# Preparation and Structure of $F_3As-Au^+SbF_6^-$ , the Structures of $Au(CO)_2^+$ and $Au(PF_3)_2^+$

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Dedicated to Professor Arndt Simon on the Occasion of his 60th Birthday

**Abstract.** AuF<sub>3</sub>, Au(SbF<sub>6</sub>)<sub>2</sub>, or [Au(SbF<sub>6</sub>)<sub>2</sub> · Au(AuF<sub>4</sub>)<sub>2</sub>] react with AsF<sub>3</sub> in HF/SbF<sub>5</sub> under formation of F<sub>3</sub>As–Au<sup>+</sup>SbF<sub>6</sub><sup>-</sup>. This is stable to about 0 °C. The crystal structure reveals strong cationic-anionic interactions through one fluorine atom so that a description as F<sub>3</sub>As–Au–F...SbF<sub>5</sub> is also possible (a = 798.3(1), b = 912.0(2), c = 1076.3(2) pm,  $\beta$  = 96.25°, space group P2<sub>1</sub>/n). A similar reaction with CO affords [Au(CO)<sub>2</sub><sup>+</sup>]<sub>2</sub>SbF<sub>6</sub><sup>-</sup> · Sb<sub>2</sub>F<sub>11</sub><sup>-</sup> (a = 1404.8(1), b = 622.86(3), c = 1130.2(1) pm, space group Pmma). The cations in these compounds have the expected linear geometry. Reaction with PF<sub>3</sub> affords Au(PF<sub>3</sub>)<sub>2</sub>+SbF<sub>6</sub><sup>-</sup> (a = 825.5(2), b = 824.4(2), c = 876.4(3) pm,  $\gamma$  = 119.99°, space group P2<sub>1</sub>/n).

**Keywords:** Gold; Gold(I) fluoride; Gold(I) carbonyl; Crystal structure

# Darstellung und Kristallstruktur von $F_3AsAu^+SbF_6^-$ , die Strukturen von Au(CO)<sub>2</sub><sup>+</sup> und Au(PF<sub>3</sub>)<sub>2</sub><sup>+</sup>

**Inhaltsübersicht.** AuF<sub>3</sub>, Au(SbF<sub>6</sub>)<sub>2</sub>, or  $[Au(SbF_6)_2 \cdot Au(AuF_4)_2]$ reagieren mit AsF<sub>3</sub> in HF/SbF<sub>5</sub> Lösung unter Bildung von F<sub>3</sub>As-Au<sup>+</sup>SbF<sub>6</sub><sup>-</sup>. Dieses ist bis etwa 0 °C stabil. Die Kristallstrukturanalyse zeigt starke Wechselwirkungen zwischen Kation und Anion, so daß die Verbindung auch als F<sub>3</sub>As-Au-F...SbF<sub>5</sub> beschrieben werden kann (a = 798.3(1), b = 912.0(2), c = 1076.3(2) pm,  $\beta$  = 96.25°, Raumgruppe P2<sub>1</sub>/n). Die analoge Reaktion mit CO ergibt  $[Au(CO)_2^+]_2SbF_6^-$ . Sb<sub>2</sub>F<sub>11</sub><sup>-</sup> (a = 1404.8(1), b = 622.86(3), c = 1130.2(1) pm, Raumgruppe Pmma). Die Kationen in diesen Verbindungen haben die erwartete lineare Anordnung. Reaktion mit PF<sub>3</sub> ergibt Au(PF<sub>3</sub>)<sub>2</sub><sup>+</sup>SbF<sub>6</sub><sup>-</sup> (a = 825.5(2), b = 824.4(2), c = 876.4(3) pm,  $\gamma$  = 119.99°, Raumgruppe P2<sub>1</sub>/n).

