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<td>Author(s)</td>
<td>Mak, Kar Hang Garvin; Chan, Pek Ke; Fan, Wai Yip; Ganguly, Rakesh; Leong, Weng Kee</td>
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Photochemical Reaction of Cp*Ir(CO)$_2$ with C$_6$F$_5$X (X = CN, F): The Formation of Diiridium(II) Complexes

Kar Hang Garvin Mak,$^1$ Pek Ke Chan,$^1$ Wai Yip Fan,$^{1,*}$ Rakesh Ganguly,$^2$ Weng Kee Leong,$^{2,*}$

$^1$Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543
$^2$Division of Chemistry and Biological Chemistry, Nanyang Technological University, 21 Nanyang Link, Singapore 637371

Abstract

Visible light irradiation of Cp*Ir(CO)$_2$, 1, in pentafluorobenzonitrile resulted in the formation of two isomeric diiridium(II) complexes [Cp*Ir(μ-CO)(C$_6$F$_4$CN)]$_2$, 3, and [Cp*Ir(CO)(C$_6$F$_4$CN)]$_2$, 4, while the analogous reaction of 1 in hexafluorobenzene to give [Cp*Ir(μ-CO)(C$_6$F$_5$)]$_2$, 3a, required UV irradiation. Complex 4 isomerizes to 3 under visible light irradiation. A reaction pathway to 4 involving aromatic nucleophilic substitution has been proposed on the basis of experimental and computational data. The isomerisation of 4 to 3 is believed to proceed via a radical species resulting from homolytic fission of the Ir-Ir bond.

Introduction

Iridium complexes generally have the oxidation states +1 and +3; Ir(II) complexes are uncommon and those containing diiridium(II) are rarer still. In the reported examples, they are typically synthesized via oxidative addition of a substrate across the two iridium centers of a diiridium(I) species, and the resulting iridium(II) atoms are bridged by a ligand such as acetato, sulfido, sulfonylamido or pyrazolato.$^{1,2,3,4}$ To date, there are only five known examples of diiridium(II) complexes containing no bridging ligands across the Ir-Ir bond, three of which contain large chelating ligands that seemingly stabilize the iridium(II) centers,$^{5,6,7}$ the fourth contains a chelating ligand that is apparently too bulky to bridge the
metal centers,\textsuperscript{8} and the fifth which was synthesized via deprotonation of a bridged cationic
dimeric species (Figure 1).\textsuperscript{9}

![Chemical structures and reactions](image)

Figure 1. The only five known diiridium(II) complexes without a ligand bridging the Ir-Ir
bond.

Sometime ago, we reported that the reaction of \(\text{Cp}^*\text{Ir(CO)}_2\), \textit{1}, with
pentafluorobenzonitrile in the presence of water gave the metallocarboxylic acid species
\(\text{Cp}^*\text{Ir(CO)}(\text{COOH})(\text{C}_6\text{F}_5\text{CN})\), \textit{2},\textsuperscript{10} and a reaction pathway based on the nucleophilicity of \textit{1},\textsuperscript{11}
and the susceptibility of perfluorinated aromatic rings towards nucleophilic aromatic
substitution,\textsuperscript{12} was proposed (Scheme 1). Our earlier attempts at trapping the intermediate \textit{A}
were unsuccessful which we presumed may be due to its susceptibility to hydrolysis. Under
scrupulously dry conditions, however, we observed an unusual reaction leading to the
formation of diiridium(II) complexes, which we wish to report here.
Results and Discussion

