Inorganica Chimica Acta 385 (2012) 164–169

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Synthesis and reactivity of bis(diphenylphosphino)amine ligands and their application in Suzuki cross-coupling reactions

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ARTICLE INFO

Article history:
Received 27 July 2011
Received in revised form 20 December 2011
Accepted 26 January 2012
Available online 1 February 2012

Keywords:
Bis(phosphino)amine
Palladium complex
X-ray structure
Catalysis
Suzuki reaction

ABSTRACT

Two new bis(diphenylphosphino)amines, *N,N*-bis(diphenylphosphino)benzidine **1** and *N,N*-bis(diphenylphosphino)-3,3-dimethoxybenzidine **2** were prepared by aminolysis. Their corresponding oxides, sulfides and selenides were readily prepared by reaction with hydrogen peroxide, elemental sulfur or grey selenium, respectively. Symmetric dinuclear palladium and platinum complexes were also isolated from the reaction with $[M(cod)Cl_2]$ (M = Pd or Pt, cod = cycloocta-1,5-diene). All compounds were characterized by IR and NMR spectroscopy and elemental analysis and the structure of $[(Ph_2P)_2N–C_6H_4–C_6H_4–N(PPh_2)_2]$ was determined by single crystal X-ray diffraction. The catalytic activity of palladium complexes in Suzuki coupling reactions was also investigated.

1. Introduction

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 [1]. To date, a number of such systems with a variety of backbone frameworks have been synthesized and their transition metal chemistry has been explored [2]. Potentially this ligand family is attractive since their various structural modifications are accessible via simple P–N bond formation. The effect of ligand type on structure and reactivity of transition metal complexes is an important topic of research in coordination and organometallic chemistry [3]. Ligands containing direct phosphorus–nitrogen bonds are quite attractive as structural modifications can be introduced via simple P–N bond formation [4] and they have proved to be versatile ligands, and varying the substituents on both to P- and N-centers gives rise the changes in the P–N–P angle and to conformation around the P-centers [5]. Small variations in the ligands can cause significant changes in their coordination behavior and the structural features of the resulting complexes [6].

Because of their remarkable catalytic potential and their large versatility, palladium complexes have become the most popular organometallics used in organic synthesis [7]. In particular, palladium catalyzes most of the carbon–carbon bond formation reactions, such as Heck and Suzuki reactions, [8] which are powerful tools for the preparation of unsymmetrical biaryl and stilbene compounds [9] and represent essential steps in the synthesis of many compounds including herbicides [10] and natural products [11].

In our previous studies, we have shown that many bis(aminophosphine) palladium(II) complexes can be used in Heck and Suzuki cross-coupling reactions. 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, herein we describe the synthesis and characterization of two new bis(phosphine)amine ligands and their reactivity towards chalcogens and with transition metal complexes. The application of the Pd(II) complexes as pre-catalysts in Suzuki cross-coupling reactions is also described.

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 $[M(cod)Cl_2]$ (M = Pd, Pt; cod = cycloocta-1,5-diene) were prepared according to literature procedures [12,13]. Other starting materials were obtained from commercial sources and were used as received. NMR spectra were obtained on a Bruker AV400 spectrometer operating at the appropriate frequencies using $SiMe_4$ (for ^1H and ^{13}C) as internal and 85% H_3PO_4 (for ^{31}P) as external references. IR spectra were recorded on a Mattson 1000 ATI UNICAM FT-IR spectrometer in the range 4000–400 cm^{-1} in KBr matrices. Elemental analyses

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doi:10.1016/j.ica.2012.01.057

were carried out using a Fisons EA 1108 CHNS-O instrument. GC analyses were performed on a HP 6890 N 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 with a Gallenkamp MID 350 BM 2.5 apparatus.

2.1. Synthesis of $[(Ph_2P)_2N–C_6H_4–C_6H_4–N(PPh_2)_2]$ **1**

Chlorodiphenylphosphine (2.395 g, 10.86 mmol) was added dropwise into a solution of benzidine (0.500 g, 2.71 mmol) and triethylamine (1.23 g, 12.2 mmol) in dichloromethane (25 mL) at 0 °C, the resulting suspension was stirred for 1 h and then the solvent was removed under reduced pressure. The remaining solid was consecutively washed with distilled water (25 mL) and diethyl ether (3 × 10 mL), and dried in *vacuum* to produce a white solid. Yield: 2.17 g (86.8%), mp: 210–211 °C ^{1}H NMR (ppm, $CDCl_3$): δ {6.66 (d, 4H, $^3J_{HH}$ = 7.9 Hz, H-2), 7.07 (d, 4H, $^3J_{HH}$ = 7.9 Hz, H-3), 7.29–7.38 (m, 40H)} (Ar). ^{13}C-{^{1}H} NMR (ppm, $CDCl_3$): δ 145.30 (d, C-1, $^1J_{31P-13C}$ = 17.15 Hz), 130.69 (C-4), 127.30 (C-3), 116.27 (d, C-2, $^1J_{31P-13C}$ = 12.3 Hz), 140.16 (d, $^1J_{31P-13C}$ = 12.2 Hz, *i*-carbon atoms of phenyls), 131.33 (d, $^2J_{31P-13C}$ = 7.6 Hz, *o*-carbon atoms of phenyls), 131.13 (s, *p*-carbon atoms of phenyls), 128.56 (t, $^3J_{31P-13C}$ = 6.1 Hz, *m*-carbon atoms of phenyls), assignment was based on the ^{1}H-^{13}C HETCOR spectrum. ^{31}P-{^{1}H} NMR (ppm, $CDCl_3$): δ 68.4 (s). Selected IR (ν, cm^{-1}): 901 (P–N–P), 1431 (P-Ph). $C_{60}H_{48}N_2P_4$: Calc.: C, 78.25; H, 5.25; N, 3.04. Found: C, 77.87; H, 5.11; N, 2.83%.

