# Base-Promoted Selective Activation of Benzylic Carbon−Hydrogen Bonds of Toluenes by Iridium(III) Porphyrin

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$K_2CO_3$ and NaOPh promoted the rate of benzylic carbon−hydrogen bond activation (BnCHA) of toluenes with iridium(III) porphyrin carbonyl chloride (Ir(ttp)Cl(CO)) to give iridium porphyrin benzyls in high yields. Mechanistic studies suggested that $K_2CO_3$ initially converted Ir(ttp)Cl(CO) to Ir(ttp)X (X $= OH^-, KCO_3^-$), which reacted very fast with toluenes to yield Ir(ttp)H. Ir(ttp)H then reduced the carbonyl ligand in unreacted Ir(ttp)Cl(CO) to yield Ir(ttp)Me. Ir(ttp)H also dimerized dehydrogenatively to give $[Ir(ttp)]_2$, especially promoted in the presence of base, which further reacted with toluenes to yield iridium benzyls. Weaker base of NaOPh converted Ir(ttp)Cl(CO) to Ir(ttp)OPh, which selectively promoted BnCHA to yield iridium benzyls.

## Introduction

Selective intermolecular carbon−hydrogen bond activation (CHA) by transition metal complexes is an important area of research in organometallic chemistry for the controlled activation and functionalization of hydrocarbons.[1] The activation of toluenes is particularly important since the catalytic functionalization of toluenes can yield industrially important chemicals such as benzyl alcohols,[2] benzaldehydes,[3] and benzoic acids.[4] The selectivity of benzylic CHA (BnCHA) for functionalization is therefore important as competitive aromatic CHA (ArCHA) has been reported.[5]

CHA by low valent Rh(I)[6] and Ir(I)[7] complexes have been extensively studied. The commonly accepted mechanism involves classical oxidative addition pathway to give Rh(III) and Ir(III) products.[1a,e] CHA by high valent Rh(III)[8,9] and Ir(III)[10,11] complexes have also been investigated, and various mechanisms are proposed: oxidative addition via M(III)-M(V)-M(III) species (M = Rh[8] or Ir[11a,c]), σ-bond metathesis,[8,10,11f] and heterolytic cleavage.[12] Rh(V)[13] and Ir(V)[14] complexes were even observed in the analogous silicon−hydrogen bond activation. However, no Rh(V) and Ir(V) complexes formed by CHA have been directly observed. This makes CHA by Rh(III) and Ir(III) complexes mechanistically intriguing since the mechanistic details of CHA by high-valent Rh(III) and Ir(III) complexes have not been fully defined.

We have reported that Rh(III) and Ir(III) porphyrins are unique high valent complexes in undergoing CHA. Selective aldehydic CHA of aryl aldehydes by $Rh^{III}$(ttp)Cl[8] and $Ir^{III}$(ttp)-Cl(CO)[10] (ttp = tetrakis(*p*-tolyl)porphyrin dianion) without ArCHA have been observed. We have discovered that in the absence of base, Rh(ttp)Cl reacted with toluene to give both ArCHA and BnCHA products. With $K_2CO_3$ added, the rates of reactions were enhanced, and only selective BnCHA products in high yields were isolated for a variety of functionalized toluenes.[9] We thus have extended our investigation of CHA of

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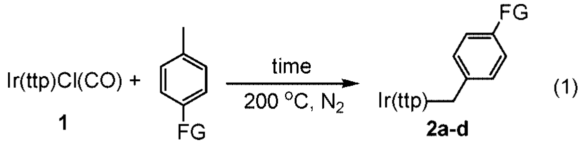
**Table 1. CHA of Toluenes with Ir(ttp)Cl(CO)**



| entry | FG | time/d | yield **2**/% |
|---|---|---|---|
| 1 | Me | 3.5 | **2a** (56) |
| 2 | H | 9 | **2b** (55) |
| 3 | F | 9 | **2c** (75) |
| 4 | $NO_2$ | 1 | decomp. |

**Table 2. Base Effect on CHA of Toluene with Ir(ttp)Cl(CO)**

$$\underset{\mathbf{1}}{\mathrm{Ir(ttp)Cl(CO)}} + \mathrm{PhCH_3} \xrightarrow[200\ ^\circ\mathrm{C,\ time,\ N_2}]{\text{base}} \underset{\mathbf{2b}}{\mathrm{Ir(ttp)Bn}} + \underset{\mathbf{3}}{\mathrm{Ir(ttp)Me}} \tag{2}$$

| entry | base (equiv) | time | yield **2b** (%) | yield **3** (%) |
|---|---|---|---|---|
| 1 | $NaNH_2$ (10) | 0.25 h | 43 | 13 |
| 2 | NaOH (10) | 1 h | 34 | 7 |
| 3 | $Cs_2CO_3$(20) | 0.5 h | 37 | 4 |
| 4 | $K_2CO_3$ (20) | 3 h | 66 | 3 |
| 5 | NaOPh (20) | 2 d | 78 | |
| 6 | NaF (20) | 6 d | 96 | |

toluenes with iridium porphyrin. We now report that NaOPh can promote the rate and selectivity of BnCHA with iridium porphyrin.

## Result and Discussion

Initially, Ir(ttp)Cl(CO) did not react with toluene at 150 °C in 3 days. A very slow reaction occurred at 200 °C in 9 days to give Ir(ttp)Bn in 55% yield (Table 1, eq 1, entry 2). *p*-Xylene and 4-fluorotoluene also reacted slowly to generate BnCHA complexes (Table 1, entries 1 and 3). 4-Nitrotoluene decomposed Ir(ttp)Cl(CO) (Table 1, entry 4). Likely, the low reactivity is due to the coordinative saturation of Ir(ttp)Cl(CO).

In view of successful base-promoted BnCHA by Rh(ttp)Cl,[9] various bases were examined. Coordinating organic base, pyridine, and noncoordinating bulky organic base, 2,6-di-*tert*-butylpyridine were not effective at all. Improvements in rate enhancement and yields were observed with inorganic bases (Table 2, eq 2). Stronger inorganic bases[15] led to shorter reaction times but lower yields of Ir(ttp)Bn and lower selectivity as Ir(ttp)Me also formed (Table 2, entries 1–4). Weaker bases of NaOPh and NaF[15] reacted more slowly, but they were more selective in BnCHA to yield Ir(ttp)Bn only (Table 2, entries 5 and 6). $K_2CO_3$ and NaOPh were therefore selected as the optimized bases to further examine the scope of base-promoted BnCHA since they reacted sufficiently fast and gave higher yields of Ir(ttp)Bn in higher selectivity. The optimized amount of base was found to be 20 equivalents with reference to Ir(ttp)Cl(CO) since a lower equivalent of $K_2CO_3$ (10 equiv) slowed down the reaction rates (Table 3, eq 3, entries 1 and 2), and a higher equivalent of $K_2CO_3$ (30 equiv) gave similar yields of Ir(ttp)Bn and Ir(ttp)Me in 2 h (Table 3, entry 3 and 4).

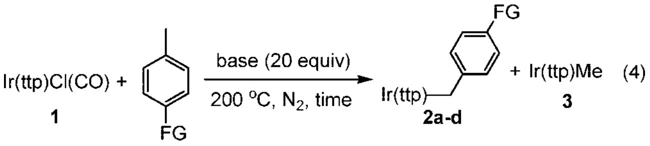
$K_2CO_3$ and NaOPh were also used in the reactions of Ir(ttp)Cl(CO) with various 4-substituted toluenes (Table 4, eq 4). Both bases enhanced BnCHA with the stronger base $K_2CO_3$ showing a larger rate enhancement than NaOPh (Table 4, entries 1–3). NaOPh was more selective without any Ir(ttp)Me formed and generally higher yielding in BnCHA when compared with $K_2CO_3$. Furthermore, 4-nitrotoluene successfully reacted to give **2d** (Table 4, entry 4).

**Table 3. Optimization of Base Equivalent in CHA of Toluenes with Ir(ttp)Cl(CO)**

$$\underset{\mathbf{1}}{\mathrm{Ir(ttp)BnCl(CO)}} + \mathrm{PhCH_3} \xrightarrow[\text{temp, N}_2]{\mathrm{K_2CO_3},\ \text{time}} \underset{\mathbf{2b}}{\mathrm{Ir(ttp)Bn}} + \underset{\mathbf{3}}{\mathrm{Ir(ttp)Me}} \tag{3}$$

| entry | $K_2CO_3$(equiv) | temp/°C | time | yield **2b**/% | yield **3**/% |
|---|---|---|---|---|---|
| 1 | 10 | 150 | 3 d | 63 | 1 |
| 2 | 20 | 150 | 2 d | 66 | 3 |
| 3 | 20 | 200 | 3.5 h | 61 | 7 |
| 4 | 30 | 200 | 2 h | 60 | 7 |

**Table 4. Effect of $K_2CO_3$ and NaOPh on CHA of Toluene with Ir(ttp)Cl(CO)**



| | | entry A ($K_2CO_3$) | | | entry B (NaOPh) | |
|---|---|---|---|---|---|---|
| entry | FG | time/h | yield (%) | | time/h | yield (%) |
| 1 | Me | 1 | **2a** (41) | **3** (1) | 24 | **2a** (67) |
| 2 | H | 3.5 | **2b** (61) | **3** (7) | 48 | **2b** (78) |
| 3 | F | 2 | **2c** (62) | | 12 | **2c** (78) |
| 4 | $NO_2$ | 0.1 | **2d** (80) | | 0.1 | **2d** (43) |

**Synthesis of Authentic Samples.** Iridium porphyrin benzyls **2a**, **2b**, **2c**, and **2e** were successfully synthesized by reductive benzylation of Ir(ttp)Cl(CO) (eq 5).[16–18] Ir(ttp)Cl(CO) was first reduced by $NaBH_4$ with base to yield $Ir(ttp)^-$, which was then further reacted with benzyl bromides to yield iridium benzyls.

$$\mathrm{Ir(ttp)Cl(CO)} \xrightarrow[\substack{2.\ p\text{-FG-C}_6\text{H}_4\text{CH}_2\text{Br, 2 h} \\ \text{THF, 80 °C, N}_2}]{1.\ \mathrm{NaBH_4,\ NaOH,\ 2\ h}} \begin{array}{r} \mathrm{Ir(ttp)Bn}\text{-}p\text{-FG} \\ \mathrm{FG = Me,\ \mathbf{2a},\ 52\%;} \\ \mathrm{H,\ \mathbf{2b},\ 67\%;} \\ \mathrm{F,\ \mathbf{2c},\ 54\%;} \\ {}^t\mathrm{Bu,\ \mathbf{2e},\ 65\%} \end{array} \tag{5}$$

**X-ray Details.** The collection and processing parameters of single-crystal data for complexes **2a**, **2d**, and **2e** are given in Table 5 and Supporting Information. Table 6 lists the selected bond lengths and angles. The bond lengths of Ir−C in $Ir(ttp)CH_2Ar$ and Ir−C−$C_{aryl}$ angles are not affected by the *para*-substituents (Table 6). In the solid state, **2a**, **2d**, and **2e** adopt monomeric structures. However, due to the rotation of the molecule of **2d**, disorder of the X-ray structure results. Both disordered and simplified ORTEP drawings of **2d** are reported in Supporting Information. As a representative, Figure 1 shows the molecular structure of Ir(ttp)Bn($p$-$^t$Bu) (**2e**) (30% thermal ellipsoids).

**Mechanism: No Base.** Scheme 1 illustrates the proposed mechanism for the reactions without and with bases. In the absence of a base (Scheme 1, Pathway **I**), Ir(ttp)Cl(CO) presumably reacts with the benzylic C−H bond of toluene,

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**Table 5. Crystal Data and Summary of Data Collection and Refinement for 2a, 2d, and 2e**

| param | **2a** | **2d** | **2e** |
|---|---|---|---|
| formula | $C_{56}H_{45}N_4Ir.2H_2O$ | $C_{55}H_{42}N_5O_2Ir$ | $C_{59}H_{51}N_4Ir$ |
| cryst size (mm) | 0.40 × 0.30 × 0.20 | 0.40 × 0.30 × 0.20 | 0.40 × 0.30 × 0.20 |
| fw | 1002.19 | 997.14 | 1008.24 |
| cryst syst | monoclinic | monoclinic | monoclinic |
| space group | P2 (1)/c | P2(1)/c | P2 (1)/n |
| $a$ (Å) | 13.870 (3) | 7.6573 (12) | 12.755 (3) |
| $b$ (Å) | 22.020 (4) | 16.574 (3) | 22.544 (6) |
| $c$ (Å) | 15.361 (3) | 21.973 (3) | 16.701 (4) |
| α (deg) | 90 | 90 | 90 |
| $\beta$(deg) | 95.34 (3) | 90.180 (3) | 100.692 (6) |
| $\gamma$ (deg) | 90 | 90 | 90 |
| $V$, Å$^3$ | 4671.3 (16) | 2788.7 (7) | 4719 (2) |
| $Z$ | 4 | 2 | 4 |
| $D_{\mathrm{calcd}}$, Mg/m$^3$ | 1.425 | 1.188 | 1.419 |
| radiation ($\lambda$), Å | 0.71073 | 0.71073 | 0.71073 |
| $\theta$ range, deg | 2.11 to 25.00 | 1.54 to 28.02 | 1.53 to 25.00 |
| F(000) | 2024 | 1000 | 2040 |
| reflcns collcd | 8575 | 18222 | 25303 |
| indpndt rflns | 8215 | 6677 | 8315 |
| data/restraints/params | 8215/0/568 | 6677/155/631 | 8315/0/577 |
| goodness of fit | 1.043 | 1.095 | 1.074 |
| final $R_1{}^a/wR_2{}^b$ [$I > 2\sigma(I)$] | 0.0503/0.1372 | 0.0582/0.1621 | 0.0422/0.1022 |
| final $R_1{}^a/wR_2{}^b$ (all data) | 0.0945/0.1569 | 0.1024/0.1925 | 0.0658/0.1198 |
| $w_1/w_2{}^c$ | 0.0768/4.5632 | 0.1088/0.0000 | 0.0664/0.3854 |

[a] $R_1 = \Sigma\,(|F_0| - |F_c|)/\Sigma\,|F_0|$. [b] $wR_2 = \Sigma\,\{\Sigma[w(F_0{}^2 - F_c{}^2)^2]/\Sigma\,[w(F_0{}^2)^2]\}^{1/2}$. [c] Weighting scheme $w^{-1} = \sigma^2\,(F_0{}^2) + (w_1\,P)^2 + w_2P$, where $P = (F_0{}^2 + 2F_c{}^2)/3$.

