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**Grushin et al.**

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(54) **ELECTROLUMINESCENT IRIIDIUM COMPOUNDS WITH FLUORINATED PHENYLPYRIDINES, PHENYLPYRIMIDINES, AND PHENYLQUINOLINES AND DEVICES MADE WITH SUCH COMPOUNDS**

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(58) **Field of Search** ..... 546/2; 556/40, 556/136, 137; 313/504; 428/690, 917; 257/40, 257/98; 438/29, 69, 82, 99

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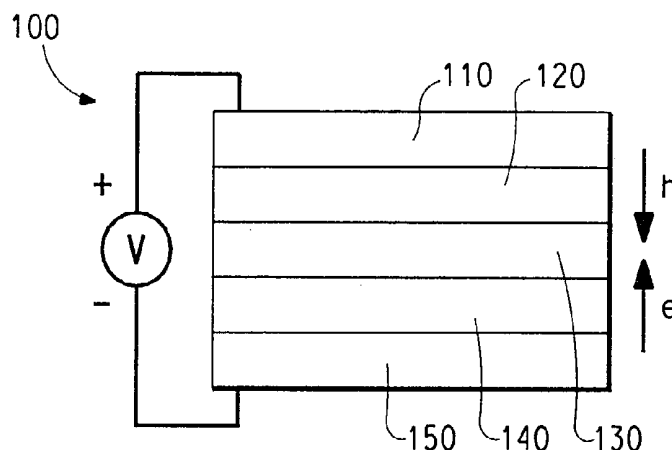
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*Primary Examiner*—Erik Kielin

(57) **ABSTRACT**

The present invention is generally directed to electroluminescent Ir(III) compounds, the substituted 2-phenylpyridines, phenylpyrimidines, and phenylquinolines that are used to make the Ir(III) compounds, and devices that are made with the Ir(III) compounds.

**1 Claim, 1 Drawing Sheet**



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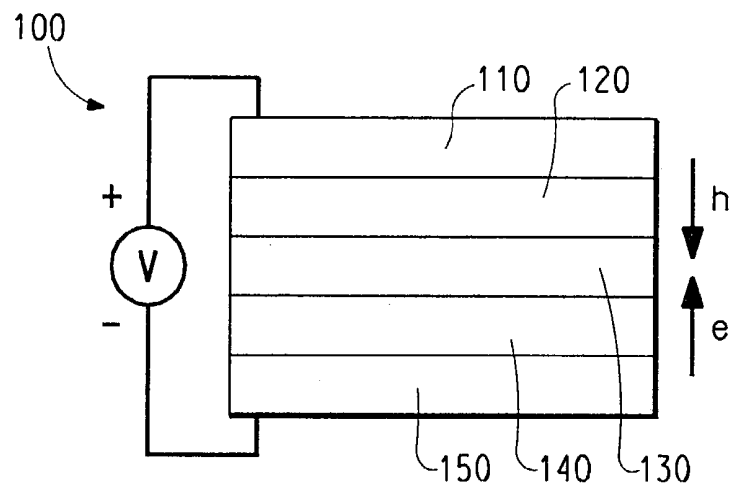


FIG. 1

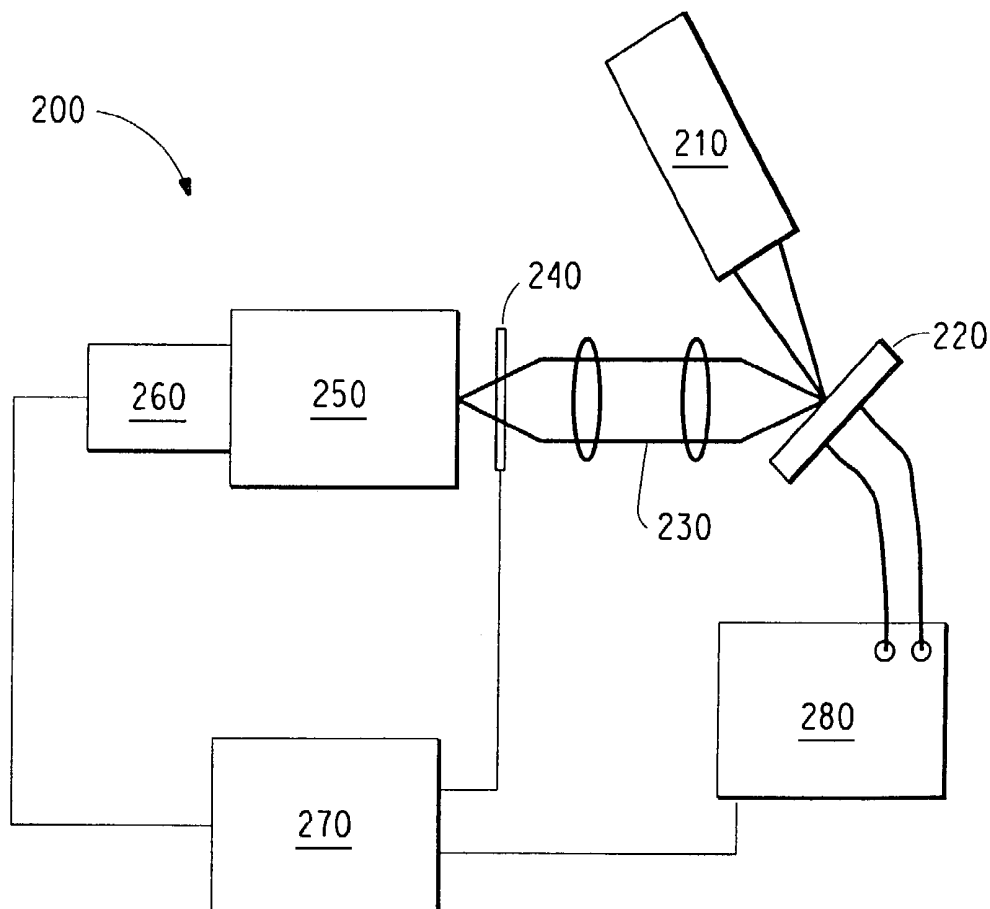


FIG. 2

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**ELECTROLUMINESCENT IRIIDIUM  
COMPOUNDS WITH FLUORINATED  
PHENYLPYRIDINES,  
PHENYLPYRIMIDINES, AND  
PHENYLQUINOLINES AND DEVICES MADE  
WITH SUCH COMPOUNDS**

**BACKGROUND OF THE INVENTION**

**1. Field of the Invention**

This invention relates to electroluminescent complexes of iridium(III) with fluorinated phenylpyridines, phenylpyrimidines, and phenylquinolines. It also relates to electronic devices in which the active layer includes an electroluminescent Ir(III) complex.

**2. Description of the Related Art**

Organic electronic devices that emit light, such as light-emitting diodes that make up displays, are present in many different kinds of electronic equipment. In all such devices, an organic active layer is sandwiched between two electrical contact layers. At least one of the electrical contact layers is light-transmitting so that light can pass through the electrical contact layer. The organic active layer emits light through the light-transmitting electrical contact layer upon application of electricity across the electrical contact layers.

It is well known to use organic electroluminescent compounds as the active component in light-emitting diodes. Simple organic molecules such as anthracene, thiadiazole derivatives, and coumarin derivatives are known to show electroluminescence. Semiconductive conjugated polymers have also been used as electroluminescent components, as has been disclosed in, for example, Friend et al., U.S. Pat. No. 5,247,190, Heeger et al., U.S. Pat. No. 5,408,109, and Nakano et al., Published European Patent Application 443 861. Complexes of 8-hydroxyquinolate with trivalent metal ions, particularly aluminum, have been extensively used as electroluminescent components, as has been disclosed in, for example, Tang et al., U.S. Pat. No. 5,552,678.

Burrows and Thompson have reported that fac-tris(2-phenylpyridine) iridium can be used as the active component in organic light-emitting devices. (*Appl. Phys. Lett.* 1999, 75, 4.) The performance is maximized when the iridium compound is present in a host conductive material. Thompson has further reported devices in which the active layer is poly(N-vinyl carbazole) doped with fac-tris[2-(4',5'-difluorophenyl)pyridine-C<sup>2</sup>,N]iridium(III). (*Polymer Preprints* 2000, 41(1), 770.)

However, there is a continuing need for electroluminescent compounds having improved efficiency.

**SUMMARY OF THE INVENTION**

The present invention is directed to an iridium compound (generally referred as "Ir(III) compounds") having at least two 2-phenylpyridine ligands in which there is at least one fluorine or fluorinated group on the ligand. The iridium compound has the following First Formula:



where:

x=0 or 1, y=0, 1 or 2, and z=0 or 1, with the proviso that:

x=0 or y+z=0 and

when y=2 then z=0;

L'=a bidentate ligand or a monodentate ligand, and is not a phenylpyridine, phenylpyrimidine, or phenylquinoline; with the proviso that:

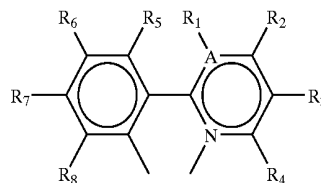
2

when L' is a monodentate ligand, y+z=2, and

when L' is a bidentate ligand, z=0;

L''=a monodentate ligand, and is not a phenylpyridine, and phenylpyrimidine, or phenylquinoline; and

L<sup>a</sup>, L<sup>b</sup> and L<sup>c</sup> are alike or different from each other and each of L<sup>a</sup>, L<sup>b</sup> and L<sup>c</sup> has structure (I) below:



(I)

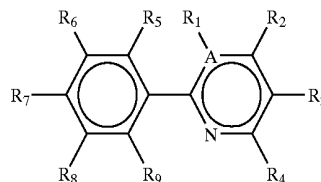
wherein:

adjacent pairs of R<sub>1</sub>-R<sub>4</sub> and R<sub>5</sub>-R<sub>8</sub> can be joined to form a five- or six-membered ring,

at least one of R<sub>1</sub>-R<sub>8</sub> is selected from F, C<sub>n</sub>F<sub>2n+1</sub>, OC<sub>n</sub>F<sub>2n+1</sub>, and OCF<sub>2</sub>X, where n=1-6 and X=H, Cl, or Br, and

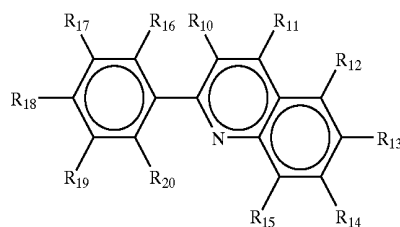
A=C or N, provided that when A=N, there is no R<sub>1</sub>.

