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Iron(0), rhodium(I) and palladium(II) complexes with *p*-(*N*,*N*-dimethylaminophenyl) diphenylphosphine and the application of the palladium complex as a catalyst for the Suzuki–Miyaura cross-coupling reaction

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The reaction of *p*-(*N*,*N*-dimethylaminophenyl)diphenylphosphine [$PPh_2(p\text{-}C_6H_4NMe_2)$] with [$Fe_3(CO)_{12}$], [$Rh(CO)_2Cl]_2$ and $PdCl_2$ resulted in three new mononuclear complexes, {$Fe(CO)_4[\eta^1\text{-(P)-}PPh_2(p\text{-}C_6H_4NMe_2)]$} (1a), *trans*-{$Rh(CO)Cl[\eta^1\text{-(P)-}PPh_2(p\text{-}C_6H_4NMe_2)]_2$} (2) and *trans*-{$PdCl_2[\eta^1\text{-(P)-}PPh_2(p\text{-}C_6H_4NMe_2)]_2$} (3), respectively. A small amount of dinuclear nonmetal-metal bonded complex, {$Fe_2(CO)_8[\mu\text{-(P,N)-}PPh_2(p\text{-}C_6H_4NMe_2)]$} (1b), was also isolated as a side product in the reaction of [$Fe_3(CO)_{12}$]. The complexes were characterized by elemental analyses, mass, IR, UV–vis, ^1H, ^{13}C (except 1b) and $^{31}P\{^1H\}$ NMR spectroscopy. The Pd complex 3 effectively catalyzes the Suzuki–Miyaura cross-coupling reactions of aryl halides with arylboronic acids in water–isopropanol (1 : 1) at room temperature. Excellent yields (up to 99% isolated yield) were achieved. The effects of different solvents, bases, catalyst quantities were also evaluated.

Keywords: aminophosphine ligand; metal complex; Suzuki-Miyaura reaction; aqueous solvent; room temperature

Introduction

During the last two decades, transition metal complexes bearing phosphorous and nitrogen donor atoms occupying the same ligand framework have received tremendous interest because of their structural diversity, unusual reactivity and catalytic applications.[1,2] Previous studies have demonstrated that metal complexes containing such ligands can be exploited as catalysts for a number of reactions, including rhodium-catalyzed hydrogenation and hydroformylation reactions,[3–5] palladium-catalyzed cross-coupling reactions[6–10] and iron-catalyzed polymerization reactions.[11,12] It is now well established that the ligand backbones play a dominant role in the performance of such phosphine-based catalysts. Until now, the major focus has been given to P,N donor ligands that have flexible backbone unit, because the metal complexes with such ligands often exhibit hemilabile behavior, i.e. reversible decoordination and coordination of the weakly bonded atom.[2,13,14] On the other hand, ligands possessing rigid and robust backbones have received relatively less attention. *p*-(*N*,*N*-Dimethylaminophenyl)diphenylphosphine [$PPh_2(p\text{-}C_6H_4NMe_2)$], is one of the least studied rigid backbone P,N-based phosphine ligand. A literature survey revealed only a few complexes with this ligand, e.g. iron,[15] cyclometallated palladium,[16,17] rhodium,[18] copper[19] and tungsten complexes.[20] Thus, in order to extend the scope of this ligand further, we report here the synthesis and characterization of Fe(0), Rh(I) and Pd(II) complexes with $PPh_2(p\text{-}C_6H_4NMe_2)$.

Palladium-catalyzed Suzuki–Miyaura cross-coupling reactions, involving aryl halides with arylboronic acids in the presence of a base, have emerged as one of the most versatile methods for the formation of C–C bonds.[21] For many years, phosphines have been the most commonly employed ligands for this reaction. Some of the most influential phosphine-based ligands used in Suzuki–Miyaura reactions are simple tertiary,[22,23] hemilabile-type,[24–26] sterically crowded biphenyl-type[27,28] and other electron-rich phosphines.[29,30] In fact, there exist two reports in which P,N-based ligands containing a *p*-phenyl backbone resulted in dramatic performances in cross-coupling reactions.[31,32] Thus, as part of our ongoing research into Suzuki–Miyaura reactions,[33,34] we explored the catalytic potential of the palladium–phosphine complex **3** for the Suzuki–Miyaura reaction of aryl halides with arylboronic acids. The effects of different solvents, bases and catalyst quantities were also evaluated.

Experimental Section

General Information

The starting complex [$Fe_3(CO)_{12}$] was purchased from Acros Chemicals. [$Rh(CO)_2Cl]_2$ and the ligand, *p*-(*N*,*N*-dimethylaminophenyl)diphenylphosphine [$PPh_2(p\text{-}C_6H_4NMe_2)$], were purchased from Aldrich. $PdCl_2$ and other necessary chemicals were purchased from Rankem, India. The solvents used were of analytical grade and distilled prior to utilization. Elemental analyses were recorded by using an Elementar Vario EL III Carlo Erba 1108.

