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Gold(II) Halide Complexes, [AuX₃]⁻, from Organogold(III) Precursors

Miguel Baya,[a] Alberto Pérez-Bitrián,[a] Sonia Martínez-Salvador,[a] Antonio Martín,[a] José M. Casas,[a] Babil Menjón*[a], and Jesús Orduna[b]

Dedicated to Dr. Cristina Bohanna on the occasion of her 50th birthday

Abstract: The mononuclear gold(II) halide complexes [AuCl₃]⁻ and [AuBr₃]⁻ are formed in the gas phase by collision-induced homolytic splitting of the only Au–C bond in the monoalkylgold(III) precursors [CF₃AuX₃]⁻. The geometries of the whole series of [AuX₃]⁻ complexes (X = F, Cl, Br, I) have been calculated by DFT methods. It has also been found that the neutral AuX₂ molecules behave as unsaturated species, showing significant affinity for an additional X⁻ ligand. Moreover, in the open-shell [AuX₃]⁻ anions, homolytic splitting of one of the Au–X bonds and formation of the lower-valent [AuX₂]⁻ anions is favored over non-reducing halide dissociation. They should therefore be prone to undergo disproportionation.

Since the indirect detection of triatomic AuX₂ halides in the gas phase (X = Cl, Br),[1] there has been increasing interest in the study of mononuclear gold(II) halides, pseudohalides and the like.[2,3] These open-shell d⁹ derivatives, however, are elusive in the condensed phase,[4–7] and their detection has been possible thanks to unimolecular techniques either in matrices or in the gas phase.[3,8] Little is known, however, about their chemical behavior thus far.[9] Here we report on the unexpected formation of the mononuclear [AuCl₃]⁻ and [AuBr₃]⁻ anions by homolytic splitting of the only Au–C bond in the monoalkyl gold(III) precursors [CF₃AuX₃]⁻ (X = Cl, Br) in the gas phase. This experimental detection prompted us to evaluate the affinity of the neutral AuX₂ halides for an additional X⁻ ligand to afford the [AuX₃]⁻ anions (ligand association) as well as the relationship of the latter singly-charged species with their oxidized neutral AuX₃ counterparts (redox processes).

The monoalkyl gold(III) derivatives [PPh₄][CF₃AuX₃] (X = Cl, Br, I) have been prepared by X₂ addition to the corresponding organogold(I) precursor [PPh₄][CF₃AuX] (Scheme 1). They have been isolated as stable solids in good yields. The coordination environment of the gold center changes from linear to square-planar upon oxidation (Figure 1).[10] In the ¹⁹F NMR spectra of the oxidized species **2**, the CF₃ signals show steady upfield shift with increasing the electronegativity of the halide (Figure S1). This trend is opposite to that observed in their corresponding gold(I) precursors **1**.[11] It is worth noting that the anion of **2a** as

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well as the fluoro-complex [CF₃AuF₃]⁻ had been previously detected in solution,[12] but not isolated.[13]
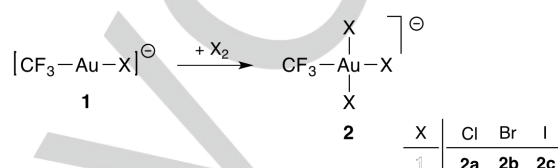
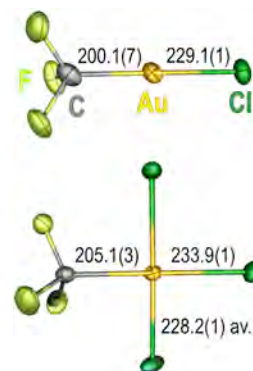**Scheme 1.** Synthesis of the anionic monoalkylgold(III) derivatives **2**. In all cases the cation is [PPh₄]⁺.

Figure 1. Displacement-ellipsoid diagrams (50% probability) of the [CF₃AuCl]⁻ and [CF₃AuCl₃]⁻ anions as found in single crystals of **1a** and **2a**. Selected bond lengths (pm) and atom labeling as indicated.

In contrast to the well-established chemistry of arylgold(III) derivatives with a single Au–C bond,[14] monoalkylgold(III) complexes are still rare.[15] In fact, no alkyl [RAuX₃]⁻ species seems to have been isolated thus far.

