# Synthesis and Reactivity of Nonbridged Metal−Metal Bonded Rhodium and Iridium Phenanthroline-Based $N_2O_2$ Dimers

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Nonbridged metal dimers of phenanthroline-based $N_2O_2$ ligands of rhodium and iridium have been synthesized from the reactions of metal hydrides with TEMPO (2,2′,6,6′-tetramethylpiperidinyloxy). Modification of phenathroline ligands has led to more lipophilic metal complexes. The oxidative additions of the metal dimers with methyl iodide, silane, and hydrogen have been studied.

Nonbridged $d^7-d^7$ dimeric metal−metal bonded complexes of rhodium[1−15] and iridium[16−20] have attracted considerable interest owing to their rich chemistry and unique structural features. The fairly extensive chemistry of the nonbridged metal−metal bonded complexes is exemplified by the porphyrin ligand class. This class of metal porphyrin dimer complexes, especially that of rhodium, undergo facile dissociation to yield extremely reactive metal-centered radicals. These rhodium monomers undergo halogen abstraction,[21] olefin insertion,[21] novel carbon−hydrogen bond activation, especially the activation of methane,[22−25] and carbon−carbon bond activation by sterically hindered rhodium porphyrin monomers.[19c] Electrocatalytic reduction of oxygen via a four-electron process catalyzed by iridium porphyrins has also been reported.[17,20]

The rhodium porphyrin chemistry has been extended to complexes with nonmacrocyclic ligand systems which have the potential to manifest more versatile reaction pathways and thus faster substrate reactions than those observed for rigid tetradentate macrocyclic complexes.[26−30] Wayland et al. reported the synthesis and the chemistry of [*N*,*N*′-ethylenebis(3,5-di-*tert*-butylsalicylaldiminato)]rhodium(II) dimer, $[(ttbs)Rh]_2$, with $H_2$, CO, and $CH_2{=}CH_2$.[26,27] Eisenberg and co-workers reported that the tetradentate dianionic Schiff base ligand $H_2bu_4$ (salophen) reacts with $[RhCl(C_2H_4)_2]_2$ and $NR_4OH$ (R = n-Bu, Et) to produce the complexes RhR-($bu_4$salophen) (R = n-Bu, Et), which undergo photolysis under a hydrogen atmosphere to generate RhH-($bu_4$salophen) and the corresponding alkanes.[28,29]

1,10-Phenanthroline (Phen) with phenolic moieties at 2,9-positions bearing a similar $N_2O_2$ donor set is a relatively unexplored $N_2O_2$ system.[31] Compared to the Schiff base, bearing relatively sensitive imine bonds,[32] the phenanthroline skeleton is less susceptible to decomposition by redox reaction and hydrolysis due to its more robust pyridine ring.[33] Therefore, their metal complexes may be more robust and efficient reagents and catalysts. We now report the synthesis and chemistry of these rhodium and iridium nonbridged metal−metal bonded dimers of 1,10-phenanthroline type $N_2O_2$ ligands (Figure 1).

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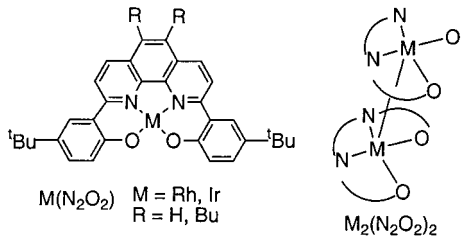


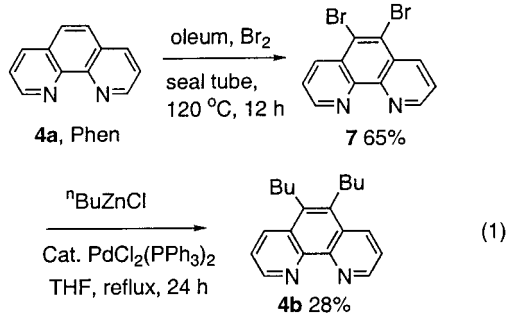

**Figure 1.**

## Results and Discussion

The synthetic routes of two $N_2O_2$ ligands, 9-bis(5-*tert*-butyl-2-hydoxyphenyl)-1,10-phenanthroline ($H_2$bpp, **6a**)[33] and the more lipophilic 2,9-bis(5-*tert*-butyl-2-hydoxyphenyl)-5,6-di-*n*-butyl-1,10-phenanthroline ($H_2$bbpp, **6b**), are shown in Scheme 1**.** The synthesis of the $N_2O_2$ ligand $H_2$bpp [2,9-bis(5-*tert*-butyl-2-hydoxyphenyl)-1,10-phenanthroline followed a modified Sauvage procedure for the preparation of 2,9-disubstituted phenanthrolines.[31] Nucleophilic addition of the lithium reagent 2-bromo-1-methoxyl-4-*tert*-butylbenzene **3** to 1,10-phenanthroline followed by oxidation with manganese dioxide yielded **5a** in 80% yield. Demethoxylation with pyridinium hydrochloride gave $H_2$bpp **6a** in 80% yield.

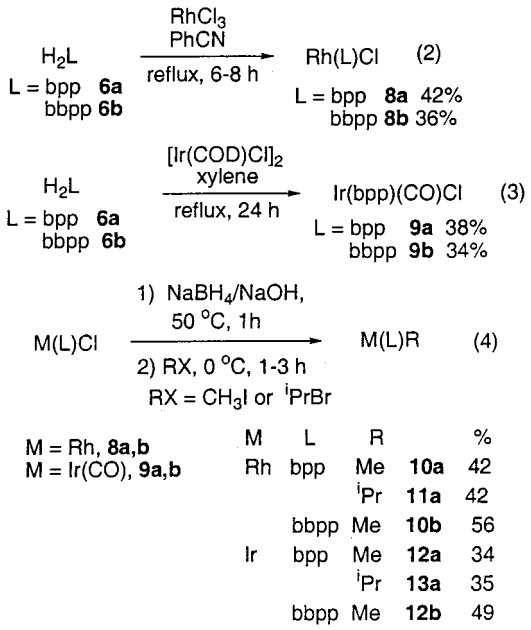
Since the lipophilicity of the $N_2O_2$ ligand is important for studying the chemistry of their metal complexes, a more lipophilic derivative was prepared. As the more convenient incorporation of an alkyl group in the phenoxy groups was found to be less effective in enhancing the solubility, functionalization of 1,10-phenanthroline for the preparation of alkyl Phen was sought. 2,9-Bis-(5-*tert*-butyl-2-hydoxyphenyl)-5,6-di-*n*-butyl-1,10-phenanthroline ligand ($H_2$bbpp, **6b**) was chosen as the target with alkyl groups introduced at the 5- and 6-positions. For positions 3 and 8, alkyl groups introduced will hamper the synthesis of the $N_2O_2$ ligand at the subsequent nucelophilic substitution step due to steric hindrance. For positions 4 and 7, alkyl groups have been introduced.[34] The synthesis however is very lengthy. Positions 5 and 6 are the most ideal as 5,6-dibromo-Phen **7** is conveniently prepared from Phen via bromination.[35] Furthermore, the substituent electronic effect is too remote to affect the chemistry at the $N_2O_2$ core.

5,6-Dibutyl-Phen was prepared by a bromination/cross-coupling route. 5,6-Dibromo-Phen **7** was synthesized in 65% yield by the improved bromination of Phen with $Br_2$ in oleum at 120 °C for 12 h in a sealed tube (eq 1). In an open system,[35] a much lower yield of only




(1)

30% was obtained. 5,6-Dibromo-Phen **7** then underwent Negishi cross-coupling[36] with BuZnBr catalyzed by $PdCl_2(PPh_3)_2$ to yield 5,6-dibutyl-Phen **4b** in 28% yield (eq 4).[37] The corresponding Kumada coupling[36] with Grignard reagents was less effective.




| M | L | R | | % |
|---|---|---|---|---|
| Rh | bpp | Me | **10a** | 42 |
| | | $^i$Pr | **11a** | 42 |
| | bbpp | Me | **10b** | 56 |
| Ir | bpp | Me | **12a** | 34 |
| | | $^i$Pr | **13a** | 35 |
| | bbpp | Me | **12b** | 49 |

The synthetic route of 2,9-bis(5-*tert*-butyl-2-hydoxyphenyl)-5,6-di-*n*-butyl-1,10-phenanthroline ligand ($H_2$bbpp, **6b**) is shown in Scheme 1. The aryllithium reagent of **3** underwent nucleophilic substitution at the 2,9-positions of **5b** after oxidative re-aromatization to produce **5b** in 75% yield. **5b** was then demethylated with py·HCl at 210 °C for 4 h to produce **6b** in 85% yield.

