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Base-Promoted Selective Aryl C−Cl Cleavage by Iridium(III) Porphyrins via a Metalloradical Ipso Addition−Elimination Mechanism

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Supporting Information

ABSTRACT: Base-promoted aryl carbon−chlorine bond (Ar−Cl) cleavage by iridium(III) porphyrin carbonyl chloride (Ir^{III}(ttp)(CO)Cl; ttp = 5,10,15,20-tetrakis(*p*-tolyl)porphyrinato dianion) was achieved in the presence of K_2CO_3 to give iridium(III) porphyrin aryls (Ir^{III}(ttp)Ar). Mechanistic studies revealed that K_2CO_3 promotes the reduction of Ir(ttp)(CO)Cl to give the iridium(II) porphyrin dimer intermediate $[Ir^{II}(ttp)]_2$. $[Ir(ttp)]_2$ is the source of Ir^{II}(ttp) metalloradical, which cleaves Ar−Cl to give Ir(ttp)Ar and a chlorine radical ($Cl^{\bullet}$) via radical ipso substitution in an addition−elimination pathway. $Cl^{\bullet}$ reacts with $[Ir(ttp)]_2$ to yield Ir(ttp)Cl for subsequent base-promoted reduction and Ir(ttp) for radical chain propagation. Additionally, the base-promoted Ar−Cl cleavage of chlorobenzene (PhCl) by Ir(ttp)(CO)Cl gives both Ir(ttp)Ph and 1,4-bis-iridium(III)-porphyrin benzene, Ir^{III}(ttp)(*p*-C_6H_4)Ir^{III}(ttp). The reactive $Cl^{\bullet}$ can simultaneously react with PhCl via homolytic aromatic substitution to give 1,4-dichlorobenzene, which further undergoes double Ar−Cl cleavage to form Ir(ttp)(*p*-C_6H_4)Ir(ttp).

$Ir^{III}(ttp)(CO)Cl \xrightarrow{OH^-} Ir^{III}(ttp)OH \xrightarrow[-1/2H_2O_2]{} 1/2[Ir^{II}(ttp)]_2 \xrightarrow[-Cl^{\bullet}]{Ar-Cl} Ir^{III}(ttp)Ar$

ttp = 5,10,15,20-tetra-*p*-tolylporphyrinato dianion

INTRODUCTION

Aryl carbon−chlorine bond (Ar−Cl) cleavage by transition-metal complexes is of significant importance in organic synthesis[1] and chemical waste treatments for environmental protection.[2] Aryl chlorides (ArCl) can act as a cheaper aryl source in transition-metal-catalyzed carbon−carbon[1a,b] and carbon−heteroatom[1c,d] bond coupling reactions, though the Ar−Cl bond is stronger and is more difficult to cleave in comparison with Ar−Br and Ar−I bonds. Transition-metal-mediated hydrodechlorination of chlorinated dioxins and polychlorinated biphenyls also provides an alternative treatment method to substantially lower the toxicity of halogenated chemical wastes.[2]

Ar−Cl cleavage is generally achieved by using electron-rich d^8 and d^{10} transition metals.[3,4] Group 9 metal(I) complexes have also been adopted to achieve selective Ar−Cl cleavage. For examples, Rh^{I}PNP (PNP = bis(2-(diisopropylphosphino)-4-methylphenyl)-amino)[3c] and Vaska's[3e] complexes undergo oxidative addition with Ar−Cl. Alternatively, Ar−Cl cleavage can also occur via homolytic pathways with metalloradicals. Recently, a group 9 Co(0) metalloradical, [2,6-bis(dimethylphenyliminoethyl)-pyridine]cobalt(0), was found to cleave Ar−Cl via chlorine atom abstraction to yield Co^{I}−Ar and Co^{I}−Cl.[5]

One of the challenges of selective Ar−Cl cleavage is the competitive aryl C−H (Ar−H) activation of ArCl.[6−8] Kinetic C−H activation and thermodynamic C−Cl cleavage of chlorobenzene (PhCl) by neutral $(PNP)Ir^{I}$,[6] as well as both kinetic and thermodynamic ortho-Ar−H activation of PhCl by cationic $[(PNP^*)Ir^{I}]^+$ (PNP* = 2,6-bis(di-*tert*-butylphosphinomethyl)-pyridine),[7] have been reported. Additionally, ortho-Ar−H activation of PhCl by the complex $[Cp^*_2Zr^{IV}CH_3]^+$ initially occurs to give $[Cp^*_2Zr^{IV}(C_6H_4(o\text{-}Cl))]^+$, which gradually undergoes intramolecular Ar−Cl cleavage via β-Cl elimination with the proposed formation of a benzyne intermediate to give the complex Zr^{IV}(Ar)(Cl).[8] The selection of transition metals and reaction conditions are thus important to achieve selective Ar−Cl cleavage.

Our group has been interested in selective bond cleavage by high-valent rhodium(III)[9] and iridium(III) porphyrin complexes.[10] Recently, we have reported the base-promoted selective Ar−Br and Ar−I cleavage by iridium(III) porphyrin carbonyl chloride (Ir^{III}(ttp)(CO)Cl) to yield iridium(III) porphyrin aryls (Ir^{III}(ttp)Ar).[10d,e] Mechanistic studies suggested that base (OH^-) can promote the reduction of Ir^{III}(ttp)(CO)Cl to iridium(II) porphyrin dimer ($[Ir^{II}(ttp)]_2$) via the intermediacy of iridum(III) porphyrin hydroxo (Ir^{III}(ttp)OH). $[Ir(ttp)]_2$ is the source of Ir^{II}(ttp) metalloradical, which cleaves the Ar−Br and Ar−I bonds via radical ipso substitution in an addition−elimination pathway (ipso substitution, addition−elimination, abbreviated as ISAE) to give Ir(ttp)Ar as a new, alternative reactivity mode of Ar−X cleavage.[10d,e]

In order to investigate the effect of Ar−X bond strength on the chemoselectivity of Ar−X and Ar−H cleavage in ArX substrates with Ir(ttp)(CO)Cl under basic conditions, we have further extended the substrate scope from ArBr and ArI to ArCl. We have discovered that base-promoted, selective Ar−Cl cleavage by Ir(ttp)(CO)Cl can also be achieved via Ir^{II}(ttp)-mediated ipso substitution of Ar−Cl to give Ir(ttp)Ar. We now report the reaction scope and detailed mechanistic studies of base-promoted Ar−Cl cleavage by Ir(ttp)(CO)Cl.

RESULTS AND DISCUSSIONS

Optimization of Ph−Cl Cleavage. Initially, Ir(ttp)(CO)Cl (**1a**) reacted with PhCl (1.1 equiv) in benzene at 200 °C in 7 days to give only a trace of Ir(ttp)Ph (**2a**; 2%) and unreacted **1a** was

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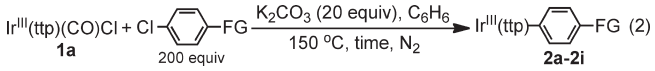
Table 1. Optimization of Ph−Cl Cleavage by Ir(ttp)(CO)Cl

				yield, %[a]			
entry	amt of PhCl, equiv	amt of K_2CO_3, equiv	time	**1a** (recovered)	**2a**	**3**	Ir(ttp)CH_3
1	1.1	0	7 d	78	2[b]	0	0
2	1.1	20	1 d	0	31	3	3
3	50	20	12 h	0	57	3	5
4	200	20	7 h	0	75	2[b,d]	0
5	200	20	22 h[c]	0	74	5[b,e]	0

[a] Isolated yield. [b] NMR yield. [c] Reaction was run at 150 °C. [d] A trace of 1,4-$Cl_2C_6H_4$ (1%) was detected by GC-MS analysis. [e] A trace of 1,4-$Cl_2C_6H_4$ (0.4%) was detected by GC-MS analysis.

Table 2. Substrate Scope of Base-Promoted Ar−Cl Cleavage



entry	FG	time, h	Ir(ttp)Ar (yield, %)[a]	entry	FG	time, h	Ir(ttp)Ar (yield, %)[a]
1	OMe	36	**2b** (76)[b]	6	CO_2Me	46	**2f** (70)[b]
2	Me	36	**2c** (32)[c]	7	CHO	22	**2g** (69)[e,f]
3	H	22	**2a** (74)[d]	8	CF_3	168	**2h** (68)[g]
4	F	36	**2d** (67)	9	CN	24	**2i** (51)[h]
5	Cl	84	**2e** (100)				

[a] Isolated yield. [b] Ir(ttp)CH_3[11] in 3% yield was also isolated. [c] Ir(ttp)Bn(*p*-Cl) (**2j**) in 18% isolated yield and Ir(ttp)CH_3[11] in 2% NMR yield were also formed. [d] Ir(ttp)(*p*-C_6H_4)Ir(ttp) in 5% NMR yield was also formed, and a trace of 1,4-$Cl_2C_6H_4$ (0.4%) was detected by GC-MS analysis. [e] Ir(ttp)(PPh_3)C_6H_4(*p*-CHO) was isolated by adding PPh_3. [f] Aldehydic C−H activation also occurred to give Ir(ttp)(PPh_3)C(O)C_6H_4(*p*-Cl) (**2k**) in <1% yield. [g] A trace of PhCl (0.4%) was detected by GC-MS analysis. [h] Ir(ttp)(PPh_3)C_6H_4(*p*-CN) was isolated by adding PPh_3.

recovered in 78% yield (Table 1, eq 1, entry 1). When K_2CO_3 (20 equiv) was added, the reaction of **1a** with PhCl (1.1 equiv) was complete at 200 °C in 1 day to give **2a** in 31% yield and a trace of Ir(ttp)CH_3[11] (3%) and the unexpected Ir(ttp)(*p*-C_6H_4)Ir(ttp) (**3**; 3%) (Table 1, entry 2). In order to increase the product yields, the PhCl loading was increased. A 50 equiv amount of PhCl increased the yield of **2a** to 57% (Table 1, entry 3). Increasing the PhCl loading to 200 equiv further promoted the yield of **2a** to 75% after 7 h (Table 1, entry 4). The PhCl loading was thus optimized to be 200 equiv. The reaction conditions of base-promoted Ph−Cl cleavage by **1a** were further optimized at a lower temperature of 150 °C and a longer time of 22 h (Table 1, entry 5). Ph−Cl cleavage rather than Ar−H activation of PhCl occurred to give **2a**, since **1a** reacted with PhCl (50 equiv) and K_2CO_3 in benzene-d_6 at 200 °C to give **2a** only without any Ir(ttp)C_6D_5.

Substrate Scope of ArCl. Under the optimal reaction conditions, **1a** generally reacted with a variety of ArCl species to give Ir(ttp)Ar in moderate to high yields via selective Ar−Cl cleavage with high functional compatibility (Table 2, eq 2). Notably, in the reactions with 4-chlorobenzaldehyde and 4-chlorobenzonitrile, brown precipitates were initially formed without the successful isolation of Ir(ttp)Ar. Presumably, coordination oligomers of Ir(ttp)C_6H_4(*p*-CN)[10e,12] and Ir(ttp)C_6H_4(*p*-CHO)[10e,13] at the trans vacant site of the neighboring Ir(ttp)Ar form. Addition of PPh_3 resulted in the isolation of monomeric Ir(ttp)(PPh_3)Ar (Table 2, entries 7 and 9).[10e]

The chemoselectivity of Ar−Cl cleavage in ArCl becomes lower, compared with that of the ArBr and ArI substrates.[10d,e] While selective Ar−Br cleavage of 4-bromotoluene[10d] and 4-bromobenzaldehyde[10e] with **1a** and K_2CO_3 occurred to yield only Ir(ttp)(*p*-Tol) (**2c**) and Ir(ttp)(PPh_3)C_6H_4(*p*-CHO) (**2g**) (upon addition of PPh_3), competitive benzylic C−H bond activation of 4-chlorotoluene occurred to give Ir(ttp)Bn(*p*-Cl) (**2j**) in 18% yield (Table 2, entry 2),[14] and competitive aldehydic C−H bond activation of 4-chlorobenzaldehyde took place to give a trace of Ir(ttp)(PPh_3)C(O)C_6H_4(*p*-Cl) (**2k**) (Table 2, entry 7).[14]

Ir^{II} for Ph−Cl Cleavage. To investigate the reaction mechanism of base-promoted Ar−Cl cleavage by **1a**, the reaction of **1a** with Cs_2CO_3 (20 equiv)[15] and PhCl (50 equiv)[16] in benzene-d_6 at 150 °C was monitored in a sealed NMR tube. After 3.5 h, Ir(ttp)H (**4a**) and [Ir(ttp)]$_2$ (**5**) in 26% and 7% yields, respectively, were observed (eq 3a). After 18 days, **1a**, **4a**, and **5** were consumed to give Ir(ttp)Ph (**2a**), Ir(ttp)(*p*-C_6H_4)Ir(ttp) (**3**), and Ir(ttp)CH_3[11] in 56%, 6%, and 6% yields, respectively (eq 3b). Ir(ttp)H and [Ir(ttp)]$_2$ were the observed intermediates.

