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PAPER

Iridium(III) complexes with polypyridine ligands coordinated as *N*-heterocyclic carbenes. Synthesis, structure and photophysical properties†‡Salvador Conejero,^a Celia Maya,^a Margarita Paneque,^a Ana Petronilho,^a Manuel L. Poveda,^{*a} Florencia Vattier,^a Eleuterio Álvarez,^a Ernesto Carmona,^{*a} Antonio Laguna^{*b} and Olga Crespo^b

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Unsaturated [Tp^{Me2}Ir(III)] fragments, readily generated from compounds [Tp^{Me2}Ir(C₆H₅)₂(N₂)], (**1a**) and [Tp^{Me2}Ir(η⁴-CH₂=C(Me)C(Me)=CH₂)] (**1b**) (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate), induce the isomerisation of the polypyridines, 2,2'-bipyridine, 1,10-phenanthroline and 2,2':6'2''-terpyridine, to form complexes that contain the carbene tautomer of these ligands. For terpy, a binuclear compound has also been isolated, in which this molecule bridges two Ir(III) centres, thanks to its coordination as a bidentate *N*-heterocyclic carbene. The new compounds have been structurally authenticated by X-ray crystallography and their photophysical properties have been investigated.

Introduction

Pyridine and substituted pyridines, in particular polypyridines such as 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen) and 2,2':6'2''-terpyridine (terpy), constitute an important family of aromatic heterocycles which are widely used as ligands in coordination and organometallic chemistry,¹ as well as in homogeneous catalysis² and supramolecular chemistry.³ Transition metal compounds of polypyridine ligands feature, in addition, advantageous photophysical and redox properties⁴ that confer them with high value as new materials⁵ and biological probes.⁶ These properties have, for instance, led to their utilisation in the photocatalytic reduction of CO₂,⁷ in water oxidation,⁸ or as phosphorescent dopants of OLEDs and other optical devices.⁹

Recent work from several research groups, including our own, has revealed that some substituted pyridines and related heterocycles can undergo a metal-promoted rearrangement to form *N*-heterocyclic carbene (pyridylidene-type¹⁰) structures. Early work on Os^{11a} and later on Rh,^{11b} was followed by our first communication in this field.^{12a} Related tautomerisations induced by Mn,¹³ Re,¹⁴ Ru,¹⁵ Os,¹⁶ Rh,¹⁷ and Ir^{12b-g} also became available. For some of these systems it is not entirely understood why the

tautomerisation of the pyridine ligand becomes favoured over *N*-coordination. However, for that based on the [Tp^{Me2}Ir(III)] fragment (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate), a combination of experimental and theoretical studies has provided a clear picture of this reactivity.¹⁸ Thus, only for 2-substituted pyridines are the carbene tautomers thermodynamically preferred over their *N*-adduct counterparts, due to steric repulsion (F-strain¹⁹) between the [Tp^{Me2}IrR₂] fragment and the substituent in the 2-position of the pyridine ring.

The polypyridines bpy, phen and terpy may be viewed as 2-substituted pyridines and therefore a similar tautomerisation can be expected to lead to a new coordination mode of these ubiquitous ligands, as *N*-heterocyclic carbenes (NHC). With few exceptions, these polypyridines form *N*-chelate structures with transition metals, bpy and phen behaving as bidentate and terpy as tridentate.¹ However, on some occasions C–H bond activation at one of the aromatic rings allows for mixed *C*- and *N*-bonding, giving rise to κ²-*C,N* (bpy) or κ³-*C,N,N'* (terpy) coordination modes²⁰ (Fig. 1). The resulting cyclometallated complexes²¹ also feature good photophysical properties. Monodentate *N*-coordination of bpy and phen has been proposed in several instances,²² but it has been corroborated by X-ray crystallography only rarely.²³ Monodentate, *N*-binding of terpy is uncommon too.²⁴

Recently, we have communicated that bpy, phen and terpy^{12c,d} undergo isomerisation to their corresponding NHC tautomers in

Fig. 1 Cyclometallated structures derived from bpy and terpy.

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Fig. 2 The two types of 16 e[−], reacting intermediates, $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{III})$ fragments studied in this work.

the coordination sphere of the two unsaturated fragments represented in Fig. 2. Fragment **a** is readily generated by dissociation of dinitrogen from $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_6\text{H}_5)_2(\text{N}_2)]^{25a}$ (**1a**), whereas **b** is produced, also smoothly, from the Ir(I) complex $[\text{Tp}^{\text{Me}_2}\text{Ir}(\eta^4\text{-CH}_2=\text{C}(\text{Me})\text{C}(\text{Me})=\text{CH}_2)]$ (**1b**),^{25b} as demonstrated by its reactions with Lewis bases.^{25c} Here we provide full details of this work. To avoid unnecessary repetition, we focus data analysis on the NMR properties of compounds **2** and **6** (not discussed in the preliminary reports^{12c,d}) and on the newly described complexes **4a–6a**.

Since the investigation of the optical properties of transition metal complexes of polypyridine ligands is an active and important field of research,²⁶ we have investigated the photoluminescence properties of the new compounds. Few Ir(III) compounds bearing NHC ligands have been investigated in this regard and studies on complexes with pyridylidene-like ligands are even more scarce.²⁷

Results and discussion

Synthesis of pyridylidene complexes

In accord with previous work from our laboratory with monopyridines, heating a solution of **1a** in benzene, at 90 °C, in the presence of bpy, led to the formation of the NHC complex **2a** (isolated as an orange crystalline solid) in spectroscopic yields higher than 90% (¹H NMR). No intermediates were detected for this bpy reaction (Scheme 1, $[\text{Ir}] = \text{Tp}^{\text{Me}_2}\text{Ir}$ throughout the manuscript), even at lower temperatures (60 °C) and this is at variance with the behaviour ascertained for $\text{NC}_5\text{H}_4\text{-2-Ph}$, that under these latter conditions provided the aquo complex **3a** (Scheme 1), due to the action of adventitious water.¹⁸ Nevertheless, a related aquo complex **4a** was isolated from the reaction of **1a** and phen (*vide infra*). At room temperature the ¹H NMR spectrum of **2a** exhibits broad signals due to a fluxional process. Low temperature NMR (CD_2Cl_2) permits the observation of two rotamers (*ca.* 20 : 1 ratio) which exist as a consequence of hindered rotation around the Ir–C_{carbene} bond. The major rotamer is that shown in Scheme 1, with the N–H unit pointing towards the phenyl ligands. In the minor one, the N–H bond faces the chelating Tp^{Me_2} ligand. In both cases, in the ¹H NMR spectrum, strongly deshielded resonances are recorded for the N–H protons (14.60 and 12.40 ppm for the major and minor rotamers respectively), suggesting their participation in intramolecular N–H...N hydrogen bonding. Notice that this hydrogen bond must be

Scheme 1 Reactivity of complex **1a** with 2-phenylpyridine and bpy.

