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Synthesis and characterization of ether-derivatized aminophosphines and their application in C–C coupling reactions

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ABSTRACT

Four new bis(phosphino)amine ligands $(Ph_2P)_2N$-C_6H_3-R, where R = 3,5-OMe (**1**), 2,5-OMe (**2**), 2,4-OMe (**3**) or 3,4-OMe (**4**), were prepared via aminolysis of the corresponding dimethoxyanilines with 2 equiv. of diphenylphosphine chloride in the presence of triethyl amine. Oxidation of these ligands with aqueous H_2O_2, elemental S_8 or Se powder afforded the corresponding chalcogen oxides **1a**–**4a**, sulfides **1b**–**4b** and selenides **1c**–**4c** in good yields. Reaction of **1**–**4** with $[MCl_2(cod)]$ (M = Pt, Pd; cod = cycloocta-1,5-diene) in equimolar ratios afforded *cis*-$[MCl_2\{(Ph_2P)_2N$-C_6H_3-R$\}]$ (M = Pt; R = 3,5-OMe **1d**, R = 2,5-OMe **2d**, R = 2,4-OMe **3d**, and R = 3,4-OMe **4d**. M = Pd; R = 3,5-OMe **1e**, R = 2,5-OMe **2e**, R = 2,4-OMe **3e**, and R = 3,4-OMe **4e**). Similarly, reaction of $[Cu(CH_3CN)_4]PF_6$ with the **1**–**4** in 1:2 ratio gave $[Cu\{(Ph_2P)_2N$-C_6H_3-R$\}_2]PF_6$ (R = 3,5-OMe **1f**, 2,5-OMe **2f**, 2,4-OMe **3f** and 3,4-OMe **4f**). All new compounds were fully characterized by spectroscopy and elemental analysis and the molecular structures of seven representative compounds were determined by single-crystal X-ray crystallography. In addition, the palladium complexes were investigated as pre-catalysts in C–C coupling reactions.

1. Introduction

The synthesis and coordination chemistry of phosphorus(III) ligands containing P–N linkages continues to receive widespread attention [1,2]. In particular, bis(phosphino)amines including (diphenylphosphino)aniline derivatives are frequently encountered due to their facile synthesis, relatively high stability [3] and applications in catalysis [4]. Indeed, an extensive library of P–N bond containing ligands has been constructed [5,6]. Functionalization of the aminophosphines allows their electronic and steric properties to be tuned which in turn modulates catalytic activity. In addition, the oxidized forms of the bis(phosphino)amine $RN(P(:E)R_2)_2$ (where E = O, S or Se) can be used as precursors in the synthesis of small-membered ring systems [7].

Palladium-catalysed couplings have become an indispensable tool in organic synthesis [8] since they are tolerant to a wide variety of functional groups. Over the years studies have revealed the crucial role played by the ancillary ligands in the efficiency of these reactions. For example, electron-rich alkyl-phosphines [9] and carbenes [10] have received increasing interest in recent years, but the phosphine ligands and the phosphine–palladium complexes are unstable at elevated temperatures, placing significant limits on their synthetic utility. Therefore, from a practical point of view, the development of more stable ligands leading to more reactive catalysts is of importance.

The ancillary ligands coordinated to a metal center have a number of important roles in homogeneous catalysis, not only providing a stabilizing effect, but also governing activity and selectivity. Recently it has been shown that *N,N*-bis(diphenylphosphino)aniline palladium(II) complexes offer distinctive benefits in Heck coupling reactions [11,12]. In a continuation of our studies on aminophosphines [13,14], we decided to prepare a series of bis(phosphino)amines possessing electron-donating methoxy-substituents on an aryl ring and explore their chemistry and catalytic function when coordinated to palladium, and we report the outcome of these studies herein.

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; cod = cycloocta-1,5-diene) [15,16] and $[Cu(CH_3CN)_4]PF_6$ [17] were prepared according to literature procedures. Other starting materials are commercially available and were used as received.

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NMR spectra were obtained on a Bruker Avance 400 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 reference. IR spectra were recorded on a Mattson 1000 ATI UNICAM FT-IR spectrometer in the range 4000–400 cm^{-1} in KBr matrices. Elemental analysis was carried out using a Fisons EA 1108 CHNS-O instrument. Melting points were determined in capillary tubes on a Gallenkamp MID 350 BM 2.5 apparatus.

2.1. General procedure for preparation of **1–3**

Ph_2PCl (2.88 g, 13.1 mmol) was added to a solution of the dimethoxyaniline (1.00 g, 6.53 mmol) and NEt_3 (1.45 g, 14.3 mmol) in CH_2Cl_2 (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 washed with distilled water and then with diethyl ether, and dried under vacuum.

2.1.1. N,N-Bis(diphenylphosphino)-3,5-dimethoxyaniline, $[(Ph_2P)_2N\text{-}C_6H_3\text{-}(3,5\text{-}OCH_3)]$ (**1**)

Yield: 2.63 g, (77.4%). M.p. 130–132 °C. *Anal.* Calc. for $C_{32}H_{29}NO_2P_2$: C, 73.70; H, 5.61; N, 2.69. Found: C, 73.91; H, 5.65; N, 2.61%. ^{31}P NMR (ppm, $CDCl_3$): δ 68.6 (s). ^1H NMR (ppm, $CDCl_3$): δ 5.80 (s, 2H), 6.13 (s, 1H), 7.30–7.41 (m, 20H, Ar), 3.36 (s, 6H, CH_3). ^{13}C NMR (ppm, $CDCl_3$): δ C_{Arm}, 160.0, 149.0, 139.2, 133.3, 129.1, 128.0, 107.2, 98.5. C_{OCH_3}, 55.0. IR (cm^{-1}): υ 2831 (CH of OMe), 915 (P–N).

2.1.2. N,N-Bis(diphenylphosphino)-2,5-dimethoxyaniline, $[(Ph_2P)_2N\text{-}C_6H_3\text{-}(2,5\text{-}OCH_3)]$ (**2**)

Yield: 2.51 g, (73.8%). M.p. 147–149 °C. *Anal.* Calc. for $C_{32}H_{29}NO_2P_2$: C, 73.70; H, 5.61; N, 2.69. Found: C, 73.89; H, 5.63; N, 2.66%. ^{31}P NMR (ppm, $CDCl_3$): δ 64.7 (s). ^1H NMR (ppm, $CDCl_3$): δ 6.33 (s, 1H), 6.65 (s, 2H), 7.33 (broad singlet, 20 H, Ar), 3.38 (s, 3H, CH_3), 3.32 (s, 3H, CH_3). ^{13}C NMR (δ ppm, $CDCl_3$): C_{Arm}, 152.7, 150.4, 140.1, 137.6, 133.4, 128.7, 127.8, 115.8, 112.4, 112.1. C_{OCH_3}, 55.4, 55.0. IR (cm^{-1}): υ 2840 (CH of OMe), 896 (P–N).

2.1.3. N,N-Bis(diphenylphosphino)-2,4-dimethoxyaniline, $[(Ph_2P)_2N\text{-}C_6H_3\text{-}(2,4\text{-}OCH_3)]$ (**3**)

Yield: 2.26 g, (66.5%). M.p. 120–121 °C. *Anal.* Calc. for $C_{32}H_{29}NO_2P_2$: C, 73.70; H, 5.61; N, 2.69. Found: C, 73.95, H, 5.68; N, 2.59%. ^{31}P NMR (ppm, $CDCl_3$): δ 66.1 (s). ^1H NMR (ppm, $CDCl_3$): δ 6.15 (q, 1H), 6.23 (d, 1H), 6.70 (d, 1H), 7.28–7.52 (m, 20H, Ar), 3.74 (s, 3H, CH_3), 3.27 (s, 3H, CH_3). ^{13}C NMR (δ ppm, $CDCl_3$): C_{Arm}, 158.6, 156.8, 134.6, 132.3, 131.3, 130.5, 130.4, 127.8, 103.2, 99.0, C_{OCH_3}, 55.4; 54.3. IR (cm^{-1}): υ 2837 (CH of OMe), 835 (P–N).

2.2. Preparation of N,N-bis(diphenylphosphino)-3,4-dimethoxyaniline, $[(Ph_2P)_2N\text{-}C_6H_3\text{-}(3,4\text{-}OCH_3)]$ (**4**)

Ph_2PCl (2.88 g, 13.1 mmol) was added to a solution of the 3,4-dimethoxyaniline (1.00 g, 6.53 mmol) and NEt_3 (1.45 g, 14.3 mmol) in tetrahydrofurane (25 ml) at 0 °C. The resulting suspension was stirred for 1 h and then filtered in vacuo to separate the $Et_3N{\cdot}HCl$ salt by-product. The solvent was removed under reduced pressure and the remaining viscous product was washed with a small amount of diethyl ether and dried under vacuum.

