

Synthesis of gold(I)-trifluoromethyl complexes and their role in generating spectroscopic evidence for a gold(I)-difluorocarbene species

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Dedicated to the memory of Professor Edwin D. Stevens.

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Abstract: Readily-prepared and bench-stable $[\text{Au}(\text{CF}_3)(\text{NHC})]$ compounds were synthesized using new methodologies, starting from $[\text{Au}(\text{OH})(\text{NHC})]$, $[\text{Au}(\text{Cl})(\text{NHC})]$ or $[\text{Au}(\text{L})(\text{NHC})]\text{HF}_2$ precursors (NHC = N-heterocyclic carbene). The mechanism of formation of these species was investigated. Consequently, a new and straightforward strategy for the mild and selective cleavage of a single carbon-fluorine bond from $[\text{Au}(\text{CF}_3)(\text{NHC})]$ complexes was attempted and found to be reversible in the presence of an additional nucleophilic fluoride source. This straightforward technique has led to the unprecedented spectroscopic observation of a gold(I)-NHC difluorocarbene species.

Introduction

Organic compounds containing a CF_3 moiety are of increasing importance to the pharmaceutical and agrochemical industries.^[1] The incorporation of fluorinated functional groups can enhance many properties such as the solubility, bioavailability and metabolic stability of a drug target.^[2] Radiolabeled fluorinated

(^{18}F) organic compounds are also essential tools for positron emission tomography (PET).^[3]

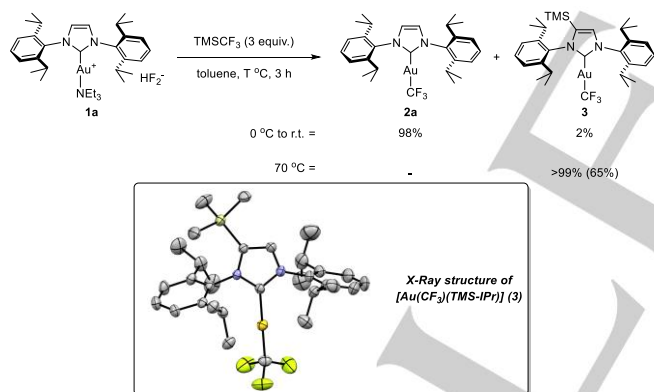
A trifluoromethyl group can be introduced in several ways and a large number of these methods make use of transition metals.^[4] The use of *in situ* generated or well-defined CF_3 -based complexes of transition metals, such as Pd, Cu, or Ag, in the selective trifluoromethylation of aromatic substrates is well-documented.^{[24]-[25]} Recent independent reports, by Vicente^[26] and Toste^[3d] on the synthesis and reactivity of Au(I)- and Au(III)-NHC trifluoromethyl complexes (NHC = N-heterocyclic carbene), have shown that these species can indeed set up new C- CF_3 bonds on complex aliphatic and aromatic organic compounds. Toste and co-workers also demonstrated that the net C- CF_3 bond construction is achieved through a sequence of i) fluoride abstraction to form a gold(III)-difluorocarbene intermediate, ii) followed by migratory insertion and iii) C-F reductive elimination.^[3d] This feature was successfully applied to the synthesis of ^{18}F -radiolabeled CF_3 -containing compounds, thus demonstrating the usefulness of this protocol for preparing potential tracers for use in PET. Gold difluorocarbenes are quite

elusive, postulated as intermediates in several mechanistic investigations, yet never observed spectroscopically, to the best of our knowledge. The potential application of such species, especially the $\text{CF}_3 \rightarrow \text{CF}_2 \rightarrow \text{CF}_3$ sequence highlighted in the work of Toste, is of great interest to us. The possibility of applying a similar process to access Au(I)-difluorocarbenes through fluoride abstraction of the parent Au(I)-trifluoromethyl complexes is therefore very tempting.

Aligned with our recent efforts to develop silver-free methodologies to access well-defined metal-NHC complexes, we herein report new methods to access the $[\text{Au}(\text{CF}_3)(\text{NHC})]$ complexes. These species were shown to generate a stable and spectroscopically detectable Au(I)-difluorocarbene complex, *via* selective and reversible C-F bond cleavage.

