Evidence for Direct Transmetalation of Au^{III}−F with Boronic Acids

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S *Supporting Information*

ABSTRACT: The underlying reactivity of Au^{III}−F species with aryl boronic acids has been studied in detail taking advantage of four novel, stable difluoro-[(C^N)AuF$_2$], arylmonofluoro-[(C^N)AuArF], and alkylmonofluoro-[(C^N)AuAlkF] gold(III) complexes, prepared and isolated in monomeric form. We provide the first experimental evidence for a direct Au^{III}−F/B trans-metalation preceding the Csp^2−Csp^2 or Csp^3−Csp^2 bond formation.

Transmetalation is a fundamental step in metal catalyzed cross-coupling reactions.[1] The prominent role of Suzuki reactions in modern synthetic chemistry[2a] has fostered efforts toward establishing a detailed mechanistic basis for the interaction of boron reagents with Pd^{II} species.[2b−e] Gold-catalyzed oxidative couplings have recently emerged as powerful complementary tools for the efficient formation of Csp^3−Csp^2, Csp^2−Csp^2, and Csp−Csp^2 bonds.[3] Interestingly, boronic acids are involved as productive reaction partners in many of these transformations.[4] While Au^I−B transmetalation has been studied in detail,[5] examples of Au^{III}/B transmetalation are less abundant. Pioneering studies by Bochmann and co-workers showed that κ^3-[(C^N^C)Au(OX)] complexes react smoothly with aryl boronic acids in the absence of external base to produce the corresponding arylation products [(C^N^C)-AuAr].[6] Our group also demonstrated that [(Ph$_3$P)Au(C$_6$F$_5$)-Cl$_2$] react with electron deficient aryl boronic acids (Ar^{F}B-(OH)$_2$) under neutral conditions to form stable [(Ph$_3$P)Au-(C$_6$F$_5$)Ar^{F}Cl] species.[7] These processes showcase the synergistic combination of Au^{III} and B; however, most gold catalyzed oxidative-cross couplings involving boronic acids as reaction partners employ Selectfluor as stoichiometric oxidant, and thus, Au^{III}−F species have been invoked as the key partners of boron species toward the formation of new C−C bonds.[4b−f] Such putative Au^{III}−F intermediates remain largely elusive due to their intrinsic unstable character,[8] and thus, the nature of the interaction Au^{III}−F/B is still a matter of intense discussion. In a seminal contribution toward the understanding of these transformations, Toste et al. showed that *in situ* generated *cis*-[(NHC)AuMeF$_2$] species (NHC: *N*-heterocyclic carbene), in equilibrium with the corresponding dimer, rapidly react with aryl boronic acids to produce toluene derivatives (Scheme 1A).[9] Since the electronics on the boronic acid did not affect the reaction outcome, a single step bimolecular reductive elimination (**I**) rather than a conventional two-step trans-metalation and reductive elimination pathway was proposed for the Csp^3−Csp^2 bond formation, a hypothesis also supported by DFT calculations.[4f] Recently, You et al.[10] managed to establish

