

# Reactions of Cp\*Ir(CO)<sub>2</sub> with Pentafluorobenzonitrile: Half-Sandwich

## Iridium Complexes Cp\*Ir(CO)(p-C<sub>6</sub>F<sub>4</sub>CN)(X)

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### Abstract

The reaction of Cp\*Ir(CO)<sub>2</sub> (**1**) with pentafluorobenzonitrile in the presence of a base afforded the diaryl complex Cp\*Ir(CO)(p-C<sub>6</sub>F<sub>4</sub>CN)<sub>2</sub> (**4**). The reaction proceeds via the metallacarboxylic acid Cp\*Ir(CO)(p-C<sub>6</sub>F<sub>4</sub>CN)(COOH) (**2**). The latter can be decarboxylated in the presence of a base to the hydrido species Cp\*Ir(CO)(p-C<sub>6</sub>F<sub>4</sub>CN)(H) (**5**), which can then undergo hydride-chloride exchange to Cp\*Ir(CO)(p-C<sub>6</sub>F<sub>4</sub>CN)(Cl) (**6a**). In the presence of air and water, the reaction of **1** with pentafluorobenzonitrile afforded a complex formulated as Cp\*Ir(CO)(p-C<sub>6</sub>F<sub>4</sub>CN){C(OH)(NH<sub>2</sub>)C<sub>6</sub>F<sub>5</sub>} (**7a**); this is also available from the reaction of **2** with pentafluorobenzamide in the presence of aqueous NaOH.

**Keywords:** Iridium, pentafluorobenzonitrile, restricted rotation

### Introduction

The iridium carbonyl complex Cp\*Ir(CO)<sub>2</sub> (**1**) holds a special place in the development of organometallic chemistry as it was among the earliest example of an organometallic complex that could activate, under photochemical conditions, the C-H bond in alkanes.<sup>1</sup> In our own studies, we had recently reported that it reacted with pentafluorobenzonitrile, in the presence of water, to afford the metallocarboxylic acid species Cp\*Ir(CO)(p-C<sub>6</sub>F<sub>4</sub>CN)(COOH) (**2**).<sup>2</sup> In subsequent attempts at elucidating the reaction pathway for this, we found that visible light irradiation under anhydrous conditions led to the formation of two isomeric diiridium(II) complexes [Cp\*Ir(μ-CO)(p-C<sub>6</sub>F<sub>4</sub>CN)]<sub>2</sub> (**3**) and

[Cp\*Ir(CO)(*p*-C<sub>6</sub>F<sub>4</sub>CN)]<sub>2</sub> (**3'**).<sup>3</sup> In the presence of other additives, however, different Cp\*Ir(III)-containing products were obtained. We wish to report here our findings for these, as well as the related reactivity of **2** and **3**.

## Results and Discussion

Stirring a solution of **1** in C<sub>6</sub>F<sub>5</sub>CN in the presence of basic alumina or NaOH pellets gave quantitative conversion to Cp\*Ir(CO)(*p*-C<sub>6</sub>F<sub>4</sub>CN)<sub>2</sub> (**4**), which has been completely characterised, including by a single crystal X-ray crystallographic study; the ORTEP plot, together with selected bond parameters, are given in Figure 1. The closest known analogue is Cp\*Ir(CO)(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, for which the crystal structure has not yet been reported.<sup>4</sup>

