

Orange-Red Phosphorescent Iridium(III) Complexes Bearing **Bisphosphine Ligands: Synthesis, Photophysical and Electrochemical** Properties, and DFT Calculations

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Supporting Information

ABSTRACT: Nine new phosphorus-coordinated iridium(III) complexes of the form $[Ir(C^N)_2(P^P)]PF_6$, $[Ir(F-piq)_2(xantphos)]PF_6$ (1), $[Ir(F-piq)_2(binap)]PF_6$ (2), [Ir(F-piq)₂(dppp)]PF₆ (3), [Ir(Me-piq)₂(xantphos)]PF₆ (4), [Ir(Me-piq)₂(binap)]PF₆ (5), $[Ir(Me-piq)_2(dppp)]PF_6$ (6), $[Ir(CF_3O-piq)_2(xantphos)]PF_6$ (7), $[Ir(CF_3O-piq)_2(xantphos)_$ $piq)_2(binap)]PF_6(8)$, and $[Ir(CF_3O-piq)_2(dppp)]PF_6(9)$ (F-piq = 1-(4-fluorophenyl)isoquinoline, Me-piq = 1-(p-tolyl)isoquinoline, CF₃O-piq = 1-(4-(trifluoromethoxy)phenyl)isoquinoline, xantphos = 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene, binap = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, dppp = 1,3-bis-(diphenylphosphanyl)propane), have been synthesized and fully characterized. The crystal structures of 1, 7, and 9 have been determined by X-ray analysis. The most



representative molecular orbital energy-level diagrams and the lowest energy electronic transitions of 1-9 have been calculated with density functional theory (DFT) and time-dependent DFT (TD-DFT). All of the complexes are orange-red emissive with quantum efficiencies of 3.2-24.4% and lifetimes of $1.77-3.19\ \mu s$ in degassed CH_2Cl_2 solution at room temperature. These research results reveal that the Me-piq C^N ligand and xantphos P^P ligand are beneficial for a red shift of absorption and emission wavelength. Complex 4 has better charge transfer ability, which probably promises its use as a red-phosphorescent material.

INTRODUCTION

During the last few decades, a considerable amount of interest has been drawn to the application of iridium(III) complexes in white organic light-emitting diodes (WOLEDs) and full-color displays.¹⁻⁵ For the realization of white emission, it is essential to obtain high efficiency and color purity for the three primary blue-, green-, and red-emitting materials.^{6,7} Indeed, true red emitters are more difficult because their luminescent quantum yields tend to be lower due to the smaller energy gap.^{8,9} Therefore, our goal is to design novel red-emissive Ir(III) complexes with larger quantum yields, for the realization of highly efficient WOLEDs.

Studies on photoluminescent iridium complexes bearing diphosphine ligands have been carried out in recent years due to their chemical stability, excellent color tunability, and high quantum efficiencies. In 2013, a series of Ir(III) complexes with bent-diphosphine ligands were first reported by Hor et al. These complexes covered a broad emission range from 472 nm (blue) to 569 nm (orange) with quantum efficiencies up to 0.38 at room temperature.¹⁰ More recently, Zysman-Colman and co-workers prepared 13 cationic iridium(III) complexes of the form $[Ir(C^N)_2(P^P)]PF_6$. All of the complexes were sky blue emissive, but their photoluminescence quantum yields (Φ_{PL}) were generally low.¹¹ However, to date, there have been no

more reports of red phosphors with the motif [Ir- $(C^N)_2(P^P)]PF_6.$

In order to push the emission of $[Ir(C^N)_2(P^P)]PF_6$ complexes further into the red region, one key requirement is to choose a suitable C^N cyclometalating ligand. Iridium(III) complexes with 1-phenylisoquinoline (piq) are well-known as red-emitting materials. The first important example was the $[Ir(piq)_3]$ complex, which emitted red phosphorescence with a wavelength maximum at 620 nm and showed good red color purity with CIE characteristics (0.68, 0.32).¹² Afterward, numerous substituted bis(1-phenylisoquinolinato) cyclometalating iridium complexes were reported, such as [Ir- $(piq)_2(acac)$] $(\lambda_{em} 622 \text{ nm})$,¹³ [Ir $(piq-F)_2(acac)$] $(\lambda_{em} 600$ mm),¹³ [Ir(5-f-1piq)₂(acac)] (λ_{em} 632 nm),¹⁴ [Ir(5-f-1fpi-q)₂(acac)] (λ_{em} 609 nm),¹⁴ and *mer*-[Ir(1-piq)₂(ppy)] (λ_{em} 620 nm).¹⁵

Herein, we incorporated three piq-based C^N ligands (F-piq, Me-piq, and CF₃O-piq) and three steric blocking diphosphine P[^]P ligands (xantphos, binap, and dppp) to yield an array of nine cationic Ir(III) species (Figure 1). Their electrochemical and optical properties have been measured and analyzed. Again,

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Figure 1. Chemical structures of complexes 1–9.

the absorption spectra are rationalized on the basis of density functional theory (DFT) and time-dependent DFT (TD-DFT). The luminescent properties have been investigated both in the solid state and in solution (at room temperature and 77 K).

RESULTS AND DISCUSSION

Synthesis and Characterization. The syntheses of the piq-based cyclometalating ligands 3a-c and their derived complexes 1-9 are shown in Scheme 1. These compouds 3a-cwere prepared by the Suzuki coupling reaction between 1chloroisoquinoline and the corresponding substituted boronic acid (2a-c) under palladium catalysis in good yields (91.8-94.6%). Cyclometalated Ir(III) dichloro-bridged dimers, [Ir- $(C^N)_2(\mu$ -Cl)]_2, were synthesized by iridium trichloride hydrate with 2.2 equiv of 3a-c in a 2:1 mixture of 2ethoxyethanol and deionized water according to a similar method reported by Nonoyama.¹⁶ Then the new phosphoruscoordinated iridium(III) complexes 1-9 were obtained by the reaction of $[Ir(C^N)_2(\mu-Cl)]_2$ with bisphosphine ligands $(P_1 P_3$) in CH₂Cl₂/MeOH (1/1) followed by addition of excess NH₄PF₆. All of these new compounds were characterized by ¹H, ¹³C, and ³¹P NMR spectroscopy and ESI-MS spectrometry. In ¹H NMR spectra, the ratio of the C[^]N to P[^]P ligands is 2:1,

