Reactivity Studies of Cationic Au(III) difluorides supported by N-ligands

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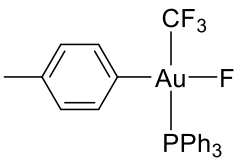
ABSTRACT

The reactivity of difluoro Au(III) cations supported by pyridine or imidazole ligands is reported. The Au(III)-F bond is found to be susceptible to metathesis by TMS reagents and reagents bearing acidic protons such as H-CC-Ph and HOAc. In the latter case the reactions are slower than analogous reactions reported by other groups where strong -trans donors are present opposite the Au-F bond. This, coupled with the inability to effect metathesis on only one Au-F bond in our system indicates the -trans effect is a key consideration in Au-F chemistry.

INTRODUCTION

The chemistry of organometallic and coordination complexes containing an Au-F bond is underdeveloped, with only 8 unique compounds for Au(I)[1-6] and 15 for Au(III)[7-16] as well as a single Au(II) complex[17] having been characterized by X-ray crystallography. The first was described in 2005, with most examples being reported in the past 5 years as interest in the area increases. Representative examples for Au(III) are shown in compounds **1-4**. However, despite being relatively few in number the existing reports demonstrate that there is potential for taking advantage of this functionality in a variety of interesting contexts. For example substituting the Au-F groups for aryl using boron-based transmetalating reagents has been shown to result in C-C bond formation by reductive elimination from the Au centre (Scheme 1).[10] Csp^3-F bond formation via reductive elimination was also demonstrated from related compounds.[11]



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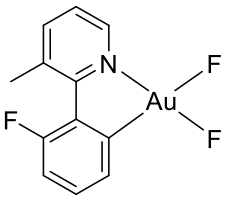

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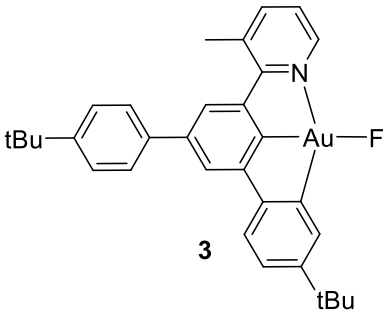

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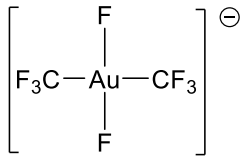

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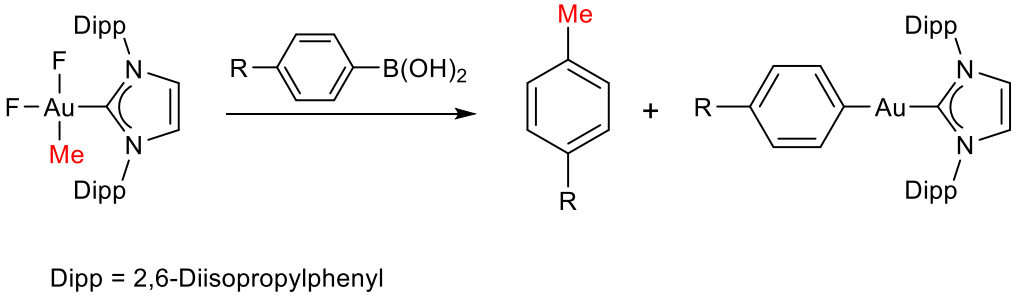
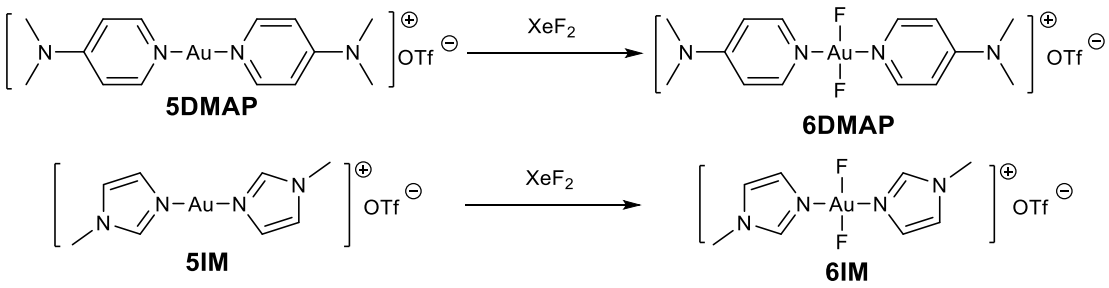


Dipp = 2,6-Diisopropylphenyl

Scheme 1. Reactivity reported by Toste for transmetallation of Au-F by boronic acids.