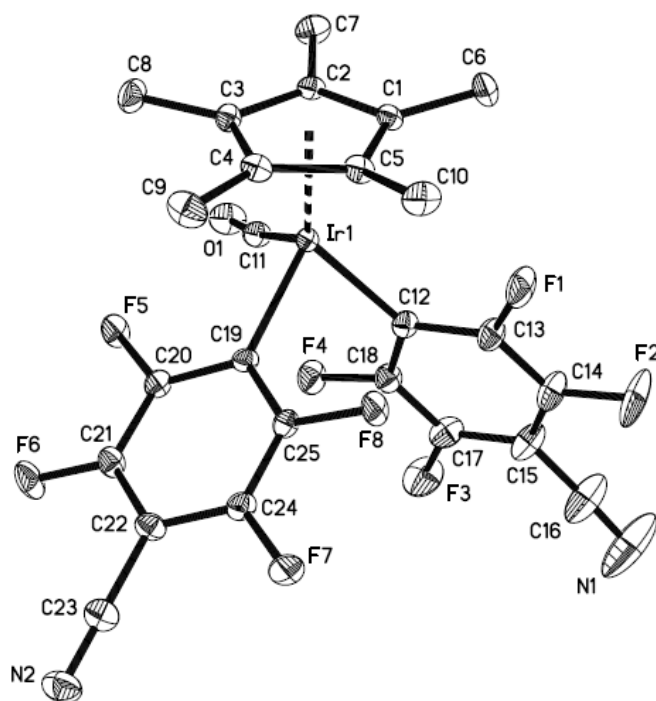
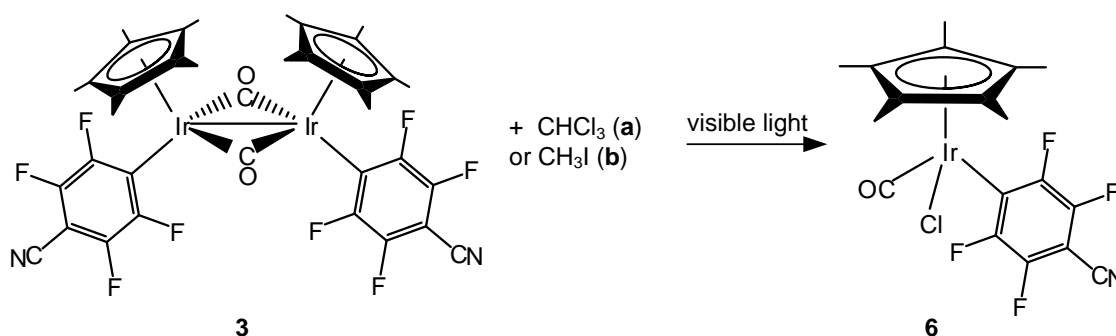


Figure 1. ORTEP plot of **4** showing the atomic numbering scheme, with thermal ellipsoids drawn at 50% probability level and hydrogen atoms omitted for clarity. Selected bond distances [Å] and angles [deg]: Ir(1)-C(11), 1.866(4); Ir(1)-C(19), 2.068(3); Ir(1)-C(12), 2.095(3); C(11)-Ir(1)-C(19), 97.24(14); C(11)-Ir(1)-C(12), 90.42(15); C(19)-Ir(1)-C(12), 84.00(12).

The possible precursors to **4** included **2** and **3**, but the latter was ruled out on the basis that the formation of **4** did not require visible light irradiation (but see later). On the other hand, the reaction of **2** with  $C_6F_5CN$  in the presence of aqueous NaOH afforded **4** as the only iridium-containing product. Decarboxylation of **2** occurred in the presence of aqueous NaOH to afford the hydrido species  $Cp^*Ir(CO)(p-C_6F_4CN)(H)$  (**5**) quantitatively. Although leaving a solution of **5** in chloroform to stand eventually gave complete conversion to  $Cp^*Ir(CO)(p-C_6F_4CN)(Cl)$  (**6a**), it did not react with  $C_6F_5CN$ . Complex **6a** could also be obtained quantitatively from the reaction of **3** in the presence of visible light with  $CHCl_3$ ; reaction with  $CH_3I$  afforded the iodo analogue  $Cp^*Ir(CO)(p-C_6F_4CN)(I)$  (**6b**) (Scheme 1). The structures of both **6a** and **6b** have been confirmed by single crystal X-ray crystallographic studies; the ORTEP plot for **6b**, together with selected bond parameters, is given in Figure 2.



