ARTICLE

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

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Readily-prepared and bench-stable [Au(CF_3)(NHC)] compounds were synthesised using new methodologies, starting from [Au(OH)(NHC)], [Au(Cl)(NHC)] or [Au(L)(NHC)]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 [Au(CF_3)(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] Radiolabelled 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.[4-23] 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 $CF_3 \rightarrow CF_2 \rightarrow CF_3$ 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 [Au(CF_3)(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 [Au(CF_3)(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 [Au(IPr)(NEt_3)]HF_2 (**1a**) with excess Me_3SiCF_3 ($TMSCF_3$; Ruppert-Prakash reagent) at 0 °C delivered [Au(CF_3)(IPr)] (**2a**) in quantitative yield (Scheme 1). ^{19}F NMR spectroscopic analysis showed that trace amounts of another

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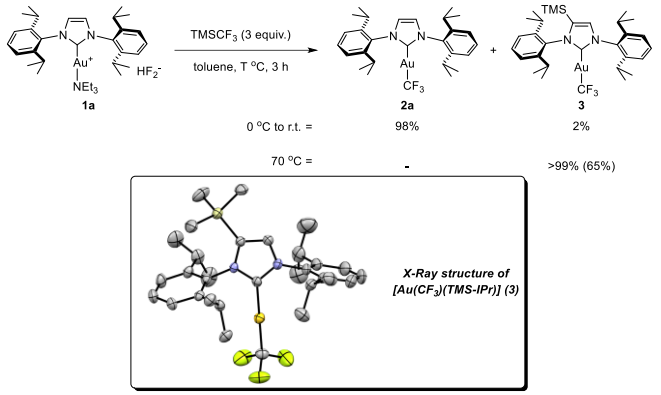
† Electronic Supplementary Information (ESI) available: NMR spectra of new compounds and complexes prepared during this study. Mechanistic investigations and DFT calculations described during this study. See DOI: 10.1039/x0xx00000x

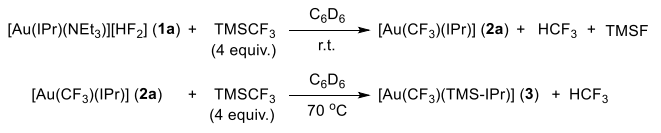
CF_3-containing compound (**3**) (δ_F = -28.27 ppm) were present in addition to **2a** (δ_F = -28.46 ppm) in a 2:98 ratio, respectively.



Scheme 1. Reaction of **1a** with $TMSCF_3$ 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]

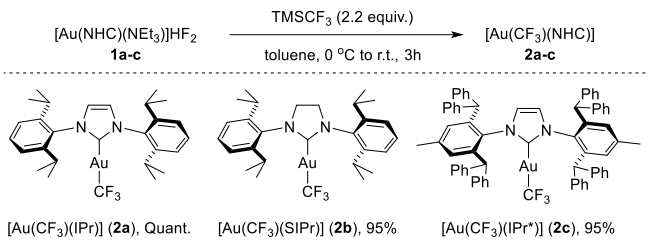
When the reaction was carried out at 70 °C, **3** was obtained as the sole product in 65% isolated yield. After full characterisation and X-ray analysis, **3** was identified as [Au(CF_3)(TMS-IPr)], presenting a trimethylsilyl (TMS) group incorporated into the NHC ligand (Scheme 1). While a copper analogue 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 $TMSCF_3$ at room temperature, bifluoride complex **1a** reacts rapidly to deliver **2a**, presumably *via* the initial formation of [Au(F)(IPr)] (**4**). Vicente *et al.*[26] have shown that **4**, prepared *in situ* using AgF, readily reacts with $TMSCF_3$ to form **2a**. HCF_3 and TMSF were observed in the ^{19}F NMR spectrum of the reaction, offering additional support for the proposed mechanism. Heating **2a** with excess $TMSCF_3$ gives complete conversion to **3** after 3 h, ruling out the involvement of gold (bi)fluorides in the pathway that installs a TMS group on the NHC.



