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Two-, Three-, and Four-Coordination at Gold(I) Supported by the Bidentate Selenium Ligand $[Ph_2P(Se)NP(Se)Ph_2]^-$

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Treatment of the gold(I) halide complexes LAuCl (L = PMe_3, PPh_3, $CNC_6H_3Me_2$-2,6) with $K[Ph_2P(Se)NP(Se)Ph_2]$ provides the gold−selenium coordination compounds [{$N(Ph_2PSe)_2$-*Se,Se′*}AuL]. However, on standing for a number of days, the complex [{$N(Ph_2PSe)_2$-*Se,Se′*}$AuPMe_3$] gains a phosphine to provide the bis(phosphine) species [{$N(Ph_2PSe)_2$-*Se,Se′*}$Au(PMe_3)_2$]. Treatment of the $K[Ph_2P(Se)NP(Se)Ph_2]$ ligand with $[(Ph_3PAu)_3O]BF_4$ allows the isolation of [{$N(Ph_2PSe)_2$-*Se,Se′*}$(AuPPh_3)_2]BF_4$. Reaction of the complex $[(dppm)(AuCl)_2]$ with $AgSO_3CF_3$ followed by addition of the ligand $K[Ph_2P(Se)NP(Se)Ph_2]$ results in the formation of [{$N(Ph_2PSe)_2$-*Se,Se′*}$Au_2(dppm)]OSO_2CF_3$ and treatment of [(tht)AuCl] (tht = tetrahydrothiophene) with an equimolar quantity of $K[Ph_2P(Se)NP(Se)Ph_2]$ affords the complex [{$N(Ph_2PSe)_2$-*Se,Se′*}$_2Au_2$]. The compounds [{$N(Ph_2PSe)_2$-*Se,Se′*}$Au_2(dppm)]OSO_2CF_3$, [{$N(Ph_2PSe)_2$-*Se,Se′*}$AuPPh_3$] and [{$N(Ph_2PSe)_2$-*Se,Se′*}$Au(PMe_3)_2$] have been investigated crystallographically. The results reveal that the metal centers are two-, three-, and four-coordinate, respectively. The cationic, eight-membered ring complex bearing the dppm ligand displays transannular aurophilic bonding and is further associated into dimers via intermolecular gold−selenium contacts. The six-membered rings in the other two structures have C_2-symmetrical twist conformations, however, the Au(I) coordination sphere in $[N(PPh_2Se)_2]AuPPh_3$ is not fully symmetrical. The Au−Se bond lengths increase dramatically as the coordination number of the metal atom becomes larger.

Introduction

Gold metal has a remarkable affinity for the heavy chalcogen elements.[1] This is particularly true for tellurium and leads to the phenomenon that, next to gold and its alloys, gold tellurides are the only binary gold minerals found in nature. The gold−selenium solid-state chemistry is also rich in binary and polynary systems[2] which are of interest in the context of interfaces between gold metal and gold alloys and II/VI or I/III/VI semiconductors.

Another topical area of gold−selenium chemistry is the use of gold chalcogen compounds in chemotherapy.[3]

Though by no means as developed as the corresponding sulfur chemistry, gold(I) compounds of selenium have therefore received some recent attention. Probably due to the lack of commercially available selenol compounds, the number of known selenolate complexes grew slowly. A triethylphosphinegold(I) complex of a glucose residue reminiscent of auranofin[4] was patented in 1983 but it was only later that the complexes $[(Ph_3P)AuSeR]$ (R = organyl), $[(dppm)(AuSePh)_2]$ were reported.[5] As part of a study of pseudohalide ligands, the selenocyanate analogues $[(Ph_3P)AuSeCN]$ and $[(dppm)(AuSeCN)_2]$ were prepared in 1971.[6] A gold(I) complex bearing the biorelevant 1-selenoglucose ligand has also been synthesized[7] as have complexes of the selenium homologue of urea.[8,9]

The dinuclear species $[(Ph_3PAu)_2SePh]SbF_6$[5] and $[(Ph_3PAu)_2Se]$[9] were reported at the beginning of the past decade and the latter has recently proved to be an excellent precursor for the preparation of aurated hypervalent selenium compounds. Though the complexes $[(Ph_3PAu)_3Se]Cl$[10] and $[(Ph_3PAu)_4Se](OTf)_2$[11] had previously been prepared using other methods, the complex $[(Ph_3PAu)_2Se]$ provided routes to all members of the homoleptic series $[(Ph_3PAu)_nSe](OTf)_{n-2}$ ($n = 3-6$).[12] This work also incorporated the use of a bisphosphine precursor $[(dppf)Au_2]Se$, as well as theoretical calculations on the species prepared.

