DOI: 10.1002/ejic.201100055

Synthesis, Structures, and Unique Luminescent Properties of Tridentate C^C^N Cyclometalated Complexes of Iridium

Yuji Koga,*[a] Marina Kamo,[a] Yuji Yamada,[a] Taisuke Matsumoto,[b] and Kouki Matsubara*[a]

Keywords: Synthesis design / Iridium / N ligands / Luminescence / Near-infrared emission

The first C^C^N cyclometalated complexes of iridium that bear tridentate pyridylbiphenylene ligands are reported herein. These complexes were synthesized in good yields by means of the directed C–C bond activation of biphenylene with the assistance of pyridyl group precoordination. Their photoluminescent performances were also studied and show unique luminescent properties at longer wavelengths in the near-infrared range than that of previously synthesized C^N^C cyclometalated iridium complexes.

Introduction

Recently, phosphorescent materials have been widely reported as organic electroluminescent devices,[1,2] sensor materials,[3] and bioimaging probes.[4] Phosphorescent materials are expected to exhibit higher luminescent efficiency than fluorescent ones, because both triplet and singlet excitons generate in 3:1 ratios when excited. Iridium,[5] platinum,[6] and rhenium compounds[7] are chemically stable and can emit several colors of light even at room temperature. Quite recently, luminescence in the near-infrared range has also been reported.[8] Cyclometalated complexes of iridium that bear conjugated chelate ligands have attracted attention in these studies because these compounds have great potential to exhibit highly efficient luminescence at room temperature.[5] Tris(phenylpyridine)iridium, [Ir(ppy)$_3$], in which ppy is 2-phenylpyridine, and its analogues are well known as stable and efficient luminescent materials.[5a] Some examples of these are shown in Figure 1. Williams et al.[9] have reported that iridium complexes that bear tridentate conjugated ligands exhibit higher quantum yields [Φ = 0.76: for [Ir(dpyx)(ppy)Cl], in which dpyx is 1,3-bis(2-pyridyl)-4,6-dimethylbenzene] than that of the bidentate analogue *fac*-[Ir(ppy)$_3$] (Φ = 0.40). Haga et al. have also shown the effectiveness of tridentate ligands in other luminescent organometallic compounds.[10] These high luminescent efficiencies are believed to be derived from two facts: cyclometalated tridentate ligands allow easy electron transfer between the conjugated π orbital and the metal d orbital due to a large overlap, and the rigid structure derived from the strong tridentate coordination including metal–carbon σ bonds makes the complex stable[11] and suppresses the radiationless deactivation process.

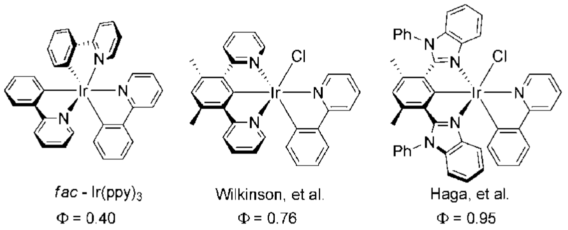


Figure 1. Structures of bidentate and tridentate complexes of iridium.

The above findings prompted us to design new C^C^N-type tridentate ligands to study the luminescent properties of iridium complexes. To the best of our knowledge, there have been no reported C^C^N complexes. Previous synthetic approaches using pyridylbiphenyl with iridium chloride to obtain the iridium complexes have been unsuccessful.[12] Only DFT calculations of a gold complex that bears such tridentate ligands are reported, and this study compares the orbital relationships and luminescent properties of C^C^N with its analogues, C^N^C, N^C^N, and N^N^C.[13] We describe here a synthetic route to the iridium C^C^N cyclometalated complexes using pyridylbiphenylene as a starting compound to form a C^C^N cyclometalated moiety, as oxidative addition of the C–C bond of biphenylene to iridium has been reported previously.[14] As a result, we have successfully prepared a series of C^C^N cyclometalated iridium complexes for the first time, determined these structures, and examined the luminescent properties.

---

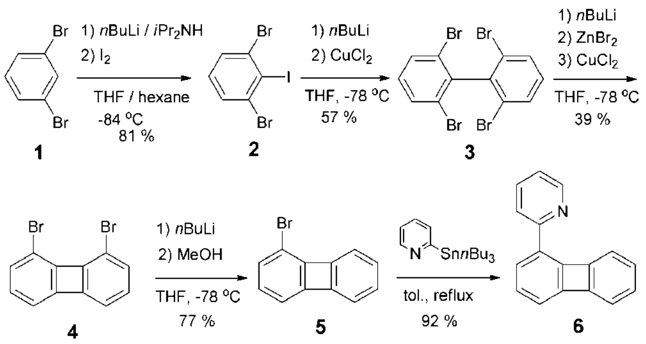
[a] Department of Chemistry, Fukuoka University,
8-19-1 Nanakuma, Fukuoka 814-0180, Japan
Fax: +81-92-865-6030
E-mail: y-koga@fukuoka-u.ac.jp
kmatsuba@fukuoka-u.ac.jp
[b] Analytical Center, Institute for Materials Chemistry and Engineering, Kyushu University,
6-1 Kasuga, Fukuoka 816-8580, Japan

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201100055.

Results and Discussion

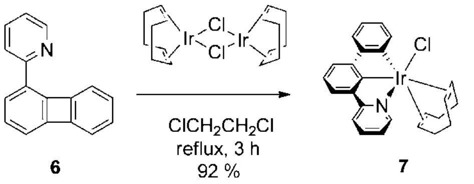
Syntheses of Pyridylbiphenylene and Iridium Complexes

The synthetic scheme to obtain pyridylbiphenylene (**6**) is shown in Scheme 1, in which *m*-dibromobenzene (**1**) was used as the starting material and the target compound **6** was isolated from the reaction of bromobiphenylene (**5**) with 2-(tributylstannyl)pyridine by means of Stille coupling in excellent yield.[9]



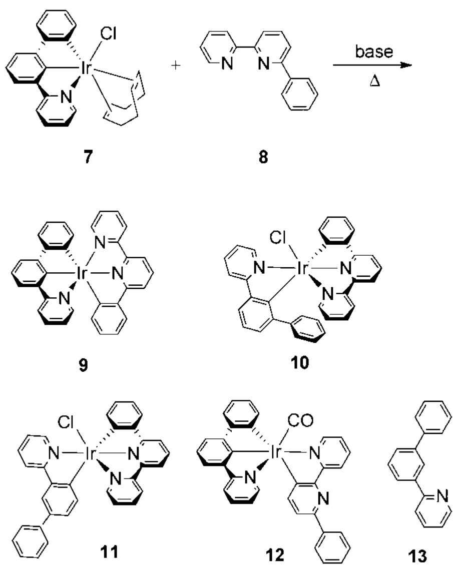
Scheme 1. Synthetic route for **6**.

The reaction of chloro(1,5-cyclooctadiene)iridium(I) dimer [{IrCl(cod)}$_2$] with **6** (2 equiv.) in 1,2-dichloroethane under reflux conditions gave the first C^C^N cyclometalated complex of iridium, [IrCl(cod)(C^C^N-pybp)] (**7**, in which pybp is pyridylbiphenyl) in 92% yield (Scheme 2). As observed in the ^{1}H NMR spectra of the crude mixture, no other complexes were formed through oxidative addition of the biphenylene C–C bonds in **6**, furthest from the pyridine ring.



Scheme 2. Preparation of **7** from [{IrCl(cod)}$_2$] and **6**.

The formation of **7** encouraged us to synthesize a new series of luminescent complexes of iridium by its reaction with conjugated aromatic compounds. The reaction of **7** with 6-phenyl-2,2′-bipyridyl (**8**) in glycerol at 130–200 °C in the presence of a base formed a complicated mixture (Scheme 3). As shown in Table 1, a small amount of the target product **9** along with byproducts **10**–**13** were isolated by chromatography. Unfortunately, the yields of **9** were less than 5%, and even when the reaction was conducted at lower temperatures, 160 and 130 °C, the yields did not improve (Table 1, entries 8–10). Under most reaction conditions, reductive elimination of the C^C^N ligand occurs to form iridium complexes **10** and **11** (entry 1) or 3-pyridylbiphenyl (**13**) (entries 2–10) in low to moderate yields, probably following the oxidative addition of some C–H bonds in **8** to generate a hydride species. Thus, we found that the bases were not effective for halogen extraction in this reaction. When two equivalents of **8** were used without the base, only **10** was formed, and the isolated yield was up to 65% by recrystallization from chloroform/ethyl acetate (entry 2).



Scheme 3. The reaction of **7** with **8** in the presence of base.

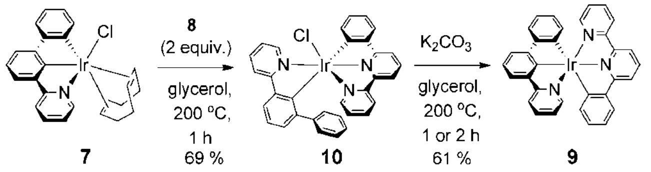
Table 1. The reaction of iridium complex **7** with 6-phenylbipyridyl **8** (1 equiv.).