**Table 6. Selected Bond Lengths and Bond Angles of Compounds 2a, 2d, and 2e**

| entry | FG | Ir−C length (Å) | Ir−C−$C_{\mathrm{aryl}}$ bond angle (deg) |
|---|---|---|---|
| 1 | Me, **2a** | 2.089 (9) | 115.2 (6) |
| 2 | $NO_2$, **2d** | 2.186 (4)[a] | 114.8 (4)[b] |
| 3 | $^t$Bu, **2e** | 2.073 (6) | 117.1 (4) |

[a] Average of 2 Ir−C bond lengths from 2 kinds of disordered structures. [b] Average of 4 Ir−C−$C_{\mathrm{aryl}}$ bond angles from 4 kinds of disordered structures.

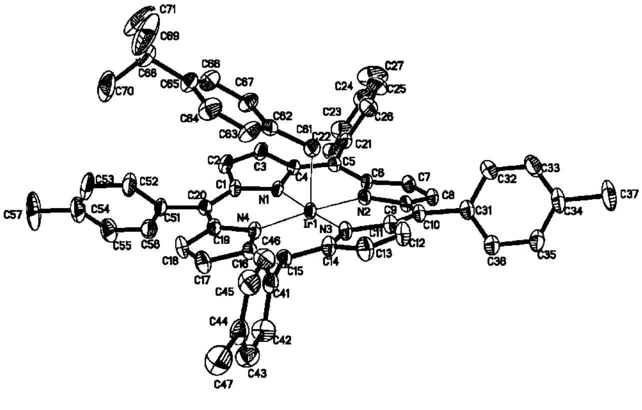

**Figure 1.** ORTEP drawing of Ir(ttp)Bn($p$-$^t$Bu) (**2e**) in 30% probability displacement ellipsoids.

which is a sterically more accessible bond than arene C−H bonds, via $\sigma$-bond metathesis[10,11f] or its variant form of internal electrophilic substitution (IES).[19] Complete dissociation of Ir(ttp)Cl(CO) into $\mathrm{Ir(ttp)}^{+10,20}$ for BnCHA is less probable, and this can be attributed into 2 reasons. (i) $\mathrm{Ir(ttp)BF_4}$ (an inseparable mixture of $\mathrm{Ir(ttp)BF_4}$ and $\mathrm{Ir(ttp)(CO)BF_4}$)[10] with the much less coordinating $BF_4^-$ reacted with toluene at 200 °C in 2 h to generate only Ir(ttp)($p$-tol) in 26% yield via electrophilic aromatic substitution[21] without any Ir(ttp)Bn (eq 6). (ii) Ir(ttp)($p$-tol) did not further react with toluene at 200 °C in 1.5 days to yield any Ir(ttp)Bn, and therefore it is not an intermediate to give Ir(ttp)Bn. The dissociation of $Cl^-$ from Ir(ttp)Cl(CO) does take part during BnCHA because of the decreased rate in the reaction between Ir(ttp)Cl(CO) and toluene added with CsCl (10 equiv) at 200 °C to yield Ir(ttp)Bn in 61% yield with unreacted Ir(ttp)Cl(CO) recovered in 12% yield in 15 days (eq 7). BnCHA without base does not involve Ir(ttp)H as the intermediate since no Ir(ttp)H was observed in the course of the reaction of Ir(ttp)Cl(CO) with $p$-xylene (100 equiv) in $C_6D_6$ at 200 °C in 22 days to yield Ir(ttp)Bn($p$-Me) in 47% yield.

$$\mathrm{Ir(ttp)BF_4} + \mathrm{PhCH_3} \xrightarrow{200\ {}^\circ\mathrm{C,\ 2\ h,\ N_2}} \underset{26\%}{\mathrm{Ir(ttp)}(p-\mathrm{tol})} + \text{“}\mathrm{HBF_4}\text{”} \quad (6)$$

$$\mathrm{Ir(ttp)Cl(CO)} + \mathrm{PhCH_3} \xrightarrow[15\ \mathrm{d,\ N_2}]{200\ {}^\circ\mathrm{C,\ CsCl\ (10\ equiv)}} \underset{61\%}{\mathrm{Ir(ttp)Bn}} + \overset{\text{unreacted}}{\underset{12\%}{\mathrm{Ir(ttp)Cl(CO)}}} \quad (7)$$

**Mechanism: Strong Base.** In the presence of a strong base (Scheme 1, Pathway **II**) such as $K_2CO_3$, which is a precursor of hydroxide generated by thermal hydrolysis of carbonate at 200 °C with a small amount of water present,[22] or NaOH, Ir(ttp)X (X = $OH^-$, $KCO_3^-$) **A** probably forms first by rapid ligand substitution.[11f,23] Ir(ttp)X further reacts with toluene to yield Ir(ttp)H.[17,24] This is supported by the initial formation of Ir(ttp)H as the only iridium porphyrin species in the independent reaction of Ir(ttp)Cl(CO) with $\mathrm{Ph^{13}CH_3}$ (50 equiv) and $Cs_2CO_3$

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[19] In the internal electrophilic substitution (IES) mechanism, the lone pair on an M-X ligand forms an X-H bond, while the orbital making up the M-X bond turns into a coordinating lone pair (ref 12).

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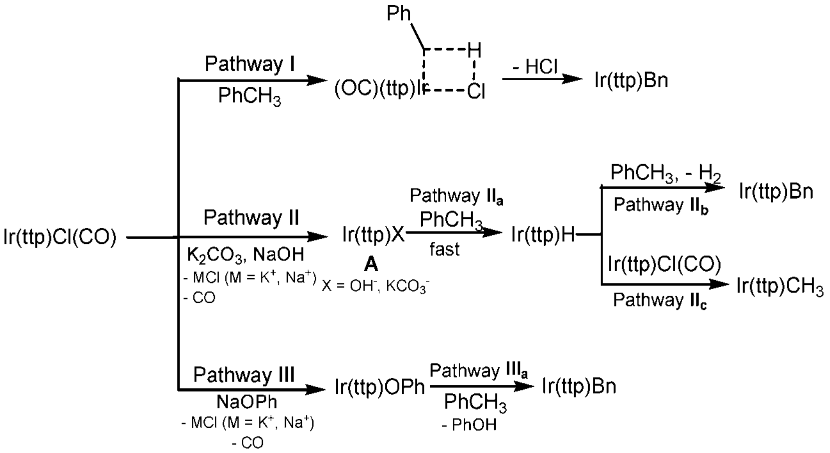
**Scheme 1. Mechanism of Benzylic CHA and Generation of Ir(ttp)Me**



in $C_6D_6$ at 150 °C in 30 min (eq 8). The characteristic high field hydride signal was observed at −57.4 ppm by $^1$H NMR spectroscopy. However, no benzyl alcohol was observed by GC-MS analysis in the reaction mixture of Ir(ttp)Cl(CO) with toluene and NaOH (20 equiv) or $K_2CO_3$ (20 equiv) at 200 °C. As the fate of the organic coproducts remains unclear, we can only conclude that toluene is a hydride donor or reducing agent. The detailed mechanism of conversion of Ir(ttp)Cl(CO) to Ir(ttp)H with toluene and bases is still unclear. As Ir(ttp)OH could not be successfully prepared from the reaction of Ir(ttp)Cl(CO) with KOH, its observation in the reaction mixture remains difficult. Presumably, Ir(ttp)X reacts very rapidly with toluene to give Ir(ttp)H (Scheme 1, Pathway $\mathbf{II_a}$) which further reacts with toluene to yield Ir(ttp)Bn (Scheme 1, Pathway $\mathbf{II_b}$). The intermediacy of Ir(ttp)H was further established by the separate reaction of Ir(ttp)H with toluene at 200 °C in 1 h to give Ir(ttp)Bn in 48% yield (eq 9).

$$\mathrm{Ir(ttp)Cl(CO)} + \underset{50\text{ equiv}}{\mathrm{Ph^{13}CH_3}} \xrightarrow[150\ ^\circ\mathrm{C},\ 30\text{ min}]{\mathrm{Cs_2CO_3}\ (20\text{ equiv}),\ \mathrm{C_6D_6}} \underset{81\%}{\mathrm{Ir(ttp)H}} \quad (8)$$

$$\mathrm{Ir(ttp)H} + \mathrm{PhCH_3} \xrightarrow{200\ ^\circ\mathrm{C},1\text{ h},\ \mathrm{N_2}} \underset{48\%}{\mathrm{Ir(ttp)Bn}} \quad (9)$$

Ir(ttp)H can also reduce unreacted Ir(ttp)Cl(CO) to Ir(ttp)Me (Scheme 1, Pathway $\mathbf{II_c}$). $Ph^{13}CH_3$ reacted with Ir(ttp)Cl(CO) and $Cs_2CO_3$ at 150 °C in 2 h to give Ir(ttp)$^{13}CH_2Ph$ and Ir(ttp)Me in 8% and 17% yield, respectively (eq 10). No Ph-$^{13}CH_3$ cleavage occurred. As the reduction of CO by transition metal hydride species to yield metal methyl complexes has been widely reported,[25,26] it is highly likely that $PhCH_3$ reduces Ir(ttp)Cl(CO) to Ir(ttp)H, which further reduces unreacted Ir(ttp)Cl(CO), most likely the CO ligand, to Ir(ttp)Me. Indeed, Ir(ttp)H (4 equiv) with $Cs_2CO_3$ (20 equiv) were found to reduce Ir(ttp)Cl(CO) (1 equiv) in toluene-$d_8$ at 150 °C in 4 days to yield Ir(ttp)Bn-$d_7$ (19%) and Ir(ttp)Me (10%) (eq 11). The presence of base is important in the reduction of Ir(ttp)Cl(CO) as the reaction of Ir(ttp)H (4 equiv) with Ir(ttp)Cl(CO) (1 equiv) without any base in toluene-$d_8$ was incomplete even at 200 °C in 19 days, yielding Ir(ttp)Bn-$d_7$ (23%) and Ir(ttp)-Me (5%) with unreacted Ir(ttp)Cl(CO) and Ir(ttp)H (eq 12). Therefore, the Ir(ttp) anion, which is formed by deprotonation of Ir(ttp)H with base, is probably the reacting species. The base-promoted reduction of Ir(ttp)Cl(CO) with Ir(ttp)H was also successfully carried out in $C_6D_6$ in 150 °C to yield Ir(ttp)Me in 10% yield (eq 13).

$$\mathrm{Ir(ttp)Cl(CO)} + \mathrm{Ph^{13}CH_3} \xrightarrow[150\ ^\circ\mathrm{C},\ 2\text{ h}]{\mathrm{Cs_2CO_3}\ (20\text{ equiv})} \underset{8\%}{\mathrm{Ir(ttp)^{13}CH_2Ph}} + \underset{17\%}{\mathrm{Ir(ttp)CH_3}} \quad (10)$$

$$\underset{4\text{ equiv}}{\mathrm{Ir(ttp)H}} + \underset{1\text{ equiv}}{\mathrm{Ir(ttp)Cl(CO)}} \xrightarrow[150\ ^\circ\mathrm{C},\ 4\text{ d}]{\mathrm{Cs_2CO_3}\ (20\text{ equiv}),\ \mathrm{C_6D_5CD_3}} \underset{19\%}{\mathrm{Ir(ttp)Bn}\text{-}d_7} + \underset{10\%}{\mathrm{Ir(ttp)CH_3}} \quad (11)$$

$$\underset{4\text{ equiv}}{\mathrm{Ir(ttp)H}} + \underset{1\text{ equiv}}{\mathrm{Ir(ttp)Cl(CO)}} \xrightarrow[200\ ^\circ\mathrm{C},\ 19\text{ d}]{\mathrm{C_6D_5CD_3}} \underset{23\%}{\mathrm{Ir(ttp)Bn}\text{-}d_7} + \underset{5\%}{\mathrm{Ir(ttp)CH_3}} + \underset{23\%}{\overset{\text{unreacted}}{\mathrm{Ir(ttp)Cl(CO)}}} + \underset{19\%}{\overset{\text{unreacted}}{\mathrm{Ir(ttp)H}}} \quad (12)$$

$$\underset{4\text{ equiv}}{\mathrm{Ir(ttp)H}} + \underset{1\text{ equiv}}{\mathrm{Ir(ttp)Cl(CO)}} + \xrightarrow[150\ ^\circ\mathrm{C},\ 11\text{ d}]{\mathrm{Cs_2CO_3}\ (100\text{ equiv}),\ \mathrm{C_6D_6}} \underset{10\%}{\mathrm{Ir(ttp)CH_3}} (13)$$

Ir(ttp)Me is not an intermediate of Ir(ttp)Bn as it reacted slowly with toluene at 200 °C in 14 days to yield only a trace of Ir(ttp)Bn with the recovery of Ir(ttp)Me in 46% yield, and it reacted with toluene and $K_2CO_3$(20 equiv) at 200 °C in 3 days to yield a trace of Ir(ttp)Bn with the recovery of Ir(ttp)Me in 92% yield.

**Mechanism of Ir(ttp)Me Generation.** The source of proton in the methyl group of Ir(ttp)Me is probably from water. In view of the rapid generation of Ir(ttp)H without Ir(ttp)D in the reaction of Ir(ttp)Cl(CO) with toluene-$d_8$ (50 equiv) and $Cs_2CO_3$ (20 equiv) at 150 °C in 20 min, water, which is intrinstically present in trace amount in base used, probably acts as an alternative proton source for the generation of Ir(ttp)H. However, no reaction occurred when Ir(ttp)Cl(CO) and water (100 equiv) in benzene were heated at 200 °C for 8 days to yield Ir(ttp)Me. Thus, water does not directly react with the CO ligand in Ir(ttp)Cl(CO) to yield Ir(ttp)Me. Indeed, base is also essential in the formation of Ir(ttp)Me. It is proposed that Ir(ttp)D was generated and rapidly exchanged with the trace of water present to yield Ir(ttp)H before reducing CO in Ir(ttp)Cl(CO) to yield Ir(ttp)Me (eq 14). In fact, facile proton exchange of Ir(ttp)D with $H_2O$ (50 equiv) added with $Cs_2CO_3$ (40 equiv) in $C_6D_6$ at 150 °C did occur to yield Ir(ttp)H (eq 15). Complete conversion

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[25] Transition-metal coordinated CO can be reduced by hydride sources to yield metal-methyl complexes. (a) Treichel, P. M.; Shubkin, R. L. *Inorg. Chem.* **1967**, *6*, 1328–1334. (b) Lapinte, C.; Catheline, D.; Astruc, D. *Organometallics* **1988**, *7*, 1683–1691.

