## Bis(trifluoromethylselenato(0))metallates(I) of Silver and Gold, $[M(SeCF_3)_2]^-$ (M = Ag, Au)

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Received March 14th, 2005.

Dedicated to Professor Herbert W. Roesky on the Occasion of his 70<sup>th</sup> Birthday

Abstract. Ligand exchange reactions of  $[NMe_4]SeCF_3$  or  $[Cs(15-Crown-5)_2]SeCF_3$  with Ag[BF<sub>4</sub>] and AuCl gave the corresponding bis(trifluoromethylselenato(0))metallates  $[Ag(SeCF_3)_2]^-$  and  $[Au(SeCF_3)_2]^-$  in good yields. All compounds were characterized by NMR spectroscopic means and ESI mass spectrometry. Cation exchange with [PNP]Cl ([PNP] = bis(triphenylphosphoranylidene)-ammonium) yielded the corresponding [PNP] salts. The single cry-

### stal structure of [PNP][Au(SeCF<sub>3</sub>)<sub>2</sub>] was elucidated by XRD measurements (P2<sub>1</sub>/a; a = 1712.0(1), b = 1142.5(1), c = 2013.6(1) pm; $\beta$ = 112.10(1)°; Z = 4).

**Keywords:** Silver; Gold; Trifluoromethylselenates(0); Synthesis; Structure

### Introduction

In previous papers we have presented a more or less general approach for the syntheses of trifluoromethylchalcogenates(0),  $[ECF_3]^-$  (E = S [1], Se [2], Te [3]) (Eq. (1)) starting from tetramethylammonium fluoride,  $[NMe_4]F$ , trimethyl(-trifluoromethyl)silane, Me<sub>3</sub>SiCF<sub>3</sub>, and the corresponding chalcogen.

$$Me_{3}SiCF_{3} + E + [NMe_{4}]F \rightarrow [NMe_{4}]ECF_{3} + Me_{3}SiF$$
(1)

These convenient syntheses open new possibilities to investigate ligand exchange reactions of these derivatives with inorganic [4] and organic [5] substrates. The good access to the corresponding tellurates [4] encouraged us to investigate bis(trifluoromethylselenato(0))metallates of group 11 elements.

CuSeCF<sub>3</sub> [6] or AgSeCF<sub>3</sub> [7] have been used for the direct introduction of a SeCF<sub>3</sub> group into organic, inorganic and metal-organic compounds under different conditions but characterization is solely based on <sup>19</sup>F NMR spectroscopic data. CuSeCF<sub>3</sub> was prepared via the reaction of (CF<sub>3</sub>Se)<sub>2</sub> and elemental copper [6] according to Eq. (2).

$$CF_3SeSeCF_3 + 2 Cu \rightarrow 2 CuSeCF_3$$
 (2)

Although reactions of  $C(Se)F_2$  with AgF are mentioned in the literature [7] (Eq (3)), few details are reported about stability and reactivity of the resulting compound, Ag-SeCF<sub>3</sub>.

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$$F_2C=Se + AgF \rightarrow AgSeCF_3$$
 (3)

AgSeCF<sub>3</sub> has alternatively been prepared from the reactions of  $B(SeCF_3)_3$  and AgF [7] (Eq. (4)) or AgCF<sub>3</sub> and elemental selenium [8] (Eq. (5)).

$$B(SeCF_3)_3 + 3 \text{ AgF} \xrightarrow{150 \text{ °C}} 3 \text{ AgSeCF}_3 + BF_3$$
(4)

$$AgCF_3 + Se \xrightarrow{r.t.} AgSeCF_3 + ...$$
 (5)  
EtCN

In this paper, we report about syntheses and characterization of salts with the anions  $[M(SeCF_3)_2]^-$  (M = Ag, Au).

### **Results and Discussion**

The number of selenato complexes of group 11 elements is still limited to few structurally characterized examples [9-11]. Among them mainly polymeric compounds of general formula [AgSeR]<sub>n</sub> (n = 4, 6, 8,  $\infty$ ; R = organic group) are mentioned. By contrast, gold(I) chemistry with these class of ligands is dominated by mononuclear [9] and dinuclear [10] complexes incorporating organophosphorus ligands. To our knowledge, the carborane-selenato aurate(I), [Au(SeC<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)<sub>2</sub>]<sup>-</sup>, displays the only (so far not structurally characterized) example of a gold species with the gold atom exclusively co-ordinated by two selenium atoms [11].

