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Selective Au–C Cleavage in (C^N^C)Au(III) Aryl and Alkyl Pincer Complexes

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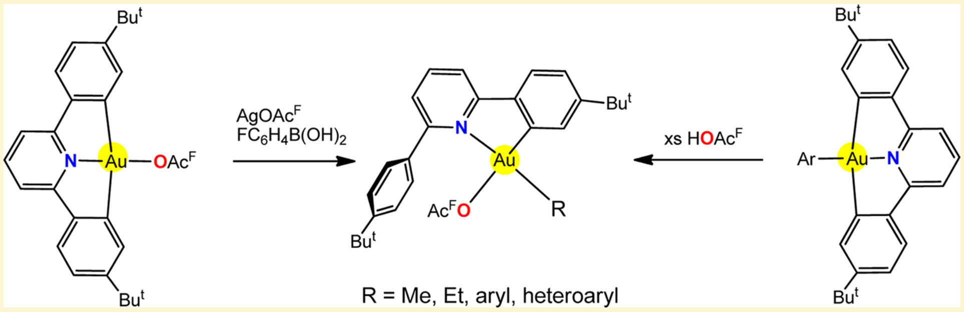
Supporting Information



ABSTRACT: Treatment of gold(III) pincer complexes (C^N^C)*AuX with trifluoroacetic acid (X = C_6F_5, thiophenyl, Me, Et) or of (C^N^C)*AuOAc^F with AgOAc^F/arylboronic acids leads to the selective cleavage of a C–Au bond under mild conditions to give the bidentate complexes (HC-C^N)*Au(X)(OAc^F) [(C^N^C)* = 2,6-($C_6H_3Bu^t)_2$pyridine]. Alkylation of (C^N^C)*Au(OAc^F) with AlR_3 (R = Me, Et) proved to be a high-yielding route to gold(III) alkyls. Au–C cleavage significantly influences reactivity, e.g., with boronic acids. The photoemission of the cleavage product (HC-C^N)*Au(C_6H_4F)(OAc^F) is about an order of magnitude more intense than that of its tridentate parent compound.

Gold(III) complexes with bidentate and tridentate cyclometalated phenylpyridine ligands of the types (C^N)-AuX_2 and (C^N^C)AuX have attracted much attention in recent years, mainly because of their interesting photophysical properties and antitumor activities.[1−4] The pincer complexes (C^N^C)AuX are very attractive since the rigid ligand framework with *trans*-oriented Au–C bonds is particularly structurally and chemically robust and provides excellent stability toward reductive elimination, which is the prevalent reaction path of Au(III) complexes with more labile ligands.[5] It now appears that these C^N^C pincer complexes may be more reactive that previously thought, particularly in the presence of silver salts, which are often components in gold catalyst mixtures.

We have recently reported the synthesis of (C^N^C)*AuX complexes with labile and/or basic ligands X = OAc^F, OMe, and OH (OAc^F = CF_3CO_2), as well as the facile reaction of (C^N^C)*AuOH with arylboronic acids to give gold aryls (C^N^C)*AuAr. The latter show aryl-modulated photoemissions in solution [(C^N^C)* = 2,6-($C_6H_3Bu^t)_2$pyridine].[6] We show here that one of the gold–phenyl bonds of the pincer framework can undergo unexpectedly facile and selective cleavage with AgOAc^F or HOAc^F to give bidentate (C^N)-gold(III) aryls or alkyls.

In contrast to the reaction of boronic acids with (C^N^C)*AuOH, there was no reaction with *p*-fluorophenylboronic acid when (C^N^C)*AuOAc^F (**1**) was used as the starting material. However, we found that in the presence of AgOAc^F **1** was readily converted to a new compound, (HC-C^N)*Au(C_6H_4F)(OAc^F) (**2**), a product of Au–C bond protolysis, which was obtained in 76% yield (Scheme 1). In order to test whether Ag$^+$ was necessary for this cleavage, the aryls (C^N^C)*AuAr (**3a**, Ar = 2-thiophenyl; **3b**, Ar = C_6F_5) were treated with HOAc^F in dichloromethane, which also gave cleanly the Au–C cleaved products **4** and **5**, respectively.[7] Electrophilic attack occurs exclusively on the phenyl-C of the pincer ligand, while the aryl or alkyl ligands *trans* to the pyridine donor are not affected. There is no reaction with weaker acids, such as CH_3COOH.

