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Systematic Evaluation of the Electronic Effect of Aluminum-Containing Ligands in Iridium-Aluminum and Rhodium-Aluminum Bimetallic Complexes

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Abstract

Pyridinemethanolate and oxyquinoline derivatives of previously reported late transition metal-aluminum heterobimetallic complexes containing iridium and rhodium have been synthesized and characterized. A combination of experimental and computational data permits a direct comparison of the electronic effects of each novel aluminum-containing ligand in our library on the late transition metal centers. Alongside electronic data of previously reported oxypyridine bridged systems, we conclude that the addition of a dialkylaluminum(X) (X= anion) fragment does not significantly perturb the electron donor ability of the bridging ligand. Anions bound to the aluminum are also shown to behave similarly. The overall library, thus, suggests that the best predictor of the electron donor ability of an alkylaluminum-containing ligand to a transition metal is the donor power of the bridging ligand.

Graphical Abstract

*Electron Donor Power is
Dependent on Bridge
Structure*

A library of structurally analogous heterobimetallic complexes are investigated to determine the electron donor power of an aluminum-containing ligand on a late transition metal. The donor

ability is found to be predictable based on the donor ability of the bridging ligand. Anion effects are found to be minimal.

Introduction

The investigation of the chemistry of multimetallic systems has seen a significant uptick over the past decade. A majority of the focus has been on heterobimetallic systems consisting of two transition metal centers, with the ultimate aspiration being chemical bond activation by combining unique properties of both metals. This has yielded significant success across a diverse range of systems.¹⁻⁷ More recently emergent are heterobimetallic systems containing one transition metal and one p-block element. It is within this area that our lab holds an interest; specifically, in the application of aluminum to heterobimetallic systems. Although there has been extensive investigation of analogous transition metal-boron complexes,⁸⁻²³ relatively little research has been done on heterobimetallic complexes of aluminum and a transition metal.²⁴⁻³⁵ Our interest in aluminum stems from its potency as a Lewis acid as well as its increased electropositive, oxophilic nature relative to boron.

Of the few aluminum-containing heterobimetallics known, many incorporate early transition metals and have olefin polymerization applications.³⁶⁻⁴¹ In contrast, our lab is chiefly interested in combining electron-rich, late transition metals with aluminum to take advantage of potential synergistic Lewis acid/base pair behavior. The late transition metal-aluminum bonding motif has been found to be useful for both stoichiometric and catalytic bond activations.^{15,24,27,28}

Recently, we published a trio of studies investigating the electronic structure and reactivity of a series of iridium-aluminum and rhodium-aluminum complexes wherein the metals were bridged by regioisomers of oxypyridine (Figure 1).⁴²⁻⁴⁴ Our most recent study highlighted the correlation between regiosubstitution of the oxypyridine bridge and the resultant donor power of the aluminum-containing ligand to the late transition metal. The observed trend in donor power among regioisomers was explainable via a simple resonance analysis of the organic bridge.⁴⁴ In all cases, addition of the nitrate-bound dialkylaluminum moiety into the transition metal-oxypyridine skeleton resulted in a mild increase in the electron donor strength, relative to a proton, of the bridging ligand.⁴⁴ Observation of electronic trends in our oxypyridine-bridged complexes constitutes the first-step toward a thorough understanding of how changes in the structure of an aluminum-based ligand affects the electronic properties of the heterobimetallic complex.

Establishment of an expansive library of electron-donor parameters for aluminum containing ligands will be valuable for future design of catalytic systems. The work herein dramatically expands upon our previously reported system and presents electronic data for a new suite of heterobimetallics bridged by regioisomers of pyridinemethanolate and oxyquinoline. We also present additional oxypyridine complexes in which the nitrate ion, bound inner-sphere to aluminum, is replaced with trifluoromethanesulfonate. The novel heterobimetallics have been thoroughly spectroscopically characterized and computationally analyzed to determine the electron donor power of each aluminum-containing ligand. Electronic data obtained from this study are tabulated and compared with that from our previous reports.^{42,44} Finally,

trends relating the structural features of the aluminum-containing ligands and their donor ability are discussed. Gratifyingly, our hypothesis derived from our previous publications, that the donor strength of aluminum-containing ligands correlates to the donor strength of the bridge between the two metal centers, is supported by the expanded library.

Results and Discussion

Synthesis.

Synthesis of our new suite of heterobimetallic complexes was undertaken using the “transition metal first” strategy commonly exploited in our laboratory.^{42,44} Vaska’s complex, $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$ (**1a**) or its rhodium congener, $[\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$ (**1b**, NOTE: all complexes denoted “a” contain Ir and complexes denoted “b” contain Rh), were first reacted with a silver salt in the presence of the desired pyridinemethanol (Scheme 1), hydroxypyridine (Scheme 2), or hydroxyquinoline bridging ligand (Scheme 3) resulting in complexes **8a–17b**. Monometallic precursors were then reacted with triisobutylaluminum to generate the desired bimetallics **18a–21b** (Scheme 4). All newly synthesized complexes have been fully characterized by NMR and IR spectroscopy, as well as elemental analysis. Full synthetic details for each complex can be found in the Experimental details below.

Pyridinemethanol complexes of iridium **8a–10a** and rhodium **8b–10b** were synthesized via reaction of silver nitrate with the appropriate Vaska’s complex precursor at room temperature. Single crystals of **8a–10a** and **8b–10b** have been obtained and their solid-state structures determined (Figure 2). Two isomeric crystalline polymorphs were obtained for **9b** (see Supplemental Information). X-ray data support a square planar geometry expected for complexes of Ir(I) and Rh(I), with the exception of the 2-pyridinemethanol complex of rhodium (**8b**) in which the ligand was found to chelate to rhodium through nitrogen and oxygen in the solid state. It is worth noting that the chelation observed in the crystal structure of **8b** is not likely to occur in solution. Attempts to calculate a 5-coordinate complex led only to the formation of the expected 4-coordinate species. In all structures the ligand was found to bind to the transition metal via nitrogen. Bond lengths within the pyridine moiety [1.302–1.422 Å] are consistent with those of an aromatic ring, as is expected in this nonconjugated system, and bond lengths between the transition metal and nitrogen are within the normal range for iridium-pyridine [2.097 Å, 2.101 Å, 2.125 Å] and rhodium-pyridine [2.097 Å, 2.125 Å, 2.125 Å] complexes.

Replacement of silver nitrate with silver triflate in the synthetic protocol led to the formation of complexes **11a**, **11b**, **12a**, and **12b** (Scheme 1). Analogous complexes containing 2-pyridine methanol were not included in this study due to the inability to synthesize the aluminum-containing bimetallic derivatives of **8a** and **8b** (*vide infra*). Spectral characteristics for **11a–12b** were consistent with those observed for the corresponding nitrate complexes **9a–10b**. This was unsurprising as the Vaska’s complex cation only weakly interacts with the associated non-coordinating anion.

In an effort to further study the influence of the counterion on our final bimetallic systems, we also sought to synthesize the triflate analogues of our previously reported hydroxypyridine complexes (Scheme 2). Monometallic hydroxypyridine complexes of

iridium (**13a,14a**) were obtained in moderate yield. The corresponding 4-hydroxypyridine complex of iridium was not cleanly obtained. The 2-hydroxypyridine complex **13a** was obtained as an isomeric mixture. Based on our previous work, we assert that the isomers obtained are those derived from O-bound 2-pyridone and N-bound 2-hydroxypyridine, present in a 1:1 ratio based on integration of the ^1H and ^{31}P NMR spectra.⁴² Rhodium complex **13b** was then synthesized to confirm the extension of any electronic perturbation caused by triflate to a second transition metal. Like **13a**, **13b** was obtained as a mixture of isomers. This stands in contrast to the nitrate analog (**2b**) which was obtained as a single, O-bound isomer.⁴² We attribute this difference to weaker hydrogen bonding between the N-H proton, as observed in the crystal structure of **2b**, and the triflate anion.

Finally, we wanted to probe the effect of an extended π -system within the bridge on ligand donor power. To do so, we synthesized hydroxyquinoline complexes of iridium (**15a–17a**) and rhodium (**15b–17b**, Scheme 3). Synthesis was carried out using silver nitrate in a manner analogous to that described above. However, in most cases, ligand exchange took significantly longer to proceed to completion (60 hours vs. 18 hours). After optimization of reaction time, high-purity product was obtained in moderate to excellent yield.

Upon successful synthesis of monometallic precursors we then moved on to synthesis of the desired heterobimetallics. The aluminum-containing heterobimetallic complexes of iridium (**18a–21a**) and rhodium (**18b–21b**) were synthesized by adding triisobutylaluminum to the appropriate precursor, similar to our previous approach (Scheme 4, for full details, see the Experimental Section).⁴⁴ The ^1H NMR spectra of complexes **18a–21a** and **18b–22b** contain diagnostic proton signals between δ –0.29 ppm and δ 0.02 ppm similar to those observed in our previous reports.^{42–44} Observed second-order doublets of doublets correspond to the diastereotopic methylene protons α to the aluminum center. Diastereotopic alkyls indicate the aluminum center is tetrahedral *in situ* and bound to the oxygen atom of the hydroxyquinoline bridge, two chemically equivalent alkyls, and the nitrate or triflate moiety.²⁷ Al NMR could not be obtained for this, or any subsequent, complex due to fast quadrupolar relaxation of the aluminum nucleus. Fast relaxation occurs due to the relatively low symmetry around the aluminum center. Density Functional Theory geometry optimizations support a tetrahedral aluminum coordination for complexes **18a–21a** and **18b–22b**.

Synthesis of the oxyquinoline-bridged bimetallics **18a–20b** proceeded easily. The precursor was suspended in THF solvent and a solution of triisobutylaluminum in THF was added dropwise. The solvent was removed under vacuum upon full dissolution of the suspended solids (indicating full conversion of starting material to product). The resulting solid was washed with pentane to remove excess aluminum reagent. Bimetallic complexes were found to be stable in solution for several days under inert atmosphere.

