Half-Sandwich Rh(Cp*) and Ir(Cp*) Complexes with Oxygen Atom Transfer Reagents as Ligands

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ABSTRACT. Rhodium(Cp*) and iridium(Cp*) complexes with bidentate ligands and a coordinated oxygen atom transfer reagent as the final ligand in the d⁶ coordination sphere are described (Cp* = η^5 -pentamethylcyclopentadienyl). A Rh(Cp*) cation with a pyridyl-benzamide bidentate ligand resistant to insertion and a coordinated oxygen atom transfer reagent, 2-*tert*-butylsulfonyliodosylbenzene (sPhIO), was isolated in the solid state. In anhydrous solution, the sPhIO ligand was reduced over 24 hours, and a solvent-stabilized, 16-electron rhodium complex was formed. Oxygen atom transfer either led to unobserved oxidative degradation of a small fraction of the rhodium species, or formed the iodoxyarene, sPhIO₂, via a known disproportionation reaction. The reduced oxidant, sPhI, did not coordinate to rhodium, but the 16-electron cation was readily trapped by water. The organometallic Ir(Cp*) backbone with cyclometalated 2-phenylpyridine (phpy) formed stable complexes with the mild oxygen atom

transfer reagents pyridine-*N*-oxide and 4-methoxy-pyridine-*N*-oxide. Oxygen atom transfer from the coordinated *N*-oxides was induced by thermolysis or photolysis and initially led to decomposition of a small fraction of the samples. The liberated pyridine derivatives displaced coordinated *N*-oxides and somewhat limited decomposition of the Ir(Cp*)(phpy) backbone. Neither oxygen atom insertion into the metal-carbon bond of coordinated phpy nor metal-oxo complexes were observed.

Abstract Graphic

Ligand Substitution or Cp* Oxidation after Oxygen Atom Transfer

Graphical abstract synopsis

Three new rhodium(Cp*) and iridium(Cp*) complexes with bidentate ligands and coordinated oxygen atom transfer reagents are described. Oxygen atom transfer was promoted by heat or light irradiation. The reactivity of each of the three compounds is explored.

Keywords

rhodium, iridium; oxygen atom transfer; photolysis; thermolysis

INTRODUCTION

Oxygen atom transfer (OAT) is a method to probe the oxidation chemistry of transition metal complexes.¹ OAT reagents have practical value as terminal oxidants in metal-catalyzed processes, such as alkene epoxidation.² They are also useful for fundamental studies, which show that OAT can induce insertion reactions at a metal center³ or generate a metal-oxo species in a single step (Scheme 1).⁴ While metal-oxo complexes have been proposed as reactive intermediates in biological applications,⁵ industrial applications,⁶ and water oxidation catalysis,⁷ they are often difficult to detect or study. Metal-oxo compounds of the late transition metals (groups 9-11) are especially rare,⁸ as the metal-oxo bond is destabilized by electronic repulsion between filled $d\pi$ -orbitals on the metal and filled p-orbitals on the oxo ligand.⁹ By combining oxygen atom transfer reagents with labile Cp* derivatives of rhodium and iridium we have been able to probe the scope of reactions available to these strong oxidants.

Scheme 1. Oxygen atom transfer to a metal can induce insertion reactions (a) or oxidation to a metal-oxo complex (b).

Oxygen atom transfer to a metal can be initiated by ligation of a nucleophilic OAT reagent to a vacant metal coordination site. Subsequent oxidation of the metal generates the metal-oxo double bond and liberates the reduced OAT fragment. Recent efforts utilizing labile late transition metal complexes revealed unexpected OAT to the labile ligand.¹⁰ While coordination of nucleophilic OAT reagents typically forms transient intermediates, some stable metal complexes with coordinated OAT reagents have been isolated. Such compounds serve as well-defined starting points for OAT reactions because the initial metal-oxygen bond is already established. Oxygen atom transfer can be triggered by heat or light. For example, iron and

manganese complexes with coordinated perchlorate anions (ClO_4^-) have been oxidized to their respective oxo compounds by photolysis resulting in extrusion of chlorate (ClO_3^-).¹¹ In addition, a polypyridyl iron compound with coordinated iodosylbenzene has been reported, and this iron compound oxidized sulfides to sulfoxides when heated, presumably due to formation of an intermediate iron-oxo complex.¹² Even a ruthenium complex with a *pendant* pyridine-*N*-oxide ligand furnished a ruthenium-oxo compound upon photolysis.¹³ *N*-oxides also coordinate to platinum and rhodium compounds, generating stable models of intermediates proposed in oxygen functionalization reactions.¹⁴⁻¹⁵ A $\text{Rh}(\text{Cp}^*)$ complex with a coordinated iodosylbenzene derivative and an $\text{Ir}(\text{Cp}^*)$ compound with a coordinated pyridine-*N*-oxide are also known, but oxidation to form terminal metal-oxo complexes was not described.^{10,16} Compounds with coordinated OAT reagents are relatively easy to handle and serve as well-defined precursors for oxygen atom transfer reactions. Activation of coordinated OAT reagents with heat or light, therefore, is an attractive method to probe either oxidation to form an oxo complex or alkyl/aryl migration to the oxygen atom of the OAT reagent.

