# ORGANOMETALLICS

# Base-Promoted Selective Aryl Carbon–Bromine Bond Cleavage by Iridium(III) Porphyrin for Iridium(III) Porphyrin Aryl Synthesis: A Metalloradical Ipso Addition-Elimination Mechanism

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Supporting Information

ABSTRACT: K<sub>2</sub>CO<sub>3</sub> was found to promote selective aryl carbon-bromine bond (Ar-Br) cleavage by a high-valent iridium(III) porphyrin carbonyl chloride  $(Ir^{III}(ttp)(CO)Cl, ttp = 5,10,15,20$ -tetra-*p*-tolylporphyrinato dianion) in benzene ttp = 5,10,15,20-tetrakis(*p*-tolyl)porphyrinato dianion solvent at elevated temperature to give iridium(III) porphyrin aryls (Ir<sup>III</sup>(ttp)Ar) in

 $Ir^{III}(ttp)(CO)CI \xrightarrow{OH^-}_{-1/2''H_2O_2''} Ir^{II}(ttp) \cdot \xrightarrow{Ar-Br}_{-Br^{\bullet}} Ir^{III}(ttp)Ar$ 

high yields. Ir(ttp)(CO)Cl is reduced in alkaline media to give an [Ir(ttp)]<sub>2</sub> intermediate. [Ir(ttp)]<sub>2</sub> then cleaves the Ar-Br bond via a radical-type addition-elimination reaction (radical ipso -substitution) to yield Ir(ttp)Ar and a bromine radical.

roup 9 metal(II) complexes are metalloradicals which have Gbeen widely studied in organometallic chemistry.<sup>1</sup> A wellknown example of group 9 metal(II) complexes is the metalloporphyrin radical ( $M^{II}(por)$ , M = Co, Rh, Ir).  $M^{II}(por)$  exhibits unique chemical reactivity in the bond activation of small molecules, such as olefins,<sup>2</sup> carbon monoxide,<sup>2b</sup>  $H_{2,3}$  C(sp<sup>3</sup>)-H,  $^{3a,4}$  C(sp<sup>3</sup>)-Br,  $^{5}$  and C(sp<sup>3</sup>)-C(sp<sup>3</sup>)<sup>6</sup> bonds. They have also been utilized as catalysts in various chemical transformations, including the polymerization,<sup>7</sup> cyclopropanation,<sup>8</sup> and aziridination of olefins,<sup>9</sup> as well as C-H amination.<sup>10</sup>

However, the cleavage of aryl-halogen bonds (Ar-X) by group 9 metalloporphyrin radicals is still unprecedented. To our knowledge, the only reported Ar-X cleavages mediated by group 9 metalloradicals are the reaction of 2-iodopyridine with metalloradicals are the reaction of 2-lodopyndine with pentacyanocobaltate(II) ( $[Co^{II}(CN)_5]^{3-}$ ) to give  $[Co^{III}(CN)_5I]^{3-}$ and  $[Co^{III}(CN)_5(2-pyridyl)]^{3-11}$  and the reaction of Ar–X (X = Cl, Br, I) with (L)Co<sup>0</sup> (L = 2,6-bis[2,6-dimethylpheny-liminoethyl]pyridine) to give (L)Co<sup>I</sup>–X and (L)Co<sup>I</sup>–Ar,<sup>12</sup> via halogen atom abstraction by Co radicals. While Ar–X cleavage via oxidative addition of Co(I),<sup>13</sup> Rh(I),<sup>14</sup> and Ir(I)<sup>15</sup> to M<sup>III</sup>-(Ar)(X) has been commonly reported, Ar-X cleavage with group 9 metalloradicals remains underdeveloped.