In contrast, synthesis of bimetallic complexes containing triflate anions or pyridine methanol bridges was not straightforward. Complexes **21a** and **21b** could be obtained in moderate yield and characterized by ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR. However, they decomposed in solution over a few hours. Satisfactory $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were not recorded due to decomposition and solubility limitations. The corresponding bimetallic derived from 3-

hydroxypyridine complex **14a** was so unstable it could not be cleanly isolated and characterized, even at low temperature. This stands in sharp contrast to nitrate complexes **5a** and **5b** which are relatively stable in solution. Iridium complex **5a** is stable for at least a month, while rhodium complex **5b** decomposes with a half-life of approximately 5 days.⁴² We attribute the difference to a weaker interaction between the anion and aluminum. We have previously observed oligomeric decomposition of our bimetallic species in which the nitrate anion is displaced by a second oxypyridine.⁴² This is likely more favorable with triflate. The instability of the bimetallic product from **14a** discouraged us from attempting to synthesize **14b**, as the rhodium-derived bimetallics have generally been found to be less stable.⁴²

Similar challenges were met when attempting to synthesize bimetallic complexes bridged by regioisomers of pyridinemethanol. We first attempted to react 2-pyridine methanol complexes **8a** and **8b** with triisobutylaluminum. Rather than obtaining the desired bimetallic, abstraction of pyridinemethanol was observed to generate the monometallic aluminum complex **23** (Scheme 5). This abstraction is no doubt preferred due to formation of the stable, 5-membered ring chelate at aluminum. The structure of **23** was confirmed via independent synthesis.

The only pyridinemethanol complex from which a stable heterobimetallic complex could be derived was **9b**. Triisobutylaluminum was added dropwise to a solution of **9b** in THF which had been chilled to -78°C . Solvent was removed as the reaction warmed to room temperature to isolate the desired product **22b**. Following a similar procedure for iridium complex **9a** and 4-pyridinemethanol derivatives **10a** and **10b** led to intractable mixtures of products. Although synthesis of the additional pyridinemethanol-derived heterobimetallics proved untenable, the successful synthesis of **22b**, along with the suite of other mono- and heterobimetallics discussed herein, led to the collection and analysis of significant data regarding the electronic effect of ligand modification.

Electronic Effect of Ligands

We are interested in quantifying the electron donor capability of aluminum-containing ligands and parameterizing the donor power as a function of specific characteristics of the ligand. In this study we compare several independent variables: 1) the number of bonds between aluminum and the transition metal, 2) the structure and conjugation of the bridging ligand, and 3) the anion present in the system, which coordinates aluminum in the zwitterionic bimetallic complexes. We find that variables 1 and 3 have little or no effect on the electron donor ability of the aluminum-containing ligand. Rather, the donor ability of the aluminum containing ligand is predictably determined solely by the structure of the bridging moiety.

We measured electron donor effects in three ways. First, we calculated an expected carbonyl stretching frequency for the CO ligand bound to the late transition metal. Second, we measured the CO stretching frequency experimentally using IR spectroscopy. Finally, we measured the reduction potential for the bimetallic complex. The measured reduction potential is presumed to be the M^+/M^0 reduction ($\text{M} = \text{Ir}, \text{Rh}$) rather than a reduction of the

potentially redox-active bridging ligand; it shifts systematically as a function of the transition metal employed and occurs at similar potentials for oxyquinoline, oxypyridine, and pyridinemethanolate-bridged complexes. Were the bridging ligands the site of reduction we would expect to see a much more dramatic shift in reduction potential when comparing pyridinemethanolate and oxyquinoline complexes, though some degree of orbital delocalization between the unoccupied metal d -orbital and a vacant π^* orbital of the bridge cannot be rigorously excluded. Observed reductions are irreversible, so we define our measured potential as E_{pc} , the peak of the cathodic wave obtained on reduction. For full CV data, see the Supplemental Information. A tabulation of all electron-donor data (from this study and our previous work) can be found in Table 1. For reference, the E_{pc} of Vaska's complex (**1a**) and its rhodium analogue (**1b**) are -2.11 V and -2.05 V, respectively.

First, in all cases, the observed reduction potentials and IR data indicate that the ligand effects are consistent across both iridium and rhodium. While the absolute numbers differ due to the transition metal (Ir is easier to reduce and a better π -acid due to population of 5d orbitals, as opposed to 4d orbitals in Rh), the trends are identical. What we are measuring is a true ligand electronic effect.

Second, variation of the ancillary ligands at aluminum within the range of this study does not perturb the electronics. We have previously observed a minimal impact of changing the aluminum-bound alkyl group from isobutyl to ethyl.⁴² Similarly, switching from nitrate to triflate (**5a** vs **21a**, **5b** vs **21b**) did not significantly alter the donor power of the aluminum-containing ligand. The only noticeable effect of switching anions was a marked decrease in the stability of the complex. Thus, when designing aluminum-containing ligands, one should target the anion that imparts the most stability without worrying about significant electronic perturbation, so long as the chosen anions are similar in nature.

Finally, the addition of aluminum minimally perturbs the electronics of the system. In other words, replacement of a proton with a diisobutylaluminum(X) (X= nitrate, triflate) group does not impart a significant electronic change on the system. The aluminum moiety is a very weak electron donor, relative to H. Additionally, the *magnitude* of the change when adding aluminum to the ligand is fairly consistent. This further supports a conclusion we have posited;⁴⁴ namely, that the interaction of the aluminum center with the bridging ligand is purely inductive. We would expect conjugated (oxypyridine and hydroxyquinoline) systems to behave differently than nonconjugated systems (pyridinemethanol) if there were significant transmission of electronic information through the π -system of the bridge. Because the observed electronic influence is an inductive effect on the bridging aromatic ring, the number of bonds separating the two metal centers is relatively inconsequential (see **18a-20a**, and **18b-20b**). Instead, it is the donor ability of the bridging ligand itself that determines the overall donor ability of the aluminum-containing ligand. We expect this trend to be highly general with one notable exception: systems in which there is a direct M-Al bond. In these systems the metals are in direct electronic communication and the influence on any bridging ligands should be a secondary consideration.

Conclusions

We have extended our library of monometallic and heterobimetallic rhodium and iridium complexes derived from Vaska's complex. Electronic data in the form of carbonyl stretching frequencies (ν_{CO}) as well as reduction potentials (E_{pc}) have been collected for each complex to determine the influence of the aluminum center on the electronic structure at the transition metal. Carbonyl stretching frequencies were computed with Density Functional Theory and directly measured via infrared spectroscopy, while reduction potentials were measured via cyclic voltammetry. Analysis of the combined electronic data resulted in significant revelations.

First, ligand electronic effects are consistent across both iridium and rhodium metal centers suggesting that our observed trends are a result of ligand variation. Exchange of a proton for a dialkylaluminum(X) moiety has a minimal impact on the electron density at the transition metal. Interestingly, though small, this exchange did yield *quantitatively consistent* electronic changes, in support of our hypothesis that the interaction between the aluminum moiety and the bridging ligand is inductive in nature.⁴⁴ Changing the inner-sphere oxyanion at aluminum was also found to have minimal effect on the overall system.

Finally, and most importantly, we can now accurately *predict* what the donor ability of an alkylaluminum-containing ligand will be based on our knowledge of the donor ability of the bridging ligand itself (assuming there is no direct bond between the two metals). This has the potential to be very powerful, as electron donor parameters exist for a large number of organic ligands.⁴⁵⁻⁴⁷ When designing ligands for eventual catalytic applications we can use these tabulated data as a proxy for the aluminum-containing ligands desired. Alternatively, we can calculate the donor ability of the bridging ligand using our Vaska's complex framework and extrapolate. It will be interesting to see if this trend holds for other Group 13 Lewis acids, which will be the focus of future work in our laboratory.

Experimental Details

Synthetic Methods.

Syntheses and manipulations were performed in a nitrogen-filled Inert Technologies glovebox or using standard Schlenk techniques unless otherwise specified. Deuterated solvents were purchased from Cambridge Isotope Laboratories, dried over molecular sieves or calcium hydride, and stored in the glovebox over molecular sieves prior to use. $\text{Ir}(\text{PPh}_3)_2\text{Cl}(\text{CO})$ and $\text{Rh}(\text{PPh}_3)_2\text{Cl}(\text{CO})$ were synthesized according to methods established in the literature.⁴⁸ All other reagents and solvents used were commercially available and used without further purification unless specified. Aluminum reagents, pyridinemethanolate ligands, and oxypyridine ligands were stored in a nitrogen glovebox prior to use. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a 400 MHz JEOL spectrometer and referenced to the residual solvent peak.⁴⁹ Infrared spectra were recorded on a PerkinElmer Frontier FT-IR spectrometer. Spectra were measured in air-free solution cells (dichloromethane) prepared in the glovebox. Elemental analyses were performed by Robertson Microlit Laboratories.

[Ir(PPh₃)₂(CO)(2-pyridinemethanol)][NO₃] (8a).—In the glovebox, 200 mg (0.256 mmol) of Ir(PPh₃)₂(CO), 45.7mg (0.269 mmol) of AgNO₃, and 26 μ L (29.4 mg, 0.269mmol) of 2-pyridinemethanol were suspended in 25 mL of dichloromethane in a 50 mL Schlenk flask and stirred overnight. After 18 h, stirring was stopped and the reaction mixture filtered through Celite. The filtrate volume was reduced until a precipitate was observed (approximately 5 mL of solvent). A volume of 15 mL of pentane was added to precipitate the remaining product. The solid was washed with benzene (3x 5mL), collected by filtration and recrystallized by layering a saturated solution of crude material in dichloromethane with pentane to yield pure product. Yield: 151.8 mg (69%). ¹H NMR (400 MHz, C₆D₆) δ 8.28 (d, J = 5.1 Hz, 1H), 7.88 (q, J = 5.7 Hz, 12H), 7.36 (s, 1H), 7.10 – 6.86 (m, 18H), 6.59 (d, J = 7.9 Hz, 1H), 6.53 (dd, J = 7.1, 5.5 Hz, 1H), 4.57 (s, 2H). ³¹P{¹H} NMR (162 MHz, C₆D₆) δ 27.74. IR (dichloromethane solution): $\nu_{\text{CO-carbonyl}}$ = 1994 cm⁻¹. Elemental Analysis (with 0.5 molecules of dichloromethane from precipitation): Calculated C 54.52, H 4.00, N 2.92; Measured C 55.15, H 3.97, N 3.53.

