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Iridium(I)-salicylaldiminato-cyclooctadiene complexes used as catalysts for phenylborylation

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Abstract

Iridium(I) salicylaldiminato-cyclooctadiene complexes, Ir(–*o*-O–C_6H_4–CH=N–R)(cod) (R = CH_2Ph (**1**), Ph (**2**); cod = 1,5-cyclooctadiene), have been prepared, characterized and used as catalysts for arylborylation via C–H activation. With **1** as a catalyst, isolated yields of up to 91% has been achieved for the borylation of benzene by bis(pinacolato)diboron in the presence of *tetra*-2-pyridinylpyrazine and an ionic liquid. The catalytic system could be recycled for at least three times without loss of activity.

Keywords: Iridium(I) salicylaldiminato-cyclooctadiene complexes; Arylborylation; Catalyst recycle; Ionic liquid

1. Introduction

Organoboric acids constitute an important class of compounds that are widely used in Suzuki cross-coupling reactions to form various C–C bonds [1,2]. Commonly used methods to synthesize arylboronic acids are the alkylation of trialkylborates or haloboranes with organomagnesium (Grignard) or aryl lithium reagents at low temperature [3]. These methods are not general in that they require the prior preparation of extremely basic and nucleophilic organometallic species that tolerate only a restricted number of functional groups. In addition, the yields in these reactions are usually fairly modest (ca. 50%). The preparation of the Grignard and organolithium reagents from ArCl is difficult and often requires the use of the less readily available arylbromides. Thus, there is a great deal of interest in the development of robust and highly efficient catalytic methods for the production of organoboronic acids. Palladium(0) species produced *in situ* from palladium(II) complexes, such as $PdCl_2$ (dppf), have been reported to be active catalysts for the cross-coupling reactions of the pinacol esters of diboronic acid with haloarenes in homogeneous systems [4]. More recently, Rh, Ir, and Re complexes also have been explored in the direct borylation of hydrocarbons to provide alkyl- and aryl-boron compounds via C–H activation (see Scheme 1) [5]. These are economical, efficient, and environmentally benign protocols for the preparation of various organoboron compounds.

The borylations of unreactive arenes were demonstrated in the early 1990s by Marder [6] and Hartwig [7] and coworkers. Thermally-induced transition metal-catalyzed aromatic C–H borylation with Ir complexes was described by Smith and Iverson [8]. These workers obtained B–C bond formation from the reaction of benzene and pinacolborane (HBpin) catalyzed by a Cp^*Ir complex in the presence of PMe_3. Further work saw the development of other active catalysts, such as, (η^5-C_9H_7)Ir(cod) [9] and $Cp^*Rh(\eta^4$-$C_6Me_6)$ [10]. Although yields from the reactions

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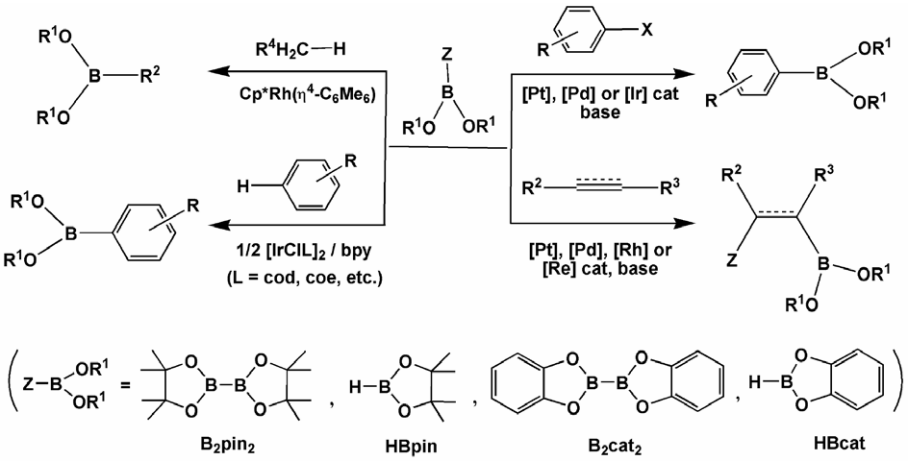


Scheme 1. Direct borylation of alkene, alkyne and arenas.

were moderate to high, the elevated temperatures and long reaction times proved to be an inconvenience in the synthesis of arylboronate compounds.

