Influence of the Bite Angle of Dianionic C,N,C-Pincer Ligands on the Chemical and Photophysical Properties of Iridium(III)- and Osmium(IV)-Hydride Complexes

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ABSTRACT: The study of the reactions of $\text{IrH}_5(\text{P}^i\text{Pr}_3)_2$ (**1**) with 2,6-diphenylpyridine and 2-phenoxy-6-phenylpyridine and the photophysical characterization of some of the resulting compounds, as well as their osmium-counterparts, reveal that the bite angle of dianionic C,N,C-pincer ligands has a marked influence on the chemical and photophysical properties of iridium(III)- and osmium(IV)-hydride complexes. Complex **1** promotes a double *o*-CH bond activation of both disubstituted pyridines. The reaction with 2,6-diphenylpyridine directly leads to $\text{IrH}\{\kappa^3\text{-C,N,C-(C}_6\text{H}_4\text{-py-C}_6\text{H}_4)\}(\text{P}^i\text{Pr}_3)_2$ (**2**), whereas the activation of 2-phenoxy-6-phenylpyridine is sequential and slower. Initially, the phenyl activation gives $\text{IrH}_2\{\kappa^2\text{-C,N-(C}_6\text{H}_4\text{-py-OPh)}\}(\text{P}^i\text{Pr}_3)_2$ (**3**), which subsequently evolves to $\text{IrH}\{\kappa^3\text{-C,N,C-(C}_6\text{H}_4\text{-py-OC}_6\text{H}_4)\}(\text{P}^i\text{Pr}_3)_2$ (**4**). Complexes **2** and **4** are Brønsted bases, which react with $\text{HBF}_4\cdot\text{OEt}_2$. The protonation of the hydride position is elusive; the proton of the acid is selectively added to one of the metalated substituents. Thus, the reaction with **2** affords $[\text{IrH}\{\kappa^3\text{-C,N,(C-H)-(C}_6\text{H}_4\text{-py-Ph)}\}(\text{P}^i\text{Pr}_3)_2]\text{BF}_4$ (**5**), in which the formed C-H bond remains coordinated. The protonation of **4** selectively occurs at the phenoxy substituent to give the five-coordinate cationic complex $[\text{IrH}\{\kappa^2\text{-C,N-(C}_6\text{H}_4\text{-py-OPh)}\}(\text{P}^i\text{Pr}_3)_2]\text{BF}_4$ (**6**) bearing a free OPh group. In contrast to **5**, complex **6** inserts acetylene and phenylacetylene into the Ir-H bond to yield $[\text{Ir}\{(E)\text{-CH=CHR}\}\{\kappa^2\text{-C,N-(C}_6\text{H}_4\text{-py-OPh)}\}(\text{P}^i\text{Pr}_3)_2]\text{BF}_4$ ($R = \text{H}$ (**7**), Ph (**8**)). Complexes **2** and **4** and their osmium(IV)-counterparts $\text{OsH}_2\{\kappa^3\text{-C,N,C-(C}_6\text{H}_4\text{-py-C}_6\text{H}_4)\}(\text{P}^i\text{Pr}_3)_2$ (**A**) and $\text{OsH}_2\{\kappa^3\text{-C,N,C-(C}_6\text{H}_4\text{-py-OC}_6\text{H}_4)\}(\text{P}^i\text{Pr}_3)_2$ (**B**) are phosphorescent emitters, which display emission wavelengths between 473 nm and 619 nm and quantum yields between 0.03 and 0.96 depending upon the metal center and the presence or absence of the oxygen atom in the pincer ligand.

INTRODUCTION

Pincer ligands are currently having a tremendous impact on the transition metal chemistry.¹ They have shown noticeable ability to stabilize a wide range of complexes,² which has allowed the discovery of uncommon compounds as the *mer*-tris(boryl) derivative $\text{Ir}(\text{Bcat})_3\{\kappa^3\text{-P,O,P-[xant(P}^i\text{Pr}_2)_2]\}$ ($\text{xant(P}^i\text{Pr}_2)_2 = 9,9\text{-dimethyl-4,5-bis(diisopropylphosphino)xanthene}$), which challenges the concept of *trans*-influence.³ Pincer ligands are flexible or rigid. The former can change their coordination mode from *mer* to *fac*, in addition to display hemilability.⁴ As a consequence, they adapt to the requirements of the different intermediates of the catalytic cycles.⁵ There are rigid ligands that cooperate with the metal undergoing reversible chemical transformations during the catalysis.⁶ Both facts have opened novel approaches to catalytic processes.⁷ The use of pincer ligands allows improving the stability and photophysical properties of phosphorescent emitters.⁸ Initially, there was the perception that these ligands should produce a reduction of the emission efficiency, due to structural distortions induced by their rigidity.⁹ Nevertheless, the increase of strength of the metal-ligand binding appears to disfavor the thermal induced quenching.¹⁰ Pincer ligands also form groupings with metals that act as a cofactor in natural enzymes.¹¹ The impressive

development of this chemistry is a direct consequence of the progressive understanding of the role that the coordination parameters of these ligands play in the stability and properties of the complexes. Between these parameters, the bite angles merit particular attention.

The bite angles favor particular coordination polyhedra around the metal center and therefore condition the stability of some oxidation states. As a proof of concept of this, it has been recently shown that the pincer ligand of the dihydride-osmium(IV) cation $[\text{OsH}_2\{\kappa^3\text{-C,N,N'-(C}_6\text{H}_4\text{-py-Mepz)}\}(\text{P}^i\text{Pr}_3)_2]^+$ ($\text{C}_6\text{H}_5\text{-py-Mepz} = 2\text{-(1-methyl-1H-2}\lambda^4\text{-pyrazol-2-yl)-6-phenylpyridine}$) imposes a *trans*-C-Os-N angle of about 150°, which favors a pentagonal bipyramid arrangement while strongly deviates from the ideal value of 180° for an octahedral structure.¹² In this way, the *trans*-C-Os-N angle stabilizes the oxidation state +4 while destabilizes the oxidation state +2 of the metal center. The difference in stability between the oxidation states is revealed by the deprotonation of the dihydride cation, which generates a neutral monohydride-osmium(II) species. The latter is unstable and evolves into a new dihydride-osmium(IV) compound (Scheme 1). The process changes the nature of the pincer from monoanionic-C,N,N' to dianionic-C,N,C'.

Scheme 2. Reactions of $\text{OsH}_6(\text{P}^i\text{Pr}_3)_2$ with 2,6-diphenylpyridine and 2-phenoxy-6-phenylpyridine¹⁴

Scheme 1. Transformation from a Monoanionic C,N,N'- to a Dianionic C,N,C'-Pincer Ligand in Osmium Complexes¹²

The bite angles of the pincer can be selectively modified by means of the introduction of fine changes in the ligand, away from the donor atoms. The introduction of an oxygen atom between the pyridine and one of the phenyl units of 2,6-diphenylpyridine gives rise to 2-phenoxy-6-phenylpyridine. In agreement with the noticeable ability of the d^2 -hexahydride $\text{OsH}_6(\text{P}^i\text{Pr}_3)_2$ to activate sigma-bonds,¹³ it reacts with both molecules to afford compressed dihydride derivatives bearing a dianionic C,N,C'-donor ligand. The difference between them has a notable chemical influence.¹⁴ While 2,6-diphenylpyridine favors the formation of osmium(IV) compounds, 2-phenoxy-6-phenylpyridine stabilizes osmium(II) elongated dihydrogen species. The derivatives of the former have also higher tendency to undergo the reductive elimination of the cyclometalated heterocycle (Scheme 2).

