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α- and *β*-Fluorine Elimination Reactions Induced by Reduction of Iridium−Fluoroalkyl Complexes. Selective Formation of Fluoroalkylidene and Hydrofluoroalkene Ligands

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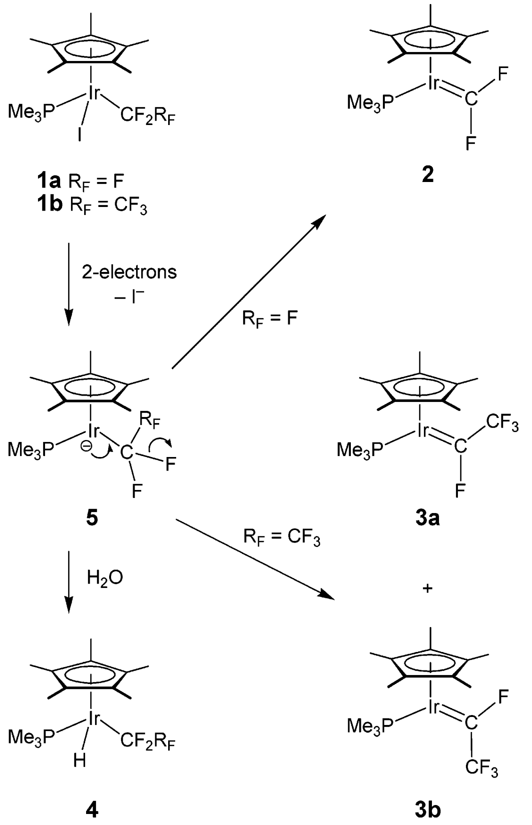
Summary: Two-electron reduction of the perfluoroalkyl complexes $Cp^*Ir(CO)(CF_2R_F)(I)$ $[R_F = F, CF_3, CF_2CF_3]$ *occurs by α-fluorine elimination to give the perfluoroalkylidene complexes* $Cp^*(CO)Ir{=}CFR_F$*; when* $R_F = CF_3$*, the E-isomer predominates, while when* $R_F = CF_2CF_3$*, the Z-isomer is preferred. No β-fluorine elimination is observed in these reactions, but when no α-fluorines are present, reduction of* $Cp^*Ir(CO)(CH_2CF_2R_F)(I)$ $[R_F = F, CF_3]$ *occurs cleanly by β-fluorine elimination to afford a new route to the hydrofluoroalkene compounds* $Cp^*Ir(CO)(CH_2{=}CFR_F)$ $[R_F = F, CF_3]$*.*

Despite the strength of the carbon−fluorine bond,[1,2] fluorines attached to carbon atoms that are directly ligated to certain transition metals can be remarkably labile,[3−11] even to the point of activation with weak acids.[12−14] Recently we reported that a different form of α-C−F bond activation occurs during reduction of iridium(III) fluoroalkyl complexes using sodium naphthalenide (NaNp) or potassium graphite (KC_8) as electron sources, thereby providing a simple route to neutral perfluoroalkylidene compounds.[15] Specifically, as shown in Scheme 1, reduction of trifluoromethyl derivative **1a** afforded **2**, while corresponding reduction of **1b** generated an initial 6:1 mixture of stereoisomers **3a** and **3b**, which subsequently converted to the thermodynamically favored *E*-stereoisomer **3a**. The mechanism of this reduction process is clearly complex, especially when using heterogeneous reagents such as KC_8. In particular the question of whether C−F bond activation results from direct reduction at the metal center (sphaerointraneous) or by direct reduction of an α-CF bond (ligandintraneous) was unclear, especially since direct reduction of C−F bonds in aliphatic fluorocarbons can be effected under similar conditions.[16−18] Here we present some additional insight into this reaction and provide an extension to the first examples of *β*-fluorine elimination reactions from fluoroalkyl ligands to give coordinated fluoroalkenes.

Scheme 1



We initially reported that formation of perfluoroalkylidene compounds **2** and **3** was always accompanied by small amounts

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(1) Smart, B. E. *Mol. Struct. Eng.* **1986**, *3*, 141−191.

(2) Smart, B. E. Fluorocarbons. In *Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds.; Wiley, New York: 1983; Chapter 14, pp 603−655.

(3) Appleton, T. G.; Berry, R. D.; Hall, J. R.; Neale, D. W. *J. Organomet. Chem.* **1989**, *364*, 249−273.

