## An 18+ $\delta$ iridium dimer releasing metalloradicals spontaneously<sup>†</sup>

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Reductive elimination of a bridged chlorine from a diiridium(III) core,  $[(dfpbo)_2Ir(\mu-Cl)]_2$  (dfpbo = 2-(3.5-difluorophenyl)benzoxazolato-N,C<sup>2</sup>), afforded an iridium dimer,  $[(fpbo)_2Ir]_2(\mu-Cl)$ , showing an 18+ $\delta$  structure with a bent bridge, which can release metalloradicals spontaneously in solution at room temperature.

Iridium metalloradicals are known to play an important role in the investigation of DNA oxidative chemistry, energy transfer in biological systems, and organometallic substrate transformations.<sup>1</sup> Mostly, iridium metalloradicals are generated by the dissociation of unstable molecules, for example, via a photochemical, chemical or electrochemical reaction.<sup>2</sup> The concept of  $18+\delta$  was introduced in 1988, in which the value of  $\delta$  reflects the degree of electron residing on the metal centre.<sup>3</sup> Since then, very few 18+δ complexes have been described.<sup>4</sup> Such complexes are difficult to synthesize and isolate due to their propensity to undergo further reactions such as ligand dissociation, and the reduction or oxidation of metal atoms. Our interest in the iridium radical chemistry has discovered a novel diiridium compound showing an  $18+\delta$  structure which can spontaneously release iridium metalloradicals under ambient temperature. We report here the isolation and characterization of this title compound.

Reaction of  $[(dfpbo)_2 Ir(\mu-Cl)]_2 (dfpbo = 2-(3.5-difluorophenyl)$ benzoxazolato-N,C<sup>2</sup>)<sup>5</sup> with potassium carbonate in a solventsystem of toluene and ethoxyethanol afforded an unusual iridium $dimer <math>[(dfpbo)_2 Ir]_2(\mu-Cl)$  (1) (Scheme S1, ESI†).‡ A single-crystal X-ray structure determination confirmed the dimeric nature of 1 (Fig. 1). The Ir1–Cl–Ir2 and Cl–Ir1–Ir2 angles are 76.21(3) and 51.90(3)°, respectively. This structure possesses a bent single bridge connecting the two iridium core. The Ir–Ir bond length of 3.0433(3) Å is similar to those of previously reported complexes of single bridged iridium dimer, such as  $\{[Cp*Ir(CO)H]_2(\mu-H)\}BAr'_4$ (2.928 Å) and  $\{[Cp*Ir(PMe_3)H]_2(\mu-H)\}PF_6$  (2.983 Å).<sup>6</sup>

The (FAB+) (Fast Atom Bombardment) spectrum of 1 (Fig. S1, ESI<sup>†</sup>) shows a medium-intensity complex pattern of molecular peaks:  $[Ir_2(dfpbo)_4(Cl)]^+$ :  $[^{193}Ir, ^{193}Ir, ^{35}Cl$  and  $^{193}Ir, ^{191}Ir, ^{37}Cl, m/z$  1341 (15%)]. A high-intensity pattern of peaks of radicalcation was also observed:  $[(dfpbo)_2Ir]^{++}$  [ $^{193}Ir, m/z$  653 (38%) and  $^{191}Ir, m/z$  651 (32%)], which reveals that compound 1 is



**Fig. 1** ORTEP plots of **1**. Thermal ellipsoids are drawn at the 30% probability level and hydrogen atoms are omitted for clarity.

readily dissociated to form the relatively stable metalloradical  $[(dfpbo)_2Ir]^*$ . Furthermore, two of these metalloradicals could combine with each other to form a binuclear species:  $[(dfpbo)_2Ir]_2$  [<sup>193</sup>Ir, <sup>193</sup>Ir, *m/z* 1307 (2.2%) and <sup>193</sup>Ir, <sup>191</sup>Ir, *m/z* 1305 (1.1%)].

The frozen-solution (77 K, in toluene) EPR spectrum of compound 1 displays an isotropic signal at g = 2.0009, characteristic of an organic centered radical (Fig. 2(a)), which, with no resolvable iridium hyperfine, suggests that only a very small degree of spinfree electron is delocalized from the dfpbo ligands to the metal.<sup>7</sup> At



**Fig. 2** EPR spectra of **1** in toluene after degassing at (a) 77 K, and (b) 298 K. EPR settings: microwave frequency, 9.879 GHz; microwave power, 10.080 mW; number of scans, 1.

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Full experimental details, analytical data and X-ray details for 1, 4 and 5; mass spectral data for 1; a table of Cartesian coordinates, SOMO and LUMO orbital compositions for 1. CCDC reference numbers for compounds 1, 4 and 5, 778557–778559. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00605j



Fig. 3 Electron density of the SOMO (left) and LUMO (right) in [(fpbo)<sub>2</sub>Ir]<sub>2</sub>(µ-Cl).

