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Synthesis of Iridium Pyridinyl N-Heterocyclic Carbene Complexes and Their Catalytic Activities on Reduction of Nitroarenes

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Coordination of iridium(I) metal ions with a pyridinyl imidazol-2-ylidene ligand (**pyN^C-R**) [R = Me, mesityl(2,4,6-trimethylphenyl)] that processes bulky substituents has been investigated. The iridium carbene complexes [(*C*-**pyN^C-R**)IrCl(COD)] (COD = 1,5-cyclooctadiene) are prepared via transmetalation from the corresponding silver carbene complexes. Upon the abstraction of chloride, the chelation of **pyN^C** becomes feasible, resulting in the formation of [*C*,*N*-(**pyN^C-R**)Ir(COD)](BF_4) (**4**). The coordinated COD of complex **4** can be replaced by carbon monoxide to yield the corresponding carbonyl species [*C*,*N*-(**pyN^C-R**)Ir$(CO)_2$](BF_4). The labile nature of the pyridinyl nitrogen donor is readily replaced by acetonitrile, as is evidenced by the NMR study. All iridium complexes show catalytic activity on the hydrogen-transfer reduction of carbonyl and nitro functionalities. By manipulation of the reaction conditions, the iridium-catalyzed reduction of nitroarenes can selectively provide aniline or azo compounds as the desired product.

Introduction

In recent years, the use of N-heterocyclic carbenes as ligands for transition-metal ions in catalysis has increased significantly because of the effect of their strong σ-donor nature on the stabilization of metal ions.[1] Among the various metal ions, applications of the iridium carbene complexes in homogeneous catalysis have also been reported.[2−9] It is known that N-heterocyclic carbeneiridium complexes can catalyze the Oppenauer-type oxidation,[2] hydrogen-transfer reduction of carbonyl compounds,[3] cyclization of alkynylcarboxylic acids,[4] hydrogenation of olefins,[5] hydrosilylation,[6] hydroamination,[7] C−H activation,[8] and bornylation.[8] However, to our knowledge, the use of iridium carbene complexes for catalytic reduction of nitro compounds has not been reported before.

Hydrogenation of functionalized nitrobenzenes produces anilines, which are important intermediates for the manufacture of a variety of agrochemicals, pharmaceuticals, dyes, and pigments. Reduction of nitro compounds can be carried out in the gas or liquid phase by using metal catalysts.[10]

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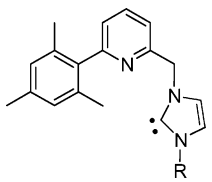
However, hydrogenation of aromatic nitro compounds poses problems, particularly for those with other reducible groups in the reaction. Alternatively, the hydrogen-transfer reduction offers a promising solution because of its selectivity.[10] Herein, we report the preparation and characterization of a series of new pyridinylcarbene (denoted as **pyN^C-R**) iridium(I) complexes as well as their catalytic activities toward the hydrogen-transfer reduction of nitroarenes under mild reaction conditions.



R = Mes, Me

pyN^C-R

Experimental Section

General Information. Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ or acetone-d_6 on either a Bruker AM-300 or AVANCE 400 spectrometer. Chemical shifts are given in parts per million relative to Me_4Si for ^1H and $^{13}C\{^1H\}$ NMR. IR spectra were measured on a Nicolet Magna-IR 550 spectrometer (Series II) as KBr pellets, unless otherwise noted.

All reactions and manipulations were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl. Dichloromethane was dried over CaH_2 and distilled under nitrogen. Other solvents were degassed before use. Chemicals were purchased from a commercial source and used without further purification. The preparation methods of (6-mesitylpyridin-2-yl)methanol and complex **2b** are described in the literature.[11a]

1-(6-Mesityl-2-picolyl)-3-methylimidazolium Bromide (1a). A solution of (6-mesitylpyridin-2-yl)methanol (1.03 g, 4.53 mmol) in dichloromethane (20 mL) was cooled in an ice bath. Phosphorus tribromide (1.2 mL, 12.8 mmol) was slowly added to the above solution, and the resulting solution was stirred at room temperature overnight. Water (5 mL) was then added to quench the excess of PBr_3, and the solution was neutralized by sodium bicarbonate. The organic portion was separated and dried over magnesium sulfate. To this solution was added methylimidazole (0.4 g, 4.9 mmol). The mixture was heated to reflux for 12 h, and the desired product precipitated as a white solid from the solution. The solid was collected and recrystallized from alcohol to give the desired bromide as a white powder (88%). ^1H NMR (400 MHz, $CDCl_3$): δ 10.36 (s, 1H), 7.75−7.69 (m, 2H), 7.52−7.50 (m, 2H), 7.13 (dd, 1H, J = 6.8 and 1.6 Hz), 6.85 (s, 2H), 5.71 (s, 2H), 4.00 (s, 3H), 2.24 (s, 3H), 1.85 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.9, 152.0, 137.7, 137.5, 137.1, 136.6, 135.1, 128.1, 124.9, 123.1, 122.1, 121.7, 54.0, 36.7, 21.0, 20.2. Anal. Calcd for $C_{19}H_{22}N_3Br$: C, 61.30; H, 5.96; N, 11.29. Found: C, 61.11; H, 6.08; N, 11.44.

Silver Complex 2a. A solution of **1a** (397 mg, 1.07 mmol), silver oxide (124 mg, 0.54 mmol), and sodium iodide (160.4 mg, 1.07 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 24 h. Filtration of the reaction mixture through Celite gave a colorless solution, which was then concentrated. Upon the addition of hexane to the crude reaction mixture, complex **2a** was precipitated and isolated as a white solid (545 mg, 97%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.69 (dd, 1H, J = 7.6 and 7.6 Hz, *Py*), 7.54 (d, 1H, J = 7.6 Hz, *Py*), 7.12 (d, 1H, J = 7.6 Hz, *Py*), 7.10 (m, 1H, *Im*), 6.89 (s, 2H, *Mes*), 6.86 (d, 1H, J = 1.2 Hz, *Im*), 5.52 (s, 2H), 3.87 (s, 3H), 2.29 (s, 3H), 1.94 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 184.7 (Ag−*C*), 159.5, 155.5, 137.5, 137.1, 135.4, 128.2, 124.0, 121.9, 121.4, 121.0, 57.0, 39.1, 21.2, 20.4. Anal. Calcd for $C_{38}H_{42}Ag_2I_2N_6$: C, 43.37; H, 4.02; N, 7.99. Found: C, 43.37; H, 4.09; N, 7.97.

