Full Paper

Applied Organometallic Chemistry

Received: 5 June 2009 Revised: 8 September 2009 Accepted: 26 September 2009 Published online in Wiley Interscience: 26 November 2009

(www.interscience.com) DOI 10.1002/aoc.1576

Synthesis and characterization of new (*N*-diphenylphosphino)-isopropylanilines and their complexes: crystal structure of $(Ph_2P{=}S)NH{-}C_6H_4{-}4{-}CH(CH_3)_2$ and catalytic activity of palladium(II) complexes in the Heck and Suzuki cross-coupling reactions

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Three new (*N*-diphenylphosphino)-isopropylanilines, having isopropyl substituent at the carbon 2- (1) 4- (2) or 2,6- (3) were prepared from the aminolysis of chlorodiphenylphosphine with 2-isopropylaniline, 4-isopropylaniline or 2,6-diisopropylaniline, respectively, under anaerobic conditions. Oxidation of 1,2 and 3 with aqueous hydrogen peroxide, elemental sulfur or gray selenium gave the corresponding oxides, sulfides and selenides $(Ph_2P{=}E)NH{-}C_6H_4{-}2{-}CH(CH_3)_2$, $(Ph_2P{=}E)NH{-}C_6H_4{-}4{-}CH(CH_3)_2$ and $(Ph_2P{=}E)NH{-}C_6H_4{-}2,6{-}\{CH(CH_3)_2\}_2$, where E = O, S, or Se, respectively. The reaction of $[M(cod)Cl_2]$ (M = Pd, Pt; cod = 1,5-cyclooctadiene) with two equivalents of 1,2 or 3 yields the corresponding monodendate complexes $[M((Ph_2P)NH{-}C_6H_4{-}2{-}CH(CH_3)_2)_2Cl_2]$, M = Pd 1d, M = Pt 1e, $[M((Ph_2P)NH{-}C_6H_4{-}4{-}CH(CH_3)_2)_2Cl_2]$, M = Pd 2d, M = Pt 2e and $[M((Ph_2P)NH{-}C_6H_4{-}2,6{-}(CH(CH_3)_2)_2)_2Cl_2]$, M = Pd 3d, M = Pt 3e, respectively. All the compounds were isolated as analytically pure substances and characterized by NMR, IR spectroscopy and elemental analysis. Furthermore, representative solid-state structure of $[(Ph_2P{=}S)NH{-}C_6H_4{-}4{-}CH(CH_3)_2]$ (2b) was determined using single crystal X-ray diffraction technique. The complexes 1d–3d were tested and found to be highly active catalysts in the Suzuki coupling and Heck reaction, affording biphenyls and stilbenes, respectively. **Copyright © 2009 John Wiley & Sons, Ltd.**

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

Keywords: aminophosphine; crystal structure; catalysis; Heck reaction; Suzuki coupling

Introduction

The effects of ligands on structure and reactivity of transition metal complexes are important topics of research in coordination and organometallic chemistry as well as in homogeneous catalysis.[1] The large impact of phosphine ligand has become evident from the important discovery of the Wilkinson hydrogenation catalyst.[2] Thus, there is immense interest in the development of new phosphorus(III) ligands for various applications, principally those of homogeneous metal-catalyzed reactions.[3] Phosphorus–nitrogen containing ligands have particular use in catalysis where it is necessary for part of ligand to dissociate to allow an organic fragment to coordinate and undergo transformations. Small variations in the ligands can cause significant changes in their coordination behavior and the structural features of the resulting complexes.[4] The presence of P–N ligands enables many different and important catalytic processes to occur including Heck[5,6] and Suzuki[7,8] reactions.

Because of their remarkable catalytic potential and their large versatility, palladium complexes have become the most popular organometallics used in organic synthesis.[9] In particular, palladium catalyzes most of the carbon–carbon bond formation reactions such as Heck and Suzuki reactions,[10] which are powerful tools for the preparation of unsymmetrical biaryl[11,12] and stilbene compounds.[13] Recently, various bulky and electron-

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rich phosphanes have been developed as ligands to promote the cross-coupling reactions.[14] We have shown that aminophosphine and bis(aminophosphine) palladium(II) complexes offer distinct advantages over the Pd–phosphine system in the Suzuki and Heck cross-coupling reactions.[15,16]

Herein, we report the preparation of the three new (*N*-diphenylphosphino)isopropylanilines, having isopropyl substituent at the carbon 2- (**1**), 4- (**2**) or 2,6- (**3**) from the aminolysis of the respective aniline with one equivalent of chlorodiphenylphosphine in the presence of a base, as well as their oxides (a), sulfides (b), selenides (c) and complexes with Pd^{2+} (d) and Pt^{2+} (e). The structures of all new compounds were elucidated by a combination of multinuclear NMR spectroscopy, IR spectroscopy and elemental analysis. Furthermore, the X-ray crystal structure of (*N*-diphenylthiophosphino)-4-isopropylaniline, [(Ph_2P═S)NH–C_6H_4–4-$CH(CH_3)_2$] (**2b**) was determined, and pertinent features of this structure were described. In addition, extending our program in the design and study to develop useful catalysts for the C–C coupling reaction, palladium complexes were tested as catalyst in the Suzuki–Heck type coupling reactions.

