

# Preparation of Phosphorescent Iridium(III) Complexes with a Dianionic C,C,C,C-Tetradentate Ligand

*Miguel A. Esteruelas,<sup>\*,a</sup> Ana M. López,<sup>a</sup> Enrique Oñate,<sup>a</sup> Ainhoa San-Torcuato,<sup>a</sup> Jui-Yi Tsai,<sup>b</sup> and Chuanjun Xia<sup>b</sup>*

<sup>a</sup>Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Centro de Innovación en Química Avanzada (ORFEO-CINQA), Universidad de Zaragoza - CSIC, 50009 Zaragoza (Spain)

<sup>b</sup>Universal Display Corporation, 375 Phillips Boulevard, Ewing, New Jersey 08618 (USA).

ABSTRACT The preparation and photophysical properties of heteroleptic iridium(III) complexes, containing a dianionic C,C,C,C-tetradentate ligand and a cyclometalated phenylpyridine group are described. Complex  $[\text{Ir}(\mu\text{-OMe})(\text{COD})]_2$  (**1**, COD = 1,5-cyclooctadiene) reacts with 1,1-diphenyl-3,3-butylenediimidazolium iodide

([PhIm(CH<sub>2</sub>)<sub>4</sub>ImPh]I<sub>2</sub>), in the presence NaO<sup>t</sup>Bu, to give [Ir(μ-I){κ<sup>4</sup>-C,C,C,C-[C<sub>6</sub>H<sub>4</sub>Im(CH<sub>2</sub>)<sub>4</sub>ImC<sub>6</sub>H<sub>4</sub>]}] (2), which leads to {[Ir{κ<sup>4</sup>-C,C,C,C-[C<sub>6</sub>H<sub>4</sub>Im(CH<sub>2</sub>)<sub>4</sub>ImC<sub>6</sub>H<sub>4</sub>]}] (μ-OH)(μ-OMe)} (3) by treatment firstly with silver trifluoromethanesulphonate (AgOTf) in acetone-dichloromethane and subsequently with KOH in methanol. The reaction of 2 with AgOTf and acetonitrile affords the bis(solvento) complex [Ir{κ<sup>4</sup>-C,C,C,C-[C<sub>6</sub>H<sub>4</sub>Im(CH<sub>2</sub>)<sub>4</sub>ImC<sub>6</sub>H<sub>4</sub>]}](CH<sub>3</sub>CN)<sub>2</sub>OTf (4). The latter promotes the pyridyl-supported heterolytic *ortho*-CH bond activation of the phenyl group of 2-phenylpyridine, 2-(2,4-difluorophenyl)pyridine, 2-(*p*-tolyl)pyridine and 5-methyl-2-phenylpyridine to yield Ir{κ<sup>4</sup>-C,C,C,C-[C<sub>6</sub>H<sub>4</sub>Im(CH<sub>2</sub>)<sub>4</sub>ImC<sub>6</sub>H<sub>4</sub>]}{κ<sup>2</sup>-C,N-[Ar-py]} (Ar-py = C<sub>6</sub>H<sub>4</sub>-py (5), C<sub>6</sub>H<sub>2</sub>F<sub>2</sub>-py (6), C<sub>6</sub>H<sub>3</sub>Me-py (7), C<sub>6</sub>H<sub>4</sub>-Mepy (8)) using (piperidinomethyl)polystyrene as an external base. Complexes 5–8 are blue-green emitters, which display short lifetimes (0.6–4.8 μs) and quantum yields close to the unity in both doped poly(methylmethacrylate) (PMMA) films at 5 wt% and in 2-methyltetrahydrofuran at room temperature.

## INTRODUCTION

The straightforward manner in which the photophysical properties of phosphorescent emitters can be tuned by combining different ligands in the coordination sphere of the metal center has positioned the heteroleptic iridium(III) complexes at the forefront of modern photochemistry.<sup>1</sup> As a consequence, several classes of compounds of this type have been reported, being the focus mainly centered on [3b+3b+3b'] derivatives<sup>2</sup> which are easily obtained via [Ir(μ-Cl)(3b)<sub>2</sub>]<sub>2</sub> dimers.<sup>3</sup> Because each compound has its own photophysical properties, the development of heteroleptic emitters undergoes two main problems: the existence of several isomers with

different stereochemistry for a given stoichiometry and their marked trend to reach the ligands redistribution equilibrium.<sup>4</sup>

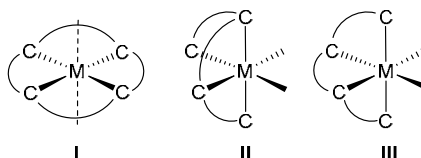
A promising strategy to mitigate these problems is to link the donor groups coordinated at the metal center. The generation of ligands with higher denticity reduces both the number of possible isomers and the number of compounds in the mixtures due to ligand redistribution issues. Furthermore, recent studies indicate that the link favors narrow and bluer emissions. This, which is highly desirable for OLED display applications, seems to be related to less pronounced differences between the excited-state structure and the ground-state structure.<sup>1,5</sup>

Cyclometalated phenylpyridines were initially the most used 3b ligands.<sup>6</sup> However, they are being replaced by cyclometalated aryl-N-heterocyclic carbenes (Ar-NHCs) because of the latter effectively raise the LUMO energy, which gives rise to a wider band gap and therefore more energetic emissions. In addition, their electronic properties ensures that deactivating ligand-field states remain higher in energy than the emissive triplet state.<sup>7</sup> The applicability of NHC groups needs their coordination, which requires specific procedures. In this context, the cleanest method is the direct metalation of imidazolium or benzimidazolium salts.<sup>8</sup> If one links two cyclometalated Ph-NHC groups with a flexible chain, through the nitrogen atoms, one can generate a dianionic C,C,C,C-tetradentate ligand and therefore [6tt+3b] (tt = tetradentate) phosphorescent heteroleptic iridium(III) derivatives.

Tetradentate ligands are less common than those with one, two, or three donor atoms and carbon is also a less frequent donor atom than nitrogen, phosphorus, arsenic, oxygen, or sulfur.<sup>9</sup> Thus, although the boom of the NHCs has given rise in recent years to interesting complexes containing tetradentate ligands based on one, two, three, and four NHC groups, those coordinating four C-donor atoms are very scarce.<sup>10</sup> The great majority of C,C,C,C-donors ligands

are neutral macrocycles based on four NHC moieties, which coordinate to generate a plane (**I**),<sup>11</sup> with some exceptions.<sup>12</sup> A few acyclic system have been also described, which stabilize structures **II**<sup>13</sup> (Chart 1).

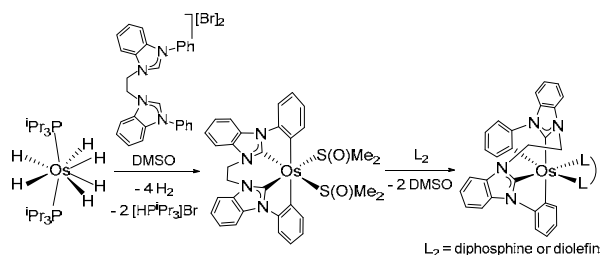
### Chart 1. Structures Stabilized by C,C,C,C-Tetradentate Ligands



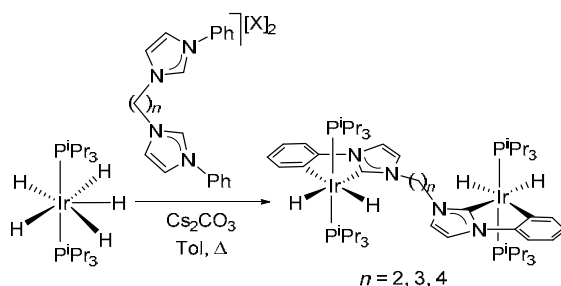
The generation of tetradentate ligands based on two cyclometalated Ar-NHC moieties requires the chelating coordination of a bidentate bis(N-phenyl)-substituted-bis(NHC) ligand and the subsequent C-directed *ortho*-CH bond activation of both N-phenyl substituents.<sup>14</sup> The chelating versus bridging coordination of bis(NHC) ligands is an unresolved issue.<sup>15</sup> It has been suggested that the length of the linker between theazole rings plays a main role in the type of coordination.<sup>16</sup> However, the problem is much more complex. Recently, we have shown that the d<sup>2</sup>-hexahydride OsH<sub>6</sub>(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub> promotes the direct metalation of the benzimidazolium units and the *ortho*-CH bond activation of both phenyl substituents of 1,1'-diphenyl-3,3'-ethylenedibenzimidazolium to give Os{κ<sup>4</sup>-C,C,C,C-[C<sub>6</sub>H<sub>4</sub>BzIm(CH<sub>2</sub>)<sub>2</sub>BzImC<sub>6</sub>H<sub>4</sub>]}L<sub>2</sub> derivatives, containing a dianionic C,C,C,C-tetradentate ligand (Scheme 1).<sup>5b</sup> In contrast to the d<sup>2</sup>-hexahydride, the d<sup>4</sup>-pentahydride IrH<sub>5</sub>(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub> reacts with 1,1'-diphenyl-3,3'-alkylenediimidazolium halides ([C(CH<sub>2</sub>)<sub>n</sub>(HImC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]X<sub>2</sub>; n = 2, 3, 4) to yield the dinuclear derivatives {[IrH<sub>2</sub>(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub>]<sub>2</sub>[μ-(CH<sub>2</sub>)<sub>n</sub>(ImC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>]} (n = 2, 3, 4), regardless of the length of the chain between the imidazolylidene groups (Scheme 2),<sup>17</sup> although the steric hindrance of both polyhydrides is the same. The tetradentate ligand of Os{κ<sup>4</sup>-C,C,C,C-[C<sub>6</sub>H<sub>4</sub>BzIm(CH<sub>2</sub>)<sub>2</sub>BzImC<sub>6</sub>H<sub>4</sub>]}L<sub>2</sub> avoids a four-planar coordination, whereas it favors sawhorse-type dispositions (**II** and **III** in Chart 1). The reason for this preference appears to be electronic,

because the observed arrangement for the donor atoms is not determined by the presence of the linker between the benzimidazolylidene groups and is as that found in complexes containing two independent orthometalated N-phenylbenzimidazolylidene ligands.<sup>5b</sup>

**Scheme 1. Reaction of OsH<sub>6</sub>(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub> with 1,1'-Diphenyl-3,3'-ethylenedibenzimidazolium<sup>5b</sup>**



**Scheme 2. Reactions of IrH<sub>5</sub>(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub> with 1,1'-Diphenyl-3,3'-alkylenediimidazolium<sup>17</sup>**



This paper shows an entry to iridium(III) emitters of the class [6tt+3b], which display quantum yields close to the unity, and at the same time demonstrates that the synthetic precursor plays a key role in the coordination mode of tetradentate bis(N-phenyl)-bis(NHC) ligands.

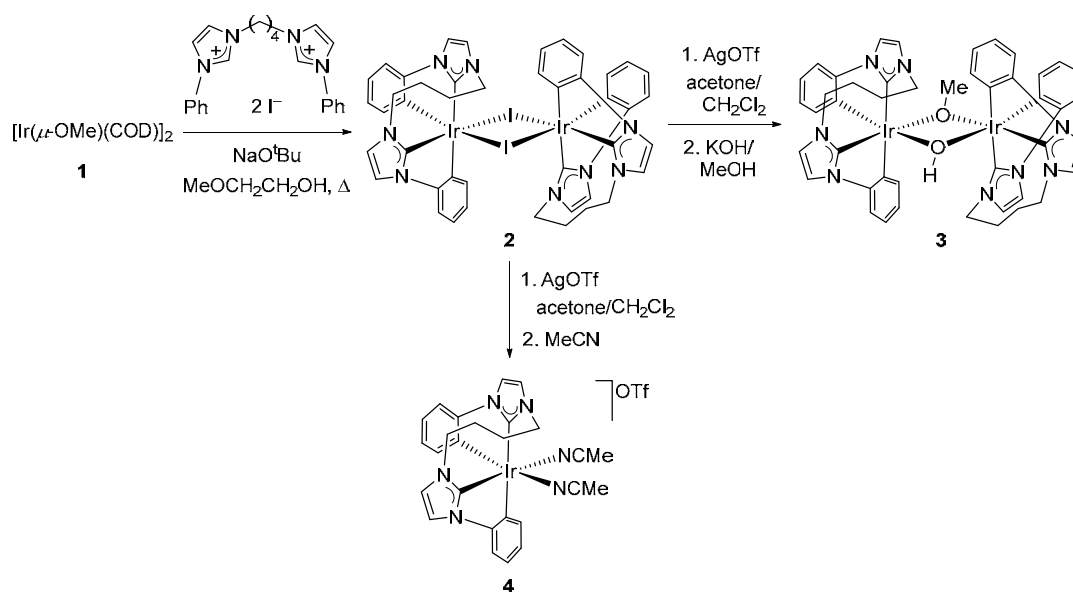
**RESULTS AND DISCUSSION**

**The Synthetic Precursor.** Dimers  $[\text{Ir}(\mu\text{-Cl})\{\kappa^2\text{-C,C-(C}_6\text{R}_4\text{-NHC)}\}_2]_2$  have shown to be useful synthetic precursors to prepare iridium(III) emitters of the class [3b+3b+3b'], with two cyclometalated Ar-NHC ligands, which are the counterparts of our target [6tt+3b] compounds. They are usually obtained from the reactions of the known complex  $[\text{Ir}(\mu\text{-Cl})(\text{COD})]_2$  (COD = 1,5-cyclooctadiene) with the corresponding imidazolium or benziimidazolium chloride in the

presence of a base and their X-ray structures reveal that the NHC groups are mutually *trans* disposed at the coordination sphere of each iridium(III).<sup>7b,c</sup> As a consequence, the resulting [3b+3b+3b'] derivatives also show a mutually *trans* NHC arrangement.<sup>7d-f,i</sup> We decided to explore this synthetic strategy to prepare [6tt+3b] derivatives containing two cyclometalated Ar-NHC moieties linked by a butylene chain, given that the use of the pentahydride IrH<sub>5</sub>(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub> as synthetic precursor had previously led to a compound with a bridging bis(NHC) ligand.<sup>17</sup> However, a more suitable precursor than [Ir( $\mu$ -Cl)(COD)]<sub>2</sub> would be the methoxide-counterpart [Ir( $\mu$ -OMe)(COD)]<sub>2</sub> (**1**), since the methoxide ligand of this type of dimers has proven to allow the direct metalation of imidazolium and benzimidazolium salts.<sup>18</sup>