[26] The carbonyl group of Rh(ttp)C(O)Ph was proposed to be reduced by Rh(ttp)H to yield Rh(ttp)Bn (ref 8).

of Ir(ttp)H to Ir(ttp)D with $D_2O$ (50 equiv) in $C_6D_6$ added with $Cs_2CO_3$ (40 equiv) in the same reaction conditions of BnCHA confirms the occurrence of proton exchange (eq 16). Therefore, only Ir(ttp)H was present without any Ir(ttp)D during CO reduction (eq 14). The conversion of Ir(ttp)D to Ir(ttp)H is likely due to the base-promoted proton transfer via Ir(ttp) dimer, $[\mathrm{Ir(ttp)}]_2$,[27] which was observed in the proton exchange of Ir(ttp)D with $H_2O$ (eq 15) and Ir(ttp)H with $D_2O$ (eq 16).

$$\mathrm{Ir(ttp)Cl(CO)} + \underset{\text{50 equiv}}{\mathrm{C_6D_5CD_3}} \xrightarrow[\text{14 d}]{150\ ^\circ\mathrm{C},\ \mathrm{Cs_2CO_3}\text{ (20 equiv)},\ \mathrm{C_6D_6}} \underset{42\%}{\mathrm{Ir(ttp)Bn}\text{-}d_7} + \underset{34\%}{\mathrm{Ir(ttp)CH_3}} \quad (14)$$

$$\mathrm{Ir(ttp)D} + \underset{\text{50 equiv}}{\mathrm{H_2O}} \xrightarrow[\text{13 h}]{150\ ^\circ\mathrm{C},\ \mathrm{Cs_2CO_3}\text{ (40 equiv)},\ \mathrm{C_6D_6}} \underset{43\%}{\mathrm{Ir(ttp)H}} \quad (15)$$

$$\mathrm{Ir(ttp)H} + \underset{\text{50 equiv}}{\mathrm{D_2O}} \xrightarrow[\text{36 h}]{150\ ^\circ\mathrm{C},\ \mathrm{Cs_2CO_3}\text{ (40 equiv)},\ \mathrm{C_6D_6}} \underset{20\%}{\mathrm{Ir(ttp)D}} \quad (16)$$

The incorporation of proton from water into Ir(ttp)Me is further confirmed by the addition of $D_2O$ to the base-promoted reactions of toluene. When toluene-$d_8$, $Cs_2CO_3$ (20 equiv), and $D_2O$ (10 equiv) were reacted with Ir(ttp)Cl(CO) at 150 °C, a mixture of $\mathrm{Ir(ttp)CH_3}$ and $\mathrm{Ir(ttp)CD_3}$ formed at a ratio of 5.45: 1 (eq 17a). When the amount of $D_2O$ was increased to 50 equiv, the ratio of $\mathrm{Ir(ttp)CH_3/Ir(ttp)CD_3}$ became 2.54:1 with an increase in the proportion of $\mathrm{Ir(ttp)CD_3}$ (eq 17b). The addition of $D_2O$ (50 equiv) still did not give $\mathrm{Ir(ttp)CD_3}$ in 100% yield.

$$\mathrm{Ir(ttp)Cl(CO)} + \mathrm{C_6D_5CD_3} + \underset{\substack{\text{(a) (20 equiv)}\\ \text{(b) (50 equiv)}}}{\mathrm{D_2O}} \xrightarrow[\substack{\text{3 h, 150 °C}\\ \text{3 h, 150 °C}}]{\mathrm{Cs_2CO_3}\text{ (20 equiv)}} \underset{\substack{33\%\\ 14\%}}{\mathrm{Ir(ttp)Bn}\text{-}d_7} + \underset{\substack{5.45:1\\ \text{total yield: }34\%\\ 2.54:1\\ \text{total yield: }27\%}}{\mathrm{Ir(ttp)CH_3} + \mathrm{Ir(ttp)CD_3}} \quad (17)$$

The base-promoted reactions of toluene by Ir(ttp)Cl(CO) with various other bases were also studied at 150 °C (Table 7, eq 18). The rates of reactions and the ratios of Ir(ttp)CH$_3$/Ir(ttp)Bn increased with more basic salts (MOH > $M_2CO_3$) (Table 7, entries 2–5). Furthermore, the Ir(ttp)Me/Ir(ttp)Bn ratio increased down the group of metal ions in the bases (Cs > K > Na > Li, Table 7, entries 1–6). The above trends can be rationalized by the nucleophilicity of a base. A more nucleophilic $OH^-$ reacts faster than $CO_3^{2-}$ in ligand substitution with Ir(ttp)Cl(CO) to give Ir(ttp)X (X: $OH^-$ > $MCO_3^-$, Scheme 1, Pathway **II**), which also reacts faster with toluene to produce Ir(ttp)H (Scheme 1, pathway **II$_a$**). Further reaction of Ir(ttp)H with toluene forms Ir(ttp)Bn (Scheme 1, Pathway **II$_b$**) or with unreacted Ir(ttp)-Cl(CO) to yield Ir(ttp)Me (Scheme 1, Pathway **II$_c$**).

**Table 7. Base Effect on the Formation of Ir(ttp)Me**

$$\mathrm{Ir(ttp)Cl(CO)} + \mathrm{PhCH_3} \xrightarrow[150\ ^\circ\mathrm{C,time,\ N_2}]{\text{base (equiv)}} \underset{\mathbf{2b}}{\mathrm{Ir(ttp)Bn}} + \underset{\mathbf{3}}{\mathrm{Ir(ttp)CH_3}} \quad (18)$$

| entry | base (equiv) | time | yield of **2b**/% | yield of **3**/% | total yield/% | ratio of **2b**: **3** |
|---|---|---|---|---|---|---|
| 1 | LiOH.H$_2$O (10) | 3 d | 62 | 23 | 85 | 2.70:1 |
| 2 | NaOH (10) | 1 d | 44 | 21 | 65 | 2.10:1 |
| 3 | KOH (10) | 1 h | 27 | 24 | 51 | 1.13:1 |
| 4 | Na$_2$CO$_3$ (20) | 10 d | 79 | 10 | 89 | 7.90:1 |
| 5 | K$_2$CO$_3$ (20) | 2 d | 66 | 3 | 69 | 22.0:1 |
| 6 | Cs$_2$CO$_3$ (20) | 1 h | 46 | 35 | 81 | 1.31:1 |

With a stronger base, more rapid deprotonation of Ir(ttp)H gives $[\mathrm{Ir(ttp)}]^-M^{+17}$ (Scheme 2, pathway **I**). The Ir(ttp) anion then attacks the CO ligand of Ir(ttp)Cl(CO) followed by dissociation of $Cl^-$ to give presumably Ir(ttp)C(O)Ir(ttp) **B**[28] (Scheme 2, Pathway **II**), which dissociates homolytically and rapidly to yield the $\mathrm{Ir^{II}}$(ttp) radical and $\mathrm{Ir^{III}}$(ttp)C(O) carbon-centered radical[29] **C** (Scheme 2, Pathway **II$_a$**). The $\mathrm{Ir^{III}}$(ttp)C(O) radical probably further reacts with Ir(ttp)H to give Ir(ttp)CHO and $\mathrm{Ir^{II}}$(ttp) radicals[27b,30] (Scheme 2, Pathway **III**). Ir(ttp)CHO is further reduced by Ir(ttp)H to yield Ir(ttp)Me[31] (Scheme 2, pathway **IV**). In view of the higher yield of Ir(ttp)Me with a stronger base in base-promoted BnCHA, the Ir(ttp) anion is probably the reacting species for Ir(ttp)Me formation (Scheme 2, pathways **II–IV**).

**Mechanism of Ir(ttp)Bn Formation.** $[\mathrm{Ir(ttp)}]_2$ is probably another reacting species to generate Ir(ttp)Bn in base-promoted BnCHA. The formation of $[\mathrm{Ir(ttp)}]_2$ was supported by its observation in 41% yield in the reaction of Ir(ttp)Cl(CO) with toluene-$d_8$ (50 equiv) and $Cs_2CO_3$ in $C_6D_6$ at 150 °C in 1 h (eq 19). The spectroscopic identification of $[\mathrm{Ir(ttp)}]_2$ was confirmed using an authentic sample of $[\mathrm{Ir(ttp)}]_2$[27a] generated by the reaction of Ir(ttp)H with 2,2,6,6-tetramethylpiperidinooxy (TEMPO) in $C_6D_6$ at room temperature for 5 min. Indeed, $[\mathrm{Ir(ttp)}]_2$ did react rapidly with toluene at 200 °C in 90 min to yield Ir(ttp)Bn in 46% yield (eq 20).

$$\mathrm{Ir(ttp)Cl(CO)} + \underset{\text{50 equiv}}{\mathrm{C_6D_5CD_3}} \xrightarrow[\text{1 h}]{150\ ^\circ\mathrm{C},\ \mathrm{Cs_2CO_3}\text{ (20 equiv)},\ \mathrm{C_6D_6}} \underset{38\%}{\mathrm{Ir(ttp)H}} + \underset{41\%}{[\mathrm{Ir(ttp)}]_2} + \underset{2\%}{\mathrm{Ir(ttp)Bn}\text{-}d_7} + \underset{14\%}{\mathrm{Ir(ttp)Me}} \quad (19)$$

$$[\mathrm{Ir(ttp)}]_2 + \mathrm{PhCH_3} \xrightarrow[\mathrm{N_2}]{1.5\text{ h, }200\ ^\circ\mathrm{C}} \underset{46\%}{\mathrm{Ir(ttp)Bn}} \quad (20)$$

$[\mathrm{Ir(ttp)}]_2$ is formed by the thermal (eqs 21 and 22) and base-promoted (eq 23) dehydrogenative dimer formation from Ir(ttp)H. Ir(ttp)H remained unreacted at room temperature in 2 h but reacted rapidly at 150 °C to give $[\mathrm{Ir(ttp)}]_2$ in 74% yield in 1 h (eq 21). This shows that high temperature is required for dimer formation from Ir(ttp)H. Alternatively, in the separate reaction of Ir(ttp)H with toluene (50 equiv) in $C_6D_6$ at 150 °C, $[\mathrm{Ir(ttp)}]_2$ was formed in 66% yield as the major species in 30 min prior to reacting with toluene to yield Ir(ttp)Bn (eq 22). Rh(oep)H (oep = octaethylporphyrin dianion) has also been

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(27) The authentic sample of $[\mathrm{Ir(ttp)}]_2$ was synthesized using the same method to synthesize $[\mathrm{Ir(oep)}]_2$ by reacting Ir(oep)H and TEMPO. (a) Chan, K. S.; Leung, Y.-B. *Inorg. Chem.* **1994**, *3*, 3187. The chemical shifts and splitting patterns of $[\mathrm{Ir(ttp)}]_2$ in $^1$H NMR spectrocscopy was similar to that of $[\mathrm{Rh(ttp)}]_2$. For $[\mathrm{Ir(ttp)}]_2$: $^1$H NMR ($C_6D_6$) $\delta$ 9.48 (d, 4 H, *o*-phenyl), 8.33 (s, 8 H, pyrrole), 7.65 (d, 4 H, *o′*-phenyl), 2.46 (s, 12 H, *p*-methyl); m and *m′*-phenyl hydrogens are obscured by solvent (7.15). For $[\mathrm{Rh(ttp)}]_2$: $^1$H NMR ($C_6D_6$) $\delta$ 9.64 (d, 4 H, *o*-phenyl), 8.63 (s, 8 H, pyrrole), 7.75 (d, 4 H, *o′*-phenyl), 2.50 (s, 12 H, *p*-methyl); m and *m′*-phenyl hydrogens are obscured by solvent (7.15). (b) Wayland, B. B.; Voorhees, S. L. V.; Charles Wilker, C. *Inorg. Chem.* **1986**, *25*, 4039–4042.

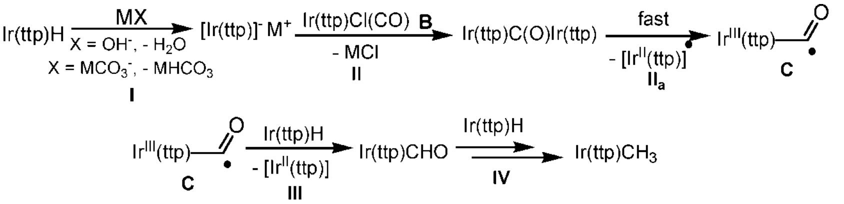
(28) An analogue of Ir(ttp)C(O)Ir(ttp), Rh(oep)C(O)Rh(oep), had been reported. (a) Wayland, B. B.; Woods, B. A.; Coffin, V. L. *Organometallics,* **1986**, *5*, 1059–1062. (b) Coffin, V. L.; Brennen, W.; Wayland, B. B. *J. Am. Chem. Soc.* **1988**, *110*, 6063–6069.

(29) Cui, W.; Li, S.; Wayland, B. B. *J. Organomet. Chem.* **2007**, *692*, 3198–3206.

(30) (a) Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333–4335. (b) Wayland, B. B.; Sherry, A. E.; Poszmik, G.; Bunn, A. G. *J. Am. Chem. Soc.* **1992**, *114*, 1673–1681.

