## **ORGANOMETALLICS**

# Base-Promoted C–O Bond Cleavage of Primary Alcohols by Iridium(III) Porphyrin Chloride

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 ABSTRACT: Various Ir(por)-benzyls and Ir(por)-alkyls (por = porphyrinato dianion ligand) were successfully synthesized with benzyl and 1° alkyl alcohols by C-O bond cleavage with Ir(ttp)(CO)Cl (ttp = 5.10.15.20-tetraphenylporphyrinato
 Ir(ttp)(CO)Cl + R-OH KOH(10 equiv) / CeH6 or PhCN,150 °C / Ir(ttp)R R = 1°alkyl, benzyl

C–O bond cleavage with Ir(ttp)(CO)Cl (ttp = 5,10,15,20-tetraphenylporphyrinato dianion) in alkaline media. The alkylation products were afforded in up to 92%

yields. Mechanistic investigations suggest that both the  $Ir(ttp)^-$  anion and Ir(ttp)H are key intermediates via a hydrogen-borrowing pathway.

#### INTRODUCTION

Iridium porphyrin alkyls, Ir(por)R (por = porphyrinato dianion ligand), as intriguing organometallic complexes have been widely utilized in many fields, including molecular recognition, anticancer drugs, sensors, catalysis, etc.<sup>1</sup> Serving as catalysts, they can activate various chemical bonds. For example, they can effectively catalyze the N-H, C-H, and Si-H bond insertion with ethyl diazoacetate in high yields.<sup>1d,e</sup> Ir(por)R are also effective and robust catalysts for the cyclopropanation of olefin with diazo compounds.<sup>1f</sup> More interestingly, iridium porphyrin alkyls can catalyze the hydrogenolysis of the carbon-carbon  $\sigma$  bond of [2.2]paracyclophane with H<sub>2</sub>O as the hydrogen source under neutral conditions. Mechanistic investigations reveal that the active catalyst is the iridium porphyrin hydride.<sup>2</sup> Hence, developing efficient strategies to access various iridium porphyrin alkyls remain an attractive research field.

The synthesis of iridium porphyrin alkyls was first reported by Ogoshi in 1978 involving the transmetalation between Ir(oep)(CO)Cl (oep = 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion) and MeLi or nucleophilic substitution between  $Ir(oep)^{-}$  and MeI to generate Ir(oep)Me (Scheme 1a).<sup>3</sup> The oxidative addition of alkyl C-H bonds by  $[Ir(por)]_2$ represents another important method to form iridium porphyrin alkyls, which was discovered by Wayland in 1986 (Scheme 1b).<sup>4</sup> In 2008, our group developed the basepromoted benzylic C-H bond activation of various PhCH<sub>3</sub> species by Ir(ttp)(CO)Cl (ttp = 5,10,15,20-tetraphenylporphyrinato dianion) providing different Ir(ttp)Bn species (Scheme 1c).<sup>5</sup> Recently, we have expanded the scope of alkylating substrates to alkyl halides, including 1°, 2°, and 3° alkyls, for the preparation of Ir(ttp)-alkyls from Ir(ttp)(CO)Cl in good yields under user-friendly aerobic conditions (Scheme  $1c).^{6}$ 

Generally, under neutral or basic conditions alkyl alcohols are not good alkylating agents due to the poor leaving ability of hydroxide and the strong carbon–OH bond strengths (such as 92.0 kcal/mol in Me–OH and 79.9 kcal/mol in PhCH<sub>2</sub>–

OH).<sup>7</sup> Therefore, both acid-catalyzed nucleophilic substitutions and conversion of the hydroxyl group into better leaving groups followed by substitution are popular strategies.<sup>8</sup> We previously have reported the direct cleavage of the C–OH bond in methanol by Ir(ttp)(CO)Cl to give Ir(ttp)Me under solvent-free and basic conditions, in which Ir(ttp)H was proposed as the active species to cleave the C–O bond likely via  $\sigma$ -bond metathesis to give Ir(ttp)Me.<sup>9</sup> In this work, we have successfully expanded the scope of the alcohols to benzyl alcohols and other aliphatic alcohols with  $\beta$  hydrogens. Ir(ttp)(CO)Cl can efficiently cleave the benzylic C–OH bond in toluene solvent or aliphatic C–OH bond in benzonitrile solvent to give Ir(ttp)Bn or Ir(ttp)-alkyls, respectively.

#### RESULTS AND DISCUSSION

**Reaction Discovery.** Previously, we reported that Rh-(ttp)Cl could cleave the C–OH bond of benzyl alcohols and aliphatic alcohols in benzonitrile solvent under basic conditions at 120 °C to form Rh(ttp)Bn and Rh(ttp)-alkyls, respectively.<sup>10</sup> Considering the analogous reactivity of Ir(por) complexes to Rh(por) complexes in bond activation, we anticipated that the C–O bonds of various alcohols could be cleaved with Ir(ttp)(CO)Cl (1a) under the above conditions.

When we examined the reaction between Ir(ttp)(CO)Cl(1a) and benzyl alcohol (2a) with  $K_2CO_3$  as a base in benzonitrile solvent at 120 °C under an  $N_2$  atmosphere, to our delight, the C–O cleavage product, Ir(ttp)Bn (3a), was isolated in 29% yield (eq 1). Then, we further pursued optimizing the reaction conditions.

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## Scheme 1. Synthesis of Ir(por)R (por = Porphyrinato Dianion, R = Alkyls)

#### a) Ogoshi (1975) CH<sub>3</sub>Li Ir(oep)(CO)CI -Ir(oep)Me THF. reflux Ir(oep)(CO)CI 1) NaBH<sub>4</sub>/NaOH 2) CH<sub>3</sub>I (excess) lr(oep)Me b) Wayland (1986) $[Ir(oep)]_2$ + CH<sub>3</sub>C(O)H $\frac{r.r.}{-Ir(oep)H}$ Ir(oep)CH<sub>2</sub>C(O)H c) Our group ( Chan 2008, 2015) r.t $Ir(ttp)(CO)CI + PhCH_3 \xrightarrow{r.t.} Ir(ttp)CH_2Ph$ Chan 2008, 61% $Ir(ttp)(CO)CI + R-X \xrightarrow{KOH} Ir(ttp)R$ Chan 2015 X = Cl. Br. I $R = 1^{\circ}, 2^{\circ}, 3^{\circ}$ alkyl This work Ir(ttp)(CO)CI + R-OH $\frac{KOH}{C_6H_6 \text{ or PhCN}, 150 \degree C}$ Ir(ttp)R R = 1ºalkvl, benzvl Ir(oep)R, X = H, Y = EtIr(ttp)R, X = p-tolyl, Y = HIr(por)R

1a	2a		3a	
	(100 equiv)	N <sub>2</sub> , 120 °C, 19 h PhCN	29%	(1)
lr(ttp)Cl(CO) +	PhCH <sub>2</sub> OH	10 equiv K <sub>2</sub> CO <sub>3</sub>	lr(ttp)CH₂Ph	

