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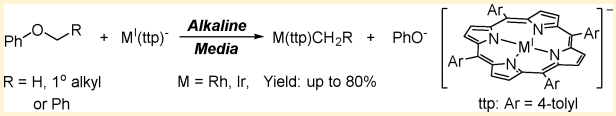
Alkyl Carbon–Oxygen Bond Cleavage of Aryl Alkyl Ethers by Iridium–Porphyrin and Rhodium–Porphyrin Complexes in Alkaline Media

Chen Chen and Kin Shing Chan*

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

Supporting Information

ABSTRACT: Alkyl C–O bond cleavage in aryl alkyl ethers was achieved with Rh(ttp)Cl (**1a**; ttp = 5,10,15,20-tetrakis(*p*-tolyl)-porphyrinato dianion) together with competitive alkyl C–H bond activation in alkaline media. In contrast, selective alkyl C–O bond cleavage occurred with the iridium–porphyrin Ir(ttp)(CO)Cl (**1b**)/KOH. Mechanistic investigations indicate the coexistence of $M^{I}(ttp)^{-}$ and $M_2^{II}(ttp)_2$ (M = Rh, Ir) under basic conditions. With a weaker Rh(ttp)–Rh(ttp) bond, $Rh^{II}(ttp)\cdot$ metalloradical exists in an appreciable amount to cleave the alkyl C–H bond, competing with the alkyl C–O bond cleavage via $Rh^{I}(ttp)^{-}$. In contrast, the more nucleophilic $Ir^{I}(ttp)^{-}$ cleaves the alkyl C–O bond exclusively.



INTRODUCTION

The carbon–oxygen (C–O) bond is among the most common linkages in nature.[1] Recently, C–O bond cleavage has drawn much attention due to its application in natural product synthesis and biomass utilization.[2] Ether cleavage or O-dealkylation is primarily used as a deprotection method of the hydroxyl group in synthetic chemistry,[3] such as the debenzylation of PhOBn with H_2 catalyzed by Pd/C.[4]

Etheric C–O cleavage is usually a Brønsted- or Lewis-acid-catalyzed process by activating the C–O bond with protonation or coordination.[5,6] In the absence of acids, extremely basic conditions are needed, such as in the case of the [1,2]-Wittig rearrangement of ethers to give secondary or tertiary alcohols in the presence of alkyl lithium compounds.[7]

The transition-metal-mediated C–O bond activation of ethers has been widely investigated due to the importance of this fundamental step both in catalytic and stoichiometric transformations.[5,8] The $C(sp^2)$–O bond activation of aryl ethers by transition-metal complexes via oxidative addition has been systematically studied,[8,9] while the $C(sp^3)$–O bond activation is less commonly encountered.[10] Ittel and Tolman reported the alkyl C–O bond activation of anisole via oxidative addition by a $Fe^{0}(dmpe)_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$) intermediate in 1978 (Scheme 1A).[11] Later, Milstein and co-workers discovered that an electrophilic Pd(II) or Ni(II) species was likely to function as a Lewis acid to promote the alkyl C–O bond cleavage of a bisphosphinated aryl methyl ether (Scheme 1B).[8] A unique C–O cleavage mode induced by C–H oxidative addition with an iridium PCP-type pincer ligand has been disclosed by Goldman and co-workers (Scheme 1C).[12] Recently, Gryko and co-workers reported a nucleophilic substitution of (allyloxy)arenes with reduced Vitamine B_{12} species (Co^{I}) to cleave the alkyl C–O bond (Scheme 1D).[13] However, this method is limited to allyl aryl ethers. Aside from the above strategies for $C(sp^3)$–O bond activation, other methods on etheric $C(sp^3)$–O bond cleavage have seldom been reported.[14]

Group 9 $M^{I}(por)^{-}$ (M = Rh, Ir; por = porphyrinato dianion) anions show "super nucleophilic"[15] character toward alkyl iodide, lactones, and epoxides in these substitution reactions.[16] The typical method to generate $M^{I}(por)^{-}$, however, requires an anaerobic atmosphere and expensive $NaBH_4$ to reduce $M^{III}(por)Cl$.[16] Recently, our group has developed a more convenient method by using KOH as the reducing agent to generate $M^{I}(por)^{-}$ in aerobic conditions. $M^{I}(por)^{-}$ is in equilibria with $M^{II}(por)\cdot$ and M(por)H under basic conditions.[17] Both Rh(ttp)Cl and Ir(ttp)(CO)Cl in the presence of KOH can cleave the C–O bond of CH_3–OH to give $M(ttp)CH_3$. $Ir^{I}(ttp)^{-}$ is the proposed nucleophile to displace hydroxide in CH_3–OH, while Rh(ttp)H undergoes σ-bond metathesis with CH_3–OH to give $Rh(ttp)CH_3$.[18] Wayland has also demonstrated the water-soluble $Ir^{I}(tspp)^{-}$ (tspp = tetra(*p*-sulfonatophenyl)porphyrinato dianion) catalyzed the C–O bond cleavage of CD_3OD with Ir(tspp)D to give $Ir(tspp)CD_3$.[19] However, the activation of the reactive O–H bond competed with the alkyl C–O bond in the reaction process.[18,19] In aryl alkyl ethers, the PhO^{-} is a better leaving group than OH^{-} in CH_3–OH, and the $C(sp^2)$–O bond is inert toward nucleophilic substitution;[20] the alkyl $C(sp^3)$–O bond is therefore more likely to be selectively substituted by $M^{I}(por)^{-}$ (M = Rh, Ir) anions. As far as we know, such a metal-centered anion-complex-mediated nucleophilic substitution of aryl alkyl ethers with the displacement of phenoxide under alkaline conditions remains unusual. In addition, the generated M(por)alkyls may serve as intermediates for alkyl C–O bond hydrogenolysis through M(por)–C bond hydrogenation with water.[21] Herein, we report the KOH-promoted alkyl C–O bond activation of

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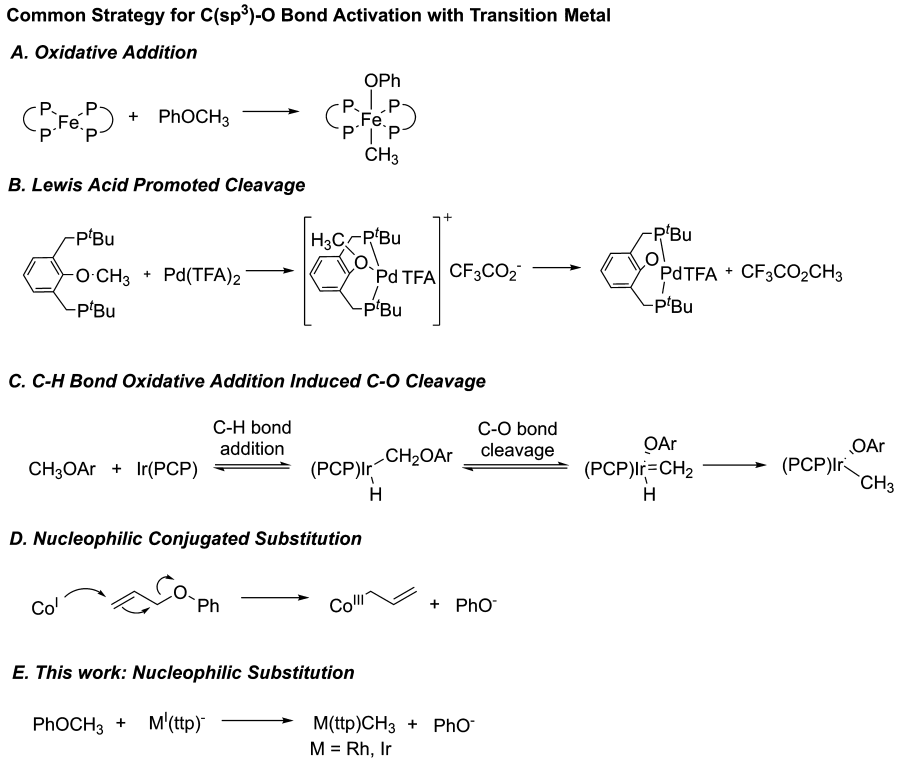
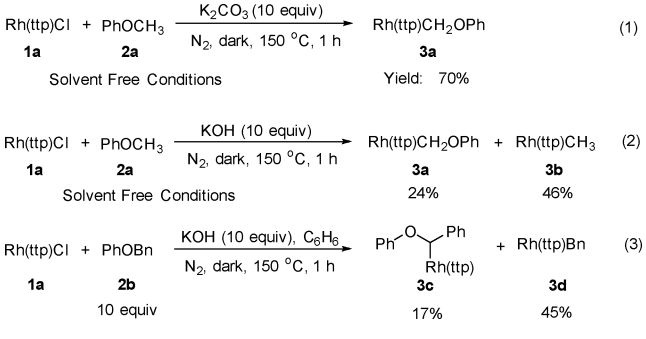
Scheme 1. Transition-Metal-Mediated C(sp^3)−O Bond Cleavage



aryl alkyl ethers with rhodium−porphyrin and iridium−porphyrin complexes to yield the corresponding M(por)alkyls via the proposed $M^I(por)^-$ (M = Rh, Ir)-anion-mediated displacement of phenoxide.

