Selective room temperature hydrogenolysis of aromatic fluorocarbons mediated by a low-valent zirconium complex

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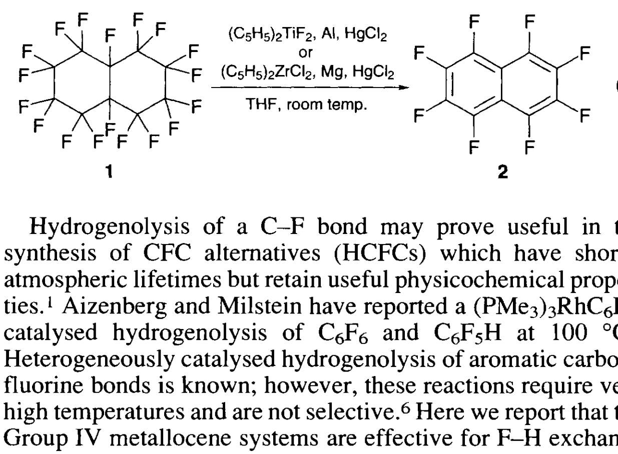
Treatment of fluorinated aromatic compounds with $(C_5H_5)_2ZrCl_2$, $HgCl_2$, Mg or $(C_5H_5)_2ZrCl_2$, PMe_3, Mg results in selective room temperature hydrogenolysis of aromatic C–F bonds.

The selective functionalization of highly fluorinated organic molecules is challenging because of the great strength of the carbon–fluorine bond. The lack of chemical reactivity exhibited by fluorocarbons has frequently been exploited in useful technological and medical applications.[1] Unfortunately, this chemical inertness also translates into environmental persistence since these compounds are quite difficult to degrade.[1]

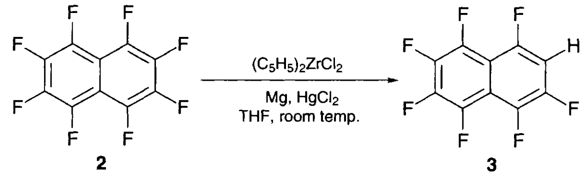
We have been interested in the development of transition metal catalysts for the activation and functionalization of C–F bonds.[2] Whereas several reports from our group and others have demonstrated that a variety of organometallic complexes are capable of promoting stoichiometric C–F bond activation under mild conditions,[3] only recently has homogeneous catalytic C–F bond activation in saturated perfluorocarbons been noted. In this latter chemistry, low-valent titanocene and zirconocene complexes serve as catalysts in the synthesis of octafluoronaphthalene **2** from perfluorodecalin **1** in the presence of amalgamated aluminum or magnesium which serve as the terminal reductant [eqn. (1)].[4]



(1)

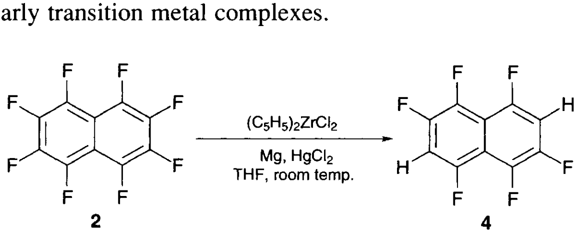
Hydrogenolysis of a C–F bond may prove useful in the synthesis of CFC alternatives (HCFCs) which have shorter atmospheric lifetimes but retain useful physicochemical properties.[1] Aizenberg and Milstein have reported a $(PMe_3)_3RhC_6F_5$-catalysed hydrogenolysis of C_6F_6 and C_6F_5H at 100 °C.[5] Heterogeneously catalysed hydrogenolysis of aromatic carbon–fluorine bonds is known; however, these reactions require very high temperatures and are not selective.[6] Here we report that the Group IV metallocene systems are effective for F–H exchange in aromatic fluorocarbons. This work provides the first examples of selective room temperature hydrogenolysis of strong aromatic C–F bonds by a soluble transition metal complex.