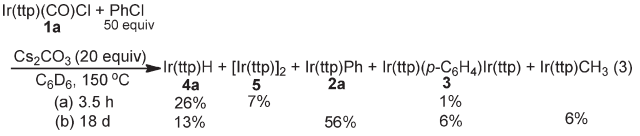


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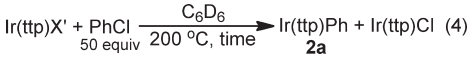
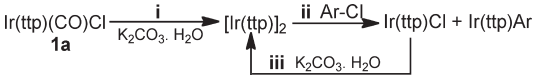
Table 3. Relative Reactivities of Possible Ir(ttp) Species in Ph−Cl Cleavage



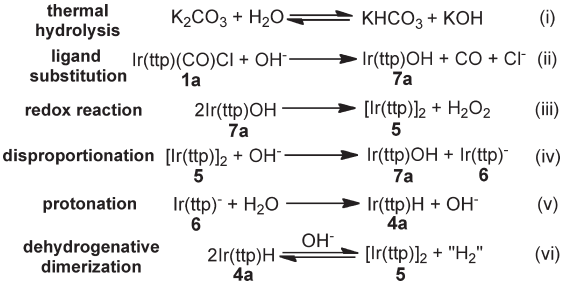
entry	Ir(ttp)X′	time	yield, %[a] Ir(ttp)Ph	Ir(ttp)Cl
1	$Ir(ttp)^-K^+$ (**6**)[b]	4 d	50	
2	Ir(ttp)H (**4a**)	4 d	67	4[c]
3	1/2[Ir(ttp)]$_2$ (**5**)	5 h	57[d]	4[c]

[a] Isolated yield. [b] In the form of $Ir(ttp)^-[K(18\text{-crown-}6)]^+$. [c] Ir(ttp)(CO)Cl (**1a**) was isolated. [d] Ir(ttp)(*p*-C_6H_4)Ir(ttp) (**3**) was also formed in 3% NMR yield.

Scheme 1. General Mechanism of Base-Promoted Ar−Cl Cleavage



Scheme 2. Reduction of Ir(ttp)(CO)Cl to [Ir(ttp)]$_2$ and Ir(ttp)H

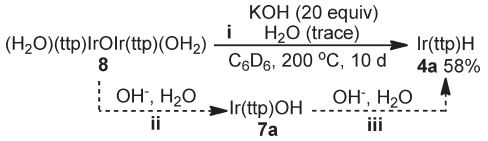


In principle, $Ir(ttp)^-$ (**6**) could also be generated via the deprotonation of Ir(ttp)H with K_2CO_3.[10d] To identify the iridium porphyrin intermediate for Ar−Cl cleavage, the relative reactivities of $Ir(ttp)^-$, Ir(ttp)H, and [Ir(ttp)]$_2$ were compared by reacting with PhCl (50 equiv) in benzene-d_6 at 200 °C (Table 3, eq 4). $Ir(ttp)^-K^+$ and Ir(ttp)H reacted slowly in 4 days to give Ir(ttp)Ph (Table 3, entries 1 and 2). [Ir(ttp)]$_2$ reacted the fastest (5 h) to give Ir(ttp)Ph in 57% yield with a trace of Ir(ttp)(CO)Cl (4%)[17] and Ir(ttp)(*p*-C_6H_4)Ir(ttp) (3%) (Table 3, entry 3). [Ir(ttp)]$_2$ is thus the most probable intermediate for Ph−Cl cleavage.

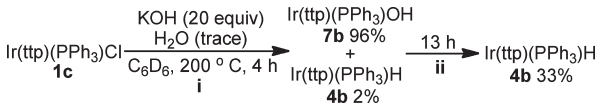
Mechanism (Base-Promoted). The mechanism of base-promoted Ar−Cl cleavage by **1a** (Scheme 1) is generally similar to the previously reported mechanism of Ar−Br and Ar−I cleavage,[10d,e] involving (i) the base-promoted reduction of **1a** to [Ir(ttp)]$_2$, (ii) Ar−Cl cleavage by [Ir(ttp)]$_2$ to give Ir(ttp)Ar and Ir(ttp)Cl, and (iii) recycling of Ir(ttp)Cl via base-promoted reduction. The detailed mechanisms are described below.

Base-Promoted Reduction of Ir(ttp)(CO)Cl to [Ir(ttp)]$_2$ and Ir(ttp)H. Previously, we ruled out the possibility of reduction of **1a** to Ir(ttp)H and then [Ir(ttp)]$_2$, via the nucelophilic attack of OH^- to the CO ligand in **1a**, followed by the decarboxylation of $Ir(ttp)CO_2H$.[10d,e] Instead, base most likely acts as a reducing agent to reduce the Ir(III) center of **1a** to $[Ir^{II}(ttp)]_2$.[10d,e]

Scheme 3. Conversion of (H_2O)(ttp)IrOIr(ttp)(OH_2) to Ir(ttp)H via Ir(ttp)OH



Scheme 4. Base-Promoted Reduction of Ir(ttp)(PPh_3)Cl



Scheme 2 depicts the mechanism of base-promoted reduction of **1a** to [Ir(ttp)]$_2$ for Ar−Cl cleavage.

OH^-, which is generated from the thermal hydrolysis of K_2CO_3[18] with the residual water[19] in benzene solvent (eq i in Scheme 2), reacts with **1a** via ligand substitution to give Ir(ttp)OH (**7a**) and gaseous CO (eq ii).[10d,e] Ir(ttp)OH then converts to [Ir(ttp)]$_2$ and H_2O_2 via the reduction of the Ir(III) center by the hydroxo ligand (eq iii).[10d,e] In the absence of or at a low concentration of ArCl, [Ir(ttp)]$_2$ simultaneously undergoes rapid disproportionation with OH^- to give Ir(ttp)OH and $Ir(ttp)^-$ (eq iv).[20] Ir(ttp)OH is recycled for subsequent redox reaction, whereas $Ir(ttp)^-$ is protonated by residual water to give Ir(ttp)H (eq v).[21] Ir(ttp)H can undergo thermal and base-promoted dehydrogenative dimerization to regenerate [Ir(ttp)]$_2$ via an equilibrium (eq vi).[10d]

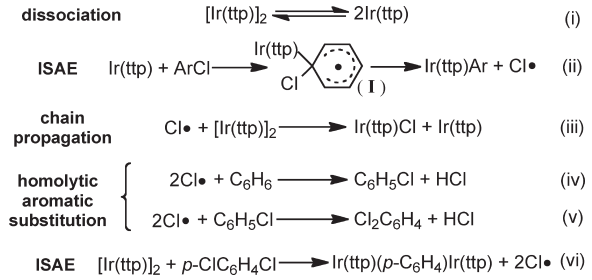
To support the above proposal (Scheme 2), a sample of Ir(ttp)OH (**7a**) is needed to demonstrate the conversion of Ir(ttp)OH intermediate to Ir(ttp)H. However, Ir(ttp)OH could not be prepared by reacting the electrophilic "$Ir(ttp)SbF_6$" (**1b**) (as a inseparable mixture of $Ir(ttp)SbF_6$ and $Ir(ttp)(CO)SbF_6$ prepared in irreproducible ratios)[10e] with CsOH in benzene-d_6 at room temperature, due to the instantaneous formation of Ir(ttp)H in 95% yield.[10e] Previously, we have used (H_2O)(ttp)IrOIr(ttp)(OH_2) (**8**) as a precursor of Ir(ttp)OH via KOH-promoted hydrolysis (Scheme 3, path ii).[10e] **8** reacted with KOH (20 equiv) and residual water in benzene-d_6 at 200 °C in 10 days to give Ir(ttp)H in 58% yield (Scheme 3, path i), supporting the intermediacy of Ir(ttp)OH for Ir(ttp)H formation (Scheme 3, paths ii and iii).[10e]

To independently validate the proposed reaction steps in Scheme 2, we further adopted the coordinatively saturated and less reactive Ir(ttp)(PPh_3)Cl (**1c**) to study the base-promoted reduction processes. **1c** was prepared in 65% yield by reacting **1a** with excess PPh_3 (5 equiv) in benzene at 200 °C for 1 day.

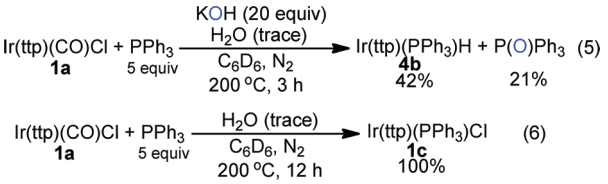
(a). Evidence for Scheme 2, eq ii. **1c** reacted with KOH in benzene-d_6 at 200 °C in 4 h to give the more stable, coordinatively saturated Ir(ttp)(PPh_3)OH (**7b**) in 96% yield accompanied by a trace amount of Ir(ttp)(PPh_3)H (**4b**) (2%) (Scheme 4, path i). Ligand substitution of **1a** with OH^- to form Ir(ttp)OH is thus supported.

(b). Evidence for Scheme 2, eq iii. In the reaction of **1c** with KOH, **7b**, once formed, was further converted to **4b** in 33% yield[22] in 13 h (Scheme 4, path ii). The hydroxo ligand acts as a reducing agent to reduce the Ir(III) center of **7b** to give $Ir^{II}(ttp)(PPh_3)$ or $[Ir^{II}(ttp)PPh_3]_2$ for subsequent rapid reaction to yield **4b** (Scheme 2, eqs iii−v). The conversion of **7b** to Ir(ttp)(PPh_3)/[Ir(ttp)(PPh_3)]$_2$ and H_2O_2 can be supported by

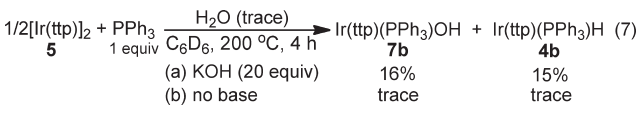
Scheme 5. Reaction of ArCl with $[Ir(ttp)]_2$ in Benzene



the detection of H_2O_2 (Scheme 2, eq iii). The direct detection of H_2O_2, however, is difficult, as it can rapidly disproportionate into H_2O and O_2 in the presence of a base catalyst.[23] Instead, H_2O_2 can be indirectly detected by reacting with excess PPh_3 as a H_2O_2 trap to produce $P(O)Ph_3$.[24,25] Indeed, **1a** reacted with KOH and residual water in the presence of excess PPh_3 (5 equiv) in benzene-d_6 at 200 °C in 3 h to give Ir(ttp)(PPh_3)H (**4b**; 42%) and a moderate yield of $P(O)Ph_3$ (21%) (eq 5). Without KOH, **1a** only reacted with excess PPh_3 under identical conditions in 12 h to yield **1c** only without any **4b** (eq 6). The results reveal that OH^- is oxidized to produce H_2O_2, whereas Ir(III) is reduced to Ir(II) which finally gives Ir(ttp)H.