RESULTS AND DISCUSSION

Alkyl C−O Bond Cleavage of Aryl Alkyl Ethers by Rhodium−Porphyrin Complexes. On the basis of the optimal reaction conditions in the reported C−O bond cleavage of methanol with Rh(ttp)Cl (**1a**),[18b] 10 equiv of K_2CO_3 at 150 °C and solvent-free conditions were applied for the investigation of the alkyl C−O bond cleavage of anisole (**2a**). However, only alkyl C−H bond activation (CHA) occurred to give 70% yield of **3a** (eq 1). Compounds with



similar structures have been reported in our previous work.[22] When the stronger base of KOH was employed, the alkyl C−O bond-activation (COA) product was achieved (**3b**) in 46% yield as well as alkyl C−H activation product (**3a**) in 24% yield (eq 2). A similar result was obtained when the more reactive benzyl phenyl ether (**2b**) was employed with **3c** and **3d**, obtained in 17% and 45% yields, respectively (eq 3). This alkyl C−O bond cleavage is distinct, since the C−O bonds of ethers are usually stable under basic conditions.[6] Figures 1,2 illustrate the molecular structures of **3a** and **3c**. The collection and

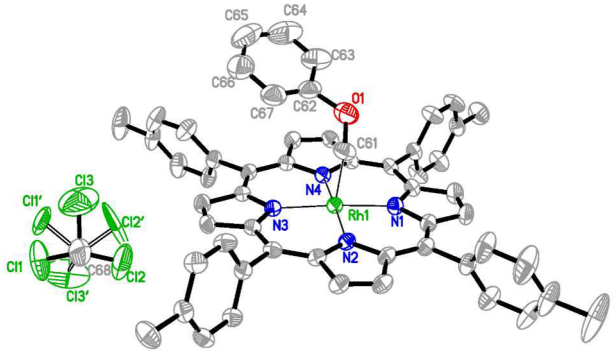


Figure 1. ORTEP drawing of $Rh(ttp)CH_2OPh{\cdot}0.5CHCl_3$ (**3a**·0.5$CHCl_3$), with 50% probability displacement ellipsoids. **3a** selected bond length (Å): Rh(1)−C(61): 2.031(6).

processing parameters of single-crystal data for **3a** and **3c** are shown in the Supporting Information.

On the basis of the reported mechanism on the alkyl C−H bond activation with $Rh^{II}(por)\cdot$[23] and the alkyl C−O bond activation with $Rh^I(por)^-$,[16c,17a] Scheme 2 depicts the proposed mechanism for the reaction between aryl alkyl ethers with Rh(por) complexes. In basic media, Rh(ttp)Cl (**1a**) undergoes ligand substitution with OH^- to form Rh(ttp)OH, which then generates $Rh^{II}_2(ttp)_2$ and H_2O_2 through reductive dimerization.[24] $Rh^{II}_2(ttp)_2$ reacts with excess OH^- to yield an equilibrium mixture of $Rh^I(ttp)^-$ and Rh(ttp)OH.[25,17a] $Rh_2(ttp)_2$ dissociates into a $Rh^{II}(ttp)\cdot$ metalloradical, which then undergoes bimetalloradical C−H bond activation to give Rh(ttp)alkyl and Rh(ttp)H, analogous to that of CH_4 and toluene (Scheme 2, Pathway A).[23] Alternatively, the nucleophilic $Rh^I(ttp)^-$ undergoes

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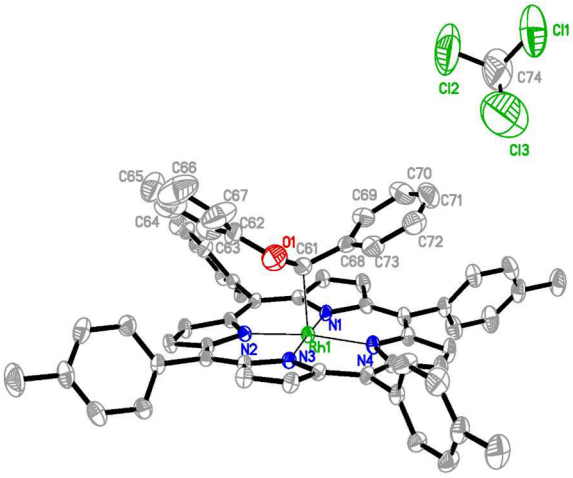
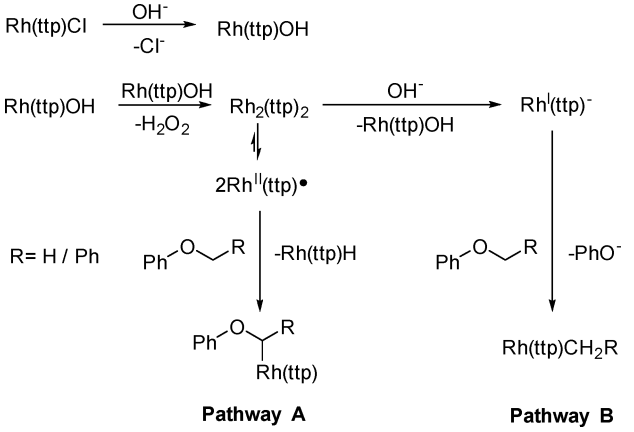


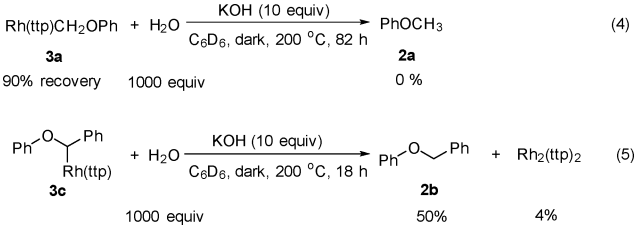
Figure 2. ORTEP drawing of Rh(ttp)CHPh(OPh)·$CHCl_3$ (**3c**·$CHCl_3$), with 50% probability displacement ellipsoids. **3c** selected bond length (Å): Rh(1)−C(61): 2.059(6).

Scheme 2. Proposed Mechanism for COA and CHA of Aryl Alkyl Ethers with Rhodium−Porphyrin Complexes



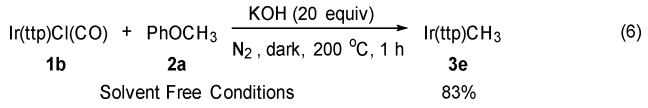
parallel nucleophilic substitution at the alkyl carbon center to cleave the C−O bond (Scheme 2, Pathway B).[16c,17a]

Since rhodium−porphyrin alkyls undergo hydrolysis with water to give the corresponding alkanes,[26] the hydrolysis of **3a** and **3c** in basic conditions was further examined for the regeneration of **2a** and **2b** from **3a** and **3c**, respectively. Rh(ttp)CH_2OPh (**3a**) was found to be very stable toward hydrolysis at 200 °C for 82 h without any anisole (**2a**) formed (eq 4). The hydrolysis rate of **3c**, being a Rh(ttp)-2°



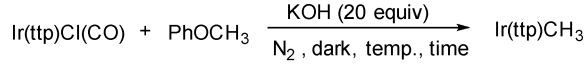
alkyl, was much faster to regenerate 50% of benzyl phenyl ether (**2b**) in 18 h (eq 5). However, the hydrolysis rate was still too slow compared with the formation rate of CHA product **3c**. Thus, it was difficult to eliminate C−H bond-activation product through hydrolysis in the reaction process.

Alkyl C−O Bond Cleavage of Aryl Alkyl Ethers by Iridium−Porphyrin Complexes. With the partial success of alkyl C−O bond cleavage between aryl alkyl ethers and Rh(ttp)Cl (**1a**)/KOH, we then examined the chemistry with more nucleophilic $Ir^{I}(ttp)^{-}$, generated from the reaction of Ir(ttp)(CO)Cl (**1b**) with KOH, in order to achieve selective alkyl C−O bond cleavage. We adapted the reaction conditions of the C−O cleavage of MeOH[18a] by using 20 equiv of KOH at 200 °C in solvent-free conditions to investigate the alkyl C−O bond cleavage of anisole (**2a**) with Ir(ttp)(CO)Cl (**1b**). To our delight, the alkyl C−O bond activation of anisole proceeded selectively to give Ir(ttp)CH_3 (**3e**) with a high yield of 83% (eq 6). With this initial success, the reaction conditions were further optimized.



