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Synthesis and Photophysical Properties of Bis-Cyclometallated Iridium(III)–Styryl Complexes and Their Saturated Analogues

Marc Lepeltier,[a] Terence Kwok-Ming Lee,[b] Kenneth Kam-Wing Lo,*[b] Loic Toupet,[c] Hubert Le Bozec,[a] and Véronique Guerchais*[a]

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This manuscript reports the synthesis and photophysical investigation of a series of Ir^{III} complexes $Ir(C^{\wedge}N)_2(O^{\wedge}O)$ which are functionalized in the *para* position of the pyridine ring by styryl groups substituted with electron-donor and -acceptor end groups. The saturated derivative $Ir(C^{\wedge}N$-ppy-4-$CH_2CH_2C_6H_4OMe)_2(O^{\wedge}O$-acac) (**4a**-$H_2$) was formed from $[Ir(C^{\wedge}N$-ppy-4-$CH{=}CHC_6H_4OMe)_2]_2(\mu\text{-}Cl)_2$ (**3a**) at 140 °C, whereas at 80 °C the parent unsaturated complexes $Ir(C^{\wedge}N$-ppy-4-$CH{=}CHC_6H_4R)_2(O^{\wedge}O)$ [$O^{\wedge}O$ = acac, R = OMe (**4a**), NEt_2 (**4b**), H (**4c**), NO_2 (**4d**); $O^{\wedge}O$ = dpm, R = OMe (**5a**), NEt_2 (**5b**)] were isolated. The saturated complex **4a**-H_2 exhibits intense green emission with a 36 % quantum yield at 298 K. The styryl complexes **4a**–**4d**, **5a** and **5b** are very weakly emissive at 298 K, but show intense red luminescence in alcohol glass at 77 K. The amino- and nitro-substituted complexes **4b** and **4d** give low-energy emission (λ_{em} = 651 and 647 nm, respectively). The emissive states of these complexes are believed to possess predominant triplet intra-ligand charge-transfer (^{3}ILCT) and metal-to-ligand charge-transfer (^{3}MLCT) character, respectively.
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Introduction

There is a growing interest in the study and design of luminescent heavy-transition-metal complexes for their potential applications in optoelectronic devices such as light-emitting diodes (OLEDs) and luminescent probes for biomolecules.[1–3] Iridium complexes, homoleptic and heteroleptic, featuring cyclometallated phenylpyridine (ppy) ligands and relative derivatives have been extensively studied in recent years. The emission is believed to arise from a strong mixing between the MLCT and LC excited states. The colour of the emission depends highly on the choice of the cyclometallating ligand, and efforts are focused on the design and synthesis of new ligands for optimization of the luminescence properties.[4,5] In this context, we have started a research program on the luminescence properties of functionalized styryl Ir complexes in order to study the influence of the ligand modification on the photophysical properties of the resulting complexes. The synthesis of tris-chelate iridium(III) complexes is, in fact, very versatile; this requires drastic conditions and depends on the nature of the cyclometallating ligands used.[6] In a recent attempt to prepare tris-cyclometallated iridium(III)–styryl complexes *fac*-$Ir(C^{\wedge}N$-ppy-4-$CH{=}CHC_6H_4R)_3$ [R = OMe (**2a**), NEt_2 (**2b**)] by the classical route, that is, from the corresponding bis-cyclometallated chloro-bridged dimers **3a**,**3b** and 4-(donor-substituted-styryl)-2-phenylpyridines **1a**,**1b** in refluxing glycerol, we observed the unexpected formation of the fully saturated complexes **2**-H_2.[7a] To overcome this problem, an alternative smooth procedure was developed by direct functionalization of the tris-chelate-methyl complex *fac*-$Ir(C^{\wedge}N$-ppy-4-$Me)_3$. However, this very attractive "chemistry-on-the-complex" procedure was restricted to only donor-substituted styryl derivatives and did not allow the introduction of acceptor end groups.

We showed that extension of the ligand π-conjugation induces a strong redshift of the emission band of more than 100 nm relative to the unsubstituted complex $Ir(C^{\wedge}N$-ppy$)_3$ (in 77 K glass, **2a**-H_2 and **2a** emit at 496 and 616 nm, respectively). Moreover, the presence of a donor-acceptor D–A interaction by introducing a diethylamino group instead of a methoxy group leads to an additional redshift of 35 nm (λ_{em} = 651 nm for **2b** in 77 K glass). In order to rationalize the electronic effects of the styryl end group, we have directed our studies towards the corresponding neutral heteroleptic bis-cyclometallated complexes $Ir(C^{\wedge}N$-ppy-4-$CH{=}CHC_6H_4R)_2(O^{\wedge}O)$ containing different end groups from strong donors to strong acceptors (R = NEt_2, OMe, H, NO_2). Bis-cyclometallated species, where the third ligand $O^{\wedge}O$ is an anionic acetylacetonate (acac) or dipyvaloylme-

[a] Sciences Chimiques de Rennes, UMR 6626 CNRS – Université de Rennes 1,
Campus de Beaulieu, 35042 Rennes Cedex, France
E-mail: veronique.guerchais@univ-rennes1.fr
[b] Department of Biology and Chemistry, City University of Hong Kong,
Tat Chee Avenue, Kowloon, Hong Kong, P. R. China
E-mail: bhkenlo@cityu.edu.hk
[c] Groupe Matière Condensée, UMR 6626 CNRS – Université de Rennes 1,
Campus de Beaulieu, 35042 Rennes Cedex, France
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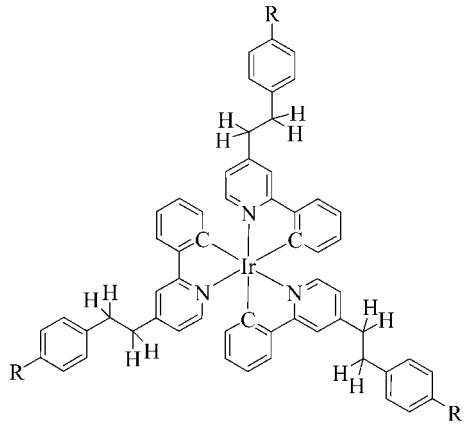
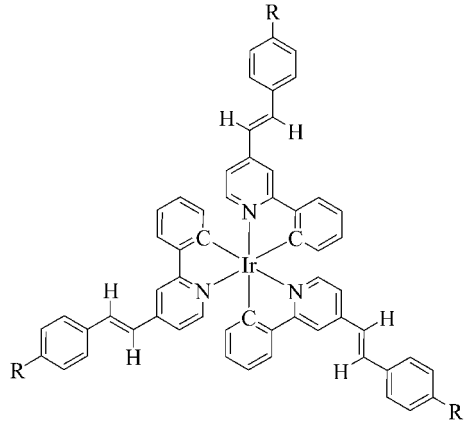


2a-H_2: R = OMe, **2b**-H_2: R = NEt_2



2a: R = OMe, **2b**: R = NEt_2

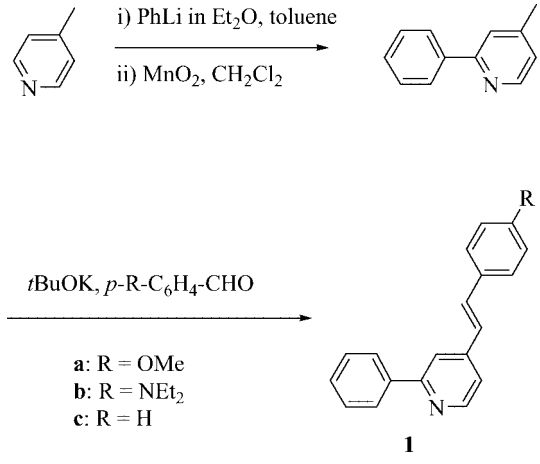
thane (dpm) ligand, are easily accessible whatever the nature of R. The photophysical properties of these neutral Ir(*C*^*N*-ppy)$_2$(*O*^*O*) derivatives have been shown to be very similar to those of the corresponding tris-cyclometallated species.[4] The hydrogenation reaction of the styryl C=C double bond observed during the course of the synthesis of tris-cyclometallated complexes is inhibited in this case, simply by lowering the reaction temperature.

We report here the synthesis and spectroscopic characterization of a new family of bis-cyclometallated iridium–styryl complexes and the saturated complex Ir(*C*^*N*-ppy-4-$CH_2CH_2C_6H_4OMe)_2$(*O*^*O*-acac) (**4a**-H_2); the effects of the styryl substituent R on their photophysical properties will be discussed. The synthesis and X-ray crystal structures of the free ligands will also be described.

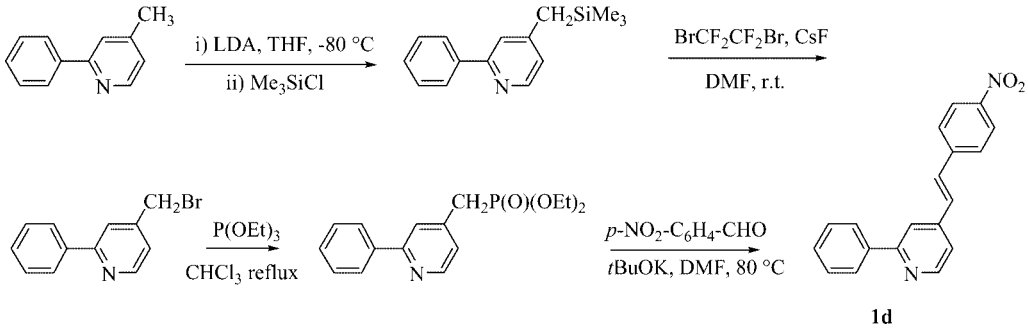
Results and Discussion

Synthesis of the Ligands

The donor-substituted phenylpyridine derivatives, the methoxy-, diethylamino- and non-substituted 4-styryl-2-phenylpyridine derivatives (ppy-4-CH=CHC_6H_4R) [R = OMe (**1a**), NEt_2 (**1b**), H (**1c**)], were obtained from 4-picoline in a two-step procedure. The first step was the phenylation at the α position, upon addition of PhLi followed by oxidation with MnO_2.[8] Then deprotonation of the methyl group with *t*BuOK and condensation with the appropriate aldehyde *p*-R-C_6H_4-CHO (R = OMe, NEt_2, H) afforded, by in situ dehydration, the expected unsaturated derivatives **1** (Scheme 1). Compounds **1a**–**1c** were purified by crystallization from a mixture of toluene/pentane and were isolated in 86, 96 and 34% yield, respectively, from ppy-4-Me (4-methyl-2-phenylpyridine). In all cases, the *E* configuration of the C=C double bond was confirmed by the presence of an AB system with a characteristic $^3J_{H–H}$ coupling of 16 Hz. We did not observe any photoisomerization process $E \rightarrow Z$ in acidic medium or under sunlight (vide infra).



Scheme 1.



Scheme 2.

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The described procedure cannot be applied to benzaldehyde featuring an electron-withdrawing group.[9] The nitro derivative **1d** was prepared by a different procedure (Scheme 2). This synthesis involved a Wadsworth–Emmons reaction between the (diethylphosphoryl)methyl-2-phenylpyridine and *p*-nitrobenzaldehyde. The phosphonate derivative was prepared in a two-step procedure, following the method described for 2,2′-bipyridines.[10–12] The first step was the deprotonation of the methyl precursor ppy-4-Me and subsequent addition of TMSCl to give 4-(trimethylsilylmethyl)-2-phenylpyridine; the latter was then converted into the 4-(bromomethyl)-2-phenylpyridine, and eventually the phosphonate derivative was formed by means of an Arbuzov reaction. Compound **1d** was isolated in an overall yield of 33%. The *E* configuration was ascertained by the presence of the AB system which appears at δ = 7.42 (^3J = 16 Hz) and 7.28 ppm.