в

which suggests that the chemical formula of each Ir(III) complex is $[Ir(C^N)_2(P^P)]PF_6$. The ³¹P NMR spectra for complexes **1–9** show singlet resonances from –30.70 to –10.63 ppm, indicating the two phosphorus atoms in the P^P ligand, whereas the septets at around –144 ppm are characteristic of the PF₆ anion. The ESI-MS spectra give diagnostic peaks which are ascribed to $[Ir(C^N)_2(P^AP)]^+$. Complexes **1–9** were further characterized by FT-IR, and the purity was confirmed by elemental analysis. The IR spectra of complexes **1–9** have almost the same tendency, which reveal the strong P–F stretches of the PF₆⁻ group in the range of 843–846 cm⁻¹.

Structural Description. Single-crystal structures of 1, 7, and 9 were obtained through X-ray diffraction analysis, and the ORTEP diagrams are shown in Figure 2. The crystallographic data and structure refinement details are given in Table S1 in the Supporting Information; selected bond lengths and bond angles are collected in Table S2 in the Supporting Information. These iridium(III) complexes have a distorted-octahedral coordination geometry around Ir, retaining the *cis*-C,C and *trans*-N,N configuration of the C^N cyclometalating ligands.¹⁷ Meanwhile, the two phosphorus atoms of the P^P ligand are disposed trans with respect to the carbon atoms of the C^N ligand. All of the Ir–C (2.028(4)-2.065(5) Å), Ir–N

Scheme 1. Synthetic Routes of Ir(III) Complexes 1-9



Figure 2. Molecular structures of complexes 1, 7, and 9. PF_6^- counterions, solvent molecules, and hydrogen atoms are omitted for clarity.

(2.060(4)-2.091(4) Å), and Ir–P bond lengths (2.4248(13)-2.5113(12) Å) are close to those in previously reported iridium complexes bearing phosphine ligands.^{18,19}

The P-Ir-P angles can be seen to vary in a regular manner. The P-Ir-P bond angles $(96.35(4)-97.85(4)^{\circ})$ of complexes 1 and 7 with the xantphos ligand are significantly greater than the P-Ir-P bond angle $(94.49(4)^{\circ})$ of complex 9 with a dppp ligand. This is apparently due to the size of the chelate formed by the P^P ligand at the metal center. To accommodate the varying sizes of chelate rings, the Ir-P bonds are found to vary in consequence, those in complexes 1 and 7 with an eightmembered chelate ring showing longer Ir-P bonds (2.4959(13)-2.5113(12) Å) in comparison to those in complex 9 with a six-membered chelate ring (2.4248(13) - 2.4504(13) Å). Additionally, one of the phenyl rings is almost fixed in a parallel position with the isoquinoline ring, whereas another phenyl ring is twisted out of planarity from the aforementioned fragment by $27.231(116)^{\circ}$ (1), $25.618(107)^{\circ}$ (7), and $22.295(144)^{\circ}$ (9), respectively.

Photophysical Properties. The UV–vis absorption spectra of complexes 1-9 in CH_2Cl_2 solution at room temperature are depicted in Figure 3, and the data are provided in Table 1.

Similar to the case for many other cationic $[Ir(C^N)_2(P^P)]^+$ iridium complexes found in the literature,^{20–22} the absorption spectra of complexes **1–9** are dominated by multiple bands



Figure 3. UV–vis spectra of complexes $1\!-\!9$ in CH_2Cl_2 at room temperature.

originating from ligand-centered $\pi - \pi^*$ transitions and MLCT transitions. The intense bands at higher energies (240–320 nm) are assigned to the spin-allowed ligand-centered (LC) ${}^1\pi - \pi^*$ transitions. The weaker bands at lower energies (320–500 nm) are attributed to charge transfer transitions, with their nature being both spin-allowed (singlet to singlet metal to ligand charge transfer, ${}^1\text{MLCT}$) and spin-forbidden (singlet to triplet metal to ligand charge transfer (${}^3\text{MLCT}$) and ligand-centered ${}^3\pi - \pi^*$ transition).

From Table 1, it is found that the xantphos ancillary ligand of complexes 1, 4, and 7 and the Me-piq cyclometalating ligand of complexes 4-6 both can cause an absorption maximum red shift in the latter low-energy region. Consequently, complex 4 has the longest absorption wavelength (425 nm). In addition, from the absorption edges (395–425 nm) of complexes 1-9, their corresponding optical energy gaps (E_g) are estimated to be 2.92–3.14 eV, which correlates well with the variation rules of the HOMO–LUMO energy gaps discussed below.

The normalized emission spectra of 1-9 in the CH_2Cl_2 solution (at room temperature and 77 K) and in the solid state are given in Figure 4. The corresponding data are also given in Table 1.

Under photoexcitation, all Ir(III) complexes in solution at room temperature emit intense orange to red light with emission maxima bunched between 589 and 619 nm (Figures 4a and 5). Meanwhile, the emission spectra are broad and structureless, indicating that the emissive excited states are dominantly the ³MLCT character.^{27,28} It should be noted that the emission wavelengths for 1, 4, and 7 are red-shifted relative to other series of complexes 2–3, 5–6, and 8–9, respectively. Moreover, complex 4 exhibits emission spectra even more red shifted in comparison to the other complexes (1 and 7) of the series. Thus, the emission spectrum of 4 (λ_{em} 619 nm) is in the expected red region. The results are in good agreement with those of the lowest-energy electronic transition in the above UV–vis spectra.

