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The metal vapor synthesis and reactions of bis(trifluoromethyl)gold-μ-halide dimers

Norem, Nathan Thomas, Ph.D.
Rice University, 1989
RICE UNIVERSITY

THE METAL VAPOR SYNTHESIS AND REACTIONS OF BIS(TRIFLUOROMETHYL)GOLD-\(\mu\)-HALIDE DIMERS

by

Nathan Thomas Norem

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS OF THE DEGREE DOCTOR OF PHILOSOPHY

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HOUSTON, TEXAS
APRIL, 1988
ABSTRACT

The Metal Vapor Synthesis and Reactions of Bis(trifluoromethyl)gold-μ-halide Dimers

by

Nathan Thomas Norem

The metal vapor synthesis of two novel bis(trifluoromethyl)gold-μ-halide dimers was accomplished by the codeposition of gold atoms with freons (CF₃X; X=Br, I) at -196°C. The reactor, the reaction procedures and conditions, and the isolation and purification techniques are described here. Solution IR, ¹⁹F NMR, mass spectrometry, and x-ray crystallography were used to characterize the two compounds.

Both compounds showed moderate vapor pressures and were treated with thallium hexafluoroacetylacetonate, phosphorus trifluoride, and tris(trifluoromethyl)phosphine in an attempt to synthesize monomeric compounds with higher vapor pressures. The dimers were decomposed by PF₃ and did not react with P(CF₃)₃; neither reaction yielded soluble gold compounds detectable by mass spectrometry. Reaction with Tl(hfacac) resulted in an unstable oily product which gave a mass spectrum characteristic of bis(trifluoromethyl)gold hexafluoroacetylacetonate. This compound decomposed readily and resisted isolation. All of the isolated gold compounds were light sensitive. The bis(trifluoromethyl)gold-μ-halide dimers were resistant to air oxidation.
ACKNOWLEDGEMENTS

In regards to my progress in the science of chemistry, I must acknowledge the support of my advisor, Dr. J. L. Margrave, who not only taught me, respected me, and presided over a group of good people to work around, but also gave me occasional wild ideas that actually worked. I must also acknowledge Dr. B. A. Sosinsky who gave me a lesson in life and experience with some chemical systems which were interesting; would that things had worked out better. Assistance in my research was also generously given by Dr. Ken Whitmire. I acknowledge the contributions to my life of Drs. R. R. Kintner, A. Viste, W. Gildseth, M. Hanson, and R. Landborg of the Augustana College (SD) Chemistry Department.

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Chapter 1

Introduction and Background

Metal Vapor Synthesis

Preparative scale syntheses in low temperature reactors began with the work of Timms and Margrave in their study of SiF$_2$ reactions with several different substrates$^{1,2}$ and the carbon arc work of Skell and Westcott.$^3$ A short while later Timms initiated the first studies of elemental metal vapors and their reactions with organic substrates.$^4$ The first great success of metal vapor synthesis was the synthesis of the stable organometallic compound bis( benzene) chromium.$^5$ The new technique produced in one step, relatively cleanly and in higher yield, a compound which had required two steps and the separation of a number of different products in the earlier “wet chemistry” syntheses.$^6$ This technique was quickly adopted by others and proved to be quite general in its ability to produce bisarene chromium compounds cleanly from the metal and the appropriate arene.$^7,8$ The early work by Timms also showed that the technique was not limited to making organometallic compounds in which
all constituent parts were considered zero-valent. Timms synthesized ferrocene directly from iron vapor and cyclopentadiene.4

Metal vapor synthesis is an attractive technique because of its inherent simplicity. It is a solvent-less technique so that the experimenter need not worry about selecting a solvent of appropriate polarity, coordinating ability, or inertness. Metal atoms coming into the reaction are unbiased by ligands that could impose steric or electronic preferences to disguise or distort inherent properties of the atomic orbitals. This lack of valence electron donors, the proclivity of some metal atoms to seek different oxidation states, and the absence of more reactive species in the reaction medium, serve as driving forces that cause the metal atoms to react with substrates which would otherwise be too inert for reaction. The absence of solvents and counterions restricts the number of reactants available, thereby limiting to some extent the number of possible side reactions which might otherwise occur. Since the metal atoms have high kinetic energies from the vaporization procedure and have all their potentially bonding orbitals available to react, they are capable of undergoing many types of reactions. Klabunde has studied a variety of reactions in this field and has described the following seven reaction types:

1. Abstraction - removal of an atom from the substrate by the metal.
2. Electron-transfer processes - removal of an electron, generally from the substrate by the metal.
3. Oxidative addition processes - oxidative insertion of a metal into a bond of the substrate.
4. Simple orbital mixing processes - \( \pi \) or \( \sigma \) complexes are formed.
5. Substitution processes - high-temperature species displace part of the substrate.

6. Disproportionation and ligand transfer processes - reactive species coordinate to groups from the substrate.

7. Cluster formation processes - the reactive species bonds with itself. These small clusters may still react with the substrate although they are generally less likely to produce discreet organometallic compounds.\(^9\)

While the number of reactions occurring during a single experiment is generally limited to just one or two of these processes at any particular stage, the vaporization, cocondensation, warm-up, and recovery steps of a typical experiment expose the reactants and intermediates to several different environments which may lead to a multiplicity of products. Many investigators, each with his own aims, chemical emphases, and experimental techniques, are examining the myriad aspects of this burgeoning field.\(^10\)

Organogold Chemistry

Gold, which has always attracted people of all classes and vocations, came under the scrutiny of organometallic chemists quite early in the history of the field,\(^11\) but as with the alchemists, the chemists came up short in their first efforts.\(^12\) Even this noble metal, though, could not withstand the tremendous onslaught of work by C. S. Gibson, beginning in 1907 with the synthesis of \(\text{AuMe}_2\text{Br}\) by the Grignard reaction of gold
tribromide with an ethereal solution of magnesium ethyl bromide.\textsuperscript{13} Twenty-three years later, through the application of the cryoscopic method of molecular weight determination, Gibson proved it to be the dimer.\textsuperscript{14} The crystal structure of this compound was finally established by Gibson in 1937 when the state of the art in x-ray crystallography allowed him to obtain sufficiently good x-ray photographs to determine rough values for bond angles and lengths of the central square made up of the gold and bromine atoms before the x-rays decomposed the crystal.\textsuperscript{15} In 1977 Komiya \textit{et al.} published the structure of the monomethyl dibromogold dimer which was synthesized by the bromination of the dimethylmonobromogold dimer.\textsuperscript{16} The presence of both methyl groups on one of the gold atoms is noted as further proof of the instability of monoalkylgold(III) complexes. To this day there are no unambiguous examples of monoalkylgold(III) complexes.

