

Gold Fluorides

Gold(I) Fluorohalides: Theory and Experiment

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Dedicated to Prof. Dr. Elena Lalinde on the occasion of her 60th birthday

Abstract: The anionic trifluoromethylgold(I) derivatives $[\text{CF}_3\text{AuX}]^-$, which have been prepared and isolated as their $[\text{PPh}_4]^+$ salts in good yield, undergo thermally induced difluorocarbene extrusion in the gas phase, giving rise to the mixed gold(I) fluorohalide complexes $[\text{F}-\text{Au}-\text{X}]^-$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$). These triatomic species have been detected by tandem mass spectrometry (MS2) experiments and their properties have been analyzed by DFT methods. The CF_2 extrusion mechanism from the $\text{Au}-\text{CF}_3$ moiety serves as a model for the CF_2 insertion into the $\text{Au}-\text{F}$ bond, since both reactivity channels are connected by the microreversibility principle.

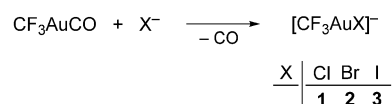
Gold halides are simple chemical species of great theoretical and practical importance.^[1] The binary halides AuX , AuX_2 , AuX_3 , and AuF_5 exhibit quite different properties when associated in the condensed phase or as single molecules,^[2] either in the gas phase or trapped in inert matrices.^[3,4] Thus, genuine gold(II) chloride, AuCl_2 , has only been detected in the gas phase,^[5] whereas a solid with identical stoichiometry is, in fact, a mixed-valence species best formulated as $\text{Au}[\text{Au}^{\text{III}}\text{Cl}_4]$.^[6] Moreover, the instability of gold(I) fluoride, AuF , in the condensed phase seems to derive from intermolecular processes leading to disproportionation into Au^0 and AuF_3 rather than from intrinsic thermodynamic reasons.^[7,8]

On the whole and despite intensive research on the subject, gold fluorides still today remain challenging and rare species; especially those with the metal in low oxidation state.^[9] A few ligand-supported gold(I) fluorides stabilized by neutral donors are currently known. Thus, the AuF moiety is known to form loose complexes with noble gases, FAuNg ($\text{Ng}=\text{Ne}, \text{Ar}, \text{Kr}, \text{Xe}$),^[3,10] and much more robust complexes with NHC ligands

that enable their isolation in the condensed phase: $[\{(\text{NHC})\text{Au}\}_n(\mu-\text{F})]^{(n-1)+}$ ($n=1$ or 2 ; $\text{NHC}=1,3$ -bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene).^[11] To the best of our knowledge, however, no anionic gold(I) fluoride derivative is currently known apart from the symmetric $[\text{AuF}_2]^-$ complex recently detected by Rijs and O'Hair in the sequential decomposition of $[\text{Au}(\text{OAc}^{\text{F}})_2]^-$ in the gas phase ($\text{OAc}^{\text{F}}=\text{CF}_3\text{CO}_2$).^[12]

Herein we report the experimental detection of the whole series of mixed gold(I) fluorohalides $[\text{F}-\text{Au}-\text{X}]^-$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) in the gas phase, together with their optimized equilibrium structures and their calculated stabilities. The mechanism of CF_2 insertion into the $\text{Au}-\text{F}$ bond to give a CF_3 group offers new insight into the relation and mutual transformation of these fundamental C_1 fluorocarbon units.

The trifluoromethylgold(I) derivatives $[\text{PPh}_4][\text{CF}_3\text{AuX}]$ (1–3) are obtained and isolated as pure substances by the procedure used to prepare the bromo derivative,^[13] which involves replacing the highly labile CO ligand in the gold carbonyl derivative CF_3AuCO ^[14] with the corresponding halide (Scheme 1).^[15]



Scheme 1. Method to synthesize the organogold(I) derivatives 1–3 (see the Supporting Information for details). In all cases the cation is $[\text{PPh}_4]^+$.

Geometry optimizations of the mixed $[\text{CF}_3\text{AuX}]^-$ derivatives at the DFT/M06 level of calculation yield linear structures (Figure 1) with the geometric parameters given in Table 1. The optimized geometry of the $[\text{CF}_3\text{AuBr}]^-$ anion in the gas phase shows reasonable agreement with that experimentally established for compound 2 in the solid state (X-ray diffraction).^[13] The $\text{Au}-\text{CF}_3$ distance shows little variation with the halide going from chlorine (206.1 pm) to iodine (208.8 pm), and the $\text{Au}-\text{X}$ distances are just marginally longer than those calculated for the symmetric halides $[\text{AuX}_2]^-$ (Table 1; Supporting Information, Table S1). In the ^{19}F NMR spectra of compounds 1–3, the signal corresponding to the CF_3 group suffers a steady downfield shift with increasing electronegativity of the halide ligand: $\text{I} < \text{Br} < \text{Cl}$ (Supporting Information, Figure S1). This means that the F atoms are deshielded in the same order.

