Cyclic Dinuclear Gold(I) Complexes: The Crystal Structure of Bis-μ-[(diphenylphosphino)(diphenylphosphinoselenoyl)methane]-digold(I) Bis(perchlorate)

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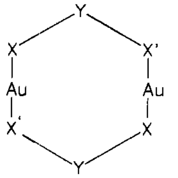
[(CO)AuCl] reacts with equimolar amounts of $Ph_2PCH_2P(Se)Ph_2$ (dpmSe) to afford $ClAuPh_2PCH_2P(Se)Ph_2$, in which dpmSe is bound to gold in a monodentate fashion by phosphorus. Subsequent reaction of this 1:1 complex with $AgClO_4$ results in the formation of the 10-membered ring complex **4** which crystallizes in the monoclinic space group $P2_1/n$ with approximately centrosymmetric dicationic units, in which two gold(I) atoms are doubly bridged by two dpmSe ligands coordinated by phosphorus and selenium. The coordination at the gold atoms deviates from linearity and implies an Au···Au interaction with the gold(I) atoms separated by a distance of 3.020(1) Å.

As evidenced by the number of review articles and monographs published in recent years[1-6], inorganic and organometallic chemistry of gold is an ever expanding area of research. For the purpose of promoting metal nucleation, which is important, for example, in the controlled deposition of gold in micro-electronics and electron microscopy, extensive studies habe been undertaken on dinuclear gold(I) complexes. Initial studies focused on 1,3-difunctional ligands, and several compounds with the 8-membered ring structure **1** have been synthesized.



1

(charges omitted)

X = PPh_2 ; Y = CH[7], CH_2[8], NH[9]
X = PMe_2 ; Y = CH_2[10]
X = CH_2 ; Y = PR_2[11, 12]
X = $CH(PPh_3)$; Y = CO[13]
X = S ; Y = CNR_2[14], $P(OR)_2$[15], COR[16], NR_2[14a], PR_2[14a, 15]
X = S ; X' = PR_2 ; Y = CH_2[17]
X = S ; X' = CH_2 ; Y = PR_2[18a]
X = S ; X' = $CH(PPh_2Me)$; Y = PPh_2[18b]

Short transannular Au···Au contacts are observed in all of these complexes. Weak bonding appears to be operative perpendicular to the linear X–Au–X' axes and can be described as a $5d^{10}$-$5d^{10}$ interaction based on a mixing with the 6s orbitals[19], whose energy is lowered by relativistic effects[20,21]. Many authors, however, have suggested that there are no significant bonding interactions involved as short Au–Au distances are perhaps not surprising for gold atoms constrained by ring geometry and the small bite of the 1,3-difunctional ligands. The frequency of occurrence of short Au–Au distances in various other types of complexes, however, is not consistent with this view.

Clearly, the fixation of metal atoms in close geometrical proximity becomes less favourable as the number of atoms separating the ligand donor atoms increases. A recent report[22] has provided evidence for the existence of an attractive interaction between gold(I) centres based on changes in the conformation of the butadiene skeleton. The *s-trans* ground state geometry of 2,3-bis(diphenylphosphino)-1,3-butadiene is abandoned upon double complexation with AuCl, and the two gold atoms are brought into contact at a distance of 3.023(1) Å. If it is assumed that the *s-trans* to *s-cis* reorientation is caused by Au···Au attraction, the bond energy is estimated to be in the order of 7 kcal/mol. This result is in good agreement with that arrived at for the analogous system with the 1,4-difunctional ligand 1,1'-bis(diphenylphosphino)bicyclopropyl[23]. In the 10-membered ring complex $[Au_2(SCH_2CH_2PEt_2)_2]$ the S–Au–P angle of 173.5° is also adduced as evidence for a Au···Au interaction[17] since the deviation from linearity is such as to bring the metal atoms closer together.

In an effort to further investigate the influence of the weak attractive force between closed-shell (d^{10}-d^{10}) centres on the positioning of substituents bound to the metal atoms, gold(I) complexes with the asymmetric Group 15/Group 16 donor ligand dpmSe $[Ph_2PCH_2P(Se)Ph_2]$ have been synthesized. Despite the existence of naturally occurring mixed Au/Ag selenides[24], very few compounds containing a gold(I)–selenium linkage have been described[25-28] and, consequently, little is known about their structure, chemistry, and possible applications.