X-ray Crystal Studies of 1a, 1b and 1d

The styryl derivatives **1a**, **1b** and **1d** were characterized by X-ray diffraction studies (Figures 1, 2 and 3, respectively). Crystals were obtained by slow diffusion of pentane in toluene solutions of **1a**, **1b** and **1d**. Selected distances and angles are listed in Table 1. Derivatives **1a**, **1b** and **1d** crystallized as dimers. The two molecules are almost identical, except in the case of **1b** for which the conformation about the C12–C9 bond is different; *s-cis* and *s-trans* isomers (C12–C13 and C9–C10) are observed. In all compounds, the *E* configuration of the C=C double bond of the styryl group is confirmed; the C12–C13 bond length in **1a** and **1d** is characteristic of a double bond and compares well with that of the bipyridine analogues.[9] In contrast, the C12–C13 distance in **1b** is significantly shorter, probably because of the crystal packing. In the *s-trans* isomer, the

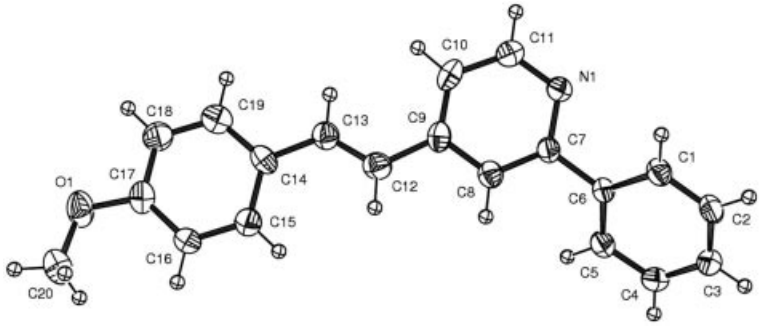

Figure 1. ORTEP drawing of **1a**.

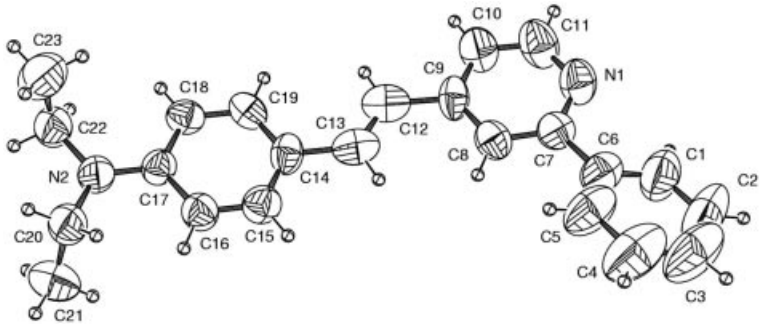

Figure 2. ORTEP drawing of **1b**. Only the *s-cis* isomer is shown for clarity.

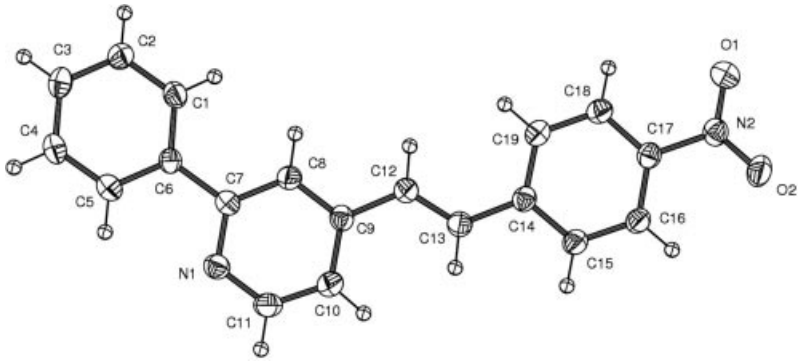

Figure 3. ORTEP drawing of **1d**.

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phenyl group is tilted relative to the adjacent pyridine ring (dihedral angle N1–C7–C6–C1 –25.35°), whereas the planarity is better for the *s-cis* isomer (dihedral angle 3.63°). The styryl group is almost coplanar with the nitrogen ring in the former isomer, whereas the deviation is about 20° in the latter isomer.

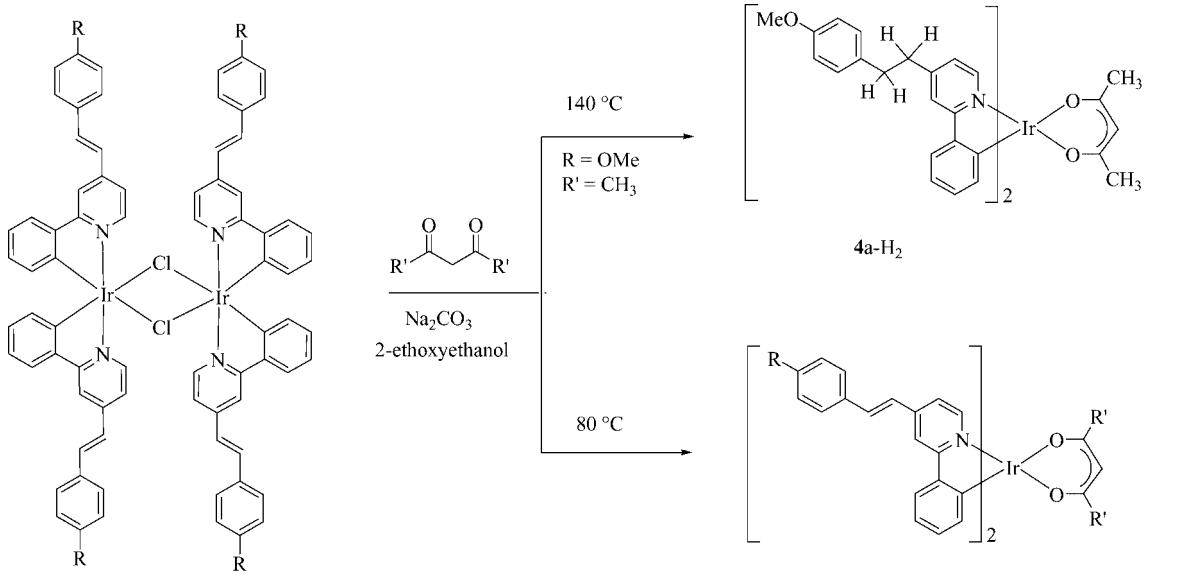
Table 1. Selected bond lengths [Å] and angles [°] for **1a**, **1b** and **1d**.

Compound	**1a**	**1b** (*s-trans*)	**1b** (*s-cis*)	**1d**
C12–C13	1.328(7)	1.260(5)	1.285(5)	1.340(3)
C13–C14	1.453(6)	1.522(6)	1.468(6)	1.463(3)
C9–C12	1.497(6)	1.509(6)	1.505(6)	1.474(3)
N1–C7	1.353(6)	1.338(5)	1.329(5)	1.350(3)
C6–C7	1.489(6)	1.451(6)	1.474(6)	1.492(3)
C7–C8	1.389(6)	1.390(5)	1.374(5)	1.397(3)
C12–C13–C14	127.9(5)	128.6(5)	128.4(5)	126.6(2)
C9–C12–C13	123.6(4)	125.6(5)	126.1(5)	125.0(2)
N1–C7–C6	116.0(4)	115.9(5)	116.8(5)	116.2(2)
C7–C6–C1	119.3(4)	120.8(6)	121.3(6)	121.9(2)
C11–N1–C7	115.5(4)	117.3(4)	117.5(4)	116.8(2)

Synthesis of the Metal Complexes

The precursor dimers $[Ir(C^{\wedge}N\text{-ppy-4-CH=CHC}_6H_4R)_2]_2(\mu\text{-Cl})_2$ [R = OMe (**3a**), NEt_2 (**3b**), H (**3c**), NO_2 (**3d**)] were prepared following classical procedures starting from $IrCl_3{\cdot}nH_2O$ (140 °C).[13,14] For comparison, we also prepared the methyl complex $[Ir(C^{\wedge}N\text{-ppy-4-Me})_2]_2(\mu\text{-Cl})_2$ (**3e**).[15] Compounds **3a**–**3d** were isolated as orange powders and **3e** as a yellow powder. They are sparingly soluble in CH_2Cl_2. The NO_2-derivative **3d** is too insoluble in CD_2Cl_2 to be characterized by ^1H NMR spectroscopy, but dissolution in DMSO gives rise to the formation of the DMSO adduct $[Ir(C^{\wedge}N\text{-ppy-4-CH=CHC}_6H_4NO_2)_2(DMSO)(Cl)]$ (**3d**-DMSO). Such solvation by strong coordinating solvents (H_2O, CH_3CN, DMF) has been already reported; the reaction products were not isolated because of re-formation of the corresponding chloro-bridged dimer.[16] The ^1H NMR spectrum of the DMSO adduct **3d**-DMSO shows two different sets of signals for the magnetically nonequivalent C^N ligands. For instance, two pyridine signals (py^6) are observed at low field at δ = 9.82 and 9.50 ppm. The ^1H NMR spectra of crude **3a**–**3c** show the presence of only one set of signals which is attributed to the racemic mixture ($\Delta\Delta/\Lambda\Lambda$) as indicated by a characteristic low-field doublet at δ = 9.15 ppm (**3a**) for the pyridine proton in the 6-position. The *E* ($^3J_{H-H}$ = 16 Hz) configuration of the double bond of the styryl group of **3** was maintained during the synthesis. Exposure of the CD_2Cl_2 solutions of **3a**–**3c** to sunlight for a few hours, however, resulted in the appearance of new aromatic signals. Several doublets from δ = 9.28 ppm to δ = 9.04 ppm were then observed for the proton H^6 of the pyridine ring of **3a**. We assume that *trans*/*cis* isomerization of the C=C double bond occurs under these conditions (vide infra).

Dimers were then converted upon cleavage of the chloro bridges with bidentate ligands, such as 1,3-diketonates, into mononuclear complexes. We used acetylacetone (acacH) and dipivaloylmethane (dpmH). Treatment of **3a** with acacH and Na_2CO_3 in 2-ethoxyethanol at 140 °C led to the formation of the bis-cyclometallated complex **4a**-H_2, in which the C=C double bonds of the styryl groups were hydrogenated (Scheme 3). Moreover, the free hydrogenated ligand $HC^{\wedge}N\text{-}H_2$ **1a**-H_2 was also isolated. Compound **4a**-H_2 was obtained as a yellow powder, and its structure was confirmed by ^1H- and ^{13}C NMR spectroscopy and elemental analysis. The methylene protons appear as multiplets at



Scheme 3. Synthesis of the bis-cyclometallated complexes: influence of the reaction temperature.

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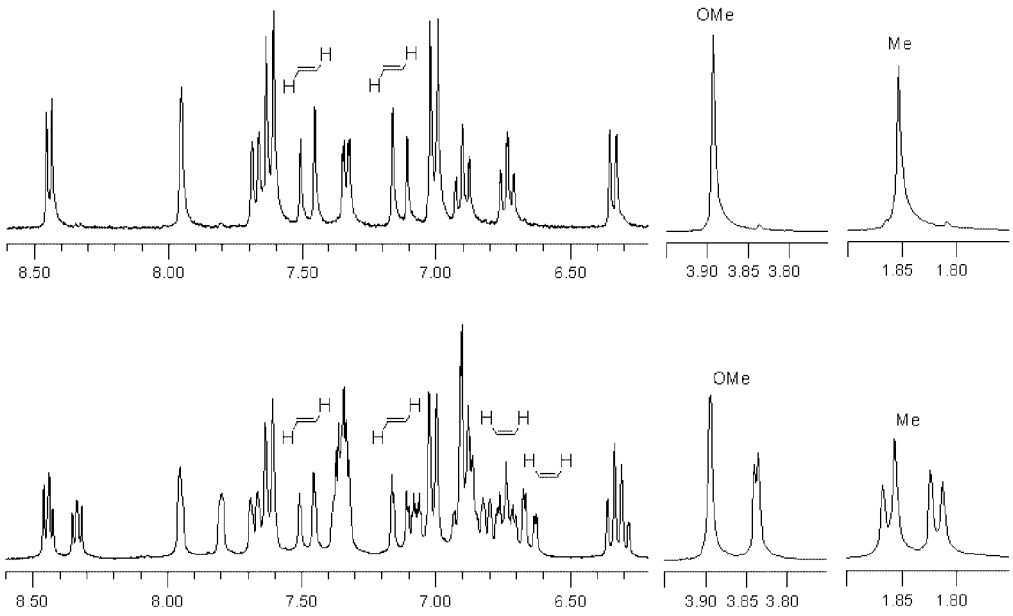
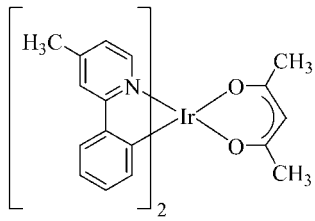


Figure 4. NMR spectra (δ values given in ppm) of **4a**: before (top) and after (bottom) exposure for one hour in the sunlight.