The mononuclear organogold(I) halides 1–3 are thermally stable compounds. To the best of our knowledge, no related

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$[\text{CH}_3\text{AuX}]^-$ species have been obtained yet in the condensed phase, and only recently has the heavier $[\text{CH}_3\text{Au}]^-$ derivative been detected to arise by oxidative addition of $\text{I}-\text{CH}_3$ to the bare Au^- anion in the gas phase.^[16] A related organocopper(I) derivative, $[\text{CF}_3\text{Cu}]^-$, was proposed as a key intermediate in Cu-assisted arene trifluoromethylation processes, but it was not detected.^[17] Compounds 1–3 show reasonable stability towards ligand scrambling that might otherwise lead to the symmetric species $[\text{CF}_3\text{AuCF}_3]^-$ and $[\text{AuX}_2]^-$. In fact, no such rearrangement was experimentally observed to occur in solution at room temperature.^[18] Moreover, given their anionic nature, compounds 1–3 are ideal species for mass-spectrometry studies, which should provide valuable information on fundamental processes taking place at the unimolecular level.^[19]

Negatively charged $[\text{CF}_3\text{AuX}]^-$ complexes are efficiently transferred to the gas-phase by electrospray ionization (ESI) techniques starting from room-temperature $\text{CH}_2\text{Cl}_2/\text{MeOH}$ solutions of the pure compounds 1–3. Their standard MS show no

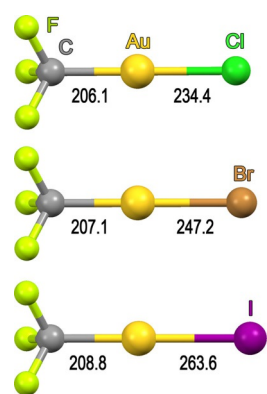


Figure 1. Geometries of the anionic $[\text{CF}_3\text{AuX}]^-$ derivatives optimized at the DFT/M06 level with relevant structural parameters indicated (see Table 1).

sign of ligand scrambling. Upon collision-induced activation of mass-selected $[\text{CF}_3\text{AuX}]^-$ ions, the mixed $[\text{F}-\text{Au}-\text{X}]^-$ ions are formed and clearly detected in all three cases (Figure 2, Scheme 2). These experimental conditions preclude side-reactions, such as ligand scrambling and/or disproportionation that might hinder the preparation of the $[\text{F}-\text{Au}-\text{X}]^-$ species in the condensed phase. Halide dissociation (Scheme 2b) is a competing process that is also observed to occur in all cases (Supporting Information, Figures S2–S4). Calculated $\text{Au}-\text{X}$ bond dissociated energies $[\text{kcal mol}^{-1}]$ in the $[\text{CF}_3\text{AuX}]^-$ complexes are as follows: 68.9 (Cl) > 65.7 (Br) > 63.7 (I).

Table 1. Interatomic distances [pm] in the equilibrium structures obtained for the linear $[\text{CF}_3\text{AuX}]^-$ and $[\text{FAuX}]^-$ anions at the DFT/M06 level of calculation. ^[a]						
	$[\text{CF}_3\text{AuX}]^-$		$[\text{FAuX}]^-$		$[\text{AuX}_2]^-$	$\text{AuX}^{[b]}$
X	Au–C ^[c]	Au–X	Au–F ^[d]	Au–X	Au–X	Au–X
Cl	206.1	234.4	201.3	229.7	231.8	222.6
Br	207.1 ^[e]	247.2 ^[e]	201.9	242.1	244.7	233.9
I	208.8	263.6	202.9	257.3	261.7	250.6

[a] Data corresponding to symmetric $[\text{AuX}_2]^-$ anions and diatomic AuX molecules are also included for comparison. All the triatomic species are exactly linear, as are the $[\text{CF}_3\text{AuX}]^-$ anions. [b] Values taken from Ref. [21]. [c] Similar Au–C distances were found in the crystal structures of the homoleptic salts $[\text{N}(\text{PPh}_3)_2][\text{Au}(\text{CF}_3)_2]$ (206.5(6) pm)^[36] and $[\text{PPh}_4][\text{Au}(\text{CF}_3)_2]$ (203.3(2) pm).^[14a] [d] In the free diatomic AuF molecule, $\text{Au}-\text{F} = 191.84$ pm.^[8] [e] Experimental interatomic distances in the crystal of $[\text{PPh}_4][\text{CF}_3\text{AuBr}]$ are as follows: $\text{Au}-\text{C}$ 211.9(5) pm and $\text{Au}-\text{Br}$ 240.5(1) pm.^[13]