Lower temperature catalytic systems were developed by Miyaura and co-workers from the reaction of commercially available Ir(I) precursors $[IrCl(cod)]_2$ (cod = 1,5-cyclooctadiene) or $[IrCl(coe)_2]_2$ (coe = cyclooctene) with the strongly electron-donating 2,2′-bipyridine ligand. These Ir catalysts proved to be highly efficient in the direct borylation of arenes and heteroarenes by bis(pinacolato)diboron (B_2pin_2) under mild, room temperature conditions [11]. Extended studies showed that the Ir complexes having OH, OPh or OMe ligands in place of the Cl atom also performed well in the synthesis of arylboronates at room temperature [12]. Experimental and computational studies of this catalytic system lead to the identification and isolation of an Ir(III) tris(boryl) intermediate as well as an Ir(V) complex thought to be important in the catalytic mechanism [13]. Of late, N-heterocyclic carbene complexes of Ir(I) were shown to exhibit high activity in aromatic borylation at relatively mild temperatures (40–45 °C) and reaction times of between 9 and 12 h [14]. While these systems provide feasible synthesis conditions for arylboronation, they are not reusable, which contributes greatly to the cost of such synthetic schemes.

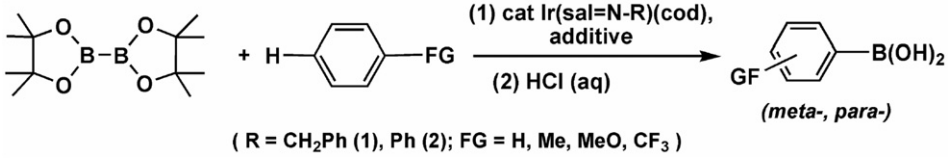
Herein, we report our preliminary results regarding the syntheses of iridium(I) salicylaldiminato-cyclooctadiene complexes as reusable catalysts for the C–H borylation of arenes by B_2pin_2 as outlined in Scheme 2.

2. Results and discussion

2.1. Synthesis and characterization of Ir(I) complexes

Iridium(I) salicylaldiminato-cyclooctadiene complexes, Ir(–*o*-O–C_6H_4–CH=N–CH_2Ph)(cod) **1** and Ir(–*o*-O–C_6H_4–CH=N–Ph)(cod) **2** have been prepared in 82% and 68% yields, respectively, from the reaction of the corresponding Schiff bases and commercially available $[IrCl(cod)]_2$ (see Supplementary material for detail synthetic procedures and characterization). The salicylidenebenzylamine and salicylideneaniline were first deprotonated with NaH to produce their Na salts as intermediates, which reacted with $[IrCl(cod)]_2$ to produce complexes **1** and **2**. The synthesis of **2** from the reaction of $[IrOCH_3(cod)]_2$ and salicylideneaniline was reported earlier but no yields were quoted [15]. The solid state structures of **1** and **2** were determined (see the Supplementary material) and are shown in Fig. 1. As can be seen in Fig. 1, both complexes show that the Schiff base and the cod ligands are arranged about the central Ir to give a square planar coordination of the metal; the O–Ir–N bond angles in **1** and **2** are 90.7(3)° and 90.37(14)°, respectively. These angles are essentially the same as the value of 90.2(4)° found for the equivalent angle in Ir(–*o*-O–C_6H_4–CH=N–*o*-tol)(cod) [15]. The Ir–N bond lengths in **1** (2.066(9) Å) and **2** (2.073(3) Å) are slightly greater than their Ir–O bond distances (**1**, 2.020(7) Å, **2**, 2.029(3) Å).