As part of our continuing interest in bond cleavage chemistry by high-valent iridium(III) porphyrins,<sup>4d,16</sup> we sought to investigate the aryl-bromine bond (Ar-Br) cleavage by Ir<sup>III</sup>(ttp)-(CO)Cl (1a; ttp = tetra-*p*-tolylporphyrinato dianion). We found that ArBr reacted with Ir(ttp)(CO)Cl in the presence of base to give ipso-substituted iridium(III) porphyrin aryls (Ir<sup>III</sup>(ttp)Ar). The reaction is apparently intriguing, as a direct metathesis process would give an energetically uphill BrCl coproduct. Mechanistically, the formation of any Ir(V) porphyrin intermediate is difficult in electronics and sterically demanding, with three non-porphyrin ligands located in a cis position. In exploring this bond activation, we discovered that base can reduce Ir(ttp)-(CO)Cl to a metalloradical dimer intermediate,  $[Ir^{II}(ttp)]_2$  (step i in Scheme 1), which then undergoes an unprecedented radicalScheme 1. Discovery of This Work

$$Ir^{III}(ttp)(CO)CI \xrightarrow[K_2CO_3, KOH)]{I/2[Ir^{II}(ttp)]_2} \xrightarrow[II]{Ar-Br} Ir^{III}(ttp)Ar + Br$$

type ipso substitution with Ar-Br<sup>17</sup> via an addition-elimination reaction to give Ir<sup>III</sup>(ttp)Ar (step ii in Scheme 1). We now report the results and mechanistic studies of the Ar-Br cleavage.

**Results and Discussion.** Ir(ttp)(CO)Cl(1a) initially reacted very slowly with PhBr (1.1 equiv) in benzene solvent at 200 °C in 7 days to give Ir(ttp)Ph (2e) in only 9% yield. Upon the addition of  $K_2CO_3$  (20 equiv), the reaction was complete in 2 days to yield 2e quantitatively (Table 1, eq 1, entry 5). 2e was formed from Ph-Br cleavage rather than the C-H activation of benzene, since 1a reacted with PhBr (1.1 equiv) and  $K_2CO_3$  (20 equiv) in benzene- $d_6$  at 200 °C in 10 days to give **2e** quantitatively without any  $Ir(ttp)C_6D_5$ . This base-promoted reaction is general for various ArBr species to give high yields of Ir(ttp)Ar bearing different functional groups (Table 1). 4,4'-Dibromobiphenyl also reacted with 1a and K<sub>2</sub>CO<sub>3</sub> sequentially to give  $Ir(ttp)(p-C_6H_4)_2(p-Br)(2q)$  and then  $Ir(ttp)(p-C_6H_4)_2(p-Br)(2q)$  $C_6H_4)_2Ir(ttp)$  (3) (Scheme 2). The new convenient synthesis of iridium(III) porphyrin aryls eliminates the use of Grignard<sup>19</sup> or organolithium<sup>20</sup> reagents required in the traditional synthesis.

In order to understand the reaction mechanism, the reaction of 1a with PhBr (1.1 equiv) and the stronger base  $Cs_2CO_3$  (20 equiv) in benzene- $d_6$  at a lower temperature of 150 °C was monitored by <sup>1</sup>H NMR spectroscopy to observe any intermediates formed (eq 2; Table S1 in the Supporting Information).<sup>21</sup> After 3 h, 2e in 30% yield was formed together with intermediates  $Ir^{III}(ttp)H$  (4) and  $[Ir^{II}(ttp)]_2$  (5) in 13% and 1% yields, respectively (eq 2a). After 60 h, 1a, 4, and 5 were completely consumed to yield 2e quantitatively (eq 2b). The base has promoted the reduction of 1a to 4 and 5.

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Table 1. Substrate Scope of Ar-Br Cleavage