Phosphineselenide ligands have been used to ligate gold in a number of examples of the form $[Ph_3PSeAuR]$ (R = organyl),[13,14] $[(Ph_3PSe)Au(PPh_3)]SbF_6$ and $[(Ph_3PSe)_2Au]SbF_6$.[15] The

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asymmetric ligand dppmSe has also been employed to form a structurally characterized 10-membered ring system [(dppmSe)-Au_2]ClO_4[16] and as a supporting ligand for investigations into nonconventional hydrogen-bonding systems.[17]

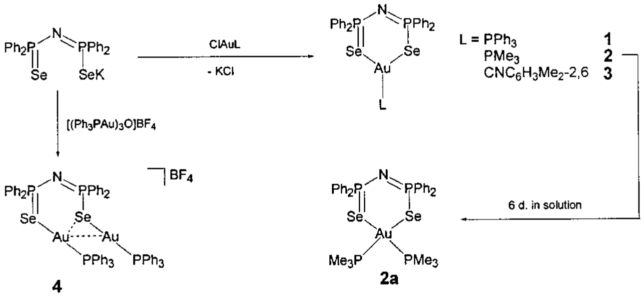
A number of selenium-bound, heteroleptic gold complexes have been prepared using the mixed chalcogen ligand, 4,5-diselenolate-1,3-dithiole-2-thione (dsit) such as the cyclic example [(dsit)Au_2(dppm)]. Interestingly, the use of a zinc complex (NBu_4)[Zn(dsit)] as ligand transfer agent was found to be favorable to direct addition of the selenium ligand.[18]

The versatility of the dichalcogenoimidodiphosphinato anions [$R_2P(E)NP(E)R_2$]$^-$ as ligands remained largely neglected for many years after their synthesis by Schmidpeter in the 1960s.[19] Recently, interest has been renewed in their coordination abilities and they have found use in a number of diverse areas such as catalysis,[20] NMR shift reagents,[21] and selective metal extractants.[22] Ligands with mixed chalcogen donors [$R_2P(O)NP(E)R_2$]$^-$ (E = S, Se) have also been prepared.[23] The preparation by Woollins and co-workers of the selenium analogue[24] in 1995 has led to a sizable number of metal diselenoimidodiphosphinate complexes being reported.[24,25]

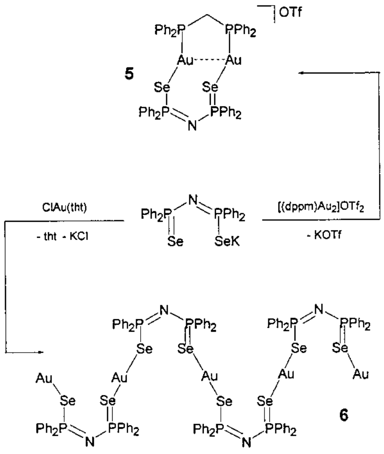
Gold has been shown to readily coordinate selenium species in accordance with its "soft" nature and this potential was touched upon in a recent report concerning the [$R_2P(Se)NP(Se)R_2$]$^-$ ligand.[26]

As part of an ongoing study of the coordination of sulfur and selenium ligands at gold(I) centers, we present here an investigation into the coordination chemistry of the diselenoimidodiphosphinate anion as a ligand for gold(I) mono- and bisphosphine complexes. Compounds of the formula [{N($Ph_2PSe)_2$-*Se,Se′*}AuL] (L = PPh_3, **1**; PMe_3, **2**) were prepared along with an isonitrile gold diselenoimidodiphosphinate species [{N($Ph_2PSe)_2$-*Se,Se′*}AuCN$C_6H_3Me_2$-2,6] (**3**) which was intended to provide a phosphine-free example for comparison but proved highly insoluble in common laboratory solvents. The oxonium compound [($Ph_3PAu)_3O$]BF_4 was found to react with K[$Ph_2P(Se)NP(Se)Ph_2$] to provide the cationic complex [{N($Ph_2PSe)_2$-*Se,Se′*}($AuPPh_3)_2$]BF_4 (**4**). To investigate the possibility of ring formation, two bimetallic examples were prepared. The complex [{N($Ph_2PSe)_2$-*Se,Se′*}Au_2(dppm)]OSO_2CF_3 (**5**) yielded suitable crystals for an X-ray diffraction study that confirmed its cyclic nature. The second example [{N($Ph_2PSe)_2$-*Se,Se′*}$_2Au_2$] (**6**), free of auxiliary ligands, however, proved insoluble, probably due to the formation of a polymeric structure (Scheme 2). The structural studies reveal that the gold center in the [{N($Ph_2PSe)_2$-*Se,Se′*}AuL] complexes [L = PPh_3 (**1**); ($PMe_3)_2$ (**2a**)] is able to display different coordination numbers (3 or 4) depending on the phosphine present. The ability of gold(I) to show higher coordination numbers than that found in the usual linear species has been the subject of a recent review.[27] Probably owing to steric crowding, no aurophilic interactions are observed in complexes **1** and **2a**, in contrast to the cyclic species [{N($Ph_2PSe)_2$-*Se,Se′*}Au_2(dppm)]OSO_2CF_3 (**5**) which has a transannular gold−gold contact of 3.2687(4) Å and exhibits intermolecular gold−selenium contacts.