(31) The reduction of a carbonyl ligand coordinated to transition metal to yield methyl ligand had been reported to proceed via a metal-formyl intermediate. Thus, Ir(ttp)CHO was proposed to be formed in the reduction of Ir(ttp)Cl(CO) by Ir(ttp)H.[25b]

**Scheme 2. Mechanism of Reduction of Ir(ttp)Cl(CO) by Ir(ttp)H to Generate Ir(ttp)Me**



reported to react to yield $[Rh(oep)]_2$ and $H_2$.[32] In the presence of $Cs_2CO_3$ (20 equiv) (eq 23), a small amount of $[Ir(ttp)]_2$ in 25% yield had already formed from the dehydrogenative dimerization of Ir(ttp)H at ambient temperature, and a high yield of $[Ir(ttp)]_2$ in 89% yield was formed in 30 min. Thus, the base also promoted the dimer formation of Ir(ttp)H to $[Ir(ttp)]_2$. Indeed, the base promoted the rate of BnCHA with Ir(ttp)H since the reaction of Ir(ttp)H with toluene (50 equiv) in $C_6D_6$ at 150 °C with $Cs_2CO_3$ (20 equiv) was complete to yield Ir(ttp)Bn in 55% in 6 days (eq 24), whereas the same reaction without base was still incomplete in 6 days (eq 25). Base probably deprotonates Ir(ttp)H to give the Ir(ttp) anion[17] for faster formation of $[Ir(ttp)]_2$, which in turn leads to faster rate of BnCHA.

$$2\mathrm{Ir(ttp)H} \xrightarrow[1.5\ \mathrm{h},\ 150\ ^\circ\mathrm{C}]{\mathrm{C_6D_6}} \underset{74\%}{[\mathrm{Ir(ttp)}]_2} + \mathrm{H_2} \tag{21}$$

$$\mathrm{Ir(ttp)H} + \underset{50\ \mathrm{equiv}}{\mathrm{PhCH_3}} \xrightarrow[150\ ^\circ\mathrm{C},\ 30\ \mathrm{min}]{\mathrm{C_6D_6}} \underset{5\%}{\mathrm{Ir(ttp)H}} + \underset{66\%}{[\mathrm{Ir(ttp)}]_2} + \underset{4\%}{\mathrm{Ir(ttp)Bn}} \tag{22}$$

$$\mathrm{Ir(ttp)H} + \underset{50\ \mathrm{equiv}}{\mathrm{PhCH_3}} \xrightarrow[150\ ^\circ\mathrm{C},\ 30\ \mathrm{min}]{\mathrm{Cs_2CO_3\ (20\ equiv),\ C_6D_6}} \underset{2\%}{\mathrm{Ir(ttp)H}} + \underset{89\%}{[\mathrm{Ir(ttp)}]_2} + \underset{4\%}{\mathrm{Ir(ttp)Bn}} \tag{23}$$

$$\mathrm{Ir(ttp)H} + \underset{50\ \mathrm{equiv}}{\mathrm{PhCH_3}} \xrightarrow[150\ ^\circ\mathrm{C},\ 6\ \mathrm{d}]{\mathrm{Cs_2CO_3\ (20\ equiv),\ C_6D_6}} \underset{55\%}{\mathrm{Ir(ttp)Bn}} \tag{24}$$

$$\mathrm{Ir(ttp)H} + \underset{50\ \mathrm{equiv}}{\mathrm{PhCH_3}} \xrightarrow[150\ ^\circ\mathrm{C},\ 6\ \mathrm{d}]{\mathrm{C_6D_6}} \underset{37\%}{\mathrm{Ir(ttp)H}} + \underset{40\%}{\mathrm{Ir(ttp)Bn}} \tag{25}$$

$[Ir(ttp)]_2$ probably reacts with toluene to yield both Ir(ttp)Bn and Ir(ttp)H, likely in a termolecular mechanism[33] analogous to BnCHA with Rh(tmp) (tmp = tetramesitylporphyrin dianion) radical[33b] and toluene. Indeed, $[Ir(oep)]_2$ has been reported to react with toluene to yield both Ir(oep)Bn and Ir(oep)H.[34] However, direct reaction of Ir(ttp)H with toluene to yield Ir(ttp)Bn and $H_2$ cannot be excluded. $[Ir(ttp)]_2$ probably reacts faster with toluene than Ir(ttp)H. It is because Ir(ttp)H, which was generated from the reaction of $[Ir(ttp)]_2$ with toluene, was consumed slowly in the reaction of Ir(ttp)H with toluene (50 equiv) in $C_6D_6$ at 150 °C (eq 25). Ir(ttp)Me was probably not generated from $[Ir(ttp)]_2$ as it did not form in the reaction of $[Ir(ttp)]_2$ with toluene (50 equiv) at 150 °C both with and without $Cs_2CO_3$ (20 equiv) (eqs 24 and 25).

**Mechanism: Weak Base.** In the presence of the weak base of NaOPh (Scheme 1, Pathway **III**), Ir(ttp)Cl(CO) undergoes ligand substitution[35] with NaOPh to give Ir(ttp)OPh. This is confirmed by the rapid conversion of Ir(ttp)Cl(CO) to Ir(ttp)OPh in 95% yield in the reaction of Ir(ttp)Cl(CO) with toluene (100 equiv) and NaOPh (20 equiv) in benzene-$d_6$ in 2 h as observed by $^1$H NMR spectroscopy (eq 26). The identity of Ir(ttp)OPh was confirmed by an authentic sample of Ir(ttp)OPh prepared in 86% yield by reacting Ir(ttp)Cl(CO) with NaOPh (2 equiv) in benzene at 150 °C for 12 h. Ir(ttp)OPh then reacts with toluene to yield Ir(ttp)Bn (Scheme 1, Pathway **III$_a$**). The intermediacy of Ir(ttp)OPh was supported by the reaction of Ir(ttp)OPh with toluene-$d_8$ at 200 °C in 1 day to yield Ir(ttp)Bn-$d_7$ in 75% isolated yield and PhOH in 31% yield by GC-MS analysis (eq 27). The absence of signals of Ir(ttp)H and benzyl phenyl ether[36] by $^1$H NMR spectroscopy in the reaction of Ir(ttp)OPh with toluene (100 equiv) in $C_6D_6$ at 200 °C for 10 days further supported the direct reaction of Ir(ttp)OPh with toluene to yield Ir(ttp)Bn and PhOH. The slower substitution of chloride by the less nucleophilic phenoxide anion (Scheme 1, Pathway **III**) and the lower reactivity of Ir(ttp)OPh with its bulky and less basic phenoxide anion (Scheme 1, Pathway **III$_a$**) account for the longer reaction time of BnCHA with NaOPh than with $K_2CO_3$.

$$\mathrm{Ir(ttp)Cl(CO)} + \underset{20\ \mathrm{equiv}}{\mathrm{NaOPh}} \xrightarrow[200\ ^\circ\mathrm{C},\ 2\ \mathrm{h}]{\mathrm{PhCH_3\ (100\ equiv),\ C_6D_6}} \underset{95\%}{\mathrm{Ir(ttp)OPh}} \tag{26}$$

$$\mathrm{Ir(ttp)OPh} \xrightarrow{\mathrm{C_6D_5CD_3},\ 200\ ^\circ\mathrm{C},\ 1\ \mathrm{d},\ \mathrm{N_2}} \underset{75\%}{\mathrm{Ir(ttp)Bn}\text{-}d_7} + \underset{31\%}{\mathrm{PhOH}} \tag{27}$$

Scheme 3 lists more detailed mechanisms for the BnCHA step with Ir(ttp)X (X = $OH^-$, $KCO_3^-$, $OPh^-$) with two major possible classes: (i) oxidative addition and (ii) $\sigma$-bond metathesis and its variants (Scheme 3). Oxidative addition (Scheme 3, Pathway **i**) involves the *cis*-addition of the $PhCH_2$−H bond to Ir(ttp)X to generate a 7-coordinate Ir(V) intermediate with three substituents on the *cis*-face of a porphyrin ligand, which is too crowded for reaction. Therefore, oxidative addition is less likely to occur. Classical $\sigma$-bond metathesis (Scheme 3, Pathway **ii**), and one of its variant forms, $\sigma$-complex-assisted metathesis ($\sigma$-CAM)[37] (Scheme 3, Pathway **iii**), involves the concerted rearrangement of bonds through a 4-center, 4-electron transition state. However, they are less favorable as suggested by the very slow analogous reaction of Ir(ttp)Me with toluene at 200 °C in

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[32] Wayland, B. B.; Del Rossi, K. J. *J. Organomet. Chem.* **1984**, *276*, C27–C30.

[33] (a) Sherry, A. E.; Wayland, B. B. *J. Am. Chem. Soc.* **1990**, *112*, 1259–1261. (b) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 5305–5311. (c) Zhang, X.-X.; Wayland, B. B. *J. Am. Chem. Soc.* **1994**, *116*, 7897–7898. (d) Cui, W.; Zhang, X. P.; Wayland, B. B. *J. Am. Chem. Soc.* **2003**, *125*, 4994–4995.

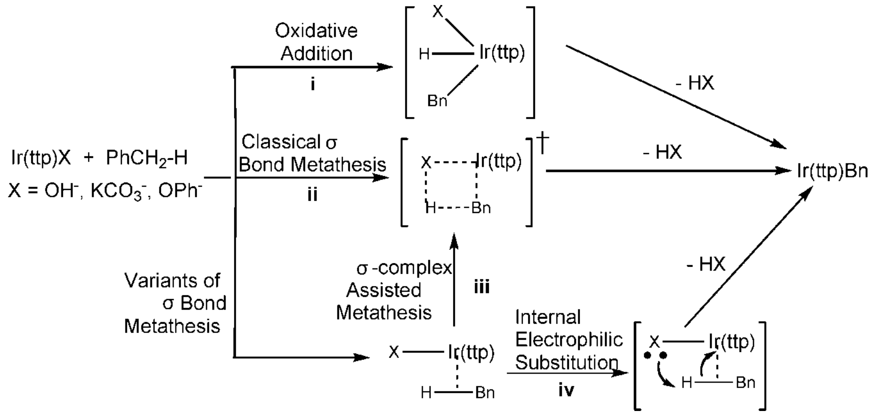
[34] Del Rossi, K. J.; Wayland, B. B. *J. Chem. Soc. Chem. Commun.* **1986**, 1653–1655.

[35] Rees, W. M.; Churchill, M. R.; Fettinger, J. C.; Atwood, J. D. *Organometallics* **1985**, *4*, 2179–2185.

[36] Wiles, C.; Watts, P.; Haswell, S. J.; Pombo-Villar, E. *Tetrahedron* **2005**, *61*, 10757–10773.

[37] The difference between $\sigma$-complex-assisted metathesis and classical $\sigma$-bond metathesis in CHA is that the former involves the pre-coordination of the C-H bond to the metal center before concerted bond rearrangement, whereas the latter involves the direct concerted rearrangement of bonds. Perutz, R. N.; Sabo-Etienne, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 2578–2592.

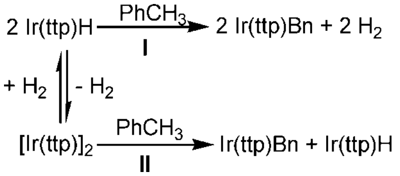
**Scheme 3. Four Possible Mechanisms of Base-Promoted BnCHA Steps**



14 days to give just a trace of Ir(ttp)Bn with the recovery of Ir(ttp)Me in 46% yield. Another refinement of classical $\sigma$-bond metathesis, the internal electrophilic substitution (IES)[12] (Scheme 3, Pathway **iv**), is probably the more likely mechanism with the participation of the lone electron pair of the oxygen atom of the phenoxide ligand. The oxygen in the phenoxide ligand in Ir(ttp)OPh is $sp^3$ hybridized with the filled $p$-type lone pair orbital of oxygen conjugated with the $\pi$ system of the aromatic group. As the distortion of the $p$ orbital of oxygen from the $\pi$ system of the aromatic group in phenol at high temperature has been reported[38] with the low energy barrier for OH rotation about the C−O bond in phenol (3.47 kcal/mol),[39] it is highly probable that the filled $p$ orbital of oxygen does not further overlap with the $\pi$ system of the aromatic group in the phenoxide ligand at the reaction temperature of 200 °C. The electron density of the $p$ orbital of oxygen in the phenol group can be enhanced and freely available to abstract the proton of toluene during IES.

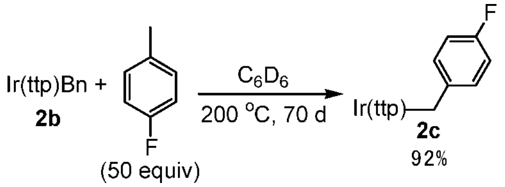
**Isotope Effect.** The observed isotope effect $(k_H/k_D)_{obs}$ for the BnCHA of toluene with Ir(ttp)Cl(CO) was measured by a competition experiment with an equimolar mixture of solvent toluene and toluene-$d_8$. At 200 °C, $(k_H/k_D)_{obs}$ was measured to be 2.37 without base after 9 days, 2.16 with $K_2CO_3$ after 3.5 h, and 2.18 with NaOPh after 2 days by $^1$H NMR spectroscopy. These values suggest that the cleavages of benzylic C−H bonds are involved in or occur prior to the rate-determining steps in the BnCHA. The observed isotope effect $(k_H/k_D)_{obs}$ for BnCHA of toluene at 200 °C with Ir(ttp)H and $[Ir(ttp)]_2$ was measured to be 2.30 and 2.10, resepectively, which are similar to $(k_H/k_D)_{obs}$ of 2.16 in BnCHA with Ir(ttp)Cl(CO) and $K_2CO_3$ at 200 °C. This implies that both Ir(ttp)H and $[Ir(ttp)]_2$ are the intermediates involved in the rate-determining step (RDS) in the base-promoted BnCHA of toluene with Ir(ttp)Cl(CO) (Scheme 1, pathway **II$_b$**). Moreover, a pre-equilibrium[40] exists between Ir(ttp)H and $[Ir(ttp)]_2$ prior to BnCHA at 200 °C (Scheme 4), and the generation of $[Ir(ttp)]_2$ from Ir(ttp)H is facile at high temperature as supported by independent experiments (eqs 21 and 22), especially in the presence of base (eq 23).

**Scheme 4. Parallel BnCHA of Toluene with Ir(ttp)H and $[Ir(ttp)]_2$**



Since the kinetic isotope effect (KIE) of the BnCHA of toluene with Rh(tmp) is 6.5[33b] and a linear transition state was suggested, the small KIE in BnCHA with iridium porphyrin cannot be accounted totally by the analogous linear transition state proposed in the BnCHA of toluene by $[Ir(ttp)]_2$. Probably a parallel pathway of BnCHA by Ir(ttp)H with a bent transition state can rationalize the small observed values (Scheme 4, Pathway **I**).

Ir(ttp)Bn did not react with 4-fluorotoluene (50 equiv) in $C_6D_6$ at 200 °C in 3 days without base. In 6 days, Ir(ttp)Bn reacted with 4-fluorotoluene and the ratio of Ir(ttp)Bn/Ir(ttp)Bn($p$-F) was found to be 11.5:1. Ir(ttp)Bn was completely consumed only after 70 days to yield Ir(ttp)Bn($p$-F) in 92% yield (eq 28). Besides, Ir(ttp)Bn did not react with toluene-$d_8$ (50 equiv) added with $K_2CO_3$ (20 equiv) in $C_6D_6$ at 200 °C in 18 h, but it reacted at a longer time of 4 days to yield Ir(ttp)Bn-$d_7$ with the ratio of Ir(ttp)Bn/Ir(ttp)Bn-$d_7$ of 26.8:1 (eq 29). After 14 days, the ratio of Ir(ttp)Bn/Ir(ttp)Bn-$d_7$ was found to be 3.57:1. Therefore, these results suggest that reactions of Ir(ttp)Bn with toluene-$d_8$ to give Ir(ttp)Bn-$d_7$ without and with base do not significantly affect the $(k_H/k_D)_{obs}$ values in the time scale of BnCHA. The $(k_H/k_D)_{obs}$values are generally truly kinetic values.

