Syntheses of Acyliridium Porphyrins by Aldehydic Carbon−Hydrogen Bond Activation with Iridium(III) Porphyrin Chloride and Methyl

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Acyliridium porphyrins were synthesized by the reactions of aryl aldehydes with iridium(III) porphyrin chloride and methyl under solvent-free conditions with high yields. Selective aldehydic carbon hydrogen bond activation (CHA) was observed without any aromatic CHA in all the cases. Mechanistic investigation on the reactions with Ir(ttp)Cl(CO) suggested that (ttp)Ir cation was a likely intermediate of aldehydic CHA, whereas the CHA with Ir(ttp)Me underwent an oxidative addition or σ bond metathesis pathway. These reactions provided a facile synthesis of (arylacyl)iridium porphyrins.

Introduction

The cleavage of carbon hydrogen bonds using transition metal complexes plays an important role in converting saturated hydrocarbons to functionalized organic compounds.[1,2] Carbon−hydrogen bond activation (CHA) with late transition metal complexes has attracted much interest[3] due to the wide functional group tolerance in substrates of these complexes. Acyl transition metal complexes are important compounds because they are intermediates in carbonylation and decarbonylation reactions of aldehydes and ketones.[4] The syntheses of acylmetal complexes are often accessible via the aldehydic CHA reactions of RCHO with low-valent transition metal complexes. Although the examples of aldehydic CHA with iridium are abundant, most of the activations were focused on iridium(I).[5] In sharp contrast, the aldehydic CHA with Ir(III) complexes are much less reported, with Cp*$IrMe_2$(DMSO)[6] and Cp*IrMe(OTf)[7] being the two most studied complexes. Furthermore, the Ir(I) complexes always gave iridium acyl hydrides, while Ir(III) afforded iridium alkyls after facile decarbonylation.[6,7]

Previously, we have reported the selective, aldehydic CHA of aromatic aldehydes with Rh^{III}(ttp)Cl (ttp = tetrakis(4-tolyl)-porphyrinato dianion) to give acylrhodium porphyrins.[8] In exploring the CHA chemistry of metalloporphyrins, we have discovered that aldehydes reacted with both Ir(ttp)Cl(CO) and Ir(ttp)Me in solvent-free conditions selectively at the aldehydic carbon−hydrogen bond to afford stable acyliridium porphyrins. These reactions provide clean and convenient syntheses of Ir-(ttp)COR and illustrate a unique type of CHA by high-valent iridium(III) complexes.

Results and Discussion

Ir(ttp)Cl(CO) **(1)** reacted with PhCHO under solvent-free conditions to give Ir(ttp)COPh **(2a)** in the absence of light under nitrogen. Initially, Ir(ttp)Cl(CO) **(1)** reacted with benzaldehyde at 100 °C for 2 days to give only trace amount of Ir(ttp)COPh. At 150 °C after 2 days, a higher yield of 16% of Ir(ttp)COPh was obtained. When the temperature was increased to 200 °C, 62% yield of Ir(ttp)COPh was obtained after 2 days. Since Ir-(ttp)Cl(CO) is reactive toward common solvents such as THF, ether, and toluene under high temperature, excess substrates were used as solvent. This CHA reaction was very selective, without any aromatic CHA product or other iridium porphyrin alkyl formed at various temperatures (Table 1, eq 1). The aldehydic CHA of Ir(ttp)Cl(CO) appeared to be cleaner than that of Rh(ttp)Cl as no Ir(ttp)Bn was observed.[8]

When the optimized reaction conditions were applied to various 4-substituted aryl aldehydes, highly selective aldehydic CHA was found to afford the acyl complexes Ir(ttp)COAr **(2a−g)** as the sole liphophilic products in moderate to good yields (Table 2, eq 2). According to thin layer chromatography analysis and NMR spectrum of the crude reaction mixture, no other iridium porphyrin aryl was observed. Both the reaction yields and rates were affected by the electronic effect of some of the substituents. 4-Fluorobenzaldehyde gave the highest product yield of **2e** in 92% in 15 h (entry 5), and the reaction with 4-(α,α,α-trifluoromethyl)benzaldehyde only took 6 h to give 70% yield of **2g** (entry 7), whereas 4-methylbenzaldehyde reacted with Ir(ttp)Cl(CO) at 200 °C in 4 days to give only

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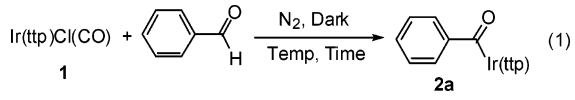
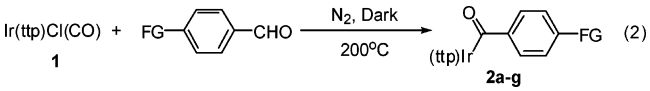
Table 1. Optimization of CHA of PhCHO with Ir(ttp)Cl(CO)



entry	temp (°C)	time (d)	isolated yield (%)
1	100	2	trace
2	150	2	16
3	200	2	62

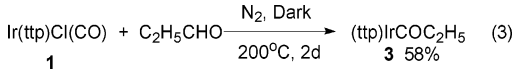
Table 2. CHA of Aryl Aldehydes with Ir(ttp)Cl(CO)



entry	FG	time	isolated compd (yield, %)
1	H	2 d	**2a** (62)
2	OMe	2.5 d	**2b** (62)
3	Me	4 d	**2c** (42)
4	^{t}Bu	1.5 d	**2d** (47)
5	F	15 h	**2e** (92)
6	Cl	1.5 d	**2f** (57)
7	CF[3]	6 h	**2g** (70)

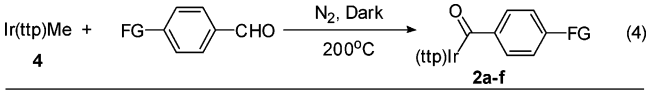
42% yield of **2c** (entry 3). 4-Methoxylbenzaldehyde reacted with Ir(ttp)Cl(CO) to produce **2b** in 62% yield (entry 2). In contrast, it reacted with Rh(ttp)Cl to give no arylrhodium complex but only 11% yield of Rh(ttp)Me.[8] Unfortunately, 4-(*N*,*N*-dimethyamino)benzaldehyde and 4-cyanobenzaldehyde gave unidentified products.