As the temperature is decreased to 77 K, marked variations are noted in the emission spectra (Figure 4b). For complexes 2-3, 5-6, and 8-9, a significant hypsochromic shift in emission maxima is seen. The shift occurs because the relaxation rate of the solvent is strongly dependent on temperature, as illustrated by Balter et al.²⁹ In contrast, the emission bands of complexes 1, 4, and 7 show a slight bathochromic shift. It is conceivable that the phenomenon depends on the change of $P^{A}P$ ancillary ligands. Namely, the structural relaxation of iridium complexes with the xantphos ligand was not suppressed at lower temperature. Additionally, the vibrational structure in emission spectra at 77 K is present, since at low temperature the fine structure of different vibronic levels of $S_1 \rightarrow S_0$ is not affected by the collision–inactivation.³⁰ For solid-state emissions (Figure 4c), all of these complexes have a stronger bathochromic effect and broader emission in comparison to those in the solution state, which is consistent with the excimer formation arising from $\pi - \pi$ stacking

Table 1. Optoelectronic Characterization of Complexes 1-9

			emission									
	absorption		solution							solid		
complex	$\lambda_{abs} (nm)^a$	$E_{g} (eV)^{b}$	$\lambda_{\rm em}^{\rm RT} ({\rm nm})^a$	$\Phi_{\rm em}~(\%)^c$	$\tau \ (\mu s)^a$	$k_{\rm r} (10^5 {\rm s}^{-1})^d$	$k_{\rm nr} \ (10^5 \ { m s}^{-1})^d$	$ au_{\rm r} \ (\mu {\rm s})^d$	$\lambda_{\mathrm{em}}^{}77\mathrm{K}} (\mathrm{nm})^{e}$	$\lambda_{\rm em}~({\rm nm})$	$\Phi_{abs} (\%)^{f}$	electrohem ^a E _{ox} (V)
1	297, 361, 416	2.98	611	3.2	2.66	0.12	3.64	83.1	613 (654)	622	17.1	0.99
2	285, 338, 373, 411	3.02	598	24.4	3.19	0.77	2.37	13.1	587 (631)	617	30.1	0.96
3	277, 365, 398	3.12	589	5.5	2.01	0.27	4.70	36.5	581 (625)	594	17.7	0.95
4	272, 355, 425	2.92	619	4.0	2.33	0.17	4.12	58.3	620 (663)	625	12.2	0.90
5	290, 339, 377, 411	3.02	596	6.4	2.73	0.23	3.43	42.7	594 (637)	611	28.8	0.91
6	286, 357, 403	3.08	589	6.2	2.05	0.30	4.58	33.1	588 (635)	600	21.7	0.97
7	291, 356, 405	3.06	610	4.6	2.58	0.18	3.70	56.1	617 (658)	621	17.7	1.05
8	282, 340, 375, 410	3.03	602	12.8	2.83	0.45	3.08	22.1	588 (633)	602	34.8	1.05
9	278, 363, 395	3.14	593	9.8	1.77	0.55	5.10	18.1	584 (611)	571 (602)	21.0	1.04

^{*a*}Data were collected from degassed CH₂Cl₂ solutions at room temperature. ^{*b*}The optical energy gap $E_{\rm g}$ determined from the absorption onset. ^{*c*}*fac*-Ir(ppy)₃ as reference standard (0.4).⁴⁴ ^{*d*}Radiative decay rate ($k_{\rm r}$), nonradiative decay rate ($k_{\rm nr}$), and pure radiative lifetime ($\tau_{\rm r}$) estimated from the measured quantum yields and lifetimes. ^{*c*}Data were collected from degassed CH₂Cl₂ solutions at 77 K. ^{*f*}The solid-state absolute quantum yields were measured by employing an integrating sphere.



Figure 4. Normalized emission spectra of 1-9 in the CH₂Cl₂ solution at room temperature (a) and 77 K (b) and in the solid state (c).



Figure 5. Photo showing PL of 1-9 (from left to right) in solution (in CH₂Cl₂ under irradiation by a UV lamp at 365 nm).

interactions in the solid state.³¹ Specifically, a structured vibronic emission profile is found for complex **9** in the solid

state at room temperature, which is indicative of a mixing of ${}^{3}LC ({}^{3}\pi-\pi^{*})$ and ${}^{3}CT ({}^{3}MLCT)$ excited states.³²⁻³⁴

Phosphorescence relative quantum yields (Φ_{em}) of 1–9 in dichloromethane solution were measured to be 3.2-24.4% (Table 1) at room temperature by using the typical phosphorescent fac-Ir(ppy)₃ as a standard ($\Phi = 0.40$). The quantum efficiency of complex 2 (24.4%) is higher relative to those of complexes 1 (3.2%) and 3 (5.5%). Possibly, this is because the steric hindrance of the bulky diphosphine ligands prevents deactivation of the emitters by limiting energy transfer between the complexes.¹⁰ A similar effect is also observed for complexes 5 (6.4%) and 8 (12.8%), respectively. The introduction of the electron-withdrawing group (-F) in complex 2 results in a dramatic increase in the phosphorescence quantum yield. It can be surmised that the presence of the C-F bonds leads to the reduced radiationless deactivation rate.^{35,36} Furthermore, the solid-state absolute quantum yields (Φ_{abs}) of 1–9 were measured to be 12.2–34.8% (Table 1) by employing an integrating sphere. We note that the Φ_{abs} values of these complexes are noticeably improved. Obviously, the Φ_{abs} values of 2, 5, and 8 are much higher than those of other complexes in the corresponding series. This proves again the aforementioned steric hindrance effect of the binap ligand.

Phosphorescence (solution) is obtained in all cases with microsecond lifetimes at room temperature, ranging from 1.77 to 3.19 μ s, which suggests a possible triplet nature of the emissive excited state. Interestingly, complexes 3, 6, and 9 have significantly shorter excited-state lifetimes than analogues 1–2, 4–5, and 7–8. Such results indicate that the three Ir complexes possess effective T₁ to S₀ radiative relaxation, which is beneficial for the OLED operation.