δ = 3.14 ppm (δ = ^{13}C 37.5 ppm) and 3.07 ppm (δ = ^{13}C 35.7 ppm). Such a hydrogenation reaction could be mediated by Ir species which are known to catalyse hydrogen transfer reductions.[17] This feature was also observed in the attempted synthesis of the parent tris-cyclometallated styryl species **2**. Since the saturated derivative Ir(*C*^*N*-ppy-$CH_2CH_2C_6H_4OMe)_3$ was formed, an alternative synthesis involving functionalization after complexation was developed.[7a] It is likely that the drastic conditions used for the synthesis of Ir complexes, the presence of an alcohol (hydrogen donor) and a base all favour this process. It is noteworthy that the dimers **3** were not hydrogenated since no base was present in the reaction medium.

Concerning the bis-cyclometallated mononuclear species (the oxygenated derivatives **4** and **5**), side hydrogenation reactions could be avoided by performing the syntheses at lower temperature, namely 80 °C instead of 140 °C. Selective formation of the styryl complexes Ir(*C*^*N*-ppy-4-$CH=CHC_6H_4R)_2$(*O*^*O*) [O^O = acac, R = OMe (**4a**), NEt_2 (**4b**), H (**4c**), NO_2 (**4d**); O^O = dpm, R = OMe (**5a**), NEt_2 (**5b**)] can occur at this reaction temperature (Scheme 3). Compounds were isolated in excellent yield (ca. 90%) as red-brown powders. Similarly, the saturated complex Ir(*C*^*N*-ppy-4-Me)$_2$(*O*^*O*-acac) (**4e**) was isolated as a yellow compound. The cleavage of the dimers occurred with retention of the configuration, that is, the resulting products **4a**–**4d**, **5a** and **5b** have C_2 symmetry.

We note that the aromatic regions of the ^{1}H NMR spectra of **4** and **5** are similar to those of dimers **3**; the aromatic signals appear in the same order. For example, the lowest field signal ($\delta \approx$ 8.30 ppm) is assigned to the proton in the α position of the nitrogen atom of the pyridine ring as a characteristic signature, in contrast to that of the tris-chelate species, which is due to the pyridine proton H^3. Upon exposure of CH_2Cl_2 solutions to sunlight, the complexes



4e

4a–**4c**, **5a** and **5b**, like the dimer precursors, undergo partial isomerization of the C=C double bond leading to the formation of three isomers (*E*/*E*, *E*/*Z*, *Z*/*Z*). For instance, the ^{1}H NMR spectra display two sets of signals for vinylic protons of the *cis*-alkenyl group of the *E*/*Z* and *Z*/*Z* isomers of **4a**; one signal is located at δ = 6.65 ppm ($^3J_{H-H}$ = 12 Hz, the second doublet is masked), and the second set is found at δ = 7.49 and 7.14 ppm, as the result of the splitting of the former AB system of the *E*/*E* isomer (Figure 4). It is noteworthy that the NO_2 derivative **4d** was not prone to isomerization under such conditions; no change was observed by ^{1}H NMR spectroscopy.

Absorption and Emission Properties of the Ligands and Complexes

The photophysical data of the free ligands **1a**–**1d** in CH_2Cl_2 solutions at 298 K are presented in Table 2. Compounds **1a**, **1c** and **1d** display an intense absorption band between 290–390 nm that is assigned to a ligand-centred (^{1}LC) ($\pi \rightarrow \pi^*$) transition (Figure 5). The strong absorption bands of compounds **1c** and **1d** are comparable to those of their non-phenylated counterparts, namely styrylpyridine and (*p*-nitrostyryl)pyridine [292 nm (31300 $M^{-1}cm^{-1}$) and

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Table 2. Absorption and emission spectroscopic data of ppy-4-CH=CHC$_6$H$_4$R (**1**) in CH_2Cl_2 at 298 K.

	R	λ_{max}/nm (ε/M^{-1}cm^{-1})	λ_{em}/nm	Φ[a]
1a	OMe	264 (16000), 309 sh (23000), 310 sh (23000), 327 (29000)	404	0.008
1b	NEt_2	251 (27000), 277 sh (18000), 335 (9400), 382 (17000)	487	0.078
1c	H	262 (24000), 312 (33000), 328 sh (20000)	364	–
1d	NO_2	257 (25000), 335 (33000)	–	–

[a] Emission quantum yields were determined using quinine sulfate as the standard.

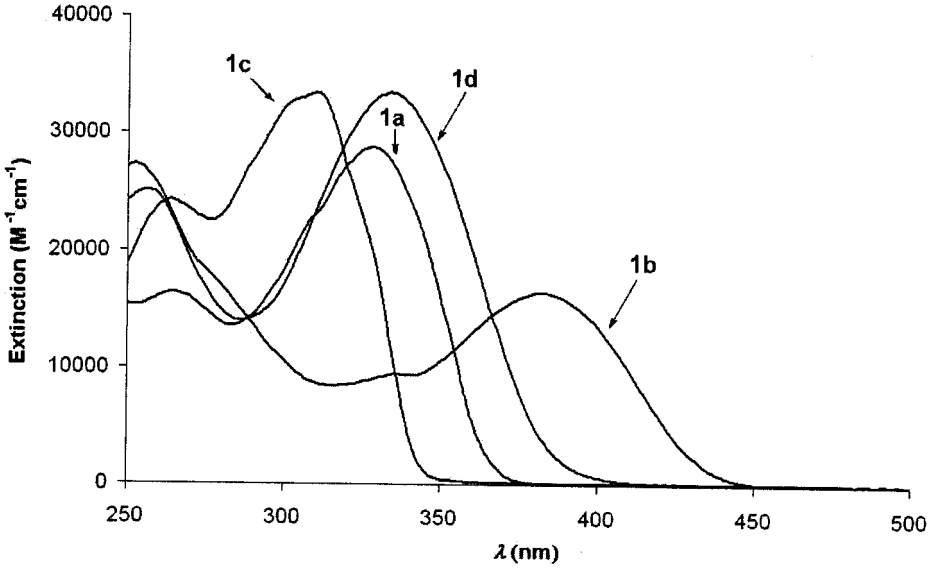

Figure 5. Absorption spectra of ppy-4-CH=CHC$_6$H$_4$R **1a**–**d** in CH_2Cl_2 solutions at 298 K.

332 nm (30875 M^{-1}cm^{-1}) in CH_3CN, respectively].[18] Interestingly, the absorption spectrum of the amino-styryl ligand **1b** shows a strong band at 382 nm (17000 M^{-1}cm^{-1}) which can be assigned to an intra-ligand charge-transfer (^{1}ILCT) transition from the electron-donating amino group to the electron-accepting pyridine ring via the π-linker styryl group. This intense and structureless band is typical for "push-pull" molecules and compares well with that found for the related bipyridine derivative bpy-4-styryl-NEt_2, for which absorption maximum occurs at 394 nm in CH_3CN.[19]

Compounds **1a**–**1c** are fluorescent upon photoexcitation. The emission colour of the compounds in CH_2Cl_2 at 298 K ranges from blue to green (Figure 6), depending on the identity of the substituent R. The emission energy decreases in the order **1c** (364 nm) > **1a** (404 nm) > **1b** (487 nm),

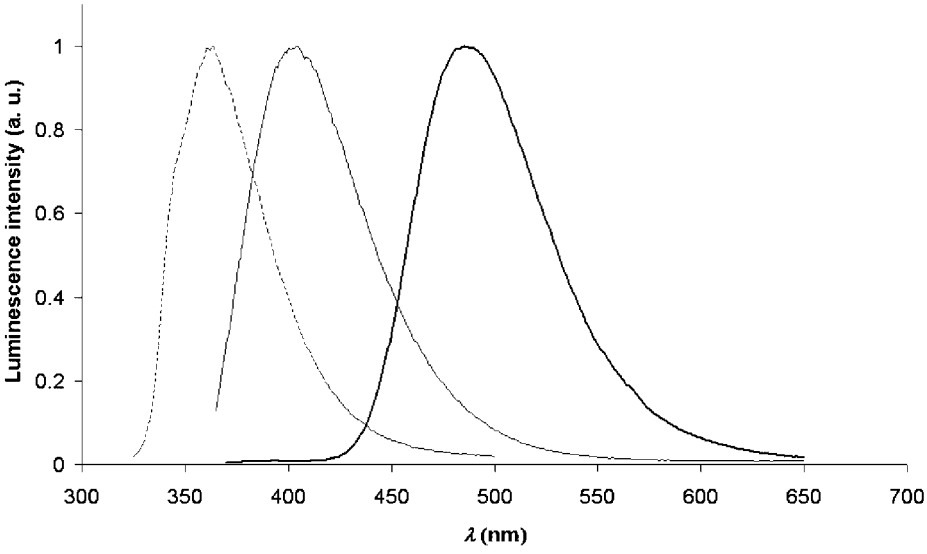

Figure 6. Normalized emission spectra of ppy-4-CH=CHC$_6$H$_4$R **1a** (−), **1b** (−) and **1c** (---) in CH_2Cl_2 solutions at 298 K.

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which is consistent with the electron-donating ability of the substituent R. Compound **1d** is non-emissive. The observation of a positive solvatochromic shift on the emission band of **1b** in solvents ranging from toluene to DMSO, is in agreement with a charge-transfer emissive state (Table 3, Figure 7). The emission quantum yields for **1a** and **1b** are comparable to those reported for the bpy-styryl-4-R derivatives (R = NBu_2, 3.6%;[19] R = OOct, 1%).[9]

Table 3. Absorption and emission wavelengths of **1b** in various solvents at 298 K.

Solvent	λ_{abs}/nm	λ_{em}/nm
Toluene	383	457
Acetone	384	495
CH_2Cl_2	382	488
Ethanol	386	510
DMSO	395	517

The absorption spectra of the dimers **3a**–**3d** show intense bands between 250–350 nm (Table 4), which are assigned to ^{1}LC ($\pi\rightarrow\pi^*$) transitions of the cyclometallated ligands. The characteristic ^{1}ILCT absorption band of **3b** occurs at 431 nm. The redshift of 48 nm compared to the absorption band of the free ligand is ascribed to the increased electron-accepting properties of the pyridine ring after its coordination to the iridium(III) centre. A similar shift was observed for related $[M(bpy\text{-}4\text{-}CH{=}CHC_6H_4R)_3]^{2+}$ complexes.[20] Moderately intense bands are present in the lower energy region (450–550 nm). The absorption bands of **3c** at 467 nm and **3d** at 500 nm are tentatively assigned to an admixture of ^{1}MLCT/^{3}MLCT transitions. The nitro group of **3d** significantly shifts the MLCT absorption band to lower energy (500 nm), compared with that of the styryl derivative **3c** (467 nm). The shift is attributed to the strong electron-accepting properties of the nitro substituent, which substantially lower the LUMO of the complex.[7b] The MLCT transition of **3b** is not clearly resolved and is probably embedded in the intense and broad ILCT band.

