

Cationic Iridium(III) Complexes Bearing Phosphaalkene and 2-Pyridylphenyl Ligands

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Received March 22, 2007

The reactions of $[\text{Ir}(\text{ppy})_2(\text{H}_2\text{O})_2](\text{OTf})$ ($\text{ppy} = 2\text{-pyridylphenyl}$) with 1,2-diaryl-3,4-bis[(2,4,6-tri-*tert*-butylphenyl)phosphinidene]cyclobutenes (DPCB-Y) afford $[\text{Ir}(\text{ppy})_2(\text{DPCB-Y})](\text{OTf})$ ($\text{Y} = \text{CF}_3$ (**1**), H (**2**), and OMe (**3**)) in high yields. The 2-(2-pyridyl)phosphaethene ($\text{P}^{\wedge}\text{N}$) analogue $[\text{Ir}(\text{ppy})_2(\text{P}^{\wedge}\text{N})](\text{OTf})$ (**4**) is prepared in a similar manner. Complexes **1–4** are characterized by elemental analysis, NMR and electronic spectroscopy, cyclic voltammetry, and/or X-ray structural analysis.

Introduction

The appropriate choice of ancillary ligands is essential to gain desirable functions of transition metal complexes. From the electronic point of view, ancillary ligands are classified as σ -donors and π -acceptors. The former includes nitrogen bases such as dimines and bipyridines, phosphines, N-heterocyclic carbenes, and cyclopentadienyl derivatives; their properties may be finely tuned by chemical modifications. On the other hand, ancillary ligands that are strong π -acceptors are limited. Although carbon monoxide is a typical π -acceptor, this molecule is generally reactive toward organometallic compounds and its chemical modification is infeasible. This situation has urged us to examine a new type of π -accepting ligand 1,2-diaryl-3,4-bis-[(2,4,6-tri-*tert*-butylphenyl)phosphinidene]cyclobutenes (DPCB-Y), whose electronic and steric properties can be controlled by introducing a variety of substituents to the backbone.^{1,2} The most striking feature of DPCB-Y is the extremely low-lying π^* -orbitals spread over the diphosphinidene-cyclobutene skeleton to induce strong π -back-donation from transition metals.³

This paper reports the synthesis, structures, and properties of cationic iridium(III) complexes bearing 2-pyridylphenyl (ppy) and DPCB-Y ligands. Over the past years, a number of studies have been carried out on the photophysical properties of octahedral d^6 Ru(II), Os(II), Rh(III), and Ir(III) complexes,^{4–6} because of their potential applications to photoreductants,⁷ emissive materials,^{8–11} and chemical sensors.¹² In 2003, Nazeeruddin *et al.* reported a new series of Ir(III) complexes (NBu_4)- $[\text{Ir}(\text{ppy})_2(\text{CN})_2]$, $(\text{NBu}_4)[\text{Ir}(\text{ppy})_2(\text{NCS})_2]$, and $(\text{NBu}_4)[\text{Ir}(\text{ppy})_2(\text{NCO})_2]$ ($\text{ppy} = 2\text{-pyridylphenyl}$), which exhibit blue, green,

and yellow emission, respectively.¹³ The marked variation in the emission color is mainly due to the difference in the metal t_{2g} orbital levels dependent on ancillary ligands. In this study, we examined the π -accepting ability of DPCB-Y ligands in $[\text{Ir}(\text{ppy})_2(\text{DPCB-Y})]^+$ complexes. It was found that the oxidation potential is rather sensitive to the substituents of DPCB-Y ligands. The synthesis of a related 2-(2-pyridyl)phosphaethene complex is also reported.