In another embodiment, the present invention is directed to substituted 2-phenylpyridine, phenylpyrimidine, and phenylquinoline precursor compounds from which the above Ir(III) compounds are made. The precursor compounds have a structure (II) or (III) below:



(II)

where A and R<sub>1</sub>-R<sub>8</sub> are as defined in structure (I) above, and R<sub>9</sub> is H.



(III)

where:

at least one of R<sub>10</sub>-R<sub>19</sub> is selected from F, C<sub>n</sub>F<sub>2n+1</sub>, OC<sub>n</sub>F<sub>2n+1</sub>, and OCF<sub>2</sub>X, where n=1-6 and X=H, Cl, or Br, and R<sub>20</sub> is H.

It is understood that there is free rotation about the phenyl-pyridine, phenyl-pyrimidine and the phenyl-quinoline bonds. However, for the discussion herein, the compounds will be described in terms of one orientation.

In another embodiment, the present invention is directed to an organic electronic device having at least one emitting layer comprising the above Ir(III) compound, or combinations of the above Ir(III) compounds.

As used herein, the term "compound" is intended to mean an electrically uncharged substance made up of molecules that further consist of atoms, wherein the atoms cannot be separated by physical means. The term "ligand" is intended to mean a molecule, ion, or atom that is attached to the coordination sphere of a metallic ion. The term "complex", when used as a noun, is intended to mean a compound having at least one metallic ion and at least one ligand. The term "group" is intended to mean a part of a compound, such a substituent in an organic compound or a ligand in a complex. The term "facial" is intended to mean one isomer of a complex,  $\text{Ma}_3\text{b}_3$ , having octahedral geometry, in which the three "a" groups are all adjacent, i.e. at the corners of one face of the octahedron. The term "meridional" is intended to mean one isomer of a complex,  $\text{Ma}_3\text{b}_3$ , having octahedral geometry, in which the three "a" groups occupy three positions such that two are trans to each other. The phrase "adjacent to," when used to refer to layers in a device, does not necessarily mean that one layer is immediately next to another layer. On the other hand, the phrase "adjacent R groups," is used to refer to R groups that are next to each other in a chemical formula (i.e., R groups that are on atoms joined by a bond). The term "photoactive" refers to any material that exhibits electroluminescence and/or photosensitivity.

#### DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram of a light-emitting device (LED).

FIG. 2 is a schematic diagram of an LED testing apparatus.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The Ir(III) compounds of the invention have the First Formula  $\text{Ir}(\text{III})\text{L}^a\text{L}^b\text{L}^c\text{L}^d$ , above.

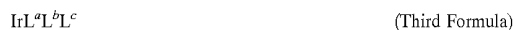
The above Ir(III) compounds are frequently referred to as cyclometalated complexes: Ir(III) compounds having the following Second Formula is also frequently referred to as a bis-cyclometalated complex:



where:

y, z,  $\text{L}^a$ ,  $\text{L}^b$ ,  $\text{L}^c$ , and  $\text{L}^d$  are as defined in the First Formula above.

Ir(III) compounds having the following Third Formula is also frequently referred to as a tris-cyclometalated complex:



where:

$\text{L}^a$ ,  $\text{L}^b$  and  $\text{L}^c$  are as defined in the First Formula described above.

The preferred-cyclometalated complexes are neutral and non-ionic, and can be sublimed intact. Thin films of these materials obtained via vacuum deposition exhibit good to excellent electroluminescent properties. Introduction of fluorine substituents into the ligands on the iridium atom increases both the stability and volatility of the complexes. As a result, vacuum deposition can be carried out at lower temperatures and decomposition of the complexes can be avoided. Introduction of fluorine substituents into the ligands can often reduce the non-radiative decay rate and the self-quenching phenomenon in the solid state. These reductions can lead to enhanced luminescence efficiency. Variation of substituents with electron-donating and electron-

withdrawing properties allows for fine-tuning of electroluminescent properties of the compound and hence optimization of the brightness and efficiency in an electroluminescent device.

While not wishing to be bound by theory, it is believed that the emission from the iridium compounds is ligand-based, resulting from metal-to-ligand charge transfer. Therefore, compounds that can exhibit electroluminescence include those of compounds of the Second Formula  $\text{IrL}^a\text{L}^b\text{L}^c\text{L}^d$ , above, and the Third Formula  $\text{IrL}^a\text{L}^b\text{L}^c$ , above, where all  $\text{L}^a$ ,  $\text{L}^b$ , and  $\text{L}^c$  in the Third Formula are phenylpyridines, phenylpyrimidines, or phenylquinolines. The  $\text{R}_1$ - $\text{R}_8$  groups of structures (I) and (II), and the  $\text{R}_{10}$ - $\text{R}_{19}$  groups of structure (III) above may be chosen from conventional substituents for organic compounds, such as alkyl, alkoxy, halogen, nitro, and cyano groups, as well as fluoro, fluorinated alkyl and fluorinated alkoxy groups. The groups can be partially or fully fluorinated (perfluorinated). Preferred iridium compounds have all  $\text{R}_1$ - $\text{R}_8$  and  $\text{R}_{10}$ - $\text{R}_{19}$  substituents selected from fluoro, perfluorinated alkyl ( $\text{C}_n\text{F}_{2n+1}$ ) and perfluorinated alkoxy groups ( $\text{OC}_n\text{F}_{2n+1}$ ), where the perfluorinated alkyl and alkoxy groups have 1-6 carbon atoms, or a group of the formula  $\text{OCF}_2\text{X}$ , where  $\text{X}=\text{H}$ ,  $\text{Cl}$ , or  $\text{Br}$ .

It has been found that the electroluminescent properties of the cyclometalated iridium complexes are poorer when any one or more of the  $\text{R}_1$ - $\text{R}_8$  and  $\text{R}_{10}$ - $\text{R}_{19}$  groups is a nitro group. Therefore, it is preferred that none of the  $\text{R}_1$ - $\text{R}_8$  and  $\text{R}_{10}$ - $\text{R}_{19}$  groups is a nitro group.

The nitrogen-containing ring can be a pyridine ring, a pyrimidine or a quinoline. It is preferred that at least one fluorinated substituent is on the nitrogen-containing ring; most preferably  $\text{CF}_3$ .

Any conventional ligands known to transition metal coordination chemistry is suitable as the  $\text{L}'$  and  $\text{L}''$  ligands. Examples of bidentate ligands include compounds having two coordinating groups, such as ethylenediamine and acetylacetonate, which may be substituted. Examples of monodentate ligands include chloride and nitrate ions and mono-amines. It is preferred that the iridium complex be neutral and sublimable. If a single bidentate ligand is used, it should have a net charge of minus one (-1). If two monodentate ligands are used, they should have a combined net charge of minus one (-1). The bis-cyclometalated complexes can be useful in preparing tris-cyclometalated complexes where the ligands are not all the same.

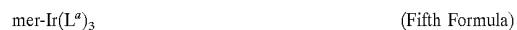
In a preferred embodiment, the iridium compound has the Third Formula  $\text{IrL}^a\text{L}^b\text{L}^c$  as described above.

In a more preferred embodiment,  $\text{L}^a=\text{L}^b=\text{L}^c$ . These more preferred compounds frequently exhibit a facial geometry, as determined by single crystal X-ray diffraction, in which the nitrogen atoms coordinated to the iridium are trans with respect to carbon atoms coordinated to the iridium. These more preferred compounds have the following Fourth Formula:



where  $\text{L}^a$  has structure (I) above.

The compounds can also exhibit a meridional geometry in which two of the nitrogen atoms coordinated to the iridium are trans to each other. These compounds have the following Fifth Formula:



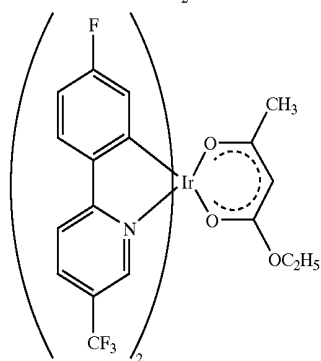
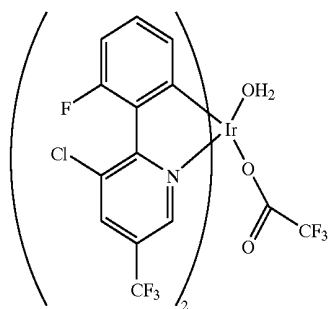
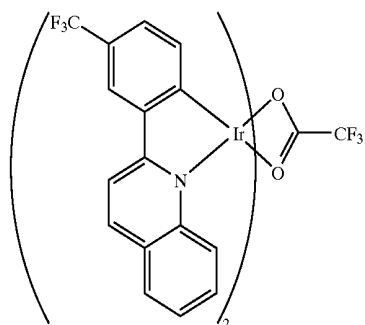
where  $\text{L}^a$  has structure (I) above.

