

A Carbene-Stabilized Gold(I) Fluoride: Synthesis and Theory

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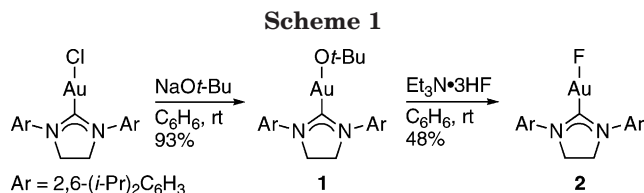
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Summary: The first isolable gold(I) fluoride complex, stabilized by an *N*-heterocyclic carbene (NHC) ligand, has been isolated in two-coordinate monomeric form. DFT calculations show significant $p\pi/d\pi$ interactions between fluoride and gold(I) and indicate a substantial negative charge on fluorine.

Fluoride complexes of the late transition metals raise interesting questions in bonding and display unusual reactivity. The fluoride ion, according to hard/soft acid–base theory,¹ is mismatched with the cations formed by late transition metals in low oxidation states. Its π -donating ability, moreover, can lead to destabilizing interactions with filled *d* orbitals.^{2–5} The resulting metal–fluorine bonds tend to be labile and reactive.³ Such complexes have excited considerable synthetic interest, greatly intensified in recent years;⁴ they have been studied in the context of C–F bond cleavage⁵ and formation⁶ and as precatalysts in a wide range of other organic transformations.⁷

Perhaps the most mismatched of all transition-metal fluorides, gold(I) fluoride, was once thought impossible to prepare.⁸ Only recently detected in the gas phase, AuF has been studied as a discrete molecule,⁹ and as noble gas^{10a,b} and CO^{10c} adducts. *N*-Heterocyclic carbene (NHC) ligands,¹¹ particularly of the type developed by Arduengo and co-workers,¹² appeared ideally suited



to the stabilization of a molecular gold(I) fluoride complex. Such ligands have found recent use in the synthesis of new gold complexes,^{13,14a} and the nature of the bonding between NHCs and group 11 metals has been investigated theoretically.¹⁴ This report describes the synthesis of the first isolable fluoride of gold(I). Density functional calculations find significant splitting of the metal *d*-orbital energies through σ and π interactions with fluorine. The considerable negative charge on fluorine leads to weak hydrogen-bonding interactions with the C–H bonds of dichloromethane.

The known (SIPr)AuCl^{13g} (SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) is converted to (SIPr)-AuOt-Bu (**1**) in high yield by reaction with 1 equiv of NaOt-Bu in benzene solution (Scheme 1). An analogous route has been used to prepare (phosphine)gold(I) alkoxides; relatively few in number, these complexes display interesting reactivity based on the lability of the gold(I)–alkoxide bond.^{15,16} This first (NHC)gold(I) alkoxide is expected to be a versatile precursor to other new gold(I) complexes.

Addition of 1 equiv of HF, in the relatively benign form of triethylamine tris(hydrofluoride) (Et₃N·3HF), to

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a benzene solution of **1** resulted in the formation of a colorless precipitate. The product after filtering, washing, and drying in vacuo was identified by ^1H NMR as unsolvated (SIPr)gold(I) fluoride (**2**). Small amounts of a byproduct complex, as yet unidentified, must be removed by recrystallization to obtain analytically pure samples. Although the use of $\text{Et}_3\text{N}\cdot 3\text{HF}$ to generate late-transition-metal fluorides by protonolysis of a suitable precursor is well established,^{6a,17} no reports describe the isolation of a gold(I) fluoride by this (or any other) method. It is worth noting that treatment of $(\text{Ph}_3\text{P})\text{AuCl}$ with AgF leads to the formation of $\{[(\text{Ph}_3\text{P})\text{Au}]_3\text{O}\}^+[\text{H}_2\text{F}_3]^-$ and that the gold(I)–oxo bonds do not react with the dihydrotrifluoride anion to form gold(I)–fluoride bonds.¹⁸

In the solid state, **2** is stable indefinitely when protected from light. In CD_2Cl_2 solution, complex **2** displays substantial decomposition after 1 day ($\sim 25\%$) to a mixture of unidentified byproducts, as judged by ^1H NMR. The ^{19}F NMR spectrum of **2** shows a single peak at -247.0 ppm. In the ^{13}C NMR spectrum, the resonance for the gold-bound carbon is split into a doublet by dipolar coupling to fluorine ($^2J_{\text{C-F}} = 61$ Hz), indicating that the complex is monomeric in solution. The IR spectrum of **2** shows a strong band, absent from the spectrum of $(\text{SIPr})\text{AuCl}$, at 500 cm^{-1} , similar to the frequency estimated for Au-F ($\omega_e \approx 500\text{ cm}^{-1}$) in the gas phase.^{9b}