Anal. Calc. for $C_{32}H_{29}NO_2P_2$: C, 73.70; H, 5.61; N, 2.69. Found: C, 73.87; H, 5.64; N, 2.56%. ^{31}P NMR (ppm, $CDCl_3$): δ 71.1 (s). ^1H NMR (ppm, $CDCl_3$): δ 5.84 (s, 1H), 6.20 (d, 1H), 6.45 (d, 1H), 7.29–7.35 (m, 20 H, Ar), 3.74 (s, 3H, CH_3), 3.18 (s, 3H, CH_3). ^{13}C NMR (δ ppm, $CDCl_3$): C_{Arm}, 147.7, 146.6, 139.7, 139.4, 133.4, 129.1, 128.0, 121.4, 113.4, 110.2, (C_{OCH_3}, 55.8, 55.1. IR data (cm^{-1}): υ 2839 (CH of OMe), 910 (P–N).

2.3. General procedure for synthesis of **1a–4a**

A thf (10 ml) solution of the *N,N*-bis(diphenylphosphino)dimethoxyaniline (**1**–**4**) (0.100 g, 0.192 mmol) and aqueous H_2O_2 (30% w/w, 0.435 g, 0.383 mmol) was stirred for 1 h. The solution was evaporated to dryness under reduced pressure to give the corresponding oxide derivative (**1a**–**4a**) as a solid.

2.3.1. N,N-Bis(diphenyloxophosphino)-3,5-dimethoxyaniline, $[(Ph_2P(O))_2N\text{-}C_6H_3\text{-}(3,5\text{-}OCH_3)]$ (**1a**)

Yield: 0.0816 g, (76.9%). Mp. 212–213 °C. *Anal.* Calc. for $C_{32}H_{29}NO_4P_2$: C, 69.44; H, 5.28; N, 2.53%. Found: C, 69.53; H, 5.23; N, 2.40%. ^{31}P NMR (ppm, $CDCl_3$): δ 22.0 (s). ^1H NMR (ppm, $CDCl_3$): δ 5.95 (s, 1H), 6.68 (s, 2H), 7.21–7.89 (m, 20H, Ar), 3.58 (s, 6H, CH_3). IR data (cm^{-1}): υ 2845 (CH of OMe), 1202 (P–O), 920 (P–N).

2.3.2. N,N-Bis(diphenyloxophosphino)-2,5-dimethoxyaniline, $[(Ph_2P(O))_2N\text{-}C_6H_3\text{-}(2,5\text{-}OCH_3)]$ (**2a**)

Yield: 0.0971 g, (91.5%). M.p. 165–167 °C. *Anal.* Calc. for $C_{32}H_{29}NO_4P_2$: C, 69.44; H, 5.28; N, 2.53. Found: C, 69.38; H, 5.20; N, 2.38%. ^{31}P NMR (ppm, $CDCl_3$): δ 26.1 (s). ^1H NMR (ppm, $CDCl_3$): δ 6.25 (d, 1H), 6.47 (d, 1H), 7.11 (s, 1H), 7.25–7.93 (m, 20H, Ar), 3.56 (s, 3H, CH_3), 3.51 (s, 3H, CH_3). IR data (cm^{-1}): υ 2839 (CH of OMe), 1221 (P–O), 958 (P–N).

2.3.3. N,N-Bis(diphenyloxophosphino)-2,4-dimethoxyaniline, $[(Ph_2P(O))_2N\text{-}C_6H_3\text{-}(2,4\text{-}OCH_3)]$ (**3a**)

Yield: 0.0758 g, (71.4%). M.p. 205–207 °C. *Anal.* Calc. for $C_{32}H_{29}NO_4P_2$: C, 69.44; H, 5.28; N, 2.53. Found: C, 69.41; H, 5.18; N, 2.46%. ^{31}P NMR (ppm, $CDCl_3$): δ 25.1 (s). ^1H NMR (ppm, $CDCl_3$): δ 5.85 (d, 1H), 6.20 (d, 1H), 7.21–7.95 (m, 21H, Ar) 3.63 (s, 3H, CH_3), 3.48 (s, 3H, CH_3). IR data (cm^{-1}): υ 2841 (CH of OMe), 1228 (P–O), 958 (P–N).

2.3.4. N,N-Bis(diphenyloxophosphino)-3,4-dimethoxyaniline, $[(Ph_2P(O))_2N\text{-}C_6H_3\text{-}(3,4\text{-}OCH_3)]$ (**4a**)

Yield: 0.0535 g, (50.4%). M.p. 131–133 °C. *Anal.* Calc. for $C_{32}H_{29}NO_4P_2$: C, 69.44; H, 5.28; N, 2.53. Found: C, 69.35; H, 5.24; N, 2.37%. ^{31}P NMR (ppm, $CDCl_3$): δ 29.5 (s). ^1H NMR (ppm, $CDCl_3$): δ 6.43 (d, 1H), 6.65 (s,1H), 6.86 (s,1H), 7.05–7.92 (m, 20H, Ar), 3.75 (s, 3H, CH_3), 3.64 (s, 3H, CH_3). IR data (cm^{-1}): υ 2838 (CH of OMe), 1196 (P–O), 968 (P–N).

2.4. General procedure for synthesis of **1b–4b** and **1c–4c**

Elemental sulfur (0.0123 g, 0.384 mmol) was added to a solution of *N,N*-bis(diphenylphosphino)dimethoxyaniline (**1**–**4**) (0.100 g, 0.192 mmol) in thf (10 ml) and the reaction mixture was heated to reflux for 5 h. The volume of the solvent was concentrated in vacuo to 1–2 ml and addition of *n*-hexane (15 ml) gave the sulfide derivative (**1b**–4**b**) as a solid which was collected by filtration. In a similar manner the selenide derivatives were synthesized from **1**–**4** (0.100 g, 0.192 mmol) and selenium powder (0.0303 g, 0.384 mmol).

2.4.1. N,N-Bis(diphenylthiophosphino)-3,5-dimethoxyaniline, $[(Ph_2P(S))_2N\text{-}C_6H_3\text{-}(3,5\text{-}OCH_3)]$ (**1b**)

Yield: 0.0634 g, (56.5%). M.p 237–238 °C. *Anal.* Calc. for $C_{32}H_{29}NO_2P_2S_2$: C, 65.63; H, 4.99; N, 2.39; S, 10.94. Found: C, 65.56; H, 4.81; N, 2.35; S, 10.88%. ^{31}P NMR (ppm, $CDCl_3$): δ 68.4 (s). ^1H NMR (ppm, $CDCl_3$): δ 5.94 (s, 1H), 7.04 (s, 2H), 7.23–8.14 (m, 20H, Ar), 3.56 (s, 6H, CH_3). IR data (cm^{-1}): υ 2839 (CH of OMe), (920) P–N, 654 (P–S).

*2.4.2. N,N-Bis(diphenylthiophosphino)-2,5-dimethoxyaniline, [$(Ph_2P(S))_2N$-C_6H_3-(2,5-OCH_3)] (**2b**)*

Yield: 0.0397 g, (70.7%). M.p. 215–217 °C. *Anal.* Calc. for $C_{32}H_{29}NO_2P_2S_2$: C, 65.63; H, 4.99; N, 2.39; S, 10.94. Found: C, 65.68; H, 4.86; N, 2.32; S, 10.85%. ^{31}P NMR (ppm, $CDCl_3$): δ 67.5 (s). ^{1}H NMR (ppm, $CDCl_3$): δ 6.07 (d, 1H), 6.49 (d, 1H), 6.93 (s, 1H), 7.14–7.95 (m, 20H, Ar), 3.44 (s, 3H, CH_3), 3.22 (s, 3H, CH_3). IR data (cm^{-1}): υ 2839 (CH of OMe), 920 (P–N), 656 (P–S).

*2.4.3. N,N-Bis(diphenylthiophosphino)-2,4-dimethoxyaniline, [$(Ph_2P(S))_2N$-C_6H_3-(2,4-OCH_3)] (**3b**)*

Yield: 0.0706 g, (62.9%). M.p. 197–199 °C. *Anal.* Calc. for $C_{32}H_{29}NO_2P_2S_2$: C, 65.63; H, 4.99; N, 2.39; S, 10.94. Found: C, 65.53; H, 4.83; N, 2.29; S, 10.79%. ^{31}P NMR (ppm, $CDCl_3$): δ 67.9 (s). ^{1}H NMR (ppm, $CDCl_3$): δ 5.69 (d, 1H), 6.08 (q, 1H). 7.14–8.18 (m, 21H,Ar), 3.59 (s, 3H, CH_3), 3.20 (s, 3H, CH_3). IR data (cm^{-1}): υ 2837 (CH of OMe), 908 (P–N), 700 (P–S).