Scheme 1

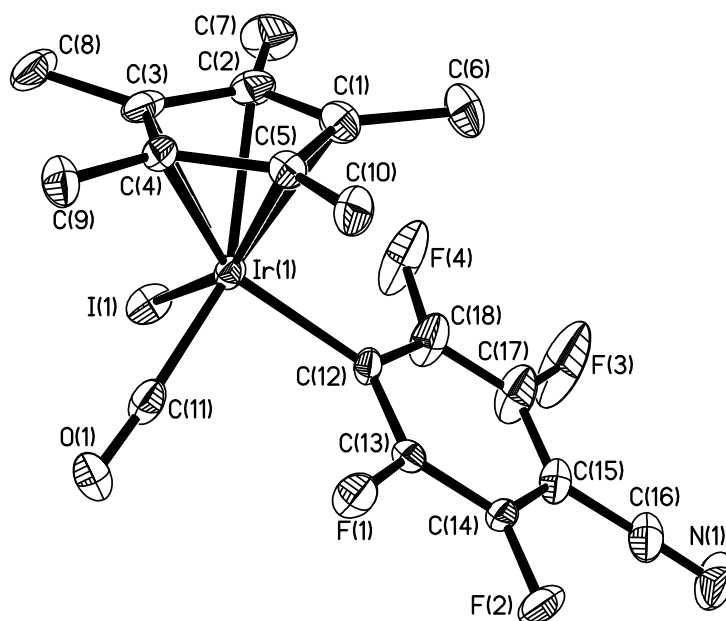
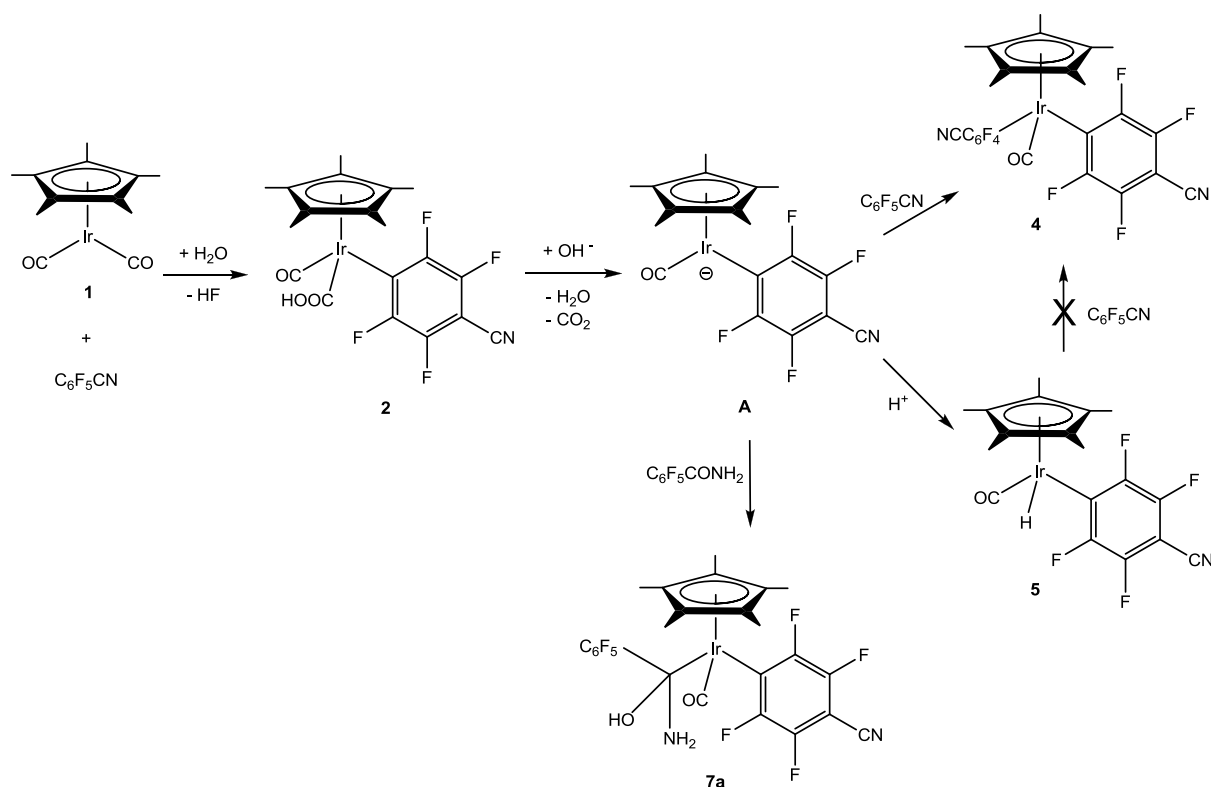


Figure 2. ORTEP plot of **6b** showing the atomic numbering scheme, with thermal ellipsoids drawn at 50% probability level and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir(1)-I(1) = 2.6967(5); Ir(1)-C(11) = 1.891(7); Ir(1)-C(12) = 2.084(6); O(1)-C(11) = 1.108(8); C(16)-N(1) = 1.122(9); C(15)-C(16) = 1.441(9); C(12)-Ir(1)-I(1) = 91.58(16); C(11)-Ir(1)-C(12) = 91.9(2).