Ir(ttp)Cl(CO) also showed high selectivity in reactions with aliphatic aldehydes. Ir(ttp)Cl(CO) reacted with the enolizable aldehyde C_2H_5CHO to give only the aldehydic CHA product Ir(ttp)COC_2H_5 (**3**) in 58% yield, without any reaction at the α-carbonyl C−H bond (eq 3). In contrast, Rh(ttp)Cl reacted with aliphatic aldehydes at 200 °C in 2 days poorly to give very low yields of acylrhodium porphyrins.[8] Furthermore, Rh(oep)ClO_4 (oep = octaethylporphyrinate), being more Lewis acidic, reacted with enolizable carbonyls at the α-carbonyl C−H bond.[9] Iridium complexes, being more electron rich and less Lewis acidic, likely underwent selective "oxidative addition" at the aldehydic C−H bond. Sterically hindered ^{t}BuCHO however failed to give an acyliridium complex.



Ir(ttp)Cl(CO) is coordinatively saturated and might not be very reactive. Therefore, the coordinatively unsaturated and electron-rich Ir(ttp)Me **(4)** was then examined.[8,10] To our delight, successful aldehydic CHA occurred. The yields and reaction rates were enhanced when compared with those of Ir(ttp)Cl(CO) (Table 3, eq 4). As shown in Table 3, the reaction rates varied with some substituents. The shortest reaction time was

Table 3. CHA of Aryl Aldehydes with Ir(ttp)Me



entry	FG	time (h)	isolated compd (yield, %)
1	H	5	**2a** (71)
2	OMe	4	**2b** (73)
3	Me	6.5	**2c** (55)
4	^{t}Bu	31	**2d** (74)
5	F	2	**2e** (88)
6	Cl	18	**2f** (63)
7	CF[3]	1.5	**2g** (62)

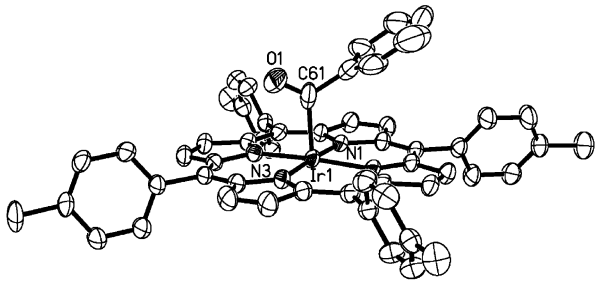


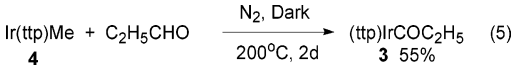
Figure 1. ORTEP drawing of Ir(ttp)COPh (**2a**).

Table 4. Selected Bond Lengths and Bond Angles of Compounds 2a−f

entry	FG	Ir−C(O) length (Å)	Ir−C(O)−C_{aryl} bond angle (deg)
1	H, **2a**	2.038(12)	118.8(7)
2	OMe, **2b**	2.292(11)	117.6(8)
3	Me, **2c**	1.978(14)	116.4(8)
4	^{t}Bu, **2d**	2.004(15)	119.9(10)
5	F, **2e**	1.997(9)	117.9(6)
6	Cl, **2f**	1.970(3)	117.45(16)

obtained by using 4-$CF_3C_6H_4CHO$ (Table 3, entry 7), while the longest reaction time was required by 4-*tert*-butylbenzaldehyde (Table 3, entry 4).

No obvious improvement was observed in the CHA of sterically unhindered aliphatic aldehydes with Ir(ttp)Me. Ir(ttp)Me reacted with C_2H_5CHO to give **3** in 55% yield after 2 days (eq 5). The bulky ^{t}BuCHO remained unreactive.



The carbonyl stretching frequencies of Ir(ttp)COAr appear from 1660 to 1680 cm^{-1}. They are lower than those of Rh(ttp)COAr ranging from 1690 to 1720 cm^{-1}.[8] Apparently, the stronger iridium to carbonyl electron donation may cause the lowering in stretching frequencies.

X-ray Details. The collection and processing parameters of single-crystal data for complexes **2a**−**f** are given in the Supporting Information. Table 4 lists selected bond lengths and angles. The bond lengths of Ir−C are similar to the reported Rh−C bond lengths in Rh(ttp)COR (1.95−1.98 Å)[8] and the Ir−C(O)−C_{aryl} angles are not affected by the *para*-substitutents (Table 4). Moreover, from the calculated dihedral angles and atom displacements (Supporting Information), all iridium atoms do not lie in the defined 24-atom least-squares plane but deviate from the plane. In the solid state, **2a**,**c**−**f** adopt monomeric structures, whereas **2b** is a coordination polymer, in which the oxygen atom of the OMe moiety is coordinated to another Ir(III) center forming a polymeric chain. However, due to the rotation of the molecule, C═O in the carbonyl group and C−O in the methoxyl group appeared identical, which caused the disorder of the X-ray structure. As a representative, Figure 1 shows the molecular structure of Ir(ttp)COPh **(2a)** (30% thermal ellipsoids).

