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Methylation of Amines and Ketones with Methanol Catalyzed by an Iridium Complex Bearing a 2-Hydroxypyridylmethylene Fragment

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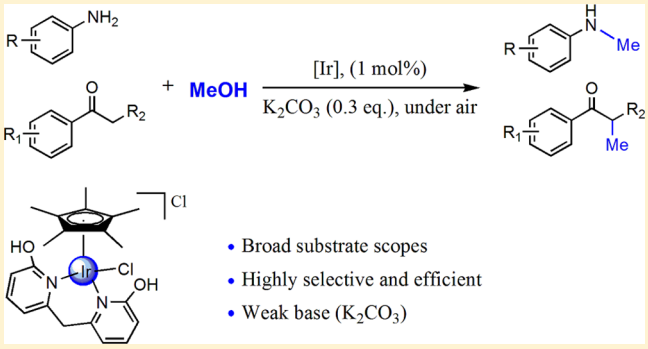
Supporting Information

ABSTRACT: Reaction of complex [Cp*Ir-($HOC_5H_3CH_2C_5H_3OH$)Cl][Cl] (**1**) with AgOTf generated the product [Cp*Ir($HOC_5H_3CH_2C_5H_3OH$)(H_2O)][OTf]$_2$ (**2**), which was further transformed to the complex [Cp*Ir-($OC_5H_3CH_2C_5H_3O$)(H_2O)] (**3**) in the presence of *t*-BuONa via −OH deprotonation. Complexes **1**−**3** exhibited high activity for the methylation of amines and ketones. These C−C and C−N coupling reactions proceeded in air with 1 mol % catalyst loading in the presence of K_2CO_3.



INTRODUCTION

The borrowing hydrogen (BH) reaction, which is also known as hydrogen autotransfer, has become an elegant protocol for the coupling of C−C and C−N bonds during the past years.[1] Traditional methods for methylation of amines, ketones, or other methylene compounds are usually dependent on the utilization of toxic methyl halides and excess base.[2] As methanol is an abundant, atom-economical and environmentally friendly C_1 source, transition-metal-based BH methylation using methanol as a C_1 source for the selective transformation of C−H and N−H bonds to C−CH_3 and N−CH_3 bonds has received increasing attention in green chemistry.[3] For example, several catalysts have been applied to the methylation of ketones to construct C−CH_3 bonds,[4] and more studies have been reported for *N*-methylation of amines to construct N−CH_3 bonds.[5]

Although significant achievements have been made, strong bases (NaOH, *t*-BuONa, KOH, *t*-BuOK, and *t*-BuOLi) are usually necessary in two such kinds of reactions.[4,5] Recently, the Li group developed a new Cp*Ir complex **a** bearing a 2,2′-bibenzimidazole functional ligand with protic hydrogens and studied its catalytic reactivity for *N*-methylation of various amines with methanol in the presence of a weak base (Cs_2CO_3) (Figure 1, left).[5g] When aniline was used as the substrate, the yield reached 98% in 12 h with 1 mol % of catalyst and 0.3 equiv of Cs_2CO_3 at 120 °C. When Cp*Ir complexes with 2-hydroxypyridine derivatives, which were reported by Fujita, Yamaguchi, and co-workers,[6] were tried as catalysts under the same conditions, the results were not very good. For example, the yield was decreased to 90% when complex **b**[6c] was used as the catalyst (Figure 1, middle). When Cs_2CO_3 was replaced by a weaker base (K_2CO_3), a relatively low yield (84%) was obtained.[5g]

More recently, our group designed the ruthenium hydride complex **c** based on the ligand [$HOC_5H_3NCH_2C_5H_3NC_5H_3NOH$], which contains one −$CH_2C_5H_3OH$ and one −C_5H_3OH located at the 6- and 2-positions of the middle pyridyl ring. When it was treated with 2 equiv of *t*-BuOK, **c** was transformed into **d** via selective deprotonation, which means that the −OH group of −$C_5H_3CH_2C_5H_3OH$ is more acidic than that of −$C_5H_3C_5H_3OH$ (Scheme 1).[7] Hence, by the introduction of a methylene group into the 6,6′-dihydroxy-2,2′-bipyridine part of complex **b**, the acidity of the resulting complex will increase, and it might achieve better catalytic activity for N−CH_3 and C−CH_3 coupling in the presence of a weaker base (Figure 1, right). Herein we report the synthesis and reactivity of the new Cp*Ir complex [Cp*Ir($HOC_5H_3CH_2C_5H_3OH$)Cl][Cl] (**1**), bearing a 2-hydroxy-6-((6-hydroxypridin-2-yl)methyl)pyridine ligand ($HOC_5H_3CH_2C_5H_3OH$, $\mathbf{L_1}$) (Figure 1, right). In addition, it showed high catalytic efficiency for the methylation of amines and ketones with methanol, in the presence of K_2CO_3.

