Acetylides for the Preparation of Phosphorescent Iridium(III) Complexes: Iridaoxazoles and Their Transformation into Hydroxycarbenes and N,C(sp^3),C(sp^2),O-Tetradentate Ligands

Maria Benítez, María L. Buil, Miguel A. Esteruelas,* Susana Izquierdo, Enrique Oñate, and Jui-Yi Tsai

ABSTRACT: The preparation of three families of phosphorescent iridium(III) emitters, including iridaoxazole derivatives, hydroxycarbene compounds, and N,C(sp^3),C(sp^2),O-tetradentate containing complexes, has been performed starting from dimers vis-[Ir(μ-η^2-C≡CR)(κ^2-C,N-(MeC_6H_5-py))]_2 (R = Bu (1a), Ph (1b)). Reactions of 1a with benzamide, acetamide, phenylacetamide, and trifluoroacetamide lead to the iridaoxazole derivatives Ir[κ^2-C,O-[C(CH_3-Bu)NC(R)O]]{κ^2-C,N-(MeC_6H_5-py)}_2 (R = Ph (2), Me (3), CH_3Ph (4), CF_3 (5)) with a fac disposition of carbons and heteroatoms around the metal center. In 2-methyltetrahydrofuran and dichloromethane, water promotes the C=N bond of the iridaoxazole ring of 3–5 to form amide–iridium(III)–hydroxycarbene derivatives Ir[κ^1-N-[NHC(R)O]-{κ^2-C,N-(MeC_6H_5-py)}_2]C(=C(CH_3-Bu)OH) (R = Me (6), CH_3Ph (7), CF_3 (8)). In contrast to 1a, dimer 1b reacts with benzamide and acetamide to give Ir[κ^2-N,C,C,O-{-py-MeC_6H_5-C(CH_2-C_6H_5)NHC(R)O}]_2{κ^2-C,N-(MeC_6H_5-py)} (R = Ph (9), Me (10)), which bear a N,C(sp^3),C(sp^2),O-tetradentate ligand resulting from a triple coupling (an alkynyl ligand, an amide, and a coordinated aryl group) and a C–H bond activation at the metal coordination sphere. Complexes 2–4 and 6–10 are emissive upon photoexcitation, in orange (2–4), green (6–8), and yellow (9 and 10) regions, with quantum yields between low and moderate (0.01–0.50) and short lifetimes (0.2–9.0 μs).

1. INTRODUCTION

The development of phosphorescent emitters, including those of iridium(III), mainly focuses on organic synthesis. Interesting chromophores and ancillary ligands are prepared by purely organic methods. Subsequently, they are coordinated to an appropriate 5d metal center by conventional procedures involving the activation of some of their σ bonds or directly. Once located in the coordination sphere of the metal, they can be modified by subsequent selective functionalization; a noticeable employed procedure involves C-H bromination of one or more ligands followed by a palladium-promoted Suzuki–Miyaura cross-coupling. A common feature of such emitters is their structural monotony. In the most classical complexes of this class, such as the iridium(III) species having two orthometalated arylypyridine groups, such monotony is clearly evident in the systematically mutually trans arrangement of the heterocycles, with a few rare exceptions. Alternative procedures have been scarcely investigated (Scheme 1). Teets’ research group and in less extension Kinzhalov, Luzyanin, and coworkers have built ancillary ligands at the metal coordination sphere of bis(cyclometalated arylypyridine)iridium(III) complexes, using coordinated arylicarbene as building blocks. Their reactions with amines have generated a variety of acyclic aryldiaminocarbene auxiliary ligands by the nucleophilic addition of the amine to the C(sp) carbon atom. In some cases, the aryl substituent of the resulting monodentate diaminocarbene was subsequently cyclometalated (a in Scheme 1) to afford interesting heterolytic tris-cyclometalated iridium(III) blue-green emitters of class [3b + 3b + 3b′] (3b = 3e donor bidentate ligand). Reactions of bis(arylisocyanide) precursors with hydrazine directly afforded related emitters where the 3b′ ligand is a Chugaev-type carbene (b in Scheme 1). Inspired by previous work about osmium chemistry, we have recently described a methodology of synthesis that, applied to the preparation of phosphorescent complexes, allows to generate emitters of the class [3b + 3b + 3b′] with an asymmetrical β-diketenate ligand. The procedure involves the anti-addition of the O–H bond of a dihydroxo-bridged dimer [Ir(μ-OH)(3b)]_2 to the
C−C triple bond of activated alkynes and the C−C double bond of α,β-unsaturated ketones (c in Scheme 1).9

Synthetic procedures summarized in Scheme 1 have certainly allowed to generate novel ancillary ligands. However, the emitters maintain the mutually trans arrangement of the heterocycles of the chromophores. A recent review about some advances in synthesis of molecular heteroleptic osmium and iridium phosphorescent emitters has pointed out that improvements in the field would come over as a consequence of the development of new procedures of organometallic synthesis,10 for which the handling of alternative starting complexes is crucial. Dimers trans-[Ir(μ-Cl)(3b)2]2 have been traditionally the usual starting point for the preparation of heteroleptic emitters of classes [3b + 3b + 3b′]11 and [3b + 3b + 2m + 1m′]12 (2m = 2e donor monodentate, 1m = 1e donor monodentate). A handicap of these dimers, which appears to be responsible for the lack of structural diversity between the resulting emitters, is the retention of the stereochemistry of their mononuclear half during the emitter preparation process. In the search for starting materials to the synthesis of [3b + 3b + 3b′] emitters with a cis arrangement of the heterocycles of the 3b ligands, we recently replaced the chloride bridges of dimers trans-[Ir(μ-Cl)(3b)2]2 by acetylides. The action provided us two synthetic improvements: the mononuclear fragments of the new dimers trans-[Ir(μ-η2-C≡CR)(3b)2]2 change the relative positions of the donor atoms of one of the 3b chelates to afford counterparts cis-[Ir(μ-η2-C≡CR)(3b)2]2 with cis-heterocycles, in contrast to the chloride dimers as was desired, whereas the acetylide modifies and enhances the reactivity of the carbon atoms of the triple bond to be converted into an interesting building block, which generates new types of ligands. We thus prepared iridaimidazo[1,2-a]pyridine emitters of an octahedral structure with a fac disposition of carbon and nitrogen atoms (Scheme 2).13