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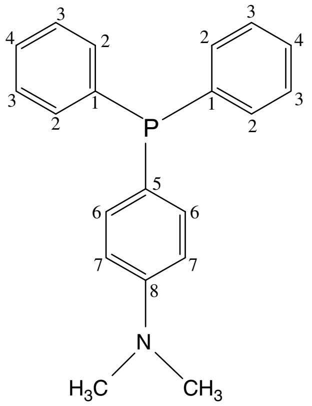


Scheme 1. Numbering of atom positions in phenyl rings.

IR spectra were recorded in KBr using a Shimadzu IR prestige-21 FTIR spectrophotometer in the range 4000–250 cm^{-1}. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded in $CDCl_3$ operating at 300.13 and 121.50 MHz, respectively, on a Bruker 300 MHz spectrometer. The ^{13}C NMR spectra were recorded on a Jeol JNM-ECS 400 MHz spectrometer operating at 100.52 MHz. The ^1H and ^{13}C NMR assignments were made with respect to the labeling chart (Scheme 1). The UV–vis spectra of the complexes were recorded on a Shimadzu UV 1700. The FAB mass spectra were recorded on a Jeol SX 102/DA-6000 mass spectrometer using argon/xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature. The electrospray mass spectra were recorded on a Thermo Finnigan LCQ Advantage max ion trap mass spectrometer. The ion spray voltage was set at 5.3 kV and the capillary voltage was 34 V.

Synthesis of $\{Fe(CO)_4[\eta^1\text{-}(P)\text{-}PPh_2(p\text{-}C_6H_4NMe_2)]\}$ (1a) and $\{Fe_2(CO)_8[\mu\text{-}(P,N)\text{-}PPh_2(p\text{-}C_6H_4NMe_2)]\}$ (1b)

To a tetrahydrofuran solution of $[Fe_3(CO)_{12}]$ (302 mg; 0.60 mmol), $PPh_2(p\text{-}C_6H_4NMe_2)$ (366 mg; 1.2 mmol) was added. The reaction mixture was refluxed under nitrogen for 3 h, during which time the color of the solution changed from green to dark brown. After cooling, the reaction mixture was filtered and the solvent was removed under reduced pressure to afford a dark brown solid. The residue was dissolved in minimum amount of CH_2Cl_2 and then chromatographed on a silica gel column. Elution of hexane–CH_2Cl_2 (80 : 20) gave complex **1a** as a dark brown solid and **1b** as a yellow solid.

*Complex **1a***

Yield: 52%. Anal. calcd for $C_{24}H_{20}NO_4PFe$: C, 60.89% (60.91); H, 4.23%; N, 2.96%. Found: C, 60.16%; H, 4.21%; N, 2.93%. MS-ESI $m/z = 474$ $[M + 1]^+$, 445 $[M - CO]^+$; 418 $[M - 2CO + 1]^+$; 306 $[PPh_2(p\text{-}C_6H_4NMe_2) + 1]^+$. IR (KBr): 2044(s), 1971(s), 1930(s) cm^{-1}, ν(CO). UV–vis ($CHCl_3$): λ_{max}(nm), 290, 243. ^1H NMR (δ ppm): 7.42–7.67 (m, 12H, Ph, $H^{2,3,4,6}$), 6.71–6.69 (m,2H,Ph,H^7), 3.02 (s,6H,CH_3). ^{13}C NMR (δ ppm): 213.85 (CO), 151.68 (C^8), 135.02 (C^1), 133.03 (C^6), 132.93 (C^2), 130.51 (C^4), 128.56 (C^3), 128.46 (C^5), 111.42 (C^7), 40.31 (CH_3); $^{31}P\{^1H\}$ NMR (δ ppm): 46.05(s).

*Complex **1b***

Yield: 12%. Anal. calcd for $C_{28}H_{20}O_8NPFe_2$: C, 52.41%; H, 3.12%; N, 2.18%. Found: C, 51.91%; H, 3.10%; N, 2.21%. MS-ESI $m/z = 643$ $[M + 2]^+$, 627 $[M - CH_3 - 1]^+$; 474 $[M - Fe(CO)_4 + 1]^+$; 306 $[PPh_2(p\text{-}C_6H_4NMe_2) + 1]^+$. IR (KBr): 2040 (s), 1959 (w), 1930 (m), 1926 (w) cm^{-1}, ν(CO). UV–vis ($CHCl_3$): λ_{max}(nm): 292, 244. ^1H NMR (δ ppm): 7.27–7.67 (m, 12H, Ph, $H^{2,3,4,6}$), 6.71–6.69 (m, 2H, Ph, H^7), 4.13 (s, 6H, CH_3). $^{31}P\{^1H\}$ NMR (δ ppm): 68.18(s).