We believe the main reason for the lack of reports of Au-F containing compounds stems from the relative weakness and therefore high reactivity of the bond. For example in compound **4** Menjón and co-workers found that the weakness of the Au-F bond resulted in the fluoride being easily replaced by the other halides.[13] Pyridine based systems have been used to "tame" the reactivity of the Au-F bond by Riedel and co-workers,[18] and we recently reported a family of cationic complex with two Au(III)-F bonds *trans* to one another supported by either pyridine or imidazole ligands (**6DMAP**, **6IM**, Scheme 2).[14] Given the cationic nature of the complex, high oxidation state of Au and the weak *trans* donating ability of the fluorides with respect to each other, this class of compound contain some of the shortest, strongest Au-F bonds reported to date at 1.90 Å.



Scheme 2. Synthetics pathway for **6DMAP** and **6IM**.

Only the $[AuF_4]^-$ anion has been structurally determined to have a bond as short at 1.899-1.901 Å,[18] the typical range for an Au-F bond is 2-2.2 Å. Gas phase AuF_3 is also slightly shorter at

1.88 Å.[19] This feature of having a short, strong Au-F bond makes our compounds ideal as a relatively stable platform to explore the possibilities of Au-F chemistry within a coordination complex.

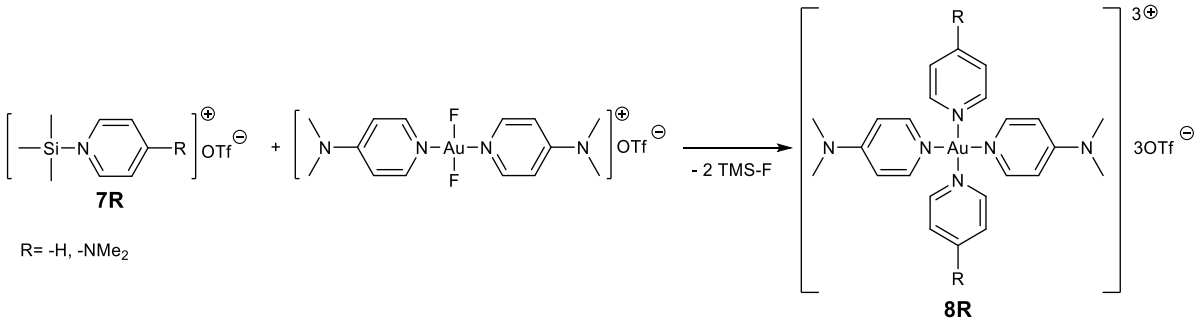
RESULTS AND DISCUSSION

Delivery of fragments to Au using TMS reagents

Delivery of pyridine

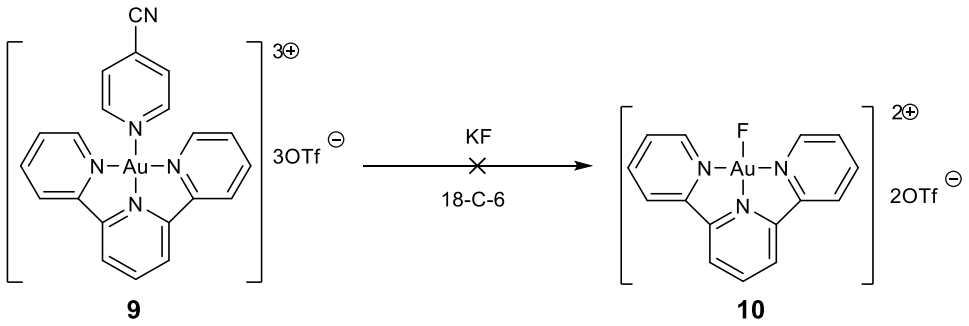
Trimethylsilyl (TMS) reagents are often used to deliver fragments to species containing X-F bonds owing to the high thermodynamic stability of the Si-F bond. To date there has been only one report of manipulating an Au-F bond with -TMS in which Riedel replaced an Au(III)-F with chloride or triflate of an NHC-AuF_3 complex using the corresponding -TMS reagent.[15]

To demonstrate that our Au(III)-F system was compatible with TMS metathesis reactions we sought to generate a known compound, tetrakis pyridine species **8H**.[20] The TMS-pyridine cations **7R** were generated by direct reaction between TMS-OTf and the appropriate pyridine following literature procedure, and can be isolated and stored for future use.[21] The reaction of two equivalents of **7H** with **6DMAP** in CH_3CN resulted in the generation of **8H** over 4 days (Scheme 3). During monitoring of the reaction, TMS-F could be observed *in situ* by ^{19}F NMR, with a diagnostic singlet at -157 ppm.[22] The conversion is quantitative as determined by ^{1}H NMR spectroscopy and the isolated yield of **8H** was 84%, demonstrating that TMS metathesis reactions are compatible with this system. The same conversion was also observed using **7NMe$_2$** giving the homoleptic trication **8NMe$_2$**.