In a similar manner as described for the corresponding trifluoromethyl tellurato derivatives [4], the tetramethylammonium derivatives  $[NMe_4][Ag(SeCF_3)_2]$  and  $[NMe_4][Au(-SeCF_3)_2]$  are obtained from the reactions of  $[NMe_4]SeCF_3$ with Ag[BF<sub>4</sub>] and AuCl, respectively, in 2 : 1 molar ratios. Reactions with  $[Cs(15\text{-crown-}5)_2]SeCF_3$  proceed in a similar manner but do not allow the isolation of pure compounds (Eq. (6)).

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$$MX + 2[CAT]SeCF_3 \xrightarrow{r.t.} [CAT][M(SeCF_3)_2] + [CAT]X \quad (6)$$

 $MX = Ag[BF_4], AuCl; [CAT] = [NMe_4], [Cs(15-Crown-5)_2]$ 

The low solubility of  $[NMe_4][BF_4]$  and  $[NMe_4]Cl$ , respectively, in EtCN opens a direct access to the corresponding selenato metallates after distilling off all volatile components under reduced pressure. Unfortunately, the cesium salts  $[Cs(15\text{-}crown-5)_2][Ag(SeCF_3)_2]$  and  $[Cs(15\text{-}crown-5)_2][BF_4]$  respectively  $[Cs(15\text{-}crown-5)_2][Au(SeCF_3)_2]$  and  $[Cs(15\text{-}crown-5)_2]Cl$  could not be separated from each other so far neither by extraction nor by fractionated crystallization.

Ligand exchange of [NMe<sub>4</sub>] into [PNP] proceeds nearly quantitatively again making use of the low solubility of [NMe<sub>4</sub>]Cl in MeCN (Eq. (7)).

$$[NMe_4][M(SeCF_3)_2] + [PNP]Cl \xrightarrow{r.t.} [PNP][M(SeCF_3)_2] + [NMe_4]Cl MeCN$$
(7)

$$M = Ag$$
,  $Au$ ;  $PNP = Ph_3P = N = PPh_3$ 

While the  $[NMe_4]$  and [PNP] derivatives are isolated as colourless to ochre solids decomposing above 100 °C,  $[Cs(15-Crown-5)_2][M(SeCF_3)_2]$  (M = Ag, Au) form waxy materials melting not significantly above room temperature (Ag) or even below (Au) due to significant impurities of  $[Cs(15-crown-5)_2][BF_4]$  and  $[Cs(15-crown-5)_2]Cl$ , respectively.

Room temperature <sup>19</sup>F, <sup>77</sup>Se and <sup>13</sup>C NMR spectra of [CAT][M(SeCF<sub>3</sub>)<sub>2</sub>] (CAT = NMe<sub>4</sub>, PNP, Cs(15-crown-5)<sub>2</sub>) in CD<sub>3</sub>CN at room temperature do not deviate from each other indicating complete dissociation. Sharp signals are detected for the argentate at  $\delta(^{19}F) = -15.8$  (s, <sup>2</sup>J(<sup>77</sup>Se,F) = 54 Hz,  $W_{1/2} \approx 8$  Hz),  $\delta(^{77}Se) = 128$  (q, <sup>2</sup>J(<sup>77</sup>Se,F) = 54 Hz) and  $\delta(^{13}C) = 125.9$  (q, <sup>1</sup>J(F,C) = 329 Hz) and the aurate at  $\delta(^{19}F) = -17.0$  (s, <sup>2</sup>J(<sup>77</sup>Se,F) = 44 Hz,  $W_{1/2} \approx 5$  Hz),  $\delta(^{77}Se) = 237$  (q, <sup>2</sup>J(<sup>77</sup>Se,F) = 44 Hz) and  $\delta(^{13}C) = 126.8$  (q, <sup>1</sup>J(F,C) = 330 Hz)

The negative ESI mass spectrum of the argentate  $[Ag(SeCF_3)_2]^-$  shows the anion peak (M<sup>-</sup> = 405 m/z) with 100 % intensity and the peak of  $[Ag_2(SeCF_3)_3]^-$  with 76 % intensity. No evidence is found for higher aggregates as observed in mass spectra of the corresponding tellurium derivative [4]. Signals of low intensity with masses of 530 and 275 m/z indicate the formation of the ions  $[Ag_2(SeCF_3)_2F]^-$  and  $[Ag(SeCF_3)F]^-$ , respectively, which are formed by loss of SeCF<sub>2</sub>.