After an apparent break from this work, or forays into other areas,
Gibson returned to this area in the 1930’s and 40’s and solved the structure of his [Au(CH₃)₂(μ-Br)]₂; he not only broke the ground in the field but harvested a great deal of its yield. He expanded his investigations into derivatives of the bromide compound by synthesizing and studying the iodine-bridged complex. Other ligands included pseudohalogens such as cyanide, thiocyanate, pyridine, and dibenzylsulphide; bidentate ligands like ethylenediamine, dithio-oxamide, and dicarboxylic acid which formed other bridged gold dimers; and acetylacetone and dithiocarbamate ligands which formed monomers of the dimethyl- and diethylgold complexes.¹⁷

The next major investigator to work in the field was Coates, beginning in the late 1950’s, who expanded the work by reacting phosphine complexes of the gold(I) halides with organolithium compounds to synthesize a whole series of organogold(I) phosphines.¹⁸ He was followed by Hüttel in the mid-1960’s who sought to prepare a cyclopentadienylgold(I) complex, but found it to be a monohapto (i.e. bonding through just one of the atoms in the ligand; the numeric prefix on “hapto” indicates the number of ligand atoms considered to be bonded to the metal atom), σ-bonded compound rather than a π-bonded sandwich complex.¹⁹ Hüttel made some rather unstable gold(I) π-complexes and a few even less stable gold(III) π-complexes, none of which appear to be more than the dihapto complexation of one double bond.²⁰

Finally in the late 1960’s, Tobias became involved in the isolation and characterization of a group of tetramethylaurate(III) anions.²¹
\[(\text{CH}_3)_2\text{AuP(C}_6\text{H}_5)_3 + \text{CH}_3\text{Li} \xrightarrow{\text{Et}_2\text{O}} \text{Li}^+\text{[Au(CH}_3)_4]^- + \text{P(C}_6\text{H}_5)_3}\]

This work helped to clarify an earlier claim by Gilman, in 1948, of the synthesis of an unstable trimethylgold from the reaction of methyllithium with gold tribromide at -65°C; the product decomposed at -40°C.\(^{22}\) This work also lent support to the proposal by Belluco \textit{et al.} of a trimethylgold intermediate in the decomposition of \(\text{Me}_4\text{Pb}\) by \(\text{AuCl}_3\).\(^{23}\)

With the possible exception of the aforementioned low temperature work, organogold chemistry is very strongly ruled by the electronic configuration of the metal atom. Gold(I) has the closed shell electronic configuration of \([\text{Xe}]4f^{14}5d^{10}\) leading to diamagnetic complexes with a coordination number of two and with linear stereochemistry predominating. This behavior, combined with the chemical softness (i.e. its relatively large size, low oxidation states compared to atomic number, high polarizability, and its preference for bonding with ligands of a similar nature) and low oxygen affinity of the atom, leads to the unusual case of the acetylacetonates being carbon-bonded.\(^{24}\)

\[
\begin{align*}
\text{R}_3\text{P} & \xrightarrow{\text{Au}} \text{CH} \\
\quad & \text{C}=\text{O} \\
\text{H}_3\text{C} & \\
\quad & \text{C}=\text{O} \\
\text{H}_3\text{C} &
\end{align*}
\]

Likewise all known gold(III) complexes are in a low-spin 5d\(^8\) electronic configuration and show a great preference for a four coordinate
square-planar stereochemistry, as seen with the bridging halogen compounds where the satisfaction of the four coordination sites seems to be of primary importance. There are a few known exceptions wherein the nature of the ligands has caused the gold to adopt either five-coordinate, e.g., trichlorobisquinolylgold(III)\textsuperscript{25}, or even six-coordinate configurations, e.g., diiodobis(\textit{o}-phenylenebis(dimethylarsine))gold(III) iodide.\textsuperscript{26} In such cases the coordination number has been expanded by occupying two or more of the preferred equatorial sites around the gold atom with a soft, zero-valent, generally bidentate ligand which forces the anions to occupy axial sites in the coordination sphere. The configuration of the coordination sphere for the Li\textsuperscript{+} [Au(CH\textsubscript{3})\textsubscript{4}] compound is unknown.

The restrictive geometries generally require that the stereochemistry of dialkylgold complexes be \textit{cis}, except in the unusual ylid complexes.\textsuperscript{27}
The reasons given for this preference for the cis-stereochemistry include the theory that the available orbitals for bonding by gold(III) are the 5d_x^2-y^2, 6s, 6p_x, and 6p_y, in order of decreasing stability. The two methyl groups will prefer to form strong σ-bonds to the lower energy orbitals, i.e. the 5d and 6s, leaving the 6p orbitals for the other ligands. Since the ds hybrid orbitals have lobes directed 90° to each other, this requires the cis-isomer to be formed.²⁸ There is also the theory of antisymbiosis which suggests that two soft ligands, such as the methyls, in mutually trans positions will have a destabilizing effect on each other when attached to a soft metal ion such as gold.²⁹

Perfluoroorganogold Chemistry

The perfluoroorganic chemistry of gold has lagged far behind its organic chemistry for several practical reasons. This parallels the general delay which perfluoroorganic chemistry has displayed in the field of organic chemistry. It would seem that there have been a large number of organometallic chemists who were simply awaiting the creation of new ligands by their organic counterparts. The preferred perfluoromethylating agent, trifluoromethyl iodide, was unknown until 1948, but by 1949 it had been used in the synthesis of bis(trifluoromethyl)-mercury.³⁰ It was not until 1976, however, that a trifluoromethylgold complex was reported by Puddephatt.³¹ This report was of a nuclear magnetic resonance study of the products formed in situ by the reactions of trifluoromethyl iodide with methylgold(I) complexes.
The relative dearth of activity in the field of perfluoroalkylgold chemistry can also be linked to the scarcity of suitable perfluoroalkylating agents. There are no perfluoroalkyl Grignard reagents and no good lithium or aluminum perfluoroalkyls. Even the aforementioned bis(trifluoromethyl)mercury has proven to be much inferior to the analogous dimethylmercury as a ligand-exchange reagent. It has only been through the recent combination of metal vapor techniques with radio frequency discharge generated plasmas of \( \text{C}_2\text{F}_6 \) and isolation of the trimethylphosphine adducts, that Lagow has succeeded in preparing compounds which have more than one trifluoromethyl group attached to a metal.\(^{32}\) By using a specially designed metal vapor reactor with a rotating cold-finger and radio-frequency plasma generator, Lagow synthesized an \([\text{Au}(\text{CF}_3)_3]\) intermediate from gold vapors and plasma-generated trifluoromethyl radicals at -196°C. He stabilized the compound by dripping the melting matrix into trimethylphosphine as an intermediate step before the warm-up to room temperature.\(^{33}\)

\[
\text{Au} + 3 \cdot \text{CF}_3 \xrightarrow{-196^\circ \text{C}} \begin{bmatrix} \text{CF}_3 \mid \text{Au} \text{CF}_3 \\ \text{F}_3\text{C} \end{bmatrix} \xrightarrow{-78^\circ \text{C}} \begin{bmatrix} \text{F}_3\text{C} \mid \text{Au} \text{CF}_3 \\ \text{F}_3\text{C} \end{bmatrix} \]

There has been an increased interest in the field of perfluoroalkyl organometallic chemistry with the metals of groups VIII\(^{34}\) and IIb\(^{35}\) so that it may just be a matter of time before there is also success with the
metals of group Ib.$^{36}$

In the area of perfluoroarylgold chemistry there has been more activity. Early success was reported in 1969 by Vaughan and Sheppard with the synthesis of tris(pentafluorophenyl)gold(III).$^{37}$ They reported it as a solvent stabilized product of the Grignard reaction of gold trichloride with pentafluorophenylmagnesium bromide at -60°C which remained stable at room temperature as long as it remained solvated. It could be stabilized by the addition of triphenylphosphine. The decomposition products were metallic gold and decafluoro-biphenyl when solvent was removed in the absence of a stabilizing ligand.

