Synthesis, structural characterization and the first electroluminescent properties of tris- and bis-cycloiridiated complexes of sterically hindered electron-poor 2-(3,5-bis(trifluoromethyl)phenyl)-4-trifluoromethylpyridine†

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An application of the new sterically hindered electron-poor 2-(3,5-bis(trifluoromethyl)phenyl)-4-trifluoromethylpyridine [HC N] (1) in the one-step high temperature cyclometalation by Ir^{III}Cl₃ in the presence of $Ag^{I}OC(O)CF_{3}$ resulted in the synthesis of tris-cyclometalated complexes $[C^{\Lambda}N]_{2}Ir[C^{\Lambda}C]$ (3) and $[C^N]_{i}$ Ir (5). A neutral silver cluster with a repeating unit of hexa-silver groups in an infinite chain of (2) was isolated from the above reaction as well. When this cyclometalation was carried out in trimethylphosphate at lower temperature, bis-cyclometalated derivatives $[C^N]_2 Ir(\mu-Cl)_2 Ir[C^N]_2$ (6), $[C^{N}]_{2}Ir[\eta^{2}-(O(C(^{B}u))_{2}CH]$ (7), and $[C^{N}]_{2}Ir(\mu-O-P(OMe)_{2}-O)_{2}Ir[C^{N}]_{2}$ (8) were synthesized. According to X-ray analyses complex (3), while trivalent, contains four cyclometalated single Ir–C bonds. One of the Ir-C bonds, next to the nitrogen atom of the C^C pyridinium ligand, was found to be the shortest to date (1.977(4) Å) for a single bond between iridium and carbon atoms. The coordination of the C^AC ligand in (3) to iridium has a decidedly interesting bonding pattern and can be explained by various formulations. The first one is considering this ligand as a monoanionic chelating ligand, in which the second coordination site arises from a carbene or azomethine ylide. Overall the best single picture may be a dianionic ligand making two "normal" Ir-C bonds, in which the ligand just happens to contain a pyridinium function that compensates for one negative charge on the iridium. LEDs constructed with compounds (7) and (8) give blue-green emission with peak electroluminescent efficiency of 15 and 2 cd A^{-1} , respectively. An LED constructed with compound (5) gives a yellowish emission with peak electroluminescent efficiency of 5.5 cd A^{-1} .

Introduction

Tennant discovered the element iridium over 200 years ago in the black residues remaining from the treatment of platinum ores.¹ Since then iridium has been linked to phenomena ranging from the disappearance of dinosaurs² to organic light emitting diodes (OLEDs).³ Particularly, bis- and tris-cyclometalated (N^C) complexes of Ir^{III} with 2-phenylpyridine ligands (Type A in Scheme 1) have been used widely as one of the promising electroluminescent materials for OLED technology. The emission colors from these complexes depends on the choice of cyclometalated ligand, ranging from blue-green, to green and to red. The introduction of trifluoromethyl groups in the *para-* and *ortho*-positions to the



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iridium atom in the phenyl moiety of the cyclometaled ligand (Type **B** in Scheme 1) was found to hypochromically shift the emission to the blue part of the spectrum.⁴ The blue emissive materials are among the most sought after components for an emerging OLED technology.

In our quest for blue phosphorescent materials, we decided to synthesize bis- and tris-cyclometalated (N^C) complexes of Ir^{III} with 2-phenylpyridine ligands bearing three trifluoromethyl groups: two in the phenyl moiety (like in Type **B** in Scheme 1) and one additional group in the pyridine moiety *para* to the nitrogen (Type **C** in Scheme 1). There are two effects of the trifluoromethyl group in the Ir-cyclometalated complexes. The first one is the strong electron withdrawing effect on the ligand π -system, and the second is to provide steric protection around the metal, which is an important parameter for increasing the intensity of the emission.⁴

In this report we describe the isolation of several luminescent bis- and tris-cyclometalated (N^C) Ir-complexes based on a new sterically hindered fluorinated 2-(3,5-bis(trifluoromethyl)phenyl)-4-trifluoromethylpyridine 1. The high temperature cyclometalation of 1 by Ir^{III}Cl₃ in the presence of Ag^IOC(O)CF₃ afforded the neutral silver cluster 2 containing six silver atoms, the first mono-nuclear trivalent iridium complex 3 with four cyclometalated iridium–carbon bonds with a decidedly interesting bonding pattern, bipyridine 4 and target tris-cyclometalated product 5. Bis-cyclometalated derivatives 6–8 were prepared through the cyclometalation of 1 in trimethylphosphate as a medium.

Results and discussion

Synthesis of 2-(3,5-bis(trifluoromethyl)phenyl)-4-trifluoromethylpyridine 1

The palladium-catalysed Suzuki cross-coupling reaction between 2-chloro-4-trifluoromethylpyridine and 3,5-bis(trifluoromethyl)-phenylboronic acid was used to prepare 2-(3,5-bis(trifluoromethyl)-phenyl)-4-trifluoromethylpyridine **1** (Scheme 2).



The synthetic protocol involves Pd_2dba_3/di -*tert*-butyl-trimethylsilylanylmethylphosphine as the catalyst in the presence of caesium fluoride in 1,4-dioxane as the solvent. The yield of 2-(3,5-bis-trifluoromethyl-phenyl)-4-trifluoromethylpyridine **1**

was 18.0 g (91.0%) after distillation as a colorless liquid with bp 84–86 °C/0.1 mmHg. The ¹⁹F NMR spectrum of 1 contains two chemical shifts at $\delta = -62.37$, which corresponds to the trifluoromethyl groups of the phenyl moiety, and at $\delta = -64.30$, which corresponds to the trifluoromethyl groups of the pyridine moiety, with the expected ratio between them as two to one. The cyclometalation experiments with compound 1 are described in the following sections.