$\frac{Ir(ttp)(CO)CI + Br}{1a} + \frac{1}{1.1 \text{ equiv}} + \frac{1}{C_6H_6, 200 \text{ °C}, \text{ time}, N_2} + Ir(ttp) + \frac{1}{2} r^3 (1)$							
entry <sup>a</sup>	FG	time/h	product (yield/%) <sup>b</sup>	entry <sup>a</sup>	FG	time/h	product $(yield/\%)^b$
1	p-OMe	9	<b>2a</b> (89)	9	p-Cl	24	<b>2i</b> (72)
2	p- <sup>t</sup> Bu	15	<b>2b</b> (86)	10	<i>p</i> -CO <sub>2</sub> Me	36	<b>2</b> j (84)
3	p-Me	11	<b>2c</b> (73)	11	p-C(O)Me	19	<b>2</b> k (82)
4	p-SiMe <sub>3</sub>	15	<b>2d</b> (80)	12	p-CF <sub>3</sub>	24	<b>2l</b> (72)
5	<i>р-</i> Н	48	<b>2e</b> (100)	13	p-NO <sub>2</sub>	6	<b>2m</b> (63)
6	p-NPhth <sup>c</sup>	27	<b>2f</b> (68)	14	<i>m</i> -OMe	17	<b>2n</b> (83)
7	<i>p</i> -F	20	<b>2</b> g (99)	15	<i>m</i> -Me	14	<b>2o</b> (85)
8	p-Br	36	<b>2h</b> (76)	16	<i>m</i> -NO <sub>2</sub>	16	<b>2p</b> (84)

<sup>*a*</sup> The intermediate Ir(ttp)(CO)Br(1b) was observed in the course of the reaction and was completely consumed to yield Ir(ttp)Ar upon prolonged heating. <sup>*b*</sup> Isolated yield. <sup>*c*</sup> NPhth = phthalimide.

Scheme 2. Synthesis of  $Ir(ttp)(p-C_6H_4)_2Ir(ttp)$ 

$1a \frac{Br}{(10 \text{ equiv})} Br}{K_2CO_3 (20 \text{ equiv})} Ir(ttp)}$	- <b>√ →</b> -Br <b>2q</b> 73%	
	1a (1.1 equiv)           K <sub>2</sub> CO <sub>3</sub> (20 equiv)           C <sub>6</sub> H <sub>6</sub> , 200 °C, 36 h, N <sub>2</sub>	<mark>}∕−</mark> lr(ttp) 3 75%

lr(ttp)(CO)Cl	+ PhBr - C	s <sub>2</sub> CO <sub>3</sub> (20 equiv	$\frac{1}{1}$ lr(ttn)Ph +	lr(ttn)H +	[lr(ttp)]	(2)
1a	1.1 equiv	C <sub>6</sub> D <sub>6</sub> , 150 °C	2e	<b>4</b>	<b>5</b>	(~)
		(a) 3 h	30%	13%	1%	
		(b) 60 h	100%			

Ir<sup>II</sup> for Ar-Br Cleavage. In the base-promoted Ar-Br cleavage, Ir(ttp)H and  $[Ir(ttp)]_2$  were the observed intermediates (eq 2a). Ir(ttp)H rapidly underwent dehydrogenative dimerization in benzene to give  $[Ir(ttp)]_2$  both on heating and as promoted by  $K_2CO_3$ , as shown by independent experiments (eqs 3a and 3b).<sup>4d,22</sup> Ir(ttp)<sup>-</sup> (6), although it is not observed, could also be produced in a low concentration in benzene via the deprotonation of Ir(ttp)H with base, as Ir(ttp)H is acidic enough.<sup>16b</sup> Thus,  $Ir(ttp)H_{2}$  [Ir(ttp)]<sub>2</sub>, and Ir(ttp)<sup>-</sup> can coexist in equilibria in benzene.<sup>16b</sup> Their relative reactivities with ArBr (1.1 equiv) were thus compared independently at 200 °C in benzene-d<sub>6</sub> to establish the intermediate for Ar-Br cleavage (Table S4 in the Supporting Information). In Ph-Br cleavage, the relative reaction rates of  $[Ir(ttp)]_2$ , Ir(ttp)H, and  $Ir(ttp)^{-}$  were estimated to be about 10 000:20:1, by comparing the time required for complete consumption of iridium porphyrin species. Such a reactivity trend was also observed in the reactions with both electron-rich  $(p-MeO)C_6H_4Br$  and electron-poor  $(p-NO_2)C_6H_4Br$ . Additionally,  $Ir(ttp)^{-}K^{+}$  was nonproductive in the Ar-Br cleavage of  $(p-MeO)C_6H_4Br$  but rather reacted to give  $Ir(ttp)CH_3$ , probably via nucleophilic substitution of Me-OC<sub>6</sub>H<sub>4</sub>(p-Br).<sup>23</sup> Thus, [Ir(ttp)]<sub>2</sub> is the most probable intermediate for Ar-Br cleavage to give Ir(ttp)Ar and  $Ir(ttp)Br^{24}$  (Table 2, entries 3, 6, and 9).

