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ARTICLE

Synthesis and Reactivity of Iridium(I) Fluorido Complexes: Oxidative Addition of SF_4 at *trans*-$[Ir(F)(CO)(PEt_3)_2]$

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Dedicated to Prof. Manfred Scheer on the Occasion of his 65th Birthday

Abstract. The facile access to the Vaska type fluorido complexes *trans*-$[Ir(F)(CO)(PR_3)_2]$ [**6**: R = Et, **7**: R = Ph, **8**: R = *i*Pr, **9**: R = Cy, **10**: R = *t*Bu] was achieved by halide exchange at *trans*-$[Ir(Cl)(CO)(PR_3)_2]$ (**1**–**5**) with Me_4NF. Furthermore, the reaction of complex **6** with SF_4 gave *cis*,*trans*-$[Ir(F)_2(SF_3)(CO)(PEt_3)_2]$ (**11**), whereas **8**–**10** did not react. Reactivity studies revealed that **11** can selectively be manipulated at the sulfur atom by hydrolysis or fluoride abstraction to give *cis*,*trans*-$[Ir(F)_2(SOF)(CO)(PEt_3)_2]$ (**12**) and *cis*,*trans*-$[Ir(F)_2(SF_2)(CO)(PEt_3)_2][AsF_6]$ (**13**), respectively.

Introduction

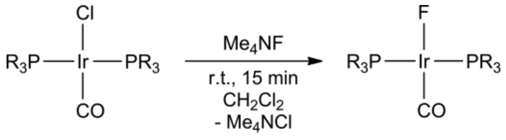
Fluorinated transition metal complexes are highly interesting substances.[1] Fluorido complexes of late transition metals can enable unique reaction pathways when compared to the reactivity of the corresponding metal complexes of the heavier halides.[1a,1b,2] The preparation of transition metal fluorido complexes can be achieved either by treatment of metal fluorides with ligand precursors, by fluorination of suitable complexes or by the activation of element–fluorine bonds.[1a,1b,2l,3] Apart from C–F bond activation reactions,[2e,2f,2h,2l,4] this also includes reactions with SF_4 or SF_6.[5] SF_4 is typically used as a tool for the fluorination of oxygen containing compounds, but has so far received only little attention in transition metal chemistry.[5b,6] Replacement of a fluoride in SF_4 by nitrogen atoms or a bulky aryl group led to the discovery and commercialization of several deoxyfluorinating agents like Fluolead™, DAST, MOST or Deoxo-Fluor®.[7] The derivatives often show a higher selectivity in fluorination, but they are not as versatile when compared with SF_4.[6b,8]

Examples for transition metal derivatives of sulfur fluorides are scarce, but DFT calculations suggest the general feasibility of metal bound SF units.[5e,5f,9] All experimentally available SF_3 complexes include only platinum group metal compounds.[5b–5h] The most stable and best characterized derivatives are *trans*-$[Ir(Cl)(F)(SF_3)(CO)(PEt_3)_2]$ and *trans*-$[Pt(F)(SF_3)(PR_3)_2]$ (R = *i*Pr, Cy).[5c–5h] The complexes *trans*-$[Pt(F)(SF_3)(PR_3)_2]$ (R = *i*Pr, Cy) were applied in deoxyfluorination reactions of ethanol or benzophenone.[5e,5h,10] Note that the reaction of SF_4 with **7** at 178 K to form a mixture of compounds with *cis*,*trans*-$[Ir(F)_2(SF_3)(CO)(PPh_3)_2]$ as main product was also reported.[5h] This demonstrates the influence of the fluorido ligand on the S–F bond cleavage in SF_4, because the chlorido complex **2** did give the respective SF_3 complex only at 323 K.[5h] Other conversions at Vaska-type rhodium complexes were described as well, but the procedures always resulted in a mixture of products.[5g] However, we recently reported on the selective formation of *cis*,*trans*-$[Rh(F)_2(SF_3)(CO)(PEt_3)_2]$ by oxidative addition of SF_4 at *trans*-$[Rh(F)(CO)(PEt_3)_2]$. The complex was characterized by NMR spectroscopy and is only stable at low temperature in solution.[5f]

In this contribution we report on the development of a reaction route to access iridium(I) fluorido carbonyl complexes. *trans*-$[Ir(F)(CO)(PEt_3)_2]$ (**6**) is a useful starting compound for the synthesis of an iridium SF_3 complex, which can be handled in solution at room temperature. Reactivity studies towards hydrolysis and the Lewis acid AsF_5 are also presented.

Results and Discussion

Treatment of *trans*-$[Ir(Cl)(CO)(PR_3)_2]$ with Me_4NF in dichloromethane gave *trans*-$[Ir(F)(CO)(PR_3)_2]$ [**6**: R = Et, **7**: R = Ph, **8**: R = *i*Pr, **9**: R = Cy, **10**: R = *t*Bu] as the product of chlorine-fluorine exchange reactions (Scheme 1). Furthermore,



1 - 5 **6 - 10**

R = Et, Ph, *i*Pr, Cy, *t*Bu

Scheme 1. Preparation of *trans*-$[Ir(F)(CO)(PR_3)_2]$ [**6**: R = Et, **7**: R = Ph, **8**: R = *i*Pr, **9**: R = Cy, **10**: R = *t*Bu].

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the isotopologue of **6**, *trans*-[Ir(F)(^{13}CO)(PEt$_3$)$_2$] (**6′**) was obtained when *trans*-[Ir(Cl)(^{13}CO)(PR$_3$)$_2$] (**6′**) was treated with Me$_4$NF. The complex *trans*-[Ir(F)(CO)(PPh$_3$)$_2$] (**7**) has been described in the literature and was identified by its NMR and IR spectroscopic data (Table 1).[11] Comparable fluorination reactions with Me$_4$NF in dichloromethane were reported before, for instance at rhodium and palladium complexes.[2c,5f]

Table 1. Selected IR and NMR spectroscopic data for complexes *trans*-[Ir(F)(CO)(PR_3)$_2$] (**6**–**10**) (in cm^{-1}, δ in ppm, J in Hz).

