

Supporting Information for

(Phosphine chalcogenide)gold(I) halides and their halogenation products; some novel structures

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1. Experimental Details

Methods and materials: Reactions were carried out under a dry nitrogen atmosphere with standard Schlenk techniques with a high vacuum line. The glassware was flame dried prior to use. Solvents were dried and purified by a SPS-System from MBraun and stored over molecular sieve (4 Å) until they were needed. The ^{31}P -NMR spectra were recorded on a Bruker DPX 200 (200 MHz) device. Chemical shifts are reported in ppm (parts per million). Elemental analyses were carried out with a Vario Micro Cube System. All starting materials were purchased from Aldrich or Acros and used without further purification. $\text{dppn}^{[1]}$, $\text{dppnSe}^{[2]}$, $\text{dppmSAuBr}^{[3]}$, $\text{dppmSAuI}^{[3]}$, $\text{dppmSeAuI}^{[3]}$, $\text{dppbzSAuBr}^{[3]}$, $\text{Ph}_3\text{PSAuBr}^{[4]}$ and $\text{Ph}_3\text{PSeAuBr}^{[4]}$, were prepared according to the literature procedures.

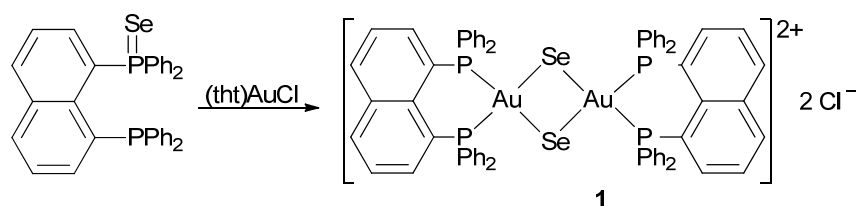
[1] A. Karacar, H. Thönnessen, P. G. Jones, R. Bartsch, R. Schmutzler, *Heteroatom Chem.*, 1997, **8**, 539-550.

[2] A. Karacar, M. Freytag, H. Thönnessen, J. Omelanczuk, P. G. Jones, R. Bartsch, R. Schmutzler, *Z. Anorg. Allg. Chem.*, 2000, **626**, 2361-2372.

[3] Routine syntheses – details to be published.

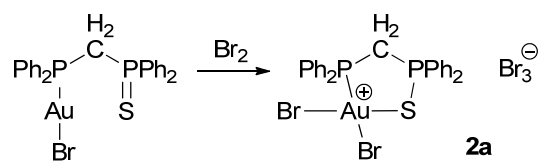
[4] a) M. S. Hussain, *Acta Cryst.*, 1987, **C43**, 450-453; M. S. Hussain, *J. Chem. Cryst.*, 1986, **16**, 91-99; P. G. Jones and E. Bembenek, *J. Cryst. Spect. Res.*, 1992, **22**, 397-401.

Reaction of dppnSe with $(\text{tht})\text{AuCl}$



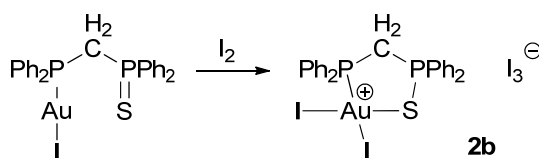
To a solution of 1,8-bis(diphenylphosphino)naphthalene monoselenide (500 mg, 0.87 mmol) in dichloromethane (25 mL) was added under stirring a solution of $(\text{tht})\text{AuCl}$ (279 mg, 0.87 mmol) in dichloromethane (15 mL). The reaction mixture which turned black immediately was stirred for other 10 minutes. The solvent was then removed in vacuum. The dark brown residue has a very low solubility. A part of it was recrystallized by diffusion of pentane into a saturated dichloromethane solution. Crystals suitable for X-ray analysis could be obtained from a deuterated chloroform solution. ^{31}P -NMR (200 MHz, CDCl_3): δ 13.68 (s). MS (NSI), m/z (%): 773.0 (100, $[(\text{dppnSeAu})_2]$), 1581.0 (27, $[(\text{dppnSeAu})_2+\text{Cl}]$).

Bromination of dppmSAuBr



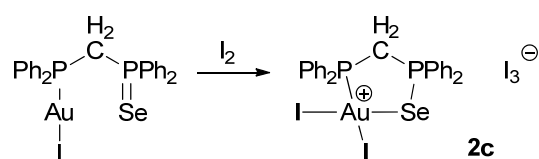
To a solution of dppmSAuBr (200 mg, 0.29 mmol) in dichloromethane (15 mL) was added an excess of bromine. The resulting red reaction mixture was stirred for five minutes at room temperature. Then stirring was stopped and the mixture was covered with a layer of pentane. After one week at 3 °C **2a** was obtained as red crystals of low solubility. **Elemental analysis:** Found: C 29.64, H 2.19, S 3.17 for C₂₅H₂₂AuBr₅P₂S: C 29.20, H 2.31, S 3.27.