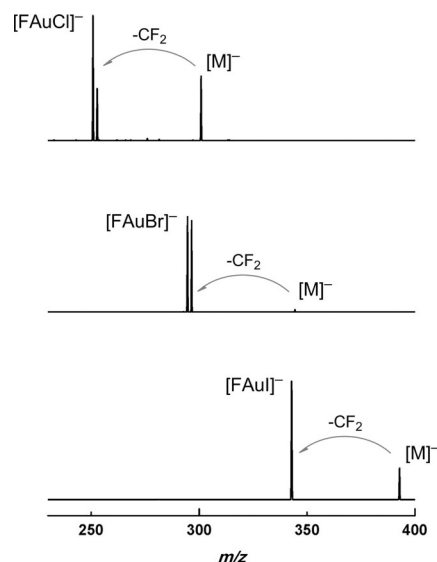
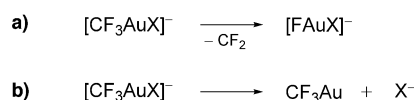


Figure 2. Detection of the mixed $[\text{FAuX}]^-$ anions ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) formed by collision-induced dissociation of the corresponding $[\text{CF}_3\text{AuX}]^-$ species (labeled $[\text{M}]^-$) in quadrupole ion-trap MS^2 experiments.



Scheme 2. Competing dissociation processes undergone by the $[\text{CF}_3\text{AuX}]^-$ anions in the gas phase.

Geometry optimizations of the triatomic $[\text{F}-\text{Au}-\text{X}]^-$ anions were performed to find out their structural arrangement and the results were characterized vibrationally (see the Supporting Information for details). All three anions show a linear structure with $C_{\infty v}$ symmetry (Figure 3) and the interatomic distances given in Table 1. Taking the neutral diatomic AuF molecule as a reference ($\text{Au}-\text{F}$ 191.84 pm),^[8] the coordination of an additional X^- ligand results in elongation of the $\text{Au}-\text{F}$ bond by ca. 10 pm,^[20] thus becoming comparable to the bond length observed in the neutral $\text{FAu}(\text{NHC})$ complex ($\text{Au}-\text{F}$ 202.8(8) pm).^[11b] In the same way, the $\text{Au}-\text{X}$ bond is elongated by a similar amount with respect to the diatomic AuX molecules^[21] upon F^- coordination. Addition of F^- to the heavier gold halides, AuX , was precisely the method originally suggested by Schwerdtfeger to prepare the mixed $[\text{F}-\text{Au}-\text{X}]^-$ derivatives.^[22] However, we are not aware that this method has yielded any positive results so far.

In the absence of external acids,^[23] decomposition of trifluoromethyl metal derivatives is commonly assumed to follow the tautomeric equilibrium shown in Scheme 3a as identified by

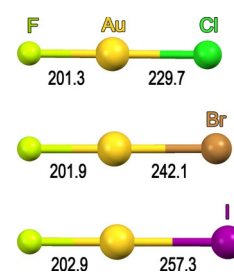
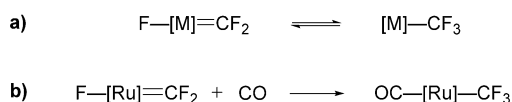


Figure 3. Geometries of the mixed $[\text{FAuX}]^-$ anions optimized at the DFT/M06 level with relevant structural parameters indicated (see Table 1).



Scheme 3. Tautomeric equilibrium applying to trifluoromethyl metal derivatives: a) in general, and b) evidenced in ruthenium(II) systems; [Ru] = (R₃P)RuH(CO) and PR₃ = P*i*Pr₃, P*Me*tBu₂.^[24]

Caulton in organoruthenium systems (Scheme 3b).^[24] This mechanism was also suggested to apply to the decomposition of [CF₃MR]⁻ ions in the gas phase (M = Cu, Ag, Au; R = F, CF₃, OAc^F).^[12] With regard to our own system, this mechanism is commented on in detail in the Supporting Information.

We have now found a lower-energy path for the [CF₃AuX]⁻ decomposition that differs from the standard mechanism as no difluorocarbene metal intermediate [M]CF₂ is involved. This alternative mechanism (Figure 4) comprises the following

