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A Novel Cyclometalated Dimeric Iridium Complex, $[(dfpbo)_2Ir]_2$ [dfpbo = 2-(3,5-Difluorophenyl)benzoxazolato-*N*,$C^{2'}$], Containing an Unsupported $Ir^{II}-Ir^{II}$ Bond

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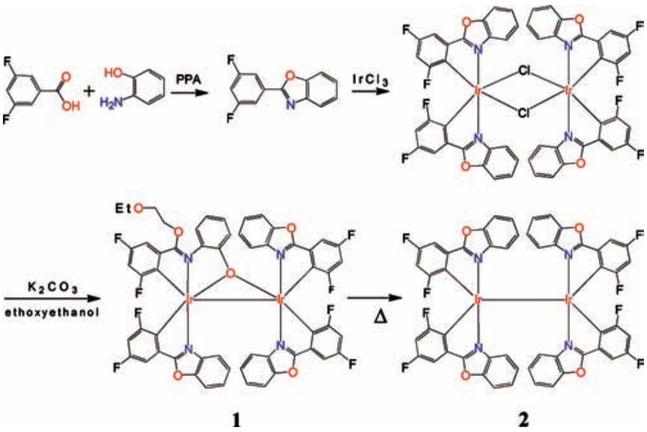
An unusual iridium complex, $[(dfpbo)_2Ir]_2$ [dfpbo = 2-(3,5-difluorophenyl)benzoxazolato-*N*,$C^{2'}$], which is the first dimeric iridium complex composed of two bis-cyclometalated Ir^{II} structures connected by an unsupported $Ir^{II}-Ir^{II}$ bond, has been synthesized and fully characterized. Under mild conditions of neutral pH at room temperature, this complex dissociated spontaneously to form the stable radical $[Ir(dfpbo)_2]^{\bullet}$.

Since Nonoyama developed a method to prepare cyclometalated Ir^{III} Cl-bridged dimers,[1] hundreds of bis-cyclometalated or tris-cyclometalated Ir^{III} complexes have been prepared by using these kinds of dimers as starting materials, which have received considerable attention in photonic applications.[2] Besides the Cl-bridged dimers, multinuclear iridium complexes with unsupported Ir−Ir bonding are rare but important.[3] The first complex of this type was discovered in 1985,[4a] and until now, only five examples had been reported.[4] Owing to their rarity, these compounds have not been employed to further investigate the iridium chemistry.

Scheme 1. Synthesis of Complexes **1** and **2**



Herein, we report the preparation and characterization of a novel diiridium compound, $[(dfpbo)_2Ir]_2$ [**2**; dfpbo = 2-(3,5-difluorophenyl)benzoxazolato-*N*,$C^{2'}$; Scheme 1), which is the first iridium complex composed of two bis-cyclometalated Ir^{II} structures linked only by an unsupported $Ir^{II}-Ir^{II}$ bond. This dimeric complex possesses a special structural character different from that of the traditional bridged dimers and exhibits particular reactivities.

As shown in Scheme 1, when the solution of $(dfpbo)_2Ir(\mu\text{-}Cl)_2Ir(dfpbo)_2$[5] in ethoxyethanol was stirred under basic and anaerobic conditions, an electrophilic C atom of an oxazole ring in $(dfpbo)_2Ir(\mu\text{-}Cl)_2Ir(dfpbo)_2$ was attacked by the nucleophile, the ethoxyethoxide ion, to form an *o*-[(3,5-difluorophenyl)ethoxyethoxylmethyl]iminophenoxide ion. Two μ-Cl atoms were then excluded by this iminophenoxide ion

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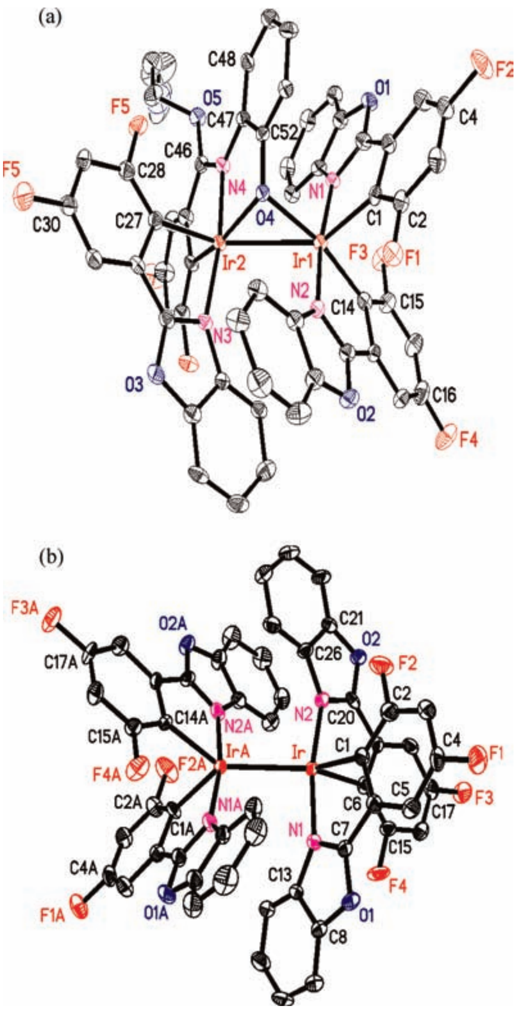

