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Cross-coupling reactions in water using ionic liquid-based palladium(II)–phosphinite complexes as outstanding catalysts

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Two new phosphinite ligands based on ionic liquids [(Ph₂PO)C₇H₁₄N₂Cl]Cl (1) and [(Cy₂PO)C₇H₁₄N₂Cl]Cl (2) were synthesized by reaction of 1-(3-chloro-2-hydoxypropyl)-3-methylimidazolium chloride, [C₇H₁₅N₂OCl]Cl, with one equivalent of chlorodiphenyl-phosphine or chlorodicyclohexylphosphine, respectively, in anhydrous CH₂Cl₂ and under argon atmosphere. The reactions of 1 and 2 with MCl₂(cod) (M = Pd, Pt; cod = 1,5-cyclooctadiene) yield complexes *cis*-[M([(Ph₂PO)C₇H₁₄N₂Cl]Cl)₂Cl₂] and *cis*-[M(Cy₂PO) C₇H₁₄N₂Cl]Cl)₂Cl₂], respectively. All complexes were isolated as analytically pure substances and characterized using multi-nuclear NMR and infrared spectroscopies and elemental analysis. The catalytic activity of palladium complexes based on ionic liquid phosphinite ligands 1 and 2 was investigated in Suzuki cross-coupling. They show outstanding catalytic activity in coupling of a series of aryl bromides or aryl iodides with phenylboronic acid under the optimized reaction conditions in water. The complexes provide turnover frequencies of 57 600 and 232 800 h⁻¹ in Suzuki coupling reactions of phenylboronic acid with *p*-bromoacetophenone or *p*-iodoacetophenone, respectively, which are the highest values ever reported among similar complexes for Suzuki coupling reactions in water as sole solvent in homogeneous catalysis. Furthermore, the palladium complexes were also found to be highly active catalysts in the Heck reaction affording *trans*-stilbenes. Copyright © 2014 John Wiley & Sons, Ltd.

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Keywords: ionic liquid; phosphinite; Suzuki coupling; Heck reaction; palladium; platinum

Introduction

Palladium complexes have become the most popular organometallics used in organic synthesis due to their remarkable catalytic potential and their great versatility.^[1,2] Especially, palladium catalysts have been used in most of the carbon-carbon bond formation reactions such as the Heck and Suzuki reactions^[3,4] which are powerful tools for the preparation of unsymmetric biaryl^[5,6] and stilbene compounds^[7] and have been widely employed in the synthesis of pharmaceuticals, herbicides, natural products and advanced materials.^[8-10] Most palladium-catalysed Suzuki coupling reactions are performed in organic solvents. However, the use of an environmentally friendly reaction medium, minimization of reaction steps, higher yields and faster reaction remain challenges in the context of green chemistry for the Suzuki coupling reaction.^[11] In this regard, the use of water, the most abundant and non-toxic solvent for organic reactions, is becoming more important due to increasing environmental, economic and safety concerns.^[12-14] So far, a variety of catalytic systems have been reported for the Suzuki coupling reaction in water, in spite of which they may be less efficient than in a suitable organic solvent.[15-17] Palladium catalysts with phosphine ligands,^[18] carbene ligands,^[19] palladacycle^[20] and other coordinate ligands^[21,22] have shown high activity in Suzuki coupling reactions in water. However, the development of easily available or readily prepared and inexpensive palladium catalysts with outstanding activity towards

Suzuki-Miyaura cross-coupling reactions in the sole solvent of water is a highly attractive aim.

Metal-containing ionic liquids are considered as promising new materials that combine the properties of ionic liquids with additional intrinsic magnetic, spectroscopic or catalytic properties, depending on the incorporated metal ion.^[23] Ionic liquids that contain palladium, ruthenium, platinum, gold and aluminium

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(alsoiron, nickel, zinc or copper) have been used successfully in catalysis.^[24,25] Several metal (Pd, Ru, Rh, V) complex catalysts with imidazolium tags also have been used in chemical transformations such as hydrogenation, ring-closing olefin metathesis, and Heck and Suzuki cross-coupling reactions.^[26–29]

Extending our study to develop useful and very effective catalysts, in the present article we describe the synthesis of the ionic liquid compound 1-(3-chloro-2-hydoxypropyl)-3-methylimidazolium chloride and its corresponding phosphinite ligands with palladium(II) and platinum(II) metals. We also investigated the catalytic activities of palladium complexes in the Suzuki and Heck cross-coupling reactions. Furthermore, the structures of all new compounds were elucidated using a combination of multinuclear NMR spectroscopy, infrared spectroscopy and elemental analysis.

Experimental

General

Unless otherwise stated, all reactions were carried out under an atmosphere of argon using conventional Schlenk glassware. Solvents were dried using established procedures and distilled under argon immediately prior to use. Analytical grade and deuterated solvents were purchased from Merck. PPh₂Cl, PCy₂Cl, epichlorohydrin and 1-methylimidazole were purchased from Fluka and were used as received. The starting materials $[MCl_2(cod)]$ (M = Pd, Pt; cod = 1,5cyclooctadiene) were prepared according to literature procedures.^[30,31] Fourier transform infrared (IR) spectra were recorded using attenuated total reflection apparatus with a PerkinElmer Spectrum 100 Fourier transform spectrophotometer. ¹H NMR (400.1 MHz), ¹³C NMR (100.6 MHz) and ³¹P-{¹H} NMR (162.0 MHz) spectra were recorded using a Bruker AV400 spectrometer, with δ referenced to external tetramethylsilane and 85% H₃PO₄, respectively. Elemental analysis of carbon, hydrogen and nitrogen was carried out with a Costech Combustion System CHNS-O instrument. Melting points were determined using a Gallenkamp Model apparatus with open capillaries.