2.2. Synthesis of $(Ph_2P)_2N–C_6H_3–(o\text{-}OCH_3)–C_6H_3–(o\text{-}OCH_3)–N(PPh_2)_2$ **2**

Chlorodiphenylphosphine (1.806 g, 8.19 mmol) was added dropwise, to a solution of 3,3-dimethoxybenzidine (0.500 g, 2.05 mmol) and triethylamine (0.900 g, 8.89 mmol) in dichloromethane (15 mL) at 0 °C, with vigorous stirring. The mixture was stirred at 0 °C for 1 h, and then the solvent was removed under reduced pressure. Thf (10 mL) was added to form a white precipitate (triethylammmonium chloride) that was removed by filtration under argon and the solvent was then removed under vacuum. The brown solid was dried in *vacuum*. Yield: 1.43 g (71.3%), mp: 195–197 °C. ^{1}H NMR (ppm, $CDCl_3$): δ {6.91–7.99 (m, 46H, Ar), 3.48 (s, 6H, OCH_3). ^{13}C-{^{1}H} NMR (ppm, $CDCl_3$): δ 148.16 (C-3), 134.50 (C-2), 131.48 (C-6), 128.03 (C-5), 118.38 (C-1), 110.23 (C-4), 54.7 (OCH_3), 138.93 (d, $^1J_{31P-13C}$ = 21.5 Hz, *i*-carbon atoms of phenyls), 131.92 (d, $^2J_{31P-13C}$ = 24.5 Hz, *o*-carbon atoms of phenyls), 130.57 (s, *p*-carbon atoms of phenyls), 128.84 (d, $^3J_{31P-13C}$ = 7.0 Hz, *m*-carbon atoms of phenyls), assignment was based on the ^{1}H–13C HETCOR spectrum. ^{31}P-{^{1}H} NMR (ppm, $CDCl_3$): δ 68.8 (s). Selected IR (ν, cm^{-1}): 893 (P–N–P), 1439 (P-Ph), 2853 (OMe). $C_{62}H_{52}N_2P_4O_2$: Calc.: C, 75.91; H, 5.34; N, 2.86. Found: C, 75.63; H, 5.12; N, 2.86%.

2.3. Synthesis of $(Ph_2P(O))_2N–C_6H_4–C_6H_4–N(P(O)Ph_2)_2$ **1a**

Aqueous hydrogen peroxide (30%, w/w, 0.0492 g, 0.434 mmol) was added dropwise to a suspension of **1** (0.100 g, 0.109 mmol) in thf (20 mL) and the mixture was stirred for 2 h at room temperature. The volume of the solvent was reduced under *vacuum* to ca. 1–2 mL and *n*-hexane (25 mL) was added to afford **1a** as a white solid which was collected by suction filtration and dried in *vacuum*. Yield: 0.214 g (88.1%), mp: 275–277 °C. ^{1}H NMR (ppm, $CDCl_3$): δ {6.91 (d, 4H, $^3J_{HH}$ = 8.5 Hz), 7.18–7.37 (m, 28H), 7.81–7.86 (m, 16H)} (Ar). ^{31}P-{^{1}H} NMR (ppm, $CDCl_3$): δ 24.5 (s). Selected IR (ν, cm^{-1}): 908 (P–N–P), 1216 (P═O), 1447 (P-Ph). $C_{60}H_{48}N_2P_4O_4$: Calc.: C, 73.17; H, 4.91; N, 2.84. Found: C, 72.79; H, 4.73; N, 2.66%.

