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Fluorine

Conversion of a Au^I Fluorido Complex into an *N*-Fluoroamido Derivative: N–F versus Au–N Reactivity

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Abstract: The Au^I complex [Au{N(F)SO_2Ph}(SPhos)] (SPhos = dicyclohexyl(2′,6′-dimethoxy[1,1′-biphenyl]-2-yl)phosphane) (**2**) bearing a fluoroamido ligand has been synthesized by reaction of the fluorido complex [Au(F)(SPhos)] (**1**) with NFSI (NFSI = *N*-fluorobenzenesulfonimide). A reaction with CO resulted in an unprecedented insertion into the N–F bond at **2**. With the carbene precursor N_2CH(CO_2Et) N–F bond cleavage gave the Au–F bond insertion product [Au{CHF-(CO_2C_2H_5)}(SPhos)] (**7**). The presence of CN*t*Bu led to Au–N cleavage at **2** and concomitant amide formation to give the cationic complex [Au(CN*t*Bu)(SPhos)][N-(F)SO_2Ph)] (**5**), which reacted further to give F*t*Bu as well as the cyanido complex [Au(CN)(SPhos)] (**6**). These results led to the development of a process for the amination of electrophilic organic substrates by transfer of the fluoroamido group NF(SO_2Ph)^−.

Au^I fluorido complexes can serve as unique precursors to install new ligands at the Au^I center and access organic Au derivatives.[1] In catalytic hydrofluorination reactions they presumably serve as resting states.[2] In addition, Au fluorido complexes have been identified as important intermediates in Au^III-catalyzed C–C coupling and fluorination reactions.[3]

Toste and Bergman et al. reported on the synthesis of a series of Au^I amido complexes [Au(NR^1R^2)(IPr)] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene, R^1 = H, *i*Pr, R^2 = *i*Pr, Ph, *t*Bu) by reactions of the chlorido complex [Au(Cl)(IPr)] with the respective lithium salts LiNR^1R^2. They also demonstrated the ability to transfer the amido group onto organic molecules by reaction with benzyl bromide, resulting in benzyldiisopropylamine.[4] Later, Nolan et al. delivered an alternative synthetic method by reaction of [Au(OH)(IPr)] with the respective amines.[5] In a recent contribution, Finze et al. showed the ability of Cu^I and Ag^I compounds to transfer a N(CF_3)_2 group to benzylic bromides or α-bromoesters at 80 °C. The complexes were

synthesized from the salts M[N(CF_3)_2] (M = Rb, Cs) and were remarkably stable.[6] The compounds [M(CO)Cl_2(PEt_3)_2(NF_2)] (M = Ir, Rh) have been obtained by oxidative addition of NF_2Cl to M^I Vaska type precursors.[7]

NFSI (NFSI = *N*-fluorobenzenesulfonimide), which is primarily used as an electrophilic fluorination agent,[8] can also fluorinate metal centres as well as ligands in the coordination sphere of transition metals.[9] In general, electrophilic fluorination can be initiated by an initial electron transfer step or alternatively proceed via a concerted reaction pathway, although differences might be subtle and also depend on the substrates.[8c, 10] Alternatively, NFSI can be used to introduce amino groups into organic molecules, forming C–N bonds, usually via radical reactions.[11] Examples include many different functionalizations at *sp^2*-carbon atoms by copper, palladium or iron catalysis[12] as well as transition metal-free aminations.[13] Similar transition metal catalysts can also be used in amination reactions at *sp^3*-carbon atoms with NFSI.[14] In addition, NFSI has been applied in aminofluorination reactions of olefins in processes that are often mediated by transition metal catalysts.[15]

In this contribution we report on a synthetic route to access a Au^I fluoroamido complex from a Au^I fluorido precursor by reaction with NFSI. The fluoroamido ligand N(F)SO_2Ph reveals an extraordinary reactivity: whereas CO inserts into the N–F bond, treatment with organyl halides led to a unique C–N coupling by transfer of the fluoroamido N(F)SO_2Ph group to yield NFSI derivatives.