[(*C*-pyN^C-Me)Ir(COD)Cl] (3a). A mixture of silver complex **2a** (200 mg, 0.19 mmol) and $[IrCl(COD)]_2$ (127 mg, 0.19 mmol) in dichloromethane (25 mL) was stirred at room temperature for 3 h. The resulting solution was filtered through Celite, followed by concentration and crystallization from CH_2Cl_2/hexane to afford a yellow solid of the desired iridium complex (230 mg, 97%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.71 (dd, 1H, J = 7.6 and 7.6 Hz, *Py*), 7.51 (d, 1H, J = 7.6 Hz, *Py*), 7.12 (d, 1H, J = 7.6 Hz, *Py*), 6.92 (s, 2H, *Mes*), 6.88 (s, 1H, *Im*), 6.78 (s, 1H, *Im*), 6.13 (d, 1H, J = 14.8 Hz, C*H*$_2$), 5.48 (d, 1H, J = 14.8 Hz, C*H*$_2$), 4.63−4.59 (m, 2H, *COD*), 3.96 (s, 3H, N*Me*), 2.98 (br, 1H, *COD*), 2.87 (br, 1H, *COD*), 2.31 (s, 3H, *Me*), 2.00 (s, 6H, *Me*), 2.24−1.63 (m, 8H, *COD*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 179.8 (Ir−*C*), 158.7, 155.4, 137.1, 137.0, 135.1, 128.0, 123.6, 121.8, 120.8, 120.0, 85.0 (*COD*), 84.5 (*COD*), 56.0 (*CH*$_2$), 52.1 (*COD*), 51.8 (*COD*), 37.7 (N*Me*), 34.2 (*COD*), 33.4 (*COD*), 30.2 (*COD*), 29.5 (*COD*), 21.5, 20.6. Anal. Calcd for $C_{27}H_{33}ClIrN_3$: C, 51.70; H, 5.30; N, 6.70. Found: C, 51.37; H, 4.98; N, 6.45.

[(*C*-pyN^C-Mes)Ir(COD)Cl] (3b). The procedure for the preparation of **3b** is similar to that for **3a**. Yield: yellow solid (73%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (dd, 1H, J = 7.2 and 7.2 Hz, *Py*), 7.63 (d, 1H, J = 7.2 Hz, *Py*), 7.18 (d, 1H, J = 1.6 Hz, *Im*), 7.16 (d, 1H, J = 7.2 Hz, *Py*), 7.01 (s, 1H, *Mes*), 6.92 (s, 2H, *Mes*), 6.87 (s, 1H, *Mes*), 6.70 (d, 1H, J = 1.6 Hz, *Im*), 6.21 (d, 1H, J = 15.2 Hz, C*H*$_2$), 5.71 (d, 1H, J = 15.2 Hz, C*H*$_2$), 4.46−4.45 (m, 2H, *COD*), 2.88−2.85 (m, 1H, *COD*), 2.67−2.64 (m, 1H, *COD*), 2.35 (s, 6H, *Me*), 2.32 (s, 3H, *Me*), 2.03 (m, 2H, *COD*), 1.99 (s, 6H, *Me*), 1.95−1.86 (m, 2H, *COD*), 1.82 (s, 3H, *Me*), 1.79−1.75 (m, 2H, *COD*), 1.53−1.29 (m, 4H, *COD*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 179.6 (Ir−*C*), 159.1, 155.7, 138.1, 137.1, 137.0, 136.6, 136.4, 135.5, 135.1, 133.9, 129.0, 128.0, 127.7, 123.5, 122.4, 121.3, 120.9, 83.4, 83.2, 56.4 (*CH*$_2$), 52.3, 51.3, 34.6, 32.8, 29.8, 29.1, 21.5, 21.4, 20.6, 20.0, 18.1. HR-FAB for $[M - Cl]^+$: calcd, 696.2930 ($C_{35}H_{41}N_3{}^{193}Ir$); found, 696.2936. Anal. Calcd for $C_{35}H_{41}ClIrN_3$: C, 57.48; H, 5.65; N, 5.75. Found: C, 57.03; H, 5.33; N, 5.45.

[(*C,N*-pyN^C-Me)Ir(COD)](BF$_4$) (4a). A mixture of **3a** (100 mg, 0.159 mmol) and silver tetrafluoroborate (32 mg, 0.16 mmol) in CH_2Cl_2 (25 mL) was stirred under nitrogen at the ambient temperature for 1 h. The mixture was filtered through Celite, and the filtrate was added dropwise to a hexane solution. The desired product was precipitated as a brown-red solid (96 mg, 89%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.08 (dd, 1H, J = 7.6 and 0.8 Hz, *Py*), 7.93 (dd, 1H, J = 7.6 and 7.6 Hz, *Py*), 7.59 (d, 1H, J = 1.6 Hz, *Im*), 7.31 (dd, 1H, J = 7.6 and 0.8 Hz, *Py*), 7.03 (s, 1H, *Mes*), 6.91 (s, 1H, *Mes*), 6.89 (d, 1H, J = 1.6 Hz, *Im*), 5.90 (d, 1H, J = 14.8 Hz, C*H*$_2$), 5.85 (d, 1H, J = 14.8 Hz, C*H*$_2$), 4.19−4.15 (m, 1H, *COD*), 3.79 (s, 3H, *NMe*), 3.76−3.73 (m, 1H, *COD*), 3.47−3.43 (m, 1H, *COD*), 2.92−2.86 (m, 1H, *COD*), 2.36 (s, 3H, *Me*), 2.2−2.17 (m, 2H, *COD*), 2.07 (s, 3H, *Me*), 1.85−1.79 (m, 5H, *Me* and *COD*), 1.51−1.42 (m, 1H, *COD*), 1.23−1.08 (m, 3H, *COD*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 173.0 (Ir−*C*), 160.9, 153.7, 139.4, 139.0, 137.5, 135.5, 134.7, 128.5, 128.1, 128.0, 124.7, 122.2, 122.0, 86.3 (*COD*), 84.0 (*COD*), 60.9 (*COD*), 55.2 (*CH*$_2$), 54.0