 (28)

$$\underset{\mathbf{2b}}{\mathrm{Ir(ttp)Bn}} + \mathrm{C_6D_5CD_3(50\ equiv)} \xrightarrow[200\ ^\circ\mathrm{C},\ 4\ \mathrm{d}]{\mathrm{K_2CO_3\ (20\ equiv),\ C_6D_6}} \underset{26.8:1}{\mathrm{Ir(ttp)Bn{:}Ir(ttp)Bn}\text{-}d_7} \quad (29)$$

**Hammett Plot.** In order to gain preliminary electronic effects of toluenes on base-promoted BnCHA, the Hammett plot was constructed from competition experiments using an equimolar mixture of 4-substituted toluenes (100 equiv) and toluene (100 equiv) with Ir(ttp)Cl(CO) and $K_2CO_3$ (20 equiv) at 200 °C in benzene (Table 8, eq 30). Because of the very slow reacton of benzyl exchange of Ir(ttp)Bn with 4-fluorotoluene (eq 28) and

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(38) Pratt, D. A.; de Heer, M. I.; Mulder, P.; Ingold, K. U. *J. Am. Chem. Soc.* **2001**, *123*, 5518–5526.

(39) Zierkiewicz, W.; Michalska, D.; Hobza, P. *Chem. Phys. Lett.* **2004**, *386*, 95–100.

(40) An anologue of Ir(ttp)H, Rh(oep)H, was in equilibrium with $[Rh(oep)]_2$ and $H_2$ (ref 32).

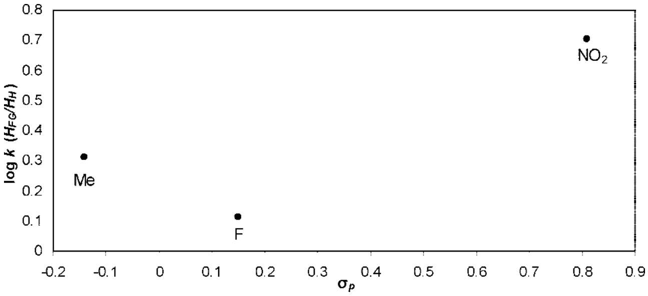
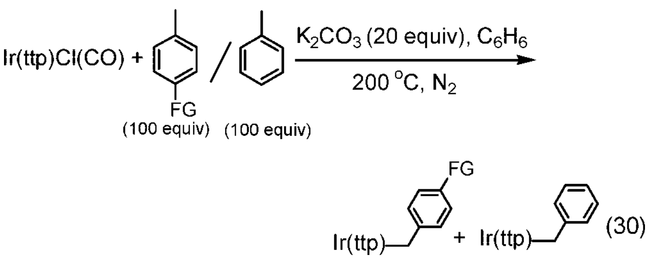


**Figure 2.** Hammett plot of base-promoted BnCHA of toluenes with Ir(ttp)Cl(CO).

**Table 8. Competition Experiments of Benzylic CHA**



| entry | $p$-FG | $\sigma_p$[a] | log $k$ ($H_{FG}/H_H$) |
|---|---|---|---|
| 1 | Me | −0.14 | 0.3118 |
| 2 | F | 0.15 | 0.1149 |
| 3 | $NO_2$ | 0.81 | 0.7048 |

[a] $\sigma_p$: *para*-substituent constant.

toluene-$d_8$ (eq 29), the ratios of both iridium porphyrin benzyls formed were genuine kinetic values. Figure 2 shows a nonlinear free energy relationship in the Hammett plot using the substituent constant $\sigma_p$.[41] Therefore, the rate-determining step of the multistepwise reactions likely changes with the *para* substituents of toluenes.

## Conclusions

In summary, we have discovered that the rates of benzylic carbon−hydrogen bond activation of toluenes by Ir(ttp)Cl(CO) were greatly enhanced by the presence of inorganic bases. Strong inorganic base $K_2CO_3$ generated both benzylic CHA complexes of iridium porphyrin benzyls and methyl. Weak inorganic base NaOPh selectively promoted BnCHA to yield benzylic CHA complexes only. With a strong base (e.g., $Cs_2CO_3$, KOH), Ir(ttp)H and $[Ir(ttp)]_2$ were the probable intermediates observed in the formation of Ir(ttp)Me and Ir(ttp)Bn, respectively. With a weak base NaOPh, Ir(ttp)OPh was the intermediate observed in the reaction. Ir(ttp)OPh likely underwent internal electrophilic substitution in BnCHA with toluene.

## Experimental Section

Unless otherwise noted, all reagents were purchased from commercial suppliers and directly used without further purification. Hexane was distilled from anhydrous calcium chloride. Benzene and toluene were distilled from sodium. Thin layer chromatography was performed on precoated silica gel 60 $F_{254}$ plates. Ir(ttp)Cl(CO),[16] $Ir(ttp)BF_4$ (an inseparable mixture of $Ir(ttp)(CO)BF_4$ and $Ir(ttp)BF_4$),[10] Ir(ttp)Me,[16] and Ir(ttp)Bn[16] were prepared according to the literature procedures. Neutral alumina (Merck, 70-230 mesh)/$H_2O$ (10:1 v/v) and silica gel (Merck, 70-230 mesh) were used for column chromatography.

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker DPX-300 at 300 and 75 MHz, respectively. Chemical Shifts were referenced with the residual solvent protons in $C_6D_6$ ($\delta$ = 7.15 ppm), $CDCl_3$ ($\delta$ = 7.26 ppm), or tetramethylsilane ($\delta$ = 0.00 ppm) in $^1$H NMR spectra, and $CDCl_3$ ($\delta$ = 77.16 ppm) or THF-$d_8$ ($\delta(\beta\text{–}CH_2)$ = 25.62 ppm) in $^{13}$C NMR spectra as the internal standards. Chemical shifts ($\delta$) were reported as part per million (ppm) in ($\delta$) scale downfield from TMS. Coupling constants ($J$) were reported in Hertz (Hz). High resolution mass spectra (HRMS) were performed on a ThermoFinnigan MAT 95 XL mass spectrometer in fast atom bombardment (FAB) mode using 3-nitrobenzyl alcohol (NBA) matrix and $CH_2Cl_2$ as solvent, and electrospray ionization (ESI) mode using $MeOH/CH_2Cl_2$ (1:1) as solvent.

**Independent Synthesis of (Porphyrinato)iridium(III) Benzyls [Ir(por)R].** Synthesis of (5,10,15,20-tetratolylporphyrinato)(4-methylbenzyl)iridium(III) by reductive benzylation of Ir(ttp)Cl(CO) is described as a typical example for the preparation of (porphyrinato)iridium(III) benzyl complexes.[16]

**(5,10,15,20-Tetrakis(*p*-tolyl)porphyrinato)(4-methylbenzyl)iridium(III) [Ir(ttp)Bn(*p*-Me)] (2a).** A suspension of Ir(ttp)Cl(CO) (100 mg, 0.11 mmol) in THF (50 mL) and a solution of $NaBH_4$ (153 mg, 67 $\mu$L, 1.08 mmol) in aqueous NaOH (1.0 M, 3.0 mL) were purged separately with $N_2$ for 15 min. The solution of $NaBH_4$ was added slowly to the suspension of Ir(ttp)Cl(CO) via a cannula. The mixture was heated at 70 °C under $N_2$ for 2 h in a Teflon screw-capped 250 mL round-bottomed flask to give a deep brown suspension. The mixture was then cooled to room temperature under $N_2$, and 4-methylbenzyl bromide (200 mg, 1.08 mmol) was added. The reaction mixture was further heated at 70 °C under $N_2$ for 2 h. A reddish brown suspension was formed. The reaction mixture was worked up by extraction with $CH_2Cl_2/H_2O$. The combined organic extract was dried ($MgSO_4$), filtered, and dried by rotary evaporation. The reddish brown residue was purified by column chromatography over alumina (70-230 mesh), eluting with a solvent mixture of $CH_2Cl_2$ and hexane (1:2). The major brown fraction was collected to give a brown solid (55 mg, 0.057 mmol, 52%) as the product after rotary evaporation. The product was further purified by recrystallization from $CH_2Cl_2/CH_3OH$. $R_f$ = 0.60 (1:1 hexane/$CH_2Cl_2$). $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ −4.01 (s, 2 H, $H_{29}$), 1.69 (s, 3 H, $H_{34}$), 2.69 (s, 12 H, $H_{25\text{–}28}$), 3.07 (d, 2 H, $J$ = 7.8 Hz, $H_{30,31}$), 5.69 (d, 2 H, $J$ = 7.8 Hz, $H_{32,33}$), 7.51 (d, 4 H, $J$ = 5.7 Hz, $H_{17,19,21,23}$), 7.53 (d, 4 H, $J$ = 5.7 Hz, $H_{18,20,22,24}$), 7.92 (d, 4 H, $J$ = 8.4 Hz, $H_{10,12,14,16}$), 8.00 (d, 4 H, $J$ = 8.4 Hz, $H_{9,11,13,15}$), 8.46 (s, 8 H, $H_{1\text{–}8}$). $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ −13.8, 21.2, 21.7, 124.1, 124.2, 127.1, 127.6, 131.3, 132.1, 133.7, 133.9, 137.2, 138.3, 139.0, 143.4. HRMS (ESIMS): Calcd for $[C_{56}H_{45}N_4Ir]^+$: $m/z$ 966.3268. Found: $m/z$ 966.3262. The single crystal used for X-ray diffraction crystallography was grown from $CH_2Cl_2$/MeOH.

**(5,10,15,20-Tetrakis(*p*-tolyl)porphyrinato)(4-fluorobenzyl)iridium(III) [Ir(ttp)Bn(*p*-F)] (2c).** 4-Fluorobenzyl bromide (204 mg, 135 $\mu$L, 1.08 mmol) was used. Brown solid (58 mg, 0.059 mmol, 54%) was obtained. $R_f$ = 0.60 (1:1 hexane/$CH_2Cl_2$). $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ −4.05 (s, 2 H, $H_{29}$), 2.69 (s, 12 H, $H_{25\text{–}28}$), 3.07 (dd, 2 H, $J_{HH}$ = 8.4 Hz, $^4J_{HF}$ = 6.0 Hz, $H_{30,31}$), 5.56 (dd, 2 H, $J_{HH}$ = 8.7 Hz, $^3J_{HF}$ = 8.9 Hz, $H_{32,33}$), 7.51 (d, 4 H, $J$ = 7.2 Hz, $H_{17,19,21,23}$), 7.53 (d, 4 H, $J$ = 7.2 Hz, $H_{10,12,14,16}$), 7.94 (d, 4 H, $J$ = 6.9 Hz, $H_{10,12,14,16}$), 8.00 (d, 4 H, $J$ = 7.8 Hz, $H_{9,11,13,15}$), 8.48 (s, 8 H, $H_{1\text{–}8}$). $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ −15.1, 21.7, 112.7 (d, $^2J_{CF}$= 21 Hz), 124.2, 125.2 (d, $^3J_{CF}$ = 7.7 Hz), 127.7, 131.4, 133.8, 137.1, 137.3, 138.9, 143.3, 157.1 (d, $^1J_{CF}$ = 241 Hz). HRMS (FABMS): Calcd for $[C_{55}H_{42}N_4FIr]^+$: $m/z$ 970.3017. Found: $m/z$ 970.3036.

**(5,10,15,20-Tetrakis(*p*-tolyl)porphyrinato)(4-*tert*-butylbenzyl)iridium(III) [Ir(ttp)Bn(*p*-$^t$Bu)] (2e).** 4-*tert*-Butylbenzyl bromide (245 mg, 1.08 mmol) was used. Brown solid (72 mg, 0.072

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(41) Isaacs, N. S. *Physical Organic Chemistry*; ELBS, Longman: Avon, U.K., 1987.

mmol, 65%) was obtained. $R_f = 0.62$ (1:1 hexane/$CH_2Cl_2$). $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ −4.02 (s, 2 H, $H_{29}$), 0.98 (s, 9 H, $H_{34–36}$), 2.69 (s, 12 H, $H_{25–28}$), 3.14 (d, 2 H, $J = 8.1$ Hz, $H_{30,31}$), 5.92 (d, 2 H, $J = 8.1$ Hz, $H_{32,33}$), 7.50 (d, 4 H, $J = 6.3$ Hz, $H_{17,19,21,23}$), 7.52 (d, 4 H, $J = 6.3$ Hz, $H_{18,20,22,24}$), 7.98 (d, 4 H, $J = 6.3$ Hz, $H_{10,12,14,16}$), 7.99 (d, 4 H, $J = 6.3$ Hz, $H_{9,11,13,15}$), 8.44 (s, 8 H, $H_{1–8}$). $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ −13.6, 21.7, 30.9, 34.3, 123.3, 123.7, 124.2, 127.5, 127.6, 131.3, 133.7, 133.9, 137.2, 138.1, 139.0, 143.4, 145.2. HRMS (FABMS): Calcd for $[C_{59}H_{51}N_4Ir]^+$: *m/z* 1008.3737. Found: *m/z* 1008.3733. The single crystal used for X-ray diffraction crystallography was grown from $CH_2Cl_2$/MeOH.

**Preparation of (5,10,15,20-Tetrakis(*p*-tolyl)porphyrinato)-methyliridium(III) hydride [Ir(ttp)H] (4).** Ir(ttp)H was prepared according to the literature procedure for the synthesis of Ir(oep)H.[17] A suspension of Ir(ttp)Cl(CO) (100 mg, 0.11 mmol) in THF (50 mL), a solution of $NaBH_4$ (153 mg, 67 $\mu$L, 1.08 mmol) in aqueous NaOH (1.0 M, 3.0 mL), and concentrated HCl (10 mL) in water (200 mL) were purged separately with $N_2$ for 15 min. The solution of $NaBH_4$ was added slowly to the suspension of Ir(ttp)Cl(CO) via a cannula. The mixture was heated at 70 °C under $N_2$ for 2 h in a Teflon screw-capped 250 mL round-bottomed flask to give a deep brown suspension. The mixture was then cooled in an ice–water bath under $N_2$, and HCl solution was added via a cannula. The reaction mixture was stirred in an ice–water bath under $N_2$ until a reddish brown precipitate formed. The precipitate was collected under $N_2$ by suction filtration and washed with water to give **4** (83 mg, 0.097 mmol, 88%). $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ −57.6 (s, 1 H, $H_{29}$), 2.68 (s, 12 H, $H_{25–28}$), 7.50 (d, 8 H, $J = 7.2$ Hz, $H_{17–24}$), 8.00 (d, 8 H, $J = 6.9$ Hz, $H_{9–16}$), 8.57 (s, 8 H, $H_{1–8}$). $^{13}C$ NMR (THF-$d_8$, 75 MHz)$\delta$ 21.9, 124.5, 128.3, 128.6, 132.0, 134.9, 138.1, 140.5, 144.8. HRMS (FABMS): Calcd for $[C_{48}H_{47}N_4Ir]^-$: *m/z* 862.2653. Found: *m/z* 862.2640.

