

Bis(carbonyl)gold(I) Undecafluorodiantimonate(V),  
 [Au(CO)<sub>2</sub>][Sb<sub>2</sub>F<sub>11</sub>]: Synthesis, Vibrational and <sup>13</sup>C NMR  
 Study, and the Molecular Structure of Bis(acetonitrile)gold(I)  
 Hexafluoroantimonate(V), [Au(NCCH<sub>3</sub>)<sub>2</sub>][SbF<sub>6</sub>]

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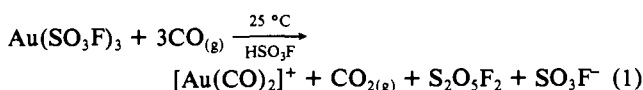
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**Abstract:** The synthesis of the bis(carbonyl)gold(I) salt, [Au(CO)<sub>2</sub>][Sb<sub>2</sub>F<sub>11</sub>], is achieved in a two-step procedure: the reduction of gold(III) fluorosulfate, Au(SO<sub>3</sub>F)<sub>3</sub>, in HSO<sub>3</sub>F to give Au(CO)SO<sub>3</sub>F as an intermediate, followed by solvolysis in liquid antimony(V) fluoride in the presence of carbon monoxide. The use of <sup>13</sup>CO or C<sup>18</sup>O permits the synthesis of the corresponding isotopically labeled salts. The compound is thermally stable up to 130 °C. The cation has D<sub>∞h</sub> symmetry, and all seven fundamentals, three Raman and four IR active modes, are observed. A normal coordinate analysis (NCA) and general valence force-field (GVFF) calculations are carried out and allow comparison to the isoelectronic and isosteric molecular species Hg(CN)<sub>2</sub> and [Au(CN)<sub>2</sub>]<sup>-</sup>. The near absence of gold to carbon π-back donation in [Au(CO)<sub>2</sub>]<sup>+</sup> is manifested in strong carbon-oxygen bonds and consequently rather weak gold-carbon bonds, reflected in the highest CO-stretching frequencies so far observed for a metal carbonyl derivative with 2254 (ν<sub>1</sub>) and 2217 (ν<sub>3</sub>) cm<sup>-1</sup> and a stretching force constant of 20.1 × 10<sup>2</sup> Nm<sup>-1</sup>. In the <sup>13</sup>C NMR spectrum a single-line resonance at 174 ppm is attributed to [Au(<sup>13</sup>CO)<sub>2</sub>]<sup>+</sup>, while the [Au(<sup>13</sup>CO)]<sup>+</sup> chemical shift changes from 162 ppm in HSO<sub>3</sub>F to 158 ppm in magic acid (HSO<sub>3</sub>F/SbF<sub>5</sub>). The resonances for [Au(<sup>13</sup>CO)<sub>2</sub>]<sup>+</sup> and [Au(<sup>13</sup>CO)]<sup>+</sup> in the same solution are found to undergo coalescence at elevated temperature indicative of slow CO exchange. The coalescence temperature is solvent dependent, 325 K in HSO<sub>3</sub>F and 395 K in the more dilute HSO<sub>3</sub>F/SbF<sub>5</sub> mixture. Attempts to recrystallize [Au(CO)<sub>2</sub>][Sb<sub>2</sub>F<sub>11</sub>] from acetonitrile result in the formation of single crystals of [Au(NCCH<sub>3</sub>)<sub>2</sub>][SbF<sub>6</sub>] instead. The compound crystallizes in a cubic unit cell, space group Pa $\bar{3}$ , with a = 10.250 (2) Å and Z = 4. The structure was determined by Patterson and Fourier methods and refined by least-squares techniques to R = 0.023 and R<sub>w</sub> = 0.024 for 147 reflections with I > 3σ(I). The crystal contains linear [Au(NCCH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> cations and octahedral [SbF<sub>6</sub>]<sup>-</sup> anions, with normal dimensions.

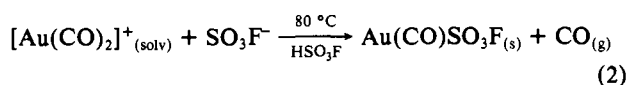
## Introduction

A small number of carbonyl derivatives of gold have been synthesized to date.<sup>1,2</sup> Of this small group, carbonyl gold(I) chloride, Au(CO)Cl, has been known since 1925.<sup>3</sup> Its vibrational spectrum<sup>4</sup> and molecular structure<sup>5</sup> are published, and a number of its reactions have been studied.<sup>1,2</sup> For over 65 years Au(CO)Cl has remained the sole member in this select group of compounds.

Recently four additional carbonyl gold(I) derivatives have been reported. They include carbonyl gold(I) fluorosulfate, Au(CO)SO<sub>3</sub>F, which is formed via the solvated bis(carbonyl)gold(I) cation [Au(CO)<sub>2</sub>]<sup>+</sup> as intermediate,<sup>6</sup> when gold tris(fluorosulfate), Au(SO<sub>3</sub>F)<sub>3</sub>, dissolved in fluorosulfuric acid is reduced by carbon monoxide according to



followed by thermal decomposition



and isolated by sublimation in quantitative yield.

The [Au(CO)<sub>2</sub>]<sup>+</sup> cation, also present in [Au(CO)<sub>2</sub>][UF<sub>6</sub>],<sup>7</sup> is formed in anhydrous HF according to



Finally, a report on the formation and characterization of thermally unstable Au(CO)Br has appeared recently.<sup>8</sup>

In addition to these mononuclear carbonyl gold(I) derivatives, a dinuclear, mixed valency (+1,+3) compound of the composition Au<sub>2</sub>(CO)Cl<sub>4</sub> is known,<sup>9</sup> and several studies of gold(0) carbonyls are reported, among them matrix-isolated Au(CO)<sub>2</sub><sup>10</sup> and Au(CO),<sup>11</sup> studied by ESR<sup>10,11</sup> and vibrational spectroscopy.<sup>10</sup> They exhibit extremely low thermal stability, and their vibrational

spectra show no resemblance to carbonyl gold(I) derivatives, which are the subject of this study.

Of the carbonyl gold(I) derivatives, the bis(carbonyl)gold(I) cation, [Au(CO)<sub>2</sub>]<sup>+</sup>, deserves particular attention for three reasons: (a) it is the only thermally stable binary gold carbonyl species reported so far, and other thermally stable binary bis(carbonyl) transition metal compounds are unknown; (b) the CO stretching frequencies, with an average value of 2231 cm<sup>-1</sup> for [Au(CO)<sub>2</sub>]<sup>+</sup><sub>(solv)</sub>, are the highest observed so far for any metal carbonyl species,<sup>6</sup> well above the value of 2143 cm<sup>-1</sup> for free CO;<sup>12</sup> and (c) it is one of the few linear five-atomic species that belong to the point group D<sub>∞h</sub>, and a comparison to [Au(CN)<sub>2</sub>]<sup>-</sup> and Hg(CN)<sub>2</sub> seems most appropriate.

Unfortunately, the limited thermal stability of [Au(CO)<sub>2</sub>][U-F<sub>6</sub>]<sup>7</sup> and the observed band overlap with vibrations due to HSO<sub>3</sub>F or SO<sub>3</sub>F<sup>-</sup> in the case of [Au(CO)<sub>2</sub>]<sup>+</sup><sub>(solv)</sub>,<sup>6</sup> have prevented a complete vibrational analysis of this ion so far.

In the present study these limitations are overcome by the synthesis of a new bis(carbonyl)gold(I) derivative, [Au(CO)<sub>2</sub>][Sb<sub>2</sub>F<sub>11</sub>]. The solid is thermally stable up to 130 °C and permits the recording of the complete vibrational spectrum of [Au(CO)<sub>2</sub>]<sup>+</sup>.

(1) Puddephatt, R. J. *The Chemistry of Gold*; Elsevier: Amsterdam, 1978.

(2) Puddephatt, R. J. *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, U.K., 1987; Vol. 7, p 861.

(3) (a) Manchot, W.; Gall, H. *Chem. Ber.* **1925**, *58B*, 2175. (b) Kharash, M. S.; Isbell, H. S. *J. Am. Chem. Soc.* **1930**, *52*, 2919.

(4) (a) Belli Dell'Amico, D.; Calderazzo, F.; Dell'Amico, G. *Gazz. Chim. Ital.* **1977**, *107*, 101. (b) Calderazzo, F. *Pure Appl. Chem.* **1978**, *50*, 49. (c) Browning, J.; Goggin, P. L.; Goodfellow, R. J.; Norton, M. J.; Rattray, A. J. M.; Taylor, B. F.; Mink, J. J. *Chem. Soc., Dalton Trans.* **1977**, 2061.

(5) Jones, P. G. Z. *Naturforsch.* **1982**, *37B*, 823.

(6) Willner, H.; Aubke, F. *Inorg. Chem.* **1990**, *29*, 2195.

(7) Adelhelm, M.; Bacher, W.; Höhn, E. G.; Jacob, E. *Chem. Ber.* **1991**, *124*, 1559.

(8) Belli Dell'Amico, D.; Calderazzo, F.; Robino, P.; Serge, A. *Gazz. Chim. Ital.* **1991**, *121*, 51; *J. Chem. Soc., Dalton Trans.* **1991**, 3017.

(9) Belli Dell'Amico, D.; Calderazzo, F.; Marchetti, F. *J. Chem. Soc., Dalton Trans.* **1976**, 1829.

(10) McIntosh, D.; Ozin, G. A. *Inorg. Chem.* **1977**, *16*, 51.

(11) Kasai, P. H.; Jones, P. M. *J. Am. Chem. Soc.* **1985**, *107*, 6385.

(12) Herzberg, G. *Spectra of Diatomic Molecules*; 2nd ed.; D. Van Nostrand: New York, 1950.

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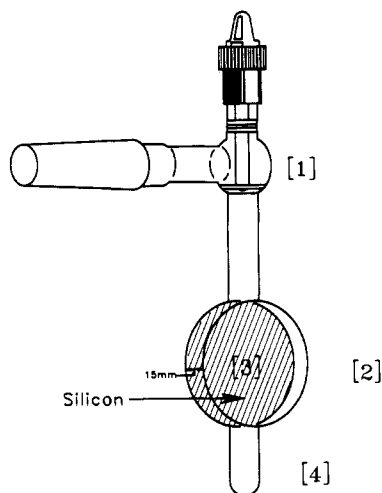


Figure 1. Infrared cell, fitted with silicon windows.

With the aid of <sup>13</sup>C and <sup>18</sup>O, isotopic substitution valence force field calculations are conducted, and <sup>13</sup>C NMR spectra of HSO<sub>3</sub>F solutions allow identification of [Au(<sup>13</sup>CO)<sub>2</sub>]<sup>+</sup><sub>(solv)</sub> and the monocarbonyl gold(I) cation [Au(<sup>13</sup>CO)]<sup>+</sup><sub>(solv)</sub>.

Finally, the attempted recrystallization of [Au(CO)<sub>2</sub>][Sb<sub>2</sub>F<sub>11</sub>] from acetonitrile results in CO elimination and the formation of a crystalline, white salt of the composition [Au(NCCH<sub>3</sub>)<sub>2</sub>][SbF<sub>6</sub>]. The molecular structure of this compound is determined by single-crystal X-ray diffraction.

