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COMMUNICATION

Halogenation of (phosphine chalcogenide)gold(1) halides; some unexpected products[†]

Christina Taouss and Peter G. Jones*

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The monoselenide of 1,8-bis(diphenylphosphino)naphthalene reacts with (tht)AuCl to give the gold(III) system $[(dppnAuSe)_2]^{2+} 2Cl^-$ (1); bromination of the bromogold(I) complex of the 1,2-bis(diphenylphosphino)methane monosulfide ligand furnishes the tribromide salt (2a) of a gold(III) cation [LAuBr₂]⁺; bromination of the bromogold(I) complex of the 1,2-bis(diphenylphosphino)benzene monosulfide ligand leads to a mixed bromide/tetrabromoaurate salt (3) of a heterocyclic dication involving a [-PPh₂-S-PPh₂-]²⁺ moiety; analogous reactions of triphenylphosphine sulfide and selenide complexes lead to tetrabromoaurate salts (4a and 4b) of the (bromochalcogeno)phosphonium cations Ph₃PEBr⁺.

Phosphine chalcogenides $R_3P = E$ (E = O, S, Se; the R groups may be different or form part of ring systems) are well-known compounds that can act as ligands. In particular, gold(I) complexes of the type R_3PEAuX (X = halogen) have been reported by several groups; they are synthesized by direct reaction of the phosphine chalcogenide with L'AuX, where L' is an easily displaced ligand such as tetrahydrothiophene (tht) or Me₂S.¹ Similarly, diphosphine dichalcogenides have been shown to form gold(I) complexes such as XAuEP(CH₂)_nPEAuX,² although no X-ray structures of these halogen derivatives were reported. To the best of our knowledge, however, few gold(I) complexes of diphosphine monochalcogenides are known; this may in part be associated with the difficulties of obtaining some of the ligands in a pure state.³ The compound ClAuPh₂PCH₂P(=Se)Ph₂ (dppmSeAuCl) was synthesized by Schmidbaur and used to prepare the cyclic dication [(dppmSe)₂Au₂]²⁺;⁴ we determined the X-ray structure of dppmSeAuCl,⁵ and of two salts of the tetrahedral Au(I) cation $[(dppmSe)_2Au]^+.^6$

Many gold(I) complexes of the type LAuX (L = phosphine, X = Cl, Br) undergo oxidative addition with elemental chlorine or bromine to give the gold(III) complexes LAuX₃.⁷ With iodine, the halogenation depends strongly on electronic and steric effects of the ligand; complexes with small trialkylphosphines are readily oxidised, whereas those with more bulky ligands are not. Where no

oxidation occurs, the gold(I) complexes may crystallise as adducts with elemental iodine.⁷

As regards the halogenation of phosphine chalcogenides themselves, du Mont showed that the iodination of phosphine selenides leads to $[R_3PSeI]^+$ cations.⁸ Reaction of phosphine selenides with elemental bromine, in contrast, leads to hypervalent compounds R_3PSeBr_2 with a T-shaped structure at selenium in the solid state. The addition of bromine to such a dibromide was assumed to give R_3PSeBr^+ derivatives, but these were never isolated.^{9,10}

We wished to combine these various fields of investigation by synthesizing new gold(I) halide derivatives with diphosphine monochalcogenide ligands (E = S, Se) and oxidizing both these and the known monophosphine chalcogenide complexes with halogens. Here we present some unexpected and novel products of these reactions.

