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Reactivity Studies of Cationic Au(III) Difluorides Supported by N Ligands

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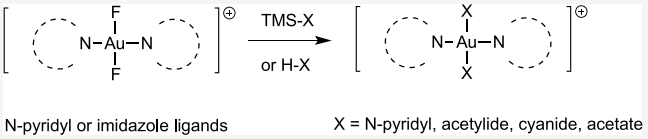
ABSTRACT: The reactivity of difluoro Au(III) cations supported by pyridine or imidazole ligands is reported. The Au(III)−F bond is found to be susceptible to metathesis by TMS reagents and reagents bearing acidic protons such as H−CC−Ph and HOAc. In the last case the reactions are slower than analogous 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 that the *trans* effect is a key consideration in Au−F chemistry.



INTRODUCTION

The chemistry of organometallic and coordination complexes containing a Au−F bond is underdeveloped, with only eight unique compounds for Au(I)[1−6] and 16 for Au(III)[7−17] as well as a single Au(II) complex[18] 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 has increased. 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 reagents has been shown to result in C−C bond formation by reductive elimination from the Au center (Scheme 1A).[10] The mechanism for this reaction was proposed to be via a concerted mechanism in which the boron abstracts the Au−F simultaneously with C−C bond formation. C(sp^3)−F bond formation via reductive elimination was also demonstrated from related compounds.[11] Nevado reported a system based on derivatives of compound **2** with evidence for direct transmetalation of the B−C bond onto Au(III), followed by reductive elimination of C−C from Au (Scheme 1B).[8] Several earlier systems were reported using boron-based reagents to generate C−C bonds in Au(I)/Au(III) redox couples using Selectfluor as an oxidant, but the proposed Au(III)−F intermediates were not isolated.[19−22] The formation of a C−F bond on a propargyl acetate by Au(I)/Au(III) and Selectfluor through a Au−F intermediate has also been reported.[23]

Nevado has also demonstrated activation of C−H bonds by isolable Au(III)−F to introduce acetylide (Scheme 1C)[9] and formate (Scheme 1D)[17] fragments onto gold, the latter being the first example of a Au(III) formate. The use of an Au(III)−F intermediate for Sonogashira type reactions has also been proposed again using Selectfluor as an oxidant for Au(I).[24]

We believe the main reason for the lack of reports of isolated 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,[25] and we recently reported a family of cationic complexes with two Au(III)−F bonds *trans* to one another supported by either pyridine or imidazole ligands (**6DMAP** and **6IM**; Scheme 2).[14] Given the cationic nature of the complex, the high oxidation state of Au, and the weak *trans*-donating ability of the fluorides with respect to each other, this class of compound contains some of the shortest, strongest Au−F bonds reported to date at 1.90 Å.

Only the $[AuF_4]^-$ anion has been structurally determined to have a bond as short at 1.899−1.901 Å;[25] the typical range for an Au−F bond is 2−2.2 Å. Nevado has reported Au−F bonds as short as 1.94 Å in compound **2** and related analogues, for the Au−F bond trans to pyridine. The Au−F bonds *trans* to the formally anionic phenyl donor in these complexes is longer at 2.01−2.02 Å.[8] This bond in gas-phase AuF_3 is also relatively short at 1.88 Å.[26] 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.

