

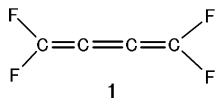
Reductive Activation of Carbon–Fluorine Bonds in Perfluoroalkyl Ligands: An Unexpected Route to the Only Known Tetrafluorobutatriene Transition Metal Complex: $\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)(2,3\text{-}\eta^2\text{-CF}_2\text{=C=C=CF}_2)$

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Although tetrafluorobutatriene (**1**) was first prepared more than 40 years ago,¹ only recently has its low-temperature molecular structure been reported, following development of a more efficient synthesis.² Originally described as a “treacherously explosive” liquid, even at its melting point of $-5\text{ }^\circ\text{C}$,¹ and more recently shown to decompose slowly even at $-80\text{ }^\circ\text{C}$, it is clearly a highly reactive molecule. However, many unstable or labile organic molecules have been trapped and stabilized via transition metal coordination,^{3–6} and we have extended this series recently to include reactive fluorocarbons such as tetrafluorobenzynes in complexes such as $\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{C}_6\text{F}_4)$.^{7–9} Here, we report an in situ synthesis of tetrafluorobutatriene within the coordination sphere of iridium, using a novel route involving the reductive activation of saturated carbon–fluorine bonds.

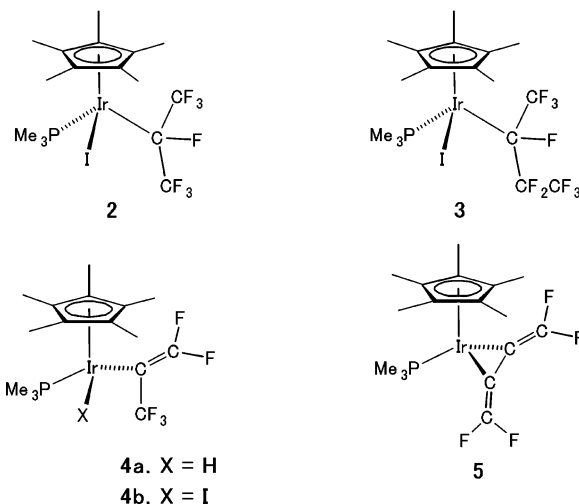


The chemistry of aliphatic carbon–fluorine bonds is limited by their thermodynamic stability and kinetic inertness. Among others,^{10–16} we have been interested in using transition metals to help activate C–F bonds, with eventual conversion to C–H and C–C compounds.^{17–20} In the free state, aliphatic C–F bond activation has been realized only under strongly reducing conditions, with the low-lying σ^* orbital of a tertiary C–F bond usually providing the Achilles’ heel²¹ of the molecule, with generation of aromatic organic products and formation of strong metal–fluoride bonds often providing some thermodynamic driving force.^{22–28}

With these factors in mind, we decided to test whether the vulnerability of tertiary C–F bonds to reduction includes those that are part of a secondary fluoroalkyl group σ -bonded to a transition metal center, anticipating that coordination stabilization of any otherwise reactive species might be achieved.

The starting complexes **2** and **3** were prepared by oxidative addition of the appropriate secondary perfluoroalkyl iodide to $\text{Cp}^*\text{Ir}(\text{CO})_2$, followed by carbonyl displacement by PMe_3 .²⁹ Treatment of **2** with 3 equiv of sodium naphthalenide ($\text{NaC}_{10}\text{H}_8$) in THF afforded the previously reported unsaturated hydride complex **4a**,³⁰ with apparent reductive loss of iodide and two fluoride anions. The source of the hydride is presumably the reaction solvent. Two equivalents of $\text{NaC}_{10}\text{H}_8$ affords a mixture of **4a** and the corresponding iodo analogue **4b**, which has been crystallographically characterized,³¹ and more than 3 equiv of $\text{NaC}_{10}\text{H}_8$ results in no further reaction of **4a**. In contrast, the *sec*-butyl analogue **3** reacts with 6 equiv of $\text{NaC}_{10}\text{H}_8$ to afford the tetrafluorobutatriene complex

5. Fewer than 6 equiv of $\text{NaC}_{10}\text{H}_8$ affords a complex mixture of products, some of which clearly contain Ir–H bonds by NMR spectroscopy.



