

## Synthesis and Luminescence of a Charge-Neutral, Cyclometalated Iridium(III) Complex Containing N<sup>∧</sup>C<sup>∧</sup>N- and C<sup>∧</sup>N<sup>∧</sup>C-Coordinating Terdentate Ligands

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The first examples of iridium(III) complexes containing a terdentate, N<sup>∧</sup>C<sup>∧</sup>N-coordinated 1,3-di(2-pyridyl)benzene derivative, cyclometalated at C2 of the benzene ring, are reported. This mode of binding becomes significant only if competitive cyclometalation at C4/C6 is blocked, and the ligand 1,3-di(2-pyridyl)-4,6-dimethylbenzene (dpyxH) has been prepared to achieve this condition. The charge-neutral complex [Ir(dpyx)(dppy)], **2**, (dppyH<sub>2</sub> = 2,6-diphenylpyridine) has been isolated, containing dpyx and dppy bound to the metal through one and two carbon atoms, respectively. A terpyridyl analogue, [Ir(dpyx)(tppy)](PF<sub>6</sub>)<sub>2</sub>, **3**, (tppy = 4'-tolylterpyridine) has also been prepared and its X-ray crystal structure determined, confirming the N<sup>∧</sup>C<sup>∧</sup>N binding mode of dpyx. Complex **2** emits strongly in degassed solution at 295 K ( $\lambda_{\text{max}} = 585$  nm,  $\phi = 0.21$ ,  $\tau = 3900$  ns, in CH<sub>3</sub>CN). In solution, the excited state can also undergo photodissociation, through cleavage of one of the Ir–C(dppy) bonds.

Luminescent iridium(III) complexes with polypyridyl and related cyclometalating ligands have been the subject of intense recent interest.<sup>1–3</sup> The polypyridyl complexes are typically characterized by long-lived emissive excited states of primarily <sup>3</sup> $\pi$ – $\pi^*$  character,<sup>2</sup> whereas cyclometalated complexes containing C<sup>∧</sup>N-coordinating ligands, such as 2-phenylpyridine (ppy), often display intense emission from states with substantial <sup>3</sup>MLCT character.<sup>3</sup> The complex *fac*-

[Ir(ppy)<sub>3</sub>] has enjoyed particular attention recently, following the demonstration that it can act as a triplet-harvesting agent when incorporated into electroluminescent devices, with accompanying large gains in efficiency.<sup>3b</sup> The charge neutrality of this system is an attractive feature for such applications. Cyclometalated iridium complexes are also strong photoreductants, allowing them to be used as sensitizers for electron-transfer reactions.<sup>4</sup> Owing to this rich combination of properties, such compounds are attractive building blocks for constructing larger supramolecular assemblies, for example, in systems designed to carry out energy- and electron-transfer processes.<sup>1</sup>

With respect to such applications, a six-coordinate complex containing two *terdentate* ligands can offer two important advantages over complexes with three bidentate ligands, such as [Ir(ppy)<sub>3</sub>], in the same way that bis-terpyridylmetal complexes have structural advantages over their tris-bipyridyl counterparts.<sup>5</sup> First, the latter are normally chiral, so that a mixture of diastereomers is formed when two or more such complexes are linked together; in contrast, bis-terdentate complexes are achiral. Second, complexes with two terdentate ligands have axial symmetry, which allows three or more such components to be connected linearly and without problems of geometrical isomerism. Cationic Ir(III) complexes incorporating terdentate N<sup>∧</sup>N<sup>∧</sup>C- or C<sup>∧</sup>N<sup>∧</sup>C-coordinating ligands have been reported recently.<sup>6</sup> However, ligands offering N<sup>∧</sup>C<sup>∧</sup>N coordination have not been investigated with Ir(III), despite their favorable effect on the luminescence of complexes with Ru(II),<sup>7</sup> Os(II),<sup>7</sup> and Pt(II),<sup>8</sup> and no charge-neutral bis-terdentate Ir(III) complexes have been reported. In this contribution, we describe the first example of a

