

Fluorination Reactions at a Platinum Carbene Complex: Reaction Routes to SF₃, S(=O)F and Fluorido Complexes

Dilcan Dirican,^[a] Maria Talavera,^[a] and Thomas Braun^{*[a]}

Abstract: The electron-rich Pt complex [Pt(IMes)₂] (IMes: [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolinyldiene]) can be used as precursor for the syntheses of a variety of fluorido ligand containing compounds. The sulfur fluoride SF₄ undergoes a rapid oxidative addition at Pt⁰ to yield *trans*-[Pt(F)(SF₃)(IMes)₂]. A photolytic reaction of SF₆ at [Pt(IMes)₂] in the presence of IMes gave the fluorido complexes *trans*-[Pt(F)₂(IMes)₂] and *trans*-[Pt(F)(SF₃)(IMes)₂] along with *trans*-[Pt(F)(SOF)(IMes)₂] and *trans*-[Pt(F)(IMes')(IMes)] (IMes': cyclometalated IMes

ligand), the latter being products produced by reaction with adventitious water. *trans*-[Pt(F)(SOF)(IMes)₂] and *trans*-[Pt(F)₂(IMes)₂] were synthesized independently by treatment of [Pt(IMes)₂] with SOF₂ or XeF₂. A reaction of [Pt(IMes)₂] with a HF source gave *trans*-[Pt(H)(F)(IMes)₂], and an intermediate bifluorido complex *trans*-[Pt(H)(FHF)(IMes)₂] was identified. Compound *trans*-[Pt(H)(F)(IMes)₂] converts in the presence of CsF into *trans*-[Pt(F)(IMes')(IMes)].

Introduction

Transition metal fluorido complexes often display unique properties when compared to other halogenido analogues.^[1] Reaction pathways include metal-mediated fluorination reactions, but transition metal fluorides can also play a role in catalytic reaction cycles, for instance in borylation reactions. Such transformations can impart C–F bond activation reactions of highly fluorinated organic compounds to access fluorinated building blocks.^[2] Catalytic fluorination reactions can occur via transition metal fluorination with nucleophilic or electrophilic fluorinating agents.^[1f,i,k,3] However, other strategies to synthesize particular fluorido complexes are based on oxidative addition reactions, for instance with XeF₂, or on ligand exchange reactions involving fluoride sources like AgF and HF.^[1j,4]

At Pt, various Pt fluorido complexes were prepared by treatment of iodo complexes with AgF by the research groups of Vigalok, Wendt, Beyzavi, Shahsavari and Beweries.^[5] Seppelt et al. and Perutz et al. described routes to access fluorido complexes by treatment of methyl or hydrido compounds with HF sources.^[6] Other conversions include the generation of fluorido complexes by treatment of Pt precursors with NFSI (NFSI: *N*-fluorobenzenesulfonimide), or Selectfluor (*N*-chloromethyl-*N'*-fluorotriethylenediammonium bis

(tetrafluoroborate).^[3b,7] Love and co-workers reported on C–F bond activation reactions to result in Pt(IV) fluorido complexes.^[2g,u,3c,8] Another method to access Pt fluorido complexes imparts fluorination with XeF₂. Thus, oxidative addition reactions of XeF₂ at Pt(II) yielded Pt(IV) difluorido compounds.^[9] Treatment of monoaryl Pt(IV) complexes with electrophilic fluorinating agents like XeF₂ can lead to C–F bond formation as shown by Gagné, Vigalok and Vedernikov.^[7,10] Similar reactions with diaryl ligand containing Pt resulted in difluorination at the metal along with reductive elimination of biaryl compounds.^[5a,11] Alternatively, it was demonstrated that metal-bound alkyne ligands at Pt(0) are fluorinated by XeF₂ yielding β-fluorovinyl Pt(II) complexes, which can undergo further fluorination processes to give *ortho*-metalated Pt(IV) fluorido compounds.^[3d] Platinum fluorido complexes can generally play certain roles in metal-mediated fluorination and defluorination reactions.^[1a,m,2a,c,e,g,m,p,u,3c,10]

