Reaction Mechanism

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Insertion of CS_2 into Iridium–Fluorine Bonds**

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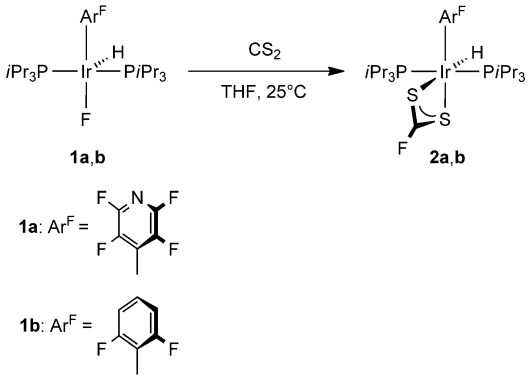
Because of the major importance of fluorinated organic molecules in material sciences,[1] drug development,[2] agrochemistry,[1b,3] and as [^{18}F] PET tracers,[4] it is desirable to expand the chemist's toolbox for fluorination methods and to understand their reaction mechanisms. Transition-metal-mediated fluorination methods can be considered as a smart alternative when compared to conventional fluorination methods.[5] Catalytic procedures often allow a nucleophilic or electrophilic fluorination under mild reaction conditions and considerable progress has been made in the last decade.[6,7] A fluorination step to form a C–F bond generally proceeds either by a transition-metal fluorido complex as an intermediate or by fluorination of a ligand. For the former pathway reductive elimination can lead to C–F bonds.[8]

Insertion reactions into metal–fluorine bonds would also be an interesting approach for transition-metal-mediated C–F bond-formation reactions, but so far they have hardly been identified. The formation of (β-fluorovinyl)gold complexes by reaction of gold(I) fluorides with alkynes has been reported but the conversions proceed, most likely, by an intermolecular fluorination.[9] To the best of our knowledge, the formation of the fluorodithiocarbonato complex [Pt(κ^2-(*S*,*S*)-S_2CF)(PPh$_3$)$_2$][HF$_2$] from a reaction of [Pt(F)(PPh$_3$)$_2$][HF$_2$] with CS_2 represents a unique example for which the formation of a C–F bond by an intermolecular insertion of a substrate into a metal–fluorine bond was suggested.[10,11] However, the compound was characterized by infrared spectroscopy and single-crystal structure analysis, but the identity of the bifluoride anion [F···F 2.84(2) Å] is ambiguous.[12]

Herein we report on the synthesis of iridium(III) fluorodithiocarbonato complexes by insertion of CS_2 into the Ir–F bond of the iridium(III) fluorides *trans*-[Ir(Ar^F)(F)(H)(P*i*Pr$_3$)$_2$] (**1a**: Ar^F = 4-C_5NF_4; **1b**: Ar^F = 2-$C_6H_3F_2$; Scheme 1).[13] The insertion mechanism is supported by density-functional theory (DFT) calculations.

Treatment of a solution of **1a** in THF with CS_2 led to the formation of *trans*-[Ir(4-C_5NF_4)(H)(κ^2-(*S*,*S*)-S_2CF)(P*i*Pr$_3$)$_2$] (**2a**) at room temperature (Scheme 1). The ^{13}C-labeled isotopologue *trans*-[Ir(4-C_5NF_4)(H)(κ^2-(*S*,*S*)-$S_2{}^{13}$CF)(P*i*Pr$_3$)$_2$] ([^{13}C]-**2a**) can be obtained by a comparable procedure using $^{13}CS_2$. Analogously, *trans*-[Ir(2-$C_6H_3F_2$)(H)(κ^2-(*S*,*S*)-S_2CF)(P*i*Pr$_3$)$_2$] (**2b**) is formed by a reaction of **1b** with CS_2 in THF at room temperature.



Scheme 1. Syntheses of **2a** and **2b**. THF = tetrahydrofuran.

The ^{31}P{^{1}H} NMR spectrum of **2a** displays a doublet at δ = 9.7 ppm ($^2J_{F,P}$ = 5.8 Hz) for the phosphorus atoms in a mutually *trans* arrangement. The ^{19}F{^{1}H} NMR spectrum shows a broad singlet at remarkably low field at δ = 96.8 ppm and four multiplets (δ = −98.4, −99.8, −108.8, −117.2 ppm) in a 1:1:1:1:1 ratio. Whereas the four multiplets indicate a restricted rotation of the tetrafluoropyridyl ligand about the metal–carbon bond,[13,14] the singlet at δ = 96.8 ppm can be assigned to the fluorine atom of the fluorodithiocarbonato ligand. For the isotopologue [^{13}C]-**2a** an additional coupling constant of $^1J_{C,F}$ = 395 Hz is observed. The IR (ATR) spectrum of **2a** displays an absorption band at 2218 cm^{-1} for the IrH moiety.[13,14b,15] The complex **2b** shows comparable spectroscopic data to that of **2a**.