The absorption spectra of the bis-cyclometallated acac (**4a**–**4d**) and dpm (**5a** and **5b**) complexes closely resemble those of the corresponding dimers. The absorption features originate mainly from the $Ir(C^{\wedge}N)_2$ moieties (Figure 8,

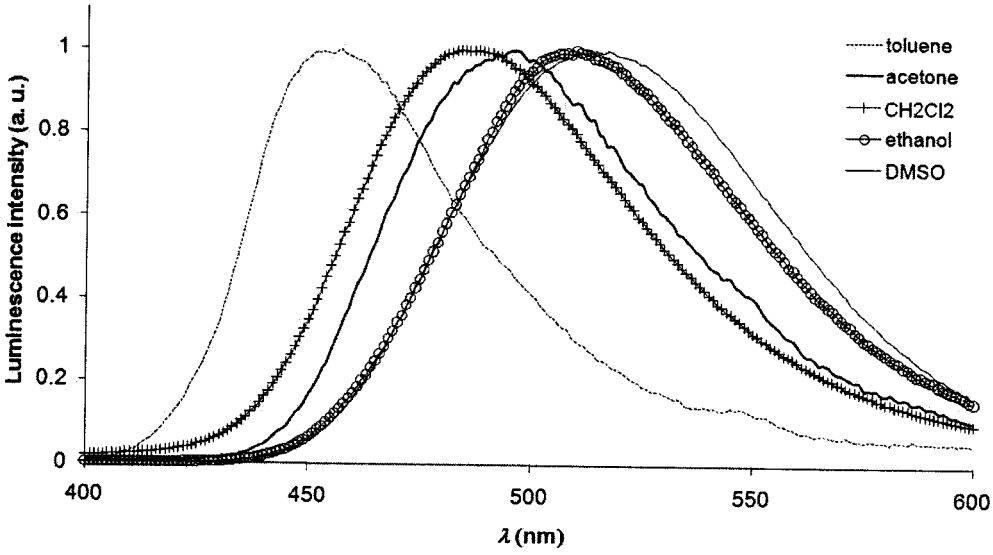

Figure 7. Emission spectra of ppy-4-CH=$CHC_6H_4NEt_2$ (**1b**) in different solvents in fluid solutions at 298 K.

Table 4. Photophysical data for the styryl-containing complexes.

	R	λ_{abs}/nm (ε/M^{-1} cm^{-1})[a]	λ_{em}/nm[b]	τ_o/μs[b]
$[Ir(C^{\wedge}N\text{-ppy-4-CH}{=}CHC_6H_4R)_2]_2(\mu\text{-Cl})_2$ (**3a**–**3d**)				
3a	OMe	256, 303, 328, 374, 407 sh, 455	611 (max.), 674, 744 sh	5.0
3b	NEt_2	261, 293, 404 sh, 431, 473 sh	651 (max.), 713, 796 sh	20.4
3c	H	271, 311, 371, 411 sh, 467	605 (max.), 664, 729 sh	2.9
3d	NO_2	262, 331, 392 sh, 432 sh, 500, 552 sh	639, 660 (max.), 727 sh	1.0
$Ir(C^{\wedge}N\text{-ppy-4-CH}{=}CHC_6H_4R)_2(O^{\wedge}O)$ (**4a**–**4d**, **5a**, **5b**)				
4a	OMe	270 (62000), 330 (45000), 373 (39000), 415 sh (21000), 475 (5300)	613 (max.), 673, 740 sh	4.6
5a	OMe	266 (62000), 327 (48000), 377 (39000), 418 sh (21000), 476 (7200)	616 (max.), 676, 759 sh	2.9
4b	NEt_2	265 (40000), 410 (23000), 433 (26000), 480 sh (5500)	651 (max.), 715	12.1
5b	NEt_2	263 (35000), 412 (38000), 438 (42000), 482 sh (8500)	651 (max.), 717	9.1
4c	H	268 (44000), 306 (45000), 370 (25000), 410 sh (12000), 468 (4700)	609 (max.), 667, 734 sh	2.2
4d	NO_2	263 (38000), 282 (36000), 332 (48000), 400 (33000), 442 sh (18000), 518 (5200)	647 (max.), 705, 788 sh	1.0

[a] In CH_2Cl_2 at 298 K (the extinction coefficients for complexes **3a**–**3d** could not be determined with accuracy because of the low solubility of the complexes). [b] In CH_2Cl_2/EtOH/MeOH (1:4:1, v/v/v) at 77 K.

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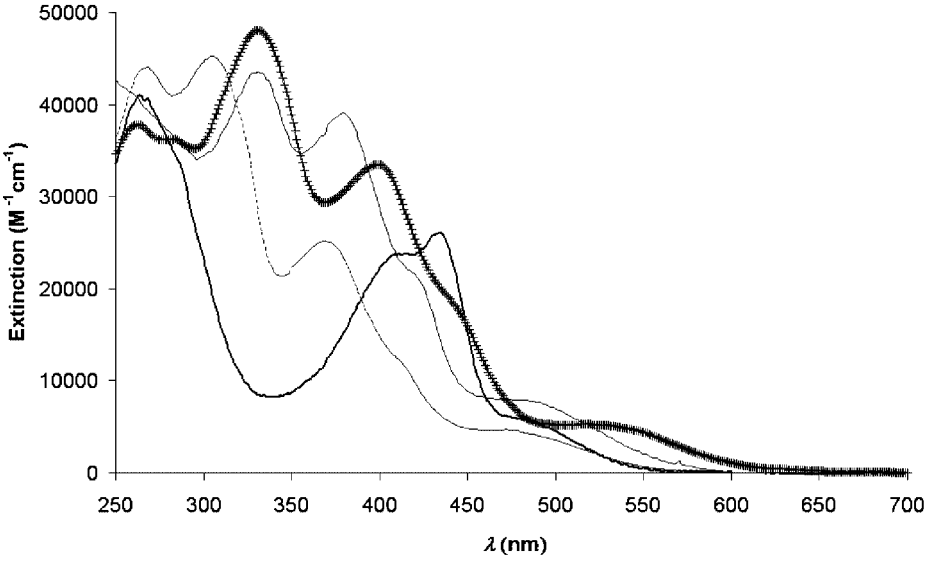

Figure 8. Absorption spectra of **4a** (−), **4b** (−), **4c** (---) and **4d** (+++) in 2-Me-THF solutions at 298 K.

Table 4). For example, the ligand-centred bands of **4a** (373 nm) and **4b** (433 nm) are comparable to that of their respective dimeric precursors **3a** and **3b**. The dpm complexes **5a** and **5b** display similar absorption features. Analogous findings were observed for the related complexes Ir($C^{\wedge}N$)$_2$($O^{\wedge}O$).[4a,4b]

The saturated complex **4a**-H_2 exhibits a strong LC absorption band at 337 nm (Table 5, Figure 9). Since no ILCT band is present, the ^{1}MLCT and mixed ^{1}MLCT/^{3}MLCT transitions are observed at 403, 460 and 485 nm, respectively, with tailings extended to 500 nm. The singlet and triplet MLCT bands for Ir($C^{\wedge}N$-ppy)$_2$($O^{\wedge}O$-acac) were

Table 5. Photophysical data for the alkyl-substituted complexes **3e**, **4e** and **4a**-H_2.

	λ_{abs}/nm (ε/M^{-1} cm^{-1})[a]	T/K	λ_{em}/nm	Φ	τ_o/μs
3e	262 (62000), 330 (12000), 400 (6300), 450 (3700), 480 (950)	298[a]	507 (max), 534 sh, 590 sh	0.0039[c]	0.7
		77[b]	494 (max), 531, 572 sh	–	4.4
4e	261 (37000), 336 (9200), 400 sh (4100), 450 sh (2600), 483 sh (900)	298[a]	511, 544 sh	0.51[d]	1.4
		77[b]	497 (max), 534, 577 sh	–	4.7
4a-H_2	265 (40000), 337 (11000), 403 sh (4900), 460 sh (3000), 485 sh (1500)	298[a]	516, 549 sh	0.36[d]	1.3
		77[b]	496 (max), 531, 579 sh	–	3.8

[a] CH_2Cl_2. [b] CH_2Cl_2/EtOH/MeOH (1:4:1, v/v/v). [c] $[Ru(bpy)_3]^{2+}$ was used as the standard. [d] Quinine sulfate was used as the standard.

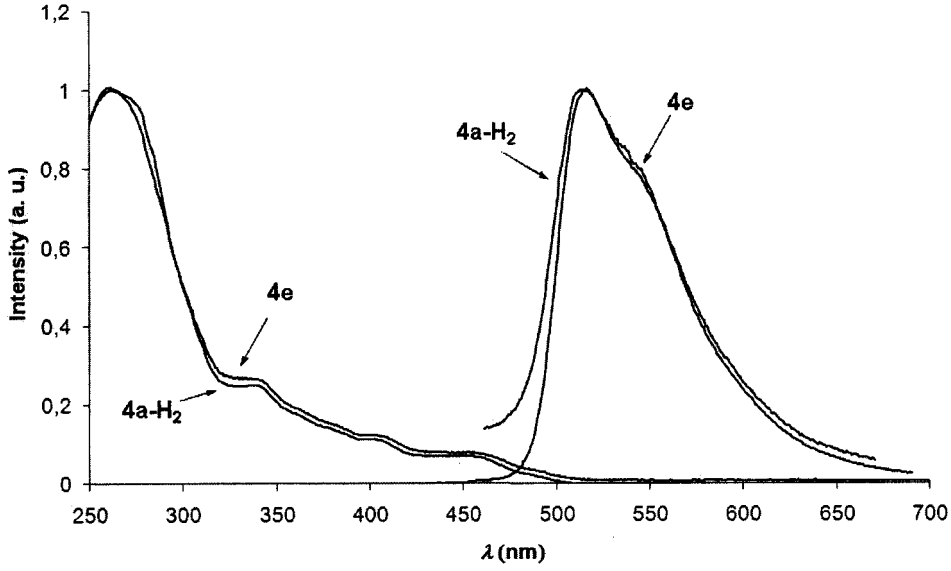

Figure 9. Absorption and emission spectra of **4e** and **4a**-H_2 in CH_2Cl_2 solutions at 298 K.

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found at 412, 460 and 490 nm, respectively. Thus, addition of the alkyl group $CH_2CH_2C_6H_4OMe$ to the ppy ligand causes no significant changes.[4a]

Upon excitation, complex **4a**-H_2 in CH_2Cl_2 solution at 298 K shows strong green emission (Figure 9, Table 5). The emission properties of this complex are very similar to those of the dimethyl complexes $Ir(dmppy)_3$[15] and $Ir(dmppy)_2(acac)$[21] [Hdmppy = 4-methyl-2-(4-methylphenyl)pyridine]. The presence of a methyl or an alkyl group such as CH_2CH_2-C_6H_4OMe in the *para* position of the pyridine ring brings no significant effects to the photophysical properties of these types of complexes. The emission of **4a**-H_2 is assigned to a state of an admixture of ^{3}MLCT and ^{3}LC character.[4a,22]

The emission data for complexes **3a**–**3d**, **4a**–**4d**, **5a** and **5b** are summarized in Table 4. All the styryl complexes show very weak emission in fluid solutions at room temperature (Figure 10).[7] In alcohol glass at 77 K, they become strongly emissive. The emission bands of the complexes show rich vibronic structures with progressional spacings of ca. 1400 cm^{-1}, typical of C=C aromatic stretching. The emission behaviour of the complexes depends strongly on the cyclometallating ligands, whereas the ancillary ligands acac and dpm O^O or the chloro bridge play a minor role. For these reasons, only the emission properties of the acac complexes **4a**–**4d** are discussed.