**Preparation of (5,10,15,20-Tetrakis(*p*-tolyl)porphyrinato)(phenoxy)iridium(III) [Ir(ttp)OPh] (5).** Ir(ttp)Cl(CO) (50 mg, 0.054 mmol), NaOPh (12.5 mg, 0.11 mmol), and benzene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 150 °C under $N_2$ for 12 h. The solvent was then removed under vacuum, and the reddish orange residue was purified by column chromatography over silica gel (70-230 mesh), eluting with $CHCl_3$. The major reddish orange fraction was collected to give **5** (44.4 mg, 0.047 mmol, 86%). $R_f = 0.30$ ($CHCl_3$). $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 1.89 (d, 2 H, $J = 8.1$ Hz, $H_{29,30}$), 2.79 (s, 12 H, $H_{25–28}$), 5.66 (t, 2 H, $J = 7.8$ Hz, $H_{31,32}$), 5.83 (t, 1 H, $J = 7.2$ Hz, $H_{33}$), 7.65 (d, 8 H, $J = 7.8$ Hz, $H_{17–24}$), 8.14 (d, 4 H, $J = 8.1$ Hz, $H_{1–8}$), 8.20 (d, 4 H, $J = 8.1$ Hz, $H_{9,11,13,15}$), 8.99 (s, 8 H,$H_{1–8}$). $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 21.7, 116.2, 119.5, 122.3, 125.7, 127.5, 127.8, 131.7, 134.2, 134.6, 137.7, 138.6, 141.4, 158.6. The determination of the molecular mass $M^+$ of Ir(ttp)OPh by FAB or ESI mass spectroscopy (MS) was unsuccessful, with the FABMS only showing the metalloporphyrin peak $[Ir(ttp)]^+ = 861$. The growth of a single crystal of Ir(ttp)OPh from $CH_2Cl_2$/MeOH or $CH_2Cl_2$/hexane for X-ray diffraction crystallography was also unsuccessful with the decomposition of Ir(ttp)OPh in the solvent.

**Reaction of Ir(ttp)$BF_4$ with Toluene: Synthesis of (5,10,15,20-Tetrakis(*p*-tolyl)porphyrinato)(4-tolyl)iridium(III) [Ir(ttp)(*p*-tol)] (6).** Ir(ttp)$BF_4$ [Ir(ttp)(CO)$BF_4$/Ir(ttp)$BF_4$ (10:1 ratio in $^1H$ NMR)][10] (15.0 mg, 0.015 mmol) and toluene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 2 h. The solvent was then removed under vacuum, and the reddish brown residue was purified by column chromatography over alumina (70-230 mesh), eluting with a solvent mixture of $CH_2Cl_2$ and hexane (1:1). The major orange fraction was collected to give **6** (3.6 mg, 0.004 mmol, 26%). $R_f = 0.40$ (1:1 hexane/$CH_2Cl_2$). $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 0.47 (d, 2 H, $J = 8.4$ Hz), 1.10 (s, 3 H), 2.68 (s, 12 H, $H_{25–28}$), 4.56 (d, 2 H, $J = 8.4$ Hz), 7.50 (d, 8 H, $J = 8.1$ Hz, $H_{17,19,21,23}$), 8.00 (d, 8 H, $J = 8.1$ Hz, $H_{17,19,21,23}$), 8.57 (s, 8 H). $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 19.3, 21.7, 89.8, 124.2, 124.3, 127.6, 128.6, 129.2, 131.6, 133.8, 134.2, 137.4, 138.8, 143.1. HRMS (FABMS): Calcd for $[C_{55}H_{43}N_4Ir]^+$: *m/z* 952.3111. Found: *m/z* 952.3119.

**Preparation of (5,10,15,20-Tetrakis(*p*-tolyl)porphyrinato)iridium(II) Dimer [[Ir(ttp)]$_2$] (7).** $[Ir(ttp)]_2$ was prepared using the literature method for the preparation of $[Ir(oep)]_2$.[30] Ir(ttp)H (4.2 mg, 0.005 mmol) and 2,2,6,6-tetramethylpiperidinooxy (TEMPO) (1.1 mg, 0.007 mmol) were added to a Rotaflo screw-capped NMR tube. Benzene-$d_6$ (0.50 mL) was added to the tube under $N_2$. The reaction mixture was degassed for three freeze–thaw−pump cycles in the tube and then flame-sealed under vacuum. Compound **7** was observed by $^1H$ NMR spectroscopy. $^1H$ NMR ($C_6D_6$) $\delta$ 9.48 (d, 4 H, *o*-phenyl), 8.33 (s, 8 H, pyrrole), 7.65 (d, 4 H, *o′*-phenyl), 2.46 (s, 12 H, *p*-methyl); m and *m′*-phenyl hydrogens are obscured by solvent (7.15).

**Reaction of Ir(ttp)Cl(CO) with Toluene.** Ir(ttp)Cl(CO) (30.0 mg, 0.032 mmol) and toluene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 9 days. The solvent was then removed under vacuum, and the reddish brown residue was purified by column chromatography over silica gel (70-230 mesh), eluting with a solvent mixture of $CH_2Cl_2$ and hexane (1:1). The major orange fraction was collected to give **2b** (16.8 mg, 0.018 mmol, 55%).

**General Procedures for Reactions of Ir(ttp)Cl(CO) with Toluene and Various Ligands or Bases. Addition of 10 Equiv of 2,6-Di-*tert*-butylpyridine.** Ir(ttp)Cl(CO) (30.0 mg, 0.032 mmol), 2,6-di-*tert*-butylpyridine (61.2 mg, 72 $\mu$L, 0.32 mmol), and toluene (2 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 10 days to give **2b** (17.5 mg, 0.018 mmol, 58%).

**Addition of 10 Equiv of CsCl.** Ir(ttp)Cl(CO) (15.5 mg, 0.017 mmol), CsCl (28 mg, 0.17 mmol), and toluene (1.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 15 days. The solvent was then removed under vacuum, and the reddish brown residue was purified by column chromatography over alumina (70-230 mesh), eluting with a solvent mixture of $CH_2Cl_2$ and hexane (1:4) to obtain the brown fraction of **2b** (9.7 mg, 0.010 mmol, 61%). $CH_2Cl_2$/hexane (1:1) was then used to isolate the red fraction of unreacted Ir(ttp)Cl(CO) (1.8 mg, 0.002 mmol, 12%).

**Addition of 10 Equiv of $NaNH_2$.** Ir(ttp)Cl(CO) (20.0 mg, 0.022 mmol), $NaNH_2$ (8.6 mg, 0.22 mmol), and toluene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 15 min. The solvent was then removed under vacuum, and the reddish brown residue was purified by column chromatography over alumina (70-230 mesh), eluting with a solvent mixture of $CH_2Cl_2$ and hexane (1:1). Compounds **2b** and **3** with the same $R_f = 0.50$ ($CH_2Cl_2$/hexane = 1: 1) were collected in one portion, and the ratio was determined by $^1H$ NMR spectroscopy from the integration of the methyl protons of the Ir-$CH_2$Ar group of **2b** and the methyl protons of the Ir-Me group of Ir(ttp)Me. Compound **2b** (9.0 mg, 0.0095 mmol, 43%) and Ir(ttp)Me (0.3 mg, 0.0003 mmol, 13%) were obtained.

**Addition of 10 Equiv of NaOH.** Ir(ttp)Cl(CO) (20.0 mg, 0.022 mmol), NaOH 12.3 mg, 0.22 mmol), and toluene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 1 h to give **2b** (7.1 mg, 0.0075 mmol, 34%) and Ir(ttp)Me (0.1 mg, 0.0002 mmol, 7%).

**Addition of 20 Equiv of $Cs_2CO_3$.** Ir(ttp)Cl(CO) (20.0 mg, 0.022 mmol), $Cs_2CO_3$ (140 mg, 0.43 mmol), and toluene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 1 h to give **2b** (7.7 mg, 0.008 mmol, 37%) and Ir(ttp)Me (0.8 mg, 0.0009 mmol, 4%).

**Addition of 10 Equiv of $K_2CO_3$.** Ir(ttp)Cl(CO) (30.0 mg, 0.032 mmol), $K_2CO_3$(45 mg, 0.32 mmol), and toluene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 150 °C under $N_2$ for 2 days to give **2b** (19.5 mg, 0.020 mmol, 63%) and Ir(ttp)Me (0.3 mg, 0.0003 mmol, 1%).

**Addition of 20 Equiv of $K_2CO_3$.** Ir(ttp)Cl(CO) (30.0 mg, 0.022 mmol), $K_2CO_3$(59 mg, 0.43 mmol), and toluene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at selected temperatures under $N_2$. At 150 °C, the reaction was complete in 2 days to give **2b** (18.8 mg, 0.020 mmol, 61%) and Ir(ttp)Me (0.9 mg, 0.0009 mmol, 3%). At 200 °C, the reaction was complete in 3.5 h to give **2b** (12.8 mg, 0.013 mmol, 61%) and Ir(ttp)Me (1.3 mg, 0.002 mmol, 7%).

**Addition of 30 Equiv of $K_2CO_3$.** Ir(ttp)Cl(CO) (30.0 mg, 0.022 mmol), $K_2CO_3$(90 mg, 0.65 mmol), and toluene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 2 h to give **2b** (18.5 mg, 0.019 mmol, 60%) and Ir(ttp)Me (2.0 mg, 0.002 mmol, 7%).

**Addition of 20 Equiv of NaOPh.** Ir(ttp)Cl(CO) (20.0 mg, 0.022 mmol), NaOPh (50 mg, 0.43 mmol), and toluene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 2 days to give **2b** (16.2 mg, 0.017 mmol, 78%).

**Addition of 20 Equiv of NaF.** Ir(ttp)Cl(CO) (20.0 mg, 0.022 mmol), NaF (18 mg, 0.43 mmol), and toluene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 6 days to give **2b** (19.8 mg, 0.021 mmol, 96%).

**Reaction of Ir(ttp)Cl(CO) with *p*-Xylene.** Ir(ttp)Cl(CO) (30.0 mg, 0.032 mmol) and *p*-xylene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 3.5 days. The solvent was then removed under vacuum, and the reddish brown residue was purified by column chromatography over alumina (70-230 mesh), eluting with a solvent mixture of $CH_2Cl_2$ and hexane (1:1) as the eluent. The major orange fraction was collected to give **2a** (17.3 mg, 0.018 mmol, 56%).

**General Procedures for the Reactions of Ir(ttp)Cl(CO) with *p*-Xylene and Various Bases. Addition of 20 Equiv of $K_2CO_3$.** Ir(ttp)Cl(CO) (20.0 mg, 0.022 mmol), $K_2CO_3$ (59 mg, 0.43 mmol), and *p*-xylene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 1 h. The solvent was then removed under vacuum, and the reddish brown residue was purified by column chromatography over silica gel (70-230 mesh), eluting with a solvent mixture of $CH_2Cl_2$ and hexane (1:1). Compound **2a** and Ir(ttp)Me with the same $R_f = 0.50$ ($CH_2Cl_2$/hexane = 1:1) were collected in one portion, and the ratio was determined by $^1H$ NMR spectroscopy from the integration of the methyl protons of the Ir-$CH_2$Ar group of **2a** and the methyl protons of the Ir-Me group of Ir(ttp)Me. Compound **2a** (8.7 mg, 0.009 mmol, 41%) and Ir(ttp)Me (0.2 mg, 0.0002 mmol, 1%) were obtained.

**Addition of 20 Equiv of NaOPh.** Ir(ttp)Cl(CO) (20.0 mg, 0.022 mmol), NaOPh (50.0 mg, 0.43 mmol), and *p*-xylene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 1 h. Compound **2a** (14.2 mg, 0.015 mmol, 67%) was obtained.

**Reaction of Ir(ttp)Cl(CO) with 4-Fluorotoluene.** Ir(ttp)Cl(CO) (30.0 mg, 0.032 mmol) and 4-fluorotoluene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 9 days. The solvent was then removed under vacuum, and the reddish brown residue was purified by column chromatography over silica gel (70-230 mesh), eluting with a solvent mixture of $CH_2Cl_2$ and hexane (1:1). The major orange fraction was collected. Compound **2c** (23.2 mg, 0.024 mmol, 75%) was obtained.

**General Procedures for the Reactions of Ir(ttp)Cl(CO) with 4-Fluorotoluene and Various Bases. Addition of 20 Equiv of $K_2CO_3$.** Ir(ttp)Cl(CO) (20.0 mg, 0.022 mmol), $K_2CO_3$ (59 mg, 0.43 mmol), and 4-fluorotoluene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 2 h. Compound **2c** (13.6 mg, 0.014 mmol, 62%) was obtained.

**Addition of 20 Equiv of NaOPh.** Ir(ttp)Cl(CO) (20.0 mg, 0.022 mmol), NaOPh (50.0 mg, 0.43 mmol), and 4-fluorotoluene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 12 h. Compound **2c** (16.6 mg, 0.017 mmol, 78%) was obtained.

**Reaction of Ir(ttp)Cl(CO) with 4-Nitrotoluene.** Ir(ttp)Cl(CO) (30.0 mg, 0.032 mmol) and 4-nitrotoluene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 1 day. Decomposition of Ir(ttp)Cl(CO) resulted.