Results and Discussion

The synthesis of $[\text{Au}(\text{CF}_3)(\text{NHC})]$ complexes was initially undertaken as we strived to develop silver-free methodologies^{[26]-[27]} to access these compounds in an efficient, straightforward and practical manner. The bench-stable bifluoride compounds^[28] were used as a starting point. The reaction of $[\text{Au}(\text{IPr})(\text{NEt}_3)]\text{HF}_2$ (**1a**) with excess Me_3SiCF_3 (TMSCF₃; Ruppert-Prakash reagent) at 0 °C delivered $[\text{Au}(\text{CF}_3)(\text{IPr})]$ (**2a**) in quantitative yield (Scheme 1). ¹⁹F NMR spectroscopic analysis showed that trace amounts of another CF₃-containing compound (**3**) ($\delta_{\text{F}} = -28.27$ ppm) were present in addition to **2a** ($\delta_{\text{F}} = -28.46$ ppm) in a 2:98 ratio, respectively.

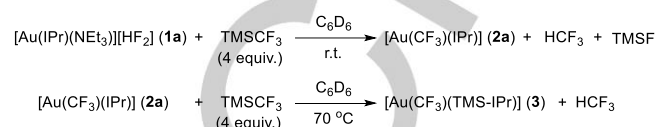


Scheme 1. Reaction of **1a** with TMSCF₃ at different temperatures and the molecular structure of **3** as determined by single-crystal X-ray diffraction analysis. Thermal displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms and all solvent molecules are omitted for clarity.^[29]

When the reaction was carried out at 70 °C, **3** was obtained as the sole product in 65% isolated yield. After full characterization and X-ray analysis, **3** was identified as $[\text{Au}(\text{CF}_3)(\text{TMS-IPr})]$, presenting a trimethylsilyl (TMS) group incorporated into the NHC ligand (Scheme 1). While a copper analogue is known,^[19] to the best of our knowledge, this is the first example for gold-NHC complexes.

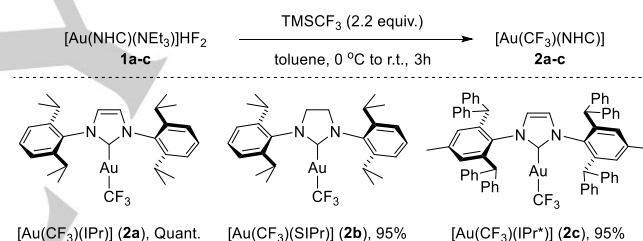
Several NMR-scale reactions were conducted to better understand the reaction mechanism (Scheme 2). In the presence of excess TMSCF₃ at room temperature, bifluoride complex **1a** reacts rapidly to deliver **2a**, presumably *via* the initial formation of

$[\text{Au}(\text{F})(\text{IPr})]$ (**4**). Vicente *et al.*^[26] have shown that **4**, prepared *in situ* using AgF, readily reacts with TMSCF₃ to form **2a**. HCF₃ and TMSF were observed in the ¹⁹F NMR spectrum of the reaction, offering additional support for the proposed mechanism. Heating **2a** with excess TMSCF₃ gives complete conversion to **3** after 3 h, indicating that **2a** could be a key intermediate in the pathway that installs a TMS group on the NHC. Though, it should be noted that alternative pathways involving a direct route from **1a** to **3** cannot be entirely ruled out.



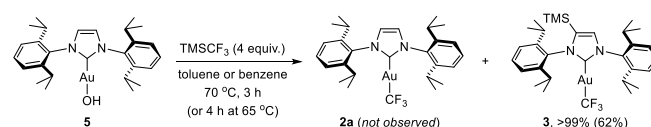
Scheme 2. Mechanistic probing of the bifluoride route

This methodology was extended to obtain SIPr (**2b**) and IPr* (**2c**) analogues in high yield and selectivity (Scheme 3). The incorporation of TMS into the backbone of **2c** was not possible under these conditions as either starting materials or decomposition (after prolonged reaction time) were obtained. It should be noted that complexes **2a** and **2b** have already been reported by Vicente and co-workers.^[26]



