Charged cyclometalated iridium(III) complexes that have large electrochemical gap

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Abstract

Bis-cyclometalated cationic Ir(III) diimine complexes [Ir(C^N)2(N^N)](PF6) with 1-phenylpyrazoles (C^N) and 1-(4'-tert-butyl-2'-pyridyl)pyrazole (N^N) are white solids that have absorption onset below 425 nm and electrochemical gap of up to 3.5 V.

1. Introduction

Cyclometalated iridium(III) complexes are finding increasing application in electro-luminescent devices as emitters[1–8] and as electronic materials [9–11]. Recently, He et al reported that Ir(III) complexes with 1-(2'-pyridyl)pyrazole (1, Chart 1) emit blue-green phosphorescence from a predominantly ligand centered 3(π–π') excited state [12]. We considered that the redox and optical properties of 1 could be tuned by replacing a pyridine in the cyclometalating ligand with a pyrazole. We reasoned that the pyrazole is a weaker π-acceptor and a weaker σ-donor than the pyridine [13], and that the pyrazole ligands have π–π* transitions at higher energy than the analogous pyridine derivatives [14]. Here, we describe a successful application of this approach to access cationic bis-cyclometalated Ir(III) complexes that have a high-energy absorption onset and a large electrochemical gap.

2. Results and discussion

Scheme 1 shows a new neutral ligand L that was prepared by a non-catalyzed C–N coupling reaction of pyrazole with 2-chloro-4-tert-butylypyridine in DMSO, in the presence of potassium tert-butoxide as a base [15]. The pyridyl ring was modified with a bulky tert-butyl group to improve solubility of the Ir(III) complexes and to reduce the intermolecular interaction between them in the solid state.

Two new complexes, 3 (3H and 3F), were prepared by reaction of the neutral ligand with a cyclometalated Ir(III) precursor [Ir(C^N)2(μ-Cl)]2 (Scheme 1). The complexes were purified by column chromatography (on silica) and by re-crystallization; they were characterized by elemental analysis, ESI+ MS, and NMR spectroscopy.

Fig. 1 shows the X-ray molecular structure of complex 3F. The metal ion is in a distorted octahedral [Ir(C^N)2(N^N)]+ coordination environment with the two nitrogen atoms of the cyclometalating ligands in a pyrazole. We reasoned that the pyrazole is a weaker π-acceptor and a weaker σ-donor than the pyridine [13], and that the pyrazole ligands have π–π* transitions at higher energy than the analogous pyridine derivatives [14]. Here, we describe a successful application of this approach to access cationic bis-cyclometalated Ir(III) complexes that have a high-energy absorption onset and a large electrochemical gap.

Keywords: Iridium, Cyclometalation, Complex, Pyrazole, Electrochemistry

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The first oxidation process in 3 is quasi-reversible. Although both the forward and the return waves are observed, their peak separation is wider compared to that for the standard (Fc+/Fc couple [16]) and strongly depends on the scan rate (Table S2, Supporting Information). The oxidation potential undergoes a positive shift by 320 mV on fluorination of the phenyl ring of the cyclometalating ligand (Table 2). The first reduction is irreversible; its potential undergoes a positive shift by 70–90 mV on fluorination (Table 2). The redox properties of 3 were compared to those of 1 and 2 [12,14]. The oxidation potential is similar for the complexes that have either a 2,4-difluorophenyl (3F ≈ 1F ≈ 2F ≈ 1.2 V) or a phenyl (3H ≈ 1H ≈ 2H ≈ 0.9 V) as an aryl substituent (Table 2). The 300 mV difference in the potential between these two series reflects the strong electron-withdrawing properties of the fluorine and suggests that the oxidation is localized on a metal-aryl fragment.

Table 1
Selected bond lengths (Å) in complex 3F.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Complex</th>
<th>Solvent</th>
<th>E$_{1/2}$/V</th>
<th>E$^\text{red}$/V</th>
<th>D$E$/V$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir–C</td>
<td>3H</td>
<td>CH$_3$CN</td>
<td>0.94 (98)$^c$</td>
<td>-2.31$^d$</td>
<td>3.25</td>
</tr>
<tr>
<td></td>
<td>1H</td>
<td>CH$_3$CN</td>
<td>0.88</td>
<td>-2.19</td>
<td>3.07</td>
</tr>
<tr>
<td></td>
<td>2H</td>
<td>CH$_3$CN</td>
<td>0.95</td>
<td>-1.89</td>
<td>2.84</td>
</tr>
<tr>
<td></td>
<td>3F</td>
<td>CH$_3$CN</td>
<td>1.25</td>
<td>-1.83</td>
<td>3.08</td>
</tr>
</tbody>
</table>

$^c$ Quasi-reversible; the anodic/cathodic peak separation is given in brackets.