RESULTS AND DISCUSSION

Synthesis and Characterization of Ligand and Complexes. As shown in Scheme 2, $\mathbf{L_1}$ was obtained by the reaction of HBr (40% in water) with 2-methoxy-6-((6-methoxypyridin-2-yl)methyl)pyridine at reflux for 3 h in 92% yield. When $\mathbf{L_1}$ was treated with $[Cp^*IrCl_2]_2$ in boiling CH_3OH for 6 h, the yellow product [Cp*Ir-($HOC_5H_3CH_2C_5H_3OH$)(Cl)][Cl] (**1**) was isolated in 90%

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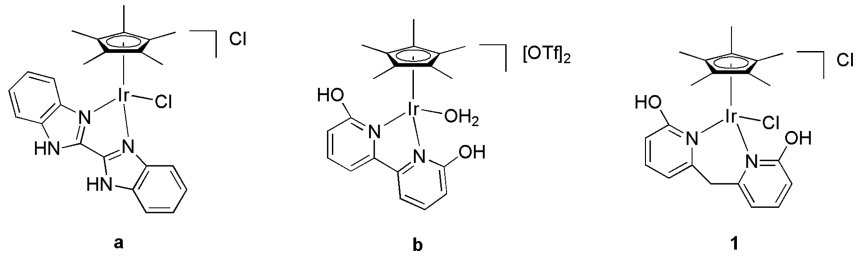
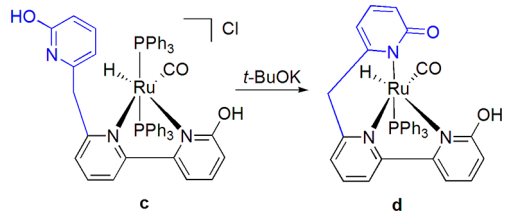
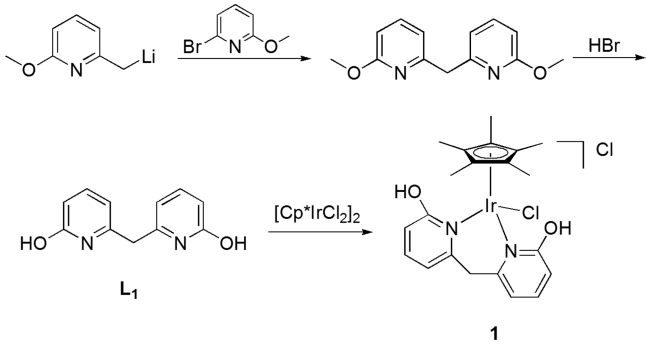


Figure 1. Li's iridium complex **a** (left), Fujita's iridium complex **b** (middle), and complex **1** in this work (right).

Scheme 1. Selective Deprotonation from Complex c to d



Scheme 2. Synthesis of Compounds L_1 and 1



yield. The ^{1}H NMR spectrum of **1** in d_6-DMSO exhibits one singlet at 11.60 ppm for its two −OH groups, three signals between 7.36 and 6.05 ppm for its aromatic protons, one singlet at 3.66 ppm for its methylene protons, and one singlet for the Cp* at 1.63 ppm. In principle, the methylene protons are diastereotopic and should appear as two doublets rather than one singlet. This phenomenon might be because the difference in the chemical shifts of these two diastereotopic protons is zero, resulting in the collapse of two doublets to one singlet.[8]

The molecular structure of **1** was further confirmed by X-ray crystallography (Figure 2). The cation is mirror symmetrical, with a symmetric Ir(1)−C(6)−Cl(1) plane. The central Ir atom is coordinated with two pyridyl groups, one Cp* group, and one Cl atom. The two pyridyl rings are not coplanar, with an C(5)−C(6)−C(5A) angle of 113.1(6)°. The Ir(1)−N(1) and Ir(1)−Cl(1) distances are 2.152(4) and 2.4235(15) Å, respectively, comparable to those of complex **b** shown in Figure 1.[6c]

Complex **1** was further treated with AgOTf in water at room temperature, and $[Cp^*Ir(HOC_5H_3CH_2C_5H_3OH)(H_2O)]$-$[OTf]_2$ (**2**) was produced in 82% yield (Scheme 3).[9] The ^{1}H NMR signals for the −OH groups, aromatic protons, and Cp* protons of **2** are similar to those of **1**. Differently, the $-CH_2-$ signals of complex **2** appear as two doublets at 4.52 and 3.65 ppm. In the presence of 2 equiv of *t*-BuONa, **2** was transformed into the complex $[Cp^*Ir(OC_5H_3CH_2C_5H_3O)$-

