Formation of Dinuclear-Iridium Complexes by NHC-Supported C–H Bond Activation

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ABSTRACT: The formation of dinuclear-iridium complexes by NHC-supported aryl–CH bond activation reactions is reported. Complex $\text{IrH}_5(\text{P}^i\text{Pr}_3)_2$ (**1**) reacts with 1,3-bis(3-methylimidazolium)benzene bis(tetrafluoroborate) ($[\text{C}_6\text{H}_4(\text{HImMe})_2][\text{BF}_4]_2$) to give the dinuclear species $\{[\text{IrH}_2(\text{P}^i\text{Pr}_3)_2][\mu\text{-C}_6\text{H}_2(\text{ImMe})_2]\}$ (**2**), with a core formed by five fused rings. Complex **1** also reacts with 1,1'-diphenyl-3,3'-alkylenediimidazolium dihalides ($[(\text{CH}_2)_n(\text{HImC}_6\text{H}_5)_2]\text{X}_2$; $n = 2, 3, 4$). The reactions lead to the dinuclear complexes $\{[\text{IrH}_2(\text{P}^i\text{Pr}_3)_2][\mu\text{-(CH}_2)_n(\text{ImC}_6\text{H}_4)_2]\}$ ($n = 2$ (**3**), 3 (**4**), 4 (**5**)). These compounds can be described as two six-coordinate d^6 -iridium-dihydride metal fragments containing an orthometalated phenylimidazolylidene, which are connected through an alkylene linker. In contrast to the diimidazolium salts, 1,1'-diphenyl-3,3'-methylenedibenzimidazolium dibromide ($[\text{CH}_2(\text{HBzImC}_6\text{H}_5)_2]\text{Br}_2$) reacts with **1** to give a 1:1 mixture of the mononuclear complexes $\text{IrH}_2\text{Br}\{\kappa\text{-N'-(HBzImC}_6\text{H}_5)\}(\text{P}^i\text{Pr}_3)_2$ (**6**) and $\text{IrH}_2\{\kappa^2\text{-C,C'-(MeBzImC}_6\text{H}_4)\}(\text{P}^i\text{Pr}_3)_2$ (**7**). The latter and its analogous $\text{IrH}_2\{\kappa^2\text{-C,C'-(PhBzImC}_6\text{H}_4)\}(\text{P}^i\text{Pr}_3)_2$ (**8**) can be also obtained, as pure solids, by means of the reactions of **1** with 1-methyl-3-phenylbenzimidazolium tetrafluoroborate and 1,3-diphenylbenzimidazolium chloride, respectively.

INTRODUCTION

Applications of transition metal complexes containing N-heterocyclic carbenes (NHCs) include catalysis,¹ medicine,² or material science,³ among other fields. This fact has awakened the interest of the organometallic chemists for this family of ligands.⁴ However, they are more than stabilizing groups; recent results prove that they are also excellent directors and assistants in reactions of general interest, such as the activation of σ -bonds.⁵

The applicability of NHC groups as directors for σ -bond activation processes needs their previous coordination, while the NHC coordination occurs after the σ -bond cleavage in the NHC-assisted reactions.⁶ In both cases, the NHC-metalation requires the use of specific procedures. Without a shadow of a doubt, the cleanest method is the direct metalation of imidazolium or benzimidazolium salts.⁷

Polyhydrides of platinum group metals are a class of transition metal complexes of exceptional interest due to their ability to activate σ -bonds. This inclination allows them to interact with a wide range of fields, including those where the usage of NHCs is relevant.⁸ Furthermore, the hydride ligands are basic enough to produce the deprotonation of imidazolium and benzimidazolium salts. Thus, the d^4 -pentahydride $\text{IrH}_5(\text{PPh}_3)_2$ ⁹ (Scheme 1) and the d^2 -hexahydride $\text{OsH}_6(\text{P}^i\text{Pr}_3)_2$ ¹⁰ (Scheme 2) have shown to react with these salts to afford hydride complexes containing an NHC ligand, as a result of the direct or chelate-supported heterolytic C–H bond activation of the cation. The NHC ligand shows normal or abnormal coordination depending upon the anion and the bulkiness of

Scheme 1. Reactions of $\text{IrH}_5(\text{PPh}_3)_2$ with Imidazolium Salts

ligands resulting from the metalation of the salts collected in Chart 1, and their applicability as support for aryl C–H bond activation reactions.

RESULTS AND DISCUSSION

1,3-Bis(3-methylimidazolium)benzene. The behavior of **1** does not follow the general trend of promoting the C–H activation at position 2 of the aryl linker between the heterocycles. As a consequence, the metalation of the imidazolium groups does not give rise to a C,C,C-pincer ligand. In contrast to the expected one, the treatment of toluene solutions of **1** with 1.0 equiv of the salt **I**, in the presence of 5.0 equiv of cesium carbonate,¹⁸ under reflux, for 20 h leads to the dinuclear species $\{[\text{IrH}_2(\text{P}^i\text{Pr}_3)_2]_2[\mu\text{-C}_6\text{H}_2(\text{ImMe})_2]\}$ (**2**), as a result of the metalation of both imidazolium groups and the double C–H bond activation of the linker, at positions 4 and 6, by two different iridium centers (eq 1). In contrast to **1**, the d^2 -hexahydride $\text{OsH}_6(\text{P}^i\text{Pr}_3)_2$ reacts with the diiodide salt of the cation of **I** to afford a cationic d^4 -osmium-dihydride containing the expected C,C,C-pincer ligand (Scheme 2).^{5c} In this context, it should be pointed out that Braunstein and co-workers have shown that the directed-imidazolylidene single C–H bond activation at position 4 of the aryl linker of 1,3-bis(3-butylimidazol-2-ylidene)benzene is kinetically favored with regard to the formation of C,C,C-pincer iridium complexes, when the known dimer $[\text{Ir}(\mu\text{-Cl})(\text{COD})]_2$ is used as the starting material.¹⁹ The double C–H bond activation shown in eq 1 is notable. A similar double C–H bond activation promoted by the dimer $[\text{Ir}(\mu\text{-Cl})(\text{COD})]_2$ has been observed by Danopoulos and coworkers for the pyridine linker of 2,6-bis[3-(2,6-diisopropylphenyl)imidazolylidene]pyridine. However, in contrast to **2**, the resulting dinuclear species is highly unstable above -30°C , which has prevented its full characterization.²⁰ A double C–H bond activation as that observed for **I** has been also described for 2,6-bis[1-[(4-methylphenyl)imino]ethyl]pyridine and 1,3-bis[1-[(4-methylphenyl)imino]ethyl]benzene, which react with $\text{OsH}_6(\text{P}^i\text{Pr}_3)_2$ to give stable aromatic 1,7-diosma-2,4,6-triaza-*s*-indacene and 1,7-diosma-pyrrolo[3,4,*f*]isindole derivatives, respectively.²¹