Entry	Solvent	Base	*T* [°C]	*t* [h]	Yields [%]					Recovery [%]	
					9	**10**	**11**	**12**	**13**	**7**	**8**
1	glycerol	–	200	1	0	26(40[a])	trace(22[a])	0	0	0	0
2[b]	glycerol	–	200	1	0	69	0	0	0	0	–[c]
3	glycerol	K_2CO_3	200	1	5	trace	trace	4	13	0	0
4	glycerol	Cs_2CO_3	200	1	2	trace	trace	3	16	0	0
5	glycerol	K_3PO_4	200	1	5	8[d]	16[d]	1	34	0	45[d]
6	ethylene glycol	K_2CO_3	195	1	trace	0	0	12	35	0	9
7	glycerol	K_2CO_3	160	1	2	11	trace	3	17	21	11
8	glycerol	K_2CO_3	160	24	3	trace	trace	6	7	0	0
9	glycerol	K_2CO_3	130	24	4	7	trace	2	10	19[a]	8[a]
10	2-ethoxyethanol	K_2CO_3	130	24	0	0	0	15	28	0	5

[a] The yields were determined by the ^{1}H NMR spectra of the mixture from the integrated ratio of each product. [b] Two equiv. of compound **8** were used only in this reaction. [c] We did not determine the yield of **8** in this reaction; however, it proceeded almost quantitatively. [d] The yields were roughly determined including some negligible contaminations.

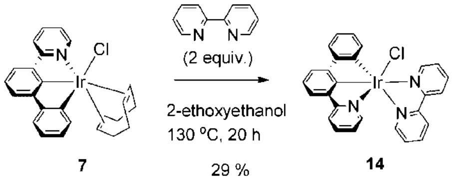
On the other hand, the undesired directed C–H bond activation of **8** also proceeded to form **12** in the presence of base in low yields (entries 3–10).

Fortunately, we discovered that **10** was an intermediary product in the generation of **9**, which never formed in the absence of base. As shown in Scheme 4, when a solution of **10** was heated with K_2CO_3 at 200 °C for 1 or 2 h, we observed two sets of signals assigned as **9** and **10** in a 2:1 ratio in the ^1H NMR spectrum of the crude mixture. By using silica gel column chromatography we could isolate **9** in 61% yield, and the overall yield from **7** was 42%.



Scheme 4. Preparation of **9**.

We also tried a reaction of a bidentate ligand, 2,2′-bipyridyl, with which *ortho*-metalation does not proceed, in contrast to 6-phenylbipyridyl. Successfully, a simple ligand-exchange reaction proceeded to form iridium complex **14** in 29% isolated yield as a result of the reaction of **7** with 2 equiv. of 2,2′-bipyridyl in 2-ethoxyethanol at 130 °C for 20 h (Scheme 5).



Scheme 5. Preparation of **14**.

Characterization of Iridium Complexes 7, 9–12, and 14

The isolated iridium complexes **7**, **9**–**12**, and **14** were characterized by ^1H and ^{13}C NMR spectroscopy, IR, UV, and ESI-MS. The structures of some complexes (**7**, **10**–**12**) were determined by single-crystal X-ray diffraction studies. The ^1H NMR spectrum for **7** demonstrated the existence of the biphenylpyridine ligand and cyclooctadiene in a 1:1 ratio, as calculated from the integrated ratios of the assigned proton signals in these ligands. The expected formation of the tridentate ligand has clearly occurred as determined by detection of the characteristic downfield shift of the ^{13}C resonances due to the two iridium-bound quaternary carbon atoms at δ = 172.4 and 167.0 ppm. Also, the typical downfield shift of the signals due to the four protons in the pyridine ring − δ = 7.86–9.18 ppm in **7**, down from δ = 7.41–8.71 ppm in **13** − supported the coordination of the pyridine group. Finally, we confirmed the structure of **7** on the basis of X-ray crystallography. As shown in Figure 3 (a), the pyridylbiphenylene ligand took an almost planar conformation and shows the conjugated plane as expected. The tridentate ligand, η^4-cyclooctadiene, and chlorine made a distorted octahedral trivalent iridium structure. The bond length between the iridium and the center carbon, Ir1–C11, was 2.002(3) Å, which was in the range of an iridium–carbon single bond. Those between the iridium and the side carbon and nitrogen atoms, Ir1–C17 and Ir1–N1, were 2.112(3) and 2.203(3) Å, respectively. These lengths are a little longer than that of the Ir1–C11 bond length,[15] and a representative list of the bond lengths and angles in **7** and the other structures is shown in Table 2.

Table 2. Representative bond lengths [Å] and angles [°] for **7**, **10**, and **12**.

Bond lengths		Bond angles	
7			
Ir1–Cl1	2.3887(8)	Cl1–Ir1–C11	96.83(9)
Ir1–N1	2.203(3)	N1–Ir1–C11	76.75(12)
Ir1–C11	2.002(3)	N1–Ir1–C17	152.09(12)
Ir1–C17	2.112(3)	C11–Ir1–C17	78.51(13)
C5–C6	1.459(4)		
C10–C12	1.476(5)		
C18–C19	1.404(5)		
C22–C23	1.381(5)		
10			
Ir1–Cl1	2.4916(14)	Cl1–Ir1–N1	93.89(14)
Ir1–N1	2.050(5)	Cl1–Ir1–C11	173.53(16)
Ir1–N2	2.127(5)	N1–Ir1–N3	176.43(19)
Ir1–N3	1.984(5)	N2–Ir1–C33	160.3(2)
Ir1–C11	2.031(5)		
Ir1–C33	2.019(5)		
C5–C6	1.462(9)		
C10–C12	1.503(9)		
12			
Ir1–N1	2.165(6)	N1–Ir1–C11	78.8(3)
Ir1–N2	2.160(6)	N1–Ir1–C17	159.2(3)
Ir1–C11	1.983(6)	N2–Ir1–C24	78.3(2)
Ir1–C17	2.075(7)	Ir1–C34–O1	174.5(6)
Ir1–C24	2.053(7)		
Ir1–C34	1.900(8)		
O1–C34	1.133(9)		
C27–C28	1.468(10)		

The ^1H NMR spectrum of **9** shown in Figure 2 has all the signals and coupling patterns assigned by using two-dimensional NMR spectroscopic studies. The full results from these studies are provided in the Supporting Information. All the signals from both the ^1H and ^{13}C NMR spectra were observed independently, thus demonstrating its asymmetric structure. The ESI-MS spectrum of the protonated compound, calculated as *m*/*z* = 654.1521 ($C_{33}H_{23}N_3Ir^+$) and observed as *m*/*z* = 654.2411, showed no existence of chlorine, and the observed isotopic distribution was in good agreement with the calculated one.

The ^1H NMR spectrum for **10** in the aromatic region showed 23 independent signals, one more than **9**. The presence of a chlorine atom close to the α-proton in one of the pyridyl groups was indicated by the appearance of a downshifted doublet signal at δ = 10.20 ppm. This was further supported by two-dimensional NMR spectroscopy and it was confirmed by X-ray crystallography as shown in Fig-

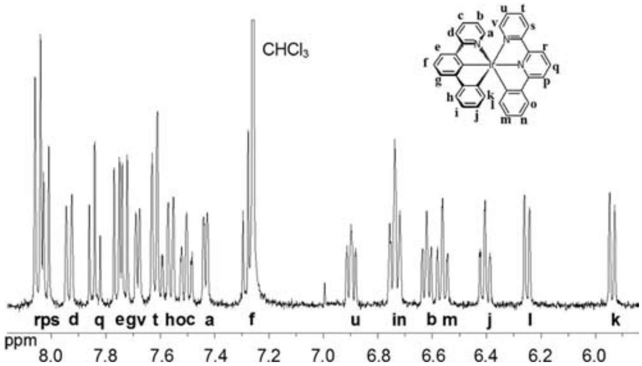


Figure 2. ^1H NMR spectrum for **9** (400 MHz, in $CDCl_3$).

ure 3 (b). The structure showed a pseudo-octahedral conformation, composed of a chloride ligand, bidentate C^N-pyridylbiphenyl, and tridentate N^N^C-phenylbipyridyl. Interestingly, one of the phenyl groups in the bidentate C^N-pyridylbiphenyl forms π–π stacking with the center pyridyl group of the tridentate N^N^C-phenylbipyridyl at a distance of 3.9 Å. In solution, five independent ^1H NMR spectroscopic resonances due to the stacking phenyl group suggested that the rigid conformation is the same as in the solid state.

Similar signals to those for **10** were observed in the ^1H NMR spectrum for **11**, in that the number of the protons in **11** was 23, and a doublet signal appeared at δ = 10.24 ppm. ESI-MS spectra for **10** and **11** both showed the typical separated patterns of the same isotopes, *m*/*z* = 654.2 and 652.2 as dechlorinated major signals. These observations indicate that **10** and **11** are structurally different isomers. The equivalent signals in the ^1H NMR spectrum for **11** around δ = 7.3–7.4 ppm are assigned to five protons in a phenyl group, of which free rotation of the C–C single bond is possible, which stands in sharp contrast to the case of **10**. Preliminary single-crystal X-ray diffraction study for **11** agreed well with these spectral observations and this is shown in the Supporting Information.