Figure 1. ORTEP plots of (a) **1** and (b) **2**. Thermal ellipsoids are drawn at the 30% probability level, and H atoms are omitted for clarity.

via intramolecular substitution, and a red intermediate, (dfpbo)(R)Ir(μ-*o*-OC$_6$H$_r$)Ir(dfpbo)$_2$ (**1**; R = *N*-[(3,5-difluorophenyl)ethoxyethoxylmethyl]imino-*N*,*C*$^{2'}$), was isolated and structurally characterized (Figure 1a). This intermediate is dimeric and consists of two distorted-octahedral moieties linked by an Ir−Ir bond [Ir1−Ir2 = 2.9024(6) Å] and stabilized by a bridged O atom. It is worth noting that one of these distorted-octahedral moieties possesses a tetracyclometalated structure, i.e., incorporating two N^Ir^C rings, an N^Ir^O ring, and a three-membered ring composed of two Ir atoms and a bridged O atom.[6] Complex **1** decomposed gradually to form a red complex **2** with a moderate yield (40%).

A single-crystal X-ray determination shows that complex **2** is a dimeric iridium complex consisting of two dicyclometalated moieties linked only by an unsupported Ir^{II}−Ir^{II} bond (Figure 1b). The unsupported Ir−Ir distance of 2.7357(10) Å in **2** is similar to those of previously reported complexes, such as [Ir$_2$Cl$_2$(CO)$_4$(η^1-NP-Fc]$_2$] [2.7121(8) Å][4b] and [CP*Ir(CO)H]$_2$ [2.730(1) Å].[4c] In complex **2**, the Ir atoms are five-coordinated with distorted-trigonal-bipyramidal (DTBP) geometry, which is different from those of the previously reported complexes with octahedral or pseudooctahedral geometry. The phenyl fragments of cyclometalated ligands of complex **2** prefer to be in the equator of the DTBPs, adopting a *cis*-C−C-*trans*-N−N chelate disposition, which implies that there is a stronger trans influence of the phenyl group over that of the benzoxazolyl. To release the steric repulsion between the bulky groups, the two cyclometalated ligands are positioned nearly perpendicular to each other (dihedral angle = 84°) and the two DTBPs adopt a staggered geometry (the N$_1$−Ir$_1$−Ir$_2$−N$_{1A}$ twist angle = 22.2°). By the values of the bond angles (Table S2 in the Supporting Information) of the DTBP geometries ($\angle$N$_1$−Ir$_1$−N$_2$ = 169.4°, $\angle$C$_1$−Ir$_1$−C$_{14}$ = 84.9°, $\angle$C$_1$−Ir−Ir$_A$ = 136.1°, and $\angle$C$_{14}$−Ir−Ir$_A$ = 139.0°, respectively), the steric hindrance between the two DTBPs must be very large. The (FAB$^+$) (fast atom bombardment) spectrum of **2** (Figure S1 in the Supporting Information) shows a medium-intensity complex pattern of molecular peaks: [Ir$_2$(dfpbo)$_4$]$^+$ [^{193}Ir, ^{193}Ir, *m/z* 1307 (17%), ^{193}Ir, ^{191}Ir, *m/z* 1305 (29%), and ^{191}Ir, ^{191}Ir, *m/z* 1303 (20%), respectively]. Furthermore, a high-intensity pattern of peaks resulting from breaking of the unsupported Ir−Ir bond was observed: [Ir(dfpbo)$_2$]$^+$ [^{193}Ir, *m/z* 653 (47%) and ^{191}Ir, *m/z* 651 (28%)], which reveals that the homolytically cleaved fragments of complex **2**, [Ir(dfpbo)$_2$]$^+$, are quite stable in the gas phase. Interestingly, when complex **2** was dissolved in dichloromethane at room temperature, some of the molecules of complex **2** dissociated spontaneously. The unsupported Ir^{II}−Ir^{II} bond in a molecule of complex **2** was broken, and a free radical, [Ir (dfpbo)$_2$]$^\bullet$, was formed.[7] The solution of complex **2** in dichloromethane at 77 K shows a very low intensity of the electron paramagnetic resonance (EPR) signal (Figure 2a), and the intensity of the signal increases readily when the temperature rises to 298 K (Figure 2b, g_{iso} = 2.005), which reveals that