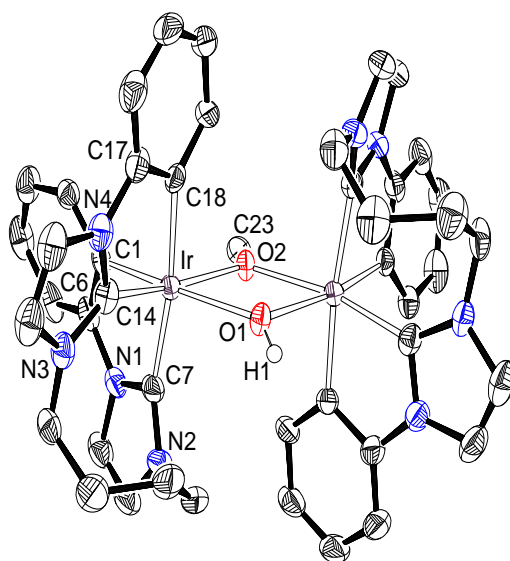
Treatment of 2-methoxyethanol suspensions of **1** with 3.4 equivalents of 1,1'-diphenyl-3,3-butylenediimidazolium iodide ([PhIm(CH<sub>2</sub>)<sub>4</sub>ImPh]I<sub>2</sub>), in the presence of sodium *tert*-butoxide (NaO<sup>t</sup>Bu), at 130 °C, for 6 hours produces the precipitation of the dimer [Ir( $\mu$ -I){ $\kappa^4$ -C,C,C,C-[C<sub>6</sub>H<sub>4</sub>Im(CH<sub>2</sub>)<sub>4</sub>ImC<sub>6</sub>H<sub>4</sub>]}]<sub>2</sub> (**2**), as a white solid in 65% yield (Scheme 3). Interestingly, its <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, in dichloromethane-*d*<sub>2</sub>, at room temperature shows two resonances for the metalated NHC-carbon atoms, at 175.6 and 153 ppm, and two resonances for the metalated phenyl-carbon atoms, at 150.7 and 131.7 ppm. This reveals that the imidazolylidene units of **2** are mutually *cis* disposed, in contrast to that observed for related dimers containing two free cyclometalated Ar-NHC ligands. So, unlike the osmium complexes Os{ $\kappa^4$ -C,C,C,C-[C<sub>6</sub>H<sub>4</sub>BzIm(CH<sub>2</sub>)<sub>2</sub>BzImC<sub>6</sub>H<sub>4</sub>]}L<sub>2</sub> shown in Scheme 1, the linker between the NHC units of **2** is determinant to place the donor atoms in their positions at the coordination sphere of the metal centers.

### Scheme 3. Synthesis of the Precursors



Treatment of **2** firstly with silver trifluoromethanesulphonate ( $\text{AgOTf}$ ) in acetone-dichloromethane and subsequently with  $\text{KOH}$  in methanol produces the replacement of the double iodide bridge by a mixed hydroxide-methoxide bridge. The resulting dimer  $\{[\text{Ir}\{\kappa^4\text{-C,C,C,C-[C}_6\text{H}_4\text{Im}(\text{CH}_2)_4\text{ImC}_6\text{H}_4]\}\}_2(\mu\text{-OH})(\mu\text{-OMe})\}$  (**3**), was isolated in 47% yield, also as a white solid. Like for **2**, the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3**, in dichloromethane- $d_2$ , at room temperature displays two resonances for the metalated NHC-carbon atoms, at 182.7 and 160.9 ppm, and two resonances for the metalated phenyl-carbon atoms, at 156.8 and 133.0 ppm, indicating that the arrangement of the C-donor atoms around the metal center of **2** is kept in **3**. This was confirmed by means of the X-ray diffraction analysis of the structure of the latter (Figure 1). The structure has a  $C_2$  axis, which contains the oxygen atoms of the bridge. As a consequence, the tetradentate ligands are oriented in *anti*-disposition. In agreement with the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra, the coordination polyhedron around each iridium atom can be described as a distorted octahedron with the imidazolylidene of a cyclometalated Ph-NHC moiety *trans* to the orthometalated phenyl of the other one ( $\text{C7-Ir-C18} = 172.1(2)^\circ$ ), whereas the hydroxide

ligand lies *trans* to the remaining orthometalated phenyl (O1–Ir–C1 = 169.97(18)°) and the methoxide ligand is *trans* to the remaining imidazolylidene (O2–Ir–C14 = 168.81(18)°). The separation between the metal center and the phenyl *trans* to the hydroxide ligand (Ir–C1 = 2.019(5) Å) is about 0.05 Å shorter than the separation between the iridium atom and the phenyl *trans* to the imidazolylidene (Ir–C18 = 2.066(6) Å). Similarly, the separation between the metal center and the imidazolylidene *trans* to the methoxide ligand (Ir–C14 = 1.963(5) Å) is about 0.05 Å shorter than the separation between the iridium atom and imidazolylidene situated *trans* to the phenyl (Ir–C7 = 2.051(6) Å). The Ir–OH and Ir–OMe bond lengths of 2.190(4) (Ir–O1) and 2.123(3) (Ir–O2) Å, respectively, compare well with those reported for double hydroxide<sup>19</sup> and methoxide<sup>20</sup> bridges in iridium(III) complexes.



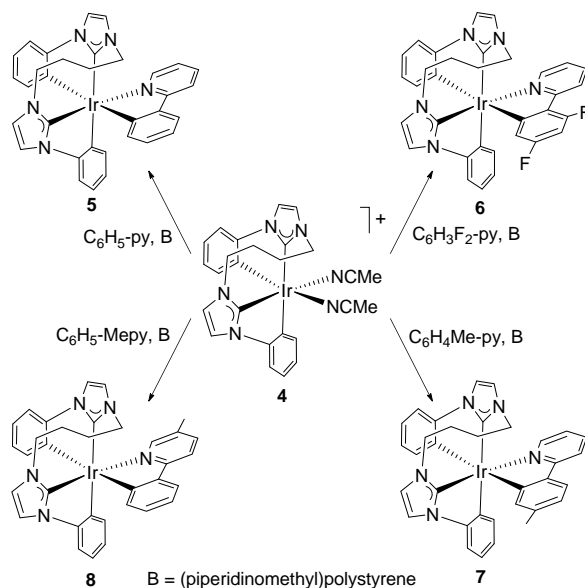
**Figure 1.** Molecular diagram of **3** (50% probability ellipsoids). Hydrogen atoms (except H1) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir–C1 = 2.019(5), Ir–C7 = 2.051(6), Ir–C14 = 1.963(5), Ir–C18 = 2.066(6), Ir–O1 = 2.190(4), Ir–O2 = 2.123(3); C7–Ir–C18 = 172.1(2), O1–Ir–C1 = 169.97(18), O2–Ir–C14 = 168.81(18), C1–Ir–C18 = 93.3(2), C7–Ir–C14 = 97.6(2).



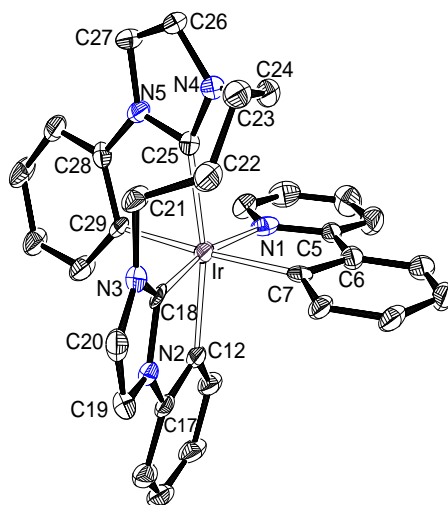
The removal of the iodide ligands of **2** with AgOTf in acetone-dichloromethane leads to a complex mixture of solvento species, which in acetonitrile affords the mononuclear bis(acetonitrile) derivative  $[\text{Ir}\{\kappa^4\text{-C,C,C,C-[C}_6\text{H}_4\text{Im(CH}_2\text{)}_4\text{ImC}_6\text{H}_4\text{]}\}(\text{CH}_3\text{CN})_2]\text{OTf}$  (**4**). This salt was isolated as a white solid in 71% yield. The demolishing of the dinuclear structure does not give rise to any change in the disposition of the C-donor atoms of the tetradentate ligand. Thus, in agreement with **2** and **3**, the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4**, in dichloromethane- $d_2$ , at room temperature shows two resonances for the inequivalent metalated imidazolylidene carbon atoms, at 170.9 and 151.1 ppm, and two resonances for the inequivalent metalated phenyl carbon atoms, at 146.8 and 124.6 ppm.

**Preparation and Characterization of [6tt+3b] Complexes.** The bis(acetonitrile) complex **4** is an excellent synthetic precursor to prepare [6tt+3b] complexes containing a cyclometalated phenylpyridine ligand. The procedure implies pyridyl-supported heterolytic *ortho*-CH bond activation reactions, on the phenyl group, which use (piperidinomethyl)polystyrene as an external base. The reactions were carried out in fluorobenzene under reflux and are compatible with substituents at both the pyridyl and phenyl groups (Scheme 4). Thus, under the above mentioned conditions, the treatment of **4** with 1.0 equivalent of 2-phenylpyridine ( $\text{C}_6\text{H}_5\text{-py}$ ), 2-(2,4-difluorophenyl)pyridine ( $\text{C}_6\text{H}_3\text{F}_2\text{-py}$ ), 2-(*p*-tolyl)pyridine ( $\text{C}_6\text{H}_4\text{Me-py}$ ), and 5-methyl-2-phenylpyridine ( $\text{C}_6\text{H}_5\text{-Mepy}$ ) affords the respective derivatives  $\text{Ir}\{\kappa^4\text{-C,C,C,C-[C}_6\text{H}_4\text{Im(CH}_2\text{)}_4\text{ImC}_6\text{H}_4\text{]}\}\{\kappa^2\text{-C,N-[Ar-py]}\}$  (Ar-py =  $\text{C}_6\text{H}_4\text{-py}$  (**5**),  $\text{C}_6\text{H}_2\text{F}_2\text{-py}$  (**6**),  $\text{C}_6\text{H}_3\text{Me-py}$  (**7**),  $\text{C}_6\text{H}_4\text{-Mepy}$  (**8**)), which were isolated as analytically pure yellow solids in high yields (80–95%) without further purification.

#### Scheme 4. Preparation of [6tt+3b] Complexes



The stereochemistry of the obtained [6tt+3b] complexes was confirmed by means of the X-ray diffraction analysis of **5**. Its structure (Figure 2) reveals that the relative disposition of the donor atoms of the tetradentate ligands does not change in the new octahedral environment, i.e., the imidazolylidene of a cyclometalated Ph-NHC unit is situated *trans* to the orthometalated phenyl of the other one ( $C25-Ir-C12 = 167.2(2)^\circ$ ). Furthermore, it proves that from the two possible isomers resulting from the cyclometalation of the phenylpyridine, pyridine *trans* to phenyl and pyridine *trans* to imidazolylidene, the latter is regioselectively formed with pyridine–iridium–imidazolylidene and phenyl–iridium–phenyl angles of  $167.2(2)$  ( $N1-Ir-C18$ ) and  $170.9(2)^\circ$  ( $C7-Ir-C29$ ) respectively. The iridium–imidazolylidene distances of  $1.956(6)$  ( $Ir-C18$ ) and  $2.072(6)$  ( $Ir-C25$ ) Å and the iridium–phenyl bond lengths of  $2.062(6)$  ( $Ir-C12$ ),  $2.090(6)$  ( $Ir-C7$ ), and  $2.115(6)$  ( $Ir-C29$ ) Å compare well with those of **3**.