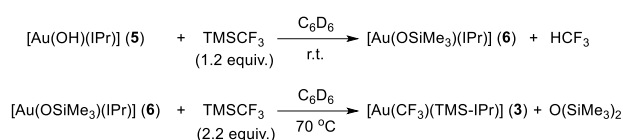
Scheme 3. Synthesis of $[\text{Au}(\text{CF}_3)(\text{NHC})]$ complexes (**2a-c**) starting from **1a-c**.^[29]

In an effort to employ simpler starting materials, commercially-available $[\text{Au}(\text{OH})(\text{IPr})]$ ^[30] (**5**) was used instead of $[\text{Au}(\text{IPr})(\text{NEt}_3)]\text{HF}_2$. However, under the room temperature procedure, no **2a** or **3** was formed, but a new product (**6**) was observed. Under harsher conditions (70 °C; 4 equiv. TMSCF₃), $[\text{Au}(\text{CF}_3)(\text{TMS-IPr})]$ (**3**) was selectively obtained in 62% isolated yield (Scheme 4). Complex **6** was later identified as $[\text{Au}(\text{OTMS})(\text{IPr})]$ ^[31] (Scheme 5).



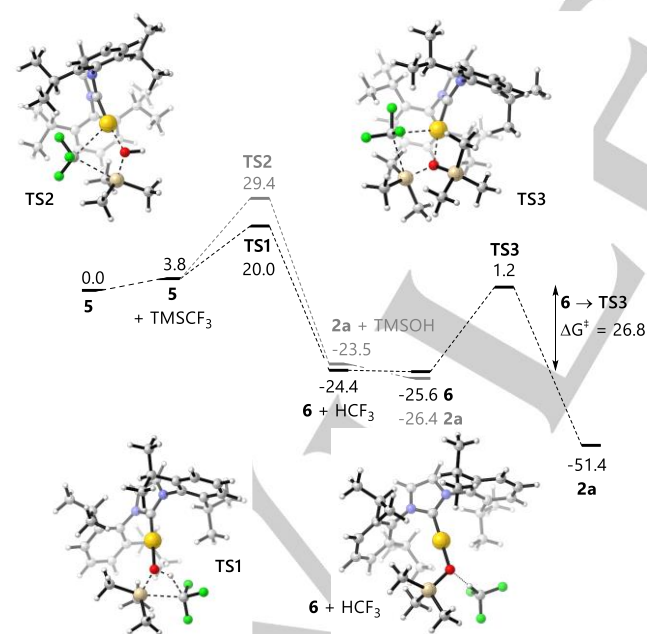
Scheme 4. Synthesis of **3** *via* the reaction of **5** with TMSCF₃.

By reacting **5** with 1.2 equiv. of TMSCF₃ at r.t., complex **6** and HCF₃ are observed by NMR spectroscopy. The formation of intermediate **6** halts any further reactivity at low temperatures, mainly due to the lower nucleophilicity of the OTMS group.



Scheme 5. Mechanistic probing of the hydroxide route.