Experimental Section

Materials and Methods

All reactions and manipulations were performed under argon unless otherwise stated. 2-Isopropylaniline, 4-isopropylaniline, 2,6-diisopropylaniline and Ph_2PCl were purchased from Fluka and used directly. Analytical grade and deuterated solvents were purchased from Merck. The starting materials [MCl_2(cod)] (M = Pd, Pt, cod = 1,5-cyclooctadiene)[17,18] were prepared according to literature procedures. Solvents were dried using the appropriate reagents and distilled prior to use. Infrared spectra were recorded as KBr disks in the range 4000–400 cm^{-1} on a Mattson 1000 ATI Unicam FT-IR spectrometer. ^1H (400.1 MHz), ^{13}C NMR (100.6 MHz) and $^{31}P–\{^1H\}$ NMR (162.0 MHz) spectra were recorded on a Bruker Avance 400 spectrometer, with δ referenced to external TMS and 85% H_3PO_4, respectively. GC analyses were performed on an HP 6890N gas chromatograph equipped with capillary column (5% biphenyl, 95% dimethylsiloxane, 30 m × 0.32 mm × 0.25 μm). Elemental analysis was carried out on a Fisons EA 1108 CHNS-O instrument. Melting points were determined by Gallenkamp Model apparatus with open capillaries.

Synthesis of Ligands

Preparation of (N-diphenylphosphino)-2-isopropylaniline, ***1***

Chlorodiphenylphosphine (0.33 g, 1.41 mmol) was added dropwise over a period of 20 min to a stirred solution of 2-isopropylaniline (0.20 g, 1.41 mmol) and triethylamine (0.14 g, 1.41 mmol) in THF–CH_2Cl_2 (1 : 2) (30 ml) at 0 °C with vigorous stirring. The mixture was stirred at room temperature (r.t.) for 2 h, and the solvent was removed under reduced pressure. After addition of THF, the white precipitate (triethylammonium chloride) was filtered off under argon and the solvent removed *in vacuo*, which was washed with cold diethyl ether (2 × 15 ml) and dried *in vacuo* to produce dark yellow viscous oil compound **1**; yield 0.43 g (92%). $^{31}P–\{^1H\}$ NMR (162.0 MHz, $CDCl_3$): δ = 29.0 (s) ppm (see Supporting Information for ^1H and ^{13}C NMR data). IR (KBr): υ = 899 (P–N), 1439 (P–Ph), 3391 (N–H) cm^{-1}. $C_{21}H_{22}NP$ (319.39 g mol^{-1}): calcd C 78.98, H 6.94, N 4.39; found C 78.87, H 6.85, N 4.35

Preparation of (N-diphenylphosphino)-4-isopropylaniline, ***2***

A dry and degassed THF (50 ml) solution of 4-isopropylaniline (0.38g, 2.75 mmol) was cooled to −78 °C in an acetone and dry ice bath. To the cooled solution was added dropwise a hexane solution of *n*-BuLi (2 ml, 2.75 mmol) over 1 h. After the addition the mixture was stirred at −78 °C for 1 h and another 30 additional minutes at room temperature. The reaction solution was cooled to −78 °C again and a solution of diphenylchlorophosphine (0.64 g, 2.75 mmol) in THF (10 ml) was added dropwise to the reaction medium. Stirring was continued for a further 1 h at −78 °C. Then the cooling bath was removed and the mixture was stirred overnight at room temperature. The solution was evaporated to dryness *in vacuo* and CH_2Cl_2 (30 ml) was added. Lithium chloride, which precipitated, was removed by filtration under argon and then the volatiles was evaporated *in vacuo* to leave a yellow viscous oil compound **2**; yield 0.85 g (97%). $^{31}P–\{^1H\}$ NMR (162.0 MHz, $CDCl_3$): δ = 31.8 (s) ppm (see Supporting Information for ^1H and ^{13}C NMR data). IR (KBr): υ = 899 (P–N), 1439 (P–Ph), 3377 (N–H) cm^{-1}. $C_{21}H_{22}NP$ (319.39 g mol^{-1}): calcd C 78.98, H 6.94, N 4.39; found C 78.85, H 6.87, N 4.34.

Preparation of (N-diphenylphosphino)-2,6-diisopropylaniline, ***3***

Chlorodiphenylphosphine (1.10 g, 4.75 mmol) was added dropwise over a period of 30 min to a stirred solution of 2,6-diisopropylaniline (0.94 g, 4.75 mmol) and triethylamine (0.49 g, 4.75 mmol) in CH_2Cl_2 (50 ml) at 0 °C with vigorous stirring. The mixture was stirred at r.t. for 2 h, and the solvent was removed under reduced pressure. After addition of dry diethyl ether, the white precipitate (triethylammonium chloride) was filtered off under argon and the solvent removed *in vacuo* which was washed with cold diethyl ether (2 × 15 ml) and dried *in vacuo* to produce yellow viscous oil compound **3**; yield 1.65 g (96%). $^{31}P–\{^1H\}$ NMR (162.0 MHz, $CDCl_3$): δ = 45.5 (s) ppm (see Supporting Information for ^1H and ^{13}C NMR data). IR (KBr): υ = 802 (P–N), 1438 (P–Ph), 3344 (N–H) cm^{-1}. $C_{24}H_{28}NP$ (361.47 g mol^{-1}): calcd C 79.75, H 7.81, N 3.88; found C 79.68, H 7.77, N 3.85.

Synthesis and Characterization of Chalcogenides

See Supporting Information.

Synthesis of Complexes

Preparation of dichlorobis((N-diphenylphosphino)-2-isopropylaniline)palladium(II), ***1d***

[Pd(cod)Cl_2] (0.10 g, 0.36 mmol) and **1** (0.23 g, 0.72 mmol) were dissolved in dry THF (25 ml) and stirred for 3 h. The volume was concentrated to ca. 1–2 ml under reduced pressure and addition of diethyl ether (20 ml) gave **1d** as a clear yellow solid. The product was collected by filtration and dried *in vacuo*; yield 0.26 g (89%); m.p. >300 °C (dec.). $^{31}P–\{^1H\}$ NMR (162.0 MHz, DMSO): δ = 38.9 (s) ppm (see Supporting Information for ^1H and ^{13}C NMR data). IR (KBr): υ = 893 (P–N), 1442 (P–Ph), 3446 (N–H) cm^{-1}. $C_{42}H_{44}N_2P_2PdCl_2$ (816.11 g mol^{-1}): calcd C 61.81, H 5.43, N 3.43; found C 61.74, H 5.36, N 3.40.

