Synthesis and structures of gold(I) phosphine complexes containing monoanionic selenocarbamate ester ligands

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ABSTRACT

A series of mono- and dinuclear gold(I) phosphine complexes of the type [Au{SeC(OMe)=NPh}(P)] [P = PPh_3, PTA, P(o-tolyl)$_3$, P(p-MeOC$_6$H$_4$)$_3$] and [Au$_2${SeC(OMe)=NPh}$_2$(μ-PP)] (PP = dppm, dppe, dppp, dppf, dppee) were prepared from the reaction of the appropriate chlorogold(I) phosphine complexes with *N*-phenyl-*O*-methylselenocarbamide in the presence of base. These new complexes were fully characterised by spectroscopic techniques and, in several cases, by X-ray crystallography. The differences in the solid-state structures of these selenium complexes were compared with those of some sulfur analogues.

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1. Introduction

The chemistry of gold(I) phosphine complexes with sulfur ligands is today a well-established field. A vast number of such compounds have been prepared and some interesting applications have emerged from their supramolecular structures, luminescence properties and their biological activity [1]. Particularly in medicinal applications, gold thiolate complexes have shown much promise; in fact the gold(I) compounds Auranofin, Myocrisin and Solgonal (Fig. 1) have been in clinical use against rheumatoid arthritis for more than 30 years [2].

In marked contrast, the chemistry of gold(I) complexes containing organic selenium ligands is a relatively unexplored field. The comparatively small number of known gold–selenium compounds are generally derived from selenium derivatives which are either commercially available or easily accessible including NCSe$^-$, $H_2NC(Se)NH_2$, PhSe$^-$, Ph_3PSe, [Ph$_2$P(Se)NP(Se)Ph$_2$]$^-$ and Ph$_2$P(Se)CH$_2$P(Se)PPh$_2$ [3–12]. More recently, some highly luminescent clusters containing the Au$_3$Se core have also been reported [13,14]. Selenocarbamate esters, specifically *N*-phenyl-*O*-alkylselenocarbamides, have been known for more than 35 years but have so far been completely neglected as ligands in coordination chemistry [15]. There exists only one report of a metal complex containing *N*-phenyl-*O*-methylselenocarbamide acting as a neutral Se-donor ligand to a cobalt(II) centre [15]. However, to date no complexes containing deprotonated, monoanionic *N*-aryl-*O*-akyl-selenocarbamate ligands are known. Given that gold(I) phosphine complexes containing ArNHC(S)OMe (Ar = Ph, 4-NO$_2$C$_6$H$_4$) form a variety of supramolecular structures and are also strongly luminescent [16–19], we were interested in exploring the so far unknown chemistry of their selenium counterparts, in particular focusing on *N*-phenyl-*O*-methylselenocarbamate. The results of this investigation are presented herein [20].

2. Results and discussion

N-phenyl-*O*-methylselenocarbamide is accessible in good yield by treatment of PhNCSe with MeOH as reported by Barton in 1994 [21]. The X-ray crystal structure of the compound was recently reported by us [22]. The reaction of *N*-phenyl-*O*-methylselenocarbamide with appropriate amounts of either mononuclear or binuclear chlorogold(I) phosphine complexes in the presence of base affords the colourless or pale-yellow gold(I) complexes [Au{SeC(OMe)=NPh}(P)] [P = PPh_3 (**1**), PTA (**2**), P(o-tolyl)$_3$ (**3**), P(p-MeOC$_6$H$_4$)$_3$ (**4**)] and [Au$_2${SeC(OMe)=NPh}$_2$(μ-PP)] (PP = dppm (**5**), dppe (**6**), dppp (**7**), dppee (**8**), dppf (**9**)], respectively (Scheme 1).

The new gold complexes were fully characterised by various spectroscopic methods, including ^{1}H and ^{31}P NMR spectroscopy, IR spectroscopy and mass spectrometry. The combination of the relatively poor solubility and stability of the compounds in solution combined with the low sensitivity of the ^{77}Se nucleus (7.63% natural abundance) did not allow us to obtain any ^{77}Se NMR spectra. The chemical shifts of the singlet resonances in the ^{31}P NMR spectra of complexes **1–9** are in the range typically observed for

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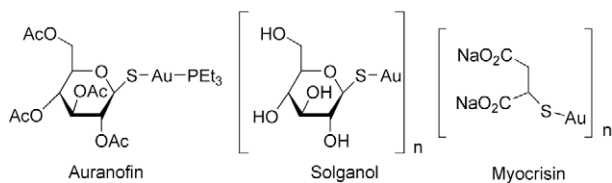 *E-mail address:* fmohr@uni-wuppertal.de (F. Mohr).

