

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

Chi Wai Cheung and Kin Shing Chan*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, People's Republic of China

Received July 25, 2007

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 $Ir^{III}(ttp)Cl(CO)^{10}$ ($ttp = tetrakis(p\text{-tolyl})porphyrin$ 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

* Corresponding author. E-mail: ksc@cuhk.edu.hk.

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

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 ₂ CO ₃ (20)	0.5 h	37	4
4	K ₂ CO 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(tp)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(tp)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(tp)Cl(CO) (Table 1, entry 4). Likely, the low reactivity is due to the coordinative saturation of Ir(tp)Cl(CO).

In view of successful base-promoted BnCHA by Rh(tp)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 bases¹⁵ led to shorter reaction times but lower yields of Ir(tp)Bn and lower selectivity as Ir(tp)Me also formed (Table 2, entries 1–4). Weaker bases of NaOPh and NaF¹⁵ reacted more slowly, but they were more selective in BnCHA to yield Ir(tp)Bn only (Table 2, entries 5 and 6). K₂CO₃ 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(tp)Bn in higher selectivity. The optimized amount of base was found to be 20 equivalents with reference to Ir(tp)Cl(CO) since a lower equivalent of K₂CO₃ (10 equiv) slowed down the reaction rates (Table 3, eq 3, entries 1 and 2), and a higher equivalent of K₂CO₃ (30 equiv) gave similar yields of Ir(tp)Bn and Ir(tp)Me in 2 h (Table 3, entry 3 and 4).

K₂CO₃ and NaOPh were also used in the reactions of Ir(tp)Cl(CO) with various 4-substituted toluenes (Table 4, eq 4). Both bases enhanced BnCHA with the stronger base K₂CO₃ showing a larger rate enhancement than NaOPh (Table 4, entries

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

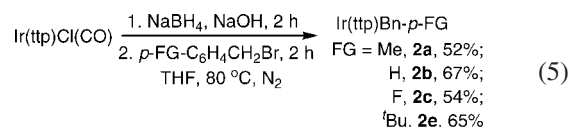
entry	K ₂ CO ₃ (equiv)	temp/°C	time	yield 2b /%	yield 3 /%
1	10	150	3 d	63	1
2	20	150	2 d	66	3
3	20	200	3.5 h	61	7
4	30	200	2 h	60	7

Table 4. Effect of K₂CO₃ and NaOPh on CHA of Toluene with Ir(tp)Cl(CO)

entry	FG	entry A (K ₂ CO ₃)		entry B (NaOPh)	
		time/h	yield (%)	time/h	yield (%)
1	Me	1	2a (41)	24	2a (67)
2	H	3.5	2b (61)	48	2b (78)
3	F	2	2c (62)	12	2c (78)
4	NO ₂	0.1	2d (80)	0.1	2d (43)

1–3). NaOPh was more selective without any Ir(tp)Me formed and generally higher yielding in BnCHA when compared with K₂CO₃. Furthermore, 4-nitrotoluene successfully reacted to give **2d** (Table 4, entry 4).

Synthesis of Authentic Samples. Iridium porphyrin benzyls **2a**, **2b**, **2c**, and **2e** were successfully synthesized by reductive benzylation of Ir(tp)Cl(CO) (eq 5).^{16–18} Ir(tp)Cl(CO) was first reduced by NaBH₄ with base to yield Ir(tp)[–], which was then further reacted with benzyl bromides to yield iridium benzyls.



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(tp)CH₂Ar 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(tp)Bn(*p*-^tBu) (**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(tp)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

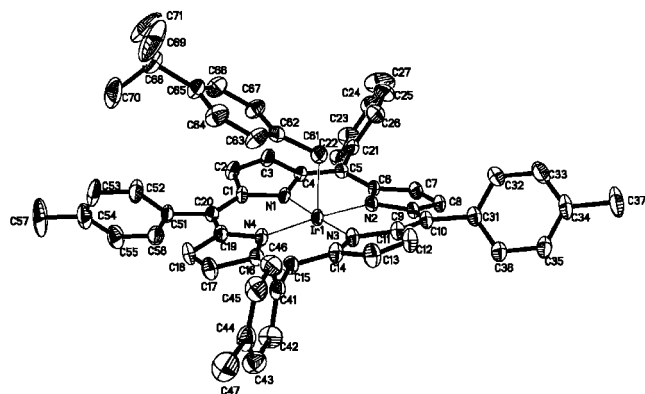
param	2a	2d	2e
formula	C ₅₆ H ₄₅ N ₄ Ir·2H ₂ O	C ₅₅ H ₄₂ N ₅ O ₂ Ir	C ₅₉ H ₅₁ N ₄ Ir
cryst size (mm)	0.40 × 0.30 × 0.20	0.40 × 0.30 × 0.20	0.40 × 0.30 × 0.20
fw	1002.19	997.14	1008.24
cryst syst	monoclinic	monoclinic	monoclinic
space group	P2 (1)/c	P2(1)/c	P2 (1)/n
a (Å)	13.870 (3)	7.6573 (12)	12.755 (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
β (deg)	95.34 (3)	90.180 (3)	100.692 (6)
γ (deg)	90	90	90
V, Å ³	4671.3 (16)	2788.7 (7)	4719 (2)
Z	4	2	4
D _{calcd} , Mg/m ³	1.425	1.188	1.419
radiation (λ), Å	0.71073	0.71073	0.71073
θ range, deg	2.11 to 25.00	1.54 to 28.02	1.53 to 25.00
F(000)	2024	1000	2040
reflcs collcd	8575	18222	25303
indpdnt 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 > 2σ(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 $R_1 = \sum (|F_o| - |F_c|) / \sum |F_o|$. ^b $wR_2 = \sum \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$. ^c Weighting scheme $w^{-1} = \sigma^2 (F_o^2) + (w_1 P)^2 + w_2 P$, where $P = (F_o^2 + 2F_c^2)/3$.

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

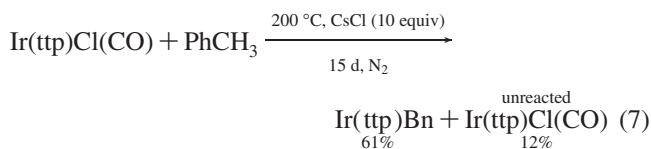
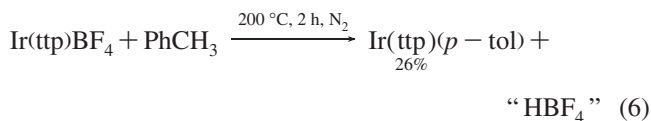
entry	FG	Ir—C length (Å)	Ir—C—C _{aryl} bond angle (deg)
1	Me, 2a	2.089 (9)	115.2 (6)
2	NO ₂ , 2d	2.186 (4) ^a	114.8 (4) ^b
3	^t Bu, 2e	2.073 (6)	117.1 (4)

^a Average of 2 Ir—C bond lengths from 2 kinds of disordered structures. ^b Average of 4 Ir—C—C_{aryl} bond angles from 4 kinds of disordered structures.

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

which is a sterically more accessible bond than arene C—H bonds, via σ -bond metathesis^{10,11f} or its variant form of internal electrophilic substitution (IES).¹⁹ Complete dissociation of Ir(ttp)Cl(CO) into Ir(ttp)^{+10,20} for BnCHA is less probable, and this can be attributed into 2 reasons. (i) Ir(ttp)BF₄ (an inseparable mixture of Ir(ttp)BF₄ and Ir(ttp)(CO)BF₄)¹⁰ with the much less coordinating BF₄[−] reacted with toluene at 200 °C in 2 h to

generate only Ir(ttp)(*p*-tol) in 26% yield via electrophilic aromatic substitution²¹ 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 C₆D₆ at 200 °C in 22 days to yield Ir(ttp)Bn(*p*-Me) in 47% yield.



