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Cyclometalated Iridium(III) Complexes with Ligand Effect on Catalytic Carbon-Hydrogen Bond Activation of Toluene in High-Performance

Tsun-Ren Chen,*[a] Pei-Chun Liu,[a] Hsiu-Pen Lee,[a] Fang-Siou Wu[a] and Kelvin H.-C. Chen[a]

Abstract: New cyclometalated iridium (III) complexes are designed, prepared and applied to a catalytic system for carbon-hydrogen bond activation (CHA) of toluene using a clean, highly efficient and environmentally friendly process. These complexes have the general formula $(C\hat{}N)_2Ir(N\hat{}O)$. The C^N ligands are monoanionic bidentate cyclometalating ligands, including 2-phenylpyridinato (ppy), 2-phenylbenzoxazolato (pbo) and 2-(3.5-difluorophenyl)benzoxazolato (dfpbo), respectively; the (N^O) ligand is also a monoanionic bidentate cyclometalating ligand, picolinato (pic). Complexes $(ppy)_2Ir(pic)$ (**1**), $(pbo)_2Ir(pic)$ (**2**) and $(dfpbo)_2Ir(pic)$ (**3**) are structurally characterized by ^1H NMR, ^{13}C NMR, FAB-MS and X-ray crystallography. The activation energies needed for the catalytic CHA oxidation of toluene when using complexes **1**-**3** as catalysts are quite low, between 14.4 and 25.5 kcal mol^{-1}. The catalytic frequencies (TOF) are fairly high (up to 4.0×10^3 $Mol_{toluene}$ $Mol_{catalyst}^{-1}$ h^{-1}) with excellent reliability; the turnover number (TON) can reach 2.40×10^4 $Mol_{toluene}$ $Mol_{catalyst}^{-1}$ after 6 hours of processing time. A combination of catalytic tests, studies with density functional theory (DFT), X-Ray absorption near edge structure (XANES) and kinetic modeling is used to derive detailed insights into the characteristics of the catalysts and their effect on the reactions featured in the CHA oxidation of toluene.

Introduction

Carbon-hydrogen bond activation (CHA), used to functionalize saturated hydrocarbons to form a variety of organic compounds, is an important process and widely applied in various fields.[1-6] As to the hydrocarbons, the C-H bond is inert and has a fairly strong bond energy, so a major challenge for CHA is how to activate the bond and lower the energy needed. Much effort has been dedicated to seeking out powerful candidates for CHA catalysts. An early example of homogeneously metal-catalyzed CHA is known as the Shilov system.[7] Since Bergman, in 1984, discovered that the products of the C-H oxidative addition reaction of aromatic and aliphatic compounds could be isolated by using d^8-CP*Ir(PMe_3) as the catalyst,[8,9] the scope of developing catalysts for CHA has been widened to include a variety of complexes, for example, iridium,[10-12] palladium,[13-16] platinum,[17-20] rhenium,[21-24] rhodium[25-29] and ruthenium.[30-34] Although these studies reported certain achievements, some issues still required further research. For example, some reported complexes have an acceptable reactivity (the turnover frequency (TOF) may be higher than 10), but a low reliability (the turnover number (TON) may be less than 100), or some complexes are active but not easily prepared and too unstable to be stored. Therefore, our aim is to provide some ideas on obtaining catalysts for a high-performance CHA. Those catalysts should be stable and easy to prepare and their characteristics able to be systematically tuned.

In 1993, the Ir(III) complex CP*Ir(PMe_3)(Me)(OTf) which was prepared could undergo a mild and selective reaction with C-H bonds in arenes and alkanes. This complex had a better performance for CHA than that of low-valent iridium complexes.[35] Until now, the use of the Ir(III) complex for CHA has rarely been reported.[36,37] In other fields, Ir(III) complexes with bidentate ligands, including carbon-nitrogen (C^N), nitrogen-oxygen (N^O) and nitrogen-nitrogen (N^N), have been widely applied to organic light-emitting diodes (OLEDs),[38,39] biolabeling,[40,41] dye-sensitized solar cells (DSCs)[42,43] and the photoreaction of water,[44,45] in which most of the bidentate ligands could be easily prepared and have a steady bond to a metal center. Also, the character of the ligands was flexible and could be modified. In general, the bidentate ligands C^N and N^O are ionic, whereas the ligand N^N is neutral, which means that ligands C^N and N^O could form a tighter bond to the central metal than the ligand N^N. Moreover, since the bond energy of metal-carbon is different from that of metal-oxygen, the stability and activity of a complex composed of various bidentate ligands could be finely and widely tuned.

Results and Discussion

Synthesis and Structure. Previously, we discovered that an 18+δ iridium dimer possessing a benzoxazole ligand can spontaneously release metalloradicals, which promotes two types of reactions: the carbon-hydrogen bond activation and a rare but important carbon-carbon bond activation (CCA) for ketones and aldehydes.[46] We also discovered that the diiridium bimetallic complexes having a benzoxazole ligand exhibit a *special type* of oxidation-reduction reaction which directly splits the carbonate into carbon monoxide and oxygen via a low-energy pathway without the need of a sacrificial reagent.[47] This means that such complexes are active for various reaction systems, including CHA. However, CHA was not a major type of reaction in our previous report; moreover, metalloradicals are quite unstable and hard to control. Therefore, we designed

