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

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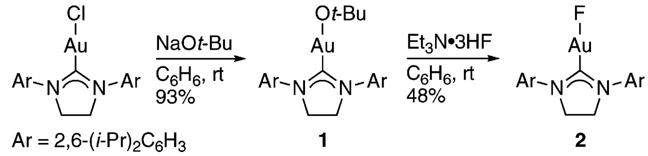
Summary: The first isolable gold(I) fluoride complex, stabilized by an N-heterocyclic carbene (NHC) ligand, has been isolated in two-coordinate monomeric form. DFT calculations show significant pπ/dπ interactions between fluoride and gold(I) and indicate a substantial negative charge on fluorine.

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 cleavage[5] and formation[6] 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.

Scheme 1



The known (SIPr)AuCl[13g] (SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) is converted to (SIPr)AuO*t*-Bu (**1**) in high yield by reaction with 1 equiv of NaO*t*-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) (Et$_3$N·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 ^{1}H 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 $Et_3N{\cdot}3HF$ 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 $(Ph_3P)AuCl$ with AgF leads to the formation of $\{[(Ph_3P)Au]_3O\}^+[H_2F_3]^-$ 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 (~25%) to a mixture of unidentified byproducts, as judged by ^{1}H 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 ($^2J_{C-F} = 61$ Hz), indicating that the complex is monomeric in solution. The IR spectrum of **2** shows a strong band, absent from the spectrum of (SIPr)AuCl, at 500 cm^{-1}, similar to the frequency estimated for Au−F ($\omega_e \approx 500$ 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 $[(Cy_3P)Pd(Ph)F]_2$.[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] Geometry 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.

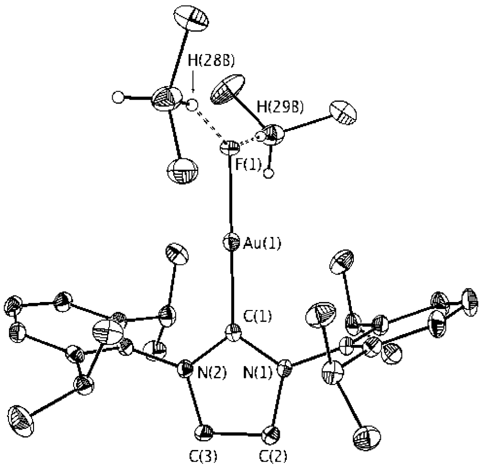

Figure 1. X-ray crystal structure of the gold fluoride **2**·$2CH_2Cl_2$, shown as 50% ellipsoids. Solvent hydrogen atoms are calculated; ligand hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Au(1)−F(1) = 2.0281(17), Au(1)−C(1) = 1.956(3), C(1)−N(1) = 1.338(3), C(1)−N(2) = 1.342(3), N(1)−C(2) = 1.472(4), N(2)−C(3) = 1.481(3), C(2)−C(3) = 1.534(4), F(1)−H(28B) = 2.287, F(1)−H(29B) = 2.243; C(1)−Au(1)−F(1) = 177.22(9), N(1)−C(1)−N(2) = 108.7(3).

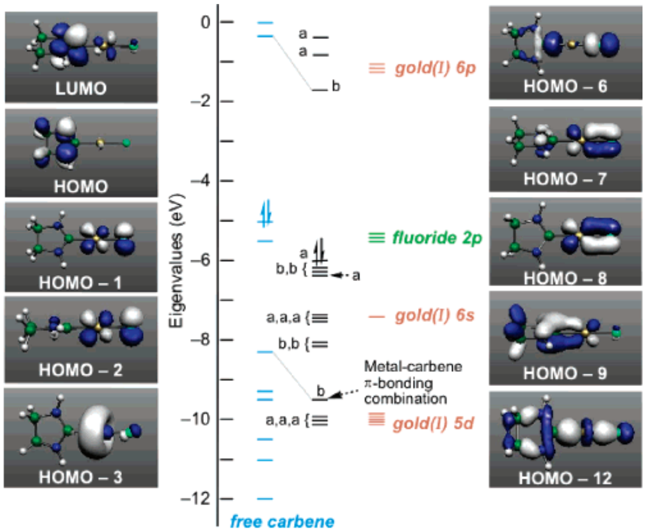

Figure 2. Kohn−Sham orbital energy-level diagram for the gold model complex **A**. Orbital eigenvalues of the carbene are those of the geometry-optimized, free ligand; those of gold are of Au$^+$, and those of fluorine are of F$^-$. All values include implicit solvation by CH_2Cl_2 ($\epsilon = 8.93$)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

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 $C_{27}H_{38}N_2AuF{\cdot}2CH_2Cl_2$ are as follows. A total of 57 714 reflections were collected in the θ range 1.80−26.37°, of which 6492 were unique ($R_{int} = 0.0351$). 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 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, β = 98.695(1)°, V = 3171.4(2) Å^3, Z = 4, ρ_{calcd} = 1.626 g/cm^3, $F(000)$ = 1544.

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[21] In contrast, certain (NHC)Au(I) complexes do show aurophilic interactions; the X-ray crystal structure of (NHC)AuCl (where NHC = 1,3-dimethylimidazol-2-ylidene), for example, displays Au−Au distances of ca. 3.54 Å[13f].

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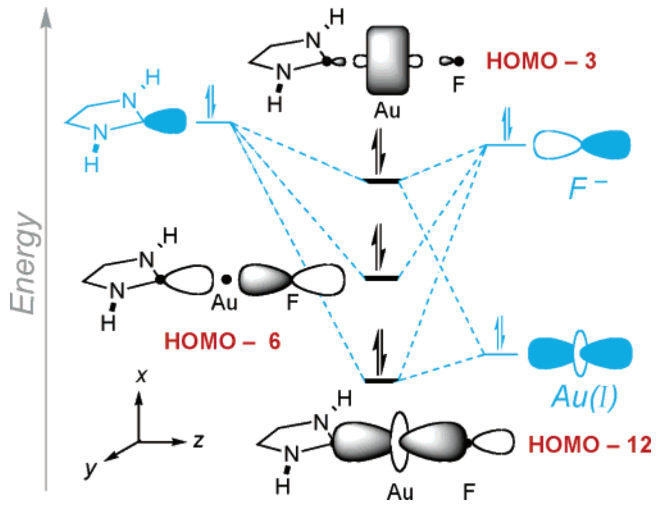

Figure 3. Qualitative energy diagram for the interaction of the Au^+ d_{z^2} orbital with F^- and NHC σ-donor orbitals.

immediately below the HOMO in energy are dπ−pπ antibonding combinations between gold and fluoride. Mulliken population analysis[23] 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 fluorine 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 order[25] (in the Löwdin basis) is 0.933.

Three filled orbitals arise from the $C_{carbene}$−Au−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 fluorine 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**·$2CH_2Cl_2$ 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 fluorine 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 fluorine 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 fluorine, 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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[28] For comparative listings of calculated atomic charges, including Mulliken charges, see Tables S2 and S4.

[29] Table S3 gives interatomic distances calculated with explicit solvation.