The mass spectrum of the aurate,  $[Au(SeCF_3)_2]^-$ , is dominated by the anion peak (100 %) and a peak of 34 % intensity for  $[Au(SeCF_3)F]^-$ . This fragmentation is similar to that of the corresponding tellurato aurate [4] exhibiting



Fig. 1 View of [PNP][Au(SeCF<sub>3</sub>)<sub>2</sub>] showing the labeling scheme of the anion and the displacement ellipsoids at the 50 % probability level; interatomic distances/pm and angles/deg (with estimated standard deviations in parentheses):

Se1-Au1 238.8(1), Se2-Au1 239.3(1), Se1-C1 190.9(7), Se2-C2 191.8(6), C1-F11 133.3(7), C1-F12 133.7(8), C1-F13 135.6(7), C2-F23 133.3(7), C2-F22 134.3(7), C2-F21 135.0(6), N1-P1 158.4(4), N1-P2 158.7(4), Se1-Au1-Se2 172.7(1), Au1-Se1-C1 102.7(2), Au1-Se2-C2 101.3(2), P1-N1-P2 138.0(3). Hatoms are omitted for clarity.



**Fig. 2** The packing diagram for [PNP][Au(SeCF<sub>3</sub>)<sub>2</sub>] viewed along b-axis.

that  $[Au(SeCF_3)_2]^-$  is monomeric in solution and does not tend to build higher aggregates as the argentate does.

Among the selenato gold compounds analyzed by XRD measurements [10, 11], [PNP][Au(SeCF<sub>3</sub>)<sub>2</sub>] (Figures 1 and 2, Table 1) represents the first example of a gold-selenato

empirical formula	C28H20NF6P2AuSe2
formula mass /g mol <sup><math>-1</math></sup>	1031.46
data collection	
diffractometer	STOE IPDS II
radiation	Mo-K $\alpha$ , $\lambda = 71.073$ pm
temperature /K	150(2)
index range	$-21 \le h \le 19$
	$-14 \le k \le 14$
	$-25 \le 1 \le 25$
rotation angle range	$0^{\circ} \leq \omega \leq 180^{\circ}; \gamma = 0^{\circ}$
	$0^{\circ} \leq \omega \leq 94^{\circ}; \gamma = 90^{\circ}$
increment	$\Delta \omega = 1^{\circ}$
no. of images	274
exposure time /min	4
detector distance /mm	120
$2 \cdot \theta$ range /deg	1.9 - 54.8
total data collected	42807
unique data	7994
observed data	6811
Rmarg	0.0817
absorption correction	numerical, after crystal shape
	optimization [16, 17]
transmission min / max	0.0941 / 0.3815
crystallographic data [18]	
crystal size /mm	$0.2 \cdot 0.2 \cdot 0.2$
colour, habit	colourless, block
crystal system	monoclinic
space group	$P_{2_1/a}$ (no. 14)
a /pm	1711.98(6)
b /pm	1142.54(4)
c /pm	2013.64(9)
β/deg	112.097(3)
volume /nm <sup>3</sup>	3.6494(2)
Z	4
$\rho_{cala}/Mg m^{-3}$	1.877
u/mm <sup>-1</sup>	6 174
F(000)	1984
structure analysis and refinement*	
structure determination	SIR-92 [19] and SHELX-97 [20]
no. of variables	453
R indexes $[I > 2\sigma I]$	$R_1 = 0.0443$
$wR_2 = 0.1108$	1
R indexes (all data)	$wR_2 = 0.1145$
$R_1 = 0.0517$	
goodness of fit (S <sub>abs</sub> )	1.029
goodness of fit $(S_{all})$	1.029
largest difference map	-1.794 / 5.410
hole / peak /e $10^{-6}$ pm <sup>-3</sup>	