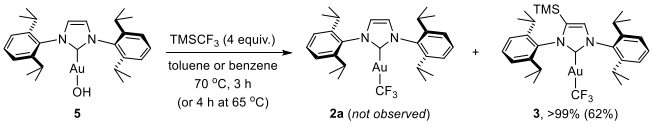
Scheme 2. Mechanistic probing of the bifluoride route.

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]



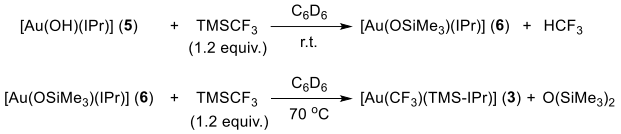
Scheme 3. Synthesis of [Au(CF_3)(NHC)] complexes (**2a-c**) starting from **1a-c**.[29]

In an effort to employ simpler starting materials, commercially-available [Au(OH)(IPr)][30] (**5**) was used instead of [Au(IPr)(NEt_3)]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. $TMSCF_3$), [Au(CF_3)(TMS-IPr)] (**3**) was selectively obtained in 62% isolated yield (Scheme 4). Complex **6** was later identified as [Au(OTMS)(IPr)][31] (Scheme 5).



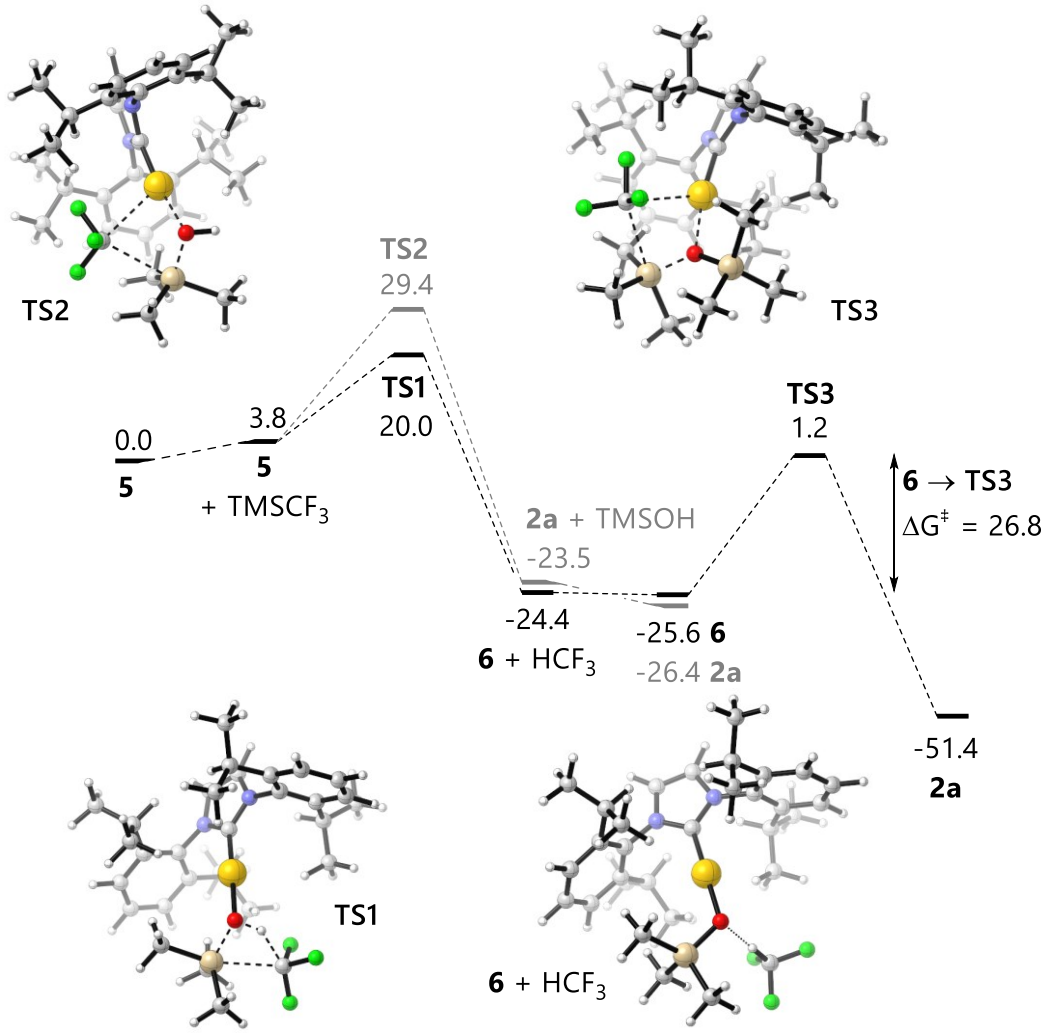
Scheme 4. Synthesis of **3** *via* the reaction of **5** with $TMSCF_3$.