**Figure 2.** Molecular diagram of **5** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir–N1 = 2.096(6), Ir–C7 = 2.090(6), Ir–C12 = 2.062(6), Ir–C18 = 1.956(6), Ir–C25 = 2.072(6), Ir–C29 = 2.115(6); N1–Ir–C18 = 167.2(2), C7–Ir–C29 = 170.9(2), C12–Ir–C25 = 167.2(2), N1–Ir–C7 = 78.9(2), C12–Ir–C18 = 79.7(2), C25–Ir–C29 = 77.8(2).

The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra **5–8**, in dichloromethane- $d_2$ , at room temperature are consistent with the structure shown in Figure 2 and agree well with those of **2–4**. Thus, they show two resonances for the inequivalent metalated imidazolylidene carbon atoms, at about 176 and 165 ppm, and two resonances for the metalated carbon atoms of the inequivalent phenyl groups of the tetradentate ligand, between 152 and 155 ppm. The resonance corresponding to the metalated carbon atom of the bidentate C,N-donor ligand appears between 171 and 173 ppm for **5**, **7**, and **8** and at 179.8 ppm for **6**.

As it has been previously mentioned, the [3b+3b+3b'] iridium complexes containing two free cyclometalated Ph-NHC ligands display octahedral environments with the NHC units disposed mutually *trans*. In this context, it should be pointed out that the linkage of the cyclometalated

moieties with a butylene chain allows to isolate species with an arrangement NHC *trans* to phenyl.

**Photophysical and Electrochemical Properties of the [6tt+3b] Complexes.** UV/vis absorption data of  $1.0\text{--}6.5 \times 10^{-5}$  M 2-methyltetrahydrofuran (MeTHF) solutions of complexes **5–8**, at room temperature, are collected in Table 1. The spectra of the four complexes are similar (Figures S19 – S22 in the Supporting Information), showing three different zones: 230–300, 320–410, and  $>420$  nm. Time-dependent DFT calculations (B3LYP-GD3//SDD(f)/6-31G\*\*), computed in tetrahydrofuran as solvent, indicate that the absorptions at the highest energy region correspond mainly to  $^1\pi\text{--}\pi^*$  interligand and intraligand transitions. The bands in the region of moderate energy are due to allowed spin metal-to-phenylpyridine charge transfer ( $^1\text{MLCT}$ ) mixed with NHC-to-phenylpyridine transitions. The weak absorption tails after 420 nm are usually assigned to formally spin-forbidden  $^3\text{MLCT}$  transitions, caused by the large spin-orbit coupling introduced by the iridium center.<sup>21</sup>

The oxidation and reduction potentials of **5–8** were measured by cyclic voltammetry in degassed acetonitrile solutions and referenced vs Fc/Fc<sup>+</sup>. The data are collected on Table 2. The four complexes exhibit an irreversible oxidation peak potential in the region 0.23–0.41 V and a quasi-reversible reduction in the narrow region from –2.94 to –3.02 V. The electrochemical gap is in agreement with the calculated HOMO-LUMO gap (Table 2, Tables S10–S13, and Figures S23–S26) and with those previously reported for neutral iridium complexes containing two free cyclometalated NHC ligands with the NHC disposed mutually *trans*.<sup>7d,e,g</sup>

**Table 1. Selected Experimental UV-Vis Absorptions for 5–8 (in MeTHF) and Computed TD-DFT (in THF) Vertical Excitation Energies and their Major Contributions**

Complex	$\lambda_{\text{exp}}$ (nm)	$\epsilon \times 10^{-3}$ (M <sup>-1</sup> ·cm <sup>-1</sup> )	Excitation energy (nm)	Oscillator strength, <i>f</i>	Transition	Contrib (%)
<b>5</b>	244	16.5	238	0.0678	HOMO-5 → LUMO+2	63
	272	24.5	279	0.0684	HOMO-6 → LUMO	83
	344	4.0	345	0.0495	HOMO-2 → LUMO	85
	376	2.6	381	0.0250	HOMO-1 → LUMO	98
	402	2.1	409	0.0246	HOMO → LUMO	98
	444	1.1				
<b>6</b>	234	94.1	242	0.0648	HOMO-4 → LUMO+3	48
	266	56.8	278	0.1028	HOMO-6 → LUMO	55
					HOMO-3 → LUMO+1	26
	324	12.3	336	0.0119	HOMO → LUMO+1	96
	342	6.7	343	0.0399	HOMO-2 → LUMO	94
	374	3.8	374	0.0250	HOMO-1 → LUMO	97
	400	2.7	401	0.0165	HOMO → LUMO	97
	430	1.0				
<b>7</b>	234	137	243	0.0555	HOMO-4 → LUMO+3	58
	272	40.3	289	0.1577	HOMO-5 → LUMO	39
					HOMO-3 → LUMO+1	32
	342	5.2	342	0.0519	HOMO → LUMO+1	90
	376	2.9	376	0.0249	HOMO-1 → LUMO	98
	404	2.4	404	0.0284	HOMO → LUMO	98
	440	1.0				
<b>8</b>	234	43.9	254	0.0603	HOMO-9 → LUMO	69
	272	27.8	287	0.1571	HOMO-3 → LUMO+1	33
					HOMO-5 → LUMO	32
					HOMO-1 → LUMO+3	14
	340	4.8	341	0.0335	HOMO → LUMO+1	78
					HOMO-2 → LUMO	18
	376	2.6	377	0.0259	HOMO-1 → LUMO	98
	404	2.1	405	0.0284	HOMO → LUMO	98
440	0.9					

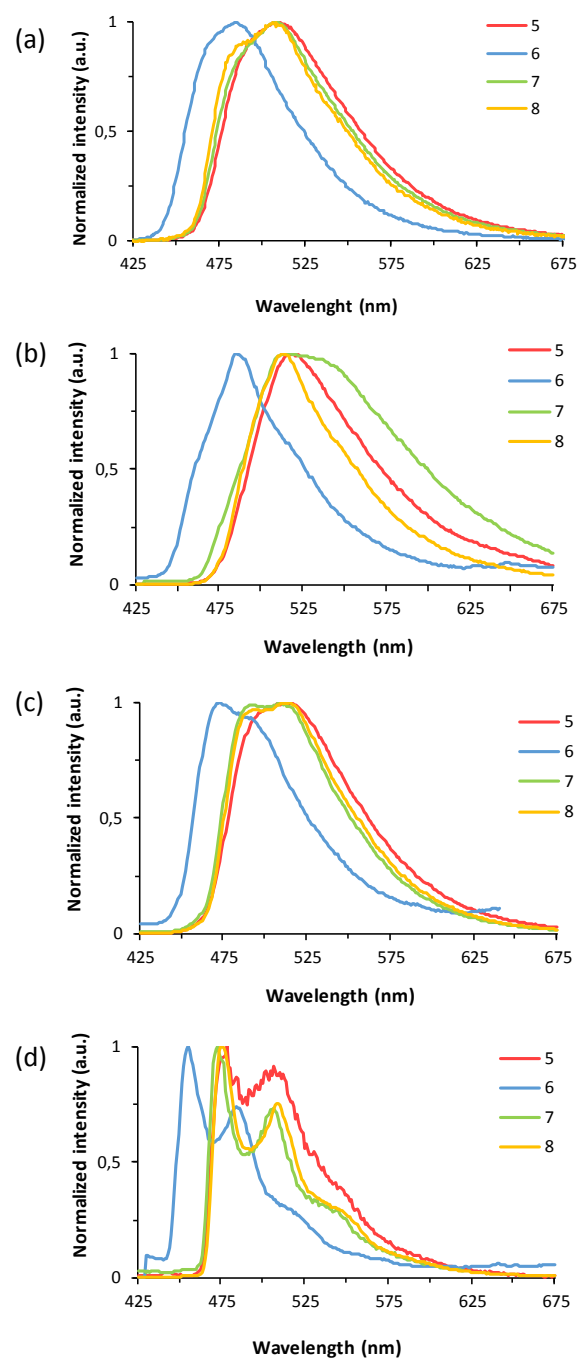
**Table 2. Electrochemical and DFT MO Energy Data for Complexes 5–8**

Complex	$E_{\text{ox}}$ (V) <sup>a</sup>	$E_{\text{red}}$ (V) <sup>a</sup>	$E_{\text{ox}} - E_{\text{red}}$ (V)	HOMO (eV) <sup>b</sup>	LUMO (eV) <sup>b</sup>	HLG (eV) <sup>b,c</sup>
<b>5</b>	0.26	-2.94	3.20	-4.86	-1.10	3.76
<b>6</b>	0.41	-2.94	3.35	-4.97	-1.16	3.81
<b>7</b>	0.23	-3.02	3.25	-4.84	-1.05	3.79
<b>8</b>	0.23	-3.02	3.25	-4.84	-1.06	3.78

<sup>a</sup>Measured in degassed acetonitrile solution ( $10^{-3}$  M) / [Bu<sub>4</sub>N]PF<sub>6</sub> (0.1 M), vs Fc/Fc<sup>+</sup> at 0.1 V·s<sup>-1</sup>, at room temperature. <sup>b</sup>Values from electronic structure DFT calculations. <sup>c</sup>HLG = LUMO – HOMO.

Complexes **5–8** are emissive in the blue-green spectral region upon photoexcitation, in doped poly(methylmethacrylate) (PMMA) films at 5 wt% and in powder at room temperature and in 2-methyltetrahydrofuran at room temperature and 77 K, displaying bands centered between 455 and 520 nm. Figure 3 depicts the emission spectra, whereas Table 3 summarizes calculated and experimental wavelengths, lifetimes, quantum yields at room temperature in PMMA films and 2-methyltetrahydrofuran solutions, and radiative and nonradiative rate constants. The emission spectra in PMMA films, in neat solid powders, and in 2-methyltetrahydrofuran at room temperature show broad structureless bands. However, the spectra in glassy 2-methyltetrahydrofuran, at 77 K, display vibronic fine structures which are consistent with a notable contribution of ligand centered  $^3\pi-\pi^*$  transitions to the excited state. The emission maxima further undergo a blue shift, which has been attributed to a significant additional  $^3\text{MLCT}$  character of the excited state at room temperature.<sup>7d,22</sup> The nature of the substituents of the cyclometalated phenylpyridine has a moderated influence on the emission. Thus, while the methyl substituted complexes **7** and **8** display emission wavelengths similar to the unsubstituted derivative **5**, the emission wavelength of the fluoride disubstituted compound **6** undergoes a

higher energy shift of about 30 nm. This blue shift is in agreement with the higher HOMO-LUMO gap of **6** with regard to those of **5**, **7**, and **8**. It should be noted that although the reduction potentials of the four complexes are similar, the oxidation potential of **6** is higher. The lifetimes are short lying in the range 0.6–4.8  $\mu\text{s}$ , whereas the quantum yields, measured in PMMA films are in all cases close to the unity (0.87–0.96), whereas are approximately 1 for **5**, **7**, and **8** and 0.73 for **6** in solution at room temperature. In this context, it should be mentioned that, as far as we know, the highest quantum yield reported for complexes with two free cyclometalated aryl-NHC ligands is 0.79.<sup>7c</sup> In PMMA films, the radiative rate constants are one order of magnitude higher than the nonradiative rate constants for **5**, **7**, and **8** whereas are of the same order of magnitude for **6**. The radiative rate constants in PMMA films and solution are comparable. The exceptional quantum yields in solution suggest that the rigidity of the structure imposed by the linker between the carbene moieties plays a main role in the brightness of the emitters.



**Figure 3.** Emission spectra in 5 wt% PMMA films at 298 K (a), in neat solid powders at 298 K (b), in MeTHF at 298K (c), and in MeTHF at 77 K (d) for complexes **5–8**.

