 (d, 2H, $^{3}J = 7.7$ Hz, $\underline{H}$-3), 7.21 (t, 2H, $^{3}J = 7.4$ Hz, $\underline{H}$-7), 7.66–7.79 (m, 20H), 8.35 (br, 1H, NH). $^{13}C\{^{1}H\}$ NMR (ppm, $CDCl_3$): δ 144.2 ($\underline{C}$-1), 142.2 ($\underline{C}$-4), 134.5 (d, $^{1}J_{(^{31}P-^{13}C)} = 17.0$ Hz, *i*-carbons of phenyls), 134.1 (s, *p*-carbons of phenyls), 133.8 (t, *o*-carbons of phenyls, $^{2}J_{(^{31}P-^{13}C)} = 6.2$ Hz), 129.9 (t, *m*-carbons of phenyls, $^{3}J_{(^{31}P-^{13}C)} = 6.0$ Hz), 129.7 ($\underline{C}$-5), 129.1 ($\underline{C}$-7), 127.8 ($\underline{C}$-6), 121.5 ($\underline{C}$-8), 118.7 ($\underline{C}$-3), 115.8 ($\underline{C}$-2), assignment was based on the ^{1}H-^{13}C HETCOR and ^{1}H-^{1}H COSY spectra. $^{31}P\{^{1}H\}$ NMR (ppm, $CDCl_3$): δ 21.2 (s, $^{1}J_{Pt-P}$: 3335.8 Hz). Selected IR (υ, cm^{-1}): 894 (P–N–P), 1,440 (P–Ph), 3,326 (N–H). $C_{36}H_{30}N_2P_2PtCl_2$ (mw: 818.6 g/mol): calcd. C, 52.8; H, 3.7; N, 3.4; found C, 52.7; H, 3.5; N, 3.2%.

*Synthesis of dichloro{N,N-bis(diphenylphosphino)-2-aminofluorene}platinum(II), (**2e**)*

A solution of $[Pt(cod)Cl_2]$ (0.07 g, 0.18 mmol) and (**2**) (0.10 g, 0.18 mmol) in thf (15 mL) was stirred for 1 h at room temperature. The volume was reduced to ca. 1–2 mL under reduced pressure, and addition of diethyl ether (15 mL) gave **2e** as a white solid which was filtered off and dried in vacuum. Yield: 0.08 g (53. %), mp: 251–253 °C (dec.). ^{1}H NMR (ppm, $CDCl_3$): δ 7.29–7.68 (m, 19H, aromatic hydrogens and *m-*, *p*-hydrogens of phenyls), 8.04 (br, 8H, *o*-hydrogens of phenyls), 3.62 (s, 2H, $\underline{C}H_2$). $^{13}C\{^{1}H\}$ NMR (ppm, $CDCl_3$): δ {144.4, 143.3, 141.5, 140.1, 139.4, 131.2, 127.2, 126.1, 125.1, 124.1, 120.5, 120.2 (($\underline{C}$-1)-($\underline{C}$-11), $\underline{C}$-13)}, 136.5 (d, $^{1}J_{(^{31}P-^{13}C)} = 15.6$ Hz, *i*-carbons of phenyls), 36.6 ($\underline{C}H_2$), 133.8 (t, $^{3}J_{(^{31}P-^{13}C)} = 6.4$ Hz, *o*-carbons of phenyls), 133.3 (s, *p*-carbons of phenyls), 129.2 (t, $^{3}J_{(^{31}P-^{13}C)} = 6.3$ Hz, *m*-carbons of phenyls), assignment was based on the ^{1}H-^{13}C HETCOR and ^{1}H–^{1}H COSY spectra. $^{31}P\{^{1}H\}$ NMR (ppm, $CDCl_3$): δ 21.3 (s, $^{1}J_{Pt-P}$: 3337.1 Hz). Selected IR (υ, cm^{-1}): 903 (P–N–P), 1435 (P–Ph). $C_{37}H_{29}NP_2PtCl_2$ (mw: 815.6 g/mol): calcd. C, 54.5; H 3.6; N 1.7; found C, 54.0; H 3.4; N 1.6%.

General procedure for Suzuki coupling reactions

Complex (**1d**) or (**2d**), (0.01 mmol), aryl bromide (1.0 mmol), phenylboronic acid (1.5 mmol), Cs_2CO_3 (2 mmol) and dioxane (3 mL) were placed in a Schlenk tube under argon, and the mixture was heated at 80 °C for 2.0 h. After the completion of the reaction, the mixture was cooled and extracted with ethyl acetate/hexane (1:5). The extract was 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 by GC and ^{1}H NMR, and yields are based on the aryl bromide.

General procedure for Heck reactions

Complex (**1d**) or (**2d**), (0.01 mmol), aryl bromide (1.0 mmol), styrene (1.5 mmol), K_2CO_3 (2 mmol), and DMF (3 mL) were placed in a Schlenk tube under argon, and the mixture was heated at 120 °C for 1.5 h. After completion of the reaction, the mixture was cooled and extracted with ethyl acetate/hexane (1:5). The extract was 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 by GC and ^{1}H NMR, and yields are based on the aryl bromide.

Conclusion and perspectives

In conclusion, we have synthesized two new bis(phosphino)amines and their derivatives including oxides, sulfides, selenides, as well as transition metal complexes. The ligands coordinate in a *cis*-fashion to both Pd(II) and Pt(II), as indicated by $^{31}P\{^{1}H\}$ NMR spectroscopy. Furthermore, we have investigated the application of these complexes in the Suzuki and Heck coupling of aryl bromides. The two platinum complexes showed no catalytic activity, probably due to strong Pt–C bonds. In contrast, both palladium complexes were active catalysts for the Suzuki and Heck reactions. In both cases, the catalytic activities were higher in reactions of aryl bromides with electron-withdrawing substituents than those with electron-releasing substituents. Following our previous studies that have shown Pd complexes of ether-derivatized aminophosphines to be highly effective catalysts for C–C cross-coupling reactions [18, 19], we decided to compare catalytic activities of these Pd complexes with those of the present bis(diphenylphosphino)amines (**1**) and (**2**). Higher yields of biphenyl were obtained with **1d** and **2d** as compared with the other palladium-bis(phosphino)amine complexes, possessing electron-donating methoxy substituents. Although the present ligands are unstable, they can be handled in air. The palladium and platinum complexes described in this paper are air-stable, both in the solid state and in solution. All materials could be handled in air although the coupling reactions were conducted under an inert atmosphere. In summary, we have shown that new P–N–P ligands and their palladium complexes have various advantages, as follows: (1) the ligands are easily prepared from commercially available and inexpensive starting materials; (2) the catalysts can be handled in air; (3) reaction times are reduced and do not require an induction period.

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