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Synthesis and characterization of palladium(II) and platinum(II) metal complexes with iminophosphine ligands: X-ray crystal structures of platinum(II) complexes and use of palladium(II) complexes as pre-catalysts in Heck and Suzuki cross-coupling reactions

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Abstract The reactions of *N*-(2(diphenylphosphino) benzylidene) (phenyl) methanamine, $Ph_2PPhNHCH_2$-C_5H_4N, **1** and *N*-(2-(diphenylphosphino) (benzylidene) (thiophen-2-yl) methanamine, $Ph_2PPhNHCH_2$-C_4H_3S, **2** with MCl_2(cod) and MCl(cod)Me (M = Pd, Pt; cod = 1,5-cyclooctadiene) yield the new complexes [M($Ph_2PPhNHCH_2$-C_5H_4N)Cl_2], M = Pd**1a**, Pt**1b**, [M($Ph_2PPhNHCH_2$-C_5H_4N)ClMe], M = Pd**1c**, Pt **1d**, [M($Ph_2PPhNHCH_2$-C_4H_3S)Cl_2], M = Pd**2a**, Pt **2b**, and [M($Ph_2PPhNHCH_2$-C_4H_3S)ClMe], M = Pd**2c**, Pt **2d**, respectively. The new compounds were isolated as analytically pure crystalline solids and characterized by ^{31}P-, ^{1}H-NMR, IR spectroscopy, electro spray ionization-mass spectrometry (ESI-MS) and elemental analysis. The representative solid-state molecular structures of the platinum complexes **1b** and **2b** were determined using single crystal X-ray diffraction analysis and revealed that the complexes exhibit a slightly distorted square-planar geometry. Furthermore, the palladium complexes were tested as potential catalysts in the Heck and Suzuki cross-coupling reactions.

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Introduction

Phosphorus–nitrogen containing ligands have particular use in catalysis where it is necessary for part of the ligand to dissociate to allow an organic fragment to coordinate and undergo transformations [1]. Small variations in these ligands can cause significant changes in their coordination behavior and the structural features of the resulting complexes [2]. Tertiary phosphines have long been used in the synthesis of transition metal complexes with catalytic properties, especially with electron-rich transition metals like nickel, rhodium, platinum and palladium [3–5]. In particular, palladium complexes containing phosphine ligands serve as highly active catalysts for the formation of carbon–carbon bonds [6].The palladium-catalyzed formation of biaryls from aryl halides with arylboronic acids (the Suzuki reaction) [7, 8] and the arylation and alkenylation of olefins (the Heck reaction) [9] have become mainstays of modern synthetic organic chemistry for the formation of carbon–carbon bonds.

In recent years, the Heck and Suzuki reactions have found widespread applications in synthetic organic chemistry and materials science [10]. Their popularity stems in part from their tolerance of many functional groups, which allows them to be employed in the synthesis of highly complex molecules [11]. The palladium-catalyzed Suzuki and Heck cross-coupling reactions are powerful tools for the preparation, respectively, of unsymmetrical biaryl [12] and stilbene compounds [13] which have been applied to many areas, including herbicides [14] and natural product synthesis [15]. Recently, various bulky and electron-rich phosphines have been developed as ligands to promote the cross-coupling reactions [16, 17].

Herein, we investigated the coordination behavior of iminophosphines toward palladium(II) and platinum(II).

The structures of all new compounds have been elucidated by a combination of NMR spectroscopy, IR spectroscopy, elemental analysis and X-ray crystallography. In addition, extending our program in the design and development of useful catalysts for the C–C coupling reaction, we tested the activities of the palladium complexes as potential catalysts in Suzuki–Heck-type coupling reactions.

Experimental

All manipulations were carried out under an atmosphere of nitrogen or argon using standard Schlenk techniques. All glassware was thoroughly dried at 210 °C for at least 4 h prior to use. The ligands **1–2** [18], complexes **1a**, **1c**, **2a**, **2c** [19], **1b**, **2b** [20], [$PdCl_2(COD)$] [21, 22], [PdClMe(COD)] [23], [$PtCl_2(COD)$] [24, 25], [PtClMe(COD)] [23, 26] were prepared as described in the literature.