As depicted in eqn. 2, reaction of 0.66 mmol octafluoronaphthalene **2** with 0.46 mmol $(C_5H_5)_2ZrCl_2$ with Mg (9.47 mmol)–$HgCl_2$ (0.48 mmol) as the terminal reductant in THF at room temperature for 2 h affords 1,3,4,5,6,7,8-heptafluoronaphthalene **3** in 97% yield (0.44 mmol).† Deuterium incorporation in **3** from [$^2H_8$]THF indicates that the solvent is the proton source. Control experiments demonstrate that **2** does not exhibit any reactivity with activated magnesium in the absence of the metallocene. Interestingly, compound **2** was found to react with excess sodium benzophenone radical anion, but complete defluorination to carbon and fluoride ions occurred.[8]



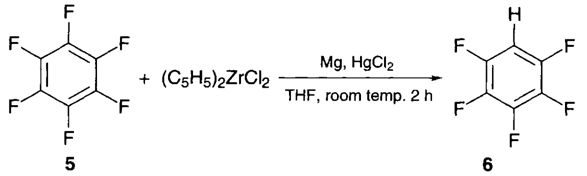
(2)

Prolonged reaction times (13 h) result in multiple F–H exchanges to generate 1,3,4,5,7,8-hexafluoronaphthalene **4**[7] as the only observable product as illustrated below in eqn. 3. The formation of compound **4** suggests that the hydrogenolysis process is highly regioselective although a small amount (less than 5%) of the 1,3,4,5,6,8-hexafluoronaphthalene isomer is observed. Similar selectivities are observed in classical nucleophilic displacement reactions of polyfluoroaromatic compounds.[7] The facile scission of the C–F linkage in preference to the C–H bond in **3** is interesting. However, this selectivity might be rationalized if one considers the known fluorophilicity of early transition metal complexes.



(3)

This chemistry is also useful for the functionalization of polyfluorobenzene compounds. For example, reaction of **5** (0.69 mmol) with 0.47 mmol $(C_5H_5)_2ZrCl_2$ in the presence of Mg (9.63 mmol), $HgCl_2$ (0.49 mmol) as the terminal reductant for 2 h at room temperature quantitatively affords pentafluorobenzene **6** in 93% yield (0.44 mmol) as determined using ^{19}F NMR spectroscopy[9] and confirmed by comparison with a commercial sample [eqn. (4)]. As above, deuterium incorporation was observed in [$^2H_8$]THF. Moreover, extended reaction times (24 h) result in the production of 1,2,4,5-tetrafluorobenzene.[9] Importantly, hexafluorobenzene does not exhibit any reactivity with activated magnesium in the absence of metallocene and Na–Ph_2CO does not react with this substrate.



(4)

Although the above chemistry clearly demonstrates the crucial role of the metallocene in the hydrogenolysis reaction we were concerned about environmental complications prompted by the presence of mercury in the reaction mixture. Thus, it is significant that the transformations illustrated in eqns. 2–4 can also be accomplished by treatment of the fluoroaromatic compounds with $(C_5H_5)_2ZrCl_2$ in the presence of magnesium and excess trimethylphosphine. Rausch and co-workers[10] have shown that $(C_5H_5)_2Zr(PMe_3)_2$, generated from the reduction of $(C_5H_5)_2ZrCl_2$ with magnesium in THF in the presence of PMe_3, serves as a versatile source of '$(C_5H_5)_2Zr$.' Importantly, the aromatic fluorocarbons do not exhibit any reaction chemistry with magnesium and/or trimethylphosphine in the absence of the metallocene.