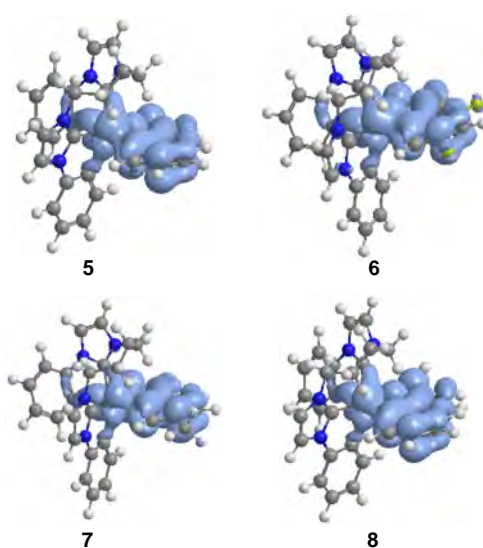


**Table 3. Photophysical Data for Complexes 5–8**

Complex	Calcd $\lambda_{em}^a$ (nm)	Media (T/K)	$\lambda_{em}$ (nm)	$\lambda_{exc}$ (nm)	$\tau$ ( $\mu$ s)	$\phi$	$k_r$ ( $s^{-1}$ ) <sup>b</sup>	$k_{nr}$ ( $s^{-1}$ ) <sup>b</sup>	$k_r/k_{nr}$
<b>5</b>		PMMA film (298)	509	407	1.7	0.93	$5.5 \times 10^5$	$4.1 \times 10^4$	13.3
		powder (298)	519	475	1.1				
	505	MeTHF (298)	510	431	3.9	~1	$2.6 \times 10^5$		
		MeTHF (77)	478, 506	439	4.8				
<b>6</b>		PMMA film (298)	485	401	1.3	0.87	$6.7 \times 10^5$	$1.0 \times 10^5$	6.7
		powder (298)	485	450	0.7				
	478	MeTHF (298)	473	394	1.6	0.73	$4.6 \times 10^5$	$1.7 \times 10^5$	2.7
		MeTHF (77)	455, 484	396	3.1				
<b>7</b>		PMMA film (298)	509	401	1.7	0.93	$5.5 \times 10^5$	$4.1 \times 10^4$	13.3
		powder (298)	517	470	0.6				
	500	MeTHF (298)	492	424	3.1	~1	$3.2 \times 10^5$		
		MeTHF (77)	473, 506	429	4.5				
<b>8</b>		PMMA film (298)	508	403	1.8	0.96	$5.3 \times 10^5$	$2.2 \times 10^4$	24.0
		powder (298)	513	475	1.1				
	501	MeTHF (298)	492	425	2.4	~1	$4.2 \times 10^5$		
		MeTHF (77)	476, 510	429	4.4				

<sup>a</sup>Predicted from TD-DFT calculations in THF at 298 K. <sup>b</sup>Calculated according to the equations  $k_r = \phi/\tau$  and  $k_{nr} = (1 - \phi)/\tau$ , where  $k_r$  is the radiative rate constant,  $k_{nr}$  is the nonradiative rate constant,  $\phi$  is the quantum yield, and  $\tau$  is the excited-state lifetime.

The emissions can be attributed to  $T_1$  excited states originated by HOMO→LUMO charge transfer transitions. Figure 4 displays the spin density distribution calculated for the  $T_1$  states at their minimum energy geometry. In accordance with this, good agreement is observed between the experimental wavelengths and those calculated by estimating the difference in energy between the optimized triplet state and the singlet state  $S_0$ , in tetrahydrofuran.



**Figure 4.** Unpaired electron spin-contours density (0.03 au) calculated for the  $T_1$  states of complexes **5–8**.

## CONCLUDING REMARKS

This study shows the discovery of a family of iridium(III) emitters of the class [6tt+3b], which contain a C,C,C,C-tetradentate ligand and display quantum yields close to the unity. In addition, the study reveals that there are marked differences in stereochemistry and photophysical features between the compounds with two free cyclometalated aryl-NHC ligands and those bearing the NHC moieties linked by a butylene chain.

The coordination mode of bis(N-phenyl)-bis(NHC) ligands depends upon the metal precursor. In contrast to the pentahydride  $\text{IrH}_5(\text{P}^i\text{Pr}_3)_2$ , that reacts with 1,1-diphenyl-3,3-butylenediimidazolium iodide to afford a bis(NHC) bridge, the known dimer  $[\text{Ir}(\mu\text{-OMe})(\text{COD})]_2$  metalates the cation of this salt to generate a C,C,C,C-tetradentate ligand, formed by two cyclometalated Ph-NHC moieties linked by a butylene chain, which coordinates to only one iridium atom. The resulting species is easily transformed into the cation  $[\text{Ir}\{\kappa^4\text{-C,C,C,C-[C}_6\text{H}_4\text{Im}(\text{CH}_2)_4\text{ImC}_6\text{H}_4]\}(\text{CH}_3\text{CN})_2]^+$ , which promotes the pyridyl supported heterolytic *ortho*-CH bond activation of the phenyl group of phenylpyridines to give the [6tt+3b] complexes in almost quantitative yield. In contrast to the complexes with two free cyclometalated aryl-NHC ligands, the structures of these compounds have the NHC moieties of the tetradentate ligand disposed mutually *cis*. The rigidity imposed by the chain not only changes the disposition of the donor atoms in the coordination sphere of the metal, but also produces an increase of the quantum efficiency. Thus, they are blue-green emitters, which display short lifetimes (0.6–4.8  $\mu\text{s}$ ) and reach quantum yields close to the unity, upon photoexcitation, in both doped poly(methylmethacrylate) (PMMA) films at 5 wt% and in 2-methyltetrahydrofuran at room temperature.

In conclusion, the linkage of chelate ligands with alkylene chains allows to stabilize particular isomers of heteroleptic iridium(III) emitters, containing three bidentate units, and reduces the mixtures due to ligand redistribution. Furthermore, the rigidity imposed by the chain increases the quantum efficiency.

## EXPERIMENTAL SECTION

Reactions were performed under argon with dried solvents using Schlenk-tube techniques. Instrumental methods used for characterization, X-ray information, and DFT computational details are given in the Supporting Information. Chemical shifts (in ppm) are referenced to

residual solvent peaks ( $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ) or external  $\text{CFCl}_3$  ( $^{19}\text{F}$ ) whereas coupling constants  $J$  are given in hertz. Complex  $[\text{Ir}(\mu\text{-OMe})(\text{COD})]_2$  (**1**)<sup>23</sup> and 1,1'-diphenyl-3,3'-butylenediimidazolium iodide<sup>24</sup> were prepared according to the published methods.

**Preparation of  $[\text{Ir}(\mu\text{-I})\{\kappa^4\text{-C,C,C,C-[C}_6\text{H}_4\text{Im(CH}_2)_4\text{ImC}_6\text{H}_4\}]\}_2$  (**2**).** A mixture of **1** (213.2 mg, 0.322 mmol), 1,1'-diphenyl-3,3'-butylenediimidazolium iodide (654 mg, 1.09 mmol), and sodium tert-butoxide (154.5 mg, 1.61 mmol) in 15 mL of 2-methoxyethanol was heated at 130 °C in a Schlenk flask with a Teflon stopcock for 6 h. During this time a white solid appeared. The resulting suspension was transferred to a Schlenk flask. After cooling to room temperature, the white solid was decanted, washed with methanol (4 x 3 mL) and dried in vacuo. Yield: 276 mg (65%). Anal. Calcd for  $\text{C}_{44}\text{H}_{40}\text{I}_2\text{Ir}_2\text{N}_8$ : C, 40.06; H, 3.06; N, 8.50. Found: C, 40.19; H, 3.39; N, 8.09. HRMS (electrospray,  $m/z$ ): Calcd for  $\text{C}_{22}\text{H}_{20}\text{IrN}_4$   $[\text{M}/2 - \text{I}]^+$ : 533.1312; found 533.1312.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  8.75 (m, 2H, Ph), 7.67 (d, 2H,  $^3J_{\text{H-H}} = 2.0$ , Im), 7.28 (d, 2H,  $^3J_{\text{H-H}} = 2.1$ , Im), 7.25 (m, 4H, Ph), 7.22 (d, 2H,  $^3J_{\text{H-H}} = 2.0$ , Im), 7.15 (m, 2H, Ph), 7.01 (dd, 2H,  $^3J_{\text{H-H}} = 7.7$ ,  $^4J_{\text{H-H}} = 1.3$ , Ph), 6.68 (ddd, 2H,  $^3J_{\text{H-H}} = ^3J_{\text{H-H}} = 7.4$ ,  $^4J_{\text{H-H}} = 1.3$ , Ph), 6.55 (d, 2H,  $^3J_{\text{H-H}} = 2.1$ , Im), 6.36 (ddd, 2H,  $^3J_{\text{H-H}} = ^3J_{\text{H-H}} = 7.4$ ,  $^4J_{\text{H-H}} = 1.3$ , Ph), 6.18 (dd, 2H,  $^3J_{\text{H-H}} = 7.7$ ,  $^4J_{\text{H-H}} = 1.3$ , Ph), 5.27, 3.61, 3.40, 2.44 (all m, 2H each,  $\text{NCH}_2$ ), 2.13, 2.03, 1.93, 1.48 (all m, 2H each,  $\text{NCH}_2\text{CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.63 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  175.6, 153.0 (both IrC Im), 150.7 (IrC Ph), 147.7, 146.3 (both NC Ph), 141.3, 136.3 (both CH Ph), 131.7 (IrC Ph), 126.3, 124.4 (both CH Ph), 122.8 (CH Im), 121.9, 121.6 (both CH Ph), 120.5, 115.7, 114.4 (all CH Im), 111.3, 110.5 (both CH Ph), 51.8, 48.1 (both  $\text{NCH}_2$ ), 29.4, 26.0 (both  $\text{NCH}_2\text{CH}_2$ ).

**Preparation of  $[\text{Ir}\{\kappa^4\text{-C,C,C,C-[C}_6\text{H}_4\text{Im(CH}_2)_4\text{ImC}_6\text{H}_4\}]\}_2(\mu\text{-OH})(\mu\text{-OMe})$  (**3**).** A solution of silver trifluoromethanesulfonate (86.0 mg, 0.335 mmol) in 5 mL of acetone was added to a suspension of **2** (201.0 mg, 0.152 mmol) in dichloromethane (20 mL). The suspension was

stirred in the dark at room temperature, for 1 h. Then, it was filtered through Celite to remove the precipitated AgI. The solvent of the filtrate was almost removed in vacuo. The addition of diethyl ether (3 mL) caused the precipitation of a white solid that was dried in vacuo. The white solid was dissolved in MeOH (7 mL) and a solution of KOH (18.8 mg, 0.335 mmol) in MeOH (3 mL) was added to the previous one. After 2 hours at room temperature, a white solid was formed. It was decanted and washed with further portions of MeOH (3 x 3 mL). Yield: 80 mg (47%). Anal. Calcd for C<sub>45</sub>H<sub>44</sub>Ir<sub>2</sub>N<sub>8</sub>O<sub>2</sub>: C, 48.55; H, 3.98; N, 10.06. Found: C, 48.31; H, 3.89; N, 9.99. HRMS (electrospray, *m/z*): calcd for C<sub>22</sub>H<sub>20</sub>IrN<sub>4</sub> [Ir{C<sub>6</sub>H<sub>4</sub>Im(CH<sub>2</sub>)<sub>4</sub>ImC<sub>6</sub>H<sub>4</sub>}]<sup>+</sup>: 533.1312; found 533.1394. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 7.56 (d, 2H, <sup>3</sup>J<sub>H-H</sub> = 2.0, CH Im), 7.47 (dd, 2H, <sup>3</sup>J<sub>H-H</sub> = 7.1, <sup>4</sup>J<sub>H-H</sub> = 1.4, CH Ph), 7.29 (d, 2H, <sup>3</sup>J<sub>H-H</sub> = 2.1, CH Im), 7.14 (m, 2H, CH Ph), 7.08 (ddd, 2H, <sup>3</sup>J<sub>H-H</sub> = <sup>3</sup>J<sub>H-H</sub> = 7.4, <sup>4</sup>J<sub>H-H</sub> = 1.4, CH Ph), 6.98 (dd, 2H, <sup>3</sup>J<sub>H-H</sub> = 7.6, <sup>4</sup>J<sub>H-H</sub> = 1.4, CH Ph), 6.89 (dd, 2H, <sup>3</sup>J<sub>H-H</sub> = 7.1, <sup>4</sup>J<sub>H-H</sub> = 1.4, CH Ph), 6.86 (d, 2H, J<sub>H-H</sub> = 2.0, CH Im), 6.65 (ddd, 2H, <sup>3</sup>J<sub>H-H</sub> = <sup>3</sup>J<sub>H-H</sub> = 7.4, <sup>4</sup>J<sub>H-H</sub> = 1.5, CH Ph), 6.51 (d, 2H, <sup>3</sup>J<sub>H-H</sub> = 2.1, CH Im), 6.30 (ddd, 2H, <sup>3</sup>J<sub>H-H</sub> = <sup>3</sup>J<sub>H-H</sub> = 7.4, <sup>4</sup>J<sub>H-H</sub> = 1.3, CH Ph), 6.21 (dd, 2H, <sup>3</sup>J<sub>H-H</sub> = 7.6, <sup>4</sup>J<sub>H-H</sub> = 1.5, CH Ph), 3.45, 3.29, 3.02 (all m, 2H each, NCH<sub>2</sub>), 2.48 (s, 3H, OCH<sub>3</sub>), 2.38 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 2.16 (m, 2H, NCH<sub>2</sub>), 1.75, 1.64, 1.24 (all m, 2H each, NCH<sub>2</sub>CH<sub>2</sub>), -0.77 (s, 1H, OH). <sup>13</sup>C{<sup>1</sup>H} NMR (100.63 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 182.7, 160.9 (both IrC Im), 156.8 (IrC Ph), 148.8, 148.4 (both NC Ph), 139.4, 137.7 (both, CH Ph), 133.0 (IrC Ph), 124.2, 123.7 (both CH Ph), 123.1 (CH Im), 121.0, 120.6 (both, CH Ph), 120.2, 114.6, 114.4 (all CH Im), 110.4, 109.4 (both CH Ph), 57.3 (s, OCH<sub>3</sub>), 49.0, 47.7 (both NCH<sub>2</sub>), 29.8, 21.9 (both, NCH<sub>2</sub>CH<sub>2</sub>).