2.4. Synthesis of $(Ph_2P(O))_2N–C_6H_3–(o\text{-}OCH_3)–C_6H_3–(o\text{-}OCH_3)–N(P(O)Ph_2)_2$ **2a**

Aqueous hydrogen peroxide (30%, w/w, 0.0462 g, 0.408 mmol) was added dropwise to a suspension of **2** (0.100 g, 0.102 mmol) in thf (20 ml) and the mixture was stirred for 2 h at room temperature. The volume of solvent was reduced under *vacuum* to ca. 1–2 mL and *n*-hexane (15 mL) was added to give **2a** as a light grey solid which was collected by suction filtration and dried in *vacuum*. Yield: 0.0833 g (78.2%), mp: 233–235 °C. ^{1}H NMR (ppm, $CDCl_3$): δ {7.14-7.56 (m, 30H), 7.75–7.91 (m, 16H)} (Ar), 3.50 (s, 6H, OCH_3). ^{31}P-{^{1}H} NMR (ppm, $CDCl_3$): δ 29.6 (s). Selected IR (ν, cm^{-1}): 912 (P–N–P), 1221 (P═O), 1439 (P-Ph), 2852 (OMe). $C_{62}H_{52}N_2P_4O_6$: Calc. C, 71.26; H 5.02; N, 2.68. Found: C, 70.89; H, 4.84; N, 2.51%.

2.5. Synthesis of $(Ph_2P(S))_2N–C_6H_4–C_6H_4–N(P(S)Ph_2)_2$ **1b**

Compound **1** (0.100 g, 0.109 mmol) and elemental sulfur (0.0139 g, 0.434 mmol) were heated to reflux in thf (25 mL) for 5 h. After allowing the mixture to cool to room temperature the white solid was collected by suction filtration and dried in *vacuum*. Yield: 0.0788 g (69.2%), mp: 331–333 °C. ^{1}H NMR (ppm, $CDCl_3$): δ {6.82 (d, 4H, $^3J_{HH}$ = 8.5 Hz), 7.19–7.29 (m, 24H), 7.58 (d, 4H, $^3J_{HH}$ = 8.3 Hz), 8.06–8.11 (q, 16H, $^3J_{HH}$ = 7.0 Hz)} (Ar) ^{31}P-{^{1}H} NMR (ppm, $CDCl_3$): δ 69.1 (s). Selected IR (ν, cm^{-1}): 657 (P = S), 889 (P–N–P), 1447 (P-Ph). $C_{60}H_{48}N_2P_4S_4$: Calc. C, 68.69; H, 4.61; N, 2.67. Found: C, 68.35; H, 4.46; N, 2.52%.

2.6. Synthesis of $(Ph_2P(S))_2N–C_6H_3–(o\text{-}OCH_3)–C_6H_3–(o\text{-}OCH_3)–N(P(S)Ph_2)_2$ **2b**

Compound **2** (0.100 g, 0.102 mmol) and elemental sulfur (0.0131 g, 0.409 mmol) were heated to reflux in thf (25 mL) for 5 h. After allowing the mixture to cool to room temperature, the white solid was collected by suction filtration and dried in *vacuum*. Yield: 0.0791 g (69.9%), mp: 281–283 °C. ^{1}H NMR (ppm, $CDCl_3$): δ {7.10–7.23 (m, 14H), 7.36–7.49 (16H), 7.87–8.29 (m, 16H)} (Ar), 3.37 (s, 6H, OCH_3). ^{31}P-{^{1}H} NMR (ppm, $CDCl_3$): δ 69.1 (s). Selected IR (ν, cm^{-1}): 650 (P–S), 912 (P–N–P), 1439 (P-Ph), 2838 (OMe). $C_{62}H_{52}N_2P_4S_4$: Calc.: C, 67.13; H, 4.73; N, 2.53. Found: C, 66.78; H, 4.52; N, 2.33%.

2.7. Synthesis of $(Ph_2P(Se))_2N–C_6H_4–C_6H_4–N(P(Se)Ph_2)_2$ **1c**

Compound **1** (0.100 g, 0.109 mmol) and grey selenium (0.0343 g, 0.434 mmol) were heated to reflux in thf (25 mL) for 5 h. After allowing the mixture to cool to room temperature the white solid was collected by suction filtration and dried in *vacuum*. Yield: 0.0831 g (61.9%), mp: 271–273 °C. ^{1}H NMR (ppm, $CDCl_3$): δ {6.82 (d, 4H, $^3J_{HH}$ = 8.3 Hz), 7.21–7.30 (m, 24H), 7.59 (d, 4H, $^3J_{HH}$ = 7.6 Hz), 8.12–8.18 (q, 16H, $^3J_{HH}$ = 7.4 Hz)} (Ar) ^{31}P-{^{1}H} NMR (ppm, $CDCl_3$): δ 69.7 (s). Selected IR (ν, cm^{-1}): 565 (P═Se), 889 (P–N–P), 1439 (P-Ph). $C_{60}H_{48}N_2P_4Se_4$: Calc.: C, 58.27; H, 3.91; N, 2.27. Found: C, 57.91; H, 3.68; N, 2.12%.

