DOI: 10.1002/ejic.201001184

C–F Bond Activation of Highly Fluorinated Molecules at Rhodium: From Model Reactions to Catalysis

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Dedicated to Prof. Erhard Kemnitz on the occasion of his 60th birthday

Keywords: C–F activation / Fluoroorganics / Fluorine / Rhodium / Homogeneous catalysis

Rhodium complexes are excellent tools for the activation of aromatic and olefinic carbon–fluorine bonds. C–F bond cleavage reactions are key steps for the derivatization of highly fluorinated compounds via stoichiometric or catalytic reaction pathways. The reaction routes involve hydrodefluorinations, but also the selective introduction of functional groups at distinctive positions, to provide access to new fluorinated building blocks. One can identify two general types of rhodium precursors that can induce the C–F activation step. Cyclopentadienyl compounds have been applied for thermal and photochemical C–F bond cleavage reactions of aromatics in solution, but oxidative addition steps have also been investigated in matrix isolation studies at low temperature. Square-planar hydrido, silyl, and boryl complexes are often involved in unique stoichiometric and catalytic processes for the derivatization of aromatics and olefins.

Introduction

The importance of fluorinated compounds is not only reflected by their significance in countless technological applications and their use in daily life, but also by their role at the leading edge of many new developments.[1] It is therefore no surprise that fluorine chemistry has been subject to quite a lot of reviews and books, which give a comprehensive insight into the key role that fluorine and its compounds play in many branches of chemistry, technology, and even medicine.[2] Agrochemistry and pharmaceuticals certainly benefit from fluoroorganics,[3] so does the chemistry of materials and polymers.[4] From a thermodynamic point of view, the C–F bond is exceptionally strong,[5] which is one of the reasons for the unique nature of fluorinated compounds.[6] Incorporation of fluorine atoms can lead to high stability, but also to a distinctly altered reactivity of

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Thomas Braun did his undergraduate and graduate studies at the University of Würzburg (Germany) and received his doctoral degree under the supervision of Helmut Werner. After a short period at the University of Rennes (France) with Pierre H. Dixneuf he moved in 1997 to York (UK), where he was a post-doctoral fellow with Robin N. Perutz. In 2000 he joined the research group of Peter Jutzi at the University of Bielefeld (Germany) to finish his habilitation in 2003. After a short stay as lecturer at the University of Kassel in 2006, he moved in 2007 to the Humboldt University of Berlin, where he is Professor for Inorganic Chemistry and currently Head of Department. He is vice-chair of the DFG Research Training Group (Graduiertenkolleg) "Fluorine as Key Element", which is a joint program of the Free University of Berlin and the Humboldt University of Berlin. Presently, he also serves as chair of the fluorine subject group of the German Chemical Society (GDCh). His main research interests are C–F and C–H activation reactions at transition metals, fluoro complexes as fluorinating agents, metal-mediated oxygenation reactions, as well as the synthesis of highly reactive silyl and boryl complexes and their application in catalysis. Thomas Braun received the Wöhler Award for Young Scientists of the GDCh in 2006 and the RSC Fluorine Chemistry Prize in 2007.

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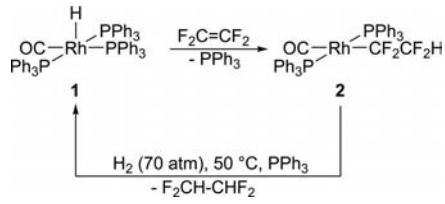
fluorinated compounds in comparison to their nonfluorinated counterparts. However, one has also to take into account that the high stability and relative inertness of some fluoroorganics are not always desirable features. Highly fluorinated molecules like perfluorocarbons have been applied as inert refrigerants[7] and as solvents or ligands in synthesis and catalysis,[2b,8] yet their chemical resistance is a reason for their environmental persistence.[9]

There is considerable interest in the development of new reaction routes to access fluorinated building blocks. One unique pathway to synthesize fluoroorganic compounds is based on a transition-metal-mediated derivatization of highly fluorinated precursors. Such an approach can involve C–F bond cleavage reactions, which then open up unique reaction pathways.[10] Thus, fluoroorganic compounds can undergo hydrodefluorination reactions at transition-metal complexes (i.e. the replacement of a C–F by a C–H moiety).[10,11] Such a reaction sequence might also be relevant for the conversion of perfluorocarbons into environmentally more benign hydrofluorocarbons.[9d,9e] In addition, C–F bond cleavage reactions open up an opportunity for the introduction of functional groups at distinctive positions. This approach may provide access to new organic building blocks of higher value, which are not accessible otherwise. This Microreview focuses on rhodium-mediated C–F activation pathways.

Accessing Fluorinated Building Blocks via C–F Bond Activation

In order to employ transition-metal-mediated activation and derivatization reactions successfully, several issues have to be addressed. One major challenge is the C–F bond cleavage step. Usually, this requires the formation of a thermodynamically more stable bond. This can, for example, be achieved by the generation of a metal–fluorine bond by C–F oxidative addition reactions, which, for instance, occur at nickel,[12] palladium,[13] platinum,[12a,14] and rhodium (vide infra).[15] Hydrodefluorination of a C–F unit by transition-metal hydrides might also involve the formation of transition-metal fluorides.[10,11] Alternative C–F activation routes include the generation of Si–F,[16] B–F,[16e,17] and Al–F bonds,[18] or HF.[10,11,19] Another challenge, which has to be taken into account often, is the possible kinetic inertness of a C–F bond. For example, DFT (B3LYP) investigations for the activation of 1,4-difluorobenzene at {(Cp)Rh(PH_3)} (Cp = η^5-C_5H_5) revealed that the energetic difference between the C–H activation product [(Cp)Rh($C_6F_2H_3$)(H)(PH_3)] and the C–F activation product [(Cp)Rh(C_6FH_4)(F)(PH_3)] is only marginal.[20] In fact, the formation of the C–F activation oxidative addition product is slightly favored by 2.7 kcal/mol. This suggests that the lack of reactivity of the C–F bond, which has been experimentally observed with {(Cp)Rh(PMe_3)}, is of kinetic origin. Indeed, the activation barrier for a concerted oxidative addition of the C–F bond in 1,4-difluorobenzene turned out to be considerably higher than that for C–H activation. The poor Rh–C interaction in the transition state may be an important factor for the high activation energy for the C–F bond cleavage reaction.[20]

Once a fluorinated organic precursor has been activated at a transition-metal center, a derivatization step of the fluorinated ligand might be required to access a functionalized moiety. This can be difficult to achieve, because fluoroorganic ligands – when attached to a transition metal – often show a dramatically altered reactivity relative to that of their nonfluorinated counterparts.[21] This is, for example, illustrated by the considerably strong linkage of the fluoroalkyl group to rhodium in [Rh(CF_2CF_2 H)(CO)(PPh_3)$_2$] (**2**). The latter complex can be synthesized by insertion of tetrafluoroethylene into the Rh–H bond of [Rh(H)(CO)(PPh_3)$_3$] (**1**).[22] Formation of the hydrogenation product, 1,1,2,2-tetrafluoroethane, occurs only under relatively harsh conditions, that is, 70 bar hydrogen pressure at 50 °C (Scheme 1). Note that this demonstrates on the other hand that the unusual electronic properties of fluorinated ligands can also have a stabilizing influence on coordination compounds, which might sometimes allow the detection or isolation of reactive intermediates.[21]



Scheme 1. Hydrogenation of tetrafluoroethylene at rhodium.

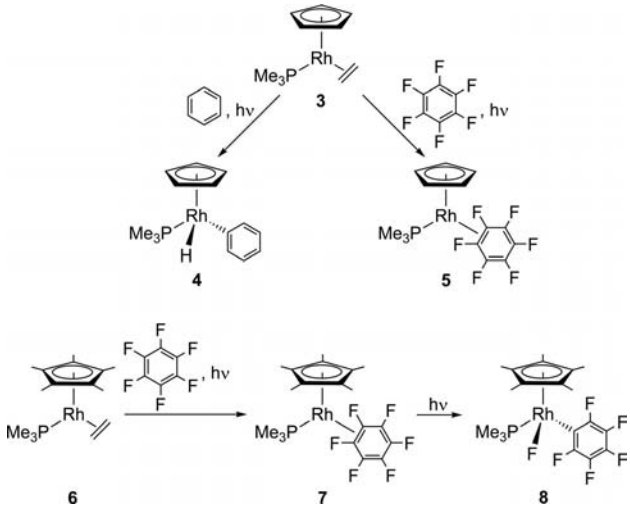
Finally, after successful derivatization and release of any fluoroorganic product, the resulting coordination compound might show a distinctively decreased or a complete absence of reactivity towards C–F bond cleavage. Therefore, in order to develop a cyclic process, usually a highly reactive transition-metal species that is capable of C–F activation has to be (re)generated.

All these requirements can often be met by suitable rhodium complexes, which have been used to derivatize fluorinated arenes and alkenes. There is, to the best of our knowledge, only one report on a rhodium-mediated intermolecular C–F bond cleavage reaction in the literature involving fluorinated alkanes.[23] Herein, we would like to present a detailed insight into the rhodium-mediated C–F bond activation reactions of aromatics and olefins. First, the initial C–F bond cleavage reactions will be described. Cyclopentadienyl compounds and square-planar 16-electron rhodium complexes can be identified as two important types of starting compounds. Then, the functionalization of fluorinated entities in the coordination sphere of the metal will be presented, including stoichiometric and catalytic derivatization reactions of fluorinated substrates at rhodium.

C–F Bond Cleavage Reactions

Rhodium–Cyclopentadienyl Complexes

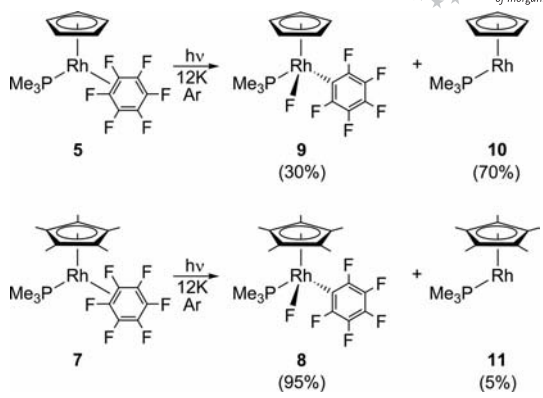
One of the first investigations of C–F bond activation reactions at rhodium were probably triggered by studies on C–H bond activation in aromatic compounds. In 1989, Perutz and co-workers reported their results on the photolytic activation of benzene at a {(Cp)Rh(PMe_3)} moiety.[24] They postulated an η^2-precoordination of benzene prior to the oxidative addition step of a C–H bond to give [(Cp)Rh(H)(C_6H_5)(PMe_3)] (**4**). The η^2-intermediate complex could not be isolated, but photolysis of [(Cp)Rh(η^2-C_2H_4)(PMe_3)] (**3**) in perfluorobenzene yielded the η^2 complex [(Cp)Rh(η^2-C_6F_6)(PMe_3)] (**5**) (Scheme 2). An oxidative addition of the aromatic C–F bond in C_6F_6 was achieved by photolysis of the Cp* complex [(Cp*)Rh(η^2-C_2H_4)(PMe_3)] (**6**) (Cp* = η^5-C_5Me_5) in perfluorobenzene (Scheme 2).[25] Initially, the η^2 complex [(Cp*)Rh(η^2-C_6F_6)(PMe_3)] (**7**) was generated.[26] Complex **7** underwent oxidative addition of a C–F bond under further irradiation to yield [(Cp*)Rh(F)(C_6F_5)(PMe_3)] (**8**). In contrast, the analogous cyclopentadienyl complex **5** did not show any signs for an oxidative addition.