Melting points were determined on a Kofler hot stage microscope (Reichart Thermovar) and are uncorrected. Microanalysis data were obtained using a Carlo Erba EA1108 elemental analyzer. Infrared Spectra were recorded on a Perkin-Elmer 1000 FT-IR spectrometer, as KBr discs for solids. All data are given in wavenumbers (cm^{-1}). ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian Unity-400 instrument. Mass spectra (EI) were recorded using a JEOL-MATE(II) GC–MS instrument. X-ray intensity data were collected on a Nonius Kappa-CCD diffractometer with 1.5 kW graphite monochromated Mo-Kα radiation.

Preparation of **1d**

To a CH_2Cl_2 solution (5 mL) of the ligand, $Ph_2PPhNHCH_2–C_5H_4N$ (ca. 0.2–0.3 mmoL), was added a CH_2Cl_2 solution (15 mL) of [PtClMe(COD)]. A yellow precipitate formed immediately. The reaction mixture was allowed to stir at room temperature for 6 h and the yellow crude product filtered off. The product was then washed three times with 10 mL CH_2Cl_2 and dried *in vacuo* to give a yellow powder. Yield 78 %. m.p. 213–215 °C. $C_{26}H_{24}ClN_2PPt$: Found: C, 51.8 %; H, 4.1 %; N, 2.5 %. Calcd. C, 51.9 %; H, 4.4 %; N, 2.8 %. IR($\upsilon_{C=N}$, imine: cm^{-1}): 1,630(s). ^{1}H NMR: (dmso-d_6) δ 8.50 (dd, 1H, $J = 1.6, 4.8$ Hz), 8.33 (s, 1H), 8.32 (d, 1H, $J = 2.2, 8.3$ Hz), 7.99 (td, 1H, $J = 1.8, 7.7$ Hz, ArH), 7.63 (m, 1H, ArH), 7.58 (m, 1H, ArH), 7.46 (m, 3H, ArH), 7.39 (m, 4H, ArH), 7.16 (m, 5H, ArH), 7.06 (dd, 1H, $J = 7.4, 9.7$ ArH), 5.48 (s, 2H), 0.60 (d, 3H, $J = 3.1$ Hz, CH_3). ^{31}P NMR: δ 9.28 J(Pt–P) = 3,782.6 Hz. EI-MS: *m/z* 590.68 $[M–Cl]^+$.

Preparation of **2d**

Using a procedure similar to that described above, reaction of $Ph_2PPhNHCH_2–C_4H_3S$ with $Pd[COD]Cl_2$ in CH_2Cl_2 at room temperature afforded complex **2d** as a yellow crystalline powder. Yield 75 %. m.p. 230–233 °C. $C_{25}H_{23}ClNSPPt$: Found: C, 48.3 %; H, 3.8 %; N, 2.3 %; S, 4.9 %. Calcd. C, 48.6 %; H, 3.7 %; N, 2.2 %; S, 4.9 %. IR($\upsilon_{C=N}$, imine: cm^{-1}): 1,627(s). ^{1}H NMR: (dmso-d_6) δ_H 8.73 (s, 1H), 7.69 (m, 10H, ArH), 7.17 (m, 2H, ArH), 6.90 (dd, 1H, $J = 3.5$ Hz, $J = 5.1$ Hz, ArH), 6.75 (ddd, 1H $J = 3.4$ Hz, $J = 5.1$ Hz, $J = 12.1$ Hz), 6.51 (dd, 1H $J = 1.0$ Hz, $J = 3.4$ Hz), 6.46 (dd, 1H $J = 1.0$ Hz, $J = 3.4$ Hz), 5.824 (s, 2H), 0.31 (dd, 3H $J = 3.7$ Hz, J = 40 Hz, CH_3). ^{31}P NMR: δ 8.20 (s) J (Pt–P) = 3,748 Hz. EI-MS: *m/z* : 595.45 $[M–Cl]^{+\cdot}$

Table 1 Crystal data and structure refinement parameters for complexes **1b** and **2b**