**Temperature and Solvent Effect.** When the reaction temperature was increased from 120 to 150 °C, the yield of the desired product Ir(ttp)Bn (3a) did not obviously change but there was a higher reaction rate (Table 1, entries 1 and 2). Therefore, 150 °C was chosen to be the optimal reaction

Table 1. Temperature a	nd Solvent	t Effects	on the	С-О
Cleavage of Benzyl Alco	hol			

Ir(ttp)Cl(CO) + PhCH <sub>2</sub> OH (100 equiv)		10 equiv K <sub>2</sub> N <sub>2</sub> , temp, ti solven	<mark>CO<sub>3</sub>→</mark> Ir(ti me t	lr(ttp)CH <sub>2</sub> Ph	
1a	2a			3a	
entry	solvent	temp/°C	time/h	yield/% <sup>a</sup>	
1	benzonitrile	120	19	29	
2	benzonitrile	150	5	28	
3		150	48	50	
4	acetonitrile	150	24	trace	
5	isopropyl alcohol	150	24	trace	
6	anisole	150	48	4 <sup><i>b</i>,<i>c</i></sup>	
7	benzene	150	48	84	

 $^a$ Isolated yield.  $^{b1}{\rm H}$  NMR yield.  $^c{\rm A}$  17% NMR yield of Ir(ttp)CH\_3 was afforded.

temperature. Subsequently, various solvents were further examined to optimize the reaction conditions. When the reaction proceeded under solvent-free conditions, the product Ir(ttp)Bn (**3a**) was afforded in 50% yield after 48 h (Table 1, entry 3). Only a trace amount of Ir(ttp)Bn (**3a**) was observed in acetonitrile or isopropyl alcohol solvent (Table 1, entries 4 and 5). Using anisole as the solvent, a 4% yield of Ir(ttp)Bn (**3a**) was produced with a 17% yield of Ir(ttp)CH<sub>3</sub> from the cleavage of the alkyl PhO–Me bond (Table 1, entry 6).<sup>11</sup> The optimal result was obtained in benzene solvent, and Ir(ttp)Bn (**3a**) was formed in 84% yield after 48 h (Table 1, entry 7). Therefore, we chose benzene as the optimal solvent to further optimize the reaction conditions.

Base and Base-Loading Effects. Without any base, Ir(ttp)(CO)Cl(1a) did not react with benzyl alcohol (2a) at 150 °C for 48 h with quantitative recovery of 1a (Table 2,

Table 2.	Base	and	Base-Loading	Effects	on	the	С-0
Cleavage	e of B	enzyl	Alcohol				

		base	(n equiv)	
	(100 equiv)	N <sub>2</sub> , 15 C	50 °C, time	
1a	2a			3a
entry	base	n	time/h	yield/% <sup>a</sup>
1		0	48	0
2	K <sub>2</sub> CO <sub>3</sub>	10	48	84
3	КОН	10	2	89
4	КОН	20	2	88
5	КОН	5	2	80
<sup><i>a</i></sup> Isolated yield.				

entry 1). When 10 equiv of KOH was used instead of  $K_2CO_3$  as the base, the reaction gave a higher product yield of 89% with a shorter reaction time of only 2 h (Table 2, entry 3). There was not an obvious influence on the yield and reaction time when the loading of KOH was increased from 10 to 20 equiv (Table 2, entry 4). A slightly lower yield of 80% was afforded when 5 equiv of KOH was added. The yield did not vary greatly, probably because the solubility of KOH in benzene is low and the solution is already saturated with 5 equiv of KOH. A 10 equiv amount of KOH was thus found to be suitable.

**Benzyl Alcohol Loading Effects.** When both 50 and 30 equiv of benzyl alcohol were used in this transformation, the reaction efficiency was similar to that of 100 equiv of benzyl alcohol in rates and yields (Table 3, entries 1-3). A lower

Table 3. Benzyl Alcohol Loading	Effects	on	the	C-C	)
Cleavage of Benzyl Alcohol					

Ir(ttp)Cl(CO) +	PhCH <sub>2</sub> OH	KOH (10 equiv)	Ir(ttp)CH <sub>2</sub> Ph
	( <mark>n</mark> equiv)	N <sub>2</sub> , 150 <sup>o</sup> C, time C <sub>6</sub> H <sub>6</sub>	
1a	2a		3a
entry	n	time/h	yield/% <sup>a</sup>
1	100	2	89
2	50	2	89
3	30	2	88
4	10	5	81

<sup>a</sup>Isolated yield.

benzyl alcohol loading of 10 equiv resulted in a slightly lower yield of Ir(ttp)Bn (3a) (81%) in 5 h (Table 3, entry 4). Therefore, 30 equiv of benzyl alcohol loading was used in further studies.

**Substrate Scope.** The optimal reaction conditions were found to require Ir(ttp)(CO)Cl, 30 equiv of benzyl alcohol, and 10 equiv of KOH as a base in benzene at 150 °C. Various substituted benzyl alcohols were then investigated under the optimal conditions. The results demonstrated that the reaction could tolerate various functional groups such as methyl, methoxyl, *tert*-butyl, and trifluoromethyl (Table 4). Both

Table 4. Scope of Substituted Benzyl Alcohols

lr(ttp)Cl(CO)	+ R (30 equiv)	0H <u>10 equiv KOH</u> N <sub>2</sub> , 150 °C, 2 h C <sub>6</sub> H <sub>6</sub>	R Ir(ttp)
1a	2		3
entry		R	yield/% <sup>a</sup>
1	Н	(2a)	88 ( <b>3</b> a)
2	4-	<i>t</i> -Bu (2b)	92 (3b)
3	4-	Me (2c)	87 ( <b>3c</b> )
4	4-	OMe ( <b>2d</b> )	84 ( <b>3d</b> )
5	4-	$CF_3$ (2e)	86 ( <b>3e</b> )
<sup><i>a</i></sup> Isolated yiel	d.		

electron-rich and electron-poor benzyl alcohols 2a-e gave good yields of the corresponding C–O cleavage products 3a-e (Table 4, entries 1–5). 4-Methylbenzyl alcohol (2c) reacted to give the desired Ir(ttp)CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(4-Me) (3c) in 87% yield without any benzylic C–H activation products (Table 4, entry 3). 4-Methoxybenzyl alcohol (2d) underwent chemoselective C–O cleavage to produce Ir(ttp)CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(4-OMe) (3d) in 62% yield (Table 4, entry 4).<sup>11</sup> Halogen-containing benzyl alcohols were not suitable, presumably because the aryl carbon–halogen bonds were more easily cleaved than alkyl carbon–oxygen bonds with iridium porphyrin complexes under the basic conditions.<sup>12</sup>