The reaction of 1 in dry C₆F₅CN (scrupulously pre-dried or in the presence of molecular sieves) under irradiation with a tungsten lamp (or more slowly under ambient light) gave a dark red suspension. Spectroscopic analysis indicated the presence of one major product, the diiridium(II) species [Cp*Ir(µ-CO)(C₆F₄CN)]₂, 3, and a minor isomer 4; the yield of the latter could be increased by shortening the reaction time (Scheme 2). The two isomers decomposed on silica and could not be separated by fractional crystallization, but fractional crystallisation afforded diffraction-quality crystals of both. In the presence of even adventitious moisture, complex 2 was obtained quantitatively instead.
In contrast, while 1 reacted with C₆F₅CN and water under ambient conditions to yield the metallocarboxylic acid 2, there was no analogous reaction with C₆F₆. Complex 1 did react with C₆F₆ (10 mg/ml), however, under UV irradiation to give Cp*Ir(CO)(η²-C₆F₆), 5, and [Cp*Ir(CO)(C₆F₅)]₂, 3a, in a 5:1 ratio; a similar UV irradiation of 1 in C₆F₅CN gave an intractable mixture. Both 3a and 5 have also been characterised spectroscopically and by single crystal X-ray crystallographic studies (Scheme 3). These products were also unstable on silica gel. Irradiation of a more dilute solution (4.4 mg/ml) gave only 5, and prolonging the irradiation caused precipitation of a tan solid which contained a mixture of unidentified products. Heating the reaction mixture containing 1 and 5 at 80 °C also did not result in the formation of 3a. These results suggested that 5 was unlikely to be the precursor to 3a.

Scheme 3

The decarbonylation of 1 under UV photoexcitation to form Cp*Ir(CO), 1*,13 has been well studied in relation to C-H bond activation,13,14,15 and was thus a possible precursor to 3a and 5. However, that the UV-vis spectrum of 1 showed that a strong absorption band at 297 nm but absorbed poorly in the 350 – 500 nm (visible) region, suggested that 1* was unlikely to be responsible for the formation of 3 and 4 from C₆F₅CN. This difference in reactivity may be attributed to the increased susceptibility to nucleophilic attack of C₆F₅CN compared to C₆F₆; the latter could only react with the highly reactive 16e− species 1* (to form 5), or a UV-photoexcited 1 having increased nucleophilicity (to eventually form 3a).16
Conversion of 4 to 3

NMR analyses showed that with increasing irradiation time, the amount of unreacted 1 and 4 decreased relative to 3 until only the latter remained, suggesting that 4 converted irreversibly to 3 upon visible light irradiation. Synchronous opening of the two bridging carboxyls does not result in any change of the relative stereochemistry about the two iridium centres. The conversion of 4 to 3 must therefore involve cleavage of the Ir-Ir bond. Homolytic cleavage of the Ir-Ir bond to give the radical species [Cp*Ir(CO)(C₆F₄CN)]•, C, rather than a [Cp*Ir(CO)(C₆F₄CN)]⁺ [Cp*Ir(CO)(C₆F₄CN)]⁻ ion pair was supported by the observation that 3 reacted quantitatively in the presence of visible light with CHCl₃ to form Cp*Ir(CO)(C₆F₄CN)(Cl), 6. The reaction failed to proceed in the absence of visible light irradiation, and species such as Cp*Ir(CO)(C₆F₄CN)(CHCl₂), which may be expected from heterolytic cleavage of the Ir-Ir bond, was not observed.

The Gibbs free energies for 3 and 4, and for their respective stereoisomers 3’ and 4’, respectively, were computed (Figure 2). Compound 3 was computed to be 29.6 kJ/mol higher in energy than 4 in the gas phase, but the situation was reversed when solvated; it was 12.3 kJ/mol lower in energy in C₆F₅CN. This can be rationalized by the high polarity of 3 (19.6 D) and low polarity of 4 (0.0024 D), and accounted for why 3 was the major product in the reaction and why it was energetically favoured in a polar environment; irradiation of a solution of 1 in a less polar mixture of C₆F₅CN and C₆F₆ (1:1, v/v) for 24 h gave a 9:1 mixture of 3 and 4. The computed energies suggested that 4 first splits homolytically into two [Cp*Ir(CO)(C₆F₄CN)]• radicals, which would recombine, effectively with rotation of one of them about the Cp*-Ir axis, to generate 3’ but subsequent bridging of the Ir-Ir bond by the CO ligands to 3 was favoured.
Figure 2. Relative energies of 3, 4 and their hypothetical isomers 3′ and 4′.

