Hydrogenolysis of Aliphatic Carbon−Fluorine Bonds in Fluoroalkyl−Iridium Complexes to Give Hydrofluorocarbons

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The chemical inertness of saturated perfluorocarbons (PFCs) arises in large part from the strength of the aliphatic C−F bond, the strongest single bond formed by carbon.[1] The stoichiometric and catalytic activation of these normally inert C−F bonds has been the subject of considerable interest among transition metal chemists.[2−4] In contrast to aromatic fluorocarbons for which a variety of functionalization reactions have been reported,[3,5−7] the aliphatic C−F bonds in saturated PFCs have no strong binding site for interaction with a metal center. It is not surprising that reports of their activation reactions with transition-metal centers almost invariably involve the metal acting as a reductant or a catalytic electron shuttle.[8−10] Other strongly reducing conditions using ammonia, alkali metals, metal oxalate salts, and elemental carbon have been reported.[11−14] Nonreducing conditions involving abstraction of fluorine by lanthanide and actinide complexes have also been reported.[15,16] In all of these reactions, the thermodynamic driving force is usually provided by formation of strong metal−fluorine bonds or high lattice energy metal fluorides.[4,13]

While organometallics bearing aliphatic fluoroalkyl groups have been known since the early days of organotransition-metal chemistry,[17−21] the saturated fluoroalkyl chains in these complexes are usually inert. However, the α-fluorines in such compounds are unusually reactive in the presence of strong Lewis acids,[22−26]

Scheme 1
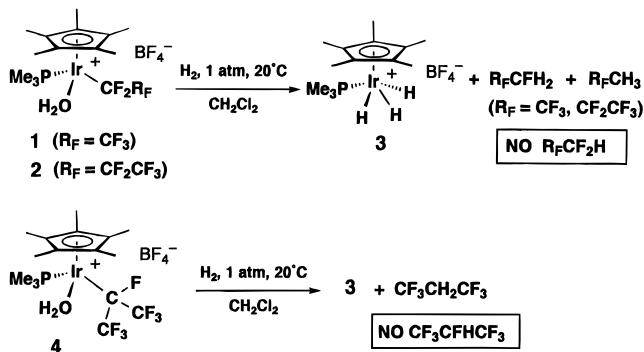
exogenous protic acids,[27−30] or protons from intramolecular water[31,32] as fluoride acceptors; subsequent hydrolysis of the α-CF$_2$ to a ketone or CO occurs, with strong HF and CO bonds providing thermodynamic compensation for breaking the strong CF bonds. Here we report the first examples of hydrogenolysis of the α-CF$_2$ groups in some iridium fluoroalkyls using *dihydrogen under ambient conditions*.

The cationic (aqua)(fluoroalkyl)iridium complexes **1** and **2**[33] can be prepared from the corresponding iodides as previously described for rhodium analogues.[31] Treating methylene chloride solutions of **1** or **2** with dihydrogen results in clean and rapid formation of the known iridium trihydride **3**, whose ^{1}H, ^{19}F, and ^{31}P NMR data are consistent with those previously reported[34,35] and that of an independently prepared sample. The fate of the fluoroalkyl ligand was an approximately 1:1 mixture of two hydrofluorocarbon (HFC) compounds, identified as R$_F$CFH$_2$ and R$_F$CH$_3$ (R$_F$ = CF$_3$, CF$_3$CF$_2$) by ^{19}F NMR spectroscopy.[36] No trace of the monohydrogenated species, CF$_3$CF$_2$H or CF$_3$CF$_2$CF$_2$H were observed. Similarly treatment of the corresponding perfluoroiso-propyl complex **4**[33] with H$_2$ affords only **3** and CF$_3$CH$_2$CF$_3$ with no observable trace of CF$_3$CFHCF$_3$ (Scheme 1). These observations represent, to our knowledge, the first examples of the hydrogenolysis of aliphatic CF bonds in the coordination sphere of a transition metal. Furthermore, the reaction is selective for H$_2$, with no observable hydrolysis of the fluoroalkyl group, even in the presence of the water originally present in the coordination