SF₄ and its derivatives are applied for deoxyfluorination reactions, for instance of ketones or alcohols.^[12] At rhodium, iridium and platinum centers, SF₄ converts by oxidative addition into SF₃ fluorido complexes.^[13] SF₆, on the other hand, is fairly inert and applied as dielectric in high-voltage power devices. Reactivity studies of SF₆ at transition metal complexes are rare. They led to the generation of a variety of metal fluorido complexes as it was shown by Ernst, Limberg, or Braun et al.^[14] Remarkably, the reaction of SF₆ at the platinum phosphine complexes [Pt(PR₃)₂] (R=Cy, *i*Pr) in the presence of free phosphine enabled the generation of λ⁴-trifluoro sulfonyl ligands to yield *trans*-[Pt(F)(SF₃)(PR₃)₂].^[13d,15] It was additionally shown that the sulfur(VI) fluorides SF₅X (X=Cl, CF₃) react with iron, rhodium, iridium or platinum complexes to result in a complete defluorination at sulfur by fluorination of the metal centres.^[16] Peacock and co-workers proposed the formation of a SF₅ complex by reaction of [Pt(*E*-PhC=CPh)(PPh₃)₂] with SF₅Cl, but this report was not confirmed further.^[16c,17] However, the generation of SF₅[−] anions was observed at rhodium complexes

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when $[\text{Rh}(\text{X})(\text{CO})(\text{IMes})_2]$ ($\text{X} = \text{F}, \text{Cl}$) was reacted with SF_5Cl .^[18] Note that Pt(0) complexes are generally suitable for the element-fluorine bond activation as it was shown for instance by Braunschweig and Finze et al. with BF_3 and PF_5 as substrates.^[19]

In this contribution we report on the reactivity of the electron-rich carbene complex $[\text{Pt}(\text{IMes})_2]$ (**1**, IMes: (1,3-bis(2,4,6-trimethylphenyl)-2-imidazolynylidene)) towards the sulfur fluorides SF_4 , SOF_2 and SF_6 . The generation of sulfanyl ligands and fluoro complexes was observed. The latter were synthesized independently by investigating the reactivity of $[\text{Pt}(\text{IMes})_2]$ towards HF sources and XeF_2 .

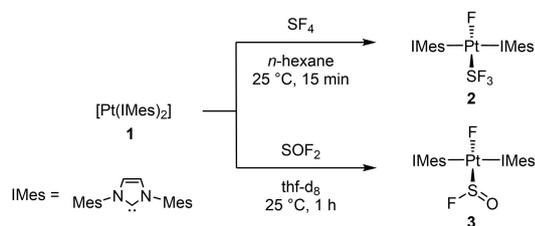
Results and Discussion

Treatment of $[\text{Pt}(\text{IMes})_2]$ (**1**) with SF_4 gave the trifluorosulfanyl fluoro complex $\text{trans}[\text{Pt}(\text{F})(\text{SF}_3)(\text{IMes})_2]$ (**2**) (Scheme 1). The conversion resembles the reactions of $[\text{Pt}(\text{PR}_3)_2]$ ($\text{R} = \text{Cy}, i\text{Pr}$) with SF_4 , which led to the formation of $\text{trans}[\text{Pt}(\text{F})(\text{SF}_3)(\text{PR}_3)_2]$.^[13d] The ^{19}F NMR data of **2** are comparable to those of the phosphine analogues $\text{trans}[\text{Pt}(\text{F})(\text{SF}_3)(\text{PR}_3)_2]$ ($\text{PR}_3 = \text{PCy}_3, \text{P}i\text{Pr}_3$). The ^{19}F NMR spectrum shows a doublet with Pt satellites ($^2J_{\text{F,Pt}} = 86 \text{ Hz}$) at $\delta = 60.9 \text{ ppm}$ for the two axial fluorine atoms of the sulfanyl ligand of a trigonal-bipyramidal configuration at sulfur, when taking the electron lone pair at sulfur into account (Figure 1). The signal exhibits a coupling of $^2J_{\text{F,F}} = 71 \text{ Hz}$ to the equatorial fluorine atom at the SF_3 group. The resonance for the latter appears at higher field at $\delta = -67.9 \text{ ppm}$ as a triplet with Pt satellites ($^2J_{\text{F,Pt}} = 297 \text{ Hz}$). The signal for the metal-bound fluoro ligand is found as a singlet with Pt satellites ($^1J_{\text{F,Pt}} =$