(4) Clark, G. R.; Hoskins, S. V.; Roper, W. R. *J. Organomet. Chem.* **1982**, *234*, C9−C12.

(5) Burrell, A. K.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R. *J. Organomet. Chem.* **1994**, *482*, 261−269.

(6) Michelin, R. A.; Ros, R.; Guadalupi, G.; Bombieri, G.; Benetollo, F.; Chapuis, G. *Inorg. Chem.* **1989**, *28*, 840−846.

(7) Koola, J. D.; Roddick, D. M. *Organometallics* **1991**, *10*, 591−597.

(8) Crespi, A. M.; Shriver, D. F. *Organometallics* **1985**, *4*, 1830−1835.

(9) Richmond, T. G.; Shriver, D. F. *Organometallics* **1984**, *3*, 305−314.

(10) Richmond, T. G.; Crespi, A. M.; Shriver, D. F. *Organometallics* **1984**, *3*, 314−319.

(11) Reger, D. L.; Dukes, M. D. *J. Organomet. Chem.* **1978**, *153*, 67−72.

(12) Garratt, S. A.; Hughes, R. P.; Kovacik, I.; Ward, A. J.; Willemsen, S.; Zhang, D. *J. Am. Chem. Soc.* **2005**, *127*, 15585−15594.

(13) Hughes, R. P.; Laritchev, R. B.; Zakharov, L. N.; Rheingold, A. L. *J. Am. Chem. Soc.* **2005**, *127*, 6325−6334.

(14) Hughes, R. P.; Zhang, D.; Zakharov, L. N.; Rheingold, A. L. *Organometallics* **2002**, *21*, 4902−4904.

(15) Hughes, R. P.; Laritchev, R. B.; Yuan, J.; Golen, J. A.; Rucker, A. N.; Rheingold, A. L. *J. Am. Chem.* Soc. **2005**, *127*, 15020−15021.

(16) Burdeniuc, J.; Jedlicka, B.; Crabtree, R. H. *Chem. Ber./Recl.* **1997**, *130*, 145−154.

(17) Kiplinger, J. L.; Richmond, T. G. *J. Am. Chem. Soc.* **1996**, *118*, 1805−1806.

(18) Stoyanov, N. S.; Ramchandani, N.; Lemal, D. M. *Tetrahedron Lett.* **1999**, *40*, 6549−6552.

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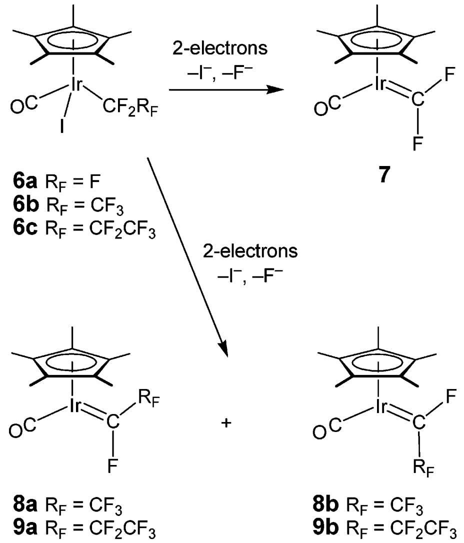
Scheme 2



of the hydrido complexes **4**.[15] We have subsequently observed that absolutely rigorous exclusion of traces of water in the reaction system results in complete suppression of byproducts **4**, suggesting that the hydride ligand resulted from adventitious protic interception of an anionic intermediate **5** in the reduction process. Consequently a reasonable hypothesis for formation of alkylidene products can be formulated as proceeding via initial two-electron reduction at iridium with loss of iodide to give anion **5**, followed by an α-fluoride elimination to generate the iridium−carbon double bond in products **2** and **3**, as shown in Scheme 1.

Reasoning that such an anionic intermediate might be formed more readily if the PMe_3 ligand were replaced by the stronger π-acceptor CO, the analogous precursor **6a** was subjected to reduction with two-electron equivalents of NaNp, KC_8, or magnesium graphite[19,20] to afford clean conversion to the difluorocarbene compound **7** (Scheme 2).[21] The carbene complex **7** was characterized by a single-crystal X-ray diffraction study.[22] There are two independent molecules in the asymmetric unit. One shows complete CF_2/CO disorder, and the other is perfectly ordered; an ORTEP diagram of the ordered molecule is shown in Figure 1.