*2.4.4. N,N-Bis(diphenylthiophosphino)-3,4-dimethoxyaniline, [$(Ph_2P(S))_2N$-C_6H_3-(3,4-OCH_3)] (**4b**)*

Yield: 0.0551 g, (49.1%). M.p. >200 °C (dec.) *Anal.* Calc. for $C_{32}H_{29}NO_2P_2S_2$: C, 65.63; H, 4.99; N, 2.39; S, 10.94. Found: C, 65.49; H, 4.87, N, 2.28; S, 10.86%. ^{31}P NMR (ppm, $CDCl_3$): δ 73.6 (s). ^{1}H NMR (ppm, $CDCl_3$): δ 6.36–8.13 (m, 23H, Ar), 3.65 (d, 6H, CH_3). IR data (cm^{-1}): υ 2831 (CH of OMe), 949 (P–N), 725 (P–S).

*2.4.5. N,N-Bis(diphenylselenophosphino)-3,5-dimethoxyaniline, [$(Ph_2P(Se))_2N$-C_6H_3-(3,5-OCH_3)] (**1c**)*

Yield: 0.0658 g, (50.5%). M.p. 215–216 °C. *Anal.* Calc. for $C_{32}H_{29}NO_2P_2Se_2$: C, 56.57; H, 4.30; N, 2.06. Found: C, 56.45, H, 4.21, N, 1.99%. ^{31}P NMR (ppm, $CDCl_3$): δ 69.1 (s). $^1J_{P-Se}$: 796 Hz. ^{1}H NMR (ppm, $CDCl_3$): δ 5.96 (s, 1H), 7.09 (s, 2H), 7.22–8.21 (m, 20H, Ar), 3.57 (s, 6H, CH_3). IR data (cm^{-1}): υ 2840 (CH of OMe), 915 (P–N), 558 (P–Se).

*2.4.6. N,N-Bis(diphenylselenophosphino)-2,5-dimethoxyaniline, [$(Ph_2P(Se))_2N$-C_6H_3-(2,5-OCH_3)] (**2c**)*

Yield: 0.0917 g, (70.4%). M.p. 175–177 °C. *Anal.* Calc. for $C_{32}H_{29}NO_2P_2Se_2$: C, 56.57; H, 4.30; N, 2.06. Found: C, 56.49; H, 4.20; N, 1.97%. ^{31}P NMR (ppm, $CDCl_3$): δ 65.2 (s). J_{P-Se}: 807 Hz. ^{1}H NMR (ppm, $CDCl_3$): δ 6.03 (d, 1H), 6.50 (d, 1H), 7.01 (d, 1H), 7.12–7.94 (m, 20H, Ar), 3.46 (s, 3H, CH_3), 3.17 (s, 3H, CH_3). IR data (cm^{-1}): υ 2839 (CH of OMe), 914 (P–N), 560 (P–Se).

*2.4.7. N,N-Bis(diphenylselenophosphino)-2,4-dimethoxyaniline, [$(Ph_2P(Se))_2N$-C_6H_3-(2,4-OCH_3)] (**3c**)*

Yield: 0.0738 g, (61.4%). M.p. 231–233 °C. *Anal.* Calc. for $C_{32}H_{29}NO_2P_2Se_2$: C, 56.57; H, 4.30; N, 2.06. Found: C, 56.40, H, 4.18, N, 1.94%. ^{31}P NMR (ppm, $CDCl_3$): δ 65.9 (s). $^1J_{P-Se}$: 802 Hz. ^{1}H NMR (ppm, $CDCl_3$): δ 5.67 (d, 1H), 6.10 (q, 1H), 7.09–7.89 (m, 21H, Ar), 3.62 (s, 3H, CH_3), 3.19 (s, 3H, CH_3). IR data (cm^{-1}): υ 2838 (CH of OMe), 906 (P–N), 571 (P–Se).

*2.4.8. N,N-Bis(diphenylselenophosphino)-3,4-dimethoxyaniline, [$(Ph_2P(Se))_2N$-C_6H_3-(3,4-OCH_3)] (**4c**)*

Yield: 0.0919 g, (76.5%). M.p. >200 °C (dec.) *Anal.* Calc. for $C_{32}H_{29}NO_2P_2Se_2$: C, 56.57; H, 4.30; N, 2.06. Found: C, 56.38, H, 4.17; N, 1.92%. ^{31}P NMR (ppm, $CDCl_3$): δ 69.8 (s). $^1J_{P-Se}$: 805 Hz. ^{1}H NMR (ppm, $CDCl_3$): δ 6.35–8.24 (m, 23H, Ar), 3.65 (d, 6H, CH_3). IR data (cm^{-1}): υ 2835 (CH of OMe), 911 (P–N), 554 (P–Se).

*2.5. General procedure for synthesis of **1d–4d** and **1e–4e***

A solution of [$PtCl_2$(cod)] (0.0717 g, 0.192 mmol) and *N,N*-bis(diphenylphosphino) dimethoxyaniline (**1–4**) (0.100 g, 0.192 mmol) in CH_2Cl_2 (10 ml) was stirred at RT for 1 h. The volume of the solvent was concentrated to 1–2 ml under reduced pressure and addition of Et_2O (15 ml) gave the platinum complexes (**1d–4d**) as solids which were isolated by filtration and dried in vacuo. In a similar manner the palladium complexes (**1e–4e**) were prepared from **1–4** (0.100 g, 0.192 mmol) and [$PdCl_2$(cod)] (0.0546 g, 0.192 mmol).

*2.5.1. {N,N-Bis(diphenylphosphino)-3,5-dimethoxyaniline}platinum(II)chloride, [$PtCl_2${$(Ph_2P)_2N$-C_6H_3-(3,5-OMe)}] (**1d**)*

Yield: 0.118 g, (78.1%). M.p. 315–316 °C. *Anal.* Calc. for $C_{32}H_{29}NO_2P_2PtCl_2$: C, 48.81; H, 3.71; N, 1.78. Found: C, 48.72; H, 3.66; N, 1.71%. ^{31}P NMR (ppm, $CDCl_3$): δ 20.0 (t); $^1J_{Pt-P}$: 3414 Hz. ^{1}H NMR (ppm, $CDCl_3$): δ 5.60 (s, 2H), 6.24 (s, 1H), 7.51–7.91 (m, 20H, Ar), 3.35 (s, 6H, CH_3). IR data (cm^{-1}): υ 2841 (CH of OMe), 901 (P–N).

*2.5.2. {N,N-Bis(diphenylphosphino)-2,5-dimethoxyaniline}platinum(II)chloride, [$PtCl_2${$(Ph_2P)_2N$-C_6H_3-(2,5-OMe)}] (**2d**)*

Yield: 0.132 g, (87.4%). M.p. 309–311 °C. *Anal.* Calc. for $C_{32}H_{29}NO_2P_2PtCl_2$: C, 48.81; H, 3.71; N, 1.78. Found: C, 48.75; H, 3.67; N, 1.73%. ^{31}P NMR (ppm, $CDCl_3$): δ 22.9 (t). $^1J_{Pt-P}$: 3344 Hz. ^{1}H NMR (ppm, $CDCl_3$): δ 5.68 (d, 1H), 6.58 (d, 1H), 6.75 (d, 1H), 7.47–7.92 (m, 20H), 3.24 (s, 3H, CH_3), 2.94 (s, 3H, CH_3). IR data (cm^{-1}): υ 2837 (CH of OMe), 908 (P–N).

*2.5.3. {N,N-Bis(diphenylphosphino)-2,4-dimethoxyaniline}platinum(II)chloride, [$PtCl_2${$(Ph_2P)_2N$-C_6H_3-(2,4-OMe)}] (**3d**)*

Yield: 0.111 g, (73.5%). M.p. >200 °C (dec.) *Anal.* Calc. for $C_{32}H_{29}NO_2P_2PtCl_2$: C, 48.81; H, 3.71; N, 1.78. Found: C, 48.69; H, 3.64; N, 1.68%. ^{31}P NMR (ppm, DMSO-d_6): δ 22.5 (t). J_{Pt-P}: 3229 Hz. ^{1}H NMR (ppm, DMSO-d_6): δ 6.25 (t, 2H), 6.43 (d, 1H), 7.40–7.81 (m, 20H, Ar), 3.66 (s, 3H, CH_3), 2.80 (s, 3H, CH_3). IR data (cm^{-1}): υ 2839 (CH of OMe), 891 (P–N).