Examples of compounds of the Fourth Formula and Fifth Formula above are given in Table 1 below:

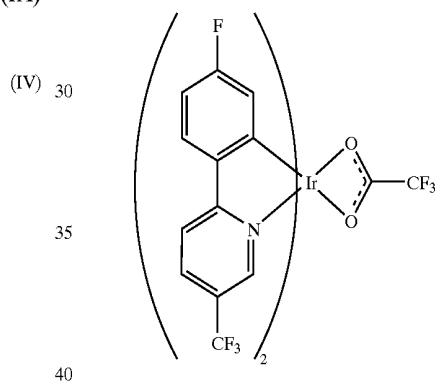
TABLE 1

Compound	A	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	R <sub>7</sub>	R <sub>8</sub>	Formula
1-a	C	H	H	CF <sub>3</sub>	H	H	H	H	H	Fourth
1-b	C	H	H	CF <sub>3</sub>	H	H	H	F	H	Fourth
1-c	C	H	H	CF <sub>3</sub>	H	F	H	H	H	Fourth
1-d	C	H	H	H	H	F	H	H	H	Fourth
1-e	C	H	H	CF <sub>3</sub>	H	H	CF <sub>3</sub>	H	H	Fourth
1-f	C	H	H	H	H	H	CF <sub>3</sub>	H	H	Fourth
1-g	C	H	H	H	H	H	H	F	H	Fourth
1-h	C	Cl	H	CF <sub>3</sub>	H	H	H	H	H	Fourth
1-i	C	H	H	CF <sub>3</sub>	H	H	H	OCH <sub>3</sub>	H	Fourth
1-j	C	H	H	CF <sub>3</sub>	H	H	F	H	H	Fourth
1-k	C	H	H	NO <sub>2</sub>	H	H	CF <sub>3</sub>	H	H	Fourth
1-l	C	H	H	CF <sub>3</sub>	H	H	H	OCF <sub>3</sub>	H	Fourth
1-m	N	—	CF <sub>3</sub>	H	H	H	H	F	H	Fourth
1-q	C	H	H	CF <sub>3</sub>	H	H	OCH <sub>3</sub>	H	H	Fourth
1-r	C	H	OCH <sub>3</sub>	H	H	H	H	CF <sub>3</sub>	H	Fourth
1-s	C	H	H	H	H	F	H	F	H	Fourth and Fifth
1-t	C	H	H	CF <sub>3</sub>	H	H	F	H	F	Fifth
1-u	C	H	H	CF <sub>3</sub>	H	F	H	F	H	Fifth
1-v	C	H	H	CF <sub>3</sub>	H	H	H	F	H	Fifth

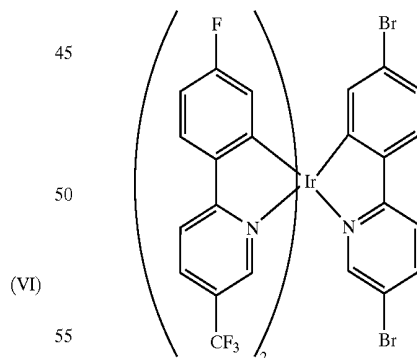
Examples compounds of the Second Formula  $\text{IrL}^a\text{L}^b\text{L}^c$  above include compounds 1-n, 1-o, 1-p, 1-w and 1-x, respectively having structure (IV), (V), (VI), (IX) and (X) below:



(IV) 30 -continued

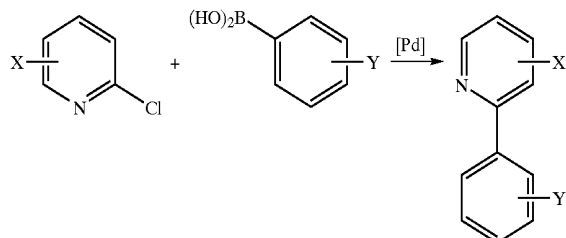


(V) 45 (X)



The iridium complexes of the Third Formula  $\text{IrL}^a\text{L}^b\text{L}^c$  above are generally prepared from the appropriate substituted 2-phenylpyridine, phenylpyrimidine, or phenylquinoline. The substituted 2-phenylpyridines, phenylpyrimidines, and phenylquinolines, as shown in Structure (II) above, are prepared, in good to excellent yield, using the Suzuki coupling of the substituted 2-chloropyridine, 2-chloropyrimidine or 2-chloroquinoline with arylboronic acid as

described in O. Lohse, P. Thevenin, E. Waldvogel *Synlett*, 1999, 45–48. This reaction is illustrated for the pyridine derivative, where X and Y represent substituents, in Equation (1) below:



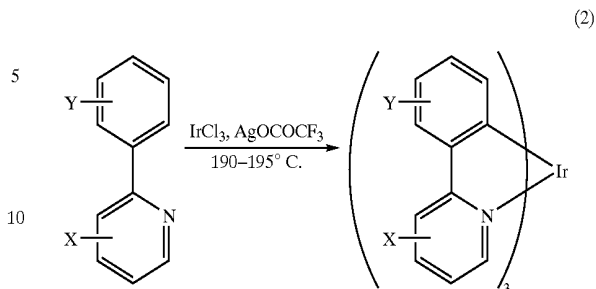
Examples of 2-phenylpyridine and 2-phenylpyrimidine compounds, having structure (II) above, are given in Table 2 below:

TABLE 2

Compound	A	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	R <sub>7</sub>	R <sub>8</sub>	R <sub>9</sub>
2-a	C	H	H	CF <sub>3</sub>	H	F	H	H	H	H
2-b	C	H	H	CF <sub>3</sub>	H	H	CF <sub>3</sub>	H	H	H
2-c	C	H	H	NO <sub>2</sub>	H	H	CF <sub>3</sub>	H	H	H
2-d	C	H	H	CF <sub>3</sub>	H	H	F	H	H	H
2-e	C	H	H	CF <sub>3</sub>	H	H	H	CH <sub>3</sub> O	H	H
2-f	C	Cl	H	CF <sub>3</sub>	H	H	H	H	H	H
2-g	C	H	H	H	CH <sub>3</sub>	H	H	F	H	H
2-h	N	—	H	H	H	H	H	F	H	H
2-i	C	H	H	CF <sub>3</sub>	H	H	H	CF <sub>3</sub> O	H	H
2-j	N	—	CF <sub>3</sub>	H	H	F	H	H	H	H
2-k	C	H	H	CF <sub>3</sub>	H	H	H	F	H	H
2-l	C	CF <sub>3</sub>	H	H	H	H	H	H	H	H
2-m	C	Cl	H	CF <sub>3</sub>	H	H	H	F	H	H
2-n	C	CF <sub>3</sub>	H	H	H	H	H	F	H	H
2-o	C	CF <sub>3</sub>	H	H	H	H	H	CH <sub>3</sub> O	H	H
2-p	C	Cl	H	CF <sub>3</sub>	H	H	H	CH <sub>3</sub> O	H	H
2-q	N	—	CF <sub>3</sub>	H	H	H	H	F	H	H
2-r	C	Cl	H	CF <sub>3</sub>	H	H	H	H	H	F
2-s	C	H	H	CF <sub>3</sub>	H	H	H	H	H	H
2-t	C	CL	H	H	H	F	H	H	H	H
2-v	C	H	H	CF <sub>3</sub>	H	H	CH <sub>3</sub> O	H	H	H
2-w	C	H	CH <sub>3</sub> O	H	H	H	H	CF <sub>3</sub>	H	H
2-x	C	H	H	H	H	H	F	F	H	H
2-y	C	H	H	CF <sub>3</sub>	H	H	F	H	F	H
2-z	C	H	H	CF <sub>3</sub>	H	F	H	F	H	H
2-aa	C	H	H	Br	H	H	H	Br	H	H

One example of a substituted 2-phenylquinoline compound, having structure (III) above, is compound 2-u, which has R<sub>17</sub>=CF<sub>3</sub> and R<sub>10</sub>–R<sub>16</sub> and R<sub>18</sub>–R<sub>20</sub>=H.

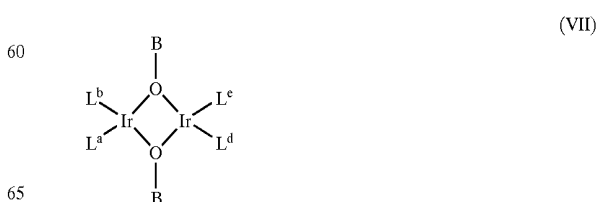
The 2-phenylpyridines, pyrimidines, and quinolines thus prepared are used for the synthesis of the cyclometalated iridium complexes. A convenient one-step method has been developed employing commercially available iridium trichloride hydrate and silver trifluoroacetate. The reactions are generally carried out with an excess of 2-phenylpyridine, pyrimidine, or quinoline, without a solvent, in the presence of 3 equivalents of AgOCOCF<sub>3</sub>. This reaction is illustrated for a 2-phenylpyridine in Equation (2) below:



The tris-cyclometalated iridium complexes were isolated, purified, and fully characterized by elemental analysis, <sup>1</sup>H and <sup>19</sup>F NMR spectral data, and, for compounds 1-b, 1-c, and 1-e, single crystal X-ray diffraction. In some cases, mixtures of isomers are obtained. Often the mixture can be used without isolating the individual isomers.

