Journal of Organometallic Chemistry 693 (2008) 2693–2699

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

Synthesis of new aminophosphine complexes and their catalytic activities in C–C coupling reactions

Nermin Biricik [a,*], Feyyaz Durap [a], Cezmi Kayan [a], Bahattin Gümgüm [a], Nevin Gürbüz [b], İsmail Özdemir [b], Wee Han Ang [c], Zhaofu Fei [c], Rosario Scopelliti [c]

[a] Department of Chemistry, University of Dicle, 21280 Diyarbakir, Turkey
[b] Department of Chemistry, University of İnönü, 44280 Malatya, Turkey
[c] Institut de Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

ARTICLE INFO

Article history:
Received 17 March 2008
Received in revised form 6 May 2008
Accepted 6 May 2008
Available online 22 May 2008

Keywords:
Aminophosphine
Synthesis
Oxidation
X-ray structures
Catalysis

ABSTRACT

Two new aminophosphines, benzyl-N(Ph_2P)$_2$ and 2-picolyl-N(Ph_2P)$_2$, have been synthesized. Oxidation of the aminophosphines with either hydrogen peroxide, elemental sulfur and selenium gave the corresponding oxides, sulfides and selenides benzyl-N(Ph_2P=E)$_2$ and 2-picolyl-N(Ph_2P=E)$_2$, where E = O, S, or Se. Complexes [benzyl-N(Ph_2P)$_2$]MCl_2 and [2-picolyl-N(Ph_2P)$_2$]MCl_2, where M = Pd, Pt, were obtained by the reaction of the aminophosphines with MCl_2(cod). The new compounds were characterised by NMR, IR spectroscopy and microanalysis. Furthermore, representative solid-state structures of the palladium and platinum complexes were determined using single crystal X-ray diffraction analysis. The palladium complexes were further investigated as potential catalysts in C–C coupling reactions.

1. Introduction

The chemistry of aminophosphines containing direct P–N bonds is one of the interesting and challenging areas in the main group chemistry [1]. Among the numerous aminophosphines, bis(diphenylphosphino)alkylamine derivatives are particularly interesting due to their facile synthesis, relatively higher stability and their ability to chelate transition metals such as palladium, platinum, copper [2,3]. Functionalized aminophosphines with additional donor groups attached onto the amine or phosphine backbones are particularly interesting since the functional group can be modified to tune the chemical and physical properties of the final product. Many aminophosphine ligands and their complexes have been investigated as co-catalysts in a number of catalytic processes [4,5]. In addition, some aminophosphines and derivatives have also been investigated as anticancer drugs [6], herbicides and antimicrobial agents, as well as neuroactive agents [7,8].

The synthesis of bis(diphenylphosphino)alkylamine is usually achieved in high yield *via* the aminolysis method, which allows the incorporation of additional functional groups such as O- and N-donors [9,10], or π-donors such as ally group [11]. The presence of the bulky groups attached to the phosphorus center renders the aminophosphine more stable against hydrolysis [12]. The substituents at the amine backbone can also play an important role in determining the outcome of the products [13]. In a recent study [14], we found that electron-donating groups often lead to the exclusive formation of aminophosphines [P^{III}–N–P^{III}], whereas the electron-withdrawing groups, such as nitrile, trifluoromethyl at the *ortho*-position can lead to formation of iminobiphosphine [P^{III}–P^{V}=N] species.

The palladium-catalyzed reactions of aryl chlorides with arylboronic acid (the Suzuki reaction) and with alkenes (the Heck reaction) are among the most common methods for C–C bond formation and has attracted much current interest [15,16]. Recently, various bulky and electron-rich phosphanes have been developed as ligands to promote the cross-coupling reaction [17]. The ligands may afford coordinatively unsaturated monophosphane-ligated complexes and accelerate the catalytic steps, that is, oxidative addition, transmetalation, and reductive elimination. We have shown that *N,N*-bis(diphenylphosphino)aniline palladium(II) complexes offer distinctive advantages as possible alternatives for Pd/phosphine systems in the Heck coupling reactions [18].

Herein, we describe the synthesis of new aminophosphines and corresponding oxides and complexes with selected transition metals (Pd, Pt). The compounds were fully characterized using multinuclear NMR spectroscopic methods and the solid-state structure of the metal complexes was established by single crystal X-ray

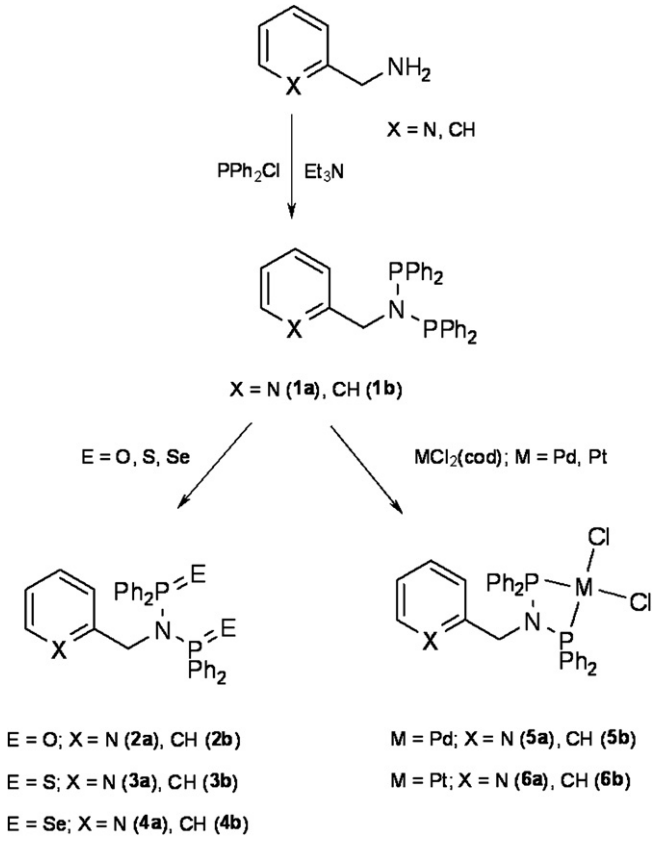
* Corresponding author.
E-mail address: nbiricik@dicle.edu.tr (N. Biricik).