By reacting **5** with 1.2 equiv. of $TMSCF_3$ at r.t., complex **6** and HCF_3 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.



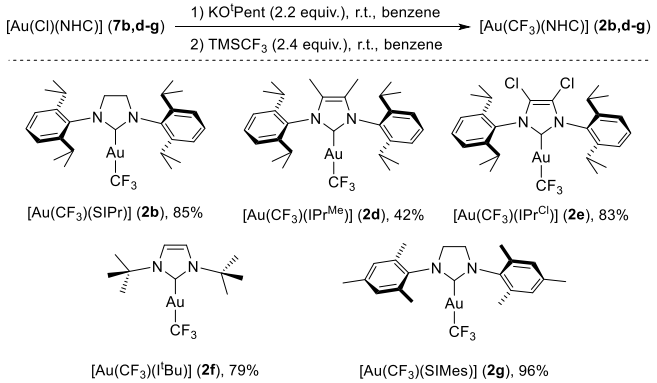
Scheme 5. Mechanistic probing of the hydroxide route.

Previous mechanistic studies on the reactivity of [Au(OH)(NHC)] with organosilanes (aryl-Si$(OR)_3$) point to a concerted transmetallation pathway being in play, which could afford [Au(CF_3)(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 HCF_3. However, upon mixing **2a** with TMSOH in C_6D_6, no reaction occurred. Furthermore, DFT calculations (Scheme 6) showed that the reaction from **5** to directly form **6** and HCF_3 proceeds *via* a four-membered transition state (TS1), rather than *via* initial formation of **2a** and TMOSH. A higher energy barrier ($\Delta G^{\ddagger}$) is observed for TS2 than for TS1 (20 kcal.mol^{-1} *vs* 29.4 kcal.mol^{-1}, respectively), making TS1 the more favourable transition state. The further reaction of **6** with $TMSCF_3$ only occurs at temperatures above 65 °C, and is highly selective for the formation of [Au(CF_3)(TMS-IPr)], similarly to the bifluoride pathway (Scheme 5). Consistent with this, the barrier for the reaction of [Au(OTMS)(IPr)] with $TMSCF_3$ (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 $TMSCF_3$ and [Au(OH)(IPr)].

[Au(Cl)(NHC)][33] complexes are readily-prepared and often commercially available; the direct synthesis of [Au(CF_3)(NHC)] complexes from these precursors was successfully achieved *via in situ* formation of *tert*-pentoxide intermediates [Au(O^{t}Pent)(NHC)] (**Fout! Verwijzingsbron niet gevonden.**), which then undergo reaction with $TMSCF_3$, in a similar approach to the work of Vicic on [Cu(CF_3)(NHC)][19] and of Komiya on [Au(CF_3)(PR_3)].[34]



Scheme 7. Synthesis of [Au(CF_3)(NHC)] complexes starting from their gold(I)-Cl analogues (**7**).[29]

Highest conversions were reached using benzene as solvent, and optimisation of the stoichiometry led to the successful synthesis of five [Au(CF_3)(NHC)] complexes in moderate to excellent yields (**Fout! Verwijzingsbron niet gevonden.**).