Scheme 1. Synthesis and Reactivity of Au^{III}−F with Boronic Acids
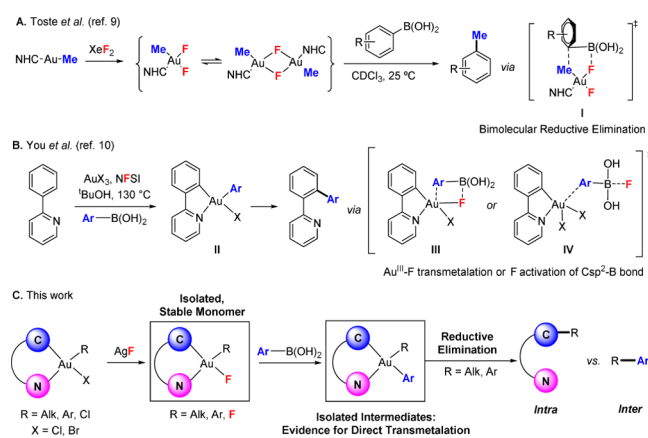
a catalytic cycle in which 2-(aryl)pyridine substrates react with gold in the presence of *N*-fluorobenzenesulfonimide (NFSI) and aryl boronic acids to produce the corresponding cross-coupling products via reductive elimination on biaryl gold(III) intermediate **II** (Scheme 1B).[11] Here, the role of fluorine remains unclear as Csp^2−Au^{III}−F species **III** can be proposed to precede transmetalation, or alternatively, noncoordinated fluoride anions produced *in situ* might be responsible for the C−B cleavage (**IV**).[12] Thus, even if Au^{III} is isoelectronic to Pd^{II}, our understanding of the interaction Au^{III}−F/B and of the specific nature of the individual steps forging the new C−C bonds (direct transmetalation or bimolecular reductive elimination) is still limited and mostly restricted to indirect experimental evidence. Here we present the synthesis of monomeric, easy to handle Csp^2−Au^{III}-bis and monofluoride complexes together with a detailed study on their reactivity with aryl boronic acids. Our results provide experimental evidence for the ability of Au^{III}−F species to undergo "classical" transmetalation with aryl boronic acids by isolation of the corresponding transmetalation products. We also demonstrate that, in contrast to previously studied systems,[9] the product formation is indeed governed by both the electronic and steric features of the organic residue on the boronic acid (Scheme 1C).

As seen in Scheme 1, methods to produce Au^{III}−F species *in situ* have mostly relied on the reaction of (NHC)- or (C^N)-stabilized gold(I) complexes with strong oxidants such as XeF$_2$ or NFSI.[8−10] Recently, our group reported the synthesis of a

novel class of pincer κ^3-[(N^C^C)AuCl] complexes in which a facile Cl/F ligand exchange reaction in the presence of AgF successfully yielded the corresponding fluorides κ^3-[(N^C^C)-AuF].[13] Aware of the ability of 2-phenylpyridine based ligands (C^N) to stabilize electron deprived gold(III) species,[14] *cis*-dichloro-2-(2-fluorophenyl)- and 2-(3,4,5-trimethoxyphenyl)-3-methylpyridine-gold(III) complexes **1** and **2** were treated with AgF in dichloromethane at room temperature producing the corresponding difluorides **3** and **4** in high yields.[15] Interestingly, [(C^N)AuArBr] **5** and [(C^N)AuMeBr] **6**[16] were also efficiently transformed under similar conditions into the corresponding monofluoride species [(C^N)AuRF] **7** (R = 3,5-(CF$_3$)$_2$-C$_6$H$_3$) and **8** (R = Me) (Scheme 2).

Scheme 2. Synthesis of Csp²–Au^{III}-bis and Monofluoride Complexes via Halogen/F Exchange Reactions
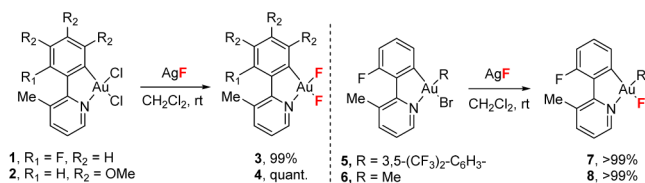
The monomeric structure of Au^{III}–F complexes **3**, **4**, **7**, and **8** could be confirmed by ^{19}F-NMR as well as by successful X-ray diffraction analysis of the corresponding crystals.[17] As expected, the Au^{III}–F bond *trans* to the strong σ-donor aryl ligand is substantially elongated compared to the one *trans* to the pyridino moiety, particularly in the case of electron-rich (C^N) precursors. Distorted square planar geometries were observed for all complexes, with a more acute angle observed in compound **7** compared to that measured in the difluoride complexes **3** and **4** (Figure 1). Differences in the ^{19}F NMR of
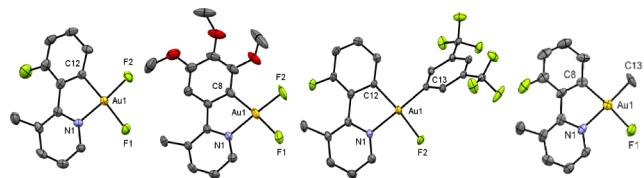