From the quantum yields $\Phi_{\rm em}$ and the τ lifetime values, the radiative decay rate $(k_{\rm r})$, the nonradiative decay rate $(k_{\rm nr})$, and the pure radiative lifetime $(\tau_{\rm r})$ were calculated for a series of complexes through the equations $k_{\rm r} = \Phi_{\rm em}/\tau$, $k_{\rm nr} = (1 - \Phi_{\rm em})/\tau$, τ_r^{37} and $\tau_{\rm r} \approx \tau/\Phi_{\rm em}^{38}$ (see Table 1). Thus, the emission quantum yield $(\Phi_{\rm em})$ is generally formulated as $\Phi_{\rm em} = k_{\rm r}/(k_{\rm r} + k_{\rm nr})$. From the equation, we can conclude that a large $k_{\rm r}$ and a small $k_{\rm nr}$ are required to increase the quantum yield. For 2, the $k_{\rm r}$ value is the largest and the $k_{\rm nr}$ value is the smallest within the investigated complexes, which makes it distinctive as being the most strongly emissive in the family of complexes. The radiative lifetime $(\tau_{\rm r})$ was deduced to be 13.1–83.1 μ s for all complexes 1–9. This value is comparable to that of the red-emitting Ir(III) complexes.

Theoretical Calculations. Density functional theory (DFT) and time-dependent DFT (TD–DFT) calculations have been performed for complexes 1–9 to gain insights into the lowest-energy electronic transition. The HOMO–LUMO energy-level diagrams for these complexes and the energy gap are presented in Figure 6. The calculated spin-allowed electronic transitions are provided in Table 2 and compared with the experimental absorption spectral data.

As seen in Figure 6, the HOMOs of 1–9 are mainly dominated by iridium d orbitals and π orbitals of phenyl and pyridine rings of the two cyclometalating ligands, along with a minor contribution from the ancillary ligand. Meanwhile, the LUMO/LUMO+1 are mostly located on π^* orbitals of phenyl and pyridine rings of the two cyclometalating ligands. Therefore, the lowest-energy electronic transition (HOMO \rightarrow LUMO, HOMO \rightarrow LUMO+1) of these Ir(III) complexes 1–9 are ascribed as MLCT, LL'CT, and ILCT $\pi \rightarrow \pi^*$

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Figure 6. Molecular orbital energy-level diagrams of HOMOs and LUMOs in iridium complexes 1-9.

Table 2. Main Experimental	and Calculated Op	ptical Transitions for	Complexes 1-9
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complex		HOMO (eV)	LUMO (eV)	LUMO+1 (eV)	oscillation strength (eV)	calcd (nm)	exptl (nm)
1	HOMO \rightarrow LUMO+1	-6.065	-2.493	-2.427	0.0791	412	416
2	$HOMO \rightarrow LUMO$	-6.109	-2.511		0.0865	415	411
3	HOMO \rightarrow LUMO+1	-6.101	-2.464	-2.395	0.1441	399	398
4	HOMO \rightarrow LUMO+1	-5.889	-2.412	-2.352	0.0652	429	425
5	HOMO \rightarrow LUMO	-5.958	-2.410		0.0860	425	411
6	HOMO \rightarrow LUMO+1	-5.929	-2.385	-2.318	0.1284	415	403
7	HOMO \rightarrow LUMO+1	-6.136	-2.550	-2.497	0.0732	415	405
8	HOMO \rightarrow LUMO	-6.172	-2.581		0.0926	417	410
9	HOMO \rightarrow LUMO+1	-6.225	-2.576	-2.520	0.1243	403	395

transitions,³⁹ which are consistent with the actual absorptions (Table 2).

In Figure 6, the HOMO levels of complexes 4-6 are distinctly greater than those of the other two families of complexes 1-3 and 7-9, owing to the increases in the electron density around the iridium center provided by the electrondonating methyl group on the C^N ligand. The increase in HOMO levels reduces the HOMO-LUMO energy gap, thereby leading to red-shifted emission. For complexes 4-6, the HOMO-LUMO gap of 4 is the smallest of all complexes, which is dependent on the nature of the ancillary ligand. However, while simply replacing the P^P ancillary ligand results in a slight change in HOMO value, further replacing the $-CH_3$ substituent group on cyclometalating ligands leads to a significant change in HOMO energy level. This behavior, in combination with the aforementioned emission spectra, supports the supposition that the cyclometalating ligand with electron-donating group plays an important role in the redshifted emission. This observation agrees well with the photophysical properties discussed above.

Electrochemical Properties. The electrochemical behaviors of these iridium complexes were investigated by cyclic voltammetry. The electrochemical waves are shown in Figure S1 in the Supporting Information, and the oxidation potentials (E_{ox}) are compiled in Table 1. All nine complexes introduced in this work exhibit quasi-reversible monoelectronic oxidation peaks around 0.90–1.05 V. The oxidation processes are linked to metal-centered orbitals with a contribution from the phenyl part of cyclometalated fragments, which was confirmed by our DFT calculations (Figure 6). It is assumed that pure metal-

centered oxidations are reversible and the irreversibility increases as the contribution to the HOMO of the cyclometalating phenyl(s) increases.^{40,41} From Table 1, it can be seen that the E_{ox} values are in the order 4-6 < 1-3 < 7-9, which is consistent with the actual electron-donating ability of $-CH_3 > -F > -OCF_3$. These findings indicate the electrondonating $(-CH_3)$ group can improve the HOMO energy levels, while the electron-withdrawing fluorine atom lower them effectively, especially $- OCF_3$ group. The variation tendency is approximately consistent with DFT calculations.

CONCLUSION

In conclusion, nine orange to red emitting cationic heteroleptic iridium(III) complexes incorporating bisphosphine ancillary ligands have been synthesized and characterized. Their photophysical properties, theoretical calculations, and electrochemical behaviors have been investigated. The molecular structures of complexes 1, 7, and 9 reveal that they all possess pseudo-octahedral coordination geometry. Analyses of DFT and TD-DFT calculations indicate that the lowest-energy electronic transitions are attributed to MLCT, LL'CT, and ILCT $\pi \to \pi^*$ transitions. However, the emission spectra in solution at room temperature are broad and structureless, suggesting that the lowest excited states are dominantly ³MLCT excitations. Through optimization of three C^N cyclometalating ligands (F-piq, Me-piq, and CF₃O-piq) and three P^AP ancillary ligands (xantphos, binap, and dppp), we have rationally designed the red-emitting complex 4 (λ_{em} 619 nm), which would be a potential candidate for red phosphorescent materials.

