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# Application of *N*,*N*-bis(diphenylphosphino)aniline palladium(II) complexes as pre-catalysts in Heck coupling reactions

**Bahattin Gümgüm[1]*, Nermin Biricik[1], Feyyaz Durap[1], Ismail Özdemir[2], Nevin Gürbüz[2], Wee Han Ang[3] and Paul J. Dyson[3]**

[1]Department of Chemistry, University of Dicle, 21280 Diyarbakir, Turkey
[2]Department of Chemistry, University of Inönü, 44280 Malatya, Turkey
[3]Institut des Sciences et Ingenierie Chimiques, Ecole Polytechnique Federale de Lausanne (EPFL) CH-1015 Lausanne, Switzerland

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**Palladium(II) complexes with *N*,*N*-bis(diphenylphosphino)aniline ligands catalyse the Heck reaction between styrene and aryl bromides, affording stilbenes in good yield. The structures of two of the complexes used as pre-catalysts have been determined by single-crystal X-ray diffraction. Copyright © 2007 John Wiley & Sons, Ltd.**

**KEYWORDS:** aminophosphines; bis(diphenylphosphino)aniline; catalysis; Heck reaction; N,P ligands; palladium complexes; X-ray structure

## INTRODUCTION

Aminophosphines which bear phosphorus and nitrogen as donor atoms have attracted considerable interest in recent years because of their versatile coordination chemistry[1–3] and their potential use in catalytic applications.[4–6] In the last decade a large number of complexes with aminophosphine ligands have been evaluated in different catalysed reactions including allylic alkylation,[7–10] amination,[11–13] Heck,[14–21] Sonogashira,[22] Suzuki,[23–27] hydroformylation,[28–32] hydrogenation[33–37] and polymerization[38–42] reactions. Indeed, the Heck reaction is a very important carbon–carbon bond-forming reaction and has been applied to a variety of complex natural product syntheses.[17,43–45]

In general, formation of stilbene from arylhalogenide and styrenes is a widely used model to evaluate the catalytic activity of new ligands in the Heck reaction.[44] Reetz *et al.*[14] reported the preparation of a dendritic diphenylphosphinoamine-palladium complex and stilbene was recovered in up to 89% yield from coupling of bromobenzene with styrene in the presence of the catalyst. Heck coupling of *p*-anisyl bromide with styrene was investigated using iminophosphines as co-catalyst and the methoxystilbene product was obtained with a conversion of 78%.[19] Recently, the reaction between bromobenzene and styrene was performed using palladium complexes with N, P ligands and stilbenes were obtained with yields up to 86%.[21]

Following on from previous studies,[46–52] herein we report on the activity of some *N*,*N*-bis(diphenylphosphino)aniline palladium(II) complexes as pre-catalysts in the Heck reaction. The solid-state structures of two of the pre-catalysts is also described.

## EXPERIMENTAL

The ligands (**1–5**)[53,54] and the palladium complexes (**1a–5a**)[55–59] were prepared according to literature procedures. Heck coupling reactions were conducted as follows: aminophosphine-palladium complexes (**1a–5a**; 1.0 mmol%), aryl bromide (1.0 mmol), styrene (1.5 mmol), $K_2CO_3$ (2 mmol) and dioxane (3 ml) were placed in a Schlenk tube and the mixture was heated to 80 °C for 6 or 16 h. After reaction, the mixture was cooled, and the product extracted with ethylacetate/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

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*Correspondence to: Bahattin Gümgüm, Department of Chemistry, University of Dicle, 21280 Diyarbakir, Turkey.
E-mail: bgumgum@dicle.edu.tr
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was checked by NMR and GC, and yields are based on arylbromide.

## Structure determination in the solid state

Data collection for **1a** and **4a** was performed on a four-circle Kappa goniometer equipped with an Oxford Diffraction KM4 Sapphire CCD at 140 K and data reduction performed using CrysAlis RED.[60] Structural solution was performed using SiR92,[61] structural refinement using the SHELX97 software package,[62] and graphical representations of the structures were made with Diamond.[63] 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 were applied using DELABS.[64] Relevant crystallographic data are compiled in Table 1. CCDC 635782 and 635783 contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