DFT calculations were performed to model the reaction of **1a** with CS_2 to give **2a**.[16] The formation of **2a** is predicted to be exothermic by an energy difference of −12.0 kJ mol^{-1}. In accordance with the NMR data the computed molecular structure of **2a** exhibits a distorted octahedral arrangement as it is depicted in Figure 1. The S_2CF moiety coordinates through its two sulfur atoms, which are located in the *trans* positions to the metal-bound hydrogen atom and to the tetrafluoropyridyl ligand. Note that the fluorodithiocarbonato ligand features a surprisingly short C–F bond length of 1.320 Å. For the above-mentioned cation [Pt(κ^2-(*S*,*S*)-S_2CF)(PPh$_3$)$_2$]$^+$ a C–F bond length of 1.27(3) Å was determined by X-ray crystallography.[11] Similar short C–F bonds have been found for 2-fluoroamidinium, 2-fluoroimidazolinium, and 2-fluoroimidazolium cations.[17]

Two possible reaction pathways for the formation of **2a** have been considered (Scheme 2). Pathway A features

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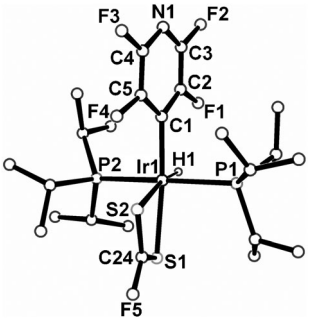


Figure 1. Computed structure of **2a**. The hydrogen atoms of the isopropyl groups are omitted for clarity. Selected distances [Å] and angles [°]: Ir1–P1 2.466, Ir1–P2 2.401, Ir1–C1 2.062, Ir1–H1 1.575, Ir1–S1 2.499, Ir1–S2 2.605, S1–C24 1.677, S2–C24 1.667, C24–F5 1.320; P1-Ir1-P2 170.9, C1-Ir1-H1 86.7, C1-Ir1-S1 172.0, C1-Ir1-S2 103.2, S1-C24-S2 120.5, S1-C24-F5 119.5, S1-C24-S2 120.5.

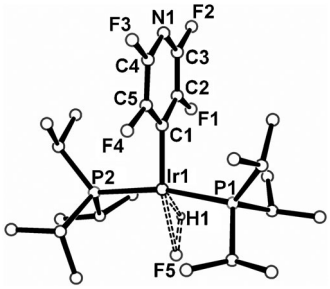
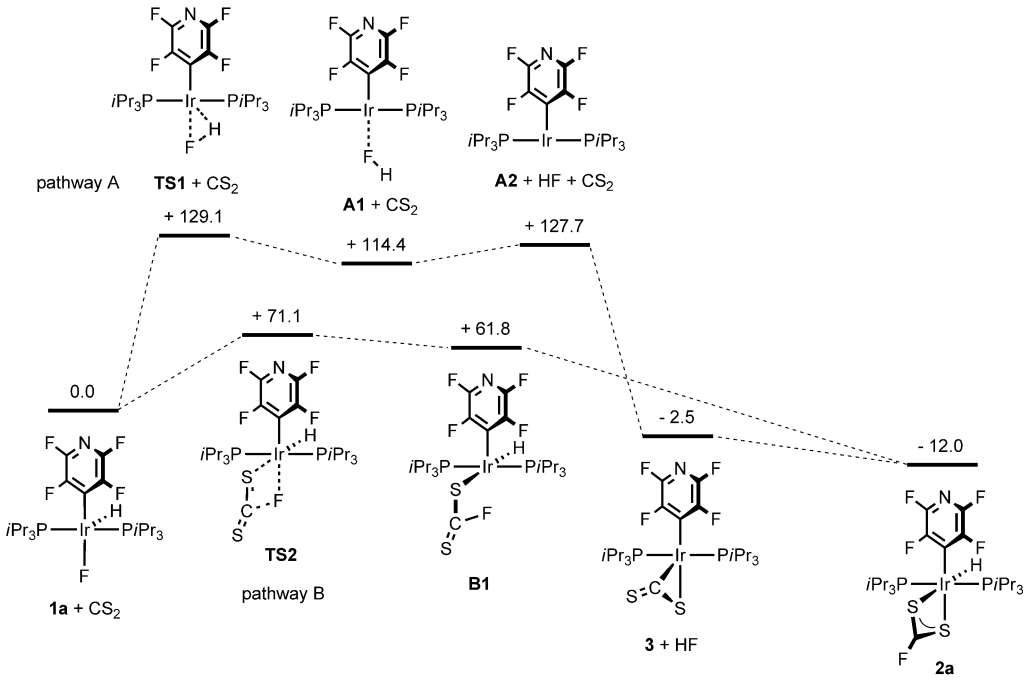