Since 1976, Usón, et al. have been using the pentafluorophenyl ligand extensively to stabilize gold anions in a whole series of salts containing the bis(pentafluorophenyl)aurate(I) and the mono-, tris-, and tetrakis-(pentafluorophenyl)aurate(III) ions.$^{38}$

His best starting material for the wide range of tetraalkylamine-stabilized anions is trichlorotetrahydrothiophen gold, Cl₃Au(tht), which is air- and thermally-stable, but from which the (tht) ligand is readily replaced by other neutral ligands.$^{39}$
Background of this work

The original goal of this work was to synthesize an organogold compound which would have a reasonably high vapor pressure, i.e., several hundred Torr, at room temperature. It was decided that the ideal product molecule should most likely be some type of small perfluoroalkyl (ideally trifluoromethyl) complex which might require a non-traditional synthetic technique. Standard techniques had proven to work only for the alkyl compounds and perfluoroaryl compounds, such as Usón’s pentafluorophenyl gold salts which, being large and ionic, did not offer much hope of displaying the desired properties.

The initial thrust was towards the design of a radio frequency discharge plasma device to produce trifluoromethyl radicals coupled with a metal atom reactor along the lines of Lagow’s apparatus for his work with nickel and palladium.\textsuperscript{32} It was anticipated that such a reaction would not lead directly to any desired product, as the optimum product would be either the one-coordinate trifluoromethylgold or the three-coordinate tris(trifluoromethyl)gold. Both intermediates would be unstable in the absence of stabilizing ligands which made it necessary to include such ligands in the reaction.\textsuperscript{22,23} Work was begun to allow for the introduction of the necessary stabilizing ligand vapor in such a way as to have it available during the warm-up without having it involved in the desired reaction. Our intention was to alternate the introduction of the reactant and the ligand in an attempt to layer them and to allow the reactions to occur in the
frozen matrix or quite early in the warm-up process; this technique is somewhat different from the way in which Lagow arranged his reactor to make the (CF$_3$)$_2$Au(PMe$_3$)$_2$.\textsuperscript{33}

But the trifluoromethyl plasma idea was not the only one to be found in the group. Along with Dr. John Bell (who had just returned from a post-doctoral appointment with M. L. H. Green and with his new expertise had modified the metal vapor synthesis reactor), a codeposition experiment was performed with gold and trifluoromethyl iodide. The product was characterized as bis(trifluoromethyl)gold-μ-iodide dimer, the first bis(trifluoromethyl)gold complex known, and although it was far from being the volatile compound desired, it was an entry into an area which held promise.

Metal vapor syntheses were used to produce the starting dimeric compounds for use in wet chemistry synthetic efforts towards stabilizing perfluoroalkylgold monomers. The metal atom reactor also found use in some additional reactions with other ligands in efforts to synthesize directly other perfluoroalkyl- or perfluorophosphorusgold compounds.
References and Notes


10 The following, along with reference 7, offer a fairly complete coverage of the foundations of this field:


11 For a more detailed account of the development of the chemistry see:


Chapter 2

Metal Vapor Synthesis Reactor Design
and General Procedures

Reactor Design

The trifluoromethylgold complexes were prepared from elemental gold and the appropriate freons in a metal vapor synthesis reactor, a modified "Green" design, (Figure 2.1) built by Dr. John P. Bell similar to a design with which he became familiar during a post-doctoral stay in the group of Dr. Malcolm L. H. Green. The metal and ligand vapors were condensed upon the inner surface of a 6-inch diameter Kimax pipe which had been reduced at the top to fit a male 24/40 standard taper joint. It was sealed onto the stainless steel base with an O-ring. Another O-ring, resting on the outside flare of the base of the pipe, served as the seal to a stainless steel sleeve wrapped with insulation which contained a liquid nitrogen bath during the course of a reaction. A drain valve near the bottom of the sleeve allowed the liquid nitrogen to be removed at the end of the cocondensation to facilitate the warm-up process. Below the bottom of the sleeve, the base of
FIGURE 2-1

METAL VAPOR SYNTHESIS REACTOR

A. Kimax bell jar
B. Insulated stainless steel sleeve
C. Liquid nitrogen
D. Ligand inlet system
E. Heating tape
F. Tungsten/alumina furnace
G. Inert gas inlet
H. Water-cooled electrodes
I. To rough pump
J. To vacuum system
the bell jar was wrapped with heating tape to prevent the O-ring at the base from freezing and leaking. The base was a stainless steel flange with an O-ring groove matching that of the Kimax pipe and a raised lip surrounding the central hole. This flange was sealed to the aluminum reactor base by an O-ring. The water-cooled electrodes, constructed of concentric copper tubing, were fed through the base by means of nylon Swagelock fittings to keep them electrically insulated. The electrodes were cooled by a water recirculation system with a heat exchanger cooled by chilled water. The tops of the electrodes were threaded and slotted to allow the ends of the furnace wires to be clamped between two knurled nuts. The furnaces were Sylvania Emissive Products CS-1008 integral alumina coated tungsten. The ligands, typically stable organic compounds, were introduced into the reactor through a system of 1/4-inch stainless steel tubing and were dispersed onto the matrix surface by a circular tube, with holes drilled into it at approximately half-inch intervals; it was located approximately at the same level as the furnace. For higher boiling ligands, the inlet tubing was wrapped with heating tape to facilitate the vaporization of the compounds. The rate of introduction for higher boiling ligands was monitored by dropping the liquid from a calibrated dropping funnel. The addition of lower boiling and gaseous ligands was monitored by a Hastings LF-300 mass flow-meter. A valve connected to a cylinder of argon was located in the reactor base, allowing the reactor to be repressurized with inert gas during the work-up.

The reactor was built in the center of a Formica-laminated, inch-
FIGURE 2-2

SETUP FOR THE
METAL VAPOR SYNTHESIS REACTOR

A. Inert gas cylinder
B. Ligand lecture bottle
C. Mass flowmeter
D. Rough pump
E. Reaction chamber
F. Thermocouple gauges
G. Vacuum trap
H. Gate valve
I. Diffusion pump
J. Electronics rack
thick table top supported by a Unistrut frame with its accessories arranged around it as shown in Figure 2-2. The vacuum system associated with the reactor consisted of a Precision Scientific Model 150 rotary oil pump and an NRC Model VHS-6 high capacity diffusion pump. Connected to the reactor chamber by a six-inch gate valve, the diffusion pump opened under a stainless steel liquid nitrogen vacuum trap which protected the pump from condensable vapors during the reactions. The vacuum was monitored by means of Consolidated Vacuum Corporation thermocouple gauges on the rough pump manifold and the reaction chamber, and by a Veeco cold cathode gauge on the reaction chamber.

The electrical power for the furnace was supplied by a Crittenden Model 13960 step-down transformer controlled by a Powerstat variac. A Pyro micro-optical pyrometer, viewing through a mirror set over a window on the top plug, allowed one to read the static temperature at which vaporization takes place. A control panel with rheostats controlled the heating tapes around the base of the reactor and around the ligand inlet tube.

General Reaction Procedure

In preparation for an experiment, the gold was pre-melted to clean and degas it before weighing the furnace and metal to ascertain the initial weight. The furnace was then connected to the water-cooled electrodes by tightening the leads between the knurled nuts. The ligand was also
degassed if necessary before it was weighed and connected onto the ligand inlet system. The O-rings were greased with Dow Corning silicone grease and placed in their grooves and the bell jar placed accordingly. The heating tape and the insulated stainless steel sleeve were placed around the bell jar; the O-ring at the base of the insulated sleeve was greased with petroleum jelly to help it contain the liquid nitrogen, and the nuts tightened. The inert gas line was shut off at the reactor while the ligand inlet system was opened completely up to the valve on the bulb or cylinder and the system was pumped down with the rough pump. When the thermocouple gauge on the rough pump manifold read about 100 millitorr, the system was opened up to the diffusion pump. The system was evacuated for several hours, at which time the cold cathode gauge normally indicated a chamber pressure in the $10^{-5}$ range.