[Rh(PPh₃)₂(CO)(2-pyridinemethanol)][NO₃] (8b).—In the glovebox, 200 mg (0.256 mmol) of Ir(PPh₃)₂(CO), 45.7mg (0.269 mmol) of AgNO₃, and 26 μ L (29.4 mg, 0.269mmol) of 2-pyridinemethanol were suspended in 25 mL of dichloromethane in a 50 mL Schlenk flask and stirred overnight. After 18 h, stirring was stopped and the reaction mixture filtered through Celite. The filtrate volume was reduced until a precipitate was observed (approximately 5 mL of solvent). A volume of 15 mL of pentane was added to precipitate the remaining product. The solid was washed with benzene (3x 5mL), collected by filtration and recrystallized by layering a saturated solution of crude material in dichloromethane with pentane to yield pure product. Yield: 185.5 mg (84%). ¹H NMR (400MHz, C₆D₆) δ 8.28 (d, J = 4.9 Hz, 1H), 7.86 (q, J = 6.3 Hz, 12H), 7.06 – 6.99 (m, 18H), 7.36 (s, 1H), 6.59 (d, J = 7.8 Hz, 1H), 6.53 (t, J = 6.8 Hz, 1H), 4.57 (s, 2H). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂) δ 148.72, 137.92, 134.30 (t, J = 6.2 Hz), 131.42 (t, J = 6.2 Hz), 129.27 (t, J = 5.7 Hz), 125.00, 123.22, 66.04. ³¹P{¹H} NMR (162 MHz, C₆D₆) δ 31.03 (d, J = 137.7 Hz). IR (dichloromethane solution): $\nu_{\text{CO-carbonyl}}$ = 2006 cm⁻¹. Elemental Analysis (with 0.5 molecules of benzene from washing): Calculated C 63.82, H 4.66, N 3.24; Measured C 64.03, H 4.56, N 3.43.

[Ir(PPh₃)₂(CO)(3-pyridinemethanol)][NO₃] (9a).—In the glovebox, 200 mg (0.256 mmol) of Ir(PPh₃)₂(CO), 45.7mg (0.269 mmol) of AgNO₃, and 26 μ L (29.4 mg, 0.269mmol) of 3-pyridinemethanol were suspended in 25 mL of dichloromethane in a 50 mL Schlenk flask and stirred overnight. After 18 h, stirring was stopped and the reaction mixture filtered through Celite. The filtrate volume was reduced until a precipitate was observed (approximately 5 mL of solvent). A volume of 15 mL of pentane was added to precipitate the remaining product. The solid was washed with benzene (3x 5mL), collected by filtration and recrystallized by layering a saturated solution of crude material in dichloromethane with pentane to yield pure product. Yield: 173.1 mg (79%). ¹H NMR (400MHz, CD₂Cl₂) δ 7.62 – 7.50 (m, 13H), 7.50 – 7.36 (m, 20H), 6.60 (t, J = 6.4 Hz, 1H), 4.06 (s, 2H). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂) δ 148.03, 134.40 (t, J = 6.3 Hz), 131.83, 129.94 (t, J = 27.9 Hz), 129.34 (t, J = 5.3 Hz), 128.68, 125.57, 60.88. Quaternary carbons not detected due to slow relaxation. ³¹P{¹H} NMR (162 MHz, CD₂Cl₂) δ 27.70. IR

(dichloromethane solution): $\nu_{\text{CO-carbonyl}} = 1996 \text{ cm}^{-1}$. Elemental Analysis (with 1 molecule of dichloromethane from precipitation): Calculated C 52.80, H 3.93, N 2.80; Measured C 52.25, H 3.91, N 2.84.

[Rh(PPh₃)₂(CO)(3-pyridinemethanol)][NO₃] (9b).—In the glovebox, 200 mg (0.256 mmol) of Ir(PPh₃)₂(CO), 45.7 mg (0.269 mmol) of AgNO₃, and 26 μL (29.4 mg, 0.269 mmol) of 3-pyridinemethanol were suspended in 25 mL of dichloromethane in a 50 mL Schlenk flask and stirred overnight. After 18 h, stirring was stopped and the reaction mixture filtered through Celite. The filtrate volume was reduced until a precipitate was observed (approximately 5 mL of solvent). A volume of 15 mL of pentane was added to precipitate the remaining product. The solid was washed with benzene (3x 5mL), collected by filtration and recrystallized by layering a saturated solution of crude material in dichloromethane with pentane to yield pure product. Yield: 112.9 mg (51%). ¹H NMR (400MHz, CD₂Cl₂) δ 7.57 – 7.45 (m, 20H), 7.39 (t, J = 7.4 Hz, 13H), 6.65 (s, 1H), 4.15 (s, 2H). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂) δ 149.32, 134.24 (t, J = 6.6 Hz), 131.58, 130.64 (t, J = 23.7, 22.9 Hz), 129.86, 129.35 (t, J = 5.1 Hz), 124.94, 61.21. Quaternary carbons not detected due to slow relaxation. ³¹P{¹H} NMR (162 MHz, CD₂Cl₂) δ 32.27 (d, J = 129.8 Hz). IR (dichloromethane solution): $\nu_{\text{CO-carbonyl}} = 2007 \text{ cm}^{-1}$. Elemental Analysis (with 0.5 molecule of benzene from washing): Calculated C 63.82, H 4.66, N 3.24; Measured C 64.14, H 4.55, N 3.25.

[Ir(PPh₃)₂(CO)(4-pyridinemethanol)][NO₃] (10a).—In the glovebox, 200 mg (0.256 mmol) of Ir(PPh₃)₂(CO), 45.7mg (0.269 mmol) of AgNO₃, and 26 μL (29.4 mg, 0.269mmol) of 4-pyridinemethanol were suspended in 25 mL of dichloromethane in a 50 mL Schlenk flask and stirred overnight. After 18 h, stirring was stopped and the reaction mixture filtered through Celite. The filtrate volume was reduced until a precipitate was observed (approximately 5 mL of solvent). A volume of 15 mL of pentane was added to precipitate the remaining product. The solid was washed with benzene (3x 5mL), collected by filtration and recrystallized by layering a saturated solution of crude material in dichloromethane with pentane to yield pure product. Yield: 72 mg (33%). ¹H NMR (400MHz, CD₂Cl₂) δ 7.59 – 7.45 (m, 20H), 7.44 – 7.38 (m, 12H), 6.73 (d, J = 5.8 Hz, 2H), 4.49 (s, 2H). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂) δ 149.41, 135.25, 134.38 (t, J = 6.3 Hz), 131.87, 129.98 (t, J = 27.4 Hz), 129.35 (t, J = 5.3 Hz), 128.34, 123.64, 61.91. ³¹P{¹H} NMR (162 MHz, CD₂Cl₂) δ 27.35. IR (dichloromethane solution): $\nu_{\text{CO-carbonyl}} = 1996 \text{ cm}^{-1}$. Elemental Analysis (with 1 molecule of dichloromethane from precipitation): Calculated C 52.80, H 3.93, N 2.80; Measured C 53.27, H 4.20, N 2.81.

[Rh(PPh₃)₂(CO)(4-pyridmemethanol)][NO₃] (10b).—In the glovebox, 200 mg (0.256 mmol) of Ir(PPh₃)₂(CO), 45.7 mg (0.269 mmol) of AgNO₃, and 26 μL (29.4 mg, 0.269mmol) of 4-pyridinemethanol were suspended in 25 mL of dichloromethane in a 50 mL Schlenk flask and stirred overnight. After 18 h, stirring was stopped and the reaction mixture filtered through Celite. The filtrate volume was reduced until a precipitate was observed (approximately 5 mL of solvent). A volume of 15 mL of pentane was added to precipitate the remaining product. The solid was washed with benzene (3x 5mL), collected by filtration and recrystallized by layering a saturated solution of crude material in

dichloromethane with pentane to yield pure product. Yield: 186.6 mg (84%). ^1H NMR (400MHz, CD_2Cl_2) δ 7.57 – 7.43 (m, 20H), 7.42 – 7.37 (m, 12H), 6.76 (d, J = 5.6 Hz, 2H), 4.50 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) 149.51, 134.21 (t, J = 6.7 Hz), 131.65, 130.64 (t, J = 23.3 Hz), 129.39 (t, J = 5.1 Hz), 123.22, 62.14. Quaternary carbons not detected due to slow relaxation. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 32.00 (d, J = 130.2 Hz). IR (dichloromethane solution): $\nu_{\text{CO-carbonyl}}$ = 2006 cm^{-1} . Elemental Analysis: Calculated C 62.48, H 4.51, N 3.39; Measured C 61.67, H 4.49, N 3.43.

[Ir(PPh₃)₂(CO)(3-pyridinemethanol)][SO₃CF₃] (11a).—In the glovebox, 639 mg (0.819 mmol) of Ir(PPh₃)₂(CO), 231 mg (0.898 mmol) of AgSO₃CF₃ and 87 μL (0.898 mmol) of 3-pyridinemethanol were suspended in 25 mL of dichloromethane in a 50 mL Schlenk flask and stirred overnight. After 18 h, stirring was stopped and the reaction mixture filtered through Celite. The filtrate volume was reduced until a precipitate was observed (approximately 10 mL of solvent). A volume of 20 mL of pentane was added to precipitate the remaining product. The solid was collected by filtration and recrystallized by layering a saturated solution of crude material in dichloromethane with pentane to yield pure product. Yield: 420 mg (53%). ^1H NMR (400MHz, CD_2Cl_2) δ 7.55 – 7.51 (m, 12H), 7.50 – 7.45 (m, 7H), 7.41 – 7.35 (m, 13H), 7.32 (d, J = 8.1 Hz, 1H), 6.65 (d, J = 6.9 Hz, 1H), 4.01 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) δ 148.96, 148.08, 136.70, 134.92, 134.05 (t, J = 6.3 Hz), 131.50, 129.29, 129.00 (t, J = 5.3 Hz), 125.34, 60.56. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 27.70. IR (dichloromethane solution): $\nu_{\text{CO-carbonyl}}$ = 1998 cm^{-1} . Elemental Analysis (with 0.5 molecule of dichloromethane from precipitation): Calculated C 51.12, H 3.66, N 1.34; Measured C 50.83, H 3.69, N 1.70.