In this paper we describe the preparation and crystal structure of bis-μ-[(diphenylphosphino)(diphenylphosphinoselenoyl)methane]-digold(I) bis(perchlorate) (**4**), which is isolated in the crystalline form as $[Au_2(Ph_2PCH_2P(Se)Ph_2)_2](ClO_4)_2 \cdot CH_3(CO)CH_3 \cdot 1.5\ CH_2Cl_2$.

Results

[(CO)AuCl] reacts with dpmSe in equimolar proportions to afford – with CO evolution – the 1:1 complex **2** in high yields, whose composition is confirmed by analytical and spectroscopic data. Addition of a second mol of [(CO)AuCl] to **2** results in the formation of $Ph_2PCH_2P(Se)Ph_2(AuCl)_2$ (**3**). This 2:1 complex decomposes in solution, and addition of one equivalent of dpmSe produces complex **2** suggesting that the Au–Se bond is relatively weak and easily cleaved. Reaction of dpmSe with two equivalents of [(CO)AuCl] also affords complex **3**. Reaction of **2** with $AgClO_4$ in equimolar

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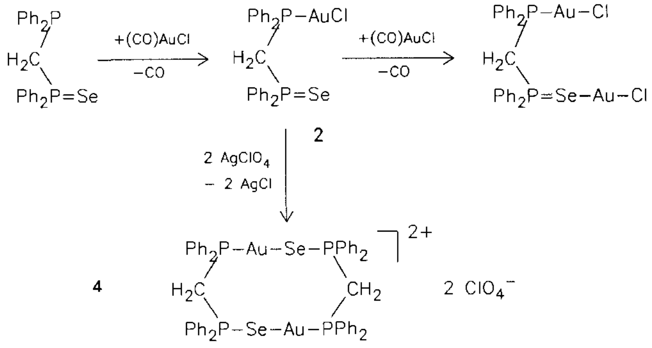
proportions results in the formation of the 10-membered ring complex **4**.



Crystal Structure of $[Au_2(Ph_2PCH_2P(Se)Ph_2)_2](ClO_4)_2 \cdot CH_3COCH_3 \cdot 1.5\ CH_2Cl_2$

Compound **4** crystallizes in the monoclinic space group $P2_1/n$ with two molecules in the unit cell. The crystal structure consists of discrete dications $[Au_2(Ph_2PCH_2P(Se)Ph_2)_2]^{2+}$ having noncrystallographic C_2 symmetry (Figure 1). The perchlorate anions are present, as expected, as noncoordinated counterions. The crystal contains one molecule of acetone and at least one molecule of CH_2Cl_2 per formula unit. A satisfactory model of the crystal structure is obtained with an additional half molecule of CH_2Cl_2 per formula unit. Further evidence for this formulation is provided by ^{1}H-NMR spectroscopy and microanalytical data. Refinement of the structure is complicated by the absorption corrections necessary for gold[6c] and the inaccuracy of light atom positions brought about by the dominance of the X-ray scattering power of the heavy atoms Au and Se. Consequently, a number of the bond lengths and bond angles have relatively high standard deviations (Table 1). All of the bond lengths and angles within the 10-membered ring could, however, be accurately determined.

The two gold(I) atoms are doubly bridged by two dpmSe ligands by phosphorus and selenium coordination, resulting in a folded 10-membered ring system (Figure 2). A comparison of the bond lengths and bond angles in the free ligand[29] with those in **4** shows that these parameters have changed very little upon complexation, with a few exceptions: The P–C–P angles in **4** [117.3(7) and 118.4(8)°] are clearly larger than the corresponding angle in free dpmSe [110.6(2)°]. Similarly, the $C_{phenyl}-P-C_{phenyl}$ angle about the phosphorus(III) atoms increases from 100.7(2) to 108.2(7) and 107.1(7) upon complexation with gold(I). The P–Se bonds in the dication [2.175(4) and 2.180(5) Å] are, as expected, longer than the P=Se bond in free dpmSe [2.103(1) Å].