GC Analyses

GC analyses were performed using a Shimadzu 2010 Plus gas chromatograph equipped with a capillary column (5% biphenyl, 95% dimethylsiloxane; $30 \text{ m} \times 0.32 \text{ mm}$ inner diameter $\times 0.25 \text{ µm}$ film thickness). The GC parameters for Suzuki–Miyaura coupling reactions were as follows: initial temperature, $50 \,^{\circ}$ C; initial time, 1 min; solvent delay, 3.70 min; temperature ramp 1, $10 \,^{\circ}$ C min⁻¹; final temperature, $150 \,^{\circ}$ C; temperature ramp 2, $15 \,^{\circ}$ C min⁻¹; final temperature, $250 \,^{\circ}$ C; final time, 20.67 min; injector port temperature, $250 \,^{\circ}$ C; detector temperature, $250 \,^{\circ}$ C; injection volume, $2.0 \,^{\mu}$ L Parameters for Heck coupling reactions were as follows: initial temperature, $50 \,^{\circ}$ C; initial time, 1 min; solvent delay, $3.53 \,^{\circ}$ Sin; temperature ramp, $13 \,^{\circ}$ C min⁻¹; final temperature, $300 \,^{\circ}$ C; final time, $40.46 \,^{\circ}$ C; injection volume, $2.0 \,^{\mu}$ L

General Procedure for Suzuki–Miyaura Cross-Coupling Reaction

Palladium complexes based on the ionic liquid phosphinite ligands (**1a** and **2a**, 0.001 mmol), aryl bromide/chloride/iodide (1.0 mmol), phenylboronic acid (1.5 mmol), base (2 mmol) and solvent (3 ml)

were added to a Schlenk tube under argon atmosphere or in air and the reaction was followed at various conditions and parameters (temperature, time, base, etc.). 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 using flash chromatography on silica gel. The purity of the compounds was checked immediately using GC and ¹H NMR. Yields are based on aryl halides.

General Procedure for Heck Coupling Reaction

Palladium complexes based on the ionic liquid phosphinite ligands (**1a** and **2a**, 0.01 mmol), aryl bromide/chloride/iodide (1.0 mmol), styrene (1.5 mmol), base (2 mmol) and solvent (3 ml) were added to a Schlenk tube under argon atmosphere or in air and the reaction was monitored at various conditions and parameters (temperature, time, base, etc.). 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 using flash chromatography on silica gel. The purity of the compounds was checked immediately using GC and ¹H NMR. Yields are based on aryl halides.

Synthesis and Characterization of Ligands and Their Complexes

General procedure for the synthesis of phosphinites (1 and 2)

A dry and degassed CH_2CI_2 (20 ml) solution of 1-(3-chloro-2-hydroxypropyl)-3-methylimidazolium chloride under argon atmosphere (0.100 g, 0.467 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 (0.293 ml, 0.467 mmol). After the addition, the mixture was stirred at -78 °C for 1 h and for an additional 30 min at room temperature. The reaction solution was cooled to -78 °C again, and a solution of chlorodiphenylphosphine for 1 or chlorodicyclohexylphosphine for 2 (0.467 mmol) in CH_2CI_2 (10 ml) was added dropwise to the reaction medium. Stirring was maintained for a further 1 h at -78 °C. Then the cooling bath was removed and the mixture was stirred for another 1 h at room temperature. Precipitated lithium chloride was removed by filtration under argon and then the volatiles were evaporated *in vacuo* to leave viscous oily phosphinite ligand 1 or 2.

Synthesis of 1-{3-chloro-2-[(diphenylphosphanyl)oxy]propyl}-3methylimidazolium chloride [(Ph₂PO)C₇H₁₄N₂Cl]Cl (1). Yield 0.180 g, 96.8%. ¹H NMR (400.1 MHz, CDCl₃, δ , ppm): 10.14 (s, 1H, – (CH₃)NCHN–), 7.13–7.78 (m, 12H, P(C₆H₅)₂ + –NCHCHN–), 4.94 (m, 1H, NCH₂, (a)), 4.71 (br, 1H, –CHOP), 4.57 (m, 1H, NCH₂, (b)), 3.91 (m, 1H, –CH₂Cl, (a)), 3.85 (m, 1H, –CH₂Cl, (b)), 3.80 (s, 3H, NCH₃). ¹³C NMR (100.6 MHz, CDCl₃, δ , ppm): 36.55 (NCH₃), 45.14 (–CH₂Cl), 52.52 (NCH₂), 78.45 (d, ²J = 23.1 Hz, (–CHOP), 122.59, 122.90 (–NCHCHN–), 129.53 (d, ³J_{31P-13C} = 10.1 Hz, *m*-P(C₆H₅)₂), 131.41 (*p*-P(C₆H₅)₂), 135.26 (d, ²J_{31P-13C} = 19.6 Hz, *o*-P(C₆H₅)₂), 140.65 (d, ¹J_{31P-13C} = 47.8 Hz, *i*-P(C₆H₅)₂), 138.17 (–(CH₃)NCHN–); the assignment was based on the ¹H–¹³C HETCOR, DEPT and ¹H–¹H COSY spectra. ³¹P-{¹H} NMR (162.0 MHz, CDCl₃, δ , ppm): 118.46 (s, OPPh₂). IR (ν , cm⁻¹): 3053 (aromatic C–H), 1434 (P–Ph), 1060 (O–P). Anal. Calcd for C₁₉H₂₄N₂OCl₂P (398.29 g mol⁻¹) (%): C, 57.30; H, 6.07; N, 7.03. Found (%): C, 57.18; H, 6.00; N, 6.96.