To expand the synthetic application of this alkylating methodology, other 1° alkyl alcohols were then investigated. Under the above optimal conditions, MeOH (2f) was first attempted. but no desired Ir(ttp)Me (3f) product was observed. In view of the fact that benzonitrile as a solvent is successful in the reaction of Rh(ttp)Cl cleaving the C-O bond of alkyl alcohols, we again ran the reaction between Ir(ttp)(CO)Cl (1a) and 100 equiv of MeOH in benzonitrile solvent. To our delight, the reaction was complete in 2 h and gave Ir(ttp)Me (3f) in 88% yield (Table 5, entry 1), which was higher than that under the previously reported solventless conditions giving a 70% yield.<sup>9</sup> Using these conditions, other alkyl alcohols with  $\beta$ -hydrogens, such as EtOH, n-PrOH, n-BuOH, n-pentanol, and n-octanol, were also screened, and moderate to good yields of Ir(ttp)-alkyls 3g-l were obtained in 24 h (Table 5, entries 2-6). The yields slightly decreased with increasing alkyl chain length, possibly due to product decomposition by the facile  $\beta$ -hydride elimination.<sup>13</sup> 5-Hexen-1-ol was also a suitable substrate even with a reactive alkene moiety and gave the corresponding alkylating product in 64% yield, suggesting that this approach can potentially be used to prepare more valuable and functionalized Ir(ttp)-alkyls (Table 5, entry 7).

**Mechanistic Studies.** It has been reported that Ir(ttp)-(CO)Cl could readily be reduced to  $[Ir(ttp)]_2$  and  $Ir(ttp)^-$  in

#### Table 5. Scope of Alkyl Alcohols

Ir(ttp)CI(CO		10 equiv KOH	Ir(tto)P	
	(100	N <sub>2</sub> , 150 °C, time	II (up)ix	
	(100 equiv)	PhCN		
1a	2		3	
entry	ROH	time/h	yield/% <sup>a</sup>	
1	CH <sub>3</sub> OH (2f)	2	88 ( <b>3f</b> )	
2	EtOH (2g)	24	83 ( <b>3g</b> )	
3	<i>n</i> -PrOH (2h)	24	79 (3h)	
4	n-BuOH (2i)	24	73 ( <b>3i</b> )	
5	<i>n</i> -pentanol (2j)	24	71 ( <b>3</b> j)	
6	n-octanol (2k)	24	70 ( <b>3</b> k)	
7	5-hexen-1-ol (2l)	24	64 ( <b>3l</b> )	
<sup><i>a</i></sup> Isolated yield.				

the presence of KOH.<sup>11,12a</sup> We propose that Ir(ttp)(CO)CI(1a) first undergoes ligand dissociation and ligand substitution with KOH to give Ir(ttp)OH, which then undergoes fast reductive dimerization to form  $Ir_2(ttp)_2$  and  $H_2O_2$ . Excess KOH could reduce  $Ir_2(ttp)_2$  to  $Ir(ttp)^-$ . Meanwhile,  $Ir(ttp)^-$  is also protonated to Ir(ttp)H by residual water in the solvent.<sup>12a</sup> These three Ir(ttp) species are possible dominant active intermediates for the various bond activations and exist in equilibria under basic conditions, as depicted in Scheme 2.<sup>3,12a</sup>

#### Scheme 2. Equilibria between Iridium Porphyrin Intermediates

$$\begin{array}{c|c} Ir(ttp)(CO)CI & \xrightarrow{OH^-} & Ir(ttp)OH \\ \hline & & \\ Ir(ttp)OH & -H_2O_2 \\ & & \\ Ir_2(ttp)_2 & \xrightarrow{OH^+, -Ir(ttp)OH} & Ir(ttp)^- & \xrightarrow{H_2O, -OH^-} & Ir(ttp)H \end{array}$$

In addition,  $[Ir(ttp)]_2$  has been ruled out to be an intermediate in the C–O cleavage of MeOH by Ir(ttp)(CO)Cl in alkaline media.<sup>9</sup> Therefore, we proposed that similar mechanistic pathways operate in benzene or benzonitrile solvent. Therefore, the reactivities of only  $Ir(ttp)^-$  and Ir(ttp)H as the probable intermediates toward C–O bond cleavage of benzyl alcohol were examined individually.

When Ir(ttp)H (1b) was reacted with 30 equiv of benzyl alcohol at 150 °C in  $C_6D_6$  for 24 h under  $N_2$ , no C–O bond cleavage product Ir(ttp)CH<sub>2</sub>Ph (3a) was observed (Scheme 3A). Thus, Ir(ttp)H (1b) alone is unlikely to be the active intermediate.

Ir(ttp)<sup>-</sup> was then generated in situ from the deprotonation of Ir(ttp)H (1b) (the  $pK_a$  of Ir(ttp)H is 15)<sup>9</sup> with KOH in  $C_6D_6$  and reacted with 30 equiv of benzyl alcohol to form the C–O cleavage product Ir(ttp)Bn in 78% yield in 2 h (Scheme 3,B). These outcomes imply two mechanistic possibilities: (1) the Ir(ttp)<sup>-</sup> anion directly cleaves the C–O bond of benzyl alcohol possibly by an  $S_N$ 2-like pathway and (2) KOH is essential and plays a promoting role in the C–O cleavage reaction with Ir(ttp)H. We support the second mechanistic proposal because hydroxide is a very poor leaving group under basic conditions.

In order to gain some mechanistic understanding of the electronic effects of C-O bond cleavage, a series of competition experiments using an equimolar mixture of 4-substituted benzyl alcohol and benzyl alcohol with Ir(ttp)-

Article

Ir(ttp)CH<sub>2</sub>Ph

#### Scheme 3. Reaction of Ir(ttp)H and Ir(ttp)<sup>-</sup> toward the C-O bond Cleavage of Benzyl Alcohol

#### A. Ir(ttp)H Ir(ttp)H + PhCH<sub>2</sub>OH -(30 equiv)

	(30 equiv)	N <sub>2</sub> , 150 °C, 24 h C <sub>6</sub> D <sub>6</sub>	0%
1b	2a		3a

#### B. Ir(ttp)

Ir(tto)H		10 equiv KOH	Ir(ttp)CH. Ph
n(up)n		N <sub>2</sub> , 150 °C, 2 h	
	(30 equiv)	C <sub>6</sub> D <sub>6</sub>	78%
1b	2a		3a

(CO)Cl and KOH (30 equiv) at 150  $^\circ \rm C$  in benzene were conducted.

Table 6 summarizes the results. On the basis of these results, a Hammett plot was then constructed and showed that the

### Table 6. Competition Reaction between Substituted BnOH and BnOH with Ir(ttp)Cl(CO)

lr(ttp)Cl(CO)	+ OH +		equiv KOH 150 °C, 2 h	Ir(t	tp) + Ir(ttp)
1a	(30 equiv)	(30 equiv)	C <sub>6</sub> H <sub>6</sub>	3a	GF 3
			yield	l/% <sup>a</sup>	
entry	FG	$\sigma_{ m p}$	3a	3	$\log(k_{ m FG}/k_{ m H})$
1	CH <sub>3</sub>	-0.17	35	60	0.230
2	OCH <sub>3</sub>	-0.27	21	57	0.431
3	CF <sub>3</sub>	0.54	52	44	-0.079
<sup>a</sup> NMR y	rield.				

electron-withdrawing group  $(-CF_3)$  decreased the rate of C– O cleavage (Figure 1). This finding also disfavors the S<sub>N</sub>2-like pathway, since an electron-withdrawing group is a better leaving group.