227 Hz) at $\delta = -318.7 \text{ ppm}$, which is a typical chemical shift for transition metal bound fluoro ligands.^[1e,i,2h,3b,d,5a,6b,8d,11b,13d,15,20] The two IMes ligands give one set of signals in the ^1H and ^{13}C $\{^1\text{H}\}$ NMR spectra. On ^{13}C labeling of the carbene carbon atom at IMes the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{trans}[\text{Pt}(\text{F})(\text{SF}_3)(^{13}\text{C}\text{IMes})_2]$ (**2'**) revealed a doublet at $\delta = 169.5 \text{ ppm}$ with a coupling to the metal bound fluoride ($^2J_{\text{C,F}} = 6 \text{ Hz}$) and Pt satellites ($^1J_{\text{C,Pt}} = 1123 \text{ Hz}$).

The above mentioned trigonal-bipyramidal geometry at the sulfur atom was also confirmed by DFT calculations of **2** (BP86/def2-SVP).^[13d-f] The frontier orbital analysis revealed that the electron pair is reflected by the HOMO (Figure 2). Hence, the λ^4 -trifluoro sulfanyl ligand can be considered as an one-electron donor or two-electron donor, when the sulfanyl group is considered to be anionic.^[21]

A reaction of $[\text{Pt}(\text{IMes})_2]$ (**1**) with SF_6 for 4 h at 60°C in a PFA tube did result in a depletion of the sulfur fluoride, but only a mixture of platinum containing products was observed consisting of $\text{trans}[\text{Pt}(\text{F})(\text{SOF})(\text{IMes})_2]$ (**3**), $\text{trans}[\text{Pt}(\text{H})(\text{F})(\text{IMes})_2]$ (**4**) and $\text{trans}[\text{Pt}(\text{F})(\text{IMes}')(\text{IMes})]$ (**5**) (IMes' = cyclometalated IMes ligand) in a ratio of 1:1.2:1.6. In addition, the complexes $\text{trans}[\text{Pt}(\text{F})_2(\text{IMes})_2]$ (**6**) and $\text{cis}[\text{Pt}(\text{H})_2(\text{IMes})_2]$ (*cis*-**7**) were identified in traces. Apparently, adventitious water hampered the generation of a SF_3 ligand containing complex. The reaction was then performed in the presence of additional IMes, which could trap generated HF formed by hydrolysis, but also act as an acceptor for fluorine atoms during the course of the SF_6 activation. As mentioned above, the conversion of SF_6 at $[\text{Pt}(\text{PR}_3)_2]$ ($\text{R} = \text{Cy}, i\text{Pr}$) is promoted by phosphine to give $\text{trans}[\text{Pt}(\text{F})(\text{SF}_3)(\text{PR}_3)_2]$ and F_2PR_3 .^[13d,15] Yet, reactions of $[\text{Pt}(\text{IMes})_2]$ (**1**) with SF_6 in the presence of IMes at higher temperatures in toluene- d_8 were again not selective, but after 8 h small amounts of the sulfanyl complex $\text{trans}[\text{Pt}(\text{F})(\text{SF}_3)(\text{IMes})_2]$ (**2**) were detected. A better conversion was found upon irradiation of SF_6 with **1** and IMes for 40 min at 311 nm in toluene- d_8 to result in the generation of $\text{trans}[\text{Pt}(\text{F})(\text{SF}_3)(\text{IMes})_2]$ (**2**), $\text{trans}[\text{Pt}(\text{F})(\text{SOF})(\text{IMes})_2]$ (**3**), $\text{trans}[\text{Pt}(\text{F})_2(\text{IMes})_2]$ (**6**) and $\text{trans}[\text{Pt}(\text{F})(\text{IMes}')(\text{IMes})]$ (**5**) in a ratio of 1:0.9:0.4:1.7 (Scheme 2), as well as small amounts of the fluorinated carbene IMes- F_2 (IMes- $\text{F}_2 = \text{C}_2\text{H}_2(\text{NMe}_2)_2\text{CF}_2$). An addi-