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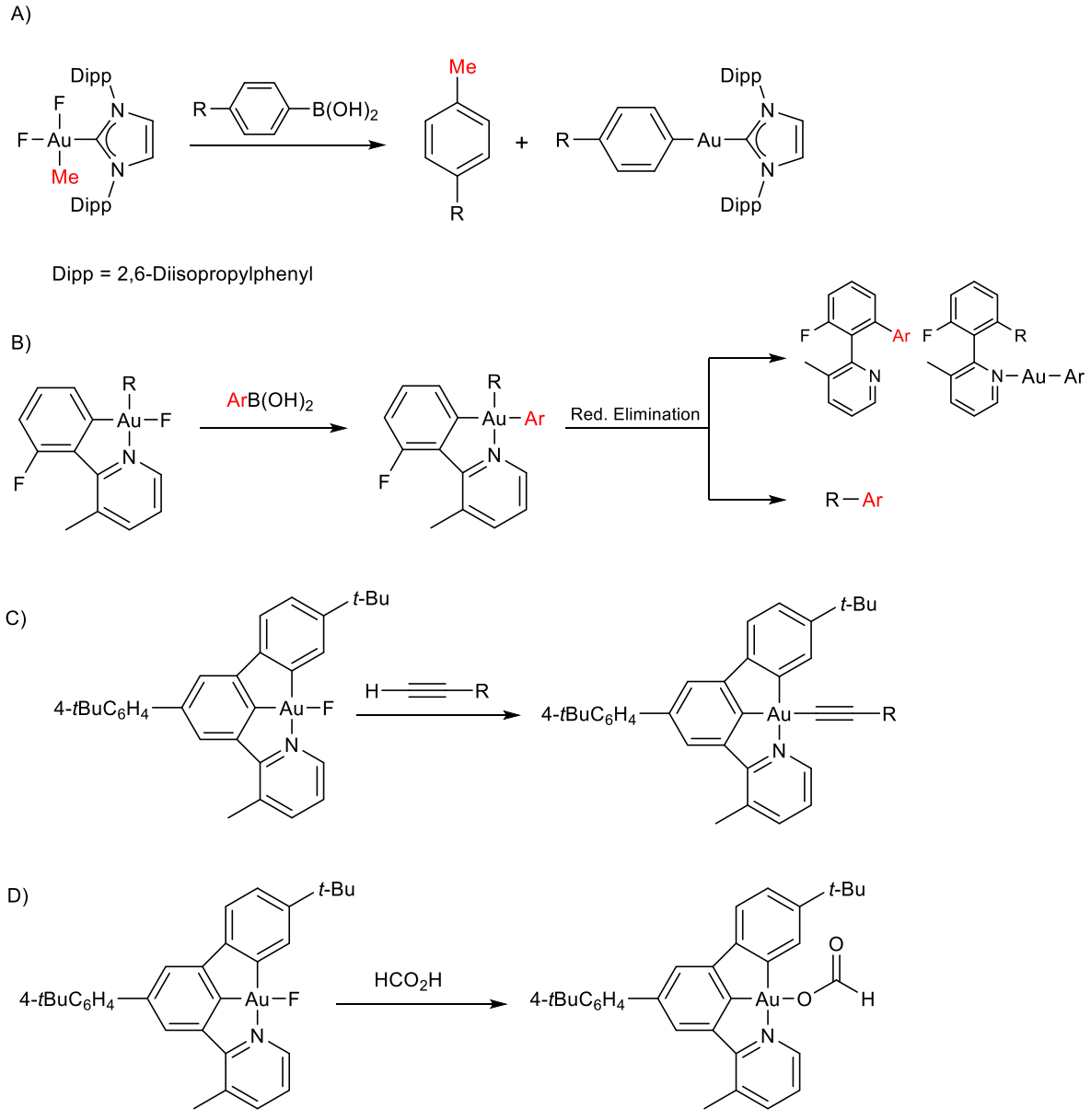
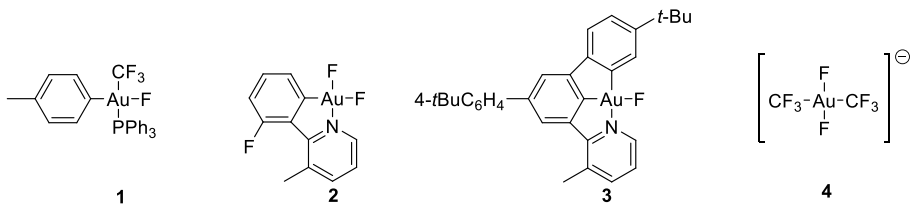
Scheme 1. (A) Reactivity Reported by Toste between Au−F and Boronic Acids, (B) the First Direct Evidence for Transmetalation between Au−F and Boronic Acids by Nevado, Where Arylated Intermediates Were Isolated and C−C Reductive Elimination Products Varied Depending on the R and Aryl Group Substituents, (C) Reactivity of Au−F with Terminal Alkynes Reported by Nevado, and (D) Generation of the First Gold Formate from Au−F and Formic Acid





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 E−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 bond with chloride or teflate 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, the tetrakis(pyridine) species **8R**.[27] The TMS−pyridine cations **7R** were generated by a direct reaction between TMS−OTf and the appropriate pyridine following the literature procedure and can be isolated and stored for future