Single crystals of **2** were grown by vapor diffusion of hexanes into a concentrated CH_2Cl_2 solution. Analysis by X-ray diffraction (Figure 1)¹⁹ reveals a monomeric structure, with nearly linear coordination geometry, in the solid state. The gold–fluorine bond length ($2.0281(17)$ Å) is slightly longer than that determined for AuF in the gas phase (1.918 Å).^{9b} Two CH_2Cl_2 molecules were also present in the asymmetric unit, with calculated positions of solvent C–H bonds closely approaching the fluoride. Similar hydrogen-bonding interactions have also been observed by Grushin and co-workers for the dimeric $[(\text{Cy}_3\text{P})\text{Pd}(\text{Ph})\text{F}]_2$.²⁰ The closest separation between Au centers, at $8.1779(3)$ Å, is much more than twice the van der Waals radius of Au (1.66 Å) and falls well outside those observed for complexes with aurophilic Au–Au interactions.²¹

To understand the gold–fluorine interactions in **2**, we have carried out density functional calculations on the model complex **A**, in which the N-aryl groups of **2** are replaced by hydrogen. Implicit solvation by CH_2Cl_2 was included in all calculations through the polarizable continuum model of Tomasi and collaborators.²² Geom-

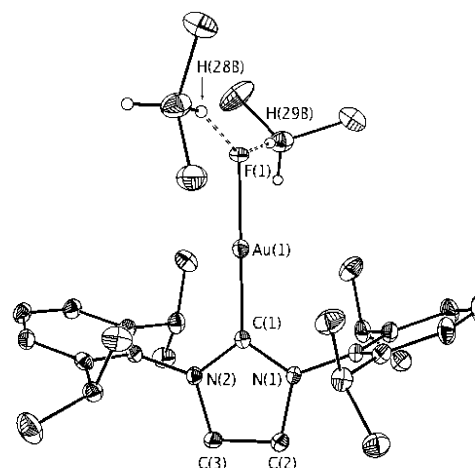


Figure 1. X-ray crystal structure of the gold fluoride **2**· $2\text{CH}_2\text{Cl}_2$, shown as 50% ellipsoids. Solvent hydrogen atoms are calculated; ligand hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): $\text{Au}(1)\text{--F}(1) = 2.0281(17)$, $\text{Au}(1)\text{--C}(1) = 1.956(3)$, $\text{C}(1)\text{--N}(1) = 1.338(3)$, $\text{C}(1)\text{--N}(2) = 1.342(3)$, $\text{N}(1)\text{--C}(2) = 1.472(4)$, $\text{N}(2)\text{--C}(3) = 1.481(3)$, $\text{C}(2)\text{--C}(3) = 1.534(4)$, $\text{F}(1)\text{--H}(28\text{B}) = 2.287$, $\text{F}(1)\text{--H}(29\text{B}) = 2.243$; $\text{C}(1)\text{--Au}(1)\text{--F}(1) = 177.22(9)$, $\text{N}(1)\text{--C}(1)\text{--N}(2) = 108.7(3)$.

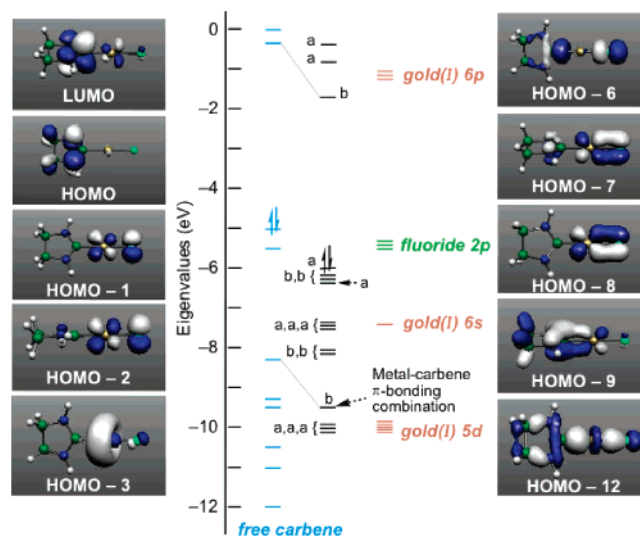


Figure 2. Kohn–Sham orbital energy-level diagram for the gold model complex **A**. Orbital eigenvalues of the carbene are those of the geometry-optimized, free ligand; those of gold are of Au^+ , and those of fluorine are of F^- . All values include implicit solvation by CH_2Cl_2 ($\epsilon = 8.93$) at 298.15 K. Images of selected orbitals are given in the insets.

etry optimizations converged to potential-energy minima having all-real calculated vibrational frequencies. Figure 2 gives an orbital energy level diagram, with images of selected molecular orbitals.