lr/ttm\⊔		Inreacted Ir(ttp)H	+ [lr(ttp)]	(2)
n(up)⊓ ⊿	200 °C, 2 min	<b>1</b>	5 [II((Lp)]]2	(3)
-	(a) no base	81%	19%	
(b)	K <sub>2</sub> CO <sub>3</sub> (20 equiv	v) 40%	55%	

Mechanism of Ir(ttp)(CO)CI Reduction. We propose two possible mechanisms for base-promoted Ar-Br cleavage by Ir(ttp)(CO)Cl (1a) to give Ir(ttp)Ar (Scheme 3).

*Mechanism 1.*  $OH^-$ , which can be generated from the thermal hydrolysis of  $K_2CO_3^{25}$  with residual  $H_2O^{26}$  in benzene at 200 °C (eqs  $i_a$  and  $i_b$ ), undergoes nucleophilic attack to the CO ligand of **1a** to give Ir(ttp)CO<sub>2</sub>H and Cl<sup>-</sup> (eq ii). Ir(ttp)CO<sub>2</sub>H then decarboxylates to give Ir(ttp)H and CO<sub>2</sub> (eq iii),<sup>27,28</sup> in line with the known transition-metal-mediated water-gas shift reaction.<sup>27–29</sup>

Ir(ttp)H further undergoes dehydrogenative dimerization via an equilibrium to give  $[Ir(ttp)]_2$  (eq iv).  $[Ir(ttp)]_2$  finally reacts with ArBr to give Ir(ttp)Ar and Ir(ttp)Br (eq v).

*Mechanism 2.* 1a undergoes CO dissociation to give Ir(ttp)Cl (eq vi), which further reacts with OH<sup>-</sup> to give the proposed Ir(ttp)OH via ligand substitution (eq vii).<sup>30</sup> Ir(ttp)OH then gives [Ir(ttp)]<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> via the reduction of the Ir<sup>III</sup> center by the hydroxo ligand (eq viii),<sup>16c,31</sup> since the one-electron reduction of first-row transition-metal porphyrins by OH<sup>-</sup> in aprotic solvents has been reported.<sup>32</sup> The H<sub>2</sub>O<sub>2</sub> formed rapidly disproportionates into H<sub>2</sub>O and O<sub>2</sub>, catalyzed by OH<sup>-</sup> (eq ix).<sup>33</sup> In a low concentration or the absence of ArBr, [Ir(ttp)]<sub>2</sub> can react competitively with residual water in benzene to give Ir(ttp)OH and the observed Ir(ttp)H (eq x).<sup>16c,34</sup> In a productive process, [Ir(ttp)]<sub>2</sub> reacts with ArBr to give Ir(ttp)Ar and Ir(ttp)Br (eq xi). Ir(ttp)Br, once formed, can further react with CO dissociated from **1a** to form Ir(ttp)(CO)Br (**1b**) (eq xii). Both Ir(ttp)Br and Ir(ttp)(CO)Br continue to undergo base-promoted Ar–Br cleavage to give Ir(ttp)Ar (eqs vi–viii and xi).