**General Procedures for the Reactions of Ir(ttp)Cl(CO) with 4-Nitrotoluene and Various Bases. Addition of 20 Equiv of $K_2CO_3$: Synthesis of (5,10,15,20-Tetrakis(*p*-tolyl)porphyrinato)(4-nitrobenzyl)iridium(III) [Ir(ttp)Bn(*p*-$NO_2$)] (2d).** Ir(ttp)-Cl(CO) (20.0 mg, 0.022 mmol), $K_2CO_3$ (59 mg, 0.43 mmol), and 4-nitrotoluene (1.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 5 min. The solvent was then removed under vacuum, and the reddish brown residue was purified by column chromatography over alumina (70-230 mesh), eluting with a solvent mixture of $CH_2Cl_2$ and hexane (1:2). The major orange fraction was collected to give **2d** (17.3 mg, 0.017 mmol, 80%). $R_f = 0.50$ (1:1 $CH_2Cl_2$/hexane). $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ –3.84 (s, 2 H, $H_{29}$), 2.70 (s, 12 H, $H_{28}$), 3.07 (d, 2 H, $J = 7.5$ Hz, $H_{30,31}$), 6.70 (d, 2 H, $J = 7.5$ Hz, $H_{32,33}$), 7.52 (d, 4 H, $J = 7.3$ Hz, $H_{17,19,21,23}$), 7.54 (d, 4 H, $J = 7.5$ Hz, $H_{18,20,22,24}$), 7.91 (d, 4 H, $J = 7.3$ Hz, $H_{10,12,14,16}$), 7.98 (d, 4 H, $J = 7.2$ Hz,$H_{9,11,13,15}$), 8.50 (s, 8 H,$H_{1–8}$). $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ –16.7, 21.7, 121.2, 123.9, 124.2, 127.4, 127.8, 130.6, 131.5, 133.7, 133.8, 137.5, 138.6, 143.0. HRMS (FABMS): Calcd for $[C_{55}H_{42}N_5O_2Ir]^+$: *m/z* 997.2962. Found: *m/z* 997.2948. The single crystal used for X-ray diffraction crystallography was grown from $CH_2Cl_2$/MeOH.

**Addition of 20 Equiv of NaOPh.** Ir(ttp)Cl(CO) (20.0 mg, 0.022 mmol), NaOPh (50.0 mg, 0.43 mmol), and 4-nitrotoluene (1.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 5 min. Compound **2d** (9.3 mg, 0.0093 mmol, 43%) was obtained.

**Reaction of Ir(ttp)H with Toluene.** Ir(ttp)H (20.0 mg, 0.023 mmol) and toluene (2.0 mL) were degassed for three freeze–thaw–pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 1 h. The solvent was then removed under vacuum, and the reddish brown residue was purified by column chromatography over alumina (70-230 mesh), eluting with a solvent mixture of $CH_2Cl_2$ and hexane (1:1). Compound **2b** (10.5 mg, 0.011 mmol, 48%) was obtained.

**Reaction of Ir(ttp)Me with Toluene.** Ir(ttp)Me[16] (10.0 mg, 0.011 mmol) and toluene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200

°C under $N_2$ for 14 days. The solvent was then removed under vacuum, and the reddish brown residue was purified by column chromatography over silica gel (70-230 mesh), eluting with a solvent mixture of $CH_2Cl_2$ and hexane (1:1). A trace of **2b** was observed in crude $^1H$ NMR only and could not be isolated. Ir(ttp)Me (4.6 mg, 0.005 mmol, 46%) was recovered.

**Reaction of Ir(ttp)Me with Toluene and $K_2CO_3$.** Ir(ttp)Me (10.0 mg, 0.011 mmol), $K_2CO_3$ (32 mg, 0.23 mmol), and toluene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 3 days. The solvent was then removed under vacuum, and the reddish brown residue was purified by column chromatography over silica gel (70-230 mesh), eluting with a solvent mixture of $CH_2Cl_2$ and hexane (1:1). A trace of **2b** was observed in crude $^1H$ NMR only and cannot be isolated. Ir(ttp)Me (9.2 mg, 0.011 mmol, 92%) was recovered.

**Reaction of Ir(ttp)(*p*-Tol) with Toluene.** Ir(ttp)(*p*-Tol) (5.0 mg, mmol) and toluene (1.0 mL) was degassed for three freeze–thaw–pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 1.5 days. No Ir(ttp)Bn and only unreacted Ir(ttp)(*p*-Tol) were observed by thin-layer chromatography.

**Reaction of Ir(ttp)Bn with 4-Fluorotoluene.** Compound **2b** (5.0 mg, 0.005 mmol), 4-fluorotoluene (28.9 mg, 29 $\mu$L, 0.26 mmol), and benzene-$d_6$ (0.50 mL) were degassed for three freeze–thaw–pump cycles in a Teflon screw-capped NMR tube and then flame-sealed under vacuum. The reaction mixture was covered by aluminum foil and heated at 200 °C in a sand bath. In the course of the reaction, the amount of **2b** was decreasing, while **2c** was increasing. After 6 days, the ratio of **2b**/**2c** was found to be 11.5:1 as observed by $^1H$ NMR spectroscopy using the *ortho*-phenyl protons of $IrCH_2Ar$ in **2b** and **2c**. After 70 days, all **2b** was consumed to give **2c** (92%, NMR yield) using benzene as the internal reference.

**Reaction of Ir(ttp)Bn with Toluene-$d_8$ and $K_2CO_3$.** Compound **2b** (6.1 mg, 0.006 mmol), toluene-$d_8$ (32.1 mg, 34 $\mu$L, 0.32 mmol), $K_2CO_3$ (18 mg, 0.13 mmol), and benzene-$d_6$ (0.60 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped NMR tube and then flame-sealed under vacuum. The reaction mixture was covered by aluminum foil and heated at 200 °C in a sand bath. In the course of the reaction, the amount of **2b** was decreasing, while **2b-$d_7$** was increasing. After 4 days, the ratio of **2b**/**2b-$d_7$** was found to be 26.8:1 observed by $^1H$ NMR spectroscopy (integration of benzylic proton = 2.000, the integration of pyrrole signal was set as 8.29). After 14 days, the ratio of **2b**/**2b-$d_7$** was found to be 3.57:1 as measured by FABMS. The recovery yield of **2b** was 74% (NMR yield), and the yield of **2b-$d_7$** was 21% (NMR yield) using benzene as the internal reference. The amount of toluene was increasing in the course of reaction indicated by the increased intensity of methyl protons of toluene at 2.70 ppm.

**Reaction of Ir(ttp)Cl(CO) with *p*-Xylene in $C_6D_6$.** Ir(ttp)Cl(CO) (5.8 mg, 0.006 mmol), *p*-xylene (66.6 mg, 77 $\mu$L, 0.63 mmol), and benzene-$d_6$ (0.50 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped NMR tube and then flame-sealed under vacuum. The reaction mixture was covered by aluminum foil and heated at 200 °C in a sand bath. In the course of the reaction, the amount of Ir(ttp)Cl(CO) was decreasing, while **2a** was increasing. After 22 days, **2a** (47%, NMR yield) and unreacted Ir(ttp)Cl(CO) (31%, NMR yield) were observed using the methyl protons of *p*-xylene as the reference.

**Reaction of Ir(ttp)Cl(CO) with $Ph^{13}CH_3$ and $Cs_2CO_3$.** Ir(ttp)Cl(CO) (5.8 mg, 0.006 mmol), $Ph^{13}CH_3$ (29 mg, 33 $\mu$L, 0.31 mmol), $Cs_2CO_3$ (41 mg, 0.13 mmol), and benzene-$d_6$ (0.50 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped NMR tube and then flame-sealed under vacuum. The reaction mixture was covered by aluminum foil and heated at 150 °C in an oil bath. Ir(ttp)H (81%, NMR yield) was observed as an only intermediate in 30 min. Besides, Ir(ttp)Cl(CO) (10.0 mg, 0.011 mmol), $Cs_2CO_3$ (70 mg, 0.22 mmol), and $Ph^{13}CH_3$ (0.10 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped NMR tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ in an oil bath for 2 h. The solvent was then removed under vacuum, and the reddish brown residue was purified by column chromatography over alumina (70-230 mesh), eluting with a solvent mixture of $CH_2Cl_2$ and hexane (1:1). The major orange fraction was collected to give Ir(ttp)$^{13}CH_2Ph$ (8%, NMR yield estimated from crude $^1H$ NMR as it could not be isolated) and Ir(ttp)Me (1.6 mg, 0.002 mmol, 17%). HRMS (FABMS): Calcd for $[C_{54}{}^{13}CH_{43}N_4Ir]^+$: *m*/*z* 953.3145. Found: *m*/*z* 953.3154.

**Reduction of Ir(ttp)Cl(CO) by Ir(ttp)H with $Cs_2CO_3$. (i) In toluene-$d_8$.** Ir(ttp)H (15.3 mg, 0.018 mmol), Ir(ttp)Cl(CO) (4.1 mg, 0.004 mmol), $Cs_2CO_3$ (29 mg, 0.089 mmol), and toluene-$d_8$ (0.50 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped NMR tube and then flame-sealed under vacuum. The reaction mixture was covered by aluminum foil and heated at 150 °C in an oil bath. Ir(ttp)H was consumed after 4 days. The crude product was dried under vacuum. The products were purified by alumina column chromatography to give Ir(ttp)Bn-$d_7$ (19%, 4.0 mg, 0.004 mmol) and Ir(ttp)Me (10%, 2.0 mg, 0.002 mmol). HRMS (FABMS): Calcd for $[C_{55}H_{36}D_7N_4Ir]^+$: *m*/*z* 959.3551. Found: *m*/*z* 959.3554.

**(ii) In benzene-$d_6$.** Ir(ttp)H (7.1 mg, 0.008 mmol), Ir(ttp)Cl(CO) (1.9 mg, 0.002 mmol), $Cs_2CO_3$ (67 mg, 0.21 mmol), and benzene-$d_6$ (0.50 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped NMR tube and then flame-sealed under vacuum. The reaction mixture was covered by aluminum foil and heated at 150 °C in an oil bath. Ir(ttp)H was consumed after 11 days. Ir(ttp)Me (10%, NMR yield) was obtained using $C_6D_6$ as the internal standard.

**Reduction of Ir(ttp)Cl(CO) by Ir(ttp)H.** Ir(ttp)H (16.3 mg, 0.019 mmol), Ir(ttp)Cl(CO) (4.3 mg, 0.005 mmol), and toluene-$d_8$ (0.50 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped NMR tube and then flame-sealed under vacuum. The reaction mixture was covered by aluminum foil and heated at 150 °C in an oil bath. Some Ir(ttp)H remained unreacted after 7 days. The reaction temperature was increased to 200 °C for 19 days. The crude product was dried under vacuum. The products were purified by alumina column chromatography. Ir(ttp)Bn-$d_7$ (23%, 5.5 mg, 0.005 mmol) and Ir(ttp)Me (5%, 1.0 mg, 0.001 mmol) were obtained. Unreacted Ir(ttp)Cl(CO) (23%, NMR yield) and Ir(ttp)H (19%, NMR yield) were estimated from crude $^1H$ NMR.

**Reaction of Ir(ttp)Cl(CO) with $H_2O$.** Ir(ttp)Cl(CO) (9.1 mg, 0.010 mmol), $H_2O$ (17.7 $\mu$L, 0.98 mmol), and benzene (1.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube and then flame-sealed under vacuum. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 8 days. No Ir(ttp)Me was generated, and Ir(ttp)Cl(CO) remained unreacted.

**Reaction of Ir(ttp)Cl(CO) with toluene-$d_8$ and $Cs_2CO_3$.** Ir(ttp)Cl(CO) (9.7 mg, 0.010 mmol), toluene-$d_8$ (53 mg, 56$\mu$L, 0.52 mmol), $Cs_2CO_3$ (68 mg, 0.21 mmol), and benzene-$d_6$ (0.50 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped NMR tube and then flame-sealed under vacuum. The reaction mixture was covered by aluminum foil and heated at 150 °C in an oil bath. All Ir(ttp)Cl(CO) was consumed, and Ir(ttp)H (38%, NMR yield) and $[Ir(ttp)]_2$ (41%, NMR yield) were obtained after 1 h. All Ir(ttp)H was consumed in 14 days to yield Ir(ttp)Bn-$d_7$ (42%, NMR yield) and Ir(ttp)Me (34%, NMR yield) using residual protons of benzene as the internal reference.

**Reaction of Ir(ttp)D with $H_2O$ and $Cs_2CO_3$.** Ir(ttp)D (3.7 mg, 0.004 mmol), $H_2O$ (3.9 mg, 3.9$\mu$L, 0.21 mmol), $Cs_2CO_3$ (56 mg, 0.17 mmol), and benzene-$d_6$ (0.50 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped NMR tube and then flame-sealed under vacuum. The reaction mixture was covered by aluminum foil and heated at 150 °C in an oil bath. All Ir(ttp)D was consumed to yield Ir(ttp)H (43%, NMR yield) after 13 h using residual protons of benzene as the internal reference.

**Reaction of Ir(ttp)H with $D_2O$ and $Cs_2CO_3$.** Ir(ttp)H (3.2 mg, 0.004 mmol), $D_2O$ (3.7 mg, 3.3$\mu$L, 0.19 mmol), $Cs_2CO_3$ (48 mg, 0.15 mmol), and benzene-$d_6$ (0.50 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped NMR tube and then flame-sealed under vacuum. The reaction mixture was covered by aluminum foil and heated at 150 °C in an oil bath. All Ir(ttp)H was consumed to yield Ir(ttp)D (20%, NMR yield) after 36 h using residual protons of benzene as the internal reference.

**Reaction of Ir(ttp)Cl(CO) with toluene-$d_8$, $D_2O$, and $Cs_2CO_3$. (i) $D_2O$ (20 Equiv).** Ir(ttp)Cl(CO) (15.1 mg, 0.019 mmol), toluene-$d_8$ (1.0 mL), $D_2O$ (3.3 mg, 3.0$\mu$L, 0.16 mmol), and $Cs_2CO_3$(106 mg, 0.33 mmol) were degassed for three freeze–thaw–pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 150 °C under $N_2$ for 3 h. The solvent was then removed under vacuum, and the reddish brown residue was purified by column chromatography over alumina (70-230 mesh), eluting with a solvent mixture of $CH_2Cl_2$ and hexane (1:2). Ir(ttp)Bn-$d_7$ (5.1 mg, 0.005 mmol, 33%) and a mixture of Ir(ttp)Me and Ir(ttp)$CD_3$ (4.9 mg, 0.006 mmol, 34%) were obtained. The ratio of Ir(ttp)Me/Ir(ttp)$CD_3$ was found to be 5.45:1 (methyl proton from Ir(ttp)Me = 2.535, the integration of pyrrole signal from both Ir(ttp)Me and Ir(ttp)$CD_3$ was set as 8.000).

**(ii) $D_2O$ (50 Equiv).** Ir(ttp)Cl(CO) (14.5 mg, 0.016 mmol), toluene-$d_8$ (1.0 mL), $D_2O$ (15.7 mg, 16 $\mu$L, 0.78 mmol), and $Cs_2CO_3$(102 mg, 0.31 mmol) were degassed for three freeze–thaw–pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 150 °C under $N_2$ for 3 h. The solvent was then removed under vacuum, and the reddish brown residue was purified by column chromatography over alumina (70-230 mesh), eluting with a solvent mixture of $CH_2Cl_2$ and hexane (1:2). Ir(ttp)Bn-$d_7$ (2.1 mg, 0.002 mmol, 14%) and a mixture of Ir(ttp)Me and Ir(ttp)$CD_3$ (3.8 mg, 0.004 mmol, 27%) were obtained. The ratio of Ir(ttp)Me:Ir(ttp)$CD_3$ was found to be 2.54:1 (methyl proton from Ir(ttp)Me = 2.153; the integration of pyrrole signal from both Ir(ttp)Me and Ir(ttp)$CD_3$ was set as 8.000).