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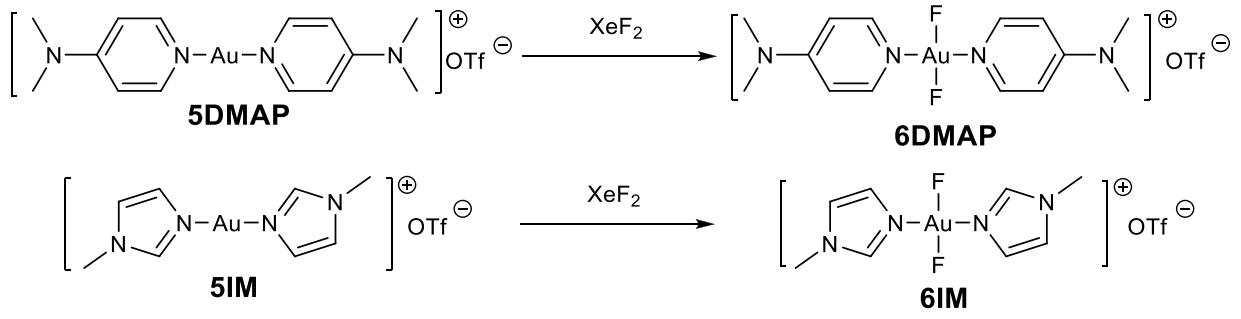
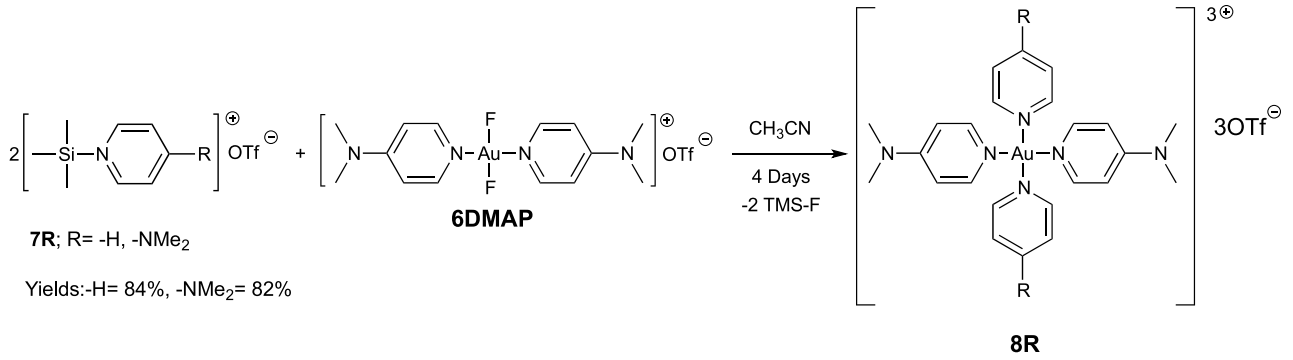
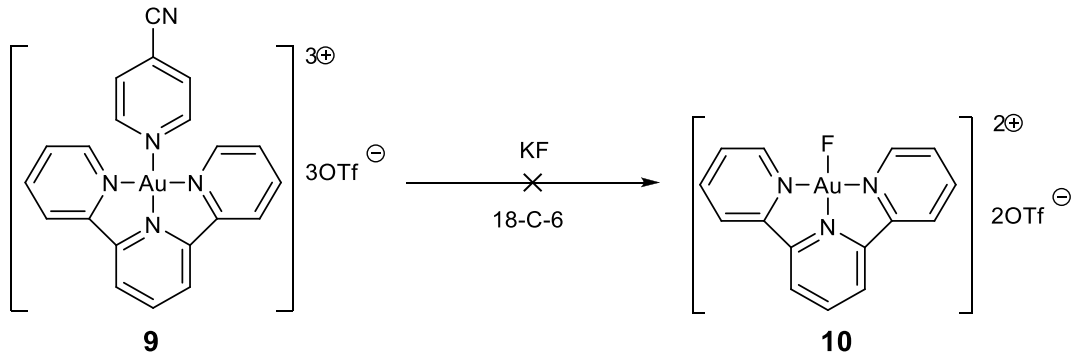
Scheme 2. Synthetic Pathway for 6DMAP and 6IM