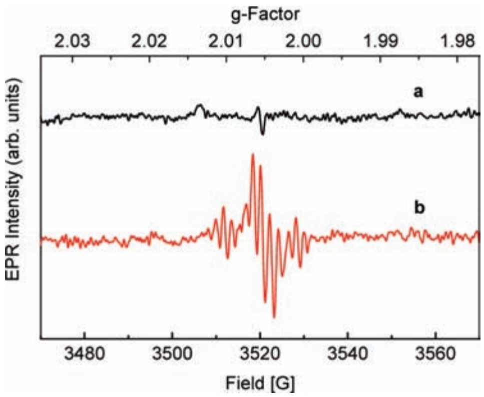

Figure 2. EPR spectra of **2** in dichloromethane after degassing at (a) 77 K and (b) 298 K. EPR settings: microwave frequency, 9.879 GHz; microwave power, 5.063 mW; number of scans, 4.

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(7) The concentrations of metalloradicals depend on the constants (^1k_q, ^3k_q, k_d, and k_D) and the quantum yield to form radical species: Caspar, J. V.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 3029. Some similarity to the measuring radical signal by using dichloromethane as the solvent may be found, for instance, in the reported case of the EPR study of the fluorophore−metal interaction: Carano, M.; Cicogna, F.; Houben, J. L.; Ingrosso, G.; Marchetti, F.; Mottier, L.; Paolucci, F.; Pinzino, C.; Roffia, S. *Inorg. Chem.* **2002**, *41*, 3396.

the radical formation is thermoinduced.[8] Organoiridium radicals possess high reactivity in a variety of catalytic and electron-transfer reactions[8b,9] and play an important role in the mechanism of many synthetic oxygenating catalysts.[10] Most organoiridium radicals are prepared by electrochemical,[11] photoinduced,[8a,12] or charge-transfer processes.[8a,13] The thermoinduced process for the formation of organoiridium radicals at room temperature in this report is the first case. The cyclic voltammogram of complex **2** (Figure S2 in the Supporting Information), recorded in dichloromethane at a slow scan rate, 80 mV s^{-1}, shows a reversible wave at very low oxidation potential, 0.12 V, versus Fc/Fc^+, which is associated with electrogeneration of the monocationic species $[Ir(dfpbo)_2]^+$.[8b,14]

In solution, **2** appears orange in color. The absorptions at 241 and 302 nm are attributable to $\pi-\pi^*$ transitions, and a lower-energy (LE) absorption band at 462 nm is also observed (Figure S3 in the Supporting Information). In order to gain insight of this LE band, density functional theory calculations were performed on **2** at the B3LYP/LANL2DZ level, which is implemented in the *Gaussian 03* software package.[15] Coordinates are directly from X-ray crystallography. The results show that the highest occupied molecular orbital is a σ-type bonding orbital (35% from two Ir atoms and 65% from the ligands), whereas the lowest unoccupied molecular orbital is a π-type bonding orbital (24% from Ir atoms and 76% from the ligands). The LE band thus can be assigned as a $\sigma(ML) \rightarrow \pi(ML)$ transition (Figure S4 in the Supporting Information).

In summary, a novel cyclometalated iridium complex, $[(dfpbo)_2Ir]_2$ (**2**), has been prepared and fully characterized. The unsupported $Ir^{II}-Ir^{II}$ bond of complex **2** exhibits unique character, and this kind of compound can serve for the mechanistic investigations of catalytic and electron-transfer reactions and as the starting materials for the preparation of new kinds of compounds possessing special characteristics.

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Supporting Information Available: X-ray crystallographic data in CIF format for **1**and **2**; tables containing listing of crystal and data collection parameters, atomic coordinate and isotropic thermal parameters, bond distances, bond angles, photophysical spectra, details of experimental procedures, and characterization data for **1**and **2**; mass spectral data for **2**; a table of Cartesian coordinates, HOMO and LUMO orbital compositions and diagrams for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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