Treatment of the Au^I fluorido complex [Au(F)(SPhos)] (SPhos = dicyclohexyl(2′,6′-dimethoxy[1,1′-biphenyl]-2-yl)phosphane) (**1**) with NFSI resulted in the formation of FSO_2Ph as well as the fluoroamido compound [Au{N-(F)SO_2Ph}(SPhos)] (**2**) (Scheme 1). The reaction to **2** also proceeds at 213 K, but no intermediates were observed by NMR spectroscopy. To the best of our knowledge, fluoroamido complexes are unprecedented in the literature. Complex **2** exhibits a doublet in the ^31P{^1H} NMR spectrum at 36.9 ppm with a coupling constant to the nitrogen-bound fluorine of ^3*J*_FP = 7 Hz. In the ^19F NMR spectrum a doublet

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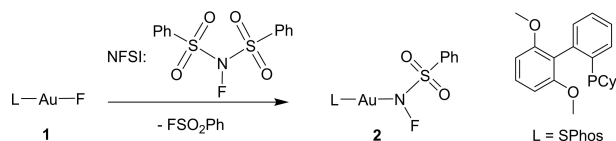
Scheme 1. Synthesis of **2** by reaction of [Au(F)(SPhos)] (**1**) with NFSI.

at −89.6 ppm was observed with the same coupling constant. FSO$_2$Ph was identified by the singlet in the ^{19}F NMR spectrum at 65.5 ppm, which is in agreement with previously reported values in the literature.[16]

Suitable single crystals for X-ray diffraction of [Au{N(F)SO$_2$Ph}(SPhos)] (2) were obtained and the molecular structure is depicted in Figure 1.[17] The Au1–N1 distance is with 2.059(3) Å comparable or longer compared to the separations in [Au(NiPr$_2$)(SIPr)] (SIPr = 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene, 1.967-(4) Å)[4] and [Au(N(H)R)(IPr)] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene, R = aromatic rings, 1.979(15)–2.035(4) Å).[5] Only a compound bearing a 5-chloropyrimidine substituted amido ligand possessed a comparable Au–N distance with 2.042(8) Å.[5] This might indicate that electron-withdrawing amines at the fluoroamido moiety increase this separation. The N1–F1 bond length in 2 of 1.445(3) Å is longer as the one in NFSI (1.422(3) Å),[18] but comparable to separations in other organic molecules bearing N(F)SO$_2$Ph groups (1.417(2)–1.432(3) Å).[19] The N1 atom is located 0.45 Å above the Au1/S1/F1 plane with the sum of angles at N1 being 339°, which suggests an arrangement between trigonal-pyramidal and trigonal-planar.

Mechanistically, the formal insertion of a nitrene moiety into the Au–F bond might occur via a nucleophilic attack of the fluorido ligand in 1 at the sulfur at the NFSI to give FSO$_2$Ph and the amido ligand. Alternatively, we can't exclude an initial dissociation of fluoride allowing for NFSI to bind to the Au center. A subsequent attack of the fluoride results then in the generation of 2. Fluoride dissociation at Au centers has been proposed in catalytic hydrofluorination reactions.[2a] Another possibility might consist of an oxidative addition of NFSI at 1, followed by an attack of a fluoride at the SO$_2$Ph group to generate a nitrene complex [Au(F)(=NSO$_2$Ph)(SPhos)]. The latter will equilibrate with compound 2. Note that oxidation steps with NFSI or Selectfluor have been proposed for a few catalytic cycles involving Au^I/Au^{III} intermediates,[3f,20] but, to the best of our knowledge, no oxidation products with NFSI have been identified. Note also that neither complex [Au(Cl)(SPhos)] nor [Au(SPhos)][B(C$_6$F$_5$)$_4$] do react with NFSI, not even at 363 K. However, treatment of [Au(Cl)(SPhos)] with a
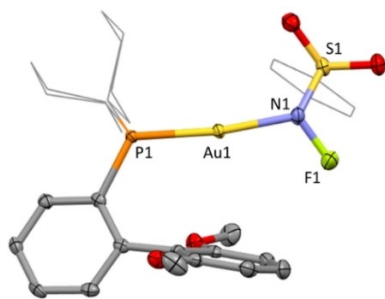
mixture of KF and NFSI led to the formation of compound 2, albeit with a low conversion. It has been reported that FSO$_2$Ph and K[N(F)SO$_2$Ph] are generated by a reaction of KF with NFSI.[21] Generally, it is known that hard nucleophiles attack at the sulfur of NFSI, whereas soft nucleophiles react at the fluorine atom of NFSI.[10d]

Next, the properties of the N–F bond of [Au{N-(F)SO$_2$Ph}(SPhos)] (2) were evaluated. Interestingly, 2 showed no reactivity towards acetylacetone, 1,3-diphenyl-1,3-dicarbonyls or styrene, which react readily with NFSI.[8b,15b] Thus, complex 2 does not show evidence of reactivity as an electrophilic fluorinating agent towards the substrates tested. In addition, treatment of 2 with ClSO$_2$Ph did not lead to the generation of NFSI and the rather stable complex [Au(Cl)(SPhos)]. DFT calculations were performed to evaluate the different behavior of 2 in contrast to NFSI, (see the Supporting Information for the Computational Details). While no significant difference in the charge analyses were found, the NBO orbitals revealed that part of the LUMO of the NFSI is located at the N–F bond. In contrast, the LUMO of 2 is not located at the N–F bond.