In this article, three new late transition metal compounds with coordinated oxygen atom transfer reagents are reported. The OAT reaction is investigated for each of these compounds by photolysis or thermolysis, and the reactivity of each compound is described.

RESULTS AND DISCUSSION

A $\text{Rh}(\text{Cp}^*)$ complex with a coordinated iodosylbenzene derivative. Compound **1**, $\text{Rh}(\text{Cp}^*)[(3,5\text{-bis(trifluoromethyl)benzoyl})(2\text{-(2-pyridyl)phenyl)amide}]\text{Cl}$, was synthesized from $[\text{Rh}(\text{Cp}^*)\text{Cl}_2]_2$ and the proligand 3,5-bis(trifluoromethyl)-*N*-(2-(2-pyridyl)phenyl)benzamide by following a procedure described for metalation of the same proligand with $[\text{Ir}(\text{Cp}^*)\text{Cl}_2]_2$.¹⁰

Deprotonation of the proligand by the insoluble NaH base, followed by filtration of the THF solution onto solid $[\text{Rh}(\text{Cp}^*)\text{Cl}_2]_2$, yielded complex **1** after stirring overnight (Scheme 2). The product was stable to both air and water.

Scheme 2. Synthesis of $\text{Rh}(\text{Cp}^*)$ compound **1**.

Abstraction of the chloride from the $\text{Rh}(\text{Cp}^*)$ compound **1** was accomplished with $\text{Na}[\text{B}(\text{Ar}^{\text{F}})_4]$ in the presence of 2-*tert*-butylsulfonyliodosylbenzene (sPhIO, Scheme 3).¹⁷⁻¹⁹ The sPhIO-Rh adduct (**2**) was transiently stable in solution at room temperature, and ^1H NMR spectroscopy confirmed that sPhIO had coordinated to rhodium. The aromatic region of the

Scheme 3. Synthesis of a $\text{Rh}(\text{Cp}^*)$ complex with a coordinated iodosylbenzene derivative.

spectrum of **2** revealed the 11 resonances expected for the pyridyl-benzamide ligand, and four additional resonances were identified (2 doublets, 2 triplets) belonging to the sPhIO ligand. A nine-proton ^tBu resonance singlet appeared at 1.30 ppm, a chemical shift which is upfield of the ^tBu resonances for both non-coordinated sPhIO and sPhI (1.40 ppm and 1.38 ppm, respectively). An upfield shift of the ^tBu resonance was also observed for coordinated sPhIO in a sPhIO- $\text{Rh}(\text{Cp}^*)$ compound.¹⁶ Additionally, the ^{13}C NMR spectrum of **2** revealed that the carbon bonded to iodine of coordinated sPhIO resonated at 121.4 ppm, about 4 ppm below the parallel carbon resonance of sPhIO (117.9) and far below sPhI (94.6).¹⁷ This downfield shift is a clear indication that iodine is bound to oxygen,¹⁷ and confirms that sPhIO is indeed coordinated to rhodium.

Samples of the sPhIO-Rh adduct **2** were found to be analytically pure by elemental analysis. Compound **2** is a rare example of a metal compound with a coordinated iodosylarene derivative.^{12,20}

When chloride abstraction was monitored *in situ* at 0 °C by ¹H NMR spectroscopy, compound **1** reacted immediately, but an intermediate species distinct from **2** was observed (compound **3**, Scheme 4). The intermediate species **3** converted to the sPhIO-Rh compound **2** over several minutes. The NMR spectrum indicated that some sPhIO was not coordinated to

Scheme 4. Observation of intermediate **3** when chloride abstraction from **1** was monitored *in situ* at 0 °C.

rhodium when intermediate **3** was in solution. We postulated that chloride abstraction slowed at lower temperatures, and that chloride-bridged rhodium dimers could form transiently. To test this hypothesis, compound **1** was treated with one-half an equivalent of Na[B(Ar^F)₄] at room temperature. The species identified by ¹H NMR spectroscopy was the same as the intermediate species observed at 0 °C, confirming the assignment of compound **3** as a chloride-bridged dinuclear rhodium species (Scheme 5). Independently synthesized dinuclear compound **3** reacted with sPhIO to form a 1:1 mixture of compounds **1** and **2** (identified by ¹H NMR spectroscopy).

Scheme 5. Independent synthesis of dimer **3**.