Synthesis of $\{Rh(CO)Cl[\eta^1\text{-}(P)\text{-}PPh_2(p\text{-}C_6H_4NMe_2)]_2\}$ (2)

A solution of the $PPh_2(p\text{-}C_6H_4NMe_2)$ ligand (251 mg; 0.824 mmol) in 30 ml of CH_2Cl_2 was added dropwise to a solution of $[Rh(CO)_2Cl]_2$ (160 mg; 0.412 mmol) in 45 ml of CH_2Cl_2 for about 10 min. The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 1 h. The color of the solution changed from yellow to dark brown. The solvent was evaporated partially in open atmosphere and, on treatment with 10 ml of hexane, complex **2** was precipitated as a bright yellow solid which was washed with hexane and dried *in vacuo*. Yield: 96%. Anal. calcd for $C_{41}H_{40}N_2OP_2ClRh$; C, 63.38%; H, 5.15%; N, 3.60%. Found: C, 62.78%; H, 5.12%; N, 3.57%. MS-FAB $m/z = 775$ $[M - 2]^+$, 741 $[M - Cl - 1]^+$; 712 $[M - Cl - CO - 2]^+$; 304 $[PPh_2(p\text{-}C_6H_4NMe_2) - 1]^+$. IR (KBr): 1975 cm^{-1} ν(CO). UV–vis (CH_2Cl_2): λ_{max} (nm), 285. ^1H NMR (δ ppm): 7.64–7.70 (m, 8H, Ph, H^3), 7.38–7.50 (m, 16H, Ph, $H^{2,4,6}$), 6.68–6.72 (m, 4H, Ph, H^7), 2.98 (s, 12H, CH_3). ^{13}C NMR (δ ppm): 184.21 (CO), 153.48 (C^8), 136.93 (C^1), 133.13 ($C^{2,6}$), 131.88 (C^4), 131.79 (C^3), 128.33 (C^5),111.67 (C^7), 39.56 (CH_3). $^{31}P\{^1H\}$NMR (δ ppm): 42.83 (d, $J_{Rh-P} = 178$ Hz).

Synthesis of the Complex $\{PdCl_2\text{-}[\eta^1\text{-}(P)\text{-}PPh_2(p\text{-}C_6H_4NMe_2)]_2\}$ (3)

A solution of the ligand $PPh_2(p\text{-}C_6H_4NMe_2)$ (345 mg; 1.13 mmol) in 20 ml acetonitrile was added dropwise to a solution of $PdCl_2$ (100 mg; 0.56 mmol) in 10 ml of acetonitrile. The resultant solution was refluxed under an N_2 atmosphere for 3 h. A yellow-colored compound was precipitated. After filtration and washing the residue with acetonitrile, complex **3** was isolated as a bright yellow solid. Yield: 86%. Anal. calcd for $C_{40}H_{40}Cl_2N_2P_2Pd$: C, 60.97; H, 5.11; N, 3.55. Found: C, 59.87; H, 5.09; N, 3.53. MS-ESI $m/z = 665$ $[M - C_6H_4NMe_2]^+$, 484 $[M - \{PPh_2(p\text{-}C_6H_4NMe_2)\} + 1]^+$, 448 $[M - Cl - [PPh_2(p\text{-}C_6H_4NMe_2)] + 1]^+$; 306 $[PPh_2(p\text{-}C_6H_4NMe_2) + 1]^+$. IR (KBr): 433 cm^{-1}, ν(Pd–P); 358 cm^{-1}, ν(Pd–Cl). ^1H NMR (δ ppm): 7.60–7.67 (m, 8H, Ph, H^3), 7.21–7.41 (m, 16H, $H^{2,4,6}$), 6.67–6.69 (m, 4H, H^7), 2.98 (s, 12H, CH_3). ^{13}C NMR (δ ppm): 151.28 (C^8), 136.73 (C^1) 134.56 (C^6), 134.01 (C^2), 129.93 (C^4), 129.63(C^3), 127.69(C^5), 111.23(C^7), 40.03 (CH_3). $^{31}P\{^1H\}$: 22.12 (s); UV-vis ($CHCl_3$): λ_{max} (nm), 334, 400.

General Information about Catalytic Experiments

The Suzuki–Miyaura cross-coupling reactions were carried out under aerobic conditions. The progress of the reactions was monitored by thin-layer chromatography using aluminum-coated TLC plates (Merck) under UV light. The products were purified by column chromatographic technique using silica gel (60–120 mesh). The various products separated were characterized by melting point, mass spectroscopy and ^1H NMR spectroscopy, and compared with the authentic samples. Mass spectra of the compounds were recorded in on a Jeol GCmate instrument in EI^+ mode. The melting points were determined using Buchi B450 melting point apparatus.