Iodination of dppmSAuI



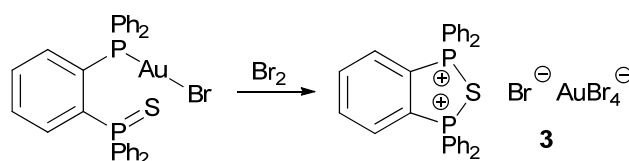
To a solution of dppmSAuI (150 mg, 0.2 mmol) in dichloromethane was added a solution of iodine (103 mg, 0.4 mmol) in dichloromethane. Evaporation of the solvent in vacuum and recrystallization from dichloromethane/pentane gave **2b** as a black crystalline solid of low solubility. **Elemental analysis:** Found: C 24.06, H 1.78, S 2.57 for C₂₅H₂₂AuI₅P₂S: C 23.99, H 1.86, S 2.59.

Iodination of dppmSeAuI



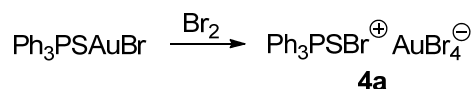
To a solution of dppmSeAuI (200 mg, 0.25 mmol) in dichloromethane (10 mL) was added a solution of iodine (130 mg, 0.5 mmol) in dichloromethane. Evaporation of the solvent in vacuum and recrystallization from dichloromethane/pentane gave **2c** as a black crystalline solid of low solubility. **Elemental analysis:** Found: C 23.19, H 1.71 for C₂₅H₂₂AuI₅P₂Se: C 22.90, H 1.81.

Bromination of dppbzSAuBr



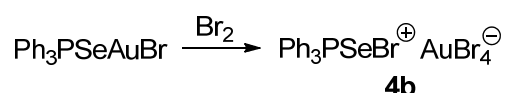
To a solution of dppbzSAuBr (140 mg, 0.19 mmol) in dichloromethane (20 mL) was added an excess of bromine. The reaction mixture was stirred several minutes at room temperature. Then it was covered with a layer of pentane and stored at 3°C. After one week crystals suitable for X-ray analysis were obtained. Evaporation of the solvent in vacuum gave pure **3** as a red solid in quantitative yield. **Elemental analysis:** Found: C 33.52, H 2.25, S 2.98 for C₃₀H₂₄AuBr₅P₂S: C 34.32, H 2.78, S 3.60. **³¹P-NMR** (200 MHz, CDCl₃): δ 50.16 (s).

Bromination of Ph₃PSAuBr



An excess of bromine (40 μL) was added under stirring to a solution of Ph₃PSAuBr (200 mg, 0.35 mmol) in dichloromethane (10 mL). After a few minutes stirring was stopped and the reaction mixture was covered with a layer of pentane and stored at 3 °C. The resulting red solid was recrystallized again from dichloromethane and pentane. **³¹P-NMR** (200 MHz, CD₃CN): δ 49.44 (s).