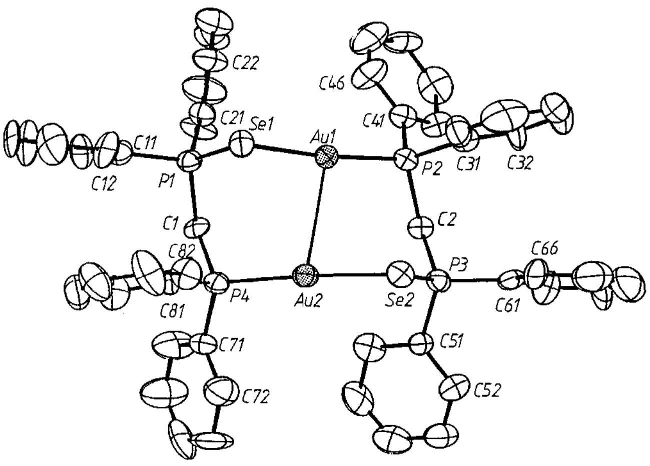


Figure 1. Molecular structure of the dication $[Au_2(Ph_2PCH_2P(Se)Ph_2)_2]^{2+}$ in compound **4** with the atomic numbering scheme. (Hydrogen atoms omitted for clarity)

Table 1. Selected distances [Å] and angles [°] for the dication in compound **4**. (Estimated standard deviations in units of the last significant figure are given in parentheses)

Au1-Au2	3.020(1)	Au1-Se1	2.438(2)
Au1-P2	2.265(4)	Au2-Se2	2.431(2)
Au2-P4	2.271(5)	Se1-P1	2.175(4)
Se2-P3	2.180(5)	P1-C1	1.80(1)
P1-C11	1.79(2)	P1-C21	1.78(1)
P2-C2	1.83(1)	P2-C31	1.81(2)
P2-C41	1.79(1)	P3-C2	1.83(1)
P3-C51	1.83(1)	P3-C61	1.80(2)
P4-C1	1.85(1)	P4-C71	1.82(1)
P4-C81	1.81(2)		
Au2-Au1-Se1	84.0(1)	Au2-Au1-P2	101.5(1)
Se1-Au1-P2	174.5(1)	Au1-Au2-Se2	83.3(1)
Au1-Au2-P4	101.1(1)	Se2-Au2-P4	175.5(1)
Au1-Se1-P1	94.8(1)	Au2-Se2-P3	97.7(1)
Se1-P1-C1	115.9(4)	Se1-P1-C11	108.1(5)
C1-P1-C11	108.3(7)	Se1-P1-C21	110.9(6)
C1-P1-C21	105.9(6)	C11-P1-C21	107.5(7)
Au1-P2-C2	113.1(5)	Au1-P2-C31	112.9(5)
C2-P2-C31	106.9(6)	Au1-P2-C41	111.0(5)
C2-P2-C41	104.2(6)	C31-P2-C41	108.2(7)
Se2-P3-C2	114.2(5)	Se2-P3-C51	112.9(5)
C2-P3-C51	105.1(6)	Se2-P3-C61	107.6(5)
C2-P3-C61	108.4(7)	C51-P3-C61	108.5(7)
Au2-P4-C1	111.5(5)	Au2-P4-C71	112.9(5)
C1-P4-C71	104.4(6)	Au2-P4-C81	113.7(5)
C1-P4-C81	106.7(6)	C71-P4-C81	107.1(7)
P1-C1-P4	117.3(7)	P2-C2-P3	118.4(8)

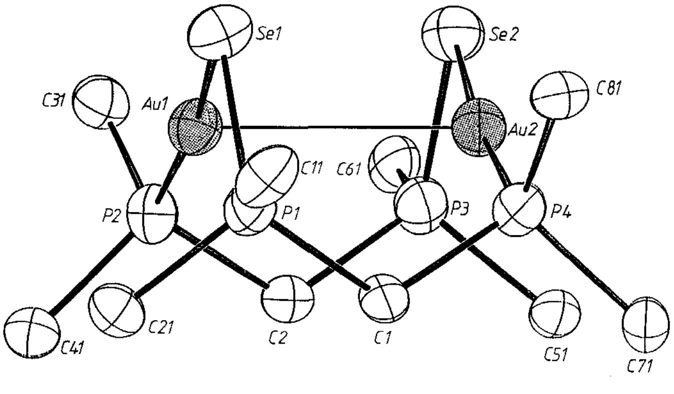


Figure 2. A view of the dication $[Au_2(Ph_2PCH_2P(Se)Ph_2)_2]^{2+}$ of compound **4** showing the folding of the 10-membered ring which allows a transannular Au···Au contact

