Reductive Defluorination of Saturated Perfluorocarbons by Organometallic Nucleophiles[†]

Roger G. Harrison and Thomas G. Richmond*

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

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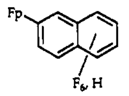
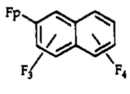
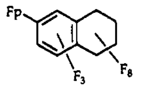
Saturated perfluorocarbons are remarkably resistant to chemical attack by most reagents. For example, recent estimates place the atmospheric lifetime of perfluorocarbons at greater than 2000 years.[1] These substrates provide a challenge for synthetic chemists akin to that of saturated hydrocarbons where significant progress in the activation and functionalization of C–H bonds has been made by organometallic chemists over the past decade.[2] Nearly all examples[3] of well-defined C–F activation by transition-metal complexes noted to date have involved unsaturated or aromatic substrates.[4] In this communication, we report that Fp^-[Fp = $CpFe(CO)_2$] can defluorinate perfluoromethylcyclohexane and perfluorodecalin at or below room temperature and that iron-bound fluorinated aromatic compounds can be isolated from these reactions. Our work was prompted by recent reports concerning reactivity exhibited by these substrates with arenethiolate nucleophiles[5] and with organic electron donors under ultraviolet irradiation.[6] Of particular relevance is the selective reduction of perfluorodecalin to perfluoronaphthalene noted by Pez and coworkers upon treatment with sodium benzophenone ketyl in THF.[7] Although high-temperature metal-catalyzed defluorination of these substrates is used in the synthesis of perfluoroaromatics,[8] these are the first reported reactions of transition-metal organometallic reagents with saturated fluorocarbons in homogeneous solution.[9]

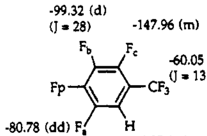
A solution of 1.0 mmol of perfluorodecalin ($C_{10}F_{18}$) and 6.0 mmol of NaFp was prepared in THF solution at –78 °C, and an IR spectrum recorded after 15 min at room temperature showed that all the anion had reacted and Fp_2 was detected as the dominant organometallic product. Weaker bands (ν_{CO} = 2032, 1982 cm^{-1}) consistent with FpR products,[10] where R represents organic fragments derived from perfluorodecalin, were also evident. Unreacted $C_{10}F_{18}$ (0.50 mmol quantified by GC) was removed under vacuum, and 0.20 g of yellow FpR (ca. 0.4 mmol, 90% based on $C_{10}F_{18}$) and 2.2 mmol of Fp_2 (73% yield based on iron) were isolated by chromatography on silica. Although full spectroscopic characterization of the FpR products has not yet been achieved because of separation difficulties, mass spectral analysis confirms the presence of a minimum of three products as depicted below. Extraction of the residue into aqueous solution gave 4.8 mmol of fluoride (53% yield based on $C_{10}F_{18}$) as quantified with a fluoride-ion-sensitive electrode and confirmed by ^{19}F NMR spectroscopy.







Although the above reaction clearly demonstrates that Fp^- can reductively defluorinate and aromatize $C_{10}F_{18}$, we further explored this chemistry with perfluoromethylcyclohexane ($C_6F_{11}CF_3$) in hope of obtaining simpler organometallic products which could be more fully characterized. In 40 mL of THF, 6.0 mmol of NaFp was treated with 1.0 mmol of $C_6F_{11}CF_3$, and after 4 h at room temperature the following products were obtained: 0.26 mmol of unreacted $C_6F_{11}CF_3$, 2.1 mmol of Fp_2, 4.5 mmol of fluoride ion, and 86 mg (ca. 0.23 mmol, 31% based on $C_6F_{11}CF_3$) of **1–3** isolated as a yellow oil. Proposed structures with ^{19}F ($\delta(CCl_3F)$ and *J* in Hz) and ^1H NMR spectroscopic data are shown below.



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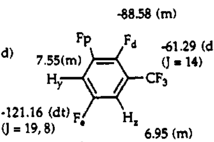

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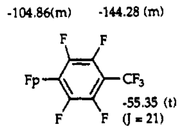

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Compound **1** (ν_{CO} = 2306, 1991 cm^{-1}) typically represents 80% of this mixture as determined by ^{19}F NMR spectroscopy, although more **2** is obtained with higher $Fp^-/C_6F_{11}CF_3$ ratios. Compound **3** previously has been prepared by King and Bisnette[10] by treatment of Fp^- with perfluorotoluene. The molecular formulas of **1** and **2** were confirmed by high-resolution exact mass measurements.[11] Assignment of the stereochemistry of **1** is based on the observation of two distinct resonances in the ^{19}F NMR spectrum (δ –80.78 F_a (dd), –99.32 F_b (d)) which are deshielded by the Fp substituent, along with a doublet for the CF_3 at δ –60.05 coupled to F_c (δ –147.96, m). The magnitudes of the coupling constants, decoupling experiments, and spin simulations are also consistent with these assignments. A highly coupled multiplet is observed for the aromatic hydrogen in **1**, and the cyclopentadienyl resonance appears at δ 5.24. The aromatic proton in **1** results from hydrogen atom abstraction from THF (deuterium incorporation was observed in THF-d_8). In the case of **2**, F_d is observed as a multiplet arising from coupling to F_e, and the CF_3 group and F_e is an apparent doublet of triplets coupled to F_d, H_y, and H_z. Hydrogen abstraction from solvent is well precedented[12] in the reaction chemistry of fluoroaromatics with excess Fp^- and probably accounts for the formation of **2**.

Transition-metal nucleophiles have long been known to displace fluoride from highly fluorinated arenes and alkenes to afford metal arene[10] and vinyl complexes, respectively.[13] This work provides the first examples of such reactivity with saturated

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[†] Dedicated to Professor Robert W. Parry: teacher, friend, and colleague.

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perfluorocarbons. Perfluoromethylcyclohexane was found to react with Na/Ph_2CO but overreduction and complete defluorination to carbon occurred.[7] The less reducing Fp^- reagent thus affords some selectivity in these reactions compared to simple alkali metal/organic radical anion reducing agents. Aside from the photochemical process,[6] a tertiary C–F bond appears to be required for productive reaction chemistry, and the formation of aromatic products is also crucial in defining the above reactivity patterns. Electrochemical measurements suggest that initial reduction of tertiary fluorocarbons is more facile than for secondary systems.[7,14] Accordingly, perfluorocyclohexane does not appear to react with Fp^- although some Fp_2 was detected, probably as a result of reaction with perfluoromethylcyclopentane impurities in commercial samples of perfluorocyclohexane.[15] Of several other organometallic nucleophiles studied, $[Re(CO)_5]^-$ slowly reacted with perfluorodecalin to afford $Re_2(CO)_{10}$ and fluoride ion, but the weaker nucleophile $[CpMo(CO)_3]^-$ did not. This trend in reactivity corresponds with the reducing power of the organometallic anion[16] and is consistent with single electron transfer to the fluorocarbon as the first step in the reaction mechanism. Initial activation of the fluorocarbon appears to be the slow step in these reactions since unreacted starting material can be recovered in these reactions with subsequent defluorination and formation of the aromatic products as rapid events. Mechanistic studies on this intriguing transformation are in progress.

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