Mechanism 1 is unlikely to operate. Since OH<sup>-</sup> reduces 1a to Ir(ttp)H via the consumption of CO to give CO<sub>2</sub> (eqs ii and iii in Scheme 3), subsequent reaction of  $[Ir(ttp)]_2$  with ArBr would only give both Ir(ttp)Ar and Ir(ttp)Br with each of them in a maximum yield of 50% (eq v in Scheme 3). However, no Ir(ttp)Br ( $\delta$ (pyrrole H) ~8.9 ppm)<sup>24</sup> was observed in the crude reaction mixtures of the base-promoted Ar–Br cleavage by 1a by <sup>1</sup>H NMR spectroscopy, and the isolated yields of Ir(ttp)Ar are consistently much higher than 50% (Table 1).

Instead, mechanism 2 operates. The  $Ir(ttp)(CO)Br (1b)^{35}$ intermediate was formed in the base-promoted Ar-Br cleavage by 1a (Table 1), strongly supporting the CO dissociation pathway (eq vi in Scheme 3). 1b was completely consumed to yield Ir(ttp)Ar (Table 1), most likely because 1b is further reduced by OH<sup>-</sup> to yield  $[Ir(ttp)]_2$  for further Ar-Br cleavage (eqs vi-viii and xi in Scheme 3). Further studies are ongoing to gain the understanding of the reduction of 1a and 1b by OH<sup>-</sup>.

#### Mechanism (1)

$K_2CO_3 + H_2O \longrightarrow KHCO_3 + KOH$	(i <sub>a</sub> )
$K_2CO_3 + H_2O \longrightarrow 2KOH + CO_2$	(i <sub>b</sub> )
$Ir(ttp)(CO)CI + OH \rightarrow Ir(ttp)CO_2H + CI$	(ii)
$Ir(ttp)CO_2H \longrightarrow Ir(ttp)H + CO_2$	(iii)
2 lr(ttp) H  [ $lr(ttp)$ ] <sub>2</sub> + H <sub>2</sub>	(iv)
$[Ir(ttp)]_2 + ArBr \longrightarrow Ir(ttp)Ar + Ir(ttp)Br$	(v)
2Ir(ttp)(CO)CI + ArBr + 2OH <sup>-</sup> → Ir(ttp)Ar + Ir(ttp)Br + H <sub>2</sub>	2 + 2CO <sub>2</sub> + 2Cl <sup>-</sup>
Mechanism (2)	
$lr(ttp)(CO)X \longrightarrow lr(ttp)X + CO$ X = CL Br	(vi)
$Ir(ttp)X + OH^- \rightarrow Ir(ttp)OH + X^-$ X = CI, Br	(vii)
$2 \text{Ir(ttp)OH} \longrightarrow [\text{Ir(ttp)}]_2 + \text{H}_2\text{O}_2$	(viii)
$H_2O_2 \xrightarrow{OH^-} H_2O + 1/2O_2$	(ix)
$[lr(ttp)]_2 + H_2O \longrightarrow lr(ttp)OH + lr(ttp)H$	(x)
$[Ir(ttp)]_2 + ArBr \longrightarrow Ir(ttp)Ar + Ir(ttp)Br$	(xi)
Ir(ttp)Br + CO Ir(ttp)(CO)Br	(xii)
2lr(ttp)(CO)Cl + ArBr + 2OH <sup>-</sup> → lr(ttp)Ar + lr(ttp)(CO)Br + C	O + H <sub>2</sub> O + 1/2O <sub>2</sub> + 2Cl <sup>-</sup>

*Ar*–*Br* Cleavage Mechanism. Ar–Br cleavage by  $[Ir(ttp)]_2$  likely goes through radical ipso substitution via the addition– elimination reaction (ISAE) (Scheme 4) rather than a direct bromine atom abstraction.<sup>36</sup> We propose that  $[Ir(ttp)]_2$  initially dissociates into an Ir(ttp) metalloradical (eq i).<sup>2b,3a</sup> Ir(ttp) then attacks the ipso carbon of ArBr to give an Ir(ttp)–cyclohexadienyl radical intermediate (I), which subsequently dissociates into Ir(ttp)Ar and a bromine atom (Br<sup>•</sup>) via radical ipso substitution (eq ii).<sup>17</sup> Br<sup>•</sup> further reacts with  $[Ir(ttp)]_2$  to form Ir(ttp)Br and another Ir(ttp) for chain propagation (eq iii). Thus, the Ar–Br cleavage operates in a radical-chain mechanism. Consequently, some Br<sup>•</sup> can leak out from the chain reaction and react with benzene solvent to give PhBr (eq iv).<sup>37</sup>

The ISAE of ArBr with  $[Ir(ttp)]_2$  (Scheme 4) can be supported by three lines of evidence.