Preparation of dichlorobis((N-diphenylphosphino)-4-isopropylaniline)palladium(II), ***2d***

[Pd(cod)Cl_2] (0.10 g, 0.36 mmol) and **2** (0.23 g, 0.72 mmol) were dissolved in dry THF (25 ml) and stirred for 2 h. The volume was

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concentrated to ca. 1–2 ml under reduced pressure and addition of diethyl ether (20 ml) gave **2d** as a yellow solid. The product was collected by filtration and dried *in vacuo*; yield 0.27 g (92%); m.p. 264–266 °C. $^{31}P-\{^1H\}$ NMR (162.0 MHz, DMSO): $\delta = 36.6$ [(s), *cis*-isomer], 34.1 [(s), *trans*-isomer] ppm (see Supporting Information for ^1H and ^{13}C NMR data). IR (KBr): $\upsilon = 917$ (P–N), 1434 (P–Ph), 3425 (N–H) cm^{-1}. $C_{42}H_{44}N_2P_2PdCl_2$ (816.11 g mol^{-1}): calcd C 61.81, H 5.43, N 3.43; found C 61.74, H 5.39, N 3.40.

Preparation of dichlorobis((N-diphenylphosphino)-2,6-diisopropylaniline)palladium-(II), ***3d***

$[Pd(cod)Cl_2]$ (0.08 g, 0.28 mmol) and **3** (0.20 g, 0.56 mmol) were dissolved in dry CH_2Cl_2 (20 ml) and stirred for 2 h. The volume was concentrated to ca. 1–2 ml under reduced pressure and addition of diethyl ether (25 ml) gave **3d** as a clear yellow solid. The product was collected by filtration and dried *in vacuo*; yield: 0.21 g, 84%; m.p. 249–251 °C. $^{31}P-\{^1H\}$ NMR (162.0 MHz, DMSO): $\delta = 64.1$ (s) ppm (see Supporting Information for ^1H and ^{13}C NMR data). IR (KBr): $\upsilon = 802$ (P–N), 1438 (P–Ph), 3262 (N–H) cm^{-1}. $C_{48}H_{56}N_2P_2PdCl_2$ (900.27 g mol^{-1}): calcd C 64.04, H 6.27, N 3.11; found C 63.96; H 6.21; N 3.09.

Preparation of dichlorobis((N-diphenylphosphino)-2-isopropylaniline)platinum(II), ***1e***

$[Pt(cod)Cl_2]$ (0.14 g, 0.36 mmol) and **1** (0.23 g, 0.72 mmol) were dissolved in dry THF (25 ml) and stirred for 3 h. The volume was concentrated to ca. 1–2 ml under reduced pressure and addition of diethyl ether (20 ml) gave **1e** as a white solid. The product was collected by filtration and dried *in vacuo*; yield 0.29 g (89%); m.p. 209–211 °C. $^{31}P-\{^1H\}$ NMR (162.0 MHz, DMSO): $\delta = 28.6$ [(s) ppm, $J_{(PPt)}$: 3924.0 Hz] (see Supporting Information for ^1H and ^{13}C NMR data). IR (KBr): $\upsilon = 918$ (P–N), 1439 (P–Ph), 3435 (N–H) cm^{-1}. $C_{42}H_{44}N_2P_2PtCl_2$ (904.77 g mol^{-1}): calcd C 55.76, H 4.90, N 3.09; found C 55.69, H 4.85, N 3.05.

Preparation of dichlorobis((N-diphenylphosphino)-4-isopropylaniline)platinum(II), ***2e***

$[Pt(cod)Cl_2]$ (0.14 g, 0.36 mmol) and **2** (0.23 g, 0.72 mmol) were dissolved in dry THF (25 ml) and stirred for 2 h. The volume was concentrated to ca. 1–2 ml under reduced pressure and addition of diethyl ether (20 ml) gave **2e** as a yellow solid. The product was collected by filtration and dried *in vacuo*; yield 0.31 g (95%); m.p. 190–192 °C. $^{31}P-\{^1H\}$ NMR (162.0 MHz, DMSO): $\delta = 32.6$ [(s), *cis*-isomer, $J_{(PPt)}$: 3926.0 Hz], 24.1 [(s), *trans*-isomer, $J_{(PPt)}$: 3336.0 Hz] (see Supporting Information for ^1H and ^{13}C NMR data). IR (KBr): $\upsilon = 910$ (P–N), 1435 (P–Ph), 3417 (N–H) cm^{-1}. $C_{42}H_{44}N_2P_2PtCl_2$ (904.77 g mol^{-1}): calcd C 55.76, H 4.90, N 3.10; found C 55.71, H 4.84, N 3.05.

Preparation of dichlorobis((N-diphenylphosphino)-2,6-diisopropylaniline)platinum-(II), ***3e***

$[Pt(cod)Cl_2]$ (0.10 g, 0.28 mmol) and **3** (0.20 mg, 0.56 mmol) were dissolved in dry CH_2Cl_2 (20 ml) and stirred for 2 h. The volume was concentrated to ca. 1–2 ml by evaporation under reduced pressure and addition of diethyl ether (25 ml) gave **3e** as a white solid. The product was collected by filtration and dried *in vacuo*; yield 0.22 g, 80%; m.p. 294–296 °C. $^{31}P-\{^1H\}$ NMR (162.0 MHz, DMSO): $\delta = 28.4$ [(s) ppm, $J_{(PPt)}$: 3893.0 Hz] (see Supporting Information for ^1H and ^{13}C NMR data). IR (KBr): $\upsilon = 833$ (P–N), 1438 (P–Ph), 3413 (N–H) cm^{-1}. $C_{48}H_{56}N_2P_2PtCl_2$ (988.93 g mol^{-1}): calcd C 58.30, H 5.71, N 2.83; found C 58.22, H 5.66, N 2.80.