In order to evaluate the catalytic efficiencies of **1** and **2** in aromatic C–H borylation, benzene was used as the com-



Scheme 2. Iridium(I) salicylaldiminato-cyclooctadiene complexes catalyzed borylation.

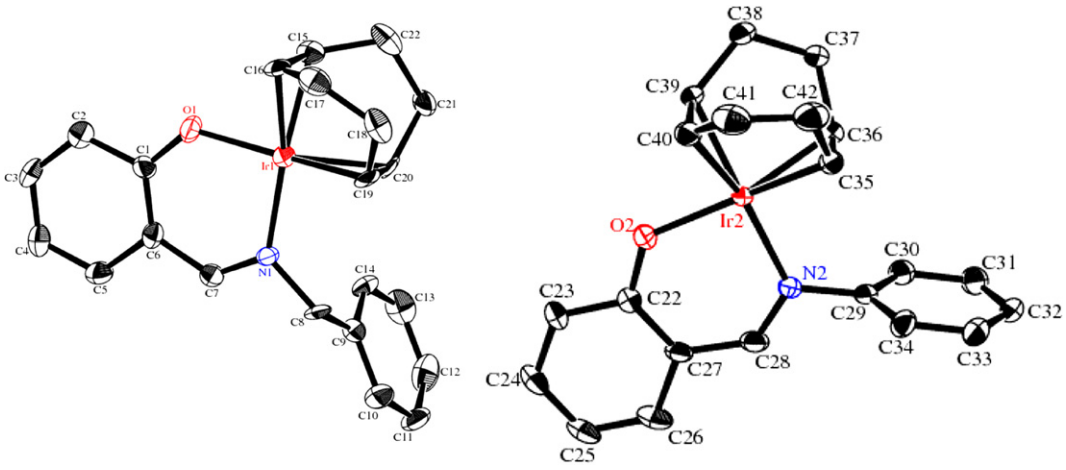


Fig. 1. Molecular structure **1** (left) and **2** (right).

mon substrate with B_2pin_2 as the borolating agent. The solvents were either excess benzene or a mixture of the ionic liquid, tributyltetradecylphosphonium dodecylbenzenesulfonate, (TBPD) and dichloromethane (see the Supplementary material for the detail catalyst evaluation). To probe the effects of added bases, which were found to be necessary by Hartwig [11,12], the reactions were run in the presence of different ligands, as listed in Table 1. The two polydentate bases, Tpy (tetra-2-pyridinylpyrazine) and Bpy (2,2′-bipyridine) were much more effective activating agents than were the momonentate bases, even py. Hartwig observed that in the borylation of aromatic compounds using the precatalyst, $[IrCl(cod)]_2$ activated by substituted bpy, the planarity of the activating base was important [11,12]. On the other hand, Hermann and co-workers found that a number of bis(carbene) Ir complexes were effective catalysts for the syntheses of a series of arylboronic acids from their corresponding aryls and pinicolborane, without base activation [14]. The data in Table 1 show that compounds **1** and **2** required base activation similar to the $[IrCl(cod)]_2$, even though **1** and **2** are monomeric compounds in which the salicylaldiminato ligands are planar. In addition, Table 1 shows that, except for the runs in which Na_2CO_3 and Bpy acted as the bases, catalyst **1** was ~35% more effective than was catalyst **2**.

Table 1
Phenylborylation catalyzed by **1** and **2** with various additives[a]

Cat	L[b]					
	PPh_3	Py	Bpy	TPy	Cs_2CO_3	Na_2CO_3
1	23[c]	30	63	70	15	6
2	14	22	65	52	10	8

[a] All catalytic reactions were conducted under argon atmosphere at 80 °C for 21 h. Reaction mixture consisted of 1.0 mmol B_2pin_2, 0.015 mmol of Ir(I) precursor and 0.03 mmol ligand, 20.0 ml benzene.
[b] PPh_3 = triphenylphosphine, Py = pyridine, TPy = tetra-2-pyridinylpyrazine, Bpy = 2, 2′ − bipyridine.
[c] Isolated yield (%) after hydrolysis and flash chromatography.