Synthesis 1-{3-chloro-2-[(dicyclohexylphosphanyl)oxy]propyl}-3methylimidazolium chloride [(Cy_2PO)- $C_7H_{14}N_2CI$]Cl (**2**). Yield 0.183 g, 95.5%. ¹H NMR (400.1 MHz, CDCI₃, δ , ppm): 10.48 (s, 1H, – (CH₃)NCHN–), 7.64, 7.45 (2×s, 2H, –NCHCHN–), 4.84 (m, 1H, NCH₂, (a)), 4.53 (m, 1H, NCH₂, (b)), 4.16 (br, 1H, –CHOP), 4.10 (s, 3H, NCH₃), 3.83 (m, 1H, –CH₂Cl, (a)), 3.68 (m, 1H, –CH₂Cl, (b)), 1.00–1.95 (m, 22H, protons of P(C₆H₁₁)₂). ¹³C NMR (100.6 MHz, CDCl₃, δ , ppm): 26.20, 26.27, 26.64, 26.85, 26.98, 27.21 (CH₂ of P(C₆H₁₁)₂), 37.20 (d, ¹*J* = 15.1 Hz, CH of P(C₆H₁₁)₂), 36.77 (NCH₃), 44.05 (–CH₂Cl), 52.34 (NCH₂), 77.32 (d, ²*J* = 22.7 Hz, –CHOP), 123.05, 123.43 (–NCHCHN–), 138.67 (–(CH₃)NCHN–); the assignment was based on the ¹H–¹³C HETCOR, DEPT and ¹H–¹H COSY spectra. ³¹P-(¹H) NMR (162.0 MHz, CDCl₃, δ , ppm): 148.76 (s, OPCy₂). IR (ν , cm⁻¹): 2923, 2850 (aliphatic C–H), 1446 (P–Cy), 1059 (O–P). Anal. Calcd for C₁₉H₃₆N₂OCl₂P (410.39 g mol⁻¹) (%): C, 55.61; H, 8.84; N, 6.83. Found (%): C, 55.56; H, 8.71; N, 6.70.

Synthesis of Metal (Pd(II), Pt(II)) Complexes

Pd(II) complex 1a

[Pd(cod)Cl₂] (0.036 g, 0.126 mmol) and **1** (0.100 g, 0.251 mmol) were dissolved in dry CH₂Cl₂ (25 ml) under argon atmosphere and stirred for 15 min at room temperature. The volume was concentrated to ca 1-2 ml under reduced pressure, and addition of petroleum ether (20 ml) gave the corresponding Pd(II) complex as a clear yellow solid. The product was collected by filtration and dried in vacuo. Yield 0.095 g, 77.7%; m.p. 143–145 °C. ¹H NMR (400.1 MHz, DMSO-d₆, δ, ppm): 9.23 (s, 2H, –(CH₃)NCHN–), 7.42–7.78 (m, 24H, P (C₆H₅)₂ + -NCHCHN-), 5.98 (br, 2H, -CHOP), 4.81 (m, 4H, NCH₂), 4.11 (br, 4H, -CH₂Cl), 3.77 (s, 6H, NCH₃). ¹³C NMR (100.6 MHz, DMSO-d₆, δ , ppm): 36.44 (NCH₃), 45.56 (–CH₂Cl), 51.41 (NCH₂), 78.13 (d, ²J=22.9 Hz, -CHOP), 123.63, 124.13 (-NCHCHN-), 128.28 $(m-P(C_6H_5)_2)$, 131.30, $(p-P(C_6H_5)_2)$, 131.63 $(o-P(C_6H_5)_2)$, 137.60 ((CH₃)NCHN–), 139.25 (d, ${}^{1}J_{31P-13C} = 38.2$ Hz, *i*-P(C₆H₅)₂); the assignment was based on the ${}^{1}H-{}^{13}C$ HETCOR, DEPT and ${}^{1}H-{}^{1}H$ COSY spectra. ³¹P-{¹H} NMR (162.0 MHz, DMSO-*d*₆, *δ*, ppm): 104.59; (CDCl₃, δ_{i} ppm): 107.20 (s, Pd–OPPh₂). IR (KBr, v_{i} cm⁻¹): 3053 (aromatic C-H), 1436 (P-Ph), 1045 (O-P), 301, 281 (Pd-Cl). Anal. Calcd for C₃₈H₄₈N₄O₂P₂PdCl₆ (973.91 g mol⁻¹) (%): C, 46.87; H, 4.97; N, 5.75. Found (%): C, 46.79; H, 4.90; N, 5.68.

