FEATURE ARTICLE

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Carbon–fluorine bond activation—looking at and learning from unsolvated systems†

Ulf Mazurek* and Helmut Schwarz*
Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany.
E-mail: Helmut.Schwarz@www.chem.tu-berlin.de; Fax: (+49)30-314-21102

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The selective activation of a particular bond in a molecule has always been a desideratum in chemical synthesis. This Feature Article focuses on studying the mechanisms operative in the activation of carbon–fluorine bonds beyond solvated systems, *i.e.*, on surfaces and in the gas phase. Side glances to reactions in solutions, however, are incorporated when appropriate.

Introduction

Despite its apparent omnipresence, the question 'Have you already tried your reaction in isopropanol?' is *not* what chemistry is about. In contrast, first and foremost chemistry is about the understanding of how atoms and molecules behave, why they do so, and, of course, how to affect their behaviour in a desired way. As far as synthesis is concerned, chemistry is the science of both forming and breaking bonds in a selective manner. Referring to the latter point, this article addresses the selective activation of carbon–fluorine bonds. As shown in Table 1, the bond dissociation energy (BDE) of a C–F bond is larger than that of any other C–X single bond, thus turning its activation into a subject of both vital and diversified research. Recent reviews of C–F bond activation are mostly oriented towards solvated systems covering, *e.g.*, oxidative addition to low-valent transition metals,[1] use of metal complexes,[2,3] activation of perfluoro alkanes and arenes,[4] the importance of organometallic fluorides,[5] and the use of magnesium.[6]

Table 1 Bond dissociation energy (BDE) values (kcal mol^{-1}) of C–X bonds

Bond	BDE	
C–H	96–99	ref. [7]
C–O	85–91	ref. [7]
C–N	69–75	ref. [7]
C–S	61	ref. [7]
H_3C–Cl	85	ref. [7]
H_3C–Br	70	ref. [7]
H_3C–I	57	ref. [7]
H_3C–F	109.0	ref. [4]
H_2FC–F	122.0	ref. [4]
HF_2C–F	128.0	ref. [4]
F_3C–F	129.7	ref. [4]
F_3C_6–F	116	ref. [8]

Helmut Schwarz was born in Nickenich (now Rhineland-Palatinate). He studied chemistry at the Technische Universität Berlin and received his PhD with Professor Ferdinand Bohlmann in 1972. Professor Schwarz's research interest concerns gas-phase chemistry in its broadest sense and covers chemical systems as diverse as small organic molecules and actinoid polycations. The numerous awards he has received include the Leibniz-Forschungspreis (1990), the J. J. Thomson Medal in Gold (1994), the Liebig Medal (1998), the Prelog Medal in Gold (2000), the Field–Franklin Award (2001) and the Otto-Hahn-Preis für Chemie und Physik (2003). Professor Schwarz is co-editor of the International Journal of Mass Spectrometry and an Editorial Board Member of Helvetica Chimica Acta. Currently, rather than listening to Mozart's unparalleled music, he serves as Vice Presidents of the Berlin-Brandenburg (formerly Prussian) Academy of Sciences and the German Research Foundation (DFG).

Ulf Mazurek was born in Dresden (then East Germany). He studied chemistry at the Technische Universität Dresden, the Ludwig-Maximilians-Universität München, and—as a Fulbright scholar—The University of Georgia, Athens, GA. He received his PhD with Professor Schwarz in Berlin in 2002. His major research interests concern reaction mechanisms, chemical kinetics and—in a broader sense—the understanding of complex systems.

Due to limited space allocated for this Feature Article, its focus is on surface and gas-phase reactions. It turned out that mass spectrometry is a useful tool to analyse the products of such reactions; thus, ionic species will be addressed here frequently. On the other hand, solvated systems—being most important from the point of actual synthetic chemistry—will not be discussed. However, recent studies since the reviews mentioned above should not be ignored. They focused on metal complexes of, *e.g.*, Ti,[9] Zr,[10–12] Fe,[13] Ni,[14,15] Ru,[16,17] Rh,[18–22] Re,[23] Os,[24] Ir,[25,26] and Yb.[27] While not directly connected to carbon–fluorine bond *activation*, it appears that enzymes can be employed to *form* such bonds.[28] Only recently, nickel-mediated C–F bond activation of heteroaromatics has been featured in this journal.[29]