Mechanism: Ir(ttp)Cl(CO). Scheme 1 shows the proposed mechanism of the aldehydic CHA with Ir(ttp)Cl(CO). Initially, Ir(ttp)Cl(CO) undergoes loss of chloride ion at 200 °C to give the coordinatively unsaturated Ir(ttp) cation **A**,[11] possibly with

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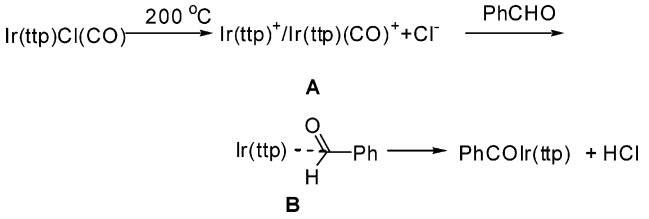
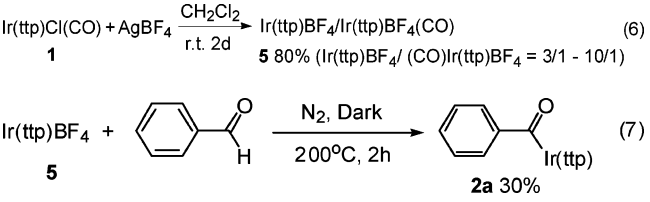
Scheme 1. Mechanism of Aldehydic CHA with Ir(ttp)Cl(CO)

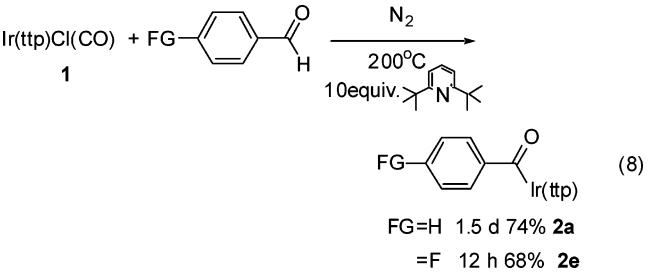


partial dissociation of CO ligand. The carbonyl oxygen of aryl aldehyde then coordinates to the Ir(ttp) cation to give **B**. Finally, the aldehydic C−H bond is activated via heterolysis to give Ir(ttp)COAr and a proton.

The formation of the Ir(ttp) cation intermediate was supported by the rate-accelerated reaction of "Ir(ttp)BF_4". "Ir(ttp)BF_4" was synthesized as an inseparable mixture of Ir(ttp)BF_4 and Ir(ttp)-BF_4(CO) (Ir(ttp)BF_4:(CO)Ir(ttp)BF_4 = 3:1−10:1) from the reaction of $AgBF_4$ with Ir(ttp)Cl(CO) (eq 6). Then "Ir(ttp)BF_4" reacted much faster with PhCHO at 200 °C in just 2 h to give Ir(ttp)COPh **(2a)** in 30% yield (eq 7) comparing with Ir(ttp)-Cl(CO) which took 2 days. The lower yield for **5** was likely due to its thermal decomposition or other side reactions.

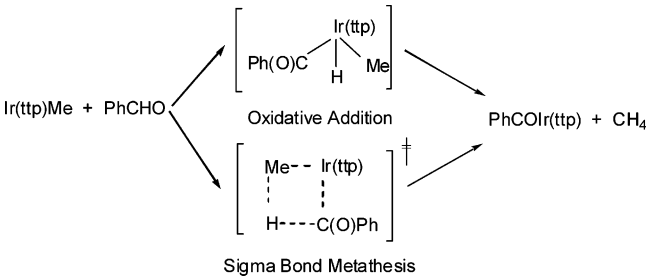


The heterolysis step was substantiated by the rate enhancement with added 2,6-di-*tert*-butylpyridine in the reaction of Ir-(ttp)Cl(CO) with PhCHO (eq 8) (Table 2, entry 1). Likely, the 2,6-di-*tert*-butylpyridine promoted the abstraction of proton in the aryl aldehyde iridium porphyrin complex **B**. Such base-enhanced CHA reactions have been recently reported.[12,13] No obvious rate enhancement was observed in the reaction between Ir(ttp)Cl(CO) and 4-FC_6H_4CHO (eq 8) (Table 2, entry 3). We do not understand the difference. The fluoro group may compete to coordinate to the Ir(ttp) cation and lowers the concentration of Ir−aldehyde complex. Therefore, the base-promoting effect of this substrate is not prominent.

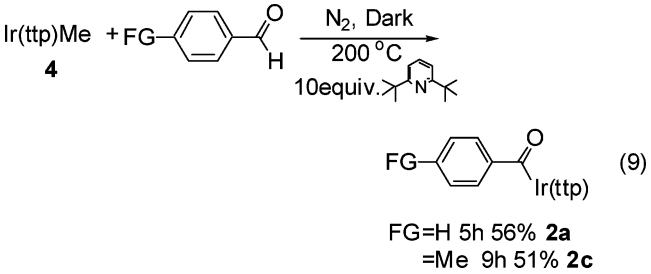


Mechanism: Ir(ttp)Me. The mechanism of CHA by Ir(ttp)-Me appears to undergo an associative type mechanism of either oxidative addition or σ-bond metathesis[2,11] rather than dissociative homolysis or heterolysis (Scheme 2). The Ir−Me bond is stronger than Rh−Me bond, which is about 58 kcal/mol.[14] At 200 °C, the rate of homolysis or heterolysis of Ir−Me is too slow to be a viable pathway. The addition of Ph_3P to Ir(ttp)Me