A similar P–Se bond length [2.187(5) Å] is found in $(Ph_3PSe)AuCl$[19], but the Au–Se bond in this complex [2.371(2) Å] is considerably shorter than those in **4** [2.438(2) and 2.431(2) Å]. Other Au–Se bond lengths determined to date lie in the range of 2.425 to 2.551 Å[25a,30,31], but the gold complexes concerned are too few in number and too varied to enable any useful comparisons to be made. The Au–P(III) bond lengths in **4** [2.271(5) and 2.265(4) Å] are characteristic of similar gold(I)–phosphine linkages[8].

As the Au–Se–P(V) angles of 94.8(1) and 97.7(1)° are smaller than the corresponding angle in $(Ph_3PSe)AuCl$ [100.1(1)°], the P(V) atoms in **4** exert even a closer approach to the gold atoms (3.401 and 3.475 Å cf. 3.947 Å). These obtuse angles presumably reflect the repulsive effect of the non-bonded selenium electrons.

Interestingly, the Se–Au–Au angles in the dication are not 90° but considerably smaller [84.0(1) and 83.3(1)°], resulting in shorter distances of the selenium atoms to the gold(I) atom to which they are not bound [Au1···Se2: 3.650(1) Å; Au2···Se1: 3.677(1) Å]. These distances are, however, still longer than the sum of the van der Waals radii (3.6 Å)[32].

The coordination at the gold atoms deviates substantially from linearity [Se1–Au1–P2: 174.5(1)°; Se2–Au2–P4: 175.5(1)°] and implies the presence of an Au···Au interaction. The gold(I) atoms are brought into contact at a distance of 3.020(1) Å, which is comparable to that found in many of the 8-membered ring systems. $[Au_2S_8]^{2-}$ is also a 10-membered ring complex with a short Au–Au contact (3.12 Å) and an associated distortion from linearity at gold (S–Au–S: 166.4°)[33]. It is interesting to note that the Au–Au contact in **4** is shorter than that in the similar 10-membered ring complex $[Au_2(SCH_2CH_2PEt_2)_2]$ with Au–Au = 3.104 Å[17], but is considerably longer than in $[Au_2(Me_2PCH_2CH_2PMe_2)_2]^{2+}$ with an Au–Au range of 2.872(2) to 2.974(3) Å (variations with the counteranion)[10].

The Au, Se, and P atoms in complex **4** are not coplanar; rather, the P–Au–Se units are twisted relative to one another with dihedral angles of P2–Au1–Au2–Se2 = 49.41° and P4–Au2–Au1–Se1 = 48.14° (Figure 2). This feature also prevails in the 10-membered rings of $[Au_2S_8]^{2-}$ [33], $[Au_2(Me_2PCH_2CH_2PMe_2)_2]^{2+}$ [10], $[Au_2PCH_2CH_2PMe_2)_2]^{2+}$ [10], $[Au_2(SCH_2CH_2PEt_2)_2]$[17].

In summary, the structure of the dication in compound **4** provides additional and virtually unequivocal evidence for attractive transannular Au(I)···Au(I) interactions. These forces prove to be strongly conformation-determining in these classes of complexes, and therefore related complexes can be predicted to adopt similar structures. In the absence of such forces quite different conformations would be expected.

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Experimental

All reactions were carried out in oven-dried Schlenk glassware using standard inert-atmosphere techniques. All solvents were dried and freshly distilled before use. – NMR: Jeol GX 270 and GX 400. – MS: Varian MAT CH 7.

(Diphenylphosphino)(diphenylphosphinoselenoyl)methane, dpmSe, was prepared as described[29].