Fig. 1. Gold thiolate complexes used in medicine.

phosphine gold(I) complexes. Deprotonation of the N-phenyl-O-methylselenocarbamide is confirmed in both the ^{1}H and IR spectra by the absence of signals due to the NH group. In addition, the C–N stretching frequencies in the IR spectra of complexes 1–9 are shifted to higher wavenumbers (by ca. 100 cm^{-1}) compared to that of the (protonated) free ligand, consistent with an increase in the C–N bond order. These selenium complexes thus represent the very first examples of metal complexes containing deprotonated

N-phenyl-O-methylselenocarbamate. Whilst we were unable to obtain X-ray quality crystals of the mononuclear derivatives 1–5, we were able to determine the solid-state structures of the binuclear complexes 6, 7 and 9. The molecular structures of these compounds are shown in Figs. 2–4 and selected geometric parameters are collected in Table 1.

The two independent gold atoms in 6 each exist in a distorted linear geometry defined by the selenium and phosphorus atoms. Key differences in geometric parameters describing the N-phenyl-O-methylselenocarbamate ligand compared with the neutral N-phenyl-O-methylselenocarbamide molecule are evident. Most noteworthy is the elongation of the C–Se bond to 1.921(14) and 1.902(15) Å in the anion compared with 1.8322(19) Å in the neutral molecule [22]. This difference is associated with concomitant shortening of the C1–N1 and C35–N2 bond distances to 1.289(17) and 1.277(18) Å, respectively, compared with 1.328(2) Å [22], consistent with significant double bond character in the C1–N1 and C35–N2 bonds. In terms of angles, the Se–C–N
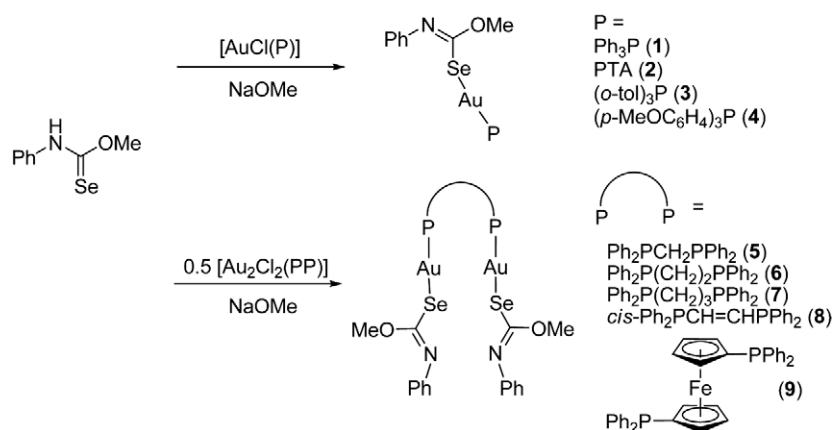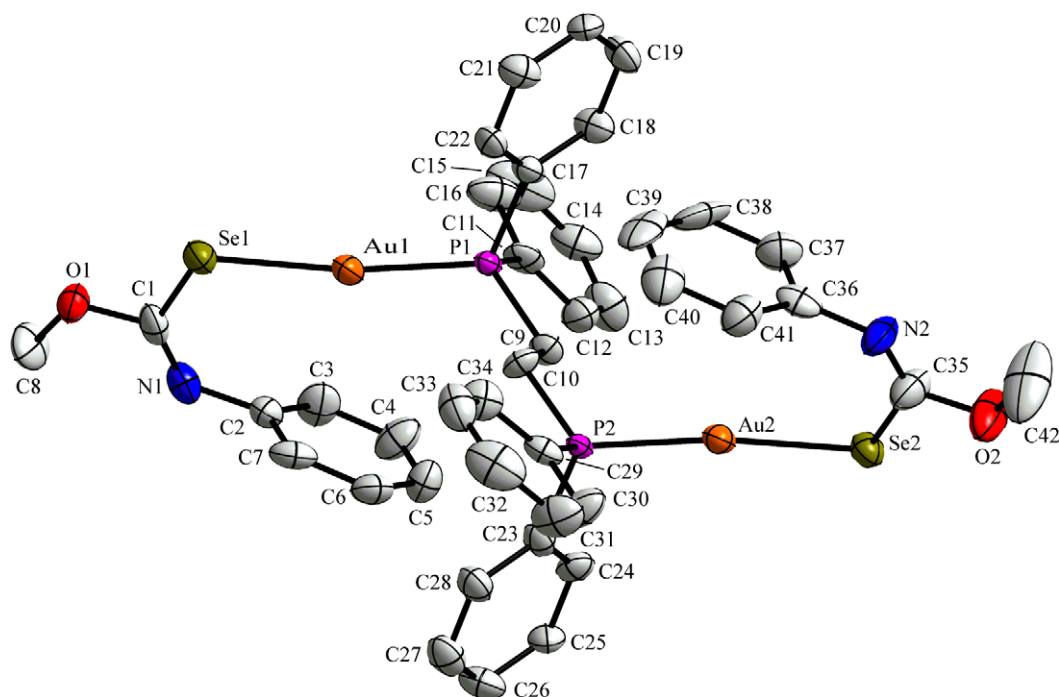

Scheme 1.

