Organogold Compounds

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[Au(CF$_3$)(CO)]: A Gold Carbonyl Compound Stabilized by a Trifluoromethyl Group**

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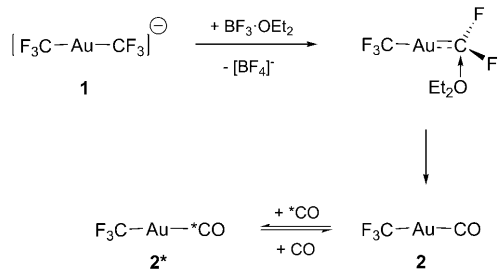
Dedicated to José M. Casas on the occasion of his 50th birthday

Gold nanoparticles (Au NPs)[1] are attracting increasing interest in the scientific community as new and fascinating properties are being discovered with potential applications in the fields of technology,[2] chemistry,[3] and biomedicine.[4] Within the realm of chemistry, Au NPs have been found to act as efficient catalysts in an ever-growing number of chemical processes.[5] The performances achieved, however, seem to be highly dependent on the size, shape, and morphology of these Au NPs,[6] and thus new efficient and reliable methods to prepare them are being eagerly sought.[7] A recently reported procedure[8] to obtain monodisperse Au NPs with circa 28.7 nm average size consists of hydrolysis of the homoleptic trifluoromethyl derivative $[Au(CF_3)_2]^-$; this synthesis was suggested to proceed through "an intermediately formed, short-lived species $AuCF_3{\cdot}CO$." Herein we present the synthesis, isolation, and characterization of this unstable and highly reactive intermediate species, which is one of the very few gold carbonyl derivatives isolated in the condensed phase.[9]

Low-temperature treatment of $[PPh_4][Au(CF_3)_2]$ (**1**)[10] with $BF_3{\cdot}OEt_2$ in CH_2Cl_2 cleanly affords the carbonyl derivative $[Au(CF_3)(CO)]$ (**2**).[11] No decomposition is observed throughout the process, provided that moisture is carefully excluded from the reaction medium. The reaction path depicted in Scheme 1 is proposed in analogy with results obtained in platinum chemistry.[12] The first step would involve α-fluoride abstraction from the starting material **1** by the etherate $BF_3{\cdot}OEt_2$, thus giving rise to a transient difluorocarbene species that could possibly be stabilized by base coordination before further evolving into the final product **2**.[13] Transformation of **1** into **2** is evidenced by the shift of the CF_3 signal in the ^{19}F NMR spectrum from $\delta = -28.6$ to -31.1 ppm and the appearance of a sharp, strong band at 2180 cm^{-1} in the IR spectrum that can be assigned to the ν(CO) vibration mode. The frequency of this absorption is even higher than that observed for [AuCl(CO)] (2162 cm^{-1} in CH_2Cl_2 solution),[14,15] and is similar to that reported for the mixed-valence compound $[Cl_3Au(\mu\text{-}Cl)Au(CO)]$ (2180 cm^{-1} in $SOCl_2$ solution).[15,16] The high ν(CO) frequency denotes that the CO molecule in **2** is acting predominantly as a σ-donor ligand;[17] it also confirms the electron-withdrawing character of the CF_3 group, which has been recently questioned.[18] Compound **2** readily undergoes CO exchange with free ^{13}CO at atmospheric pressure to give the labeled species $[Au(CF_3)(^{13}CO)]$ (**2***). This labeling experiment enables the CO signal to be unambiguously located in the ^{13}C NMR spectrum ($\delta_C = 183.0$ ppm), as coupling with the F nuclei is clearly observed (Figure 1a). Furthermore, the ^{19}F NMR signal of **2*** appears to be split into a doublet with the same coupling constant: $^3J(^{13}C,^{19}F) = 15.7$ Hz (Figure 1b).

Compound **2** is extremely water-sensitive and suffers massive decomposition to Au^0 under the action of moisture.



Scheme 1. Suggested reaction path for the transformation of **1** (cation: $[PPh_4]^+$) into **2**, and the observed CO exchange in **2**.