Novel CF_3-complex [Au(CF_3)(TMS-IPr)] (**3**) proved to be an interesting case. The most intriguing discovery came when a

sample of **3** was analysed by high resolution mass spectroscopy (using APCI-ASAP). The expected $[M\text{-}CF_3]^+$ fragment was not observed, but instead the $[M\text{-}F]^+$ 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, $[Au(CF_2)(TMS\text{-}IPr)]BF_4$ (**8**), *via* α-F abstraction (Scheme 8). Though unsuccessful in isolating a gold(I)-CF_2 complex, the work of Menjón and co-workers was instrumental in pointing out the possibility of activating C-F bonds in Au-CF_3 complexes using Lewis acids.[35]

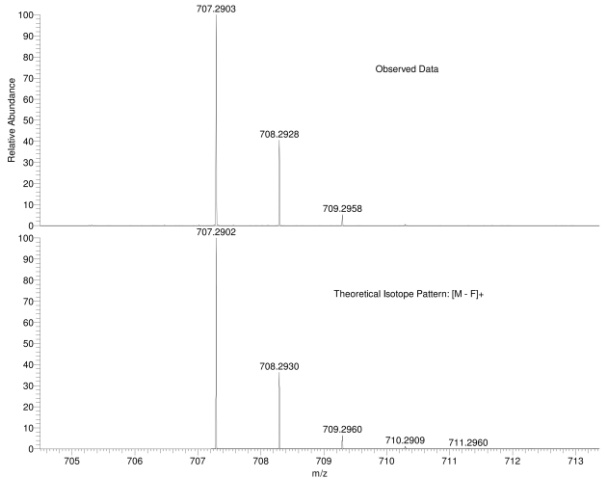
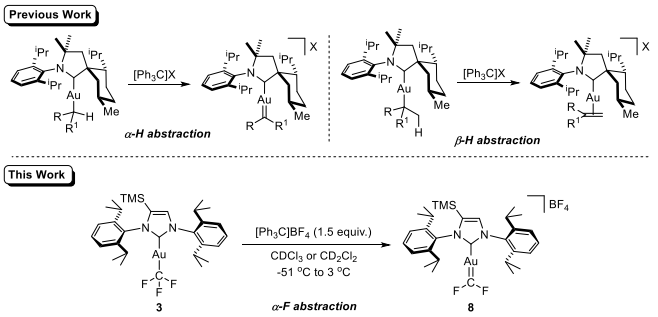


Figure 1. The HRMS spectra of complex **3**.

Previous work by Bertrand[36] and co-workers on α- and β-hydride abstraction from CAAC-stabilised alkylgold(I) complexes, affording cationic gold(I) complexes, served as further inspiration (Scheme 8). Complex **3** reacted with a carbenium salt, $[Ph_3C]BF_4$, in an NMR tube under inert conditions, and was analysed at temperatures between -51 °C and 3 °C.



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

At temperatures below -16 °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 °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.

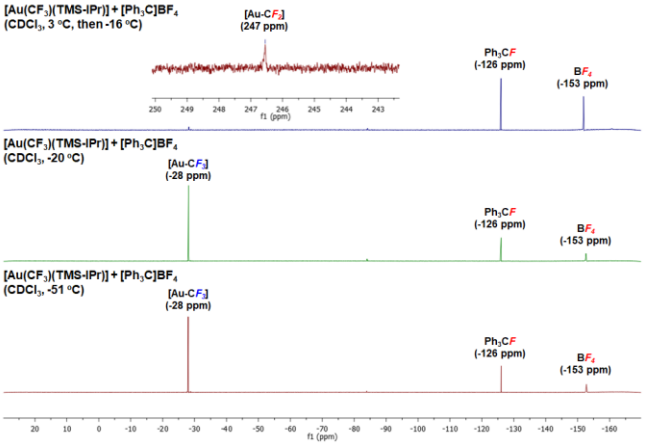


Figure 2. $^{19}F\{^1H\}$ NMR spectra of the VT experiment reacting **3** (1 equiv.) with $[Ph_3C]BF_4$ (1.5 equiv.) in $CDCl_3$.

^1H and $^{13}C\{^1H\}$ NMR spectra were also successfully recorded (at -16 °C), however, subsequent DEPTQ NMR spectroscopic analysis indicated the formation of $[Au(CO)(TMS\text{-}IPr)]^+$ (δ_C = 182.9 ppm).[35,39] In addition, DFT calculations successfully predicted the NHC carbene signal (N*C*N) of the CO complex to be at 181 ppm (see Table S1).

Two signals on the initial $^{13}C\{^1H\}$ NMR spectrum (δ_C = 210 and 177 ppm) stood out; one of which should be attributed to the N*C*N 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 *C*F_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.