Mechanism: Strong Base. In the presence of a strong base (Scheme 1, Pathway II) such as K₂CO₃, 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[−], KCO₃[−]) 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 Ph¹³CH₃ (50 equiv) and Cs₂CO₃

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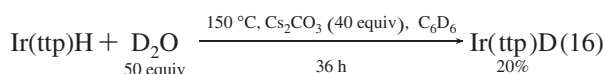
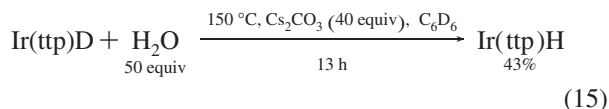
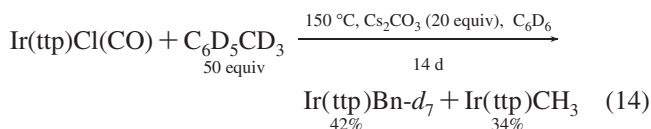
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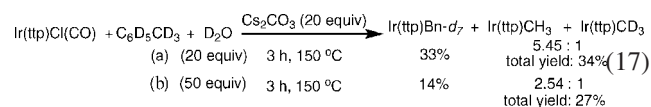
(19) In the internal electrophilic substitution (IES) mechanism, the lone pair on an M—X ligand forms an X—H bond, while the orbital making up the M—X bond turns into a coordinating lone pair (ref 12).

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of Ir(tpp)H to Ir(tpp)D with D₂O (50 equiv) in C₆D₆ added with Cs₂CO₃ (40 equiv) in the same reaction conditions of BnCHA confirms the occurrence of proton exchange (eq 16). Therefore, only Ir(tpp)H was present without any Ir(tpp)D during CO reduction (eq 14). The conversion of Ir(tpp)D to Ir(tpp)H is likely due to the base-promoted proton transfer via Ir(tpp) dimer, [Ir(tpp)]₂,²⁷ which was observed in the proton exchange of Ir(tpp)D with H₂O (eq 15) and Ir(tpp)H with D₂O (eq 16).

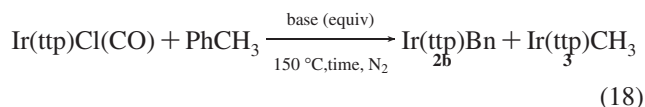


The incorporation of proton from water into Ir(tpp)Me is further confirmed by the addition of D₂O to the base-promoted reactions of toluene. When toluene-*d*₈, Cs₂CO₃ (20 equiv), and D₂O (10 equiv) were reacted with Ir(tpp)Cl(CO) at 150 °C, a mixture of Ir(tpp)CH₃ and Ir(tpp)CD₃ formed at a ratio of 5.45:1 (eq 17a). When the amount of D₂O was increased to 50 equiv, the ratio of Ir(tpp)CH₃/Ir(tpp)CD₃ became 2.54:1 with an increase in the proportion of Ir(tpp)CD₃ (eq 17b). The addition of D₂O (50 equiv) still did not give Ir(tpp)CD₃ in 100% yield.



The base-promoted reactions of toluene by Ir(tp)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(tp)CH₃/Ir(tp)Bn increased with more basic salts (MOH > M₂CO₃) (Table 7, entries 2–5). Furthermore, the Ir(tp)Me/Ir(tp)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 CO₃^{2−} in ligand substitution with Ir(tp)Cl(CO) to give Ir(tp)X (X: OH[−] > MCO₃[−], Scheme 1, Pathway **II**), which also reacts faster with toluene to produce Ir(tp)H (Scheme 1, pathway **II_a**). Further reaction of Ir(tp)H with toluene forms Ir(tp)Bn (Scheme 1, Pathway **II_b**) or with unreacted Ir(tp)Cl(CO) to yield Ir(tp)Me (Scheme 1, Pathway **II_c**).

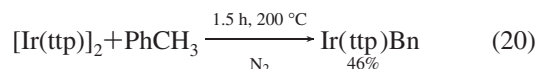
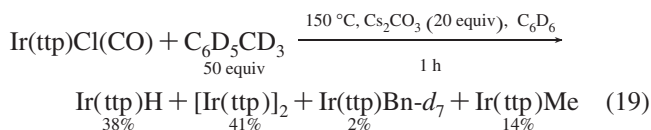
Table 7. Base Effect on the Formation of Ir(ttp)Me



entry	base (equiv)	time	yield of 2b /%	yield of 3f /%	total yield/%	ratio of 2b : 3f
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 $[\text{Ir}(\text{ttp})]^{-}\text{M}^{+17}$ (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 Ir^{II}(ttp) radical and Ir^{III}(ttp)C(O) carbon-centered radical²⁹ **C** (Scheme 2, Pathway **II**_a). The Ir^{III}(ttp)C(O) radical probably further reacts with Ir(ttp)H to give Ir(ttp)CHO and Ir^{II}(ttp) radicals^{27b,30} (Scheme 2, Pathway **III**). Ir(ttp)CHO is further reduced by Ir(ttp)H to yield Ir(ttp)Me³¹ (Scheme 2, pathway **IV**). In view of the higher yield of Ir(ttp)Me with a stronger base in base-promoted BrCHA, 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. [Ir(ttp)]₂ is probably another reacting species to generate Ir(ttp)Bn in base-promoted BnCHA. The formation of [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 Cs₂CO₃ in C₆D₆ at 150 °C in 1 h (eq 19). The spectroscopic identification of [Ir(ttp)]₂ was confirmed using an authentic sample of [Ir(ttp)]₂^{27a} generated by the reaction of Ir(ttp)H with 2,2,6,6-tetramethylpiperidinoxyl (TEMPO) in C₆D₆ at room temperature for 5 min. Indeed, [Ir(ttp)]₂ did react rapidly with toluene at 200 °C in 90 min to yield Ir(ttp)Bn in 46% yield (eq 20).



[Ir(tpp)]₂ is formed by the thermal (eqs 21 and 22) and base-promoted (eq 23) dehydrogenative dimer formation from Ir(tpp)H. Ir(tpp)H remained unreacted at room temperature in 2 h but reacted rapidly at 150 °C to give [Ir(tpp)]₂ in 74% yield in 1 h (eq 21). This shows that high temperature is required for dimer formation from Ir(tpp)H. Alternatively, in the separate reaction of Ir(tpp)H with toluene (50 equiv) in C₆D₆ at 150 °C, [Ir(tpp)]₂ was formed in 66% yield as the major species in 30 min prior to reacting with toluene to yield Ir(tpp)Bn (eq 22). Rh(oep)H (oep = octaethylporphyrin dianion) has also been

(27) The authentic sample of $[\text{Ir}(\text{ttp})]_2$ was synthesized using the same method to synthesize $[\text{Ir}(\text{oep})]_2$ by reacting $\text{Ir}(\text{oep})\text{H}$ and TEMPO. (a) Chan, K. S.; Leung, Y.-B. *Inorg. Chem.* **1994**, *33*, 3187. The chemical shifts and splitting patterns of $[\text{Ir}(\text{ttp})]_2$ in ^1H NMR spectroscopy was similar to that of $[\text{Rh}(\text{ttp})]_2$. For $[\text{Ir}(\text{ttp})]_2$: ^1H NMR (C_6D_6) δ 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 $[\text{Rh}(\text{ttp})]_2$: ^1H NMR (C_6D_6) δ 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.

