DOI: 10.1002/ejic.201100917

Synthesis, Structure and Reactivity of Iridium Hydrido Fluorido Complexes

Paul Kläring,[a] Ann-Katrin Jungton,[a] Thomas Braun,*[a] and Carsten Müller[b]

Keywords: Fluorinated ligands / Hydride ligands / Iridium / Fluorination

The oxidative addition of HF at *trans*-[Ir(Ar^F)(η^2-C_2H_4)($PiPr_3$)$_2$] (**1a**: Ar^F = 4-C_5NF_4; **1b**: Ar^F = 2-$C_6H_3F_2$) affords the fluorido complexes *trans*-[Ir(Ar^F)(F)(H)($PiPr_3$)$_2$] (**2a**: Ar^F = 4-C_5NF_4; **2b**: Ar^F = 2-$C_6H_3F_2$). The hydrido fluorido complex **2a** is also accessible by means of the reaction of the hydroxido complex *trans*-[Ir(4-C_5NF_4)(H)(OH)($PiPr_3$)$_2$] (**3a**) with $Et_3N{\cdot}3HF$. Both compounds **2a** and **2b** react with CO to give the carbonyl complexes *trans*-[Ir(4-C_5NF_4)(F)(H)(CO)($PiPr_3$)$_2$] (**4a**: Ar^F = 4-C_5NF_4; **4b**: Ar^F = 2-$C_6H_3F_2$). In the presence of traces of water, a slow reaction of **2a** with CO_2 yields the hydrogencarbonato complex *trans*-[Ir(4-C_5NF_4)(H)(κ^2-(*O*,*O*)-O_2COH)($PiPr_3$)$_2$] (**5a**). Upon using **2a** or **2b** as fluorinating agent, Ph_3SiH could be converted into Ph_3SiF and CH_3C(O)Cl into CH_3C(O)F.

Introduction

The interest in transition-metal-mediated fluorido complexes has increased rapidly in the last two decades because of their remarkable reactivity[1] and their role as possible intermediates in C–F bond activation reactions[2] or transition-metal-mediated fluorination reactions.[3] Various transition-metal-mediated fluorination reactions can be accomplished by nucleophilic or electrophilic fluorination of a transition-metal-bound substrate.[3,4] C–F bond-forming reactions with the participation of transition-metal fluorides are also known.[3,5] The formation of fluoroaromatics by reductive elimination as C–F bond-forming step from transition-metal aryl fluorides has been a challenge for a long time, but considerable progress has been made in the last decade.[3,6] Recently, Watson and Buchwald et al. developed a palladium catalyst that allows the catalytic fluorination of aryl halides and triflates when using CsF or AgF as fluorinating agent.[7] In this case, the reductive elimination of aryl fluorides is achieved by a decreased electron density at the metal centre as a consequence of a sterically demanding phosphane ligand, which blocks the fourth coordination site at the palladium aryl fluorido intermediate.

Transition-metal fluorido complexes can, for instance, be prepared by oxidative addition of a C–F bond.[2b–2e,2g,8] Other reactions include the oxidation of a transition-metal complex with XeF_2[9] or with elemental fluorine[10] as well as conversions that involve HF or its derivatives.[11] However, the most common procedures represent halide exchange reactions when using metal fluorides such as KF, CsF, TlF, AgF or other nucleophilic fluoride sources.[5,7,12]

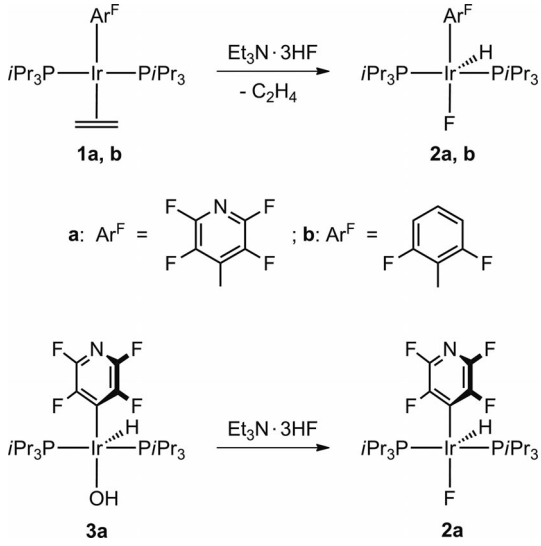
Herein we report the synthesis of the Ir^{III}–fluorido–hydrido complexes *trans*-[Ir(Ar^F)(F)(H)($PiPr_3$)$_2$] (**2a**: Ar^F = 4-C_5NF_4; **2b**: Ar^F = 2-$C_6H_3F_2$) by oxidative addition of HF when using $Et_3N{\cdot}3HF$ as the HF source. Studies on their reactivity towards CO, Ph_3SiH and CH_3C(O)Cl are also described.

Results and Discussion

Treatment of the Ir^I ethylene complexes *trans*-[Ir(Ar^F)(η^2-C_2H_4)($PiPr_3$)$_2$] (**1a**: Ar^F = 4-C_5NF_4; **1b**: Ar^F = 2-$C_6H_3F_2$)[13] with $Et_3N{\cdot}3HF$ in THF at room temperature led to the formation of fluorido hydrido complexes *trans*-[Ir(Ar^F)(F)(H)($PiPr_3$)$_2$] (**2a**: Ar^F = 4-C_5NF_4; Ar^F = **2b**: 2-$C_6H_3F_2$) (Scheme 1). Compound **2a** can also be synthesized by a reaction of the hydrido hydroxido complex *trans*-[Ir(4-C_5NF_4)(H)(OH)($PiPr_3$)$_2$] (**3a**) with $Et_3N{\cdot}3HF$ (Scheme 1).[14] Mechanistically, this conversion might proceed by an oxidative addition of HF at a reactive 14-electron species, which can be formed by reductive elimination of water from **3a**. It was shown before that **3a** is susceptible to the reductive elimination of water.[14,15] However, a protonation of the hydroxido ligand to give water and **2a** is also conceivable.

The $^{31}P\{^1H\}$ NMR spectrum of **2a** displays a doublet of doublets at δ = 39.5 ppm ($^2J_{F,P}$ = 16.3 Hz, $^4J_{F,P}$ = 9.4 Hz) for the phosphane ligands in a *trans* configuration. Four multiplets in a 1:1:1:1 ratio can be found in the $^{19}F\{^1H\}$ NMR spectrum for the fluorine atoms of the tetrafluoropyridyl ligand. This indicates a hindered rotation about the Ir–C bond.[13,16] A broad singlet at δ = –267.4 ppm verifies the presence of the fluorido ligand.[9h,12a,17] The signal remains broad at low temperature (223 K). The hydrido li-

[a] Humboldt-Universität zu Berlin,
Department of Chemistry,
Brook-Taylor-Straße 2, 12489 Berlin, Germany
Fax: +49-30-2093-3913
E-mail: thomas.braun@chemie.hu-berlin.de
[b] Freie Universität Berlin,
Department of Chemistry and Biochemistry,
Takustraße 3, 14195 Berlin, Germany
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201100917.



Scheme 1. Synthesis of the Ir^{III} fluorido hydrido complexes **2a** and **2b**.

gand gives rise to a multiplet at δ = –40.28 ppm in the ^{1}H NMR spectrum, which simplifies to a triplet ($^2J_{H,P}$ = 12.0 Hz) upon ^{19}F decoupling and to a doublet of doublets upon ^{31}P decoupling ($^2J_{H,F}$ = 12.1 Hz, $^4J_{H,F}$ = 2.8 Hz). The IR spectrum of **2a** shows an absorption band at $\tilde{\nu}$ = 455 cm^{-1}, which could possibly be assigned to the Ir–F stretching vibration.[18] A DFT frequency-mode analysis shows frequencies at 445 cm^{-1} for a coupled H–Ir–F vibration and at 2482 cm^{-1} (very weak) for the Ir–H stretching vibration. An absorption band for the Ir–H vibration was not found in the IR spectrum of **2a**. Comparable spectroscopic data were found for the difluorophenyl fluorido complex *trans*-[Ir(2-$C_6H_3F_2$)(F)(H)(P*i*Pr$_3$)$_2$] (**2b**).