EXPERIMENTAL SECTION

General Methods. NMR spectra were recorded on a Bruker AM 400 MHz instrument (¹H, 400 MHz; ¹³C, 100 MHz; ³¹P, 162 MHz). Chemical shifts were reported in ppm relative to $\mathrm{Me}_4\mathrm{Si}$ as internal standard. ESI-MS spectra were recorded on an Esquire HCT-Agilent 1200 LC/MS spectrometer. The elemental analyses were performed on a Vario EL Cube Analyzer system. IR spectra were taken on a Nicolet 6700 FTIR spectrometer (400-4000 cm⁻¹) with KBr pellets. UV-vis spectra were recorded on a Hitachi U3900/3900H spectrophotometer. Fluorescence spectra were carried out on a Hitachi F-7000 spectrophotometer as deaerated CH₂Cl₂ solutions at room temperature and 77 K, as well as for the neat solid powders. The absolute quantum efficiencies (Φ_{abs}) in the solid state were measured on a PL quantum yield measurement system (Hamamatsu, Model C9920-01). Luminescence lifetime curves were measured on an Edinburgh Instruments FLS920P fluorescence spectrometer, and the data were treated as one-order exponential fitting using OriginPro 8 software. All solutions were deaerated by nitrogen bubbling for 30 min before measurements.

The luminescence quantum efficiencies in solution were calculated by comparison of the fluorescence intensities (integrated areas) of the standard sample *fac*-Ir(ppy)₃ and the unknown sample according to the equation^{42–44}

$$\Phi_{\rm unk} = \Phi_{\rm std} \left(\frac{I_{\rm unk}}{I_{\rm std}} \right) \left(\frac{A_{\rm std}}{A_{\rm unk}} \right) \left(\frac{\eta_{\rm unk}}{\eta_{\rm std}} \right)^2$$

where Φ_{unk} and Φ_{std} are the luminescence quantum yield values of the unknown sample and fac-Ir(ppy)₃ solutions ($\Phi_{std} = 0.4$),⁴⁴ respectively, I_{unk} and I_{std} are the integrated fluorescence intensities of the unknown sample and fac-Ir(ppy)₃ solutions, respectively, A_{unk} and A_{std} are the absorbance values of the unknown sample and fac-Ir(ppy)₃ solutions at their excitation wavelengths, respectively, and the η_{unk} and η_{std} terms represent the refractive indices of the corresponding solvents (pure solvents were assumed).

X-ray Structure Determination. X-ray diffraction data were collected with an Agilent Technologies Gemini A Ultra diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.7107$ Å) and Cu K α radiation ($\lambda = 1.5418$ Å) at room temperature. Data collection and reduction were processed with CrysAlisPro software.⁴⁵ All of the structures were solved using Superflip⁴⁶ and refined using SHELXL-2014⁴⁷ within Olex2.⁴⁸ All non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in calculated positions and refined as riding atoms with a uniform value of U_{iso} .

Electrochemical Measurements. Cyclic voltammetry (CV) was performed on a CHI 1210B electrochemical workstation, with a glassy-carbon electrode as the working electrode, a platinum wire as the counter electrode, an Ag/Ag^+ electrode as the reference electrode, and 0.1 M *n*-Bu₄NClO₄ as the supporting electrolyte.

Computational Details. All calculations were carried out with Gaussian 09 software package.⁴⁹ Density functional theory (DFT) and time-dependent DFT (TD-DFT) were employed with no symmetry constraints to investigate the optimized geometries and electron configurations with the Becke three-parameter Lee–Yang–Parr (B3LYP) hybrid density functional theory.^{50–52} The LANL2DZ basis set was used to treat the Ir atom, whereas the 6-31G* basis set was used to treat C, H, O, N, F, and P atoms. Solvent effects were considered within the SCRF (self-consistent reaction field) theory using the polarized continuum model (PCM) approach to model the interaction with the solvent.^{53,54}

Materials. IrCl₃·3H₂O and other chemicals were obtained from commercial sources and used without further purification. All solvents were purified and dried by standard procedures. All of the reactions

dealing with air-sensitive reactions were carried out under a nitrogen atmosphere.

Syntheses. 1-(4-Fluorophenyl)isoquinoline (F-piq, 3a). To a degassed solution of 1-chloroisoquinoline (1.0 g, 6.11 mmol) and (4fluorophenyl)boronic acid (2a; 940 mg, 6.72 mmol) in 1,4-dioxane (20 mL) was added Pd(dppf)Cl₂ (0.21 g, 0.31 mmol) and potassium phosphate (1.27 g, 9.17 mmol), and then the reaction mixture was degassed under vacuum and charged with N2. The mixture was heated to 80 °C and stirred for 10 h under a nitrogen atmosphere. The mixture was poured into water and extracted multiple times with ethyl acetate. The combined organic phases were washed with brine and dried over Na₂SO₄. After concentration, the residue was purified by column chromatography to give the desired compound 3a (1.28 g, yield 93.8%) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.60 (d, J = 6.0 Hz, 1H, Py-H), 7.97 (d, J = 8.4 Hz, 1H, Ar-H), 7.93 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.79–7.84 (m, 4H, Ar-H, Py-H), 7.73–7.78 (m, 2H, Ar-H), 7.59 (t, J = 8.0 Hz, 1H, Ar-H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.53, 143.87, 142.08, 137.03, 134.11, 132.30, 130.79, 130.68, 128.05, 127.43, 126.71, 126.48, 121.19, 118.74, 116.46, 112.56. MS (ESI): m/z 224.1 [M + 1]⁺

1-(*p*-Tolyl)isoquinoline (Me-piq, **3b**). A procedure analogous to that described for compound **3a** was used with (4-methylphenyl)boronic acid (**2b**) instead of (4-fluorophenyl)boronic acid (**2a**) to afford **3b** as a white solid. Yield: 94.6%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.60 (d, *J* = 6.0 Hz, 1H, Py-H), 8.13 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.87 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.51–7.70 (m, 5H, Ar-H, Py-H), 7.28–7.36 (m, 2H, Ar-H), 2.47 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 160.92, 142.32, 138.59, 137.00, 136.82, 130.06, 129.98, 129.16, 127.81, 127.18, 127.08, 126.88, 119.83, 21.49. MS (ESI): *m*/z 220.1 [M + 1]⁺, 242.2 [M + Na]⁺.