Scheme 3. Synthesis of **8R** using **7R** and **6DMAP.**

If only one equivalent of **7R** is used, no product consistent with a [tris-pyridine Au(III)-F]$^{2+}$ compound was observed. After 3 days in solution **7R** and **6DMAP** were still present, along with TMS-F, a small amount of HF and the Au(I) compound **5DMAP**. Riedel reported observation of HF in pyridyl-Au(III) fluorides in some cases and also that certain ratios of pyridine:F^- result in unstable complexes.[18] We have not been successful in generating **10** by attempted displacement of one pyridine from **9** using 1 equivalent of KF (scheme 4), which results in decomposed reaction mixtures, indicating that Au(III) bearing one fluoride and 3 N-ligands may not be a stable class of compounds.

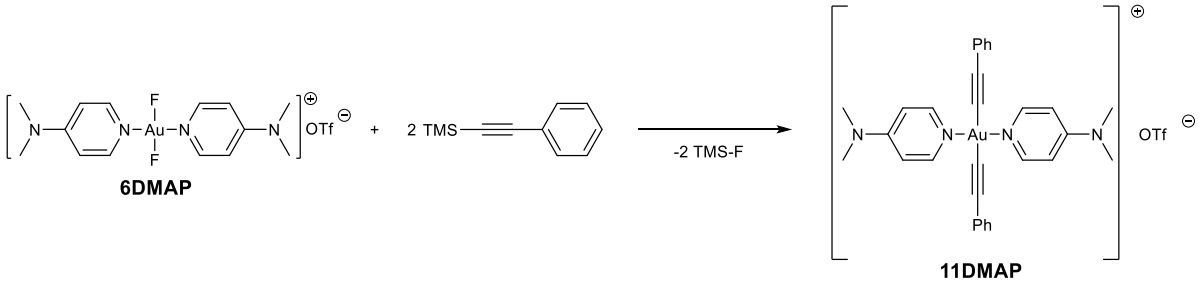


Scheme 4. Observed reactivity between **9** and KF.

Delivery of phenyl acetylene

Au(III) acetylides are of interest as they often give compounds containing interesting luminescent properties.[9, 23, 24] To determine if Au-F can be switched for an acetylide functionality **6DMAP** was reacted with 2 equivalents of TMS-CC-Ph in CH_3CN. TMS-F was

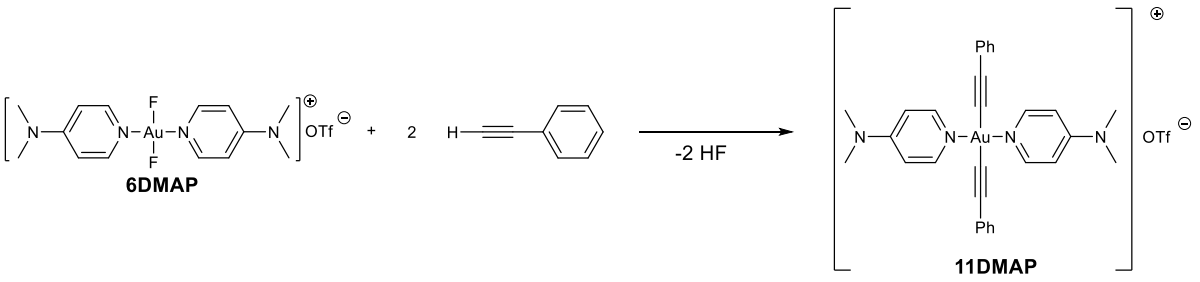
observed in the ^{19}F NMR, and **6DMAP** was completely consumed within one hour. After workup, mass spectrometry and NMR studies were consistent with complex **11DMAP**, which was isolated in 60% yield (Scheme 5). **11DMAP** is still isolated as the exclusive Au-acetylide product if less than 2 stoichiometric equivalents of TMS-CC-Ph are used. We hypothesize this is due to the superior -*trans* donating ability of the acetylide which renders the opposite fluorine atom much more reactive for the second substitution to occur.



Scheme 5. Synthesis of **11DMAP** from TMS-CC-Ph and **6DMAP**.