Synthesis, structural and bonding studies of the tris-cyclometalated derivatives (3 and 5)

One-step synthesis leading directly to tris-cyclometalated Ir^{III} complexes was reported by the reaction of Ir^{III}Cl₃ with 2phenylpyridines in the presence of Ag^I trifluoroacetate.⁴ Ag^I trifluoroacetate was used to facilitate tris-cyclometalation by generating in situ IrIII trifluoroacetate, which is a more active triscycloiridation agent than Ir^{III}Cl₃.⁴ We decided to synthesize the tris-cyclometalated complex by the above one-pot method from 2-(3,5-bis(trifluoromethyl)phenyl)-4-trifluoromethylpyridine 1 and Ir^{III}Cl₃/Ag^I trifluoroacetate (Scheme 3). Unexpectedly, several compounds in this reaction were isolated with unusual bonding patterns: the neutral silver cluster 2 containing six silver atoms, the first mono-nuclear trivalent iridium complex 3 with four cyclometalated iridium-carbon bonds with a decidedly interesting bonding pattern, bipyridine 4 and the target tris-cyclometalated product 5. The isolated yields of compounds 2-5 were rather low, varying from 3.4% for **4** to 9.8% for **2**.



Scheme 3 Cyclometalation of 1 by $Ir^{III}Cl_3$ in the presence of AgOC(O)CF₃. There is one trifluoroacetate ligand per silver atom in 2. The silver and oxygen atoms in brackets are from neighboring repeating units.

The 2-phenylpyridine ligands 1 behave in 2 as blocking groups or terminators to prevent further aggregation of silver trifluoroacetate moieties in two dimensions: above and below the infinite chain of silver atoms (Scheme 3 and Fig. 1).⁵



Fig. 1 An ORTEP drawing of centrosymmetric dimer 2. The phenyl moieties of the 2-phenylpyridine ligands 1 are assembled in face-to-face mode of π - π stacking. The centroid-centroid contacts between the phenyl groups in 2 are 3.96 Å. The mean planes of the two phenyl groups are tilted by 11.2°. The hydrogen and fluorine atoms are omitted for clarity. Thermal ellipsoids drawn to the 20% probability level. Symmetry operation codes are designated on atom labels with A = (x, y, z), B = (1 - x, -y, -z), C = (1 + x, y, z) and D = (2 - x, -y, -z).

Cluster 2 contains two kinds of silver atoms: the two peripheral three-coordinate silver atoms each connected with two nitrogen atoms of two ligands 1; and a four-atom flat core with two six-coordinate and two seven-coordinate silver atoms in the center of the cluster (Scheme 3). Within the four atoms, the Ag–Ag distances are 3.00 Å, which are less than 3.4 Å (less than twice the van der Waals radius of a silver atom). The central cage is perfectly planar, in contrast to the butterfly geometry previously observed for four-

atom grouping in silver clusters.^{5d} The repeating units in the cluster are bridged together by six-coordinate silver atoms forming Ag– O–Ag four-membered rings. Complex **3** was isolated as dark gold crystals with orange photoluminescence. The diamagnetic nature of **3** (judging from sharp lines in the NMR spectra of **3**) suggests a trivalent status. In a four-valent state, complex **3** should be paramagnetic, consistent with a d⁵ iridium. According to X-ray analysis, the nitrogen atoms coordinated to iridium are in *cis*positions (N1 and N15 atoms in Fig. 2).



Fig. 2 An ORTEP drawing of 3. The shortest Ir-C(30) bond length is 1.977(4) Å. Thermal ellipsoids drawn to the 30% probability level. All hydrogen atoms and pentane solvent molecule are removed for clarity.

The bond between iridium and carbon next to the nitrogen atom of the C^C pyridinium ligand was found to be among the shortest for cyclometalated Ir–C bonds (1.977(4) Å, Table 1). The recent account⁶ of Ir–C bonds of tris-cyclometalated structures gives a range from 2.024(6) to 2.151(9) Å for the 2-phenylpyridine derivatives. The second Ir–C bond length of this C^C pyridinium ligand (2.065(4) Å) is within the range found for other Ir–C bonds in this report with the same cyclometalated N^C ligand 1 (Table 1, structure 5) and within the literature data.⁶ Both of these Ir–C bonds are under the same *trans*-influence of the nitrogen atoms of the pyridine rings. The bonding pattern of the C^C pyridinium ligand to iridium is not a trivial issue, but it can be rationalized (formulated) by the structures depicted in Scheme 4.

The experimental values from the X-ray analyses for a single bond length between iridium and N-heterocyclic carbenes vary from 2.019 Å to 2.055 Å.⁷ Our corresponding value for the Ir–C

Table 1 Selected bond lengths (Å) for 3, 5, 7 and 8

	3	5	7	8	
Ir–C	1.977(4), Ir-C30	N/A	N/A	N/A	
Ir–C	2.136(4), Ir-C11	2.156(7), Ir-C11	2.039(5), Ir-C11	2.022(8), Ir-C13	
Ir–C	2.119(4), Ir-C24	2.122(7), Ir-C39	2.030(5), Ir-C25	2.013(8), Ir-C28	
Ir–C	2.065(4), Ir-C45	2.061(6), Ir-C25	N/A	N/A	
Ir–N	2.125(3)	2.123(5)	2.032(4)	2.037(6)	
Ir–N	2.123(3)	2.051(5)	2.031(4)	2.026(6)	
Ir–N	N/A	2.048(5)	N/A	N/A	



Scheme 4 Three plausible modes of bonding in complex 3.

bond in complex **3** is even shorter at 1.977(4) Å. However, this distance is longer than the Ir=C double bond (1.904 Å) observed in a known alkylidene complex $[Cp^*(PiPr_3)Ir=CPh_2]$. This C–Ir distance in **3** is shorter than typical single Ir–C bonds (2.1 Å).⁸

The resonance of the carbene moiety is a very characteristic feature for iridium–carbene complexes in the ¹³C NMR spectum. It appears downfield between $\delta = 155$ and 181 ppm.⁷ The most downfield signal in the ¹³C NMR spectra of **3** has a chemical shift at $\delta = 187.24$ ppm (Table 2), which is in agreement with the carbene formulation. In the reference compounds, the chemical shifts for the Ir–C carbon atoms in tris-cyclometalated complex **5** appear upfield with respect to **3**.