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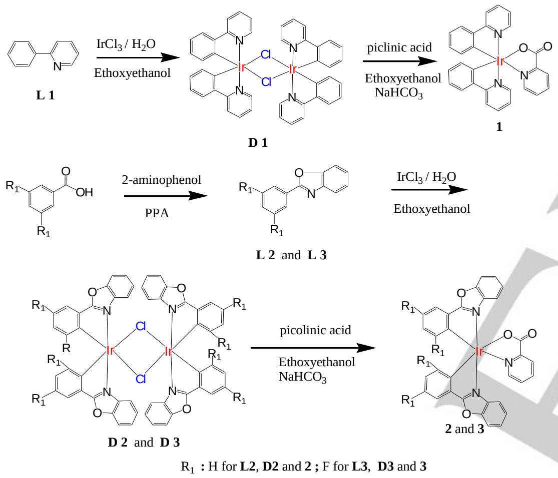
iridium complexes composed of an N^O and two C^N ligands, which are six-coordinate complexes with a stable octahedral geometry. In mild reaction conditions, for example, by heating or irradiating with light, this kind of complex first releases the N^O ligand to form a four-coordinate intermediate with the vacant coordination sites required for oxidative addition, in which the characteristic of the C^N ligand obviously affects the property of the intermediate.

Scheme 1 shows the synthesis of the ligands and the iridium complexes. Complexes **1**-**3** have a general formula $[(C^{\wedge}N)_2Ir(N^{\wedge}O)]$, where C^N is a monoanionic cyclometalating ligand, including 2-phenylpyridinato (ppy), 2-phenylbenzoxazolato (pbo) and 3.5-difluorophenyl benzoxazolato (dfpbo), respectively; and N^O is the picolinato group (pic), and also a monoanionic bidentate ligand. All the iridium dimers and iridium complexes were purified and identified by ^{1}H NMR, ^{13}C NMR, FAB-MS spectrometry and elemental analyses; complexes **1**-**3** were characterized by a single-crystal X-ray analysis.



Scheme 1. Synthetic route of C^N ligands and complexes **1**-**3**.

The single-crystal structures of complexes **1**-**3** are represented with ORTEP diagrams in Figure 1, where complex **1** belongs to the monoclinic space group P 21 and complexes **2** and **3** belong to the monoclinic space group P 21/c, respectively. Selected bond distances and angles are listed in Table 1. The diversity of the space groups for this series of complexes suggested that the packing of these complexes was sensitive to the substituent of the ligands.[48]

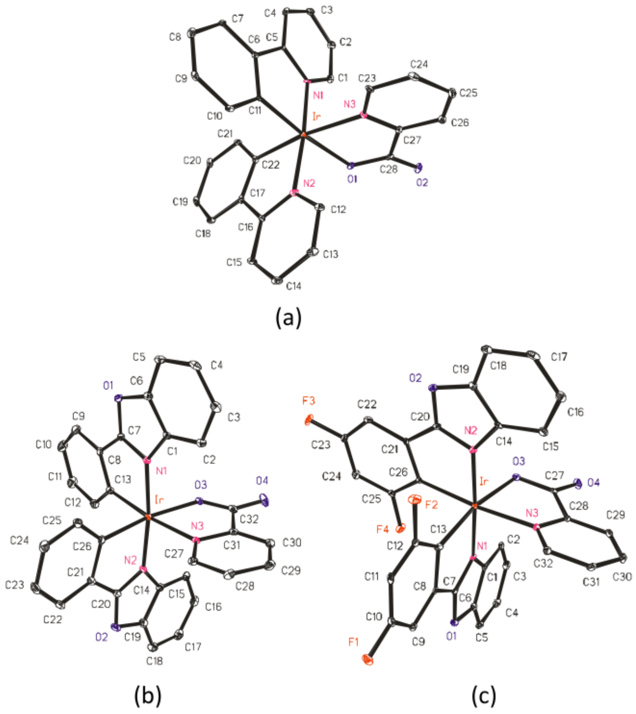


Figure 1. ORTEPdiag ram of (a) $(ppy)_2$ Ir(pic) (**1**), (b) $(pbo)_2Ir(pic)$ (**2**), and (c) $(dfpbo)_2$ Ir(pic) (**3**). Thermal ellipsoids are draw at the 20% probability level. The hydrogen atoms and solvent are omitted for clarity..

Table 1. Selected Bond Distance (Å) and Bond Angles for Complexes **1**-**3**

	complex / parameter	1	2	3
Bond length (Å)	Ir -N(1)	2.042(4)	2.043(2)	2.032(2)
	Ir -N(2)	2.052(5)	2.025(2)	2.043(2)
	Ir -N(3)	2.141(4)	2.120(2)	2.101(2)
	Ir -C(A)^a	2.003(5)	2.015(3)	2.028(3)
	Ir -C(B)^b	2.012(5)	2.009(3)	2.045(3)
	Ir –O(A)^c	2.157(4)	2.1461(17)	2.129(2)
Bond angle (º)	N(1)-Ir-N(2)	175.67(18)	173.28(9)	176.87(10)
	C(A)^a -Ir-O(A)^c	174.24(18)	171.83(10)	168.17(10)
	C(B)^b -Ir-N(3)	171.69(19)	173.19(9)	174.56(11)
	N(1)-Ir-C(A)^a	81.3(2)	79.88(10)	79.87(12)
	N(2)-Ir-C(B)^b	80.1(2)	80.00(10)	79.84(11)

[a] represented the atom label C(11) of complex **1**, or C(13) of complex **2** and **3** on the x-ray crystal structures. [b] represented the atom label C(12) of complex **1**, or C(26) of complex **2** and **3**. [c] represented the atom label O(1) of complex **1**, or O(3) of complex **2** and **3**.