Unsymmetrical diphosphine monochalcogenides were prepared from bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)benzene (dppbz) and 1,8-bis(diphenylphosphino)naphthalene (dppn) according to literature methods.^{11,12} For the dppm and dppbz chalcogenides, the corresponding gold(I) halides were obtained for X = Cl, Br by reaction of the ligand with (tht)AuX; as expected, the gold centres are coordinated by the phosphine donors. Reaction of the chlorides with an excess of potassium iodide in dichloromethane/water gave the gold(I) iodides.^{24,7,13}

For dppnSe, however, the reaction with (tht)AuCl does not lead to the expected gold(I) complex (dppnSe)AuCl. Instead, a dark brown gold(III) complex of the same stoichiometry (1) is obtained (Scheme 1); the selenium has dissociated from the dppn but still forms part of the product. In its ³¹P-NMR spectrum 1 displays a singlet at 13.7 ppm. X-ray structure analysis‡ showed that 1 crystallises in the space group $P\overline{1}$ with half a cation (Fig. 1), one chloride and three chloroform molecules in the asymmetric unit. The gold centre has an approximately square planar geometry and is coordinated to both phosphorus atoms of the dppn ligand and to two selenium atoms. Inversion symmetry completes the central



Scheme 1 Reaction of dppnSe with (tht)AuCl.

Institut für Anorganische und Analytische Chemie, Technische Universität Carolo-Wilhelmina, Hagenring 30, D-38106 Braunschweig, Germany. E-mail: p.jones@tu-bs.de; Fax: +49 531-391-5387; Tel: +49 531-391-5382 † Electronic supplementary information (ESI) available. CCDC reference numbers 837547–837553. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11476j



Fig. 1 Crystal structure of the cation $[(dppnAuSe)_2]^{2+}$ in 1 (H atoms omitted). Selected bond lengths [Å] and angles [°]: P1–Au 2.323(3), P2–Au 2.341(3), Au–Se 2.443(2), Au–Se' 2.451(2); P1–Au–P2 87.64(10), P1–Au–Se' 92.29(8), P2–Au–Se 98.91(8), Se–Au–Se' 81.08(5), Au–Se–Au' 98.92(5).

 Au_2Se_2 four-membered ring,¹⁴ in which the gold has an oxidation state of +III while the selenium can be formally regarded as -II (selenide).

In order to investigate the halogenation products, the gold(I) complexes were treated with the corresponding halogen in dichloromethane. Various types of products were observed, which seem to depend on the steric requirements of the ligand.

For dppmSeAuBr, the halogenation product could not be identified. The other dppmS and dppmSe complexes react with two mole equivalents of halogen X_2 , whereby gold(I) is oxidised to gold(III) with concomitant ring closure involving the formation of an Au–E bond, leading to the products dppmEAu $X_2^+ X_3^-$ (**2a–c**; Scheme 2, Fig. 2), which are not isostructural. Such five-membered auracycles are known for Au(I) (see above) but not for Au(III).



Scheme 2 Halogenation of (dppmE)AuX with E = S, X = Br (a); E = S, X = I (b) and E = Se, X = I (c).

Halogenation of the (dppbzSe)gold(I) complexes caused separation of elemental selenium and led to the gold(III) compounds dppbzAuI₂⁺I₃⁻⁷ and dppbzAuBr₃.¹⁵ The bromogold(I) derivative of dppbzS, in contrast, is oxidized by two mole equivalents of bromine to the mixed bromide/tetrabromoaurate salt of an unusual heterocyclic dication, formally (1,1,3,3)tetraphenylbenzo[d]-(2,1,3)thiadiphosphol-1,3-diium, analogous to the as yet unknown acyclic species [Ph₃P-S-PPh₃]²⁺ (Scheme 3).



Scheme 3 Bromination of (dppbzS)AuBr.



Fig. 2 Crystal structure of 2a (H atoms omitted). Selected bond lengths [Å] and angles [°]: P1–S 2.048(2), P2–Au 2.307(2), S–Au 2.330(2), Au–Br1 2.458(1), Au–Br2 2.429(1); P1–S–Au 103.86(6), P2–Au–S 94.19(5), P2–Au–Br2 88.53(4), Br2–Au–Br1 92.18(2), Br1–Au–S 85.07(4).

The 31 P-NMR spectrum of the gold(I) complex shows two doublets at 44.5 and 26.8 ppm with a coupling of 17 Hz, whereas for **3** a singlet at 50.2 ppm is observed.