Fig. 2. Molecular structure of complex 6. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms and the solvent CH$_2$Cl$_2$ molecule have been omitted for reasons of clarity.
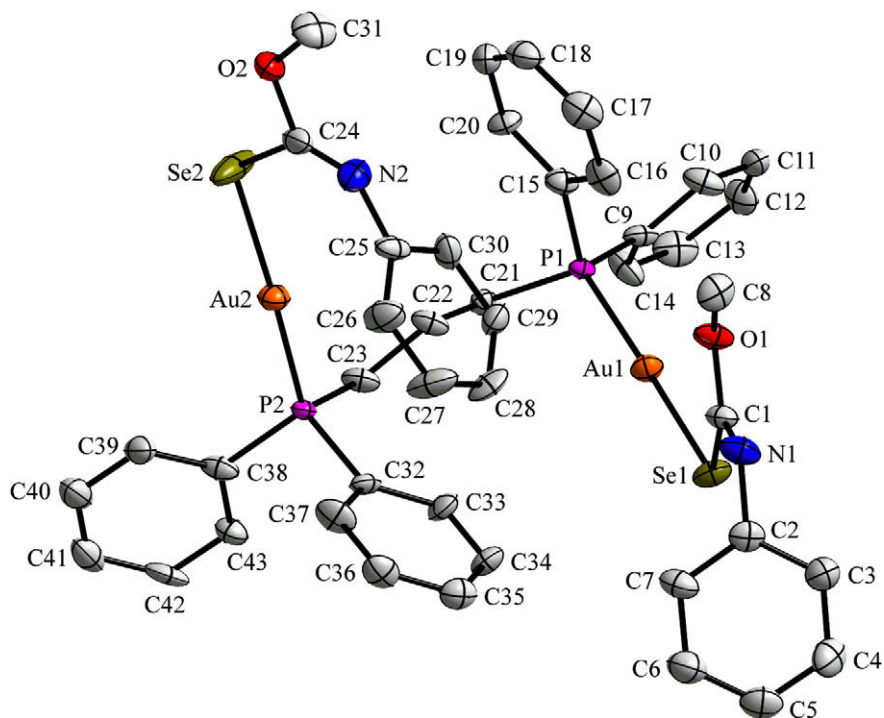
Fig. 3. Molecular structure of complex **7**. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for reasons of clarity.
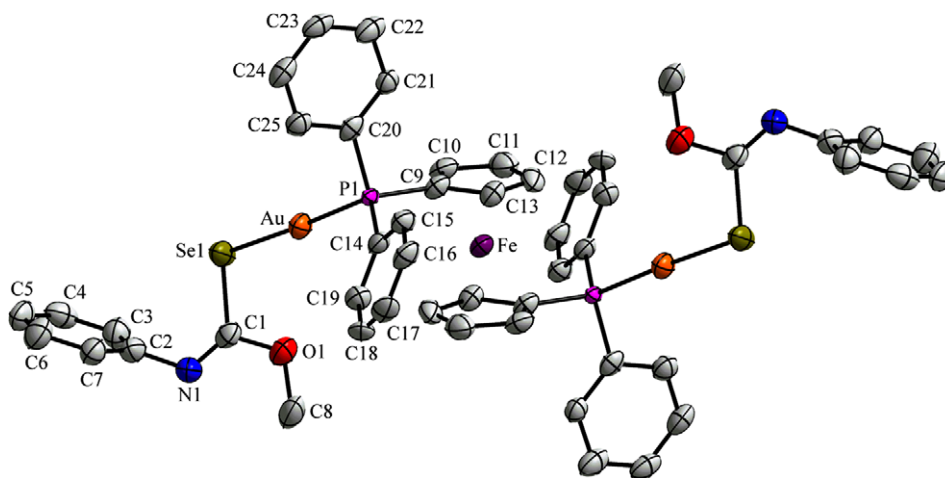

Fig. 4. Molecular structure of complex **9**. Displacement ellipsoids are shown at the 50% probability level. The Fe atom is located on a crystallographic centre of inversion; unlabelled atoms are related by the symmetry operation $1 - x$, $1 - y$, $-z$. Hydrogen atoms and the solvent CH_2Cl_2 molecule have been omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) for complexes **6**, **7** and **9**.

