# Carbon−Fluorine Bond Hydrogenolysis in Perfluoroethyl−Iridium Complexes To Give HFC-134a Involves Heterolytic Activation of $H_2$

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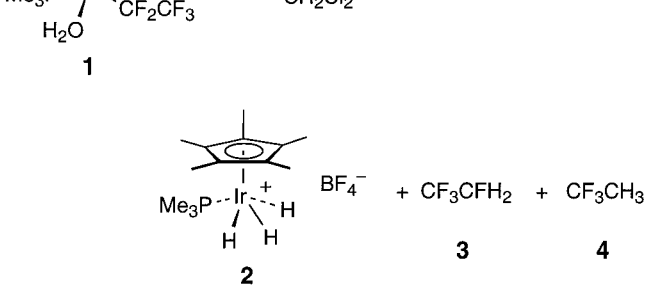
*Received March 26, 2002*

*Summary: Reaction of Cp*Ir(PMe$_3$)(CF$_2$CF$_3$)H with CH$_3$CO$_2$D affords mostly Cp*Ir(PMe$_3$)(CFHCF$_3$)(O$_2$CCH$_3$), while the corresponding reaction of Cp*Ir(PMe$_3$)(CF$_2$CF$_3$)D with CH$_3$CO$_2$H affords mostly Cp*Ir(PMe$_3$)(CFDCF$_3$)(O$_2$CCH$_3$). These results are consistent with external protonation of the CF bond and migration of the originally present H (or D) from Ir to C and suggest that the previously reported CF bond hydrogenolysis using dihydrogen proceeds via heterolytic activation of the H$_2$ molecule at iridium.*



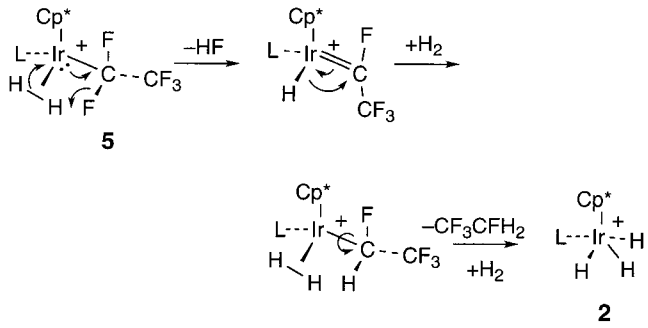
Hydrofluorocarbons (HFCs) are of significant importance as replacements for chlorofluorocarbons (CFCs); for example, $CF_3CFH_2$ (HFC-134a) is the replacement refrigerant for $CF_2Cl_2$ (CFC-12).[1,2] Recently we reported on the extremely facile hydrogenolysis of aliphatic carbon−fluorine bonds in cationic fluoroalkyl complexes of iridium, including the perfluoroethyl complex **1**, by simple treatment with $H_2$ gas under ambient conditions. The iridium is converted cleanly to the known trihydride cation **2**, while the fluoroalkyl group in **1** is liberated




mostly as HFC-134a (**3**) with some additional **4**.[3] This reaction provides a stoichiometric model for the study of aliphatic CF bond hydrogenolysis reactions, which have been previously observed in the heterogeneous catalytic hydrogenation of fluoroalkenes[4−6] and the catalytic dimerization of fluoroalkenes.[7,8]

In our initial report, we suggested the mechanism shown in Scheme 1, with protonation of the α-C−F bond occurring via the cationic dihydrogen complex **5**, formed

**Scheme 1**[a]




[a] L = PMe$_3$.

by displacement of water from **1**.[3] Here we report mechanistic studies that define more clearly the role of **5** in the series of events leading to the eventual hydrogenolysis of the C−F bonds in compound **1**.

We reasoned that a cationic $\eta^2$-$H_2$ intermediate such as **5** could be approached in an alternative fashion, by protonation of an Ir−H bond in an appropriate neutral precursor. Fortunately, the hydrido complex **6** and its deuterio analogue **7** are readily prepared from **1** using the methodology already reported.[9] To test whether elimination of HF occurs directly from an intermediate dihydrogen complex, or its dihydride tautomer, reactions of **6** and **7** with $CH_3CO_2H$ and $CH_3CO_2D$ were examined.