The number of heteroaromatic organic molecules that might be in principle employed as a part of the chromophores or ancillary ligands of the emitters is extremely large.14 The formal replacement of a CH unit at a molecule of this type by an isolobal metal fragment, formed by a transition metal and its associated ligands, generates metalaheteroaromatic derivatives. Such compounds have a tremendous conceptual interest, since the metal fragment adds metal properties and organometallic reactivity to the aromatic organic heterocycle.15 Although the iridium−pyridine bond prevents the full aromaticity of the bicycle, the iridaimidazo[1,2-a]pyridine emitters shown in Scheme 2 are examples of this class of organometallic molecules. Previously, a few phosphorescent aromatic iridacarbocyclic derivatives had been reported.16 Metalaheteroaromatic compounds are mono- and polycyclic species bearing a main-group heteroatom. The first monocycles containing two main-group heteroatoms, osmaoxazole derivatives, were reported a few months ago. They were prepared by deprotonation of hydrideosmaoxazolium salts, which were generated via amidate intermediates. Such transient species resulted from the addition of the hydroxide group of the cation [OsH(OH)(≡CPh)(IPr)(PPr3)]+ (IPr = 1,3-bis(2,6-dioisopropylphenyl)imidazolylidene) to an external nitrile or

Scheme 1. Previous Procedures to Build Ancillary Ligands of Iridium(III) Emitters at the Metal Coordination Sphere

Scheme 2. Synthesis of Iridaimidazo[1,2-a]pyridine Emitters
directly through displacement of the hydroxide group by an amidate anion. Once the amidate is generated, it cyclizes with the alkylidyne ligand to form the five-membered ring (Scheme 3). The formation of the osmaoxazoles exhibited in Scheme 3 resembles the cyclization shown in Scheme 2. In both cases, a nucleophilic nitrogen atom of a doubly deprotonated NH$_2$ molecule adds to the $\alpha$-atom of a C-donor ligand. Such similarity prompted us to investigate the addition of amides to the dimers cis-[Ir($\mu^2$-$\xi^2$-$\eta^2$=C=C)CR]$_2$R$_2$ (R = Bu, Ph), in the search for novel families of iridium(III) emitters. This paper reports about the synthesis and photophysical properties of complexes of three different unprecedented families of phosphorescent iridium(III) emitters. This paper reports about the synthesis and photophysical properties of complexes of three different unprecedented families of phosphorescent iridium(III) emitters of classes [3b + 3b + 3b = 6tt = 6e donor tetradentate], including the first iridaoxazole derivatives, hydroxycarbene compounds, and N$_2$C$_2$O-Tetradentate containing complexes. The described preparations illustrate alternative synthetic procedures in the generation of phosphorescent emitters and highlight again the utility of alkynyl ligands as building blocks in organometallic synthesis.

2. RESULTS AND DISCUSSION

2.1. Iridaoxazole Derivatives. Treatment of suspensions of the tert-butylacetylide dimer cis-[Ir($\mu^2$-$\xi^2$-$\eta^2$=C=C)Bu]$_2$(x$^2$-C$_2$N-(MeC$_6$H$_4$Ph)py)$_2$ (1a), in toluene, with 2–3 equiv of benzamide, acetamide, phenylacetamide, and trifluoroacetamide, at 120 °C leads to the respective iridaoxazole derivatives Ir[x$^2$-C$_2$O-(C(CH$_3$Bu)NC(R)O)](x$^2$-C$_2$N-(MeC$_6$H$_4$Ph)py)$_2$ (R = Ph (2), Me (3), CH$_3$Ph (4), CF$_3$ (5)). Their formation is illustrated in Figure 1b. Canonical form that describe the metalacycle bonding situation.

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The amide to the metal-acetylide moiety occurs with retention of the stereochemistry around each iridium center. Thus, its coordination polyhedron can be described as an octahedron formed by three (carbon, heteroatom)-chelating groups with a fac dispositions of carbons and heteroatoms. The iridaoxazole ring is planar. The maximum deviation from the best plane through the atoms Ir, C(1), N(3), C(7), and O(1) is
0.0275(11) Å and involves C(1). The bond lengths in the sequence C(1)−N(3)−C(7)−O(1) of 1.343(3), 1.360(3), and 1.263(3) Å are intermediate between those expected for single and double bonds, as expected for the contribution of both resonance forms \( f_1 \) and \( f_2 \) to the structure (Figure 1b) and compare well with the analogous ones in the osmaoxazole derivatives \( \text{OsX}[\kappa^2\cdot C_2\cdot O_2\cdot \{C(\text{Ph})NC(\text{R})\cdot O\}]\) (IPr) (PPPr) \((X = H, R = \text{Ph}; X = C\equiv\text{CPh}, R = \text{Me}) \). In spite of its planarity and the bond length values, the iridaoxazole ring is scarcely aromatic, as revealed by the poorly negative value of the nuclear independent chemical shifts (NICS) computed at the center of the ring and out of plane at 1 Å above and below of +17.8, −3.0, and −3.2 ppm. The low aromaticity of these iridaoxazoles was furthermore confirmed by a NICS scan (Figure S1) and the anisotropy of the induced current density (ACID) method, which clearly shows the lack of a diatropic current within the ring (Figure S2). The main difference between the iridaoxazoles here reported and the osmaoxazoles previously described appears to be in the M−C bond of the metaladeterorying. This bond appears to have an M-to-C back bonding component weaker in the formers than in the second ones. Consistent with this, comparative NBO7 analysis of the osmium derivative \( \text{OsH}[\kappa^2\cdot C_2\cdot O_2\cdot \{C(\text{Ph})NC(\text{CH}_3)\cdot O\}]\) (IPr) (PPPr) and the iridium counterpart (Figure S3a) revealed that the Wiberg bond index of the M−C bond of the five-membered ring is 1.28 for osmaoxazole, while it has a value of only 0.84 for iridaoxazole. In agreement with this, \( \pi \) NBO orbitals of the five-membered metalaoxazole rings (Figure S3b) indicate that the resonance form \( f_1 \) is the major contribution to the osmaoxazole structure, while \( f_2 \) is the most relevant for the iridaoxazole structure. As a consequence of the weak back bonding, the metalated carbon atom of the iridaoxazole ring of 2−5 seems to undergo a noticeable electron deficiency in comparison with the analogous atom of the osmaoxazoles. In this context, it should be pointed out that the resonance corresponding to the metalated carbon atom of the metaladeterorying in the \( ^{13}\text{C}[^1\text{H}] \) NMR spectra of 2−5 appears in the 267−280 ppm range, shifted about 40 ppm to lower field with regard to the osmaoxazole derivatives.