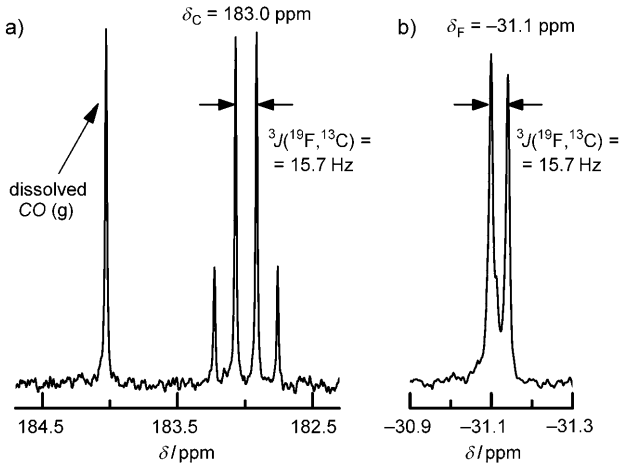


Figure 1. Low-temperature NMR spectra and selected parameters for compound **2*** in CD_2Cl_2 solution: a) ^{13}C, b) ^{19}F. The signal corresponding to dissolved $^{13}CO(g)$ appears at $\delta = 184.0$ ppm in the ^{13}C NMR spectrum (a).

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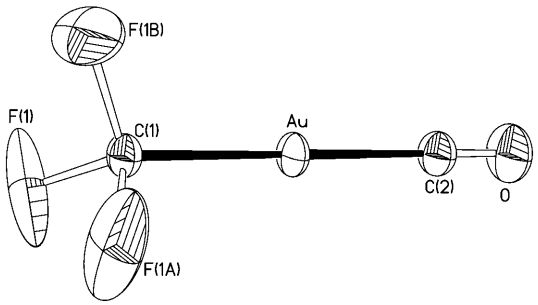

Figure 2. Thermal ellipsoid diagram (50% probability) of the [Au(CF$_3$)(CO)] molecule. Selected bond lengths [pm] and angles [°]: Au–C(1) 204.7(14), Au–C(2) 197.7(16), C(2)–O 108(2), C(1)–F 132.6(10), C(1)-Au-C(2) 180.0(3), Au-C(2)-O 180.0(18), F-C(1)-Au 114.3(7), F-C(1)-F′ 104.2(8).

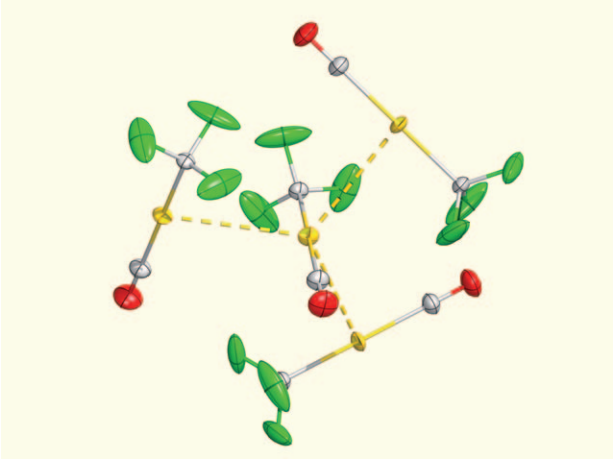

Figure 3. Local environment of each [Au(CF$_3$)(CO)] molecule in the crystal lattice, including indications of the aurophilic interactions with three equidistant neighbor molecules. Au yellow, C gray, F green, O red. Au···Au = 345.9(1) pm.

This extreme water sensitivity is the reason why compound **2** is indeed a short-lived intermediate under the wet conditions required to produce the hydrolysis of $[Au(CF_3)_2]^-$.[8] Under strictly anhydrous conditions, however, compound **2** can be isolated as light yellow crystals.[11] The ν(CO) frequency observed in the solid state (2194 cm^{-1}) is similar to that found in [Au(OSO$_2$F)(CO)] (2195 cm^{-1}),[19] but is still significantly lower than that reported for the cationic species $[Au(CO)_2][Sb_2F_{11}]$ (2254 cm^{-1}).[20]

The crystal and molecular structures of **2** have been established by single-crystal X-ray diffraction methods.[21–23] The only crystallographically independent F$_3$C–Au–CO molecule (Figure 2) longitudinally coincides with a C_3 axis and therefore has a symmetry-imposed linear C–Au–C≡O arrangement. The Au–CO bond length (197.7(16) pm) is virtually identical to that found in the cationic species $[Au(CO)_2]^+$ (197.1(8) pm)[24] and is comparable to that reported for [AuCl(CO)] (193(2) pm);[25] it is, however, significantly longer than that found in the tetrahedrally coordinated compound [Au{BH(pz*)$_3$}(CO)] (186.2(9) pm; pz* = 3,5-bis(trifluoromethyl)pyrazolyl).[26] The long Au–CO bond in **2** is a further indication of the mainly σ-donor character of the CO ligand.[17] Each of the Au$^{\text{I}}$ centers (closed d^{10} shell) shows weak aurophilic interactions (Au···Au = 345.9(1) pm)[27] with three symmetry-related Au$^{\text{I}}$ neighbors located in a plane perpendicular to the C–Au–CO axis (Figure 3), yielding an extended three-dimensional network of aurophilic interactions. The weak nature of these aurophilic interactions is also in keeping with the hard character or the CF$_3$ group and the poor σ-donating ability of the CO ligand that should result in a diminished electron density on the Au center.[28]