	6	**7**	**9**[a]
Au1–P1, Au2–P2	2.267(3), 2.261(3)	2.262(3), 2.265(3)	2.270(2)
Au1–Se1, Au2–Se2	2.4172(13), 2.4162(13)	2.4072(12), 2.3991(14)	2.4048(12)
C–Se1, C–Se2	1.921(14), 1.902(15)	1.924(10), 1.895(13)	1.935(10)
C–N1, C–N2	1.289(17), 1.277(18)	1.273(14), 1.259(16)	1.239(13)
Se1–Au1–P1, Se2–Au2–P2	172.05(8), 172.86(8)	177.57(8), 168.21(8)	176.36(6)
Au1–Se1–C, Au2–Se2–C	104.5(4), 103.6(5)	98.6(3), 109.3(3)	98.8(3)

[a] Molecule is disposed about a crystallographic centre of inversion.

angles open up by over 10° to 132.9(10) and 134.1(11)° compared with 122.07(14)° in the neutral molecule and the remaining angles about the quaternary carbon atom each contracting about 5° [22]. Similar observations were made when comparing geometric parameters of the related thiocarbamate phosphine gold(I) complexes [16–19] and their neutral precursors [23–25] whereupon it was concluded that the anion was functioning as a thiolate ligand. Similar trends are found in the molecular structures of each

of **7** and **9**; the latter molecule is centrosymmetric with the iron atom located on a crystallographic centre of inversion.

An interesting observation in the structures is the relative orientations of the selenocarbamate anions. In **6**, the anions are orientated so as to place the aromatic ring in close proximity of the gold centre. The Au1, 2···Cg separations are 3.304(3) and 3.289(4) Å, respectively where Cg is the ring centroid of the C2–C7 and C36–C41 aromatic rings, respectively. In **7**, the Au1 atom forms a more conventional intramolecular Au···O interaction of 3.091(7) Å whereby a Au···π interaction persists for the Au2 atom, with Au2···Cg(C25–C30) = 3.646(5) Å. In centrosymmetric **9**, a Au···O1 interaction of 3.146(9) Å is noted. The appearance of both orientations of the selenocarbamate anion in **7** suggests that each conformation is of comparable energy. A recent systematic study of related phosphinegold thiocarbamate structures demonstrated electronic and steric control of intramolecular Au···π interactions [19]; a review of intermolecular Au···π contacts as a supramolecular synthon has also appeared recently [26].

An important difference between the structures of **6, 7**, and **9** on the one hand and the thiolate counterparts on the other is noted. Thus, whereas aurophilic interactions are absent in **6, 7**, and **9**, these are present in each of the thiolate derivatives [17]. This observation is correlated with the electronegativity differences between the sulfur and selenium donor atoms. Despite the absence of aurophilic interactions in **6, 7**, and **9**, other intermolecular contacts serve to consolidate the respective crystal structures.

In **6**, intermolecular Au···Se and C–H···Se contacts link molecules into supramolecular chains, as illustrated in Fig. 5a. The Au1···Se2^i and Au2···Se1^{ii} separations of 3.7423(15) and 3.7356(17) Å, respectively, are well within the sum of the van der Waals radii of gold and selenium, being 4.4 Å [27]; symmetry operations i: $x, -1 + y, z$ and ii: $x, 1 + y, z$. The Au···Se interactions are supported by C–H···Se contacts [C22–H···Se2^i = 2.89 Å, C22···Se2^i = 3.821(6) Å with angle at H22 = 167°; C24–H···Se1^{ii} = 2.91 Å, C24···Se1^{ii} = 3.842(6) Å with angle at H24 = 168°]. Globally, the chains pack in the *ab*-plane with layers stacked in the *c*-direction being interspersed by the dichloromethane molecules of crystallisation. Similar Au···Se interactions are found in the structure of **7** but involve only the Au1 and Se2^i atoms with a distance of 3.873(2) Å; symmetry operation i: $x, -y, -\frac{1}{2} + z$. These contacts are reinforced by C–H···O [C4–H···O2^{ii} = 2.47 Å, C4···O2^{ii} = 3.373(16) Å with angle at H4 = 160° for ii: $x, y, -1 + z$] and C–H···Se [C33–H···Se2^i = 2.85 Å, C33···Se2^i = 3.632(11) Å with angle at H33 = 141°] contacts to form a supramolecular chain along the *c*-direction. The most prominent intermolecular interactions operating in the crystal structure of **9** are of the type C–H···Se and involve the complex and solvent dichloromethane molecules of crystallisation. The weak nature of these interactions accounts for the disorder observed for the dichloromethane molecules, see Experimental, whereby these are disposed about a centre of inversion and occupy two positions of equal weight. Nevertheless, a recognisable supramolecular aggregation pattern, namely a chain, is evident, Fig. 5c. The parameters defining this interaction are C26–H···Se1 = 2.97 Å, C26–H···Se1 = 3.75(4) Å with an angle at H26a = 137°. Globally, the chains superimpose upon each other so that in a sense channels along the *a*-direction are formed in which reside the dichloromethane molecules.