Scheme 1



Scheme 2



Experimental Section

General Information. The experiments were carried out routinely in air. NMR: JEOL GX 400 spectrometer using deuterated solvents with the usual standards at 25°C. MS: Varian MAT311A instrument (FAB, *p*-nitrobenzyl alcohol). The complexes [LAuCl] (L = PMe_3, PPh_3),[28] [(dppm)($AuCl)_2$],[28] [(2,6-$C_6H_3Me_2NC$)AuCl],[29] and [($Ph_3PAu)_3O$]BF_4[30] and the ligand K[$Ph_2P(Se)NP(Se)Ph_2$][24] were prepared following literature procedures.

[{N($Ph_2PSe)_2$-*Se,Se′*}$AuPPh_3$] (1). An acetone solution (5 mL) of K[$Ph_2P(Se)NP(Se)Ph_2$] (59 mg, 0.10 mmol) was added dropwise to a

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Table 1. Crystal Data, Data Collection, and Structure Refinement of Compounds **1**, **2a**, and **5**

	1	**2a**	**5**·CH_2Cl_2
empirical formula	$C_{42}H_{35}AuNP_3Se_2$	$C_{30}H_{38}AuNP_4Se_2$	$C_{51}H_{44}Au_2Cl_2F_3NO_3P_4SSe_2$
M	1001.51	891.38	1554.57
crystal system	Triclinic	Orthorhombic	Triclinic
space group	$P\bar{1}$	*F*dd2	$P\bar{1}$
a/Å	9.0980(1)	21.5152(2)	11.3563(4)
b/Å	12.0153(2)	31.0765(6)	15.2646(4)
c/Å	18.6794(3)	9.5041(1)	15.5717(5)
α/deg	77.791(1)	90	108.839(1)
β/deg	79.768(1)	90	91.216(1)
γ/deg	74.661(1)	90	90.904(1)
U/Å^3	1908.64(5)	6354.6(2)	2575.8(1)
ρ_{calc}/g cm^{-3}	1.743	1.863	2.004
Z	2	8	2
μ(Mo Kα)/cm^{-1}	59.18	71.44	74.23
T/K	193	143	143
unique reflections	11619	1701	9723
refined parameters	442	173	622
R1 [$I > 2\sigma(I)$]	0.0409	0.0217	0.0449
wR2	0.0809	0.0556	0.0948
weighting scheme[a]	a = 0.0177	*a* = 0.0065	*a* = 0.0353
	b = 7.60	*b* = 111.32	*b* = 11.28
σ_{fin}(max/min)/eÅ^{-3}	0.873/−1.935	0.825/−1.768	1.672/−1.628

[a] wR2= $\{[\sum w(F_o2 - F_c2)^2]/\sum[w(F_o2)^2]\}^{1/2}$; w = $1/[\sigma^2(F_o2) + (ap)^2 + bp]$; $p = (F_o2 + 2F_c2)/3$.

stirred solution of [Ph_3PAuCl] (50 mg, 0.10 mmol) in dichloromethane (15 mL). After stirring for 2 h, all solvent was removed and the crude product dissolved in dichloromethane (20 mL) and filtered through diatomaceous earth to remove KCl. After concentration of the solution to ca. 10 mL, pentane (20 mL) was carefully added to precipitate a colorless solid. This was washed with pentane (20 mL) and dried. Yield: 79% (80 mg). MS (FAB) *m*/*e* = 1001, 11% [M]$^+$. ^{31}P NMR (CD_2Cl_2): 25.4 (s, PPh_2, J_{PSe} = 570.2 Hz), 37.5 (s, PPh_3) ppm. ^{1}H NMR (CD_2Cl_2): 7.39, 7.97 (m × 2, 35 H, C_6H_5) ppm. Anal. Calcd for $C_{42}H_{35}AuNP_3Se_2$: C, 50.32; H, 3.62; N, 1.40%. Found: C, 50.28; H, 3.43; N, 1.28%.

[{N(Ph_2PSe)$_2$-*Se,Se′*}AuPMe$_3$] (2). An acetone solution (5 mL) of K[$Ph_2P(Se)NP(Se)Ph_2$] (94 mg, 0.16 mmol) was added dropwise to a stirred solution of [Me_3PAuCl] (50 mg, 0.16 mmol) in dichloromethane (15 mL). After stirring for 2 h, all solvent was removed and the crude product dissolved in dichloromethane (20 mL) and filtered through diatomaceous earth to remove KCl. After concentration of the solution to ca. 10 mL, pentane (20 mL) was carefully added to precipitate a colorless solid. This was washed with pentane (20 mL) and dried. Yield: 80% (105 mg). MS (FAB) *m*/*e* = 817, 8% [M]$^+$, 273, 7% [$AuPMe_3$]$^+$. ^{31}P NMR (CD_2Cl_2): −6.3 (s, PMe_3), 26.3 (s, PPh_2, J_{PSe} = 589.0 Hz) ppm. ^{1}H NMR (CD_2Cl_2): 1.39 (d, 9 H, CH_3, J_{HP} = 1.49 Hz), 7.37, 7.97, 8.02 (m × 3, 20 H, C_6H_5) ppm. Anal. Calcd for $C_{27}H_{29}AuNP_3Se_2$: C, 39.77; H, 3.59; N, 1.72%. Found: C, 39.92; H, 3.82; N, 1.69%.