Results and Discussion

Synthesis. A variety of iridium(III) complexes bearing 2-pyridylphenyl (ppy) ligands have been synthesized from $[\text{Ir}$ -

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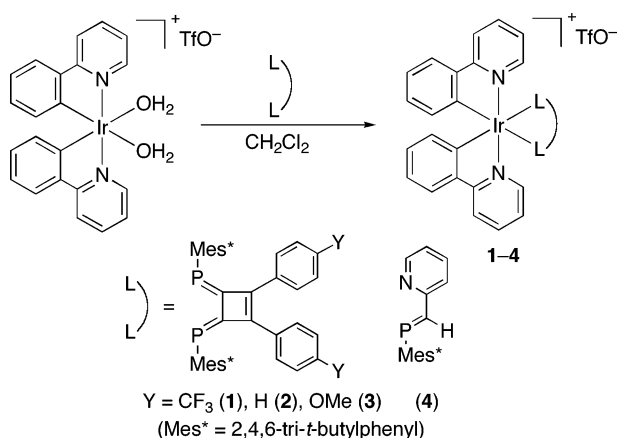
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Scheme 1



(ppy)₂(μ-Cl)₂.^{14–18} Accordingly, we first examined the reaction of this complex with DPCB-Y. However, no coordination of DPCB-Y took place. We therefore introduced a more labile complex, [Ir(ppy)₂(H₂O)₂](OTf),¹⁹ which smoothly underwent substitution of H₂O ligands with DPCB-Y to give 1–3 (Scheme 1). The reaction cleanly proceeded in CH₂Cl₂ at room temperature, and analytically pure compounds were obtained simply by evaporating the solvent, followed by washing the resulting solids with Et₂O (84–92% yields). The 2-(2-pyridyl)phosphathene (P[^]N) complex 4 was synthesized in a similar manner

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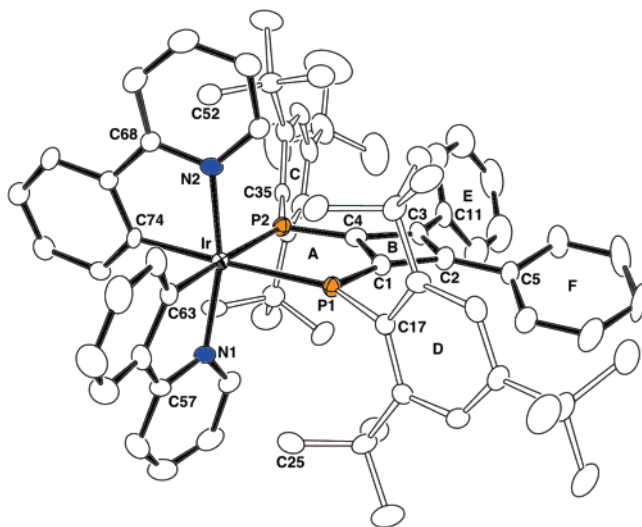


Figure 1. ORTEP drawing of 2·(2THF) with thermal ellipsoids at the 50% probability level. Hydrogen atoms, counteranion, and two molecules of THF are omitted for clarity.

(86% yield). To our knowledge, complexes 1–4 are the first examples of iridium(III) complexes bearing sp²-hybridized phosphorus ligands. Complexes 1–3 are stable in the solid state as well as in poorly coordinating solvents such as CH₂Cl₂, CHCl₃, and THF, but easily dissociate the DPCB-Y ligands in MeCN. On the other hand, complex 4 was stable even in MeCN.

Characterization. Complexes 1–4 were identified by elemental analysis and NMR spectroscopy. As a representative example, complex 1 exhibited aromatic proton signals assignable to ppy ligands in a range typical for Ir(III) ppy complexes (δ 5.75–9.88).²⁰ The *tert*-butyl protons of 2,4,6-tri-*tert*-butylphenyl groups (Mes*) were observed as three sets of singlets at δ 0.77 (18H), 1.26 (18H), and 1.75 (18H), showing hindered rotation around the C(Mes*)–P bonds, making the two *ortho tert*-butyl groups nonequivalent. The ³¹P{¹H} NMR chemical shift (δ 130.6) was considerably higher than that of free DPCB-CF₃ (δ 180.7). Complexes 2 and 3 showed similar spectroscopic features.