(c). Evidence for Scheme 2, eqs iv and v. In the presence of PPh_3 as a stabilizing ligand, $[Ir(ttp)]_2$ reacted with KOH and residual water in benzene-d_6 at 200 °C in 4 h to yield **7b** (16%) and **4b** (15%) in around a 1:1 ratio.[20] Without KOH, $[Ir(ttp)]_2$/PPh_3 only reacted with residual water in 4 h to give only a trace of **7b** and **4b** (eq 7b), supporting the promoting effect of OH^- in the disproportionation of $[Ir(ttp)]_2$. We are not very clear about the reason of low yields of **7b** and **4b**. Probably, the coordinatively saturated $[Ir^{II}(ttp)(PPh_3)]_2$ decomposes much faster either with heat at 200 °C or in the presence of H_2O_2.[26]



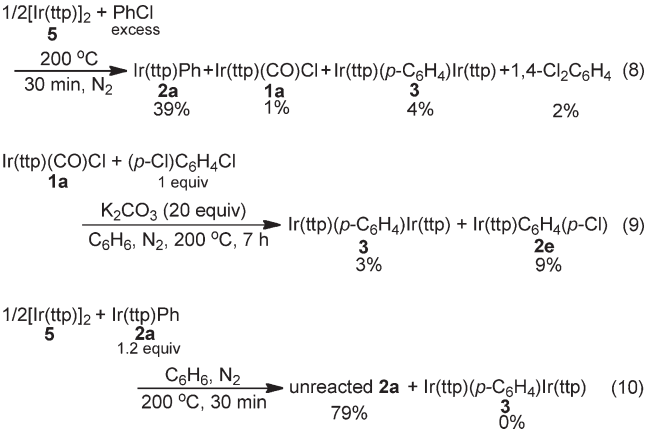
Ar—Cl Cleavage by $[Ir^{II}(ttp)]_2$ in Benzene. The mechanism of $[Ir(ttp)]_2$-mediated Ar—Cl cleavage is similar to that of Ar—Br and Ar—I cleavage.[10d,e] We propose that $[Ir(ttp)]_2$ initially dissociates into $Ir^{II}(ttp)$ (Scheme 5, eq i).[27] Ir(ttp) then reacts with ArCl via radical ipso substitution in an addition—elimination pathway (ISAE)[10d,e] to give Ir(ttp)Ar and a very reactive chlorine radical ($Cl^•$) via the intermediacy of an Ir(ttp)—cyclohexadienyl radical (**I**) (Scheme 5, eq ii). $Cl^•$ reacts with $[Ir(ttp)]_2$ to give Ir(ttp)Cl and another Ir(ttp) (Scheme 5, eq iii). Ir(ttp)Cl is recycled via a base-promoted reduction (Scheme 2), whereas Ir(ttp) further reacts via radical chain propagation (Scheme 5, eq ii).

$Cl^•$ can leak out from the chain reaction and reacts with benzene solvent to give PhCl via homolytic aromatic substitution (HAS) (Scheme 5, eq iv).[28,29] When PhCl is used as a substrate (Ar = Ph), $Cl^•$ also reacts with excess PhCl to yield dichlorobenzene via HAS (Scheme 5, eq v).[28,30] 1,4-Dichlorobenzene can further react with $[Ir(ttp)]_2$ to give Ir(ttp)(p-C_6H_4)Ir(ttp) (**3**) via double Ar—Cl cleavage (Scheme 5, eq vi).[31]

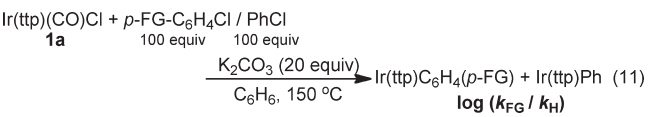
The following two lines of evidence[10d,32] can support the ISAE mechanism of ArCl by $[Ir(ttp)]_2$:

(a). Detection of Organic Coproducts Originating from $Cl^•$.[32] In the base-promoted (p-CF_3)C_6H_4—Cl cleavage by **1a**, a trace of PhCl was detected by GC-MS analysis (Table 2, entry 8). This supports the HAS of (p-CF_3)C_6H_4—Cl with $[Ir(ttp)]_2$ intermediate to give $Cl^•$, which further reacts with benzene to give PhCl (Scheme 5, eqs ii and iv).[29,33]

Additionally, in the base-promoted Ph—Cl cleavage by **1a**, a trace of 1,4-dichlorobenzene (1,4-$Cl_2C_6H_4$) was detected by GC-MS analysis (Table 1, entries 4 and 5). Most likely, the HAS of PhCl with $[Ir(ttp)]_2$ gives $Cl^•$, which further reacts with excess PhCl to give 1,4-$Cl_2C_6H_4$ (Scheme 5, eqs ii and v).[30,34] Indeed, $[Ir(ttp)]_2$ reacted with neat PhCl at 200 °C to give Ir(ttp)Ph, Ir(ttp)(CO)Cl,[17] Ir(ttp)(p-C_6H_4)Ir(ttp), and 1,4-$Cl_2C_6H_4$ in 39%, 1%, 4%, and 2% yields, respectively (eq 8). Most likely, the coproduct 1,4-$Cl_2C_6H_4$ further reacts with $[Ir(ttp)]_2$ to give a trace of **3** (Scheme 5, eq vi). This can be supported by the reaction of **1a** with 1,4-$Cl_2C_6H_4$ (1 equiv) and K_2CO_3 in benzene at 200 °C in 7 h to give a trace of **3** (eq 9).[35] The formation of **3** via HAS of Ir(ttp)-Ph with $[Ir(ttp)]_2$ is excluded, as **5** did not react with **2a** to give **3** (eq 10).



(b). Rate Enhancement by Para Substituents (p-FGs) in ArCl.[32] In the competition reaction of an equimolar ratio of para-substituted ArCl (p-FG-C_6H_4Cl) and PhCl with **1a** and K_2CO_3 (eq 11), both the electron-donating and -withdrawing p-FGs promoted the rate of Ar—Cl cleavage, as shown in the V-shaped Hammett plot (Figure 1).[36] The results suggest that the Ir(ttp)—cyclohexadienyl radical intermediate is formed and stabilized by resonance with the p-FG group (Figure 2).[37]



Other Mechanistic Possibilities of Ar—Cl Cleavage. Two other possible mechanisms of Ar—Cl cleavage to give Ir(ttp)Ar are (A) the elimination—addition reaction of ArCl with $Ir(ttp)^-$ (Scheme 6, mechanism A) and (B) chlorine atom abstraction by $[Ir(ttp)]_2$ (Scheme 6, mechanism B).

Mechanism A. The intermediate $Ir(ttp)^-$ can in principle abstract a proton from the para-substituted ArCl, and a chloride

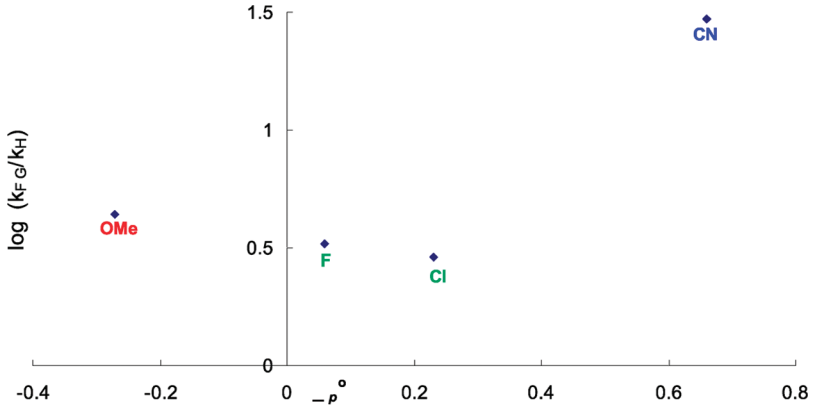


Figure 1. Hammett plot of Ar−Cl cleavage using the Hammett constants σ_p^o.

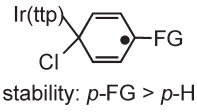
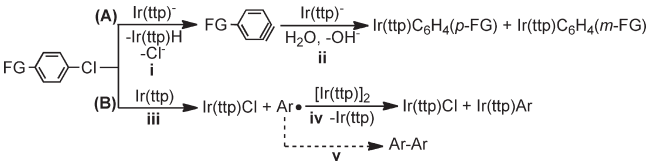
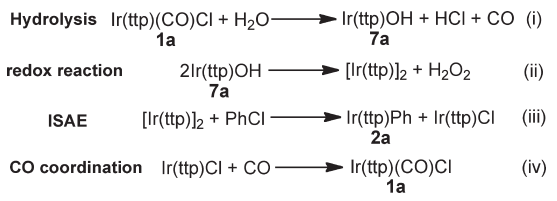


Figure 2. Stabilization of the Ir(ttp)−cyclohexadienyl intermediate by para substituents.

Scheme 6. Other Possible Mechanisms of Ar−Cl Cleavage



Scheme 7. Mechanism of Ph−Cl Cleavage without Base



ion is then eliminated to give an aryne (Scheme 6, path i). Subsequent reaction of the aryne with $Ir(ttp)^-$ and residual water yields both iridium(III) porphyrin para- and meta-substituted aryls (Scheme 6, path ii). Mechanism A is ruled out due to the absence of $Ir(ttp)C_6H_4$(*m*-FG) in the base-promoted Ar−Cl cleavage of para-substituted ArCl by **1a** (Table 2).

Mechanism B. Ir(ttp), dissociated from the intermediate $[Ir(ttp)]_2$, can directly abstract a chlorine atom ($Cl^•$) from ArCl to give Ir(ttp)Cl and Ar• (Scheme 6, path iii). $Ar^•$ further reacts with $[Ir(ttp)]_2$ to give Ir(ttp)Ar (Scheme 6, path iv) or leaks from the chain reactions and dimerizes to yield biaryls (Scheme 6, path v). Mechanism B is also ruled out, since the ratio of Ir(ttp)Cl to Ir(ttp)Ar is much less than 1 (Table 3, entry 3)[10d] and no biphenyl was detected in the reaction of $[Ir(ttp)]_2$ with PhCl (eq 8).

Mechanism (without Base). Without base, **1a** reacted slowly and incompletely with PhCl (1.1 equiv) in benzene at 200 °C in 7 days to give a trace of **2a** (2%) (Table 1, entry 1). It is likely that the residual water[19] in benzene hydrolyzes **1a** slowly to give Ir(ttp)OH, HCl, and CO (Scheme 7, eq i). Ir(ttp)OH then rapidly converts to $[Ir(ttp)]_2$ and H_2O_2 (Scheme 7, eq ii). $[Ir(ttp)]_2$ further cleaves the Ph−Cl bond via an ISAE mechanism to give **2a** and Ir(ttp)Cl (Scheme 7, eq iii). Ir(ttp)Cl finally reacts with CO to give back **1a** (Scheme 7, eq iv).

CONCLUSION

In summary, we have discovered base-promoted selective Ar−Cl cleavage by high-valent Ir(ttp)(CO)Cl in benzene solvent. Mechanistic studies reveal that OH^- promotes the reduction of Ir(ttp)(CO)Cl to $[Ir(ttp)]_2$, which then cleaves the Ar−Cl bond via a radical ipso addition−elimination mechanism to give Ir(ttp)Ar and a chlorine radical. The chlorine radical further reacts with $[Ir(ttp)]_2$ to give Ir(ttp)Cl and simultaneously reacts with excess benzene and ArCl via homolytic aromatic substitution to give the chlorinated aromatic compounds.

EXPERIMENTAL SECTION

General Procedures. 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 benzene-d_6 were distilled from sodium and were stored in a Teflon screw capped tube under nitrogen prior to use. All reactions were carried out without light irradiation by wrapping with aluminum foil. The reactions in Teflon screw capped Schlenk tubes were heated in heat blocks on heaters, whereas the reactions in sealed NMR tubes were heated in GC ovens. The reaction mixtures should be handled with care and with safety precautions (e.g., protective shield), as explosion may occur at high temperatures (150−200 °C). Thin-layer chromatography was performed on precoated silica gel 60 F_{254} plates. Ir(ttp)(CO)Cl (**1a**),[17] "Ir(ttp)SbF_6" (**1b**),[10e] Ir(ttp)(*p*-TolCN)Cl,[10e] Ir(ttp)CH_3,[17] Ir(ttp)H (**4a**),[10a] Ir(ttp)(PPh_3)H (**4b**),[10c] $[Ir(ttp)]_2$ (**5**),[10a] $Ir(ttp)^-$-$[K(18\text{-crown-}6)]^+$ (**6**),[10c] Ir(ttp)OH (**7a**),[10e] and (H_2O)(ttp)IrOIr(ttp)-(H_2O) (**8**)[10e] had been characterized and were prepared according to the literature procedures. Ir(ttp)Ar (**2a**−**i**) and Ir(ttp)(*p*-C_6H_4)Ir(ttp) (**3**) have been characterized.[10d,e] Silica gel (Merck, 70−230 mesh), and neutral alumina (Merck, activity I, 70−230 mesh) added with H_2O (~10/1 v/v), were used for column chromatography.