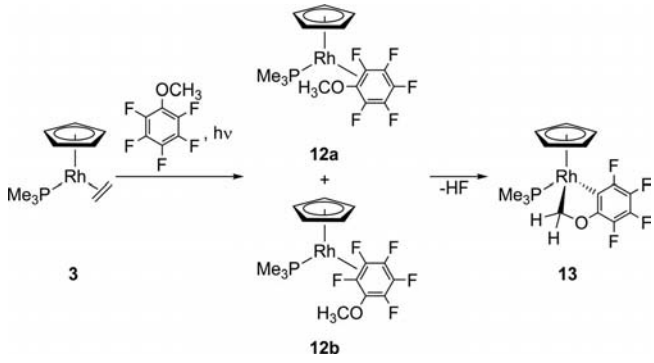
Scheme 2. Reactivity of [(Cp)Rh(η^2-C_2H_4)(PMe_3)] (**3**) and [(Cp*)Rh(η^2-C_2H_4)(PMe_3)] (**6**) upon photolysis in benzene or perfluorobenzene.

Further studies in Ar matrices at 12 K revealed that the sterically less crowded complex, [(Cp)Rh(η^2-C_6F_6)(PMe_3)] (**5**), mainly extrudes perfluorobenzene upon photolysis, to give the 16-electron species [(Cp)Rh(PMe_3)] (**10**) but also the oxidative addition product [(Cp)Rh(F)(C_6F_5)(PMe_3)] (**9**). With [(Cp*)Rh(η^2-C_6F_6)(PMe_3)] (**7**), the formation of the C–F activation product [(Cp*)Rh(F)(C_6F_5)(PMe_3)] (**8**), as well as the generation of small amounts of complex [(Cp*)Rh(PMe_3)] (**11**) were observed (Scheme 3).[27]

Irradiation of pentafluoroanisole with [(Cp)Rh(η^2-C_2H_4)(PMe_3)] (**3**) gave initially the η^2 complexes **12a** and **12b** (Scheme 4).[28] A subsequent C–F bond activation at the *ortho*-position to the methoxy group yielded the metallacycle [(Cp)Rh(κ^2-$CH_2OC_6F_4$)(PMe_3)] (**13**). Here, the formation of HF represents a considerable thermodynamic driving force.



Scheme 3. Oxidative additions of C_6F_6 in Ar matrices at 12 K.



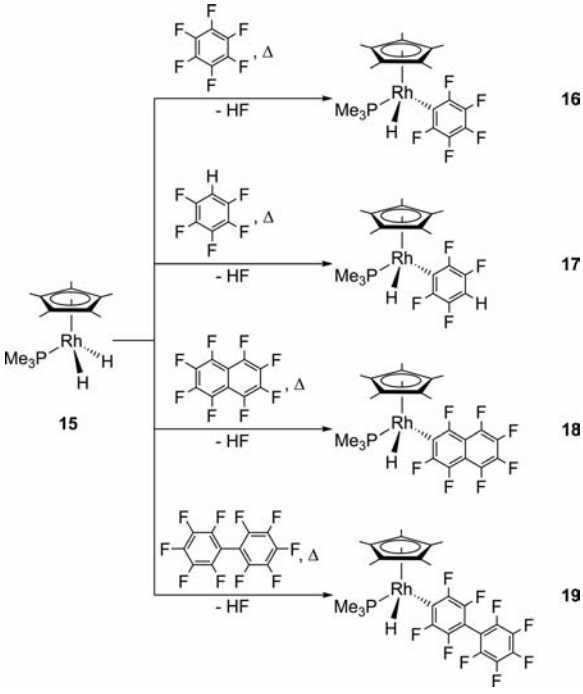
Scheme 4. C–F bond activation of pentafluoroanisole at [(Cp)Rh(η^2-C_2H_4)(PMe_3)] (**3**).

Heating of the rhodium(III) complex [(Cp*)Rh(H)(C_6H_5)(PMe_3)] (**14**) in the presence of several fluorobenzenes revealed that in all cases C–H activation is favored over C–F activation.[29] In contrast, [(Cp*)Rh(H)$_2$(PMe_3)] (**15**) reacted with pentafluorobenzene, perfluorobenzene, perfluoronaphthalene, and perfluorobiphenyl to yield the fluoroaryl complexes **16**–**19** (Scheme 5).[30]

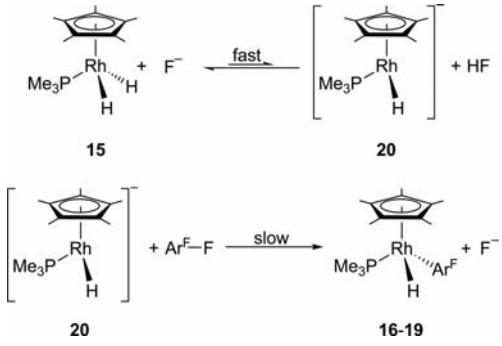
Kinetic studies indicated that the reactions are initiated by the generation of fluoride.[30] There is evidence that the active species for the C–F bond cleavage step is the anion [(Cp*)Rh(H)(PMe_3)]$^-$ (**20**), which is formed by deprotonation of **15** with fluoride (Scheme 6). Nucleophilic attack of **20** at the highly fluorinated aromatic substrates gives **16**–**19** and regenerates the catalytically active species F^-. In the presence of pyridine or additional fluoride ions, the reactions occurred much faster than they did in neat benzene.

Saunders and co-workers reported several intramolecular carbon–carbon coupling reactions by simultaneous C–F and C–H activation reactions.[31] For instance, the dimeric complex [(Cp*)Rh(Cl)(μ-Cl)]$_2$ (**21**) reacts with bis(pentafluorophenyl)phosphanylethane to give the coupling product **22** (Scheme 7).

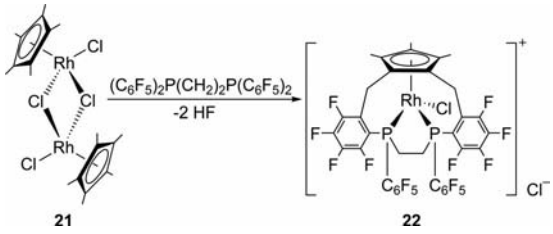
Further examples of intramolecular C–F bond activation reactions were investigated by Hughes and co-workers at cationic rhodium complexes.[10k,32] The fluoroalkyl groups



Scheme 5. C–F activation of highly fluorinated arenes at [(Cp*)-$Rh(H)_2(PMe_3)$] (**15**).

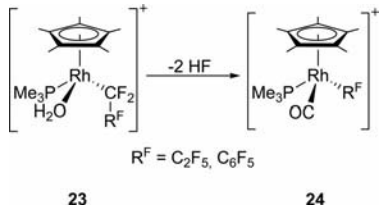


Scheme 6. Mechanism for C–F bond activation at [(Cp*)Rh-$(PMe_3)(H)_2$] (**15**).



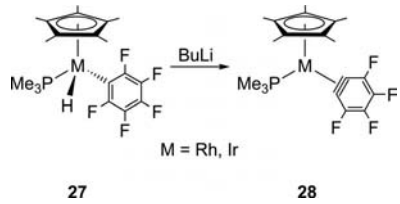
Scheme 7. C–C coupling by simultaneous C–F and C–H activation.

in **23** are hydrolyzed by coordinated water to give carbonyl complexes (compound **24**, Scheme 8). Comparable reactions at iridium complexes have also been described.[32b,32c,33]



Scheme 8. Hydrolysis of fluoroalkyl groups by coordinated water in rhodium–fluoroalkyl complexes.

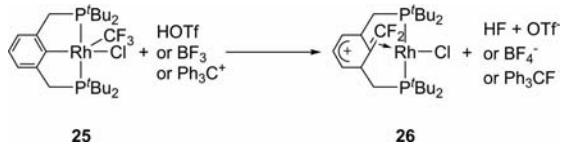
A striking example for an intramolecular C–F bond activation is the formation of the tetrafluorobenzyne complexes $[(Cp^*)M(\eta^2\text{-}C_6F_4)(PMe_3)]$ (**28**) (M = Rh, Ir). They could be generated by treatment of the pentafluorophenyl compounds $[(Cp^*)M(H)(C_6F_5)(PMe_3)]$ (**27**) with *n*BuLi (Scheme 9).[34]



Scheme 9. Formation of tetrafluorobenzyne complexes.

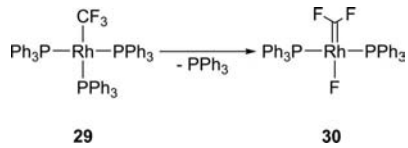
16-Electron Rhodium Compounds

A carbon–fluorine bond activation induced by Lewis acids was reported by Milstein and co-workers. The pincer complex **25** reacted with BF_3 or a tritylium cation, but also with HOTf, to give **26** (Scheme 10).[35]



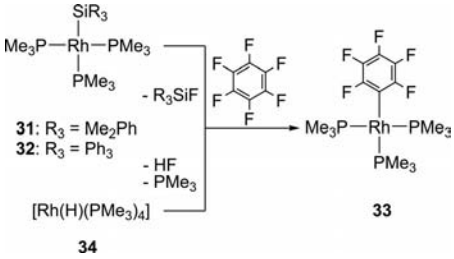
Scheme 10. C–F activation induced by HOTf or Lewis acids.

A remarkable example for an intramolecular C–F activation reaction was reported by Grushin, Macgregor, and co-workers for the 16-electron complex $[Rh(CF_3)(PPh_3)_3]$ (**29**). Migration of a fluorine atom from the trifluoromethyl group to the metal and loss of triphenylphosphane gave the difluorocarbene complex $[Rh(F)(CF_2)(PPh_3)_2]$ (**30**) (Scheme 11).[36] A comparable reaction sequence has been reported by Caulton et al. at ruthenium.[37]



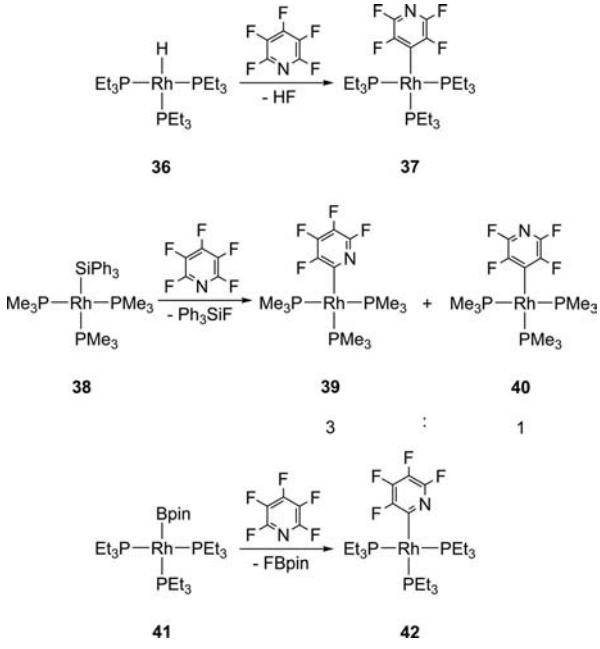
Scheme 11. Intramolecular C–F activation to give the difluorocarbene complex **30**.

In 1994, Milstein and Aizenberg showed that the rhodium silyl complexes $[Rh(SiR_3)(PMe_3)_3]$ (**31**: R_3 = Me_2Ph; **32**: $R_3 = Ph_3$) react with perfluorobenzene to yield $[Rh(C_6F_5)(PMe_3)_3]$ (**33**) and the corresponding fluorosilanes (Scheme 12).[16a] The same complex could be generated by reaction of perfluorobenzene with the hydrido complex $[Rh(H)(PMe_3)_4]$ (**34**). Hydrogen fluoride is formed as a byproduct (Scheme 12).[19a] Similarly, pentafluorobenzene reacted by C–F activation with the rhodium silyl and hydrido complexes **31**, **32**, and **34**. The activation product $[Rh(C_6HF_4)(PMe_3)_3]$ (**35**) could not be isolated, yet it seems to be reasonable to postulate an activation at the 4-position of pentafluorobenzene.