Figure 1. Solid-state molecular structures of (from left to right) [(N^C)AuF$_2$] complexes **3**, **4** and [(N^C)AuRF] **7**, **8** with atoms drawn using 50% probability ellipsoids and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: **3**, Au(1)–F(1) = 2.014(3), Au(1)–F(2) = 1.951(4); **4**, Au(1)–F(1) = 2.025(4), Au(1)–F(2) = 1.940(3); **7**, Au(1)–F(2) = 2.011(4); **8**, Au(1)–F(1) = 2.023(7); and angles [deg]: **3**, N(1)–Au(1)–F(1) = 94.80(17); **4**, N(1)–Au(1)–F(1) = 93.98(16); **7**, N(1)–Au(1)–F(2) = 91.6(2); **8**, N(1)–Au(1)–F(1) = 92.5(3).

these complexes are also diagnostic, with the signals of F-*trans* to the phenyl ring appearing at higher fields compared to those opposite to the pyridino group (**3**: F(1), −252.4 ppm; F(2), −191.8 ppm. **4**: F(1), −281.2 ppm; F(2), −170.8 ppm. **7**: F(2), −208.5 ppm. **8**: F(1), −220.8 ppm).[15]
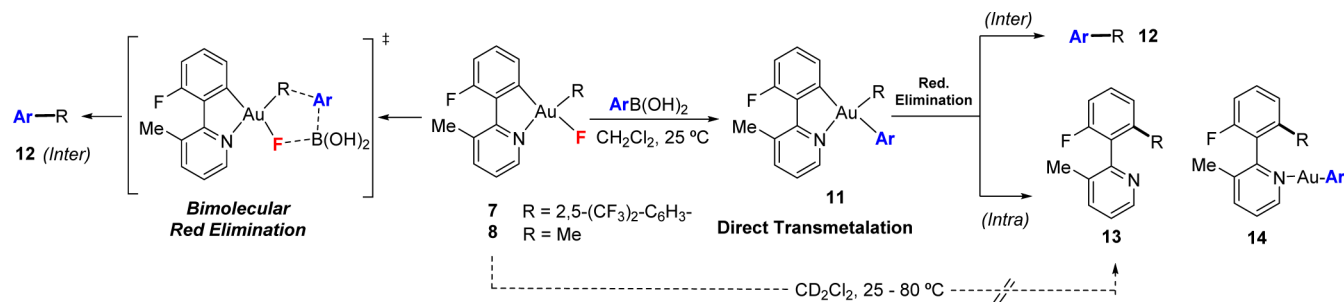
The reactivity of these discrete Csp²–Au^{III}–F complexes with different aryl boronic acids was explored next. Interestingly, the reaction of **3** with two equivalents of (pentafluorophenyl)boronic acid furnished the corresponding bis-aryl complexes [(C^N)Au(C$_6$F$_5$)$_2$] **9a** in 81% yield, thus demonstrating that Csp²–Au^{III}–F species can react with boronic acids via a direct transmetalation (Scheme 3).