**Metalations of Ligands.** Rh(bpp)Cl **8a**, Rh(bbpp)-Cl **8b**, Ir(bpp)(CO)Cl **9a**, and Ir(bbpp)(CO)Cl **9a** were synthesized by the metalation of $H_2$bpp **6a** and $H_2$bbpp **6b** with $RhCl_3$[19,38] and $[Ir(COD)_2Cl]_2$[39] in 42, 36, 38, and 34% yield, respectively (eqs 2 and 3). The solubilities of the metal complexes of bpp were found to be poor in most organic solvents, while that of bbpp was much better. For example, **8a** and **8b** dissolved sparingly in $CHCl_3$, while **9a** and **9b** dissolved well.

IR streching frequencies of CO groups in Irbpp(CO)-Cl **9a** and Irbbpp(CO)Cl appeared at 2049 and 2052 $cm^{-1}$, suggesting little difference in the electronic property of the ligands.

**Synthesis of M(L)R (M = Rh, Ir).** M(L)R (L = bpp, bbpp; M = Rh, Ir(CO); and R = Me, $^i$Pr) were synthesized by the reductive alkylation of M(L)Cl with $NaBH_4$/RX (eq 4).[40] Upon addition of $NaBH_4$, the orange suspension of Rh(L)Cl and Ir((L)(CO)Cl changed into intense deep brown in color, which indicated the successful reduction of $Rh^{III}$ and $Ir^{III}$ into $Rh^{I}$ and $Ir^{I}$,

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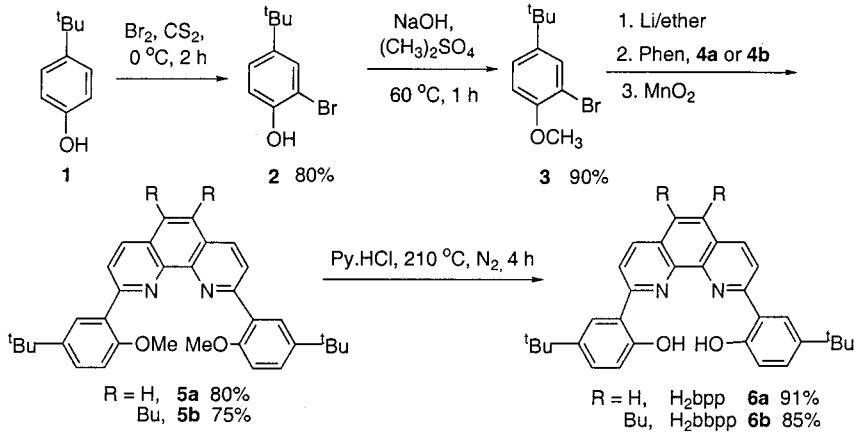
**Scheme 1**




respectively. Subsequent oxidative addition with alkyl halides produced metal alkyls (eq 4).

In the $^1$H NMR spectrum, the Rh−$CH_3$ resonance in Rh(bpp)Me **10a** appeared at 0.51 ppm in DMSO-$d_6$ with $J_{Rh-H}$ equal to 2.4 Hz. The Ir−$CH_3$ resonance in Ir(bpp)-Me **10b** appeared at 0.04 ppm in DMSO-$d_6$. The chemical shifts of the $^i$Pr group in Rh(bpp)$^i$Pr **11a** were −0.55 (=CH−) and −0.07 ($CH_3$), and those in Ir(bpp)$^i$Pr **13a** were −0.85 (=CH−) and −0.67 ($CH_3$). The methyl signal of Rh−$CH_3$ in Rh(bbpp)Me **10b** appeared at 0.51 ppm in $CDCl_3$ with $J_{Rh-H}$ equal to 2.1 Hz. The methyl signal of Ir−$CH_3$ in Ir(bbpp)Me **12b** appeared at 0.35 ppm in $CDCl_3$. These chemical shifts and coupling constants are similiar to that of close anaologues of Rh(SB)Me(py) (SB = *N*,*N*′-ethylenebis(salicylideneiminato))[41] with the Rh−$CH_3$ appearing at 1.3 ppm [$(CD_3)_2SO$] and $J^{103}_{Rh-H}$ = 3.0 Hz.

The five-coordinate square planar complex M(L)R readily formed a six-coordinate complex with ligands. $PPh_3$ reacted with Rh(bpp)Me **10a** to give Rh(bpp)Me-($PPh_3$) **14** in DMSO-$d_6$ with the doublet of the methyl signal changed into a double doublet in the $^1$H NMR spectrum (eq 5). Furthermore, the $^{31}$P NMR showed that a doublet appeared at 47.39 ppm with $J_{Rh-P}$ = 138 Hz.

$$\underset{\textbf{10a}}{\text{Rh(bpp)Me}} + \text{PPh}_3 \longrightarrow \underset{\textbf{14}}{\text{Rh(bpp)(Me)(PPh}_3\text{)}} \quad (5)$$

$$\text{M(L)Cl} \xrightarrow[\text{2) HCl, 0 °C, 1-3 h}]{\text{1) NaBH}_4\text{/NaOH, 50 °C, 1h}} \text{M(L)H} \quad (6)$$

M = Rh **8a,b**
M = Ir(CO) **9a,b**

| M | L | | % |
|---|---|---|---|
| Rh | bpp | **15a** | 78 |
| | bbpp | **15b** | 70 |
| Ir | bpp | **16a** | 52 |
| | bbpp | **16b** | 62 |

**Synthesis of M(L)H.** Syntheses of M(L)H (M = Rh, Ir) were accomplished by the reductive protonation of M(L)Cl with $NaBH_4/H^+$ (eq 6). The characteristic IR stretching frequencies of Rh−H and Ir−H fell at 2225 and 2046 $cm^{-1}$, respectively, without any significant electronic effect exerted by the ligands.

In the $^1$H NMR spectrum, the hydride peak of Rh-(bpp)H **14a** appeared as a doublet at −22.85 ppm with $J_{Rh-H}$ = 37.3 Hz. The hydride peak of Irbpp(H) **15a** appeared at −22.04 ppm in DMSO-$d_6$ added with $CF_3SO_3H$.[41] $CF_3SO_3H$ was necessarily added to prevent M(bpp)H from dissociation into M(bpp) anion, which may lead to decomposition.[42] The hydride peak of Rh(bppp)H **15b** appeared as a doublet at −20.27 ppm with $J_{Rh-H}$ = 44.4 Hz in $CD_3OD$-$d_4$ added with a small amount of $CF_3SO_3H$. The hydride peak of Ir(bbpp)H **16b** appeared at −20.23 ppm in $CD_3OD$-$d_4$. The solubilities of the metal hydrides of the bbpp ligand were much better without the need of polar DMSO solvent.

The $N_2O_2$-metal hydrides exibihited typical insertion and coordination chemistry. Styrene reacted with Rh(bpp)H **14a** in THF to give the addition product of Rh(bpp)($CH_2CH_2Ph$) **17a** quantitatively (eq 7). Ir(bpp)H **15a** formed a six-coordination adduct with $PPh_3$ in DMSO-$d_6$. The hydride singlet appeared at −22.04 ppm and was split into a doublet with $J_{P-H}$ = 15.8 Hz (eq 8).

$$\underset{\textbf{16a}}{\text{Ir(bpp)H}} + \text{PPh}_3 \longrightarrow \underset{\textbf{17a}}{\text{Ir(bpp)(H)(PPh}_3\text{)}} \quad (7)$$

$$\underset{\textbf{15a}}{\text{Rh(bpp)H}} + \text{PhCH=CH}_2 \xrightarrow{\text{THF}} \underset{\textbf{18}}{\text{Rh(bpp)(CH}_2\text{CH}_2\text{Ph)}} \quad (8)$$

**Synthesis of $M_2(bpp)_2$ (M = Rh, Ir).** Three general methods exist for synthesizing rhodium and iridium metal−metal bonded complexes: (i) photolysis of metal alkyls;[19] (ii) aerobic oxidation of rhodium hydride;[6,7] and (iii) reaction of metal hydride with TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl).[19a,b] The first method usually requires long reaction time and is highly dependent on both the quantum yields of the metalloporphyrin alkyls and the experimental conditions. The second method is difficult because overoxidation of the air-sensitive metal−metal bonded dimer is possible. The third one is the most convenient and efficient since it is high yielding and excess TEMPO and TEMPOH coproduct are easily removed by vacuum evaporation.[19a,b]

$M_2(L)_2$ were synthesized in high yields by the reaction of M(L)H with TEMPO (eq 9). The chemical shifts of

$$\text{M(bpp)H} + \text{TEMPO} \xrightarrow[\text{N}_2\text{, 2-4 h}]{\text{THF}} \text{M}_2\text{(bpp)}_2 \quad (9)$$

| M | L | M(L)H | | $M_2L_2$ | % yield |
|---|---|---|---|---|---|
| Rh | bpp | **15a** | TEMPO = | **19a** | 95 |
| Rh | bbpp | **15b** | | **19b** | 95 |
| Ir | bpp | **16a** | | **20a** | 92 |
| Ir | bbpp | **16b** | | **20b** | 90 |

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the metal−metal bonded dimers of nonmacrocylic ligands are very distinctive. As DMSO used in NMR analysis is a coordinating solvent, formation of complexes with a metal−metal dimer is possible. Furthermore, two coordination modes of either O- or S-bonded ligands are feasible. Infrared spectra have been utilized in distinguishing between O- and S-bonded ligands.[43] DMSO solvent likely coordinated to the Rh dimer as in $Rh_2(O_2CCH_3)_4(Me_2SO)_2$ with sulfur as the donor atom, which was indicated by an upward shift of $\nu_{SO}$ ($\nu_{S-O}$ = 1086 $cm^{-1}$, for free DMSO, $\nu_{S-O}$ = 1050 $cm^{-1}$ [44]). From the IR spectrum, the peak at 1086 $cm^{-1}$ was assigned to the coordinated S−O stretching frequency in DMSO-$d_6$ solution of $Rh_2(bpp)_2$ **19a**. The S−O stretching frequency was red-shifted by 36 $cm^{-1}$ in DMSO. In the case of $Ir_2(bpp)_2$ **20a**, the coordination mode of DMSO-$d_6$ was the same as that of $Rh_2(bpp)_2$ **20a** because the S−O stretching frequency appeared at 1085 $cm^{-1}$.