2.8. Synthesis of $(Ph_2P(Se))_2N–C_6H_3–(o\text{-}OCH_3)–C_6H_3–(o\text{-}OCH_3)–N(P(Se)Ph_2)_2$ **2c**

Compound **2** (0.100 g, 0.102 mmol) and grey selenium (0.0322 g, 0.408 mmol) were heated to reflux in thf (25 mL) for 5 h. After allowing the mixture to cool to room temperature the white solid was collected by suction filtration and dried in *vacuum*. Yield: 0.0977 g (73.9%), mp: 343–345 °C. ^{1}H NMR (ppm, $CDCl_3$): δ {7.11–7.50 (m, 16H), 7.92–8.37 (m, 30H)] (Ar), 3.36 (s, 6H, OCH_3). ^{31}P-{^{1}H} NMR (ppm, $CDCl_3$): δ 67.6 (s). Selected IR (ν, cm^{-1}): 554

(P=Se), 901 (P–N–P), 1439 (P-Ph), 2838 (OMe). $C_{62}H_{52}N_2P_4Se_4$: Calc.: C, 57.42; H, 4.04; N, 2.16. Found: C, 57.09; H, 3.86; N, 2.01%.

2.9. Synthesis of $[PdCl_2\{(Ph_2P)_2N–C_6H_4–C_6H_4–N(PPh_2)_2PdCl_2\}]$ **1d**

$[Pd(cod)Cl_2]$ (0.0619 g, 0.217 mmol) and **1** (0.100 g, 0.109 mmol) were dissolved in thf (25 mL) and stirred for 1 h at room temperature. The volume of the solvent was reduced to ca. 1–2 mL by evaporation under reduced pressure and diethyl ether (15 mL) was added to afford **1d** as a light yellow solid which was collected by suction filtration and dried in *vacuum*. Yield: 0.107 g (77.3%), mp: >300 °C (dec.). ^{1}H NMR (ppm, $CDCl_3$): δ {6.53 (d, 4H, $^3J_{HH}$ = 8.5 Hz), 7.27–7.38 (m, 14H), 7.64–7.87 (m, 30H)} (Ar). ^{31}P-{^{1}H} NMR (ppm, $CDCl_3$): δ 34.9 (s). Selected IR (ν, cm^{-1}): 893 (P–N–P), 1440 (P-Ph). $C_{60}H_{48}N_2P_4Pd_2Cl_4$: Calc. C, 56.50; H, 3.79; N, 2.20. Found: C, 56.13; H, 3.61; N, 2.04%.

2.10. Synthesis of $[PdCl_2\{(Ph_2P)_2N–C_6H_3–(o\text{-}OCH_3)–C_6H_3–(o\text{-}OCH_3)–N(PPh_2)_2\}PdCl_2]$ **2d**

$[Pd(cod)Cl_2]$ (0.0581 g, 0.204 mmol) and **2** (0.100 g, 0.102 mmol) were dissolved in thf (15 mL) and stirred for 1 h at room temperature. The volume of the solvent was reduced to ca. 1–2 mL by evaporation under reduced pressure and diethyl ether (15 mL) was added to afford **2d** as a yellow solid which was collected by suction filtration and dried in *vacuum*. Yield: 0.0893 g (65.6%), mp: 262–264 °C. ^{1}H NMR (ppm, $CDCl_3$): δ 6.90–7.82 (m, 46H, Ar); 3.87 (s, 6H, OCH_3). ^{31}P-{^{1}H} NMR (ppm, $CDCl_3$): δ 41.4 (s). Selected IR (ν, cm^{-1}): 892 (P–N–P), 1438 (P-Ph), 2857 (OMe). $C_{62}H_{52}N_2P_4O_2Pd_2Cl_4$: Calc.: C, 55.76; H, 3.92; N, 2.10. Found: C, 55.49; H, 3.75; N, 1.96%.

2.11. Synthesis of $[PtCl_2\{(Ph_2P)_2N–C_6H_4–C_6H_4–N(PPh_2)_2\}PtCl_2]$ **1e**

$[Pt(cod)Cl_2]$ (0.0812 g, 0.217 mmol) and **1** (0.100 g, 0.109 mmol) were dissolved in dry thf (25 mL) and stirred for 1 h. The volume of the solvent was reduced to ca. 1–2 mL by evaporation under reduced pressure and diethyl ether (15 mL) was added to afford **1e** as a white solid which was collected by suction filtration and dried in *vacuum*. Yield: 0.114 g (72.2%), mp: >300 °C (dec.). ^{1}H NMR (ppm, $CDCl_3$): δ {6.53 (d, 4H, $^3J_{HH}$ = 8.5 Hz), 7.27–7.38 (m, 14H), 7.64–7.87 (m, 30H)} (Ar). ^{31}P-{^{1}H} NMR (ppm, $CDCl_3$): δ 20.5 (s, $^1J_{Pt–P}$: 3421.0 Hz). Selected IR (ν, cm^{-1}): 906 (P–N–P), 1439 (P-Ph). $C_{60}H_{48}N_2P_4Pt_2Cl_4$: Calc.: C, 49.60; H, 3.33; N, 1.93. Found: C, 49.24; H, 3.17; N, 1.75%.