Complex	ν(CO)	δ(^{19}F)	$^2J_{\mathrm{P,F}}$	δ(^{31}P)
6	1925	–265	33	25.6
7 [11]	1943	–254	30	24.4
8	1916	–256	26	49.5
9	1924	–255	26	39.3
10	1910	–243	24	71.5

Slow evaporation of a saturated *n*-hexane solution at room temperature produced crystals suitable for X-ray diffraction of **9** (Figure 1, left) and **10** (Figure 1, right). The CO and fluorido ligand in **9** are disordered. The asymmetric unit for complex **10** contains three molecules of which one reveals a disorder of the F, Ir and CO positions (Figure S31, Supporting Information). The bond lengths and angles found for all molecules of **10** are comparable, and hence only one is discussed in the following. The complexes *trans*-[Ir(F)(CO)(PCy$_3$)$_2$] (**9**) and *trans*-[Ir(F)(CO)(P*t*Bu$_3$)$_2$] (**10**) exhibit an approximately square-planar coordination about the iridium center. Only a slight deviation from the ideal geometry is found for *trans*-[Ir(F)(CO)(PCy$_3$)$_2$] (**9**) with ligand–iridium–ligand angles of 88.37(2)° (F1–Ir1–P1) and 178.33(5)° (F1–Ir1–C1). A stronger distortion is observed for *trans*-[Ir(F)(CO)(P*t*Bu$_3$)$_2$] (**10**) indicated by the F2–Ir2–C2 and P4–Ir2–P3 angles [169.88(13)° and 172.98(3)°], most probably due to the sterical demand of the *t*Bu groups at the phosphorus atoms. A nearly linear coordination of the carbonyl ligand to the metal center is revealed by the Ir–C–O angles of 176.3(12)° (**9**) and 176.4(3)° for (**10**) showing the expected bond lengths for the Ir–C [1.838(11) Å for **9**, 1.800(3) Å for **10**] as well as for the C–O [1.156(11) Å for **9**, 1.174(4) Å for **10**] distances.[12] The metal carbon distance in **9** is longer than in *trans*-[Ir(Cl)(CO)(PCy$_3$)$_2$] (**4**) [Ir–C: 1.788(10) Å],[13] which is also observed when comparing the analogous rhodium complexes.[5f,13–14] The Ir–F distances [1.965(5) Å for **9**, 1.9846(19) Å for **10**] are well comparable to these in other iridium(I) fluorido complexes as well as to the one observed in *trans*-[Ir(F)(CO)(P{C$_6$H$_4$-2-CH$_3$)$_3$}$_2$].[15]

The ^{19}F NMR spectrum of the complex **6** reveals one signal at δ = –265 ppm which appears as a triplet ($^2J_{\mathrm{F,P}}$ = 33 Hz) and can be assigned to an iridum(I) bound fluorine atom with two phosphorus nuclei in a *cis* position.[11c,11d,12b,15a,15b,15e] The isotopologue *trans*-[Ir(F)(^{13}CO)(PEt$_3$)$_2$] (**6′**) shows a doublet of triplets [$^2J_{\mathrm{C,F}}$ = 84 Hz], caused by the coupling of the carbon atom of the carbonyl ligand to the fluorine atom in the *trans* position.[5f,16] The ^{31}P{^{1}H} NMR spectrum of compound **6** exhibits a single resonance at δ = 25.6 ppm showing the respective $^2J_{\mathrm{P,F}}$ doublet coupling. An additional doublet coupling can be detected for the ^{31}P{^{1}H} NMR spectrum of the isotopologue **6′** with a $^2J_{\mathrm{C,P}}$ *cis*-coupling of 10 Hz.[17] Compound **6′** reveals the expected doublet of triplet pattern in the ^{13}C{^{1}H} NMR spectrum in the range of iridium(I) bound carbonyl ligands at δ = 174.1 ppm.[17,18] A very intense absorption band at 1925 cm^{-1} for the CO stretch mode can be detected in the IR spectrum of **6** (1878 cm^{-1} for **6′**) which is well comparable to the known iridium based Vaska type complexes.[12a,19] Compound **6** shows a significantly lower wavenumber than the compounds bearing heavier halogenido ligands.[19] This phenomenon has already been discussed in the literature. It has been proposed that the fluorido ligand acts as a better π-donor than the other halogenido ligands.[1a–1d] A push-pull interaction has also been reasoned for the stronger π backbonding from the metal to the ligand.[2k,20] The NMR and IR spectroscopic data of the complexes **7**–**10** are very similar to those of **6** and are therefore not discussed (see Supporting Information and Table 1).

The fluorido complex **6** readily reacted with equimolar amounts of SF$_4$ in [D$_8$]THF, [D$_8$]toluene or CD$_2$Cl$_2$ below 263 K to give *cis,trans*-[Ir(F)$_2$(SF$_3$)(CO)(PEt$_3$)$_2$] (**11**) (Scheme 2). When introducing SF$_4$ to **6′** the formation of the isotopomer *cis,trans*-[Ir(F)$_2$(SF$_3$)(^{13}CO)(PEt$_3$)$_2$] (**11′**) was observed. Attempts to isolate **11** resulted in the decomposition of