**Preparation of [Ir{κ<sup>4</sup>-C,C,C,C-[C<sub>6</sub>H<sub>4</sub>Im(CH<sub>2</sub>)<sub>4</sub>ImC<sub>6</sub>H<sub>4</sub>]}(CH<sub>3</sub>CN)<sub>2</sub>][OTf] (4)** A solution of silver trifluoromethanesulfonate (87.6 mg, 0.341 mmol) in 5 mL of acetone was added to a suspension of **2** (204.5 mg, 0.155 mmol) in dichloromethane (20 mL). The suspension was

stirred in the dark at room temperature, for 1 h. Then, it was filtered through Celite to remove the precipitated AgI. The solvent of the filtrate was almost removed in vacuo. The addition of diethyl ether (3 mL) caused the precipitation of a white solid that was dried in vacuo. The solid was dissolved in acetonitrile (5 mL) forming a colorless solution. The solvent was almost removed under reduced pressure and the addition of diethyl ether (3 mL) caused the precipitation of a white solid that was washed with further portions of diethyl ether (3 x 3 mL). Yield: 168 mg (71%). Anal. Calcd for C<sub>27</sub>H<sub>26</sub>F<sub>3</sub>IrN<sub>6</sub>O<sub>3</sub>S: C, 42.45; H, 3.43; N, 11.00; S, 4.20. Found: C, 42.53; H, 3.65; N, 10.82; S, 4.55. HRMS (electrospray, *m/z*): calcd for C<sub>24</sub>H<sub>23</sub>IrN<sub>5</sub> [M - NCCH<sub>3</sub>]<sup>+</sup> 574.1578; found 574.1662. IR (cm<sup>-1</sup>): ν(CN) 2260 (br, m), ν(CF<sub>3</sub> + SO<sub>3</sub>) 1250, 1222, 1148, 1027 (m). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 7.86 (m, 1H, Ph), 7.65 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 2.0, Im), 7.37 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 2.1, Im), 7.28 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 2.0, Im), 7.23 (m, 3H, Ph), 7.11 (dd, 1H, <sup>3</sup>J<sub>H-H</sub> = 7.6, <sup>4</sup>J<sub>H-H</sub> = 1.3, Ph), 6.86 (ddd, 1H, <sup>3</sup>J<sub>H-H</sub> = <sup>3</sup>J<sub>H-H</sub> = 7.6, <sup>4</sup>J<sub>H-H</sub> = 1.4, Ph), 6.74 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 2.1, Im), 6.53 (ddd, 1H, <sup>3</sup>J<sub>H-H</sub> = <sup>3</sup>J<sub>H-H</sub> = 7.6, <sup>4</sup>J<sub>H-H</sub> = 1.3, Ph), 6.34 (dd, 1H, <sup>3</sup>J<sub>H-H</sub> = 7.6, <sup>4</sup>J<sub>H-H</sub> = 1.4, Ph), 4.72, 4.33, 3.57 (all m, 1H each, NCH<sub>2</sub>), 2.38 (m, 1H, NCH<sub>2</sub>CH<sub>2</sub>), 2.37, 2.32 (both s, 3H each, CH<sub>3</sub>CN), 2.14 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 1.92, 1.81 (both m, 1H each, NCH<sub>2</sub>CH<sub>2</sub>). <sup>19</sup>F NMR (282.33 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ -78.9 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (100.63 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 170.9, 151.1 (both IrC Im), 147.5, 147.3 (both NC Ph), 146.8 (IrC Ph), 137.9, 135.4, 126.5, 125.2 (all CH Ph), 124.6 (IrC Ph), 123.6, 123.5 (both CH Ph), 123.4, 122.0 (both CH Im), 120.1, 118.3 (both CH<sub>3</sub>CN), 116.5, 115.2 (both CH Im), 111.8, 111.7 (both CH Ph), 51.8, 48.1 (both NCH<sub>2</sub>), 30.1, 24.3 (both NCH<sub>2</sub>CH<sub>2</sub>), 4.3, 4.1 (both CH<sub>3</sub>).

**Preparation of Ir{κ<sup>4</sup>-C,C,C,C-[C<sub>6</sub>H<sub>4</sub>Im(CH<sub>2</sub>)<sub>4</sub>ImC<sub>6</sub>H<sub>4</sub>]}{κ<sup>2</sup>-C,N-[C<sub>6</sub>H<sub>4</sub>-py]} (5).** A mixture of **4** (268 mg, 0.351 mmol), (piperidinomethyl)polystyrene (100 mg, 0.351 mmol), and 2-phenylpyridine (50.1 μL, 0.351 mmol) was refluxed in 10 mL of fluorobenzene for 5h. After

cooling at room temperature, the resulting suspension was filtered through Celite. The oily residue remaining in the Schlenk flask was washed with dichloromethane (2 x 3 mL). The filtrate and washings were combined and the solvent removed under reduced pressure. The obtained yellow solid was washed with diethyl ether (3 x 3 mL). Yield: 193 mg (80%). Anal. Calcd for  $C_{33}H_{28}IrN_5$ : C, 57.71; H, 4.11; N, 10.20. Found: C, 57.49; H, 4.30; N, 9.84. HRMS (electrospray,  $m/z$ ): calcd for  $C_{33}H_{29}IrN_5 [M + H]^+$  688.2048; found 688.2042.  $^1H$  NMR (300 MHz,  $CD_2Cl_2$ , 298 K):  $\delta$  7.86 (d, 1H,  $^3J_{H-H} = 8.0$ , py), 7.75 (dd, 1H,  $^3J_{H-H} = 5.6$ ,  $^4J_{H-H} = 1.3$ , py), 7.69 (d, 1H,  $^3J_{H-H} = 7.8$ , Ph), 7.58 (ddd, 1H,  $^3J_{H-H} = ^3J_{H-H} = 8.0$ ,  $^4J_{H-H} = 1.3$ , py), 7.51 (d, 1H,  $^3J_{H-H} = 1.9$ , Im), 7.41 (d, 1H,  $^3J_{H-H} = 2.1$ , Im), 7.20 (d, 1H,  $^3J_{H-H} = 7.4$ , Ph), 7.16 (d, 1H,  $^3J_{H-H} = 7.3$ , Ph), 7.00-6.82 (m, 4H, Ph), 6.80 (d, 1H,  $^3J_{H-H} = 1.9$ , Im), 6.78 (d, 1H,  $^3J_{H-H} = 2.1$ , Im), 6.77-6.71 (m, 4H, 1H py + 3H Ph), 6.67 (ddd, 1H,  $^3J_{H-H} = ^3J_{H-H} = 7.3$ ,  $^4J_{H-H} = 1.0$ , Ph), 6.38 (dd, 1H,  $^3J_{H-H} = 7.3$ ,  $^4J_{H-H} = 1.0$ , Ph), 3.74 (m, 1H,  $NCH_2$ ), 3.54 (m, 2H,  $NCH_2$ ), 2.55 (m, 1H,  $NCH_2$ ), 2.36 (m, 1H,  $NCH_2CH_2$ ), 2.10 (m, 2H,  $NCH_2CH_2$ ), 1.49 (m, 1H,  $NCH_2CH_2$ ).  $^{13}C\{^1H\}$  NMR (75.47 MHz,  $CD_2Cl_2$ , 298 K):  $\delta$  176.7 (IrC Im), 172.2 (IrC Ph), 169.0 (NC py), 165.2 (IrC Im), 154.6, 153.7 (both IrC Ph), 151.0 (CH py), 148.6, 146.6, 145.0 (all C Ph), 139.54, 139.51 (both CH Ph), 135.6 (CH py), 132.8, 128.7, 125.7, 124.7, 124.2, 121.9 (all CH Ph), 121.5 (CH py), 120.7 (CH Im), 120.3 (CH Ph), 120.1 (CH Im), 119.7 (CH Ph), 118.9 (CH py), 116.3, 114.0 (both CH Im), 110.9, 110.4 (both CH Ph), 50.9, 47.9 both ( $NCH_2$ ), 29.9, 26.4 (both  $NCH_2CH_2$ ).

**Preparation of  $Ir\{\kappa^4-C,C,C,C-[C_6H_4Im(CH_2)_4ImC_6H_4]\}\{\kappa^2-C,N-[C_6H_2F_2-py]\}$  (6).** A mixture of **4** (220 mg, 0.288 mmol), (piperidinomethyl)polystyrene (82 mg, 0.288 mmol), and 2-(2,4-difluorophenyl)pyridine (45  $\mu$ L, 0.288 mmol) was refluxed in 10 mL of fluorobenzene for 5h. After cooling at room temperature, the resulting suspension was filtered through Celite. The solvent was removed under reduced pressure and the addition of diethyl ether resulted on a

precipitation of a yellow solid that was washed with diethyl ether (3 x 3 mL). Yield: 170 mg (82%). Anal. Calcd for C<sub>33</sub>H<sub>26</sub>F<sub>2</sub>IrN<sub>5</sub>: C, 54.83 H, 3.63; N, 9.69. Found: C, 54.85 H, 3.54; N, 9.34. HRMS (electrospray, *m/z*): calcd for C<sub>33</sub>H<sub>27</sub>F<sub>2</sub>IrN<sub>5</sub> [M + H]<sup>+</sup> 724.1860; found 724.1897. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 8.25 (dd, 1H, <sup>3</sup>J<sub>H-H</sub> = 8.0, <sup>4</sup>J<sub>H-H</sub> = 1.5, py), 7.82 (dd, 1H, <sup>3</sup>J<sub>H-H</sub> = 5.7, <sup>4</sup>J<sub>H-H</sub> = 1.0, py), 7.61 (dd, 1H, <sup>3</sup>J<sub>H-H</sub> = 8.0, <sup>4</sup>J<sub>H-H</sub> = 1.0, py), 7.52 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 2.0, Im), 7.41 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 2.1, Im), 7.21 (m, 2H, Ph), 6.98 (ddd, 1H, <sup>3</sup>J<sub>H-H</sub> = <sup>3</sup>J<sub>H-H</sub> = 7.5, <sup>4</sup>J<sub>H-H</sub> = 1.7, Ph), 6.93 (ddd, 1H, <sup>3</sup>J<sub>H-H</sub> = 7.5, <sup>4</sup>J<sub>H-H</sub> = 1.3, Ph), 6.82 (d, 1H, J<sub>H-H</sub> = 2.0, Im), 6.78-6.68 (m, 5H, 1H Im + 1H py + 3H Ph), 6.39 (dd, 1H, <sup>3</sup>J<sub>H-H</sub> = 7.2, <sup>4</sup>J<sub>H-H</sub> = 1.3, Ph), 6.32 (m, 2H, dfp), 3.72, 3.62, 3.54, 2.50 (all m, 1H each, NCH<sub>2</sub>), 2.24, 2.16, 2.07, 1.53 (all m, 1H each, NCH<sub>2</sub>CH<sub>2</sub>). <sup>19</sup>F NMR (282.33 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ -111.14 (ddd, F<sup>2</sup>, <sup>4</sup>J<sub>F-F</sub> = <sup>3</sup>J<sub>F-H</sub> = 8.9, <sup>5</sup>J<sub>F-H</sub> = 2.4), -112.46 (ddd, F<sup>4</sup>, <sup>4</sup>J<sub>F-F</sub> = <sup>3</sup>J<sub>F-H</sub> = <sup>3</sup>J<sub>F-H</sub> = 8.9). <sup>19</sup>F{<sup>1</sup>H} NMR (282.33 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ -111.14 (d, F<sup>2</sup>, <sup>4</sup>J<sub>F-F</sub> = 8.9), -112.46 (d, F<sup>4</sup>, <sup>4</sup>J<sub>F-F</sub> = 8.9). <sup>13</sup>C{<sup>1</sup>H} NMR (100.63 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 179.8 (dd, <sup>3</sup>J<sub>C-F</sub> = 2.9, <sup>3</sup>J<sub>C-F</sub> = 4.6, IrC dfp), 176.3 (s, IrC Im), 165.6 (d, <sup>3</sup>J<sub>C-F</sub> = 7.9, NC py), 164.3 (s, IrC Im), 163.4 (dd, <sup>1</sup>J<sub>C-F</sub> = 255.3, <sup>3</sup>J<sub>C-F</sub> = 10.8, CF), 162.6 (dd, <sup>1</sup>J<sub>C-F</sub> = 260.6, <sup>3</sup>J<sub>C-F</sub> = 11.5, CF), 153.6 (s, IrC Ph), 152.3 (dd, <sup>5</sup>J<sub>C-F</sub> = 2.2, IrC Ph *trans* to C<sub>6</sub>H<sub>2</sub>F<sub>2</sub>-py), 151.2 (s, CH py), 148.5, 146.6 (both s, C Ph), 139.3 (s, CH Ph), 136.2 (s, CH py), 133.0 (s, CH Ph), 128.7 (d, <sup>2</sup>J<sub>C-F</sub> = 2.5, C-py dfp), 126.0, 125.1 (both s, CH Ph), 123.0 (d, <sup>4</sup>J<sub>C-F</sub> = 22.5, CH py), 122.4 (s, CH Ph), 121.7 (s, CH py), 121.0 (s, CH Im), 120.9 (s, CH Ph), 120.6 (s, CH Im), 119.8 (dd, <sup>2</sup>J<sub>C-F</sub> = 13.6, <sup>4</sup>J<sub>C-F</sub> = 2.8, CH dfp), 116.7 (s, CH Im), 114.3 (s, CH Im), 111.2 (s, CH Ph), 110.9 (s, CH Ph), 95.8 (dd, <sup>2</sup>J<sub>C-F</sub> = <sup>2</sup>J<sub>C-F</sub> = 27.5, CH dfp), 51.3, 48.0 (both s, NCH<sub>2</sub>), 30.2, 26.5 (both s, NCH<sub>2</sub>CH<sub>2</sub>).