## Introduction

Gold(I) fluoride does not exist in condensed phase [1]. At first glance this is surprising, since AgF is a very stable fluoride. But CuF also does not seem to have existed so far. An Au-F molecule is a bound species, as has been shown by ionisation-reneutralisation mass spectrometry on fragments of  $AuF_3$  [2]. The bond energy of the molecule has been so determined as 73 kcal/mol<sup>-1</sup>, which agrees well with the latest *ab initio* calculation of 3.1 eV (= 69 kcal mol<sup>-1</sup>) [3]. AuF has clearly a tendency to disproportionate into Au and AuF<sub>3</sub>. Preparation of AuF in condensed phase should therefore be done under very special conditions guaranteeing enough reaction speed but avoiding its disproportionation. This ought to be difficult [4]. Another unfulfilled goal in gold chemistry is the isolation of a gold cation L-Au<sup>+</sup>, or even Au<sup>+</sup>.  $R_3P-Au^+$  can be generated in situ from  $R_3P-AuCl$ 

and TIBF<sub>4</sub> or AgBF<sub>4</sub> [5, 6]. Such "cationic" gold compounds serve in solution as highly efficient catalysts for the addition of alcohols to alkynes [7]. Another way to approach a gold(I) cation is the stabilization by two weakly complexing ligands, such as CH<sub>3</sub>–CN. [Au(NC–C<sub>6</sub>H<sub>5</sub>)<sub>2</sub><sup>+</sup>] salts can be isolated [8], and a single crystal structure of [Au(NC–CH<sub>3</sub>)<sub>2</sub><sup>+</sup>]SbF<sub>6</sub><sup>-</sup> is even known [9].

In the present study we tried to approach both aims, a gold(I) fluoride and a Au<sup>+</sup> ion, by a special route, without fully reaching either one of them. We consider the oxidation state +1 as low, since the existence of AuF<sub>3</sub> and AuF<sub>5</sub> [10] shows that the formation of high oxidation states does not cause great difficulties. There is a general rule that has only been written down occasionally [11], namely, that high oxidation states are preferentially found in highly basic solutions and, in turn, low oxidation states in strongly acidic solutions. AuF<sub>6</sub><sup>-</sup> is thus easily formed in presence of strong bases like CsF or XeF<sub>6</sub> and, alternatively, Au<sup>2+</sup> can be generated in anhydrous HF as Au(SbF<sub>6</sub>)<sub>2</sub> [12]. It should be noted that true Au<sup>2+</sup> compounds are rare [13].

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# Results

If  $AuF_3$  is reduced to  $Au^{2+}$  in anhydrous HF, further reduction might be possible in super acidic media. For this purpose we added  $SbF_5$  to the HF, thus working in the strongest known acid [14]. We added  $AsF_3$  as a mild reducing agent which, as it turned out, also acts as a mild complexation agent:

# $AuF_3 + SbF_5 + 2AsF_3 \rightarrow F_3As - Au^+SbF_6^- + AsF_5$

Colorless crystals are formed, and the reaction is nearly quantitative. Au $(SbF_6)_2$  and  $[Au(SbF_6)_2Au(AuF_4)]$  [12] work as well. But substitution of  $SbF_5$  by the less strong Lewis acid AsF<sub>5</sub> does not work, and phosphanes such as trimethyl- or triphenylphosphane as reducing agents resulted in complex mixtures that could not be separated so far.

The crystal structure of  $F_3As-Au^+SbF_6^-$  is shown in Fig. 1, see also Table 1. At a first glance it is obvious that there are no weak  $Au(I) \cdots Au(I)$  interactions which are otherwise so common in gold chemistry [15]. The shortest  $Au \cdots Au \cdots$  distance is 510.9(1) pm. The F<sub>3</sub>As-Au part of the molecular unit seems normal. Of interest is the positioning of one fluorine atom between Au and Sb. The As-Au. F fragment is essentially linear  $(172.6(2)^\circ)$ . This particular F atom clearly belongs at first to the SbF<sub>6</sub><sup>-</sup> anion. However, the usual octahedral structure of this anion is strongly distorted in so far as this special Sb-F bond distance is enlarged to 193.4(6) pm. The other Sb-F bonds are 185–189 pm long. The Au $\cdots$ F distance is 211.8(6) pm. The AuF molecule should have a bond length of 194 pm, according to *ab initio* calculations [3]. The comparison with similarly unknown F-Au-F<sup>-</sup> may be more revealing, for which a bond length of 203 pm is calculated [16]. Bond lengths in  $AuF_3$  are between 186.6(3) (terminal) and 199.8(2) (bridge) [17], and in Au(SbF<sub>6</sub>)<sub>2</sub> four Au···F contacts are between 209(2) and 215(2) pm long [12]. The best description for  $F_3As-Au^+SbF_6^-$  is that of an ion pair between the elusive L-Au<sup>+</sup> cation and the weakly coordinating  $SbF_6^$ anion. Such complexes for other than gold compounds are well known [18]. The fluoride ion affinity of  $F_3As-Au^+$  must be large, otherwise the distortion of