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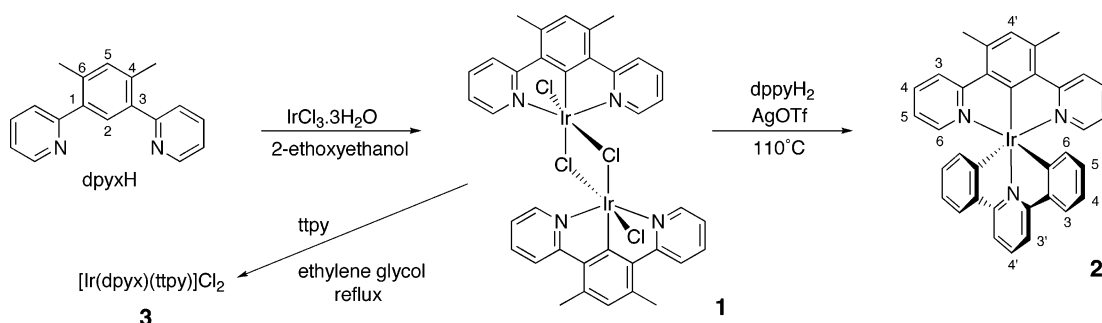
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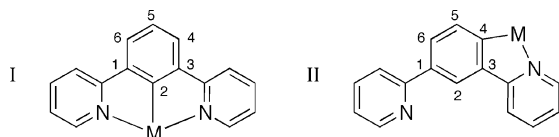
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Scheme 1



charge-neutral cyclometalated complex of iridium(III) containing two terdentate ligands, binding via  $N\wedge C\wedge N$  and  $C\wedge N\wedge C$  coordination modes, the first example of such a coordination arrangement in transition metal chemistry.

Our initial efforts to prepare such a complex were focused on the attempted introduction of 1,3-di(2-pyridyl)benzene (dpyb) into the coordination sphere of Ir(III), as an  $N\wedge C\wedge N$ -coordinating ligand (mode I), as observed for Ru(II), Os(II), and Pt(II).<sup>7,8</sup> However, reaction of dpybH with  $IrCl_3 \cdot 3H_2O$ , under a range of conditions, resulted primarily in complexation through binding mode II, in which the ligand binds bidentately, in the same way as ppy.



Clearly, cyclometalation at the C4 position of the phenyl ring must be kinetically favored over reaction at the more hindered C2 position. We reasoned that this undesired binding mode could be blocked through the introduction of substituents at the 4 and 6 positions of the central ring. The new ligand 1,3-di(2-pyridyl)-4,6-dimethylbenzene (dpyxH, Scheme 1) was therefore prepared by palladium-catalyzed cross-coupling of 4,6-dibromo-*meta*-xylene with 2-tri-*n*-butylstannyl-pyridine. Subsequent reaction of dpyxH with  $IrCl_3 \cdot 3H_2O$  in 2-ethoxyethanol led to a product of low solubility in all common solvents, the  $^1H$  NMR spectrum of which, after dissolution in  $d_6$ -DMSO, showed the same 2-fold symmetry as the ligand, but with no H2 resonance and with a substantial upfield shift of the H5 resonance, consistent with the expected effect of cyclometalation at C2. An X-ray diffraction study of a single crystal obtained from DMSO solution revealed the structure to be  $[Ir(dpyx)Cl_2(DMSO)]$ , containing dpyx bound in the desired manner (mode I), and with DMSO coordinated through sulfur, trans to the cyclometalated carbon. Mass spectrometry (MALDI) suggests that the initially formed insoluble solid is the dimer **1**, which undergoes bridge cleavage in coordinating solvents, such as DMSO, to give the corresponding solvate.

To introduce the second  $C\wedge N\wedge C$ -coordinating ligand onto the metal, the reaction of **1** with 2,6-diphenylpyridine

(dppyH<sub>2</sub>) was investigated. The preparation of bis-terpyridyl iridium complexes is notoriously difficult, requiring forcing conditions, normally in ethylene glycol at reflux.<sup>2</sup> In the present instance, the use of such conditions (and other variants including the addition of silver salts to promote the dechlorination of the intermediate) consistently failed to provide the desired complex **2**.  $^1H$  NMR spectroscopy of the main product obtained upon chromatographic separation revealed bidentate binding of dppy, as a  $C\wedge N$ -coordinated ligand, with the second phenyl group unbound. The sixth coordination site might be occupied by a weakly bound solvent molecule. The desired complex **2**, containing bis-cyclometalated dppy, was finally obtained as an orange solid by heating **1** with silver triflate in molten dppy at 110 °C, in the absence of any other solvent, followed by chromatographic purification. The structure of this tetracyclic complex (i.e., incorporating four  $N\wedge M\wedge C$  rings) was confirmed by  $^1H$ - $^1H$  COSY and NOESY NMR spectroscopy and by electron-ionization mass spectrometry. Solvent-free conditions have previously been reported as successful alternatives to the usual solution-based methods in the preparation of  $[Ir(ppy)_3]$  and derivatives;<sup>9</sup> the extension of such an approach to the present system is facilitated by the relatively low melting point of dppyH<sub>2</sub> (74–76 °C).