[Rh(PPh₃)₂(CO)(3-pyridinemethanol)][SO₃CF₃] (11b).—In the glovebox, 566 mg (0.819 mmol) of Rh(PPh₃)₂(CO), 231 mg (0.449 mmol) of AgSO₃CF₃ and 87 μL (0.898 mmol) of 3-pyridinemethanol were suspended in 25 mL of dichloromethane in a 50 mL Schlenk flask and stirred overnight. After 18 h, stirring was stopped and the reaction mixture filtered through Celite. The filtrate volume was reduced until a precipitate was observed (approximately 10 mL of solvent). A volume of 20 mL of pentane was added to precipitate the remaining product. The solid was collected by filtration and recrystallized by layering a saturated solution of crude material in dichloromethane with pentane to yield pure product. Yield: 450 mg (56%). ^1H NMR (400MHz, CD_2Cl_2) δ 7.55 – 7.45 (m, 20H), 7.39 (m, 13H), 6.62 (s, 1H), 4.04 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) δ 148.89, 148.13, 133.84 (t, J = 6.6 Hz), 131.31, 131.06, 130.10 (t, J = 23.3 Hz), (t, J = 5.1 Hz), 122.48, 119.29. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 32.42 (d, J = 129.2 Hz). IR (dichloromethane solution): $\nu_{\text{CO-carbonyl}}$ = 2009 cm^{-1} . Elemental Analysis (with 0.5 molecule of dichloromethane from precipitation): Calculated C 55.90, H 4.01, N 1.46; Measured C 55.63, H 3.77, N 1.84.

[Ir(PPh₃)₂(CO)(4-pyridinemethanol)][SO₃CF₃] (12a).—In the glovebox, 323 mg (0.409 mmol) of Ir(PPh₃)₂(CO), 115 mg (0.449 mmol) of AgSO₃CF₃ and 49 mg (0.449 mmol) of 4-pyridinemethanol were suspended in 25 mL of dichloromethane in a 50 mL Schlenk flask and stirred overnight. After 18 h, stirring was stopped and the reaction mixture filtered through Celite. The filtrate volume was reduced until a precipitate was observed (approximately 10 mL of solvent). A volume of 20 mL of pentane was added to precipitate

the remaining product. The solid was collected by filtration and recrystallized by layering a saturated solution of crude material in dichloromethane with pentane to yield pure product. Yield: 97 mg (22%). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.61 – 7.46 (m, 18H), 7.40 (t, J = 7.3 Hz, 12H), 7.35 (d, J = 6.6 Hz, 2H), 6.70 (d, J = Hz, 2H), 4.45 (d, J = 4.8 Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) δ 149.27, 134.04 (t, J = 6.3 Hz), 131.55, 129.63 (t, J = 27.5 Hz), 129.02 (t, J = 5.3 Hz), 123.28, 61.51. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 27.34. IR (dichloromethane solution): $\nu_{\text{CO-carbonyl}}$ = 1997 cm^{-1} . Elemental Analysis (with 0.5 molecule of dichloromethane from precipitation): Calculated C 51.12, H 3.66, N 1.34; Measured C 50.56, H 3.66, N 1.45.

[Rh(PPh₃)₂(CO)(4-pyridinemethanol)][SO₃CF₃] (12b).—In the glovebox, 283 mg (0.409 mmol) of Rh(PPh₃)₂(CO), 115 mg (0.449 mmol) of AgSO₃CF₃ and 49 mg (0.449 mmol) of 4-pyridinemethanol were suspended in 25 mL of dichloromethane in a 50 mL Schlenk flask and stirred overnight. After 18 h, stirring was stopped and the reaction mixture filtered through Celite. The filtrate volume was reduced until a precipitate was observed (approximately 10 mL of solvent). A volume of 20 mL of pentane was added to precipitate the remaining product. The solid was collected by filtration and recrystallized by layering a saturated solution of crude material in dichloromethane with pentane to yield pure product. Yield: 89 mg (23%). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.59 – 7.44 (m, 19H), 7.46 – 7.35 (m, 13H), 6.68 (d, J = 5.7 Hz, 2H), 4.45 (d, J = 5.1 Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) δ 155.43, 149.33, 133.83 (t, J = 6.6 Hz), 131.36, 130.15 (t, J = 23.7 Hz), 129.08 (t, J = 5.1 Hz), 122.94, 122.40, 119.22, 61.60. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 32.06 (d, J = 128.9 Hz). IR (dichloromethane solution): $\nu_{\text{CO-carbonyl}}$ = 2008 cm^{-1} . Elemental Analysis: Calculated C 57.84, H 4.08, N 1.53; Measured 57.41, H 3.88, N 1.78.

[Ir(PPh₃)₂(CO)(2-hydroxypyridine)][SO₃CF₃] (13a).—In the glovebox, 800 mg (1.03 mmol) of Ir(PPh₃)₂(CO), and 106 mg (1.12 mmol) of 2-hydroxypyridine were weighed to a 50 mL Schlenk flask. 287 mg (1.12 mmol) of AgSO₃CF₃ was added. 30 mL of dry dichloromethane was then added. The flask was sealed with a septum, removed from the glovebox, and stirred under a positive pressure of argon overnight in the absence of light. After 18 h, stirring was stopped and the reaction mixture filtered through Celite. The filtrate volume was reduced until a precipitate was observed (approximately 10 mL of solvent). A volume of 20 mL of pentane was added to precipitate the remaining product. The solid was collected by filtration and recrystallized by layering a saturated solution of crude material in dichloromethane with pentane to yield pure product. The resulting yellow solid was collected by filtration. Yield: 356 mg (48 %). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.71 – 7.50 (m, 12H), 7.47 – 7.31 (m, 18H), 7.08 (d, J = 5.9 Hz, 1H), 7.01 (t, J = 8.1 Hz, 1H), 6.31 (d, J = 8.4 Hz, 1H), 6.12 (t, 1H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 28.67, 26.82. IR: $\nu_{\text{CO-carbonyl}}$ = 1986 cm^{-1} . Elemental Analysis (with 1 molecule of dichloromethane from precipitation): Calculated C 49.21, H 3.47, N 1.30; Measured C 49.35, H 3.19, N 1.48.

[Rh(PPh₃)₂(CO)(2-hydroxypyridine)][SO₃CF₃] (13b).—In the glovebox, 955 mg (1.4 mmol) of Rh(PPh₃)₂(CO), and 123 mg (1.3 mmol) of 4-hydroxypyridine were weighed to a 50 mL Schlenk flask. 345 mg (1.3 mmol) of AgSO₃CF₃ was added. 30 mL of dry dichloromethane was then added. The flask was sealed with a septum, removed from the

glovebox, and stirred under a positive pressure of argon overnight in the absence of light. After 18 h, stirring was stopped and the reaction mixture filtered through Celite. The filtrate volume was reduced until a precipitate was observed (approximately 10 mL of solvent). A volume of 20 mL of pentane was added to precipitate the remaining product. The solid was collected by filtration and recrystallized by layering a saturated solution of crude material in dichloromethane with pentane to yield pure product. The resulting yellow solid was collected by filtration as a mixture of two isomers. Yield: 543 mg (68 %). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.76 – 7.54 (m, 24H), 7.51 – 7.29 (m, 36H), 7.20 (s, 1H), 7.12 (d, J = 5.8 Hz, 1H), 7.02 (t, J = 7.8 Hz, 1H), 6.95 (t, J = 8.0 Hz, 1H), 6.28 (d, J = 8.5 Hz, 1H), 6.12 (t, J = 6.4 Hz, 1H), 6.08 (t, J = 6.9 Hz, 1H), 5.91 (d, J = 9.0 Hz, 1H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 32.66 (d, J = 130.1 Hz), 30.81 (d, J = 128.1 Hz). IR: $\nu_{\text{CO-carbonyl}}$ = 1994 cm^{-1} . Elemental Analysis (with 2 molecules of benzene from washing): Calculated C 62.56, H 4.49, N 1.33; Measured C 62.15, H 4.36, N 1.34.

[Ir(PPh₃)₂(CO)(3-hydroxypyridine)][SO₃CF₃] (14a).—In the glovebox, 800 mg (1.03 mmol) of Ir(PPh₃)₂(CO), and 106 mg (1.12 mmol) of 3-hydroxypyridine were weighed to a 50 mL Schlenk flask. 287 mg (1.12 mmol) of AgSO₃CF₃ was added. 30 mL of dry dichloromethane was then added. The flask was sealed with a septum, removed from the glovebox, and stirred under a positive pressure of argon overnight in the absence of light. After 18 h, stirring was stopped and the reaction mixture filtered through Celite. The filtrate volume was reduced until a precipitate was observed (approximately 10 mL of solvent). A volume of 20 mL of pentane was added to precipitate the remaining product. The solid was collected by filtration and recrystallized by layering a saturated solution of crude material in dichloromethane with pentane to yield pure product. The resulting yellow solid was collected by filtration. Yield: 532 mg (63 %). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.60 (dtd, J = 8.6, 5.8, 1.4 Hz, 1H), 7.54 – 7.45 (m, 1H), 7.41 (ddt, J = 8.4, 6.9, 1.2 Hz, 1H), 7.29 (d, J = 2.7 Hz, 0H), 7.02 (d, J = 5.4 Hz, 0H), 6.84 (dd, J = 9.4, 2.0 Hz, 0H), 6.44 (dd, J = 8.6, 5.4 Hz, 0H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) δ 174.92, 155.77, 139.96 (d, J = 81.9 Hz), 134.08 (t, J = 6.3 Hz), 131.38, 129.64 (t, J = 27.4 Hz), 128.88 (t, J = 5.3 Hz), 125.77, 125.02, 122.20, 119.02. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 27.49. IR: $\nu_{\text{CO-carbonyl}}$ = 1994 cm^{-1} . Elemental Analysis: Calculated C 52.22, H 3.57, N 1.42; Measured C 51.73, H 3.31, N 1.62.