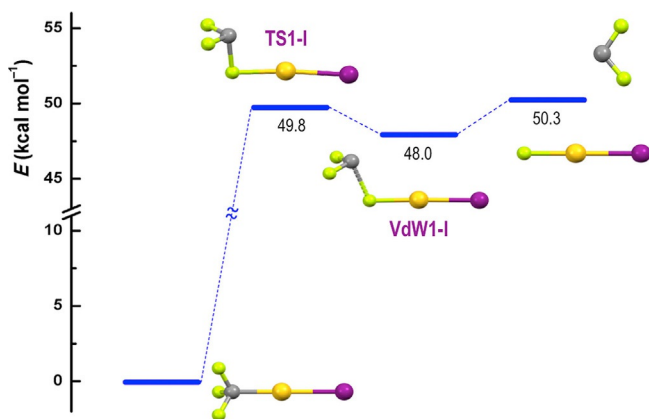
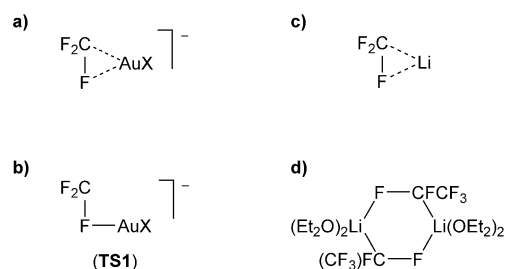


Figure 4. Energy profile of the lower-energy CF₂ extrusion path from the organogold [CF₃Au]⁻ derivative (see the Supporting Information, Figures S7 and S8 for structural details of the intermediates involved). The same but reverse profile applies to the CF₂ insertion into the Au–F bond. For color code, see Figure 1.

steps: 1) weakening of the Au–C bond in favor of a Au–F bond through a transient η²-coordinated F₂C–F unit (Scheme 4a); 2) complete loss of the Au–C interaction in the transition state (TS1), which features an uncommon fluoride-bridging F₂C–F–[Au] unit (Scheme 4b); and 3) release of the unsaturated :CF₂ unit from the ensuing van der Waals complex (VdW1) that leaves the triatomic [F–Au–X]⁻ species. The last step involves just a small dissociation threshold of <3 kcal mol⁻¹.

Owing to the microreversibility principle, the mechanism just discussed also applies to the :CF₂ insertion into the Au–F bond. Thus, the interaction of free :CF₂ with the electron density of the F ligand results in slight stabilization and entails little structural modification in any of the moieties involved. This interaction confirms the inherently ambiphilic character of the singlet fluorinated divalent carbon atom that bears both a lone pair and an empty p orbital, the latter being involved in partial F(p)→C(p) π-donation.^[25–29] The strengthening of this



Scheme 4. Structural patterns involving C–F···M interactions: a) transient species formed upon thermal excitation of [CF₃AuX]⁻; b) transition state in the CF₂ extrusion/insertion path given in Figure 4 (see the Supporting Information, Figure S7 for structural details); c) global minimum calculated for LiCF₃ in the gas phase;^[33a] d) central core of the Li(CF₂CF₃)₂·2Et₂O dimer in the crystal.^[32]

F₂C···F–[Au] interaction in the initial van der Waals complex leads to significant elongation of the Au–F bond, which, in the transition state (Au–F ca. 215 pm; Scheme 4b), is substantially longer than in the fluoride-bridged dinuclear complex [((NHC)Au)₂(μ-F)][BF₄] (Au–F 206.0(1) pm).^[11a] The metallotropic shift from F to C through a transient Au(η²-F–CF₂) species (Scheme 4a) leads to the final insertion product [CF₃AuX]⁻. Along the reaction path, the carbon atom gradually increases the number of substituents from two in the initial carbene to three in the transition state and four in the final product. The global insertion process takes place in an almost barrierless way and results in large stabilization, so it might be experimentally feasible.^[30]

It is worth noting that the structures of both the transition state and the transient species referred to in the mechanism just discussed find support in the chemistry of lithium carbenoids.^[31] Thus, the bridging role of the F–C unit was substantiated in the crystal structure of the Li(CF₂CF₃)₂·2Et₂O dimer (Scheme 4d),^[32] while a Li(η²-F–CF₂) interaction was found to be the global minimum for LiCF₃ in the gas phase (Scheme 4c).^[33] Both perfluoroalkyl lithium systems are known to release the corresponding fluorinated carbene upon LiF elimination in a sometimes violent process.^[34] Considering that our gold systems also release CF₂ without the need of any actual metal carbene intermediate, they can properly be termed gold carbenoids.^[35]

In summary, the anionic organogold(I) [CF₃AuX]⁻ complexes (X = Cl, Br, I) are found to perform as gold carbenoids, since they undergo CF₂ extrusion in the gas phase affording the mixed gold(I) fluorohalide [F–Au–X]⁻ complexes. The experimental detection of these simple, triatomic species demonstrates that AuF can indeed be stabilized by heavier-halide coordination, as formerly suggested by Schwerdtfeger.^[22] These species might, however, be difficult to isolate in the condensed phase unless facile ligand scrambling is precluded. An unconventional CF₂ insertion/extrusion mechanism not involving any metal carbene intermediate has been identified, which might be relevant to difluoromethylation processes mediated by late transition metals.

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Keywords: difluorocarbene · gold carbenoids · gold fluorides · organogold compounds · trifluoromethyl compounds

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