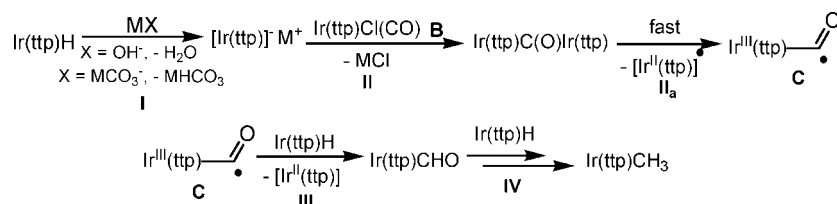
(28) An analogue of $\text{Ir}(\text{tp})\text{C}(\text{O})\text{Ir}(\text{tp})$, $\text{Rh}(\text{oe})\text{C}(\text{O})\text{Rh}(\text{oe})$, had been reported. (a) Wayland, B. B.; Woods, B. A.; Coffin, V. L. *Organometallics*, **1986**, 5, 1059–1062. (b) Coffin, V. L.; Brennen, W.; Wayland, B. B.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

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

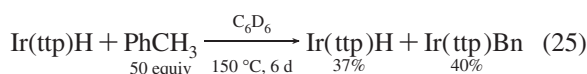
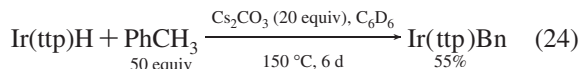
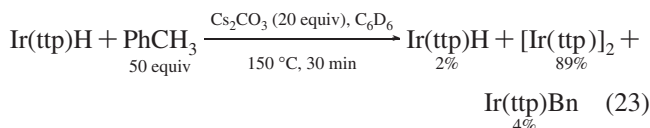
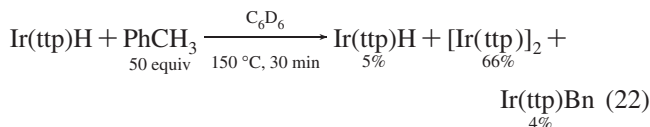
(30) (a) Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333–4335. (b) Wayland, B. B.; Sherry, A. E.; Poszmik, G.; Bunn, A. G. *J. Am. Chem. Soc.* **1992**, *114*, 1673–1681.

(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, $\text{Ir}(\text{ttp})\text{CHO}$ was proposed to be formed in the reduction of $\text{Ir}(\text{ttp})\text{Cl}(\text{CO})$ by $\text{Ir}(\text{ttp})\text{H}$.^{25b}

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

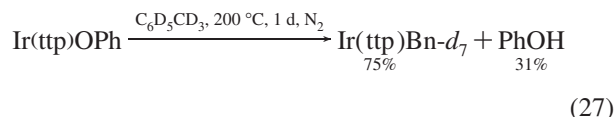
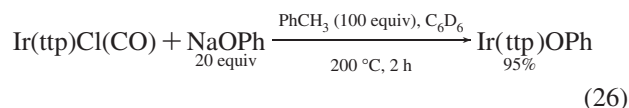


reported to react to yield $[\text{Rh}(\text{oep})]_2$ and H_2 .³² In the presence of Cs_2CO_3 (20 equiv) (eq 23), a small amount of $[\text{Ir}(\text{tp})]_2$ in 25% yield had already formed from the dehydrogenative dimerization of $\text{Ir}(\text{tp})\text{H}$ at ambient temperature, and a high yield of $[\text{Ir}(\text{tp})]_2$ in 89% yield was formed in 30 min. Thus, the base also promoted the dimer formation of $\text{Ir}(\text{tp})\text{H}$ to $[\text{Ir}(\text{tp})]_2$. Indeed, the base promoted the rate of BnCHA with $\text{Ir}(\text{tp})\text{H}$ since the reaction of $\text{Ir}(\text{tp})\text{H}$ with toluene (50 equiv) in C_6D_6 at 150 °C with Cs_2CO_3 (20 equiv) was complete to yield $\text{Ir}(\text{tp})\text{Bn}$ in 55% in 6 days (eq 24), whereas the same reaction without base was still incomplete in 6 days (eq 25). Base probably deprotonates $\text{Ir}(\text{tp})\text{H}$ to give the $\text{Ir}(\text{tp})$ anion¹⁷ for faster formation of $[\text{Ir}(\text{tp})]_2$, which in turn leads to faster rate of BnCHA .



$[\text{Ir}(\text{tp})]_2$ probably reacts with toluene to yield both $\text{Ir}(\text{tp})\text{Bn}$ and $\text{Ir}(\text{tp})\text{H}$, likely in a termolecular mechanism³³ analogous to BnCHA with $\text{Rh}(\text{tmp})$ (tmp = tetramesitylporphyrin dianion) radical^{33b} and toluene. Indeed, $[\text{Ir}(\text{oep})]_2$ has been reported to react with toluene to yield both $\text{Ir}(\text{oep})\text{Bn}$ and $\text{Ir}(\text{oep})\text{H}$.³⁴ However, direct reaction of $\text{Ir}(\text{tp})\text{H}$ with toluene to yield $\text{Ir}(\text{tp})\text{Bn}$ and H_2 cannot be excluded. $[\text{Ir}(\text{tp})]_2$ probably reacts faster with toluene than $\text{Ir}(\text{tp})\text{H}$. It is because $\text{Ir}(\text{tp})\text{H}$, which was generated from the reaction of $[\text{Ir}(\text{tp})]_2$ with toluene, was consumed slowly in the reaction of $\text{Ir}(\text{tp})\text{H}$ with toluene (50 equiv) in C_6D_6 at 150 °C (eq 25). $\text{Ir}(\text{tp})\text{Me}$ was probably not generated from $[\text{Ir}(\text{tp})]_2$ as it did not form in the reaction of $[\text{Ir}(\text{tp})]_2$ 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**), $\text{Ir}(\text{tp})\text{Cl}(\text{CO})$ undergoes ligand substitution³⁵ with NaOPh to give $\text{Ir}(\text{tp})\text{OPh}$. This is confirmed by the rapid conversion of $\text{Ir}(\text{tp})\text{Cl}(\text{CO})$ to $\text{Ir}(\text{tp})\text{OPh}$ in 95% yield in the reaction of $\text{Ir}(\text{tp})\text{Cl}(\text{CO})$ with toluene (100 equiv) and NaOPh (20 equiv) in benzene- d_6 in 2 h as observed by ^1H NMR spectroscopy (eq 26). The identity of $\text{Ir}(\text{tp})\text{OPh}$ was confirmed by an authentic sample of $\text{Ir}(\text{tp})\text{OPh}$ prepared in 86% yield by reacting $\text{Ir}(\text{tp})\text{Cl}(\text{CO})$ with NaOPh (2 equiv) in benzene at 150 °C for 12 h. $\text{Ir}(\text{tp})\text{OPh}$ then reacts with toluene to yield $\text{Ir}(\text{tp})\text{Bn}$ (Scheme 1, Pathway **III**_a). The intermediacy of $\text{Ir}(\text{tp})\text{OPh}$ was supported by the reaction of $\text{Ir}(\text{tp})\text{OPh}$ with toluene- d_8 at 200 °C in 1 day to yield $\text{Ir}(\text{tp})\text{Bn-}d_7$ in 75% isolated yield and PhOH in 31% yield by GC-MS analysis (eq 27). The absence of signals of $\text{Ir}(\text{tp})\text{H}$ and benzyl phenyl ether³⁶ by ^1H NMR spectroscopy in the reaction of $\text{Ir}(\text{tp})\text{OPh}$ with toluene (100 equiv) in C_6D_6 at 200 °C for 10 days further supported the direct reaction of $\text{Ir}(\text{tp})\text{OPh}$ with toluene to yield $\text{Ir}(\text{tp})\text{Bn}$ and PhOH . The slower substitution of chloride by the less nucleophilic phenoxide anion (Scheme 1, Pathway **III**) and the lower reactivity of $\text{Ir}(\text{tp})\text{OPh}$ 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 .