The complexes **2**, **5** and **6a** also failed to give **3** even in a reducing environment (zinc powder), indicating that these may also be excluded as possible precursors to **3**. It is therefore plausible that the formation of **4** proceeded via an anionic intermediate  $[\text{Cp}^*\text{Ir}(\text{CO})(p\text{-C}_6\text{F}_4\text{CN})]^-$  (**A**) (Scheme 2). Intermediate **A** is analogous to the reported anionic complex  $[\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{H})]\text{Li}$ , which has been reported to be active in C-F activation.<sup>5</sup>



Scheme 2

We believe that generation of the proposed anionic intermediate **A** also accounted for the observation that the reaction of **1** with  $\text{C}_6\text{F}_5\text{CN}$  in the presence of air yielded a mixture containing a species which has been formulated as  $\text{Cp}^*\text{Ir}(\text{CO})(p\text{-C}_6\text{F}_4\text{CN})[\text{C}(\text{OH})(\text{NH}_2)(\text{C}_6\text{F}_5)]$  (**7a**) and  $\text{C}_6\text{F}_5\text{CONH}_2$ , in ~1:1 molar ratio. The identity of the amide was confirmed by a single crystal x-ray crystallographic study,<sup>6</sup> and was likely the result of base catalysed hydrolysis of  $\text{C}_6\text{F}_5\text{CN}$ ; stirring a mixture of  $\text{C}_6\text{F}_5\text{CN}$  with one equivalent of aqueous  $\text{NaOH}$  gave  $\text{C}_6\text{F}_5\text{CONH}_2$  in ~48% yield, but no reaction occurred in the absence of a base.

The species **7a** decomposed on silica gel and on standing, and its formulation was proposed on the basis of its spectroscopic evidence. It was also obtained as the major product when freshly prepared **2** was reacted with one equivalent of  $\text{C}_6\text{F}_5\text{CONH}_2$  in the presence of aqueous  $\text{NaOH}$ . As hemiaminal groups typically undergo dehydration to an imine, this may likely be the reason for the precipitation of unidentified solids upon leaving a solution of **7a**

to stand. The involvement of **3** or **5** as intermediates can also be ruled out as we have found that **5** did not react with  $C_6F_5CONH_2$ , and that the formation of **7a** did not depend on visible light irradiation. It was thus likely that under the reaction conditions, the intermediate **A** that was formed also acted as a base to generate  $C_6F_5CONH_2$  from  $C_6F_5CN$ . Consistent with this was the observation that **2** reacted with  $PhCONH_2$  and  $^tBuCONH_2$  in the presence of aqueous NaOH to afford the analogues  $Cp^*Ir(CO)(p-C_6F_4CN)[(C(OH)(NH_2)(R))]$  (R = Ph (**b**) and  $^tBu$  (**c**)).

#### *VT-NMR studies*

The room temperature  $^{19}F\{^1H\}$  NMR spectrum of **6a** showed one small broad signal for the F atoms *ortho* to the iridium atom and a sharp multiplet for the *meta* F's, while that of **6b** showed two broad signals for the *ortho* F atoms and one sharp multiplet for the *meta* F atoms; these were suggestive of restricted rotation of the  $C_6F_4CN$  ring. The  $^{19}F\{^1H\}$  NMR spectra of **6a** over the temperature 20 °C to -60 °C are shown in Figure 3, and shows that on cooling to 0 °C, the  $F_{ortho}$  signal at -35.1 ppm collapsed into the baseline and gradually re-emerged as two sharp signals at -32.7 and -37.8 ppm as the temperature was decreased to below about -20 °C. Similarly, the  $F_{meta}$  signal was also split into two sharp signals, at -57.7 and -58.8 ppm, at temperatures below about -30 °C. Since the room temperature spectrum of **6b** clearly showed two signals for the *ortho* F's, it indicated that the restricted rotation increased with the size of the halogen ligand on the iridium center. Restricted rotation of perfluorinated rings have been studied with  $C_6F_5S$ ,<sup>7</sup>  $(C_6F_5)_3P$ ,<sup>8</sup> and the  $C_6F_5$  ligands.<sup>9</sup>