Crystal Structure of 2. The X-ray diffraction analysis of 2 was performed for single crystals grown by slow diffusion of a THF solution into Et₂O at room temperature. Figure 1 illustrates the molecular structure, which adopts a typical octahedral geometry around iridium, taking the *cis*-C,C and *trans*-N,N disposition of the ppy ligands. Selected bond distances and angles are listed in Table 1. The Ir–C (2.045(5), 2.042(5) Å) and Ir–N (2.078(4), 2.072(4) Å) lengths are within the range reported for bipyridine and diphosphine analogues (1.99–2.06 Å for Ir–C, 1.98–2.08 Å for Ir–N).^{15f,17,18} On the other hand, the N–Ir–N (165.56(16)°) angle is significantly smaller than that of the related complexes, probably due to steric repulsion between the pyridine rings and the Mes* groups (C, D); the interatomic distances between the carbons C25···C57 (3.216(7) Å) and C52···C68 (3.221(7) Å) are much shorter than the sum (3.7 Å) of the effective van der Waals radii of methyl groups (2.0 Å) and the half-thickness of the π -electron cloud of aromatic rings (1.7 Å). The coordination plane A consisting of Ir, P1, C1, C4, and P2 atoms is coplanar to the cyclobutene ring B, but almost perpendicular to the Mes* rings (C and D) on the phosphorus atoms.

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Table 1. Selected Bond Distances (Å) and Angles (deg) for 2·(2THF)

Ir–P1	2.5281(13)	Ir–N1	2.078(4)
Ir–P2	2.5228(16)	Ir–N2	2.072(4)
Ir–C63	2.045(5)	P1–C1	1.682(5)
Ir–C74	2.042(5)	P2–C4	1.674(5)
C1–C4	1.494(7)	C2–C3	1.388(7)
C1–C2	1.498(7)	C2–C5	1.464(6)
C3–C4	1.475(7)	C3–C11	1.472(7)
P1–Ir–P2	81.85(5)	C1–P1–C17	106.9(2)
N1–Ir–N2	165.56(16)	C4–P2–C35	104.7(2)
C63–Ir–C74	85.54(19)		
A–B	0.74(35)	B–E	58.40(19)
A–C	85.53(11)	B–F	23.48(32)
A–D	88.44(13)		

Table 2. Electrochemical Data for 1–4^a

redox	<i>E</i> _{pa} (V) vs Fc/Fc ⁺
[1]/[1] ⁺	+1.37
[2]/[2] ⁺	+1.30
[3]/[3] ⁺	+0.92
[4]/[4] ⁺	+1.15

^a In CH₂Cl₂ (0.1 M *n*Bu₄NBF₄) at room temperature, sweep rate 50 mV s^{−1}.

The 1,2-diphenyl-3,4-diphosphinidenecyclobutene skeleton of the DPCB-H ligand notably changed bond distances upon the coordination, involving elongation of the C2–C3 bond (+0.5%) and shortening of the C1–C4 (−2.7%), C2–C5 (−0.5%), and C3–C11 (−1.0%) bonds as compared with free DPCB-H.²¹ As previously pointed out for PtMe₂(DPCB-H),³ these structural variations are attributable to the occurrence of π -back-donation from the *t*_{2g} orbitals of iridium to the π^* -orbitals of the DPCB-H ligand, while the magnitude of variation is somewhat smaller than that of the platinum complex.

Electrochemical Analysis. The cyclic voltammograms of 1–4 showed one irreversible one-electron oxidation wave in the region 0.92–1.37 V vs Fc/Fc⁺. As seen from Table 2, the oxidation potentials are sensitive to the substituent Y on the DPCB-Y ligands. Thus, the CF₃ group in 1 causes a positive shift, whereas the OMe group in 3 causes a negative shift. The large cathodic shift by 450 mV in 1 compared with 3 is ascribable to the strong electron-withdrawing nature of the CF₃ group, which induces π -back-donation from the iridium center through the π -conjugation system spread over the 1,2-diphenyl-3,4-diphosphinidenecyclobutene skeleton. On the basis of the oxidation potentials, the *t*_{2g} orbital levels are estimated to be in the order 3 > 4 > 2 > 1.

