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Selective Aromatic C−H Hydroxylation Enabled by η^6-Coordination to Iridium(III)

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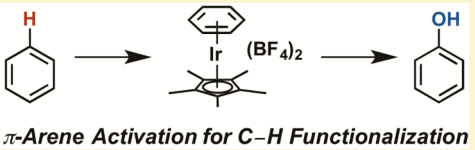
Supporting Information

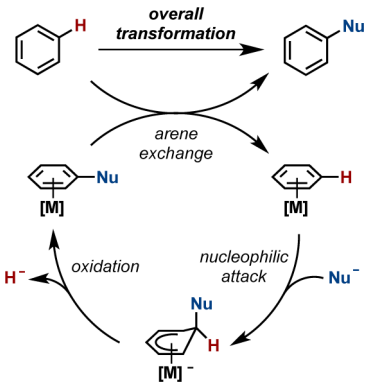
ABSTRACT: We report an aromatic C−H hydroxylation protocol in which the arene is activated through η^6-coordination to an iridium(III) complex. η^6-Coordination of the arene increases its electrophilicity and allows for high positional selectivity of hydroxylation at the site of least electron density. Through investigation of intermediate η^5-cyclohexadienyl adducts and arene exchange reactions, we evaluate incorporation of arene π-activation into a catalytic cycle for C−H functionalization.



INTRODUCTION

Transition metal-mediated C−H functionalization methods typically involve the formation of a metal−carbon σ-bond through oxidative addition, σ-bond metathesis, or electrophilic metalation.[1] Slow metalation processes, due to the strength and low polarity of the aromatic C−H bond, are difficult to overcome and hinder the improvement of current methodologies. We identified η^6-coordination of the aromatic π-system to a transition metal as an alternative activation manifold that could facilitate aromatic C−H functionalization. The catalytic cycle we envision involves nucleophilic attack on an η^6-coordinated arene, oxidation of the resulting η^5-cyclohexadienyl adduct, and arene exchange (Scheme 1). By employing nucleophilic functionalization reagents, as opposed to the conventionally used electrophilic reagents, the π-activation mode is well suited for the formation of C−X bonds, where X is an electronegative atom, such as O, N, or F. Additional benefits of the π-activation approach include the ability to target aromatic rings without introduction of a coordinating directing group and the reversal of positional selectivity observed for traditional C−H functionalization chemistry. Herein, we present C−H hydroxylation utilizing iridium(III) η^6-arene complexes and demonstrate the first use of oxygen nucleophiles for C−H functionalization with transition metal η^6-arene complexes. We anticipate that these advances in stoichiometric C−O bond formation will provide valuable insight for translation into a catalytic cycle.

Scheme 1. C−H Functionalization Utilizing η^6-Arene Activation



Several strategies have been employed to form metal−carbon σ-bonds as intermediates for subsequent functionalization, despite the slow C−H metalation of arenes. The use of coordinating directing groups for both *ortho*[2] and *meta*[3] C−H functionalization has been thoroughly explored by several groups to enforce intramolecularity for the difficult metalation step. However, introduction and further modification of a directing group increases step count and is often challenging. On the other hand, C−H metalation without a coordinating directing group typically requires an excess of arene (i.e., as solvent) to increase the concentration of substrate. Notable exceptions include iridium-catalyzed borylation[4] and rhodium-catalyzed silylation.[5] An opposing strategy is to avoid formation of a metal−carbon σ-bond altogether, such as electrophilic aromatic substitution, radical rebound by high valent metal complexes,[6] or reactions that proceed through a radical addition to an arene. For example, MacMillan's iridium-catalyzed trifluoromethylation[7] and our group's palladium and silver cocatalyzed C−H imidation[8] utilize transition metal catalysts to form reactive radical species that interact with the aromatic substrate. In an effort to expand upon methods that do not rely upon formation of a metal−carbon σ-bond during catalysis, we focused on utilizing η^6-arene complexes to provide a different mechanism for C−H functionalization.

η^6-Coordination of an arene has long been recognized as a tool for *umpolung* aromatic substitution chemistry, which facilitates nucleophilic attack on otherwise unactivated aromatic