Scheme 2 Reaction of complex **1b** with bpy.

strong enough to overcome the destabilizing interaction of the two C–H units next to the central C_q–C_q bond of the pyridylidene ligand that is responsible for the *anti* disposition of the two nitrogens in free bpy.

The Ir(I) precursor **1b** promoted a similar tautomerism of bpy (Scheme 2), to form the corresponding carbene derivative **2b**. By similarity with the already reported reactions of **1b** and different Lewis bases,^{25c,28} coordination to the Ir centre induces a change in the coordination mode of the butadiene ligand from $\eta^4:\pi^2$ -diene to $\eta^2:\sigma^2$ -enediyl, with concomitant oxidation of Ir(I) to Ir(III). Compound **2b** is also an orange crystalline solid of moderate stability in air, particularly in the solid state. Interestingly, and in contrast with **2a**, sharp ¹H NMR resonances are observed in this case at room temperature, as only one rotamer is present in CDCl_3 solutions, this being the one depicted in the Scheme (NOESY evidence). The N–H...N hydrogen nucleus resonates at 12.60 ppm, *ca.* 2 ppm higher field with respect to the related rotamer of **2a**, but this only reflects the existence of an intrinsic effect that is observed when the related pyridylidene structures of the **a** and **b** systems are compared.

The related 1,10-phenanthroline molecule reacted similarly with complexes **1a** and **1b**, under otherwise identical reaction conditions, to generate complexes **5a** and **5b**, respectively (Scheme 3). Spectroscopic yields for compound **5** were similar to those for **2**, but the yields of isolated products were lower, as a result of the partial decomposition of the complexes during their chromatographic purification. The spectroscopic data for **5** resemble closely those for **2** (see Experimental section), hinting at phen coordination as a monodentate NHC-type ligand. Complexes **2** and **5** constitute the only reported examples of bpy and

Scheme 3 Reactivity of complexes **1a**, **b** against phen. Scheme 4 Reaction of complex **1a** with terpy.

phen monodentate *N*-heterocyclic carbene (or alternatively ylidic) coordination to a metal centre. This binding mode has been confirmed by X-ray studies (*vide infra*).

The reaction of **1a** with phen at $60\text{ }^\circ\text{C}$ allowed isolation of the aquo-phenyl-pyridyl complex **4a**, analogous to the structurally characterized (X-ray crystallography) compound **3a** of Scheme 1.¹⁸ IR and NMR data for **4a** resemble those of **3a**. At room temperature NMR signals for the water protons are not discernible, but upon cooling at $-70\text{ }^\circ\text{C}$ a resonance at 16.60 ppm can be observed (16.90 for **3a**). Once more mimicking the behaviour of **3a**,¹⁸ heating a pure sample of **4a** in C_6H_6 at $90\text{ }^\circ\text{C}$, labilizes the coordinated molecule of water and permits activation of a molecule of benzene, with formation of the bis-(phenyl) phen-derived carbene complex **5a** (Scheme 3).

The importance of terpy in coordination chemistry and in related fields of research²⁹ made it an obvious choice to study this reactivity. It was soon disclosed that heating a benzene solution of complex **1a** and terpy (1 : 1 ratio) at $90\text{ }^\circ\text{C}$ produced the expected pyridylidene complex, **6a**, as the major product (Scheme 4). The reaction also generated other complexes that could not be characterized. NMR data (CD_2Cl_2 , $-50\text{ }^\circ\text{C}$) for the new compound demonstrated the existence in solution of a 5 : 1 mixture of two rotamers with the major one (depicted in the Scheme) exhibiting a *cis-trans* arrangement of its pyridyl rings and having its N–H moiety directed toward the coordinated C_6H_5 groups according to the NOESY spectrum.^{12a,18}

Complex **1b** gave rise to a related NHC structure, **6b**, under analogous conditions, but as represented in Scheme 5, a binuclear compound **7b**, was also generated. In the latter species

Scheme 5 Reactivity of complex **1b** with terpy.

terpy bridges the two iridium centres, binding to each as a carbene, thereby providing an unprecedented structure. Not unexpectedly, we found that the proportion of **6b** and **7b** in the reaction mixture depends upon the molar ratio of **1b** and terpy employed in the reaction. Hence, it changes from 4 : 1 for an Ir : terpy proportion of 1 : 2, to 1 : 3 if the concentration of **1b** is double that of terpy. Consequently, adding additional amounts of complex **1b** to either of the above mixtures led to an increase in the quantities of the binuclear complex, **7b**, formed. Similarly, reaction of isolated samples of **6b** with 1 equiv of **1b** yielded exclusively complex **7b**.

The mono- and bi-metallic carbenes, **6b** and **7b**, were separated by column chromatography and crystallized from diethyl ether : hexane and THF : pentane solvent mixtures, respectively. The NOESY spectrum of **6b** indicates that no intramolecular N–H...N hydrogen bonding exists in the only rotamer detected in $CDCl_3$ solution (its N–H resonates at 11.80 ppm) and this structure has been confirmed by X-ray studies (Fig. 5, see below). Complexes **6a** and **6b** may feature different conformations in solution due to steric reasons. If **6b** was to adopt the intramolecular hydrogen-bonding arrangement found in **6a** the terminal pyridyl substituent would experience an important repulsive interaction with the methyl substituent of the diene ligand. In fact, and as discussed below (Fig. 5), the “expected” conformation of the carbene ligand of **6b** was found in a second solid state polymorph subjected to X-ray studies, this being a rotamer (not detected in $CDCl_3$) in which the N–H is pointing towards the Tp^{Me_2} ligand. A similar reasoning may be applied for the solution structure found for complex **7b**. In $CDCl_3$ at $25\text{ }^\circ\text{C}$, and despite the structure found in the solid state (Fig. 6, see below), a symmetrical species is found with their N–H protons resonating at 11.76 ppm, a chemical shift coincident with that of **7a**.

