# Well defined difluorogold(III) complexes supported by N-ligands

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Stable difluorogold(III) complexes can be easily synthesized either via oxidation of N-ligated cationinc Au(I) precursors using XeF_2 or from tricationic Au(III) precursors by displacement of the N-ligands using fluoride from economical KF. X-ray crystallographic studies of the bisimidazole ligated derivative shows the shortest Au-F bond known in a gold complex.

Gold-fluorine chemistry is of increasing interest primarily due to the potential for using gold catalysis to generate new fluorine containing molecules.[1] However, well defined organometallic or coordination compounds of Au(III) fluorides are exceedingly rare, with only a total of 10 having been crystallographically characterized in 7 unique reports (e.g. **1-3**).[2-8] Solution-phase chemistry of anionic $[(CF_3)_3Au-F]^-$ complexes has also been recently reported.[9] Despite their rarity, they have been shown useful in studying reductive elimination and transmetallation processes from Au(III) as well as the formation of luminescent complexes, led by the groups of Toste and Nevado. Au(I)-F complexes are similarly rare, with only a total of 8 examples with crystallographic characterization, often as bridging fluorides between formally cationic Au(I) centres and BF_4 or PF_6 counteranions.[10-15] There is also a single Au(II) example.[16]
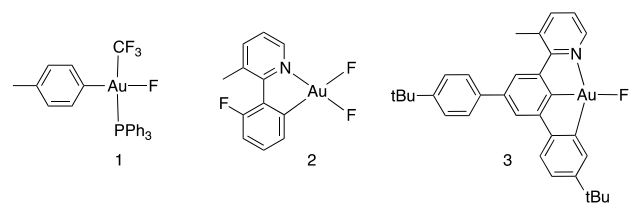
Recently Riedel reported that pyridine ligands were effective in stabilizing Au(III) fluorides. In their case pyridine/fluoride exchange resulted in a mixture of compounds dominated by pyridine-AuF_3 and bispyridine-AuF_2 could be precipitated but was not crystallographically characterized or isolated in a pure form. Careful ^{19}F NMR and mass spectrometry analysis allowed for identification of the complexes in the mixture (Scheme 1).[17] The reaction mixtures decomposed in solution over the course 1 or 2 days with elimination of 2-fluoropyridine.
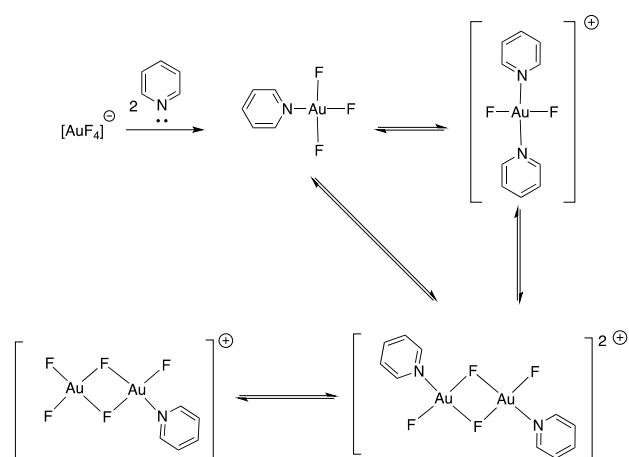

Scheme 1. Species observed in the reaction of pyridine with tetrafluoroaurate.

We have also found that pyridine ligands (starting from homoleptic Au(I) and Au(III) pyridine ligated precursors) are effective in the synthesis and stabilization of Au(III) functionalities involving small anionic fragments, including rare hydroxides.[18, 19] In this work we report the first examples of well defined isolated

trans-difluorogold(III) complexes, supported by pyridine or imidazole N-based ligands including crystallographic characterization for the imidazole derivative.

The reaction of Au(I) starting complex **4NMe₂** with XeF₂ (Scheme 2) in CHCl₃ in a polyethylene centrifuge tube resulted in a yellow solid which was washed with CHCl₃. A sample was dissolved in CD₃CN for NMR studies which showed a singlet at -249 ppm as well as the peak arising from triflate at -79 ppm in the ¹⁹F NMR spectrum. The former chemical shift is consistent with the range for Au(III) pyridine fluorides in the Riedel work.[17] ¹H NMR spectroscopy was consistent with a single compound containing 4-DMAP. Mass spectrometry in CH₃CN showed signals arising from **5NMe₂**, a fragment having lost a fluoride, as well as starting material **4NMe₂**. Many attempts at growing single crystals, however only poorly diffracting micro/polycrystalline material was obtained. The structural solution from multiple data sets was sufficient to identify the compound as the cationic Au(III)difluoride **5NMe₂**, however were of much too poor quality to allow for satisfactory refinement.