Unless otherwise noted, all the reaction mixtures were degassed for three freeze−thaw−pump cycles and were then back-filled with N_2 in the Teflon screw capped Schlenk tubes, or flame-sealed under vacuum in the Teflon screw capped NMR tubes. In sealed NMR tube experiments, the residual benzene proton signal was used as an internal standard to

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estimate the NMR yields of iridium porphyrin species by ^{1}H NMR spectroscopy.

A trace of residual water was always present in benzene-d_6 ($\delta(H_2O)$ ~0.4 ppm).[19] The amount of residual water (~0.2−2 equiv with reference to the iridium porphyrin species) in benzene-d_6 in sealed NMR tube experiments was estimated by ^{1}H NMR spectroscopy by taking the ratio between the proton signal of residual water and that of porphyrin's pyrrole of iridium porphyrin species. The yields of Ir(ttp)-(p-C_6H_4)Ir(ttp) (**3**) and [Ir(ttp)]$_2$ (**5**) were based on the number of moles of iridium porphyrin ring (Ir(ttp)) incorporated into the complexes.

Experimental Instrumentation. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Brüker DPX-300 instrument at 300, 75, and 122 MHz, respectively, or a Brüker AV-400 instrument at 400, 100, and 162 MHz, respectively. Chemical shifts were referenced with the residual solvent protons in C_6D_6 (δ 7.15 ppm), $CDCl_3$ (δ 7.26 ppm), or tetramethylsilane (TMS) (δ 0.00 ppm) in ^{1}H NMR spectra as the internal standards and in $CDCl_3$ (δ 77.16 ppm), C_6D_6 (δ 128.06 ppm), or THF-d_8 ($\delta(\beta$-$CH_2)$ 25.62 ppm) in ^{13}C NMR spectra as the internal standards. H_3PO_4 (85% solution) (δ 0.00 ppm) in C_6D_6 was referenced as the external standard in ^{31}P NMR spectra. Chemical shifts (δ) are reported as parts per million (ppm) in the δ scale downfield from TMS. Coupling constants (J) are reported in hertz (Hz).

High-resolution mass spectra (HRMS) were performed on a ThermoFinnigan MAT 95 XL mass spectrometer in fast atom bombardment (FAB) mode using 3-nitrobenzyl alcohol (NBA) matrix and CH_2Cl_2 as solvent or electrospray ionization (ESI) mode using MeOH/CH_2Cl_2 (1/1) as solvent.

Gas chromatography−mass spectrometric (GC-MS) analysis was conducted on a Shimadzu GCMS-2010Plus instrument using a Rtx-5MS column (30 m × 0.25 mm). The column oven temperature and injection temperature were 50.0 and 250 °C, repsectively. Helium was used as a carrier gas. Flow control mode was chosen as linear velocity (36.3 cm s^{-1}) with a pressure of 53.5 kPa. The total flow, column flow, and purge flow were 24.0, 1.0, and 3.0 mL min^{-1}, respectively. Split mode inject with split ratio 20.0 was applied. After injection, the column oven temperature was kept at 50 °C for 5 min and the temperature was then elevated at a rate of 20 °C min^{-1} for 10 min up to 250 °C. The temperature of 250 °C was kept for a further 5 min.

Experimental Procedures. *Preparation of Chloro(triphenylphosphine)(5,10,15,20-tetrakis(p-tolyl)porphyrinato)iridium(III), [Ir(ttp)-(PPh$_3$)Cl] (**1c**).* Ir(ttp)(CO)Cl (**1a**; 100 mg, 0.11 mmol), PPh_3 (142 mg, 0.54 mmol, 5 equiv), and benzene (4 mL) were heated in a Teflon screw capped tube at 200 °C under N_2 for 1 day. The solvent was dried, and the reaction mixture was purified by column chromatography with alumina using $CHCl_3$ as the eluent. The major red solution was collected and then dried under vacuum. The product was further recrystallized using CH_2Cl_2/hexane to obtain a red solid of Ir(ttp)(PPh_3)Cl (**1c**; 81.5 mg, 0.070 mmol, 65%). R_f = 0.15 ($CHCl_3$). ^{1}H NMR (C_6D_6, 300 MHz): δ 2.39 (s, 12 H), 4.27 (dd, 6 H, $^3J_{PH}$ = 9.0 Hz, $^3J_{HH}$ = 8.6 Hz), 6.33 (t, 6 H, $^3J_{HH}$ = 7.4 Hz), 6.55 (t, 3 H, $^3J_{HH}$ = 7.2 Hz), 7.14 (d, 4 H, $^3J_{HH}$ = 7.9 Hz), 7.35 (d, 4 H, $^3J_{HH}$ = 7.5 Hz), 7.78 (d, 4 H, $^3J_{HH}$ = 7.4 Hz), 7.93 (d, 4 H, $^3J_{HH}$ = 7.3 Hz), 8.84 (s, 8 H). ^{13}C NMR (THF-d_8, 300 MHz): δ 21.9, 123.5, 126.0 (d, $^1J_{PC}$ = 53.2 Hz), 127.9 (d, $^2J_{PC}$ = 15.7 Hz), 128.1, 128.6, 130.2, 132.1 (d, $^3J_{PC}$ = 9.0 Hz), 132.4, 134.8, 135.6, 138.1, 140.5, 143.4. ^{31}P NMR (C_6D_6, 162 MHz): δ −37.5 (br) (Figure S2d in the Supporting Information). HRMS (FABMS): calcd for $[C_{66}H_{51}N_4PClIr]^+$ ($[M]^+$) m/z 1158.3164, found m/z 1158.3199.

*Preparation of p-Chlorobenzyl(5,10,15,20-Tetrakis(p-tolyl)porphyrinato)-iridium(III), Ir(ttp)Bn(p-Cl) (**2j**).* A suspension of Ir(ttp)(CO)Cl (84 mg, 0.091 mmol) in THF (20 mL) in a Teflon screw capped 250 mL round-bottomed flask and a solution of $NaBH_4$ (68.7 mg, 1.82 mmol) in aqueous NaOH (1.0 M, 1.5 mL) were purged with N_2 for 15 min separately. The solution of $NaBH_4$ was added slowly into the suspension of Ir(ttp)(CO)Cl via a cannula under N_2. The mixture was heated at 50 °C under N_2 for 2 h to give a deep brown solution. The mixture was then cooled to room temperature, and p-chlorobenzyl bromide (92 mg, 0.45 mmol) was added under N_2. The reaction mixture was further heated at 50 °C for 2 h. The reaction mixture was dried and purified by column chromatography with alumina using CH_2Cl_2/hexane (1/2) as eluent. The major deep brown fraction was collected and dried. The product was recrystallized in CH_2Cl_2/hexane to obtain a deep brown solid of Ir(ttp)Bn(p-Cl) (**2j**; 61 mg, 0.062 mmol, 68%). R_f = 0.67 (CH_2Cl_2/hexane 1/1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ −4.02 (s, 2 H), 2.69 (s, 12 H), 3.04 (d, 2 H, J = 8.4 Hz), 5.84 (d, 2 H, J = 8.4 Hz), 7.53 (d, 4 H, J = 7.8 Hz), 7.55 (d, 4 H, J = 8.1 Hz), 7.94 (d, 4 H, J = 7.5 Hz), 8.02 (d, 4 H, J = 7.8 Hz), 8.49 (d, 8 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ −15.7, 21.7, 124.1, 125.3, 126.2, 127.7, 131.4, 133.7, 133.9, 137.3, 138.8, 140.3, 143.2. HRMS (FABMS): calcd for $[C_{55}H_{42}N_4ClIr]^+$ ($[M]^+$) m/z 986.2722, found m/z 986.2730.

*Preparation of (p-Chlorobenzoyl)(triphenylphosphine)(5,10,15,20-tetrakis(p-tolyl)porphyrinato)iridium(III), Ir(ttp)(PPh$_3$)C(O)C$_6$H$_4$(p-Cl) (**2k**).* Ir(ttp)CH_3 (62 mg, 0.072 mmol), 4-chlorobenzaldehyde (506 mg, 3.6 mmol, 50 equiv), and benzene (2 mL) were heated in a Teflon screw capped tube at 200 °C under N_2 for 14 days. The reaction mixture was then dried and further purified by column chromatography over silica gel using CH_2Cl_2/hexane (2/1) as eluent to obtain an orange solid of Ir(ttp)C(O)C_6H_4(p-Cl)[10f] (42 mg, 0.042 mmol, 58%). Ir(ttp)C(O)-C_6H_4(p-Cl) was then reacted with PPh_3 (110 mg, 0.42 mmol, 10 equiv) in $CHCl_3$ (4 mL) in a Teflon screw capped tube in air at 50 °C for 30 min. The deep reddish brown reaction mixture was dried and purified by column chromatography over alumina using CH_2Cl_2/hexane (1/3) as eluent to obtain a reddish brown solid of Ir(ttp)(PPh_3)C(O)C_6H_4(p-Cl) (**2k**; 45 mg, 0.036 mmol, 50% with reference to Ir(ttp)CH_3). R_f = 0.67 (CH_2Cl_2/hexane 1/1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.22 (d, 2 H, J = 8.4 Hz), 2.23 (s, 12 H), 4.05 (br, 6 H), 5.85 (d, 2 H, J = 8.0 Hz), 6.54 (t, 6 H, J = 6.8 Hz), 6.85 (t, 3 H, J = 7.2 Hz), 7.48 (d, 8 H, J = 8.0 Hz), 7.69 (d, 4 H, J = 8.0 Hz), 7.80 (d, 4 H, J = 7.6 Hz), 8.48 (s, 8 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.6, 118.5, 118.6, 122.8, 125.3, 127.0 (d, J = 7.6 Hz), 127.1, 127.6, 127.9, 128.1, 128.3, 130.0 (d, $^1J_{PC}$ = 30.5 Hz), 130.8 (d, $^2J_{PC}$ = 11.5 Hz), 131.7, 133.8, 134.5, 137.0, 139.1, 142.4. HRMS (FABMS): calcd for $[C_{73}H_{56}N_4ClOPIr]^+$ ($[M + H]^+$): m/z 1263.3503, found m/z 1263.3500.

*Preparation of Phenyl(triphenylphosphine)(5,10,15,20-tetrakis-(p-tolyl)porphyrinato)iridium(III), Ir(ttp)(PPh$_3$)Ph (**2l**).* Ir(ttp)Ph (21.6 mg, 0.023 mmol), triphenylphosphine (60 mg, 0.23 mmol, 10 equiv), and benzene (2 mL) were heated in a Teflon screw capped tube at 120 °C under N_2 for 30 min. The reaction mixture was then dried, purified by column chromatography over alumina using CH_2Cl_2/hexane (1/1) as an eluent, and further recrystallized with CH_2Cl_2/CH_3OH to obtain a deep reddish brown solid of Ir(ttp)(PPh_3)Ph (**2l**; 21.9 mg, 0.018 mmol, 79%). R_f = 0.51 (CH_2Cl_2/hexane 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.37 (dd, 2 H, $^3J_{HH}$ = 7.0 Hz, $^4J_{PH}$ = 6.4 Hz), 2.65 (s, 12 H), 4.12 (dd, 6 H, $^3J_{PH}$ = 8.1 Hz, $^3J_{HH}$ = 8.1 Hz), 4.71 (t, 2 H, $^3J_{HH}$ = 7.1 Hz), 5.13 (t, 1 H, $^3J_{HH}$ = 7.0 Hz), 6.54 (t, 6 H, $^3J_{HH}$ = 7.0 Hz), 6.85 (t, 3 H, $^3J_{HH}$ = 7.3 Hz), 7.41 (d, 4 H, $^3J_{HH}$ = 7.7 Hz), 7.45 (d, 4 H, $^3J_{HH}$ = 7.7 Hz), 7.63 (d, 4 H, $^3J_{HH}$ = 7.4 Hz), 7.79 (d, 4 H, $^3J_{HH}$ = 7.5 Hz), 8.42 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.6, 119.2, 122.8, 122.9, 126.9 (d, $^3J_{PC}$ = 8 Hz), 127.0, 127.4, 128.0, 128.9 (d, $^1J_{PC}$ = 25 Hz), 130.9 (d, $^2J_{PC}$ = 11 Hz), 131.7, 133.8, 134.6, 136.9, 139.2, 142.4. HRMS (FABMS): calcd for $[C_{72}H_{56}N_4PIr]^+$ m/z 1200.3866, found m/z 1200.3861.