Complex **2** was isolated as a white solid in almost quantitative yield and characterized by X-ray diffraction analysis. Figure 1 shows a view of the structure of the molecule, which proves the creation of the polycyclic system. This diiridapolycyclic core, formed by five fused rings, is almost planar. The greatest deviation from the best plane through the eighteen atoms is $0.170(2)$ Å and involves to Ir(2). In spite of the planarity, the nucleus-independent chemical shift (NICS)²² values computed at the [3+1] ring critical point (NICS(0)) are only significantly negative for the imidazolylidene rings (-9.0 and -9.4 ppm) and for the central six-membered ring (-6.8), whereas the values for the five-membered heterometalacycles (-0.3 and -1.2 ppm) are slightly negative. This suggests that only the five-membered rings of the corners and the central six-

membered ring are really aromatic units whereas the heterometalacycles show marginal aromaticity. The lack of aromaticity in the heterometalacycles is consistent with the distance between the imidazolylidene nitrogen atoms N(2) and N(3) and the C(5) and C(9) carbon atoms of the central six-membered ring ($1.423(5)$ and $1.431(5)$ Å, respectively), which are about 0.05 Å longer than the C–N bond lengths within the imidazolylidene rings ($1.360(5)$ – $1.384(6)$ Å). It should be also pointed out that both iridium-imidazolylidene bond lengths of $2.057(4)$ (Ir(1)–C(1)) and $2.053(5)$ (Ir(2)–C(11)) Å are about 0.08 Å shorter than the distances between the iridium atoms and the metalated carbon atoms of the central six-membered ring of $2.137(4)$ (Ir(1)–C(6)) and $2.132(4)$ (Ir(2)–C(8)) Å. This is in full agreement with that recently observed for d^4 -osmium-trihydride derivatives containing an orthometalated phenylimidazolylidene ligand. DFT calculations using AIM and NBO methods suggest that this is due to a significant π -backdonation from a doubly occupied $d_z(\text{M})$ atomic orbital to the p_z atomic orbital at the carbene carbon atom.^{5f} The coordination polyhedron around both iridium atoms can be rationalized as a distorted octahedron with *trans*-phosphines (P(1)–Ir(1)–P(2) = $160.37(4)^\circ$ and P(3)–Ir(2)–P(4) = $156.63(5)^\circ$) and with the hydride ligands lying in the plane of the polycycle. This donor atoms distribution gives rise to equivalent metal fragments with inequivalent hydride ligands. The ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, in benzene- d_6 , at room temperature are consistent with this. Thus, the ^1H NMR spectrum shows two hydride resonances at -13.57 and -15.00 ppm, which appear as doublet of triplets with a H–H coupling constant of 4 Hz and H–P coupling constants of 21.1 and 19.4 Hz, respectively. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the metalated carbon atoms display at 181.7 (C(1) and C(11)) and 141.1 (C(6) and C(8)) ppm triplets with C–P coupling constants of 7.0 and 5.9 Hz, respectively. The equivalent phosphines give rise to a singlet at 29.1 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum.

Figure 1. Molecular diagram of **2** (50% probability ellipsoids). Hydrogen atoms (except the hydride ligands) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir(1)–C(1) = $2.057(4)$, Ir(1)–C(6) = $2.137(4)$, Ir(2)–C(11) = $2.053(5)$, Ir(2)–C(8) = $2.132(4)$, N(1)–C(1) = $1.366(5)$, N(1)–C(3) = $1.381(6)$, N(2)–C(1) = $1.377(5)$, N(2)–C(4) = $1.373(5)$, N(2)–C(5) = $1.423(5)$, N(3)–C(9) = $1.431(5)$, N(3)–C(11) = $1.372(6)$, N(3)–C(12) = $1.384(6)$, N(4)–C(11) = $1.360(5)$, N(4)–C(13) = $1.383(7)$; P(1)–Ir(1)–P(2) = $160.37(4)$, P(3)–Ir(2)–P(4) = $156.63(5)$, C(1)–Ir(1)–C(6) = $78.03(17)$, C(8)–Ir(2)–C(11) = $78.08(17)$, C(1)–Ir(1)–H(01) = $171.3(14)$, C(6)–Ir(1)–H(02) = $177.3(14)$, C(6)–Ir(1)–H(02) = $177.3(14)$, C(11)–Ir(2)–H(04) = $172.4(15)$.

1,1'-Diphenyl-3,3'-alkylenediimidazolium. The dications with ethylene, propylene, and butylene linkers also afford dinuclear species. Treatment of toluene solutions of **1** with 1.0 equiv of 1,1'-diphenyl-3,3'-ethylenediimidazolium dibromide, 1,1'-diphenyl-3,3'-propylenediimidazolium dibromide, and 1,1'-diphenyl-3,3'-butylenediimidazolium diiodide, in the presence of 5 equiv of cesium carbonate, under reflux, for 24 h leads to the dinuclear complexes $\{[\text{IrH}_2(\text{P}^i\text{Pr}_3)_2]_2[\mu-(\text{CH}_2)_n(\text{ImC}_6\text{H}_4)_2]\}$ ($n = 2$ (**3**), 3 (**4**), 4 (**5**)), as a result of the metalation and phenyl-orthometalation of each phenylimidazolium unit of the salts, promoted by different metal centers. This generates two six-coordinate d^6 -iridium-dihydride metal fragments containing an orthometalated phenylimidazolylidene ligand, which are connected through an alkylene linker (eq 2). The formation of **3** is surprising for us, since we have recently observed that the related salt 1,1'-diphenyl-3,3'-ethylenedibenzimidazolium dibromide reacts with the d^2 -hexahydride $\text{OsH}_6(\text{P}^i\text{Pr}_3)_2$, which has similar steric requirements as **1**, to give complexes containing a $\text{C}_{\text{aryl}}\text{C}_{\text{NHC}}\text{C}_{\text{NHC}}\text{C}_{\text{aryl}}$ -tetradentate ligand, resulting from the metalation and phenyl-orthometalation of both phenylbenzimidazolium units of the salt on the same metal center (Scheme 2).¹¹ This difference in behavior between **1**, a d^4 -species, and $\text{OsH}_6(\text{P}^i\text{Pr}_3)_2$, a d^2 -species, seems to indicate that not only the steric requirement of the starting material but also the electronic properties of its metal center should be taken into account in order to rationalize the coordination fashion of the C-donor ligands resulting from the metalation of salts of type **II**.

The dinuclear character of **3–5**, which were isolated as white solids in 40–50% yield, was confirmed by means of the X-ray structure of **3**. Figure 2 shows a view of the dinuclear complex, in which the chemically and crystallographically equivalent metal fragments adopt an *anti*-disposition.²³ The coordination polyhedron around the iridium atoms can be described as a distorted octahedron with *trans*-phosphines ($\text{P}(1)\text{--Ir--P}(2) = 162.93(3)$). The perpendicular plane is formed by the C,C-chelate ligand and the hydrides. The iridium-imidazolylidene and iridium-aryl distances agree well with those of **2**. Similarly to the latter, the first of them ($\text{Ir}(\text{C}(1)) = 2.041(3)$ Å) is about 0.09 Å shorter than the second one ($\text{Ir}(\text{C}(6)) = 2.132(3)$ Å).