**Figure 1.** Hammett plot of base-promoted Bn–OH cleavage using the Hammett constants.

On the basis of the above experimental findings and the previous investigations on the C–O bond cleavage of CH<sub>3</sub>OH,<sup>9</sup> a possible mechanism is proposed for the C–O cleavage in primary alcohols using benzyl alcohol as an example (Scheme 4). First, a small amount of PhCH<sub>2</sub>O<sup>-</sup> anion is produced by deprotonation of PhCH<sub>2</sub>OH (2a) with KOH and reacts with Ir(ttp)(CO)Cl (1a) via ligand substitution to generate the Ir(ttp)OCH<sub>2</sub>Ph intermediate.<sup>14</sup> Alternatively, Ir(ttp)OCH<sub>2</sub>Ph can be generated by the reaction between PhCH<sub>2</sub>OH (2a) and Ir(ttp)OH from the ligand substitution of Ir(ttp)(CO)Cl (1a) and KOH. Ir(ttp)OCH<sub>2</sub>Ph then undergoes  $\beta$ -H elimination with KOH to yield the Ir(ttp)<sup>-</sup> anion



and benzaldehyde.<sup>14,15</sup> Ir(ttp)<sup>-</sup> can also be protonated to Ir(ttp)H (1b) by H<sub>2</sub>O (the p $K_a$  of Ir(ttp)H is 15).<sup>9,16</sup> Subsequently, the nucleophilic Ir(ttp)<sup>-</sup> anion attacks the carbonyl carbon in benzaldehyde to give the  $\alpha$ -hydroxyalkyl complex Ir(ttp)CH(OH)Ph upon protonation with H<sub>2</sub>O.<sup>9,17</sup> Finally, Ir(ttp)CH(OH)Ph can be reduced by Ir(ttp)H (1b) to the desired C–O cleavage product Ir(ttp)CH<sub>2</sub>Ph (3a) and Ir(ttp)OH, probably via  $\sigma$ -bond metathesis.<sup>10</sup> Then, Ir(ttp)-OH is either reused to react with PhCH<sub>2</sub>OH (2a) or converted directly to the Ir(ttp)<sup>-</sup> anion according to the pathway in Scheme 2. In benzonitrile solvent for aliphatic alcohols, the (PhCN)Ir(ttp)<sup>-</sup> anion is formed by the solvent ligation of the Ir(ttp)<sup>-</sup> anion is more nucleophile, because the (PhCN)Ir(ttp)<sup>-</sup> anion is more nucleophilic than the Ir(ttp)<sup>-</sup> anion.<sup>10,16</sup>

#### CONCLUSION

In short, the alkylation of Ir(por)s was successfully achieved with benzyl and alkyl alcohols as the alkylating reagents. This C–O bond cleavage reaction could proceed smoothly in benzene or benzonitrile solvent under basic conditions and gave up to a 92% yield of Ir(ttp) complexes. Mechanistic investigations suggest that both the  $Ir(ttp)^-$  anion and Ir(ttp)H are key intermediates for this C–O cleavage. The reaction involves a hydrogen-borrowing pathway via Ir(ttp)H.

#### EXPERIMENTAL SECTION

Unless otherwise noted, all materials were purchased from commercial suppliers and directly used without further purification. Benzene for the reaction was distilled from sodium. Hexane for chromatography was distilled from anhydrous calcium chloride. All reactions were protected from light by wrapping with aluminum foil. The reaction mixtures in Teflon screw-capped pressure tubes were heated in heat blocks on heaters and monitored by thin-layer chromatography (TLC) performed on Merck precoated silica gel 60 F254 plates. Silica gel (Merck, 70–230 and 230–400 mesh) was used for column chromatography in air. Ir(ttp)Cl(CO) (1a)<sup>13</sup> and It(ttp) H (1b)<sup>5</sup> have been characterized and were prepared according to the literature processes.

<sup>1</sup>H NMR spectra were recorded on a Bruker AV400 instrument at 400 MHz. Chemical shifts were referenced with the residual solvent protons in CDCl<sub>3</sub> ( $\delta$  7.26 ppm) and C<sub>6</sub>D<sub>6</sub> ( $\delta$  7.15 ppm). All Ir(ttp)-alkyl compounds are known compounds, and their characterization data are in accordance with those previously reported.<sup>5,6,11,13</sup> Unless otherwise specified, the coupling constant *J* refers to H–H coupling.

Reaction of Ir(ttp)CI(CO) and Benzyl Alcohol with K2CO3 in PhCN at 120 °C. Ir(ttp)Cl(CO) (1a; 11.6 mg, 0.0125 mmol), K<sub>2</sub>CO<sub>3</sub> (17.3 mg, 0.125 mmol), and benzyl alcohol (2a; 135.2 mg, 1.25 mmol) were added into benzonitrile (1.5 mL) in a Teflon screwcapped tube, degassed for three freeze-pump-thaw cycles, refilled with N2, and heated at 120 °C for 19 h. After the excess benzyl alcohol and benzonitrile were removed by vacuum distillation, the solid mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> and filtered through a short pipet column chromatograph on silica gel with CH<sub>2</sub>Cl<sub>2</sub> to give the red crude product. The crude product was further purified by a precoated silica gel TLC plate with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1/1) to give Ir(ttp)Bn<sup>5</sup> (3a; 3.5 mg, 0.0037 mmol) in 19% yield. <sup>1</sup>H NMR  $(CDCl_3, 400 \text{ MHz}): \delta -3.97 \text{ (s, 2 H), } 2.71 \text{ (s, 12 H), } 3.18 \text{ (d, 2 H, J)}$ = 7.4 Hz), 5.92 (t, 2 H, J = 7.6 Hz), 6.49 (t, 1 H, J = 7.2 Hz), 7.55 (t, 8 H, J = 6.8 Hz), 7.99 (d, 4 H, J = 7.4 Hz), 8.04 (d, 4 H, J = 7.1 Hz), 8.49 (s, 8 H).

Reaction of Ir(ttp)Cl(CO) and Benzyl Alcohol with  $K_2CO_3$  in PhCN at 150 °C. Ir(ttp)Cl(CO) (1a; 11.6 mg, 0.0125 mmol),  $K_2CO_3$  (17.3 mg, 0.125 mmol), and benzyl alcohol (2a; 135.2 mg, 1.25 mmol) were added into benzonitrile (1.5 mL) in a Teflon screwcapped tube, degassed for three freeze–pump–thaw cycles, refilled with  $N_{2^{\prime}}$  and heated at 150 °C for 5 h. After the excess benzyl alcohol and benzonitrile were removed by vacuum distillation, the solid mixture was then extracted with  $CH_2Cl_2$  and filtered through a short pipet column chromatograph on silica gel with  $CH_2Cl_2$  to give the red crude product. The crude product was further purified by a precoated silica gel TLC plate with  $CH_2Cl_2$ /hexane (1/1) to give Ir(ttp)Bn (3a; 3.3 mg, 0.0035 mmol) in 28% yield.