Reaction Conditions Optimization. *Temperature Effect.* The reaction temperature was first optimized. At 120 °C, the reaction required 4 h to give Ir(ttp)CH_3 (**3e**) in 55% yield (Table 1, entry 1). When the temperatures were raised to

Table 1. Temperature Effect[a]



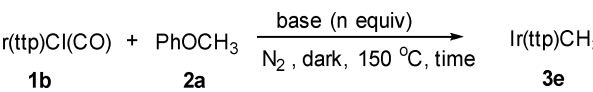
entry	temp/°C	time/h	yield/%
1	120	4	55
2	150	2	87
3	180	1	87
4	200	1	83

[a]Ir(ttp)(CO)Cl (**1b**) (0.010 mmol) with 1.0 mL of anisole.

150−200 °C, the reactions took 1 to 2 h to complete to give similar yields of **3e** (Table 1, entries 2 to 4). Therefore, 150 °C was chosen as the optimal temperature to allow milder conditions.

Base and Base-Loading Effects. Without any base, Ir(ttp)(CO)Cl (**1b**) did not react with anisole (**2a**) at 150 °C for 14 h with quantitative recovery of **1b** (Table 2, entry 1). When a weak base of K_2CO_3 was employed, Ir(ttp)CH_3 (**3e**) was only obtained in 6% yield (Table 2, entry 3). Thus, KOH was found to be the optimal base (Table 2, entry 2). When 10 equiv of KOH was added, Ir(ttp)Me (**3e**) was obtained in 82% yield at 150 °C for 2 h (Table 2, entry 5). A lower KOH

Table 2. Base and Base-Loading Effects[a]



entry	base	*n*	time/h	yield/%
1[b]	KOH	0	14	0
2	KOH	20	2	87
3	K_2CO_3	20	10	6
4	KOH	5	2	71
5	KOH	10	2	82
6	KOH	30	2	81

[a]Ir(ttp)(CO)Cl (**1b**) (0.010 mmol) with 1.0 mL of anisole. [b]Ir(ttp)(CO)Cl (**1b**) recovered quantitatively.

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loading of 5 equiv resulted in a 71% yield of Ir(ttp)CH_3 (**3e**), also in 2 h (Table 2, entry 4). With higher loadings of KOH at 20 and 30 equiv, the reaction efficiency was similar in rates and yields (Table 2, entries 2, 5, and 6). Therefore, 10−30 equiv of KOH were all effective, and 10 equiv of KOH was used in further studies.

Substrate Scope. Various primary alkyl aryl ethers were then investigated. Alkyl C−O bond cleavage occurred selectively to give high product yields with Ir(ttp)(CO)Cl (**1b**)/KOH (Table 3, entries 1 to 4). The reaction with low melting-point

Table 3. Substrate Scope for Alkyl C−O Bond Cleavage[a]

Ir(ttp)Cl(CO) (**1b**) + PhOR (**2a-e**) → KOH (10 equiv), N_2, dark, 150 °C, time → Ir(ttp)R (**3e-h**)

entry	R	time/h	yield/%
1	Me (**2a**)	2	82 (**3e**)
2	Et (**2c**)	2	87 (**3f**)
3	^{n}Pr (**2d**)	2	85 (**3g**)
4[b]	Bn (**2b**)	2	82 (**3h**)
5[c]	allyl (**2e**)	4	Ir(ttp)^{n}Pr (**3g**): 35%

[a]Ir(ttp)(CO)Cl (**1b**) (0.010 mmol) with 1 mL of substrate in solvent-free conditions. [b]BnOPh (**2b**) (10 equiv) in benzene solvent. [c]Ir(ttp)$CH_2CH_2CH_2OPh$ (**3i**) (20%) was also isolated.

solid PhOBn (**2b**) (mp = 39−41 °C) (10 equiv) was conducted in benzene solvent and completed in 2 h to afford Ir(ttp)Bn (**3h**) in 82% yield (Table 3, entry 4). When allyl

Table 4. Alkyl C−O Bond Cleavage of PhOBn(*p*-FG) in Benzene[a]

Ir(ttp)Cl(CO) (**1b**) + PhOBn(*p*-FG) (**2f-h**, 10 equiv) → KOH (10 equiv), C_6H_6, N_2, dark, 150 °C, 2 h → Ir(ttp)Bn(*p*-FG) (**3j-l**)

entry	FG	yield[b]/%
1	OMe (**2f**)	71 (**3j**)
2	Cl (**2g**)	66 (**3k**)
3	CF_3 (**2h**)	68 (**3l**)

[a]Ir(ttp)(CO)Cl (**1b**) (0.010 mmol) with 1.0 mL of benzene. [b]NMR yield calculated using diphenylmethane as the internal standard.

phenyl ether was employed, 35% of Ir(ttp)^{n}Pr (**3g**) was isolated together with 20% yield of Ir(ttp)$CH_2CH_2CH_2OPh$ (**3i**) formed from the 1,2-insertion with Ir(ttp)H.[19,27] (Table 3, entry 5) As for the 2° alkyl phenyl ether of isopropyl phenyl ether, no Ir(ttp)alkyl was observed. The nucleophilic substitution of the isopropyl group is likely too sterically demanding. Ir(ttp)Et (**3f**) was further characterized by single-crystal X-ray diffraction, and its structure is shown in Figure 3.

When the para-substituted aryl phenyl ethers PhOBn(*p*-FG) (FG = OMe, Cl, CF_3) (**2f−h**) reacted with Ir(ttp)(CO)Cl (**1b**), Ir(ttp)Bn(*p*-FG) was achieved in moderate to high yields from 66−71% (Table 4, entries 1 to 3) with high chemoselectivity. The substrate-bearing aryl C−Cl bond (**2g**) underwent selective alkyl C−O bond cleavage without interference from C−Cl bond activation, which has been reported by our group before.[28]

Mechanistic Investigation. Like the Rh(ttp) analogue, the four Ir(ttp) species: $Ir^I(ttp)^-$, $Ir^{II}(ttp)\cdot$, Ir(ttp)H, and Ir(ttp)-OH have been reported to exist in equilibria in basic conditions as depicted in Scheme 3.[16a,28,29] Ir(ttp)(CO)Cl (**1b**) undergoes

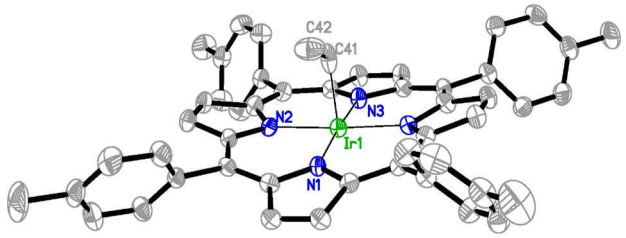
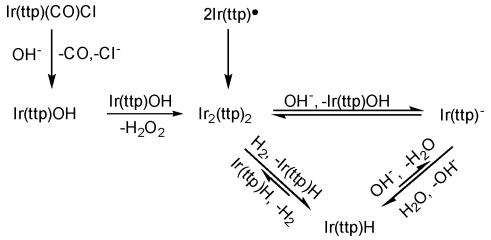


Figure 3. ORTEP drawing of Ir(ttp)CH_2CH_3 (**3f**), with 50% probability displacement ellipsoids. **3f** selected bond length (Å): Ir(1)−C(41): 1.969(12).

Scheme 3. Equilibria between Iridium−Porphyrin Intermediates under the Optimized Reaction Conditions



ligand dissociation and ligand substitution with OH^- to give Ir(ttp)OH, which undergoes fast reductive dimerization to generate $Ir_2(ttp)_2$ and H_2O_2 at 150 °C.[28] $Ir_2(ttp)_2$ will be reduced by excess OH^- to give $Ir^I(ttp)H^-$,[29] and it can be protonated by residual water to form Ir(ttp)H.[16a] Therefore, $Ir_2(ttp)_2$ (**1d**), $Ir^I(ttp)^-$, and Ir(ttp)H (**1c**) are the three dominant possible intermediates coexisting in the reaction mixture. The reactivity of the three possible intermediates toward alkyl C−O bond cleavage were then examined individually.

Ir(ttp)H (**1c**) reacted with anisole at 150 °C for 2 h to give only trace amounts of Ir(ttp)Me (**3e**) and the aromatic CHA product **3m** (Scheme 4A). The reaction of Ir(ttp)H (**1c**) with PhOBn (**2b**) gave the benzylic C−H activation product **3n** in around 60% yield (Scheme 4A), similar to the benzylic CHA of $PhCH_3$ by Ir(ttp)H to afford Ir(ttp)CH_2Ph.[30] Alkyl C−O bond cleavage of both anisole (**2a**) and PhOBn (**2b**) does not occur with Ir(ttp)H. Therefore, Ir(ttp)H (**1c**) is unlikely to be the intermediate to cleave the alkyl C−O bond.