*Preparation of Triphenylphosphine Oxide, P(O)Ph$_3$ (**9**).* The typical synthetic method for the preparation of $P(O)Ph_3$ is the oxidation of PPh_3 by H_2O_2.[25a] PPh_3 (64 mg, 0.24 mmol), H_2O_2 (30% solution, 2.5 mL, 24.4 mmol of H_2O_2 (100 equiv)), and benzene (2 mL) were heated in a Teflon screw capped tube under N_2 at 200 °C for 12 h. The reaction mixture was then purified by column chromatography with silica gel using $CHCl_3$ as eluent. The product was crystallized by CH_2Cl_2/hexane to yield P(O)Ph_3 (**9**; 50.7 mg, 0.18 mmol, 76%). ^{1}H NMR (C_6D_6, 400 MHz):

δ 6.96−7.03 (m, 9 H), 7.74 (ddd, 6 H, $^3J_{PH}$ = 11.5 Hz, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.5 Hz). The observation of $^4J_{HH}$ is dependent on the concentration of $P(O)Ph_3$. ^{31}P NMR (C_6D_6, 162 MHz): δ 25.2 (hept, $^3J_{PH}$ = 11.3 Hz). HRMS (ESIMS): calcd for $[C_{18}H_{15}OPNa]^+$ ($[M + Na]^+$) m/z 301.0753, found m/z 301.0748.

Optimization of Base-Promoted Ph−Cl Cleavage by Ir(ttp)(CO)Cl. The experimental procedures of the reaction of Ir(ttp)(CO)Cl with PhCl (1.1 equiv) in benzene at 200 °C without and with K_2CO_3 are described as typical examples.

(a). Reaction of Ir(ttp)(CO)Cl with PhCl (1.1 equiv) at 200 °C. Ir(ttp)(CO)Cl (20 mg, 0.022 mmol), PhCl (2.7 mg, 2.4 μL, 0.024 mmol), and benzene (2 mL) were heated in a Teflon screw capped tube at 200 °C under N_2 for 7 days. The solvent was then removed under vacuum, and the crude products were purified by column chromatography over silica gel with CH_2Cl_2/hexane (2/1) as eluent. The major red fraction was collected to give unreacted Ir(ttp)(CO)Cl (15.7 mg, 0.017 mmol, 78%). Ir(ttp)Ph was also formed in a trace amount, but it could not be isolated by column chromatography, due to its decomposition in silica gel. The yield of Ir(ttp)Ph (**2a**; 2%, NMR yield) was estimated by using the isolated yield of unreacted Ir(ttp)(CO)Cl and the porphyrin's pyrrole proton ratio Ir(ttp)(CO)Cl:Ir(ttp)Ph (~39:1) in the crude products estimated by ^1H NMR spectroscopy.

(b). Reaction of Ir(ttp)(CO)Cl with PhCl (1.1 equiv) and K_2CO_3 at 200 °C. Ir(ttp)(CO)Cl (19.7 mg, 0.021 mmol), K_2CO_3 (59.0 mg, 0.43 mmol), PhCl (2.6 mg, 2.4 μL, 0.023 mmol), and benzene (2 mL) were heated at 200 °C under N_2 for 1 day to yield Ir(ttp)Ph (**2a**; 6.2 mg, 0.007 mmol, 31%), Ir(ttp)(p-C_6H_4)Ir(ttp) (**3**; 0.5 mg, 0.0006 mmol, 3%), and Ir(ttp)CH_3 (1.1 mg, 0.0006 mmol, 3%) isolated in a single fraction (alumina, CH_2Cl_2/hexane (1/2)). The yields of the three products were estimated by using the total isolated yield and the pyrrole proton ratio **3**:**2a**:Ir(ttp)CH_3 in the isolated products by ^1H NMR spectroscopy.

(c). Reaction of Ir(ttp)(CO)Cl with PhCl (50 equiv) and K_2CO_3 at 200 °C. Ir(ttp)(CO)Cl (9.7 mg, 0.010 mmol), K_2CO_3 (29 mg, 0.21 mmol), PhCl (59 mg, 53 μL, 0.53 mmol), and benzene (1 mL) were heated at 200 °C under N_2 for 12 h to give Ir(ttp)Ph (5.6 mg, 0.006 mmol, 57%), Ir(ttp)(p-C_6H_4)Ir(ttp) (0.6 mg, 0.0003 mmol, 3%), and Ir(ttp)CH_3 (0.5 mg, 0.0005 mmol, 5%).

(d). Reaction of Ir(ttp)(CO)Cl with PhCl (200 equiv) and K_2CO_3 at 200 °C. Ir(ttp)(CO)Cl (10.9 mg, 0.012 mmol), K_2CO_3 (33 mg, 0.24 mmol), PhCl (265 mg, 240 μL, 2.4 mmol), and benzene (1 mL) were heated at 200 °C under N_2 for 7 h to give Ir(ttp)Ph (8.3 mg, 0.009 mmol, 75%) and Ir(ttp)(p-C_6H_4)Ir(ttp) (2%, NMR yield). 1,4-Dichlorobenzene in 1% yield was also detected by GC-MS analysis using 4-chlorotoluene as an internal standard (GC6 in the Supporting Information).

(e). Reaction of Ir(ttp)(CO)Cl with PhCl (200 equiv) and K_2CO_3 at 150 °C. Ir(ttp)(CO)Cl (9.8 mg, 0.011 mmol), K_2CO_3 (29 mg, 0.21 mmol), PhCl (239 mg, 216 μL, 2.1 mmol), and benzene (1 mL) were heated at 200 °C under N_2 for 22 h to give Ir(ttp)Ph (7.4 mg, 0.008 mmol, 74%) and Ir(ttp)(p-C_6H_4)Ir(ttp) (5%, NMR yield). 1,4-Dichlorobenzene in 0.4% yield was also detected by GC-MS analysis using 4-chlorotoluene as an internal standard (GC7 in the Supporting Information).

Scope of Base-Promoted Aryl C−Cl Cleavage: Reactions of 4-Substituted Aryl Chlorides (200 equiv) with Ir(ttp)(CO)Cl and K_2CO_3 (20 equiv). The experimental procedure of the reaction of Ir(ttp)(CO)Cl with 4-chloroanisole (200 equiv) and K_2CO_3 (20 equiv) is described as a typical example.

(a). Reaction with 4-Chloroanisole. Ir(ttp)(CO)Cl (9.6 mg, 0.010 mmol), K_2CO_3 (29 mg, 0.21 mmol, 20 equiv), 4-chloroanisole (296 mg, 254 μL, 2.1 mmol), and benzene (1 mL) were heated in a Teflon screw capped tube at 150 °C under N_2 for 36 h. The crude product was dried under vacuum and then purified by column chromatography over alumina with CH_2Cl_2/hexane (1/2) as eluent to give Ir(ttp)C_6H_4(p-OMe) (**2b**;[10d] 7.6 mg, 0.008 mmol, 76%) and Ir(ttp)CH_3 (0.3 mg, 0.0003 mmol, 3%) in a single fraction. The ratio **2b**:Ir(ttp)CH_3 was estimated by using the porphyrin's pyrrole proton ratio **2b**:Ir(ttp)CH_3 in the isolated product mixture by ^1H NMR spectroscopy.

(b). Reaction with 4-Chlorotoluene. Ir(ttp)(CO)Cl (9.5 mg, 0.010 mmol), K_2CO_3 (28 mg, 0.21 mmol, 20 equiv), 4-chlorotoluene (260 mg, 243 μL, 2.1 mmol, 200 equiv), and benzene (1 mL) were heated at 150 °C under N_2 for 36 h to give Ir(ttp)(p-Tol) (**2c**;[10d] 3.1 mg, 0.003 mmol, 32%), Ir(ttp)Bn(p-Cl) (**2j**; 1.8 mg, 0.002 mmol, 18%), and Ir(ttp)CH_3 (0.3 mg, 0.0003 mmol, 3%) in a single fraction by column chromatography.

(c). Reaction with 1-Chloro-4-fluorobenzene. Ir(ttp)(CO)Cl (10.4 mg, 0.011 mmol), K_2CO_3 (31 mg, 0.23 mmol, 20 equiv), 1-chloro-4-fluorobenzene (294 mg, 240 μL, 2.3 mmol), and benzene (1 mL) were heated at 150 °C under N_2 for 36 h to give Ir(ttp)C_6H_4(p-F) (**2d**;[10d] 7.2 mg, 0.008 mmol, 67%).

(d). Reaction with 1,4-Dichlorobenzene. Ir(ttp)(CO)Cl (10.7 mg, 0.012 mmol), K_2CO_3 (32 mg, 0.23 mmol, 20 equiv), 1,4-dichlorobenzene (340 mg, 2.3 mmol), and benzene (1 mL) were heated at 150 °C under N_2 for 3.5 days to give Ir(ttp)C_6H_4(p-Cl) (**2e**;[10d] 11.2 mg, 0.012 mmol, 100%).

(e). Reaction with Methyl 4-Chlorobenzoate. Ir(ttp)(CO)Cl (10.2 mg, 0.011 mmol), K_2CO_3 (30.5 mg, 0.22 mmol, 20 equiv), methyl 4-chlorobenzoate (376 mg, 2.2 mmol), and benzene (1 mL) were heated at 150 °C under N_2 for 46 h to give Ir(ttp)C_6H_4(p-C(O)Me) (**2f**;[10d] 7.7 mg, 0.008 mmol, 70%) and Ir(ttp)CH_3 (0.3 mg, 0.0003 mmol, 3%).

(f). Reaction with 4-Chlorobenzaldehyde. Ir(ttp)(CO)Cl (10.8 mg, 0.012 mmol), K_2CO_3 (32 mg, 0.023 mmol, 20 equiv), 4-chlorobenzaldehyde (328 mg, 2.3 mmol), and benzene (1 mL) were heated at 150 °C under N_2 for 22 h. PPh_3 (30.6 mg, 0.12 mmol, 10 equiv) was then added under N_2, and the reaction mixture was further heated at 120 °C for 1 h to give Ir(ttp)(PPh_3)C_6H_4(p-CHO) (**2g**;[10e] 9.9 mg, 0.008 mmol, 69%) and a trace of Ir(ttp)(PPh_3)C(O)C_6H_4(p-Cl) (**2k**; <1%).

(g). Reaction with 4-Chlorobenzotrifluoride. Ir(ttp)(CO)Cl (10.6 mg, 0.011 mmol), K_2CO_3 (33 mg, 0.23 mmol, 20 equiv), 4-chlorobenzotrifluoride (414 mg, 2.3 mmol), and benzene (1 mL) were heated at 150 °C under N_2 for 7 days to give Ir(ttp)C_6H_4(p-CF_3) (**2h**;[10d] 7.9 mg, 0.008 mmol, 68%). PhCl (0.4%) was also detected by GC-MS analysis using 4-chlorotoluene as an internal standard (GC5 in the Supporting Information).

(h). Reaction with 4-Chlorobenzonitrile. Ir(ttp)(CO)Cl (10.6 mg, 0.011 mmol), K_2CO_3 (32 mg, 0.23 mmol, 20 equiv), 4-chlorobenzonitrile (315.6 mg, 2.3 mmol, 200 equiv), and benzene (1 mL) were heated at 150 °C under N_2 for 1 day. PPh_3 (30.1 mg, 0.11, 10 equiv) was then added under N_2, and the reaction mixture was further heated at 120 °C for 1 h to give Ir(ttp)(PPh_3)C_6H_4(p-CN) (**2i**; 7.3 mg, 0.006 mmol, 51%).