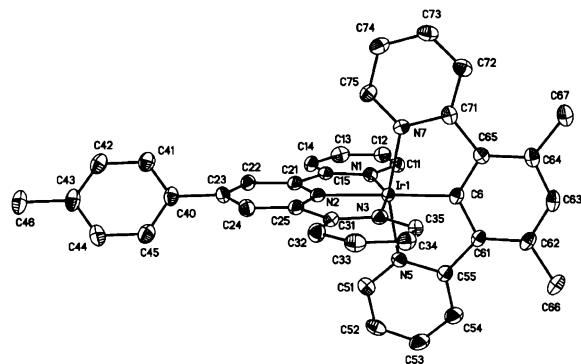
The related complex **3**, which contains an  $N\wedge N\wedge N$ -coordinated terpyridine in place of dppy, could be obtained under more conventional conditions, by refluxing **1** with 4'-tolylterpyridine in ethylene glycol for 1 h. An X-ray diffraction study of a single crystal of this complex confirms the  $N\wedge C\wedge N$  binding mode of dpyx and the mutually orthogonal orientation of the ligands (Figure 1).<sup>10</sup>

The absorption spectrum of complex **2** in acetonitrile solution (Figure 2) displays strong bands in the far-UV region [244 nm (53 900 L mol<sup>-1</sup> cm<sup>-1</sup>), 269 nm (46 900 L mol<sup>-1</sup> cm<sup>-1</sup>)], assigned to  $^1\pi$ - $\pi^*$  transitions of the ligands. There are also two well-resolved sets of weaker bands, one in the near-UV range and the other extending well into the visible region [458 nm, (5510 L mol<sup>-1</sup> cm<sup>-1</sup>), 481 nm (6820 L mol<sup>-1</sup> cm<sup>-1</sup>).

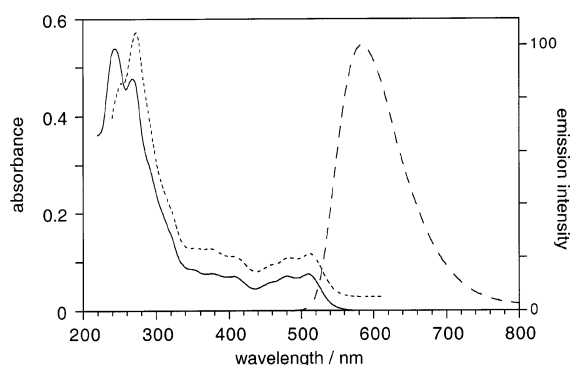
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(10) Crystal data for complex **3**: C<sub>43</sub>H<sub>38</sub>F<sub>12</sub>IrN<sub>5</sub>OP<sub>2</sub>,  $M = 1122.92$ , orthorhombic, space group  $Pbca$ ,  $a = 12.7455(2)$  Å,  $b = 19.0106(3)$  Å,  $c = 33.9410(5)$  Å,  $U = 8223.9(2)$  Å<sup>3</sup>,  $T = 120(2)$  K,  $Z = 8$ ,  $D_c = 1.814$  g cm<sup>-3</sup>,  $\mu = 3.423$  mm<sup>-1</sup>, 52 795 reflections collected, of which 10 414 were independent ( $R_{int} = 0.0534$ ). Final  $R(F) = 0.0372$  [ $I > 2 \sigma(I)$  data], and  $wR(F^2) = 0.0905$  (all data).



**Figure 1.** Structure of the cation in complex **3**, crystallized as the  $\text{PF}_6^-$  salt from acetone; displacement ellipsoids shown at 50% probability level. Selected bond lengths (Å) and angles ( $^\circ$ ): Ir(1)–C(6), 1.954(4); Ir(1)–N(5), 2.046(3); Ir(1)–N(7), 2.047(3); Ir(1)–N(1), 2.046(3); Ir(1)–N(2), 2.030(3); Ir(1)–N(3), 2.052(3); C(6)–Ir(1)–N(2), 175.76(14); C(6)–Ir(1)–N(5), 80.03(15); N(5)–Ir(1)–N(7), 160.25(13); N(1)–Ir(1)–N(2), 78.82(13); N(1)–Ir(1)–N(3), 158.19(13); N(1)–Ir(1)–N(5), 90.58(13); N(1)–Ir(1)–N(7), 91.74(13) (see Supporting Information).



**Figure 2.** Complex **2**: absorption spectrum (solid line), luminescence emission spectrum (dashed line,  $\lambda_{\text{ex}} = 480$  nm), and excitation spectrum (dotted line,  $\lambda_{\text{em}} = 585$  nm, offset for clarity) in  $\text{CH}_3\text{CN}$  at 295 K.