1-(Pyrididin-2-yl)-pyridinium perchlorates resembling the core of the C^C cyclometalated ligand of **3** are known.⁹ The most downfield signals in the ¹³C NMR spectrum of reported 1-(pyrididin-2-yl)-pyridinium perchlorates were observed between $\delta = 155$ and 158 ppm, which corresponds to the carbon atoms connected to the pyridinium nitrogen. Compound **3** exhibits chemical shifts close to that range, but more deshielded.

2,2'- Or 2,4'-bipyridine ligands with one nitrogen atom quaternized are known to undergo mono-C-cyclometalation to form Pt^{II} and Pd^{II} complexes with an internal pyridinium fragment.¹⁰ Our studies did not begin with the pyridinium salt of the C^C cyclometalated ligand of 3, but rather this ligand structure had to be generated in situ. The mechanism of the formation of this ligand and ultimately complex 3 itself seems to involve highly reactive intermediates, like pyridine-2 radicals. The pyridine radicals generated in situ by the different methods are known to convert to 4,4'- or 2,2'-bipyridines.¹¹ The pyridine radicals generated in the presence of other aromatic substrates form various isomeric heteroaromatic products including the pyridinium salts.¹² The cyclometalation of ligand 1 by IrCl₃ was carried out at high temperatures from 180 to 190 °C for 58 hours. Under these harsh conditions the silver cluster 2 could generate pyridinyl radicals, which in turn are responsible for the formation of **3** and **4**. The dimerization of the pyridinyl

radicals in the presence of trifluoacetate anions can lead to the formation of the intermediate pyridinium salt, parent to the C^C ligand in 3, as in Scheme 2. This intermediate pyridinium salt could be incorporated in to complex 3 upon subsequent cyclometalation. The pyridinyl radical can attack the tris-cyclometalated complex 5 with subsequent rearrangements leading to 3. The studies of the thermal stability of Ag^I complexes with pyridines show decomposition occurs above 130 °C.13 This simple test of the stability of silver cluster 2 reveals that it deposits a silver mirror upon heating to 200 °C. However, it is hard to carry out ESR studies on the radical species formed because these temperatures lie outside the range of our ESR instrumentation. Further studies of the mechanism of formation of compounds 2 and 3 have not been pursued at this point. Besides thermal decomposition of silver clusters leading to pyridine radicals, several plausible routes can be envisioned for the formation of the observed products. Silver catalyzed oxidation of starting ligand 1 to biphenyl derivatives with subsequent cyclometalation, or thermal decomposition of iridium cyclometalated complexes leading to products 4 and 3, are just two of the additional possibilities.

The ORTEP drawing of tris-cyclometalated complex **5** is shown in Fig. 3. In contrast to the previously reported sterically less bulky fluorinated analogs, **5** exists as a meridional isomer, not the facial isomer.⁴ When the complex assumes a meridional conformation, sterical repulsion between the C^N ligands is reduced.⁶

Synthesis and structural studies of the bis-cyclometalated derivatives (6–8)

The bis-cyclometalation of 2-(3,5-bis(trifluoromethyl)phenyl)-4trifluoromethylpyridine **1** was carried out in trimethylphosphate. Electrophilic reactions, like cyclometalation, in trimethylphosphate take place at lower temperature in many difficult cases.¹⁴ The Ir^{III} -bridged di-chloride dimer **6** was precipitated from the trimethylphosphate solution by dilution with diethyl ether

Table 2 ¹³C NMR data for carbon atoms attached to iridium in complexes 3 and 5

	3			5		
Cyclometalated	C^N	C^N	C^C	C^N	C^N	C^N
Ligand	1	1	Pyridinium	1	1	1
δ (ppm)	169.06	168.23	187.24, 154.65	172.14	167.36	152.07



Scheme 5 The cyclometalation of 2-(3,5-bis(trifluoromethyl)phenyl)-4-trifluoromethylpyridine 1 in trimethylphosphate and related transformations.



Fig. 3 ORTEP drawing of tris-cyclometalated complex 5. This is a meridional isomer. The shortest Ir-C(25) bond length is 2.061(6) Å. Thermal ellipsoids drawn to the 50% probability level. Only one of two molecules in the asymmetric unit is depicted and all hydrogen atoms are removed for clarity.

(Scheme 5). Complex 6 reacted with 2,2,6,6-tetramethyl-heptane-3,5-dione and tetrabutylammonium hydroxide in THF to yield bis-cyclometalated complex 7.