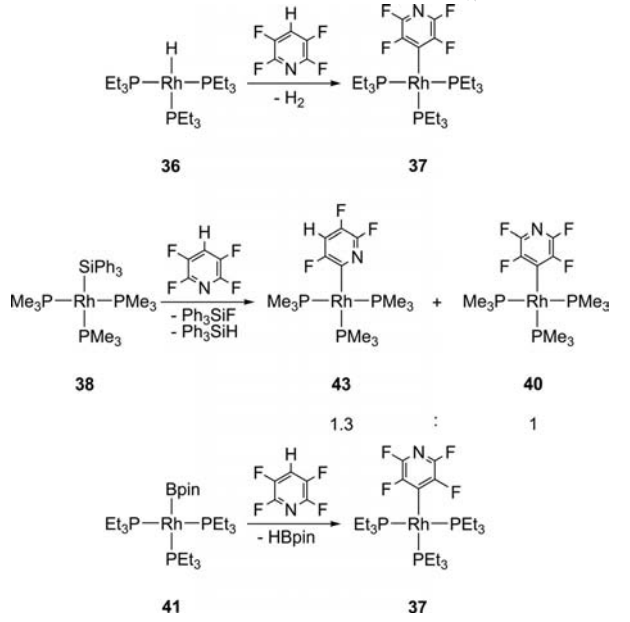
Scheme 12. Activation of perfluorobenzene at $[Rh(SiR_3)(PMe_3)_3]$ (**31**, **32**) and $[Rh(H)(PMe_3)_4]$ (**34**).

It has also been demonstrated that treatment of the hydrido complex $[Rh(H)(PEt_3)_3]$ (**36**) with pentafluoropyridine leads selectively to an activation at the 4-position to give $[Rh(4\text{-}C_5NF_4)(PEt_3)_3]$ (**37**) (Scheme 13).[19e] Note that complex **37** is also the product of a C–H activation of 2,3,5,6-tetrafluoropyridine (Scheme 14).



Scheme 13. C–F bond activation of pentafluoropyridine.

Perutz, Marder, and co-workers investigated the reactivity of highly fluorinated pyridines towards the silyl complex $[Rh(SiPh_3)(PMe_3)_3]$ (**38**). A reaction with pentafluoropyridine resulted in C–F bond cleavage at the 2- and the 4-positions to yield $[Rh(2\text{-}C_5NF_4)(PMe_3)_3]$ (**39**) and $[Rh(4\text{-}C_5NF_4)(PMe_3)_3]$ (**40**) in a 3:1 ratio (Scheme 13). The latter can also be generated by C–H activation of 2,3,5,6-tetrafluoropyridine (Scheme 14). Similar amounts of the C–F activation product $[Rh\{2\text{-}C_5(4\text{-}H)NF_3\}(PMe_3)_3]$ (**43**) were also formed. The activation of 2,3,5,6-tetrafluoro-4-methylpyridine at $[Rh(SiPh_3)(PMe_3)_3]$ (**38**) takes place at the 2-position to give $[Rh\{2\text{-}C_5NF_3(4\text{-}Me)\}(PMe_3)_3]$ (**44**).[16e]



Scheme 14. C–H bond activation of 2,3,5,6-tetrafluoropyridine.

A selective C–F activation of pentafluoropyridine at the 2-position to furnish $[Rh(2\text{-}C_5NF_4)(PEt_3)_3]$ (**42**) has been achieved by using the rhodium(I) boryl complex $[Rh(Bpin)(PEt_3)_3]$ (**41**) (HBpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolane, pinacolborane) as starting compound (Scheme 13).[17b] In this case, the reaction's thermodynamic driving force is the formation of the B–F bond. However, a reaction of complex **41** with 2,3,5,6-tetrafluoropyridine led to the formation of $[Rh(4\text{-}C_5NF_4)(PEt_3)_3]$ (**37**) and HBpin (Scheme 14). In contrast, treatment of **41** with benzene gave the hydrido complex, $[Rh(H)(PEt_3)_3]$ (**36**), and the phenyl boronato ester PhBpin.[17b]

Milstein and Aizenberg proposed an electron-transfer mechanism for C–F activation reactions of fluorinated benzenes at hydrido complex $[Rh(H)(PMe_3)_4]$ (**31**). It has been suggested that the conversion proceeds via a hydrido radical cation $[Rh(H)(PMe_3)_4]^{+\cdot}$ and a fluoroarene radical anion $[Ar^F–F]^{\cdot-}$.[16a,19a] An alternative mechanism has been put forward for the activation of pentafluoropyridine at $[Rh(Bpin)(PEt_3)_3]$ (**41**).[17b] It involves the addition of a C–F bond across the Rh–B moiety via a four-centered transition state. Evidence is provided by DFT calculations (BP 86) on the model complex $[Rh(Bpin)(PMe_3)_3]$. Both the C–F bond concerted oxidative additions and the boryl-assisted processes were calculated for activations at the 2- and the 4-position in pentafluoropyridine. It turned out that a

boryl-assisted C–F activation shows a kinetic preference for activation at the 2-position, whereas a concerted oxidative addition at the rhodium center would favor the 4-position. The boryl-assisted pathway is, therefore, in accordance with the experimental observations. One factor that might contribute to the preferential accessibility of the boryl-assisted process is the short Rh···N contact in the transition state (2.22 Å, Figure 1). Comparable ligand-assisted reaction pathways have been suggested for reactions of fluoroorganic moieties at electron-rich iridium, platinum, and nickel complexes. Here the C–F bond cleavage occurs by addition across an M–P bond.[14a,14b,38,39]

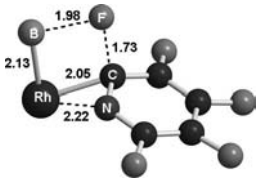
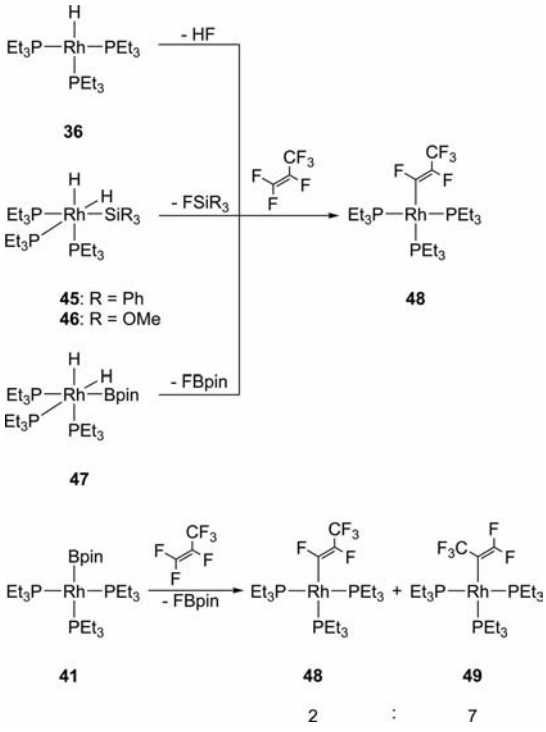


Figure 1. Part of the computed transition state of a boryl-assisted C–F bond activation of pentafluoropyridine at [Rh(Bpin)(PMe_3)$_3$]. Distances are given in Å. Reprinted with permission from ref.[17b] Copyright 2010 Wiley-VCH.

Hydrido complex [Rh(H)(PEt_3)$_3$] (**36**), as well as the hydrido–silyl complexes *cis-fac*-[Rh(H)$_2$(SiR_3)(PEt_3)$_3$] (**45**, **46**), and the hydrido boryl complex *cis-fac*-[Rh(H)$_2$(Bpin)(PEt_3)$_3$] (**47**) are capable of activating fluorinated olefins such as hexafluoropropene. Treatment with hexafluoropropene yielded rhodium(I) complex [Rh{(*Z*)-CF=CF(CF_3)}(PEt_3)$_3$] (**48**) as activation product as well as hydrogen fluoride, fluorosilanes, or FBpin (Scheme 15).[16c,16d,17a,19b]



Scheme 15. C–F activation of hexafluoropropene at rhodium hydrido, silyl, and boryl complexes.

However, in the case of the rhodium(I) boryl complex [Rh(Bpin)(PEt_3)$_3$] (**41**), the reaction led to the formation of complex **48** only as a byproduct, whereas the main product was identified as [Rh{C(CF_3)=CF_2}(PEt_3)$_3$] (**49**) (Scheme 15).[17b]

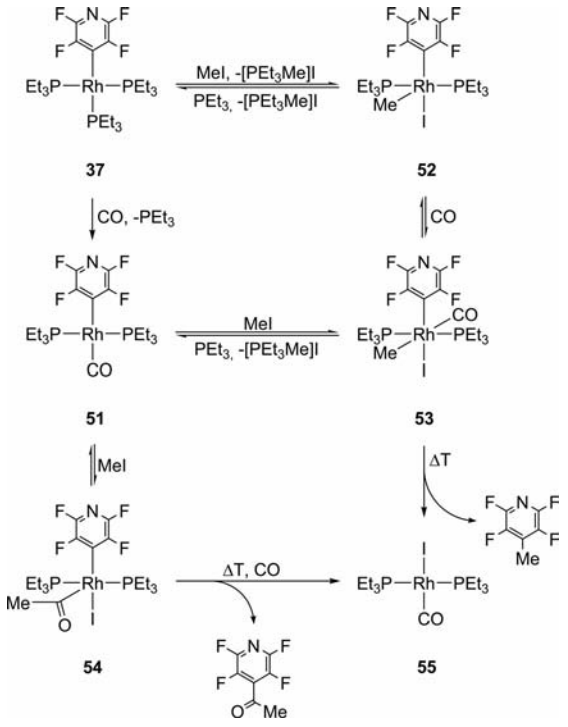
In addition to the reactions described above, there are a few reports on intermolecular and intramolecular C–F activation and derivatization reactions of fluoroolefins at iridium compounds, most notably reported by Cowie and co-workers, who presented a binuclear approach for the activation of fluoroethylenes.[10d,40]

Derivatization Reactions of Aromatics

Jones and co-workers demonstrated that the C–F activation product [(Cp*)Rh(H)(C_6F_5)(PMe_3)] (**16**) eliminates pentafluorobenzene in the presence of an excess of hexafluorobenzene or dihydrogen, but this reaction could not be carried out catalytically.[30] However, Grushin and Young reported that 1-fluoronaphthalene as well as monofluorobenzenes can be hydrodefluorinated catalytically by [Rh(H)(Cl)$_2$(PCy_3)$_2$] (**50**) in the presence of dihydrogen (ca. 6 bar) and sodium hydroxide, though these conversions did not lead to fluorinated products.[41]