Reactions on surfaces

Reactions on surfaces may appear as a slightly esoteric field of research. Actually, they are not, for understanding the mechanisms underlying chemical processes to occur at the surface–vacuum interface is essential in materials science, including, *e.g.*, semiconductor doping, ion beam etching, and surface hardening by oxide or nitride formation. Reactions on surfaces have been pioneered by Cooks and co-workers.[30] In 1994, they studied the formation of transition-metal fluoride monocations from fluorinated self-assembled monolayers (F-SAM).[31] In more detail, the reactions of Ti^+, Cr^+, Fe^+, Mo^+, and W^+ with (i) a self-assembled monolayer of $CF_3(CF_2)_{11}(CH_2)_2S$–Au on a gold film and (ii) an 8 μm layer of $F[CF(CF_3)CF_2O]_{27(ave)}CF_2CF_3$ on stainless steel were investigated at varying collision energies of the metal cations (20–60 eV), yielding fluorinated ions up to TiF_3^+, CrF_2^+, FeF_2^+, MoF_4^+, and WF_5^+, respectively.

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† Dedicated to Professor Heribert Offermanns on the occasion of his 65th birthday.

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When the ‘projectiles’ bombarding the F-SAM were changed to metal-carbonyl cations (metal = Cr, Mo, and W), cyclopentadienyl (Cp) complexes (Fe), or chlorides (Ti), respectively, both loss and exchange of ligands were observed. For instance, accelerating $TiCl_2^+$ to a collision energy of 60 eV and colliding it with F-SAM gives rise to cations TiF^+, TiF_2^+, TiF_3^+, $TiClF^+$, $TiClF_2^+$, and $TiCl_2F^+$. Extending their study even further, the authors undertook angle-resolved measurements with W^+ which revealed a one-step mechanism for the abstraction of fluorine atoms as evident from the decrease of average W^+ fluorination upon lowering the scattering angle. If, in contrast, the tungsten cation was abstracting fluorine atoms by ‘rolling over’ the monolayer’s surface, the opposite result would have been observed. Nonetheless, the tungsten ion apparently gets bound to the surface for a short period of time losing a substantial part of its kinetic energy.

Later, Cooks and co-workers employed silylium cations as reaction partners to hydroxyl-terminated (HO-SAM), hydrocarbon (H-SAM), and fluorocarbon (F-SAM) self-assembled monolayers.[32] Except for the transhalogenation reaction $SiCl_3^+ \rightarrow SiCl_2F^+$, ligand loss from both $SiCl_3^+$ and $Si(C_2H_5)_4^+$ dominated the product spectrum while Si–F bond formation was not as pronounced as one might have expected. This result corresponds to collisions of Si^+ with F-SAM, yielding SiF^+ as the most abundant ion.[33] The latter study, however, covers the reactions of group 13 through 17 cations with F-SAM in much more detail than can be discussed here. The overall picture is that multiple C–F bond activation increases with the collision energy. In addition, it increases with the group number; in a given group, it rises with the mass of the colliding cation.

A study on the collisions of BBr_n^+ ($n = 0$–2) with F-SAM[34] revealed new insight into the thermochemistry of ion-surface reactions. It turned out that BF_2^+ appears at lower collision energies and is more abundant at all collision energies examined than BF^+. While the preference for BF_2^+ formation corresponds to gas-phase enthalpy data, its relatively low abundance indicates a considerable reaction barrier. Cooks and co-workers concluded the formation of BF_2^+ to proceed by simultaneous reactions with two C–F bonds. For BBr^+, formation of $BBrF^+$ dominated while the yield of BF_2^+ was significantly lower. Finally, BBr_2^+ did not undergo fluorine atom addition but underwent halogen–halogen atom exchange, yielding $BBrF^+$ and—at higher collision energies and in lower abundances—BF_2^+.

Wysocki and co-workers showed that C–F bond activation occurs upon 30 eV collisions of CD_3^+ cations with CF_3-terminated SAM surfaces.[35] More than 80% of the total ion intensity is being lost in this process which the authors concluded to be F^- abstraction from the SAM terminus.