As Figure 1 shows, the three complexes adopted distorted octahedral coordination geometry around the iridium, and the two C^N ligands preferred a cis-C−C and a trans-N−N chelate disposition. The bond lengths of the Ir− C_{av} bond for complexes **1**-**3** were 2.008(5), 2.012(3) and 2.037(3) Å, respectively, which implied that the bidentate ligand C^N of **1** formed the strongest σ_{Ir-C} bond to the central metal, and that of **3** had the weakest bond. Therefore, the C^N ligand of **1** should have a higher trans-effect and so lengthen the bond distances between the metal and N^O ligand. As can be seen in Table 2, the bond lengths of Ir−N(pic) and Ir−O(pic) of complex **1** were 2.141(4) and 2.157(4) (Å), respectively, and so longer than the bond lengths of complex **2** (Ir−N(pic) = 2.120(2); Ir−O(pic) = 2.1461(17) Å) or **3** (Ir−N(pic) = 2.101(2); Ir−O(pic) = 2.129(2) Å), which implied that the structure of **1** was the most unstable and the structure of **3** the most stable. The thermal gravimetric analyses (TGA) (Figure 2) showed that complex **2** initially lost the lattice solvent at 120℃ and completely released the N^O ligand at 400℃, and complex **1** and **3** completely released the N^O ligand at 360 and 414℃, respectively.

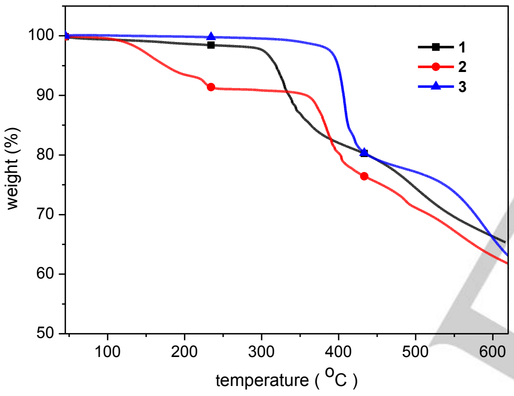


Figure 2. Thermal gravimetric analyses (TGA) for complexes 1-3: samples were heated up under nitrogen at a pressure of 1 atm with a heating rate of 10 °C min^{-1} and finished at 620 °C.

Electrochemical Properties. Cyclic voltammetry (CV) was performed using a CHI voltammetric analyzer under a nitrogen atmosphere. The supporting electrolyte of 0.1 M tetra(n-butyl)ammonium hexafluorophosphate ($Bu_4N^+ \cdot PF_6^-$) in anhydrous dichloromethane (DCM) was used as the solvent, a glassy-carbon rod as the working electrode, a platinum wire as the counter electrode and an Ag/Ag+ electrode as the reference electrode. The CV curves of complexes **1**−**3** had a reversible route in the range of 1.0-1.6 V versus the ferrocene/ferrocenium (Fc/Fc$^+$) redox couple (Figure 3).[49]

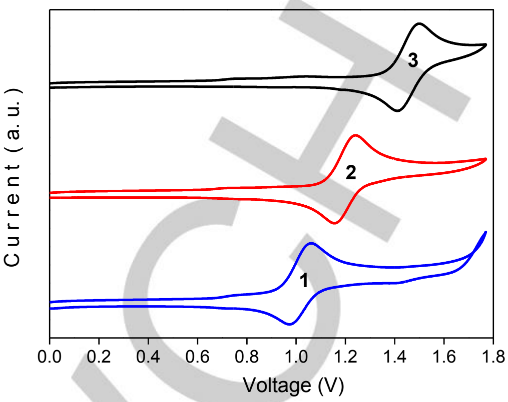


Figure 3. Cyclic voltammograms of complexes **1**−**3**

As shown in Figure 3, complexes **1**−**3** were quite stable under the oxidative and reductive reactions. The first oxidation potentials (E_{ox}^1) of complexes **1**−**3** were 1.05, 1.23 and 1.49 V, respectively. By the equation: HOMO (eV) = $-\{4.8 + [(E_{ox}^1 \text{of complex}) - (E_{ox}^1 \text{of Fc/Fc}^+)]\}$,[50] we obtained the HOMO level of complexes **1**−**3** of -5.37, -5.55 and -5.81 eV, respectively, which showed the HOMO of complex **3** to be more stable than that of complex **1** or **2**.

Theoretical Calculations and X-Ray absorption near edge structure spectra (XANES). computational study was performed on the materials, including ligands, complexes, reaction intermediates and adducts, to investigate the characteristics of the molecules and their structural effect on the CHA. Theoretical calculations were performed using the program package Gaussian 03 and employing Becke's three-parameter B3LYP for C, H, F, O and N and the LANL2DZ basis set for the Ir element.[51] Partial charges were calculated according to the Mulliken, APT (atomic polar tensors) and NPA (natural population).