The molecular structures of **2a** and **2b** were determined by X-ray diffraction analyses at 100 K (Figures 1 and 2). Suitable crystals of **2a** were grown from an *n*-pentane solution at 243 K; crystals of **2b** were obtained by slow evaporation of the solvent from an *n*-hexane solution. Selected bond lengths and angles are summarized in Table 1. Both molecules **2a** and **2b** show an approximately square-planar arrangement of the metal-bound fluorine atom, the metal-bound carbon atom of the aryl unit and the phosphane ligands, which are in a mutually *trans* configuration. The hydrido ligand was located for neither **2a** nor **2b** but is expected to occupy an apical coordination site, which results in an overall square-pyramidal structure. DFT calculations for **2a** and **2b** verify the suggested square-pyramidal structures and the apical position of the metal-bound hydrogen atoms (see the Supporting Information; Figures 3 and 4). The Ir–F bond lengths [**2a** 2.039(2) Å, **2b** 2.0508(17) Å] are comparable to those in other Ir^{III} fluorido complexes, as, for example, in [Ir{η^5-$C_5(CH_3)_4(CH_2CH_3)$}(F)(Ph)(PMe_3)] [2.069(4) Å], [Ir(Cp*)(F)(R^F)(PMe_3)] [2.070(2) Å for R^F = CF_2CF_3; 2.055(3) Å for R^F = $CF_2CF_2CF_3$; 2.074(3) Å for R^F = $CF(CF_3)_2$] and [Ir(F)(H)$_2$(P*t*Bu$_2$Ph)$_2$]

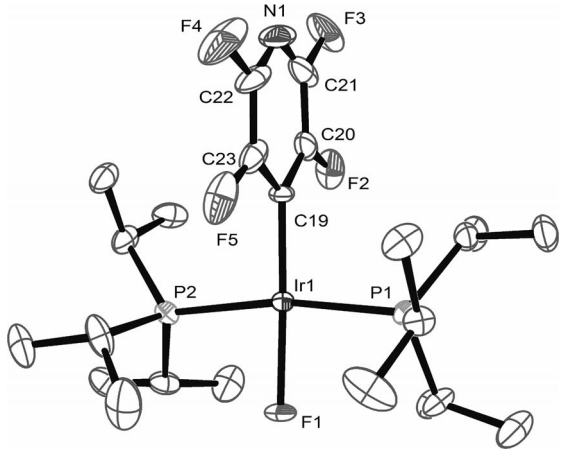


Figure 1. An ORTEP diagram of **2a**. Ellipsoids are drawn at the 50% level; hydrogen atoms at the *i*Pr groups are omitted for clarity.

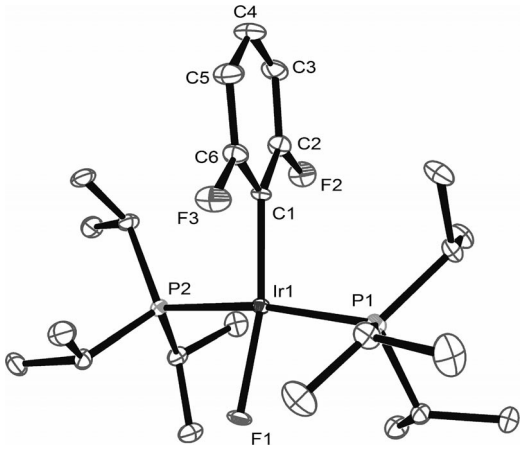


Figure 2. An ORTEP diagram of **2b**. Ellipsoids are drawn at the 50% level; hydrogen atoms at the aromatic ring and at the *i*Pr groups are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] in *trans*-[Ir(4-C_5NF_4)(F)(H)(P*i*Pr$_3$)$_2$] (**2a**) and *trans*-[Ir(2-$C_6H_3F_4$)(F)(H)(P*i*Pr$_3$)$_2$] (**2b**) with estimated standard deviations in parentheses.

Compound **2a**		Compound **2b**	
Ir1–P1	2.3425(9)	Ir1–P1	2.3292(7)
Ir1–P2	2.3518(10)	Ir1–P2	2.3255(7)
Ir1–F1	2.039(2)	Ir1–F1	2.0508(17)
Ir1–C19	1.998(3)	Ir1–C1	2.018(3)
C19–C20	1.388(5)	C1–C2	1.392(4)
C20–C21	1.397(7)	C2–C3	1.387(4)
C21–N1	1.324(10)	C3–C4	1.381(5)
C22–N1	1.293(10)	C4–C5	1.389(5)
C22–C23	1.364(6)	C5–C6	1.387(4)
C19–C23	1.401(5)	C1–C6	1.395(4)
C20–F2	1.347(6)	C20–F2	1.371(3)
C21–F3	1.334(7)	C21–F3	1.377(3)
C22–F4	1.341(7)		
C23–F5	1.359(6)		
P1–Ir1–P2	169.85(3)	P1–Ir1–P2	170.24(3)
P1–Ir1–C19	93.30(11)	P1–Ir1–C1	95.85(8)
P2–Ir1–C19	96.81(11)	P2–Ir1–C1	92.90(8)
P1–Ir1–F1	85.99(8)	P1–Ir1–F1	86.52(5)
P2–Ir1–F1	83.87(8)	P2–Ir1–F1	86.44(5)
C19–Ir1–F1	172.39(13)	C1–Ir1–F1	162.44(10)

[2.045(9) Å].[5a,12a,12c] The calculation of the structural index parameter τ, introduced by Addison and Reedijk et al., furnishes a value of $\tau = 0.04$ for **2a** and $\tau = 0.13$ for **2b**.[19] Whereas τ is close to zero for square-pyramidal structures, τ is equal to unity for trigonal-bipyramidal systems.

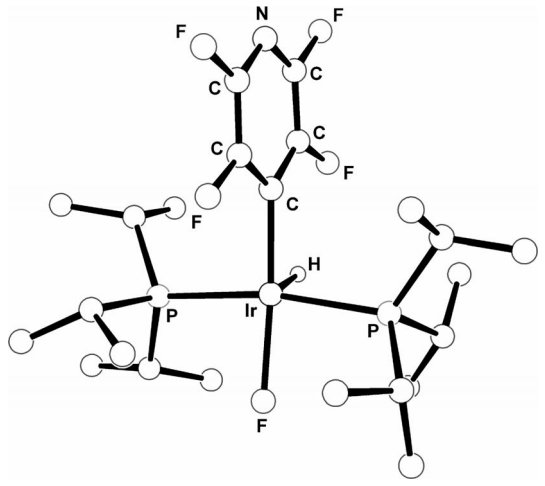


Figure 3. DFT-optimized structure for **2a**. The hydrogen atoms at the *i*Pr groups are omitted for clarity.