**Reaction of Ir(ttp)Cl(CO) and Benzyl Alcohol with K<sub>2</sub>CO<sub>3</sub> at 150 °C.** Ir(ttp)Cl(CO) (1a; 11.6 mg, 0.0125 mmol) and K<sub>2</sub>CO<sub>3</sub> (17.3 mg, 0.125 mmol) were added into benzyl alcohol (1.5 mL) in a Teflon screw-capped tube, degassed for three freeze–pump–thaw cycles, refilled with N<sub>2</sub>, and heated at 150 °C for 48 h. After the excess benzyl alcohol was removed by vacuum distillation, the solid mixture was then extracted with  $CH_2Cl_2$  and filtered through a short pipet column chromatograph on silica gel with  $CH_2Cl_2$  to give the red crude product. The crude product was further purified by a precoated silica gel TLC plate with  $CH_2Cl_2$ /hexane (1/1) to give Ir(ttp)Bn (3a; 6.0 mg, 0.0063 mmol) in 50% yield.

**Reaction of Ir(ttp)Cl(CO) and Benzyl Alcohol with K<sub>2</sub>CO<sub>3</sub> in CH<sub>3</sub>CN at 150 °C. Ir(ttp)Cl(CO) (1a; 11.6 mg, 0.0125 mmol), K<sub>2</sub>CO<sub>3</sub> (17.3 mg, 0.125 mmol), and benzyl alcohol (2a; 135.2 mg, 1.25 mmol) were added into acetonitrile (1.5 mL) in a Teflon screw-capped tube, degassed for three freeze–pump–thaw cycles, refilled with N<sub>2</sub>, and heated at 150 °C for 24 h. After the excess benzyl alcohol and acetonitrile were removed by vacuum distillation, the solid mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> and filtered through a short pipet column chromatograph on silica gel with CH<sub>2</sub>Cl<sub>2</sub> to give the red crude product. The <sup>1</sup>H NMR spectrum was recorded for the crude product. Ir(ttp)Bn (3a) was formed in trace amounts.** 

**Reaction of Ir(ttp)CI(CO) and Benzyl Alcohol with K<sub>2</sub>CO<sub>3</sub> in Isopropyl Alcohol at 150 °C.** Ir(ttp)CI(CO) (1a; 11.6 mg, 0.0125 mmol), K<sub>2</sub>CO<sub>3</sub> (17.3 mg, 0.125 mmol), and benzyl alcohol (2a; 135.2 mg, 1.25 mmol) were added into isopropyl alcohol (1.5 mL) in a Teflon screw-capped tube, degassed for three freeze–pump–thaw cycles, refilled with N<sub>2</sub>, and heated at 150 °C for 24 h. After the excess benzyl alcohol and isopropyl alcohol were removed by vacuum distillation, the solid mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> and filtered through a short pipet column chromatograph on silica gel with CH<sub>2</sub>Cl<sub>2</sub> to give the red crude product. The <sup>1</sup>H NMR spectrum was recorded for the crude product. Ir(ttp)Bn (3a) was formed in trace amounts.

Reaction of Ir(ttp)Cl(CO) and Benzyl Alcohol with  $K_2CO_3$  in Anisole at 150 °C. Ir(ttp)Cl(CO) (1a; 11.6 mg, 0.0125 mmol),

 $K_2CO_3$  (17.3 mg, 0.125 mmol), and benzyl alcohol (2a; 135.2 mg, 1.25 mmol) were added into anisole (1.5 mL) in a Teflon screwcapped tube, degassed for three freeze–pump–thaw cycles, refilled with N<sub>2</sub>, and heated at 150 °C for 48 h. After the excess benzyl alcohol was removed by vacuum distillation, the solid mixture was then extracted with  $CH_2Cl_2$  and filtered through a short pipet column chromatograph on silica gel with  $CH_2Cl_2$  to give the red crude product. The NMR yield of Ir(ttp)Bn (3a) was determined to be 4% using dichloroethane as the internal standard.

Reaction of Ir(ttp)Cl(CO) and Benzyl Alcohol with  $K_2CO_3$  in Benzene at 150 °C. Ir(ttp)Cl(CO) (1a; 11.6 mg, 0.0125 mmol),  $K_2CO_3$  (17.3 mg, 0.125 mmol), and benzyl alcohol (2a; 135.2 mg, 1.25 mmol) were added into benzene (1.5 mL) in a Teflon screwcapped tube, degassed for three freeze–pump–thaw cycles, refilled with N<sub>2</sub>, and heated at 150 °C for 48 h. After the excess benzyl alcohol and benzene were removed by vacuum distillation, the solid mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> and filtered through a short pipet column chromatograph on silica gel with CH<sub>2</sub>Cl<sub>2</sub> to give the red crude product. The crude product was further purified by a precoated silica gel TLC plate with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1/1) to give Ir(ttp)Bn (3a; 10.0 mg, 0.0035 mmol) in 84% yield.

**Reaction of Ir(ttp)Cl(CO) and Benzyl Alcohol without Base.** Ir(ttp)Cl(CO) (1a; 11.6 mg, 0.0125 mmol) and benzyl alcohol (2a; 41.0 mg, 0.375 mmol) were added into benzene (1.5 mL) in a Teflon screw-capped tube, degassed for three freeze-pump-thaw cycles, refilled with  $N_{2}$ , and heated at 150 °C for 48 h. No desired Ir(ttp)Bn was formed, as determined by TLC and <sup>1</sup>H NMR.

Reaction of Ir(ttp)Cl(CO) and Benzyl Alcohol with KOH (10 equiv) at 150 °C. Ir(ttp)Cl(CO) (1a; 11.6 mg, 0.0125 mmol), KOH (7.0 mg, 0.125 mmol), and benzyl alcohol (2a; 135.2 mg, 1.25 mmol) were added into benzene (1.5 mL) in a Teflon screw-capped tube, degassed for three freeze–pump–thaw cycles, refilled with N<sub>2</sub>, and heated at 150 °C for 2 h. After the excess benzyl alcohol and benzene were removed by vacuum distillation, the solid mixture was then extracted with  $CH_2Cl_2$  and filtered through a short pipet column chromatograph on silica gel with  $CH_2Cl_2$  to give the red crude product. The crude product was further purified by a precoated silica gel TLC plate with  $CH_2Cl_2$ /hexane (1/1) to give Ir(ttp)Bn (3a; 10.6 mg, 0.0111 mmol) in 89% yield.