Summarising the studies referred to so far, many of the results show that reaction exothermicity governs C–F bond activation; nonetheless, reaction barriers may come into play as was shown for brominated borinium ions.[34]

A completely different approach to C–F bond activation was used by Myli and Grassian[36] who allowed nickel (100) surfaces to be covered by trifluoromethyl iodide under ultrahigh-vacuum conditions. Temperature-programmed desorption revealed the activation of both C–I and C–F bonds, upon which about 90% of the trifluoromethyl iodide decomposed on Ni(100) forming I, NiF_2, and CF_3 as dominating products. When molecular hydrogen was present, however, hydrogenolysis yielding HF and CH_2F_2 occurred as well.

Reactions in the gas phase

Due to the possibility to extensively control ligation of species and details of reaction conditions, low-pressure gas-phase experiments have emerged as perfect tools to investigate intrinsic properties of the reacting species. As mentioned above, advanced mass spectrometry is a prime analytical method; thus, all of the results discussed below originate from mass-spectrometric investigations, and three conceptually different approaches to the subject will be presented here.

Endothermic reactions

While studies on C–F bond activation on surfaces are primarily associated with Cooks’ laboratory, the detailed investigations of endothermic gas-phase reactions are so with that of Armentrout employing a guided ion-beam technique. As early as 1983, the investigation of the Ni^+/C_2F_4 system revealed the generation of NiF^+, $NiCF_2^+$, and $NiC_2F_3^+$.[37] Both the first and the last of these ionic products originate from C–F bond activation. This picture is paralleled by the formation of both NiF^+ and CF_3^+ from Ni^+ and CF_4. Later, the reactions of CF_4 with He^+, Ne^+, and Ar^+,[38] fluoride anion abstraction from CF_4,[39] and the ion–molecule reactions of O^+ and O_2^+ with both CF_4 and C_2F_6[40] were investigated in Armentrout’s laboratory as well. While these chemical transformations may appear to be of pure academic interest only, their understanding proved essential to surface-etching processes in, *e.g.*, the semiconductor industry. In none of the studies,[38–40] CF_4^+ was detected. In contrast, electron abstraction from CF_4 is immediately followed by fluorine atom dissociation, thus yielding CF_3^+. At higher collision energies, fragmentation of the perfluorinated hydrocarbons quite naturally provided pronounced yields of CF_n^+ ($n = 1$–3) cations. Overall, the appearance energies of the particular reaction channels correlate with the noble gases’ ionisation energies and the electronic energy levels of CF_4.[38] When oxygen comes into play, however, fluoride anion abstraction from the carbon centres is the lowest-energy channel, followed by the generation of fluorinated carbonyl cations. $C_2F_5^+$ was found to undergo C–C bond fission easily, and fluorinated carbonyl cations were generated from both CF_4 and C_2F_6 except for the O^+/C_2F_6 system.[40]

Activation of C–F bonds in $C_6F_6^+$ by collision with noble gas atoms (He, Ne, Ar, Xe)[41] revealed the existence of two dissociation reaction channels, one following statistical theories but the other causing a non-statistical behaviour of the collision complex. However, an explanation of the non-statistical reaction channel relying on the polarisability of the colliding noble gas atom[41] appears a little bit questionable because there is no quantitative correlation between polarisability and the fraction of non-statistical C–F bond cleavage.

Exothermic reactions

To the best of our knowledge, the first *thermal* C–F bond activation by an exothermic gas-phase reaction was reported by Jones and McDonald in 1988.[42] Quite remarkably, the *anionic* manganese carbonyl complex $Mn(CO)_3^-$ was capable of intitiating vicinal defluorination of F_2CCF_2, F_2CCHF, FHCCHF, and F_3CCF_3 while in the products $F_2Mn(XC_2Y)^-$ (X, Y = F, H) the negative charge remained on the metal centre.

Non-endothermic C–F bond activation by *cations* in the gas phase was first observed for the generation of FeF^+ from FeO^+ and C_6F_6.[43] Subsequently, lanthanoid cations were focussed upon, as first represented by Pr^+[44] and later investigated in a systematic way.[45] The reactions of praseodymium cations with fluorinated organic substrates are straightforward, and their results are instructive: (i) C–H bonds do not get activated, neither by ground-state nor by electronically or kinetically excited atomic Pr^+. (ii) C–F bond activation by ground-state praseodymium cations is limited to CH_3F and C_6F_6 whereas excited cations also activate C_2F_6, CHF_3, and even CF_4. Neglecting possible reaction barriers, this observation allows for an estimation of BDE(Pr^+–F) of roughly 120–125 kcal mol^{-1} (see Table 1 for reference data). (iii) Whenever possible, a second fluorine atom transfer onto the praseodymium cation takes place, may it be in one reaction step for polyfluorinated substrates or in two reaction steps for their monofluorinated counterparts. A third fluorine-atom transfer, however, is unfavoured compared to fluoride-anion transfer as evident from reaction of Pr^+ with SF_6. (iv) When weaker C–X bonds are present in the substrate as, *e.g.*, in mixed halocarbons, these weaker bonds get preferentially activated.