[{N(Ph_2PSe)$_2$-*Se,Se′*}Au(CNC$_6$H$_3$Me$_2$-2,6)] (3). An acetone solution (5 mL) of K[$Ph_2P(Se)NP(Se)Ph_2$] (80 mg, 0.14 mmol) was added dropwise to a stirred solution of [(2,6-$Me_2C_6H_3NC$)AuCl] (50 mg, 0.14 mmol) in dichloromethane (15 mL) causing immediate precipitation of a colorless product. After stirring for 2 h, all solvent was removed and the crude material washed with water (30 mL) and filtered. The colorless product was washed with pentane (20 mL) and dried. Yield: 59% (71 mg). MS (FAB) *m*/*e* = 740, 2% [M − $CNC_6H_3Me_2$]$^+$. IR (Nujol/KBr plates): 2147 [ν(CN)] cm^{-1}. NMR: Due to insolubility in all available deuterated solvents, no NMR data could be obtained. Anal. Calcd for $C_{33}H_{29}AuN_2P_2Se_2.2CH_2Cl_2$: C, 40.41; H, 3.20; N, 2.69%. Found: C, 40.68; H, 2.81; N, 2.18%.

[{N(Ph_2PSe)$_2$-*Se,Se′*}(AuPPh$_3$)$_2$]BF$_4$ (4). A dichloromethane (20 mL) solution of [(Ph_3PAu)$_3$O]BF_4 (100 mg, 0.068 mmol), K[$Ph_2P(Se)NP(Se)Ph_2$] (59 mg, 0.102 mmol) and $NaBF_4$ (8 mg, 0.073 mmol) were stirred for 2 h. The solution was filtered through diatomaceous earth and the solvent volume of the filtrate reduced to ca. 5 mL. Diethyl ether was then added to precipitate the colorless product which was filtered, washed with diethyl ether (10 mL) and dried. Yield: 65% (102 mg). The product was recrystallized from chloroform/diethyl ether. MS (FAB) *m*/*e* = 1462, 58% [M]$^+$; 1199, 16% [M − PPh_3]$^+$; 721, 57% [Au(PPh_3)$_2$]$^+$; 460, 100% [$AuPPh_3$]$^+$. ^{31}P NMR (CD_2Cl_2): 24.7 (s, PSe, J_{PSe} = 503.0 Hz), 35.3 (s, PPh_3) ppm. ^{1}H NMR (CD_2Cl_2): 7.55, 8.16 (m × 2, 50 H, C_6H_5) ppm. Anal. Calcd for $C_{60}H_{50}Au_2BF_4NP_4Se_2.2CHCl_3$: C, 41.69; H, 2.93; N, 0.78%. Found: C, 41.62; H, 2.91; N, 0.73%.

[{N(Ph_2PSe)$_2$-*Se,Se′*}Au$_2$(dppm)]OSO$_2$CF$_3$ (5). An ice-cooled tetrahydrofuran solution (5 mL) of $AgOSO_2CF_3$ (61 mg, 0.24 mmol) was added dropwise to a stirred tetrahydrofuran solution (10 mL) of (dppm)(AuCl)$_2$ (100 mg, 0.12 mmol) at 0°C. After 45 min. stirring, this suspension was filtered into a solution of K[$Ph_2P(Se)NP(Se)Ph_2$] (68 mg, 0.12 mmol) in tetrahydrofuran (5 mL), also at 0°C. The reaction was stirred for 2 h and methanol added (15 mL). Reduction in solvent volume caused the precipitation of a colorless solid. This was filtered, washed with methanol (10 mL), pentane (10 mL) and dried. Yield: 70% (120 mg). MS (FAB) *m*/*e* = 1326, 86% [M + 4H]$^+$; 939, 7% [M − (dppm)]$^+$; 778, 2% [M − (N(Ph_2PSe)$_2$]$^+$. ^{31}P NMR (CD_2Cl_2): 24.4 (s, PSe, J_{PSe} = 499.0 Hz), 33.2 (s, dppm) ppm. ^{1}H NMR (CD_2Cl_2): 3.43 (t, 2 H, CH_2, J_{HP} = 11.25 Hz) 7.25, 7.41, 7.83 (m × 3, 40 H, C_6H_5) ppm. Anal. Calcd for $C_{50}H_{42}Au_2F_3NO_3P_4SSe_2$: C, 40.86; H, 2.88; N, 0.95%. Found: C, 40.45; H, 2.73; N, 0.77%.

[{N(Ph_2PSe)$_2$-*Se,Se′*}$_2$Au$_2$] (6). An acetone solution (5 mL) of K[$Ph_2P(Se)NP(Se)Ph_2$] (91 mg, 0.16 mmol) was added dropwise to a stirred solution of [(tht)AuCl] (50 mg, 0.16 mmol) in dichloromethane (15 mL) causing immediate precipitation of a colorless product. After stirring for 2 h, all solvent was removed and the crude material washed with water (30 mL) and filtered. The colorless product was washed with water (20 mL) and pentane (20 mL) and dried. Yield: 69% (80 mg). NMR: Due to insolubility in all available deuterated solvents, no NMR data could be obtained. Anal. Calcd for $C_{48}H_{40}Au_2N_2P_4Se_4.CH_2Cl_2$: C, 37.64; H, 2.71; N, 1.79%. Found: C, 37.35; H, 2.79; N, 1.66%.