**Fig. 1** View of one unit  $F_3As-Au^+SbF_6^-$ , ORTEP, ellipsoids represent 50% probability.

the  $SbF_6^-$  anion cannot be explained, since it can compete with the extreme high fluoride ion affinity of  $SbF_5$ . A more extreme view of the molecular unit would be a  $SbF_5$  adduct of  $F_3As$ -AuF.

All attempts failed to generate  $F_3As$ -AuF from the compound. It would only need the reaction with strongly basic fluorides such as CsF or NOF in the HF solvent in order to trap out Cs<sup>+</sup>SbF<sub>6</sub><sup>-</sup> or NO<sup>+</sup>SbF<sub>6</sub><sup>-</sup>. But even under the most carefully controlled reaction conditions at -78° immediate decomposition to elemental gold is observed.

## Crystal Structure of $[Au(CO)_2^+]_2SbF_6^-Sb_2F_{11}^-$

By replacing of the reducing and complexing agent AsF<sub>3</sub> with CO in unhydrous HF we hoped to obtain Au(CO)<sup>+</sup>SbF<sub>6</sub><sup>-</sup> as an analogue to known Au(CO)<sup>+</sup>SO<sub>3</sub>F<sup>-</sup> [19]. However, the reaction proceeds to Au(CO)<sub>2</sub><sup>+</sup>, a cation that is also known [9, 19] in form of the salt Au(CO)<sub>2</sub><sup>+</sup>Sb<sub>2</sub>F<sub>11</sub><sup>-</sup>. To the best to our knowledge crystal structure data of the Au(CO)<sub>2</sub><sup>+</sup> cation are missing. Our product turned out to be  $[Au(CO)_2^+]_2SbF_6 \cdot Sb_2F_{11}^-$ . The crystal structure is shown in Fig. 2, see also Table 1.

The Au(CO)<sub>2</sub><sup>+</sup> cations appear in two different crystallographic forms, which are both nearly or completely linear. The cation Au(CO)<sub>2</sub><sup>+</sup>(II) is twofold disordered, so that the estimated standard deviations are much larger than for Au(CO)<sub>2</sub><sup>+</sup>(I). The following discussion of bond lengths is therefore only based on Au(CO)<sub>2</sub><sup>+</sup>(I). The Au–C distance, see Table 1, is 197.1(8) pm long, in good agreement with the latest *ab initio* calculations. These predict distances between