0022-328X/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2008.05.010

diffraction analyses. With a view to develop useful catalysts for C–C coupling reactions, the palladium complexes were further investigated as potential catalyst precursor for Suzuki-Heck type coupling reactions.

2. Results and discussions

The new aminophosphines **1a** and **1b** were prepared from the commercially available amines via the classical aminolysis reaction with diphenylphosphine chloride in dichloromethane (see Scheme 1) [19]. The reaction of Ph_2PCl with 2-picolylamine and benzylamine yielded products with single resonances δ 62.6 ppm for **1a** and 60.2 ppm for **1b**, respectively in their ^{31}P NMR spectra in high yield. No formation of iminobiphosphine species (Ph_2P–PPh_2=NC_5H_4X, where X = N, CH) was observed. The chemical shift of compound **1a** is shifted downfield with respect to compound **1b**, although they both lie in the expected region of 60–70 ppm [20]. In the ^1H NMR spectra, the aminophosphines displayed overlapped multiplets in the region of 6.70–8.10 ppm for the aromatic H-atoms, whereas the CH_2 groups lie at 4.69 ppm for **1a** and 4.51 ppm for **1b**, respectively. Both compounds **1a** and **1b** are stable in air, presumably due to the presence of bulky phenyl groups, and can be washed with water to remove traces of $Et_3N \cdot HCl$ byproduct. However, in solution, they undergo decomposition in time.



Scheme 1. Synthetic route of *N,N*-bis(diphenylphosphino)anilines by the aminolysis reaction of H_2N–CH_2–C_5H_4X (X = N, CH) with Ph_2PCl, and their oxidation and complexation reactions.

Oxidation of **1a** and **1b** with either hydrogen peroxide, elemental sulfur and selenium gave the corresponding oxides **2a** and **2b**, sulfides **3a** and **3b** and selenides **4a** and **4b** (Scheme 1). As expected, the oxidation reaction using aqueous H_2O_2 was very rapid for both complexes and took place at ambient conditions spontaneously, with a small amount of hydrolysis product formed as evidenced by the signal at about 20.0 ppm for the $Ph_2P(O)H$ in the ^{31}P–$\{^1H\}$ NMR spectra. In contrast, oxidation with sulfur or selenium had to be carried out at elevated temperatures and a stepwise oxidation process was further observed. For example, in the sulfurization of **1a**, resonances due the starting compound **1a** (62.6 ppm), the mono-oxidized intermediate (62.5 ppm and 72.4 ppm) and the desired product **3a** (72.3 ppm) were observed at the beginning of the reaction. This is not surprising since elemental sulfur and selenium are weaker oxidizing agents than hydrogen peroxide and that the phosphorous atoms are rendered less reactive due to the bulky phenyl groups [21,22]. After the completion of the reaction, the signals of the starting compound **1a** and the mono-oxidized intermediate disappeared leaving the resonance at 72.3 ppm due to the desired product **3a**. Attempts to control the reaction conditions to yield the mono-oxidized intermediates were unsuccessful.

The ^{31}P NMR spectra of **2a** and **2b** displayed singlets at 30.6 ppm and 30.3 ppm, respectively, suggesting both phosphorus atoms are chemically-equivalent in the solution. Similarly, single resonances were also found in the ^{31}P NMR spectra of **3a** and **3b**, at 72.3 ppm and 71.8 ppm, and in those of **4a** and **4b**, at 71.9 ppm and 72.3 ppm, respectively. The structures of the oxidized derivatives **2a** and **2b**, sulfides **3a** and **3b** and selenides **4a** and **4b** were further confirmed by using microanalysis and IR spectroscopy, and found to be in good agreement with the theoretical values [23]. It is interesting to note that the ^{31}P NMR chemical shift of **1a** is nearly no different from that of the compound **1b** despite

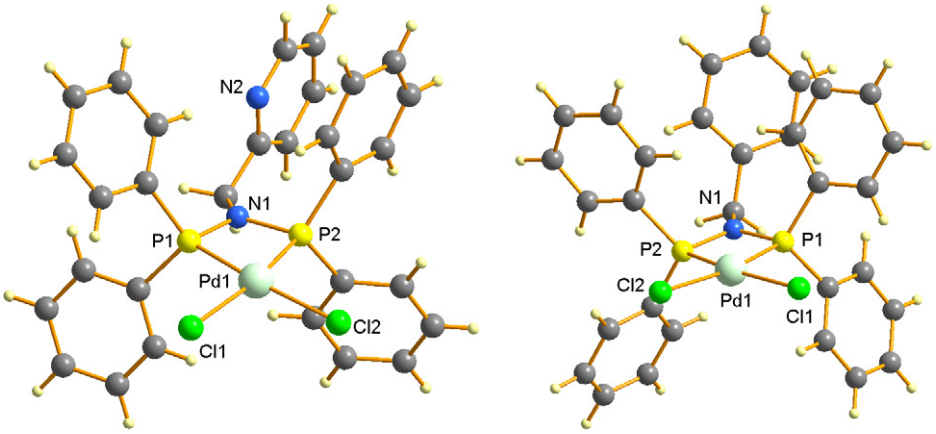


Fig. 1. Ball and stick representation of **5a** (left) and **5b** (right); atoms of spheres of arbitrary radii. Dichloromethane solvent molecules are omitted for clarity.