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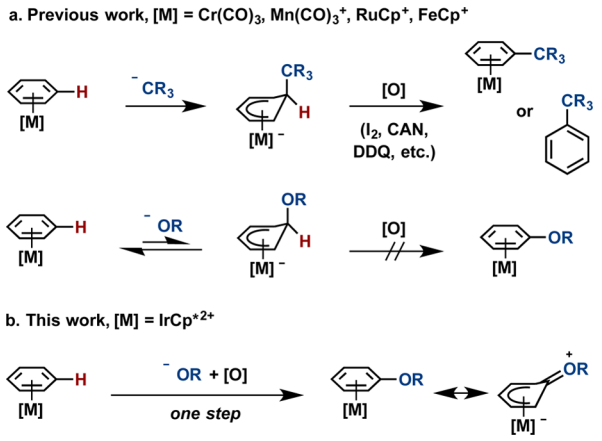
π-systems.[9,10] Nucleophilic attack at C−H bonds is well established with a variety of transition metal complexes, such as η^6-arene complexes of the $[Cr(CO)_3]$, $[Mn(CO)_3]^+$, $[FeCp]^+$, $[RuCp]^+$, and $[IrCp^*]^{2+}$ fragments, and is kinetically preferred over C−X bonds[9a] in most cases. Strong nucleophiles, such as some carbanions, form stable η^5-cyclohexadienyl adducts via irreversible nucleophilic attack.[9,11] Stable adducts can be oxidized in a subsequent step to provide overall C−H-functionalized products (Scheme 2). However,

Scheme 2. C−H Functionalization via Nucleophilic Attack on η^6-Arene Complexes

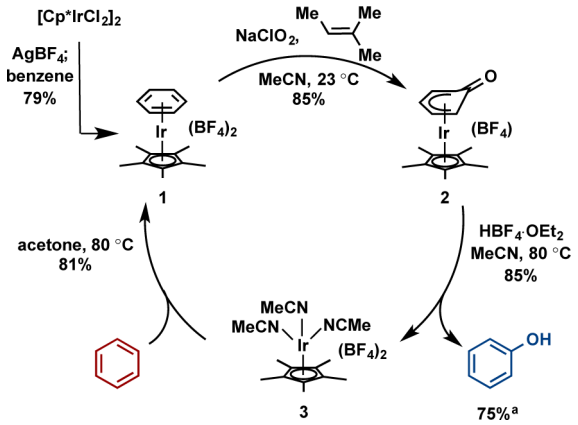


the use of heteroatomic nucleophiles (HNR_2, ^-OR, etc.) for this two-step sequence is quite limited, because η^5-cyclohexadienyl adduct formation is usually reversible with equilibrium favoring the starting materials.[12,13] Furthermore, an example where nucleophilic attack and oxidation have occurred in the same reaction vessel at the same time, as is necessary for a catalytic reaction and is reported here, is unprecedented. We targeted C−H hydroxylation as a reaction that would be an advancement of known stoichiometric η^6-arene chemistry, as well as a desirable synthetic transformation.[14]

RESULTS AND DISCUSSION

We identified air- and moisture-stable arene complex **1**[15] as a good target for studying the desired oxidation reaction, due to its high electrophilicity.[16] Complex **1** is readily synthesized from commercially available $[Cp^*IrCl_2]_2$ by chloride abstraction with $AgBF_4$ (Scheme 3). Upon addition of $NaClO_2$, in conjunction with 2-methyl-2-butene as an HOCl scavenger,[17] **1** is converted directly into η^5-phenoxo complex **2**[18] within 3 h at 23 °C in 85% yield. The conversion of **1** into **2** is an overall aromatic C−H to C−O bond transformation that represents both the nucleophilic attack and oxidation steps of the proposed catalytic cycle from Scheme 1. Importantly, the control reaction using uncoordinated benzene instead of complex **1** results in no formation of phenol. By increasing the electrophilicity of the arene complex and identifying the appropriate functionalization reagent ($NaClO_2$), nucleophilic attack and oxidation occur concurrently, which circumvents issues of an unfavorable equilibrium for the initial attack step. To the best of our knowledge, no other transition metal η^6-arene complex has afforded hydroxylated aromatic products through initial nucleophilic attack at a C−H bond.

Scheme 3. Synthetic Cycle for Oxidation of Benzene to Phenol

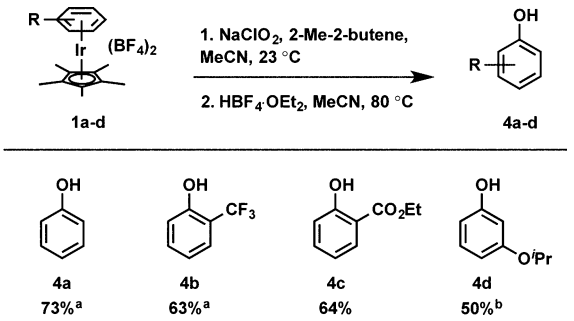


[a]Isolated as the aryl *p*-toluenesulfonate due to volatility of phenol.

After protonation of **2** and heating at 80 °C in acetonitrile, phenol is recovered in 75% isolated yield and tris(acetonitrile) complex **3** is isolated in 85% yield. The iridium can be recycled to convert complex **3** into **1** in 81% yield by heating in a 1:1 mixture of benzene and acetone. In this way, all steps of the proposed catalytic cycle have been demonstrated individually.