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Table 1. Crystal Data and Structure Refinement for Complexes **2a**, **3b**, and **5b**

complex	**2a**	**3b**	**5b**
formula	$C_{19}H_{21}AgIN_3$	$C_{35}H_{41}ClIrN_3$	$C_{29}H_{29}BF_4IrN_3O_2{\cdot}CHCl_3$
fw	526.16	731.36	849.93
T, K	295(2)	295(2)	295(2)
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a, Å	7.0698(1)	9.8802(1)	7.7440(1)
b, Å	8.3572(2)	12.2907(1)	20.6300(2)
c, Å	17.2918(4)	26.4927(3)	21.1440(2)
α, deg	91.228(1)	90	89.8300(8)
β, deg	91.613(1)	93.446(1)	86.0530(8)
γ, deg	107.051(1)	90	87.2310(8)
V, Å^3; *Z*	975.90(4); 2	3211.31(6); 4	3365.99(6); 4
d(calcd), Mg/m^3	1.791	1.513	1.677
F(0,0,0)	512	1464	1664
crystal size, mm^3	0.20 × 0.15 × 0.10	0.20 × 0.18 × 0.15	0.25 × 0.20 × 0.15
rflcns collected	7316	20471	21420
indep rflcns	4402 (R_{int} = 0.0308)	7340 (R_{int} = 0.0416)	11820 (R_{int} = 0.0382)
θ range, deg	1.18−27.49	1.83−27.49	2.17−25.00
refined method		full-matrix least squares on F^2	
GOF on F^2	0.974	1.162	1.180
R indices [$I > 2\sigma(I)$]	R1 = 0.0356, wR2 = 0.1137	R1 = 0.0352, wR2 = 0.0894	R1 = 0.0728, wR2 = 0.2076

(*COD*), 37.2 (*NMe*), 35.6 (*COD*), 31.6 (*COD*), 30.1 (*COD*), 27.6 (*COD*), 21.6 (*Me*), 21.5 (*Me*), 21.4 (*Me*). Anal. Calcd for $C_{27}H_{33}BF_4IrN_3$: C, 47.79; H, 4.90; N, 6.19. Found: C, 47.43; H, 4.54; N, 5.97.

[(*C*,*N*-pyN^C-Mes)Ir(COD)](BF$_4$) (4b). The procedure for the preparation of **4b** is similar to that for **4a**. Yield: brown-red solid (105 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.19 (d, 1H, *J* = 8.0 Hz, *Py*), 7.96 (dd, 1H, *J* = 8.0 and 7.6 Hz, *Py*), 7.89 (s, 1H, *Im*), 7.30 (d, 1H, *J* = 7.6 Hz, *Py*), 6.96 (s, 1H, *Mes*), 6.92 (s, 2H, *Im* + *Mes*), 6.84 (s, 1H, *Mes*), 6.68 (s, 1H, *Mes*), 6.07 (d, 1H, *J* = 14.4 Hz, C*H*$_2$), 5.97 (d, 1H, *J* = 14.4 Hz, C*H*$_2$), 4.46−4.43 (m, 1H, *COD*), 3.50−3.42 (m, 2H, *COD*), 2.54−2.46 (m, 1H, *COD*), 2.35 (s, 3H, *Me*), 2.30 (s, 3H, *Me*), 2.19 (s, 3H, *Me*), 2.15−2.10 (m, 2H, *COD*), 1.99−1.65 (m, 6H, *COD*), 1.97 (s, 3H, *Me*), 1.91 (s, 3H, *Me*), 1.63 (s, 3H, *Me*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 171.3 (Ir−*C*), 161.5, 153.8, 139.4, 139.1, 139.0, 137.5, 136.3, 135.1, 135.0, 134.8, 134.3, 128.8, 128.6, 128.5, 127.8, 127.7, 86.2, 80.3, 60.0, 58.3, 55.7 (*C*H$_2$), 36.8, 33.6, 28.8, 26.5, 24.1, 21.5, 21.4, 21.3, 18.7, 18.4. Anal. Calcd for $C_{35}H_{41}BF_4IrN_3$: C, 53.71; H, 5.28; N, 5.37. Found: C, 53.21; H, 5.01; N, 5.05.

[(*C*,*N*-pyN^C-Me)Ir(CO)$_2$](BF$_4$) (5a). Carbon monoxide gas was passed through a solution of **4a** (10 mg, 0.015 mmol) in dichloromethane (25 mL) with stirring for 3 h. The solution slowly turned yellow. The reaction mixture was filtered through Celite, and the filtrate was concentrated. Recrystallization of the residue from a solution of chloroform and hexane gave **5a** as a yellow crystalline solid (9 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.23 (d, 1H, *J* = 7.6 Hz, *Py*), 8.14 (dd, 1H, *J* = 7.6 and 7.6 Hz, *Py*), 7.79 (s, 1H, *Im*), 7.47 (d, 1H, *J* = 7.6 Hz, *Py*), 7.18 (s, 1H, *Im*), 7.02 (s, 1H, *Mes*), 7.00 (s, 1H, *Mes*), 5.96 (d, 1H, *J* = 14.0 Hz, C*H*$_2$), 5.44 (d, 1H, *J* = 14.0 Hz, C*H*$_2$), 3.86 (s, 3H, N*Me*), 2.39 (s, 3H, *Me*), 2.10 (s, 3H, *Me*), 1.74 (s, 3H, *Me*). ^{13}C{^{1}H} NMR (100 MHz, CDCl3): *δ* 179.2 (*C*O), 170.3 (*C*O), 169.7 (Ir−*C*), 163.3, 154.1, 141.5, 140.3, 138.0, 135.3, 134.5, 128.9, 128.8, 127.8, 125.6, 123.5, 123.0, 54.5 (*C*H$_2$), 37.7 (N*Me*), 21.7, 21.4, 21.3. IR (KBr, cm^{-1}): *ν*(CO) 2064 (s), 2004 (s). Anal. Calcd for $C_{21}H_{21}BF_4IrN_3O_2$: C, 40.26; H, 3.38; N, 6.71. Found: C, 40.01; H, 3.00; N, 6.35.