Treatment of **6** with $CH_3CO_2H$ readily affords complex **8** as a 2:1 mixture of diastereomers, along with 1 equiv of HF. Analogous treatment of **7** with $CH_3CO_2D$ affords the same diastereomeric ratio of the deuterio complex **9**. This reaction provides a model for the first events in the overall hydrogenolysis reaction using $H_2$, in which the C−F bond is broken and the new C−H bond is formed. In this case, instead of reaction with additional $H_2$, the coordinating anion acetate traps the iridium cation. The diastereomers of complex **8** can be prepared independently by oxidative addition of $CF_3CFHI$

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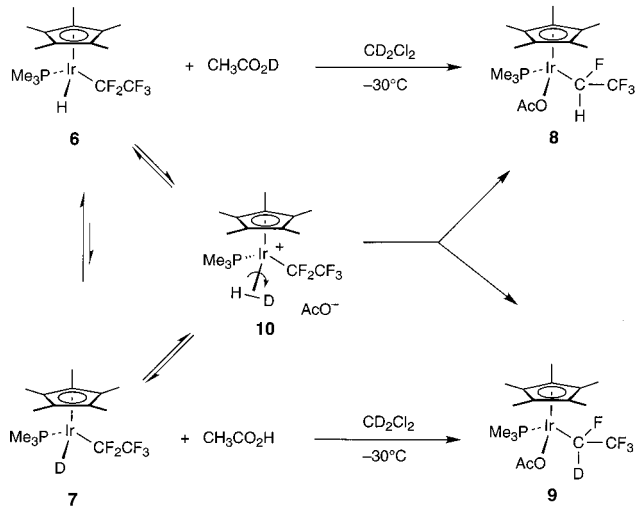
10.1021/om020225d CCC: $22.00 
Publication on Web 06/19/2002

**Scheme 2**

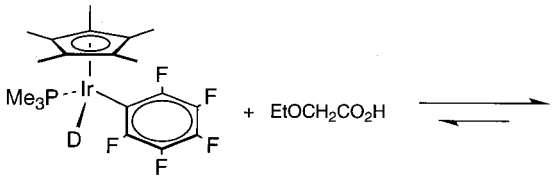



to $Cp^*Ir(CO)_2$ to give $Cp^*Ir(CFHCF_3)(CO)I$,[10] treatment with $PMe_3$ to give $Cp^*Ir(CFHCF_3)(PMe_3)I$,[11] and finally reaction with $Ag(O_2CCH_3)$[12] and have been fully characterized by spectroscopy and by microanalysis. These diastereomers can be separated by crystallization and are configurationally stable at room temperature.

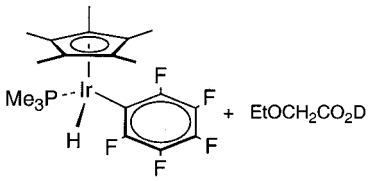
Treatment of **6** with $CH_3CO_2D$ in $CD_2Cl_2$ at −30 °C affords a 90% yield of the same mixture of diastereomers of **8**, along with about 10% of the corresponding deuterio analogue **9** (Scheme 2). Treatment of **7** with acetic acid affords 80% of **9** along with 20% of **8**. These results are clearly inconsistent with protonation of the α-CF bond occurring directly from the common $\eta^2$-HD intermediate **10**, in which complete scrambling of H and D should be facile and from which an identical mixture of **8** and **9** is expected. These observations are consistent with external $H^+$ (or $D^+$) being responsible for protonation of the CF bond and the D (or H) originally present on the metal migrating to form the new C−D (or C−H) bond. The isotopic impurity present in each reaction is consistent with some equilibration, presumably via $\eta^2$-HD intermediate **10**, but this is clearly significantly slower than the rate of protonation at F. The differential amount of isotopic impurity in each reaction is consistent with the expected equilibrium isotope effect[13,14] favoring **6** (with an Ir−H bond) and $CH_3CO_2D$, over **7** (with an Ir−D bond) and $CH_3CO_2H$; consequently, the rate of isotopic leakage from **7** to **6** should exceed the reverse rate.