Complex	1b	2b
Empirical formula	$C_{25}H_{21}Cl_2N_2PPt$	C_{25} H_{22} Cl_2 N P Pt S, 0.5(C H_2 Cl_2)
Formula weight	646.40	707.92
T/K	173(2)	173(2)
λ/Å	0.71073	0.7103
Crystal system	Triclinic	Monoclinic
Space group	P −1	P 21/c
a	9.9684(14)	9.9635(7)
b	10.4129(15)	19.0185(14)
c	12.526(3)	16.0155(9)
α(°)	97.687(5)	90
β(°)	98.363(5)	122.751(3)
γ(°)	114.499(3)	90
$V(Å^3)$	1,143.1(4)	2,552.3(3)
Z	2	4
$Density_{calc}$ (mg/mL)	1.878	1.779
Absorption coefficient (mm^{-1})	6.457	5.869
F(000)	624	1,328
Crystal size (mm)	0.07 × 0.06 × 0.04	0.08 × 0.05 × 0.03
Theta range for data collection (°)	2.20–27.09	2.14–28.72
Limiting indices	$-12 \le h \le 7$, $-11 \le k \le 13$, $-16 \le 1 \le 16$	$-13 \le h \le 13$, $-25 \le k \le 25$, $-18 \le 1 \le 18$
Reflections collected/ unique	16,090/4,994 [*R*(int) = 0.0580]	30,138/6,590 [*R*(int) = 0.0524]
Completeness of theta max. and min. transmission	27.09 (99.3 %)	28.72 (99.7 %)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	4,994/0/280	6,590/8/270
Goodness-of-fit on F^2	1.005	1.053

Scheme 1 Synthesis of the platinum methylchloride complexes

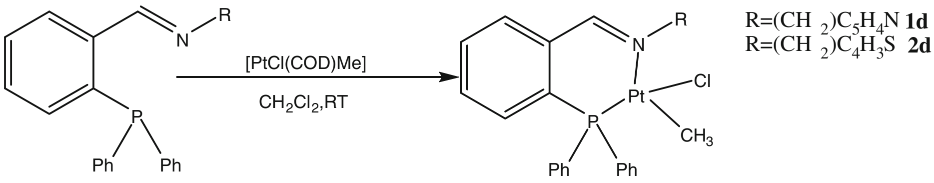


Table 2 Selected bond distances and angles for the platinum complex **1b**

Bond distances (Å)		Bond angles(°)	
Pt(1)–N(1)	2.040(4)	N(1)–Pt(1)–P(1)	88.47(12)
Pt(1)–P(1)	2.1999(13)	N(1)–Pt(1)–Cl(2)	176.70(12)
Pt(1)–Cl(2)	2.2840(12)	P(1)–Pt(1)–Cl(2)	91.76(5)
Pt(1)–Cl(1)	2.3806(14)	N(1)–Pt(1)–Cl(1)	91.27(12)
P(1)–C(20)	1.803(5)	P(1)–Pt(1)–Cl(1)	178.20(5)
P(1)–C(14)	1.815(5)	Cl(2)–Pt(1)–Cl(1)	88.60(5)

Table 3 Selected bond distances and angles for the platinum complex **2b**

Bond distances (Å)		Bond angles(°)	
Pt(1)–N(1)	2.032(5)	N(1)–Pt(1)–P(1)	86.13(14)
Pt(1)–P(1)	2.2084(13)	N(1)–Pt(1)–Cl(2)	178.42(14)
Pt(1)–Cl(2)	2.2901(15)	P(1)–Pt(1)–Cl(2)	95.36(5)
Pt(1)–Cl(1)	2.3639(14)	N(1)–Pt(1)–Cl(1)	89.48(14)
P(1)–C(20)	1.811(5)	P(1)–Pt(1)–Cl(1)	174.05(5)
P(1)–C(9)	1.823(5)	Cl(2)–Pt(1)–Cl(1)	89.06(6)

General procedure for Suzuki coupling reactions

The Iminophosphine palladium(II) complex (**1a**–**2a**, 0.01 mmoL), aryl bromide (1.0 mmoL), phenylboronic acid (1.5 mmoL), Cs_2CO_3 (2 mmoL) and dioxane (3 mL) were added to a Schlenk tube under argon atmosphere and the mixture was heated at 60 °C. After 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 immediately by GC and NMR and yields are based on aryl bromide.