The ^{19}F NMR spectrum of **5** shows two fluorine resonances at $\delta -72.46$ and -102.37 , which appear as a classic AA'XX' coupling pattern, with $^2J_{\text{F}(\text{AX})} = 95.5\text{ Hz}$, $^5J_{\text{F}(\text{XX}')} = 35.5\text{ Hz}$, $^5J_{\text{F}(\text{AA}')} = 4.5\text{ Hz}$, and $^5J_{\text{F}(\text{AX}')} = 4.0\text{ Hz}$. The structure is unambiguously defined by means of a single-crystal X-ray diffraction study; an ORTEP representation of the structure is shown in Figure 1 (C–C and C–F distances in the cumulene ligand are given in Table 1).³¹

The tetrafluorobutatriene ligand adopts the expected conformation with the center double bond coordinated to iridium. The coordinated C–C bond distance [1.418(5) Å] is dramatically longer than the corresponding distance in tetrafluorobutatriene [1.2679(5) Å], presumably due to strong back-bonding from iridium to an antibonding π^* orbital of the ligand. This elongation is accompanied by significant bending of the ligand, with C–C–C angles of about 140° . Similar features have been observed in the structures of other metal complexes of hydrocarbon trienes of this type.^{32–37} Quite unexpected, however, is the significant shortening of the two flanking noncoordinated fluorinated double bonds, with a mean value of 1.281(4) Å, as compared to the value of 1.3162(3) Å in the free triene. One might perhaps expect lengthening of these bonds if the *s*-character in the C–C σ -bond orbitals of the two center carbon atoms is reduced on bending the triene. Other coordinated butatrienes do not show this bond shortening,^{32–37} nor do mono- or dianions of butatrienes,^{38,39} and its origins remain to be explored in more detail. The Ir–P [2.2530(9) Å] and Ir–Cp(centroid) [1.873(3) Å] are very similar to those reported for the analogous complex of tetrafluorobenzynes [2.2573(13) and 1.858(3) Å].^{7,8}

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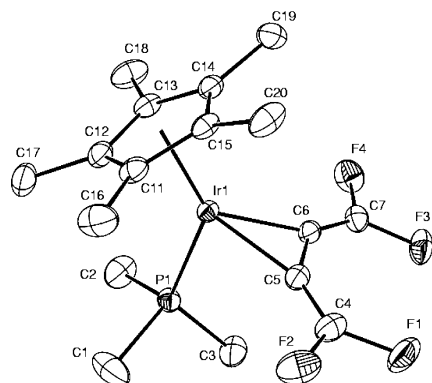
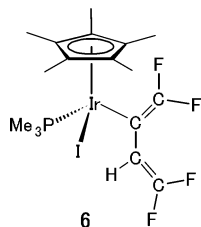


Figure 1. ORTEP diagram for **5** with ellipsoids drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Ir(1)–C(5), 2.039(3); Ir(1)–C(6), 2.042(3); Ir(1)–P(1), 2.2530(9); C(5)–Ir(1)–C(6), 40.66(13); C(4)–C(5)–C(6), 142.3(3); C(7)–C(6)–C(5), 140.4(3). C–C and C–F distances in the cumulene ligand are given in Table 1.

Table 1. Bond Lengths (Å) for the Tetrafluorobutatriene Ligand in Complex **5** and in Free Tetrafluorobutatriene **1**²

	C(4)–C(5)	C(5)–C(6)	C(6)–C(7)	C(4)–F(1)	C(4)–F(2)	C(7)–F(3)	C(7)–F(4)
1 ²	1.3162(3)	1.2679(5)		1.3198(3)	1.3222(3)		
5	1.279(4)	1.418(5)	1.283(4)	1.352(4)	1.348(4)	1.346(3)	1.343(4)

In solution, one of the Ir–C bonds of compound **5** easily undergoes protonation by weak acids such as lutidinium iodide to give the butadienyl complex **6**, but, as with the perfluoroaryl complexes produced by protonation of the perfluorobenzene complex Cp*Ir(PMe₃)(C₆F₄), treatment of **6** with the stronger acid CF₃CO₂H for several hours is required to cleave the remaining Ir–C bond to produce Cp*Ir(PMe₃)(CF₃CO₂)₂.⁹ The tetrafluorobutatriene ligand in **5** is not displaced by exchange with CO at 80 °C.



The mechanism and generality of this method for the introduction of unsaturation in fluorinated ligands remains to be explored in detail. For example, it is interesting that reduction of **3** affords the butatriene ligand by consumption of six electrons, but reduction of **2** only results in consumption of three electrons, stopping at the perfluoropropenyl ligand without proceeding further to, for example, a tetrafluoroallene ligand. Nevertheless, this methodology promises to be of general interest and utility for the preparation of other transition metal complexes of strained or otherwise unstable fluorocarbon ligands by reduction of appropriate precursors. Further studies are underway and will be reported in due course.

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Supporting Information Available: Synthetic and spectroscopic data for compounds **4b**, **5**, and **6**; tables of crystallographic and refinement data, atomic coordinates and anisotropic thermal parameters, bond lengths and angles, H atom coordinates, and isotropic thermal parameters for **4b** and **5** (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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