Upon standing at 23 °C in anhydrous solution, sPhIO-rhodium adduct **2** converted to a different species over 24 hours (91% overall yield, as determined by ¹H NMR spectroscopy). Conversion to the new rhodium species was concomitant with the appearance of sPhI in the ¹H

NMR spectra, indicating that product formation was contingent on oxygen atom transfer (Scheme 6). The new species was determined to be the solvent-stabilized, unsaturated $[\text{Rh}(\text{Cp}^*)(\kappa^2\text{-pyridyl-benzamide})]$ cation (**4**), and this assignment was verified in a separate reaction by adding compound **1** and one equivalent of $\text{Na}[\text{B}(\text{Ar}^{\text{F}})_4]$ to dichloromethane- d_2 under strictly anhydrous conditions (Scheme 6). The ^1H NMR spectra of the two species formed from compounds **1** and **2** were essentially identical. Coordination of sPhI was ruled out by mixing compound **1**, $\text{Na}[\text{B}(\text{Ar}^{\text{F}})_4]$, and sPhI in anhydrous dichloromethane- d_2 . The presence of sPhI did not change the chemical shifts of the rhodium complex **4** in solution. Solvent-stabilized, 16-electron $\text{Rh}(\text{Cp}^*)$ cations have been reported with different bidentate ligands.¹⁶

Scheme 6. Reaction of compound **2** (top) and *in situ* chloride abstraction from **1** (bottom) yield the solvent-stabilized complex **4**.

The net result of oxygen atom transfer is not known since the final destination of the oxygen atom that was transferred away from sPhIO could not be ascertained. At least two explanations could account for oxygen atom transfer without oxygen atom incorporation into the rhodium product. One explanation is that a small fraction (<10%) of the sPhIO-Rh adduct **2** begins to decompose upon oxygen atom transfer to the metal (Cp* ligand oxidation is well-known for $\text{Ir}(\text{Cp}^*)$ compounds).²¹ If decomposition products of rhodium are susceptible to further oxidation, dissociation of sPhIO from **2** and oxidation of the compromised rhodium species is possible. A small fraction of the rhodium in solution, therefore, could be oxidized by multiple equivalents of the sPhIO reagent. One would expect to see roughly a 1:1 ratio of

complex **4** to sPhI at the end of the reaction. Another possible explanation arises from the known disproportionation reaction of iodosylbenzene reagents. It is thermodynamically favorable for two equivalents of sPhIO to disproportionate into one equivalent each of sPhI (2-*tert*-butylsulfonyliodobenzene) and the sparingly soluble sPhIO₂ (2-*tert*-butylsulfonyliodoxybenzene).¹⁷ Disproportionation, followed by precipitation of half an equivalent of sPhIO₂, could account for the lack of oxygen atom incorporation into the rhodium product **4**. In this situation, one would expect to see only one-half an equivalent of sPhI relative to **4**. We favor the first explanation, as a full equivalent of sPhI is generated during conversion to the unsaturated, 16-electron rhodium cation **4**. The presence of sPhIO₂ was not discerned by ¹H NMR spectroscopy, and no precipitate was evident during the reaction.

The unsaturated, 16-electron rhodium complex **4** was readily trapped by adding water to form the aqua adduct, [Rh(Cp*)(κ²-pyridyl-benzamide)(OH₂)]⁺ (compound **5**, Scheme 7). X-ray analysis on a crystal suitable for diffraction confirmed the identity of the final product, and the structure of the cation is shown in Figure 1. Notably, the benzamide oxygen atom forms a hydrogen bond to one of the hydrogens of the coordinated water (1.66 Å). The hydrogens on the water were located from the electron difference map and the positions refined isotropically. The benzamide C-O bond distance (1.27 Å) and C-N bond distance (1.32 Å) were typical values expected for amide bonds. Importantly, the ¹H NMR spectrum of the isolated crystals was the same as the ¹H NMR spectrum of the rhodium compound formed upon addition of water, ensuring that the final species in this reaction cascade was indeed the aqua adduct **5**.

Scheme 7. Addition of water to compound **4** yields complex **5**.

The overall reaction scheme, starting from chloride abstraction from rhodium compound **1**, is shown in the Supporting Information. The unsaturated, 16-electron $[\text{Rh}(\text{Cp}^*)(\kappa^2\text{-pyridyl-benzamide})]^+$ compound **4** is not observed if the conversion of the sPhIO-Rh adduct **2** is allowed to occur in solvent that has not been rigorously dried. In this case, growth of the diagnostic signals for sPhI in the ^1H NMR spectra is observed concomitantly both with the growth of

Figure 1. ORTEP drawing of **5**, with partial numbering scheme (50% probability thermal ellipsoids). The anion and hydrogen atoms (except for the aqua hydrogen atoms) have been omitted for clarity. Selected bond lengths (Å): Rh₁ – O₁ 2.1914(14), Rh₁ – N₁ 2.1108(16), Rh₁ – N₂ 2.1007(16), O₂ – C₁₂ 1.268(2), N₂ – C₁₂ 1.324(3), O₂ ... H_{1B} 1.66(3).

diagnostic signals of the aqua adduct **5** and with the disappearance of resonances for the sPhIO adduct **2** over 24 hours. The sPhIO reagent, therefore, is a stronger ligand than water. At low water concentrations, compounds **4** and **5** were found to be in rapid equilibrium by ^1H NMR spectroscopy. A terminal rhodium-oxo complex was not observed at any point in the reaction sequence.