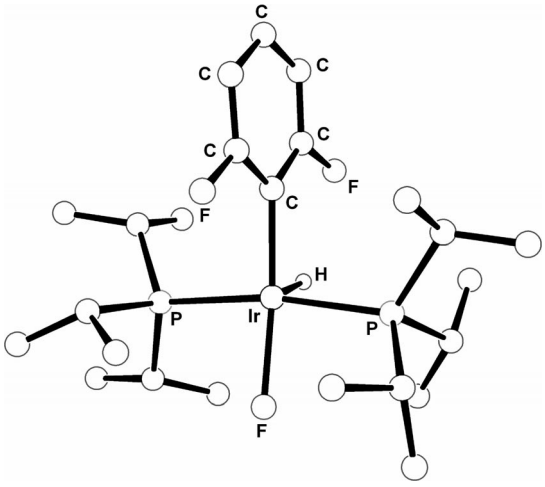
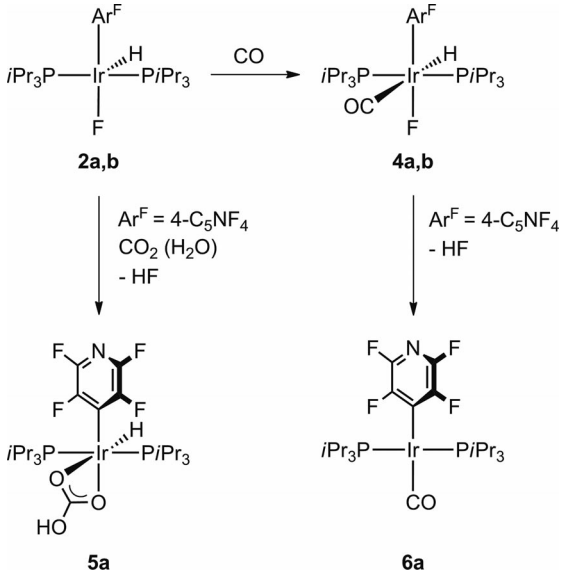


Figure 4. DFT-optimized structure for **2b**. The hydrogen atoms at the aromatic ring and at the *i*Pr groups are omitted for clarity.

Treatment of **2a** or **2b** with CO afforded the formation of the carbonyl complexes *trans*-[Ir(Ar^F)(F)(H)(CO)($PiPr_3$)$_2$] (**4a**: Ar^F = 4-C_5NF_4; **4b**: Ar^F = 2-$C_6H_3F_2$) (Scheme 2). In solution, **4a** decomposes slowly at room temperature to form the Ir^I carbonyl complex *trans*-[Ir(4-C_5NF_4)(CO)($PiPr_3$)$_2$] (**6a**), which was characterized before.[13] An insertion of the carbonyl ligand into the Ir–F bond to give a fluoroacyl species[9a,9b] was not observed. We also have no indication for the reductive elimination of 2,3,5,6-tetrafluoropyridine or even pentafluoropyridine.[6,7,20]



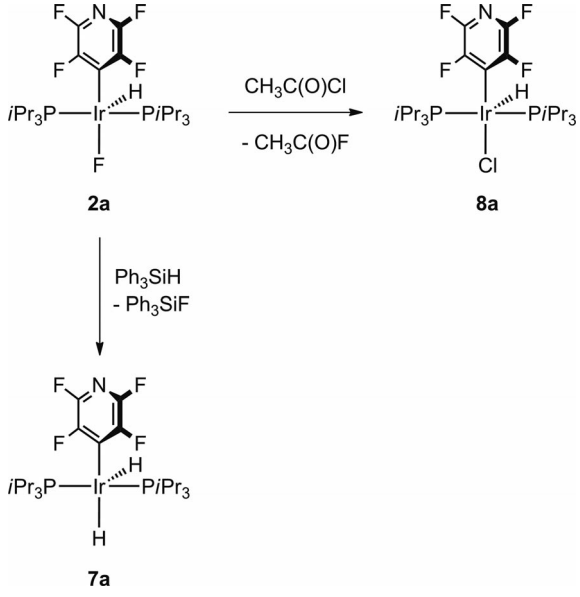
Scheme 2. Reactivity of **2a** and **2b** towards CO and CO_2/H_2O.

The $^{31}P\{^1H\}$ NMR spectrum of **4a** displays a doublet at $\delta = 21.4$ ppm with a coupling constant of $^2J_{F,P} = 22.0$ Hz, which indicates a *cis* configuration of the phosphane groups and the fluorido ligand. Four multiplets in the $^{19}F\{^1H\}$ NMR spectrum indicate a hindered rotation of the tetrafluoropyridyl ligand about the Ir–C bond.[13,16] A broad singlet can be found at $\delta = -444.3$ ppm for the metal-bound fluorine atom.[5a,9h,17] The ^1H NMR spectrum of **4a** shows a multiplet for the hydrido ligand at $\delta = -5.90$ ppm. The multiplet simplifies to a triplet ($^2J_{H,P} = 15.2$ Hz) upon ^{19}F decoupling and to a doublet of doublets ($^2J_{H,F} = 14.8$ Hz, $^4J_{H,F} = 9.6$ Hz) upon ^{31}P decoupling. The *trans* configuration of the hydrido and the carbonyl ligand was verified by determination of the $^2J_{H,C}$ coupling constant of 53.0 Hz in the isotopomer *trans*-[Ir(4-C_5NF_4)(F)(H)(^{13}CO)($PiPr_3$)$_2$] (**4a′**), which is characteristic of a *trans* arrangement.[21] The IR spectrum of **4a** exhibits an absorption band at 2170 cm^{-1} for the Ir–H vibration, and one at 2010 cm^{-1} for the C≡O vibration of the carbonyl ligand.[13,14] Comparable spectroscopic data have been found for *trans*-[Ir(2-$C_6H_3F_2$)(F)(H)(CO)($PiPr_3$)$_2$] (**4b**) and *trans*-[Ir(2-$C_6H_3F_2$)(F)(H)(^{13}CO)($PiPr_3$)$_2$] (**4b′**).

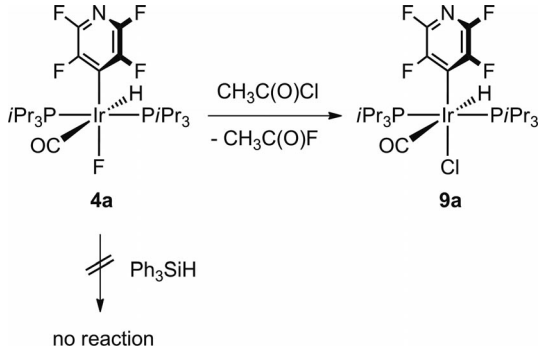
Treatment of a solution of **2a** with CO_2 showed initially no reactivity of **2a** towards CO_2. However, after several days the formation of *trans*-[Ir(4-C_5NF_4)(H){κ^2-(*O,O*)-O_2COH}($PiPr_3$)$_2$] (**5a**) could be detected by NMR spectroscopy (Scheme 2).[14] We presume that in the presence of adventitious water the hydrido hydroxido complex *trans*-[Ir(4-C_5NF_4)(H)(OH)($PiPr_3$)$_2$] was generated, which reacts rapidly with CO_2 to give **5a**, which was reported previously.[14]

Tertiary silanes can be considered to be good reagents for the replacement of a fluorido by a hydrido ligand.[22] Indeed, treatment of **2a** or **2b** with an excess amount of Ph_3SiH afforded the formation of Ph_3SiF and the corresponding dihydrido complexes *trans*-[Ir(Ar^F)(H)$_2$($PiPr_3$)$_2$] (**7a**: Ar^F = 4-C_5NF_4; **7b**: Ar^F = 2-$C_6H_3F_2$) (Scheme 3),

which were described and characterized before.[13] In addition to the signals of **7a** or **7b**, the ^{19}F NMR spectra of the reaction mixtures showed a singlet at δ = –169.2 ppm with ^{29}Si satellites ($^1J_{F,Si}$ = 282.5 Hz) for Ph_3SiF.[23] The presence of Ph_3SiF was also confirmed by an $^1H,^{29}Si$ HMBC NMR spectrum, which shows a doublet at $\delta(^{29}Si)$ = –3.5 ppm ($^1J_{F,Si}$ = 284 Hz).[23] Note that complex **4a** does not react with Ph_3SiH (Scheme 4).



Scheme 3. Reactivity of **2a** towards Ph_3SiH and $CH_3C(O)Cl$.



Scheme 4. Reactivity of **4a** towards $CH_3(O)Cl$.