Scheme 1. S–F oxidative addition reactions at $[\text{Pt}(\text{IMes})_2]$ (**1**).

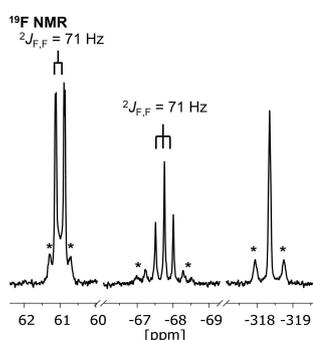


Figure 1. Parts of the ^{19}F NMR spectrum of $\text{trans}[\text{Pt}(\text{F})(\text{SF}_3)(\text{IMes})_2]$ (**2**); *Pt satellites.

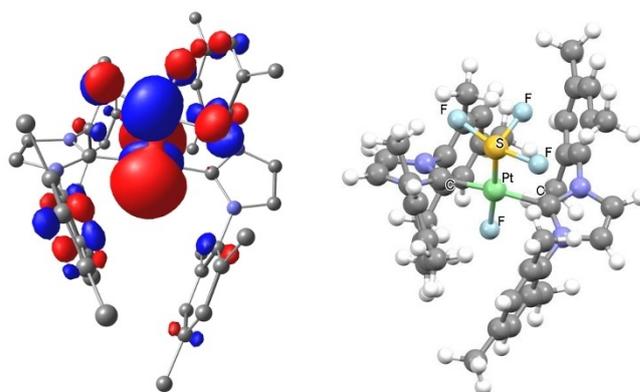
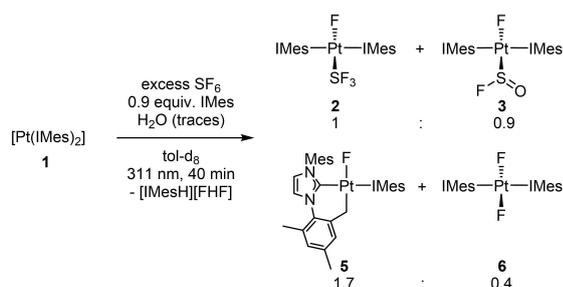


Figure 2. HOMO (left) of the DFT-optimized structure (right) of $\text{trans}[\text{Pt}(\text{F})(\text{SF}_3)(\text{IMes})_2]$ (**2**); BP86/def2-SVP with RECP for the Pt center, Grimme-D3 dispersion correction with Becke-Johnson damping.



Scheme 2. Reaction of SF_6 at $[\text{Pt}(\text{IMes})_2]$ (**1**) in the presence of IMes yielding sulfur fluoride groups and fluoro ligands at $\text{Pt}(\text{II})$.

tional platinum compound was observed in traces, which could not be characterized further (see Supporting Information). The added IMes acts mainly as base, giving upon reaction with HF $[\text{IMesH}][\text{FHF}]$, which precipitated out of the reaction solution.^[22] When ^{13}C labeled $^{13}\text{IMes}$ was added instead of IMes , $^{13}\text{IMesH}][\text{FHF}]$ was furnished.