Mechanistic investigations

The most likely reaction pathway by which 3 and 4 were formed was via reductive coupling of the acyl fluoride intermediate B with the elimination of oxalyl fluoride, either directly or via some other intermediate(s). However, our attempts to detect oxalyl fluoride or its hydrolysis product, oxalic acid, were unsuccessful. The reaction of 1 with C₆F₅CN (and molecular sieves) in the dark showed ~90% conversion after 24 h. The IR spectrum did not contain any absorption peak indicative of a -COF group, nor was there any resonance at around -53 ppm in the ¹⁹F NMR spectrum, which would have been indicative of a -COF group attached to an Ir(III) centre.¹⁷ These ruled out the presence of B but the spectroscopic data were assignable to a mixture of two unknown compounds D and E, in a 5:2 ratio.
Variable temperature $^{19}$F NMR experiments showed no evidence of exchange between their signals, suggesting that they were separate species.

Both D and E were converted quantitatively to 6 upon standing in chloroform over an extended period of time, and upon visible light irradiation in $C_6F_5CN$, completely converted to 3 after 24 h. Freshly prepared 3 in $C_6F_5CN$ showed no reaction upon stirring in complete darkness for 24 h. These observations indicated that D and E were precursors to 3. Although we have not been able to assign definitive identities to them, we propose that they may be zwitterionic Meisenheimer-type complexes of the formula Cp*Ir(CO)$_2$(CFC$_5$F$_4$CN), from which loss of a CO and light-activated dissociation of a fluorine atom would lead to C (Scheme 4). We have studied the formation of such a complex computationally and found that the Gibbs free energy for its formation from 1 and $C_6F_5CN$ was +83 kJ mol$^{-1}$.

![Scheme 4](image)

Crystallographic Discussion

The X-ray crystal structures of 3, 3a, 4 and 5 have all been determined; the ORTEP plots for 3 and 4 are shown in Figure 3. There are two crystallographically independent molecules found in the crystals of 3 and 3a; a common atomic numbering scheme and
selected bond parameters are given in Table 1. The molecular structures of 3 and 3a are essentially the same; the perfluoroaryl rings are oriented perpendicular to the plane defined by the bridging carbonyls, and are eclipsed and parallel to each other.

Table 1. Common atomic numbering scheme and selected bond parameters for 3 and 3a.

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<th>Complex</th>
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<th>3a (X = F)</th>
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<td>Bond length (Å)</td>
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<td>Molecule B</td>
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<td>φ (°)</td>
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φ = angle between the C(1)-Ir(1)-Ir(2)-C(2) and C(3)-Ir(1)-Ir(2)-C(4) planes.
Figure 3. ORTEP plots of one of the crystallographically independent molecules of 3 (top), and 4 (bottom). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.
The molecule of 4 sits on a crystallographic inversion centre and the C₈F₄CN rings are also parallel but *trans* with respect to each other across the Ir-Ir bond. Unlike in 3 and 3a, the CO ligands are in terminal positions. Interestingly, they are also oriented essentially perpendicular to the plane defined by the carboxyls and the iridium atoms ($\phi = 87.3^\circ$). This mutually *trans* arrangement of the ligands is unique; the four known diiridium(II) complexes containing no bridging ligands that have been crystallographically studied have their ligands arranged in a staggered conformation, and we believe that it can be traced to the HOMO-2 orbital, which was computed to have $\pi$-type symmetry, thus restricting rotation about the Ir-Ir bond (Figure 4). The Ir-Ir bond of 4 (2.8442(6) Å) is clearly longer than those in 3 (2.7655(5) and 2.7485(5) Å) and 3a (2.7576(8) and 2.7583(8) Å). It is also longer than those of the other known diiridium(II) complexes containing no bridging ligands; the next closest is that found in the complex containing tetracyanobisimidazole ligands (2.826(2) Å).