Upon treatment of **2a** with acetyl chloride, a quantitative conversion occurs at room temperature within a few minutes. Acetyl fluoride and the hydrido chlorido complex *trans*-[Ir(4-C_5NF_4)(Cl)(H)(P*i*Pr$_3$)$_2$] (**8a**) were detected by NMR spectroscopy (Scheme 3). The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at δ = 33.5 ppm for the phosphane ligands, which are in a mutual *trans* configuration. Four signals in the ^{19}F NMR spectrum can be assigned to the fluorine atoms of the tetrafluoropyridyl ligand in **8a**. A quartet at δ = 48.6 ppm ($^3J_{H,F}$ = 7.2 Hz) indicates the presence of acetyl fluoride.[24] In the ^1H NMR spectrum, a doublet of triplets at δ = –41.15 ppm ($^2J_{H,P}$ = 12.4 Hz, $^4J_{H,F}$ = 5.7 Hz) can be found for the hydrido ligand.

A reaction of the fluorido hydrido carbonyl complex *trans*-[Ir(4-C_5NF_4)(F)(H)(CO)(P*i*Pr$_3$)$_2$] (**4a**) with acetyl chloride gave also acetyl fluoride and *trans*-[Ir(4-C_5NF_4)(Cl)(H)(CO)(P*i*Pr$_3$)$_2$] (**9a**) (Scheme 4). A singlet at δ = 13.1 ppm in the $^{31}P\{^1H\}$ NMR spectrum of **9a** could be assigned to the phosphanes in a mutual *trans* position. Again four multiplets in the $^{19}F\{^1H\}$ NMR spectrum indicate a restricted rotation of the tetrafluoropyridyl ligand about the Ir–C bond.[13,16] The ^1H NMR spectrum of **9a** shows a multiplet at δ = –7.99 ppm, which simplifies to a triplet upon ^{19}F decoupling ($^2J_{H,P}$ = 16.2 Hz) and to a doublet upon ^{31}P decoupling ($^4J_{H,F}$ = 15.3 Hz). For the isotopomer *trans*-[Ir(4-C_5NF_4)(Cl)(H)(^{13}CO)(P*i*Pr$_3$)$_2$] (**9a′**) a carbon–hydrogen coupling of 54.4 Hz indicates a *trans* arrangement of the hydrido and the carbonyl ligand. The IR spectrum of **9a** displays two absorption bands at $\tilde{\nu}$ = 2276 cm^{-1} for the Ir–H moiety and at $\tilde{\nu}$ = 2015 cm^{-1} for the C≡O vibration.

Conclusion

In this paper, we have reported the synthesis of the fluorido hydrido complexes *trans*-[Ir(Ar^F)(F)(H)(P*i*Pr$_3$)$_2$] (**2a**: Ar^F = 4-C_5NF_4; **2b**: Ar^F = 2-$C_5H_3F_2$) by oxidative addition of HF at *trans*-[Ir(Ar^F)(η^2-C_2H_4)(P*i*Pr$_3$)$_2$] (**1a**: Ar^F = 4-C_5NF_4; **1b**: Ar^F = 2-$C_6H_3F_2$) species. Reactivity studies reveal that *trans*-[Ir(4-C_5NF_4)(F)(H)(P*i*Pr$_3$)$_2$] (**2a**) and its derivative *trans*-[Ir(4-C_5NF_4)(F)(H)(CO)(P*i*Pr$_3$)$_2$] (**4a**) act as a source of fluoride to convert acetyl chloride into acetyl fluoride. However, we did not observe the formation of C–H or C–F bonds by reductive elimination, whereas an HF elimination occurs from *trans*-[Ir(4-C_5NF_4)(F)(H)(CO)(P*i*Pr$_3$)$_2$] (**4a**) to yield *trans*-[Ir(4-C_5NF_4)(CO)(P*i*Pr$_3$)$_2$] (**6a**).

Experimental Section

General: All experiments were performed with a Schlenk line under an atmosphere of argon or in an argon-filled glovebox with oxygen levels below 10 ppm. All solvents were dried by stirring with Na/K and then distilled under an atmosphere of argon. ^{13}CO was commercially available from Sigma Aldrich. Compounds *trans*-[Ir(4-C_5NF_4)(η^2-C_2H_4)(P*i*Pr$_3$)$_2$] (**1a**) and *trans*-[Ir(2-$C_6H_3F_2$)(η^2-C_2H_4)(P*i*Pr$_3$)$_2$] (**1b**) were prepared according to the literature.[13] The NMR spectra were recorded with a Bruker DPX 300 NMR spectrometer at 298 K. The ^1H NMR spectroscopic chemical shifts were referenced to residual C_6D_5H at δ = 7.16 ppm or [D$_7$]THF at δ = 1.72 ppm. The ^{19}F NMR spectra were referenced to external C_6F_6 at δ = –162.9 ppm and the $^{31}P\{^1H\}$ NMR spectra were referenced externally to H_3PO_4 at δ = 0.0 ppm. Microanalyses were performed with a HEKAtech Euro EA elemental analyzer. Infrared spectra were recorded with a a Bruker Vertex 70 spectrometer equipped with an ATR unit (diamond).

***trans*-[Ir(4-C_5NF_4)(F)(H)(P*i*Pr$_3$)$_2$] (2a):** A solution of *trans*-[Ir(4-C_5NF_4)(η^2-C_2H_4)(P*i*Pr$_3$)$_2$] (**1a**) (238 mg, 0.345 mmol) in THF (21 mL) was treated with $Et_3N{\cdot}3HF$ (23 μL, 0.141 mmol) at room temperature. The reaction mixture turned from dark red to orange. After stirring for 16 h, all the volatile compounds were removed under vacuum and the residue was then extracted with *n*-pentane (10 mL). The volatile compounds were evaporated under vacuum

from the extract and a yellow powder remained; yield 161 mg (68%). $C_{23}H_{43}F_5IrNP_2$ (682.75): calcd. C 40.46, H 6.35, N 2.05; found C 40.89, H 6.36, N 2.10. IR (ATR): $\tilde{\nu}$ = 455 cm^{-1} (Ir–F). ^1H NMR (300.1 MHz, C_6D_6): δ = 2.17 (dsept, $^3J_{H,H}$ = 7.1, $^2J_{H,P}$ = 7.1 Hz, 6 H, CH), 1.01 (dd, $^3J_{H,H}$ = 7.1, $^3J_{H,P}$ = 7.1 Hz, 18 H, CH_3), 0.98 (dd, $^3J_{H,H}$ = 7.1, $^3J_{H,P}$ = 7.1 Hz, 18 H, CH_3), –40.28 ppm (tdd, $^2J_{H,P}$ = 12.0, $^2J_{H,F}$ = 12.1, $^4J_{H,F}$ = 2.8 Hz, 1 H, IrH); the coupling constants were obtained from $^1H\{^{19}F\}$ and $^1H\{^{31}P\}$ NMR spectra. $^{19}F\{^1H\}$ NMR (282.4 MHz, C_6D_6): δ = –98.8 (m, 1 F), –102.3 (m, 1 F), –123.8 (m, 1 F), –126.4 (m, 1 F), –267.4 ppm (br. s, 1 F). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ = 39.5 ppm (dd, $^2J_{F,P}$ = 16.3, $^4J_{F,P}$ = 9.4 Hz).

***trans*-[Ir(2-$C_6H_3F_2$)(F)(H)(P*i*Pr$_3$)$_2$] (2b):** $Et_3N{\cdot}3HF$ (150 µL, 0.920 mmol) was added to a solution of *trans*-[Ir(2-$C_6H_3F_2$)(η^2-C_2H_4)(P*i*Pr$_3$)$_2$] (**1b**) (300 mg, 0.459 mmol) in THF (20 mL). The solution turned from dark red to orange while being stirred at room temperature. After 16 h, all the volatile compounds were removed under vacuum and the residue was washed with *n*-pentane (10 mL) to yield 226 mg of an oily orange residue. The residue was then dissolved in THF (15 mL), and the solution was treated with CsF (798 mg, 5.253 mmol) at 323 K for 2 h to remove residual HF. After filtration, the volatile compounds were removed under vacuum from the filtrate. An orange oil remained; yield 221 mg (74%). ^1H NMR (300.1 MHz, C_6D_6): δ = 6.76–6.49 (br. m, 3 H, 2-$C_6H_3F_2$), 2.35 (dsept, $^3J_{H,H}$ = 7.1, $^2J_{H,P}$ = 7.1 Hz, 6 H, CH), 1.15 (dd, $^3J_{H,H}$ = 7.1, $^3J_{H,P}$ = 7.1 Hz, 36 H, CH_3), –40.08 ppm (m, 1 H, IrH); the $^3J_{H,H}$ coupling constant was determined by a ^{31}P decoupling experiment. $^{19}F\{^1H\}$ NMR (282.4 MHz, C_6D_6): δ = –88.3 (m, 1 F), –91.3 (m, 1 F), –267.0 ppm (br. s, 1 F). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ = 37.7 ppm (dd, $^2J_{F,P}$ = 17.2, $^4J_{F,P}$ = 4.3 Hz).