Figure 2. Molecular diagram of **3** (50% probability ellipsoids). Hydrogen atoms (except the hydride ligands) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): $\text{Ir--C}(1) = 2.041(3)$, $\text{Ir--C}(6) = 2.132(3)$, $\text{C}(1)\text{--N}(1) = 1.369(4)$, $\text{C}(1)\text{--N}(2) = 1.354(4)$; $\text{P}(1)\text{--Ir--P}(2) = 162.93(3)$, $\text{C}(1)\text{--Ir--C}(6) = 78.00(13)$, $\text{C}(1)\text{--Ir--H}(02) = 171.6(12)$, $\text{C}(6)\text{--Ir--H}(01) = 175.3(11)$.

The ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **3–5**, in benzene- d_6 or dichloromethane- d_2 , at room temperature are consistent with the structure shown in Figure 2. Thus, the ^1H NMR spectra show two resonances for the inequivalent hydride ligands at -14 and -15 ppm, which are observed as double triplets with a H-H coupling constant of 4 Hz and H-P coupling constants between 18 and 21 Hz. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, the metalated carbon atoms of the chelate display triplets ($^2J_{\text{C-P}} = 5\text{--}8$ Hz) at about 183 ppm (Im) and between 150 and 152 ppm (C_6H_4). The equivalent phosphines generate a singlet at around 30 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra.

1,1'-Diphenyl-3,3'-methylenedibenzimidazolium. This cation shows a different behavior to that observed for the cations of type **II** salts. In contrast to the latter, it undergoes the rupture of one of the C-N bonds between the methylene linker and one of the phenylbenzimidazolium units. Thus the treatment of toluene solutions of **1** with 1.0 equiv of 1,1'-diphenyl-3,3'-methylenedibenzimidazolium dibromide, in the presence of 5.0 equiv of cesium carbonate, under reflux, for 5 h leads to a 1:1 mixture of the mononuclear complexes $\text{IrH}_2\text{Br}\{\kappa\text{-}N\text{-(HBzImC}_6\text{H}_5)\}(\text{P}^i\text{Pr}_3)_2$ (**6**) and $\text{IrH}_2\{\kappa^2\text{-C,C-(MeBzImC}_6\text{H}_4)\}(\text{P}^i\text{Pr}_3)_2$ (**7**), according to eq 3. The low tendency of **1** to promote the formation of complexes containing chelate ligands, generated by coordination of bis-NHC groups, along with the small size of the linker between the phenylbenzimidazolium moieties could explain the behavior of **III**. The size of the linker appears to prevent the formation of a dinuclear complex related to **3–5** as a consequence of the steric hindrance experienced by the triisopropylphosphine ligands face to face coordinated at two different metal fragments.

Complexes **6** and **7** were characterized by X-ray diffraction analysis. Figure 3 shows a view of the structure of **6**, whereas Figure 4 shows a drawing of **7**. Both structures prove the mononuclear character of these compounds. The coordination polyhedron around the iridium atoms can be rationalized as a distorted octahedron with *trans*-phosphines (P(1)-Ir-P(2) = 164.86(3)° for **6** and 157.91(3)° for **7**). For **6**, the perpendicular plane is formed by the inequivalent hydrides H(01) and H(02), the bromide *trans* disposed to H(01) (Br-Ir-H(01) = 176.9(13)°) and the N-coordinate phenylbenzimidazole ligand *trans*-disposed to H(02) (N(1)-Ir-H(02) = 178.8(13)°). For **7**, the perpendicular plane is formed by the hydrides and the orthometalated phenylbenzimidazolylidene ligand, which acts with a bite angle of 77.73(13)°. The Ir-NHC and Ir-aryl distances of 2.023(3) (Ir(1)-C(1)) and 2.112(3) (Ir-C(4)) Å, respectively, agree well with the related parameters of **2** and **3**. Similarly to the latter and that observed for related d⁴-osmium-trihydride complexes with the same ligand,^{5f} the first of them is about 0.09 Å shorter than the second one.

The NMR spectra of **6** and **7**, in benzene-d₆, at room temperature are consistent with their respective structures. In agreement with the presence of two inequivalent hydride ligands in both compounds, the ¹H NMR spectra contain two high field resonances at -22.39 and -24.08 ppm for **6** and at -12.83 and -14.36 ppm for **7**, which are observed as doublet of triplets with a H-H coupling constant between 4 and 8 Hz and H-P coupling constants between 15 and 21 Hz. In the ¹³C{¹H} NMR spectrum of **7**, the metalated carbon atoms of the orthometalated phenylbenzimidazolylidene ligand give rise to triplets (²J_{C-P} = 5-7 Hz) at 198.0 (C(1)) and 151.4 (C(4)) ppm. The ³¹P{¹H} NMR spectra of both compounds show a singlet at 30 ppm.

Figure 3. Molecular diagram of **6** (50% probability ellipsoids). Hydrogen atoms (except the hydride ligands) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir-N(1) = 2.205(3), Ir-Br(1) = 2.6582(7); P(1)-Ir-P(2) = 164.86(3), Br(1)-Ir-H(01) = 176.9(13), N(1)-Ir-H(02) = 178.8(13).

Figure 4. Molecular diagram of **7** (50% probability ellipsoids). Hydrogen atoms (except the hydride ligands) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir-C(1) = 2.023(3), Ir-C(4) = 2.112(3); P(1)-Ir-P(2) = 157.91(3), C(1)-Ir-C(4) = 77.73(13), C(1)-Ir-H(02) = 170.4(12), C(4)-Ir-H(01) = 168.1(12).

Complex **7** and its analogous IrH₂{κ²-C,C-(PhBzImC₆H₄)}(PⁱPr₃)₂ (**8**) can be prepared as pure white solids, in isolated yields about 40%, by means of the reactions of **1** with 1-methyl-3-phenylbenzimidazolium tetrafluoroborate and 1,3-diphenylbenzimidazolium chloride, in the presence of cesium carbonate, in toluene, under reflux (eq 4).

The ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra of **8**, in benzene-d₆, at room temperature are in full agreement with those of **7**. In the ¹H NMR spectrum, the most noticeable resonances are the corresponding to the hydride ligands, which appear at -13.29 and -14.35 ppm as doublet (²J_{H-H} = 4.1 Hz) of triplets (²J_{H-P} = 21.5 and 19.3 Hz, respectively). In the ¹³C{¹H} NMR spectrum, the metalated carbon atoms of the chelate ligand display triplets (²J_{C-P} = 7 Hz) at 197.2 (BzIm) and 152.1 (C₆H₄) ppm. The ³¹P{¹H} NMR spectrum shows a singlet at 30.2 ppm.

CONCLUDING REMARKS

This study has revealed that the d⁴-pentahydride IrH₅(PⁱPr₃)₂ has a marked tendency to form dinuclear complexes, promoting the metalation and NHC-supported aryl-CH bond activation of arylbenzimidazolium salts. This trend is higher than its inclination to form mononuclear species containing C,C,C-pincer and C,C,C,C-tetradentate ligands.