Scheme 2. Two Possible Mechanisms of Aldehydic CHA with Ir(ttp)Me



only gave coordination product (the ^{1}H NMR spectrum showed upfield shifts of PPh_3 signals and the methyl group signal, split into a doublet with J_{PH} = 7.2 Hz), which completely shuts down the CHA reaction and further suggests the requirement of a vacant coordination site in the reaction with Ir(ttp)Me, by an associative mechanism. Furthermore, addition of 2,6-di-*tert*-butylpyridine did not change the rate and yield of reaction (eq 9). Therefore, heterolysis is excluded. Most likely, the "internal base" of methyl group possibly reacts with PhCHO in a cis-manner either by oxidative addition or σ-bond metathesis (Scheme 2) to give Ir(ttp)COPh.



Conclusions

Facile syntheses of stable iridium acyl complexes were achieved through clean and selective aldehydic CHA with high-valent Ir(III) complexes. Preliminary mechanistic experiments suggest Ir(ttp)Cl(CO) likely activates aldehydes in an electrophilic manner with subsequent heterolysis while Ir(ttp)Me undergoes either an oxidative addition or a σ-bond metathesis pathway.

Experimental Section

Unless otherwise noted, all reagents were purchased from commercial suppliers and purified before use. Hexane for chromatography was distilled from anhydrous calcium chloride. Tetrahyrofuran (THF) was distilled from sodium benzophenone ketyl prior to use. Ir(ttp)Cl(CO)[15] and Ir(ttp)Me[15] were prepared according to the literature procedure. Thin layer chromatography was performed on precoated silica gel 60 F_{254} plated. Silica gel (Merck, 70−230) was used for column chromatography in air.

^{1}H NMR spectra were recorded on a Bruker DPX 300 (300 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in C_6D_6 (δ 7.16 ppm) or $CDCl_3$ (δ 7.26 ppm) or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported in part per million (ppm). ^{13}C NMR spectra were recorded on a Bruker DPX 300 (75 MHz) spectrometer or a Varian XL-400 (100 MHz) and referenced to $CDCl_3$ (δ 77.10 ppm) spectra. Coupling constant (J) were reported

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in hertz (Hz). High-resolution mass spectra (HRMS) were performed on a Thermofinnign MAT 95 XL in FAB (using 3-nitrobenzyl alcohol (NBA) matrix and CH_2Cl_2 as solvent) and ESI (MeOH:CH_2Cl_2 = 1:1 as solvent) modes.

The CHA reactions were carried out in N_2 in dark with the reaction flasks covered with aluminum foil. Unless otherwise stated, the reactions were carried in duplicate and the yields were the average results. The products were purified by column chromatography and ascertained to be pure by ^{1}H NMR spectroscopy.

Preparation of Starting Materials. (5,10,15,20-Tetratolylporphyrinato)iridium(III) Tetrafluoroborate, Ir(ttp)BF_4/(CO)Ir(ttp)BF_4 (5). Ir(ttp)Cl(CO) (60 mg, 0.065 mmol) and $AgBF_4$ (97.5 mg, 0.50 mmol) was added into anhydrous CH_2Cl_2 (50 mL), and the mixture was stirred for 2 days at room temperature. The color of the mixture changed from red to reddish brown after 2 days. Since the product was not stable during column chromatography on silica gel, the mixed products were isolated by filtration and purified by recrystallization from CH_2Cl_2/hexane. The product ratio was calculated from integration of the porphyrin peaks on the ^{1}H NMR spectrum (49.1 mg, 0.052 mmol, 80%, ratio of Ir(ttp)BF_4/(CO)Ir(ttp)BF_4 was batch dependent, ranging from 3:1 to 10:1). R_f = 0.41 (EA). ^{1}H NMR (300 MHz, $CDCl_3$): (A) peaks of (CO)Ir(ttp)BF_4, δ 2.73 (s, 12H), 7.59 (t, 8H, J = 6.6 Hz), 8.07 (d, 4H, J = 11.7 Hz), 8.16 (d, 4H, J = 7.5 Hz), 9.08 (s, 8H); (B) peaks of Ir(ttp)BF_4, δ 2.72 (s, 12H), 7.59 (t, 8H, J = 6.6 Hz), 8.07 (d, 4H, J = 11.7 Hz), 8.16 (d, 4H, J = 7.5 Hz), 9.02 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): (A) peaks of (CO)Ir(ttp)BF_4, δ 141.6, 138.2, 137.5, 133.9, 132.1, 131.3, 128.0, 127.6, 122.8, 21.7; (B) peaks of Ir(ttp)BF_4, 141.5, 138.4, 138.0, 134.7, 133.7, 128.3, 127.7, 123.0, 21.7. The existence of the CO group was demonstrated by both IR (KBr, cm^{-1}) ν(C═O) 2063 (s) and the peak of the CO group found in the ^{13}C NMR spectrum of **5** (δ = 131.3).