X-ray structural studies

The solid state structures of the molecules of the following complexes have been determined by X-ray crystallography (Table 1 and ESI†): compounds **2a** and **2b** derived from bpy; **5a** and **5b** with a phen-derived carbene; and **6b** and **7b**, which correspond, respectively, to the mononuclear and binuclear carbene

Table 1 Summary of crystallographic data and structure refinement results for **2a**, **2b**, **5a**, **5b**, **6b_Monoclinic**, **6b_Triclinic** and **7b**

	2a	2b	5a	5b	6b_Monoclinic	6b_Triclinic	7b
Formula	C ₃₇ H ₄₀ BIrN ₈	C ₃₁ H ₄₀ BIrN ₈ ·CHCl ₃	C ₃₉ H ₄₀ BIrN ₈	C ₃₃ H ₄₀ BIrN ₈	C ₃₆ H ₄₃ BIrN ₉	2(C ₃₆ H ₄₃ BIrN ₉)·C ₄ H ₁₀ O	C ₅₇ H ₇₅ B ₂ Ir ₂ N ₁₅ ·C ₄ H ₈ O
Fw	799.78	847.09	823.80	751.74	804.80	1683.73	1448.44
Unicrystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	8.6033(4)	12.3193(2)	8.6897(3)	10.3338(12)	12.0676(3)	10.2938(15)	10.9949(9)
<i>b</i> (Å)	10.1856(5)	18.7027(3)	20.2130(6)	10.3616(12)	22.2040(7)	11.8722(17)	17.1764(14)
<i>c</i> (Å)	22.8839(12)	15.1514(3)	20.1292(6)	16.4268(18)	13.7392(4)	16.064(2)	17.3819(14)
α (°)	91.5241(10)	90.00	90.00	82.641(3)	90.00	100.103(4)	104.057(2)
β (°)	99.3171(10)	101.0050(10)	102.0930(10)	78.022(2)	108.8360(10)	102.473(3)	102.058(2)
γ (°)	102.172(1)	90.00	90.00	66.061(3)	90.00	95.845(3)	93.350(2)
<i>V</i> (Å ³)	1930.53(17)	3426.75(10)	3457.13(19)	1570.7(3)	3484.25(17)	1867.1(4)	3093.4(4)
<i>Z</i> , <i>F</i> (000)	2, 800	4, 1688	4, 1648	2, 752	4, 1616	1, 850	2, 1452
<i>D</i> _{calc} (Mg m ^{−3})	1.376	1.642	1.583	1.589	1.534	1.497	1.555
μ (mm ^{−1})	3.493	4.166	3.903	4.287	3.872	3.617	4.351
θ_{max} (°)	30.6	30.5	33.1	30.7	30.5	26.8	26.4
Temp (K)	136(2)	273(2)	173(2)	100(2)	173(2)	223(2)	173(2)
No. reflns collected	56 043	95 300	63 240	14 998	91 260	44 999	40 562
No. reflns used	11 771	10 496	13 022	9284	10 431	7919	12 549
No. of param.	424	418	452	400	435	480	797
<i>R</i> ₁ (<i>F</i>) [<i>F</i> ² > 2σ(<i>F</i> ²)] ^a	0.0370	0.0328	0.0284	0.0394	0.0226	0.0499	0.0498
w <i>R</i> ₂ (<i>F</i> ²) ^b (all data)	0.0815	0.0874	0.0571	0.0706	0.0533	0.1364	0.1021
<i>S</i> ^c (all data)	1.023	1.042	1.061	0.953	1.041	1.115	1.001

^a *R*₁(*F*) = $\sum(|F_o| - |F_c|)/\sum|F_o|$ for the observed reflections [*F*² > 2σ(*F*²)]. ^b w*R*₂(*F*²) = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$. ^c *S* = $\{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$; (*n* = number of reflections, *p* = number of parameters).

Fig. 3 X-Ray molecular structures of complexes **2a** and **2b**.

Fig. 4 X-Ray molecular structures of complexes **5a** and **5b**.

complexes of terpy. ORTEP drawings for the bpy- and phen-derived complexes are collected in Fig. 3 and 4 respectively and for terpy-derived complexes in Fig. 5 and 6. Complex **6b** has been isolated as two polymorphs with different molecular structures and the results of the X-ray studies can be found in Fig. 5.

As can be seen in Fig. 3, the structure of the molecules of complex **2** in the solid state coincides with that proposed for the major solution rotamer on the basis of NMR studies (*i.e.* with the N–H bond pointing toward the hydrocarbonyl groups). The suggested intramolecular hydrogen bond involving the N–H of the carbene ring and the N atom of the other ring, is evinced in the solid state by the almost co-planar distribution of the rings (dihedral angles 5–6°) and by a short N–H...H distance of *ca.* 2.2 Å, which is significantly smaller than the sum of the van der Waals radii of H (1.2 Å) and N (1.5 Å).³⁰

The considerations made above regarding the existence of an intramolecular N–H...H hydrogen bond and with respect to some of the bonding parameters of the C-donor ligands are applicable to other complexes structurally characterized in this work (Fig. 4, 5 and 6). Remarkably, in all the complexes the Ir–C_{carbene} distances cluster in the narrow range of *ca.*

Fig. 5 The X-ray molecular structure of two polymorphs of complex **6b** which contain different molecular architectures of this compound.

Fig. 6 X-Ray molecular structure of complex **7b**.

1.94–1.97 Å, slightly longer than those previously determined³¹ for related O-stabilized carbene complexes. For the phen- and terpy containing carbene complexes, the Ir–C_{carbene} bond is also shorter by about 0.1 Å than the Ir–C σ bonds (*ca.* 2.05–2.08 Å).

Finally, in this regard, in the binuclear complex **7b** the three aromatic rings are far from being co-planar. Indeed, the ring that contains N(13) forms a torsion angle of 38.2(3)° with the central N(14) heterocycle, whereas the angle between the latter and the N(15) ring is somewhat smaller (*ca.* 19.3(3)°). Rather than forming N–H...N bonds, the N–H groups in this molecule participate in hydrogen bond-type interactions with the π electrons of the unsaturated C(17)–C(18) and C(38)–C(39) *ene* units (*ca.* 2.32 and 2.50 Å, respectively). These interactions are similar to those found in related systems.³²

Photophysical properties

The absorption and emission of complexes **2a,b**, **5a,b**, **6a,b** and **7b** have been studied.

DRUV spectra

The DRUV spectra of all the complexes display broad bands with several maxima. These bands reach almost the 600 nm region (Fig. 7, Table 2). Absorptions attributed to $\pi \rightarrow \pi^*$ transitions in the 260 nm region have been found in the tris(pyrazolyl)borate and tris(3,5-Me₂pyrazolyl)borate ligands.³³

The bands observed at lower energies fit with the excitation maxima found in the luminescence steady state spectra and their nature could be attributed (*vide infra*) to metal to ligand charge transfer (MLCT) transitions.