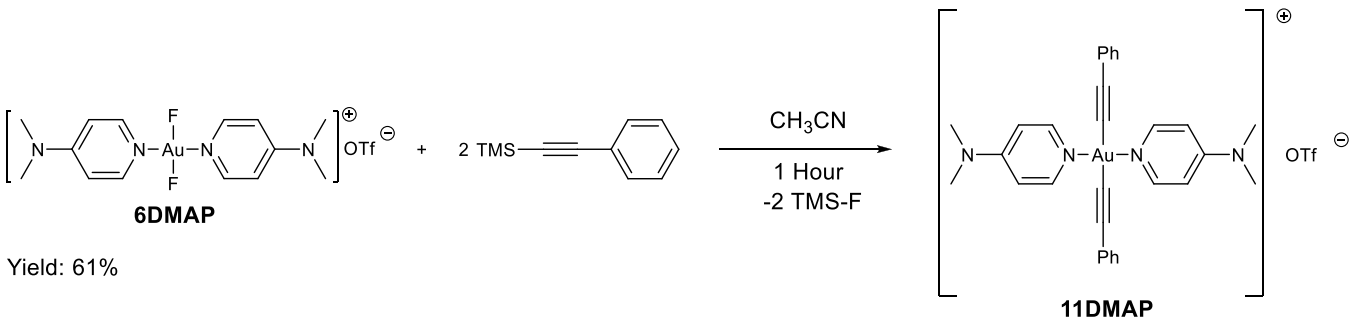
Scheme 3. Synthesis of 8R using 7R and 6DMAP



Scheme 4. Observed Reactivity between 9 and KF



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



use.[28] The reaction of 2 equiv of **7R** with **6DMAP** in CH_3CN resulted in the generation of **8R** 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.[29] The conversion is quantitative, as determined by ^{1}H NMR spectroscopy, and the isolated yield of **8R** 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$_2$**.

If only 1 equiv of **7R** was 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 the observation of HF in pyridyl−

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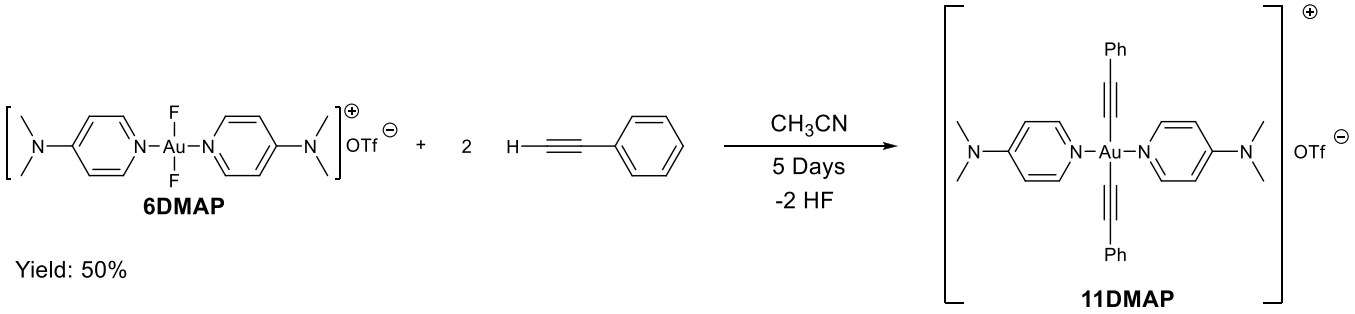
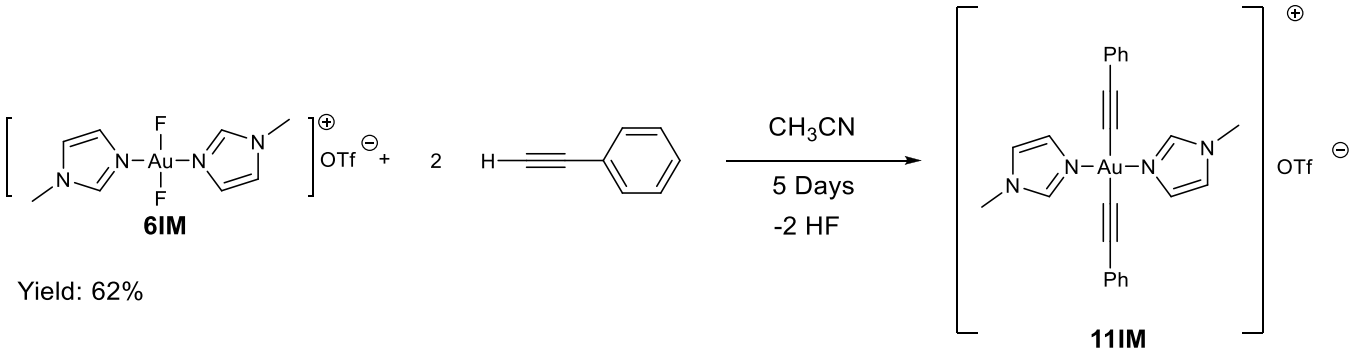
Scheme 6. Observed reactivity between 6DMAP and H−CC−Ph