Mechanistically, it was suggested in the literature that the activation of SF_6 can be initiated by a SET from the metal to SF_6 to give the $\text{SF}_6^{\cdot-}$ radical anion.^[13g,14a-c,23] This process might be facilitated by irradiation; and photocatalytic conversions of SF_6 were described.^[23b,c,f,g,i] Fast decomposition of $\text{SF}_6^{\cdot-}$ can then lead either to $\text{SF}_5^{\cdot-}$ and F^{\cdot} or SF_5^{\cdot} and F^- depending on the electron excess energy.^[24] Other assumptions include a nucleophilic attack of strong nucleophiles at SF_6 .^[25]

The SF_6 activation at $[\text{Pt}(\text{IMes})_2]$ (**1**) to yield $\text{trans}-[\text{Pt}(\text{F})(\text{SF}_3)(\text{IMes})_2]$ (**2**) is accompanied by the generation of $\text{trans}-[\text{Pt}(\text{F})_2(\text{IMes})_2]$ (**6**). Thus, **1** seems to act as additional acceptor of fluorine atoms. Note also that a photolytic SF_6 activation at 311 nm with IMes has been reported to produce $\text{IMes}-\text{F}_2$ and the thiourea derivative $\text{IMes}=\text{S}$, but a much longer reaction time was required to achieve a considerable conversion.^[23b] However, such a background reaction seems not to occur as no thiourea derivative was detected, even when ^{13}C labeled $^{13}\text{IMes}$ was added to the reaction mixture instead of IMes . Only traces of $^{13}\text{IMes}-\text{F}_2$ were then found in solution.

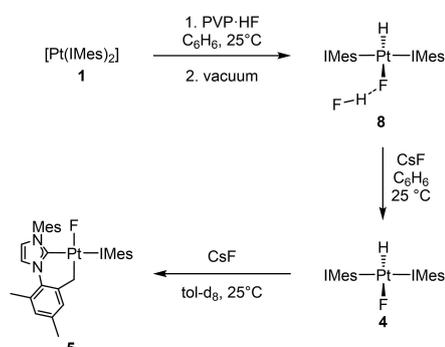
A partial reaction of **2** with adventitious water would yield $\text{trans}-[\text{Pt}(\text{F})(\text{SOF})(\text{IMes})_2]$ (**3**) and HF . In turn, the presence of HF can lead by reaction with **1** to the formation of $\text{trans}-[\text{Pt}(\text{H})(\text{F})(\text{IMes})_2]$ (**4**), which then can produce $\text{trans}-[\text{Pt}(\text{F})(\text{IMes})(\text{IMes})]$ (**5**) by cyclometalation (see below). An independent experiment showed that $\text{trans}-[\text{Pt}(\text{F})_2(\text{IMes})_2]$ (**6**) is not prone for a cyclometalation process. In another independent reaction it was shown, that the irradiation of $\text{trans}-[\text{Pt}(\text{H})(\text{F})(\text{IMes})_2]$ (**4**) in the presence of free IMes at 311 nm leads to the formation of $[\text{IMesH}][\text{FHF}]$, which also explains the absence of **4** in the product mixture.

To verify the identity of the complexes **3–6** reaction routes for their independent preparations were developed. Thus, complex $\text{trans}-[\text{Pt}(\text{F})(\text{SOF})(\text{IMes})_2]$ (**3**) was synthesized by treatment of $[\text{Pt}(\text{IMes})_2]$ (**1**) with SOF_2 (Scheme 1). An oxidative addition of SOF_2 at a metal center under preservation of the $\text{S}(\text{=O})\text{F}$ function is to the best of our knowledge unprecedented. Reactions of SOF_2 at fine powdered $\text{Ag}(0)$, $\text{Cu}(0)$ and $\text{Zn}(0)$ as