2.12. Synthesis of $[PtCl_2\{(Ph_2P)_2N–C_6H_3–(o\text{-}OCH_3)–C_6H_3–(o\text{-}OCH_3)–N(PPh_2)_2\}PtCl_2]$ **2e**

$[Pd(cod)Cl_2]$ (0.0762 g, 0.204 mmol) and **2** (0.100 g, 0.102 mmol) were dissolved in thf (15 mL) and stirred for 1 h at room temperature. The volume of the solvent was reduced to ca. 1–2 mL by evaporation under reduced pressure and diethyl ether (15 mL) was added to afford **2e** as a white solid which was collected by suction filtration and dried in *vacuum*. Yield: 0.118 g (76.5%), mp: 195–198 °C. ^{1}H NMR (ppm, $CDCl_3$): δ 7.13–7.90 (m, 46H, Ar), 3.91 (s, 6H, OCH_3). ^{31}P-{^{1}H} NMR (ppm, $CDCl_3$): δ 19.5 (s, $^1J_{Pt–P}$: 3110.2 Hz). Selected IR (ν, cm^{-1}): 925 (P–N–P), 1438 (P-Ph), 2852 (OMe). $C_{62}H_{52}N_2P_4O_2Pt_2Cl_4$: Calc.: C, 49.22; H, 3.46; N, 1.85. Found: C, 48.85; H, 3.31; N, 1.72%.

2.13. General procedure for the Suzuki coupling reaction

The palladium complexes (**1d** or **2d**) (0.01 mmol, 1%), arylbromide (1.0 mmol), phenylboronic acid (1.5 mmol), Cs_2CO_3 (2.0 mmol) and 1,4-dioxane (3 mL) were placed into a Schlenk tube and the mixture was heated to 80 °C for 1.5 h. The progress of the reaction was monitored by GC. Upon completion, the mixture was cooled, the product extracted with ethyl acetate/hexane (1:5), filtered through silica gel with copious washing, concentrated and purified by flash chromatography on silica gel. The purity of the compounds was determined by NMR and GC, and yields are based on arylbromide.

Table 1
Crystal data and details of the structure determination for 1.

	1
Chemical formula	$C_{72}H_{60}N_2P_4$
Formula weight	1077.10
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	8.7561(9)
b (Å)	16.4593(16)
c (Å)	19.728(2)
α (°)	90
β (°)	100.113(11)
γ (°)	90
V (Å^3)	2799.0(5)
Z	4
D_{calc} (g cm^{-3})	1.278
$F(000)$	1132
μ (mm^{-1})	0.182
T (K)	140(2)
λ (Å)	0.71073
Measured reflections	22586
Unique reflections	5685
Unique reflections [$I > 2\sigma(I)$]	2949
Data/parameters	5685/352
R^a [$I > 2\sigma(I)$]	0.0606
$wR2^a$ (all data)	0.1310
Goodness-of-fit (GOF)[b]	0.906

[a] $R = \sum||F_0| - |F_c||/\Sigma|F_0|$, $wR2 = \{\sum[w(F_0^2 - F_c^2)2]/\sum[w(F_0^2)^2]\}^{1/2}$.
[b] $GOF = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$ where n is the number of data and p is the number of parameters refined.

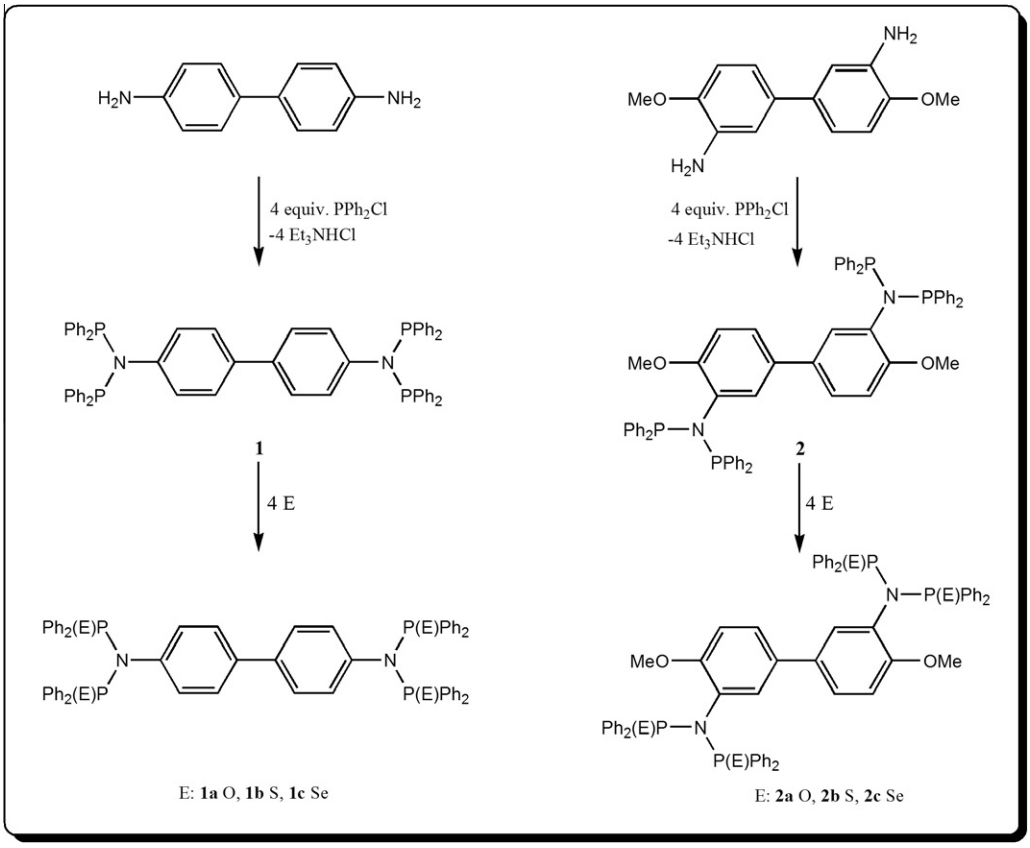
2.14. X-ray diffraction structure analysis

