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<td><strong>Author(s)</strong></td>
<td>Mak, Garvin Kar Hang; Chan, Pek Ke; Fan, Wai Yip; Leong, Weng Kee; Li, Yongxin</td>
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Reactions of Cp*Ir(CO)₂ with Pentafluorobenzonitrile: Half-Sandwich

Iridium Complexes Cp*Ir(CO)(p-C₆F₄CN)(X)

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Abstract

The reaction of Cp*Ir(CO)₂ (1) with pentafluorobenzonitrile in the presence of a base afforded the diaryl complex Cp*Ir(CO)(p-C₆F₄CN)₂ (4). The reaction proceeds via the metallacarboxylic acid Cp*Ir(CO)(p-C₆F₄CN)(COOH) (2). The latter can be decarboxylated in the presence of a base to the hydrido species Cp*Ir(CO)(p-C₆F₄CN)(H) (5), which can then undergo hydride-chloride exchange to Cp*Ir(CO)(p-C₆F₄CN)(Cl) (6a). In the presence of air and water, the reaction of 1 with pentafluorobenzonitrile afforded a complex formulated as Cp*Ir(CO)(p-C₆F₄CN){C(OH)(NH₂)C₆F₅} (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)₂ (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.¹ 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-C₆F₄CN)(COOH) (2).² 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-C₆F₄CN)]₂ (3) and
[Cp*Ir(CO)(p-C₆F₄CN)]₂ (3').³ 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 C₆F₅CN in the presence of basic alumina or NaOH pellets gave quantitative conversion to Cp*Ir(CO)(p-C₆F₄CN)₂ (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)(C₆H₅)₂, for which the crystal structure has not yet been reported.⁴

![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 C₆F₅CN 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-C₆F₅CN)(H) (5) quantitatively. Although leaving a solution of 5 in chloroform to stand eventually gave complete conversion to Cp*Ir(CO)(p-C₆F₅CN)(Cl) (6a), it did not react with C₆F₅CN. Complex 6a could also be obtained quantitatively from the reaction of 3 in the presence of visible light with CHCl₃; reaction with CH₃I afforded the iodo analogue Cp*Ir(CO)(p-C₆F₅CN)(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 [Cp*Ir(CO)(ρ-C₆F₄CN)]⁻ (A) (Scheme 2). Intermediate A is analogous to the reported anionic complex [Cp*Ir(PMe₃)(H)]Li, which has been reported to be active in C-F activation.⁵
We believe that generation of the proposed anionic intermediate A also accounted for the observation that the reaction of 1 with C₆F₅CN in the presence of air yielded a mixture containing a species which has been formulated as Cp*Ir(CO)(p-C₆F₄CN)[C(OH)(NH₂)(C₆F₅)] (7a) and C₆F₅CONH₂, in ~1:1 molar ratio. The identity of the amide was confirmed by a single crystal x-ray crystallographic study, and was likely the result of base catalysed hydrolysis of C₆F₅CN; stirring a mixture of C₆F₅CN with one equivalent of aqueous NaOH gave C₆F₅CONH₂ 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 C₆F₅CONH₂ in the presence of aqueous 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 C₆F₅CONH₂, 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 C₆F₅CONH₂ from C₆F₅CN. Consistent with this was the observation that 2 reacted with PhCONH₂ and tBuCONH₂ in the presence of aqueous NaOH to afford the analogues Cp*Ir(CO)(p-C₆F₅CN)[(C(OH)(NH₂)(R)] (R = Ph (b) and tBu (c)).

VT-NMR studies

The room temperature ¹⁹F{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 C₆F₅CN ring. The ¹⁹F{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 C₆F₅S₇ (C₆F₅)₃P,⁸ and the C₆F₅ ligands.⁹
Although it has not proven possible to separate the complexes 7 cleanly from the amide and small amounts of 4, their $^{19}$F{${}^{1}$H} NMR spectra also clearly indicated restricted rotation of the C$_6$F$_4$CN ring. At ambient temperature, only the meta F resonances were visible but at -60 °C, for example, that for 7a showed a total of seven resonances in a 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 $F_{\text{ortho}}$ resonances in the absence of exchange ($\delta\nu$),$^{10}$ 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 Cp*Ir(CO)(p-C$_6$F$_4$CN)(X).
Table 1. Free energy of activation for the –C₆F₄CN ring restricted rotation.