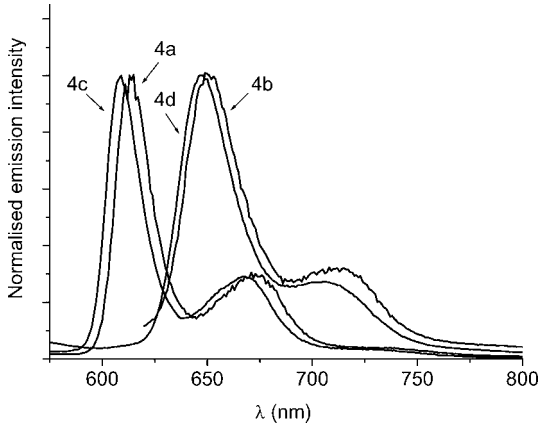

Figure 10. Emission spectra of complexes **4a**–**4d** in CH_2Cl_2/EtOH/MeOH (1:4:1, v/v/v) at 77 K.

At 77 K, complexes **4a**–**4d** emit in the red region from 609 to 788 nm with a lifetime in the microsecond timescale. As expected, increasing the π-conjugation of the C^N ligand induces a bathochromic shift of the emission band; for example, the emission of $Ir(C^N\text{-ppy})_2(O^O\text{-acac})$ shifts from 516 to 548 nm when benzoquinoline is used as the C^N ligand.[4a,4b] In this work, a shift from green to red emission is observed after the addition of a styryl group to the ppy ligand. The emission energy difference is significant [$Ir(C^N\text{-ppy})_2(O^O\text{-acac})$ in 77 K glass, λ_{em} = 492 nm; for **4c**, λ_{em} = 609 nm]. This is also in line with the data observed for the saturated complex **4a**-H_2; breaking the conjugation of the styryl group gives rise to green emission. Substitution of the hydrogen atom in **4c** by a methoxy end group has no marked effects on the emission maximum. In both cases, the emission is believed to arise from an admixture of ^{3}MLCT and ^{3}IL states. In contrast, substitution by an amino group induces a redshift to 651 nm in **4b**. It is likely that the presence of an amino group results in ^{3}ILCT character in the emissive states of **4b** and **5b**. The nitro-derivative **4d** also gives low-energy emission (λ_{em} = 647 nm). Owing to the strong electron-accepting properties of the nitro substituent, the emissive state of complex **4d** should possess predominantly ^{3}MLCT character, resulting from the stabilization of the π*-acceptor orbitals of the C^N ligand.[7]

Conclusions

A new family of bis-cyclometallated iridium(III)–styryl complexes were prepared. Reduction of the C=C double bond can be avoided by performing the synthesis under mild reaction conditions. Low-temperature glass of all the styryl complexes **4a**–**4d**, **5a** and **5b** gives intense red emission upon photoexcitation. Compared with the unmodified $[Ir(C^N\text{-ppy})_2(O^O)]$ complexes, large bathochromic shifts in emission energy were achieved by adding a conjugated styryl group to the ppy ligand and by introducing a strong electron-withdrawing nitro group. Incorporation of a diethylamino substituent into the cyclometallating ligand leads to a switch of emissive-state character from ^{3}MLCT to ^{3}ILCT, resulting in increased emission lifetimes. We anticipate that these luminescent iridium(III) complexes can act as interesting building blocks for luminescent macromolecular architectures.

Experimental Section

All manipulations were performed using Schlenk techniques under argon. All solvents were dried and purified by standard procedures. All starting materials were used as received. NMR spectra were recorded with Bruker DPX-200, AV 300 or AV 500 MHz spectrometers. ^{1}H and ^{13}C chemical shifts are given versus $SiMe_4$ and were determined by reference to residual ^{1}H and ^{13}C solvent signals. ^{31}P chemical shifts are given versus ext. H_3PO_4 (85%). Attribution of carbon atoms was based on HMBC, HMQC and COSY experiments. UV/Vis absorption spectra were recorded using a UVIKON 9413 spectrophotometer, and emission spectra were measured with a PTI C 60 fluorescence spectrophotometer. High resolution mass spectra (HRMS) were performed using a MS/MS ZABSpec TOF at the CRMPO (Centre de Mesures Physiques de l'Ouest) in Rennes. Elemental analyses were performed by the Service central d'analyse du CNRS at Vernaison. Cyclic voltammograms were recorded using a PAR model 273 Autolab. The working electrode was polished Pt, the counter electrode was a Pt wire, and a saturated calomel electrode (SCE) was used as the reference electrode. The Cp_2Fe/Cp_2Fe^+ redox couple was used as a secondary internal reference.

Luminescence quantum yields were measured by the optically dilute method[23] using an aerated aqueous solution of $[Ru(bpy)_3]Cl_2$ (Φ_{em} = 0.028) or quinine sulfate in 1 N H_2SO_4 as the standard solutions.[24] Low-temperature (77 K) glass photophysical measurements were performed with the sample loaded in a quartz tube inside a quartz-walled Dewar flask filled with liquid nitrogen. The

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excitation source for emission lifetime measurements was the 355 nm output (third harmonic) of a Quanta-Ray Q-switched GCR-150–10 pulsed Nd-YAG laser. Luminescence decay signals from a Hamamatsu R928 photomultiplier tube were converted to potential changes by a 50 Ω load resistor and then recorded with a Tektronix Model TDS 620A digital oscilloscope.

Synthesis of 4-Methyl-2-phenylpyridine: To a solution of 4-methylpyridine (5 g, 53.8 mmol) in toluene (70 mL) was added a freshly prepared solution of PhLi in Et_2O (70 mL) [from PhBr (22.6 mL, 215 mmol) and Li metal (2.98 g, 430 mmol)]. After 24 h of stirring, the solution was hydrolysed with water (150 mL), and the compound was extracted with CH_2Cl_2 (3 × 200 mL). The organic phase was dried with $MgSO_4$, and MnO_2 (56 g, 645 mmol) was added. The solution was stirred for 3 h, filtered and the solvent was evaporated. Chromatography on silica gel using heptane/ethyl acetate (90:10) gave ppy-4-Me as orange crystals. Yield 4.57 g (50%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.55 (d, ^3J = 4.8 Hz, 1 H, py^6), 7.98 (m, 2 H, Ph *ortho*), 7.55 (d, ^4J = 1 Hz, 1 H, py^3), 7.43 (m, 3 H, Ph *meta* and *para*), 7.05 (dd, ^3J = 4.8 Hz, ^4J = 1 Hz, 1 H, py^5), 2.41 (s, 3 H, CH_3) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 157.2 (C^4-py), 149.4 (C^6-py), 147.7 (C^2-py), 139.5 (Ph *ipso*), 128.8 (Ph *para*), 128.7 (Ph *meta*), 126.9 (Ph *ortho*), 123.1 (C^5-py), 121.1 (C^3-py), 21.1 (CH_3) ppm. HRMS: calcd. for $C_{12}H_{11}N$ [M]$^+$ 169.0892; found 169.0885.

Synthesis of Pyridines 1a–1c: 4-Methyl-2-phenylpyridine (0.5 g, 2.96 mmol), the appropriate aldehyde [4-methoxybenzaldehyde, 4-(diethylamino)benzaldehyde or benzaldehyde (3.5 mmol)] and *t*BuOK (0.4 g, 3.5 mmol) were dissolved in DMF (20 mL). The reaction mixture was refluxed for 3 h, and then CH_2Cl_2 (150 mL) was added. The organic phase was washed with water and an aqueous solution of 1 M KOH, and dried with $MgSO_4$. The product was crystallized from a toluene/pentane mixture.

4-(4-Methoxystyryl)-2-phenylpyridine (1a): White powder. Yield 0.73 g (86%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.66 (d, ^3J = 5 Hz, 1 H, py^6), 8.07 (m, 2 H, Ph *ortho*), 7.77 (s, 1 H, py^3), 7.53 (m, 4 H, C_6H_4 and Ph *meta*), 7.47 (m, 1 H, Ph *para*), 7.31 (m, 2 H, =CH and py^5), 6.96 (m, 3 H, =CH and C_6H_4), 3.85 (s, 3 H, OCH_3) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 160.2 (C^1-C_6H_4), 158.0 (C^2-py), 150.0 (C^6-py), 145.8 (C^4-py), 139.6 (Ph *ipso*), 132.6 (=CH), 129.0 (Ph *para*, C^4-C_6H_4), 128.8 (Ph *meta*), 128.5 (C^3-C_6H_4), 127.0 (Ph *ortho*), 124.0 (=CH), 119.0 (C^5-py), 117.9 (C^3-py), 114.3 (C^2-C_6H_4), 55.4 (OCH_3) ppm. HRMS: calcd. for $C_{20}H_{17}NO$ [M]$^+$ 287.1310; found 287.1307. $C_{20}H_{17}NO$ (287.36): calcd. C 83.60, H 5.96, N 4.87, O 5.57; found C 83.22, H 5.85, N 4.87, O 5.76.

4-[*p*-(Diethylamino)styryl]-2-phenylpyridine (1b): Yellow powder. Yield 0.93 g (96%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.64 (d, ^3J = 5.1 Hz, 1 H, py^6), 8.09 (m, 2 H, Ph *ortho*), 7.78 (s, 1 H, py^3), 7.54 (m, 2 H, Ph *meta*), 7.48 (m, 3 H, C_6H_4 and Ph *para*), 7.33 (d, ^3J = 16.2 Hz, 1 H, =CH), 7.30 (d, ^3J = 5.1 Hz, 1 H, py^5), 6.89 (d, ^3J = 16.2 Hz, 1 H, =CH), 6.71 (d, ^3J = 8.8 Hz, 2 H, C_6H_4), 3.42 (q, ^3J = 7.1 Hz, 4 H, CH_2), 1.23 (t, ^3J = 7.1 Hz, 6 H, CH_3) ppm. ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ = 157.5 (C^2-py), 149.8 (C^6-py), 148.3 (C^1-C_6H_4), 146.5 (C^4-py), 139.8 (Ph *ipso*), 133.4 (=CH), 128.8 (Ph *para*), 128.7 (Ph *meta*, C^3-C_6H_4), 126.9 (Ph *ortho*), 123.2 (C^4-C_6H_4), 120.5 (=CH), 118.7 (C^5-py), 117.3 (C^3-py), 111.5 (C^2-C_6H_4), 44.4 (CH_2), 12.7 (CH_3) ppm. HRMS: calcd. for $C_{23}H_{23}N_2$ [M]$^+$ 328.1940; found 328.1941. $C_{23}H_{24}N_2$ (328.46): calcd. C 84.11, H 7.37, N 8.53; found C 84.10, H 7.49, N 8.56.

2-Phenyl-4-styrylpyridine (1c): White powder. Yield 0.26 g (34%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.69 (d, ^3J = 5 Hz, 1 H, py^6), 8.07 (m, 2 H, Ph *ortho*), 7.81 (s, 1 H, py^3), 7.60 (m, 2 H, Ph* *ortho*), 7.53 (m, 3 H, Ph *para* and *meta*), 7.49 (m, 3 H, Ph* *para* and *meta*), 7.39 (m, 1 H, =CH), 7.35 (m, 1 H, py^5), 7.12 (d, ^3J = 16 Hz, 1 H, =CH) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 158.1 (C^2-py), 150.0 (C^6-py), 145.4 (C^4-py), 139.5 (Ph *ipso*), 136.2 (Ph* *ipso*), 133.1 (=CH), 129.0 (Ph/Ph* *para*), 128.9 (Ph/Ph* *meta*), 128.8 (Ph/Ph* *para* and *meta*), 127.1 (Ph* *ortho*), 127.0 (Ph *ortho*), 126.3 (=CH), 119.2 (C^5-py), 118.1 (C^3-py) ppm. HRMS: calcd. for $C_{19}H_{15}N$ [M]$^+$ 257.1205; found 257.1214. $C_{19}H_{15}N$ (257.34): calcd. C 88.68, H 5.88, N 5.44; found C 88.86, H 5.98, N 5.29.