1-(4-(Trifluoromethoxy)phenyl)isoquinoline (*CF*₃O-piq, **3c**). A procedure analogous to that described for compound **3a** was used with 4-(trifluoromethoxy)phenyl)boronic acid (**2c**) instead of (4-fluorophenyl)boronic acid (**2a**) to afford **3c** as a white solid. Yield: 91.8%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.59–8.60 (m, 1H, Py-H), 8.04 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.85 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.62–7.74 (m, 4H, Ar-H, Py-H) 7.52 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.39 (d, *J* = 8.0 Hz, 2H, Ar-H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 159.03, 149.48, 141.86, 137.99, 136.83, 131.41, 130.17, 127.46, 127.04, 126.93, 126.46, 120.69, 120.34. MS (ESI): *m*/*z* 290.1 [M + 1]⁺, 312.1 [M + Na]⁺.

 $[lr(F-piq)_2(xantphos)]PF_6$ (1). A mixture of $IrCl_3 \cdot 3H_2O$ (1.0 mmol) and the ligand 3a (2.2 mmol) in 6 mL of ethoxyethanol and H_2O (2/1 v/v) was heated to reflux at 120 $^\circ C$ for 12 h under a nitrogen atmosphere. Upon cooling to room temperature, the red precipitate was collected by filtration and washed with water and cooled MeOH. After drying, the chloro-bridged dimer complex 4a was used directly in the next step without further purification. A mixture of the above dimer complex 4a (100 mg) and P_1 ligand (2.5 equiv) was dissolved in 6 mL of DCM and MeOH (2/1 v/v), heated to 40 °C, and stirred for 19 h under a nitrogen atmosphere. After the mixture was cooled to room temperature, NH₄PF₆ (5.0 equiv) was added. The mixture was stirred at room temperature for 1 h and then evaporated to dryness. The solid was purified by column chromatography to afford pure complex 1. Yield: 53%. ¹H NMR (400 MHz, DMSO): δ (ppm) 8.63 (d, J = 8.4 Hz, 2H), 8.33(d, J = 8.4 Hz, 2H), 8.14-8.16 (m, 2H),7.96-8.02 (m, 6H), 7.67 (d, J = 7.6 Hz, 2H), 7.48 (d, J = 6.8 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.26 (t, J = 7.6 Hz, 2H), 7.07 (t, J = 7.6 Hz, 4H), 6.94–6.99 (m, 6H), 6.74–6.83 (m, 6H), 6.61 (dt, J₁ = 8.4 Hz, J₂ = 2.4 Hz, 2H, 6.33 (t, J = 8.0 Hz, 4H), 5.19 (t, J = 8.8 Hz, 2H), 1.48(s, 6H). 13 C NMR (100 MHz, DMSO): δ (ppm) 145.51, 141.99, 140.01, 136.45, 136.35, 133.12, 132.70, 132.24, 132.09, 131.98, 131.89, 130.34, 130.13, 129.92, 129.83, 128.72, 128.37, 127.85, 127.22, 126.55, 126.48, 125.19, 124.79, 121.95, 120.08, 116.76, 116.40, 115.94, 115.75, 115.32, 115.10, 109.97, 109.74, 35.20, 28.56. ³¹P NMR (162 MHz, DMSO): δ (ppm) –20.87, –144.18 (hept). MS (ESI): m/z 1215.3 [M $- PF_6$]⁺ (calcd 1215.3). Anal. Calcd for C₆₉H₅₀F₈IrN₂OP₃: C, 60.92; H, 3.71; N, 2.06. Found: C, 60.15; H, 3.76; N, 2.01. IR (KBr pellet, cm⁻¹): 3061 (w), 2965 (w), 2856 (w), 1576 (m), 1406 (m), 1240

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(m), 1193 (m), 1087 (w), 843 (s), 744 (m), 695 (m), 557 (w), 515 (m).

[*Ir*(*F*-*piq*)₂(*binap*)]*PF*₆ (2). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.39 (d, *J* = 8.4 Hz, 2H), 7.85–7.94 (m, 6H), 7.70–7.77 (m, 6H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.34–7.46 (m, 8H), 6.94–7.02 (m, 4H), 6.86– 6.91 (m, 4H), 6.73 (t, *J* = 7.6 Hz, 4H), 6.73 (d, *J* = 9.2 Hz, 4H), 6.50– 6.58 (m, 8H), 6.07 (d, *J* = 8.4 Hz, 2H), 5.31–5.34 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 147.19, 140.86, 136.47, 135.53, 135.48, 135.44, 134.01, 132.71, 132.66, 132.62, 130.08, 129.77, 128.81, 128.11, 128.01, 127.97, 127.92, 127.86, 127.42, 127.34, 127.30, 126.66, 126.31, 120.35, 117.24, 117.05, 110.49, 110.27. ³¹P NMR (162 MHz, CDCl₃): δ (ppm) –11.49, –144.17 (hept). MS (ESI): *m*/*z* 1259.3 [M – PF₆]⁺ (calcd 1259.3). Anal. Calcd for C₇₄H₅₀F₈IrN₂P₃: C, 63.29; H, 3.59; N, 1.99. Found: C, 63.38; H, 3.47; N, 2.05. IR (KBr pellet, cm⁻¹): 3058 (w), 2918 (w), 2853 (w), 1583 (m), 1543 (w), 1383 (w), 1252 (s), 1220 (m), 843 (s), 740 (m), 699 (m), 558 (w), 517 (w).