Single-crystal X-ray diffraction analysis of $(Ph_2PS)NH-C_6H_4-4-CH(CH_3)_2$, 2b

A suitable prismatic colorless crystal of **2b** was glued to a thin quartz glass and mounted on the goniometry of an Enraf Nonious CAD4 difractometer. Intensity data were collected at room temperature by operating in $\omega/2\theta$ scan mode with graphite monochromated MoK_α radiation, $\lambda = 0.71073$ Å (operating at 40 kV and 40 mA). Data reduction was performed using XCAD4.[19] The structure was solved by direct methods and refinement using the program SHELX[20] in the WinGX package.[21] A full-matrix least-squares refinement on F^2 converged at $R = 0.0484$. Semi-empirical absorption corrections were applied using psi-scans.[22] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the N and C19 atoms are taken from a difference Fourier map and their positional parameters fixed, while the other hydrogen atoms are in calculated positions using the riding method with $U_{iso}(H) = 1.5\,U_{eq}(CH_3)$ and $U_{iso}(H) = 1.2\,U_{eq}(C)$. The hydrogen bond and molecular packing geometry of the title molecule was calculated with PLATON.[23] The graphical representations of the structure were made with ORTEP[24] and MERCURY.[25]

General Procedure for the Suzuki Coupling Reaction

Complexes **1–3d** (0.01 mmol), aryl bromide (1.0 mmol), phenylboronic acid (1.5 mmol), Cs_2CO_3 (2 mmol) and dioxane (3 ml) were placed into a small Schlenk tube in argon atmosphere and the mixture was heated at 80 °C for 7.0 h for **1d**, at 80 °C for 6.0 h for **2d** and at 70 °C for 4.0 h for **3d**. After completion of the reaction, the mixture was cooled, 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 NMR and yields are based on aryl bromide.

General Procedure for the Heck Coupling Reaction

Complexes **1–3d** (0.01 mmol), aryl bromide (1.0 mmol), styrene (1.5 mmol), K_2CO_3 (2 mmol) and DMF (3 ml) for **1–3d** were placed into a small Schlenk tube in argon atmosphere and the mixture was heated to 120 °C for **1–3d.** After completion of the reaction, the mixture was cooled, 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 NMR and yields are based on aryl bromide.

Results and Discussion

Aminolysis appears to be the most common method used for the synthesis of phosphinoamines and bis(phosphino)amines,[26,27] whereby the solvent has a significant influence on the rate and product of the aminolysis. (*N*-diphenylphosphino)isopropylanilines, having isopropyl substituent at the carbon 2- (**1**) or 2,6- (**3**) were easily prepared from the aminolysis of $H_2N-C_6H_4-2-CH(CH_3)_2$ or $H_2N-C_6H_4-2,6-\{CH(CH_3)_2\}_2$, respectively, with one equivalent of chlorodiphenylphosphine in the presence of triethylamine at 0 °C using $THF-CH_2Cl_2$ (1 : 2) and CH_2Cl_2 as solvents, respectively. Compounds **1** and **3** were isolated as viscous oily compounds

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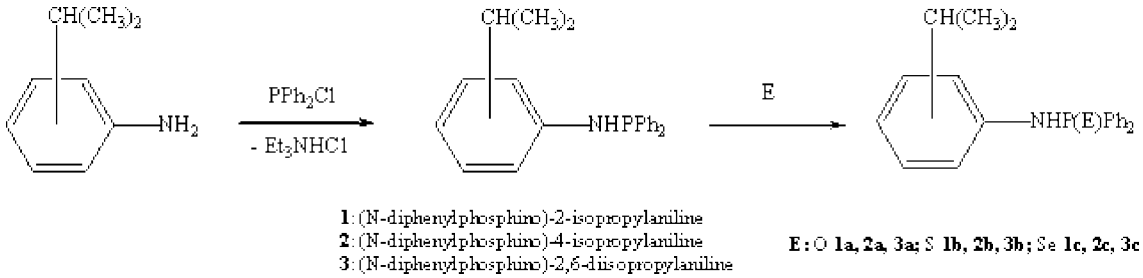
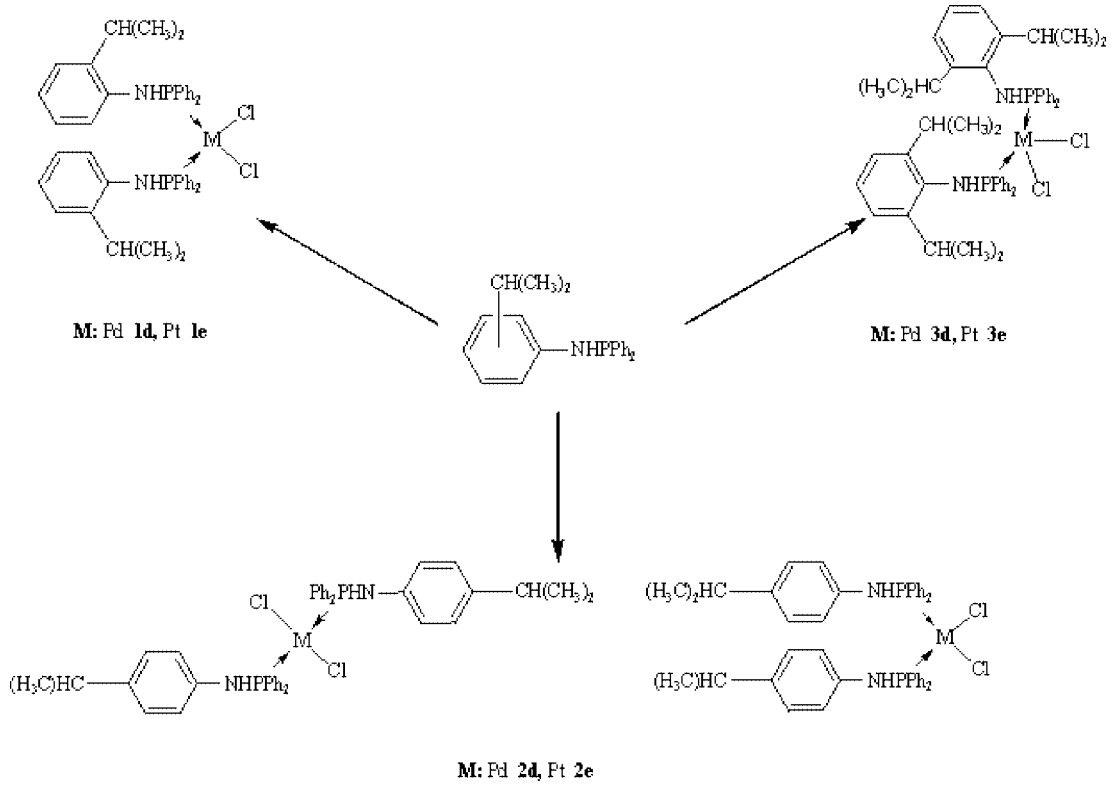