Osmium(IV)^{12,15} and mainly iridium(III)¹⁶ ions have proven to form efficient phosphorescent emissive molecules. Among the chromophores employed, orthometalated phenylpyridines occupy a prominent place. They generate five-membered heterometalaring with N-M-C angles of about 80°. The introduction of a spacer between the pyridine and aryl groups to form a six-membered cycle opens the N-M-C angle until about 90°. Although a few emitters of this class have been described, the effect of the aperture on the photophysical properties is not clear yet.¹⁷ We have recently reported the preparation and photophysical properties of complex $\text{Ir}\{\kappa^3\text{-N,C,N-(py-C}_6\text{HMe}_2\text{-py)}\}\{\kappa^3\text{-C,N,C'-(C}_6\text{H}_4\text{-py-OC}_6\text{H}_4)\}$ (Chart 1), bearing a dicyclopentylated 2-phenoxy-6-phenylpyridine, which gives rise to N-Ir-C angles of both 79.13(14)° and 88.56(14)°. This compound is green emissive with a quantum yield of 0.87 in a doped poly(methyl methacrylate) film.¹⁸

Chart 1. A Bis(tridentate) Ir(III) Complex with a Dicyclopentylated 2-phenoxy-6-phenylpyridine¹⁸

The d^4 -pentahydride $\text{IrH}_5(\text{P}^i\text{Pr}_3)_2$ displays a similar ability to the d^2 -hexahydride $\text{OsH}_6(\text{P}^i\text{Pr}_3)_2$ to activate C-H bonds.^{13a,19} Polyhydride-promoted C-H bond activation reactions have been revealed as a useful procedure to prepare phosphorescent emitters of both osmium²⁰ and iridium.²¹ Our interest in sigma-bond activation reactions and in the influence of the bite angles of the pincer ligands on the chemistry and the photophysical properties of their complexes, prompted us to study the reactivity of $\text{IrH}_5(\text{P}^i\text{Pr}_3)_2$ towards 2,6-diphenylpyridine and 2-phenoxy-6-phenylpyridine and to compare the emissive properties of the resulting hydride-iridium(III) complexes with those of the compressed dihydride-osmium(IV) compounds **A** and **B** shown in Scheme 2.

This paper shows that the introduction of an oxygen atom between the pyridine and one of the phenyl rings of 2,6-diphenylpyridine, to afford 2-phenoxy-6-phenylpyridine, increases the reactivity and the efficiency of iridium(III) emitters containing these ligands. However, an opposite effect is observed for osmium(IV).

RESULTS AND DISCUSSION

C-H Bond Activation Reactions. Pentahydride $\text{IrH}_5(\text{P}^i\text{Pr}_3)_2$ (**1**) promotes the *o*-CH bond activation of both substituents of 2,6-diphenylpyridine and 2-phenoxy-6-phenylpyridine. Interestingly, the rate of the C-H rupture depends upon the substituent. Thus, the phenyl activation is much faster than that of the phenoxy group.

The reaction of **1** with 2,6-diphenylpyridine in toluene under reflux leads to the monohydride-iridium(III) derivative $\text{IrH}\{\kappa^3\text{-C,N,C'-(C}_6\text{H}_4\text{-py-C}_6\text{H}_4)\}(\text{P}^i\text{Pr}_3)_2$ (**2**), which was isolated as a yellow solid in 52%, after 14 h (Scheme 3), and characterized by X-ray diffraction analysis. Figure 1 shows a view of the structure, which proves the formation of the C,N,C'-pincer

ligand as a result of a double hydride-mediated C-H bond activation. The coordination polyhedron around the iridium atom can be described as a distorted octahedron with *trans* phosphines (P(1)-Ir-P(2) = 158.78(2)°). The perpendicular plane is formed by the C,N,C-ligand, coordinated *mer* with C(1)-Ir-C(13), C(1)-Ir-N(1), and C(13)-Ir-N(1) angles of 157.14(8), 78.59(8), and 78.55(8)°, respectively, and the hydride ligand disposed *trans* to the pyridyl group of the pincer (H(01)-Ir-N(1) = 175.6(9)°). According to the presence of the hydride, the ¹H NMR spectrum of the molecule, in benzene-*d*₆, at room temperature contains at -15.38 ppm a triplet with an H-P coupling constant of 20.1 Hz. In the ¹³C{¹H} NMR spectrum, the metalated carbon atoms of the pincer display a triplet (²*J*_{C-P} = 9 Hz) at 165.2 ppm. The ³¹P{¹H} NMR spectrum shows a singlet at 4.4 ppm, in agreement with equivalent phosphines.

Scheme 3. Reaction of IrH₅(PⁱPr₃)₂ with 2,6-diphenylpyridine

Figure 1. Molecular diagram of complex **2** (ellipsoids shown at 50% probability). All hydrogen atoms (except the hydride) are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir-P(1) = 2.3371(8), Ir-P(2) = 2.3297(7), Ir-N(1) = 2.0663(18), Ir-C(1) = 2.102(2), Ir-C(13) = 2.120(2), Ir-H(01) = 1.583(10); P(1)-Ir-P(2) = 158.78(2), H(01)-Ir-N(1) = 175.6(9), C(1)-Ir-C(13) = 157.14(8), C(1)-Ir-N(1) = 78.59(8), C(13)-Ir-N(1) = 78.55(8).

The activation of both substituents of 2-phenoxy-6-phenylpyridine needs one week, under the same conditions as those employed for the activation of 2,6-diphenylpyridine. Furthermore, in contrast to the latter, the process is sequential. Initially, the phenyl activation takes place to form the dihydride intermediate IrH₂{κ²-C,N-(C₆H₄-py-OPh)}(PⁱPr₃)₂ (**3**). Spectroscopic features of **3** are: two doublets of triplets (²*J*_{H-P} = 20.4 and 18.6 Hz and ²*J*_{H-H} = 5.1 Hz) at -12.72 and -21.67 ppm, due to the hydride ligands, in the ¹H NMR spectrum; a triplet (²*J*_{C-P} = 7 Hz) at 180.3 ppm, corresponding to the metalated carbon atom, in the ¹³C{¹H} NMR spectrum; and a sin-

glet at 29.2 ppm, in the ³¹P{¹H} NMR spectrum. It subsequently evolves to the double activation product IrH{κ³-C,N,C-(C₆H₄-py-OC₆H₄)}(PⁱPr₃)₂ (**4**) releasing a hydrogen molecule (Scheme 4). Complex **4** was isolated as a bright yellow solid in 50% yield. Its ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra, in benzene-*d*₆, at room temperature agree well with those of **2**. In the ¹H NMR spectrum, the hydride resonance appears at -18.54 ppm as a triplet with an H-P coupling constant of 19.5 Hz. The ¹³C{¹H} NMR spectrum displays triplets (²*J*_{C-P} = 9 Hz) at 166.8 and 130.7 ppm for the metalated carbon atoms. The ³¹P{¹H} NMR spectrum shows a singlet at 2.1 ppm.

Scheme 4. Reaction of IrH₅(PⁱPr₃)₂ with 2-phenoxy-6-phenylpyridine

Protonation Reactions. Complexes **2** and **4** are Brønsted bases, which react with HBF₄·OEt₂, in dichloromethane, at room temperature. In both cases, the protonation of the hydride position is elusive; the proton of the acid is selectively added to one of the metalated substituents. The addition gives salts with the metal center six- or five-coordinate depending upon the presence of the oxygen atom in the pincer.

The reaction of **2** with the acid leads to [IrH{κ³-C,N,(C-H)-(C₆H₄-py-Ph)}(PⁱPr₃)₂]BF₄ (**5**), in which the formed C-H bond remains coordinated to the metal center to in this way afford a six-coordinate iridium(III) species, bearing a pincer ligand bonded to the metal through a phenyl C-H agostic bond (Scheme 5). The salt was isolated as a pale yellow solid in 88% yield and characterized by X-ray diffraction analysis. The structure, which has two cations chemically equal but crystallographically independent in the asymmetric unit (Figure 2 shows one of them), proves the selective protonation of one of the metalated phenyl groups of **2** and the coordination of the generated sigma bond. Thus, the octahedral polyhedron around the iridium(III) center resembles that of **2** with the sigma bond in the position of one of the metalated carbon atoms. The agostic interaction is strongly supported by the Ir(1)-C(13) (2.660(3) and 2.696(2) Å), Ir(1)-H(13) (1.99(3) and 2.12(3) Å), and C(13)-H(13) (1.01(3) and 0.92(3) Å) bond lengths, which compare well with those reported for other Ir-H-C agostic interactions.²² The *r*_{bp} value of 0.89 Å lies in the range corresponding to relatively strong interactions.^{14,23} The distances between the agostic C(13) atom and the metal center are 0.66-0.70 Å longer than the distances between the latter and the metalated C(1) atom (2.004(2) and 1.998(2) Å).