Pd(II) complex 2a

[Pd(cod)Cl₂] (0.035 g, 0.122 mmol) and 2 (0.100 g, 0.244 mmol) were dissolved in dry CH₂Cl₂ (25 ml) under argon atmosphere and stirred for 15 min at room temperature. The volume was concentrated to ca 1-2 ml under reduced pressure, and addition of petroleum ether (20 ml) gave the corresponding Pd(II) complex as a clear yellow solid. The product was collected by filtration and dried in vacuo. Yield 0.097 g, 79.8%; m.p. 178–180 °C. ¹H NMR (400.1 MHz, DMSO- d_{6} , δ , ppm): 9.25 (s, 2H, -(CH₃)NCHN-), 7.81-7.86 (2×s, 4H, -NCHCHN-), 5.74 (br, 2H, -CHOP), 4.63 (m, 4H, NCH2), 4.27 (m, 2H, -CH₂Cl, (a)), 4.09 (m, 2H, -CH₂Cl, (b)), 3.88 (s, 6H, NCH₃), 2.67 (m, 2H, CH of $P(C_6H_{11})_2$ (a)), 2.33 (m, 2H, CH of $P(C_6H_{11})_2$ (b)), 1.15–1.72 (m, 40H, CH₂ of $P(C_6H_{11})_2$). ¹³C NMR (100.6 MHz, DMSO-d₆, δ , ppm): 26.75, 26.90, 27.04, 27.15, 27.38, 27.71 (CH₂ of $P(C_6H_{11})_2)$, 36.51 (NCH₃), 41.23 (d, ¹J = 33.7 Hz, CH of $P(C_6H_{11})_2)$, 45.98 (–CH₂Cl), 51.48 (NCH₂), 77.94 (d, ²J = 20.5 Hz, –CHOP), 123.63, 124.04 (-NCHCHN-), 137.74 (-(CH₃)NCHN-); assignment was based on the ¹H-¹³C HETCOR, DEPT and ¹H-¹H COSY spectra. ³¹P-{¹H} NMR (162.0 MHz, DMSO-*d*₆, *δ*, ppm): 129.77 (s, Pd–OPCy₂); (CDCl₃, δ, ppm): 132.48 (s, Pd–OPCy₂). IR (v, cm⁻¹): 2926, 2852 (aliphatic C–H), 1436 (P–Cy), 1036 (O–P), 303, 283 (Pd–Cl). Anal. Calcd for $C_{38}H_{72}N_4O_2P_2PdCl_6$ (998.10 g mol⁻¹) (%): C, 45.73; H, 7.27; N, 5.61. Found (%): C, 45.67; H, 7.20; N, 5.55.

Pt(II) complex 1b

[Pt(cod)Cl₂] (0.047 g, 0.126 mmol) and 1 (0.100 g, 0.251 mmol) were dissolved in dry CH₂Cl₂ (25 ml) under argon atmosphere and stirred overnight at room temperature. The volume was concentrated to ca 1-2 ml under reduced pressure, and addition of petroleum ether (20 ml) gave the corresponding Pt(II) complex as a white solid. The product was collected by filtration and dried in vacuo. Yield 0.104 g, 78.2%; m.p. 197–209 °C. ¹H NMR (400.1 MHz, CDCl₃, δ, ppm): 9.15 (s, 2H, -(CH₃)NCHN-), 7.42-8.07 (m, 20H, P(C₆H₅)₂), 7.02 (d, 2H, J = 1.7 Hz, -NCHCHN-), 6.98 (d, 2H, J = 1.7 Hz, -NCHCHN-), 5.62 (m, 2H, NCH₂, (a)), 4.25 (m, 2H, NCH₂, (b)), 3.97 (s, 6H, NCH₃), 3.95 (br, 2H, -CHOP), 3.51 (m, 2H, -CH₂Cl, (a)), 3.37 (m, 2H, -CH₂Cl, (b)). ¹³C NMR (100.6 MHz, CDCl₃, δ, ppm): 36.07 (NCH₃), 43.02 (–CH₂Cl), 47.18 (NCH₂), 73.06 (d, ²J=21.8 Hz, -CHOP), 120.80, 123.49 (-NCHCHN-), 128.66 (s, $p-P(C_6H_5)_2$), 131.68 (d, ${}^{3}J_{31P-13C} = 10.1$ Hz, $m-P(C_6H_5)_2)$, 134.41 (d, ${}^2J_{31P-13C} = 13.2$ Hz, $o-P(C_6H_5)_2)$, 137.56 $((CH_3)NCHN-)$, 141.75 (d, ${}^{1}J_{31P-13C} = 44.2 \text{ Hz}$, *i*-P(C_6H_5)₂); assignment was based on the ¹H–¹³C HETCOR, DEPT and ¹H–¹H COSY spectra. ³¹P-{¹H} NMR (162.0 MHz, CDCl₃, δ , ppm): 77.12 (s, $J_{(PPt)} = 4273.6$ Hz, Pt-OPPh₂). IR (v, cm⁻¹): 3053 (aromatic C-H), 1436 (P-Ph), 1045 (O-P), 303, 283 (Pt-Cl). Anal. Calcd for C₃₈H₄₈N₄O₂P₂PtCl₆ (1062.57 g mol⁻¹) (%): C, 42.95; H, 4.55; N, 5.27. Found (%): C, 42.88; H, 4.49; N, 5.21.