Kinetic studies under pseudo-first-order conditions[15] indicate that there is at most a very small kinetic isotope effect on this reaction, with the following second-order rate constants $k$ (L mol$^{-1}$ s$^{-1}$) at −30 °C: **6**/$D^+$, [0.95 (±0.04)] × $10^{-3}$; **7**/$H^+$, [1.20 (±0.04)] × $10^{-3}$; **6**/$H^+$, [1.24 (±0.04)] × $10^{-3}$; **7**/$D^+$, [1.13 (±0.04)] × $10^{-3}$. Kinetic data measured over the temperature range from −25 to −40 °C afford values for the free energy of activation $\Delta G^{\ddagger} = 64 \pm 2$ kJ mol$^{-1}$ in each case.

Using stronger acids such as $CF_3SO_3H$ and $CF_3CO_2H$ leads to immeasurably fast rates under these conditions. It seems likely, therefore, that protonation of the CF bond by external acid is rate limiting, with an early transition state perhaps accounting for the negligible isotope effect. In agreement with the observation that H/D scrambling via **10** is considerably slower than protonation of the α-CF bond, the second-order rate constant for H/D exchange to equilibrate pentafluorophenyl complexes **11** and **12**[16] (in which no competitive CF bond activation occurs) is [6.5 (±0.2)] × $10^{-5}$ at 25 °C, and the expected equilibrium isotope effect[13,14] is reflected in the value of $K_{eq} = 2.6$ (±0.2).




**11**




**12**

(10) $Cp^*Ir(CO)_2$ in $CH_2Cl_2$ was treated with $ICHFCF_3$ (1 equiv) for 3 h at 0 °C and an additional 2 h at ambient temperature, to give $Cp^*Ir(CO)(CHFCF_3)I$ (94%); Major isomer (ratio 4:1): $^1$H NMR ($CD_2Cl_2$) δ 2.09 (s, 15H, Cp*), 7.35 (dq, 1H, $^2J_{FH}$ = 46.4 Hz, $^3J_{FH}$ = 10.8 Hz, CHF); $^{19}$F NMR ($CD_2Cl_2$) δ −76.5 (dd, 3F, $^3J_{FH}$ = 10.8 Hz, $^3J_{FF}$ = 15.3 Hz, $CF_3$), −193.9 (dq, 1F, $^2J_{FH}$ = 46.4 Hz, $^3J_{FF}$ = 15.3 Hz, CHF). Minor isomer: $^1$H NMR ($CD_2Cl_2$) δ 2.05 (s, 15H, Cp*), 6.00 (dq, 1H, $^2J_{FH}$ = 47.4 Hz, $^3J_{FH}$ = 10.3 Hz, CHF); $^{19}$F NMR ($CD_2Cl_2$) δ −75.5 (dd, 3F, $^3J_{FH}$ = 10.3 Hz, $^3J_{FF}$ = 15.8 Hz, $CF_3$), −174.2 (dq, 1F, $^2J_{FH}$ = 47.4 Hz, $^3J_{FF}$ = 15.8 Hz, CHF. Anal. Calcd: C, 26.76; H, 2.76. Found: C, 26.69; H, 2.63.