Figure 4. Computed molecular structure of 4 (left) and its HOMO-2 (right).
The ORTEP plot for 5 is shown in Figure 5, together with selected bond parameters. The molecule has a η²-coordinated C₆F₆ ligand, and the associated bond parameters are similar to those of three other group 9 complexes containing such a moiety which have been structurally characterised, viz., CpIr(C₂H₄)(η²-C₆F₆), 5a,¹⁸ CpRh(PMe₃)(η²-C₆F₆), 5b,¹⁹ and (η⁵: η¹-C₅H₅SiMe₂CH₂PPh₂)Rh(η²-C₆F₆), 5c.²⁰ An almost planar C₆F₄ unit is retained; the C(1)-C(2)-C(3)-C(3A) dihedral angle is only 1.4°, and F(2) and F(3) are bent out of the arene ring plane by 2.9° and 5.5°, respectively. The coordinated C=C bond (C(1)-C(1A) = 1.465(11) Å) is significantly lengthened compared to that of free C₆F₆ (1.394 Å) and the C-C bond lengths for the rest of the ring resemble those of a free diene, with a short (C(2)-C(3)), medium (C(3)-C(3A)), short (C(3A)-C(2A)) pattern, as observed for 5a-c. The fluorine atoms (F(1) and F(1A)) on the carbon atoms bonded to the Ir atom bend strongly away from the plane of the aromatic ring; the dihedral angle between the C₆ ring plane and the F(1)-C(1)-C(1A)-F(1A) plane is 47.0°, similar to that reported for 5a (47.9°) but larger than those for the Rh complexes (43.8° and 38.0°, for 5b and 5c, respectively), and is probably a consequence of the larger size of Ir compared to Rh. Thus the C₆F₆ ligand resembles a coordinated alkene in geometry.

Concluding remarks

We have reported here the unusual formation of two isomeric diiridium(II) complexes 3 and 4 from the visible light irradiation of Cp*Ir(CO)₂ in pentafluorobenzonitrile; the generation of an analogue from hexafluorobenzene occurred less readily. Complex 4 is one of the few examples of such a species that does not contain a bridging ligand across the Ir-Ir bond, and it appears to be the less stable isomer. The reaction pathway is believed to proceed via initial nucleophilic attack on the aromatic ring followed by generation of an organometallic radical species C. Although the precise role of irradiation in the reaction remains unclear, it has a decided role in the isomerisation of 4 to 3, which is believed to
proceed via C resulting from homolytic fission of the Ir-Ir bond. Complex 4, and probably 3 as well, is therefore a ready precursor for the organometallic radical [Cp*Ir(CO)(C₆F₄CN)]•, and we are in the process of further exploration of its chemistry.

Figure 5. ORTEP plot showing the molecular structure of 5, with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and angles [deg]: Ir(1)-C(4) = 1.863(9); Ir(1)-C(1) = 2.071(6); C(4)-O(4) = 1.124 (11); F(1)-C(1) = 1.390(6); F(2)-C(2) = 1.340(8); F(3)-C(3) = 1.351(7); C(1)-C(1A) = 1.465(11); C(1)-C(2) = 1.469(9); C(2)-C(3) = 1.317(10); C(3)-C(3') = 1.428(13); C(1)-C(2)-C(3)-C(3A) = 1.4(6).

Experimental Section

General Procedures. All reactions and manipulations were performed under argon using standard Schlenk techniques unless stated otherwise. Visible light irradiation was carried out
using a Phillips 60 W commercial light bulb. UV irradiation was carried out using a 450 W medium pressure mercury lamp (peak emission at 254 nm). NMR spectra were recorded on a Jeol ECA400 or ECA400SL NMR spectrometer as CDCl₃ solutions unless otherwise stated; ¹H chemical shifts reported were referenced against the residual proton signals of the solvent. ¹⁹F chemical shifts reported were referenced against external trifluoroacetic acid; designations of the F atoms are with respect to the iridium atom. Electrospray ionization (ESI) mass spectra were obtained on a Thermo Deca Max (LCMS) mass spectrometer with an ion-trap mass detector at 15 eV, 40 °C using direct injection of sample. Fast atom bombardment (FAB) mass spectra were obtained on a Finnigan MAT95XL-T spectrometer in a 3NBA matrix (FAB). All elemental analyses were performed by the microanalytical laboratory at NUS. Cp*Ir(CO)₂, ¹ and Cp*Ir(CO)(COOH)(C₆F₄CN), ² were prepared according to their published methods. All other reagents were from commercial sources and used without further purification.