Reaction of Aromatic Aldehydes with Ir(ttp)Cl(CO) and Ir(ttp)Me. (5,10,15,20-Tetratolylporphyrinato)(benzoyl)iridium(III), C_6H_5COIr(ttp) (2a). Method A1. Ir(ttp)Cl(CO) (20.4 mg, 0.022 mmol) was added into benzaldehyde (1.0 mL). The red suspension was then heated at 200 °C under N_2 in the dark for 2 days. After 2 days, the mixture turned into dark red in color. Excess benzaldehyde was removed by vacuum distillation. The dark red crude product was then purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (2:1) to give C_6H_5COIr(ttp) (**2a**) as an orange red solid (13.2 mg, 0.014 mmol, 62%), which was further recrystallized from CH_2Cl_2/MeOH. R_f = 0.67 (1:2 hexane/CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.57 (d, 2 H, J = 8.1 Hz), 2.70 (s, 12 H), 5.99 (t, 2 H, J = 7.8 Hz), 6.42 (t, 1 H, J = 7.8 Hz), 7.52 (t, 8 H, J = 6.0 Hz), 7.96 (d, 4 H J = 7.8 Hz), 8.01 (d, 4H, J = 7.8 Hz), 8.62 (s, 8 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.2, 116.9, 124.4, 126.1, 128.1, 132.0, 134.2, 134.6, 138.0, 139.4, 143.4 167.4. HRMS (ESIMS): calcd for $(C_{55}H_{41}N_4OIr+Na)^+$, m/z 989.2802; found, m/z 989.2807. IR (KBr, cm^{-1}): ν(C═O) 1665 (s). The sample for elemental analysis and single crystal was grown from CH_2Cl_2/toluene, and X-ray analysis showed that there was one toluene molecule/iridium porphyrin complex. Anal. Calcd for $C_{55}H_{41}N_4OIr$·toluene: C, 70.36; H, 4.67; N, 5.29. Found: C, 70.68; H, 4.89; N, 4.94.

Method A2. Ir(ttp)Cl(CO) (14.8 mg, 0.016 mmol) and 10 equiv of 2,6-di-*tert*-butylpyridine were dissolved in benzaldehyde (1.0 mL). The red reaction mixture was heated at 200 °C under N_2 in the dark for 1.5 days. The orange red solid was isolated after column chromatography (11.4 mg, 0.012 mmol, 74%).

Method B1. Ir(ttp)Me (14.8 mg, 0.017 mmol) was dissolved in benzaldehyde (1.0 mL). The red reaction mixture was heated at 200 °C under N_2 in the dark for 5 h. The orange red solid was isolated after column chromatography (11 mg, 0.011 mmol, 71%).

Method B2. Ir(ttp)Me (17.8 mg, 0.020 mmol) and 10 equiv of 2,6-di-*tert*-butylpyridine were dissolved in benzaldehyde (1.0 mL). The red reaction mixture was heated at 200 °C under N_2 in the dark for 5 h. The orange red solid was isolated after column chromatography (11 mg, 0.011 mmol, 56%).

Method C. "Ir(ttp)BF_4" (14.9 mg, 0.016 mmol) was dissolved in benzaldehyde (1.0 mL). The red reaction mixture was heated at 200 °C under N_2 in the dark for 2 h. The orange red solid was isolated after column chromatography (4.5 mg, 0.005 mmol, 30%).

(5,10,15,20-Tetratolylporphyrinato)(4-methoxylbenzoyl)iridium(III), 4-MeOC_6H_4COIr(ttp) (2b). Method A. The suspension of Ir(ttp)Cl(CO) (24.1 mg, 0.026 mmol) and anisaldehyde (1.0 mL) was heated at 200 °C under N_2 in the dark for 2.5 days to give a dark red solution. Excess anisaldehyde was removed by vacuum distillation. The reaction mixture was then isolated by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (2:1) to give 4-MeOC_6H_4COIr(ttp) **(2b)** as an orange red solid (16.0 mg, 0.016 mmol, 62%), which was further recrystallized from CH_2Cl_2/MeOH. R_f = 0.41 (1:2 hexane/CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.57 (d, 2 H, J = 8.7 Hz), 2.69 (s, 12 H), 3.45 (s, 3 H), 5.55 (d, 2 H, J = 9.0 Hz), 7.52 (d, 8 H, J = 8.1 Hz), 7.93 (d, 4 H, J = 7.8 Hz), 8.02 (d, 4 H, J = 5.7 Hz), 8.64 (s, 8 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.2, 55.5, 111.2, 118.9, 124.4, 128.2, 132.0, 134.2, 134.6, 138.0, 139.4, 143.5, 157.4. HRMS (ESIMS): calcd for $[C_{56}H_{43}N_4O_2Ir + H]^+$, m/z 997.3088; found, m/z 997.3072. IR (KBr, cm^{-1}): ν(C═O) 1674 (s). Anal. Calcd for $C_{56}H_{43}N_4O_2Ir$: C, 67.52; H, 4.35; N, 5.62. Found C, 67.83; H, 4.45; N, 5.41. A single crystal for X-ray diffraction analysis was grown from CH_2Cl_2/toluene.

Method B. Ir(ttp)Me (26.6 mg, 0.030 mmol) was dissolved in anisaldehyde (1.0 mL). The red reaction mixture was heated at 200 °C under N_2 in the dark for 4 h. The orange red solid was isolated after column chromatography (22.1 mg, 0.022 mmol, 73%).