 Table 1 Crystal Data and Structure Refinement Parameters for

 [PNP][Au(SeCF<sub>3</sub>)<sub>2</sub>]

#### [PNP][Au(SeCF<sub>3</sub>)<sub>2</sub>]

$$\begin{split} &R_1 = \Sigma \||F_o| - |F_c|| / \Sigma |F_o|, \ wR_2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w (|F_o|^2)^2 |F_o|^2)^2 / \Sigma w (|F_o|^2)^2 |F_o|^2 |F_o|^2 / (n-p) ]^{1/2}, \ with \ w = 1 / [\sigma^2 (F_o)^2 + (0.0428 \cdot P)^2 + 18.5046 \cdot P], \ were \ P = (F_o^2 + 2F_c^2) / 3. \ F_c^* = k \ F_c [1+0.001 \cdot |F_c|^2 \lambda^3 / \sin(2\theta)]^{-1/4}. \end{split}$$

\* All H atoms were placed in idealized positions and constrained to ride on their parent atom.

compound with a discrete quasi-linear Se-Au-Se unit (172.7°) where neither gold atoms nor selenium atoms are co-ordinated by more than two ligands. It crystallizes isostructurally with the corresponding tellurato aurate in the monoclinic space group P2<sub>1</sub>/a (a = 1712.0(1), b = 1142.5(1), c = 2013.6(1) pm;  $\beta$  = 112.10(1)°; Z = 4) with well separated cations and anions. In the crystal packing, the anions are layered in channels formed by the space-demanding [PNP]<sup>+</sup> ions.

Au-Se bond lengths of 238.8 pm and 239.3 pm are shorter than those in the derivative  $[Au(SeC_2B_{10}H_{11})PPh_3]$  (241.7 pm) [11] and further compounds mentioned [10]. This shortening might be attributed to the strong electron withdrawing nature of the trifluoromethyl group bond to selenium compared with less electron withdrawing groups in the other structures.

### **Experimental Part**

Schlenk techniques were used throughout all manipulations. NMR spectra were recorded on Bruker AC 200 (<sup>1</sup>H, <sup>19</sup>F, <sup>13</sup>C) and AV-ANCE 400 (<sup>77</sup>Se) spectrometers. External standards were used in all cases (<sup>1</sup>H, <sup>13</sup>C: Me<sub>4</sub>Si; <sup>19</sup>F: CCl<sub>3</sub>F; <sup>77</sup>Se: Me<sub>2</sub>Se). Acetone-d<sub>6</sub> was used as an external lock (5 mm tube) in reaction control measurements while an original sample of the reaction mixture was measured in a 4 mm insert. Negative ESI mass spectra in MeCN solutions were run on a Finnigan MAT 900 apparatus with a flow rate of 2 µl/min. Intensities are referenced to the most intense peak of a group. Isotope patterns for comparison were calculated with the program Isopro [12]. Visible decomposition points were determined using the Stuart melting point apparatus SMP10. C, H and N analyses were carried out with a HEKAtech Euro EA 3000 apparatus. Details of crystal data and structure refinement parameters for [PNP][Au(SeCF<sub>3</sub>)<sub>2</sub>] are summarised in Table 1.

The following derivatives were prepared according to literature procedure: [NMe<sub>4</sub>]SeCF<sub>3</sub> [2], [PNP]Cl [13], AuCl [14]. Ag[BF<sub>4</sub>] (Apollo) was used as received.