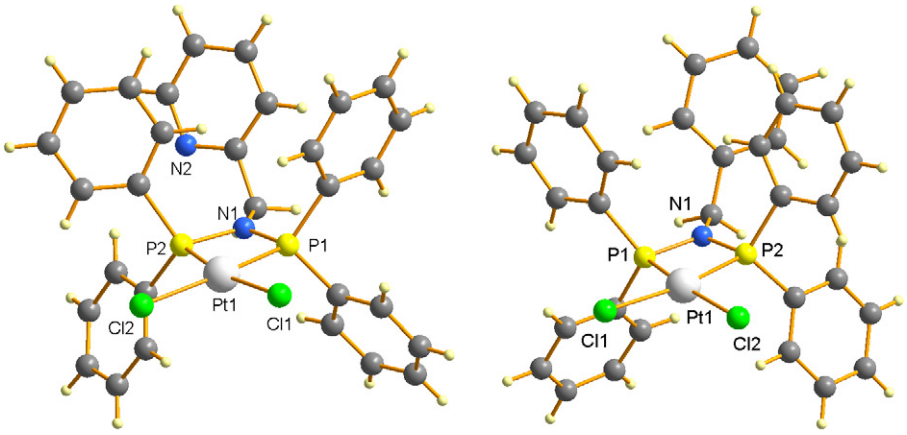


Fig. 2. Ball and stick representation of **6a** (left) and **6b** (right); atoms of spheres of arbitrary radii. Dichloromethane solvent molecules are omitted for clarity.

the presence of the pyridyl group in the former. This indicates that the pyridyl group has little or no electronic influence on the phosphorus centre. Same trends were also observed in **2a** and **2b**, **3a** and **3b**, and **4a** and **4b**.

Reactions of **1a** and **1b** with MCl_2(cod) (where M = Pd, Pt; cod = cyclooctadiene) in dichloromethane gave the corresponding complexes **5a–6b** (see Scheme 1). In both complexes **5a** and **6a**, the nitrogen atoms in the pyridyl group were not involved in any coordination to the metal centres because the phosphorus atoms in the aminophosphine ligand are much stronger donor centres and thus, coordination to the metal centre take place preferentially at the phosphorus atoms.

In the ^{31}P NMR spectra, the chemical shifts of **5a** and **5b** 34.2 ppm and 34.3 ppm, respectively, are similar and within the expected range of other reported structurally similar complexes, where an electron-withdrawing group is attached to the aniline ring [13–15]. In the ^{1}H NMR spectra, the chemical shifts of the CH_2 groups lie at δ 4.30 and 4.24 ppm, slightly upfield (4.69,4.51) with respect to aminophosphines **1a** and **1b**.

Single crystals of **5a–6b** suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into dichloromethane solutions of the respective complexes (see Figs. 1 and 2). The crystallographic data are listed in Table 1 and key bond parameters are given in Table 2. In general, the bond distances and angles between **5a** and **5b** and between **6a** and **6b** in the solid state are very similar, with minimal structural differences due to the replacement of the pyridyl group with the phenyl group. Similarly, their P–N bond distances are within expected values in comparison to similar aminophosphine-transition metal structures [11–15].

All **5a–6b** complexes form metallacycles, with the aminophosphine ligands chelating the metal centre at both phosphine positions. The metallacycles are nearly planar with P(1)–Pd(1)–P(2)–N(1) torsion angles of −4.44(7)° and −2.57(11)° in **5a** and **5b**,

Table 1
Crystallographic data for **5a–6b**

Chemical formula	**5a** · $C_{30}H_{26}Cl_2N_2P_2Pd$	**5b** · $0.5C_4H_{10}OC_{31}H_{27}Cl_2NP_2Pd \cdot 0.5C_4H_{10}O$	**6a** · $CH_2Cl_2C_{30}H_{26}Cl_2N_2P_2Pt \cdot CH_2Cl_2$	**6b** · $CH_2Cl_2C_{31}H_{27}Cl_2NP_2Pt \cdot CH_2Cl_2$
Formula weight	653.77	689.84	827.38	826.39
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$
A (Å)	11.9233(17)	11.0527(13)	9.7892(8)	11.0779(9)
B (Å)	18.3698(19)	18.3272(12)	18.3095(16)	18.3443(9)
C (Å)	13.3486(11)	15.5888(11)	17.9375(11)	15.5624(12)
α (°)	90	90	90	90
β (°)	108.944(8)	93.534(7)	98.485(6)	94.266(7)
γ (°)	90	90	90	90
Volume (Å^3)	2765.4(5)	3151.7(5)	3179.8(4)	3153.8(4)
Z	4	4	4	4
D_{calc} (g cm^{-3})	1.570	1.454	1.728	1.740
F(000)	1320	1404	1616	1616
μ mm^{-1})	1.003	0.885	4.874	4.913
T (K)	100(2)	100(2)	140(2)	140(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Measured reflections	50239	62809	18358	22484
Unique reflections	4861	5548	5338	7560
Unique reflections [$I > 2\sigma(I)$]	4220	4360	3809	5429
No. of data/restraints/parameters	4861/0/334	5548/43/379	5338/0/361	7560/48/361
R^a[$I > 2\sigma(I)$]	0.0255	0.0396	0.0561	0.0990
wR_2[a] (all data)	0.0509	0.0888	0.1229	0.2059
Goodness-of-fit (GoF)[b]	1.163	1.127	1.042	1.279

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.
[b] $\mathrm{GoF} = \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$, where n is the number of data and p is the number of parameters refined.