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<tr>
<th>Compound</th>
<th>Tₐ of Fortho signals (K)</th>
<th>δν at 213 K (Hz)</th>
<th>ΔG‡ at Tₐ (kJ mol⁻¹)</th>
</tr>
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<tbody>
<tr>
<td>Cp*Ir(CO)(p-C₆F₄CN)(Cl), 6a</td>
<td>273</td>
<td>1915</td>
<td>+ 48</td>
</tr>
<tr>
<td>Cp*Ir(CO)(p-C₆F₄CN)[C(OH)(NH₂)(C₆F₅)], 7a</td>
<td>293</td>
<td>5451</td>
<td>+ 49</td>
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<tr>
<td>Cp*Ir(CO)(p-C₆F₄CN)[C(OH)(NH₂)(Ph)], 7b</td>
<td>253</td>
<td>5964</td>
<td>+ 42</td>
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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-C₆F₄CN)₂ was formed. In the absence of the base, the metallacarboxylic acid Cp*Ir(CO)(p-C₆F₄CN)(COOH) was obtained, the decarboxylation of which gave the hydrido species Cp*Ir(CO)(p-C₆F₄CN)(H), which may undergo hydride-chloride exchange with halogenated solvents to form the halide species Cp*Ir(CO)(p-C₆F₄CN)(X). In the presence of air and water, the reaction afforded a complex formulated as Cp*Ir(CO)(p-C₆F₄CN)[C(OH)(NH₂)C₆F₅] (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-C₆F₄CN)]⁺.
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 CDCl$_3$ solutions; $^1$H chemical shifts reported were referenced against the residual proton signals of the solvent. $^{19}$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 CH$_2$Cl$_2$ as solvent on a Bruker ALPHA FTIR spectrometer at a resolution of 2 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 °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,$^{11}$ 2,$^2$ and 3,$^3$ 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 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)(p-C$_6$F$_4$CN)(Cl) (6a). The same observations can be made if an NMR sample of 3 was left in CDCl$_3$ for a few hours. Replacing CHCl$_3$ with CH$_3$I (1 ml) gave Cp*Ir(CO)(p-C$_6$F$_4$CN)(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). ν\textsubscript{CO}: 2053 (vs) cm\textsuperscript{-1}. \textsuperscript{1}H NMR: δ 1.94 (s, 15H, CH\textsubscript{3}). FAB-MS: +538 [M-CO+H], +530 [M-Cl].

HR-FAB-MS: calcd for C\textsubscript{18}H\textsubscript{15}F\textsubscript{4}NO\textsuperscript{193}\textsuperscript{Ir}: [M-Cl]: 530.0714, found: 530.0697.

Data for 6b: Yield = quantitative (spectroscopic); 11 mg, 0.017 mmol (89%, isolated). ν\textsubscript{CO}: 2046 (vs) cm\textsuperscript{-1}. \textsuperscript{1}H NMR: δ 2.07 (s, 15H, CH\textsubscript{3}). ESI-MS: +689 [M+MeOH], +530 [M-I].

Anal. Calcd for C\textsubscript{18}H\textsubscript{15}F\textsubscript{4}IrNO: C, 32.93; H, 2.30; N, 2.13. Found: C, 32.71; H 2.29; N, 2.00.

Synthesis of Cp\textsuperscript{*}Ir(CO)(p-C\textsubscript{6}F\textsubscript{4}CN), 4 To a carius tube containing 2, freshly prepared from 1 (10 mg, 0.0261 mmol), C\textsubscript{6}F\textsubscript{5}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 \textsuperscript{1}H NMR spectrum showed only the presence of 4. A \textsuperscript{19}F{\textsuperscript{1}H} NMR spectrum showed that a small amount of C\textsubscript{6}F\textsubscript{5}CONH\textsubscript{2} was obtained as a side product. Yield = quantitative (spectroscopic); 15 mg, 0.021 mmol (82%, isolated). ν\textsubscript{CO}: 2045 (vs) cm\textsuperscript{-1}. \textsuperscript{1}H NMR: δ 2.02 (s, 15H, CH\textsubscript{3}). \textsuperscript{19}F NMR: δ -33.6 (m, 2F, \textit{F\textsubscript{ortho}}), -59.3 (m, 2F, \textit{F\textsubscript{meta}}). ESI-MS: +705 [M+H]. Anal. Calcd for C\textsubscript{25}H\textsubscript{15}F\textsubscript{8}IrN\textsubscript{2}O: C, 42.68; H, 2.15; N, 3.98. Found: C, 42.46; H 2.09; N, 3.85.

Synthesis of Cp\textsuperscript{*}Ir(CO)(p-C\textsubscript{6}F\textsubscript{4}CN)(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 $^1$H NMR spectrum showed the presence of 5 and 6a. After the solution was left to stand in CDCl$_3$ for a longer period of time, only 6a could be observed in the spectrum. Yield (spectroscopic) = ~90%. v$_{CO}$: 2014 (vs) cm$^{-1}$. $^1$H NMR: δ 2.08 (s, 15H, CH$_3$), -14.72 (s, 1H, Ir-H). $^{19}$F NMR: δ -32.3 (m, 2F, F$_{ortho}$), -60.2 (m, 2F, F$_{meta}$)

**Synthesis of Cp*$^{8}$Ir(CO)(C$_6$F$_4$CN)(C(OH)(NH$_2$)C$_6$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), C$_6$F$_5$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 $^1$H and $^{19}$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 C$_6$F$_5$CN after the synthesis of 2. Leaving a solution of 7a in CDCl$_3$ to stand resulted in precipitation and apparent decomposition to unidentified compounds. Repeating the procedure with PhCONH$_2$ (3 mg, 0.0248 mmol) or $^1$BuCONH$_2$ (3 mg, 0.0297 mmol) in place of C$_6$F$_5$CONH$_2$ yielded 7b or 7c, respectively, as the major product.

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

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

**Data for 7c:** Yield (spectroscopic) = ~60%. $^1$H NMR: δ 1.88 (s, 15H, CH$_3$), 1.13 (s, 9H, $^1$Bu). $^{19}$F NMR: -59.2 (m, 2F, F$_{meta}$). ESI-MS: ESI: +631 [M-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 Kα radiation, with the SMART suite of programs.\textsuperscript{12} Data were processed and corrected for Lorentz and polarization effects with SAINT,\textsuperscript{13} and for absorption effects with SADABS.\textsuperscript{14} Structural solution and refinement were carried out with the SHELXTL suite of programs.\textsuperscript{15} 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\textsubscript{2}Cl\textsubscript{2} 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. Variable temperature \textsuperscript{19}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.
References