The highest occupied molecular orbital (HOMO) distribution of the anions of the C^N ligand, including 2-phenylpyridinato (ppy^{-1}) 2-phenylbenzoxazole (pbo^{-1}) and 2-(3.5-difluorophenyl)benzoxazole (dfpbo^{-1}), are shown in Figure 4. These anions resulted from removing the proton of the carbon (denoted as C_2) being a meta position to pyridyl or benzoxazole group can be stabilized by the resonance of the aromatic substituents. Also, since C_2 is a γ-atom to the nitrogen of the pyridyl or benzoxazole group, this kind of anion could chelate to metal to form a stable five-membered ring. The HOMOs of the anions were mainly composed of the atomic orbitals of carbons C_1, C_2 and C_3, and the negative charge was most localized on the C_2. The Mulliken atomic charges on C_2 of ppy^{-1}, pbo^{-1} and dfpbo^{-1} were -0.3831, -0.3769 and -0.3340, respectively, which implied that the ligand ppy provided the highest negative charge to the central metal and that the dfpbo delivered the lowest charge.

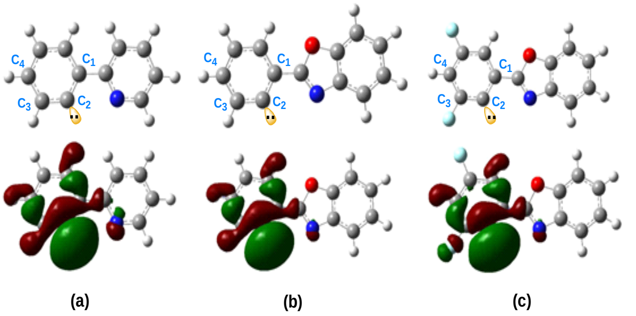


Figure 4. Computational structure and the HOMO distribution of the anions of (a) 2-phenylpyridine (ppy^{-1}), (b) 2-phenylbenzoxazole (pbo^{-1}), and (c) 2-(3.5-difluorophenyl) benzoxazole ($dfpbo^{-1}$)

Because the partial negative charge on C_2 of ppy^{-1} was higher than that of pbo^{-1} or $dfpbo^{-1}$, the partial positive charge on the iridium atom of **1** should be lower than that of **2** or **3**. The calculation data showed the Mulliken atomic charge on the iridium of **1** to be 0.91 lower than that of **2** (0.95) or **3** (1.04). The computational results were verified by the normalized X-Ray absorption near edge structure (XANES) spectra at the Ir L3-edge for complexes **1**-**3** (Figure 5). Complex **3** (Figure 5c) had the highest partial positive charge on the iridium atom, complex **2** (Figure 5b) the second highest and complex **1** (Figure 5a) the lowest.[52] It is to be noted that, in general, a complex with a higher partial positive charge on metal would be a better electrophile by attracting the substrates of electron donors, thus being more active for oxidative addition.

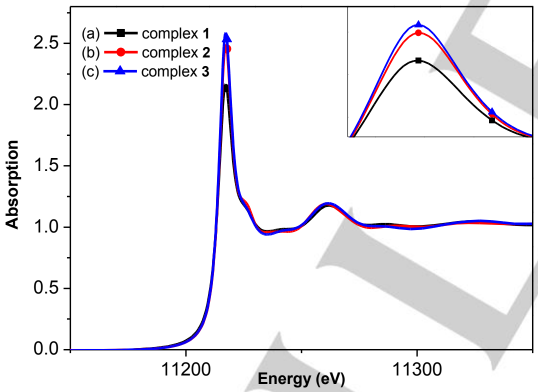


Figure 5. Ir L3-edge XANES of crystalline (a) (■) $[(pp)_2Ir^{IV}(pic)]$ (**1**), (b) (●) $[(pbo)_2Ir^{IV}(pic)]$ (**2**), and (c) (▲) $[(dfpbo)_2Ir^{IV}(pic)]$ (**3**). A Si (111) double crystal monochromator was employed for energy scanning. Fluorescence data were obtained at room temperature using an Ar-filled ionization chamber detector, each sample was scanned 3 times for averaging.

Performance on CHA for Toluene. All solutions of complexes 1-3 exhibited catalytic activity for the CHA oxidation of benzylic compounds; A proposed catalytic cycle for the CHA process was showed as Figure 6 via radical reaction that are selective for the most highly substituted or benzylic CH bonds.[53-55] The mechanism containing six steps:

(a) coordination of an oxygen to the intermediate **Im**;
(b) abstraction of a hydrogen atom from the C-H bond of toluene;
(c) rebound of the newly formed OH group to the benzylic radical to form benzyl alcohol;
(d) abstraction a hydrogen atom from the C-H bond of benzyl alcohol;
(e) rebound of the newly formed OH group to the radical to restore **Im** and give benzaldehyde hydrate;
(f) releasing of a water to form benzaldehyde.