$^d$ Irreversible process; the reduction peak potential is reported.

$^b$ D$E$ = E$_{1/2}$ – E$^\text{red}$.

$^a$ Relative to Fc$^+/$/Fc. On glassy carbon working electrode, in the presence of 0.1 M (NBu$_4$)$_2$PF$_6$, at scan rate 100 mV/s. Estimated error: ±50 mV. The anodic/cathodic peak separation for the standard, Fc$^+/$/Fc couple [16], was 68–88 mV in CH$_3$CN; 83–88 mV in DMF.

Fig. 1. Structure of 3F (50% probability ellipsoids; H atoms, PF$_6$ anion, and co-crystallized diethyl ether molecule omitted; ORTEP). Heteroatoms are shown as octant ellipsoids: Ir, black; N, shaded; F, clear.
The reduction potential of the complexes appears to be determined by the neutral ligand: \((3 \approx -2.3 \, \text{V}) < (1 \approx -2.2 \, \text{V}) < (2 \approx -1.9 \, \text{V})\). We consider the pyridyl ring of ligand \(L\) to be the main electron acceptor in \(3\). The negative shift of the reduction potential of \(3\) by 90–120 mV with respect to that of \(1\) \([12]\) arises from the presence of an electron-donating tert-butyl group in the neutral ligand and from the replacement of a pyridine with a pyrazole, a weaker \(\pi\)-acceptor \([13]\), in the cyclometalating ligand.

\(3\)H has an electrochemical gap of 3.2 V that on fluorination increases to 3.5 V \(3\) (Table 2). To our knowledge, the value of the electrochemical gap in \(3\) is the highest reported for a cationic bis-cyclometalated Ir(III) complex with a neutral dimine ligand \(\text{(Table 2) \([12,14,17,18]\).}\\

The complexes \(3\) are white solids and give colorless solutions in polar organic solvents. The electronic absorption spectra of \(3\) in dichloromethane do not have strong transitions in the visible range \(3\) (Table 3, Fig. 3 and Fig. S2, Supporting Information). The absorption onset, defined as a wavelength above which \(\varepsilon < 0.1\%\) \(\varepsilon_{\text{max}}\), is observed at 425 nm in \(3\)H; it is blue-shifted to 400 nm in the fluorinated complex \(3\)F (Fig. 3). The shorter wavelength of an absorption onset \(\text{(Table 3)}\) corresponds to a larger value of the electrochemical gap \(3\) (Table 2); therefore, we assign the lowest energy absorption onset \(\text{(Table 3)}\) to the \(\text{(metal and} \, \text{aryl)-to-pyridyl} \, \text{charge transfer.}\\

\(3\) do not display luminescence at 400–700 nm in 10–4 M dichloromethane solutions at room temperature under near-UV excitation; the upper limit of their quantum yield is 0.05%. We attribute the lack of luminescence of \(3\) to the quenching of a ligand-centered or charge-transfer excited state by proximate non- emissive \(d-d\) metal states; the same deactivation mechanism has been suggested for the cyclometalated Ir(III) complexes with 1-phenylpyrazoles \([19–22]\).

In conclusion, 1-(4'-tert-butyl-2'-pyridyl)pyrazole and 1-(2',4'-R2-phenyl)pyrazole \((R = H \text{ or} F)\) form cationic bis-cyclometalated Ir(III) complexes \([\text{Ir(C^N)2(N^N)}]^+\) that have high-energy absorption onset and large electrochemical gap. A facile modification of these ligands opens opportunities for the development of functional Ir(III) complexes.

3. Experimental

Purification, crystal growth, and handling of all compounds were carried out under air. All products were stored in the dark.