Although an electron-transfer pathway cannot be ruled out, an attractive mechanistic rationale consistent with the above results would involve the formal oxidative addition of the aromatic carbon-fluorine bond at a low-valent '$(C_5H_5)_2Zr$' followed by rapid homolytic cleavage of the Zr–C bond (in the presence of added reductant) and abstraction of H from the THF solvent by the resulting pentafluorophenyl radical. The oxidative addition of 2-haloalkenes to '$(C_5H_5)_2Zr$' has recently been demonstrated.[11] Radical-based hydrogen fluorine exchange using $(C_5H_5)_3UCMe_3$ has been noted by Andersen and Bergman.[12] Consistent with this mechanism is the important observation that the related pentafluorophenyl titanium complexes $(C_5H_5)_2Ti(C_6F_5)F$ and $(C_5H_5)_2Ti(C_6F_5)_2$, afford pentafluorobenzene upon treatment with Mg, $HgCl_2$.

We have shown that low-valent zirconocene species can mediate the hydrogenolysis of strong aromatic C–F bonds at room temperature. Coupled with our group's existing defluorination chemistry, this hydrogenolysis process should allow for the development of metal-based catalysts capable of effecting the hydrogenation of halocarbons.

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Footnote

† All new compounds exhibited satisfactory GC/MS and NMR data in accord with their assigned structures. Known compounds were identified by comparison of their ^{19}F NMR spectra to commercial samples. Yields were determined by ^{19}F NMR using added C_6H_5F as an internal standard with $CFCl_3$ as the external reference at δ 0.00.

References

1 *Organofluorine Chemistry: Principles and Commercial Applications*, ed. R. E. Banks, B. E. Smart and J. C. Tatlow, Plenum, New York, 1994; M. Hudlicky and A. E. Pavlath, *Chemistry of Organic Fluorine Compounds II. A Critical Review*, ACS Monograph 187, Washington DC, 1995 and references cited therein.

2 For a comprehensive review of C–F activation by metal reagents see: J. L. Kiplinger, T. G. Richmond and C. E. Osterberg, *Chem. Rev.*, 1994, **94**, 373.

3 For recent examples of C–F activation processes employing transition metal complexes: B. K. Bennett, R. G. Harrison and T. G. Richmond, *J. Am. Chem. Soc.*, 1994, **116**, 11 165; J. Burdeniuc, W. Chupka and R. H. Crabtree, *J. Am. Chem. Soc.*, 1995, **117**, 10 119.

4 J. L. Kiplinger and T. G. Richmond, *J. Am. Chem. Soc.*, 1996, **118**, 1805.

5 M. Aizenberg and D. Milstein, *Science*, 1994, **265**, 359; M. Aizenberg and D. Milstein, *J. Am. Chem. Soc.*, 1995, **117**, 8674.

6 R. E. Florin, W. J. Pummer and L. A. Wall, *J. Res. Natl. Bur. Stand.*, 1959, **62**, 119; M. Hudlicky, *Chemistry of Organic Fluorine Compounds*, 2nd edn., Wiley, New York, 1976, pp. 174–178.

7 R. K. Atwal and R. Bolton, *Aust. J. Chem.*, 1987, **40**, 241; R. Bolton and J. P. B. Sandall, *J. Chem. Soc., Perkin Trans. 2*, 1978, 746.

8 J. A. Marsella, A. G. Gilicinski, A. M. Coughlin and G. P. Pez, *J. Org. Chem.*, 1992, **57**, 2856.

9 C. H. Dungan and J. R. van Wazer, *Compilation of Reported ^{19}F NMR Chemical Shifts*, Wiley, New York, 1970.

10 L. B. Kool, M. D. Rausch, H. G. Alt, M. Herberhold, B. Honold and U. Thewalt, *J. Organomet. Chem.*, 1987, **320**, 37.

11 T. Takahashi, M. Kotora, R. Fischer, Y. Nishihara and K. Nakajima, *J. Am. Chem. Soc.*, 1995, **117**, 11 039.

12 M. Weydert, R. A. Andersen and R. G. Bergman, *J. Am. Chem. Soc.*, 1993, **115**, 8837.

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