of its operation have been previously described.[13] Briefly, metal ions were generated by laser desorption/ionization by focusing the beam of a Nd:YAG laser (Spectron Systems, 1064 nm) onto a high-purity rod of the desired transition metal, which is affixed in the external ion source. The ions are extracted from the source and transferred into the analyzer cell by a system of electric potentials and lenses. The ion source, transfer system, and ICR cell are differentially pumped by three turbomolecular pumps (Balzers TPU 330 for source and cell, respectively, and Balzers TPU 50 in the middle of the transfer system). After deceleration, the ions are trapped in the field of the superconducting magnet (Oxford Instruments), which has a maximum field strength of 7.05 T. The metal's most abundant isotope is isolated by using FERETS[14] and allowed to react with the substrate, which is present with a constant pressure of the order of 10^{-8} mbar; reaction times are typically 1-10 s. For collisional cooling of eventually formed excited states and removal of kinetic energy remaining from the transfer, as well as for CID experiments,[6] argon was present as a buffer gas with a constant pressure of $(1-5) \times 10^{-7}$ mbar, as measured with an uncalibrated ionization gauge (Balzers IMG 070). All functions of the instrument were controlled by a Bruker Aspect 3000 minicomputer; broad-band spectra were recorded with a fast ADC, digitized as 64K or 128K data points and zero-filled[15] to 256K before Fourier transformation. Reaction products were unambiguously identified by double-resonance and MS/MS techniques.[5]

The isocyanates were synthesized and fully characterized by using established procedures, purified by preparative gas chromatography, and carefully degassed by multiple freeze-pump-thaw cycles immediately before the experiments. The label content was determined with NMR and mass spectrometry techniques.

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Synthesis and Characterization of Bis(trifluoromethyl)gold μ-Halide Dimers: X-ray Structural Characterization of $[Au(CF_3)_2(\mu\text{-}I)]_2$

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Perfluoroalkyl complexes of metal atoms have received attention owing to the importance of fluorocarbons in important materials applications. For example, trifluoromethyl metal complexes often show enhanced volatility, which make them potentially useful in vapor deposition studies. Gold complexes hold particular interest because of desirable electrical properties of gold for electronics manufacture. In spite of this, very few (trifluoromethyl)gold complexes have been reported. In 1976 Johnson and Puddephatt synthesized the first (trifluoromethyl)gold complexes by the oxidative addition CF_3I to methylgold phosphine complexes.[1] These products were characterized by ^{19}F NMR spectroscopy but were not isolated. It has only been with the recent combination of metal vapor techniques and radio frequency discharge generated plasmas of C_2F_6 that Lago et al. have succeeded in preparing compounds that have more than one trifluoromethyl group attached to a metal.[2] Unstable $Au(CF_3)_3$ synthesized from gold vapors and plasma-generated trifluoromethyl radicals at −196 °C is stabilized by addition of PMe_3.[3] More recently, Fackler, Lagow, and co-workers have prepared CF_3 derivatives of gold(II) ylide complexes by exchange reactions between $Cd(CF_3)_2$(glyme) and $[Au(CH_2)_2PPh_2]_2Br_2$.[4] Sanner, Sacher, and Droege have stabilized (trifluoromethyl)gold halide complexes with PMe_3, PEt_3, and PPh_3.[5] In this paper we report the vapor deposition synthesis of the dimeric bis(trifluoromethyl)gold(III) bromide and iodide complexes and the X-ray structural characterization of the iodide complex.

Table I. Crystallographic Data Collection Parameters for Compound Ib

emp formula	$Au_2C_4F_{12}I_2$	fw	923.77
space group	$P2_1/n$ (*no.* 14)	T, °C	23
a, Å	7.5963 (8)	λ(Mc Kα), Å	0.71069
b, Å	7.295 (1)	ρ, g/cm^3	4.31
c, Å	13.057 (1)	μ, cm^{-1}	257.62
β, deg	100.710 (7)	T_{max}/T_{min}	1.000/0.2847
V, Å^3	711.0 (1)	R^a	0.039
Z	2	$R_w{}^a$	0.053

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w\{|F_o| - |F_c|\}^2/\sum w|F_o|^2]^{1/2}$. The function minimized during least squares was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$.