**Preparation of Ir{κ<sup>4</sup>-C,C,C,C-[C<sub>6</sub>H<sub>4</sub>Im(CH<sub>2</sub>)<sub>4</sub>ImC<sub>6</sub>H<sub>4</sub>]}{κ<sup>2</sup>-C,N-[C<sub>6</sub>H<sub>3</sub>Me-py]} (7).** It was prepared following the procedure described for **6** starting from **4** (115 mg, 0.150 mmol), (piperidinomethyl)polystyrene (43 mg, 0.150 mmol), and 2-(*p*-tolyl)pyridine (25 μL, 0.150



mmol). Yellow solid. Yield: 95 mg (90 %). Anal. Calcd for C<sub>34</sub>H<sub>30</sub>IrN<sub>5</sub>: C, 58.27 H, 4.31; N, 9.99. Found: C, 58.69 H, 4.17; N, 9.74. HRMS (electrospray, *m/z*): calcd for C<sub>34</sub>H<sub>31</sub>IrN<sub>5</sub> [M + H]<sup>+</sup> 702.2205; found 702.2212. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 7.81 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 8.2, py), 7.72 (m, 1H, py), 7.58 (m, 1H, C<sub>6</sub>MeH<sub>3</sub>), 7.54 (m, 1H, py), 7.51 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 2.0, Im), 7.41 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 2.2, Im), 7.19 (m, 2H, Ph), 6.95 (m, 1H, Ph), 6.89 (m, 1H, Ph), 6.80 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 2.0, Im), 6.79 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 2.2, Im), 6.74-6.65 (m, 6H, 1H py + 3H Ph + 2H C<sub>6</sub>MeH<sub>3</sub>), 6.39 (dd, 1H, <sup>3</sup>J<sub>H-H</sub> = 7.2, <sup>4</sup>J<sub>H-H</sub> = 1.2, Ph), 3.75 (m, 1H, NCH<sub>2</sub>), 3.54 (m, 2H, NCH<sub>2</sub>), 2.57 (m, 1H, NCH<sub>2</sub>CH<sub>2</sub>), 2.38 (m, 1H, NCH<sub>2</sub>CH<sub>2</sub>), 2.13 (s, 3H, CH<sub>3</sub>), 2.07 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 1.47 (m, 1H, NCH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75.48 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 176.9 (IrC Im), 172.2 (IrC C<sub>6</sub>H<sub>3</sub>Me), 169.1 (NC py), 165.4 (IrC Im), 154.9, 154.0 (both IrC Ph), 151.0 (CH py), 148.7, 146.8 (both C Ph), 142.7 (C C<sub>6</sub>H<sub>3</sub>Me(-py)), 140.6 (CH C<sub>6</sub>H<sub>3</sub>Me), 139.6 (CH Ph), 138.4 (C C<sub>6</sub>H<sub>3</sub>Me(-CH<sub>3</sub>)), 135.6 (CH py), 133.0, 125.8, 124.8 (all CH Ph), 124.3 (CH C<sub>6</sub>H<sub>3</sub>Me), 122.0 (CH Ph), 121.2 (CH py), 121.1 (CH C<sub>6</sub>H<sub>3</sub>Me), 120.8 (CH Im), 120.3 (CH Ph), 120.2 (CH Im), 118.7 (CH py), 116.5, 114.1 (both CH Im), 111.0, 110.6 (both CH Ph), 50.9, 48.0 (both NCH<sub>2</sub>), 29.9, 26.7 (both NCH<sub>2</sub>CH<sub>2</sub>), 22.0 (CH<sub>3</sub>).

**Preparation of Ir{κ<sup>4</sup>-C,C,C,C-[C<sub>6</sub>H<sub>4</sub>Im(CH<sub>2</sub>)<sub>4</sub>ImC<sub>6</sub>H<sub>4</sub>]}{κ<sup>2</sup>-C,N-[C<sub>6</sub>H<sub>4</sub>-Mepy]} (8).** It was prepared following the procedure described for **6** starting from **4** (125 mg, 0.164 mmol), (piperidinomethyl)polystyrene (47 mg, 0.164 mmol), and 5-methyl-2-phenylpyridine (28 mg, 0.164 mmol). Yellow solid. Yield: 110 mg (95%). Anal. Calcd for C<sub>34</sub>H<sub>30</sub>IrN<sub>5</sub>: C, 58.27 H, 4.31; N, 9.99. Found: C, 58.48 H, 4.47; N, 9.72. HRMS (electrospray, *m/z*): calcd for C<sub>34</sub>H<sub>31</sub>IrN<sub>5</sub> [M + H]<sup>+</sup> 702.2205; found 702.2203. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 7.75 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 8.3, py), 7.64 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 7.8, Ph), 7.53 (d, 1H, <sup>4</sup>J<sub>H-H</sub> = 0.9, NCH py), 7.53 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 2.0, Im), 7.42 (dd, 1H, <sup>3</sup>J<sub>H-H</sub> = 8.3, <sup>4</sup>J<sub>H-H</sub> = 0.9, py), 7.40 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 2.1, Im), 7.20 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 7.8,

Ph), 7.17 (d, 1H,  $^3J_{\text{H-H}} = 7.3$ , Ph), 6.97 (m, 1H, Ph), 6.89 (ddd, 1H,  $^3J_{\text{H-H}} = ^3J_{\text{H-H}} = 7.5$ ,  $^4J_{\text{H-H}} = 1.3$ , Ph), 6.86-6.81 (m, 2H, Ph), 6.80 (d, 1H,  $^3J_{\text{H-H}} = 2.0$ , Im), 6.77 (d, 1H,  $^3J_{\text{H-H}} = 2.1$ , Im), 6.77-6.72 (m, 3H, Ph), 6.67 (ddd, 1H,  $^3J_{\text{H-H}} = ^3J_{\text{H-H}} = 7.2$ ,  $^4J_{\text{H-H}} = 1.0$ , Ph), 6.39 (dd, 1H,  $^3J_{\text{H-H}} = 7.2$ ,  $^4J_{\text{H-H}} = 1.0$ , Ph), 3.75 (m, 1H, NCH<sub>2</sub>), 3.54 (m, 2H, NCH<sub>2</sub>), 2.56 (m, 1H, NCH<sub>2</sub>), 2.34 (m, 1H, NCH<sub>2</sub>CH<sub>2</sub>), 2.10 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 2.02 (s, 3H, CH<sub>3</sub>), 1.50 (m, 1H, NCH<sub>2</sub>CH<sub>2</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  176.8 (IrC Im), 171.2 (IrC Ph), 166.5 (NC py), 165.4 (IrC Im), 155.0, 153.9 (both IrC Ph), 151.0 (CHN py), 148.6, 146.7, 145.3 (all C Ph), 139.6, 139.5 (both CH Ph), 136.6 (CH py), 133.0 (CH Ph), 131.3 (CCH<sub>3</sub>), 128.5, 125.9, 124.8, 123.9, 122.0 (all CH Ph), 120.8, 120.4 (both CH Im), 119.8 (CH Ph), 118.5 (CH py), 116.5, 114.1 (both CH Im), 110.5 (CH Ph), 51.0, 48.0 (both NCH<sub>2</sub>), 30.1, 26.5 (both NCH<sub>2</sub>CH<sub>2</sub>), 18.5 (CH<sub>3</sub>).

## ASSOCIATED CONTENT

**Supporting Information.** The following files are available free of charge.

General information, crystallographic data for complexes **3** and **5**, computational details,  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  APT NMR of the complexes **2–8**, experimental and computed UV/vis spectra, frontier molecular orbitals, cyclic voltammograms, and normalized excitation and emission spectra for complexes **5–8** (PDF)

Cartesian coordinates of compounds **5–8** (XYZ)

## Accession Codes

CCDC 1580312 (**3**) and 1580313 (**5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto: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.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: maester@unizar.es.

### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

## ACKNOWLEDGMENT

Financial support from the Spanish MINECO (Projects CTQ2017-82935-P, Red de Excelencia Consolider CTQ2016-81797-REDC), Gobierno de Aragón (E35), FEDER, and the European Social Fund (FSE) is acknowledged.

## REFERENCES

(1) See for example: (a) Ulbricht, C.; Beyer, B.; Friebe, C.; Winter, A.; Schubert, U. S. Recent Developments in the Application of Phosphorescent Iridium(III) Complex Systems. *Adv. Mater.* **2009**, *21*, 4418–4441. (b) You Y.; Park, S. Y. Phosphorescent iridium(III) complexes: toward high phosphorescence quantum efficiency through ligand control. *Dalton Trans.* **2009**, 1267–1282. (c) Chi, Y.; Chou, P.-T. Transition-metal phosphors with cyclometalating ligands: fundamentals and applications. *Chem. Soc. Rev.* **2010**, *39*, 638–655. (d) Liu, Z.; Bian, Z.; Huang, C. Luminescent iridium complexes and their applications. *Top. Organomet. Chem.* **2010**, *28*, 113–142. (e) Fan, C.; Yang, C. Yellow/orange emissive heavy-metal complexes as phosphors in monochromatic and white organic light-emitting devices. *Chem. Soc. Rev.* **2014**, *43*, 6439–6469. (f) Zanoni, K. P. S.; Coppo, R. L.; Amaral, R. C.; Iha, N. Y. M. Ir(III) complexes designed for light-emitting devices: beyond the luminescence color array. *Dalton Trans.* **2015**, *44*, 14559–

14573. (g) Omae, I. Application of the five-membered ring blue light-emitting iridium products of cyclometalation reactions as OLEDs. *Coord. Chem. Rev.* **2016**, *310*, 154–169.

(2) 3 is the number of electrons donated by the ligands, whereas b and b' indicate the denticity of the ligands (bidentate). See: Esteruelas, M. A.; Oñate, E.; Palacios, A. U. Selective Synthesis and Photophysical Properties of Phosphorescent Heteroleptic Iridium(III) Complexes with Two Different Bidentate Groups and Two Different Monodentate Ligands. *Organometallics* **2017**, *36*, 1743–1755.