Evidence for the carbonyl ligand in **12** was provided by several spectroscopic analyses. The IR spectrum showed a very strong single absorbance at 1995 cm^{-1}, assigned as the CO stretching band, and a ^{13}C NMR spectroscopic resonance in the lowest field at δ = 174 ppm due to the quaternary CO carbon was also observed. The ESI-MS spectrum supported the atomic composition of $[C_{33}H_{22}N_3Ir/CO/Na]^+$ for **12** as expected. Finally, the structure was confirmed by X-ray crystallography as shown in Figure 3 (c). The existence of the tridentate C^C^N-pyridylbiphenylene in **12** is significant in that it shows that such coordination modes are thermally stable in the reaction of **7** with pyridyl ligands. We assumed that the carbonyl group in **12** was introduced from the alcoholic solvents or M_2CO_3, in which M was K or Cs. A small amount of **12** is formed upon addition with K_3PO_4 (Table 1, entry 5), and the dependence of the yield of **12** on the solvents (Table 1, entries 9 and 10) suggests that the carbonyl group can be derived from the solvents by means of a C–C bond-cleavage reaction. Formation of a carbonyl complex of iridium in 2-ethoxyethanol with base has previously been reported in the literature.[16] Nineteen independent signals in the ^1H NMR spectrum of **14** due to 19 aromatic protons indicate that there are no non-iridium bound aromatic groups. The typical down-field doublet signal at δ = 10.19 ppm, assigned to an α-proton of the pyridyl group, strongly indicates the chlorine atom remains in **14**, similar to **10** and **11**.

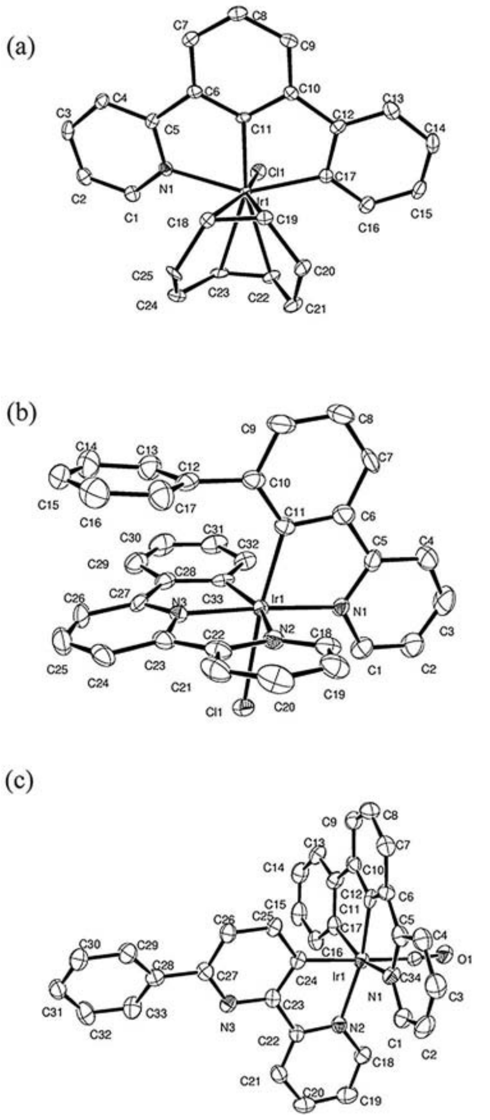
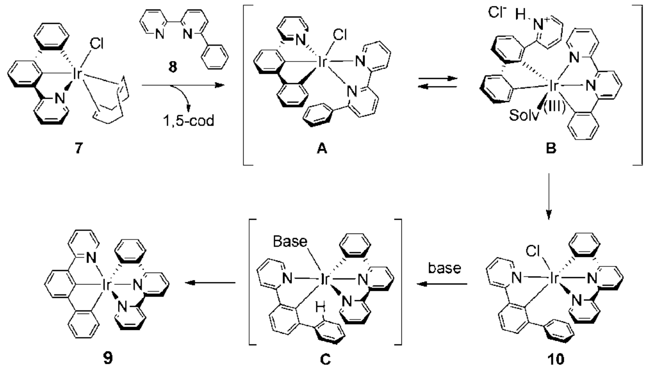


Figure 3. ORTEP drawings of (a) **7**, (b) **10**, and (c) **12** (50% probability of thermal ellipsoids). All hydrogen atoms are omitted for clarity.

Reaction Mechanism to Form 10 and 9

We considered the reaction mechanism in the stepwise formation of **10** and then **9** from **7**. As for the formation of **10** in the absence of the base, it is easily imagined that the ligand-exchange reaction of η^4-cyclooctadiene with the bipyridyl group in **8** proceeds to form an unknown product **A** as an intermediate. The formation of intermediate **A** was shown to be possible by the reaction of **7** with 2,2′-bipyridyl to form **14**, a similar complex to **A**. However, **A** was not detected when the reaction was carried out at the same temperature, 130 °C, as that at which **14** formed. Because free pyridylbiphenyl and any decomposed products were not observed in the crude mixture of the reaction without the base (Table 1, entry 2), some intramolecular interconversion could occur after ligand substitution of **7** with phenylbipyridyl. Formation of an iridium(III) intermediate **B** (Scheme 6) might be possible through elimination of chloride anion and pyridinium cation formed by cleavage of the aromatic C–H bond in phenylbipyridyl from **A**. Formation of the cation was partly evidenced by addition of AgOTf into the reaction mixture to form a complex mixture and not **10**. The high reaction temperature prevented further investigation. We found that **10** is one of the intermediates for efficient production of **9**, which might be formed through formation of an intermediate **C** from **10**. Transmetallation of chloride in **10** and removal of proton accompanied by the Ir–C bond formation might form **9** as proposed in Scheme 6. It is noteworthy that **9** is thermally more stable than **10** in the presence of base, as expected.



Scheme 6. Proposed reaction mechanism to form **10** and **9**.

Although we have poor information to help us to understand why the yields were quite low when the base was initially added to **7**, we found that **7** is unstable in the presence of base. Addition of K_2CO_3 to a solution of **7** forms many decomposed products, such as pyridylbiphenyl **13**, upon heating at 160 °C for 1 h, whereas no decomposition occurred under the same conditions without the base.

Luminescence

Photoluminescent spectroscopy for the complexes **9–12** and **14** was measured in CH_2Cl_2 (1.0×10^{-5} M) (Figure 4). The wavelengths at the maximum intensity in the UV/Vis and luminescent spectra are listed in Table 3. Remarkably, all the cyclometalated iridium complexes except **12** have quite unique luminescent wavelengths in the deep red (650 nm) to near infrared (730 nm) range. The C^C^N cyclometalated complexes **9** and **14** showed similar weak broad luminescent spectra from 600 nm to more than 800 nm, in which the wavelengths at the maximum intensity were both about 730 nm. In contrast, the luminescent spectra for the carbonyl complex **12** showed a characteristic blueshift to 525 nm as the wavelength at the maximum intensity, apparently due to the existence of the acceptor, CO ligand.[17] On the other hand, it is interesting that the wavelengths in the luminescent spectra for the tridentate C^N^N cyclometalated complexes **10** and **11** were both 650 nm, which were about 80 nm shorter than that observed in the spectra for the C^C^N complexes **9** and **14**. The X-ray diffraction study for **10** indicated the existence of π–π-stacking interaction between the aromatic groups of the bidentate pyridylbiphenylene and tridentate phenylbipyridyl ligands. However, any influence of that interaction on the luminescence behavior of **10** was not detected compared with that of **11**. This is a similar result to that reported in a literature,[18] although another recent report showed a significant effect on the luminescent properties.[19] The lu-

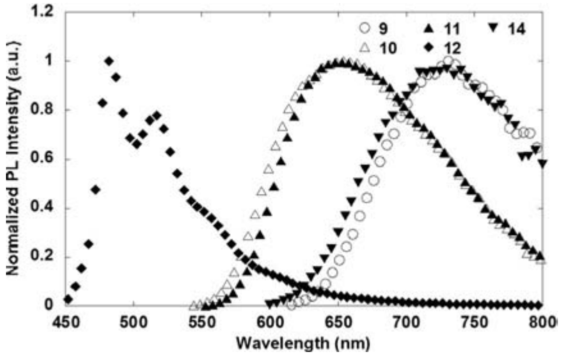


Figure 4. Photoluminescence spectra (1.0×10^{-5} M in CH_2Cl_2) for **9**, **10**, **11**, **12**, and **14**, for which the irradiated wavelengths were 400 nm. Another irradiation wavelength around 400 nm did not affect the shapes of the spectra for all the compounds.

Table 3. Absorption and luminescent properties for **9**–**12**, and **14**.