According to the results of X-ray analysis, complex 7 was found to be a *trans*-N,N-isomer (Fig. 4). Prolonged heating of complex 6 in trimethylphosphate was found to form complex 8 with two bridged dimethoxyphosphate moieties (Scheme 4). The structure of 8 was confirmed by X-ray analysis (Fig. 5). It was



Fig. 4 ORTEP drawing of complex 7. This is a *trans*-N,N-isomer. The shortest Ir-C(25) bond length is 2.030(5) Å. Thermal ellipsoids drawn to the 50% probability level. All hydrogen atoms are removed for clarity.

observed to be the *trans*-N,N isomer. The eight-membered ring formed by the bridging iridium dimethoxyphosphate groups has a chair conformation. There is an averaging between the phosphoryl (P=O) and single phosphorus–oxygen (P–O) bonds in **8**. The averaged P–O bond in the ring system of **8** is 1.483(5) Å, which is shorter than the average single bond between phosphorus and the *exo* methoxy group in complex **8** (1.5745(5) Å). The shortest Ir–C(8) bond length is 2.013(8) Å in **8**, which is positioned *trans* to the oxygen atom connected to phosphorus.



Fig. 5 ORTEP drawing of centrosymmetric dimer **8**. The shortest Ir–C(8) bond length is 2.013(8) Å. Thermal ellipsoids drawn to the 30% probability level. Hydrogen atoms, disordered CF₃ positions and dimethylphosphate are removed for clarity. Symmetry operation codes are designated on atom labels with A = (2 - x, -y, -z).

The order of the *trans* influence on the Ir–C bond length in complexes **3**, **5**, **7**, **8** bearing the same (N^{\land}C) cyclometalated 2-(3,5-bis(trifluoromethyl)phenyl)-4-trifluoromethylpyridine 1 ligand can be summarized as follows: C > N > O–(C) > O–(P).

The longest $Ir-C(sp^2)$ bonds have been found to be in *trans* positions to carbon, then in *trans* positions to nitrogen, then in *trans* positions to oxygen connected to carbon and the shortest $Ir-C(sp^2)$ bonds have been found when the carbon lies *trans* to oxygen connected to phosphorus. This sequence correlates perfectly with the electronegativities of these elements in the Periodic Table of elements. One exception in this series is the Ir-C bond formed by "carbene" carbon in complex **3**, which is *trans* to nitrogen (Table 1, second column for C^C cyclometalated ligand).

Photoluminescent and electroluminescent properties of cyclometalated complexes

Thin film absorption, luminescence, and excitation spectra of cyclometalated Ir compounds **5**, **7**, and **8** are shown in Fig. 6–8. Compound **3** showed thermal decomposition upon sublimation and was not studied for these properties. Luminescent wavelengths for all compounds studied are in the blue-green region. In all cases, the excitation spectra agree with the absorption spectra (Fig. 6–8). The peak luminescent wavelengths are summarized in Table 3. The similarity between the spectra indicates that the luminance mainly originates from the fluorinated phenylpyridine ligand perturbed by the charge transfer interaction with Ir. The presence of the third ligand has only a minor effect on the photo-luminescent spectrum. Compound **5** shows less vibronic structure than compounds **7** and



Fig. 6 Thin film absorption (+), excitation (•), and luminescence spectra (\bigcirc) of compound **5**, thickness 120 nm. Excitation spectrum was monitored at 500 nm. Luminescence spectrum was excited at 350 nm.



Fig. 7 Thin film absorption (+), excitation (\bullet) , and luminescence spectra (\bigcirc) of compound 7, thickness 150 nm. Excitation spectrum was monitored at 490 nm. Luminescence spectrum was excited at 350 nm.



Fig. 8 Thin film absorption (+), excitation (\bullet) , and luminescence spectra (\bigcirc) of compound **8**, thickness 150 nm. Excitation spectrum was monitored at 490 nm. Luminescence spectrum was excited at 350 nm.

Table 3 Summary of the photoluminescent and electroluminescent data for cyclometalated Ir compounds

	Peak electroluminescence efficiency/cd A ⁻¹	Electroluminescence peak wavelength/nm	Photoluminescence, peak wavelength/nm
Compound 5	5.5 at 15 V	597	497
Compound 7 Compound 8	2 at 17 V	500	492 493

8, which could indicate the existence of a stronger metalligand charge transfer interaction in that compound.

Preliminary device work was done using compounds 5, 7, and 8 as the electroluminescent emitters. The device configuration consists of ITO as the anode, MPMP (30 nm) as the hole transport material, Ir emitters (40 nm), DPA (10 nm) as the electron transport material, AlQ (30 nm) as the electron injection material, and LiF/Al as the cathode. Molecular structures of the materials used are shown in Scheme 6.



Compound 7 gives blue-green electroluminescence with a peak located at 492 nm. The maximal electroluminescence efficiency is 15 cd A^{-1} at 12 V. Compound 8 gives green electroluminescence with a peak located at 500 nm and a maximal electroluminescence efficiency of 2 cd A^{-1} at 17 V. Compound 5 gives yellowish electroluminescence at 597 nm with a peak efficiency of 5.5 cd A^{-1} at 15 V. These results are displayed in Fig. 9–11 and summarized in Table 3.



Fig. 9 (a) Electroluminescent efficiency vs voltage for compound 5; (b) comparison of photoluminescent and electroluminescent spectra of compound 5.



Fig. 10 (a) Electroluminescent efficiency *vs* voltage for compound **7**; (b) comparision of photoluminescent and electroluminescent spectra of compound **7**.





Fig. 11 (a) Electroluminescent efficiency *vs* voltage for compound 8; (b) comparision of photoluminescent and electroluminescent spectra of compound 8.