[Ir(PPh₃)₂(CO)(5-hydroxyquinoline)][NO₃] (15a).—In the glovebox, 201 mg (0.247 mmol) Ir(PPh₃)₂Cl(CO) and 38.1 mg (0.263 mmol) 5-hydroxyquinoline were weighed to a 100 mL round-bottom flask. 62 mg (0.36 mmol) AgNO₃ was added. 50 mL of dry dichloromethane was then added. The flask was sealed with a septum, removed from the glovebox, and stirred under a positive pressure of argon for 60 hours in the absence of light. The resulting suspension was returned to the glovebox and filtered through Celite to remove silver chloride and excess silver nitrate. The solvent volume was then reduced to approximately 5 mL under vacuum and the product precipitated by the addition of pentane. The resulting bright yellow solid was collected by filtration. Yield: 224 mg (95%). ^1H NMR (400 MHz, CD_2Cl_2) δ 11.54 (s, 1H), 8.33 (d, J = 8.4 Hz, 1H), 7.93 – 7.75 (m, 2H), 7.46 – 7.37 (m, 19H), 7.33 – 7.23 (m, 12H), 7.04 (d, J = 7.8 Hz, 1H), 6.58 (dd, J = 8.4, 5.1 Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) δ 155.13, 150.77, 146.55, 136.59, 134.58, 133.90, 133.84 (t, J = 6.3 Hz), 133.77, 132.75, 131.39, 129.67 (t, J = 27.6 Hz), 128.66 (t, J = 5.3 Hz),

122.38, 119.32, 115.94, 111.34. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 27.2. IR: $\nu_{\text{CO-carbonyl}}$ = 1994 cm^{-1} . Elemental Analysis (with 2 molecules of dichloromethane from precipitation): Calculated C 51.39, H 3.68, N 2.50; Measured C 51.99, H 3.63, N 2.59.

[Rh(PPh₃)₂(CO)(5-hydroxyquinolme)][NO₃] (15b).—In the glovebox, 199 mg (0.288 mmol) Rh(PPh₃)₂Cl(CO) and 42.3 mg (0.291 mmol) 5-hydroxyquinoline were weighed to a 100 mL round-bottom flask. 56 mg (0.33 mmol) AgNO₃ was added. 25 mL of dry dichloromethane was then added. The flask was sealed with a septum, removed from the glovebox, and stirred under a positive pressure of argon for 24 hours in the absence of light. The resulting suspension was returned to the glovebox and filtered through Celite to remove silver chloride and excess silver nitrate. The solvent volume was then reduced to approximately 5 mL under vacuum and the product precipitated by the addition of pentane. The resulting pale-yellow solid was collected by filtration. The product was recrystallized by layering dichloromethane with pentane. Yield: 162 mg (65%). ^1H NMR (400 MHz, CD_2Cl_2) δ 8.31 (d, J = 8.4 Hz, 1H), 7.78–7.87 (m, 2H), 7.69 (s, 1H), 7.39 (q, J = 7.1, 6.7 Hz, 18H), 7.26 (t, J = 7.6 Hz, 12H), 7.01 (dd, J = 7.8, 0.9 Hz, 1H), 6.61 – 6.50 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) δ 155.49, 151.36, 138.52, 135.20, 134.04, 134.04 (t, J = 6.4 Hz), 132.89, 131.59 (t, J = 23.1 Hz), 130.59, 129.10 (t, J = 4.7 Hz), 126.26, 119.68, 116.57, 111.45. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 32.7 (d, J_{PRh} = 129.1 Hz). IR: $\nu_{\text{CO-carbonyl}}$ = 2005 cm^{-1} . Elemental Analysis (with 1.5 molecules of dichloromethane from precipitation): Calculated C 57.63, H 4.07, N 2.83; Measured C 57.26, H 3.96, N 2.73.

[Ir(PPh₃)₂(CO)(6-hydroxyquinoline)][NO₃] (16a).—In the glovebox, 201 mg (0.247 mmol) Ir(PPh₃)₂Cl(CO) and 38.1 mg (0.263 mmol) 5-hydroxyquinoline were weighed to a 100 mL round-bottom flask. 60 mg (0.30 mmol) AgNO₃ was added. 50 mL of dry dichloromethane was then added. The flask was sealed with a septum, removed from the glovebox, and stirred under a positive pressure of argon for 60 hours in the absence of light. The resulting suspension was returned to the glovebox and filtered through Celite to remove silver chloride and excess silver nitrate. The solvent volume was then reduced to approximately 5 mL under vacuum and the product precipitated by the addition of pentane. The resulting greenish yellow solid was collected by filtration. Yield: 142 mg (60%). ^1H NMR (400 MHz, CD_2Cl_2) δ 11.00 (s, 1H), 8.40 (d, J = 9.4 Hz, 1H), 7.65 (d, J = 4.6 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.49 – 7.35 (m, 18H), 7.29 (t, J = 7.6 Hz, 12H), 7.26 (d, J = 2.7 Hz, 1H), 7.01 (d, J = 2.6 Hz, 1H), 6.52–6.58 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) δ 158.67, 147.45, 141.20, 136.94, 135.30, 134.26 (t, J = 6.3 Hz), 131.97, 131.79, 129.99 (t, J = 27.6 Hz), 129.13, 129.07 (t, J = 5.3 Hz), 129.02, 128.00, 125.18, 121.39, 109.96. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 27.1. IR: $\nu_{\text{CO-carbonyl}}$ = 1995 cm^{-1} . Elemental Analysis (with 1.5 molecules of dichloromethane from precipitation): Calculated C 52.86, H 3.74, N 2.60; Measured C 52.55, H 3.61, N 2.51.

[Rh(PPh₃)₂(CO)(6-hydroxyquinoline)][NO₃] (16b).—In the glovebox, 201 mg (0.291 mmol) Rh(PPh₃)₂Cl(CO) and 44.0 mg (0.303 mmol) 5-hydroxyquinoline were weighed to a 100 mL round-bottom flask. 60 mg (0.35 mmol) AgNO₃ was added. 50 mL of dry dichloromethane was then added. The flask was sealed with a septum, removed from the glovebox, and stirred under a positive pressure of argon for 60 hours in the absence of light.

The resulting suspension was returned to the glovebox and filtered through Celite to remove silver chloride and excess silver nitrate. The solvent volume was then reduced to approximately 5 mL under vacuum and the product precipitated by the addition of pentane. The resulting pale-yellow solid was collected by filtration. Yield: 162 mg (64%). ^1H NMR (400 MHz, CD_2Cl_2) δ 11.02 (s, 1H), 8.23 (d, J = 9.1 Hz, 1H), 7.60 (d, J = 8.3 Hz, 1H), 7.46 – 7.37 (m, 18H), 7.29 (t, J = 7.6 Hz, 12H), 7.25 – 7.23 (m, 1H), 6.97 (s, 1H), 6.55 (t, J = 6.8 Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) δ 158.47, 147.69, 141.04, 136.72, 134.02 (t, J = 6.6 Hz), 131.60, 131.19, 130.53 (t, J = 22.8 Hz), 129.13 (t, J = 5.2 Hz), 128.69, 128.19, 125.08, 121.33, 109.97. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 32.5 (d, $J_{\text{P,Rh}}$ = 128.9 Hz). IR: $\nu_{\text{CO-carbonyl}}$ = 2005 cm^{-1} . Elemental Analysis (with 1.5 molecules of dichloromethane from precipitation): Calculated C 57.63, H 4.07, N 2.83; Measured C 56.43, H 3.95, N 2.75.

[Ir(PPh₃)₂(CO)(7-hydroxyquinoline)][NO₃] (17a).—In the glovebox, 208 mg (0.267 mmol) Ir(PPh₃)₂Cl(CO) and 41.8 mg (0.288 mmol) 5-hydroxyquinoline were weighed to a 100 mL round-bottom flask. 50 mg (0.29 mmol) AgNO₃ was added. 50 mL of dry dichloromethane was then added. The flask was sealed with a septum, removed from the glovebox, and stirred under a positive pressure of argon for 60 hours in the absence of light. The resulting suspension was returned to the glovebox and filtered through Celite to remove silver chloride and excess silver nitrate. The solvent volume was then reduced to approximately 5 mL under vacuum and the product precipitated by the addition of pentane. The resulting bright yellow solid was collected by filtration. Yield: 167 mg (66%). ^1H NMR (400 MHz, CD_2Cl_2) δ 12.06 (bs, 1H), 8.05 (d, J = 2.3 Hz, 1H), 7.86 – 7.82 (m, 1H), 7.62 – 7.53 (m, 13H), 7.38 – 7.27 (m, 18H), 7.25 (d, J = 8.9 Hz, 1H), 7.05 (dd, J = 8.9, 2.3 Hz, 1H), 6.53 (dd, J = 8.0, 5.4 Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) δ 163.83, 161.90, 137.78, 136.10, 134.85, 134.49 (t, J = 6.3 Hz), 131.44, 130.30 (t, J = 27.4 Hz), 129.58, 128.95 (t, J = 5.3 Hz), 122.65, 118.00, 117.03, 109.07. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 26.4. JR: $\nu_{\text{CO-carbonyl}}$ = 1995 cm^{-1} . Elemental Analysis (with 2 molecules of dichloromethane from precipitation): Calculated C 51.39, H 3.68, N 2.50; Measured C 51.34, H 3.53, N 2.63.

[Ph(PPh₃)₂(CO)(7-hydroxyquinoline)][NO₃] (17b).—In the glovebox, 202 mg (0.292 mmol) Rh(PPh₃)₂Cl(CO) and 42.4 mg (0.292 mmol) 7-hydroxyquinoline were weighed to a 100 mL round-bottom flask. 60 mg (0.35 mmol) AgNO₃ was added. 50 mL of dry dichloromethane was then added. The flask was sealed with a septum, removed from the glovebox, and stirred under a positive pressure of argon for 60 hours in the absence of light. The resulting suspension was returned to the glovebox and filtered through Celite to remove silver chloride and excess silver nitrate. The solvent volume was then reduced to approximately 5 mL under vacuum and the product precipitated by the addition of pentane. The resulting pale-yellow solid was collected by filtration. The product was recrystallized by layering dichloromethane with pentane. Yield: 162 mg (72%). ^1H NMR (400MHz, CD_2Cl_2) δ 11.89 (s, 1H), 7.91 (d, J = 2.2 Hz, 1H), 7.85 (d, J = 5.3 Hz, 1H), 7.56 – 7.48 (m, 12H), 7.36 – 7.22 (m, 19H), 7.18 (d, J = 8.9 Hz, 1H), 6.98 (dd, J = 8.9, 2.1 Hz, 1H), 6.51 (dd, J = 8.0, 5.2 Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) δ 161.45, 150.20, 147.97, 137.18, 133.93 (t, J = 6.6 Hz), 130.87, 130.47 (t, J = 23.3 Hz), 129.22, 128.63 (t, J = 5.1 Hz), 128.43, 122.05, 117.57, 108.84. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 32.0 (d, $J_{\text{P,Rh}}$ = 129.3 Hz). IR:

$\nu_{\text{CO-carbonyl}} = 2007 \text{ cm}^{-1}$. Elemental Analysis (with 1.5 molecules of dichloromethane from precipitation): Calculated C 57.63, H 4.07, N 2.83; Measured C 57.49, H 3.89, N 2.88.