### Experimental Section

**(a) Chemicals.** Gold powder of 99.99% purity was obtained from ABCR, Karlsruhe, Germany. HSO<sub>3</sub>F (technical grade) and SbF<sub>5</sub> of 98% purity were obtained from Bayer A.G. Leverkusen and Merck, Darmstadt, respectively. Both were purified first by distillation at atmospheric pressure and then by trap-to-trap distillation in vacuo. Bis(fluoro-sulfuryl)peroxide, S<sub>2</sub>O<sub>6</sub>F<sub>2</sub>, was prepared by the catalytic fluorination (AgF<sub>2</sub>) of SO<sub>3</sub>.<sup>13</sup> SO<sub>2</sub>ClF was obtained from SO<sub>2</sub>Cl<sub>2</sub> by partial halogen exchange with NaF.<sup>14</sup> Gold trifluoride was obtained by fluorination (with F<sub>2</sub>) of anhydrous AuCl<sub>3</sub>,<sup>15</sup> which in turn was prepared from AuCl<sub>3</sub>·2H<sub>2</sub>O (99.9% purity, ABCR, Karlsruhe) by treatment with SOCl<sub>2</sub>. The solvents CH<sub>3</sub>CN (99.5% pure, Merck, Darmstadt) and SO<sub>2</sub> (99.5% Bayer A.G. Leverkusen) were dried by storing over P<sub>4</sub>O<sub>10</sub>. The gases CO (98%, Linde A.G.), <sup>13</sup>CO (<sup>13</sup>C enrichment 99%, M.S.D. Isotopes, Montreal, P.Q.), and C<sup>18</sup>O (<sup>18</sup>O enrichment 99.6%, Matthey, Karlsruhe) were dried by cooling to -196 °C during vacuum transfer.

**(b) Instrumentation.** <sup>13</sup>C NMR spectra were obtained on a Bruker MSL200 FT spectrometer operating at 50.330 MHz. Liquid samples were contained in sealed-off tubes of 5 mm o.d. and placed in the center of 10 mm o.d. tubes fitted with rotationally symmetrical Teflon stem valves (Young, London, UK). CDCl<sub>3</sub>, used as lock and as external reference, was added to the outer tube. For measurement above 30 °C, D<sub>2</sub>SO<sub>4</sub> was used. With D<sub>2</sub>SO<sub>4</sub> as lock, <sup>13</sup>CO<sub>2</sub> present in the samples was used as internal reference.

Solid-state spectra using magic angle spinning (MAS) were recorded using a broad band probe, MAS DLK, 39–82 MHz (Bruker), with rotational frequencies between 1500 and 4000 Hz. Details and parameters are as follows: spectral width 828 ppm, delay time 5 s, pulse angle 20°, 500 acquisitions, pulse programme SOLIDC2. Samples were filled inside the drybox into a rotor made from ZrO<sub>2</sub> with an airtight Kel-F lid and insert.

Raman spectra were obtained on a Bruker FT instrument type FRA 106, either at the University of Munich (Prof. Schnöckel) or at Bruker Instruments in Karlsruhe (Dr. Sawatzki). Liquid samples were contained in 5-mm o.d. NMR tubes, and solids were filled into 2-mm o.d. capillaries.

Infrared spectra were recorded with two FT-IR spectrometers: a Bruker IFS-66v instrument with the range of 4000–50 cm<sup>-1</sup> and a Nicolet MX-1 spectrometer operating between 4000 and 400 cm<sup>-1</sup>. For all vibrational spectroscopic measurements, the spectral resolution was 4 cm<sup>-1</sup>.

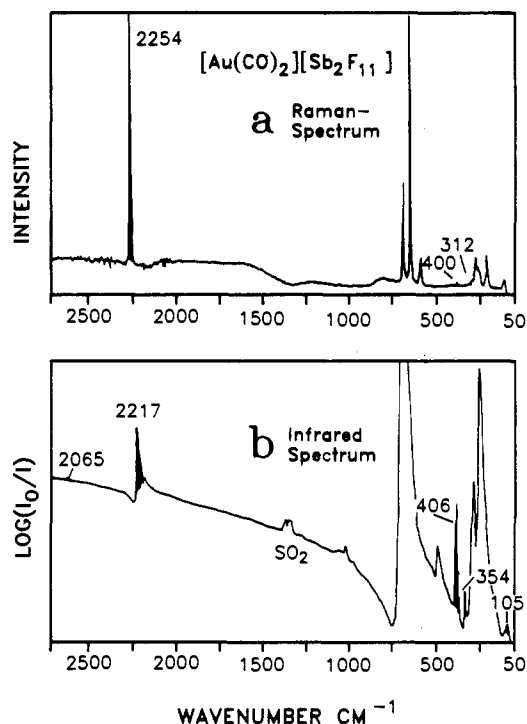


Figure 2. Vibrational spectra of solid [Au(CO)<sub>2</sub>][Sb<sub>2</sub>F<sub>11</sub>]: (a) Raman spectrum and (b) IR spectrum.

IR spectra of dissolved samples were obtained on thin films between two silicon discs (Wacker Chemie, Burghausen, Germany), 0.5-mm thick and 45-mm in diameter. The silicon discs were mounted in an airtight Teflon sample holder.

In order to record IR spectra of solid [Au(CO)<sub>2</sub>][Sb<sub>2</sub>F<sub>11</sub>] in the spectral range of 4000–50 cm<sup>-1</sup>, a special sample preparation technique was developed. The sample cell is shown in Figure 1. A pair of silicon windows [3] was attached 15-mm apart with epoxy glue to the cell body [2]. The device was found to be vacuum tight between +100 and -120 °C. In a typical experiment, the carefully dried cell was charged inside the inert-atmosphere box with about 20 mg of solid [Au(CO)<sub>2</sub>][Sb<sub>2</sub>F<sub>11</sub>]. The cell was evacuated, and about 2–4 mmol of dry SO<sub>2</sub> were condensed in vacuo onto the sample, contained in the cold finger [4]. The cell was subsequently warmed to -20 °C in an ethanol bath and shaken until the solid had completely dissolved. The solution was distributed evenly over the silicon windows on the inside of the cell by further shaking the contents. While the cell was still cold, it was connected to the vacuum line with the windows in a horizontal position and allowed to warm up slowly. Evaporation of SO<sub>2</sub> produced a thin layer of [Au(CO)<sub>2</sub>][Sb<sub>2</sub>F<sub>11</sub>] on the surface of the silicon windows. Complete removal of SO<sub>2</sub> was ensured by briefly heating the cell to 80 °C in a water bath.

Gaseous and volatile reagents and products were measured in a vacuum line of known volume. Pressure measurements were made with a Setra capacity manometer type 280E (Setra Instruments, Acton, Mass). Synthetic reactions were carried out in various glass reactors (25–100-mL volume) fitted with Teflon stem valves (Young, London, UK) and Teflon-coated stirring bars.

Solid materials were manipulated either inside an inert-atmosphere box (Braun, Munich, Germany) filled with argon with a residual moisture content of less than 0.1 ppm or a Vacuum Atmosphere Corporation Drilab filled with dry N<sub>2</sub> as described before.<sup>6</sup> Solutions in HSO<sub>3</sub>F were prepared in an evacuable box (Mecaplex, Grenchen, Switzerland) filled with N<sub>2</sub>. Microanalyses were performed either by Beller Laboratories Göttingen, Germany or Mr. P. Borda, Department of Chemistry, UBC, Vancouver, Canada.

**(c) X-ray Diffraction.** A summary of the crystal data for [Au(NCCH<sub>3</sub>)<sub>2</sub>][SbF<sub>6</sub>] is given in Table I. The unit cell parameters were obtained by least-squares refinement for 22 reflections with 2θ = 41–45°. Intensity measurements were made on a Rigaku AFC6S diffractometer using graphite monochromatized Mo Kα radiation. The intensities of three standard reflections, remeasured every 200 reflections throughout the data collection, declined by 1.75%, and a linear correction factor was applied to the data to account for this minor decay. A full octant was collected (2θ(max) = 59.7°, h, k, l ≥ 0) giving a total of 1823 measured reflections. A preliminary examination of the data suggested m3 Laue symmetry. The data were then reprocessed and corrected for Lorentz and polarization factors, and an empirical absorption correction (ψ scan)

(13) Cady, G. H.; Shreeve, J. M. *Inorg. Synth.* 1963, 7, 124.

(14) Tullock, C. W.; Coffman, D. D. *J. Org. Chem.* 1960, 25, 2016.

(15) Brauer, G. *Handbuch der Präparativen Anorganischen Chemie*; Enke, F. Publishing Co.; Stuttgart, 1975; Vol. 1, p 250.

was applied, and the data merged ( $R_{\text{int}} = 10.5\%$ ) to give 527 independent measured reflections.

The gold and antimony atoms were located on independent  $\bar{3}$  sites, 4(b) and 4(a), by a careful examination of the distribution of diffracted intensity within the reflection parity groups; the two heavy atoms were found to be pseudo-body-centered with respect to each other. The methyl carbon atom was then located on the body diagonal 3-fold axis (position 8(c)), approximately equidistant between the two heavy atoms, by an examination of the low-weight peaks in the Patterson function. A difference Fourier map calculated after isotropic least-squares refinement of this model revealed the positions of all three remaining non-hydrogen atoms: the carbon and nitrogen atoms of the cyanide group on the 3-fold axis (8(c)) and the fluorine atom, F, in a general position (24(d)). All of the non-hydrogen atoms were refined anisotropically with the parameters of the atoms on crystallographic special positions suitably restrained. In the later stages of the refinement a peak corresponding to the position of the one independent methyl group hydrogen atom was located in a difference map. The hydrogen atom was included in this position, with its thermal parameter refined. Published neutral-atom scattering factors and anomalous dispersion corrections for non-hydrogen atoms were used.<sup>16</sup> Final atomic coordinates and equivalent isotropic thermal parameters, bond lengths, and bond angles are tabulated and mentioned in the discussion section. A more detailed summary of the crystallographic data is found in the supplementary material. An ORTEP diagram<sup>17</sup> of the structure will also be discussed.

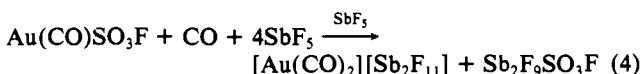
**Synthetic Reactions.** (a)  $[\text{Au}(\text{CO})_2][\text{Sb}_2\text{F}_{11}]$ . In a typical preparation a reactor was charged with 197 mg (1.0 mmol) of gold powder. About 2 g of  $\text{HSO}_3\text{F}$  and 1 g of  $\text{S}_2\text{O}_6\text{F}_2$  were added in vacuo, and the mixture was warmed to 80 °C and magnetically stirred until all gold powder had dissolved (1 h). After cooling the mixture to room temperature, the excess  $\text{S}_2\text{O}_6\text{F}_2$  was removed in vacuo, and 4 mmol CO were admitted to the reactor with the flask cooled to -196 °C. At this temperature the vapor pressure of CO was approximately 580 mbar. In order to effect a complete condensation of expensive, isotopically labeled carbon monoxide ( $^{13}\text{CO}$  or  $\text{C}^{18}\text{O}$ ), a stream of liquid helium was directed toward the precooled (-196 °C) flask. Approximately 1 L of helium was needed for a single condensation step.

The reaction mixture was allowed to warm to room temperature, and the yellow solution was stirred vigorously until it became colorless (approximately 10 h were needed). All volatile products were removed in vacuo with the reactor initially at room temperature and then at 50–60 °C for 3 h. To the residue, found to be pure, solid  $\text{Au}(\text{CO})\text{SO}_3\text{F}$ , about 10 g of  $\text{SbF}_5$ , and 2 mmol of CO were condensed in vacuo. After warming the mixture to 50 °C under constant stirring, two separate liquid phases were noticed. Upon further warming to 75 °C for 1 h a single phase had formed. On cooling to room temperature, two phases separated out again. Excess  $\text{SbF}_5$  and the reaction product  $\text{Sb}_2\text{F}_9\text{SO}_3\text{F}$  were removed in vacuo, and the denser of the two phases was left as residue. The initial weight of ~910 mg suggested a composition of  $\text{Au}(\text{CO})_2\text{-Sb}_4\text{F}_{21}$ , but after pumping at 80 °C the residue solidified and 730 mg (1.03 mmol) of  $[\text{Au}(\text{CO})_2][\text{Sb}_2\text{F}_{11}]$  were obtained. The white, crystalline material was found to be stable to 130 °C without apparent evolution of CO and melted in a sealed capillary at 156 °C. Anal. Calcd for  $\text{Au}_2\text{C}_2\text{F}_{11}\text{Sb}_2\text{O}_2$ : Au, 27.9; C, 3.40; Sb, 34.5. Found: Au, 29.5; C, 3.57; Sb, 33.9.