Monitoring the Intermediates in Base-Promoted Ph−Cl Cleavage by Ir(ttp)(CO)Cl in Benzene-d_6. (a). With K_2CO_3. Ir(ttp)(CO)Cl (4.6 mg, 0.005 mmol), K_2CO_3 (13.7 mg, 0.10 mmol, 20 equiv), PhCl (28 mg, 25 μL, 0.25 mmol, 50 equiv), and benzene-d_6 (0.5 mL) were heated in a sealed NMR tube under vacuum at 200 °C. The course of the reaction was monitored by ^1H NMR spectroscopy. Only Ir(ttp)H was observed as an intermediate in the course of the reaction. After 4 days, all Ir(ttp)(CO)Cl and Ir(ttp)H were consumed to give Ir(ttp)Ph, Ir(ttp)(p-C_6H_4)Ir(ttp), and Ir(ttp)CH_3 in 91%, 1%, and 1% NMR yields, respectively. No Ir(ttp)C_6D_5 was formed, as the proton signal ratio pyrrole H:meta phenyl H of Ir−Ph is 8:2 in the isolated product of Ir(ttp)Ph by column chromatography.

(b). With Cs_2CO_3. Ir(ttp)(CO)Cl (4.3 mg, 0.005 mmol), Cs_2CO_3 (30 mg, 0.09 mmol, 20 equiv), PhCl (26 mg, 24 μL, 0.23 mmol, 50 equiv), and benzene-d_6 (0.5 mL) were heated in a Teflon screw capped NMR tube at 150 °C. The course of the reaction was monitored by ^1H NMR spectroscopy. Ir(ttp)H and $[Ir(ttp)]_2$ were observed as the intermediates. After 18 days, the reaction was incomplete, as unreacted Ir(ttp)H was still observed. The reaction mixture was further heated at 200 °C for 60 h to form Ir(ttp)Ph, Ir(ttp)(p-C_6H_4)Ir(ttp), and

Ir(ttp)CH_3 in 71%, 6%, and 4% NMR yields, respectively (Table S1 and Figure S1 in the Supporting Information).

Relative Reactivities of Possible Iridium Porphyrin Intermediates in Ph−Cl Cleavage. (a). Reaction with Ir(ttp)$^-$. Ir(ttp)$^-$[K(18-crown-6)]$^+$ was prepared quantitatively from the reaction of Ir(ttp)H (4.6 mg, 0.005 mmol) with KOH (3.0 mg, 0.05 mmol, 10 equiv) and 18-crown-6 ether (4.3 mg, 0.016 mmol, 3 equiv) in THF (0.5 mL) at 150 °C under N_2 for 45 min in a Teflon screw capped NMR tube.[10c] THF was then dried under vacuum, and PhCl (30.0 mg, 27 μL, 0.27 mmol, 50 equiv) and benzene-d_6 (0.5 mL) were added under N_2. The reaction mixture was then heated in a sealed NMR tube at 200 °C, and the reaction was monitored by ^{1}H NMR spectroscopy. After 4 days, all Ir(ttp)$^-$[K(18-crown-6)]$^+$ was consumed to give Ir(ttp)Ph (2.5 mg, 0.003 mmol, 50%), which was isolated by column chromatography.

(b). Reaction with Ir(ttp)H.[10b] Ir(ttp)H (4.8 mg, 0.006 mmol), PhCl (31.3 mg, 28 μL, 0.28 mmol, 50 equiv), and benzene-d_6 (0.5 mL) were heated in a sealed NMR tube at 200 °C, and the reaction was monitored by ^{1}H NMR spectroscopy. After 4 days, all Ir(ttp)H was consumed to form Ir(ttp)Ph (3.5 mg, 0.004 mmol, 67%) and Ir(ttp)(CO)Cl (0.2 mg, 0.0002 mmol, 4%), which were isolated by column chromatography.

(c). Reaction with [Ir(ttp)]$_2$. [Ir(ttp)]$_2$[10b] was prepared quantitatively from the reaction of Ir(ttp)H (4.5 mg, 0.005 mmol) with (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO; 0.9 mg, 0.006 mmol) in benzene (0.5 mL) in a Teflon screw capped NMR tube under N_2. The solvent was removed under vacuum, and PhCl (29.4 mg, 26.5 μL, 0.26 mmol, 50 equiv) and benzene-d_6 (0.5 mL) were added into the tube under N_2. The reaction mixture was then heated in a sealed NMR tube under vacuum at 200 °C, and the reaction was monitored by ^{1}H NMR spectroscopy. After 5 h, all [Ir(ttp)]$_2$ was consumed to form Ir(ttp)Ph (2.8 mg, 0.003 mmol, 57%) and Ir(ttp)(CO)Cl (0.2 mg, 0.0002 mmol, 4%), which were isolated by column chromatography. Ir(ttp)-(*p*-C_6H_4)Ir(ttp) (3%, NMR yield) was also formed, and its yield was estimated by using the yield of Ir(ttp)Ph and the pyrrole proton ratio Ir(ttp)Ph:Ir(ttp)(*p*-C_6H_4)Ir(ttp) in the crude reaction mixture by ^{1}H NMR spectroscopy.

Reaction of Ir(ttp)(PPh$_3$)Cl with KOH. (a). In Sealed NMR Tube. Ir(ttp)(PPh$_3$)Cl (**1c**; 4.5 mg, 0.004 mmol), KOH (4.4 mg, 0.08 mmol), and benzene-d_6 (0.5 mL) were heated in a sealed NMR tube at 200 °C for 4 h to form Ir(ttp)(PPh$_3$)OH (**7b**; δ(pyrrole) 8.80) and Ir(ttp)-(PPh$_3$)H (**4b**; δ(pyrrole) 8.74 ppm) in 96% and 2% NMR yields, respectively, using residual benzene as an internal standard. The reaction mixture was further heated for 13 h to form Ir(ttp)(PPh$_3$)H (**7b**) in ∼33% NMR yield. Residual water (∼1.7 equiv) was observed by ^{1}H NMR spectroscopy. Characterization data for Ir(ttp)(PPh$_3$)OH (**7b**) are as follows. ^{1}H NMR (C_6D_6, 300 MHz): δ −9.35 (s, 1 H, $^3J_{PH}$ = 7.5 Hz), 2.40 (s, 12 H), 4.29 (dd, 6 H, $^3J_{PH}$ = 8.9 Hz, $^3J_{HH}$ = 8.7 Hz), 6.36 (t, 6 H, $^3J_{HH}$ = 7.2 Hz), 6.56 (t, 3 H, $^3J_{HH}$ = 7.1 Hz), 7.17 (d, 4 H, $^3J_{HH}$ = 7.2 Hz), 7.35 (d, 4 H, $^3J_{HH}$ = 7.5 Hz), 7.82 (d, 4 H, $^3J_{HH}$ = 7.5 Hz), 7.92 (d, 4 H, $^3J_{HH}$ = 7.5 Hz), 8.81 (s, 8 H). ^{13}C NMR (C_6D_6 , 100 MHz): δ 21.2, 122.8, 126.7, 126.9 (*d*, $^1J_{PC}$ = 17 Hz), 131.0, (d, $^3J_{PC}$ = 9 Hz), 131.7, 133.8, 134.9, 136.7, 139.5, 142.9. One set of porphyrin's tolyl meta carbon signals and PPh$_3$'s ipso and para phenyl carbon signals were obscured by residual benzene carbon signals. ^{31}P NMR (C_6D_6, 122 MHz): δ −34.9 (d, $^3J_{PC}$ = 7.2 Hz) (Figure S2e in the Supporting Information). HRMS (FABMS): calcd for [$C_{66}H_{52}N_4OPIr$]$^+$ ([M]$^+$) *m*/*z* 1140.3502, found *m*/*z* 1140.3545.

(b). In Teflon Screw Capped Tube. Ir(ttp)(PPh$_3$)Cl (**1c**; 5.2 mg, 0.004 mmol), KOH (5.0 mg, 0.10 mmol), and benzene-d_6 (0.5 mL) were heated in a Teflon screw capped tube at 200 °C for 30 min to form Ir(ttp)(PPh$_3$)H (**4b**; δ(pyrrole H) 8.75 ppm), Ir(ttp)(PPh$_3$)OH (**7b**; δ(pyrrole H) 8.81 ppm), and unreacted Ir(ttp)(PPh$_3$)Cl (**1c**; δ(pyrrole H) 8.84 ppm) in 31%, 17%, and 29% NMR yields, respectively, by ^{1}H NMR spectroscopy using a quantified amount of tetrakis(trimethylsilyl)-silane (TMS_4Si) as an internal standard. The reaction mixture was subjected to HRMS analysis, and no (Ph$_3$P)(ttp)IrOIr(ttp)(PPh$_3$), (Ph$_3$P)-(ttp)IrOIr(ttp), or (ttp)IrOIr(ttp) was detected.

Reaction of Ir(ttp)(PPh$_3$)H with KOH (20 equiv). Ir(ttp)H (**4a**; 4.7 mg, 0.005 mmol), PPh$_3$ (1.4 mg, 0.005 mmol), KOH (6.1 mg, 0.11 mmol), and benzene-d_6 (0.5 mL) were added to a Teflon screw capped NMR tube under N_2. The reaction mixture changed to reddish brown instantaneously at room temperature to generate in situ Ir(ttp)(PPh$_3$)H (**4b**) quantitatively.[10c] The reaction mixture containing Ir(ttp)(PPh$_3$)H and KOH was then heated in a sealed NMR tube at 200 °C for 3 days. Ir(ttp)(PPh$_3$)H was stable on heating and in basic media, as it was recovered in 98% NMR yield.

Reaction of PPh$_3$ with Possible Oxygen Sources (Table S2 in the Supporting Information). The experimental procedure of the reaction of PPh$_3$ with oxygen in air is described as a typical example.

(a). With Oxygen in Air. PPh$_3$ (8.6 mg, 0.033 mmol) and benzene (1 mL) were heated in air (∼3 equiv of O_2) at 200 °C in a Teflon screw capped tube in 12 h. The reaction mixture was dried under vacuum. A quantified amount of TMS_4Si was added as an internal standard, and benzene-d_6 was further added for ^{1}H NMR spectroscopy. No P(O)Ph$_3$ was formed (<1% NMR yield), and unreacted PPh$_3$ was recovered in 89% NMR yield. The number of moles of O_2 in air (*n*) was calculated by using the ideal gas equation: $n = (PV)/(RT) \times 21\%$, where P = 101325 N m^{-2}, $V \approx 13 \times 10^{-6}$ m^3, R = 8.314 J K^{-1} mol^{-1}, T = 298 K, and 21% is the percentage of O_2 in air. Thus, *n* is found to be 0.11 mmol (∼3 equiv with reference to PPh$_3$).

(b). With H_2O. PPh$_3$ (8.6 mg, 0.033 mmol), water (3.0 μL, 0.16 mmol, 5 equiv), and benzene (1 mL) were heated in a Teflon screw capped tube under N_2 at 200 °C in 12 h. No P(O)Ph$_3$ was formed (<1% NMR yield), and unreacted PPh$_3$ was recovered in 94% NMR yield.

(c). With KOH. PPh$_3$ (8.7 mg, 0.033 mmol), KOH (37.2 mg, 0.66 mmol, 20 equiv), and benzene (1 mL) were heated in a Teflon screw capped tube under N_2 at 200 °C in 12 h. No P(O)Ph$_3$ was formed (<1% NMR yield), and unreacted PPh$_3$ was recovered in 75% NMR yield.

(d). With H_2O_2. PPh$_3$ (17.5 mg, 0.067 mmol), H_2O_2 (30% solution, 15.1 mg, 13.6 μL, 0.1334 mmol of H_2O_2 (2 equiv)), and benzene (2 mL) were heated in a Teflon screw capped tube under N_2 at 200 °C. The reaction was complete in 1 h, as determined by thin-layer chromatography. P(O)Ph$_3$ (**9**) was formed in 86% NMR yield.

(e). Without Oxygen Sources. PPh$_3$ (8.6 mg, 0.033 mmol) and benzene (1 mL) were heated in a Teflon screw capped tube under N_2 at 200 °C in 12 h. No P(O)Ph$_3$ was formed (<1% NMR yield), and unreacted PPh$_3$ was recovered in 75% NMR yield.