(5,10,15,20-Tetratolylporphyrinato)(4-methylbenzoyl)iridium(III), 4-MeC_6H_4COIr(ttp) (2c). Method A. The suspension of Ir(ttp)Cl(CO) (22.5 mg, 0.024 mmol) and 4-methylbenzaldehyde (1.0 mL) was heated at 200 °C under N_2 in the dark for 4 days to give a dark red solution. Excess 4-methylbenzaldehyde was removed by vacuum distillation. The reaction mixture was then purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (2:1) to give 4-MeC_6H_4COIr(ttp) **(2c)** as an orange red solid (10.0 mg, 0.010 mmol, 42%), which was further recrystallized from CH_2Cl_2/MeOH. R_f = 0.54 (1:2 hexane/CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.88 (s, 3 H), 2.48 (d, 2 H, J = 8.0 Hz), 2.69 (s, 12 H), 5.78 (d, 2 H, J = 7.4 Hz), 7.53 (d, 8 H, J = 7.7 Hz), 7.90 (d, 4 H, J = 6.6 Hz), 8.02 (d, 4 H, J = 6.2 Hz), 8.63 (s, 8 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 22.2, 116.8, 124.4, 126.7, 128.1, 132.0, 134.2, 134.6, 138.0, 139.5, 143.5, 167.6. HRMS (ESIMS): calcd for $[C_{56}H_{43}N_4OIr + H]^+$, m/z 981.3139; found, m/z 981.3134. IR (KBr, cm^{-1}): ν(C═O) 1674 (s). The sample for elemental analysis was grown from CH_2Cl_2/MeOH and vacuum-dried at 100 °C for 2 days. Anal. Calcd for $C_{56}H_{43}N_4OIr$: C, 68.62; H, 4.42; N, 5.71. Found: C, 68.35; H, 4.49; N, 5.59. A single crystal for X-ray diffraction analysis was grown from CH_2Cl_2/toluene.

Method B1. Ir(ttp)Me (13.6 mg, 0.016 mmol) was dissolved in 4-methylbenzaldehyde (1.0 mL). The red reaction mixture was heated at 200 °C under N_2 in the dark for 6.5 h. The orange red solid was isolated after column chromatography (7.9 mg, 0.0080 mmol, 52%).

Method B2. Ir(ttp)Me (17.4 mg, 0.020 mmol) and 10 equiv of 2,6-di-*tert*-butylpyridine were dissolved in 4-methylbenzaldehyde (1.0 mL). The red reaction mixture was heated at 200 °C under N_2 in the dark for 9 h. The orange red solid was isolated after column chromatography (10.0 mg, 0.010 mmol, 51%).

(5,10,15,20-Tetratolylporphyrinato)(4-*tert*-butylbenzoyl)iridium(III), 4-*tert*-BuC_6H_4COIr(ttp) (2d). Method A. The suspension of Ir(ttp)Cl(CO) (37.2 mg, 0.040 mmol) and 4-*tert*-butylbenzaldehyde (1.0 mL) was heated at 200 °C under N_2 in the dark for 1.5 days to give a dark red solution. Excess 4-*tert*-butylbenzalde-

hyde was removed by vacuum distillation. The reaction mixture was then isolated by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (2:1) to give 4-^{t}BuC$_6$H$_4$COIr(ttp) **(2d)** as an orange red solid (19.5 mg, 0.019 mmol, 47%), which was further recrystallized from CH_2Cl_2/MeOH. R_f = 0.64 (1:2 hexane/CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.957 (s, 9 H), 2.56 (d, 2 H, J = 8.1 Hz), 2.77 (s, 12 H), 5.99 (d, 2 H, J = 8.1 Hz), 7.52 (d, 8 H, J = 8.1 Hz), 7.95 (d, 4 H, J = 6.9 Hz), 8.02 (d, 4 H, J = 7.2 Hz), 8.62 (s, 8 H). HRMS (ESIMS): calcd for $[C_{59}H_{49}N_4OIr + H]^+$, m/z 1023.3608; found, m/z 1023.3603. IR (KBr, cm^{-1}): ν(C═O) 1660 (s). The sample for elemental analysis was grown from CH_2Cl_2/MeOH and dried at 100 °C in vacuum for 2 days. Anal. Calcd for $C_{59}H_{49}N_4OIr$: C, 69.32; H, 4.83; N, 5.48. Found: C, 69.20; H, 4.88; N, 5.25. A single crystal for X-ray diffraction analysis was grown from CH_2Cl_2/toluene/THF.

Method B. Ir(ttp)Me (25.3 mg, 0.029 mmol) was dissolved in 4-*tert*-butylbenzaldehyde (1.0 mL). The red reaction mixture was heated at 200 °C under N_2 in the dark for 31 h. The orange red solid was isolated after column chromatography (22.0 mg, 0.022 mmol, 74%).

(5,10,15,20-Tetratolyporphyrinato)(4-fluorobenzoyl)iridium(III), 4-FC$_6$H$_4$COIr(ttp) (2e). Method A1. The suspension of Ir(ttp)Cl(CO) (17.8 mg, 0.019 mmol) and 4-fluorobenzaldehyde (1.0 mL) was heated at 200 °C under N_2 in the dark for 15 h to give a dark red solution. Excess 4-fluorobenzaldehyde was removed by vacuum distillation. The reaction mixture were then purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (2:1) to give 4-FC$_6$H$_4$COIr(ttp) **(2e)** as an orange red solid (17.4 mg, 0.018 mmol, 92%), which was further recrystallized from CH_2Cl_2/MeOH. R_f = 0.56 (1:2 hexane/CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.52 (dd, 2 H, J = 3.3, 5.4 Hz), 2.70 (s, 12 H), 5.69 (t, 2 H, J = 8.7 Hz), 7.54 (t, 8 H , J = 6.6 Hz), 7.96 (d, 4 H, J = 8.4 Hz), 8.01 (d, 4 H, J = 7.8 Hz), 8.66 (s, 8 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.1, 112.7 (d, J = 11.0 Hz), 119.0 (d, J = 4.0 Hz), 124.4, 128.1 (d, J = 3.2 Hz), 132.0, 134.3 (d, J = 9.8 Hz), 138.0, 139.2, 143.3, 158.7. HRMS (ESIMS): calcd for $[C_{55}H_{40}N_4OFIr + H]^+$, m/z 985.2888; found, m/z 985.2882. IR (KBr, cm^{-1}): ν(C═O) 1682 (s). A single crystal for X-ray diffraction analysis was grown from CH_2Cl_2/toluene.