Scheme 5. Protonation of Complex 2

Figure 2. Molecular diagram of one of the two independent cations of **5** in the asymmetric unit (ellipsoids shown at 50% probability). All hydrogen atoms (except the hydride and the agostic hydrogen) are omitted for clarity. Selected bond distances (Å) and angles (deg) for both cations: Ir(1)-P(1) = 2.3654(6), 2.3798(6); Ir(1)-P(2) = 2.3642(7), 2.3787(6); Ir(1)-N(1) = 2.097(2), 2.1105(19); Ir(1)-C(1) = 2.004(2), 1.998(2); Ir(1)-C(13) = 2.660(3), 2.696(2); Ir(1)-H(01) = 1.574(10), 1.573(9); Ir(1)-H(13) = 1.99(3), 2.12(3); C(13)-H(13) = 1.01(3), 0.92(3); P(1)-Ir-P(2) = 159.67(2), 160.49(2); H(01)-Ir(1)-N(1) = 177.4(9), 175.4(9); C(1)-Ir(1)-C(13) = 153.69(9), 152.91(9), C(1)-Ir(1)-N(1) = 80.66(9), 80.81(9).

The agostic hydrogen atom H(13) is involved in several dynamic processes, in dichloromethane solution (Scheme 6), in agreement with that previously observed for the related (compressed dihydride)-osmium cation $[\text{OsH}_2\{\kappa^3\text{-C}_6\text{H}_4\text{py-Ph}\}(\text{P}^i\text{Pr}_3)_2]^+$ shown in Scheme 2.¹⁴ These processes are revealed by the variation of the ^1H NMR spectrum of **5** as a function of temperature (Figure 3). It exchanges its position with the free *o*-hydrogen atom of its own phenyl group. According to this, between 183 and 213 K, the spectra show a broad resonance centered at 5.76 ppm for both aromatic hydrogen atoms. The process should imply the dissociation of the sigma bond from the metal coordination sphere to afford an unsaturated five-coordinate intermediate (C), in which the free phenyl substituent of the pyridine could rotate around the pyridine-phenyl bond (a). This atom also exchanges its position with the hydride ligand. Thus, between 213 and 223 K, the above mentioned signal coalesces with the hydride resonance (δ -14.15; $^2J_{\text{H-P}} = 16.6$ Hz) to disappear under the baseline, between 223 and 313 K. The exchange could take place via a dihydride-iridium(V) species (D), which should involve the hydride ligand and the coordinated sigma C-H bond by means of a rapid equilibrium of oxidative addition-reductive

elimination (b). Furthermore, the H(13) hydrogen atom undergoes an exchange between equivalent positions of both phenyl groups when the reductive elimination in the iridium(V) intermediate implies the metalated carbon atom C(1). This process is supported by the broadening and the decrease in the number of aromatic resonances, which is also observed between 223 and 313 K (c). In contrast to the hydride ligand and the agostic hydrogen atom H(13), the phosphines are not involved in any fluxional process. In agreement with this and their equivalent character, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** shows a singlet at 15.6 ppm, which is temperature invariant between 183 and 313 K.

Figure 3. Partial view (aromatic and hydride regions) of the ^1H NMR spectrum (300 MHz, CD_2Cl_2) of **5** as a function of temperature.

Scheme 6. Exchange Processes in Complex 5

The protonation of the metalated phenoxy substituent is favored with regard to the protonation of the metalated phenyl group. Thus, complex **4** selectively adds the proton of the acid to the metalated carbon atom of the former (Scheme 7); any evidence of the protonation of the metalated phenyl substituent was not found. This is consistent with that previously observed for the related dihydride-osmium(IV) complex $\text{OsH}_2\{\kappa^3\text{-}$

C,N,*C*-(*C*₆H₄-py-OC₆H₄)}(PⁱPr₃)₂ (**B** in Scheme 2).¹⁴ Furthermore, in a similar manner to that shown in Scheme 2, but in contrast to **5**, the metal center of the resulting salt [IrH{κ²-*C,N*-(*C*₆H₄-py-OPh)}(PⁱPr₃)₂]BF₄ (**6**) does not coordinate the formed C-H bond. This low coordinating ability of the *o*-CH bonds of the phenoxy group explains why their activation is significantly slower than that of the *o*-CH bonds of the phenyl substituent (Scheme 3 *versus* Scheme 4).

Scheme 7. Protonation of Complex 4

Complex **6** was isolated as an orange solid in 84% yield and was characterized by X-ray diffraction analysis. The structure (Figure 4) proves the unsaturated character of the metal center. The coordination polyhedron around the iridium atom can be rationalized as a square pyramid with the metalated carbon atom C(1) of the phenyl substituent in the apex. At the base, the nitrogen atom of the pyridine group lies *trans* to the hydride (N(1)-Ir-H(01) = 174.0(9)°) along with the phosphines, which are also disposed *trans* (P(1)-Ir-P(2) = 164.49(19)°). The four atoms forming the base are approximately in a plane. The greatest deviation from the best plane through them is 0.11(1) Å and involves to H(01). In agreement with the presence of the hydride ligand, the ¹H NMR spectrum of the complex, in dichloromethane-*d*₂, at room temperature shows a triplet (²*J*_{H-P} = 16.4 Hz) at -14.05 ppm. In the ¹³C{¹H} NMR spectrum, the resonance corresponding to the metalated carbon atom C(1) is observed at 119.5 ppm (²*J*_{C-P} = 7 Hz). The ³¹P{¹H} NMR spectrum displays a singlet at 25.3 ppm, in accordance with the equivalence of the phosphines.

Figure 4. Molecular diagram of complex **6** (ellipsoids shown at 50% probability). All hydrogen atoms (except the hydride) are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir-P(1) = 2.3514(5), Ir-P(2) = 2.3449(5), Ir-N(1) = 2.1465(16), Ir-C(1) = 1.9803(19), Ir-H(01) = 1.45(2); P(1)-Ir-P(2) = 164.485(19); H(01)-Ir-N(1) = 174.0(9), C(1)-Ir-N(1) = 79.50(7).

Insertion Reactions. The presence or absence of an oxygen atom between the pyridine and one of the phenyl groups determine the coordination of the C-H bond formed in the protonation reactions shown in Schemes 5 and 7 and this has certainly a crucial influence in the reactivity of the resulting cations. As a consequence, there are significant differences in the behavior of **5** and **6**, which can be associated to the saturated character of the former and the unsaturated nature of the metal center of the second one. Thus, while complex **5** does not react with terminal alkynes, acetylene and phenylacetylene insert into the Ir-hydride bond of **6** to give the corresponding alkenyl derivatives [Ir{(E)-CH=CHR}{κ²-*C,N*-(*C*₆H₄-py-OPh)}(PⁱPr₃)₂]BF₄ (R = H (**7**), Ph (**8**)). These salts were isolated as orange solids in almost quantitative yield (>90%), according to Scheme 8.

Scheme 8. Insertion Reactions

The vinyl derivative **7** was characterized by X-ray diffraction analysis. The structure (Figure 5) confirmed the success of the insertion reactions. The geometry around the iridium atom resembles that of its precursor **6** with the carbon atom C(1) of the vinyl group at the position of the hydride, whereas the metalated carbon atom of the phenyl substituent of the pyridine (C(3)) remains at the apex of the pyramid. Like in **6**, the metal center and the four atoms of the vertexes of the base are approximately in a plane. The greatest deviation from the best plane through them is 0.098(1) Å and involves to P(2). The angles P(1)-Ir-P(2) and C(1)-Ir-N(1) are 171.72(3)° and 178.10(11)°, respectively. The Ir-C(1) bond length of 2.043(3) Å, which is about 0.04 Å longer than the Ir-C(3) distance of 2.000(3) Å, compares well with the Ir-alkenyl bond lengths previously reported for related compounds.^{21,24} The ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra of both **7** and **8**, in dichloromethane-*d*₂, at room temperature are consistent with the structure shown in Figure 5. In the ¹H NMR spectra, the most noticeable features are the alkenyl resonances, which appear at 9.18, 6.11, and 5.42 ppm for **7** and at 9.64 and 6.53 ppm for **8**, and the ²*J*_{H-H} value of 18.0 Hz observed in the alkenyl resonances of the latter that strongly supports an *E*-stereochemistry at the C-C double bond. The ¹³C{¹H} NMR spectra show the signal corresponding to the metalated carbon atom of the phenyl group at about 115 ppm, whereas those due to the alkenyl carbon atoms are observed at 140.1 (C_α) and 120.3 (C_β) ppm for **7** and at 133.1 (C_α) and 133.2 (C_β) ppm for **8**. The ³¹P{¹H} NMR spectra display a singlet between 5 and 6 ppm.