well as laser-ablated $\text{U}(0)$ atoms led to fluorination and sulfurization of the metals, and in the latter case $\text{U}(\text{O})(\text{S})(\text{F})_2$ was furnished.^[26] Treatment of the metal oxides Ag_2O , CuO and ZnO with SOF_2 resulted in the fluorination of the metal and release of SO_2 .^[26a] The sulfur-bound fluorine atom in **3** reveals a resonance in the ^{19}F NMR spectrum at low field at $\delta = -7.3$ ppm as a singlet with Pt satellites ($^2J_{\text{F,Pt}} = 140$ Hz). Comparable data were described for other metal bound $\text{S}(\text{=O})\text{F}$ groups.^[13d,15] The resonance for the fluoro ligand appears at $\delta = -289.2$ ppm as a singlet ($^1J_{\text{F,Pt}} = 826$ Hz) at a typical range for metal bound fluorides.^[1e,i,2h,3b,d,5a,6b,8d,11b,13d,15,20,27] The $^{13}\text{C}\{^1\text{H}\}$ NMR resonance for the ^{13}C labeled carbene complex $\text{trans}-[\text{Pt}(\text{F})(\text{SOF})(^{13}\text{IMes})_2]$ (**3'**) appears at $\delta = 174.2$ ppm as a doublet with a coupling of $^2J_{\text{C,F}} = 5$ Hz to the fluoro ligand ($^1J_{\text{C,Pt}} = 1199$ Hz). The distorted tetrahedral geometry at the sulfur atom was confirmed by DFT calculations of **3** (BP86/def2-SVP). The frontier orbital analysis revealed that the electron pair resembles the HOMO (see Supporting Information).

In order to investigate the possible generation of the cyclometalated complex $\text{trans}-[\text{Pt}(\text{F})(\text{IMes})(\text{IMes})]$ (**5**) from the hydrido fluoro compound $\text{trans}-[\text{Pt}(\text{H})(\text{F})(\text{IMes})_2]$ (**4**), the reactivity of $[\text{Pt}(\text{IMes})_2]$ (**1**) towards a HF source was studied to access **4**. Treatment of **1** with an excess of the hydrogen fluoride source PVP-HF (PVP-HF = Poly-[4-vinylpyridiniumpoly (hydrogenfluoride)]) led to oxidative addition of HF followed by the formation of a bifluoro ligand in the coordination sphere of Pt (Scheme 3). Removal of the solvent from the product solution under reduced pressure afforded the bifluoro complex $\text{trans}-[\text{Pt}(\text{H})(\text{FHF})(\text{IMes})_2]$ (**8**). Transition metal complexes with hydrido bifluoro ligands are described in the literature and often result from reaction of the corresponding hydrido compounds with an excess HF or coordination of HF at fluoro ligands.^[1j,3b,5d,6b,9a,27] A subsequent conversion of **8** into the fluoro complex $\text{trans}-[\text{Pt}(\text{H})(\text{F})(\text{IMes})_2]$ (**4**) was successful by removal of HF from the ligand sphere by addition of CsF to a solution of **8** in C_6H_6 (Scheme 3).

Compound $\text{trans}-[\text{Pt}(\text{H})(\text{FHF})(\text{IMes})_2]$ (**8**) exhibits in the ^1H NMR spectrum a resonance for the proton in the FHF entity at $\delta = 12.91$ ppm as a broad doublet with a coupling constant of 372 Hz to the distal fluorine. The hydrido ligand gives a doublet at $\delta = 27.37$ ppm with Pt satellites ($^2J_{\text{H,Pt}} = 130$, $^1J_{\text{H,Pt}} = 1623$ Hz) and $^1\text{H}\{^{19}\text{F}\}$ NMR measurements confirm the coupling to the



Scheme 3. Generation and reactivity of the hydrido fluoro $\text{Pt}(\text{II})$ complex **4**.