Table 2
Key bond distances (Å) and angles (°) for **5a–6b**

	5a	5b	6a	6b
M–P_{ave}[a]	2.228	2.218	2.208	2.202
M–Cl_{ave}[a]	2.365	2.370	2.360	2.358
P–N_{ave}	1.705	1.706	1.717	1.706
P(1)–P(2)	2.6146(10)	2.5920(14)	2.618(3)	2.605(5)
N(1)–C(1)	1.482(3)	1.495(5)	1.475(10)	1.492(17)
P(1)–M–P(2)[a]	71.85(2)	71.49(4)	72.71(9)	72.54(13)
Cl(1)–M–Cl(2)[a]	93.88(3)	96.75(4)	92.88(9)	92.50(14)
P(1)–N(1)–P(2)	100.17(11)	98.93(17)	99.4(4)	99.6(6)
P(1)–M–P(2)–N(1)[a]	−4.44(7)	−2.57(11)	1.0(3)	0.6(4)

[a] M = Pd for **5a** and **5b**; M = Pt for **6a** and **6b**.

and P(1)–Pt(1)–P(2)–N(1) torsion angles of 1.0(3)° and 0.6(4)° in **6a** and **6b**, respectively. The P–Pd–P angles in **5a** and **5b** of 71.85(2)° and 71.48(3)° are slightly smaller than that of P–Pt–P angles in **6a** and **6b** of 72.71(9)° and 72.54(13)°, presumably due to the smaller size of the palladium atom compared to that of the platinum.

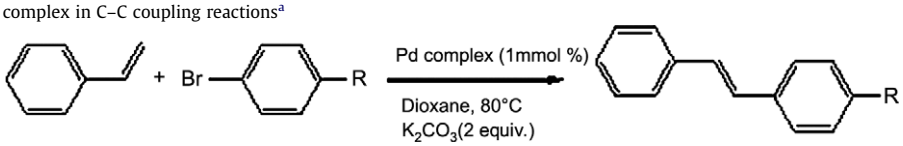
3. Catalysis

Palladium complexes in general can be used as catalyst-precursors in a number of C–C coupling reactions [24,25]. In a real catalytic process, the palladium complexes are believed to be reduced to zero-valent palladium which in many cased are nanosized particles that can direct interact with the substrate [26]. The catalytic activities of the complexes depend largely on the ability of the ligands to activate and stabilize the zero-valent palladium nanoparticles. For this purpose, many palladium complexes are prepared using bulky phosphine ligands. Since both complexes **5a** and **5b** are structurally very similar, it is interesting to compare their catalytical activities in C–C coupling reactions.

The Heck reaction has shown to be very useful for the preparation of disubstituted olefins. The rate of coupling depends on a variety of parameters such as temperature, solvent, base and catalyst loading. Use of 0.01 mmol, 1% palladium complex, 2 mmol K_2CO_3 in dioxane at 80 °C led to the best conversion within 6 h. We initially evaluated the catalytic activity of palladium complexes for the coupling of 4-bromoacetophenone with styrene (Table 3, entry 1). Control experiments indicate that the coupling reaction did not occur in the absence of **5a** or **5b**. Under these reaction conditions a wide range of aryl bromides bearing electron-donating or electron-withdrawing groups react with styrene affording the coupled products in optimum yields 84–95% (Table 3, entries 1, 2 and 4). Enhancements in activity, although less significant, are also observed employing 4-bromobenzaldehyde instead of 4-bromoacetophenone (entries 1, 2).

In order to survey the parameters for the Suzuki reaction, we chose to examine Cs_2CO_3, K_2CO_3, and K_3PO_4 as base and dioxane as the solvent, found that the reactions performed in dioxane with Cs_2CO_3 at 80 °C appeared to be best. We started our investigation with the coupling of 4-bromooacetophenone and phenylboronic acid, in the presence of complexes (**5a**, **5b**). Table 4 summarizes the results obtained in the presence of **5a**, **5b** (Table 4, entries 1–4). The scope of the cross-coupling reaction with respect to the aryl bromide component was also investigated. It can be seen that **5b** is an effective complex for the coupling of unactivated, activated and deactivated bromides.

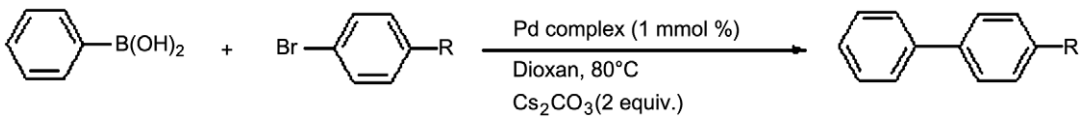
Table 3
Catalytic activity of palladium complex in C–C coupling reactions[a]



Entry	R	Yield (%)	
		5a	**5b**
1	$COCH_3$	41	95
2	CHO	39	84
3	H	31	55
4	OCH_3	37	85
5	CH_3	9	17

[a] Reaction conditions: 1.0 mmol of R-C_6H_4X-*p*, 1.5 mmol of styrene, 2 mmol K_2CO_3, 1 mmol% Pd complex, dioxane (3 mL) at 80 °C. Reaction time was 6 h with the exception of entry 4 which was 16 h. Reactions were monitored by GC. Purity of compounds was checked by NMR and yields are based on aryl bromide.

Table 4
Catalytic activity of palladium complex in C–C coupling reactions[a]



Entry	R	Yield (%)	
		5a	**5b**
1	$COCH_3$	94	93
2	CHO	74	86
3	OCH_3	94	89
4	H	88	90

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

4. Conclusion

In conclusion, we have prepared two aminophosphines and their derivatives including oxides, sulfides, selenides, as well as transition–metal complexes containing Pd, Pt centres. All these new compounds were characterized using NMR and IR spectroscopy, with two representative structures studied by single crystal X-ray diffraction analysis. Although the substituents on the amines are different, they exhibit similar reactivities towards different oxidants due to the presence of the bulky diphenyl groups at the phosphorus atom. In addition, they also show similar coordination properties towards Pd and Pt. However, they show different catalytic activities in C–C coupling reactions. The palladium complexes exhibit high catalytic activity in the C–C coupling reactions. The procedure is simple and efficient towards various aryl bromides and does not require induction period.