Electronic Spectra. Figure 2 shows the absorption spectra of DPCB-Y and P[^]N ligands. The DPCB-Y ligands displayed strong absorptions with a shoulder in the UV and visible regions. The absorption bands at around 330 nm are assigned to π – π^* transitions.²² As expected for π -conjugated molecules, DPCB-OMe exhibited the absorption maximum at the longest wavelength (λ_{max} = 335 (OMe), 328 (H), 329 nm (CF₃)). The P[^]N ligand showed two absorption bands at the maxima of 283 and 328 nm, which are tentatively assigned to π – π^* transitions of the pyridine and phosphalkene parts, respectively. The longer wavelength for the phosphalkene part is consistent with the previous MO calculation for phosphathene showing an extremely low-lying π^* -orbital and a moderately high-lying π -orbital across the P=C bond.³

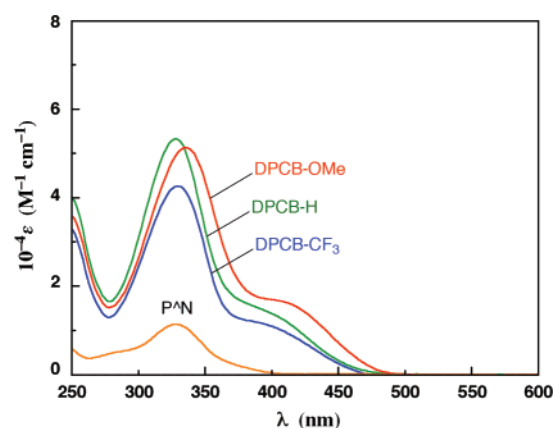
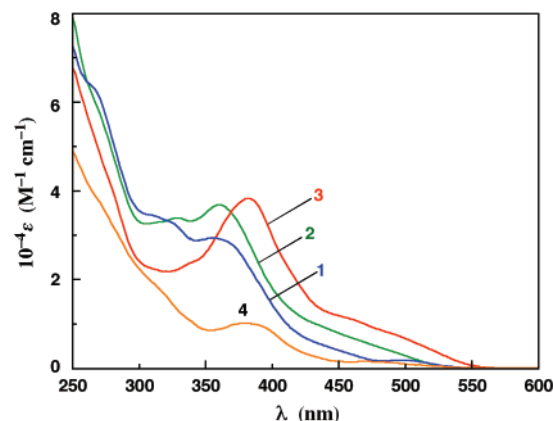
**Figure 2.** Absorption spectra of phosphalkene ligands.**Figure 3.** Absorption spectra of iridium(III) complexes 1–4.

Figure 3 compares the UV–vis spectra of 1–4. All complexes showed strong absorptions at 250–300 nm due to the spin-allowed π – π^* transitions of the ppy ligands.^{9j,14,16–19} The other π – π^* transitions arising from the phosphalkene parts were observed in the region 356–382 nm with a broad shoulder band at 400–550 nm. The latter absorptions are significantly red-shifted as compared with the corresponding free ligands, showing the occurrence of extended π -conjugation through π -back-bonding between iridium and the phosphalkenes. Since the π -back-donation should stabilize the metal *t*_{2g} orbitals, a blue-shift of the MLCT band of the Ir(ppy)₂ moiety was also expected. However, the corresponding absorption was not clearly observed due to the overlap with much stronger π – π^* transition bands.

Emission spectra of 1–4 were measured in a degassed chloroform solution at room temperature. No notable emission was observed for 2 and 3. On the other hand, 1 and 4, bearing DPCB-CF₃ and P[^]N ligands, exhibited bluish-green (λ_{em} = 492 nm, Φ_{em} = 0.02) and green (λ_{em} = 513 nm, Φ_{em} = 0.03) luminescence, respectively. The emission maxima were in significantly shorter wavelength regions than that of [Ir(ppy)₂-(bpy)]⁺ (λ_{em} = 600 nm),^{14g} and comparable to that of [Ir(ppy)₂(CN)₂][−] (λ_{em} = 470, 502 nm) and [Ir(ppy)₂(NCS)₂][−] (λ_{em} = 506, 520 nm), having electron-withdrawing ligands.¹³

Conclusion

We have synthesized a new series of cationic iridium(III) complexes bearing phosphalkene and 2-pyridylphenyl ligands and examined their electrochemical and photophysical properties. It has been confirmed that the metal *t*_{2g} levels can be tuned by chemical modification of the phosphalkene ligands. The

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DPCB- CF_3 ligand in **1** serves as a particularly effective π -acceptor to cause bluish-green luminescence at 492 nm.