Table 1. Selected Experimental UV-Vis Absorptions for 2, 4, A, and B (in MeTHF) and Computed TD-DFT (in THF) Vertical Excitation Energies and their Major Contributions

complex	λ_{exp}^a (nm)	$\epsilon \times 10^{-3}$ ($\text{M}^{-1} \cdot \text{cm}^{-1}$)	excitation energy (nm)	oscillator strength, f	orbital contribution
2	240	19.6	245	0.3643	HOMO-1 $\rightarrow$ LUMO+4 (79%)
	274	15.4	283	0.1688	HOMO-4 $\rightarrow$ LUMO+1 (79%)
	354	5.3	338	0.1317	HOMO-2 $\rightarrow$ LUMO (89%)
	424	0.8	421 (S_1)	0	HOMO $\rightarrow$ LUMO (99%)
			461 (T_1)	0	HOMO-1 $\rightarrow$ LUMO+1 (65%)
					HOMO-3 $\rightarrow$ LUMO+1 (17%)
4	226	30.1	226	0.1208	HOMO-3 $\rightarrow$ LUMO+3 (38%)
					HOMO-1 $\rightarrow$ LUMO+6 (15%)
	254	26.1	259	0.1303	HOMO-3 $\rightarrow$ LUMO+1 (51%)
					HOMO $\rightarrow$ LUMO+4 (25%)
	310	8.6	311	0.1333	HOMO-3 $\rightarrow$ LUMO (92%)
	366	5.3	355	0.106	HOMO-1 $\rightarrow$ LUMO (92%)
	400	1.5	396 (S_1)	0.00029	HOMO $\rightarrow$ LUMO (99%)
			441 (T_1)	0	HOMO-1 $\rightarrow$ LUMO (36%)
A					HOMO-3 $\rightarrow$ LUMO (28%)
					HOMO $\rightarrow$ LUMO (18%)
	302	7.7	284	0.179	HOMO-3 $\rightarrow$ LUMO+1 (72%)
	314	3.1	305	0.0725	HOMO-2 $\rightarrow$ LUMO (79%)
	394	2.8	373	0.099	HOMO-1 $\rightarrow$ LUMO (63%)
	430	0.8	416	0.0273	HOMO $\rightarrow$ LUMO+1 (86%)
B	464	0.4	466 (S_1)	0.0008	HOMO $\rightarrow$ LUMO (99%)
			498 (T_1)	0	HOMO $\rightarrow$ LUMO (95%)
	272	6.6	263	0.2814	HOMO-2 $\rightarrow$ LUMO+1 (49%)
					HOMO-5 $\rightarrow$ LUMO (40%)
	292	5.7	291	0.1994	HOMO $\rightarrow$ LUMO+3 (83%)
	336	1.9	318	0.0908	HOMO-1 $\rightarrow$ LUMO+1 (63%)
	404	1.3	392	0.0782	HOMO-1 $\rightarrow$ LUMO (95%)
	462	0.4	455 (S_1)	0.0091	HOMO $\rightarrow$ LUMO (98%)
			488 (T_1)	0	HOMO $\rightarrow$ LUMO (89%)

^a Measured in 2-MeTHF with a concentration of 7.5×10^{-5} M (**2** and **4**) and 4.0×10^{-4} M (**A** and **B**) at room temperature.

Figure 5. Molecular diagram of complex **7** (ellipsoids shown at 50% probability). All hydrogen atoms (except those of the vinyl moiety) are omitted for clarity. Selected bond distances (Å) and angles (deg): Ir(1)-P(1) = 2.3930(8), Ir(1)-P(2) = 2.3943(8), Ir(1)-N(1) = 2.163(2), Ir-C(3) = 2.000(3), Ir(1)-C(1) = 2.043(3), C(1)-C(2) = 1.330(4), P(1)-Ir(1)-P(2) = 171.72(3); C(1)-Ir(1)-N(1) = 178.10(11), C(3)-Ir(1)-N(1) = 78.95(11).

Photophysical and Electrochemical Properties of 2 and 4 and their Dihydride-Osmium(IV) Counterparts. Selected UV/vis absorption data for 2-methyltetrahydrofuran (MeTHF) solutions of the molecular monohydride complexes **2** and **4** at room temperature are collected in Table 1, along with those of the dihydride-osmium(IV) counterparts $\text{OsH}_2\{\kappa^3\text{-C,N,C-(C}_6\text{H}_4\text{-py-C}_6\text{H}_4)\}(\text{P}^i\text{Pr}_3)_2$ and $\text{OsH}_2\{\kappa^3\text{-C,N,C-(C}_6\text{H}_4\text{-py-OC}_6\text{H}_4)\}(\text{P}^i\text{Pr}_3)_2$ (**A** and **B**, respectively, in Scheme 2) which are included for comparative purpose. Time dependent DFT calculations (B3LYP-GD3//SDD(f)6-31G**), performed in tetrahydrofuran as solvent were also performed in order to assign the absorptions. The spectrum of **2** (Figure S23) shows the three different zones typical of this type of compounds: <300, 300-400, >400 nm.²⁵ The absorptions of the highest energy region correspond mainly to $^1\pi\text{-}\pi^*$ intra-C,N,C-ligand transitions, whereas the bands between 300 and 400 nm are due to allowed spin metal-to-C,N,C-ligand charge transfer ($^1\text{MLCT}$) mixed with C,N,C-to-C,N,C- and phosphine-to-C,N,C-transitions. The very weak absorption tails after 400 nm are assigned to formally spin-forbidden $^3\text{MLCT}$ transitions caused by the large spin-orbit coupling introduced by the iridium center. The spectrum of **4** (Figure S24) is similar. However, the calculations suggest that the absorptions between 250 and 400 nm are $^1\text{MLCT}$ mixed with $^1\pi\text{-}\pi^*$ intra-C,N,C-ligand transitions. The spectra of **A** and **B** (Figures S25 and S26) can be rationalized similarly to that of **2**. At energies

Table 2. Electrochemical and DFT MO Energy Data for Complexes 2, 4, A, and B

complex	$E_{1/2}^{\text{ox } a}$ (V)	observed (eV)			calculated (eV)		
		HOMO ^b	E_{00}^c	LUMO ^d	HOMO ^e	LUMO ^e	HLG ^{e,f}
2	-0.02	-4.78	2.53	-2.25	-4.85	-1.02	3.83
4	0.25	-5.05	2.67	-2.38	-4.92	-1.09	3.83
A	-0.06	-4.74	2.41	-2.33	-4.56	-1.05	3.51
B	-0.09	-4.71	2.39	-2.32	-4.56	-1.11	3.45

^a Measured in CH₂Cl₂ (**2** and **B**, 1×10^{-3} M) or CH₂Cl₂-MeCN (**4** and **A**, 5×10^{-4} M)/[Bu₄N]PF₆ (0.1 M) solutions under argon, vs Fc/Fc⁺ at 0.1 V/s, at room temperature. ^b HOMO = $-[E^{\text{ox}}$ vs Fc/Fc⁺ + 4.8] eV. ^c E_{00} = onset of emission in MeTHF at rt. ^d LUMO = HOMO + E_{00} . ^e Values from electronic structure DFT calculations. ^f HLG = LUMO – HOMO.

higher than 320 nm for **A** and 290 nm for **B**, the observed bands can be assigned to ¹ π - π^* intra-C,N,C-ligand transitions, whereas in the intermediate region until about 470 nm they appear to correspond to ¹MLCT mixed with C,N,C-to-C,N,C- and phosphine-to-C,N,C-transitions. For these compounds, very weak absorption tails at energies lower than 470 nm are also observed, which are assigned to formally spin-forbidden ³MLCT transitions caused by the large spin-orbit coupling introduced by the osmium center.