*2.5.4. {N,N-Bis(diphenylphosphino)-3,4-dimethoxyaniline}platinum(II)chloride, [$PtCl_2${$(Ph_2P)_2N$-C_6H_3-(3,4-OMe)}] (**4d**)*

Yield: 0.134 g, (88.7%). M.p. >240 °C (dec.) *Anal.* Calc. for $C_{32}H_{29}NO_2P_2PtCl_2$: C, 48.81; H, 3.71; N, 1.78. Found: C, 48.66, H, 3.61; N, 1.65%. ^{31}P NMR (ppm, $CDCl_3$): δ 25.3 (t). $^1J_{P-Pt}$: 3325 Hz. ^{1}H NMR (ppm, $CDCl_3$): δ 6.33–7.78 (m, 23H, Ar), 3.61 (d, 6H, CH_3). IR data (cm^{-1}): υ 2835 (CH of OMe), 913 (P–N).

*2.5.5. {N,N-Bis(diphenylphosphino)-3,5-dimethoxyaniline}palladium(II)chloride, [$PdCl_2${$(Ph_2P)_2N$-C_6H_3-(3,5-OMe)}] (**1e**)*

Yield: 0.104 g, (77.6%). M.p. 289–290 °C. *Anal.* Calc. for $C_{32}H_{29}NO_2P_2PdCl_2$: C, 55.00; H, 4.18; N, 2.00. Found: C, 55.21, H, 4.25; N, 1.89%. ^{31}P NMR (ppm, $CDCl_3$): δ 34.1 (s). ^{1}H NMR (ppm, $CDCl_3$): δ 5.66 (s, 2H), 6.23 (s, 1H), 7.52–7.98 (m, 20H, Ar), 3.37 (s, 6H, CH_3). IR data (cm^{-1}): υ 2839 (CH of OMe), 909 (P–N).

*2.5.6. {N,N-Bis(diphenylphosphino)-2,5-dimethoxyaniline}palladium(II)chloride, [$PdCl_2${$(Ph_2P)_2N$-C_6H_3-(2,5-OMe)}] (**2e**)*

Yield: 0.0967 g, (72.2%). M.p. 285–287 °C. *Anal.* Calc. for $C_{32}H_{29}NO_2P_2PdCl_2$: C, 55.00; H, 4.18; N, 2.00. Found: C, 55.13; H, 4.19; N, 1.88%. ^{31}P NMR (ppm, $CDCl_3$): δ 38.2 (s). ^{1}H NMR (ppm, $CDCl_3$): δ 5.77 (s, 1H), 6.59 (d, 1H), 6.76 (d, 1H), 7.46–7.98 (m, 20H, Ar), 3.25 (s, 3H, CH_3), 2.98 (s, 3H, CH_3). IR data (cm^{-1}): υ 2837 (CH of OMe), 908 (P–N).

*2.5.7. {N,N-Bis(diphenylphosphino)-2,4-dimethoxyaniline}palladium(II)chloride, [$PdCl_2${$(Ph_2P)_2N$-C_6H_3-(2,4-OMe)}] (**3e**)*

Yield: 0.111 g, (82.8%). M.p. 281–283 °C. *Anal.* Calc. for $C_{32}H_{29}NO_2P_2PdCl_2$: C, 55.00; H, 4.18; N, 2.00. Found: C, 55.07, H, 4.16, N, 1.93%. ^{31}P NMR (ppm, DMSO-d_6): δ 37.9 (s). ^{1}H NMR (ppm, DMSO-d_6): δ 6.26 (t, 2H), 6.47 (d, 1H), 7.62–7.83 (m, 20H, Ar), 3.66 (s, 3H, CH_3), 2.81 (s, 3H, CH_3). IR data (cm^{-1}): υ 2837 (CH of OMe), 893 (P–N).

*2.5.8. {N,N-Bis(diphenylphosphino)-3,4-dimethoxyaniline}palladium(II)chloride, [$PdCl_2${$(Ph_2P)_2N$-C_6H_3-(3,4-OMe)}] (**4e**)*

Yield: 0.119 g, (88.8%). M.p. >240 °C (dec.) *Anal.* Calc. for $C_{32}H_{29}NO_2P_2PdCl_2$: C, 55.00; H, 4.18; N, 2.00. Found: C, 55.16; H, 4.22; N, 1.94%. ^{31}P NMR (ppm, DMSO-d_6): δ 34.9 (s). ^{1}H NMR (ppm, DMSO-d_6): δ 5.45 (s, 1H), 6.40 (d, 1H), 6.79 (d, 1H), 7.69–7.85 (m, 20H, Ar), 3.63 (d, 6H, CH_3). IR data (cm^{-1}): υ 2839 (CH of OMe), 926 (P–N).

*2.6. General procedure for preparation of **1f–4f***

To a solution of *N,N*-bis(diphenylphosphino)dimethoxyaniline (**1–4**) (0.100 g, 0.192 mmol) in CH_2Cl_2 (10 ml), $[Cu(CH_3CN)_4]PF_6$ (0.0357 g, 0.096 mmol) was added and the resulting solution was stirred at RT for 1 h. The majority of solvent was removed under reduced pressure and addition of Et_2O (15 ml) gave the corresponding copper complexes (**1f**–**4f**) as solids which were isolated by filtration, washed with Et_2O (5 ml) and dried in vacuo.

*2.6.1. Bis[N,N-bis(diphenylphosphino)-3,5-dimethoxyaniline)copper(1)] hexafluorophosphate, [Cu{Ph_2P)$_2$N-C_6H_3-(3,5-OMe)}$_2$]PF_6 (**1f**)*

Yield: 0.0970 g, (80.8%). M.p. 191–193 °C. *Anal.* Calc. for $C_{64}H_{58}N_2O_4P_5F_6Cu$: C, 61.42; H, 4.67; N, 2.24. Found: C, 61.53; H, 4.75; N, 2.13%. ^{31}P NMR (ppm, $CDCl_3$): δ 87.6 (s). $\delta_{(PF6)}$: −144.5 (m). $^1J_{P-F}$: 711 Hz. ^{1}H NMR (ppm, $CDCl_3$): δ 5.45 (s, 2H), 6.18 (s, 1H), 7.30–7.52 (m, 20H, Ar), 3.25 (s, 6H, CH_3). IR data (cm^{-1}): υ 2837 (CH of OMe), 844 (P–N).

*2.6.2. Bis[N,N-bis(diphenylphosphino)-2,5-dimethoxyaniline)copper(1)] hexafluorophosphate, [Cu{Ph_2P)$_2$N-C_6H_3-(2,5-OMe)}$_2$]PF_6 (**2f**)*

Yield: 0. 101 g, (84.2%). M.p. 204–206 °C. *Anal.* Calc. for $C_{64}H_{58}N_2O_4P_5F_6Cu$: C, 61.42; H, 4.67; N, 2.24. Found: C, 61.37, H, 4.61; N, 2.07%. ^{31}P NMR (ppm, $CDCl_3$): δ 88.8 (s). $\delta_{(PF6)}$: −144.3, $^1J_{P-F}$: 712 Hz. ^{1}H NMR (ppm, $CDCl_3$): δ 5.78 (s, 1H), 6.42 (d, 1H), 6.63 (d, 1H), 7.27–7.47 (m, 20H, Ar), 3.21 (s, 3H, CH_3), 2.75 (s, 3H, CH_3). IR data (cm^{-1}): υ 2839 (CH of OMe), 900 (P–N).

*2.6.3. Bis[N,N-bis(diphenylphosphino)-2,4-dimethoxyaniline)copper(1)] hexafluorophosphate, [Cu{Ph_2P)$_2$N-C_6H_3-(2,4-OMe)}$_2$]PF_6 (**3f**)*

Yield: 0.103 g, (85.8%). m.p. >200 °C (dec.) *Anal.* Calc. for $C_{64}H_{58}N_2O_4P_5F_6Cu$: C, 61.42; H, 4.67; N, 2.24. Found: C, 61.49, H, 4.69; N, 2.10%. ^{31}P NMR (ppm, $CDCl_3$): δ 89.0 (s). $\delta_{(PF6)}$: −144.3, J_{P-F}: 712 Hz. ^{1}H NMR (ppm, DMSO-d_6): δ 6.10 (q, 2H), 6.24 (d, 1H), 7.26–7.54 (m, 20H, Ar), 3.61 (s, 3H, CH_3), 2.67 (s, 3H, CH_3). IR data (cm^{-1}): υ 2837 (CH of OMe), 888 (P–N).

*2.6.4. Bis[N,N-bis(diphenylphosphino)-3,4-dimethoxyaniline)copper(1)] hexafluorophosphate, [Cu{Ph2P)2N-C6H3-(3,4-OMe)}2]PF6 (**4f**)*

Complex **4f** could not be isolated in pure form. It decomposes rapidly. ^{31}P NMR (reaction medium, ppm, $CDCl_3$): δ 87.6 (s). $\delta_{(PF6)}$: −144.3, J_{P-F}: 712 Hz.