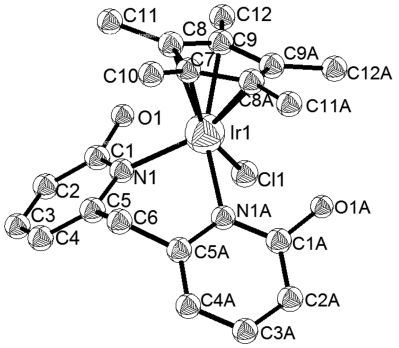


Figure 2. Molecular structure of complex **1**. Hydrogen atoms, solvent, and Cl^- anion have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ir(1)−N(1), 2.152(4); Ir(1)−N(1A), 2.149(2); Ir(1)−Cl(1), 2.4235(15); Ir(1)−C(7), 2.155(4); Ir(1)−C(8), 2.178(5); Ir(1)−C(9), 2.164(6); N(1)−Ir(1)−N(1A), 86.0(2); N(1)−Ir(1)−Cl(1), 86.09(11); N(1A)−Ir(1)−Cl(1), 86.09(11).

$(H_2O)]$ (**3**) in 80% yield (Scheme 3).[10] No −OH signal is shown in the ^{1}H NMR spectrum of complex **3**.

Catalysis. Complexes **1**-**3** were first tested as catalysts for the *N*-methylation of amines. To find the optimal conditions, the reaction of aniline with methanol was selected as the model reaction (Table 1). At 120 °C, in the presence of 0.3 equiv of base, with 1 mol % of complexes **1**−**3** and 2 mL of CH_3OH, the reactions proceeded well in air. It can be seen that the catalytic activity of complexes **1**−**3** was almost identical when Cs_2CO_3 was used as the base (Table 1, entries 1−3), suggesting their similar catalytic processes.[9,11] Complex **1** was then selected as the catalyst for such a transformation because it was more easily synthesized. Two other weak bases, K_2CO_3 and Na_2CO_3, were then tested. K_2CO_3 revealed 93% conversion, similar to that of Cs_2CO_3, while Na_2CO_3 showed worse results (Table 1, entries 4 and 5). In comparison to complex **b** with 6,6′-dihydroxy-2,2′-bipyridine, **1** exhibited higher efficiency when K_2CO_3 was used as the base (93% vs 84%).[5g] In the absence of a base, complex **1** showed no activity, while complex **3** gave a 31% conversion (Table 1, entries 6 and 7). The reaction did not proceed without a base (Table 1, entry 8). When the reactions were carried out with 0.5 mol % catalyst or at 90 °C, the yields were much lower (Table 1, entries 9 and 10). It should be noted that no *N*,*N*-dimethylated product was detected according to GC analysis.

On the basis of the results above, various aromatic amines were tested for the methylation reaction and the results are given in Table 2. Reactions of brominated anilines gave the corresponding products in 62−90% yields (Table 2, entries 2−4). It is obvious that ortho-substituted aniline was less active than meta- and para-substituted anilines due to steric hindrance. An electron-withdrawing amine, 4-aminobenzoni-

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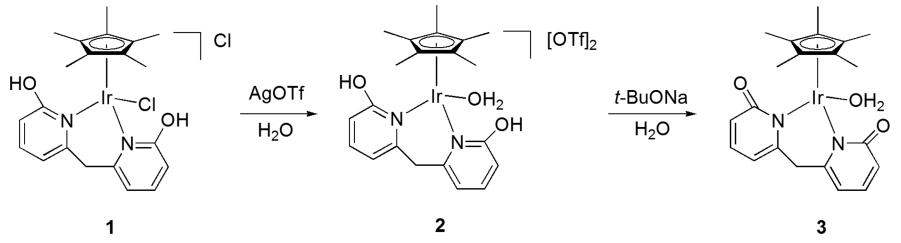
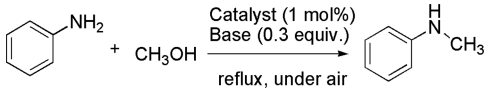
Scheme 3. Synthesis of Complexes 2 and 3



1 2 3

Table 1. Optimization of Reaction Conditions for the Synthesis of *N*-Methylaniline[a]



entry	cat.	base	yield (%)[b]
1	**1**	Cs_2CO_3	94
2	**2**	Cs_2CO_3	92
3	**3**	Cs_2CO_3	93
4	**1**	K_2CO_3	93
5	**1**	Na_2CO_3	79
6	**1**	No base	0
7	**3**	No base	31
8	No Cat.	K_2CO_3	0
9[c]	**1**	K_2CO_3	80
10[d]	**1**	K_2CO_3	61