A systematic investigation of lanthanoid cations (with the exception of radioactive Pm^+)[45] revealed an insightful correlation between the second ionisation energy of the metal and the corresponding reactivity towards fluorohydrocarbons. While not being so pronounced when fluorobenzene was taken as sole reference, the correlation became striking when more substrates where used to comprise the relative reactivity as shown in Figs. 1 and 2.

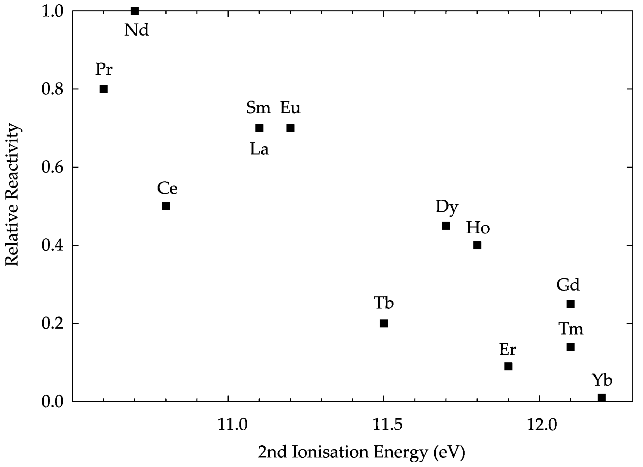

Fig. 1 Relative reactivity of Ln^+ with fluorobenzene with regard to F atom abstraction. Adapted, with permission, from ref. [45]. Copyright 1996 American Chemical Society.

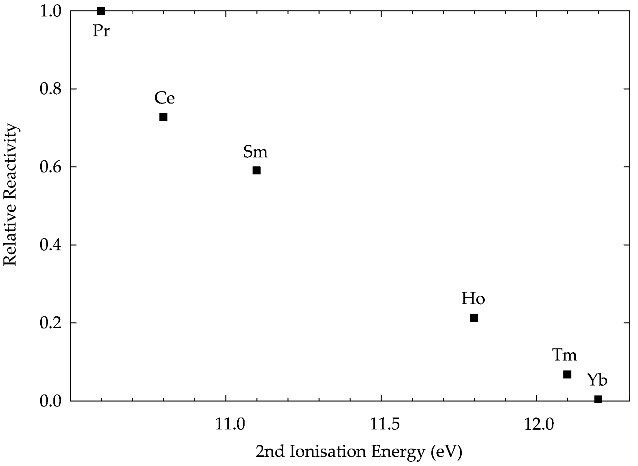

Fig. 2 Normalised sum of the relative reactivities of Ln^+ with fluoromethane, 1,1-difluoroethane, fluorobenzene, and hexafluorobenzene, with regard to F atom abstraction. Adapted, with permission, from ref. [45]. Copyright 1996 American Chemical Society.

From this correlation, it was straightforward to postulate the single-electron transfer (SET) or ‘harpoon’ mechanism depicted in Fig. 3 and to assume the electron transfer to be the rate-determining step in the reaction sequence.

$$Ln^+ + R\text{–}F \longrightarrow [Ln^+\cdots F\text{–}R \xrightarrow{SET} Ln^{2+}\cdots F^-\cdots R] \longrightarrow LnF^+ + R^\bullet$$

Fig. 3 Proposed mechanism of the C–F bond activation by Ln^+. Adapted, with permission, from ref. [45]. Copyright 1996 American Chemical Society.

With regard to Ce^+ and Ho^+, detailed high-level quantum mechanical calculations[46] confirmed the ‘harpoon mechanism’. Furthermore, the counterintuitive fluorobenzene’s higher reactivity compared to that of fluoromethane (see Table 1 for bond dissociation energies) was found to originate from stabilisation of a non-linear transition structure by the benzene’s π system. Subsequent quantum-mechanical calculations by Liu and co-workers on the reactions of fluoromethane with La^+[47] or Ce^+, Pr^+, and Yb^+,[48] respectively, only confirm the original results.[44–46]

When the reactions of main-group Ca^+ (*IE* = 11.87 eV, ref. [49]) with organofluorides were investigated both experimentally and theoretically,[50] the ‘harpoon mechanism’ was found also for this cation as shown in Fig. 4.