Iridium(Cp*) complexes with coordinated pyridine-*N*-oxides. Synthesis of $\text{Ir}(\text{Cp}^*)(\text{phpy})$ cations with coordinated pyridine-*N*-oxides was accomplished in one step ($\text{Cp}^* = \eta^5\text{-pentamethylcyclopentadienyl}$, $\text{phpy} = \text{cyclometalated 2-phenylpyridine}$). Chloride abstraction

from Ir(Cp*)(phpy)Cl in the presence of stoichiometric pyridine-*N*-oxide yielded the pyridine-*N*-oxide adducts (Scheme 8). The choice of pyridine-*N*-oxide affected the stability of the Ir(Cp*)(phpy) adduct. Stable products could be formed using pyridine-*N*-oxide (compound **6**) and 4-methoxy-pyridine-*N*-oxide (compound **7**), but decomposition was observed when the stronger OAT reagent, 4-nitro-pyridine-*N*-oxide, was tried. The electron-withdrawing nitro group destabilizes the nitrogen-oxygen bond of the *N*-oxide. That OAT occurred spontaneously from 4-nitro-pyridine-*N*-oxide suggested that OAT might be promoted starting from coordinated pyridine-*N*-oxide and 4-methoxy-pyridine-*N*-oxide. Stable coordination of these two *N*-oxides in complexes **6** and **7** allowed for monitoring OAT reactions initiated by thermolysis or photolysis.

Scheme 8. Synthesis of Ir(Cp*) complexes **6** and **7** with coordinated *N*-oxides.

Thermolysis. Compound **6** was dissolved in dichloromethane-*d*₂ and heated at 80 °C in a sealed NMR tube for 16 hours (Scheme 9a). ¹H NMR spectroscopy after heating revealed that all of compound **6** had reacted, but the reaction was not clean. The major product was identified as the pyridine adduct, [Ir(Cp*)(phpy)(pyridine)]⁺, which was formed in 35% yield. The identity of the product was verified by comparison to a known sample of [Ir(Cp*)(phpy)(pyridine)]⁺, which was generated *in situ* by adding pyridine to the acetonitrile adduct, [Ir(Cp*)(phpy)(NCCH₃)]⁺.²² An additional 43% of the iridium species might be accounted for by summing the integrals of two resonances in the alkyl region (the resonances might correspond to -CH₃ groups of the Cp* ligand), but these minor species could not be identified because the ¹H NMR spectrum was complex. At least 22% of the iridium starting material suffered decomposition of the organic ligands and was invisible by ¹H NMR spectroscopy, but the percentage of iridium that

experienced organic ligand oxidation may have reached as high as 65%. Shorter reaction times (4 hours) resulted in only partial conversion of compound **6**, but no new intermediates were observed, and ligand decomposition was still implicated. Cp* ligand degradation is often observed under oxidative stress at iridium.²¹

The presence of $[\text{Ir}(\text{Cp}^*)(\text{phpy})(\text{pyridine})]^+$ can be accounted for by ligand substitution of pyridine for pyridine-*N*-oxide at compound **6**. Pyridine is the byproduct of oxygen atom transfer from pyridine-*N*-oxide. Presumably, coordination of pyridine limits oxidative degradation of the organometallic $\text{Ir}(\text{Cp}^*)(\text{phpy})$ backbone by preventing OAT to iridium. No evidence of oxygen atom insertion into the iridium-carbon bond of coordinated phpy was observed, although the isoelectronic nitrene insertion into the iridium-carbon bond of coordinated phpy at $[\text{Ir}(\text{Cp}^*)(\text{phpy})(\text{NCCH}_3)]^+$ has been documented.²² In addition, oxygen atom insertion into the rhodium-carbon bond of coordinated phpy at a $\text{Rh}(\text{Cp}^*)$ complex has been observed.¹⁶ Oxygen atom insertion does not occur in the thermolysis reaction presented here.

Thermolysis of the 4-methoxy-pyridine-*N*-oxide adduct **7** at 75 °C for 16 hours was also performed (Scheme 9b). It was found that complex **7** did not react as quickly as compound **6**,

Scheme 9. Thermolysis of compound **6** (a) and compound **7** (b).

which is expected because 4-methoxy-pyridine-*N*-oxide is a milder OAT reagent than pyridine-*N*-oxide. Conversion to the 4-methoxy-pyridine adduct, $[\text{Ir}(\text{Cp}^*)(\text{phpy})(\text{4-methoxy-pyridine})]^+$, had reached 44% after 16 hours, but 29% of starting compound **7** still remained. Oxygen atom

insertion into the iridium-carbon bond of coordinated phpy was not observed, and no evidence of an iridium-oxo compound was obtained spectroscopically. Instead, OAT was believed to cause oxidative degradation of at least 20% of the iridium starting material **7**. The results of these two thermolysis reactions are similar to what was observed in thermolysis reactions of platinum and rhodium compounds with coordinated pyridine-*N*-oxide ligands.¹⁵