Single crystals of **1** suitable for X-ray diffraction analysis were obtained by recrystallization in benzene. The solid state structure of this compound was established by single crystal X-ray diffraction and the details of the structure determination are given in Table 1.

Data collection was performed at low temperature using Mo Kα radiation. An Oxford Diffraction Sapphire/KM4 CCD, having a kappa geometry goniometer, was employed to measure the diffraction data of **1**. Data reduction was carried out by means of Crysalis PRO [14] and then corrected for absorption [15]. Solution and refinement were calculated by SHELX [16]. Structure was refined using full-matrix least-squares on F^2 with all non hydrogen atoms anisotropically defined. Hydrogen atoms were placed in calculated positions and then refined as isotropic with free coordinates and U_{iso}.

3. Results and discussion

The bis(phosphino)amine ligands *N*,*N*-bis(diphenylphosphino)benzidine **1** and *N*,*N*-bis(diphenylphosphino)-3,3-dimethoxybenzidine **2** were prepared via aminolysis between benzidine or 3,3-dimethoxybenzidine with two equivalents of Ph_2PCl in the presence of Et_3N (Scheme 1) [17]. The reactions were monitored by ^{31}P-{^{1}H} NMR spectroscopy which indicated that the reactions had reached completion within 1 h. Compound **1** is an air-stable solid and therefore the Et_3NHCl by-product could be removed easily by washing with distilled water, whereas **2** is unstable and was purified by extraction into dry thf.



Scheme 1. Synthesis of **1** and **2** and their chalcogen (O, S and Se) derivatives.

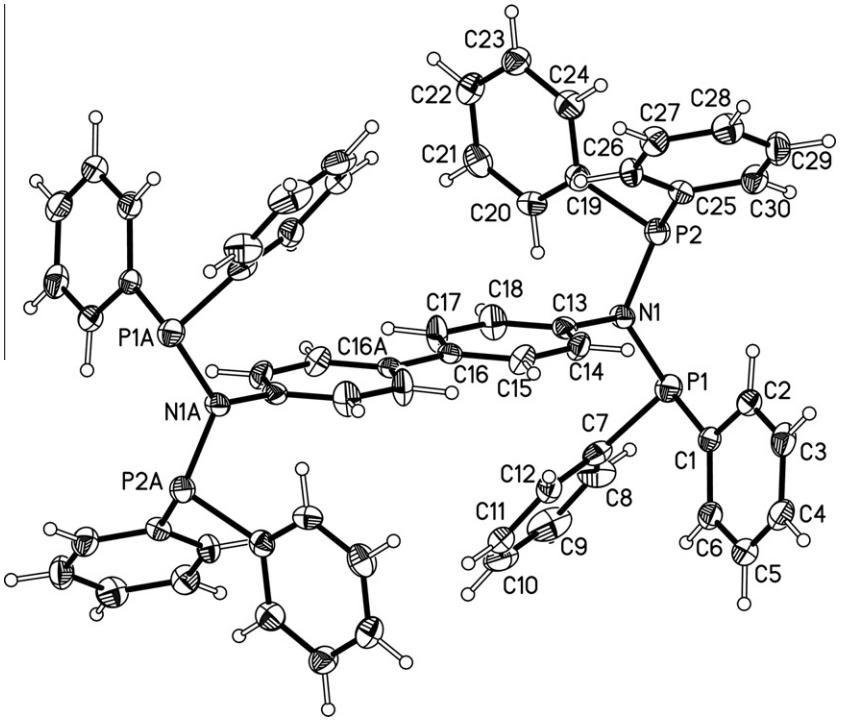
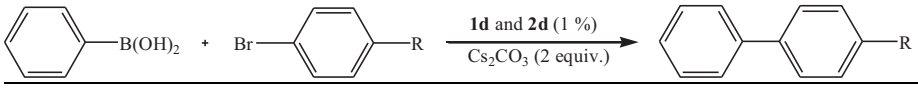
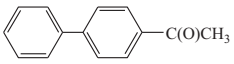
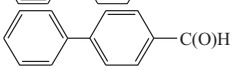
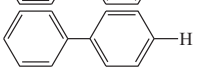
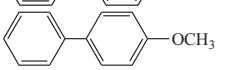
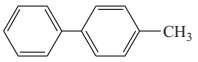