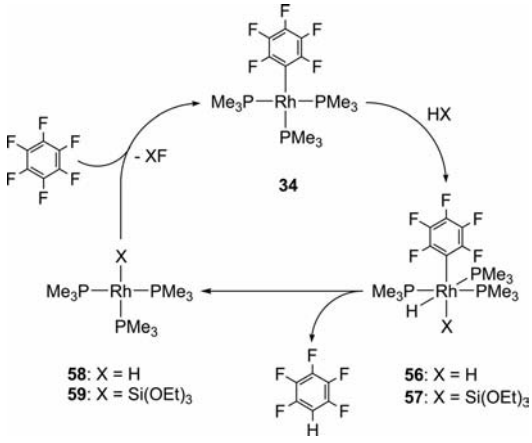
Some derivatization reactions of pentafluoropyridine could be observed with complex [Rh(4-C_5F_4N)(PEt_3)$_3$] (**37**), which is the C–F activation product of pentafluoropyridine.[19e] Treatment of **37** with CO gave the square-planar rhodium(I) compound *trans*-[Rh(4-C_5F_4N)(CO)(PEt_3)$_2$] (**51**) (Scheme 16). A reaction with methyl iodide afforded the oxidative addition product *trans*-[Rh(I)(Me)(4-C_5F_4N)(PEt_3)$_2$] (**52**) and PEt_3, which is trapped by excess MeI to give a phosphonium salt. Complex **52** also reacted with CO to give the carbonyl complex *trans*-[Rh(I)(Me)(4-C_5F_4N)(CO)(PEt_3)$_2$] (**53**), in which the CO and Me groups are in a mutual *trans*-position. Complex **53** is not stable in solution and isomerizes slowly to give the acyl compound *trans*-[Rh(I){C(O)Me}(4-C_5F_4N)(PEt_3)$_2$] (**54**) by a C–C coupling reaction. In the presence of PEt_3, **53** slowly forms *trans*-[Rh(4-C_5NF_4)(CO)(PEt_3)$_2$] (**51**) together with the phosphonium salt [PEt_3Me]I. One possibility for the conversion of **53** into **54** is, therefore, that it occurs via **51**. Indeed, carbonyl complex **51** reacts with MeI to yield **54**. Heating of complexes **53** and **54** led to the generation of *trans*-[Rh(I)(CO)(PEt_3)$_2$] (**55**) as well as 2,3,5,6-tetrafluoro-4-methylpyridine and 2,3,5,6-tetrafluoro-4-acylpyridine, respectively. Both highly fluorinated pyridines represent examples for the derivatization of pentafluoropyridine by C–C coupling reactions. Unfortunately, **55** could not be applied as starting compound in C–F bond activation reactions.[19e]

Treatment of the activation product of hexafluorobenzene [Rh(C_6F_5)(PMe_3)$_3$] (**33**) with dihydrogen or triethoxysilane led to the formation of the rhodium(III) complexes *mer*-[Rh(H)(X)(C_6F_5)(PMe_3)$_3$] [**56**: X = H; **57**: X = Si(OEt)$_3$] (Scheme 17).[16a,19a] A comparable reaction could



Scheme 16. Reactivity of [Rh(4-C_5F_4N)(PEt_3)$_3$] (**37**) towards CO and MeI.

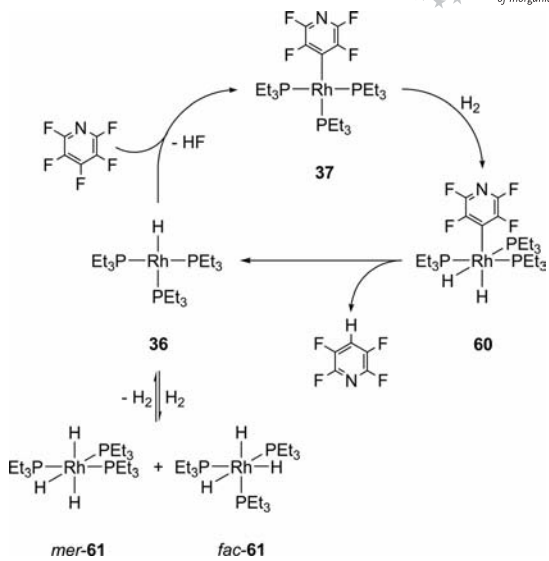
be observed starting from [Rh(4-C_5F_4N)(PEt_3)$_3$] (**37**). Oxidative addition of dihydrogen produced *mer*-[Rh(H)$_2$(4-C_5F_4N)(PEt_3)$_3$] (**60**) (Scheme 18).[42]



Scheme 17. Cyclic process for the hydrodefluorination of hexafluorobenzene.

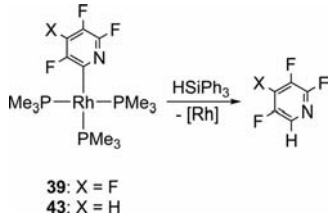
The mono- and dihydrido complexes **56**, **57**, and **60** are not stable, and elimination of the hydrodefluorinated organic molecules was observed (Schemes 17 and 18).[16a,19a,42] In all cases, the resulting organometallic species **36**, **58**, or **59** are capable of C–F activation reactions. Note that **36** reacts further with H_2 to give *mer*- and *fac*-[Rh(H)$_3$(PEt_3)$_3$] (**61**), which are resting states of a putative catalytic cycle (Scheme 18).[42]

Marder, Perutz, and co-workers reported a stoichiometric hydrodefluorination of fluoropyridines by using silanes as hydrogen source. The C–F activation products [Rh(2-



Scheme 18. Cyclic process for the hydrodefluorination of pentafluoropyridine.

C_5F_4N)(PMe_3)$_3$] (**39**) and [Rh{2-C_5(4-H)F_3N}(PMe_3)$_3$] (**43**) react with triphenylsilane to give 2,3,4,5-tetrafluoropyridine and 2,3,5-trifluoropyridine, respectively (Scheme 19). Interestingly, the C–F activation product [Rh(4-C_5F_4N)(PMe_3)$_3$] (**40**) does not react with triphenylsilane.[16e]

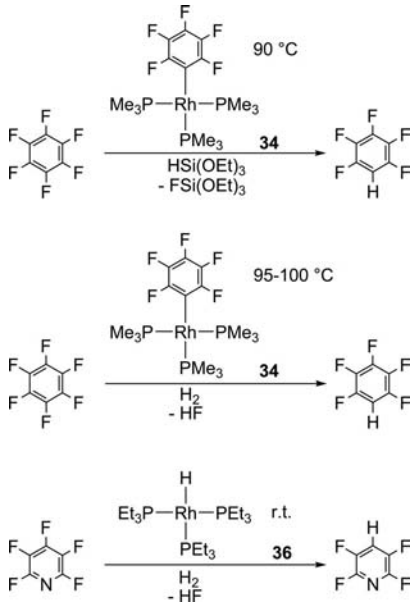


Scheme 19. Formation of fluoropyridines.

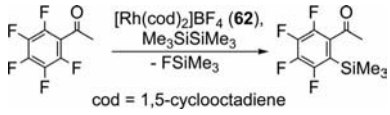
Based on the cyclic processes shown in Schemes 17 and 18, catalytic hydrodefluorination reactions were developed (Scheme 20). Hexafluorobenzene has been successfully converted into pentafluorobenzene with a turnover number (TON) of up to 114 at 90–100 °C. Pentafluorobenzene could be hydrodefluorinated selectively, yielding 1,2,4,5-tetrafluorobenzene with a TON of 55.5.[19a] The catalytic hydrodefluorination of pentafluoropyridine with dihydrogen as hydrogen source was achieved at room temperature.[42]

A remarkable way to derivatize pentafluoroacetophenone by silylation was reported by Murai et al. With a TON of 6, pentafluoroacetophenone could be silylated at the *ortho*-position with hexamethyldisilane in the presence of the cationic complex [Rh(cod)$_2$]BF_4 (**62**) (Scheme 21).[43]

C–F activation products **34**, **39**, **40**, and **43**–**44** are useful precursors for borylation of the fluoroaromatic ligands. With two equivalents of B_2cat_2 (Bcat = B{1,2-$O_2C_6H_4$}), the free boronato esters Ar^FBcat and the triboryl complex *fac*-[Rh(Bcat)$_3$(PMe_3)$_3$] (**63**) were generated (Scheme 22).[16e] These derivatization reactions were the

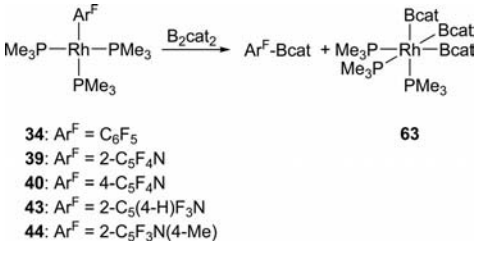


Scheme 20. Catalytic hydrodefluorination reactions of highly fluorinated arenes.



Scheme 21. Catalytic silylation of pentafluoroacetophenone.

first C–F bond borylation steps that have been reported. However, rhodium(III) complex **63** seems to be a thermodynamic sink, and catalytic conversions could not be achieved.

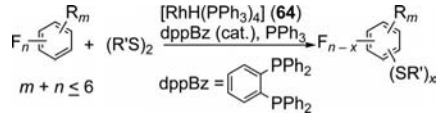


Scheme 22. Borylation of fluorinated arenes.

Very recently, the catalytic borylation of pentafluoropyridine at the 2-position was reported. In the presence of 2.5 mol-% [Rh(Bpin)$(PEt_3)_3$] (**41**), B_2pin_2 and pentafluoropyridine can be converted into the 2-boronato ester (Scheme 23). Note that the hexamethyldisilane has been used as a solvent, partly because the boryl complex **41** reacts with benzene to give the phenyl boronato ester and the rhodium–hydrido complex [Rh(H)$(PEt_3)_3$] (**36**).[17b] The formation of the latter would lead to an activation of pentafluoropyridine at the 4-position and, therefore, to a loss of regioselectivity. The catalytic C–F activation and derivatization of pentafluoropyridine at the 2-position is particularly uncommon, whereas functionalization reactions at the 4-position, by nucleophilic attack, by radical pathways, and even by cross coupling reactions, are well-known.[10,12,13,44]

Scheme 23. Catalytic borylation of pentafluoropyridine at the 2-position.

An example for catalytic C–S bond formation based on C–F activation of fluorinated arenes was reported by Yamaguchi et al. The rhodium(I) hydrido complex [Rh(H)$(PPh_3)_4$] (**64**) catalyzes the reaction of various fluorobenzenes with disulfides in the presence of phosphanes to yield thioethers (Scheme 24).[45] Thiophenolate moieties selectively replace the aromatic fluorides – other functional groups such as R = CN, NO_2, $COCH_3$, Cl, Br do not react.



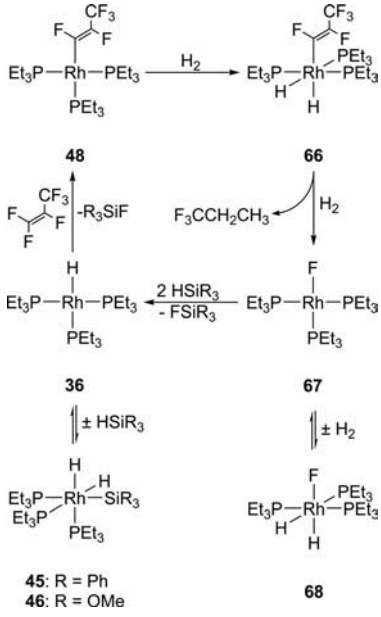
Scheme 24. Catalytic synthesis of thioethers from fluorobenzenes.