Upon discovery of the above C−H oxidation protocol, the effect of arene substitution on selectivity was investigated (Table 1). Interestingly, C−O bond formation occurs

Table 1. Effect of Arene Substitution on Site Selectivity of C−H Hydroxylation



[a]Isolated as the aryl *p*-toluenesulfonate due to volatility of phenol. [b]^{i}PrCN used instead of MeCN for step 2; isolated as a 95:5 mixture of *meta*:*para* isopropoxyphenol.

selectively *ortho* to electron-withdrawing groups, as in the case of trifluorotoluene complex **1b** and ethyl benzoate complex **1c**. Only one isomeric product was observed in the reactions of both **1b** and **1c**. C−O bond formation was observed primarily *meta* to the resonance electron-donating group in isopropoxybenzene complex **1d**. A small amount (5%) of the *para* hydroxylation product was also isolated from the reaction of **1d**.

While nucleophilic addition of carbanions to η^6-arene complexes has been shown to occur with similar selectivity,[9a,b,19] typical C−H hydroxylation chemistry does not proceed in such high selectivity. In addition, the positional selectivity of the products in Table 1 is opposite that of most C−H oxidation protocols, which broadly rely on the arene to act as nucleophile. For example, Siegel reported aromatic C−H hydroxylation using phthaloyl peroxide and observed only *ortho* and *para*

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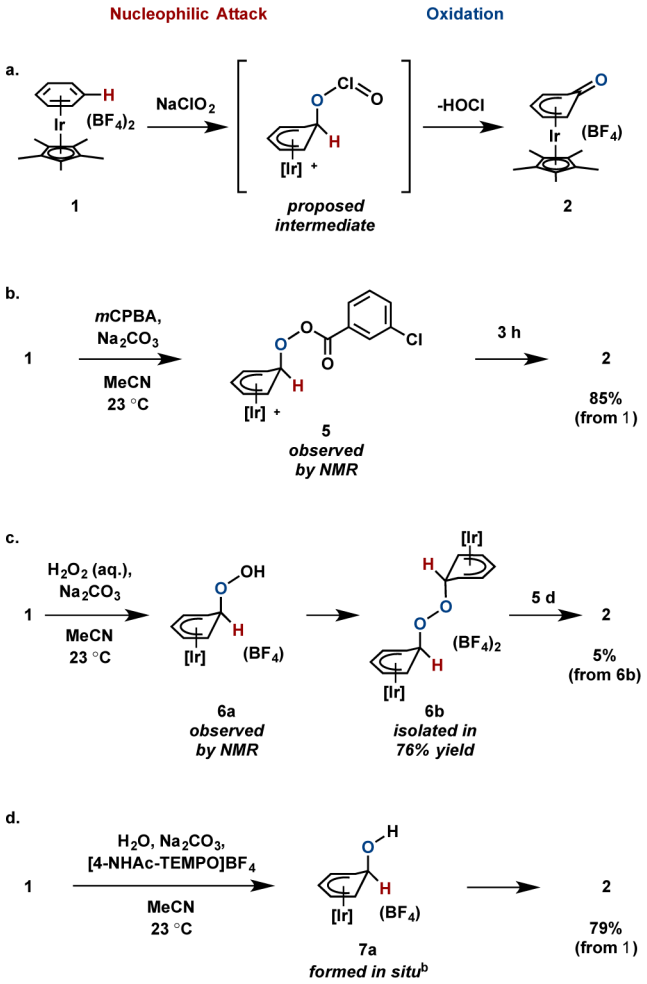
products (o:p = 1.4:1.0) for anisole, a substrate with a single resonance donor.[20] Similarly, Sanford reported a palladium-catalyzed acetoxylation that gives C−O bond formation predominantly *meta* to the electron-withdrawing trifluoromethyl group (o:m:p = 1:78:21).[21] In contrast, by enhancing the electrophilicity of the arene through η^6-coordination, our protocol has the potential to complement these selectivities, with hydroxylation occurring at the position of least electron density.

With the goal of catalysis in mind, we examined more closely the mechanism of the promising C−H hydroxylation protocol described above. The C−H to C−O transformation can be divided into two general steps: nucleophilic attack to form an η^5-cyclohexadienyl adduct, followed by oxidation to form η^5-phenoxo complex **2** (Scheme 4a). While there are reports of

Scheme 4. C−O Bond Formation via η^5-Cyclohexadienyl Adducts[a]



[a][Ir] = [Cp*Ir(III)]. [b]Complex **7a** may be isolated in the absence of [4-NHAc-TEMPO]BF_4. See the SI for details.

nucleophilic attack on complex **1**, albeit with stronger nucleophiles than $NaClO_2$,[16b] the oxidation step is unprecedented. Only starting material (**1**) and final product (**2**) could be observed in the $NaClO_2$ oxidation reaction when monitored by ^{1}H NMR spectroscopy. We, therefore, were prompted to investigate other nucleophile/oxidant combinations that react with **1** to learn about the nucleophilic attack and oxidation steps that lead to C−O bond formation.