***trans*-[Ir(4-C_5NF_4)(F)(H)(CO)(P*i*Pr$_3$)$_2$] (4a):** A solution of *trans*-[Ir(4-C_5NF_4)(F)(H)(P*i*Pr$_3$)$_2$] (**2a**) (21 mg, 0.031 mmol) in C_6D_6 (0.6 mL) was treated with CO gas at room temperature. The solution turned pale yellow within seconds. The NMR and IR spectra revealed a quantitative conversion into *trans*-[Ir(4-C_5NF_4)(F)(H)(CO)(P*i*Pr$_3$)$_2$] (**4a**). After storage at room temperature for several days, the formation of *trans*-[Ir(4-C_5NF_4)(CO)(P*i*Pr$_3$)$_2$] (**6a**) was detected in the reaction mixture. Analytical data for *trans*-[Ir(4-C_5NF_4)(F)(H)(CO)(P*i*Pr$_3$)$_2$] (**4a**): IR (ATR): $\tilde{\nu}$ = 2170 (Ir–H), 2010 cm^{-1} (C≡O). ^1H NMR (300.1 MHz, C_6D_6): δ = 2.10 (dsept, $^3J_{H,H}$ = 7.1, $^2J_{H,P}$ = 7.1 Hz, 6 H, CH), 1.03 (dd, $^3J_{H,H}$ = 7.1, $^3J_{H,P}$ = 7.1 Hz, 18 H, CH_3), 0.98 (dd, $^3J_{H,H}$ = 7.1, $^3J_{H,P}$ = 7.1 Hz, 18 H, CH_3), –5.90 ppm (tdd, $^2J_{H,P}$ = 15.2, $^2J_{H,F}$ = 9.6, $^4J_{H,F}$ = 14.8 Hz, 1 H, IrH); the coupling constants were obtained from the $^1H\{^{31}P\}$ and $^1H\{^{19}F\}$ NMR spectra. $^{19}F\{^1H\}$ NMR (282.4 MHz, C_6D_6): δ = –98.5 (m, 1 F), –98.9 (m, 1 F), –109.4 (m, 1 F), –113.5 (m, 1 F), –444.3 ppm (br. s, 1 F). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ = 21.4 ppm (d, $^2J_{F,P}$ = 22.0 Hz). The isotopomer *trans*-[Ir(4-C_5NF_4)(F)(H)(^{13}CO)(P*i*Pr$_3$)$_2$] (**4a′**) can be prepared analogously upon treatment of **2a** with ^{13}CO. Analytical data for **4a′**: ^1H NMR (300.1 MHz, C_6D_6): δ = 2.10 (dsept, $^3J_{H,H}$ = 7.1, $^2J_{H,P}$ = 7.1 Hz, 6 H, CH), 1.03 (dd, $^3J_{H,H}$ = 7.1, $^3J_{H,P}$ = 7.1 Hz, 18 H, CH_3), 0.98 (dd, $^3J_{H,H}$ = 7.1, $^3J_{H,P}$ = 7.1 Hz, 18 H, CH_3), –5.90 ppm (tddd, $^2J_{H,C}$ = 53.0, $^2J_{H,P}$ = 15.2, $^2J_{H,F}$ = 9.6, $^4J_{H,F}$ = 14.8 Hz, 1 H, IrH); the coupling constants were obtained from the $^1H\{^{31}P\}$ and $^1H\{^{19}F\}$ NMR spectra. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ = 21.4 ppm (dd, $^2J_{F,P}$ = 22.0, $^2J_{C,P}$ = 6.2 Hz). Complex **6a** was identified by comparison of the NMR spectroscopic data with the literature data.[13]

***trans*-[Ir(2-$C_6H_3F_2$)(F)(H)(CO)(P*i*Pr$_3$)$_2$] (4b):** A slow stream of CO was bubbled through a solution of *trans*-[Ir(2-$C_6H_3F_2$)(F)(H)(P*i*Pr$_3$)$_2$] (**2b**) (175 mg, 0.271 mmol) in THF (5 mL) at room temperature. The solution turned from yellow to pale yellow within seconds. All volatile compounds were removed under vacuum to yield a yellow residue; yield 170 mg (93%). IR (ATR): $\tilde{\nu}$ = 2209 (Ir–H), 2003 cm^{-1} (C≡O). ^1H NMR (300.1 MHz, C_6D_6): δ = 6.76–6.49 (br. m, 3 H, 2-$C_6H_3F_2$), 2.28 (dsept, $^3J_{H,H}$ = 7.1, $^2J_{H,P}$ = 7.1 Hz, 6 H, CH), 1.19 (dd, $^3J_{H,H}$ = 7.1, $^3J_{H,P}$ = 7.1 Hz, 18 H, CH_3), 1.10 (dd, $^3J_{H,H}$ = 7.1, $^3J_{H,P}$ = 7.1 Hz, 18 H, CH_3), –5.51 (tdd, $^2J_{H,P}$ = 15.7, $^2J_{H,F}$ = 9.3, $^4J_{H,F}$ = 14.0, 1 H, IrH); the coupling constants were obtained from the $^1H\{^{31}P\}$ and $^1H\{^{19}F\}$ NMR spectra. ^{19}F NMR (282.4 MHz, C_6D_6): δ = –73.4 (m, 1 F), –76.8 (m, 1 F), –441.0 (br. s, 1 F). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ = 20.0 (d, $^2J_{F,P}$ = 19.5 Hz). Treatment with ^{13}CO forms the isotopomer *trans*-[Ir(2-$C_6H_3F_2$)(F)(H)(^{13}CO)(P*i*Pr$_3$)$_2$] (**4b′**). $^{31}P\{^1H\}$ NMR for **4b′** (121.5 MHz, C_6D_6): δ = 20.7 ppm (dd, $^2J_{F,P}$ = 19.3, $^2J_{C,P}$ = 6.0 Hz).

Treatment of *trans*-[Ir(4-C_5NF_4)(F)(H)(P*i*Pr$_3$)$_2$] (2a) with Ph_3SiH: Compound **2a** (6 mg, 0.009 mmol) was dissolved in C_6D_6 (0.7 mL). Then Ph_3SiH (15 mg, 0.058 mmol) was added to the solution, which turned from yellow to orange within minutes. *cis*–*trans*-[Ir(4-C_5NF_4)(H)$_2$(P*i*Pr$_3$)$_2$] (**7a**) and Ph_3SiF could be detected by NMR spectroscopy. Complex **7a** was identified by comparison of the NMR spectroscopic data with the literature data.[13] Analytical data for Ph_3SiF: ^{19}F NMR (282.4 MHz, C_6D_6): δ = –169.2 ppm (s, with ^{29}Si satellites, $^1J_{F,Si}$ = 282.5 Hz). ^1H,^{29}Si HMBC (79.5 MHz, C_6D_6): δ(^{29}Si,^1H) = –3.5/7.7 ppm (d, $^1J_{F,Si}$ = 284 Hz); **2b** reacts with Ph_3SiH in a similar manner to form Ph_3SiF and **7b**.