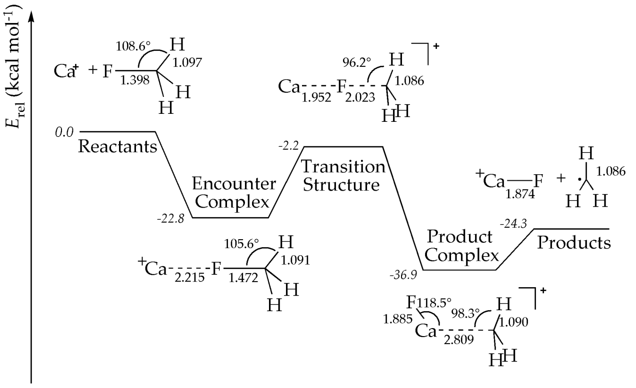

Fig. 4 Schematic potential energy surface (PES) of the $Ca^+ + CH_3F$ reaction. Adapted, with permission, from ref. [50]. Copyright 1997 Elsevier Science B. V. Energies (numbers in italics) are given in kcal mol $^{-1}$, bond lengths in Å, and bond angles in degrees.

C–F bond activation in the *cationic* complex MCF_3^+ (M = Fe, Co) causing formation of $FM^+\cdots F_2C$ were investigated both experimentally and theoretically[51] but will not be discussed here due to space limitations. The niobium cation, on the other hand, deserves special monitoring. Nb^+ undergoes a truly remarkable fourfold fluorine-atom abstraction from C_6F_6 to form NbF_4^+ in a *single* collision,[52] thus corresponding to the twofold C–F bond activation in one step by Pr^+[44] and the above-mentioned behaviour of W^+ on surfaces.[31] Quantum-mechanical calculations of the niobium system suggest a sequential intramolecular fluorine abstraction from the hexafluorobenzene molecule[52] as shown in Fig. 5.

‘Unreactive’ cations

Another approach to the subject discussed here was chosen recently by our group. Generally unreactive atomic Cr^+, whose ground-state inertness is easily explained by reference to its electronic configuration $3d^5$ ($^6S_{5/2}$), activates up to four C–F bonds in hexafluoroacetone,[53] thus making them susceptable to hydrolysis. This hydrolytic C–F bond cleavage is noteworthy because hexafluoroacetone itself is not sensitive to water; in contrast, C_3F_6O is commercially available in the form of sesqui- and trihydrates. Furthermore, it is only the inertness of Cr^+ towards water which enables the C–F bond activation reactions shown in Fig. 6: If Cr^+ cations were more reactive towards water, the metal cations would have been consumed prior to the (comparatively slow) complexation with hexafluoroacetone.

As shown by deliberate decomposition of $CrC_3HF_3O_3^+$, a key intermediate of the reaction sequence depicted in Fig. 6, no oxidative addition of the chromium cation precedes the bond activation.[53,54] Thus, in contrast to the electron transfer mechanism discussed above, the bond activation proceeds by simple coordination of the chromium cation. A related way of C–F bond activation by a nearby cation in solution was observed by Lectka and co-workers[55] in an *o,o′*-disubstituted biphenyl molecule but caused an intramolecular fluoride ion shift as shown in Fig. 7.

Also caused by the electron-withdrawing effect of a cation, the complete hydrolysis of a difluorobenzyl group followed by CO generation, was observed in solution by Hughes and co-workers[19] as shown in Fig. 8.