[a]Conditions unless specified otherwise: aniline (1 mmol), methanol (2 mL), base (0.3 equiv), air, catalyst (1 mol %), 120 °C, 12 h. [b]Yields determined by GC analysis by using *p*-xylene as the internal standard. [c]Reaction was carried out with 0.5 mol % of catalyst. [d]Reaction was carried out at 90 °C.

trile, was selectively monomethylated to give the desired product in 94% yield (Table 2, entry 5). An electron-donating amine was also selectively monomethylated to form the corresponding *N*-methylamine in good yield (Table 2, entry 6). 2-Aminopyridine, 2-naphthylamine, and benzooxazol-2-ylamine were also tested, and the corresponding products were isolated in high yields (Table 2, entries 7−9). In addition, the catalyst was available for *p*-toluenesulfonamide and benzenesulfonamide, affording the desired products in 93% and 94% yields, respectively (Table 2, entries 10 and 11). In addition, an aliphatic amine (phenethylamine) was used with Cs_2CO_3 to give the *N*,*N*-dimethylated product in high yield (Table 2, entry 12).[5g]

Complex **1** was also applied for the methylation of ketones. The reactions of a series of phenyl ketones with methanol were conducted, and the results are given in Table 3. Propiophenone was converted to the methylation product in high isolated yield (Table 3, entry 1). Similar to the *N*-methylation of amines, electron-withdrawing groups in ortho, meta, and para positions of propiophenones also decreased the yields (Table 3, entries 2−4). Electron-donating propiophenones were selectively monomethylated to form the corresponding ketones in good yields (Table 3, entries 5 and 6). Valerophenone was also tested, and the corresponding product was isolated in 92% yield (Table 3, entry 7).

The reaction mechanisms of our work might be consistent with relevant literature reports (Scheme 4).[4d,g,5a,g,11,12] For *N*-methylation, the first step is to generate the unsaturated intermediate **4** by a reaction with base when complex **1** is used as the catalyst. **4** can also be formed through the loss of the coordinated water from complex **3**. Then the intermediate **4** accepts a proton from methanol to afford the iridium methoxy species **5**, which loses one molecule of formaldehyde to generate the iridium hydride species **6**. The formaldehyde and amine are condensed into unsaturated imine, accompanied by the release of one molecule of water. The hydride on iridium and the proton on the ligand of **6** transfer simultaneously to the C═N bond to give the desired product, and the unsaturated intermediate **4** is regenerated. A similar mechanism for *C*-methylation is proposed as well. The nucleophilic carbon anion of ketone is formed and condensed with formaldehyde to give an *α*,*β*-unsaturated ketone. In a similar way, the methylated product is produced through hydrogen transfer from iridium hydride species **6**.

CONCLUSIONS

In summary, three iridium complexes bearing a 2-hydroxy-6-((6-hydroxypridin-2-yl)methyl)pyridine ligand have been synthesized and applied to the methylation of amines and ketones using methanol. These iridium complexes were efficient for such transformations in the presence of a weak base (0.3 equiv of K_2CO_3) in air. Our current work provides alternative methods for the coupling of C−C and C−N bonds, especially when the substrates are sensitive to strong bases. Other experimental studies are ongoing to explore more active transition-metal catalysts.

EXPERIMENTAL SECTION

All manipulations were carried out under an atmosphere of dry nitrogen using vacuum-line and oven-dried standard Schlenk techniques if not otherwise specified. All solvents were distilled from the appropriate drying agents under N_2 before use. All reagents were obtained from commercial suppliers and used without further purification. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer. The ^1H NMR chemical shifts were referenced to the residual solvent as determined relative to Me_4Si (δ 0 ppm). The $^{13}C\{1H\}$ chemical shifts were reported in ppm relative to the carbon resonance of $CDCl_3$ (77.0 ppm) or d_6-DMSO (39.5 ppm). Elemental analyses were performed on a PerkinElmer 240C analyzer. High-resolution mass spectra (HR-MS) were recorded on a Varian 7.0 T FTICR-MS by the ESI technique. IR spectra were recorded on a Nicolet iS5 FT-IR spectrometer. For single-crystal X-ray diffraction, suitable crystals were placed in a cooled N_2 stream at 173(2) K on a Bruker D8 Quest X-ray diffractometer. Data collections were performed using four-circle kappa diffractometers equipped with CCD detectors. Data were reduced and then corrected for absorption.[13] Solution, refinement, and geometrical calculations for all crystal structures were performed by SHELXTL.[14] All GC measurements were performed on Agilent GC7890A equipment using an Agilent 19091B-102 (25 m, 220 μm) column.