Derivatization Reactions of Fluoroolefins

One example for a catalytic hydrodefluorination reaction at fluoroolefins was reported in 2006 by McNeill and Peterson. The rhodium(I) chlorido complex [Rh(Cl)$(PPh_3)_3$] (**65**) could be used to catalyze the hydrodefluorination of vinyl fluoride in the presence of $HSiEt_3$ to give ethylene.[46a] Using dihydrogen instead of triethylsilane did not lead to the formation of ethylene as hydrodefluorination product, but yielded the hydrogenation product fluoroethane.[46b] McNeill and Peterson could also show that 1-chloro-1-fluoroethylene and both *cis*- and *trans*-1-chloro-2-fluoroethylene preferably undergo hydrodechlorination reactions with H_2 and $HSiEt_3$ to yield vinyl fluoride, which then can be hydrodefluorinated in the presence of triethylsilane.[46]

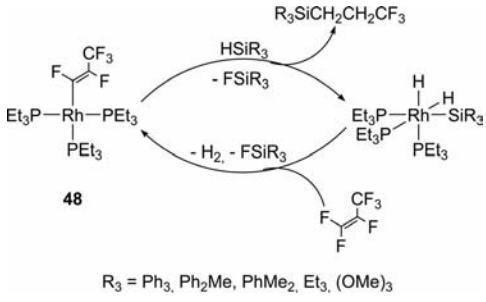
The C–F activation product of hexafluoropropene, [Rh{(*Z*)-CF=CF(CF_3)}$(PEt_3)_3$] (**48**), reacted with dihydrogen to give the dihydrido complex *mer*-[Rh$(H)_2${(*Z*)-CF=CF(CF_3)}$(PEt_3)_3$] (**66**), but this rhodium(III) species did not eliminate the hydrodefluorination product (*E*)-1,2,3,3,3-pentafluoropropene. Instead, reaction with additional dihydrogen yielded 1,1,1-trifluoropropane as well as the rhodium(I) fluoro complex [Rh(F)$(PEt_3)_3$] (**67**) and *cis-mer*-[Rh$(H)_2$(F)$(PEt_3)_3$] (**68**), which is in equilibrium with **67** (Scheme 25).[16c,19b] Fluoro complexes are highly reactive species and, in general, late-transition-metal fluoro compounds offer an interesting and fascinating chemistry.[16c,19b,38c,47] The development of a cyclic process by regeneration of the rhodium hydrido species [Rh(H)$(PEt_3)_3$] (**36**) from **67** was achieved by using tertiary silanes.[16c,48]

The formation of the exceptionally strong Si–F bond provides a reaction pathway that leads to the rhodium(III) dihydrido silyl complexes *cis-fac*-[Rh(H)$_2$(SiR$_3$)(PEt$_3$)$_3$] (**45**: R = Ph; **46**: R = OMe). They are suitable precursors for C–F activation reactions, because they are in equilibrium with **36** (Scheme 15).[16c,16d,19b]



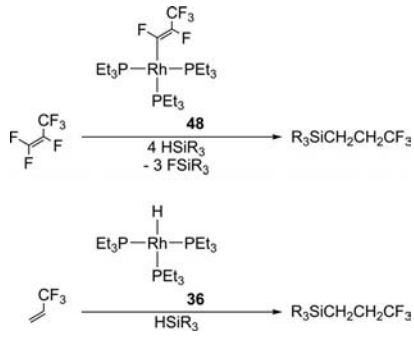
Scheme 25. Cyclic process for the formation of 1,1,1-trifluoropropane by hydrodefluorination of hexafluoropropene with H_2.

When tertiary silanes instead of dihydrogen were used, the hydrodefluorination led to different products. Reactions of [Rh{(*Z*)-CF=CF(CF$_3$)}(PEt$_3$)$_3$] (**48**) with an excess of silane yielded (3,3,3-trifluoropropyl)silanes and not 1,1,1-trifluoropropane (Scheme 26). The resulting rhodium(III) compounds can be used again as starting compounds for the activation of hexafluoropropene, as mentioned before.



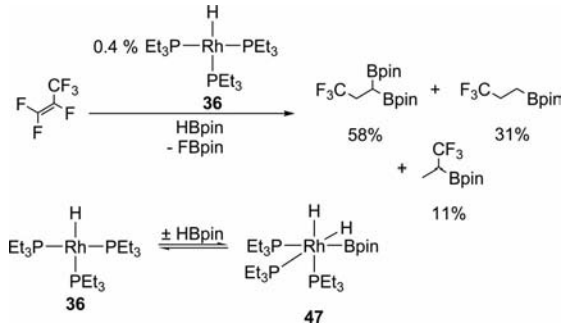
Scheme 26. Cyclic process for the formation of (3,3,3-trifluoropropyl)silanes.

Consequently, complex [Rh{(*Z*)-CF=CF(CF$_3$)}(PEt$_3$)$_3$] (**48**) catalyzes the reaction of hexafluoropropene with HSiR$_3$ [R$_3$ = Ph$_3$, Ph$_2$Me, PhMe$_2$, Et$_3$, (OMe)$_3$] to yield the corresponding (3,3,3-trifluoropropyl)silanes R$_3$SiCH$_2$CH$_2$CF$_3$ (Scheme 27). The latter silanes can also be synthesized by catalytic hydrosilylation of 3,3,3-trifluoropropene with [Rh(H)(PEt$_3$)$_3$] (**36**) as a catalyst (Scheme 27).[16d] It seems to be plausible that this step plays a certain role in the conversion of hexafluoropropene into R$_3$SiCH$_2$CH$_2$CF$_3$.



Scheme 27. Catalytic formation of (3,3,3-trifluoropropyl)silanes.

Another spin-off was observed upon using boranes instead of silanes for a catalytic derivatization of hexafluoropropene. A stoichiometric conversion revealed that treatment of *cis-fac*-[Rh(H)$_2$(Bpin)(PEt$_3$)$_3$] (**47**), which is in equilibrium with **36** and HBpin, with an excess of pinacolborane in the presence of hexafluoropropene led to three different trifluoropropyl-1,3,2-dioxaborolanes and the C–F activation product [Rh{(*Z*)-CF=CF(CF$_3$)}(PEt$_3$)$_3$] (**48**).[17a] In subsequent catalytic experiments, [Rh(H)(PEt$_3$)$_3$] (**36**) was used for the borylation reaction of the fluorinated precursor (Scheme 28). Thus, hexafluoropropene was converted into the trifluoropropyl-1,3,2-dioxaborolanes in the presence of HBpin. The main products are (pinB)$_2$-CHCH$_2$CF$_3$ and (pinB)CH$_2$CH$_2$CF$_3$. Minor amounts of the CH$_3$C(CF$_3$)H(Bpin) could also be detected.[17a]



Scheme 28. Catalytic formation of trifluoropropyl-1,3,2-dioxaborolanes.

Conclusions

Rhodium complexes are excellent tools for C–F activation and derivatization of highly fluorinated precursors. Catalytic hydrodefluorination reactions of highly fluorinated arenes could be elaborated. However, it has to be emphasized that a lot of other transition-metal-catalyzed hydrodefluorination reactions have also been developed, for example, with group 4,[11] group 5,[10l,49] or group 8[11i,16h] complexes, or even with cerium compounds.[11e]

What makes rhodium complexes especially valuable for a derivatization of fluorinated compounds is their capability to replace C–F units selectively by C–Si, C–B, and C–S moieties. This led to a development of new reaction routes for the synthesis of higher-value fluorinated organic compounds, some of which are not accessible otherwise.

C–F bond activation of fluoroalkanes at transition-metal complexes still represents a challenge.[10] Striking results for the C–F bond activation of highly fluorinated alkyl groups were reported by Ozerov[10j,50] and Müller.[51] Silylium cations such as $[Et_3Si]^+[CHB_{11}H_5Cl_6]^-$ could be applied as catalysts for hydrodefluorination reactions in the presence of tertiary silanes. These hydrodefluorination routes are remarkable, because they proved to tolerate aryl halides. Thus, they show a completely different selectivity in comparison to most other C–F activation processes at late transition metals, which favor the cleavage of sp^2 over sp^3 C–F moieties.[10j]

Acknowledgments

The corresponding author's research on C–F activation at rhodium has been supported by the Deutsche Forschungsgemeinschaft (DFG) and the Fonds der Chemischen Industrie. The Berlin DFG Research Training Group "Fluorine as Key Element" is gratefully acknowledged. Collaborations and discussions in this research area with Erhard Kemnitz (HU Berlin), Dieter Lentz (FU Berlin), Stuart A. Macgregor (Heriot-Watt, Edinburgh), John E. McGrady (Oxford), Robin N. Perutz (York), and Udo Radius (Würzburg) were and are very beneficial and fruitful. Important contributions have been made by many students, mainly Daniel Noveski, Falk Wehmeier, Kai Altenhöner, Michael Teltewskoi, and Anna Lena Raza.

[1] R. E. Banks (Ed.), *Fluorine Chemistry at the Millenium. Fascinated by Fluorine*, Elsevier, Amsterdam, **2000**.

[2] a) T. Hiyama, T. Kusumoto, Y. Morizawa, M. Shimizu, *Organofluorine Compounds: Chemistry and Applications*, Springer, Berlin, **2000**; b) J. A. Gladysz, D. P. Curra, I. T. Horvath (Eds.), *Handbook of Fluorous Chemistry*, Wiley-VCH, Weinheim, **2004**; c) R. D. Chambers (Ed.), *Functionalized Inorganic Fluorides*, John Wiley & Sons Ltd., Sussex, **2010**; d) D. B. Harper, D. O'Hagan, C. D. Murphy, *The Handbook of Environmental Chemistry, vol. 3P* (Ed.: G. W. Gribble), Springer, Heidelberg, **2003**, p. 141; e) A. Tressaud, G. Haufe (Eds.), *Fluorine and Health*, Elsevier, Amsterdam, **2008**; f) A. Tressaud, *Fluorine and the Environment*, Elsevier, Amsterdam, **2006**; g) V. Gouverneur, M. Tredwell, *Science of Synthesis Vol. 34: Fluorine* (Ed.: J. M. Percy), Thieme Verlag, Stuttgart, **2006**.

[3] a) A. M. Thayer, *Chem. Eng. News* **2006**, *84*, 15; b) K. Müller, C. Faeh, F. Diederich, *Science* **2007**, *317*, 1881; c) J.-P. Bégué, D. Bonnet-Delpon, *Bioorganic and Medicinal Chemistry of Fluorine*, John Wiley & Sons, Inc., Hoboken, New York, **2008**.

[4] a) M. P. Krafft, J. G. Riess, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1185; b) S. Ebnesajiad, P. R. Khaladkar, *Fluoropolymer Applications in Chemical Processing Industries: The Definitve User's Guide and Databook*, William Andrew Publishing, Norwich, N. Y., **2004**; c) B. Ameduri, B. Boutevin (Eds.), *Well-Architectured Fluoropolymers: Synthesis Properties and Applications*, Elsevier, Amsterdam, **2004**; d) J. Scheirs, *Fluoropolymers – Technology, Markets and Trends*, Rapra, Shewbury, UK, **2001**; e) G. Hougham, P. E. Cassidy, K. Johns, T. Davidson (Eds.), *Fluoropolymers 2: Properties*, Kluwer/Plenum, New York, **1999**; f) S. Rüdiger, U. Gross, E. Kemnitz, *J. Fluorine Chem.* **2007**, *128*, 353; g) E. Kemnitz, D. H. Menz, *Prog. Solid State Chem.* **1998**, *26*, 97; h) T. Krahl, E. Kemnitz, *J. Fluorine Chem.* **2006**, *127*, 663.

[5] a) B. E. Smart, *Mol. Struct. Eng.* **1986**, *3*, 141; b) B. E. Smart in *Fluorocarbons* (Ed.: S. Patai, Z. Rappoport), Wiley, New York, **1983**, p. 603.

[6] a) D. M. Lemal, *J. Org. Chem.* **2004**, *69*, 1; b) D. O'Hagan, *Chem. Soc. Rev.* **2008**, *37*, 308.

[7] K. P. Shine, W. T. Sturges, *Science* **2007**, *315*, 1804.