Photolysis. In an attempt to stabilize potentially reactive species formed during photolysis reactions, all photolysis experiments were conducted at -10 °C (470 nm light). Irradiation of pyridine-*N*-oxide adduct **6** for 4 hours at -10 °C resulted in only partial conversion of the starting compound (Scheme 10a). The original compound **6** still accounted for 64% of the iridium species in solution, while 27% of the iridium had converted to the pyridine adduct, $[\text{Ir}(\text{Cp}^*)(\text{phpy})(\text{pyridine})]^+$. At most, only 9% of the sample suffered Cp* ligand degradation, but the photolysis reaction still resembled the thermolysis reaction for pyridine-*N*-oxide adduct **6**. Irradiation of compound **7** at -10 °C for 4 hours resulted in no reaction (Scheme 10b). It is possible that the reaction was too slow to be monitored at -10 °C, or that irradiation did not trigger oxygen atom transfer. Another possibility is that breaking the nitrogen-oxygen bond of the coordinated *N*-oxide is reversible, rapidly reforming the nitrogen-oxygen bond. A reversible bond-breaking reaction has been identified by femtosecond laser flash spectroscopic study of a ruthenium compound with a coordinated pyridine-*N*-oxide.¹³ The possibility of a degenerate,

Scheme 10. Photolysis of compound **6** (a) and compound **7** (b).

reversible reaction would be more likely with compound **7** than with compound **6** because 4-methoxy-pyridine is more easily oxidized to an *N*-oxide than pyridine.

In neither the thermolysis nor photolysis experiments could any evidence be obtained for oxo complexes or oxygen atom insertion into the metal-carbon bond of coordinated phpy. Instead, the predominant molecular products were $[\text{Ir}(\text{Cp}^*)(\text{phpy})(\text{pyridine})]$ cations, formed by displacement of *N*-oxides by liberated pyridines. Oxidative ligand degradation was also implicated, especially for the more reactive OPy adduct **6**. This suggests that the $\text{Ir}(\text{Cp}^*)(\text{phpy})$ backbone is unlikely to support oxygen atom insertion into the iridium-carbon bond of coordinated phpy.

CONCLUSIONS

Three new late transition metal complexes with coordinated oxygen atom transfer reagents are described. A $\text{Rh}(\text{Cp}^*)$ complex with a pyridyl-benzamide bidentate ligand bearing a coordinated sPhIO oxygen atom transfer reagent (**2**) was isolated in the solid state. In anhydrous solution, the compound converted to a solvent-stabilized, 16-electron complex (**4**) as sPhIO dissociated and reacted. It is believed that a small fraction of the $\text{Rh}(\text{Cp}^*)$ complex **2** in solution decomposed (Cp^* ligand oxidation) and consumed multiple equivalents of the sPhIO oxidant. The reduced oxidant, sPhI, did not coordinate to the 16-electron complex, but water readily trapped the unsaturated compound and formed an isolable adduct (**5**). The organometallic $\text{Ir}(\text{Cp}^*)(\text{phpy})$ backbone formed stable cationic compounds with the OAT reagents pyridine-*N*-oxide and 4-methoxy-pyridine-*N*-oxide. Thermolysis or photolysis of these compounds generally resulted in formation of the $[\text{Ir}(\text{Cp}^*)(\text{phpy})(\text{pyridine})]^+$ adducts. In each of the three compounds studied, some Cp^* ligand oxidation was either observed or suggested by the experimental data.

In no instance was oxidation to a metal-oxo complex or oxygen atom insertion into the bidentate ligand observed.

EXPERIMENTAL

Materials and methods. All reactions were performed under an atmosphere of dry argon using standard Schlenk and drybox techniques, unless noted otherwise. Argon was purified by passage through columns of BASF R3-11 catalyst and 4 Å molecular sieves. Methylene chloride, hexane, and pentane were purified under an argon atmosphere and distilled over calcium hydride. All other chemicals were used as received without further purification. ^1H and ^{13}C NMR spectra were recorded on Bruker AVANCEIII400, AVANCEIII500, and AVANCEIII600 spectrometers. ^1H NMR and ^{13}C NMR chemical shifts were referenced to residual ^1H and ^{13}C signals of the deuterated solvents. Yields of NMR reactions were determined using the resonances of the $[\text{B}(\text{Ar}^{\text{F}})_4]$ anion as an internal standard. X-ray diffraction studies were conducted on a Bruker-AXS SMART APEX-II diffractometer. Crystals were selected and mounted using a paratone oil on a MiteGen mylar tip. Elemental analyses were performed by Robertson Microlit Laboratories of Madison, NJ. **CAUTION:** An explosion hazard has been reported using the initially published procedure for preparation of the oxygen atom transfer reagent 2-*tert*-butylsulfonyliodosylbenzene (sPhIO).¹⁷⁻¹⁸ In this work we have used a recent procedure published by Lin.¹⁹

Irradiation experiments. Solutions of compounds **6** and **7** were prepared in NMR tubes in dichloromethane- d_2 . The NMR tubes were placed in a Thermo NesLab CB-80 cooled to -10 °C, and were irradiated for four hours with 470 nm LED light strips. The solutions were then analyzed by ^1H NMR spectroscopy.