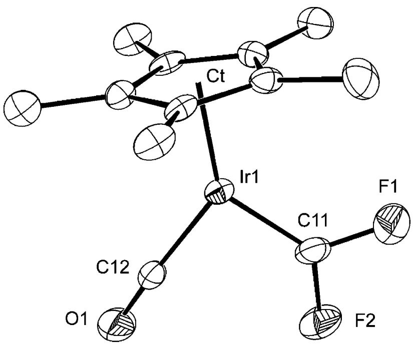


Figure 1. ORTEP diagram of the non-hydrogen atoms of **7**, showing the partial atom-labeling scheme. Thermal ellipsoids are shown at the 30% level. Selected bond distances (Å) and angles (deg): Ir1−C11, 1.855(13); C11−F1, 1.340(13); C11−F2, 1.325(12); Ir1−C12, 1.839(9); C12−O1, 1.136(11), Ir1−Ct, 1.902(10); Ir1−C11−F1, 124.7(8); Ir1−C11−F2, 131.7(9); F1−C11−F2, 103.5(10); C12−Ir1−C11, 91.7(5).

Corresponding reduction of the perfluoroethyl and perfluoropropyl analogues demonstrates some remarkable stereoselectivity. Reduction of **6b** affords initially exclusively the *E*-perfluoroethylidene complex **8a**, which slowly isomerizes at room temperature to a 2:1 *E*/*Z*-isomer mixture of **8a**/**8b**.[21] Unfortunately compounds **8** did not provide X-ray-quality crystals, but structural isomer assignments were straightforward using $^{19}F\{^1H\}$ HOESY experiments.[15,23−25] In dramatic contrast, reduction of perfluoropropyl analogue **6c** afforded initially the *Z*-perfluoropropylidene isomer **9b**, which slowly isomerizes to give a 2:1 *Z*/*E*-isomer mixture of **9b**:**9a**.[21] Once again isomer assignments were straightforward using $^{19}F\{^1H\}$ HOESY experiments, and the structure of the major stereoisomer **9b** was confirmed crystallographically; an ORTEP diagram is shown in Figure 2.[26] Clearly the α-fluoride elimination during the reduction of **6b** and **6c** occurs under conditions of kinetic control and shows dramatically different stereoselectivity depending on the fluoroalkyl ligand. The thermodynamics of the equilibrium between *E*- and *Z*-isomers of perfluoroalkylidene ligands is also highly dependent on the fluoroalkyl substituent, perhaps reflecting some subtle steric interactions between the alkylidene substituents and the ancillary ligands.

If an iridium-based anion analogous to **5** (Scheme 1) is indeed the intermediate that precedes α-fluoride elimination to give the fluoroalkylidene ligands, the fate of such an intermediate in the absence of α-fluorines was of considerable interest. When **10a** was reduced by two-electron equivalents of magnesium graphite, the 1,1-difluoroethylene complex **11** was produced cleanly via a β-fluoride elimination reaction (Scheme 3).[27] The complex crystallizes on a mirror plane, and the CH_2 and CF_2 groups are completely disordered; an ORTEP diagram of the 50% occupancy structure is shown in Figure 3, but the disorder allows no comparison of Ir−C parameters involving the fluorinated alkene.[28] In solution, observation of two ^{19}F and

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(19) Fürstner, A.; Csuk, R.; Rohrer, C.; Weidmann, H. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1729−1734.

(20) Csuk, R.; Glaenzer, B. I.; Fürstner, A. *Adv. Organomet. Chem.* **1988**, *28*, 85−137.