Experimental Section

General Considerations. All manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques unless otherwise noted. NMR spectra were recorded on a Varian Mercury 300 spectrometer at room temperature. Chemical shifts are reported in δ , referenced to ^1H (of residual protons) and ^{13}C signals of deuterated solvents as internal standards or to the ^{31}P signal of 85% H_3PO_4 as an external standard. Elemental analysis was performed on a Perkin-Elmer 2400 II CHN analyzer. UV-vis absorption and emission spectra were recorded on JASCO V-560 and Hitachi F-2500 spectrometers, respectively. Dichloromethane was dried over CaH_2 and distilled prior to use. Diethyl ether and THF were distilled from sodium benzophenone ketyl before use. The compounds $[\text{Ir}(\text{ppy})_2(\text{H}_2\text{O})_2](\text{OTf})$,¹⁹ DPCB-Y ($\text{Y} = \text{CF}_3$, H, OMe)³ and 2-(2-pyridyl)phosphathene ($\text{P}^{\wedge}\text{N}$)²³ were synthesized by published procedures. Other chemicals were purchased and used as received.

Synthesis of $[\text{Ir}(\text{ppy})_2(\text{DPCB-}\text{CF}_3)](\text{OTf})$ (1**).** To a solution of $[\text{Ir}(\text{ppy})_2(\text{H}_2\text{O})_2](\text{OTf})$ (50.3 mg, 0.0734 mmol) in CH_2Cl_2 (2.0 mL) was added DPCB- CF_3 (65.5 mg, 0.0745 mmol) with constant stirring. The yellow solution immediately turned red. After stirring at room temperature for 2 h, volatiles were removed under reduced pressure. The residue was washed with Et_2O and hexane at 0°C and was dried under reduced pressure to give an orange powder of **1**. Yield: 104 mg (92%). Mp: 195°C . ^1H NMR (CDCl_3): δ 0.77 (s, 18H, *o*-Bu), 1.26 (s, 18H, *p*-Bu), 1.75 (s, 18H, *o*-Bu), 5.75 (d, $J_{\text{HH}} = 7.3$ Hz, 2H, ppy), 6.55 (d, $J_{\text{HH}} = 8.2$ Hz, 4H, ppy), 6.76 (t, $J_{\text{HH}} = 7.0$ Hz, 2H, ppy), 6.85 (t, $J_{\text{HH}} = 7.1$ Hz, 2H, ppy), 7.13 (s, 2H, Mes*), 7.20 (d, $J_{\text{HH}} = 8.6$ Hz, 4H, ppy), 7.47 (d, $J_{\text{HH}} = 7.0$ Hz, 2H, ppy), 7.50 (s, 2H, Mes*), 7.60 (t, $J_{\text{HH}} = 5.9$ Hz, 2H, ppy), 8.01 (d, $J_{\text{HH}} = 7.5$ Hz, 2H, ppy), 8.22 (t, $J_{\text{HH}} = 7.7$ Hz, 2H, ppy), 9.88 (d, $J_{\text{HH}} = 5.5$ Hz, 2H, ppy). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 31.0 (*p*- CMe_3), 32.7 (*o*- CMe_3), 33.5 (*o*- CMe_3), 35.1 (*p*- CMe_3), 37.3 (*o*- CMe_3), 38.3 (*o*- CMe_3), 120.8, 121.0 (q, $J_{\text{FC}} = 321$ Hz, OTf), 122.7, 123.2, 123.3 (q, $J_{\text{FC}} = 273$ Hz, CF_3), 123.5, 124.3, 125.4, 125.5, 126.1 (m), 127.7, 130.1, 131.1, 131.6, 131.9, 140.3, 142.8 (dd, $J_{\text{PC}} = 107$, 9.8 Hz, $\text{P}=\text{CC}$), 143.6, 153.7, 155.5 (dd, $J_{\text{PC}} = 56$, 36 Hz), 156.1, 157.0, 157.7, 167.5, 182.6 (t, $J_{\text{PC}} = 21$ Hz, $\text{P}=\text{C}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 130.6 (s). Anal. Calcd for $\text{C}_{77}\text{H}_{82}\text{F}_9\text{IrN}_2\text{O}_3\text{P}_2\text{S}$: C, 60.03; H, 5.36; N, 1.82. Found: C, 59.76; H, 5.22; N, 1.83.