(3) (a) Stringer, B. D.; Quan, L. M.; Barnard, P. J.; Wilson, D. J. D.; Hogan, C. F. Iridium Complexes of N-Heterocyclic Carbene Ligands: Investigation into the Energetic Requirements for Efficient Electrogenenerated Chemiluminescence. *Organometallics* **2014**, *33*, 4860–4872. (b) Kim, T.; Lee, J.; Lee, S. U.; Lee, M. H. *o*-Carboranyl–Phosphine as a New Class of Strong-Field Ancillary Ligand in Cyclometalated Iridium(III) Complexes: Toward Blue Phosphorescence. *Organometallics* **2015**, *34*, 3455–3458. (c) Lee, Y. H.; Park, J.; Lee, J.; Lee, S. U.; Lee, M. H. Iridium Cyclometalates with Tethered *o*-Carboranes: Impact of Restricted Rotation of *o*-Carborane on Phosphorescence Efficiency. *J. Am. Chem. Soc.* **2015**, *137*, 8018–8021. (d) Li, T.-Y.; Liang, X.; Zhou, L.; Wu, C.; Zhang, S.; Liu, X.; Lu, G.-Z.; Xue, L.-S.; Zheng, Y.-X.; Zuo, J.-L. Synthesis and characterization of efficient luminescent materials based on 2,1,3-benzothiadiazole with carbazole moieties. *Inorg. Chem.* **2015**, *54*, 161–173. (e) Nguyen, V. H.; Khoo, R. S. H.; Yip, J. H. K. Ir(2-Phenylpyridine)<sub>2</sub>(benzene-1,2-dithiolate) Anion as a Diastereoselective Metalloligand and Nucleophile: Stereoelectronic Effect, Spectroscopy, and Computational Study of the Methylated and Aurated Complexes and their Oxygenation Products. *Inorg. Chem.* **2015**, *54*, 2264–2277. (f) Radwan, Y. K.; Maity, A.; Teets, T. S. Manipulating the Excited States of Cyclometalated Iridium Complexes with  $\beta$ -Ketoiminate and  $\beta$ -Diketimate

Ligands. *Inorg. Chem.* **2015**, *54*, 7122–7131. (g) Kumar, S.; Hisamatsu, Y.; Tamaki, Y.; Ishitani, O.; Aoki, S. Design and Synthesis of Heteroleptic Cyclometalated Iridium(III) Complexes Containing Quinoline-Type Ligands that Exhibit Dual Phosphorescence. *Inorg. Chem.* **2016**, *55*, 3829–3843. (h) Yi, S.; Kim, J.-H.; Cho, Y.-J.; Lee, J.; Choi, T.-S.; Cho, D. W.; Pac, C.; Han, W.-S.; Son, H.-J.; Kang, S. O. Stable Blue Phosphorescence Iridium(III) Cyclometalated Complexes Prompted by Intramolecular Hydrogen Bond in Ancillary Ligand. *Inorg. Chem.* **2016**, *55*, 3324–3331. (i) Axtell, J. C.; Kirlikovali, K. O.; Djurovich, P. I.; Jung, D.; Nguyen, V. T.; Munekiyo, B.; Royappa, A. T.; Rheingold, A. L.; Spokoyny, A. M. Blue Phosphorescent Zwitterionic Iridium(III) Complexes Featuring Weakly Coordinating nido-Carborane-Based Ligands. *J. Am. Chem. Soc.* **2016**, *138*, 15758–15765. (j) Umamahesh, B.; Karthikeyan, N. S.; Sathiyarayanan, K. I.; Malicka, J. M.; Cocchi, M. Tetrazole iridium(III) complexes as a class of phosphorescent emitters for high-efficiency OLEDs. *J. Mater. Chem. C* **2016**, *4*, 10053–10060. (k) Yu, T.; Yang, F.; Chen, X.; Su, W.; Zhao, Y.; Zhang, H.; Li, J. Synthesis and characterization of green-emitting Ir(III) complexes based on a functionalized benzimidazole ligand. *New J. Chem.* **2017**, *41*, 2046–2054. (l) Jing, Y.-M.; Zhao, Y.; Zheng, Y.-X. Photoluminescence and electroluminescence of iridium(III) complexes with 2',6'-bis(trifluoromethyl)-2,4'-bipyridine and 1,3,4-oxadiazole/1,3,4-thiadiazole derivative ligands. *Dalton Trans.*, **2017**, *46*, 845–853. (m) Benjamin, H.; Liang, J.; Liu, Y.; Geng, Y.; Liu, X.; Zhu, D.; Batsanov, A. S.; Bryce, M. R. Color Tuning of Efficient Electroluminescence in the Blue and Green Regions Using Heteroleptic Iridium Complexes with 2-Phenoxyoxazole Ancillary Ligands. *Organometallics* **2017**, *36*, 1810–1821. (n) Pal, A. K.; Henwood, A. F.; Cordes, D. B.; Slawin, A. M. Z.; Samuel, I. D. W.; Zysman-Colman, E. Blue-to-Green Emitting Neutral Ir(III) Complexes Bearing Pentafluorosulfonyl Groups: A Combined Experimental and Theoretical Study. *Inorg. Chem.* **2017**, *56*, 7533–7544. (o) Davidson, R.; Hsu, Y.-T.; Bhagani, ., Yufit, D.;

Beeby, A. Exploring the Chemistry and Photophysics of Substituted Picolinate Positional Isomers in Iridium(III) Bisphenylpyridine Complexes. *Organometallics* **2017**, *36*, 2727–2735.

(4) See for example: Baranoff, E.; Curchod, B. F. E.; Frey, J.; Scopelliti, R.; Kessler, F.; Tavernelli, I.; Rothlisberger, U.; Grätzel, M.; Nazeeruddin, Md. K. Acid-Induced Degradation of Phosphorescent Dopants for OLEDs and Its Application to the Synthesis of Tris-heteroleptic Iridium(III) Bis-cyclometalated Complexes. *Inorg. Chem.* **2012**, *51*, 215–224.

(5) (a) Xia, C.; Tsai, J.-Y.; Esteruelas, M. A.; Gómez, R.; Oliván, M.; Oñate, E. Organic Electroluminescent Materials and Devices. Patent Application 14/996448, 2016. (b) Alabau, R. G.; Esteruelas, M. A.; Oliván, M.; Oñate, E.; Palacios, A. U. Tsai, J.-Y.; Xia, C. Osmium(II) Complexes Containing a Dianionic CCCC-Donor Tetradentate Ligand. *Organometallics*, **2016**, *35*, 3981–3995. (c) Alabau, R. G.; Esteruelas, M. A.; Oliván, M.; Oñate, E. Preparation of Phosphorescent Osmium(IV) Complexes with N,N',C and C,N,C'-Pincer Ligands. *Organometallics*, **2017**, *36*, 1848–1859.

(6) Baranoff, E.; Yum, J.-H.; Graetzel, M.; Nazeeruddin, Md. K. Cyclometallated iridium complexes for conversion of light into electricity and electricity into light. *J. Organomet. Chem.* **2009**, *694*, 2661–2670.

(7) (a) Chang, C.-F.; Cheng, Y.-M.; Chi, Y.; Chiu, Y.-C.; Lin, C.-C.; Lee, G.-H.; Chou, P.-T.; Chen, C.-C.; Chang, C.-H.; Wu, C.-C. Highly Efficient Blue-Emitting Iridium(III) Carbene Complexes and Phosphorescent OLEDs. *Angew. Chem. Int. Ed.* **2008**, *47*, 4542–4545. (b) Chien, C.-H.; Fujita, S.; Yamoto, S.; Hara, T.; Yamagata, T.; Watanabe M.; Mashima K. Stepwise and one-pot syntheses of Ir(III) complexes with imidazolium-based carbene ligands. *Dalton Trans.* **2008**, 916–923. (c) Tsurugi, H.; Fujita, S.; Choi, G.; Yamagata, T.; Ito, S.; Miyasaka, H.;

Mashima, K. Carboxylate Ligand-Induced Intramolecular C-H Bond Activation of Iridium Complexes with N-Phenylperimidine-Based Carbene Ligands. *Organometallics*, **2010**, *29*, 4120–4129. (d) Hsieh, C.-H.; Wu, F.-I.; Fan, C.-H.; Huang, M.-J.; Lu, K.-Y.; Chou, P.-Y.; Yang, Y.-H. O.; Wu, S.-H.; Chen, I.-C.; Chou, S.-H.; Wong, K.-T.; Cheng, C.-H. Design and Synthesis of Iridium Bis(carbene) Complexes for Efficient Blue Electrophosphorescence. *Chem. Eur. J.* **2011**, *17*, 9180–9187. (e) Lu, K.-Y.; Chou, H.-H.; Hsieh, C.-H.; Yang, Y.-H. O.; Tsai, H.-R.; Tsai, H.-Y.; Hsu, L.-C.; Chen, C.-Y.; Chen, I.-C.; Cheng, C.-H. Wide-Range Color Tuning of Iridium Biscarbene Complexes from Blue to Red by Different N<sup>N</sup> Ligands: an Alternative Route for Adjusting the Emission Colors. *Adv. Mater.* **2011**, *23*, 4933–4937. (f) Zhou, Y.; Jia, J.; Li, W.; Fei, H.; Zhou, M. Luminescent biscarbene iridium(III) complexes as living cell imaging reagents. *Chem. Commun.*, **2013**, *49*, 3230–3232. (g) Li, H.; Yin, Y.-M.; Cao, H.-T.; Sun, H.-Z.; Wang, L.; Shan, G.-G.; Zhu, D.-X.; Su, Z.-M.; Xie, W.-F. Efficient greenish-blue phosphorescent iridium(III) complexes containing carbene and triazole chromophores for organic light-emitting diodes. *J. Organomet. Chem.* **2014**, *753*, 55–62. (h) Shang, X.; Han, D.; Zhan, Q.; Zhang, G.; Li, D. DFT and TD-DFT Study on the Electronic Structures and Phosphorescent Properties of a Series of Heteroleptic Iridium(III) Complexes. *Organometallics*, **2014**, *33*, 3300–3308. (i) Leopold, H.; Císařová, I.; Strassner, T. Phosphorescent C<sup>^</sup>C\* Cyclometalated Thiazol-2-ylidene Iridium(III) Complexes: Synthesis, Structure, and Photophysics. *Organometallics* **2017**, *36*, 3016–3018.

(8) (a) Hahn, F. E.; Jahnke, M. C. Heterocyclic Carbenes: Synthesis and Coordination Chemistry. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122–3172. (b) Díez-González, S.; Marion, N.; Nolan, S. P. N-Heterocyclic Carbenes in Late Transition Metal Catalysis. *Chem. Rev.* **2009**, *109*, 3612–3676. (c) Esteruelas, M. A.; López, A. M.; Oliván, M. Polyhydrides of Platinum Group

Metals: Nonclassical Interactions and  $\sigma$ -Bond Activation Reactions. *Chem. Rev.* **2016**, *116*, 8770–8847.

(9) *Comprehensive Coordination Chemistry II, from Biology to Nanotechnology*; Lever, A. B. P., Vol. Ed.; Elsevier: Amsterdam, 2004; Vol. 1.

(10) (a) Hu, X.; Castro-Rodriguez, I.; Meyer, K. Dioxygen Activation by a Low-Valent Cobalt Complex Employing a Flexible Tripodal N-Heterocyclic Carbene Ligand. *J. Am. Chem. Soc.* **2004**, *126*, 13464–13473. (b) Liu, B.; Xia, Q.; Chen, W. Direct Synthesis of Iron, Cobalt, Nickel, and Copper Complexes of N-Heterocyclic Carbenes by Using Commercially Available Metal Powders. *Angew. Chem. Int. Ed.* **2009**, *48*, 5513–5516. (c) Lu, C.; Gu, S.; Chen, W.; Qiu, H. Platinum(II) complexes with polydentate N-heterocyclic carbenes: synthesis, structural characterization and hydrosilylation catalysis. *Dalton Trans.* **2010**, *39*, 4198–4204. (d) Raba, A.; Cokoja, M.; Ewald, S.; Riener, K.; Herdtweck, E.; Pöthig, A.; Herrmann, W. A.; Kühn, F. E. Synthesis and Characterization of Novel Iron(II) Complexes with Tetradentate Bis(N-heterocyclic carbene)–Bis(pyridine) (NCCN) Ligands. *Organometallics* **2012**, *31*, 2793–2800. (e) Liu, X.; Chen, W. Synthesis of ruthenium(II) complexes of tetradentate bis(N-pyridylimidazolylidenyl)methane and their reactivities towards N- donors. *Dalton Trans.* **2012**, *41*, 599–608. (f) Käß, M.; Hohenberger, J.; Adelhardt, M.; Zolnhofer, E. M.; Mossin, S.; Heinemann, F. W.; Sutter, J.; Meyer, K. Synthesis and Characterization of Divalent Manganese, Iron, and Cobalt Complexes in Tripodal Phenolate/N-Heterocyclic Carbene Ligand Environments. *Inorg. Chem.* **2014**, *53*, 2460–2470. (g) Fleetham, T.; Li, G.; Wen, L.; Li, J. Efficient “Pure” Blue OLEDs Employing Tetradentate Pt Complexes with a Narrow Spectral Bandwidth. *Adv. Mater.* **2014**, *26*, 7116–7121. (h) Weiss, D. T.; Anneser, M. R.; Haslinger, S.;



Pöthig, A.; Cokoja, M.; Basset, J.-M.; Kühn, F. E. NHC Versus Pyridine: How “Teeth” Change the Redox Behavior of Iron(II) Complexes. *Organometallics* **2015**, *34*, 5155–5166.