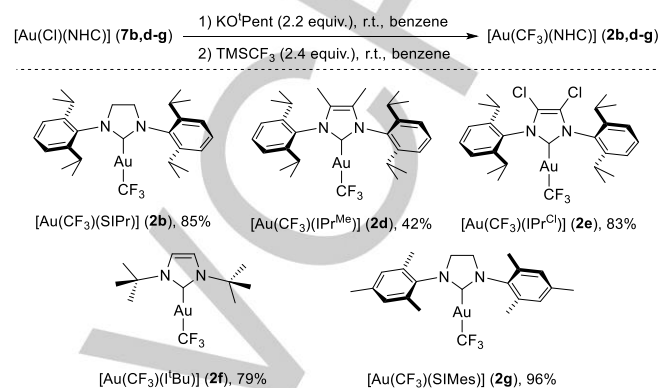
Previous mechanistic studies on the reactivity of $[\text{Au}(\text{OH})(\text{NHC})]$ with organosilanes (aryl-Si(OR)₃) point to a concerted transmetalation pathway being in play, which could afford $[\text{Au}(\text{CF}_3)(\text{IPr})]$ (**2a**) and TMSOH as intermediates.^[32] The latter two would then react with each other *via* an acid-base reaction, due to the low pK_a of TMSOH (*ca.* 12), affording **6** and HCF₃. However, upon mixing **2a** with TMSOH in C₆D₆, no reaction occurred. Furthermore, DFT calculations were carried out at the BP86-D3(BJ)/6-311+G(2d,2p)+LANL2TZ(f)//BP86-D3(BJ)/6-31G(d)+LANL2TZ(f) level of theory in benzene solution (SMD model) (Scheme 6). These showed that the reaction from **5** to directly form **6** and HCF₃ proceeds *via* a four-membered transition state (TS1), rather than *via* initial formation of **2a** and TMSOH. A higher energy barrier (ΔG^\ddagger) is observed for TS2 than for TS1 (20 kcal.mol⁻¹ vs 29.4 kcal.mol⁻¹, respectively), making TS1 the more favorable transition state. The further reaction of **6** with TMSCF₃ only occurs at temperatures above 65 °C, and is highly selective for the formation of $[\text{Au}(\text{CF}_3)(\text{TMS-IPr})]$, similarly to the bifluoride pathway (Scheme 5). Consistent with this, the barrier for the reaction of $[\text{Au}(\text{OTMS})(\text{IPr})]$ with TMSCF₃ (TS3, 26.8 kcal.mol⁻¹) is higher than that for TS1, necessitating higher reaction temperatures (Scheme 6).



Scheme 6. DFT calculations of the reaction between TMSCF₃ and $[\text{Au}(\text{OH})(\text{IPr})]$.

$[\text{Au}(\text{Cl})(\text{NHC})]$ ^[33] complexes are readily-prepared and often commercially available; the direct synthesis of $[\text{Au}(\text{CF}_3)(\text{NHC})]$ complexes from these precursors was successfully achieved *in situ* formation of *tert*-pentoxide intermediates

$[\text{Au}(\text{O}^i\text{Pent})(\text{NHC})]$ (Scheme 7), which then undergo reaction with TMSCF₃, in a similar approach to the work of Vicic on $[\text{Cu}(\text{CF}_3)(\text{NHC})]$ ^[19] and of Komiya on $[\text{Au}(\text{CF}_3)(\text{PR}_3)]$.^[34] Highest conversions were reached using benzene as solvent, and optimization of the stoichiometry led to the successful synthesis of five $[\text{Au}(\text{CF}_3)(\text{NHC})]$ complexes in moderate to excellent yields (Scheme 7).



Scheme 7. Synthesis of $[\text{Au}(\text{CF}_3)(\text{NHC})]$ complexes starting from their gold(I)-Cl analogues (**7**).^[29]

Novel CF₃-complex $[\text{Au}(\text{CF}_3)(\text{TMS-IPr})]$ (**3**) proved to be an interesting case. The most intriguing discovery came when a sample of **3** was analyzed by high resolution mass spectroscopy (using APCI-ASAP). The expected $[\text{M} - \text{CF}_3]^+$ fragment was not observed, but instead the $[\text{M} - \text{F}]^+$ fragment was prominent (Figure 1). This suggested to us the potential formation of a difluorocarbene gold species. This result hinted at the possibility of accessing difluorocarbene gold complex, $[\text{Au}(\text{CF}_2)(\text{TMS-IPr})\text{BF}_4]$ (**8**), *via* α -F abstraction (Scheme 8). Though unsuccessful in isolating a gold(I)-CF₂ complex, the work of Menjón and co-workers was instrumental in pointing out the possibility of activating C-F bonds in Au-CF₃ complexes using Lewis acids.^[35]