*Reaction of Ir(ttp)(CO)Cl (**1a**) with KOH and Excess PPh$_3$ (5 equiv).* Ir(ttp)(CO)Cl (10 mg, 0.011 mmol), KOH (12.1 mg, 0.22 mmol), PPh$_3$ (14.2 mg, 0.054 mmol), and benzene-d_6 (1 mL) were heated in a Teflon screw capped tube under N_2 for 3 h, and the reaction mixture changed from deep red to deep brown. Tetrakis(trimethylsilyl)-methane (TMS_4Si) in a quantitative amount was added into the reaction mixture as an internal standard. Ir(ttp)(PPh$_3$)H (**4b**) and P(O)Ph$_3$ (**9**) were formed in 42% and 21% NMR yields, respectively, with reference to Ir(ttp)(CO)Cl added. Unreacted PPh$_3$ was recovered in 70% yield with reference to PPh$_3$ added (Figure S3a in the Supporting Information). The formation of P(O)Ph$_3$ in the reaction was confirmed by ^{1}H NMR spectroscopy using the authentic sample of P(O)Ph$_3$. Characterization data for P(O)Ph$_3$ formed in the reaction are as follows. ^{1}H NMR (C_6D_6, 400 MHz): δ(*o*-phenyl H) 7.75 (dd, $^3J_{PH}$ = 12.0 Hz, $^3J_{HH}$ = 7.6 Hz). The P(O)Ph$_3$'s phenyl meta and para protons are obscured by the excess PPh$_3$'s phenyl meta and para protons. ^{31}P NMR (C_6D_6, 162 MHz): 24.9 (br) (Figure S3b in the Supporting Information). HRMS (ESIMS): calcd for [$C_{18}H_{15}OPNa$]$^+$ ([M + Na]$^+$): *m*/*z* 301.0753, found *m*/*z* 301.0750.

*Reaction of Ir(ttp)(CO)Cl (**1a**) with Excess PPh$_3$ (5 equiv) without Base.* Ir(ttp)(CO)Cl (**1a**; 10.3 mg, 0.011 mmol), PPh$_3$ (14.6 mg, 0.056 mmol), and benzene-d_6 (1 mL) were heated in a Teflon screw capped tube under N_2 for 12 h. TMS_4Si in a quantitative amount was added to

the reaction mixture as an internal standard. Ir(ttp)(PPh_3)Cl was formed quantitatively, and P(O)Ph_3 was observed in ~5% NMR yield, with reference to Ir(ttp)(CO)Cl added. Unreacted PPh_3 and P(O)Ph_3 were observed in 69% and 1% NMR yields, respectively, with reference to PPh_3 added. The formation of P(O)Ph_3 was presumably due to the oxidation of PPh_3 with residual O_2 catalyzed by iridium porphyrin species.

Reaction of [Ir(ttp)]$_2$/PPh_3 in Benzene-d_6. (a). Without Addition of KOH. Ir(ttp)H (**4a**; 3.8 mg, 0.004 mmol), (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO; 1.0 mg, 0.005 mmol), and benzene (0.5 mL) were mixed in a Teflon screw capped NMR tube under N_2 to form [Ir(ttp)]$_2$ quantitatively.[10a] The reaction mixture was dried under vacuum for a few hours to remove the solvent, unreacted TEMPO, and TEMPOH coproduct. PPh_3 (1.2 mg, 0.004 mmol) and benzene-d_6 (0.5 mL) were added into the tube under N_2. The reaction mixture changed to red instantaneously. Reddish brown precipitate was formed, probably due to the formation of insoluble [Ir(ttp)(PPh_3)]$_2$. The reaction mixture was then sealed in an NMR tube under vacuum. As shown by ^{1}H NMR spectroscopy, all unreacted [Ir(ttp)]$_2$ was consumed, and scarce Ir(ttp)(PPh_3)OH (**7b**) was observed. The reaction mixture was then heated at 200 °C for 4 h to yield Ir(ttp)(PPh_3)H (**4b**) and Ir(ttp)(PPh_3)OH (**7b**) in trace amounts (<5% NMR yields) estimated by adding TMS_4Si (0.000 29 mmol, from standard TMS_4Si/benzene solution) as the internal standard (Table S3 and Figure S4a in the Supporting Information). Residual water (~1 equiv) was estimated by ^{1}H NMR spectroscopy.

(b). With Addition of KOH (20 equiv). [Ir(ttp)]$_2$ was prepared in a Teflon screw capped NMR tube similar to the procedure as shown in (a). PPh_3 (1.2 mg, 0.004 mmol), KOH (5.0 mg, 0.088 mmol), and benzene-d_6 (0.5 mL) were added into the NMR tube under N_2. The reaction mixture was then sealed in the NMR tube under vacuum. The reaction mixture changed to red instantaneously. Reddish brown precipitate was formed, probably due to the formation of insoluble [Ir(ttp)(PPh_3)]$_2$. As shown by ^{1}H NMR spectroscopy, all unreacted [Ir(ttp)]$_2$ was consumed, and scarce Ir(ttp)(PPh_3)OH (**7b**) was observed. The reaction mixture was heated at 200 °C for 4 h to yield Ir(ttp)(PPh_3)H (**4b**) and Ir(ttp)(PPh_3)OH (**7b**) in 15% and 16% NMR yields, respectively. The yield of Ir(ttp)(PPh_3)OH (**7b**) was estimated by adding TMS_4Si (0.000 29 mmol, from standard TMS_4Si/benzene solution) as the internal standard. The yield of Ir(ttp)(PPh_3)H (**4b**) was estimated by using the yield of Ir(ttp)(PPh_3)OH (**7b**) and the ratio of porphyrin's pyrrole proton signals for Ir(ttp)(PPh_3)H and Ir(ttp)(PPh_3)OH (1.0:1.1) (Table S3 and Figure S4b in the Supporting Information). Residual water (~1 equiv) was estimated by ^{1}H NMR spectroscopy.

Reaction of Sulfuryl Chloride with Benzene. SO_2Cl_2 (25.0 mg, 15 μL, 0.19 mmol) and benzene (1 mL) were heated in a Teflon screw capped tube under N_2 at 200 °C in 90 min. The PhCl formed (20%) was quantified by GC-MS analysis using 4-chlorotoluene as an internal standard (GC3 in the Supporting Information). The product yield was calculated with reference to the number of Cl atoms in SO_2Cl_2. The formation of PhCl was confirmed by the commercial sample of PhCl.

Reaction of Sulfuryl Chloride with PhCl. SO_2Cl_2 (25.0 mg, 15 μL, 0.19 mmol) and excess PhCl (1 mL) were heated in a Teflon screw capped tube under N_2 at 200 °C for 90 min. 1,4-$Cl_2C_6H_4$ (6%), 1,2-$Cl_2C_6H_4$ (4%), 1,3-$Cl_2C_6H_4$ (<1%), and chloro-substituted biphenyls (1%) were detected by GC-MS analysis using 4-chlorotoluene as an internal standard, in which the product yields were calculated with reference to the number of Cl atoms in SO_2Cl_2 (GC4 in the Supporting Information). The formation of 1,4-$Cl_2C_6H_4$ and 1,2-$Cl_2C_6H_4$ in the reaction was confirmed by the commercial samples, whereas the formation of 1,3-$Cl_2C_6H_4$ and chloro-substituted biphenyls was confirmed by the GC-MS library.

Reaction of [Ir(ttp)]$_2$ with PhCl. [Ir(ttp)]$_2$ was prepared quantitatively from the reaction of Ir(ttp)H (5.6 mg, 0.006 mmol) with (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO; 1.1 mg, 0.007 mmol) in benzene (0.5 mL) in a Teflon screw capped tube.[10a] The solvent, unreacted TEMPO, and TEMPOH coproduct were removed under vacuum. PhCl (1 mL) was then added under N_2. The reaction mixture was heated in a Teflon screw capped tube at 200 °C for 30 min. The organic fraction was collected under vacuum by a cold trap with liquid N_2 and was then subjected to GC-MS analysis. 1,4-$Cl_2C_6H_4$ (2% yield, with reference to Ir(ttp) monomer used) was detected using 4-chlorotoluene as an internal standard (GC8 in the Supporting Information). The crude products were purified by column chromatography in a single fraction to yield Ir(ttp)Ph (2.4 mg, 0.003 mmol, 39%) and Ir(ttp)(CO)Cl (<0.1 mg, 0.000 01 mmol, ~1%). Ir(ttp)(*p*-C_6H_4)Ir(ttp) (4%, NMR yield) was also formed, and its yield was estimated by using the isolated yield of Ir(ttp)Ph and the pyrrole proton ratio Ir(ttp)Ph:Ir(ttp)(*p*-C_6H_4)Ir(ttp) in the reaction mixture by ^{1}H NMR spectroscopy.

Reaction of Ir(ttp)(CO)Cl with 1,4-Dichlorobenzene (1 equiv) and K_2CO_3. Ir(ttp)(CO)Cl (11.0 mg, 0.012 mmol), K_2CO_3 (33 mg, 0.24 mmol, 20 equiv), 1,4-dichlorobenzene (1.8 mg, 0.012 mmol, 1 equiv), and benzene (1 mL) were heated in a Teflon screw capped tube at 200 °C in 7 h under N_2 to give Ir(ttp)C_6H_4(*p*-Cl) (1.1 mg, 0.001 mmol, 9%), Ir(ttp)CH_3 (0.1 mg, 0.0002 mmol, 1%), and Ir(ttp)(*p*-C_6H_4)Ir(ttp) (3%, NMR yield) by column chromatography. Unreacted Ir(ttp)H (7%, NMR yield) was also recovered. The NMR yields of products were estimated by using the isolated yield of Ir(ttp)C_6H_4(*p*-Cl) and the pyrrole proton ratio Ir(ttp)H:Ir(ttp)(*p*-C_6H_4)Ir(ttp):Ir(ttp)C_6H_4(*p*-Cl) in the crude reaction mixture by ^{1}H NMR spectroscopy.

Reaction of Ir(ttp)Ph with [Ir(ttp)]$_2$. Ir(ttp)H (**4a**; 8.4 mg, 0.010 mmol), (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO; 1.5 mg, 0.010 mmol), and benzene (1 mL) were mixed in a Teflon screw capped tube under N_2 to form [Ir(ttp)]$_2$ quantitatively.[10a] The reaction mixture was dried under vacuum for a few hours to remove the solvent, unreacted TEMPO, and TEMPOH coproduct. Ir(ttp)Ph (10.6 mg, 0.011 mmol, 1.2 equiv) was added into the tube under N_2, and the reaction mixture was further heated at 200 °C under N_2 for 30 min. No Ir(ttp)(*p*-C_6H_4)Ir(ttp) was observed in the crude reaction mixture by ^{1}H NMR spectroscopy. Unreacted Ir(ttp)Ph (8.2 mg, 0.009 mmol, 79%) was isolated by column chromatography.

Competition Reactions with Para-Substituted ArCl and PhCl. The experimental procedure of the competition reaction between 4-chloroanisole and PhCl with Ir(ttp)(CO)Cl and K_2CO_3 is described as an example.

(a). 4-Chloroanisole. Ir(ttp)(CO)Cl (8.5 mg, 0.009 mmol), K_2CO_3 (25 mg, 0.18 mmol, 20 equiv), 4-chloroanisole (131.1 mg, 113 μL, 0.92 mmol, 100 equiv), PhCl (103.5 mg, 93.5 μL, 0.92 mmol, 100 equiv), and benzene (1 mL) were heated in a Teflon scew capped tube at 150 °C under N_2 for 35 h. The kinetic ratio Ir(ttp)C_6H_4(*p*-OMe):Ir(ttp)Ph was estimated to be 4.39:1.00 by ^{1}H NMR spectroscopy by taking the ratio of the meta aryl proton signal ratio of (ttp)Ir−Ar. The crude product was then purified by column chromatography over alumina with CH_2Cl_2/hexane (1/1) as eluent to yield Ir(ttp)C_6H_4(*p*-OMe) (5.9 mg, 0.006 mmol, 66%), Ir(ttp)Ph (1.7 mg, 0.002 mmol, 19%) (ratio 3.5:1), and Ir(ttp)CH_3 (0.2 mg, 0.0003 mmol, 3%).