The reaction was performed under argon. Pyrazole \((440 \, \text{mg, 6.46 mmol, excess, Aldrich})\) and potassium tert-butoxide \((714 \, \text{mg, 6.36 mmol, excess, Acros})\) were dissolved at RT in dry and degassed DMSO \((3 \, \text{mL, Acros, 99.8%, ExtraDry, over Molecular Sieves, AcroSeal}^\circ\text{)}\). 2-Chloro-4-tert-butylpyridine \((1 \, \text{g, 5.89 mmol} \text{ [23,24]})\) was added. The reaction mixture was stirred at 140°C for 9 h to give orange solution. It was cooled to RT. It was extracted with water and ether. Organic layer was washed with water to extract DMSO. Purification by chromatography \((\text{run twice; silica, 2 × 25 cm})\) removed the starting material \((\text{hexane/CH2Cl2; 3/1–1/1})\) and recovered the product \((0.5\% \text{ CH2OH in CH2Cl2})\). The product was isolated as colourless oil that crystallized to a pale yellow solid after a week of standing: 923 mg \((4.59 \, \text{mmol, 78%}, \text{Anal. Calcd for C17H15N3 (MW 281.27): C, 71.61; H, 7.51; N, 20.88.} \text{Found: C, 72.13; H, 7.54; N, 20.71.} \text{H NMR (400 MHz, CDCl3; py = pyridine; pz = pyrazole): } \delta = 8.58 \text{ (dd, } J = 2.8, 0.8 \, \text{Hz, 1H, pz), 8.32 (dd, } J = 5.6, 0.4 \, \text{Hz, 1H, py), 8.00 (m, 1H, py), 7.76 (m, 1H, pz), 7.20 (m, 1H, py), 6.47 (m, 1H, pz), 1.39 (s, 9H, tert-butyl) \text{[25,26]}.} \text{13C NMR (100 MHz, CDCl3; } \delta = 163.54 \text{ (C, py), 152.03 (C, py), 148.02 (CH, py), 141.97 (CH, pz), 127.36 (CH, py), 119.04 (CH, py), 109.52 (CH, py), 107.78 (CH, pz), 35.38 (tert-butyl, C), 30.72 (tert-butyl, CH3) [25,26]. GC-El+ MS: m/z 201 (M+, 100%), 186 ([M–CH4]+, 95%).\\

The reactions were performed under argon and in the absence of light. The solvents were de-oxygenated by bubbling with Ar, but they were not dried. Cyclometalated precursor \([\text{Ir(C^N)2(μ-Cl)]2} \text{ [27]}\) was dissolod in CH2Cl2 \((40 \, \text{mL})\) at RT. After addition of CH2OH \((5 \, \text{mL})\) and ligand \(L\) (excess), the reaction mixture was stirred at 40°C overnight to give colourless or pale brown solution. It was evaporated to dryness. The work-up and further synthetic details are provided below. The complexes are air- and moisture-stable white solids; to the naked eye they appear to be non-emissive at RT under excitation with 365 nm light in the solid state, in CH2Cl2 solution, or on silica TLC plate.

\(3\)H: The reaction was performed with \([\text{Ir(ppz)2(μ-Cl)]2} \text{ (100 mg, 0.097 mmol; } \text{ppz = 1-phenylpyrazole-N',C'-})\) and \(L\) \((50 \, \text{mg, 0.25 mmol, excess})\). Purification by chromatography \((\text{silica, 15 g})\) removed the impurities \((1–3% \text{ CH2OH in CH2Cl2})\). The target fractions were evaporated. Dry residue was dissolved in CH2OH \((4 \, \text{mL})\), and the complex was precipitated by KPF6 \((305 \, \text{mg, 1.66 mmol, in 10 mL of water, excess, Alfa Aesar}). More water \((15 \, \text{mL})\) was added. The resulting suspension was stirred \((30 \, \text{min})\) and filtered. The complex was washed with water and ether. It was re-crystallized by pouring its solution in CH2Cl2 \((2 \, \text{mL})\) to ether \((30 \, \text{mL})\). The product was filtered and washed with

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**Table 3** Optical absorption of new compounds.

| Compound | \(\lambda_{\text{max}}/\text{nm} (\varepsilon/10^3 \, \text{M}^{-1} \, \text{cm}^{-1})\) | \(\lambda_{\text{onset}}/\text{nm}\)
|---|---|---
| \(L\) | 253 (11), 281 (10), 305 (0.9, sh) | 330
| \(3\)H | 258 (39), 310 (12, sh), 377 (1.1, sh) | 425
| \(3\)F | 253 (44) | 400

\(a\) In CH2Cl2, at room temperature, in the range 250–500 nm. Estimated errors: ±1 nm for \(\lambda_{\text{max}}\); ±5 nm for \(\lambda_{\text{onset}}\); ±5% for \(\varepsilon\).

\(b\) Defined as a wavelength above which \(\varepsilon < 0.1\%_{\text{max}}\).