The experiment was begun by filling the vacuum trap and the insulated sleeve with liquid nitrogen. After the vacuum stabilized, the variac was turned on and the furnace brought slowly up to temperature while the ligand inlet system was first shut off and then adjusted for desired flow after the ligand container was opened. Cocondensation usually continued at least an hour, at most three, during which time the furnace condition, the ligand flow, and the level of liquid nitrogen surrounding the bell jar were monitored.

Once the cocondensation part of the experiment was over, either at the end of a specified time or at the exhaustion of the supply of one of the reactants, the current to the furnace was turned off, the ligand supply was shut off, the vacuum was cut off, and the system was allowed to warm up.
For the experiments with volatile ligands, the vacuum system was
switched over to a line with a rough pump and a liquid nitrogen trap to
condense the unreacted ligand during the early stage of the warm-up. The
reactor was allowed to warm to a temperature at which the wash-down
solvent would not freeze on the surface; the reactor was pressurized with
the inert gas; and the top plug was exchanged with a septum cap through
which two cannulas (flexible double-ended needles) were inserted. One
cannula had its other end through a septum in a Schlenk tube containing
the wash-down solvent into which argon was being blown. Another
cannula was connected to a tube leading through a septum into the top of a
Schlenk filter filled with Celite. Some wash-down solvent was then sprayed
onto the interior of the bell jar to wash the melted matrix off the walls and
dissolve what it could of the products. The resulting slurry was contained
between the raised wall on the flange and the bottom of the bell jar until it
was pulled off through the second cannula. All of the insolubles, including
unreacted gold, were filtered off onto the Celite, the soluble products being
carried through the filter into the receiving flask. A determination of the
amount of each reactant used was made by weighing the furnace and the
ligand bulb or lecture bottle.

The soluble products were then concentrated by vacuum distilling
the solvent off on a Schlenk line. Normally a different, more nonpolar,
solvent was then transferred into the flask to dissolve selectively any
neutral organometallics. These products were then transferred to another
Schlenk flask, the solvent again removed by vacuum distillation, and the
septum cap replaced with a cold finger. The flask was connected to a
vacuum line, the cold finger filled with liquid nitrogen, and the
organometallic product sublimed. A drybox was used to transfer the cold
finger and the sublimate to another Schlenk flask where the product was
washed off with a minimum of pentane. The cold finger was replaced with
a septum cap and the solvent was vacuum distilled until the solution
became cloudy, at which time the flask was placed in a freezer and left
overnight to allow the product to crystallize.

The recrystallized product was weighed to determine overall yield,
based on the amount of metal vaporized. Normal procedure required the
combination of the products of several metal vapor syntheses to provide the
starting material for further experiments because of the small amounts
normally synthesized and the relatively high molecular weights of the
bis(trifluoro-methyl)gold-μ-halide dimers. The products were stored under
nitrogen in Schlenk flasks in a freezer to reduce the likelihood of thermal
decomposition.

The reactor was cleaned by wiping off the interior surfaces with
Kimwipes soaked with acetone several successive times. When necessary,
the bell jar was cleaned with a dilute hydrochloric acid solution, and the
metal parts of the reactor were cleaned by scouring them with steel wool.
The bottom of the reactor was lined with aluminum foil to catch residues
which fell during the experiments and wash-down solvent which failed to
reach the reactor walls during the wash-down procedure. This foil was
replaced when it became noticeably dirty or after a wash-down where
solvent was spilled onto the bottom of the reactor. In between reactions the
reactor was left under vacuum. Experience proved this to be necessary in
obtaining a good vacuum since even the most careful matrix wash-down resulted in some solvent getting into small crevices in the reactor base.

Schlenk Line and Procedures

For the isolation and further reactions of the products of the metal vapor synthesis reactions, a double manifold Schlenk line was built. It was constructed with a vacuum manifold and an inert gas manifold interconnected with five three-way, oblique bore stopcocks. The ends of each manifold had a 0.5 mm valve for direct connection to auxiliary apparatus, such as the flask which served as a large volume vacuum trap when distilling off the wash-down solvent from the metal vapor synthesis reactions. The valves were connected to the Schlenk glassware by 1/4-inch I.D. rubber vacuum tubing.

The vacuum manifold was pumped by a Welch Duo-Seal Model 1400 rotary oil pump. A vacuum trap between the manifold and the pump protected the pump from condensable solvent vapors and augmented the pumping of the system. A Consolidated Vacuum Corporation thermocouple gauge continuously monitored the pressure in the manifold. The inert gas manifold was connected directly to a cylinder of pre-purified nitrogen.

A set of Schlenk glassware was built for the manipulation of compounds. It consisted of elongated flasks with 24/40 standard taper male joints and a set of filter tubes and specialty glassware with 24/40 standard
taper female joints. All of the flasks and filter tubes and most of the specialty glassware had side arms with ground-glass stopcocks for connection to the Schlenk line.

Before use, all flasks and special set-ups were evacuated on the Schlenk line and back-filled with nitrogen. Solvents were transferred by cannula. Glassware was cleaned by scrubbing, when necessary, soaking in a potassium hydroxide/ethanol bath, followed by a dilute HCl bath, rinsing with de-ionized water, and drying in an oven kept at 180°C

Reagents and Purification Procedures

The gold was cut from gold calorimeter capsules obtained from Dr. Margrave. The trifluoromethyl bromide and phosphorus trifluoride were from the Matheson Gas Co. The trifluoromethyl iodide was synthesized by Dr. Bell. The thallium ethoxide and hexafluoroacetylacetone were from Aldrich. The solvents used were distilled from appropriate drying agents, sodium/potassium amalgam for the diethyl ether and pentane, and phosphorus pentoxide for the dichloromethane. The diethyl ether was stored over molecular sieves until it was added to the still. The distilled solvents were degassed on the Schlenk line before use. The Celite was kept in a drying oven at 180°C until it was put into a Schlenk funnel, which was immediately evacuated while the Celite was still hot to remove as much water or other adsorbed volatiles as possible.
References and Notes

1 For general information on Schlenk techniques see:
Chapter 3

Metal Vapor Synthesis of
Bis(trifluoromethyl)gold-μ-halide Dimers

Background

Since this project had the goal of making perfluoroalkylgold complexes with as few other ligands as possible, a clean metal vapor synthesis was quite attractive. The gold would enter the reaction devoid of other ligands allowing the design of the final ligand sphere, provided the gold would react with the trifluoromethyl ligand.