(b)  $[\text{Au}(\text{CH}_3\text{CN})_2][\text{SbF}_6]$ . In an attempt to recrystallize  $[\text{Au}(\text{C}-\text{O})_2][\text{Sb}_2\text{F}_{11}]$ , about 40–50 mg of this material was dissolved in dry acetonitrile, resulting in immediate release of gas (CO). The resulting white crystals were isolated by slow solvent evaporation in vacuo, studied by single-crystal X-ray diffraction, and analyzed by Mr. P. Borda of the Department of Chemistry at UBC. Anal. Calcd for  $\text{Au}_2\text{C}_4\text{F}_6\text{H}_6\text{N}_2\text{Sb}$ : C, 9.33; H, 1.17; N, 5.43. Found: C, 9.40; H, 1.19; N, 5.37.

## Results and Discussion

(a) **Synthesis.** The conversion of  $\text{Au}(\text{CO})\text{SO}_3\text{F}$  in the presence of CO to  $[\text{Au}(\text{CO})_2][\text{Sb}_2\text{F}_{11}]$  according to



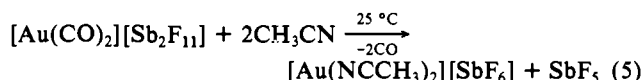
follows published precedents. Using this approach, main group, organometallic, or transition metal fluorosulfates are solvolyzed in an excess of antimony(V) fluoride to allow the syntheses of fluoroantimonate derivatives such as  $\text{Br}_2[\text{Sb}_3\text{F}_{16}]$ ,<sup>18a</sup>  $[(\text{CH}_3)_2\text{-Sn}][\text{Sb}_2\text{F}_{11}]_2$ ,<sup>18b</sup> or  $\text{Pd}[\text{SbF}_6]_2$ .<sup>18c</sup>

(16) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, UK (present distribution D. Reidel: Dordrecht, The Netherlands), 1974; Vol. IV, pp 99–102, 149.

The attempted synthesis of monocarbonyl gold(I) hexafluoroantimonates(V) from  $\text{Au}(\text{CO})\text{SO}_3\text{F}$  without additional CO leads to viscous, poorly defined liquids of varying composition. Similarly, the initial product, after removal of excess  $\text{SbF}_5$  and the rather volatile product  $\text{Sb}_2\text{F}_9\text{SO}_3\text{F}$ ,<sup>19</sup> is a viscous phase of the approximate composition  $\text{Au}(\text{CO})_2\text{Sb}_4\text{F}_{21}$  from which solid  $[\text{Au}(\text{CO})_2][\text{Sb}_2\text{F}_{11}]$  is obtained by heating to 80 °C in vacuo.

The white solid shows reasonable thermal stability and may be heated to 130 °C without any detectable loss of mass. Attempts to follow the thermal decomposition of  $[\text{Au}(\text{CO})_2][\text{Sb}_2\text{F}_{11}]$  by differential thermal analysis (DTA) up to 400 °C indicate continuous decomposition and result eventually in the formation of a fine layer of gold on the surface of the crucible and thermocouple. Distinct intermediates such as a gold monocarbonyl compound or a gold(I) fluoroantimonate are not detected and remain, just like  $\text{AuF}^{20}$  and  $\text{AuSO}_3\text{F}$ ,<sup>6</sup> elusive.

Facile substitution of CO is observed when an attempt is made to recrystallize  $[\text{Au}(\text{CO})_2][\text{Sb}_2\text{F}_{11}]$  from acetonitrile

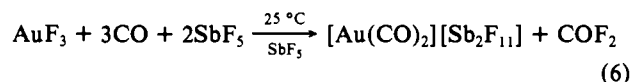


Bis(acetonitrile)gold(I) hexafluoroantimonate(V) is isolated in the form of square, crystalline plates, which are suitable for a molecular structure determination by single-crystal X-ray diffraction. The most likely byproduct,  $\text{SbF}_5\text{-NCCH}_3$ , is reportedly soluble in an excess of acetonitrile<sup>21</sup> and is not isolated here.

Cationic gold(I) complexes of the type  $\text{AuL}_2^+$  with nitrogen donor ligands are rare. In this case a relevant precedent,  $[\text{Au}(\text{NCCH}_3)_2][\text{SbCl}_6]$ , exists<sup>22a</sup> and is characterized by its IR spectrum.<sup>22b</sup> In addition, the cation  $[\text{Au}(\text{NCCH}_3)_2]^+$  is readily obtained by anodic oxidation of gold in acetonitrile and used in the determination of stability constants of various gold(I) complexes.<sup>12</sup> Its standard reduction potential is known.<sup>22c</sup>

The displacement of CO by other ligands is, in the case of  $\text{Au}(\text{CO})\text{Cl}$ , frequently used in the synthesis of various gold(I) complexes.<sup>12</sup> It is anticipated that this compound will play a useful role in the synthesis of cationic complexes of the type  $[\text{AuL}_2]^+$ .

There is an alternative single-step synthetic route to  $[\text{Au}(\text{C}-\text{O})_2][\text{Sb}_2\text{F}_{11}]$  which appears to proceed according to the general equation



Upon combining the reagents,  $\text{AuF}_3$  turns immediately black, and the reaction mixture becomes very viscous. Within 8 h the viscosity of the reaction mixture decreases, and within 3 days all the  $\text{AuF}_3$  has dissolved. Removal of all volatiles allows isolation of  $[\text{Au}(\text{CO})_2][\text{Sb}_2\text{F}_{11}]$ . This alternate route may be used because of its simplicity, where  $\text{AuF}_3$  is more readily available than  $\text{Au}(\text{SO}_3\text{F})_3$ .

The bis(carbonyl)gold(I) salt  $[\text{Au}(\text{CO})_2][\text{Sb}_2\text{F}_{11}]$  is very soluble in dry  $\text{SO}_2$ . The resulting solutions are stable at room temperature for several days. The solubility in  $\text{SO}_2\text{FCl}$  is considerably lower, and a  $\text{SO}_2\text{FCl}/\text{SO}_2$  mixture of a 100:1 volume ratio is suitable as solvent in attempts to recrystallize  $[\text{Au}(\text{CO})_2][\text{Sb}_2\text{F}_{11}]$  by slowly reducing the volume of the solution. However, attempts to obtain single crystals in this manner for a molecular structure determination have been unsuccessful so far.

(17) *TEXSAN/TEXRAY*; Structure Analysis Package Version (5.0) Molecular Structure Corporation: The Woodlands, TX 77381; 1989.

(18) (a) Wilson, W. W.; Thompson, R. C.; Aubke, F. *Inorg. Chem.* **1980**, *19*, 1489. (b) Mallela, S. P.; Yap, S.; Sams, J. R.; Aubke, F. *Rev. Chim. Miner.* **1986**, *23*, 572. (c) Cader, M. S. R.; Aubke, F. *Can. J. Chem.* **1989**, *67*, 1700.

(19) Wilson, W. W.; Aubke, F. *J. Fluorine Chem.* **1979**, *13*, 431.

(20) Müller, B. *J. Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 861.

(21) Kolditz, L.; Rehak, W. *Z. Anorg. Allg. Chem.* **1966**, *342*, 32.

(22) (a) Zuur, A. P.; Groeneveld, W. P. *Recl. Trav. Chem. Pay-Bas* **1967**, *86*, 1089. (b) Reedijk, J.; Zuur, A. P.; Groeneveld, W. L. *Recl. Trav. Chem. Pay-Bas* **1967**, *86*, 1127. (c) Johnson, P. R.; Pratt, J. M.; Tilley, R. I. *J. Chem. Soc., Chem. Commun.* **1978**, 606.

In summary, the cation [Au(CO)<sub>2</sub>]<sup>+</sup> appears to exist either in HSO<sub>3</sub>F solution<sup>6</sup> or as a solid, together with very weak nucleophiles as counter anions like [UF<sub>6</sub>]<sup>-7</sup> or [Sb<sub>2</sub>F<sub>11</sub>]<sup>-</sup>. A monocarbonyl gold(I) cation [Au(CO)]<sup>+</sup> has remained elusive in solid compounds. A copper analogue is found in [Cu(CO)][AsF<sub>6</sub>]<sup>23</sup> while for Ag(CO)B(OTeF<sub>5</sub>)<sub>4</sub><sup>24</sup> covalent bonding of the B(OTeF<sub>5</sub>)<sub>4</sub> group to silver is observed.

All observations made here and elsewhere strongly suggest that carbonyl derivatives of group 11 metals are different from conventional transition metal carbonyls in four major respects: (i) they are either cations or cationic in nature with the metal in the +1 oxidation state, bonded to highly electronegative and weakly nucleophilic anions or anionic ligands, and strong protonic acids or superacids are frequently used in their synthesis and generation; (ii) they may not obey the effective atomic rule; (iii) CO appears to be weakly bound and replaceable; and (iv) their thermal stability increases with the decreasing basicity of the counter anion. This is best illustrated for [Au(CO)<sub>2</sub>]<sup>+</sup>, where stability toward CO cleavage follows the order SO<sub>3</sub>F<sup>-</sup> < [UF<sub>6</sub>]<sup>-</sup> < [Sb<sub>2</sub>F<sub>11</sub>]<sup>-</sup>.

Interestingly, solid, well-characterized and thermally stable binary, cationic bis(carbonyl) salts are obtained only for gold but not for copper or silver.

A final comment concerns the general synthetic route to carbonyl gold(I) derivatives. With suitable gold(I) precursors frequently either unknown<sup>20</sup> or difficult to obtain,<sup>1,2</sup> metallic gold or the more stable and available gold(III) derivatives AuCl<sub>3</sub>,<sup>3</sup> AuBr<sub>3</sub>,<sup>8</sup> Au(SO<sub>3</sub>F)<sub>3</sub>,<sup>6</sup> or AuF<sub>3</sub> take their place. Oxidation of gold by UF<sub>6</sub> is so far only employed in the synthesis of [Au(CO)<sub>2</sub>][UF<sub>6</sub>],<sup>7</sup> while reductive carbonylation under mild conditions appears to be more generally applicable, as exemplified by the syntheses of Au(CO)Cl,<sup>3</sup> Au(CO)SO<sub>3</sub>F,<sup>6</sup> Au(CO)Br,<sup>8</sup> and [Au(CO)<sub>2</sub>][Sb<sub>2</sub>F<sub>11</sub>] from either Au(SO<sub>3</sub>F)<sub>3</sub> or AuF<sub>3</sub>.

(b) **Vibrational Spectra.** (i) **The Assignment of Fundamentals for [Au(CO)<sub>2</sub>]<sup>+</sup>.** For the five atomic linear [Au(CO)<sub>2</sub>]<sup>+</sup> cation of point group D<sub>∞h</sub>, the irreducible representation of normal vibrations is

$$\Gamma_{\text{vib}} = 2\Sigma_g^+[\nu_1, \nu_2 (\text{Ra}, \text{p})] + 2\Sigma_u^+[\nu_3, \nu_4 (\text{IR})] + \Pi_g[\nu_5 (\text{Ra}, \text{dp})] + 2\Pi_u[\nu_6, \nu_7 (\text{IR})]$$

Of the expected seven fundamental vibrations, four have been identified in previous studies,<sup>6,7</sup> but only the two CO stretching modes  $\nu_1$  and  $\nu_3$ , observed for [Au(CO)<sub>2</sub>]<sup>+(solv)</sup>, appear to be correctly assigned.<sup>6</sup> In order to identify and assign all seven fundamental vibrations unambiguously, the vibrational spectra of both 1 M solutions of [Au(CO)<sub>2</sub>]<sup>+</sup> in HSO<sub>3</sub>F and solid [Au(CO)<sub>2</sub>][Sb<sub>2</sub>F<sub>11</sub>] are investigated and CO with the natural isotope distribution as well as isotopically enriched <sup>13</sup>C and <sup>18</sup>O are employed. In HSO<sub>3</sub>F solution with SO<sub>3</sub>F<sup>-</sup> as counterion the solvent bands are identified by comparison with previous reports.<sup>25,26</sup> For solid [Au(CO)<sub>2</sub>][Sb<sub>2</sub>F<sub>11</sub>], all fundamentals of the [Au(CO)<sub>2</sub>]<sup>+</sup> cation are identified, with anion bands assigned by comparison with published precedents.<sup>27-29</sup> Examples of an infrared and Raman spectrum are shown in Figure 2.