General Procedure for the Suzuki–Miyaura Reactions of Aryl Halides using Complex 3 as Catalyst

A 50 ml round-bottomed flask was charged with a mixture of aryl halide (1 mmol), arylboronic acid (1.1 mmol), K_2CO_3 (3 mmol), complex **3** (appropriate quantity) and solvent (6 ml). The mixture was stirred at room temperature for the required time. After completion, the mixture was diluted with water (20 ml) and extracted with ether (3 × 20 ml). The combined extract was washed with brine (3 × 20 ml) and dried over Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel, ethyl acetate–hexane, 1 : 9) to obtain the desired products.

Results and Discussion

Synthesis and Characterization of {$Fe(CO)_4[\eta^1$-(P)-$PPh_2(p$-$C_6H_4NMe_2)]$} (1a) and {$Fe_2(CO)_8[\mu$-(P,N)-$PPh_2(p$-$C_6H_4NMe_2)]$} (1b)

The reaction of $[Fe_3(CO)_{12}]$ with phosphine-based ligands to synthesize mono- and binuclear complexes is well established but, in the majority of cases, addition of a decarbonylating agent such as trimethylamine N-oxide is required.[35] In this work, we have found that the reaction of $[Fe_3(CO)_{12}]$ with *p*-(*N*,*N*-dimethylaminophenyl)diphenylphosphine [$PPh_2(p$-$C_6H_4NMe_2)$] in refluxing THF proceeded without the addition of a decarbonylating agent to produce a mononuclear complex, {$Fe(CO)_4[\eta^1$-P-$PPh_2(p$-$C_6H_4NMe_2)]$} (**1a**) as the major product along with a small amount of nonmetal–metal bonded binuclear complex, {$Fe_2(CO)_8[\mu$-P,N-$PPh_2(p$-$C_6H_4NMe_2)]$} (**1b**) as a minor product (Scheme 2). The yields of the complexes were 52 and 12% respectively. The elemental analyses and ESI-mass spectra of the complexes were in excellent agreement with the proposed compositions. For example, the ESI-mass spectrum of complex **1a** showed a high-intensity molecular ion peak at $m/z = 474$ (100%) along with two fragment ion peaks at $m/z = 445$ and 418, corresponding to the sequential loss of two CO ligands. The IR spectra of **1a** in KBr exhibited three distinct terminal ν(CO) bands at 2044s, 1971s and 1930s cm^{-1}; this pattern is consistent with the other reported tetracarbonyl iron complexes.[36,37] The number and intensities of CO stretching frequencies are often used to draw conclusions about axial and equatorial arrangement of ligands in complexes of the type $Fe(CO)_4$(phosphine).[36,38] Thus, based on the ν(CO) values of some reported $Fe(CO)_4$(phosphine)-type complexes,[36,38–40] we propose that the phosphine ligand in complex **1a** is axially located. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at δ 46.05 ppm. Compared with the free ligand (δ −6.0 ppm), complex **1a** shows a downfield shift of about 52 ppm indicates coordination of the aminophosphine ligand through the phosphorus atom. The ^1H NMR spectra of the complex shows, in addition to the aromatic proton, a strong singlet at δ 3.02 ppm, which is almost the same as that of the free ligand, indicating that the amine group is not involved in coordination. The ^{13}C NMR spectra of the complex **1a** shows aromatic resonances in the range δ 111–152 ppm, carbonyl resonance at δ 213.85 ppm and methyl resonance at δ 40.31 ppm The ESI-mass spectrum of complex **1b** shows a very strong molecular ion peak at $m/z = 643$ (100%). The infra-red spectra of the complex **1b** show four terminal ν(CO) bands in the range 2040–1926 cm^{-1}, which is in good agreement with the infra-red data of the previously reported nonmetal–metal bonded $[Fe_2(CO)_8(\mu$-phosphine)].[41,42] The absence of any band in the range 1850–1700 cm^{-1} suggests the absence of any bridging carbonyl group in **1b.** The ^1H NMR data clearly show the coordination of the ligand through the N-atom, as the methyl proton has shifted significantly downfield compared with the free ligand or η^1-(P)-coordinated complex **1a**. Compared with the complex **1a**, the $^{31}P\{^1H\}$ NMR of complex **1b** shows a downfield shift of about 22 ppm, indicating bidentate nature of the ligand in complex **1b**.