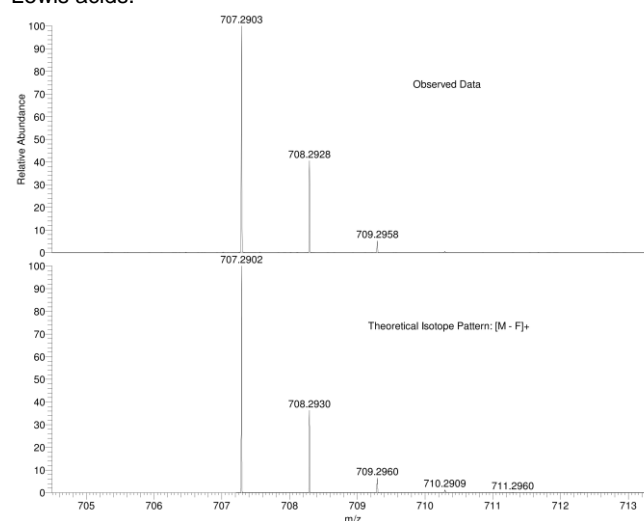
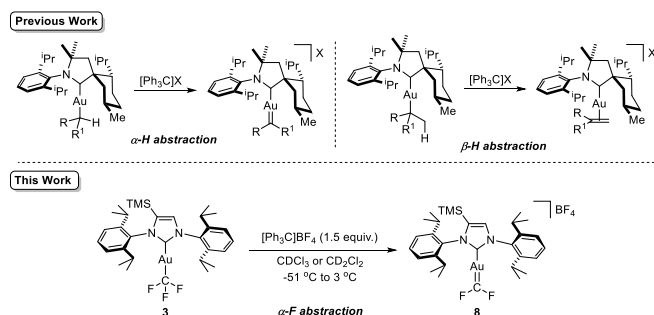


Figure 1. The HRMS spectra of complex **3**.

Previous work by Bertrand^[36] and co-workers on α - and β -hydride abstraction from CAAC-stabilized alkylgold(I) complexes, affording cationic gold(I) complexes, served as further inspiration (Scheme 8). Complex **3** reacted with a carbenium salt, $[\text{Ph}_3\text{C}]\text{BF}_4$, in an NMR tube under inert conditions, and was analyzed at temperatures between $-51\text{ }^\circ\text{C}$ and $3\text{ }^\circ\text{C}$.



Scheme 8. The work on α -F abstraction inspired by reports on α -H and β -H abstraction.

At temperatures below $-16\text{ }^\circ\text{C}$, the reaction was sluggish, although the presence of trityl fluoride (Ph_3CF) was a clear indication that fluoride abstraction had occurred (Figure 2). As the temperature was increased to $3\text{ }^\circ\text{C}$, the CF_3 signal for **3** disappeared; ^{19}F NMR spectroscopic analysis between 0 and 300 ppm confirmed the presence of a signal at 247 ppm, which was attributed to the CF_2 moiety of difluorocarbene gold complex **8** (Figure 2). To the best of our knowledge, this is the first observation by ^{19}F NMR spectroscopy of a gold difluorocarbene complex; although the shift is higher than expected, compared to previously observed transition metal difluorocarbene complexes^[37] (80–128 ppm). Contrary to previous observations,^[38] complex **8** appears to be sufficiently stable to allow observation by NMR spectroscopy.

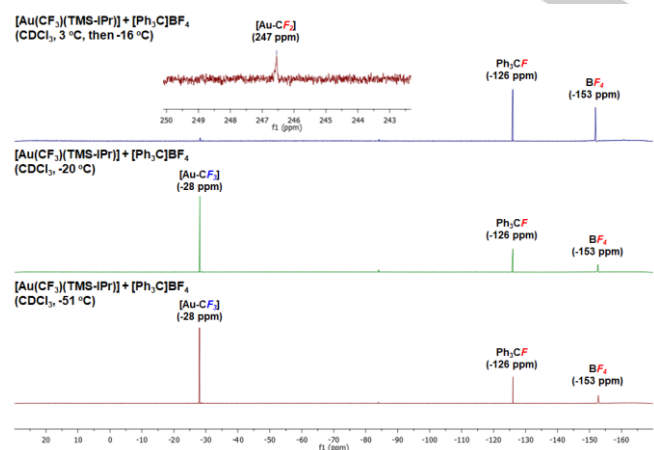


Figure 2. $^{19}\text{F}\{^1\text{H}\}$ NMR spectra of the VT experiment reacting **3** (1 equiv.) with $[\text{Ph}_3\text{C}]\text{BF}_4$ (1.5 equiv.) in CDCl_3 . In the top spectrum, at complete consumption of the gold- CF_3 complex, the integral ratio of $\text{Ph}_3\text{CF}/\text{BF}_4$ is 1:6, which correlates well with the 1.5 equivalents of $[\text{Ph}_3\text{C}]\text{BF}_4$ added at the start.