Scheme 3 lists more detailed mechanisms for the BnCHA step with $\text{Ir}(\text{tp})\text{X}$ ($\text{X} = \text{OH}^-, \text{KCO}_3^-, \text{OPh}^-$) with two major possible classes: (i) oxidative addition and (ii) σ -bond metathesis and its variants (Scheme 3). Oxidative addition (Scheme 3, Pathway **i**) involves the *cis*-addition of the $\text{PhCH}_2\text{-H}$ bond to $\text{Ir}(\text{tp})\text{X}$ to generate a 7-coordinate $\text{Ir}(\text{V})$ 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 σ -bond metathesis (Scheme 3, Pathway **ii**), and one of its variant forms, σ -complex-assisted metathesis (σ -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 $\text{Ir}(\text{tp})\text{Me}$ with toluene at 200 °C in

(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.

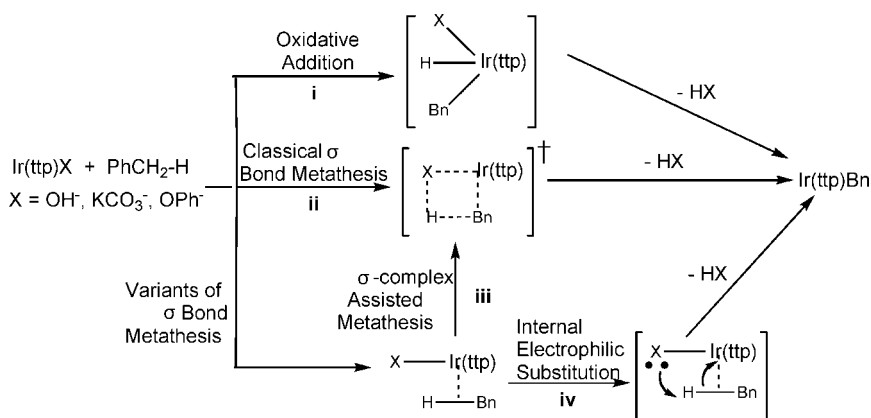
(34) Del Rossi, K. J.; Wayland, B. B. *J. Chem. Soc. Chem. Commun.* **1986**, 1653–1655.

(35) Rees, W. M.; Churchill, M. R.; Fettingner, 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 σ -complex-assisted metathesis and classical σ -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.

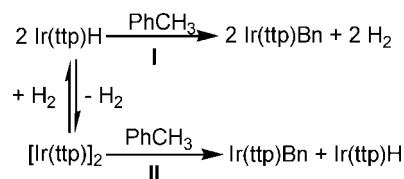
Scheme 3. Four Possible Mechanisms of Base-Promoted BnCHA Steps



14 days to give just a trace of Ir(tpp)Bn with the recovery of Ir(tpp)Me in 46% yield. Another refinement of classical σ -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(tpp)OPh is sp^3 hybridized with the filled p -type lone pair orbital of oxygen conjugated with the π system of the aromatic group. As the distortion of the p orbital of oxygen from the π system of the aromatic group in phenol at high temperature has been reported³⁸ 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 π 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.

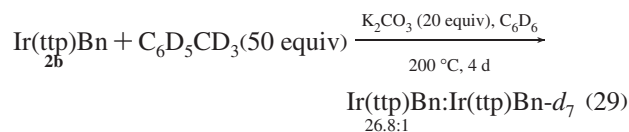
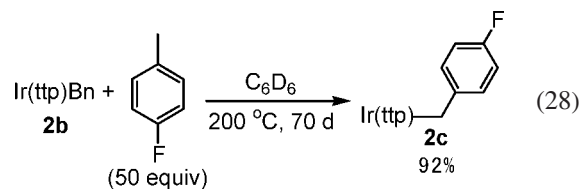
Isotope Effect. The observed isotope effect $(k_H/k_D)_{\text{obs}}$ for the BnCHA of toluene with Ir(tpp)Cl(CO) was measured by a competition experiment with an equimolar mixture of solvent toluene and toluene- d_8 . At 200 °C, $(k_H/k_D)_{\text{obs}}$ was measured to be 2.37 without base after 9 days, 2.16 with K_2CO_3 after 3.5 h, and 2.18 with NaOPh after 2 days by ^1H 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 $(k_H/k_D)_{\text{obs}}$ for BnCHA of toluene at 200 °C with Ir(tpp)H and [Ir(tpp)]₂ was measured to be 2.30 and 2.10, respectively, which are similar to $(k_H/k_D)_{\text{obs}}$ of 2.16 in BnCHA with Ir(tpp)Cl(CO) and K_2CO_3 at 200 °C. This implies that both Ir(tpp)H and [Ir(tpp)]₂ are the intermediates involved in the rate-determining step (RDS) in the base-promoted BnCHA of toluene with Ir(tpp)Cl(CO) (Scheme 1, pathway **II**_b). Moreover, a pre-equilibrium⁴⁰ exists between Ir(tpp)H and [Ir(tpp)]₂ prior to BnCHA at 200 °C (Scheme 4), and the generation of [Ir(tpp)]₂ from Ir(tpp)H is facile at high temperature as supported by independent experiments (eqs 21 and 22), especially in the presence of base (eq 23).

Since the kinetic isotope effect (KIE) of the BnCHA of toluene with Rh(tmp) is 6.5^{33b} and a linear transition state was

Scheme 4. Parallel BnCHA of Toluene with Ir(tpp)H and [Ir(tpp)]₂

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(tpp)]₂. Probably a parallel pathway of BnCHA by Ir(tpp)H with a bent transition state can rationalize the small observed values (Scheme 4, Pathway **I**).

Ir(tpp)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(tpp)Bn reacted with 4-fluorotoluene and the ratio of Ir(tpp)Bn/Ir(tpp)Bn(*p*-F) was found to be 11.5:1. Ir(tpp)Bn was completely consumed only after 70 days to yield Ir(tpp)Bn(*p*-F) in 92% yield (eq 28). Besides, Ir(tpp)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(tpp)Bn- d_7 with the ratio of Ir(tpp)Bn/Ir(tpp)Bn- d_7 of 26.8:1 (eq 29). After 14 days, the ratio of Ir(tpp)Bn/Ir(tpp)Bn- d_7 was found to be 3.57:1. Therefore, these results suggest that reactions of Ir(tpp)Bn with toluene- d_8 to give Ir(tpp)Bn- d_7 without and with base do not significantly affect the $(k_H/k_D)_{\text{obs}}$ values in the time scale of BnCHA. The $(k_H/k_D)_{\text{obs}}$ values are generally truly kinetic values.



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(tpp)Cl(CO) and K_2CO_3 (20 equiv) at 200 °C in benzene (Table 8, eq 30). Because of the very slow reaction of benzyl exchange of Ir(tpp)Bn with 4-fluorotoluene (eq 28) and

(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 analogue of Ir(tpp)H, Rh(oep)H, was in equilibrium with [Rh(oep)]₂ and H₂ (ref 32).

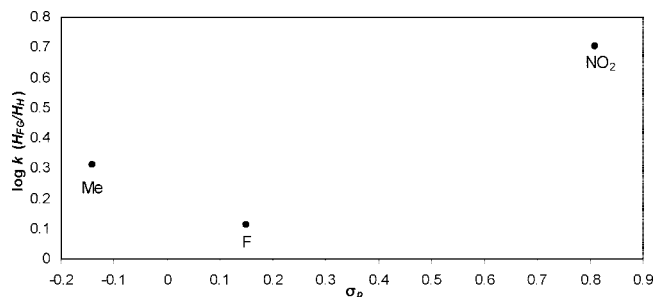


Figure 2. Hammett plot of base-promoted BnCHA of toluenes with Ir(tp)Cl(CO).