Method A2. Ir(ttp)Cl(CO) (15.3 mg, 0.016 mmol) and 10 equiv of 2,6-di-*tert*-butylpyridine were dissolved in 4-fluorobenzaldehyde (1.0 mL). The red reaction mixture was heated at 200 °C under N_2 in the dark for 12 h. The orange red solid was isolated after column chromatography (11.0 mg, 0.011 mmol, 68%).

Method B. Ir(ttp)Me (22.0 mg, 0.025 mmol) was dissolved in 4-fluorobenzaldehyde (1.0 mL). The red reaction mixture was heated at 200 °C under N_2 in the dark for 1.5 h. The orange red solid was isolated after column chromatography (21.7 mg, 0.022 mmol, 88%).

(5,10,15,20-Tetratolyporphyrinato)(4-chlorobenzoyl)iridium(III), 4-ClC$_6$H$_4$COIr(ttp) (2f). Method A. The suspension Ir(ttp)Cl(CO) (22.5 mg, 0.024 mmol) and 4-chlorobenzaldehyde (1.0 mL) was heated at 200 °C under N_2 in the dark for 1.5 days to give a dark red solution. Excess 4-chlorobenzaldehyde was removed by vacuum distillation. The reaction mixture were then isolated by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (2:1) to give 4-ClC$_6$H$_4$COIr(ttp) **(2f)** as an orange red solid (14.0 mg, 0.014 mmol, 57%), which was further recrystallized from CH_2Cl_2/MeOH. R_f = 0.72 (1:2 hexane/CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.47 (d, 2 H, J = 8.1 Hz), 2.70 (s, 12 H), 5.97 (d, 2 H, J = 8.1 Hz), 7.55 (t, 8 H, J = 7.4 Hz), 7.92 (d, 4 H, J = 7.8 Hz), 8.02 (d, 4 H, J = 7.5 Hz), 8.66 (s, 8 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.9, 117.9, 124.1, 125.9, 127.8, 128.0, 131.8, 133.8, 134.2, 137.8, 138.9, 143.0, 165.9. HRMS (ESIMS): calcd for $[C_{55}H_{40}N_4OClIr + H]^+$, m/z 1001.2593; found, m/z 1001.2600. IR (KBr, cm^{-1}): ν(C═O) 1663 (s). The sample for elemental analysis was grown from CH_2Cl_2/MeOH and vacuum-dried at 100 °C for 2 days. Anal. Calcd for $C_{55}H_{40}N_4OClIr$: C, 66.02; H, 4.03; N, 5.60. Found: C, 65.62; H, 4.03; N, 5.27. A single crystal for X-ray diffraction analysis was grown from CH_2Cl_2/toluene.

Method B. Ir(ttp)Me (20.8 mg, 0.024 mmol) was dissolved in 4-chlorobenzaldehyde (1.0 mL). The red reaction mixture was heated at 200 °C under N_2 in the dark for 18 h. The orange red solid was isolated after column chromatography (15.0 mg, 0.015 mmol, 63%).

(5,10,15,20-Tetratolyporphyrinato)(4-(α,α,α-trifluoromethyl)-benzoyl)iridium(III), 4-CF$_3$C$_6$H$_4$COIr(ttp) (2g). Method A. The suspension of Ir(ttp)Cl(CO) (30.6 mg, 0.033 mmol) and 4-(α,α,α-trifluoromethyl)benzaldehyde (1.0 mL) was heated at 200 °C under N_2 in the dark for 6 h to give a dark red solution. Excess 4-(α,α,α-trifluoromethyl)benzaldehyde was removed by vacuum distillation. The reaction mixture were then isolated by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (2:1) to give 4-CF$_3$C$_6$H$_4$COIr(ttp) **(2g)** as an orange red solid (24.0 mg, 0.023 mmol, 70%), which was further recrystallized from CH_2Cl_2/MeOH. R_f = 0.56 (1:2 hexane/CH_2Cl_2). ^{1}H NMR (300 MHz, C_6D_6): δ 2.43 (s, 12 H), 2.74 (d, 2 H, J = 8.2 Hz), 6.03 (d, 2 H, J = 8.0 Hz), 7.34 (t, 8 H, J = 6.6 Hz), 7.95 (d, 4 H, J = 8.4 Hz), 8.14 (d, 4 H, J = 7.8 Hz), 8.85 (s, 8 H). HRMS (FABMS): calcd for $[C_{56}H_{40}N_4OF_3Ir]^+$, m/z 1034.2778; found m/z 1.34.2787. IR (KBr, cm^{-1}): ν(C═O) 1672 (s). Anal. Calcd for $C_{56}H_{40}N_4OF_3Ir$: C, 65.04; H, 3.90; N, 5.41. Found: C, 65.52; H, 4.04; N, 5.36.

Method B. Ir(ttp)Me (21.3 mg, 0.024 mmol) was dissolved in 4-(α,α,α-trifluoromethyl)benzaldehyde (1.0 mL). The red reaction mixture was heated at 200 °C under N_2 in the dark for 1.5 h. The orange red solid was isolated after column chromatography (15.7 mg, 0.015 mmol, 62%).