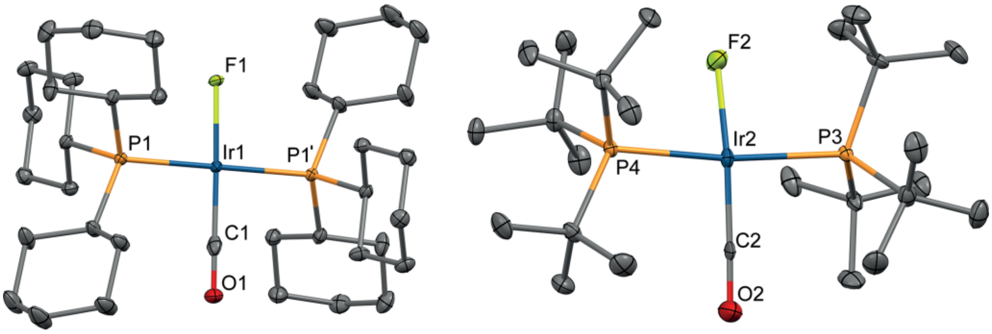


Figure 1. ORTEP diagram of *trans*-[Ir(F)(CO)(PCy$_3$)$_2$] (**9**) (left) and *trans*-[Ir(F)(CO)(P*t*Bu$_3$)$_2$] (**10**) (right). Ellipsoids are drawn at 50 % probability. All hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /° with estimated standard deviations in parentheses: **9**: Ir1–F1 1.965(5), Ir1–C1 1.838(11), Ir1–P1 2.3266(4), O1–C1 1.156(11); F1–Ir1–P1 88.37(2), F1–Ir1–C1 178.33(5), Ir1–C1–O1 178.99(11); **10**: Ir2–F2 1.9846(19), Ir2–C2 1.800(3), Ir2–P3 2.3810(9), Ir2–P4 2.3901(8), O2–C2 1.174(4), P3–Ir2–P4 172.98(3), P4–Ir2–F2 85.17(6), P4–Ir2–C2 93.96(10), F2–Ir2–C2 169.88(13), Ir2–C2–O2 176.4(3).

the complex giving $SPEt_3$ along with F_2PEt_3 and unidentified iridium species.[21] Based on ^{19}F NMR spectroscopy **11** was assumed to be one of four products in the reaction of *trans*-[Ir(NCS)(CO)$(PEt_3)_2$] with SF_4, which was reported by Murdoch.[5h] No oxidative addition of SF_4 was observed for **8–10** but the formation of traces of the respective difluorophosphoranes and phosphine sulfides where detected by ^{19}F and ^{31}P{^{1}H} NMR spectroscopy when the reaction mixtures were heated up to 323 K.[21a,22] Comparable observations were reported for analogous rhodium compounds, and it was reasoned that the steric demand of the phosphine ligands plays a crucial role.[5f]

6 **11**

Scheme 2. Formation of *cis,trans*-[Ir(F)$_2$(SF$_3$)(CO)(PEt$_3$)$_2$] (**11**).

DFT calculations were carried out on *cis,trans*-[Ir(F)$_2$(SF$_3$)(CO)(PR$_3$)$_2$] (**11**: R = Et; R = *i*Pr) (see SI), and both complexes converged into stable structures. Furthermore, the calculated reaction enthalpies for the formation of *cis,trans*-[Ir(F)$_2$(SF$_3$)(CO)(PR$_3$)$_2$] (**11**: R = Et; R = *i*Pr) from *trans*-[Ir(F)(CO)(PR$_3$)$_2$] (**6**: R = Et, **8**: R = *i*Pr) and SF_4 both indicate the general feasibility of these reactions, whereas the formation of **11** was found to be more exergonic. However, as stated above, *cis,trans*-[Ir(F)$_2$(SF$_3$)(CO)(P*i*Pr$_3$)$_2$] was not observed experimentally. The analysis of the frontier orbitals of **11** reveals a HOMO, which is located at the sulfur atom and resembles an electron lone pair (Figure 2). The λ^4-trifluorosulfanyl ligand should, therefore, be regarded as a one-electron donor.[5e,5f,9g]

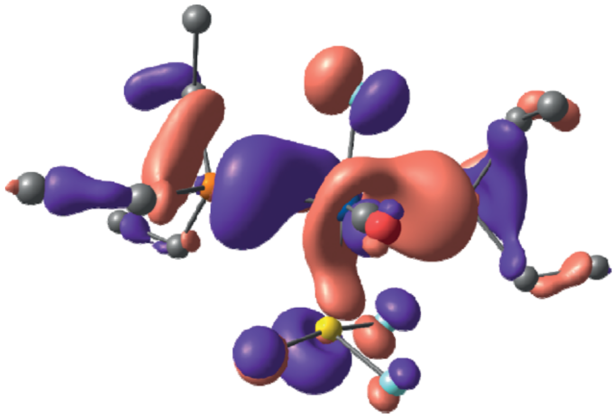


Figure 2. HOMO of the DFT-optimized structure of *cis,trans*-[Ir(F)$_2$(SF$_3$)(CO)(PEt$_3$)$_2$] (**11**). Hydrogen atoms at the phosphine ligands are omitted for clarity.

At 243 K the ^{19}F NMR spectrum of **11** shows four resonances at δ = 67.5, –64.9, –314.6 and –366.6 ppm which integrate in a ratio of 2:1:1:1 (Figure 3). The broad signal at δ = 67.5 ppm can be assigned to the two fluorine atoms in the axial positions of the trigonal bipyramidal configuration about the sulfur atom, and the resonance at –64.9 ppm to the one in the equatorial position.[5d–5h] The signal for the sulfur bound fluorine atom at higher field shows a $^2J_{F,F}$ triplet splitting of 71 Hz which is in good accordance with fluorine-fluorine couplings in sulfur(IV) compounds.[5c,5e,7a,7b,23] When cooling the sample to 203 K the resonance for the axial fluorine atoms at sulfur splits into two broad signals, indicating a dynamic behavior on the NMR timescale.

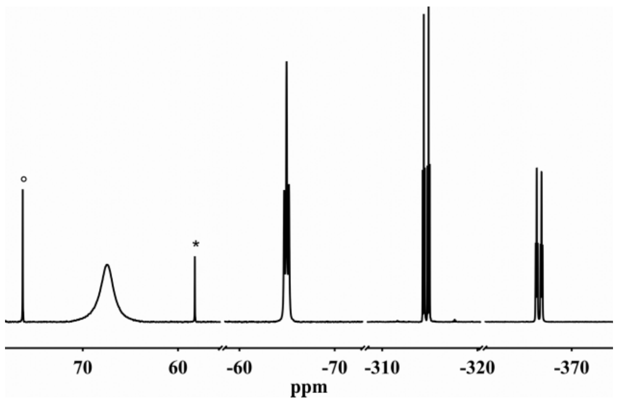


Figure 3. ^{19}F NMR spectrum (282.4 MHz) of *cis,trans*-[Ir(F)$_2$(SF$_3$)(CO)(PEt$_3$)$_2$] (**11**) at 243 K (° SOF_2; * SF_6).

