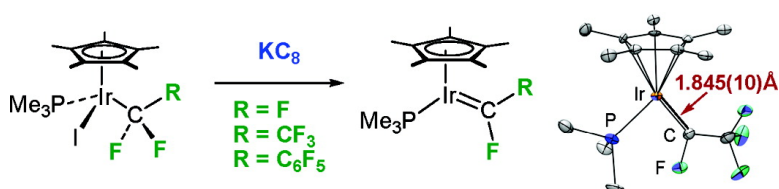


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## A Simple Route to Difluorocarbene and Perfluoroalkylidene Complexes of Iridium

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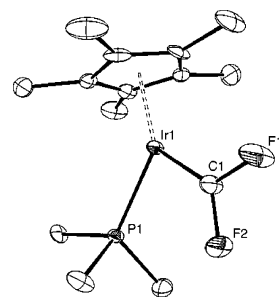
Received July 29, 2005; E-mail: rph@dartmouth.edu

Difluorocarbene complexes of transition metals are rare and are almost invariably produced from precursors containing a CF<sub>3</sub> ligand.<sup>1</sup> Cationic difluorocarbene species have been produced by fluoride abstraction from the trifluoromethyl ligand by various Lewis acids,<sup>2–5</sup> and neutral difluorocarbene complexes have been obtained either by  $\alpha$ -fluorine (or chlorine) elimination reactions<sup>6–8</sup> or, more recently, by olefin metathesis of 1,1-difluoroethylene.<sup>9</sup> With the exception of a single spectroscopically characterized cationic perfluoropropylidene complex,<sup>2</sup> no perfluoroalkylidene compounds have been reported. Here we report a simple route to isolable neutral difluorocarbene and perfluoroalkylidene complexes of iridium.

The C–F bond is the strongest covalent bond to carbon,<sup>10</sup> but the electronegativity of fluorine also ensures that C–F  $\sigma^*$  antibonding orbitals are relatively low lying, allowing their activation by reduction. Exhaustive reduction of halofluorocarbons to carbon has been studied as a way to dispose of environmentally harmful fluorocarbons, with the fate of fluorine as an alkali metal fluoride providing a powerful thermodynamic driving force for the overall reaction.<sup>11–13</sup> In some cases, fluorocarbon rings can be partially reduced to the fluorinated aromatic molecules, providing a useful method of producing high value organics from saturated precursors.<sup>12,14</sup> In contrast, the selective reductive activation of saturated fluorocarbons is exceptionally rare.<sup>15,16</sup> Tertiary C–F bonds usually provide the Achilles' heel<sup>17</sup> for these reductive processes.

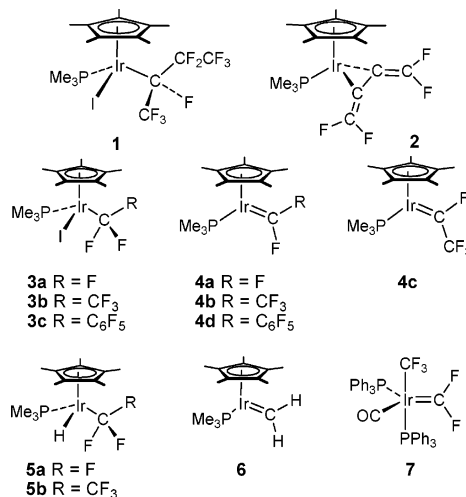
We have demonstrated recently that a metal center can serve as a stabilizing template for reduction of a perfluoroalkyl ligand to generate an unsaturated fluorinated ligand; the perfluoro-*sec*-butyl ligand in **1** was reduced to afford the first example of a transition metal **2** containing a tetrafluorobutatriene ligand.<sup>18</sup>