Scheme 1. Synthesis of (*N*-diphenylphosphino)-2-isopropylaniline, $(Ph_2P)NH-C_6H_4-2-CH(CH_3)_2$, (*N*-diphenylphosphino)-4-isopropylaniline, $(Ph_2P)NH-C_6H_4-4-CH(CH_3)_2$ and (*N*-diphenylphos-phino)-2,6-diisopropylaniline, $(Ph_2P)NH-C_6H_4-2,6-\{CH(CH_3)_2\}_2$ and their chalcogenides.

in high yields (92 and 96%, respectively) under anaerobic conditions. However, the attempt to prepare (*N*-diphenylphosphino)-4-isoprophylaniline (**2**) hardly succeed, due to the formation of *N*,*N*-bis(diphenylphosphino)-4-isopropylaniline, $[(Ph_2P)_2N-(C_6H_4)-4-CH(CH_3)_2]$. Therefore, the preparation of **2** was achieved only with one equivalent of Ph_2PCl, in the presence of *n*-BuLi at $-78\,^{\circ}C$ as a yellow viscous oil compound (97%) (Scheme 1).

The $^{31}P-\{H\}$ NMR spectra taken from the crude solutions of **1–3** display in addition to the prominent single resonances at 29.0, 31.8 or 45.5 ppm for the main products **1–3**, respectively, two doublets at 16.8 ppm and −22.1 ppm with a $^{1}J_{(PP)}$ value of 286 Hz, indicating the formation of iminobiphosphine [-N=PPh_2-PPh_2] structure.[28] Additionally, the observation of a singlet at δ −14.3 ppm and doublets at δ 34.4 ppm and at δ −23.7 ppm with $^{1}J_{(PP)}$ 218 Hz indicates the formation of PPh_2PPh_2 and $P(O)Ph_2PPh_2$, respectively. These by-products were easily removed by washing with copious amount of dry diethyl ether. The compounds **1–3** are not stable in solution toward oxidation when exposed to air or moisture. The solution of **1–3** in $CDCl_3$, prepared under anaerobic conditions, oxidized gradually to give respective oxide and bis(diphenylphosphino)monoxide $[P(O)Ph_2PPh_2]$ derivatives.

Compounds **1–3** were fully characterized by NMR, IR spectroscopy and elemental analysis. The IR spectra of **1–3** showed characteristic absorption bands at 3391, 3377 and 3344 cm^{-1}, respectively, due to υ(N–H) stretching. The $^{31}P-\{^{1}H\}$ NMR spectra of compounds **1–3** showed single resonances at 29.0, 31.8 and 45.5 ppm, respectively, comparable to those of other aminophosphines.[29] The phenyl carbons displayed well-resolved signals in the $^{13}C-\{^{1}H\}$ NMR spectra. In the P(III) compounds **1–3**, the coupling constant between *i*-carbon and the phosphorus was relatively small, $^{1}J(PC)$ = 13.1, 20.0 and 16.0 Hz, respectively, while the couplings between *o*-carbon and the phosphorus were relatively large, $^{2}J(PC)$ = 21.1, 21.1 and 20.0 Hz, respectively. The coupling constants between *m*-carbon and the phosphorus were $^{3}J(PC)$ = 6.0, 6.0 and 6.0 Hz, respectively, and



Scheme 2. Reactions of aminophosphines **1,2** or **3** with $[M(cod)Cl_2]$ (M = Pd, Pt).

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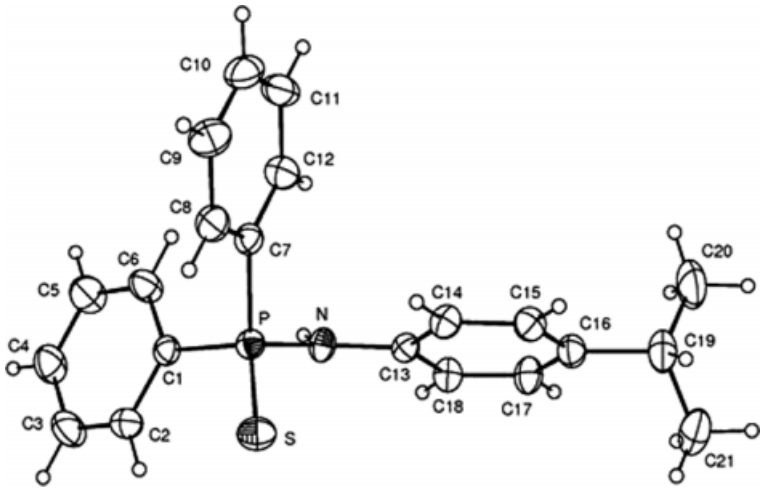

Figure 1. ORTEP drawing of the title compound **2b** with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

the coupling between *p*-carbon and the phosphorus was not observed.