Fig. 1. ORTEP plot of **1** showing the labeling scheme (solvent is omitted for clarity). Main bond lengths [Å] and angles [°]: P1–N1 = 1.738(3); P2–N1 = 1.725(3); N1–C13 = 1.439(4); C16–C16A = 1.489(6); C13–N1–P2 = 122.9(2); C13–N1–P1 = 122.7(2); P2–N1–P1 = 114.0(1). Letter A indicates the following symmetry transformation: $-x$, $-y$, $-z$.

The ^{31}P-{^{1}H}NMR spectra of **1** and **2** contain singlets at δ(P) 68.4 ppm and δ(P) 68.8, respectively, similar to those found for closely related systems [18–21]. Solutions of **1** and **2** in $CDCl_3$, prepared under anaerobic conditions, are unstable and decompose slowly to give the

Table 2
The Suzuki coupling reactions of aryl bromides with phenylboronic acid.



Entry	R	Cat	Product	Conv. (%)	Yield (%)	TOF (%)
1	4-CH3C(O)-	**1d**		99	98	67
		2d		95	93	62
2	4-CH(O)-	**1d**		95	90	60
		2d		97	96	64
3	4-H	**1d**		88	87	58
		2d		81	78	52
4	4-CH_3O-	**1d**		64	61	41
		2d		65	63	42
5	4-CH_3-	**1d**		74	71	47
		2d		75	73	49

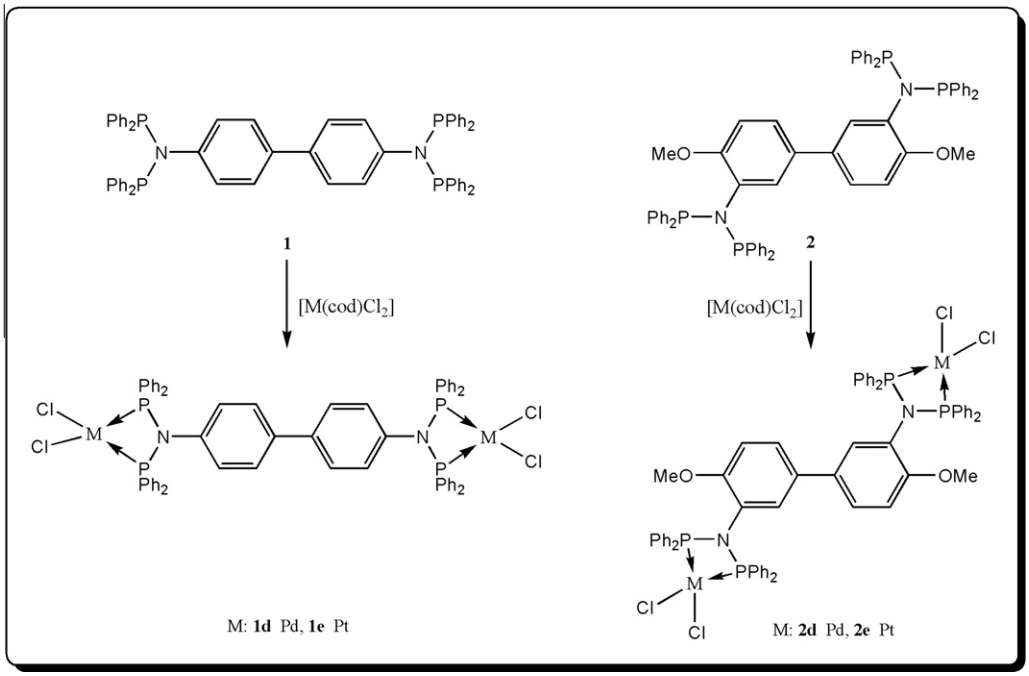
Conditions: 1.0 mmol of *p*-R-C_6H_4Br aryl bromide, 1.5 mmol of phenylboronic acid, 2.0 mmol Cs_2CO_3, 0.01 mmol (1%) catalyst, dioxane (3.0 mL). Purity of compounds was assessed by NMR and yields are based on the arylbromide. All reactions were monitored by GC; 80 °C, 1.5 h. TOF = (mol product/mol cat) × h^{-1}. The GC-yield was obtained using diethyleneglycol-di-*n*-butylether as an internal standard.

corresponding oxide and $[P(O)Ph_2PPh_2]$, the latter indicated by signals at δ 34.60 (d) ppm and δ −24.30 (d) ppm, ($^1J_{(P-P)}$ = 226 Hz). The ^1H NMR spectra of **1** and **2** exhibit no NH resonance in accord with complete N–H substitution. Characteristic J(^{31}P–^{13}C) coupling constants of the carbons of the phenyls rings are observed in the ^{13}C NMR spectra, which are consistent with the literature values for related compounds [5,22]]. Other pertinent spectroscopic and analytical data are provided in the Section 2.