3. Experimental

3.1. General

^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a 400 MHz Bruker ARX spectrometer. Chemical shifts are quoted relative to external TMS (^{1}H) and 85% H_3PO_4 (^{31}P); coupling constants are reported in Hertz. Electrospray mass spectra were measured on a Bruker MicroTOF spectrometer in positive ion mode. IR spectra were run as KBr pellets on a Bruker Tensor 27 instrument. Elemental analyses were performed by staff of the microanalytical laboratory of the University of Wuppertal. Although the products were air-stable, all reactions were routinely carried out under dried dinitrogen. *N*-Phenyl-*O*-methylselenocarbamate was prepared as described previously [21,22]. The chlorogold(I) phosphine complexes were prepared by the reaction of [AuCl(tht)] [28] (tht = tetrahydrothiophene) with appropriate amounts of the phosphines. All other chemicals and solvents (anhydrous grade) were sourced commercially and used as received.

3.2. Preparation of the gold(I) complexes

To a solution of PhNHC(Se)OMe (0.1 mmol) in 5 mL MeOH was added NaOMe (0.007 g, 0.13 mmol) followed by appropriate quantities of the chlorogold(I) phosphine complexes (1 equiv. of the mononuclear and 0.5 equiv. of the dinuclear compounds, respectively). The mixture was allowed to stir at room temperature for *ca.* 18 h. After this time the mixture was evaporated to dryness and the resulting solid residue was extracted into CH_2Cl_2 (2 × 5 mL) and passed through Celite. Addition of Et_2O precipitated the products, which were isolated by filtration, washed with Et_2O and dried. Using this procedure the following complexes were prepared.

3.2.1. [Au{SeC(OMe)=NPh}(PPh$_3$)] (**1**)

0.059 g, 88%, colourless solid. ^{1}H NMR (CD$_2$Cl$_2$): δ = 7.49 (m, 15H, Ph$_3$P), 7.04 (t, *J* = 7.6 Hz, 2H, *meta*-PhN), 6.74 (m, 3H, *ortho/para*-PhN), 3.87 (s, 3H, OCH$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 39.83. IR (KBr disk): 1625 cm^{-1} ν(C–N). Anal. Calc. for C$_{26}$H$_{23}$AuNOPSe · ¼CH$_2$Cl$_2$ (693.60): C, 45.46; H, 3.42; N, 2.02. Found: C, 45.58; H, 3.48; N, 1.86%.

3.2.2. [Au{SeC(OMe)=NPh}(PTA)] (**2**)

0.040 g, 70%, colourless solid. ^{1}H NMR (CD$_2$Cl$_2$): δ = 7.38 (t, *J* = 7.6 Hz, 2H, *meta*-PhN), 7.04 (t, *J* = 7.6 Hz, 1H, *para*-PhN), 6.71 (d, *J* = 7.6 Hz, 2H, *ortho*-PhN), 4.35 (AB quart., *J* = 13.2 Hz, 6H, NCH$_2$N), 4.10 (s, 6H, PCH$_2$N), 3.83 (s, 3H, OCH$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = −48.05. IR (KBr disk): 1612 cm^{-1} ν(C–N). Anal. Calc. for C$_{14}$H$_{20}$AuN$_4$OPSe · 2CH$_2$Cl$_2$ (737.09): C, 26.07; H, 3.28; N, 7.60. Found: C, 25.79; H, 3.16; N, 7.97%.

3.2.3. [Au{SeC(OMe)=NPh}{P(o-tolyl)$_3$}] (**3**)

0.048 g, 67%, colourless solid. ^{1}H NMR (CD$_2$Cl$_2$): δ = 7.48 (t, *J* = 7.6 Hz, 3H, H4 *o*-tol$_3$P), 7.38 (t, *J* = 7.1 Hz, 3H, H3 *o*-tol$_3$P), 7.21 (t, *J* = 7.6 Hz, 3H, H5 *o*-tol$_3$P), 7.13 (t, *J* = 7.6 Hz, 2H, *meta*-PhN), 6.99 (dd, *J* = 7.6 Hz, 3H, H6 *o*-tol$_3$P), 6.88 (t, *J* = 7.1 Hz, 1H, *para*-PhN), 6.77 (d, *J* = 7.6 Hz, 2H, *ortho*-PhN), 3.79 (s, 3H, OCH$_3$,), 2.64 (s, 9H, *o*-tol$_3$P). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 21.25. IR (KBr disk): 1628 cm^{-1} ν(C–N). Anal. Calc. for C$_{29}$H$_{29}$AuNOPSe (714.45): C, 48.75; H, 4.09; N, 1.96. Found: C, 48.61; H, 4.02; N, 1.96%.