$Ir_2(ttp)_2$ (**1d**) reacted with anisole (**2a**) to give trace amounts of Ir(ttp)Me (**3e**) (Scheme 4B). The reaction of $Ir_2(ttp)_2$ (**1d**) with PhOBn (**2b**) gave the benzylic C−H bond-activation product (**3n**) in 40% yield in 2 h with no Ir(ttp)Bn (**3h**) formed (Scheme 4B). Thus, $Ir_2(ttp)_2$ (**1d**) is also not the intermediate for alkyl C−O bond cleavage.

$Ir^I(ttp)^-$ was prepared independently from the deprotonation of Ir(ttp)H with KOH[18a] and reacted with **2a** and **2b**, respectively, to give the corresponding C−O cleavage products in 54 and 22% yield in 2 h (Scheme 4C). The results strongly support that $Ir^I(ttp)^-$ is the intermediate to cleave the alkyl C−O bond.

To gain further understanding on the stereoelectronic nature of the alkyl C−O bond-cleavage process, the competition experiments between equal molar mixtures of PhOMe (**2a**), PhOEt (**2c**), and PhO^{n}Pr (**2d**) were conducted (Table 5, entries 1 to 3). The relative reactivity followed the trend: **2a**/**2c**/**2d** = 1:1.7:3.2, which is not consistent with a typical S_N2 process. The reaction between Ir(ttp)Me (**3e**) and PhO^{n}Pr (**2d**) gave 5% of Ir(ttp)^{n}Pr (**3g**) with mostly 95% yield recovery of **3e**; thus, the

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Scheme 4. Reactivity of Three Possible Intermediates toward Alkyl C−O Bond Cleavage

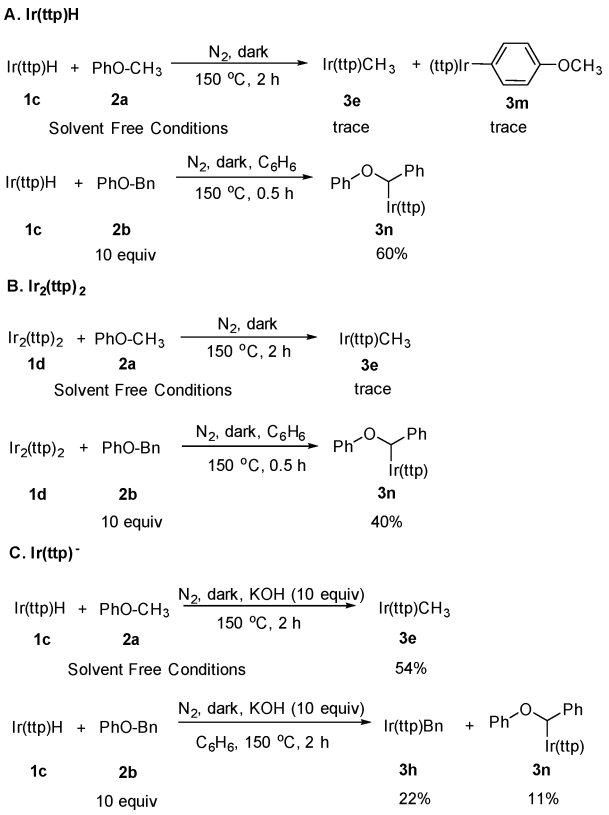
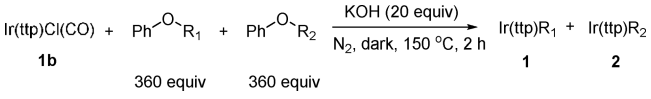


Table 5. Relative Reactivity of Primary Alkyl Phenyl Ethers[a]



entry	R_1	R_2	1 yield: 2 yield[b]	total yield (%)
1	Me	Et	**3e**/**3f** = 1:1.7	63
2	Me	^{n}Pr	**3e**/**3g** = 1:3.2	79
3	Et	^{n}Pr	**3f**/**3g** = 1:1.8	71

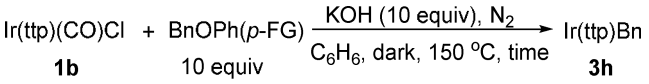
[a]Ir(ttp)(CO)Cl (**1b**), 0.010 mmol. [b]Ratio calculated according to the ^{1}H NMR of the crude mixture.

ratios measured were the kinetic ones. We do not fully understand the underlying reason for the reactivity trend at this stage.

In the reaction process, the starting material Ir(ttp)(CO)Cl (**1b**) was completely consumed rapidly within the first 10 min, while the formation of product was much slower and took about 2 h. Therefore, the C−O bond-cleavage step is the rate-determining step in the multistepwise reaction. Competition reactions between para-substituted PhOBn(*p*-FG) (**2f**−**h**) and PhOBn (**2b**) were conducted to investigate on the electronic nature of the C−O cleavage step. The reaction between Ir(ttp)Bn (**3h**) and PhOBn(*p*-CF_3) (**2h**) under the optimized reaction conditions gave quantitative recovery of Ir(ttp)Bn (**3h**) and without any potential Ir(ttp)Bn(*p*-CF_3) (**3l**) formed, so the product ratios measured were the kinetic ratios (eq S1). Then, competition experiments between an equimolar mixture of PhOBn(*p*-FG) (FG = OMe, Cl and CF_3) (**2f**−**h**) and PhOBn (**2b**) with Ir(ttp)(CO)Cl (**1b**) and KOH in benzene were conducted and yielded the product ratio between Ir(ttp)$CH_2C_6H_4$(*p*-FG) and Ir(ttp)CH_2Ph. The calculated ratios were close to 1 (Table S1). Thus, no significant reactivity difference was observed and para-substituents on the benzyl group have little electronic effect on the alkyl C−O bond-cleavage process.

Therefore, further efforts were taken for the reaction with BnOPh(*p*-FG) (FG = OMe, CN) (**2i**, **2j**) to compare the reaction times of each substrate for a qualitative understanding of the electronic effect on the alkyl C−O bond-cleavage rate. BnOPh(*p*-CN) (**2j**), with a strong electron-withdrawing group, showed the fastest reaction rate, taking 0.5 h to complete, while the reaction of BnOPh(*p*-OMe) (**2i**) required 3 h. (Table 6, entries 1 to 3) On the basis of these findings, an S_N2-like transition state is deduced for the C−O cleavage process (Figure 4). The $Ir^I(ttp)^-$ anion attacks the benzylic carbon with a heterolytic C−O cleavage. The incipient phenoxide is stabilized by an electron-withdrawing group, such as a CN group in the transition state to result in a shorter reaction time.

Table 6. Comparison of Reaction Time of Ir(ttp)(CO)Cl with BnOPh(*p*-FG)[a]



entry	FG	time (h)	yield[b] (%)
1	OMe (**2i**)	3	71
2	H (**2b**)	2	82
3	CN (**2j**)	0.5	81

[a]Ir(ttp)(CO)Cl (**1b**) (0.010 mmol) with 1.0 mL of benzene. [b]Yield calculated using diphenylmethane as the internal standard.

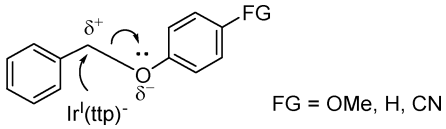


Figure 4. Alkyl C−O bond cleavage via an S_N2-like transition state.

Comparison of Rhodium−Porphyrins and Iridium−Porphyrins in Alkyl C−O Bond Cleavage. Alkyl C−O bond cleavage with Ir(ttp)(CO)Cl (**1b**)/KOH was achieved with high chemoselectivity. However, C−H bond activation occurred parallel with alkyl C−O bond activation in the rhodium case. We rationalize that $Ir^I(ttp)^-$ is more nucleophilic than $Rh^I(ttp)^-$ in basic conditions, allowing it to more easily substitute the alkyl C−O bond because of the higher pK_a of Ir(ttp)H (~15)[16a] compared with that of Rh(ttp)H (~11).[31] Alternatively, with a stronger Ir−Ir bond (~24 kcal/mol),[32] $Ir^{II}_2(ttp)_2$ cannot dissociate into $Ir^{II}(ttp)\cdot$ as fast and extensively as the rhodium−porphyrin analogue (Rh−Rh bond: ~16 kcal/mol)[33] to activate the C−H bond.

CONCLUSION

The alkyl C−O bond cleavage of aryl alkyl ethers was successfully achieved by Rh(ttp)Cl (**1a**) and Ir(ttp)(CO)Cl (**1b**) in basic media. Competitive alkyl C−H bond activation occurred with Rh(ttp)Cl (**1a**), while selective alkyl C(sp^3)−O bond cleavage was achieved exclusively with Ir(ttp)(CO)Cl (**1b**). $M^I(ttp)^-$ (M = Rh, Ir) was proposed to be the intermediate to cleave the alkyl C(sp^3)−O bond via nucleophilic substitution.