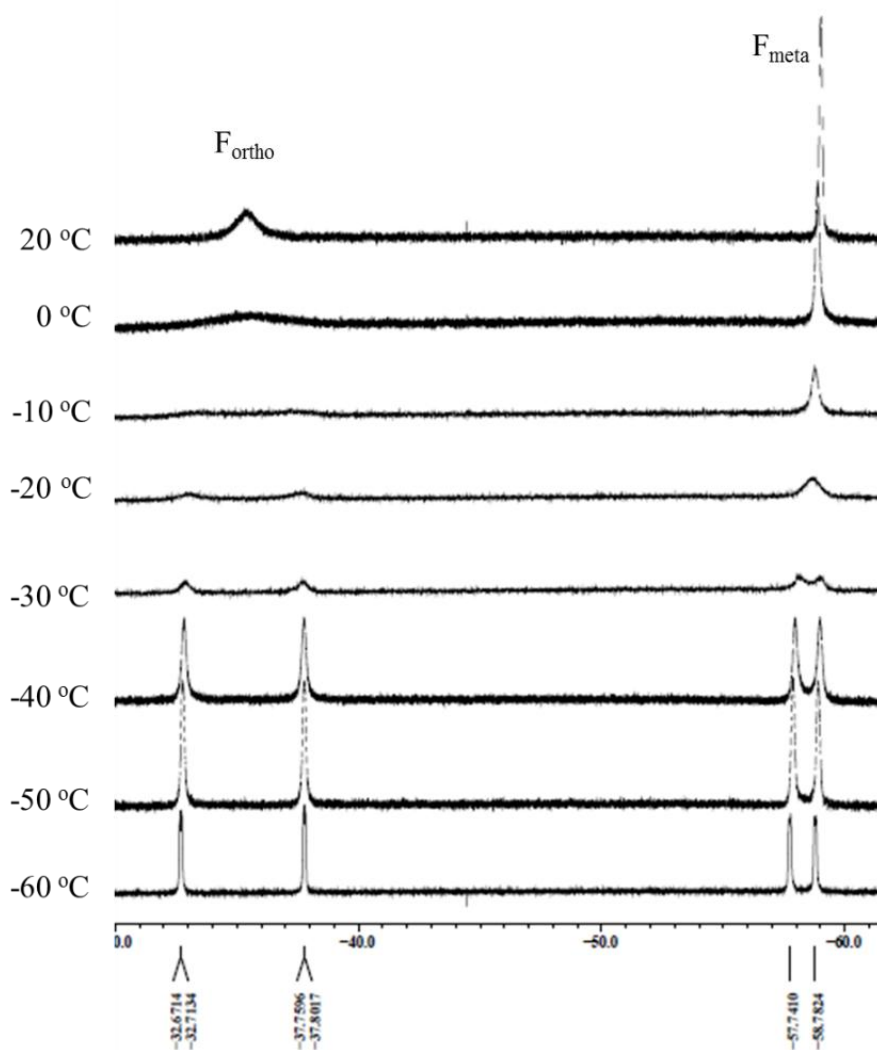


Figure 3. Variable temperature  $^{19}\text{F}$  NMR spectra of **6a**.

Although it has not proven possible to separate the complexes **7** cleanly from the amide and small amounts of **4**, their  $^{19}\text{F}\{^1\text{H}\}$  NMR spectra also clearly indicated restricted rotation of the  $\text{C}_6\text{F}_4\text{CN}$  ring. At ambient temperature, only the *meta* F resonances were visible but at  $-60\text{ }^\circ\text{C}$ , for example, that for **7a** showed a total of seven resonances in a 1: 1: 1: 1: 2: 1: 2 integration ratio. On the basis of the observed coalescence temperatures ( $T_c$ ) and the differences in frequency of the  $\text{F}_{\text{ortho}}$  resonances in the absence of exchange ( $\delta\nu$ ),<sup>10</sup> the free energies of activation ( $\Delta G^\ddagger$ ) for the restricted rotation of the perfluoroarene ring in **6a**, **7a** and **7b** have been estimated (Table 1). The values are consistent with the increased steric bulk of X in the complexes  $\text{Cp}^*\text{Ir}(\text{CO})(p\text{-C}_6\text{F}_4\text{CN})(\text{X})$ .