For the two metal fluorido ligands in **11** sharp doublets of triplets at δ = –314.6 and –366.6 ppm appear in the ^{19}F NMR spectrum at a characteristic chemical shift.[15a,24] Both show a $^2J_{F,F}$ coupling of 143 Hz indicating a mutual *cis* arrangement.[15a,24b] Additionally the triplet couplings of 34 Hz and 29 Hz suggest that both metal fluorides have two phosphine ligands in a *cis* position.[15a,24d] The ^{13}C labeled isotopologue **11′** doesn't show further splitting of the signals for the sulfur bound fluorine atoms, but an additional doublet splitting of 77 Hz and 5 Hz is observed for the resonances of the metal fluorides at δ = –314.6 and –366.6 ppm, respectively.[5f,16,24d–24f] A larger $^2J_{F,C}$ coupling of the carbonyl ligand to a fluoride in the *trans* position than to a fluoride in the *cis* position has been observed before, and this allows for an assignment of both resonances.[5f,24d–24f] Thus, the signal at at δ = –314.6 ppm is attributed to the fluorido ligand *trans* to the carbonyl ligand and the resonance at δ = –366.6 ppm to the fluorido ligand *cis* to the carbonyl ligand.[5h,15a,24b,24e,24f]

At 203 K the ^{31}P{^{1}H} NMR spectrum of **11** shows one extremely broadened resonance at around $\delta \approx 13$ ppm (Figure 4). This broadening is presumably due to a hindered rotation of the λ^4-trifluorosulfanyl group about the Ir–S bond. Similar fluxionalities have been observed for the above mentioned iridium, rhodium and platinum complexes.[5c–5h] Increasing the temperature resulted at 298 K in a doublet of doublet pattern due to coupling to the two fluorine atoms in the *cis* position of the phosphines (Figure S15, Supporting Information). An additional doublet splitting of 7 Hz is detected in the ^{31}P{^{1}H} NMR spectrum of **11′** at 298 K indicating a *cis* arrangement of the carbonyl ligand to the phosphine ligands. The above mentioned couplings are also observed in the ^{13}C{^{1}H} NMR spectrum of **11′** (Figure S19, Supporting Information), which shows a doublet of triplets of doublets in the expected range

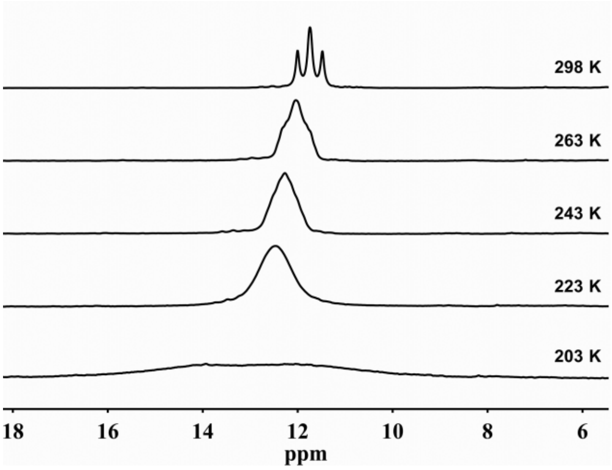
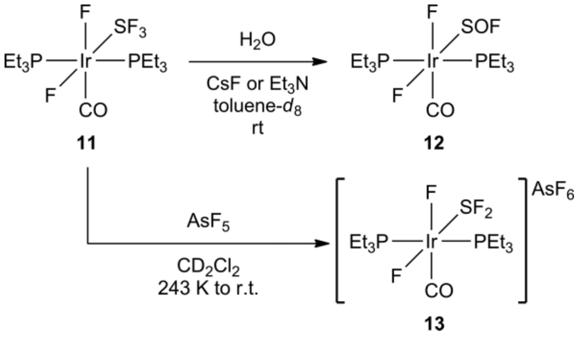


Figure 4. Variable temperature $^{31}P\{^1H\}$ NMR spectra (121.5 MHz) of *cis,trans*-$[Ir(F)_2(SF_3)(CO)(PEt_3)_2]$ (**11**).

for CO ligands in iridium(III) carbonyl complexes at δ = 160.3 ppm.[24d,24f,25]

The trifluorosulfanyl complex **11** is very much prone to hydrolysis. Treatment of **11** with H_2O in the presence of an excess of CsF resulted in the formation of *cis,trans*-$[Ir(F)_2(SOF)(CO)(PEt_3)_2]$ (**12**) (Scheme 3). The addition of CsF or Et_3N is needed to remove the HF, which is formed by the hydrolysis. However, complex **12** converts further into a mixture of compounds within 2 days, of which **6**, $SPEt_3$ and F_2PEt_3 were identified based on $^{31}P\{^1H\}$ and ^{19}F NMR spectroscopy (Figure S21, Supporting Information).[21]



Scheme 3. Reactivity of *cis,trans*-$[Ir(F)_2(SF_3)(CO)(PEt_3)_2]$ (**11**).

The ^{19}F NMR spectrum of **12** shows three resonances at δ = 0.7, –318.3 and –337.6 ppm of equal intensity. The broad multiplet at δ = 0.7 ppm can be assigned to the fluorine atom of the SOF unit, which is in accordance with literature data.[5e,5h] A doublet of triplets for one of the iridium bound fluorides is observed at δ = –318.3 ppm exhibiting couplings to a fluoride as well as two phosphorus atoms in the *cis* position ($^2J_{F,F}$ = 140, $^2J_{F,P}$ = 32 Hz).[5c,5f,15a,24b,24d–24f] For the other metal bound fluorine at δ = –337.6 ppm a broad doublet with the $^2J_{F,F}$ of 140 Hz is detected.[5f,15a,24b,24e]