Ir(PPh₃)₂(CO)(5-oxyquinoline-[Al(ⁱBu)₂NO₃]) (18a)—In the glovebox, 60 mg (0.063 mmol) [Ir(PPh₃)₂(CO)(5-hydroxyquinoline)][NO₃] was weighed to a 10 mL Schlenk flask. The solid was suspended in 2 mL THF. Then, 26 μL Al(ⁱBu)₃ (33 mg, 0.167 mmol) was added via microliter syringe. The flask sides were washed down with an additional 3 mL THF. The suspension was stirred until it became a golden yellow solution (all solids dissolved); approximately 5 minutes. The solvent was then removed in vacuo. The resulting pale-yellow solid was washed twice with 3 mL pentane to remove excess Al(ⁱBu)₃ and dried. Yield: 68 mg (98 %). ¹H NMR (400 MHz, CD₂Cl₂) δ 8.33 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.48 – 7.36 (m, 28H), 7.29 (tt, *J* = 7.2, 1.4 Hz, 12H), 7.24 (d, *J* = 8.2 Hz, 1H), 6.70 (dd, *J* = 7.9, 0.9 Hz, 1H), 6.44 (dd, *J* = 8.3, 5.2 Hz, 1H), 1.92 – 1.80 (m, 4H), 0.92 (d, *J* = 6.6 Hz, 12H), –0.01 (d, *J* = 7.0 Hz, 4H). (101 MHz, CD₂Cl₂) δ 136.23, 135.22, 134.24 (t, *J* = 6.5 Hz), 133.53, 131.68, 130.20 (t, *J* = 27.0 Hz), 128.97 (t, *J* = 5.3 Hz), 128.49, 125.81, 122.81, 114.08, 30.48, 26.70, 24.84, 22.75. Quaternary carbons not detected due to slow relaxation. ³¹P{¹H} NMR (162 MHz, CD₂Cl₂) δ 27.24. IR: $\nu_{\text{CO-carbonyl}} = 1993 \text{ cm}^{-1}$. Elemental Analysis: Calculated C 59.39, H 4.98, N 2.47; Measured 54.94, H 4.67, N 2.58; consistent with hydrolysis of alkyl groups during analysis and crystallization with one equivalent of THF. Predicted for Ir(PPh₃)₂(CO)(5-oxyquinoline-[Al(OH)₂NO₃])•THF: C 55.40, H 4.28, N 2.58.

Rh(PPh₃)₂(CO)(5-oxyquinoline-[Al(ⁱBu)₂NO₃]) (18b)—In the glovebox, 60 mg (0.070 mmol) [Rh(PPh₃)₂(CO)(5-hydroxyquinoline)][NO₃] was weighed to a 10 mL Schlenk flask. The solid was suspended in 2 mL THF. Then, 26 μL Al(ⁱBu)₃ (33 mg, 0.167 mmol) was added via microliter syringe. The flask sides were washed down with an additional 3 mL THF. The suspension was stirred until it became a dark yellow-orange solution (all solids dissolved); approximately 5 minutes. The solvent was then removed in vacuo. The resulting pale-yellow solid was washed twice with 3 mL pentane to remove excess Al(ⁱBu)₃ and dried. Yield: 67 mg (96 %). ¹H NMR (400 MHz, CD₂Cl₂) δ 8.31 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.44 – 7.37 (m, 19H), 7.28 (td, *J* = 7.0, 6.5, 1.5 Hz, 12H), 7.21 (d, *J* = 8.2 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.45 (dd, *J* = 8.3, 5.1 Hz, 1H), 1.91 – 1.78 (m, 2H, peak overlaps with THF impurity), 0.92 (d, *J* = 6.5 Hz, 12H), –0.01 (d, *J* = 7.0 Hz, 4H). ¹³C{¹H} (101 MHz, CD₂Cl₂) δ 150.88, 134.06 (t, *J* = 6.6 Hz), 133.27, 131.51, 130.75 (t, *J* = 23.9 Hz), 129.03 (t, *J* = 5.4 Hz), 128.70, 125.81, 118.66, 113.84, 30.48, 28.44, 24.84, 22.75. Quaternary carbons not detected due to slow relaxation. ³¹P{¹H} NMR (162 MHz, CD₂Cl₂) δ 32.77 (d, *J_{P, Rh}* = 129.3 Hz). IR: $\nu_{\text{CO-carbonyl}} = 2003 \text{ cm}^{-1}$. Elemental Analysis: Calculated C 64.67, H 5.43, N 2.69; Measured 60.98, H 4.33, N 2.74; consistent with partial hydrolysis of alkyl groups during analysis and crystallization with one equivalent of THF. Predicted for Rh(PPh₃)₂(CO)(5-oxyquinoline-[Al(OH)₂NO₃])•THF: C 60.37, H 4.66, N 2.82.

Ir(PPh₃)₂(CO)(6-oxyquinoline-[Al(ⁱBu)₂NO₃]) (19a)—In the glovebox, 162 mg (0.170 mmol) [Ir(PPh₃)₂(CO)(6-hydroxyquinoline)][NO₃] was weighed to a vial. 3 mL diethyl ether was added, generating a suspension. Separately, a solution of Al(ⁱBu)₃ in diethyl ether was prepared (200 μL in 10 mL). 2.2 mL of the aluminum stock solution (1 equivalent) was

added dropwise at room temperature over the course of 5 minutes. A yellow solution with a sticky precipitate was observed. The solution was passed through a 2-micron syringe filter to remove remaining solid, and subsequently dried *in vacuo*. The obtained yellow solid was washed with hexane. The product was further purified by layering a solution of the product in dichloromethane with pentane and recrystallization via slow diffusion at -35° . Yield: 86 mg (46 %). ^1H NMR (400 MHz, CD_2Cl_2) δ 8.29 (d, $J = 9.2$ Hz, 1H), 7.53 (s, 1H), 7.49 – 7.41 (m, 12H), 7.42 – 7.37 (m, 6H), 7.29 (tt, $J = 7.0, 1.5$ Hz, 12H), 7.16 (d, $J = 7.1$ Hz, 1H), 7.09 – 7.00 (m, 2H), 6.70 (d, $J = 2.6$ Hz, 1H), 6.44 (dd, $J = 8.3, 5.2$ Hz, 1H), 1.85 – 1.72 (m, 2H), 0.88 (dd, $J = 6.6, 1.6$ Hz, 12H), 0.02 – -0.16 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) δ 162.47, 145.67, 140.43, 136.05, 134.21 (t, $J = 6.3$ Hz), 132.61, 131.70, 130.08 (t, $J = 27.4$ Hz), 129.97, 128.99 (t, $J = 5.2$ Hz), 128.69, 127.18, 120.62, 112.80, 28.38, 26.60, 24.83, 22.75. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 27.07. IR: $\nu_{\text{CO-carbonyl}} = 1994\text{ cm}^{-1}$. Elemental Analysis: Calculated C 64.67, H 5.43, N 2.69; Measured 52.36, H 4.35, N 2.80; consistent with hydrolysis of alkyl groups during analysis and crystallization with one equivalent of DCM. Predicted for $\text{Ir}(\text{PPh}_3)_2(\text{CO})(6\text{-oxyquinoline-}[\text{Al}(\text{OH})_2\text{NO}_3])\bullet\text{DCM}$: C 51.47, H 3.68, N 2.55.

$\text{Rh}(\text{PPh}_3)_2(\text{CO})(6\text{-oxyquinoline-}[\text{Al}(\text{iBu})_2\text{NO}_3])$ (19b)—In the glovebox, 132 mg (0.153 mmol) $[\text{Rh}(\text{PPh}_3)_2(\text{CO})(6\text{-hydroxyquinoline})][\text{NO}_3]$ was weighed to a vial. 3 mL diethyl ether was added, generating a suspension. Separately, a solution of $\text{Al}(\text{iBu})_3$ in diethyl ether was prepared (200 μL in 10 mL). 2.0 mL of the aluminum stock solution (1 equivalent) was added dropwise at room temperature over the course of 5 minutes. A pale red-yellow solution with a sticky precipitate was observed. The solution was passed through a 2-micron syringe filter to remove remaining solid, and subsequently dried *in vacuo*. The obtained beige solid was washed with hexane. The product was further purified by layering a solution of the product in dichloromethane with pentane and recrystallization via slow diffusion at -35° . Yield: 94 mg (61 %). ^1H NMR (400 MHz, CD_2Cl_2) δ 8.10 (d, $J = 9.1$ Hz, 1H), 7.57 (d, $J = 5.1$ Hz, 1H), 7.47 – 7.30 (m, 19H), 7.25 (t, $J = 7.5$ Hz, 12H), 7.00 (dd, $J = 9.1, 2.7$ Hz, 1H), 6.63 (d, $J = 2.6$ Hz, 1H), 6.41 (dd, $J = 8.3, 5.0$ Hz, 1H), 1.81 – 1.72 (m, 2H), 0.85 (dd, $J = 6.5, 2.2$ Hz, 12H), 0.02 – -0.25 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) δ 161.93, 145.52, 139.92, 135.50, 133.65 (t, $J = 6.6$ Hz), 131.45, 131.15, 130.25 (t, $J = 23.7$ Hz), 129.52, 128.69 (t, $J = 5.1$ Hz), 128.33, 127.00, 120.15, 112.43, 28.07, 28.02, 26.24, 22.38. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 32.65 (d, $J_{\text{P-Rh}} = 130.1$ Hz). IR: $\nu_{\text{CO-carbonyl}} = 2005\text{ cm}^{-1}$. Elemental Analysis: Calculated C 64.67, H 5.43, N 2.69; Measured 56.84, H 4.79, N 3.05; consistent with hydrolysis of alkyl groups during analysis and crystallization with one equivalent of DCM. Predicted for $\text{Rh}(\text{PPh}_3)_2(\text{CO})(6\text{-oxyquinoline-}[\text{Al}(\text{iBu})_2\text{NO}_3])\bullet\text{DCM}$: C 56.03, H 4.00, N 2.78.