The iridium complexes having the Second Formula IrL<sup>a</sup>L<sup>b</sup>L<sup>c</sup> above, may, in some cases, be isolated from the

reaction mixture using the same synthetic procedures as preparing those having Third Formula IrL<sup>a</sup>L<sup>b</sup>L<sup>c</sup> above. The complexes can also be prepared by first preparing an intermediate iridium dimer having structure VII below:



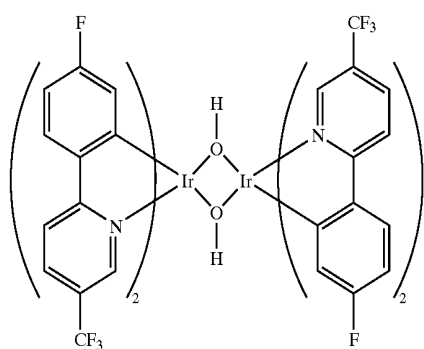
wherein:

B=H, CH<sub>3</sub>, or C<sub>2</sub>H<sub>5</sub>, and

L<sup>a</sup>, L<sup>b</sup>, L<sup>c</sup>, and L<sup>d</sup> can be the same or different from each other and each of L<sup>a</sup>, L<sup>b</sup>, L<sup>c</sup>, and L<sup>d</sup> has structure (I) above.

The iridium dimers can generally be prepared by first reacting iridium trichloride hydrate with the 2-phenylpyridine, phenylpyrimidine or phenylquinoline, and adding NaOB.

One particularly useful iridium dimer is the hydroxo iridium dimer, having structure VIII below:



This intermediate can be used to prepare compound 1-p by the addition of ethyl acetoacetate.

#### Electronic Device

The present invention also relates to an electronic device comprising at least one photoactive layer positioned between two electrical contact layers, wherein the at least one layer of the device includes the iridium complex of the invention. Devices frequently have additional hole transport and electron transport layers. A typical structure is shown in FIG. 1. The device **100** has an anode layer **110** and a cathode layer **150**. Adjacent to the anode is a layer **120** comprising hole transport material. Adjacent to the cathode is a layer **140** comprising an electron transport material. Between the hole transport layer and the electron transport layer is the photoactive layer **130**.

Depending upon the application of the device **100**, the photoactive layer **130** can be a light-emitting layer that is activated by an applied voltage (such as in a light-emitting diode or light-emitting electrochemical cell), a layer of material that responds to radiant energy and generates a signal with or without an applied bias voltage (such as in a photodetector). Examples of photodetectors include photoconductive cells, photoresistors, photoswitches, phototransistors, and phototubes, and photovoltaic cells, as these terms are describe in Markus, John, *Electronics and Nucleonics Dictionary*, 470 and 476 (McGraw-Hill, Inc. 1966).

The iridium compounds of the invention are particularly useful as the photoactive material in layer **130**, or as electron transport material in layer **140**. Preferably the iridium complexes of the invention are used as the light-emitting material in diodes. It has been found that in these applications, the fluorinated compounds of the invention do not need to be in a solid matrix diluent in order to be effective. A layer that is greater than 20% by weight iridium compound, based on the total weight of the layer, up to 100% iridium compound, can be used as the emitting layer. This is in contrast to the non-fluorinated iridium compound, tris(2-phenylpyridine) iridium (III), which was found to achieve maximum effi-

ciency when present in an amount of only 6–8% by weight in the emitting layer. This was necessary to reduce the self-quenching effect. Additional materials can be present in the emitting layer with the iridium compound. For example, a fluorescent dye may be present to alter the color of emission. A diluent may also be added. The diluent can be a polymeric material, such as poly(N-vinyl carbazole) and polysilane. It can also be a small molecule, such as 4,4'-N, N'-dicarbazole biphenyl or tertiary aromatic amines. When a diluent is used, the iridium compound is generally present in a small amount, usually less than 20% by weight, preferably less than 10% by weight, based on the total weight of the layer.

In some cases the iridium complexes may be present in more than one isomeric form, or mixtures of different complexes may be present. It will be understood that in the above discussion of OLEDs, the term "the iridium compound" is intended to encompass mixtures of compounds and/or isomers.

To achieve a high efficiency LED, the HOMO (highest occupied molecular orbital) of the hole transport material should align with the work function of the anode, the LUMO (lowest un-occupied molecular orbital) of the electron transport material should align with the work function of the cathode. Chemical compatibility and sublimation temp of the materials are also important considerations in selecting the electron and hole transport materials.

The other layers in the OLED can be made of any materials which are known to be useful in such layers. The anode **110**, is an electrode that is particularly efficient for injecting positive charge carriers. It can be made of, for example materials containing a metal, mixed metal, alloy, metal oxide or mixed-metal oxide, or it can be a conducting polymer. Suitable metals include the Group 11 metals, the metals in Groups 4, 5, and 6, and the Group 8–10 transition metals. If the anode is to be light-transmitting, mixed-metal oxides of Groups 12, 13 and 14 metals, such as indium-tin-oxide, are generally used. The IUPAC numbering system is used throughout, where the groups from the Periodic Table are numbered from left to right as 1–18 (CRC Handbook of Chemistry and Physics, 81<sup>st</sup> Edition, 2000). The anode **110** may also comprise an organic material such as polyaniline as described in "Flexible light-emitting diodes made from soluble conducting polymer," *Nature* vol. 357, pp 477–479 (11 Jun. 1992). At least one of the anode and cathode should be at least partially transparent to allow the generated light to be observed.

Examples of hole transport materials for layer **120** have been summarized for example, in Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, Vol. 18, p. 837–860, 1996, by Y. Wang. Both hole transporting molecules and polymers can be used. Commonly used hole transporting molecules are: N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD), 1,1-bis[(di-4-tolylamino) phenyl]cyclohexane (TAPC), N,N'-bis(4-methylphenyl)-N,N'-bis(4-ethylphenyl)-[1,1'-(3,3'-dimethyl) biphenyl] 4,4'-diamine (ETPD), tetrakis-(3-methylphenyl)-N,N,N',N'-2,5-phenylenediamine (PDA), a-phenyl-4-N,N-diphenylaminostyrene (TPS), p-(diethylamino) benzaldehyde diphenylhydrazone (DEH), triphenylamine (TPA), bis[4-(N,N-diethylamino)-2-methylphenyl](4-methylphenyl)methane (MPMP), 1-phenyl-3[p-(diethylamino) styryl]-5-[p-(diethylamino)phenyl] pyrazoline (PPR or DEASP), 1,2-trans-bis(9H-carbazol-9-yl)cyclobutane (DCZB), N,N,N',N'-tetrakis(4-methyl-phenyl)-(1,1'-biphenyl)-4,4'-diamine (TTB), and porphyrinic compounds, such as copper phthalocyanine. Commonly used hole transporting



polymers are polyvinylcarbazole, (phenylmethyl)polysilane, and polyaniline. It is also possible to obtain hole transporting polymers by doping hole transporting molecules such as those mentioned above into polymers such as polystyrene and polycarbonate.

Examples of electron transport materials for layer 140 include metal chelated oxinoid compounds, such as tris(8-hydroxyquinolato)aluminum ( $\text{Alq}_3$ ); phenanthroline-based compounds, such as 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (DDPA) or 4,7-diphenyl-1,10-phenanthroline (DPA), and azole compounds such as 2-(4-biphenyl)-5-(4-*t*-butylphenyl)-1,3,4-oxadiazole (PBD) and 3-(4-biphenyl)-4-phenyl-5-(4-*t*-butylphenyl)-1,2,4-triazole (TAZ). Layer 140 can function both to facilitate electron transport, and also serve as a buffer layer or confinement layer to prevent quenching of the exciton at layer interfaces. Preferably, this layer promotes electron mobility and reduces exciton quenching.

The cathode 150, is an electrode that is particularly efficient for injecting electrons or negative charge carriers. The cathode can be any metal or nonmetal having a lower work function than the anode. Materials for the cathode can be selected from alkali metals of Group 1 (e.g., Li, Cs), the Group 2 (alkaline earth) metals, the Group 12 metals, including the rare earth elements and lanthanides, and the actinides. Materials such as aluminum, indium, calcium, barium, samarium and magnesium, as well as combinations, can be used. Li-containing organometallic compounds can also be deposited between the organic layer and the cathode layer to lower the operating voltage.

It is known to have other layers in organic electronic devices. For example, there can be a layer (not shown) between the conductive polymer layer 120 and the active layer 130 to facilitate positive charge transport and/or band-gap matching of the layers, or to function as a protective layer. Similarly, there can be additional layers (not shown) between the active layer 130 and the cathode layer 150 to facilitate negative charge transport and/or band-gap matching between the layers, or to function as a protective layer. Layers that are known in the art can be used. In addition, any of the above-described layers can be made of two or more layers. Alternatively, some or all of inorganic anode layer 10, the conductive polymer layer 120, the active layer 130, and cathode layer 150, may be surface treated to increase charge carrier transport efficiency. The choice of materials for each of the component layers is preferably determined by balancing the goals of providing a device with high device efficiency.

It is understood that each functional layer may be made up of more than one layer.

The device can be prepared by sequentially vapor depositing the individual layers on a suitable substrate. Substrates such as glass and polymeric films can be used. Conventional vapor deposition techniques can be used, such as thermal evaporation, chemical vapor deposition, and the like. Alternatively, the organic layers can be coated from solutions or dispersions in suitable solvents, using any conventional coating technique. In general, the different layers will have the following range of thicknesses: anode 110, 500–5000 Å, preferably 1000–2000 Å; hole transport layer 120, 50–1000 Å, preferably 200–800 Å; light-emitting layer 130, 10–1000 Å, preferably 100–800 Å; electron transport layer 140, 50–1000 Å, preferably 200–800 Å; cathode 150, 200–10000 Å, preferably 300–5000 Å. The location of the electron-hole recombination zone in the device, and thus the emission spectrum of the device, can be affected by the relative thickness of each layer. Thus the thickness of the electron-

transport layer should be chosen so that the electron-hole recombination zone is in the light-emitting layer. The desired ratio of layer thicknesses will depend on the exact nature of the materials used.