X-ray Crystallography. Specimens of suitable quality and size of compounds **1**, **2a**, and **5** were mounted on the ends of quartz fibers in F06206R oil and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo Kα radiation. The structures were solved by a combination of direct methods (SHELXS-97) and difference Fourier syntheses and refined by full matrix least-squares calculations on F^2 (SHELXL-97). The thermal motion was treated anisotropically for all non-hydrogen atoms. All hydrogen atoms were calculated and allowed to ride on their parent atoms with fixed isotropic contributions. Further information on crystal data, data collection and structure refinement are summarized in Table 1. Important interatomic distances and angles are shown in the corresponding Figure Captions.

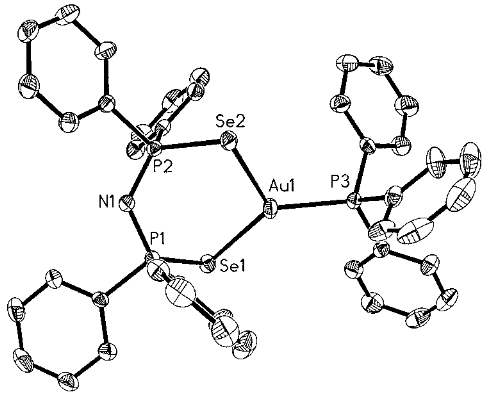

Figure 1. Molecular structure of compound **1** (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: Au1−P3 2.2786(9), Au1−Se1 2.5271(4), Au1−Se2 2.6341(4), Se1−P1 2.1768(9), Se2−P2 2.169(1), P1−N1 1.600(3); P2−N1 1.596(3); P3−Au1−Se1 133.06(3), P3−Au1−Se2 114.24(3), Se2−Au1−Se1 112.69(1), Au1−Se1−P1 92.84(3), Se1−P1−N1 117.9(1), P1−N1−P2 128.2(2), N1−P2−Se2 117.4(1), P2−Se2−Au1 93.79(3).

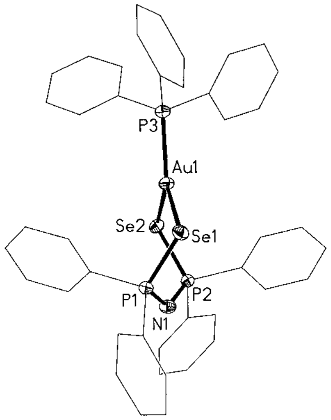

Figure 2. Side-on view of compound **1** showing twisted conformation.

Synthesis and Characterization of Complexes. Addition of an acetone solution of K[$Ph_2P(Se)NP(Se)Ph_2$] to dichloromethane solutions of the gold(I) halide complexes [LAuCl] (L = PMe_3, PPh_3, CNC_6H_3-Me_2-2,6) provided the target complexes [{N($SePPh_2$)$_2$-*Se*,*Se′*}AuL] as crystalline products in good yield (Scheme 1). In addition to a singlet at 37.5 ppm in the ^{31}P NMR spectrum for the triphenylphosphine group, the presence of the selenium ligand in the complex [{N(Ph_2PSe)$_2$-*Se*,*Se′*}$AuPPh_3$] (**1**) was confirmed by a resonance at 25.4 ppm showing a ^{31}P-^{77}Se coupling of 570 Hz. Similarly, the trimethylphosphine analogue [{N(Ph_2PSe)$_2$-*Se*,*Se′*}$AuPMe_3$] (**2**) gave rise to resonances at 26.3 (J_{PSe} = 589 Hz) and −6.3 ppm. The molecular mass pattern of the ion observed for **2** at *m*/*e* = 817 in the FAB mass spectrum corresponded well to the calculated isotopic distribution. The xylylisonitrile species [{N(Ph_2PSe)$_2$-*Se*,*Se′*}Au($CNC_6H_3Me_2$-2,6)] (**3**) proved to be insufficiently soluble in common laboratory solvents to allow a spectroscopic investigation but its composition was confirmed by elemental analysis and FAB mass spectrometry. The isonitrile ligand gave rise to a ν(CN) absorption at 2147 cm^{-1} in the solid-state infrared spectrum.

Single crystals of **1** were grown from a dichloromethane/diethyl ether mixture and were found to be suitable for a structural study (Figures 1 and 2). The same crystallization process for complex **2** took considerably longer (6 days) and yielded smaller single crystals. One of these was used for a structural analysis which surprisingly revealed a four-coordinate, bis(trimethylphosphine)gold center (complex **2a**) shown in Figures 3 and 4. The partial conversion to **2a** is thought to arise from a slow dissociation process in **2** to provide the additional phosphine ligand. A dichloromethane solution of **2**, stirred for a week, also yields this bis(phosphine) species **2a** in small amounts.