Synthesis of $[\text{Ir}(\text{ppy})_2(\text{DPCB-H})](\text{OTf})$ (2**).** Compound **2** was synthesized as an orange powder similarly to **1**, using $[\text{Ir}(\text{ppy})_2(\text{H}_2\text{O})_2](\text{OTf})$ (50.0 mg, 0.0729 mmol), CH_2Cl_2 (2 mL), and DPCB-H (55.3 mg, 0.0732 mmol). Yield: 88.5 mg (86%). Mp: 256°C . ^1H NMR (CDCl_3): δ 0.78 (s, 18H, *o*-Bu), 1.27 (s, 18H, *p*-Bu), 1.73 (s, 18H, *o*-Bu), 5.76 (dd, $J_{\text{HH}} = 7.7$, 2.9 Hz, 2H, ppy), 6.44 (d, $J_{\text{HH}} = 7.7$ Hz, 4H, ppy), 6.74 (t, $J_{\text{HH}} = 7.7$ Hz, 2H, ppy), 6.82 (t, $J_{\text{HH}} = 7.2$ Hz, 2H, ppy), 6.91 (t, $J_{\text{HH}} = 7.9$ Hz, 4H, ppy), 7.13 (d, $J_{\text{HH}} = 2.6$ Hz, 2H, Mes*), 7.15 (t, $J_{\text{HH}} = 8.1$ Hz, 2H, ppy), 7.44 (d, $J_{\text{HH}} = 6.8$ Hz, 2H, ppy), 7.46 (s, 2H, Mes*), 7.54 (t, $J_{\text{HH}} = 6.1$ Hz, 2H, ppy), 7.99 (d, $J_{\text{HH}} = 7.1$ Hz, 2H, ppy), 8.20 (t, $J_{\text{HH}} = 7.5$ Hz, 2H, ppy), 9.93 (d, $J_{\text{HH}} = 4.9$ Hz, 2H, ppy). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 31.1 (*p*- CMe_3), 32.6 (*o*- CMe_3), 33.5 (*o*- CMe_3), 35.1 (*p*- CMe_3), 37.2 (*o*- CMe_3), 38.2 (*o*- CMe_3), 120.6, 121.0 (q, $J_{\text{FC}} = 321$ Hz, OTf), 122.4, 122.8, 123.4, 124.0, 124.1, 126.3 (m), 127.4, 128.4, 128.7, 129.9, 129.9, 131.2, 139.9, 143.4 (dd, $J_{\text{PC}} = 107$, 9.2 Hz, $\text{P}=\text{CC}$), 143.7, 153.1, 155.9, 157.1 (t, $J_{\text{PC}} = 4.3$ Hz), 157.2 (dd, $J_{\text{PC}} = 55$, 35 Hz), 157.4, 167.6 (t, $J_{\text{PC}} = 2.6$

Table 3. Crystallographic Data for **2**·(2THF)

color	red
habit	block
cryst size (mm)	$0.10 \times 0.06 \times 0.06$
formula	$\text{C}_{83}\text{H}_{100}\text{F}_3\text{IrN}_2\text{O}_5\text{P}_2\text{S}$
fw	1548.85
<i>a</i> (Å)	14.266(6)
<i>b</i> (Å)	24.292(9)
<i>c</i> (Å)	21.352(8)
β (deg)	92.193(3)
<i>V</i> (Å ³)	7394(5)
cryst syst	monoclinic
space group	<i>P</i> 21/ <i>c</i>
<i>Z</i>	4
θ range (deg)	3.03–27.48
no. of reflns collected	57 524
no. of indep reflns	16 695 [$R_{\text{int}} = 0.0882$]
completeness to θ	98.4%
goodness-of-fit on F^2	1.112
final <i>R</i> indices [$I > 2\sigma(I)$]	$R1 = 0.0604$, $wR2 = 0.1052$
<i>R</i> indices (all data)	$R1 = 0.0907$, $wR2 = 0.1165$

H), 184.1 (t, $J_{\text{PC}} = 21$ Hz, $\text{P}=\text{C}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 119.7 (s). Anal. Calcd for $\text{C}_{75}\text{H}_{84}\text{F}_3\text{IrN}_2\text{O}_3\text{P}_2\text{S}$: C, 64.13; H, 6.03; N, 1.99. Found: C, 64.48; H, 5.99; N, 2.04.