It is understood that the efficiency of devices made with the iridium compounds of the invention, can be further improved by optimizing the other layers in the device. For example, more efficient cathodes such as Ca, Ba or LiF can be used. Shaped substrates and novel hole transport materials that result in a reduction in operating voltage or increase quantum efficiency are also applicable. Additional layers can also be added to tailor the energy levels of the various layers and facilitate electroluminescence.

The iridium complexes of the invention often are phosphorescent and photoluminescent and may be useful in applications other than OLEDs. For example, organometallic complexes of iridium have been used as oxygen sensitive indicators, as phosphorescent indicators in bioassays, and as catalysts. The bis cyclometalated complexes can be used to synthesize tris cyclometalated complexes where the third ligand is the same or different.

## EXAMPLES

The following examples illustrate certain features and advantages of the present invention. They are intended to be illustrative of the invention, but not limiting. All percentages are by weight, unless otherwise indicated.

### Example 1

This example illustrates the preparation of the 2-phenylpyridines and 2-phenylpyrimidines which are used to form the iridium compounds.

The general procedure used was described in O. Lohse, P. Thevenin, E. Waldvogel *Synlett*, 1999, 45–48. In a typical experiment, a mixture of 200 ml of degassed water, 20 g of potassium carbonate, 150 ml of 1,2-dimethoxyethane, 0.5 g of  $\text{Pd}(\text{PPh}_3)_4$ , 0.05 mol of a substituted 2-chloropyridine (quinoline or pyrimidine) and 0.05 mol of a substituted phenylboronic acid was refluxed (80–90° C.) for 16–30 h. The resulting reaction mixture was diluted with 300 ml of water and extracted with  $\text{CH}_2\text{Cl}_2$  (2×100 ml). The combined organic layers were dried over  $\text{MgSO}_4$ , and the solvent removed by vacuum. The liquid products were purified by fractional vacuum distillation. The solid materials were recrystallized from hexane. The typical purity of isolated materials was >98%. The starting materials, yields, melting and boiling points of the new materials are given in Table 3. NMR data and analytical data are given in Table 4.

TABLE 3

Preparation of 2-Phenyl Pyridines, Phenylpyrimidines and Phenylquinolines		
Compound	Yield in %	B.p./mm Hg (m.p.) in ° C.
2-s	70	—
2-a	72	—
2-b	48	—
2-u	75	(76–78)
2-c	41	(95–96)
2-d	38	(39–40)
2-e	55	74.5/0.1
2-g	86	71–73/0.07
2-t	65	77–78/0.046
2-k	50	(38–40)
2-m	80	72–73/0.01

TABLE 3-continued

Preparation of 2-Phenyl Pyridines, Phenylpyrimidines and Phenylquinolines		
Compound	Yield in %	B.p./mm Hg (m.p.) in ° C.
2-f	22	52–33/0.12
2-v	63	95–96/13
2-w	72	
2-x	35	61–62/0.095
2-y	62	(68–70)
2-z	42	66–67/0.06 (58–60)
2-aa	60	

TABLE 4

Properties of 2-Phenyl Pyridines, Phenylpyrimidines and Phenylquinolines			
Compound	<sup>1</sup> H NMR	<sup>19</sup> F NMR	Analysis %, found (calc.) or MS (M <sup>+</sup> )
2-s	7.48(3H), 7.70(1H), 7.83(1H), 7.90(2H), 8.75(1H)	–62.68	C, 64.50 (64.57) H, 3.49 (3.59) N, 6.07 (6.28)
2-a	7.19(1H), 7.30(1H), 7.43(1H), 7.98(2H), 8.07(1H), 9.00(1H)	–60.82(3F, s), –116.96(1F, m)	C, 59.56 (59.75) H, 3.19 (2.90) N, 5.52 (5.81)
2-b	7.58(1H), 7.66(1H), 7.88(1H), 8.03(1H), 8.23(1H), 8.35(1H), 8.99(1H)	–62.75(3F, s), –63.10(3F, s)	C, 53.68 (53.60) H, 2.61 (2.40) N, 4.53 (4.81)
2-u	7.55(1H), 7.63(1H), 7.75(2H), 7.89(2H), 8.28(2H), 8.38(1H), 8.50(1H)	–62.89(s)	C, 69.17 (70.33) H, 3.79 (3.66) N, 4.88 (5.12)
2-c	7.53(1H), 7.64(1H), 7.90(1H), 8.18(1H), 8.30(1H), 8.53(1H), 9.43(1H)	–62.14(s)	C, 53.83(53.73) H, 2.89 (2.61) N, 9.99 (10.44)
2-d	7.06(1H), 7.48(1H), 7.81(3H), 8.01(1H), 8.95(1H)	–62.78(3F, s), –112.61 (1F, m)	C, 59.73 (59.75) H, 2.86 (2.90) N, 5.70 (5.81)
2-e	3.80(3H), 6.93(2H), 7.68(1H), 7.85(1H), 7.96(2H), 8.82(1H)	–62.63 (s)	C, 61.66 (61.90) H, 3.95 (4.04) N, 5.53 (5.38)
2-g	2.70(3H), 7.10(3H), 7.48(1H), 7.60(1H), 8.05(2H)	–114.03 (m)	C, 76.56 (77.00) H, 5.12 (5.30) N, 5.43 (7.50)
2-t	7.10(2H), 7.35(2H), 7.96(1H)	–62.73 (3F, s), –113.67	C, 50.51 (52.17) H, 1.97

TABLE 4-continued

Properties of 2-Phenyl Pyridines, Phenylpyrimidines and Phenylquinolines			
Compound	<sup>1</sup> H NMR	<sup>19</sup> F NMR	Analysis %, found (calc.) or MS (M <sup>+</sup> )
5			
	8.78(1H),	(1F, m)	(2.17) N, 5.09 (5.07)
10 2-k	7.08(2H), 7.62(1H), 7.90(3H), 8.80(1H),	–62.75 (3F, s) –111.49 (m)	C, 60.39 (59.75), H, 3.38 (2.90), N, 5.53 (5.51)
2-m	7.10(2H), 7.80(2H), 8.00(1H), 8.75(1H),	–62.63 (3F, s) –111.24 (m)	C, 52.13 (52.17) H, 2.16 (2.17) N, 4.85 (5.07)
15			
2-f	7.55(3H), 7.77(2H), 8.06(1H),	–62.57(s)	257(M <sup>+</sup> , C <sub>12</sub> H <sub>7</sub> F <sub>3</sub> CIN <sup>+</sup> ), 222(M–Cl)
20 2-v	3.8(3H), 6.95(1H), 7.30(1H), 7.50(1H), 7.58(1H), 7.75(1H), 7.90(1H), 8.87(1H)	–62.70 ppm	C, 61.66(61.37), H, 3.98(3.67), N, 5.53(5.48)
2-w	8.54(1H, d), 8.21(2H, d), 7.70(2H, d), 7.24(1H, s), 6.82(1H, dd), 3.91(3H, s)	–63.08(3F, s)	
30			
2-x	6.9(2H, m), 7.18(2H, m), 7.68(2H, m), 7.95(1H, m), 8.65(1H, m);	–109.70(1F, m), –113.35(1F, m).	
35			
2-y	6.94(1H), 7.62(2H), 7.82(1H), 8.03(1H), 8.96(1H);	–62.72(3F, s), –109.11(2F, m)	
40			
2-z	6.85(1H), 6.93(1H), 7.80, 7.90, 8.05(3H), 8.89(1H);	–62.80(3F, s), –107.65(1F, m), –112.45(1F, m).	
45			
2-aa	7.70(3H, m), 7.85(3H, m), 7.80, 7.90, 8.85(1H, m).		

## Example 2

This example illustrates the preparation of iridium compounds of the Fourth Formula fac-Ir(L<sup>n</sup>)<sub>3</sub> above.

In a typical experiment, a mixture of IrCl<sub>3</sub>.nH<sub>2</sub>O (53–55% Ir), AgOCOCF<sub>3</sub> (3.1 equivalents per Ir), 2-arylpyridine (excess), and (optionally) a small amount of water was vigorously stirred under N<sub>2</sub> at 180–195° C. (oil bath) for 2–8 hours. The resulting mixture was thoroughly extracted with CH<sub>2</sub>Cl<sub>2</sub> until the extracts were colorless. The extracts were filtered through a silica column to produce a clear yellow solution. Evaporation of this solution gave a residue which was treated with methanol to produce colored crystalline tris-cyclometalated Ir complexes. The complexes were separated by filtration, washed with methanol, dried under vacuum, and (optionally) purified by crystallization, vacuum sublimation, or Soxhlet extraction. Yields: 10–82%. All materials were characterized by NMR spectroscopic data

and elemental analysis, and the results are given in Table 5 below. Single-crystal X-ray structures were obtained for three complexes of the series.

#### Compound 1-b

A mixture of  $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$  (54% Ir; 508 mg), 2-(4-fluorophenyl)-5-trifluoromethylpyridine, compound kk (2.20 g),  $\text{AgOCOCF}_3$  (1.01 g), and water (1 mL) was vigorously stirred under a flow of  $\text{N}_2$  as the temperature was slowly (30 min) brought up to 185° C. (oil bath). After 2 hours at 185–190° C. the mixture solidified. The mixture was cooled down to room temperature. The solids were extracted with dichloromethane until the extracts decolorized. The combined dichloromethane solutions were filtered through a short silica column and evaporated. After methanol (50 mL) was added to the residue the flask was kept at –10° C. overnight. The yellow precipitate of the tris-cyclometalated complex, compound b, was separated, washed with methanol, and dried under vacuum. Yield: 1.07 g (82%). X-Ray quality crystals of the complex were obtained by slowly cooling its warm solution in 1,2-dichloroethane.