$\text{Ir}(\text{PPh}_3)_2(\text{CO})(7\text{-oxyquinoline-}[\text{Al}(\text{iBu})_2\text{NO}_3])$ (20a)—In the glovebox, 60 mg (0.063 mmol) $[\text{Ir}(\text{PPh}_3)_2(\text{CO})(7\text{-hydroxyquinoline})][\text{NO}_3]$ was weighed to a 10 mL Schlenk flask. The solid was suspended in 2 mL THF. Then, 26 μL $\text{Al}(\text{iBu})_3$ (33 mg, 0.167 mmol) was added via microliter syringe. The flask sides were washed down with an additional 3 mL THF. The suspension was stirred until it became a golden yellow solution (all solids dissolved); approximately 5 minutes. The solvent was then removed *in vacuo*. The resulting pale-yellow solid was washed twice with 3 mL pentane to remove excess $\text{Al}(\text{iBu})_3$ and dried.

Yield: 65 mg (94 %). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.80 (d, J = 2.2 Hz, 1H), 7.63 (d, J = 5.4 Hz, 1H), 7.53 (dtd, J = 8.6, 5.9, 1.4 Hz, 12H), 7.44 (d, J = 7.8 Hz, 1H), 7.38 – 7.31 (m, 6H), 7.30 – 7.24 (m, 12H), 7.18 (d, J = 9.0 Hz, 1H), 6.97 (dd, J = 8.9, 2.2 Hz, 1H), 6.29 (dd, J = 7.9, 5.4 Hz, 1H), 1.86 – 1.76 (m, 2H, peak overlaps with THF impurity), 0.89 (dd, J = 6.5, 2.8 Hz, 12H, peak overlaps with pentane impurity), -0.03 – -0.16 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) δ 166.20, 163.89, 149.63, 137.16, 136.23, 134.42 (t, J = 6.6 Hz), 131.49, 131.40, 130.48 (t, J = 27.3 Hz), 128.89 (t, J = 5.6 Hz), 127.45, 125.81, 123.66, 111.64, 30.49, 28.42, 26.66, 24.84. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 27.15. IR: $\nu_{\text{CO-carbonyl}}$ = 1994 cm^{-1} . Elemental Analysis: Calculated C 59.39, H 4.98, N 2.47; Measured 57.53, H 4.84, N 2.45; consistent with partial hydrolysis of alkyl groups during analysis and crystallization with one equivalent of THF. Predicted for $\text{Ir}(\text{PPh}_3)_2(\text{CO})(7\text{-oxyquinoline-}[\text{Al}(\text{OH})(i\text{Bu})\text{NO}_3])\bullet\text{THF}$: C 57.69, H 5.31, N 2.45.

$\text{Rh}(\text{PPh}_3)_2(\text{CO})(7\text{-oxyquinoline-}[\text{Al}(i\text{Bu})_2\text{NO}_3])$ (20b)—In the glovebox, 60 mg (0.070 mmol) $[\text{Rh}(\text{PPh}_3)_2(\text{CO})(7\text{-hydroxyquinoline})][\text{NO}_3]$ was weighed to a 10 mL Schlenk flask. The solid was suspended in 2 mL THF. Then, 26 μL $\text{Al}(i\text{Bu})_3$ (33 mg, 0.167 mmol) was added via microliter syringe. The flask sides were washed down with an additional 3 mL THF. The suspension was stirred until it became a dark yellow solution (all solids dissolved); approximately 5 minutes. The solvent was then removed in vacuo. The resulting pale-yellow solid was washed twice with 3 mL pentane to remove excess $\text{Al}(i\text{Bu})_3$ and dried. Yield: 59 mg (84 %). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.70 (d, J = 2.2 Hz, 1H), 7.68 (dt, J = 5.3, 1.3 Hz, 1H), 7.56 – 7.42 (m, 12H), 7.45 (d, J = 8.3 Hz, 1H), 7.41 – 7.33 (m, 6H), 7.32 – 7.21 (m, 12H), 7.14 (d, J = 8.9 Hz, 1H), 6.94 (dd, J = 8.9, 2.2 Hz, 1H), 6.30 (dd, J = 7.9, 5.3 Hz, 1H), 1.86 – 1.75 (m, 2H, peak overlaps with THF impurity), 0.89 (dd, J = 6.6, 3.0 Hz, 12H, peak overlaps with pentane impurity), -0.03 – -0.13 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) δ 165.71, 162.83, 136.59, 135.85, 133.86, 130.83, 130.66, 128.62, 128.57, 126.91, 125.43, 122.47, 116.03, 111.35, 30.11, 28.05, 25.61, 24.46. δ 166.09, 163.21, 150.04, 149.41, 136.96, 136.23, 134.24 (t, J = 6.6 Hz), 131.34, 131.30, 131.03 (t, J = 24.7 Hz), 128.94 (t, J = 5.5 Hz), 127.29, 125.81, 116.41, 30.48, 28.43, 25.99, 24.84. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 32.8 (d, $J_{\text{P,Rh}}$ = 130.5 Hz). IR: $\nu_{\text{CO-carbonyl}}$ = 2004 cm^{-1} . Elemental Analysis: Calculated C 64.67, H 5.43, N 2.69; Measured 61.56, H 5.37, N 2.78; consistent with partial hydrolysis of alkyl groups during analysis and crystallization with one equivalent of THF. Predicted for $\text{Rh}(\text{PPh}_3)_2(\text{CO})(7\text{-oxyquinoline-}[\text{Al}(\text{OH})(i\text{Bu})\text{NO}_3])\bullet\text{THF}$: C 62.67, H 5.26, N 2.71.

$[\text{Ir}(\text{PPh}_3)_2(\text{CO})(2\text{-oxypyridine-Al}(\text{OSO}_2\text{CF}_3)(i\text{Bu})_2)]$ (21a)—In the glovebox, 50 mg (0.051 mmol) of $[\text{Ir}(\text{PPh}_3)_2(\text{CO})(2\text{-hydroxypyridine})][\text{SO}_3\text{CF}_3]$ was weighed to a 10 mL Schlenk flask. The solid was suspended in 2 mL of THF. Then, 14 μL (11 mg, 0.055 mmol) of $\text{Al}(i\text{Bu})_3$ was added via microliter syringe. The flask sides were washed down with an additional 3 mL of THF. The suspension was stirred until it became a golden yellow solution (all solids dissolved); approximately 2 minutes. The solvent was then removed in vacuo. The resulting brown solid was washed twice with 3 mL of pentane to remove excess $\text{Al}(i\text{Bu})_3$ and dried. Yield: 6 mg (12 %). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.63 – 7.51 (m, 14H), 7.47 – 7.30 (m, 22H), 6.92 (t, J = 8.1 Hz, 1H), 6.69 (d, J = 6.0 Hz, 1H), 6.28 (d, J = 8.6 Hz, 1H), 5.68 (t, 1H), 1.74 – 1.62 (m, 3H), 0.94 – 0.85 (m, 17H), 0.87 (s, 12H), -0.12 (d, J = 7.0 Hz,

3H), $-0.11 - -0.29$ (m, 6H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 27.00. IR: $\nu_{\text{CO-carbonyl}} = 1983\text{ cm}^{-1}$. Elemental Analysis: Calculated C 54.63, H 4.76, N 1.23; Measured 48.00, H 4.30, N 1.19; consistent with hydrolysis of alkyl groups during analysis and crystallization with 0.5 equivalents of DCM. Predicted for $\text{Ir}(\text{PPh}_3)_2(\text{CO})(2\text{-oxypyridine-Al}(\text{OH})_2\text{OSO}_2\text{CF}_3] \bullet 0.5\text{DCM}$: C 48.26, H 3.73, N 1.26.

[Rh(PPh₃)₂(CO)(2-oxypyridine-Al(OSO₂CF₃)(ⁱBu)₂)] (21b).—In the glovebox, 50 mg (0.056 mmol) of $[\text{Rh}(\text{PPh}_3)_2(\text{CO})(2\text{-hydroxypyridine})][\text{SO}_3\text{CF}_3]$ was weighed to a 10 mL Schlenk flask. The solid was suspended in 2 mL of THF. Then, 15 μL (12 mg, 0.060 mmol) of $\text{Al}(\text{iBu})_3$ was added via microliter syringe. The flask sides were washed down with an additional 3 mL of THF. The suspension was stirred until it became a golden yellow solution (all solids dissolved); approximately 2 minutes. The solvent was then removed in vacuo. The resulting brown solid was washed twice with 3 mL of pentane to remove excess $\text{Al}(\text{iBu})_3$ and dried. Product was recrystallized by layering dichloromethane with pentane. Yield: 7 mg (14 %). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.59 – 7.47 (m, 12H), 7.46 – 7.39 (m, 6H), 7.44 – 7.30 (m, 12H), 6.96 (t, $J = 1.1$ Hz, 1H), 6.77 (d, $J = 5.9$ Hz, 1H), 6.27 (d, $J = 8.6$ Hz, 1H), 5.71 (t, $J = 6.5$ Hz, 1H), 1.78 – 1.66 (m, 2H), 0.94 – 0.83 (m, 12H), $-0.06 - -0.26$ (m, 4H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 32.22 (d, $J = 133.2$ Hz). IR: $\nu_{\text{CO-carbonyl}} = 1992\text{ cm}^{-1}$. Elemental Analysis: Calculated C 59.26, H 5.16, N 1.33; Measured C 52.29, H 4.38, N 1.26; consistent with hydrolysis of alkyl groups during analysis and crystallization with 0.5 equivalents of DCM. Predicted for $\text{Rh}(\text{PPh}_3)_2(\text{CO})(2\text{-oxypyridine-Al}(\text{OH})_2\text{OSO}_2\text{CF}_3] \bullet 0.5\text{DCM}$: C 52.42, H 3.70, N 1.39.