The observed vibrational frequencies as well as a vibrational assignment of the bands due to solid [Au(CO)<sub>2</sub>][Sb<sub>2</sub>F<sub>11</sub>] and [Au(CO)<sub>2</sub>]<sup>+(solv)</sup> are listed in Tables II and III, respectively, together with the corresponding bands of the <sup>13</sup>C and <sup>18</sup>O isotopomers.

As observed previously in alkali metal salts of the isoelectronic anion [Au(CN)<sub>2</sub>]<sup>-30</sup> only weak interionic coupling is observed. Probably the only indication of such coupling is very weak bands

Table I. Selected Crystallographic Data for [Au(NCCH<sub>3</sub>)<sub>2</sub>][SbF<sub>6</sub>]

formula	C <sub>4</sub> H <sub>8</sub> AuF <sub>6</sub> N <sub>2</sub> Sb
formula wt	514.81
crystal system	cubic
space group	<i>Pa</i> $\bar{3}$ (no. 205)
<i>a</i> (Å)	10.250 (2)
<i>V</i> (Å <sup>3</sup> )	1076.9 (3)
<i>Z</i>	4
<i>T</i> (K)	294
$\rho_c$ (g cm <sup>-3</sup> )	3.17
$\lambda$ (Å)	0.71069
$\mu$ (Mo <i>K</i> α) cm <sup>-1</sup>	1614
transmission factors	0.40–1.00
<i>R</i>	0.023
<i>R<sub>w</sub></i>	0.024
no. of independent measd reflns	527
reflcs with <i>I</i> ≤ 3σ( <i>I</i> )	147
no. of parameters refined	25

interpreted as satellites bands of  $\nu_3$  at 2176 and 2239 cm<sup>-1</sup>, respectively, which are also found in the IR spectra of the isotopomers and are possibly caused by a correlation field splitting of  $\nu_3$ . Alternatively, the presence of trace amounts of a second, possibly nonlinear or nonsymmetrical Au(CO)<sub>2</sub> species may have caused these very weak bands.

The accuracy of IR band positions and of the isotope shifts for solids is judged to be 1–2 cm<sup>-1</sup>. For solutions of [Au(CO)<sub>2</sub>]<sup>+</sup> in HSO<sub>3</sub>F, all band positions are completely reproducible, and an accuracy of ±0.5 cm<sup>-1</sup> is suggested. The accuracy limit in band positions of Raman bands is generally judged to be ±1 cm<sup>-1</sup>.

The band assignments for [Au(CO)<sub>2</sub>]<sup>+</sup> (Table IV) are based on the observed band intensities in the IR and Raman spectra as a reflection of the mutual exclusion principle. In addition, comparison to the reported vibrational spectrum of [Au(CN)<sub>2</sub>]<sup>-30,31</sup> model calculations and a normal coordinate analysis (to be discussed) also aid in the assignments.

Of the four stretching vibrations ( $\nu_1$ – $\nu_4$ ), the two CO stretches have been assigned already on [Au(CO)<sub>2</sub>]<sup>+</sup> solutions.<sup>6</sup> For solid [Au(CO)<sub>2</sub>][Sb<sub>2</sub>F<sub>11</sub>], very slightly higher frequencies of 2254 and 2217 cm<sup>-1</sup> are observed in the Raman and IR spectra, respectively. A plausible cause is a very weak solvation effect, resulting in a very slight frequency lowering, or a small difference in anion basicity between SO<sub>3</sub>F<sup>-</sup>/HSO<sub>3</sub>F and [Sb<sub>2</sub>F<sub>11</sub>]<sup>-</sup>. Nevertheless, a comparison of the data in Tables II and III clearly indicates that the species giving rise to the vibrational spectra are identical in solution and in the solid state. A slightly higher anion basicity for [UF<sub>6</sub>]<sup>-</sup> than for [Sb<sub>2</sub>F<sub>11</sub>]<sup>-</sup> is seen as a likely cause for the observation of  $\nu_3$  at 2200 cm<sup>-1</sup> in [Au(CO)<sub>2</sub>][UF<sub>6</sub>].<sup>7</sup>

Of the remaining stretching vibrations,  $\nu_2$ , the symmetric Au–CO stretch, is observed at 400 cm<sup>-1</sup> as a very weak band in the Raman spectrum of [Au(CO)<sub>2</sub>][Sb<sub>2</sub>F<sub>11</sub>]. For [Au(CN)<sub>2</sub>]<sup>-30</sup>  $\nu_2$  is of similar low intensity. Furthermore, a very weak IR band at 2605 cm<sup>-1</sup> corresponds to the most intense combination band,  $\nu_2 + \nu_3$ , reported for [Au(CN)<sub>2</sub>]<sup>-31</sup> From the band position of  $\nu_3$  found for [Au(CO)<sub>2</sub>][Sb<sub>2</sub>F<sub>11</sub>], a value of 388 cm<sup>-1</sup> is obtained for  $\nu_2$ , with the difference to 400 cm<sup>-1</sup> attributed to anharmonicity.

For the asymmetric Au–CO stretch  $\nu_4$ , IR-active bands at 406 and 354 cm<sup>-1</sup> may be considered. Model calculations in  $\Sigma_u^+$  and  $\Pi_u$  using these frequencies suggest isotope shifts (*I*/*II*) of either 13.5/2.6 or 4.6/9.6 cm<sup>-1</sup>. The observed isotope shift of 4.5/9 listed in Table IV strongly supports the assignment of the band at 354 cm<sup>-1</sup> as  $\nu_4$ , and it appears that the previously proposed assignment of these two IR-active bands for [Au(CO)<sub>2</sub>][UF<sub>6</sub>]<sup>7</sup> should be reversed. The assignment of the remaining bands in the deformation range is straightforward.

When the fundamental vibrations of the two isoelectronic and isosteric ions [Au(CO)<sub>2</sub>]<sup>+</sup> and [Au(CN)<sub>2</sub>]<sup>-</sup> are compared, it is noticeable that for the bis(carbonyl)gold(I) cation the ligand stretching and deformation modes are found at higher and the gold–ligand vibrations at lower frequencies than observed for the bis(cyanide)gold(I) complex. An analogous situation is encoun-

(23) Desjardins, C. D.; Edwards, D. B.; Passmore, J. *Can. J. Chem.* **1979**, *57*, 2714.

(24) Hurlburt, P. K.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1991**, *113*, 6277.

(25) Savoie, R.; Giguère, P. A. *Can. J. Chem.* **1964**, *42*, 277.

(26) (a) Gillespie, R. J.; Robinson, E. A. *Can. J. Chem.* **1962**, *40*, 644. (b) Gillespie, R. J.; Robinson, E. A. *Can. J. Chem.* **1962**, *40*, 675.

(27) Gillespie, R. J.; Landa, B. *Inorg. Chem.* **1973**, *12*, 1383.

(28) Bonnet, B.; Mascherpa, G. *Inorg. Chem.* **1980**, *19*, 785.

(29) Craig, N. C.; Fleming, G. F.; Pranata, J. *J. Am. Chem. Soc.* **1985**, *107*, 7324.

(30) Chadwick, B. M.; Frankiss, S. G. *J. Mol. Struct.* **1976**, *31*, 1.

(31) Jones, L. H. *J. Chem. Phys.* **1957**, *27*, 468.

**Table II.** Vibrational Frequencies [cm<sup>-1</sup>] and Assignments for [Au(CO)<sub>2</sub>][Sb<sub>2</sub>F<sub>11</sub>], [Au(<sup>13</sup>CO)<sub>2</sub>][Sb<sub>2</sub>F<sub>11</sub>], and [Au(C<sup>18</sup>O)<sub>2</sub>][Sb<sub>2</sub>F<sub>11</sub>]<sup>a</sup>

[Au(CO) <sub>2</sub> ][Sb <sub>2</sub> F <sub>11</sub> ]				[Au( <sup>13</sup> CO) <sub>2</sub> ][Sb <sub>2</sub> F <sub>11</sub> ]		[Au(C <sup>18</sup> O) <sub>2</sub> ][Sb <sub>2</sub> F <sub>11</sub> ]		assignments			
IR	int	Raman	int	IR	Raman	IR	Raman	Au(CO) <sub>2</sub> <sup>+</sup> D <sub>∞h</sub>		Sb <sub>2</sub> F <sub>11</sub> <sup>-</sup> D <sub>4h</sub>	
2605	vw			2547		2545		Σ <sub>u</sub> <sup>+</sup>	ν <sub>2</sub> +ν <sub>3</sub>		
2239	vw			2187		2188		Σ <sub>u</sub> <sup>+</sup>	ν <sub>3</sub> '		
		2254	vs		2199		2203	Σ <sub>g</sub> <sup>+</sup>	ν <sub>1</sub>		
2217	s			2165		2165		Σ <sub>u</sub> <sup>+</sup>	ν <sub>3</sub>		
2176	w			2125		2124		Σ <sub>u</sub> <sup>+</sup>	ν <sub>3</sub> '		
713	sh			714		713		A <sub>2u</sub>	ν <sub>as</sub>	(SbF <sub>6</sub> ) <sub>ax</sub>	
		697	s		697		697	A <sub>1g</sub>	ν <sub>s</sub>	(SbF <sub>6</sub> ) <sub>ax</sub>	
689	vs			689		689		E <sub>u</sub>	ν <sub>as</sub>	(SbF <sub>6</sub> ) <sub>4eq</sub>	
662	sh			663		663		A <sub>2u</sub>	ν	(SbF <sub>6</sub> ) <sub>4eq</sub>	
		653	vs		653		653	A <sub>1g</sub>	ν <sub>s</sub>	(SbF <sub>6</sub> ) <sub>4eq</sub>	
		598	m		599		598	E <sub>g</sub> /B <sub>1g</sub>	ν <sub>as</sub>	(SbF <sub>6</sub> ) <sub>4eq</sub>	
503	m			503		502		A <sub>2u</sub>	ν <sub>as</sub>	(SbF <sub>6</sub> ) <sub>4eq</sub>	
406	m			392		403		Π <sub>u</sub>	ν <sub>6</sub>		
		400	vw					Σ <sub>g</sub> <sup>+</sup>	ν <sub>2</sub>		
354	w			348		344		Σ <sub>u</sub> <sup>+</sup>	ν <sub>4</sub>		
		312	sh					Π <sub>g</sub>	ν <sub>5</sub>		
307	s			307		308		E <sub>u</sub>	δ <sub>ip</sub>	(SbF <sub>6</sub> ) <sub>ax</sub>	
		293	m		293		293	A <sub>1g</sub>	δ <sub>oop</sub>	(SbF <sub>6</sub> ) <sub>ax</sub>	
		279	w		279		279	B <sub>1g</sub>	δ <sub>ip</sub>	(SbF <sub>6</sub> ) <sub>ax</sub>	
267	s			266		266		A <sub>2u</sub>	δ <sub>oop</sub>	(SbF <sub>6</sub> ) <sub>ax</sub>	
230	sh	229	m	230		230		B <sub>2g</sub> /E <sub>u</sub>		(SbF <sub>6</sub> ) <sub>ax</sub>	
		131	w		131		131	E <sub>g</sub>			
105	vw			105		100		Π <sub>u</sub>	ν <sub>7</sub>		

<sup>a</sup> Abbreviations: vw = very weak, s = strong, w = weak, vs = very strong, m = medium, sh = shoulder, s = symmetrical, oop = out of plane, as = asymmetrical, ip = in plane.