In the $^{31}P\{^1H\}$ NMR spectrum of **12**, an AB pattern can be observed (Figure 5, bottom). The spectrum has been simulated (Figure 5, top) and the phosphine ligands couple to three fluorine atoms as well as the other phosphorus nucleus in the *trans* position ($^2J_{P,P}$ = 342 Hz).[5c,5g,5h,26] The $^2J_{P,F}$ couplings appear in the typical range (A: 32, 28 Hz, B: 29, 33 Hz).[5c,5f,15a,24d,24f] The $^3J_{P,F}$ couplings of the phosphine ligands to the sulfur bound fluorine atom of 7 Hz (A) and 10 Hz (B) are comparable to the ones found in *trans*-$[Pt(F)(SOF)(PCy_3)_2]$ (**18**), *trans*-$[Ir(Cl)(F)(SF_3)(CO)(PEt_3)_2]$ (**14**) and *trans*-$[Pt(F)(SF_3)(PR_3)_2]$ (R = *i*Pr, Cy) (**15**).[5c,5e]

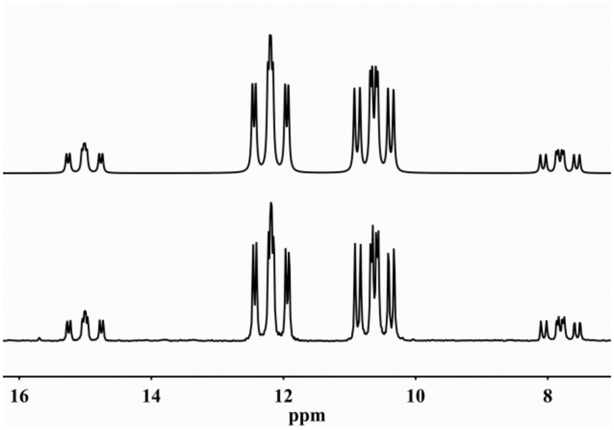


Figure 5. Section of the simulated (top) and experimental (bottom) $^{31}P\{^1H\}$ NMR spectrum of *cis,trans*-$[Ir(F)_2(SOF)(CO)(PEt_3)_2]$ (**12**) at 298 K. The following shifts and coupling constants were obtained from the simulation: δ = 13.1 (P_a, $^2J_{Pa,Pb}$ = 342.0, $^2J_{Pa,F}$ = 27.6, $^2J_{Pa,F}$ = 33.6, $^3J_{Pa,F}$ = 5.5 Hz) and 9.7 (P_b, $^2J_{Pa,Pb}$ = 342.0, $^2J_{Pb,F}$ = 32.6, $^2J_{Pb,F}$ = 28.6, $^3J_{Pb,F}$ = 10.8 Hz) ppm.

By addition of equimolar amounts of AsF_5 to **11** a sulfur bound fluoride of the SF_3 unit can be abstracted to give *cis,trans*-$[Ir(F)_2(SF_2)(CO)(PEt_3)_2][AsF_6]$ (**13**) along with unknown impurities (about 2 % based on the $^{31}P\{^1H\}$ NMR spectrum; Figure S25, Supporting Information) (Scheme 3). Evaporation of the solvent resulted in a brownish oil as well as in an increasing amount of the side products. Similar reactions are reported for *trans*-$[Ir(Cl)(F)(SF_3)(CO)(PEt_3)_2]$ and *trans*-$[Pt(F)(SF_3)(PR_3)_2]$ (R = *i*Pr, Cy) yielding with BF_3 *trans*-$[Ir(Cl)(F)(SF_2)(CO)(PEt_3)_2][BF_4]$ and *trans*-$[Pt(F)(SF_2)(PR_3)_2][BF_4]$ (R = *i*Pr, Cy), respectively.[5c,5e]

Four resonances were observed in the ^{19}F NMR spectrum of the SF_2 complex **13** at δ = –36.8, –65.7, –334.8 and –336.6 ppm in an integral ratio of 2:6:1:1 (Figure S26, Supporting Information). The most lowfield shifted resonance appears as a triplet of doublet of doublets ($^3J_{F,P}$ = 14, $^3J_{F,F}$ = 11, $^3J_{F,F}$ = 8 Hz) and is in good accordance with a cationic SF_2 ligand bound to a transition metal center.[5c,5e,5h] A broad signal at δ = –65.7 ppm ($\Delta\nu_{1/2}$ = 1190 Hz) appears for the anion AsF_6^-.[27] The two resonances for the metal bound fluorides in **13** at δ = –334.8 and –336.6 ppm show a typical $^2J_{F,F}$ coupling of 157 Hz accompanied by a strong roof effect for both doublet of triplet of triplets.[5f,15a,24b,24e] The coupling to the equivalent phosphorus atoms of the phosphine ligands in the *cis* position results in a $^2J_{F,P}$ coupling constant of 32 Hz and 37 Hz, respectively.[5c,5f,15a,24d,24f] A coupling to the two sulfur bound fluorine atoms is also observed in both resonances, exhibiting $^3J_{F,F}$ couplings of 11 Hz and 8 Hz. Comparable couplings have been observed for other iridium(III) and platinum(II) complexes.[5c,5e,24d,24f,28]

At 263 K, the $^{31}P\{^1H\}$ NMR spectrum shows a doublet of doublet of triplets at $\delta = 24.6$ ppm for **13** with corresponding coupling constants.[5c,5e] The IR spectrum of the obtained oil shows prominent absorption bands at 692 cm^{-1} and 675 cm^{-1}, which can be attributed to modes of the hexafluoroarsenate anion (Figure S37, Supporting Information).[27a,29] The CO stretching mode at 2064 cm^{-1} confirms the presence of an iridium compound in oxidation state +III.[15a,24c,30]

Conclusions

In conclusion, we reported on the selective formation of *cis*,*trans*-$[Ir(F)_2(SF_3)(CO)(PEt)_2]$ (**11**) by reaction with SF_4. As starting compound *trans*-$[Ir(F)(CO)(PR_3)_2]$ [**6**: R = Et, **7**: R = Ph, **8**: R = *i*Pr, **9**: R = Cy, **10**: R = *t*Bu] has to be prepared by exchange of the chlorido ligand. It is intriguing that only the latter complex **6** and *trans*-$[Ir(F)(CO)(PPh_3)_2]$ react with SF_4 to yield the oxidative addition product, whereas *trans*-$[Ir(F)(CO)(PR_3)_2]$ [**8**: R = *i*Pr, **9**: R = Cy, **10**: R = *t*Bu] do not react.