Synthesis and Characterization of {$Rh(CO)Cl[\eta^1$-(P)-$PPh_2(p$-$C_6H_4NMe_2)]_2$} (2)

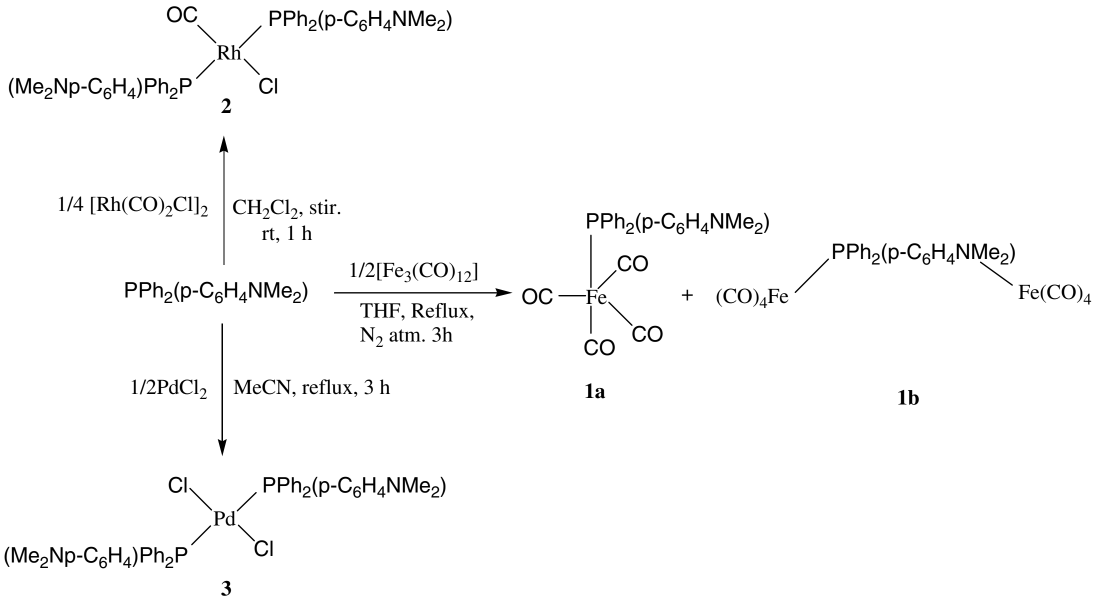
The chlorobridged dimer, $[Rh(CO)_2Cl]_2$, undergoes a bridge splitting reaction with four molar equivalents of the aminophosphine ligand, $PPh_2(p$-$C_6H_4NMe_2)$ in CH_2Cl_2 to yield monocarbonyl complex {$Rh(CO)Cl[\eta^1$-(P)-$PPh_2(p$-$C_6H_4NMe_2)]_2$} (**2**) (Scheme 2), in which the two aminophosphine ligands are bonded to rhodium center through phosphorous atoms. Elemental analyses and FAB-mass spectra of the complex **2** are consistent with the above formulation. In the mass spectra, complex **2** shows a low-intensity molecular ion peak at $m/z = 775$ along with a moderate intense peak due to M − Cl. The base peak appears at $m/z = 714$ (100%), which corresponds to the $[Rh(PPh_2(p$-$C_6H_4NMe_2)_2]^+$ fragment, formed by the removal of CO and Cl^- ion from the complex. The IR spectrum of complex **2** in KBr shows one strong terminal ν(CO) band at 1975 cm^{-1}, consistent with square planar Rh(I) carbonyl complex. The ^{31}P NMR spectra of the complex show one doublet at δ 42.83 ppm ($J_{RhP} = 178$ Hz). Theoretically there are two possibilities that the two phosphorus atoms occupy either the mutual *trans* or *cis* position. However, the presence of a single ^{31}P NMR signal and the high J_{RhP} value indicate two phosphorous atoms occupying a mutual *trans* position.[43,44] The ^1H NMR spectra of the complex **2** shows the aromatic protons as multiplets in the range δ 6.58–7.70 ppm. The methyl proton appears at δ 2.98 ppm, which is almost same as the free ligand, indicating that the NMe_2 group does not take part in bonding. The ^{13}C NMR spectra show carbonyl resonance at δ 184.21 ppm, methyl resonance at δ 39.56 ppm and aromatic carbon resonances in the range 111–154 ppm.

Synthesis and Characterization of {$PdCl_2$-$[\eta^1$-(P)-PPh_2(p-$C_6H_4NMe_2)]_2$} (3)

Treatment of $PdCl_2$ with two equivalents of the ligand, $PPh_2(p$-$C_6H_4NMe_2)$, in refluxing acetonirile under an N_2 atmosphere afforded the mononuclear complex, {$PdCl_2$-$[\eta^1$-(P)-$PPh_2(p$-$C_6H_4NMe_2)]_2$} (**3**) (Scheme 2) as an air-stable solid. Similar to complexes **1** and **2**, the elemental analyses and mass spectra are in good agreement with the proposed composition. The coordination of the aminophosphine ligand through phosphorus atom was confirmed by $^{31}P\{^1H\}$-NMR spectroscopy, which showed a singlet at δ 22.12 ppm and, compared with the free ligand this value had shifted 28 ppm downfield. The ^1H NMR spectra show, in addition to aromatic protons, a sharp singlet at δ 2.98 for methyl protons, which is almost same of that of the free ligand, clearly indicating that the amine group is not involved in coordination. The ^{13}C NMR-spectra show characteristic resonances for the aromatic as well as methyl carbon. The far-IR spectra of the complex shows a strong band at 358 cm^{-1}, consistent with *trans* disposition of the two chlorides.[45] In general, two bands are expected for a *cis*-isomer.[45]

Suzuki–Miyaura Cross-coupling Reactions using Palladium Complex 3 as Catalyst

It is now well established that palladium complexes containing phosphine-based ligands are excellent catalysts for



Scheme 2. Synthesis of the complexes **1a, 1b, 2** and **3**.