Synthesis of 2-Methoxy-6-((6-methoxypyridin-2-yl)methyl)-pyridine. A solution of *n*-BuLi (6.5 mL, 2.4 M, 15.6 mmol) in 10 mL of dry THF was added to 2-methoxy-6-methylpyridine (2.0 g, 15.6 mmol) in THF (25 mL) at −78 °C. When the temperature was raised

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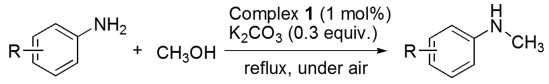
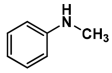
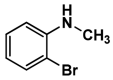
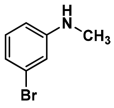
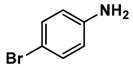
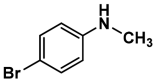
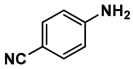
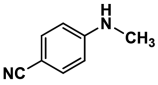
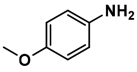
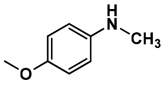
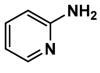
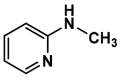
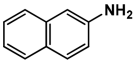
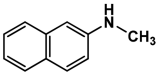
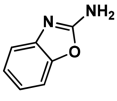
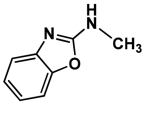
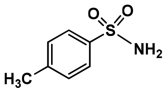
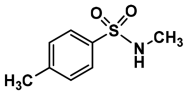
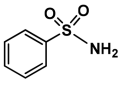
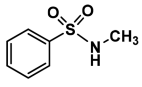
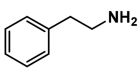
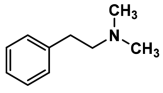
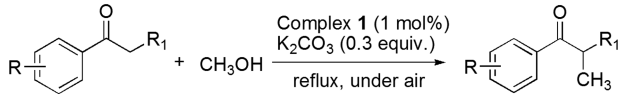
Table 2. Ir-Catalyzed Selective Monomethylation of Anilines or Sulfonamides Using Methanol[a]

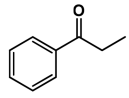
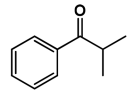
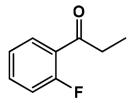
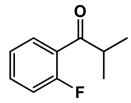
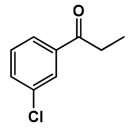
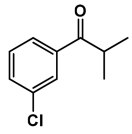
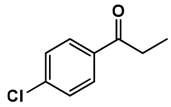
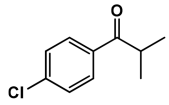
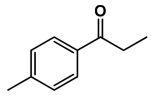
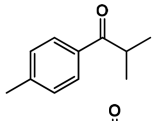
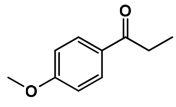
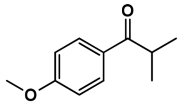
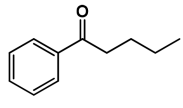
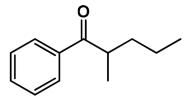


entry	substrate	product	isolated yield (%)[b]
1			91
2			62
3			75
4			90
5			94
6			89
7			83
8			88
9			90
10			93
11			94
12[c]			89

[a]Conditions: aniline (1 mmol), methanol (2 mL), base (0.3 equiv), air, catalyst (1 mol %), 120 °C, 12 h. [b]Yield of isolated product. [c]Reaction was carried out with Cs_2CO_3.

Table 3. Ir-Catalyzed Selective Monomethylation of Propiophenone Derivatives Using Methanol[a]



entry	substrate	product	isolated yield (%)[b]
1			92
2			67
3			78
4			80
5			94
6			93
7			92

[a]Conditions: aniline (1 mmol), methanol (2 mL), base (0.3 equiv), air, catalyst (1 mol %), 120 °C, 12 h. [b]Yield of isolated product.

to −20 °C, 2-bromo-6-methoxypyridine (1.3 g, 7.8 mmol) was added. The reaction mixture was stirred at −20 °C for 3 h and left at room temperature overnight. After the addition of 15 mL of water, the water phase was extracted with CH_2Cl_2. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, v/v 5/1) to give 2-methoxy-6-((6-methoxypyridin-2-yl)methyl)-pyridine (0.97 g, 56%). HR-MS (ESI, *m/z*): calcd for $C_{13}H_{14}N_2O_2$ + H, 231.1134; found, 231.1137. Anal. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.84; H, 6.13; N, 12.21. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.52 (t, *J* = 7.6 Hz, 2H), 6.84 (d, *J* = 7.2 Hz, 2H), 6.59 (d, *J* = 8.4 Hz, 2H), 4.15 (s, 2H), 3.94 (s, 6H). ^{13}C NMR (100 Hz, $CDCl_3$, ppm): 163.6, 157.3, 138.9, 116.0, 107.8, 53.3, 46.4.