### 2.2. Hydroxycarbene Compounds

The electron deficiency at the metalated carbon atom of iridaoxazole ring (C(1)) was confirmed by the hydrolysis of the Ir−C(1) bond of 3−5 in relatively polar solvents, such as 2-methyltetrahydrofuran (2-MeTHF) and dichloromethane, at room temperature. The hydrolysis occurs with small amounts of water (>10 equiv) and generates a hydroxycarbene ligand and an amide. The latter would initially coordinate in a \( \kappa^1\cdot \text{O} \)-fashion, forming intermediates \( c \). These species should exchange the donor atom of the amide to afford the hydrolysis products, complexes \( \text{Ir}[\kappa^1\cdot \text{N} \cdot \{\text{NHC}(\text{R})\cdot \text{O}\}]\{\kappa^2\cdot C_2\cdot N\cdot (\text{MeC}_6\text{H}_3\cdot p\cdot \text{py})\}\) \((R = \text{Me} (6), \text{CH}_2\text{Ph} (7), \text{CF}_3 (8))\), probably through a dissociation−coordination process or alternatively via slippage of the metal center by an O−C−N path. In spite of the usual low stability of the hydroxycarbene groups, which normally undergo deprotonation to afford acyl derivatives,19 complexes 6−8 are surprisingly stable and were isolated as yellow solids in 40−70% yields after 24 h of reaction (Scheme S5).

The formation of these unusual species was confirmed by means of the X-ray diffraction analysis structure of 7 (Figure 2a) and 8 (Figure 2b).20 In both cases, the hydrolysis occurs keeping the stereochemistry of the metal center. Thus, in a ligand arrangement resembling the octahedral disposition described for 2, the hydroxycarbene ligand is disposed trans to the pyridyl group of a tolylpyridine chelate (C(1)−Ir−N(2) = 169.03(17)° (7), 170.1(3)° and 171.7(3)° (8)), whereas the amide anion lies trans to the metalated tolyl group of the other one (N(3)−Ir−C(15) = 164.99(16)° (7), 165.3(4)° and 179.0(3)° (8)). In agreement with the hydroxycarbene nature of the monodentate C-donor ligand, angles around the C(1) atom are in the range 112−129°. The presence of a hydroxycarbene ligand in 6−8 is also strongly supported by the \( ^{13}\text{C}[^1\text{H}] \) NMR spectra of these compounds, in dichloromethane-d6, at room temperature, which show a singlet at about 230 ppm due to the C(sp3) atom.

An extended view of the structures (Figure 3) reveals that two molecules of both compounds are associated by means of hydrogen bonds to form dimers. This intermolecular interaction involves the hydrogen atom of the hydroxycarbene of one of them and the oxygen atom of the amide group of the other. The association takes place between identical molecules in the case of 7, while two different conformers associate in 8. They result from the rotation of the amide group around the Ir−N axis. In addition to this intermolecular hydrogen bond, intramolecular oxygen−hydrogen interactions are also observed, although there are significant differences between the complexes. For 7 (Figure 3a), it is only observed for the hydrogen acceptor molecule and implies to the hydrogen atom of the hydroxycarbene ligand and the oxygen atom of the amide group. Complex 8 further displays a second intramolecular interaction, which occurs in the hydrogen donor molecule and associates the hydrogen atom of the amide group and the oxygen atom of the hydroxycarbene ligand (Figure 3b). This second interaction is a consequence of the disposition of the NH hydrogen atom in the involved conformer, which points out the oxygen atom of the hydroxycarbene ligand. As a consequence of the interactions, the separations between the involved atoms lie in the range 2.092−2.196 Å, which are significantly shorter than the sum of the van der Waals radii of hydrogen and oxygen \((r_{vdw}(\text{H}) = 1.20 \text{ Å}, r_{vdw}(\text{O}) = 1.52 \text{ Å})\), whereas the angles O−
H–O are close to the linearity with values between 146° and 163°. The association is broken in dichloromethane-d_2 at room temperature as is supported by 1H-DOSY experiments. Pulse field gradient (PFG) NMR method allows to measure diffusion rate of molecules in solution, which depends on the molecular size and the hydrodynamic volume. At 303 K, the diffusion coefficients obtained from the solutions of 7 and 8 in dichloromethane-d_2 are 1.48 × 10^{-9} m^2 s^{-1} and 1.06 × 10^{-10} m^2 s^{-1}, respectively. These values allow to calculate hydrodynamic radius of 5.32 and 3.81 Å, which agrees well with those obtained from the X-ray diffraction analysis structures for the monomers, 5.81 and 3.72 Å, respectively.

The substituent at the carbon atom situated between the heteroatoms of the iridaoxazole cycle has a marked influence on the stability of the five-membered ring toward the hydrolysis. In contrast to alkyl groups, a phenyl substituent prevents the reaction with water, most probably as consequence of its hyperconjugation capacity. Thus, complex 2 does not undergo hydrolysis in opposition to compounds 3–5.

### 2.3. \( \text{N},\text{C}(sp^3),\text{C}(sp^3),\text{O}-\text{Tetrade} \text{ntate Conta} \text{ining Complexes} \)

The substituent of the acetylide bridges of dimers cis-\([\text{Ir}(\mu^2-\eta^2-\text{C}≡\text{CR})\{\text{x}^2-\text{C}_5\text{N}-(\text{MeC}_6\text{H}_3\text{-py})\}_2]\); (1) has a paramount relevance in the synthetic performance of the carbon