Complex	Absorption λ_{max} [nm] (ε/10^3 mol^{-1} [dm^{3}cm^{-1}]) [a]	Emission λ_{max} [nm][b]	Φ[c]
9	272 (36.8), 286 (32.9), 317 (19.9), 405 (12.1), 431 (11.4), 456 (8.4)	730	1.5×10^{-3}
10	272 (32.5), 295 (26.3), 348 (12.7), 396 (5.9), 425 (4.4)	655	7.4×10^{-3}
11	268 (46.1), 398 (35.0), 353 (11.1), 402 (5.7), 430 (4.4)	650	9.8×10^{-3}
12	252 (47.7), 272 (40.4), 310 (21.6), 350 (14.8), 384 (9.7)	485, 515	4.2×10^{-2}
14	287 (36.6), 303 (24.1), 393 (10.3), 418 (10.6), 439 (8.2)	725	8.5×10^{-4}

[a] Absorption data for the iridium complexes in CH_2Cl_2 solution at room temperature. [b] Luminescence data for the iridium complexes in CH_2Cl_2 solution at room temperature. [c] Luminescence quantum yield, measured using $Ru(bpy)_3Cl_2$ as the standard (Φ = 0.028).

minescence quantum yields, which were measured using [Ru(bpy)$_3$Cl$_2$] as the standard (Φ = 0.028), were all disappointingly small. Such low luminescent efficiency of tridentate cyclometalated iridium complexes has also been reported previously.[5d,20]

Consideration for Luminescent Properties

Although poor emission intensities of these complexes disappointed us (for example, the quantum yield Φ of **9** was under 0.01), the range of the wavelengths for these complexes was characteristic and needs further explanation. On the basis of DFT calculations, we compared the HOMO and LUMO energy band gap of **9** with those of an iridium complex **X** that bear dpyx and dppy as N^C^N and C^N^C cyclometalated ligands, respectively. Figure 5 illustrates the HOMO and LUMO energy correlations of **9** and **X**[21] and shows the effects of these tridentate cyclometalated ligands on the frontier orbitals. The energy levels of the center metal orbital in these complexes are the same because they have the same numbers of carbon and nitrogen atoms bound to iridium. However, it is of interest that the energy diagram suggests that the high energy levels of both the π and π* orbitals in the C^C^N ligand, and the low energy levels of those in the N^N^C of **9**, can induce a narrower energy band gap between the HOMO (the occupied iridium d orbital) and LUMO (π* of N^C^C ligand) than that of **X**. This narrow band gap may result in the typical redshift we have seen in the C^C^N cyclometalated complexes. A recent calculation study that compared some gold complexes that bear the same tridentate ligands also showed a higher energy of the unoccupied MO of the C^C^N cyclometalated ligand than that of C^N^C ligand.[22]

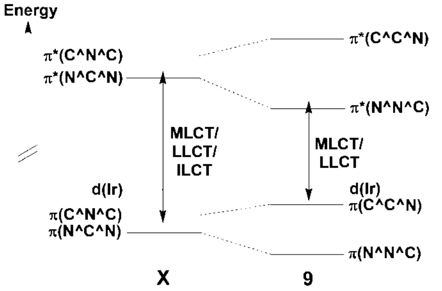


Figure 5. Simplified schematic energy-level diagram of the iridium complexes **9** and **X**. Long-wavelength emission in **9** is attributed to a narrow-energy band gap of the MLCT between d(Ir) and π*(N^N^C). "Double-ζ"-quality basis sets were employed for the ligands (6-31G) and the Ir (LANL2DZ).

As for the unexpected low photoluminescence intensity in these C^C^N cyclometalated complexes, we considered that one of the subsequent hypotheses that arose from the DFT calculation results of **9**, which were conducted with double-ζ-quality basis sets for the ligands (6-31G) and Ir (LANL2DZ), clearly explains the phenomenon. The energy level of the π orbital of the N^N^C ligand in **9** is lower than that of the π orbital of the N^C^N ligand in X. The orbitals, d(Ir) and π(C^C^N ligand), are closely located, which resulted in energy transfer from both the metal and the ligand to the π*(N^N^C) orbital in the other ligand. Thus they are MLCT and LLCT by irradiation. Such a high degree of LLCT character in the excited state could lead to the low luminescent ability of iridium in the relaxation process similar to a previously reported iridium complex that bear tridentate ligands, [Ir(N^C^N)-(N^N^N)]$^{2+}$.[9] The calculated HOMO orbital in **9** showed delocalization of electron density in both the metal and the C^C^N ligand as shown in Figure 6.

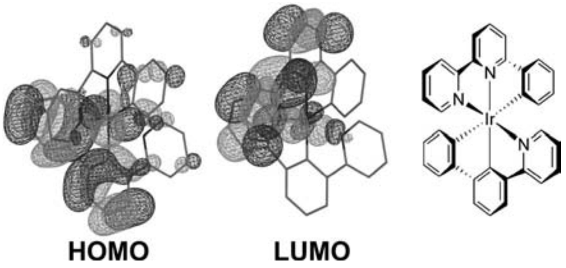


Figure 6. Electron-density maps of the HOMO (left) and LUMO (right) for **9** calculated by density functional theory (DFT) based on B3LYP 6-31G for the ligand and LANL2DZ for iridium atom.

We also discussed a possibility for the photochemical instability of **9**, which could lead to low photoluminescence intensity. A previous study demonstrated photochemical decomposition of an iridium complex that bear tridentate C^N^C and N^C^N cyclometalated ligands (**X**) in CH$_2$Cl$_2$ when irradiated with visible light for 5 min.[9] However, under similar conditions to the literature, photoirradiation of **9** using 400 nm light from a 150 W xenon lamp for 5 min did not decrease the photoluminescence intensity of **9**, as shown in Figure 7. In addition, we did not detect any change in the ^{1}H NMR spectra for the solution of **9** in CDCl$_3$ after photoirradiation for 1 h with the lamp without any filters, thereby indicating the remarkable toughness of **9** against light, which is in sharp contrast to that of **X**. Thus, we concluded that the low luminescent ability in **9** was not derived from the photochemical decomposition process. However, the photochemical stability of **9** is good information for us to use in the design of new luminescent iridium complexes that bear tridentate ligands.

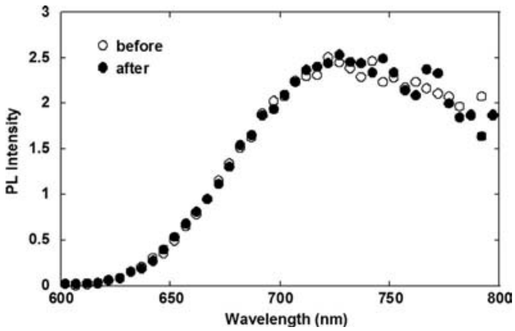


Figure 7. Photoluminescent spectra for **9** before (○) and after (●) photoirradiation using a 400 nm light for 5 min in CH$_2$Cl$_2$.

Conclusion

New C^C^N cyclometalated iridium complexes that bear tridentate 3-pyridylbiphenyl were synthesized by means of directed oxidative addition of the C–C bond of pyridylbiphenylene with chloro(1,5-cyclooctadiene)iridium(I) dimer, [{IrCl(cod)}$_2$]. The reaction of the iridium complex, [IrCl(cod)(C^C^N-pyridylbiphenyl)] (**7**) with 6-phenyl-2,2′-bipyridyl in the presence of base at 130–200 °C formed several products, most of which were isolated and structurally characterized. [Ir(C^C^N-pyridylbiphenyl)(C^N^N-phenylbipyridyl)] (**9**) and [IrCO(C^C^N-pyridylbiphenyl)(N^C-phenylbipyridyl)] (**12**) were good examples of C^C^N cyclometalated complexes. Two structural isomers of [IrCl(C^N-pyridylbiphenyl)(C^N^N-phenylbipyridyl)] (**10** and **11**) were two examples of C^N^N cyclometalated complexes. Compound **9** was afforded in good yield through the formation of the intermediate **10**, which can be isolated in high yield from the reaction of **7** with 6-phenyl-2,2′-bipyridyl (2 equiv.) in the absence of base. The reaction of **7** with 2,2′-bipyridyl also gave a C^C^N cyclometalated complex, [IrCl(N^N-bipyridyl)(C^C^N-pyridylbiphenyl)] (**14**). The photoluminescent performances of the isolated complexes were also studied. Despite low luminescent intensity, **9** and **14** showed luminescence at longer wavelengths than that of previous C^N^C cyclometalated iridium complexes, due to the high π*-orbital energy of C^C^N pyridylbiphenyl ligand.

Experimental Section

General: All experiments for synthesis of the iridium complexes were carried out under an argon atmosphere using standard Schlenk techniques unless otherwise noted. The solvents, glycerol, 2-ethoxyethanol, and ethylene glycol, were stored under 4 Å molecular sieves and degassed before use. Other reagents were used as received. Column chromatography of products was carried out using silica gel [Kanto Kagaku, silica gel 60N (spherical, neutral)]. Preparative TLC was prepared with the same silica gel on a glass plate (20 cm × 20 cm). The ^{1}H NMR spectra were taken with a VARIAN Mercury Y plus 400 MHz spectrometer at room temperature. Chemical shifts (δ) were recorded in ppm from the solvent signal. IR spectra were recorded in cm^{-1} with a Perkin–Elmer Spectrum One spectrometer equipped with a universal diamond ATR. UV/Vis spectra were measured with a JASCO V-550 UV/Vis spectrophotometer. Photoluminescent spectra were recorded with a Hitachi F-7000 fluorescence spectrophotometer. All the samples were dissolved in CH_2Cl_2. The quantum yields were calculated from the luminescent spectra, calibrated by the standard solution, [Ru(bpy)$_3$Cl$_2$] solution in water (quantum yield 0.028). The elemental analysis was carried out with a YANACO CHN Corder MT-5 auto-sampler. Electrospray ionization time-of-flight mass spectrometry (ESI-TOF MS) was carried out with a JEOL JMS-T100 mass spectrometer. The sample solutions in methanol were directly infused using methanol as solvent stream. The synthesis of the organic compounds **2**–**4** was carried out according to the literature.[23] Although the synthesis of **5** has been reported previously,[24] we developed an alternative route to **5** from **4**, details of which are shown in the Supporting Information.