Table 1. Free energy of activation for the  $-C_6F_4CN$  ring restricted rotation.

Compound	$T_c$ of $F_{ortho}$ signals (K)	$\delta\nu$ at 213 K (Hz)	$\Delta G^\ddagger$ at $T_c$ (kJ mol <sup>-1</sup> )
$Cp^*Ir(CO)(p-C_6F_4CN)(Cl)$ , <b>6a</b>	273	1915	+ 48
$Cp^*Ir(CO)(p-C_6F_4CN)[C(OH)(NH_2)(C_6F_5)]$ , <b>7a</b>	293	5451	+ 49
$Cp^*Ir(CO)(p-C_6F_4CN)[C(OH)(NH_2)(Ph)]$ , <b>7b</b>	253	5964	+ 42

## Conclusion

We have found that the reaction of  $Cp^*Ir(CO)_2$  with pentafluorobenzonitrile followed a complex network of pathways that depended on the conditions used. In the presence of aqueous NaOH, the diaryl complex  $Cp^*Ir(CO)(p-C_6F_4CN)_2$  was formed. In the absence of the base, the metallacarboxylic acid  $Cp^*Ir(CO)(p-C_6F_4CN)(COOH)$  was obtained, the decarboxylation of which gave the hydrido species  $Cp^*Ir(CO)(p-C_6F_4CN)(H)$ , which may undergo hydride-chloride exchange with halogenated solvents to form the halide species  $Cp^*Ir(CO)(p-C_6F_4CN)(X)$ . In the presence of air and water, the reaction afforded a complex formulated as  $Cp^*Ir(CO)(p-C_6F_4CN)[C(OH)(NH_2)C_6F_5]$  (**7a**), presumably via hydrolysis of some of the nitrile to the amide. These reactions presumably proceeded via the formation of a carbonylate intermediate  $[Cp^*Ir(CO)(p-C_6F_4CN)]^-$ .

## 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. NMR spectra were recorded on a Jeol ECA400 or ECA400SL NMR spectrometer as  $\text{CDCl}_3$  solutions;  $^1\text{H}$  chemical shifts reported were referenced against the residual proton signals of the solvent.  $^{19}\text{F}$  chemical shifts reported were referenced against external trifluoroacetic acid; designations of the F atoms are with respect to the iridium atom. Solution IR spectra were obtained with  $\text{CH}_2\text{Cl}_2$  as solvent on a Bruker ALPHA FTIR spectrometer at a resolution of  $2\text{ cm}^{-1}$  using a solution IR cell with NaCl windows and a pathlength of 0.1 mm. Electrospray ionization (ESI) mass spectra were obtained on a Thermo Deca Max (LCMS) mass spectrometer with an ion-trap mass detector at 15 eV,  $40\text{ }^\circ\text{C}$  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. The complexes **1**,<sup>11</sup> **2**,<sup>2</sup> and **3**,<sup>3</sup> were prepared according to the published methods. All other reagents were from commercial sources and used without further purification.

**Reaction of 3 with alkyl halides.** To a carius tube containing **3** (10 mg, 0.0095 mmol) was added  $\text{CHCl}_3$  (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  $^1\text{H}$  NMR spectrum showed quantitative conversion to  $\text{Cp}^*\text{Ir}(\text{CO})(p\text{-C}_6\text{F}_4\text{CN})(\text{Cl})$  (**6a**). The same observations can be made if an NMR sample of **3** was left in  $\text{CDCl}_3$  for a few hours. Replacing  $\text{CHCl}_3$  with  $\text{CH}_3\text{I}$  (1 ml) gave  $\text{Cp}^*\text{Ir}(\text{CO})(p\text{-C}_6\text{F}_4\text{CN})(\text{I})$  (**6b**). Both products 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.

Data for **6a**: Yield = quantitative (spectroscopic); 10 mg, 0.018 mmol (94%, isolated).  $\nu_{\text{CO}}$ : 2053 (vs)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$  1.94 (s, 15H,  $\text{CH}_3$ ). FAB-MS: +538 [M-CO+H], +530 [M-Cl]<sup>+</sup>. HR-FAB-MS: calcd for  $\text{C}_{18}\text{H}_{15}\text{F}_4\text{NO}^{193}\text{Ir}$ : [M-Cl]<sup>+</sup>: 530.0714, found: 530.0697.