Table 8. Competition Experiments of Benzylic CHA

$$\text{Ir}(\text{tp})\text{Cl}(\text{CO}) + \text{C}_6\text{H}_5\text{FG} + \text{C}_6\text{H}_5 \xrightarrow[200\text{ }^\circ\text{C, N}_2]{\text{K}_2\text{CO}_3 (20\text{ equiv}), \text{C}_6\text{H}_6}$$

 (100 equiv) (100 equiv)

$$\text{Ir}(\text{tp})\text{CH}_2\text{C}_6\text{H}_4\text{FG} + \text{Ir}(\text{tp})\text{CH}_2\text{C}_6\text{H}_5 \quad (30)$$

entry	<i>p</i> -FG	σ_p^a	$\log k (H_{\text{FG}}/H_{\text{H}})$
1	Me	-0.14	0.3118
2	F	0.15	0.1149
3	NO ₂	0.81	0.7048

^a σ_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 σ_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(tp)Cl(CO) were greatly enhanced by the presence of inorganic bases. Strong inorganic base K₂CO₃ 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., Cs₂CO₃, KOH), Ir(tp)H and [Ir(tp)]₂ were the probable intermediates observed in the formation of Ir(tp)Me and Ir(tp)Bn, respectively. With a weak base NaOph, Ir(tp)Oph was the intermediate observed in the reaction. Ir(tp)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 F₂₅₄ plates. Ir(tp)-Cl(CO),¹⁶ Ir(tp)BF₄ (an inseparable mixture of Ir(tp)(CO)BF₄ and Ir(tp)BF₄),¹⁰ Ir(tp)Me,¹⁶ and Ir(tp)Bn¹⁶ were prepared according to the literature procedures. Neutral alumina (Merck, 70-230 mesh)/

H₂O (10:1 v/v) and silica gel (Merck, 70-230 mesh) were used for column chromatography.

¹H NMR and ¹³C 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 C₆D₆ (δ = 7.15 ppm), CDCl₃ (δ = 7.26 ppm), or tetramethylsilane (δ = 0.00 ppm) in ¹H NMR spectra, and CDCl₃ (δ = 77.16 ppm) or THF-*d*₈ (δ (β -CH₂) = 25.62 ppm) in ¹³C NMR spectra as the internal standards. Chemical shifts (δ) were reported as part per million (ppm) in (δ) 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 CH₂Cl₂ as solvent, and electrospray ionization (ESI) mode using MeOH/CH₂Cl₂ (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(tp)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(tp)Bn(*p*-Me)] (2a). A suspension of Ir(tp)Cl(CO) (100 mg, 0.11 mmol) in THF (50 mL) and a solution of NaBH₄ (153 mg, 67 μ L, 1.08 mmol) in aqueous NaOH (1.0 M, 3.0 mL) were purged separately with N₂ for 15 min. The solution of NaBH₄ was added slowly to the suspension of Ir(tp)Cl(CO) via a cannula. The mixture was heated at 70 $^\circ$ C under N₂ 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 N₂, and 4-methylbenzyl bromide (200 mg, 1.08 mmol) was added. The reaction mixture was further heated at 70 $^\circ$ C under N₂ for 2 h. A reddish brown suspension was formed. The reaction mixture was worked up by extraction with CH₂Cl₂/H₂O. The combined organic extract was dried (MgSO₄), 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 CH₂Cl₂ 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 CH₂Cl₂/CH₃OH. *R*_f = 0.60 (1:1 hexane/CH₂Cl₂). ¹H NMR (CDCl₃, 300 MHz) δ -4.01 (s, 2 H, H₂₉), 1.69 (s, 3 H, H₃₄), 2.69 (s, 12 H, H₂₅₋₂₈), 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, H₁₋₈). ¹³C NMR (CDCl₃, 75 MHz) δ -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 [C₅₆H₄₅N₄Ir]⁺; *m/z* 966.3268. Found: *m/z* 966.3262. The single crystal used for X-ray diffraction crystallography was grown from CH₂Cl₂/MeOH.

(5,10,15,20-Tetrakis(*p*-tolyl)porphyrinato)(4-fluorobenzyl)iridium(III) [Ir(tp)Bn(*p*-F)] (2c). 4-Fluorobenzyl bromide (204 mg, 135 μ L, 1.08 mmol) was used. Brown solid (58 mg, 0.059 mmol, 54%) was obtained. *R*_f = 0.60 (1:1 hexane/CH₂Cl₂). ¹H NMR (CDCl₃, 300 MHz) δ -4.05 (s, 2 H, H₂₉), 2.69 (s, 12 H, H₂₅₋₂₈), 3.07 (dd, 2 H, *J*_{HH} = 8.4 Hz, ⁴*J*_{HF} = 6.0 Hz, H_{30,31}), 5.56 (dd, 2 H, *J*_{HH} = 8.7 Hz, ³*J*_{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, H₁₋₈). ¹³C NMR (CDCl₃, 75 MHz) δ -15.1, 21.7, 112.7 (d, ²*J*_{CF} = 21 Hz), 124.2, 125.2 (d, ³*J*_{CF} = 7.7 Hz), 127.7, 131.4, 133.8, 137.1, 137.3, 138.9, 143.3, 157.1 (d, ¹*J*_{CF} = 241 Hz). HRMS (FABMS): Calcd for [C₅₅H₄₂N₄FIr]⁺; *m/z* 970.3017. Found: *m/z* 970.3036.

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

(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) δ -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, $\text{H}_{30,31}$), 5.92 (d, 2 H, $J = 8.1$ Hz, $\text{H}_{32,33}$), 7.50 (d, 4 H, $J = 6.3$ Hz, $\text{H}_{17,19,21,23}$), 7.52 (d, 4 H, $J = 6.3$ Hz, $\text{H}_{18,20,22,24}$), 7.98 (d, 4 H, $J = 6.3$ Hz, $\text{H}_{10,12,14,16}$), 7.99 (d, 4 H, $J = 6.3$ Hz, $\text{H}_{9,11,13,15}$), 8.44 (s, 8 H, H_{1-8}). ^{13}C NMR (CDCl_3 , 75 MHz) δ -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 $[\text{C}_{59}\text{H}_{51}\text{N}_4\text{Ir}]^+$: m/z 1008.3737. Found: m/z 1008.3733. The single crystal used for X-ray diffraction crystallography was grown from $\text{CH}_2\text{Cl}_2/\text{MeOH}$.

Preparation of (5,10,15,20-Tetrakis(*p*-tolyl)porphyrinato)-methyliridium(III) hydride [Ir(tp)H] (4). Ir(tp)H was prepared according to the literature procedure for the synthesis of Ir(oep)H.¹⁷ A suspension of Ir(tp)Cl(CO) (100 mg, 0.11 mmol) in THF (50 mL), a solution of NaBH_4 (153 mg, 67 μL , 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(tp)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) δ -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 ($\text{THF}-d_8$, 75 MHz) δ 21.9, 124.5, 128.3, 128.6, 132.0, 134.9, 138.1, 140.5, 144.8. HRMS (FABMS): Calcd for $[\text{C}_{48}\text{H}_{47}\text{N}_4\text{Ir}]^-$: m/z 862.2653. Found: m/z 862.2640.