Synthesis of L_1. A solution of 2-methoxy-6-((6-methoxypyridin-2-yl)methyl)pyridine (1.3 g, 5.6 mmol) in 10 mL of HBr (40% in water) was heated at reflux for 3 h. After it was cooled to room temperature, the yellow solution was neutralized by slow addition of a saturated aqueous solution of NaOH. The resulting white precipitate was filtered and then dried to afford $\mathbf{L_1}$ as a white solid (1.1 g, 92%). Mp: 181 °C. HR-MS (ESI, *m/z*): calcd for $C_{11}H_{10}N_2O_2$ + H, 203.0821; found, 203.0820. Anal. Calcd for $C_{11}H_{10}N_2O_2$: C, 65.34; H, 4.98; N, 13.85. Found: C, 65.35; H, 4.94; N, 13.88. ^{1}H NMR (400 MHz, d_6-DMSO, ppm): 11.61 (s, 2H), 7.37 (dd, *J* = 9.2, 6.8 Hz, 2H), 6.21 (d, *J* = 9.2 Hz, 2H), 6.06 (d, *J* = 6.8 Hz, 2H), 3.67 (s, 2H). No satisfactory ^{13}C NMR data could be obtained due to low solubility.

Synthesis of 1. A solution of $\mathbf{L_1}$ (0.1 g, 0.5 mmol) and $[Cp^*IrCl_2]_2$ (0.2 g, 0.25 mmol) was refluxed in dried CH_3OH (30 mL) with stirring for 6 h. The mixture was cooled to room temperature, and the yellow precipitate was collected, washed with ether, and dried under vacuum to provide **1** (0.26 g, 90%). Single crystals suitable for X-ray crystallographic determination were grown with $CH_2Cl_2/CH_3OH/n$-hexane at ambient temperature. Mp: 203 °C. Anal. Calcd for $C_{21}H_{25}Cl_2IrN_2O_2$: C, 42.00; H, 4.20; N, 4.66. Found: C, 42.13; H, 4.22; N, 4.59. ^{1}H NMR (400 MHz, d_6-DMSO, ppm): 11.60 (s, 2H), 7.36 (dd, *J* = 6.8, 6.0 Hz, 2H), 6.21 (d, *J* = 6.8 Hz, 2H), 6.06 (d, *J* = 6.0 Hz, 2H), 3.66 (s, 2H), 1.63 (s, 15H). No satisfactory ^{13}C NMR data could be obtained due to low solubility.

Synthesis of 2. AgOTf (0.08 g, 0.32 mmol) was added to a solution of **1** (0.1 g, 0.16 mmol) in H_2O (10 mL) with stirring for 1 h