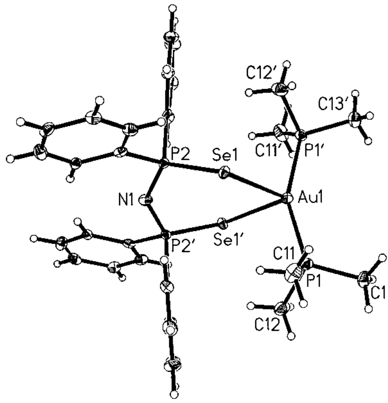

Figure 3. Molecular structure of compound **2a** (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: Au1−P1/P1′ 2.333(2), Au1−Se1/Se1′ 2.9230(7), Se1−P2 2.122(2), P2−N1 1.600(4); P1−Au1−P1′ 153.5(1), P1−Au1−Se1 96.16(5), P1′-Au1-Se1 102.05(5), Se1−Au1−Se1′ 92.90(3), Au1−Se1−P2 108.88(5), Se1−P2−N1 120.6(3), P2−N1−P2′ 135.0(7).

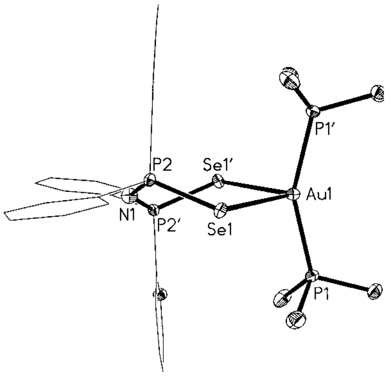

Figure 4. Side-on view of compound **2a** showing twisted conformation.

Treatment of the K[$Ph_2P(Se)NP(Se)Ph_2$] ligand with the oxonium species [$(Ph_3PAu)_3O$]BF_4 results in the isolation of [{N(Ph_2PSe)$_2$-*Se*,*Se′*}($AuPPh_3$)$_2$]BF_4 (**4**) in good yield (Scheme 1). A strong (58%) molecular ion is observed at *m*/*e* = 1462 in the FAB mass spectrum for the cation in addition to diagnostic fragmentation of phosphine (*m*/*e* = 1199) and a gold-phosphine unit (*m*/*e* = 721).

In situ preparation of the complex [(dppm)($AuOSO_2CF_3$)$_2$] at low temperature from [(dppm)$(AuCl)_2$] and 2 equiv of $AgOSO_2CF_3$ was followed by addition of K[$Ph_2P(Se)NP(Se)Ph_2$]. The resulting crystalline product [{N(Ph_2PSe)$_2$-*Se*,*Se′*}Au_2(dppm)]OSO_2CF_3 (**5**) shown in Scheme 2, gave rise to two resonances in the ^{31}P NMR spectrum at 24.4 and 33.2 ppm, the former displaying a J_{PSe} coupling of 499 Hz. A structural study was undertaken and demonstrated that the complex formed was indeed cyclic in nature, consisting of an eight-membered ring showing a transannular gold−gold interaction of 3.2687(4) Å (Figures 5−7). It is interesting to note that no ionization takes place to form the homoleptic gold species [$(dppm)_2(Au)_2$]$^{2+}$ and [{N(Ph_2PSe)$_2$-*Se*,*Se′*}$_2Au_2$], a tendency that has often been observed in other cases.[31] The complex [{N(Ph_2PSe)$_2$-*Se*,*Se′*}$_2Au_2$] (**6**) with the same composition as the neutral species above can, however, be prepared by reaction of equimolar quantities of [(tht)AuCl] (tht = tetrahydrothiophene) and K[$Ph_2P(Se)NP(Se)Ph_2$]. The colorless product that precipitated immediately on addition of the ligand, proved insoluble in all common laboratory solvents including hot dimethylformamide. It is likely that it adopts a polymeric structure in the solid state (Scheme 2).

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(31) Bauer, A.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **1997**, 1115. Bauer, A.; Schmidbaur, H. *J. Am. Chem. Soc.* **1996**, *118*, 5324.

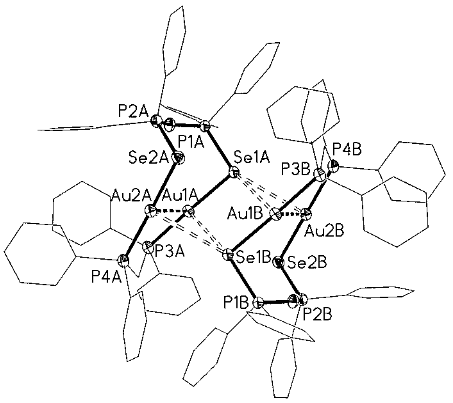

Figure 5. Dimeric units of compound **5** (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Au2B···Se1A 3.447(1), Au1B···Se1A 3.331(1) Å.