As the crystal structure of **2** confirms, the reaction is regioselective, leading exclusively to the isomer where the C_6H_4F ligand is located *trans* to the pyridine donor. The crystal structure of **1** was determined for comparison (Figure 1). In the bidentate complex, both the Au–OAc^F and the Au–N distances are significantly elongated compared to **1**, due to the *trans* influence of the strong aryl σ-donor, suggesting a loosening of the pyridine coordination. The Au–O distance of 2.130(5) Å in complex **2** suggests a weak bond to the anion similar to that found in the triflate complex (tpy)Au(Me)(OTf) (2.1382(17) Å) (tpy = *p*-tolylpyridine anion).[8]

In an effort to attempt the synthesis of related gold(III) alkyl complexes, the reaction of **1** with trialkylaluminum reagents was explored, which generated the corresponding complexes (C^N^C)*AuR (**6a**, R = Me; **6b**, R = Et) in yields of 60% and

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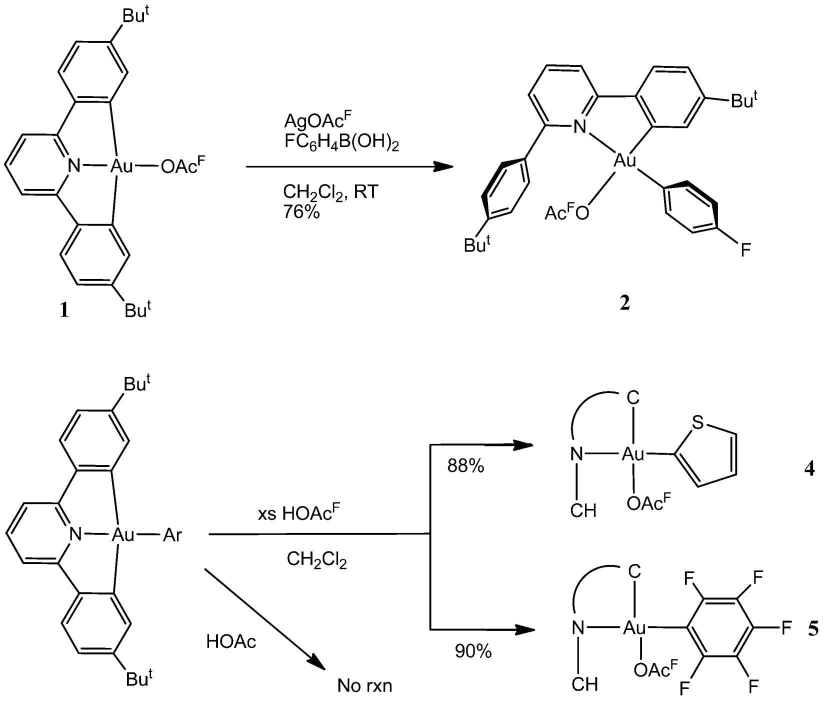
Scheme 1



3a, Ar = 2-C$_4$H$_3$S
3b, Ar = C$_6$F$_5$

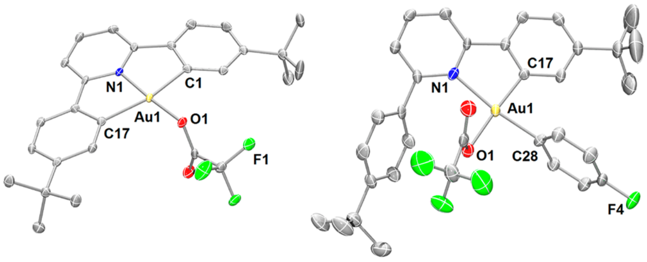


Figure 1. Molecular structures of **1** (left) and **2** (right). Ellipsoids are drawn at 50% probability. Selected bond distances (Å) and angles (deg): **1**: Au−C(1) 2.060(4), Au−C(17) 2.069(4), Au−N 1.959(3), Au−O(1) 2.019(3); N(1)−Au−O(1) 175.46(7). **2**: Au−C(17) 2.017(7), Au−C(28) 2.029(7), Au−O(1) 2.130(5), Au−N(1) 2.164(6); N(1)−Au−C(28) 172.4(2).