- Higher ratio of Ir(ttp)Ar to Ir(ttp)Br. In the reactions of [Ir(ttp)]<sub>2</sub> with various (p-FG)C<sub>6</sub>H<sub>4</sub>Br (FG = H, OMe, NO<sub>2</sub>), the ratios of Ir(ttp)Ar to Ir(ttp)Br are consistently greater than 1 (Table S4 in the Supporting Information) due to the Br<sup>•</sup> leakage (eq ii in Scheme 4).
- (2) Detection of PhBr. [Ir(ttp)]<sub>2</sub> reacted with (p-<sup>t</sup>Bu)C<sub>6</sub>H<sub>5</sub>Br (1.1 equiv) in C<sub>6</sub>H<sub>6</sub> at 200 °C to give Ir(ttp)C<sub>6</sub>H<sub>4</sub>(p-<sup>t</sup>Bu) (47%), Ir(ttp)Br (~39%), and PhBr (1%),<sup>38</sup> as detected by GC-MS analysis (eq 4). The detection of PhBr firmly supports the ISAE of Ar-Br by Ir(ttp) to give Br<sup>•</sup> for PhBr formation (eqs ii and iv in Scheme 4).

$$\frac{1/2[Ir(ttp)]_{2} + (p^{-t}Bu)C_{6}H_{4}Br}{5} \frac{C_{6}H_{6}, N_{2}}{1.1 \text{ equiv}} \frac{1/2[Ir(ttp)C_{6}H_{4}(p^{-t}Bu) + Ir(ttp)Br + PhBr}{200 \text{ }^{\circ}C} (4)$$

(3) Rate enhancement by para substituents (p-FGs) in ArBr. Both the electron-rich and -poor para-substituted ArBr promoted the rate of base-promoted Ar-Br cleavage by 1a, as shown by the V-shaped Hammett plots (Table S5 and Figure S5 in the Supporting Information). Such a reactivity trend is attributed to the stabilization of the Ir(ttp)-cyclohexadienyl radical intermediate via resonance interactions with both the electron-donating COMMUNICATION

# Scheme 4. Radical Ipso Substitution of ArBr by $[Ir(ttp)]_2$





**Figure 1.** Stabilization of the Ir(ttp)-cyclohexadienyl intermediate by various substituents.

and -withdrawing *p*-FGs only, but not with the *m*-FGs (Figure 1; Table S6 and Schemes S3–S7 in the Supporting Information).<sup>39</sup> Indeed, such a reactivity pattern has also been observed in radical ipso substitution of Ar–Br with sulfur-centered radicals.<sup>17e</sup>

**Conclusion.** In summary, we have discovered base-promoted selective Ar–Br cleavage by high-valent Ir(ttp)(CO)Cl. Mechanistic studies suggest that OH<sup>-</sup> likely promotes the reduction of Ir(ttp)(CO)Cl to  $[Ir(ttp)]_2$ , which then cleaves the Ar–Br bond via radical ipso substitution to give Ir(ttp)Ar. Further mechanistic studies are ongoing.

# ASSOCIATED CONTENT

**Supporting Information.** Sequence of reactions monitored by <sup>1</sup>H NMR spectroscopy, supplementary experimental results, table and figure of crystallographic data for complex **3** (CIF and PDF), GC-MS analysis, and <sup>1</sup>H and <sup>13</sup>C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) No electrophilic aromatic substitution ( $S_EAr$ ) of benzene solvent by 1a occurs in basic media to yield 2e. We reasoned that 1a rapidly reacts with base to yield Ir(ttp)OH, which contains a poor leaving hydroxo ligand and thus is not Lewis acidic enough to undergo  $S_EAr$  of benzene. Furthermore, Ir(ttp)OH undergoes rapid reduction to  $[Ir^{II}(ttp)]_2$ , which is not reactive toward benzene.