Single crystals of **1** were obtained by slow evaporation from benzene at room temperature. The solid state structure of **1** is shown in Fig. 1 and its geometric parameters are given in the caption, and general crystallographic data are shown in Table 2. Compound **1** crystallizes in space group $P2_1/c$ with four molecules in the unit cell, the molecule itself shows a perfect C_i symmetry, having a center of inversion at the midpoint of the C–C single bond of the biphenyl moiety. The nitrogen atom shows a planar geometry [sum of angles = 359.6(2)°] with a P–N–P angle of 114.0(1)° due to the steric hindrance of the PPh_2 groups. The C–N distance [1.439(4) Å] is slightly smaller than those found for $PhN(PPh_2)_2$ [23], presumably due to the electronic effect of the biphenyl moiety. The biphenyl moiety is tilted by 98.3° compared to the plane made by P1, N1 and P2. This almost perpendicular orientation reduces the very high steric congestion within the molecule.

Reaction of **1** and **2** with aqueous H_2O_2, elemental sulfur or selenium powder in thf affords the corresponding oxides (**1a** and **2a**), sulfides (**1b** and **2b**) and selenides (**1c** and **2c**), which were characterized by analytical and spectroscopic methods. The ^{31}P NMR spectra of the oxides contain singlet resonances at 24.5 and 29.6 ppm for **1a** and **2a**, respectively. Similarly, singlet resonances are observed for **1b** and **2b** at 69.1 ppm and for **1c** and **2c** at 69.7 and 67.6 ppm, respectively. The ^{31}P NMR resonances of these chalcogenes are within the anticipated ranges [3,19,22a] and in the case of the selenides $^1J_{P-Se}$ satellites of ca. 800 Hz are observed that are characteristic of phosphine selenide systems.

Bis(phoshino)amines tend to react spontaneous with H_2O_2 at room temperature, whereas reaction with elemental sulfur or



Scheme 2. Reaction of $[M(cod)Cl_2]$ (M = Pd or Pt; cod = cycloocta-1,5-diene) with **1** and **2** to give the corresponding metal complexes.

selenium require elevated temperatures, especially for phosphorus compounds with bulky phenyl-substituent groups [24]. The selenium compounds decompose, to deposit elemental selenium, upon exposure to air [22a], and therefore must be handled under an inert atmosphere.

Reaction of **1** and **2** with [M(cod)Cl_2] (M = Pd or Pt; cod = cyclo-octa-1,5-diene) in CH_2Cl_2 affords the palladium complexes (**1d** and **2d**) and the platinum complexes (**1e** and **2e**) in good yield (Scheme 2). The $^{31}P\{^1H\}$ NMR spectra of the complexes contain singlet resonances at 34.9 and 41.4 ppm for **1d** and **2d** and at 19.5 and 20.5 ppm for **1e** and **2e**, respectively. The spectra of the platinum complexes also exhibit $^1J_{P-Pt}$ couplings of 3200–3400 Hz, consistent with the expected cis-geometry [25]]. The ^{31}P NMR chemical shifts of the complexes are in keeping with structurally related compounds [3,19,20].

4. Suzuki coupling reactions

The palladium complexes **1d** and **2d** were evaluated as pre-catalysts in the Suzuki reaction of selected aryl bromides with phenylboronic acid initially under similar conditions to those reported elsewhere [26]. Following optimization of the reaction, a catalyst loading of 0.01 mmol was employed together with Cs_2CO_3 as the base in dioxane at 80 °C. Control experiments showed that in the absence of the catalyst no reaction took place. In the presence of 0.01 mmol of **1d** or **2d**, however, *p*-bromoacetophenone, *p*-bromobenzaldehyde, *p*-bromobenzene, *p*-bromotoluene and *p*-bromoanisole react cleanly with phenylboronic acid to give appropriate the cross-coupling products in high yield (Table 2). As expected, the yields of the coupling product in reactions of aryl bromides with electron-withdrawing substituents are higher than those with an electron-releasing substituent. It is worth noting that ligand **2** is unstable (see above), but once coordinated to the palladium(II) center, appears to be stable and robust.

5. Conclusions

In conclusion, two new bis(diphenylphosphino)amines and their oxides, sulfides and selenides have been prepared. In addition, the coordination behaviour of ligands **1** and **2** towards palladium(II) and platinum(II) were described. We also demonstrated the application of palladium complexes of these bis(phosphino)amine 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 **1e** and **2e** system exhibited no catalytic activity. Only the palladium complexes were found to show catalytic activity in both the Suzuki coupling reactions of aryl bromides. In both cases, the catalytic activities of complexes **1d** and **2d** 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.

Acknowledgement

Financial support from Dicle University Research Fund (Project number: DUBAP-06-FF-07) is gratefully acknowledged.

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