Chloro[(diphenylphosphino)(diphenylphosphinoselenoyl)methane]gold(I) (**2**): A suspension of 0.42 g (1.6 mmol) of [(CO)AuCl] in CH_2Cl_2 (15 ml) was treated with a solution of 0.75 g (1.6 mmol) of dpmSe in the same solvent (15 ml). Evolution of CO was observed. After stirring the reaction mixture for ca. 30 min at room temp., *n*-hexane was added. The volume of the solvent was then reduced in vacuo until precipitation began. More *n*-hexane was added to the reaction mixture to ensure complete precipitation. The white precipitate was filtered, washed with *n*-hexane, and dried under reduced pressure. Yield 0.95 g (85%), m.p. 177°C. – ^1H NMR ($CDCl_3$, 20°C): δ = 3.9 (app. t, A_2XY, 2H, CH_2); 7.3–7.8 (m, 20H, Ph). – ^{13}C NMR (CD_2Cl_2, 20°C): δ = 32.5 (app. t, AXY, CH_2); 128.0–133.5 (m, Ph). – ^{31}P NMR (CD_2Cl_2, 20°C): δ = 18.4 [d, AX, J = 22 Hz, P(III)]; 28.2 [d, AX, J = 22 Hz, ^1J(P–Se) = 745 Hz, P(V)]. – MS (FD): m/z (%) = 696 [M^+] (55.1); 464.1 [M^+ – AuCl] (100).

$C_{25}H_{22}AuClP_2Se$ (695.8) Calcd. C 43.15 H 3.19 Au 28.31
Found C 42.98 H 3.29 Au 29.50

Dichloro[(diphenylphosphino)(diphenylphosphinoselenoyl)methane]digold(I) (**3**): A suspension of 0.26 g (1.0 mmol) of [(CO)AuCl] in CH_2Cl_2 (10 ml) was treated with a CH_2Cl_2 solution of 0.70 g (1.0 mmol) of **2**. CO evolution was observed, and a very dark yellow solution resulted to which *n*-hexane was added. The resultant tan precipitate was filtered, washed with *n*-hexane, and dried under reduced pressure. Yield 0.65 g (70%), m.p. 140°C (dec.). – ^1H NMR ($CDCl_3$, 20°C): δ = 4.14 (t, A_2XY, J = 12.2 Hz, 2H, CH_2); 7.3–7.8 (m, 20H, Ph). – ^{31}P NMR ($CDCl_3$, 20°C): δ = 18.8 [d, AX, J = 13 Hz, P(III)]; 26.8 [d, AX, J = 13 Hz, ^1J(P–Se) = 585 Hz, P(V)].

$C_{25}H_{22}Au_2Cl_2P_2Se$ (928.2)
Calcd. C 32.35 H 2.39 Au 42.44 Cl 7.64
Found C 34.26 H 2.89 Au 41.40 Cl 6.91

Bis-μ-[(diphenylphosphino)(diphenylphosphinoselenoyl)methane]-digold(I) Bis(perchlorate) (**4**): A solution of 0.90 g (1.29 mmol) of **2** in CH_2Cl_2 (15 ml) was treated with 0.27 g (1.29 mmol) of $AgClO_4$. The reaction mixture was stirred vigorously at room temp. for ca. 2 h. The precipitated AgCl was filtered, and acetone was added to the clear yellow filtrate. The volume of the solvent was then reduced in vacuo until precipitation began. To ensure complete precipitation *n*-hexane was added. The resultant white precipitate was filtered, washed with *n*-hexane and dried under reduced pressure. Yield 0.55 g (80%), m.p. 180°C (dec.). – ^1H NMR ($CDCl_3$, 20°C): δ = 4.6 (m, A_2XY, 4H, CH_2); 7.4–7.8 (m, 40H, Ph). – ^{31}P NMR (CD_2Cl_2, 20°C): δ = 26.1 [br. s, AA'XX', ^1J(P–Se) = 536 Hz, P(V)]; 27.2 [br. s, AA'XX', P(III)].