Scheme 3. Reaction of [(C^N)AuF$_2$] 3 with Aryl Boronic Acids

R = 2,3,4,5,6-pentafluoro **9a**, 81%   **9b**, -
R = 4-*tert*-butyl   **10a**, -   **10b**, 72%
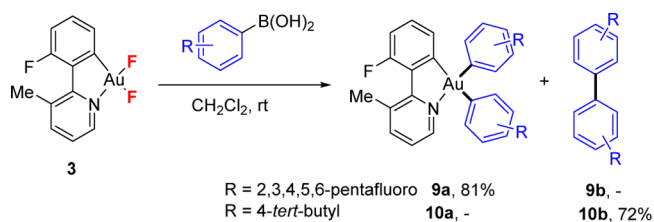
The reaction with (4-*tert*-butylphenyl)boronic acid yielded homocoupling product **10b** in 72% yield as a result of a facile reductive elimination between the two electron-rich aromatic residues. It is important to note that cross-coupling products stemming from a reductive elimination with the 2-phenyl-pyridine ligand were not detected in the reaction mixtures.
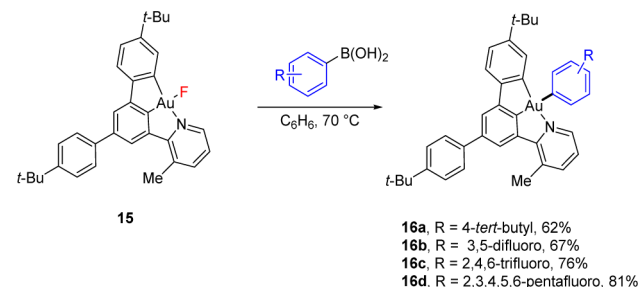
The reactivity of monofluoride complexes **7** and **8** was also investigated. As shown in Table 1, a bimolecular reductive elimination pathway would deliver the *intermolecular* cross-coupling products (**12**). If a direct transmetalation were to take place via **11**, both *intra-* and *intermolecular* reductive elimination products (**12** vs **13/14**)[18] could be observed. The reaction of 4-(*tert*butylphenyl)- and 4-(fluorophenyl)boronic acids (**A**, **B**) with **7** in dichloromethane at room temperature produced both *inter-* (**12A** and **12B**) and *intramolecular* (**13**) reductive elimination products in comparable yields (Table 1, entries 1, 2). Monitoring by ^{1}H NMR the reaction of **7** with 4-(*tert*butylphenyl)boronic acid (**A**) at −40 °C enabled us to detect a new species, which was assigned to transmetalation product **11A**. Upon warming to room temperature, reductive elimination products are observed suggesting that the cross-coupling products observed in entries 1 and 2 can stem from the corresponding direct transmetalation intermediates **11** (see SI).[15] Interestingly, the reaction of **7** with (pentafluorophenyl)-boronic acid (**C**) produced preferentially product **13** in 81% yield showing that sterically encumbered, electron deprived intermediates favor the corresponding *intramolecular* reductive elimination process (entry 3). An equally sterically demanding, but less electronically deprived partner, such as (2,4,6-trifluorophenyl)boronic acid (**D**), enabled the isolation of transmetalation product **11D** in 51% yield (entry 4). Compound **11D** undergoes quantitative reductive elimination to **13** upon heating (see SI).[15] The reaction of complex **8** with 4-(*tert*butylphenyl)boronic acid **A** delivered intermolecular reductive elimination **12A′**, together with homocoupling product **10b** (entry 5).[19] In contrast, the reactions with pentafluorophenyl- and 2,3,6-trifluorophenyl boronic acid furnished exclusively *intramolecular* reductive elimination products **14C** and **14E** in high yields (entries 6, 7). As such, the reaction outcome seems to be governed by both the electronic and steric features of the organic residue on the boron counterpart as well as by the electronic nature of the cycloaurated complex, thus hinting toward the involvement of transmetalation intermediates **11** in these transformations, in contrast to a potential bimolecular reductive elimination pathway in which the electronic features of the boron reagent would not be expected to play such an important role.[9] These results highlight the mechanistic diversity underlying gold-catalyzed oxidative couplings combining Selectfluor and boronic acids. For preliminary results on a catalytic version of these transformations, see section S6 in the SI.[15]