Synthesis of $[\text{Ir}(\text{ppy})_2(\text{DPCB-OMe})](\text{OTf})$ (3**).** Compound **3** was synthesized as a red powder similarly to **1**, using $[\text{Ir}(\text{ppy})_2(\text{H}_2\text{O})_2](\text{OTf})$ (50.2 mg, 0.0732 mmol), CH_2Cl_2 (2 mL), and DPCB-OMe (59.6 mg, 0.0731 mmol). Yield: 89.9 mg (84%). Mp: 197°C . ^1H NMR (CDCl_3): δ 0.79 (s, 18H, *o*-Bu), 1.30 (s, 18H, *p*-Bu), 1.72 (s, 18H, *o*-Bu), 3.72 (s, 6H, OMe), 5.76 (dd, $J_{\text{HH}} = 5.1$ Hz, 2H, ppy), 6.34 (d, $J_{\text{HH}} = 9.0$ Hz, 4H, ppy), 6.42 (d, $J_{\text{HH}} = 9.0$ Hz, 4H, ppy), 6.73 (t, $J_{\text{HH}} = 6.9$ Hz, 2H, ppy), 6.82 (t, $J_{\text{HH}} = 7.5$ Hz, 2H, ppy), 7.19 (s, 2H, Mes*), 7.44 (d, $J_{\text{HH}} = 7.5$ Hz, 2H, ppy), 7.47 (s, 2H, Mes*), 7.50 (t, $J_{\text{HH}} = 6.0$ Hz, 2H, ppy), 7.97 (d, $J_{\text{HH}} = 7.7$ Hz, 2H, ppy), 8.15 (t, $J_{\text{HH}} = 7.4$ Hz, 2H, ppy), 9.94 (d, $J_{\text{HH}} = 5.1$ Hz, 2H, ppy). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 31.2 (*p*- CMe_3), 32.6 (*o*- CMe_3), 33.5 (*o*- CMe_3), 35.1 (*p*- CMe_3), 37.3 (*o*- CMe_3), 38.3 (*o*- CMe_3), 55.2 (OMe), 114.0, 120.4, 121.0 (q, $J_{\text{FC}} = 321$ Hz, OTf), 121.2, 122.5, 122.7, 123.5, 123.9, 124.1, 126.8, 129.5, 129.9, 131.2, 139.7, 143.7, 143.8 (dd, $J_{\text{PC}} = 106$ and 8.6 Hz, $\text{P}=\text{CC}$), 153.1, 156.1, 156.3 (dd, $J_{\text{PC}} = 54$, 34 Hz), 157.3 (t, $J_{\text{PC}} = 4.3$ Hz), 157.6, 160.7, 167.8 (t, $J_{\text{PC}} = 2.9$ Hz), 184.5 (t, $J_{\text{PC}} = 20$ Hz, $\text{P}=\text{C}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 110.8 (s). Anal. Calcd for $\text{C}_{77}\text{H}_{88}\text{F}_3\text{IrN}_2\text{O}_5\text{P}_2\text{S}$: C, 63.14; H, 6.06; N, 1.91. Found: C, 63.15; H, 6.01; N, 1.67.