General procedure for the Heck coupling reaction

The Iminophosphine palladium(II) complex (**1a**–**2a**, 0.01 mmoL), aryl bromide (1.0 mmoL), styrene (1.5 mmoL), K_2CO_3 (2 mmoL), DMF (3 mL) for **1a** and dioxane (3 mL) for **2a** were added to a Schlenk tube under argon atmosphere and the mixture was heated to 100 °C. After 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 immediately by GC and NMR and yields are based on aryl bromide.

X-ray crystal structure determination

Crystals suitable for single crystal X-ray diffraction for complexes **1b** and **2b** were obtained by slow evaporation of a dmso-d_6-CH_2Cl_2 solution of the complex at room temperature. All X-ray intensity data were collected on a Bruker APEX-II 4K-CCD diffractometer with 1.5 kW graphite monochromated Mo-Kα radiation.

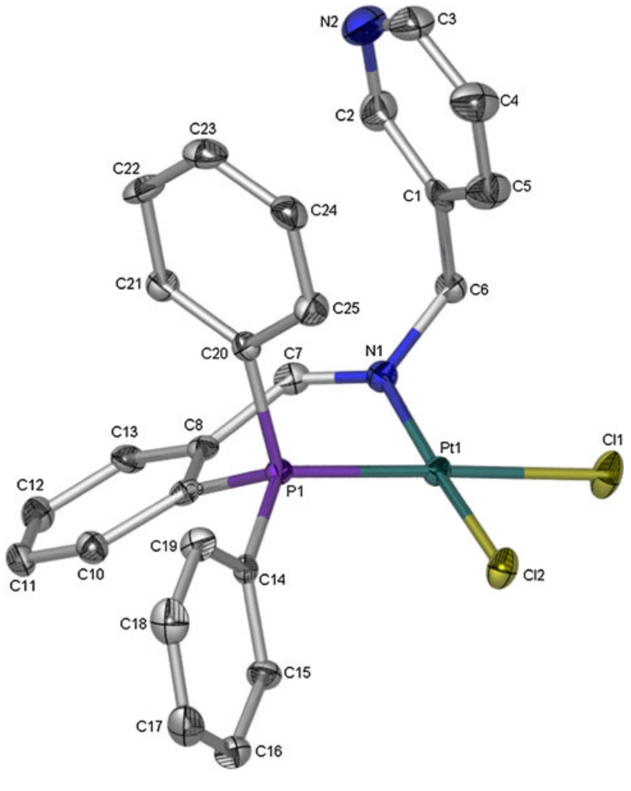


Fig. 1 The molecular structure of **1a** showing the atomic *numbering*. All non-hydrogen atoms were presented with ellipsoidal model with probability level 40 %. All hydrogen atoms are omitted for clarity

The structures were solved by direct methods using SHELXS-97 and refined employing full-matrix least-squares with the program SHELXL-97 refining on F^2. Packing diagrams were produced using the program Pov-Ray and graphic interface X-seed [27]. Crystallographic data for the structure determinations are listed in Table 1.

Results and discussion

Treatment of the iminophosphine ligands **1** and **2** with MCl_2(cod) and MCl_2(cod)Me (M = Pd, Pt; cod = 1,5-cyclooctadiene) in CH_2Cl_2 at room temperature afforded the palladium and platinum iminophosphine complexes **1a**, **1b**, **1c**, **2a**, **2b**, **2c** [19, 20]. The platinum methyl chloride complexes **1d** and **2d** were obtained from the reaction of the ligands **1** and **2** with [PtCl(COD)Me], respectively (Scheme 1).