### *Synthesis of bis*(15-crown-5)cesium trifluoromethylselenate(0), [Cs(15-Crown-5)<sub>2</sub>]SeCF<sub>3</sub>

3.80 g (25 mmol) well-dried and finely powdered CsF are dissolved in a solution of 9.74 ml (50 mmol) 15-crown-5 in 200 ml dimethoxvethane at ambient temperature. After cooling to -30 °C, 1.97 g (25 mmol) red selenium are added in one portion. Finally 3.75 ml (28 mmol) Me<sub>3</sub>SiCF<sub>3</sub> are poured into the well-stirred suspension. Stirring is maintained for 30 minutes at -30 °C and afterwards the reaction mixture is allowed to warm to room temperature overnight. After a total reaction time of approximately 16 hours the colour of the mixture has changed into orange and some greyochre solid has precipitated. The composition is controlled by <sup>19</sup>F NMR spectroscopy. Volatile products (Me<sub>3</sub>SiF, excess Me<sub>3</sub>SiCF<sub>3</sub>, traces of  $CF_3H$  and  $Se(CF_3)_2$ ) and the solvent are removed under reduced pressure giving a grey residue. [Cs(15-crown-5)<sub>2</sub>]SeCF<sub>3</sub> is separated from the residue by repeated extraction with MeCN (3-4 times). The selenate crystallizes upon removal of MeCN under reduced pressure at ambient temperature. The pale ochre product is vacuum dried and obtained in a yield of 30 % (5.40 g).

## Bis(15-crown-5) cesium trifluoromethylselenate(0), [Cs(15-Crown-5)<sub>2</sub>]SeCF<sub>3</sub>

Pale ochre crystals, visible m.p. 102-104 °C (molten glas-capillary), 160-165 °C (onset of dec.).

NMR data (CD<sub>3</sub>CN) and MS spectra (neg. ESI) of the anion are in absolute agreement with those published in a previous paper [2]. NMR data for [Cs(15-crown-5)<sub>2</sub>]<sup>+</sup>: <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta = 3.56$ (s). <sup>13</sup>C NMR (CD<sub>3</sub>CN):  $\delta = 69.5$  (t, <sup>1</sup>*J*(C,H) = 141 Hz). Analytical data  $C_{21}H_{40}F_3O_{10}CsSe$  (721.40): C 35.69 (calc. 34.96); H 5.86 (5.59) %.

## Reactions of [NMe<sub>4</sub>]SeCF<sub>3</sub> and Ag[BF<sub>4</sub>]

In a typical procedure, 0.57 g (2.57 mmol) [NMe<sub>4</sub>]SeCF<sub>3</sub> were dissolved in 10 ml EtCN at ambient temperature. Directly after addition of 0.25 g (1.28 mmol) Ag[BF<sub>4</sub>] to the primarily rose-coloured solution, a colourless solid began to precipitate, while the colour of the reaction mixture changed into pale yellow. The reaction mixture was stirred for one hour and ongoing of the reaction was monitored by <sup>19</sup>F NMR spectroscopy. Stirring was terminated after approximately two hours and [NMe<sub>4</sub>][BF<sub>4</sub>] was filtered off. Evaporation of MeCN in vacuo afforded [NMe<sub>4</sub>][Ag(SeCF<sub>3</sub>)<sub>2</sub>] in 91 % yield (0.56 g) as an ochre solid.

# Tetramethylammonium[bis(trifluoromethylselenato(0)) argentate(I)], $[NMe_4][Ag(SeCF_3)_2]$

Colourless crystals, visible m.p. 170  $^{\circ}$ C (onset of decomposition (darkening); complete decomposition with gas evolution at 195 – 200  $^{\circ}$ C).

Analytical data  $C_6H_{12}AgF_6NSe_2$  (477.95): C 15.71 (calc. 15.08); H 2.67 (2.53); N 2.97 (2.93) %.

<sup>19</sup>F NMR (CD<sub>3</sub>CN):  $\delta$  = -15.9 (s, <sup>2</sup>*J*(<sup>77</sup>Se,F) = 54 Hz; <sup>1</sup>*J*(F,C) = 322.9 Hz). <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  = 3.16 (s). <sup>77</sup>Se NMR (CD<sub>3</sub>CN):  $\delta$  = 128 (q, <sup>2</sup>*J*(Se,F) = 54 Hz). <sup>13</sup>C NMR (CD<sub>3</sub>CN):  $\delta$  = 125.9 (q, <sup>1</sup>*J*(F,C) = 329 Hz, CF<sub>3</sub>), 55.6 (q of decets, <sup>1</sup>*J*(C,H) = 144 Hz, <sup>3</sup>*J*(C,H) = 3.5 Hz, NMe<sub>4</sub>).