To probe the reactivity of compounds **1–3**, reactions with aqueous hydrogene peroxide, elemental sulfur and gray selenium were carried out (Scheme 1). The oxides **1a, 2a** and **3a** were easily prepared by addition of excess aqueous hydrogen peroxide to **1,2** or **3**, respectively. The $^{31}P-\{^{1}H\}$ NMR spectra of **1a–3a** showed singlets at δ(P) 16.8, 22.1, and 25.2 ppm which were shifted towards higher magnetic field by 12.2, 9.7, and 20.3 ppm compared with the parent compounds **1–3**, respectively.

The sulfides **1b–3b** and selenides**1c–3c** were prepared by the addition of elemental S and Se to**1–3** in THF, respectively. The $^{31}P-\{^{1}H\}$ NMR showed single resonances at δ(P) 52.8 ppm, δ(P) 56.1 ppm and δ(P) 60.8 ppm for **1b–3b**, respectively. Compounds **1c–3c** were analyzed by $^{31}P-\{^{1}H\}$ NMR spectroscopy, which exhibited singlet resonances at 49.3, 52.6, and 58.1 ppm, with $^{1}J(^{31}P\text{-}^{77}Se)$ of 791, 762, and 770 Hz, respectively.

The coordination chemistry of the ligands **1–3** was studied by forming palladium and platinum complexes. The reaction of $[M(cod)Cl_2]$ (M = Pd, Pt; cod = 1,5-cyclooctadiene) with two equivalents of **1–3** in dichloromethane at room temperature afforded the corresponding monodendate complexes $[M\{(Ph_2P)NH-C_6H_4-2-CH(CH_3)_2\}_2Cl_2]$, M = Pd **1d**, M = Pt **1e**, $[M\{(Ph_2P)NH-C_6H_4-4-CH(CH_3)_2\}_2Cl_2]$, M = Pd **2d**, M = Pt **2e** and $[M\{(Ph_2P)NH-C_6H_4-2,6-(CH(CH_3)_2)_2\}_2Cl_2]$, M = Pd **3d**, M = Pt **3e**, respectively, as the main products in high yields (80–90%; Scheme 2). In the complexes **1d–3d** and **1e–3e**, the nitrogen atom of the amine group was not involved in coordination to the metal centers because the phosphorus atoms are much stronger donors and thus coordination to the metal center takes place preferentially at the phosphorus atoms. The formation of complexes**1d,3d, 1e** and **3e** was followed by $^{31}P-\{^{1}H\}$ NMR spectra which gave singlet signals growing at δ 38.9, 64.1, 28.6 and 28.4 ppm for **1d,3d, 1e** and **3e**, respectively. The complexes **1e** and**3e** showed large $^{1}J_{PtP}$ coupling 3924 and 3893 Hz, respectively, which are characteristic of phosphines having mutually *cis*-arrangement.[30] The $^{31}P-\{^{1}H\}$-NMR spectra of complexes **2d** and **2e** showed two sharp singlets at δ 36.6, 34.1 and 32.6, 24.1 ppm with relative intensity ratios of ~5 : 3 and ~3 : 2, attributable to the mixture of

Table 1. Crystal data and results of structure refinement for **2b**

Formula	$[\{(C_6H_5)_2PS\}NH\ C_6H_4\ CH(CH_3)_2]$
Formula weight (g mol^{-1})	351.44
Crystal system, space group	Monoclinic, P $2_1/n$
Unit cell dimensions (Å, deg)	$a = 12.253(2)$, $b = 9.7934(10)$, $c = 15.932(2)$, $\beta = 92.628(10)$
Cell volume (Å^3)/Z	1909.8(4)/4
Calculated density (g cm^{-3})	1.222
Crystal color/shape/size (mm)	colorless/prism/0.4 × 0.3 × 0.3
F(000)	744
Absorption coefficient (mm^{-1})	0.255
Absorption correction type	Psi-scan
T_{max}/T_{min}	0.912/0.935
θ-range for data collection (deg)	2.44–26.3
Limiting indices	$-15 \le h \le 15$, $-12 \le k \le 0$, $-19 \le l \le 19$
Reflections collected/unique	7725/3881 [$R_{int} = 0.0484$]
Data/parameters/restraints	3881/221/2
Goodness-of-fit on F^2	1.097
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0460$, $wR_2 = 0.1243$
Largest difference peak and hole (e Å^{-3})	0.249, −0.392

Further details on the structural investigation are available on request from the Cambridge Crystallographica Data Centre, quoting the depository number CCDC 720017.