The electrochemical properties of the iridium complexes **2** and **4** and the comparative osmium derivatives **A** and **B** were studied by cyclic voltammetry in 0.1 M solutions of Bu₄NPF₆ in dichloromethane or dichloromethane-acetonitrile (1:1) and referenced versus Fc/Fc⁺. The relevant data are given in Table 2. All complexes show oxidation waves; however, reduction waves are not observed within the solvents electrochemical window. The iridium complexes show a quasi-reversible oxidation peak at -0.02 V (**2**) and 0.25 V (**4**), whereas the osmium compounds exhibit quasi-reversible oxidation peaks at -0.06 V (**A**) and -0.09 V (**B**). They were assigned to metal-centered Ir^{III}/Ir^{IV} and Os^{IV}/Os^V redox couples, respectively.²⁶ The HOMO energy levels determined from the oxidation potentials are in good agreement with those obtained from DFT calculations. Similarly, the LUMO energy levels determined from the onsets of the emission spectra,²⁷ in MeTHF, at room temperature show the same trend that those obtained from DFT calculations.

Iridium complexes **2** and **4** and their osmium counterparts **A** and **B** are phosphorescent emitters upon photoexcitation, in a doped poly(methyl methacrylate) (PMMA) film at 5 wt %, at room temperature and in MeTHF at room temperature and at 77 K. Figure 6 shows the emission spectra, whereas Table 3 collects calculated and experimental wavelengths, observed lifetimes, quantum yields, and radiative and non-radiative rate constants. The observed lifetimes for the four complexes are short, lying in the range 0.3–9.9 μ s. In contrast to the lifetimes, the quantum yields and/or the emission wavelengths undergo a dramatic dependence upon the presence of the oxygen atom in the C,N,C-pincer, for both iridium and osmium.

Complex **2** is a modest emitter, which displays a broad structureless band in the green region of the spectrum (540 nm), with a quantum yield of 0.21, in PMMA. In 2-MeTHF solution, the emission is shifted toward the orange region (601 nm (298 K) and 581 nm (77 K)) keeping the quantum yield (0.23). The introduction of an oxygen atom between the pyridine ring and one of its substituents gives rise to a noticeable shift of the emission toward higher energy and a significant increase of the efficiency of the emitter. Thus, complex **4** emits in the green-blue region (544–473 nm), with quantum yields of 0.87 in PPMA and 0.96 in 2-MeTHF at room temperature. In 2-

MeTHF at 77 K, the spectrum shows vibronic fine structure in agreement with a significant contribution of ligand-centered ³ π - π^* transitions to the excited state.^{27a,28} For osmium, an opposite effect is observed. Both compounds **A** and **B** emit in the yellow region. However, while complex **A** is a notable osmium(IV) emitter, which displays quantum yields of 0.28 in PPMA and 0.56 in 2-MeTHF at room temperature, complex **B** is poorly emissive with quantum yields lower than 0.10; i.e., in the osmium case, the introduction of an oxygen atom between the pyridine ring and one of its substituents ruins the efficiency of the emitter.

Figure 6. Emission spectra of complexes **2**, **4**, **A**, and **B** recorded in 5 wt % PMMA films at 298 K (a), in MeTHF at 298 K (b), and in MeTHF at 77 K (c).

Table 3. Emission Properties of Complexes 2, 4, A, and B

complex	calc λ_{em}^a (nm)	media (T, K)	λ_{em} (nm)	λ_{exc} (nm)	τ_{obs} (μ s)	Φ	k_r^b (s^{-1})	k_{nr}^b (s^{-1})	k_r/k_{nr}
2		PMMA (298)	540	367	0.6	0.21	3.5×10^5	1.3×10^6	0.2
	562	MeTHF (298)	601	356	0.3	0.23	7.7×10^5	2.6×10^6	0.3
		MeTHF (77)	581	357	5.2				
4		PMMA (298)	481, 513, 543 (sh)	370	1.5	0.87	5.8×10^5	8.7×10^4	6.6
	488	MeTHF (298)	482, 515, 544 (sh)	367	2.0	0.96	4.8×10^5	2.0×10^4	24
		MeTHF (77)	473, 509, 538	370	6.7				
A		PMMA (298)	550, 585 (sh)	391	2.9	0.28	9.7×10^4	2.5×10^5	0.4
	565	MeTHF (298)	553, 589	393	4.1	0.56	1.4×10^5	1.1×10^5	1.2
		MeTHF (77)	532, 574, 619 (sh)	391	4.1				
B		PMMA (298)	561	405	3.3	0.08	2.4×10^4	2.8×10^5	0.08
	571	MeTHF (298)	582	402	9.9	0.03	3.0×10^3	9.8×10^4	0.03
		MeTHF (77)	540, 564	402	3.0				

^a Predicted from TD-DFT calculations in THF at 298 K by estimating the energy difference between the optimized T₁ and singlet S₀ state. ^b Calculated according to the equations $k_r = \Phi/\tau_{obs}$ and $k_{nr} = (1 - \Phi)/\tau_{obs}$, where k_r is the radiative rate constant, k_{nr} is the nonradiative rate constant, Φ is the quantum yield, and τ_{obs} is the excited-state lifetime.

The emissions can be attributed to T₁ excited states. According to this, there is good agreement between the experimental and calculated emissions by estimating the difference in energy between the optimized triplet states T₁ and the singlet states S₀ in THF. Figure 7 shows the spin-density distribution calculated for the T₁ states of the four emitters at their minimum-energy geometries. These geometries show again a marked dependence on the oxygen atom between the pyridine and a phenyl group. While for iridium it favors the octahedral geometry of the T₁ state as a consequence of the proximity of the pyridine-Ir-phenoxo angle to the ideal value of 90°, for osmium it disfavors the pentagonal bipyramidal arrangement of the T₁ state due to the deviation of the pyridine-Os-phenoxo angle from the ideal value of 72°.

Figure 7. DFT calculated spin density for the T₁ states of complexes 2, 4, A, and B at 0.002 au contour level.

CONCLUDING REMARKS

This study reinforces the key role of the bite angle of pincer ligands in the chemistry and properties of the complexes that they stabilize.

Our results reveal that the pentahydride IrH₅(PⁱPr₃)₂ promotes the pyridine-directed *o*-CH bond activation of both substituents of 2,6-diphenylpyridine and 2-phenoxy-6-phenylpyridine. The activation of the phenyl groups is faster than the activation of the phenoxy substituent as a consequence of the lower coordination ability of the *o*-CH bonds of the latter. The reactions leads to octahedral (PⁱPr₃)₂HIr(III)-complexes, which coordinate the dianionic C,N,C-pincer ligands resulting from the activations. These compounds are Brønsted bases. The position of their nucleophilic center depends upon the presence or absence of the oxygen atom between the pyridine group and one of its substituents. The protonation of the hydride position is always elusive, whereas the proton addition to the metalated carbon atom of the phenoxy group is favored with regard to the proton addition to the metalated carbon atom of the phenyl substituent. However, in contrast to the regenerated phenoxy substituent, the formed *o*-CH bond in the phenyl group remains coordinated to the metal center. This subtle difference has a crucial influence in the behavior of the resulting monohydride cationic complexes. While the compound bearing a free phenoxy substituent reacts with alkynes by insertion of the hydrocarbon into the Ir-H bond, the monohydride containing the coordinated *o*-CH phenyl bond is inert.