Preparation of 1-(Pyridine-2-yl)biphenylene (6): Compound **5** (120 mg, 0.5 mmol), 2-(tributylstannyl)pyridine (230 mg, 0.6 mmol), lithium chloride (85 mg, 2.0 mmol), and dichlorobis(triphenylphosphane)palladium (7.3 mg, 0.01 mmol) were added to a 20 mL Schlenk tube. The mixture was dissolved in toluene (2.5 mL). The tube was refilled with argon and equipped with a reflux condenser. The solution was heated under reflux for 15 h with stirring. After cooling to room temperature, a saturated aqueous solution of potassium fluoride (2.5 mL) was added and stirred for 30 min. After the suspension was filtered, the solution was extracted with dichloromethane (2.5 mL × 3), dried under $MgSO_4$, and filtered. Removal of the solvent under reduced pressure gave a yellow liquid. Compound **6** was purified after silica gel column chromatography by eluting with hexane, as a yellow liquid (110 mg, 92% yield). ^{1}H NMR (CDCl$_3$): δ = 8.71 (d, *J* = 4.4 Hz, 1 H, H^6-py), 7.76 (t, *J* = 7.6 Hz, 1 H, H^4-py), 7.63 (d, *J* = 8.0 Hz, 1 H, H^3-py), 7.41 (d, *J* = 8.4 Hz, 1 H, H^2-biph), 7.22 (t, *J* = 7.6 Hz, 1 H, H^5-py), 6.95–6.93 (m, 1 H, H^6-biph), 6.86 (t, *J* = 7.8 Hz, 1 H, H^3-biph), 6.82–6.80 (m, 2 H, H$^{5/8}$-biph), 6.69 (m, 1 H, H^7-biph), 6.66 (d, *J* = 6.8 Hz, 1 H, H^4-biph) ppm. ^{13}C NMR (CDCl$_3$): δ = 154.7 (C^2-py), 151.5 (quat.), 151.4 (quat.), 151.3 (quat.), 149.7 (C^6-py), 149.1 (quat.), 136.4 (C^4-py), 130.3 (C^1-biph), 129.0 (C^3-biph), 128.7 (C^8-biph), 128.3 (C^5-biph), 126.1 (C^2-biph), 122.1 (C^5-py), 120.7 (C^3-py), 118.8 (C^6-biph), 117.3 (C^4-biph), 117.1 (C^7-biph) ppm. GC–MS (EI): *m*/*z* calcd. for $C_{17}H_{11}N$: 229.089; found 229.018 [M$^+$]. $C_{17}H_{11}N + H_2O$ (247.29): calcd. C 82.57, H 5.30, N 5.66; found C 82.30, H 5.01, N 5.96.

Preparation of 7: 1-(Pyridine-2-yl)biphenylene (0.71 g, 3.1 mmol), [{IrCl(cod)}$_2$] (1.0 g, 1.6 mmol), and 1,2-dichloroethane (15 mL) were added to a 20 mL Schlenk tube. The solution was stirred at room temperature for 30 min and then at 95 °C for 3 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residual orange solid was dissolved in dichloromethane. Addition of ethyl acetate lead to precipitation of the product **7** (1.66 g, 92% yield). ^{1}H NMR (CDCl$_3$): δ = 9.18 (d, *J* = 5.8 Hz, 1 H, H^6-C^C^*N*), 7.97–7.90 (m, 2 H, H$^{3/4}$-C^C^*N*), 7.88–7.86 (m, 1 H, H^6-C^C^N), 7.61–7.55 (m, 2 H, H^3-C^C^N/H^3-C^C^N), 7.52 (d, *J* = 7.8 Hz, 1 H, H^5-C^C^N), 7.37 (t, *J* = 6.2 Hz, 1 H, H^5-C^C^*N*), 7.20–7.15 (m, 2 H, H$^{4/5}$-C^C^N), 7.12 (t, *J* = 7.6 Hz, 1 H, H^4-C^C^N), 5.88–5.80 (m, 1 H, C*H*-cod), 5.16–5.08 (m, 1 H, C*H*-cod), 3.16–3.06 (m, 2 H, C*H*-cod), 2.92–2.72 (m, 2 H, C*H*$_2$-cod), 2.45–2.34 (m, 2 H, C*H*$_2$-cod), 2.33–2.13 (m, 2 H, C*H*$_2$-cod), 2.01–1.78 (m, 2 H, C*H*$_2$-cod) ppm. ^{13}C NMR (CDCl$_3$): δ = 172.4 (C^1-C^C^N), 167.0 (C^1-C^C^N), 152.3 (C^2-C^C^*N*), 151.5 (C^6-C^C^*N*), 150.1 (C^2-C^C^N), 140.6 (C^6-C^C^N), 138.7 (C^2-C^C^N), 138.4 (C^4-C^C^*N*), 135.2 (C^6-C^C^N), 127.4 (C^4-C^C^N), 123.8 (C^4-C^C^N), 123.8 (C^5-C^C^N), 122.9 (C^4-C^C^N), 121.6 (C^3-C^C^N), 121.6 (C^3-C^C^N), 121.3 (C^5-C^C^N), 120.0 (C^3-C^C^*N*), 105.3 (*C*H-cod), 104.4 (*C*H-cod), 85.09 (*C*H-cod), 79.26 (*C*H-cod), 33.64 (*C*H$_2$-cod), 31.54 (*C*H$_2$-cod), 27.95 (*C*H$_2$-cod), 26.34 (*C*H$_2$-cod) ppm. ESI-MS: *m*/*z* calcd. for $[C_{26}H_{27}NClIr + H]^+$: 566.123; found 566.142. $C_{25}H_{23}ClIrN$ (565.13): calcd. C 53.13, H 4.10, N 2.48; found C 52.91, H 4.03, N 2.36.

General Reactions of 7 with 1-Phenylbipyridine (8): In a typical example, **7** (28 mg, 0.05 mmol), 1-phenylbipyridine (13 mg, 0.055 mmol), K_2CO_3 (35 mg, 0.25 mmol), and glycerol (1.0 mL) were added to a 20 mL Schlenk tube. The solution was stirred at 200 °C for 1 h. After cooling, water (5 mL) was added and extracted with dichloromethane (5 mL × 3). The solution was dried under Na_2SO_4 and filtered. Removal of the solvent under reduced pressure gave a brown solid. Separation of the products using silica gel column chromatography by eluting with dichloromethane/methanol gave **9**–**13**.

Compound 11: (orange crystals, trace amount): ^{1}H NMR (CDCl$_3$): δ = 10.2 (d, *J* = 6.0 Hz, 1 H, H^6-C^C^*N*), 8.03 (t, *J* = 8.2 Hz, 2 H, H^4-C^C^*N*/H^3-N^N^C), 7.92 (d, *J* = 6.0 Hz, 1 H, H^6-N^N^C), 7.89–7.83 (m, 3 H, H^4-C^C^*N*/H^5-N^N^C/H^5-N^N^C), 7.80–7.74 (m, 3 H, H^3-C^C^N/H^4-N^N^C/H^4-N^N^C), 7.55 (d, *J* = 7.6 Hz, 1 H, H^3-N^N^*C*), 7.43 (d, *J* = 8.0 Hz, 2 H, H$^{2/6}$-C^C^N), 7.38–7.22 (m, 5 H, H$^{3/5}$-C^C^N/H^5-C^N^*N*/H^3-N^N^C), 6.89–6.81 (m, 3 H, H^5-C^C^N/H$^{5/6}$-N^N^*C*), 6.34 (d, *J* = 7.2 Hz, 1 H, H^6-N^N^*C*), 6.23 (d, *J* = 7.2 Hz, 1 H H^6-C^C^N) ppm. ^{13}C NMR (CDCl$_3$): δ = 167.8 (quat.), 166.6 (quat.), 157.7 (quat.), 155.3 (quat.), 151.2, 149.9, 149.8 (quat.), 147.4 (quat.), 144.9 (quat.), 143.6 (quat.), 141.6 (quat.), 137.5, 137.0, 136.3, 133.9 (quat.), 132.5, 131.0, 130.7, 128.6, 128.5, 126.8 (C$^{2/6}$-C^C^N), 126.4 (C$^{3/5}$-C^C^N), 126.3, 125.3, 122.8, 122.4, 122.2, 121.4, 118.5, 118.2, 117.2 ppm. ESI-MS: *m*/*z* calcd. for $[C_{33}H_{23}N_3ClIr - Cl]^+$: 654.152; found 654.148. $C_{33}H_{23}ClIrN_3 + H_2O$ (707.24): calcd. C 56.04, H 3.56, N 5.94; found C 56.20, H 3.65, N 5.83.

Compound 12: (yellow crystals, 4% yield): ^{1}H NMR (CDCl$_3$): δ = 9.31 (d, *J* = 5.6 Hz, 1 H, H^6-N^N^C), 8.74 (d, *J* = 8.4 Hz, 1 H, H^3-N^N^C), 8.11 (t, *J* = 7.8 Hz, 1 H, H^4-N^N^C), 7.94 (t, *J* = 8.4 Hz, 2 H, H$^{3/6}$-C^C^*N*), 7.88 (d, *J* = 7.2 Hz, 2 H, H$^{2/6}$-N^N^*C*), 7.71 (t, *J* = 7.2 Hz, 1 H, H^4-C^C^*N*), 7.70 (d, *J* = 7.6 Hz, 1 H, H^3-C^C^N), 7.65 (d, *J* = 8.0 Hz, 1 H, H^5-C^C^N), 7.60 (d, *J* = 7.6 Hz, 1 H, H^3-C^C^N), 7.52 (t, *J* = 6.4 Hz, 1 H, H^5-N^N^C), 7.39–7.30 (m, 3 H, H^4-C^C^N/H$^{3/5}$-N^N^*C*), 7.27 (t, 1 H, H^4-N^N^*C*), 7.04 (d, *J* = 8.0 Hz, 1 H H^5-N^N^C), 6.98–6.89 (m, 2 H, H^4-C^C^N/H^5-C^C^*N*), 6.68 (t, *J* = 7.4 Hz, 1 H, H^5-C^C^N), 6.59 (d, *J* = 7.2 Hz, 1 H, H^6-C^C^N), 6.42 (d, *J* = 8.0 Hz, 1 H, H^4-N^N^C) ppm. ^{13}C NMR (CDCl$_3$): δ = 174.1 (CO), 166.9 (quat.), 164.6 (quat.), 164.2 (quat.), 162.1 (quat.), 159.9 (quat.), 154.4 (quat.), 151.6, 151.4 (quat.), 151.0 (quat.), 150.8, 141.4, 139.9 (quat.), 139.7 (quat.), 137.4, 137.4 (quat.), 137.2, 134.3, 128.4 (C$^{2/6}$-C^C^N), 128.0, 126.3, 125.0 (C$^{3/5}$-C^C^N), 123.1, 123.1, 122.8, 122.2, 121.8, 121.5, 121.2, 121.0, 120.0 ppm. IR: $\tilde{\nu}$ = 1995 (ν_{CO}) cm^{-1}. ESI MS: *m*/*z* calcd. for $[C_{34}H_{23}N_3OIr + Na]^+$: 704.129; found 704.224. $C_{34}H_{22}N_3OIr + H_2O$ (698.79): calcd. C 58.44, H 3.46, N 6.01; found C 58.30, H 3.72, N 5.71.