MS (neg. ESI in MeCN):  $m/z = 659.9 ([Ag_2(SeCF_3)_3]^-, 76\%),$ 530.1 ( $[Ag_2(SeCF_3)_2F]^-, 4\%$ ); 404.5 ( $[Ag(SeCF_3)_2]^-, 100\%$ ), 274.7 ( $[Ag(SeCF_3)F]^-, 9\%$ ).

All attempts to grow single crystals suitable for XRD measurements failed.

## Synthesis of $[PNP][Ag(SeCF_3)_2]$

To a solution of 0.13 g (0.27 mmol)  $[NMe_4][Ag(SeCF_3)_2]$  in 5 ml MeCN a solution of 0.16 g (0.28 mmol) [PNP]Cl in 5 ml MeCN was added in one portion. Directly after mixing both solutions, the reaction mixture became turbid and stirring was maintained for 30 minutes until the signal of  $[NMe_4]^+$  could no more be detected in the <sup>1</sup>H-NMR spectrum. After inert filtration from  $[NMe_4]Cl$ , all volatile components were distilled off in vacuo giving  $[PNP][Ag(-SeCF_3)_2]$  as a pale-brown crystalline solid in 90 % yield (0.23 g).

## Bis(triphenylphosphoranyliden)ammonium bis(trifluoromethyselenato(0))argentate(I), [PNP][Ag(SeCF<sub>3</sub>)<sub>2</sub>]

Pale brown crystals, visible m.p.  $135 \,^{\circ}$ C (onset of decomposition, > 170  $^{\circ}$ C complete decomposition with gas evolution).

NMR data collected at room temperature in  $CD_3CN$  for the cation  $[PNP]^+$  (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P) are in absolute agreement with literature data [15], those of the anion  $[Ag(SeCF_3)_2]^-$  (<sup>13</sup>C, <sup>19</sup>F, <sup>77</sup>Se) in absolute agreement with those of the tetramethylammonium salt. Also values in negative ESI mass spectra do not deviate from those obtained for the tetramethylammonium salt. Attempts to measure <sup>1</sup>D-

 $^{109}\text{Ag-NMR}$  spectra or  $^{109}\text{Ag},\,^{19}\text{F}$  HMBC spectra failed through rapid ligand exchange of the SeCF3-groups.

Elemental analysis for  $C_{38}H_{30}F_6NAgP_2Se_2$  (942.39) at ambient temperature was not sufficient due to rapid decomposition of the compound on exposure to ambient atmosphere.

## Reactions of [Cs(15-crown-5)<sub>2</sub>]SeCF<sub>3</sub> and Ag[BF<sub>4</sub>]

To a well stirred solution of pale brown solution of 0.69 g (0.96 mmol)  $[Cs(15-Crown-5)_2]SeCF_3$  in 10 ml EtCN 0.10 g (0.51 mmol) Ag[BF<sub>4</sub>] was added in one portion at room temperature. The colour of the mixture changed into dark brown directly after addition of the silver salt. Stirring was maintained for one hour; during this period the reaction mixture became turbid. The solution was decanted from a minor amount of solid and evaporated to dryness. Repeated washing of the residue with diethylether followed by evaporation gave a waxy material which contained ca. 55 % [Cs(15-Crown-5)\_2][Ag(SeCF\_3)\_2] and ca. 45 % [Cs(15-Crown-5)\_2][BF<sub>4</sub>] (<sup>19</sup>F NMR; elemental analysis).

NMR data (CD<sub>3</sub>CN) of the product mixture were in absolute agreement with those given above.

## Reactions of [NMe<sub>4</sub>]SeCF<sub>3</sub> and AuCl

In a similar manner as described for the argentate,  $[NMe_4][Au(-SeCF_3)_2]$  was prepared from 0.21 g (0.90 mmol) AuCl and 0.40 g (1.80 mmol)  $[NMe_4]SeCF_3$  in 78 % yield (0.40 g) after re-crystallization from cold MeCN as a colourless solid.

Tetramethylammonium[bis(trifluoromethylselenato(0)) aurate(I)], [NMe<sub>4</sub>][Au(SeCF<sub>3</sub>)<sub>2</sub>]

Colourless crystals, visible m.p. 120  $^{\circ}\mathrm{C}$  (onset of decomposition (darkening)).