proximal fluoride in the *trans* position. In the ^{19}F NMR spectrum two resonances of equal intensity were found. One signal appears at $\delta = -179.1$ ppm as a broadened doublet with a coupling constant of $^1J_{\text{F,H}} = 373$ Hz to the FHF proton and is assigned to the distal fluorine. ^[1j,3b,6b,14d,28] The signal for the proximal fluorine atom was detected at $\delta = -269.5$ ppm as a broadened multiplet with a coupling to Pt of $^1J_{\text{F,Pt}} = 714$ Hz. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the ^{13}C labeled isotopologue **8'** revealed a broadened ^{13}C signal at 180.6 ppm with Pt satellites ($^1J_{\text{C,Pt}} = 1070$ Hz). The ATR IR spectrum of **8** shows vibrational bands at $\tilde{\nu} = 420$ and 445 cm^{-1} , which can be assigned to Pt-F vibrations. ^[3b,d,5b,13d,15,29] Strong absorption bands for the stretching vibration of Pt-H appear at $\tilde{\nu} = 2314\text{ cm}^{-1}$, which has been confirmed by DFT calculations. Additionally, two broad vibrational bands for the FHF unit are present in the IR spectrum of **8** at $\tilde{\nu} = 2453\text{ cm}^{-1}$ and $\tilde{\nu} = 1906\text{ cm}^{-1}$. For comparison, the vibrational modes for the FHF unit in *trans*-[Pt(H)(FHF)(P*i*Pr₃)₂] appear at $\tilde{\nu} = 2273$ and 1903 cm^{-1} and for [Pt(PhC=CFPh)(FHF)-{κ²(*P*,*M*)-*i*PrPC₂H₄NMe₂}] at $\tilde{\nu} = 2495$ and 1807 cm^{-1} . ^[3b,6b] The vibration bands for the FHF ligand in **8** appear at higher wavenumbers than the data for bifluorido salts ($\tilde{\nu} = 1284$ – 1372 cm^{-1}), which demonstrates that the hydrogen bonding interaction in the FHF ligand is asymmetric. ^[1j,30]

The hydrido ligand in **4** appears as a doublet with satellites in the ^1H NMR spectrum at $\delta = -24.50$ ppm ($^2J_{\text{H,F}} = 102$ Hz, $^1J_{\text{H,Pt}} = 1361$ Hz). It couples to the fluoride, the signal of which is observed in the ^{19}F NMR spectrum as a doublet with satellites at $\delta = -281.5$ ppm ($^1J_{\text{F,Pt}} = 521$ Hz, PtF). Note that for the bifluorido complex **8** a larger Pt,F coupling was found when compared to the one in **4**. Analogous observations were reported for *trans*-[Pt(H)(X)(PR₃)₂] (X = F, FHF; R = Cy, *i*Pr). ^[6b,15] The IR spectrum of **4** exhibits a vibrational band for Pt-H at $\tilde{\nu} = 2188\text{ cm}^{-1}$ and for Pt-F at $\tilde{\nu} = 413\text{ cm}^{-1}$, which is in accordance with DFT calculations. ^[3b,d,5b,13d,15,29]

As speculated, once the fluorido ligand in **4** is not stabilized by HF coordination, further reactivity was observed, which was monitored by ^{19}F NMR spectroscopy. A decrease of the intensities of the resonances for **4** were observed along with the increasing intensity of a compound for which we propose the cyclometalated structure *trans*-[Pt(F)(IMes')(IMes)] (**5**, Scheme 3). However, the reaction was very slow and not selective, and several unknown hydrido species were detected. The latter remain unidentified (see Supporting Information). Nevertheless, this outcome indicates that such a reaction step might play a role during the SF₆ activation process, although reaction times are not consistent. Cyclometalation was observed before at complexes comprising the {Pt(CH₃)(NHC)} entity to yield the cyclometalated product and methane. ^[31] The signal for the fluorido ligand in **5** is found at $\delta = -292.6$ ppm in the ^{19}F NMR spectrum as a singlet with Pt satellites ($^1J_{\text{F,Pt}} = 414$ Hz). Furthermore, two signals for the metal-bound carbon atoms in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the isotopologue *trans*-[Pt(F)(¹³IMes')(¹³IMes)] (**5'**) confirm the presence of two inequivalent carbene ligands. They appear at $\delta = 184.3$ and 180.2 ppm as doublets of doublets ($^2J_{\text{C,F}} = 4$, $^2J_{\text{C,C}} = 48$ Hz) and both reveal a *cis*-coupling to the fluorido ligand.