#### Compound 1-e

A mixture of  $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$  (54% Ir; 504 mg), 2-(3-trifluoromethylphenyl)-5-trifluoromethylpyridine, compound bb (1.60 g), and  $\text{AgOCOCF}_3$  (1.01 g) was vigorously stirred under a flow of  $\text{N}_2$  as the temperature was slowly (15 min) brought up to 192° C. (oil bath). After 6 hours at 190–195° C. the mixture solidified. The mixture was cooled down to room temperature. The solids were placed on a silica column which was then washed with a large quantity of dichloromethane. The residue after evaporation of the filtrate was treated with methanol to produce yellow solid. The solid was collected and purified by extraction with dichloromethane in a 25-mL micro-Soxhlet extractor. The yellow precipitate of the tris-cyclometalated complex, compound e, was separated, washed with methanol, and dried under vacuum. Yield: 0.59 g (39%). X-Ray quality crystals of the complex were obtained from hot 1,2-dichloroethane.

#### Compound 1-d

A mixture of  $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$  (54% Ir; 508 mg), 2-(2-fluorophenyl)-5-trifluoromethylpyridine, compound aa (1.53 g), and  $\text{AgOCOCF}_3$  (1.01 g) was vigorously stirred under a flow of  $\text{N}_2$  at 190–195° C. (oil bath) for 6 h 15 min. The mixture was cooled down to room temperature and then extracted with hot 1,2-dichloroethane. The extracts were filtered through a short silica column and evaporated. Treatment of the residue with methanol (20 mL) resulted in precipitation of the desired product, compound d, which was separated by filtration, washed with methanol, and dried under vacuum. Yield: 0.63 g (49%). X-Ray quality crystals of the complex were obtained from dichloromethane/methanol.

#### Compound 1-i

A mixture of  $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$  (54% Ir; 503 mg), 2-(4-trifluoromethoxyphenyl)-5-trifluoromethylpyridine, compound ee (2.00 g), and  $\text{AgOCOCF}_3$  (1.10 g) was vigorously stirred under a flow of  $\text{N}_2$  at 190–195° C. (oil bath) for 2 h 45 min. The mixture was cooled down to room temperature and then extracted with dichloromethane. The extracts were filtered through a short silica column and evaporated. Treatment of the residue with methanol (20 mL) resulted in precipitation of the desired product, compound i, which was separated by filtration, washed with methanol, and dried under vacuum. The yield was 0.86 g. Additionally, 0.27 g of the complex was obtained by evaporating the mother liquor and adding petroleum ether to the residue. Overall yield: 1.13 g (72%).

#### Compound 1-q

A mixture of  $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$  (54% Ir; 530 mg), 2-(3-methoxyphenyl)-5-trifluoromethylpyridine (2.50 g),  $\text{AgOCOCF}_3$  (1.12 g), and water (1 mL) was vigorously stirred under a flow of  $\text{N}_2$  as the temperature was slowly (30 min) brought up to 185° C. (oil bath). After 1 hour at 185° C. the mixture solidified. The mixture was cooled down to room temperature. The solids were extracted with dichloromethane until the extracts decolorized. The combined dichloromethane solutions were filtered through a short silica column and evaporated. The residue was washed with hexanes and then recrystallized from 1,2-dichloroethane-hexanes (twice). Yield: 0.30 g.  $^{19}\text{F}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20° C.),  $\delta$ : –63 (s).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20° C.),  $\delta$ : 8.1 (1H), 7.9 (1H), 7.8 (1H), 7.4 (1H), 6.6 (2H), 4.8 (3H). X-Ray quality crystals of the complex (1,2-dichloroethane, hexane solvate) were obtained from 1,2-dichloroethane-hexanes. This facial complex was orange-photoluminescent.

Compounds 1-a, 1-c, 1-f through 1-h, 1-j through 1-m, and 1-r were similarly prepared. In the preparation of compound 1-j, a mixture of isomers was obtained with the fluorine in either the  $\text{R}_6$  or  $\text{R}_8$  position.

TABLE 5

Compound	Analysis (calcd (found))	NMR ( $\text{CD}_2\text{Cl}_2$ , 25° C.)
1-a	C: 50.3(50.1) H: 2.5(2.7) N: 4.9(4.9) Cl: 0.0(0.2)	$^1\text{H}$ : 6.8(1H), 6.9(1H), 7.0(1H), 7.8 (2H), 7.95(1H), 8.1(1H) $^{19}\text{F}$ : –63.4
1-b	C: 47.4(47.3) H: 2.0(2.1) N: 4.6(4.4)	$^1\text{H}$ : 6.4(1H), 6.75(1H), 7.7(1H), 7.8 (1H), 7.95(1H), 8.05(1H) $^{19}\text{F}$ : –63.4(s); –109.5(ddd)
1-c	C: 47.4(47.2) H: 2.0(2.0) N: 4.6(4.5)	$^1\text{H}$ : 6.6(1H), 6.7(1H), 6.9(1H), 7.8 (1H), 8.0(1H), 8.6(1H) $^{19}\text{F}$ : –63.5(s); –112.8(ddd)
1-d	C: 55.9(56.1) H: 3.0(3.2) N: 5.9(5.8)	$^1\text{H}$ : 6.6(2H), 6.8(1H), 7.0(1H), 7.6 (1H), 7.7(1H), 8.4(1H) $^{19}\text{F}$ : –115.0(ddd)
1-e	C: 44.1(43.3) H: 1.7(2.1) N: 3.9(3.6)	$^1\text{H}$ : 6.9(1H), 7.1(1H), 7.8(1H), 8.0 (2H), 8.2(1H) $^{19}\text{F}$ : –63.0(1F), –63.4(1F)
1-f	C: 50.4(50.5) H: 2.5(2.7) N: 4.9(4.9)	$^1\text{H}$ : 6.9(1H), 7.1(2H), 7.6(1H), 7.8 (1H), 7.9(1H), 8.1(1H) $^{19}\text{F}$ : –62.4
1-g	C: 55.9(56.3) H: 3.0(3.2) N: 5.9(6.0)	$^1\text{H}$ : 6.4(1H), 6.7(1H), 7.0(1H), 7.6 (1H), 7.7(2H), 7.9(1H) $^{19}\text{F}$ : –112.6(ddd)
1-h	C: 51.0(45.2) H: 2.1(2.3) N: 4.9(4.2)	$^1\text{H}$ : 6.8(1H), 6.95(1H), 7.05(1H), 7.7 (1H), 8.0(1H), 8.9(1H) $^{19}\text{F}$ : –63.3
1-i	C: 49.4(49.3) H: 2.9(2.8) N: 4.4(4.4)	$^1\text{H}$ : 3.6(3H), 6.3(1H), 6.6(1H), 7.7 (2H), 7.85(1H), 7.95(1H) $^{19}\text{F}$ : –63.2
1-j	C: 47.4(47.4) H: 2.0(2.3) N: 4.6(4.7)	$^1\text{H}$ : 6.7(m), 7.1(m), 7.5(m), 7.6(m), 7.7(m), 8.0(m), 8.2(m) $^{19}\text{F}$ : 8 s resonances (–63.0–63.6) and 8 ddd resonances (–92.2–125.5)
1-k	C: 43.5(44.0) H: 1.8(2.1) N: 8.5(8.4)	$^1\text{H}$ : 6.9(1H), 7.15(1H), 8.1(1H), 8.3 (1H), 8.45(1H), 8.6(1H) $^{19}\text{F}$ : –62.9
1-l	C: 42.2(42.1) H: 1.6(1.8) N: 3.8(3.7)	$^1\text{H}$ : 6.5(1H), 6.7(1H), 7.75(1H), 7.85 (1H), 8.0(1H), 8.1(1H) $^{19}\text{F}$ : –58.1(1F), –63.4(1F)

#### Example 3

This example illustrates the preparation of iridium complexes of the Second Formula  $\text{IrL}^a\text{L}^b\text{L}^c\text{L}^d\text{L}^e\text{L}^f$ , above,

#### Compound 1-n

A mixture of  $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$  (54% Ir; 510 mg), 2-(3-trifluoromethylphenyl)quinoline (1.80 g), and silver trifluoroac-

etate (1.10 g) was vigorously stirred at 190–195° C. for 4 hours. The resulting solid was chromatographed on silica with dichloromethane to produce a mixture of the dicyclo-metalated complex and the unreacted ligand. The latter was removed from the mixture by extraction with warm hexanes. After the extracts became colorless the hexane-insoluble solid was collected and dried under vacuum. The yield was 0.29 g. <sup>19</sup>F NMR: –63.5 (s, 6F), –76.5 (s, 3F). The structure of this complex was established by a single crystal X ray diffraction study.

#### Compound 1-o

A mixture of IrCl<sub>3</sub>·nH<sub>2</sub>O (54% Ir; 500 mg), 2-(2-fluorophenyl)-3-chloro-5-trifluoromethylpyridine (2.22 g), water (0.3 mL), and silver trifluoroacetate (1.00 g) was stirred at 190° C. for 1.5 hours. The solid product was chromatographed on silica with dichloromethane to produce 0.33 g of a 2:1 co-crystallized adduct of the dicyclo-metalated aqua trifluoroacetato complex, compound 1-p, and the unreacted ligand. <sup>19</sup>F NMR: –63.0 (9F), –76.5 (3F), –87.7 (2F), –114.4 (1F). The co-crystallized phenylpyridine ligand was removed by recrystallization from dichloromethane-hexanes. The structures of both the adduct and the complex were established by a single crystal X-ray diffraction study.