**Table III.** Vibrational Frequencies [cm<sup>-1</sup>] of [Au(CO)<sub>2</sub>]<sup>+</sup> in HSO<sub>3</sub>F Solution<sup>a</sup>

[Au(CO) <sub>2</sub> ] <sup>+</sup>				[Au( <sup>13</sup> CO) <sub>2</sub> ] <sup>+</sup>		[Au(C <sup>18</sup> O) <sub>2</sub> ] <sup>+</sup>		assignments in point group D <sub>∞h</sub>	
IR	int	Raman	int	IR	Raman	IR	Raman		
2599	vw			2542		2537		Σ <sub>u</sub> <sup>+</sup>	ν <sub>2</sub> +ν <sub>3</sub>
		2246.0	vs		2194.5		2197.0	Σ <sub>g</sub> <sup>+</sup>	ν <sub>1</sub>
2210.5	s			2160.0		2158.5		Σ <sub>g</sub> <sup>+</sup>	ν <sub>3</sub>
352.0	w			347.5		343.0		Σ <sub>u</sub> <sup>+</sup>	ν <sub>4</sub>
		312.5	w		303.5		309.0	Π <sub>g</sub>	ν <sub>5</sub>
		[(CO)Au( <sup>13</sup> CO)] <sup>+</sup>					[(CO)Au(C <sup>18</sup> O)] <sup>+</sup>		C <sub>∞v</sub>
2233.5	m	2233.5	s			2234.5	2234.5	Σ <sup>+</sup>	ν <sub>1</sub>
2172.0	s	2172.0	m			2173.0	2173.0	Σ <sup>+</sup>	ν <sub>2</sub>

<sup>a</sup> For abbreviations see table II.

**Table IV.** Fundamental Frequencies [cm<sup>-1</sup>] of [Au(CO)<sub>2</sub>]<sup>+</sup> and [Au(CN)<sub>2</sub>]<sup>-</sup> and Isotope Shifts between [Au(CO)<sub>2</sub>]<sup>+</sup> and [Au(<sup>13</sup>CO)<sub>2</sub>]<sup>+</sup> (I) and [Au(C<sup>18</sup>O)<sub>2</sub>]<sup>+</sup> (II)

[Au(CO) <sub>2</sub> ] <sup>+</sup>	I <sup>b</sup>	II <sup>b</sup>	[Au(CN) <sub>2</sub> ] <sup>-a</sup>	assignments
2254	51.5 (52.4)	49 (50.7)	2162	Σ <sub>g</sub> <sup>+</sup> ν <sub>1</sub>
400	6.5 <sup>c</sup> (6.5)	10 <sup>c</sup> (14.2)	440	Σ <sub>g</sub> <sup>+</sup> ν <sub>2</sub>
2217	50.5 (50.3)	52 (51.8)	2142	Σ <sub>u</sub> <sup>+</sup> ν <sub>3</sub>
354	4.5 (4.6)	9 (9.6)	426	Σ <sub>u</sub> <sup>+</sup> ν <sub>4</sub>
312	9.0 (9.2)	3.5 (3.3)	302	Π <sub>g</sub> ν <sub>5</sub>
406	14 (13.5)	3 (2.6)	390	Π <sub>u</sub> ν <sub>6</sub>
105	0 (0.2)	5 (4.6)	120	Π <sub>u</sub> ν <sub>7</sub>

<sup>a</sup> Averaged values from refs 30 and 31. <sup>b</sup> Values in parentheses calculated from the force field given in Table V. <sup>c</sup> Calculated from (ν<sub>2</sub> + ν<sub>3</sub>) - ν<sub>3</sub>, Table III.

tered when the isoelectronic species HCO<sup>+</sup> 32-34 and HCN<sup>35</sup> are compared, with frequencies for HCO<sup>+</sup> and HCN quoted in this order in cm<sup>-1</sup>. ν<sub>3</sub>, 2183.9496<sup>32</sup> - 2097;<sup>35</sup> ν<sub>2</sub>, 828.235<sup>33</sup> - 712,<sup>35</sup> and ν<sub>1</sub>, 3088.7395<sup>34</sup> - 3311.<sup>35</sup>

(ii) **Band Assignment of the Anion [Sb<sub>2</sub>F<sub>11</sub>]<sup>-</sup>.** The vibrational spectrum of [Sb<sub>2</sub>F<sub>11</sub>]<sup>-</sup> has been reported previously for [XeF]-[Sb<sub>2</sub>F<sub>11</sub>],<sup>27</sup> Cs[Sb<sub>2</sub>F<sub>11</sub>],<sup>28</sup> and [C<sub>3</sub>F<sub>3</sub>][Sb<sub>2</sub>F<sub>11</sub>].<sup>29</sup> However, the reported data are not completely consistent, measurements in the

lower spectral region are limited, and vibrational assignments are incomplete. The detailed measurements on [Au(CO)<sub>2</sub>][Sb<sub>2</sub>F<sub>11</sub>] described here permit a more complete description and assignment of the vibrational spectrum of [Sb<sub>2</sub>F<sub>11</sub>]<sup>-</sup>.

According to single-crystal X-ray diffraction studies of [H<sub>3</sub>F<sub>2</sub>][Sb<sub>2</sub>F<sub>11</sub>]<sup>36</sup> and [BrF<sub>4</sub>][Sb<sub>2</sub>F<sub>11</sub>],<sup>37</sup> the bis(octahedral) [Sb<sub>2</sub>F<sub>11</sub>]<sup>-</sup> ion appears to be present in both compounds in an eclipsed form (D<sub>4h</sub> symmetry), with the bridging fluorine atom depending on the cation either in a symmetrical [H<sub>3</sub>F<sub>2</sub>][Sb<sub>2</sub>F<sub>11</sub>]<sup>36</sup> or an asymmetrical position [BrF<sub>4</sub>][Sb<sub>2</sub>F<sub>11</sub>].<sup>37</sup>

Since in the Raman spectrum of [Au(CO)<sub>2</sub>][Sb<sub>2</sub>F<sub>11</sub>] a band at 503 cm<sup>-1</sup> (assigned as νSbFSb) is not observed, the mutual exclusion principle appears to be obeyed, which in turn is consistent with D<sub>4h</sub> symmetry, and the assignment proposed in Table II is based on this assumption. For D<sub>4h</sub> symmetry the irreducible representation of normal vibrations is as follows:

$$\Gamma_{\text{vib}} = 4A_{1g} (\text{Ra,p}) + A_{1u} + 4A_{2u} (\text{IR}) + 2B_{1g} (\text{Ra,dp}) + B_{1u} + B_{1g} (\text{Ra,dp}) + 2B_{2u} + 4E_g (\text{Ra,dp}) + 5E_u (\text{IR})$$

Of the expected nine IR-active (4ν, 5δ) and eleven Raman-active (5ν, 6δ) modes, seven modes in each group are observed according to Table II. The proposed band assignment is based on observed intensities and the reported assignments for the related [SbF<sub>6</sub>]<sup>-</sup> anion.<sup>38</sup>

(iii) **The Normal Coordinate Analysis of [Au(CO)<sub>2</sub>]<sup>+</sup>.** For the calculation of a general valence force field (GVFF) for [Au-

(32) Foster, S. C.; McKellar, A. R. W.; Sears, T. J. *J. Chem. Phys.* **1984**, *81*, 578.

(33) Kawaguchi, K.; Yamada, C.; Saito, S.; Hirota, E. *J. Chem. Phys.* **1985**, *82*, 1750.

(34) Amano, T. *J. Chem. Phys.* **1983**, *79*, 3595.

(35) Siebert, H. *Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie*; Springer Verlag: Berlin, 1966; p 45.

(36) Mootz, D.; Bartmann, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 391.

(37) Lind, M. D.; Christe, K. O. *Inorg. Chem.* **1972**, *11*, 608.

(38) Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley-Interscience: New York, 1986.

**Table V.** Inner Force Constants<sup>a</sup> for [Au(CO)<sub>2</sub>]<sup>+</sup>, [Au(CN)<sub>2</sub>]<sup>-</sup>, and Hg(CN)<sub>2</sub>

$f_i$	[Au(CO) <sub>2</sub> ] <sup>+</sup>	[Au(CN) <sub>2</sub> ] <sup>-c</sup>	Hg(CN) <sub>2</sub> <sup>c</sup>
$f_r$	20.1 ± 0.1	17.6 ± 0.2	18.1 ± 0.2
$f_R$	2.16 ± 0.03	2.78 ± 0.03	2.59 ± 0.03
$f_{rr}$	0.15 ± 0.1	0.0 ± 0.2	0.0 ± 0.2
$f_{RR}$	0.54 ± 0.03	0.42 ± 0.03	0.12 ± 0.02
$f_{Rr}$	0.45 ± 0.2	0.3 ± 0.15	0.05 ± 0.15
$f_{Rr}$	0.0 ± 0.2	0.0 ± 0.15	0.0 ± 0.15
$f_\alpha$	0.77 ± 0.09		
$f_\beta$	0.268 ± 0.02		
$f_{\alpha\beta}$	-0.015 ± 0.015		
$f_{\beta\beta}$	0.015 ± 0.02		

<sup>a</sup> 10<sup>2</sup> Nm<sup>-1</sup>, bending force constants and bending-stretching constants normalized on 10<sup>-10</sup> m. <sup>b</sup> r, R,  $\alpha$ ,  $\beta$  and refer to the bond CX, AuC, the angle CAuC, and XCAu, respectively. <sup>c</sup> Reference 39.

(CO)<sub>2</sub>]<sup>+</sup>, previously derived vibrational equations for five atomic linear species are used.<sup>39</sup> Data input involves the vibrational frequencies and isotope shifts listed in Table IV. The necessary structural parameters have not yet been obtained, but it is possible to predict the C–O distance in [Au(CO)<sub>2</sub>]<sup>+</sup> with a high degree of precision and to estimate the Au–C distance.

For the C–O distance in [Au(CO)<sub>2</sub>]<sup>+</sup> a value of 1.11 Å is obtained, when the relationship between bond distance [Å] and force constant [ $\times 10^2$  Nm<sup>-1</sup>] is extrapolated from CO (1.1283/19.0),<sup>40</sup> over CO<sup>+</sup> (1.1151/19.8)<sup>40</sup> to [Au(CO)<sub>2</sub>]<sup>+</sup> where  $f_r$  is found to be 20.1 (see below). Suitable data for reliable Au–C distances are not available however. From the molecular structures of Au(CO)Cl<sup>5</sup> and [Au(CN)<sub>2</sub>]<sup>-</sup>,<sup>41</sup> values for  $d_{(Au-C)}$  of 1.93 and 1.97 Å, respectively, are obtained. The corresponding force constants in 10<sup>2</sup> Nm<sup>-1</sup> are 2.83<sup>4c</sup> and 2.78,<sup>30</sup> respectively, for Au(CO)Cl and [Au(CN)<sub>2</sub>]<sup>-</sup>. If these values are compared to the Au–C force constant of 2.16  $\times 10^2$  Nm<sup>-1</sup>, calculated below, a value of 2.05 Å for  $d_{(Au-C)}$  appears reasonable.

The error limits included for internal force constants (Table V) are the result of inaccuracies in the measurement of isotope shifts and the lack of complete agreement of solutions based on isotope shifts I and II. Also included in Table V are the valence-force constants for [Au(CN)<sub>2</sub>]<sup>-</sup><sup>39</sup> and Hg(CN)<sub>2</sub>.<sup>39</sup> For all three complexes the interaction force constants,  $f_{rr}$  and  $f_{RR}$ , have values of approximately zero, which implies that these interactions do not play a significant role here.

As can be seen from Table V, the C–X (X = O or N) force constant  $f_r$  increases from the anion [Au(CN)<sub>2</sub>]<sup>-</sup> over neutral species Hg(CN)<sub>2</sub> to [Au(CO)<sub>2</sub>]<sup>+</sup>, while the M–C (M = Au or Hg) force constant  $f_R$  decreases in the same order, consistent with a decrease of metal to ligand  $\pi$ -back donation.

The conclusion that  $\pi$ -back donation is at a minimum for [Au(CO)<sub>2</sub>]<sup>+</sup> may be extended from a comparison of the five-atom linear species to other carbonyl species (Table V). Their stretching frequencies and stretching force constants  $f_r$  are summarized in Table VI. As can be seen, a higher force constant than calculated for [Au(CO)<sub>2</sub>]<sup>+</sup> is found only for HCO<sup>+</sup>, where  $\pi$ -back donation is impossible.