However, it is remarkable that a reaction of [Au{N-(F)SO$_2$Ph}(SPhos)] (2) with CO resulted in the insertion of CO into the N–F bond to yield [Au{N(C{O}F)SO$_2$Ph}-(SPhos)] (3) (Scheme 2). When the same reaction was performed with ^{13}CO, the isotopomer [Au{N(^{13}C{O}F)SO$_2$Ph}(SPhos)] (3′) was obtained. The ^{19}F NMR spectrum of 3 showed a singlet at 6.9 ppm, which splits into a doublet for 3′ with a coupling constant of $^1J_{CF}$ = 289 Hz. A doublet for the carbonyl carbon atom of 3′ was observed at 147.5 ppm in the ^{13}C{^{1}H} NMR spectrum. The vibrational band for the carbonyl moiety of 3 was found at 1765 cm^{-1} in the IR spectrum. This band is redshifted to 1722 cm^{-1} for 3′.

To the best of our knowledge, an insertion of CO into a N–F bond is unprecedented. No intermediates could be identified by monitoring the conversions at low temperature by NMR spectroscopy. Addition of 2,2,6,6-tetramethyl-piperidin-1-yl)oxyl (TEMPO) did not impede the reaction, suggesting no radical intermediates. We speculate that a dissociation of fluoride might initiate the reaction. Note that NFSI itself does not react with CO. A few examples of a formal insertion of CO into an N–Cl bond have been described. Those include an intramolecular rearrangement[22] as well as a palladium catalyzed reaction[23] to afford R$_2$NC-

Figure 1. Molecular structure of [Au{N(F)SO$_2$Ph}(SPhos)] (2) in the solid state. Cyclohexyl as well as phenyl groups are drawn as a wireframe and thermal ellipsoids are depicted at 50% probability. Hydrogen atoms have been omitted.
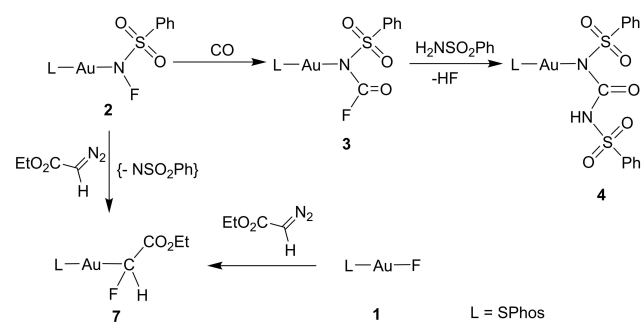
Scheme 2. N–F bond cleavage reactions at [Au{N(F)SO$_2$Ph}(SPhos)] (2).

(O)Cl from R_2NCl (R = alkyl substituents). It was also shown that treatment of $(CF_3SO_2)(C_4F_9SO_2)NCl$ with CO results in the formation of $(CF_3SO_2)(C_4F_9SO_2)NC(O)Cl$ at room temperature.[24]

Since acyl fluorides tend to be very reactive, compound **3** was treated with NH_2SO_2Ph to obtain a derivative. Indeed, the formation of $[Au\{N(C\{O\}N\{H\}SO_2Ph)SO_2Ph\}(SPhos)]$ (**4**) as well as the elimination of HF were observed (Scheme 2). The isotopologue $[Au\{N(^{13}C\{O\}N\{H\}SO_2Ph)\text{-}SO_2Ph\}(SPhos)]$ (**4′**) was obtained when **3′** was treated with the amine. The absorption band for the carbonyl moiety was found at 1672 cm^{-1} in the IR spectrum of **4**, and appeared redshifted to 1631 cm^{-1} for **4′**. Suitable crystals for XRD studies were obtained for **4** (see Supporting Information). The molecular structure confirms the identity of **3** further.