The comparison of the behavior of this pentahydride and that previously described for the related d²-osmium-hexahydride OsH₆(PⁱPr₃)₂^{Se,f,h,11} shows noticeable differences in reactivity. Because the steric hindrance of both polyhydrides is similar, this indicates that the coordination fashion of the ligands generated from the C-H bond activation processes of the starting salts depends not only of the steric requirement of the metal fragments and

generated ligands but also of the electronic properties of the metal center of the starting complex.

The steric hindrance of the co-ligands of the metal fragment can also determine the stability of the ligands generated from the C–H bond activations of the starting salts, when the linker between the NHC moieties is very short and the metal centers are enforced to lie very close. In such case, the splitting of the bond between the linker and one of the NHC moieties can take place.

In conclusion, bis-NHC ligands can be used to promote NHC-supported aryl-CH bond activations. These processes lead to dinuclear complexes containing C,C-linker-C,C-bridge ligands or mononuclear species with C,C,C-pincer or C,C,C,C-tetradentate ligands depending upon the steric requirement of both starting complexes and salts and the electronic properties of the metal center of the starting complexes.

EXPERIMENTAL SECTION

General Information. All reactions were carried out with rigorous exclusion of air using Schlenk techniques. Solvents (except methanol that was dried and distilled under argon) were obtained oxygen- and water-free from a solvent purification apparatus. ^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a 300 or 400 MHz NMR spectrometer. Chemical shifts (expressed in parts per million) 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 ($N = {}^2J_{\text{H-P}} + {}^4J_{\text{H-P}}$ for ^1H ; $N = {}^1J_{\text{C-P}} + {}^3J_{\text{C-P}}$ for ^{13}C), are given in hertz. Attenuated total reflection infrared spectra (ATR-IR) of solid samples were run on a FT-IR spectrometer. High-resolution electrospray mass spectra were acquired using a hybrid quadrupole time-of-flight spectrometer. $\text{IrH}_2(\text{P}^i\text{Pr}_3)_2$,²⁴ 1,3-bis(3-methylimidazolium)benzene bis(tetrafluoroborate),^{5c} 1,1'-diphenyl-3,3'-ethylenediimidazolium dibromide,¹⁶ 1,1'-diphenyl-3,3'-propylenediimidazolium dibromide,¹⁶ 1,1'-diphenyl-3,3'-butylenediimidazolium diiodide,¹⁶ and 1,1-diphenyl-3,3-methylenediimidazolium dibromide,¹⁶ 1-phenyl-3-methylbenzimidazolium tetrafluoroborate,^{5f} and 1,3-diphenylbenzimidazolium chloride,²⁵ were prepared according to the published methods.

Preparation of $\{[\text{IrH}_2(\text{P}^i\text{Pr}_3)_2]_2[\mu\text{-C}_6\text{H}_2(\text{ImMe})_2]\}$ (2). Complex 1 (228 mg, 0.440 mmol), 1,3-bis(3-methylimidazolium)benzene bis(tetrafluoroborate) (184 mg, 0.440 mmol) and cesium carbonate (724 mg, 2.20 mmol) were mixed in toluene (10 mL). The resulting mixture was refluxed for 20 hours and then was cooled to room temperature. The mixture was filtered through Celite and the solvent was removed in vacuo. The addition of methanol caused the precipitation of a white solid and that was washed with methanol (3 x 3 mL) and dried in vacuo. Yield: 280 mg (99%). Suitable crystals for X-ray diffraction analysis were grown by slow diffusion of methanol into a concentrate solution of the solid in toluene at -30°C. Anal. Calcd. for $\text{C}_{50}\text{H}_{100}\text{Ir}_2\text{N}_4\text{P}_4$: C 47.45, H 7.96; N 4.43. Found: C 47.69, H 7.90, N 4.51. HRMS (electrospray, m/z): calcd for $\text{C}_{50}\text{H}_{100}\text{Ir}_2\text{N}_4\text{P}_4$ $[\text{M}+\text{H}]^+$: 1265.6208; found 1265.5364. IR (cm^{-1}): $\nu(\text{Ir-H})$ 2159 (w), 2090 (w). ^1H NMR (300 MHz, C_6D_6 , 298 K): δ 8.51 (s, 1H, Ph), 7.22 (d, ${}^3J_{\text{H-H}} = 2.0$, 2H, Im), 7.00 (s, 1H, Ph), 6.41 (d, ${}^3J_{\text{H-H}} = 2$, 2H, Im), 3.61 (s, 6H, NCH_3), 2.08 (m, 12H, $\text{PCH}(\text{CH}_3)_2$), 1.22 (dvt, $N = 12.9$, ${}^3J_{\text{H-H}} = 6.6$, 36H, $\text{PCH}(\text{CH}_3)_2$), 1.06 (dvt, $N = 12.9$, ${}^3J_{\text{H-H}} = 6.6$, 36H, $\text{PCH}(\text{CH}_3)_2$), -13.57 (td, ${}^2J_{\text{H-P}} = 21.1$, ${}^2J_{\text{H-H}} = 4.0$, 2H, Ir-H *trans* Im), -15.00 (td, ${}^2J_{\text{H-P}} = 19.5$, ${}^2J_{\text{H-H}} = 4.0$, 2H, Ir-H *trans* Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz, C_6D_6 , 298 K): δ 29.1 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, C_6D_6 , 298 K): δ 181.7 (t, ${}^2J_{\text{C-P}} = 7.0$, NCN), 159.6 (s, NCCH Ph), 144.1 (t, ${}^2J_{\text{C-P}} = 5.9$, IrC Ph), 143.5 (s, NC Ph), 117.3 (s, CH Im), 114.1 (s, CH Im), 94.6 (s, IrCCH Ph), 39.2 (s, NCH_3), 27.6 (vt, $N = 27.24$ Hz, $\text{PCH}(\text{CH}_3)_2$), 20.1 and 19.9 (both s, $\text{PCH}(\text{CH}_3)_2$).