The interplay between gold and CO has been a fascinating subject for over a century. As early as 1905, J. Donau reported that action of CO on aqueous $[AuCl_4]^-$ solutions produced red colloidal gold.[29] The procedure has been conveniently modified and newly exploited to efficiently produce sub-10 nm Au NPs,[30] ultrathin gold nanowires (Au NWs),[31] and also plasmonic nanoparticles with highly regular Au shell layers.[32] Moreover, one of the most characteristic and thoroughly studied reactions catalyzed by Au NPs is the low-temperature oxidation of CO.[33] It is precisely the combination of the reducing ability of CO and the readiness with which gold is reduced that can be considered the main reason for the paucity of well-defined isolated carbonyl derivatives.[9] In fact, to our knowledge, compound **2** is the only gold carbonyl derivative stabilized by an organyl group.[34] Lower stabilities would be anticipated for the lighter isoleptic species [M(CF$_3$)(CO)] (M = Cu, Ag) considering the behavior of the [MCl(CO)] series: Au > Cu > Ag.[35] The methyl derivative [Au(CH$_3$)(CO)] would also be expected to be substantially less stable than **2**, given the lower stability of the related species [Au(CH$_3$)(CNMe)] with respect to its fluorinated homologue [Au(CF$_3$)(CNMe)].[36]

The isolation of [Au(CF$_3$)(CO)] (**2**) underlines the importance of gold carbonyl derivatives as intermediate species in the preparation of Au NPs. Preliminary results reveal that the CO molecule in **2** can be readily replaced by a number of other ligands. Therefore, compound **2** can be considered as a valuable synthon of the "Au(CF$_3$)" fragment that may find wide use in gold chemistry.[37]

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[11] Synthetic procedure: $BF_3{\cdot}OEt_2$ (38 μL, 0.30 mmol) was added to a solution of **1** (0.20 g, 0.30 mmol) in CH_2Cl_2 (10 mL) at −78 °C and under exclusion of light. The mixture was allowed to react for 4 h while the temperature rose to 0 °C, and the initially yellow solution gradually faded. Addition of pre-cooled *n*-hexane (20 mL) to the now colorless solution caused the precipitation of a white solid, which was filtered off. By allowing the filtrate to stand at −60 °C, light yellow crystals of **2** were obtained, which were filtered, washed with cold *n*-pentane (3 mL), and vacuum dried, while maintaining the temperature at −78 °C to avoid decomposition (0.03 g, 0.10 mmol, 34 % yield). Crystals of **2** quickly darken at room temperature and/or when exposed to moist air. No satisfactory elemental analyses were obtained owing to the instability of the substance.

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[21] Crystal data for **2**: C_2AuF_3O, $M_r = 293.99$; crystal size: $0.41 \times 0.37 \times 0.13$ mm^3; space group $I2_13$; $a = b = c = 968.170(10)$ pm, $V = 0.907517(16)$ nm^3; $Z = 8$; $\rho_{calcd} = 4.303$ g cm^{-3}; $\mu = 32.361$ mm^{-1}; graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm); $T = 100(2)$ K; range for data collection: $4.21 \le \theta \le 28.59°$; reflections collected/unique: 2912/376 ($R_{int} = 0.0760$); Oxford Diffraction Xcalibur CCD diffractometer. The diffraction frames were integrated and corrected for absorption using the CrysAlis RED package.[22] Lorentz and polarization corrections were applied. The structure was solved by direct methods, and refinement against F^2 with SHELXL-97[23] converged to final residual indices of $R_1 = 0.0252$, $wR_2 = 0.0645$ [$I > 2\sigma(I)$] and $R_1 = 0.0253$, $wR_2 = 0.0645$ (all data). GoF = 1.056. CCDC 813000 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[37] **Note added in proof (20.5.2011)**: After submission of this article, two reports have appeared on the synthesis and characterization of cationic gold(I) carbonyl compounds with the formula

[Au(L)(CO)][SbF_6], where L is trimesitylphosphine[37a] or an *N*-heterocyclic carbene ligand.[37b] Their high ν(CO) values (ca. 2195 cm^{-1}) and their long Au–CO distances have been attributed mainly to the electrostatic effect of the cationic $[Au(L)]^+$ fragment on the polarization of the C≡O bond. Such an explanation, although appealing, cannot be invoked in the case of our neutral compound [Au(CF_3)(CO)], for which similar ν(CO) values are observed. No aurophilic interactions were observed in these newly reported cationic compounds.

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