[(*C*,*N*-pyN^C-Mes)Ir(CO)$_2$](BF$_4$) (5b). The procedure for the preparation of **5b** is similar to that for **5a**. Yield: yellow crystalline solid (40.1 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.36 (d, 1H, *J* = 7.2 Hz, *Py*), 8.17 (dd, 1H, *J* = 8.0 and 7.2 Hz, *Py*), 8.08 (s, 1H, *Im*), 7.47 (d, 1H, *J* = 8.0 Hz, *Py*), 6.97 (s, 2H, *Mes*), 6.95 (s, 1H, *Im*), 6.94 (s, 2H, *Mes*), 6.00−5.60 (br, 2H, C*H*$_2$), 2.34 (s, 6H, *Me*), 1.97 (s, 6H, *Me*), 1.93 (s, 6H, *Me*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 172.0 (*C*O), 171.3 (*C*O), 167.3 (Ir−*C*), 164.1, 153.9, 141.8, 140.1, 140.0, 135.8, 133.4, 129.0, 128.5, 128.3, 126.0, 124.0, 123.5, 54.7 (*C*H$_2$), 21.6, 21.5, 18.4. IR (KBr, cm^{-1}): *ν*(CO) 2071 (s), 2004 (s). Anal. Calcd for $C_{29}H_{29}BF_4IrN_3O_2$: C, 47.68; H, 4.00; N, 5.75. Found: C, 47.32; H, 3.73; N, 5.55.

General Procedures for the Reduction of Benzophenone. A mixture of benzophenone (2.5 mmol), the iridium complex (2.5 × 10^{-3} mmol), and KOH (0.1 M) in isopropyl alcohol (2 mL) was heated under refluxing temperature for 12 h. Upon cooling, the solvent was removed under reduced pressure and the residue was dissolved in 1 mL of CH_2Cl_2 for gas chromatography (GC) analysis. Product analysis was also performed by a ^{1}H NMR spectroscopic method. The results are summarized in Table 4.

General Procedures for the Reduction of Nitroarenes. Catalytic reactions were typically performed with 1 mmol of substrate, the iridium complex, and KOH in isopropyl alcohol (4 mL) under nitrogen. The progress of the reaction was monitored by ^{1}H NMR at regular intervals. The reaction mixture was passed through Celite to remove the metal species and salts. The filtrate was concentrated and identified by GC and ^{1}H NMR. In the case of the azo products, the reaction mixture was chromatographed on silica gel with elution of dichloromethane/ethyl acetate and the colored fraction was collected. The desired product was obtained upon concentration and characterized by ^{1}H NMR spectroscopy. Spectral data of all known compounds are consistent with those reported in the literature. Spectral data of the products are provided in the Supporting Information. All results are summarized in Tables 5 and 6.

Crystallography. Crystals suitable for X-ray determination were obtained for **2a**, **3b**, and **5b** by recrystallization at room temperature. Cell parameters were determined by a Siemens SMART CCD diffractometer. Crystal data of these complexes are listed in Table 1. All ORTEP plots are drawn with 30% probability ellipsoids and partial labeling for clarity in Figures 1−3. Other crystallographic data are presented as Supporting Information.

Results and Discussion

Preparation of Iridium Complexes. The method for the preparation of iridium carbene complexes is similar to that

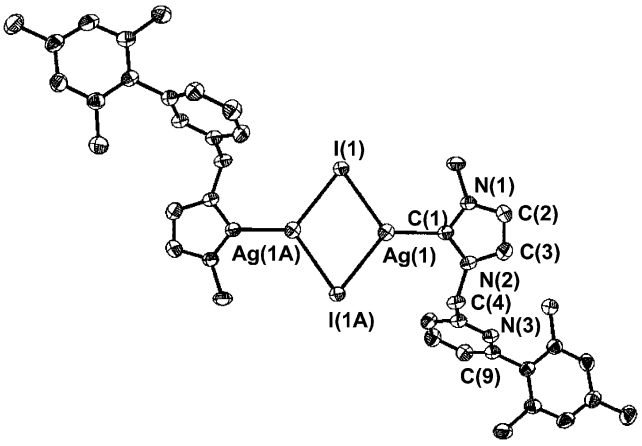


Figure 1. ORTEP plot of complex **2a** (drawn with 30% probability ellipsoids): Ag−C 2.150(3) Å, C(1)−N(1) 1.337(4) Å, C(1)−N(2) 1.364-(5) Å, C(1)−Ag(1)−I(1) 125.68(9)°, Ag(1)−I(1)−Ag(1A) 74.62(1)°.

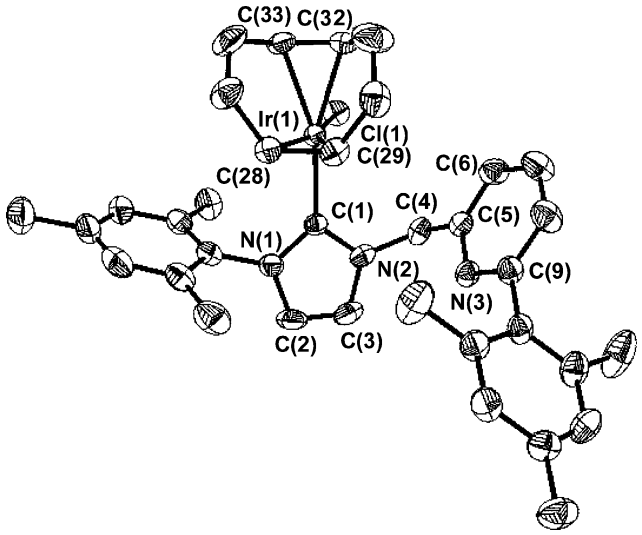


Figure 2. Molecular structure of **3b** (drawn with 30% probability ellipsoids).

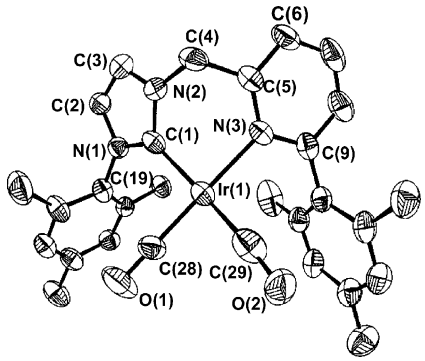
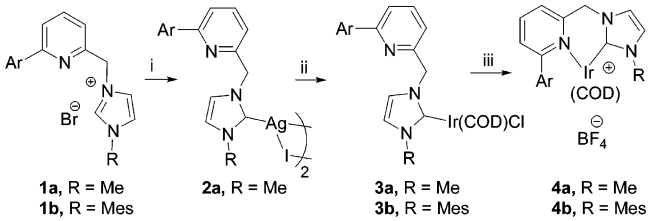


Figure 3. ORTEP plot of the cationic portion of complex **5b** (drawn with 30% probability ellipsoids).