All other metal carbonyls as well as CO<sup>+</sup> and CO exhibit lower  $\nu_{CO}$  values and smaller stretching force constants. Even if additional literature data<sup>39</sup> for M(CO)<sub>6</sub>, Fe(CO)<sub>5</sub>, or Ni(CO)<sub>4</sub> are included, it is apparent that higher stretching frequencies and hence less  $\pi$ -back donation are observed for group 11 metals. Within this group no clear metal dependence of  $\nu_{CO}$  can be demonstrated, because chemically different species are reported for Cu(I), Ag(I), and Au(I), respectively. Where comparable compounds are studied, e.g., for Cu(CO)Cl and Au(CO)Cl, a somewhat higher  $\nu_{CO}$  value is observed for the gold(I) derivative.

Within a group of compounds with a common metal (I) center,  $\nu_{CO}$  increases for Au(CO)X with decreasing basicity of X (X = Br < Cl < SO<sub>3</sub>F), as discussed for Cu(CO) derivatives<sup>23</sup> and

**Table VI.** Stretching Frequencies and Force Constants of CO in Some Carbonyls and Related Species

compound <sup>a</sup>	$\nu_{CO}$ <sup>b</sup> [cm <sup>-1</sup> ]	$f_r$ [ $\times 10^2$ Nm <sup>-1</sup> ]	ref
CO <sub>(g)</sub>	2143	18.6	12
CO <sup>+</sup> <sub>(g)</sub>	2184	19.3	12
HCO <sup>+</sup> <sub>(g)</sub>	2184	21.3	42
W(CO) <sub>6(g)</sub>	2126	17.2	39
Cr(CO) <sub>6(g)</sub>	2119	17.2	39
[Re(CO) <sub>6</sub> ] <sup>+</sup> <sub>(sol)<sup>c</sup></sub>	2197	18.1	39
Cu(CO)Cl <sup>d</sup>	2157	18.3	e
[Cu(CO)] [AsF <sub>6</sub> ]	2180	19.2	23
Ag(CO)B(OTeF <sub>5</sub> ) <sub>4</sub>	2204	19.6	24
Au(CO)Br <sub>(sol)<sup>f</sup></sub>	2153		8
Au(CO)Cl	2170	19.0	4
Au(CO)SO <sub>3</sub> F	2196	19.5	6
[Au(CO) <sub>2</sub> ][Sb <sub>2</sub> F <sub>11</sub> ]	2235.5	20.1	this work

<sup>a</sup> Unless otherwise stated, spectra are obtained on solid compounds.

<sup>b</sup> For M(CO)<sub>6</sub> species, the frequency of the  $\nu_1[A_{1g}]$  modes listed here, and for [Au(CO)<sub>2</sub>]<sup>+</sup> the average CO stretching frequency is given.

<sup>c</sup> Dissolved in CH<sub>3</sub>CN. <sup>d</sup> In Ar matrix. <sup>e</sup> Plitt, H. S. Ph.D. Thesis, University of Munich, Germany, 1991, 106. <sup>f</sup> Dissolved in CH<sub>2</sub>Cl<sub>2</sub>.

observed for Au(I) derivatives. For [Au(CO)<sub>2</sub>]<sup>+</sup>, including the solvated species, the order of increasing  $\nu_{CO}$  appears to be [UF<sub>6</sub>]<sup>-</sup> < SO<sub>3</sub>F<sup>-</sup>/HSO<sub>3</sub>F < [Sb<sub>2</sub>F<sub>11</sub>]<sup>-</sup>, with a similar dependency on anion basicity evident. For [Au(CO)<sub>2</sub>]<sup>+</sup> the facile replacement of CO by CH<sub>3</sub>CN observed in this study is now readily explained by the weak gold–carbon bond.

(c) <sup>13</sup>C Nuclear Magnetic Resonance Studies. The use of <sup>13</sup>C-labeled gold(I) carbonyl derivatives in vibrational spectroscopy, discussed in the preceding section, is extended to a <sup>13</sup>C NMR study in fluorosulfuric acid with two objectives: (i) to arrive at an assignment of resonances observed for reactants and reaction products during the formation of carbonyl gold(I) species in HSO<sub>3</sub>F, in order to allow a comparison with previous work<sup>8,43</sup> on group 11 carbonyl derivatives, and (ii) to follow formation and CO exchange reactions of dissolved Au(CO)SO<sub>3</sub>F and [Au(CO)<sub>2</sub>]<sup>+</sup> in HSO<sub>3</sub>F by <sup>13</sup>C NMR.

In all instances only single resonance lines are obtained. Fine structure due to coupling between <sup>13</sup>C and <sup>197</sup>Au ( $I = 3/2$ ) is not observed, consistent with previous observations.<sup>8</sup> The starting material <sup>13</sup>CO gives a resonance at 184 ppm (relative to TMS) at ~2 atm pressure and -60 °C, in complete agreement with previous measurements in aprotic solvents.<sup>8,44</sup> An intensity comparison to the reference CDCl<sub>3</sub> suggests a solubility of <sup>13</sup>CO in HSO<sub>3</sub>F of the order of 10<sup>-2</sup>–10<sup>-3</sup> M. Oxidation of <sup>13</sup>CO by S<sub>2</sub>O<sub>8</sub>F<sub>2</sub> in HSO<sub>3</sub>F produces a second resonance at 125 ppm, which is attributed to <sup>13</sup>CO<sub>2</sub> by comparison with a previous report.<sup>45</sup>

These initial observations allow two conclusions: (a) the <sup>13</sup>C chemical shifts of <sup>13</sup>CO and <sup>13</sup>CO<sub>2</sub> in HSO<sub>3</sub>F do not vary from shifts measured in aprotic solvents, and (b) oxidation of CO by S<sub>2</sub>O<sub>8</sub>F<sub>2</sub> produces CO<sub>2</sub> as the only detectable product. The phosgene analogue CO(SO<sub>3</sub>F)<sub>2</sub><sup>46</sup> decomposes rapidly to CO<sub>2</sub> and S<sub>2</sub>O<sub>8</sub>F<sub>2</sub> in HSO<sub>3</sub>F as suggested previously.<sup>6</sup>

Reaction of <sup>13</sup>CO with a ~1 M solution of Au(SO<sub>3</sub>F)<sub>3</sub> in HSO<sub>3</sub>F at -50 °C produces three resonances in the <sup>13</sup>C NMR spectrum, a very intense resonance at 174 ppm and two weak signals at 162 and 125 ppm, respectively. The peak at 125 ppm is attributed to <sup>13</sup>CO<sub>2</sub>, and all <sup>13</sup>CO appears to be completely consumed. When the volume of the solution is reduced in vacuo at 25 °C, the resonance at 125 ppm due to <sup>13</sup>CO<sub>2</sub> disappears and the peak at 174 ppm diminishes in intensity, while the resonance at 162 steadily gains intensity and becomes at high solute concentration the only observable signal. Assignment of the 162-ppm resonance as due to [Au(<sup>13</sup>CO)]<sup>+</sup> is consistent with the reported course of the reaction between CO and Au(SO<sub>3</sub>F)<sub>3</sub> in HSO<sub>3</sub>F to

(41) Schubert, R. J.; Range, K. J. Z. Naturforsch. 1990, 456, 629.

(42) Hirota, E.; Endo, J. J. Mol. Spectrosc. 1988, 127, 524.

(43) Souma, Y.; Iyoda, J.; Sano, H. Inorg. Chem. 1976, 15, 968.

(44) Ettinger, R.; Blume, P.; Patterson, A.; Lauterbur, P. C. J. Chem. Phys. 1960, 33, 1547.

(45) Kalinowski, H. O.; Berger, S.; Braun, S. <sup>13</sup>C-NMR Spectroscopy; Wiley-Interscience: New York, 1988.

(39) Jones, L. H. Inorganic Vibrational Spectroscopy; Marcel Dekker: New York, 1971; Vol. 1, p 122.

(40) Huber, K. P.; Herzberg, G. Constants of Diatomic Molecules; Van Nostrand: New York, 1979.

**Table VII.**  $^{13}\text{C}$  Chemical Shifts of Coinage Metal Carbonyls and Related Compounds

compound	solvent	$T$ [K]	$\delta^a$ [ppm]	ref
$^{13}\text{CO}$	$\text{HSO}_3\text{F}$	210	184	this work
$^{13}\text{CO}_2$	$\text{HSO}_3\text{F}$	220	125	this work
$[\text{Au}(^{13}\text{CO})_2]^+$	$\text{HSO}_3\text{F}$	220–330	174	this work
$[\text{Au}(^{13}\text{CO})]^+$	$\text{HSO}_3\text{F}/\text{SbF}_5$ 1:1	220–330	158	this work
$[\text{Au}(^{13}\text{CO})]^+$	$\text{HSO}_3\text{F}$	220–330	162	this work
$\text{Au}(^{13}\text{CO})\text{Cl}$	$\text{CD}_2\text{Cl}_2$	205	172	8
$\text{Au}(^{13}\text{CO})\text{Br}$	$\text{CD}_2\text{Cl}_2$	205	174	8
$[\text{Cu}(^{13}\text{CO})]^+$	$\text{HSO}_3\text{F}/\text{H}_2\text{SO}_4$	303	169.0	43
$[\text{Ag}(^{13}\text{CO})_2]^+$	$\text{HSO}_3\text{F}$	303	172.2	43
$[\text{Cu}(^{13}\text{CO})_n]^{+b}$	$c$	213–243	$170. \pm 1$	43
$\text{Cr}(^{13}\text{CO})_6$	$\text{CH}_2\text{Cl}_2$	$d$	212.3	45 <sup>e</sup>

<sup>a</sup> Relative to TMS. <sup>b</sup>  $n = 1, 3, \text{ or } 4$ . <sup>c</sup> Various very strong protonic acids. <sup>d</sup> Temperature not stated. <sup>e</sup> Gansow, O. A.; Kimura, B. Y.; Dobson, G. R.; Brown, R. A. *J. Am. Chem. Soc.* **1971**, *93*, 5922.

produce solid  $\text{Au}(\text{CO})\text{SO}_3\text{F}$ .<sup>6</sup> Ionic dissociation of  $\text{Au}(\text{CO})\text{SO}_3\text{F}$  in solution to give  $[\text{Au}(\text{CO})]^+$  and  $\text{SO}_3\text{F}^-$  is consistent with the excellent ionizing ability of  $\text{HSO}_3\text{F}$ .<sup>47,48</sup>

Gradual addition of  $\text{SbF}_5$  to a solution of  $[\text{Au}(^{13}\text{CO})]^+$  in  $\text{HSO}_3\text{F}$  causes a small shift of the  $^{13}\text{C}$  single line resonance to lower frequencies, which at a concentration of about 50 mol %  $\text{SbF}_5$  is observed at 158 ppm. Differences in the acidity of the solvating medium or, alternatively, weak coordination of  $[\text{Au}(^{13}\text{CO})]^+$  to the self-ionization ions  $\text{SO}_3\text{F}^-$  and  $[\text{SbF}_n(\text{SO}_3\text{F})_{6-n}]^-$ ,<sup>48</sup> respectively, are likely reasons for the small shift.

Assignment of the resonance at 174 ppm as due to  $[\text{Au}(^{13}\text{CO})_2]^+$  is consistent with earlier suggestions based on vibrational spectra<sup>6</sup> and supported by two observations. MAS (magic angle spinning) spectra of solid  $[\text{Au}(^{13}\text{CO})_2][\text{Sb}_2\text{F}_{11}]$  have a resonance at 174 ppm, and solutions of the solid in either  $\text{HSO}_3\text{F}$  or  $\text{SO}_2$  show a single peak in the same position in both solvents. In magic acid the resonance for  $[\text{Au}(^{13}\text{CO})_2]^+$  remains at 174 ppm.