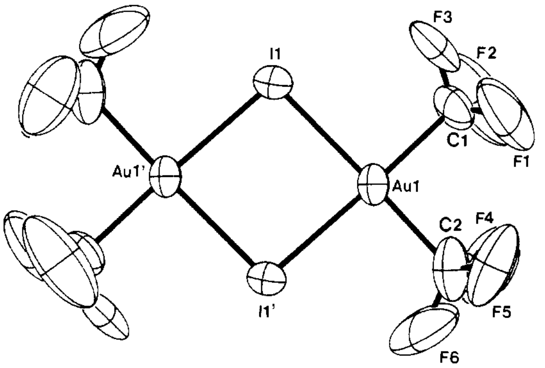

Figure 1. ORTEP diagram of $[Au(CF_3)_2(\mu\text{-}I)]_2$, showing 50% anisotropic thermal ellipsoids and atom labeling.

Experimental Section

Synthesis of $[Au(CF_3)_2(\mu\text{-}X)]_2$ (X = Br (Ia), I (Ib)). A typical reaction consisted of cocondensation of about 0.75 g (3.81 mmol) of gold with about 50 g (335.8 mmol) of bromotrifluoromethane over a period of about 1.5 h in an apparatus that has been previously described.[6] The bell jar upon which the reagents were condensed was then washed with diethyl ether (total volume ~400 mL) from which 250 mg (16%) of the $[Au(CF_3)_2(\mu\text{-}Br)]_2$ was isolated. A similar procedure was followed by using CF_3I and gold (100:1) with a yield of 8%. The compounds Ia and Ib are sublimable (room temperature 10^{-2} Torr) orange to brownish orange solids with melting points 90-94 °C (Ia) and 136-137 °C (Ib). Mass spectra showed the parent ions in both cases (Ia, *m/e* 832; Ib *m/e* 924). ^{19}F NMR: $\delta = -71.4$ (Ia), −73.7 ppm (Ib) (CF_3CO_2H reference). Both compounds are moderately air and light sensitive. Recrystallization from pentane gave diamond-shaped crystals suitable for X-ray diffraction.

X-ray Analyses of Ia and Ib. X-ray diffraction data for both Ia and Ib were collected on a Rigaku AFC5S fully automated single-crystal X-ray diffractometer using graphite-monochromated Mo Kα radiation.

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Table II. Atomic Positions and B_{eq} for Compound Ib

atom	x	y	z	B_{eq}, Å^2
Au1	0.93096	0.21215	0.41116 (4)	3.65 (2)
I1	1.2111 (1)	−0.0105 (2)	0.45534 (8)	4.73 (5)
C1	1.051 (3)	0.362 (3)	0.308 (2)	5.4 (8)
C2	0.0705 (3)	0.389 (3)	0.382 (2)	7 (1)
F1	0.956 (2)	0.391 (3)	0.219 (1)	14 (1)
F2	1.116 (4)	0.502 (3)	0.341 (2)	17 (2)
F3	1.178 (3)	0.288 (3)	0.284 (2)	18 (2)
F4	0.752 (3)	0.557 (2)	0.405 (2)	13 (1)
F5	0.629 (2)	0.382 (2)	0.288 (1)	12 (1)
F6	0.594 (3)	0.389 (3)	0.382 (2)	7 (1)

Table III. Bond Distances (Å) and Angles (deg) for Compound Ib

Distances			
Au1–C1	2.07 (2)	Au1–C2	2.12 (2)
Au1–I1	2.654 (1)	Au1–I1′	2.658 (1)
C1–F1	1.26 (2)	C1–F2	1.18 (2)
C1–F3	1.20 (3)	C2–F4	1.30 (2)
C2–F5	1.26 (2)	C2–F6	1.22 (3)
Angles			
C1–Au1–C2	89.9 (9)	C1–Au1–I1	91.9 (6)
C1–Au1–I1′	177.7 (6)	C2–Au1–I1	177.8 (6)
C2–Au1–I1′	92.4 (6)	I1–Au1–I1′	85.74 (3)
F2–C1–F3	100 (2)	F2–C1–F1	108 (2)
F2–C1–Au1	116 (2)	F3–C1–F1	100 (2)
F3–C1–Au1	114 (1)	F1–C1–Au1	116 (1)
F6–C2–F5	107 (2)	F6–C2–F4	106 (2)
F6–C2–Au1	112 (1)	F5–C2–F4	109 (2)
F5–C2–Au1	111 (2)	F4–C2–Au1	111 (2)

Crystals of Ia were of poor quality with a low percentage of observed data, but unit cell constants (a = 7.444(8) Å, b = 7.20 (2) Å, c = 12.41 (4) Å, β = 99.0 (2)°) and preliminary structure solution showed Ia to be isomorphous to Ib. Because of the limited data quality, those results are not presented here. Data collection and refinement parameters for Ib are provided in Table I. The structure was solved by using the program MITHRIL[7] and refined to convergence by using TEXSAN (version 2.0).[8] The data were corrected for LP and polarization effects and absorption (empirical ψ scans).