Table 2. Coordination geometry around the P atom for **2b** (Å, deg)

P–S	1.9447(9)	S–P–N	115.53(8)
P–N	1.6603(18)	S–P–C1	115.39(8)
P–C1	1.805(2)	S–P–C7	111.51(8)
P–C7	1.807(2)	N–P–C7	106.99(11)
N–H	0.9417(18)	N–P–C1	99.44(10)
		C1–P–C7	106.92(10)

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cis- and *trans*- forms of **2d** and **2e**, respectively. From the $^{31}P-\{^{1}H\}$ NMR data it can be concluded that **2d** and **2e** are on the verge of preferential *cis*- and *trans*-geometry. Upon redisolving and stirring for 24 h, no change in the *cis* : *trans* ratio was observed. It is difficult to make an unequivocal assignment of the signals to the respective isomers. However, in the case of complex **2e**, an assigment can be made on the basis of ^{1}J(Pt–P) coupling constants. It is known that in platinum(II) complexes $PtCl_2(PR_3)_2$, the ^{1}J(Pt–P) coupling constant in the *cis*-isomer is larger than that in the *trans*-isomer.[31,32] Therefore, the signal with the large $^{1}J(^{135}Pt-^{31}P)$ coupling constant of 3926.0 Hz for **2e** is assigned to the *cis* arrangement of phosphines around the platinum(II) center while the signal with the small ^{1}J ($^{135}Pt-^{31}P$) coupling constant of 3336.0 Hz is assigned to the *trans* arrangement. The chemical shifts for **2d** can help us in assigning the signals to the respective isomer. By comparing to the literature values, the signal at δ 36.6 ppm was tentatively assigned to the *cis*-isomer and the one at δ 34.1 ppm to the *trans*-isomer. In the nonchelating phosphine complexes, the phosphorus signal of the *cis*-isomers has been always observed at lower field than that of the *trans*-isomer.[33,34] In the IR spectra, the υ(P–N) vibrations were observed as very strong bands at ca. 893, 917, 802 for **1d–3d** and 918, 910, and 833 cm^{-1} for **1e–3e**. Furthermore, ^{1}H NMR spectral data of the complexes **1d–3d** and **1e-3e** were consistent with the structures proposed and the compositions of the six complexes were confirmed by elemental analysis.

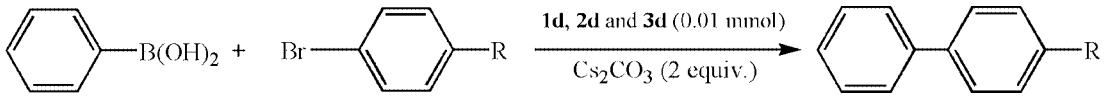
Palladium(II) complexes were found to be stable in the solid state, but decomposed in solution when exposed to air. The decomposition of the complexes was followed *in situ* by ^{31}P NMR spectroscopy. The resonances corresponding to complexes **1d–3d** gradually disappeared with concomitant formation of $Ph_2P(O)H$ and $Ph_2P(O)OH$ as indentified by signals at δ = 21 and 35 ppm, respectively.[35]

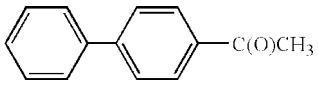
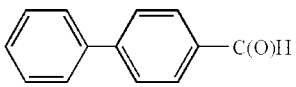
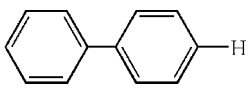
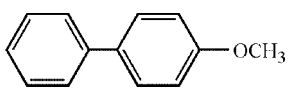
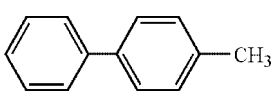
A single crystal of $[(Ph_2P{=}S)NH-C_6H_4-4\text{-}CH(CH_3)_2]$ **2b** suitable for X-ray diffraction studies was obtained by slow diffusion of diethyl ether into solution of the compound in dichloromethane.

Solid-state Crystal Structure of $[(Ph_2P{=}S)NH-C_6H_4-4\text{-}CH(CH_3)_2]$, 2b

The compound $(Ph_2P{=}S)NH-C_6H_4-4\text{-}CH(CH_3)_2$ crystallizes in monoclinic crystal system with an asymmetric unit formula of $PNSC_{21}H_{22}$ (Fig. 1). The crystallographic data are listed in Table 1. The bond distances and bond angles around the P atom are given in Table 2. The P atom has a distorted tetrahedral coordination sphere consisting of one N, one S and two C atoms of the phenyl rings at bond distances P–S = 1.9447(9), P–N = 1.6603(18), P–C1 = 1.805(2) and P–C7 = 1.807(2) Å. The bond angles within the coordination sphere are close to the ideal value of 109°,

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



Entry	R	Cat	Product	Conv.(%)	Yield(%)
1	4-$CH_3C(O)$-	**1d**		94.36	92.25
2		**2d**		91.74	90.33
3		**3d**		92.20	89.23
4	4-CH(O)-	**1d**		93.85	93.46
5		**2d**		95.73	94.62
6		**3d**		88.46	87.52
7	4-H	**1d**		82.20	75.78
8		**2d**		73.34	69.78
9		**3d**		82.28	81.85
10	4-CH_3O-	**1d**		75.45	72.68
11		**2d**		64.34	61.36
12		**3d**		70.83	67.51
13	4-CH_3-	**1d**		74.85	70.84
14		**2d**		70.30	63.08
15		**3d**		65.18	60.08

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 catalyst, dioxane (3.0 ml). Purity of compounds was checked by NMR and yields are based on arylbromide. All reactions were monitored by GC, 80 °C, 7.0 h for **1d**; 80 °C, 6.0 h for **2d**; 70 °C, 4.0 h for **3d**.

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except the N–P–C1 angle of 99.44(10)°. The distortion of this angle from ideal tetrahedral geometry is a consequence of the steric repulsion in the (*N*-diphenylphosphino)-2-isopropylaniline molecule.