Treatment of *trans*-[Ir(4-C_5NF_4)(F)(H)(P*i*Pr$_3$)$_2$] (2a) with $CH_3C(O)Cl$: $CH_3C(O)Cl$ (6 µL, 0.084 mmol) was added to a solution of **2a** (53 mg, 0.078 mmol) in THF (12 mL). NMR spectra of the mixture revealed the presence of *trans*-[Ir(4-C_5NF_4)(Cl)(H)(P*i*Pr$_3$)$_2$] (**8a**) and $CH_3C(O)F$ only. Compound **8a** was isolated by evaporation of the volatile compounds from the reaction mixture. Analytical data for **8a**: $C_{23}H_{43}ClF_4IrNP_2$ (699.21): calcd. C 39.51, H 6.20, N 2.00; found C 39.17, H 6.29, N 1.49. ^1H NMR (300.1 MHz, C_6D_6): δ = 2.34 (dsept, $^3J_{H,H}$ = 7.1, $^2J_{H,P}$ = 7.1 Hz, 6 H, CH), 0.98 (dd, $^3J_{H,H}$ = 7.1, $^3J_{H,P}$ = 7.1 Hz, 36 H, CH_3), –41.15 ppm (dt, $^2J_{H,P}$ = 12.4, $^4J_{H,F}$ = 5.7 Hz, 1 H, IrH). ^{19}F NMR (282.4 MHz, C_6D_6): δ = –99.5 (m, 1 F), –101.3 (m, 1 F), –121.6 (m, 1 F), –127.6 ppm (m, 1 F). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ = 33.5 ppm (s). Analytical data for $CH_3C(O)F$: ^{19}F NMR (282.4 MHz, C_6D_6): δ = 48.6 ppm (q, $^3J_{H,F}$ = 7.2 Hz).

Treatment of *trans*-[Ir(4-C_5NF_4)(F)(H)(CO)(P*i*Pr$_3$)$_2$] (4a) with $CH_3C(O)Cl$: A solution of **4a** (18 mg, 0.025 mmol) in C_6D_6 (0.7 mL) was treated with $CH_3C(O)Cl$ (2 µL, 0.028 mmol). The quantitative formation of *trans*-[Ir(4-C_5NF_4)(Cl)(H)(P*i*Pr$_3$)$_2$] (**9a**) and $CH_3C(O)F$ was detected by NMR spectroscopy. Evaporation of the volatile compounds afforded complex **9a** as a pale yellow powder. Analytical data for **9a**: $C_{24}H_{43}ClF_4IrNOP_2$ (727.22): calcd. C 39.64, H 5.96, N 1.93; found C 39.68, H 6.48, N 1.93. IR (ATR): $\tilde{\nu}$ = 2276 (Ir–H), 2015 cm^{-1} (C≡O). ^1H NMR (300.1 MHz, C_6D_6): δ = 2.16 (dsept, $^3J_{H,H}$ = 7.1, $^2J_{H,P}$ = 7.1 Hz, 6 H, CH), 1.06 (dd, $^3J_{H,H}$ = 7.1, $^3J_{H,P}$ = 7.1 Hz, 18 H, CH_3), 0.95 (dd, $^3J_{H,H}$ = 7.1, $^3J_{H,P}$ = 7.1 Hz, 18 H, CH_3), –7.99 ppm (dt, $^2J_{H,P}$ = 16.2, $^4J_{H,F}$ = 15.3 Hz, 1 H, IrH). ^{19}F NMR (282.4 MHz, C_6D_6): δ = –97.4 (m, 1 F), –97.8 (m, 1 F), –105.4 (m, 1 F), –110.0 ppm (m, 1 F). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ = 13.1 ppm (s).

Structure Determination: Yellow crystals of **2a** were obtained by slow evaporation of the solvent from an *n*-pentane solution at 243 K. Suitable crystals of **2b** were grown from an *n*-hexane solution at room temperature. The diffraction data were collected with a STOE IPDS 2Θ diffractometer at 100 K. Crystallographic data are depicted in Table 2. The structures were solved with direct methods

(SHELXTL PLUS or SIR97) and refined with the full-matrix least-squares method on F^2 (SHELXL-97).[25] Hydrogen atoms were placed at calculated positions and refined using a riding model. The hydrogen atoms bound at iridium were not located.

Table 2. Crystallographic data.

	2a	**2b**
Crystal dimensions [mm^3]	$0.07 \times 0.06 \times 0.05$	$0.32 \times 0.30 \times 0.08$
Crystal colour	orange	yellow
Empirical formula	$C_{23}H_{43}F_5IrNP_2$	$C_{24}H_{46}F_3IrP_2$
M_r	682.75	645.78
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a [Å]	9.2726(2)	8.3249(3)
b [Å]	24.0899(4)	10.2917(3)
c [Å]	11.8937(3)	16.4867(5)
α [°]	–	79.991(2)
β [°]	90.025(2)	83.239(3)
γ [°]	–	71.438(2)
V [Å^3]	2656.77(10)	1315.73(7)
Z	4	2
$D_{calcd.}$ [mg m^{-3}]	1.707	1.630
μ(Mo-K_α) [mm^{-1}]	5.193	5.226
θ range [°]	2.35 to 30.49	2.11 to 29.18
Reflns. collected	15607	24890
Indep. reflns.	8092	7075
R_{int}	0.0289	0.1067
Completeness	99.7	99.5
Absorption correction	numerical	numerical
GoF on F^2	0.992	1.126
R_1, wR_2 (all data)	0.0418, 0.0785	0.0247, 0.0670
R_1, wR_2 [$I_0 > 2\sigma(I_0)$]	0.0316, 0.0758	0.0225, 0.0664
Max diff. peak/hole [e Å^{-3}]	1.363 / –2.404	1.204 / –3.237

CCDC-841984 (for **2a**) and -841983 (for **2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Computational details for **2a** and **2b** for this article is available.

Acknowledgments

The authors gratefully acknowledge support from the GRK "Fluorine as a Key Element" funded by the Deutsche Forschungsgemeinschaft. We would like to thank Dr. B. Braun and Dr. S. Mebs for helpful discussions concerning the X-ray crystal-structure analyses as well as Prof. B. Paulus (FU Berlin) for support with the DFT calculations. We acknowledge D. Warner, L. Zámostná and T. Ahrens for experimental assistance.

[1] a) N. M. Doherty, N. W. Hoffman, *Chem. Rev.* **1991**, *91*, 553–573; b) E. F. Murphy, R. Murugavel, H. W. Roesky, *Chem. Rev.* **1997**, *97*, 3425–3468; c) H. W. Roesky, I. Haiduc, *J. Chem. Soc., Dalton Trans.* **1999**, 2249–2264; d) A. Mezzetti, C. Becker, *Helv. Chim. Acta* **2002**, *85*, 2686–2703; e) V. V. Grushin, *Acc. Chem. Res.* **2010**, *43*, 160–171.

[2] Reviews on C–F bond activations: a) J. L. Kiplinger, T. G. Richmond, C. E. Osterberg, *Chem. Rev.* **1994**, *94*, 373–431; b) J. Burdeniuc, B. Jedlicka, R. H. Crabtree, *Chem. Ber./Recueil* **1997**, *130*, 145–154; c) T. G. Richmond, *Angew. Chem.* **2000**, *112*, 3378–3380; *Angew. Chem. Int. Ed.* **2000**, *39*, 3241–3244; d) T. Braun, R. N. Perutz, *Chem. Commun.* **2002**, 2749–2757; e) W. D. Jones, *Dalton Trans.* **2003**, 3991–3995; f) U. Mazurek, H. Schwarz, *Chem. Commun.* **2003**, 1321–1326; g) H. Torrens, *Coord. Chem. Rev.* **2005**, *249*, 1957–1985; h) R. N. Perutz, T. Braun, *Comprehensive Organometallic Chemistry III, Vol. 1* (Eds.: R. H. Crabtree, M. P. Mingos), Elsevier, Oxford **2007**, p. 725; i) H. Amii, K. Uneyama, *Chem. Rev.* **2009**, *109*, 2119–2183; j) G. Meier, T. Braun, *Angew. Chem.* **2009**, *121*, 1575–1577; *Angew. Chem. Int. Ed.* **2009**, *48*, 1546–1548; k) R. P. Hughes, *Eur. J. Inorg. Chem.* **2009**, 4591–4606; l) T. G. Driver, *Angew. Chem.* **2009**, *121*, 8116–8119; *Angew. Chem. Int. Ed.* **2009**, *48*, 7974–7976; m) A. D. Sun, J. A. Love, *Dalton Trans.* **2010**, *39*, 10362–10374; n) T. Braun, F. Wehmeier, *Eur. J. Inorg. Chem.* **2011**, 613–625; o) E. Clot, O. Eisenstein, N. Jasim, S. A. Macgregor, J. E. McGrady, R. N. Perutz, *Acc. Chem. Res.* **2011**, *44*, 333–348.