In a reaction analogous to that with $NaClO_2$, complex **1** reacts with *m*-chloroperbenzoic acid (*m*CPBA) in the presence of Na_2CO_3 to give η^5-phenoxo complex **2** in 85% yield (Scheme 4b). Furthermore, an η^5-cyclohexadienyl adduct of *m*-chloroperbenzoate (**5**) was observed when the reaction was followed by ^{1}H NMR spectroscopy. Adduct **5** could not be isolated due to its propensity to form complex **2**, but it was distinguished by the significant upfield shift of the observed ^{1}H NMR and ^{13}C NMR signals, compared to those of η^6-arene complex **1**, a feature characteristic of all known η^5-cyclohexadienyl adducts.[22] After comparing adduct **5** with the proposed η^5-cyclohexadienyl adduct of chlorite, we hypothesized that a cyclic five- or six-membered transition state for *syn* elimination might facilitate oxidation.

To probe the hypothesis of a cyclic transition state, we next evaluated hydrogen peroxide, a nucleophilic oxidant that would not be expected to readily undergo *syn* elimination after attack on complex **1**. Reaction of **1** with H_2O_2 and Na_2CO_3 resulted in a dialkylated peroxide η^5-cyclohexadienyl adduct (**6b**), which, unlike **5**, could be isolated and characterized (Scheme 4c). Monoalkylated peroxide adduct **6a** could be observed by NMR and is likely on-path in the formation of **6b**. Adduct **6b** was observed to form complex **2** in low conversion (5%) over the course of 5 days, which suggests a different mechanism for oxidation, or at least one that was significantly slowed when using H_2O_2, and supported our hypothesis of *syn* elimination in the cases of $NaClO_2$ and *m*CPBA.

To further probe possible mechanisms for C−H oxidation, we attempted to decouple the nucleophile and oxidant but maintain the possibility for a cyclic transition state for *syn* elimination. Reaction of complex **1**, H_2O, Na_2CO_3, and [4-NHAc-TEMPO]BF_4, a reagent known for oxidation of alcohols to aldehydes or ketones,[23] results in isolation of complex **2** in 79% yield. Formation of adduct **7a** is observed, and the adduct can be isolated if the reaction is run in the absence of oxidant. Previously reported mechanistic investigations for alcohol oxidation with [4-NHAc-TEMPO]BF_4 suggest that oxidation proceeds through a five-membered transition state.[24]

Based on the observed positional selectivity and the formation of η^5-cyclohexadienyl adducts with oxygen nucleophiles, our mechanistic hypothesis for the C−O bond forming reaction involves nucleophilic attack of chlorite on arene complex **1** in analogy to nucleophilic attack of chlorite on an aldehyde in the Lindgren−Pinnick oxidation.[25] Nucleophilic attack is quickly followed by oxidation, possibly through a *syn* elimination, to generate η^5-phenoxo complex **2** and hypochlorous acid.

Ultimately, our goal is to develop the selective C−H oxidation described above into a catalytic reaction. Initial experiments have indicated that each step in the cycle shown in Scheme 3 involves conditions that are not compatible with those for the other steps. For example, $NaClO_2$ is known to decompose under acidic conditions (pH < 2 in aqueous solutions),[26] while complex **2** requires strong acid for protonation and displacement from iridium. In addition, tris(acetonitrile) complex **3** forms readily from **2** under acidic conditions. However, benzene does not easily displace acetonitrile ligands to re-form **1** unless a solvent less coordinating than acetonitrile is used (e.g., acetone). Preliminary progress toward a catalytic cycle has shown that use of 3-methyl-2-oxazolidinone, a solvent with high dielectic

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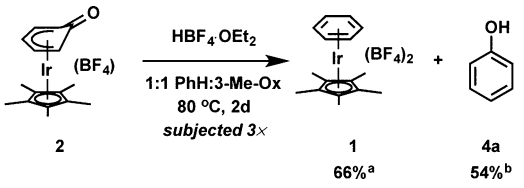
constant,[27] allows for direct conversion of complex **2** into starting arene complex **1**, with release of phenol (Scheme 5).

Scheme 5. Direct Formation of 1 from 2



[a]Yield determined by ^{1}H NMR. [b]Isolated as the aryl *p*-toluenesulfonate due to volatility of phenol. 3-Me-Ox = 3-methyl-2-oxazolidinone.

High conversion of this reaction was not observed due to an unfavorable equilibrium constant for arene exchange. However, the conversion could be improved by removing the phenol product and resubjecting the mixture of complexes **1** and **2** to the reaction conditions. While the change in solvent can promote direct transformation of **2** into **1**, the issue of incompatibility between $NaClO_2$ and strong acid remains unsolved.

