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Organometallic Transformations Demonstrate That Fluorocarbons Are Reactive Molecules

Thomas G. Richmond*

Fluorine forms the strongest single bond to carbon. The great strength of this bond, along with the small size and high electronegativity of fluorine, conspire to give rise to the unusual properties associated with highly fluorinated organic molecules.[1] Indeed, the most characteristic chemical property of fluorocarbons is their *lack* of reactivity. The stability imparted by the C–F bond leads to the long atmospheric lifetimes of chlorofluorocarbons (CFCs); saturated perfluorocarbons (PFCs) are even more stable, with CF_4 having an estimated stratospheric lifetime of more than 10000 years.[2]

The unique properties of fluorinated groups have long been exploited by organometallic chemists to stabilize unusual molecules and provide a benchmark for comparisons with analogous hydrocarbon ligands.[3, 4] Current activity has focused on the preparation of highly fluorinated ligands that contain "fluorous ponytails". These "ponytails" impart solubility in PFC solvents, a property which is necessary for application in "fluorous" biphase chemistry.[5] This technique exploits the unusual solubility properties of PFCs to address the technologically important problem of the separation of PFC-containing catalysts or reagents from hydrocarbon-soluble products. Clearly the success of this strategy requires that the PFC phase remains inert under the reaction conditions. This article will trace recent developments in the reaction chemistry of saturated PFCs and PFC ligands in organometallic complexes with an emphasis on how organometallic reagents enable transformations to be performed under remarkably mild conditions.[6]

The advances in the reaction chemistry of totally saturated PFCs and CFCs with special focus on the defluorination chemistry were summarized by Saunders in 1996.[7] Strong reducing agents mineralize PFCs and CFCs but partial and selective C–F activation has been achieved under homogeneous conditions with the sodium benzophenone radical anion or with cobaltocene in the presence of lithium trifluoromethanesulfonate.[8] Metal – organic electron donors have been applied to the synthesis of organofluorine compounds (Scheme 1).[9]

Catalytic defluorination chemistry has been achieved utilizing early transition metallocenes ($[Cp_2TiF_2]$, $[Cp_2ZrCl_2]$)

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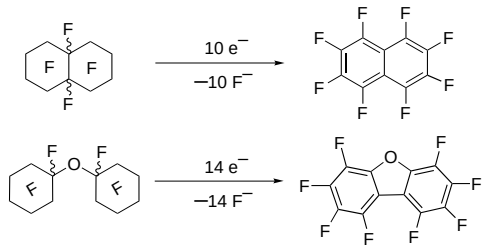
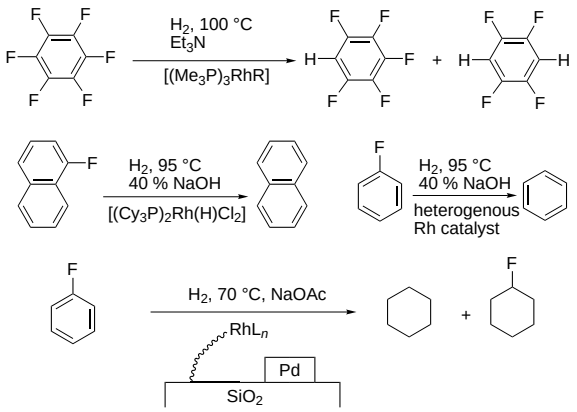


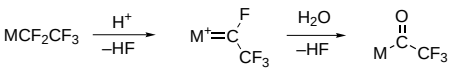
Scheme 1. Examples of reductive defluorination chemistry applied to the synthesis of perfluoroaromatics.