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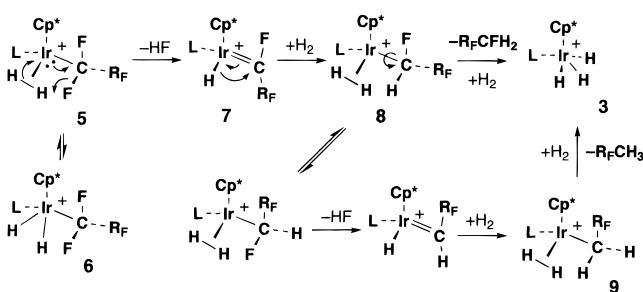(21) Stone, F. G. A. *Endeavour* **1966**, *25*, 33−38.
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(33) **1**; IR (KBr), ν_{OH} = 3422 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.70 (s, 15H, C$_5$Me$_5$); 1.68 (d, J_{PH} = 11 Hz, 9H, PMe$_3$); ^{19}F NMR (CDCl$_3$), δ −82.29 (s, 3F, CF$_3$); −82.22 (d, J_{AB} = 303, 1F, C$_\alpha$F$_A$); −90.10 (d, J_{AB} = 303, 1F, C$_\alpha$F$_B$); −150.33 (s, 4F, BF$_4$); ^{31}P{^{1}H}NMR (CDCl$_3$), δ −23.48 (dd, J_{PF} = 8.0, PMe$_3$). **2**; IR (KBr), ν_{OH} = 3340 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.71 (d, J_{HH} = 2 Hz, 15H, C$_5$Me$_5$); 1.70 (d, J_{PH} = 11 Hz, 9H, PMe$_3$); ^{19}F NMR (CD$_2$Cl$_2$), δ −79.32 (t, J_{FF} = 12, 3F, CF$_3$); −71.96 (m, J_{AB} = 261, 1F, C$_\alpha$F$_A$); −94.96 (m, J_{AB} = 261, 1F, C$_\alpha$F$_B$); −116.40 (m, 2F, C$_\beta$F$_2$); −149.67 (s, 4F, BF$_4$); ^{31}P{^{1}H}NMR (CD$_2$Cl$_2$), δ −21.71 (br s, PMe$_3$). **4**; IR (KBr), ν_{OH} = 3442 cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$), δ 1.66 (dd, J_{PH} = 11 Hz, J_{HF} = 2 Hz, 9H, PMe$_3$); 1.61 (s, 15H, C$_5$Me$_5$). ^{19}F NMR (CD$_2$Cl$_2$), δ −69.91 (s, 6F, CF$_3$); −149.56 (s, 4F, BF$_4$); −180.50 (s, 1F, CF). ^{31}P{^{1}H}NMR (CD$_2$Cl$_2$), δ −69.90 (br s, PMe$_3$) Satisfactory microanalysis data were obtained for all new compounds.
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Scheme 2[a]

[a] (L = PMe₃).

sphere. The HFC products themselves are of unusual interest; CF_3CFH_2 (HFC-134a) is the replacement refrigerant for CF_2Cl_2 (CFC-12),[37,38] and similar HFCs are used as inhalation anesthetics.[39]

Our working mechanistic hypothesis is shown in Scheme 2. Dihydrogen is known to displace H_2O from a variety of metal centers;[40] analogous reaction here would afford **5**, which may be in equilibrium with its dihydride tautomer **6**. The dihydrogen complex is likely to have the more acidic H[41−46] and can play a role analogous to that of intramolecular water in the previously reported hydrolysis reactions.[31,32] Protonation of an α-CF with loss of HF afford the alkylidene(hydride) **7**; such fluoroalkylidene complexes are known to undergo facile migration of H to C,[28,47−49] and coordination of more H_2 affords **8**, which either reductively eliminates R_FCFH_2 at this stage or undergoes a second α-CF activation with loss of HF to give **9**. Subsequent H migration, H_2 coordination, and elimination from **9** affords R_FCH_3; incorporation of the third molecule of H_2 converts the cationic iridium center to the observed trihydride **3**. We hypothesize that no elimination of R_FCF_2H occurs from intermediate **5**, because the M-CF_2R_F bond is too strong; however once partial replacement of F by H has occurred, elimination from **8** or **9** is considerably more facile. Support comes from experimental[50] and theoretical[51,52] studies

which indicate that perfluoroalkyl−metal bonds are indeed stronger than those of hydrocarbon analogues or partially fluorinated alkyls.[51] Furthermore, thermal reductive elimination from $CF_3CH_2(H)Pt$ complexes has been shown to be facile,[53] but, in contrast to the photochemical reductive elimination of CF_3H from a $CF_3(H)Pt$ complex,[54] corresponding thermal elimination from the same complex has not been observed.[55] We cannot exclude a mechanism involving α−F elimination as a prelude to elimination of HF directly from the metal; equilibria between trifluoromethyl and difluoromethylene(fluoride) complexes have been reported recently.[47]

The hydrogenolysis manifold shown in Scheme 2 can be entered by generating the putative intermediate **5** in another way. Complex **2** reacts with 1,8-bis(dimethylamino)naphthalene (Proton Sponge)[56] in a beautifully clean and quantitative reaction with loss of H_2O, and generation of the fluoroalkyl(hydride) complex **10**,[57] along with the known organic product **12**.[58] This represents
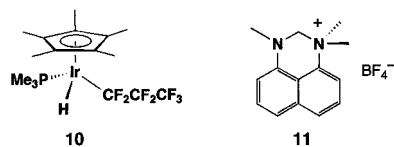
an unusual, but not unprecedented,[58] instance of Proton Sponge acting not as a base, but as a formal hydride donor. In agreement with our hypothesis, **10** shows no sign of reductive elimination of R_FCF_2H at temperatures up to 150 °C, at which point it decomposes to afford a library of volatile organics sufficiently diverse that we have not attempted to penetrate it. Complex **10** does not react with H_2 alone, but protonation using triflic acid rapidly affords the triflate salt of **3** and the same mixture of HFCs $CF_3CF_2CFH_2$ and $CF_3CF_2CH_3$, presumably via initial formation of **5**.

In summary, introduction of dihydrogen cis to a perfluoroalkyl ligand in these cationic iridium complexes results in hydrogenolysis and elimination of perfluoroalkyl ligands as useful HFCs. This new reactivity of perfluoroalkyl ligands may be general, and preliminary experiments indicate that similar chemistry can be achieved with analogous cobalt complexes.[59] This chemistry potentially opens the way to mild synthesis of environmentally friendly hydrofluorocarbons. Further mechanistic studies are in progress.

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