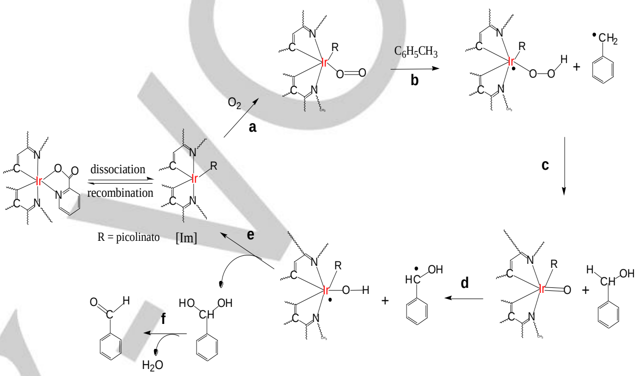


Figure 6. A proposed catalytic cycle for the CHA oxidation of benzylic compounds

In order to evaluate the reactivity and reliability of complexes **1**-**3** for carbon-hydrogen bond activation, we applied them in catalytic reaction systems to convert toluene to benzaldehyde and to investigate the reaction rate, rate constant and activation energy (Ea) for the CHA oxidation of toluene. The experimental data are summarized in Table 2. As benzaldehyde was the only detectable product under the reaction condition, the calibration curve of the standard solutions containing toluene and benzaldehyde was used to monitor the progress of the reactions. The reaction solution was stirred well under air to keep the concentration of oxygen constant.

Table 2. Reaction rate, rate constants and activation energy for the CHA oxidation of net toluene by using complexes **1**-**3** as catalysts

Cat.		rate (μM s^{-1})				k^g M^{-1} s^{-1}	^{h} E_a kcal/mol
		C_1^a	C_2^b	C_3^c	C_4^d		
1	T_1^e	0.009	0.014	0.007	0.011	0.338	25.5
	T_2^f	0.080	0.115	0.059	0.088	2.861	
2	T_1	0.017	0.029	0.013	0.022	0.681	23.1
	T_2	0.125	0.183	0.095	0.140	4.585	
3	T_1	0.076	0.126	0.064	0.105	3.246	14.4
	T_2	0.266	0.437	0.219	0.363	11.189	

[a] 0.1mM of catalyst in net toluene ([toluene] = 9.39 M), [b] 0.2mM of catalyst in net toluene, [c] 0.1mM of catalyst in a reaction solution consisted of 80% of toluene and 20% of 1,2-dichlorobenzene (v/v) ([toluene]=7.51M); [d] 0. 2mM of catalyst in a reaction solution consisted of 80% of toluene and 20% of 1,2-dichlorobenzene. [e] 333K of reaction temperature; [f] 353K of reaction

temperature. [g] rate constant(x10^{-6}) [h] average of activation energy.

For the CHA oxidation of net toluene ([toluene] = 9.39 M), the reaction rates using 0.1m M of complexes **1**-**3** as catalysts at a 60℃ reaction temperature were 0.009, 0.017 and 0.076 μM s^{-1}, respectively, which showed complex **3** to be a most powerful catalyst for CHA. At an 80℃ reaction temperature, the reaction rates for complexes **1**-**3** were 0.080, 0.125 and 0.266 μM s^{-1}. All reaction rates showed an obvious increase, although the reaction rate of complex **1** increased more sharply than that of complex **2** or **3**, which implied that the activation energy of the reaction using complex **1** as catalyst was higher than that of complex **2** or **3**.

With 0.2 mM of catalyst for net toluene at a 60℃ reaction temperature, the reaction rates of complexes **1**-**3** were 0.014, 0.029 and 0.126 μM s^{-1}, respectively, which showed that the catalytic reaction proceeded in an order of 0.67 with respect to complexes **1**-**3** when the concentration of the complex ranged between 0.1 and 0.2 mM. For the CHA oxidation of 80% (v/v) toluene in dichlorobenzene ([toluene] = 7.51M) with 0.1 mM of catalyst at a 60℃ reaction temperature, the reaction rates of complexes **1**-**3** were 0.007, 0.013 and 0.064 μM s^{-1}, respectively, which showed that the catalytic reaction was first order to toluene.

The experimental data also showed that complex **1** had lower rate constants (k^{333} = 0.34 x 10^{-6} M^{-1} s^{-1}, k^{353} = 2.86 x 10^{-6} M^{-1} s^{-1}) with a higher activation energy (Ea = 25.5 kcal/mol), and that complex **3** exhibited higher rate constants (k^{333} = 3.25 x 10^{-6} M^{-1} s^{-1}, k^{353} = 11.19 x 10^{-6} M^{-1} s^{-1}) with a lower activation energy (Ea = 14.4 kcal/mol) (Figure 7). This result demonstrated that the C^N ligand of complex **3** (dfpbo) better stabilized the transition state in the CHA reaction. As we know that the dissociation energy of the C-H bond in hydrocarbon is quite high (~105 kcal mol^{-1}), this was a robust chemical bond and could be hardly cleaved. In most cases, some active reactants, such as halogens or radical species, should be used to supply chemical energy, and some stoichiometric amounts of sacrificial materials should be supplied to the systems. It is of considerable significance that by using cyclometalated iridium complexes as catalysts, the activation energy needed was quite low (~ 20 kcal/mol), the reaction was exergonic and no sacrificial material was needed.