and amalgamated aluminum or magnesium as the final reductant.[10] Crabtree and co-workers developed a photochemical defluorination system based on decamethylferrocene and pioneered PFC functionalization chemistry utilizing gas-phase Hg-sensitized photolysis in the presence of ammonia.[11] All of these reactions (with the exception of a $[Cp_2ZrCl_2]$/Mg/Hg system,[10] which reduces perfluorocyclohexane to 1,2,4,5-tetrafluorobenzene) exploit the enhanced reactivity of tertiary C–F bonds, which has been termed the "Achilles Heel" of perfluorocarbons, to initiate reductive defluorination.[12] The common theme in these defluorination transformations is electron transfer in the presence of a Lewis acidic metal cation. Simple hydrogenation of a PFC (either free or as part of a ligand) under mild conditions was unknown until the report by Hughes and Smith (ref. [16]) discussed below. In contrast, significant progress has been made in the hydrogenolysis of aromatic C–F bonds in both homogeneous and heterogeneous systems, including some examples of catalytic hydrogenation (Scheme 2).[13]



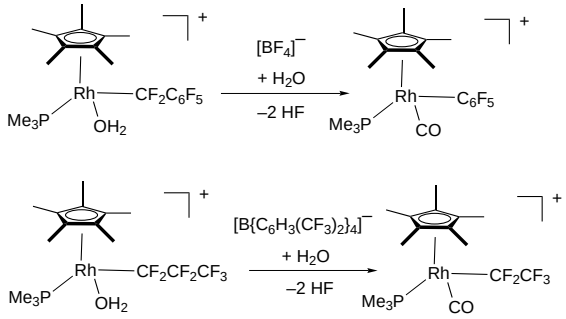
Scheme 2. Hydrogenolysis of aromatic C–F bonds with H_2.

An important exception to the inert nature of perfluorocarbon ligands is the Lewis or proton acid enhanced hydrolysis of α-fluorine atoms made thermodynamically feasible by the formation of strong C–O and H–F bonds and kinetically accessible by the stabilization of a carbene intermediate by the transition metal [Eq. (1)].[14]



(1)

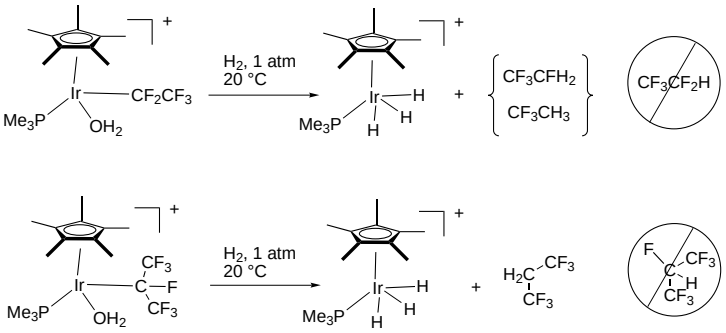
Hughes and co-workers recently illustrated the subtle nuances of this reaction in a series of cationic rhodium(III) complexes in which coordinated water is demonstrated to be sufficiently acidic to hydrolyze the α-fluorines of a perfluorobenzyl group into HF and coordinated CO (Scheme 3).[15]



Scheme 3. Hydrolysis of α-carbon–fluorine bonds activated by a rhodium(III) center.

The enhanced activity of coordinated water is demonstrated by the absence of reactivity in acetone, which displaces the water ligand. To effect the same transformation in the less reactive perfluoropropyl system, the non-hydrogen-bonding ion $[B(3,5\text{-}(CF_3)_2C_6H_3)]^-$ is required to enhance the activity of the bound water. In addition to the unusually mild conditions for C–F hydrolysis, this work provides evidence that coordination to a metal center enhances the reactivity of water and this activity can be influenced by the hydrogen-bonding properties of the counterion.

Treatment of the analogous iridium(III) complexes with hydrogen (1 atm) at room temperature results in a facile hydrogenolysis of the α-CF_2 group and the production of hydrofluorocarbons (CF_3CFH_2 and CF_3CH_3 in an approximate 1:1 mixture), and the known iridium trihydride as illustrated for the pentafluoroethyl compound (Scheme 4).[16]



Scheme 4. Production of HCFCs by hydrogenolysis of with H_2 at an iridium(III) center.

Interestingly, the reaction is selective for H_2 and no hydrolysis products are detected despite the presence of the aqua ligand in the iridium complex. A series of reactions consistent with the absence of mono-hydrogen containing products is given in Scheme 5.