**Reactions of $M_2(L)_2$.** $M_2(L)_2$ underwent characteristic oxidative addition with MeI, $Et_3SiH$, and $H_2$. $Rh_2(bpp)_2$ **19a** reacted with MeI to yield Rh(bpp)Me **12a** and Rh(bpp)I **25a** in 32% and 28% yield, respectively (eq 10). $Rh_2(bpp)_2$ **19a** reacted with $Et_3SiH$ to produce Rh(bpp)($SiEt_3$) **21** and Rh(bpp)H **15a** in 42% and 36% yield, respectively (eq 11). $Rh_2(bpp)_2$ **20a** and $Ir_2(bpp)_2$ **20b** reacted with $H_2$ to produce Rh(bpp)H **15a** and Ir(bpp)H **16a** both in 90% yield (eq 12).

$$M_2(L)_2 + CH_3I \xrightarrow[\text{r.t., 2 h}]{\text{THF}} M(L)Me + M(L)I \quad (10)$$

| M | L | $M_2L_2$ | M(L)Me | M(L)I |
|---|---|---|---|---|
| Rh | bpp | **19a** | **10a** 32% | **21a** 28% |
| Rh | bbpp | **19b** | **10b** 83% | **21b** 25% |
| Ir | bbpp | **20b** | **12b** 32% | **22b** 28% |

$$Rh_2(bpp)_2 \text{ (19a)} \xrightarrow[\text{r.t., 2 h}]{Et_3SiH,\ \text{THF}} Rh(bpp)(SiEt_3) + Rh(bpp)H \quad (11)$$

**23a**, 42% **15a** 36%

$$M_2(L)_2 + H_2 \xrightarrow[\text{r.t., 2 h}]{\text{DMSO-}d_6 \text{ or MeOH-}d_4} M(L)H \quad (12)$$

| M | L | $M_2L_2$ | M(L)H |
|---|---|---|---|
| Rh | bpp | **19a** | **15a** 90% |
| Rh | bbpp | **19b** | **15b** 90% |
| Ir | bpp | **20a** | **16a** 90% |
| Ir | bbpp | **20b** | **16b** 85% |

**Reactions of $M_2(bbpp)_2$.** The metal dimers $M_2(bbpp)_2$ (M = Rh, Ir) underwent oxidative addition with MeI to yield M(bbpp)Me (M = Rh, 33%; M = Ir, 36%) and M(bbpp)I (M = Rh, 25%; M = Ir, 24%), respectively, as shown in eq 16.

$Rh_2(bbpp)_2$ **19b** and $Ir_2(bbpp)_2$ **20b** reacted with $H_2$ to produce Rh(bbpp)H **15b** and Ir(bbpp)H **16b** in 90% and 85% yield, respectively (eq 12).

In summary, nonbridged metal dimers of phenanthroline-based $N_2O_2$ ligands of rhodium and iridium have been synthesized from the reactions of metal hydrides with TEMPO. Modification of phenanthroline ligands has led to more lipophilic metal complexes. The oxidative additions of the metal dimers with methyl iodide, silane, and hydrogen have been successfully carried out.

## Experimental Section

All manipulations were performed under nitrogen by vacuum line techniques or in a Braun MB 150 M glovebox. $^1H$ NMR spectra were recorded on either a Bruker DPX-300 (300 MHz) or a Bruker AMX-500 (500 MHz) spectrometer. Chemical shifts ($\delta$) were reported with reference to the residual $CHCl_3$ ($\delta$ 7.24 ppm) in $CDCl_3$ or DMSO ($\delta$ 2.49 ppm) in DMSO-$d_6$. $^{13}C$ NMR spectra were recorded on a Bruker DPX-300 (75 MHz) spectrometer. $^{31}P$ NMR spectra were recorded on a Bruker AMX-500 ($H_3PO_4$ was used as internal standard) spectrometer. The coupling constants ($J$) are reported in hertz (Hz). Low-resolution mass spectra were recorded on a VG7070F mass spectrometer. High-resolution mass spectra were recorded on a Bruker APEX 47e FT-ICR mass spectrometer. IR spectra were obtained on a Perkin-Elmer 1600 FT-IR spectrophotometer. UV−vis spectra were recorded on a Hitachi U-3300 spectrophotometer. Yields were reported in either isolated yield or NMR yield using the residue solvent proton as the internal standard.

**2,9-Bis(5-*tert*-butyl-2-methoxyphenyl)-1,10-phenanthroline (5a).**[33] The anisole **3** (15.5 g, 0.064 mol) in anhydrous ether (20 mL) was transferred slowly to dried freshly cut lithium metal (0.98 g, 0.14 mol) in anhydrous ether (10 mL) via a cannula. The mixture was refluxed for 1 h under nitrogen, and the aryllithio reagent was then transferred dropwise to 1,10-phenanthroline (1.44 g, 8.0 mmol) in anhydrous toluene (15 mL) via a cannula under nitrogen to give a red solution. The mixture was allowed to stir for 48 h at 40 °C. the solution was then cooled to 5 °C, and water (30 mL) was added under nitrogen to hydrolyze the reaction mixture. The organic layer was collected, and the aqueous layer was extracted with $CH_2Cl_2$. $MnO_2$ (5.0 g, 57 mmol) was added to the organic solution, and the mixture was stirred for 8 h and then dried over $MgSO_4$. After filtration and removal of solvent, a brown oil was collected and purified by column chromatography ($R_f$ = 0.30, hexane/ethyl acetate = 3:1) to give a white solid (11.6 g, 80%) as the product. Mp: 115−118 °C ($CH_2Cl_2$/hexane). $^1H$ NMR ($CDCl_3$, 250 MHz): $\delta$ 1.37 (s, 18 H), 3.81 (s, 6 H), 6.95 (d, 2 H, $J$ = 8.8 Hz), 7.40 (dd, 2 H, $J$ = 2.4, 8.8 Hz), 7.78 (s, 2 H), 8.04 (d, 2 H, $J$ = 2.4 Hz), 8.06 (d, 2 H, $J$ = 8.5 Hz), 8.20 (d, 2 H, $J$ = 8.5 Hz). $^{13}C$ NMR ($CDCl_3$, 75 MHz): $\delta$ 31.68, 34.22, 55.94, 111.22, 125.96, 126.84, 127.42, 128.97, 129.74, 135.01, 143.60, 155.13, 157.23. MS (*m/e*, %, relative intensity): 504 ($M^+$, 69), 503 (100), 486 (61). HRMS calcd for $C_{34}H_{36}N_2O_2$: 504.2777. Found: 504.2777. IR (neat): 2959, 1586, 1494, 1265 $cm^{-1}$.