The assignments of the  $^{13}\text{C}$  chemical shifts discussed here (Table VII) are compared to previously reported shifts for various metal carbonyl derivatives.<sup>8,43,49</sup> It appears that all coinage metal carbonyl derivatives have single line resonances with chemical shifts at higher fields (and lower frequencies) relative to  $^{13}\text{CO}$ , while transition metal carbonyls and their derivatives<sup>49</sup> have resonances at the low field side of  $^{13}\text{CO}$ .

There is some similarity in the  $^{13}\text{C}$  chemical shifts for the group 11 carbonyl derivatives, particularly when  $[\text{Au}(^{13}\text{CO})_2]^+$  and  $[\text{Au}(\text{CO})\text{X}]$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ )<sup>8</sup> are compared. A difference is noted for the carbonyl copper(I) cations  $[\text{Cu}(\text{CO})_n]^+$  ( $n = 1, 3, \text{ or } 4$ ), which show closely spaced chemical shifts of  $170 \pm 1$  ppm in various protonic solvents at  $-30$  to  $-60$  °C,<sup>43</sup> while for  $[\text{Au}(^{13}\text{CO})]^+$  and  $[\text{Au}(^{13}\text{CO})_2]^+$ , well-separated peaks at 162 and 174 ppm are observed in  $\text{HSO}_3\text{F}$ .

Some doubt exists regarding the composition of the  $\text{Ag}(\text{I})\text{-CO}$  species observed previously in solution,<sup>43,50</sup> based on reported IR and Raman data. The Raman active in-phase CO stretch,  $\nu_1$  is observed at lower frequencies than the IR active  $\nu_3$ , which is highly unusual in view of our findings for  $[\text{Au}(\text{CO})_2]^+$  and previous work on  $[\text{Au}(\text{CN})_2]^-$ ,  $\text{Hg}(\text{CN})_2$ ,<sup>39</sup> and  $\text{C}_3\text{O}_2$ .<sup>51</sup> It is surprising to us that in these previous studies<sup>43,50</sup> the possible presence of  $[\text{Ag}(\text{CO})]^+$  is not considered, in view of the recent isolation of  $\text{Ag}(\text{CO})\text{B}(\text{OTeF}_3)_4$ <sup>24</sup> and the well-documented thermal instability of  $\text{Ag}(\text{I})$  carbonyls in  $\text{H}_2\text{SO}_4$ .<sup>52</sup>

As suggested by the rapid CO exchange for  $\text{Au}(\text{CO})\text{X}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ),<sup>8</sup> the compounds and the rather poorly characterized

(46) Lustig, M. *Inorg. Chem.* **1965**, *4*, 1828.

(47) (a) Thompson, R. C. *Inorganic Sulphur Chemistry*; Nickless, G., Ed.; Elsevier: Amsterdam, The Netherlands, 1968; p 821. (b) Gillespie, R. J. *Acc. Chem. Res.* **1968**, *1*, 202.

(48) Olah, G.; Prakash, S. G. K.; Sommer, J. *Superacids*; Wiley: New York, NY, 1985.

(49) Mann, B. E. *J. Chem. Soc., Dalton Trans.* **1973**, 2012.

(50) Neppel, A.; Hickey, J. P.; Butler, I. S. *J. Raman Spectrosc.* **1979**, *8*, 57.

(51) Long, D. H.; Murfin, S. F.; Williams, A. C. *Proc. R. Soc. London* **1954**, *A233*, 251.

(52) Manchot, W.; König, J. *Chem. Ber.* **1927**, *60*, 2183.

**Table VIII.** Atomic Coordinates (Fractional) and  $B(\text{eq})^a$  ( $\text{\AA}^2$ ) for  $[\text{Au}(\text{NCCH}_3)_2][\text{SbF}_6]$ 

atom	Wyckoff			$B(\text{eq})$
	notation	$x$	$y$	
Au	4(b)	1/2	1/2	4.76
Sb	4(a)	0	0	4.49
F	24(d)	0.1686 (5)	-0.0393 (6)	0.0478 (5)
N	8(c)	0.3893 (6)	0.3893	0.3893
C(1)	8(c)	0.328 (1)	0.328	0.328
C(2)	8(c)	0.246 (1)	0.246	0.246
H	24(d)	0.295	0.170	0.215

<sup>a</sup>  $B(\text{eq}) = \frac{8}{3\pi} \times \text{trace of orthogonalized } U_{ij}$ . <sup>b</sup>  $B(\text{iso})$ .

**Table IX.** Bond Lengths ( $\text{\AA}$ ) and Angles (deg) with Estimated Standard Deviations for  $[\text{Au}(\text{NCCH}_3)_2][\text{SbF}_6]$ 

Bond Lengths							
Au	N	1.97 (1)	N	C(1)	1.08 (1)		
Sb	F	1.841 (5)	C(1)	C(2)	1.47 (2)		
Bond Angles							
N	Au	N'	180.00	F	Sb	F'	180.00
Au	N	C(1)	180.00	F	Sb	F''	89.2 (2)
N	C(1)	C(2)	180.00	F	Sb	F'''	90.8 (2)

**Table X.** Interionic Distances ( $\text{\AA}$ )<sup>a</sup>

atom	atom	distance	atom	atom	distance
Au	F	3.455 (5)	F	N	3.181 (6)
Au	H	3.51	F	H	3.46
F	H	2.42	F	C(1)	3.52 (1)
F	H	3.04	F	H	3.56
F	C(1)	3.179 (7)	N	H	3.53
F	C(2)	3.122 (7)			

<sup>a</sup> Contacts out to 3.60  $\text{\AA}$ . Estimated standard deviations in the least significant figure are given in parentheses.

carbonyl cations of  $\text{Cu}(\text{I})$  and  $\text{Ag}(\text{I})$ <sup>43</sup> in solution of strong protonic acids appear to be of limited thermal stability, and undergo CO exchange. This has led in the case of the carbonyl cations of  $\text{Ag}(\text{I})$  and  $\text{Cu}(\text{I})$  to their use as effective carbonylation catalysts.<sup>53</sup>

There is evidence for CO exchange between the gold(I) carbonyl cations as well. There is fast CO exchange when  $[\text{Au}(^{12}\text{CO})_2]^+$  is added to a solution of  $[\text{Au}(^{13}\text{CO})_2]^+$  in  $\text{HSO}_3\text{F}$  to give isotopically mixed  $[\text{Au}(^{12}\text{CO})(^{13}\text{CO})]^+$  within a minute after mixing. This exchange can only be observed by vibrational spectroscopy, because the  $^{13}\text{C}$  chemical shift remains unchanged while  $\nu_{\text{CO}}$  changes (Table III).

Slow CO exchange is observed for mixtures of  $[\text{Au}(^{13}\text{CO})_2]^+$  and  $[\text{Au}(^{13}\text{CO})]^+$  which may be studied by  $^{13}\text{C}$  NMR. When a solution in  $\text{HSO}_3\text{F}$  with a gold(I) concentration of 1 M and an intensity ratio of the 174 to the 162-ppm resonance of approximately 1:1.5 is heated from 17 to 52 °C, initial line broadening of both resonances is noted, which eventually leads to coalescence. Finally at 52 °C a single resonance at 167 ppm with a line width at half peak height of about 100 Hz is observed. The chemical shift of 167 ppm reflects the concentration ratio of the two contributing carbonylgold(I) cations. Four spectra in this series are shown (Figure 3).

When an equimolar amount of  $\text{SbF}_5$  is added to this solution, coalescence of both resonances is observed at  $\sim 125$  °C. There are two possible explanations for the change in coalescence temperature: (a) a greater stabilization of  $[\text{Au}(\text{CO})_2]^+$  in  $\text{HSO}_3\text{F}/\text{SbF}_5$  which in turn may suggest a dissociative pathway for the CO exchange and (b) a dilution effect suggesting a bimolecular reaction. Clarification is expected from a kinetic study of the CO exchange between the two carbonyl gold(I) cations (currently underway), which should shed some light on the exchange mechanism.

In summary,  $^{13}\text{C}$  nuclear magnetic resonance spectra support the presence of two distinct carbonyl gold(I) species in  $\text{HSO}_3\text{F}$ ,

(53) (a) Souma, Y.; Sano, H. *J. Org. Chem.* **1973**, *38*, 2016. (b) Souma, Y.; Sano, H. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3273. (c) Souma, Y.; Sano, H. *J. Org. Chem.* **1973**, *38*, 3633.

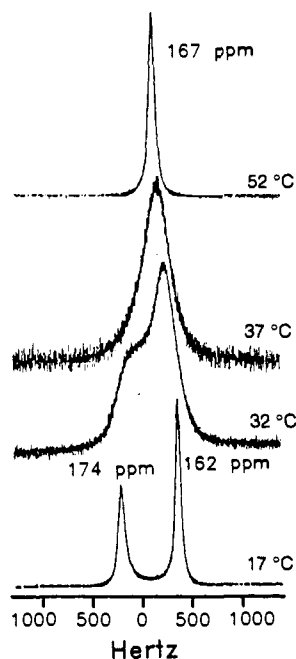


Figure 3. The <sup>13</sup>C NMR spectra of a mixture of [Au(<sup>13</sup>CO)]<sup>+</sup> and [Au(<sup>13</sup>CO)<sub>2</sub>]<sup>+</sup> in HSO<sub>3</sub>F between 17 °C and 52 °C.

[Au(CO)]<sup>+</sup><sub>(solv)</sub> and [Au(CO)<sub>2</sub>]<sup>+</sup><sub>(solv)</sub>. Only at an elevated temperature is CO exchange between both observed on the NMR time scale. The presence of more extensively carbonylated species as suggested for Cu(I)<sup>43</sup> is not observed nor expected, considering the great tendency of gold(I) to form linear complexes exclusively.<sup>1,2</sup>

(d) **The Molecular Structure of Bis(acetonitrile)gold(I) Hexafluoroantimonate(V), [Au(NCCH<sub>3</sub>)<sub>2</sub>][SbF<sub>6</sub>].** The crystal data are summarized in Table I. More detailed information on the crystal data, intensity measurements, structure solution, and refinement are found in the supplementary material, together with a packing diagram of the molecular ions in the cubic unit cell. A detailed view of the molecular structure of the cation [Au(NCCH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> and the [SbF<sub>6</sub>]<sup>-</sup> anion is shown in Figure 4. The positional parameters, intramolecular distances, and bond angles are summarized in Tables VIII and IX, respectively. Interionic distances up to 3.6 Å are shown in Table X.

Bis(acetonitrile)gold(I) hexafluoroantimonate(V), [Au(NCCH<sub>3</sub>)<sub>2</sub>][SbF<sub>6</sub>], crystallizes in the form of cubic crystals with *a* = 10.250 (2) Å, space group *Pa*3̄ (no. 205). The heavy atoms, Au and Sb, form a NaCl-type lattice. The linear [Au(NCCH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> cation is found on the body diagonal of the unit cell. As a consequence of the cubic symmetry of the crystal, the molecular structures of both the [Au(NCCH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> cation and the [SbF<sub>6</sub>]<sup>-</sup> anion are very regular and highly symmetrical. Both acetonitrile ligands are symmetrically coordinated, resulting in a completely linear alignment of seven atoms with all bond angles 180°. The two terminal CH<sub>3</sub> groups are staggered with respect to each other, resulting in *D*<sub>3d</sub> symmetry for the cation.

The Au–N distances, at 1.97 (1) Å, are relatively short in comparison to reported distances which are frequently longer than 2.0 Å.<sup>54</sup> Only for sodium bis(*N*-methylhydantoinato)gold(I) tetrahydrate<sup>55</sup> are average Au–N distances of 1.94 Å mentioned in a preliminary report. Frequently, however, the determination of light-atom positions in the presence of gold is of limited accuracy.<sup>54</sup>

The remaining bond parameters of the coordinated NCCH<sub>3</sub> ligand compare very well with those of recently reported transition metal complexes of cobalt(II)<sup>56a</sup> and osmium(II),<sup>56b</sup> even though

(54) (a) Jones, P. G. *Gold Bull* 1981, 14, 102; 1981, 14, 159; 1983, 16, 114; 1986, 19, 46. (b) Melnik, M.; Parish, R. V. *Coord. Chem. Rev.* 1986, 10, 157.