 Table 1
 Important Bond Lengths/pm and Angles/°

| $F_3As-Au^+SbF_6^-$  |                  | $[Au(CO)_2^+]_2 \cdot SbF_6^- \cdot Sb_2F_{11}^-$ |                    |
|----------------------|------------------|---|--------------------|
| Au(1)–F(1)           | 211.8(6)         | Au(1)–C(1)  | 197.2(8)           |
| Au(1)-As(1)          | 226.8(1)         | Au(2) - C(2)                                      | 198.2(21)          |
| Sb(1) - F(1)         | 193.4(6)         | Au(2)-(C3)  | 196.2(17)          |
| Sb(1)-F(2)           | 188.06(7)        | C(1) - O(1)                                       | 110.7(9)           |
| Sb(1)-F(3)           | 187.5(7)         | C(2) - O(2)                                       | 111.1(22)          |
| Sb(1)-F(4)           | 186.2(6)         | C(3) - O(3)                                       | 115.3(17)          |
| Sb(1)-F(5)           | 183.3(7)         | Sb(1)-F(11,12,14)                                 | 185.5(5)-186.4(3)  |
| Sb(1)-F(6)           | 186.7(7)         | Sb(1)-F(13)                                       | 202.5(2)           |
| As(1) - F(7)         | 167.0(7)         | Sb(2)-F(21-23)                                    | 185.5(7)-188.3(3)  |
| As(1) - F(8)         | 168.5(7)         | C(1) - Au(1) - C(1)                               | 176.4(4)           |
| As(1)-F(9)           | 167.8(6)         | C(2)-Au(2)-C(2)                                   | 180.0              |
| Au(1)-F(1)-Sb(1)     | 127.9(3)         | C(3)-Au(2)-C(3)                                   | 180.0              |
| As(1) - Au(1) - F(1) | 172.6(2)         | Au(1)-C(1)-O(1)                                   | 177.7(7)           |
| F(1)-Sb(1)-F         | 84.8(3)-88.7(3), | Au(2)-C(2)-O(2)                                   | 179.6(15)          |
|                      | 177.5(3)         |   |                    |
| F–As(1)–F            | 98.0(4)-98.4(4)  | Au(2)-C(3)-C'(3)                                  | 180.0              |
|                      |                  | Sb(1)-F(13)-Sb(1)                                 | 152.5(3)           |
|                      |                  | F-Sb(1)-F   | 85.4(2)-94.7(2),   |
|                      |                  |   | 171.5(2)-178.8(2)  |
|                      |                  | F-Sb(2)-F   | 89.5(2)-90.5(2)    |
|                      |                  | $\mathrm{Au}(\mathrm{PF}_3)_2^+\mathrm{SbF}_6^-$  |                    |
|                      |                  | Au–P  | 225.3(3)           |
|                      |                  | P–F   | 150.2(1)-153.6(2)  |
|                      |                  | Sb-F(1-3)   | 184.6(1)-190.1(1)  |
|                      |                  | P-Au-P  | 180.0              |
|                      |                  | F-P-F   | 99.2(12)-104.6(12) |
|                      |                  | F–Sb–F  | 86.06(4)-93.94(4), |
|                      |                  |   | 180.0              |



**Fig. 2** Crystal structure of one unit of  $[Au(CO)_2^+]_2 \cdot SbF_6^- \cdot SbF_{11}^-$ , ORTEP, ellipsoids represent 50% probability. The disorder of the Au  $(CO)_2^+(II)$  cation is indicated by broken lines. Atoms not indexed are those generated by the crystallographic mirror planes.

198.8 and 203.0 pm depending on the approximation used for the electron correlation [20]. The C–O bond length is found to be 110.8(9) pm and predicted to lie between 112.2 and 114.2 pm [20]. Free, gaseous CO has a C–O bond length of 112.82 pm. Au(CO)<sub>2</sub><sup>+</sup>, among other noble metal carbonyls, has been the focus of a discussion that arose from naming them "nonclassical" carbonyls [21, 22], because they have a CO stretching frequency (or its weighed average) above 2143 cm<sup>-1</sup>, the wave number for free carbon monoxide. In  $Au(CO)_2^+$  the averaged CO stretching frequency is 2235.5 cm<sup>-1</sup> [9]. Of course i.r. frequencies are a much more sensitive probe for bond strengths than bond distances, particularly if, as here, very strong (and short) bonds are involved. But it can be noted that the CO bond length in  $Au(CO)_2^+$  is indeed shorter than in free CO.

In the isoelectronic cation  $Hg(CO)_2^{2+}$  the C–O bond length is found to be equally short: 110.4(12) pm, and the averaged CO stretching frequency has the highest reported value so far (2279.5 cm<sup>-1</sup>) [23]. In isoelectronic  $Ag(CO)_2^+$  the averaged CO stretching frequency is 2208 cm<sup>-1</sup>, but unfortunately the CO bond lengths (107(5) and 109(5) have such a large estimated standard deviation that these values cannot be used in this discussion [24]. Cu(CO)<sub>2</sub><sup>+</sup>, however, has CO distances of 110.9(3) and 111.5(3) pm [25]. So it seems that CO bond lengths, only if precise enough, can also be used as indicator for the bonding type towards transition metal centers.