(21) **7**: A mixture of potassium graphite (0.2441 g, 1.81 mmol) and magnesium chloride (0.0872 g, 0.916 mmol) in THF (3 mL) was refluxed (30 min) and then cooled to room temperature. Cp*Ir(CO)(CF_3)(I) (0.100 g, 0.181 mmol) was added as a solution in THF (3 mL) and the suspension allowed to stir at room temperature (1 h). The solvent was removed and the product extracted into hexanes. Filtration and removal of solvent afforded a yellow solid (37 mg, 50%): IR (hexanes) ν_{CO} 1999 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6, 21 °C) δ 1.78 (s, C_5Me_5); ^{19}F NMR (470.35 MHz, C_6D_6, 21 °C) δ 57.03 (d, $^2J_{AB}$ = 90 Hz, 1F, $C_\alpha F_A$), 57.88 (d, $^2J_{AB}$ = 90 Hz, 1F, $C_\alpha F_B$). **8**: prepared similarly from Cp*Ir(CO)(CF_2CF_3)(I) as a mixture of isomers **8a**:**8b** = 10:1; IR (hexanes) ν_{CO} 2010 cm^{-1}; major isomer, ^{1}H NMR (500 MHz, C_6D_6, 21 °C) δ 1.69 (s, C_5Me_5); ^{19}F NMR (470.35 MHz, C_6D_6, 21 °C) δ −73.19 (d, $^3J_{FF}$ = 12 Hz, 3F), −0.07 (q, $^3J_{FF}$ = 12 Hz, 1F); minor isomer, ^{1}H NMR (500 MHz, C_6D_6, 21 °C) δ 1.68 (s, C_5Me_5); ^{19}F NMR (470.35 MHz, C_6D_6, 21 °C) δ −72.93 (d, $^3J_{FF}$ = 10 Hz, 3F), 9.58 (q, $^3J_{FF}$ = 10 Hz, 1F). **9**: similarly prepared from Cp*Ir(CO)($CF_2CF_2CF_3$)(I) (0.036 g, 0.055 mmol) as a mixture of isomers **9b**:**9a** in a ratio of 4:1. **9b**: IR (hexanes) ν_{CO} 2011 cm^{-1}; ^{1}H NMR (C_6D_6, 500 MHz) δ 1.70 (s, C_5Me_5); ^{19}F NMR (C_6D_6, 470.35 MHz) δ 4.3 (tq, $^3J_{FF}$ = 18, $^4J_{FF}$ = 8, 1F, CFC_2F_5), −81.9 (dt, $^4J_{FF}$ = 8, $^3J_{FF}$ = 3, 3F, CF_3), −113.2 (dq, $^3J_{FF}$ = 18, $^3J_{FF}$ = 3, 2F, CF_2). **9a**: IR (hexanes) ν_{CO} 2011 cm^{-1}; ^{1}H NMR (C_6D_6, 500 MHz) δ 1.69 (s, C_5Me_5); ^{19}F NMR (C_6D_6, 470.35 MHz) δ 12.8 (tq, $^3J_{FF}$ = 18, $^4J_{FF}$ = 9, 1F, CFC_2F_5), −82.0 (dt, $^4J_{FF}$ = 8, $^3J_{FF}$ = 3, 3F, CF_3), −113.7 (d, $^3J_{FF}$ = 19, 2F, CF_2).

(22) Crystallographic data for **7**: $C_{12}H_{15}F_2IrO$, fw = 405.44, monoclinic, space group $P2_1/n$, a = 8.017(2) Å, b = 21.124(6), c = 15.011(4) Å, β = 98.755(5)°, V = 2512.5(12) Å^3, Z = 8, T = 213(2) K, ρ_{calcd} = 2.144 g·cm^{-3}, 9183 unique reflections, R (wR_2) = 0.0422 (0.1011) for 316 variables and 4209 reflections ($I > 2\sigma(I)$), GOF = 1.036.

(23) Macchioni, A. *Eur. J. Inorg. Chem.* **2003**, 195−205.

(24) Hughes, R. P.; Zhang, D.; Ward, A. J.; Zakharov, L. N.; Rheingold, A. L. *J. Am. Chem. Soc.* **2004**, *126*, 6169−6178.

(25) Macchioni, A. *Chem. Rev.* **2005**, *105*, 2039−2073.

(26) Crystallographic data for **9b**: $C_{14}H_{15}F_6IrO$, fw = 505.46, triclinic, space group $P\bar{1}$, a = 8.3030(14) Å, b = 8.7600(15), c = 11.424(2) Å, α = 81.286(2)°, β = 88.961(2)°, γ = 75.301(2)°, V = 794.3(2) Å^3, Z = 2, T = 208(2) K, ρ_{calcd} = 2.113 g·cm^{-3}, 9355 unique reflections, R (wR_2) = 0.0516 (0.1294) for 204 variables and 3600 reflections ($I > 2\sigma(I)$), GOF = 1.128.