Preparation of 10: The product was similarly obtained from **7** (28 mg, 0.05 mmol) and 1-phenylbipyridine (26 mg, 0.11 mmol) in glycerol (1.0 mL). The red crystals of **10** were obtained from the dichloromethane/ethyl acetate solution (0.24 g, 69% yield). ^{1}H NMR (CDCl$_3$): δ = 10.20 (d, *J* = 8.0 Hz, 1 H, H^6-C^C^*N*), 8.06 (d, *J* = 6.8 Hz, 1 H, H^3-C^C^*N*), 7.90–7.82 (m, 2 H, H^4-C^C^*N*/H^6-N^N^C), 7.80–7.75 (m, 2 H, H$^{3/5}$-C^C^N), 7.70 (d, *J* = 8.0 Hz, 1 H, H^6-C^C^N), 7.41 (t, *J* = 8.8 Hz, 2 H, H^3-N^N^C/H^3-N^N^C), 7.30–7.17 (m, 4 H, H^4-C^C^N/H^5-C^C^*N*/H$^{4/5}$-N^N^C), 6.94–6.78 (m, 4 H, H$^{4/5}$-C^C^N/H^4-N^N^C/H^5-N^N^*C*), 6.73 (t, *J* = 7.4 Hz, 2 H, H^3-C^C^N/H^4-N^N^*C*), 6.40 (d, *J* = 7.5 Hz, 1 H, H^4-C^C^N), 6.34 (d, *J* = 7.4 Hz, 1 H, H^5-N^N^C), 6.16 (d, *J* = 7.2 Hz, 1 H, H^3-N^N^*C*), 6.08 (d, *J* = 7.5 Hz, 1 H, H^6-N^N^*C*) ppm. ^{13}C NMR (CDCl$_3$): δ = 167.6 (quat.), 167.0, 159.4 (quat.), 155.7 (quat.), 152.2, 150.0 (quat.), 150.0, 148.1 (quat.), 146.7 (quat.), 145.6 (quat.), 144.5 (quat.), 140.9 (quat.), 137.4 (quat.), 136.6, 136.3, 132.4, 132.3, 130.4, 129.3, 128.0, 127.4, 126.5, 126.2, 125.9, 124.9, 123.0, 122.6, 122.2, 121.6, 120.6, 119.0, 118.2, 117.5 ppm. ESI MS: *m*/*z* calcd. for $[C_{33}H_{23}N_3ClIr - Cl]^+$: 654.152; found 654.215. $C_{33}H_{23}ClIrN_3 + H_2O$ (707.24): calcd. C 56.04, H 3.56, N 5.94; found C 56.05, H 3.56, N 6.02.

Preparation of 9: Compound **10** (35 mg, 0.05 mmol), K_2CO_3 (35 mg, 0.25 mmol), and glycerol (1.0 mL) were added to a 20 mL Schlenk tube. The solution was stirred at 200 °C for 1 h. After cooling, water (5 mL) was added and extracted with dichloromethane (5 mL × 3). The solution was dried under Na_2SO_4 and filtered. Removal of the solvent under reduced pressure gave a brown solid. Silica gel column chromatography by eluting with dichloromethane gave **9** (20 mg, 61% yield). ^{1}H NMR (CDCl$_3$): δ = 8.06–8.01 (m, 3 H, H^3-N^N^C/H$^{3/5}$-N^N^C), 7.94 (d, *J* = 8.0 Hz, 1 H, H^3-C^C^*N*), 7.84 (t, *J* = 6.8 Hz, 1 H, H^4-N^N^C), 7.77–7.73 (m, 2 H, H$^{3/5}$-C^C^N), 7.68 (d, *J* = 5.6 Hz, 1 H, H^6-N^N^C), 7.63–7.56 (m, 3 H, H^3-C^C^N/H^4-N^N^*C*/H^3-N^N^*C*), 7.50 (t, *J* = 7.4 Hz, 1 H, H^4-C^C^*N*), 7.44 (d, *J* = 5.6 Hz, 1 H, H^6-C^C^*N*), 7.30–7.26 (m, 1 H, H^4-C^C^N), 6.89 (t, *J* = 9.8 Hz, 1 H, H^5-N^N^C), 6.74 (t, *J* = 7.6 Hz, 2 H, H^4-C^C^N/H^4-N^N^*C*), 6.62 (t, *J* = 6.2 Hz, 1 H, H^5-C^C^*N*), 6.56 (t, *J* = 8.0 Hz, 1 H, H^5-N^N^*C*), 6.41 (t, *J* = 7.2 Hz, 1 H, H^5-C^C^N), 6.26 (t, *J* = 7.6 Hz, 1 H, H^6-N^N^*C*), 5.94 (d, *J* = 7.6 Hz, 1 H, H^6-C^C^N) ppm. ^{13}C NMR (CDCl$_3$): δ = 186.7 (quat.), 168.0 (quat.), 164.0 (quat.), 158.3 (quat.), 156.1 (quat.), 152.7 (quat.), 152.6, 152.4 (quat.), 151.3 (quat.), 149.7, 148.2 (quat.), 144.0 (quat.), 138.9 (quat.), 136.3, 135.5, 135.5, 134.5, 132.2, 130.1, 126.1, 124.8, 124.5, 122.3, 120.9, 120.5, 120.2, 120.1, 119.9, 119.8, 119.7, 119.7, 119.0, 117.3, 116.2 ppm. ESI-MS: *m*/*z* calcd. for $[C_{33}H_{22}N_3Ir + H]^+$: 654.152; found 654.234. $C_{33}H_{22}IrN_3 + H_2O$ (670.78): calcd. C 59.09, H 3.61, N 6.26; found C 59.38, H 3.87, N 6.01.

Preparation of 14: Compound **7** (0.028 g, 0.050 mmol), 2,2′-bipyridine (0.016 g, 0.1 mmol), and 2-ethoxyethanol (5 mL) were added to a 20 mL Schlenk tube. The solution was stirred at 130 °C for 20 h. After the solvents were evaporated under reduced pressure, a residual brown solid was obtained. Silica gel column chromatography by eluting with dichloromethane and methanol in a 98:2 ratio and subsequent preparative TLC afforded red crystals of **14** (8.8 mg, 29% yield). ^{1}H NMR (CDCl$_3$): δ = 10.2 (d, *J* = 5.2 Hz, 1 H, H^6-N^N), 8.19 (d, *J* = 8.4 Hz, 1 H, H^3-N^N), 8.08 (t, *J* = 7.8 Hz, 1 H, H^4-N^N), 7.91 (d, *J* = 8.0 Hz, 1 H, H^3-N^*N*), 7.87 (d, *J* = 7.6 Hz, 1 H, H^3-C^C^*N*), 7.83–7.76 (m, 3 H, H^6-C^C^*N*/H^5-N^N/H^4-N^*N*), 7.59 (d, *J* = 6.6 Hz, 3 H, H$^{3/5}$-C^C^N/H^6-N^*N*), 7.53 (d, *J* = 7.2 Hz, 1 H, H^3-C^C^N), 7.42 (t, *J* = 7.8 Hz, 1 H, H^4-C^C^*N*), 7.15 (t, *J* = 7.6 Hz, 1 H, H^4-C^C^N), 6.89 (t, *J* = 6.4 Hz, 1 H, H^5-N^*N*), 6.80–6.74 (m, 2 H, H^4-C^C^N/H^5-C^C^*N*), 6.59 (t, *J* = 7.4 Hz, 1 H, H^5-C^C^N), 6.22 (d, *J* = 7.2 Hz, 1 H, H^6-C^C^N) ppm. ^{1}H NMR ([D$_6$]DMSO): δ = 9.84 (d, *J* = 5.0 Hz, 1 H, H^6-N^N), 8.77 (d, *J* = 8.2 Hz, 1 H, H^3-N^N), 8.49 (d, *J* = 8.2 Hz, 1 H, H^3-N^*N*), 8.34 (t, *J* = 7.2 Hz, 1 H, H^4-N^N), 8.17 (d, *J* = 8.1 Hz, 1 H, H^3-C^C^*N*), 8.06 (t, *J* = 6.5 Hz, 1 H, H^5-N^N), 7.84–7.67 (m, 4 H, H$^{4/6}$-C^C^*N*/H$^{4/6}$-N^*N*), 7.51 (d, *J* = 7.4 Hz, 1 H, H^3-C^C^N), 7.47 (d, *J* = 5.8 Hz, 1 H, H^5-C^C^N), 7.40 (d, *J* = 7.4 Hz, 1 H, H^3-C^C^N), 7.13–7.02 (m, 3 H, H^4-C^C^N/H^5-C^C^*N*/H^5-N^*N*), 6.64 (t, *J* = 7.3 Hz, 1 H, H^4-C^C^N), 6.42 (t, *J* = 7.3 Hz, 1 H, H^5-C^C^N), 5.99 (d, *J* = 7.2 Hz, 1 H, H^6-C^C^N) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 174.5 (quat.), 166.4 (quat.), 158.0 (quat.), 156.4 (quat.), 155.2 (quat.), 152.2, 151.4 (quat.), 150.2, 148.2, 145.3 (quat.), 140.5 (quat.), 138.1, 137.7, 135.9, 133.6, 127.9, 127.2, 125.1, 124.0, 123.7, 122.6, 121.9, 121.8, 121.3, 120.2, 120.1, 119.8 ppm. ESI-MS: *m*/*z* calcd. for $[C_{27}H_{19}N_3ClIr + Na]^+$: 636.079; found 636.097. $C_{27}H_{19}ClN_3Ir$ (613.13): calcd. C 52.89, H 3.12, N 6.85; found C 53.06, H 3.24, N 6.57.