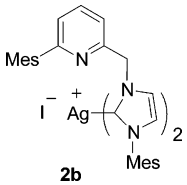
of the rhodium complexes prepared in our laboratory.[11a] In brief, the pyridinylimidazolium salt **1**, the precursor for the carbene ligand, was prepared by a simple substitution reaction of 2-(bromomethyl)-6-mesitylpyridine with the corresponding imidazole. Deprotonation of the imidazolium salt **1** with a strong base, which was expected to produce the corresponding free carbene, unfortunately failed presumably because of interference from the deprotonation of benzylic methylene protons.[12] Alternatively, the imidazolium salt **1** was converted into its silver carbene complex (Scheme 1) via the reaction of **1** with excess of Ag_2O in a dichloromethane solution.[13] The $^{13}C\{^1H\}$ NMR spectrum of the silver complex **2a** shows a characteristic shift for Ag−C(carbene) at δ 184.7, which is reasonably assigned to the 2*C*-imidazol-2-ylidene(carbene) carbon, whereas Ag−C(carbene) for complex **2b** appears at δ 183.5 and is in a similar range as that for Ag−C(carbene).[13] These spectral data clearly illustrate the formation of a silver carbene complex.

Scheme 1 [a]



[a] Ar = mesityl. (i) Ag_2O, NaI. (ii) $[Ir(COD)Cl]_2$. (iii) $AgBF_4$.

Further structural confirmation is given by X-ray analyses. The ORTEP plot of **2a** is shown in Figure 1, while the crystal structure of **2b** has been reported previously.[11a] Unlike **2b**, the molecule comprises two silver atoms bridged by iodide atoms, while the ligand **pyN^C-Me** acts as monodentate from the carbene end. The four-membered ring defined by Ag-(1)−I(1)−Ag(1A)−I(1A) is in a planar arrangement. The long distance of Ag−Ag (3.40 Å) indicates no metal−metal interaction.[11b] The Ag−C bond length is 2.150(3) Å, similar to that of complex **2b** [2.108(4) Å].

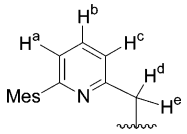


2b

Treatment of $[Ir(COD)Cl]_2$ with the silver carbene complexes **2** in dichloromethane at ambient temperature gave the desired iridium complexes **3** as yellow solids in excellent yields. Characterization of these complexes, **3a** and **3b**, was performed by both spectroscopic and elemental analyses. $^{13}C\{^1H\}$ NMR data for the coordinating carbene carbons appear at δ 179.8 for **3a** and δ 179.6 for **3b**, suggesting the formation of the Ir−C bond. These signals are all in the typical range for Ir−C(carbene) observed for the analogues.[14] The ^1H NMR shifts corresponding to the proton of the pyrindinyl ring are essentially similar to those of the silver complexes (Table 2), indicating that the pyridinyl nitrogen donor remains uncoordinated. Furthermore, ^1H NMR spectra

(12) McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 741.
(13) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972.
(14) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663.

Table 2. ^{1}H NMR Spectral Data for Pyridinyl Hydrogen Atoms in Silver and Iridium Complexes



complex	H^a	H^b	H^c	H^d; H^e
2a	7.54 (d, J = 7.6 Hz)	7.69(dd, J = 7.6 and 7.6 Hz)	7.12 (d, J = 7.6 Hz)	
2b[a]	7.45 (d, J = 8.0 Hz)	7.74 (dd, J = 8.0 and 8.0 Hz)	7.16 (d, J = 8.0 Hz)	
3a	7.51 (d, J = 7.6 Hz)	7.71 (dd, J = 7.6 and 7.6 Hz)	7.12 (d, J = 7.6 Hz)	6.13 (d, J = 14.8 Hz); 5.48 (d, J = 14.8 Hz)
3b	7.63 (d, J = 7.2 Hz)	7.77 (dd, J = 7.2 and 7.2 Hz)	7.16 (d, J = 7.2 Hz)	6.21 (d, J = 15.2 Hz); 5.71 (d, J = 15.2 Hz)
4a	7.93 (dd, J = 7.6 and 0.8 Hz)	8.08 (dd, J = 7.6 and 7.6 Hz)	7.31(dd, J = 7.6 and 0.8 Hz)	5.90 (d, J = 14.8 Hz); 5.85 (d, J = 14.8 Hz)
4b	8.19 (d, J = 8.0 Hz)	7.96 (dd, J = 8.0 and 7.6 Hz)	7.30 (d, J = 7.6 Hz)	6.07 (d, J = 14.4 Hz); 5.97 (d, J = 14.4 Hz)
5a	8.23 (d, J = 7.26 Hz)	8.14 (dd, J = 7.6 and 7.6 Hz)	7.47 (d, J = 7.6 Hz)	5.96 (d, J = 14.0 Hz); 5.44 (d, J = 14.0 Hz)
5b	8.36 (d, J = 7.2 Hz)	8.17 (dd, J = 8.0 and 7.2 Hz)	7.47 (d, J = 8.0 Hz)	6.00−5.60 (br, 2H)

[a] Reference 11a.

