

Cobaltocenium Fluoride: A Novel Source of "Naked" Fluoride Formed by Carbon–Fluorine Bond Activation in a Saturated Perfluorocarbon[†]

Brian K. Bennett, Roger G. Harrison, and Thomas G. Richmond*

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

Received May 31, 1994

There continues to be considerable interest in the generation of highly nucleophilic sources of fluoride, often termed "naked" fluoride,¹ for applications in organic² and inorganic synthesis.³ Most approaches involve synthesis of elaborate counterions⁴ followed by ion exchange or reaction with HF and appropriate drying procedures.^{5–7} Although saturated perfluorocarbons are normally chemically inert, recent studies in our lab⁸ as well as by others⁹ have identified several modes of reactivity for these substrates.¹⁰ In this work we report that perfluorodecalin affords a novel source of fluoride ion upon treatment with the one-electron reductant cobaltocene. The resulting cobaltocenium fluoride salt provides a useful source of anhydrous fluoride ion, which is capable of providing nucleophilic fluoride for chloride metathesis with a variety of organic and inorganic substrates.

Treatment of an excess of perfluorodecalin (dried by distillation from P₂O₅) with Cp₂Co (Cp = C₅H₅) in toluene solution for 4 h at room temperature under a nitrogen atmosphere results

in precipitation of an extremely hygroscopic greenish yellow solid, which was isolated in 96% yield after filtration and washing with THF. The thermally sensitive powder (mp 78–90 °C dec) is identified as [Cp₂Co]F on the basis of its reaction chemistry and spectroscopic properties. Although this powder is stable for more than 1 week at –10 °C, partial decomposition to a purple solid is evident after 6 h at room temperature. A 1953 reference by Fischer and Jira to aqueous solutions of [Cp₂Co]F appears to be the only mention of this material in the chemical literature.¹¹ Fluoride ion analysis of [Cp₂Co]F using an ion-sensitive electrode gave a 1.02:1 ratio of fluoride: cobaltocenium ions.¹² Essentially quantitative adduct formation is observed upon treatment with inorganic Lewis acids such as BF₃·OEt₂ or SO₂ to afford the known [Cp₂Co][BF₄]¹³ and previously unknown [Cp₂Co][FSO₂]¹⁴ salts. For comparison purposes, [Cp₂Co][HF₂] was prepared by ion exchange (Dowex 1-X8 anion exchange resin charged with [HF₂][–]) in acetonitrile with [Cp₂Co]Cl followed by recrystallization from CH₂Cl₂/Et₂O. This brilliant yellow salt is also hygroscopic but, in contrast to a published report,¹⁵ is thermally stable and exhibits the expected ¹H (δ 16.1 (t), ¹J_{HF} = 121 Hz, HF₂[–]; δ 5.83 (s), C₅H₅) and ¹⁹F (δ –153.6 (d), ¹J_{HF} = 121 Hz) NMR spectroscopic signals in CD₂Cl₂.¹⁶ In contrast to [Cp₂Co]F, [Cp₂Co][HF₂] does not react with SO₂. Due to the reactive nature of the fluoride ion, spectroscopic samples of [Cp₂Co]F usually contained about 25% bifluoride ion¹⁷, but the dominant signal in the ¹⁹F NMR spectrum in CD₂Cl₂ at –10 °C appeared as a broad singlet (ν_{1/2} = 28 Hz) at δ –110 ppm and is assigned to fluoride ion. The bifluoride signal in this sample is sharp, with ¹J_{HF} coupling observed in both the ¹H and ¹⁹F NMR spectra, so exchange with fluoride is slow on the NMR time scale. The fluoride resonance is about 13 ppm upfield of the fluoride signal observed for [Me₄N]⁺[F[–]] in this solvent, perhaps as a consequence of interaction with the cobaltocenium fragment.⁵ The cyclopentadienyl proton resonance (δ 5.77 ppm) is also broad but is consistent with the [Cp₂Co]⁺ group. Addition of water sharpens the cyclopentadienyl peak, presumably by sequestering the fluoride by hydrogen bonding and reaction to form bifluoride. Low-temperature NMR measurements failed to resolve additional spectroscopic features, but ion pairing or even a cobalt–fluoride covalent bond with concomitant cyclopentadienyl ring slippage¹⁸ cannot be ruled out on the basis of the available data. However, the low solubility of the material in solvents such as THF and the measured molar conductances of 98 S cm^{–1} mol^{–1} in CH₃CN and 36 S cm^{–1} mol^{–1} in CH₂Cl₂ argue for an ionic formulation.¹⁹ Similarly, the properties of this material are inconsistent with an η⁴-fluorocyclopentadiene²⁰ formulation.

[†] Dedicated to Professor Fred Basolo on the occasion of his 75th birthday.