Figure 2. Computed structure for the transition state (**TS1**) of the reductive elimination of HF from **1a**. The hydrogen atoms of the isopropyl groups are omitted for clarity. Selected distances [Å] and angles [°]: Ir1–C1 1.980, Ir1–H1 1.650, Ir1–F5 2.337, F5–H1 1.240; P1-Ir1-P2 167.2, C1-Ir1-H1 129.5, C1-Ir1-F5 159.9.

a reductive elimination of HF and subsequent coordination of CS_2 at the metal center and fluorination of the CS_2 ligand with HF. The second pathway B involves a concerted mechanism which is characterized by an insertion of CS_2 into the Ir–F bond. The formation of the reactive 14-electron iridium(I) intermediate *trans*-{Ir(4-C_5NF_4)(P*i*Pr$_3$)$_2$} (**A2**; pathway A) via a three-membered transition state was found to have an activation energy of $+129.1\ kJ\,mol^{-1}$. The structure of transition-state **TS1** is depicted in Figure 2 and is characterized by a simultaneous elongation of the Ir–F bond (2.337 Å) and the Ir–H bond (1.650 Å). The H···F separation is significantly shorter (1.240 Å) compared to that in **1a** (2.929 Å). For an HF molecule solid-state X-ray and gas-phase neutron diffraction experiments revealed H–F separations in a range from 0.92 Å to 0.97 Å, which is in accordance with a computed distance of 0.918 Å.[18] The complex *trans*-{Ir(4-C_5NF_4)(FH)(P*i*Pr$_3$)$_2$} (**A1**) is formed as a shallow intermediate, which then releases HF to yield *trans*-{Ir(4-C_5NF_4)-(P*i*Pr$_3$)$_2$} (**A2**). The subsequent coordination of CS_2 to the 14-electron intermediate **A2** results in the formation of *trans*-[Ir(4-C_5HF_4)(κ^2-(*C*,*S*)-*SCS*)(P*i*Pr$_3$)$_2$] (**3**) at $-2.5\ kJ\,mol^{-1}$. Note that the formal reductive elimination of HF from *trans*-[Ir(4-C_5NF_4)(F)(H)(CO)(P*i*Pr$_3$)$_2$] (**4**) was observed before.[13]

The computed reaction profile for pathway B, which involves the concerted insertion of CS_2 into the metal–fluorine bond, proceeds via a four-membered transition state (**TS2**) at $+71.1\ kJ\,mol^{-1}$ (Figure 3). The Ir–F separation of 2.197 Å in **TS2** shows an incipient Ir–F bond cleavage and a significant elongation when compared to the Ir–F distance in **1a** (crystal structure: 2.039(2) Å, computed: 2.076 Å). The simultaneous formation of the C–F bond and Ir–S bond is demonstrated by a C···F distance of 1.739 Å and an Ir···S distance of 2.609 Å. Comparable four-membered transition states were also discussed for the reverse reaction—a concerted C–F bond cleavage either by β-fluoride elimination or a metathesis-like mechanism.[19] Note that an interaction of CS_2 with the Ir center requires a vacant coordination site at the metal. The LUMO of **1a** has σ-antibonding character in the Ir–H bond, but is essentially metal-centered with one lobe



Scheme 2. Energy profile for the reaction of **1a** with CS_2. Calculated energies are given in $kJ\,mol^{-1}$ and include a zero-point correction.