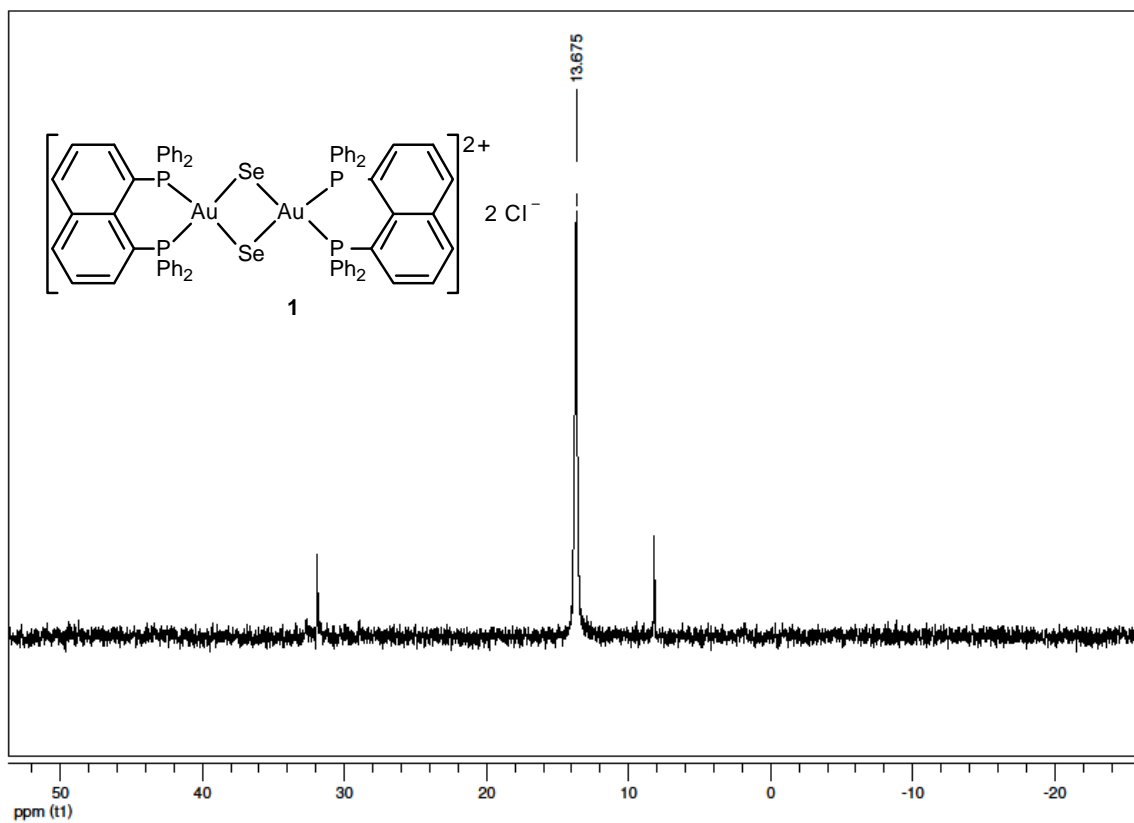
Bromination of Ph₃PSeAuBr



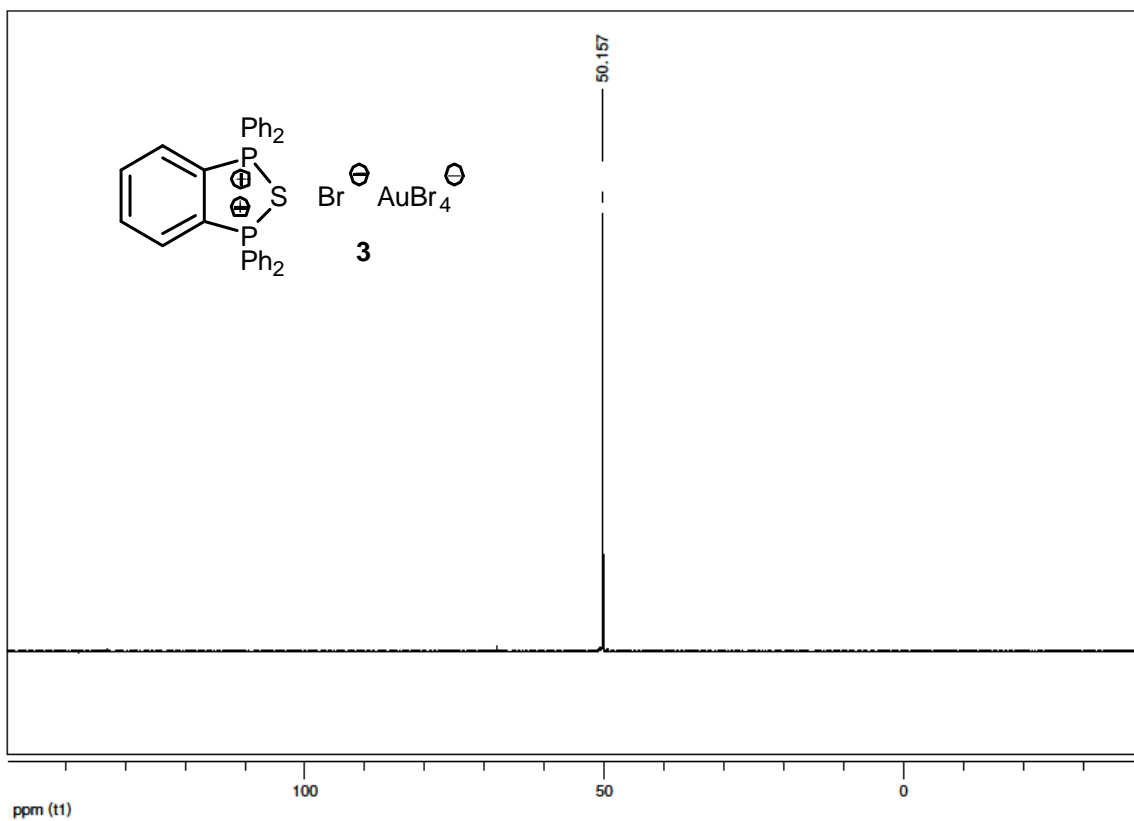
An excess of bromine (40 μL) was added under stirring to a solution of Ph₃PSeAuBr (200 mg, 0.32 mmol) in dichloromethane (10 mL). After a few minutes stirring was stopped and the reaction mixture was covered with a layer of pentane and stored at 3 °C. After 24 hours crystals suitable for X-ray analysis were obtained. Decanting the solvent and drying the residue in vacuum gave pure **4b** as a red crystalline solid. **Elemental analysis:** Found: C 23.05, H 1.61 for C₁₈H₁₅AuBr₅PSe: C 23.33, H 1.74. **³¹P-NMR** (200 MHz, CD₃CN): δ 52.30 (s).