There are more than 10000 CO bond lengths of metal carbonyl compounds deposited in the Cambridge Data index [26], and one can arrive at the conclusion that the CO bond length, if only precise enough, is be an indicator for the bond order [27]. However, it is of course difficult to compare values

**Table 2**C-O bond length of some typical binary metal car-<br/>bonyls in the solid and gas phase. ND = neutron diffraction,<br/>XD = x ray diffraction, ED = electron diffraction

| $Cr(CO)_{6}$<br>$Mo(CO)_{6}$<br>$W(CO)_{6}$<br>$V(CO)_{6}$<br>$Fe(CO)_{5}$<br>$Ni(CO)_{4}$<br>$Cu(CO)_{4}^{+}$<br>$Co(CO)_{4}^{-}$ | XD 113.8–114.1(1) [28]<br>XD 112.5(5) [30]<br>XD 113.5–115.5 [32]<br>XD 112.3(2)–113.6(3) [34]<br>XD 111.7(2)–113.6(2) [35, 36]<br>XD 112.5(3)–112.8(2) [35]<br>XD 110.9–111.4(3) [25]<br>XD 110.9–111.4(3) [25] | ND 114.1 [28, 29]<br>ED 114.5(2) [31]<br>ED 114.8(3) [31]<br>ED 113.8(2) [33]<br>ED 114.5 [37]<br>ED 114.1(2) [38] |
|--|--|--|
|--|--|--|

from crystal structures measured at different temperatures and also with and without correction for liberation.

Here we want to compare the values presented above only to a few archetypal binary metal carbonyls, see Table 2. It is clear that here the CO bond lengths are all larger than in  $Au(CO)_2^+$ . The influence of the charge is seen in the sequence  $Co(CO)_4^-$ ,  $Ni(CO)_4$ , and  $Cu(CO)_4^+$ .

# $Au(PF_3)_2^+SbF_6^-$

By replacing the reducing and complexing agent AsF<sub>3</sub> with PF<sub>3</sub> we have obtained Au(PF<sub>3</sub>)<sub>2</sub><sup>+</sup>SbF<sub>6</sub><sup>-</sup>. This has previously been prepared from Au(CO)<sub>2</sub><sup>+</sup> by a replacement reaction with PF<sub>3</sub> [40]. We also hoped again in vain, to obtain the complex cation F<sub>3</sub>PAu<sup>+</sup>. Since Au(PF<sub>3</sub>)<sub>2</sub><sup>+</sup> is otherwise completely characterized, we report here the missing crystal structure. Our compound crystallized as Au(PF<sub>3</sub>)<sub>2</sub><sup>+</sup>SbF<sub>6</sub><sup>-</sup>, while the previously described material is Au(PF<sub>3</sub>)<sub>2</sub><sup>+</sup>Sb<sub>2</sub>F<sub>11</sub><sup>-</sup>. The structure solution and refinement posed some space group problems, see Table 3. The structure is solved as



**Fig. 3** Crystal structure of one unit of  $Au(PF_3)_2^+SbF_6^-$ , ORTEP, ellipsoids represent 50% probability. Atoms not indexed are those generated by the center of symmetry.

a twin in  $P2_1/n$ . The close to hexagonal crystal symmetry indicates the problems with twinning. Certainly the fairly high conventional R factor can be so explained.

The result is shown in Fig. 3 and Table 1. The P–Au–P frame work is linear, and all bond lengths and angles are in the expected region. Due to the center of symmetry the  $PF_3$  groups are staggered, whereas the vibrational spectra have been interpreted though with caution, in terms of an eclipsed configuration.

## Experimental

General: Moisture sensitive materials were handled in an argon glove box with less than 1 ppm water content. NMR spectra were taken on a Jeol 90 MHz multinuclear instrument with CFCl<sub>3</sub> as external standard for <sup>19</sup>F measurement. Raman spectra were taken on a Bruker RFS 100 S instrument, with Nd YAG laser excitation of 1064 nm. X-ray single crystal data were obtained by mounting a suitable crystal with help of a special device [41] under nitrogen cooling on a Bruker SMART CCD 1000 TM diffractometer, with MoK $\alpha$ (= 71.1069 pm) radiation, graphite monochromator, a scan width of 0–3 in  $\omega$ , and exposure time of 10 sec./frame, detector-crystal distance 4.0 cm. A full shell of data up to  $2\theta = 66^{\circ}$ was measured by 1800 frames. Data were reduced to intensities, corrected for background, and an empirical absorption correction was done by equalizing multiple symmetry equivalent reflections ("Sadabs"). Structures were solved [42] and refined [43] by the SHELX programs.