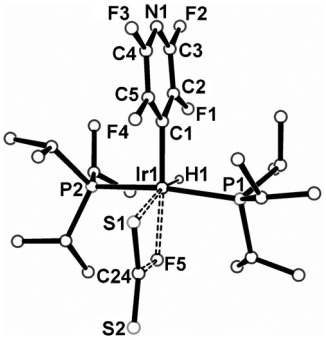
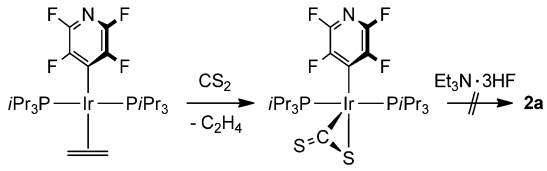


Figure 3. Computed structure for the transition state (**TS2**) of the insertion of CS_2 into the Ir–F bond of **1a**. The hydrogen atoms of the isopropyl groups are omitted for clarity. Selected distances [Å] and angles [°]: Ir1–C1 2.016, Ir1–H1 1.556, Ir1–S1 2.609, Ir1–F5 2.197, S1–C24 1.634, S2–C24 1.586, C24–F5 1.739; P1-Ir1-P2 165.5, C1-Ir1-H1 84.2, C1-Ir1-S1 108.6, C1-Ir1-F5 173.6, S1-C24-S2 148.8, S1-C24-F5 101.5, S1-C24-S2 109.7.



Scheme 3. Synthesis of *trans*-[Ir(4-C_5NF_4)(κ²-(*C*,*S*)-*SCS*)($PiPr_3$)$_2$] (**3**).

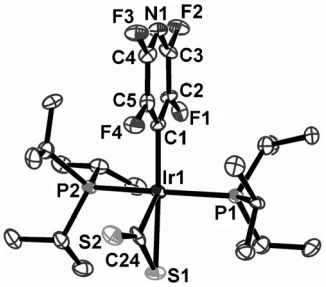


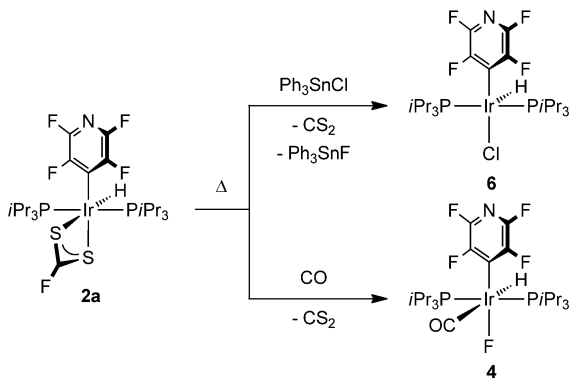
Figure 4. An ORTEP diagram of **3**. Ellipsoids are drawn at the 50% probability level. hydrogen atoms are omitted for clarity. Selected bond length [Å] and angles [°] with standard deviations in parentheses and computed values in italics: Ir1–P1 2.391(3) *2.449*, Ir1–P2 2.375(5) *2.446*, Ir1–C1 2.038(9) *2.052*, Ir1–C24 1.987(9) *1.973*, Ir1–S1 2.459(2) *2.477*, S1–C24 1.697(12) *1.685*, S2–C24 1.602(11) *1.620*; P1-Ir1-P2 166.58(9) *169.6*, C1-Ir1-C24 124.4(4) *129.4*, C1-Ir1-S1 169.3(3) *171.6*, Ir1-C24-S1 83.3(4) *84.8*, Ir1-C24-S2 136.2(7) *134.3*, S1-C24-S2 140.4(7) *140.8*.

pointing towards the vacant *trans* position of the metal-bound hydrogen atom of **1a** (see the Supporting Information). As the reaction proceeds, **TS2** links to a shallow intermediate (**B1**) at $+61.8\ kJ\,mol^{-1}$, and features a monodentate fluorodithiocarbonato ligand. The C–F separation of 1.388 Å in **B1** reveals the C–F bond formation, whereas an Ir···F distance of 2.620 Å denotes only a weak interaction between the metal and the fluorine atom.[20] Subsequently, a rotation about the C–S bond and coordination of the second sulfur atom to Ir results in the formation of **2a**. Overall, the reaction pathway B is computed to be kinetically favored over the alternative route including HF elimination and CS_2 coordination (pathway A). In addition, a mechanism which involves a metallophosphorane intermediate generated by initial migration of the fluorine atom to one of the phosphorous atoms was computed to be unfavorable by an energy of $+272.6\ kJ\,mol^{-1}$.[8b,d,21]

Note that it was reported before that the reaction of **1a** with CO_2 results in the formation of the hydrogencarbonato complex *trans*-[Ir(4-C_5NF_4)(H)(κ²-(*O*,*O*)-O_2COH)($PiPr_3$)$_2$] (**7**) in the presence of traces of water.[13] An insertion of CO_2 into the Ir–F bond of **1a** was not observed. We also computed the formation of the putative insertion product *trans*-[Ir(4-C_5NF_4)(H)(κ²-(*O*,*O*)-O_2COF)($PiPr_3$)$_2$] by DFT calculations and found it to be endothermic by $+32.9\ kJ\,mol^{-1}$. Furthermore, several attempts to optimize a transition state comparable to **TS2** only converged to the structures of **1a** and CO_2.