The structure of **3** was determined by X-ray analysis (Fig. 3). It crystallizes in the triclinic space group $P\bar{1}$; within the asymmetric unit are two independent dications, two bromide anions, each coordinating to one of the dications, together with two tetrabromoaurate(III) anions and one dichloromethane molecule. Two equivalent dications are bridged by two bromide anions coordinating weakly to the sulphur atoms to complete a fourmembered S_2Br_2 ring with $S \cdots Br 3.108(4)$ Å.



Fig. 3 Crystal structure of one inversion-symmetric $[(dppbzS)_2Br_2]^{2+}$ unit in 3 (H atoms omitted). Selected bond lengths [Å] and angles [°]: P1–S1 2.121(4), P2–S1 2.114(4), S1…Br1 3.108(4), S1…Br1' 3.108(4); P1–S1–P2 95.90(17), Br1…S1…Br1' 101.95(9), P1–S1…Br1' 84.73(14), P2–S1…Br1 77.35(13), S1…Br1…S1' 78.05(9).

Bromination of the known gold(I) complexes $Ph_3PEAuBr^1$ led to tetrabromoaurate salts **4a** and **4b** of (bromochalcogeno)phosphonium cations (Scheme 4), which show a downfield shift in the ³¹P-NMR spectrum in comparison to the gold(I) complexes; **4a** shows a singlet at 49.4 ppm and **4b** a

Ph₃PEAuBr $\xrightarrow{2 \text{ Br}_2}$ Ph₃PEBr $\xrightarrow{\oplus}$ AuBr $\xrightarrow{\oplus}$ 4a,b

Scheme 4 Halogenation of $Ph_3PEAuBr$ with E = S(a) and E = Se(b).

singlet at 52.3 ppm. The values for the gold(1) complexes are 49.4 and 30.0, respectively.

The structures of **4a** and **4b**, which are not isostructural, were determined by X-ray analysis. Ph₃PSeBr⁺ AuBr₄⁻ (**4b**) crystallizes in the triclinic space group $P\overline{1}$ with one cation and two half anions in the asymmetric unit. The Se–Br bond length is 2.3121(4) Å and the Br \cdots Br contact between cation and anion is 3.4009(5) Å. Compound **4b** represents the first successful isolation and structure determination of an R₃PSeBr⁺ cation.

For phosphane sulfides, which are weaker donors than the selenides towards dihalogen molecules, no such adducts are known so far. The crystal structure of the Ph₃PSBr⁺ AuBr₄⁻ salt **4a**, shown in Fig. 4, is the first crystal structure of any species with a P–S–Br unit, according to the Cambridge Structural Database (2010 version). It crystallizes in the monoclinic space group $P2_1/n$ with one formula unit in the asymmetric unit. The Br \cdots Br contact of 3.151(1) Å is very short and is comparable with the value of 3.123(2) Å in the adduct Ph₃PBr₂.¹⁶



Fig. 4 Crystal structure of $Ph_3PSBr^+AuBr_4^-$ (H atoms omitted). Selected bond lengths [Å] and angles [°]: P–S 2.085(2), Br1–S 2.202(2), Br1··· Br2 3.151(1); P–S–Br1 101.31(6), S–Br1··· Br2 174.79(4), Br1··· Br2–Au 99.41(2).

More gold(I) complexes with various mono- and diphosphine chalcogenide ligands are currently being synthesised with a view to investigating their halogenation products; studies on gold complexes with diphosphane dichalcogenide ligands are in progress.

Notes and references

‡ **X-Ray structure determinations**: Data were collected at 100 K on an Oxford Diffraction Xcalibur E diffractometer using monochromated Mo-Kα radiation. Structures were refined using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany).