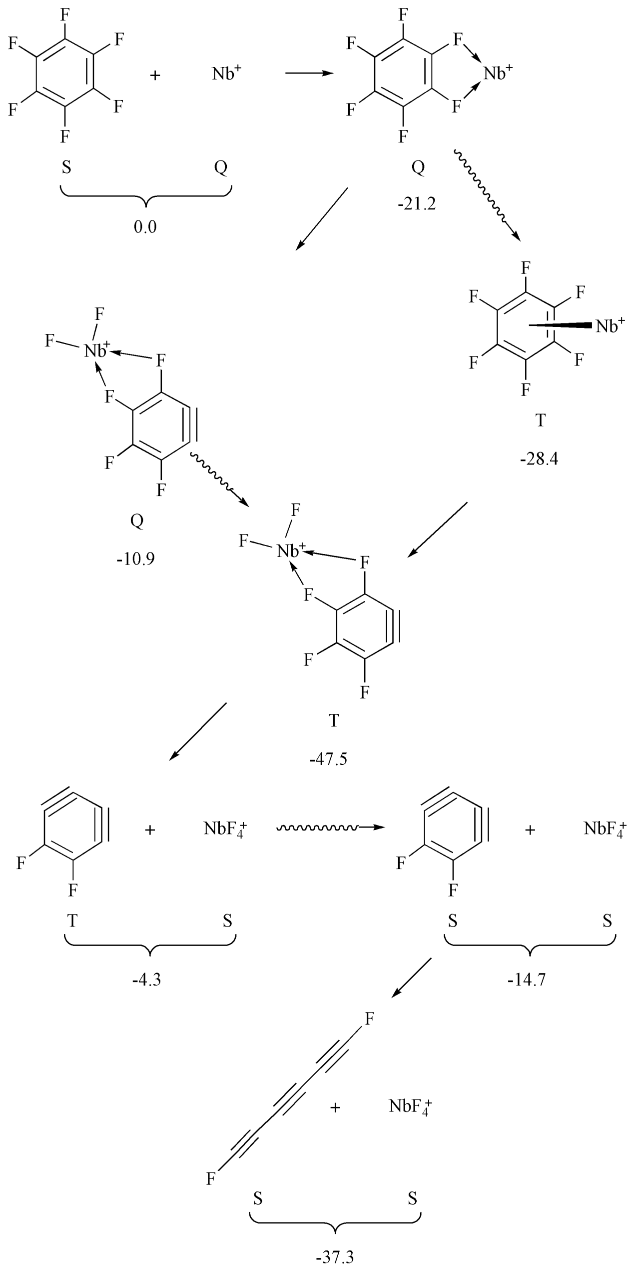

Fig. 5 Proposed mechanism for 4 F transfer from C_6F_6 onto Nb^+. Adapted, with permission, from ref. [52]. Copyright 2002 American Chemical Society. Computed relative enthalpies at 298 K are given in kcal mol^{-1} with respect to the reactants. The multiplicities are indicated as S (singlet), T (triplet), and Q (quintet; the 'quartet' in ref. [52] is a typographical error).

$$CrC_3F_6O^+ \xrightarrow[-HF]{+H_2O} [CrC_3HF_5O_2^+] \xrightarrow[-HF]{} CrC_3F_4O_2^+ \xrightarrow[-HF]{+H_2O} CrC_3HF_3O_3^+$$

$$\begin{tikzcd} CrC_3HF_3O_3^+ \arrow[r, "+H_2O"] & CrC_3H_3F_3O_4^+ \arrow[r, "+H_2O"] \arrow[d, "\pm H_2O"', "-HF"] & CrC_3H_5F_3O_5^+ \arrow[r, "+H_2O"] & CrC_3H_7F_3O_6^+ \\ & CrC_3H_2F_2O_4^+ \arrow[r, "+H_2O"] & CrC_3H_4F_2O_5^+ \arrow[r, "+H_2O"] & CrC_3H_6F_2O_6^+ \end{tikzcd}$$

Fig. 6 Major reactions of Cr^+-coordinated hexafluoroacetone, C_3F_6O, with water. Adapted, with permission, from ref. [53]. Copyright 2002 Wiley-VCH.

Consequently, C–F bond activation by an adjacent cation—whether it be a rather unreactive metal cation,[53] a carbocation,[55] or a coordinating water molecule[19]—might allow a new access to carbon–fluorine bond activation.

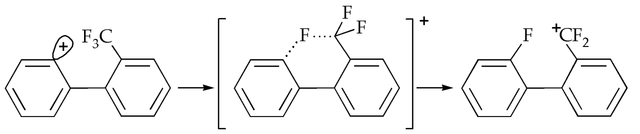

Fig. 7 Intramolecular fluoride anion shift in a biphenyl system. Adapted, with permission, from ref. [55]. Copyright 1997 American Chemical Society.