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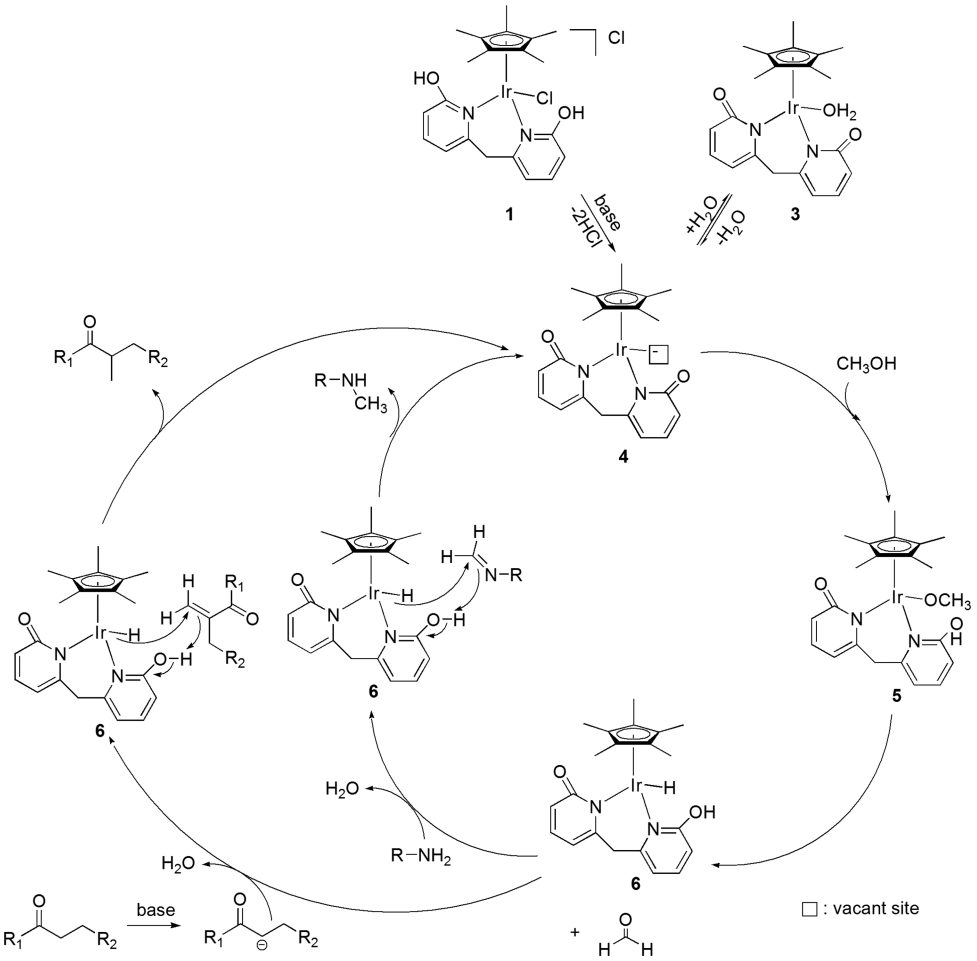
Scheme 4. Proposed Mechanism of Methylation with Iridium Catalysts



at room temperature. Then the precipitate was filtered and the solution was concentrated. The crude product was recrystallized with CH_2Cl_2/ether to give **2** as a yellow powder (0.1 g, 82%). Mp: 217 °C. Anal. Calcd for $C_{23}H_{27}F_6IrN_2O_9S_2$: C, 32.66; H, 3.22; N, 3.31. Found: C, 32.65; H, 3.27; N, 3.28. ^{1}H NMR (400 MHz, d_6-DMSO, ppm): 13.35 (s, 2H), 7.88 (t, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 4.52 (d, J = 14.4 Hz, 1H), 3.89 (s, 2H), 3.65 (d, J = 14.4 Hz, 1H), 1.58 (s, 15H). ^{13}C NMR (100 Hz, d_6-DMSO, ppm): 163.7, 153.3, 143.7, 125.9, 122.7, 119.5, 117.1, 116.3, 111.4, 100.9, 87.7, 46.6, 9.6.

Synthesis of 3. *t*-BuONa (0.023 g, 0.24 mmol) was added to a solution of **2** (0.1 g, 0.12 mmol) in H_2O (10 mL) with stirring for 1 h. Then the precipitate was filtered and the solution was concentrated. The crude product was recrystallized with CH_2Cl_2/ether to give **3** as a yellow powder (0.05 g, 80%). Mp: 201 °C. Anal. Calcd for $C_{21}H_{25}IrN_2O_3$: C, 46.22; H, 4.62; N, 5.13. Found: C, 46.15; H, 4.61; N, 5.34. ^{1}H NMR (400 MHz, d_6-DMSO, ppm): 7.03 (dd, J = 6.8, 5.2 Hz, 2H), 6.10 (d, J = 5.2 Hz, 2H), 5.97 (d, J = 6.8 Hz, 2H), 3.65 (d, J = 11.6 Hz, 1H), 3.34 (s, 2H), 3.29 (d, J = 11.6 Hz, 1H), 1.60 (s, 15H). ^{13}C NMR (100 Hz, d_6-DMSO, ppm): 169.8, 153.6, 138.1, 114.4, 105.4, 49.1, 9.8.

General Procedure for the Methylation of Amines and Ketones. In air, in a 25 mL Schlenk tube, a mixture of amine or ketone (1.0 mmol), methanol (2 mL), complex **1** (6 mg, 1 mol %), and K_2CO_3 (0.041g, 0.3 equiv) was stirred at 120 °C for 12 h; it was cooled to room temperature and 0.1 mL of the reaction mixture was sampled and immediately diluted with 5 mL of CH_2Cl_2 precooled to 0 °C for GC analysis to calculate the conversion and product selectivity of the reaction. After the reaction was completed, the reaction mixture was condensed under reduced pressure and subjected to purification by flash silica gel column chromatography to afford the target product, which was identified by NMR analyses. All analytical data of the known compounds are consistent with those reported in the literature.