Synthesis of $\text{Rh}(\text{Cp}^*)[(3,5\text{-bis(trifluoromethyl)benzoyl})(2\text{-(2-pyridyl)phenyl)amide}]\text{Cl}$ (1**).** A mixture of 130 mg NaH (5.4 mmol), 415 mg proligand 3,5-bis(trifluoromethyl)-*N*-(2-(2-pyridyl)phenyl)benzamide (1.0 mmol), and 25 mL of THF were stirred for 1.5 hours and then filtered by cannula onto 300 mg $[\text{Rh}(\text{Cp}^*)(\text{Cl})_2]_2$ (0.49 mmol). The rhodium dimer had been dried by heating at 40 °C under high vacuum the previous night. After stirring the reaction mixture overnight, dichloromethane was added until the colored solids dissolved. The mixture was filtered by cannula and the solvent was removed under reduced pressure. The solid was redissolved in minimal dichloromethane and slowly added to chilled (-78 °C), rapidly stirring

pentane (35 mL). The mixture was filtered via cannula, and the solid was placed under high vacuum overnight while heating at 40 °C. An orange powder was isolated (542 mg, 81%). Anal. Calcd. (found) for $C_{30}H_{26}N_2F_6RhOCl$: C, 52.76 (52.63); H, 3.84 (3.78); N, 4.10 (3.98). 1H NMR (600 MHz, CD_2Cl_2) δ 9.01 (d, J = 4.8, 1H), 7.93 (td, J = 7.8 and 1.2, 1H), 7.85 (d, J = 7.8, 1H), 7.79 (s, 2H), 7.66 (s, 1H), 7.58 (dd, J = 7.8 and 1.2, 1H), 7.40 (td, J = 6.6 and 1.2, 1H), 7.07 (td, J = 7.8 and 1.2, 1H), 6.97 (t, J = 7.2, 1H), 6.60 (d, J = 7.8, 1H), 1.43 (s, 15H). $^{13}C\{^1H\}$ NMR (150 MHz, CD_2Cl_2) δ 171.3, 156.8, 155.1, 149.9, 142.5, 138.9, 131.8, 130.9, 130.6, 130.5 (q, 2 bond J_{C-F} = 33), 130.3, 128.9, 123.9, 123.8 (q, 1 bond J_{C-F} = 272), 123.1, 122.4 (septet, 3 bond J_{C-F} = 3), 122.0, 94.6 (d, J_{C-Rh} = 8), 8.7.

Synthesis of $[Rh(Cp^*)\{(3,5\text{-bis(trifluoromethyl)benzoyl}(2\text{-(2-pyridyl)phenyl)amide}\}(sPhIO)][B(Ar^F)_4]$ (2). A 100 mL Schlenk flask was charged with 200 mg compound **1** (0.29 mmol), 280 mg $Na[B(Ar^F)_4]$ (0.32 mmol), 108 mg *sPhIO* (0.32 mmol), and 20 mL dichloromethane. The reaction was stirred for 1 hour at 0 °C and then filtered via cannula. The solvent of the filtrate was reduced to a minimal volume and then added slowly to 25 mL of chilled (-78 °C), rapidly stirring pentane (30 mL). The mixture was filtered and the solid was placed under high vacuum for 1 hr. Product **2** was isolated as an orange solid (380 mg, 70%). Anal. Calcd. (found) for $C_{72}H_{51}BF_{30}IN_2O_4RhS$: C, 46.72 (46.98); H, 2.78 (2.98); N, 1.51 (1.45). 1H NMR (500 MHz, CD_2Cl_2 , 10 °C) δ 8.92 (d, J = 5.5, 1H), 8.14 (d, J = 8.5, 1H), 8.03 (t, J = 7.0, 1H), 8.00 (t, J = 7.5, 1H), 7.95 (d, J = 7.5, 1H), 7.88 (d, J = 8.0, 1H), 7.80 (s, 1H), 7.72 (s, 8H), 7.72 (overlapping triplet, 1H), 7.66 (s, 2H), 7.63 (m, 1H), 7.55 (s, 4H), 7.50 (t, J = 6.5, 1H), 7.16 (m, 2H), 6.58 (m, 1H), 1.33 (s, 15H), 1.30 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2 , -10 °C, one carbon merged to others) δ 171.9, 161.8 (1:1:1:1 quartet, J_{C-B} = 50), 156.0, 152.1, 145.0, 140.1, 135.9, 134.8, 133.6, 132.3, 131.2, 131.1, 130.9 (q, 2 bond J_{C-F} = 33), 130.8, 130.6, 129.6, 128.8 (q, 2 bond J_{C-F} = 31), 128.1, 127.6, 125.2, 124.9, 124.5 (q, 1 bond J_{C-F} = 270), 124.3, 123.3 (septet, 3 bond J_{C-F} = 3), 122.9 (q, 1 bond J_{C-F} = 272), 121.4, 117.6 (septet, 3 bond J_{C-F} = 4), 94.9 (d, J_{C-Rh} = 8), 63.5, 22.9, 8.6.