![Figure 2](image-url) (a) ORTEP diagram of complex 7. Only significant hydrogen atoms are shown for clarity. Selected bond lengths (Å) and angles (deg): Ir–N(1) = 2.129(4), Ir–N(2) = 2.127(4), Ir–N(3) = 2.171(3), Ir–C(1) = 1.984(5), Ir–C(15) = 1.994(4), Ir–C(27) = 2.016(4), N(3)–C(7) = 1.265(6), O(1)–C(1) = 1.323(6), O(2)–C(7) = 1.238(6), C(1)–Ir–N(2) = 169.03(17), C(27)–Ir–N(1) = 169.89(15), C(15)–Ir–N(3) = 164.99(16), O(1)–C(1)–Ir = 118.1(3), C(2)–C(1)–Ir = 128.8(3). (b) ORTEP diagram of complex 8. Only significant hydrogen atoms are shown for clarity. Selected bond lengths (Å) and angles (deg): Ir(1)–N(1) = 2.137(8), 2.119(8); Ir(1)–N(2) = 2.121(8), 2.141(7); Ir(1)–N(3) = 2.212(5), 2.198(5); Ir(1)–C(1) = 1.971(8), 1.979(7); Ir(1)–C(15) = 2.002(6), 2.024(9); Ir(1)–C(21) = 2.020(8), 1.987(7); N(3)–C(7) = 1.267(8), 1.287(6); O(1)–C(1) = 1.302(10), 1.339(9); O(2)–C(7) = 1.199(8), 1.212(10); C(1)–Ir(1)–N(2) = 170.1(3), 171.7(3); C(21)–Ir(1)–N(1) = 170.1(3), 170.8(3); C(15)–Ir(1)–N(3) = 165.3(4), 179.0(3); O(1)–C(1)–Ir(1) = 119.8(5), 116.3(5); C(2)–C(1)–Ir(1) = 127.3(5), 129.3(5).

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atoms of the triple bond as building block. Treatment of thephenylacetylide derivative cis-[Ir(μ−η²-C≡CPh)(κ²-C,N-(MeC₆H₄py)])₂] (1b), in toluene, with benzamide and acetamide, under the same conditions as those previously mentioned for the formation of 2–5 leads to complexes Ir[κ²-N,C,C'/O-ppy-MeC₆H₄-C(CH₂-C₆H₄)NHC(R)O]/(κ²-C,N-(MeC₆H₄py)](R = Ph (9), Me (10)), in contrast to the tert-butylacetylide counterpart 1a (Scheme 4).

The phenylacetylide bridge of 1b undergoes a three-component coupling involving the nitrogen atom of the amide, the C₆ atom of the bridge, and the metalated carbon atom of one of the cyclometalated tolylpyridines (Scheme 6).

The coupling can be viewed as the migratory insertion of an electron deficient Ir–C double bond of a transient iridaoxazole intermediate d into one of the cis-disposed cyclometalated aryl groups of the chromophores; i.e., the smaller bulky and less electron donor ability of the phenyl group in comparison to tert-butyl one appears to destabilize the iridaoxazole, favoring the migration of one of the metalated tolyl groups from the metal to the carbon atom of the iridaoxazole Ir–C bond. The triple coupling to give e, along with the metalation of such phenyl substituent, generates an asymmetrical 6e-donor N,C(sp²),C(sp²)-tetradentate ligand, which defines two different five-membered rings and other of six members. The metalation of the agostic phenyl substituent of the iridaoxazole ring of e, to afford 9 and 10, involves a hydrogen transfer from the coordinated C₆atom to the azole N-atom. The process could be rationalized as an intermolecular heterolytic C−H bond activation promoted by an external iridaoxazole base.

Iridium(III) emitters with nonplanar tetradentate ligands are uncommon, particularly those bearing different bidentate moieties, and in special when the donor atoms of such moieties are different in identity and nature, as is occurring in 9 and 10. Furthermore, in contrast to our new compounds, such ligands are generated from the coordination of organic molecules previously prepared.

Complexes 9 and 10 might be described as pseudotris(heteroleptic) species, since bearing three different 3e donor bidentate units. Iridium(III) emitters of class [3b + 3b’ + 3b’’] are certainly the most challenging because of allowing a better tuning of designed photophysical properties and because they are the most difficult of preparing. Complexes 9 and 10 were isolated as analytically pure yellow solids, in low yield (9–14%), after the corresponding purification of the reaction crude, which also contained several unidentified species, by column chromatography. The formation of their novel tetradentate moiety was confirmed by the X-ray diffraction analysis structure of 10. Figure 4 shows a view of the molecule. The coordination around the iridium center can be idealized as an octahedron with the pyridyl and metalated phenyl groups of the tetradentate ligand mutually arranged trans (N(1)–Ir–C(6) = 167.47(14)°). The perpendicular plane is defined by the five-membered ring, resulting from the transient iridaoxazole d, and the metalated tolylpyridine. The junction C(sp³) atom of the tetradentate ligand is disposed trans to the pyridyl group (C(1)–Ir–N(2) = 172.18(14)°), whereas the oxygen atom locates trans to the metalated carbon atom of the tolyl group (O(1)–Ir–C(23) = 178.46(15)°). Noticeable NMR features of 9 and 10, in dichloromethane-d₄, at room temperature are two doublets (J ≈ 15.4 Hz) at about 4.1 and 3.2 ppm in the ¹H, due to the CH₂ group of the benzyl moiety of the tetradentate ligand, and a singlet around 54 ppm in the ¹³C(¹H), corresponding to the junction C(sp³) atom.

2.4. Photophysical and Electrochemical Properties of the Generated Emitters. Figures S4–S11 provide UV–vis spectra of 10⁻³ M solutions of the new complexes 2–4 and 6–10, in 2-MeTHF or toluene, at room temperature, whereas Table 1 offers a summary of characteristic absorptions. Spectra display the typical pattern for iridium(III) species, showing the usual three energy regions: <300, 350–450, and >450 nm. According to time-dependent DFT (TD-DFT) calculations (B3LYP-D3//SDD(f)/6-31G**) in THF, the higher energy
(<300 nm) bands correspond to $^{1}\pi^{*}-\pi^{*}$ intra- and interligand transitions, while spin-allowed charge transfers from metal-to-ligand combined with ligand-to-ligand or intraligand appear in the region of intermediate energy (350–450 nm). Formally spin-forbidden transitions, generated by large spin–orbit coupling as a consequence of the iridium presence, are also evident after 450 nm. They are mainly HOMO-to-LUMO for 2−8 and HOMO-to-LUMO combined with HOMO-to-LUMO + 1 ($\approx 60\% : 30\%$) for 9 and 10. In this context, it should be pointed out that the marked contribution of the iridoxazol ligand to the LUMO of 2–5, which increases in the sequence $3 < 4 < 2 \approx 5$, as the methyl substituent of 3 changes to CH$_3$Ph, Ph, and CF$_3$ in 4, 2, and 5. At the time, the HOMO−LUMO gap diminishes; while this gap is about 3.9 eV for 3 (Me) and 4 (CH$_3$Ph), it lies in the range 3.4−3.5 eV for 2 (Ph) and 5 (CF$_3$). The HOMO−LUMO gap for the [3b + 3b + 2 + 1 m'] complexes 6−8 is similar to that of 3 and 4 (Table 2). Figures S9−S17 give views of the frontier orbitals.