Table 1. Reaction of [(N^C)AuRF] 7 and 8 with Aryl Boronic Acids[a]

			product distribution[b,c]			
entry	starting material[a]	Ar	11	12	13	14
1	7, R = 3,5-(CF$_3$)$_2$-C$_6$H$_3$	4-tBu-C$_6$H$_4$- (A)	–	12A, 57%	40%	–
2	"	4–F-C$_6$H$_4$- (B)	–	12B, 32%	68%	–
3	"	C$_6$F$_5$- (C)	–	–	81%	–
4	"	2,4,6-C$_6$F$_3$H$_2$- (D)	11D, 51%	–	19%	–
5	8, R = Me	4-tBu-C$_6$H$_4$- (A)	–	12A', 33%[d,e]	traces	–
6	"	C$_6$F$_5$- (C)	–	–	–	14C, 88%
7	"	2,3,6-C$_6$F$_3$H$_2$- (E)	–	–	–	14E, 74%

"–": not observed. [a]No intramolecular reductive elimination was observed in complexes 7 and 8 even after prolonged heating at 80 °C.[15] [b]Reaction conditions: ArB(OH)$_2$ (1.2 equiv), CH$_2$Cl$_2$, 25 °C, 30 min to 1 h. [c]Transmetalation intermediates 11A (R = 3,5-(CF$_3$)$_2$-C$_6$H$_3$) and 11A' (R = Me) were observed when the reaction was performed at −40 °C. Warming up the reaction to 25 °C delivers cross coupling products (see SI). [d]29% yield of homocoupling product 10b could be isolated. [e]Reaction with boronic acid B showed a similar outcome.

The ability of Csp²−Au^III−F species to undergo direct transmetalation with aryl boronic acids was further confirmed with κ³-[(N^C^C)AuF] species.[13] As shown in Scheme 4, the

Scheme 4. Reaction of κ³-[(N^C^C)AuF] 15 with Aryl Boronic Acids

16a, R = 4-tert-butyl, 62%
16b, R = 3,5-difluoro, 67%
16c, R = 2,4,6-trifluoro, 76%
16d, R = 2,3,4,5,6-pentafluoro, 81%

reaction of 15 with (4-tertbutylphenyl)boronic acid delivered complex 16a in 62% yield. Pentafluoro-, 3,5-difluoro-, and 2,4,6-trifluorophenyl boronic acids delivered aryl biscyclometalated complexes κ³-[(N^C^C)AuAr] 16b−d in high yields.

These tranformations showcase that a direct transmetalation Au^III−F/B is indeed possible regardless of the electronic nature of the boronic acid provided enough stabilization is in place to prevent the reductive elimination to give a new Csp²−Csp² bond. The structures of complexes 9a, 11D, 14C, 15, 16a, and 16b could be unambiguously established by X-ray diffraction analysis.[17]

In conclusion we report here the synthesis, isolation, and characterization of four novel, difluoro-[(C^N)AuF$_2$], arylmonofluoro-[(C^N)AuArF], and alkylmonofluoro-[(C^N)-AuAlkF] gold(III) complexes isolated in monomeric form via facile X/F exchange reactions. The underlying reactivity of the Au^III−F bond with aryl boronic acids has been studied in detail under neutral reaction conditions. Importantly, we provide the first experimental evidence for a direct Au^III−F/B trans-

metalation preceding the Csp²−Csp² or Csp²−Csp³ bond formation. Our results thus showcase that different mechanistic scenarios can operate in gold-catalyzed oxidative couplings involving Selectfluor and boronic acids.

■ **ASSOCIATED CONTENT**

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b07763.

Compound synthesis and characterization (PDF)
Crystallographic data for compounds 1, 2, 3, 4, 5, 7, 8, 9a, 11D, 14C, 15, 16a, and 16b (CIF)

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Notes
The authors declare no competing financial interest.

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(18) Note that compound **13** shown in Table 1 is formed from the corresponding complexes **14** upon purification via column chromatography in silica gel.

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