In Situ Synthesis of $[Rh_2(Cp^*)_2\{(3,5\text{-bis(trifluoromethyl)benzoyl}(2\text{-(2-pyridyl)phenyl)amide}\}_2Cl][B(Ar^F)_4]$ (3). An NMR tube was charged with 6.5 mg of rhodium compound **1** (0.010 mmol), 4.2 mg $Na[B(Ar^F)_4]$ (0.005 mmol, one-half equivalent), and 0.4 mL dichloromethane- d_2 . The NMR tube was shaken until the reagents dissolved, and the solution was analyzed by 1H NMR spectroscopy. 1H NMR (400 MHz, CD_2Cl_2) δ 8.89 (d, J = 5.2, 2H),

7.99 (t, $J = 7.6$, 2H), 7.90 (d, $J = 7.6$, 2H), 7.72 (s, 8H), 7.72 (overlapping singlet, 2H) 7.61 (s, 4H), 7.61 (overlapping multiplet, 2H), 7.56 (s, 4H), 7.44 (t, $J = 6.0$, 2H), 7.09 (m, 4H), 6.54 (m, 2H), 1.36 (s, 30H).

In Situ Synthesis of $[\text{Rh}(\text{Cp}^*)\{(3,5\text{-bis(trifluoromethyl)benzoyl})(2\text{-(2-pyridyl)phenyl)amide}\}(\text{CD}_2\text{Cl}_2)][\text{B}(\text{Ar}^{\text{F}})_4]$ (4). A screw-cap NMR tube was tightly sealed in a glovebox after adding 5 mg of rhodium compound **1** (0.007 mmol), 7 mg $\text{Na}[\text{B}(\text{Ar}^{\text{F}})_4]$ (0.008 mmol), and 0.4 mL dichloromethane- d_2 . The NMR tube was shaken until the reagents dissolved, and the solution was allowed to sit for one hour before being analyzed by ^1H and ^{13}C NMR spectroscopy. Compound **4** could also be formed by dissolving compound **2** in dichloromethane- d_2 and allowing it to react for 24 hours at room temperature (91% conversion by ^1H NMR spectroscopy). ^1H NMR (600 MHz, CD_2Cl_2) δ 9.06 (d, $J = 5.4$, 1H), 7.96 (td, $J = 7.8$ and 1.8, 1H), 7.83 (s, 1H), 7.75 (d, $J = 7.8$, 1H), 7.72 (s, 8H), 7.72 (overlapping doublet, 1H), 7.66 (s, 2H), 7.66 (overlapping doublet, 1H), 7.66 (overlapping triplet, 1H), 7.55 (s, 4H), 7.55 (overlapping triplet, 1H), 7.41 (t, $J = 8.4$, 1H), 1.60 (s, 15H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CD_2Cl_2) δ 178.7, 162.1 (1:1:1:1 quartet, $J_{\text{C-B}} = 50$), 156.2, 153.8, 142.2, 141.0, 135.2, 132.7, 132.3, 132.2 (q, 2 bond $J_{\text{C-F}} = 33$), 130.8, 129.2 (q, 2 bond $J_{\text{C-F}} = 32$), 128.4 (two overlapping singlets), 127.8, 127.1, 126.9, 126.1, 125.5, 124.9 (q, 1 bond $J_{\text{C-F}} = 270$), 122.9 (q, 1 bond $J_{\text{C-F}} = 270$), 117.8 (septet, 3 bond $J_{\text{C-F}} = 4.5$), 95.2 (d, 2 $J_{\text{C-Rh}} = 7.5$), 9.1.

Synthesis of $[\text{Rh}(\text{Cp}^*)\{(3,5\text{-bis(trifluoromethyl)benzoyl})(2\text{-(2-pyridyl)phenyl)amide}\}(\text{OH}_2)][\text{B}(\text{Ar}^{\text{F}})_4]$ (5). Full conversion from compound **4** to compound **5** could be accomplished by exposing a solution of compound **4** in dichloromethane to air for 24 hours. The volume of the solution was then reduced to a minimal volume, and pentane was layered on top of the solution to initiate crystallization of compound **5**. Red crystals suitable for X-ray diffraction were obtained. Using Olex2,²³ the structure was solved with the olex2.solve structure solution program using charge flipping and refined with the ShelXL refinement package using least squares minimisation.²⁴ Crystal Data for $\text{C}_{67}\text{H}_{52}\text{BF}_{30}\text{N}_2\text{O}_2\text{Rh}$ ($M = 1600.82$): triclinic, space group P-1 (no. 2), $a = 13.8704(4)$ Å, $b = 16.6146(5)$ Å, $c = 17.7823(5)$ Å, $\alpha = 117.3448(15)^\circ$, $\beta = 94.7820(14)^\circ$, $\gamma = 107.4986(14)^\circ$, $V = 3350.85(18)$ Å³, $Z = 2$, $T = 100$ K, $\mu(\text{CuK}\alpha) = 3.241$ mm⁻¹, $D_{\text{calc}} = 1.587$ g/mm³, 124912 reflections measured ($5.796 \leq 2\theta \leq 140.148$), 12352 unique ($R_{\text{int}} = 0.0375$, $R_{\text{sigma}} = 0.0184$) which were used in all calculations. The final R_1 was 0.0303 ($I > 2\sigma(I)$) and wR_2 was 0.0769 (all data), with a goodness-of-fit on $F^2 =$

1.038. ^1H NMR (600 MHz, CD_2Cl_2) δ 8.68 (d, $J = 5.4$, 1H), 8.13 (t, $J = 7.8$, 1H), 8.05 (d, $J = 7.8$, 1H), 7.79 (s, 1H), 7.72 (s, 8H), 7.68 (m, 1H), 7.63 (d, $J = 6.0$, 1H), 7.55 (s, 4H), 7.51 (s, 2H), 7.25 (m, 2H), 6.67 (m, 1H), 1.82 (broad singlet, H_2O), 1.42 (s, 15H).