2.2. Catalytic evaluation of Ir(I) complexes in benzylic borylation

Since the most advantageous reaction mixture was catalyst **1** with TPy, this combination was used to investigate the advantages of different reaction conditions; the results of this study are given in Table 2. As can be seen, normal reaction aids such as ultrasonication and increasing the temperature had an inverse effect on the yield [16–18]. The only yield enhancement was found on the addition of the ionic liquid, TBPD, giving a yield of 91%.

The maximum turnover number for the phenylborylation of benzene by bis(pinacolato)diboron, in the presence of **1** was determined by running the reaction at 100 °C for 40 h in a 0.015 mol% loading of catalyst **1** in benzene solvent. After hydrolysis and flash chromatography, phenylboronic acid was isolated in 67% yield (4467 turnovers). It is of interest to note that this yield was slightly lower than that listed in Table 1 even though the reaction time was extended. The results to date indicate that an increase in temperature results in lower yields. It was found that the addition of extra TPy had no positive effect on the activity of complex **1**. On the other hand, the catalytic activity of **1** is found to be strongly influenced by the choice of solvent.

Table 2
Phenylborylation with different methodology using catalyst **1** and TPy ligand[a]

Method	MW[b]	((((c	Autoclave[d]	IL[e]	Standard[f]	HBpin[g]
Yield (%)	17	28	53	91	70	43

[a] Conditions are same as described in Table 1.
[b] Reaction mixture was heated at 130 °C using microwaves for 1 h.
[c] Reaction mixture was heated at 80 °C in ultrasonic bath for 3 h.
[d] Reaction mixture was heated at 180 °C in high pressure reactor for 14 h.
[e] 3.0 ml benzene with additional 2.0 ml each of dichloromethane and the ionic liquid TBPD as solvent at 80 °C for 21 h.
[f] 20.0 ml benzene as solvent at 80 °C for 21 h.
[g] Same conditions with standard method except using HBpin instead B_2pin_2.

Table 3
Effect of aromatic substituent groups on the arylborylation using catalyst **1** and TPy ligand[a]

FG	H	Me	OMe	CF_3
Yield (%, *m*:*p*)[b]	70	62 (1.5)	67 (1.1)	86 (1.3)
Yield (%, *m*:*p*)[c]	70	64 (1.6)	65 (1.0)	87 (1.6)
Yield (%, *m*:*p*)[d]	91	–	71 (0.7)	89 (0.9)

[a] Conditions are same as described in Table 1 except for CF_3 which was operated for 8 h. Reaction mixture consisted of 1.10 mmol B_2pin_2, 0.015 mmol of Ir(I) precursor and 0.03 mmol ligand, 1.00 mmol arenes and 10.0 ml dichloromethane as solvent (for FG = H, 20.0 ml benzene was used as both substrate and solvent).

[b] Isolated yield (%) after hydrolysis and flash chromatography. The ratios of *meta*-/*para*- (*m*:*p*) were determined by NMR spectroscopy.

[c] Obtained from 10-fold of arenes with B_2pin_2 with similar standard process.