2.7. General procedure for the Heck coupling reactions

The palladium pre-catalyst (**1e–4e**, 1.0%), aryl bromide (1.0 mmol), styrene (1.5 mmol), K_2CO_3 (2 mmol) and dioxane (3 ml) were added to a Schlenk tube and the mixture was heated to 80 °C for 6 h. The reaction mixture was cooled to RT, and the products extracted with ethyl acetate/hexane (1:5), filtered through a pad of silica gel with copious washing, concentrated and purified by flash chromatography on silica gel. The purity of the compounds was checked by ^{1}H NMR and GC, and the yields are based on the aryl bromide.

2.8. General procedure for the Suzuki coupling reactions

The palladium pre-catalyst (**1e–4e**, 1.0%), aryl bromide (1.0 mmol), phenylboronic acid (1.5 mmol), Cs_2CO_3 (2 mmol), dioxane (3 ml) were added to a small Schlenk tube in air and the mixture was heated to 80 °C for 2 h. The reaction mixture was cooled to RT, extracted with ethyl acetate/hexane (1:5), filtered through a pad of silicagel 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.

2.9. Crystallography

Data collection for the crystal structures were performed at low temperature using Mo Kα radiation. An Oxford Diffraction Sapphire/KM4 CCD was employed for **2b, 1d, 3d, 3e, 4e** and the remaining crystals were measured on a Bruker APEX II CCD. Both diffractometers have a kappa geometry goniometer. Data were reduced using CRYSALIS PRO [18] (**2b, 1d, 3d, 3e, 4e**), and EvalCCD [19] (**1c, 1e**) and then corrected for absorption [20] Solution and refinement for all crystal structures were performed by SHELXTL [21]. All structures were refined using full-matrix least-squares on F^2 with all non hydrogen atoms anisotropically defined. Hydrogen atoms were placed in calculated positions by means of the "riding" model. Relevant crystallographic data are compiled in Table 1.

3. Results and discussion

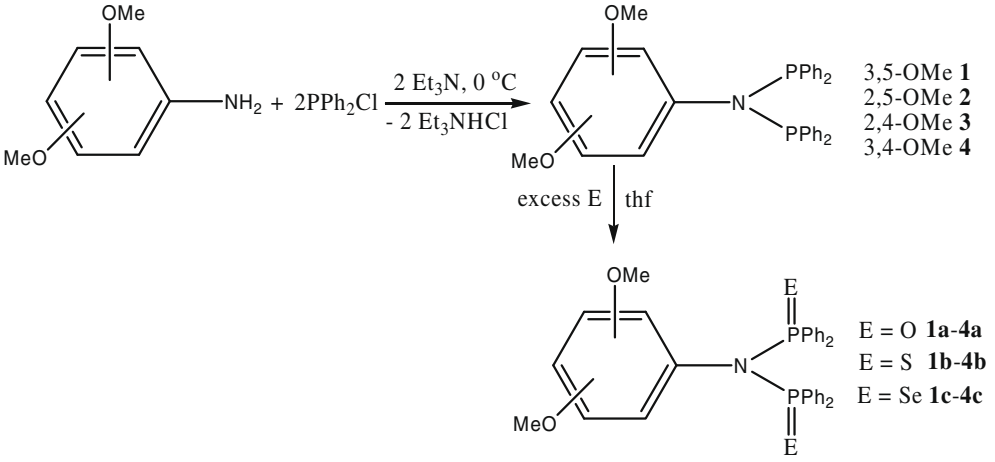
Aminolysis of chlorophosphines is an efficient method for preparing aminophosphines of general formula $R_2PN(H)R'$ or $(R_2P)_2NR'$ [22]. The outcome of the aminolysis reaction is influenced by the amine, the nature of the auxiliary base, and the solvent [23]. For the synthesis of the new bis(phosphino)amine ligands $(Ph_2P)_2N$-C_6H_3-R (R = 3,5-OMe **1**, 2,5-OMe **2**, 2,4-OMe **3**, 3,4-OMe **4**) aminolysis was achieved using Et_3N as the auxiliary base in dichloromethane (Scheme 1). The reaction also proceeds in diethyl ether but at considerably increased reaction times. The reaction in dichloromethane was monitored by ^{31}P NMR spectroscopy and completed within 1 h. Ligands **1**–**3** are air-stable solids that can even be purified by washing with water. In contrast, **4** is very sensitive towards moisture and rapidly decomposes upon exposure the air. The ^{31}P NMR spectra of **1–4** display singlet resonances at δ 68.6, 64.7, 66.1 and 71.1 ppm, respectively, these values being within the range found in structurally similar compounds [3,5,28]. The ^{1}H NMR spectra of **1–4** verify that complete N–H substitution has taken place and the ^{13}C NMR spectra further corroborate the proposed structures. Other pertinent spectroscopic and analytical data are given in Section 2.

Oxidation of **1–4** with aqueous H_2O_2, elemental sulfur or selenium powder in thf gave the corresponding oxides **1a–4a**, sulfides **1b–4b** and selenides **1c–4c** (Scheme 1) which were characterized

Table 1
Crystal data and details of the structure determination for: **1c, 2b, 1d, 1e, 3d, 3e, 4e**.

	1c	2b	1d	1e	3d	3e	4e
Chemical formula	$C_{32}H_{29}NO_2P_2Se_2$	$C_{32}H_{29}NO_2P_2S_2$	$C_{33}H_{31}Cl_4NO_2P_2Pt$	$C_{33}H_{31}Cl_4NO_2P_2Pd$	$C_{33}H_{31}Cl_4NO_2P_2Pt$	$C_{33}H_{31}Cl_4NO_2P_2Pd$	$C_{32}H_{29}Cl_2NO_2P_2Pd$
Formula weight	679.42	585.62	872.42	783.73	872.42	783.73	698.80
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/m$	$P2_1/m$	$P2_1$
a (Å)	10.2911(7)	11.4109(3)	12.6683(2)	12.6796(12)	8.7362(6)	8.7055(5)	8.7866(2)
b (Å)	12.5722(4)	15.8705(3)	14.6175(2)	14.5834(11)	16.1198(8)	16.1646(7)	20.5582(4)
c (Å)	12.8041(10)	16.7331(3)	18.6772(3)	18.6795(16)	12.0028(8)	11.9720(7)	9.1715(2)
α (°)	90.435(5)	90	90	90	90	90	90
β (°)	103.529(6)	104.136(2)	102.8190(15)	102.323(8)	109.248(5)	109.050(7)	111.509(3)
γ (°)	113.087(5)	90	90	90	90	90	90
V (Å^3)	1472.49(16)	2938.55(11)	3372.42(9)	3374.5(5)	1595.82(18)	1592.45(15)	1541.34(6)
Z	2	4	4	4	2	2	2
D_{calc} (g cm^{-3})	1.532	1.324	1.718	1.543	1.816	1.634	1.506
F(0 0 0)	684	1224	1712	1584	856	792	708
μ (mm^{-1})	2.650	0.321	4.604	0.993	4.865	1.052	0.909
T (K)	100	140	140	100	140	140	140
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Measured reflections	33 475	24 415	21 014	78 418	13 826	11 098	13 691
Unique reflections	6737	5964	5713	7747	3352	3221	5739
Unique reflections [$I > 2\sigma(I)$]	5307	4428	5201	5247	2583	2971	5058
Data/parameters	6737/352	5964/352	5713/419	7747/416	3352/214	3221/214	5739/361
R[a] [$I > 2\sigma(I)$]	0.0363	0.0337	0.0207	0.0709	0.0404	0.0501	0.0359
$wR2$[a] (all data)	0.0645	0.0807	0.0530	0.1170	0.0838	0.1390	0.0653
Goodness-of-fit (GOF)[b]	1.132	1.010	1.032	1.160	0.949	1.148	1.046

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



Scheme 1. Synthesis of bis(phosphino)amines **1–4** and their oxides **1a–4a**, sulfides **1b–4b** and selenides **1c–4c**.

by analytical and spectroscopic methods, and furthermore, in the case of **1c** and **2b**, by X-ray crystallography. The ^{31}P NMR spectra of the oxides **1a–4a** display singlets at δ 22.0, 26.1, 25.1 and 29.5 ppm, the sulfides **1b–4b** at δ 68.4, 67.5, 67.9 and 73.6 ppm, and the selenides **1c–4c** at δ 69.1, 65.2, 65.9 and 69.8 ppm, respectively. The ^{31}P NMR resonances of these chalcogenes are consistent with similar compounds [14]. During the oxidation reaction of **1–4** with elemental sulfur and selenium, stepwise oxidation is observed, typical of bis(phosphorus) compounds with (bulky) diphenyl substituents [24]. In the case of the selenides satellites with $^1J_{P-Se}$ of about 800 Hz are observed, slightly larger than those observed with alkyl substituents (772–776 Hz) [25]. The IR spectra contain absorptions at 800–900 cm^{-1} corresponding to the P–N–P bonds. The P=O bonds in **1a–4a** exhibits vibrations around 1200 cm^{-1}, and bands between 654 and 725 cm^{-1} that are characteristic of the P=S bonds are observed in **1b–4b** and vibrations between 554 and 571 cm^{-1} ascribed to P=Se bonds are observed in **1c–4c**.