Luminescence

All the complexes exhibit red emissions in the solid state. Compounds **2a**, **6b** and **7b** are only luminescent at room temperature (**2a**) or 77 K (**6b** and **7b**). The rest are emissive both at room and low temperature (Table 2). The emission bands are broad and display a more or less resolved shoulder at higher energies, which could point out to a non-simple origin (Fig. 8).

Octahedral Ir(III) complexes have been extensively studied, and among them cyclometallated derivatives.^{9b,34} Three main

transitions have been described: metal centered (MC, $d \rightarrow d$), intraligand (IL $\pi \rightarrow \pi^*$) and metal to ligand charge transfer (MLCT) transitions. Many Ir(III) compounds are luminescent with emissions which spread in the visible region.

The nature of these emissions is frequently phosphorescent, which are favored by spin–orbit coupling frequently observed in heavy metal complexes. The emissions have been proposed to originate from ³IL ($\pi \rightarrow \pi^*$) or ³MLCT [$d(\text{Ir}) \rightarrow \pi^*$] transitions or even mixtures of ³IL ($\pi \rightarrow \pi^*$) and ^{1,3}MLCT. On many occasions a mixed character has been claimed. Ligand substitutions or slight modifications of them may lead to changes in the energies of the HOMO and LUMO orbitals, leading to changes in the emission energies. For the free ligand tris-[3-(2-pyridyl)pyrazol-1yl]-hydroborate, moderately intense, short lived fluorescence (≈ 340 nm) in fluid solution at 298 K has been described.³⁵ In a rigid matrix at 77 K the short lived fluorescence is accompanied by a very long lived and highly structured phosphorescence band with a maximum at 455 nm. Also, blue emissions (between 379 and 392 nm), upon excitation at 350 nm, attributed to LMCT transitions have been reported for the vanadium complexes³³ [HB(pz)₃VO(ph-acac)], [HB(3,5-Me₂pz)₃VO(ph-acac)] and [V₂O₄[HB(pz)₃]₂]. The complexes reported here display emissions at much lower energies which points out to a relevant role of the iridium atom in the luminescence. The lifetime values measured at room temperature fit with phosphorescent processes. The emission energies observed for the complexes

Fig. 7 DRUV spectrum of complex **5b** as an example of those of the complexes studied.

Fig. 8 Normalized emission (right) and excitation (left) spectra of compound **5b** at room temperature (in blue) and 77 K (in green) as an example of those of the complexes studied.

Table 2 Summary of photophysical data for new compounds

Compound	DRUV ^a		298 K ^b	τ^c	77 K ^b
2a	293, 371, 420, 499	250–552 (0.5)	582, 674 (sh)	0.26, 0.1d	Not emissive
5a	285, 394, 503	250–586 (3.5)	589, 660 (sh)	0.12, 0.03 ^d	584, 665 (sh)
6a	298, 389	250–588 (0.7)	631, 663 (sh)	0.05	620, 665 (sh) Not well defined
2b	313, 384, 518	250–593 (0.3)	619, 663 (sh)	0.03, 0.008 ^d	601, 663 (sh)
5b	287, 319	250–607 (2)	610, 666 (sh)	0.05, 0.002 ^d	600, 654 (sh)
6b	306, 386, 517, 554	250–614 (1.7)	Not emissive		616, 668 (sh)
7b	326, 380, 530	250–634 (0.7)	Not emissive		659, 721 (sh)

^a Left column: Maxima (in nm). Right column: Range (in nm) and maximum of the most intense maximum (in Kubelka Munk units). ^b Emission maxima in nm. ^c Lifetime values at room temperature in μs . ^d Values for a second order exponential fitting of the data.

presented here are very similar and there is not a clear trend upon modification of two Ph groups by the $\eta^2:\sigma^2$ coordinated enediyl ligand (when comparing **2a** and **2b**; **5a** and **5b**; **6a** and **6b**) or when modifying the carbene (for example when comparing **2a** with **5a** and **6a**; or **4a** with **5a** and **6a**). When comparing complexes $[\text{Re}(\text{CO})_3(\text{N-N})(\text{btpz})]$ ($\text{N-N} = \text{bipy}, \text{phen}; \text{btpz} = 3,5\text{-bis(trifluoromethyl)pyrazolate}$) no important changes in the emission energies have been found.³⁶ We propose that metal to ligand charge transfer transitions [³MLCT] are the origin of the red emissions observed for the complexes. Both ligands, pyrazolate or/and the pyridylidene-moieties could contribute to the observed emissions.

The non-emissive behavior of complexes **6b** and **7b** at room temperature could be explained by quenching of the excited state by radiationless processes, which compete with the emission. These non-radiative processes are, in general, more active at room temperature. On the other hand, competition of the radiative state with the non-radiative $d_\pi \rightarrow d_{\sigma^*}$ transition has been described.^{27f} If such a non-radiative state is near enough to the emissive one, the latter could suffer thermal deactivation at high temperature. This could be another explanation for the non-emissive character of **6b** and **7b** at room temperature. Carbene ligands are high field ligands and we could expect the $d_\pi \rightarrow d_{\sigma^*}$ state to be far enough from the emissive excited state, but the data could indicate that this is not the case for all the complexes.

Conclusions

The work reported in this paper confirms that the tautomerisation of polypyridines 2,2'-bipyridine, 1,10-phenanthroline and 2,2':6',2''-terpyridine by unsaturated $[\text{Tp}^{\text{Me}_2}\text{IrR}_2]$ fragments (where R represents a hydrocarbyl group) is a general reaction that permits access to a new coordination mode of these common ligands as *N*-heterocyclic carbenes (or ylidic-type ligands). The complexes exhibit similar absorption and emissive properties. The absorptions at higher energies correspond with the excitation maxima in the steady state excitation spectra. We propose that metal to ligand (pyridylidene or/and pyrazol) charge transfer transitions [³MLCT] originate the red emissions observed for the complexes.

Experimental

General remarks

Infrared spectra were obtained from a Bruker Vector 22 spectrometer. The NMR instruments were Bruker DRX-500, DRX-400 and DPX-300 spectrometers. Spectra were referenced to external SiMe_4 (δ 0 ppm) using the residual protio solvent peaks as internal standards (¹H NMR experiments) or the characteristic resonances of the solvent nuclei (¹³C NMR experiments). Spectral assignments were made by routine one- and two-dimensional NMR experiments where appropriate. All manipulations were performed under dry, oxygen-free dinitrogen, following conventional Schlenk techniques. The complexes $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_6\text{H}_5)_2(\text{N}_2)]^{25a}$ and $[\text{Tp}^{\text{Me}_2}\text{Ir}(\eta^4\text{-CH}_2=\text{C}(\text{Me})\text{C}(\text{Me})=\text{CH}_2)]^{25b}$

were obtained by published procedures. DRUV (diffuse reflectance UV-V) spectra were recorded on an Evolution 600 spectrophotometer. The solid samples were prepared by mixing the compounds with dried silica to allow a homogeneous powder and with a Praying Mantis integrating sphere. Steady-state photoluminescence spectra were recorded in a Jobin-Yvon Horiba Fluorolog FL-3-11 spectrofluorometer. An IBH 5000F coaxial nanosecond flashlamp was used for the lifetime measurements (chi-square between 0.97 and 1.6).