4R; R = -H, -NMe₂
A = BF₄ for 4H, OTf for 4NMe₂
5R
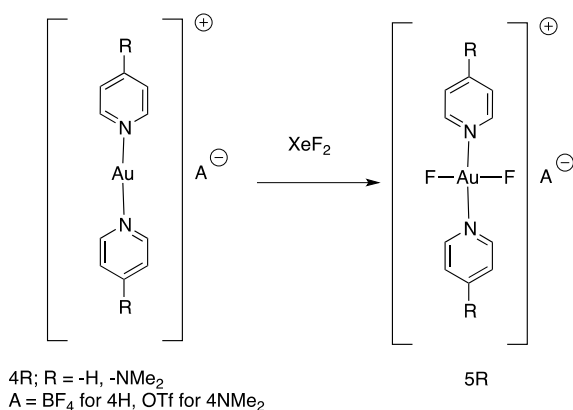
Scheme 2. Synthesis of **5R** (R = -NMe₂, -H) using XeF₂.

The same reaction using the Au(I) bispyridine complex **4H** (as the BF₄⁻ salt in CH₂Cl₂, which resulted in a cleaner reaction than in CHCl₃ for this analogue) gave the same results with a ¹⁹F NMR shift of -237 ppm and signals in the mass spectrum arising from **5H** and a trispyridine-monofluoride Au(III) complex as well as **4H**. Unfortunately in this case no crystals of diffraction quality could be obtained. However based on the NMR and mass spectral studies we are confident the product is **5H**, although the stereochemistry of the fluorides relative to the pyridine cannot be confirmed from these data.

To obtain material that might give better quality diffracting crystals the ligand was changed to N-methylimidazole. The Au(I) starting complex **4IM** was achieved via adapting the standard synthetic protocol of Lin and using N-methylimidazole as the ligand in place of 4-DMAP.[20] The same cation has previously been reported as an [AuCl₂]⁻ salt.[21] Addition of XeF₂ (Scheme 3) using the same protocol as the pyridine ligands gave the expected results, with in this case the Au(III)-F ¹⁹F{¹H} chemical shift at -284 ppm and a clean ¹H NMR spectrum for the isolated material. The mass spectrum showed cationic fragments **5IM** and starting material **4IM**. Single crystals were grown from CD₃CN/Et₂O, which were of high quality and allowed for a satisfactory structural solution and refinement (Figure 1).
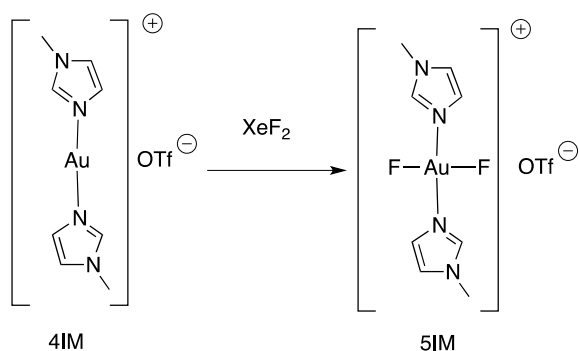
Scheme 3. Synthesis of **5IM** using XeF$_2$.

While the yields for these reactions are good, ranging from 73 to 81%, XeF$_2$ is not an ideal agent for introducing fluorine, due to its high cost, toxicity and relative difficulty in handling.[22] Therefore, having established the viability and spectroscopic characteristics of the Au(III) fluorides described above we sought a synthetic method that used a more economical and easily handled fluoride source, KF. Ritter and co-workers described the displacement of pyridine ligands from Pd(IV) species using a mixture of KF and 18-crown-6 as a solubilizing agent.[23] Therefore we envisioned the use of the Au(III) pseudo-homoleptic tetrakis pyridine trications **6R** developed in our group to achieve this.[18] Compound **6NMe$_2$** was previously reported and the syntheses of **6H** and **6IM** was accomplished by adapting the procedure and reacting **4H** or **4IM** with the I(III) reagent [PhI(4-cyanopyridine)$_2$][OTf]$_2$.
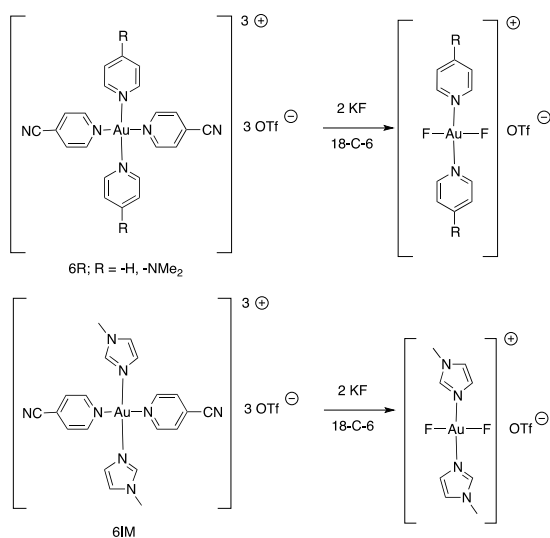
Scheme 4. Synthesis of **5R** and **5IM** using KF.