*Materials.* Commercially available unhydrous HF was vacuum distilled twice on a metal vacuum line.  $SbF_5$  and  $AsF_3$  are vacuum distilled once. AuF<sub>3</sub> was prepared by heating elemental gold with an excess fluorine overnight at 200 °C in a 150 ml monel autoclave equipped with an Autoclave Eengineering stainless steel valve.

 $[Au(SbF_6)_2 \cdot Au(AuF_4)_2]$  is the best starting material for  $F_3AsAu^+SbF_6^-$ . According to the literature it is prepared from elemental gold,  $SbF_5$ ,  $F_2$ , and HF [12]. Therefore we describe here a simple conversion of  $AuF_3$  into  $[Au(SbF_6)_2 \cdot Au(AuF_4)_2]$ .

 Table 3 Experimental details of the crystal structure determinations

|                             | $F_3AsAu^+SbF_6^-$          | $\begin{matrix} [\text{Au}(\text{CO})_2^+]_2 \cdot \\ \text{SbF}_6^- \cdot \text{Sb}_2 \text{F}_{11}^- \end{matrix}$ | $\operatorname{Au}(\operatorname{PF}_3)_2^+\operatorname{SbF}_6^-$ |
|-----------------------------|-----------------------------|--|--|
| size/mm                     | $0.3 \times 0.3 \times 0.1$ | $0.3 \times 0.1 \times 0.1$  | $0.2 \times 0.2 \times 0.2$  |
| a/pm                        | 798.3(2)                    | 1404.78(8)   | 825.5(2)   |
| b/pm                        | 912.0(2)                    | 622.86(3)  | 824.4(2)   |
| c/pm                        | 1076.3(3)                   | 1130.20(6)   | 876.4(3)   |
| $\alpha / \circ$            | 90                          | 90   | 90   |
| β/°                         | 96.25(4)                    | 90   | 90   |
| γ/°                         | 90                          | 90   | 119.997(6)   |
| $V/(10^6 \text{ pm}^3)$     | 778.9                       | 988.9  | 516.5  |
| T/°C                        | -143                        | -125   | -125   |
| Space group                 | $P2_1/n$                    | Pmma   | $P2_1/n$   |
| Z                           | 4                           | 2  | 2  |
| color                       | colorless                   | colorless  | colorless  |
| $\mu/\text{mm}^{-1}$        | 26.6                        | 18.99  | 17.25  |
| $2\theta_{\rm max}^{\circ}$ | 60                          | 66   | 66   |
| measured reflections        | 2343                        | 2501   | 4798   |
| independent reflexes        | 2166                        | 1766   | 1331   |
| R <sub>int</sub>            | 0.02                        | 0.06   | 0.10   |
| parameters                  | 110                         | 98   | 77   |
| $\hat{R}(Fo > 4\sigma(Fo))$ | 0.04                        | 0.03   | 0.06   |
| wR <sub>2</sub>             | 0.11                        | 0.06   | 0.17   |

In a glove box 400 mg (1.57 mmol) AuF<sub>3</sub> are weighed into a 14 mm diameter poly-(perfluoro) vinylether-tetrafluoroethylen (PFA) tube. The tube is closed by a metal valve which is in turn connected to a metal vacuum line. 2 g (9.2 mmol) SbF<sub>5</sub> and HF are condensed to it. At room temperature the mixture is shaken for 4 hrs. The insoluble, orange AuF<sub>3</sub> is converted into dark red, similar insoluble [Au(SbF<sub>6</sub>)<sub>2</sub> · Au(AuF<sub>4</sub>)<sub>2</sub>]. After pumping off all volatile materials the compound is obtained essentially quantitatively. Further characterization see [12].