The highest occupied Kohn–Sham orbital (HOMO) of **A** arises from the NHC π system, with contributions from the four backbone C–H bonding orbitals. Three orbitals resulting from gold–fluoride interactions are only slightly lower in energy. The two molecular orbitals

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(19) Crystal data for $\text{C}_{27}\text{H}_{38}\text{N}_2\text{AuF}\cdot 2\text{CH}_2\text{Cl}_2$ are as follows. A total of 57 714 reflections were collected in the θ range $1.80\text{--}26.37^\circ$, of which 6492 were unique ($R_{\text{int}} = 0.0351$). A semiempirical absorption correction was applied. The least-squares refinement converged normally with residuals of $R1(F > 4\sigma(F)) = 0.0228$, $wR2 = 0.0628$, and $\text{GOF} = 1.095$ based on F^2 (all data). Monoclinic, space group $P2_1/n$, $a = 12.4390(4)$ Å, $b = 16.3588(5)$ Å, $c = 15.7664(6)$ Å, $\beta = 98.695(1)^\circ$, $V = 3171.4(2)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.626\text{ g/cm}^3$, $F(000) = 1544$.

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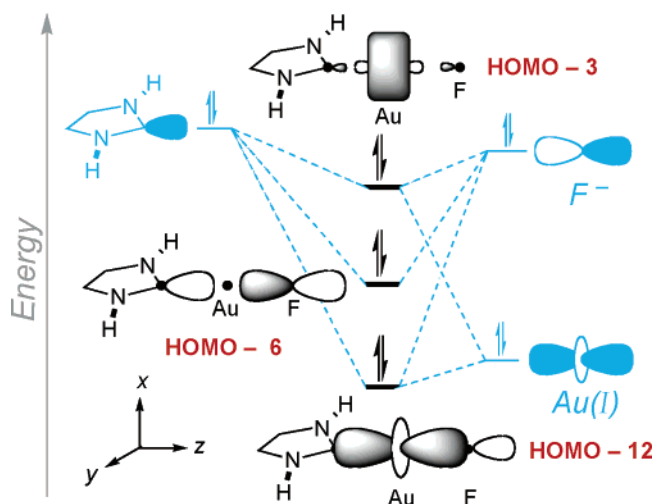


Figure 3. Qualitative energy diagram for the interaction of the Au^+ d_z^2 orbital with F^- and NHC σ -donor orbitals.

immediately below the HOMO in energy are $d\pi-p\pi$ antibonding combinations between gold and fluoride. Mulliken population analysis²³ indicates that the HOMO - 1 and HOMO - 2 consist of 36.5 and 34.8% Au character respectively, with fluoride contributing 60.0 and 59.5%. Their nearest Au-F π -bonding counterparts are the HOMO - 7 (43.4% Au, 37.1% F) and HOMO - 8 (60.7% Au, 36.7% F). In contrast, a computational study of d^8 iridium complexes [*trans*-(H_3P)₂Ir(CO)X] found that the Ir d and fluoride p atomic orbitals interact only slightly, and that the higher-energy π^* combinations comprise almost purely metal-based combinations.²⁴ Apart from the participation of fluoride, the orbitals resulting from metal-carbene π interactions in **A** (LUMO, HOMO - 1, HOMO - 2, HOMO - 7, HOMO - 8, HOMO - 9) resemble those encountered previously.¹⁴ All potential π^* combinations between Au and F are maximally occupied, and the Wiberg Au-F bond order²⁵ (in the Löwdin basis) is 0.933.

Three filled orbitals arise from the $\text{C}_{\text{carbene}}-\text{Au}-\text{F}$ σ interactions, as illustrated in Figure 3. The HOMO - 3 has d_z^2 symmetry along the Au-F axis with σ -antibonding character toward fluoride. The intermediate orbital in this series is the HOMO - 6; it is an antiphase combination of the F p_z and an sp^2 hybrid on the carbene

C and is essentially nonbonding toward gold. The primary C-Au-F σ -bonding orbital is the HOMO - 12, a constructive overlap of the gold $5d_z^2$ orbital and lobes of σ symmetry on fluoride and carbon.

A natural population analysis carried out for **A**^{26,27} found electrostatic charges of 0.42 for Au, -0.77 for F, and 0.20 for the carbenic carbon.²⁸ Further calculations were carried out on **A**·2 CH_2Cl_2 to examine the nature of the hydrogen-bonding interaction. Explicit solvation of fluoride by CH_2Cl_2 perturbs the electronic structure of **A** only minimally. Geometry optimization indicates a small distension of the interacting C-H bonds, and the gold-fluorine bond lengthens by 0.021 Å.²⁹ Natural electrostatic charges indicate appreciable polarization of the solvate C-H bonds: the hydrogens near fluoride acquire charges of +0.317 each. For comparison, the charge calculated for hydrogens in isolated CH_2Cl_2 (in a solvent continuum) is +0.295. The electrostatic charge calculated for fluoride is approximately unchanged at -0.77.

In conclusion, the first isolable gold(I) fluoride has been synthesized and structurally characterized. DFT calculations find a large partial negative charge on fluoride, and a slight lengthening of the Au-F bond, with polarization of the solvent C-H bonds, through hydrogen bonding with dichloromethane. Reactivity studies on this and related complexes are in progress.

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Supporting Information Available: Text, tables, and figures detailing the synthesis and characterization of **1** and **2**, structural parameters for **2**, and computational details for **A**; crystallographic data for **2** are also provided as a CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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