Pt(II) complex 2b

[Pt(cod)Cl₂] (0.046 g, 0.122 mmol) and **2** (0.100 g, 0.244 mmol) were dissolved in dry CH₂Cl₂ (25 ml) under argon atmosphere and stirred overnight at room temperature. The volume was concentrated to ca 1-2 ml under reduced pressure, and addition of petroleum ether (20 ml) gave the corresponding Pt(II) complex as a white solid. The product was collected by filtration and dried in vacuo. Yield 0.102 g, 77.2%; m.p. 99–101 °C. ¹H NMR (400.1 MHz, CDCl₃, δ, ppm): 9.90 (s, 2H, -(CH₃)NCHN-), 7.47, 7.43 (2×s, 4H, -NCHCHN-), 5.95 (br, 2H, -CHOP), 5.16 (m, 2H, NCH2, (a)), 4.62 (m, 2H, NCH2, (b)), 4.10 (s, 6H, NCH₃), 4.25 (m, 2H, -CH₂Cl, (a)), 3.95 (m, 2H, -CH₂Cl, (b)), 2.71 (m, 4H, CH of P(C₆H₁₁)₂), 1.26–2.38 (m, 40H, CH₂ of P(C₆H₁₁)₂). ¹³C NMR (100.6 MHz, CDCl₃, δ, ppm): 26.38, 26.49, 27.13, 27.31, 27.61, 28.38 (CH₂ of P(C₆H₁₁)₂), 37.28 (NCH₃), 39.95 (d, ¹J = 35.2 Hz, CH of $P(C_6H_{11})_2)$, 45.60 (-CH₂Cl), 52.18 (NCH₂), 77.35 (d, ²J=21.2Hz, -CHOP), 122.85, 123.30 (-NCHCHN-), 137.91 (-(CH₃)NCHN-); assignment was based on the ¹H-¹³C HETCOR, DEPT and ¹H-¹H COSY spectra. ³¹P-{¹H} NMR (162.0 MHz, CDCl₃, δ , ppm): 97.24 (s, $J_{(PPt)} =$ 4082.4 Hz, Pt–OPCy₂). IR (KBr, v, cm⁻¹): 2926, 2852 (aliphatic C–H), 1436 (P-Cy), 1036 (O-P), 328, 278 (Pt-Cl). Anal. Calcd for C₃₈H₇₂N₄O₂P₂PtCl₆ (1086.76 g mol⁻¹) (%): C, 42.00; H, 6.68; N, 5.16. Found (%): C, 41.90; H, 6.58; N, 5.09.

Results and Discussion

Synthesis and Characterization of Ligands and Their Metal Complexes

The synthesis of 1-(3-chloro-2-hydroxypropyl)-3-methylimidazolium chloride, $[C_7H_{15}N_2OCI]CI$, was accomplished in one step from the reaction of 1-methylimidazole and epichlorohydrin in ethanol at room temperature, according to literature procedures.^[32] 1-(3-Chloro-2-hydroxypropyl)-3-methylimidazolium chloride was characterized using elemental analysis, IR spectroscopy, TGA–DTA and multinuclear NMR spectroscopies and also X-ray analysis (to be published elsewhere). As shown in Scheme 1, phosphinite ligands **1** and **2** were synthesized^[33] from the starting materials PPh₂CI and PCy₂CI, respectively, in CH₂Cl₂ solution by the hydrolysis method.^[34,22]



Scheme 1. Synthesis of compounds $[(Ph_2PO)C_7H_{14}N_2CI]CI (1), [(Cy_2PO)C_7H_{14}N_2CI]CI (2), [Pd ((Ph_2PO)C_7H_{14}N_2CI)_2CI_2]CI_2 (1a), [Pd((Cy_2PO)C_7H_{14}N_2CI)_2CI_2]CI_2 (2a), [Pt((Ph_2PO)C_7H_{14}N_2CI)_2CI_2]CI_2 (1b) and [Pt((Cy_2PO)C_7H_{14}N_2CI)_2CI_2]CI_2 (2b). (i) 1 equiv. Ph_2PCI or Cy_2PCI, 1 equiv.$ *n* $-BuLi, CH_2CI_2; (ii) 0.5 equiv. [M(cod)CI_2] (M = Pd, Pt), CH_2CI_2.$

The coordination chemistry of ligands 1 and 2 was studied by forming their palladium and platinum complexes. Reaction of 1 or 2 with [Pd(cod)Cl₂] gives the corresponding Pd(II) complexes 1a and 2a in high yields (*ca* 80%). In the ³¹P-(¹H} NMR spectra, each of 1a and 2a gives one signal at 107.20 and 132.48 ppm, respectively, which are within the expected range of other reported structurally similar complexes (Fig. S1).^[22,38,39] Typical spectra of these complexes are illustrated in the supporting information. Both of the isolated dichloropalladium(II) complexes 1a and 2a are found

to have the *cis* configuration, characteristic of phosphinites having mutual *cis* arrangement.^[41–43] The ¹³C-{¹H} NMR spectra display well-resolved signals for the phenyls and cyclohexyl carbons, respectively.^[44] Furthermore, the ¹H NMR spectral data of complexes **1a** and **2a** are consistent with the proposed structures, and the compositions of the two complexes have been further confirmed by elemental analysis and IR spectroscopy, and found to be in good agreement with the theoretical data. Other pertinent spectroscopic and analytic data are given in the experimental section.

Based on the above information, we also examined the coordination chemistry of **1** and **2** with $[Pt(cod)Cl_2]$ precursor. The reaction of $[Pt(cod)Cl_2]$ with two equivalents of **1** or **2** leads to the formation of complexes **1b** and **2b**, respectively, in high yields as the main products. In both complexes, the phosphinites bind the metal centre as monodentate ligand. The formation of compounds **1b** and **2b** was followed by monitoring the ${}^{31}P{}{}^{1}H$ NMR spectra, which show single resonances at

77.12 and 97.24 ppm, respectively, consistent with structures of the anticipated complexes (supporting information).^[45] The complexes **1b** and **2b** exhibit large ${}^{1}J_{PtP}$ coupling of 4273.6 and 4082.4 Hz, respectively, which are characteristic of phosphinites having mutual *cis* arrangement (Fig. S2).^[46–48] ¹H NMR spectral data of **1b** and **2b** are consistent with the proposed structures. Furthermore, in the ${}^{13}C{}^{1}H$ NMR spectra of **1b** and **2b**, $J({}^{31}P{}^{-13}C)$ coupling constants are measured for the carbons of the phenyl rings and cyclohexyl moiety, and they are consistent with the literature values.^[49,50] The structural compositions of complexes **1b** and **2b**