When compared to the analogous rhodium compound *cis*,*trans*-$[Rh(F)_2(SF_3)(CO)(PEt)_2]$, complex **11** shows an enhanced stability allowing for manipulations at room temperature, although an isolation was not possible. SF_3 complexes are very rare, but the hydrolysis of **11** as well as the reaction with a Lewis acid is in accordance with the behavior of other transition metal or organo substituted λ^4-trifluorosulfanyl units.[5c,5e,7a,7c,31]

Experimental Section

General Methods and Instrumentation: The synthetic work was carried out with a Schlenk line or in a glove box in an atmosphere of argon. All reactions involving SF_4 and AsF_5 were performed on a stainless steel vacuum line with a defined volume. The reactions were performed in 15 mm o.d. and 3.8 mm o.d. PFA tubing.

Caution! Sulfur tetrafluoride and arsenic pentafluoride are highly toxic gases. Exposure to these chemicals can cause serious injuries.

All solvents were purified and dried by conventional methods and distilled under an atmosphere of argon before use or directly condensed into the reaction vessel. The complexes *trans*-$[Ir(Cl)(CO)(PR_3)_2]$[**1**: R = Et , **2**: R = Ph, **3**: R = *i*Pr, **4**: R = Cy] were prepared based on literature-known procedures. The preparation of *trans*-$[Ir(Cl)(CO)(P\mathit{t}Bu_3)_2]$ (**5**) was done analogous. SF_4 (99 %), AsF_5 (99.9 %) and Me_4NF were obtained from ABCR and used without further purification. Traces of thionyl fluoride and SF_6 were present in sulfur tetrafluoride but did not interfere with the chemistry. The NMR spectra were acquired with a Bruker DPX 300 or a Bruker Avance 300 spectrometer. The ^1H and $^{13}C\{^1H\}$ NMR chemical shifts were referenced to residual C_6D_5H at $\delta = 7.15$ ppm $CDHCl_2$ at $\delta = 5.32$ ppm or toluene-d_7 at $\delta = 2.09$ ppm. The $^{13}C\{^1H\}$ NMR chemical shifts were referenced to $[D_8]$toluene at $\delta = 137.84$ ppm. The ^{19}F NMR spectra were referenced to external $CFCl_3$ at $\delta = 0.0$ ppm and the $^{31}P\{^1H\}$ NMR spectra to external 85 % H_3PO_4 at $\delta = 0.0$ ppm. IR spectra were recorded with a Bruker Vertex 70 spectrometer that was equipped with an ATR unit (diamond). Mass spectra were measured with a Micromass Q-TOF-2 mass spectrometer, which was equipped with a Linden LIFDI source (Linden CMS GmbH). Microanalyses were performed with a HEKAtech Euro EA Elemental Analyzer.

Structure Determination of Complexes 9 and 10: The data were collected at a BRUKER D8 VENTURE area detector, Mo-K_α radiation ($\lambda = 0.71073$ Å). All measurements were performed at 100(2) K. Multi-scan absorption corrections implemented in SADABS were applied to the data.[32] The structures were solved by intrinsic phasing method (SHELXT-2015) and refined by full-matrix least square procedures based on F^2 with all measured reflections (SHELXL-2015) with anisotropic temperature factors for all non-hydrogen atoms.[33] All hydrogen atoms were added geometrically and refined on using a riding model.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1976836 (**9**) and CCDC-1976842 (**10**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

General Procedure for the Synthesis of *trans*-$[Ir(F)(CO)(PR_3)_2]$: A PFA tube was loaded with Me_4NF (1.2 equiv.) and $[Ir(Cl)(CO)(PR_3)_2]$ (**1–5**) (1 equiv.) dissolved in CH_2Cl_2 was added. After 15 min the solvent was removed in vacuo and the residue was extracted with *n*-hexane. Removing all volatiles from the extract gave **6** as a yellow oil and **7–10** as yellow powders in 98 %, 80 %, 97 %, 82 % and 93 % yield.

Analytical Data for *trans*-$[Ir(F)(CO)(PEt_3)_2]$ (6): ^1H NMR (300.1 MHz, C_6D_6, 298 K): $\delta = 1.81$ (mq, $^3J_{H,H} = 7.5$ Hz, 12 H, $PC\mathit{H}_2CH_3$), 1.06 ppm (mt, $^3J_{H,H} = 7.5$ Hz, 18 H, $PCH_2C\mathit{H}_3$); $^3J_{H,H}$- and $^3J_{H,P}$-coupling constants were determined from a $^1H\{^{31}P\}$ NMR spectrum. **^{19}F NMR** (282.4 MHz, C_6D_6, 298 K): $\delta = -264.8$ ppm (t, $^2J_{F,P} = 33$ Hz). **$^{31}P\{^1H\}$ NMR** (121.5 MHz, C_6D_6, 298 K): $\delta = 25.9$ ppm (d, $^2J_{P,F} = 33$ Hz) ppm. **MS** (LIFDI TOF, toluene): calcd. for $C_{13}H_{30}FIrOP_2^+$ $[M^+]$: *m/z* 476.5, found: 476.2. **IR** (ATR, diamond): $\tilde{\nu} = 1925$ (vs, CO), 490 (m, Ir–F) cm^{-1}. Complex *trans*-$[Ir(F)(^{13}CO)(PEt_3)_2]$ (**6′**) was prepared in a similar manner by using *trans*-$[Ir(Cl)(^{13}CO)(PEt_3)_2]$ (**1′**). Selected spectroscopic data for **6′**: **$^{13}C\{^1H\}$ NMR** (75.5 MHz, $[D_8]$toluene, 298 K): $\delta = 174.1$ ppm (dt, $^2J_{C,F} = 84$, $^2J_{C,P} = 10$ Hz). **^{19}F NMR** (282.4 MHz, C_6D_6, 298 K): $\delta = -264.8$ ppm (dt, $^2J_{C,F} = 84$, $^2J_{F,P} = 33$ Hz). **$^{31}P\{^1H\}$ NMR** (121.5 MHz, $[D_8]$toluene, 298 K): $\delta = 25.9$ ppm (dd, $^2J_{P,F} = 33$, $^2J_{C,P} = 10$ Hz). **IR** (ATR, diamond): $\tilde{\nu} = 1878$ (vs, ^{13}CO) cm^{-1}.