Aiming to gain insight into the fundamental properties of our monoalkylgold(III) complexes **2**, the unimolecular decomposition of the [CF₃AuX₃]⁻ anions was studied in the gas phase by tandem mass spectrometry (Figures S4–S8).[16] The iodo-derivative [CF₃AuI₃]⁻ cleanly undergoes iodine elimination regenerating the parent species [CF₃AuI]⁻ in the reverse process of that given in Scheme 1.[17] All the decomposition paths undergone by the lighter species [CF₃AuCl₃]⁻ and [CF₃AuBr₃]⁻ also involve reduction (Scheme 2). Thus, elimination of CF₃X or X₂ results in two-electron reduction (reductive elimination). Quite unexpectedly, however, a one-electron reduction is also detected, which involves the homolytic cleavage of the Au–CF₃ bond and formation of the [AuX₃]⁻ anion. Such three-coordinate gold(II) species had been suggested to be involved in the chemical, photochemical or radiolytic reduction of the square-

planar $[AuX_4]^-$ complexes.[18] Recently, the $[AuCl_3]^-$ anion was observed to arise by fragmentation of $[AuCl_4]^-$ in a photochemically excited state.[19] We have additionally found that collision-induced dissociation of the $[AuX_3]^-$ species (X = Cl, Br) proceeds under homolytic splitting of a Au–X bond and formation of the gold(I) linear derivatives $[AuX_2]^-$ (Figures S9 and S10). No halide dissociation was observed in any of the fragmentation processes discussed.
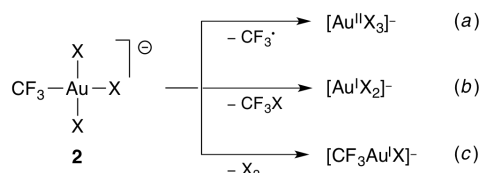
Scheme 2. General fragmentation paths observed for the monoalkylgold(III) derivatives **2** in the gas phase (Figures S4–S8). They involve metal reduction by one (path *a*) or two units (paths *b* and *c*). Path *b* is common to all three halogens (X = Cl, Br, I), whereas halogen dissociation (path *c*) is not observed for **2a** (X = Cl) and the radical path (*a*) is not observed for **2c** (X = I).

Homolytic cleavage of M–C bonds is a fundamental process widely found in main-group organoelement chemistry,[20] but much less common in organotransition-metal compounds.[21] The Au–C homolysis observed in our trifluoromethyl compounds **2** seems to be a distinct feature of these monoalkylgold(III) complexes.[22] The calculated Au–C bond enthalpy is shown in Table 1.
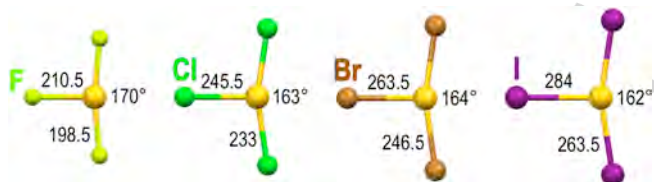
Figure 2. T-shaped polytopes for the $[AuX_3]^-$ anions optimized at the DFT/M06 level and identified as minima in the potential energy surface. Selected bond lengths [pm] and angles [°] are indicated together with atom labeling.

We have optimized the geometries of the whole series of $[AuX_3]^-$ anions[23] and have found that the T-shaped structures are energy minima in all cases (Figure 2). On the other hand, Y-shaped structures are identified as transition states (Figure S16). Trigonal planar or pyramidal polytopes are not stationary points in any of these systems. The T-shaped structures of these open-shell, anionic $[AuX_3]^-$ species (d^9) show noticeable differences with those of the monomeric, diamagnetic AuX_3 molecules (d^8), which had been thoroughly studied by theoretical and experimental methods.[3,24,25] First, they are energy minima for all halide ligands, including iodide (Figure 2), whereas in the neutral case, monomeric AuI_3 is better described as a side-on iodine adduct of gold(I) iodide: $IAu(I_2)$.[25,26] The Au–X distances within each T-shaped neutral AuX_3 molecule are all virtually identical (Figure S14).[25a] In the $[AuX_3]^-$ anions, however, the Au–X distance in the stem of the T is consistently longer by ~15

pm than those found in the crosspiece (Figure 2). This difference can be ascribed to the fact that the spin density in the open-shell complexes is located mainly in the stem axis (Figure 3). It is worth noting that the spin density gradually shifts along this axis from the metal to the X ligand on going down the halogen group (Table 1). The relationship between the mononuclear, T-shaped $[AuX_3]^-$ and AuX_3 species is given by the vertical electron-detachment energy of the former or the electron affinity of the later (Scheme 3). The large values calculated (Table 1) qualify even the heaviest T-shaped AuX_3 species as superhalogens.[27]
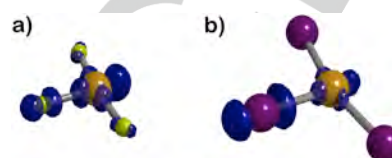
Figure 3. Spin density contour of (a) the lightest $[AuF_3]^-$ and (b) the heaviest $[AuI_3]^-$ anions according to the values given in Table 1. (Full set in Figure S15)