**Synthesis of 2,9-Bis (5-*tert*-butyl-2-hydroxyphenyl)-1,10-phenanthroline, $H_2$bpp (6a).** Pyridine (16 mL) was placed in a 100 mL two-necked round flask fitted with a thermometer and a funnel. With rapid stirring concentrated hydrochloric acid (17.6 mL) was added. The flask was equipped for distillation, and water was distilled from the mixture until its internal temperature rose to 210 °C. After cooling to 140 °C, 2,9-bis(5-*tert*-butyl-2-methoxyphenyl)-1,10-phenanthroline (**6b**) was added as a solid, and the reaction flask was fitted with a reflux condenser connected to a source of nitrogen. The yellow mixture was stirred and refluxed for 3 h (210 °C). To the cooled mixture was added water (70 mL), and the solution was extracted with $CHCl_3$, washed with saturated NaCl solution, and dried ($MgSO_4$). After removal of solvent, a yellow solid was collected as the product (4.3 g, 91% yield). $R_f$ = 0.6 (hexane/ethyl acetate, 1:1). Mp: 150−152 °C (hexane/ethyl

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acetate). $^1$H NMR ($CDCl_3$, 300 MHz, ppm): $\delta$ 1.40 (s, 18 H), 7.22 (s, 2 H), 7.44 (s, 2 H), 7.60 (s, 2 H), 7.85 (s, 2 H), 8.07 (d, 2 H, $J$ = 8.7 Hz), 8.15 (d, 2 H, $J$ = 8.7 Hz), 14.26 (s, 2 H). $^{13}$C NMR ($CDCl_3$, 75 MHz, ppm): $\delta$ 32.22, 34.82, 118.84, 119.30, 120.00, 123.74, 126.41, 127.68, 130.19, 138.04, 141.74, 142.02, 158.66, 158.71. UV−vis ($CHCl_3$, nm, log $\epsilon$): 364 (4.78). IR (neat film, cm$^{-1}$): 3412 ($\nu_{O-H}$), 1641, 1540, 1407, 1186, 971, 915, 882. MS (relative intensity, %): 476 ($M^+$, 92), 461 (98), 445 (26), 433 (13), 405 (14), 377 (5.5), 267 (2.2), 209 (5.6). Anal. Calcd for $C_{32}H_{32}N_2O_2$: C, 80.64; H, 6.77; N, 5.88. Found: C, 80.00; H, 6.92; N, 5.71.

**Synthesis of 5,6-Dibromo-1,10-phenanthroline (7).**[35] 1,10-Phen **4a** (0.9 g, 5 mmol) and fuming sulfuric acid (containing 30% $SO_3$, 7 mL) were loaded into a 15 mL tube. After the tube was cooled, bromine (0.3 mL, 1 mmol) was added with a syringe, then the tube was sealed under vacuum. After it was heated for 12 h at 120 °C in an oil bath, the tube was broken carefully. The brown solution was poured into ice water, neutralized with ammonia hydroxide to pH 3, and filtered, and the yellow solid was recrystallized from ethanol. 5,6-Dibromo-1,10-phenanthroline (**7**) was obtained in 65% yield. $R_f$ = 0.34 ($CH_2Cl_2$). Mp: 221−223 °C ($CH_2Cl_2$/MeOH) (lit.[35] 223 °C). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.70 (dd, 2 H, $J$ = 4.2 Hz), 8.74 (dd, 2 H, $J$ = 1.5 Hz), 9.18 (dd, 2 H, $J$ = 1.5 Hz). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 124.58, 125.26, 128.69, 137.49, 145.22, 150.96. MS (EI, % relative intensity): 339 ($M^+$ + 1, 11), 338 ($M^+$, 52), 336 ($M^+$ − 1, 26), 260 (99), 179 (60), 152 (26), 125 (14).

**Synthesis of 5,6-Dibutyl-1,10-phenanthroline, Pd-($PPh_3$)$_2$$Cl_2$, Catalyzed Reactions.** To THF (20 mL) saturated with anhydrous $ZnCl_2$ (11 mmol) at −78 °C was added dropwise n-BuLi (11 mmol) in hexane. The resulting mixture was then slowly warmed to room temperature in 2 h to form BuZnCl. To a suspension of 5,6-dibromo-Phen **7** and Pd($PPh_3$)$_2$-$Cl_2$ (10 mol %) in THF (20 mL) was added dropwise BuZnCl at room temperature. The solution was heated to reflux for 24 h under nitrogen. Water was then added, the layers were separated, and the aqueous phase was extracted with $Et_2O$. The combined organic layer was washed with $H_2O$, dried over $MgSO_4$, filtered, and evaporated to dryness. The residue was subjected to column chromatography using a hexane/ethyl acetate (1:1) to give **4b** in 28% yield. $R_f$ = 0.75 (hexane/ethyl acetate = 1:1). Mp: 218−220 °C (hexane/ethyl acetate). $^1$H NMR ($CDCl_3$, 300 MHz, ppm): $\delta$ 0.94 (t, 6 H, $J$ = 7.3 Hz), 1.46 (m, 4 H), 1.84 (m, 4 H), 3.15 (t, 4 H, $J$ = 8.0 Hz), 7.45 (dd, 2 H, $J$ = 4.2 Hz, 3.9 Hz), 8.04 (dd, 2 H, $J$ = 6.6 Hz, 1.6 Hz), 9.02 (dd, 2 H, $J$ = 2.8 Hz, 1.6 Hz). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 13.93, 22.77, 31.79, 39.04, 122.22, 125.29, 126.92, 136.08, 145.20, 163.05. MS (EI, % relative intensity): 295 ($M^+$, 52), 281 (9), 267 (18), 253 (26), 239 (99), 221 (16.2), 195 (42), 183 (71), 149 (35). HRMS *m/e* calcd for $C_{20}H_{24}N_2$: 292.1939. Found: 292.1852.

**Synthesis of 2,9-Bis(5-*tert*-butyl-2-hydroxyphenyl)-5,6-di-*n*-butyl-1,10-phenanthroline, $H_2$bbpp (6b).** Pyridine (8 mL) was placed in a 100 mL two-necked round flask fitted with a thermometer and a funnel. With rapid stirring concentrated hydrochloric acid (8.8 mL) was added. The flask was equipped for distillation, and water was distilled from the mixture until its internal temperature rose to 210 °C. After cooling to 140 °C, 2,9-bis(5-*tert*-butyl-2-methoxyphenyl)-5,6-di-*n*-butyl-1,10-phenanthroline (**5b**) (0.2 g, 0.32 mmol) was added as a solid, and the reaction flask was fitted with a reflux condenser connected to a source of nitrogen. The yellow mixture was stirred and refluxed for 3 h (210 °C). To the cooled mixture was added water (70 mL), and the solution was extracted with $CHCl_3$, washed with saturated NaCl solution, and dried ($MgSO_4$). After removal of solvent, a yellow solid was collected as the product **6b** (0.16 g, 85% yield). $R_f$ = 0.65 (hexane/EA, 1:1). Mp: 184−186 °C (hexane/ethyl acetate). UV−vis ($CHCl_3$, nm, log $\epsilon$) 364 (4.78). IR (neat film) 3408, 2918, 1649, 1568, 1420, 1266, 883 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 0.87 (t, 3 H, $J$ = 8.5 Hz), 1.33 (s, 18 H), 1.44 (m, 4 H), 1.79 (m, 4 H), 3.35 (t, 4 H, $J$ = 6.9 Hz), 7.40 (dd, 2 H, $J$ = 6.9 Hz, 2.2 Hz), 7.68 (s, 2 H), 7.80 (d, 2 H, $J$ = 2.2 Hz), 8.13 (d, 2 H, $J$ = 8.8 Hz), 8.27 (d, 2 H, $J$ = 8.7 Hz), 14.23 (s, 2 H). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 13.78, 21.90, 32.16, 34.33, 34.82, 35.35, 118.85, 119.41, 120.86, 124.13, 126.54, 127.81, 130.57, 138.61, 142.08, 158.34, 158.76. MS (FAB): 588 ($M^+$). HRMS *m/e* calcd for $C_{40}H_{48}N_2O_2$: 588.3710. Found: 588.3744.

**Synthesis of Rhodium 2,9-Bis(5-*tert*-butyl-2-hydroxyphenyl)-1,10-phenanthroline Chloride, Rh(bpp)Cl (8a).** The ligand $H_2$bpp **6a** (100 mg, 0.21 mmol) and $RhCl_3$·$3H_2O$ (66.3 mg, 0.25 mmol) were added into PhCN (10 mL) and heated to reflux for 6−8 h under nitrogen. The color of the solution changed from yellow to red, and an orange precipitate formed. PhCN was distilled in a vacuum. The residue was washed with $CH_2Cl_2$/hexane (1:1), and an orange solid was obtained after filtration. The orange solid was put in a Soxlet extractor and extracted with $CH_2Cl_2$/hexane (1:1) to wash away the remaining ligand. The resulting orange solid was dried over vacuum at 80 °C for 12 h (54 mg, 42% yield). $R_f$ = 0.20 ($CH_2Cl_2$/MeOH, 95:5); mp > 350 °C. $^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta$ 1.36 (s, 18 H), 6.54 (s, 2 H), 7.15 (d, 2 H, $J$ = 8.1 Hz), 7.36 (d, 2 H, $J$ = 4.8 Hz), 8.10 (s, 2 H), 8.40 (s, 2 H), 9.08 (s, 2 H). UV−vis ($CH_2Cl_2$): 461, 671, 693, 707, 721. MS (FAB, relative intensity, %): 612 ($M^+$, 55), 577 (99), 562 (49), 547 (19), 477 (27), 307 (11). HRMS *m/e* calcd for $RhC_{32}H_{30}N_2O_2Cl$: 612.1045. Found: 612.1063.