#### Example 4

This example illustrates the preparation of an hydroxo iridium dimer, having structure (VIII) above.

A mixture of IrCl<sub>3</sub>·nH<sub>2</sub>O (54% Ir; 510 mg), 2-(4-fluorophenyl)-5-trifluoromethylpyridine (725 mg), water (5 mL), and 2-ethoxyethanol (20 mL) was vigorously stirred under reflux for 4.5 hours. After a solution of NaOH (2.3 g) in water (5 mL) was added, followed by 20 mL of water, the mixture was stirred under reflux for 2 hours. The mixture was cooled down to room temperature, diluted with 50 mL of water, and filtered. The solid was vigorously stirred under reflux with 30 mL of 1,2-dichloroethane and aqueous NaOH (2.2 g in 8 mL of water) for 6 hours. The organic solvent was evaporated from the mixture to leave a suspension of an orange solid in the aqueous phase. The orange solid was separated by filtration, thoroughly washed with water, and dried under vacuum to produce 0.94 g (95%) of the iridium hydroxo dimer (spectroscopically pure). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): –1.0 (s, 1H, IrOH), 5.5 (dd, 2H), 6.6 (dt, 2H), 7.7 (dd, 2H), 7.9 (dd, 2H), 8.0 (d, 2H), 9.1 (d, 2H). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>): –62.5 (s, 3F), –109.0 (ddd, 1F).

#### Example 5

This example illustrates the preparation of bis-cyclometalated complexes from an iridium dimer.

#### Compound 1-p

A mixture of the iridium hydroxo dimer (100 mg) from Example 4, ethyl acetoacetate (0.075 mL; 4-fold excess), and dichloromethane (4 mL) was stirred at room temperature overnight. The solution was filtered through a short silica plug and evaporated to give an orange-yellow solid which was washed with hexanes and dried. The yield of the complex was 109 mg (94%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 1.1 (t, CH<sub>3</sub>), 3.9 (dm, CH<sub>2</sub>), 4.8 (s, CH<sub>3</sub>COCH), 5.9 (m), 6.7 (m), 7.7 (m), 8.0 (m), 8.8 (d). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>): –63.1 (s, 3F), –63.2 (s, 3F), –109.1 (ddd, 1F), –109.5 (ddd). Analysis: Calcd: C, 44.9; H, 2.6; N, 3.5. Found: C, 44.4; H, 2.6; N, 3.3.

#### Compound 1-w

A solution of hydroxo iridium dimer from Example 4 (0.20 g) in THF (6 mL) was treated with 50 mg of trifluoroacetic acid, filtered through a short silica plug, evaporated to ca. 0.5 mL, treated with hexanes (8 mL), and left overnight. The yellow crystalline solid was separated, washed with hexanes, and dried under vacuum. Yield (1:1 THF solvate): 0.24 g (96%). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20° C.), δ: –63.2 (s, 3F), –76.4 (s, 3F), –107.3 (ddd, 1F). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20° C.), δ: 9.2 (br s, 1H), 8.2 (dd, 1H), 8.1 (d, 1H), 7.7 (m, 1H), 6.7 (m, 1H), 5.8 (dd, 1H), 3.7 (m, 2H, THF), 1.8 (m, 2H, THF).

#### Compound 1-x

A mixture of the trifluoroacetate intermediate, compound 1-w (75 mg), and 2-(4-bromophenyl)-5-bromopyridine (130 mg) was stirred under N<sub>2</sub> at 150–155° C. for 30 min. The resulting solid was cooled to room temperature and dissolved in CH<sub>2</sub>Cl<sub>2</sub>. The resulting solution was filtered through silica gel and evaporated. The residue was washed several times with warm hexanes and dried under vacuum to leave a yellow, yellow-photoluminescent solid. Yield: 74 mg (86%). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20° C.), δ: –63.1 (s, 3F), –63.3 (s, 3F), –108.8 (ddd, 1F), –109.1 (ddd, 1F). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20° C.), δ: 8.2 (s), 7.9 (m), 7.7 (m), 7.0 (d), 6.7 (m), 6.2 (dd), 6.0 (dd). The complex was meridional, with the nitrogens of the fluorinated ligands being trans, as confirmed by X-ray analysis.

#### Example 6

This example illustrates the preparation of iridium compounds of the Fifth Formula mer-Ir(L<sup>a</sup>)<sub>3</sub> above.

#### Compound 1-s

This complex was synthesized in a manner similar to compound 1-n. According to the NMR, TLC, and TGA data, the result was an approximately 1:1 mixture of the facial and meridional isomers.

#### Compound 1-t

A mixture of IrCl<sub>3</sub>·nH<sub>2</sub>O (54% Ir; 0.40 g), 2-(3,5-difluorophenyl)-5-trifluoromethylpyridine (1.40 g), AgOCOCF<sub>3</sub> (0.81 g), and water (0.5 mL) was vigorously stirred under a flow of N<sub>2</sub> as the temperature was slowly (30–40 min) brought up to 165° C. (oil bath). After 40 min at 165° C. the mixture solidified. The mixture was cooled down to room temperature. The solids were extracted with dichloromethane until the extracts decolorized. The combined dichloromethane solutions were filtered through a short silica column and evaporated. The residue was thoroughly washed with hexanes and dried under vacuum. Yield: 0.53 g (49%). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20° C.), δ: –63.55 (s, 3F), –63.57 (s, 3F), –63.67 (s, 3F), –89.1 (t, 1F), –100.6 (t, 1F), –102.8 (dd, 1F), –118.6 (ddd, 1F), –119.3 (ddd, 1F), –123.3 (ddd, 1F). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20° C.), δ: 8.4 (s), 8.1 (m), 7.9 (m), 7.6 (s), 7.5 (m), 6.6 (m), 6.4 (m). The complex was meridional, as was also confirmed by X-ray analysis.

#### Compound 1-u

This complex was prepared and isolated similarly to compound 1-q, then purified by crystallization from 1,2-dichloroethane-hexanes. The yield of the purified product was 53%. The complex is mer, as follows from the NMR data.

<sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20° C.), δ: –63.48 (s, 3F), –63.52 (s, 6F), –105.5 (ddd, 1F), –105.9 (ddd, 1F), –106.1 (ddd, 1F), –107.4 (t, 1F), –107.9 (t, 1F), –109.3 (t, 1F). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20° C.), δ: 8.6 (m), 8.3 (s), 8.2 (s), 8.1 (m), 7.9 (m), 7.6 (m), 6.6 (m), 6.4 (m), 6.0 (m), 5.8 (m).

## Compound 1-v

This mer-complex was prepared in a manner similar to compound 1-w, using the trifluoroacetate dicyclopentadienyl intermediate, compound 1-x, and 2-(4-fluorophenyl)-5-trifluoromethylpyridine. <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20° C.), δ: -63.30 (s, 3F), -63.34 (s, 3F), -63.37 (s, 3F), -108.9 (ddd, 1F), -109.0 (ddd, 1F), -109.7 (ddd, 1F). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20° C.), δ: 8.3–7.6 (m), 6.7 (m), 6.6 (dd), 6.3 (dd), 6.0 (dd). This yellow-luminescent merisinal complex isomerised to the green luminescent facial isomer, compound 1-b, upon sublimation at 1 atm.

## Example 7

This example illustrates the formation of OLEDs using the iridium complexes of the invention.

Thin film OLED devices including a hole transport layer (HT layer), electroluminescent layer (EL layer) and at least one electron transport layer (ET layer) were fabricated by the thermal evaporation technique. An Edward Auto 306 evaporator with oil diffusion pump was used. The base vacuum for all of the thin film deposition was in the range of 10<sup>-6</sup> torr. The deposition chamber was capable of depositing five different films without the need to break up the vacuum.

An indium tin oxide (ITO) coated glass substrate was used, having an ITO layer of about 1000–2000 Å. The substrate was first patterned by etching away the unwanted ITO area with 1N HCl solution, to form a first electrode pattern. Polyimide tape was used as the mask. The patterned ITO substrates were then cleaned ultrasonically in aqueous detergent solution. The substrates were then rinsed with distilled water, followed by isopropanol, and then degreased in toluene vapor for ~3 hours.

The cleaned, patterned ITO substrate was then loaded into the vacuum chamber and the chamber was pumped down to 10<sup>-6</sup> torr. The substrate was then further cleaned using an oxygen plasma for about 5–10 minutes. After cleaning, multiple layers of thin films were then deposited sequentially onto the substrate by thermal evaporation. Finally, patterned metal electrodes of Al were deposited through a mask. The thickness of the film was measured during deposition using a quartz crystal monitor (Sycon STC-200). All film thickness reported in the Examples are nominal, calculated assuming the density of the material deposited to be one. The completed OLED device was then taken out of the vacuum chamber and characterized immediately without encapsulation.

A summary of the device layers and thicknesses is given in Table 6. In all cases the anode was ITO as discussed above, and the cathode was Al having a thickness in the range of 700–760 Å. In some of the samples, a two-layer electron transport layer was used. The layer indicated first was applied adjacent to the EL layer.