The HOMO energy levels DFT-calculated for 2 and 6−10 nicely agree with those experimentally obtained from the electrochemical study of these compounds. Figure S22 shows the voltammograms, which were measured in dichloromethane, under argon, using [Bu$_4$N]PF$_6$ as supporting electrolyte (0.1 M). All compounds display reversible oxidations from Ir(III) to Ir(IV) and from Ir(IV) to Ir(V) between 0.00 and 1.05 V (Table 2). Reductions were not detected between −1.5 and 1.5 V.
Table 2. Electrochemical and DFT Molecular Orbitals
Energy Data for 2–10

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<th>complex</th>
<th>$E_{1/2}^0$ vs Fe/Fe$^+$ (V)</th>
<th>obs (eV)</th>
<th>calc (eV)</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>HOMO$^a$</td>
<td>HOMO</td>
</tr>
<tr>
<td>2</td>
<td>0.44, 1.05</td>
<td>−5.24</td>
<td>−5.18</td>
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<tr>
<td>3</td>
<td></td>
<td>−5.18</td>
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<td>4</td>
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<td>−5.18</td>
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<tr>
<td>5</td>
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<td>−5.36</td>
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<tr>
<td>6</td>
<td>0.37, 0.86</td>
<td>−5.17</td>
<td>−5.08</td>
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<td>7</td>
<td>0.37, 0.87</td>
<td>−5.17</td>
<td>−5.08</td>
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<td>0.01, 0.79</td>
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<td>−4.65</td>
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<td>10</td>
<td>0.00, 0.73</td>
<td>−4.80</td>
<td>−4.64</td>
</tr>
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</table>

$^a$HOMO = $-[E_{1/2}^0$ vs Fe/Fe$^+$ + 4.8] eV. $^b$HGL = LUMO − HOMO.

Table 3 summarizes features of emissions, upon photoexcitation, of iridoazoxole complexes 2–4, hydroxycarbene compounds 6–8, and tetradentate derivatives 9 and 10. The measurements were carried out in a doped poly-(methyl methacrylate) (PMMA) film at 5 wt %, at room temperature, and 2-MeTHF (2 and 6–10) or toluene (3 and 4) at room temperature and at 77 K. Figure 5 collects the spectra of the three classes of emitters recorded under the above mentioned experimental conditions. Emissions take place from the respective $T_1$ excited states, as is supported by the experimental wavelength values, which are consistent with the difference in energy, calculated in THF, between the optimized triplet states $T_1$ and the singlet states $S_0$.

Iridoazoxoles complexes 2–4 are poor orange emitters (578–639 nm), which display low quantum yields (<10). Ring opening hydrolysis of iridoazole results in a blue shift of the emission and a significant increase of the quantum yields. Thus, the hydroxycarbene compounds 6–8 are green emitters (476–556 nm), which beam with moderated efficiency; particularly in the case of 7. The quantum yields of latter reach values of 0.44 in PMMA and 0.17 in 2-MeTHF. By their part, the tetradentate derivatives 9 and 10 are yellow emitters (520–558 nm), which show quantum yields in PMMA higher than those of 6–8, around 0.50. Like for the hydroxycarbene compounds, the efficiency of both drops in solution. This appears to be due to a significant rise of the nonradiative rate constants in solution, suggesting a strong energy dissipation through mechanical processes. The lifetimes are short with values in the range 0.2–9.0 μs.

3. CONCLUDING REMARKS

This study has revealed that the alkynyl ligands of dimers cis-[Ir(μ-$η^2$-C≡CR)(k²-C₆N·(MeC₆H₁-py))₂]₂ are building

| Table 3. Photophysical Data of Complexes 2–4 and 6–10 |
|---------------------------------|-----------------|-------------|----------|----------|----------|----------|----------|
| calc $\lambda_{em}$ (nm) | media (T/K) | $\lambda_{em}$ (nm) | $\tau$ (μs) | $\Phi$ | $k_r$ (s⁻¹) | $k_{nr}$ (s⁻¹) | $k_r/k_{nr}$ |
| complex 2 | 627 PMMA (298) | 627 | 2.5 | 0.04 | 1.6 × 10⁴ | 3.8 × 10³ | 0.04 |
|           | 2-MeTHF (298) | 628 | 0.9 | 0.01 | 1.1 × 10⁴ | 1.1 × 10³ | 0.01 |
|           | 2-MeTHF (77) | 600, 639 | 1.5 | | | | |
| complex 3 | 536 PMMA (298) | 581 | 1.4 | 0.08 | 5.7 × 10⁴ | 6.6 × 10³ | 0.09 |
|           | Toluene (298) | 590 | 0.4 | 0.07 | 1.8 × 10⁴ | 2.3 × 10³ | 0.08 |
|           | Toluene (77) | 578 | 4.0 | | | | |
| complex 4 | 553 PMMA (298) | 592 | 0.9 | 0.08 | 8.9 × 10⁴ | 1.0 × 10³ | 0.09 |
|           | Toluene (298) | 600 | 0.4 | 0.06 | 1.5 × 10⁴ | 2.4 × 10³ | 0.06 |
|           | Toluene (77) | 584 | 3.8 | | | | |
| complex 6 | 500 PMMA (298) | 492, 516 | 1.4 | 0.29 | 2.1 × 10⁴ | 5.1 × 10³ | 0.41 |
|           | 2-MeTHF (298) | 497, 520 | 1.2 | 0.10 | 8.3 × 10³ | 7.5 × 10³ | 0.11 |
|           | 2-MeTHF (77) | 478, 513, 555 | 4.3 | | | | |
| complex 7 | 504 PMMA (298) | 490, 515 | 1.5 | 0.44 | 2.9 × 10⁴ | 3.7 × 10³ | 0.78 |
|           | 2-MeTHF (298) | 492, 515 | 1.2 | 0.12 | 1.0 × 10⁴ | 7.3 × 10³ | 0.14 |
|           | 2-MeTHF (77) | 477, 512, 542 | 4.6 | | | | |
| complex 8 | 440 PMMA (298) | 483, 511, 553 | 1.5 | 0.11 | 7.3 × 10⁴ | 5.9 × 10³ | 0.12 |
|           | 2-MeTHF (298) | 490, 515 | 1.8 | 0.07 | 3.9 × 10⁴ | 5.2 × 10³ | 0.08 |
|           | 2-MeTHF (77) | 476, 509, 548 | 5.0 | | | | |
| complex 9 | 542 PMMA (298) | 540 | 0.7 | 0.50 | 7.1 × 10⁴ | 7.1 × 10³ | 1.00 |
|           | 2-MeTHF (298) | 544 | 0.2 | 0.04 | 2.0 × 10⁴ | 4.8 × 10³ | 0.04 |
|           | 2-MeTHF (77) | 520, 556 | 7.5 | | | | |
| complex 10 | 540 PMMA (298) | 546 | 1.5 | 0.45 | 3.0 × 10⁵ | 3.7 × 10⁴ | 0.81 |
|           | 2-MeTHF (298) | 546 | 0.8 | 0.12 | 1.5 × 10⁵ | 1.1 × 10⁴ | 0.14 |
|           | 2-MeTHF (77) | 523, 558 | 9.0 | | | | |