Reaction of Ir(ttp)Cl(CO) and Benzyl Alcohol with KOH (20 equiv) at 150 °C. Ir(ttp)Cl(CO) (1a; 11.6 mg, 0.0125 mmol), KOH (14.0 mg, 0.250 mmol), and benzyl alcohol (2a; 135.2 mg, 1.25 mmol) were added into benzene (1.5 mL) in a Teflon screw-capped tube, degassed for three freeze–pump–thaw cycles, refilled with  $N_2$ , and heated at 150 °C for 2 h. The desired Ir(ttp)Bn (3a; 10.5 mg, 0.011 mmol) was obtained in 88% yield.

Reaction of Ir(ttp)Cl(CO) and Benzyl Alcohol with KOH (5 equiv) at 150 °C. Ir(ttp)Cl(CO) (1a; 11.6 mg, 0.0125 mmol), KOH (3.5 mg, 0.0625 mmol), and benzyl alcohol (2a; 135.2 mg, 1.25 mmol) were added into benzene (1.5 mL) in a Teflon screw-capped tube, degassed for three freeze–pump–thaw cycles, refilled with  $N_2$ , and heated at 150 °C for 2 h. The desired Ir(ttp)Bn (3a; 9.5 mg, 0.010 mmol) was obtained in 80% yield.

**Reaction of Ir(ttp)Cl(CO) and Benzyl Alcohol (50 equiv) at 150** °C. Ir(ttp)Cl(CO) (1a; 11.6 mg, 0.0125 mmol), KOH (7.0 mg, 0.125 mmol), and benzyl alcohol (**2a**; 67.6 mg, 0.625 mmol) were added into benzene (1.5 mL) in a Teflon screw-capped tube, degassed for three freeze–pump–thaw cycles, refilled with N<sub>2</sub>, and heated at 150 °C for 2 h. After the excess benzyl alcohol and benzene were removed by vacuum distillation, the solid mixture was then extracted with  $CH_2Cl_2$  and filtered through a short pipet column chromatograph on silica gel with  $CH_2Cl_2$  to give the red crude product. The crude product was further purified by a precoated silica gel TLC plate with  $CH_2Cl_2$ /hexane (1/1) to give Ir(ttp)Bn (**3a**; 10.6 mg, 0.0111 mmol) in 89% yield.

**Reaction of Ir(ttp)Cl(CO) and Benzyl Alcohol (30 equiv) at 150** °C. Ir(ttp)Cl(CO) (1a; 11.6 mg, 0.0125 mmol), KOH (7.0 mg, 0.125 mmol), and benzyl alcohol (2a; 41.0 mg, 0.375 mmol) were added into benzene (1.5 mL) in a Teflon screw-capped tube, degassed for three freeze-pump-thaw cycles, refilled with N<sub>2</sub>, and heated at  $150\ ^{\circ}\mathrm{C}$  for 2 h. The desired Ir(ttp)Bn (3a; 10.5 mg, 0.011 mmol) was obtained in 88% yield.

**Reaction of Ir(ttp)Cl(CO) and Benzyl Alcohol (10 equiv) at 150** °C. Ir(ttp)Cl(CO) (1a; 11.6 mg, 0.0125 mmol), KOH (7.0 mg, 0.125 mmol), and benzyl alcohol (2a; 13.5 mg, 0.125 mmol) were added into benzene (1.5 mL) in a Teflon screw-capped tube, degassed for three freeze–pump–thaw cycles, refilled with  $N_2$ , and heated at 150 °C for 5 h. The desired Ir(ttp)Bn (3a; 9.6 mg, 0.010 mmol) was obtained in 88% yield.

**Reaction of Ir(ttp)Cl(CO) and 4-***tert***-Butylbenzyl Alcohol.** Ir(ttp)Cl(CO) (**1a**; 11.6 mg, 0.0125 mmol), KOH (7.0 mg, 0.125 mmol), and 4-*tert*-butylbenzyl alcohol (**2b**; 61.6 mg, 0.375 mmol) were added into benzene (1.5 mL) in a Teflon screw-capped tube, degassed for three freeze–pump–thaw cycles, refilled with N<sub>2</sub>, and heated at 150 °C for 2 h. After the excess alcohol and benzene were removed by vacuum distillation, the solid mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> and filtered through a short pipet column chromatograph on silica gel with CH<sub>2</sub>Cl<sub>2</sub> to give the red crude product. The crude product was further purified by a precoated silica gel TLC plate with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1/1) to give Ir(ttp)(4-*t*-Bu)Bn<sup>5</sup> (**3b**; 11.6 mg, 0.0115 mmol) in 92% yield. <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  –3.99 (s, 2 H), 1.02 (s, 9 H), 2.72 (s, 12 H), 3.18 (d, 2 H, *J* = 8.1 Hz), 5.97 (d, 2 H, *J* = 8.1 Hz), 7.55 (t, 8 H, *J* = 6.7 Hz), 8.03 (t, 8 H, *J* = 6.9 Hz), 8.47 (s, 8 H).

**Reaction of Ir(ttp)Cl(CO) and 4-Methylbenzyl Alcohol.** Ir(ttp)Cl(CO) (**1a**; 11.6 mg, 0.0125 mmol), KOH (7.0 mg, 0.125 mmol), and 4-methylbenzyl alcohol (**2c**; 45.8 mg, 0.375 mmol) were added into benzene (1.5 mL) in a Teflon screw-capped tube, degassed for three freeze–pump–thaw cycles, refilled with N<sub>2</sub>, and heated at 150 °C for 2 h. After the benzene were removed by vacuum distillation, the solid mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> and filtered through a short pipet column chromatograph on silica gel with CH<sub>2</sub>Cl<sub>2</sub> to give the red crude product. The crude product was further purified by a precoated silica gel TLC plate with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1/1) to give Ir(ttp)(4-Me)Bn<sup>5</sup> (**3c**; 10.5 mg, 0.0109 mmol) in 87% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  –4.00 (s, 2 H), 1.71 (s, 3 H), 2.71 (s, 12 H), 3.11 (d, 2 H, *J* = 7.9 Hz), 5.72 (d, 2 H, *J* = 7.8 Hz), 7.55 (t, 8 H, *J* = 6.2 Hz),7.95 (d, 4 H, *J* = 6.3 Hz), 8.05 (d, 4 H, *J* = 7.3 Hz), 8.48 (s, 8 H).