$C_{50}H_{44}Au_2Cl_2O_8P_4Se_2$ (1519.5) Calcd. C 39.52 H 2.92
Found C 39.01 H 3.10

Crystal Structure Determination: $C_{50}H_{44}Au_2Cl_2O_8P_4Se_2 \cdot 1.5\ CH_2Cl_2 \cdot C_3H_6O$, M_r = 1705.04, monoclinic, space group $P2_1/n$, a = 17.604(2), b = 19.948(2), c = 18.450(2) Å, β = 104.45(1)°, V = 6274.0 Å^3, Z = 4, $d_{calcd.}$ = 1.805 g/cm^3, μ(Mo-K_α) = 61.7 cm^{-1}, $F(000)$ = 3292 e, T = 23°C. Enraf-Nonius CAD4 diffractometer, Mo-K_α radiation, λ = 0.71069 Å, graphite monochromator. A suitable crystal (0.20 mm × 0.25 mm × 0.40 mm) was sealed into a glass capillary under argon. The integrated intensities of 11780 reflections were measured up to $(\sin\Theta/\lambda)_{max}$ = 0.594 Å^{-1} using Θ-2Θ scan techniques ($\Delta\omega = 0.8 + 0.35 \tan\Theta$; hkl range ±20, 23, 21) and corrected for intensity, Lp effects, and absorption effects (rel. transmission 0.799 to 1.000). From 10978 unique reflections 6334 were considered "observed" [$F_o \geq 4\sigma(F_o)$] and used in the

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters for $[Au_2(Ph_2PCH_2P(Se)Ph_2)_2](ClO_4)_2 \cdot CH_3COCH_3 \cdot 1.5\ CH_2Cl_2$ (**4** $\cdot CH_3COCH_3 \cdot 1.5\ CH_2Cl_2$)

ATOM	X/A	Y/B	Z/C	U(eq.)
AU1	0.30165(3)	0.19757(3)	0.14251(3)	0.039
AU2	0.12854(3)	0.20148(4)	0.06691(3)	0.041
SE1	0.2588(1)	0.14242(8)	0.24336(9)	0.047
SE2	0.1710(1)	0.15642(8)	-0.03893(9)	0.047
P1	0.2291(2)	0.2350(2)	0.2921(2)	0.038
P2	0.3534(2)	0.2488(2)	0.0562(2)	0.038
P3	0.2057(2)	0.2509(2)	-0.0806(2)	0.041
P4	0.0790(3)	0.2420(2)	0.1607(2)	0.040
C1	0.1550(8)	0.2857(6)	0.2323(7)	0.029
C2	0.2810(8)	0.2967(7)	-0.0128(7)	0.035
C11	0.1969(9)	0.2142(8)	0.3738(7)	0.057
C12	0.178(1)	0.1502(8)	0.3881(8)	0.056
C13	0.153(1)	0.1370(9)	0.451(1)	0.090
C14	0.151(1)	0.189(1)	0.5041(9)	0.069
C15	0.168(1)	0.253(1)	0.487(1)	0.091
C16	0.190(1)	0.2670(9)	0.4215(9)	0.054
C21	0.3132(9)	0.2876(7)	0.3208(8)	0.036
C22	0.384(1)	0.2586(8)	0.3545(9)	0.060
C23	0.448(1)	0.297(1)	0.384(1)	0.079
C24	0.443(1)	0.367(1)	0.379(1)	0.061
C25	0.374(1)	0.3979(9)	0.345(1)	0.078
C26	0.3074(9)	0.3561(8)	0.3165(9)	0.059
C31	0.3988(9)	0.1904(7)	0.0044(8)	0.038
C32	0.441(1)	0.2120(9)	-0.0444(9)	0.074
C33	0.478(1)	0.166(1)	-0.082(1)	0.079
C34	0.469(1)	0.099(1)	-0.074(1)	0.093
C35	0.424(1)	0.0766(9)	-0.027(1)	0.121
C36	0.390(1)	0.1231(9)	0.0142(9)	0.075
C41	0.4252(8)	0.3096(7)	0.0990(8)	0.041
C42	0.4451(9)	0.3622(8)	0.0580(8)	0.050
C43	0.509(1)	0.4046(8)	0.095(1)	0.071
C44	0.547(1)	0.3960(9)	0.166(1)	0.063
C45	0.522(1)	0.344(1)	0.203(1)	0.095
C46	0.463(1)	0.3018(9)	0.1704(8)	0.034
CL2	0.6392(3)	0.0169(2)	0.8290(3)	0.063
O21	0.653(1)	0.0232(9)	0.751(1)	0.177
O22	0.634(1)	0.0822(9)	0.8544(9)	0.143
O23	0.704(1)	-0.019(1)	0.866(1)	0.199
O24	0.570(1)	-0.0215(8)	0.8198(8)	0.135
C5	0.732(1)	0.0627(9)	0.6239(9)	0.062
C6	0.667(1)	0.016(1)	0.595(1)	0.094
C7	0.813(1)	0.0369(9)	0.658(1)	0.083
O3	0.7204(7)	0.1233(6)	0.6173(6)	0.076
C51	0.1240(8)	0.3100(7)	-0.1094(7)	0.037
C52	0.084(1)	0.3167(8)	-0.1823(8)	0.053
C53	0.022(1)	0.3612(9)	-0.204(1)	0.070
C54	-0.002(1)	0.3942(9)	-0.153(1)	0.074
C55	0.033(1)	0.3864(9)	-0.081(1)	0.072
C56	0.099(1)	0.3438(7)	-0.0546(9)	0.051
C61	0.2430(9)	0.2322(8)	-0.1607(8)	0.045
C62	0.263(1)	0.2837(9)	-0.2019(9)	0.064
C63	0.288(1)	0.272(1)	-0.264(1)	0.102
C64	0.294(1)	0.209(1)	-0.293(1)	0.106
C65	0.273(1)	0.155(1)	-0.252(1)	0.134
C66	0.249(1)	0.1689(9)	-0.1865(9)	0.068
C71	0.0032(8)	0.3048(8)	0.1287(8)	0.040
C72	-0.055(1)	0.289(1)	0.069(1)	0.081
C73	-0.117(1)	0.332(1)	0.041(1)	0.105
C74	-0.117(1)	0.393(1)	0.078(1)	0.102
C75	-0.059(1)	0.409(1)	0.137(1)	0.112
C76	0.000(1)	0.3654(9)	0.163(1)	0.102
C81	0.0378(9)	0.1780(7)	0.2092(8)	0.036
C82	0.044(1)	0.1116(8)	0.1933(9)	0.053
C83	0.013(1)	0.0642(9)	0.232(1)	0.071
C84	-0.024(1)	0.081(1)	0.285(1)	0.089
C85	-0.032(1)	0.150(1)	0.300(1)	0.068
C86	-0.002(1)	0.1976(9)	0.2620(9)	0.067
CL1	0.2910(4)	0.4744(2)	-0.0947(3)	0.079
O11	0.785(1)	0.0275(8)	0.476(1)	0.153
O12	0.843(1)	0.0731(8)	0.3887(8)	0.129
O13	0.7995(9)	-0.0397(8)	0.3846(8)	0.129
O14	0.712(1)	0.049(1)	0.368(1)	0.232
C3	0.818(1)	0.046(1)	0.016(1)	0.128
CL3	0.8435(5)	0.1253(4)	0.0514(4)	0.184
CL4	0.0948(5)	-0.0038(4)	0.9846(5)	0.193
C8	0.6501(9)	0.0495(9)	0.190(1)	0.033
CL6	0.6062(9)	0.1190(9)	0.128(1)	0.071
CL5	0.7456(9)	0.0242(9)	0.180(1)	0.106