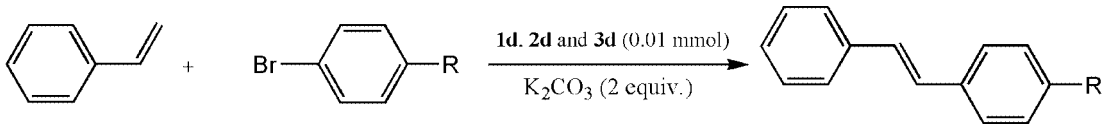
The Suzuki Coupling Reactions

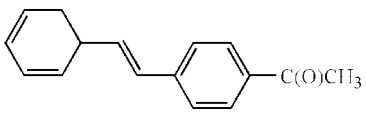
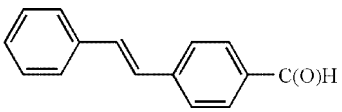
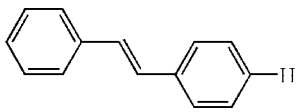
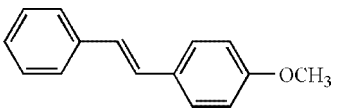
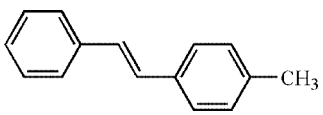
The palladium complexes **1d–3d** were tested as catalyst in the Suzuki reaction of aryl halides with boronic acid, which is one of the most efficient methods for C–C bond formation.[36] Among the bases (Cs_2CO_3, K_2CO_3 and K^tOBu) screened, Cs_2CO_3 gave the best yields. Following optimization of experiments we found that the use of 0.01 mmol the palladium complexes **1d–3d** with Cs_2CO_3 as the base at 80, 80 and 70 °C in dioxane appeared to be best, respectively. We initially tested the catalytic activity of the complexes **1d–3d** for the coupling of *p*-bromoacetophenone with phenylboronic acid and the control experiments showed that the coupling reaction does not occur in the absence of the catalyst. Under these conditions, *p*-bromoacetophenone, *p*-bromobenzaldehyde, *p*-bromobenzene, *p*-bromoanisole and *p*-bromotoluene reacted cleanly with phenylboronic acid in high yields (Table 3).

The Heck Coupling Reactions

For the choice of base, we surveyed Cs_2CO_3, K_2CO_3 and K^tOBu. Finally, we found that use of 1.0% mmol, 2 equivalents of K_2CO_3 in DMF at 120 °C for **1d–3d** led to the best conversions. We initially tested the catalytic activities of **1d–3d** for the coupling of *p*-bromoacetophenone with styrene. A control experiment indicated that the coupling reaction did not occur in the absence of **1d–3d.** Under the determined reaction conditions, a wide range of aryl bromides bearing electron-donating and electron-withdrawing groups reacted with styrene, affording the coupled products in excellent yields. As expected, electron-deficient bromides were beneficial for the conversions (Table 4). Using aryl chlorides instead of aryl bromides yielded only a small amount of stilbene derivatives under the conditions employed for bromides.

Table 4. The Heck coupling reactions of aryl bromides with styrene



Entry	R	Cat	Product	Conv.(%)	Yield(%)
1	4-$CH_3C(O)$-	**1d**		96.61	94.31
2		**2d**		93.84	91.90
3		**3d**		94.25	93.37
4	4-CH(O)-	**1d**		96.14	95.92
5		**2d**		98.28	96.71
6		**3d**		92.62	90.49
7	4-H	**1d**		75.45	70.35
8		**2d**		74.39	71.18
9		**3d**		80.05	74.80
10	4-CH_3O-	**1d**		53.55	51.29
11		**2d**		58.82	50.63
12		**3d**		55.06	53.30
13	4-CH_3-	**1d**		64.05	62.48
14		**2d**		72.30	64.56
15		**3d**		66.18	60.55

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 catalyst, DMF (3.0 ml) for **1-3d**. Purity of compounds was checked by NMR and yields are based on arylbromide. All reactions were monitored by GC: 120 °C, 2.0 h for **1d**; 120 °C, 4.0 h for **2d**; and 120 °C, 2.5 h for **3d**.

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Conclusions

In conclusion, we have shown the facile synthesis of versatile and inexpensive aminophosphine ligands **1,2** and**3**, based on 2-isopropylaniline, 4- isopropylaniline or 2,6-diisopropylaniline and their derivatives including oxides, sulfides and selenides. All these new compounds were characterized using multinuclear NMR, IR and microanalysis and also one representative structure was studied by single crystal X-ray diffraction analysis. The coordination behaviors of ligands**1–3** towards Pd(II) and Pt(II) have been described. The ligands show clear tendencies to coordinate in a *cis*-fashion to these transitions metals, as indicated by $^{31}P-\{^{1}H\}$ NMR spectroscopy. However, for complexes **2d** and **2e**, from the data $^{31}P-\{^{1}H\}$ NMR spectroscopy, it was observed that a mixture of *cis* and *trans* isomers formed. Furthermore, we have demonstrated the application of these aminophosphine ligands in the Suzuki coupling and Heck reactions of aryl halides. Because of the strength of the Pt–C bonds, the Pt(II)-bis(phosphino)amine **1–3e** system exhibited no catalytic activity.[37] Only the palladium complexes were found to show catalytic activity in both the Suzuki coupling and Heck reactions of aryl bromides. In both cases, the catalytic activities of complexes **1–3d** were found to be higher in reactions of aryl bromides with an electron-withdrawing substituent than those with an electron-releasing substituent. The catalytic activity and the yield of coupling reactions could be controlled over a wide range by variation of the coupling parameters. The procedure is quite simple and efficient towards various aryl bromides and does not require an induction period. It is likely that palladium(0) nanoclusters are formed from the reduction of palladium(II) complexes. Palladium(0) nanoclusters are active catalyst in the Suzuki and Heck reactions; however, they undergo rapid deactivation. As the only stabilizers present in the reaction medium, the aminophosphine ligands cannot provide enough stabilization for the palladium(0) nanoclusters against the aggregate to bulk palladium metal, which are catalytically inactive.

Supporting Information

Supporting information can be found in the online version of this article. CCDC holds the supplementary crystallographic data 720017 . These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax (+44) 1223-336-033; or email deposit@ccdc.cam.ac.uk.

Acknowledgment

Partial support from Turkish Academy of Sciences and Dicle University (project number DÜAPK 05-FF-27) is gratefully acknowledged

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