$^a$Calculated according to $k_r = \Phi/\tau$ and $k_{nr} = (1 - \Phi)/\tau$. 
blocks to build iridaoxazole rings, hydroxycarbene moieties, and novel 6e-donor $N,C(sp^3),C(sp^2),O$-tetradentate ligands.

Only one class of monocyclic organometallic metalaheteroaromatic compounds, bearing two main-group heteroatoms in the ring, was known as far, osmaoxazoles; their formation starting from an amidate and an alkylidyne ligand was reported some months ago. A new family of metalaoxazoles, iridaoxazoles, has been now generated using an amide and an alkynyl ligand instead of an amidate and the alkylidyne unit. It is further demonstrated that the $L^m_M$ fragment of the five-membered ring has a marked influence in the aromaticity degree of the cycle and its stability toward the hydrolysis. The results reported here point out that $L^m_M$ fragments with a low back bonding ability create a significant electron deficiency in the carbon atom of the $M-C$ bond that reduces the aromaticity of the five-membered ring and polarizes the adjacent $C-N$ bond. The increased difference in charge between the atoms of such bond enhances their affinity by the water molecule, which promotes the $C-N$ rupture to form amidate–iridium(III)–hydroxycarbene derivatives. The substituents at the carbon atoms of the iridaoxazole have also a paramount importance in the stability of the five-membered ring. In contrast to alkyl groups, a phenyl substituent situated at the carbon atom between the heteroatoms of cycle prevents the hydrolysis.

The iridaoxazole ring is the starting point not only of the hydroxycarbene moieties but also of $N,C(sp^3),C(sp^2),O$-tetradentate ligands. A significant bulkiness reduction in the $CH_2R$ group, generated in the process of the five-membered ring built, unprotects the metalated carbon atom toward the attack of one of the tolyl groups coordinated to the iridium centers in the starting dimers. The migration is the seed for the tetradentate ligands when the $R$ is a phenyl group, since the latter is able to undergo a subsequent ortho–CH bond.

Figure 5. (a) Emission spectra of 2−4 and 6−10 in 5 wt % PMMA films at 298 K. (b) Emission spectra of 2, 6−10 in 2-MeTHF and 3−4 in toluene at 298 K. (c) Emission spectra of 2, 6−10 in 2-MeTHF and 3−4 in toluene at 77 K.
activation. These tetradentate ligands are therefore the result of a triple coupling (an alkylidyn ligand, an amide, and a coordinated aryl group) and a C–H bond activation at the metal coordination sphere. Furthermore, they point out the decisive role of the alkylidyn substituent of the starting dimers in the nature of the C–C triple bond as building block.

The compounds prepared by these novel procedures represent novel families of heteroleptic iridium(III) phosphorescent emitters in the orange-green region of the emission spectrum, which display quantum yields between low and moderate and short lifetimes.

In summary, the use of dimers cis-\text{Ir}(\mu-\eta^2-C\equivC-\text{CR})\{\text{xCy} \text{C} \equiv \text{C} \text{MeC}_2(\text{py})\}_2 as starting materials allows to develop original synthetic procedures, which leads to classes of iridium(III) phosphorescent emitters different to those previously known.

4. EXPERIMENTAL SECTION

4.1. General Information. All reactions were carried out under argon with dried solvents and using Schlenk tube techniques. Instrumental methods are given in the Supporting Information. In the NMR spectra, chemical shifts (expressed in ppm) are referenced to residual solvent peaks and coupling constants (\(J\)) are given in hertz. Signals were assigned using also bidimensional NMR spectra (\(\text{IH} - \text{IH CO} \), \(\text{IH} - \text{Ip CO} \) and \(\text{IH} - \text{Ip HMBC} \))

4.1.1. Preparation of \(\text{Ir}(\mu-\eta^2-C\equivC-\text{CR})\{\text{xCy} \text{C} \equiv \text{C} \text{MeC}_2(\text{py})\}_2\) (2). To a suspension of \(1 \text{a} \) (300 mg, 0.246 mmol) in toluene (20 mL) placed in a Schlenk flask equipped with a PTFE stopcock, benzamide (60 mg, 0.492 mmol) was added. The mixture was held for 24 h at 120 °C. The red solution was cooled at room temperature and evaporated to dryness. The crude was purified by silica column chromatography (deactivated with NEt3) using toluene as eluent to get a red solid, which was washed with pentane (3 × 5 mL) and dried to vacuum (164 mg, 46%). Anal. Calc. for \(\text{C}_{25}\text{H}_{29}\text{IrN}_2\text{O}_5 \): C, 60.80; H, 4.96; N, 5.75. Found: C, 60.41; H, 4.81; N, 5.84. HRMS (electrospray, m/z): Calcld for \(\text{C}_{25}\text{H}_{29}\text{IrN}_2\text{O}_5 \): 732.2562, found: 732.2587. IR (cm\(^{-1}\)): v(CO) 1600 (m), v(C≡N) 1585 (m). H NMR (400 MHz, CDCl\(_3\), 298 K): \(\delta \) 8.46 (dd, \(J_{\text{HH}} = 8.2, J_{\text{HH}} = 1.2, 2 \text{H}, \text{CH Ph})