structure determination. The structure was solved by Patterson methods (SHELXS-86) and completed by difference Fourier syntheses (SHELX76). With the exception of the carbon and oxygen atoms of the solvent molecules and the perchlorate counterions, all nonhydrogen atoms were refined anisotropically. The hydrogen atoms (10 found, 40 calculated at idealized positions, those of CH_2Cl_2 neglected) were included in the final refinement cycles with fixed $U_{iso} = 0.05$ Å^2. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ [$w = 1/\sigma^2(F_o)$] in the final refinement cycles. 631 parameters were refined in two blocks: $R(R_w) = 0.053\ (0.051)$, $\Delta\varrho_{fin}$(max/min) = +1.45 (near half occupied CH_2Cl_2)/−0.98). The fractional atomic coordinates and equivalent isotropic displacement parameters are presented in Table 2. Further crystal structure data may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, by quoting the depository number CSD-54546, the names of the authors and the literature citation.

CAS Registry Numbers

2: 128054-46-6 / **3**: 128054-47-7 / **4**: 128054-49-9 / **4** $\cdot CH_3COCH_3 \cdot 1.5\ CH_2Cl_2$: 128054-50-2 / $Ph_2PCH_2P(Se)Ph_2$: 23176-19-4 / (CO)AuCl: 50960-82-2

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