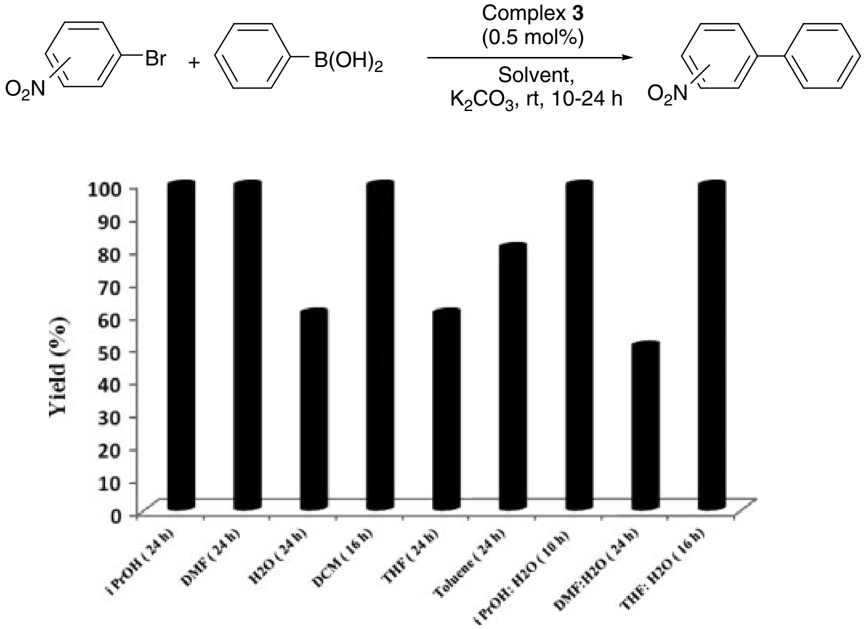


Figure 1. Effects of solvents in the Suzuki–Miyaura cross-coupling reactions of 4-bromonitrobenzene with phenylboronic acid.

Suzuki–Miyaura cross-coupling reactions; thus we attempted to use palladium complex **3** as a catalyst for the Suzuki–Miyaura reactions. In the majority of cases with phosphine-based ligands, an elevated temperature and/or use of an inert atmosphere is required for effective catalytic performance.[29,46] To investigate the effectiveness of complex **3** as a catalyst in the Suzuki–Miyaura reaction, the reaction of 4-bromonitrobenzene with phenylboronic acid was chosen as a model reaction using isopropanol as solvent, K_2CO_3 as base and 0.5 mol% complex **3** as catalyst, and performing the reaction in aerobic conditions. The reaction completed within 24 h and 99% 4-nitrobiphenyl was isolated as the sole product. Literature survey reveals that, in the Suzuki–Miyaura reaction, the use of pre-formed complexes as catalysts often shows different results[47,48] than *in situ*-generated catalysts. We found that the use of the pre-formed complex **3** gave a better result compared with the *in situ* catalyst generated from $PdCl_2$ and the aminophosphine ligand in a 1 : 2 molar ratio. Since the choice of solvents and bases greatly influences the overall catalytic performances in Suzuki–Miyaura reactions, several different solvents and bases were examined and the results are represented in Figs 1 and 2. Our results show that the reaction between 4-bromonitrobenzene and phenylboronic acid proceeded well in both protic and aprotic solvents, although significant variations in yields were noticed in some cases. Almost quantitative product formations were obtained with *iso*-propanol, ethanol, dichloromethane and dimethylformamide. Water as a solvent gave only moderate conversion, but when it