5. Experimental

All reactions were performed under argon unless otherwise stated. Ph_2PCl, 2-picolylamine and benzylamine were purchased from Fluka and used directly without further purification. $PdCl_2(cod)$ and $PtCl_2(cod)$ were prepared according to literature procedures [27,28]. Solvents were dried using the appropriate reagents and distilled prior to use. Infrared spectra were recorded as KBr pellet in the range 4000–400 cm^{-1} on a Mattson 1000 ATI UNICAM FT-IR spectrometer. ^1H NMR spectra (400 MHz) and $^{31}P–\{^1H\}$ NMR spectra (162 MHz) on a Bruker Avance 400 spectrometer. The ^1H NMR spectra were calibrated using residual undeuterated solvent peaks whereas the $^{31}P–\{^1H\}$ NMR spectra were externally calibrated using 85% H_3PO_4 solution. Microanalysis was carried out on a Fisons EA 1108 CHNS-O instrument.

5.1. Synthesis of *1a*

Ph_2PCl (4.10 g, 18.5 mmol) was added slowly to a solution of 2-picolylamine (1.00 g, 9.25 mmol) and Et_3N (1.867 g, 18.5 mmol) in CH_2C1_2 (30 mL) at 0 °C. The resulting white suspension was stirred for 3 h, and the solvent was removed under reduced pressure. The solid was washed with degassed water (3 × 10 mL) and dried in air to yield **1a** as a white solid (yield: 4.30 g, 98%; m.p.: 160–162 °C). ^1H NMR ($CDCl_3$) δ (ppm): 6.66–8.41 (m, 24H, Ar–H), 4.69 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (ppm): (C_{Arm}, 159.8; 148.6; 139.2; 135.7; 132.8; 128.8; 128.1; 121.5), (C_{CH_2}, 57.9). $^{31}P–\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 62.6 (s). Selected IR, ν (cm^{-1}): 855 (P–N–P). Anal. Calc. for $C_{30}H_{26}N_2P_2$: C, 75.62; H, 5.5; N, 5.88. Found: C, 75.46; H, 5.25; N, 5.31%.

5.2. Synthesis of *1b*

Ph_2PCl (4.10 g, 18.5 mmol) was added slowly to a solution of benzyl amine (1.00 g, 9.33 mmol) and Et_3N (1.867 g, 18.5 mmol) in CH_2C1_2 (30 mL) at 0 °C. The resulting white suspension was stirred for 1 h, and the solvent was removed under reduced pressure. The residue was washed with degassed water (3 × 10 mL) and dried in air to yield **1b** as a white solid (yield: 3.67 g, 82%; m.p.: 144–146 °C). ^1H NMR ($CDCl_3$) δ (ppm): 6.78–7.40 (m, 25H, Ar H), 4.51 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$)δ (ppm): (C_{Arm}, 139.8; 139.5; 139.3; 132.9; 132.8; 128.8; 128.1; 127.9), (C_{CH2}, 56.1). $^{31}P–\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 60.2 (s). Selected IR, ν (cm^{-1}): 835 (P–N–P). Anal. Calc. for $C_{31}H_{27}NP_2$: C, 78.32; H, 5.72; N, 2.95. Found: C, 78.61; H, 5.76; N, 3.11%.

5.3. Synthesis of *2a*

A thf solution (10 mL) of **1a** (0.20 g, 0.420 mmol) and aqueous H_2O_2 (30% w/w, 0.085 mL) was stirred for 2 h at room temperature. The solution was evaporated to dryness under reduced pressure to yield **3a** as a white solid (yield: 0.09 g, 43%; m.p.: 115–117 °C). ^1H NMR ($CDCl_3$) δ (ppm): 6.99–7.83 (m, 24H, ArH); 4.64 (s, 2H, CH_2); $^{31}P–\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 30.6 (s). Selected IR, ν (cm^{-1}): 861 (P–N–P), 1201 (P═O). Anal. Calc. for $C_{30}H_{26}N_2P_2\ O_2$: C, 70.86; H, 5.15; N, 5.51. Found: C, 70.66; H, 5.48; N, 5.23%.

5.4. Synthesis of *2b*

A thf solution (10 mL) of **1b** (0.20 g, 0.421 mmol) and aqueous H_2O_2 (30% w/w, 0,085 mL) was stirred for 2 h at room temperature. The solution was evaporated to dryness under reduced pressure to yield **2b** as a white solid (yield: 0.082 g, 41%; m.p.: 118–119 °C). ^1H NMR ($CDCl_3$) δ (ppm): 7.09–7.79 (m, 25H, ArH); 4.44 (s, 2H, CH_2); $^{31}P–\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 30.3 (s). Selected IR, ν (cm^{-1}): 843 (P–N–P), 1206 (P═O). Anal. Calc. for $C_{31}H_{27}NP_2O_2$: C, 73.37; H, 5.36; N, 2.76. Found: C, 73.68; H, 5.86; N, 2.35%.

5.5. Synthesis of *3a*

Ligand **1a** (0.20 g, 0.420 mmol) and S_8 (0.027 g, 0.840 mmol) were refluxed in thf (20 mL) for 6 h. The reaction mixture was concentrated to ca. 1–2 mL *in vacuo* and *n*-hexane (20 mL) was added. The precipitate was filtered and dried in air to yield **3a** as a white solid (yield: 0.1 g, 46%; m.p.: 147–148 °C). ^1H NMR ($CDCl_3$) δ (ppm): 6.89–8.06 (m, 24 H, Ar H); 4.72 (s, 2H, CH_2); $^{31}P–\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 72.3 (s). Selected IR, ν (cm^{-1}): 822 (P–N–P), 650 (P–S). Anal. Calc. for $C_{30}H_{26}N_2P_2\ S_2$: C, 66.65; H, 4.81; N, 5.18; S, 11.86. Found: C, 66.43; H, 5.44; N, 5.46; S, 11.08%.