The free ligands show a distinctive stretching frequency, *ν*(C=N), between 1,629 and 1,636 cm^{-1} which agrees with the previously reported values for iminophosphine ligands [28]. Upon complexation, the peaks shift to lower

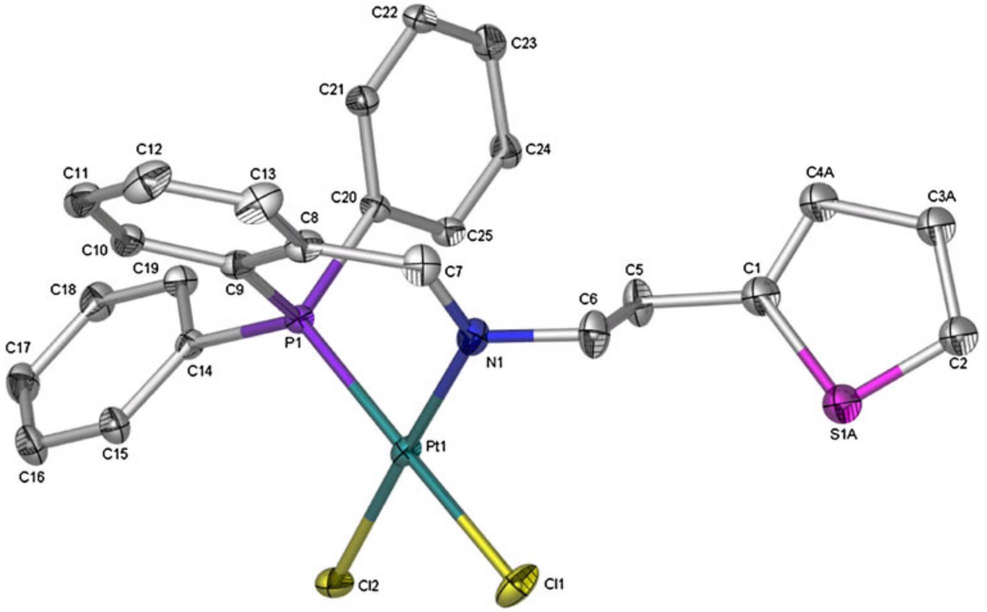
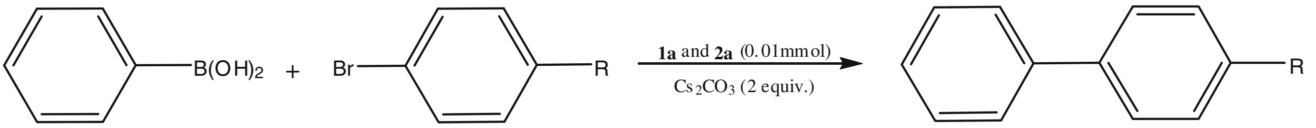
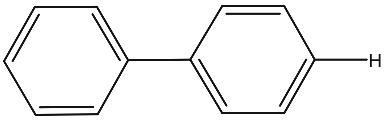
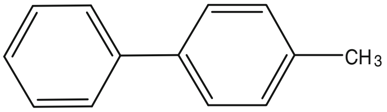
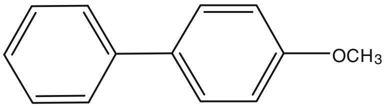
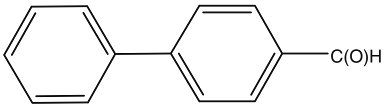


Fig. 2 The molecular structure of **2b** showing the atomic *numbering*. All non-hydrogen atoms were presented with ellipsoidal model with probability level 40 %. The thiophene *ring* was disordered over two places and only one *ring* is shown here. One dichloromethane solvent molecule and all hydrogen atoms are omitted for clarity

Table 4 The Suzuki coupling reactions of aryl bromides with phenylboronic acid[a]



Entry	*R*	Catalyst	Product	Conversion (%)	Yield (%)[b]
1	4-H	**1a**		64.5	60.4
		2a		67.8	64.3
2	4-CH_3–	**1a**		78.4	75.4
		2a		76.8	72.4
3	4-CH_3O–	**1a**		98.4	94.3
		2a		97.6	94.2
4	4-CH(O)–	**1a**		96.6	93.3
		2a		95.8	91.5

[a] 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)

[b] Purity of compounds was checked by NMR and yields are based on arylbromide. All reactions were monitored by GC: 80 °C, 2.0 h

frequencies, being observed at 1,624–1,630 cm^{-1}. This is due to increased electron density on the metal upon coordination of the imine moiety to the metal center [19, 20].