4.1.2. Preparation of \(\text{Ir}(\mu-\eta^2-C\equivC-\text{CR})\{\text{x} \text{C} \equiv \text{C} \text{MeC}_2(\text{py})\}_2\) (8). To a suspension of \(1 \text{a} \) (300 mg, 0.246 mmol) in toluene (15 mL) placed in a Schlenk flask equipped with a PTFE stopcock, acetonitrile (44 mg, 0.745 mmol) was added. The mixture was held for 24 h at 120 °C. After that time, the solution was cooled at room temperature, filtered through Celite, and evaporated to dryness. The crude was purified by column chromatography (basic Al2O3, activity grade V) using toluene as eluent to elute an impurity and then using acetonitrile to get an orange solid (105 mg, 32%). Anal. Calcld for \(\text{C}_{25}\text{H}_{34}\text{IrN}_2\text{O}_5 \): C, 57.46; H, 5.12; N, 6.28. Found: C, 57.48; H, 5.46; N, 6.32. HRMS (electrospray, m/z): Calcld for \(\text{C}_{25}\text{H}_{34}\text{IrN}_2\text{O}_5 \): 762.0392; found: 762.0395. IR (cm\(^{-1}\)): v(CO) 1600 (m), v(C≡N) 1589 (m). 1H NMR (400 MHz, CDCl\(_3\), 298 K): \(\delta \) 8.46 (dd, \(J_{\text{HH}} = 8.2, J_{\text{HH}} = 1.2, 2 \text{H}, \text{CH Ph})

4.1.3. Preparation of \(\text{Ir}(\mu-\eta^2-C\equivC-\text{CR})\{\text{x} \text{C} \equiv \text{C} \text{MeC}_2(\text{py})\}_2\) (4). To a suspension of \(1 \text{a} \) (300 mg, 0.246 mmol) in toluene (15 mL) placed in a Schlenk flask equipped with a PTFE stopcock, phenylacetonitrile (66.5 mg, 0.492 mmol) was added. The mixture was held for 24 h at 120 °C. The resulting orange solution was cooled at room temperature, filtered through Celite, and evaporated to dryness. The crude was purified by silica column chromatography (deactivated with NEt3) using pentane:dichloromethane (1:2) as eluent to get an orange solid (196 mg, 53%). Anal. Calcld for \(\text{C}_{25}\text{H}_{34}\text{IrN}_2\text{O}_5 \): C, 60.80; H, 4.96; N, 5.75. Found: C, 60.41; H, 4.81; N, 5.84. HRMS (electrospray, m/z): Calcld for \(\text{C}_{25}\text{H}_{34}\text{IrN}_2\text{O}_5 \): 732.2562, found: 732.2587. IR (cm\(^{-1}\)): v(CO) 1600 (m), v(C≡N) 1589 (m). 1H NMR (400 MHz, CDCl\(_3\), 298 K): \(\delta \) 7.68 (dd, \(J_{\text{HH}} = 8.2, \text{H}, \text{CH Ph})

4.1.4. Preparation of \(\text{Ir}(\mu-\eta^2-C\equivC-\text{CR})\{\text{x} \text{C} \equiv \text{C} \text{MeC}_2(\text{py})\}_2\) (5). To a suspension of \(1 \text{a} \) (300 mg, 0.246 mmol) in toluene (20 mL) placed in a Schlenk flask equipped with a PTFE stopcock, trifluoroacetonitrile (55.6 mg, 0.492 mmol) was added. The mixture was held for 24 h at 120 °C. The resulting red solution was cooled at room temperature, filtered through Celite, and evaporated to dryness. The addition of 10 mL of pentane to the crude causes the precipitation of a redish pink solid, which was washed with pentane (5 × 5 mL) and evaporated to dryness (212 mg, 60%). Anal. Calcld for \(\text{C}_{25}\text{H}_{34}\text{IrN}_2\text{O}_5 \): C, 53.17; H, 4.32; N, 5.81.
Found: C, 53.47; H, 4.64; N, 6.03. HRMS (electrospray, m/z): Calc. for C_{31}H_{32}F_{2}lnNO [M + H]^+: 724.2123, found: 724.2126. IR (cm⁻¹): ν(CO) 1603 (m), ν(C=O) 1588 (m), ν(CF) 1175, 1144 (s). 1H NMR (400 MHz, CDCl₃, 298 K): δ 8.04 (ddd, δ_H = 5.6, δ_H = 1.7, δ_H = 1.0, 1H, CH py), 7.93 (ddd, δ_H = 8.4, δ_H = 1.9, δ_H = 1.3, 1H, CH py), 7.87–7.78 (m, 2H, CH py), 7.63–7.57 (m, 2H, CH MeC₆H₄-py + CH py), 7.53 (d, δ_H = 7.9, 1H, CH MeC₆H₄-py), 7.26 (ddd, δ_H = 7.2, δ_H = 5.6, δ_H = 1.3, 1H, CH py), 6.98 (ddd, δ_H = 5.6, δ_H = 1.7, δ_H = 1.0, 1H, CH py); and δ_H = 5.6, δ_H = 1.7, 1H, CH py), 7.85 (ddd, δ_H = 8.4, δ_H = 1.9, δ_H = 1.3, 1H, CH py), 7.87–7.78 (m, 2H, CH py), 7.63–7.57 (m, 2H, CH MeC₆H₄-py + CH py).

CH MeC₆H₄-py, J₆ = 5.5, δ_H = 8.1, 1H, CH py), 7.27 (d, δ_H = 8.1, 1H, CH py).

CH MeC₆H₄-py, J₆ = 5.6, δ_H = 1.5, 1H, CH py).

CH MeC₆H₄-py, J₆ = 5.6, δ_H = 1.5, 1H, CH py).

CH MeC₆H₄-py, J₆ = 5.6, δ_H = 1.5, 1H, CH py).

CH MeC₆H₄-py, J₆ = 5.6, δ_H = 1.2, 1H, CH py).

CH MeC₆H₄-py, J₆ = 5.6, δ_H = 1.2, 1H, CH py).

CH MeC₆H₄-py, J₆ = 5.6, δ_H = 1.2, 1H, CH py).

CH MeC₆H₄-py, J₆ = 5.6, δ_H = 1.5, 1H, CH py).

142.7 (s, CH MeC₆H₄-py), 141.2 (s, CH MeC₆H₄-py), 141.9 (s, CH MeC₆H₄-py), 140.0 (s, CH MeC₆H₄-py), 139.3 (s, CH MeC₆H₄-py), 138.3 (s, CH MeC₆H₄-py), 138.0 (s, CH MeC₆H₄-py), 137.9 (s, CH MeC₆H₄-py), 137.3 (s, CH py), 124.5 (s, CH MeC₆H₄-py), 124.4 (s, CH MeC₆H₄-py), 124.2 (s, CH MeC₆H₄-py), 122.3 (s, CH MeC₆H₄-py), 122.2 (s, CH MeC₆H₄-py), 121.1 (s, CH py), 119.1 (s, CH py), 118.2 (s, CH py), 58.0 (s, CH₃), 31.8 (s, CH₂), 30.6 (s, CH₂, 25.8 (s, CH acylamidine), 22.1 (s, CH MeC₆H₄-py), 21.7 (s, CH MeC₆H₄-py).