3.2.4. [Au{SeC(OMe)=NPh}{P(p-MeOC$_6$H$_4$)$_3$}] (**4**)

0.034 g, 44%, colourless solid. ^{1}H NMR (CD$_2$Cl$_2$): δ = 7.37 (d, *J* = 8.1 Hz, 6H, P{*p*-MeOC$_6$H$_4$}$_3$), 7.06 (t, *J* = 7.6 Hz, 2H, *meta*-PhN), 6.94 (d, *J* = 8.1 Hz, 6H, P{*p*-MeOC$_6$H$_4$}$_3$), 6.83 (d, *J* = 8.2 Hz, 2H, *ortho*-PhN), 6.76 (t, *J* = 7.6 Hz, 1H, *para*-PhN), 3.92 (s, 3H, OCH$_3$), 3.83 (s, 9H, P{*p*-MeOC$_6$H$_4$}$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 36.45. IR (KBr disk): 1619 cm^{-1} ν(C–N). Anal. Calc. for C$_{29}$H$_{29}$AuNO$_4$PSe · ¼CH$_2$Cl$_2$ (783.68): C, 44.83; H, 3.79; N, 1.79. Found: C, 45.00; H, 3.65; N, 1.69%.

3.2.5. [Au$_2${SeC(OMe)=NPh}$_2${μ-Ph$_2$PCH$_2$PPh$_2$}] (**5**)

0.036 g, 51%, pale yellow solid. ^{1}H NMR (CD$_2$Cl$_2$): δ = 7.27–7.66 (m, 20H, Ph$_2$P), 7.07 (t, *J* = 7.6 Hz, 4H, *meta*-PhN), 6.79 (m, 6H,
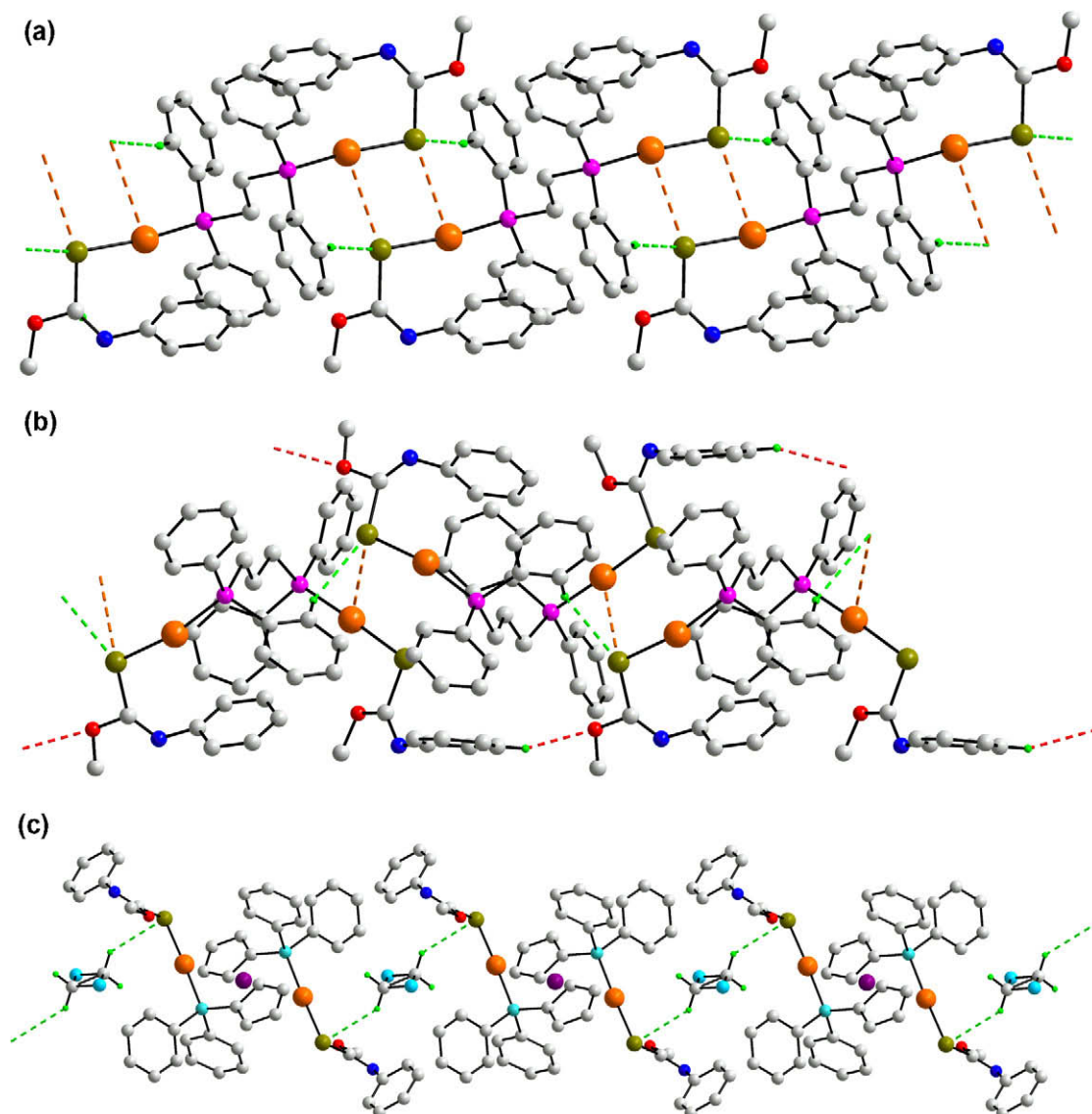
Fig. 5. Supramolecular chains in the crystal structures of **6**, **7** and **9**. (a) Complex **6**: mediated by Au⋯Se (orange dashed lines) and C–H⋯Se (green dashed lines) contacts; (b) Complex **7**: mediated by Au???Se (orange dashed lines), C–H⋯O (red dashed lines) and C–H⋯Se (green dashed lines) contacts; and (c) **9**: mediated by C–H⋯Se (green dashed lines) contacts. Note that the dichloromethane molecules of crystallisation are disordered about a crystallographic centre of inversion and that both orientations for each are shown in this figure. Hydrogen atoms not participating in intermolecular contacts leading to chains are omitted for clarity. Colour code: gold, orange; selenium, olive; iron, purple; phosphorus, pink; chloride, cyan; oxygen, red; nitrogen, blue; carbon, grey; and hydrogen, green.