CONCLUSION

In conclusion, we present aromatic C−H bond hydroxylation enabled by η^6-coordination to an iridium(III) complex that proceeds with high positional selectivity through nucleophilic attack, followed by oxidation. By conceptually reversing the role of the arene in C−H functionalization chemistry (from nucleophile to electrophile), π-arene activation provides a new platform for the synthesis of arenes that makes use of nucleophilic functionalization reagents and gives products with complementary selectivity to traditional approaches. We believe that catalytic activation of the aromatic π-system has great potential as an alternative approach to C−H functionalization chemistry.

EXPERIMENTAL SECTION

General Procedure for Synthesis of Arene Complexes 1a−d. $[Cp^*IrCl_2]_2$ (300 mg, 0.377 mmol, 1.00 equiv) and $AgBF_4$ (293 mg, 1.51 mmol, 4.00 equiv) were added to a flame-dried round-bottom flask. The flask was evacuated and backfilled with N_2. Acetone (6 mL) was then added. The mixture was allowed to stir for 30 min at 23 °C, affording a yellow solution and an off-white precipitate (AgCl). Filtration through glass wool afforded a clear yellow solution, to which arene (3 mL) was added. The mixture was stirred for 1 h at 23 °C to give a pale yellow solution and the formation of a colorless precipitate. Et_2O (5 mL) was added to this mixture. Centrifugation followed by decantation of the supernatant yielded a colorless solid, which was washed with Et_2O (10 mL). This solid was dissolved in acetonitrile (10 mL). Et_2O (10 mL) was added to the solution, affording a colorless precipitate. Centrifugation followed by decantation of the supernatant and drying under high vacuum yielded the title compound as a colorless solid.

[Cp*Ir(η^5-phenoxo)](BF$_4$) (2). Complex **1** (116 mg, 0.200 mmol, 1.00 equiv) was added to a flame-dried round-bottom flask. Acetonitrile (10 mL), a solution of 2-methyl-2-butene in THF (0.800 mL, 1.60 mmol, 8.00 equiv, 2.0 M), and freshly powdered sodium chlorite (45.2 mg, 0.400 mmol, 2.00 equiv) were then added. The mixture was allowed to stir for 3 h at 23 °C. Filtration through glass wool afforded a clear, pale yellow solution. The filtrate was concentrated to 3 mL. Et_2O (10 mL) was added to the filtrate. Centrifugation followed by decantation of the supernatant yielded a tan residue. The residue was extracted with DCM (100 mL). The extracts were filtered through glass wool and concentrated to 10 mL, and Et_2O (10 mL) was added. Centrifugation followed by decantation of the supernatant yielded a residue, which was washed with Et_2O (10 mL) and dried under high vacuum to afford 86.7 mg of the title compound as a colorless solid (85% yield). NMR spectroscopy: ^{1}H NMR (500 MHz, CD_3CN, 23 °C, δ): 6.38 (t, J = 5.5 Hz, 1H), 6.27 (dd, J = 7.5, 5.5 Hz, 2H), 5.54 (d, J = 7.5 Hz, 2H), 2.18 (s, 15H). ^{13}C NMR (125 MHz, CD_3CN, 23 °C, δ): 163.8, 100.7, 96.0, 84.6, 81.5, 10.2. FT-IR spectroscopy (neat, cm^{-1}): 3091, 3033, 1633, 1597, 1470, 1392, 1050, 1036, 694, 522, 454. Anal. Calcd for $C_{16}H_{20}BF_4IrO$: C, 37.88; H, 3.97. Found: C, 37.68; H, 4.25. HRMS-FIA (m/z): calcd for $C_{16}H_{20}OIr$ [M]$^+$, 421.1143; found 421.1147. Spectroscopic data match that reported for related compounds [(η^5-phenoxo)IrCp*]PF_6 and [(η^5-phenoxo)IrCp*]I.[18b]