Analytical Data for *trans*-$[Ir(F)(CO)(P\mathit{i}Pr_3)_2]$ (8): ^1H NMR (300.1 MHz, C_6D_6, 298 K): $\delta = 2.48$ [mhept, $^3J_{H,H} = 7.2$ Hz, 6 H, $PCH(C\mathit{H}_3)_2$], 1.31 ppm [md, $^3J_{H,H} = 7.2$ Hz, 36 H, $PCH(C\mathit{H}_3)_2$]; $^3J_{H,H}$ -coupling constants were determined from a $^1H\{^{31}P\}$ NMR spectrum. **^{19}F NMR** (282.4 MHz, C_6D_6, 298 K): $\delta = -256.0$ ppm (t, $^2J_{F,P} = 26$ Hz). **$^{31}P\{^1H\}$ NMR** (121.5 MHz, C_6D_6, 298 K): $\delta = 49.45$ ppm (d, $^2J_{P,F} = 26$ Hz). **MS** (LIFDI TOF, toluene): calcd. for $C_{19}H_{42}FIrOP_2^+$ $[M^+]$: *m/z* 560.2, found: 560.5. **IR** (ATR, diamond): $\tilde{\nu} = 1916$ (vs, CO), 487 (m, Ir–F) cm^{-1}. $C_{19}H_{42}FIrOP_2$ (560.23): calcd. C 40.77, H 7.56 %; found C 41.15, H 7.64 %.

Analytical Data for *trans*-$[Ir(F)(CO)(PCy_3)_2]$ (9): ^1H NMR (300.1 MHz, C_6D_6, 298 K): $\delta = 2.43$ [m, 6 H, $PC\mathit{H}(CH_2)_2(CH_2)_2CH_2$], 2.19 [m, 12 H, $PCH(CH_2)_2(CH_2)_2C\mathit{H}_2$], 1.76 [m, 24 H, $PCH(C\mathit{H}_2)_2(CH_2)_2CH_2$], 1.26 ppm [m, 24 H, $PCH(CH_2)_2(C\mathit{H}_2)_2CH_2$]. **$^{19}F$ NMR** (282.4 MHz, $[D_8]$toluene, 298 K):

δ = –255.0 ppm (t, $^2J_{F,P}$ = 26 Hz). **^{31}P{^{1}H} NMR** (121.5 MHz, [D$_8$]toluene, 298 K): δ = 39.3 ppm (d, $^2J_{P,F}$ = 26 Hz). **MS** (LIFDI TOF, toluene): calcd. for $C_{37}H_{66}FIrOP_2^+$ [M$^+$]: *m/z* 800.4, found: 800.7. **IR** (ATR, diamond): ṽ = 1924 (vs, CO), 490 (m, Ir–F) cm^{-1}. $C_{37}H_{66}FIrOP_2$ (644.33): calcd. C 55.54, H 8.31; found C 55.41, H 8.27.

Analytical Data for *trans*-[Ir(F)(CO)(P*t*Bu$_3$)$_2$] (10): ^{1}H NMR (300.1 MHz, [D$_8$]toluene, 298 K): δ = 1.60 (pseudo triplet, I$^3J_{H,P}$+$^5J_{H,P}$I = 11.8 Hz). **^{19}F NMR** (282.4 MHz, [D$_8$]toluene, 298 K): δ = –243.3 ppm (t, $^2J_{F,P}$ = 24 Hz). **^{31}P{^{1}H} NMR** (121.5 MHz, [D$_8$]toluene, 298 K): δ = 71.5 ppm (d, $^2J_{P,F}$ = 24 Hz). **MS** (LIFDI TOF, toluene): calcd. for $C_{25}H_{54}FIrOP_2^+$ [M$^+$]: *m/z* 644.3, found: 644.6. **IR** (ATR, diamond): ṽ = 1910 (vs, CO), 492 (m, Ir–F) cm^{-1}. $C_{25}H_{54}FIrOP_2$ (644.33): calcd. C 46.64, H 8.45; found C 46.78, H 8.54.

Formation of *cis,trans*-[Ir(F)$_2$(SF$_3$)(CO)(PEt)$_2$] (11): In a PFA tube *trans*-[Ir(F)(CO)(PEt$_3$)$_2$] (**6**) (23 mg, 0.05 mmol) was dissolved in [D$_8$]toluene. The solution was degassed in vacuo and 1 equiv. of SF_4 (0.05 mmol) was condensed into the PFA tube at 77 K. After sealing the PFA tube and storing the reaction mixture at 243 K for 16 h, *cis,trans*-[Ir(F)$_2$(SF$_3$)(CO)(PEt)$_2$] (**11**) was identified by NMR spectroscopy. Selected spectroscopic data for **11**: **^{1}H NMR** (300.1 MHz, [D$_8$]toluene, 298 K): δ = 1.94 (mq, $^3J_{H,H}$ = 7.5 Hz, 12 H, PCH_2CH$_3$), 0.96 ppm (mt, $^3J_{H,H}$ = 7.6 Hz, 18 H, PCH$_2$CH_3); the $^3J_{H,H}$-coupling constant was determined by a ^{1}H{^{31}P} NMR spectrum. **^{19}F NMR** (282.4 MHz, [D$_8$]toluene, 243 K): δ = 67.5 (br., 2F, IrSF_2F), –64.9 (t, $^2J_{F,F}$ = 71 Hz, 1F, IrSF$_2$$F$), –314.6 (dt, $^2J_{F,F}$ = 143, $^2J_{F,P}$ = 34 Hz, 1F, IrF), –366.6 ppm ($^2J_{F,F}$ = 143, $^2J_{F,P}$ = 29 Hz, 1F, IrF). **^{31}P{^{1}H}** NMR (121.5 MHz, [D$_8$]toluene, 298 K): δ = 11.7 ppm (dd, $^2J_{P,F}$ = 34, $^2J_{P,F}$ = 29 Hz).