In spite of the similarity of their photoluminescent spectra, the electroluminescent spectra show more deviations from each other. In particular, compound 5 gives a yellowish emission which is red-shifted by about 100 nm from its photoluminescent spectrum. There is little doubt that this is either excimer or exciplex emission due to molecular interaction in the solid state. Since the same hole transport (MPMP) and electron transport (DPA) layers are used for all three OLED devices and all three Ir compounds have essentially the same lumiphore (phenylpyridine ligand), but only compound 5 shows the dramatic red-shifted electroluminescence, exciplex formation between the Ir compound and the neighboring layer can be ruled out as the origin of the red-shifted luminescence. The most likely mechanism is due to excimer formation between the Ir complexes. The difference between compounds 5, 7, and 8 may be attributed to different solid state packing induced by the presence of the third ligand which is different for each compound. Therefore although the solid state photoluminescent spectra of all three compounds are similar, originating from the same fluorinated phenylpyridine ligand, the presence of the third ligand does affect solid state packing and the electroluminescent spectra. Since the effect of the third ligand shows up in the electroluminescence spectra rather than the photoluminescence spectra, it suggests that the transport of electrons and holes are affected by the presence of the third ligand. The detailed mechanism for this difference still needs to be understood with further studies.

Conclusion

The application of sterically hindered electron poor 2phenylpyridine 1 in the tris-cyclometalation by IrCl₃ resulted in the isolation of the first mono-nuclear trivalent iridium complex 3 with four cyclometalated Ir-C bonds. One of the Ir-C bonds of the C^C ligand in 3 was found to be the shortest to date (1.977(4) Å) for a single bond between iridium and carbon atoms. The mode of coordination of the C^C ligand in 3 to iridium can be explained by various formulations. The first one is considering this ligand as a monoanionic chelating ligand, in which the second coordination site arises from a carbene or azomethine ylide. The azomethine ylide/carbene question is largerly one of semantics because these are just resonance structures. Singlet carbenes coordinated to metals show small valence angles at carbon and the carbon-metal interaction is often weak and long.⁷ As was mentioned above 3 contains the shortest single Ir-C bond, this is why it may not be completely fair to formulate this C^C ligand as containing center is incorporated in a six-membered ring and not in the, more typical, five-membered ring systems, for which the major structural data are available. Overall the best single picture may be a dianionic ligand making two "normal" Ir–C bonds, in which the ligand just happens to contain a pyridinium function that compensates for one negative charge on the iridium. The thermally stable to the sublimation tris- and biscyclometalated derivatives 5, 7, and 8 were used to construct

cyclometalated derivatives 5, 7, and 8 were used to construct LED devices. Preliminary results show that they emit yellow, bluegreen and green colors correspondingly with moderate efficiencies. Further work is required to optimize the device efficiency.

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Experimental

General procedures

All air-sensitive compounds were prepared and handled under a N_2/Ar atmosphere using standard Schlenk and inertatmosphere box techniques. Anhydrous solvents were used in the reactions. Solvents were distilled from drying agents or passed through columns under an argon or nitrogen atmosphere. 3,5-Bis(trifluoromethyl)phenylboronic acid, caesium fluoride, tris(dibenzylideneacetone) dipalladium(0), trimethylphosphate, 2,2,6,6-tetramethyl-heptane-3,5-dione, tetrabutylammo-

 Table 4
 COSY data for compound 1. 1-H Chemical shifts in F1

F2	Н3	Н5	H6	H9	H11		
F2_av	8.048 8.047 7.587 8.917	7.587 8.047 7.588 8.918	8.919 8.047 7.586 8.918	8.552 8.551 7.990	7.991 8.551 7.991	F1_av 8.047 7.587 8.918 8.551 7.990	F1 H3 H5 H6 H9 H11

 Table 5
 HSQC data for compound 1 (single-bond correlation)

nium hydroxide as 55–60% solution in water were purchased from Aldrich. Iridium(+3) chloride trihydrate was purchased from Alfa Aesar. 2-Chloro-4-trifluoromethyl-pyridine was purchased from Matrix Scientific.

Syntheses

2-(3,5-Bis(trifluoromethyl)phenyl)-4-trifluoromethylpyridine (1). 15.0 g (0.058 mol) of (3,5-bis(trifluoromethyl)phenyl)boronic acid, 10.00 g (0.055 mol) of 2-chloro-4-trifluoromethylpyridine, 2.66 g (0.0029 mol) of tris(dibenzylideneacetone)dipalladium(0), 1.62 g (0.00698 mol) of di-tert-butyl-trimethylsilylmethylphosphine, 10.60 g (0.0698 mol) of caesium fluoride and 150 ml of dioxane were stirred at room temperature for 24 hours. The resulting mixture was poured into 200 ml of water and extracted twice with 200 ml of methylene chloride. The organic phase was dried on magnesium sulfate overnight and filtered. The solvent was removed on a rotovapor and the residue was purified by vacuum distillation. Yield of 2-(3,5-bis(trifluoromethyl)phenyl)-4trifluoromethylpyridine was 18.0 g (91.0%) as a colorless liquid with bp 84-86 °C/0.1 mmHg. ¹⁹F NMR (377 MHz, CD₂Cl₂) $\delta = -62.37$ (s, 6F, CF3), -64.30 (s, 3F, CF3). Anal. Calcd. for C₁₄H₆F₉N (mol. wt.: 359.19): C, 46.81; H, 1.68; F, 47.60; N, 3.90. Found: C, 46.89; H, 1.92; F, 47.50; N, 4.15%. LC/MS calculated for C₁₄H₆F₉N: 359.04. Found: 359.04.

Two-dimensional ¹H and ¹³C NMR correlation data for compound **1** (Tables 4–6), numbering of atoms in **1** is shown in Scheme 7.