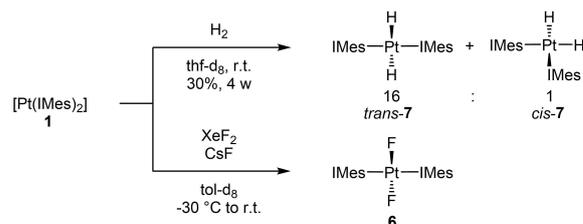
Another effort included the generation of dihydrido complexes, as *cis*-[Pt(H)₂(IMes)₂] (*cis*-**7**) was identified in traces in one of the reactions of SF₆ with [Pt(IMes)₂] (**1**). They might be generated from **1** and small amounts of H₂, the latter being formed in the cyclometallation process of **4** to yield **5**, as mentioned above. Treatment of **1** with H₂ resulted in the formation of the dihydrido complexes *cis/trans*-[Pt(H)₂(IMes)₂] (*cis/trans*-**7**) (Scheme 4). A conversion of approximately 30% was observed after four weeks to give **7** in a *cis/trans* ratio of 1:16. DFT calculations confirm that the *trans* isomer is by 42.1 kJ/mol more stable than the *cis* derivative (see Supporting Information). The IR spectrum for *trans*-[Pt(H)₂(IMes)₂] (*trans*-**7**) shows an absorption band at $\tilde{\nu} = 1652\text{ cm}^{-1}$ for the PtH₂ unit. ^[32]

Finally, the difluorido complex *trans*-[Pt(F)₂(IMes)₂] (**6**) was synthesized independently by treatment of **1** with XeF₂ in the presence of CsF at $-30\text{ }^\circ\text{C}$ (Scheme 4). Since chlorinated solvents like CH₂Cl₂ undergo rapid oxidative addition at **1** to give *trans*-[Pt(Cl)(CH₂Cl)(IMes)₂] ^[33] (**9**, see Supporting Information), toluene was used as solvent, although this can result in the fluorination of toluene by XeF₂ to give benzyl fluoride and HF, which can be trapped by the CsF. ^[34]

The ^{19}F NMR spectrum of **6** shows a singlet with Pt satellites ($^2J_{\text{F,Pt}} = 883$ Hz) at $\delta = -463.9$ ppm. Consistent to the literature, the mutually *trans*-standing fluorido ligands cause a resonance at higher field. ^[5a] On $^{13}\text{C}\{^1\text{H}\}$ labeling of the carbene carbon atom the corresponding signal in the ^{13}C NMR spectrum of **6'** at $\delta = 174.2$ ppm appears as a triplet with a coupling to the fluorido ligands of $^2J_{\text{C,F}} = 4$ Hz and to Pt of $^1J_{\text{C,Pt}} = 1086$ Hz. The ATR IR spectrum of **6** exhibits a vibrational band for Pt-F at $\tilde{\nu} = 513\text{ cm}^{-1}$.

Conclusion

In conclusion, we demonstrated that the electron-rich zerovalent Pt complex [Pt(IMes)₂] (**1**) is highly reactive and can be readily converted into various fluorinated compounds under mild conditions. At room temperature reactions take place with SF₄ and SOF₂ via oxidative addition, as well as activation of SF₆. The {Pt(IMes)₂} entity enables the stabilization of SF₃ and S(=O)F ligands in the coordination sphere of Pt(II). Such complexes are still rare and their properties have hardly been investigated. An oxidative addition of SOF₂ to a transition metal complex to yield a S(=O)F compound is unprecedented. The independent syntheses of fluorido ligand containing complexes by fluorination with a HF source or XeF₂ gave stable products.



Scheme 4. Oxidative addition reactions at [Pt(IMes)₂] (**1**).

Experimental Section

Details of experimental procedures, characterization of the complexes, NMR and IR data, as well as computational details can be found in the Supporting Information.

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Conflict of Interest

The authors declare no conflict of interest.

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