**Ir(ttp)Me Generation in Reaction of Ir(ttp)Cl(CO) with Toluene. Addition of 10 Equiv of $LiOH.H_2O$.** Ir(ttp)Cl(CO) (20.0 mg, 0.022 mmol), $LiOH.H_2O$ (9.1 mg, 0.22 mmol), and toluene (2.0 mL) were degassed for three freeze–thaw–pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 150 °C under $N_2$ for 3 days. The solvent was then removed under vacuum, and the reddish brown residue was purified by column chromatography over alumina (70-230 mesh), eluting with a solvent mixture of $CH_2Cl_2$ and hexane (1:1). Compound **2b** and Ir(ttp)Me with the same $R_f$ = 0.50 ($CH_2Cl_2$/hexane = 1: 1) were collected in one portion, and the ratio was determined by $^1$H NMR spectroscopy from the integration of the methyl protons of the Ir-$CH_2$Ar group of **2b** and the methyl protons of the Ir-Me group of Ir(ttp)Me. Compound **2b** (12.8 mg, 0.013 mmol, 62%) and Ir(ttp)Me (4.4 mg, 0.005 mmol, 23%) were obtained.

**Addition of 10 Equiv of NaOH.** Ir(ttp)Cl(CO) (20.0 mg, 0.022 mmol), NaOH (8.7 mg, 0.22 mmol), and toluene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 150 °C under $N_2$ for 1 day to give **2b** (9.1 mg, 0.010 mmol, 44%) and Ir(ttp)Me (4.0 mg, 0.005 mmol, 21%).

**Addition of 10 Equiv of KOH.** Ir(ttp)Cl(CO) (20.0 mg, 0.022 mmol), KOH (12.1 mg, 0.22 mmol), and toluene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 150 °C under $N_2$ for 1 day to give **2b** (5.6 mg, 0.006 mmol, 27%) and Ir(ttp)Me (4.5 mg, 0.005 mmol, 24%).

**Addition of 20 Equiv of $Na_2CO_3$.** Ir(ttp)Cl(CO) (20.0 mg, 0.022 mmol), $Na_2CO_3$ (46 mg, 0.43 mmol), and toluene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 150 °C under $N_2$ for 10 days to give **2b** (16.2 mg, 0.017 mmol, 79%) and Ir(ttp)Me (1.9 mg, 0.002 mmol, 10%).

**Addition of 20 Equiv of $K_2CO_3$.** Ir(ttp)Cl(CO) (20.0 mg, 0.022 mmol), $K_2CO_3$ (60 mg, 0.43 mmol), and toluene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 150 °C under $N_2$ for 2 days to give **2b** (13.6 mg, 0.014 mmol, 66%) and Ir(ttp)Me (0.6 mg, 0.0006 mmol, 3%).

**Addition of 20 Equiv of $Cs_2CO_3$.** Ir(ttp)Cl(CO) (20.0 mg, 0.022 mmol), $Cs_2CO_3$ (141 mg, 0.43 mmol), and toluene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 150 °C under $N_2$ for 1 h to give **2b** (9.5 mg, 0.010 mmol, 46%) and Ir(ttp)Me (6.6 mg, 0.008 mmol, 35%).

**Dehydrogentative Dimerization of Ir(ttp)H.** Ir(ttp)H (4.1 mg, 0.005 mmol) and benzene-$d_6$ (0.50 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped NMR tube and then flame-sealed under vacuum. The reaction mixture was covered by aluminum foil and heated at 150 °C in an oil bath. $[Ir(ttp)]_2$ (78%, NMR yield) was obtained after 90 min using residual protons of benzene as the internal reference.

**Reaction of $[Ir(ttp)]_2$ with Toluene.** Ir(ttp)H (19.9 mg, 0.023 mmol), TEMPO (5.0 mg, 0.032 mmol), and benzene (0.50 mL) were stirred in a Telfon screw-capped tube for 30 min under $N_2$ to prepare $[Ir(ttp)]_2$ *in situ*. Benzene and unreacted TEMPO were then removed under vacuum overnight. Toluene (1.0 mL) was added to the tube, and the reaction mixture was degassed for three freeze–thaw−pump cycles. The reaction mixture was covered by aluminum foil and heated at 200 °C for 90 min. Excess toluene was removed under vaccum. The brown residue was purified by column chromatography using $CH_2Cl_2$/hexane (1:2) as an eluent. Ir(ttp)Bn (10.0 mg, 0.11 mmol, 46%) was obtained.

**Reaction of Ir(ttp)H with toluene (50 Equiv) and $Cs_2CO_3$.** Ir(ttp)H (4.4 mg, 0.005 mmol), toluene (23.5 mg, 27 $\mu$L, 0.26 mmol), $Cs_2CO_3$ (33 mg, 0.10 mmol), and benzene-$d_6$ (0.50 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped NMR tube and then flame-sealed under vacuum. The reaction mixture was covered by aluminum foil and heated at 150 °C in an oil bath. Ir(ttp)H (2%, NMR yield) and $[Ir(ttp)]_2$ (89%, NMR yield), and Ir(ttp)Bn (4%, NMR yield) were obtained after 30 min using residual protons of benzene as the internal reference. The reaction was complete in 6 days to yield Ir(ttp)Bn (55%, NMR yield).

**Reaction of Ir(ttp)H with and toluene (50 Equiv).** Ir(ttp)H (4.2 mg, 0.005 mmol), toluene (22.5 mg, 26 $\mu$L, 0.24 mmol), and benzene-$d_6$ (0.50 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped NMR tube and then flame-sealed under vacuum. The reaction mixture was covered by aluminum foil and heated at 150 °C in an oil bath. Ir(ttp)H (5%, NMR yield), $[Ir(ttp)]_2$ (66%, NMR yield), and Ir(ttp)Bn (4%, NMR yield) were obtained after 30 min using residual protons of benzene as the internal reference. The reaction was still complete in 6 days to yield Ir(ttp)Bn (40%, NMR yield) and unreacted Ir(ttp)H (37%, NMR yield).

**Reaction of Ir(ttp)Cl(CO) with $PhCH_3$ and NaOPh in $C_6D_6$.** Ir(ttp)Cl(CO) (10.1 mg, 0.011 mmol), $PhCH_3$ (100.6 mg, 116 $\mu$L, 1.09 mmol), NaOPh (25 mg, 0.11 mmol), and benzene-$d_6$ (0.50 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped NMR tube and then flame-sealed under vacuum. The reaction mixture was covered by aluminum foil and heated at 200 °C in a sand bath. Ir(ttp)Cl(CO) was consumed after 2 h to give Ir(ttp)OPh (95%, NMR yield) using the methyl proton of toluene as the internal reference.

**Reaction of Ir(ttp)OPh with $PhCH_3$ in $C_6D_6$.** Ir(ttp)OPh (6.6 mg, 0.0069 mmol), $PhCH_3$ (63.7 mg, 73.5 $\mu$L, 0.69 mmol), and benzene-$d_6$ (0.50 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped NMR tube and then flame-sealed under vacuum. The reaction mixture was covered by aluminum foil and heated at 200 °C in a sand bath. In the course of the reaction, the amount of Ir(ttp)OPh was decreasing, while the amount of **2b** was increasing. Ir(ttp)OPh was consumed after 10 days to yield **2b** (80%, NMR yield), using methyl protons of $PhCH_3$ as the internal reference. No Ir(ttp)H and PhOBn were found during the course of the reaction.

**Reaction of Ir(ttp)OPh with Toluene-$d_8$.** Ir(ttp)OPh (50.0 mg, 0.052 mmol) and toluene-$d_8$ (1.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C for 1 day. The solvent was extracted under vacuum and trapped under liquid $N_2$. PhOH in 31% was detected in the solvent by GC-MS analysis using 4-*tert*-butylphenol as the internal standard. Compound **2b** (44.9 mg, 0.047 mmol, 90%) was obtained after column chromatography using alumina, eluting with a mixture of $CH_2Cl_2$/hexane (1:2).

**Isotope Effect with Ir(ttp)Cl(CO).** A premixed equimolar solvent mixture of toluene (867 mg, 1.0 mL, 9.4 mmol)/toluene-$d_8$ (940 mg, 1.0 mL, 9.4 mmol) and Ir(ttp)Cl(CO) (30.0 mg, 0.032 mmol) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 9 days. The isotope ratio of **2b** to **2b-$d_7$** was determined to be 2.37 (benzylic CHA, integration of benzylic proton = 1.407; the integration of pyrrole signal was set as 8.000) by $^1$H NMR. The isotope ratio was also measured by FABMS to be 2.40.

**Addition of 20 Equiv of $K_2CO_3$.** A premixed equimolar solvent mixture of toluene (867 mg, 1.0 mL, 9.4 mmol)/toluene-$d_8$ (940 mg, 1.0 mL, 9.4 mmol), Ir(ttp)Cl(CO) (30.0 mg, 0.032 mmol), and $K_2CO_3$ (88 mg, 0.64 mmol) was heated at 200 °C under $N_2$ for 3.5 h. The isotope ratio of **2b** to **2b-$d_7$** was determined to be 2.16 (benzylic CHA, integration of benzylic proton = 1.367; the integration of pyrrole signal was set as 8.000) by $^1$H NMR. The isotope ratio was also measured by FABMS to be 2.16.

**Addition of 20 Equiv of NaOPh.** A premixed equimolar solvent mixture of toluene (867 mg, 1.0 mL, 9.4 mmol)/toluene-$d_8$ (940 mg, 1.0 mL, 9.4 mmol), Ir(ttp)Cl(CO) (20.0 mg, 0.022 mmol), and NaOPh (51 mg, 0.44 mmol) was heated at 200 °C under $N_2$ for 2 days. The isotope ratio of **2b** to **2b-$d_7$** was determined to be 2.18 (benzylic CHA, integration of benzylic proton = 1.389; the integration of pyrrole signal was set as 8.000) by $^1$H NMR. The isotope ratio was also measured by FABMS to be 2.18.

**Isotope Effect with Ir(ttp)H.** A premixed equimolar solvent mixture of toluene (434 mg, 0.50 mL, 4.7 mmol)/toluene-$d_8$ (470 mg, 0.50 mL, 4.7 mmol) and Ir(ttp)Cl(CO) (15.0 mg, 0.017 mmol) was degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 2 h. The isotope ratio of **2b** to **2b-$d_7$** was determined to be 2.30 (benzylic CHA, integration of benzylic proton = 1.407; the integration of pyrrole signal was set as 8.000) by $^1$H NMR. The isotope ratio was also measured by FABMS to be 2.13.

**Isotope Effect with $[Ir(ttp)]_2$.** $Ir(ttp)]_2$ was prepared *in situ* by stirring Ir(ttp)H (20.8 mg, 0.024 mmol) and TEMPO (5.3 mg, 0.034 mmol) in benzene (1.0 mL) in a Teflon-screw capped tube for 0.5 h. The solvent, unreacted TEMPO, and coproduct TEMPOH were removed under vacuum overnight. A premixed equimolar solvent mixture of toluene (434 mg, 0.50 mL, 4.7 mmol)/toluene-$d_8$ (470 mg, 0.50 mL, 4.7 mmol) and $[Ir(ttp)]_2$ prepared *in situ* were degassed for three freeze–thaw−pump cycles in the Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 1.25 h. The isotope ratio of **2b** to **2b-$d_7$** was determined to be 2.10 (benzylic CHA, integration of benzylic proton = 1.354; the integration of pyrrole signal was set as 8.000) by $^1$H NMR.

**Competition Reactions in Base-Promoted BnCHA. Addition of *p*-Xylene (100 Equiv) and Toluene (100 Equiv).** Ir(ttp)Cl(CO) (15.4 mg, 0.017 mmol), $K_2CO_3$ (46 mg, 0.33 mmol), *p*-xylene (177 mg, 205 μL, 1.67 mmol), toluene (154 mg, 177 μL, 1.67 mmol), and benzene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 6 h. The ratio of **2a** to **2b** was determined to be 2.050 by $^1$H NMR spectroscopy from the integration of the *meta*-phenyl protons of Ir-$CH_2$Ar group of **2a** and **2b.**

**Addition of 4-Fluorotoluene (100 Equiv) and Toluene (100 Equiv).** Ir(ttp)Cl(CO) (16.0 mg, 0.017 mmol), $K_2CO_3$ (48 mg, 0.35 mmol), *p*-fluorotoluene (191 mg, 191 μL, 1.73 mmol), toluene (160 mg, 184 μL, 1.73 mmol), and benzene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 4.5 h. The ratio of **2c** to **2b** was determined to be 1.303 by $^1$H NMR spectroscopy from the integration of the *meta*-phenyl protons of Ir-$CH_2$Ar groups of **2c** and **2b.**

**Addition of 4-Nitrotoluene (100 Equiv) and Toluene (100 Equiv).** Ir(ttp)Cl(CO) (15.8 mg, 0.017 mmol), $K_2CO_3$ (47 mg, 0.34 mmol), 4-nitrotoluene (234 mg, 1.71 mmol), toluene (158 mg, 182 μL, 1.71 mmol), and benzene (2.0 mL) were degassed for three freeze–thaw−pump cycles in a Teflon screw-capped tube. The reaction mixture was covered by aluminum foil and heated at 200 °C under $N_2$ for 3.5 h. The ratio of **2d** to **2b** was determined to be 5.067 by $^1$H NMR spectroscopy from the integration of the *meta*-phenyl protons of Ir-$CH_2$Ar groups of **2d** and **2b.**

**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.[42] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all nonhydrogen atoms by full-matrix least-squares calculations on $F_2$ using the SHELXTL program package.[43] All hydrogen atoms were geometrically fixed using the riding model. X-ray data are listed in Table 5.

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**Supporting Information Available:** Text, tables, and figures of crystallographic data for complexes **2a**, **2d**, and **2e** (CIF and PDF), $^1$H and $^{13}$C NMR spectra for **2a**, **2c**, **2d**, **2e**, Ir(ttp)H (**4**), Ir(ttp)OPh (**5**), Ir(ttp)Ph(*p*-Me) (**6**), and $^1$H NMR spectrum for $[Ir(ttp)]_2$ (**7**). This material is available free of charge via the Internet at http://pubs.acs.org.

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