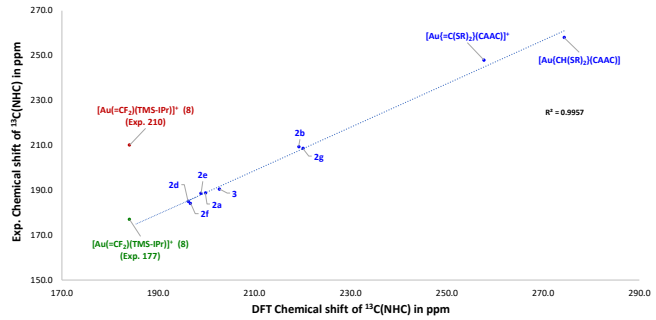


Figure 3. DFT vs experimental values plot of the ^{13}C NMR shift of C^2 carbenes (NCN) in the reported gold complexes (blue points).

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

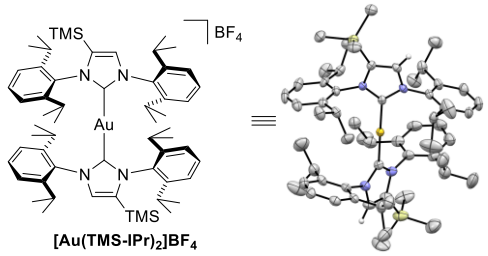


Figure 4. Molecular structure of [Au(TMS-IPr)$_2$]BF$_4$ as determined by single-crystal X-ray diffraction analysis. Thermal displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms and all solvent molecules are omitted for clarity.[29]

The fluoride abstraction reaction was attempted using **2a** and **2c**, and in both cases disappearance of the CF_3 signal and appearance of Ph_3CF 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*)]$^+$ (δ_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(CF_3)(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 [^{18}F] radiolabelling of CF_3 groups using $^{18}F^-$ sources. Our future endeavours will focus on this, as well as other types of atom substitution useful to the chemistry community.

Conclusions

In summary, three strategies to access [Au(CF_3)(NHC)] (**2**) compounds were developed starting from [Au(OH)(NHC)] (**5**), [Au(Cl)(NHC)] (**7**) or [Au(NHC)(L)]HF_2 (**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 characterised. Using the latter complex, a "one fluoride" abstraction was attempted, to afford the CF_2-adduct *via* α-*F* abstraction. In this manner, the first spectroscopic evidence for a difluorocarbene gold-NHC complex was obtained. 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(CF_3)(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 ^{19}F atom with the more valuable ^{18}F isotope, thus affording the "hot" [^{18}F]-labelled CF_3 analogue. Nonetheless, we would like to state at this point that all evidence presented here for the formation and observation of the putative difluorocarbene complex remains largely contingent on indirect evidence. Work is ongoing in our groups to further probe the mechanism of formation of the CF_2-adduct as well as its potential use in synthesis.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the Ghent University (IoF), the Special Research Fund (BOF) starting (SPN, CSJC) and advanced (SPN, KVH) grants and Research Foundation Flanders (FWO) (fellowship to SVB and grant to CSJC and KVH) for funding.

Notes and references

1 a) S. Purser, P. R. Moore, S. Swallow and V. Gouverneur, *Chem. Soc. Rev.*, 2008, **37**, 320; b) W.R., Jr., Dolbier, *The Trifluoromethyl Group*, in *Guide to Fluorine NMR for Organic Chemists*, ed. W. R. Dolbier, John Wiley & Sons, Inc., New Jersey, 2nd edition, 2016, pp. 187-235.

2 a) K. Müller, C. Faeh and F. Diederich, *Science,* 2007, **317**, 1881; b) J. Wang, M. Sánchez-Roselló, J. L. Aceña, C. del Pozo, A. E. Sorochinsky, S. Fustero, V. A. Soloshonok and H. Liu, *Chem. Rev.,* 2014, **114**, 2432; c) Y. Zhou, J. Wang, Z. Gu, S. Wang, W. Zhu, J. L. Aceña, V. A. Soloshonok, K. Izawa and H. Liu, *Chem. Rev.,* 2016, **116**, 422.