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EXPERIMENTAL SECTION

Unless otherwise noted, all of the reagents were purchased from commercial suppliers and directly used without further purification. Hexane was distilled from anhydrous calcium chloride. Benzene was distilled over sodium under nitrogen. All reactions were protected from light by wrapping with aluminum foil. The reaction in Teflon screw-capped pressure tubes were heated in heating blocks on heaters and monitored by thin-layer chromatography (TLC), whereas the reactions in sealed NMR tubes were heated in GC ovens. TLC was performed on precoated silica gel 60 F_{254} plates. Rh(ttp)Cl (**1a**),[34] Ir(ttp)Cl(CO) (**1b**),[35] Ir(ttp)H (**1c**),[30] and Ir_2(ttp)$_2$ (**1d**)[30] have been characterized and were prepared according to the literature process. Para-substituted benzyl phenyl ethers: BnOPh(*p*-FG) (FG = OMe, CN) (**2i**, **2j**) and PhOBn(*p*-FG) (FG = OMe, Cl, CF_3) (**2f**, **2g**, **2h**) have also been characterized and were prepared according to the literature method.[36] Silica gel (Merck, 70−230 and 230−400 mesh) was used in column chromatography.

^{1}H NMR spectra were recorded on a Bruker AV400 instrument at 400 MHz. Chemical shifts were referenced with the residual solvent protons in $CDCl_3$ (δ 7.26 ppm) and C_6D_6 (δ 7.15 ppm). ^{13}C NMR spectra were recorded on a Bruker AV400 (100 MHz) or a Bruker AV700 (176 MHz) spectrometer with reference to $CDCl_3$ (δ 77.1 ppm) as an internal standard. ^{19}F NMR spectra were recorded on a Bruker AV400 instrument at 376 MHz with reference to fluorobenzene (δ −113.15 ppm) as an internal standard. Chemical shifts (δ) are reported as parts per million (ppm) in δ scale downfield from TMS. Coupling constants (J) are reported in Hertz (Hz). High-resolution mass spectrometry (HRMS) was performed on a Bruker SolariX 9.4 T FTICR MS instrument in electrospray ionization (ESI) mode using MeOH/CH_2Cl_2 (1/1) as the solvent or on Bruker Autoflex speed MALDI-TOF instrument using a *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) matrix and CH_2Cl_2 as the solvent.

Single crystals were grown using a vapor diffusion method. The compound was dissolved in a solvent in a small open vial. The vial was then placed into a larger vial containing a precipitant solvent, and the outer vial was then sealed.

Reaction of Rh(ttp)Cl and Anisole with K_2CO_3. Rh(ttp)Cl (**1a**; 11.3 mg, 0.014 mmol), K_2CO_3 (18.8 mg, 0.14 mmol) and anisole (**2a**; 1.0 mL) were added in a Teflon screw-capped tube. The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated at 150 °C for 1 h until reaction completion. Excess anisole was removed by vacuum distillation. The residue was purified by pipet column chromatography on silica gel with CH_2Cl_2/hexane (1:7) to give the first fraction as Rh(ttp)CH_2OPh (**3a**; 9.2 mg, 0.0105 mmol) in 72% yield. R_f: 0.65 (hexane/CH_2Cl_2: 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ −1.74 (d, 2 H, $^2J_{Rh-H}$ = 3.4 Hz, CH_2), 2.70 (s, 12 H), 3.65−3.70 (m, 2 H), 6.37−6.45 (m, 3 H), 7.51−7.56 (m, 8 H), 7.98−8.03 (m, 8 H), 8.69 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.8, 51.9 ($^1J_{Rh-C}$ = 29.5 Hz), 112.2, 120.0, 122.6, 127.6, 127.7, 127.9, 131.7, 134.3, 134.4, 137.4, 139.6, 143.5, 154.0. HRMS (m/z) (MALDI-MS): $[M]^+$ calcd for $C_{55}H_{43}N_4RhO$ 878.2486; found 878.2450.

Reaction of Rh(ttp)Cl and Anisole with KOH. Rh(ttp)Cl (**1a**; 9.5 mg, 0.012 mmol), KOH (6.3 mg, 0.011 mmol), and anisole (**2a**; 1.0 mL) were added in a Teflon screw-capped tube. The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 150 °C for 1 h until reaction completion. The two products were purified by column chromatography on silica gel eluting with CH_2Cl_2/hexane (1:1). Rh(ttp)Me (**3b**)[23a] in 46%, and Rh(ttp)CH_2OPh (**3a**) in 24% were achieved.

Independent Synthesis of Rh(ttp)CHPh(OPh). Rh(ttp)Cl (**1a**; 9.7 mg, 0.012 mmol), K_2CO_3 (16.2 mg, 0.12 mmol) and PhOBn (**2b**; 19.2 mg, 0.11 mmol) were added in benzene (1.0 mL). The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 150 °C for 1 h until reaction completion. Benzene solvent was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel eluting with CH_2Cl_2/hexane (1:8) to give red solid product Rh(ttp)CHPh(OPh) (**3c**; 5.2 mg, 0.0054 mmol) in 45% yield. R_f: 0.77 (hexane/CH_2Cl_2: 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz, 314 K) δ −0.30 (d, 1 H, $^2J_{Rh-H}$ = 4.1 Hz, CH), 2.71 (s, 12 H), 3.20 (brs, 2 H), 4.26 (d, 2 H, $^3J_{H-H}$ = 8.1 Hz), 6.04 (t, 2 H, $^3J_{H-H}$ = 7.6 Hz), 6.39−6.49 (m, 4 H), 7.50−7.56 (m, 8 H), 7.98 (m, 8 H), 8.64 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 63.9 ($^1J_{Rh-C}$ = 29.9 Hz), 113.0, 119.7, 122.6, 124.7, 125.8, 127.4, 127.5, 127.9, 131.4, 134.0, 134.2, 137.1, 139.5, 139.8, 143.3, 143.4, 153.4. HRMS (m/z) (ESI-MS): $[M]^+$ calcd for $C_{61}H_{47}N_4RhO$ 954.2799; found 954.2784.

Reaction of Rh(ttp)Cl and Benzyl Phenyl Ether with KOH. Rh(ttp)Cl (**1a**; 9.7 mg, 0.012 mmol), KOH (7.2 mg, 0.12 mmol) and PhOBn (**2b**; 19.2 mg, 0.11 mmol) were added in benzene (1.0 mL). The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 150 °C for 1 h until reaction completion. Benzene solvent was removed by vacuum distillation. Anisole (5 μL) was added as the internal standard to calculate the NMR yields of products. Rh(ttp)Bn (**3d**)[23a] in 16%, and Rh(ttp)CHPh(OPh) (**3c**) in 41% were achieved.

Hydrolysis of Rh(ttp)CH_2OPh in Alkaline Media. Rh(ttp)-CH_2OPh (**3a**; 0.88 mg, 0.001 mmol), KOH (0.56 mg, 0.01 mmol), H_2O (18 μL, 1 mmol), and benzene-d_6 (0.5 mL) were added in a Teflon screw-capped NMR tube. The mixture was degassed for three freeze−pump−thaw cycles and then sealed in the NMR tube under vacuum. It was heated at 200 °C in the dark for 82 h. It was monitored with ^{1}H NMR spectroscopy, and the NMR yields were measured. Rh(ttp)CH_2OPh was recovered in 90% yield without any organic product formed.

Hydrolysis of Rh(ttp)CHPh(OPh) in Alkaline Media. Rh(ttp)-CHPh(OPh) (**3c**; 0.95 mg, 0.001 mmol), KOH (0.56 mg, 0.01 mmol), H_2O (18 μL, 1 mmol), and benzene-d_6 (0.5 mL) were added in a Teflon screw-capped NMR tube. The mixture was degassed for three freeze−pump−thaw cycles and then sealed in the NMR tube under vacuum. It was heated at 200 °C in the dark for 18 h. It was monitored with ^{1}H NMR spectroscopy, and the NMR yields were measured. PhOBn (**2b**) was formed in 50% yield.

Reaction of Ir(ttp)(CO)Cl and Anisole with KOH (20 Equiv) at 200 °C. Ir(ttp)(CO)Cl (**1b**; 9.7 mg, 0.010 mmol), KOH (11.9 mg, 0.21 mmol), and anisole (**2a**; 1.0 mL) were added in a Teflon screw-capped tube. The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 200 °C for 1 h until reaction completion. Excess anisole was removed by vacuum distillation. The residue was purified by pipet column chromatography on silica gel with CH_2Cl_2/hexane (1:1) to give Ir(ttp)Me[18a] (**3e**; 7.3 mg, 0.0083 mmol) in 83% yield. Ir(ttp)Me (**3e**): R_f: 0.70 (hexane/CH_2Cl_2: 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ −6.28 (s, 3 H, CH_3), 2.68 (s, 12 H), 7.50−7.53 (m, 8 H), 7.98−8.03 (m, 8 H), 8.51 (s, 8 H).