(19) Rhodium porphyrin aryls (Rh(por)Ar) can be prepared by the reaction of Rh(por)Cl with a Grignard reagent (ArMgBr). See: Chan, K. S.; Chiu, P. F.; Choi, K. S. *Organometallics* **2007**, *26*, 1117–1119.

(20) Metalloporphyrin aryls (M(por)Ar, M = Co, Rh) can be prepared by the reaction of M(por)Cl with an aryllithium. See: (a) Ogoshi, H.; Setsune, J.; Omura, T.; Yoshida, Z. J. Am. Chem. Soc. 1975, 97, 6461–6466. (b) Callot, H. J.; Cromer, R.; Louati, A.; Metz, B.; Chevrier, B. J. Am. Chem. Soc. 1987, 109, 2946–2955.

(21) The original reaction conditions ( $K_2CO_3$ , 200 °C) have been adopted initially in sealed NMR tube experiments, but no intermediates were observed. Thus, the stronger base  $Cs_2CO_3$  at 150 °C was used to achieve the successful observation of reaction intermediates.

(22) Within 2 h,  $[Ir(ttp)]_2$  was formed and gradually converted back to Ir(ttp)H, presumably via the reaction of  $[Ir(ttp)]_2$  with  $H_2$  formed (see the Supporting Information for details of the proposed interconversion between Ir(ttp)H and  $[Ir(ttp)]_2/H_2$ ). The reaction of  $[Ir(oep)]_2$  (oep = octaethylporphyrinato dianion) with  $H_2$  to give Ir(oep)H has also been reported.<sup>3a</sup>

(23) Nucleophilic substitution ( $S_N$ 2) of CH<sub>3</sub>OH by Ir(ttp)<sup>-</sup> to give Ir(ttp)CH<sub>3</sub> and OH<sup>-</sup> has been reported.<sup>16b</sup> It is likely that  $S_N$ 2 of CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>(*p*-Br) by Ir(ttp)<sup>-</sup> to form Ir(ttp)CH<sub>3</sub> and the better arylate ion leaving group, ArO<sup>-</sup>, is even more favorable.

(24) Ir(ttp)Br ( $\delta$ (pyrrole) (C<sub>6</sub>D<sub>6</sub>) ~8.9 ppm) was observed by <sup>1</sup>H NMR spectroscopy (Figure S4 in the Supporting Information) but was too unstable to be purified by column chromatography. Its formation could only be confirmed by HRMS analysis. The variable chemical shifts of the broad pyrrole signals of Ir(ttp)Br are

presumably due to the proton exchange of the sixth coordinated water in  $Ir(ttp)(H_2O)Br$ .

(25) Thomas, A. M., Jr. J. Chem. Eng. Data 1963, 8, 51-54.

(26) A trace of residual water ( $\sim 0.2-2.0$  equiv with regard to iridium porphyrin,  $\delta(H_2O) \sim 0.4$  ppm) remained in benzene- $d_6$  even though benzene- $d_6$  had been distilled over sodium and stored in a Teflon-capped Schlenk tube under N<sub>2</sub>.

(27) The decarboxylation of Ir-CO<sub>2</sub>H to Ir-H and CO<sub>2</sub> has been proposed. See: Ziessel, R. J. Am. Chem. Soc. **1993**, 115, 118–127.

(28) For the reported decarboxylation of the analogous Rh(por)-CO<sub>2</sub>H to Rh(por)H and CO<sub>2</sub>, see: Wayland, B. B.; Woods, B. A.; Pierce, R. J. Am. Chem. Soc. **1982**, 104, 302–303.

(29) Esswein, A. J.; Nocera, D. G. Chem. Rev. 2007, 107, 4022-4047.