Synthesis of $[\text{Ir}(\text{ppy})_2(\text{P}^{\wedge}\text{N})](\text{OTf})$ (4**).** Compound **4** was synthesized as a bright orange powder similarly to **1**, using $[\text{Ir}(\text{ppy})_2(\text{H}_2\text{O})_2](\text{OTf})$ (74.7 mg, 0.109 mmol), CH_2Cl_2 (3 mL), and $\text{P}^{\wedge}\text{N}$ (41.3 mg, 0.112 mmol). Yield: 95.6 mg (86%). Mp: 184°C . ^1H NMR ($\text{THF-}d_8$): δ 0.90 (s, 9H, *o*-Bu), 1.33 (s, 9H, *p*-Bu), 1.69 (s, 9H, *o*-Bu), 5.73 (t, $J_{\text{HH}} = 6.8$ Hz, 1H), 6.34 (d, $J_{\text{HH}} = 7.6$ Hz, 1H), 6.74 (t, $J_{\text{HH}} = 7.1$ Hz, 1H), 6.82 (t, $J_{\text{HH}} = 7.8$ Hz, 1H), 6.89 (t, $J_{\text{HH}} = 7.6$ Hz, 1H), 7.01 (t, $J_{\text{HH}} = 7.4$ Hz, 1H), 7.13–7.19 (m, 1H), 7.35 (t, $J_{\text{HH}} = 6.1$ Hz, 1H), 7.42 (t, $J_{\text{HH}} = 6.5$ Hz, 1H), 7.47 (s, 1H), 7.56 (s, 1H), 7.65 (d, $J_{\text{HH}} = 7.1$ Hz, 1H), 7.80 (d, $J_{\text{HH}} = 8.0$ Hz, 1H), 7.92–8.08 (m, 5H), 8.16 (d, $J_{\text{HH}} = 3.9$ Hz, 1H), 8.18 (d, $J_{\text{HH}} = 4.1$ Hz, 1H), 8.22 (d, $J_{\text{HH}} = 5.3$ Hz, 1H), 8.81 (d, $J_{\text{PH}} = 22$ Hz, 1H, $\text{P}=\text{CH}$), 9.11 (d, $J_{\text{HH}} = 5.3$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 30.9 (*p*- CMe_3), 33.1 (*o*- CMe_3), 33.7 (*o*- CMe_3), 35.0 (*p*- CMe_3), 36.8 (*o*- CMe_3), 37.7 (*o*- CMe_3), 118.6, 119.3 (d, $J = 2.9$ Hz), 120.1, 120.7 (q, $J_{\text{FC}} = 320$ Hz, OTf), 120.7, 122.4 (d, $J = 6.3$ Hz), 122.6, 122.8, 123.0, 123.3 (d, $J = 5.8$ Hz), 123.6, 123.8, 123.9, 124.2, 124.6, 124.9 (d, $J = 5.2$ Hz), 125.4 (d, $J = 3.5$ Hz), 125.6, 125.7, 126.4, 126.6, 128.2, 129.9, 129.9, 130.3,

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131.3, 131.4 (d, $J = 6.9$ Hz), 132.6, 133.3, 134.9, 138.4, 138.7, 138.8, 139.1, 139.3, 139.9, 140.5 (d, $J = 2.9$ Hz), 142.0 (d, $J = 5.8$ Hz), 142.7, 143.1, 143.5, 144.3, 145.4, 149.0, 149.5, 150.4, 151.1, 151.8, 151.9, 152.8, 153.3, 154.3, 154.4, 155.8, 156.4, 160.5 (d, $J = 4.6$ Hz), 165.8, 166.6 (d, $J = 6.3$ Hz), 167.9, 168.5, 168.9, 204.3. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 244.3 (s). Anal. Calcd for $\text{C}_{47}\text{H}_{50}\text{F}_3\text{IrN}_3\text{O}_3\text{PS}$: C, 55.50; H, 4.95; N, 4.13. Found: C, 55.31; H, 5.21; N, 4.03.

X-ray Crystal Structure Determination of 2. The intensity data were collected on a Rigaku Mercury CCD diffractometer at 173 K with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71070$ Å). The structure was solved by DIRDIF99²⁴ and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).²⁵ All hydrogen atoms were placed using AFIX instructions, while

other atoms were refined anisotropically. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Center (CCDC No. 638281). Crystallographic data for **2**·(2THF) are summarized in Table 3.

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research on Priority Areas (No. 18064010, "Synergy of Elements") from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

Supporting Information Available: Crystallographic data for **2** in cif format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM700275S