 Table 1
 Comparison of selected bond lengths (Å) and angles (°) of 1

 from crystallography and DFT calculation

	Ir–Ir	Ir–Cl	Ir–N	$\Psi^{a}$
X-Ray	3.0433(3)	2.4658(14)	2.030(4)	10.4
			2.062(4)	168.9
DFT	3.042	2.465	2.029	10.36
			2.061	168.85

<sup>a</sup> Torsional angles N1-Ir-Ir-N1a and N2-Ir-Ir-N2a respectively.

room temperature, the solution of compound **1** in toluene shows a complicated EPR spectrum, Fig. 2(b), implying that there may have more than one paramagnetic species exist in the solution system and whose spectra overlap with each other.<sup>8</sup>

DFT (B3LYP/LANL2DZ level) calculation on 1 provide insight into the electronic structure of 1. The X-ray structure of 1 was used as an initial geometry for optimization. The metrical parameters obtained from the X-ray structure and DFT calculation are in good agreement (Table 1). The singly occupied molecular orbital (SOMO) calculated for compound 1 is composed of 4.5% d(Ir) and 94.3%  $\pi$  (dfpbo) and the lowest unoccupied molecular orbital (LUMO) is composed of 15% d(Ir) and 84.5%  $\pi$  (dfpbo) (Fig. 3), which implies that the unpaired electron is mostly delocalized onto the four ligands dfpbo and gives rise to the characteristic of an ligand centered radical for compound 1 in frozen solution.<sup>7</sup> As the unpaired electron is mostly distributed over the ligands, there is only a part of the unpaired electron located on the metal centre; therefore, this complex could be categorized as an  $18+\delta$ compound. This delocalization stabilized the structure of 1 and led to the isolation of this compound.

To understand the formal charge of iridium atoms in compound 1, the normalized X-ray absorption near edge structure (XANES) spectra at the Ir K-edge of compound 1 was obtained (Fig. 4(b)). For comparison, the spectra of  $[(dfpbo)_2Ir^{II}(\mu-Cl)]_2$  (Fig. 4(a)) and  $[(dfpbo)_2Ir^{II}]_2$  (Fig. 4(c)) were also acquired. The white line intensity of compound 1 in Fig. 4 shows that the iridium atoms in 1 have a formal oxidation between +3 and +2.<sup>9</sup> As the odd electron is mostly delocalized on the ligands, the metal atoms possess more



**Fig. 4** Ir K-edge XANES of crystalline (a)  $[(dfpbo)_2Ir^{II}(\mu-CI)]_2$ , (b) compound **1**, and (c)  $[(dfpbo)_2Ir^{II}]_2$ . 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.

positive charge; therefore, the XANES data of complex 1 is similar to that of  $[(dfpbo)_2Ir^{II}(\mu-Cl)]_2$  rather than that of  $[(dfpbo)_2Ir^{II}]_2$ .

Two iridium dimers,  $[(dfpbo)_2Ir]_2$  (3)<sup>10</sup> and  $[(dfpbo)_2Ir(\mu-Cl)]_2^5$ were obtained when the temperature of the solution 1 was increased to about 100 °C. Complex 3 (40% yield) should come from the recombination of two iridium radicals [(dfpbo)<sub>2</sub>Ir]<sup>2</sup> 2a, and the iridium dimer  $[(dfpbo)_2Ir(\mu-Cl)]_2$  (40% yield) should come from the recombination of two iridium radicals [(dfpbo)<sub>2</sub>Ir(µ-Cl)]<sup>•</sup> 2b, (Scheme 1). The reactivity of these iridium radicals have been the subject of two studies, a carbon-hydrogen bond activation (CHA) and a rare but important carbon-carbon bond activation (CCA) for substrates.11 An illustration of CHA is that an unsaturated ketone, chalcone, could be converted to a 1,3diketone, dibenzoylmethane, in the presence of trace amount of water and these iridium radicals via a radical-assisted oxidation. The dibenzoylmethane formed could act as an ancillary ligand and coordinate to the iridium radical 2a, [(dfpbo)<sub>2</sub>Ir], to produce a stable cyclometalated iridium complex  $[(dfpbo)_2 Ir(dbm)] (dbm =$ dibenzoylmethanate) (4) (Scheme 1). For the reaction mentioned



Scheme 1 Formation of iridium metalloradicals from 1, and the reactions.

above, two iridium radicals **2b**,  $[(dfpbo)_2Ir(\mu-Cl)]^*$ , could combine with each other to form an iridium dimer  $[(dfpbo)_2Ir(\mu-Cl)]_2$ . Cyclometalated iridium complexes with ancillary ligands have been widely investigated recently because they can be used as emissive dopants in organic light emitting devices (OLEDs), photocatalysts for CO<sub>2</sub> reduction, photooxidants, and biological reagents.<sup>12</sup> The metalloradical reaction described herein provides a useful way to prepare cyclometalated iridium complexes.<sup>‡</sup> An example of CCA is that an aldehyde, 3,5-dibromobenzaldehyde, could react with iridium radical [(dfpbo)\_2Ir]<sup>+</sup> to introduce a carbonyl into the metal centre readily to obtain a carbonyl product [(dfpbo)\_2Ir(dbp)(CO)] (dbp = 3,5-dibromophenyl)) (**5**) by the oxidative addition and retromigration insertion (Scheme 1), which provides an approach to prepare iridium carbonyl complexes under mild condition.<sup>‡</sup>

In conclusion, we present an unusual iridium compound possessing a bent single bridge. The structural study shows that this compound holds an  $18+\delta$  electron configuration, in which the unpaired electron is mostly delocalized onto the four dfpbo ligands. This compound could spontaneously release iridium metalloradicals at ambient temperature in solution, and the metalloradicals could activate many kinds of substrates, such as alkene, ketones, and aldehydes. The reactivity of this compound suggests that it could be a key precursor in the explorations for iridium chemistry and materials science.