Results and Discussion

The reaction of gold atoms with CF_3X, where X = Br or I, produces bis(trifluoromethyl)halogold complexes that exist as dimers in the solid state and in the gas phase. Ib (Figure 1) contains two gold atoms each of which is ligated by two trifluoromethyl groups and connected to each other via two bridging iodide ligands in a fashion similar to that of other known nonfluorinated alkylgold halides. The gold atoms have a square-planar geometry with the sum of the bond angles about the metal being 359.94°. The molecule is situated such that the center of the Au_2X_2 parallelogram is a crystallographic inversion center. There is no Au–Au bond. The fluorine atoms show some disorder about the 3-fold axis of the CF_3 moiety as is common for this group. Atomic positions and B_{eq} values are provided in Table II, while bond angles and distances are given in Table III. The Au–C distances are comparable to those found for other square-planar alkyl- and arylgold complexes such as $[Br_2Au(\mu\text{-}Br)_2AuMe_2]$ (2.12 (1) Å),[9] $[Au(CH_2)_2PPh_2]_2(CF_3)_2$ (2.140 (7) Å),[4] $[Me_2AuOH]_4$ (2.05 Å average),[10] $Au_2[(CH_2)_2PPh_2]_2(Me)Br$ (2.159 (2) Å),[11] $Au(C_6F_5)_2Cl(PPh_3)$ (2.12 (9), 2.18 (10) Å),[12] etc.[13]

This work represents the first structural characterization of stable unsubstituted (trifluoromethyl)gold halide compounds produced via metal atom reactions and indicates that such simple compounds are not inherently unstable. Previous work with (trifluoromethyl)gold complexes formed by atom vapor reactions employed PMe_3 to stabilize the product $Au(CF_3)_3$.[3] Bis(trifluoromethyl)gold halide dimers have recently been prepared[5], but the synthetic route was not straightforward, involving first synthesis of CF_3AuL followed by reaction with CF_3I, which was shown to follow a radical pathway. CF_3Br was unreactive under these conditions. Thus, the atom reactor synthesis represents at the moment the only known method to unsubstituted (trifluoromethyl)gold halide complexes, but the stability of these compounds suggests that other higher yield synthetic routes might be found.

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Registry No. Ia, 123204-35-3; Ib, 123204-36-4; CBr_3I, 14349-80-5; CF_3I, 2314-97-8; Au, 7440-57-5.

Supplementary Material Available: Tables of crystallographic data collection and refinement parameters and anisotropic thermal parameters (2 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Nuclear Magnetic Resonance Studies of Hydroquinone Dianion Bridged Iron(III) Porphyrin Dimers[†]

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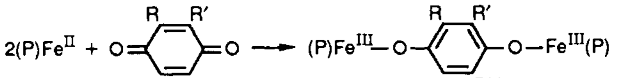
The reaction of iron(III) arylporphyrin complexes, $(P)Fe^{III}Ar$, with dioxygen produces a variety of products, which depend on the reaction conditions.[1] One of these is the dimer $(P)Fe^{III}(1,4\text{-}OC_6H_4O)Fe^{III}(P)$, a species previously isolated and characterized in the solid state by Kessel and Hendrickson.[2,3] Such dimers are readily prepared by the reaction of an iron(II) complex with a p-benzoquinone (eq 1).[2-4] Mössbauer spectra indicate that



(1)

these are high-spin ($S = {}^5/_2$) iron(III) species.[2] Magnetic susceptibility studies show evidence of weak antiferromagnetic exchange with J values between −3.6 and −15.5 cm^{-1}.[2] Consequently, it may be anticipated that their ^1H NMR spectra will resemble those of high-spin iron(III) porphyrin complexes[5-7] rather than those of the much more strongly antiferromagnetically coupled μ-oxo compounds $(P)Fe^{III}OFe^{III}(P)$, where J is about −150 cm^{-1}.[8,9] In order to facilitate the detection of the diiron complexes and

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[†] Abbreviations used: P, porphyrin dianion; TTP, tetra-p-tolylporphyrin dianion; OEP, octaethylporphyrin dianion; Ar, aryl group.

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