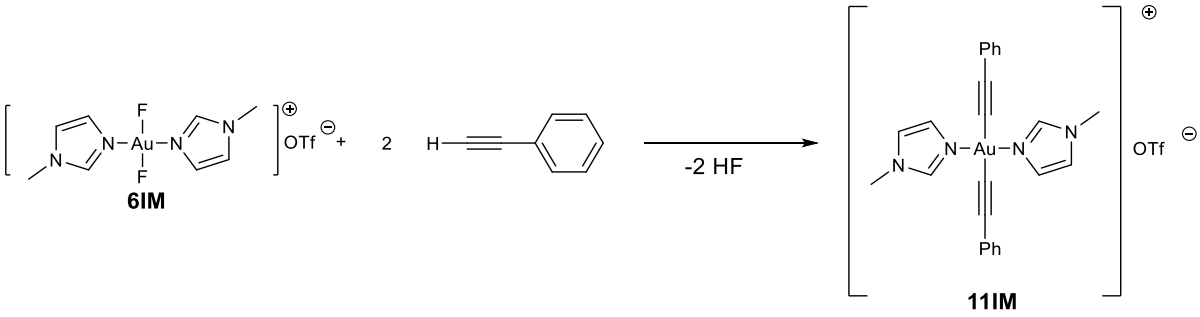
Delivery of phenyl acetylene by C-H activation

TMS elimination, while effective, suffers from high cost and a low atom efficiency. Having established the stability of compound **11DMAP** we sought to synthesize it directly from H-CC-Ph. Reaction of **6DMAP** with 2 equivalents of H-CC-Ph in CH_3CN resulted in a slow conversion to **11DMAP** and elimination of HF as monitored by ^{19}F and ^{1}H NMR over the course of 5 days (Scheme 6). **11DMAP** was isolated in 50% yield, comparable to the reaction with TMS-CC-Ph. Nevado reported a similar reaction with an analogue of compound **3**, proceeding in excellent yields at room temperature within 3 hours.[9] The extended reaction time in our system is likely due to the labilizing effect of the -*trans* anionic organometallic group in **3** as compared to ours with a -*trans* F. As with the -TMS reaction only substitution of both Au-F bonds in **6DMAP** is observed with H-CC-Ph using substoichiometric amounts, consistent with the newly introduced acetylide group rendering the -*trans* F much more reactive.



Scheme 6. Observed reactivity between **6DMAP** and H-CC-Ph.

Though **11DMAP** can be formed via direct reaction with both H-CC-Ph and TMS-CC-Ph, the reaction between TMS-CC-Ph and **6IM** resulted in complex mixtures where **11IM** was observable *in situ* but not isolable. However, when reacted with H-CC-Ph, **11IM** was isolated cleanly in 60% yield after five days (Scheme 7). The reason for the differing reactivity with TMS-CC-Ph between **6DMAP** and **6IM** is unclear but indicates within this system substitution of related ligands for each other can have an impact on reaction outcome and it is useful to have a library of related complexes at hand.

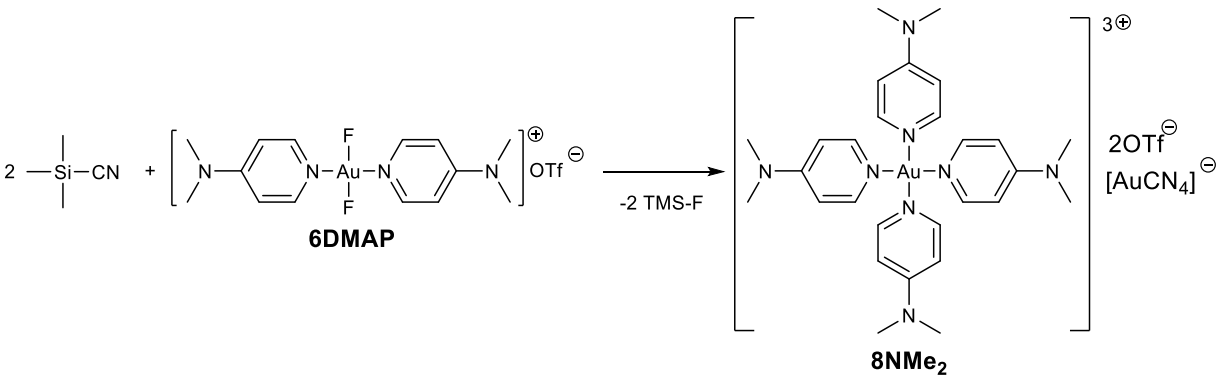


Scheme 7. Synthesis of **11IM** using **6IM** and H-CC-Ph.