Preparation of (5,10,15,20-Tetrakis(*p*-tolyl)porphyrinato)(phenoxy)iridium(III) [Ir(tp)OPh] (5). Ir(tp)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) δ 1.89 (d, 2 H, $J = 8.1$ Hz, $\text{H}_{29,30}$), 2.79 (s, 12 H, H_{25-28}), 5.66 (t, 2 H, $J = 7.8$ Hz, $\text{H}_{31,32}$), 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, $\text{H}_{9,11,13,15}$), 8.99 (s, 8 H, H_{1-8}). ^{13}C NMR (CDCl_3 , 75 MHz) δ 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(tp)OPh by FAB or ESI mass spectroscopy (MS) was unsuccessful, with the FABMS only showing the metalloporphyrin peak $[\text{Ir}(\text{tp})]^+ = 861$. The growth of a single crystal of Ir(tp)OPh from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ or $\text{CH}_2\text{Cl}_2/\text{hexane}$ for X-ray diffraction crystallography was also unsuccessful with the decomposition of Ir(tp)OPh in the solvent.

Reaction of Ir(tp)BF₄ with Toluene: Synthesis of (5,10,15,20-Tetrakis(*p*-tolyl)porphyrinato)(4-tolyl)iridium(III) [Ir(tp)(*p*-tol)] (6). Ir(tp)BF₄ [Ir(tp)(CO)BF₄/Ir(tp)BF₄ (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) δ 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, $\text{H}_{17,19,21,23}$), 8.00 (d, 8 H, $J = 8.1$ Hz, $\text{H}_{17,19,21,23}$), 8.57 (s, 8 H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 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 $[\text{C}_{55}\text{H}_{43}\text{N}_4\text{Ir}]^+$: m/z 952.3111. Found: m/z 952.3119.

Preparation of (5,10,15,20-Tetrakis(*p*-tolyl)porphyrinato)iridium(II) Dimer [Ir(tp)]₂ (7). [Ir(tp)]₂ was prepared using the literature method for the preparation of [Ir(oep)]₂.³⁰ Ir(tp)H (4.2 mg, 0.005 mmol) and 2,2,6,6-tetramethylpiperidinoxy (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) δ 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(tp)Cl(CO) with Toluene. Ir(tp)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(tp)Cl(CO) with Toluene and Various Ligands or Bases. Addition of 10 Equiv of 2,6-Di-*tert*-butylpyridine. Ir(tp)Cl(CO) (30.0 mg, 0.032 mmol), 2,6-di-*tert*-butylpyridine (61.2 mg, 72 μL , 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(tp)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%). $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1:1) was then used to isolate the red fraction of unreacted Ir(tp)Cl(CO) (1.8 mg, 0.002 mmol, 12%).

Addition of 10 Equiv of NaNH₂. Ir(tp)Cl(CO) (20.0 mg, 0.022 mmol), NaNH₂ (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 $R_f = 0.50$ ($\text{CH}_2\text{Cl}_2/\text{hexane} = 1:1$) 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_2Ar group of **2b** and the methyl protons of the Ir-Me group of Ir(tp)Me. Compound **2b** (9.0 mg, 0.0095 mmol, 43%) and Ir(tp)Me (0.3 mg, 0.0003 mmol, 13%) were obtained.

Addition of 10 Equiv of NaOH. Ir(tp)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(tp)Me (0.1 mg, 0.0002 mmol, 7%).

Addition of 20 Equiv of Cs₂CO₃. Ir(tp)Cl(CO) (20.0 mg, 0.022 mmol), Cs₂CO₃ (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 N₂ for 1 h to give **2b** (7.7 mg, 0.008 mmol, 37%) and Ir(tp)Me (0.8 mg, 0.0009 mmol, 4%).

Addition of 10 Equiv of K₂CO₃. Ir(tp)Cl(CO) (30.0 mg, 0.032 mmol), K₂CO₃ (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 N₂ for 2 days to give **2b** (19.5 mg, 0.020 mmol, 63%) and Ir(tp)Me (0.3 mg, 0.0003 mmol, 1%).

Addition of 20 Equiv of K₂CO₃. Ir(tp)Cl(CO) (30.0 mg, 0.022 mmol), K₂CO₃ (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 N₂. At 150 °C, the reaction was complete in 2 days to give **2b** (18.8 mg, 0.020 mmol, 61%) and Ir(tp)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(tp)Me (1.3 mg, 0.002 mmol, 7%).

Addition of 30 Equiv of K₂CO₃. Ir(tp)Cl(CO) (30.0 mg, 0.022 mmol), K₂CO₃ (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 N₂ for 2 h to give **2b** (18.5 mg, 0.019 mmol, 60%) and Ir(tp)Me (2.0 mg, 0.002 mmol, 7%).

Addition of 20 Equiv of NaOph. Ir(tp)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 N₂ for 2 days to give **2b** (16.2 mg, 0.017 mmol, 78%).

Addition of 20 Equiv of NaF. Ir(tp)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 N₂ for 6 days to give **2b** (19.8 mg, 0.021 mmol, 96%).

Reaction of Ir(tp)Cl(CO) with *p*-Xylene. Ir(tp)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 N₂ 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 CH₂Cl₂ 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(tp)Cl(CO) with *p*-Xylene and Various Bases. Addition of 20 Equiv of K₂CO₃. Ir(tp)Cl(CO) (20.0 mg, 0.022 mmol), K₂CO₃ (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 N₂ 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 CH₂Cl₂ and hexane (1:1). Compound **2a** and Ir(tp)Me with the same *R_f* = 0.50 (CH₂Cl₂/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–CH₂Ar group of **2a** and the methyl protons of the Ir–Me group of Ir(tp)Me. Compound **2a** (8.7 mg, 0.009 mmol, 41%) and Ir(tp)Me (0.2 mg, 0.0002 mmol, 1%) were obtained.

Addition of 20 Equiv of NaOph. Ir(tp)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 N₂ for 1 h. Compound **2a** (14.2 mg, 0.015 mmol, 67%) was obtained.

Reaction of Ir(tp)Cl(CO) with 4-Fluorotoluene. Ir(tp)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 N₂ 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 CH₂Cl₂ 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(tp)Cl(CO) with 4-Fluorotoluene and Various Bases. Addition of 20 Equiv of K₂CO₃. Ir(tp)Cl(CO) (20.0 mg, 0.022 mmol), K₂CO₃ (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 N₂ for 2 h. Compound **2c** (13.6 mg, 0.014 mmol, 62%) was obtained.

Addition of 20 Equiv of NaOph. Ir(tp)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 N₂ for 12 h. Compound **2c** (16.6 mg, 0.017 mmol, 78%) was obtained.

Reaction of Ir(tp)Cl(CO) with 4-Nitrotoluene. Ir(tp)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 N₂ for 1 day. Decomposition of Ir(tp)Cl(CO) resulted.

General Procedures for the Reactions of Ir(tp)Cl(CO) with 4-Nitrotoluene and Various Bases. Addition of 20 Equiv of K₂CO₃: Synthesis of (5,10,15,20-Tetrakis(*p*-tolyl)porphyrinato)(4-nitrobenzyl)iridium(III) [Ir(tp)Bn(*p*-NO₂)] (**2d**). Ir(tp)Cl(CO) (20.0 mg, 0.022 mmol), K₂CO₃ (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 N₂ 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 CH₂Cl₂ 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 CH₂Cl₂/hexane). ¹H NMR (CDCl₃, 300 MHz) δ –3.84 (s, 2 H, H₂₉), 2.70 (s, 12 H, H₂₈), 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}). ¹³C NMR (CDCl₃, 75 MHz) δ –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 [C₅₅H₄₂N₅O₂Ir]⁺: *m/z* 997.2962. Found: *m/z* 997.2948. The single crystal used for X-ray diffraction crystallography was grown from CH₂Cl₂/MeOH.