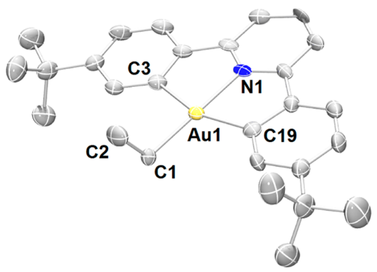


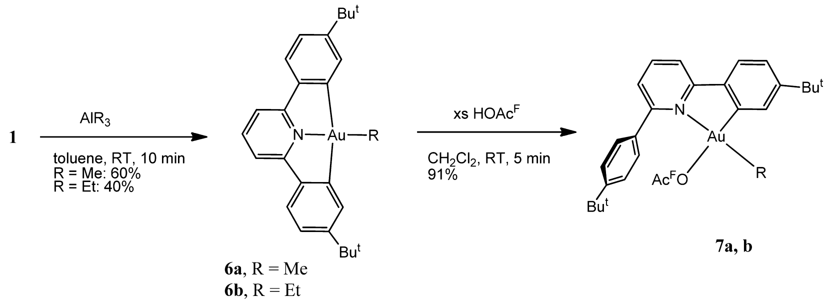
Figure 2. Molecular structure of (C^N^C)*AuEt (**6b**). Ellipsoids are drawn at 50% probability. Selected bond distances (Å) and angles (deg): Au−C(1) 2.042(8), Au−N(1) 2.051(7), Au−C(3) 2.092(8), Au−C(19) 2.075(9); C(1)−Au−N(1) 179.2(3).

40%, respectively, with some losses in the case **6b** due to its high solubility. The structure of **6b** is shown in Figure 2. In line with the *trans* influence of the alkyl σ-donor, the Au−N distance in **6b** is elongated compared to the corresponding Au(III) hydroxide[6] and trifluoroacetate complexes. Treatment of **6a,b** with HOAc^F afforded the expected complexes (HC-C^N)*AuR(OAc^F) **7a,b** in essentially quantitative yields (Scheme 2). Heyn, Tilset, and co-workers recently synthesized the related gold methyl compound (tpy)AuMe(Cl) by alkylation of (tpy)AuCl$_2$ with SnMe$_4$; however, this reaction was accompanied by extensive reduction to gold metal and gave the Au(III) methyl complex in only 8% yield.[8] By contrast, reduction to gold metal was not in evidence during the formation of **6a,b** using aluminum alkyls.

Given that the gold(III) aryls **3** showed interesting photoluminescence,[6] the photoemission behavior of **2** and **4** was investigated for comparison. Surprisingly, bidentate **2** showed a strongly increased solution photoemission intensity and quantum yield ($\Phi_P = 1.0 \times 10^{-1}$) compared to tridentate (C^N^C)*AuC$_6$H$_4$F ($\Phi_P = 1.3 \times 10^{-2}$), while the emission wavelengths of both compounds remain essentially identical (Figure 3).[9] By contrast, compound **1**, which has the same number of C, N, and O donors as **2** but in a different configuration, shows no photoluminescence. Photoemission in (C^N^C)*AuC$_6$H$_4$F is from a ligand-based triplet state and shows vibrational fine structure. This is also observed for **2**. By contrast, the thiophenyl compound **4** luminesces much less strongly than its (C^N^C)-ligated precursor **3a**. The origin of these variations is as yet unclear.

In conclusion, we have shown that tridentate C^N^C gold pincer complexes are readily converted into bidentate analogues by Au−C bond cleavage with AgOAc^F or simply HOAc^F. Such cleavage has a significant impact on reactivity, as shown by the failure of (C^N^C)*AuOAc^F to react with boronic acids unless AgOAc^F is present. Tridentate and bidentate gold alkyl complexes are similarly accessible through high-yielding alkylations with AlR$_3$. In all cases the electrophilic

Scheme 2



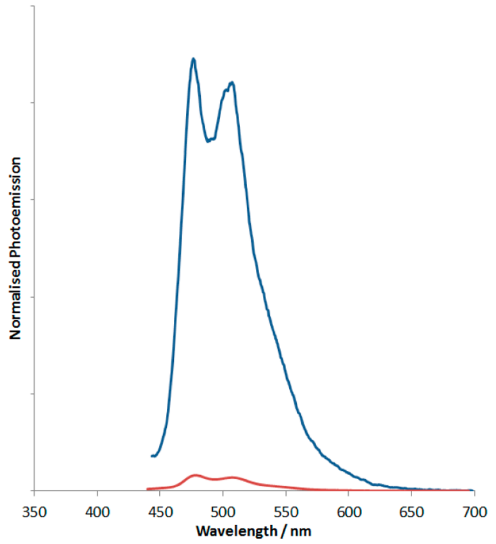


Figure 3. Normalized photoemission of (C^N^C)*Au(C_6H_4F) (red) and complex **2** (blue).

cleavage is selective for the Au−phenyl bond of the pincer ligand, while unconstrained alkyl, aryl, or heteroaryl bonds are not attacked.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and full characterization data (EA, ^{1}H, ^{13}C NMR data for **2**−**7**; crystallographic experimental details and structural data for **1**, **2**, and **6b**). This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(7) A reviewer raised the point that the cleavage may be the result of an Au(III)−Ag$^+$ metallophilic interaction. We believe that the cleavage in the presence of AgOAcF is most simply explained by the generation of HOAc^F by adventitious water.

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