(11) (a) Findlay, N. J.; Park, S. R.; Schoenebeck, F.; Cahard, E.; Zhou, S.; Berlouis, L. E. A.; Spicer, M. D.; Tuttle, T.; Murphy, J. A. Reductions of Challenging Organic Substrates by a Nickel Complex of a Noninnocent Crown Carbene Ligand. *J. Am. Chem. Soc.* **2010**, *132*, 15462–15464. (b) Bass, H. M.; Cramer, S. A.; Price, J. L.; Jenkins, D. M. 18-Atom-Ringed Macrocyclic Tetra-imidazoliums for Preparation of Monomeric Tetra-carbene Complexes. *Organometallics* **2010**, *29*, 3235–3238. (c) Lu, Z.; Cramer, S. A.; Jenkins, D. M. Exploiting a dimeric silver transmetallating reagent to synthesize macrocyclic tetracarbene complexes. *Chem. Sci.* **2012**, *3*, 3081–3087. (d) Meyer, S.; Klawitter, I.; Demeshko, S.; Bill, E.; Meyer, F. A Tetracarbene–Oxoiron(IV) Complex. *Angew. Chem. Int. Ed.* **2013**, *52*, 901–905. (e) Bass, H. M.; Cramer, A. S.; McCullough, A. S.; Bernstein, K. J.; Murdock, C. R.; Jenkins, D. M. Employing Dianionic Macrocyclic Tetracarbenes To Synthesize Neutral Divalent Metal Complexes. *Organometallics* **2013**, *32*, 2160–2167. (f) Kupper, C.; Schober, A.; Demeshko, S.; Bergner, M.; Meyer, F. An Exclusively Organometallic {FeNO}<sup>7</sup> Complex with Tetracarbene Ligation and a Linear FeNO Unit. *Inorg. Chem.* **2015**, *54*, 3096–3098. (g) Anneser, M. R.; Haslinger, S.; Pöthig, A.; Cokoja, M.; Basset, J.-M.; Kühn, F. E. Synthesis and Characterization of an Iron Complex Bearing a Cyclic Tetra-N-heterocyclic Carbene Ligand: An Artificial Heme Analogue? *Inorg. Chem.* **2015**, *54*, 3797–3804. (h) Chandrachud, P. P.; Bass, H. M.; Jenkins, D. M. Synthesis of Fully Aliphatic Aziridines with a Macrocyclic Tetracarbene Iron Catalyst. *Organometallics* **2016**, *35*, 1652–1657. (i) Kupper, C.; Rees, J. A.; Dechert, S.; DeBeer, S.; Meyer, F. Complete Series of {FeNO}<sup>8</sup>, {FeNO}<sup>7</sup>, and {FeNO}<sup>6</sup> Complexes Stabilized by a Tetracarbene Macrocycle. *J. Am. Chem. Soc.* **2016**, *138*, 7888–7898. (j) Anneser, M. R.;

Haslinger, S.; Pöthig, A.; Cokoja, M.; D'Elia, V.; Högerl, M. P.; Basset, J.-M.; Kühn, F. E. Binding of molecular oxygen by an artificial heme analogue: investigation on the formation of an Fe–tetracarbene superoxo complex. *Dalton Trans.*, **2016**, *45*, 6449–6455. (k) Altmann, P. J.; Weiss, D. T.; Jandl, C.; Kühn, F. E. Exploring Coordination Modes: Late Transition Metal Complexes with a Methylene-bridged Macrocyclic Tetra-NHC Ligand. *Chem. Asian J.* **2016**, *11*, 1597–1605.

(12) Park, S. R.; Findlay, N. J.; Garnier, J.; Zhou, S.; Spicer, M. D.; Murphy, J. A. Electron transfer activity of a cobalt crown carbene complex. *Tetrahedron* **2009**, *65*, 10756–10761.

(13) (a) Weiss, D. T.; Altmann, P. J.; Haslinger, S.; Jandl, C.; Pöthig, A.; Cokoja, M.; Kühn, F. E. Structural diversity of late transition metal complexes with flexible tetra-NHC ligands. *Dalton Trans.* **2015**, *44*, 18329–18339. (b) Hollering, M.; Weiss, D. T.; Bitzer, M. J.; Jandl, C.; Kühn, F. E. Controlling Coordination Geometries: Ru–Carbene Complexes with Tetra-NHC Ligands. *Inorg. Chem.* **2016**, *55*, 6010–6017.

(14) Albrecht, M. Cyclometalation Using d-Block Transition Metals: Fundamental Aspects and Recent Trends. *Chem. Rev.* **2010**, *110*, 576–623.

(15) (a) Albrecht, M.; Miecznikowski, J. R.; Samuel, A.; Faller, J. W.; Crabtree, R. H. Chelated Iridium(III) Bis-carbene Complexes as Air-Stable Catalysts for Transfer Hydrogenation. *Organometallics* **2002**, *21*, 3596–3604. (b) Mata, J. A.; Chianese, A. R.; Miecznikowski, J. R.; Poyatos, M.; Peris, E.; Faller, J. W.; Crabtree, R. H. Reactivity Differences in the Syntheses of Chelating N-Heterocyclic Carbene Complexes of Rhodium Are Ascribed to Ligand Anisotropy. *Organometallics* **2004**, *23*, 1253–1263. (c) Leung, C. H.; Incarvito, C. D.; Crabtree, R. H. Interplay of Linker, N-Substituent, and Counterion Effects in

the Formation and Geometrical Distortion of N-Heterocyclic Biscarbene Complexes of Rhodium(I). *Organometallics* **2006**, *25*, 6099–6107. (d) Wang, X.; Liu, S.; Weng, L.-H.; Jin, G.-X. Preparation and Structure of Mono- and Binuclear Half-Sandwich Iridium, Ruthenium, and Rhodium Carbene Complexes Containing 1,2-Dichalcogenolao 1,2-Dicarba-*closo*-Dodecaboranes. *Chem. - Eur. J.* **2007**, *13*, 188–195. (e) Zamora, M. T.; Ferguson, M. J.; McDonald, R.; Cowie, M. Carbene-anchored/pendent-imidazolium species as precursors to di-N-heterocyclic carbene-bridged mixed-metal complexes. *Dalton Trans.* **2009**, 7269–7287. (f) Graeupner, J.; Hintermair, U.; Huang, D. L.; Thomsen, J. M.; Takase, M.; Campos, J.; Hashmi, S. M.; Elimelech, M.; Brudvig, G. W.; Crabtree, R. H. Probing the Viability of Oxo-Coupling Pathways in Iridium-Catalyzed Oxygen Evolution. *Organometallics* **2013**, *32*, 5384–5390.

(16) Poyatos, M.; Mata, J. A.; Peris, E. Complexes with Poly(N-heterocyclic carbene) Ligands: Structural Features and Catalytic Applications. *Chem. Rev.* **2009**, *109*, 3677–3707.

(17) Esteruelas, M. A.; López, A. M.; Oñate, E.; San-Torcuato, A.; Tsai J.-Y.; Xia, C. Formation of Dinuclear Iridium Complexes by NHC-Supported C–H Bond Activation. *Organometallics* **2017**, *36*, 699–707.

(18) See for exemple: (a) Hahn, F. E.; Holtgrewe, C., Pape, T.; Martin, M.; Sola, E.; Oro, L. A. Iridium Complexes with N-Allyl-Substituted Benzimidazol-2-ylidene Ligands and Their Application in Catalytic Transfer Hydrogenation. *Organometallics* **2005**, *24*, 2203–2209. (b) Jiménez, M. V.; Fernández-Tornos, J.; Pérez-Torrente, J. J.; Modrego, F. J.; Winterle, S.; Cunchillos, C.; Lahoz, F. J.; Oro, L. A. Iridium(I) Complexes with Hemilabile N-Heterocyclic Carbenes: Efficient and Versatile Transfer Hydrogenation Catalysts. *Organometallics* **2011**, *30*, 5493–5508. (c) Peñafiel, I.; Pastor, I. M.; Yus, M.; Esteruelas, M. A.; Oliván, M. Preparation,

Hydrogen Bonds, and Catalytic Activity in Metal-Promoted Addition of Arylboronic Acids to Enones of a Rhodium Complex Containing an NHC Ligand with an Alcohol Function. *Organometallics* **2012**, *31*, 6154–6161. (d) Blanco, M.; Álvarez, P.; Blanco, C.; Jiménez, M. V.; Fernández-Tornos, J.; Pérez-Torrente, J. J.; Oro, L. A.; Menéndez, R. Enhanced Hydrogen-Transfer Catalytic Activity of Iridium N-Heterocyclic Carbenes by Covalent Attachment on Carbon Nanotubes. *ACS Catal.* **2013**, *3*, 1307–1317.

(19) (a) Ogo, S.; Makihara, N.; Kanedo, Y.; Watanabe, Y. pH-Dependent Transfer Hydrogenation, Reductive Amination, and Dehalogenation of Water-Soluble Carbonyl Compounds and Alkyl Halides Promoted by Cp\*Ir Complexes. *Organometallics* **2001**, *20*, 4903–4910. (b) Ionkin, A. S.; Wang, Y.; Marshall, W. J.; Petrov, V. A. Synthesis, structural characterization, and initial electroluminescent properties of bis-cycloiridiated complexes of 2-(3,5-bis(trifluoromethyl)phenyl)-4-methylpyridine. *J. Organomet. Chem.* **2007**, *692*, 4809–4827. (c) Meier, S. K.; Young, K. J. H.; Ess, D. H.; Tenn, W. J., III; Oxgaard, J.; Goddard, W. A., III; Periana, R. A. Heterolytic Benzene C-H Activation by a Cyclometalated Iridium(III) Dihydroxo Pyridyl Complex: Synthesis, Hydrogen-Deuterium Exchange, and Density Functional Study. *Organometallics* **2009**, *28*, 5293–5304.

(20) Yuan, X.; Zhang, S.; Ding, Y. Isolation, characterization and photophysical properties of a 2-(4,6-difluorophenyl)pyridyl Iridium(III) methoxide dimeric complex. *Inorg. Chem. Commun.* **2012**, *17*, 26–29.

(21) See for example refs 2, 3d,e, 7d-h, and: (a) Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Kwong, R.; Tsyba, I.; Bortz, M.; Mui, B.; Bau, R.; Thompson, M. E. Synthesis and Characterization of Phosphorescent Cyclometalated Iridium Complexes. *Inorg.*

*Chem.* **2001**, *40*, 1704–1711. (b) Li, J.; Djurovich, P. I.; Alleyne, B. D.; Yousufuddin, M.; Ho, N. N.; Thomas, J. C.; Peters, J. C.; Bau, R.; Thompson, M. E. Synthetic Control of Excited-State Properties in Cyclometalated Ir(III) Complexes Using Ancillary Ligands. *Inorg. Chem.* **2005**, *44*, 1713–1727. (c) Sajoto, T.; Djurovich, P. I.; Tamayo, A.; Yousufuddin, M.; Bau, R.; Thompson, M. E. Blue and Near-UV Phosphorescence from Iridium Complexes with Cyclometalated Pyrazolyl or N-Heterocyclic Carbene Ligands. *Inorg. Chem.* **2005**, *44*, 7992–8003.

(22) Zaroni, K. P. S.; Kariyazaki, B. K.; Ito, A.; Brennaman, M. K.; Meyer, T. J.; Iha, N. Y. M. Blue-Green Iridium(III) Emitter and Comprehensive Photophysical Elucidation of Heteroleptic Cyclometalated Iridium(III) Complexes. *Inorg. Chem.* **2014**, *53*, 4089–4099.

(23) Usón, R.; Oro, L. A. Cabeza, J. Dinuclear methoxy, cyclooctadiene, and barrelene complexes of rhodium(I) and iridium(I). *Inorg. Synth.* **1985**, *23*, 126–130.

(24) Riederer, S. K. U.; Gigler, P.; Högerl, M. P.; Herdtweck, E.; Bechlars, B.; Herrmann, W. A.; Kühn, F. E. Impact of Ligand Modification on Structures and Catalytic Activities of Chelating Bis-Carbene Rhodium(I) Complexes. *Organometallics* **2010**, *29*, 5681–5692.

SYNOPSIS: Binding of a bis(aryl-N-heterocyclic carbene) as a tetradentate ligand to iridium(III) combined with a cyclometalated phenylpyridine ligand leads to complexes that are highly efficient blue-green emitters with quantum yields close to the unity.

For Table of Contents Only