Delivery of -CN via TMS

Next, we investigated the reactivity of TMS-CN with **6DMAP**. Upon reaction for 3 hours in CH_3CN **6DMAP** was consumed and TMS-F was generated as monitored by ^{19}F NMR spectroscopy. Initially we believed that the fluorides had been substituted by CN groups,

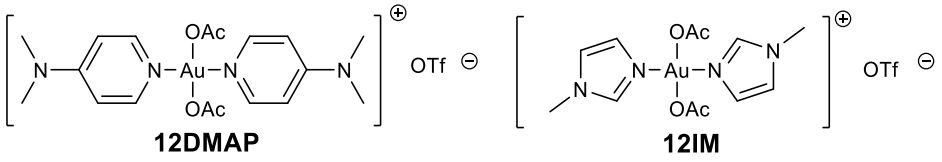
following an analogous pathway to the process involving TMS-CC-Ph and **6DMAP**. However, further analysis of the reaction products via mass spectrometry and ^{1}H NMR revealed the presence of both $[Au(CN)_4]^-$ and **8NMe$_2$**, respectively (Scheme 8). Single crystals were grown via CH_3CN/Et_2O vapour diffusion. Crystallographic studies showed a salt with co-crystallisation of $[Au(CN)_4]^-$, OTf^- and the **8NMe$_2$** trication. We speculate that the target species bis-cyano bis-pyridyl complex was formed temporarily via ligand delivery from TMS, however this species then undergoes ligand exchange to produce the observed products. This scrambling behaviour has previously been observed with halides of Au(III).[25]



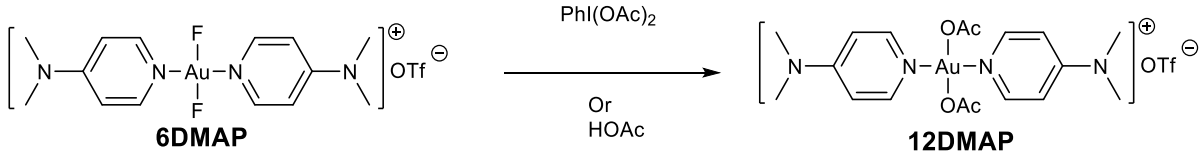
Scheme 8. Observed reactivity between TMS-CN and **6DMAP**.

Reaction of Au(III) difluorides with PhI(OAc)$_2$

Previous efforts in our lab to synthesize diacetate compounds **12DMAP** and **12IM** have been unsuccessful as combination of **5DMAP** and $PhI(OAc)_2$ resulted in no reaction, likely due to the relatively modest oxidative ability of $PhI(OAc)_2$.[26]



Recently we reported that the cationic difluorogold systems (**6DMAP**, **6IM**) can undergo metathesis reactions with $[PhI(pyridine)_2]^{2+}$ species via nucleophilic attack from fluoride onto the iodine resulting in transfer of pyridine to the gold and generation of $PhIF_2$.[27] To investigate if **6DMAP** can also react with I(III) species bearing anionic ligands to give **12DMAP**, which we were unable to synthesize oxidatively from Au(I), it was reacted with $PhI(OAc)_2$ in CH_3CN, resulting in a colour change from yellow to orange. After two hours, the *in situ* ^{19}F NMR showed generation of $PhIF_2$ as a singlet at -176 ppm.[28] The mixture was reacted for 30 hours, resulting in isolation of a bright orange solid after workup. ^1H NMR spectroscopy of the isolated material was consistent with a compound containing 4-DMAP and acetate in a 1:1 ratio and mass spectrometry studies showed an ion with an m/z of 559.2, consistent with cation **12DMAP** (Scheme 9).



Scheme 9. Observed reactivity of **6DMAP** and $PhI(OAc)_2$ or acetic acid.

Reaction of Au(III) difluorides with HOAc

Attempts to generate **12DMAP** using HOAc from **8R** starting material were not successful, giving complex mixtures. The reaction was only successful if the Au(III) centre was supported by a bidentate or tridentate pyridyl ligand.[29] In situ monitoring of the reaction of **6DMAP** with HOAc in CD_3CN showed a set of ^1H NMR signals identical to **12DMAP**. **12DMAP** could be isolated in 86% yield. The above two reactions giving diacetate compounds demonstrate cases where a product can be achieved from an Au-F bond that could not be accessed via other available methods. In attempts to obtain single crystals for X-ray studies for structural confirmation of the transformation, as we were unable to grow suitable crystals of the above

compounds, we sought to synthesize **12IM**. In the reaction of **6IM** with HOAc ^{1}H NMR and mass spectral data consistent with **12IM** were observed. This was confirmed by X-ray structural studies on single crystals grown via vapour diffusion of Et_2O into a CH_3CN solution of the cation. As expected, the acetate ligands are orientated -*trans* to one another (Figure 1). Nevado and co-workers have generated Au(III)-formates from the direct reaction of formic acid and Au(III)-F.[30]