**Computational studies.** The reaction energetics for the reactions were studied by DFT theory utilising the Becke's three parameter hybrid function, ²² and Lee-Yang-Parr's gradient-corrected correlation function (B3LYP). ²³ The LANL2DZ (Los Alamos Effective Core Potential Double-ζ) basis set was employed for all atoms. ²⁴ Excited state calculations were carried out with the TD method using the same basis set. ²⁵ For calculations involving solvated species, the Onsager model was employed. The dielectric constant for the solvent C₆F₅CN was estimated as 21, based on its polarity of 2.4 D compared to that of 2.9 D in acetone which has a dielectric constant of 20.7. Harmonic frequencies were calculated at the optimized geometries to characterize stationary points as equilibrium structures with all real frequencies, and to evaluate zero-point energy (ZPE) corrections. All calculations were performed using the Gaussian 09 suite of programs. ²⁶
Optimisation of the structure of the solvated Meisenheimer zwitterion was first carried out in the gas phase to give a structure in which the C₆F₄CN ring was oriented parallel to the Cp* ring. The cavity radius (a₀) of this was used to optimise the zwitterion in the solvated phase to the structure depicted in Scheme 4. The cavity volume for this was then calculated and the new value of a₀ employed to re-optimise the structure.

**Synthesis of [Cp*Ir(µ-CO)(C₆F₄CN)]₂, 3 and 4.** To a carius tube containing dried 4 Å molecular sieves (7 pieces), 1 (25 mg, 0.0653 mmol) and C₆F₅CN (0.25 ml, 0.383 g, 1.98 mmol) were added. The yellow solution was irradiated with a tungsten lamp and stirred slowly at room temperature for 24 h. A red suspension was formed. Volatiles were removed under reduced pressure and the remaining red residue was re-suspended in ether (10 ml). After collection of a reddish-orange powder via filtration, it was washed with ether (5 ml) and dried under reduced pressure to yield spectroscopically pure 3.

When the reaction was only carried out for 4 h, the terminal CO isomer [Cp*Ir(CO)(C₆F₄CN)]₂, 4, was obtained together with 3 as a side product. X-ray diffraction quality crystals of 4 were grown from a dichloromethane/hexane solution of a mixture of 3 and 4 at room temperature.

3: Yield (spectroscopic): ~90% to quant. ν_{CO} (CH₂Cl₂): 1770 (vs); ¹H NMR: δ 1.83 (s, 30H) ppm; ¹⁹F NMR: δ -36.2 (m, 2F, F_{ortho}), -60.9 (m, 2F, F_{meta}) ppm; FAB-MS⁺ (m/z): 1058 [M], 1030 [M-CO], 530 [M/2], 502 [M/2-CO]; Elemental analysis: Found: C, 40.68; H 2.79; N, 2.74; calcd: C, 40.83; H, 2.86; N, 2.65.

4: Yield (spectroscopic): max ~50%. ν_{CO} (CH₂Cl₂): 2051 (vs); ¹H NMR: δ 1.49 (s, 30H) ppm; ¹⁹F NMR: δ -34.5 (m, 2F, F_{ortho}), -59.9 (m, 2F, F_{meta}) ppm.