2. NMR Spectra

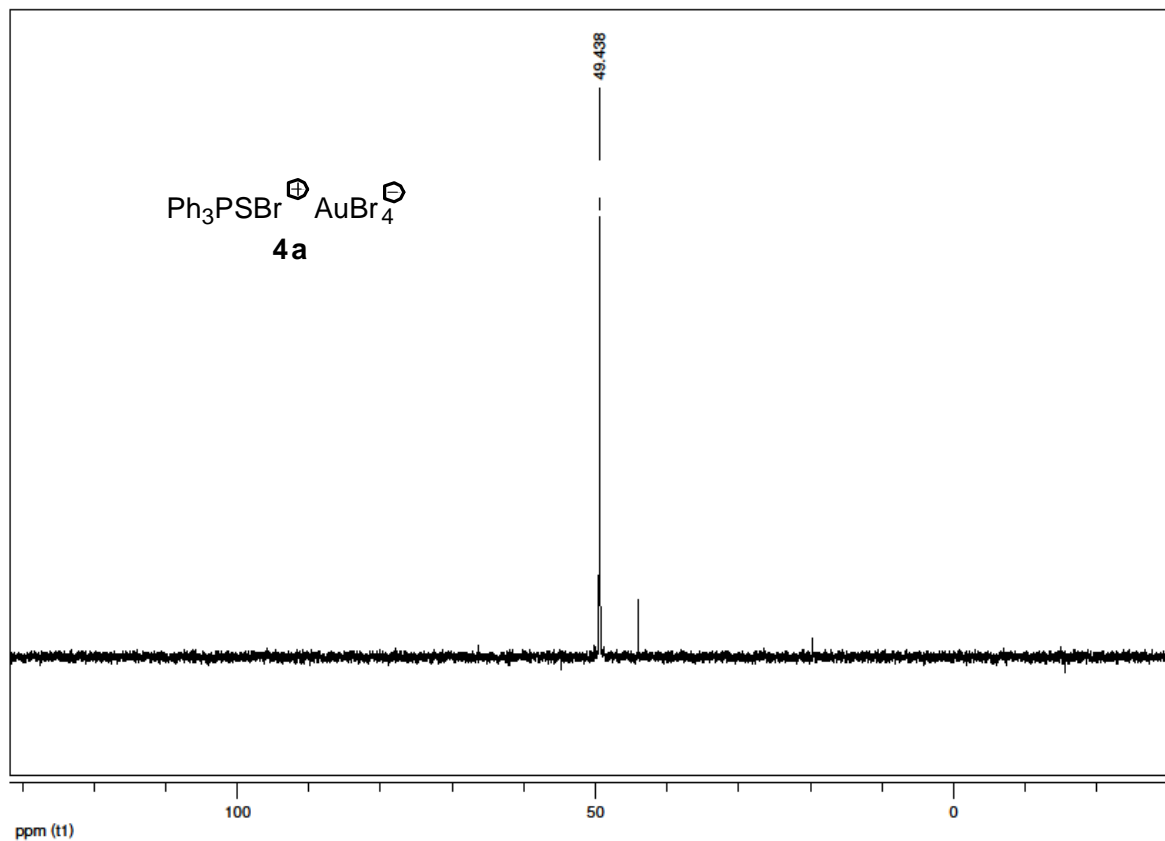
^{31}P -NMR (CDCl_3)



^{31}P -NMR (CDCl_3)



³¹P-NMR (CD₃CN)



³¹P-NMR (CD₃CN)