Addition of 20 Equiv of NaOph. Ir(tp)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 N₂ for 5 min. Compound **2d** (9.3 mg, 0.0093 mmol, 43%) was obtained.

Reaction of Ir(tp)H with Toluene. Ir(tp)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 N₂ 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 CH₂Cl₂ and hexane (1:1). Compound **2b** (10.5 mg, 0.011 mmol, 48%) was obtained.

Reaction of Ir(tp)Me with Toluene. Ir(tp)Me¹⁶ (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 N₂ 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 CH₂Cl₂ and hexane (1:1). A trace of **2b** was observed in crude ¹H NMR only and could not be isolated. Ir(tp)Me (4.6 mg, 0.005 mmol, 46%) was recovered.

Reaction of Ir(tp)Me with Toluene and K₂CO₃. Ir(tp)Me (10.0 mg, 0.011 mmol), K₂CO₃ (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 N₂ 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 CH₂Cl₂ and hexane (1:1). A trace of **2b** was observed in crude ¹H NMR only and cannot be isolated. Ir(tp)Me (9.2 mg, 0.011 mmol, 92%) was recovered.

Reaction of Ir(tp)(*p*-Tol) with Toluene. Ir(tp)(*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 N₂ for 1.5 days. No Ir(tp)Bn and only unreacted Ir(tp)(*p*-Tol) were observed by thin-layer chromatography.

Reaction of Ir(tp)Bn with 4-Fluorotoluene. Compound **2b** (5.0 mg, 0.005 mmol), 4-fluorotoluene (28.9 mg, 29 μL, 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 IrCH₂Ar 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(tp)Bn with Toluene-*d*₈ and K₂CO₃. Compound **2b** (6.1 mg, 0.006 mmol), toluene-*d*₈ (32.1 mg, 34 μL, 0.32 mmol), K₂CO₃ (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(tp)Cl(CO) with *p*-Xylene in C₆D₆. Ir(tp)Cl(CO) (5.8 mg, 0.006 mmol), *p*-xylene (66.6 mg, 77 μL, 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(tp)Cl(CO) was decreasing, while **2a** was increasing. After 22 days, **2a** (47%, NMR yield) and unreacted Ir(tp)Cl(CO) (31%, NMR yield) were observed using the methyl protons of *p*-xylene as the reference.

Reaction of Ir(tp)Cl(CO) with Ph¹³CH₃ and Cs₂CO₃. Ir(tp)Cl(CO) (5.8 mg, 0.006 mmol), Ph¹³CH₃ (29 mg, 33 μL, 0.31 mmol), Cs₂CO₃ (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(tp)H (81%, NMR yield) was observed as an only intermediate in 30 min. Besides, Ir(tp)Cl(CO) (10.0 mg,

0.011 mmol), Cs₂CO₃ (70 mg, 0.22 mmol), and Ph¹³CH₃ (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 N₂ 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 CH₂Cl₂ and hexane (1:1). The major orange fraction was collected to give Ir(tp)¹³CH₂Ph (8%, NMR yield estimated from crude ¹H NMR as it could not be isolated) and Ir(tp)Me (1.6 mg, 0.002 mmol, 17%). HRMS (FABMS): Calcd for [C₅₄¹³CH₄₃N₄Ir]⁺: *m/z* 953.3145. Found: *m/z* 953.3154.

Reduction of Ir(tp)Cl(CO) by Ir(tp)H with Cs₂CO₃. (i) In toluene-*d*₈. Ir(tp)H (15.3 mg, 0.018 mmol), Ir(tp)Cl(CO) (4.1 mg, 0.004 mmol), Cs₂CO₃ (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(tp)H was consumed after 4 days. The crude product was dried under vacuum. The products were purified by alumina column chromatography to give Ir(tp)Bn-*d*₇ (19%, 4.0 mg, 0.004 mmol) and Ir(tp)Me (10%, 2.0 mg, 0.002 mmol). HRMS (FABMS): Calcd for [C₅₅H₃₆D₇N₄Ir]⁺: *m/z* 959.3551. Found: *m/z* 959.3554.

(ii) In benzene-*d*₆. Ir(tp)H (7.1 mg, 0.008 mmol), Ir(tp)Cl(CO) (1.9 mg, 0.002 mmol), Cs₂CO₃ (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(tp)H was consumed after 11 days. Ir(tp)Me (10%, NMR yield) was obtained using C₆D₆ as the internal standard.

Reduction of Ir(tp)Cl(CO) by Ir(tp)H. Ir(tp)H (16.3 mg, 0.019 mmol), Ir(tp)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(tp)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(tp)Bn-*d*₇ (23%, 5.5 mg, 0.005 mmol) and Ir(tp)Me (5%, 1.0 mg, 0.001 mmol) were obtained. Unreacted Ir(tp)Cl(CO) (23%, NMR yield) and Ir(tp)H (19%, NMR yield) were estimated from crude ¹H NMR.

Reaction of Ir(tp)Cl(CO) with H₂O. Ir(tp)Cl(CO) (9.1 mg, 0.010 mmol), H₂O (17.7 μL, 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 N₂ for 8 days. No Ir(tp)Me was generated, and Ir(tp)Cl(CO) remained unreacted.

Reaction of Ir(tp)Cl(CO) with toluene-*d*₈ and Cs₂CO₃. Ir(tp)Cl(CO) (9.7 mg, 0.010 mmol), toluene-*d*₈ (53 mg, 56 μL, 0.52 mmol), Cs₂CO₃ (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(tp)Cl(CO) was consumed, and Ir(tp)H (38%, NMR yield) and [Ir(tp)]₂ (41%, NMR yield) were obtained after 1 h. All Ir(tp)H was consumed in 14 days to yield Ir(tp)Bn-*d*₇ (42%, NMR yield) and Ir(tp)Me (34%, NMR yield) using residual protons of benzene as the internal reference.

Reaction of Ir(tp)D with H₂O and Cs₂CO₃. Ir(tp)D (3.7 mg, 0.004 mmol), H₂O (3.9 mg, 3.9 μL, 0.21 mmol), Cs₂CO₃ (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(tp)D was consumed to yield Ir(tp)H (43%, NMR yield) after 13 h using residual protons of benzene as the internal reference.

Reaction of Ir(tp)H with D₂O and Cs₂CO₃. Ir(tp)H (3.2 mg, 0.004 mmol), D₂O (3.7 mg, 3.3 μ L, 0.19 mmol), Cs₂CO₃ (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(tp)H was consumed to yield Ir(tp)D (20%, NMR yield) after 36 h using residual protons of benzene as the internal reference.

Reaction of Ir(tp)Cl(CO) with toluene-*d*₈, D₂O, and Cs₂CO₃. (i) D₂O (20 Equiv). Ir(tp)Cl(CO) (15.1 mg, 0.019 mmol), toluene-*d*₈ (1.0 mL), D₂O (3.3 mg, 3.0 μ L, 0.16 mmol), and Cs₂CO₃ (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 N₂ 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 CH₂Cl₂ and hexane (1:2). Ir(tp)Bn-*d*₇ (5.1 mg, 0.005 mmol, 33%) and a mixture of Ir(tp)Me and Ir(tp)CD₃ (4.9 mg, 0.006 mmol, 34%) were obtained. The ratio of Ir(tp)Me/Ir(tp)CD₃ was found to be 5.45:1 (methyl proton from Ir(tp)Me = 2.535, the integration of pyrrole signal from both Ir(tp)Me and Ir(tp)CD₃ was set as 8.000).