Data for **6b**: Yield = quantitative (spectroscopic); 11 mg, 0.017 mmol (89%, isolated).  $\nu_{\text{CO}}$ : 2046 (vs)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$  2.07 (s, 15H,  $\text{CH}_3$ ). ESI-MS: +689 [M+MeOH]<sup>+</sup>, +530 [M-I]<sup>+</sup>. Anal. Calcd for  $\text{C}_{18}\text{H}_{15}\text{F}_4\text{IrNO}$ : C, 32.93; H, 2.30; N, 2.13. Found: C, 32.71; H 2.29; N, 2.00.

**Synthesis of  $\text{Cp}^*\text{Ir}(\text{CO})(p\text{-C}_6\text{F}_4\text{CN})_2$ , **4**** To a carius tube containing **2**, freshly prepared from **1** (10 mg, 0.0261 mmol),  $\text{C}_6\text{F}_5\text{CN}$  (0.25 ml, 0.383 g, 1.98 mmol), sodium hydroxide pellets (200 mg, 5.00 mmol), ether (1 ml) and deionized water (0.25 ml) were added. Effervescence was observed immediately. The resulting orange mixture was stirred for 24 h, after which a cream colour paste was obtained. The paste was shaken with dichloromethane (5 ml) and deionized water (5 ml), after which the organic layer was filtered through celite to obtain a pale yellow solution. Volatiles were removed from the filtrate under reduced pressure to give pale yellow solids. A  $^1\text{H}$  NMR spectrum showed only the presence of **4**. A  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum showed that a small amount of  $\text{C}_6\text{F}_5\text{CONH}_2$  was obtained as a side product. Yield = quantitative (spectroscopic); 15 mg, 0.021 mmol (82%, isolated).  $\nu_{\text{CO}}$ : 2045 (vs)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$  2.02 (s, 15H,  $\text{CH}_3$ ).  $^{19}\text{F}$  NMR:  $\delta$  -33.6 (m, 2F,  $F_{ortho}$ ), -59.3 (m, 2F,  $F_{meta}$ ). ESI-MS: +705 [M+H]<sup>+</sup>. Anal. Calcd for  $\text{C}_{25}\text{H}_{15}\text{F}_8\text{IrN}_2\text{O}$ : C, 42.68; H, 2.15; N, 3.98. Found: C, 42.46; H 2.09; N, 3.85.

**Synthesis of  $\text{Cp}^*\text{Ir}(\text{CO})(p\text{-C}_6\text{F}_5\text{CN})(\text{H})$ , **5**** To a carius tube containing **2**, freshly prepared from **1** (10 mg, 0.0261 mmol), sodium hydroxide pellets (200 mg, 5.00 mmol), ether (1 ml) and deionized water (0.25 ml) were added. Effervescence was observed immediately. The resulting orange mixture was stirred for 1 h with no colour change. The mixture was extracted with ether (2 x 2 ml), after which the organic layer was filtered through celite to obtain an orange solution. Volatiles were removed from the filtrate under reduced pressure to

give an orange residue. A  $^1\text{H}$  NMR spectrum showed the presence of **5** and **6a**. After the solution was left to stand in  $\text{CDCl}_3$  for a longer period of time, only **6a** could be observed in the spectrum. Yield (spectroscopic) = ~90%.  $\nu_{\text{CO}}$ : 2014 (vs)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$  2.08 (s, 15H,  $\text{CH}_3$ ), -14.72 (s, 1H, Ir-H).  $^{19}\text{F}$  NMR:  $\delta$  -32.3 (m, 2F,  $F_{\text{ortho}}$ ), -60.2 (m, 2F,  $F_{\text{meta}}$ )