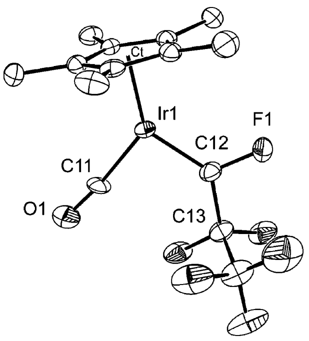
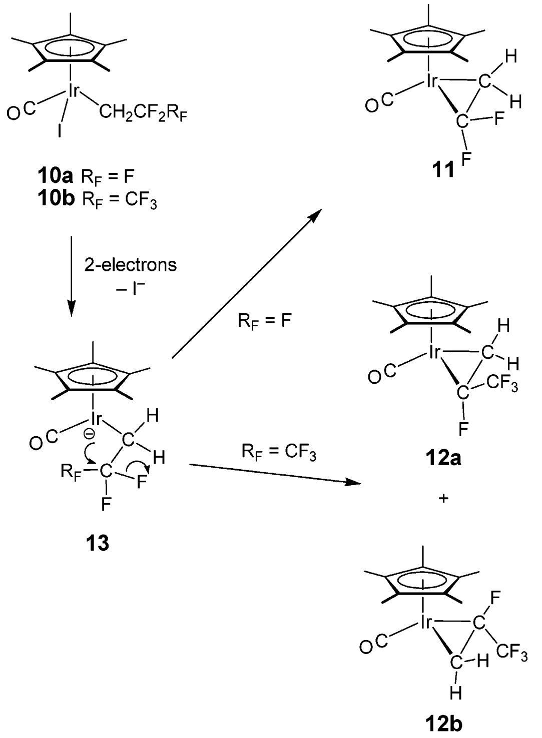


Figure 2. ORTEP diagram of the non-hydrogen atoms of **9b**, showing the partial atom-labeling scheme. Thermal ellipsoids are shown at the 30% level. Selected bond distances (Å) and angles (deg): Ir1−C12, 1.880(10); C12−F1, 1.361(12); C12−C13, 1.517(13); Ir1−C11, 1.826(8); C11−O1, 1.155(12), Ir1−Ct, 1.886(10); C11−Ir1−C12, 95.2(4); F1−C12−Ir1, 122.1(7); F1−C12−C13, 104.2(8); C13−C12−Ir1, 133.6(8).

Scheme 3



two ^{1}H NMR resonances for the coordinated fluoroalkene is consistent with the expected high energy for propeller rotation in an alkene complex of a d^8 ML$_4$ fragment.[29,30]

Analogous reduction of **10b** shows significant kinetic diastereoselectivity to afford a 2:1 mixture of hydrofluoroalkene complexes **12a** and **12b**, the composition of which remains unchanged at room temperature.[27] ^{19}F{^{1}H} HOESY NMR experiments demonstrate that the major isomer has the relative (R_{Ir},S_C)(R_C,S_{Ir}) configurations shown (Scheme 3), with the Cp* and CF$_3$ groups proximal to each other. However, on heating in refluxing toluene, this 2:1 ratio changes to 1:8, indicating that the initially predominant (R_{Ir},S_C)(R_C,S_{Ir}) diastereomer is clearly formed under conditions of kinetic control during reduction. This methodology provides a new and potentially useful way of making coordinated hydrofluoroolefins within the coordination sphere. For example, although it is quite stable once formed, complex **11** cannot be easily prepared by simple olefin substitution; a solution of Cp*Ir(CO)$_2$ and CH$_2$=CF$_2$ undergoes no reaction at either room or elevated temperatures.

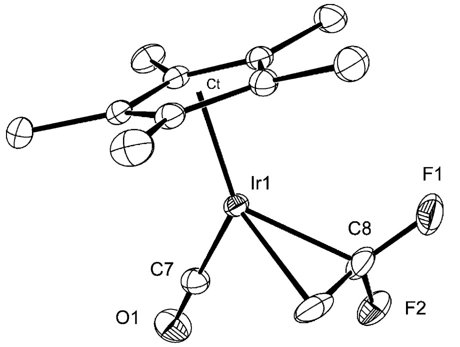


Figure 3. ORTEP diagram of the non-hydrogen atoms of **11**, showing the partial atom-labeling scheme. Thermal ellipsoids are shown at the 30% level. The molecule resides on a crystallographic mirror plane, and the olefin is end-for-end disordered. Half-occupancy fluorine sites are shown. Selected bond distances (Å): Ir1−C7, 1.837(6); O1−C7, 1.160(7); Ir1−Ct, 1.899(6).