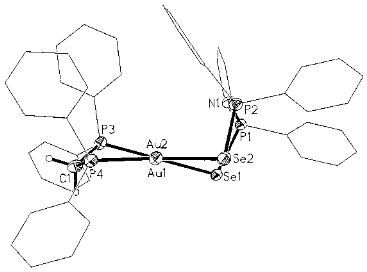

Figure 6. Side-on view along the axis of the two gold atoms for compound **5**.

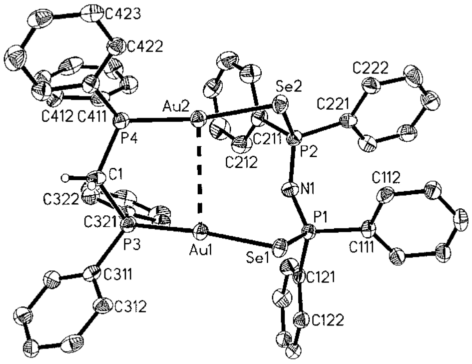

Figure 7. Molecular structure of compound **5** (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: Au1−P3 2.265(2), Au1−Se1 2.4280(7) Au1···Au2 3.2687(4), Au2−P4 2.263(2), Au2−Se2 2.4209(8), Se1−P1 2.201(2), Se2−P2 2.198(2), P1−N1 1.593(6), P2−N1 1.586(6), P3−C1 1.817(7), P4−C1 1.819(8); Se1−Au1−P3 174.71(5), Au1−P3−C1 112.9(2), C1−P4−Au2 113.9(2), P4−Au2−Se2 171.16(5), Au2−Se2−P2 98.22(6), Se2−P2−N1 118.3(2), P2−N1−P1 135.4(4), N1−P1−Se1 116.1(2), P1−Se1−Au1 97.76(5).

The luminescence properties of some of the compounds detailed above are currently under investigation.

Crystal and Molecular Structures

Crystals of complex **1** are triclinic, of space group $P\bar{1}$, with $Z = 2$ molecules related by a center of inversion in the unit cell. The individual molecule has no crystallographically imposed symmetry but, neglecting the orientation of the phenyl groups, the geometry of the skeleton approaches quite closely the requirements of point group C_2 (Figure 1). The quasi-2-fold axis passes through the atoms N, Au1, and P3. The six-membered ring is in a twist conformation (Figure 2). The gold atom is planar three-coordinate with a bond angles sum of 359.99°, but the two angles P3−Au1−Se differ quite significantly [P3−Au1−Se1 133.06(3), P3−Au1−Se2 114.24(3)°] as do the two pairs of Au−Se and P−Se bond lengths: Au1−Se1 2.5271(4)/ Au1−Se2 2.6341(4); P1−Se1 2.177(1)/P2−Se2 2.169(1) Å. In the structure of the analogous sulfur complex [{$N(Ph_2PS)_2$-*S, S′*}$AuPPh_3$], the Au−S distances differ by over 0.6 Å leading to pronounced asymmetry in the six-membered ring.[32] The data for **1** suggest that the bonding between gold and selenium is weaker for Se2 than for Se1. By contrast the two endocyclic angles N−P−Se are virtually identical [N1−P1−Se1 117.9(1)°, N1−P2−Se2 117.5(1)°] and the bond lengths N1−P1 1.600(3)/N1−P2 1.596(3) Å [at an angle P1−N1−P2 128.3(2)°] are almost equidistant, showing that the phosphazene unit of the bidentate ligand remains highly symmetrical in its complex (**1**). It should be noted that these results are in agreement with data published for a compound where the Ph_3P ligand is replaced by $Ph_2PNHP(O)Ph_2$.[26] The distortions at the three-coordinate gold atom in this reference molecule are even greater, but this may be caused by an extensive hydrogen-bonding network and by a different boatlike conformation of the six-membered ring.

Crystals of complex **2a** are orthorhombic, in space group *Fdd*2, with $Z = 8$ molecules in the unit cell. The crystallographically imposed symmetry of the individual molecules calls for a 2-fold axis passing through the atoms N1 and Au1 (Figure 3). The six-membered ring has a twist conformation (Figure 4) as encountered already for complex **1**. The gold atom has a coordination number of 4, however the geometry deviates very strongly from the idealized tetrahedral symmetry. This is most obvious from the large angle P1−Au1−P1′ 153.5(1)° which is closer to 180° than to the 109° required for an undistorted tetrahedron. The complex can therefore be described as a combination of the linear $[(Me_3P)_2Au]^+$ cation and the bidentate $[N(PPh_2Se)_2]^-$ anion in which the approach of the latter causes the distortion of the former. In this context it should be noted that the two Au−Se contacts [2.9230(7) Å] are much longer (in excess of 10%) than those in complex **1** indicating much weaker interactions in **2a**.

It is not surprising that the P−Se bond lengths are shorter [2.122(2) Å] for **2a** than for **1**, and that all endocyclic angles are larger: P2−N1−P2′ 135.0(7), N1−P2−Se1 120.6(3)°. The "natural" bite angle of the open phosphazene ligand is therefore largely unaffected by the metal atom.