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were also successfully recorded (at $-16\text{ }^\circ\text{C}$), however, subsequent DEPTQ NMR spectroscopic analysis indicated the formation of $[\text{Au}(\text{CO})(\text{TMS-IPr})]^+$ ($\delta_{\text{C}} =$

182.9 ppm).^{[35],[39]} In addition, DFT calculations successfully predicted the NHC carbene signal (NCN) of the CO complex to be at 181 ppm (see Table S1).

Two signals on the initial $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum ($\delta_{\text{C}} = 210$ and 177 ppm) stood out; one of which should be attributed to the NCN carbene of complex **8**. By plotting the DFT vs the experimental values of the ^{13}C NMR shift of C^2 carbenes (NHC ligands) for the complexes reported herein (Figure 3), we determined that the peak at 177 ppm fits best the assignment of the TMS-IPr carbene signal. Gold-CAAC complexes before and after α -hydride abstraction from the work of Bertrand^[36] and co-workers were also added to the plot to further test the correlation of our calculations (see Table S1 and Figure S13). Despite our effort, the ^{13}C signal of the CF_2 moiety was not observed; this is not surprising since this type of weak signal is expected to be lost within the noise background or buried within the other signals, especially considering that the recorded spectrum herein is not of a pure sample (as it is a crude reaction mixture NMR), and that decomposition is noticeable after prolonged ^{13}C NMR analysis. The peak at 210 ppm does fit the right shift for the CF_2 's ^{13}C NMR signal; however, the lack of any coupling and the relatively high intensity of the peak do not support its assignment to the CF_2 moiety at this time.

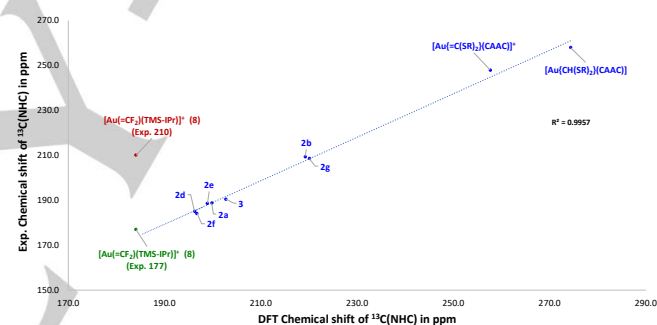


Figure 3. DFT vs experimental values plot of the ^{13}C NMR shift of C^2 carbenes (NCN) in the reported gold complexes (blue points). DFT NMR calculations for this part were performed with the ADF software at the PBE0 level of theory. Scalar relativistic effects were included *via* the zeroth-order regular approximation ZORA. All electronTZ2P basis set was used on all atoms. The chemical shielding calculations were performed by the tools included in package.

Multiple unsuccessful attempts were made to obtain single crystals suitable for X-ray diffraction analysis. However, one of the possible decomposition by-products, $[\text{Au}(\text{TMS-IPr})_2]\text{BF}_4$, was observed and characterized by single-crystal X-ray diffraction (Figure 4).