Table 3. Selected Bond Distances and Bond Angles of Iridium Carbene Complexes **3b** and **5b**

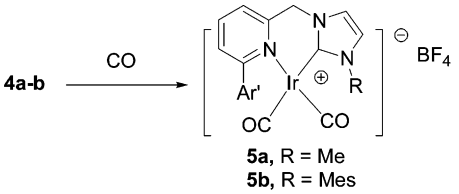
complex	**3b**, X = Cl(1)	**5b**, X = N(3)
Ir(1)−C(1)	2.040(5)	2.05(1)
Ir(1)−C(28)	2.098(4)	1.81(2)
Ir(1)−C(29)	2.099(5)	1.87(2)
Ir(1)−C(32)	2.180(5)	
Ir(1)−C(33)	2.167(5)	
Ir(1)−X	2.385(1)	2.14(1)
N(1)−C(1)−Ir(1)	129.9(3)	136.3(9)
N(2)−C(1)−Ir(1)	126.4(3)	120.2(9)
C(1)−Ir(1)−X	91.2(1)	86.2(4)
C(1)−Ir(1)−C(28)	92.2(2)	93.8(6)
C(1)−Ir(1)−C(29)	91.8(2)	84.5(7)
C(28)−Ir(1)−C(29)	39.8(2)	84.5(7)

of both **3a** and **3b** display an AM type of splitting pattern for the methylene protons (H^d and H^e, respectively). The detailed coordination sphere around the metal center of **3b** is confirmed by the X-ray crystal structural analysis.

The complete molecular structure of **3b** is shown in Figure 2. Selected bond distances and bond angles are listed in Table 3. The structural determination shows that the molecular geometry around the iridium ion is in square-planar arrangement with two coordination sites occupied by carbene and chloride in a cis fashion. The average distance of Ir−C(COD) trans to the carbene donor (2.17 Å) appears to be longer than those in the cis arrangement (2.10 Å), suggesting that the σ-donor nature of the diaminocarbene is stronger than that of the chloride. No major deviation was observed in the bond lengths (Table 3). It is noted that the imidazol-2-ylidene ring is bisected with the coordination plane by ca. 73.2°.

The chelation of **pyN^C-R** toward the iridium center can be achieved by the treatment of **3** with an equimolar amount of $AgBF_4$, leading to the ligand substitution of chloride by the pyridinyl nitrogen. The appearance of δ 173.30 for **4a** and δ 171.3 for **4b** in the $^{13}C\{^1H\}$ NMR spectra was assigned to the carbene carbon atoms, which are essentially similar to those of **3a** and **3b**. All of the ^{1}H NMR signals of the pyridinyl hydrogen atoms in **4a** and **4b** are shifted downfield relative to those in the silver complexes and **3a** and **3b**, indicating chelation of the **pyN^C-R** ligand. It is noticed that ^{1}H NMR spectra of **4a** and **4b** exhibit an AB type of splitting pattern for the methylene protons (Table 2). Besides the spectral data, elemental analyses are consistent with the proposed formula.

Under an atmospheric pressure of carbon monoxide, a stirred solution of **4a** and **4b** gave the carbonyl-substituted iridium complexes **5a** and **5b**, respectively (eq 1). IR spectra of these complexes show two carbonyl stretching bands at 2064 and 2004 cm^{-1} for **5a** as well as 2071 and 2004 cm^{-1} for **5b**, characteristic of the iridium dicarbonyl moiety. The coordination of the strong π-acid ligands around the metal center causes the downfield shift of the pyridinyl protons in the ^{1}H NMR spectrum (Table 2). In addition to the spectral data, an X-ray single-crystal structure of **5b** was determined to confirm the coordination environment of the complex.



5a, R = Me
5b, R = Mes

(1)

An ORTEP diagram of **5b** is represented in Figure 3, and selected bond distances and bond angles can be found in Table 3. As expected, the geometry around the metal center is square-planar, with the chelating **pyN^C-Me** [bite angle 86.2(4)°] and two carbonyl ligands. The chelating ring is adopted into a boat conformation, which allows the two methylene protons to be in different environments, which is in agreement with the spectroscopic observation. The ^{1}H NMR shifts of $-CH_2-$ appear as two sets of doublets at δ 5.96 and 5.44 with the germinal coupling constant ∼14 Hz. All M−C bond lengths, including Ir−C(carbene) [2.05(1) Å] and Ir−C(carbonyl) [1.81(2) and 1.87(2) Å], lie in the

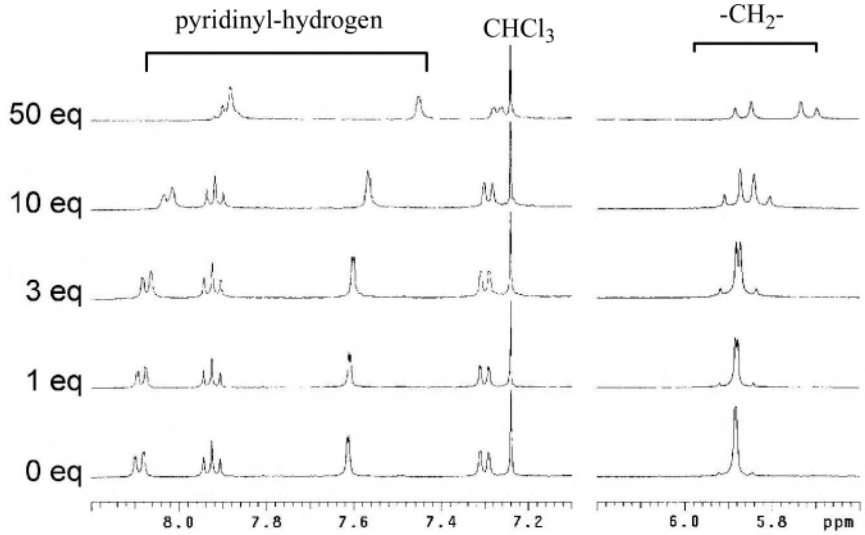


Figure 4. ^{1}H NMR spectra of **4a** in the presence of various amounts of acetonitrile in $CDCl_3$.

normal range, except the angle of N(1)−C(1)−Ir [136.3-(9)°]. The large deviation from 120° of this angle is presumably caused by the steric interaction of the mesityl group and the carbonyl ligand around the metal center. It is also noticed that the Ir−C(carbonyl) trans to the carbene moiety appears to be longer than that of the cis orientaion by about 0.06 Å, as anticipated, because of the trans influence.

Ligand Lability. Nitrogen-donor ligands are, in general, more labile than those containing the more strongly binding carbene donors. In solution, the pyridinyl nitrogen donor of **4** undergoes dissociation with added acetonitrile, and NMR experiments were applied to study the exchange. Various amounts of acetonitrile were added to a $CDCl_3$ solution of **4a** (0.01 M), and the ^{1}H NMR spectra of these samples were recorded at ambient temperature (Figure 4). As the concentration of acetonitrile is increased, the signals of the pyridinyl hydrogen atoms and the methylene unit broaden. In addition, the resonances of the pyridinyl hydrogen atoms shift upfield, whereas the splitting patterns corresponding to the methylene unit are changed from the AB system to the AM system. For the ^{1}H NMR spectrum of **4a** in the presence of excess of acetonitrile, both the chemical shifts and the splitting pattern resemble those of complex **3a** in $CDCl_3$, indicating that the coordinating pyridinyl nitrogen has been replaced by the acetonitrile. Complex **4b** behaves similarly.