3 a) S. Preshlock, M. Tredwell and V. Gouverneur, *Chem. Rev.,* 2016, **116**, 719. Selected examples of setting up ^{18}F-labelled CF_3 moieties: b) M. Huiban, M. Tredwell, S. Mizuta, Z. Wan, X. Zhang, T. L. Collier, V. Gouverneur and J. Passchier, *Nature Chem.,* 2013, **5**, 941; c) C. W. Kee, O. Tack, F. Guibbal, T. C. Wilson, P. G. Isenegger, M. Imiołek, S Verhoog, M. Tilby, G. Boscutti, S. Ashworth, J Chupin, R. Kashani, A. W. J. Poh, J. K. Sosabowski, S. Macholl, C. Plisson, B. Cornelissen, M. C. Willis, J. Passchier, B. G. Davis and V. Gouverneur, *J. Am. Chem. Soc.,* 2020, **142**, 1180; d) M. D. Levin, T. Q. Chen, M. E. Neubig, C. M. Hong, C. A. Theulier, I. J. Kobylianskii, M. Janabi, J. P. O'Neil and F. Dean Toste, *Science,* 2017, **356**, 1272.

4 O. A. Tomashenko and V. V. Grushin, *Chem. Rev.,* 2011, **111**, 4475.

5 K. A. McReynolds, R. S. Lewis, L. K. G. Ackerman, G. G. Dubinina, W. W. Brennessel and D. A. Vicic, *J. Fluor. Chem.,* 2010, **131**, 1108.