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



Au(III) fluorides in some cases and also reported that certain pyridine:F^- ratios result in unstable complexes.[25] We have not been successful in generating **10** by attempted displacement of one pyridine from **9** using 1 equiv of KF (Scheme 4), which results in decomposed reaction mixtures, indicating that Au(III) bearing one fluoride and three N ligands may not be a stable class of compounds.

Delivery of Phenylacetylene. Au(III) acetylides are of interest, as they often give compounds containing interesting luminescent properties.[9,30−32] To determine if Au−F can be switched for an acetylide functionality, **6DMAP** was reacted with 2 equiv of TMS−CC−Ph in CH_3CN. TMS−F was observed in the ^{19}F NMR, and **6DMAP** was completely consumed within 1 h. After workup, mass spectrometry and NMR studies were consistent with the 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 equiv of TMS−CC−Ph is used. We hypothesize that 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. We have been unable to obtain single crystals suitable for X-ray diffraction studies to confirm if the acetylide fragments are orientated *cis* or *trans* about the Au(III) center. However, in all cases where we have obtained X-ray structures for this family of Au(III)−pyridyl-supported cations the strongest and weakest pairs of *trans* donors are oriented *trans* to one another;[14,27,33] therefore, we surmise the arrangement in **11DMAP** is most likely *trans*. This arrangement is also observed in other structurally characterized Au(III) difluorides bearing two other monodentate ligands such as $-CF_3$.[13]

Delivery of Phenylacetylene 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. The reaction of **6DMAP** with 2 equiv of H−CC−Ph in CH_3CN over 5 days with protection from light resulted in a conversion to **11DMAP** and elimination of HF, as monitored by ^{19}F and ^1H NMR (Scheme 6). **11DMAP** was isolated in 50% yield, comparable to that for the reaction with TMS−CC−Ph. Nevado reported a similar reaction with an analogue of compound **3**, proceeding with excellent yields at room temperature within 3 h.[9] The extended reaction time in our system is likely due to the labilizing effect of the *trans* anionic organometallic group in **3** in comparison 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.

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 **6IM** was reacted with H−CC−Ph, **11IM** was isolated cleanly in 60% yield after 5 days (Scheme 7). The reason for the differing reactivity with TMS−CC−Ph between **6DMAP** and **6IM** is unclear but indicates within this system that the substitution of related ligands for each other can have an effect on the reaction outcome and it is useful to have a library of related complexes at hand.

Delivery of −CN via TMS. Next, we investigated the reactivity of TMS−CN with **6DMAP**. Upon reaction for 3 h 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 a pathway analogous to the process involving TMS−CC−Ph and **6DMAP**. However, further analysis of the reaction products via mass spectrometry and ^1H NMR revealed the presence of both $[Au(CN)_4]^-$ and **8NMe$_2$**, respectively