TABLE 6

Alq <sub>3</sub> = tris(8-hydroxyquinolato) aluminum DDPA = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline Ir(ppy) <sub>3</sub> = fac-tris(2-phenylpyridine) iridium MPMP = bis[4-(N,N-diethylamino)-2-methylphenyl] (4-methylphenyl)methane			
Sample	HT layer (Thickness, Å)	EL layer (Thickness, Å)	ET layer (Thickness, Å)
Com- parative	MPMP (528)	Ir(ppy) <sub>3</sub> (408)	DDPA (106) + Alq <sub>3</sub> (320)
1	MPMP(520)	Compound 1-b (499)	DDPA (125) + Alq <sub>3</sub> (365)
2	MPMP(541)	Compound 1-b (580)	DDPA (407)

TABLE 6-continued

Alq <sub>3</sub> = tris(8-hydroxyquinolato) aluminum DDPA = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline Ir(ppy) <sub>3</sub> = fac-tris(2-phenylpyridine) iridium MPMP = bis[4-(N,N-diethylamino)-2-methylphenyl] (4-methylphenyl)methane			
Sample	HT layer (Thickness, Å)	EL layer (Thickness, Å)	ET layer (Thickness, Å)
3	MPMP(540)	Compound 1-e (499)	DDPA (112) + Alq <sub>3</sub> (340)
4	MPMP(525)	Compound 1-k (406)	DDPA (106) Alq <sub>3</sub> (341)
5	MPMP(570)	Compound 1-i (441)	DDPA (107) + Alq <sub>3</sub> (339)
6	MPMP(545)	Compound 1-j (462)	DDPA (111) + Alq <sub>3</sub> (319)
7	MPMP(643)	Compound 1-g (409)	DDPA (112) + Alq <sub>3</sub> (361)
8	MPMP(539)	Compound 1-f (430)	DDPA (109) + Alq <sub>3</sub> (318)
9	MPMP(547)	Compound 1-a (412)	DDPA (105) + Alq <sub>3</sub> (300)
10	MPMP(532)	Compound 1-h (457)	DDPA (108) + Alq <sub>3</sub> (306)
11	MPMP(603)	Compound 1-d (415)	DDPA (111) + Alq <sub>3</sub> (303)
12	MPMP(551)	Compound 1-c (465)	DDPA (106) + Alq <sub>3</sub> (313)
13	MPMP(520)	Compound 1-l (405)	DDPA (410)
14	MPMP(504)	Compound 1-b (400)	DDPA (393)
15	MPMP(518)	Compound 1-b (153)	DDPA (418)
16	MPMP(556)	Compound 1-m (416)	DDPA (430)
17	MPMP(520)	Compound 1-n (419)	DDPA (420)
18	MPMP(511)	Compound 1-o (412)	DDPA (413)
19	MPMP(527)	Compound 1-p (425)	DDPA (412)
20	MPMP(504)	Compound 1-q (417)	DPA (407)
21	MPMP (525)	Compound 1-t (419)	DPA (416)
22	MPMP (520)	Compound 1-u (421)	DPA (405)

The OLED samples were characterized by measuring their (1) current-voltage (I-V) curves, (2) electroluminescence radiance versus voltage, and (3) electroluminescence spectra versus voltage. The apparatus used, **200**, is shown in FIG. 2. The I-V curves of an OLED sample, **220**, were measured with a Keithley Source-Measurement Unit Model **237**, **280**. The electroluminescence radiance (in the unit of Cd/m<sup>2</sup>) vs. voltage was measured with a Minolta LS-110 luminescence meter, **210**, while the voltage was scanned using the Keithley SMU. The electroluminescence spectrum was obtained by collecting light using a pair of lenses, **230**, through an electronic shutter, **240**, dispersed through a spectrograph, **250**, and then measured with a diode array detector, **260**. All three measurements were performed at the same time and controlled by a computer, **270**. The efficiency of the device at certain voltage is determined by dividing the electroluminescence radiance of the LED by the current density needed to run the device. The unit is in Cd/A.

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The results are given in Table 7 below:

TABLE 7

Electroluminescent Properties of Iridium Compounds				
Sample	Peak Radiance, Cd/m <sup>2</sup>	Efficiency at peak radiance, Cd/A	Peak efficiency, Cd/A	Approximate Peak Wavelengths, nm
Comparative	540	0.39	0.48	522
1	at 22 V 1400	3.4	11	525
2	at 21 V 1900	5.9	13	525
3	at 25 V 830	1.7	13.5	525
4	at 18 V 7.6	0.005	0.13	521
5	at 27 V 175	0.27	1.8	530, 563
6	at 25 V 514	1.5	2.2	560
7	at 20 V 800	0.57	1.9	514
8	at 26 V 1200	0.61	2	517
9	at 28 V 400	1.1	4	545
10	at 18 V 190	2.3	3.3	575
11	at 16 V 1150	1.2	3.8	506, 526
12	at 25 V 340	0.49	2.1	525
13	at 20 V 400	3	5	520
14	at 21 V 1900	5	9	525
15	2500	6	11	525
16	100	0.17	0.2	560
17	at 27 V 3.5	0.005	0.014	575
18	at 28 V 30	0.08	0.16	590
19	at 26 V 2000	6	8	532
20	at 21 V 350	0.60	1.6	595
21	at 26 V 1200		5	545
22	at 22 V 80		1	540
	at 19 V			

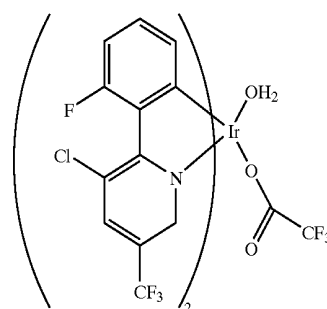
The peak efficiency is the best indication of the value of the electroluminescent compound in a device. It gives a measure of how many electrons have to be input into a device in order to get a certain number of photons out (radiance). It is a fundamentally important number, which reflects the intrinsic efficiency of the light-emitting material. It is also important for practical applications, since higher efficiency means that fewer electrons are needed in order to achieve the same radiance, which in turn means lower power consumption. Higher efficiency devices also tend to have longer lifetimes, since a higher proportion of injected electrons are converted to photons, instead of generating heat or causing an undesirable chemical side reactions. Most of the iridium complexes of the invention have much higher peak efficiencies than the parent fac-tris(2-phenylpyridine) iridium complex. Those complexes with lower efficiencies

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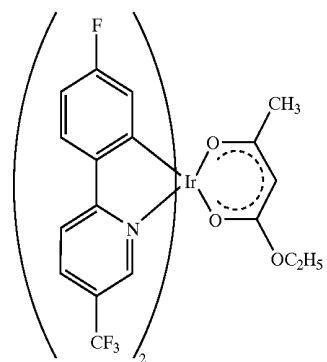
may also find utility as phosphorescent or photoluminescent materials, or as catalysts, as discussed above.

What is claimed is:

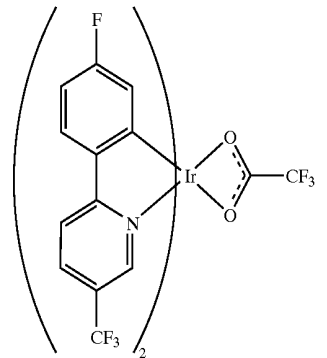
1. A compound having a structure selected from structures (V), (VI), (IX) and (X) below:



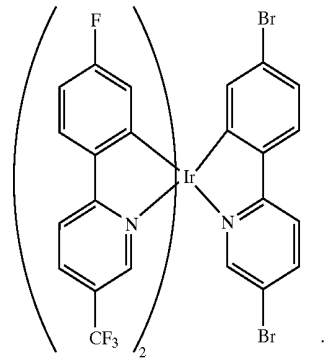
(V)



(VI)



(IX)



(X)

\* \* \* \* \*

专利名称(译)	具有氟化苯基吡啶，苯基嘧啶和苯基喹啉的电致发光铱化合物和用这些化合物制成的装置		
公开(公告)号	<a href="#">US6979739</a>	公开(公告)日	2005-12-27
申请号	US10/459946	申请日	2003-06-12
[标]申请(专利权)人(译)	Grushin向量VLADIMIR PETROV维亚切斯拉夫·á 王瑛		
申请(专利权)人(译)	Grushin向量VLADIMIR PETROV维亚切A. 王莹		
当前申请(专利权)人(译)	E·I·杜邦和公司		
[标]发明人	GRUSHIN VLADIMIR PETROV VIACHESLAV A WANG YING		
发明人	GRUSHIN, VLADIMIR PETROV, VIACHESLAV A. WANG, YING		
IPC分类号	H01L51/50 C07D213/26 C07D213/30 C07D213/61 C07D213/68 C07D215/04 C07D215/12 C07D239/26 C07F15/00 C09K11/06 H01L51/00 H01L51/30 H05B33/14 C07F17/02 B32B19/00 B32B9/00 H01J1/62 H01J63/04 H01L35/24 H01L33/00 H01L21/00 H01L51/40		
CPC分类号	C07D213/26 C07D213/61 C07D213/68 C07D215/04 C07D239/26 C07F15/0033 C09K11/06 H01L51/0084 H01L51/0085 H05B33/14 C07D213/30 Y10S428/917 C09K2211/1007 C09K2211/1011 C09K2211/1014 C09K2211/1029 C09K2211/185 H01L51/005 H01L51/50 H01L51/5012		
优先权	60/224273 2000-08-10 US 60/215362 2000-06-30 US		
其他公开文献	US20050165235A1		
外部链接	<a href="#">Espacenet</a> <a href="#">USPTO</a>		

# 摘要(译)

本发明一般涉及电致发光Ir ( III ) 化合物，用于制备Ir ( III ) 化合物的取代的2-苯基吡啶，苯基嘧啶和苯基喹啉，以及用Ir ( III ) 化合物制备的器件。