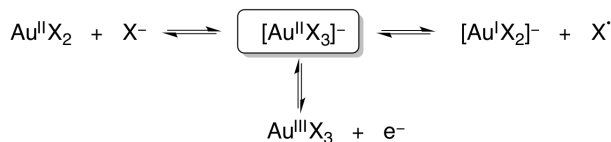**Table 1.** Relevant parameters calculated for the mononuclear $[AuX_3]^-$ species[a]

	X = F	X = Cl	X = Br	X = I
$[X_3Au–CF_3]^-$ bond enthalpy [kJ mol^{-1}]	278	208	183	155
X^- dissociation enthalpy [kJ mol^{-1}][b]	290	219	201	179
$X^•$ dissociation enthalpy [kJ mol^{-1}][c]	166	120	90	81
vertical detachment energy [eV][d]	5.19	4.90	4.71	4.26
adiabatic detachment energy [eV][e]	4.64	4.56	4.41	3.82
spin density on Au (%)[f]	62	42	31	21
spin density on stem X (%)[f]	26	37	46	52

[a] All the indicated properties and processes involve T-shaped minima (Figure 2) and have been calculated in the gas phase. [b] Heterolytic Au–X dissociation enthalpy as indicated in Scheme 3 (left). [c] Homolytic Au–X bond dissociation enthalpy as indicated in Scheme 3 (right). [d] The oxidized species is in an excited state. [e] The oxidized species is in the ground state. [f] Based on Mulliken charges and populations; the unassigned spin density is located symmetrically on the X ligands at the crosspiece (*cf.* Figure S15).

We have found that the neutral AuX_2 molecules behave as typical unsaturated species. Thus, the coordination of an additional X^- ligand (Scheme 3, left) is clearly exergonic in all cases (Table 1) with enthalpy values between −179 (X = I) and −290 (X = F) kJ mol^{-1} in the gas phase, which denotes significant ligand affinity. The least endergonic fragmentation process of these $[AuX_3]^-$ anions, however, does not involve dissociation of a X^- ligand (reverse process), but rather homolytic cleavage of a Au–X bond with release of a halogen atom $X^•$ and formation of the linear $[AuX_2]^-$ anions (Scheme 3, right). This lower-energy decomposition channel (Table 1) has been actually established to operate on the $[AuCl_3]^-$ and $[AuBr_3]^-$

anions by MS^3 experiments (Figures S9 and S10) as indicated above. The ability of Au^{II} to oxidize X$^-$ ligands to X$^\bullet$ atoms indicates a marked tendency of the species under study to undergo disproportionation.[28]

$$Au^{II}X_2 + X^- \rightleftharpoons [Au^{II}X_3]^- \rightleftharpoons [Au^IX_2]^- + X^\bullet$$

$$[Au^{II}X_3]^- \rightleftharpoons Au^{III}X_3 + e^-$$

Scheme 3. Processes connecting the anionic gold(II) [AuX$_3$]$^-$ complexes with relevant neighbor species.

In brief, the gold(II) halide complexes [AuX$_3$]$^-$ (X = Cl, Br) arise from the organogold(III) precursors [CF$_3$AuX$_3$]$^-$ by Au–C homolytic cleavage in the gas phase. The neutral AuX$_2$ molecules attain substantial stabilization by halide coordination. The [AuX$_3$]$^-$ anions thereby formed show T-shaped structures as energy minima for all halides. Dissociation of X$^\bullet$ atoms from these anions with one-electron metal reduction is energetically favored over halide dissociation even at the unimolecular level. This radical process underlies the tendency of simple gold(II) species to undergo dismutation. The [AuX$_3$]$^-$ anions (d^9) build the open-shell bridge between the diamagnetic neighbors, [PtX$_3$]$^-$ (d^8)[29] and [HgX$_3$]$^-$ (d^{10}),[30] of the relativistic triad.

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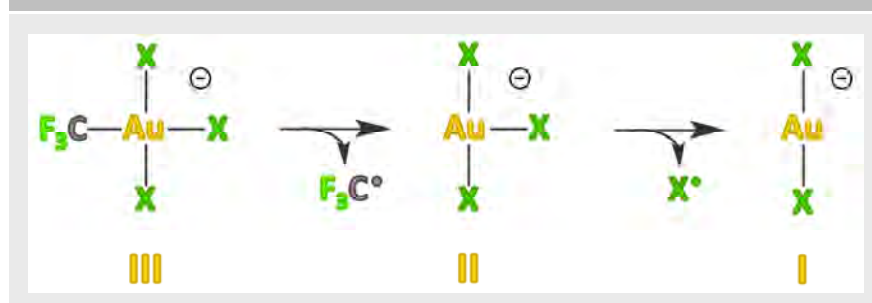
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Golden Countdown: One-electron reductions in cascade are observed for the monoalkylgold(III) [CF$_3$AuX$_3$]$^-$ complexes in the gas phase (X = Cl, Br) that result from the stepwise homolytic cleavage of Au–C and Au–X bonds.