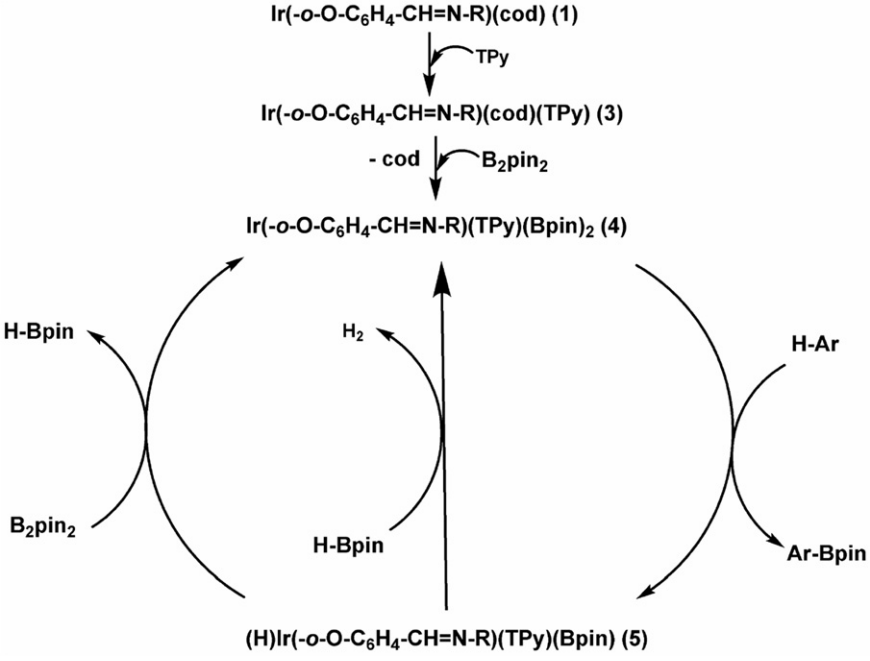
[d] From ionic liquid medium.

In the ionic liquid, TBPD, a tremendous increase in catalytic efficiency was observed, with phenylboronic acid being formed in 91% yield. The same lot of complex **1**/base could be reused three times without any obvious drop in catalytic activity. Compound **1**/base seems to be the first reported example of a reusable imine-based catalyst for arylborylation reactions.

It is of interest to note, that reactions using either **2** or $[IrCl(cod)]_2$ as the precatalyst with TPy and B_2Pin_2 in the TBPD/dichloromethane solvent produced only low yields (<15% by NMR) of the arylborylation product. It is surprising that the presence of the ionic liquid produces such dramatically different effects on the three supposedly similar catalytic systems.

The results of a study of the effects of the substituent groups on the aryl are summarized in Table 3. It can be seen that for mono-substituted benzenes of the form C_6H_5R (R = H, CH_3, OCH_3 and CF_3), only the *meta*- and *para*-disubstituted products were observed. The lack of formation of any *ortho*-products, irrespectively of the electron-donating or electron-withdrawing properties of the substituents, seems to be due to steric effects. Under the same conditions as those in Table 1, the ratios of *meta*- to *para*-isomers in the products ranged from 1.5:1 for R = CH_3 to 1.1:1 for R = OMe. These ratios are significantly less than the values of 3.0:1, 2.3:1 and 2.2:1 for R = OCH_3, CF_3 and CH_3, respectively, reported by Hartwig and co-workers, using a $[IrCl(cod)]_2$/bpy catalyst system [11]. Given that the statistical *meta*/*para* ratio would be 2:1, it is not apparent why the catalytic system used by Hartwig would favor substitution at the *meta*-position, while our Ir(–*o*-O–C_6H_4–CH=N–CH_2Ph)(cod)/TPy system would give preference to *para*-substitution. The table also shows that this preference for *para*-substitution is enhanced by the presence of the ionic liquid (Table 3, d). It might be that the ionic liquid can stabilize greater charge separation, thereby favoring a more remote substitution. Table 3 also shows that the electron withdrawing CF_3 group gives rise to an 86% yield in 8 h, while the electron-donating OCH_3 group resulted in only a 67% yield after 21 h. This increased reactivity of the electron poor arenes was also found for the $[IrCl(cod)]_2$/bpy catalyst system [11]. When excess arenes (10-fold) were used, neither the yields nor the selectivity changed materially (Table 3, c).