In 1976, Puddephatt synthesized the first gold complexes which incorporated trifluoromethyl ligands by the oxidative addition reaction of trifluoromethyl iodide with methylgold(l)phosphines.\(^1\) These products were synthesized and characterized by \(^{19}\text{F} \) NMR in situ in sealed NMR tubes and not isolated. By 1981, Lagow had demonstrated that nickel and palladium atoms would react in a trifluoromethyl plasma to form complexes with two trifluoromethyl groups, using the stabilizing ligand trimethylphosphine to synthesize \((\text{CF}_3)_2\text{Ni(PMe}_3)_3\) and \((\text{CF}_3)_2\text{Pd(PMe}_3)_2\).\(^2\)
At virtually the same time, Morrison had demonstrated that this type of molecule could also be made with the third row metal, platinum. This synthesis involved a ligand exchange reaction with \((CF_3)_2Cd\cdot glyme\) (glyme = MeOCH\(_2\)CH\(_2\)OMe) and this time triethylphosphine stabilized the product, \((CF_3)_2Pt\cdot(PEt_3)_2\). These products were isolated from the reaction mixture before being characterized by both proton and \(^{19}F\) NMR.

Plans were made to modify the existing metal atom reactor to allow for codeposition of gold with radio frequency discharge generated trifluoromethyl plasma in a parallel with Lagow's work. At this time the compounds under consideration for use as stabilizing ligands were trifluorophosphine and tris(trifluoromethyl)phosphine.

The mechanics of the project changed when Bell codeposited gold and trifluoromethyl iodide and produced the first bis(trifluoromethyl)gold iodide. The yield was low, 0.272\%, and the product was less trifluoromethylated (by comparison to the tris(trifluoromethyl)gold monomer which had been the hoped for product) and less volatile than desired.

The typical reaction forming the bis(trifluoromethyl)gold-\(\mu\)-iodide dimer consisted of the cocondensation of about 2 g. (10.15 mmol) gold with about 25 g. (127.6 mmol) trifluoromethyl iodide for a ligand to metal ratio of 12.5:1 over the course of approximately 1.5 hours. The wash-down procedure involved spraying the inside of the bell jar and siphoning out about a dozen 50 ml. aliquots of diethyl ether for a total solvent volume of about 600 ml. From this was isolated roughly 12.74 mg. (0.0137 mmol) of bis(trifluoromethyl)gold-\(\mu\)-iodide dimer, a 0.272\% yield based on metal.
vaporized.

The typical reaction forming the bis(trifluoromethyl)gold-µ-bromide dimer consisted of the cocondensation of about 0.75 g. (3.81 mmol) gold with about 50 g. (335.8 mmol) trifluoromethyl bromide for a ligand to metal ratio of 88:1 over the course of approximately 1.5 hours. The wash-down procedure involved spraying the inside of the bell jar and siphoning out about eight 50 ml. aliquots of diethyl ether for a total solvent volume of about 400 ml. From this was isolated roughly 250 mg. (0.301 mmol) of bis(trifluoromethyl)gold-µ-bromide dimer, a 15.8% yield based on metal vaporized.

Characterization of Bis(trifluoromethyl)gold-µ-iodide Dimer

The reaction of gold vapor with trifluoromethyl iodide in the metal vapor synthesis reactor yielded just one product which was soluble in, and isolatable from, diethyl ether. By increasing the ratio of ligand to metal from 12.5:1 to approximately 100:1, the yield for the reaction, based on the amount of gold vaporized, was increased from the initial 0.272% to 8% indicating that a major competing reaction in the synthesis was gold cluster formation. The dark reddish-brown product sublimed at 40°C (10⁻³ Torr) and crystallized from pentane in diamond-shaped prisms. The compound was found to have a melting point of 136-7°C with no decomposition although upon exposure to light or air it began to show noticeable decomposition within a week and created a noticeable reddish film on the interior of its glass container.
The compound was characterized by infrared spectroscopy (Figure 3-1); $^{19}$F NMR (in CDCl$_3$, ext. ref. F$_3$CCOOH) $\delta$ = -73.7 (broad singlet); and mass spectrometry (Figure 3-2) where m/e 924 (M$^+$, 0.04%), 69 (CF$_3^+$, 100%).

The molecular geometry was determined by x-ray crystal diffraction, performed by Dr. Kenton Whitmire, which refined half of the molecule, the atomic positions in the other half were determined by symmetry functions. See Table 3-1 for the crystal data, Table 3-2 for the bond lengths, and Table 3-3 for the bond angles.

The ORTEP diagram (Figure 3-3) gives an indication of the extent of the surface area that is covered by the fluorine atoms, the factor which is thought to enhance the vapor pressure of the compound by giving each molecule an essentially fluoride surface.

Characterization of Bis(trifluoromethyl)gold-$\mu$-bromide Dimer

Since the yield of the reaction of gold with trifluoromethyl iodide was disappointingly low, a variation was tried by codepositing the gold with trifluoromethyl bromide, also known as Freon 13B1, a more common industrial chemical than trifluoromethyl iodide and therefore more readily available. Again there was only one product which was soluble in and isolatable from diethyl ether. This product was a bright yellow compound which sublimed readily at room temperature and 10$^{-2}$ Torr. This property was encouraging but it complicated the matter of manipulating the compound on the Schlenk line without it subliming into the vacuum
FIGURE 3-1

Infrared Spectrum of Bis(trifluoromethyl)gold-μ-iodide Dimer (in CHCl₃):

<table>
<thead>
<tr>
<th>Abs (in cm⁻¹)</th>
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</thead>
<tbody>
<tr>
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<td>1147</td>
</tr>
<tr>
<td>1123</td>
</tr>
<tr>
<td>1090</td>
</tr>
<tr>
<td>1028</td>
</tr>
</tbody>
</table>

Wavenumber (cm⁻¹)
FIGURE 3-2

Mass Spectrum of Bis(trifluoromethyl)gold-μ-iodide Dimer (30 eV). Masses below 512 have been left off for clarity in limited space.
TABLE 3-1

\[ \text{[Au(CF}_3\text{)]}_2(\mu-\text{I})_2 \text{ Crystal Data:} \]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>( \text{Au}_2\text{I}_2\text{C}<em>4\text{F}</em>{12} )</td>
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<td>Formula Weight</td>
<td>923.77</td>
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<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
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<td>Lattice Parameters:</td>
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<tr>
<td>( a )</td>
<td>7.5963 (8) Å</td>
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<tr>
<td>( b )</td>
<td>7.295 (1) Å</td>
</tr>
<tr>
<td>( c )</td>
<td>13.057 (1) Å</td>
</tr>
<tr>
<td>( \beta )</td>
<td>100.710° (7)</td>
</tr>
<tr>
<td>( V )</td>
<td>711.0 (1) Å³</td>
</tr>
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<td>Space Group</td>
<td>( P2_1/n ) (#14)</td>
</tr>
<tr>
<td>Z value</td>
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<tr>
<td>( D ) calc</td>
<td>4.31 g/cm³</td>
</tr>
<tr>
<td>( F000 )</td>
<td>792</td>
</tr>
<tr>
<td>( \mu ) (Mo K(\alpha))</td>
<td>257.62 cm(^{-1})</td>
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<td>Diffractometer</td>
<td>Rigaku AFC5S</td>
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<tr>
<td>Radiation</td>
<td>Mo K(\alpha) ((\lambda=0.71069))</td>
</tr>
<tr>
<td>Temperature</td>
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</tr>
<tr>
<td>2(\theta) (max)</td>
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<td>Maximum Shift in Final Cycle</td>
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<td>Largest Peak in Final Diff. Map</td>
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</tr>
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</table>
TABLE 3-2

Intramolecular Bond Lengths (in Å) for $[\text{Au(CF}_3\text{)}_2(\mu-\text{Br})]_2$ and $[\text{Au(CF}_3\text{)}_2(\mu-\text{D})]_2$