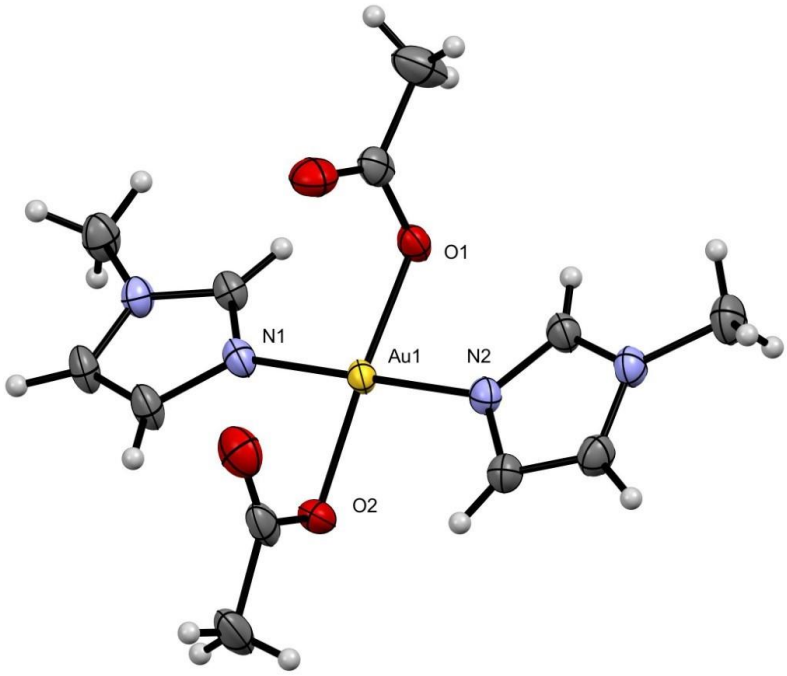
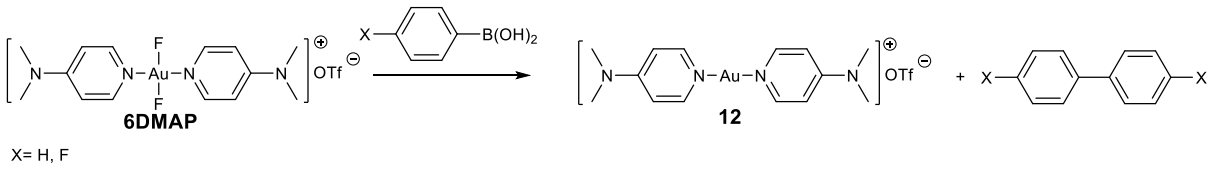


Figure 1. Solid state structure of **12IM**. Thermal ellipsoids are drawn at the 50% probability level. The triflate anion is omitted for clarity. Selected bond distances (Å) Au1-O1 1.993(2), Au1- O2 1.991(2), Au1-N1 2.004(3), Au1-N2 2.000(3).

Boronic Acids

Au(III) fluoride compounds with strong -*trans* ligands with respect to the Au-F are known to react with aryl boronic acids, giving complexes that result in C-C bond formation.[8, 10] To investigate if the more strongly bound Au-F in **6DMAP** was susceptible to aryl

transmetallation, it was reacted with $ArB(OH)_2$ (Ar = -Ph, 4-F-Ph). Over a 3 hour period, the reaction solution changed from clear yellow to a black suspension, indicative of decomposition products. In ^{1}H-NMR NMR of the suspension, both Au(I) compound **5DMAP** and the biphenyl C-C coupling product corresponding to each boronic acid were observed (Scheme 10).[31] These results are indicative of analogous transmetallation reactivity with boronic acids despite the stronger Au-F bond in **6DMAP**. The likely di-arylated intermediate then undergoes reductive elimination with C-C bond formation. This is an important observation in that some Au(III)-organo species supported by pyridine ligands may not be viable, rather being susceptible to reductive elimination.



Scheme 10. Observed reactivity between phenylboronic acids and **6DMAP**.