6 M. Chen and S. L. Buchwald, *Angew. Chem. Int. Ed.,* 2013, **52**, 11628.
7 B. R. Langlois and N. Roques, *J. Fluor. Chem.,* 2007, **128**, 1318.
8 T. Schareina, X.-F. Wu, A. Zapf, A. Cotté, M. Gotta and A. Beller, *Top Catal.,* 2012, **55**, 426.
9 J. G. MacNeil and D. J. Burton, *J. Fluor. Chem.,* 1991, **55**, 225.
10 P. Novák, A. Lishchynskyi and V. V. Grushin, *Angew. Chem. Int. Ed.,* 2012, **51**, 7767.
11 A. Lishchynskyi, M. A. Novikov, E. Martin, E. C. Escudero-Adán, P. Novák and V. V. Grushin, *J. Org. Chem.,* 2013, **78**, 11126.
12 X. Wang, Y. Xu, F. Mo, G. Ji, D. Qiu, J. Feng, Y. Ye, S. Zhang, Y. Zhang and J. Wang, *J. Am. Chem. Soc.,* 2013, **135**, 10330.
13 M. Oishi, H. Kondo and H. Amii, *Chem. Commun.,* 2009, 1909.
14 H. Morimoto, T. Tsubogo, N. D. Litvinas and J. F. Hartwig, *Angew. Chem. Int. Ed.,* 2011, **50**, 3793.
15 N. D. Litvinas, P. S. Fier and J. F. Hartwig, *Angew. Chem. Int. Ed.,* 2012, **51**, 536.
16 T. D. Senecal, A. T. Parsons and S. L. Buchwald, *J. Org. Chem.,* 2011, **76**, 1174.
17 D. A. Nagib and D. W. C. MacMillan, *Nature,* 2011, **480**, 224.
18 D. Yu, J. Shao, R. He and M. Li, *Chin. Chem. Lett.,* 2015, **26**, 564.
19 G. G. Dubinina, H. Furutachi and D. A. Vicic, *J. Am. Chem. Soc.,* 2008, **130**, 8600.
20 G. G. Dubinina, J. Ogikubo and D. A. Vicic, *Organometallics,* 2008, **27**, 6233.
21 I. Kieltsch, G. G. Dubinina, C. Hamacher, A. Kaiser, J. Torres-Nieto, J. M. Hutchison, A. Klein, Y. Budnikova and D. A. Vicic, *Organometallics,* 2010, **29**, 1451.
22 P. T. Kaplan, J. A. Lloyd, M. T. Chin and D. A. Vicic, *Beilstein J. Org. Chem.,* 2017, **13**, 2297.
23 E. Jin Cho, T. D. Senecal, T. Kinzel, Y. Zhang, D. A. Watson and S. L. Buchwald, *Science,* 2010, **328**, 1679.
24 R. J. Lundgren and M. Stradiotto, *Angew. Chem., Int. Ed.*, 2010, **49**, 9322.
25 X. Li, X. Shi, X. Li and D. Shi, *Beilstein J. Org. Chem.*, 2019, **15**, 2213.
26 M. Blaya, D. Bautista, J. Gil-Rubio and J. Vicente, *Organometallics,* 2014, **33**, 6358.
27 J. Gil-Rubio and J. Vicente, *Dalton Trans.,* 2015, **44**, 19432.
28 a) F. Nahra, S. R. Patrick, D. Bello, M. Brill, A. Obled, D. B. Cordes, A. M. Z. Slawin, D. O'Hagan and S. P. Nolan, *ChemCatChem,* 2015, **7**, 240; b) A. Gómez-Herrera, F. Nahra, M. Brill, S. P. Nolan and C. S. J. Cazin, *ChemCatChem,* 2016, **8**, 3381.
29 Crystallographic data for **2c**, **2d**, **2e**, **3** and $[Au(TMS\text{-}IPr)_2]BF_4$ can be downloaded from the Cambridge Structural Database (CSD) *via* the following link: https://www.ccdc.cam.ac.uk/structures/ (CCDC 2023143-2023147)
30 F. Nahra, S. R. Patrick, A. Collado and S. P. Nolan, *Polyhedron,* 2014, **84**, 59.
31 T. J. Robilotto, J. Bacsa, T. G. Gray and J. P. Sadighi, *Angew. Chem. Int. Ed.,* 2012, **51**, 12077.
32 L. Falivene, D. J. Nelson, S. Dupuy, S. P. Nolan, A. Poater and L. Cavallo, *ChemistryOpen,* 2016, **5**, 60.
33 a) A. Collado, A. Gomez-Suarez, A. R. Martin, A. M. Z. Slawin and S. P. Nolan, *Chem. Commun.,* 2013, **49**, 5541; b) N. V. Tzouras, F. Nahra, L. Falivene, L. Cavallo, M. Saab, K. Van Hecke, A. Collado, C. J. Collett, A. D. Smith, C. S. J. Cazin and S. P. Nolan, *Chem. Eur. J.,* 2020, **26**, 4515.
34 Y. Usui, J. Noma, M. Hirano and S. Komiya, *Inorg. Chim. Acta,* 2000, **309**, 151.
35 a) M. Baya, A. Pérez-Bitrián, S. Martínez-Salvador, J. M. Casas, B. Menjón and J. Orduna, *Chem. Eur. J.,* 2017, **23**, 1512; b) S. Martínez-Salvador, L. R. Falvello, A. Martín and B. Menjón, *Chem. Eur. J.,* 2013, **19**, 14540.
36 G. Ung and G. Bertrand, *Angew. Chem. Int. Ed.,* 2013, **52**, 11388.
37 a) G. M. Lee, D. J. Harrison, I. Korobkova and R. T. Baker, *Chem. Commun.,* 2014, **50**, 1128; b) X.-Y. Deng, J.-H. Lin and J.-C. Xiao, *Org. Lett.,* 2016, **18**, 4384; c) R. P. Hughes, R. B. Laritchev, J. Yuan, J. A. Golen, A. N. Rucker and A. L. Rheingold, *J. Am. Chem. Soc.,* 2005, **127**, 15020; d) X.-P. Fu, X.-S. Xue, X.-Y. Zhang, Y.-L. Xiao, S. Zhang, Y.-L. Guo, X. Leng, K. N. Houk and X. Zhang, *Nature Chem.,* 2019, **11**, 948; e) D. Huang, P. R. Koren, K. Folting, E. R. Davidson and K. G. Caulton, *J. Am. Chem. Soc.,* 2000, **122**, 8916.
38 A. G. Tskhovrebov, J. B. Lingnau and A. Fürstner, *Angew. Chem. Int. Ed.,* 2019, **58**, 8834.
39 C. Dash, P. Kroll, M. Yousufuddin and H. V. R. Dias, *Chem. Commun.,* 2011, **47**, 4478.