(ii) D₂O (50 Equiv). Ir(tp)Cl(CO) (14.5 mg, 0.016 mmol), toluene-*d*₈ (1.0 mL), D₂O (15.7 mg, 16 μ L, 0.78 mmol), and Cs₂CO₃ (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 N₂ 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 CH₂Cl₂ and hexane (1:2). Ir(tp)Bn-*d*₇ (2.1 mg, 0.002 mmol, 14%) and a mixture of Ir(tp)Me and Ir(tp)CD₃ (3.8 mg, 0.004 mmol, 27%) were obtained. The ratio of Ir(tp)Me:Ir(tp)CD₃ was found to be 2.54:1 (methyl proton from Ir(tp)Me = 2.153; the integration of pyrrole signal from both Ir(tp)Me and Ir(tp)CD₃ was set as 8.000).

Ir(tp)Me Generation in Reaction of Ir(tp)Cl(CO) with Toluene. Addition of 10 Equiv of LiOH·H₂O. Ir(tp)Cl(CO) (20.0 mg, 0.022 mmol), LiOH·H₂O (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 N₂ 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 CH₂Cl₂ and hexane (1:1). Compound **2b** and Ir(tp)Me with the same *R*_f = 0.50 (CH₂Cl₂/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-CH₂Ar group of **2b** and the methyl protons of the Ir-Me group of Ir(tp)Me. Compound **2b** (12.8 mg, 0.013 mmol, 62%) and Ir(tp)Me (4.4 mg, 0.005 mmol, 23%) were obtained.

Addition of 10 Equiv of NaOH. Ir(tp)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 N₂ for 1 day to give **2b** (9.1 mg, 0.010 mmol, 44%) and Ir(tp)Me (4.0 mg, 0.005 mmol, 21%).

Addition of 10 Equiv of KOH. Ir(tp)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 N₂ for 1 day to give **2b** (5.6 mg, 0.006 mmol, 27%) and Ir(tp)Me (4.5 mg, 0.005 mmol, 24%).

Addition of 20 Equiv of Na₂CO₃. Ir(tp)Cl(CO) (20.0 mg, 0.022 mmol), Na₂CO₃ (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 N₂ for 10 days to give **2b** (16.2 mg, 0.017 mmol, 79%) and Ir(tp)Me (1.9 mg, 0.002 mmol, 10%).

Addition of 20 Equiv of K₂CO₃. Ir(tp)Cl(CO) (20.0 mg, 0.022 mmol), K₂CO₃ (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 N₂ for 2 days to give **2b** (13.6 mg, 0.014 mmol, 66%) and Ir(tp)Me (0.6 mg, 0.0006 mmol, 3%).

Addition of 20 Equiv of Cs₂CO₃. Ir(tp)Cl(CO) (20.0 mg, 0.022 mmol), Cs₂CO₃ (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 N₂ for 1 h to give **2b** (9.5 mg, 0.010 mmol, 46%) and Ir(tp)Me (6.6 mg, 0.008 mmol, 35%).

Dehydrogenative Dimerization of Ir(tp)H. Ir(tp)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(tp)]₂ (78%, NMR yield) was obtained after 90 min using residual protons of benzene as the internal reference.

Reaction of [Ir(tp)]₂ with Toluene. Ir(tp)H (19.9 mg, 0.023 mmol), TEMPO (5.0 mg, 0.032 mmol), and benzene (0.50 mL) were stirred in a Teflon screw-capped tube for 30 min under N₂ to prepare [Ir(tp)]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 vacuum. The brown residue was purified by column chromatography using CH₂Cl₂/hexane (1:2) as an eluent. Ir(tp)Bn (10.0 mg, 0.11 mmol, 46%) was obtained.

Reaction of Ir(tp)H with toluene (50 Equiv) and Cs₂CO₃. Ir(tp)H (4.4 mg, 0.005 mmol), toluene (23.5 mg, 27 μ L, 0.26 mmol), Cs₂CO₃ (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(tp)H (2%, NMR yield) and [Ir(tp)]₂ (89%, NMR yield), and Ir(tp)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(tp)Bn (55%, NMR yield).

Reaction of Ir(tp)H with and toluene (50 Equiv). Ir(tp)H (4.2 mg, 0.005 mmol), toluene (22.5 mg, 26 μ 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(tp)H (5%, NMR yield), [Ir(tp)]₂ (66%, NMR yield), and Ir(tp)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(tp)Bn (40%, NMR yield) and unreacted Ir(tp)H (37%, NMR yield).

Reaction of Ir(tp)Cl(CO) with PhCH₃ and NaOPh in C₆D₆. Ir(tp)Cl(CO) (10.1 mg, 0.011 mmol), PhCH₃ (100.6 mg, 116 μ 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(tp)Cl(CO) was consumed after 2 h to give Ir(tp)OPh (95%, NMR yield) using the methyl proton of toluene as the internal reference.

Reaction of Ir(tp)OPh with PhCH₃ in C₆D₆. Ir(tp)OPh (6.6 mg, 0.0069 mmol), PhCH₃ (63.7 mg, 73.5 μ 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(tp)OPh was decreasing, while the amount of **2b** was increasing. Ir(tp)OPh was consumed after 10 days to yield **2b** (80%, NMR yield), using methyl protons of PhCH₃ as the internal reference. No Ir(tp)H and PhOBn were found during the course of the reaction.

Reaction of Ir(tp)OPh with Toluene-*d*₈. Ir(tp)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 N₂. 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 CH₂Cl₂/hexane (1:2).

Isotope Effect with Ir(tp)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(tp)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 N₂ 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 ¹H NMR. The isotope ratio was also measured by FABMS to be 2.40.

Addition of 20 Equiv of K₂CO₃. 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(tp)Cl(CO) (30.0 mg, 0.032 mmol), and K₂CO₃ (88 mg, 0.64 mmol) was heated at 200 °C under N₂ 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 ¹H 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(tp)Cl(CO) (20.0 mg, 0.022 mmol), and NaOPh (51 mg, 0.44 mmol) was heated at 200 °C under N₂ 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 ¹H NMR. The isotope ratio was also measured by FABMS to be 2.18.

Isotope Effect with Ir(tp)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(tp)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 N₂ 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 ¹H NMR. The isotope ratio was also measured by FABMS to be 2.13.

Isotope Effect with [Ir(tp)]₂. Ir(tp)]₂ was prepared *in situ* by stirring Ir(tp)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(tp)]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 N₂ 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 ¹H NMR.

Competition Reactions in Base-Promoted BnCHA. Addition of *p*-Xylene (100 Equiv) and Toluene (100 Equiv). Ir(tp)Cl(CO) (15.4 mg, 0.017 mmol), K₂CO₃ (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 N₂ for 6 h. The ratio of **2a** to **2b** was determined to be 2.050 by ¹H NMR spectroscopy from the integration of the *meta*-phenyl protons of Ir-CH₂Ar group of **2a** and **2b**.

Addition of 4-Fluorotoluene (100 Equiv) and Toluene (100 Equiv). Ir(tp)Cl(CO) (16.0 mg, 0.017 mmol), K₂CO₃ (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 N₂ for 4.5 h. The ratio of **2c** to **2b** was determined to be 1.303 by ¹H NMR spectroscopy from the integration of the *meta*-phenyl protons of Ir-CH₂Ar groups of **2c** and **2b**.

Addition of 4-Nitrotoluene (100 Equiv) and Toluene (100 Equiv). Ir(tp)Cl(CO) (15.8 mg, 0.017 mmol), K₂CO₃ (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 N₂ for 3.5 h. The ratio of **2d** to **2b** was determined to be 5.067 by ¹H NMR spectroscopy from the integration of the *meta*-phenyl protons of Ir-CH₂Ar groups of **2d** and **2b**.

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and sealed under N₂ 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.

Acknowledgment. We thank the Research Grants Council of the HKSAR, China (CUHK 400105) for financial support.

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

OM700751H

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