[Cp*Ir(MeCN)$_3$](BF$_4$)$_2$·H$_2$O (3). Complex **2** (50.8 mg, 0.100 mmol, 1.00 equiv) was added to a flame-dried round-bottom flask equipped with a reflux condenser. Acetonitrile (10 mL) and HBF_4·OEt_2 (27 μL, 0.20 mmol, 2.0 equiv) were added. The mixture was allowed to stir at 80 °C for 24 h. After cooling to ambient temperature, the reaction mixture was poured into Et_2O (100 mL). The oily precipitate was allowed to settle, and the supernatant was decanted and saved (see below). The residue was washed with Et_2O (10 mL) to afford crude material of 93% purity, as judged by ^{1}H NMR. The major impurity observed was the starting material, complex **2**. The crude material was added to a flame-dried round-bottom flask equipped with a reflux condenser. Acetonitrile (10 mL) and HBF_4·OEt_2 (27 μL, 0.20 mmol, 2.0 equiv) were added. The mixture was allowed to stir at 80 °C for 24 h. After cooling to ambient temperature, the reaction mixture was poured into Et_2O (100 mL). The oily precipitate was allowed to settle, and the supernatant was decanted. The residue was washed with Et_2O (10 mL) and dried under high vacuum to afford 54.4 mg of the title compound as a pale yellow solid (85% yield). NMR spectroscopy:[18a] ^{1}H NMR (500 MHz, CD_3CN, 23 °C, δ): 1.96 (s, 9H), 1.75 (s, 15H). ^{13}C NMR (125 MHz, CD_3NO_2, 23 °C, δ): 124.6, 94.7, 9.1, 3.7. FT-IR spectroscopy (neat, cm^{-1}): 3638, 3011, 2944, 2329, 2300, 1544, 1460, 1426, 1389, 1048, 1019, 520, 469. Anal. Calcd for $C_{16}H_{24}B_2F_8IrN_3O$: C, 29.92; H, 4.08; N, 6.54. Found: C, 30.22; H, 3.95; N, 6.64. LRMS-FIA (m/z): calcd for $C_{11}H_{15}IrNaO_2$ [M − $(CH_3CN)_3$ − H$^+$ + Na$^+$ + $(HCO_2)^-$]$^+$, 395.0599; found 395.1087. Isolation of phenyl tosylate (**4a**): Due to the volatility of phenol, the supernatant was concentrated to 20 mL, and *p*-toluenesulfonyl chloride (57.3 mg, 0.300 mmol, 3.00 equiv), 4-dimethylaminopyridine (12.2 mg, 0.100 mmol, 1.00 equiv), and triethylamine (123 μL, 0.900 mmol, 9.00 equiv) were added. The mixture was allowed to stir for 3 h at 23 °C. DCM (20 mL) and H_2O (20 mL) were added, and the reaction mixture was poured into a separatory funnel. The layers were separated. The aqueous layer was extracted with DCM (2 × 10 mL). The combined organic layers were washed with 1 M $HCl_{(aq)}$ (10 mL) and brine (10 mL), dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel eluting with a solvent mixture of Et_2O/pentane (5:95 (v/v)) to afford 18.6 mg of the title compound as a colorless solid (75% yield). Spectroscopic data matched those described in the SI for compound **4a** (p S8).

Regeneration of Complex 1 from 3. Iridium complex **3** (62.4 mg, 0.100 mmol, 1.00 equiv) was added to a 20 mL scintillation vial. Acetone (2 mL) and benzene (2 mL) were added. The vial was sealed, and the reaction mixture was allowed to stir at 80 °C for 24 h. After cooling to ambient temperature, Et_2O (15 mL) was added to the reaction mixture. Centrifugation, followed by decantation of the supernatant, gave a yellow-brown residue. Acetonitrile (3 mL) was added to the crude material, and the mixture was filtered through glass wool to give a yellow filtrate. Et_2O (10 mL) was added to the filtrate to afford a colorless precipitate. Centrifugation, followed by decantation of the supernatant, yielded a residue that was washed with Et_2O (10 mL) and dried under high vacuum to afford 46.8 mg of **1** as a colorless solid (81% yield). Spectroscopic data matched those described above for compound **1**.

General Procedure for the Synthesis of Hydroxylated Arenes 4a−d. Iridium complex **1** (116 mg, 0.200 mmol, 1.00 equiv) was added to a flame-dried round-bottom flask. Acetonitrile (10 mL), a solution of 2-methyl-2-butene in THF (0.800 mL, 1.60 mmol,

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8.00 equiv, 2.0 M), and freshly powdered sodium chlorite (45.2 mg, 0.400 mmol, 2.00 equiv) were then added. The mixture was allowed to stir for 3 h at 23 °C. Filtration through glass wool afforded a clear, pale yellow solution. The filtrate was concentrated to 2 mL, and Et_2O (15 mL) was added. The mixture was centrifuged, and the supernatant decanted. The precipitate was dissolved in acetonitrile (10 mL) and transferred to a flame-dried round-bottom flask equipped with a reflux condenser. $HBF_4{\cdot}OEt_2$ (55 μL, 0.40 mmol, 2.0 equiv) was then added. The mixture was allowed to stir for 24 h at 80 °C. After cooling to ambient temperature, the reaction mixture was filtered over a plug of silica and washed with Et_2O (200 mL). The filtrate was concentrated, and the residue was purified by column chromatography on silica gel to afford the title compound. If the organic product was volatile, the compound was tosylated before isolation (see the SI for details).