(11) A 1:1 mixture of $Cp^*Ir(CO)(CHFCF_3)I$ and $PMe_3$ in toluene was refluxed for 5 h to give $Cp^*Ir(PMe_3)(CHFCF_3)I$ as an orange solid (71%). Major isomer (ratio 6:1): $^1$H NMR ($CDCl_3$) δ 1.64 (d, 9H, $^2J_{PH}$ = 10.3 Hz, $PMe_3$), 1.89 (d, 15H, $J_{PH}$ = 2.0 Hz, Cp*), 7.05 (dqd, 1H, $^2J_{FH}$ = 46.1 Hz, $^3J_{FH}$ = 11.6 Hz, $^3J_{PH}$ = 3.4 Hz, CHF); $^{19}$F NMR ($CDCl_3$) δ −70.64 (ddd, 3F, $^3J_{FH}$ = 11.6 Hz,$^3J_{FF}$ = 16.0 Hz, $^4J_{PF}$ = 3.7 Hz, $CF_3$), −186.15 (ddq, 1F, $^2J_{FH}$ = 46.1 Hz, $^3J_{FF}$ = 16.0 Hz, $^3J_{PF}$ = 16.0 Hz, CHF); $^{31}$P{$^1$H} NMR ($CDCl_3$) δ −41.0 (d, 1P, $^3J_{PF}$ = 16.0 Hz, $^4J_{PF}$ = 3.7 Hz, $PMe_3$). Minor isomer: $^1$H NMR ($CDCl_3$) δ 1.73 (d, 9H, $^2J_{PH}$ = 10.5 Hz, $PMe_3$), 1.84 (d, 15H, $J_{PH}$ = 2.0 Hz, Cp*), 6.79 (dqd, 1H, $^2J_{FH}$ = 46.2 Hz, $^3J_{FH}$ = 13.0 Hz, $^3J_{PH}$ = 5.5 Hz, CHF); $^{19}$F NMR ($CDCl_3$) δ −69.12 (dd, 3F, $^3J_{FH}$ = 13.0 Hz,$^3J_{FF}$ = 14.3 Hz, $CF_3$), −181.36 (ddq, 1F, $^3J_{FH}$ = 13.0 Hz, $^3J_{FF}$ = 14.3 Hz, $^3J_{PF}$ = 23.3 Hz, CHF); $^{31}$P{$^1$H} NMR ($CDCl_3$) δ −37.0 (d, 1P, $^3J_{PF}$ = 23.3 Hz, $PMe_3$). Anal. Calcd: C, 28.53; H, 3.99. Found: C, 28.83; H, 3.94.

(12) A suspension of $AgOCOCH_3$ in $CH_2Cl_2$ was treated with a solution of $Cp^*Ir(PMe_3)(CHFCF_3)I$ in $CH_2Cl_2$ slowly over a time period of 15 min, followed by stirring for 3 h, filtration, and removal of the solvent to give $Cp^*Ir(PMe_3)(CHFCF_3)(OCOCH_3)$ as a pale yellow solid (96%). Major isomer (ratio 2:1): $^1$H NMR ($C_6D_6$) δ 1.30 (d, 9H, $^3J_{PH}$ = 11.0 Hz, $PMe_3$), 1.33 (d, 15H, $J_{PH}$ = 2.0 Hz, Cp*), 2.26 (s, 3H, $CH_3$), 6.81 (ddq, 1H, $^2J_{HF}$ = 50.1 Hz, $^3J_{HF}$ = 11.8 Hz, $^3J_{PH}$ = 0.7 Hz, HCF); $^{19}$F NMR ($C_6D_6$) δ −69.30 (dd, 3F, $^3J_{FF}$ =14.7 Hz, $^3J_{HF}$ = 11.8 Hz, $CF_3$), −194.26 (ddq, 1F, $^3J_{PF}$ = 38.1 Hz, $^3J_{FF}$ = 14.7 Hz, $^2J_{FH}$ = 50.1 Hz, HCF); $^{31}$P{$^1$H} NMR ($C_6D_6$) δ −31.13 (d, $^3J_{PF}$ = 38.1 Hz, $PMe_3$). Minor isomer: $^1$H NMR ($C_6D_6$) δ 1.20 (d, 9H, $^3J_{PH}$ = 10.8 Hz, $PMe_3$), 1.46 (d, 15H, $J_{PH}$ = 2.2 Hz, Cp*), 2.13 (s, 3H, $CH_3$), 6.47 (ddq, 1H, $^2J_{HF}$ = 45.9 Hz, $^3J_{HF}$ = 11.8 Hz, $^3J_{PH}$ = 7.2 Hz, HCF); $^{19}$F NMR ($C_6D_6$) δ −71.35 (dd, 3F, $^3J_{FF}$ = 14.8 Hz, $^3J_{HF}$ = 12.8 Hz, $CF_3$), −192.82 (ddq, 1F, $^3J_{PF}$ = 19.8 Hz, $^3J_{FF}$ = 14.8 Hz, $^2J_{FH}$ = 45.9 Hz, HCF); $^{31}$P{$^1$H} NMR ($C_6D_6$) δ −28.44 (d, $^3J_{PF}$ = 19.8 Hz, $PMe_3$). Anal. Calcd: C, 36.2; H, 5.01. Found: C, 36.30; H, 5.11.