In an attempt to detect formation of oxalic acid via IR spectroscopy, three cycles of freeze-pump-thaw was performed on the crude reaction mixture at the end of the reaction. The carius tube was then exposed to air, and left to thaw. After the mixture thawed, volatiles were
removed under reduced pressure, and the residue was extracted with ether. The ether extract was dried and an IR spectrum was collected using the KBr pellet method. No oxalic acid was observed.

A similar procedure was employed to monitor the ratio of 3 to 4 under varying irradiation times. After reacting for the designated number of hours, volatiles were removed under reduced pressure, and $^1$H and $^{19}$F NMR spectra were recorded.

**Reaction of 1 with C$_6$F$_5$CN in the dark** To a carius tube containing dried 4 Å molecular sieves (7 pieces) was added 1 (10 mg, 0.026 mmol) and C$_6$F$_5$CN (0.25 ml, 0.383 g, 1.98 mmol). The reaction vessel containing the yellow solution was wrapped in aluminium foil, placed inside a wooden box and stirred slowly at room temperature for 24 h. An orange solution was formed. Volatiles were removed under reduced pressure, and a $^1$H NMR spectrum of the remaining oil showed that D and E were obtained in a 5:2 ratio.

- **D**: $\nu_{CO}$ (hexane): 2019 cm$^{-1}$; $^1$H NMR: $\delta$ 1.73 (s) ppm; $^{19}$F NMR: $\delta$ -29.3 (m, 1F), -40.6 (m, 1F), -60.3 (m, 1F), -60.8 (m, 1F) ppm.
- **E**: $\nu_{CO}$ (hexane): 2002; $^1$H NMR: $\delta$ 1.76 (s) ppm; $^{19}$F NMR: $\delta$ -30.5 (m, 1F), -39.3 (m, 1F), -64.1 (m, 1F) ppm.

**Photochemical reaction of 1 and C$_6$F$_6$.** To a quartz carius tube containing 1 (20 mg, 0.0522 mmol) was added C$_6$F$_6$ (2 ml). The mixture was degassed by three cycles of freeze-pump-thaw and then irradiated for 20 h. An orange-brown solution was formed. Volatiles were removed under reduced pressure and the remaining residue was extracted with cyclohexane (20 ml). The cyclohexane extract was dried in vacuo to give a brown-yellow oil (26.9 mg). The $^1$H NMR spectrum of the oil showed the presence of 5 and 3a (5:1 ratio by integration) and small amounts of unidentified products. Recrystallization from toluene and cyclopentane gave a larger proportion of 5 in the supernatant, but complete separation was not obtained.
Prolonged irradiation led to slow precipitation of a tan solid containing a mixture of unidentified products.

X-ray diffraction-quality crystals of 5 and 3a were grown from a toluene/hexane solution of the mixture at 5 °C.

3a: Yield (spectroscopic): ~15%. $\nu_{\text{CO}}$ (cyclohexane): 1778 (vs); $^1$H NMR: $\delta$ 1.82 (s, 30H) ppm; $^{19}$F NMR: $\delta$ -39.0 (m, 2F, $F_{\text{ortho}}$), -85.2 (t, 1F, $F_{\text{para}}$), -88.5 (m, 2F, $F_{\text{meta}}$) ppm; FAB-MS+ (m/z): 523 [M/2];

5: Yield (spectroscopic): ~80%; yield (isolated): 28%. $\nu_{\text{CO}}$ (cyclohexane): 2027 (vs); $^1$H NMR: $\delta$ 1.89 (s, 15H) ppm; $^{19}$F NMR: $\delta$ -71.4 (m, 2F, $F^d$ and $F^{d A}$), -77.9 (m, 2F, $F^d$ and $F^{d A}$), -97.9 (m, 2F, $F^d$ and $F^{d A}$) ppm; FAB-MS+ (m/z): 523 [M-F], 495 [M-F-CO], 356 [M-C$_6$F$_6$];

Elemental analysis: Found: C, 39.90; H, 3.13. Calcd for C$_{17}$H$_{15}$F$_6$IrO. $\frac{1}{4}$C$_6$H$_{12}$: C, 39.50; H, 3.23.