Subsequently, the reactivity of $N_2CH(CO_2Et)$—as carbene source—towards $[Au\{N(F)SO_2Ph\}(SPhos)]$ (**2**) was studied (Scheme 2), as carbene insertion into the N–F bond in NFSI has been reported.[25] In contrast to the reactivity with CO, the formation of the complex $[Au\{CHF\text{-}(CO_2C_2H_5)\}(SPhos)]$ (**7**, 35 % NMR yield) was observed, among other unidentified products. Compound **7** is formally the product of a carbene insertion into a Au–F bond. This is consistent with an independent conversion of $[Au(F)\text{-}(SPhos)]$ (**1**) with $N_2CH(CO_2Et)$, which also yielded complex **7** (also in addition to unidentified compounds according to the ^1H and $^{13}C\{^1H\}$ NMR spectra, 78 % NMR yield). The fate of the nitrene NSO_2Ph in the conversion of **2** into **7** is unclear. We were not able to detect any follow-up products, for instance of insertion reactions with the solvent. NSO_2Ph has been reported as a reasonable leaving group for several other conversions involving NFSI, but the fate of it could also not be determined.[26] Complex **7** exhibits a doublet in the $^{31}P\{^1H\}$ NMR spectrum with a coupling constant of $^3J_{FP} = 16$ Hz at 44.4 ppm. The ^{19}F NMR spectrum shows a doublet of doublets at −212.5 ppm ($^2J_{FH} = 52$ Hz). The resonance for the CHF proton appears as a doublet of doublets at 4.87 ppm in the ^1H NMR spectrum due to couplings of $^3J_{HP} = 9$ Hz and $^2J_{FH} = 52$ Hz to the phosphorous and fluorine atoms.

Since isocyanides are isoelectronical to CO, $[Au\{N(F)SO_2Ph\}(SPhos)]$ (**2**) was treated with CNtBu. The cleavage of the Au–N bond was observed and the cationic species $[Au(SPhos)(CNtBu)]^+$ was generated (Scheme 3) in addition to the fluoroamide anion $[N(F)SO_2Ph]^−$. The identity of the cation was further confirmed by the independent generation of $[Au(SPhos)(CNtBu)][B(C_6F_5)_4]$ by treatment of $[Au(SPhos)][B(C_6F_5)_4]$ with CNtBu. The absorption band for the isocyanide ligand bound in $[Au\text{-}(SPhos)(CNtBu)][N(F)SO_2Ph]$ (**5**) appeared blueshifted to 2238 cm^{-1} in the IR spectrum when compared to the one of CNtBu (2130 cm^{-1}). This is in good agreement with data for $[Au(SIPr)(CNtBu)]^+$, which shows a band at 2244 cm^{-1}.[27] In the ^{19}F NMR spectrum of **5**, a singlet at −140.7 ppm was observed, which is assigned to the anion $[N(F)SO_2Ph]^−$. As mentioned above, Dond et al. reported on an equilibrium of KF with NFSI, forming FSO_2Ph as well as $K[N(F)SO_2Ph]$, and characterized the species $HN(F)SO_2Ph$ after acidic workup.[21] We were able to produce the anion
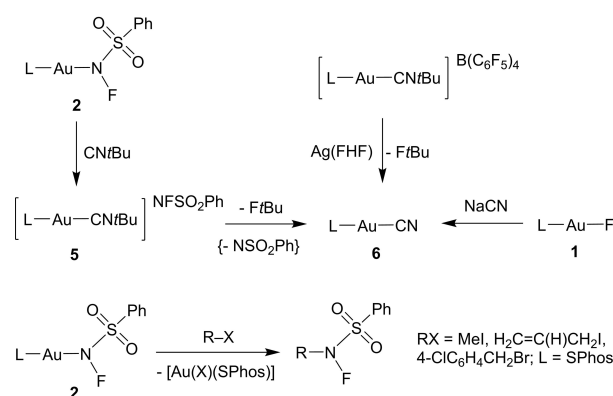
Scheme 3. Au–N bond cleavage reactions at $[Au\{N(F)SO_2Ph\}(SPhos)]$ (**2**).

$[N(F)SO_2Ph]^−$ independently by treatment of $[Me_4N]F$ with NFSI in CD_2Cl_2. The presence of the anion in **5** was then confirmed by comparison of the ^{19}F NMR data.