The ^{1}H NMR spectroscopy of **1d** showed a doublet assignable to the methyl group at δ 0.60, respectively. Complex **2d** exhibited a doublet of doublets at δ 0.31 *cis* to PPh_2, $J_{PH} = 3.8$ Hz. As expected, the Pt–H coupling is larger for the MePt *trans* to PPh_2 than for the MePt *cis* to P. The signal for the azomethine proton in the ^{1}H NMR spectra of the complexes is shifted downfield from that of the free ligand, indicating that imine nitrogen is coordinated to the metal center. Previous data for similar complexes reported the azomethine peaks as singlets [29]; in the present work, the spectra were obtained at a slightly higher field with Pt satellites $J_{PtH} = 101.3$ Hz and $J_{PtH} = 109.8$ Hz. The ^{1}H NMR spectra of the complexes show a set of resonances in the region 6.90–7.99 ppm arising from the aromatic protons of the iminophosphine ligand.

The ^{31}P NMR spectroscopy in dmso-d_6 of **1d** exhibited a singlet at δ 9.28, showing that the Pt-coordinated phosphine is considerably de-shielded compared to the free ligand **1**. The singlet has one pair of ^{195}Pt satellites with coupling constants $J_{PtP} = 3{,}782.6$ Hz. The presence of platinum satellites in the spectra of the complexes **1d** and **2d** is further evidence of coordination by the P center. Furthermore, the J_{PtP} coupling constants are of the order of magnitude expected in such complexes [30, 31].

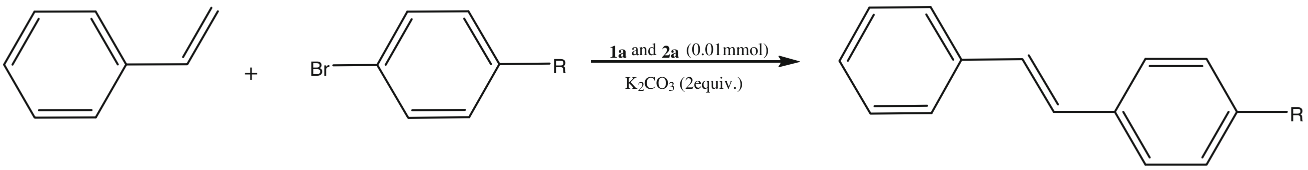
Structural description of complexes **1b** and **2b** [32, 33]

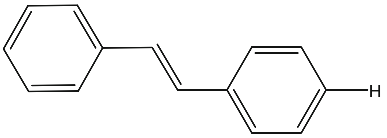
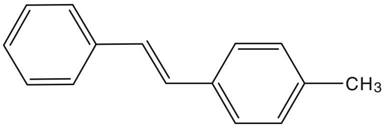
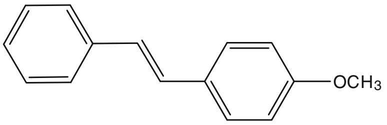
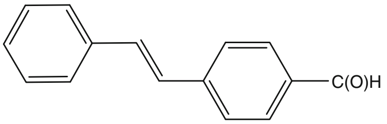
The selected bond lengths and angles for complexes **1b** and **2b** are summarized in Tables 2 and 3, and their molecular structures are shown in Figs. 1 and 2.

The platinum is in a square-planar environment and it is bound to the ligand using a K^2–N, P interaction in a *cis* fashion, with the chlorides located at the two remaining sites. However, the square-planar geometry of the platinum environment is distorted with the angles being less than 180°, N(1)–Pt(1)–Cl(2) and P(1)–Pt(1)–Cl(1) of 176.70(12)° and 178.20(5)°, respectively. The average Pt–N and Pt–P bond lengths of 2.040(4) and 2.1999(13) Å, respectively, are in the range expected for iminophosphine platinum(II) complexes. The torsion angle Pt–P–C(9)–C(8) = −36.5(4)° indicates that the $=CHC_6H_4–$ unit lies below the $PtCl_2(P,N)$ plane.