**Reaction of Ir(ttp)Cl(CO) and 4-Methoxylbenzyl Alcohol.** Ir(ttp)Cl(CO) (**1a**; 11.6 mg, 0.0125 mmol), KOH (7.0 mg, 0.125 mmol), and 4-methoxylbenzyl alcohol (**2d**; 51.8 mg, 0.375 mmol) were added into benzene (1.5 mL) in a Teflon screw-capped tube, degassed for three freeze–pump–thaw cycles, refilled with N<sub>2</sub>, and heated at 150 °C for 2 h. After the excess alcohol and benzene were removed by vacuum distillation, the solid mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> and filtered through a short pipet column chromatograph on silica gel with CH<sub>2</sub>Cl<sub>2</sub> to give the red crude product. The crude product was further purified by a precoated silica gel TLC plate with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1/1) to give Ir(ttp)(4-OMe)Bn<sup>11</sup> (**3d**; 10.3 mg, 0.0105 mmol) in 84% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  –4.04 (s, 2 H), 2.71 (s, 12 H), 3.14 (d, 2 H, *J* = 8.6 Hz), 3.46 (s, 3 H), 5.47 (d, 2 H, *J* = 8.5 Hz), 7.55 (d, 8 H, *J* = 7.4 Hz),7.97 (dd, 4 H, *J* = 7.8, 2.2 Hz), 8.04 (dd, 4 H, *J* = 7.8, 2.2 Hz), 8.48 (s, 8 H).

**Reaction of Ir(ttp)Cl(CO) and 4-Trifluoromethylbenzyl Alcohol.** Ir(ttp)Cl(CO) (1a; 11.6 mg, 0.0125 mmol), KOH (7.0 mg, 0.125 mmol), and 4-trifluoromethylbenzyl alcohol (2e; 66.1 mg, 0.375 mmol) were added into benzene (1.5 mL) in a Teflon screw-capped tube, degassed for three freeze–pump–thaw cycles, refilled with N<sub>2</sub>, and heated at 150 °C for 2 h. After the excess alcohol and benzene were removed by vacuum distillation, the solid mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> and filtered through a short pipet column chromatograph on silica gel with CH<sub>2</sub>Cl<sub>2</sub> to give the red crude product. The crude product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/MeOH to give Ir(ttp)(4-CF<sub>3</sub>)Bn<sup>11</sup> (3e; 11.0 mg, 0.0108 mmol) in 86% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  –3.91 (s, 2 H), 2.72 (s, 12 H), 3.18 (d, 2 H, *J* = 7.9 Hz), 6.14 (d, 2 H, *J* = 8.0 Hz), 7.55 (d, 8 H, *J* = 6.8 Hz), 7.94 (d, 4 H, *J* = 7.4 Hz), 8.03 (d, 4 H, *J* = 7.2 Hz), 8.51 (s, 8 H). **Reaction of Ir(ttp)Cl(CO) and Methanol.** Ir(ttp)Cl(CO) (1a; 11.6 mg, 0.0125 mmol), KOH (7.0 mg, 0.125 mmol), and methanol (**2f**; 40.1 mg, 1.25 mmol) were added into benzonitrile (1.5 mL) in a Teflon screw-capped tube, degassed for three freeze–pump–thaw cycles, refilled with N<sub>2</sub>, and heated at 150 °C for 2 h. After the excess alcohol and benzonitrile were removed by vacuum distillation, the solid mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> and filtered through a short pipet column chromatograph on silica gel with CH<sub>2</sub>Cl<sub>2</sub> to give the red crude product. The crude product was further purified by a precoated silica gel TLC plate with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1/1) to give Ir(ttp)Me<sup>6</sup> (**3f**; 9.6 mg, 0.0110 mmol) in 88% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  –6.28 (s, 3 H), 2.70 (s, 12 H), 7.54 (d, 8 H, *J* = 7.8 Hz), 8.05–8.00 (m, 8 H), 8.54 (s, 8 H).

**Reaction of Ir(ttp)Cl(CO) and Ethanol.** Ir(ttp)Cl(CO) (1a; 11.6 mg, 0.0125 mmol), KOH (7.0 mg, 0.125 mmol), and ethanol (**2g**; 57.5 mg, 1.25 mmol) were added into benzonitrile (1.5 mL) in a Teflon screw-capped tube, degassed for three freeze–pump–thaw cycles, refilled with N<sub>2</sub>, and heated at 150 °C for 24 h. After the excess alcohol and benzonitrile were removed by vacuum distillation, the solid mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> and filtered through a short pipet column chromatograph on silica gel with CH<sub>2</sub>Cl<sub>2</sub> to give the red crude product. The crude product was further purified by a precoated silica gel TLC plate with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1/1) to give Ir(ttp)Et<sup>13</sup> (**3g**; 9.2 mg, 0.0103 mmol) in 83% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  – 5.49 (s, 2 H), –4.58 (t, 3 H, *J* = 8.4 Hz), 2.70 (s, 12 H), 7.53 (t, 8 H, *J* = 6.4 Hz),7.99 (d, 4 H, *J* = 7.5 Hz), 8.05 (d, 4 H, *J* = 7.2 Hz), 8.52 (s, 8 H).

**Reaction of Ir(ttp)Cl(CO) and** *n*-**Propanol.** Ir(ttp)Cl(CO) (1a; 11.6 mg, 0.0125 mmol), KOH (7.0 mg, 0.125 mmol), and *n*-propanol (**2h**; 75.1 mg, 1.25 mmol) were added into benzonitrile (1.5 mL) in a Teflon screw-capped tube, degassed for three freeze–pump–thaw cycles, refilled with N<sub>2</sub>, and heated at 150 °C for 24 h. After the excess alcohol and benzonitrile were removed by vacuum distillation, the solid mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> and filtered through a short pipet column chromatograph on silica gel with CH<sub>2</sub>Cl<sub>2</sub> to give the red crude product. The crude product was further purified by a precoated silica gel TLC plate with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1/1) to give Ir(ttp)(*n*-Pr)<sup>13</sup> (**3h**; 8.9 mg, 0.0098 mmol) in 79% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  –5.56 (*s*, 2 H), –4.36 (sext, 2 H, *J* = 7.6 Hz), –1.65 (t, 3 H, *J* = 7.3 Hz), 2.70 (*s*, 12 H), 7.53 (t, 8 H, *J* = 7.6 Hz), 8.02 (dd, 8 H, *J* = 13.8, 6.8 Hz), 8.52 (*s*, 8 H).

**Reaction of Ir(ttp)Cl(CO) and** *n***-Butanol. Ir(ttp)Cl(CO) (1a; 11.6 mg, 0.0125 mmol), KOH (7.0 mg, 0.125 mmol), and** *n***-butanol (<b>2i**; 92.7 mg, 1.25 mmol) were added into benzonitrile (1.5 mL) in a Teflon screw-capped tube, degassed for three freeze–pump–thaw cycles, refilled with N<sub>2</sub>, and heated at 150 °C for 24 h. After the excess alcohol and benzonitrile were removed by vacuum distillation, the solid mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> and filtered through a short pipet column chromatograph on silica gel with CH<sub>2</sub>Cl<sub>2</sub> to give the red crude product. The crude product was further purified by a precoated silica gel TLC plate with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1/1) to give Ir(ttp)(*n*-Bu)<sup>6</sup> (**3i**; 8.4 mg, 0.0091 mmol) in 73% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  –5.52 (t, 2 H, *J* = 8.1 Hz), –4.44 (quint, 2 H, *J* = 7.9 Hz), –1.48 (sext, 2 H, *J* = 7.5 Hz), –0.75 (t, 3 H, *J* = 7.4 Hz), 8.05 (d, 4 H, *J* = 7.4 Hz), 8.51 (s, 8 H).