Crystals of complex **5** containing one molecule of solvent CH_2Cl_2 are triclinic, of space group $P\bar{1}$, with $Z = 2$ formula units in the unit cell. The components are related by a center of inversion. In the lattice, the cations are well separated from the anions and from the solvent molecules, however the cations are arranged in pairs with sub-van der Waals Au−Se contacts (Figure 5). The monocations form eight-membered rings in which a bis(diphenylphosphino)methane (dppm) and an imino-bis(selenodiphenyldiphosphinate) ligand bridge two gold atoms (Figures 6 and 7). The geometry of the ring approaches mirror symmetry with the reference plane passing through N1 and C1. The two gold atoms are two-coordinate, but the angles Se1−Au1−P3 174.71(5)° and Se2−Au2−P4 171.16(5)° deviate significantly from linearity. The bending of the two angles allows a mutual approach of the two metal atoms to give a transannular Au- -Au equilibrium distance of 3.2687(4) Å representing an aurophilic contact. The two Au−Se distances [Au1−Se1 2.4280(7), Au2−Se2 2.4209(8) Å] are the shortest observed for the three compounds (**1**, **2a** and **5**) and, conversely,

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[32] Haiduc, I.; Fischer, A.; Edelmann, F. T. *Rev. Roum. Chim.* 2000, **44**, 805.

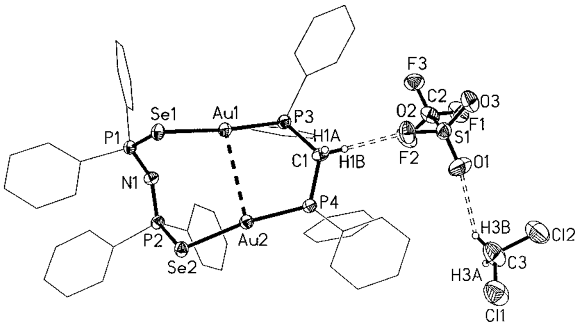

Figure 8. Hydrogen bonding between the cations, anions and solvent molecules in the structure of **$5 \cdot CH_2Cl_2$** (ORTEP drawing with 50% probability ellipsoids, phenyl-*H*-atoms omitted for clarity). C1−H1B···O2: C1−H1B 0.990, H1B···O2 2.272, C1···O2 3.182 Å, C1−H1B···O2 152.2°; C3−H3B···O1: C3−H3B 0.990, H3B···O1 2.485, C3···O1 3.341 Å, C3−H3B···O1 144.5°.

the P−Se distances are the longest [P1−Se1 2.201(2), P2−Se2 2.198(2) Å]. Variations in the endocyclic angles of the diselenide ligand in **5** as compared to **2a** are small. The data for compound **5** are in good agreement with results published for the dication $[\{Ph_2PCH_2P(Se)Ph_2\}_2Au_2]^{2+}$ which also features a strain-free ten-membered ring with transannular aurophilic bonding.[16]

In the tetranuclear dimers of the cations in complex **5**, one of the two selenium atoms (Se1) of each monomer approaches the pair of gold atoms of the neighboring monomer (Figure 5). The two resulting triangles Au1−Au2−Se1′/Au1′−Au2′−Se [with edges of Au1−Au2 3.2687(4), Au1′−Se1 3.331(1) and Au2′−Se1 3.447(1) Å] are again related by inversion symmetry. The long intercationic contacts signify that the bonding forces between the two components are weak.

Two other types of weak interactions were also detected: (a) between the cation and the anion and (b) between the anion and the solvent molecule (Figure 8). One of the two methylene hydrogen atoms of the dppm ligand (H1B) appears to be engaged in a bond to the oxygen atom O2 of the triflate anion [C1−H1B···O2 152.2°; C1−H1B 0.990 Å, O2···H1B 2.272 Å, C1···O2 3.182 Å], while a second oxygen atom of this anion (O1) forms a hydrogen bridge to one of the methylene hydrogen atoms of the dichloromethane molecule [C3−H3B···O1 144.5°; C3−H3B 0.990 Å, O1−H3B 2.485 Å, C3···O1 3.341 Å]. Interactions of this kind have been noted recently by Jones and Ahrens in a number of gold(I) and silver(I) complexes.[17]

Anisotropic thermal parameters and tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDS-167314−167316.

Conclusion

The structural chemistry of the three complexes leads to the conclusion that coordinative bonding of the diselenide ligand to gold(I) strongly depends on the coordination number of the metal atom. With an increase in coordination number of gold(I) from 2 to 4 the Au−Se distances increase drastically. Already in complex **1** with three-coordinate gold atoms, the bonding to the second selenium atom is weaker than to the other, while in complex **2a**, containing a tetracoordinate gold atom, both selenium atoms are attached only very weakly. It is therefore only in complex **5** with two-coordinate gold(I) that Au−Se contacts can attain the optimum conditions for coordinative bonding. In the quasi-linear coordination geometry, the gold atoms can establish closed-shell interactions with Au and Se centers which are virtually absent in species with higher coordination numbers.

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Supporting Information Available: Details of crystal data, data collection, and structure refinement and tables of atomic coordinates, isotropic and anisotropic thermal parameters, and all bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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