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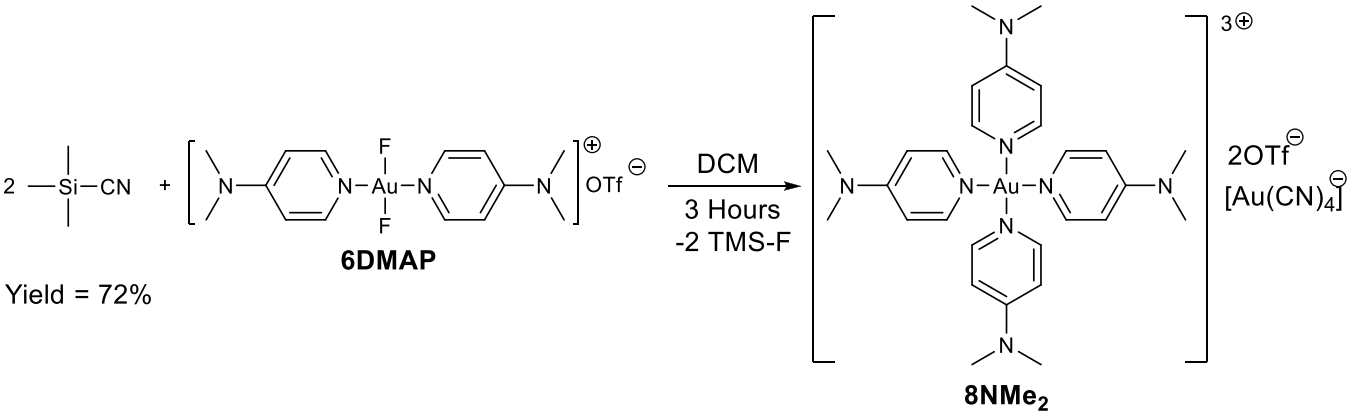
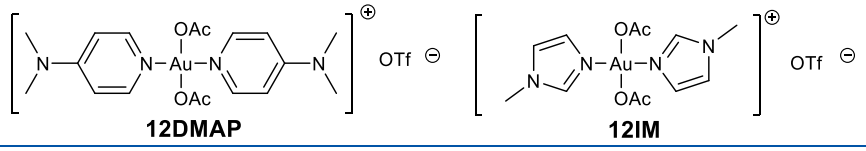
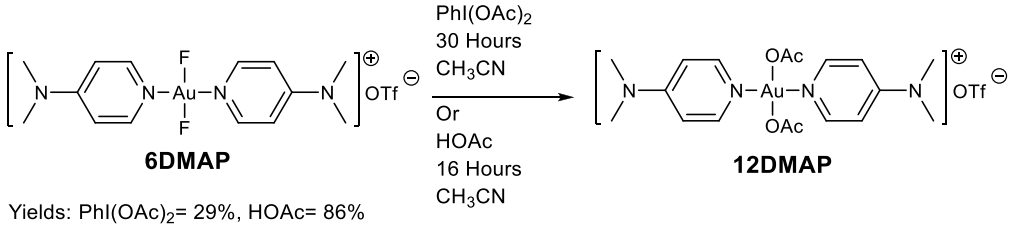
Scheme 8. Observed reactivity between TMS−CN and 6DMAP





Scheme 9. Observed Reactivity of 6DMAP and $PhI(OAc)_2$ or Acetic Acid



(Scheme 8). Single crystals were grown via CH_3CN/Et_2O vapor diffusion. Crystallographic studies showed a salt with cocrystallization of $[Au(CN)_4]^-$, OTf^-, and the **8NMe$_2$** trication. We speculate that the target bis(cyano) bis(pyridyl) complex was formed temporarily via ligand delivery from TMS; however, this species then underwent ligand exchange to produce the observed products. We have not observed such an intermediate, however. Scrambling behavior such as this has previously been observed with halides of Au(III).[33]

Reaction of Au(III) Difluorides with PhI(OAc)$_2$. Previous efforts in our laboratory to synthesize the diacetate compounds **12DMAP** and **12IM** have been unsuccessful, as the combination of **5DMAP** and $PhI(OAc)_2$ resulted in no reaction, likely due to the relatively modest oxidative ability of $PhI(OAc)_2$.[34]

Recently we reported that cationic difluorogold systems **6DMAP** and **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 $PhIF_2$.[35] 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 color change from yellow to orange. After 2 h, *in situ* ^{19}F NMR showed the generation of $PhIF_2$ as a singlet at −176 ppm.[36] The mixture was reacted for 30 h, 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 value of 559.2, consistent with the cation **12DMAP** (Scheme 9).

Reaction of Au(III) Difluorides with HOAc. Attempts to generate **12DMAP** using HOAc from the **8R** starting material were not successful, giving complex mixtures. The reaction was only successful if the Au(III) center was supported by a bidentate or tridentate pyridyl ligand.[37] *In situ* monitoring of the reaction of **6DMAP** with HOAc in CD_3CN showed a set of ^1H NMR signals identical with those of **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 ^1H NMR and mass spectral data consistent with **12IM** were observed. This was confirmed by X-ray structural studies on single crystals grown via vapor 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.[17]

Boronic Acids. Au(III) fluoride compounds with strong *trans* ligands with respect to the Au−F bond are known to react with arylboronic 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 transmetalation, it was reacted with $ArB(OH)_2$ (Ar = −Ph, 4-F−