The molecular (PⁱPr₃)₂HIr(III)-complexes and their (PⁱPr₃)₂H₂Os(IV)-counterparts stabilized by these dianionic C,N,C-pincer ligands are phosphorescent emitters upon photoexcitation. The presence of the oxygen atom between the pyridine group and one of its substituents has a dramatic influence in the luminescence of both iridium and osmium derivatives. For iridium, the presence of the oxygen atom gives rise to the shift of the emission towards higher energies and to a significant increase of the efficiency of the emitter. For osmium, the introduction of the oxygen atom ruins the efficiency of the emitter.

In summary, the reactivity and photophysical properties of transition metal complexes bearing pincer ligands can be gov-

erned by means of the introduction of fine modifications in the latter, away from the metal center, which change some of the bite angles of the pincer.

EXPERIMENTAL SECTION

General Information. All reactions were carried out with exclusion of air using Schlenk-tube techniques or in a drybox. Instrumental methods and X-ray details are given in the Supporting Information. Complex $\text{IrH}_5(\text{P}^i\text{Pr}_3)_2$ (**1**)²⁹ and 2-phenoxy-6-phenylpyridine³⁰ were prepared by the published methods. In the NMR spectra the chemical shifts (in ppm) are referenced to residual solvent peaks (^1H , $^{13}\text{C}\{^1\text{H}\}$) or external 85% H_3PO_4 ($^{31}\text{P}\{^1\text{H}\}$). Coupling constants J and N are given in hertz.

Preparation of $\text{IrH}\{\kappa^3\text{-C}_5\text{H}_4\text{-C}(\text{C}_6\text{H}_4\text{-py-C}_6\text{H}_4)\}(\text{P}^i\text{Pr}_3)_2$ (2**).** A solution of **1** (735 mg, 1.42 mmol) and 2,6-diphenylpyridine (394 mg, 1.70 mmol) in toluene (15 mL) was heated under reflux for 14 h. Solvent was removed under reduced pressure leaving a brownish crude that was precipitated with methanol (5 mL), washed with further portions of 3 mL MeOH until liquors were pale yellow, and vacuum-dried. Yellow solid. Yield: 553 mg (52%). Anal. Calcd. for $\text{C}_{35}\text{H}_{54}\text{IrNP}_2$: C, 56.58; H, 7.33; N, 1.89. Found: C, 56.41; H, 7.41; N, 1.88. HRMS (electrospray, m/z): calcd. for $\text{C}_{35}\text{H}_{54}\text{IrNP}_2$ [$\text{M}]^+$ 743.3357, found 743.3397. IR (ATR, cm^{-1}): $\nu(\text{IrH})$ 2141 (w). ^1H NMR (300 MHz, C_6D_6 , 298 K): δ 8.10 (br d, $^3J_{\text{H-H}} = 6.9$, 2H, Ph), 7.70 (dd, $^3J_{\text{H-H}} = 7.5$, $^4J_{\text{H-H}} = 1.2$, 2H, Ph), 7.35 (d, $^3J_{\text{H-H}} = 7.8$, 2H, py), 7.20 (ddd, $^3J_{\text{H-H}} = 3J_{\text{H-H}} = 6.9$, $^4J_{\text{H-H}} = 1.2$, 2H, Ph), 7.14 (m, 3H, 1H py + 2H Ph), 2.13 (m, 6H, PCH), 0.87 (dvt, $N = 12.6$, $^3J_{\text{H-H}} = 6.3$, 36H, PCHCH₃), -15.38 (t, $^2J_{\text{H-P}} = 20.1$, 1H, IrH). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz, C_6D_6 , 298 K): δ 4.4 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, C_6D_6 , 298 K): δ 167.9 (s, C py), 165.2 (t, $^2J_{\text{C-P}} = 9$, IrC), 151.3 (s, C Ph), 142.3 (s, CH Ph), 135.7 (s, CH py), 128.9, 124.4, 120.8 (all s, CH Ph), 112.9 (s, CH py), 26.3 (vt, $N = 27$, PCH), 19.0 (s, PCHCH₃).

Reaction of **1 with 2-phenoxy-6-phenylpyridine: Spectroscopic Detection of $\text{IrH}_2\{\kappa^2\text{-C}_5\text{H}_4\text{-py-O-Ph}\}(\text{P}^i\text{Pr}_3)_2$ (**3**).** A solution of **1** (200 mg, 0.39 mmol) and 2-phenoxy-6-phenylpyridine (96 mg, 0.39 mmol) in toluene (10 mL) was refluxed for 14 hours. After this time, the solvent was evaporated. NMR spectra of the crude in C_6D_6 showed the presence of **3** and **4** in a 2:1 molar ratio. Selected spectroscopic data for **3**: ^1H NMR (300 MHz, C_6D_6 , 298 K): δ 7.47 (d, $^3J_{\text{H-H}} = 7.8$, 1H, py), 6.14 (d, $^3J_{\text{H-H}} = 7.8$, 1H, py), -12.72 (td, $^2J_{\text{H-P}} = 20.4$, $^2J_{\text{H-H}} = 5.1$, 1H, IrH), -21.67 (td, $^2J_{\text{H-P}} = 18.6$, $^2J_{\text{H-H}} = 5.1$, 1H, IrH). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz, C_6D_6 , 298 K): 29.2 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, C_6D_6 , 298 K): δ 180.3 (t, $^2J_{\text{C-P}} = 7$, IrC), 171.8 (s, C Ph), 166.2, 163.3 (both s, C py), 158.6 (s, C Ph), 137.5, 112.8, 102.9 (all s, CH py).

Preparation of $\text{IrH}\{\kappa^3\text{-C}_5\text{H}_4\text{-C}(\text{C}_6\text{H}_4\text{-py-OC}_6\text{H}_4)\}(\text{P}^i\text{Pr}_3)_2$ (4**).** A solution of **1** (440 mg, 0.85 mmol) and 2-phenoxy-6-phenylpyridine (257 mg, 1.04 mmol) in toluene (10 mL) was refluxed for 1 week. Solvent was then evaporated leaving a brown crude that was purified by column chromatography in silica gel using a mixture of pentane/dichloromethane (4:1) as eluent. Bright yellow band was collected. Evaporation of this fraction led to pure **4** as a bright yellow powder. Yield: 321 mg (50%). Anal. Calcd. for $\text{C}_{35}\text{H}_{54}\text{IrNP}_2$: C, 55.39; H, 7.17; N, 1.85. Found: C, 55.33; H, 7.38; N, 1.83. HRMS (electrospray, m/z): calcd. for $\text{C}_{35}\text{H}_{54}\text{IrNP}_2$ [$\text{M}]^+$ 759.3306, found 759.3341. IR (ATR, cm^{-1}): $\nu(\text{IrH})$ 2187 (w). ^1H NMR (300 MHz, C_6D_6 , 298 K): δ 8.25 (d, $^3J_{\text{H-H}} = 7.2$, 1H, Ph), 8.17 (d, $^3J_{\text{H-H}} = 7.1$, 1H, OPh), 7.74 (dd, $^3J_{\text{H-H}} = 8.1$, $^4J_{\text{H-H}} = 1.5$, 1H, Ph), 7.34 (d, $J_{\text{H-H}} = 8.1$, 1H, py), 7.33 (d, $^3J_{\text{H-H}} = 8.1$, 1H, py), 7.18 (dd, $^3J_{\text{H-H}} = 3J_{\text{H-H}} = 8.1$, 1H, py), 7.13-7.00 (m, 3H, 2H Ph + 1H OPh), 6.91 (ddd, $^3J_{\text{H-H}} = 3J_{\text{H-H}} = 7.1$, $^4J_{\text{H-H}} = 1.5$, 1H, OPh), 6.76 (dd, $^3J_{\text{H-H}} = 7.8$, $^4J_{\text{H-H}} = 0.9$, 1H, OPh), 1.87 (m, 6H, PCH), 0.96 (dvt, $N = 13.2$, $^3J_{\text{H-H}} = 6.6$, 18H, PCHCH₃), 0.77 (dvt, $N = 12.4$, $^3J_{\text{H-H}} = 6.6$, 18H, PCHCH₃), -18.54 (t, $^2J_{\text{H-P}} = 19.5$, 1H, IrH). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz, C_6D_6 , 298 K): δ 2.1 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, C_6D_6 , 298 K): δ 169.6 (s, C py), 166.8 (t, $^2J_{\text{C-P}} = 9$, IrC Ph), 158.7 (s, C py), 156.0 (s, C OPh), 149.9 (s, CH OPh), 147.1 (s, C Ph), 144.0 (s, CH Ph), 137.3 (s, CH py), 130.7 (t, $^2J_{\text{C-P}} = 9$, IrC OPh), 128.3, 124.6 (both s, CH Ph), 122.8, 122.7 (both s, CH OPh), 120.8 (s, C Ph), 115.4, 112.1 (both s, CH py), 109.2 (s, CH OPh), 25.8 (vt, $N = 26$, PCH), 19.7, 19.2 (both s, PCHCH₃).