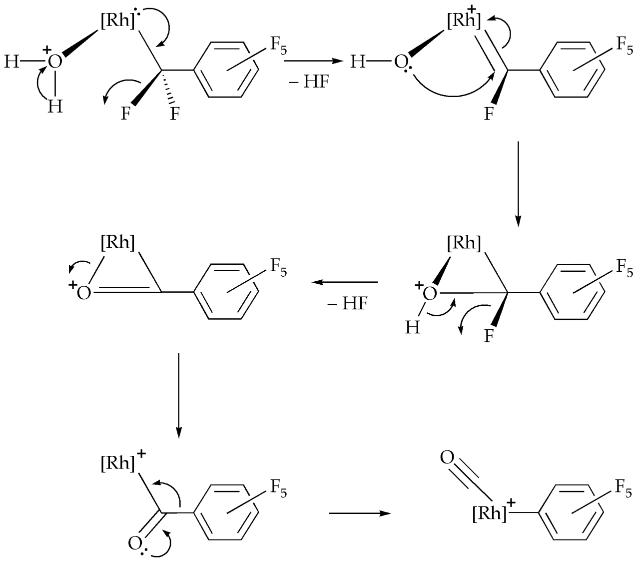

Fig. 8 C–F bond activation by Rh-coordinated water. Adapted, with permission, from ref. [19]. Copyright 1997 American Chemical Society.

Extending our observation of coordination-induced C–F bond hydrolysis, we addressed the reactions of the lesser-fluorinated substrates 1,1,1-trifluoroacetone and monofluoroacetone as well as those of the aromatic compounds pentafluorobenzaldehyde and 2,3,4,5,6-pentafluoracetophenone.[54] It turned out that Cr^+-assisted hydrolytic C–F bond activation in the gas phase is not limited to hexafluoroacetone but is most efficient for this substrate: For hexafluoroacetone, up to four C–F bonds are hydrolyzed, whereas for each of the other substrates investigated only one C–F bond per ligand molecule is involved in this reaction. On the other hand, additional ways of bond activation were observed for these substrates, namely intramolecular HF abstraction and multiple fluorine-atom abstraction from pentafluorophenyl groups.

Future perspectives

From the examples of C–F bond activation discussed above, a number of research perspectives may be derived. The overall picture is that transition metals are prime candidates for carbon–fluorine bond activation when ambient reaction conditions are desired.

From the synthetic point of view, quite clearly increasing reactivity without compromising selectivity is a permanent goal. Furthermore, catalytic procedures are always desired, and reagents being stable to both air and water are nothing one would feel sorry for. From reactions in solution not discussed here, it is evident that hexafluorobenzene is a rather benign substrate for defluorination whereas lesser fluorinated benzenes are much more difficult to activate. While this might be counter-intuitive from the point of C–F bond strength, it is easily explained by the substrates' electron affinities steadily increasing with the extent of fluorination. Thus, an electron-transfer mechanism followed by fluoride anion abstraction from the aromatic core constitutes a plausible reaction pathway, and mechanistic studies in solution should provide more insight into this point. Most pressing is, probably, the question of single-electron transfer (SET) *vs.* oxidative addition. Still addressing solvated systems, the search for optimal ligands is an everlasting effort nicely illustrated by the effect of changing phosphane ligands in ruthenium complexes.[16]

As far as the gas-phase activation by ground-state metal cations is concerned, a systematic investigation of the 'harpoon mechanism'[44,45,50] *vs.* coordination[53,54] is indicated. We suppose the respective reaction mechanisms to strongly depend on the second ionization energy of the metal involved: For a comparatively low value, electron transfer onto the fluorine atom or oxidative addition, respectively, are likely to occur, whereas a comparatively high value probably corresponds to a simple coordination. Thus, it is again the question of electron transfer onto the fluorine atom already mentioned above and the comparison of gas and condensed phases[9] which deserves prime attention.

Stereoselective transformations were not addressed in this article. However, being a constant desire in organic chemistry, asymmetric synthesis of fluorinated compounds by both enantioselective fluorination[9] and diastereoselective defluorination, *i.e.* C–F bond activation,[56] of organic compounds are beginning to make their ways into the repertoire of organic synthesis.

In conclusion, C–F bond activation constitutes a topic of prime interest, and while preferring one or other particular area of it, none of the original authors wished to reserve the field for themselves.[57,58] Thus, research on C–F bond activation is open to everyone, and the authors of this article look forward to fascinating new results.

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