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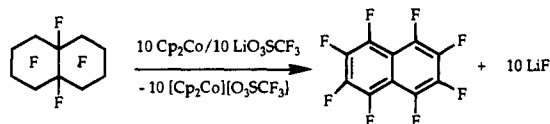
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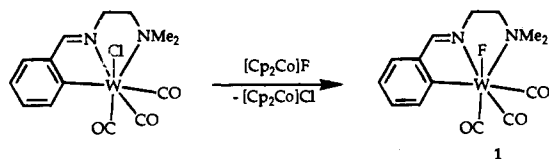
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Although the fate of the perfluorodecalin under the synthetic conditions described above has not yet been determined, treatment of $C_{10}F_{18}$ with 10 equiv of Cp_2Co in the presence of 10 equiv of $Li[O_3SCF_3]$ to scavenge the $[Cp_2Co]F$ byproduct provides a convenient synthetic route to perfluoronaphthalene,²¹ which was obtained in 53% isolated yield after a 12 h reaction in Et_2O at room temperature.

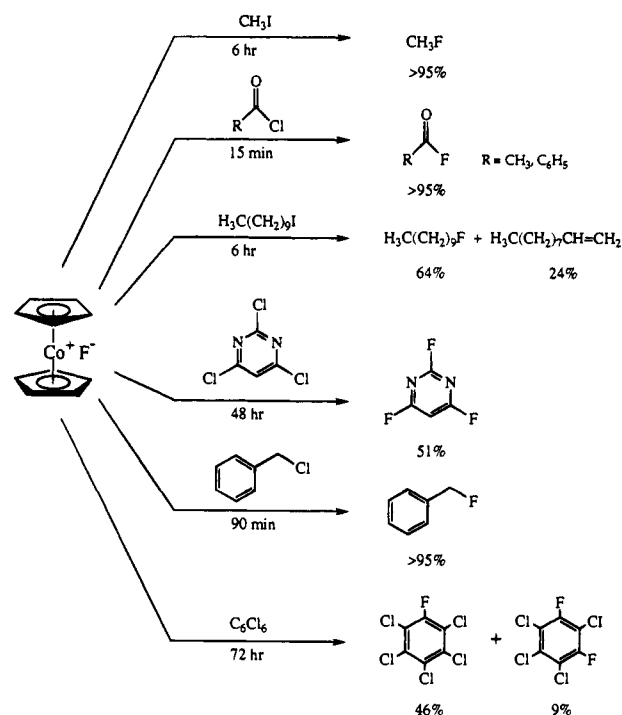


Cobaltocenium fluoride provides a potent source of nucleophilic fluoride. Reaction with Cp_2TiCl_2 affords Cp_2TiClF and then Cp_2TiF_2 in a stepwise fashion in quantitative spectroscopic yields.²² Similarly, the known tungsten fluoride²³ **1** can be easily prepared by metathesis with $[Cp_2Co]F$.



Of potentially greater significance is the ability of $[Cp_2Co]F$ to transfer fluoride to organic halides under mild conditions. Representative examples are shown in Scheme 1 for reactions conducted in THF at room temperature. Yields were determined by ^{19}F NMR spectroscopy relative to an internal standard and are not optimized. Quantitative production of acyl, benzyl, and methyl C–F bonds occurs readily at room temperature, and C–F bonds can be formed in aromatic systems activated toward nucleophilic substitution. For comparison purposes, fluorination of trichloropyrimidine with potassium fluoride requires 2 h at 310 °C in the presence of antimony trioxide,²⁴ although the recently reported HF adduct of 1,8-bis(dimethylamino)naphthalene⁷ exhibits reactivity similar to that of our reagent. The poor solubility of Me_4NF in THF⁵ is probably responsible for its inability to react with hexachlorobenzene under these conditions. Some elimination accompanied C–F bond formation from 1-iodononane. Control experiments showed that cobaltocenium bifluoride is inert under these conditions. Fluorination can even be conducted in a one-pot system, as illustrated

Scheme 1



by production of benzyl fluoride in 53% yield following addition of perfluorodecalin to a THF solution containing equimolar quantities of benzyl chloride and cobaltocene.

Perfluorodecalin provides a novel fluorine source for the generation of highly nucleophilic fluoride under strictly anhydrous conditions. It is remarkable that the relatively mild reducing agent cobaltocene ($E_{1/2} = -0.91$ V vs SCE)²⁵ is capable of inducing C–F bond activation in this substrate.^{8–10,21} In contrast to divalent lanthanide metallocenes such as $(C_5Me_5)_2Yb$, which are also capable of abstracting fluoride from a variety of organic substrates,²⁶ in the present system the fluoride remains available for further reaction chemistry. In essence, the cobaltocene fragment has the potential to act as a “fluoride shuttle” in transferring fluoride to organic and inorganic substrates. Electrochemical experiments which might make this process catalytic in cobaltocene and variation of the substituents on the cyclopentadienyl ligands which may lead to a tunable source of fluoride ion are future directions for this research which are under active exploration.

Acknowledgment. This research was supported in part by the National Science Foundation through a PYI Award to T.G.R. (CHE-895845) and the University of Utah Research Committee. T.G.R. thanks the Alfred P. Sloan Foundation for a Research Fellowship (1991–1995).

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