**Synthesis of Rhodium 2,9-Bis(5-*tert*-butyl-2-hydroxyphenyl)-5,6-di-*n*-butyl-1,10-phenanthroline Chloride, Rh-(bbpp)Cl (8b).** The ligand $H_2$bbpp **6b** (100 mg, 0.17 mmol) and $RhCl_3$·$3H_2O$ (54 mg, 20 mmol) were added into PhCN (10 mL) and heated to reflux for 6−8 h under nitrogen. The color of the solution changed from yellow to red, and an orange precipitate formed. PhCN was distilled off in a vacuum. The residue was washed with $CH_2Cl_2$/hexane (1:1), and an orange solid was obtained after filtration. The orange solid was put in a Soxlet extractor and extracted with $CH_2Cl_2$/hexane (1:1) to remove the unreacted ligand. The resulting orange solid was dried under vacuum at 80 °C for 12 h (44.3 mg, 36% yield). $R_f$ = 0.10 ($CHCl_3$). Mp > 350 °C. UV−vis (MeOH, nm): 274, 314, 475. $^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta$ 0.86 (s, 3 H), 1.13 (s, 18 H), 1.34 (s, 4 H), 1.71 (s, 4 H), 2.96 (s, 4 H), 6.60 (s, 2 H), 6.81 (s, 2 H), 7.32 (s, 2 H), 7.54 (s, 2 H), 8.27 (s, 2 H). UV−vis (MeOH, nm): 274, 314, 475. MS (FAB): 725 ($M^+$). HRMS *m/e* calcd for $RhC_{40}H_{46}N_2O_2Cl$: 724.2297. Found: 724.2321.

**Synthesis of Iridium 2,9-Bis(5-*tert*-butyl-2-hydroxyphenyl)-1,10-phenanthroline Carbonyl Chloride, Ir(bpp)-(CO)Cl (9a).** The ligand $H_2$bpp **6a** (100 mg, 0.21 mmol) and [Ir(COD)Cl]$_2$ (141 mg, 0.21 mmol) were added into xylene, and the solution was heated to reflux under nitrogen for 26 h. The color of the solution changed from yellow to red, and a red precipitate formed. After filtration, a red solid was obtained (58 mg, 38% yield). $R_f$ = 0.12 ($CH_2Cl_2$/MeOH, 95:5). $^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta$ 1.32 (s, 18 H), 7.12 (d, 2 H, $J$ = 8.7 Hz), 7.36 (d, 2 H, $J$ = 6.0 Hz), 8.10 (d, 2 H, $J$ = 7.5 Hz), 8.20 (s, 2 H), 8.78 (d, 2 H, $J$ = 9.0 Hz), 8.83 (d, 2 H, $J$ = 9.0 Hz). IR (KBr): $\nu_{Ir-CO}$ 2049 cm$^{-1}$. UV−vis ($CH_2Cl_2$): 693, 721. MS (FAB, relative intensity, %): 705 ($M^+$ − CO, 6), 667 ($M^+$ − CO − Cl, 99), 482 (12). HRMS *m/e* ($M^+$ − CO − Cl) calcd for $IrC_{32}H_{30}N_2O_2$: 665.2007. Found: 665.2047.

**Synthesis of Iridium 2,9-Bis(5-*tert*-butyl-2-hydroxyphenyl)-5,6-di-*n*-butyl-1,10-phenanthroline Carbonyl Chloride, Ir(bbpp)(CO)Cl (9b).** The ligand $H_2$bbpp **6b** (100 mg, 0.17 mmol) and [Ir(COD)Cl]$_2$ (126 mg, 0.17 mmol) were added into xylene, and the solution was heated to reflux under nitrogen for 24 h. The color of the solution changed from yellow to red, and a red precipitate formed. After filtration, a red solid was obtained as the product **9b** (48.6 mg, 34% yield). $R_f$ = 0.10 ($CHCl_3$). $^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta$ 0.91 (t, 6 H, $J$ = 7.3 Hz), 1.23 (s, 18 H), 1.38 (m, 4 H), 1.76 (t, 4 H, $J$ = 6.4 Hz),

3.10 (t, 4 H, $J$ = 8.0 Hz), 6.64 (d, 2 H, $J$ = 8.0 Hz), 6.77 (d, 2 H, $J$ = 8.4 Hz), 7.37 (s, 2 H), 7.67 (d, 2 H, $J$ = 8.1 Hz), 8.38 (d, 2 H, $J$ = 8.3 Hz). IR (KBr): $\nu_{Ir-CO}$ 2052 cm$^{-1}$. MS (FAB, % relative intensity): 840 ($M^+$, 6). HRMS *m/e* calcd for $IrC_{41}H_{46}N_2O_3Cl$: 840.2797. Found: 840.2753.

**Synthesis of Rhodium 2,9-Bis(5-*tert*-butyl-2-hydroxyphenyl)-1,10-phenanthroline Methyl, Rh(bpp)Me (10a).** To a suspension of Rh(bpp)Cl **8a** (25 mg, 0.0344 mmol) in EtOH (8 mL) was added $N_2$-purged $NaBH_4$ (3.8 mg, 0.1 mmol) in NaOH (1 M, 1 mL) through a syringe. The solution was stirred for 1 h at 50 °C under $N_2$ with the color changing from red to deep brown. The solution was then cooled to room temperature. $CH_3I$ (0.1 mL, 0.16 mmol) was added through a syringe. The solution was stirred for 1 h, and $H_2O$ (10 mL) was added. The solution was then extracted with $CH_2Cl_2$ (3 × 20 mL), dried over $MgSO_4$, and evaporated to dryness. The residue was purified by column chromatography using $CH_2Cl_2$ as the eluent to give the product (10.2 mg, 42%). $R_f$ = 0.45 (ethyl acetate). $^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta$ 0.51 (d, 3 H, $J_{Rh-H}$ = 2.5 Hz), 1.36 (s, 18 H), 7.15 (d, 2 H, $J$ = 8.8 Hz), 7.38 (dd, 2 H, $J$ = 2.4 Hz), 8.10 (d, 2 H, $J$ = 1.8 Hz), 8.14 (d, 2 H, $J$ = 2.1 Hz), 8.78 (d, 2 H, $J$ = 5.3 Hz), 8.83 (d, 2 H, $J$ = 4.9 Hz). $^{13}$C NMR (DMSO-$d_6$, 75 MHz): $\delta$ 1.54 (d, Rh−$CH_3$, $J_{Rh-C}$ = 40.8 Hz), 32.49, 34.85, 118.90, 122.72, 125.12, 125.80, 126.24, 127.49, 130.79, 136.64, 145.89, 153.57, 165.72. UV−vis ($CHCl_3$): 478 nm. MS (FAB, relative intensity, %): 593 ($M^+$ + 1, 96), 578 (59), 562 (33), 307 (22), 289 (11). HRMS *m/e* calcd for $RhC_{33}H_{33}N_2O_2$: 592.1591. Found: 592.1528.

**Synthesis of Rhodium 2,9-Bis(5-*tert*-butyl-2-hydroxyphenyl)-5,6-di-*n*-butyl-1,10-phenanthroline Methyl, Rh(bbpp)Me (10b).** To a suspension of Rh(bbpp)Cl **8b** (25 mg, 0.0345 mmol) in EtOH (8 mL) was added $N_2$-purged $NaBH_4$ (3.8 mg, 0.1 mmol) in NaOH (1 M, 1 mL) through a syringe. The color of the solution changed from orange to deep brown. After heating to 50 °C for 1 h, the solution was cooled to room temperature. $CH_3I$ (0.1 mL, 0.16 mmol) was added through a syringe. The solution was stirred for 1 h, and $H_2O$ (10 mL) was added. The solution was then extracted with $CH_2Cl_2$ (3 × 20 mL), dried over $MgSO_4$, and evaporated to dryness. The residue was purified by column chromatography using $CH_2Cl_2$ as the eluent to give the product **10b** (13.6 mg, 56% yield). $R_f$ = 0.34 ($CH_2Cl_2$). UV−vis (MeOH, nm): 410, 474. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 0.51 (d, 3 H, $J$ = 2.1 Hz), 0.95 (t, 6 H, $J$ = 7.3 Hz), 1.44 (m, 4 H), 1.74 (m, 4 h), 3.09 (t, 4 H, $J$ = 7.4 Hz), 7.63 (d, 2 H, $J$ = 6.8 Hz), 7.95 (s, 2 H), 8.22 (d, 2 H, $J$ = 8.3 Hz), 8.47 (d, 2 H, $J$ = 8.3 Hz). UV−vis (MeOH, nm): 410, 474. MS (FAB): 704 ($M^+$). HRMS *m/e* calcd for $RhC_{41}H_{49}N_2O_2$: 704.2843. Found: 704.2885.