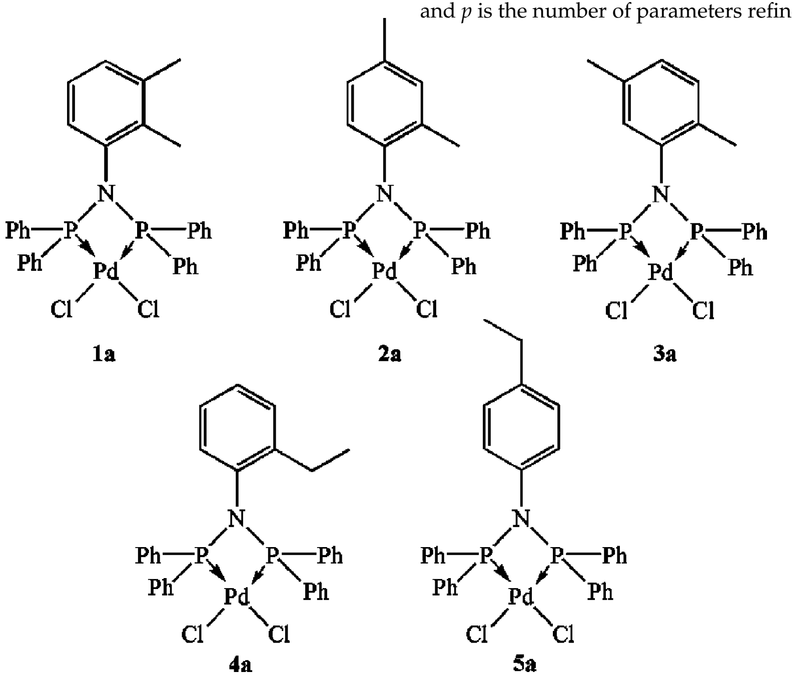
## RESULTS AND DISCUSSION

Reaction of $PdCl_2(COD)$ with **1–5** affords the expected complexes **1a–5a** shown in Scheme 1 and described previously.[55–57] The spectroscopic data for the complexes is in excellent agreement with that reported previously.

**Table 1.** Crystallographic data for **1a** and **4a**

| | 1a | 4a |
|---|---|---|
| Chemical formula | $C_{32}H_{29}Cl_2NP_2Pd$ | $C_{32}H_{29}Cl_2NP_2Pd$ |
| Fw | 666.80 | 666.80 |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ |
| $A$ (Å) | 12.6323(8) | 10.8691(4) |
| $B$ (Å) | 14.7629(10) | 47.725(2) |
| $C$ (Å) | 16.2872(9) | 17.7132(10) |
| $\alpha$ (deg) | 90 | 90 |
| $\beta$ (deg) | 100.696(5) | 100.528(4) |
| $\gamma$ (deg) | 90 | 90 |
| Volume (Å$^3$) | 2984.6(3) | 9033.6(7) |
| $Z$ | 4 | 12 |
| $D_{calc}$ (g cm$^{-3}$) | 1.484 | 1.471 |
| $F(000)$ | 1352 | 984 |
| $\mu$(mm$^{-1}$) | 0.930 | 0.922 |
| Temperature (K) | 140(2) | 140(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Measured reflections | 17533 | 53390 |
| Unique reflections | 5035 | 15811 |
| Unique reflections $[I > 2\sigma(I)]$ | 3829 | 10179 |
| No. of data/restraints/parameters | 5035/0/345 | 15811/0/1030 |
| $R^a[I > 2\sigma(I)]$ | 0.0361 | 0.0698 |
| $wR2^a$ (all data) | 0.0905 | 0.1664 |
| GooF$^b$ | 0.955 | 1.040 |

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



**Scheme 1.** Palladium complexes of *N*,*N*-bis(diphenylphosphino)dimethylanilines **1a–3a** and *N*,*N*-bis(diphenylphosphino) ethylanilines **4a–5a**.

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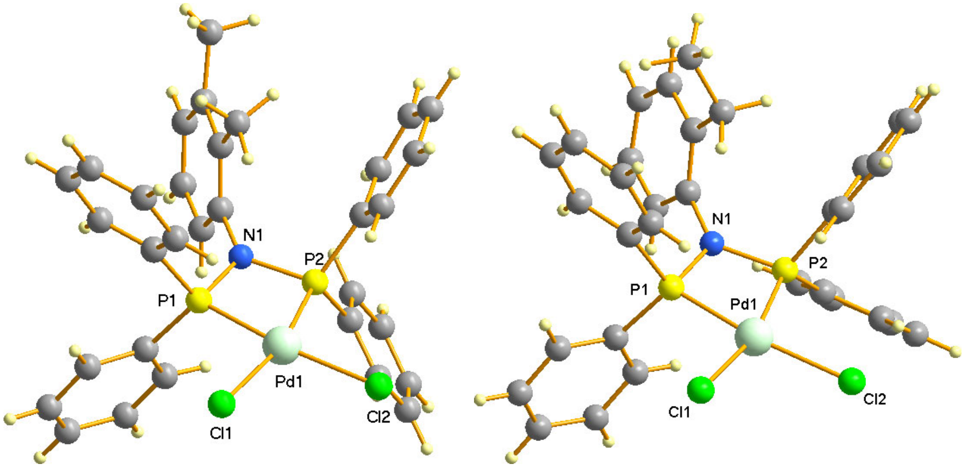
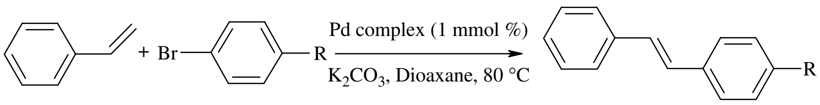