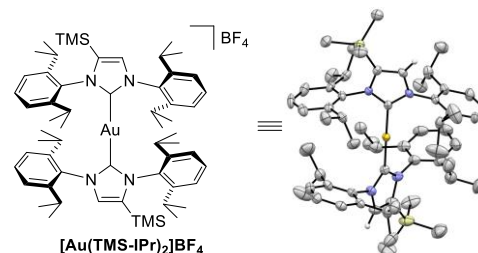


Figure 4. Molecular structure of $[\text{Au}(\text{TMS-IPr})_2]\text{BF}_4$ as determined by single-crystal X-ray diffraction analysis. Thermal displacement ellipsoids are shown at

the 50% probability level. Hydrogen atoms and all solvent molecules are omitted for clarity.²⁹

The fluoride abstraction reaction was attempted using **2a** and **2c**, and in both cases disappearance of the CF₃ signal and appearance of Ph₃CF were noted; however, **2a** only led to rapid decomposition and gold nanoparticle formation while the reaction with **2c** showed evidence of the formation of a complex that is tentatively assigned as [Au(CO)(IPr*)]⁺ ($\delta_{\text{C}} = 182.5$ ppm).^[39] Unfortunately, neither reaction allowed the analysis of tractable products.

The immediate treatment of the *in situ* formed complex **8** with a nucleophilic fluoride source (i.e. KF) resulted in the regeneration of the initial [Au(CF₃)(TMS-IPr)] complex, albeit now with a freshly replaced F atom (Figure S11). We envisage that this could lead in the future to the selective and rapid [¹⁸F] radiolabeling of CF₃ groups using ¹⁸F⁻ sources. Our future endeavors will focus on this, as well as other types of atom substitution useful to the chemistry community.

Conclusion

In summary, three strategies to access [Au(CF₃)(NHC)] (**2**) compounds were developed starting from [Au(OH)(NHC)] (**5**), [Au(Cl)(NHC)] (**7**) or [Au(NHC)(L)]HF₂ (**1**). The two reaction mechanisms, starting from **1** and **5**, were subsequently investigated. The first TMS-incorporated gold-NHC trifluoromethyl complex (**3**) was also isolated and fully characterized. Using the latter complex, a “one fluoride” abstraction was attempted, to afford the CF₂-adduct *via* α -F abstraction. In that context, the first spectroscopic evidence for a difluorocarbene gold-NHC complex was observed. This reaction was also found to be reversible in the presence of an additional nucleophilic fluoride source. This technique is novel and straightforward, allowing very short handling time and readily available reagents. The [Au(CF₃)(NHC)] compounds are bench-stable (with high tolerance to air and moisture) and can be stored for long periods (>1 year).

We anticipate that this strategy will allow us and others, in the near future, to replace a ¹⁹F atom with the more valuable ¹⁸F isotope, thus affording the “hot” [¹⁸F]-labelled CF₃ analogue. Work is ongoing in our groups to further probe the mechanism of formation of the CF₂-adduct as well as its potential use in synthesis. We are excited to see if future work by our groups or others will further support and ultimately better understand this strategy.

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The authors declare no conflict of interest.

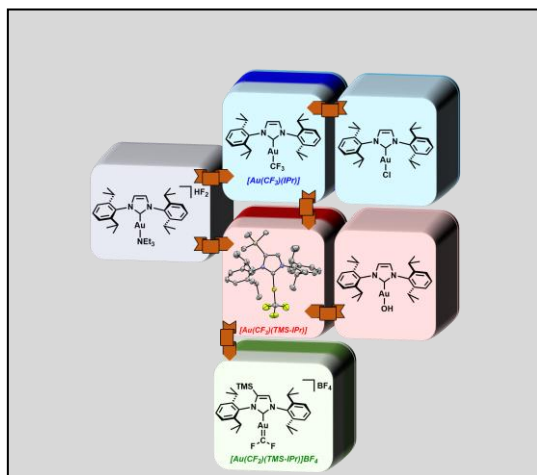
Keywords: difluorocarbene • trifluoromethyl • N-heterocyclic carbene • gold(I) • fluoride abstraction

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Entry for the Table of Contents



A new method to access $[\text{Au}(\text{CF}_3)(\text{NHC})]$ complexes has been developed, leading to the discovery of a novel trimethylsilyl incorporated gold-NHC trifluoromethyl complex. This in turn led to the development of a new and straightforward strategy for the “one fluoride” abstraction affording, for the first time, spectroscopic evidence of the corresponding gold(I)-NHC difluorocarbene analogue.