**Reaction of Ir(ttp)Cl(CO) and 1-Pentanol.** Ir(ttp)Cl(CO) (1a; 11.6 mg, 0.0125 mmol), KOH (7.0 mg, 0.125 mmol), and 1-pentanol (**2***j*; 110.0 mg, 1.25 mmol) were added into benzonitrile (1.5 mL) in a Teflon screw-capped tube, degassed for three freeze–pump–thaw cycles, refilled with N<sub>2</sub>, and heated at 150 °C for 24 h. After the excess alcohol and benzonitrile were removed by vacuum distillation, the solid mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> and filtered through a short pipet column chromatograph on silica gel with CH<sub>2</sub>Cl<sub>2</sub> to give the red crude product. The crude product was further purified by a precoated silica gel TLC plate with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1/1) to give Ir(ttp)(*n*-pentyl)<sup>o</sup> (**3***j*; 8.3 mg, 0.0089 mmol) in 71% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  –5.54 (t, 2 H, *J* = 8.4 Hz), –4.44 (quint, 2 H, *J* = 7.6 Hz), –1.52 (quint, 2 H, *J* = 7.5 Hz), –0.42 (sext, 2 H, *J* = 7.4 Hz), –0.19 (t, 3 H, *J* = 7.3 Hz), 2.70 (s, 12 H), 7.53 (t, 8 H, *J* = 6.4

Hz), 7.98 (d, 4 H, J = 7.3 Hz), 8.05 (d, 4 H, J = 7.2 Hz), 8.51 (s, 8 H).

Reaction of Ir(ttp)Cl(CO) and *n*-Octanol. Ir(ttp)Cl(CO) (1a; 11.6 mg, 0.0125 mmol), KOH (7.0 mg, 0.125 mmol) and n-octanol (2k; 162.8 mg, 1.25 mmol) were added into benzonitrile (1.5 mL) in a Teflon screw-capped tube, degassed for three freeze-pump-thaw cycles, refilled with N2, and heated at 150 °C for 24 h. After the excess alcohol and benzonitrile were removed by vacuum distillation, the solid mixture was then extracted with  $\text{CH}_2\text{Cl}_2$  and filtered through a short pipet column chromatograph on silica gel with CH2Cl2 to give the red crude product. The crude product was further purified by a precoated silica gel TLC plate with  $CH_2Cl_2$ /hexane (1/1) to give  $Ir(ttp)(n-octyl)^{6}$  (3k; 8.5 mg, 0.0087 mmol) in 70% yield. <sup>1</sup>H NMR  $(CDCl_3, 400 \text{ MHz}): \delta -5.54 \text{ (t, 2 H, } J = 8.4 \text{ Hz}), -4.44 \text{ (quint, 2 H, } J$ = 7.8 Hz), -1.51 (quint, 2 H, J = 7.5 Hz), -0.46 (quint, 2 H, J = 7.6 Hz), 0.10 (quint, 2 H, J = 7.6 Hz), 0.55 (quint, 2 H, J = 7.6 Hz), 0.63 (t, 3 H, I = 7.2 Hz), 0.87 (sext, 2 H, I = 7.8 Hz), 2.70 (s, 12 H), 7.53(t, 8 H, J = 6.9 Hz), 7.98 (d, 4 H, J = 7.6 Hz), 8.05 (d, 4 H, J = 7.6 Hz), 8.51 (s, 8 H).

Reaction of lr(ttp)Cl(CO) and 5-Hexen-1-ol. Ir(ttp)Cl(CO) (1a; 11.6 mg, 0.0125 mmol), KOH (7.0 mg, 0.125 mmol), and 5hexen-1-ol (21; 125.2 mg, 1.25 mmol) were added into benzonitrile (1.5 mL) in a Teflon screw-capped tube, degassed for three freezepump-thaw cycles, refilled with N<sub>2</sub>, and heated at 150 °C for 24 h. After the excess alcohol and benzonitrile were removed by vacuum distillation, the solid mixture was then extracted with CH2Cl2 and filtered through a short pipet column chromatograph on silica gel with CH<sub>2</sub>Cl<sub>2</sub> to give the red crude product. The crude product was further purified by a precoated silica gel TLC plate with  $\hat{CH}_2Cl_2$ /hexane (1/ 1) to give Ir(ttp)(5-hexenyl)<sup>6</sup> (31; 7.5 mg, 0.0081 mmol) in 64% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  -5.53 (t, 2 H, J = 8.2 Hz), -4.41 (quint, 2 H, J = 7.5 Hz), -1.41 (quint, 2 H, J = 7.3 Hz), 0.31 (q, 2 H, J = 7.1 Hz), 2.70 (s, 12 H), 4.10 (d, 1 H, J = 15.9 Hz), 4.37 (d, 1 H, J = 10.1 Hz), 4.64-4.74 (m, 1H), 7.53 (d, 8 H, J = 6.2Hz),7.99 (d, 4 H, J = 7.3 Hz), 8.05 (d, 4 H, J = 7.2 Hz), 8.52 (s, 8 H).

**Reaction of lr(ttp)H and Benzyl Alcohol without KOH.** Ir(ttp)H (1b; 10.8 mg, 0.0125 mmol) and benzyl alcohol (2a; 41.0 mg, 0.375 mmol) were added into benzene- $d_6$  ( $C_6D_6$ ) (1.5 mL) in a Teflon screw-capped tube, degassed for three freeze-pump-thaw cycles, refilled with N<sub>2</sub>, and heated at 150 °C for 24 h. No desired Ir(ttp)Bn was formed, as determined by TLC and <sup>1</sup>H NMR.

**Reaction of Ir(ttp)H and Benzyl Alcohol with KOH.** Ir(ttp)H (**1b**; 10.8 mg, 0.0125 mmol), KOH (7.0 mg, 0.125 mmol), and benzyl alcohol (**2a**; 41.0 mg, 0.375 mmol) were added into benzene- $d_6$  ( $C_6D_6$ ) (1.5 mL) in a Teflon screw-capped tube, degassed for three freeze-pump-thaw cycles, refilled with N<sub>2</sub>, and heated at 150 °C for 2 h. After the excess benzyl alcohol and  $C_6D_6$  were removed by vacuum distillation, the solid mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> and filtered through a short pipet column chromatograph on silica gel with CH<sub>2</sub>Cl<sub>2</sub> to give the red crude product. The crude product was further purified by a precoated silica gel TLC plate with CH<sub>2</sub>Cl<sub>2</sub>/ hexane (1/1) to give Ir(ttp)Bn (**3a**; 9.3 mg, 0.0098 mmol) in 78% yield.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00100.

Competition reactions, <sup>1</sup>H NMR spectra, and substrate scope (PDF)

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#### Notes

The authors declare no competing financial interest.

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