Synthesis of complex 2a.

The compounds $[\text{Tp}^{\text{Me}_2}\text{IrPh}_2(\text{N}_2)]$ (0.2 g, 0.3 mmol) and 2,2'-bipyridine (0.056 g, 0.36 mmol) were dissolved in 5 ml of C_6H_6 and the resulting solution was stirred at 90 °C for 4 hours. The solvent was then evaporated under vacuum and the solid residue was subjected to column chromatography on silica gel, using a hexane : diethyl ether (20 : 1) mixture as the eluent. Complex **2a** was obtained as an orange solid that can be recrystallized by dissolving it in diethyl ether, layering with hexane and allowing slow evaporation of the solvent. Yield: 40%. ¹H NMR (CD_2Cl_2 , 500 MHz, -40 °C): δ = 14.60 (br, 1 H, NH_A), 8.93 (d, 1 H, ³ J_{HH} = 4.5 Hz, H_H), 8.46 (d, 2 H, ³ J_{HH} $\approx$ 7.5 Hz, 2 H_O '), 7.93 (m, 2 H, H_E , H_F), 7.53 (br t, 1 H, H_G), 7.46 (d, 1 H, ³ J_{HH} = 7.1 Hz, H_D), 7.13 (d, 1 H, ³ J_{HH} = 8.4 Hz, H_B), 7.09 (t, 1 H, H_C), 7.07 (t, 2 H, ³ J_{HH} $\approx$ 7.5 Hz, 2 H_M '), 6.70 (t, 2 H, ³ J_{HH} $\approx$ 7.5 Hz, 2 H_P '), 6.47 (t, 2 H, ³ J_{HH} $\approx$ 7.5 Hz, 2 H_M), 6.40 (d, 2 H, ³ J_{HH} $\approx$ 7.5 Hz, 2 H_O '), 5.68, 5.67 (s, 2 : 1, 3 CH_{pz}), 2.49, 2.47, 0.78, 0.75 (s, 1 : 2 : 2 : 1, 6 Me_{pz}). ¹³C {¹H} NMR (CD_2Cl_2 , 125 MHz, -40 °C): δ = 180.2 (Ir=C), 152.9, 151.5 (1 : 2, C_{qpz}), 151.6 (CH_H), 150.1, 144.9 (C^1 , C^2), 145.9 (CH_B), 145.0 (C_{qpz}), 143.3 (2 CH_O), 140.4 (2 Ir-C Ph), 139.9 (CH_F), 137.3 (2 CH_O '), 135.6 (CH_C), 127.4 (3 C, CH_G , 2 CH_M), 127.2 (2 CH_M '), 122.7 (2 CH_P '), 121.8 (CH_E), 114.2 (CH_D), 108.9, 108.6 (1 : 2, CH_{pz}), 15.6, 15.3, 15.0, 14.9 (1 : 2 : 1 : 2, Me_{pz}). IR (KBr): $\nu(\text{N-H})$: 3265 cm^{-1} (broad; sometimes as two bands: 3220 cm^{-1} and 3290 cm^{-1}). HRMS m/z calcd $\text{C}_{37}\text{H}_{40}\text{BIrN}_8$ (expt.): 800.313427 (800.309841).

Synthesis of complex 2b.

The compound $[\text{Tp}^{\text{Me}_2}\text{Ir}(\eta^4\text{-CH}_2=\text{C}(\text{Me})\text{C}(\text{Me})=\text{CH}_2)]$ (0.15 g, 0.26 mmol) and 2,2'-bipyridine (0.056 g, 0.52 mmol) were heated, with stirring, in 5 ml of C_6H_6 at 90 °C for 20 hours.

The solvent was then evaporated under vacuum and the solid residue was subjected to column chromatography on silica gel, using a mixture of hexane : diethyl ether (20 : 1) as the eluent to obtain **2b** as a red solid. Crystallization was achieved by slow evaporation of a diethyl ether solution. Yield: 34%. ^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ = 12.60 (br, 1 H, NH_A), 8.72 (dq, 1 H, $^3J_{\text{HH}} = 4.8$, $J_{\text{HH}} \approx 1.4$ Hz, H_H), 7.80 (td, 1 H, $^3J_{\text{HH}} = 7.8$, $^4J_{\text{HH}} = 1.4$ Hz, H_F), 7.75 (dt, 1 H, H_E), 7.33 (ddd, 1 H, H_G), 7.19 (dt, 1 H, $^3J_{\text{HH}} = 7.2$, $^4J_{\text{HH}} = 1.2$ Hz, H_D), 7.04 (dt, 1 H, $^3J_{\text{HH}} = 8.6$, $^4J_{\text{HH}} = 1.2$ Hz, H_B), 6.87 (dd, 1 H, H_C), 5.69, 5.65 (s, 1 : 2, 3 CH_{pz}), 3.13 (d, 2 H, $^2J_{\text{HH}} = 14.3$ Hz, CH_HJ), 2.38, 2.36, 2.11, 1.61 (s, 2 : 1 : 1 : 2, 6 Me_{pz}), 2.34 (d, 2 H, CH_IHJ), 1.84 (s, 6 H, 2 Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz, 25 °C): δ = 185.5 ($\text{Ir}=\text{C}$), 151.1, 149.2 (1 : 2, C_{qpz}), 149.5 (C^2), 149.4 (CH_H), 145.5 (C^3), 143.9 (CH_B), 142.9, 142.0 (1 : 2, C_{qpz}), 141.8 (2 C^1), 136.9 (CH_F), 129.7 (CH_C), 123.9 (CH_G), 119.1 (CH_E), 109.8 (CH_D), 107.4, 106.2 (1 : 2, CH_{pz}), 19.5 (2 Me), 13.9, 13.0, 12.7, 11.3 (s, 2 : 1 : 2 : 1, Me_{pz}), 11.8 (2 $\text{Ir}-\text{CH}_2$). IR (KBr): $\nu(\text{N}-\text{H})$: 3140, 3120 cm^{-1} . HRMS m/z calcd $\text{C}_{31}\text{H}_{40}\text{BlrN}_8$ (expt.): 727.2993 (727.3020).