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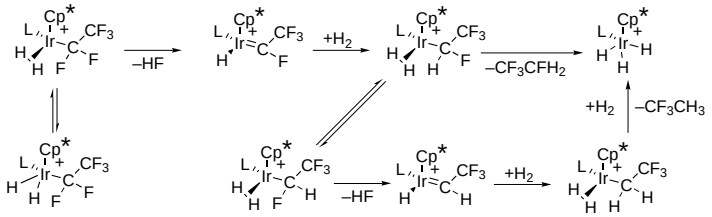
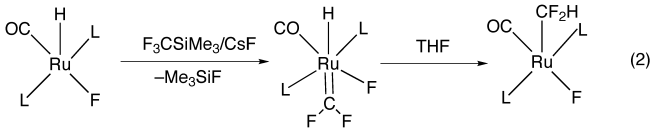


Scheme 5. Mechanistic scheme for the hydrogenolysis of perfluoroalkyl groups at an iridium(III) center ($Cp^* = C_5Me_5$).

The substitution of water by H_2 generates an η^2-dihydrogen complex; the η^2-H_2 ligand is known to be more acidic than coordinated water and this increase in acidity is sufficient to cause HF elimination and the generation of a carbene intermediate. Reductive elimination, which might be anticipated from the classical dihydride complex, is not favored because of the stability of the iridium–perfluoroalkyl bond. This hypothesis was confirmed by the independent generation of the complex $[Cp^*Ir(PMe)_3(H)(CF_2CF_2CF_3)]$ which proved to be stable to reductive elimination up to 150 °C. Importantly, protonation of this complex in the presence of H_2 affords hydrofluorocarbon species that are analogous to those in Scheme 4. Production of CF_3CH_3 suggests that hydrogenolysis of the second C–F bond competes with the reductive elimination process. An alternative mechanism which involves α-fluoro migration to the iridium center and leads to the loss of HF from the metal cannot be eliminated. Caulton and Huang have demonstrated that there is an equilibrium between Ru–CF_3 and Ru(F)(CF_2) bonding modes and that the latter species provides an example of the hydrogenolysis of a C–F bond [Eq. (2)].[17]



(2)

Note that this transformation involves the net replacement of F by H in a trifluoromethyl group. A related α-fluoro migration is important in nickel(0)-mediated transformations of perfluoroalkyl iodides.[18]

Organometallic complexes provide a versatile basis for the discovery of new reaction chemistry of fluorocarbons.[6] The work of Hughes and co-workers is particularly significant because it demonstrates how σ-coordination (M–CF_2R_F) of a fluorocarbon to a metal center can not only activate α-C–F bonds but also the relatively meek reagents (water and hydrogen). These reagents participate in the C–F bond activation that results in the synthesis of hydrofluorocarbons. Significant progress has been noted in the chemistry of highly fluorinated aromatics; this includes recent reports that range from the oligomerization of hexafluorobenzene initiated by the thermolysis of $[Cp_2Zr(C_6F_5)_2]$ to the $Ni^{(0)}$-assisted defluorination of 2,4,6-trifluoropyrimidine to prepare new pyrimidine and pyrimidinone derivatives.[19] The use of electron-rich metal centers (as well as strong organic electron donors) to mediate reductive defluorination of PFCs is now complemented by the possibility of the mild and selective reduction of PFCs by molecular hydrogen. Significant challenges remain on the way to the true catalytic functionalization (in this instance partial hydrogenation) of PFCs. Activation of PFCs by C–F oxidative addition to a transition metal as a means of entry into the hydrogenation manifold as described above has yet to be achieved. The exceptionally poor coordinating ability of PFCs ($M \leftarrow FCR_n$) mitigates against C–F activation.[20] Both technologies should prove applicable in the synthesis of fluorine-containing molecules (including hydrofluorocarbons) to replace CFCs and to aid the understanding of the scope and limitations of catalytic chemistry in the fluorous phase.

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