Reaction of 1 with *m*CPBA. Iridium complex **1** (57.9 mg, 0.100 mmol, 1.00 equiv) and sodium carbonate (106 mg, 1.00 mmol, 10.0 equiv) were added to a round-bottom flask. Acetonitrile (5 mL) was added, followed by a solution of *m*CPBA in DCM (1.00 mL, 0.100 mmol, 1.00 equiv, 0.10 M). The reaction mixture was allowed to stir for 3 h at 23 °C, during which time the mixture became cloudy with a colorless precipitate. The reaction mixture was filtered over glass wool. The filtrate was then concentrated to 2 mL, and Et_2O (10 mL) was added, affording a colorless precipitate. Centrifugation, followed by decantation of the supernatant, yielded a colorless solid. The solid was extracted with DCM (100 mL). The extracts were filtered through glass wool and concentrated to 10 mL, and Et_2O (10 mL) was added. Centrifugation, followed by decantation of the supernatant, yielded a colorless solid, which was washed with Et_2O (10 mL) and dried under high vacuum to afford 43.0 mg of **2** as a colorless solid (85% yield). Spectroscopic data matched those described above for compound **2**.

η^5-Cyclohexadienyl Adduct of *m*CPBA and 1 (5). Complex **1** (17.3 mg, 0.0300 mmol, 1.00 equiv) and Na_2CO_3 (63.6 mg, 0.600 mmol, 20.0 equiv) were added to an NMR tube. A solution of *m*CPBA in CD_3CN (1.00 mL, 0.0300 mmol, 1.00 equiv, 0.030 M) was added, and the tube was inverted once and immediately placed into the precooled (−40 °C) NMR machine. NMR spectroscopy: ^{1}H NMR (500 MHz, CD_3CN, 23 °C, δ): 7.87 (s, 1H, H6), 7.79 (d, J = 7.9 Hz, 1H, H9), 7.68 (d, J = 8.1 Hz, 1H, H7), 7.51 (dd, J = 8.0, 8.0 Hz, 1H, H8), 6.47 (t, J = 5.2 Hz, 1H, H4), 5.50 (dd, J = 5.8, 5.8 Hz, 2H, H3), 4.89 (t, J = 6.0 Hz, 1H, H1), 4.43 (dd, J = 6.1 Hz, 6.1 Hz, 2H, H2), 2.14 (s, 15H, H5). ^{13}C NMR (125 MHz, CD_3CN, 23 °C, δ): 134.4 (C7), 131.3 (C8), 129.2 (C6), 128.1 (C9), 88.5 (C3), 87.3 (C4), 72.8 (C1), 45.9 (C2), 9.9 (C5). NMR spectra also contain complex **1**, complex **2**, *m*CPBA, and *m*-chlorobenzoic acid.

Monoalkylated η^5-Cyclohexadienyl Adduct of H_2O_2 and 1 (6a). Complex **1** (29.0 mg, 0.0500 mmol, 1.00 equiv), Na_2CO_3 (10.6 mg, 0.100 mmol, 2.00 equiv), CD_3CN (1.0 mL), and H_2O_2(aq) (28 μL, 0.25 mmol, 5.0 equiv, 30 wt %) were added to a 4 mL scintillation vial. The mixture was allowed to stir for 1.5 h at 23 °C. The mixture was filtered through glass wool into an NMR tube. The yield of the title compound was determined by internal standard (dioxane) to be 68%. Dimeric adduct **6b** (see below) was observed in 8% yield. NMR spectroscopy: ^{1}H NMR (600 MHz, CD_3CN, 23 °C, δ): 9.78 (br, 1H), 6.40 (t, J = 5.2 Hz, 1H), 5.39 (dd, J = 5.8 Hz, 5.8 Hz, 2H), 4.35 (t, J = 5.9 Hz, 1H), 4.26 (dd, J = 5.9 Hz, 5.9 Hz, 2H), 2.15 (s, 15H). ^{13}C NMR (125 MHz, CD_3CN, 23 °C, δ): 98.9, 88.8, 87.5, 71.9, 47.2, 10.3.

Bisalkylated η^5-Cyclohexadienyl Adduct of H_2O_2 and 1 (6b). Complex **1** (116 mg, 0.200 mmol, 1.00 equiv), Na_2CO_3 (106 mg, 1.00 mmol, 5.00 equiv), acetonitrile (10 mL), and H_2O_2(aq) (14 μL, 0.12 mmol, 0.60 equiv, 30 wt %) were added to a 20 mL scintillation vial. The mixture was allowed to stir for 3 h at 23 °C. The mixture was filtered through glass wool, and the filtrate was concentrated to 3 mL. The solid residue was extracted with DCM (50 mL) and filtered, and the filtrate was concentrated. The solid residue was dissolved in acetonitrile (10 mL), and $NaBF_4$ (400 mg) was added. The mixture was stirred for 3 h at 23 °C. The mixture was filtered through glass wool, and the filtrate was concentrated. The solid residue was extracted with DCM (50 mL) and filtered, and the filtrate was concentrated to afford 77.8 mg of the title compound as a colorless solid (76% yield). NMR spectroscopy: ^{1}H NMR (600 MHz, CD_3CN, 23 °C, δ): 6.38 (t, J = 5.3 Hz, 2H), 5.38 (dd, J = 5.9 Hz, 5.9 Hz, 4H), 4.26 (t, J = 5.9 Hz, 2H), 4.18 (dd, J = 6.1 Hz, 6.1 Hz, 4H), 2.15 (s, 30H). ^{13}C NMR (125 MHz, CD_3CN, 23 °C, δ): 99.0, 88.8, 87.6, 70.9, 47.4, 10.3. Anal. Calcd for $C_{32}H_{42}B_2F_8Ir_2O_2$: C, 37.80; H, 4.16. Found: C, 38.03; H, 4.14. Adduct **6b** decomposes to give complex **2** upon standing in CD_3CN solution. Complex **2** is generated in 5% yield after 5 d at 23 °C.