CONCLUSIONS

The reactivity of $[Au(Pyr)_2F_2]^+$ cations was examined. They are susceptible to both -TMS and -H metathesis reactions to introduce other functionalities onto the Au(III) centre. The reactions involving acetylene (C-H) proceed more slowly than known systems with strong -trans donors opposite to the Au-F bond. The inability in our system to achieve mono-substitution with a new anionic group -trans to Au-F indicates the -trans effect is a key feature of Au(III)-F chemistry. We were able to access diacetate compounds inaccessible from oxidation of Au(I) using conventional reaction from $PhI(OAc)_2$, indicating that the Au-F bond may be a useful tool Au reactivity. Finally, boronic acids react with Au-F, consistent with related reports from other groups, and consequent C-C bond formation shows that the elementary step of reductive

elimination is a consideration in the bispyridyl Au(III) system being worked with and a possibility in related compounds going forward.

EXPERIMENTAL DETAILS:

Solvents used were dried using an Innovative Technologies Solvent Purification System. The dried solvents were stored under a N_2 atmosphere over 3 Å molecular sieves in the glovebox. Solvents for NMR spectroscopy were purchased from Cambridge Isotope Laboratories and dried by stirring for three days over CaH_2, distilled prior to use, and stored in the glovebox over 3 Å molecular sieves. **6IM**, **6DMAP** and **7R** species were synthesised via literature procedures.[14, 21] Gold powder was purchased from Precious Metals Online. All other reagents were purchased from Sigma Aldrich and used as received. All reactions were performed either within a glove box or Schlenk line under dry N_2 gas at room temperature.

X-ray Crystallography Details:

Single crystals were selected under n-paratone oil, mounted on nylon loops and placed into a cold stream (172 K) of N_2 on a Rigaku SuperNova CCD diffractometer using Cu Kα radiation. Structure solution and refinement were performed using the SHELXTL suite of software.

Reaction of 6DMAP and 7NMe$_2$.

To a solution of **6DMAP** (20 mg, 0.032 mmol) in 2 mL CH_3CN was added **7NMe$_2$** (22 mg, 0.064 mmol). The resulting solution was left to stir for 4 days producing a red solution, volatiles were removed *in vacuo* to receive a red solid. ^{1}H NMR identified the product as **8NMe$_2$** matching known literature (29 mg, 82% yield).[18]

^{1}H NMR (400 MHz, CD_3CN), δ (ppm) = 7.96 (d, 8H, *J*= 7.7), 6.71 (d, 8H, *J*= 7.7), 3.10 (s, 24H)

Reaction of 6DMAP and 7H.

To a solution of **6DMAP** (20 mg, 0.032 mmol) in 2 mL CH_3CN was added **7H** (19 mg, 0.064 mmol). The resulting solution was left to stir for 4 days producing a red solution, volatiles were removed *in vacuo* to receive a dark red solid. ^{1}H NMR identified the product as **8H** matching known literature (28 mg, 84% yield).[18]

^{1}H NMR (400 MHz, CD_3CN), δ (ppm) = 8.78 (t, 4H, *J*= 6.0 Hz), 8.37 (t, 2H, *J*= 7.7 Hz), 7.97 (d, 4H, *J*= 7.8 Hz), 7.86 (d, 4H, *J*=7.1 Hz), 6.67 (d, 4H, *J*= 7.9 Hz), 3.09 (s, 12H)

Synthesis of 11DMAP using 1-Phenyl-2-Trimethylsilylacetylene.

To a solution of **6DMAP** (39 mg, 0.062 mmol) in 4 mL CH_3CN was added 1-phenyl-2-trimethylsilylacetylene (37 µL, 0.188 mmol). The solution was stirred for 1 hour before being filtered, concentrated *in vacuo* and treated with Et_2O to receive **11DMAP** as a cream solid (30 mg, 61% yield).

^{1}H NMR (500 MHz, CD_3CN), *δ* (ppm): 8.43 (d, 4H, *J* = 7.8 Hz), 7.34-7.28 (m, 10H), 6.74 (d, 4H, *J* = 7.8 Hz), 3.12 (s, 12H)

^{13}C NMR (125 MHz, CD_3CN), *δ* (ppm): 156.6, 151.1, 132.5, 129.4, 129.0, 125.1, 109.4, 104.7, 96.90, 40.1.

ESI-MS: 643.2 $[Au(DMAP)_2(CC\text{-}Ph)_2]^+$

Synthesis of 11DMAP using Phenylacetylene.

To a solution of **6DMAP** (33 mg, 0.053 mmol) in 4 mL CH_3CN was added phenylacetylene (14 µL, 0.128 mmol). The resulting solution was stirred for five days under darkness before being filtered, concentrated *in vacuo* and treated with Et_2O to receive **11DMAP** as a cream solid (21 mg, 50% yield).

Synthesis of 11IM.