(55) Malik, N. A.; Sadler, P. J.; Neidle, S.; Taylor, G. L. *J. Chem. Soc., Chem. Commun.* 1978, 711.

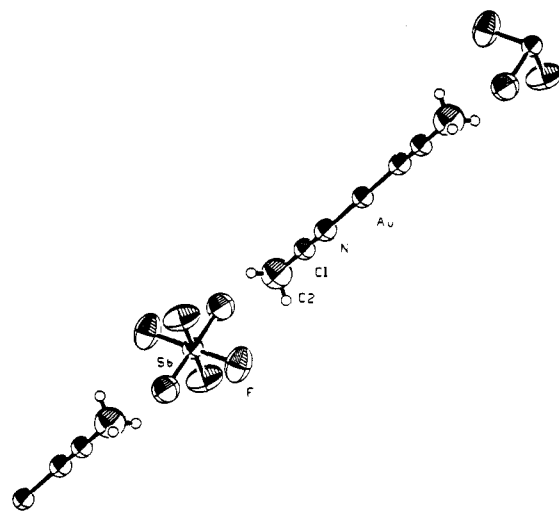


Figure 4. A 50% probability ORTEP view of [Au(NCCH<sub>3</sub>)<sub>2</sub>][SbF<sub>6</sub>] showing one complete cation–anion pair and parts of their nearest neighbors. The crystallographically independent non-hydrogen atoms are labeled.

slight departures from linearity are observed in both cases.<sup>56</sup> Comparison of the C–N bond distance of 1.08 (1) Å to that of free acetonitrile (1.1571 Å)<sup>57</sup> gives no indication of  $\pi$ -back donation.

A feature commonly observed for linear gold(I) complexes, relatively short gold–gold contacts,<sup>54</sup> is absent. Instead, as seen in Table X, very regular Au...F and Au...H contacts of 3.455 (5) and 3.51 Å, respectively, are found. The nearest Au...Au contact is 7.247 Å (*a*/√2).

The hexafluoroantimonate(V) anion is perfectly octahedral with identical Sb–F distances of 1.841 (5) Å and FSbF bond angles of 90° within error limits. Octahedral [SbF<sub>6</sub>]<sup>-</sup> anions are commonly found in alkali metal hexafluoroantimonates, e.g., LiSbF<sub>6</sub>,<sup>58</sup> even though here the Sb–F distances of 1.877 (6) Å are slightly longer. In compounds with transition metal–complex cations, the [SbF<sub>6</sub>]<sup>-</sup> anion is frequently distorted from *O<sub>h</sub>* symmetry, as is evident in two recent examples, ( $\pi^*$ -C<sub>5</sub>H<sub>5</sub>)[Ni(NCCD<sub>3</sub>)<sub>6</sub>][SbF<sub>6</sub>]<sup>59</sup> and [( $\pi$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)][SbF<sub>6</sub>],<sup>60</sup> with *C*<sub>3</sub> symmetry for the anion and Sb–F distances of 1.80 (1) and 1.83 (1) Å in the first case, and Sb–F distances between 1.806 and 1.874 Å in the second case, where the crystal data are of poor quality and FSbF bond angles are not reported.<sup>60</sup>

In summary, the cubic symmetry of [Au(NCCH<sub>3</sub>)<sub>2</sub>][SbF<sub>6</sub>], which caused initial problems in solving the structure, is responsible for the observed classical regularity of both cation and anion, with a rather unusual perfectly linear C–C–N–Au–N–C–C alignment observed for the cation.

## Conclusions and Summary

During the course of this study, the conditions required to stabilize unusual cations like [Au(CO)]<sup>+</sup> and [Au(CO)<sub>2</sub>]<sup>+</sup> have become clear. A very strong protonic acid like HSO<sub>3</sub>F<sup>47</sup> provides a suitable medium to generate both [Au(CO)]<sup>+</sup> and [Au(CO)<sub>2</sub>]<sup>+</sup>, and extremely weakly basic fluoro anions like [UF<sub>6</sub>]<sup>-7</sup> and [Sb<sub>2</sub>F<sub>11</sub>]<sup>-</sup> (the latter perhaps the weakest nucleophile<sup>61</sup>) permit isolation of solid [Au(CO)<sub>2</sub>]<sup>+</sup> compounds. Both the thermal stability of this compound, and one of the most striking features,

(56) (a) Capelle, B.; Beauchamp, A. L.; Dartiguenave, M.; Dartiguenave, Y.; Klein, H. F. *J. Am. Chem. Soc.* 1982, 104, 3891. (b) Robinson, P. D.; Ali, I. A.; Hinckley, C. C. *Acta Crystallogr.* 1991, C47, 1397.

(57) Costain, C. C. *J. Chem. Phys.* 1958, 29, 864.

(58) Burns, J. H. *Acta Crystallogr.* 1962, 15, 1098.

(59) Bougon, R.; Charpin, P.; Christe, K. O.; Isabey, J.; Lance, M.; Nierlich, M.; Vigner, J.; Wilson, W. W. *Inorg. Chem.* 1988, 27, 1389.

(60) Schumann, H.; Speis, M.; Bosman, W. P.; Smits, J. M. M.; Beurskens, P. T. J. *Organomet. Chem.* 1991, 403, 165.

(61) Mallela, S. P.; Yap, S.; Sams, J. R.; Aubke, F. *Inorg. Chem.* 1986, 25, 4327.



the very high C–O stretching frequencies, increase with decreasing counter anion basicity. Even though a molecular structure of this compound was not obtained, the careful analysis of the complete vibrational spectrum of the cation with the aid of  $^{13}\text{C}$  and  $^{18}\text{O}$  isotope substitution has allowed a normal coordinate analysis and valence force field calculations, which permit good structural insights.

The unusual bonding situation is seen as a manifestation of drastically diminished metal-to-ligand  $\pi$ -back donation. Trends in stretching force constants for the isoelectronic and isosteric series  $[\text{Au}(\text{CN})_2]^-$ ,  $\text{Hg}(\text{CN})_2$ , and  $[\text{Au}(\text{CO})_2]^+$  suggest that the gradually increasing effective nuclear charge on the metal due to the change in ionic charge is the cause for the gradually decreasing  $\pi$ -back donation in the above series. Consistent with this view is noticeable  $\pi$ -back donation, suggested by the vibrational spectrum of the matrix-isolated neutral  $\text{Au}(\text{CO})_2$ .<sup>10</sup>

It is surprising that the gold–carbon  $\sigma$  bond in  $[\text{Au}(\text{CO})_2]^+$  is sufficiently strong to permit isolation of thermally stable compounds. The thermal stability is best explained by the documented ability of gold(I) to form strong covalent, linear bonds,<sup>1,2</sup> possibly aided by relativistic effects<sup>62,63</sup> and by polar contributions to the gold–carbon bond, as suggested by the inverse relationship between thermal stability and counter anion basicity observed in this study and discussed above.

The weak gold–carbon bond allows facile replacement of CO by acetonitrile, illustrated by the conversion of  $[\text{Au}(\text{CO})_2][\text{Sb}_2\text{F}_{11}]$  to  $[\text{Au}(\text{NCCH}_3)_2][\text{SbF}_6]$ . The structure and bonding features observed for both  $[\text{Au}(\text{CO})_2]^+$  and  $[\text{Au}(\text{NCCH}_3)_2]^+$  are very similar and apparently determined by the gold(I) center, with its

strict preference for linear coordination, and its ability to form strong covalent bonds in both  $[\text{Au}(\text{NCCH}_3)_2]^+$  and  $[\text{Au}(\text{CO})_2]^+$ . In this respect gold(I) is clearly different even from the other univalent coinage metal ions, a fact best illustrated by the monomeric, linear molecular structure of  $\text{Au}(\text{CO})\text{Cl}$ <sup>5</sup> and the polymeric structure of  $\text{Cu}(\text{CO})\text{Cl}$ .<sup>64</sup> It is also noted that in  $\text{Ag}(\text{CO})\text{B}(\text{OTeF}_5)_4$ <sup>24</sup> Ag(I) is tricoordinated. In  $[\text{Au}(\text{CO})_2]^+$ , carbon monoxide takes the place of an easily interchangeable donor ligand with Au(I) as acceptor. There appears to be no need for the resulting coordination complex to have the nearest noble gas configuration for the central atom, and the effective atomic number rule is irrelevant in this case as in the case of many other group 11 carbonyl derivatives or coordination compounds of univalent gold.<sup>1,2</sup>

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**Supplementary Material Available:** Listing of crystal data, intensity measurements, structure solution and refinement, positional parameters and anisotropic thermal parameters for  $[\text{Au}(\text{NCCH}_3)_2][\text{SbF}_6]$ , and intramolecular distances and bond angles, a stereoview of the packing of the molecular ions in the unit cell, and intermolecular contacts out to 3.60 Å with a footnote (9 pages); listing of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

(62) Pyykko, P. *Chem. Rev.* 1988, 88, 563, and references therein.

(63) Schwerdtfeger, P. *J. Am. Chem. Soc.* 1989, 111, 7261.

(64) Hakansson, M.; Jagner, S. *Inorg. Chem.* 1990, 29, 5241.

## Partial Paramagnetism of the Cr–Cr Quadruple Bond

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**Abstract:** Variable-temperature NMR measurements show that  $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$  compounds (L = MeOH, H<sub>2</sub>O, py, MeCN) and closely related ones possess inherent, temperature-dependent partial paramagnetism. This may be attributed to a Boltzmann distribution between a ground state with  $S = 0$  and a low-lying ( $\sim 400$ – $1000\text{ cm}^{-1}$ ) state with  $S = 1$ . When R is kept constant (as CH<sub>3</sub>) and the Cr–Cr distance is changed by changing L, the singlet–triplet separation varies inversely with the Cr–Cr distance, suggesting that the low-lying triplet state may be the  $^3\text{A}_{2g}$  state arising from a  $\sigma^2\pi^4\delta\delta^*$  configuration. Other explanations may also be considered, and cannot be falsified conclusively. The carbamate compound  $\text{Cr}_2(\text{O}_2\text{CNEt}_2)_4(\text{NEt}_2\text{H})_2$  has also been studied. Despite the fact that the Cr–Cr distance is similar to those in the acetates, the singlet–triplet gap is much smaller, ca.  $600\text{ cm}^{-1}$ . This may be attributed to a different interaction of the carbamate ligand with the  $\delta$  orbital, as is shown by SCF–X $\alpha$  calculations.

### Introduction

From the earliest magnetic studies it has been known that  $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$  compounds display weak paramagnetism in the solid state.<sup>1</sup> There is some evidence to suggest that at least some of this, in at least some cases, is due to the presence of paramagnetic (e.g. Cr(III)) impurities. However, it has also been suggested that the paramagnetism is inherent in the  $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$  molecule owing to the fact that an  $S = 1$  state lies within  $1000\text{ cm}^{-1}$  of an  $S = 0$  ground state. Thus, Furlani<sup>2</sup> suggested that such

molecules could be regarded as antiferromagnetically coupled systems of two  $S = 2$  cores and he used a value of  $\chi = 113 \times 10^{-6}$  cgsu at 300 K (and assuming  $g = 2$ ) to get  $E = 770\text{ cm}^{-1}$  for  $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$ . The significance of  $E$  is indicated by eq 1; it is the separation between the singlet ground state and the lowest triplet state (the S–T gap).

$$\chi = \frac{2Ng^2\beta^2}{3kT} \frac{1}{1 + \frac{1}{3}e^{E/kT}} \quad (1)$$

The use of solid-state magnetic susceptibility data has significant drawbacks. To eliminate the spurious effect of paramagnetic impurities, it is necessary to carry out measurements from room temperature to very low temperatures (ca. 5 K) and then to make

(1) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Oxford University Press: Oxford, U.K., 1992; Chapter 4.

(2) Furlani, C. *Gazz. Chim. Ital.* 1957, 87, 876.