Synthesis of complex 4a.

The compound $[\text{Tp}^{\text{Me}_2}\text{IrPh}_2(\text{N}_2)]$ (0.2 g, 0.3 mmol) and 1,10-phenanthroline (0.054 g, 0.36 mmol) were dissolved in 5 ml of C_6H_6 and the resulting solution was stirred at 60 °C for 2 hours. The solvent was then removed under vacuum and the solid residue was subjected to column chromatography on silica gel, using a mixture of hexane : diethyl ether (5 : 1 $\rightarrow$ 1 : 5) as the eluent. Complex **4a** was obtained as an orange solid. Yield: 45%. ^1H NMR (CD_2Cl_2 , 500 MHz, -60 °C): δ = 9.27 (br, 1 H, $^3J_{\text{HH}} = 5.0$ Hz, H_H), 8.28 (d, 1 H, $^3J_{\text{HH}} = 8.1$ Hz, H_F), 7.98 (d, 1 H, $^3J_{\text{HH}} = 7.3$ Hz, $\text{H}_\text{o'}$), 7.70 (m, 3 H, H_D , H_E , H_G), 7.57 (d, 1 H, $^3J_{\text{HH}} = 8.7$ Hz, H_C), 7.43 (d, 1 H, $^3J_{\text{HH}} = 8.6$, H_B), 7.04 (t, 1 H, $^3J_{\text{HH}} = 7.3$ Hz, $\text{H}_\text{m'}$), 6.76 (t, 1 H, $^3J_{\text{HH}} = 7.3$ Hz, H_p), 6.65 (t, 1 H, $^3J_{\text{HH}} = 7.0$ Hz, H_m), 6.39 (d, 1 H, $^3J_{\text{HH}} = 7.2$ Hz, H_o), 5.81, 5.69, 5.59 (s, 1 H each, 3 CH_{pz}), 2.39, 2.47, 0.84, 0.78 (s, 1 : 2 : 2 : 1, 6 Me_{pz}). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 125 MHz, -60 °C): δ = 180.6 ($\text{Ir}=\text{C}$), 151.2, 150.4 (C_{qpz}), 150.4 (CH_H), 150.2, 143.2, 143.1, 142.6 (C_{qpz}), 140.5 (CH_o), 139.3 (CH_B), 138.9, 138.2, 136.3 (C_{qphen}), 138.8 ($\text{Ir}-\text{C}_{\text{Ph}}$), 135.8 (CH_F), 131.0 (CH_C), 130.1 ($\text{CH}_\text{o'}$), 128.2 (C_{qphen}), 125.7 (CH_m), 125.1 ($\text{CH}_\text{m'}$), 124.4 (CH_D), 123.8 (CH_E), 123.6 (CH_G), 121.2 (CH_p), 107.5, 107.3, 107.0 (CH_{pz}), 16.3, 13.7, 13.2, 13.1, 13.0, 11.9 (Me_{pz}). IR (nujol): $\nu(\text{O}-\text{H})$ 3605 cm^{-1} . HRMS m/z calcd $\text{C}_{331}\text{H}_{350}\text{BlrN}_8 - \text{H}_2\text{O}$ (expt.): 747.2698 (727.2707).

Synthesis of complex 5a.

The compound $[\text{Tp}^{\text{Me}_2}\text{IrPh}_2(\text{N}_2)]$ (0.2 g, 0.3 mmol) and 1,10-phenanthroline (0.054 g, 0.36 mmol) were dissolved in 5 ml of C_6H_6 and the resulting solution was stirred at 100 °C for 3 hours. The solvent was then evaporated under vacuum and the solid residue was subjected to column chromatography on silica gel, using a mixture of hexane : diethyl ether (20 : 1 $\rightarrow$ 5 : 1) as the eluent. Complex **5a** was obtained as a red solid that can be recrystallized by dissolving it in a $\text{MeOH}:\text{CH}_2\text{Cl}_2$ mixture and allowing slow evaporation of the solvent. Yield: 40%. ^1H NMR (CD_2Cl_2 , 500 MHz, -60 °C): δ = 14.92 (s, 1 H, NH_A), 9.22 (br d, 1 H, $^3J_{\text{HH}} = 5.0$ Hz, H_H), 8.59 (d, 2 H, $^3J_{\text{HH}} = 7.5$ Hz, 2 $\text{H}_\text{o'}$), 8.35 (d, 1 H, $^3J_{\text{HH}} = 8.2$ Hz, H_F), 7.78 (m, 2 H, H_D , H_G), 7.69 (d, 1 H, $^3J_{\text{HH}} = 8.9$ Hz, H_B), 7.47 (d, 1 H, $^3J_{\text{HH}} = 8.9$ Hz, H_C), 7.34 (d, 1 H, $^3J_{\text{HH}} = 8.8$ Hz, H_E), 7.10 (t, 2 H, $^3J_{\text{HH}} = 7.3$ Hz, 2 $\text{H}_\text{m'}$), 6.71 (t, 2 H, $^3J_{\text{HH}} = 7.0$ Hz, 2 H_p), 6.48 (t, 2 H, $^3J_{\text{HH}} = 7.2$ Hz, 2 H_m), 6.40 (d, 2 H, $^3J_{\text{HH}} = 7.7$ Hz, 2 H_o), 5.69 (br, 3 H, 3 CH_{pz}), 2.49, 2.48, 0.79, 0.76 (s, 1 : 2 : 1 : 2, 6 Me_{pz}). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 125 MHz, -60 °C): δ = 178.5 ($\text{Ir}=\text{C}$), 151.1, 149.7 (1 : 2, C_{qpz}), 150.0 (CH_H), 143.2 (C_{qpz}), 142.0 (CH_B), 141.0 (2 CH_o), 138.2 (2 $\text{Ir}-\text{C}_{\text{Ph}}$, 2 C_{qphen}), 136.8 (C_{qphen}), 136.5 (CH_F), 135.0 (2 $\text{CH}_\text{o'}$), 131.2 (CH_C), 127.9 (C_{qphen}), 125.7 (2 $\text{CH}_\text{m'}$), 125.6 (2 CH_m), 124.4 (CH_D), 124.3 (CH_E), 124.2 (CH_G), 120.4 (2 CH_p), 107.1, 106.7 (1 : 2, CH_{pz}), 14.2, 13.5 (1 : 5, Me_{pz}). IR (nujol): $\nu(\text{N}-\text{H})$: 3235 cm^{-1} . HRMS m/z calcd $\text{C}_{39}\text{H}_{40}\text{BlrN}_8$ (expt.): 824.3098 (824.3126). Anal. Calcd for $\text{C}_{39}\text{H}_{40}\text{BlrN}_8 \cdot \text{CH}_2\text{Cl}_2$: C, 52.9; H, 4.7; N, 12.3. Found: C, 52.9; H, 5.0; N, 12.7.