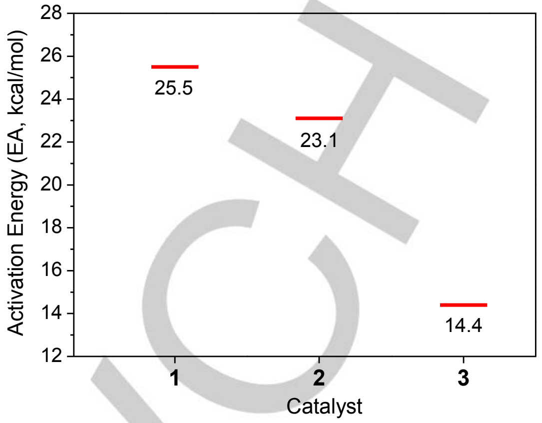


Figure 7. Activation energy (EA, kcal/mol) for the CHA oxidation of net toluene by using 0.1 mM of complexes **1**-**3** as catalysts at 100℃ of reaction temperature

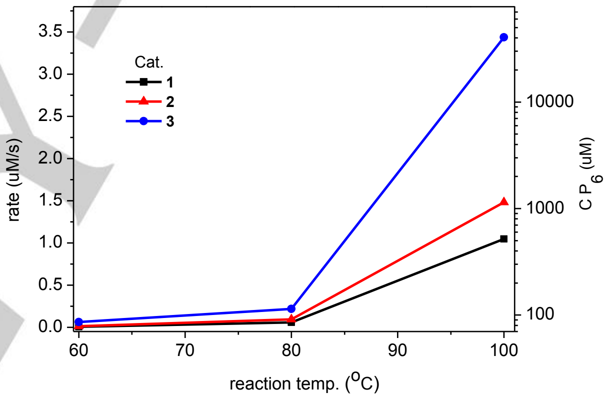


Figure 8. Reaction rate (μM/s) and the concentration of benzaldehyde accumulated after 6 hours of reaction time (CP_6, μM) for the CHA oxidation of net toluene by using complexes 100 μM of complexes **1** (■), **2** (▲), and **3** (●) as catalysts in various reaction temperature.

The activation energy needed for the CHA oxidation of toluene was so low that the reaction could take place at room temperature and that the reaction rate could increase rapidly when the reaction temperature was raised. Figure 8 shows the reaction progress for the CHA oxidation of net toluene using 0.1 mM of complexes **1**-**3** as catalysts at various reaction temperatures. At 100℃, the catalytic rates of complexes **1**-**3** were in the range of 1.04 and 3.44 μM s^{-1}; the catalytic frequencies (TOF) were 37.72, 53.35 and 123.77 $Mol_{toluene}$ $Mol_{catalyst}^{-1}$ h^{-1}, respectively; the concentration of the product after 6 hours of reaction time was 22.63, 32.01 and 74.26 mM, respectively; and the turnover number (TON_6) 226, 320 and 743 $Mol_{toluene}$ $Mol_{catalyst}^{-1}$, respectively. The data showed the performance of complexes **1**-**3** to be much better than that of previously reported catalytic CHA reactions.[56]

To investigate the influence of the concentration of the catalysts on the CHA oxidation of toluene, complexes **1**-**3** were loaded to the reaction system in various concentrations between 1.0×10^{1}

and 1.0×10^{-5} mM at a 100℃ reaction temperature. The results are summarized in Figure 10.

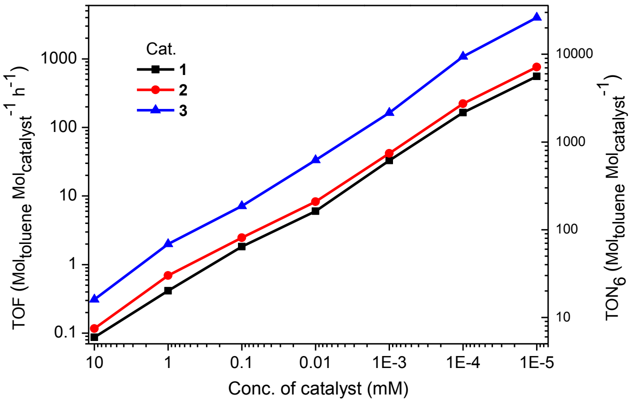


Figure 9 Catalytic frequencies (TOF) and turnover in 6 hours of processing time (TON$_6$) for the CHA oxidation of net toluene at 100℃ of reaction temperature by using complexes **1** (■), **2** (●), and **3** (▲) as catalysts in various concentrations between 1.0×10^{1} and 1.0×10^{-5}m M.

As Figure 9 shows, the TOF of the CHA oxidation for 1.0×10^{-5}m M of complexes **1**-**3** was 5.6×10^{2}, 7.6×10^{2} and 4.0×10^{3} Mol$_{toluene}$ Mol$_{catalyst}^{-1}$ h^{-1}, respectively, and the TON$_6$ 3.4×10^{3}, 4.5×10^{3} and 2.40×10^{4} Mol$_{toluene}$ Mol$_{catalyst}^{-1}$, respectively. These results were quite good, with the data also showing these complexes to be very active for CHA with an excellent reliability under processing conditions. Furthermore, when complexes **1**-**3** were applied to the reaction system in higher concentrations, the catalytic rates of the CHA oxidation for toluene increased, but those of the TON decreased, as a result of the recombination of the intermediates (**Ims**) of complexes **1**-**3** with the N^O ligand to regenerate the complexes. However, the recombination rate could be lowered by tuning the structures of the C^N and N^O ligands and a much higher throughput achieved.

As we know, the synthesis of benzaldehyde and its derivatives by oxidation of the corresponding toluenes is an important industrial process in pharmaceutical drug synthesis. The traditional technologies for the production of benzaldehyde are carried out with a stoichometric quantity of metal oxide, mineral acid and other chemicals. [57] The catalytic system discovered here would provide a green and environmentally friendly process for the production of benzaldehyde and its derivatives..