Synthesis of $[\text{Ir}(\text{Cp}^*)(\text{phpy})(\text{pyridine-}N\text{-oxide})][\text{B}(\text{Ar}^{\text{F}})_4]$ (6). A 100 mL Schlenk flask was charged with 88 mg $\text{Ir}(\text{Cp}^*)(\text{phpy})\text{Cl}$ (0.17 mmol), 159 mg $\text{Na}[\text{B}(\text{Ar}^{\text{F}})_4]$ (0.18 mmol), 18 mg pyridine- N -oxide (0.18 mmol), and 20 mL dichloromethane. The reaction was stirred for five hours at room temperature and then filtered. The solvent was removed under reduced pressure and 147 mg of a red powder was isolated (60%). Anal. Calcd. (found) for $\text{C}_{58}\text{H}_{40}\text{BF}_{24}\text{IrN}_2\text{O}$: C, 48.38 (48.16); H, 2.80 (2.75); N, 1.95 (1.99). ^1H NMR (500 MHz, CD_2Cl_2) δ 8.86 (d, $J = 6.0$, 1H), 7.82 (td, $J = 8.0$ and 1.5, 1H), 7.72 (s, 8H), 7.72 (overlapping doublet, 1H), 7.69 (d, $J = 8.0$, 1H), 7.56 (s, 4H), 7.39 (d, $J = 7.5$, 1H), 7.39 (overlapping triplet, 1H) 7.34 (td, $J = 6.5$ and 1.5, 1H), 7.15 (d, $J = 5.5$, 2H), 7.08 (td, $J = 6.5$ and 1.5, 1H), 7.00 (td, $J = 8.0$ and 1.5, 1H), 6.91 (t, $J = 7.0$, 2H), 1.67 (s, 15H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2) δ 167.5, 164.6, 162.1 (1:1:1:1 quartet, $J_{\text{C-B}} = 50$), 151.4, 145.6, 140.9, 139.6, 135.5, 135.2, 134.9, 132.0, 129.2 (q, 2 bond $J_{\text{C-F}} = 32$), 126.0, 125.0 (q, 1 bond $J_{\text{C-F}} = 271$), 124.5, 124.4, 124.3, 119.5, 117.9 (septet, 3 bond $J_{\text{C-F}} = 4$), 88.9, 9.1.

Synthesis of $[\text{Ir}(\text{Cp}^*)(\text{phpy})(4\text{-methoxy-pyridine-}N\text{-oxide})][\text{B}(\text{Ar}^{\text{F}})_4]$ (7). A 100 mL Schlenk flask was charged with 50 mg $\text{Ir}(\text{Cp}^*)(\text{phpy})\text{Cl}$ (0.10 mmol), 95 mg $\text{Na}[\text{B}(\text{Ar}^{\text{F}})_4]$ (0.11 mmol), 15 mg 4-methoxy-pyridine- N -oxide hydrate (0.11 mmol), and 20 mL dichloromethane. The reaction was stirred for four hours at room temperature and then filtered. The solvent was reduced to a minimal volume and slowly added to chilled (-78°C), rapidly stirring pentane (30 mL). The orange powder was isolated by filtration (103 mg, 72% yield). Anal. Calcd. (found) for $\text{C}_{59}\text{H}_{42}\text{BF}_{24}\text{IrN}_2\text{O}_2$: C, 48.21 (48.12); H, 2.88 (2.94); N, 1.91 (1.94). ^1H NMR (400 MHz, CD_2Cl_2) δ 8.85 (d, $J = 5.2$, 1H), 7.81 (t, $J = 7.2$, 1H), 7.73 (s, 8H), 7.73 (overlapping doublets, 2H), 7.56 (s, 4H), 7.43 (d, $J = 7.6$, 1H), 7.33 (t, $J = 5.6$, 1H) 7.09 (t, $J = 7.2$, 1H), 7.03 (t, $J = 7.6$, 1H), 6.95 (d, $J = 7.6$, 2H), 6.29 (d, $J = 7.2$, 2H), 3.71 (s, 3H), 1.66 (s, 15H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CD_2Cl_2) δ 167.5, 164.8, 164.2, 162.1 (1:1:1:1 quartet, $J_{\text{C-B}} = 50$), 151.4, 145.7, 141.7, 139.4, 135.6, 135.2, 131.8, 129.2 (q, 2 bond $J_{\text{C-F}} = 32$), 125.0 (q, 1 bond $J_{\text{C-F}} = 271$), 124.5, 124.4, 124.1, 119.5, 117.9 (septet, 3 bond $J_{\text{C-F}} = 4$), 110.9, 88.7, 57.2, 9.0.

ASSOCIATED CONTENT

Supporting Information Available: NMR spectra of new compounds and the CIF file for the structural characterization of compound **5** are provided.

Notes

The authors declare no competing financial interest.

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