Reaction of Ir(ttp)(CO)Cl and Anisole with KOH (20 Equiv) at 120 °C. Ir(ttp)(CO)Cl (**1b**; 10.6 mg, 0.011 mmol), KOH (11.8 mg, 0.21 mmol), and anisole (**2a**; 1.0 mL) were added in a Teflon screw-capped tube. The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 120 °C for 4 h to give Ir(ttp)Me (**3e**; 5.3 mg, 0.006 mmol) in 55% yield.

Reaction of Ir(ttp)(CO)Cl and Anisole with KOH (20 Equiv) at 150 °C. Ir(ttp)(CO)Cl (**1b**; 9.8 mg, 0.010 mmol), KOH (11.9 mg, 0.21 mmol), and anisole (**2a**; 1.0 mL) were added in a Teflon screw-capped tube. The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 150 °C for 2 h to give Ir(ttp)Me (**3e**; 7.6 mg, 0.087 mmol) in 87% yield.

Reaction of Ir(ttp)(CO)Cl and Anisole with KOH (20 Equiv) at 180 °C. Ir(ttp)(CO)Cl (**1b**; 10.3 mg, 0.011 mmol), KOH (12.3 mg, 0.22 mmol), and anisole (**2a**; 1.0 mL) were added in a Teflon screw-capped tube. The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 180 °C for 1 h to give Ir(ttp)Me (**3e**; 8.5 mg, 0.0097 mmol) in 88% yield.

Reaction of Ir(ttp)(CO)Cl and Anisole without KOH at 150 °C. Ir(ttp)(CO)Cl (**1b**; 9.6 mg, 0.010 mmol) and anisole (**2a**; 1.0 mL) were added in a Teflon screw-capped tube. The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 150 °C for 14 h with Ir(ttp)(CO)Cl recovered quantitatively.

Reaction of Ir(ttp)(CO)Cl and Anisole with K_2CO_3 (20 Equiv) at 150 °C. Ir(ttp)(CO)Cl (**1b**; 9.1 mg, 0.010 mmol), K_2CO_3 (28.5 mg,

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0.20 mmol), and anisole (**2a**; 1.0 mL) were added in a Teflon screw-capped tube. The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 150 °C for 10 h to give complex products. Ir(ttp)Me (**3e**) was estimated to be in 6% yield.

Reaction of Ir(ttp)(CO)Cl and Anisole with KOH (5 Equiv) at 150 °C. Ir(ttp)(CO)Cl (**1b**; 10.7 mg, 0.011 mmol), KOH (3.2 mg, 0.057 mmol), and anisole (**2a**; 1.0 mL) were added in a Teflon screw-capped tube. The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 150 °C for 2 h to give Ir(ttp)Me (**3e**; 7.2 mg, 0.0082 mmol) in 71% yield.

Reaction of Ir(ttp)(CO)Cl and Anisole with KOH (10 Equiv) at 150 °C. Ir(ttp)(CO)Cl (**1b**; 11.9 mg, 0.013 mmol), KOH (6.6 mg, 0.12 mmol), and anisole (**2a**; 1.0 mL) were added in a Teflon screw-capped tube. The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 150 °C for 2 h to give Ir(ttp)Me (**3e**; 9.3 mg, 0.011 mmol) in 82% yield.

Reaction of Ir(ttp)(CO)Cl and Anisole with KOH (30 Equiv) at 150 °C. Ir(ttp)(CO)Cl (**1b**; 9.2 mg, 0.010 mmol), KOH (18 mg, 0.32 mmol), and anisole (**2a**; 1.0 mL) were added in a Teflon screw-capped tube. The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 150 °C for 2 h to give Ir(ttp)Me (**3e**; 7.1 mg, 0.0081 mmol) in 81% yield.

Reaction of Ir(ttp)(CO)Cl and Ethoxybenzene with KOH (10 Equiv) at 150 °C. Ir(ttp)(CO)Cl (**1b**; 11.7 mg, 0.013 mmol), KOH (7.7 mg, 0.14 mmol), and ethoxybenzene (**2c**; 1.0 mL) were added in a Teflon screw-capped tube. The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 150 °C for 2 h to give Ir(ttp)Et[35] (**3f**; 9.8 mg, 0.011 mmol) in 87% yield.

Reaction of Ir(ttp)(CO)Cl and Propoxybenzene with KOH (10 Equiv) at 150 °C. Ir(ttp)(CO)Cl (**1b**; 10.6 mg, 0.011 mmol), KOH (6.7 mg, 0.12 mmol), and propoxybenzene (**2d**; 1.0 mL) were added in a Teflon screw-capped tube. The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 150 °C for 2 h to give Ir(ttp)^{n}Pr[35] (**3g**; 8.8 mg, 0.0097 mmol) in 85% yield.

Reaction of Ir(ttp)(CO)Cl and Benzyl Phenyl Ether with KOH (10 Equiv) at 150 °C. Ir(ttp)(CO)Cl (**1b**; 9.3 mg, 0.010 mmol), KOH (6.2 mg, 0.11 mmol), PhOBn (**2b**; 18.8 mg, 0.10 mmol), and benzene (1.0 mL) were added in a Teflon screw-capped tube. The mixture was degassed for three freeze−pump−thaw cycles, purged with N_2, and heated to 150 °C for 2 h until reaction completion. Benzene solvent was removed with vacuum distillation. Diphenylmethane (10 μL) was added as the internal standard. The NMR yield of Ir(ttp)Bn (**3h**)[30] was determined to be 82% by comparing the benzylic protons with the methylene protons of diphenylmethane. Ir(ttp)Bn (**3h**): R_f: 0.6 (hexane/CH_2Cl_2: 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ −3.99 (s, 2 H, CH_2), 2.68 (s, 12 H), 3.16 (d, 2 H, $^3J_{H-H}$ = 7.7 Hz), 5.90 (t, 2 H, $^3J_{H-H}$ = 7.5 Hz), 5.47 (t, 1 H, $^3J_{H-H}$ = 7.3 Hz), 7.50−7.54 (m, 8 H), 7.95−8.02 (m, 8 H), 8.46 (s, 8 H).

Independent Synthesis of Ir(ttp)$CH_2CH_2CH_2OPh$. Ir(ttp)(CO)Cl (**1b**; 23.7 mg, 0.026 mmol), KOH (14.4 mg, 0.26 mmol), allyl phenyl ether (**2e**; 35 μL, 0.25 mmol), and benzene (1.0 mL) were added in a Teflon screw-capped tube. The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 150 °C for 2 h until reaction completion. Benzene and excess allyl phenyl ether were removed with vacuum distillation. The residue was purified by pipet column chromatography on silica gel with CH_2Cl_2/hexane (1:5) to give Ir(ttp)$CH_2CH_2CH_2OPh$ (**3i**; 16.4 mg, 0.0165 mmol) in 64% yield. R_f: 0.64 (hexane:CH_2Cl_2 = 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ −5.44 (t, 2 H, $^3J_{H-H}$ = 8 Hz, $\underline{CH_2}CH_2CH_2OPh$), −3.75- −4.06 (m, 2 H, $CH_2\underline{CH_2}CH_2OPh$), 1.0 (t, 2 H, $^3J_{H-H}$ = 6.8 Hz, $CH_2CH_2\underline{CH_2}OPh$), 2.69 (s, 12 H), 5.80 (d, 2 H, $^3J_{H-H}$ = 8.0 Hz), 6.63 (t, 1 H, $^3J_{H-H}$ = 7.3 Hz), 6.87 (t, 2 H, $^3J_{H-H}$ = 7.9 Hz), 7.52 (m, 8 H), 7.93 (d, 4 H, $^3J_{H-H}$ = 7.6 Hz), 8.02−8.03 (m, 4 H), 8.51 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ -20.3, 21.8, 25.8, 63.2, 114.3, 120.1, 124.4, 127.8, 129.1, 131.6, 133.7, 134.2, 137.4, 138.9, 143.6, 158.0. HRMS (m/z) (MALDI-MS): $[M]^+$ calcd for ($C_{57}H_{47}IrN_4O$) 996.3378; found 996.3362.