Cyclometalation of 2-(3,5-bis(trifluoromethyl)phenyl)-4-trifluoromethylpyridine (1) by $Ir^{III}Cl_3$ in the presence of AgOC(O)CF₃. 13.04 g (0.0363 mol) of 2-(3,5-bis(trifluoromethyl)phenyl)-4trifluoromethylpyridine, 2.13 g (0.00604 mol) of iridium(III) chloride trihydrate, 4.80 g (0.0217 mol) of silver trifluoroacetate and 40 ml of water were stirred at room temperature under a flow

 F2	Н3	Н5	H6	H9	H11			
F2_ppm	8.040 116.655	7.580 119.771	8.911 151.787	8.545 127.680	7.983	13C 116.655 119.771 151.787 127.680 123.874	F1 C3 C5 C6 C9 C11	

Table 6 HMBC data for compound 1 (multiple-bond correlation)

F2	Н3	H5	H6	H9	H11		
F2_av	8.042 155.763 116.635 140.144 119.751	7.582 155.763 116.632 140.127 119.745	8.914 155.775 116.635 140.187 119.767	8.547 155.774 116.655	7.985 155.769	13C 155.769 116.639 140.153 119.754	F1 C2 C3 C4 C5
	151.758 123.435 140.547	151.763 123.454 140.581	151.771 123.461	140.562 127.639 132.796 123.848 124.016	140.565 127.645 132.795 123.845 124.020	151.764 123.450 140.564 127.642 132.796 123.846 124.018	C6 C7 C8 C9 C10 C11 C14



Scheme 7 Numbering of atoms in 1 for ¹H and ¹³C NMR correlation experiments.

of nitrogen for 12 hours. Then, the reaction mixture was placed into a heating bath and the temperature of the bath was gradually increased to 180 °C during 10 hours. The formed trifluoroacetic acid and water were removed from the reaction mixture by the constant flow of nitrogen. Heating was continued for the next 48 hours at the above conditions. Then, the reaction mixture was cooled to ambient temperature and dissolved in 200 ml of methylene chloride. The concentrated filtrate yielded silver cluster 2 upon standing for 12 hours at room temperature. The yield of silver cluster 2 was 2.47 g (9.8%) as colorless crystals with no mp until 200 °C. 1H NMR (500 MHz, CD2Cl2, TMS) & 7.50-9.00 (m, 12H, arom-H). ¹⁹F NMR (377 MHz, CD₂Cl₂) δ -63.72 (s, 12F, CF3), -65.67 (s, 6F, CF3), -73.60 (s, 9F, CF3). Anal. Calcd. for C₃₄H₁₂Ag₃F₂₇N₂O₆: (mol. wt.: 1381.03): C, 29.57; H, 0.88; N, 2.03. Found: C, 29.74; H, 1.03; N, 2.33%. The structure was proven by X-ray analysis. The residue from the crystallization was purified by chromatography on silica gel with petroleum ether (bp 35-60 °C)ethyl ether 10 : 1 as eluent.

Bis[4,6-bis(trifluoromethyl)-2-(4-trifluoromethyl-2-pyridinylκ*N*)**phenyl-κ***C*][**bisphenylpyridine]iridium (3).** The yield of **3** (from the above cyclometalation of **1**) was 0.74 g (4.8%) as dark gold crystals from pentane with no mp until 200 °C. ¹H NMR (500 MHz, CD₂Cl₂) δ 0.90–1.12 (br, 12H, pentane), 7.30 (m, 2H, arom-H), 7.59 (m, 3H, arom-H), 7.80 (m, 2H, arom-H), 8.05 (m, 4H, arom-H), 8.20 (m, 2H, arom-H), 8.40 (m, 3H, arom-H), 8.63 (m, 2H, arom-H), 8.90 (m, 1H, arom-H). ¹⁹F NMR (377 MHz, CD₂Cl₂) δ –57.68 to –66.64 (m, 36F, CF3). Anal. Calcd. for the pentane adduct $C_{61}H_{31}F_{36}IrN_4$ (mol. wt.: 1696.09): C, 43.20; H, 1.84; N, 3.30. Found: C, 43.41; H, 1.74; N, 3.59%. The structure was proven by X-ray analysis.

2-(3,5-Bis(trifluoromethyl)phenyl)-6-[2,4-bis(trifluoromethyl)-6-(4-trifluoromethylpyridin-2-yl)phenyl]-4-trifluoromethylpyridine

(4). The yield of 4 (from the above cyclometalation of 1) was 0.46 g (3.5%) as white crystals from pentane with mp 65.2 °C. ¹H NMR (500 MHz, CD₂Cl₂, TMS) δ 7.20 (s, 2H, arom-H), 7.51 (s, 1H, arom-H), 7.90 (m, 2H, arom-H), 8.23 (m, 2H, arom-H), 8.35 (s, 2H, arom-H), 8.63 (s, 1H, arom-H). ¹⁹F NMR (377 MHz, CD₂Cl₂) δ –57.70 (s, 3F, CF₃), –63.70 (s, 3F, CF₃), –63.78 (s, 6F, CF₃), –65.69 (s, 3F, CF₃), –65.98 (s, 3F, CF₃). Anal. Calcd. for C₂₈H₁₀F₁₈N₂ (mol. wt.: 716.36): C, 46.95; H, 1.41; N, 3.91. Found: C, 47.03; H, 1,52; N, 4.27%. LC/MS calculated for C₂₈H₁₀F₁₈N₂: 716,06. Found: 716,06. The structure was proven by X-ray analysis.