ortho/para-PhN), 3.80 (s, 6H, OCH$_3$), 1.91 (m, 2H, PCH$_2$P). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 31.22. IR (KBr disk): 1617 cm^{-1} v(C–N). Anal. Calc. for C$_{42}$H$_{40}$Au$_2$N$_2$O$_2$P$_2$Se$_2$ (1204.55): C, 40.88; H, 3.18; N, 2.33. Found: C, 40.97; H, 3.07; N, 2.14%.

3.2.6. [Au$_2${SeC(OMe)=NPh}$_2${μ-Ph$_2$P(CH$_2$)$_2$PPh$_2$}] (**6**)

0.040 g, 65%, colourless solid. ^{1}H NMR (CD$_2$Cl$_2$): δ = 7.65–7.44 (m, 20H, Ph$_2$P), 7.04 (t, *J* = 7.6 Hz, 4H, *meta*-PhN), 6.74 (m, 6H, *ortho/para*-PhN), 3.82 (s, 6H, OCH$_3$), 2.53 (m, 4H, PCH$_2$CH$_2$P). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 37.28. IR (KBr disk): 1616 cm^{-1} v(C–N). Anal. Calc. for C$_{42}$H$_{40}$Au$_2$N$_2$O$_2$P$_2$Se$_2$ (1218.58): C, 41.40; H, 3.31; N, 2.30. Found: C, 41.21; H, 3.36; N, 2.16%. Crystals suitable for X-ray diffraction were grown by slow diffusion of Et$_2$O into a CH$_2$Cl$_2$ solution of the complex.

3.2.7. [Au$_2${SeC(OMe)=NPh}$_2${μ-Ph$_2$P(CH$_2$)$_3$PPh$_2$}] (**7**)

0.020 g, 32%, colourless solid ^{1}H NMR (CD$_2$Cl$_2$): δ = 7.42–7.61 (m, 20H, Ph$_2$P), 7.01 (t, *J* = 7.6 Hz, 4H, *meta*-PhN), 6.76–6.71 (m, 6H, *ortho*, *para*-PhN), 3.89 (s, 6H, OCH$_3$), 2.63 (m, 4H, PCH$_2$CH$_2$CH$_2$P), 1.74 (m, 2H, PCH$_2$CH$_2$CH$_2$P). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 33.31. IR (KBr disk): 1613 cm^{-1} v(C–N). Anal. Calc. for C$_{43}$H$_{42}$Au$_2$N$_2$O$_2$P$_2$Se$_2$ (1232.61): C, 41.90; H, 3.43; N, 2.27. Found: C, 42.13; H, 5.76; N, 2.10%. Crystals suitable for X-ray diffraction were grown by slow diffusion of Et$_2$O into a CH$_2$Cl$_2$ solution of the complex.