Pleasingly, addition of 2 stoichiometric equivalents of KF and 6 equivalents of 18-crown-6 to **6H**, 6**NMe$_2$** and **6IM** in CH$_3$CN resulted in consumption of KF and conversion to **5H, 5NMe$_2$** and **5IM** within 30 minutes as monitored ^{19}F NMR. The compounds could be isolated from the mixture in yields ranging from 26 to 61 %, somewhat lower than the same yields using XeF$_2$. If the reactions are performed in CD$_3$CN, ^{1}H NMR spectroscopy showed the *in situ* conversion to **5R** be greater than 80% in all cases. The spatial arrangement of the pyridine ligands in **6H** (the weaker pyridine donors are always arranged in a –trans arrangement), supports a –trans arrangement of the fluorides and pyridines with respect to one another.
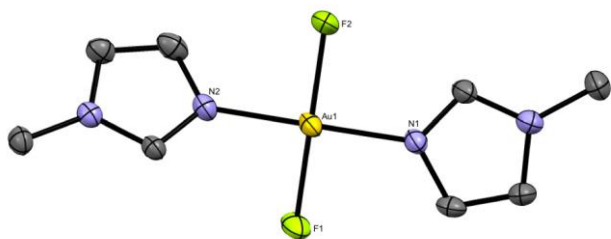
Figure 1. Solid-state structure of **5IM**. Thermal ellipsoids are depicted at 50% probability level, hydrogen atoms and triflate anion are omitted. Selected bond distances (Å): Au(1)-F(1) 1.908(3), Au(1)-F(2) 1.924(3), Au(1)-N(1) 1.985(4), Au(1)-N(2) 1.992(4).

The Au-F bond distances in **5IM** are 1.908(3) and 1.924(3) Å, the shortest known from the few previous reports of Au(III)-F bonds is 1.95 Å in complex **2** for the F trans to N,[3] with a typical range of 2-2.2 Å,[2-7] making ours the shortest known for any complex of gold. The bond distances in AuF_3 are 2.04 (bridging) and 1.91 (terminal) Å.[24] The gold atom does not participate in any substantive intermolecular interactions in the solid state. The shortest interactions with the F atoms are with H atoms bound to the aryl carbons of an imidazole ligand in an adjacent complex with an F----H separation of 2.24 Å.

Addition of excess pyridine ligand to solutions of the isolated complexes **5R** did not result in any decomposition. However if excess KF (3-4 equivalents) was used in the syntheses within 2 hours black material precipitated and the ^{19}F NMR signal arising for **5R** disappeared. We did not observe the types of products observed by Riedel in their experiments starting from $[AuF_4]^-$ and pyridine in Scheme 1.[17] Holding solutions of **5R** in dry CD_3CN under N_2 at room temperature and observing by NMR spectroscopy showed no evidence of decomposition after 2 days. If the NMR tube was stored in the ambient atmosphere decomposition (a disappearance of the ^{19}F NMR signal) and precipitation of black material was observed after 24 hours. The compounds may be stored for months in the solid-state in an N_2 filled glovebox, and a crystal left in the ambient atmosphere under n-paratone oil showed no signs of decomposition after 24 hours.

In conclusion we have reported the second crystallographically characterized example of a trans difluoride of gold, the first only having been reported very shortly before publication of this article,[8] and the first in a cationic complex. This compound **5IM** and the analogous pyridine ligated complexes are reasonably stable both in solution and in the solid state at room temperature. When using XeF_2 the syntheses are straightforward and high yielding We also demonstrated synthesis can be accomplished with F^-, a first for forming Au(III)-F species, albeit requiring an extra step to achieve the Au(III) starting material and giving lower, but still manageable isolated yields. To our knowledge, **5IM** shows the shortest Au-F bond yet described in any Au compound.

Conflicts of interest

There are no conflicts to declare.

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