[8] a) R. L. Scott, *J. Am. Chem. Soc.* **1948**, *70*, 4090; b) J. H. Hildebrand, *J. Am. Chem. Soc.* **1949**, *71*, 22; c) R. L. Scott, *J. Phys. Chem.* **1958**, *62*, 136; d) D. Gudmundsen, E. G. Hope, D. R. Paige, A. M. Stuart, *J. Fluorine Chem.* **2009**, *130*, 952; e) J. Fawcett, E. G. Hope, A. M. Stuart, A. J. West, *Polyhedron* **2006**, *25*, 1182; f) J. Fawcett, E. G. Hope, A. M. Stuart, A. J. West, *Green Chem.* **2005**, *7*, 316; g) D. J. Adams, J. A. Bennett, D. J. Cole-Hamilton, E. G. Hope, J. Hopewell, J. Kight, P. Pogorzelec, A. M. Stuart, *Dalton Trans.* **2005**, 3862; h) M. Skalický, M. Rybáčková, O. Kysilka, M. Kvíčalová, J. Cvačka, J. Čejka, J. Kvíčala, *J. Fluorine Chem.* **2009**, *130*, 966; i) L. C. Šťastná, K. Auerová, J. Kvíčala, J. Čermák, *J. Organomet. Chem.* **2007**, *692*, 1974; j) J. Čermák, L. C. Šťastná, J. Sýkora, I. Císařová, J. Kvíčala, *Organometallics* **2004**, *23*, 2850; k) T. Bříza, J. Kvíčala, O. Paleta, J. Čermák, *Tetrahedron* **2002**, *58*, 3841; l) D. J. Cole-Hamilton, *Science* **2003**, *299*, 1702; m) I. T. Horváth, J. Rábai, *Science* **1994**, *266*, 72; n) J. A. Gladysz, *Science* **1994**, *266*, 55.

[9] a) L. E. Manzer, *Chem. Ind.* **1994**, *53*, 411; b) L. E. Manzer, *Catal. Today* **1992**, *13*, 13; c) L. E. Manzer, *Science* **1990**, *249*, 31; d) V. N. M. Rao, *Organofluorine Chemistry. Principles and Commercial Applications* (Eds.: R. E. Banks, B. E. Smart, J. C. Tatlow), Plenum Press, New York, **1994**; e) E. I. Eger, J. Liu, D. D. Koblin, M. J. Laster, S. Taheri, M. J. Halsey, P. Ionescu, B. S. Chortkoff, T. Hudlicky, *Anesth. Analg.* **1994**, *79*, 245.

[10] a) T. Braun, R. N. Perutz, *Chem. Commun.* **2002**, 2749; b) J. Burdeniuc, B. Jedlicka, R. H. Crabtree, *Chem. Ber./Recueil* **1997**, *130*, 145; c) W. D. Jones, *Dalton Trans.* **2003**, 3991; d) J. L. Kiplinger, T. G. Richmond, C. E. Osterberg, *Chem. Rev.* **1994**, *94*, 373; e) T. G. Richmond, *Topics in Organometallic Chemistry, Vol. 3* (Ed.: S. Murai), Springer, Heidelberg, **1999**, p. 243; f) U. Mazurek, H. Schwarz, *Chem. Commun.* **2003**, 1321; g) H. Torrens, *Coord. Chem. Rev.* **2005**, *249*, 1957; h) R. N. Perutz, T. Braun, *Comprehensive Organometallic Chemistry III, Vol. 1* (Eds.: R. H. Crabtree, M. P. Mingos), Elsevier, Oxford, **2007**, 725; i) H. Amii, K. Uneyama, *Chem. Rev.* **2009**, *109*, 2119; j) G. Meier, T. Braun, *Angew. Chem.* **2009**, *121*, 1575; *Angew. Chem. Int. Ed.* **2009**, *48*, 1546; k) R. P. Hughes, *Eur. J. Inorg. Chem.* **2009**, 4591; l) T. G. Driver, *Angew. Chem.* **2009**, *121*, 8116; *Angew. Chem. Int. Ed.* **2009**, *48*, 7974; m) A. D. Sun, J. A. Love, *Dalton Trans.* **2010**, *39*, 10362; n) T. G. Richmond, *Angew. Chem.* **2000**, *112*, 3378; *Angew. Chem. Int. Ed.* **2000**, *39*, 3241.

[11] for hydrodefluorination reactions see for example: a) B. M. Kraft, W. D. Jones, *J. Organomet. Chem.* **2002**, *658*, 132; b) E. Clot, C. Mégret, B. M. Kraft, O. Eisenstein, W. D. Jones, *J. Am. Chem. Soc.* **2004**, *126*, 5647; c) R. P. Hughes, R. B. Laritchev, A. Williamson, C. D. Incarvito, L. N. Zakharov, A. L. Rheingold, *Organometallics* **2003**, *22*, 2134; d) B. L. Edelbach, A. K. Fazlur-Rahman, R. J. Lachicotte, W. D. Jones, *Organometallics* **1999**, *18*, 3170; e) L. Maron, E. L. Werkema, L. Perrin, O. Eisenstein, R. A. Andersen, *J. Am. Chem. Soc.* **2005**, *127*, 279; f) N. Y. Adonin, V. F. Starichenko, *Mendeleev Commun.* **2000**, *10*, 60; B. M. Kraft, R. J. Lachicotte, W. D. Jones, *Organometallics* **2002**, *21*, 727; g) S. A. Johnson, E. T. Taylor, S. J. Cruise, *Organometallics* **2009**, *28*, 3842; h) S. A. Prikhod'ko, N. Y. Adonin, D. E. Babushkin, V. N. Parmon, *Mendeleev Commun.* **2008**, *18*, 211; i) S. P. Reade, M. F. Mahon, M. K. Whittlesey, *J. Am. Chem. Soc.* **2009**, *131*, 1847; j) A. R. Fout, J. Scott, D. L. Miller, B. C. Bailey, M. Pink, D. J. Mindi-

ola, *Organometallics* **2009**, *28*, 331; k) B. C. Bailey, J. C. Huffman, D. H. Mindiola, *J. Am. Chem. Soc.* **2007**, *129*, 5302; l) V. I. Krasnov, V. E. Platonov, I. V. Beregoyava, L. N. Shohegolava, *Tetrahedron* **1997**, *53*, 1797; m) M. F. Kühnel, D. Lentz, *Angew. Chem.* **2010**, *122*, 2995; *Angew. Chem. Int. Ed.* **2010**, *49*, 2933; n) R. D. Rieth, W. W. Brennessel, W. D. Jones, *Eur. J. Inorg. Chem.* **2007**, 2839; o) B. M. Kraft, W. D. Jones, *J. Am. Chem. Soc.* **2002**, *124*, 8681; p) L. A. Watson, D. V. Yandulov, K. G. Caulton, *J. Am. Chem. Soc.* **2001**, *123*, 603; q) B. M. Kraft, R. J. Lachicotte, W. D. Jones, *J. Am. Chem. Soc.* **2000**, *122*, 8559; r) P. A. Deck, M. M. Konaté, B. V. Kelly, C. Slebodnick, *Organometallics* **2004**, *23*, 1089; s) M. W. Boukamp, J. deWolf, I. D. H. Morales, J. Gercama, A. Meetsma, S. I. Troyanov, B. Hessen, J. H. Teuben, *J. Am. Chem. Soc.* **2002**, *124*, 12956; t) C. Santamaría, R. Beckhaus, D. Haase, W. Saak, R. Koch, *Chem. Eur. J.* **2001**, *7*, 622; u) L. Bareille, S. Becht, J. L. Cui, P. Le Gendre, C. Moïse, *Organometallics* **2005**, *24*, 5802.

[12] a) M. Reinhold, J. E. McGrady, R. N. Perutz, *J. Am. Chem. Soc.* **2004**, *126*, 5268; b) D. R. Fahey, J. E. Mahan, *J. Am. Chem. Soc.* **1977**, *99*, 2501; c) L. Cronin, C. L. Higgitt, R. Karch, R. N. Perutz, *Organometallics* **1997**, *16*, 4920; d) T. Braun, L. Cronin, C. L. Higgitt, J. E. McGrady, R. N. Perutz, M. Reinhold, *New J. Chem.* **2001**, *25*, 19; e) I. Bach, K. R. Pörschke, R. Goddard, C. Kopiske, C. Kruger, A. Rufinska, K. Seevogel, *Organometallics* **1996**, *15*, 4959; f) A. Nova, M. Reinhold, R. N. Perutz, S. A. Macgregor, J. E. McGrady, *Organometallics* **2010**, *29*, 1824; g) T. Schaub, P. Fischer, A. Steffen, T. Braun, U. Radius, A. Mix, *J. Am. Chem. Soc.* **2008**, *130*, 9304; h) T. Braun, S. Parsons, R. N. Perutz, M. Voith, *Organometallics* **1999**, *18*, 1710; i) A. Steffen, M. I. Sladek, T. Braun, B. Neumann, H.-G. Stammler, *Organometallics* **2005**, *24*, 4057; j) T. Braun, M. I. Sladek, R. N. Perutz, *Chem. Commun.* **2001**, 2254; k) T. Schaub, M. Backes, U. Radius, *J. Am. Chem. Soc.* **2006**, *128*, 15964; l) S. Burling, P. I. P. Elliott, N. A. Jasim, R. J. Lindup, J. McKenna, R. N. Perutz, S. J. Archibald, A. C. Whitwood, *Dalton Trans.* **2005**, 3686; m) M. I. Sladek, T. Braun, B. Neumann, H.-G. Stammler, *J. Chem. Soc., Dalton Trans.* **2002**, 297; n) S. A. Johnson, E. T. Taylor, S. J. Cruise, *Organometallics* **2009**, *28*, 3842; o) M. E. Doster, S. A. Johnson, *Angew. Chem.* **2009**, *121*, 2219; *Angew. Chem. Int. Ed.* **2009**, *48*, 2185; p) S. A. Johnson, C. W. Huff, F. Mustafa, M. Saliba, *J. Am. Chem. Soc.* **2008**, *130*, 17278; q) S. J. Archibald, T. Braun, J. A. Gaunt, J. E. Hobson, R. N. Perutz, *J. Chem. Soc., Dalton Trans.* **2000**, 2013.

[13] a) N. A. Jasim, R. N. Perutz, A. C. Whitwood, T. Braun, J. Izundu, B. Neumann, S. Rothfeld, H.-G. Stammler, *Organometallics* **2004**, *23*, 6140; b) T. Braun, J. Izundu, A. Steffen, B. Neumann, H.-G. Stammler, *Dalton Trans.* **2006**, 5118; c) M. R. Cargill, G. Sandford, A. J. Tadeusiak, D. S. Yufit, J. A. K. Howard, P. Kilickiran, G. Nelles, *J. Org. Chem.* **2010**, *75*, 5860; d) D. Breyer, T. Braun, A. Penner, *Dalton Trans.* **2010**, *39*, 7513; e) M. Jakt, L. Johanissen, H. S. Rzepa, D. A. Widdowson, R. Wilhelm, *J. Chem. Soc. Perkin Trans. 2* **2002**, 576.

[14] a) A. Nova, S. Erhardt, N. A. Jasim, R. N. Perutz, S. A. Macgregor, J. E. McGrady, A. C. Whitwoord, *J. Am. Chem. Soc.* **2008**, *130*, 15499; b) S. A. Macgregor, D. C. Roe, W. J. Marshall, K. M. Bloch, V. I. Bakhmutov, V. V. Grushin, *J. Am. Chem. Soc.* **2005**, *127*, 15304; c) M. Crespo, J. Granell, M. Font-Badia, X. Solans, *J. Organomet. Chem.* **2004**, *689*, 3088; d) M. Crespo, M. Martines, J. Sales, *Organometallics* **1993**, *12*, 4297; e) C. M. Anderson, M. Crespo, G. Ferguson, A. J. Lough, R. J. Puddephatt, *Organometallics* **1992**, *11*, 1177; f) M. Crespo, M. Martinez, J. Sales, *J. Chem. Soc., Chem. Commun.* **1992**, 822; g) O. López, M. Crespo, M. Font-Bardía, X. Solans, *Organometallics* **1997**, *16*, 1233; h) M. Crespo, M. Martinez, E. de Pablo, *J. Chem. Soc., Dalton Trans.* **1997**, 1231; i) H. L. Buckley, A. D. Sun, J. A. Love, *Organometallics* **2009**, *28*, 6622; j) H. L. Buckley, T. Wang, O. Tran, J. A. Love, *Organometallics* **2009**, *28*, 2356; T. Wang, J. A. Love, *Organometallics* **2008**, *27*, 3290; k) T. Wang, B. J. Alfonso, J. A. Love, *Org. Lett.* **2007**, *9*, 5629; l) P. Hofmann, G. Unfried, *Chem. Ber.* **1992**, *125*, 659; m) A. Nova, P. González-Duarte, A. Lledós, R. Mas-Ballesté, G. Ujaque, *Inorg. Chim. Acta* **2006**, *359*, 3736; n) U. Mazurek, H. Schwarz, *J. Chem. Soc., Chem. Commun.* **1993**, 1321.