In complex **2b,** the ligand adopts a KP and KN coordination mode in a square-planar coordination geometry for the platinum center. The Pt(1)–N(1), Pt(1)–P(1),

Table 5 The Heck coupling reactions of aryl bromides with styrene[a]



Entry	*R*	Catalyst	Product	Conversion (%)	Yield (%)[b]
1	4-H	**1a** **2a**		64.2 60.2	59.8 55.6
2	4-CH_3–	**1a** **2a**		88.3 86.4	82.6 81.5
3	4-CH_3O–	**1a** **2a**		98.6 96.3	93.2 91.8
4	4-CH(O)–	**1a** **2a**		98.8 96.4	95.3 91.4

[a] 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 **1a** and dioxane 3.0 (mL) for **2a**

[b] Purity of compounds was checked by NMR and yields are based on arylbromide. All reactions were monitored by GC: 80 °C, 2.0 h

Pt(1)–Cl(2) and Pt(1)–Cl(2) bond lengths are in the normal ranges. The Pt–Cl bond length *trans* to the P atom (2.3639(14) Å) is longer than that *trans* to the N atom (2.2901(15) Å) owing to the stronger *trans* influence of a tertiary phosphine with respect to an imine. The bond angle at the Pt(1) atom exhibits only minor deviations from a right angle. The torsion angle Pt(1)–P(1)–C(9)–C(8) = 44.8(5)° indicates that the =CHC_6H_4– unit lies above the $PtCl_2$(P,N) plane. These deviations have been observed in similar complexes with iminophosphine ligands [34–36].

Suzuki reaction catalysis

The palladium complexes **1a** and **2a** were tested as catalysts in the Suzuki reaction of aryl bromides with boronic acid. Following optimization experiments, we found that the use of 0.01 mmoL the palladium complexes (**1a, 2a**) with Cs_2CO_3 as the base at 60 and 80 °C in dioxane appeared to be best, respectively. We initially tested the catalytic activity of the complexes (**1a, 2a**) for the coupling of *p*-bromobenzaldehyde 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*-bromobenzaldehyde, *p*-bromobenzene, *p*-bromoanisole and *p*-bromotoluene react cleanly with phenylboronic acid in high yields (Table 4).

Heck reaction catalysis

The rate of coupling is dependent on a variety of parameters such as temperature, solvent, base and catalyst loading. We found that the use of 0.01 mmoL catalyst, 2 equivalents K_2CO_3 in DMF at 80 °C for both **1a** and **2a,** led to the best conversions. We initially tested the catalytic activities of **1a** and **2a** for the coupling of *p*-bromobenzaldehyde with styrene. A control experiment indicated that the coupling reaction did not occur in the absence of **1a** and **2a.** 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. Electron-deficient bromides gave higher conversions.

Conclusion

The coordination behavior of ligands **1** and **2** toward Pd(II) and Pt(II) is described. Single crystal X-ray diffraction revealed that in complexes **1b** and **2b,** there is a slightly distorted square-planar geometry around the platinum metal center and the Pt–P distances are within the expected ranges. We have also demonstrated the application of palladium complexes of these iminophosphine ligands as pre-catalysts in the Suzuki coupling and Heck reactions of aryl halides. The Pt(II) iminophosphine **1b** and **2b** system exhibited no catalytic activity. Only the palladium complexes were found to show catalytic activity in both the Suzuki and Heck coupling reactions of aryl bromides. In both cases, the catalytic activities of complexes **1a** and **2a** were found to be higher in the reactions of aryl bromides with electron-withdrawing substituents than those with electron-releasing substituents (Table 5).

Supplementary materials

Supplementary data and figures for complexes **1b** and **2b** are available from the IUCR electronic archives (References: GO2028 and NR2014). Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 851988 and 919298 for complexes **1a** and **2b,** respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk of www: http://www.ccdc.cam.ac.uk.