Reaction of 1 with H_2O, Na_2CO_3, and [4-NHAc-TEMPO]BF_4. Iridium complex **1** (57.9 mg, 0.100 mmol, 1.00 equiv), sodium carbonate (212 mg, 2.00 mmol, 20.0 equiv), and [4-NHAc-TEMPO]BF_4 (60.0 mg, 0.200 mmol, 2.00 equiv) were added to a 20 mL scintillation vial. Acetonitrile (5 mL) and water (9.0 μL, 0.50 mmol, 5.0 equiv) were added. The reaction mixture was allowed to stir for 4 h at 23 °C. The reaction mixture was filtered over glass wool. The filtrate was then concentrated to 2 mL, and Et_2O (15 mL) was added, affording a colorless precipitate. Centrifugation, followed by decantation of the supernatant, yielded a colorless solid. The solid was extracted with DCM (50 mL). The extracts were filtered through glass wool and concentrated. The solid residue was dissolved in acetonitrile (2 mL) and Et_2O was added (10 mL) to afford a colorless precipitate. Centrifugation, followed by decantation of the supernatant, yielded a colorless solid, which was washed with Et_2O (10 mL) to afford 40.1 mg of **2** as a colorless solid (79% yield). Spectroscopic data matched those described above for compound **2**.

Arene Exchange Reaction. Iridium complex **1** (10.2 mg, 0.0200 mmol, 1.00 equiv), benzene (0.20 mL), 3-methyl-2-oxazolidinone (0.20 mL), and $HBF_4{\cdot}OEt_2$ (5.0 μL, 0.040 mmol, 2.0 equiv) were added to a 4 mL scintillation vial. The reaction mixture was allowed to stir at 80 °C for 2 d. After cooling to room temperature, Et_2O (3 mL) was added. Centrifugation, followed by decantation of the supernatant, afforded a brown oil. The supernatant was set aside and saved (see below). The brown oil was dissolved in 3-methyl-2-oxazolidinone (0.20 mL). Benzene (0.20 mL) and $HBF_4{\cdot}OEt_2$ (5.0 μL, 0.040 mmol, 2.0 equiv) were added. The reaction mixture was again allowed to stir at 80 °C for 2 d. The workup described above was repeated, and the supernatant was again saved. The resulting brown oil was dissolved in 3-methyl-2-oxazolidinone (0.20 mL) for a final time. Benzene (0.20 mL) and $HBF_4{\cdot}OEt_2$ (5.0 μL, 0.040 mmol, 2.0 equiv) were added. The reaction mixture was allowed to stir at 80 °C for 2 d. The workup described above was repeated, and the supernatant was saved. The brown oil was dissolved in acetonitrile (0.50 mL), and Et_2O (3 mL) was added. Centrifugation, followed by decantation and drying under high vacuum, afforded a colorless solid, which was analyzed by ^{1}H NMR spectroscopy to contain **1**, **2**, 3-methyl-2-oxazolidinone, and protonated *N*-methylethanolamine. The yield of **1** was determined by integration against an internal standard (dioxane, 2 μL) to be 66%. Isolation of phenyl tosylate (**4a**): Due to the volatility of phenol, the supernatant was concentrated to 5 mL, and *p*-toluenesulfonyl chloride (34.2 mg, 0.180 mmol, 9.00 equiv), 4-dimethylaminopyridine (7.2 mg, 0.060 mmol, 3.0 equiv), and triethylamine (75 μL, 0.54 mmol, 27 equiv) were added. The mixture was allowed to stir for 15 h at 23 °C. DCM (10 mL) and H_2O (10 mL) were added, and the reaction mixture was poured into a separatory funnel. The layers were separated. The aqueous layer was extracted with DCM (2 × 10 mL). The combined organic layers were washed with 1 M $HCl_{(aq)}$ (10 mL) and brine (10 mL), dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel eluting with a solvent mixture of Et_2O/pentane (5:95 (v/v)) to afford 2.7 mg of the title compound as a colorless solid (54% yield). Spectroscopic data matched those described in the SI for compound **4a** (p S8).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00731.

Additional experimental procedures and characterization data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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