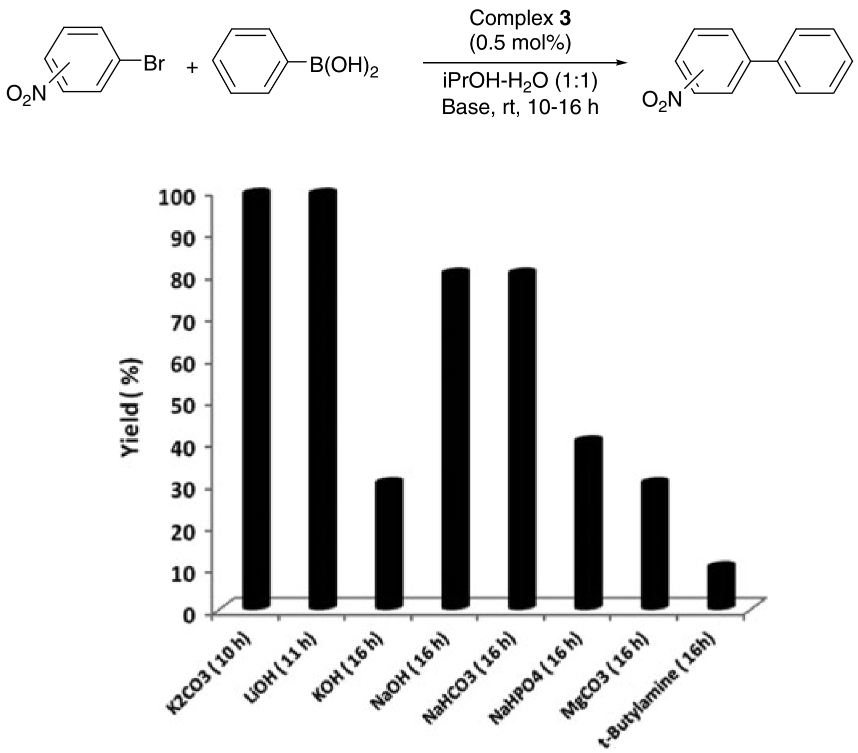


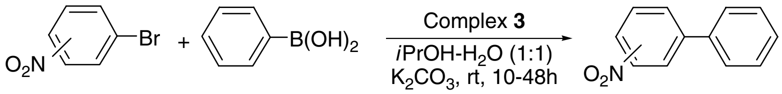
Figure 2. Effects of bases in the Suzuki–Miyaura cross-coupling reactions of 4-bromonitrobenzene with phenylboronic acid.

was used as a co-solvent with ^{i}PrOH or THF in 1 : 1 proportion, quantitative product formation was achieved in a much shorter time. For example, the reaction of 4-bromonitrobenzene with phenylboronic acid in water–^{i}PrOH resulted in the quantitative formation of coupling product in 10 h, whereas to achieve the same conversion in neat ^{i}PrOH required 24 h. Thus, for a base optimization study water–^{i}PrOH (1 : 1) was used as the solvent. Among bases, K_2CO_3 and LiOH were found to be the most effective bases whereas *tert*-butyl amine was found to be the least effective (Fig. 2). Studies on optimization of catalyst quantity (Table 1) revealed that the use of 0.5 mol% catalyst loading resulted in completion of the reaction within 10 h (entry 1). However, on decreasing the catalyst loading, the reaction time increased. A catalyst loading of 0.06 mol% was essential to maintain quantitative conversion of the product (entry 4). When the catalyst loading was decreased to 0.02 mol% (entry 5), 65% product formation was obtained in 24 h. A further decrease in catalyst loading to 0.01 mol% resulted in only 40% product formation being achieved (entry 6).

To evaluate the scope and limitations of the current procedure, the reactions of a wide array of electronically diverse aryl bromides with arylboronic acids were examined using complex **3** as the catalyst, and the results are shown in Table 2. It can be seen from Table 2 that, in general, the aryl bromides with electron-withdrawing substituents such as NO_2, CHO, CO_2Me and COOH (entries 1–4) underwent the coupling reactions in nearly quantitative yields (94–99%). The nonactivated aryl bromides (such as bromobenzene, 4-bromotolune and 4-bromoanisole) also gave the coupling products in excellent yields (entries 8–10). Interestingly, with a slightly extended reaction time, the sterically demanding substrates such as 2-bromotolune and 2-bromoanisole (entry 11 and 12) could also be coupled with phenylboronic acid to give the desired product in reasonably good yield. It is important to note that, although the electronic properties of aryl bromides have little influence on the coupling reactions, the nature of arylboronic acids has a substantial influence on the overall performance of the catalyst. For example, phenylboronic and 4-chlorophenylboronic acid were found to be extremely efficient with 4-bromonitrobenzene to afford the desired product in almost quantitative yield (Table 2, entries 1 and 5), while 3-nitrophenylboronic acid gave only 10% product formation (entry 7).