Preparation of $\{[\text{IrH}_2(\text{P}^i\text{Pr}_3)_2]_2[\mu\text{-(CH}_2)_2(\text{ImC}_6\text{H}_4)_2]\}$ (3). Complex 1 (204 mg, 0.394 mmol), 1,1'-diphenyl-3,3'-ethylenediimidazolium dibromide (187 mg, 0.394 mmol), and cesium carbonate (640 mg, 1.964 mmol) were mixed in toluene (10 mL). The resulting mixture was refluxed for 15 h. Upon cooling to room temperature, the suspension was filtered through

Celite and the solvent was removed in vacuo. The addition of methanol caused the precipitation of a white solid that was washed with methanol (3 x 3 mL) and dried in vacuo. Yield: 112 mg (42%). X-ray quality crystals were grown by slow diffusion of methanol into a concentrate solution of the solid in toluene at -30°C. Anal. Calcd. for $\text{C}_{56}\text{H}_{104}\text{Ir}_2\text{N}_4\text{P}_4$: C, 50.13 H, 7.81; N, 4.18. Found: C, 49.92; H, 7.76, N, 3.77. HRMS (electrospray, m/z): calcd for $\text{C}_{56}\text{H}_{103}\text{Ir}_2\text{N}_4\text{P}_4$ $[\text{M} - \text{H}]^+$ 1341.6388; found 1341.6110. IR (cm^{-1}): $\nu(\text{Ir-H})$ 2028(w), 1993(m), 1970(w). ^1H NMR (400 MHz, C_6D_6 , 298 K): δ 8.33 (m, 2H, CH Ph), 7.22 (d, ${}^3J_{\text{H-H}} = 2.1$, 2H, Im), 7.16 (m, 6H, Ph), 7.12 (d, ${}^3J_{\text{H-H}} = 2.1$, 2H, Im), 5.00 (s, 4H, NCH_2), 1.97 (m, 12H, $\text{PCH}(\text{CH}_3)_2$), 1.10 (dvt, $N = 13.0$, ${}^3J_{\text{H-H}} = 6.7$, 36H, $\text{PCH}(\text{CH}_3)_2$), 0.97 (dvt, $N = 12.7$, ${}^3J_{\text{H-H}} = 6.6$, 36H, $\text{PCH}(\text{CH}_3)_2$), -13.50 (td, 2H, ${}^2J_{\text{H-P}} = 20.9$, ${}^2J_{\text{H-H}} = 4.0$ Ir-H *trans* Im), -14.56 (td, 2H, ${}^2J_{\text{H-P}} = 18.7$, ${}^2J_{\text{H-H}} = 4.0$, Ir-H *trans* Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.98 MHz, C_6D_6 , 298 K): δ 29.8 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.63 MHz, C_6D_6 , 298 K): δ 183.6 (br NCN), 149.7 (t, ${}^2J_{\text{C-P}} = 7.5$, IrC Ph), 149.5 (s, NC Ph), 144.8 (s, CH Ph), 124.3 (s, CH Ph), 120.2 (s, CH Ph), 116.6 (s, CH Im), 115.9 (s, CH Im), 110.3 (s, CH Ph), 51.5 (s, NCH_2), 27.4 (vt, $N = 28.1$ Hz, $\text{PCH}(\text{CH}_3)_2$), 20.1 and 19.4 (both s, $\text{PCH}(\text{CH}_3)_2$).

Preparation of $\{[\text{IrH}_2(\text{P}^i\text{Pr}_3)_2]_2[\mu\text{-(CH}_2)_3(\text{ImC}_6\text{H}_4)_2]\}$ (4). Complex 1 (174 mg, 0.336 mmol), 1,1'-diphenyl-3,3'-propylenediimidazolium dibromide (165 mg, 0.336 mmol) and cesium carbonate (547 mg, 1.68 mmol) were mixed in toluene (10 mL). The resulting mixture was refluxed for 24 h and then was cooled to room temperature. The mixture was filtered through Celite and the solvent was removed in vacuo. The addition of methanol caused the precipitation of a white solid that was washed with methanol (3 x 3 mL) and dried in vacuo. Yield: 110 mg (48%). Anal. Calcd for $\text{C}_{57}\text{H}_{106}\text{Ir}_2\text{N}_4\text{P}_4$ (C_7H_8): C 53.1, H 7.94, N 3.87. Found: C 52.71, H 7.92, N 3.77. HRMS (electrospray, m/z): calcd for $\text{C}_{57}\text{H}_{107}\text{Ir}_2\text{N}_4\text{P}_4$ $[\text{M} + \text{H}]^+$ 1355.6678; found 1355.6545. IR (cm^{-1}): $\nu(\text{Ir-H})$ 2083 (w), 1951 (m). ^1H NMR (300 MHz, CD_2Cl_2 , 298 K): δ 7.86 (d, ${}^3J_{\text{H-H}} = 7.0$, 2H, Ph), 7.50 (d, ${}^3J_{\text{H-H}} = 1.8$, 2H, Im), 7.09 (d, ${}^3J_{\text{H-H}} = 7.0$, 2H, Ph), 6.98 (d, ${}^3J_{\text{H-H}} = 1.8$, 2H, Im), 6.88 (dd, ${}^3J_{\text{H-H}} = 7.0$, ${}^3J_{\text{H-H}} = 7.0$, 2H, CH Ph), 6.71 (dd, ${}^3J_{\text{H-H}} = 7.0$, ${}^3J_{\text{H-H}} = 7.0$, 2H, Ph), 4.45 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 2.35 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 1.89 (m, 12H, $\text{PCH}(\text{CH}_3)_2$), 0.97 (dvt, $N = 13.5$, ${}^3J_{\text{H-H}} = 6.7$, 36H, $\text{PCH}(\text{CH}_3)_2$), 0.92 (dvt, $N = 13.4$, ${}^3J_{\text{H-H}} = 6.7$, 36H, $\text{PCH}(\text{CH}_3)_2$), -13.93 (td, ${}^2J_{\text{H-P}} = 20.8$, ${}^2J_{\text{H-H}} = 3.8$, 2H, Ir-H *trans* Im), -14.96 (td, 2H, ${}^2J_{\text{H-P}} = 19.2$, ${}^2J_{\text{H-H}} = 3.1$, Ir-H *trans* Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz, CD_2Cl_2 , 298 K): δ 29.6 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, CD_2Cl_2 , 298 K): δ 183.2 (t, ${}^2J_{\text{C-P}} = 5.8$, NCN), 151.6 (t, ${}^2J_{\text{C-P}} = 7.4$, IrC Ph), 150.0 (s, NC Ph), 145.30 (s, CH Ph), 123.8 (s, CH Ph), 119.6 (s, CH Ph), 117.1 (s, CH Im), 115.9 (s, CH Im), 110.1 (s, CH Ph), 50.6 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 31.2 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 27.8 (vt, $N = 28.1$ Hz, $\text{PCH}(\text{CH}_3)_2$), 20.3 and 19.8 (both s, $\text{PCH}(\text{CH}_3)_2$).