Reaction of Aliphatic Aldehydes with Ir(ttp)Cl(CO). (5,10,-15,20-Tetratolyporphyrinato)(ethylformyl)iridium(III), CH$_3$CH$_2$-COIr(ttp) (3). Method A. Ir(ttp)Cl(CO) (19.6 mg, 0.021 mmol) was dissolved in propanal (1.0 mL), and the mixture was heated at 200 °C under N_2 in the dark for 2 days. Excess propanal was removed by vacuum distillation. The reaction mixture was then isolated by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (2:1). (The silica gel was first deactivated by the addition of water (5 mL of water/100 g of silica gel).) A red solid, $CH_3CH_2COIr(ttp)$ (**3**) (11.4 mg, 0.012 mmol, 58%), was collected and was further recrystallized from CH_2Cl_2/MeOH. R_f = 0.66 (1:2 hexane/CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ −3.20 (q, 2 H, J = 7.2, 7.5 Hz), −1.71 (t, 3 H, J = 7.2 Hz), 2.69 (s, 12 H), 7.52 (d, 8 H, J = 8.1 Hz), 8.02 (d, 8 H, J = 7.8 Hz), 8.67 (s, 8 H). HRMS (FABMS): calcd for $[C_{51}H_{41}N_4OIr + H]^+$, m/z 919.2982; found, m/z 919.2973. Anal. Calcd for $C_{51}H_{41}N_4OIr$: C, 66.72; H, 4.50; N, 6.10. Found: C, 66.89; H, 4.50; N, 6.24. IR (KBr, cm^{-1}): ν(C═O) 1682 (s).

Method B. Ir(ttp)Me (20 mg, 0.023 mmol) was added into propanal (1.0 mL). The red reaction mixture was heated at 200 °C under N_2 in the dark for 2 days. Excess propanal was removed by vacuum distillation. The orange red product was then isolated by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (2:1). (The silica gel was first deactivated by the addition of water (5 mL of water/100 g of silica gel)). Red solid **3** was collected (11.5 mg, 0.012 mmol, 55%).

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and sealed under N_2 in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation. An empirical absorption correction was applied using the SADABS program.[16] All structures were solved by direct methods and subsequent Fourier

Table 5. Crystal Data and Summary of Data Collection and Refinement for 2a−f

param	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**
formula	$C_{61}H_{48}N_4OIr$	$C_{56}H_{43}N_4O_2Ir$	$C_{56}H_{47}N_4O_3Ir$	$C_{63}H_{57}N_4O_2Ir$	$C_{62}H_{48}N_4OFIr$	$C_{62}H_{48}N_4OClIr$
cryst size (mm)	0.40 × 0.30 × 0.20	0.40 × 0.30 × 0.20	0.30 × 0.20 × 0.20	0.40 × 0.30 × 0.20	0.50 × 0.40 × 0.30	0.30 × 0.20 × 0.10
fw	1058.25	996.14	1016.18	1094.33	1076.24	1092.69
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$	$P2_1/c$	$P2/n$	$P2_1/c$	$P2_1/c$
a (Å)	11.4151(12)	8.8390(14)	13.8753(15)	20.648(3)	11.338(2)	11.239(2)
b (Å)	17.8705(18)	28.222(4)	22.280(2)	13.5262(18)	18.307(4)	18.548(3)
c (Å)	24.260(2)	22.931(4)	15.5951(16)	20.692(3)	23.902(5)	24.007(5)
α (deg)	90	90	90	90	90	90
β (deg)	98.424(2)	98.215(3)	96.397(2)	99.762(3)	99.05(3)	98.714(4)
γ (deg)	90	90	90	90	90	90
V, Å^3	4895.5(9)	5661.6(15)	4791.1(9)	5695.3(13)	4899.7(17)	4946.8(16)
Z	4	4	4	4	4	4
D_{calcd}, Mg/m^3	1.436	1.169	1.409	1.276	1.459	1.467
radiation (λ), Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
θ range, deg	1.42−25.00	1.44−25.00	1.74−25.00	1.51−25.00	2.05−25.00	1.72−25.00
F(000)	2136	2000	2048	2224	2168	2200
reflcns collcd	26 038	15 163	25 751	30 255	9106	26 270
indpndt reflcns	8607	4996	8424	10 036	8639	8715
data/restraints/params	8607/20/613	4996/0/289	8424/0/577	10036/24/631	8639/13/622	8715/7/622
goodness of fit	1.079	1.136	1.044	1.057	0.984	1.050
R_1[a] (all data)	0.0835	0.0911	0.1228	0.1345	0.1191	0.0735
wR_2[b] (all data)	0.1211	0.2055	0.1782	0.2716	0.1425	0.0983
w_1/w_2[c]	0.0243/24.8934	0.1033/64.7479	0.0632/31.2667	0.1308/34.8201	0.0596/0.0000	0.0368/2.8972

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] Weighting scheme $w^{-1} = \sigma^2(F_o^2) + (w_1P)^2 + w_2P$, where $P = (F_o^2 + 2F_c^2)/3$.

difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on F_2 using the SHELXTL program package.[17] All hydrogen atoms were geometrically fixed using the riding model. X-ray data are listed in Table 5. CIF files have been deposited in Cambridge Crystallographic Data Centre (CCDC) with reference nos. CCDC 628255−628260 corresponding to complexes **2a**−**f**, respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K (fax, (internat.) (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Text, tables, and figures of crystallographic data for complexes **2a**−**f** (CIF and PDF), ^{13}C NMR spectra for **1**, **2e**, and **5**, ^1H NMR spectra for **2e** and **5**, and an IR spectrum for **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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