4.1.8. Preparation of Ir²⁺(N,N,N′,N′′,N″-NPPhCH₂OP)(Ch₂MeC₆H₄-py)(NC₆H₄-py)(8). To a suspension of Ir(III) (150 mg, 0.208 mmol) in dichloromethane (15 mL), deoxygenated water (40 µL, 2.220 mmol) was added. The solution was stirred at room temperature for 24 h and then evaporated to dryness. The crude was washed with pentane (3 × 5 mL) affording a yellow solid (102 mg, 66%). Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane over dichloromethane solution of the compound at room temperature. Anal. Calc. for C_{31}H_{32}F_{2}lnNO: C, 51.88; H, 4.49; N, 5.67. Found: C, 51.83; H, 4.36; N, 5.75. HRMS (electrospray, m/z): Calc. for C_{31}H_{32}F_{2}lnNO [M + Na]: 764.2046, found: 764.2065. IR (cm⁻¹): ν(NH) 3385, ν(CH) 3031. IR (cm⁻¹): ν(OH) 3347, ν(NH) 3033, ν(CO) 1587 (s). 1H NMR (300 MHz, CDCl₃, 298 K): δ 13.18 (s, br, 1H, OH), 8.94 (ddd, δ_H = 5.5, δ_H = 1.7, δ_H = 0.9, 1H, CH py); and s, br, 1H, OH), 7.97 (δ_H = 8.1, 1H, CH py), 7.85 (ddd, δ_H = 8.2, 7.4, δ_H = 1.7, 1H, CH py), 7.71 (δ_H = 8.2, 7.4, δ_H = 1.7, 1H, CH py); and s, br, 1H, OH), 7.97 (δ_H = 8.1, 1H, CH py), 7.71 (ddd, δ_H = 8.2, 7.4, δ_H = 1.7, 1H, CH py), 7.56–7.47 (m, 3H, CH py, MeC₆H₄-py), 7.43 (s, 1H, CH MeC₆H₄-py), 7.31 (ddd, δ_H = 7.4, 5.5, δ_H = 1.3, 1H, CH py), 7.08 (ddd, δ_H = 5.6, δ_H = 1.5, 1H, CH py).

CH MeC₆H₄-py, J₆ = 5.6, δ_H = 1.5, 1H, CH py).

CH MeC₆H₄-py, J₆ = 5.6, δ_H = 1.5, 1H, CH py).

CH MeC₆H₄-py, J₆ = 5.6, δ_H = 1.2, 1H, CH py).

CH MeC₆H₄-py, J₆ = 5.6, δ_H = 1.2, 1H, CH py).

CH MeC₆H₄-py, J₆ = 5.6, δ_H = 1.2, 1H, CH py).

CH MeC₆H₄-py, J₆ = 5.6, δ_H = 1.2, 1H, CH py).

CH MeC₆H₄-py, J₆ = 5.6, δ_H = 1.2, 1H, CH py).

CH MeC₆H₄-py, J₆ = 5.6, δ_H = 1.2, 1H, CH py).
C₆H₅N(CH₂)₄O: C, 62.38; H, 4.30; N, 5.60. Found: C, 62.53; H, 4.00; N, 5.27. HRMS (electrospray, m/z): Calcd. for C₃₀H₂₈N₅O₁₂ [M + H⁺]: 672.2247, found: 672.2212. IR (cm⁻¹): ν(NH) 3305, ν(CO) 1596 (s). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 9.49 (d, J₃Hₓ = 5.4, 1H, CH py), 8.63 (d, J₁Hₓ = 4.8, 1H, CH py tetra), 7.99 (s, 1H, CH MeC₆H₄-py tetra), 7.89 (d, J₁Hₓ = 7.9, 1H, CH py), 7.83 (ddd, J₂Hₓ = 1.9, J₃Hₓ = 7.8, J₁Hₓ = 1.8, 1H, CH py tetra), 7.53–7.47 (m, 3H, CH py tetra + 2CH COPh), 7.34–7.35 (m, 3H, CH py + CH COPh + CH MeC₆H₄-py), 3.73 (d, J₂Hₓ = 7.8, 1H, CH MeC₆H₄-py tetra), 2.72 (t, J₁Hₓ = 7.7, 2H, CH COPh), 2.11 (d, J₁Hₓ = 7.8, 1H, CH MeC₆H₄-py tetra), 7.00 (s, 1H, NH), 6.98–6.92 (m, 2H, CH py tetra + CH CH₂Ph tetra), 6.54 (t, J₁Hₓ = 7.3, 1H, CH CH₂Ph tetra), 6.46 (d, J₃Hₓ = 7.8, 1H, CH MeC₆H₄-py), 6.24–6.35 (m, 2H, CH MeC₆H₄-py + CH CH₂Ph tetra), 5.93 (d, J₂Hₓ = 7.3, 1H, CH CH₂Ph tetra), 4.20 (d, J₃Hₓ = 15.4, 1H, CH₂), 3.29 (d, J₁Hₓ = 15.4, 1H, CH₂), 2.61 (s, 3H, CH₂ MeC₆H₄-py), 1.90 (s, 3H, CH₂ MeC₆H₄-py tetra), 1.53 (s, CH₂ MeC₆H₄-py tetra), 1.47 (s, CH₂ MeC₆H₄-py tetra), 1.36 (s, CH₂ py + CH py tetra), 1.23 (s, CH₂ py + CH py tetra), 1.15 (s, CH₂ py + CH py tetra), 1.07 (s, CH₂ py + CH py tetra), 0.86 (s, CH₂ py + CH py tetra), 0.75 (s, CH₂ py + CH py tetra). For the optimized triplet T₂, normalized excitation and emission spectra of complexes 2 and 6-10, analysis of computed UV/Vis data, theoretical analysis of molecular orbitals, spin density distribution for the optimized triplet T₂, cyclic voltammograms of complexes 2 and 6-10, normalized excitation and emission spectra of complexes 2-4 and 6-10, and NMR spectra. (PDF)

Accession Codes
CCDC 2210743–2210746 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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