(30) **1a** reacts with NaOPh to yield Ir(ttp)OPh.<sup>4d</sup> It is proposed that **1a** can also react with OH<sup>-</sup> to yield Ir(ttp)OH.

(31) OH<sup>-</sup> is reported as an efficient one-electron-reducing agent in aprotic solvents. See: Sawyer, D. T.; Roberts, J. L., Jr. *Acc. Chem. Res.* **1988**, *21*, 469–476.

(32) First-row metalloporphyrins have been reported to be reduced by OH<sup>-</sup>. as follows. (i) Fe(III) to Fe(II): (a) Shin, K.; Kramer, S. K.; Goff, H. M. *Inorg. Chem.* 1987, 26, 4103–4106. (ii) Mn(III) to Mn(III): (b) Jeon, S.; Lee, H. K.; Choi., Y. K. *Bull. Kor. Chem. Soc.* 1996, 17, 929–934.

(33) Roberts, J. L., Jr.; Sugimoto, H.; Barrette, W. C., Jr.; Sawyer, D. T. J. Am. Chem. Soc. **1985**, 107, 4556–4557.

(34) It is proposed that  $[Ir^{II}(ttp)]_2$  undergoes disproportionation with water to give Ir(ttp)OH and Ir(ttp)H. The analogous disproportionation of monomeric rhodium(II) porphyrins ( $Rh^{II}(por)$ ) with  $D_2O$  to give Rh(por)D and Rh(por)OD and with MeOH to give Rh(por)OMe and Rh(por)H have been reported; see: (a) Fu, X.; Li, S.; Wayland, B. B. *Inorg. Chem.* **2006**, *45*, 9884–9889. (b) Sarkar, S.; Li, S.; Wayland, B. B. *J. Am. Chem. Soc.* **2010**, *132*, 13569–13571.

(35) **1b** and **1a** were well-separated by TLC for identification.

(36) When the halogen atom abstraction of Ar–X occurs, the ratio of M–X to M–Ar would be larger than 1, and Ar–Ar would be formed due to the Ar<sup>•</sup> radical leakage.<sup>12</sup> However, it does not occur in the Ar–Br cleavage with [Ir(ttp)]<sub>2</sub>, since the ratio of Ir(ttp)Br to Ir(ttp)Ar is consistently less than 1 (Table S4 in the Supporting Information), and no Ar–Ar was detected via the dimerization of Ar<sup>•</sup> by GC-MS analysis in the reaction of [Ir(ttp)]<sub>2</sub> with ArBr (Ar = p-<sup>t</sup>BuC<sub>6</sub>H<sub>4</sub>) (eq 4).

(37) Benzene was shown to react with Br<sub>2</sub> (as a source of Br<sup>•</sup>) at 200 °C in 90 min to form PhBr in 83% yield, likely via homolytic aromatic substitution. For the mechanism of homolytic aromatic substitution, see: Smith, M. B.; March, J. March's Advanced Organic Chemistry: Reactions, Mechanisms and Structure, 6th ed.; Wiley: New York, 2007; Chapter 14.

(38) The experiment has been done twice to ensure the formation of a trace of PhBr (1%).

(39) In the thermal rearrangements of arylmethylenecyclopropanes, all the electron-donating and -withdrawing para substituents (p-FGs) on the aryl rings promote the rearrangement rates by stabilizing the benzyl radical intermediates via resonance, but the meta substituents (m-FGs) generally do not promote the rates. See: (a) Creary, X. J. Org. Chem. **1980**, 45, 280–284. (b) Creary, X.; Mehrsheikh-Mohammadi, M. E.; McDonald, S. J. Org. Chem. **1987**, 52, 3254–3263. The reactivity trends brought by the p-FGs and m-FGs in the thermal rearrangements of arylmethylenecyclopropanes are similar to those observed in base-promoted Ar-Br cleavage by **1a** (Table S5 and Figure S5 in the Supporting Information), further suggesting the ISAE of Ar-Br by [Ir(ttp)]<sub>2</sub> to give Ir(ttp)Ar.