**Figure 1.** Ball and stick reprsentation of complex (left) $Pd[(Ph_2P)_2N-C_6H_3-2,3-(CH_3)_2]Cl_2$ **1a** and (right) $Pd[(Ph_2P)_2N-C_6H_4-2-C_2H_5]Cl_2$ **4a**; atoms as spheres of arbitrary diameter. Key bond lengths (Å) and angles (deg) for **1a**: $Pd-P_{ave}$, 2.223; $Pd-Cl_{ave}$, 2.362; $N-P_{ave}$, 1.710; P1−Pd1−P2, 72.13(3); P1−N1−P2, 99.90(14); Cl1−Pd1−Cl2, 94.72(4). Key bond lengths (Å) and angles (deg) for **4a**: $Pd-P_{ave}$, 2.216; $Pd-Cl_{ave}$, 2.358; $N-P_{ave}$, 1.712; $P-Pd-P_{ave}$, 72.13; $P-N-P_{ave}$, 99.3; $Cl-Pd-Cl_{ave}$, 95.86. This figure is available in colour online at www.interscience.wiley.com/AOC.

**Table 2.** The Heck coupling reaction of aryl bromides with styrene



| Entry | R | Complex | Yield[a] (%) |
|---|---|---|---|
| 1 | $COCH_3$ | **1a** | 76 |
| 2 | $COCH_3$ | **2a** | 80 |
| 3 | $COCH_3$ | **3a** | 65 |
| 4 | $COCH_3$ | **4a** | 90 |
| 5 | $COCH_3$ | **5a** | 76 |
| 6 | CHO | **1a** | 80 |
| 7 | CHO | **2a** | 85 |
| 8 | CHO | **3a** | 80 |
| 9 | CHO | **4a** | 90 |
| 10 | CHO | **5a** | 82 |
| 11 | H | **1a** | 45 |
| 12 | H | **2a** | 50 |
| 13 | H | **3a** | 68 |
| 14 | H | **4a** | 30 |
| 15 | H | **5a** | 58 |
| 16 | $OCH_3$ | **1a** | 75[b] |
| 17 | $OCH_3$ | **2a** | 70[b] |
| 18 | $OCH_3$ | **3a** | 84[b] |
| 19 | $OCH_3$ | **4a** | 68[b] |
| 20 | $OCH_3$ | **5a** | 80[b] |
| 21 | $CH_3$ | **1a** | 33 |
| 22 | $CH_3$ | **2a** | 46 |
| 23 | $CH_3$ | **3a** | 34 |
| 24 | $CH_3$ | **4a** | 28 |
| 25 | $CH_3$ | **5a** | 32 |

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

[b] 80 °C, 16 h.

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In addition, single crystals of **1a** and **4a** were obtained by slow diffusion of diethyl ether into $CDCl_3$ solution of the complexes and their structures were established by single crystal X-ray diffraction (Fig. 1). Key bond lengths and angles are given in the figure caption and relevant crystallographic data are listed in Table 1. The coordination geometry around the palladium centres for both complexes are distorted square planar, with the sterically hindered *N*,*N*-bisphosphinoaniline ligands chelating the metal centre via the P-atoms. The asymmetric unit of **4a** comprises three molecules of the complex and therefore the bond angles given in the figure captions are average values. Both complexes are characterised by strained P–Pd–P angles of 72.13°, due to the disposition of the PNP ligand. The other key bond distances, namely Pd–P, Pd–Cl and N–P, are similar to related complexes.[55–57,65]

The Heck reaction is an extremely useful method for the preparation of disubstituted olefins.[44] The rate of the coupling is dependent on a variety of parameters such as temperature, solvent, base and catalyst loading. Following optimization experiments we found that the use of 1 mmol% of the palladium complex with 2 equivalents of $K_2CO_3$ in dioxane at 80 °C led to the best conversion. We initially tested the catalytic activity of the complexes for the coupling of *p*-bromoacetophenone with styrene (Table 2, entries 1–5) and the control experiment indicated that the coupling reaction did not occur in the absence of the catalyst. Under these reaction conditions a range of aryl bromides with both electron donating and withdrawing groups react with styrene affording the coupled products in good yield. Thus, *p*-bromoacetophenone, *p*-bromobenzaldehyde, bromobenzene, *p*-bromoanisole and *p*-bromotoluene react cleanly with styrene in good yields (Table 2, entries 4, 9, 13 and 18).

The palladium-bis(diphenylphosphino)aniline complexes exhibit high catalytic activity in the Heck reaction. The procedure is simple and efficient towards various aryl bromides. We have found no report on the catalytic application of such P–N–P ligands in the Heck arylation reactions and this study demonstrates that very minor modifications to the ligand have a pronounced influence on the activity of the reaction. From the data presented it is not possible to infer any trends regarding the substitution pattern on the ring with respect to activity, indicating that further studies in this area would be useful.

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