Reaction of Ir(ttp)(CO)Cl and Allyl Phenyl Ether with KOH (10 Equiv) at 150 °C. Ir(ttp)(CO)Cl (**1b**; 10.6 mg, 0.011 mmol), KOH (6.4 mg, 0.11 mmol), and allyl phenyl ether (**2e**; 1.0 mL, 7.29 mmol) were added in a Teflon screw-capped tube. The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 150 °C for 4 h until reaction completion. Excess allyl phenyl ether was removed with vacuum distillation. The residue was purified by pipet column chromatography on silica gel with CH_2Cl_2/hexane (1:7) to give Ir(ttp)^{n}Pr (**3g**; 4.0 mg, 0.0044 mmol) in 35% yield as the first fraction and CH_2Cl_2/hexane (1:5) as eluent to give Ir(ttp)$CH_2CH_2CH_2OPh$ (**3i**; 2.7 mg, 0.0027 mmol) in 20% yield.

Independent Synthesis of Ir(ttp)Bn(*p*-OMe). Ir(ttp)(CO)Cl (**1b**; 10.1 mg, 0.011 mmol), KOH (6.0 mg, 0.11 mmol), 4-methoxybenzyl phenyl ether (**2f**; 23.4 mg, 0.11 mmol), and methanol (1.0 mL) were degassed for three freeze−pump−thaw cycles in a Teflon screw-capped tube. The reaction was heated in 150 °C under N_2 in the dark for 0.5 h until reaction completion. Methanol solvent was removed with vacuum distillation. The residue was further washed with methanol to give Ir(ttp)Bn(*p*-OMe) (**3j**; 6.8 mg, 0.007 mmol) as red purple solid in 63% yield. R_f: 0.63 (hexane:CH_2Cl_2 = 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ −4.06 (s, 2 H, CH_2), 2.67 (s, 12 H), 3.12 (d, 2 H, $^3J_{H-H}$ = 8.6 Hz), 3.44 (s, 3 H), 5.45 (d, 2 H, $^3J_{H-H}$ = 8.5 Hz), 7.53 (d, 8 H, $^3J_{H-H}$ = 7.5 Hz), 7.86−8.12 (m, 8 H), 8.45 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ −13.5, 21.8, 55.1, 112.0, 124.3, 125.2, 127.7, 127.8, 131.5, 133.9, 134.0, 137.4, 139.1, 143.5, 155.4. HRMS (m/z) (ESI-MS): $[M]^+$ calcd for ($C_{56}H_{45}IrN_4O$) 982.3217; found 982.3222.

Reaction of Ir(ttp)(CO)Cl and PhOBn(*p*-OMe). Ir(ttp)(CO)Cl (**1b**; 9.2 mg, 0.010 mmol), KOH (6.0 mg, 0.11 mmol), 4-methoxybenzyl phenyl ether (**2f**; 18.8 mg, 0.095 mmol), and benzene (1.0 mL) were added in a Teflon screw-capped tube. The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 150 °C for 2 h until reaction completion. Benzene solvent was removed with vacuum distillation. The NMR yield of Ir(ttp)Bn (*p*-OMe) (**3j**) was determined to be 71% using 10 μL of diphenylmethane as the internal standard.

Reaction between Ir(ttp)(CO)Cl and PhOBn(*p*-Cl). Ir(ttp)(CO)Cl (**1b**; 9.9 mg, 0.010 mmol), KOH (6.0 mg, 0.11 mmol), 4-chlorobenzyl phenyl ether (**2g**; 23.1 mg, 0.106 mmol), and benzene (1.0 mL) were added in a Teflon screw-capped tube. The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 150 °C for 2 h until reaction completion. Benzene solvent was removed with vacuum distillation. The NMR yield of Ir(ttp)Bn(*p*-Cl)(**3k**)[28] was determined to be 66% using 10 μL of diphenylmethane as the internal standard.

Independent Synthesis of Ir(ttp)Bn(*p*-CF_3). Ir(ttp)(CO)Cl (**1b**; 9.6 mg, 0.010 mmol), KOH (6.0 mg, 0.11 mmol), 4-(trifluoromethyl)-benzyl phenyl ether (**2h**; 25.7 mg, 0.010 mmol), and methanol (1.0 mL) were added in a Teflon screw-capped tube. The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 150 °C for 0.5 h until reaction completion. Methanol solvent was removed with vacuum distillation. The residue was further washed with methanol to give Ir(ttp)Bn(*p*-CF_3) (**3l**; 8.8 mg, 0.008 mmol) as purple solid in 85% yield. R_f: 0.69 (hexane:CH_2Cl_2 = 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ −3.97 (s, 2 H, CH_2), 2.71 (s, 12 H), 3.13 (d, 2 H, $^3J_{H-H}$ = 7.9 Hz), 6.11 (d, 2 H, $^3J_{H-H}$ = 7.9 Hz), 7.54 (d, 8 H, $^3J_{H-H}$ = 7.8 Hz), 7.88 (d, 4 H, $^3J_{H-H}$ = 6.9 Hz), 8.01 (d, 4 H, $^3J_{H-H}$ = 6.6 Hz), 8.44 (s, 8 H).^{19}F NMR ($CDCl_3$, 376 MHz) δ −62.6. ^{13}C NMR ($CDCl_3$, 100 MHz) δ −16.2, 21.6, 123.0, 123.9, 124.0, 124.8 (q, $^1J_{C-F}$ = 269.0 Hz), 127.6, 137.3, 138.7, 143.1, 146.5. HRMS (m/z) (MALDI-MS): $[M]^+$ calcd for ($C_{56}H_{42}IrF_3N_4$) 1020.2989; found 1020.2985.

Reaction between Ir(ttp)(CO)Cl and PhOBn(*p*-CF_3). Ir(ttp)-(CO)Cl (**1b**; 10.7 mg, 0.011 mmol), KOH (6.0 mg, 0.11 mmol), 4-(trifluoromethyl)benzyl phenyl ether (**2h**; 26.6 mg, 0.105 mmol), and benzene (1.0 mL) were degassed for three freeze−pump−thaw cycles in a Teflon screw-capped tube. The reaction was heated in 150 °C under N_2 in the dark for 2 h until reaction completion. Benzene solvent was removed with vacuum distillation. The NMR yield of Ir(ttp)Bn(*p*-CF_3) (**3l**) was determined to be 68% using 10 μL of diphenylmethane as the internal standard.

Reaction of Ir(ttp)H with Anisole in Solvent-Free Conditions. Ir(ttp)H (**1c**; 10.3 mg, 0.012 mmol) and anisole (**2a**; 1.0 mL) were

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degassed for three freeze−pump−thaw cycles in a Teflon screw-capped tube, refilled with N_2, and heated to 150 °C for 2 h until reaction completion. Excess anisole was removed with vacuum. The ^{1}H NMR spectrum was recorded for the residue. Ir(ttp)Me (**3e**) and Ir(ttp)C_6H_4(*p*-OMe) (**3m**)[29a] were formed in trace amounts.

Independent Synthesis of Ir(ttp)CHPh(OPh). Ir(ttp)(CO)Cl (**1b**; 10.6 mg, 0.011 mmol), K_2CO_3 (14.8 mg, 0.11 mmol), PhOBn (**2b**; 10.8 mg, 0.058 mmol), and benzene (1.0 mL) were added in a Teflon screw-capped tube. The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 200 °C for 15 h. Benzene solvent was removed with vacuum distillation. The residue was purified by a precoated silica gel TLC plate with CH_2Cl_2/hexane (1:1) to give Ir(ttp)CHPh(OPh) (**3n**; 5.4 mg, 0.005 mmol) in 45% yield. R_f: 0.58 (hexane:CH_2Cl_2 = 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ −0.82 (s, 1 H, CH), 2.70 (s, 12 H), 3.31 (brs, 2 H), 4.37 (d, 2 H, $^3J_{H-H}$ = 8.0 Hz), 6.07 (t, 2 H, $^3J_{H-H}$ = 7.5 Hz), 6.32 (t, 1 H, $^3J_{H-H}$ = 7.2 Hz), 6.41−6.50 (m, 3 H), 7.51−7.56 (m, 8 H), 7.93 (d, 4 H, $^3J_{H-H}$ = 7.5 Hz), 7.99 (d, 4 H, $^3J_{H-H}$ = 7.6 Hz), 8.46 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.6, 33.6, 113.2, 119.1, 124.0, 124.1, 125.9, 127.5, 127.8, 131.2, 133.8, 133.9, 137.1, 139.0, 140.2, 143.2, 154.0. HRMS (*m*/*z*) (ESI-MS): $[M + Na]^+$ calcd for ($C_{61}H_{47}IrN_4ONa$) 1067.3285; found 1067.3276.

Reaction of Ir(ttp)H with PhOBn in Benzene. Ir(ttp)H (**1c**; 8.4 mg, 0.010 mmol), PhOBn (**2b**; 18 mg, 0.10 mmol), and benzene (1.0 mL) were added in a Teflon screw-capped tube. The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 150 °C in the dark for 0.5 h until reaction completion. Benzene solvent was removed with vacuum distillation. Diphenylmethane (10 μL) was added as the internal standard, and the NMR yield of Ir(ttp)CHPh(OPh) (**3n**) was calculated to be 60%.