X-ray Crystallography: Single crystals of **7**, **10**, and **12** for X-ray diffraction studies were grown at –30 °C from the dichloromethane/methanol solutions. All the data were collected at 123 K with a Rigaku Saturn CCD diffractometer with confocal mirror using graphite-monochromated Mo-K_α radiation (λ = 0.71070 Å). Data reductions of the measured reflections were carried out using the

Table 4. Crystallographic and measurement data for **7**, **10**, and **12**.

	7	**10**	**12**
Formula (M_r)	$C_{25}H_{23}NClIr$ (565.14)	$C_{33}H_{23}N_3ClIr$ (689.19)	$C_{34}H_{22}N_3OIr$ (680.75)
Dimensions [mm]	0.15 × 0.10 × 0.10	0.12 × 0.10 × 0.05	0.30 × 0.04 × 0.02
Crystal system / space group	monoclinic / $P2_1/c$	monoclinic / $P2_1/c$	orthorhombic / $P2_12_12_1$
a [Å]	13.471(3)	15.170(4)	12.0239(11)
b [Å]	8.2199(15)	11.074(2)	12.1198(13)
c [Å]	17.515(4)	16.250(4)	17.712(2)
β [°]	99.2534(8)	109.3040(10)	
V [Å^3]	1914.1(6)	2576.5(10)	2581.1(5)
Z	4	4	4
$D_{calcd.}$ [g cm^{-3}]	1.961	1.777	1.752
T [K]	123(1)	123(1)	123(1)
$\mu_{calcd.}$ [mm^{-1}]	7.126	5.314	5.206
F (000)	1096	1344	1328
Scan type	ω	ω	ω
$2\theta_{max}$ [°]	55.0	55.0	55.0
Independent reflections	4388 [R(int) = 0.0477]	5904 [R(int) = 0.0826]	5746 [R(int) = 0.0344]
Reflections used [$I > 2\sigma(I)$]	4080	5367	5444
Variables	254	343	352
GOF[a] on F^2	1.061	1.119	1.087
R_1/wR_2 [$I > 2\sigma(I)$][b]	0.0251/0.0576	0.0456/0.1068	0.0441/0.0781
R_1/wR_2 (all)[c]	0.0281/0.0594	0.0517/0.1111	0.0478/0.0809
ρ_{max} [e Å^{-3}]	1.662 and –0.936	2.052 and –1.391	2.420 and –1.172

[a] GOF = $[\Sigma w(F_o^2 - F_c^2)^2/(N - P)]^{1/2}$. [b] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR(F_2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

CrystalStructure (ver. 3.8) software package. The structures were solved by direct methods (SIR97)[25] and refined by full-matrix least-squares fitting based on F^2 using the PC version of SHELXL 97-2.[26] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located at ideal positions and were included in the refinement, but were restricted to ride on the atom to which they were bonded. The crystallographic and measurement data for these compounds are listed in Table 4.

CCDC-808123 (for **7**), -808124 (for **10**) and -808125 (for **12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

DFT Calculations: DFT calculations for compounds **9** and **X** were carried out with Gaussian 03 software at the Research Institute for Information Technology at Kyushu University. The B3LYP functional and "double-ζ"-quality basis sets were employed for the ligands (6-31G) and the Ir (LANL2DZ). The *xyz* coordinates of the initial structures were generated with the Chem3D Pro 8.0 software package. The fact that the obtained structures give no imaginary vibrational frequency shows that the obtained structures are energetically stable. The electron spin multitude of the compounds was set to be triplet in the calculations.

Supporting Information (see footnote on the first page of this article): Experimental details for **5**, ^{13}C and two-dimensional NMR spectra for **9** and **14**, preliminary results of X-ray crystallography for **11**, Cartesian coordinates of **9** and **X** for DFT calculations.

Acknowledgments

We thank Prof. Satoshi Kawata of Fukuoka University for the X-ray crystallography of compound **11**.

---

[1] L. S. Hung, C. H. Chen, *Mater. Sci. Eng. Rep.* **2002**, *39*, 143–222.

[2] P. I. Djurovich, M. E. Thompson, in: *Highly Efficient OLEDs with Phosphorescent Materials* (Ed.: H. Yersin), Wiley-VCH, Weinheim, Germany, **2007**, p. 131–162.

[3] a) Q. Zhao, S. Liu, M. Shi, F. Li, H. Jing, T. Yi, C. Huang, *Organometallics* **2007**, *26*, 5922–5930; b) H. Chen, Q. Zhao, Y. Wu, F. Li, H. Yang, T. Yi, C. Huang, *Inorg. Chem.* **2007**, *46*, 11075–11081; c) Q. Zhao, F. Li, S. Liu, M. Yu, Z. Liu, T. Yi, C. Huang, *Inorg. Chem.* **2008**, *47*, 9256–9264; d) W. Goodall, J. A. G. Williams, *J. Chem. Soc., Dalton Trans.* **2000**, 2893–2895; e) K. J. Arm, W. Leslie, J. A. G. Williams, *Inorg. Chim. Acta* **2006**, *359*, 1222–1232; f) M.-L. Ho, F.-M. Hwang, P.-N. Chen, Y.-H. Hu, Y.-M. Cheng, K.-S. Chen, G.-H. Lee, Y. Chi, P.-T. Chou, *Org. Biomol. Chem.* **2006**, *4*, 98–103; g) K. K.-W. Lo, J. S.-Y. Lau, D. K.-K. Lo, L. T.-L. Lo, *Eur. J. Inorg. Chem.* **2006**, 4054–4062.

[4] a) J. S.-Y. Lau, P.-K. Lee, K. H.-K. Tsang, C. H.-C. Ng, Y.-W. Lam, S.-H. Cheng, K. K.-W. Lo, *Inorg. Chem.* **2009**, *48*, 708–718; b) K. Y. Zhang, K. K.-W. Lo, *Inorg. Chem.* **2009**, *48*, 6011–6025; c) M. Yu, Q. Zhao, L. Shi, F. Li, Z. Zhou, H. Yang, T. Yi, C. Huang, *Chem. Commun.* **2008**, 2115–2117; d) K. K.-W. Lo, P.-K. Lee, J. S.-Y. Lau, *Organometallics* **2008**, *27*, 2998–3006.

[5] a) K. A. King, P. J. Spellane, R. J. Watts, *J. Am. Chem. Soc.* **1985**, *107*, 1431–1432; b) M. Maestri, V. Balzani, C. Deuschel-Cornioley, A. von Zelewsky, *Adv. Photochem.* **1992**, *17*, 1–78; c) M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, S. R. Forrest, *Appl. Phys. Lett.* **1999**, *75*, 4–6; d) J.-P. Collin, I. M. Dixon, J.-P. Sauvage, J. A. G. Williams, F. Barigelletti, L. Flamigni, *J. Am. Chem. Soc.* **1999**, *121*, 5009–5016; e) C. Adachi, M. A. Baldo, S. R. Forrest, S. Lamansky, M. E. Thompson, R. C. Kwong, *Appl. Phys. Lett.* **2001**, *78*, 1622–1624; f) C. Adachi, R. C. Kwong, P. Djurovich, V. Adamovich, M. A. Baldo, M. E. Thompson, S. R. Forrest, *Appl. Phys. Lett.* **2001**, *79*, 2082–2084; g) C. Adachi, M. A. Baldo, M. E. Thompson, S. R. Forrest, *Appl. Phys. Lett.* **2001**, *80*, 5048–5051; h) S. Lamansky, P. Djurovich, D. Murphy, F. Adbel-Razzaq, H.-E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest, M. E. Thompson, *J. Am. Chem. Soc.* **2001**, *123*, 4304–4312; i) F. Chen, Y. Yang, M. E. Thompson, J. Kido, *Appl. Phys. Lett.* **2002**, *80*, 2308–2310; j) M. K. Nazeeruddin, R. Humphry-Baker, D. Berner, S. Rivier, L. Zuppiroli, M. Graetzel, *J. Am. Chem. Soc.* **2003**, *125*,