Single-crystals of **1c** and **2b** were obtained by slow diffusion of diethyl ether into a solution of **1c** or **2b** in dichloromethane. The crystallographic data of **1c** and **2b** are listed in Table 1, and their structures are illustrated in Figs. 1 and 2. Key bond lengths and angles (provided in the figure captions) are in keeping with structurally similar compounds. The P–N distances in the selenium compound **1c** [1.727(2) and 1.722(2) Å] are slightly longer than those in the sulfur compound **2b** [1.713(14) and 1.707(15) Å] and the P(1)–N(1)–P(1) angle in **1c** is slightly larger than that in **2b** [125.97(12) and 124.50(8)°, respectively].

In order to probe the ability of **1–4** to act as ligands they were reacted with several transition metal precursors (Scheme 2). Reaction of **1–4** with equimolar quantities of [MCl_2(cod)] (M = Pt or Pd; cod = cycloocta-1,5-diene) in CH_2Cl_2 afforded the platinum(II)chloride

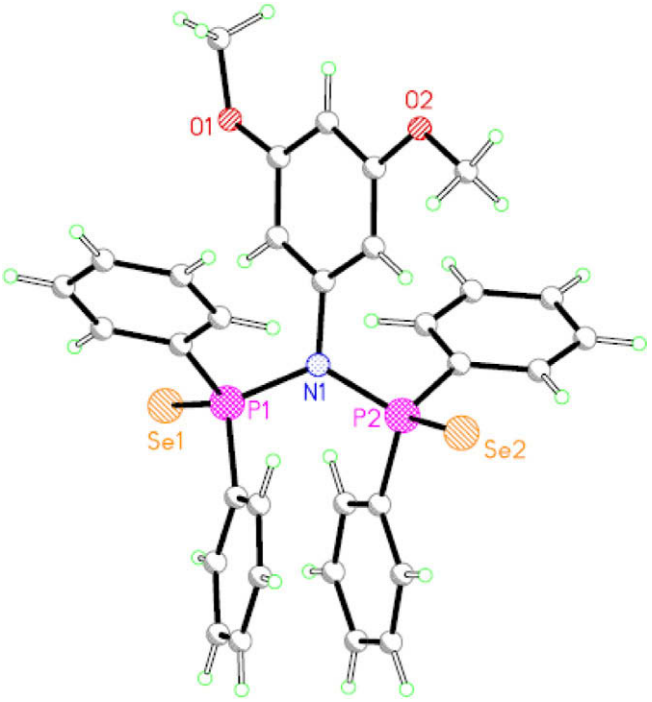


Fig. 1. Molecular structure of **1c** in the solid state. Key bond lengths (Å) and angles (°): Se(1)–P(1) 2.1092(8), Se(2)–P(2) 2.1125(8), P(1)–N(1) 1.727(2), P(1)–C(7) 1.824(3), P(1)–C(1) 1.829(3), P(2)–N(1) 1.722(2), N(1)–P(1)–Se(1), 115.59(8), N(1)–P(2)–Se(2), 115.11(8), P(2)–N(1)–P(1), 125.97(12).

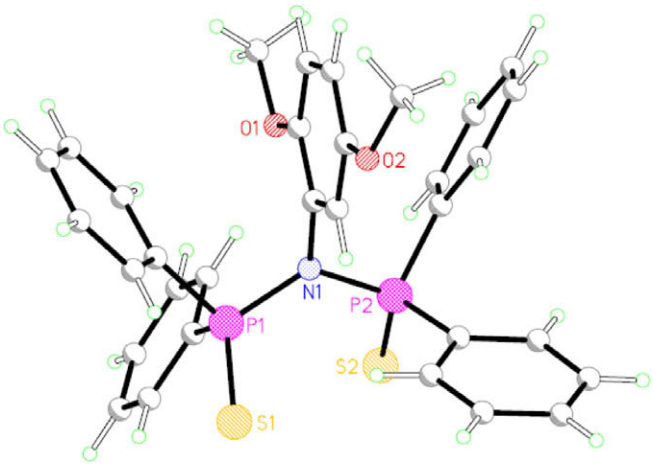
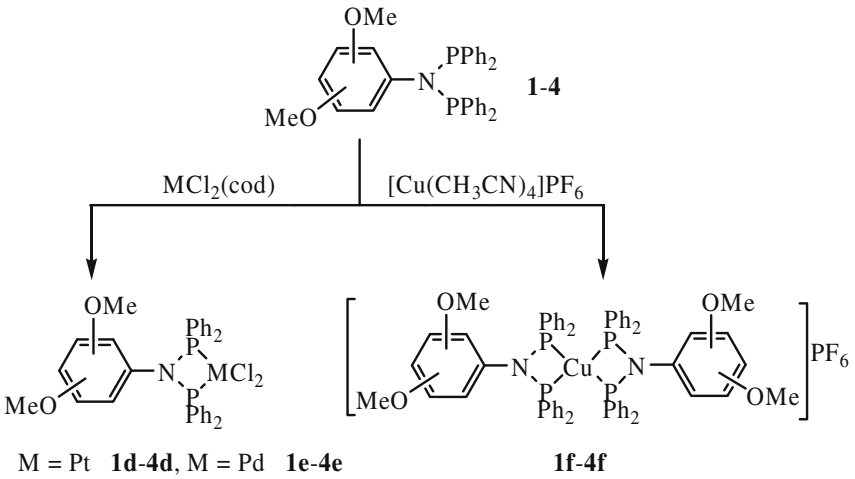


Fig. 2. Molecular structure of **2b** in the solid state. Key bond lengths (Å) and angles (°): S(1)–P(1) 1.9402(6), S(2)–P(2) 1.9370(6), P(1)–N(1) 1.7134(14), P(1)–C(1) 1.8142(18), P(1)–C(7) 1.821(2), P(2)–N(1) 1.7079(15), N(1)–P(1)–S(1) 115.03(5), N(1)–P(2)–S(2) 113.54(5), P(2)–N(1)–P(1) 124.50(8).

complexes **1d**–**4d** and the palladium(II)chloride complexes **1e**–**4e** in good yield. The ^{31}P NMR spectra of **1d**–**4d** and **1e**–**4e** display singlet resonances in the ranges 20.0–25.3 and 34.1–38.2 ppm, respectively, with the platinum complexes showing $^{1}J_{P-Pt}$ couplings of around 3400 Hz consistent with the *cis*-geometry. Reaction of **1–4** with $[Cu(CH_3CN)_4]PF_6$ in 2:1 ratio in CH_2Cl_2 gave the cationic copper complexes $[Cu\{Ph_2P)_2N\text{-}C_6H_3\text{-}R\}_2]PF_6$ (**1f**–**4f**, Scheme 2). The ^{31}P NMR spectra of **1f**–**4f** also display singlet resonances that are observed in the range 87.6–89.0 ppm together with a septet at ca. −144.4 ppm for the PF_6^- counter anion. Again, the ^{31}P NMR signals of the complexes are in keeping with structurally related compounds [3,9–11,22]. Complex **4f** is highly unstable and could not be isolated as a pure product, rapidly decomposing to give a compounds that exhibits a singlet resonance at 59.8 ppm in the ^{31}P NMR spectrum. Further spectroscopic and analytical data confirms the anticipated structures and is provided in Section 2.

Single crystals of **1d**, **1e**, **3d**, **3e** and **4e** obtained by slow diffusion of diethyl ether into solutions of the complexes in dichloromethane were analysed by single crystal X-ray diffraction and the details of the structure determinations are given in Table 1. Molecular structures of **1d**, **1e**, **3d**, **3e** and **4e** are shown in Figs. 3–7, respectively, with key bond lengths and angles listed in the captions.

There are close similarities around the 4-membered P–N–P–Pd ring in **1c, 2b, 1d, 1e, 3d**, **3e**, **4e,** with the bond distances and angles falling within narrow ranges. In the platinum complexes **1d** and **3d**, the P–Pt–P angles are 72.59(3) and 72.54(8)° and the and P–N–P angles are 98.7(3) and 99.63(12)°, respectively. The differences of the positions the methoxyl substituents have little influence on the geometry at the metal center. The P–Pd–P angles in **1e**, **3e** and **3e** [71.99(5), 72.20(6) and 72.55(5)°] are also very close and match the values observed in **1d** and **3d**, despite the smaller size of the palladium ion compared to that of the platinum ion with the P–N–P angles in **1e**, **3e** and **3e** being 99.4(4) and 98.8(3) and 99.32 (16)°, respectively.