Crystal data for 1: $C_{74}H_{58}Au_2Cl_{20}P_4Se_2$, M = 2331.94, triclinic, a = 9.974(2)Å, b = 13.760(3) Å, c = 15.679(3) Å, $\alpha = 95.70(3)^\circ$, $\beta = 97.32(3)^\circ$, $\gamma = 95.08(3)^\circ$, V = 2112.5(7) Å³, T = 100 K, space group $P\overline{1}$, Z = 1, 68021 reflections measured, 7450 independent reflections ($R_{int} = 0.186$). The final w R_2 value was 0.1695 (all data), with R_1 0.0687 ($I > 2\sigma(I)$).

Crystal data for **2a**: C₂₅H₂₂AuBr₅P₂S, M = 1012.94, monoclinic, a = 10.3072(6) Å, b = 13.378(2) Å, c = 21.0032(16) Å, $\beta = 91.302(7)^{\circ}$, V = 2895.4(5) Å³, T = 100 K, space group $P2_1/c$, Z = 4, 44975 reflections measured, 5293 independent reflections ($R_{int} = 0.089$). The final w R_2 value was 0.0300 (all data), with R_1 0.0256 ($I > 2\sigma(I)$).

Crystal data for **2b**: C₂₅H₂₂AuI₅P₂S, M = 1247.89, orthorhombic, a = 10.4495(5) Å, b = 14.0201(3) Å, c = 21.6335(5) Å, V = 3169.37(18) Å³, T = 100(2)K, space group $P2_12_12_1$, Z = 4, 80673 reflections measured, 7552 independent reflections ($R_{int} = 0.056$). The final w R_2 value was 0.0425 (all data), with R_1 0.0238 ($I > 2\sigma(I)$).

Crystal data for **2c**: $C_{25}H_{22}AuI_5P_2Se$, M = 1294.79, orthorhombic, a = 21.931(2) Å, b = 10.4353(10) Å, c = 13.7270(8) Å, V = 3141.5(5) Å³, T = 100 K, space group *Pna2*₁, Z = 4, 42845 reflections measured, 5548 independent reflections ($R_{int} = 0.157$). The final w R_2 value was 0.0490 (all data), with R_1 0.0391 ($I > 2\sigma(I)$).

Crystal data for 3: $C_{30.5}H_{25}AuBr_5ClP_2S$, M = 1117.47, triclinic, a = 14.948(2) Å, b = 16.397(3) Å, c = 16.986(3) Å, $\alpha = 117.927(15)^\circ$, $\beta = 94.835(12)^\circ$, $\gamma = 108.542(15)^\circ$, V = 3349.6(10) Å³, T = 100 K, space group $P\bar{1}, Z = 4,94741$ reflections measured, 11848 independent reflections ($R_{int} = 0.204$). The final w R_2 value was 0.0726 (all data), with R_1 0.0467 ($I > 2\sigma(I)$).

Crystal data for **4a**: $C_{18}H_{15}AuBr_5PS$, M = 890.85, monoclinic, a = 13.7340(4) Å, b = 12.2533(2) Å, c = 14.9748(4) Å, $\beta = 114.913(5)^{\circ}$, V = 2285.56(10) Å³, T = 100 K, space group $P2_1/n$, Z = 4, 58880 reflections measured, 4661 independent reflections ($R_{int} = 0.045$). The final w R_2 value was 0.0462 (all data), with R_1 0.0221 ($I > 2\sigma(I)$).

Crystal data for **4b**: $C_{18}H_{15}AuBr_5PSe$, M = 937.75, triclinic, a = 8.7461(4)Å, b = 9.4386(5)Å, c = 16.4508(7)Å, $\alpha = 84.594(4)^\circ$, $\beta = 76.871(4)^\circ$, $\gamma = 62.835(5)^\circ$, V = 1176.58(10)Å³, T = 100 K, space group $P\overline{1}$, Z = 2, 86646 reflections measured, 6278 independent reflections ($R_{int} = 0.039$). The final w R_2 value was 0.0348 (all data), with R_1 0.0170 ($I > 2\sigma(I)$).

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