[*Ir*(*F*-*piq*)₂(*dppp*)]*PF*₆ (**3**). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.31 (d, *J* = 8.4 Hz, 2H), 8.16 (d, *J* = 6.4 Hz, 2H), 7.91–7.95 (m, 2H), 7.67–7.77 (m, 8H), 7.59 (t, *J* = 8.4 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 4H), 7.98 (d, *J* = 6.4 Hz, 2H), 6.69 (dt, *J*₁ = 8.4 Hz, *J*₂ = 2.4 Hz, 2H), 6.35–7.40 (m, 10H), 6.10–6.13 (m, 2H), 3.22–3.25 (m, 2H), 3.04–3.08 (m, 2H), 2.82–3.93 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 147.15, 141.18, 136.59, 133.52, 133.48, 133.43, 132.81, 131.94, 131.36, 130.81, 130.39, 129.93, 129.54, 129.51, 129.19, 128.99, 128.11, 127.28, 127.24, 127.13, 127.08, 127.04, 126.03, 121.59, 118.54, 118.36, 110.20, 109.97, 23.68, 21.48. ³¹P NMR (162 MHz, CDCl₃): δ (ppm) –30.26, –144.17 (hept). MS (ESI): *m/z* 1049.3 [M – PF₆]⁺ (calcd 1049.3). Anal. Calcd for C₅₇H₄₄F₈IrN₂P₃: C, 57.33; H, 3.71; N, 2.35. Found: C, 57.45; H, 3.83; N, 2.25. IR (KBr pellet, cm⁻¹): 3060 (w), 2923 (w), 2853 (w), 1579 (m), 1542 (w), 1383 (w), 1195 (m), 844 (s), 745 (m), 698 (m), 560 (w), 525 (w).

[*Ir*(*Me-piq*)₂(*xantphos*)]*PF*₆ (4). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.51 (d, *J* = 8.4 Hz, 2H), 8.27 (d, *J* = 6.8 Hz, 2H), 7.93 (d, *J* = 7.6 Hz, 2H), 7.76–7.85 (m, 4H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 6.8 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 2H), 7.00 (d, *J* = 6.4 Hz, 2H), 6.92 (t, *J* = 7.2 Hz, 4H), 6.74–6.84 (m, 10H), 6.66– 6.70 (m, 2H), 6.60 (d, *J* = 7.6 Hz, 2H), 6.23 (t, *J* = 8.0 Hz, 4H), 5.54 (s, 2H), 1.71 (s, 6H), 1.50 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 153.24, 146.41, 141.50, 141.25, 136.68, 133.47, 132.90, 132.30, 131.58, 130.96, 130.39, 129.72, 129.54, 128.81, 128.30, 127.86, 127.07, 125.85, 124.76, 123.93, 120.39, 29.84, 28.81, 21.84. ³¹P NMR (162 MHz, CDCl₃): δ (ppm) –19.47, –144.21 (hept). MS (ESI): *m/z* 1207.4 [M – PF₆]⁺ (calcd 1207.3). Anal. Calcd for C₇₁H₅₆F₆IrN₂OP₃: C, 63.06; H, 4.17; N, 2.07. Found: C, 63.15; H, 4.22; N, 2.02. IR (KBr pellet, cm⁻¹): 3063 (w), 2923 (w), 2861 (w), 1588 (m), 1407 (m), 1243 (w), 1090 (w), 844 (s), 745 (m), 697 (w), 558 (w), 575 (w).

[*Ir*(*Me*-*piq*)₂(*binap*)]*PF*₆ (5). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.43 (d, *J* = 7.6 Hz, 2H), 7.81–7.91 (m, 4H), 7.67–7.72 (m, 8H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.47–7.49 (m, 8H), 6.88–7.00(m, 8H), 6.81– 7.85 (m, 4H), 6.67 (t, *J* = 7.2 Hz, 4H), 6.61 (d, *J* = 8.0 Hz, 2H), 6.43– 6.49 (m, 4H), 6.11 (d, *J* = 8.4 Hz, 2H), 5.43 (s, 2H), 1.62 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 147.59, 142.03, 139.95, 136.37, 135.67, 133.94, 132.65, 132.23, 131.90, 130.82, 129.82, 129.21, 128.68, 128.16, 127.94, 127.82, 127.67, 127.45, 127.19, 126.51, 126.47, 123.97, 119.41, 21.78. ³¹P NMR (162 MHz, CDCl₃): δ (ppm) –10.63, -144.23 (hept). MS (ESI): *m/z* 1251.4 [M – PF₆]⁺ (calcd 1251.4). Anal. Calcd for C₇₆H₅₆F₆IrN₂P₃: C, 65.37; H, 4.04; N, 2.01. Found: C, 65.43; H, 4.13; N, 1.96. IR (KBr pellet, cm⁻¹): 3052 (w), 2923 (w), 2850 (w), 1587 (m), 1440 (w), 1381 (w), 1151 (w), 1087 (w), 843 (s), 745 (m), 698 (m), 557 (w), 521 (w).

[*Ir*(*Me-piq*)₂(*dppp*)]*PF*₆ (6). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.41 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 6.4 Hz, 2H), 7.65–7.77 (m, 10H), 7.57 (t, *J* = 7.2 Hz, 2H), 7.38–7.40 (m, 2H), 7.28–7.32 (m, 4H), 6.90 (d, *J* = 6.4 Hz, 2H), 6.76 (d, *J* = 7.6 Hz, 2H), 6.36–7.41 (m, 10H), 6.20 (s, 2H), 3.17–3.21 (m, 2H), 3.04–3.08 (m, 2H), 2.85–2.92 (m, 2H), 1.98 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 147.12, 142.30, 139.52, 136.36, 133.54, 133.50, 133.46, 133.16, 131.57, 131.02, 130.78, 129.62, 128.86, 128.73, 127.73, 127.43, 127.06, 126.99, 126.95, 126.09, 123.71, 120.72, 29.80, 24.33, 21.78. ³¹P NMR (162 MHz, CDCl₃): δ (ppm) –30.70, –144.14 (hept). MS (ESI): *m/z* 1041.4 $[M - PF_6]^+$ (calcd 1041.3). Anal. Calcd for $C_{59}H_{50}F_6IrN_2P_3$: C, 59.74; H, 4.25; N, 2.36. Found: C, 59.80; H, 4.32; N, 2.28. IR (KBr pellet, cm⁻¹): 3058 (w), 2925 (w), 1669 (w), 1577 (s), 1540 (m), 1432 (m), 1383 (m), 1192 (m), 844 (s), 744 (m), 696 (m), 588 (w), 556 (m), 516 (m).