5.6. Synthesis of *3b*

Ligand **1b** (0.20 g, 0.421 mmol) and S_8 (0.027 g, 0.842 mmol) were refluxed in thf (20 mL) for 6 h. The reaction mixture was concentrated to ca. 1–2 mL *in vacuo* and *n*-hexane (20 mL) was added. The precipitate was filtered and dried in air to yield **3b** as a white solid (yield: 0.17 g, 75%; m.p.: 99–100 °C). ^1H NMR ($CDCl_3$) δ (ppm): 6.96–8.01 (m, 25 H, Ar H); 4.62 (s, 2H, CH_2); $^{31}P–\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 71.8 (s). Selected IR, ν (cm^{-1}): 822 (P–N–P), 650 (P–S). Anal. Calc. for $C_{31}H_{27}NP_2S_2$: C, 69.00; H, 5.04; N, 2.60; S, 11.88. Found: C, 69.43; H, 5.13; N, 2.49; S, 11.12%.

5.7. Synthesis of *4a*

Ligand **1a** (0.20 g, 0.420 mmol) and elemental Se (0.066 g, 0.840 mmol) were refluxed in thf (20 mL) for 6 h. The reaction mixture was concentrated to ca. 1–2 mL *in vacuo* and *n*-hexane (20 mL) was added. The precipitate was filtered and dried in air to yield **4a** as a white solid (yield: 0.123 g, 45%; m.p.: 283–285 °C). ^1H NMR ($CDCl_3$) δ (ppm): 6.89–7.79 (m, 24 H, Ar H); 4.81 (s, 2H, CH_2); $^{31}P–\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 72, $J_{(PSe)}$: 776 Hz. Selected IR, ν (cm^{-1}): 817 (P–N–P), 566 (P═Se). Anal. Calc. for $C_{30}H_{26}N_2P_2\ Se_2$: C, 56.8; H, 4.13; N, 4.42. Found: C, 56.39; H, 4.36; N, 4.31%.

5.8. Synthesis of *4b*

Ligand **1b** (0.20 g, 0.421 mmol) and elemental Se (0.064 g, 0.842 mmol) were refluxed in thf (20 mL) for 6 h. The reaction mixture was concentrated to ca. 1–2 mL *in vacuo* and *n*-hexane (20 mL) was added. The precipitate was filtered and dried in air to yield **4b** as a white solid (yield: 0.14 g, 53%; m.p.: 151–153 °C). ^1H NMR ($CDCl_3$) δ (ppm): 6.95–8.07 (m, 25 H, Ar H); 4.73 (s, 2H, CH_2); $^{31}P–\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 72.34, $J_{(PSe)}$: 772 Hz. Selected IR, ν (cm^{-1}): 822 (P–N–P), 522 (P–Se). Anal. Calc. for $C_{31}H_{27}NP_2Se_2$: C, 58.78; H, 4.30; N, 2.21. Found: C, 58.01; H, 4.34; N, 2.33%.

5.9. Synthesis of **5a**

A solution of [$PdCl_2$(cod)] (0.050 g, 0.175 mmol) and **1a** (0.083 g, 0.175 mmol) in CH_2Cl_2 (10 mL) was stirred for 1.5 h. The reaction mixture was concentrated to ca. 1–2 mL *in vacuo* and diethyl ether (20 mL) was added. The yellow precipitate was filtered and dried *in vacuo* to give **5a** (yield: 0.082 g, 75%; m.p.: >300 °C). ^{1}H NMR ($CDCl_3$) δ (ppm): 6.31–8.09 (m, 24 H, Ar H); 4.30 (s, 2H, CH_2); ^{31}P–{^{1}H} NMR ($CDCl_3$) δ (ppm): 34.2 (s). Selected IR, ν (cm^{-1}): 817 (P–N–P). Anal. Calc. for $C_{30}H_{26}N_2P_2$ $PdCl_2$: C, 55.11; H, 4.01; N, 4.28. Found: C, 55.56; H, 4.27; N, 4.48%.

5.10. Synthesis of **5b**

A solution of [$PdCl_2$(cod)] (0.050 g, 0.175 mmol) and **1b** (0.083 g, 0.175 mmol) in CH_2Cl_2 (10 mL) was stirred for 1.5 h. The reaction mixture was concentrated to ca. 1–2 mL *in vacuo* and diethyl ether (20 mL) was added. The yellow precipitate was filtered and dried *in vacuo* to give **5b** (yield: 0.090 g, 82%; m.p.: 293-295 °C). ^{1}H NMR ($CDCl_3$) δ (ppm): 6.50–7.85 (m, 25 H, Ar H); 4.24 (s, 2H, CH_2); ^{31}P–{^{1}H} NMR ($CDCl_3$) δ (ppm): 34.3 (s). Selected IR, ν(cm^{-1}): 803 (P–N–P). Anal. Calc. for $C_{31}H_{27}NP_2PdCl_2$: C, 57.03; H, 4.17; N, 2.15. Found: C, 57.37; H, 4.28; N, 2.00%.