To a solution of **6IM** (50 mg, 0.091 mmol) in 4 mL CH_3CN was added phenylacetylene (22 µL, 0.20 mmol). The resulting solution was stirred for five days under darkness prior to being filtered, concentrated to 1 mL and treated with Et_2O to receive **11IM** as a beige solid (40 mg, 62% yield).

^{1}H NMR (400 MHz, CD_3CN), δ (ppm): 8.68 (s, 2H), 7.84 (t, 2H, J= 1.7 Hz), 7.51-7.46 (m, 4H), 7.38-7.35 (m, 6H) 7.34 (t 2H J= 1.6 Hz) 3.87 (s, 6H)

^{13}C NMR (125.8 MHz, CD_3CN), δ (ppm): 142.5, 132.8, 131.0, 129.5, 129.3, 125.0, 123.6, 100.5, 98.4, 36.5.

ESI-MS: 563.1 $[Au(Methylimidazole)_2(CC\text{-}Ph)_2]^+$

Synthesis of 12IM.

To a solution of **6IM** (31 mg, 0.057 mmol) in 5 mL of CH_3CN was added 25 µL of glacial acetic acid (26 mg, 0.44 mmol). The resulting solution was stirred for 16 hours. Volatiles were removed *in vacuo* and the residue was redissolved in minimal CH_3CN and treated with Et_2O to receive **12IM** as a beige solid (22 mg, 62% yield).

^{1}H NMR (400 MHz, CD_3CN), δ (ppm): 8.09 (s, 2H), 7.31 (s, 2H), 7.18 (s, 2H), 3.83 (s, 6H), 2.07 (s, 6H)

^{13}C NMR (125 MHz, CD_3CN), δ (ppm): 176.3, 138.5, 125.8, 123.8, 36.5, 21.3.

ESI-MS:479.2 $[Au(Methylimidazole)_2(OAc)_2]^+$

Synthesis of 12DMAP.

To a solution of **6DMAP** (24 mg, 0.038 mmol) in 4 mL of CH_3CN was added 25 µL of glacial acetic acid (26 mg, 0.44 mmol). The resulting solution was stirred for 16 hours to receive an orange solution. Volatiles were then removed under reduced pressure and the residue was redissolved in minimal CH_3CN and treated with Et_2O to receive **12DMAP** as a bright orange solid (23 mg, 86% yield).

^{1}H NMR (400 MHz, CD_3CN): δ (ppm): 7.93 (d, 4H), 6.73 (d, 4H). 3.12 (s, 12H), 1.94 (s, 6H)

^{13}C NMR (125 MHz, CD_3CN), δ (ppm): 176.2, 157.0, 147.0, 109.3, 40.1, 21.2.

ESI-MS: 559.2 $[Au(DMAP)_2(OAc)_2]^+$

Reaction of $PhI(OAc)_2$ with 6DMAP.

To a solution of **6DMAP** (30 mg, 0.048 mmol) in 4 mL CH_3CN was added $PhI(OAc)_2$ (18 mg, 0.056 mmol). The resulting solution was then stirred for 30 hours, volatiles were then removed *in vacuo* to receive an orange residue. The residue was then redissolved in minimal CH_3CN and treated with Et_2O to receive a bright orange solid which was then washed with $CHCl_3$ then Et_2O to receive **12DMAP** (10 mg, 29% yield). NMR spectroscopy and mass spectrometry produced data identical to **12DMAP**.

Reaction of 6DMAP with TMS-CN.

To a suspension of **6DMAP** (39 mg, 0.062 mmol) in 5 mL DCM was added TMS-CN (16 µL, 0.13 mmol). The resulting solution was stirred for 3 hours prior to being filtered, concentrated *in vacuo* and treated with Et_2O to receive a bright orange solid. The orange solid was dissolved in CD_3CN for analysis via NMR and mass spectrometry.

ESI-MS: 300.8 $[Au(CN)_4]^-$, 248.8 $[Au(CN)_2]^-$

^{13}C NMR (125 MHz, CD_3CN), δ (ppm): **8NMe$_2$** 157.0, 146.0, 110.5, 40.3, $[Au(CN)_4]^-$, 103.1

General procedure for boronic acid reactions.

To a suspension of **6DMAP** in $CDCl_3$ was added 2 equivalents of corresponding boronic acid. For both reactions, after 3 hours at room temperature a yellow solution with a black suspension was received. NMR samples were then taken as direct aliquots of the solution for crude ^{1}H NMR analysis to observe biphenyl products.[31]

ASSOCIATED CONTENT

Supporting Information.

NMR spectra of reaction mixtures and isolated compounds. X-ray crystallographic data in .cif format has been deposited with the CCDC. CCDC reference numbers 2009722 and 2009723.

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