Hydrogen-Transfer Reduction. The hydrogen-transfer reduction of a carbonyl function catalyzed by transition-metal complexes is well-documented (Scheme 2).[15] Likewise, the iridium complexes **3**−**5**, with the mixed carbene−pyridinyl nitrogen donors, are effective for the reduction of benzophenone. A mixture of substrate, the iridium complex (0.1 mol %), and KOH (0.1 M) in isopropyl alcohol was heated to reflux for 12 h, and the product was obtained by a simple workup procedure. The results of the reduction catalyzed by **3**−**5** are compiled in Table 4.

Scheme 2

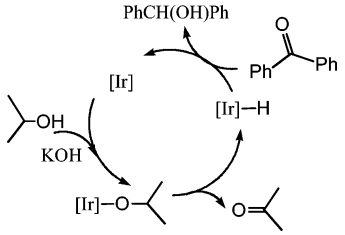


Table 4. Catalytic Transfer Hydrogenation on the Reduction of Benzophenone[a]

entry	catalyst (mol %)	yield (%)	TOF[b]
1	**3b** (0.1)	93	78
2	**3a** (0.1)	90	75
3	**4a** (0.1)	50	42
4	**4b** (0.1)	53	44
5	**5a** (0.1)	60	50

[a] Benzophenone (2.5 mmol), catalysts 2.5×10^{-3} mmol, KOH (0.1 M) in isopropyl alcohol (2 mL) under refluxing temperature for 12 h. [b] TOF = moles of product/moles of catalyst per hour.

As we can see from Table 4, complexes **3a** and **3b** with the **pyN^C-R** ligand binding in a monodentate fashion show a slightly higher catalytic activity compared to their respective chelation complexes **4a**, **4b**, and **5a**. Nevertheless, these iridium complexes show decent activity toward the hydrogen-transfer reduction of benzophenone. Under similar conditions, also noted is that the TOF in **3a** is on the same order of magnitude as that found by Hahn et al. using a five-coordinated iridium speces.[16]

The promising result on the reduction of benzophenone encouraged us to further explore the catalytic capability toward the reduction of nitroarenes. In a typical case, *p*-bromonitrobenzene, the iridium complex, solid KOH, and isopropyl alcohol were placed in a round-bottomed flask and the mixture was heated under reflux with stirring. The progress of the reaction was monitored by thin-layer chro-

(15) Recent review: Saluzzo, C.; Lemaire, M. *Adv. Synth. Catal*. **2002**, *344*, 915 and references cited therein.

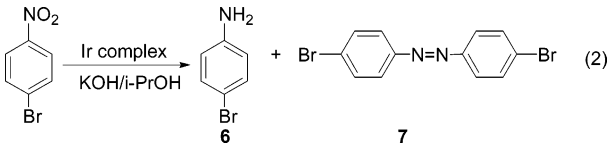
(16) Hahn, F. E.; Holtgrewe, C.; Pape, T.; Martin, M.; Sola, E.; Oro, L. A. *Organometallics* **2005**, *24*, 2203.

Table 5. Reduction of *p*-Nitrobromobenzene Using Iridium Carbene Complexes[a]

entry	catalyst concn	[KOH] (M)	temp	time (h)	conv (%)	yield[b] **6**	yield[b] **7**
1	$[Ir(COD)Cl]_2$, 6.25×10^{-4} M	1.0	reflux	24	24	30	10
2	$[Ir(COD)Cl]_2$, 2.5×10^{-3} M	1.0	reflux	12	50	49	trace
3	**3a**, 2.5×10^{-3} M	1.0	reflux	12	88	72	13
4	**3a**, 2.5×10^{-3} M	0.5	reflux	12	80	42	34
5	**3a**, 2.5×10^{-3} M	0.1	reflux	12	100	18	73
6	**3a**, 5.0×10^{-3} M	1.0	reflux	12	90	80	trace
7	**3a,** 6.25×10^{-4} M	1.0	reflux	24	96	3	81 (76)
8	**3a**, 2.5×10^{-3} M	1.0	rt	12	69	64	0
9	**3b**, 2.5×10^{-3} M	1.0	reflux	12	60	14	40
10	**4b**, 2.5×10^{-3} M	1.0	reflux	12	96	86	6
11	**4a**, 2.5×10^{-3} M	1.0	reflux	12	98	89 (81)	3
12	**5a**, 2.5×10^{-3} M	1.0	reflux	12	98	(73)	trace

[a] Reaction conditions: nitrobenzene (0.1 mmol), catalyst, and KOH in isopropyl alcohol (4 mL). [b] NMR yield, isolated yields given in parentheses.

matography. After completion, followed by the usual workup procedures on the reaction mixture, aniline was produced, accompanied by the corresponding azo product (eq 2). Accordingly, a survey on a representative reduction of 4-bromonitrobenzene with various iridium complexes was carried out, and the results are listed in Table 5.

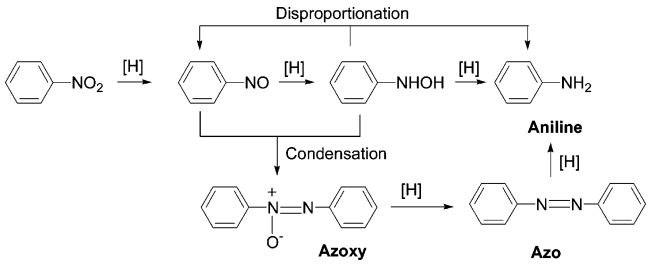


(2)

As shown in the Table 5, the conversion is faster for the iridium carbene complexes **3**−**5** as compared to $[Ir(COD)Cl]_2$, with more than 80% conversion after 12 h under refluxing conditions. There is no significant difference in activity among all iridium complexes under similar conditions. The concentration of the base and catalysts, however, could affect the selectivity of the products. Increasing the base concentration resulted in a higher amount of the reduction product **6**. On the other hand, the amount of the azo product **7** increased with the use of a lower concentration of KOH (see Table 5, entries 3−5). In principle, the catalytic path toward reduction over the formation of the azo compound **7** could be achieved if we carried the reaction under a higher dosage of catalyst (entry 6). When the reaction was carried out under a diluted concentration of the catalyst, the azo compound **7** was obtained predominately (Table 5, entry 7). This is probably attributable to the dominant metal-catalyzed hydrogen-transfer reduction, namely, that the higher concentration of catalyst favors the reduction path. The iridium complex **3a** is less active when carrying out the reduction at room temperature, with only 69% conversion over 12 h but with higher selectivity for providing solely the reduction product.