[15] a) X. Li, H. Sun, F. Yu, U. Flörke, H.-F. Klein, *Organometallics* **2006**, *25*, 4695; b) T. Zheng, H. Sun, Y. Chen, X. Li, S. Dürr, U. Radius, K. Harms, *Organometallics* **2009**, *28*, 5771; c) T. Zheng, H. Sun, J. Ding, Y. Zhang, X. Li, *J. Organomet. Chem.* **2010**, *695*, 1873; d) Z. Lian, X. Xu, H. Sun, Y. Chen, T. Zheng, X. Li, *Dalton Trans.* **2010**, *39*, 9523; e) I. M. Piglosiewicz, S. Kraft, R. Beckhaus, D. Haase, W. Saak, *Eur. J. Inorg. Chem.* **2005**, 938; f) M.-D. Su, S.-Y. Chu, *J. Am. Chem. Soc.* **1997**, *119*, 10178; g) M.-D. Su, S.-Y. Chu, *J. Am. Chem. Soc.* **1999**, *121*, 1045.

[16] a) M. Aizenberg, D. Milstein, *Science* **1994**, *265*, 359; b) J. Vela, J. M. Smith, Y. Yu, N. A. Ketterer, C. J. Flaschenriem, R. J. Lachicotte, P. L. Holland, *J. Am. Chem. Soc.* **2005**, *127*, 7857; c) D. Noveski, T. Braun, M. Schulte, B. Neumann, H.-G. Stammler, *Dalton Trans.* **2003**, 4075; d) T. Braun, F. Wehmeier, K. Altenhöner, *Angew. Chem.* **2007**, *119*, 5415; *Angew. Chem. Int. Ed.* **2007**, *46*, 5321; e) R. J. Lindup, T. B. Marder, R. N. Perutz, A. C. Whitwood, *Chem. Commun.* **2007**, 3664; f) J. Yang, M. Brookhart, *J. Am. Chem. Soc.* **2007**, *129*, 12656; g) S. P. Reade, M. F. Mahon, M. K. Whittlesey, *J. Am. Chem. Soc.* **2009**, *131*, 1847.

[17] a) T. Braun, M. Ahijado-Salomon, K. Altenhöner, M. Teltewskoi, S. Hinze, *Angew. Chem.* **2009**, *121*, 1850; *Angew. Chem. Int. Ed.* **2009**, *48*, 1818; b) M. Teltewskoi, J. A. Panetier, S. A. Macgregor, T. Braun, *Angew. Chem.* **2010**, *122*, 4039; *Angew. Chem. Int. Ed.* **2010**, *49*, 3947.

[18] a) U. Jäger-Fiedler, M. Klahn, P. Arndt, W. Baumann, A. Spannenberg, V. V. Burlakov, U. Rosenthal, *J. Mol. Catal. A* **2007**, *261*, 184; b) M. Ali, L.-P. Liu, G. B. Hammond, B. Xu, *Tetrahedron Lett.* **2009**, *50*, 4078; c) M. Klahn, C. Fischer, A. Spannenberg, U. Rosenthal, I. Krossing, *Tetrahedron Lett.* **2007**, *48*, 8900; d) J. Terao, S. A. Begum, Y. Shinohara, M. Tomita, Y. Naitoh, N. Kambe, *Chem. Commun.* **2007**, 855.

[19] a) M. Aizenberg, D. Milstein, *J. Am. Chem. Soc.* **1995**, *117*, 8674; b) T. Braun, D. Noveski, B. Neumann, H.-G. Stammler, *Angew. Chem.* **2002**, *114*, 2870; *Angew. Chem. Int. Ed.* **2002**, *41*, 2745; c) P. J. Albietz, J. F. Houlis, R. Eisenberg, *Inorg. Chem.* **2002**, *41*, 2001; d) M. K. Whittlesey, R. N. Perutz, M. H. Moore, *Chem. Commun.* **1996**, 787; e) D. Noveski, T. Braun, B. Neumann, A. Stammler, H.-G. Stammler, *Dalton Trans.* **2004**, 4106; f) P. K. Chan, W. K. Leong, *Organometallics* **2008**, *27*, 1247; g) see also: S. Rüdiger, E. Kemnitz, *Dalton Trans.* **2008**, 1117.

[20] R. Bosque, E. Clot, S. Fantacci, F. Maseras, O. Eisenstein, R. N. Perutz, K. B. Renkema, K. G. Caulton, *J. Am. Chem. Soc.* **1998**, *120*, 12634.

[21] a) A. C. Albéniz, P. Espinet, B. Martín-Ruiz, D. Milstein, *J. Am. Chem. Soc.* **2001**, *123*, 11504; b) R. López-Fernández, N. Carrera, A. C. Albéniz, P. Espinet, *Organometallics* **2009**, *28*, 4996; c) A. C. Albéniz, P. Espinet, B. Martín-Ruiz, D. Milstein, *Organometallics* **2005**, *24*, 3679; d) N. A. Barnes, A. K. Brisdon, M. Nieuwenhuyzen, R. G. Pritchard, G. C. Saunders, *J. Fluorine Chem.* **2007**, *128*, 943; e) D. G. Ho, R. Ismail, N. Franco, R. Gao, E. P. Leverich, I. Tsyba, N. N. Ho, R. Bau, M. Selke, *Chem. Commun.* **2002**, 570; f) M. Ahijado, T. Braun, D. Noveski, N. Kocher, B. Neumann, D. Stalke, H.-G. Stammler, *Angew. Chem.* **2005**, *117*, 7107; *Angew. Chem. Int. Ed.* **2005**, *44*, 6947; g) M. Ahijado-Salomon, T. Braun, A. Penner, *Angew. Chem.* **2008**, *120*, 8999; *Angew. Chem. Int. Ed.* **2008**, *47*, 8867; h) J. Vicente, J. Gil-Rubio, J. Guerrero-Leal, D. Bautista, *Dalton Trans.* **2009**, 3854; i) M. Ahijado-Salomon, A.-K. Jungton, T. Braun, *Dalton Trans.* **2009**, 7669; j) D. M. Roundhill, D. N. Lawson, G. Wilkinson, *J. Chem. Soc. A* **1968**, 845; k) R. P. Hughes, P. R. Rose, A. L. Rheingold, *Organometallics* **1993**, *12*, 3109; l) P. M. Treichel, E. Pitcher, F. G. A. Stone, *Inorg. Chem.* **1962**, *1*, 511; m) R. P. Hughes, *J. Fluorine Chem.* **2010**, *131*, 1059; n) M. Ahijado-Salomon, T. Braun, I.

Krossing, *Dalton Trans.* **2008**, 5197; o) D. Lentz, *J. Fluorine Chem.* **2004**, *125*, 853; p) D. Lentz, N. Nickelt, S. Willemsen, *Chem. Eur. J.* **2002**, *8*, 1205; q) T. Braun, B. Blöcker, V. Schorlemer, B. Neumann, A. Stammler, H.-G. Stammler, *J. Chem. Soc., Dalton Trans.* **2002**, 2213; r) M. Ahijado, T. Braun, *Angew. Chem.* **2008**, *120*, 2996; *Angew. Chem. Int. Ed.* **2008**, *47*, 2954; s) M. F. Kühnel, D. Lentz, *Dalton Trans.* **2010**, *39*, 9745; t) E. Clot, B. Oelckers, A. H. Klahn, O. Eisenstein, R. N. Perutz, *Dalton Trans.* **2003**, 4065; u) E. Clot, B. M. Besora, F. Maseras, C. Mégret, O. Eisenstein, B. Oelckers, R. N. Perutz, *Chem. Commun.* **2003**, 490; v) E. Clot, C. Mégret, O. Eisenstein, R. N. Perutz, *J. Am. Chem. Soc.* **2009**, *131*, 7817.

[22] G. Yagupsky, C. K. Brown, G. Wilkinson, *J. Chem. Soc. C* **1969**, 1244.

[23] J. Galinkina, E. Rusanov, C. Wagner, H. Schmidt, D. Strohl, S. Tobisch, D. Steinborn, *Organometallics* **2003**, *22*, 4873.

[24] S. T. Belt, S. B. Duckett, M. Helliwell, R. N. Perutz, *J. Chem. Soc., Chem. Commun.* **1989**, 928.

[25] W. D. Jones, M. G. Partridge, R. N. Perutz, *J. Chem. Soc., Chem. Commun.* **1991**, 264.

[26] C. L. Higgitt, A. H. Klahn, M. H. Moore, B. Oelckers, M. G. Partridge, R. N. Perutz, *J. Chem. Soc., Dalton Trans.* **1997**, 1269.

[27] S. T. Belt, M. Helliwell, W. D. Jones, M. G. Partridge, R. N. Perutz, *J. Am. Chem. Soc.* **1993**, *115*, 1429.

[28] M. Ballhorn, M. G. Partridge, R. N. Perutz, M. K. Whittlesey, *Chem. Commun.* **1996**, 961.

[29] A. D. Selmeczy, W. D. Jones, M. G. Partridge, R. N. Perutz, *Organometallics* **1994**, *13*, 522.

[30] B. L. Edelbach, W. D. Jones, *J. Am. Chem. Soc.* **1997**, *119*, 7734.

[31] a) M. J. Atherton, J. Fawcett, J. H. Holloway, E. G. Hope, A. Karaçar, D. R. Russell, G. C. Saunders, *J. Chem. Soc., Chem. Commun.* **1995**, 191; b) M. J. Atherton, J. Fawcett, J. H. Holloway, E. G. Hope, A. Karaçar, D. R. Russell, G. C. Saunders, *J. Chem. Soc., Dalton Trans.* **1996**, 3215; c) J. Fawcett, S. Friedrichs, J. H. Holloway, E. G. Hope, V. McKee, M. Nieuwenhuyzen, D. R. Russell, G. C. Saunders, *J. Chem. Soc., Dalton Trans.* **1998**, 1477; d) M. J. Atherton, J. Fawcett, J. H. Holloway, E. G. Hope, S. M. Martin, D. R. Russell, G. C. Saunders, *J. Organomet. Chem.* **1998**, *555*, 67; e) M. J. Atherton, J. H. Holloway, E. G. Hope, G. C. Saunders, *J. Organomet. Chem.* **1998**, *555*, 209; f) M. Nieuwenhuyzen, G. C. Saunders, *J. Organomet. Chem.* **2000**, *595*, 292; g) N. A. Barnes, A. K. Brisdon, M. Nieuwenhuyzen, R. G. Pritchard, G. C. Saunders, *J. Fluorine Chem.* **2007**, *128*, 943.

[32] a) R. P. Hughes, D. C. Lindner, A. L. Rheingold, L. M. Liable-Sands, *J. Am. Chem. Soc.* **1997**, *119*, 11544; b) R. P. Hughes, D. C. Lindner, J. M. Smith, D. Zhang, C. D. Incarvito, K.-C. Lam, L. M. Liable-Sands, R. D. Sommer, A. L. Rheingold, *J. Chem. Soc., Dalton Trans.* **2001**, 2270; c) R. P. Hughes, I. Kovacik, D. C. Lindner, J. M. Smith, S. Willemsen, D. Zhang, I. A. Guzei, A. L. Rheingold, *Organometallics* **2001**, *20*, 3190; d) R. P. Hughes, T. Le Husebo, S. M. Maddock, L. M. Liable-Sands, A. L. Rheingold, *Organometallics* **2002**, *21*, 243; e) R. P. Hughes, D. C. Lindner, L. M. Liable-Sands, A. L. Rheingold, *Organometallics* **2001**, *20*, 363; f) R. P. Hughes, D. C. Lindner, A. L. Rheingold, G. P. A. Yap, *Organometallics* **1996**, *15*, 5678; g) T. G. Richmond, *Angew. Chem. Int. Ed.* **2000**, *39*, 3241.