Scheme 2. Reactions of the bis(phosphino)amines **1–4** with $[MCl_2(cod)]$ (M = Pt, Pd) and $[Cu(CH_3CN)_4]PF_6$.

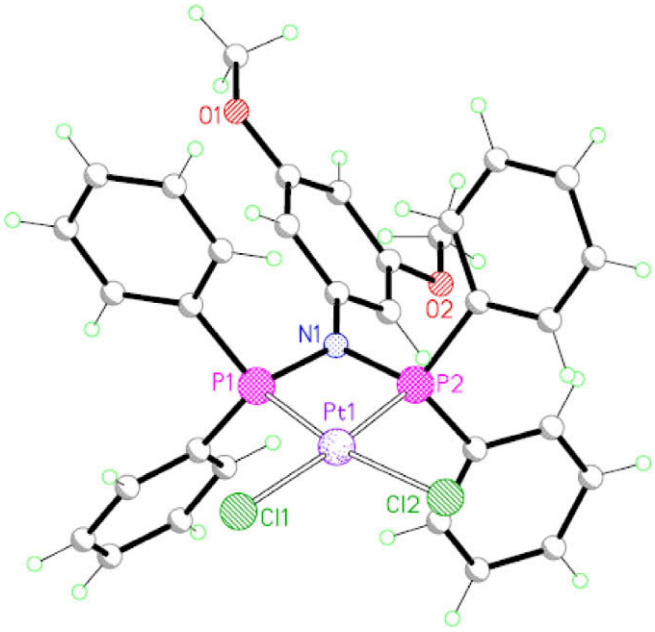


Fig. 3. Molecular structure of **1d** in the solid state. Key bond lengths (Å) and angles (°): Pt(1)–P(2) 2.1942(8), Pt(1)–P(1) 2.2111(7), Pt(1)–Cl(1) 2.3634(8), Pt(1)–Cl(2) 2.3681(7), P(1)–N(1) 1.706(2), P(1)–P(2) 2.6077(10), P(2)–N(1) 1.708(2), P(2)–Pt(1)–P(1) 72.59(3), P(2)–Pt(1)–Cl(1) 172.93(3), P(1)–Pt(1)–Cl(1) 100.57(3), P(2)–Pt(1)–Cl(2) 94.95(3), P(1)–Pt(1)–Cl(2) 167.50(3), Cl(1)–Pt(1)–Cl(2) 91.91(3), P(1)–N(1)–P(2) 99.63(12), P(2)–Pd(1)–P(1) 71.99(5), P(2)–Pd(1)–Cl(1) 171.65(5), P(1)–Pd(1)–Cl(1) 99.85(5), P(2)–Pd(1)–Cl(2) 92.72(5), P(1)–Pd(1)–Cl(2) 164.68(5), Cl(1)–Pd(1)–Cl(2) 95.46(5), P(2)–N(1)–P(1) 99.4(2).

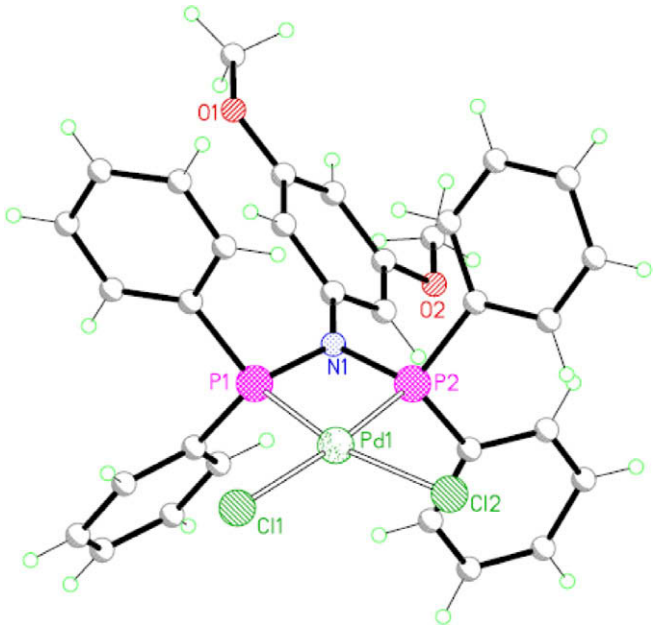


Fig. 4. Molecular structure of **1e** in the solid state. Key bond lengths (Å) and angles (°): Pd(1)–P(2) 2.2070(15), Pd(1)–P(1) 2.2358(15), Pd(1)–Cl(1) 2.3757(14), Pd(1)–Cl(2) 2.3776(14), P(1)–N(1) 1.716(4), P(1)–P(2) 2.611(2), P(2)–N(1) 1.709(4), P(2)–Pd(1)–P(1) 71.99(5), P(2)–Pd(1)–Cl(1) 171.65(5), P(1)–Pd(1)–Cl(1) 99.85(5), P(2)–Pd(1)–Cl(2) 92.72(5), P(1)–Pd(1)–Cl(2) 164.68(5), Cl(1)–Pd(1)–Cl(2) 95.46(5), P(2)–N(1)–P(1) 99.4(2).

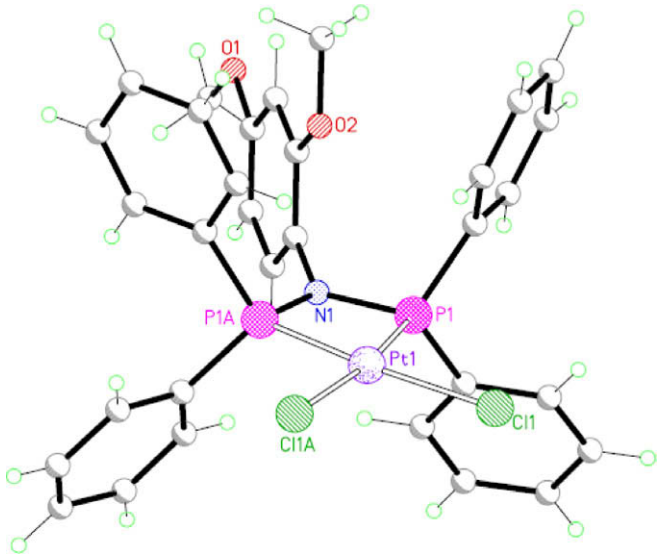


Fig. 5. Molecular structure of **3d** in the solid state. Key bond lengths (Å) and angles (°): Pt(1)–P(1) 2.2014(15), Pt(1)–P(1)#1 2.2015(15), Pt(1)–Cl(1)#1 2.3595(15), Pt(1)–Cl(1) 2.3595(15), P(1)–N(1) 1.717(4), P(1)–P(1)#1 2.605(3), N(1)–P(1)#1 1.717(4), P(1)–Pt(1)–P(1)#1 72.54(8), P(1)–Pt(1)–Cl(1)#1 170.10(5), P(1)#1–Pt(1)–Cl(1)#1 97.59(5), P(1)–Pt(1)–Cl(1) 97.59(5), P(1)#1–Pt(1)–Cl(1) 170.09(5), Cl(1)#1–Pt(1)–Cl(1) 92.26(8), P(1)#1–N(1)–P(1) 98.7(3).

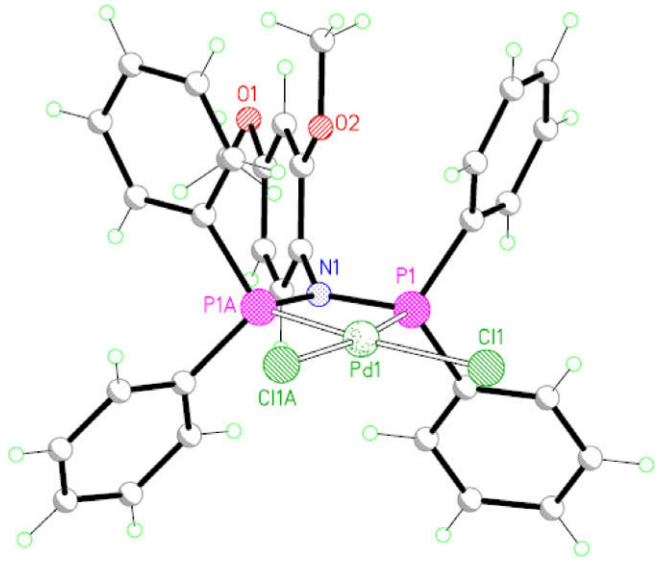


Fig. 6. Molecular structure of **3e** in the solid state. Key bond lengths (Å) and angles (°): Pd(1)–P(1)#1 2.2154(11), Pd(1)–P(1) 2.2155(11), Pd(1)–Cl(1)#1 2.3607(11), Pd(1)–Cl(1) 2.3607(11), P(1)–N(1) 1.719(4), P(1)–P(1)#1 2.611(2), N(1)–P(1)#1 1.719(4), P(1)#1–Pd(1)–P(1) 72.20(6), P(1)#1–Pd(1)–Cl(1)#1 96.20(4), P(1)–Pd(1)–Cl(1)#1 168.41(4), P(1)#1–Pd(1)–Cl(1) 168.41(4), P(1)–Pd(1)–Cl(1) 96.21(4), Cl(1)#1–Pd(1)–Cl(1) 95.39(6), P(1)–N(1)–P(1)#1 98.8(3).