Tris[4,6-bis(trifluoromethyl)-2-(4-trifluoromethyl-2-pyridinyl- κN)phenyl- κC [iridium (5). The yield of 5 (from the above cyclometalation of 1) was 1.24 g (8.1%) as colorless crystals with

no mp until 200 °C. ¹H NMR (500 MHz, CD₂Cl₂, TMS) δ 6.90 (m, 2H, arom-H), 7.30 (s, 2H, arom-H), 7.52 (s, 1H, arom-H), 7.70–7.90 (m, 3H, arom-H), 8.10–8.40 (m, 7H, arom-H). ¹⁹F NMR (377 MHz, CD₂Cl₂) δ –59.20 to –65.91 (m, 27F, CF₃). Anal. Calcd. for C₄₂H₁₅F₂₇IrN₃ (mol. wt.: 1266.76): C, 39.82; H, 1.19; N, 3.32. Found: C, 40.07; H, 1.38; N, 3.50%. The structure was proven by X-ray analysis.

Di-μ-chlorotetrakis[4,6-bis(trifluoromethyl)-2-(4-trifluoromethyl-2-pyridinyl- κ N)phenyl- κ C]diiridium (6). 5.0 g (0.0139 mol) of 2-(3,5-bis(trifluoromethyl)phenyl)-4-trifluoromethylpyridine, 2.21 g (0.00627 mol) of iridium(III) chloride trihydrate, and 40 ml of trimethylphosphate was stirred at 90 °C for 6 hours under the flow of nitrogen. The resulting solution was poured into 200 ml of diethyl ether. The formed precipitate was filtered off and dried under 1.0 mmHg vacuum. The yield of the dimer was 5.83 g (88.7%) as a yellow powder. The crude chlorodimer was used "as is" in the next steps according to established practice in cyclometalated iridium research.³

Bis[4,6-bis(trifluoromethyl)-2-(4-trifluoromethyl-2-pyridinyl- κN)phenyl- κC](2,2,6,6-tetramethyl-3,5-heptanedionato- $\kappa O,\kappa O'$)iridium (7). 2.68 g (0.00142 mol) of 6, 3.0 g (0.0163) of 2,2,6,6tetramethyl-heptane-3,5-dione, 4.0 g of a 55-60% solution of tetrabutylammonium hydroxide in water and 20 ml of THF were refluxed for 2 hours under argon atmosphere. The reaction mixture was poured into 200 ml of water and extracted twice with 200 ml of diethyl ether. The extracts were dried over magnesium sulfate overnight. The solvent was removed in a rotavapor and the residue was purified by chromatography on silica gel with petroleum ether (bp 35–60 °C)–ethyl ether 10 : 0.5 as eluent. The yield of 7 was 2.41 g (77.7%) as a yellow solid with no mp until 200 °C. ¹H NMR (500 MHz, CD₂Cl₂, TMS) δ 0.80 (s, 18H, t-Bu), 5.45 (s, 1H, H-C=), 7.20 (m, 2H, arom-H), 7.55 (m, 2H, arom-H), 8.15 (m, 6H, arom-H). ¹⁹F NMR (377 MHz, CD_2Cl_2) δ -60.44 (s, 6F, CF3), -63.07 (s, 6F, CF3), -65.74 (s, 6F, CF3). Anal. Calcd. for C₃₉H₂₉F₁₈IrN₂O₂ (mol. wt.: 1091.85): C, 42.90; H, 2.68; N, 2.57. Found: C, 43.25; H, 2.87; N, 2.71%. The structure was proven by X-ray analysis (Fig. 4).

Di-μ-(dimethylphosphato- $\kappa O, \kappa O''$)tetrakis[4,6-bis(trifluoromethyl)2-(4-trifluoromethyl-2-pyridinyl- κN)phenyl- κC]diiridium (8). 2.50 g (0.00132 mol) of 6, and 70 ml of trimethylphosphate was stirred at 90 °C for 7 days under a flow of nitrogen. The formed precipitate was filtered off and dried under 1.0 mmHg vacuum. Yield of 8 was 2.50 g (91.3%) as a bright yellow solid with no mp until 200 °C. ¹H NMR (500 MHz, CDCl₃) δ 3.70 (br, 12H, MeO), 7.40 (m, 4H, arom-H), 7.50 (m, 4H, arom-H), 8.10 (m, 4H, arom-H), 8.20 (m, 4H, arom-H), 9.00 (m, 4H, arom-H). ¹⁹P NMR (377 MHz, CDCl₃) δ 6.16 (s, 2P, OP(O)(OMe)₂). Anal. Calcd. for C₆₀H₃₂F₃₆Ir₂N₄O₈P₂ (mol. wt.: 2067.24): C, 34.86; H, 1.56; N, 2.71. Found: C, 34.90; H, 1.83; N, 2.76%. The structure was proven by X-ray analysis (Fig. 5).

X-Ray crystallography

Crystallographic data for compounds **2–4** and **5**, **7**, **8** are given in Tables 7 and 8.

CCDC reference numbers 257681-257686.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b514797b

 Table 7
 Summary of crystal data, data collection, and structural refinement parameters of 2–4