Preparation of $[\text{IrH}\{\kappa^3\text{-C}_5\text{H}_4\text{-C}(\text{C}_6\text{H}_4\text{-py-Ph})\}(\text{P}^i\text{Pr}_3)_2]\text{BF}_4$ (5**).** $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (20 μL , 0.15 mmol) was added to a solution of **2** (92 mg, 0.12 mmol) in dichloromethane (5 mL). The mixture was stirred for 10 min at room temperature and then it was concentrated to ca. 0.5 mL, precipitated with diethyl ether (5 mL), washed with further portions of Et_2O (2 x 3 mL), and vacuum-dried. Pale yellow solid. Yield: 91 mg (88%). Anal. Calcd. for $\text{C}_{35}\text{H}_{55}\text{BF}_4\text{IrNP}_2$: C, 50.60; H, 6.67; N, 1.69. Found: C, 50.77; H, 6.74; N, 1.59. HRMS (electrospray, m/z): calcd. for $\text{C}_{35}\text{H}_{55}\text{IrNP}_2$ [$\text{M}]^+$ 744.3435, found 744.3442. IR (ATR, cm^{-1}): $\nu(\text{IrH})$ 2189 (w), $\nu(\text{BF}_4)$ 1047 (s). ^1H NMR (300 MHz, CD_2Cl_2 , 298 K): δ 8.10 (m, 3H, Ar), 7.35 (m, 6H, Ar), 2.05 (m, 6H, PCH), 0.95 (dvt, $N = 13.8$, $^3J_{\text{H-H}} = 7.2$, 36H, PCHCH₃). ^1H NMR (300 MHz, CD_2Cl_2 , 188 K): δ 8.09-7.94 (m, 3H, Ar), 7.65-7.45 (m, 4H, Ar), 7.03 (dd, $J_{\text{H-H}} = J_{\text{H-H}} = 7.2$, 1H, Ar), 6.94 (dd, $J_{\text{H-H}} = J_{\text{H-H}} = 7.2$, 1H, Ar), 6.85 (d, $J_{\text{H-H}} = 7.2$, 1H, Ar), 5.76 (br, 2H, *o*-Ph), 2.45 (br, 2H, PCH), 1.85-1.20 (br m, 28H, 4H PCH + 24H PCHCH₃), 0.10 (br m, 12H, PCHCH₃), -14.15 (t, $^2J_{\text{H-P}} = 16.6$, 1H, IrH). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz, CD_2Cl_2 , 298 K): δ 18.1 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, CD_2Cl_2 , 298 K): δ 161.2 (s, C Ar), 142.7 (s, C Ar), 139.4 (s, CH Ar), 131.8 (s, CH Ar), 122.7 (s, C Ar), 120.4 (s, CH Ar), 26.0 (vt, $N = 27$, PCH), 19.2 (s, PCHCH₃).

Preparation of $[\text{IrH}\{\kappa^2\text{-C}_5\text{H}_4\text{-py-O-Ph}\}(\text{P}^i\text{Pr}_3)_2]\text{BF}_4$ (6**).** A yellow solution of **4** (400 mg, 0.53 mmol) in dichloromethane (8 mL) was treated with $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (86 μL , 0.63 mmol). The color of the solution changed immediately to orange. After 10 minutes it was concentrated to ca. 0.5 mL, precipitated with diethyl ether (5 mL), washed with further portions of Et_2O (2 x 3 mL), and dried *in vacuo*. Orange solid. Yield: 375 mg (84%). Anal. Calcd. for $\text{C}_{35}\text{H}_{55}\text{BF}_4\text{IrNP}_2$: C, 49.64; H, 6.55; N, 1.65. Found: C, 49.24; H, 6.41; N, 1.64. HRMS (electrospray, m/z): calcd. for $\text{C}_{35}\text{H}_{55}\text{IrNP}_2$ [$\text{M}]^+$ 760.3384, found 760.3390. IR (ATR, cm^{-1}): $\nu(\text{IrH})$ 2222 (w), $\nu(\text{BF}_4)$ 1046 (s). ^1H NMR (300 MHz, CD_2Cl_2 , 298 K): δ 7.92 (dd, $^3J_{\text{H-H}} = 8.1$, $^3J_{\text{H-H}} = 7.8$, 1H, py), 7.81 (d, $^3J_{\text{H-H}} = 7.8$, 1H, py), 7.58 (t, $^3J_{\text{H-H}} = 7.8$, 2H, OPh), 7.49 (dd, $^3J_{\text{H-H}} = 7.8$, $^4J_{\text{H-H}} = 1.5$, 1H, Ph), 7.44 (t, $^3J_{\text{H-H}} = 7.8$, 1H, OPh), 7.16 (d, $^3J_{\text{H-H}} = 7.8$, 2H, OPh), 6.98 (m, 2H, Ph), 6.84 (ddd, $^3J_{\text{H-H}} = 3J_{\text{H-H}} = 7.8$, $^4J_{\text{H-H}} = 1.5$, 1H, Ph), 6.68 (d, $^3J_{\text{H-H}} = 8.1$, 1H, py), 2.37 (m, 6H, PCH), 1.09 (dvt, $N = 14.4$, $^3J_{\text{H-H}} = 7.2$, 18H, PCHCH₃), 0.88 (dvt, $N = 13.8$, $^3J_{\text{H-H}} = 7.2$, 18H, PCHCH₃), -14.05 (t, $^2J_{\text{H-P}} = 16.4$, 1H, IrH). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz, CD_2Cl_2 , 298 K): δ 25.3 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, CD_2Cl_2 , 298 K): δ 165.8, 162.3 (both s, C py), 152.6 (s, C OPh), 142.0 (s, CH py), 139.0 (s, C Ph), 136.8 (s, CH Ph), 131.8 (s, CH OPh), 131.1 (s, CH Ph), 127.8 (s, CH OPh), 124.8, 123.3 (both s, CH Ph), 121.1 (s, CH OPh), 119.5 (t, $^2J_{\text{C-P}} = 7$, IrC), 114.4, 106.5 (both s, CH py), 24.9 (vt, $N = 27$, PCH), 19.5, 18.8 (both s, PCHCH₃).