Synthesis of complex 5b.

The compound $[\text{Tp}^{\text{Me}_2}\text{Ir}(\eta^4-\text{CH}_2=\text{C}(\text{Me})\text{C}(\text{Me})=\text{CH}_2)]$ (0.15 g, 0.26 mmol) and 1,10-phenanthroline (0.094 g, 0.52 mmol) were heated, with stirring, in 6 ml of C_6H_6 at 90 °C for 20 hours. The solvent was then evaporated under vacuum and the solid residue was purified by chromatography on silica gel, using a mixture of hexane : diethyl ether (20 : 1) as the eluent. A red solid was obtained in the second fraction that was crystallized from a mixture of pentane : diethyl ether (1 : 1) at -20 °C. Yield: 20%. ^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ = 13.20 (br, 1 H, NH_A), 9.00 (dd, 1 H, $^3J_{\text{HH}} = 4.2$, $^4J_{\text{HH}} = 1.6$ Hz, H_H), 8.17 (dd, 1 H, $^3J_{\text{HH}} = 8.3$ Hz, H_F), 7.63 (d, 1 H, $^3J_{\text{HH}} = 8.9$ Hz, H_E), 7.58 (d, 1 H, H_D), 7.55 (dd, 1 H, H_G), 7.25 (d, 1 H,

$^3J_{\text{HH}} = 8.9 \text{ Hz}$, H_C), 7.19 (dd, 1 H, $^4J_{\text{HH}} = 1.4 \text{ Hz}$, H_B), 5.73, 5.67 (s, 1 : 2, 3 CH_{pz}), 3.28 (d, 2 H, $^2J_{\text{HH}} = 14.0 \text{ Hz}$, $\text{CH}_1\text{CH}_\text{J}$), 2.49 (d, 2 H, $\text{CH}_1\text{CH}_\text{J}$), 2.41, 2.39, 2.19, 1.58 (s, 2 : 1 : 1 : 2, 6 Me_{pz}), 1.96 (s, 6 H, 2 Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz, 25 °C): $\delta = 189.7$ ($\text{Ir}=\text{C}$), 151.4, 149.5 (1 : 2, C_{qpz}), 149.5 (CH_H), 143.4 (CH_B), 143.1, 142.2 (1 : 2, C_{qpz}), 141.8 (2 C^1), 138.8, 138.1, 127.9, 122.4 (C^4 , C^5 , C^2 , C^3), 135.6 (CH_F), 127.4 (CH_C), 125.8 (CH_D), 122.9 (CH_G), 122.1 (CH_E), 107.6, 106.3 (2 : 1, CH_{pz}), 19.7 (2 Me), 14.1, 13.1, 12.9, 11.5 (2 : 1 : 2 : 1, Me_{pz}), 12.8 (2 $\text{Ir}-\text{CH}_2$). IR (KBr): $\nu(\text{N}-\text{H})$: 3160, 3140 cm^{-1} . HRMS m/z calcd $\text{C}_{33}\text{H}_{40}\text{BIrN}_8$ (expt.): 751.3018 (751.3020).

Synthesis of complex 6a.

The compound $[\text{Tp}^{\text{Me}_2}\text{IrPh}_2(\text{N}_2)]$ (0.2 g, 0.3 mmol) and 2,2':6',2''-terpyridine (0.083 g, 0.36 mmol) were dissolved in 8 ml of C_6H_6 and the resulting solution was stirred at 100 °C for 3 hours. The solvent was then evaporated under vacuum and the solid residue was subjected to column chromatography on silica gel, using a mixture of hexane : diethyl ether (20 : 1 $\rightarrow$ 1 : 1) as the eluent. Complex **6a** was obtained as an orange solid. Yield: 25%. ^1H NMR (CD_2Cl_2 , 500 MHz, -50°C): $\delta = 14.20$ (s, 1 H, NH_A), 9.15 (d, 1 H, $^3J_{\text{HH}} = 8.2 \text{ Hz}$, H_K), 8.79 (d, 1 H, $^3J_{\text{HH}} = 4.1 \text{ Hz}$, H_H), 8.74 (d, 2 H, $^3J_{\text{HH}} = 7.9 \text{ Hz}$, 2 $\text{H}_\text{O'}$), 8.60 (d, 1 H, $^3J_{\text{HH}} = 7.9 \text{ Hz}$, H_E), 8.08 (m, 2 H, H_B , H_J), 7.91 (d, 1 H, $^3J_{\text{HH}} = 7.9 \text{ Hz}$, H_G), 7.49 (m, 2 H, H_I , H_D), 7.10 (m, 2 H, H_C , H_B), 6.68 (t, 2 H, $^3J_{\text{HH}} = 7.3 \text{ Hz}$, 2 $\text{H}_\text{M'}$), 6.58 (t, 2 H, $^3J_{\text{HH}} = 7.3 \text{ Hz}$, 2 H_P), 6.44 (t, 2 H, $^3J_{\text{HH}} = 7.3 \text{ Hz}$, 2 H_M), 6.40 (d, 2 H, $^3J_{\text{HH}} = 7.9 \text{ Hz}$, 2 H_O), 5.70, 5.66 (s, 2 : 1, 3 CH_{pz}), 2.47, 0.78, 0.73 (s, 3 : 2 : 1, 6 Me_{pz}). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 125 MHz, -50°C): $\delta = 179.5$ ($\text{Ir}=\text{C}$), 156.5 (C^4), 154.9 (C^3), 151.1 (C_{qpz}), 149.6 (CH_K), 149.4 (C_{qpz}), 148.2 (C^1), 144.2 (C^2), 143.2 (CH_B), 143.0 (C_{qpz}), 141.1 (2 CH_O), 139.1 (2 $\text{Ir}-\text{C}_{\text{Ph}}$), 139.0 (CH_I), 137.8 (CH_F), 134.8 (2 $\text{CH}_\text{O'}$), 133.7 (CH_C), 125.1 (2 CH_M), 125.2 (2 $\text{CH}_\text{M'}$), 124.8 (CH_J), 122.7 (CH_E), 121.4 (CH_H), 120.2 (CH_G), 120.1 (2 CH_P), 113.3 (CH_D), 106.7, 106.5 (1 : 2, CH_{pz}), 13.7, 13.2, 13.3, 13.0 (1 : 2 : 1 : 2, Me_{pz}). IR (nujol): $\nu(\text{N}-\text{H})$: 3272. HRMS m/z calcd $\text{C}_{42}\text{H}_{43}\text{BIrN}_9$ (expt.): 877.3364 (877.3363). Anal. Calcd for $\text{C}_{42}\text{H}_{43}\text{BIrN}_9 \cdot 1/2\text{CH}_2\text{Cl}_2$: C, 55.9; H, 4.7; N, 13.6. Found: C, 55.8; H, 5.0; N, 13.7.