$\text{cm}^{-1}$ ), 510 nm ( $7340 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), assigned to charge-transfer transitions on the basis of related cyclometalated iridium(III) complexes.<sup>1,3</sup> The complex is strongly luminescent in degassed solution (Figure 2), displaying a broad, structureless emission band ( $\lambda_{\text{max}} = 585$  nm,  $\phi = 0.21$ , in  $\text{CH}_3\text{CN}$  at 295 K). The temporal decay of the emission follows monoexponential kinetics, with a lifetime of 3900 ( $\pm 50$ ) ns [ $77 (\pm 5)$  ns in air-equilibrated solution]. Such values are consistent with emission from a state of primarily charge-transfer character, as commonly observed for cyclometalated iridium complexes such as  $[\text{Ir}(\text{ppy})_3]$ .<sup>3</sup> The substantial red shift of the emission, compared to that displayed by *fac*- and *mer*- $[\text{Ir}(\text{ppy})_3]$  under comparable conditions ( $\lambda_{\text{max}} = 510$  and 512 nm, respectively, in  $\text{CH}_2\text{Cl}_2$ <sup>11</sup>) can be attributed to the more delocalized nature of the acceptor  $\text{N}^3\text{C}^1\text{N}^3$  ligand compared to ppy and, hence, to a lower-energy LUMO in **2**. DFT calculations confirm that the LUMO in this complex is largely localized on the  $\text{N}^3\text{C}^1\text{N}^3$  ligand, whereas the HOMO spans both the metal and fragments of the two ligands, such that the emitting state is probably best regarded as being of mixed MLCT/LC/LLCT character (see Supporting Information).

Despite the appreciable luminescence quantum yield, however, a competitive photodissociation process is observed upon prolonged irradiation in polar solvents. The decomposition product emits at higher energy ( $\lambda_{\text{max}} = 517$  nm in  $\text{CH}_3\text{CN}$ <sup>12</sup>).  $^1\text{H}$  NMR spectroscopic analysis after irradiation in acetonitrile indicates that the major compound present contains dppy bound asymmetrically as a  $\text{C}^1\text{N}^3$ -coordinating ligand with the second phenyl group unbound, indicating that cleavage of one of the mutually trans Ir–C bonds in **2** must be occurring (see Supporting Information for postulated structure of photoproduct). Such a process is also observed for the structurally similar *mer*- $[\text{Ir}(\text{ppy})_3]$ , where dissociation of one of the trans-related Ir–C bonds in the excited state is followed by isomerization to the *fac* isomer.<sup>11</sup> In contrast to *mer*- $[\text{Ir}(\text{ppy})_3]$ , however, the terdentate nature of the ligands in **2** does not allow a *fac* isomer to be formed. The photodissociation process is strongly solvent-dependent, being favored in  $\text{CH}_3\text{CN}$  and  $\text{CHCl}_3$  but greatly reduced in toluene. In the solid state, the compound is stable indefinitely and shows no evidence of decomposition even under conditions of intense irradiation that lead to rapid degradation in polar solvents. This is noteworthy, given that a major interest in such compounds lies in their use in solid-state devices. It is likely that the lability of the Ir–C(dppy) bonds in solution is the reason the  $\text{C}^1\text{N}^3\text{C}^1$ -bound product is elusive in all of the solution-based preparative routes attempted to date whereas the solvent-free route alone was successful. Interestingly,  $[\text{Ir}(\text{dppy})(\text{tppy})]^+$  displays no such instability,<sup>13</sup> which implies that the labilization of the aforesaid bonds in **2** is activated by the presence of the third cyclometalating carbon within the coordination sphere of the metal. Complex **3**, in marked contrast to **2**, is only very weakly emissive in solution at room temperature, at higher energy ( $\lambda_{\text{max}} = 560$  nm,  $\phi < 10^{-3}$  in degassed  $\text{CH}_3\text{CN}$ ).

In summary, complexes **2** and **3** are the first examples of iridium(III) complexes containing a terdentate  $\text{N}^3\text{C}^1\text{N}^3$ -coordinating ligand. This coordination mode is achieved by blocking competitive cyclometalation at C4 and C6 of the phenyl ring. Complex **2** is an intense, orange emitter and is charge-neutral, two desirable properties for many applications, including use in OLEDs. In contrast to  $[\text{Ir}(\text{ppy})_3]$ , complex **2** has axial symmetry. This feature, coupled with the accessibility of 4'-substituted dppy ligands, might render complexes of this type of interest as units in the construction of linear photoactive assemblies, among numerous other possible applications.

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**Supporting Information Available:** Details of synthesis, characterization, DFT, and crystallography. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(12) The decay kinetics of **2** at 585 nm remains monoexponential.

(13) A related complex containing bis-cyclometalated 4-tolyl-dppy and 4'-bromophenyl terpyridine has also been reported to be stable.<sup>6b</sup>