[*Ir*(*CF*₃*O*-*piq*)₂(*xantphos*)]*PF*₆ (7). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.48 (d, J = 8.4 Hz, 2H), 8.28 (d, J = 6.4 Hz, 2H), 7.98–8.01 (m, 2H), 7.80–7.92 (m, 6H), 7.48 (d, J = 6.8 Hz, 2H), 7.26–7.30 (m, 2H), 7.18 (t, J = 7.2 Hz, 2H), 7.12 (d, J = 6.4 Hz, 2H), 6.96 (t, J = 7.2 Hz, 4H), 6.84–6.88 (m, 6H), 6.64–6.78 (m, 8H), 6.24 (t, J = 8.0 Hz, 4H), 5.50 (s, 2H), 1.52 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 153.36, 146.08, 142.46, 136.85, 133.46, 133.41, 133.36, 133.00, 132.81, 132.76, 132.71, 131.85, 130.86, 130.41, 130.03, 129.74, 128.62, 128.58, 128.54, 128.29, 128.24, 128.19, 128.15, 127.42, 126.51, 126.03, 125.05, 121.83, 121.48, 114.58, 29.84, 28.72. ³¹P NMR (162 MHz, CDCl₃): δ (ppm) –20.92, –144.18 (hept). MS (ESI): *m*/z 1347.3 [M – PF₆]⁺ (calcd 1347.3). Anal. Calcd for C₇₁H₅₀F₁₂IrN₂O₃P₃: C, 57.14; H, 3.38; N, 1.88. Found: C, 57.32; H, 3.41; N, 1.86. IR (KBr pellet, cm⁻¹): 3068 (w), 2968 (w), 1584 (w), 1409 (m), 1250 (s), 1183 (m), 844 (s), 747 (m), 698 (w), 512 (w).

[*Ir*(*CF*₃*O*-*piq*)₂(*binap*)]*PF*₆ (**8**). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.40 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 8.4 Hz, 4H), 7.81–7.91 (m, 10H), 7.57 (d, J = 8.4 Hz, 2H), 7.35–7.43 (m, 8H), 6.86–6.92 (m, 6H), 6.74 (t, J = 7.2 Hz, 4H), 6.68 (d, J = 6.4 Hz, 2H), 6.62 (t, J = 8.0 Hz, 4H), 6.52 (t, J = 8.0 Hz, 4H), 6.07 (t, J = 7.6 Hz, 2H), 5.40 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.09, 148.21, 146.32, 136.24, 135.57, 133.90, 133.86, 133.04, 132.07, 131.11, 130.59, 129.47, 129.16, 128.91, 128.37, 127.81, 127.42, 127.16, 127.01, 126.77, 126.20, 126.03, 125.51, 125.32, 120.75, 119.73, 113.47. ³¹P NMR (162 MHz, CDCl₃): δ (ppm) –12.06, –144.15 (hept). MS (ESI): *m*/*z* 1391.0 [M – PF₆]⁺ (calcd 1391.3). Anal. Calcd for C₇₆H₅₀F₁₂IrN₂O₂P₃: C, 59.42; H, 3.28; N, 1.82. Found: C, 59.49; H, 3.36; N, 1.74. IR (KBr pellet, cm⁻¹): 3058 (w), 2925 (w), 2853 (w), 1579 (w), 1385 (w), 1252 (m), 1160 (s), 1089 (w), 843 (s), 745 (m), 696 (m), 521 (w). [*Ir*(*CF*₃O-*piq*)₂(*dppp*)]*PF*₆ (**9**). ¹H NMR (400 MHz, CDCl₃): δ

[*lr*(*CF*₃O-*piq*)₂(*dppp*)]*PF*₆ (**9**). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.40 (d, *J* = 8.4 Hz, 2H), 8.12 (d, *J* = 6.4 Hz, 2H), 7.66–7.77 (m, 10H), 7.58 (t, *J* = 7.2 Hz, 2H), 7.38–7.41 (m, 2H), 7.28–7.31 (m, 4H), 6.90 (d, *J* = 6.8 Hz, 2H), 6.76 (d, *J* = 8.0 Hz, 2H), 6.36–6.43 (m, 10H), 6.20 (s, 2H), 3.17–3.22 (m, 2H), 2.98–3.07 (m, 2H), 2.83– 2.92 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 148.97, 147.13, 143.25, 136.59, 133.46, 133.42, 133.38, 132.06, 131.46, 129.48, 129.44, 129.40, 129.27, 129.23, 129.18, 129.02, 128.32, 127.37, 127.18, 127.14, 127.09, 127.06, 126.19, 123.08, 122.23, 121.61, 119.05, 114.95, 23.85, 21.52. ³¹P NMR (162 MHz, CDCl₃): δ (ppm) –30.15, –144.13 (hept). MS (ESI): *m*/*z* 1181.1 [M – PF₆]⁺ (calcd 1181.2). Anal. Calcd for C₅₉H₄₄F₁₂IrN₂O₂P₃: C, 53.44; H, 3.34; N, 2.11. Found: C, 53.51; H, 3.47; N, 2.03. IR (KBr pellet, cm⁻¹): 3063 (w), 2928 (w), 1578 (m), 1437 (w), 1383 (w), 1252 (s), 1188 (m), 1094 (w), 846 (s), 746 (m), 696 (m), 647 (w), 557 (m), 518 (m).

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.7b00740.

Crystallographic data summary and selected bond distances and angles for 1, 7 and 9, cyclic voltammograms for 1–9, ¹H, ¹³C, and ³¹P (1–9) NMR spectra for 3a-3c and 1–9, and ESI-MS spectra for 1–9 (PDF)

Accession Codes

CCDC 1576155–1576157 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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