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(II)–phosphinite catalysts 1a and 2a										
Entry	Catalyst	Time (min)	Solvent	Base	Temperature (°C)	Atmosphere	Conversion (%)	Yield (%)	TOF (h^{-1})	
1	1a	30	Dioxane	K_2CO_3	100	Ar	98	97	1 940	
2	2a	45	Dioxane	K_2CO_3	100	Ar	99	98	1 307	
3	1a	30	Dioxane	K_2CO_3	100	Air	100	97	1 940	
4	2a	45	Dioxane	K_2CO_3	100	Air	98	97	1 293	
5	1a	60	DMF	K_2CO_3	110	Ar	99	99	990	
6	2a	180	DMF	K_2CO_3	110	Ar	97	95	317	
7	1a	60	DMF	K_2CO_3	110	Air	99	99	990	
8	2a	180	DMF	K_2CO_3	110	Air	98	96	320	
9	1a	1	DMF-H ₂ O (1/4)	K_2CO_3	110	Ar	99	96	57 600	
10	2a	3	DMF-H ₂ O (1/4)	K_2CO_3	110	Ar	100	98	19 600	
11	1a	1	DMF-H ₂ O (1/4)	K_2CO_3	110	Air	98	96	57 600	
12	2a	3	DMF-H ₂ O (1/4)	K_2CO_3	110	Air	100	98	19 600	
13	1a	60	DMF-H ₂ O (1/4)	K_2CO_3	25	Air	99	98	980	
14	2a	120	DMF-H ₂ O (1/4)	K_2CO_3	25	Air	99	98	490	
15	1a	1	H ₂ O	K_2CO_3	100	Ar	98	96	57 600	
16	2a	3	H ₂ O	K_2CO_3	100	Ar	97	95	19 000	
17	1a	1	H ₂ O	K_2CO_3	100	Air	98	96	57 600	
18	2a	3	H ₂ O	K_2CO_3	100	Air	99	97	19 400	
19	1a	60	H ₂ O	K_2CO_3	25	Air	99	96	960	
20	2a	180	H ₂ O	K_2CO_3	25	Air	99	97	323	

Reaction conditions: 1.0 mmol of p-CH₃C(O)C₆H₄Br aryl bromide, 1.5 mmol of phenylboronic acid, 2.0 mmol K₂CO₃, 0.001 mmol catalyst, solvent (3.0 ml). Purity of compounds was checked by ¹H NMR and yields are based on aryl bromide. All reactions were monitored using GC for **1a** and **2a**. TOF = (mol product/mol catalyst) × h⁻¹.

were further confirmed from IR spectroscopy and microanalysis, and found to be in good agreement with the theoretical data.

Suzuki-Miyaura and Mizoroki-Heck Coupling Reactions

In a pilot study to investigate the catalytic activity of palladium complexes based on ionic liquid phosphinite ligands, we initially tested the Suzuki cross-coupling reaction between aryl bromides and boronic acid.^[51] The control experiments show that the coupling reaction does not occur in the absence of the catalyst. The reaction parameters for the Suzuki cross-coupling reaction were optimized through a series of experiments. The influences of temperature, base, solvent and atmosphere were systematically studied using the coupling of *p*-bromoacetobenzene and phenylboronic acid as probe reaction. Furthermore, a change of the reaction atmosphere from an inert gas to ambient atmosphere has no negative influence on the activity of the catalysts (Table 1, entries 3, 4, 7, 8, 11, 12, 17, 18). Therefore, the coupling reactions were performed in air. Optimization studies were conducted to determine how solvent and temperature affect the coupling reaction. As demonstrated in Table 1, the best catalytic activities are not obtained until the Suzuki reaction is carried out at 100 °C in aqueous medium and DMF-H₂O (1:4) (Table 1, entries 9-20). We also find that, under identical conditions, the coupled product is obtained in higher yield at elevated temperature and the reaction occurs at room temperature (Table 1, entries 13, 14, 19 and 20). From Table 1, it can be seen that the efficiency of complexes is different from each other. For example, the Suzuki reaction with catalyst 1a always shows higher catalytic activity than that with catalyst 2a. One can also see from Table 1 that for a typical reaction of p-bromoacetobenzene and phenylboronic acid, the reaction rate is dependent on the alkyl substituents on the phosphorus atom.

In conclusion, results of the optimization studies demonstrate obviously that complex **1a** including phenyl (Ph) moieties on the phosphorus atoms is a more active and efficient catalyst leading to nearly quantitative conversions.

Encouraged by the activities obtained in these preliminary studies, optimization studies were also conducted to determine how bases affect the coupling reaction. As illustrated in Table 2, initial studies were performed using different bases (Cs₂CO₃, KOH, NaOH and KO^tBu) together with K₂CO₃ in order to optimize the reaction conditions for the coupling of p-bromoacetophenone with phenylboronic acid in the presence of complexes 1a and 2a (0.001 mmol Pd catalyst) under aerobic conditions. As evident from Table 2, the best turnover frequency (TOF) is obtained in the Suzuki reaction carried out at 100 °C, implying that K₂CO₃ as the base is the best choice for the cross-coupling reactions and other bases such as Cs₂CO₃, KOH, NaOH and K^tOBu are slightly less effective. In addition, the effect of base-to-substrate mole ratio on the coupling reaction was also investigated. Using K₂CO₃ at a base-to-substrate mole ratio of 2:1 affords the highest TOF value, while the TOF value is lower at a mole ratio of 1:1. However, increasing the base-tosubstrate mole ratio does not increase the conversion rate (Table 2, entries 11-13). The reproducibility of each catalytic reaction was confirmed by carrying out the catalytic reaction at least three times.