<table>
<thead>
<tr>
<th>Atoms</th>
<th>$[\text{Au(CF}_3\text{)}_2(\mu-\text{Br})]_2$</th>
<th>$[\text{Au(CF}_3\text{)}_2(\mu-\text{D})]_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(1)--C(1)</td>
<td>2.03(7)</td>
<td>2.07(2)</td>
</tr>
<tr>
<td>Au(1)--C(2)</td>
<td>2.03(8)</td>
<td>2.12(2)</td>
</tr>
<tr>
<td>Au(1)--X(1)</td>
<td>2.496(8)</td>
<td>2.654(1)</td>
</tr>
<tr>
<td>Au(1)--X(2)</td>
<td>2.500(8)</td>
<td>2.658(1)</td>
</tr>
<tr>
<td>F(1)--C(1)</td>
<td>1.41(9)</td>
<td>1.26(2)</td>
</tr>
<tr>
<td>F(2)--C(1)</td>
<td>1.39(7)</td>
<td>1.18(2)</td>
</tr>
<tr>
<td>F(3)--C(1)</td>
<td>1.26(7)</td>
<td>1.20(3)</td>
</tr>
<tr>
<td>F(4)--C(2)</td>
<td>1.19(8)</td>
<td>1.30(2)</td>
</tr>
<tr>
<td>F(5)--C(2)</td>
<td>1.31(7)</td>
<td>1.26(2)</td>
</tr>
<tr>
<td>F(6)--C(2)</td>
<td>1.20(1)</td>
<td>1.22(3)</td>
</tr>
</tbody>
</table>
TABLE 3-3

Intramolecular Bond Angles (in degrees) for [Au(CF$_3$)$_2$(μ-Br)]$_2$ and [Au(CF$_3$)$_2$(μ-I)]$_2$

<table>
<thead>
<tr>
<th>Atoms</th>
<th>[Au(CF$_3$)$_2$(μ-Br)]$_2$</th>
<th>[Au(CF$_3$)$_2$(μ-I)]$_2$</th>
</tr>
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<tbody>
<tr>
<td>C(1)—Au(1)—C(2)</td>
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<td>C(1)—Au(1)—X(1)</td>
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<td>91.9(6)</td>
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<td>C(1)—Au(1)—X(2)</td>
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<td>177.7(6)</td>
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<td>C(2)—Au(1)—X(1)</td>
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<td>177.8(6)</td>
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<td>C(2)—Au(1)—X(2)</td>
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<td>92.4(6)</td>
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<td>X(1)—Au(1)—X(2)</td>
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<td>94.9(3)</td>
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<tr>
<td>F(1)—C(1)—F(2)</td>
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<tr>
<td>F(1)—C(1)—F(3)</td>
<td>114(7)</td>
<td>100(2)</td>
</tr>
<tr>
<td>F(1)—C(1)—Au(1)</td>
<td>114(5)</td>
<td>116(1)</td>
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<tr>
<td>F(2)—C(1)—F(3)</td>
<td>100(6)</td>
<td>100(2)</td>
</tr>
<tr>
<td>F(2)—C(1)—Au(1)</td>
<td>110(5)</td>
<td>116(2)</td>
</tr>
<tr>
<td>F(3)—C(1)—Au(1)</td>
<td>113(6)</td>
<td>114(1)</td>
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<tr>
<td>F(4)—C(2)—F(5)</td>
<td>107(7)</td>
<td>109(2)</td>
</tr>
<tr>
<td>F(4)—C(2)—F(6)</td>
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<td>106(2)</td>
</tr>
<tr>
<td>F(4)—C(2)—Au(1)</td>
<td>115(6)</td>
<td>111(2)</td>
</tr>
<tr>
<td>F(5)—C(2)—F(6)</td>
<td>96(8)</td>
<td>107(2)</td>
</tr>
<tr>
<td>F(5)—C(2)—Au(1)</td>
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<td>111(2)</td>
</tr>
<tr>
<td>F(6)—C(2)—Au(1)</td>
<td>110(6)</td>
<td>112(1)</td>
</tr>
</tbody>
</table>
FIGURE 3-3

ORTEP DIAGRAM OF
BIS(TRIFLUOROMETHYL)GOLD-μ-IODIDE
manifold. When recrystallized from pentane, the compound formed either needles or diamond-shaped prisms. When the experiment was conducted at a ligand to metal ratio of 100:1, the overall yield (based on gold vaporized) was 18%. The compound had a melting point of 90-1°C, with no decomposition. The decomposition rate was greater than for the iodide compound upon exposure to air, and the bromide compound also displayed some light-sensitivity.

The compound was characterized by infrared spectroscopy (Figure 3-4), $^{19}$F NMR (in CDCl$_3$, ext. ref. F$_3$CCOOH) $\delta$ = -71.4 (broad singlet); and mass spectrometry (Figure 3-5) where m/e 832 (M$^+$, 0.2%), 830 (M-2, 0.45%), 828 (M-4, 0.25%), 19 (F$^+$, 100%).

The molecular geometry was determined by x-ray crystal diffractometry, performed by Jorge Gonzales, which refined half of the molecule, the atomic positions in the other half being determined by symmetry functions. See Table 3-4 for the crystal data, Table 3-2 for the bond lengths, and Table 3-3 for the bond angles. Figure 3-6 shows the ORTEP diagram generated by the data.

Discussion

These structures can be compared with each other as well as with reported structures of the dimethylmonobromogold dimer$^5$, the monomethyldibromogold dimer$^6$, and other gold compounds with related constituent atoms and geometries.$^7$ The relevant intramolecular bond
Infrared Spectrum of Bis(trifluoromethyl)gold-μ-bromide Dimer (in CHCl₃):

<table>
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<tr>
<td>1100</td>
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<tr>
<td>1040</td>
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</table>
FIGURE 3-5

Mass Spectrum of Bis(trifluoromethyl)gold-μ-bromide Dimer (70 eV).

Masses below 512 have been left off for clarity in limited space.
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<tr>
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</thead>
<tbody>
<tr>
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</tr>
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<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
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<td>Lattice Parameters:</td>
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<td>$b$</td>
<td>7.20 (2) Å</td>
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<tr>
<td>$c$</td>
<td>12.41 (4) Å</td>
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<td>$\beta$</td>
<td>99.0° (2)</td>
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<td>$V$</td>
<td>658 (2) Å$^3$</td>
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<td>Space Group</td>
<td>P2$_1$/n (#14)</td>
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<tr>
<td>$Z$ value</td>
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<td>F000</td>
<td>720</td>
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<tr>
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<td></td>
<td>Graphite-monochromated</td>
</tr>
<tr>
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<td>Maximum Shift in Final Cycle</td>
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<tr>
<td>Largest Peak in Final Diff. Map</td>
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</tbody>
</table>
FIGURE 3-6

ORTEP DIAGRAM OF
BIS(TRIFLUOROMETHYL)GOLD-μ-BROMIDE
distances and angles for the gold atom bonded to the methyl groups and the bridging bromines in [Au(CH₃)₂(μ-Br)]₂ and [Au(CH₃)Br(μ-Br)]₂ are shown in Table 3-5, using these designations for the atoms of the monomethyl dibromogold dimer:

\[ \text{Br}(2) \quad \text{Br}(1) \quad \text{C}(1) \]
\[ \text{Au}(2) \quad \text{Au}(1) \]
\[ \text{Br}(2') \quad \text{Br}(1') \quad \text{C}(1') \]

For comparison, the bond distance between the Au(2) and the terminal bromines was 2.401(2) Å and the distance between Au(2) and the bridging bromides was 2.453(2) Å; the bond angles around Au(2) are all within 0.85° of a right angle.