Preparation of $\{[\text{IrH}_2(\text{P}^i\text{Pr}_3)_2]_2[\mu\text{-(CH}_2)_4(\text{ImC}_6\text{H}_4)_2]\}$ (5). This compound was prepared as described for 4, starting from 1 (187 mg, 0.363 mmol), 1,1'-diphenyl-3,3'-butylenediimidazolium diiodide (217 mg, 0.363 mmol), and cesium carbonate (591 mg, 1.815 mmol). An off-white solid was obtained. Yield: 116 mg (47%). Anal. Calcd for $\text{C}_{58}\text{H}_{108}\text{Ir}_2\text{N}_4\text{P}_4$ C, 50.80; H, 7.96; N, 4.10. Found: C, 50.84; H, 7.34; N, 4.60. HRMS (electrospray, m/z): calcd for $\text{C}_{58}\text{H}_{107}\text{Ir}_2\text{N}_4\text{P}_4$ $[\text{M} - \text{H}]^+$ 1369.6701; found 1369.6686. IR (cm^{-1}): $\nu(\text{Ir-H})$ 1951 (br). ^1H NMR (400 MHz, CD_2Cl_2 , 298 K): δ 7.86 (d, ${}^3J_{\text{H-H}} = 7.5$, 2H, Ph), 7.49 (d, ${}^3J_{\text{H-H}} = 2.1$, 2H, Im), 7.08 (dd, ${}^3J_{\text{H-H}} = 7.5$, ${}^4J_{\text{H-H}} = 1.2$, 2H, Ph), 7.01 (d, ${}^3J_{\text{H-H}} = 2.1$, 2H, Im), 6.86 (ddd, 2H, ${}^3J_{\text{H-H}} = 7.5$, ${}^3J_{\text{H-H}} = 7.5$, ${}^4J_{\text{H-H}} = 1.2$ CH Ph), 6.69 (ddd, ${}^3J_{\text{H-H}} = 7.5$, ${}^3J_{\text{H-H}} = 7.5$, ${}^4J_{\text{H-H}} = 1.2$, 2H, Ph), 4.36 (br t, ${}^3J_{\text{H-H}} = 7.3$, 4H, NCH_2CH_2), 1.98 (m, 4H, NCH_2CH_2), 1.86 (m, 12H, $\text{PCH}(\text{CH}_3)_2$), 0.95 (dvt, $N = 13.2$, ${}^3J_{\text{H-H}} = 7.0$, 36H, $\text{PCH}(\text{CH}_3)_2$), 0.90 (dvt, $N = 12.8$, ${}^3J_{\text{H-H}} = 6.8$, 36H, $\text{PCH}(\text{CH}_3)_2$), -13.99 (td, ${}^2J_{\text{H-P}} = 20.7$, ${}^2J_{\text{H-H}} = 3.9$, 2H, Ir-H *trans* Im), -14.99 (td, ${}^2J_{\text{H-P}} = 18.5$, ${}^2J_{\text{H-H}} = 3.9$, 2H, Ir-H *trans* Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.98 MHz, CD_2Cl_2 , 298 K): δ 29.8 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.63 MHz, CD_2Cl_2 , 298 K): δ 182.7 (t, ${}^2J_{\text{C-P}} = 5.9$, NCN), 151.8 (t, ${}^2J_{\text{C-P}} = 7.0$, IrC Ph), 150.0 (s, NC Ph), 145.2 (s, CH Ph), 123.6 (s, CH Ph), 119.5 (s, CH Ph), 117.0 (s, CH Im), 115.7 (s, CH Im), 110.0 (s, CH Ph), 52.5 (s, NCH_2CH_2), 28.2 (s, NCH_2CH_2), 27.6 (vt, $N = 28.0$ Hz, $\text{PCH}(\text{CH}_3)_2$), 20.3 and 19.8 (both s, $\text{PCH}(\text{CH}_3)_2$).

Reaction of $\text{IrH}_5(\text{P}^i\text{Pr}_3)_2$ (1**) with **1**, 1'-Diphenyl-3,3'-methylenedibenzimidazolium dibromide: Formation of $\text{IrH}_2\text{Br}\{\kappa\text{-N'-(HBzImC}_6\text{H}_3)\}(\text{P}^i\text{Pr}_3)_2$ (**6**) and $\text{IrH}_2\{\kappa^2\text{-C,C'-(MeBzImC}_6\text{H}_4)\}(\text{P}^i\text{Pr}_3)_2$ (**7**).** Complex **1** (150 mg, 0.289 mmol) was mixed with 1,1'-diphenyl-3,3'-methylenedibenzimidazolium dibromide (163 mg, 0.289 mmol) and cesium carbonate (472 mg, 1.45 mmol) in toluene. The resulting mixture was refluxed for 5 h, and then was cooled to room temperature. The mixture was filtered through Celite and the solvent was removed in vacuo. The addition of methanol caused the precipitation of a yellow solid that was washed with methanol (3 x 3 mL) and dried in vacuo. The solid was a 1:1 mixture of **6** and **7** (51 mg). Two types of colorless crystals were grown in methanol at -30°C , corresponding to **6** and **7**, which were manually separated. Analytical and spectroscopic data for **6**: Anal. Calcd for $\text{C}_{31}\text{H}_{34}\text{BrIrN}_2\text{P}_2$: C 47.20; H 6.90; N 3.55. Found: C 47.20, H 6.76, N 3.68. HRMS (electrospray, m/z): calculated for $\text{C}_{18}\text{H}_{22}\text{IrP}_2$: 513.2386 $[\text{Ir}(\text{P}^i\text{Pr}_3)_2]^+$ found 513.2484. $\nu(\text{Ir-H})$ 2223(w), 2199(m). ^1H NMR (300 MHz, C_6D_6 , 298 K): δ 10.52 (s, 1H, NCHN), 8.32 (d, 1H, $^3J_{\text{H-H}} = 8.3$, Ph), 7.23 (m, 4H, BzIm), 6.98 (m, 4H, Ph), 2.25 (m, 6H, $\text{PCH}(\text{CH}_3)_2$), 1.38 (dvt, $N = 13.7$, 18H, $^3J_{\text{H-H}} = 6.4$, $\text{PCH}(\text{CH}_3)_2$), 1.05 (dvt, $N = 12.5$, $^3J_{\text{H-H}} = 6.4$, 18H, $\text{PCH}(\text{CH}_3)_2$), -22.39 (td, $^2J_{\text{H-P}} = 16.9$, $^2J_{\text{H-H}} = 7.3$, 1H, Ir-H), -24.08 (td, $^2J_{\text{H-P}} = 15.4$, $^2J_{\text{H-H}} = 7.3$, 1H, Ir-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.50 MHz, C_6D_6 , 298 K): δ 30.37 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, C_6D_6 , 298 K): δ 150.4 (s, C BzIm), 144.9 (s, NCHN), 144.4 (s, C BzIm), 133.4 (s, C Ph), 130.4 (s, 2CH Ph), 124.6 (s, CH BzIm), 123.7 (s, 2CH Ph), 122.8 (s, CH BzIm), 122.4 (s, 2CH BzIm), 111.3 (s, CH Ph), 24.6 (vt, $N = 26.4$ Hz, $\text{PCH}(\text{CH}_3)_2$), 21.2 and 19.7 (both s, $\text{PCH}(\text{CH}_3)_2$). For analytical and spectroscopic data for **7**, see below.