With the best conditions at hand, we also carried out further experiments to investigate the scope of Suzuki cross-coupling using catalysts **1a** and **2a** with various substrates, including aryl bromides, chlorides and iodides having electron-withdrawing or electron-donating substituents (Table 3, entries 1–12). Aryl iodides react with phenylboronic acid in a markedly short time of approximately 15 s and the yields of the corresponding products are very satisfactory (Table 3, entries 1–4). Encouraged by these results, we studied the reactivity between substituted aryl bromides and phenylboronic

Table 2. Suzuki coupling reactions of p-acetobromobenzene with phenylboronic acid catalysed by the palladium(II)-phosphinite catalysts 1a and 2a based on ionic liquid											
+ Br - R - Cat. (0.01 mmol) Base (2 equiv.)											
Entry	Catalyst	Time (min)	Solvent	Base	Temperature (°C)	Atmosphere	Conversion (%)	Yield (%)	TOF (h^{-1})		
1	1a	1	H ₂ O	Cs ₂ CO ₃	100	Air	95	92	55 200		
2	2a	3	H ₂ O	Cs ₂ CO ₃	100	Air	96	92	18 400		
3	1a	1	H_2O	K_2CO_3	100	Air	98	96	57 600		
4	2a	3	H_2O	K_2CO_3	100	Air	99	97	19 400		
5	1a	3	H ₂ O	NaOH	100	Air	98	97	19 400		
6	2a	8	H ₂ O	NaOH	100	Air	99	98	7 350		
7	1a	2	H_2O	KOH	100	Air	99	97	29 100		
8	2a	5	H ₂ O	KOH	100	Air	97	95	11 400		
9	1a	2	H ₂ O	K ^t OBu	100	Air	98	95	28 500		
10	2a	5	H ₂ O	K ^t OBu	100	Air	99	96	11 520		
11 ^a	1a	1	H_2O	K ₂ CO ₃	100	Air	85	81	48 600		
12 ^b	1a	1	H_2O	K_2CO_3	100	Air	98	96	57 600		
13 ^c	1a	1	H_2O	K_2CO_3	100	Air	76	72	43 200		
Reaction conditions: 1.0 mmol of aryl bromide, 1.5 mmol of phenylboronic acid, 2.0 mmol base, 0.001 mmol catalyst, water (3.0 ml) Purity of compounds was checked by ¹ H NMR and yields are based on anyl bromide. All reactions were monitored											

using GC for **1a** and **2a**. TOF = (mol product/mol catalyst) \times h⁻¹.

^aBase-to-substrate mole ratio = 1:1.

^bBase-to-substrate mole ratio = 2:1.

^cBase-to-substrate mole ratio = 5:1.

$-B(OH)_2 + X \longrightarrow -R \xrightarrow{\text{Cat.} (0.001 \text{ minol})} K_2CO_3 (2 \text{ equiv.})$
--

Entry	Х	R	Catalyst	Time (min)	Conversion (%)	Yield (%)	TOF (h^{-1})
1	I	Н	1a	0.25	98	96	230 400
2	I	Н	2a	0.75	97	95	76 000
3	I	C(O)CH ₃	1a	0.25	99	97	232 800
4	I	C(O)CH ₃	2a	0.75	99	97	77 600
5	Br	C(O)H	1a	0.5	98	96	115 200
6	Br	C(O)H	2a	2	95	92	27 600
7	Br	Н	1a	2	98	97	29 100
8	Br	Н	2a	5	97	96	11 520
9	Br	OCH ₃	1a	4	98	96	14 400
10	Br	OCH ₃	2a	7	100	96	8 229
11	Br	CH₃	1a	5	100	99	11 880
12	Br	CH ₃	2a	9	99	97	6 467

Reaction conditions: 1.0 mmol of p-RC₆H₄X aryl halogens, 1.5 mmol of phenylboronic acid, 2.0 mmol K₂CO₃, 0.001 mmol catalyst (**1a** or **2a**), water (3.0 ml). Purity of compounds was checked by ¹H NMR and yields are based on aryl halide. All reactions were monitored using GC; 100 °C. TOF = (mol product/mol catalyst) × h⁻¹.

acid. Compared to aryl iodides, the reaction takes longer (Table 3); therefore we can easily conclude that the electronic nature of the aryl bromides has a clear effect on the coupling reactions (Table 3, entries 5–12). For example, the coupling reaction of electron-rich 4-bromotoluene with phenylboronic acid has a TOF value of 11 880 h⁻¹, but for electron-deficient 4-bromobenzaldehyde, the desired coupled product is obtained with a TOF value of 115 200 h⁻¹. After obtaining such an outstanding activity in Suzuki coupling reactions of *p*-iodoacetophenone or iodobenzene with phenylboronic acid catalysed by complexes **1a** and **2a** in water, we studied the catalytic activity of complexes in the Suzuki coupling reactions of aryl chlorides with phenylboronic acid in water. However, the highest conversion reached is 63% in the presence of K₂CO₃ within 30 min in water at 100 °C and a longer reaction time

does not give any further conversion. It is well known that chlorides are generally less reactive towards Suzuki coupling reactions under the same conditions used for the coupling of bromides and iodides. The low reactivity of chlorides is usually attributed to the strength of the C–Cl bond (bond dissociation energies (kcal mol⁻¹): Ph–Cl, 96; Ph–Br, 81; Ph–I, 65), which leads to aryl chlorides being reluctant in adding oxidatively to Pd(0) centres, a critical initial step in Pd-catalysed coupling reactions.^[52,53] In addition, because of the strength of the Pt–C bonds, Pt(II)–phosphinite systems exhibit no catalytic activity in the Suzuki–Miyaura cross-coupling reaction.^[54]