Formation of hydrofluoroalkene complexes by β-fluoride elimination is shown in Scheme 3 as proceeding via anion **13** by analogy with the proposed mechanism for α-fluoride elimination shown in Scheme 1. If this is indeed the key intermediate, it is clear that in compounds with both α and β C−F bonds α-elimination occurs to the exclusion of β-elimination; only fluoroalkylidene complexes are formed, with no evidence for fluoroalkenes. Both α- and β-fluoride eliminations occur with considerable stereoselectivity under conditions of kinetic control. The origins of this selectivity and of the geometric preferences of perfluoroalkylidene ligands are under further investigation, as is the chemistry of this new family of fluorinated organometallic compounds.

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Supporting Information Available: Experimental and spectroscopic details for all new compounds, and CIF files for compounds **7**, **9b**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) **11**: A mixture of potassium graphite (0.096 g, 0.710 mmol) and magnesium chloride (0.033 g, 0.347 mmol) in THF (4 mL) was refluxed (1 h). This was allowed to cool to room temperature, and Cp*Ir(CO)(CH$_2$CF$_3$)(I) (0.037 g, 0.066 mmol) added as a solid. After stirring at room temperature (2 $^1/_2$ h) the solvent was removed and the product extracted into hexanes. After removal of the solvent the product was obtained as an off-white solid: IR (hexanes) ν_{CO} 1995 cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 500 MHz) 1.76 (ddd, $^2J_{HH}$ = 6, $^3J_{HF}$ = 9, $^3J_{HF}$ = 9, 1H, CH distal to Cp*), 1.64 (s, 15H, C$_5$Me$_5$), 1.07 (ddd, $^2J_{HH}$ = 6, $^3J_{HF}$ = 9, $^3J_{HF}$ = 9, 1H, CH proximal to Cp*); ^{19}F NMR (C$_6$D$_6$, 470.35 MHz) −83.1 (ddd, $^2J_{FF}$ = 115, $^3J_{FH}$ = 9, $^3J_{FH}$ = 9, 1F, CF distal to Cp*), −101.6 (ddd, $^2J_{FF}$ = 115, $^3J_{FH}$ = 9, $^3J_{FH}$ = 9, 1F, CF proximal to Cp*). **12**: prepared similarly from Cp*Ir(CO)(CH$_2$CF$_2$CF$_3$)(I) as two diastereomers in a ratio of 2:1. Upon refluxing in toluene (3 h) the diastereomer ratio becomes 1:8. IR (hexanes) ν_{CO} 2002 cm^{-1}. R_{Ir}, S_C (**12a**): ^{1}H NMR (C$_6$D$_6$) 2.26 (ddq, $^3J_{HF}$ = 19, $^2J_{HH}$ = 6, $^4J_{HF}$ = 1, 1H, CH distal to Cp*), 1.58 (s, 15H, Cp*), 1.45 (dd, $^3J_{HF}$ = 16, $^2J_{HH}$ = 6, 1H, CH proximal to Cp*); ^{19}F NMR (C$_6$D$_6$) −73.3 (d, $^3J_{FF}$ = 9, 3F, CF$_3$), −156.1 (ddq, $^3J_{FH}$ = 19, $^3J_{FH}$ = 16, $^3J_{FF}$ = 9, 1F, CF). R_{Ir}, R_C (**12b**): ^{1}H NMR (C$_6$D$_6$) 2.07 (dd, $^3J_{HF}$ = 19, $^2J_{HH}$ =6, 1H, CH distal to Cp*), 1.62 (s, 15H, Cp*), 1.50 (ddq, $^3J_{HF}$ = 16, $^2J_{HH}$ = 6, $^4J_{HF}$=1, 1H, CH proximal to Cp*); ^{19}F NMR (C$_6$D$_6$) −74.1 (d, $^3J_{FF}$ = 9, CF$_3$), −180.3 (ddq, $^3J_{FH}$ = 19, $^3J_{FH}$ = 16, $^3J_{FF}$ = 9, 1F, CF).

(28) Crystallographic data for **11**: C$_{13}$H$_{17}$F$_2$IrO, fw = 419.47, monoclinic, space group $P2_1/m$, a = 7.299(4) Å, b = 11.283(6) Å, c = 8.262(5) Å, β = 103.519(8)°, V = 661.6(6) Å^3, Z = 2, T = 208(2) K, ρ_{calcd} = 2.106 g·cm^{-3}, 3873 unique reflections, R (wR_2) = 0.0224 (0.0592) for 95 variables and 1590 reflections (I > 2$\sigma(I)$), GOF = 1.029.

(29) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801−3812.

(30) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *10*, 711−724.