**F<sub>3</sub>As-Au<sup>+</sup>SbF<sub>6</sub>**<sup>-</sup>. Reaction vessel is a Y-formed PFA tube system, and one end of it is closed by a metal valve, the other two ends are sealed. In one end 250 mg (1.07 mmol) AuF<sub>3</sub> or its molar equivalent [Au(SbF<sub>6</sub>)<sub>2</sub> · Au(AuF<sub>4</sub>)<sub>2</sub>] is added. 4 g HF and 280 mg (2.5 mmol) AsF<sub>3</sub> are condensed to it. The tube system is shaken for 2 hrs. at room temperature. A colorless solution and a black residue is formed. The colorless solution is decanted into the second tube, and the black residue is washed three times by a partly recondensation of HF and redecantation. Pumping on the entire system leaves colorless F<sub>3</sub>As-Au<sup>+</sup>SbF<sub>6</sub><sup>-</sup>. Single crystals are obtained by cooling the solution before pumping away the solvent. Solid F<sub>3</sub>As-Au<sup>+</sup>SbF<sub>6</sub><sup>-</sup> decomposes slowly at 0 °C, quickly at room temperature, forming elemental gold. In air rapid decomposition takes place.

Raman spectrum: 771(55), 755(20), both vAsF<sub>3</sub>, 671(100), 642(80), 588(20), all vSbF, 519(5) vAuF(?), 379(4), 351(6), 300(15), 281(20), 266(17), 228(5), 204(5), 151(20) vAs-Au(?), 120(5) cm<sup>-1</sup>. <sup>19</sup>F-nmr (CH<sub>3</sub>CN):  $\delta$  = -49.91 (AsF<sub>3</sub>),  $\delta$  = -121.1 14 line multiplett, J<sup>123</sup>Sb-F = 1937 Hz, J<sup>125</sup>Sb-F = 1050 Hz. It is not clear if this nmr spectrum stems from F<sub>3</sub>As-Au<sup>+</sup>SbF<sub>6</sub><sup>-</sup>, F<sub>3</sub>As-Au-NC-CH<sub>3</sub><sup>+</sup>SbF<sub>6</sub><sup>-</sup>, or Au(NCCH<sub>3</sub>)<sub>2</sub><sup>+</sup>SbF<sub>6</sub><sup>-</sup> + AsF<sub>3</sub>. Results of the crystal structure see Table 1, and experimental details see Table 3.

 $[Au(CO)_2]_2 \cdot SbF_6 - Sb_2F_{11} - 377 \text{ mg } (0.26 \text{ mmol}) [Au(SbF_6)_2 \cdot Au(AuF_4)_2]$  are filled into a PFA tube, 5 ml HF is distilled on it. The tube is kept on the metal vacuum line while a pressure of 3 bars CO is set over the reaction mixture that is

kept at -78 °C. Some CO is absorbed, and the crude crystalline residue has changed into a voluminous precipitate. Warming to room temperature and slow cooling to -78 °C within several days affords colorless needles. For further experimental details on Au(CO)<sub>2</sub>+Sb<sub>2</sub>F<sub>11</sub><sup>-</sup> see Lit. [9, 19]. A suitable crystal was obtained by cutting a needle to a length of 0.3 mm, and mounting it on the diffractometer as described above. Results of the crystal structure determination see Table 1, and experimental details of the crystals structure determination see Table 3.

**Au**(**PF**<sub>3</sub>)<sub>2</sub>**\*SbF**<sub>6</sub><sup>-</sup>. 377 mg (0.26 mmol) [Au(SbF<sub>6</sub>)<sub>2</sub> · Au(AuF<sub>4</sub>)<sub>2</sub>] are given into a PFA tube and 5 ml HF and approximately 250 mg (2.8 mmol) PF<sub>3</sub> then condensed into it. The tube is sealed off, warmed briefly to room temperature and than cooled slowly to  $-78 \,^{\circ}$ C within several days. Colorless crystals are formed. For further physical data on Au(PF<sub>3</sub>)<sub>2</sub>Sb<sub>2</sub>F<sub>11</sub><sup>-</sup> see Lit. [40]. One crystal is mounted on the diffractometer as described above. For results of the crystal structure determination see Table 1, and for experimental details of the crystal structure determination Table 3.

Further details of all crystal structure determinations can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-410429, 410888, 410889, the names of the author, and the journal citation.

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