Synthesis of 2-Phenyl-4-[(trimethylsilyl)methyl]pyridine: Lithium diisopropylamine, freshly prepared from diisopropylamine (6.9 mL, 47 mmol) and *n*BuLi (1.6 M in hexane, 29.6 mL, 47.3 mmol), in THF (50 mL) at –80 °C was added to a solution of 4-methyl-2-phenylpyridine (2.05 g, 12.3 mmol) in THF (15 mL) at –80 °C. The reaction mixture was stirred at –80 °C for 0.5 h and then at –10 °C for an additional 0.5 h. At –80 °C, TMSCl (1.53 mL, 17.8 mmol) was added. The reaction was quenched after 2 min of stirring by the addition of absolute ethanol (20 mL), followed by a saturated aqueous solution of $NaHCO_3$ (20 mL). Ethyl acetate (100 mL) was added, and the organic phase was washed with water (100 mL) and a saturated aqueous solution of NaCl (100 mL). The organic phase was dried with $MgSO_4$, and the solvent was evaporated to give an orange oil. Yield 2.78 g (98%). ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 8.47 (d, ^3J = 5 Hz, 1 H, py^6), 8.12 (m, 2 H, Ph *ortho*), 7.62 (s, 1 H, py^3), 7.47 (m, 3 H, Ph *meta* and *para*), 7.01 (d, ^3J = 5 Hz, 1 H, py^5), 2.29 (s, 2 H, CH_2), 0.07 (s, 9 H, $SiMe_3$) ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]acetone): δ = 156.4 (C^2-py), 150.9 (C^4-py), 149.2 (C^6-py), 139.7 (Ph *ipso*), 128.7 (Ph *para*), 128.5 (Ph *meta*), 126.7 (Ph *ortho*), 122.2 (py), 119.7 (py), 26.7 (CH_2), –2.7 ($SiMe_3$) ppm. HRMS: calcd. for $C_{15}H_{19}NSi$ [M]$^+$ 241.1313; found 241.1287.

Synthesis of 4-(Bromomethyl)-2-phenylpyridine: 2-Phenyl-4-[(trimethylsilyl)methyl]pyridine (0.66 g, 2.73 mmol) was dissolved in DMF (15 mL), and 1,2-dibromotetrafluoroethane (2.84 g, 10.9 mmol) and cesium fluoride (1.66 g, 10.9 mmol) were added. The reaction mixture was stirred at room temp. for 2 h. Ethyl acetate (50 mL) was added, and the organic phase was washed with water (3 × 50 mL). The organic phase was dried with $MgSO_4$, and the solvent was evaporated. The product was purified by column chromatography over silica [heptane/ethyl acetate (80:20)] to give a brown oil. Yield 0.55 g (81%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.68 (d, ^3J = 5 Hz, 1 H, py^6), 8.02 (m, 2 H, Ph *ortho*), 7.74 (s, 1 H, py^3), 7.50 (m, 3 H, Ph *meta* and *para*), 7.25 (d, ^3J = 5 Hz, 1 H, py^5), 4.45 (s, 2 H, CH_2) ppm. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ = 158.5 (C^2-py), 150.6 (C^6-py), 147.3 (Ph *ipso*), 139.3 (C^4-py), 129.7 (Ph *para*), 129.3 (Ph *ortho*), 127.4 (Ph *meta*), 122.4 (C^3-py), 120.8 (C^5-py), 31.4 (CH_2) ppm.

Synthesis of 4-[(Diethoxyphosphoryl)methyl]-2-phenylpyridine: To a solution of 4-(bromomethyl)-2-phenylpyridine (1.85 g, 7.46 mmol) in $CHCl_3$ (10 mL) was added triethylphosphite (10.2 mL, 9.89 g, 59.6 mmol). The reaction mixture was refluxed for 3 h. The solvent was evaporated, and the residue was washed with pentane and then dried under vacuum to give a black oil. Yield 1 g (45%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.66 (d, $^3J_{H-H}$ = 5 Hz, 1 H, py^6), 8.01 (m, 2 H, Ph *ortho*), 7.76 (s, 1 H, py^3), 7.47 (m, 3 H, Ph *meta* and *para*), 7.21 (m, 1 H, py^5), 4.09 (dq, $^3J_{H-P}$ = $^3J_{H-H}$ = 7 Hz, 4 H, Et), 3.21 (d, $^2J_{H-P}$ = 22 Hz, 2 H, CH_2P), 1.29 (t, $^3J_{H-H}$ = 7 Hz, 6 H, Et) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 157.6 (C^6-py), 149.7 (d, $^4J_{C-P}$ = 2.6 Hz, C^2-py), 141.9 (d, $^2J_{C-P}$ = 8.5 Hz, C^4-py), 139.1 (Ph *ipso*), 129.1 (Ph *para*), 128.7 (Ph *meta*), 127.0 (Ph *ortho*), 123.4 (d, $^3J_{C-P}$ = 6 Hz, C^3-py), 121.9 (d, $^3J_{C-P}$ = 6.3 Hz, C^5-py), 62.4 (d, $^1J_{C-P}$ = 6.8 Hz, CH_2), 33.7 (d, $^2J_{C-P}$ = 137.3 Hz, OEt), 16.4 (d, $^3J_{C-P}$ = 6 Hz, OEt) ppm. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ = 25.7 [P(O)(OEt)$_2$] ppm.

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Synthesis of 4-(4-Nitrostyryl)-2-phenylpyridine (1d): To a solution of 4-[(diethoxyphosphoryl)methyl]-2-phenylpyridine (0.71 g, 2.33 mmol) and *p*-nitrobenzaldehyde (0.52 g, 3.45 mmol) in THF (20 mL) was added *t*BuOK (0.65 g, 5.8 mmol). The reaction mixture was stirred for 2 h and then hydrolysed with water (20 mL). THF was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 (3 × 50 mL). The organic phase was dried with $MgSO_4$. The solvent was evaporated, and chromatography on silica gel with heptane/ethyl acetate (80:20) afforded **1d** as a yellow powder. Yield 0.640 g (91%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.74 (d, ^3J = 5 Hz, 1 H, py^6), 8.29 (d, ^3J = 8.7 Hz, 2 H, C_6H_4), 8.06 (m, 2 H, Ph *ortho*), 7.84 (s, 1 H, py^3), 7.73 (d, ^3J = 8.7 Hz, 2 H, C_6H_4), 7.53 (m, 2 H, Ph *meta*), 7.48 (m, 1 H, Ph *para*), 7.42 (d, ^3J = 16 Hz, 1 H, =CH), 7.39 (dd, ^3J = 5 Hz, ^4J = 1 Hz, 1 H, py^5), 7.28 (d, 1 H, =CH) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 158.4 (C^2-py), 150.3 (C^6-py), 147.5 (C^1-C_6H_4), 144.2 (C^4-py), 142.6 (C^4-C_6H_4), 139.2 (Ph *ipso*), 130.8 (=CH), 130.6 (=CH), 129.3 (Ph *para*), 128.9 (Ph *meta*), 127.5 (C^3-C_6H_4), 127.0 (Ph *ortho*), 124.3 (C^2-C_6H_4), 119.4 (C^5-py), 118.3 (C^3-py) ppm. HRMS: calcd. for $C_{19}H_{14}N_2O_2$ [M]$^+$ 302.1055; found 302.1059. $C_{19}H_{14}N_2O_2$ (302.33): calcd. C 75.48, H 4.67, N 9.27; found C 75.03, H 4.62, N 9.07.

Syntheses of Chloro-Bridged Dimers [Ir(*C*^*N*-ppy-4-CH=CHC$_6$H$_4$R)$_2$]$_2$(μ-Cl)$_2$ (3): A Schlenk flask was charged with $IrCl_3 \cdot 3H_2O$ (0.289 g, 0.82 mmol), the appropriate ligand H*C*^*N* (3.5 equiv.) and a mixture of 2-ethoxyethanol/water, (75:25, 10 mL). The mixture was refluxed for 24 h. The precipitate was then washed with water, ethanol and acetone.

[Ir(*C*^*N*-ppy-4-CH=CHC$_6$H$_4$OMe)$_2$]$_2$(μ-Cl)$_2$ (3a): Yield 0.62 g (95%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 9.15 (d, ^3J = 5.9 Hz, 4 H, py^6), 7.94 (s, 4 H, py^3), 7.62 (d, ^3J = 7.5 Hz, 8 H, C_6H_4), 7.39 (m, 8 H, =CH and Ph), 7.12 (d, ^3J = 16 Hz, 4 H, =CH), 6.93 (d, 4 H, py^5), 6.82 (m, 12 H, C_6H_4 and Ph), 6.32 (t, ^3J = 6.8 Hz, 4 H, Ph), 6.02 (d, ^3J = 8.0 Hz, 4 H, Ph), 3.85 (s, 12 H, OCH_3) ppm. HRMS: calcd. for $C_{80}H_{62}Cl_2{}^{193}Ir_2N_4O_4$ [M – Cl]$^+$ 1565.3876; found 1565.3893.

[Ir(*C*^*N*-ppy-4-CH=CHC$_6$H$_4$NEt$_2$)$_2$]$_2$(μ-Cl)$_2$ (3b): Yield 0.68 g (94%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.10 (d, ^3J = 6 Hz, 4 H, py^6), 7.88 (s, 4 H, py^3), 7.58 (d, 4 H, py^5), 7.44 (d, ^3J = 8.6 Hz, 8 H, C_6H_4), 7.38 (d, ^3J = 16 Hz, 4 H, =CH), 7.02 (d, ^3J = 16 Hz, 4 H, =CH), 6.86 (d, 4 H, Ph), 6.77 (t, ^3J = 7.0 Hz, 4 H, Ph), 6.68 (d, ^3J = 8.6 Hz, 8 H, C_6H_4), 6.60 (t, 4 H, Ph), 6.14 (d, ^3J = 7.0 Hz, 4 H, Ph), 3.48 (q, ^3J = 6.8 Hz, 16 H, CH_2), 1.27 (t, ^3J = 6.8 Hz, 24 H, CH_3) ppm. HRMS: calcd. for $C_{92}H_{92}Cl^{193}Ir_2N_8$ [M – Cl]$^+$ 1729.6396; found 1729.6435.

[Ir(*C*^*N*-ppy-4-CH=CHC$_6$H$_5$)$_2$]$_2$(μ-Cl)$_2$ (3c): Yield 0.54 g (89%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 9.25 (d, ^3J = 6 Hz, 4 H, py^6), 8.06 (s, 4 H, py^3), 7.71 (d, ^3J = 7.5 Hz, 4 H, Ph), 7.54 (m, 12 H, =CH and Ph *ortho*), 7.36 (m, ^3J = 16 Hz, 16 H, =CH and Ph *meta* and Ph *para*), 7.02 (d, ^3J = 6 Hz, 4 H, py^5), 6.90 (t, ^3J = 7.5 Hz, 4 H, Ph), 6.69 (t, ^3J = 6.8 Hz, 4 H, Ph), 6.09 (d, ^3J = 8.0 Hz, 4 H, Ph) ppm. HRMS: calcd. for $C_{76}H_{56}Cl_2{}^{193}Ir_2N_4$ [M]$^+$ 1480.3130; found 1480.3135.