Conclusions

In summary, three types of cyclometalated iridium (III) complex composed of various cyclometalating ligand were synthesized and fully characterized. All exhibited CHA activity for the oxidation of toluene: the activation energy was very low, between 14.4 and 25.5 kcal/mol; the turnover frequency was quite high, in the range of 5.6×10^{2} and 4.0×10^{3} Mol$_{toluene}$ Mol$_{catalyst}^{-1}$ h^{-1}; and the turnover number was also high, between 3.3×10^{4} and 2.4×10^{4} Mol$_{toluene}$ Mol$_{catalyst}^{-1}$ in the 6 hours of processing time. These complexes are quite stable and can be stored in air at room temperature for a year without obvious decomposing. A theoretical study involving density functional theory (DFT) was used to explore the relations between the structure and characteristics of the molecules. The experimental data, including X-ray analysis and X-Ray absorption near edge structure (XANES) for the single crystal of the complexes, revealed that the characteristics of the complexes were governed by the properties of the C^N ligand. . A new kind of catalytic system was discovered for the CHA of benzylic compounds, and it is a green process, not requiring a base, halogen or other sacrificial materials.

Experimental Section

Materials and methods. All solvents were of analytical reagent grade and purified according to the standard procedure, 3,5-Difluorobenzoic acid was purchased from Matrix, and IrCl$_3$.nH$_2$O was from Seedchem Co. All other chemicals including 2-phenylprydine were purchased from Acros and used as received. NMR spectra were measured on a Bruker AVIIIHD-600 MHz or a Mercury 300 MHz NMR spectrometer. UV-vis spectra were obtained from Hitachi U-3900 Spectrophotometer. Infrared spectra were recorded on Agilent Technologies Model Cary 630 FTIR instruments. X-ray Absorption Near-Edge spectroscopy (XANES) were measured on a X-ray absorption measurements of national synchrotron radiation research center (NSRRC, Taiwan). A Si (111) double crystal monochromator was employed for energy scanning. Fluorescence data were obtained at room temperature using an Ar-filled ionization chamber detector, each sample was scanned 3 times for averaging. A thermogravimetric analysis (TGA) technique was employed to study the thermal stability of the samples. The experiments were performed with a Perkin-Elmer thermal gravimetric analyzer. The samples were heated up under nitrogen at a pressure of 1 atm with a heating rate of 10 ^{o}C min^{-1} and finished at 620 ^{o}C. Mass spectra were taken with a Finnigan/Thermo Quest MAT 95XL instrument with electron impact ionization for organic compounds or fast atom bombardment for metal complexes.

Synthetic procedures

Synthesis Procedure for Ligands and Iridium Complexes. Ligands including 2-phenylbenzoxazole (L2), and 2-(3.5-difluorophenyl)benzoxazole (dfpbo) (L3) were prepared by Philips' condensation described on our previously reported procedure. The cyclometalated Ir(III) chloro-bridged dimers having a general formula (C^N)$_2$Ir(μ-Cl$_2$)Ir(C^N)$_2$ (D1−D3) were synthesized by the method also showed on our previous reports.**[58,59]**

Synthesis of bis[2-phenylpyridinato -N,C$^{2'}$]iridium(III) (picolinato) [Ir(pp)$_2$(pic)] (1). A flask was charged with 0.2g (0.18 mmol) of D1, 0.05g (4 mmol) of picolinic acid, 0.07g (0.81 mmol) of sodium bicarbonate, and 15 ml of ethoxyethanol . The solution was stirred under N$_2$ and warmed to 130 ℃. After 1.5 hr, the solution was cooled to room temperature; the reaction mixture was purified by column chromatography on silica gel with dichloromethane/n-hexane as eluent. The yield of complex 1 was 0.1827 g (79%) as yellow crystals. H NMR (300 MHz, CDCl$_3$, 298 K; δ (ppm)): 8.77 (d, *J*=5.4Hz, 1H), 8.31 (d, *J*=7.5Hz, 1H), 7.81−7.88 (m, 3H), 7.66−7.76 (m, 3H), 7.58 (t, *J*=8.1, 8.7Hz, 2H), 7.44 (d, *J*=5.4Hz, 1H), 7.31 (t, *J*=6.6, 6.3Hz, 1H), 7.11 (t, *J*=6.6, 6.3Hz, 1H), 6.70−6.94 (m, 5H), 6.39 (d, *J*=7Hz, 1H), 6.17 (d, *J*=7.5Hz, 1H). ^{13}C NMR (75 MHz, CDCl$_3$, 298 K; δ (ppm)): 169.4, 167.8, 152.4, 149.2, 144.1, 137.2, 132.7, 130.1, 129.7, 128.4, 124.5, 122.2, 121.7, 121.2, 119.2, 118.6. Anal. Calcd for $C_{28}H_{20}N_3O_2Ir$ (MW = 622.69): C, 54.01; H, 3.24; N, 6.75. Found: C, 53.67; H, 3.29; N, 6.56 %. MS (FAB; m/z): 623.1261