Although coupling reactions with aryl bromides proceeded smoothly in water–^{i}PrOH at room temperature to give the desired coupling product in good to excellent yields, under the same experimental conditions the reactions between 4-chloronitrobenzene with phenylboronic acid produced only trace amount of the cross-coupling products. Traditionally, aryl chlorides are less reactive than aryl bromides in Suzuki–Miyaura reactions and generally require more drastic conditions and/or higher catalyst loading. However, there exist a few reports in which microwave heating[49,50] or conventional heating[51,52] methodologies were successfully used to obtain the coupling products in good to excellent yields. Since only negligible amount (10%) of cross-coupling product was obtained using 0.06 mol% of the catalyst (Table 3, entry 1), we increased the catalyst quantity to 0.5 mol% (entry 2); only a slight improvement in the cross-coupling product formation was observed. However, entry 3 of Table 3 shows that the use of neat ^{i}PrOH instead of water–^{i}PrOH (1 : 1) improved the product formation significantly, and 58% cross-coupling product was isolated. Hence, further a study with aryl chlorides was performed in ^{i}PrOH with 0.5 mol% of catalyst. Besides 4-chloronitrobenzene, other electron-withdrawing substituents such as, 4-chloroacetophenone (entry 4) and 4-chlorobenzaldehyde (entry 5) gave only moderate yields. Our results also showed that, under slightly extended reaction time, nonactivated aryl chlorides such as 4-chlorobenzene and 4-

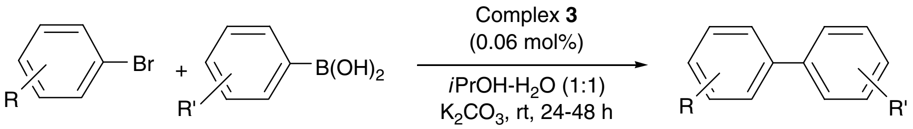
Table 1. Effect of catalyst quantity on the Suzuki–Miyaura cross coupling reactions of 4-bromonitrobenzene with phenylboronic acid[a]



Entry	Catalyst (mol%)	Time (h)	Yield (%)[b,c]
1	0.50	10	99
2	0.25	13	99
3	0.12	16	99
4	0.06	24	99
5	0.02	36	65
6	0.01	48	40

[a] Reaction conditions: 0.5 mmol 4-bromonitrobenzene, 0.55 mmol phenylboronic acid, 1.5 mmol base, solvent (6 ml). [b] Isolated yield. [c] Yields are of average of two runs.

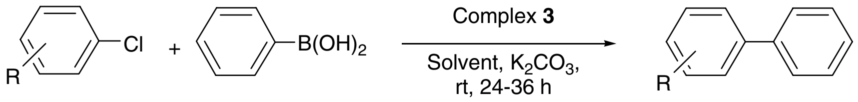
Table 2. Suzuki–Miyaura cross-coupling reactions of various aryl bromides with arylboronic acids using complex **3** as catalyst[a]



Entry	R	R′	Time (h)	Yield (%)[b,c]
1	4-NO_2	H	24	99
2	4-COMe	H	30	98
3	4-COOH	H	30	96
4	4-CHO	H	30	94
5	4-NO_2	4-Cl	24	96
6	4-NO_2	4-Me	24	90
7	4-NO_2	3-NO2	24	10
8	H	H	30	91
9	4-Me	H	30	94
10	4-OMe	H	30	93
11	2-Me	H	42	78
12	2-OMe	H	42	82

[a] Reaction conditions: 0.5 mmol aryl bromide, 0.55 mmol arylboronic acid, 1.5 mmol K_2CO_3, water–^{i}PrOH (6 ml). [b] Isolated yield. [c] Yields are of average of two runs.

Table 3. Suzuki–Miyaura cross-coupling reactions of aryl chlorides with phenylboronic acid using complex **3** as catalyst



Entry	R	Catalyst (mol%)	Solvent	Time	Yield (%)[b,c]
1	4-NO_2	0.06	^{i}PrOH–H_2O (1 : 1)	30	10
2	4-NO_2	0.5	^{i}PrOH–H_2O (1 : 1)	30	17
3	4-NO_2	0.5	^{i}PrOH	24	58
4	4-COMe	0.5	^{i}PrOH	30	43
5	4-CHO	0.5	^{i}PrOH	30	46
6	4-H	0.5	^{i}PrOH	30	36
7	4-Me	0.5	^{i}PrOH	36	26

[a] Reaction conditions: 0.5 mmol aryl chloride, 0.55 mmol phenylboronic acid, 1.5 mmol K_2CO_3, solvent (6 ml). [b] Isolated yield. [c] Yields are of average of two runs.

chlorotoluene gave relatively poor yields (entries 6 and 7). Although reduced yields of the coupling products were obtained for aryl chlorides compared with aryl bromides, these results were also significant, as we were able to use aryl chlorides as substrates in the Suzuki–Miyaura reaction at room temperature.

Conclusion

In summary, we explored the coordination ability of an aminophosphine ligand with Fe(0), Rh(I) and Pd(II). Four new complexes were synthesized and characterized by different spectroscopic techniques. The catalytic activity of the palladium complex was evaluated for Suzuki–Miyaura cross-coupling reactions of aryl halides with arylboronic acids at room temperature. Excellent yields (up to 99% isolated) were obtained with aryl bromides as substrate. The less reactive aryl chlorides could also be used as a substrate for room temperature cross-coupling reactions.

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