The gold-bromide bridging bond lengths in [Au(CF₃)₂(μ-Br)]₂ are 0.10-0.15Å shorter than the similar bonds in [Au(CH₃)₂(μ-Br)]₂ and [Au(CH₃)Br(μ-Br)]₂, while the gold-carbon bonds are also shorter by 0.09Å than in [Au(CH₃)Br(μ-Br)]₂. The most likely explanation for this observation is that the fluorides are withdrawing charge from the center of the molecule with the result being the shortening of these central bonds.

Four-coordinate gold (III) has all of its bonding orbitals filled and excess electron density occupies antibonding orbitals. Though there are no reports of bond lengths for gold to the carbon of a trifluoromethyl group, in the general literature of gold-carbon compounds the lengths range from 1.85Å (-CN) to 2.14Å (terminal alkyls) and up to 2.23Å (μ-CH₂) while
### TABLE 3-5

Bond Lengths and Angles for $[\text{Au(CH}_3\text{)}_2\mu\text{-Br}]_2^5$ and $[\text{Au(CH}_3\text{)}\text{Br}\mu\text{-Br}]_2^6$

<table>
<thead>
<tr>
<th>Atoms</th>
<th>$[\text{Au(CH}_3\text{)}_2\mu\text{-Br}]_2$</th>
<th>$[\text{Au(CH}_3\text{)}\text{Br}\mu\text{-Br}]_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(1)–C(1)</td>
<td>na*</td>
<td>2.12(1) Å</td>
</tr>
<tr>
<td>Au(1)–µ-X(1)</td>
<td>2.645(8) Å</td>
<td>2.607(2) Å</td>
</tr>
<tr>
<td>C(1)–Au(1)–C(1')</td>
<td>na</td>
<td>89.6(9)°</td>
</tr>
<tr>
<td>C(1)–Au(1)–µ-Br(1)</td>
<td>na</td>
<td>93.9(5)°</td>
</tr>
<tr>
<td>µ-Br(1)–Au(1)–µ-Br(1')</td>
<td>100°</td>
<td>82.68(7)°</td>
</tr>
<tr>
<td>Au(1)–µ-Br(1)–Au(2)</td>
<td>80°</td>
<td>94.08(5)°</td>
</tr>
</tbody>
</table>

* na indicates that this number is not available; only the atoms in the central square were sufficiently refined to report their positions.
carborane complexes of gold are assigned an average gold-carbon bond of 2.77 Å. The value measured for gold-iodide bridging bonds in AuI is 2.62 Å which is only 0.04 Å shorter than the longer bond measured in [Au(CF₃)₂(μ-I)]₂; this may indicate that the trifluoromethyls and the iodide are similar in competition for bonding electrons.

While mechanistic studies have not been carried out in sufficient depth to fully show what the intermediates are, the literature of gold⁹ and metal atom chemistry would suggest that the gold reacts with both of the products of the dissociation of the trifluoromethyl halides and forms the end product by the following sequence:

1) 2 Au + CF₃X → AuCF₃ + AuX

2) AuCF₃ + CF₃X → (CF₃)₂AuX

3) 2(CF₃)₂AuX →

This is essentially an oxidative addition process.

It is interesting to note that while the trifluoromethyl analog has resisted traditional synthetic techniques, an attempted reaction between gold atoms and methyl iodide in the metal atom reactor yielded no organometallic products.⁴ Thus it seems that Gibson's traditional techniques are necessary to synthesize the alkyl compounds while metal vapor synthesis is needed to make the perfluoroalkyl compounds.
There appeared to be no significant differences between the iodide and the bromide complexes as they both show similar solubilities in the solvents used and can be worked with using identical procedures. As can be seen from the crystal structures and crystal data, they are isostructural and isomorphous, leading to IR and NMR spectra which are very similar. In neither case were the spectra particularly illuminating as the available spectra for perfluoromethylgold compounds are quite limited. The absorptions in the infrared are due to carbon-fluorine stretching vibrations. The $^{19}$F NMR shifts can be compared with the shifts reported for $(\text{CF}_3)_2\text{M(PEt}_3)_2$ (M=Pt, Pd, Ni) which fall in the range of $\delta$= -61.1 to -64.3 (ppm vs. ext. $\text{F}_3\text{CCOOH}$),\(^{10}\) compared with shifts of -71.4 to -73.7 (ppm vs. ext. $\text{F}_3\text{CCOOH}$) found for the bis(trifluoromethyl)gold-$\mu$-halide dimers.
References and Notes


4 J. Bell, personal communication.


Chapter 4

Reactions of Bis(trifluoromethyl)gold-\(\mu\)-halide Dimers

Background

Further reactions were attempted with the bis(trifluoromethyl)gold-\(\mu\)-halide in an effort to break the halide bridges and make stable monomeric species with the expectation that such monomers would exhibit greater volatility. Proceeding on the theory that the bis(trifluoromethyl)gold-\(\mu\)-halide would display behavior somewhat analogous to the dimethylgold-\(\mu\)-halide dimers which Gibson reported,\(^1\) we began the investigation with a survey of ligands which he had used\(^2\) which were deemed appropriate to the system ultimately desired. Preference was given to the smaller perfluorinated ligands and to ligands which were substantially fluorinated with the expectation that these would contribute further to the volatility of the system.

The ideal ligand appeared to be a relatively simple mono-anionic, bidentate ligand which could displace the halides and satisfy the coordination needs of the gold without bridging. Acetylacetone fits this
description almost perfectly and is also available as hexafluoroacetyl-
acetone which would nearly satisfy the desire for a perfluoro-compound.
The hexafluoroacetylacetonate anion has but one hydrogen remaining on
the central carbon.

Next best would be a neutral monodentate ligand which would
displace neither the halide nor the trifluoromethyl groups, but would
satisfy the coordination needs of the gold and break the bridges forming the
dimers. The prime candidates here were phosphorus compounds, such as
phosphorus trifluoride and tris(trifluoromethyl)phosphine.

Experimental Procedure for Hexafluoroacetylacetone

The first step was to select the counter-ion for the reaction to form the
hexafluoroacetylacetonate. Historically the two favorite cations for this
have been sodium or thallium. Despite the advantages of using the less
toxic sodium route, the advantages of the chemically softer thallium
compound prevailed. The reaction with the bis(trifluoromethyl)gold-µ-
halide dimer was carried out in the less polar solvents in which both
reactants were more soluble and less likely to encounter species which
might cause decomposition of the gold complexes.