Encouraged by the outstanding catalytic activities obtained in the Suzuki–Miyaura cross-coupling reaction, we next extended our investigations to the Mizoroki–Heck reaction. The results are

Table 4. Heck coupling reactions of <i>p</i> -bromoacetophenone with styrene catalysed by palladium(II)-phosphinite catalysts 1a and 2a										
$H = \begin{pmatrix} 0 \\ -C \\ $										
Entry	Catalyst	Time (h)	Solvent	Base	Temperature (°C)	Atmosphere	Conversion (%)	Yield (%)	TOF (h^{-1})	
1	1a	2	DMF	K ₂ CO ₃	120	Ar	98	97	49	
2	2a	2	DMF	K ₂ CO ₃	120	Ar	99	96	48	
3	1a	2	DMF	K ₂ CO ₃	120	Air	99	97	49	
4	2a	2	DMF	K ₂ CO ₃	120	Air	98	96	48	
5	1a	8	DMF	Cs ₂ CO ₃	120	Ar	97	95	12	
6	2a	8	DMF	Cs ₂ CO ₃	120	Ar	99	96	12	
7	1a	8	DMF	Cs ₂ CO ₃	120	Air	99	97	12	
8	2a	8	DMF	Cs ₂ CO ₃	120	Air	98	95	12	

Reaction conditions: 1.0 mmol of p-CH₃C(O)C₆H₄Br aryl bromide, 1.5 mmol of styrene, 2.0 mmol base, 0.01 mmol catalyst, DMF (3.0 ml). Purity of compounds was checked by ¹H NMR and yields are based on aryl bromide. All reactions were monitored using GC for **1a** and **2a**. TOF = (mol product/mol catalyst) × h⁻¹.



Reaction conditions: 1.0 mmol of p-RC₆H₄Br aryl bromide, 1.5 mmol of styrene, 2.0 mmol K₂CO₃, 0.01 mmol catalyst (**1a** or **2a**), DMF (3.0 ml). Purity of compounds was checked by ¹H NMR and yields are based on aryl bromide. All reactions were monitored using GC; 120 °C for **1a** and **2a**. TOF = (mol product/mol catalyst) × h⁻¹.

summarized in Tables 4 and 5. It is well known that among the different methods used to form carbon-carbon bonds, palladiumcatalysed carbon-carbon bond formation between aryl halides and olefins has become an excellent tool for the synthesis of elaborate styrene derivatives.^[55,56] Furthermore, the palladium-catalysed arylation or vinylation of olefins, universally referred to as the Heck reaction, has received increasing attention in the last decade, as it is a selective method to form new carbon-carbon bonds in a single operational step.^[57,58] The reaction is appealing because of its tolerance of nearly any solvent and functional group on the substrates, its high selectivity and its moderate toxicity.^[59,60] It is a powerful and versatile method for the synthesis of polyfunctional compounds, e.g. dienes, cinnamic esters and other variously substituted olefinic compounds, which are primarily applied as dyes and UV absorbers, and as intermediates for pharmaceuticals, agrochemicals and fragrances.^[61,62]

The rate of coupling in the Heck reaction is dependent on a variety of parameters such as temperature, solvent, base and catalyst loading. Generally, the Heck reaction requires high temperatures (higher than 100 °C) and polar solvents. For the choice of base, we investigated Cs₂CO₃ and K₂CO₃ which are expected to be the best bases for this reaction. Furthermore, a change in the reaction atmosphere from an inert gas to ambient atmosphere has no negative influence on the activity of the catalysts (Table 4, entries 3, 4, 7, 8). Therefore, the coupling reactions were performed in air. Finally, from the optimization studies, we see that use of 1.0 mmol%, 2 equivalents of K₂CO₃ in DMF at 120°C for 1a and 2a leads to the best conversions with the highest TOF values. We firstly investigated the catalytic activities of 1a and 2a for the coupling of *p*-bromoacetophenone with styrene (Table 4). A control experiment indicates that the coupling reaction does not happen in the absence of 1a or 2a. Under the determined reaction conditions, a wide range of aryl bromides bearing electron-donating and electron-withdrawing groups react with styrene, affording the coupled products in moderate to good yields. As expected, electron-deficient bromides are beneficial for the conversions (Table 5). Using any chlorides instead of aryl bromides yields only small amounts of stilbene derivatives under the conditions employed for bromides.

Conclusions

This report describes for the first time the preparation and characterization of new Pd(II) and Pt(II) complexes based on ionic liquid phosphinite ligands and an investigation of their use as pre-catalysts in the Suzuki coupling and Heck reactions of aryl halides. Only the palladium complexes were found to show outstanding catalytic activity in the Suzuki coupling reactions of aryl bromides in aqueous medium. Contrary to expectation, these catalysts are not very active for the Heck reaction. But, among the reported similar palladium catalysts in homogeneous systems, the Pd(II) complexes based on ionic liquid phosphinite ligands provide record catalytic activity in the Suzuki-Miyaura coupling reaction of p-bromoacetophenone with phenylboronic acid. In addition, a change in the reaction atmosphere from an inert gas to ambient atmosphere had no negative influence on the activity of the catalysts. In both cases, the catalytic activities of these complexes were found to be higher in reactions of aryl bromides with electronwithdrawing substituents than with electron-releasing substituents. The outstanding catalytic activity and facile preparation of these catalysts raise the prospect of using this type of simply prepared material for Suzuki-Miyaura cross-coupling reactions in industrial applications as well as in small-scale organic synthesis.

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