[Rh(PPh₃)₂(CO)(3-oxymethylpyridine-Al(ONO₂)(ⁱBu)₂)] (22b).—In the glovebox, 50 mg (0.065 mmol) of $[\text{Ir}(\text{PPh}_3)_2(\text{CO})(3\text{-pyridinemethanol})][\text{NO}_3]$ was suspended in 5 mL of THF in a 10 mL Schlenk flask. In a separate pear flask, a volume of 18.17 μL (14.28 mg, 0.072 mmol) of $\text{Al}(\text{iBu})_3$ was suspended in 3 mL of THF and sealed with a septum. Both flasks were removed from the glovebox, the reaction mixture was put under argon on the Schlenk line and cooled to -78°C . The aluminum suspension was added dropwise to the stirring reaction mixture via syringe. The reaction mixture was allowed to warm to ambient temperature and solvent was removed in vacuo as soon as the reaction mixture darkened from yellow to golden in color (~ 2 min). The resulting pale-yellow solid was then returned to the glovebox and washed twice with 3 mL of pentane to remove excess $\text{Al}(\text{iBu})_3$ and dried. Yield: 30.2 mg (48%). ^1H NMR (400MHz, CD_2Cl_2) δ 8.54 (d, $J = 5.2$ Hz, 1H), 7.82 (td, $J = 7.7, 1.6$ Hz, 1H), 7.64 (q, $J = 6.0, 5.5$ Hz, 12H), 7.47 – 7.42 (m, 18H), 7.31 (d, $J = 7.9$ Hz, 1H) 6.95 (s, 1H), 5.01 (s, 2H), 1.66 (dq, $J = 13.2, 6.6$ Hz, 2H), 0.74 (dd, $J = 45.7, 6.4$, 12H), -0.12 (dd, $J = 10.2, 7.1$ Hz, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2) δ 159.41, 145.76, 138.62, 136.20, 134.57 (t, $J = 6.7$ Hz), 131.87 (t, $J = 22.5$ Hz), 131.06, 128.97 (t, $J = 5.1$ Hz), 125.81, 123.06, 63.06, 30.47, 24.83, 15.50. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2) δ 31.18 (d, $J = 132.8$ Hz). IR (dichloromethane solution): $\nu_{\text{CO-carbonyl}} = 1998\text{ cm}^{-1}$. Elemental Analysis (with 1 molecule of dichloromethane from precipitation): Calculated C 59.38, H 5.37, N 2.66; Measured C 58.89, H 5.36, N 2.91.

Al(ⁱBu)₂(2-oxymethylpyridine) (23).—In the glovebox, a solution of $\text{Al}(\text{iBu})_3$ (1.0 mL, 4.0 mmol) was generated in 10 mL of tetrahydrofuran inside a Schlenk flask. The solution

was removed from the glovebox and 2-pyridinemethanol (0.35 mL, 3.6 mmol) was added under a constant flow of nitrogen. Rapid bubbling immediately occurred. The resulting solution was allowed to stir at room temperature overnight in the glovebox. Solvent was removed *in vacuo* to give an off-white solid. Biphasic recrystallization using a benzene/pentane (v/v = 1/2) produced a pure white solid. Yield: 0.7866 g, 87%. ¹H NMR (400 MHz, Benzene-*d*₆) δ 8.35 (d, *J* = 5.4 Hz, 1H), 6.76 (t, *J* = 8.3 Hz 1H), 6.51-6.41 (m, 1H), 6.25 (d, *J* = 7.9 Hz, 1H), 4.99 (s, 2H), 2.10 (dt, *J* = 6.6 Hz, 2H), 1.22 (dd, *J* = 6.4 Hz, 12H), 0.39 (dt, *J* = 9.8 Hz, 4H). ¹³C{¹H} NMR (101 MHz, Benzene-*D*₆) δ 158.97, 147.32, 142.95, 137.77, 132.50, 114.66, 122.42, 120.00, 63.07, 29.67, 28.82, 27.58. Elemental Analysis: Calculated C 67.17, H 10.07, N 5.60; Measured C 61.06, H 8.10, N 6.09; consistent with partial hydrolysis of alkyl groups during analysis. Predicted for Al(ⁱBu)₂(2-oxymethylpyridine) + 2 Al(ⁱBu)(OH)(2-oxymethylpyridine): C 61.15, H 8.45, N 6.29.

Electrochemical Methods.

All electrochemical measurements were performed in an Inert Technologies glovebox with a dry nitrogen atmosphere using a CH Instruments 600E potentiostat. In a typical experiment, 194 mg of tetrabutylammonium hexafluorophosphate (NBu₄-PF₆) (0.500 mmol) was dissolved in 5.0 mL of dry acetonitrile along with ~2 mg of ferrocene and ~5 μmol of the substrate under investigation. Experiments were performed with a glassy carbon electrode (3 mm diameter) polished with 0.05 μm alumina for both working and auxiliary electrodes and a standard calomel reference electrode. Final data was then adjusted with the Fc⁺/Fc couple at 0.0 V.

X-ray Crystallography.

A suitable crystal of each sample was selected for analysis and mounted in a polyimide loop. All measurements were made on a Rigaku Oxford Diffraction Supernova Eos CCD with filtered Cu-Kα or Mo-Kα radiation at a temperature of 100 K. Using Olex2,⁵⁰ the structure was solved with the ShelXT structure solution program using Direct Methods and refined with the ShelXL refinement package⁵¹ using Least Squares minimization. Structures can be found at the Cambridge Crystallographic Data Centre, deposition numbers 2013740-2013746.

Computational Details.

All computations were performed using the Gaussian 16 software package.⁵² Optimized geometries, and unsealed harmonic vibrational frequencies were obtained using Density Functional Theory (DFT).⁵³ The pure hybrid B3LYP functional was used with default grid parameters.⁵⁴ The basis set for ruthenium and iridium was the Hay and Wadt basis set and effective core potential (ECP) combination (LANL2DZ)^{55,56} as modified by Couty and Hall,⁵⁷ where the two outermost p functions of Ru and Ir have been replaced by a split of the optimized 5p/6p function, respectively. Computations with phosphorous and aluminum used the standard LANL2DZ basis set/ECP combination. All carbon, nitrogen, oxygen, and hydrogen atoms utilized the 6-31G(d') basis set.⁵⁸ Spherical harmonic d functions were used throughout; i.e., there are five angular basis functions per d function. The Hessian of the energy was computed at all stationary points to confirm they were minima (no imaginary vibrational frequencies). Unscaled harmonic vibrational frequencies, zero-point energies

(ZPE) and thermal enthalpy/free energy corrections were computed at 1 atm and 298.15 K. Implicit solvation was used throughout with the CPCM model and standard cavity parameters for dichloromethane.^{59,60}

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Previously reported⁴²⁻⁴⁴ monometallic and heterobimetallic complexes of iridium and rhodium.

Figure 2.

ORTEP representations of X-ray crystal structures of **8a** (top left), **9a** (top center), **10a** (top right), **8b** (bottom left), **9b** (bottom center), and **10b** (bottom right). Ellipsoids shown at 50% probability. Arene rings on triphenylphosphine ligands truncated to show only carbon bound to phosphorous. Hydrogen atoms and nitrate counterions omitted for clarity.

Scheme 1.

Synthesis of Transition-Metal Pyridinemethanol Precursors

Scheme 2.

Synthesis of Transition-Metal Hydroxypyridine Precursors

Scheme 3.
Synthesis of Transition-Metal Hydroxyquinoline Precursors

Scheme 4.
 Synthesis of Iridium- and Rhodium-Aluminum Heterobimetallics

Table 1.

Combined Computational & Experimental CV Data and IR Data

Iridium Complexes				Rhodium Complexes			
Complex	ω_{CO} (cm ⁻¹) ^a	ν_{CO} (cm ⁻¹) ^b	E_{pc} (V vs. Fc ⁺ /Fc)	Complex	ω_{CO} (cm ⁻¹) ^a	ν_{CO} (cm ⁻¹) ^b	E_{pc} (V vs. Fc ⁺ /Fc)
2a	2011/2019 ^c	1978	-1.98 ^d	2b	2032/2039 ^c	1985	-1.89 ^d
3a	2033	1994	-1.74 ^e	3b	2054	2007	-1.71 ^e
4a	2029	1992	-1.84 ^e	4b	2052	1987	-1.84 ^e
5a	2013	1983	-2.06 ^d	5b	2033	1984	-1.97 ^d
6a	2024	1993	-1.81 ^e	6b	2045	2003	-1.85 ^e
7a	2021	1990	-1.93 ^e	7b	2045	1988	-2.00 ^e
8a	2033	1994	-1.82	8b	2052	2006	-1.84
9a	2030	1996	-1.95	9b	2050	2007	-1.85
10a	2034	1996	-1.85	10b	2049	2006	-1.83
11a	2030	1998	-1.85	11b	2043	2009	-1.86
12a	2025	1997	-1.88	12b	2047	2008	-1.82
13a	2040	1986	-1.93	13b	2049	1994	-1.89
14a	2023	1994	-2.00	14b	Complex not obtained		
15a	2031	1994	-2.02	15b	2051	2005	-1.82
16a	2031	1995	-1.83	16b	2051	2005	-1.87
17a	2030	1995	-1.98	17b	2050	2007	-1.88
18a	2024	1993	-2.09	18b	2045	2003	-1.98
19a	2026	1994	-1.99	19b	2046	2005	-2.03
20a	2025	1994	-2.08	20b	2045	2004	-1.90
21a	2017	1983	-1.95	21b	2039	1992	-1.87
22a	Complex not obtained			22b	2043	1998	-1.84

^aCalculated harmonic values.^bExperimentally determined in dichloromethane solution.^cCalculated for both possible isomers (lower-energy O-bound pyridone/higher-energy N-bound pyridine).^dValues taken from reference Brewster et al. 2018.⁴²^eValues taken from reference Brewster et al. 2020⁴⁴