[3] For transition-metal-mediated fluorination reactions, see, for example: a) E. M. Carreira, B. L. Pagenkopf, *Chem. Eur. J.* **1999**, *5*, 3437–3442; b) V. V. Grushin, *Chem. Eur. J.* **2002**, *8*, 1007–1014; c) C. Bobbio, V. Gouverneur, *Org. Biomol. Chem.* **2006**, *4*, 2065–2075; d) T. Furuya, J. E. M. N. Klein, T. Ritter, *Synthesis* **2010**, *11*, 1804–1821; e) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147–1169; f) T. Furuya, A. S. Kamlet, T. Ritter, *Nature* **2011**, *473*, 470–477; g) J. M. Brown, V. Gouverneur, *Angew. Chem.* **2009**, *121*, 8762–8766; *Angew. Chem. Int. Ed.* **2009**, *48*, 8610–8614.

[4] a) L. Hintermann, F. Läng, P. Maire, A. Togni, *Eur. J. Inorg. Chem.* **2006**, 1396–1412; b) K. L. Hull, W. Q. Anani, M. S. Sanford, *J. Am. Chem. Soc.* **2006**, *128*, 7134–7135; c) J. A. Akana, K. X. Bhattacharyya, P. Müller, J. P. Sadighi, *J. Am. Chem. Soc.* **2007**, *129*, 7736–7737; d) T. Furuya, H. M. Kaiser, T. Ritter, *Angew. Chem.* **2008**, *120*, 6082–6085; *Angew. Chem. Int. Ed.* **2008**, *47*, 5993–5996; e) T. Furuya, T. Ritter, *J. Am. Chem. Soc.* **2008**, *130*, 10060–10061; f) X. Wang, T.-S. Mei, J.-Q. Yu, *J. Am. Chem. Soc.* **2009**, *131*, 7520–7521; g) W. Wang, J. Jasinski, G. B. Hammond, B. Xu, *Angew. Chem.* **2010**, *122*, 7405–7410; *Angew. Chem. Int. Ed.* **2010**, *49*, 7247–7252; h) C. Hollingworth, A. Hazari, M. N. Hopkinson, M. Tredwell, E. Benedetto, M. Huiban, A. D. Gee, J. M. Brown, V. Gouverneur, *Angew. Chem.* **2011**, *123*, 2661–2665; *Angew. Chem. Int. Ed.* **2011**, *50*, 2613–2617.

[5] a) J. E. Veltheer, P. Burger, R. G. Bergman, *J. Am. Chem. Soc.* **1995**, *117*, 12478–12488; b) P. Barthazy, L. Hintermann, R. M. Stoop, M. Wörle, A. Mezzetti, A. Togni, *Helv. Chim. Acta* **1999**, *82*, 2448–2453; c) P. Barthazy, R. M. Stoop, M. Wörle, A. Togni, A. Mezzetti, *Organometallics* **2000**, *19*, 2844–2852; d) P. Barthazy, A. Togni, A. Mezzetti, *Organometallics* **2001**, *20*, 3472–3477.

[6] a) W. J. Marshall, V. V. Grushin, *Organometallics* **2003**, *22*, 555–562; b) V. V. Grushin, W. J. Marshall, *J. Am. Chem. Soc.* **2004**, *126*, 3068–3069; c) W. J. Marshall, V. V. Grushin, *Organometallics* **2004**, *23*, 3343–3347; d) S. A. McGregor, D. C. Roe, W. J. Marshall, K. M. Bloch, V. I. Bakhmutov, V. V. Grushin, *J. Am. Chem. Soc.* **2005**, *127*, 15304–15321; e) D. V. Yandulov, N. T. Tran, *J. Am. Chem. Soc.* **2007**, *129*, 1342–1358; f) V. V. Grushin, W. J. Marshall, *Organometallics* **2007**, *26*, 4997–5002; g) T. Furuya, T. Ritter, *J. Am. Chem. Soc.* **2008**, *130*, 10060–10061; h) A. W. Kaspi, A. Yahav-Levi, I. Goldberg, A. Vigalok, *Inorg. Chem.* **2008**, *47*, 5–7; i) N. D. Ball, M. S. Sanford, *J. Am. Chem. Soc.* **2009**, *131*, 3796–3797.

[7] D. A. Watson, M. Su, G. Teverovkiy, Y. Zhang, J. Garzía-Fortanet, T. Kinzel, S. L. Buchwald, *Science* **2009**, *325*, 1661–1664.

[8] a) M. Reinhold, J. E. McGrady, R. N. Perutz, *J. Am. Chem. Soc.* **2004**, *126*, 5268–5276; b) N. A. Jasim, R. N. Perutz, A. C. Whitwood, T. Braun, J. Izundu, B. Neumann, S. Rothfeld, H.-G. Stammler, *Organometallics* **2004**, *23*, 6140–6149; c) A. Steffen, M. I. Sladek, T. Braun, B. Neumann, H.-G. Stammler, *Organometallics* **2005**, *24*, 4057–4064; d) 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**, 3686–3695; e) T. Schaub, M. Backes, U. Radius, *J. Am. Chem. Soc.* **2006**, *128*, 15964–159645; f) T. Braun, J. Izundu, A. Steffen, B. Neumann, H.-G. Stammler, *Dalton Trans.* **2006**, 5118–5123; g) T. Wang,

B. J. Alfonso, J. A. Love, *Org. Lett.* **2007**, *9*, 5629–5631; h) T. Schaub, P. Fischer, A. Steffen, T. Braun, U. Radius, A. Mix, *J. Am. Chem. Soc.* **2008**, *130*, 9304–9317; i) S. A. Johnson, C. W. Huff, F. Mustafa, M. Saliba, *J. Am. Chem. Soc.* **2008**, *130*, 17278–17280; j) 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*, 15490–15498; k) T. Wang, J. A. Love, *Organometallics* **2008**, *27*, 3290–3296; l) H. L. Buckley, A. D. Sun, J. A. Love, *Organometallics* **2009**, *28*, 6622–6624; m) H. L. Buckley, T. Wang, O. Tran, J. A. Love, *Organometallics* **2009**, *28*, 2356–2359; n) S. A. Johnson, E. T. Taylor, S. J. Cruise, *Organometallics* **2009**, *28*, 3842–3655; o) M. E. Doster, S. A. Johnson, *Angew. Chem.* **2009**, *121*, 2219–2221; *Angew. Chem. Int. Ed.* **2009**, *48*, 2185–2187; p) A. Nova, M. Reinhold, R. N. Perutz, S. A. Macgregor, J. E. McGrady, *Organometallics* **2010**, *29*, 1824–1831; q) M. R. Cargill, G. Sandford, A. J. Tadeusiak, D. S. Yufit, J. A. K. Howard, P. Kilickiran, G. Nelles, *J. Org. Chem.* **2010**, *75*, 5860–5866; r) D. Breyer, T. Braun, A. Penner, *Dalton Trans.* **2010**, *39*, 7513–7520.