[Ir(*C*^*N*-ppy-4-CH=CHC$_6$H$_4$NO$_2$)$_2$]$_2$(μ-Cl)$_2$ (3d): Cleavage with DMSO to form [Ir(*C*^*N*-ppy-4-CH=CHC$_6$H$_4$NO$_2$)(DMSO)(Cl)] (**3d**-DMSO). Quantitative spectroscopic yield. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.82 (d, ^3J = 6.2 Hz, 1 H, py^6), 9.50 (d, ^3J = 6.2 Hz, 1 H, py^6), 8.54 (s, 1 H, py^3), 8.44 (s, 1 H, py^3), 8.35 (d, ^3J = 7.8 Hz, 2 H, C_6H_4), 8.08–7.68 (m, 12 H, C_6H_4, =CH, py^5, Ph^3), 6.95 (t, ^3J = 7.2 Hz, 1 H, Ph), 6.89 (t, ^3J = 7.4 Hz, 1 H, Ph), 6.78 (t, ^3J = 7.6 Hz, 1 H, Ph), 6.74 (t, ^3J = 7.2 Hz, 1 H, Ph), 6.34 (d, ^3J = 7.7 Hz, 1 H, Ph^6), 5.79 (d, ^3J = 7.6 Hz, 1 H, Ph^6) ppm.

[Ir(*C*^*N*(ppy-4-Me)$_2$]$_2$(μ-Cl)$_2$ (3e): Yield 0.45 g (96%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 9.10 (d, ^3J = 6 Hz, 4 H, py^6), 7.79 (br. s, 4 H, py^3), 7.57 (dd, ^3J = 7.8 Hz, ^4J = 1.3 Hz, 4 H, Ph^3), 6.83 (td, ^3J = 7.4 Hz, ^4J = 1.2 Hz, 4 H, Ph^4), 6.68 (dd, ^3J = 6 Hz, ^4J = 1.2 Hz, 4 H, py^5), 6.62 (td, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 4 H, Ph^5), 5.93 (td, ^3J = 7.8 Hz, ^4J = 1.1 Hz, 4 H, Ph^6), 2.70 (s, 12 H, CH_3) ppm. HRMS: calcd. for $C_{48}H_{38}Cl_2{}^{193}Ir_2N_4$ [M – Cl]$^+$ 1092.2200; found 1093.2206.

Syntheses of Bis-Cyclometallated Complexes Ir(*C*^*N*)$_2$(*O*^*O*) 4 and 5: In a Schlenk tube, to a 2-ethoxyethanol solution (10 mL) were added the chloro-bridged iridium dimer (0.057 mmol), 1,3-diketone (acetylacetone or dipyvaloylmethane) (0.14 mmol) and Na_2CO_3 (60 mg, 0.57 mmol). The reaction mixture was heated for 15 h. When the reaction mixture was heated at 140 °C, the hydrogenated compounds **4a**-H_2 and **1a**-H_2 were isolated, whereas at 80 °C the pure styryl derivatives **4**,**5** were obtained. After addition of water (20 mL), the precipitate was filtered and washed with water and diethyl ether. The products were then isolated as powders after crystallization from a mixture of CH_2Cl_2/Et_2O.

Ir(*C*^*N*-ppy-4-CH$_2$CH$_2$C$_6$H$_4$OMe)$_2$(acac) (4a-H$_2$): Yellow powder. Yield 0.045 g (46%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.36 (d, ^3J = 5.7 Hz, 2 H, py^6), 7.70 (s, 2 H, py^3), 7.56 (d, ^3J = 7.5 Hz, 2 H, Ph^3), 7.19 (d, ^3J = 8.2 Hz, 4 H, C_6H_4), 7.01 (d, ^3J = 6.0 Hz, 2 H, py^5), 6.88 (m, 6 H, C_6H_4 and Ph^4), 6.73 (t, ^3J = 7.5 Hz, 2 H, Ph^5), 6.24 (d, ^3J = 7.5 Hz, 2 H, Ph^6), 5.31 (s, 1 H, CH), 3.82 (s, 6 H, OCH_3), 3.14 (m, 4 H, CH_2), 3.07 (m, 4 H, CH_2), 1.83 (s, 6 H, CH_3) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 184.5 (CO), 167.6 (C^2-py), 158.2 (C^1-C_6H_4), 152.3 (C^4-py), 147.6 (C^6-py), 147.4 (C^1-Ph), 145.3 (C^2-Ph), 133.1 (C^6-Ph), 132.6 (C^4-C_6H_4), 129.4 (C^3-C_6H_4), 128.5 (C^5-Ph), 123.5 (C^3-Ph), 122.3 (C^5-py), 120.6 (C^4-Ph), 118.6 (C^3-py), 113.9 (C^2-C_6H_4), 100.2 (CH), 55.2 (OCH_3), 37.5 (CH_2), 35.7 (CH_2), 28.3 (CH_3) ppm. HRMS: calcd. for $C_{45}H_{43}{}^{193}IrN_2O_4Na$ [M + Na]$^+$ 891.2750; found 891.2770. $C_{45}H_{43}IrN_2O_4 \cdot 0.5H_2O$ (888.08): calcd. C 61.62, H 5.06, N 3.19; found C 61.59, H 4.85, N 3.13.

ppy-4-CH$_2$CH$_2$C$_6$H$_4$OMe (1a-H$_2$): Evaporation of the diethyl ether solution gave a yellow oil identified as **1a**-H_2. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.57 (d, ^3J = 4.9 Hz, 1 H, py^6), 8.02 (m, 2 H, Ph *ortho*), 7.57 (s, 1 H, py^3), 7.47 (m, 3 H, Ph *para* and *meta*), 7.15 (d, ^3J = 8.5 Hz, 2 H, C_6H_4), 7.09 (d, ^3J = 4.9 Hz, 1 H, py^5), 6.87 (d, ^3J = 8.5 Hz, 2 H, C_6H_4), 3.81 (s, 3 H, OCH_3), 2.98 (m, 4 H, CH_2) ppm. HRMS: calcd. for $C_{19}H_{19}NO$ [M]$^+$ 289.1467; found 289.1455.

Ir(*C*^*N*-ppy-4-CH=CHC$_6$H$_4$OMe)$_2$(acac) (4a): Red powder. Yield 0.092 g (93%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.45 (d, ^3J = 6.0 Hz, 2 H, py^6), 7.96 (d, ^4J = 1.7 Hz, 2 H, py^3), 7.68 (dd, ^3J = 7.7 Hz, ^4J = 1.1 Hz, 2 H, Ph^3), 7.63 (d, ^3J = 8.7 Hz, 4 H, C_6H_4), 7.49 (d, ^3J = 16.3 Hz, 2 H, =CH), 7.34 (dd, ^3J = 6 Hz, ^4J = 1.7 Hz, 2 H, py^5), 7.14 (d, ^3J = 16.3 Hz, 2 H, =CH), 7.01 (d, ^3J = 8.7 Hz, 4 H, C_6H_4), 6.91 (td, ^3J = 7.7 Hz, ^4J = 1.1 Hz, 2 H, Ph^4), 6.74 (td, ^3J = 7.7 Hz, ^4J = 1.1 Hz, 2 H, Ph^5), 6.35 (dd, ^3J = 7.7 Hz, ^4J = 1.1 Hz, 2 H, Ph^6), 5.34 (s, 1 H, CH), 3.90 (s, 6 H, OCH_3), 1.86 (s, 6 H, CH_3) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 184.7 (CO), 167.9 (C^2-py), 160.6 (C^1-C_6H_4), 147.8 (C^6-py), 147.5 (C^1-Ph), 146.3 (C^4-py), 145.2 (C^2-Ph), 134.1 (=CH), 133.3 (C^6-Ph), 128.7 (C^4-C_6H_4, C^3-C_6H_4, C^5-Ph), 123.6 (C^3-Ph), 122.8 (=CH), 120.7 (C^4-Ph), 118.5 (C^5-py), 115.4 (C^3-py), 114.3 (C^2-C_6H_4), 100.3 (CH), 55.4 (OCH_3), 28.3 (CH_3) ppm. HRMS: calcd. for $C_{45}H_{39}{}^{193}IrN_2O_4$ [M]$^+$ 864.2539; found 864.2528. In CD_2Cl_2 solution, partial isomerization of the C=C double bond occurs, and the ^{1}H NMR spectrum exhibits three isomers (*E*/*E*, *E*/*Z*, *Z*/*Z*); some signals are clearly resolved. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.45 (d, ^3J = 6.0 Hz, py^6, *E*/*E*), 8.43 (d, py^6, *E*/*Z*), 8.34 (d, py^6, *E*/*Z*), 8.33 (d,

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py[6], *Z*/*Z*), 7.96 (s, py[3], *E*/*E* and *E*/*Z*), 7.80 (d, py[3], *E*/*Z* and *Z*/*Z*), 7.49 (d, ^3J = 16.3 Hz, =CH, *E*/*E* and *E*/*Z*), 7.34 (m, py[5], *E*/*E* and *E*/*Z*), 7.14 (d, ^3J = 16.2 Hz, 2 H, =CH, *E*/*E*), 7.13 (d, ^3J = 16.2 Hz, =CH, *E*/*Z*), 7.07 (m, py[5], *E*/*Z*), 6.89 (m, =CH, *E*/*Z* and *Z*/*Z*), 6.65 (d, ^3J = 12.2 Hz, =CH, *E*/*Z* and *Z*/*Z*), 5.34 (s, 1 H, CH-acac), 3.90 (s, 6 H, OCH_3, *E*/*E* and *E*/*Z*), 3.84 (s, 6 H, OCH_3, *E*/*Z* and *Z*/*Z*), 1.87 (s, 3 H, CH_3, *E*/*Z*), 1.86 (s, 3 H, CH_3, *E*/*Z* and *E*/*E*), 1.82 (s, 6 H, CH_3, *Z*/*Z*) ppm.

Ir(*C*^*N*-ppy-4-CH=CHC$_6$H$_4$OMe)$_2$(dpm) (5a): Red powder. Yield 0.1 g (93%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.35 (d, ^3J = 6.1 Hz, 2 H, py[6]), 7.94 (d, ^4J = 1.7 Hz, 2 H, py[3]), 7.69 (d, ^3J = 7.4 Hz, 2 H, Ph[3]), 7.61 (d, ^3J = 8.8 Hz, 4 H, C_6H_4), 7.47 (d, ^3J = 16 Hz, 2 H, =CH), 7.27 (dd, ^3J = 6.1 Hz, ^4J = 1.7 Hz, 2 H, py[5]), 7.12 (d, ^3J = 16 Hz, 2 H, =CH), 7.00 (d, ^3J = 8.8 Hz, 4 H, C_6H_4), 6.89 (td, ^3J = 7.4 Hz, ^4J = 1.0 Hz, 2 H, Ph[4]), 6.72 (td, ^3J = 7.4 Hz, ^4J = 1 Hz, 2 H, Ph[5]), 6.41 (dd, ^3J = 7.4 Hz, ^4J = 1 Hz, 2 H, Ph[6]), 5.60 (s, 1 H, CH-dpm), 3.89 (s, 6 H, OCH_3), 0.98 (s, 18 H, *t*Bu) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ = 194.5 (CO), 168.2 (C[2]-py), 160.5 (C[1]-C_6H_4), 149.2 (C[1]-Ph), 147.9 (C[6]-py), 145.9 (C[4]-py), 145.1 (C[2]-Ph), 133.8 (=CH), 133.5 (C[6]-Ph), 128.8 (C[4]-C_6H_4), 128.6 (C[3]-C_6H_4), 128.4 (C[5]-Ph), 123.4 (C[3]-Ph), 123.0 (=CH), 120.2 (C[4]-Ph), 118.1 (C[5]-py), 115.0 (C[3]-py), 114.3 (C[2]-C_6H_4), 90.1 (CH), 55.3 (OCH_3), 41.0 (*t*Bu), 27.9 (CH_3) ppm. HRMS: calcd. for $C_{51}H_{51}{}^{193}IrN_2O_4$ $[M]^+$ 948.3478; found 948.3474. $C_{51}H_{51}IrN_2O_4{\cdot}2H_2O$ (968.23): calcd. C 62.24, H 5.63, N 2.85; found C 62.30, H 5.39, N 2.99.