(b). 1-Fluoro-4-chlorobenzene. Ir(ttp)(CO)Cl (8.6 mg, 0.009 mmol), K_2CO_3 (25.7 mg, 0.19 mmol, 20 equiv), 1-fluoro-4-chlorobenzene (121.4 mg, 99 μL, 0.93 mmol, 100 equiv), PhCl (104.7 mg, 95 μL, 0.93 mmol, 100 equiv), and benzene (1 mL) were heated at 150 °C under N_2 for 38 h. The kinetic ratio Ir(ttp)C_6H_4(*p*-F):Ir(ttp)Ph was found to be 3.29:1.00. Ir(ttp)C_6H_4(*p*-F) (4.4 mg, 0.005 mmol, 50%), Ir(ttp)Ph (1.4 mg, 0.001 mmol, 16%) (ratio 3.1:1), and Ir(ttp)CH_3 (0.3 mg, 0.0003 mmol, 4%) were isolated.

(c). 1,4-Dichlorobenzene. Ir(ttp)(CO)Cl (10.8 mg, 0.012 mmol), K_2CO_3 (32 mg, 0.23 mmol, 20 equiv), 1,4-dichlorobenzene (171.7 mg, 1.17 mmol, 100 equiv), PhCl (131.5 mg, 119 μL, 1.17 mmol, 100 equiv), and benzene (1 mL) were heated at 200 °C under N_2 for 60 h. The kinetic ratio Ir(ttp)C_6H_4(*p*-Cl):Ir(ttp)Ph was found to be 5.74:1.00 by averaging the original kinetic ratio (11.48:1) due to the presence of two

C−Cl bonds in 1,4-dichlorobenzene for reaction. Ir(ttp)C_6H_4(*p*-Cl) (8.0 mg, 0.008 mmol, 70%), Ir(ttp)Ph (0.9 mg, 0.001 mmol, 8%) (ratio 8.8:1), Ir(ttp)(*p*-C_6H_4)Ir(ttp) (3%, NMR yield), and Ir(ttp)CH_3 (3%, NMR yield) were isolated. The NMR yields of Ir(ttp)(*p*-C_6H_4)Ir(ttp) and Ir(ttp)CH_3 were estimated by using the isolated yield of Ir(ttp)C_6H_4(*p*-Cl) and the ratio of pyrrole proton signals Ir(ttp)C_6H_4(*p*-Cl):Ir(ttp)(*p*-C_6H_4)Ir(ttp):Ir(ttp)CH_3 in the crude products.

(d). 4-Chlorobenzonitrile. Ir(ttp)(CO)Cl (10.3 mg, 0.011 mmol), K_2CO_3 (31 mg, 0.22 mmol, 20 equiv), 4-chlorobenzonitrile (153.3 mg, 1.11 mmol, 100 equiv), PhCl (125.4 mg, 113 μL, 1.11 mmol, 100 equiv), and benzene (1 mL) were heated at 200 °C under N_2 for 3.5 days. PPh_3 (29.2 mg, 0.11 mmol, 10 equiv) was then added under N_2, and the reaction mixture was further heated at 120 °C for 30 min. The kinetic ratio Ir(ttp)(PPh_3)C_6H_4(*p*-CN):Ir(ttp)(PPh_3)Ph (**2l**) was found to be 29.8:1.00. Ir(ttp)(PPh_3)C_6H_4(*p*-CN) (4.9 mg, 0.004 mmol, 40%) and a trace of Ir(ttp)(PPh_3)Ph were isolated.

■ ASSOCIATED CONTENT

Supporting Information. Text, tables, and figures giving the sequence of reactions monitored by ^{1}H NMR spectroscopy, supplementary experimental results, GC-MS analysis, and ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Ir(ttp)CH_3 is likely formed via the base-promoted reduction of CO ligand of Ir(ttp)(CO)Cl by the Ir(ttp)H intermediate. See ref 10a for the proposed mechanism of Ir(ttp)CH_3 formation.

(12) The nitrile group in 4-bromobenzonitrile can coordinate strongly to iridium(III) porphyrin species. Indeed, **1a** has been reported to react with *p*-tolunitrile (*p*-TolCN) to yield stable, coordinatively saturated Ir(ttp)(*p*-TolCN)Cl.[10e]

(13) Water-soluble iridium(III) porphyrin, $[Ir(tspp)(H_2O)_2]^{3-}$ (tspp = tetrakis(*p*-sulfonatophenyl)porphyrinato dianion) has been reported to undergo thermodynamically favorable ligand substitution with CH_3OH to form $[Ir(tspp)(CH_3OH)_2]^{3-}$. See: Bhagan, S.; Sarkar, S.; Wayland, W. W. *Inorg. Chem.* **2010**, *49*, 6734–6739. We proposed that the nonbulky aldehydic carbonyl group (−CHO) can also bind strongly to the iridium center of Ir(ttp)Ar.

(14) The benzylic C−H bond of toluene (88.5 kcal mol^{-1}) and the aldehydic C−H bond of benzaldehyde (88.7 kcal mol^{-1}) are weaker than the Ar−Cl bond of chlorobenzene (95.5 kcal mol^{-1}). See: Luo, Y.-R. *Comprehensive Handbook of Chemical Bond Energies*; CRC Press: Boca Raton, FL, 2007. Thus, competitive cleavage between benzylic/aldehydic C−H bonds and Ar−Cl bonds can occur.

(15) Cs_2CO_3 has been adopted for the successful observations of iridium porphyrin intermediates in base-promoted Ar−Br cleavage by **1a**.[10d] Thus, it is also used in base-promoted Ph−Cl cleavage to observe the intermediates formed.

(16) A lower loading of PhCl (50 equiv) was adopted to (1) minimize the obscuration of proton signals of the iridium porphyrin intermediates by the intense and broad proton signals of a large excess of PhCl (when 200 equiv of PhCl was added) and (2) reduce the rate of consumption of iridium porphyrin intermediates for successful observation.

(17) Ir(ttp)(CO)Cl (**1a**) rather than Ir(ttp)Cl was isolated after column chromatography. The source of CO is unclear, similar to the situation of **1a** being isolated from the reaction of $[IrCOD)Cl]_2$ (COD =

1,5-cyclooctadiene) with 5,10,15,20-tetrakis(*p*-tolyl)porphyrin in refluxing *p*-xylene, even though no CO was introduced into the reaction mixture. See: Yeung, S. K.; Chan, K. S. *Organometallics* **2005**, *24*, 6426–6430.

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(19) A trace of residual water (~0.2−2 equiv with reference to iridium porphyrin, $\delta(H_2O)$ ~0.4 ppm) remained in benzene-d_6 even though benzene-d_6 had been distilled over sodium and stored in a Teflon screw capped Schlenk tube under N_2. Adventitious water was also inevitable. For the reported chemical shift of H_2O in benzene-d_6, see: Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176–2179.

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(21) The pK_a value of Ir(por)−H is generally higher than that of H_2O, as Ir(oep)H (oep = octaethylporphyrin dianion) remains unreacted in NaOH/ethanol solution to give the soluble $Ir(oep)^-$. Thus, the protonation of $Ir(por)^-$ with water would be favorable to give Ir(por)H. See: Ogoshi, H.; Setsune, J.-I.; Yoshida, Z.-I. *J. Organomet. Chem.* **1978**, *159*, 317–328.

(22) The low yield of **4b** formed was due to neither the formation of $(Ph_3P)(ttp)IrOIr(ttp)(PPh_3)$ (which was not detected by HRMS) nor the decomposition of $Ir(ttp)(PPh_3)H$ (which remained unreacted under basic conditions at 200 °C). Probably, the coordinatively saturated **7b**, or the $[Ir^{II}(ttp)(PPh_3)]_2$ intermediate formed, is less reactive and decomposes considerably at 200 °C prior to the subsequent reaction to give **4b**.

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(24) KOH, residual water, H_2O_2, and O_2 are possible oxygen sources for the oxidation of PPh_3 to form $P(O)Ph_3$. As control experiments, only H_2O_2 was shown to efficiently promote the oxidation of PPh_3 to $P(O)Ph_3$ (Table S2 in the Supporting Information). Hence, any $P(O)Ph_3$ detected can be attributed to the reaction of H_2O_2 with PPh_3.

(25) (a) H_2O_2 has been reported to react with PPh_3 to give $P(O)Ph_3$. See: Abu-Omar, M. M.; Espenson, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 272–280. (b) In the quantitative reduction of Mo(VI) and W(VI) complexes by OH^- to give Mo(V) and W(V) complexes, the coproduct H_2O_2 is trapped by PPh_3 to give $P(O)Ph_3$ in 50% yield. See: Cervilla, A. C.; Pérez-Plá, F.; Llopis, E.; Piles, M. *Dalton Trans.* **2004**, 1461–1465.

(26) No precipitate was observed after the reaction. The side products from the decomposition of the proposed $[Ir(ttp)(PPh_3)]_2$ remain unclear.

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(29) As a control experiment, SO_2Cl_2 (as a source of $Cl^\bullet$) reacted with excess C_6H_6 at 200 °C in 90 min to give PhCl in 20% yield.

(30) As a control experiment, SO_2Cl_2 (as a source of $Cl^\bullet$) reacted with excess PhCl at 200 °C in 90 min to give 1,4-$Cl_2C_6H_4$ (6%), 1,2-$Cl_2C_6H_4$ (4%), 1,3-$Cl_2C_6H_4$ (<1%), and various dichlorinated biaryls (2%). 1,4-$Cl_2C_6H_4$ and 1,2-$Cl_2C_6H_4$ are generated more than 1,3-$Cl_2C_6H_4$, since all the substituents in monosubstituted arenes are ortho and para directing.[28]

(31) With K_2CO_3, **1a** reacted with excess 1,4-dibromobenzene and 1,4-diiodobenzene to yield $Ir(ttp)C_6H_4(p\text{-}X)$ (X = Br, I), which further reacted with **1a** to yield **3**.[10e] The K_2CO_3-promoted conversion of 1,4-dichlorobenzene to **3** most likely follows analogous reaction pathways.

(32) Three lines of evidence support the ISAE mechanism of Ar−X cleavage by $[Ir(ttp)]_2$: (1) higher Ir(ttp)Ar:Ir(ttp)X ratio due to the $X^\bullet$ leakage, (2) the detection of PhX coproducts formed by the reaction of $X^\bullet$ with benzene solvent, and (3) the rate enhancement in Ar−X cleavage by all the electron-donating and -withdrawing para substituents in ArX, as shown by the V-shaped Hammett plots in the competition experiments. See ref 10d for further details.

(33) The reaction of $Cl^\bullet$ with excess $(p\text{-}CF_3)C_6H_4Cl$ to yield dichloro-substituted benzotrifluorides (p-CF_3-$C_6H_3Cl_2$) could not be excluded. However, detection of $(p\text{-}CF_3)C_6H_3Cl_2$ in the reaction mixture by GC-MS analysis was not carried out.

(34) Only 1,4-$Cl_2C_6H_4$ was detected from the reaction mixture without 1,2-$Cl_2C_6H_4$. It is proposed that the low concentration of $Cl^\bullet$ generated favors the regioselective attack of $Cl^\bullet$ at the less sterically hindered para Ar−H of PhCl to yield only 1,4-$Cl_2C_6H_4$ due to the steric strain.

(35) No $Ir(ttp)C_6H_4(p\text{-}Cl)$[10d] was observed in the reaction of **1a** with PhCl (200 equiv) and K_2CO_3 in benzene (Table 1, entries 4 and 5) or in the reaction of $[Ir(ttp)]_2$ with neat PhCl (eq 8) by ^1H NMR spectroscopy; only **3** was isolated. The reason is unclear. We proposed that the electrophilic, σ-withdrawing $Ir^{III}(ttp)$ group promotes the radical ipso substitution of $Ir^{III}(ttp)C_6H_4(p\text{-}Cl)$ by the more nucleophilic $Ir^{II}(ttp)$ metalloradical to rapidly yield **3**, whereas the π-donating p-Cl in 1,4-$Cl_2C_6H_4$ leads to a slower reaction of ipso attack by $Ir^{II}(ttp)$ to give $Ir(ttp)C_6H_4(p\text{-}Cl)$.

(36) A V-shaped Hammett plot was also obtained when using the Hammett constants σ^+_p (Figure S5b in the Supporting Information).

(37) For the details of the stabilization of Ir(ttp)−cyclohexadienyl radical by *para*-FG, see the Supporting Information in ref 10d.