Analytical data  $C_6H_{12}AuF_6NSe_2$  (567.04) C 13.41 (calc. 12.71); H, 2.60 (2.13); N 2.87 (2.47) %.

<sup>19</sup>F NMR (CD<sub>3</sub>CN):  $\delta = -17.0$  (*s*, <sup>2</sup>*J*(<sup>77</sup>Se,F) = 44 Hz; <sup>1</sup>*J*(F,C) = 329 Hz). <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta = 3.16$  (s). <sup>77</sup>Se NMR (CD<sub>3</sub>CN):  $\delta = 237$  (*q*, <sup>2</sup>*J*(Se,F) = 44 Hz). <sup>13</sup>C NMR (CD<sub>3</sub>CN):  $\delta = 126.8$  (*q*, <sup>1</sup>*J*(F,C) = 330 Hz, CF<sub>3</sub>), 55.6 (q of decets, <sup>1</sup>*J*(C,H) = 144 Hz, <sup>3</sup>*J*(C,H) = 3.5 Hz, NMe<sub>4</sub>).

MS (neg. ESI in MeCN): m/z = 494.4 ([Au(SeCF<sub>3</sub>)<sub>2</sub>]<sup>-</sup>, 100 %), 364.6 ([Au(SeCF<sub>3</sub>)F]<sup>-</sup>, 34 %).

## Synthesis of [PNP][Au(SeCF<sub>3</sub>)<sub>2</sub>]

In the same manner as described for the argentate, the tetramethylammonium derivative was converted into the [PNP]-salt starting from 0.31 g (0.55 mmol) [NMe<sub>4</sub>][Au(SeCF<sub>3</sub>)<sub>2</sub>] and 0.31 g (0.55 mmol) [PNP]Cl. 0.48 g (85 % yield) of [PNP][Au(SeCF<sub>3</sub>)<sub>2</sub>] were collected of sufficient purity. Re-crystallisation from MeCN (-21 °C) gave single crystals suitable for XRD measurements.

## Bis(triphenylphosphoranyliden)ammoniumbis(trifluoromethylselenato(0))aurate(I), $[PNP][Au(SeCF_3)_2]$

Pale orange-brown crystals, visible m.p. 115 °C (onset of decomposition(darkening)).

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NMR data collected at room temperature in CD<sub>3</sub>CN for the cation [PNP]<sup>+</sup> (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P) are in absolute agreement with literature data [15], those of the anion [Au(SeCF<sub>3</sub>)<sub>2</sub>]<sup>-</sup> (<sup>13</sup>C, <sup>19</sup>F, <sup>77</sup>Se) as well as values in the negative ESI mass spectra are in absolute agreement with those obtained for the tetramethylammonium salt.

Analytical data  $C_{38}H_{30}F_6NAuP_2Se_2$  (1031.49): C 46.75 (calc. 47.92); H 3.57 (3.17); N 2.16 (1.47) %.

### Reactions of $[Cs(15\text{-}crown-5)_2]$ SeCF<sub>3</sub> and AuCl

To a well stirred solution of pale brown solution of 0.62 g (0.86 mmol) [Cs(15-Crown-5)<sub>2</sub>]SeCF<sub>3</sub> in 10 ml EtCN 0.10 g (0.43 mmol) AuCl was added in one portion at room temperature. Directly after addition of AuCl, small quantities of a colourless solid were formed. Stirring of the reaction mixture was terminated as soon as all AuCl had been visibly dissolved. The mixture was decanted and all volatile components were removed in vacuo. The oily residue was washed twice with n-pentane and afterwards dissolved in diethylether. Storage of the ethereal solution overnight at -21 °C led to the precipitation of some colourless crystalline material which readily dissolved upon warming to ambient temperature. Evaporation of diethylether gave an orange-brown waxy material consisting of ca. 40 % [Cs(15-Crown-5)<sub>2</sub>][Au(SeCF<sub>3</sub>)<sub>2</sub>] and ca. 60 % [Cs(15-Crown-5)<sub>2</sub>]Cl (elemental analysis).

NMR data ( $CD_3CN$ ) of the product mixture were in absolute agreement with those given above.

Acknowledgements. Financial support by the Fonds der Chemischen Industrie is gratefully acknowledged.

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