To explore whether tertiary C–F bonds were essential to these metal-templated reductions, the trifluoromethyl complex, Cp\*Ir(PMe<sub>3</sub>)(CF<sub>3</sub>)I (**3a**), was prepared. Reduction in THF with 2 equiv of sodium naphthalenide or potassium graphite (KC<sub>8</sub>) afforded the difluorocarbene **4a** in up to 70% yield as a yellow crystalline compound, along with small amounts of the hydrido complex **5a**. The stability of **4a** contrasts with that of its Ir=CH<sub>2</sub> analogue **6**, which can only be observed spectroscopically in solution at low temperatures.<sup>19</sup> Compound **4a** has been crystallographically characterized (Figure 1). The Ir–C double bond distance of 1.854(11) Å is slightly shorter than that in **7** (1.874(7) Å), the only other crystallographically characterized iridium difluorocarbene complex,<sup>6</sup> and is significantly shorter than the corresponding Ir–CF<sub>3</sub> single bond distance of 2.10(2) Å in **3a**.<sup>20</sup> The P–Ir–C angle is an acute 89.1(4)°, while that from the carbene carbon to the Cp\* centroid is an obtuse 137.4(4)°; the P–Ir–Cp\*(centroid) angle of 133.5(4)° is similar to the corresponding angles in analogous complexes of



**Figure 1.** ORTEP for **4a** (ellipsoids drawn at 30% probability). Selected bond distances (Å) and angles (deg): Ir(1)–C(1), 1.854(11); C(1)–F(1), 1.295(14); C(1)–F(2), 1.352(13); Ir(1)–P(1), 2.235(2); Ir(1)–Cp\*(cent), 1.911(10); Ir(1)–C(1)–F(1), 125.1(8); Ir(1)–C(1)–F(2), 130.6(8); F(1)–C(1)–F(2), 104.3(9); P(1)–Ir(1)–Cp\*(cent), 133.5(4); P(1)–Ir(1)–C(1), 89.1(4); C(1)–Ir(1)–Cp\*(cent), 137.4(4).

tetrafluorobenzene<sup>21</sup> and tetrafluorobutatriene (**2**)<sup>18</sup> [133.9(2) and 132.8(1)°, respectively].



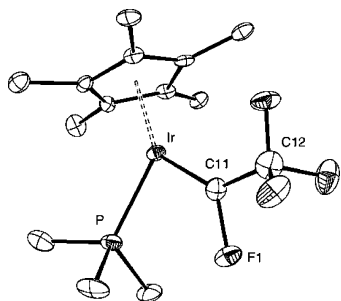
The <sup>19</sup>F NMR spectrum of **4a** illustrates that the solid-state structure is maintained in solution, with a high barrier to rotation about the iridium–carbon double bond manifested by inequivalent fluorine resonances at low field (positive) chemical shifts of  $\delta$  36.7 ppm (F<sub>2</sub>) and  $\delta$  47.3 ppm (F<sub>1</sub>). Unambiguous assignment of fluorine resonances was obtained using a <sup>19</sup>F{<sup>1</sup>H} HOESY experiment<sup>22</sup> and demonstrates that coupling of <sup>31</sup>P to the *cis*-F<sub>2</sub> (<sup>3</sup>J<sub>FP</sub> = 32 Hz) is much larger than to the *trans*-F<sub>1</sub> (<sup>3</sup>J<sub>FP</sub> = 7 Hz). The <sup>13</sup>C{<sup>1</sup>H}NMR spectrum exhibits a low field resonance at  $\delta$  180.96 ppm for the carbene carbon, very similar to the value ( $\delta$  189.9 ppm) reported for the hydrocarbon analogue **6**.<sup>19</sup>

This reductive methodology appears to be general, and reduction of perfluoroethyl precursor **3b** with excess KC<sub>8</sub> in THF affords

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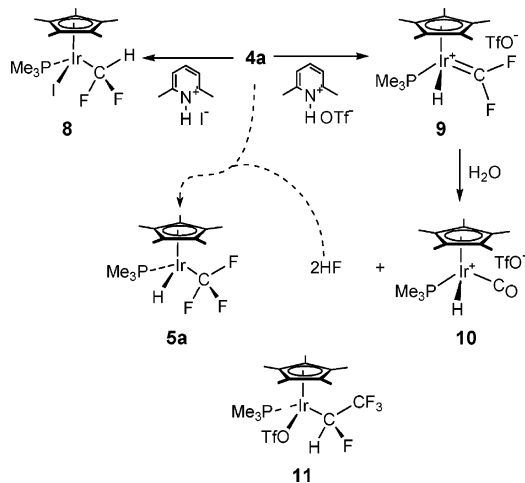
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**Figure 2.** ORTEP of **4b** (ellipsoids at 30% probability). Selected bond distances (Å) and angles (deg) are averages of four independent molecules in the asymmetric unit: Cp\*(cent)–Ir, 1.907(11); Ir–P, 2.254(3); Ir–C11, 1.845(10); C11–C12, 1.465(16); C11–F1, 1.467(13); Cp\*(cent)–Ir–P, 132.0(4); Cp\*(cent)–Ir–C11, 139.9(4); P–Ir–C11, 88.1(4); Ir–C11–F1, 126.9(7); Ir–C11–C12, 133.9(9); F–C11–C12, 99.2(9).