Thallium hexafluoroacetylacetonate is synthesized most easily from
thallium ethoxide and hexafluoroacetylacetone:

\[ \text{TlOEt} + \text{CF}_3\text{COCH}_2\text{COCF}_3 \rightleftharpoons \text{CF}_3\text{COCHCOCF}_3\text{TL} + \text{EtOH} \]
The thallium hexafluoroacetetylacetonate was isolated and then reacted with the bis(trifluoromethyl)gold-μ-bromide dimer in diethyl ether:

\[
\begin{align*}
\text{F}_3\text{C} & \quad \text{Au} & \quad \text{F}_3\text{C} \\
\text{F}_3\text{C} & \quad \text{Br} & \quad \text{Br} & \quad \text{CF}_3 \quad + \quad 2\text{TI} \\
\text{O} & \quad \text{C} & \quad \text{CH} & \quad \text{Et}_2\text{O} \\
\text{O} & \quad \text{C} & \quad \text{CH} & \quad + \quad 2\text{TI} \text{Br} \\
\text{CF}_3 & \quad \text{Au} & \quad \text{CF}_3 \\
\end{align*}
\]

When the solvent was vacuum distilled at ice-water temperature, an oily, pale yellow liquid remained. Further vacuum distillations and attempts to recrystallize the compound from pentane resulted only in loss of the product and a thin reddish film in the Schlenk line. An attempt to sublime a product from the oily liquid resulted in pale yellow frost on the liquid nitrogen filled cold finger but it quickly melted to an oil upon warming and showed little improvement in purification.

The mass spectrum (Figure 4-1) indicated a peak at 542, the expected M⁺ peak for bis(trifluoromethyl)gold hexafluoroacetetylacetonate. Other methods of characterization were unsuccessful because the compound tended to decompose rapidly on exposure to various solvents and light. The resulting complex spectra did not allow the pure compound to be differentiated from the impurities and decomposition products.
FIGURE 4-1

Mass Spectrum of Bis(trifluoromethyl)gold hexafluoroacetyladonate (50 eV)
Experimental Procedure for Phosphorus Trifluoride

The reaction with phosphorus trifluoride was much faster in several ways. No preparatory synthesis of the ligand was involved; the experiment involved simply dissolving the bis(trifluoromethyl)gold-μ-bromide dimer in ether in a sturdy Schlenk flask which was pressurized with two atmospheres of phosphorus trifluoride. The reaction was swift and noticeable as it was quite exothermic and resulted in the immediate formation of a gold mirror and some brown precipitate; no evolution of gas was observed. When the solution was analyzed by mass spectrometry, no gold was found.

An attempted metal vapor reaction of gold directly with tris(trifluoromethyl)phosphine likewise yielded no ether-soluble gold-containing products as analyzed by mass spectrometry.

Experimental Procedure for Tris(trifluoromethyl)phosphine

This reaction required the synthesis of the tris(trifluoromethyl)-phosphine$^3$. A calorimetry bomb was converted into an autoclave for the reaction of red phosphorus with trifluoromethyl iodide at 220°C for 48 hours; distillation of the products gave pure tris(trifluoromethyl)phosphine. The bis(trifluoromethyl)gold-μ-bromide dimer did not react, even upon mild heating, with the tris(trifluoromethyl)phosphine.
Results and Discussion

The hexafluoroacetylacetone product is of interest because there is no other record of a gold-hexafluoroacetylacetionate compound and it represents our only success in the attempts to synthesize a monomeric bis(trifluoromethyl) gold complex. It did not display any greater volatility than the halide dimers during Schlenk line work. The lack of stability made it a disappointment in terms of the goals of this project and it was difficult to characterize fully. Also, its physical nature (an oil) made its purification and characterization difficult. Chemically it was much less stable than the halide dimers, having a noticeably faster decomposition upon exposure to air than the bis(trifluoromethyl) gold halide dimers. The hexafluoroacetylacetone product even decomposed on contact with CDCl₃ which thwarted an attempt to take the $^{19}$F NMR spectrum. Both the $^{19}$F NMR, in d₆-benzene, and the infrared spectra of the oil were taken but the remaining reactants and broad peaks due to decomposition products masked any meaningful results and made interpretation impossible.

The phosphorus trifluoride apparently initiated decomposition of the bis(trifluoromethyl)gold-$\mu$-bromide dimer. Apparently, it was not involved in any stable complexation with the gold but rather attacked one of the ligands leading to reduction of the gold and total decomposition of the molecule.

Rather unexpectedly, the tris(trifluoromethyl)phosphine did not react. Previous studies have demonstrated the reactivity of dimethylgold halides with tertiary phosphines⁴. This work has already shown that while
the methyl and trifluoromethyl analogs share structural similarities, their syntheses and reactivities are quite different.

Because the reactions of these various ligands and the bis(trifluoromethyl)gold-μ-bromide dimer were somewhat puzzling and disappointing, they were repeated with the gold iodide dimer. The results were the same in each case. In the reaction with the thallium hexafluoromethylacetylacetonate the iodide dimer seemed to give an even lower yield than the bromide dimer, although, as alluded to earlier, the purification procedure was ineffective and perhaps led to the lesser yield. The results of these studies confirm the chemical similarities of bis(trifluoromethyl)gold bromide and iodide dimers, at least in these reactions.
References and Notes

Chapter 5

Conclusions and Proposals for Future Work

Other routes can be attempted in the search for organogold compounds, whether of high volatility or not. The work described here of making the bis(trifluoromethyl)gold-μ-halide dimers and attempting to break the dimers into perfluorinated monomers was a logical first step.

One of the difficulties in working with gold is its preference for odd numbered oxidation states and even numbered coordination sites. While its tendency to form dimers with bridging ligands was of great importance in this study, it also led to the instability when the coordination sphere was perturbed, as by phosphorus trifluoride. This suggests a further search for ligands which preferably are soft and have an odd-even mismatch in their charge vs. coordination ability.

The chemical softness of gold (i.e. its relatively large size, low oxidation states compared to atomic number, high polarizability, and its preference for bonding with ligands of a similar nature) was also a mixed blessing. While it drove the formation of the organometallic complex, on the other hand it was probably a large factor in the instability of the
hexafluoracetylacetonate complex where it had to bond through the oxygens. The possibility of reacting the gold atoms or compounds with sulphur containing compounds holds a great deal of promise. Given the chemical softness of gold, it remains somewhat curious that there was no reaction with the tris(trifluoromethyl)phosphorus. A search into the literature suggests that the problem may simply be that the low reactivity of the tris(trifluoromethyl)phosphorus offsets any benefits of its compatible softness. Although one extension of this project would be to react gold atoms with trifluoromethyl chloride, the literature of organogold chemistry suggests that the reactivity of gold with the smaller, harder chloride would be significantly less than with the bromide or iodide compounds.

Another possible direction for new synthetic work would be to codeposit gold with mixed reactants and stabilizing ligands. Or the project might include the investigation of other compounds which might dissociate and react in a manner analogous to the trifluoromethyl halides, i.e., a survey of various other Freons (C$_2$F$_5$Br, C$_2$F$_5$I, etc.) and their reactivity with gold.

The chemistry of the bis(trifluoromethyl)gold-$\mu$-halide dimers should not be considered closed. There is a whole series of complexes which Gibson made with the analogous dimethylgold-$\mu$-halide dimers and one should look at mixed alkyl/perfluoroalkyl compounds.

By getting away from the emphasis on gold, one might use other metals (Ir, Pt, Ag, Tl) generated by high temperature vaporization to react with perfluoroalkyl ligand systems. Platinum would be of interest because of the many traits it shares with its periodic neighbor gold, i.e. its size,
chemical softness, and preferred geometry. One trait that is not shared is the odd charge/even coordination dilemma, but another not shared is the ease of vaporization. For this purpose the Margrave lab has acquired the electronics for an electron gun to be incorporated into a reactor with the capabilities of attaining higher vaporization temperatures and of vaporizing greater amounts of metals. An electron gun will vaporize a conducting material without the need to have it in a refractory container. Such a reactor could eventually become a large-scale synthetic tool as it allows a continuous feed of sample material.