5.11. Synthesis of **6a**

A solution of [$PtCl_2$(cod)] (0.032 g, 0.0860 mmol) and **1a** (0.041 g, 0.0860 mmol) in CH_2Cl_2 (10 mL) was stirred for 1.5 h. The reaction mixture was concentrated to ca. 1–2 mL *in vacuo* and diethyl ether (20 mL) was added. The white precipitate was filtered and dried *in vacuo* to give **6a** (yield: 0.053 g, 83%; m.p.: >300 °C). ^{1}H NMR ($CDCl_3$) δ (ppm): 6.94–8.11 (m, 24H, Ar H); 4.23 (s, 2H, CH_2); ^{31}P–{^{1}H} NMR ($CDCl_3$) δ (ppm): 20.2, $J_{(PtP)}$: 3308 Hz. Selected IR, ν (cm^{-1}): 810 (P–N–P). Anal. Calc. for $C_{30}H_{26}N_2P_2$ $PtCl_2$: C, 48.53; H, 3.53; N, 3.77. Found: C, 48.45; H, 3.67; N, 3.88%. Slow diffusion of diethyl ether into a CH_2Cl_2 solution of 6a over 48 h gave crystals suitable for X-ray crystallography.

5.12. Synthesis of **6b**

A solution of [$PtCl_2$(cod)] (0.032 g, 0.0860 mmol) and **1b** (0.041 g, 0.0860 mmol) in CH_2Cl_2 (10 mL) was stirred for 1.5 h. The reaction mixture was concentrated to ca. 1-2 mL *in vacuo* and diethyl ether (20 mL) was added. The white precipitate was filtered and dried *in vacuo* to give **6b** (yield: 0.048 g, 76%; mp: >300 °C). ^{1}H NMR ($CDCl_3$) δ (ppm): 6.51–0.83 (m, 25H, Ar H); 4.15 (s, 2H, CH_2); ^{31}P–{^{1}H} NMR ($CDCl_3$) δ (ppm): 20.3, $J_{(PtP)}$: 3303 Hz. Selected IR, ν (cm^{-1}): 803 (P–N–P). Anal. Calc. for $C_{31}H_{27}NP_2PtCl_2$: C, 50.21; H, 3.67; N, 1.89. Found: C, 50.41; H, 3.69; N, 1.94%.

6. General procedure for the Heck coupling reactions

Aminophosphine–palladium complexes (**5a**, **5b**, 0.01 mmol, 1.0%), aryl bromide (1.0 mmol), styrene (1.5 mmol), K_2CO_3 (2 mmol) and dioxane (3 mL) were added to a small Schlenk tube and the mixture was heated at 80 °C for 6 h. At the completion of the reaction, the mixture was cooled, 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 NMR and GC and the yields are based on aryl bromide.

7. General procedure for the Suzuki coupling reaction

Aminophosphine–palladium complexes (**5a**, **5b**, 0.01 mmol, 1%), 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. At the completion of the reaction, the mixture was cooled, extracted with ethyl acetate/hexane (1:5), filtered through a pad of silicagel with copious washings, concentrated and purified by flash chromatography on silica gel. The purity of the compounds was checked by GC and NMR and yields are based on aryl chloride.

8. Structure determination in the solid-state

Relevant details on the structural refinement are given in Table 1. Data collection for **5a** and **5b** was performed a Bruker Nonius APEX II CCD at 100(2) K and data reduction using EvalCCD, while data for **6a** and **6b** was collected on a four-circle Kappa goniometer equipped with an Oxford Diffraction KM4 Sapphire CCD at 140(2) K and data reduction performed using CRYSALIS RED [29]. Structural solution was performed using SIR97 [30], structural refinement using the SHELXTL software package [31], and graphical representations of the structures were made with Diamond [32]. The structures were solved by Direct methods and refined by full-matrix least-squares refinement (against F^2), with all non-hydrogen atoms refined anisotropically. The hydrogen atoms were placed in their geometrically generated positions using the riding model and refined isotropically. Empirical absorption corrections for **5a** and **5b** were applied using SADABS and for **6a** and **6b** using DELABS [33]. Restraints were applied on the disordered diethyl ether solvent molecule in **5b** and the phenyl rings in **6b** using the SIMU and DELU commands implemented in SHELXTL.

Acknowledgement

We would like to thank Dicle University Reasearch Fund (Project no: DÜAPK-05-FF-19 and DÜBAP-06-FF-07) for financial support.

Appendix A. Supplementary material

CCDC 651937, 651938, 651939, and 651940 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] (a) F.R. Hartley, The Chemistry of Organophosphorus Compounds, vol. 1, John Wiley & Sons, Manchester, 1990;
(b) N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, Pergmon Press, Oxford, 1984. p. 619.
[2] (a) M.S. Balakrishna, V. Sreenivasa Reddy, S.S. Krishnamurthy, J.F. Nixon, J.C.T.R. Burckett St. Laurent, Coord. Chem. Rev. 129 (1994) 1;
(b) F. Agbossou, J.F. Carpentier, F. Hapiot, Coord. Chem. Rev. 178–180 (1998) 1615.
[3] (a) T. Appleby, J.D. Woollins, Coord. Chem. Rev. 235 (2002) 121;
(b) Z. Fei, P.J. Dyson, Coord. Chem. Rev. 249 (2005) 2056.
[4] (a) I. Bachert, P. Braunstein, R. Hasselbring, New J. Chem. 20 (1996) 993;
(b) I. Bachert, P. Braunstein, M.K. McCart, F. Fabrizi de Biani, F. Lashi, P. Zanello, G. Kickelbick, U. Schubert, J. Organomet. Chem. 573 (1999) 47;
(c) I. Bachert, I. Bartussek, P. Braunstein, E. Guillon, J. Rose, G. Kickelbick, J. Organomet. Chem. 580 (1999) 257.
[5] I.M.R. Zubiri, M.L. Clarke, D.F. Foster, D.J. Cole-Hamilton, A.M.Z. Slawin, J.D. Woollins, J. Chem. Soc., Dalton Trans. (2001) 969.
[6] J. Reedijk, J. Chem. Soc.,Chem. Commun. (1996) 801.
[7] (a) D.J. Birdsall, J. Green, T.Q. Ly, J. Novosad, M. Necas, A.M.Z. Slawin, J.D. Woollins, Z. Zak, Eur. J. Inorg. Chem. (1999) 1445;
(b) P. Bhattacharyya, T.Q. Ly, A.M.Z. Slawin, J.D. Woollins, Polyhedron 20 (2001) 1803.