Experimental studies gave further support for the improbability of a fluorination of coordinated CS_2. The complex *trans*-[Ir(4-C_5NF_4)(η²-CS_2)($PiPr_3$)$_2$] (**3**) was prepared on treatment of *trans*-[Ir(4-C_5NF_4)(η²-C_2H_4)($PiPr_3$)$_2$] (**5**) with CS_2 (Scheme 3). The $^{31}P\{^1H\}$ NMR spectrum of **3** shows a singlet at $\delta = 12.1$ ppm for the phosphine ligands in a mutually *trans* position. The ^{19}F NMR spectrum of **3** displays four multiplets at $\delta = -98.4$, -112.5, -118.0, and -117.2 ppm in a 1:1:1:1 ratio for the fluorine atoms of the tetrafluoropyridyl ligand. The molecular structure of **3** was also confirmed by X-ray diffraction analysis at −173 °C (Figure 4).[22] The complex **3** features an almost square-planar arrangement of the phosphine ligands (P1-Ir1-P2 166.58(9) Å), the apical carbon atom of the tetrafluoropyridyl ligand and one sulfur atom of the CS_2 ligand [C1-Ir1-S1 169.3(3)°]. The carbon atom of the CS_2 ligand is bound to the metal with an C1-Ir1-C24 angle of 124.4(4)°. The C24-S1 bond [1.697(12) Å] is found to be longer than the C24-S2 bond [1.602(11) Å], and the CS_2 moiety is bent [S1-C24-S2 140.4(7)°] in a similar fashion as reported for other compounds bearing a η²-CS_2 ligand at rhodium(I), nickel(0) or palladium(0).[23]

In accordance with the computational studies the iridium(I) complex **3** does not react with $Et_3N{\cdot}3HF$ (THF, 12 h, 50 °C, Scheme 3) or py·HF (C_6D_6, 12 h, 50 °C). Additionally, the presence of CsF or $Et_3N{\cdot}3HF$ does not have any influence on the reaction rate for the conversion of **1a** with CS_2. However, the insertion of CS_2 into the Ir–F bond of **1a** is reversible at 50 °C. The complex **1a** was observed by NMR spectroscopy. The complex **3** was not detected, but several other compounds were, and they could not be identified further. To get more insight into that reaction, **2a** was treated with Ph_3SnCl at 50 °C. This reaction led to the generation of the chlorido complex *trans*-[Ir(4-C_5NF_4)(Cl)(H)($PiPr_3$)$_2$] (**6**)[13,24] and a colorless solid, which was identified as Ph_3SnF[25] by elemental analysis and IR spectroscopy (Scheme 4). CS_2 was detected in the reaction mixture by GC/MS and ^{13}C NMR experiments. We assume that initially **1a** and CS_2 are formed from **2a** at elevated temperatures and a subsequent reaction of **1a** with Ph_3SnCl yields the chlorido



Scheme 4. Reactivity of **2a** towards Ph_3SnCl and CO.

complex **6** and Ph_3SnF. In addition, heating of **2a** in the presence of CO led also to the formation of CS_2 as well as the formation of *trans*-[Ir(4-C_5NF_4)(F)(H)(CO)(P*i*Pr_3)$_2$] (**4**; Scheme 4).[13] However, we did not observe any reaction of **2a** with metal fluorides (CsF, NaF, Me_3SnF, Ph_3SnF), nor did it react with $Et_3N{\cdot}3HF$ or Bu_4NF in THF at 50 °C to yield fluorodithiocarbonato derivatives.

In conclusion a combined experimental and computational approach revealed that an insertion of an organic substrate into a metal–fluorine bond is feasible, indeed. The insertion of CS_2 into the metal–fluorine bond of the iridium(III) fluorido complexes **1a** and **1b** yields the fluorodithiocarbonato compounds **2a** and **2b**, respectively. Computational studies support an unprecedented metathesis-like concerted mechanism, which requires a vacant coordination site at an electron-deficient metal center. The insertion of unsaturated molecules into transition-metal–fluorine bonds to achieve a C–F bond formation has to be considered as a promising alternative to ligand fluorination.

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