		2	3	4
Empi	rical formula	C ₃₄ H ₁₂ Ag ₃ F ₂₇ N ₂ O ₆	$C_{61}H_{31}F_{36}IrN_4$	$C_{28}H_{10}F_{18}N_2$
FŴ		1381.07	1696.1	716.38
Cryst	al color, form	Colourless plate	Gold block	Colourless block
Cryst	al system	Triclinic	Triclinic	Triclinic
Space	e group	$P\overline{1}$	$P\overline{1}$	PĪ
a/Å		8.2935(15)	12.9220(13)	10.4708(12)
b/Å		12.797(2)	15.9360(16)	11.8225(14)
c/Å		19.913(3)	17.7587(18)	12.6383(15)
$a/^{\circ}$		82.984(3)	67.8845(17)	104.597(2)
ß/°		83.660(3)	72.2741(17)	105.654(2)
v/°		83.647(3)	69.862(2)	105.656(2)
V/Å	3	2074.6(6)	3115.9(5)	1358.6(3)
Z		2	2	2
ρ/gc	m^{-3}	2.211	1.808	1.751
μ/mr	n^{-1}	1.572	2.295	0.191
F(000))	1324	1652	708
Cryst	al size/mm	$0.42 \times 0.42 \times 0.05$	$0.28 \times 0.20 \times 0.12$	$0.50 \times 0.36 \times 0.35$
Τ/°C	2	-100	-100	-100
Scan	mode	ω	ω	ω
Detec	ctor	Bruker-CCD	Bruker-CCD	Bruker-CCD
$\theta_{\rm max}$ /	0	28.28	28.3	28.31
No. c	bsrvd. refs	13789	18319	9024
No. u	iniq. refs	9463	13836	6203
R _{merg}	e	0.014	0.020	0.013
No. p	params	699	921	453
S^{b}		1.041	1.041	1.048
R ind	lices $[I > 2\sigma(I)]^a$	wR2 = 0.070, R1 = 0.028	wR2 = 0.094, R1 = 0.038	wR2 = 0.131, R1 = 0.050
R ind	lices (all data) ^a	wR2 = 0.073, R1 = 0.034	wR2 = 0.101, R1 = 0.048	wR2 = 0.146, R1 = 0.065
Max	diff peak, hole/e Å ⁻³)	0.621, -0.665	2.819, -0.668	0.418, -0.456

 ${}^{a}R1 = \sum ||F_{\circ}| - |F_{c}|| / \sum |F_{\circ}|, wR2 = \{\sum [w(F_{\circ}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{\circ}^{2})^{2}] \}^{1/2} \text{ (sometimes denoted as } R_{w}2). {}^{b}\text{GooF} = S = \{\sum [w(F_{\circ}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}, where n \text{ is the number of reflections, and } p \text{ is the total number of refined parameters.}$

Table 8Summary of crystal data, data collection, and structural refinement parameters of 5, 7 and 8

	5	7	8
Empirical formula FW Crystalcolor, form Crystal system Space group a/Å b/Å c/Å $a/^{\circ}$ $\beta/^{\circ}$ $\gamma/^{\circ}$ $V/Å^{3}$ Z $\rho/g \text{ cm}^{-3}$) μ/mm^{-1} F(000)	$\begin{array}{c} C_{84}H_{30}F_{54}Ir_2N_6\\ 2533.54\\ Gold \ prism\\ Monoclinic\\ C2\\ 41.862(4)\\ 9.2252(9)\\ 22.004(2)\\ 90\\ 99.2780(18)\\ 90\\ 8386.5(14)\\ 4\\ 2.007\\ 3.343\\ 4864\\ \end{array}$	$\begin{array}{c} C_{39}H_{29}F_{18}IrN_2O_2\\ 1091.84\\ Gold plate\\ Orthorhombic\\ Pbca\\ 20.852(4)\\ 16.227(3)\\ 24.092(4)\\ 90\\ 90\\ 90\\ 8152(3)\\ 8\\ 1.779\\ 3.395\\ 4256\\ \end{array}$	$\begin{array}{c} C_{34}H_{30}F_{18}IrN_2O_{12}P_3\\ 1285.71\\ \text{Yellow plate}\\ \text{Triclinic}\\ P\bar{1}\\ 10.923(6)\\ 14.898(8)\\ 15.863(8)\\ 64.147(8)\\ 85.432(9)\\ 85.384(9)\\ 2313(2)\\ 2\\ 1.846\\ 3.122\\ 1256\\ \end{array}$
Crystal size/mm $T/^{\circ}$ C Scan mode Detector $\theta_{max}/^{\circ}$ No. obsrvd. refs No. uniq. refs R_{merge} No. params S^{b} R indices $[I > 2\sigma(I)]^{a}$ R indices (all data) ^{a} Max diff peak, hole/e Å ⁻³)	$\begin{array}{c} 0.28 \times 0.28 \times 0.10 \\ -100 \\ \omega \\ \\ \text{Bruker-CCD} \\ 28.28 \\ 22126 \\ 11872 \\ 0.029 \\ 1316 \\ 1.026 \\ wR2 = 0.072, R1 = 0.032 \\ wR2 = 0.075, R1 = 0.037 \\ 2.596, -0.793 \end{array}$	$\begin{array}{l} 0.24 \times 0.14 \times 0.05 \\ -100 \\ \varpi \\ \\ \text{Bruker-CCD} \\ 28.27 \\ 50219 \\ 9831 \\ 0.074 \\ 565 \\ 1.01 \\ wR2 = 0.092, R1 = 0.041 \\ wR2 = 0.110, R1 = 0.081 \\ 2.967, -1.397 \end{array}$	0.14 × 0.06 × 0.01 -100 ω Bruker-CCD 28.39 28327 10851 0.0809 666 1.021 wR2 = 0.129, R1 = 0.058 wR2 = 0.161, R1 = 0.118 2.995, -1.587

 ${}^{a}R1 = \sum ||F_{o}| - |F_{c}|/\sum |F_{o}|, wR2 = \{\sum [w(F_{o}^{2} - F_{c}^{2})^{2}]/\sum [w(F_{o}^{2})^{2}]\}^{1/2} \text{ (sometimes denoted as } R_{w}2\text{).} {}^{b}\text{GooF} = S = \{\sum [w(F_{o}^{2} - F_{c}^{2})^{2}]/(n-p)\}^{1/2}, where n \text{ is the number of reflections, and } p \text{ is the total number of refined parameters.} \}$

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