Ir(*C*^*N*-ppy-4-CH=CHC$_6$H$_4$NEt$_2$)$_2$(acac) (4b): Orange powder. Yield 0.1 g (93%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.40 (d, ^3J = 6 Hz, 2 H, py[6]), 7.92 (s, 2 H, py[3]), 7.67 (d, ^3J = 7.5 Hz, 2 H, Ph[3]), 7.53 (d, ^3J = 8.6 Hz, 4 H, C_6H_4), 7.44 (d, ^3J = 16 Hz, 2 H, =CH), 7.31 (d, ^3J = 6 Hz, 2 H, py[5]), 7.01 (d, ^3J = 16 Hz, 2 H, =CH), 6.90 (t, ^3J = 7.5 Hz, 2 H, Ph[4]), 6.74 (m, 6 H, Ph[5], C_6H_4), 6.36 (d, ^3J = 7.5 Hz, 2 H, Ph[6]), 5.33 (s, 1 H, CH), 3.47 (q, ^3J = 6.8 Hz, 8 H, CH_2), 1.86 (s, 6 H, CH_3), 1.25 (t, ^3J = 6.8 Hz, 12 H, NEt_2) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ = 184.5 (CO), 167.7 (C[2]-py), 151.0 (C[2]-Ph), 148.6 (C[1]-C_6H_4), 147.6 (C[6]-py), 147.4 (C[1]-Ph), 146.9 (C[4]-py), 134.9 (=CH), 133.5 (C[6]-Ph), 128.9 (C[3]-C_6H_4), 128.5 (C[5]-Ph), 123.4 (C[3]-Ph), 122.9 (C[4]-C_6H_4), 120.6 (C[4]-Ph), 119.3 (=CH), 118.1 (C[5]-py), 114.9 (C[3]-py), 111.4 (C[2]-C_6H_4), 100.3 (CH), 44.4 (CH_2), 28.3 (CH_3), 12.4 (NEt_2) ppm. HRMS: calcd. for $C_{51}H_{53}{}^{193}IrN_4O_2$ $[M]^+$ 946.3802; found 946.3814. $C_{51}H_{53}{}^{193}IrN_4O_2{\cdot}H_2O$ (964.24): calcd. C 63.52, H 5.75, N 5.81; found C 63.74, H 5.30, N 6.17.

Ir(*C*^*N*-ppy-4-CH=CHC$_6$H$_4$NEt$_2$)$_2$(dpm) (5b): Red powder. Yield 0.096 g (82%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.27 (d, ^3J = 6 Hz, 2 H, py[6]), 7.90 (s, 2 H, py[3]), 7.67 (d, ^3J = 7.5 Hz, 2 H, Ph[3]), 7.51 (d, ^3J = 8.5 Hz, 4 H, C_6H_4), 7.42 (d, ^3J = 16 Hz, 2 H, =CH), 7.23 (d, ^3J = 6 Hz, 2 H, py[5]), 6.98 (d, ^3J = 16 Hz, 2 H, =CH), 6.89 (t, ^3J = 7.3 Hz, 2 H, Ph[4]), 6.74 (d, ^3J = 8.5 Hz, 4 H, C_6H_4), 6.69 (t, ^3J = 7.3 Hz, 2 H, Ph[5]), 6.42 (d, ^3J = 7.3 Hz, 2 H, Ph[6]), 5.60 (s, 1 H, CH), 3.48 (q, ^3J = 7 Hz, 8 H, CH_2), 1.19 (t, ^3J = 7 Hz, 12 H, CH_3), 0.98 (s, 18 H, *t*Bu) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ = 194.4 (CO), 167.9 (C[2]-py), 149.1 (C[1]-Ph), 148.6 (C[1]-C_6H_4), 147.7 (C[6]-py), 146.5 (C[4]-py), 145.3 (C[2]-Ph), 134.6 (=CH), 133.5 (C[6]-Ph), 128.8 (C[3]-C_6H_4), 128.2 (C[5]-Ph), 123.3 (C[3]-Ph), 122.9 (C[4]-C_6H_4), 120.1 (C[4]-Ph), 119.5 (=CH), 117.1 (C[5]-py), 114.6 (C[3]-py), 111.4 (C[2]-C_6H_4), 90.0 (CH), 44.4 (CH_2), 41.0 (*t*Bu), 27.9 (CH_3), 12.4 (NEt_2) ppm. HRMS: calcd. for $C_{57}H_{65}{}^{193}IrN_2O_4$ $[M]^+$ 1030.4742; found 1030.4736.

Ir(*C*^*N*-ppy-4-CH=CHC$_6$H$_5$)$_2$(acac) (4c): Red powder. Yield 0.082 g (90%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.48 (d, ^3J = 6 Hz, 2 H, py[6]), 7.99 (s, 2 H, py[3]), 7.68 (m, 6 H, Ph *ortho* and Ph[3]), 7.53 (d, ^3J = 16.4 Hz, 2 H, =CH), 7.45 (m, 6 H, Ph *meta* and *para*), 7.37 (dd, ^3J = 6 Hz, ^4J = 1.7 Hz, 2 H, py[5]), 7.28 (d, ^3J = 16.4 Hz, 2 H, =CH), 6.91 (t, ^3J = 7.6 Hz, 2 H, Ph[4]), 6.74 (t, ^3J = 7.6 Hz, 2 H, Ph[5]), 6.35 (d, ^3J = 7.6 Hz, 2 H, Ph[6]), 5.34 (s, 1 H, CH), 1.86 (s, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ = 184.8 (CO), 168.1, 147.9, 147.5, 145.9, 145.1, 136.0, 134.5, 133.3, 133.1, 129.1 (Ph), 128.8 (Ph), 127.3 (Ph), 125.2 (Ph), 123.7, 120.8, 118.8 (py), 115.7 (py), 100.4 (CH), 28.3 (CH_3) ppm. HRMS: calcd. for $C_{43}H_{35}{}^{193}IrN_2O_2$ $[M + H]^+$ 804.23280; found 804.2326. $C_{43}H_{35}IrN_2O_2{\cdot}2H_2O$ (840.01): calcd. C 61.48, H 4.68, N 3.33; found C 61.59, H 4.46, N 3.33.

Table 6. Crystallographic data and refinement for **1a**, **1b** and **1d**.

Compound	**1a**	**1b**	**1d**
Empirical formula	$C_{20}H_{17}NO$	$C_{23}H_{24}N_2$	$C_{20}H_{14}N_2O_2$
Formula mass	287.34	656.88	314.33
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1/n$	$P2_1$
a/Å	6.0688(2)	9.9420(10)	5.8871(2)
b/Å	7.5638(3)	11.888(2)	16.4674(6)
c/Å	32.5570(10)	33.025(6)	7.4517(3)
β/°	94.183(2)	92.96(5)	94.816(3)
V/Å^3	1490.49(9)	4936.1(1)	719.86(5)
Z	2	4	2
$D_{calcd.}$/g cm^{-3}	1.281	1.119	1.450
F(000)	608	2196	328
λ(Mo-K_α)/Å	0.71069	0.71073	0.71069
θ range/°	2.76–27.38	2.48–27.50	2.47–27.47
Data collected (*h*,*k*,*l*)	0/7, 0/9, ±42	±9, ±10, ±30	0/7, 0/21, ±9
No. of reflections collected	3557	11257	1712
No. of unique reflections	3557	11257	1712
No. of observed reflections [$I > 2\sigma(I)$]	2898	9931	1602
No. of parameters	397	596	209
Goodness-of-fit on F^2	1.039	1.023	1.069
R (all data)	0.0949, 0.2091	0.0697, 0.1565	0.0451, 0.1143
Final *R*, R_w	0.0743, 0.1887	0.044, 0.112	0.0417, 0.1114
$\Delta\rho_{max.,min.}$/e Å^{-3}	0.840, –0.259	2.4, –1.126	0.268, –0.255

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Ir($C^{\wedge}N$-ppy-4-CH=CHC$_6$H$_4$NO$_2$)$_2$(acac) (4d): Red powder. Yield 0.092 g (90%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.54 (d, ^3J = 6 Hz, 2 H, py^6), 8.32 (d, ^3J = 8.7 Hz, 4 H, C_6H_4), 8.03 (s, 2 H, py^3), 7.83 (d, ^3J = 8.7 Hz, 4 H, C_6H_4), 7.71 (d, ^3J = 7.3 Hz, 2 H, Ph^3), 7.57 (d, ^3J = 16 Hz, 2 H, =CH), 7.43 (d, ^3J = 16 Hz, 2 H, =CH), 7.40 (m, 2 H, py^5), 6.93 (t, ^3J = 6.5 Hz, 2 H, Ph^4), 6.72 (t, ^3J = 6.5 Hz, 2 H, Ph^5), 6.41 (d, ^3J = 6.5 Hz, 2 H, Ph^6), 5.35 (s, 1 H, CH), 1.87 (s, 6 H, CH_3) ppm. HRMS: calcd. for $C_{43}H_{34}{}^{193}IrN_4O_6$ [M + H]$^+$ 895.2108; found 895.2118.

Ir($C^{\wedge}N$-ppy-4-Me)$_2$(acac) (4e): Yellow powder. Yield 0.07 g (98%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.36 (d, ^3J = 5.9 Hz, 2 H, py^6), 7.74 (br. s, 2 H, py^3), 7.59 (dd, ^3J = 7.5 Hz, ^4J = 1.1 Hz, 2 H, Ph^3), 7.07 (dd, ^3J = 5.9 Hz, ^4J = 1.2 Hz, 2 H, py^5), 6.87 (td, ^3J = 7.5 Hz, ^4J = 0.9 Hz, 2 H, Ph^4), 6.71 (td, ^3J = 7.5 Hz, ^4J = 1.1 Hz, 2 H, Ph^5), 6.27 (dd, ^3J = 7.5 Hz, ^4J = 0.9 Hz, 2 H, Ph^6), 5.30 (s, 1 H, CH), 2.64 (s, 6 H, CH_3), 1.83 (s, 6 H, CH_3) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 184.6 (CO), 167.6 (C^2-py), 149.0 (C^4-py), 147.5 (C^1-Ph, C^6-py), 145.3 (C^2-Ph), 133.2 (C^6-Ph), 128.5 (C^5-Ph), 123.5 (C^3-Ph), 122.9 (C^5-py), 120.6 (C^4-Ph), 119.3 (C^3-py), 100.2 (CH), 28.3 (CH_3), 21.1 (CH_3) ppm. HRMS: calcd. for $C_{29}H_{27}{}^{193}IrN_2O_2$ [M]$^+$ 628.1703; found 628.1727.

X-ray Crystallography: Single crystals for X-ray diffraction studies were grown by slow diffusion of pentane in a toluene solution of complexes **1a**, **1b** and **1d** at 20 °C. The samples **1a** and **1d** were studied with an NONIUS Kappa CCD and **1b** with a Bruker AXS X8-APEX II with graphite-monochromatized Mo-K_α radiation. The data collection and refinement parameters are presented in Table 6. The structures were solved with SIR-97[25] which reveals the non-hydrogen atoms of the molecules. The whole structures were refined by full-matrix least-square techniques on F^2, with hydrogen atoms refined using the Riding mode. Structures were solved by Patterson or direct methods. The structures were completed by subsequent difference Fourier techniques and refined by full-matrix least-squares on F^2 (SHELXL-97) with initial isotropic parameters.[26a] Atomic scattering factors from International Tables for X-ray Crystallography. ORTEP views were realized with PLATON.[26b]

CCDC-272375 (for **1a**), -257689 (for **1b**) and -275435 (for **1d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Absorption and emission spectra of **3a** and **3d**. Comparison of the absorption and emission spectra of the acac **4a** and dpm adduct **5a**.

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