**Synthesis of Iridium 2,9-Bis(5-*tert*-butyl-2-hydroxyphenyl)-5,6-di-*n*-butyl-1,10-phenanthroline Methyl, Ir(bbpp)Me (12b).** Ir(bbpp)(CO)Cl **9b** (32 mg, 0.038 mmol) was suspended in EtOH (8 mL). $N_2$ was purged for 10 min. The solution was then heated to 50 °C. $N_2$-purged $NaBH_4$ (3.8 mg, 0.1 mmol) in NaOH (1 M, 1 mL) was added through a syringe. The solution was stirred for 1 h under $N_2$ with the color changing from red to deep brown. The solution was then cooled to room temperature. $CH_3I$ (0.1 mL, 0.16 mmol) was added through a syringe. After the solution was stirred for 1 h, water (10 mL) was added and the reaction mixture was extracted with $CH_2Cl_2$ (3 × 20 mL), dried ($MgSO_4$), and evaporated to dryness. The residue was separated by column chromatography using $CH_2Cl_2$ as the eluent to give the product **80** (14.8 mg, 49% yield). $R_f$ = 0.28 ($CH_2Cl_2$). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 0.35 (s, 3 H), 0.83 (t, 6 H, $J$ = 7.3 Hz), 1.25 (s, 18 H), 1.34 (m, 4 H), 1.71 (m, 4 H), 3.09 (t, 4 H, $J$ = 8.2 Hz), 6.76 (d, 2 H, $J$ = 7.9 Hz), 6.88 (d, 2 H, $J$ = 8.4 Hz), 7.48 (s, 4 H), 7.76 (d, 4 H, $J$ = 7.8 Hz), 8.49 (d, 4 H, $J$ = 7.8 Hz). MS (FAB, % relative intensity): 794 ($M^+$, 22). HRMS *m/e* calcd for $IrC_{41}H_{49}N_2O_2$: 792.3394. Found: 792.3356.

**Reaction of Rhodium 2,9-Bis(5-*tert*-butyl-2-hydroxyphenyl)-1,10-phenanthroline Methyl with $PPh_3$ to give Rh(bpp)(Me)($PPh_3$) (14).** $PPh_3$ (2 mg, 7.6 $\mu$mol) was added into Rh(bpp)Me **10a** (4.5 mg, 7.6 $\mu$mol) in DMSO-$d_6$ (0.4 mL), and Rh(bpp)(Me)($PPh_3$) **14** was produced. In the $^1$H NMR spectrum, the doublet of Rh−Me changed into a double doublet at 1.26 ppm with the coupling constants 7.98, 10.36, and 12.24 Hz, respectively. $^{31}$P NMR (200 MHz, $H_3PO_4$ as the external standard): $\delta$ 47.39 (d, $J_{Rh-P}$ = 138 Hz). UV−vis ($CH_2Cl_2$): 472 nm. MS (FAB, relative intensity, %): 855 ($M^+$ + 1, 4), 854 ($M^+$, 4), 839 ($M^+$ − Me, 98), 593 ($M^+$ − $PPh_3$, 17), 577 ($M^+$ − $PPh_3$ − Me, 16), 562 (36), 522 (9), 456 (2), 414 (7).

**Synthesis of Rhodium 2,9-Bis(5-*tert*-butyl-2-hydroxyphenyl)-1,10-phenanthroline Isopropyl, Rh(bpp)($^i$Pr) (11a).** Rh(bpp)Cl **8a** (25 mg, 0.040 mmol) was suspended in EtOH (8 mL). $N_2$ was purged for 10 min. The solution was then heated to 50 °C, and $N_2$-purged $NaBH_4$ (3.8 mg, 0.1 mmol) in NaOH (1 M, 1 mL) was added through a syringe. The solution was stirred for 1 h at 50 °C under $N_2$ with the color changing from red to deep brown. Then the solution was cooled to room temperature. 2-Bromopropane (0.1 mL, 0.16 mmol) was added through a syringe. The solution was stirred for 1 h. Water (10 mL) was added, the reaction mixture was extracted with $CH_2Cl_2$ (3 × 20 mL) and dried ($MgSO_4$), and the solvent was evaporated off. The residue was purified by column chromatography using $CH_2Cl_2$ as the eluent to give the product (10.2 mg, 42%). $R_f$ = 0.75 (ethyl acetate). $^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta$ −0.55 (1 H, m), −0.07 (d, 6 H, $J$ = 6.6 Hz), 1.36 (s, 18 H), 7.12 (d, 2 H, $J$ = 6.2 Hz), 7.36 (d, 2 H, $J$ = 6.9 Hz), 8.18 (m, 2 H), 8.24 (m, 2 H), 8.79 (s, 4 H). MS (FAB, relative intensity, %): 621 ($M^+$, 11), 578 ($M^+$ − $C_3H_7$, 99). HRMS calcd for $RhC_{35}H_{37}N_2O_2$: 620.1904. Found: 620.1888.

**Synthesis of Iridium 2,9-Bis(5-*tert*-butyl-2-hydroxyphenyl)-1,10-phenanthroline Methyl, Ir(bpp)Me (12a).** Ir(bpp)(CO)Cl **9a** (32 mg, 0.044 mmol) was suspended in EtOH (8 mL). $N_2$ was purged for 10 min. The solution was then heated to 50 °C. $N_2$-purged $NaBH_4$ (3.8 mg, 0.1 mmol) in NaOH (1 M, 1 mL) was added through a syringe. The solution was stirred for 1 h at 50 °C under $N_2$ with the color changing from red to deep brown. The solution was then cooled to room temperature. $CH_3I$ (0.1 mL, 0.16 mmol) was added through a syringe. The solution was stirred for 1 h, water (10 mL) was added, the reaction mixture was extracted with $CH_2Cl_2$ (3 × 20 mL) and dried ($MgSO_4$), and the solvent was evaporated off. The residue was purified by column chromatography using $CH_2Cl_2$ as the eluent to give the product (10.0 mg, 34% yield). $R_f$ = 0.62 (ethyl acetate). $^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta$ 0.04 (s, 3 H), 1.27 (s, 18 H), 7.15 (d, 2 H, $J$ = 8.7 Hz), 7.41 (d, 2 H, $J$ = 8.7 Hz), 7.69 (d, 2 H, $J$ = 3.0 Hz), 8.24 (2 H, s), 8.84 (s, 2 H), 8.89 (s, 2 H). MS (FAB, relative intensity, %): 682 ($M^+$, 99), 667 (85), 477 (17), 391 (10), 307 (29), 289 (18). HRMS *m/e* calcd for $IrC_{33}H_{33}N_2O_2$: 680.2142. Found: 680.2165.

**Synthesis of Iridium 2,9-Bis(5-*tert*-butyl-2-hydroxyphenyl)-1,10-phenanthroline Isopropyl, Ir(bpp)($^i$Pr) (13a).** Ir(bpp)(CO)Cl **9a** (36 mg, 0.050 mmol) was suspended in EtOH (8 mL). $N_2$ was purged for 10 min. The solution was then heated to 50 °C. $N_2$-purged $NaBH_4$ (3.8 mg, 0.1 mmol) in NaOH (1 M, 1 mL) was added through a syringe. The solution was stirred for 1 h at 50 °C under $N_2$ with the color changing from red to deep brown. The solution was then cooled to room temperature. 2-Bromopropane (0.1 mL, 0.16 mmol) was added through a syringe. The solution was stirred for 1 h, water (10 mL) was added, the reaction mixture was extracted with $CH_2Cl_2$ (3 × 20 mL) and dried ($MgSO_4$), and the solvent was evaporated off. The residue was separated by column chromatography using $CH_2Cl_2$ as the eluent to give the product (12.2 mg, 35%). $R_f$ = 0.72 (ethyl acetate). $^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta$ −0.85 (m, 1 H), −0.67 (d, 6 H, $J$ = 6.0 Hz), 1.32 (s, 18), 7.51 (d, 2 H, $J$ = 3.3 Hz), 7.99 (m, 2 H), 8.08 (m, 2 H), 8.36 (m, 2 H), 8.54 (m, 4 H). MS (FAB, relative intensity, %): 653 ($M^+$ − 1, 20), 615 ($M^+$ − $C_3H_7$, 4), 461 ($M^+$ − $C_3H_7$ − Ir, 9), 281 (42), 207 (39). HRMS $M^+$ − $C_3H_7$ *m/e* calcd for $IrC_{32}H_{30}N_2O_2$: 665.1907. Found: 665.1953.