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References

1. Bhattacharyya P, Woollins JD (1995) Polyhedron 14:3367
2. Aydemir M, Baysal A, Sahin E, Gumgum B, Ozkar S (2011) Inorganica Chim Acta 378:10
3. Brunner H, Zettlmeier W (1993) Handbook of enantioselective catalysis with transition metal compounds, Vols 1 and 2. VCH: Basel, New York
4. Noyori R (1994) Asymmetric catalysis in organic synthesis. Wiley, New York
5. Keim W (1990) Angew Chem Int Ed Engl 12:251
6. Punji B, Ganesamoorthy G, Balakrishna MS (2006) J Mol Catal A Chem 259:78–83
7. Miyaura N, Suzuki A (1995) Chem Rev 95:2457
8. Suzuki A (1999) J Organomet Chem 576:147
9. Heck RF, Nolley JP (1972) J Org Chem 37:2320
10. Littke AF, Fu GC (2002) Angew Chem Int Ed 41:4176–4211
11. Nicalaou KC, Sorensen EJ (1996) Classics in total synthesis. VCH, New York
12. Bedford RB (2003) Chem Commun 15:1787
13. Biricik N, Durap F, Kayan C, Gumgum B, Gurbuz N, Ozdemir I, Ang WH, Fei Z, Scopelliti R (2008) J Organomet Chem 693:2693
14. Szmant HH (1989) Organic building block of the chemical industry. Wiley, New York
15. Nicolaou KC, Li H, Body CNC, Ramanjulu JM, Yue TY, Natarajan S, Chu XJ, Brase S, Rubsam F (1999) Chem Eur J 5:2584
16. Punji B, Ganesamoorthy C, Balakrishna MS (2006) J Mol Cat 259:78

17. Aydemir M, Baysal A, Durap F, Gumgum B, Ozkar S, Yildirim LT (2009) Appl Organometal Chem 23:467–475
18. Mogorosi MM, Mahamo T, Moss JR, Mapolie SF, Slootweg JC, Lammertsma K, Smith GS (2011) J Organomet Chem 696:3585–3592
19. Chiririwa H, Moss JR, Hendricks D, Meijboom R, Muller A (2013) Transition Met Chem. doi:10.1007/s11243-012-9674-4
20. Chiririwa H, Moss JR, Hendricks D, Smith GS, Meijboom R (2013) Polyhedron 49:29–35
21. Chatt J, Vallarino LM, Venanzi LM (1957) J Chem Soc:3413
22. Bailey CT, Linsesky GCJ (1985) J Chem Educ 62:896
23. Rulke RE, Ernsting JM, Spek AL, Elsevier CJ, van Leeuwen PWNM, Vrieze K (1993) Inorg Chem 32:5769
24. McDermott JX, White JF, Whitesides GM (1976) J Am Chem Soc 98:6521
25. Drew D, Doyle JR (1990) Inorg Synth 28:346
26. Lapido FT, Anderson GK (1994) J Organomet Chem 13:303
27. Barbour LJ (2001) X-Seed: a software tool for supramolecular crystallography. J Supromol Chem 1:189
28. Ghilardi CA, Midollini S, Moneti S, Orlandini A, Scapacci G (1992) J Chem Soc, Dalton Trans 23:3371–3376
29. Fei Z, Ang WH, Zhao D, Scopelliti R, Dyson PJ (2006) Inorganica Chim Acta 359:2635–2643
30. Balakrishna MS, Krishnamurthy SS, Murugavel R, Netaji M, Mathews II (1993) J Chem Soc, Dalton Trans 3:477–482
31. Slawin AMZ, Woollins JD, Zhang Q (2001) J Chem Soc Dalton Trans 5:621–632
32. Chiririwa H, Meijboom R (2011) Acta Crystallogr Sect E Struct Rep E67:m1497
33. Chiririwa H, Muller A (2012) Acta Crystallogr Sect E Struct Rep E68:m116–m117
34. Sanchez G, Serrano JL, Moral MA, Perez J, Molins E, Lopez G (1999) Polyhedron 18:3057
35. Ankersmit HA, Bjorn HL, Kooijman H, Spek AL, Vrieze K, van Koten G (1996) Inorganica Chim Acta 252:141–155
36. Koprowski M, Sebastian RM, Maraval V, Zablocka M, Cadierno V, Donnadieu B, Igau A, Caminade AM, Majoral JP (2002) Organometallics 21:4680