The reduction steps of nitrobenzene leading to aniline are quite complex. A generally accepted mechanistic pathway is depicted in Scheme 3, in which the aniline can be obtained via either the direct reduction or the condensation followed by reduction;[17] the latter route is favorable under the basic conditions. In this work, the iridium carbene complexes are

Scheme 3



found to play a key role in the reduction of aromatic nitro compounds via a catalytic transfer hydrogenation similar to that for the reduction of carbonyl functionality. The higher concentration of KOH increases the concentration of isopropoxide, which further accelerates the ligand substitution on the metal center. The net result speeds up the β-elimination and the reduction process to yield the aniline product. Under a lower concentration of the catalyst, the base-catalyzed condensation of nitroso and hydroxyamine intermediates becomes the major pathway, yielding predominately the azo compound (Table 5, entry 7).

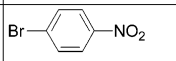
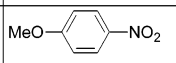
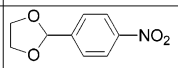
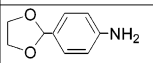
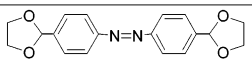
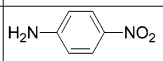
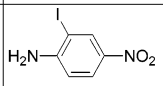
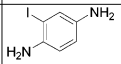
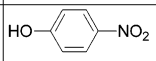
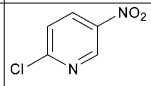
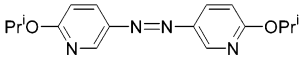
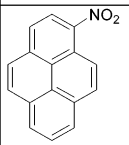
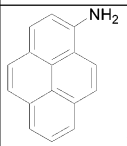
Under a similar reduction condition, we found that the iridium carbene complex catalyzes the reduction of the azo compound to aniline in a very slow manner, with less than 10% of the azo compounds converted into aniline by the use of **3a**, the result of which explains why the azo compound can be obtained as the major product.

Hydrogen-transfer reductions of various nitroarenes in the presence of catalytic amounts of iridium carbene complexes were carried out under the same reaction conditions as those described for the reduction of *p*-bromonitrobenzene, and the results are summarized in Table 6. All instances provide good yields of the desired product except when *p*-nitrophenol and 2-chloropyridine were used. It is noticed that the iodo group is largely replaced by hydrogen in the reduction of 2-iodo-4-nitroaniline (entry 5). Catalytic hydrogen-transfer reduction of 2-chloropyridine resulted in the formation of bis(6-isopropoxypyridin-3-yl)diazene in poor yield (18%), indicating that the chloride in the pyridine ring was replaced by isopropoxide.

In summary, we have successfully prepared iridium pyridinyl N-heterocyclic carbene complexes and studied their

(17) Blaser, H.-U. *Science* **2006**, *313*, 312.

Table 6. Hydrogen-Transfer Reduction of Nitroarenes[a]

entry	substrate	Catalyst, [Cat.]	base	time	products and yield[b] aniline product	azo product
1					*p*-$BrC_6H_4NH_2$	*p*-$BrC_6H_4N{=}NC_6H_4Br$-*p*
		4a, 2.5 x 10^{-3} M	[KOH] 1.0 M	24 h	89 % (81 %)	3 %
		3a, 6.25 x 10^{-4} M	[KOH] 1.0 M	24 h	3 %	81 % (74%)
2					*p*-$MeOC_6H_4NH_2$	*p*-$MeOC_6H_4N{=}NC_6H_4OMe$-*p*
		4a, 2.5 x 10^{-3} M	[KOH] 2.0 M	12 h	100% (97%)	
		4a, 6.25 x 10^{-4} M	[KOH] 1.0 M	12 h	trace	89 %(82%)
3						
		4a, 2.5 x 10^{-3} M	[KOH] 2.0 M	12 h	74 %	8 %
		3a, 6.25 x 10^{-4} M	[KOH] 0.1 M	12 h	0 %	66% (54%)
4					*p*-$H_2NC_6H_4NH_2$	
		4a, 2.5 x 10^{-3} M	[KOH] 2.0 M	12 h	(100 %)	
5						*p*-$H_2NC_6H_4NH_2$
		4a, 2.5 x 10^{-3} M	[KOH] 2.0 M	12 h	20 %	71 %
		4a, 2.5 x 10^{-3} M	[KOH] 1.0 M	12 h	0 %	(100 %)
6		**4a**, 2.5 x 10^{-3} M	[KOH] 2.0 M	12 h	No reaction	
7						
		4a, 2.5 x 10^{-3} M	[KOH] 1.0 M	12 h	(18 %)	
8						
		4a, 2.5 x 10^{-3} M	[KOH] 1.0 M	12 h	99% (96%)	

[a] Reaction conditions: substrate (1 mmol), catalyst, and KOH in isopropyl alcohol (4 mL) under refluxing temperature. [b] NMR yield, isolated yields given in parentheses.

coordination behaviors. Compared to the carbene donor, the pyridinyl nitrogen donor is more labile and is readily replaced by acetonitrile. The prepared iridium complexes have shown salient catalytic activity upon hydrogen-transfer reductions of carbonyl and nitro functionalities. More importantly, these studies explore a great potential for the selective reduction of nitroarene to aniline derivatives or azo compounds. The results should attract a broad spectrum of interest in the fields of organometallics and catalysis.

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Supporting Information Available: Complete description of the X-ray crystallographic structure determination of **2a**, **3b**, and **5b** including tables of atomic coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles provided as CIF files and spectral data of reduction products. This material is available free of charge via the Internet at http://pubs.acs.org.

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