[8] B. Gümgüm, O. Akba, F. Durap, L.T. Yıldırım, D. Ülkü, S. Özkar, Polyhedron 25 (2006) 3133.
[9] K.G. Gaw, M.B. Smith, J.W. Steed, J. Organomet. Chem. 664 (2002) 294.
[10] (a) Q. Zhang, S.M. Aucott, A.M.Z. Slawin, J.D. Woollins, Eur. J. Inorg. Chem (2002) 1635;
(b) M.L. Clarke, G.L. Holliday, A.M.Z. Slawin, J.D. Woollins, J. Derek, J. Chem. Soc., Dalton Trans. (2002) 1093;
(c) A.M.Z. Slawin, M. Wainwright, J.D. Woollins, J. Chem. Soc., Dalton Trans. (2002) 513;
(d) N. Biricik, Z. Fei, R. Scopelliti, P.J. Dyson, Helv. Chim. Acta 86 (2003) 3281.
[11] (a) A.M.Z. Slawin, H.L. Milton, J. Wheatley, J.D. Woollins, Polyhedron 23 (2004) 3125;
(b) A.M.Z. Slawin, J. Wheatley, J.D. Woollins, Phosphorus Sulfur Silicon Relat. Elem. 179 (2004) 991;
(c) A.M.Z. Slawin, J. Wheatley, J.D. Woollins, Eur. J. Inorg. Chem. (2005) 713.
[12] (a) Z. Fei, R. Scopelliti, P.J. Dyson, Eur. J. Inorg. Chem. (2003) 3527;
(b) Z. Fei, R. Scopelliti, P.J. Dyson, Eur. J. Inorg. Chem. (2004) 530;
(c) N. Biricik, Z. Fei, R. Scopelliti, P.J. Dyson, Eur. J. Inorg. Chem. (2004) 4232;
(d) I. Fernández, F. Breher, P.S. Pregosin, Z. Fei, P.J. Dyson, Inorg. Chem. 44 (2005) 7616.
[13] Z. Fei, R. Scopelliti, P.J. Dyson, Inorg. Chem. 42 (2003) 2125.
[14] Z. Fei, R. Scopelliti, P.J. Dyson, J. Chem. Soc., Dalton Trans. (2003) 2772.
[15] (a) N. Miyaruna, A. Suzuki, Chem. Rev. 95 (1995) 2457;
(b) A. Suzuki, J. Organomet. Chem. 576 (1999) 147;
(c) S.P. Stanforth, Tetrahedron 54 (1998) 263.
[16] (a) N.J. Whitcombe, K.K. Hii, S.E. Gibson, Tetrahedron 57 (2001) 449;
(b) G. T Crisp, Chem. Soc. Rev. 27 (1998) 427.
[17] V.V. Grushin, H. Alper, Top. J. Organomet. Chem. 3 (1999) 193.
[18] B. Gümgüm, N. Biricik, F. Durap, I. Özdemir, N. Gürbüz, W.H. Ang, P.J. Dyson, Appl. Organometal. Chem. 21 (2007) 711.
[19] N. Biricik, F. Durap, C. Kayan, B. Gümgüm, Heteroatom Chem. 18 (2007) 613.
[20] Z. Fei, D. Zhao, N. Biricik, R. Scopelliti, P.J. Dyson, Inorg. Chem. 43 (2004) 2228.
[21] (a) Z. Fei, I. Neda, H. Thönnessen, P.G. Jones, R. Schmutzler, Phosphorus Sulfur Silicon Relat. Elem. 131 (1997) 1;
(b) Z. Fei, H. Thönnessen, P.G. Jones, R. Schmutzler, Z. Anorg. Allg. Chem. 625 (1999) 1732.
[22] (a) Z. Fei, Y. Lu, M. Freytag, P.G. Jones, R. Schmutzler, Z. Anorg. Allg. Chem. 626 (2000) 969;
(b) Z. Fei, H. Thönnessen, P.G. Jones, L. Crowe, R.K. Harris, R. Schmutzler, Z. Anorg. Allg. Chem. 626 (2000) 1763.
[23] (a) H.L. Milton, M.V. Wheatley, A.M.Z. Slawin, J.D. Woollins, Inorg. Chem. Commun. 7 (2004) 1106;
(b) Z. Fei, W.H. Ang, D. Zhao, R. Scopelliti, P.J. Dyson, Inorg. Chim. Acta 359 (2006) 2635.
[24] N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457.
[25] B.F.G. Johnson, Top. Catal. 24 (2003) 147.
[26] (a) P. Migowski, J. Dupont, Chem. Eur. J. 13 (2006) 32;
(b) Z. Fei, T.J. Geldbach, D. Zhao, P.J. Dyson, Chem. Eur. J. 12 (2006) 2122.
[27] D. Drew, J.R. Doyle, Inorg. Synth. 13 (1972) 47.
[28] J.X. McDermott, J.F. White, G.M. Whitesides, J. Am. Chem. Soc. 98 (1976) 6521.
[29] Oxford Diffraction Ltd., Abingdon, Oxfordshire, UK, 2002.
[30] A. Altomare, M.C. Burla, G. Camalli, G. Cascarano, C. Giacovazzo, A. Gualiardi, G. Polidori, J. Appl. Cryst. 27 (1994) 435.
[31] (a) G.M. Sheldrick, University of Göttingen, Germany, 1997.;
(b) Bruker AXS, Inc., Madison, Wisconsin, 53719, USA, 1997.
[32] Diamond 3.0a, Crystal Impact GbR, Bonn, Germany.
[33] DELABS N. Walker, D. Stuart, Acta Crystallogr., Sect. A 39 (1983) 158.