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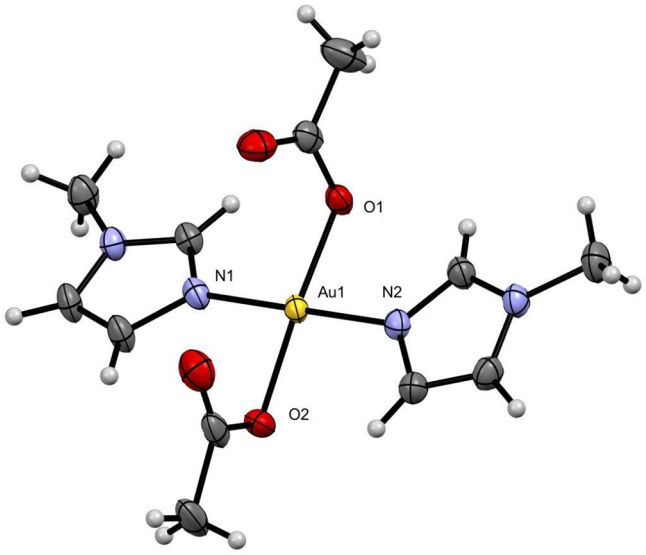


Figure 1. Solid-state structure of **12IM**. Thermal ellipsoids are drawn at the 50% probability level. The triflate anion is omitted for clarity. Selected bond distances (Å): Au1−O1 1.993(2), Au1- O2 1.991(2), Au1−N1 2.004(3), Au1−N2 2.000(3).

Ph). Over a 3 h period, the reaction solution changed from clear yellow to a black suspension, indicative of decomposition products. In ^{1}H NMR of the suspension, both the Au(I) compound **5DMAP** and the biphenyl C−C coupling product corresponding to each boronic acid were observed (Scheme 10).[38] These results are indicative of transmetalation reactivity with boronic acids despite the stronger Au−F bond in **6DMAP**. The likely diarylated intermediate then undergoes reductive elimination with C−C bond formation. A mass spectrum of the reaction mixture shows a small amount of a molecular ion with a mass consistent with this species for both X = H and X = F, but we have not been able to isolate a diarylated compound. 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.

CONCLUSIONS

The reactivity of $[Au(Py)_2F_2]^+$ cations was examined. They are susceptible to both −TMS and −H metathesis reactions to introduce other functionalities onto the Au(III) center. The reactions involving acetylene (C−H) proceed more slowly than for known systems with strong *trans* donors opposite to the Au−F bond. The inability of our system to achieve monosubstitution with a new anionic group *trans* to Au−F indicates that 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 a conventional reaction from $PhI(OAc)_2$, indicating that the Au−F bond may be a useful tool in Au reactivity. Finally, boronic acids react with Au−F, consistent with related reports from other groups, and the consequent C−C bond formation shows that the elementary step of reductive elimination is a consideration in the bis(pyridyl) 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, dried by stirring for 3 days over CaH_2, distilled prior to use, and stored in the glovebox over 3 Å molecular sieves. All NMR spectroscopy was performed on 400 or 500 MHz Bruker spectrometers at 300 K. **6IM**, **6DMAP**, and **7R** species were synthesized via literature procedures.[14,28] 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 glovebox or Schlenk line under dry N_2 gas at room temperature.

X-ray Crystallography Details. Single crystals were selected under Paratone-N 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 of CH_3CN was added **7NMe$_2$** (22 mg, 0.064 mmol). The resulting solution was stirred for 4 days, producing a red solution; volatiles were removed *in vacuo* to give a red solid. ^{1}H NMR identified the product as **8NMe$_2$**, matching known literature data (29 mg, 82% yield).[18]

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

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

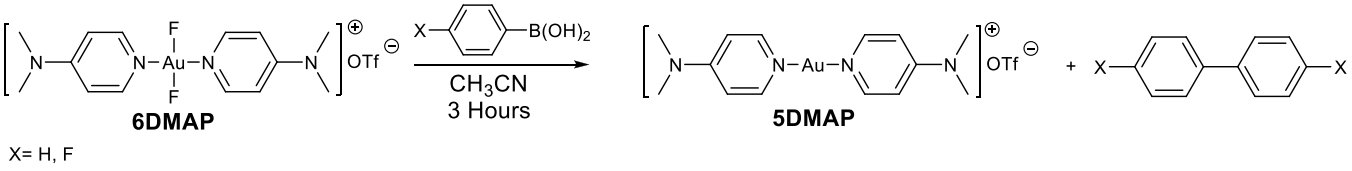
^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 8.78 (t, 4H, J = 6.0 Hz), 8.37 (t, 2H, J = 7.7 Hz), 7.97 (d, 4H, J = 7.8 Hz), 7.86 (d, 4H, J = 7.1 Hz), 6.67 (d, 4H, J = 7.9 Hz), 3.09 (s, 12H).