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**Fig. 3** Absorption spectra of the complexes \(3\)H \((8.63 \times 10^{-5} \, \text{M})\) and \(3\)F \((9.28 \times 10^{-5} \, \text{M})\) in CH2Cl2. Additional absorption spectra are provided in the Supporting Information.
ether. White solid: 124 mg (0.15 mmol, 77%). Anal. Calcd for C_{30}H_{29}F_6IrN_7P (MW 824.78): C, 43.69; H, 3.54; N, 11.89. Found: C, 43.23; H, 3.45; N, 12.27. 1H NMR (400 MHz, CD_{2}Cl_{2}): δ = 9.51 (d, J = 3.2 Hz, 1H), 8.63 (m, 2H), 8.43 (d, J = 1.6 Hz, 1H), 7.71 (d, J = 6.0 Hz, 1H), 7.61 (d, J = 2.0 Hz, 1H), 7.55 (dd, J = 6.0, 1.6 Hz, 1H), 7.45 (d, J = 2.4 Hz, 1H), 7.37 (d, J = 2.4 Hz, 1H), 7.18–7.05 (m, 2H), 6.94 (t, J = 2.4 Hz, 1H), 6.82–6.77 (m, 2H), 5.68–5.58 (m, 2H), 1.36 (s, 9H, tert-butyl). 19F NMR (376 MHz, CD_{2}Cl_{2}): δ = −72.9 (d, J_{PF} = 710 Hz, 6F, PF_{6}^−), −112.8 (d, J_{PF} = 6 Hz, 1F), −123.8 (d, J_{PF} = 6 Hz, 1F), −124.2 (d, J_{PF} = 6 Hz, 1F). 31P NMR (162 MHz, CD_{2}Cl_{2}): δ = 144.5 (septet, PF_{6}, J_{PF} = 710 Hz). ES+ TOF MS: m/z 680.21 ([M–PF_{6}^−]+, 100%).

3F: The reaction was performed with [Ir(dfppz)_{2}(μ-Cl)]_{2} [100 mg, 0.085 mmol; dfppz = 1-(2,4’-difluorophenyl)pyrazole-N^2, C^6] and L (47 mg, 0.23 mmol). Dry residue was dissolved in CH_{3}OH (5 mL), and the complex was precipitated by KPF_{6} (250 mg, 1.36 mmol, in 5 mL of water, excess). More water (10 mL) was added. The resulting suspension was stirred for 30 min and filtered. The complex was washed with water and ether. White solid: 130 mg (0.145 mmol, 85%). Anal. Calcd for C_{30}H_{29}F_{6}IrN_{7}P (MW 896.74): C, 40.18; H, 2.81; N, 10.93. Found: C, 40.26; H, 2.76; N, 10.86. 1H NMR (400 MHz, DMSO-d_{6}): δ = 9.51 (d, J = 3.2 Hz, 1H), 8.63 (m, 2H), 8.43 (d, J = 1.6 Hz, 1H), 7.71 (d, J = 6.0 Hz, 1H), 7.61 (d, J = 2.0 Hz, 1H), 7.55 (dd, J = 6.0, 1.6 Hz, 1H), 7.45 (d, J = 2.4 Hz, 1H), 7.37 (d, J = 2.4 Hz, 1H), 7.18–7.05 (m, 2H), 6.94 (t, J = 2.4 Hz, 1H), 6.82–6.77 (m, 2H), 5.68–5.58 (m, 2H), 1.36 (s, 9H, tert-butyl). 19F NMR (376 MHz, CD_{2}Cl_{2}): δ = −72.9 (d, J_{PF} = 710 Hz, 6F, PF_{6}^−), −112.3 (d, J_{PF} = 6 Hz, 1F), −112.8 (d, J_{PF} = 6 Hz, 1F), −123.8 (d, J_{PF} = 6 Hz, 1F), −124.2 (d, J_{PF} = 6 Hz, 1F). 31P NMR (162 MHz, CD_{2}Cl_{2}): δ = 144.5 (septet, PF_{6}, J_{PF} = 710 Hz). ES+ TOF MS: m/z 752.18 ([M–PF_{6}^−]+, 100%).

Acknowledgments

European Union (CELLO, STRP 248043; www.cello-project.eu), M.K.N. thanks World Class University program, funded by the Ministry of Education, Science and Technology through the National Research Foundation of Korea (No. R31-2008-000-10035-0), Department of Material Chemistry, Korea University, Chungnam 339-700, Korea.

Appendix A. Supplementary material

CCDC 833460 contains 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jica.2011.10.052.

References