In order to obtain an insight into the nature of the catalytic species, the reaction of **1** with TPy in the absence of



Scheme 3. Proposed catalyst cycle.

a borolating agent was explored. When **1** and TPy were mixed, the color of the solution changed smoothly from red brown into dark green. The product was isolated, analyzed and its NMR spectra were run. Both spectra and analysis are consistent with an Ir(–*o*-O–C_6H_4–CH=N–CH_2Ph)(cod)(TPy) (**3**) complex. This suggests a catalytic cycle shown in Scheme 3. Accordingly, B_2pin_2 could undergo oxidative addition promoting a loss of cod, giving the catalytically active species, Ir(–*o*-O–C_6H_4–CH=N–CH_2Ph)(TPy)(Bpin)$_2$ (**4**). It is assumed that the addition of the B_2pin_2 would cause the loss of cod a six coordinate Ir(III) species (**4**). Alternatively, the cod could be converted to a monodentate ligand, yielding a seven coordinate Ir complex. This would be consistent with the observation of Hartwig and co-workers, that $[IrCl(coe)_2]_2$ is just as good a catalytic precursor than is $[IrCl(cod)]_2$ [11]. Reaction with an arene to product Ar-Bpin and the six coordinate (H)Ir(–*o*-O–C_6H_4–CH=N–CH_2Ph)(TPy)(Bpin) (**5**) could easily follow. The C–H activation could proceed through either an oxidative addition/reductive elimination involving a seven coordinate Ir(V) intermediate, or a σ-bond metathesis process. Both processes have been postulate, for Ir-catalyzed borylations [13,20]. The resulting hydrido complex (**5**) could then react with a B_2pin_2 or HBpin to give (**4**) and HBpin or H_2, respectively. The cycle could then be repeated. During the cycle, ionic liquid may play an important role in the stabilization of intermediates via electrostatic interaction, which might be crucial in the decomposition step of proposed iridium(V) intermediate to form *para*-isomers of boroxines. It should be stressed that Scheme 3 represents a reasonable sequence of reactions, based on the viability of compounds **4** and **5**, neither one of these proposed intermediates have been identified. They are similar to other intermediates proposed for Ir(I)-catalyzed borylation reactions.

3. Conclusion

Ir(I) complexes, Ir(–*o*-O–C_6H_4–CH=N–CH_2Ph)(cod) **1** and Ir(–*o*-O–C_6H_4–CH=N–Ph)(cod) **2**, have been synthesized by the reaction of the sodium salts of Schiff bases salicylidenebenzylamine and salicylideneaniline with $[IrCl(cod)]_2$ and, on activation by bases, used as catalysts for arylborylation reactions. Of the two precatalysts, **1**, when activated with *tetra*-2-pyridinylpyrazine (TPy), was found to be the more active phenylborylation catalyst. In contrast to **2** and $[IrCl(cod)]_2$, the catalytic performance of **1** was enhanced when a solvent mixture of dichloromethane and the ionic liquid, tributyltetradecylphosphonium dodecylbenzenesulfonate, TBPD, was used. It was found that compound **1** is also active phenylborylation catalyst using HBpin in the presence of tetra-2-pyridinylpyrazine (TPy) in a yield of 43%. The different results found in the two catalytic systems could indicate that different mechanisms are operating. A more detailed mechanistic study and an investigation of the effects of structural modifications of the catalyst is undergoing in our laboratories.

4. Experimental

General methods. All the operations were carried out under an argon atmosphere using standard Schlenk techniques or in a glove box. Solvents diethyl ether, dichloromethane, toluene, *n*-hexane and tetrahydrofuran (THF) were purified by a solvent purification system while benzene was dried with sodium. All other reagents were used as received. Salicylidenebenzylamine and salicylidenephenylamine were prepared according to literature [19]. Elemental analyses were measured in a CHNS analyzer and melting points determined by a Büchi melting point analyzer. ^{1}H, ^{13}C and ^{11}B NMR were recorded on a Bruker Advance 400 MHz spectrometer. Chemical shifts were measured in ppm relative to TMS standard (^{1}H: 400.2 MHz, ^{13}C: 100.6 MHz, ^{11}B: 128.4 MHz). Infrared (IR) spectra were measured using a BIO-RAD spectrophotometer with KBr pellets. Rigaku Single Crystal Diffraction System was used for single crystal X-ray analysis.