8790–8797; k) E. A. Plummer, J. W. Hofstraat, L. De Cola, *Dalton Trans.* **2003**, 2080–2084; l) A. Tsuboyama, H. Iwasaki, M. Furugori, T. Mukaide, J. Kamatani, S. Igawa, T. Moriyama, S. Miura, T. Takiguchi, S. Okada, M. Hoshino, K. Ueno, *J. Am. Chem. Soc.* **2003**, *125*, 12971–12979; m) K. K.-M. Lo, C.-K. Chung, T. K.-M. Lee, L.-H. Lui, K. H.-K. Tsang, N. Zhu, *Inorg. Chem.* **2003**, *42*, 6886–6897; n) N. Yoshikawa, T. Matsumura-Inoue, *Anal. Sci.* **2003**, *19*, 761–765; o) M. Polson, S. Fracasso, V. Bertolasi, M. Ravaglia, F. Scandola, *Inorg. Chem.* **2004**, *43*, 1950–1956; p) E. Baranoff, I. M. Dixon, J.-P. Collin, J.-P. Sauvage, B. Ventura, L. Flamigni, *Inorg. Chem.* **2004**, *43*, 3057–3066; q) W.-S. Huang, J. T. Lin, C.-H. Chien, Y.-T. Tao, A.-S. Sun, Y.-S. Wen, *Chem. Mater.* **2004**, *16*, 2480–2488; r) W. Leslie, A. S. Batsanov, J. A. K. Howard, J. A. G. Williams, *Dalton Trans.* **2004**, 623–631; s) P.-T. Chou, Y. Chi, *Chem. Eur. J.* **2007**, *13*, 380–395; t) Y. Chi, P.-T. Chou, *Chem. Soc. Rev.* **2010**, *39*, 638–655.

[6] a) L. Chassot, A. von Zelewsky, *Inorg. Chem.* **1987**, *26*, 2814–2818; b) D. Sandrini, M. Maestri, V. Balzani, L. Chassot, A. von Zelewsky, *J. Am. Chem. Soc.* **1987**, *109*, 7720–7724; c) M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature* **1998**, *395*, 151–154; d) M. Hissler, J. E. McGarrah, W. B. Connick, D. K. Geiger, S. D. Cummings, R. Eisenberg, *Coord. Chem. Rev.* **2000**, *208*, 115–137; e) J. F. Michalec, S. A. Bejune, D. G. Cuttell, G. C. Summerton, J. A. Gertenbach, J. S. Field, R. J. Haines, D. R. McMillin, *Inorg. Chem.* **2001**, *40*, 2193–2200; f) V. W.-W. Yam, R. P.-L. Tang, K. M.-C. Wong, X.-X. Lu, K.-K. Cheung, N. Zhu, *Chem. Eur. J.* **2002**, *8*, 4066–4076; g) J. A. G. Williams, A. Beeby, E. S. Davies, J. A. Weinstein, C. Wilson, *Inorg. Chem.* **2003**, *42*, 8609–8611; h) V. W.-W. Yam, K. M.-C. Wong, N. Zhu, *Angew. Chem. Int. Ed.* **2003**, *42*, 1400–1403; i) C.-M. Che, W.-F. Fu, S.-W. Lai, Y.-J. Hou, Y.-L. Liu, *Chem. Commun.* **2003**, 118–119.

[7] a) D. J. Stufkens, M. P. Aarnts, B. D. Rossenaar, A. Vlcek, *Coord. Chem. Rev.* **1998**, *177*, 127–179; b) V. W.-W. Yam, Y. Yang, J. Zhang, B. W.-K. Chu, N. Zhu, *Organometallics* **2001**, *20*, 4911–4918; c) K. K.-W. Lo, W.-K. Hui, D. C.-M. Ng, K.-K. Cheung, *Inorg. Chem.* **2003**, *42*, 40–46; d) S. Ranjan, S.-Y. Lin, K.-C. Hwang, Y. Chi, W.-L. Ching, C.-S. Liu, Y.-T. Tao, C.-H. Chien, S.-M. Peng, G.-H. Lee, *Inorg. Chem.* **2003**, *42*, 1248–1255; e) T. Rajendran, B. Manimaran, R.-T. Liao, R.-J. Lin, P. Thanasekaran, G.-H. Lee, S.-M. Peng, Y.-H. Liu, I.-J. Chang, S. Rajagopal, K.-L. Lu, *Inorg. Chem.* **2003**, *42*, 6388–6394; f) K. M.-C. Wong, S. C.-F. Lam, C.-C. Ko, N. Zhu, V. W.-W. Yam, S. Roue, C. Lapinte, S. Fathallah, K. Costuas, S. Kahlal, J.-F. Halet, *Inorg. Chem.* **2003**, *42*, 7086–7097.

[8] a) E. L. Williams, J. Li, G. E. Jabbour, *Appl. Phys. Lett.* **2006**, *89*, 083506-1-3; b) J. Qiao, L. Duan, L. Tang, L. He, L. Wang, Y. Qiu, *J. Mater. Chem.* **2009**, *19*, 6573–6580.

[9] A. J. Wilkinson, H. Puschmann, J. A. K. Howard, C. E. Foster, J. A. G. Williams, *Inorg. Chem.* **2006**, *45*, 8685–8699.

[10] S. Obara, M. Itabashi, F. Okuda, S. Tamaki, Y. Tanabe, Y. Ishii, K. Nozaki, M. Haga, *Inorg. Chem.* **2006**, *45*, 8907–8921.

[11] For recent reviews for tridentate "pincer" ligands in transition metal complexes, see: a) W. Leis, H. A. Mayera, W. C. Kaska, *Coord. Chem. Rev.* **2008**, *252*, 1787–1797; b) D. Benito-Garagorri, K. Kirchner, *Acc. Chem. Res.* **2008**, *41*, 201–213; c) H. Nishiyama, *Chem. Soc. Rev.* **2007**, *36*, 1133–1141.

[12] a) N. Herron, N. S. Radu, E. M. Smith, *PCT Int. Appl.* **2005**, WO 2005124889; b) Z. Chen, C. Huang, C. Zhen, J. Yao, *PCT Int. Appl.* **2006**, WO 2006093466.

[13] B.-Z. Yang, X. Zhou, T. Liu, F.-Q. Bai, H.-X. Zhang, *J. Phys. Chem. A* **2009**, *113*, 9396–9403.

[14] a) Z. Lu, C.-H. Jun, S. R. de Gala, M. Sigalas, O. Eisenstein, R. H. Crabtree, *J. Chem. Soc., Chem. Commun.* **1993**, 1877–1880; b) K. R. Lee, M.-S. Eun, C. S. Chin, S. C. Lee, I. J. Kim, Y. S. Kim, Y. Kim, S.-J. Kim, N. H. Hur, *Dalton Trans.* **2009**, 3650–3652; c) Y. Koga, K. Ueno, K. Matsubara, *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 4204–4213.

[15] For similar longer Ir–C bond lengths, see: a) A. J. Wilkinson, A. E. Goeta, C. E. Foster, J. A. G. Williams, *Inorg. Chem.* **2004**, *43*, 6513–6515; b) K. J. H. Young, J. Oxgaard, D. H. Ess, S. K. Meier, T. Stewart, W. A. Goddard III, R. A. Periana, *Chem. Commun.* **2009**, 3270–3272; c) M. Raynal, R. Pattacini, C. S. J. Cazin, C. Vallée, H. Olivier-Bourbigou, P. Braunstein, *Organometallics* **2009**, *28*, 4028–4047.

[16] R. N. Pandey, M. Sharma, R. N. Sharma, N. Chandrashekhar, *Asian J. Chem.* **2004**, *16*, 1479–1482.

[17] W. J. Finkenzeller, P. Stößel, H. Yersin, *Chem. Phys. Lett.* **2004**, *397*, 289–295.

[18] H. J. Bolink, E. Coronado, R. D. Costa, E. Ortí, M. Sessolo, S. Graber, K. Doyle, M. Neuburger, C. E. Housecroft, E. C. Constable, *Adv. Mater.* **2008**, *20*, 3910–3913.

[19] E. C. Riesgo, Y.-Z. Hu, F. Bouvier, R. P. Thummel, D. V. Scaltrito, G. J. Meyer, *Inorg. Chem.* **2001**, *40*, 3413–3422.

[20] A. Auffrant, A. Barbieri, F. Barigelletti, J.-P. Collin, L. Flamigni, C. Sabatini, J.-P. Sauvage, *Inorg. Chem.* **2006**, *45*, 10990–10997.

[21] For similar energy calculation of an iridium complex like **X**, see: J. A. G. Williams, A. J. Wilkinson, V. L. Whittle, *Dalton Trans.* **2008**, 2081–2099.

[22] B.-Z. Yang, X. Zhou, T. Liu, F.-Q. Bai, H.-X. Zhang, *J. Phys. Chem. A* **2009**, *113*, 9396–9403.

[23] a) F. Leroux, M. Schlosser, *Angew. Chem. Int. Ed.* **2002**, *41*, 4272–4274; b) S. M. Kilyanek, X. Fang, R. F. Jordan, *Organometallics* **2009**, *28*, 300–305.

[24] J. W. Barton, K. E. Whitaker, *J. Chem. Soc. C* **1968**, 28–30.

[25] M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, *SIR2002*; **2003**.

[26] G. M. Sheldrick, *SHELXL97-2*, **1997**.

Received: January 16, 2011