Reaction of 3 with chloroform. To a carius tube containing 3 (10 mg, 0.0095 mmol) was added CHCl$_3$ (1 ml). The red solution was irradiated for 12 h under a tungsten lamp, with stirring. A yellow solution was formed within 4 h. Volatiles were removed under reduced pressure and a $^1$H NMR spectrum showed quantitative conversion to Cp*Ir(CO)(C$_6$F$_4$CN)(Cl), 6. The same observations can be made if an NMR sample of 3 was left in CDCl$_3$ for a few hours. The product could be purified by TLC with dichloromethane:hexane (2:1, v/v) as the eluent. When the reaction was performed in the dark, no reaction occurred.

6: $\nu_{\text{CO}}$ (CH$_2$Cl$_2$): 2053 (vs); $^1$H NMR: $\delta$ 1.94 (s, 15H) ppm; $^{19}$F NMR: $\delta$ -35.1 (s, br, 2F, $F_{\text{ortho}}$), -58.8 (m, 2F, $F_{\text{meta}}$) ppm; FAB-MS+ (m/z): 538 [M-CO+H], 530 [M-Cl]; HR-FAB: calcd for C$_{18}$H$_{15}$F$_4$NO$^{193}$Ir ([M-Cl]): 530.0714, found: 530.0697.

Computational studies. The reaction energetics for the reactions were studied by DFT theory utilising the Becke's three parameter hybrid function, and Lee-Yang-Parr's gradient-
corrected correlation function (B3LYP). The LANL2DZ (Los Alamos Effective Core Potential Double-ζ) basis set was employed for all atoms. For calculations involving solvated species, the Onsager model was employed. The dielectric constant (ε) of C₆F₅CN appeared to be unknown, but its polarity was reported to be ~2.4 D. As acetone, a polar non-protic solvent, has a polarity of ~2.9 D and a dielectric constant of ~20.7, dielectric constant of C₆F₅CN was assumed to be similar (ε = 21). Harmonic frequencies were calculated at the optimized geometries to characterize stationary points as equilibrium structures with all real frequencies, and to evaluate zero-point energy (ZPE) correction. All calculations were performed using the Gaussian 09 suite of programs.

Crystal structure determinations. Crystals were mounted on quartz fibres. X-ray data were collected on a Bruker AXS APEX system, using Mo Kα radiation, with the SMART suite of programs. Data were processed and corrected for Lorentz and polarization effects with SAINT, and for absorption effects with SADABS. Structural solution and refinement were carried out with the SHELXTL suite of programs. The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. Organic hydrogen atoms were placed in calculated positions, and refined with a riding model. All non-hydrogen atoms were given anisotropic displacement parameters in the final model. The crystal of 3a contained a disordered hexane solvate. This was modelled with two alternative sites of equal occupancies (0.25), with all the carbon atoms assigned a common isotropic thermal parameter, and appropriate bond restraints applied. The molecule of 5 was located across a crystallographic mirror plane and exhibited disorder of the Cp* ring about this plane.

Acknowledgment. This work was supported by an A*STAR grant (Research Grant No. 012 101 0035). K.H.G.M. would like to thank the National University of Singapore for Research Scholarships.
Supporting Information Available: Crystallographic data in CIF format, crystal and refinement data for 3, 3a, 4 and 5, and computed structures. Ordering information is given on any current masthead page.

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Visible light irradiation of Cp*Ir(CO)$_2$ in pentafluorobenzonitrile resulted in the formation of two isomeric diiridium(II) complexes [Cp*Ir(µ-CO)(C$_6$F$_4$CN)$_2$] and [Cp*Ir(CO)(C$_6$F$_4$CN)$_2$]; the latter isomerized to the latter under visible light irradiation and is believed to proceed via a radical species resulting from homolytic fission of the Ir-Ir bond. A similar reaction of 1 in hexafluorobenzene to give [Cp*Ir(µ-CO)(C$_6$F$_5$)$_2$] required UV irradiation.