4.1. Synthesis of complex Ir(–*o*-O–C_6H_4–CH=N–CH_2Ph)(cod) (*1*)

A 0.15 g (0.71 mmol) of salicylidenebenzylamine was treated with 0.14 g (3.55 mmol) of NaH (60% in mineral oil) in 75 ml diethyl ether at room temperature. After 3 h of stirring at room temperature, the mixture was filtered to remove unreacted NaH and the resulting solution added to 0.24 g (0.35 mmol) $[IrCl(cod)]_2$ in 75 ml THF at −78 °C. The mixture was kept at that temperature for 30 min and then allowed to warm to room temperature spontaneously and continuous stirring for 3 h. After the reaction process, the solvents were removed under reduced pressure and the solid was washed with benzene, filtered and dried in high vacuum to give an orange solid **1** in 82% yield (mp, 151–153 °C). Single crystal suitable for X-ray diffraction was obtained from solvents evaporation from a saturated solution **1** in CH_2Cl_2/*n*-hexane. Crystal structure and refinement data are described in Fig. 1 and Table 1. Anal. Calc. for $C_{22}H_{24}IrNO$ **1**: C, 51.71; H, 4.73; N, 2.74. Found: C, 51.85; H, 4.43; N, 2.67%. ^{1}H NMR ($CDCl_3$): $\delta = 1.725$ (d, 4H, cod-CH_2); 2.233 (t, 4H, cod-CH_2); 3.488 (s, 2H, cod-*H*C=C); 4.451 (s, 2H, cod-*H*C=C); 4.840 (s, 2H, CH_2); 6.627–7.495 (m, 9H, Ph-*H*); 8.291 (s, 1H, N=C*H*); ^{13}C NMR ($CDCl_3$): $\delta = 29.35$ (cod-*C*H$_2$); 32.66 (cod-*C*H$_2$); 54.59 (cod-*C*=C); 61.78 (*C*H$_2$); 69.90 (cod-*C*=C); 115.84–139.21 (Ph-*C*); 165.44 (Ph-*C*); 166.30 (N=*C*H). IR (KBr pellet, cm^{-1}, vs = very strong, s = strong, m = middle, w = weak): $\nu = 2998$ (w), 2972 (w), 2914 (w), 2879 (w), 2830 (w), 2361 (vs), 2342 (s), 1590 (s), 1536 (s), 1470 (m), 1435 (m), 1406 (m), 1328 (m), 1233 (w), 1199 (w), 1151 (m), 1130 (w), 1077 (w), 1023 (w), 973 (w), 895 (w), 850 (w), 807 (w), 762 (m), 738 (m), 694 (w), 683 (w), 602 (w), 488 (w), 464 (w).

4.2. Synthesis of complex Ir(–o-O–C_6H_4–CH=N–Ph)(cod) (2)

A similar procedure as the preparation of **1** was used to synthesize **2**. After purification, complex **2** was obtained in 68% yield from 0.12 g (0.60 mmol) of salicylideneaniline, 0.12 g (2.98 mmol) of NaH (60% in mineral oil) and 0.20 g (0.30 mmol) $[IrCl(cod)]_2$ in 75 ml diethyl ether. The NMR data are consistent with literature [15]. Single crystal suitable for X-ray diffraction was obtained from solvents evaporation from a saturated solution **2** in CH_2Cl_2/*n*-hexane.