the corresponding perfluoroethylidene complex as a 6:1 mixture of *E*-isomer **4b** and *Z*-isomer **4c**, along with variable small amounts of previously reported hydride **5b**.<sup>23</sup> The structure of **4b** was unambiguously defined by a crystallographic study (Figure 2). The Ir–C distance of 1.845(10) Å is indistinguishable from **4a**.

Likewise, perfluorobenzylidene **4d** can be synthesized from corresponding precursor **3c**,<sup>24</sup> with an excess of K<sub>2</sub>C<sub>8</sub> in THF. This compound is more thermally sensitive and was characterized spectroscopically. The fluorine atom on the carbene carbon has a signature downfield chemical shift at  $\delta$ 29.38 ppm with a large coupling to phosphorus ( $^3J_{FP} = 69$  Hz) and an interesting long-range coupling to the *para*-fluorine of the aromatic ring ( $^6J_{FF} = 5$  Hz), analogous to that reported for  $\alpha$ -fluoropentafluorostyrenes.<sup>25</sup>



Reaction of **4a** with 1 equiv of 2,6-lutidinium iodide (LutHI) in ether afforded **8** in a reaction characteristic of a nucleophilic carbene.<sup>1</sup> Complex **8** has been crystallographically characterized, and in solution, the H bound to C appears at low field ( $\delta$  8.65 ppm), with large  $^2J_{FH}$  (57, 55 Hz) and small  $^3J_{FH}$  (5 Hz), while the CF<sub>2</sub> fluorines appear at high field,  $\delta$  –75.99 and –80.19 ppm. However, reaction of **4a** with 1 equiv of LutHOTf in CD<sub>2</sub>Cl<sub>2</sub> at low temperatures illustrates that the protonated species present under these conditions is **9**. At –85 °C, the Ir–H appears at  $\delta$  –15.15 ppm with small (7 Hz) coupling to F, and the fluorines appear at very low field at  $\delta$  99.6 and 109.2 ppm, as expected for protonation at Ir. On warming above –50 °C, **9** reacts, presumably with adventitious moisture, to give the previously reported hydrido carbonyl compound **10**<sup>26</sup> and complex **5a**, in a 1:2 ratio. Hydrolysis of CF<sub>2</sub> ligands to give CO in cationic complexes is well-known,<sup>1–5</sup> and the resultant two molecules of HF can add to **4a** to give **5a**,

explaining the observed product ratio. This requires a different regiochemistry for addition of HF than for HI, suggesting that the difluorocarbene ligand in **4a** may be amphiphilic.<sup>27,28</sup> The behavior of **4a** is further contrasted with its congener **4b**, which reacts with LutHOTf at low temperatures to give **11** that is clearly not protonated at iridium but at carbon, as evidenced by the low field <sup>1</sup>H resonance at  $\delta$  6.67 with a large doublet coupling to a single <sup>19</sup>F (44 Hz) and quartet coupling (12 Hz) to the CF<sub>3</sub>, and the corresponding high field <sup>19</sup>F resonance at  $\delta$  –193.9 ppm. The triflate counterion is shown as coordinated in order to maintain an 18-electron structure, but we have no direct evidence for this.

These results emphasize that the kinetic site of protonation cannot be confirmed for either case, and that there is a fine balance of thermodynamic stability between metal-protonated and carbon-protonated forms that depends on the nature of the fluorinated group.

These preliminary observations indicate that the reactions of perfluoroalkylidene ligands may not parallel those of their difluorocarbene analogues, and that potentially rich new chemistry remains to be unveiled.

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**Supporting Information Available:** Experimental details for all compounds and CIF files for **3a**, **4a**, **4b**, and **8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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