**Synthesis of Rhodium 2,9-Bis(5-*tert*-butyl-2-hydroxyphenyl)-1,10-phenanthroline Hydride, Rh(bpp)H (15a).** Rh(bpp)Cl **8a** (20 mg, 0.033 mmol) was suspended in EtOH (8 mL). $N_2$ was purged for 10 min. $NaBH_4$ (8 mg, 0.10 mmol) was dissolved in NaOH (1 M, 1 mL), and $N_2$ was purged for 10 min. Then the $NaBH_4$ solution was added into the above suspension slowly with a cannula. The solution was stirred for 1 h at 50 °C under $N_2$ with the color changing from red to deep brown. The solution was then cooled to room temperature, and degassed HCl (1 M, 5 mL) was added with a cannula. A black precipitate was produced immediately. After filtration under $N_2$, the residue was washed with degassed $H_2O$ and MeOH, then dried under vacuum for 4 h, forming a yellow solid (14.4 mg, 78% yield). $^1$H NMR (DMSO-$d_6$, $CF_3SO_3H$ added, 300 MHz): $\delta$ −22.85 (d, 1 H, $J$ = 37.3 Hz), 1.49 (s, 18 H), 6.01 (d, 2 H, $J$ = 5.1 Hz), 7.75 (d, 2 H, $J$ = 7.8 Hz), 7.87 (d, 2 H, $J$ = 8.4 Hz), 8.50 (s, 2 H), 8.62 (s, 2 H), 9.22 (s, 2 H). IR (KBr): $\nu_{Rh-H}$ 2225 cm$^{-1}$. MS (FAB, % relative intensity): 579 ($M^+$, 59), 578 ($M^+ - 1$, 94), 562 (74), 547 (42), 522 (26), 506 (22).

**Synthesis of Rhodium 2,9-Bis(5-*tert*-butyl-2-hydroxyphenyl)-5,6-di-*n*-butyl-1,10-phenanthroline Hydride, Rh(bbpp)H (15b).** Rh(bbpp)Cl **8b** (20 mg, 0.028 mmol) was suspended in EtOH (8 mL). $N_2$ was purged for 10 min. $NaBH_4$ (8 mg, 0.10 mmol) was dissolved in NaOH (1 M, 1 mL), and $N_2$ was purged for 10 min. Then the $NaBH_4$ solution was added into the above suspension slowly with a cannula. The solution was stirred for 1 h under $N_2$ with the color changing from red to deep brown. The solution was then cooled to room temperature.Then degassed HCl (1 M, 5 mL) was added with a cannula, and a black precipitate was produced immediately. After filtration under $N_2$, the residue was washed with degassed $H_2O$ and MeOH, then dried under vacuum for 4 h, and a yellow solid was obtained as the product **15b** (13.5 mg, 70% yield). $^1$H NMR (DMSO-$d_6$, $CF_3SO_3H$ added, 300 MHz): $\delta$ −20.27 (d, 1 H, $J_{Rh-H}$ = 44.4 Hz), 0.91 (t, 6 H, $J$ = 6.7 Hz), 1.17 (s, 18 H), 1.42 (m, 4 H), 1.66 (m, 4 H), 2.83 (t, 4 H, $J$ = 8.1 Hz), 6.41 (d, 2 H, $J$ = 10.2 Hz), 6.77 (dd, 2 H, $J$ = 3.6 Hz), 6.94 (d, 2 H, $J$ = 8.2 Hz), 7.92 (d, 2 H, $J$ = 8.1 Hz). IR (KBr): $\nu_{Rh-H}$ 2226 cm$^{-1}$. UV−vis (MeOH, nm): 475.

**Synthesis of Iridium 2,9-Bis(5-*tert*-butyl-2-hydroxyphenyl)-1,10-phenanthroline Hydride, Ir(bpp)H (16a).** Ir(bpp)(CO)Cl **9a** (22 mg, 0.030 mmol) was suspended in EtOH (8 mL). $N_2$ was purged for 10 min. $NaBH_4$ (8 mg, 0.10 mmol) was dissolved in NaOH (1 M, 1 mL), and $N_2$ was purged for 10 min. The $NaBH_4$ solution was added into the above suspension slowly with a cannula. The solution was stirred for 1 h at 50 °C under $N_2$ with the color changing from red to deep brown. The solution was then cooled to room temperature. Then degassed HCl (1 M, 5 mL) was added with a cannula, and a black precipitate was produced immediately. After filtration under $N_2$, the brown solid was washed with degassed $H_2O$ (3 mL) and MeOH (1 mL), then dried over vacuum for 4 h to obtain the product (10.4 mg, 52% yield). $^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta$ −22.40 (s, 1 H), 1.32 (s, 18 H), 7.16 (d, 2 H, $J$ = 8.7 Hz), 7.37 (d, 2 H, $J$ = 8.4 Hz), 8.13 (s, 2 H), 8.20 (s, 2 H), 8.80 (s, 4 H). IR (KBr): $\nu_{Ir-H}$ 2046 cm$^{-1}$. MS (FAB, relative intensity, %): 668 ($M^+$, 52), 667 ($M^+ - 1$, 96), 477 ($M^+ -$ Ir, 25).

**Synthesis of Iridium 2,9-Bis(5-*tert*-butyl-2-hydroxyphenyl)-5,6-di-*n*-butyl-1,10-phenanthroline Hydride, Ir(bbpp)H (16b).** Ir(bbpp)(CO)Cl **9b** (22 mg, 0.026 mmol) was suspended in EtOH (8 mL). $N_2$ was purged for 10 min. $NaBH_4$ (8 mg, 0.10 mmol) was dissolved in NaOH (1 M, 1 mL), and $N_2$ was purged for 10 min. Then $NaBH_4$ solution was added into the above suspension slowly with a cannula. The solution was stirred for 1 h under $N_2$ with the color changing from red to deep brown. The solution was then cooled to room temperature. Then degassed HCl (1 M, 5 mL) was added with a cannula, and a black precipitate was produced immediately. After filtration under $N_2$, the brown solid was washed with degassed $H_2O$ (3 mL) and MeOH (1 mL), then dried over vacuum for 4 h to obtain the product **16b** (12.6 mg, 62% yield). $^1$H NMR (DMSO-$d_6$): $\delta$ −20.23 (s, 1 H), 0.92 (t, 6 H, $J$ = 7.3 Hz), 1.24 (s, 18 H), 1.40 (m, 4 H), 1.77 (m, 4 H), 3.02 (t, 4 H, $J$ = 7.7 Hz), 6.67 (d, 4 H, $J$ = 8.5 Hz), 6.88 (d, 4 H, $J$ = 8.4 Hz), 7.39 (d, 4 H, $J$ = 2.3 Hz), 7.62 (d, 4 H, $J$ = 8.3 Hz), 8.35 (d, 4 H, $J$ = 8.2 Hz). IR (KBr): $\nu_{Ir-H}$ 2046 cm$^{-1}$. UV−vis (MeOH, nm): 477.

**Reaction of Iridium 2,9-Bis(5-*tert*-butyl-2-hydroxyphenyl)-1,10-phenanthroline Hydride with $PPh_3$.** $PPh_3$ (2 mg, 7.6 $\mu$mol) was added into a Ir(bpp)H **16a** (5 mg, 7.6 $\mu$mol) solution in DMSO-$d_6$ (0.4 mL) under nitrogen, and (bpp)Ir(H)($PPh_3$) **17a** was obtained. $^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta$ −22.45 (d, 1 H, $J_{H-P}$ = 15.8 Hz). MS (FAB, relative intensity, %): 930 ($M^+$, 15), 929 ($M^+ - 1$, 23), 667 ($M^+ - PPh_3$, 13), 576 ($M^+ -$ Ir $- PPh_3$, 15), 518 (17), 475 (14), 383 (15).

**Synthesis of Rhodium 2,9-Bis(5-*tert*-butyl-2-hydroxyphenyl)-1,10-phenanthroline Dimer, $Rh_2$(bpp)$_2$ (19a).** To Rh(bpp)H **15a** (5 mg, 8 mmol) in degassed THF (20 mL) in a 25 mL Schlenk flask was added TEMPO (6 mg, 40 mmol). The orange color of the solution changed to pale brown immediately. After 2 h, THF, excess TEMPO, and TEMPOH were removed under high vacuum. The residue was dried for another 12 h to yield the rhodium dimer **19a** (4.5 mg, 95% yield). $^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta$ 1.03 (s, 18 H), 1.25 (s, 18 H), 6.30 (s, 4 H), 6.54 (s, 4 H), 6.80 (d, 4 H, $J$ = 6.6 Hz), 6.90 (d, 4 H, $J$ = 6.3 Hz), 7.09 (d, 4 H, $J$ = 7.2 Hz), 7.46 (d, 4 H, $J$ = 8.4 Hz). UV−vis (MeOH): 379, 392.