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## Notes and references

‡ Synthesis of 1: a flask was charged with 500 mg of  $[(fpbo)_2Ir(\mu-Cl)]_2$ (0.363 mmol) and 55 mg of anhydrous potassium carbonate (0.40 mmol). Toluene (15 ml) and ethoxyethanol (0.5 ml) were added to give a clear yellow solution, and the solution was stirred under N<sub>2</sub> and warmed to 100 °C for 24 h. After cooling to room temperature, the reaction mixture was filtered through silica gel. The filtrate was purified *via* column chromatography over silica gel using n-hexane-toluene (3:1 ratio) as eluent to obtain the pure product. Yield: 293 mg (60% based on iridium). Anal. Calcd for C<sub>52</sub>H<sub>24</sub>N<sub>4</sub>O<sub>4</sub>ClF<sub>8</sub>Ir<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 44.65; H, 1.84; N, 3.93. Found: C, 44.75; H, 1.67; N, 3.78%. 4: a mixture of chalcone (312 mg, 1.5 mmol) and compound 1 (50 mg, 0.037 mmol) in toluene (30 ml) was stirred under  $N_2$  at 110 °C for 2 d. The final solution was taken to dryness in vacuo. The residue was purified via column chromatography. Yield: 14 mg (43% based on iridium). (Anal. Calcd for C<sub>41</sub>H<sub>23</sub>F<sub>4</sub>IrN<sub>2</sub>O<sub>4</sub>: C, 56.22; H, 2.65; N, 3.20. Found: C, 56.25 H, 2.66; N, 3.21%. 5: a mixture of 3,5-dibromobenzaldehyde (396 mg, 1.5 mmol) and compound 1 (50 mg, 0.037 mmol) in toluene (30 ml) was stirred under  $N_2$  at 110 °C for 2 d. The final solution was taken to dryness in vacuo. The residue was purified via column chromatography. Yield: 16 mg (47% based on iridium). Anal. Calcd for C<sub>33</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub>Br<sub>2</sub>F<sub>4</sub>Ir: C, 43.29; H, 1.65; N, 3.06. Found: C, 43.32; H, 1.66; N, 3.07%.; IR (KBr pellet): v(CO) 2360 cm<sup>-1</sup>. Crystal data for compound 1: formula  $C_{52}H_{24}N_4O_4ClF_8Ir_2$ , M = 1340.67, orthorhombic, space group Aba2, a = 21.8706(4), b = 14.4783(3), c = 14.4783(3)16.9835(3) Å, V = 5377.81(18) Å<sup>3</sup>, Z = 4,  $\rho_c = 2.075$  g cm<sup>-3</sup>, F(000) = 3228, T = 100(2) K,  $2\theta_{max} = 58.5^{\circ}$ , 25 544 reflections collected, 6320 unique, GooF = 1.192,  $R_1 = 0.0317$ ,  $wR_2 = 0.0637$ . Crystal data for compound 4: formula C<sub>41</sub>H<sub>23</sub>F<sub>4</sub>IrN<sub>2</sub>O<sub>4</sub>, M = 875.85, triclinic, space group  $\overline{P1}$ , a =12.0381(3), b = 14.6705(4), c = 19.5320(5) Å,  $\alpha = 102.358(2)$ ,  $\beta = 95.205(2)$ ,  $\gamma = 94.203(2)^{\circ}$ ,  $V = 3340.35(15) \text{ Å}^3$ , Z = 4,  $\rho_c = 1.742 \text{ g cm}^{-3}$ , F(000) = 1712, T = 120(2) K,  $2\theta_{\text{max}} = 58.7^{\circ}$ , 29 949 reflections collected, 15 412 unique, GooF = 1.132,  $R_1$  = 0.0516, w $R_2$  = 0.1161. Crystal data for compound **5**: formula  $C_{33}H_{15}N_2O_3Br_2F_4Ir$ , M = 915.52, monoclinic, space group P21/n, a = 14.5053(3), b = 12.1682(3), c = 16.3047(3) Å,  $\beta = 102.514(2)^{\circ}, V = 102.514(2)^{\circ}$ 2809.47(10) Å<sup>3</sup>, Z=4,  $\rho_c = 2.164$  g cm<sup>-3</sup>, F(000) = 1736, T = 110(2) K,  $2\theta_{max} = 1000$  $58.4^{\circ}$ , 13 799 reflections collected, 6500 unique, GooF = 1.023,  $R_1$  = 0.0246,  $wR_2 = 0.0484.$ 

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