**Synthesis of  $\text{Cp}^*\text{Ir}(\text{CO})(\text{C}_6\text{F}_4\text{CN})[\text{C}(\text{OH})(\text{NH}_2)\text{C}_6\text{F}_5]$ , **7a**** To a carius tube containing **2**, freshly prepared from **1** (10 mg, 0.0261 mmol), sodium hydroxide pellets (200 mg, 5.00 mmol), ether (1 ml),  $\text{C}_6\text{F}_5\text{CONH}_2$  (6 mg, 0.0284 mmol) and deionized water (0.25 ml) were added. Effervescence was observed immediately. The resulting orange mixture was stirred for 24 h, after which the organic layer was orange in colour. Volatiles were removed under reduced pressure to obtain an orange oil. The  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra showed the presence of **4** and **7a**, in a 1:9 ratio. The presence of **4** was attributed to incomplete removal of  $\text{C}_6\text{F}_5\text{CN}$  after the synthesis of **2**. Leaving a solution of **7a** in  $\text{CDCl}_3$  to stand resulted in precipitation and apparent decomposition to unidentified compounds. Repeating the procedure with  $\text{PhCONH}_2$  (3 mg, 0.0248 mmol) or  $^t\text{BuCONH}_2$  (3 mg, 0.0297 mmol) in place of  $\text{C}_6\text{F}_5\text{CONH}_2$  yielded **7b** or **7c**, respectively, as the major product.

Data for **7a**: Yield (spectroscopic) = ~90%.  $\nu_{\text{CO}}$ : 2054 (vs);  $\nu_{\text{NH}}$ : 3402 (w), 3686 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$  4.56 (s, br, 1H, OH), 1.96 (s, 15H,  $\text{CH}_3$ ).  $^{19}\text{F}$  NMR:  $\delta$  -58.5 (m, 1.5F,  $F_{\text{meta}}$ ,  $\text{C}_6\text{F}_4\text{CN}$ ), -66.4 (m, 2F,  $F_{\text{ortho}}$ ,  $\text{C}_6\text{F}_5$ ), -78.8 (t, 1F,  $F_{\text{para}}$ ,  $\text{C}_6\text{F}_5$ ), -85.6 (m, 2F,  $F_{\text{meta}}$ ,  $\text{C}_6\text{F}_5$ ). ESI-MS: ESI: +741  $[\text{M}-\text{H}]^+$ .

Data for **7b**: Yield (spectroscopic) = ~90%.  $^1\text{H}$  NMR:  $\delta$  7.68 (m, 3H,  $\text{C}_6\text{H}_5$ ), 7.35 (m, 2H,  $\text{C}_6\text{H}_5$ ), 1.94 (s, 15H,  $\text{CH}_3$ ).  $^{19}\text{F}$  NMR: 20 °C  $\delta$  -58.7 (m, 2F,  $F_{\text{meta}}$ ); -60 °C: -32.1 (s, br, 1F,  $F_{\text{ortho}}$ ), -48.0 (s, br, 1F,  $F_{\text{ortho}}$ ), -58.1 (s, br, 2F,  $F_{\text{meta}}$ ). ESI-MS: ESI: +651  $[\text{M}-\text{H}]^+$

Data for **7c**: Yield (spectroscopic) = ~60%.  $^1\text{H}$  NMR:  $\delta$  1.88 (s, 15H,  $\text{CH}_3$ ), 1.13 (s, 9H,  $^t\text{Bu}$ ).  $^{19}\text{F}$  NMR: -59.2 (m, 2F,  $F_{\text{meta}}$ ). ESI-MS: ESI: +631  $[\text{M}-\text{H}]^+$

**Crystal structure determinations.** Crystals were mounted on quartz fibres. X-ray data were collected at 103(2) K on a Bruker AXS APEX system, using Mo K $\alpha$  radiation, with the SMART suite of programs.<sup>12</sup> Data were processed and corrected for Lorentz and polarization effects with SAINT,<sup>13</sup> and for absorption effects with SADABS.<sup>14</sup> Structural solution and refinement were carried out with the SHELXTL suite of programs.<sup>15</sup> The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. There was a disordered CH<sub>2</sub>Cl<sub>2</sub> solvate found in the crystals of both **6a** and **6b**. In the former, this was modelled with five alternative sites with equal occupancies, while in the latter, it was modelled with two alternative sites with occupancies summed to unity; appropriate restraints were placed on the bond and thermal displacement parameters. 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.

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**Supporting Information Available:** CCDC 940727-9 contain the supplementary crystallographic data for **4**, **6a** and **6b**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Variable temperature <sup>19</sup>F NMR spectra for **7a** and **7b**, and table of crystal and refinement data for **4**, **6a** and **6b**. Ordering information is given on any current masthead page.

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