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(15) In a typical experiment, starting materials were dissolved in methylene chloride at −78 °C, and acetic acid (10−15 equiv) was added. The sample was inserted in the probe at −50 °C, and the temperature was adjusted to the desired temperature for the experiment. Concentrations were monitored using the intensity of the Cp* signals of starting material and product.

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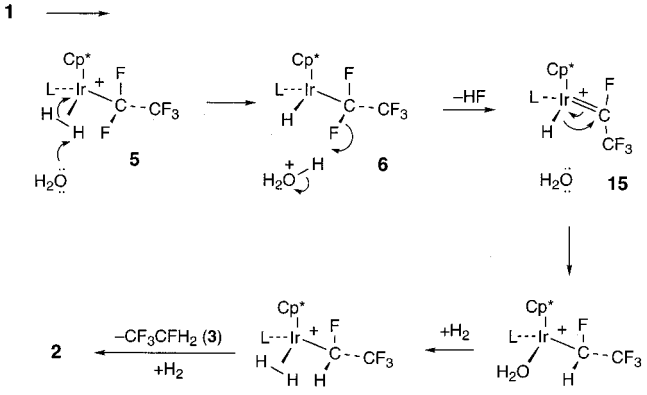
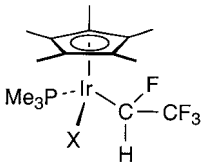
**Scheme 3**[a]




[a] L = $PMe_3$.

Also consistent with these conclusions is the observation that other exogenous fluoride acceptors trigger exactly the same reaction. Treatment of **6** with $Ph_3C^+X^-$ (X = $OT_F$, Cl) leads to formation of the corresponding products **13** and **14**.




**13** X = $CF_3SO_3$
**14** X = Cl

As a result of these experiments, we can now redefine the role of the metal in the originally observed reaction of **1** with $H_2$, as shown in Scheme 3. Binding of $H_2$ to the cationic iridium center of **1** results in displacement of water to give **5**, from which heterolytic activation of $H_2$ occurs to form the neutral iridium hydride **6** and $H^+$, presumably in the form of the $H_3O^+$ cation. C–F activation occurs by protonation of the α-CF bond by external acid[17–20] to produce HF and intermediate **15**, and migration of the hydride ligand to carbon[18,21–23] generates the new CH bond. In the absence of a good coordinating anion, more $H_2$ binds to repeat the process. Now there is an apparent competition between protonation at the Ir–C bond to afford elimination of **3** or protonation at the remaining CF bond to repeat the CF activation process, leading eventually to elimination of **4**. As we have noted previously,[3] it is remarkable that hydride migration in **15** competes to the exclusion of reaction of water with the α-carbon to give a hydrolysis reaction.[24] A similar proton-promoted CF activation in a cationic iridium complex containing a $CF_3$ ligand has been shown to be triggered by heterolytic activation of $H_2$, but hydrolysis to a CO ligand by adventitious moisture is the outcome, rather than the alternatively available H migration.[25]

The origin of the diastereoselectivity in these reactions is less clear. Since the separated diastereomers of **8** are configurationally stable in solution, the mixture of diastereomers is not a result of configurational inversion at iridium after formation of the final product, and is presumably due to some kinetically controlled outcome during the reaction sequence. The nature of the fluoroalkyl group also is important in determining the rate of CF activation; preliminary results indicate that perfluoro-*n*-propyl ligands react more slowly with acetic acid, and perfluoroisopropyl ligands are considerably less reactive. Further studies aimed at elucidating all these additional factors are in progress.

**Acknowledgment.** R.P. H. acknowledges support of this research by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We are also grateful to Professor Richard Eisenberg for an advance copy of his manuscript.[25]

**Supporting Information Available:** Text giving full synthetic and spectroscopic details for all compounds described here. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020225D



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