Synthesis of bis[2-phenylbenzoxazolato-N,$C^{2'}$]iridium(III) (picolinato) [Ir(pbo)$_2$(pic)] (2). A flask was charged with 0.5g (0.4 mmol) of D2, 0.11g (0.89 mmol) of picolinic acid, 0.15g (1.79 mmol) of sodium bicarbonate, and 15 ml of ethoxyethanol. The solution was stirred under N_2 and warmed to 130 ℃. After 2 hr, the solution was cooled to room temperature, the reaction mixture was purified by column chromatography on silica gel with dichloromethane/n-hexane as eluent. The yield of complex 2 was 0.2953g (56%) as yellow crystals. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K; δ (ppm)): 8.26(d, *J*=7.8Hz, H), 7.89−8.00 (m, 3H), 7.59−7.74 (m, 4H), 7.33 (t, *J*=11.4, 7.8Hz H), 6.77−7.01 (m, 5H), 6.68(d, *J*=7.5Hz, 1H), 6.46(d, *J*=7.8Hz, 1H), 5.64(d, *J*=8.1Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K; δ (ppm)): 178.5, 177.4, 173.5, 153.3, 150.3, 148.2, 146.7, 138.0, 134.4, 133.8, 132.4, 132.0, 130.0, 129.7, 127.9, 126.5, 126.2, 125.8, 122.1, 121.6, 117.8, 114.4, 112.2, 53.5. Anal. Calcd for $C_{32}H_{20}N_3O_4Ir\cdot CH_2Cl_2$ (MW = 787.68): C, 50.32; H, 2.82; N, 5.34. Found: C, 49.94; H, 2.86; N, 5.41 %. MS (FAB; m/z): 702.1 (Calcd MW of $C_{32}H_{20}N_3O_4Ir$ is 702.74).

Synthesis of bis[2-(3.5-difluorophenyl)benzoxazolato-N,$C^{2'}$]iridium(III) (picolinato) [Ir(dfpbo)$_2$(pic)] (3). A flask was charged with 3g (2.18 mmol) of D3, 0.59g (4.796 mmol) of picolinic acid, 0.8058g (9.592 mmol) of sodium bicarbonate, and 50 ml of ethoxyethanol. The solution was stirred under N_2 and warmed to 110 ℃. After 24 hr, the solution was cooled to room temperature; the reaction mixture was purified by column chromatography on silica gel with dichloromethane/n-hexane as eluent. The yield of complex 3 was 3.2125 g (95%) as yellow crystals. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K; δ (ppm)): 8.27 (d, *J*=1.5Hz,1 H), 8.07−7.95 (m, 3H), 7.60 (t, *J*=8.7, 7.5Hz 2H), 7.56−7.49 (m, 1H), 7.45−7.30 (m, 5H), 6.99 (t, *J*=8.1, 8.1Hz 1H), 6.44−6.72 (m, 2H) , 5.53 (d, *J*=8.1Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K; δ (ppm)): 173.7, 171.2, 168.1, 165.0, 153.0, 150.3, 149.9, 138.8, 138.5, 133.6, 128.3, 126.9, 126.0, 118.0, 114.6, 112.4, 111.6, 109.2, 107.6. Anal. Calcd for $C_{32}H_{16}N_3O_4F_4Ir$ (MW = 775.07): C, 49.59; H, 2.08; N, 5.42. Found: C, 49.99; H, 2.58; N, 5.51 %. MS (FAB; m/z):775.0786

Single Crystal X-ray Diffraction. All the crystals were obtained from a mixed solution of dichloromethane and n-hexane. The diffraction data of complexes 1-3 were collected on a Bruker SMART APEX CCD diffract meter with graphite-monochromatized Mo Kα X-ray radiation (λ = 0.71073 Å) at 110 K. All the calculations for the structure determination were carried out using SHELXS-97 package. The positions of the heavy atoms, including the iridium atoms were located by the direct method. The remaining atoms were found in a series of alternating difference Fourier maps and least-square refinement. The crystallographic data for all the structures reported here have been deposited in the Cambridge Data Centre as supplementary publication numbers CCDC # 1491980, 953384 and 953385, respectively.

Catalytic activity of catalysts. The reaction solution was stirred well under air, and the reaction temperature was well controlled in a silicon oil bath under constant temperature (±1℃). To evaluate the catalytic activity of complexes 1-3, oxidation of toluene was done by the following procedure. In round bottomed flasks, the toluene solution containing complexes 1-3 with various concentration between $1x10^{-8}$ and $1x10^{-2}$ M were prepared, and the reaction temperature was gradually increased to 100 °C and kept constant during the oxidation experiments. During the reactions, the mixtures have been continually sampling, and the concentrations of reactant and product were monitored with an instrument of the high performance liquid chromatography (HPLC)..

Theoretical Calculations. Theoretical calculations were performed with the program package Gaussian 03 by using Becke's three-parameter B3LYP for C, H, F, and N, and the LANL2DZ basis set for the Ir element. Partial charges were calculated according to the Mulliken, APT (atomic polar tensors), and NPA (natural population analysis) approaches, respectively.

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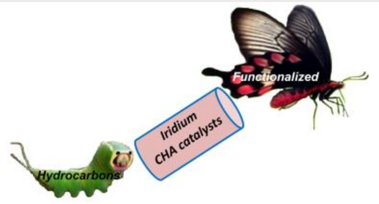
Entry for the Table of Contents

FULL PAPER

Cyclometalated Iridium(III) Complexes were designed and synthesized. All of them exhibited excellent ability for catalytic CHA oxidation of toluene by a green process with a quite low activation energy and pretty good reliability.



CHA Functionalization

Tsun-Ren Chen, Pei-Chun Liu, Hsiu-Pen Lee, Fang-Siou Wu, and Kelvin H.-C. Chen*

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Cyclometalated Iridium(III) Complexes with Ligand Effect on Catalytic Carbon-Hydrogen Bond Activation of Toluene in High-Performance