Complex *cis,trans*-[Ir(F)$_2$(SF$_3$)(^{13}CO)(PEt)$_2$] (**11′**) was prepared in a similar manner by using *trans*-[Ir(F)(^{13}CO)(PEt$_3$)$_2$] (**6′**). Selected spectroscopic data for **11′**: **^{13}C{^{1}H} NMR** (75.5 MHz, [D$_8$]toluene, 298 K): δ = 160.33 ppm (dtd, $^2J_{C,F}$ = 77, $^2J_{C,P}$ = 7, $^2J_{C,F}$ = 5 Hz). **^{19}F NMR** (282.4 MHz, [D$_8$]toluene, 298 K): δ = 67.5 (br., 2F, IrSF_2F), –64.9 (br., 1F, IrSF$_2$$F$), –314.6 (dtd, $^2J_{F,F}$ = 143, $^2J_{F,P}$ = 34, $^2J_{F,C}$ = 77 Hz, 1F, IrF), –366.6 ppm ($^2J_{F,F}$ = 143, $^2J_{F,P}$ = 29, $^2J_{F,C}$ = 5 Hz, 1F, IrF). **^{31}P{^{1}H} NMR** (121.5 MHz, [D$_8$]toluene, 298 K): δ = 11.7 ppm (ddd, $^2J_{P,F}$ = 34, $^2J_{P,F}$ = 29, $^2J_{C,P}$ = 7 Hz). **MS** (LIFDI TOF, toluene): calcd. for $C_{12}{}^{13}CH_{30}F_4IrOP_2S^+$ [M$^+$-F]: *m/z* 566.11; found: *m/z* 566.13

Formation of *cis,trans*-[Ir(F)$_2$(SOF)(CO)(PEt$_3$)$_2$] (12): A sample of *cis,trans*-[Ir(F)$_2$(SF$_3$)(CO)(PEt)$_2$] (**11**) (0.09 mmol) was prepared as described above, but either in the presence of 30 equivalents of CsF or 10 equivalents of Et$_3$N. The purity of the sample was verified by NMR spectroscopy at 243 K. The PFA tube was placed in a Young NMR tube, opened and 2 µL (1.2 Eq., 0.11 mmol) of H_2O was added with a microliter syringe at room temperature. The formation of **12** was monitored by NMR spectroscopy. Selected spectroscopic data for **12**: **^{1}H NMR** (300.1 MHz, [D$_8$]toluene, 298 K): δ = 2.06–1.73 (m, 12 H, PCH_2CH$_3$), 0.96 ppm (m, 18 H, PCH$_2$CH_3). **^{19}F NMR** (282.4 MHz, [D$_8$]toluene, 298 K): δ = 0.7 (br. m, 1F, SOF), –318.3 (dt, $^2J_{F,F}$ = 140, $^2J_{F,P}$ = 32.4 Hz, 1F, IrF), –337.6 ppm (dm, $^2J_{F,F}$ = 140 Hz, 1F, IrF). **^{31}P{^{1}H} NMR** (121.5 MHz, [D$_8$]toluene, 298 K): δ = 11.3 ppm (m, $^2J_{P,P}$ = 342, $^2J_{P,F}$ = 33, $^2J_{P,F}$ = 32, $^2J_{P,F}$ = 29, $^2J_{P,F}$ = 28, $^3J_{P,F}$ = 10, $^3J_{P,F}$ = 7 Hz). The chemical shift and the coupling constants of the ^{31}P{^{1}H} NMR spectrum were obtained by simulation.

Treatment of *cis,trans*-[Ir(F)$_2$(SF$_3$)(CO)(PEt)$_2$] (11) with AsF$_5$: A sample of *cis,trans*-[Ir(F)$_2$(SF$_3$)(CO)(PEt)$_2$] (**11**) (0.09 mmol) was prepared in CD_2Cl_2 leaving the reaction tube connected to the stainless steel line. After a reaction time of 12 h at 263 K the mixture was degassed and equimolar amounts of AsF$_5$ were condensed onto the solution. The PFA tube was sealed and transferred to the NMR spectrometer. The formation of *cis,trans*-[Ir(F)$_2$(SF$_2$)(CO)(PEt)$_2$][AsF$_6$] (**13**) was observed by NMR spectroscopy upon thawing of the mixture. Spectroscopic data for **13**: **^{1}H NMR** (300.1 MHz, CD$_2$Cl$_2$, 263 K): δ = 2.21 (mq, $^3J_{H,H}$ = 7.7 Hz, 12 H, PCH_2CH$_3$), 1.22 ppm (mt, $^3J_{H,H}$ = 7.7 Hz, 18 H, PCH$_2$CH_3); the $^3J_{H,H}$-coupling constant was determined by a ^{1}H{^{31}P} NMR spectrum. **^{19}F NMR** (282.4 MHz, CD$_2$Cl$_2$, 263 K): δ = –36.8 (tdd, 2F, SF_2), –65.7 (br., 6F, AsF_6), –334.8 (dtt, $^2J_{F,F}$ = 157, $^2J_{F,P}$ = 32, $^3J_{F,P}$ = 11 Hz, 1F, IrF), –336.6 ppm (dtt, $^2J_{F,F}$ = 157, $^2J_{F,P}$ = 37, $^3J_{F,F}$ = 8 Hz, 1F, IrF). **^{31}P{^{1}H} NMR** (121.5 MHz, CD$_2$Cl$_2$, 263 K): δ = 24.6 ppm (ddt, $^2J_{F,P}$ = 37, $^2J_{P,F}$ = 32, $^3J_{P,F}$ = 14 Hz). **IR** (ATR, diamond): ṽ = 2064 (s, CO), 692 (vs, AsF$_6$), 675 (vs, AsF$_6$) cm^{-1}.

Supporting Information (see footnote on the first page of this article): Spectra, computational details, crystallographic data.

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Synthesis and Reactivity of Iridium(I) Fluorido Complexes: Oxidative Addition of SF_4 at *trans*-$[Ir(F)(CO)(PEt_3)_2]$