Preparation of $[\text{Ir}(\text{CH}=\text{CH}_2)\{\kappa^2\text{-C}_5\text{H}_4\text{-py-O-Ph}\}(\text{P}^i\text{Pr}_3)_2]\text{BF}_4$ (7**).** An orange solution of **6** (286 mg, 0.34 mmol) in 5 mL dichloromethane was stirred for 30 min under 1 atm of acetylene. The resulting reddish suspension was filtered through Celite and this solution concentrated to ca. 0.5 mL. The addition of 5 mL of diethyl ether caused the apparition of a solid that was washed with Et_2O (3 mL) and vacuum-dried. Orange solid. Yield: 265 mg (90%). Anal. Calcd. for $\text{C}_{37}\text{H}_{57}\text{BF}_4\text{IrNP}_2$: C, 50.92; H, 6.58; N, 1.60. Found: C, 50.85; H, 6.27; N, 1.60. HRMS (electrospray, m/z): calcd. for $\text{C}_{37}\text{H}_{57}\text{IrNP}_2$ [$\text{M}]^+$ 786.3541, found 786.3512. IR (ATR, cm^{-1}): $\nu(\text{BF}_4)$ 1048 (s). ^1H NMR (300 MHz, CD_2Cl_2 , 298 K): δ 9.18 (ddt, $^3J_{\text{H-H}} = 3J_{\text{H-H}} = 15.5$, $^3J_{\text{H-P}} = 1.8$, 1H, IrCH=), 7.93 (dd, $^3J_{\text{H-H}} = 8.1$, $^3J_{\text{H-H}} = 7.8$, 1H, py), 7.79 (dd, $^3J_{\text{H-H}} = 7.8$, $^4J_{\text{H-H}} = 0.6$, 1H, py), 7.60 (m, 3H, 1H Ph + 2H OPh), 7.49 (m, 2H, 1H Ph + 1H OPh), 7.17 (dd, $^3J_{\text{H-H}} = 8.4$, $^4J_{\text{H-H}} = 0.9$, 2H, OPh), 7.07 (t, ddd, $^3J_{\text{H-H}} = 3J_{\text{H-H}} = 7.2$, 1H, Ph), 7.01 (ddd, $^3J_{\text{H-H}} = 3J_{\text{H-H}} = 7.2$, $^4J_{\text{H-H}} = 2.1$, 1H, Ph), 6.76 (dd, $^3J_{\text{H-H}} = 8.1$, $^3J_{\text{H-H}} = 0.6$, 1H, py), 6.11 (br, 1H, IrCH=CH₂), 5.42 (br d, $J_{\text{H-H}} = 15.5$, 1H, IrCH=CH₂), 2.61 (m, 6H, PCH), 1.03 (dvt, $N = 13.5$, $^3J_{\text{H-H}} = 7.2$, 18H, PCHCH₃), 0.96 (dvt, $N = 13.8$, $^3J_{\text{H-H}} = 7.2$, 18H, PCHCH₃). ^1H NMR (400 MHz, CD_2Cl_2 , 263 K): δ 9.18 (ddt, $^3J_{\text{H-H}} = 18.8$, $^3J_{\text{H-H}} = 12.2$, $^3J_{\text{H-P}} = 1.5$, 1H, IrCH=), 7.90 (dd, $^3J_{\text{H-H}} = 3J_{\text{H-H}} = 8.0$, 1H, py), 7.76 (dd, $^3J_{\text{H-H}} = 8.0$, $^4J_{\text{H-H}} = 0.6$, 1H, py), 7.60 (t, $^3J_{\text{H-H}} = 8.4$, 2H, OPh), 7.54 (d, $^3J_{\text{H-H}} = 7.6$, 1H, Ph), 7.46 (m, 2H, 1H Ph + 1H OPh), 7.15 (dd, $^3J_{\text{H-H}} = 8.4$, $^4J_{\text{H-H}} = 1.0$, 2H, OPh), 7.04 (ddd, $^3J_{\text{H-H}} = 3J_{\text{H-H}} = 7.6$, 1H, Ph), 7.00 (ddd, $^3J_{\text{H-H}} = 3J_{\text{H-H}} = 7.6$, $^4J_{\text{H-H}} = 1.8$, 1H, Ph), 6.72 (dd, $^3J_{\text{H-H}} = 8.0$, $^3J_{\text{H-H}} = 0.6$, 1H, py), 6.07 (d, $^3J_{\text{H-H}} = 12.2$, 1H,

IrCH=CH₂), 5.34 (d, ³J_{H-H} = 18.8, 1H, IrCH=CH₂), 2.59 (m, 6H, PCH), 1.05 (dvt, *N* = 13.6, ³J_{H-H} = 6.9, 18H, PCHCH₃), 0.93 (dvt, *N* = 14.0, ³J_{H-H} = 7.1, 18H, PCHCH₃). ³¹P{¹H} NMR (121.49 MHz, CD₂Cl₂, 298 K): δ 5.1 (s). ¹³C{¹H} NMR (75.48 MHz, CD₂Cl₂, 298 K): δ 166.1, 162.4 (both s, C py), 152.2 (s, C OPh), 142.8 (s, C py), 140.9 (s, C Ph), 140.1 (t, ²J_{C-P} = 10, IrCH=), 134.2 (s, CH Ph), 132.0 (s, CH OPh), 130.4 (s, CH Ph), 128.0 (s, CH OPh), 125.4, 125.0 (both s, CH Ph), 121.0 (s, CH OPh), 120.3 (t, ³J_{C-P} = 3, IrCH=CH₂), 115.9 (t, ²J_{C-P} = 6, IrC), 114.7, 107.7 (both s, CH py), 23.8 (vt, *N* = 25, PCH), 20.2, 20.1 (both s, PCHCH₃).

Preparation of [Ir{(E)-CH=CHPh}{κ²-C,N-(C₆H₄-py-OPh)}(P⁺Pr₃)₂]BF₄ (8). A solution of **6** (225 mg, 0.265 mmol) in dichloromethane (5 mL) was treated with phenylacetylene (35 μL, 0.32 mmol). The color of the solution changed from orange to red-dish. After stirring for 30 min, the solvent was concentrated to ca. 0.5 mL. Diethyl ether (5 mL) was added, resulting in the precipitation of a solid that was washed with Et₂O (3 x 3 mL) and dried *in vacuo*. Orange solid. Yield: 231 mg (92%). Anal. Calcd. for C₄₃H₆₁BF₄IrNOP₂: C, 54.43; H, 6.48; N, 1.48. Found: C, 54.30; H, 6.15; N, 1.40. HRMS (electrospray, *m/z*): calcd. for C₄₃H₆₁IrNOP₂ [M]⁺ 862.3855, found 862.3826. IR (ATR, cm⁻¹): ν(BF₄) 1051 (s). ¹H NMR (300 MHz, CD₂Cl₂, 298 K): δ 9.64 (d, ³J_{H-H} = 18.0, 1H, IrCH=), 7.97 (dd, ³J_{H-H} = 8.1, ³J_{H-H} = 7.8, 1H, py), 7.84 (d, ³J_{H-H} = 7.8, 1H, py), 7.71 (d, ³J_{H-H} = 7.8, 1H, Ph), 7.61 (t, ³J_{H-H} = 7.8, 2H, OPh), 7.53 (m, 2H, 1H Ph + 1H OPh), 7.38 (m, 4H, IrC=CPh), 7.20 (m, 3H, 2H OPh + 1H IrC=CPh), 7.10 (m, 2H, Ph), 6.81 (d, ³J_{H-H} = 8.1, 1H, py), 6.53 (d, ³J_{H-H} = 18.0, 1H, IrCH=CH), 2.53 (m, 6H, PCH), 1.02 (dvt, *N* = 13.5, ³J_{H-H} = 6.9, 18H, PCHCH₃), 0.96 (dvt, *N* = 13.8, ³J_{H-H} = 6.9, 18H, PCHCH₃). ³¹P{¹H} NMR (121.49 MHz, CD₂Cl₂, 298 K): δ 6.1 (s). ¹³C{¹H} NMR (75.48 MHz, CD₂Cl₂, 298 K): δ 166.2, 162.4 (both s, C py), 152.3 (s, C OPh), 143.1 (s, CH py), 141.1 (s, C Ph), 140.7 (s, C IrC=CPh), 134.2 (s, CH Ph), 133.2 (t, ³J_{C-P} = 3, IrCH=C), 133.1 (t, ²J_{C-P} = 11, IrCH=), 132.1 (s, CH OPh), 130.6 (s, CH Ph), 129.4 (s, CH IrCH=CPh), 128.2 (s, CH OPh), 126.2 (s, CH IrCH=CPh), 125.6, 125.3 (both s, CH Ph), 125.3 (s, CH IrCH=CPh), 121.0 (s, CH OPh), 115.6 (t, ²J_{C-P} = 6, IrC), 114.9, 108.0 (both s, CH py), 23.9 (vt, *N* = 25, PCH), 20.1, 20.0 (both s, PCHCH₃).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

General information, crystallographic data, computational details, NMR spectra, experimental and computed UV/vis spectra, frontier molecular orbitals, cyclic voltammograms, normalized excitation and emission spectra (PDF)

Cartesian coordinates of the optimized structures (XYZ)

Accession Codes

CCDC 1939003-1939006 contain the crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing 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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- Emission in MeTHF at 298 K

$\Phi = 0.23$
 $\Phi = 0.96$