4.3. Synthesis of Ir(–o-O–C_6H_4–CH=N–CH_2Ph)(cod)(TPy) (3)

In glove box, **1** (102.2 mg, 0.20 mmol) and TPy (80 mg, 0.20 mmol) were dissolved in 20 mL dry CH_2Cl_2. The reaction mixture was stirred at room temperature for 12 h. The solution was concentrated to 2 mL and precipitated with dry pentane. After filtered and dry under reduced pressure, a deep green solid was obtained in 75% yield (135 mg). Anal. Calc. for $C_{46}H_{40}IrN_7O$: C, 61.45; H, 4.48; N, 10.91. Found: C, 61.17; H, 4.41; N, 10.44%. ^{1}H NMR (CD_2Cl_2): $\delta = 1.65$ (d, 4H, cod-CH_2); 2.11 (d, 4H, cod-CH_2); 3.39 (s, 2H, cod-C*H*=C); 4.28 (s, 2H, cod-C*H*=C); 4.76 (s, 2H, CH_2–Ph); 6.56–8.49 (m, 30H, Ph–*H*, C_5H_4N and N=C*H*); ^{13}C NMR (CD_2Cl_2): $\delta = 29.32$ (cod-*C*H$_2$); 32.58 (cod-*C*H$_2$); 54.26 (cod-*C*=C); 61.83 (*C*H$_2$); 69.42 (cod-*C*=C); 116.66–139.84 (Ph-C, C_5H_4N); 148.53, 149.30, 156.99 (C_5H_4N and C_4N_2); 167.10 (N=*C*H).

4.4. Evaluation of catalytic activity

The borylation of arenes catalyzed by **1**, **2** and $[IrCl(cod)]_2$ was performed in benzene or dichloromethane (CH_2Cl_2) and an ionic liquid solvents in the presence of a basic ligand. The reactants were used in the following amount: 1.0 mmol B_2pin_2, 0.015 mmol catalyst (**1**, **2**, $[IrCl(cod)]_2$), 0.03 mmol ligand, 20 ml or 3 ml (for dichloromethane and ionic liquid solvent) benzene, 2 ml each of dichloromethane and ionic liquid tributyltetradecylphosphonium dodecylbenzenesulfonate (TBPD). The reaction was conducted at a reflux temperature 80 °C for 21 h. In addition, alternative methods were utilized in replace of the conventional way: (a) in a high pressure reactor (Parr Stirred High Pressure reactor) at 180 °C for 14 h, (b) via ultrasonic irradiation (Transsonic T750 Ultrasonic Bath) for 3 h, and (c) under microwaves (Milestone Microsynth Microwave Lab station with Lab Terminal 800 Controller) with temperature increasing from room temperature to 130 °C within 2 min and maintained at 130 °C for 1 h. After borylation, the solvent was removed under reduced pressure. Prior hydrolysis, diethyl ether was added to dissolve the obtained residue, after which 20 ml of 10% HCl (aq) was added and the mixture stirred for 4 h. Of the two layers formed, the organic layer was isolated and dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified with flash column chromatography (SiO_2) to produce the corresponding arylboronic acids (confirmed by NMR spectroscopy, see Supplementary material). For catalyst recycle runs, after the borylation reaction and removal of the solvent, the crude product of boroxines were distilled from reaction mixture under reduced pressure. The residue was reused as a catalyst mixture to undergo further runs, and the distillated sticky liquids obtained from distillation was subjected to above hydrolysis process to form products.

4.5. Determination of the maximum turnover numbers for the borylation of benzene with bis(pinacolato)diboron using catalyst 1

A 30.0 μL (0.15 μmol) solution of **1** (5.0 mM in benzene), 15.0 μL (0.30 μmol) solution of TPy (20.0 mM in benzene) in benzene were prepared in glove box. B_2pin_2 (255 mg, 1.0 mmol) in 20.0 mL benzene and prepared catalyst and ligand solutions were placed in autoclave. The reaction mixture was then heated at 100 °C for 40 h. After hydrolysis and flash chromatography as above described, phenylboronic acid was isolated in 67% yield.

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Appendix A. Supplementary material

CCDC 638193 and 638194 contain the supplementary crystallographic data for **1** and **2**. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.06.052.

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