N-Methylbenzenamine.[5g] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.17 (t, J = 7.6 Hz, 2H), 6.69 (t, J = 7.6 Hz, 1H), 6.58 (d, J = 7.6 Hz, 2H), 2.78 (s, 3H).

2-Bromo-N-methylbenzenamine.[5l] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.40 (d, J = 8.0 Hz, 1H), 7.19 (t, J = 8.0 Hz, 1H), 6.61−6.54 (m, 2H), 2.87 (s, 3H).

3-Bromo-N-methylbenzenamine.[5k] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 6.99 (t, J = 8.0 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.69 (t, J = 2.0 Hz, 1H), 6.46 (d, J = 8.0 Hz, 1H), 2.75 (s, 3H).

4-Bromo-N-methylbenzenamine.[5g] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.22 (d, J = 8.8 Hz, 2H), 6.42 (d, J = 8.8 Hz, 1H), 2.73 (s, 3H).

4-(methylamino)benzonitrile.[5g] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.42 (d, J = 8.8 Hz, 2H), 6.56 (d, J = 8.8 Hz, 2H), 2.87 (s, 3H).

4-Methoxyl-N-methylbenzenamine.[5k] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 6.78 (d, J = 8.8 Hz, 2H), 6.55 (d, J = 8.8 Hz, 1H), 3.72 (s, 3H), 2.75 (s, 3H).

N-methylpyridin-2-amine.[5g] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.07 (d, J = 4.0 Hz, 1H), 7.41 (t, J = 8.4 Hz, 1H), 6.55 (t, J = 5.2 Hz, 1H), 6.37 (d, J = 8.4 Hz, 1H), 2.89 (s, 3H).

N-Methylnaphthalen-2-amine.[5g] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.65−7.56 (m, 3H), 7.33 (t, J = 7.2 Hz, 1H), 7.17 (t, J = 7.2 Hz, 1H), 6.79−6.73 (m, 2H), 2.82 (s, 3H).

N-Methylbenzo[d]oxazol-2-amine.[5g] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.36 (d, J = 8.0 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.16 (t, J = 8.0 Hz, 1H), 7.02 (t, J = 8.0 Hz, 1H), 3.11 (s, 3H).

N,4-Dimethylbenzenesulfonamide.[5g] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.75 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 1H), 2.64 (s, 3H), 2.43 (s, 3H).

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N-Methylbenzenesulfonamide.[5g] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.87 (d, J = 7.6 Hz, 2H), 7.58 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 8.0 Hz, 2H), 2.62 (s, 3H).

N,N-Dimethylbenzeneethanamine.[15] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.26 (d, J = 7.6 Hz, 2H), 7.19 (d, J = 7.6 Hz, 2H), 2.79−2.75 (m, 2H), 2.54−2.50 (m, 2H), 2.28 (s, 3H).

2-Methyl-1-phenylpropan-1-one.[4d] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.96 (d, J = 7.2 Hz, 2H), 7.54 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.2 Hz, 2H), 3.56 (m, 1H), 1.22 (d, J = 6.8 Hz, 6H).

1-(2-Fluorophenyl)-2-methylpropan-1-one.[4d] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.77 (t, J = 7.6 Hz, 1H), 7.51−7.46 (m, 1H), 7.21 (t, J = 8.4 Hz, 1H), 7.14−7.09 (m, 1H), 3.41 (m, 1H), 1.20 (d, J = 6.8 Hz, 6H).

1-(3-Chlorophenyl)-2-methylpropan-1-one.[4d] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.92 (s, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 3.50 (m, 1H), 1.22 (d, J = 6.8 Hz, 6H).

1-(4-Chlorophenyl)-2-methylpropan-1-one.[4d] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.89 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 3.50 (m, 1H), 1.21 (d, J = 6.8 Hz, 6H).

4-Methyl-1-(2-methylphenyl)propan-1-one.[4d] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.86 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 7.6 Hz, 2H), 3.53 (m, 1H), 1.21 (d, J = 6.8 Hz, 6H).

1-(4-Methoxyphenyl)-2-methylpropan-1-one.[4d] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.95 (d, J = 7.2 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), 3.51 (m, 1H), 1.20 (d, J = 6.8 Hz, 6H).

2-Methyl-1-phenylpentan-1-one.[4d] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.95 (d, J = 7.6 Hz, 2H), 7.54 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 8.0 Hz, 2H), 3.52−3.44 (m, 1H), 1.83−1.75 (m, 1H), 1.47−1.29 (m, 3H), 1.19 (d, J = 6.8 Hz, 6H), 0.90 (d, J = 7.6 Hz, 3H).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00575.

Crystallographic details and NMR spectra of the new compounds (PDF)

Accession Codes

CCDC 1859831 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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