The compound $[Au(SPhos)(CNtBu)][N(F)SO_2Ph]$ (**5**) is not stable in solution and the elimination of FtBu was observed over the course of hours to days. The latter is revealed by a decet in the ^{19}F NMR spectrum at −130.3 ppm ($^3J_{FH} = 21$ Hz) as well as the corresponding doublet in the ^1H NMR spectrum at 1.35 ppm.[28] In addition to FtBu, the cyanido complex $[Au(CN)(SPhos)]$ (**6**) was obtained, which was also synthesized independently by treatment of $[Au(F)\text{-}(SPhos)]$ (**1**) with NaCN (Scheme 3) A doublet at 157.4 ppm in the $^{13}C\{^1H\}$ NMR spectrum with a coupling constant of $^2J_{CP} = 120$ Hz was observed for the metal-bound carbon atom, whereas the IR spectrum showed an absorption band at 2142 cm^{-1}. This is in good agreement with data for the complex $[Au(CN)(PEt_3)]$.[29] The structure was further confirmed by single crystal XRD studies (see Supporting Information). The generation of FtBu and **6** requires formally the formation of the nitrene NSO_2Ph, but again the fate of it remained elusive.

A reaction of $[Au(SPhos)(CNtBu)][N(F)SO_2Ph]$ (**5**) with an excess of $AgBF_4$ stabilized the cationic species by generating $[Au(SPhos)(CNtBu)][BF_4]$, and then no formation of FtBu was observed. Interestingly, in an alternative approach a successful fluorination is possible by treatment of $[Au(SPhos)(CNtBu)][B(C_6F_5)_4]$ with an excess of Ag-[FHF] to give FtBu and **6**. To the best of our knowledge, no report for the formation of FtBu from CNtBu exists so far. The fluorination reaction found for **5** was not observed for $[Au(SPhos)(CNCy)][N(F)SO_2Ph]$ (see Supporting Information). Note further that we were not able to prepare $[Au(SPhos)(CNAd)][N(F)SO_2Ph]$ (Ad = adamantyl), but $[Au(SPhos)(CNAd)][B(C_6F_5)_4]$ reacted with Ag[FHF] to yield AdF, albeit in small amounts, whereas $[Au(SPhos)\text{-}(CNCy)][B(C_6F_5)_4]$ did not react. Thus, the carbocation character of the organyl groups at the isocyanide ligands might be of a certain importance for the observed reactivities.

Based on the intriguing generation of $[N(F)SO_2Ph]^−$, a transfer of the fluoroamido ligand from $[Au\{N(F)SO_2Ph\}\text{-}(SPhos)]$ (**2**) to organic substrates was studied. As indicated

above, NFSI usually acts in transition-metal mediated reactions as $N(SO_2Ph)_2$ source, but not as $NF(SO_2Ph)$ source.[11] Indeed, treatment of **2** with methyl iodide at room temperature resulted in the formation of [Au(I)(SPhos)] as well as $H_3CN(F)SO_2Ph$ (Scheme 3), which was identified by comparison with the literature.[30] The amido group transfer was also readily possible with allyl iodide, yielding $H_2C=C(H)CH_2N(F)SO_2Ph$. The latter exhibits a triplet in the ^{19}F NMR spectrum at -49.5 ppm with a coupling constant of $^3J_{HF}=40$ Hz due to the coupling to the CH_2 group. The amide transfer was also possible on using a bromobenzyl organyl as it was demonstrated by treatment of **2** with 4-chlorobenzylbromide yielding (4-chlorobenzyl)$N(F)SO_2Ph$ and [Au(Br)(SPhos)].[31] No reaction was observed with methyl fluoride or benzyl fluoride. Note that F_2 gas is commonly necessary to fluorinate secondary amines, for example for the synthesis of NFSI or $H_3CN(F)SO_2Ph$.[30]

In conclusion, a unique fluoroamido gold complex [Au-{N(F)SO_2Ph}(SPhos)] (**2**) was synthesized, which revealed divergent reactivity patterns. With CO a cleavage of the N–F bond occurred to yield the N–F insertion products. On the other hand, treatment of **2** with a carbene source resulted in a formal carbene insertion into the Au–F bond. In contrast, a reaction of **2** with CN*t*Bu delivered [Au-(SPhos)(CN*t*Bu)][N(F)SO_2Ph] (**5**) providing a fluoroamido moiety, which induced a fluorination reaction of the isocyanide ligand. Ultimately, the transfer of the fluoroamido moiety from **2** to organic molecules was achieved to provide a route to *N*-fluoroamine derivatives.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

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