Preparation of $\text{IrH}_2\{\kappa^2\text{-C,C'-(MeBzImC}_6\text{H}_4)\}(\text{P}^i\text{Pr}_3)_2$ (7**):** Complex **1** (150 mg, 0.289 mmol), 1-methy-3-phenylbenzimidazolium tetrafluoroborate (87 mg, 0.289 mmol), and cesium carbonate (472 mg, 1.45 mmol) were mixed in toluene (10 mL). The resulting mixture was refluxed for 24 h and then was cooled to room temperature. The mixture was filtered through Celite and the solvent was removed in vacuo. The addition of methanol caused the precipitation of a white solid that was washed with further portions of methanol (3 x 3 mL) and dried in vacuo. Yield: 84 mg (40%). Anal. Calcd for $\text{C}_{32}\text{H}_{35}\text{IrN}_2\text{P}_2$: C 53.20; H 7.69; N 3.88. Found: C 53.24, H 7.90, N 3.48. HRMS (electrospray, m/z): calculated for $\text{IrP}_2\text{N}_2\text{C}_{32}\text{H}_{34} [\text{M} - \text{H}]^+$ 721.3387; found 721.3434. IR (cm^{-1}): $\nu(\text{Ir-H})$ 2068 (w), 1951 (w). ^1H NMR (300 MHz, C_6D_6 , 298 K): δ 8.39 (d, $^3J_{\text{H-H}} = 7.4$, 1H, Ph), 7.93 (m, 1H, BzIm), 7.89 (d, $^3J_{\text{H-H}} = 7.4$, 1H, CH Ph), 7.27 (ddd, $^3J_{\text{H-H}} = 7.4$, $^3J_{\text{H-H}} = 7.4$, $^4J_{\text{H-H}} = 1.7$, 1H, Ph), 7.21 (ddd, $^3J_{\text{H-H}} = 7.4$, $^3J_{\text{H-H}} = 7.4$, $^4J_{\text{H-H}} = 1.7$, 1H, Ph), 7.05 (m, 2H, CH BzIm), 6.96 (m, 1H, CH BzIm), 3.87 (s, 3H, NCH_3), 1.93 (m, 6H, $\text{PCH}(\text{CH}_3)_2$), 1.03 (dvt, $N = 13.3$, $^3J_{\text{H-H}} = 6.9$, 18H, $\text{PCH}(\text{CH}_3)_2$), 0.87 (dvt, $N = 13.5$, $^3J_{\text{H-H}} = 6.9$, 18H, $\text{PCH}(\text{CH}_3)_2$), -12.83 (td, $^2J_{\text{H-P}} = 21.2$, $^2J_{\text{H-H}} = 4.0$, 1H, Ir-H), -14.36 (td, $^2J_{\text{H-P}} = 19.0$, $^2J_{\text{H-H}} = 4.0$, 1H, Ir-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, C_6D_6 , 298 K): δ 30.39 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.63 MHz, C_6D_6 , 298 K): δ 198.0 (t, $^2J_{\text{C-P}} = 5.0$, NCN), 151.7 (s, NC Ph), 151.4 (t, $^2J_{\text{C-P}} = 7.1$, IrC Ph), 145.0 (s, Ph), 136.4 (s, C BzIm), 134.0 (s, C BzIm), 124.1 (s, CH Ph), 122.4 (s, CH BzIm), 121.5 (s, CH BzIm), 120.5 (s, CH Ph), 112.5 (s, CH Ph), 110.9 (s, CH BzIm), 109.4 (s, CH BzIm), 37.4 (s, NCH₃), 27.7 (vt, $N = 28.4$ Hz, $\text{PCH}(\text{CH}_3)_2$), 20.1 and 19.5 (both s, $\text{PCH}(\text{CH}_3)_2$).

Preparation of $\text{IrH}_2\{\kappa^2\text{-C,C'-(PhBzImC}_6\text{H}_4)\}(\text{P}^i\text{Pr}_3)_2$ (8**):** Complex **1** (148 mg, 0.286 mmol), 1,3-diphenylbenzimidazolium chloride (87.7 mg, 0.286 mmol) and cesium carbonate (466 mg, 1.43 mmol) were mixed with in toluene (10 mL). The resulting mixture was refluxed for 15 h and then was cooled to room temperature. The mixture was filtered through Celite and the solvent was removed in vacuo. The addition of methanol caused the precipitation of a white solid and that was washed with methanol (3 x 3 mL) and dried in vacuo. Yield: 78 mg (35%). Anal. Calcd for $\text{C}_{37}\text{H}_{37}\text{IrN}_2\text{P}_2$ (CH_3OH): C 55.93; H 7.53; N 3.43. Found: C 55.02, H 7.36, N 3.51. HRMS (electrospray, m/z): calculated for $\text{C}_{37}\text{H}_{36}\text{IrN}_2\text{P}_2 [\text{M} - \text{H}]^+$ 783.3544; found 783.3567. IR (cm^{-1}): $\nu(\text{Ir-H})$ 2071 (w), 1976 (m). ^1H NMR (400 MHz, C_6D_6 , 298 K): δ 8.39 (d, $^3J_{\text{H-H}} = 7.1$, 1H, Ph-Ir), 8.06 (d, $^3J_{\text{H-H}} = 8.0$, 1H, BzIm), 8.03 (d, $^3J_{\text{H-H}} = 7.6$, 1H, Ph-Ir), 7.78 (d, $^3J_{\text{H-H}} = 7.3$, 2H, free Ph), 7.31 (ddd, $^3J_{\text{H-H}} = 7.6$, $^3J_{\text{H-H}} = 7.6$, $^4J_{\text{H-H}} = 1.6$, 1H, Ph-Ir), 7.24 (m, 3H, free Ph + BzIm + Ph-Ir), 7.14 (m, 2H, free Ph), 7.07 (ddd, $^3J_{\text{H-H}} =$

8.0, $^3J_{\text{H-H}} = 8.0$, $^4J_{\text{H-H}} = 1.3$, 1H, BzIm), 6.95 (ddd, $^3J_{\text{H-H}} = 7.6$, $^3J_{\text{H-H}} = 7.6$, $^4J_{\text{H-H}} = 1.0$, 1H, BzIm), 1.96 (m, 6H, $\text{PCH}(\text{CH}_3)_2$), 0.98 (dvt, $N = 13.6$, $^3J_{\text{H-H}} = 6.7$, 18H, $\text{PCH}(\text{CH}_3)_2$), 0.79 (dvt, $N = 12.9$, $^3J_{\text{H-H}} = 6.7$, 18H, $\text{PCH}(\text{CH}_3)_2$), -13.29 (td, $^2J_{\text{H-P}} = 21.5$, $^2J_{\text{H-H}} = 4.1$, 1H, Ir-H), -14.354 (td, $^2J_{\text{H-P}} = 19.3$, $^2J_{\text{H-H}} = 4.1$, 1H, Ir-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.98 MHz, C_6D_6 , 298 K): δ 30.2 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.63 MHz, C_6D_6 , 298 K): δ 197.2 (t, $^2J_{\text{C-P}} = 6.7$, NCN), 152.1 (t, $^2J_{\text{C-P}} = 7.5$ IrC Ph), 151.4 (s, NC Ph-Ir), 145.2 (s, CH Ph-Ir), 140.3 (s, NC free Ph), 137.5 (s, C BzIm), 134.2 (s, C BzIm), 128.8 (s, 2CH free Ph), 128.6 (s, 2CH free Ph), 127.7 (s, CH BzIm), 124.3 (s, CH Ph-Ir), 123.0 (s, CH BzIm), 121.8 (s, CH BzIm), 120.5 (s, CH Ph-Ir), 112.9 (s, CH free Ph), 111.1 (s, CH BzIm), 110.9 (s, CH Ph-Ir), 27.6 (vt, $N = 28.3$ Hz, $\text{PCH}(\text{CH}_3)_2$), 20.3 and 19.3 (both s, $\text{PCH}(\text{CH}_3)_2$).