[9] a) A. J. Blake, R. W. Cockman, E. A. V. Ebsworth, J. H. Holloway, *J. Chem. Soc., Chem. Commun.* **1988**, 529–530; b) E. A. V. Ebsworth, N. Robertson, L. J. Yellowlees, *J. Chem. Soc., Dalton Trans.* **1993**, 1031–1038; c) S. A. Brewer, K. S. Coleman, J. Fawcett, J. H. Holloway, E. G. Hope, D. R. Russell, P. G. Watson, *J. Chem. Soc., Dalton Trans.* **1995**, 1073–1076; d) A. Yahav, I. Goldberg, A. Vigalok, *J. Am. Chem. Soc.* **2003**, *125*, 13634–13635; e) A. Yahav, I. Goldberg, A. Vigalok, *Inorg. Chem.* **2005**, *44*, 1547–1553; f) A. W. Kaspi, A. Yahav, I. Goldberg, A. Vigalok, *Inorg. Chem.* **2008**, *47*, 5–7; g) T. Furuya, T. Ritter, *J. Am. Chem. Soc.* **2008**, *130*, 10060–10061; h) J. Fawcett, D. A. J. Harding, E. G. Hope, *Dalton Trans.* **2010**, *39*, 5827–5832.

[10] a) K. S. Coleman, J. Fawcett, J. H. Holloway, E. G. Hope, R. Nassar, *J. Fluorine Chem.* **2001**, *112*, 185–189; b) K. Seppelt, *Inorg. Chem.* **2003**, *42*, 7116–7122.

[11] a) K. S. Coleman, J. H. Holloway, E. G. Hope, J. Langer, *J. Chem. Soc., Dalton Trans.* **1997**, *39*, 4555–4559; b) J. Gil-Rubio, B. Weberndörfer, H. Werner, *J. Chem. Soc., Dalton Trans.* **1999**, 1437–1444; c) M. Gorol, N. C. Mösch-Zanetti, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt, *Eur. J. Inorg. Chem.* **2004**, 2678–2682.

[12] a) A. C. Cooper, K. Folting, J. C. Huffman, K. G. Caulton, *Organometallics* **1997**, *16*, 505–507; b) C. Becker, I. Kieltsch, D. Broggini, A. Mezzetti, *Inorg. Chem.* **2003**, *42*, 8417–8429; c) C. J. Bourgeois, S. A. Garratt, R. P. Hughes, R. B. Larichev, J. M. Smith, A. J. Ward, S. Willemsen, D. Zhang, A. G. DiPasquale, L. N. Zakharov, A. L. Rheingold, *Organometallics* **2006**, *25*, 3474–3480; d) V. V. Grushin, W. J. Marshall, *J. Am. Chem. Soc.* **2006**, *128*, 12644–12645; e) V. V. Grushin, W. J. Marshall, *J. Am. Chem. Soc.* **2009**, *131*, 918–919; f) T. Furuya, D. Benitez, E. Tkatchouk, A. E. Strom, P. Tang, W. A. Goddard, T. Ritter, *J. Am. Chem. Soc.* **2010**, *132*, 3793–3807; g) N. D. Ball, J. W. Kampf, M. S. Sanford, *Dalton Trans.* **2010**, *39*, 632–640; h) A. Rossin, M. Peruzzini, F. Zanobini, *Dalton Trans.* **2011**, *40*, 4447–4452.

[13] M. Ahijado Salomon, T. Braun, I. Krossing, *Dalton Trans.* **2008**, 5197–5206.

[14] P. Kläring, S. Pahl, T. Braun, A. Penner, *Dalton Trans.* **2011**, *40*, 6785–6791.

[15] For a possible hydrolysis of fluorido complexes, see: M. C. Pilon, V. V. Grushin, *Organometallics* **1998**, *17*, 1774–1781.

[16] a) M. Ahijado, T. Braun, *Angew. Chem.* **2008**, *120*, 2996–3000; *Angew. Chem. Int. Ed.* **2008**, *47*, 2954–2958; b) G. Meier, T. Braun, *Angew. Chem.* **2011**, *123*, 3338–3342; *Angew. Chem. Int. Ed.* **2011**, *50*, 3380–3384; c) M. Ahijado Salomon, A.-K. Jungton, T. Braun, *Dalton Trans.* **2009**, 7669–7677; d) M. Ahijado Salomon, T. Braun, A. Penner, *Angew. Chem.* **2008**, *120*, 8999–9003; *Angew. Chem. Int. Ed.* **2008**, *47*, 8867–8871.

[17] a) J. Fawcett, D. A. J. Harding, E. G. Hope, K. Singh, G. A. Solan, *Dalton Trans.* **2010**, *39*, 10781–10789; b) J. Choi, D. Y. Wang, S. Kundu, Y. Choliy, T. J. Emge, K. Krogh-Jespersen, A. S. Goldman, *Science* **2011**, *332*, 1545–1548.

[18] G. Socrates, *Infrared and Raman Characteristic Group Frequencies*, Wiley, **2001**, New York, p. 305.

[19] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356.

[20] a) D. Noveski, T. Braun, B. Neumann, A. Stammler, H.-G. Stammler, *Dalton Trans.* **2004**, 4106–4119; b) T. Braun, D. Noveski, M. Ahijado, F. Wehmeier, *Dalton Trans.* **2007**, 3820–5125; c) M. Teltewskoi, J. A. Panetier, S. A. Macgregor, T. Braun, *Angew. Chem.* **2010**, *122*, 4039–4043; *Angew. Chem. Int. Ed.* **2010**, *49*, 3947–3951.

[21] A. S. Goldman, J. Halpern, *J. Organomet. Chem.* **1990**, *382*, 37–253.

[22] a) D. Noveski, T. Braun, M. Schulte, B. Neumann, H.-G. Stammler, *Dalton Trans.* **2003**, 4075–4083; b) M. Aizenberg, D. Milstein, *Science* **1994**, *265*, 359–361; c) T. Braun, F. Wehmeier, K. Altenhöner, *Angew. Chem.* **2007**, *119*, 5415–5418; *Angew. Chem. Int. Ed.* **2007**, *46*, 5321–5324; d) M. F. Kühnel, D. Lentz, *Angew. Chem.* **2010**, *122*, 2995–2998; *Angew. Chem. Int. Ed.* **2010**, *49*, 2933–2936; e) D. Noveski, T. Braun, S. Krückemeier, *J. Fluorine Chem.* **2003**, *125*, 959–966.

[23] a) C. Blankenship, S. E. Cremer, *J. Organomet. Chem.* **1989**, *371*, 19–30; b) P. D. Lickiss, R. Lucas, *J. Organomet. Chem.* **1996**, *510*, 167–172; c) O. Farooq, *J. Chem. Soc. Perkin Trans. 1* **1998**, 661–665; d) R. J. Lindup, T. B. Marder, R. N. Perutz, A. C. Whitwood, *Chem. Commun.* **2007**, 3664–3666.

[24] a) L. J. Krause, J. A. Morrison, *J. Am. Chem. Soc.* **1981**, *103*, 2995–3001; b) A. Haas, T. Maciej, *J. Fluorine Chem.* **1982**, *20*, 581–588; c) W. Dmowski, M. Kaminski, *J. Fluorine Chem.* **1983**, *23*, 219–228; d) P. E. Hansen, F. M. Nicolaisen, K. Schaumburg, *J. Am. Chem. Soc.* **1986**, *108*, 625–629; e) I. D. Gridnev, A. V. Shastin, E. S. Balenkova, *Tetrahedron* **1991**, *47*, 5577–5584; f) R. Wagner, B. Wiedel, W. Guenther, H. Goerls, E. Anders, *Eur. J. Org. Chem.* **1999**, *9*, 2383–2390.

[25] a) *SHELXTL-PLUS*, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, **1990**; G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112; b) G. Cascarano, A. Altomare, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, D. Sigli, M. C. Burla, G. Polidori, M. Camalli, *Acta Crystallogr., Sect. A* **1996**, *52*, C79.

Received: August 31, 2011
Published Online: December 21, 2011