Synthesis of 11DMAP using 1-Phenyl-2-trimethylsilylacetylene. To a solution of **6DMAP** (39 mg, 0.062 mmol) in 4 mL of CH_3CN was added 1-phenyl-2-trimethylsilylacetylene (37 μL, 0.188 mmol). The solution was stirred for 1 h before being filtered, concentrated *in vacuo*, and treated with Et_2O to give **11DMAP** as a cream-colored 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, 96.9, 40.1. ESI-MS: m/z 643.2 $[Au(DMAP)_2(CC\text{-}Ph)_2]^+$, molecular formula $AuC_{30}H_{30}N_4$, calculated mass 643.21.

Synthesis of 11DMAP using Phenylacetylene. To a solution of **6DMAP** (33 mg, 0.053 mmol) in 4 mL of CH_3CN was added phenylacetylene (14 μL, 0.128 mmol). The resulting solution was stirred for 5 days in darkness before being filtered, concentrated *in*

Scheme 10. Observed Reactivity between Phenylboronic Acids and 6DMAP



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vacuo, and treated with Et_2O to give **11DMAP** as a cream-colored solid (21 mg, 50% yield).

Synthesis of 11IM. To a solution of **6IM** (50 mg, 0.091 mmol) in 4 mL of CH_3CN was added phenylacetylene (22 μL, 0.20 mmol). The resulting solution was stirred for 5 days in darkness prior to being filtered, concentrated to 1 mL, and treated with Et_2O to give **11IM** as a beige solid (40 mg, 62% yield).

^1H 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: m/z 563.1 $[Au(methylimidazole)_2(CC-Ph)_2]^+$, molecular formula $AuC_{24}H_{22}N_4$, calculated mass 563.15.

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 h. Volatiles were removed *in vacuo*, and the residue was redissolved in minimal CH_3CN and treated with Et_2O to give **12IM** as a beige solid (22 mg, 62% yield).

^1H 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: m/z 479.2 $[Au(Methylimidazole)_2(OAc)_2]^+$, molecular formula $AuC_{12}H_{18}N_4O_4$, calculated mass 479.10.

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 h to give 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 give **12DMAP** as a bright orange solid (23 mg, 86% yield).

^1H NMR (400 MHz, CD_3CN): δ (ppm) 7.93 (d, 4H, J = 7.6 Hz), 6.73 (d, 4H, J = 7.6 Hz), 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: m/z 559.2 $[Au(DMAP)_2(OAc)_2]^+$, molecular formula $AuC_{18}H_{26}N_4O_4$, calculated mass 559.16.

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

Reaction of 6DMAP with TMS−CN. To a suspension of **6DMAP** (32 mg, 0.051 mmol) in 5 mL of DCM was added TMS−CN (14 μL, 0.11 mmol). The resulting solution was stirred for 3 h prior to being filtered, concentrated *in vacuo*, and treated with Et_2O to give a bright orange solid composed of **8NMe$_2$**, $[Au(CN)_4]^-$, and triflate anions in a 1:1:2 ratio (24 mg, 72% yield based on gold). The orange solid was dissolved in CD_3CN for analysis via NMR and mass spectrometry.

^{13}C NMR (125 MHz, CD_3CN): δ (ppm) **8NMe$_2$** 157.0, 146.0, 110.5, 40.3; $[Au(CN)_4]^-$ 103.1. ESI-MS: m/z 300.8 $[Au(CN)_4]^-$, Molecular formula AuC_4N_4, calculated mass 300.98; m/z 248.8 $[Au(CN)_2]^-$, molecular formula AuC_2N_4, calculated mass 248.97.

General Procedure for Boronic Acid Reactions. To a suspension of **6DMAP** in $CDCl_3$ was added 2 equiv of the corresponding boronic acid. For both reactions, after 3 h at room temperature a yellow solution with a black suspension was obtained. NMR samples were then taken as direct aliquots of the solution for crude ^1H NMR analysis to observe the biphenyl products.[38] Samples for mass spectrometry were diluted in CH_3CN for analysis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00429.

NMR spectra of reaction mixtures and isolated compounds (PDF)

Accession Codes

CCDC 2009722−2009723 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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