[33] a) R. P. Hughes, J. M. Smith, *J. Am. Chem. Soc.* **1999**, *121*, 6084; b) R. P. Hughes, J. M. Smith, L. M. Liable-Sands, T. E. Concolino, K.-C. Lam, C. Incarvito, A. L. Rheingold, *J. Chem. Soc., Dalton Trans.* **2000**, 873; c) R. P. Hughes, J. M. Smith, C. D. Incarvito, K.-C. Lam, B. Rhatigan, A. L. Rheingold, *Organometallics* **2002**, *21*, 2136; d) R. P. Hughes, S. Willemsen, A. Williamson, D. Zhang, *Organometallics* **2002**, *21*, 3085; e) R. P. Hughes, D. Zhang, L. N. Zakharov, A. L. Rheingold, *Organometallics* **2002**, *21*, 4902; f) R. P. Hughes, D. Zhang, A. J. Ward, L. N. Zakharov, A. L. Rheingold, *J. Am. Chem. Soc.* **2004**, *126*, 6169; g) R. P. Hughes, R. B. Larichev, L. N. Zakharov, A. L. Rheingold, *J. Am. Chem. Soc.* **2005**, *127*, 6325; h) S. A. Garratt, R. P. Hughes, I. Kovacik, A. J. Ward, S. Willemsen, D. Zhang, *J. Am. Chem. Soc.* **2005**, *127*, 15585; i) R. P. Hughes, R. B. Larichev, J. Yuan, J. A. Golen, A. N. Rucker, A. L. Rheingold, *J. Am. Chem. Soc.* **2005**, *127*, 15020; j) C. J. Bourgeois, S. A. Garratt, R. P. Hughes, R. B. Larichev, J. M. Smith, A. J. Ward, S. Willemsen, D. Zhang, A. G. Di-Pasquale, L. N. Zakharov, A. L. Rheingold, *Organometallics* **2006**, *25*, 3474; k) R. P. Hughes, R. B. Larichev, L. N. Zakharov, A. L. Rheingold, *Organometallics* **2006**, *25*, 3943; l) C. J. Bourgeois, H. Huang, R. B. Larichev, L. N. Zakharov, A. L. Rheingold, R. P. Hughes, *Organometallics* **2007**, *26*, 264.

[34] a) R. P. Hughes, A. Williamson, R. D. Sommer, A. L. Rheingold, *J. Am. Chem. Soc.* **2001**, *123*, 7443; b) R. P. Hughes, R. B. Larichev, A. Williamson, C. D. Incarvato, L. N. Zakharov, A. L. Rheingold, *Organometallics* **2002**, *21*, 4873; c) R. P. Hughes, R. B. Larichev, A. Williamson, C. D. Incarvato, L. N. Zakharov, A. L. Rheingold, *Organometallics* **2003**, *22*, 2134.

[35] a) M. E. van der Boom, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **1999**, *121*, 6652; b) M. E. van der Boom, Y. Ben-David, D. Milstein, *Chem. Commun.* **1998**, 917.

[36] J. Goodman, V. V. Grushin, R. B. Larichev, S. A. Macgregor, W. J. Marshall, D. C. Roe, *J. Am. Chem. Soc.* **2009**, *131*, 4236.

[37] a) D. J. Huang, P. R. Koren, K. Folting, E. R. Davidson, K. G. Caulton, *J. Am. Chem. Soc.* **2000**, *122*, 8916; b) D. J. Huang, K. G. Caulton, *J. Am. Chem. Soc.* **1997**, *119*, 3185; c) D. Huang, K. B. Renkema, K. G. Caulton, *Polyhedron* **2006**, *25*, 459.

[38] a) S. Erhardt, S. A. Macgregor, *J. Am. Chem. Soc.* **2008**, *130*, 15490; b) A. Nova, M. Reinhold, R. N. Perutz, S. A. Macgregor, J. E. McGrady, *Organometallics* **2010**, *29*, 1824; c) S. A. Macgregor, *Chem. Soc. Rev.* **2007**, *36*, 67; d) O. Blum, F. Frolow, D. Milstein, *J. Chem. Soc., Chem. Commun.* **1991**, 258; e) S. A. Macgregor, T. Wondimagegn, *Organometallics* **2007**, *26*, 1143; f) J. Goodman, S. A. Macgregor, *Coord. Chem. Rev.* **2010**, *254*, 1295.

[39] see also: a) V. V. Grushin, W. J. Marshall, *J. Am. Chem. Soc.* **2004**, *126*, 3068; b) S. A. Macgregor, D. C. Roe, W. J. Marshall, K. M. Bloch, V. I. Bakhmutov, V. V. Grushin, *J. Am. Chem. Soc.* **2005**, *127*, 15304.

[40] a) D. Ristic-Petrovic, M. Wang, R. McDonald, M. Cowie, *Organometallics* **2002**, *21*, 5172; b) D. J. Anderson, R. McDonald, M. Cowie, *Angew. Chem.* **2007**, *119*, 3815; *Angew. Chem. Int. Ed.* **2007**, *46*, 3741; c) M. E. Slaney, D. J. Anderson, M. J. Ferguson, R. McDonald, M. Cowie, *J. Am. Chem. Soc.* **2010**, *132*, 16544.

[41] R. J. Young Jr., V. V. Grushin, *Organometallics* **1999**, *18*, 294.

[42] T. Braun, D. Noveski, M. Ahijado, F. Wehmeier, *Dalton Trans.* **2007**, 3820–3825.

[43] Y. Ishii, N. Chatani, S. Yorimitsu, S. Murai, *Chem. Lett.* **1998**, 157.

[44] a) G. M. Brooke, *J. Fluorine Chem.* **1997**, *86*, 1; b) T. Braun, A. Steffen, V. Schorlemer, B. Neumann, H.-G. Stammler, *Dalton Trans.* **2005**, 3331; c) T. Braun, S. Rothfeld, V. Schorlemer, A. Stammler, H.-G. Stammler, *Inorg. Chem. Commun.* **2003**, *6*, 752; d) T. Braun, V. Schorlemer, B. Neumann, H.-G. Stammler, *J. Fluorine Chem.* **2006**, *127*, 367.

[45] M. Arisawa, T. Suzuki, T. Ishikawa, M. Yamaguchi, *J. Am. Chem. Soc.* **2008**, *130*, 12214.

[46] a) A. A. Peterson, K. McNeill, *Organometallics* **2006**, *25*, 4938; b) A. A. Peterson, K. A. Thoreson, K. McNeill, *Organometallics* **2009**, *28*, 5982.

[47] a) A. Mezzetti, C. Becker, *Helv. Chim. Acta* **2002**, *85*, 2686; b) V. V. Grushin, *Chem. Eur. J.* **2002**, *8*, 1006; c) V. V. Grushin, *Acc. Chem. Res.* **2010**, *43*, 160; d) E. F. Murphy, R. Murugavel, H. W. Roesky, *Chem. Rev.* **1997**, *97*, 3425; e) B. L. Pagenkopf, E. M. Carreira, *Chem. Eur. J.* **1999**, *5*, 3437; f) H. W. Roesky, I. Haiduc, *J. Chem. Soc., Dalton Trans.* **1999**, 2249; g) P. Barthazy, L. Hintermann, R. M. Stoop, M. Wörle, A. Mezzetti, A. Togni, *Helv. Chim. Acta* **1999**, *82*, 2448; h) N. M. Doherty, N. W. Hoffman, *Chem. Rev.* **1991**, *91*, 553; i) A. Steffen, T.

Braun, H.-G. Stammler, *Angew. Chem.* **2007**, *119*, 8828; *Angew. Chem. Int. Ed.* **2007**, *46*, 8674; j) V. V. Grushin, *Chem. Eur. J.* **2002**, *8*, 1006; k) D. A. Watson, M. Su, G. Teverovsky, Y. Zhang, J. Garcia-Fortanet, T. Kinzel, S. L. Buchwald, *Science* **2009**, *325*, 1661; l) T. Furuya, D. Benitez, E. Tkatchouk, A. E. Strom, P. Tang, W. A. Goddard III, T. Ritter, *J. Am. Chem. Soc.* **2010**, *132*, 3793; m) N. D. Ball, M. Sanford, *J. Am. Chem. Soc.* **2009**, *131*, 3796; n) A. W. Kaspi, A. Yahav-Levi, I. Goldberg, A. Vigalok, *Inorg. Chem.* **2008**, *47*, 5; o) P. Barthazy, R. M. Stoop, M. Wörle, A. Togni, A. Mezzetti, *Organometallics* **2000**, *19*, 2844; p) D. V. Yandulov, N. T. Tran, *J. Am. Chem. Soc.* **2007**, *129*, 1342; q) V. V. Grushin, W. J. Marshall, *Organometallics* **2007**, *26*, 4997; r) T. Fuyura, T. Ritter, *J. Am. Chem. Soc.* **2008**, *130*, 10060; s) T. Fuyura, A. E. Strom, T. Ritter, *J. Am. Chem. Soc.* **2009**, *131*, 1662; t) T. Furuya, H. M. Kaiser, T. Ritter, *Angew. Chem.* **2008**, *120*, 6082; *Angew. Chem. Int. Ed.* **2008**, *47*, 5993.

[48] D. Noveski, T. Braun, S. Krückemeier, *J. Fluorine Chem.* **2004**, *125*, 959.

[49] a) K. Fuchibe, T. Akiyama, *J. Am. Chem. Soc.* **2006**, *128*, 1434; b) K. Fuchibe, Y. Ohshima, K. Mitomi, T. Akiyama, *Org. Lett.* **2007**, *9*, 1497; c) K. Fuchibe, K. Mitomi, R. Suzuki, T. Akiyama, *Chem. Asian J.* **2008**, *3*, 261; d) K. Fuchibe, K. Mitomi, T. Akiyama, *Chem. Lett.* **2007**, *36*, 24; e) K. Fuchibe, T. Kaneko, K. Mori, T. Akiyama, *Angew. Chem.* **2009**, *121*, 8214; *Angew. Chem. Int. Ed.* **2009**, *48*, 8070.

[50] a) V. J. Scott, R. Çelenligil-Çetin, O. V. Ozerov, *J. Am. Chem. Soc.* **2005**, *127*, 2852; b) C. Douvris, E. S. Stoyanov, F. S. Tham, C. A. Reed, *Chem. Commun.* **2007**, 1145; c) C. Douvris, O. V. Ozerov, *Science* **2008**, *321*, 1188; d) C. Douvris, C. M. Nagaraja, C.-H. Chen, B. M. Foxman, O. V. Ozerov, *J. Am. Chem. Soc.* **2010**, *132*, 4946; e) see also: S. Duttwyler, C. Douvris, N. L. P. Fackler, F. S. Tham, C. A. Reed, K. K. Baldridge, J. S. Siegel, *Angew. Chem.* **2010**, *122*, 7681; *Angew. Chem. Int. Ed.* **2010**, *49*, 7519.

[51] a) R. Panisch, M. Bolte, T. Müller, *J. Am. Chem. Soc.* **2006**, *128*, 9676; b) N. Lühmann, R. Panisch, T. Müller, *Appl. Organomet. Chem.* **2010**, *24*, 533.

Received: November 8, 2010
Published Online: January 11, 2011