3.1. Heck reactions

The Heck reaction is widely used to prepare disubstituted olefins [26]. The rate of the coupling is dependent on a variety of parameters such as solvent, base, catalyst loading and temperature. Following reaction optimization we found that use of 1% of the Pd pre-catalysts (**1e–4e**) with 2 equiv. of K_2CO_3 in dioxane at 80 °C led to the good conversions within 6 h. The activity of **1e–4e** to catalyze the coupling of 4-bromoacetophenone with styrene (Table 2, entries 2 and 7) was initially evaluated (a control experiment indicated that the coupling reaction did not occur in the absence of **1e–4e**).

Under the reaction conditions, a wide range of aryl bromides bearing electron-donating or electron-withdrawing groups reacted with styrene, affording the coupled products in excellent yields.

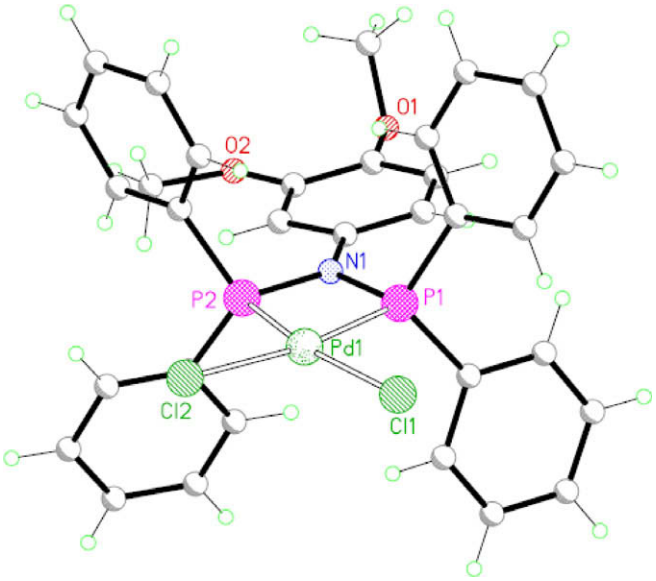
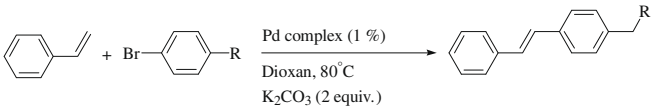


Fig. 7. Molecular structure of **4e** in the solid state. Key bond lengths (Å) and angles (°): Pd(1)–P(1) 2.2065(10), Pd(1)–P(2) 2.2069(11), Pd(1)–Cl(1) 2.3527(11), Pd(1)–Cl(2) 2.3568(10), P(1)–N(1) 1.720(3), P(1)–P(2) 2.6113(16), P(2)–N(1) 1.706(3), P(1)–Pd(1)–P(2) 72.55(5), P(1)–Pd(1)–Cl(1) 94.67(5), P(2)–Pd(1)–Cl(1) 167.08(5), P(1)–Pd(1)–Cl(2) 168.49(4), P(2)–Pd(1)–Cl(2) 96.29(4), Cl(1)–Pd(1)–Cl(2) 96.57(4), P(2)–N(1)–P(1) 99.32(16).

For substrates with electron donor groups, the palladium complexes are less active (Table 2, entries 16–23). It is interesting to note that **4e** is usually the most active pre-catalyst, especially for substrates with electron-withdrawing substitute, while all the complexes exhibit similar activities if substrates with electron-donation groups are employed. For activated substrates bearing electron-withdrawing groups, the catalytic activities of the palladium complexes **1e–4e** with ether-functionalized aminophosphines are comparable with those of ether-groups. However, for non-activated substrates the palladium complexes **1e–4e** show increased catalytic activities [27].

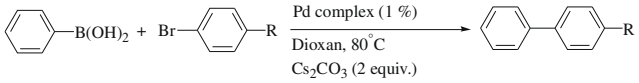
Table 2
Heck coupling reactions of aryl bromides with styrene.



Entry	R	Cat.	Yield[a] (%)
1	$COCH_3$	**1e**	65
2	$COCH_3$	**2e**	71
3	$COCH_3$	**3e**	68
4[b]	$COCH_3$	**4e**	81
5[c]	$COCH_3$	**4e**	56
6[d]	$COCH_3$	**4e**	49
7	$COCH_3$	**4e**	85
8	CHO	**1e**	76
9	CHO	**2e**	72
10	CHO	**3e**	58
11	CHO	**4e**	84
12	H	**1e**	30
13	H	**2e**	38
14	H	**3e**	66
15	H	**4e**	70
16	OCH_3	**1e**	65
17	OCH_3	**2e**	68
18	OCH_3	**3e**	69
19	OCH_3	**4e**	64
20	CH_3	**1e**	37
21	CH_3	**2e**	47
22	CH_3	**3e**	78
23	CH_3	**4e**	66

[a] *Reaction conditions:* 1.0 mmol of R-C_6H_4Br-*p*, 1.5 mmol of styrene, 2 mmol K_2CO_3, 1% Pd complex, dioxane (3 mL), 80 °C, 6 h. Purity of compounds was checked by ^{1}H NMR and yields are based on aryl bromide. All reactions were monitored by GC.
[b] Cs_2CO_3.
[c] $KOBu^t$.
[d] 50 °C.

Table 3
Suzuki coupling reactions of aryl bromides with phenylboronic acid.



Entry	R	Cat.	Yield[a] (%)
1	$COCH_3$	**1e**	95
2	$COCH_3$	**2e**	91
3	$COCH_3$	**3e**	97
4	$COCH_3$	**4e**	78[b]
5	$COCH_3$	**4e**	61[c]
6	$COCH_3$	**4e**	52[d]
7	$COCH_3$	**4e**	92
8	CHO	**1e**	88
9	CHO	**2e**	79
10	CHO	**3e**	84
11	CHO	**4e**	78
12	OCH_3	**1e**	89
13	OCH_3	**3e**	87
14	OCH_3	**4e**	89
15	H	**1e**	93
16	H	**2e**	90
17	H	**3e**	94
18	H	**4e**	95

[a] *Reaction conditions:* 1.0 mmol of R-C_6H_4Br-*p*, 1.5 mmol of phenylboronic acid, 2 mmol Cs_2CO_3, 1% Pd complex, dioxane (3 mL), 80 °C, 2 h. Purity of compounds was checked by ^{1}H NMR and yields are based on aryl bromide. All reactions were monitored by GC.
[b] K_2CO_3.
[c] $KOBu^t$.
[d] 50 °C.

3.2. Suzuki reactions

Palladium-catalysed Suzuki coupling reactions are now the method of choice for the synthesis of biaryl and heterobiaryl compounds, [28] present in numerous classes of organic compounds, such as natural products, pharmaceuticals, agrochemicals and functional materials such as liquid crystals [29]. The reaction generally results in excellent yields when performed at temperatures of 80–100 °C with aryl halides. Here, the amiophpsphine complexes **1e–4e** were performed in dioxane with Cs_2CO_3 as the base at 80 °C following reaction optimization (Table 3).

All complexes are effective pre-catalysts for the coupling of unactivated, activated and deactivated arylbromides. There does not appear to be a general trend related to the positions of the methoxyl groups in the ligands (although complex **2e** gave slightly lower yield (1–3%) compared to complexes **1e**, **3e** and **4e**). The nature of the base used strongly influences the yield of the desired products with stronger bases resulting in lower yields (Table 3, entries 4–7).

4. Conclusions

In conclusion, a series of new bis(phosphino)amines and their oxides, sulfides, selenides, and transition metal complexes have been prepared. The ligands exhibit similar reactivities towards

different oxidants and show similar coordination properties towards Pt, Pd and Cu. The palladium complexes are efficient precatalyst for C–C coupling reactions showing good activities in the Heck and Suzuki reactions, comparable or better than the other related catalysts [27].

Acknowledgements

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