Reaction of Ir_2(ttp)$_2$ with Anisole in Solvent-Free Conditions. Ir(ttp)H (**1c**; 3.0 mg, 0.003 mmol) and 2,2,6,6- tetramethylpiperidinooxy (TEMPO) (0.8 mg, 0.005 mmol) were added into a Teflon screw-capped tube under N_2. Degassed benzene (1.0 mL) was added into the tube with an airtight syringe, and the reaction mixture changed to deep brown instantaneously. Benzene solvent was removed with vacuum distillation, and the residue was further dried under vacuum for 24 h to remove the solvent, unreacted TEMPO, and TEMPOH coproduct. Degassed anisole (**2a**, 1.0 mL) was then added into the tube under N_2, and the mixture was heated to 150 °C in the dark for 2 h until reaction completion. Excess anisole was removed with vacuum. Ir(ttp)Me (**3e**) was formed in trace amounts.

Reaction of Ir_2(ttp)$_2$ with PhOBn in Benzene. Ir_2(ttp)$_2$ (**1d**; 8.1 mg, 0.009 mmol), PhOBn (**2b**; 17.3 mg, 0.09 mmol), and degassed benzene (1.0 mL) were added into the tube under N_2. The reaction mixture was heated to 150 °C for 2 h until reaction completion. Benzene solvent was removed with vacuum distillation. Diphenylmethane (10 μL) was added as the internal standard, and the NMR yield of Ir(ttp)CHPh(OPh) (**3n**) was calculated to be 40%.

Reaction of Ir(ttp)H with Anisole and KOH in Solvent-Free Conditions. Ir(ttp)H (**1c**; 8.8 mg, 0.010 mmol), KOH (6.0 mg, 0.010 mmol), and anisole (**2a**; 1.0 mL) were added into a Teflon screw-capped tube, and the reaction mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 150 °C in the dark for 2 h until reaction completion. Excess anisole was removed with vacuum. The residue was recrystallized from MeOH/DCM and washed with MeOH three times. Ir(ttp)Me (**3e**) was achieved in 54% yield.

Reaction of Ir(ttp)H with PhOBn and KOH in Benzene. Ir(ttp)H (**1c**; 9.5 mg, 0.011 mmol), KOH (6.0 mg, 0.010 mmol), PhOBn (**2b**; 20.3 mg, 0.11 mmol), and benzene (1.0 mL) were added into a Teflon screw-capped tube, and the reaction mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 150 °C in the dark for 2 h until reaction completion. Benzene solvent was removed with vacuum distillation. Diphenylmethane (10 μL) was added as the internal standard, and the NMR yield of Ir(ttp)CHPh(OPh) (**3n**) was calculated to be 11% with Ir(ttp)Bn (**3h**) in 22% yield.

Reaction of Ir(ttp)Me with Propoxybenzene. Ir(ttp)Me (**3e**; 10.6 mg, 0.012 mmol), KOH (7.4 mg, 0.13 mmol), and propoxybenzene (**2d**; 1.0 mL) were degassed for three freeze−pump−thaw cycles in a Teflon screw-capped tube. The reaction was heated in 150 °C under N_2 in the dark for 17 h. Ir(ttp)^{n}Pr (**3g**) was formed in 5% yield with 90% of Ir(ttp)Me (**3e**) recovered.

Reaction of Ir(ttp)Cl(CO) with Ethoxybenzene and Propoxybenzene. Ir(ttp)(CO)Cl (**1b**; 10.9 mg, 0.012 mmol), KOH (11.6 mg, 0.21 mmol), ethoxybenzene (**2c**; 0.506 mL, 4.0 mmol), and propoxybenzene (**2d**; 0.586 mL, 4.0 mmol) were degassed for three freeze−pump−thaw cycles in a Teflon screw-capped tube. The reaction was heated in 150 °C under N_2 in the dark for 2 h until reaction completion to give Ir(ttp)Et (**3f**; 2.7 mg) in 25% yield and Ir(ttp)^{n}Pr (**3g**; 5.0 mg) in 46% yield. The two products were purified by pipet column chromatography on silica gel eluting with CH_2Cl_2/hexane (1:1). The yield of each product was determined by an ^{1}H NMR spectrum from the integration of ethyl protons of the iridium−ethyl group of Ir(ttp)Et and the propyl protons of the iridium−propyl group of Ir(ttp)^{n}Pr.

Reaction of Ir(ttp)Cl(CO) with Anisole and Ethoxybenzene. Ir(ttp)(CO)Cl (**1b**; 10.5 mg, 0.011 mmol), KOH (12.6 mg, 0.22 mmol), ethoxybenzene (**2c**; 0.506 mL, 4.0 mmol), and anisole (**2a**; 0.435 mL, 4.0 mmol) were degassed for three freeze−pump−thaw cycles in a Teflon screw-capped tube. The reaction was heated in 150 °C under N_2 in the dark for 2 h until reaction completion to give Ir(ttp)Et (**3f**; 4.5 mg) in 40% yield and Ir(ttp)Me (**3e**; 2.6 mg) in 23% yield. The two products were purified by pipet column chromatography on silica gel eluting with CH_2Cl_2/hexane (1:1). The yield of each product was determined by an ^{1}H NMR spectrum from the integration of ethyl protons of the iridium−ethyl group of Ir(ttp)Et and the methyl protons of the iridium−methyl group of Ir(ttp)Me.

Reaction of Ir(ttp)Cl(CO) with Anisole and Propoxybenzene. Ir(ttp)(CO)Cl (**1b**; 9.3 mg, 0.010 mmol), KOH (11.3 mg, 0.20 mmol), propoxybenzene (**2d**; 0.586 mL, 4.0 mmol), and anisole (**2a**; 0.435 mL, 4.0 mmol) were degassed for three freeze−pump−thaw cycles in a Teflon screw-capped tube. The reaction was heated in 150 °C under N_2 in the dark for 2 h to give Ir(ttp)^{n}Pr (**3g**; 5.5 mg) in 61% yield and Ir(ttp)Me (**3e**; 2.0 mg) in 23% yield. The two products were purified by pipet column chromatography on silica gel eluting with CH_2Cl_2/hexane (1:1). The yield of each product was determined by an ^{1}H NMR spectrum from the integration of propyl protons of the iridium−propyl group of Ir(ttp)^{n}Pr and the methyl protons of the iridium−methyl group of Ir(ttp)Me.

Reaction of Ir(ttp)(CO)Cl and BnOPh(*p*-OMe) at 150 °C. Ir(ttp)(CO)Cl (**1b**; 10.5 mg, 0.011 mmol), KOH (6.0 mg, 0.11 mmol), 4-(benzyloxy)anisole (**2i**; 23.3 mg, 0.11 mmol), and benzene (1.0 mL) were added in a Teflon screw-capped tube. The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 150 °C for 3 h until reaction completion. Benzene solvent was removed with vacuum distillation. The NMR yield of Ir(ttp)Bn (**3h**) was determined to be 71% using diphenylmethane as the internal standard.

Reaction of Ir(ttp)(CO)Cl and BnOPh(*p*-CN) at 150 °C. Ir(ttp)(CO)Cl (**1b**; 9.2 mg, 0.010 mmol), KOH (6.0 mg, 0.11 mmol), 4-(benzyloxy)benzonitrile (**2j**; 20.5 mg, 0.10 mmol), and benzene (1.0 mL) were added in a Teflon screw-capped tube. The mixture was degassed for three freeze−pump−thaw cycles, refilled with N_2, and heated to 150 °C for 0.5 h until reaction completion. Benzene solvent was removed with vacuum distillation. The NMR yield of Ir(ttp)Bn (**3h**) was determined to be 81% using diphenylmethane as the internal standard.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00386.

Competition reactions; ^{1}H and ^{13}C NMR spectra; tables and figures outlining X-ray crystallographic data for Rh(ttp)CH_2OPh (**3a**), Rh(ttp)CHPh(OPh) (**3c**), and Ir(ttp)Et (**3f**); HRMS spectra for Rh(ttp)CH_2OPh (**3a**), Rh(ttp)CHPh(OPh) (**3c**), Ir(ttp)$CH_2CH_2CH_2$OPh

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(**3i**), Ir(ttp)Bn(*p*-OMe) (**3j**), Ir(ttp)Bn(*p*-CF_3) (**3l**), and Ir(ttp)CHPh(OPh) (**3n**) (PDF)

Accession Codes

CCDC 1552670−1552672 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

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

ORCID

Kin Shing Chan: 0000-0002-1112-6819

Notes

The authors declare no competing financial interest.

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