Structural Analysis of **2, **3**, **6**, and **7**.** X-ray data were collected on a Bruker Smart APEX CCD DUO diffractometer. Data were collected using monochromated Mo K α radiation ($\lambda = 0.71073$ Å) in the ω -scan mode. The crystals were mounted in inert oil on a glass fiber and transferred to the cold gas stream of the diffractometer. Data were collected over the complete sphere and were corrected for absorption by using a multiscan method applied with the SADABS program.²⁷ The structures were solved by Patterson or direct methods and refined by full-matrix least squares on F^2 with SHELXL97,²⁸ including isotropic and subsequently anisotropic displacement parameters. The hydrogen atoms (except hydrides) were observed in the Fourier Maps or calculated, and refined freely or using a restricted riding model. The hydrogen bonded to metal atoms were observed in the last cycles of refinement but refined too close to metals, so a restricted refinement model was used for all of them ($d(\text{Ir-H}) = 1.59(1)$ Å).

Crystal data for **2:** $\text{C}_{50}\text{H}_{100}\text{Ir}_2\text{N}_4\text{P}_4 \cdot \frac{1}{2}(\text{C}_7\text{H}_8)$, M_w 1311.69, colorless, irregular block (0.18 x 0.05 x 0.05), triclinic, space group P-1, a : 12.671(2) Å, b : 13.823(2) Å, c : 19.540(5) Å, α : 107.101(3)°, β : 94.717(3)°, γ : 113.622(2)°, $V = 2917.8(10)$ Å³, $Z = 2$, $Z' = 1$, D_{calc} : 1.493 g cm⁻³, $F(000)$: 1334, $T = 150(2)$ K, μ 4.702 mm⁻¹, 32370 measured reflections (2 θ : 3-58°, ω scans 0.3°), 14710 unique ($R_{\text{int}} = 0.0435$); min./max. transm. Factors 0.659/0.862. Final agreement factors were $R^1 = 0.0366$ (10789 observed reflections, $I > 2\sigma(I)$) and $wR^2 = 0.0804$; data/restraints/parameters 14710/7/589; GoF = 0.984. Largest peak and hole 1.354 (close to iridium atoms) and -1.278 e/Å³.

Crystal data for **3:** $\text{C}_{56}\text{H}_{104}\text{Ir}_2\text{N}_4\text{P}_4$, M_w 1341.71, colorless, irregular block (0.13 x 0.05 x 0.05), monoclinic, space group P2₁/n, a : 10.226(4) Å, b : 15.478(5) Å, c : 19.630(7) Å, β : 98.770(5)°, $V = 3070.7(19)$ Å³, $Z = 2$, $Z' = 0.5$, D_{calc} : 1.451 g cm⁻³, $F(000)$: 1364, $T = 100(2)$ K, μ 4.470 mm⁻¹, 33139 measured reflections (2 θ : 3-58°, ω scans 0.3°), 8053 unique ($R_{\text{int}} = 0.0469$); min./max. transm. Factors 0.647/0.862. Final agreement factors were $R^1 = 0.0289$ (6480 observed reflections, $I > 2\sigma(I)$) and $wR^2 = 0.0670$; data/restraints/parameters 8053/4/312; GoF = 0.988. Largest peak and hole 1.950 (close to iridium atoms) and -0.784 e/Å³.

Crystal data for **6:** $\text{C}_{31}\text{H}_{34}\text{BrIrN}_2\text{P}_2 \cdot \frac{1}{5}(\text{C}_7\text{H}_8\text{OH})$, colorless, irregular block (0.24 x 0.12 x 0.09), monoclinic, space group P2₁/c, a : 13.222(4) Å, b : 15.518(5) Å, c : 17.539(5) Å, β : 99.522(5)°, $V = 3549.0(19)$ Å³, $Z = 4$, $Z' = 1$, D_{calc} : 1.506 g cm⁻³, $F(000)$: 1620, $T = 173(2)$ K, μ 5.001 mm⁻¹, 40542 measured reflections (2 θ : 3-58°, ω scans 0.3°), 9344 unique ($R_{\text{int}} = 0.0484$); min./max. transm. Factors 0.563/0.862. Final agreement factors were $R^1 = 0.0317$ (7447 observed reflections, $I > 2\sigma(I)$) and $wR^2 = 0.0805$; data/restraints/parameters 9344/4/365; GoF = 1.015. Largest peak and hole 1.324 (close to iridium atom) and -0.701 e/Å³.

Crystal data for **7:** $\text{C}_{32}\text{H}_{35}\text{IrN}_2\text{P}_2$, M_w 721.92, colorless, irregular block (0.19 x 0.14 x 0.08), triclinic, space group P-1, a : 9.2313(11) Å, b : 10.1833(12) Å, c : 18.029(2) Å, α : 99.495(2)°, β : 93.844(2)°, γ : 100.595(2)°, $V = 1634.8(3)$ Å³, $Z = 2$, $Z' = 1$, D_{calc} : 1.467 g cm⁻³, $F(000)$: 736, $T = 173(2)$ K, μ 4.204 mm⁻¹, 17856 measured reflections (2 θ : 3-58°, ω scans 0.3°), 8219 unique ($R_{\text{int}} = 0.0261$); min./max. transm. Factors 0.679/0.862. Final agreement factors were $R^1 = 0.0285$ (7220 observed reflections, $I > 2\sigma(I)$) and $wR^2 = 0.0673$; data/restraints/parameters 8219/2/353; GoF = 1.024. Largest peak and hole 1.984 (close to osmium atom) and -0.844 e/Å³. A toluene (**2**) and methanol (**6**) crystallization molecules, along with two isopropyl groups of the phosphine ligands (**3**) were observed disordered and refined with two moieties, restrained geome-

try, isotropic displacement parameters and complementary occupancy factors.

Computational details: All calculations were performed at the DFT level using the B3LYP functional²⁹ supplemented with the Grimme's dispersion correction D3³⁰ as implemented in Gaussian09.³¹ Ir atom was described by means of an effective core potential SDD for the inner electron³² and its associated double- ζ basis set for the outer ones, complemented with a set of f-polarization functions.³³ The 6-31G** basis set was used for the H, C, N and P atoms.³⁴ The minima was verified to have no negative frequencies. The geometries were fully optimized in vacuo. The NICS values were calculated in the Ring Critical points of the ligand calculated with the AIMAll program.³⁵

ASSOCIATED CONTENT

Supporting Information

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

Crystallographic data for compounds **2**, **3**, **6**, and **7** (CIF)

Computed Cartesian coordinates of compound **2** (XYZ)

¹H NMR, ¹³C{¹H} APT, ³¹P{¹H} NMR of all the complexes (PDF)

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Notes

The authors declare no competing financial interest.

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