**Synthesis of Rhodium 2,9-Bis(5-*tert*-butyl-2-hydroxyphenyl)-5,6-di-*n*-butyl-1,10-phenanthroline Dimer, $Rh_2$(bbpp)$_2$ (19b).** To Rh(bbpp)H **15b** (5 mg, 7 mmol) in degassed THF (10 mL) in a 25 mL Schlenk flask was added TEMPO (6 mg, 40 mmol). The orange color of the solution changed to pale brown immediately. After 2 h, THF, excess TEMPO, and TEMPOH were removed under high vacuum. The residue was dried for a further 12 h to yield the product **19b** (4.2 mg, 95% yield). $^1$H NMR ($CD_3OD$-$d_4$, 300 MHz): $\delta$ 1.02 (t, 12 H, $J$ = 6.8 Hz), 1.31 (s, 18 H), 1.49 (m, 8 H), 1.87 (s, 8 H), 3.23 (t, 8 H, $J$ = 7.9 Hz), 6.81 (d, 4 H, $J$ = 2.8 Hz), 7.07 (d, 4 H, $J$ = 8.5 Hz), 7.49 (d, 4 H, $J$ = 8.6 Hz), 7.66 (s, 4 H), 8.12 (d, 4 H, $J$ = 8.2 Hz). UV−vis (MeOH, nm): 466.

**Synthesis of Iridium 2,9-Bis(5-*tert*-butyl-2-hydroxyphenyl)-1,10-phenanthroline Dimer, $Ir_2$(bpp)$_2$ (20a).** Ir(bpp)H **16a** (5 mg, 8 mmol) and TEMPO (6 mg, 40 mmol) were dissolved in degassed THF (20 mL) in a 25 mL Schlenk flask. The orange color of the solution changed to pale brown upon addition of TEMPO. After 4 h, THF, excess TEMPO, and TEMPOH were removed under high vacuum. The residue was dried for another 12 h to yield the product **20a** (4.2 mg, 92% yield). $^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta$ 1.39 (s, 36 H), 7.16 (d, 4 H, $J$ = 8.4 Hz), 7.42 (d, 4 H, $J$ = 8.0 Hz), 8.24 (s, 8 H), 8.83 (s, 4 H), 8.90 (d, 4 H, $J$ = 7.4 Hz). MS (L-SIMS): 1334 ($M^+$).

**Synthesis of Iridium 2,9-Bis(5-*tert*-butyl-2-hydroxyphenyl)-5,6-di-*n*-butyl-1,10-phenanthroline Dimer, $Ir_2$(bbpp)$_2$ (20b).** Ir(bbpp)H **16b** (5 mg, 6 mmol) and TEMPO (5 mg, 33 mmol) were dissolved in degassed THF (10 mL) in a 25 mL Schlenk flask. The orange color of the solution changed to pale brown when TEMPO was added. After 4 h, THF, excess TEMPO, and TEMPOH were removed under high vacuum. The residue was dried for a further 12 h to yield a brown solid as the product **20b** (4.0 mg, 90% yield). $^1$H NMR ($CD_3OD$-$d_4$, 300 MHz): $\delta$ 0.81 (t, 12 H, $J$ = 7.2 Hz), 1.24 (s, 36 H), 1.31 (m, 8 H), 1.67 (t, 8 H, $J$ = 7.6 Hz), 3.03 (t, 8 H, $J$ = 7.7 Hz), 6.75 (d, 4 H, $J$ = 6.5 Hz), 7.13 (d, 4 H, $J$ = 8.6 Hz), 7.53 (d, 4 H, $J$ = 8.3 Hz), 7.71 (s, 4 H), 8.21 (d, 4 H, $J$ = 8.3 Hz). UV−vis (MeOH, nm): 475.

**Reaction of $Rh_2$(bpp)$_2$ with $Et_3SiH$ and $CH_3I$.** In a glovebox, $Rh_2$(bpp)$_2$ **19a** (4 mg, 3.2 mmol) and $Et_3SiH$ or $CH_3I$ (0.11 mL, ∼2.2 mmol) and DMSO-$d_6$ (0.5 mL) were loaded into a 5 mm diameter NMR tube fitted with a vacuum-line-adapted

Teflon valve. The tube was closed, removed from the glovebox, degassed by the freeze−pump−thaw method (3 cycles), and vacuum sealed. The reaction was monitored by $^1$H NMR. After about 2 h, the reaction was completed. Rh(bpp)Me **10a**: 32% yield. Rh(bpp)I **21a**: 28% yield. $R_f$ = 0.10 ($CHCl_3$). $^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta$ 1.19 (s, 18 H), 7.54 (dd, 2 H, $J$ = 3.0, 5.1 Hz), 7.94 (dd, 2 H, $J$ = 3.0, 5.7 Hz), 8.12 (s, 2 H), 8.36 (s, 2 H), 8.59 (dd, 2 H, $J$ = 3.0, 8.8 Hz), 8.77 (d, 2 H, $J$ = 8.1 Hz). MS (FAB, relative intensity, %): 705 ($M^+$ + 1, 1), 577 ($M^+$ − I, 93). Rh(bpp)H **16a**: 36% yield. Rh(bpp)($SiEt_3$) **23a**: 42% yield, $R_f$ = 0.50 ($CH_2Cl_2$). $^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta$ 0.82 (m, 6 H), 1.07 (m, 9 H), 1.37 (s, 18 H), 7.17 (dd, 2 H, $J$ = 3.3, 8.4 Hz), 7.34 (d, 2 H, $J$ = 8.1 Hz), 8.12 (s, 2 H), 8.29 (s, 2 H), 8.80 (dd, 4 H, $J$ = 2.1, 5.4 Hz). MS (FAB, % relative intensity): 577 ($M^+$ − $SiEt_3$, 20).

**Reaction of Rhodium and Iridium 2,9-Bis(5-*tert*-butyl-2-hydroxyphenyl)-1,10-phenanthroline Dimer with $H_2$.** $H_2$ was bubbled into solutions of $Rh_2$(bpp)$_2$ **19a** (5 mg, 4 $\mu$mol) and $Ir_2$(bpp)$_2$ **20a** (5 mg, 4 $\mu$mol) in DMSO-$d_6$ (0.4 mL) under nitrogen, and the reaction was monitored by $^1$H NMR. After 2 h, Rh(bpp)H **15a** and Ir(bpp)H **16a** were obtained both in 90% yields from $^1$H NMR integration.

**Reaction of $M_2$(bbpp)$_2$ (M = Rh, Ir) with $CH_3I$.** In a glovebox, $M_2$(bbpp)$_2$ (M = Rh, 4 mg, 3.0 mmol; M = Ir, 5 mg, 3.0 mmol), $CH_3I$ (0.11 mL), and MeOH-$d_4$ (0.5 mL) were loaded into a 5 mm diameter NMR tube fitted with a vacuum-line-adapted Teflon valve. The tube was closed, removed from the glovebox, degassed by the freeze−pump−thaw method (3 cycles), and flame-sealed under vacuum. The reaction was monitored by $^1$H NMR. After 2 h, the reaction was completed. Rh(bbpp)Me **12b**: 33% yield. Rh(bupp)I **21b**: 25% yield. $R_f$ = 0.10 ($CH_2Cl_2$). $^1$H NMR ($CD_3OD$-$d_4$, 300 MHz): $\delta$ 1.82 (m, 6 H), 2.27 (m, 4 H), 2.62 (m, 4 H), 3.77 (t, 4 H, $J$ = 7.5 Hz), 6.47 (d, 2 H, $J$ = 3.6 Hz), 7.30 (dd, 2 H, $J$ = 4.5 Hz), 7.85 (d, 2 H, $J$ = 3.6 Hz), 8.13 (s, 2 H), 8.73 (s, 2 H). FABMS: 705 ($M^+$). Ir(bbpp)Me **12b**: 36% yield. Ir(bbpp)I **22b**: 24% yield. $R_f$ = 0.10 ($CH_2Cl_2$). $^1$H NMR ($CD_3OD$-$d_4$, 300 MHz): $\delta$ 0.85 (m, 6 H), 1.32 (m, 4 H), 1.71 (m, 4 H), 3.81 (t, 4 H, $J$ = 8.1 Hz), 6.90 (dd, 2 H, $J$ = 2.4, 6.0 Hz), 7.15 (dd, 2 H, $J$ = 1.5, 7.2 Hz), 7.38 (d, 2 H, $J$ = 2.7 Hz), 7.70 (d, 2 H, $J$ = 2.7 Hz), 8.20 (s, 2 H). FABMS: 905 ($M^+$). The yields were obtained from $^1$H NMR integration.

**Reaction of Rhodium and Iridium 2,9-Bis(5-*tert*-butyl-2-hydroxyphenyl)-5,6-dibutyl-1,10-phenanthroline Dimer with $H_2$.** $H_2$ was bubbled into solutions of $Rh_2$(bbpp)$_2$ **19b** (4 mg, 3.0 $\mu$mol) and $Ir_2$(bbpp)$_2$ **20b** (5 mg, 3.0 $\mu$mol) in MeOH-$d_4$ (0.4 mL) under nitrogen, and the reaction was monitored by $^1$H NMR. After 2 h, Rh(bbpp)H **15b** and Ir(bbpp)H **16b** were obtained in 90% and 85% yield, respectively, from $^1$H NMR integration.

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