Synthesis of complexes 6b and 7b. The compound $[\text{Tp}^{\text{Me}_2}\text{Ir}(\eta^4\text{-CH}_2=\text{C}(\text{Me})\text{C}(\text{Me})=\text{CH}_2)]$ (0.1 g, 0.175 mmol) and 2,2':6',2''-terpyridine (0.086 g, 0.35 mmol) were heated, with stirring, in 4 ml of C_6H_{12} at 90 °C for 20 hours. The solvent was evaporated under vacuum and the solid residue was dissolved in CH_2Cl_2 and subjected to column chromatography on silica gel, using a mixture of *n*-hexane : diethyl ether (19 : 1) to elute complex **7** as a dark red solid. A second fraction (complex **6b**) was obtained using a mixture of hexane : diethyl ether (9 : 1) as

the eluent. This compound is a bright red solid that was recrystallized from a mixture of dichloromethane : diethyl ether (**6b_Triclinic**) or dichloromethane : pentane (**6b_Monoclinic**). Yield 37%.

Complex 6b. ^1H NMR (CDCl_3 , 500 MHz, 25 °C): $\delta = 11.80$ (br, 1 H, NH_A), 8.72 (d, 1 H, H_H), 8.56 (d, 1 H, H_K), 8.54 (d, 1 H, H_G), 8.01 (t, 1 H, H_F), 7.92 (t, 1 H, H_J), 7.71 (d, 1 H, H_E), 7.59 (d, 1 H, H_D), 7.38 (dd, 1 H, H_I), 7.04 (d, 1 H, H_B), 6.95, (t, 1 H, H_C), 5.69, 5.67 (s, 1 : 2, 3 CH_{pz}), 3.14 (d, 2 H, $^2J_{\text{HH}} = 14.4 \text{ Hz}$, 2 $\text{IrCH}_\text{L}\text{H}_\text{M}$), 2.42 (d, 2 H, 2 $\text{IrCH}_\text{L}\text{H}_\text{M}$), 2.39, 2.37, 2.05, 1.62 (s, 2 : 1 : 1 : 2, 6 Me_{pz}), 1.83 (s, 6 H, 2 Me). All $^3J_{\text{HH}}$ aromatics $\approx 7.5 \text{ Hz}$ except $^3J_{\text{HI}} = 4.5 \text{ Hz}$. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz, 25 °C): $\delta = 185.7$ ($\text{Ir}=\text{C}$), 156.0 (C^4), 155.1 (C^5), 150.9, 149.3 (1 : 2, C_{qpz}), 149.8 (C^3), 148.9 (CH_H), 146.9 (C^2), 143.9 (CH_B), 143.1, 142.2 (1 : 2, C_{qpz}), 142.5 (2 C^1), 138.3 (CH_F), 137.5 (CH_J), 130.3 (CH_C), 124.3 (CH_I), 121.8, 121.8 (CH_K , CH_G), 119.2 (CH_E), 111.8 (CH_D), 107.6, 106.4 (1 : 2, CH_{pz}), 19.9 (2 Me), 14.1, 13.1, 12.8, 11.2 (2 : 1 : 2 : 1, Me_{pz}), 12.0 (2 $\text{Ir}-\text{CH}_2$, $^1J_{\text{CH}} = 121 \text{ Hz}$). IR (KBr): $\nu(\text{N}-\text{H})$ 3225, $\nu(\text{B}-\text{H})$ 2520 cm^{-1} . Anal. Calcd for $\text{C}_{36}\text{H}_{43}\text{BIrN}_9$: C, 53.7; H, 5.4; N, 15.6. Found: C, 53.9; H, 5.6; N, 15.2. HRMS m/z calcd for $\text{C}_{36}\text{H}_{43}\text{BIrN}_9$ (expt.): 804.3286 (804.3281).

Complex 7b. ^1H NMR (CDCl_3 , 400 MHz, 25 °C): $\delta = 11.76$ (br, 2 H, 2 NH_A), 8.04 (t, 1 H, H_F), 7.72 (d, 2 H, 2 H_E), 7.53 (d, 2 H, 2 H_D), 7.07 (d, 2 H, 2 H_B), 6.98 (t, 2 H, 2 H_C), 5.69, 5.66 (s, 1 : 2, 6 CH_{pz}), 3.15 (d, 4 H, $^2J_{\text{HH}} = 14.6 \text{ Hz}$, 2 $\text{IrCH}_\text{G}\text{H}_\text{H}$), 2.38 (d, 4 H, 2 $\text{IrCH}_\text{G}\text{H}_\text{H}$), 2.38, 2.36, 2.03, 1.61 (s, 2 : 1 : 1 : 2, 12 Me_{pz}), 1.81 (s, 12 H, 4 Me). All $^3J_{\text{HH}}$ aromatics $\approx 7.5 \text{ Hz}$. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz, 25 °C): $\delta = 186.0$ (2 $\text{Ir}=\text{C}$), 151.1, 149.1 (1 : 2, 6 C_{qpz}), 150.8 (2 C^3), 146.1 (2 C^2), 144.2 (2 CH_B), 143.1, 142.1 (1 : 2, C_{qpz}), 142.4 (4 C^1), 138.6 (CH_F), 130.1 (2 CH_C), 119.3 (2 CH_E), 112.3 (2 CH_D), 107.5, 106.2 (1 : 2, CH_{pz}), 19.7 (4 Me), 13.8, 12.9, 12.6, 11.1 (2 : 1 : 2 : 1, Me_{pz}), 12 (4 $\text{Ir}-\text{CH}_2$). IR (KBr): $\nu(\text{N}-\text{H})$ 3175, $\nu(\text{B}-\text{H})$ 2520 cm^{-1} . Anal. Calcd for $\text{C}_{57}\text{H}_{75}\text{B}_2\text{Ir}_2\text{N}_{15}$: C, 49.7; H, 5.5; N, 15.2. Found: C, 50.6; H, 5.7; N, 14.5.

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