3.2.8. cis-[Au$_2${SeC(OMe)=NPh}$_2${μ-Ph$_2$PHC=CHPPh$_2$}] (**8**)

0.040 g, 56%, colourless solid. ^{1}H NMR (CD$_2$Cl$_2$): δ = 6.74–7.88 (m, 32H, Ph$_2$P, Ph, HC=CH), 3.75 (s, 6H, OCH$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 19.80. IR (KBr disk): 1612 cm^{-1} v(C–N). Anal. Calc. for C$_{42}$H$_{38}$Au$_2$N$_2$O$_2$P$_2$Se$_2$ (1216.56): C, 41.47; H, 3.15; N, 2.30. Found: C, 41.83; H, 3.05; N, 2.24%.

3.2.9. [Au$_2${SeC(OMe)=NPh}$_2${μ-Ph$_2$P{(C$_5$H$_4$)$_2$Fe}PPh$_2$}] (**9**)

0.046 g, 67%, yellow solid. ^{1}H NMR (CD$_2$Cl$_2$): δ = 7.67–7.38 (m, 20H, Ph$_2$P), 7.14 (t, *J* = 7.6 Hz, 4H, *meta*-PhN), 6.87 (t, *J* = 7.63 Hz, 2H, *para*-PhN), 6.75 (d, *J* = 7.6 Hz, 4H, *ortho*-PhN), 4.46 (br. s, 8H, PC$_5$H$_4$), 3.83 (s, 6H, OCH$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 31.90. IR

Table 2
Crystallographic and refinement details of complexes **6**, **7** and **9**.

Compound	6	7	9
Formula	$C_{85}H_{82}Au_4Cl_2N_4O_4P_4Se_4$	$C_{43}H_{42}Au_2N_2O_2P_2Se_2$	$C_{51}H_{46}Au_2Cl_2FeN_2O_2P_2Se_2$
Formula weight	2522.05	1232.59	1459.44
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	$Pca2_1$	Cc	$P\bar{1}$
a (Å)	17.421(3)	11.106(4)	8.2671(8)
b (Å)	9.8508(15)	22.558(7)	13.3552(9)
c (Å)	26.095(5)	16.510(6)	13.6061(10)
	90	90	61.989(19)
β (°)	90	95.165(11)	77.22(2)
	90	90	69.87(2)
V (Å^3)	4478.2(13)	4119(2)	1242.0(3)
Z	2	4	1
T (K)	153	98	153
D_c (g cm^{-3})	1.870	1.987	1.951
$F(000)$	2396	2344	698
μ (Mo Kα) (mm^{-1})	8.337	8.998	7.859
Measured data	49 317	21 986	14 502
θ Range (°)	2.5–26.5	2.2–26.5	2.6–26.5
Unique data	9059	8049	4956
Observed data ($I \geqslant 2\sigma(I)$)	8748	7875	4609
R, observed data; all data	0.049; 0.051	0.044; 0.046	0.064; 0.070
a, b in weighting scheme	0.052, 40.534	0.070, 46.207	0.092, 5.544
R_w, observed data; all data	0.122; 0.123	0.113; 0.119	0.169; 0.178

(KBr disk): 1612 cm^{-1} ν(C–N). Anal. Calc. for $C_{50}H_{44}Au_2Fe$-$N_2O_2P_2Se_2$ (1374.54): C, 43.69; H, 3.23; N, 2.04. Found: C, 44.23; H, 3.28; N, 1.99%. Crystals suitable for X-ray diffraction were grown by slow diffusion of Et$_2$O into a CH$_2$Cl$_2$ solution of the complex.

3.3. X-ray crystallography

Intensity data sets were collected on a Rigaku AFC12/Saturn724 CCD fitted with Mo Kα radiation. The data sets were corrected for absorption based on multiple scans [29a] and reduced using standard methods [29b]. The structures were solved by direct-methods with SHELXS-97 [29c] and refined by a full-matrix least-squares procedure on F^2 using SHELXL-97 [29c] with anisotropic displacement parameters for non-hydrogen atoms and a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$). All hydrogen atoms were included in the final refinement in their calculated positions. Complex **6** was characterised as a 1:1 dichloromethane solvate (isotropic refinement) and was refined as a racemic twin precluding the determination of the absolute structure. The absolute structure of complex **7** was determined on the basis of differences in Friedel pairs included in the data set. Complex **9** was found to crystallise as a 1:1 dichloromethane solvate. The latter species was disordered about a centre of inversion (anisotropic refinement). Crystal data and refinement details are given in Table 2. Figs. 2–4, showing the atom labelling schemes, were drawn with 50% displacement ellipsoids using DIAMOND [29d]; Fig. 5 was drawn showing arbitrary spheres. Data manipulation and interpretation were accomplished using TEXSAN [29e] and PLATON [29f].

Appendix A. Supplementary material

CCDC 720530, 720531 and 720532 contain the supplementary crystallographic data for **6**, **7** and **9**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.03.032.

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